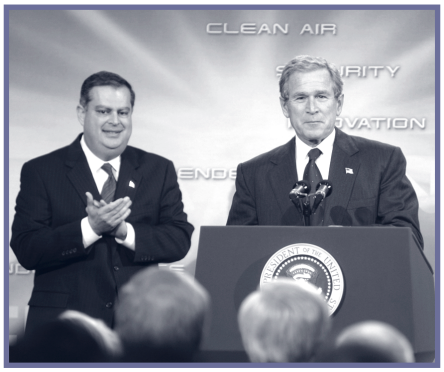
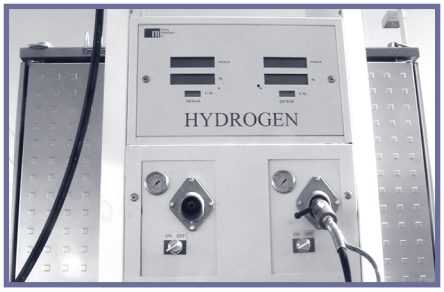
Paving the way
toward a hydrogen
energy future



Hydrogen, Fuel Cells & Infrastructure Technologies Program

2003 Merit Review and
Peer Evaluation Meeting
May 19-22, 2003 Berkeley, California



U.S. Department of Energy
Energy Efficiency and Renewable Energy

Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

DOE/GO-102003-1732
May 2003

U.S. Department of Energy
Energy Efficiency and Renewable Energy

Hydrogen, Fuel Cells & Infrastructure Technologies Program

Program Overview

Steve Chalk, Program Manager

Annual Program Review
May 19th – 22nd, 2003
Berkeley, California

President Bush Launches the Hydrogen Fuel Initiative

"Tonight I am proposing $1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles."

"A simple chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car producing only water, not exhaust fumes. With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom so that the first car driven by a child born today could be powered by hydrogen, and pollution-free."

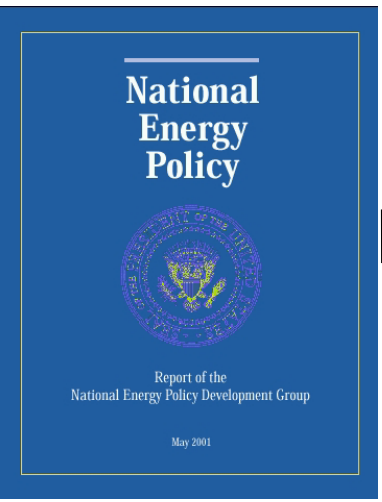
"Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy."

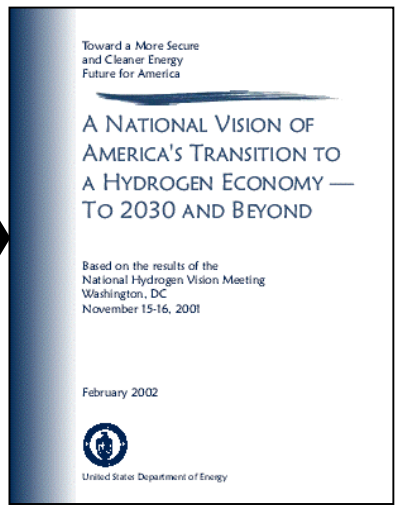
President George W. Bush
2003 State of the Union Address
January 28, 2003

Vision For The Hydrogen Economy

President Bush "Hydrogen fuel cells represent one of the most encouraging, innovative technologies of our era. …And so that's why I'm going to work with the Congress to move this nation forward on hydrogen fuel cell technologies."

-President Bush, February 6, 2003, Remarks on Energy Independence



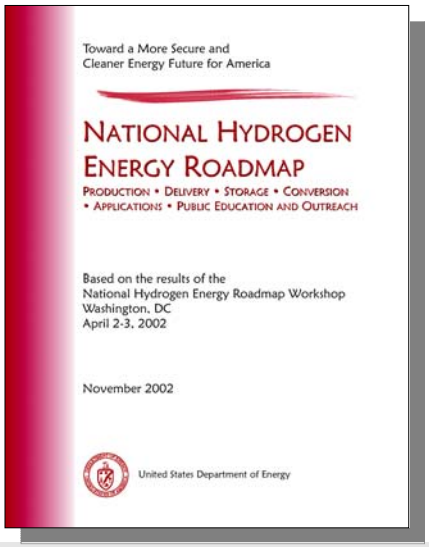


Vision for the Hydrogen Economy

Hydrogen is America's clean energy choice.

Hydrogen is flexible, affordable, safe, domestically produced, used in all sectors of the economy, and in all regions of the country.

President's Hydrogen Fuel Initiative Complements FreedomCAR


Toward a More Secure and Cleaner Energy Future for America

NATIONAL HYDROGEN ENERGY ROADMAP

PRODUCTION • DELIVERY • STORAGE • CONVERSION • APPLICATIONS • PUBLIC EDUCATION AND OUTREACH

Based on the results of the National Hydrogen Energy Roadmap Workshop Washington, DC April 2-3, 2002

November 2002

United States Department of Energy

Secretary Abraham Calls for "International Partnership for the Hydrogen Economy"
April 28, 2003

Secretary of Energy Spencer Abraham called for the development of international collaboration in advanced research and development that will support the deployment of hydrogen energy technologies. Secretary Abraham announced the initiative during a presentation to the International Energy Agency Ministerial meeting.

On January 9, 2002, Energy Secretary Abraham announced the FreedomCAR Partnership

Four "Freedom" Principles:

- Freedom from foreign petroleum dependence
- Freedom from pollutant and carbon dioxide emissions
- Freedom for Americans to drive where they want, when they want, in the vehicle of their choice
- Freedom to obtain fuel affordably and conveniently

Hydrogen Infrastructure and Fuel Cell Technologies put on an Accelerated Schedule

- **President Bush commits a total $1.7 billion over first 5 years:**
  - **$1.2 billion for hydrogen and fuel cells RD&D ($720 million in new money)**
  - **$0.5 billion for hybrid and vehicle technologies RD&D**
- **Accelerated, parallel track enables industry commercialization decision by 2015.**

Fuel Cell Vehicles in the Showroom and Hydrogen at Fueling Stations by 2020

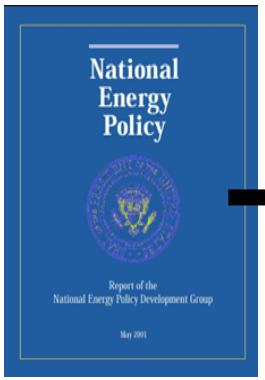
The President's FY04 Budget Request for FreedomCAR and Hydrogen Fuel Initiatives

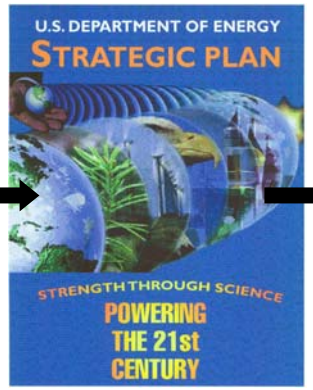
Organization	Million $
Hydrogen, Fuel Cells & Infrastructure Technologies Program (EERE)	165.5
FreedomCAR and Vehicle Technologies Program (EERE)	91.1
Office of Fossil Energy (FE)	11.5
Office of Nuclear Energy, Science and Technology (NE)	4.0
Department of Transportation (RSPA)	0.7
Total	*272.8*

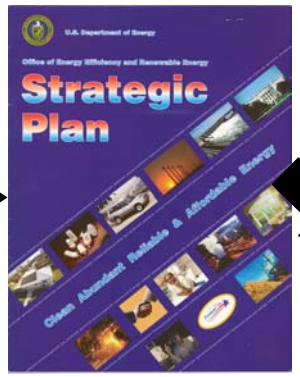
President's Office of Science and Technology Policy has formed an Interagency Hydrogen Research and Development Task Force

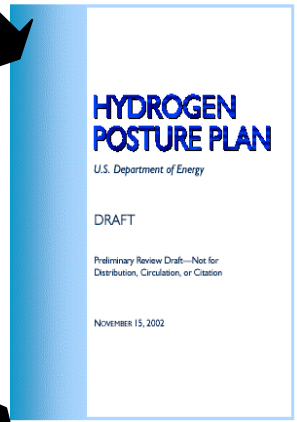
Planning

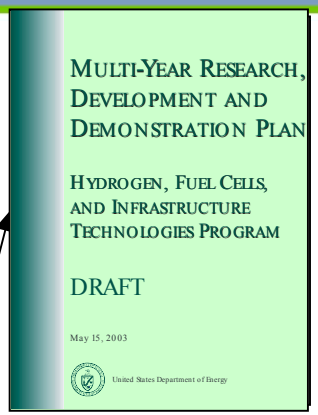
Policy

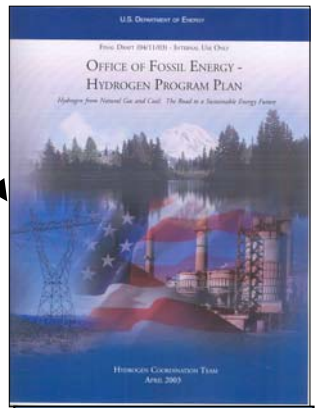




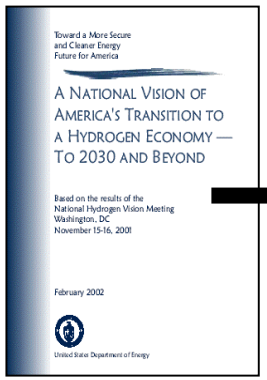


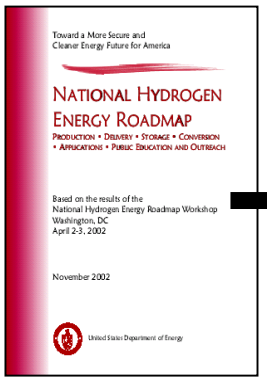


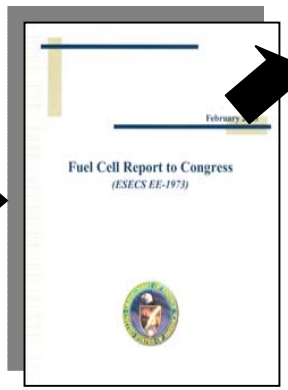




Stake-holder Input





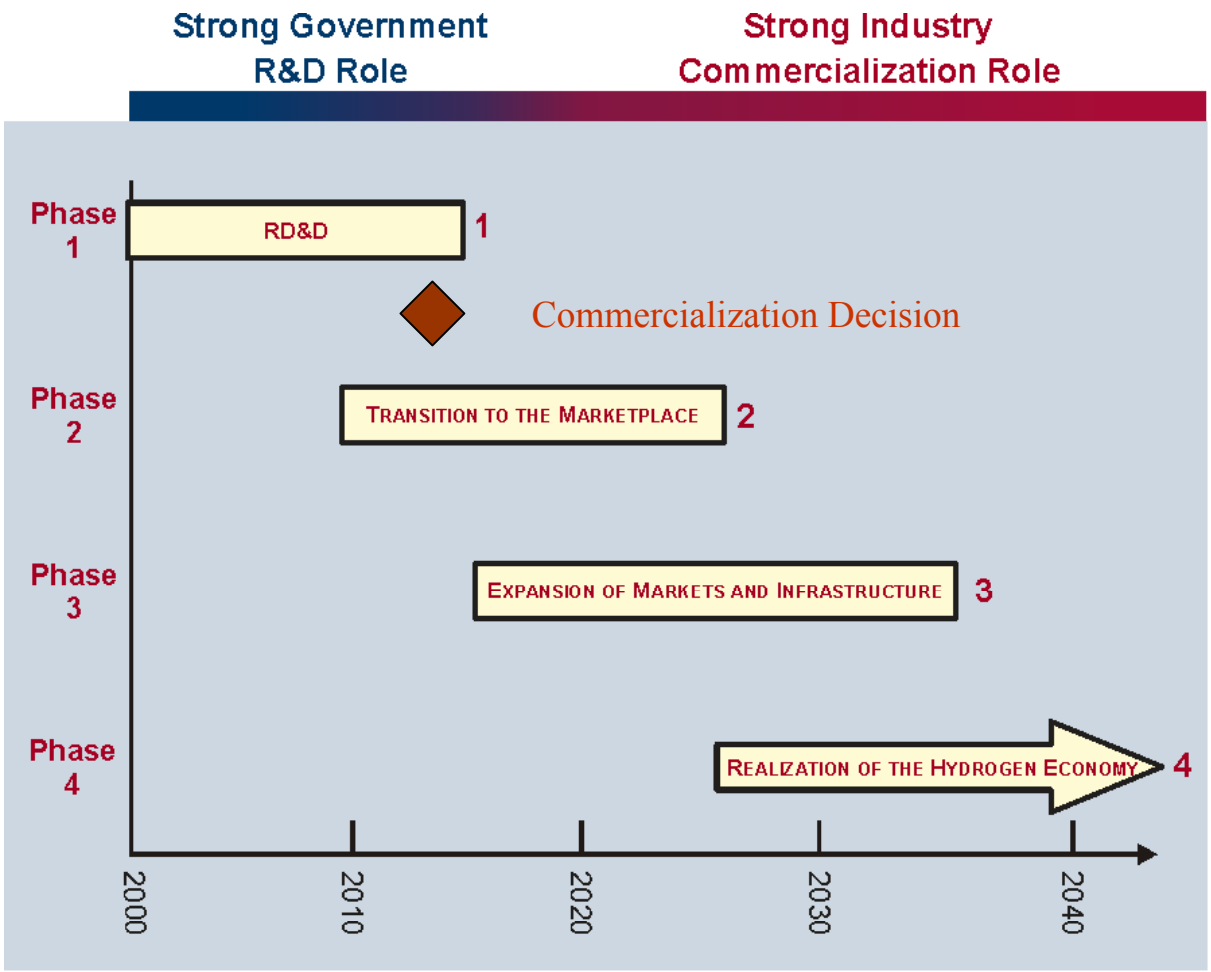


Nuclear Hydrogen Initiative Program Plan

DRAFT

www.eere.energy.gov/hydrogenandfuelcells

Timeline for Hydrogen Economy



Transitional Phases

1. **Technology Development Phase**
   H_2 power and transport systems available in select locations; limited infrastructure
2. **Initial Market Penetration Phase**
   H_2 power and transport systems begin commercialization; infrastructure investment begins with governmental policies
3. **Infrastructure Investment Phase**
   H_2 power and transport systems commercially available; infrastructure business case realized
4. **Fully Developed Market and Infrastrucure Phase**
   H_2 power and transport systems commercially available in all regions; national infrastructure

Benefits of a Hydrogen Economy

"*If we develop hydrogen power to its full potential, we can reduce our demand for oil by over **11 million barrels** per day by the year 2040.*" - President G.W. Bush

- **Energy Security**

  Can be produced from a variety of domestic sources

- **Environmental**

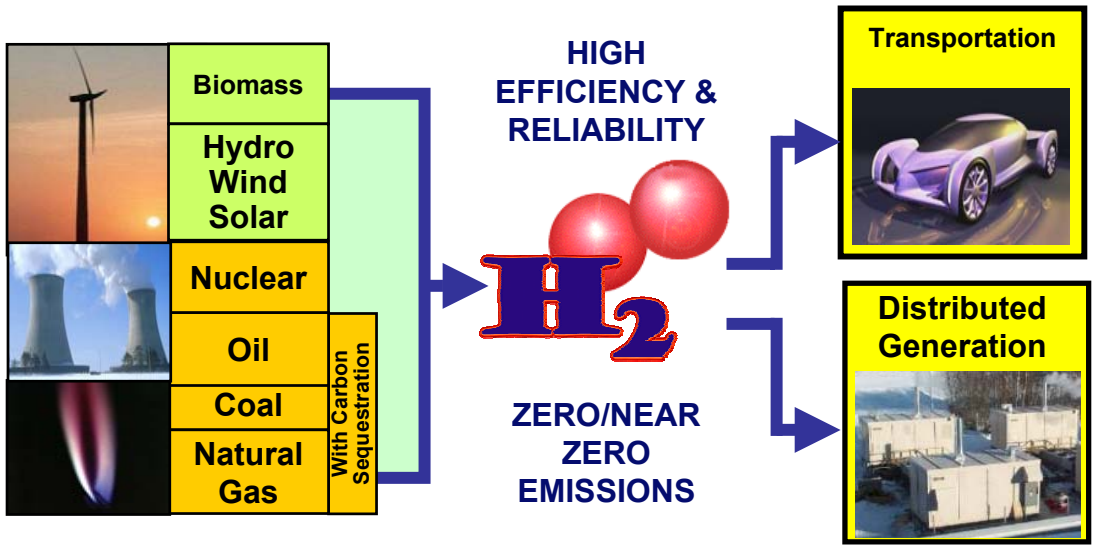
  Criteria pollutants from mobile sources eliminated

  Emissions from stationary H_2 production sites easier to control

  Greenhouse gas emissions significantly reduced

- **International Competitiveness**

  Government – sponsored R&D can help industry compete in global economy

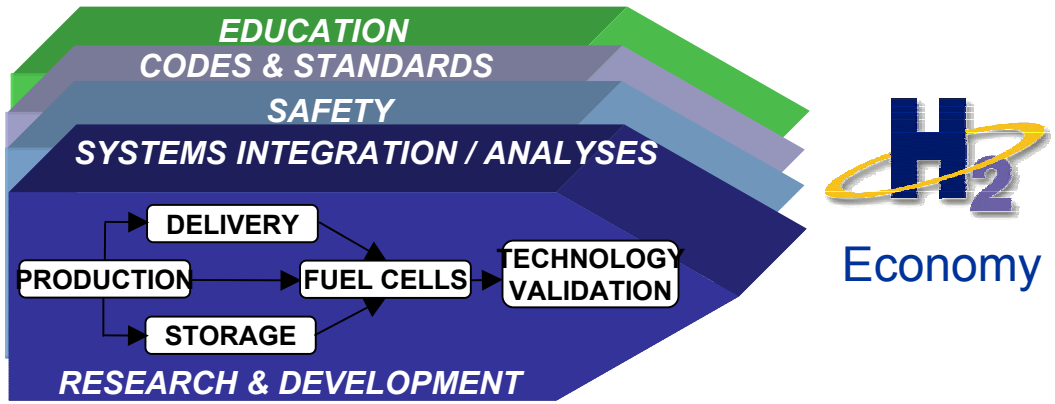


Mission Statement

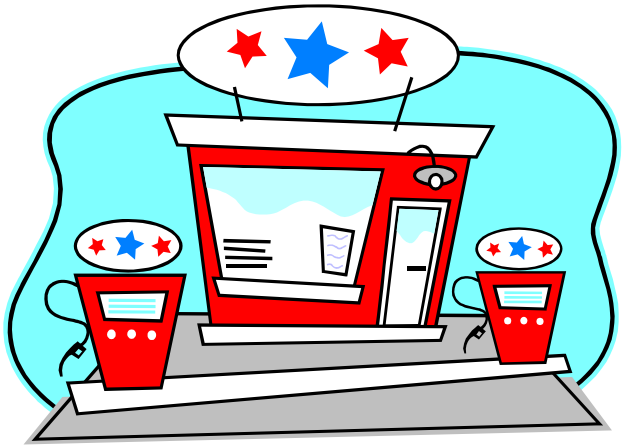
The mission of the Hydrogen, Fuel Cells & Infrastructure Technologies Program is to research, develop, and validate fuel cells and hydrogen production, delivery, and storage technologies for transportation and stationary applications.

The Program supports EERE Strategic Goals:

- Dramatically reduce dependence on foreign oil
- Promote the use of diverse, domestic, and sustainable energy resources
- Reduce carbon emissions from energy production and consumption
- Increase the reliability and efficiency of electricity generation



2002-03 Activity Highlights



Technology Validation:

Completed a 5-year project resulting in the demonstration of a multi-purpose refueling station with

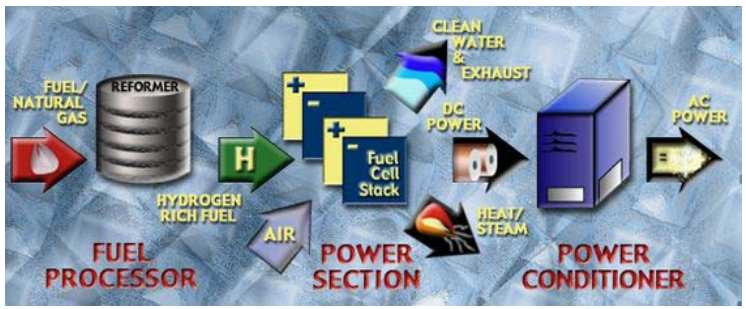
1) on-site H_2 production by reforming natural gas;
2) operating a 50 kW PEM Fuel Cell to generate electricity; and
3) dispensing compressed hydrogen for vehicles and buses.

Education:

Developed a comprehensive, long-term plan to educate multiple audiences.

Fuel Cell:

3M Corporation developed a set of high-performance, matched PEM fuel cell components and pilot manufacturing processes demonstrating high volume, high yield MEA production.



Hydrogen Vehicle/Infrastructure "Learning" Demonstration

Objectives: To conduct "learning" demonstrations that emphasize and integrate hydrogen infrastructure and hydrogen powered vehicles to validate technology status and focus future R&D directions.

Performance, durability and safety data to be collected. Vehicle-refueling interface issues will be evaluated and codes/standards will be developed.

Participants: Energy and automobile companies plus fuel cell suppliers, hydrogen technology suppliers, fleet operators, small businesses, universities, and state, local and federal governments.

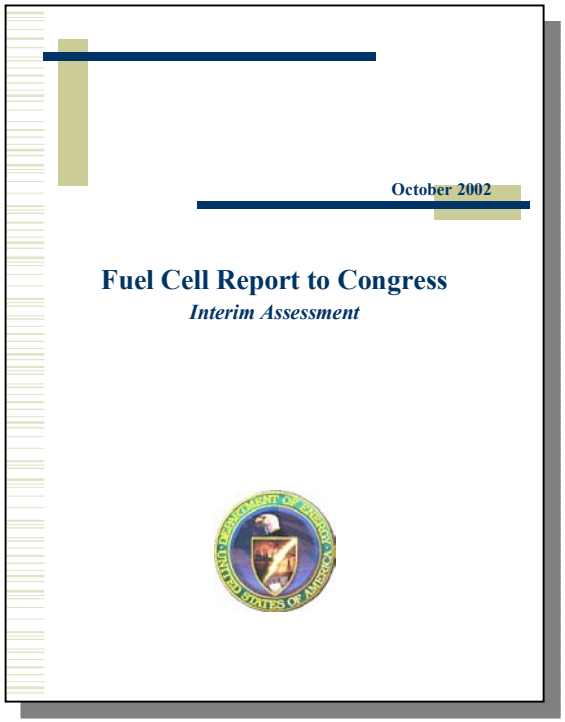
Schedule: Issue date, May

Closes, August

Awards, early 2004

Project period 2004-2008

50/50 cost shared co-operative agreements



Golden Field Office
United States Department of Energy

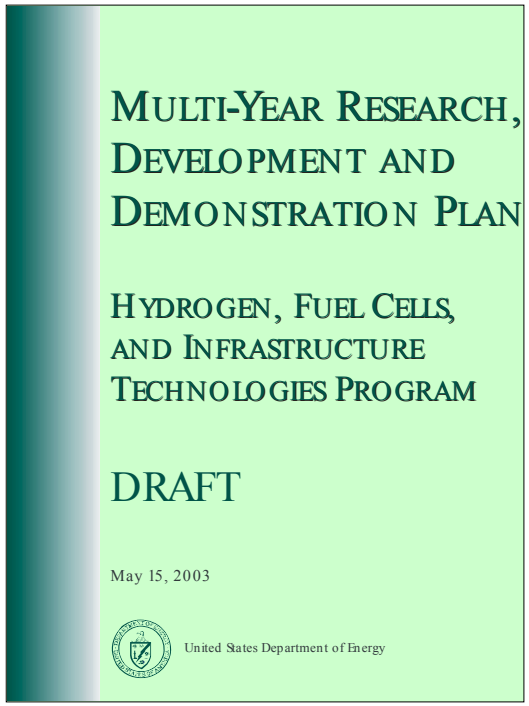
http://www.go.doe.gov

Planning Workshops and Other Stakeholder Input

Fuel Cell Report to Congress Workshops	December 2001, January-February 2002
National Hydrogen Energy Roadmap Workshop	April 2-3 2002
Hydrogen Storage Materials Workshop	August 2002, Argonne IL
DOE HFCIT Codes and Standards Meeting	August 19-20, 2002, Washington DC
International Code Council (ICC) Final Code Change Hearings held in Fort Worth, TX	In late September and early October 2002
Compressed/Liquid Hydrogen Workshop	October 2002, Detroit, MI
HFCIT Education Workshop	December 4-5, 2002, Arlington, VA
Hydrogen Infrastructure: State of Technology and Standards	January 13, 2003, Washington DC
Hydrogen Storage "Think Tank" Meeting	March 2003, Washington, DC
Harmonization of Domestic Hydrogen Standards, Codes, and Regulations	March 7, 2003, Washington DC
Technology Validation Pre-Solicitation Event	March 19, 2003, Detroit
Hydrogen Delivery Workshop	May 7-8, 2003, Washington, DC
9th Annual National Clean Cities Conference	May 20, 2003, Palm Springs
Storage Pre- Solicitation Conference	June 2003, Location TBD

Draft Multi-year Research, Development and Demonstration Plan

- Introduction
- Program Benefits
- Technology Development and Management Approach
- Technical Plan
  - Hydrogen Production
  - Hydrogen Delivery
  - Hydrogen Storage
  - Fuel Cells
  - Technology Validation
  - Codes & Standards
  - Safety
  - Education
- Systems Integration & Analyses


MULTI-YEAR RESEARCH, DEVELOPMENT AND DEMONSTRATION PLAN

HYDROGEN, FUEL CELLS, AND INFRASTRUCTURE TECHNOLOGIES PROGRAM

DRAFT

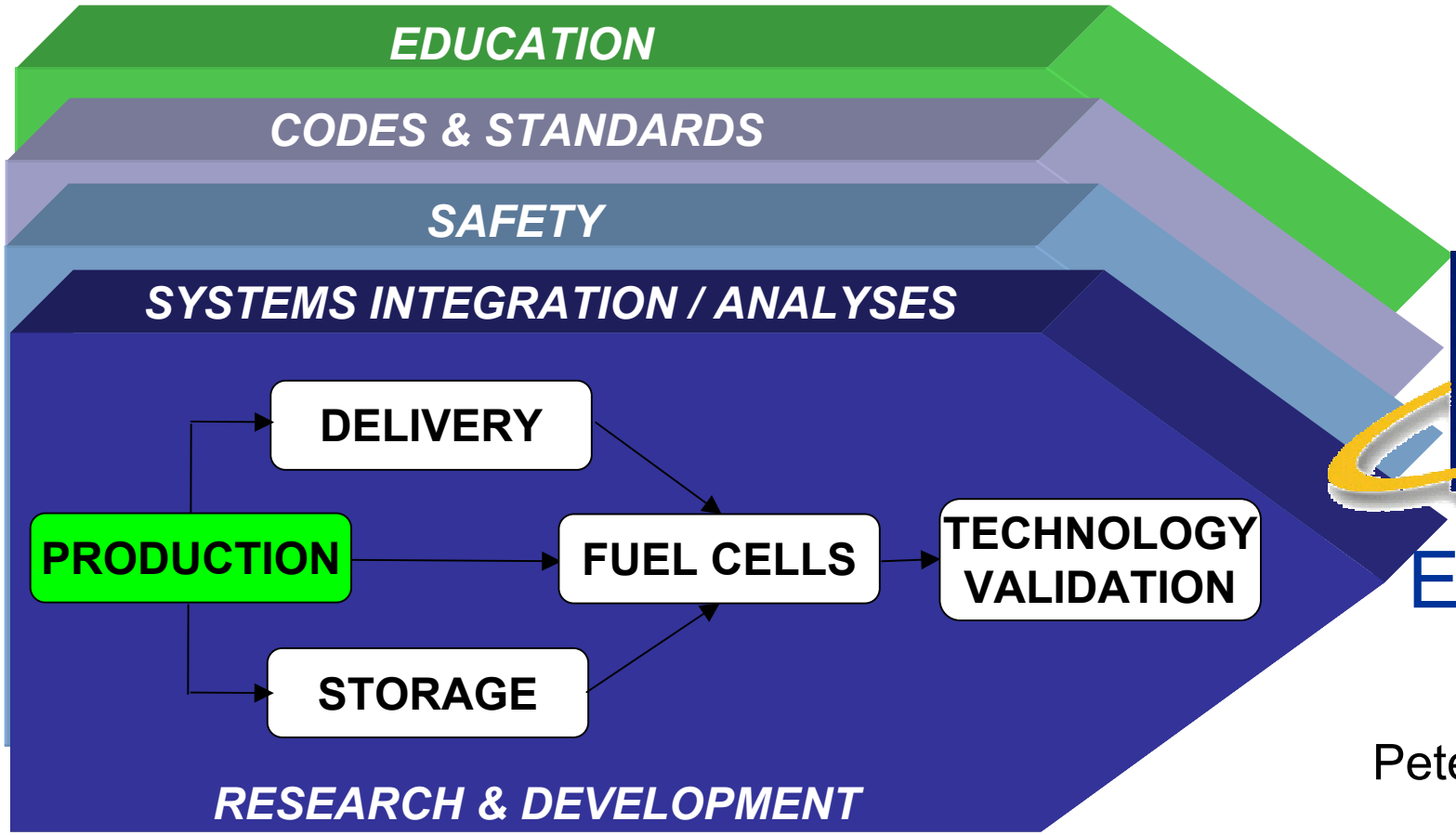
May 15, 2003

United States Department of Energy

www.eere.doe.gov/hydrogenandfuelcells

Overview of R,D& D Plans by Elements

Hydrogen Production



H2 Economy

Pete Devlin

Hydrogen Production Goals and Objectives

Goal : Research and develop low cost, highly efficient hydrogen production technologies from diverse, domestic sources, including fossil, nuclear, and renewable sources.

Objectives for 2010

- Reduce the cost of distributed production of hydrogen from natural gas and/or liquid fuels to $1.50/gallon gasoline equivalent ($1.50/kg delivered, untaxed) at the pump [without carbon sequestration];
- Develop and demonstrate technology to supply purified hydrogen from biomass at $2.60/kg at the plant gate;
- Generate hydrogen with water electrolysis at a capital cost of $250/kWe with 73% system efficiency at 5,000 psi.

Hydrogen Production

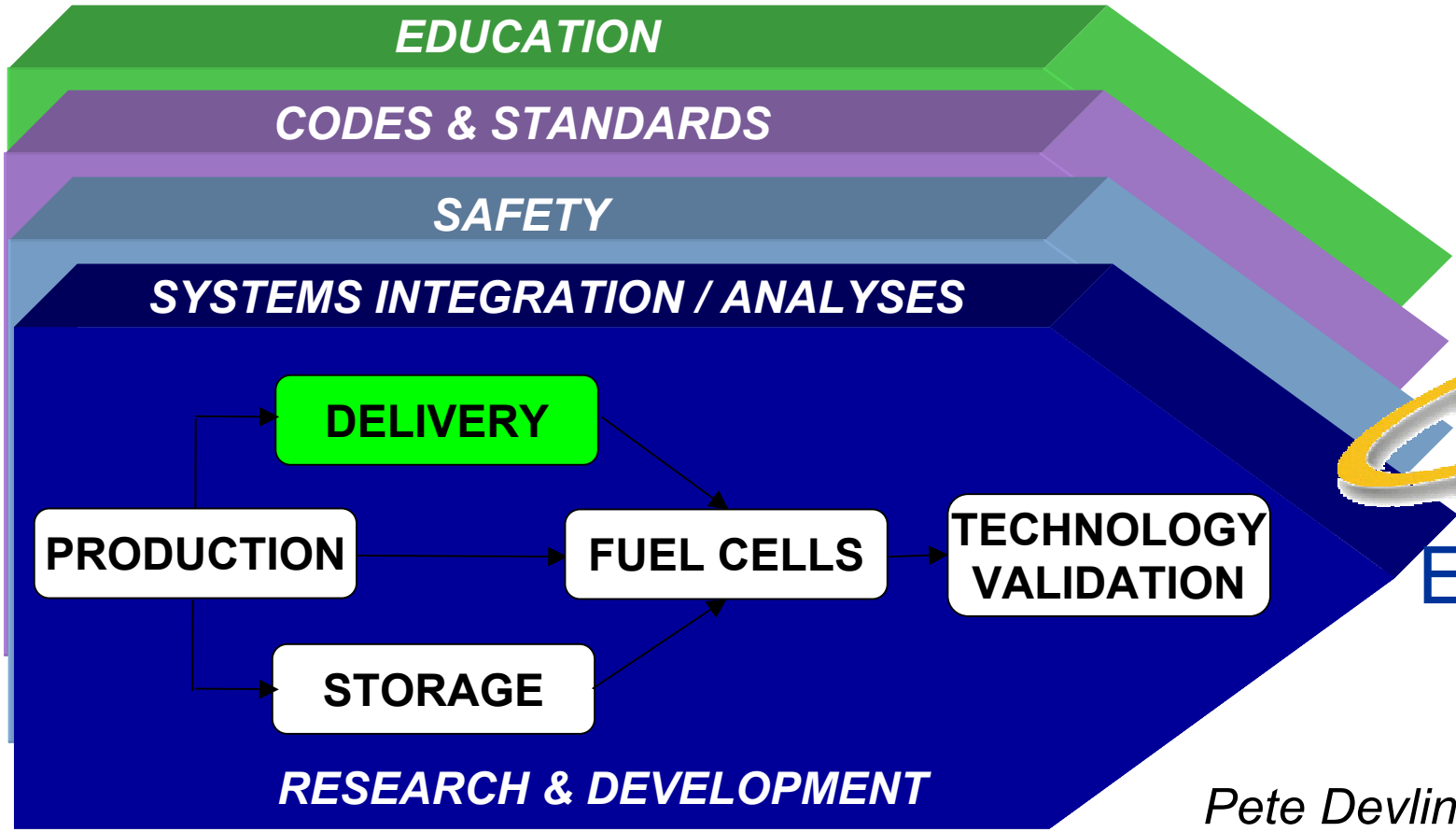
Objectives (cont'd)

- Develop advanced photolytic hydrogen generation technologies.
  - By 2015, demonstrate direct photoelectrochemical water splitting with a plant-gate hydrogen production cost of $5/kg
  - By 2015, demonstrate an engineering-scale photobiological system which produces hydrogen at a plant-gate cost of $10/kg.
- By 2015, research and develop high and ultra-high temperature thermochemical processes to convert hydrogen from high temperature heat sources (nuclear or solar).
- Evaluate other technologies that have the potential for cost effective sustainable production of hydrogen and fund appropriate research.

Hydrogen Production Key Milestones

- Develop hydrogen production technologies for distributed systems using natural gas with projected cost of $3.00/kg hydrogen at the pump, by 3rd quarter, 2004.
- Select and develop biomass gasification technologies to reduce hydrogen cost to $3.30/kg by 4th quarter, 2005.
- Develop electrolyzer technologies that reduce costs to $3.75/kg at 5,000 psi with 65% energy efficiency by 4th quarter, 2005.
- Identify or develop photoelectrochemical material that has solar-to-hydrogen efficiency of 7.5% and 1,000 durability by 4th quarter, 2005.

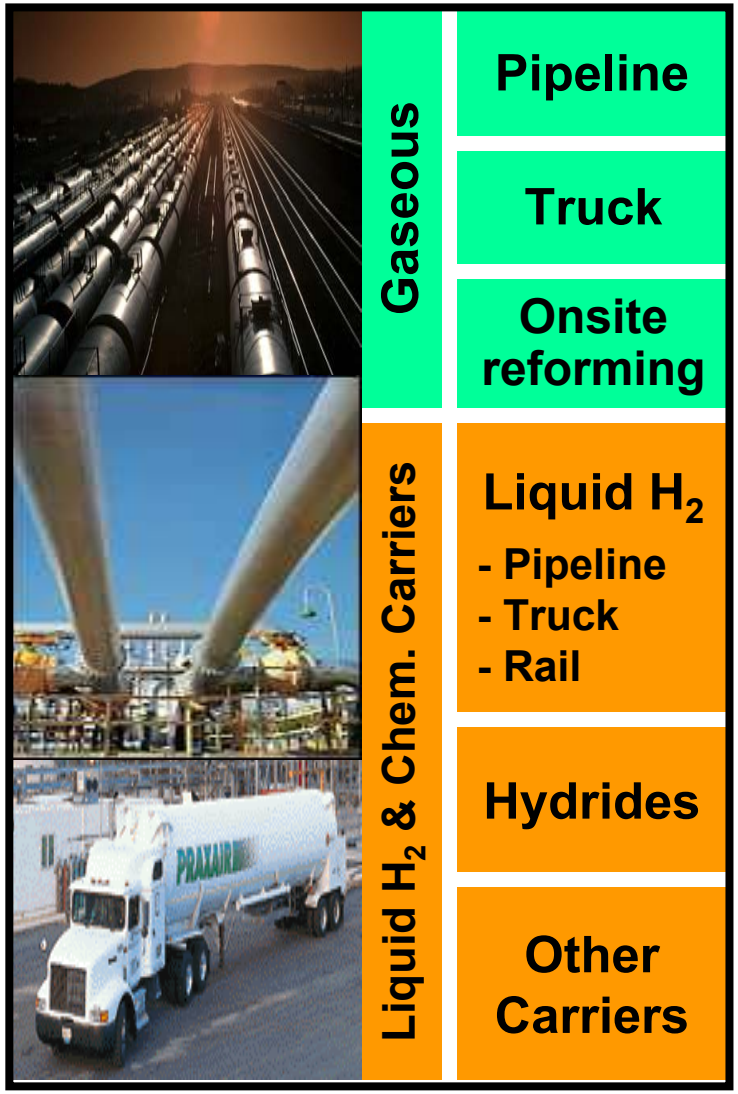
Hydrogen Delivery



H2 Economy

Pete Devlin
on behalf of Mark Paster

Hydrogen Delivery: Goal



Develop *hydrogen fuel delivery* technologies that enable the introduction and long-term viability of hydrogen as an energy carrier for transportation and stationary power.

Delivery Objectives

- By 2006, define a cost effective and energy efficient fuel delivery infrastructure for the introduction and long-term use of hydrogen for transportation and stationary power.
- By 2010, develop enabling technologies to reduce the cost of hydrogen fuel delivery from central/semi-central production facilities to the gate of refueling stations and other end users to <$0.70/kg.
- By 2010, develop enabling technologies to reduce the cost of hydrogen movement and handling within refueling stations and stationary power facilities to a vehicle or stationary power unit to <$0.60/kg.
- By 2015, develop enabling technologies to reduce the cost of hydrogen fuel delivery from the point of production to the point of use in vehicles or stationary power units to <$1.00/kg in total.

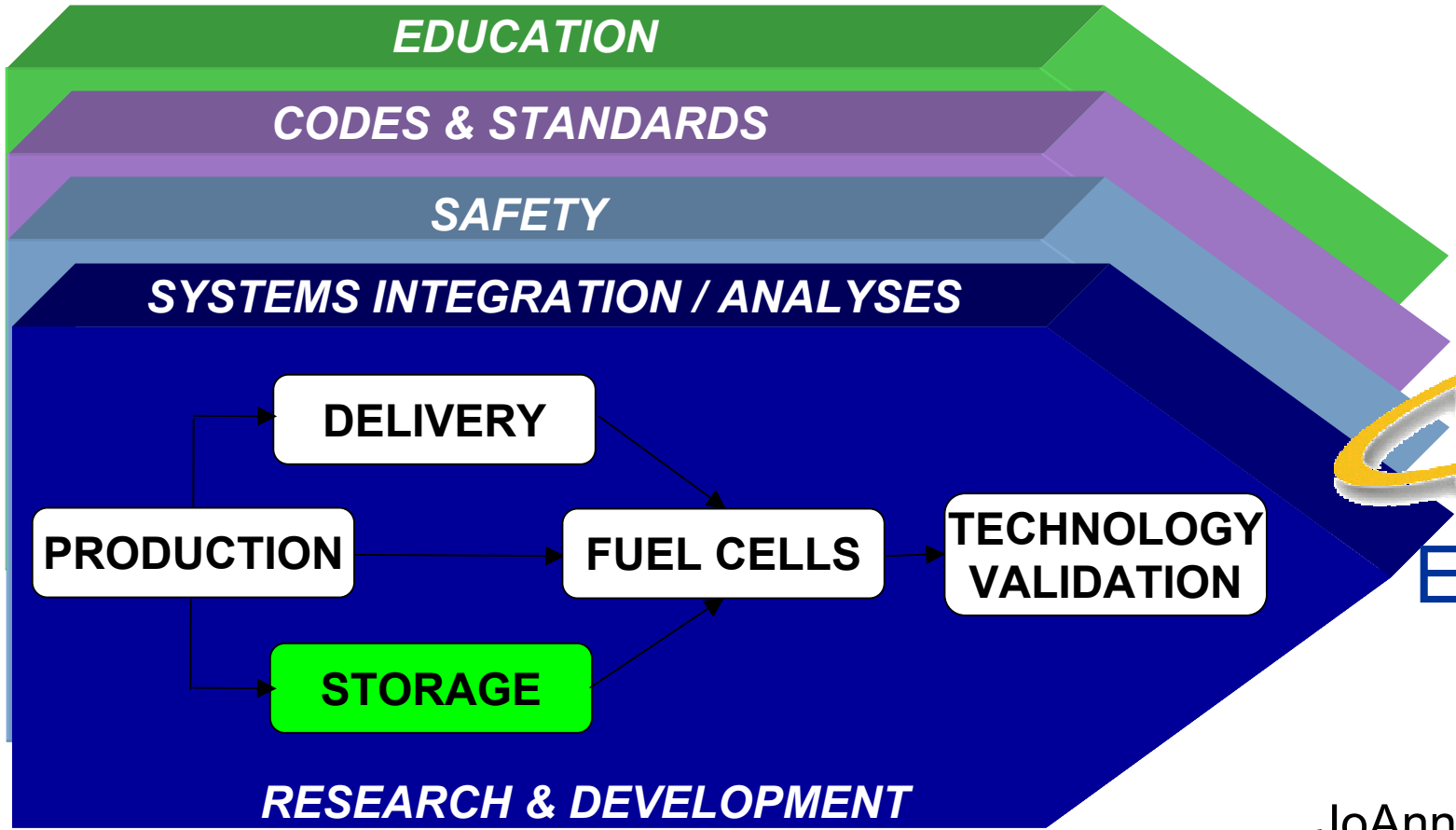
Key Delivery Milestones

Milestone	Description	Quarter (Calendar Year)
--	Complete definition of a cost effective hydrogen fuel delivery infrastructure for the introduction and long term use of hydrogen for transportation and stationary power	2Q 2005
--	Verify 20% cost reduction for hydrogen compression	4Q 2008
--	Verify 50% cost reduction for hydrogen liquefaction	4Q 2010
--	Verify 50% reduction in capital cost for hydrogen pipelines	4Q 2010

Delivery Targets/Milestones

Characteristics	Units	2003 status	2005	2010
Gaseous Hydrogen Compression				
Cost	$/kg H_2	0.18	0.17	0.14
Energy efficiency	%	90	92	95
Hydrogen Liquefaction				
Cost	$/kg H_2	1.11	1.01	0.53
Energy efficiency	%	65	70	87
Hydrogen Gas Pipelines				
Trunk lines	$/mile	1.4M	1.2M	600k
Distribution lines	$/mile	600k	500k	350k
Hydrogen Carrier Technology				
Hydrogen Content	% by wt	3	6.5	10
Energy efficiency	%	80	82	85

Hydrogen Storage



H2 Economy

JoAnn Milliken

Hydrogen Storage Technical Goal & Objectives

Goal : Develop and demonstrate viable hydrogen storage technologies for transportation and stationary applications.

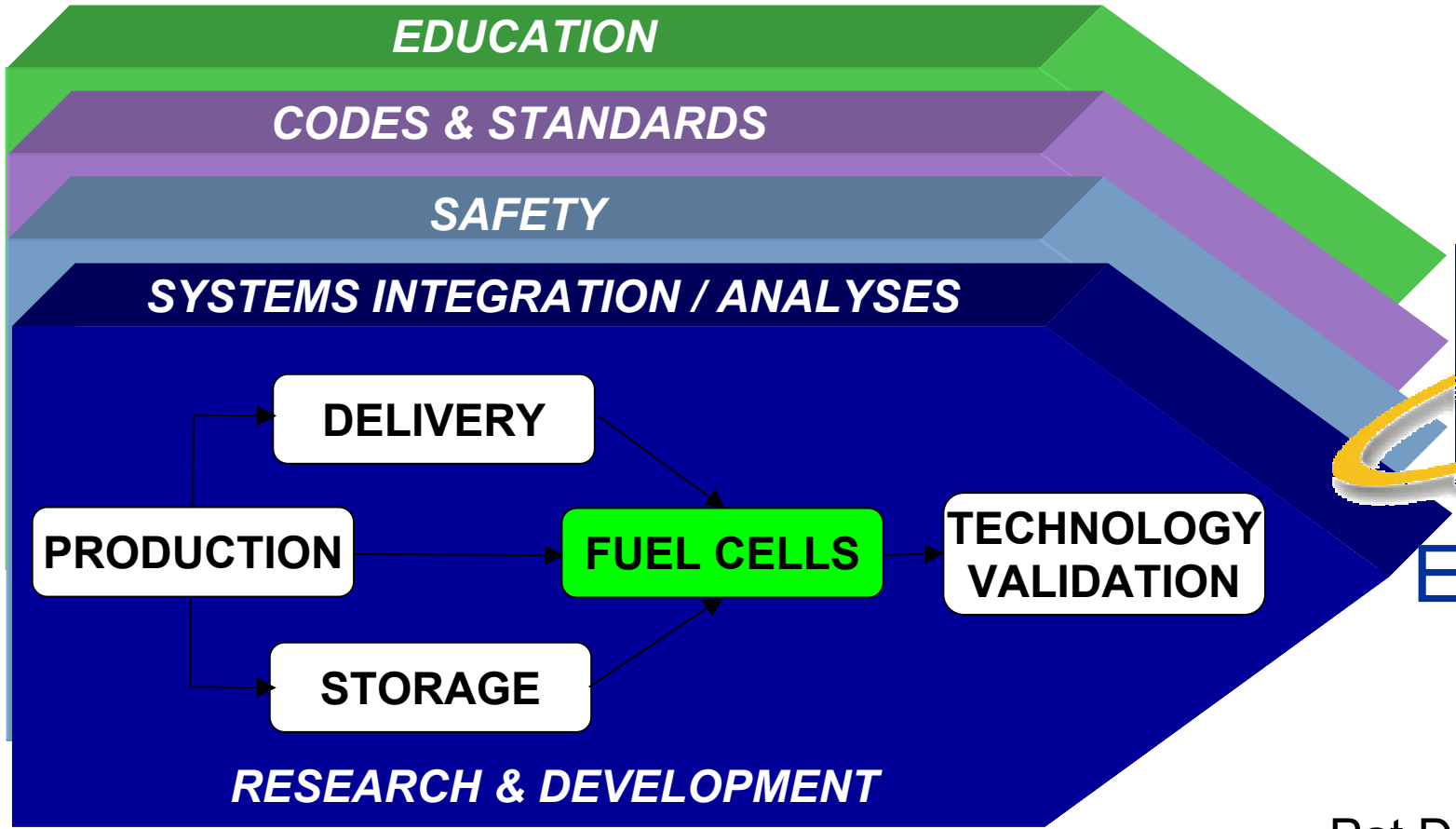
Objectives – Develop and verify:

- On-board hydrogen storage systems achieving:
  - 1.5 kWh/kg (4.5 wt%), 1.2 kWh/L, and $6/kWh by 2005
  - 2 kWh/kg (6 wt%), 1.5 kWh/L, and $4/kWh by 2010
  - 3 kWh/kg (9 wt%), 2.7 kWh/L, and $2/kWh by 2015
- Low cost, off-board hydrogen storage systems, as required for hydrogen infrastructure needs to support transportation, stationary and portable power markets by 2015.
- Vehicle interface technologies for fueling on-board hydrogen storage systems by 2015.

Hydrogen Storage Key Milestones

Milestone	Description	Quarter (Calendar Year)
6	Complete construction of reversible solid-state materials test facility	4Q, 2004
8	Go/No-Go decision on carbon nanotubes	4Q, 2005
4	Go/No-Go decision on R&D of liquid and compressed tanks	4Q, 2006

Fuel Cells



H2 Economy

Pat Davis

Fuel Cells Technical Goals & Objectives

Goal : Develop and demonstrate fuel cell power system technologies for transportation, stationary, and portable applications.

Objectives

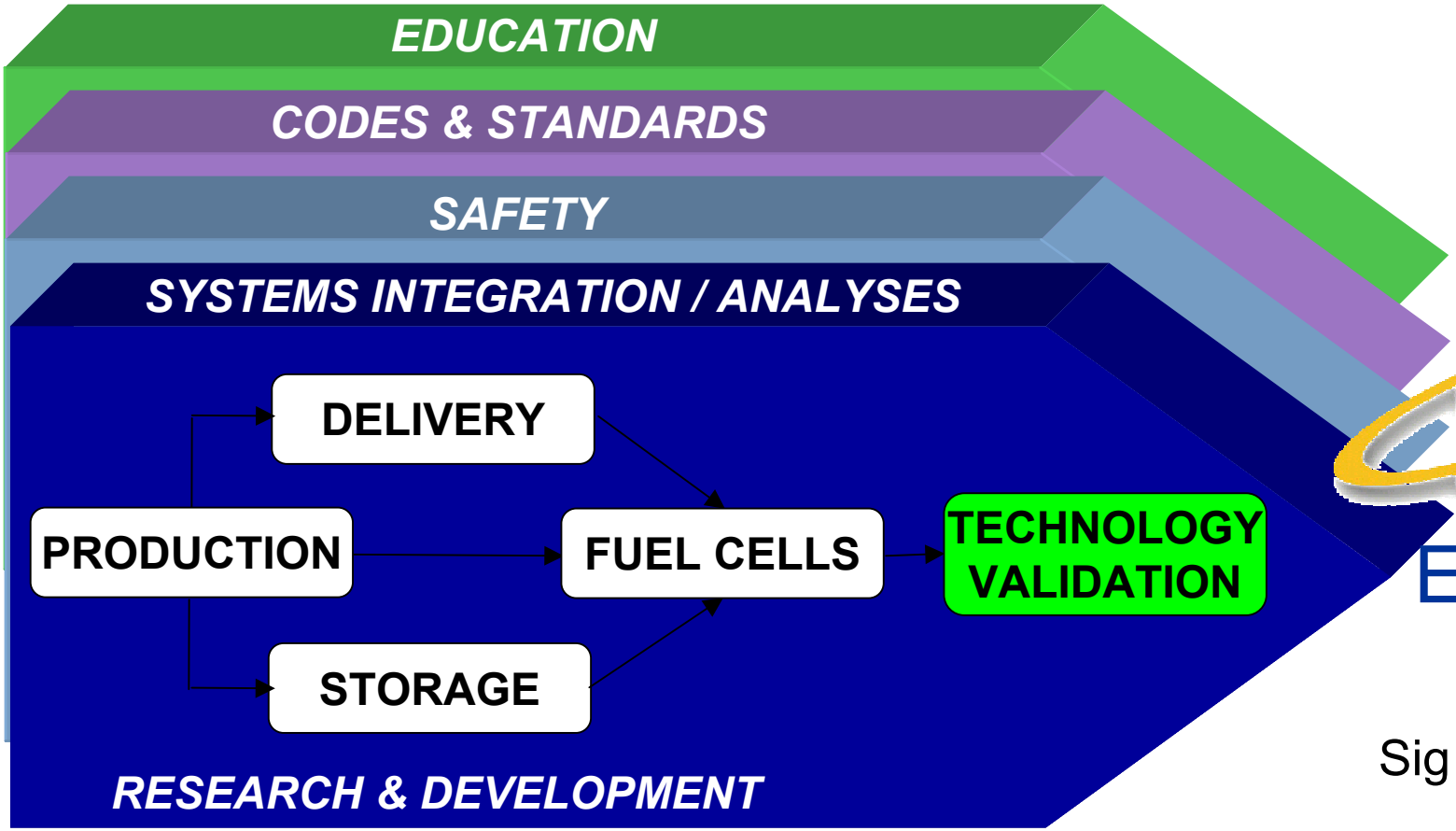
- Develop a 60% efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of $45/kW (including hydrogen storage) by 2010.
- Develop a 45% efficient reformer-based fuel cell power system for transportation operating on clean hydrocarbon or alcohol based fuel that meets emissions standards, a start-up time of 30 seconds, and a projected manufactured cost of $45/kW by 2010.
- Develop a distributed generation PEM fuel cell system operating on natural gas or propane that achieves 40% electrical efficiency and 40,000 hours durability at $750/kW by 2010.
- Develop a fuel cell system for consumer electronics with an energy density of 1,000 W-h/L by 2010.
- Develop a fuel cell system for auxiliary power units (1-3kW) with a specific power of 150 W/kg and a power density of 150 W/L by 2010.

Fuel Cells Key Milestones

Milestone	Description	Quarter (Calendar Year)
9	Go/No Go. Determine whether to continue funding of DMFC R&D for transportation applications.	3Q, 2003
11	Benchmarking of UTC Fuel Cells atmospheric 50kW system	4Q, 2003
14	Verify reproducibility of full-size bipolar plates in high-rate manufacturing processes	4Q, 2003
16	Fuel Processing Go/No Go Decision	2Q, 2004

Cross-cutting Functions

Technology Validation



H2 Economy

Sig Gronich

Technology Validation Technical Goal & Objectives

Goal : Demonstrate and validate integrated hydrogen and fuel cell technologies in a systems context under real operating conditions.

Objectives

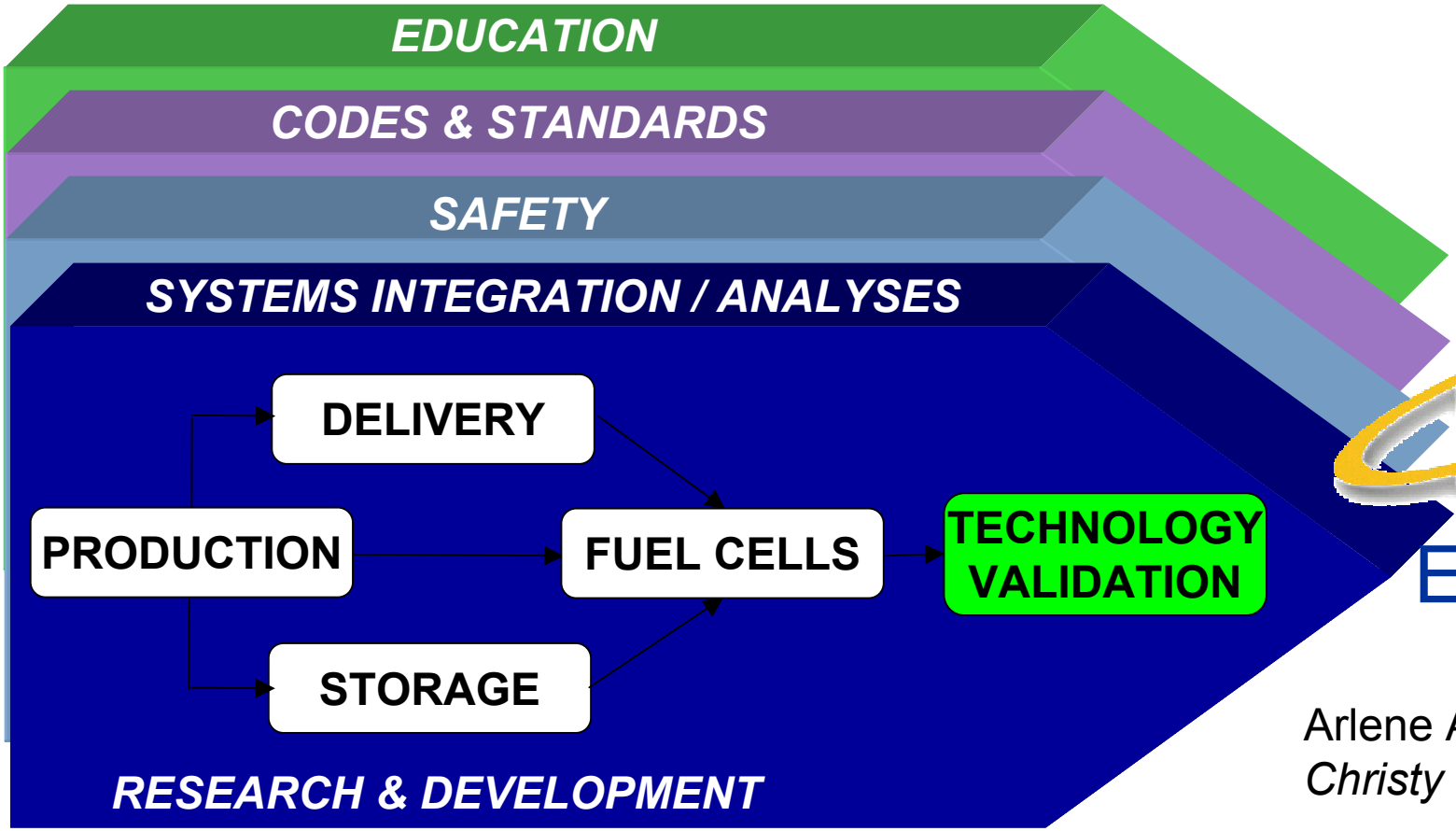
- By 2007, validate an electrolyzer at a capital cost of $300/kWe when built in quantity that is powered by a wind turbine.
- By 2008, validate hydrogen vehicles with greater than 300 miles range, 2,000 hour fuel cell durability, and $3.00/gallon (gasoline equivalent) hydrogen production cost (untaxed) and vehicles that can be safely and conveniently refueled by trained drivers.
- By 2008, validate stationary fuel cell and hydrogen ICE systems that co-produce hydrogen and electricity from non-renewable and renewable resources, and demonstrate 20,000 hour durability, greater than 40% efficiency and a price of $1,500/kW or less (for volume production).
- By 2015, validate (in collaboration with the Office of Nuclear Energy) a high-temperature electrolyzer that produces hydrogen with 40% efficiency at a price of $300/kW when in high-volume production.
- By 2008, validate a biomass to hydrogen system to produce hydrogen for $2.60/kg at the plant gate (unpressurized).

Technology Validation: Key Milestones

Milestone	Description	Date (FY)
1	Awards made to start fuel cell vehicle/infrastructure demonstration activity and for hydrogen co-production infrastructure facilities.	2Q, 2004
6	Validate fuel cell demonstration vehicle range of ~200 miles and durability of ~1,000 hours.	3Q, 2006
17	Four stations and maintenance facilities constructed with advanced sensor systems and operation procedures.	3Q, 2006

Cross-cutting Functions

Education



H2 Economy

Arlene Anderson *for* *Christy Cooper*

Education

Education Sub-Program Technical Goal & Objectives

Goal : Educate key audiences about hydrogen and fuel cell systems to facilitate commercialization and market acceptance of these technologies.

Objectives

By 2010 –

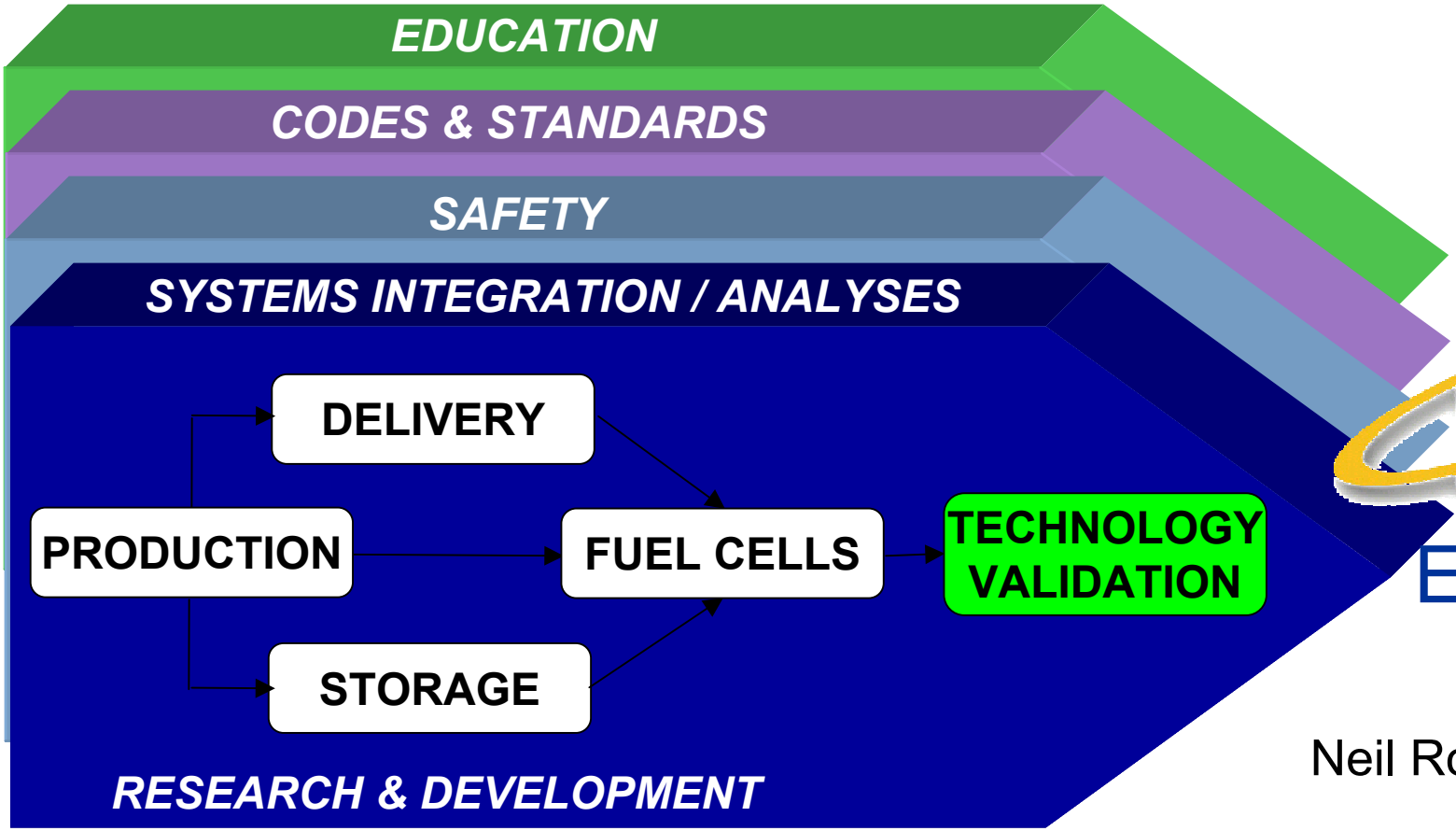
- Achieve a four-fold increase in the number of students and teachers who understand the concept of a hydrogen economy and how it may affect them
- Achieve a four-fold increase in the number of state and local government representatives who understand the concept of a hydrogen economy and how it may affect them
- Achieve a two-fold increase in the number of large-scale end-users who understand the concept of a hydrogen economy and how it may affect them
- Launch a comprehensive and coordinated public education campaign about the hydrogen economy and fuel cell technology

Education Key Milestones

Milestone	Description	Date (FY)
4	Establish educational materials library and information clearinghouse/distribution system to serve the immediate needs of multiple audiences	4Q, 2004
21	Conduct public perception analysis and publish report	4Q, 2004
5	Publish codes and standards database (in conjunction with Safety, Codes and Standards program)	3Q, 2005
6	Publish safety training materials (in conjunction with Safety, Codes and Standards program)	3Q, 2005
12	Launch coordinated materials development and teacher training/professional development program for secondary school teachers	3Q, 2005
31	Create Education Advisory Panel	4Q, 2005

Cross-cutting Functions

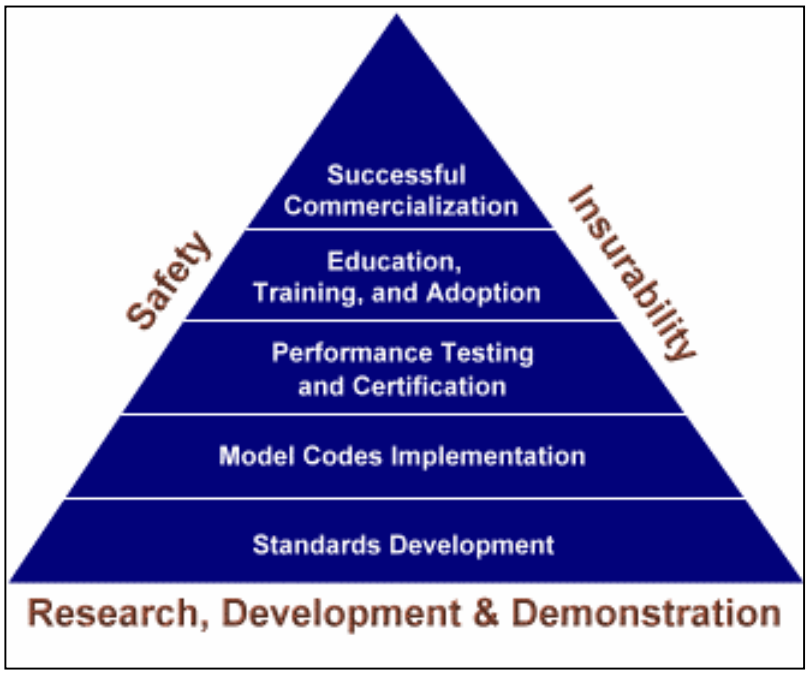
Codes and Standards



H2 Economy

Neil Rossmeissl

Hydrogen Codes & Standards



Hydrogen Codes & Standards: Goal & Objectives

Goal : Facilitate the creation and adoption of model building codes and equipment standards for hydrogen systems in commercial, residential, and transportation applications. Provide technical resources to harmonize the development of international standards among IEC, ISO, and GRPE.

Objectives

- Complete the drafting of hydrogen building codes for NFPA's hearing cycle. Facilitate in the adoption of the ICC codes in three key regions: North East, Mid-Atlantic, and Midwest, by 2005;
- Complete the adoption of the ISO standards for hydrogen refueling and storage, by 2006;
- Complete and adopt the revised NFPA 55 standard for hydrogen storage with data from Technology Validation projects and the experimental project for underground bulk storage of hydrogen, by 2008;
- Complete U.S. adoption of a Global Technical Regulation (GTR) for hydrogen fuel cell vehicles under the Global Regulation on Pollution and Efficiency Program, by 2010.

Hydrogen Codes & Standards: Key Milestones

Milestone	Description	Date (FY)
3	Collaborate with ICC and NFPA to develop first-order continuing education for code officials.	3Q, 2004
4	Establish a coordination plan with education sub-program activity to run workshops for state and local officials.	3Q, 2004
11	Initiate negotiations with critical SDOs and develop draft generic licensing agreement and estimate of costs.	4Q, 2003
24	With industry and code officials, develop templates of commercially viable footprints for fueling stations that incorporate underground and above ground storage of liquid and gaseous hydrogen.	1Q, 2004
30	Implement analytical and experimental program to support the submittal of a comprehensive vehicular safety standard as a regulation.	4Q, 2005
32	Implement research program to support five new technical committees for the key critical standards including fueling interface, power block, and fuel storage.	4Q, 2006

Hydrogen Safety

Neil Rossmeissl

Hydrogen Safety: Goal & Objectives

Goal : Develop and implement the practices and procedures that will ensure safety in the operation, handling and use of hydrogen and hydrogen systems for all DOE funded projects.

Objectives

- Draft a comprehensive safety plan to be completed in collaboration with industry. The plan will initiate the research necessary to fill safety information gaps and enable the formation of a Safety Review Panel, by 2004;
- Integrate safety procedures into all DOE project funding procurements. This will ensure that all projects that involve the production, handling, storage, and use of hydrogen incorporate project safety requirements into the procurements, by 2005;
- Publish a handbook of Best Management Practices for Safety. The Handbook will be a “living” document that will provide guidance for ensuring safety in future hydrogen endeavors, by 2010.

Hydrogen Safety: Key Milestones

Milestone	Description	Date (FY)
2	Develop in collaboration with NASA, DOT, Commerce, a search protocol on component and system safety.	1Q, 2004
12	Assemble panel of experts in hydrogen safety to provide expert technical guidance to funded projects.	4Q, 2003
17	Identify areas of additional study and research for failure modes scenarios.	3Q, 2004
21	Gather and review data to support the inclusion of hydrogen safety in procurements.	4Q, 2003
31	Establish annual review criteria for safety.	4Q, 2004

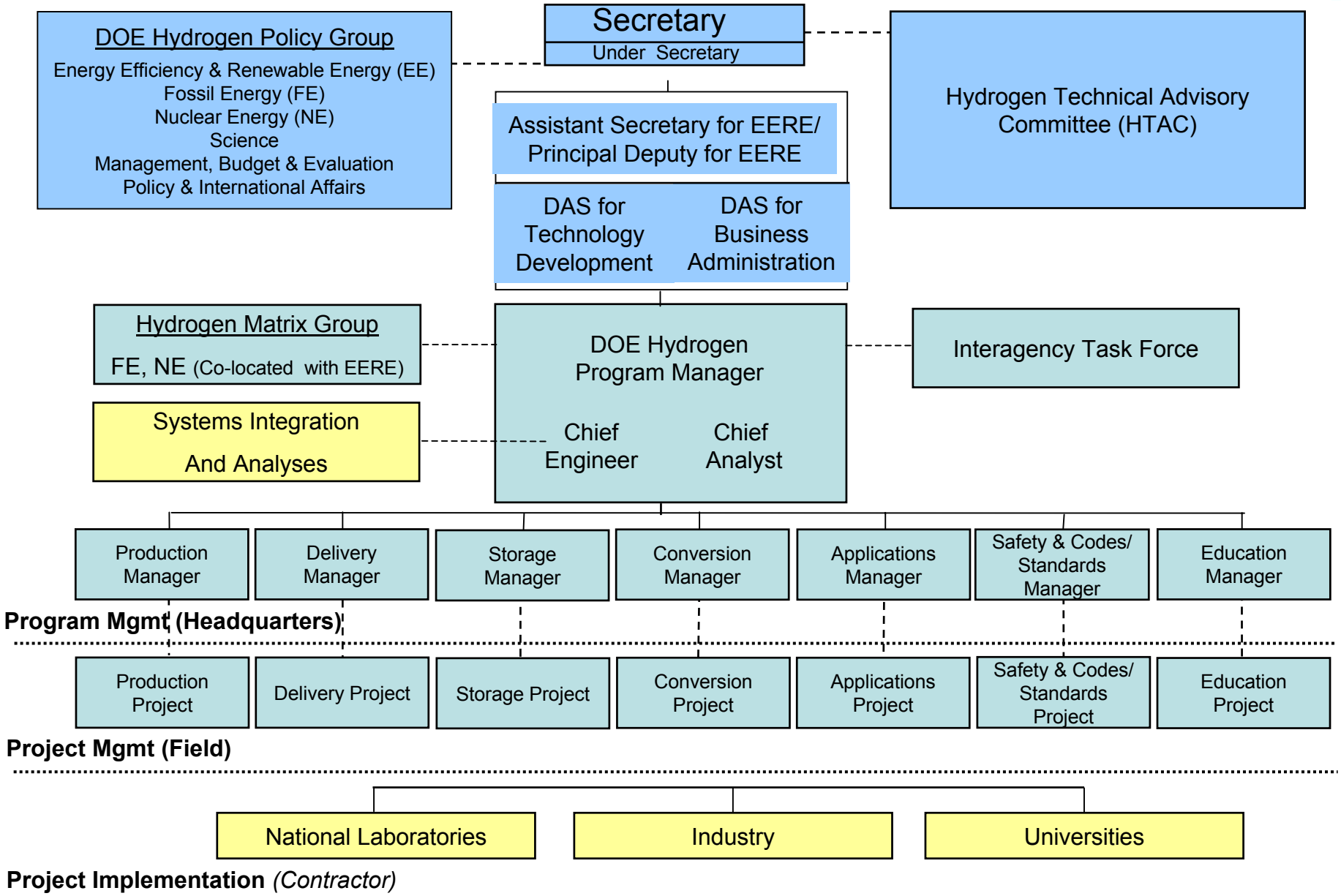
National Academy of Sciences Interim Report

- **Safety**
  The Committee recommended that DOE make significant efforts to address safety issues.
- **Systems Integration and Analyses**
  The academy recommends that R&D successes & failures be analyzed and modeled both as individual technologies, and as components parts of a greater system.
- **Exploratory Research**
  The Committee encouraged DOE to continue funding fundamental, exploratory research for promising, high-risk new technologies.
- **Organization**
  The Committee supports the DOE in its efforts to integrate various hydrogen-related RD&D programs, the Office of Science, and the private sector.

THE NATIONAL ACADEMIES
Advisers to the Nation on Science, Engineering, and Medicine

Find more information at www.nas.edu under BEES-J-02-04-A.

Proposed Management Structure



Future Directions

- **Technology Validation Projects**
  Validation and Demonstration projects will be implemented.

- **Virtual Centers for Hydrogen Storage**
  Will bring together experts from multiple fields under the direction of one lab. EERE will collaborate with the Office of Science.

- **Fuel Cell Processor Go/No-Go**
  Review in late 2004 to determine the future course of on-board vehicle fuel processing activities.

- **International Partnerships**
  Secretary announced International partnerships at IEA; US-EU co-operating on codes and standards. Working with China and India to develop Roadmaps on H2 Future.

- **Hydrogen Production from Renewables**

EERE Wind and Hydrogen Programs collaborating on study for wind-based hydrogen and electricity.

Future Opportunities

"Grand Storage Challenge"	Solicitation to be announced in June 2003. Contact: JoAnn Milliken
Hydrogen Production	Solicitation: May 2003 Contact: Pete Devlin
Fuel Cells (Portable, Auxiliary, Off-Road)	Solicitation: April 9, 2003- June 5, 2003 Contact: Pat Davis/John Garbak
Codes/Standards	Solicitation: No immediate releases Contact: Neil Rossmeissl
Technology Validation and Demonstration	Solicitation: May 2003 Contact: Sig Gronich, John Garbak
Education	Solicitation: Late Summer 2003 Contact: Christy Cooper
FutureGen	Contact: Fossil Energy and the National Energy Technology Lab (NETL) Contact: Lowell Miller

Information Resources

U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

EERE Home

Hydrogen, Fuel Cells & Infrastructure Technologies Program

About the Program | Information Resources | Financial Opportunities | Technologies

Search
Search Help
Site Map
Ask an Energy Expert

Hydrogen and fuel cells have the potential to solve several major challenges facing America today: dependence on petroleum imports, poor air quality, and greenhouse gas emissions. The Hydrogen, Fuel Cells & Infrastructure Technologies Program is working with partners to accelerate the development and successful market introduction of these technologies.

Hydrogen
Hydrogen is a clean and sustainable form of energy that can be used in mobile and stationary applications.

Fuel Cells
Fuel cells harness the chemical energy of hydrogen to generate electricity without combustion or pollution.

Safety, Codes & Standards
Codes and standards ensure the safe use of hydrogen and fuel cells.

For Students and Teachers
Learn the basics of hydrogen and fuel cells and view a fuel cell animation.

The vision of a new energy economy based on clean, renewable hydrogen is described in the National Hydrogen Energy Vision document (PDF 1 MB).

Sign up for on-line news.

Although we have a vision for a hydrogen economy, changing the way we produce and use energy is not a simple or overnight task. The National Hydrogen Energy Roadmap (PDF 2 MB) outlines the challenges we face and suggests a path forward to achieve the promise of hydrogen and fuel cells.

The first steps toward the hydrogen future are already underway. The 2002 Annual Progress Report provides a complete list of DOE-funded hydrogen and fuel cell projects for 2002.

- In November 2002, the world's first energy station featuring hydrogen and electricity co-production opened in Las Vegas, Nevada. More info
- In December 2002, DOE's education workshop kicked off a new coordinated effort to educate key audiences about hydrogen and fuel cells. More info (PDF 284 KB)

Some of the above documents are available as Adobe Acrobat PDFs. Download Acrobat Reader

NEWS
- Hydrogen Production and Delivery Pre-solicitation Announcement
  April 2003
- Energy Secretary's Comments on the Road to the Hydrogen Future
  April 14, 2003
- Portable Power, Auxiliary Power Units, and R&D for Off-Road Fuel Cell Applications Solicitation
  April 9, 2003
- More News

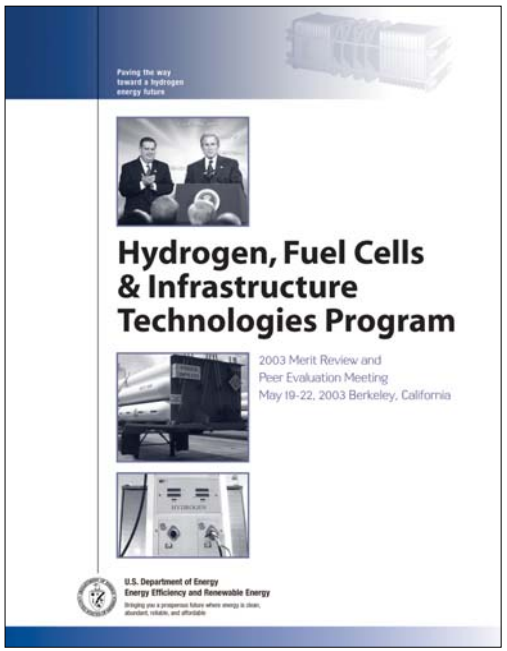
EVENTS
- 2003 Hydrogen and Fuel Cells Merit Review Meeting
  May 19-22, 2003
- More Events

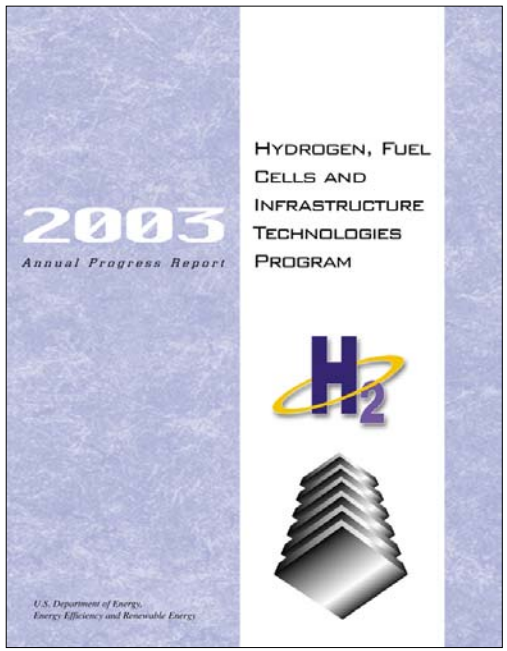
FEATURES
- Fuel Cell Report to Congress (PDF 1.18 MB)
  Download Acrobat Reader
- FreedomCAR and Fuel Initiative

Webmaster | Security & Privacy | EERE Home
U.S. Department of Energy
Content Last Updated: 04/10/2003

http://www.eere.energy.gov/hydrogenandfuelcells

Information Resources





Acknowledgements

- FreedomCAR Partners
- Reviewers
- Technical Support
- Lawrence Livermore National Lab (LLNL)

Appendix X

- Budget Information
- Responsibility Matrix

Fuel Cell Technology

Key Activity	FY 02	FY 03	FY 04 Req.	'04 Comments
Interior Appropriations in $ Millions				
Transportation Systems	**$7.5**	**$6.2**	**$7.6**	More emphasis on balance of plant systems components such as air compressors, blowers, heat exchangers, sensors, and APU's
Distributed Generation Sys.	**$5.5**	**$7.5**	**$7.5**	System durability issues, fuel processor integration and balance of plant component development
Stack Component R&D	**$12.6**	**$14.9**	**$28.0**	Emphasize basic membrane materials work, advanced catalysts/non-precious metal catalystsmaterials/manufacturing.
Fuel Processor R&D	**$20.9**	**$24.7**	**$19.0**	Decrease reflects reduced mortgages, approaching FY04 go/no go decision. Supports natural gas/propane fuel processing for distributed generation.
Technology Validation	**$0**	**$1.8**	**$15.0**	Significant increase represents first year of vehicle test and evaluation program
Technical Support	**$0.2**	**$0.4**	**$0.4**	
TOTAL	**$46.7**	**$55.5**	**$77.5**	

Hydrogen Technology

Key Activity	FY 02	FY 03	FY 04 Req.	'04 Comments
Energy & Water Appropriations in $ Millions				
Hydrogen Production & Delivery*	**$11.2**	**$11.8**	**$23.0**	Distributed natural gas reformers, and separation technologies, more emphasis on renewable production ($6M to $17M)
Hydrogen Storage	**$6.1**	**$11.3**	**$30.0**	Critical path technology! Expands current R&D and initiates research on advanced concepts such as conducting polymers and nanostructured materials.
Infrastructure Validation	**$5.7**	**$10.1**	**$13.2**	Increase for hydrogen refueling stations in support of controlled fleet demonstration project
Safety, Codes & Standards, Utilization	**$4.5**	**$4.8**	**$16.0**	Expands R&D efforts to develop critical engineering data for C&S and hydrogen safety
Education and Cross-Cutting Analyses	**$1.4**	**$2.0**	**$5.8**	Initiates national campaign to communicate hydrogen benefits and barriers. Includes only cross-cutting life cycle analysis
TOTAL	**$28.9**	**$40.0**	**$88.0**	

* EERE program activities (excludes FE ($11.5M) and NE ($4M) for FY 2004)

Responsibility Matrix

H_2 Production Team

Pete Devlin 202 586-4905 Peter.Devlin@ee.doe.gov	• Team Leader, Hydrogen Production • Overall Hydrogen Production R&D • FreedomCAR Energy Industry Expansion
Roxanne Danz 202 586-7260 Roxanne.Danz@ee.doe.gov	• Biological, Biomass, and other H2 Renewables • NAS and Roadmap coordination
Chris Bordeaux 202 586-3070 Christopher.Bordeaux@ee.doe.gov	• Integrated Power Parks/Uninterruptible Power Systems • California Fuel Cell Partnership • International Outreach (non-IEA)
Matt Kauffman 202 586-5824 Matthew.Kauffman@ee.doe..	• Cross-cutting Analyses • Electrolyzers
Arlene Anderson 202 586-3818 Arlene.Anderson@ee.doe...	• Fossil Energy Coordination on Coal-Based Production • Natural Gas, Petroleum Feedstocks/Platinum Mining • 5-Year R,D&D Plan Development
Mark Paster 202 586-2821 Mark.Paster@ee.doe.gov	• Overall Feedstock Strategy for H_2 production • High Temperature Thermochemical and Electrolysis • Hydrogen Delivery

Hydrogen Storage

JoAnn Milliken **202 586-2480** **JoAnn.Milliken@ee.doe.gov**	• **Tech Team Storage Chair** • **Overall Hydrogen Storage** • **Team Leader, Hydrogen Storage** • **Fuel Cell International Activities** • **FreedomCAR Storage & Vehicle Interface Tech Team**
Lucito Cataquiz **202 586-0729** **Lucito.Cataquiz@ee.doe.gov**	• **Support Service Contractor COTR** • **Cost/Financial Status** • **Pressurized Tanks & Hydrogen Compressors** • **Compressed/Liquid Tank Projects**
New Hire	• **New H_2 Storage Materials Virtual Centers/Projects** • **BES Liaison**
Carole Read **202 586-xxxx** **Carole.Read@ee.doe.gov**	• **New H_2 Storage Materials Virtual Centers/Projects** • **IHIG**

Fuel Cell Team

Pat Davis 202 586-8061 Patrick.Davis@ee.doe.gov	• Overall Fuel Cell Systems • FreedomCAR Fuel Cell Tech Team • Compressors/Expanders
Donna Ho 202 586-8000 Donna.Ho@ee.doe.gov	• Transportation Fuel Cells • CARAT Program
Valri Lightner 202 586-0937 Valri.Lightner@ee.doe.gov	• Fuel Processing • MEA R&D
John Garbak 202 586-1723 John.Garbak@ee.doe.gov	• Fuel Cell Vehicle Demonstration • Liaison with 21st Century Truck • Fuel Cells for APUs
Kathi Epping 202 586-7425 Kathi.Epping@ee.doe.gov	• Stationary Fuel Cells
Nancy Garland 202 586-5673 Nancy.Garland@ ee.doe.gov	• National Lab Fuel Cell R&D • Sensors • GATE Program

Cross-Cutting Functions

Sig Gronich **202 586-1623** **Sigmund.Gronich@ee.doe.gov**	• Overall Technology Validations for Transportation and Stationary Applications • Manager, Technology Validation
Christy Cooper **202 586-1885** **Christy.Cooper@ee.doe.gov**	• Education on Hydrogen and Fuel Cells
Neil Rossmeissl **202 586-8668** **Neil.Rossmeissl@ee.doe.gov**	• H_2 Codes and Standards • H_2 Safety • Hydrogen Technical Advisory Panel • IEA H_2 Agreement
Tia Alexander **202 586-9118** **Tia.Johnson@ee.doe.gov**	• Administrative Reporting and Support • Controlled Correspondence • Travel Planning and Approval • Meeting Facilitation • Foreign Visitors

Additional On-site Resources

Reeshemiah Schuler	Reeshemiah.Schuler@ee.doe.gov	202 586-8012
Bill Cleary	Bill.Cleary@ee.doe.gov	202 586-1570
Dr. John Petrovic	John.Petrovic@ee.doe.gov	202 586-8058
Lauren Inouye	Lauren.Inouye@ee.doe.gov	202 586-0894
Kristen Rannels	Kristen.Rannels@ee.doe.gov	

Additional DOE Contacts

Fossil Energy (FE)

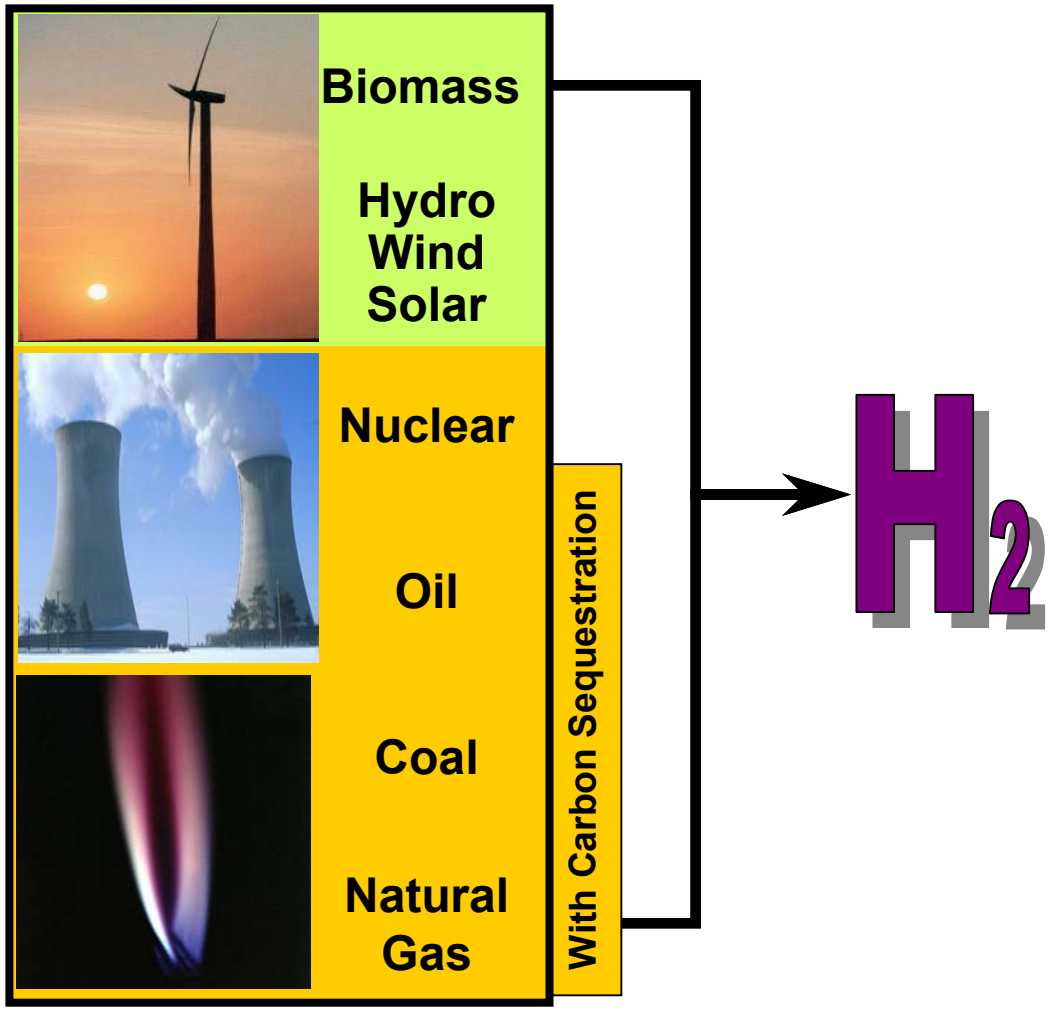
Lowell Miller	**301 903-9451**	**Lowell.Miller@hq.doe.gov**
Ed Schmetz	**301 903-3931**	**Edward.Schmetz@hq.doe.gov**
Art Hartstein	**301 903-2760**	**Arthur.Hartstein@hq.doe.gov**

Nuclear Energy (NE)

David Henderson	**301 903-3097**	**David.Henderson@hq.doe.gov**

Office of Science (SC)

John Houghton	**301 903-8288**	**JOHN.HOUGHTON@science.doe.gov**
Pat Dehmer (BES)	**301 903-3081**	**PATRICIA.DEHMER@science.doe.gov**



Biological- and Biomass-Based Hydrogen Production

Roxanne Danz

Barriers

Hydrogen Production from Biomass

BARRIERS

- Cost
- Feedstock availability
- Fermentative micro-organisms

Targets and Status

Hydrogen Production from Biomass

Characteristics	Units	2003 status	2005	2010
Central Hydrogen from Biomass via Gasification & Steam Reforming				
Total cost	$/kg H_2	3.60	3.30	2.60
Net energy ratio		28	29	34
Central Hydrogen from Biomass via Pyrolysis & Steam Reforming				
Total cost	$/kg H_2	3.80	3.70	2.90
Net energy ratio		26	27	32

Projects

Hydrogen Production from Biomass

• H_2 Production by Catalytic Reforming of Pyrolysis Vapors	NREL
• Pyrolysis of Waste Plastics and Greases	NREL
• Fluidizable Reforming Catalysts	NREL
• Bacterial Colony Fermentation	Iowa State University
• Biological Water Gas Shift	NREL

Posters

Hydrogen Production from Biomass

• Biomass-Derived H_2 from a Thermally Ballasted Gasifier	Iowa State University
• Supercritical Water Partial Oxidation	General Atomics
• Techno-Economic Analysis of H2 Production by Gasification of Biomass	Gas Technologies Institute
• Renewables Analysis	Directed Technologies, Inc.
• Biomass Pyrolysis Unit for the Production of H_2 from Peanut Shells	Clark University

Discussion Points

- Gasification and pyrolysis technologies – start moving toward system integration in addition to improving components
- Fermentation technologies – investigate this area to determine cost and production capability
- Other concepts – look for additional feasible technologies to produce hydrogen from biomass

NREL
National Renewable Energy Laboratory

Hydrogen from Biomass

Catalytic Reforming of Pyrolysis Vapors

R. Evans, L. Boyd, C. Elam, S. Czernik,
R. French, C. Feik, S Phillips, E. Chornet
National Bioenergy Center in
Collaboration with the Clark Atlanta University Team

U.S. DOE Hydrogen and Fuel Cells Merit Review Meeting

Berkeley, CA May 19-23, 2003

Project Goals

- Demonstrate the production of hydrogen from biomass by pyrolysis –steam reforming for $2.90/kg by 2010
- Barriers:
  - Vapor Conditioning
  - Catalyst Development and Regeneration
  - Reactor Configuration
  - Heat Integration
  - Deployment: H2 + Co-products
- Milestone: Verify advanced catalysts and reactor configuration for fluid bed reforming of biomass pyrolysis liquid at pilot scale (500 kg H2/day) with catalyst attrition rates < 0.01%/day. 4Q, 2009

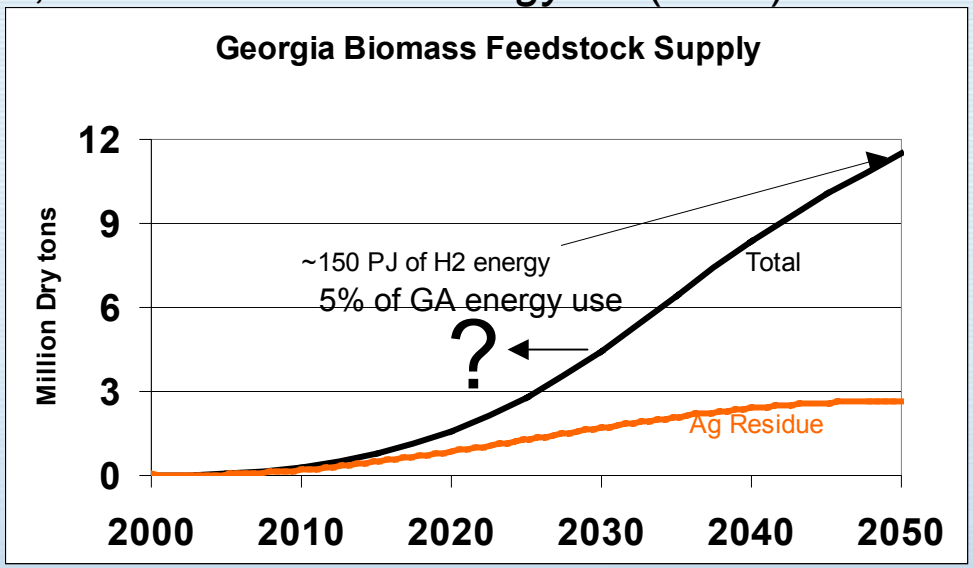
Biomass Feedstocks

$$6\ CO_2 + 6\ H_2O \xrightarrow[\text{sunlight}]{} C_6H_{12}O_6 + 6\ O_2$$

Potential : 15% of the world's energy by 2050.

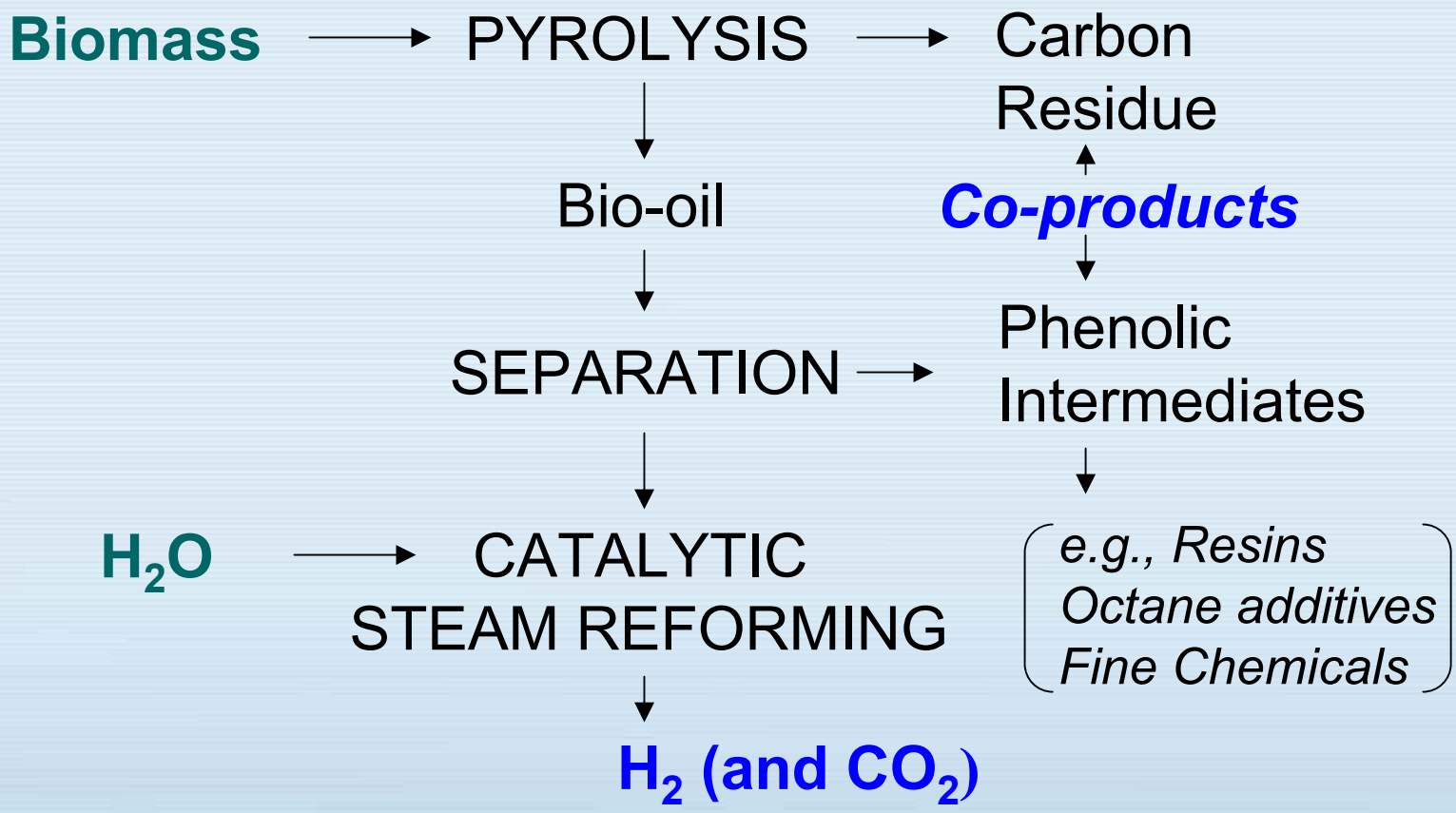
Fischer and Schrattenholzer, *Biomass and Bioenergy* 20 (2001) 151-159.

Crop residues
Forest residues
Energy crops
Animal waste
Municipal waste

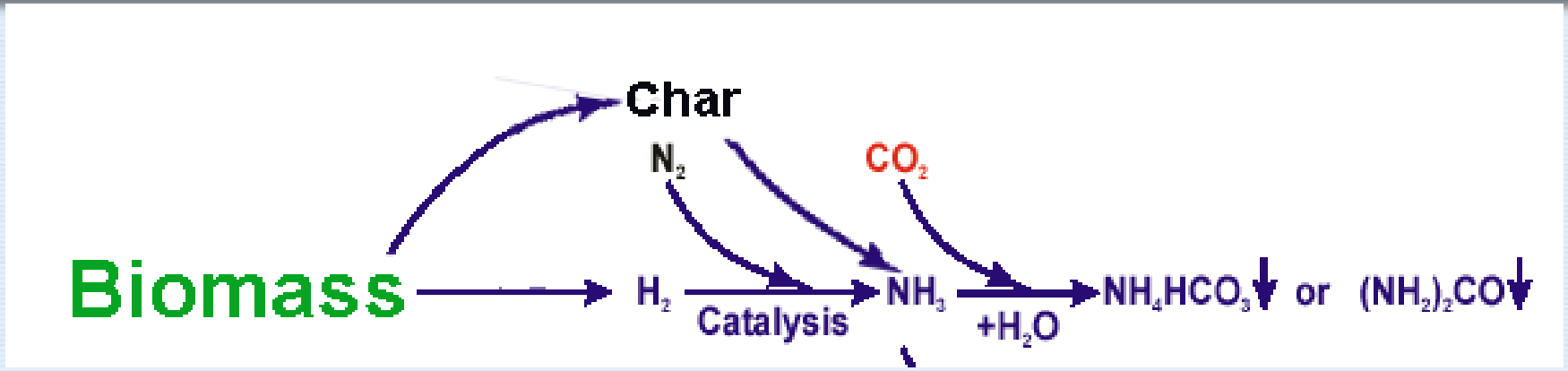


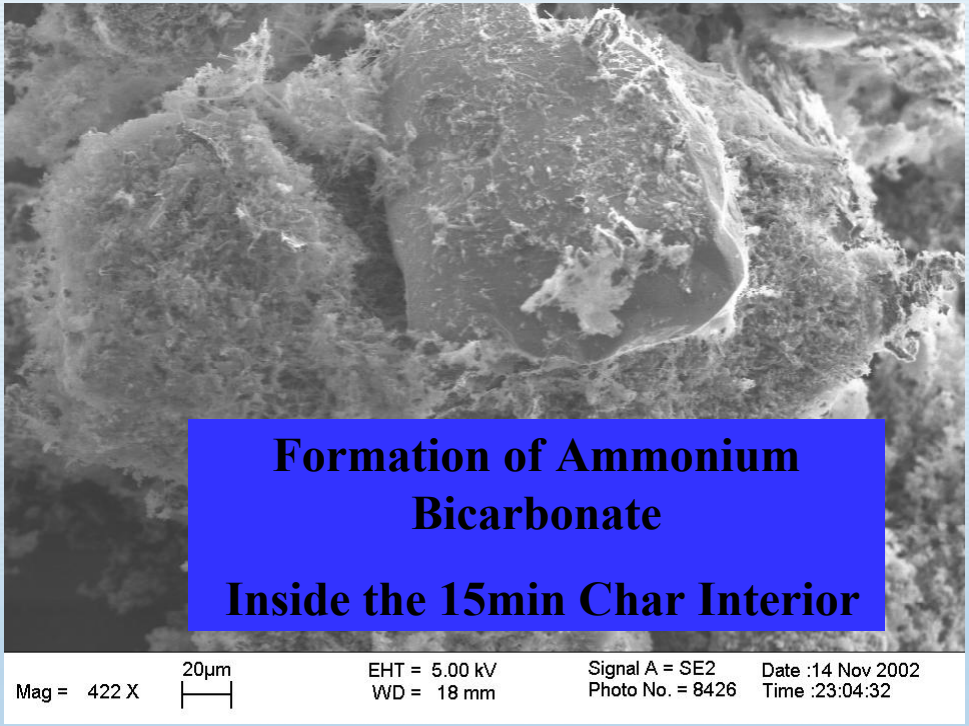
Issues: Biomass Availability and Costs

Pyrolysis Process Concept



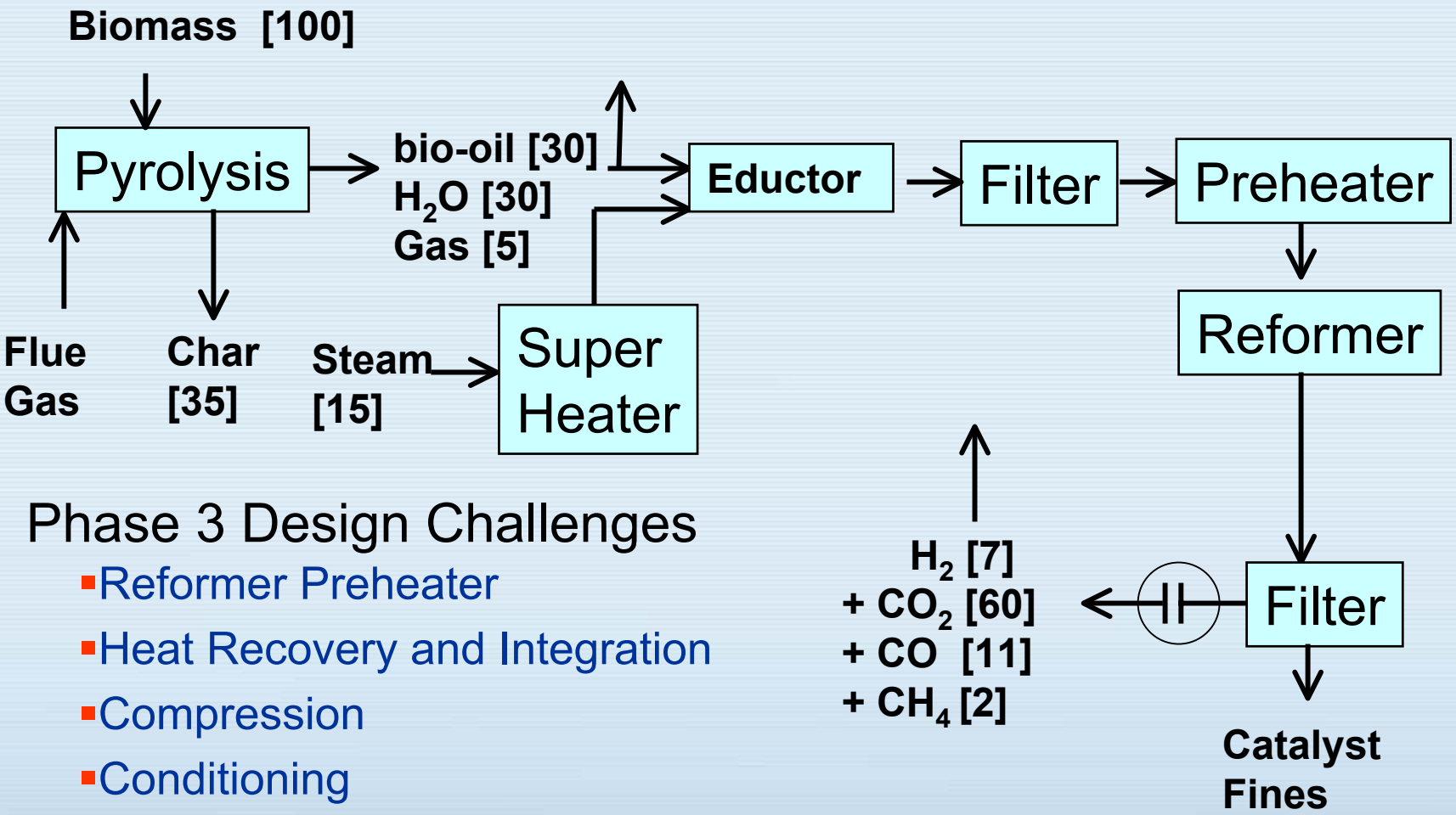
Biocarbon-Based Fertilizers





Courtesy
D. Day,
Eprida/
Scientific Carbons
Inc.

Phase 2 System

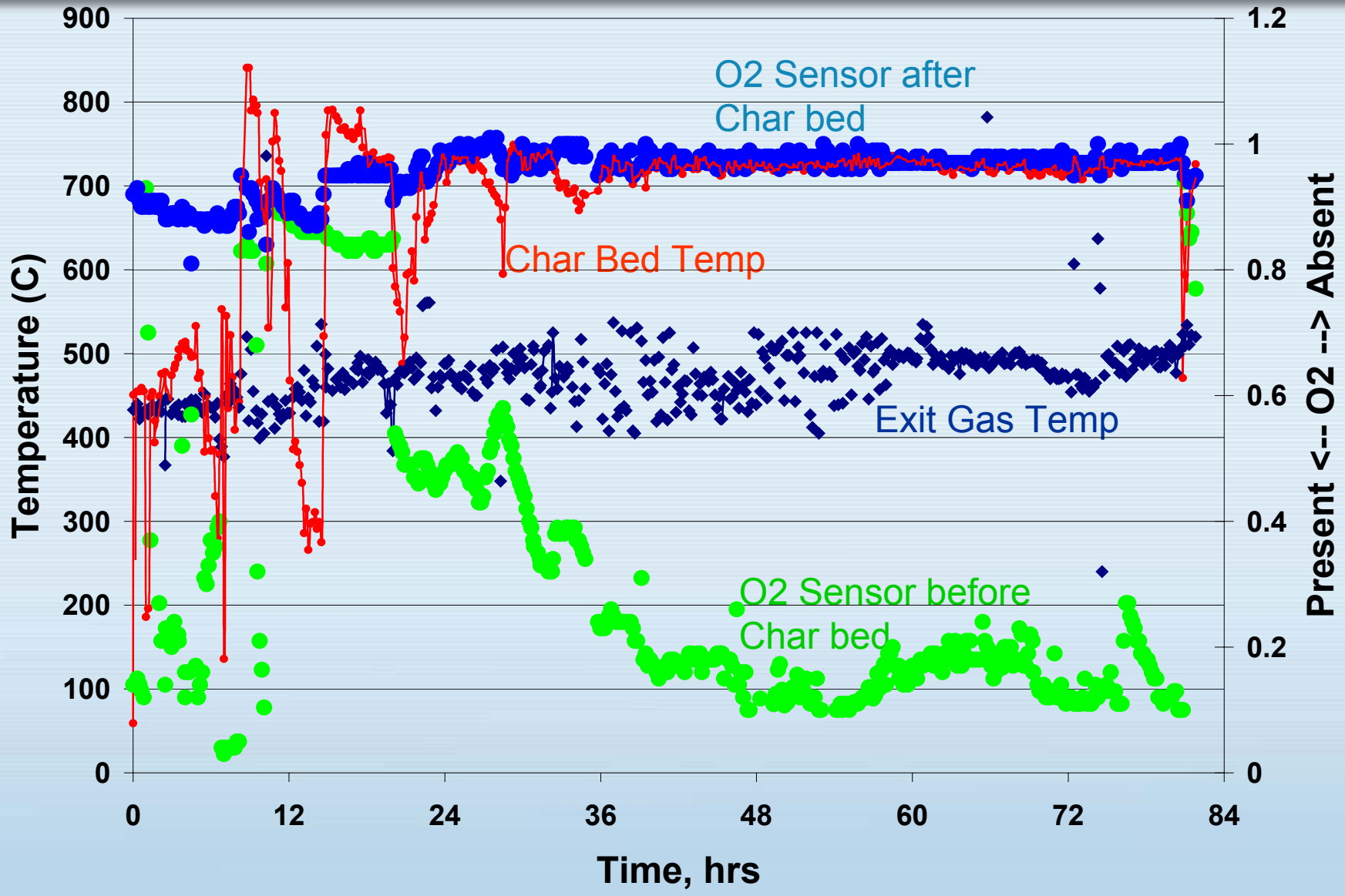


Phase 3 Design Challenges

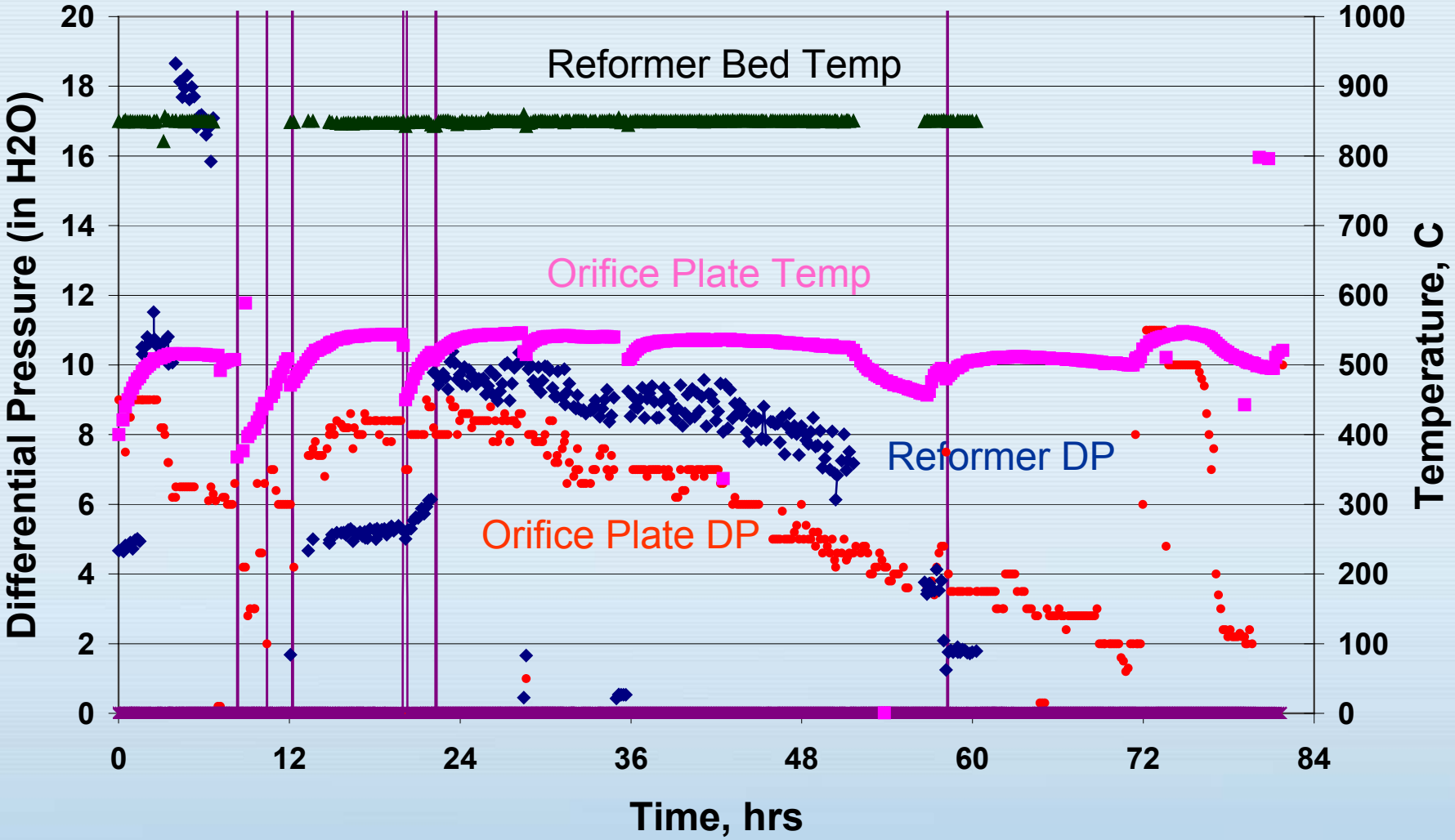
- Reformer Preheater
- Heat Recovery and Integration
- Compression
- Conditioning
- Coproduct Optimization
- Pyrolyzer Heat Optimization

Blakely Georgia Site

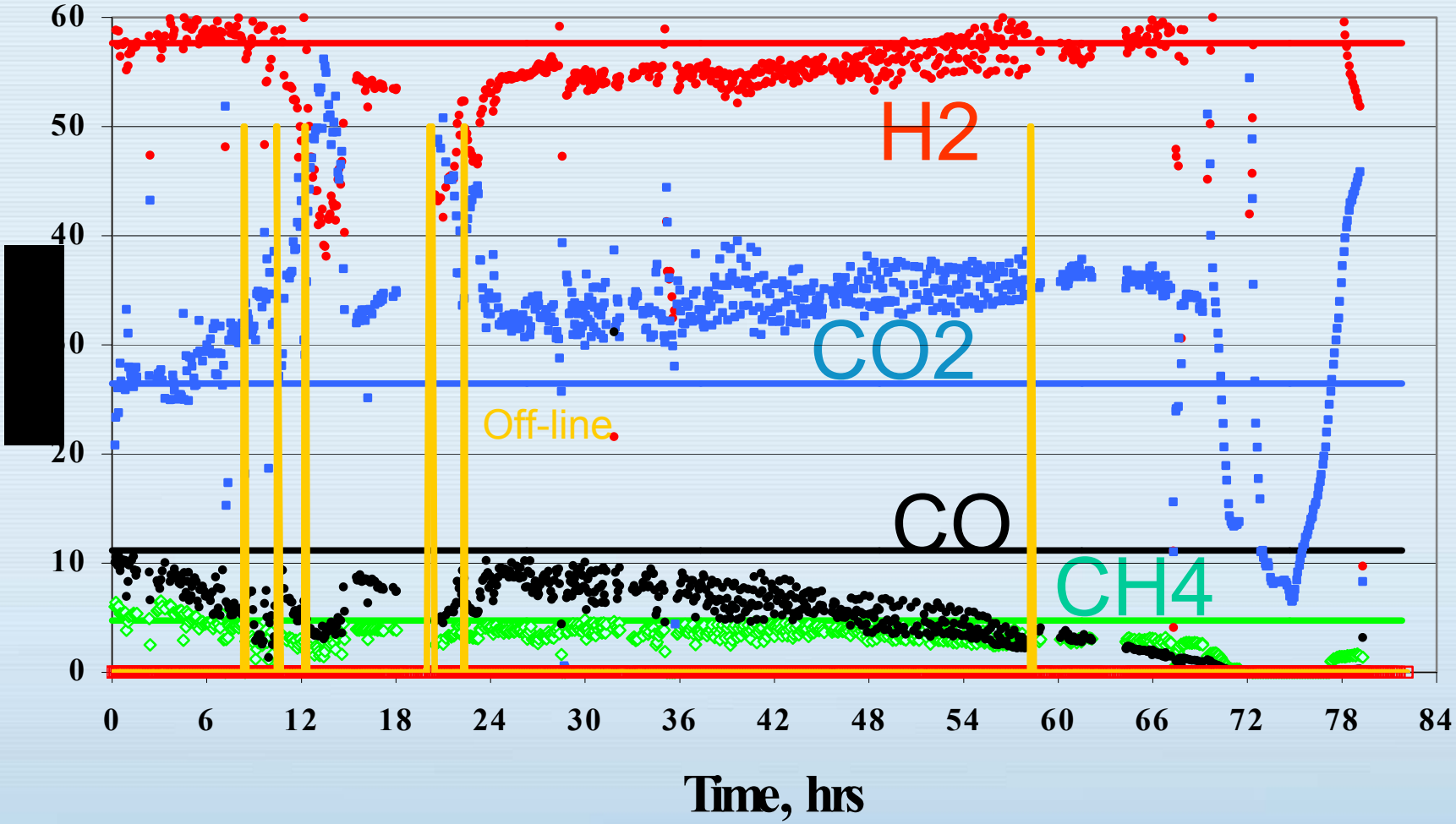
Pyrolysis Unit Performance



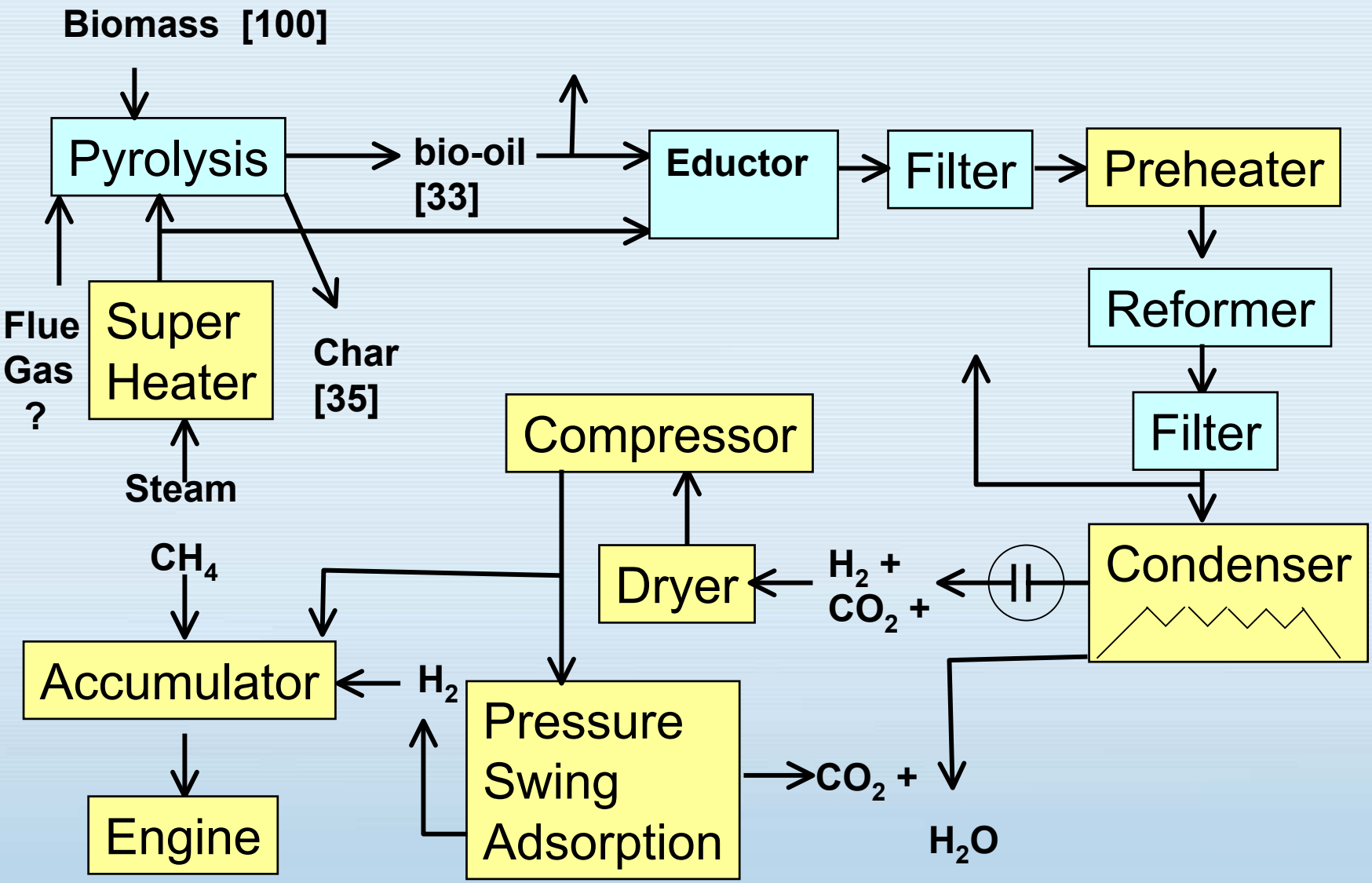
Reformer Performance



Gas Composition



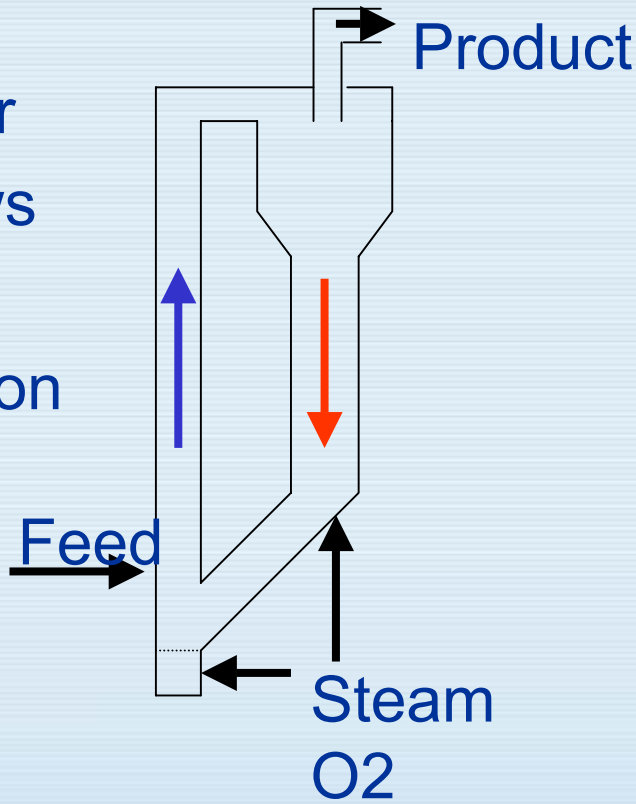
Phase 3 System



R&D	Demonstration		
	I: Initial	II: Design	III: Pilot
Process Understanding	Debugging	Development to Reduce Costs	Early Commercial
Component Technologies	Systems integration	Systems Demonstration	Communication
Scoping economics	Mass Balance	Mass & Energy Balances	Full time operation
ES&H	ES&H	ES&H	ES&H

: Circulating Fluid Bed

- Smaller Catalyst Particles → Harder
- Fluid Dynamics → Higher Gas Flows
- Direct Heating → Partial Oxidation
- Optimized Catalytic Coke Gasification

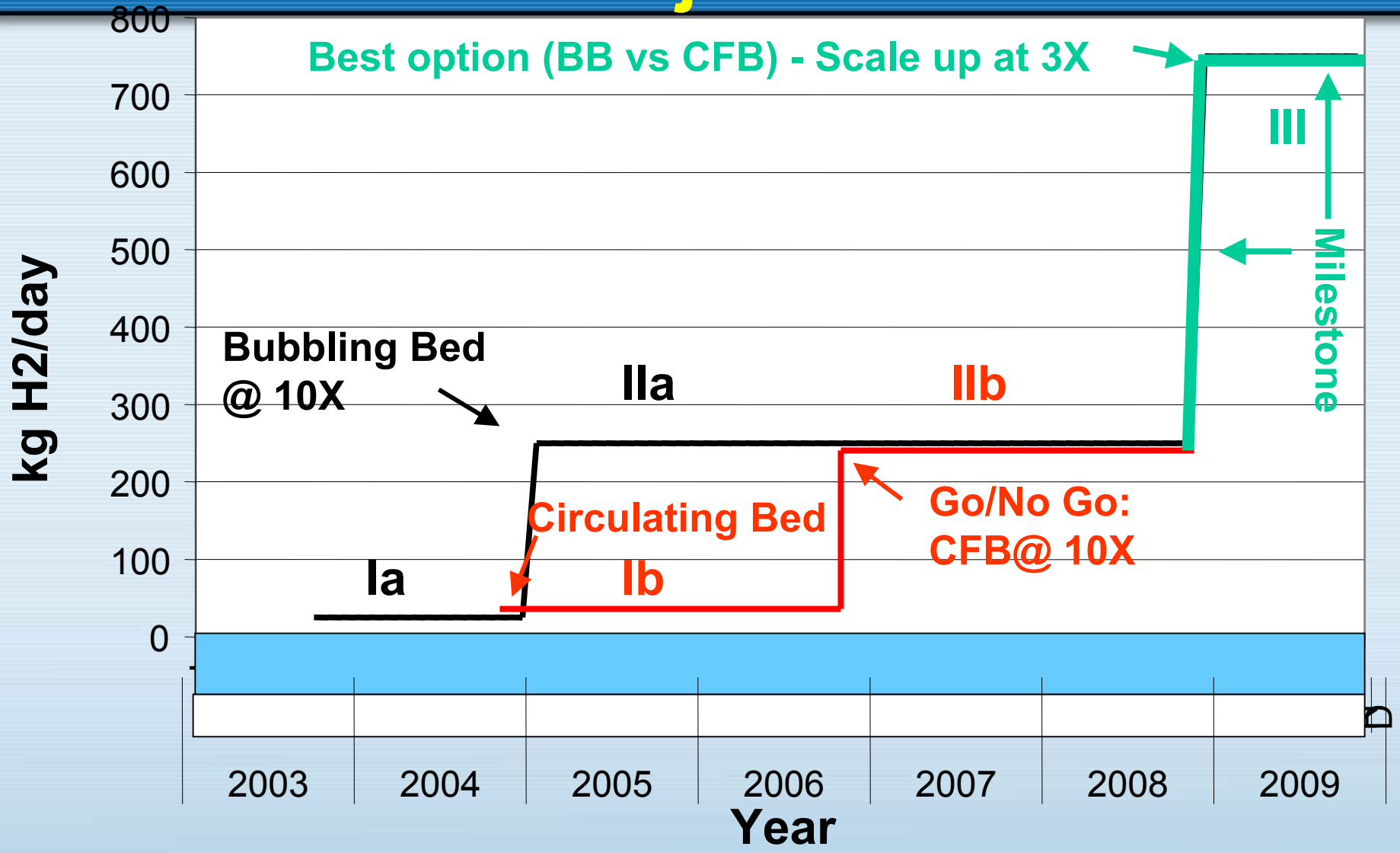


Reforming $C_xH_yO_z + H_2O \rightarrow H_2 + CO_x$

Water gas shift: $CO + H_2O \rightarrow CO_2 + H_2$

Coke Gasification: $C + H_2O \rightarrow CO + H_2$

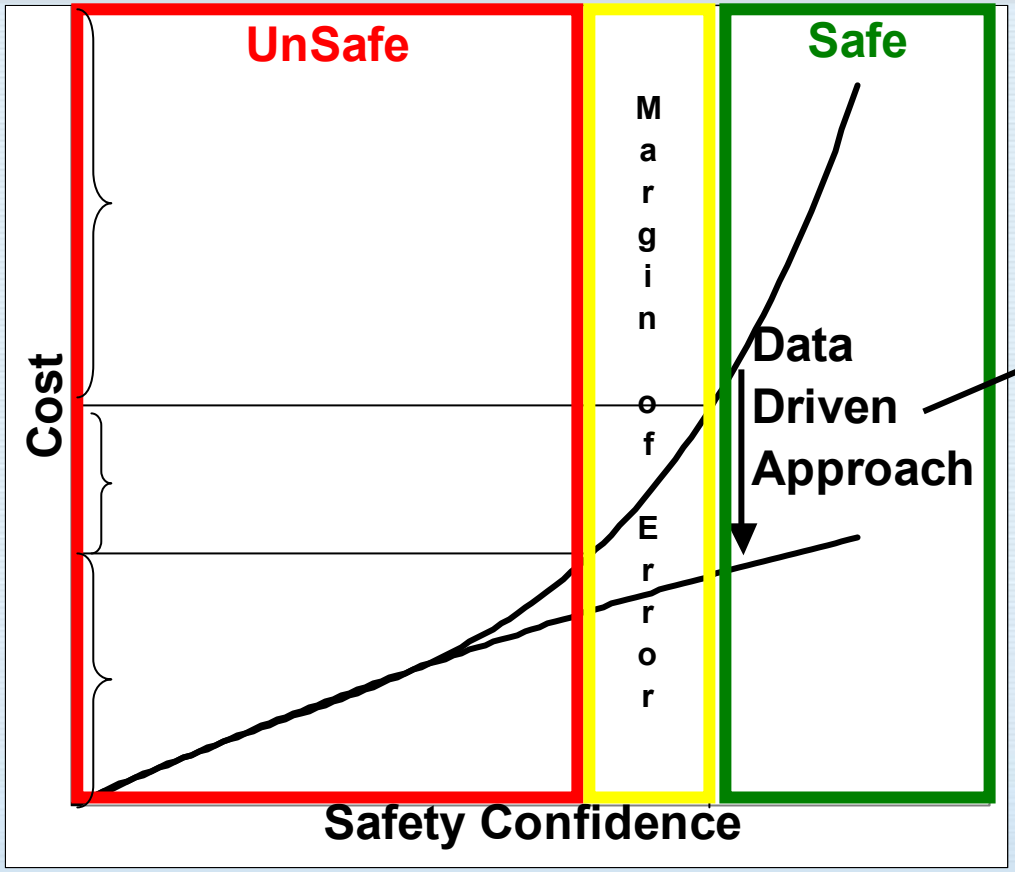
Project Time Line



FY02 Review Comments

- ***What are the Advantages of Pyrolysis/CSR vs Gasification/WGS?***
  - Distributed Resource→ Centralized Reforming
  - Coproduct → Better Economics
  - Smaller Scale → Lower Capital + Feedstock Cost
- ***Maintain a Communication Plan***
  - RACI Analysis for Phase III
- ***"Watch out for Safety"***
  - Feature Safety in Phase 3
  - Change Site to University of Georgia Biomass Research Facility to promote safety development and education and tech transfer to biomass industry

Safety Approach



U of GA Facility:

- Train the Trainers
- Process control for safety **AND** efficiency (lower cost)

Must Develop:

- A Facility to study system safety boundaries
- A Statistical Basis for Safety Confidence

NREL
National Renewable Energy Laboratory

Hydrogen from Post-Consumer Residues

S. Czernik, R. French, R. Evans, E. Chornet

National Bioenergy Center

U.S. DOE Hydrogen and Fuel Cells Merit Review Meeting

Berkeley, CA May 19-23, 2003

Goal of the Project

This work is one of three tasks in the Biomass to Hydrogen project.

Goal: develop and demonstrate technology for producing hydrogen from biomass at $2.90/kg purified hydrogen by 2010. By 2015, be competitive with gasoline.

Objectives of the Task

Explore feasibility of producing hydrogen from low-cost, potentially high-hydrogen-yield renewable feedstocks that could complement biomass, increase flexibility and improve economics of Biomass to Hydrogen process.

Can help overcome a barrier of high cost and availability of feedstock.

Demonstrate efficiency of pyrolysis/reforming technology in application to readily available post-consumer wastes: plastics, trap grease, mixed biomass and synthetic polymers.

Addresses the challenge of technology improvement.

Potential for Hydrogen

Plastics wastes: 15 Mt/year; potential for producing 6 Mt/year of hydrogen (energy equivalent 0.8×10^{18} J/year) – enough to fuel 15-20 million fuel cell vehicles

Requires development of collection programs and separation technologies.

Target streams: manufacturing residues (textiles), MRF tailings.

Trap grease recovered: 6 kg/year/person - 1.5 Mt/year; potential for 0.5 Mt/year hydrogen.

Assuming that processing costs will be comparable to those for residual oil ($0.7/kg H_2), trap grease presents a near-term market opportunity for the production of hydrogen.

Approach

Technology being developed for producing hydrogen from biomass:

- Pyrolysis or partial oxidation of biomass, plastics, and other solid organic residues.
- Catalytic steam reforming of the resulting pyrolysis gases and vapors.
- Catalytic steam reforming of biomass-derived liquid streams (trap grease).

Opportunities to co-process different feedstocks.

Process Reactions

$$\text{Polymers} \xrightarrow{500\text{-}800^{o}C} \text{Monomers and other volatile compounds}$$

$$C_nH_mO_k + (n\text{-}k)\ H_2O \xrightarrow{800^{o}C,\ cat.} n\ CO + (m/2 + n\text{-}k)\ H_2$$

$$n\ CO + n\ H2O \longleftrightarrow n\ CO_2 + n\ H_2$$

Project Timeline

Hydrogen from Post-Consumer Residues

Timeline

FY02 03 04 05 06 07 08 09

Production of Hydrogen by Catalytic Steam Reforming of Trap Grease

Reforming tests using commercial catalyst — 80% yield, 150 hours on stream, catalyst attrition losses.

Reforming tests using NREL fluidizable catalysts — 80% yield, low attrition of catalyst

Feedstock clean up strategy and long-term catalyst performance demonstration

Co-process trap grease with other biomass-derived liquids — 80% yield, low catalyst attrition, long-duration activity

Production of Hydrogen by Integrated Pyrolysis/Reforming of Plastics

Proof of Concept at Micro-Reactor/MBMS scale — Completed

Bench-scale tests using integrated bubbling bed reactor system

Bench-scale tests using plastic mixtures (gas clean up) — 80% yield from variety of feedstocks

Bench-scale co-processing of biomass and other feedstocks

Production of Hydrogen from Different Feedstocks in Support of the Scale up Effort

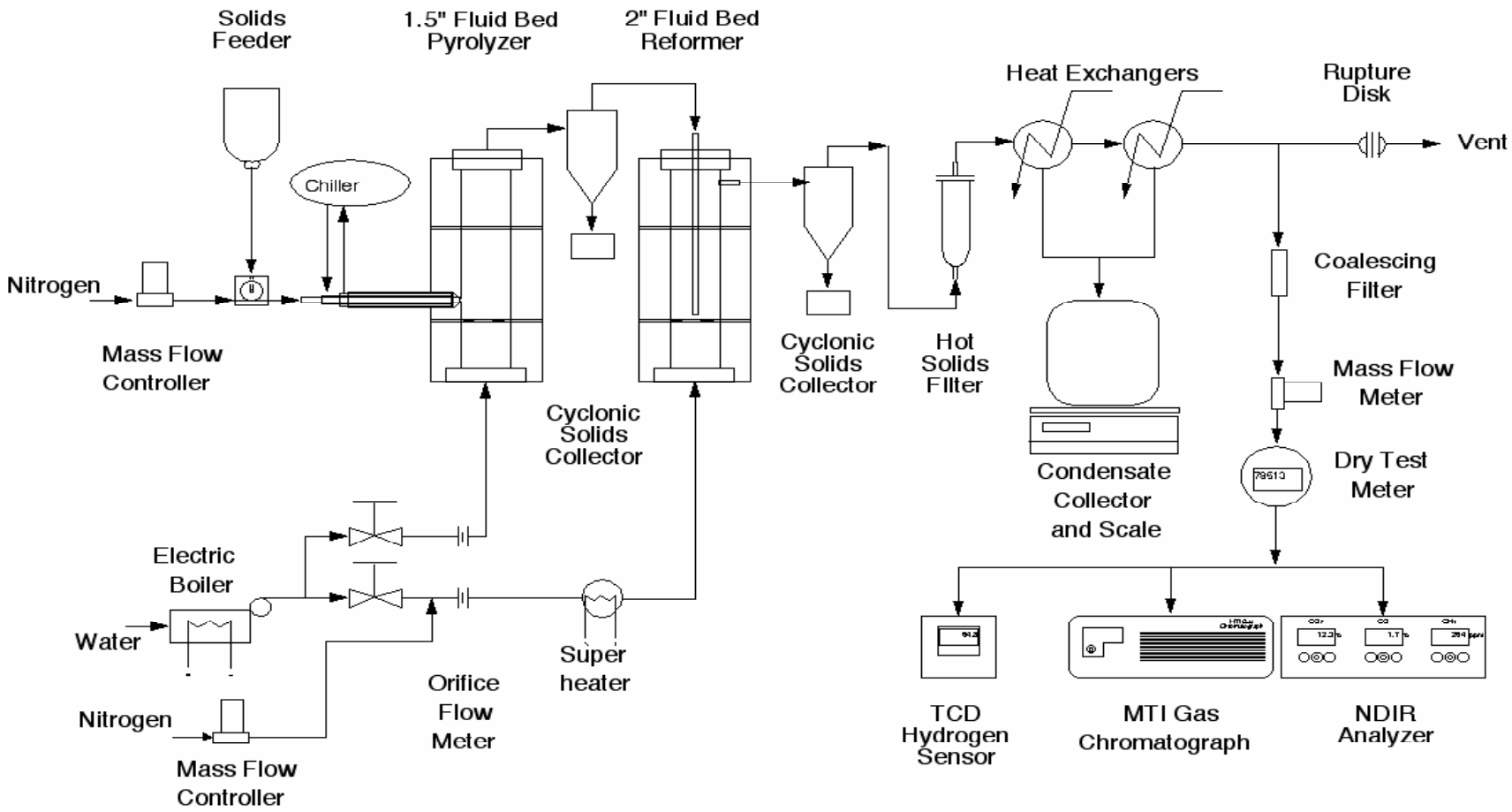
Construction of bench-scale circulating fluid bed reformer

Bubbling and circulating bed tests on flexible feedstocks

Milestones

1. Production of hydrogen from plastics by fluidized bed pyrolysis/reforming process; yield 80% of stoich. (34 g H_2/100 g PP). September 2003.
2. Demonstrate efficiency of fluidisable, attrition resistant catalyst developed at NREL for trap grease reforming; 80% of the stoich. yield (28 g H_2/100 g grease). September 2003.

Fluidized Bed Integrated Pyrolysis Reforming System



Process Conditions

Pyrolysis zone at 600 - 700°C
(Operated in both pyrolysis and POX mode)
Steam flow: 240 g/h
Feed rate: 60 g/h polypropylene

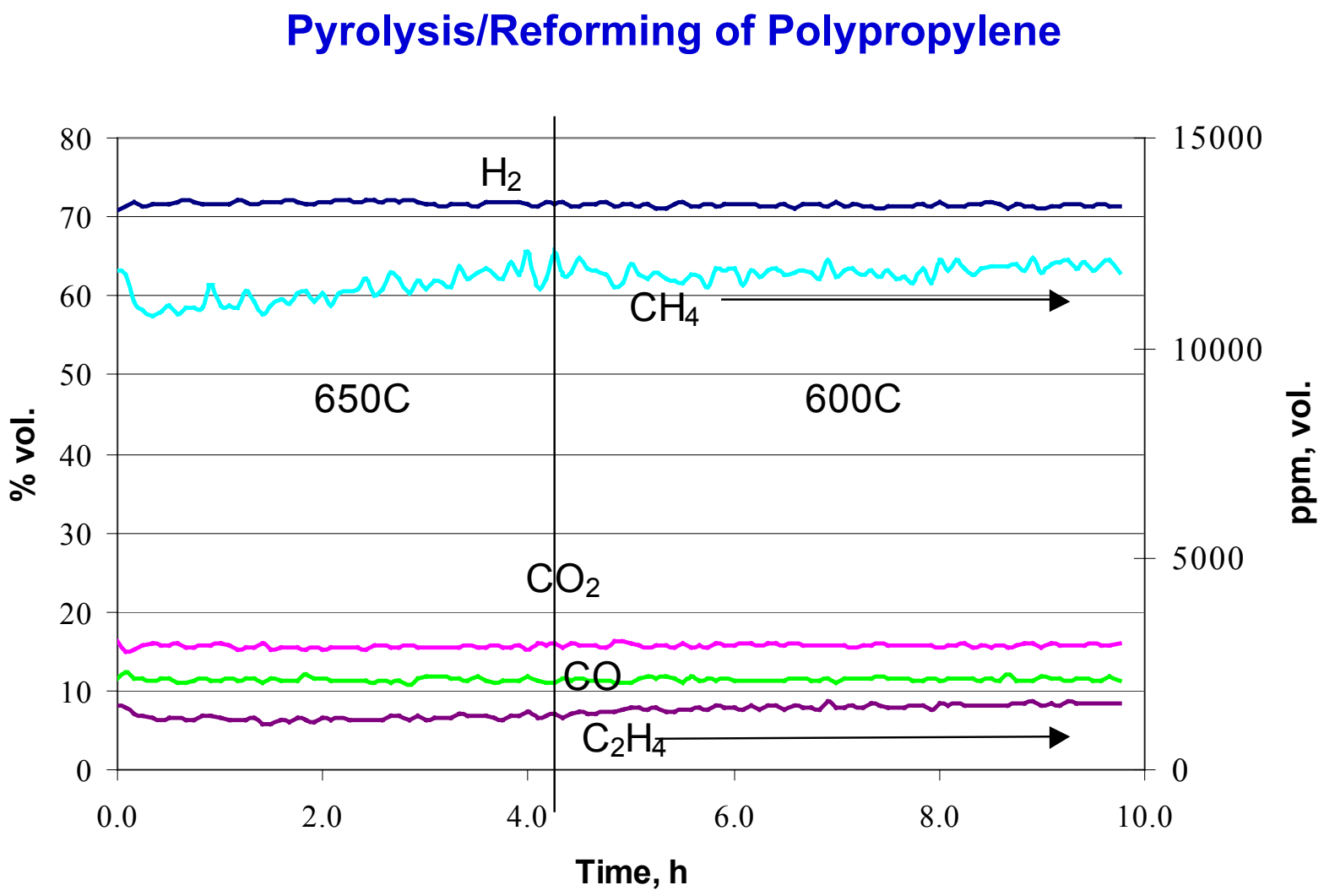
Reforming zone at 850°C

Commercial nickel-based catalyst

Molar (Steam/Carbon): 4.6

G_{C1}HSV: 1600 h^{-1}

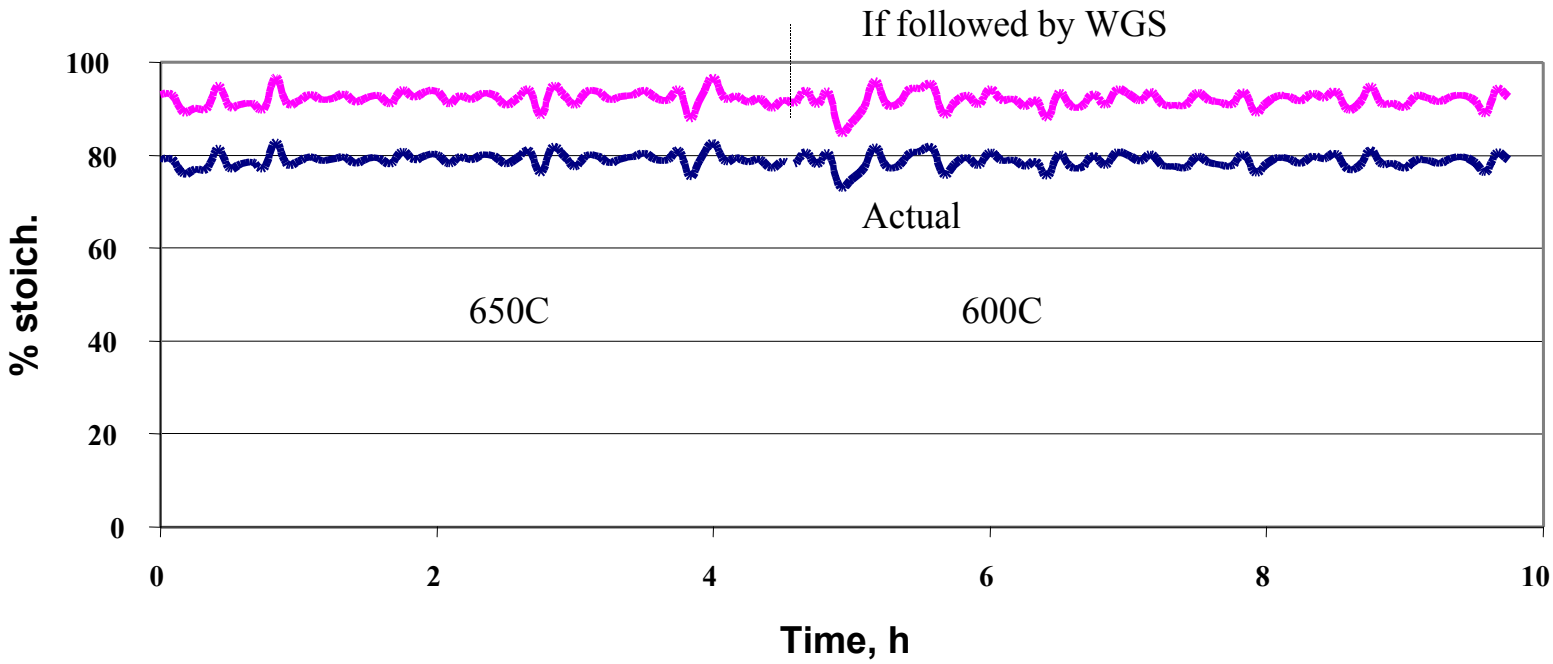
Product Gas Composition



Yield of Hydrogen

Pyrolysis/Reforming of Polypropylene

(stoich. yield: 42.9 g H_2/100 g PP)



Trap Grease

Collected from different sites in the U.S. by Pacific Biodiesel for DOE Biodiesel Program.

Mixture of C_{16} and C_{18} free fatty acids and fats;

Elemental analysis:

C: 76.2%; H: 11.8%; O: 11.9%;

N: 0.02%; S: 70 ppm; ash: 0.1%;

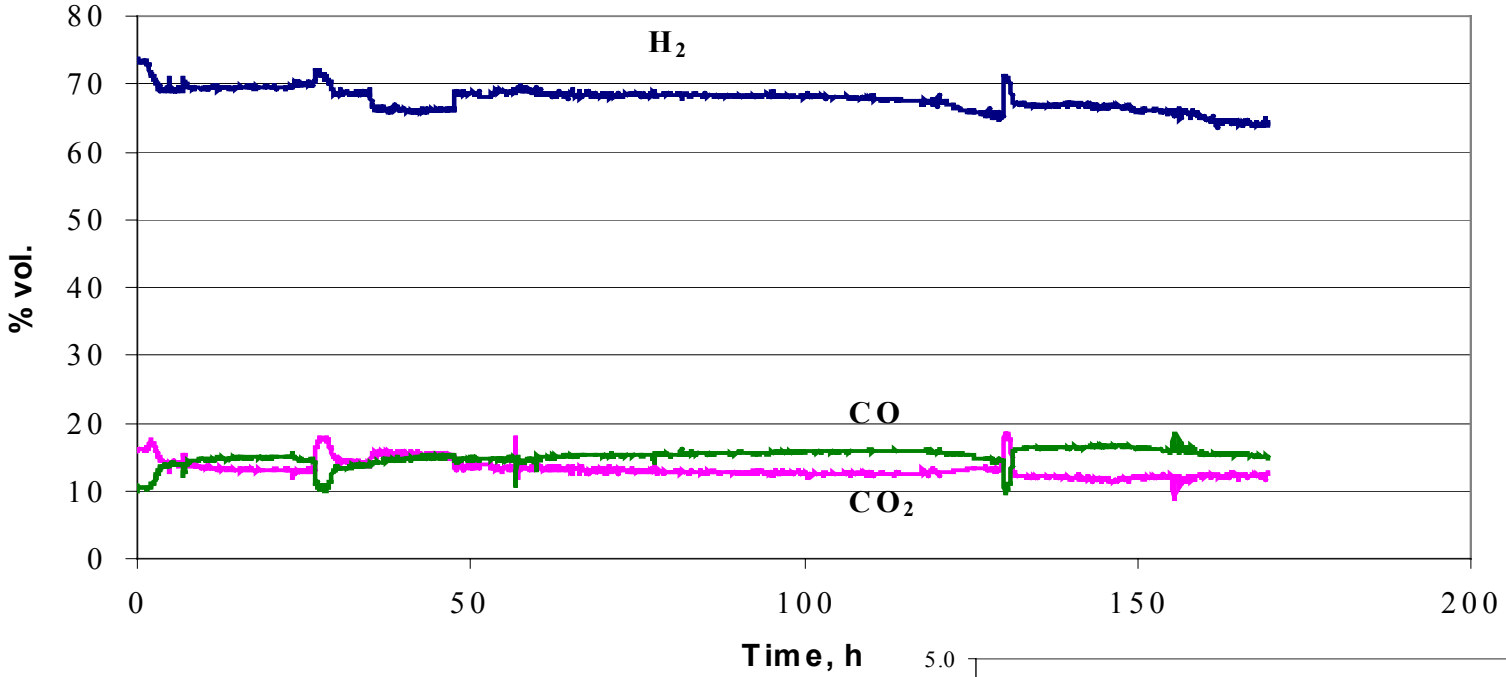
Process conditions:

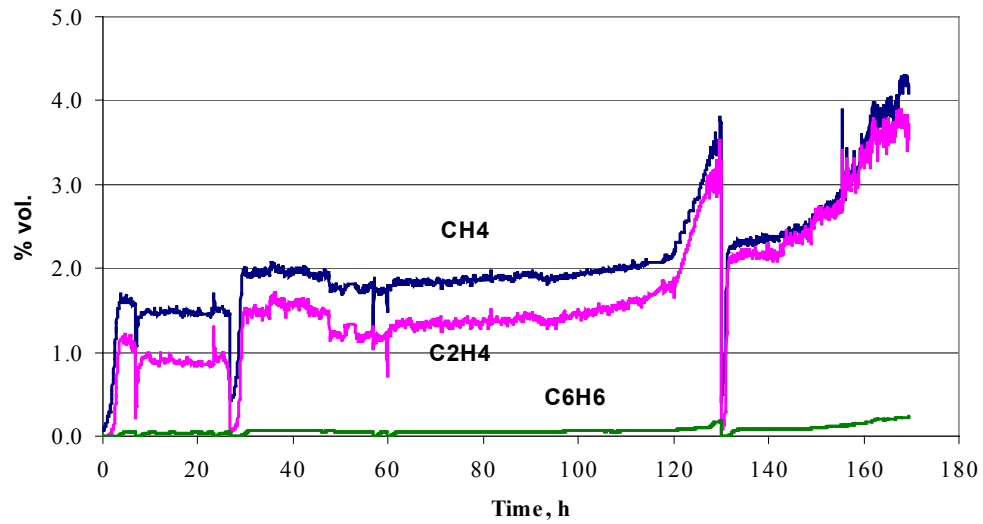
Temperature: 850°C, NREL fluidisable catalyst

Grease feed rate: 42 g/h, steam flow: 240 g/h

S/C: 5, G_{C1}HSV: 970 h^{-1}

Trap Grease Product Gas Composition

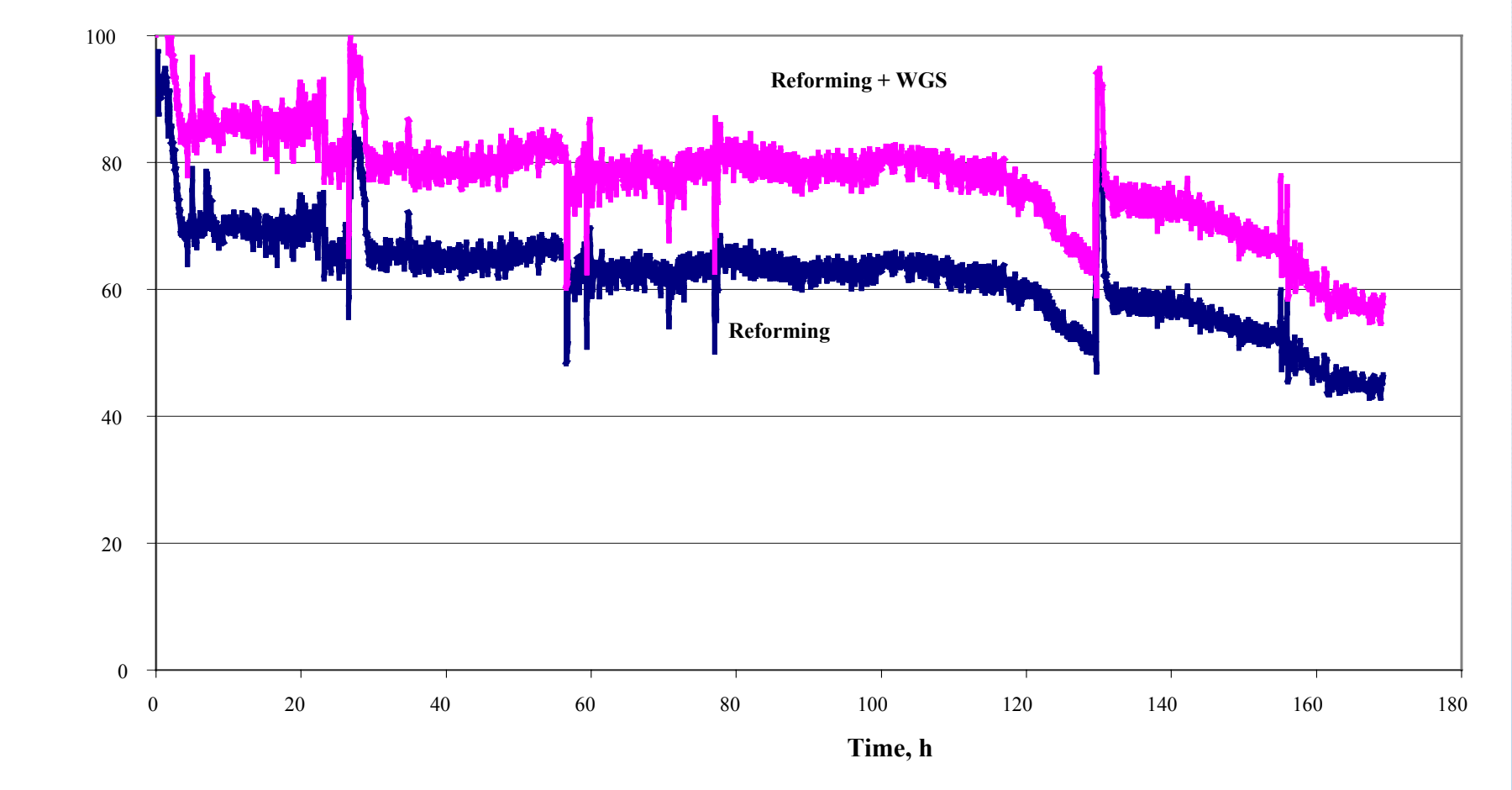




Yield of Hydrogen

Reforming Trap Grease

(Stoich. yield of H_2: 35 g/100 g grease)



Other Accomplishments

Publications:

Chornet, E. and Czernik, S., Renewable fuels: Harnessing hydrogen, **Nature 2002, 418, 928-929.**

Czernik, S., French, R., Feik, C., Chornet, E.; Hydrogen by Catalytic Steam Reforming of Liquid Byproducts from Biomass Thermoconversion Processes, **I&EC Research 2002, 41, 4209-4215.**

Record of Invention filed in U.S. DOE.

Collaboration:

Interface Research Corp., National Diesel Board, American Apparel Manufacturers Association.

Future Work

Complete milestones for FY 2003.

Demonstrate pyrolysis/reforming process for complex feedstocks (textiles, mixed plastics) using commercial and NREL developed catalysts.

Demonstrate production of hydrogen by co-processing renewable (solid and liquid biomass and wastes) and fossil (natural gas) feedstocks.

Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming

K. Magrini-Bair, S. Czernik, R. French, Y. Parent, S. Landin and S. Chornet

May 19, 2003

NREL

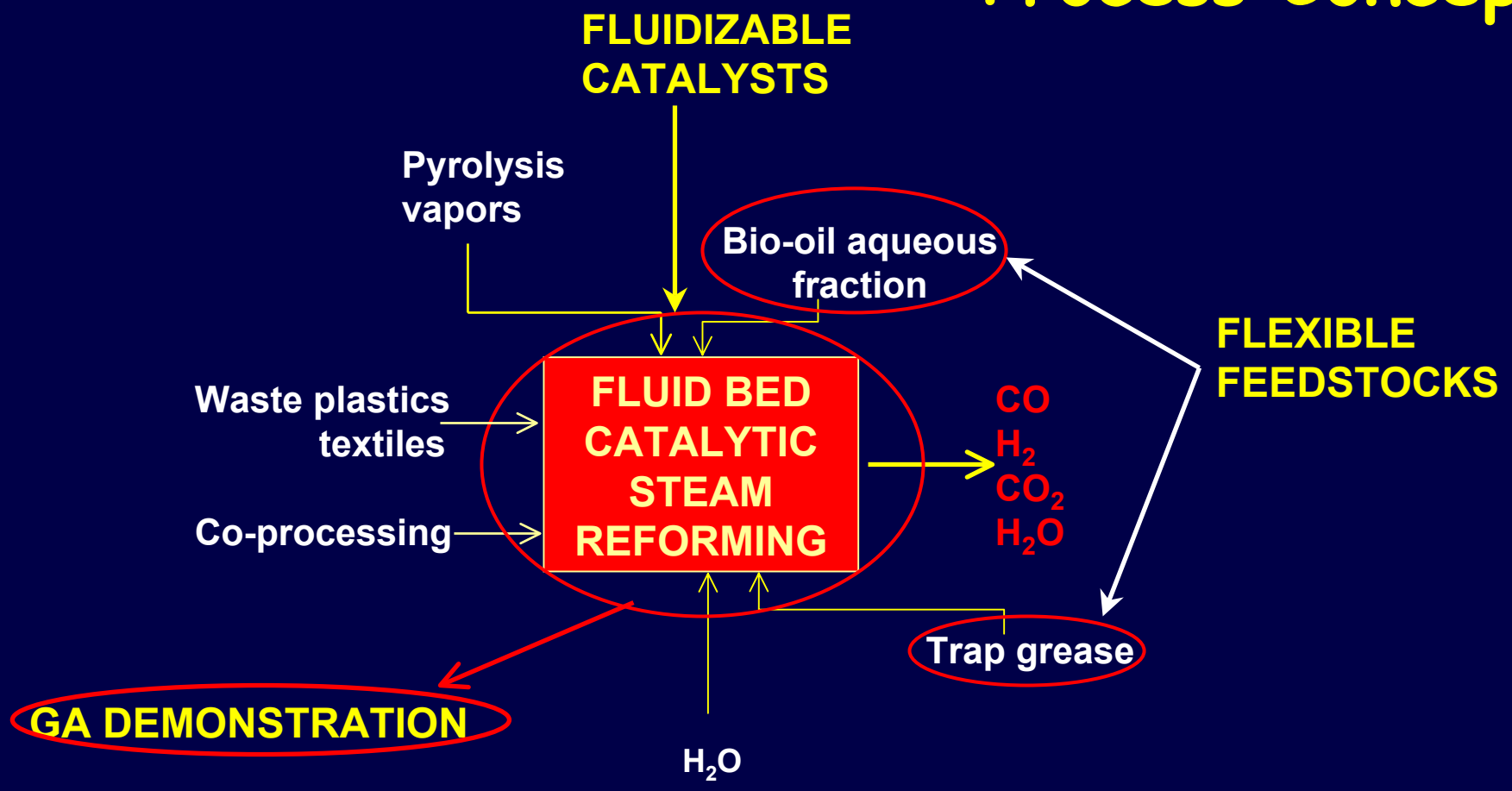
Relevance/Objective

Develop and demonstrate technology to produce hydrogen from biomass at $2.90/kg plant gate price based on 750 t/day by 2010. By 2015: be competitive with gasoline.

Technical Challenges

- Improve reforming catalysts
  - Accept flexible feedstocks
- Improve catalyst regeneration

Process Concept

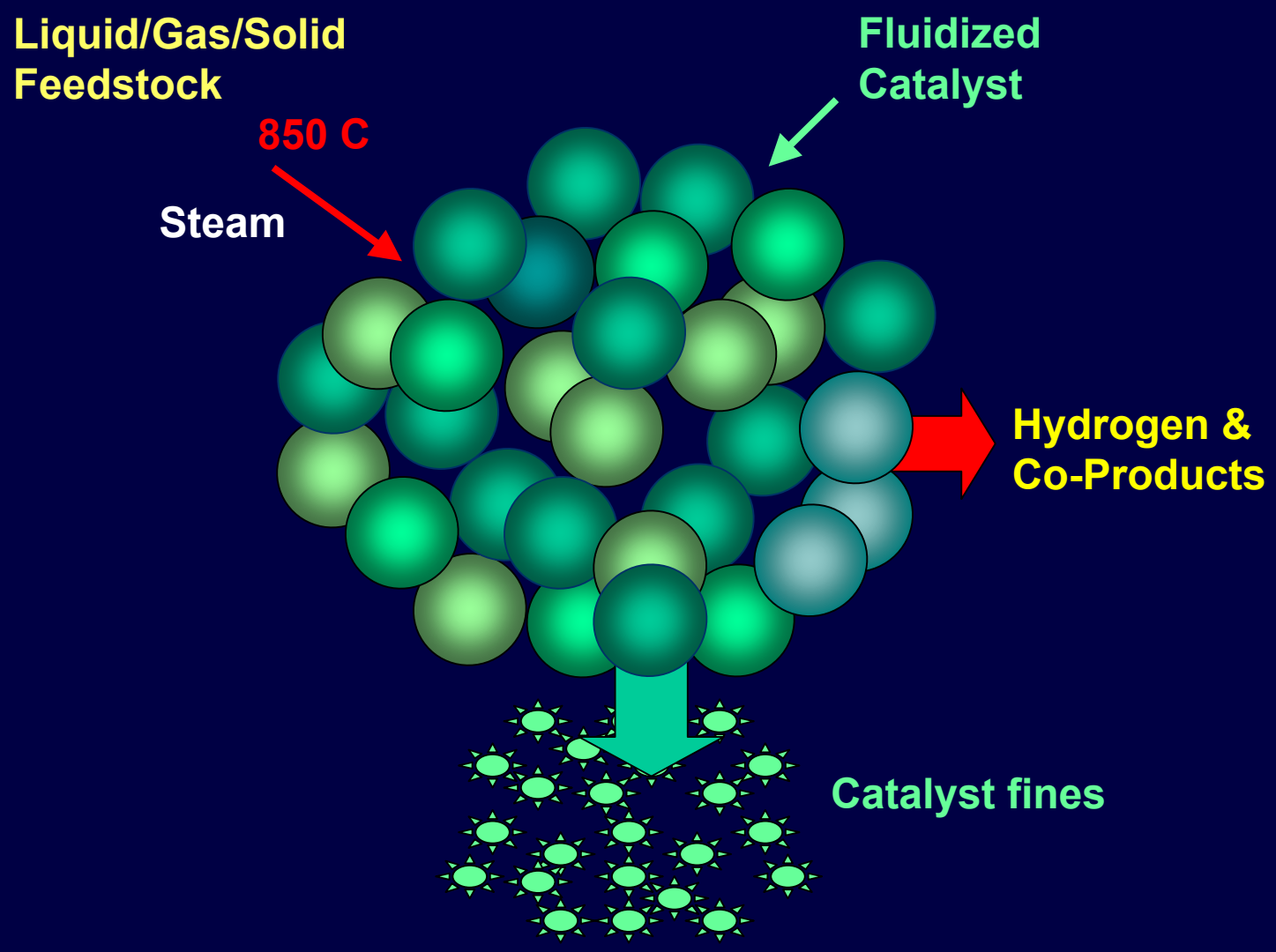


Reforming: $CxHyOz + H_2O(g) \rightarrow H_2 + xCO$

Water gas shift: $H_2O + CO \longrightarrow CO_2 + H_2$

Gasification: $C + H_2O(g) \longrightarrow COx + H_2$

Problem: Catalyst Attrition



Approach: Drivers and Impacts

- Feedstock complexity requires fluidized catalysts
- Industrial reforming catalysts exist for fixed bed processes. Industrial catalysts attrit when fluidized.
- Catalyst loss from fines causes significant performance, cost, and environmental impacts
- New markets for robust fluidizable catalysts
  - Lower Ni or non-Ni compositions
- New catalysts required for:
  - Flexible feedstock processing
  - Lower reforming temperatures

Approach/Fluidizable Catalysts

- Identify/test best industrial reforming catalysts (naptha)
- Identify/test "***off the shelf***" particulate aluminas for use as catalyst supports in fluidized bed reactors
- Formulate, evaluate and optimize ***multifunctional, multicomponent*** catalysts made from these supports
- Evaluate renewable feedstocks

Fluidizable Catalyst Development

Fluidizable Supports (bubbling bed-BB, circulating bed-CB)
- Identify industrial materials
- Assess attrition rate
- Characterize properties
- Improve/modify support preparations/CoorsTek

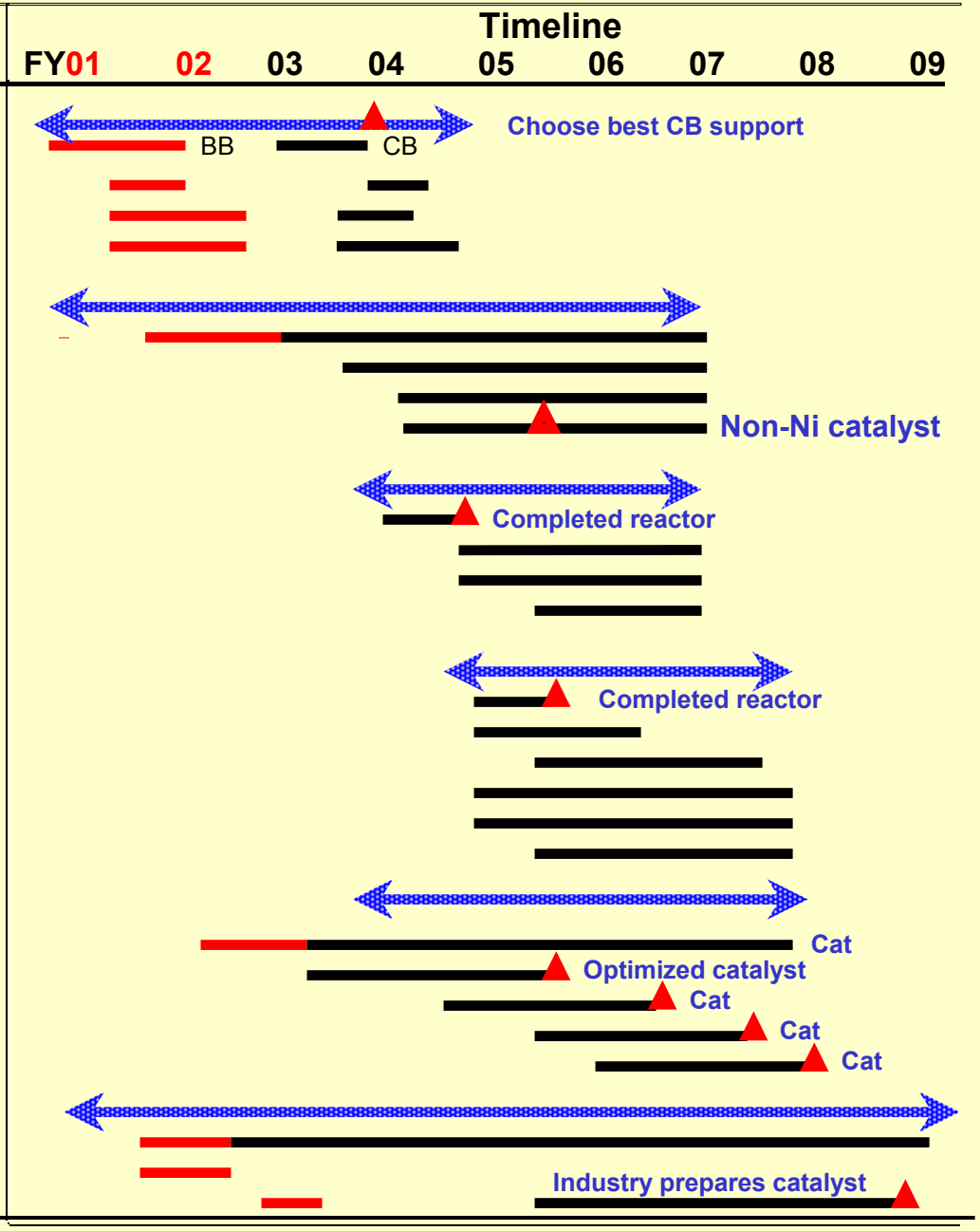
Catalyst Development
- Develop/test/optimize BB/CB catalysts
- Characterize catalysts
- Develop lower temperature catalysts
- Assess non-Ni catalysts

Rapid screen microreactor
- Design/modify existing system
- Choose/make catalyst compositions
- Screen catalysts
- Optimize compositions

Kinetics/Deactivation Mechanisms
- Add pyrolysis microreactor capability
- Coking and gasification
- Water gas shift
- Reforming
- Deactivation (S, Cl)
- Reactivation

Catalyst Design for Varied Feedstocks
- Pyrolyzed biomass liquids and vapors
- Waste grease (S)
- Waste plastics (Cl)
- Waste textiles
- Co-processing

Industrial Collaborations
- CoorsTek Ceramics/Carboceramics
- Sud Chemie
- Industry/catalyst scale up



Economic Impact of Catalyst Attrition

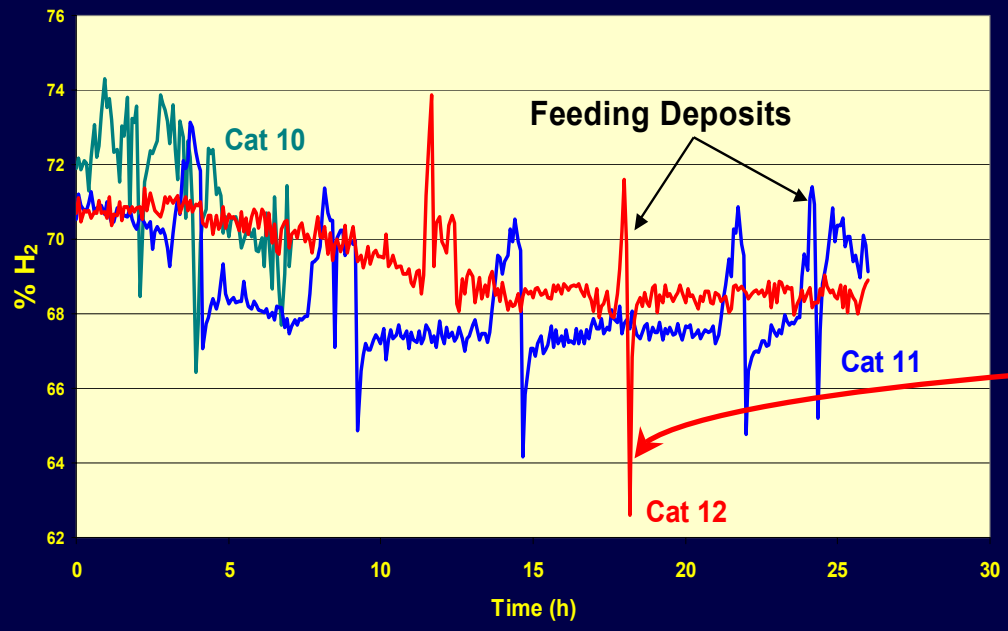
Catalyst	Wt. in Reactor (g)	Wt. out Reactor (g)	% Loss per hr	Loss Cost $/hr[2]
Best of the Industrial Catalysts				
Commercial Ni Cat. 1 (Sud Chemie C 11 NK)	292.7	208.7	0.6	19.20
Commercial Ni Cat. 2 (ICI 46-1 S)	250.2	167.1	0.7	22.40
Best of the Industrial Supports Tested				
90% Alumina	251.4	248.8	0.01	0.03
99% Alumina	298.9	299.6	0.0	0.00
NREL Catalysts				
Ni-Mg/90% Alumina[1]	250.1	250.1	0.005	0.015

Due to Catalyst Attrition

1 with Ni after methanol reforming

2 NREL and industrial catalyst costs are the same $32.00/lb. Cost per day calculated from amount of catalyst lost from reactor per hour of use.

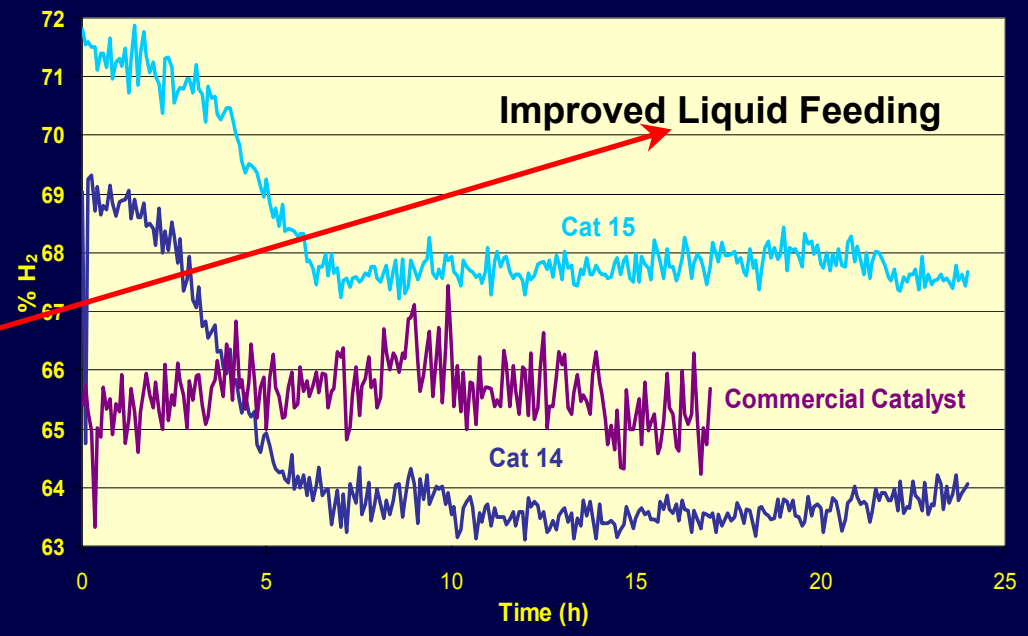
Catalyst Improvements: K_2O Improves Gasification



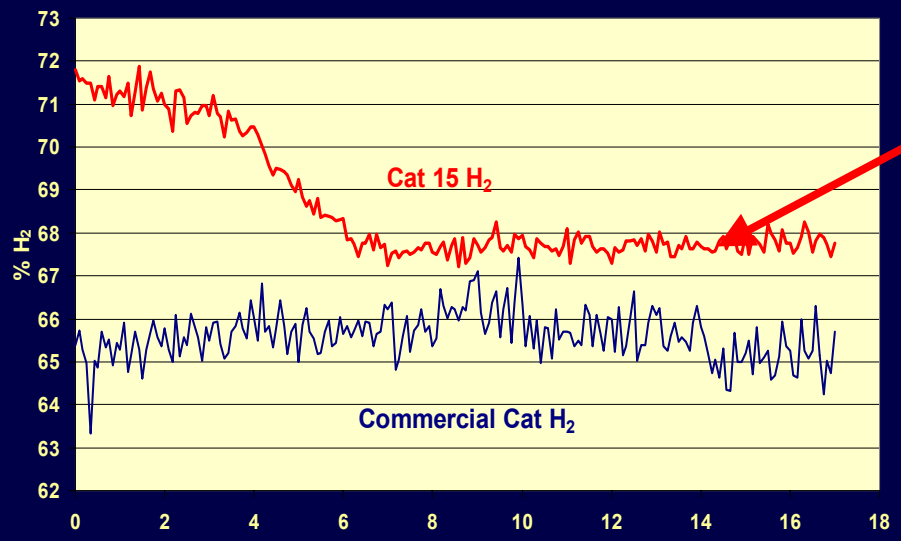
CATALYST	Wt % NiO	Wt % MgO	Wt % K_2O
CAT 10	2.0	0.2	0.07
CAT 11	2.0	1.0	0.08
CAT 12	4.0	2.0	0.09

Milestone: Improve catalyst gasification performance for pyrolysis liquid reforming

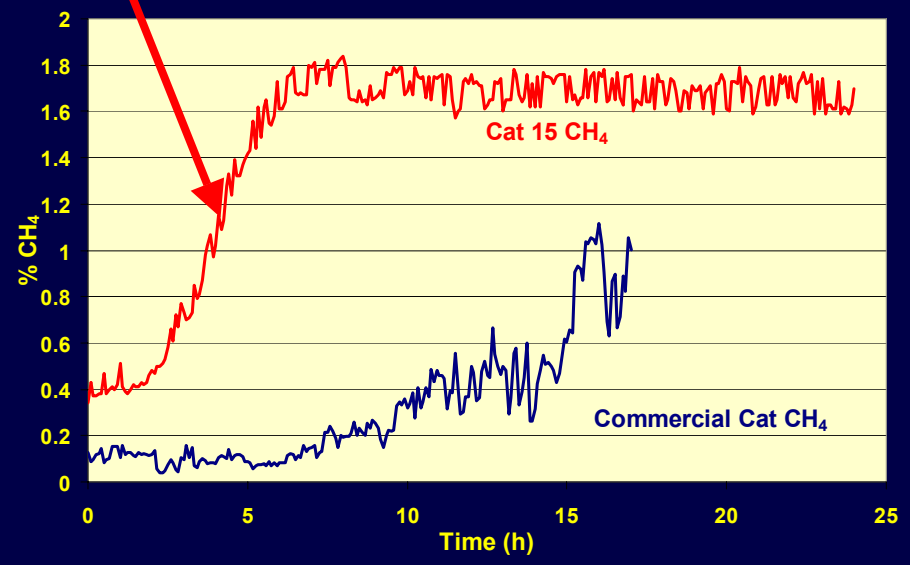
CATALYST	Wt % NO	Wt % MgO	Wt % K_2O
C 11 NK	19.0	5.0	8.0
CAT 14	2.0	0.2	0.4
CAT 15	3.5	0.4	0.7

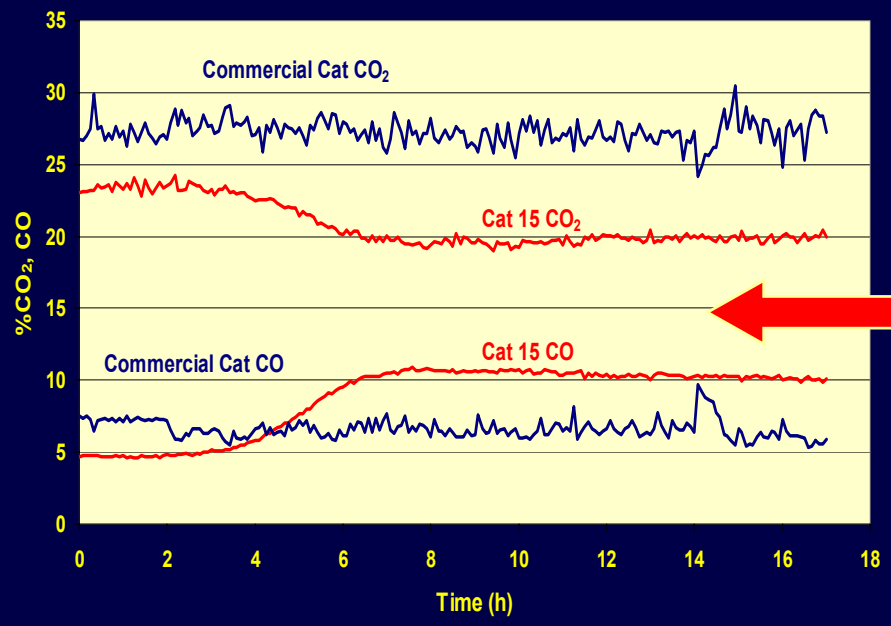


Catalyst Improvements (NREL vs. Commercial C 11)



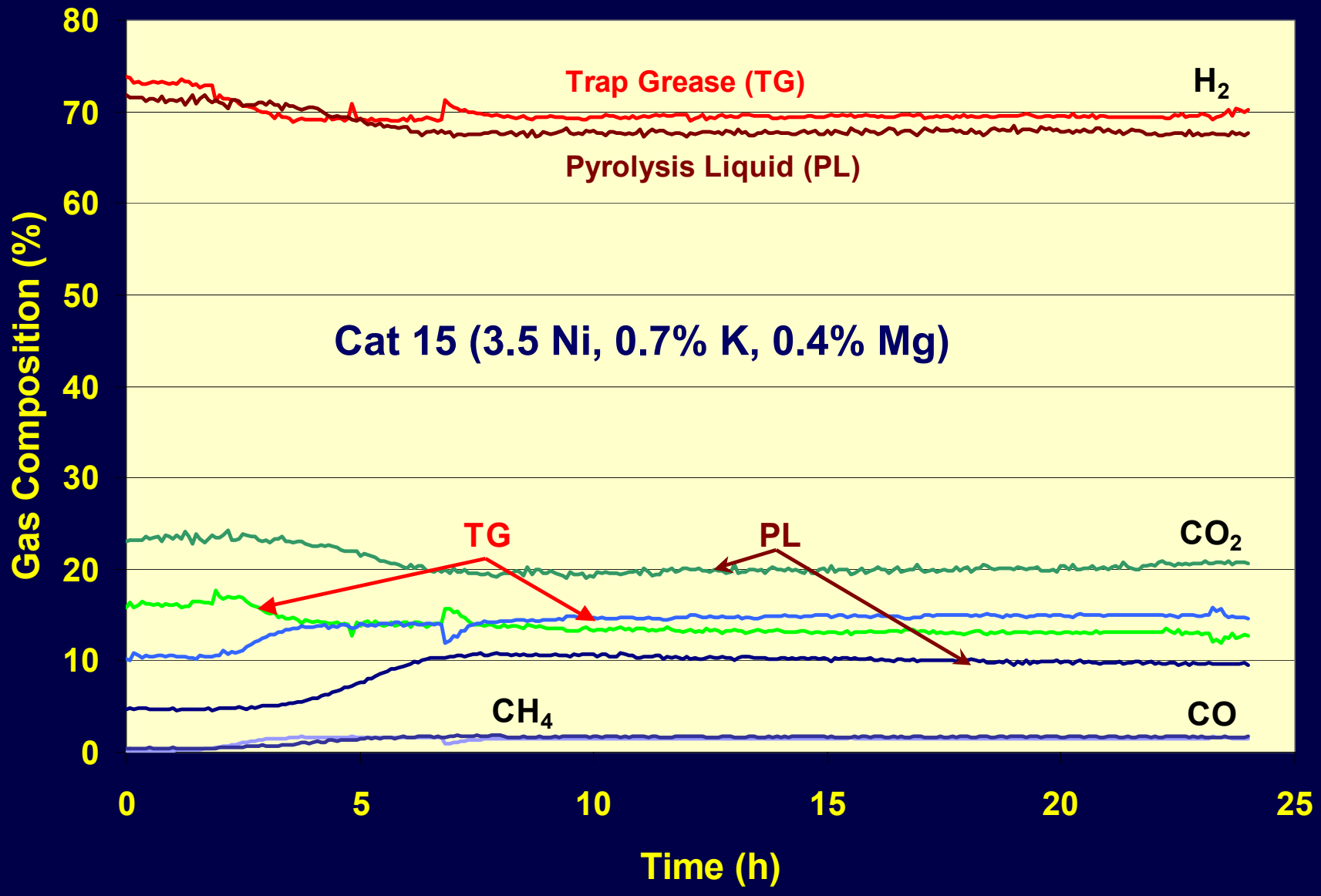
More hydrogen and methane
Need to reduce methane

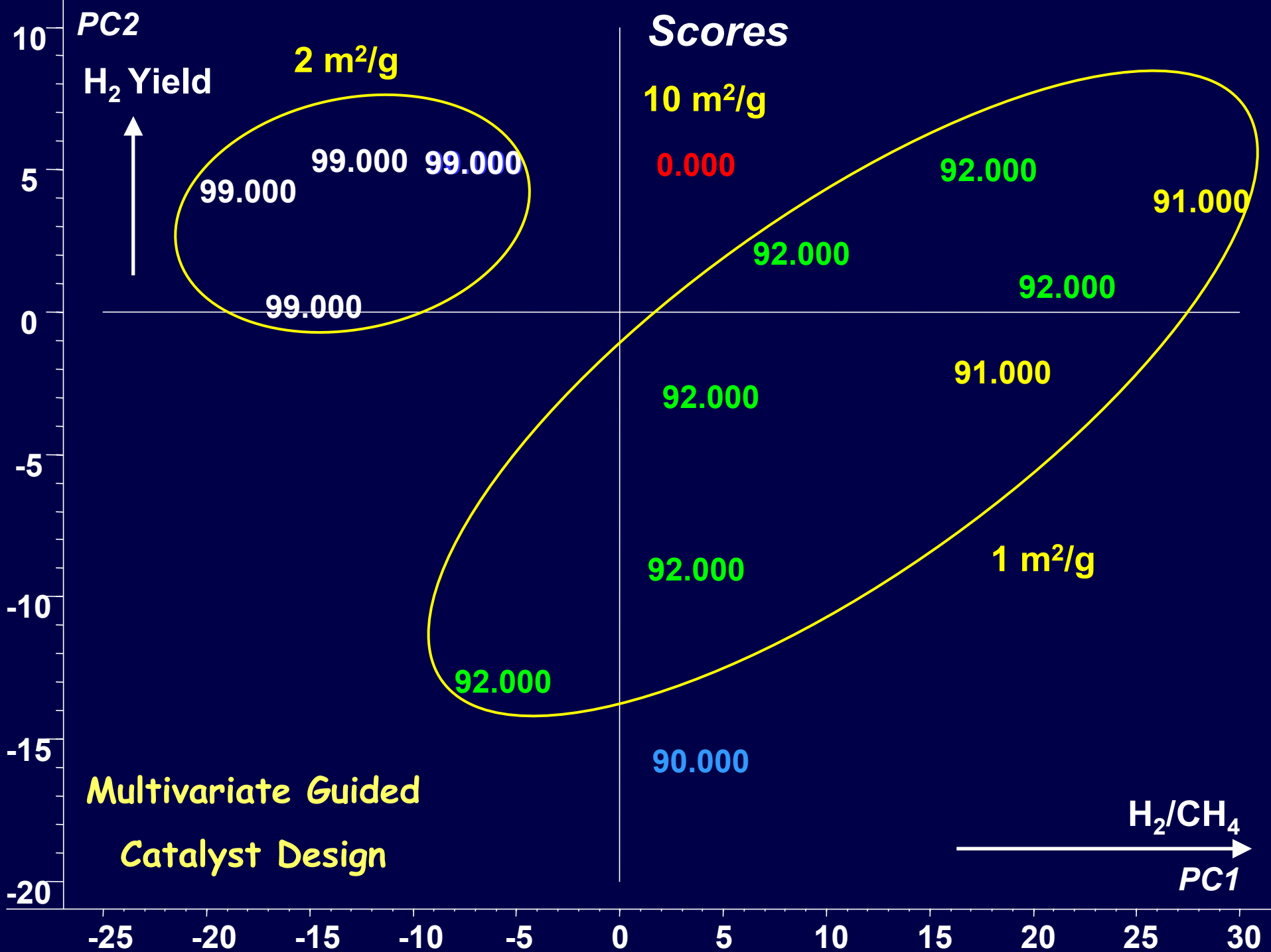




More CO_2, less CO
Need to improve WGS

Comparing Feedstocks




PC2
Scores
H2 Yield
2 m2/g
10 m2/g
99.000
99.000
99.000
99.000
0.000
92.000
91.000
92.000
92.000
91.000
92.000
92.000
1 m2/g
92.000
90.000
Multivariate Guided
Catalyst Design
H2/CH4
PC1
10
5
0
-5
-10
-15
-20
-25
-20
-15
-10
-5
0
5
10
15
20
25
30

Accomplishments/Progress

- Developed novel fluidizable reforming catalysts with CoorsTek Ceramics
- Evaluated performance of 16 catalysts for 24 hrs with pyrolysis oil-derived feedstocks
- Improved reforming activity (compared to commercial catalyst)
- Prepared a 100 lb batch of catalyst for the GA demonstration project
- Evaluating S-tolerant catalysts with waste grease

Collaborations/Technology Transfer

- CoorsTek Ceramics
  Developing fluidizable supports
- Sud Chemie
  Reforming catalyst composition
- GE Power Systems
  Fluidizable catalysts

- Article
- Record of Invention

Plans/Future Milestones

Goal: Design efficient fluidizable catalysts to produce H_2 from varied feedstocks

- Improve catalyst gasification and WGS activity
  - Develop lower temperature reforming catalysts
- Evaluate different feedstocks (pyrolysis vapors, waste grease, plastics)
  - Understand deactivation mechanisms (S, Cl)
  - Develop poison tolerant catalysts per feedstock
- Prepare/evaluate non-nickel catalysts
- Evaluate new CoorsTek supports (Zr/Al_2O_3) for circulating/bubbling reactors
- Modify/use rapid catalyst screening reactor
- Expand industrial participation in support/catalyst development

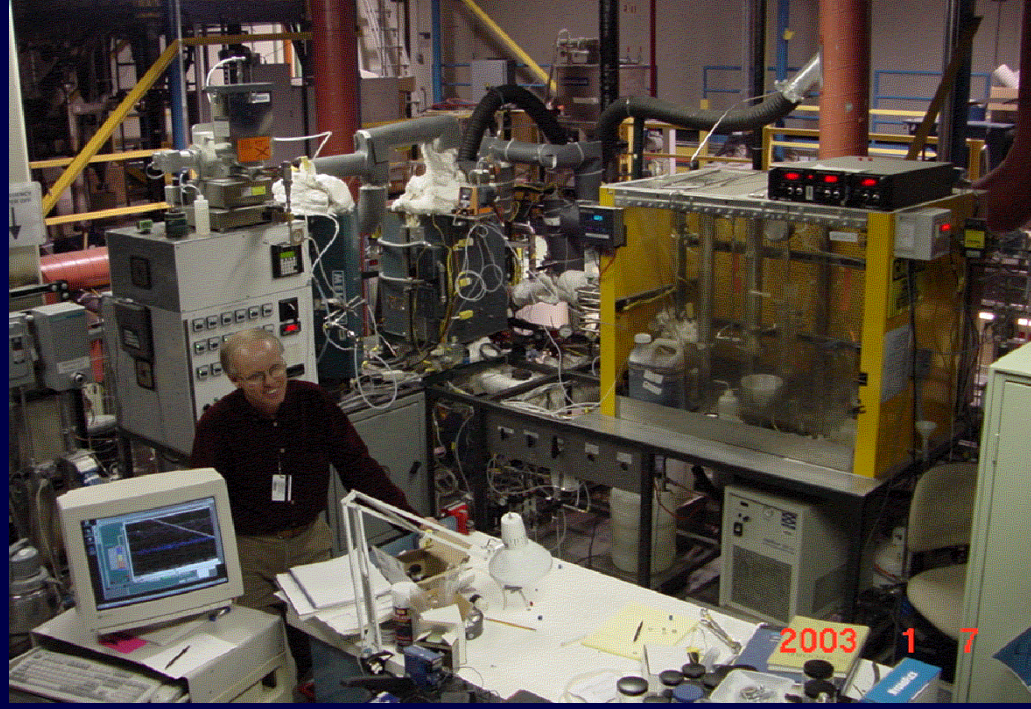
Responses to FY02 Review

- Commercial reforming catalysts attrit **(fall apart)** when fluidized
  - 3 of the best naptha reforming catalysts suffered losses > 10 wt% per day (need < 0.5 wt%/day)

- NREL catalyst composition based on commercial naptha reforming catalyst composition (Sud Chemie)

- Industrial reforming catalysts are for fixed bed use. New market is driving CoorsTek participation. IP in progress (composition of matter)

Challenges



- Real, complex feedstocks
- On-line comprehensive analysis
- Novel fluidizable catalysts
- Long term testing (>200 h)

Biohydrogen Production from Renewable Organic Wastes

May 19, 2003

Biohydrogen Production from Renewable Organic Wastes

Project Team:

PI: Dr. **ShihWu Sung**
Environmental Engineer
Iowa State University

Represented by:
Dr**. Samir Kumar Khanal**
Environmental Engineer
Iowa State University

Co-PI: Dr. **Dennis A. Bazylinski**
Microbiologist
Iowa State University

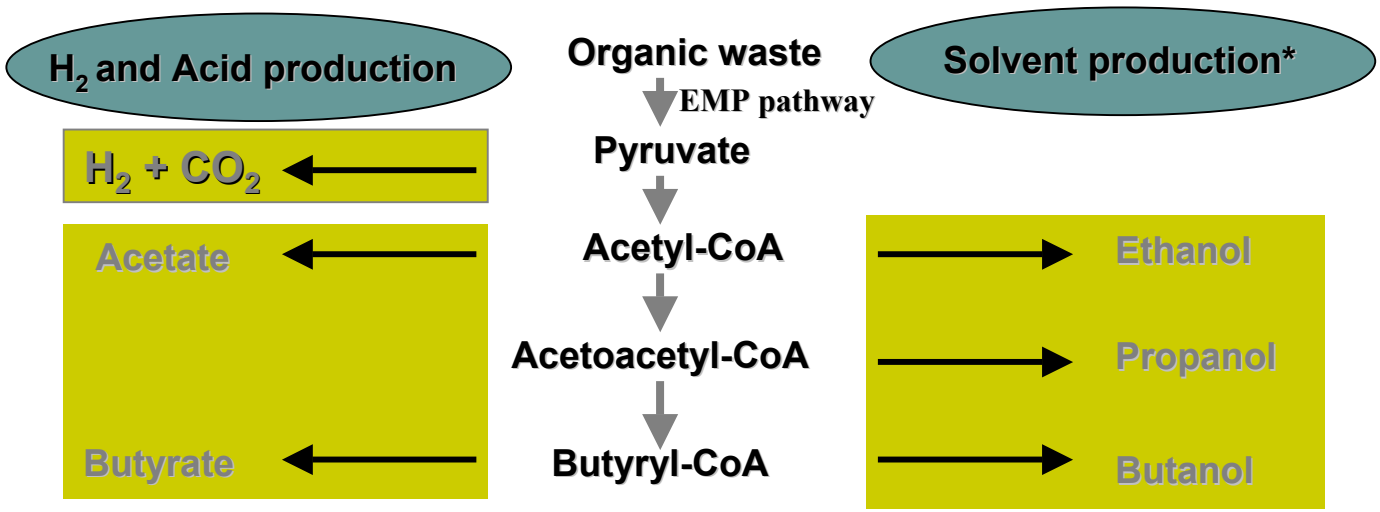
Dr. **Lutgarde Raskin**
Represented by Dr**. Jennifer J. Crawford**
Microbiologist
University of Illinois at Urbana-Champaign

Cost Sharing Partners:	**Role:**
Iowa Energy Center	Provides Pilot Testing Facility
EcoFuels Corporation	Marketing & Commercialization

Industrial Partners:	
Smithfield Foods, Inc.	Wastes Stream Provider
Excel Corporation	Wastes Stream Provider
Universal Entech, Inc.	Marketing/Commercialization

Project Goal

- Develop **Anaerobic Fermentation Process** to convert **negative value organic wastes** (a renewable source) into **hydrogen-rich gas**, which can be used as a fuel source or as a raw material for industries that utilize hydrogen



*pH below 4.5; onset stationary phase

Goals critical to the project:

- To identify and understand the **physiology of microbial populations (software)** to maximize hydrogen yield
- To **design and develop bioreactor (hardware)** to favor the growth of these microbial population

Approach

- Evaluate technical and practical **feasibility of sustainable hydrogen production** in continuous flow bioreactors using different organic waste stream

- Investigate different strategies for **selective growth of hydrogen producing bacteria** (e.g., heat selection, pH control, reactor configuration)

- Apply **nucleic acid based techniques - Terminal Restriction Fragment Length Polymorphism (T-RFLP)** for microbial identification and quantification

Project Timeline

Tasks	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
First Year (10/1/2000 - 09/30/2001)												
Task 1. Optimization of H_2 Production with Synthetic Waste Streams												
1-1 Enrichment of H_2-producing bacteria												
1-2 Influence of environmental factors												
Report												
Second Year (10/1/2001 - 9/30/2002)												
Task 2. Process Optimization of Continuous-flow Reactor												
2-1 Enhancement of hydrogen yield through heat treatment of seed sludge												
2-2 Identification and quantification of H_2-producing bacteria												
Report												
Third Year (10/1/2002 - 9/30/2003)												
Task 3. Study with Real Waste Streams												
Task 3-1a Lab-scale study using compartmentalized and two-stage sequential reactors												
Task 3-1b Pilot-scale demosntration project to study hydrogen production efficiency												
Task 3-2 Full-scale plant evaluation of hydrogen production	*Subject to funding availability*											
Task 3-3 Microbial community characterization												
Final Report												

Milestones

- **Task 1: Optimization of H_2 Production with Synthetic Waste Streams**
  - **1-1** Enrichment of H_2-producing bacteria (completed)
  - **1-2** Influence of environmental conditions (completed)

- **Task 2: Process Optimization of Continuous-flow Reactor**
  - **2-1** Enhancement of hydrogen yield through heat treatment of seed sludge (completed)
  - **2-2** Identification and quantification of H_2-producing bacteria (completed)

- **Task 3: Study with Real Waste Streams (in progress)**
  - **3-1a** Lab-scale study using compartmentalized and two-stage sequential batch reactors (50% completed)
  - **3-1b** Pilot-scale demonstration project to study hydrogen production efficiency
  - **3-2** Full-scale plant evaluation of hydrogen production
  - **3-3** Microbial community characterization

Status of Progress

Task 1: Optimization of H_2 Production with Synthetic Waste Streams

- pH of 5.5 and substrate concentration of 7.5 g COD/L - optimal for start-up
- Inocula rich in hydrogen-producing bacteria are readily available, e.g., compost, soybean soil, potato soil, anaerobic sludge
- Conversion efficiency of 20% (based on COD) with H_2 content of biogas of 55 - 82% was achieved with sucrose, starch, nonfat-dried milk, and commercial dog food
- Determination of important kinetic parameters

Status of Progress

Task 1: Optimization of H_2 Production with Synthetic Waste Streams (continue)

Biokinetic Study:

- Specific growth rate, μ

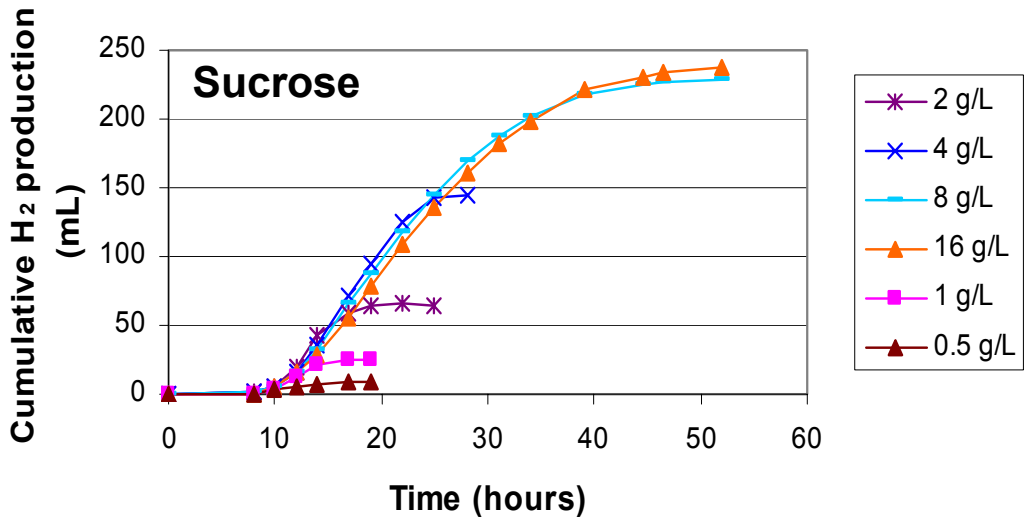
  $= 0.10\ hr^{-1}$

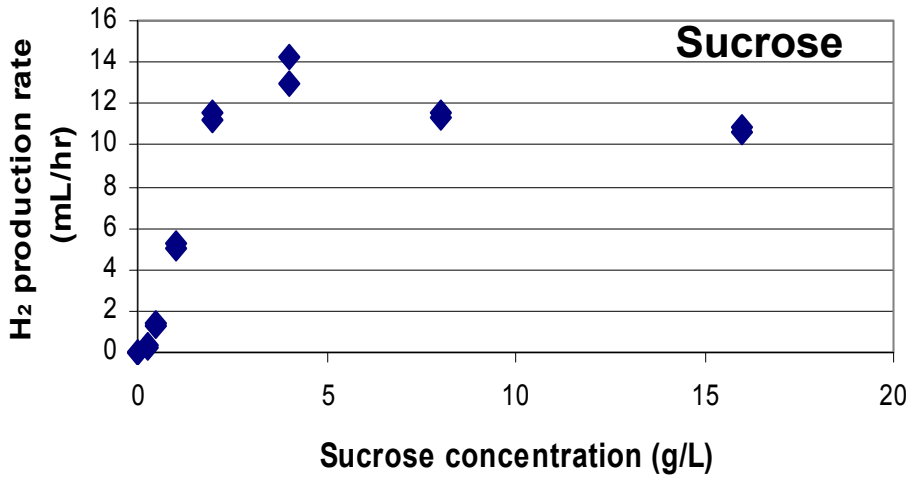
- Half velocity constant, Ks

  = 1.00 g sucrose/L

- Yield, $Y_{H/X}$ (L H_2/g VSS)

  = 0.183





Status of Progress

Task 1: Optimization of H_2 Production with Synthetic Waste Streams (continue)

Biokinetic Study:

- Specific growth rate, μ

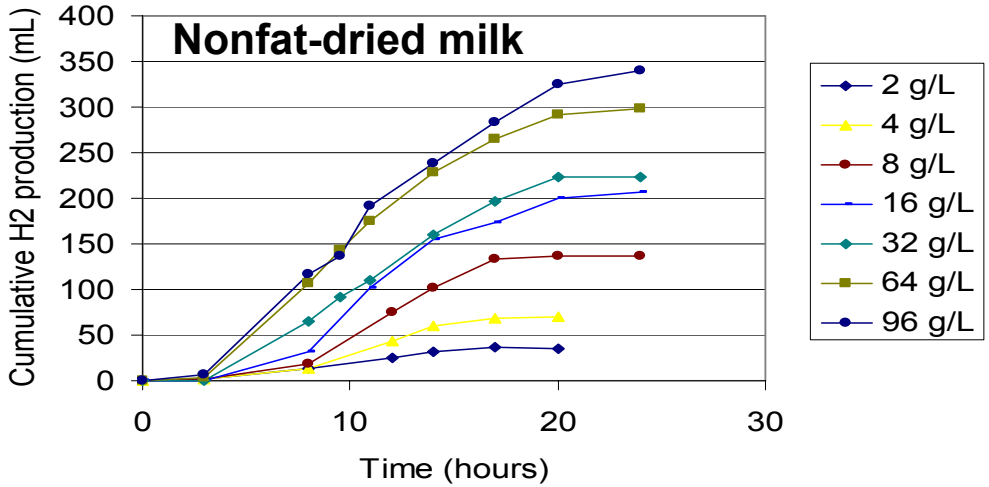
  $= 0.176\ hr^{-1}$

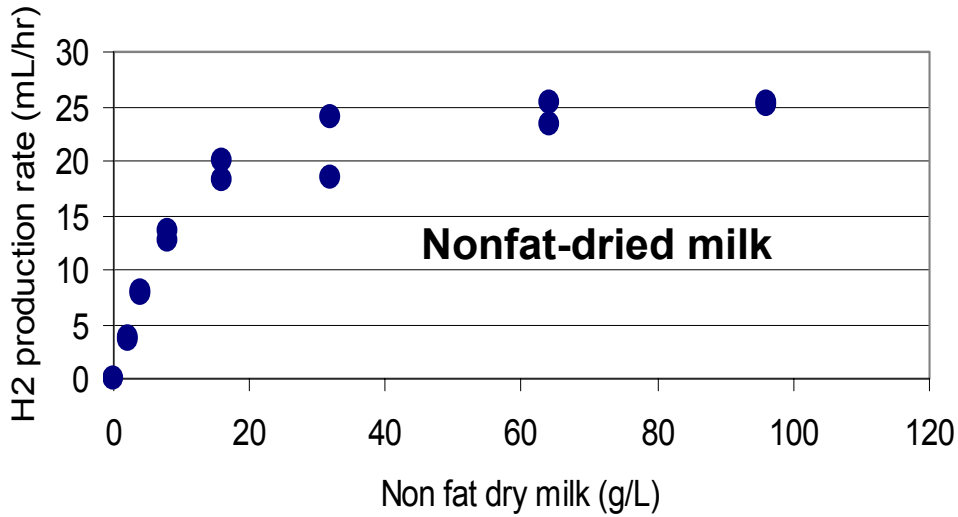
- Half velocity constant, Ks

  = 9.40 g NFDM/L

- Yield, $Y_{H/X}$ (L H_2/g VSS)

  = 0.255





Status of Progress

Task 1: Optimization of H2 Production with Synthetic Waste Streams (continue)

Biokinetic Study:

- Specific growth rate, μ

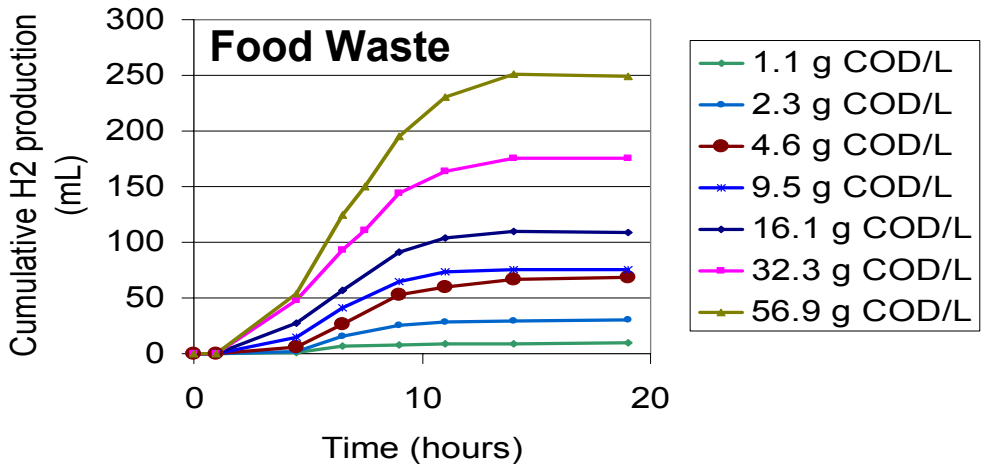
  $= 0.215\ hr^{-1}$

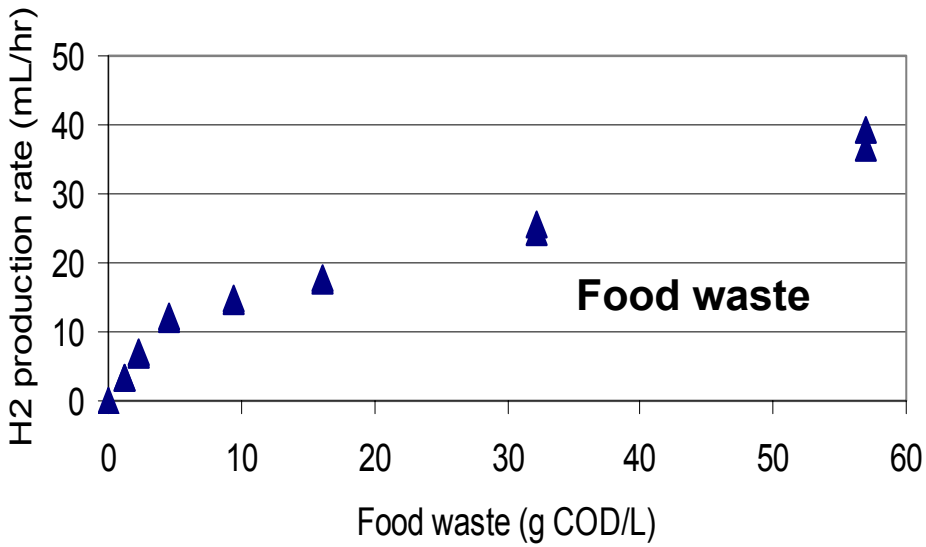
- Half velocity constant, Ks

  = 7.00 g COD/L

- Yield, $Y_{H/X}$ (L H_2/g VSS)

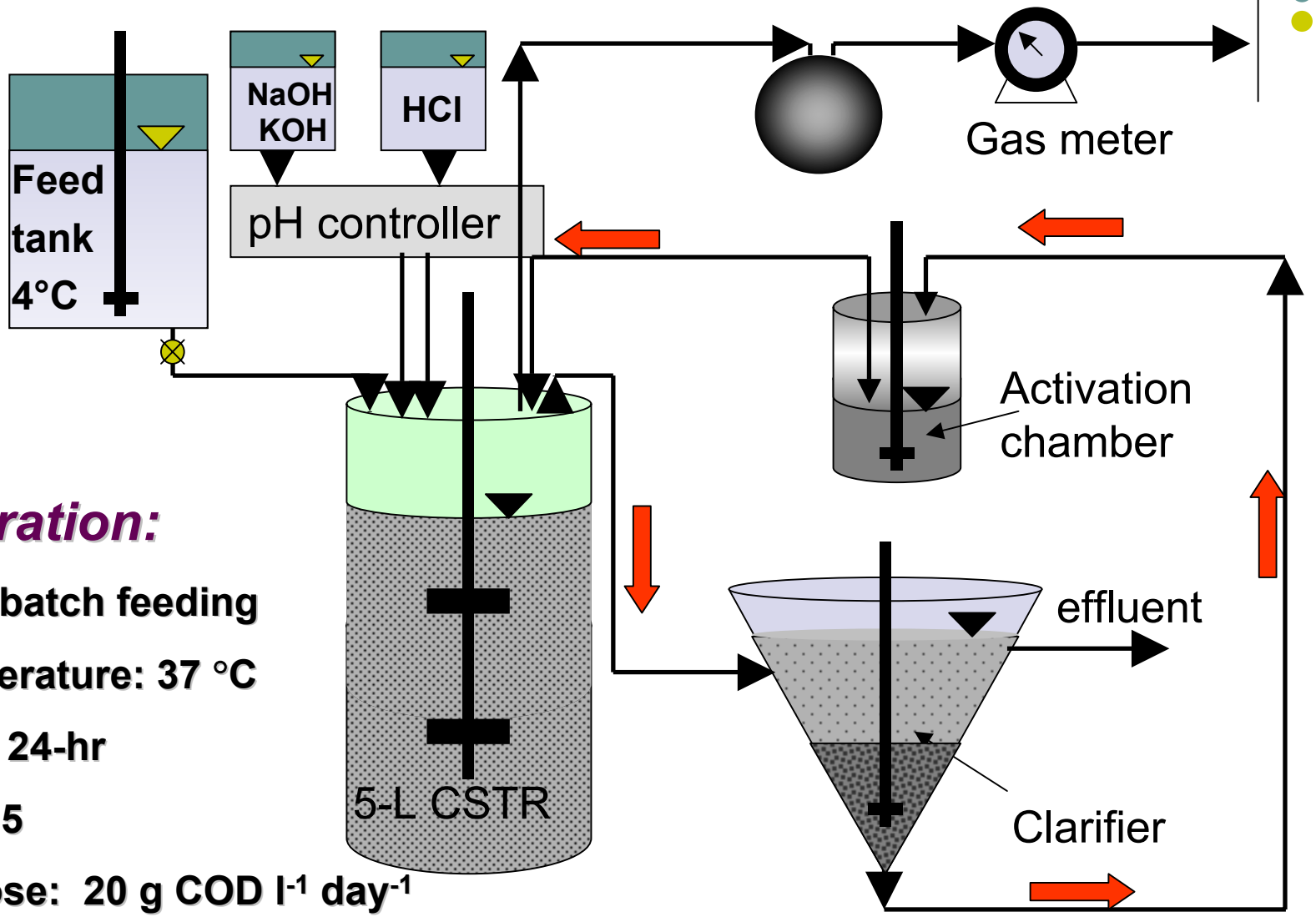
  = 0.223





Status of Progress

Task 2: Process Optimization of Continuous-flow Reactor



Operation:

Semi-batch feeding

Temperature: 37 °C

HRT: 24-hr

pH: 5.5

Sucrose: 20 g COD l^{-1} day^{-1}

Heat treatment: 100 ^{0}C for 15 min

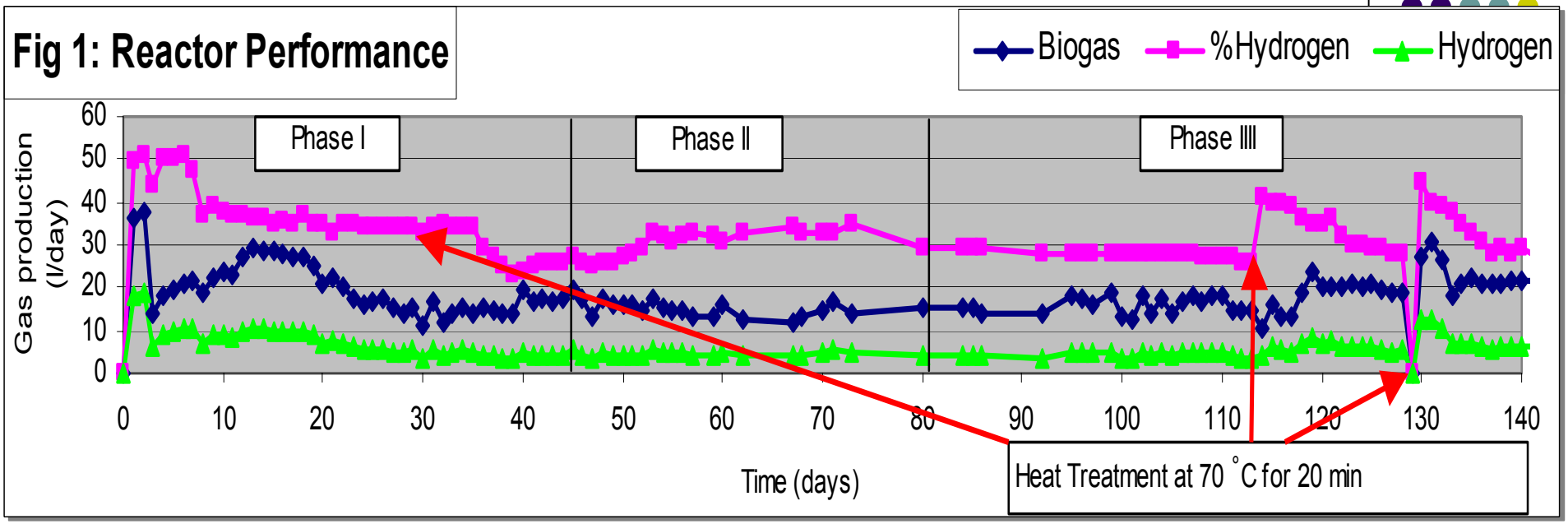
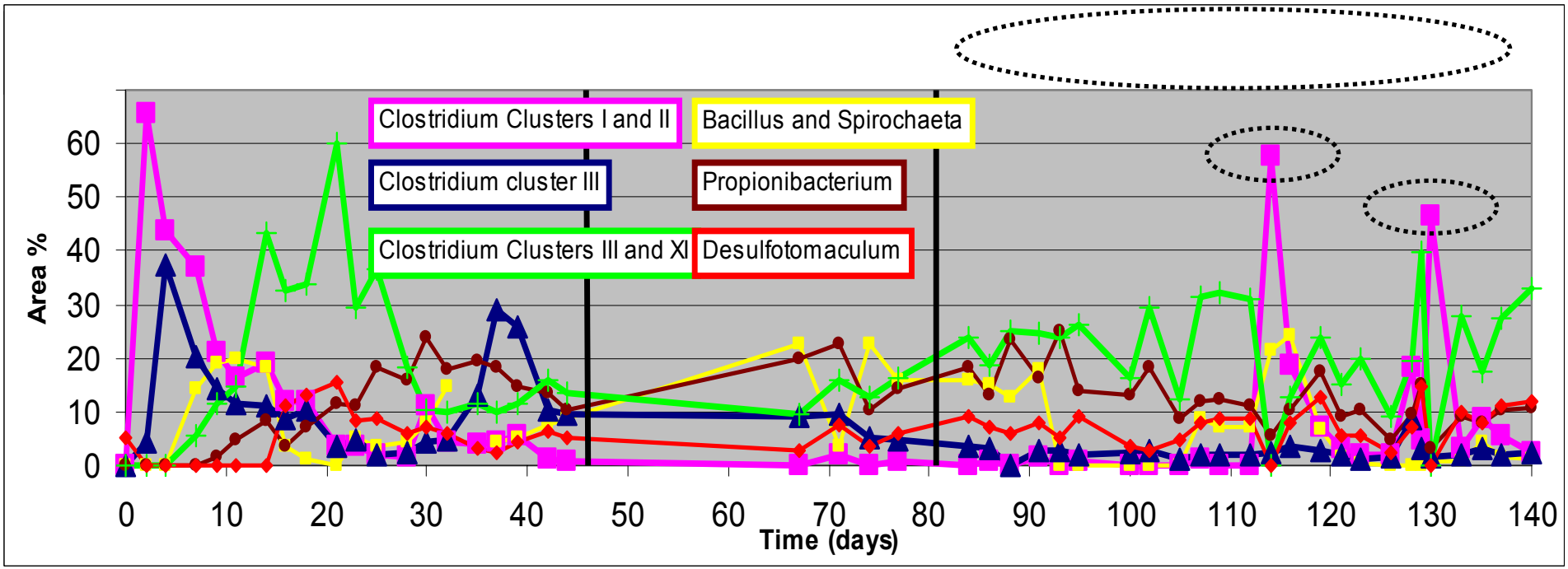


Fig 1: Reactor Performance
Biogas
%Hydrogen
Hydrogen
Phase I
Phase II
Phase IIII
Gas production (l/day)
Time (days)
Heat Treatment at 70 °C for 20 min


Clostridium Clusters I and II
Bacillus and Spirochaeta
Clostridium cluster III
Propionibacterium
Clostridium Clusters III and XI
Desulfotomaculum
Area %
Time (days)

Status of Progress

Task 2: Process Optimization of Continuous-flow Reactor (continue)

- Sustainable H_2 production was achieved by initial heat treatment followed by periodic heat treatment of reactor biomass
- Hydrogen production showed positive correlation with clostridium cluster I and II associated with heat treated biofilm and not bulk biomass
- Repeated heat treatment caused a population shift in identified *Clostridium* populations:
  - Spore germination
  - Substrate competition

Status of Progress

Task 2: Process Optimization of Continuous-flow Reactor (continue)

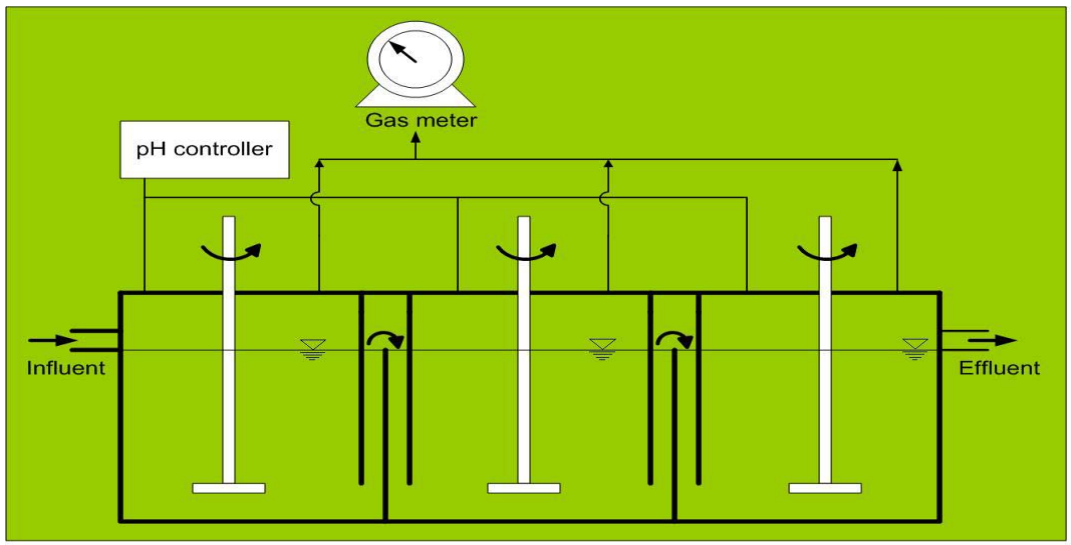
Table Anaerobic populations identified using T-RFLP analysis

1	*Clostridium cluster I & II*
2	*Bifidobacterium*
3	*Spirochaeta*
5	*Propionibacterium*
7	*Clostridium formicoaceticum (cluster XI), C.termitidis, C.aldrichii, C.cellobioparum (cluster III)*
8	*Brachyspira*
10	*C. stercorarium, C. thermolacticum (cluster III)*
11	*Desulfotomaculum*

Status of Progress

Task 3-1a: Study with Real Waste Streams (in progress)

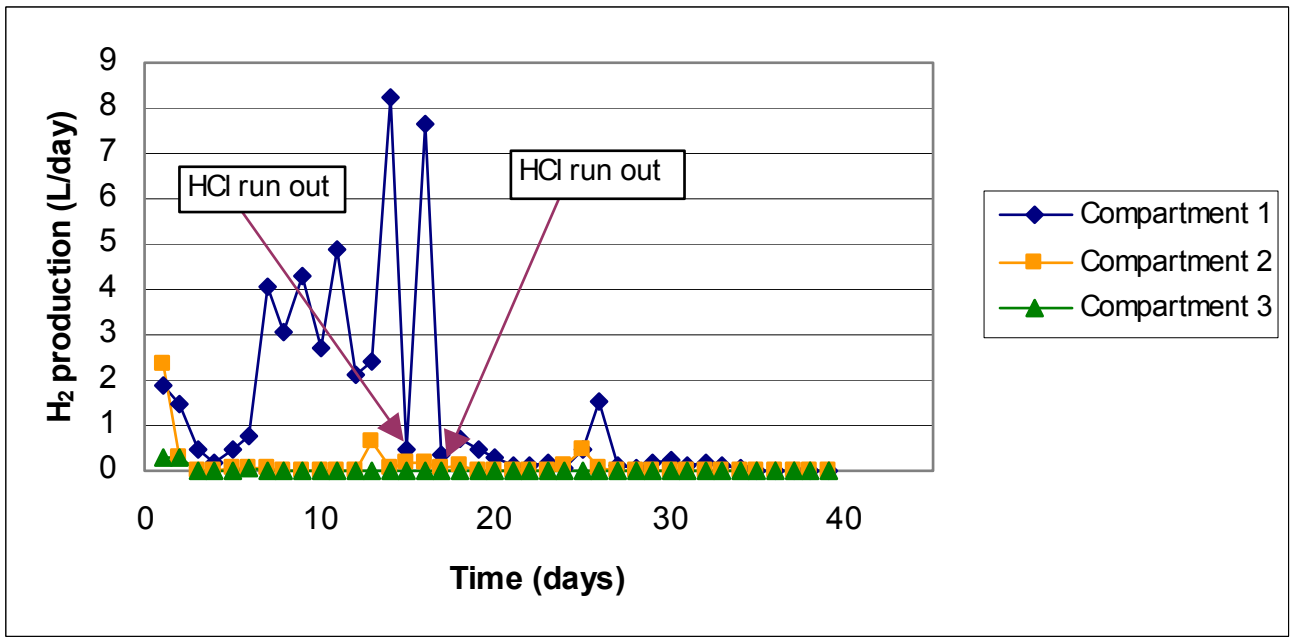
- Compartmentalized reactors (Anaerobic Baffled Reactor)
- Allow accumulation of hydrogen producers inside the reactor while maintain high organic loading rate and low HRT (favorable for hydrogen producers)
- Loading rate = 40 g COD/L/day and HRT = 9 hours



Status of Progress

Task 3-1a: Study with Real Waste Streams (in progress)

- 4 - 6 L H_2/day produced from day 7-14 of ABR operation
- Abrupt drop in hydrogen production on day 15 due to exhaust of acid that caused increase in pH to as high as 8.0
- Failure of pH controller for quick response to pH changes

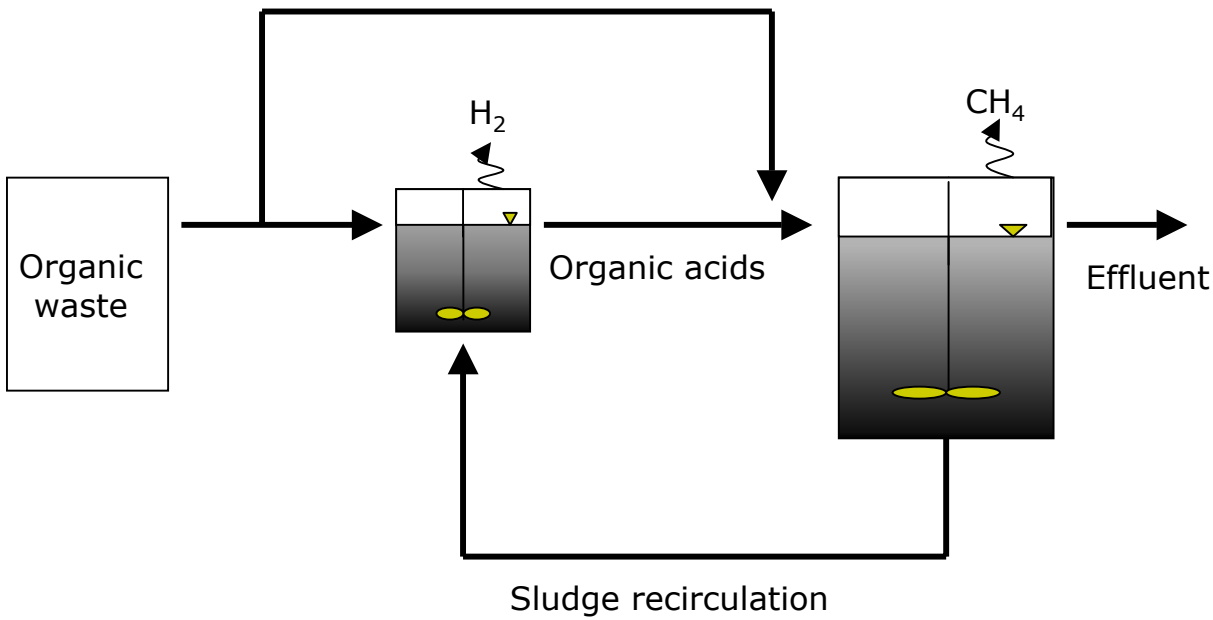


Status of Progress

Task 3-1a: Study with Real Waste Streams (in progress)

- Two-stage bioreactor: To maintain fresh microbial seed in hydrogen producing bioreactor to avoid degeneration

- To provide a favorable environment for the selective growth of hydrogen-producing bacteria in mixed microbial community: e.g. high organic loading, short hydraulic retention time, pH of 5.5



Future Work

Task 3-1b: Pilot-Scale Demonstration Project to Study Hydrogen Production Efficiency (subject to funding availability)

- Installation of pilot-scale bioreactor in IEC' BECON Facility, Nevada, IA
- Evaluation of design and critical operational parameters for hydrogen production in pilot-scale bioreactors using real waste

Task 3-2. Full-Scale Plant Evaluation (subject to funding availability)

- Evaluation of detailed design and operational guidelines for producing hydrogen from real waste

Future Work (continue)

With continuous research on process engineering and microbiology of biological hydrogen production, our research team intends to:

* **Design improved bioreactor** system that favors the selective growth of *Clostridium* cluster I and II

* Obtain operating parameters for efficient bioconversion of real waste stream: **high fructose corn syrup, corn stover, food waste, DDG** etc. to hydrogen

* Develop **nation's first biohydrogen pilot plant** using organic wastes

Cooperative Efforts

PI: Prof. Sung, Environmental Engineer at Iowa State University (ISU)

- Technology Transfer: The ISU patented TPAD to more than 20 commercial installations nationwide. The process won 1999 R&D 100 Award

Co-PI: Prof. Bazylinski, Microbiologist at ISU

- Graduate program committee member & consultant : H_2-producing cultures and sporulation

Co-PI: Prof. Raskin, Environmental Engineer at University of Illinois, Urbana-Champaign

- Expert in microbial community characterization using nucleic acid based techniques

Cost Sharing & Industrial Sharing Partners:

- **Iowa Energy Center** ($134K)**:** Providing Pilot Testing Facility in Nevada, IA
- **EcoFuels Corporation** ($20K), **Smithfield Foods, Inc., Universal Entech Inc. and Excel Corp.:** Marketing & Commercialization, Providing Waste Streams

Publications:

1. Duangmanee, T., Padmasiri, S., Simmons, J. J., Raskin, L. and Sung, S. (2002) Hydrogen production by anaerobic communities exposed to repeated heat treatment. *Water Environment Federation 74th Conference*, Chicago., IL.
2. Duangmanee, T., Chyi, Y. and Sung, S. (2002) Biohydrogen production in mixed culture anaerobic fermentation. *14th World Hydrogen Energy Conference*, Montreal, Canada.
3. Van Ginkel, S., Sung, S. and Lay, J. J.(2001) Biohydrogen production as a function of pH and substrate concentration.*Environmental Science & Technology*, 35:4726 - 4730.
4. Van Ginkel, S., Lay, J. J. and Sung, S. (2000) Biohydrogen production optimization using variable natural inocula. *Proceedings of Water Environment Federation 73rd Annual Conference*, Anaheim, CA.

Budget for 10/01/2002 to 12/31/2003

Total Budget: $ 195,000.00

Amount transferred in May (with no cost time extension up to Dec 31, 2003)
$ 115,000.00

Comments from previous review panel meeting

- Recommended that the work to be continued through development of the initial prototype system and the potential of this process for economic hydrogen production

- Pilot-scale demonstration not to be pursued – require more system optimization for higher hydrogen yield (4-6 moles H_2/mole substrate)

- The project should proceed with corn processing, rendering and other wastes

- Very good, simple process concept, very orderly experimental sequence and the work to date is very good

Biological Water Gas Shift

DOE Hydrogen, Fuel Cell, and Infrastructure Technologies Program Review

May 19-22, 2003

PIs: Ed Wolfrum and Pin-Ching Maness

Team Members: Andy Watt, Gary Vanzin

Jie Huang and Sharon Smolinski

National Renewable Energy Laboratory

Process Overview

- In the Water-gas Shift (WGS) reaction, CO is oxidized to CO_2 while water is reduced to hydrogen:

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$

- This process is used industrially to produce additional H_2 from synthesis gas streams using a 2-stage catalytic reactor (FeO/Cr at 450°C, CuO/ZnO at 250°C)
- Several strains of photosynthetic bacteria, isolated from the natural environment by NREL researchers, are able to perform the WGS reaction at ambient temperatures
- This may be an attractive alternative to conventional processes
  - Heat Integration Issues
  - Biological vs. Chemical Catalyst
  - Overall System Costs

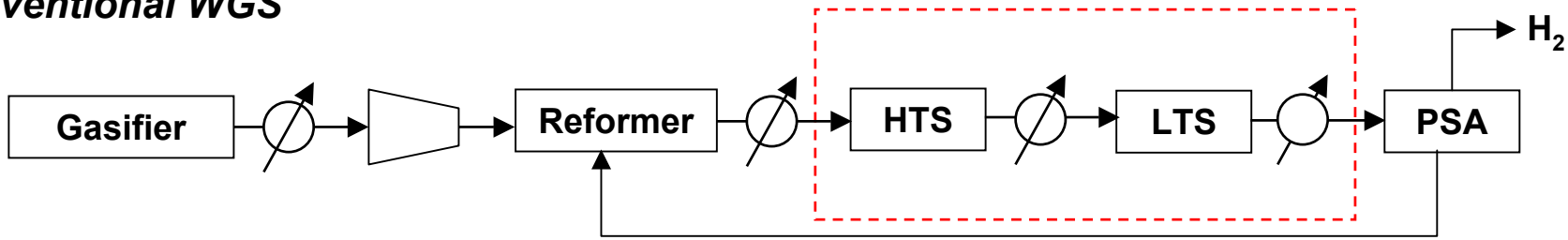
Relevance/Objective

Objective: to Improve Biological Water-Gas Shift (WGS) for Producing Biomass-Derived H_2.

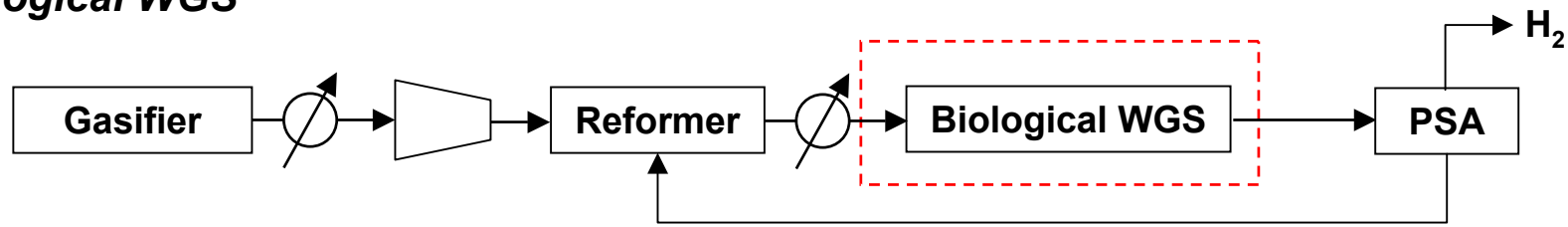
- Barrier H – Cost of Biomass-derived H_2
- Task 4 –Alternatives and Improvements to Conventional WGS
- Two Milestones
  - Verify operation of 100psi WGS Bioreactor (go/no go)
  - Demonstrate 100-L WGS Bioreactor

WGS Flow Chart - Conventional & Biological

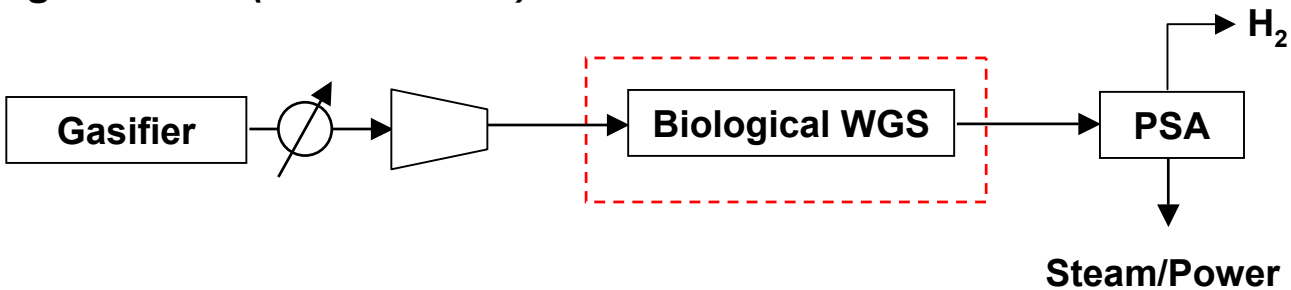
Conventional WGS



Biological WGS



Biological WGS (no Reformer)



Technical Approach

Key Challenges

- Physiology and Molecular Biology:
  - Increase specific water-gas shift rate
  - Eliminate induction period for water-gas shift
- Integrated Engineering and Operation:
  - Increase reactor productivity
  - Operate reactors at elevated pressures

Our Approach to Overcome these Challenges

- Understanding Leads to Solutions
- Physiology and Molecular Biology:
  - Understand the microbe's genetic system for genetic engineering
- Integrated Engineering and Operation:
  - Understand high-pressure bioreactor dynamics

Project Timeline - Biology

Project Steps	FY99	FY00	FY01	FY02	FY03
Improved CO shift rate by more than **5** fold by improving CO mass transfer					
Demonstrated O_2 tolerance of the hydrogenase; half-life of **21 hours** in full air					
H_2 was produced from **water** in a linked cyanobacterial-hydrogenase hybrid system					
Isolated mutants and cloned **2** water-gas shift genes					
Cloned **8** genes in the water-gas shift – manipulate genes to improve H_2 production					

Accomplishment 1:
Cloned 9 Genes in Water-gas Shift Reaction

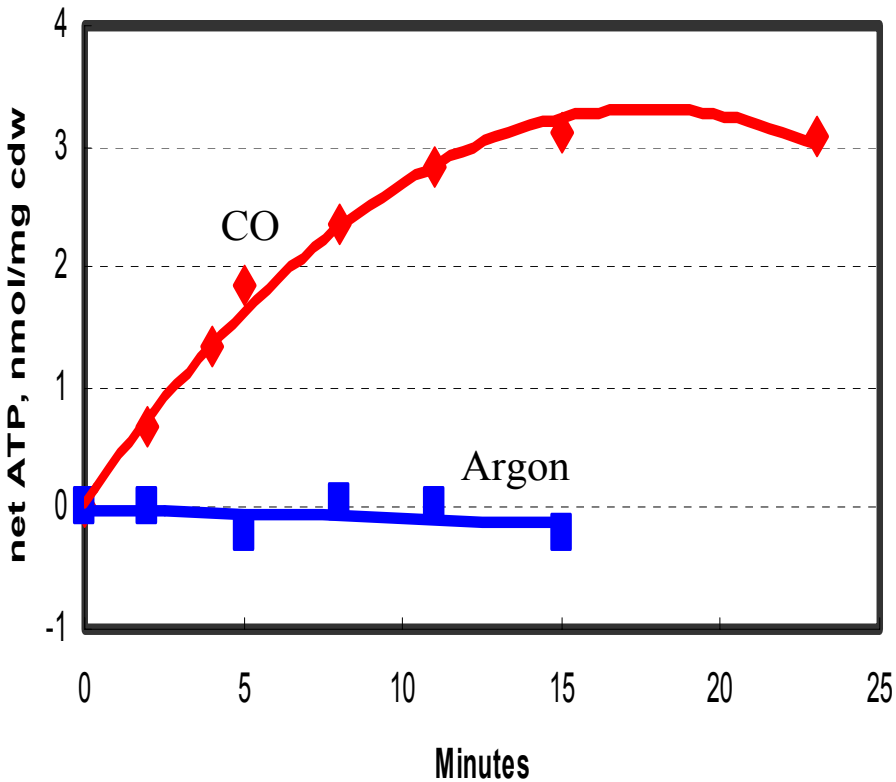
$$CO + H_2O \xrightarrow{\textit{coo}\ \text{F, S, C}} CO_2 + 2e^{-1} + 2\,H^+$$

$$2\,H^+ + 2e^{-1} \xrightarrow{\textit{coo}\ \text{M, K, L,X, U, H}} H_2$$

- 9 water-gas shift genes are completely sequenced
- WGS-genes complementation was successful, which could lead to over-expression of WGS activity
- With sequences known, these genes can be manipulated to improve H_2 production

➢ Meeting FY03 milestone of understanding genetic system of CO shift to allow for manipulations to increase H_2 production

Accomplishment 2:
Water-gas Shift Yields Energy in Darkness



- CO supports both cell growth and ATP synthesis, in darkness
- ATP can be used to regenerate more water-gas shift catalysts in darkness
- Dark bioreactor simplifies reactor design, operation, and reduces cost

Addressing Review Panel's comments that shift reaction can support cell growth yielding energy in darkness leading to sustained H_2 production

Project Timeline - Engineering

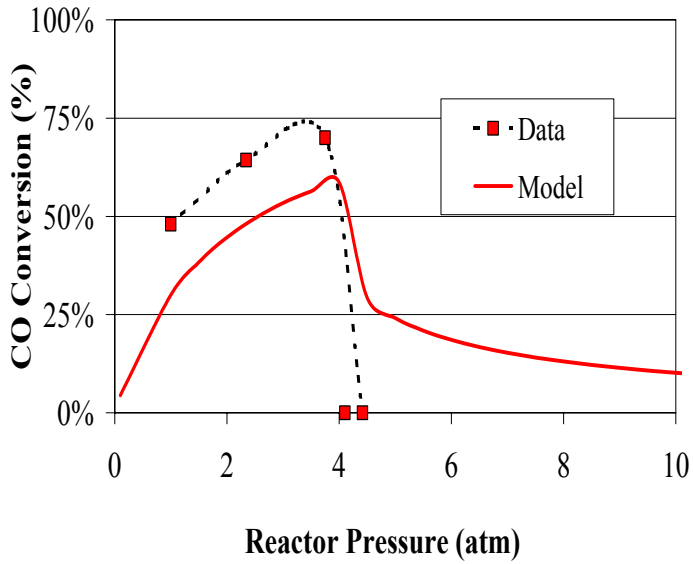
Project Steps	FY99	FY00	FY01	FY02	FY03
Test new biological WGS reactor designs					
Evaluate improved reactor internals					
Condition biomass-derived syngas; Demonstrate bioreactor operation at 5-L scale					
Operate bioreactor at P=10 atm; Measure shift kinetics of *Rx. gelatinosus*					
Determine Cause of Elevated Pressure Inhibition of WGS Reaction					

- This project has a go/no go decision in FY06 to verify 100 psi operating pressure water-gas shift bioreactor at 95% CO conversion efficiency

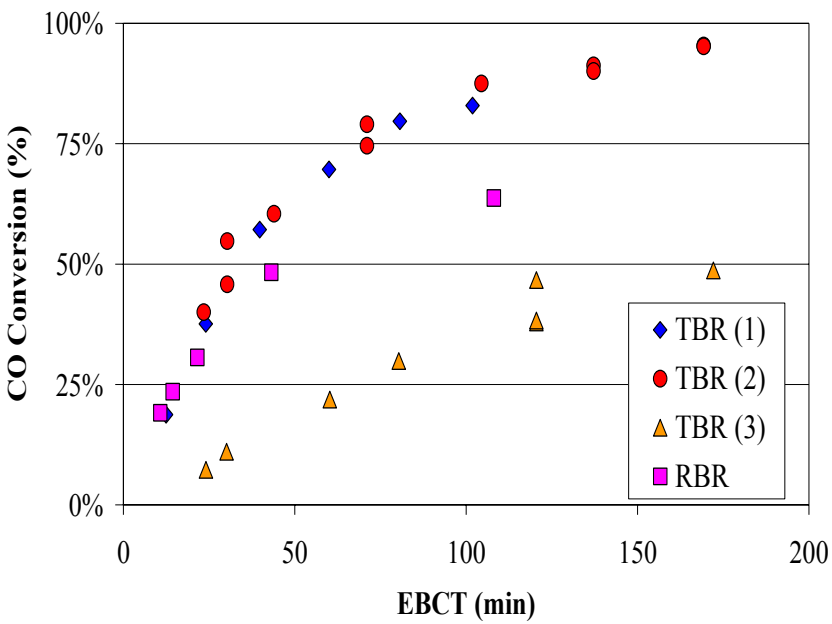
Accomplishment 3:
Elevated Pressure Bioreactor Operation

- Trickle Bed Reactor (TBR) provided good gas-liquid mass transfer, but was difficult to control and analyze
- Developed a novel Recirculating Bubble-Column Reactor (RBR) which provides good gas-liquid mass transfer, and is easier to control and analyze

RBR Design Provides Stable Operation at Elevated Pressure

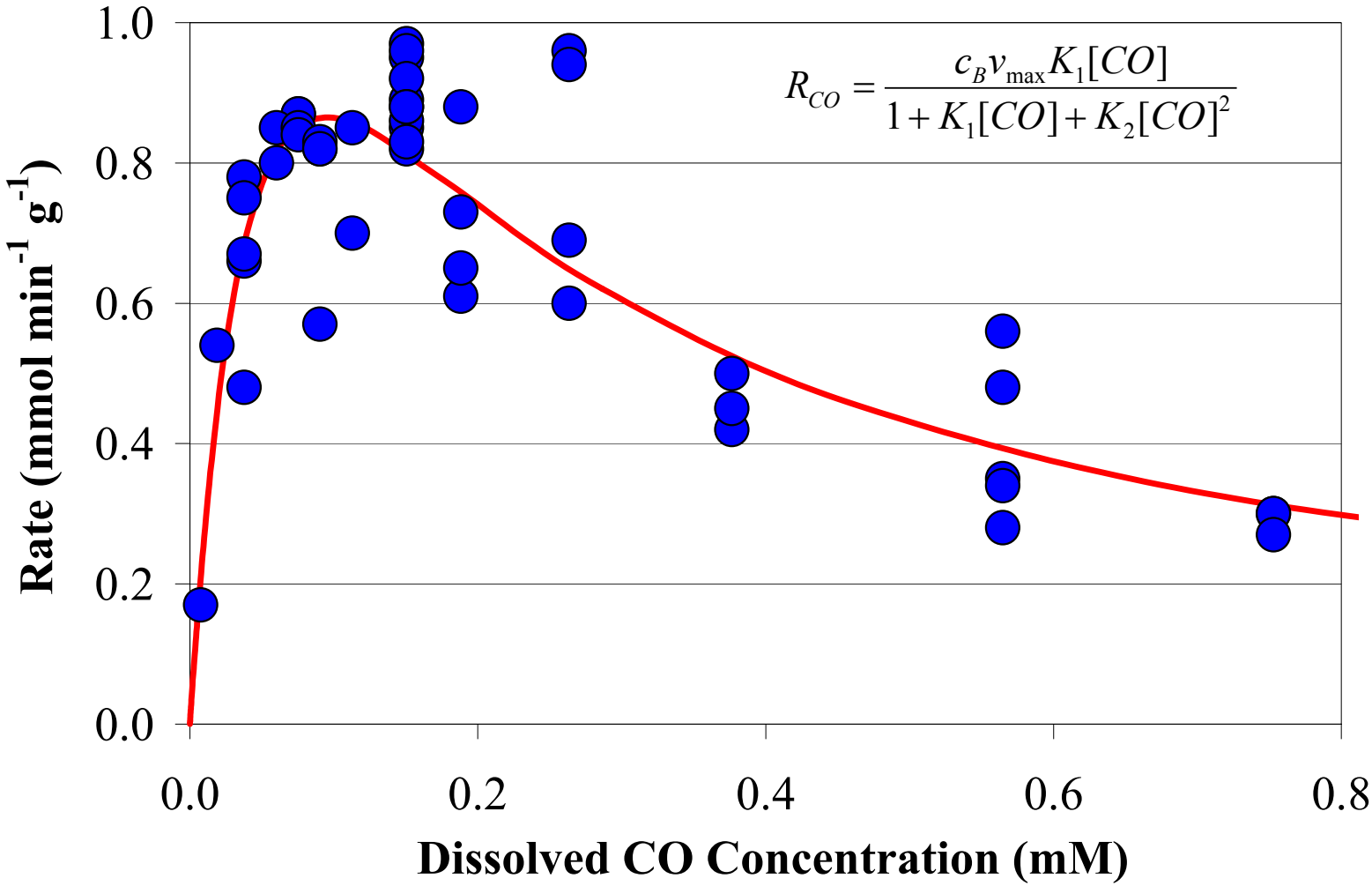


- ***Laboratory facilities can accommodate five parallel 1-L bioreactors at pressures up to 20 atm with automated GC analysis of inlet & outlet streams***



Accomplishment 4:

Intrinsic Bacterial Kinetics of *Rx. gelatinosus* CBS show Inhibition at Elevated [CO]



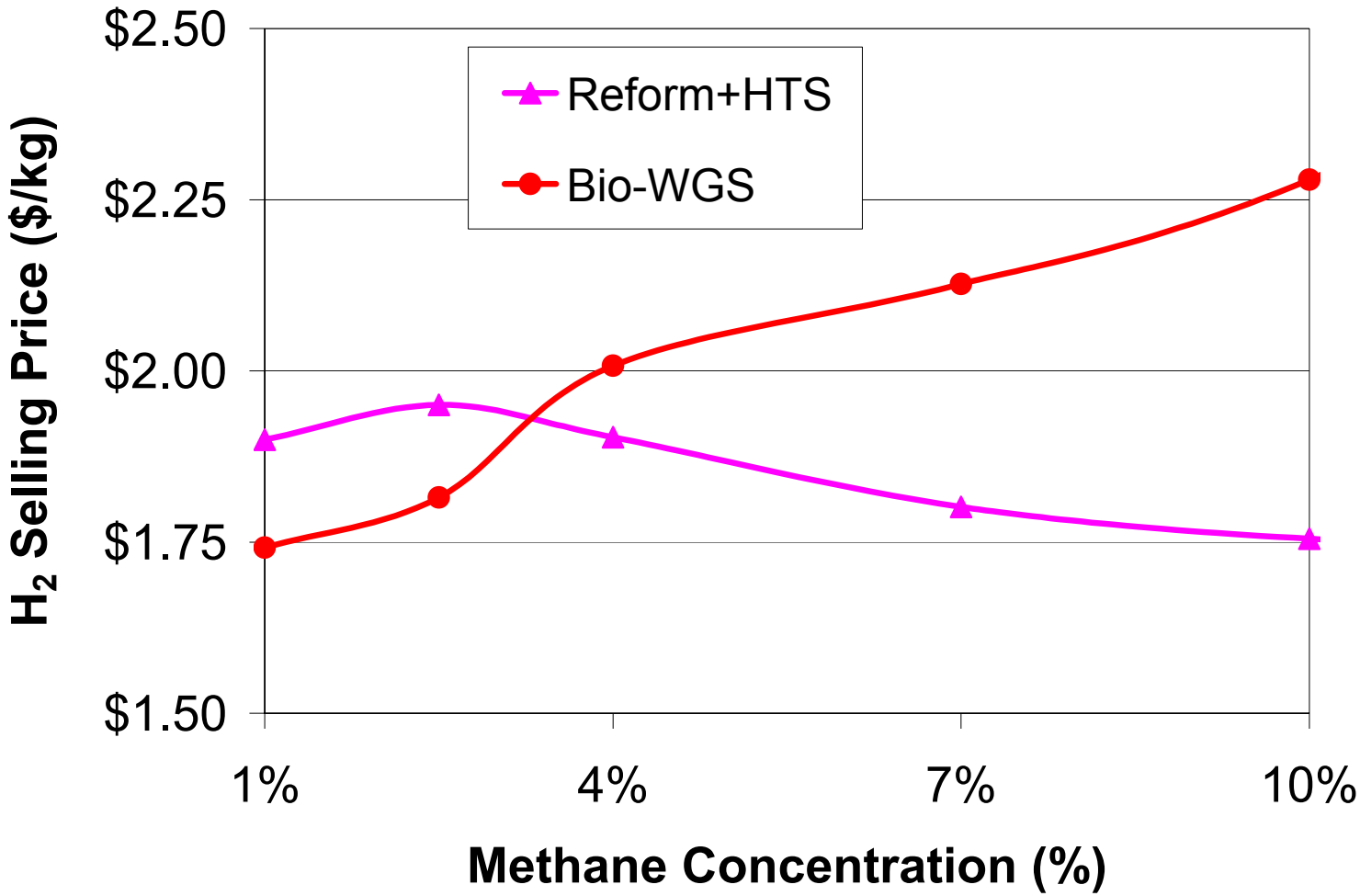
Collaborations/Industry Interactions

- Collaborations
  - Washington State University
    - Fundamental studies on the energetics of the water-gas shift pathway
  - University of Victoria (Canada)
    - Proteomics-based investigations of the water-gas shift pathway
- Industry Interactions via Work for Others
  - Oil Refinery Service Co.
    - Convert CO in refinery gas to additional hydrogen via biological water-gas shift

Publications

- Maness and Weaver. 2002. "Hydrogen production from a carbon-monoxide oxidation pathway in *Rubrivivax gelatinosus*." *International J. Hydrogen Energy*. 27: 1407-1411.
- Merida, Maness, Brown, and Levin. "Enhanced hydrogen production from indirectly heated biomass, and removal of carbon gas emission using a novel biological gas reformer. Manuscript. Accepted for publication in *International J. Hydrogen Energy.*
- Watt, Huang, Smolinski, Maness and Wolfrum. "The water-gas shift pathway in *Rubrivivax gelatinosus*." Manuscript in preparation.
- Wolfrum, Watt, Amos "Bioreactor Design Studies at Elevated Pressures", Manuscript in Preparation.
- Abstracts submitted for presentation at "12th Western Photosynthesis Conference" and "25th Symposium on Biotechnologies for Fuels and Chemicals."

Comparison of Conventional vs. Biological Water-Gas Shift; Reforming Controls Choice



Results of Techno-Economic Analysis

- The biological water-gas shift reaction (like other biological processes) is slower than the corresponding catalytic process
- The biological reactor will inevitably be larger than the corresponding chemical reactor
- Overall cost savings result from balance-of-plant considerations
- For the biological WGS process, savings result from avoiding steam reformer & associated equipment

Plans and Future Milestones - Biology

- The hydrogenase enzyme system from *Rubrivivax gelatinosus* is unique in its high rate of hydrogen evolution and its tolerance to oxygen, <u>unlike any other hydrogenases reported in literature</u>
- Continued molecular biological study of this organism could lead to other applications:
  - genetic transfer of the hydrogenase into a cyanobacterium (blue-green alga) to produce hydrogen from **water**
  - a two-stage "fermentation/photofermentation" process to convert biomass to hydrogen via fermentation and the low-value waste organic acids from which are converted into additional hydrogen in a second-stage photofermentation reaction
  - high-value co-product generation during hydrogen production
- *Milestone: increasing WGS activity two-fold through genetic engineering*

Plans and Future Milestones - Engineering

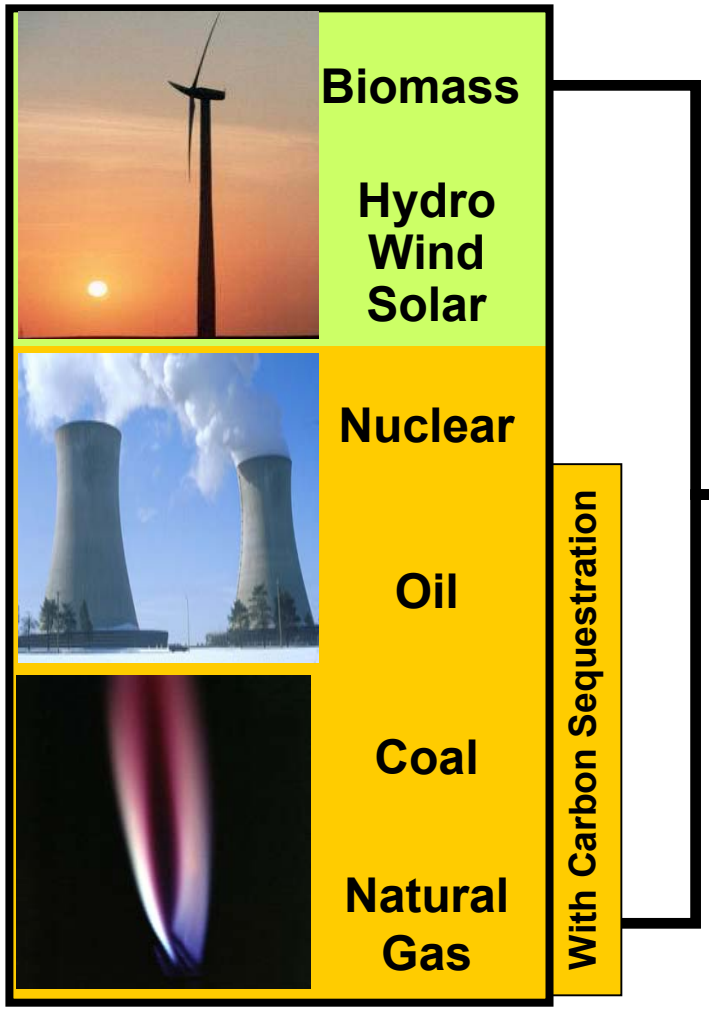
- Elevated-pressure bioreactor operation with gaseous substrates is a unique research area
- Continued research in this area could lead to process improvements and other applications:
  - niche applications for low-HC syngas streams
  - elevated pressure reactor stability issues
  - coproduct production (e.g., SCP, PHA)
  - reactor engineering for two-stage "fermentation/photofermentation" process
- *Milestone: long-term operation of laboratory-scale elevated pressure bioreactors (>4 months)*

Reviewers' Comments - Biology

- *Try to understand water-gas shift metabolic pathway and probe the genes*
  - 9 genes have been sequenced, which will be used to construct a water-gas shift metabolic pathway and to conduct genetic engineering to increase hydrogen production (accomplishment 1)
- *Demonstrate growth and energy generation in darkness*
  - We confirmed that CO supports both cell growth and ATP synthesis in darkness, both of which could sustain hydrogen production (accomplishment 2)
  - More robust dark bioreactor would lower cost of hydrogen
- *Determine lower limit to which water-gas shift can be driven by the biological system even though commercial operation may not work near this limit*
  - water-gas shift rates were determined in various CO concentrations. Results indicated that at 3.6% gaseous CO (26 μM dissolved), water-gas shift rate is 50% maximum (accomplishment 4)

Reviewers' Comments - Engineering

- *Is pH causing inhibition at elevated pressures?*
  - No; experiments with buffer disprove this; likely substrate or product inhibition
- *What will the reactor(s) look like? Low-cost reactors inconsistent with elevated pressure operation*
  - Biological reactors will be larger than corresponding high-temperature catalytic reactors; Cost savings may result from less-expensive materials, but balance-of-plant costs will likely control economics



Fossil-Based Hydrogen Production

Distributed Natural Gas

H_2

Arlene Anderson

Barriers

Fossil-Based Hydrogen Production

- Capital Costs
- O&M
- Separation Technology
- Control and Safety
- Feedstock and Water Issues

Targets and Status

Distributed Hydrogen from Natural Gas or Liquid Fuels

Characteristics	Units	2003 status	2005	2010
Reforming				
Natural gas cost	$/kg H_2	0.66	0.62	0.58
Other costs	$/kg H_2	3.08	1.36	0.24
Primary energy efficiency	% (LHV)	70	72	75
Total				
Total cost	$/kg H_2	5.06	3.00	1.50
Primary energy efficiency	% (LHV)	62	68	75

Targets and Status

Separation Membranes for H_2 Production with Palladium Membranes

Characteristics	Units	2003 status	2005	2010
Flux rate	Scfh/ft^2	60	100	200
Cost	\$/ft^2	150-200	100-150	<100
Durability	Hrs	<1000	50,000	100,000
Operating temp.	°C	300-600	300-600	300-600
Parasitic power	kWh/ 1K scfh	3.2	3.0	2.8

Projects

Fossil-Based Hydrogen Production

• Thermocatalytic CO_2-free Production of H_2 from Hydrocarbon Fuels	Florida Solar Energy Center
• Novel Catalytic Fuel Processing Using Micro-channel Steam Reforming & Advanced Separations Technology	InnovaTek
• ITM Syngas & ITM H_2: Ceramic Membrane Reactor Systems for Converting Natural Gas to H_2 & Syngas for Liquid Transportation Fuels	Air Products & Chemicals, Inc.

Projects (Continued)

Fossil-Based Hydrogen Production

• Integrated Ceramic Membrane System for H_2 Production	Praxair
• Low Cost H_2 Production Platform	Praxair
• Defect-free Thin Film Membranes for H_2 Separation & Isolation	SNL
• Hydrogen Technical Analysis	TIAX

Posters

Fossil-Based Hydrogen Production

• Reformer Model Development for Hydrogen Production	NASA Jet Propulsion Lab
• Separation Membrane Development	Westinghouse Savannah River Technology Center
• Internal Combustion Engines	SNL
• Reduced Turbine Emission Using H2-Enriched Fuels	SNL
• Water-Gas Shift Membrane Reactor Studies	NETL

Discussion Points

- WHY - Jump Start H_2 Economy
- HOW – Diverse Portfolio of Fundamental and applied cooperative RD&D
- DIRECTION – Technical Targets
- ISSUES – Feedstock Costs…..

THERMOCATALYTIC CO_2-FREE PRODUCTION OF HYDROGEN FROM HYDROCARBON FUELS

Nazim Muradov, Franklyn Smith
Florida Solar Energy Center

U.S. DOE Hydrogen and Fuel Cell Merit Review Meeting

Berkeley, May 19, 2003

Relevance/Objective:

Objective: To develop an economically viable process for centralized and distributed production of hydrogen and carbon from hydrocarbon fuels with minimal CO_2 emissions.

Relevance to DOE/FreedomCAR/ Hydrogen technical targets and barriers

(From Table 4.1.1.) Distributed Production of H_2 from Natural Gas and Liquid Fuels

Characteristics	Units	2003 Status	2005 Target	2005, Expected
Cost	\$/kg H_2	5.06	3.00	2.50 - 3.00*
Primary energy efficiency	%(LHV)	62	68	70**

* If carbon sold at >\$0.30 /kg

** Total energy efficiency

4.1.3.2.1 (D) **CO_2 Emissions.** It is significantly more challenging to cost effectively sequester these [distributed] smaller volume carbon emissions than at central hydrogen production facilities that use fossil fuels. This production route should remain limited …. until some cost effective carbon sequestration option for distributed production is discovered.

Approach

The approach is based on thermocatalytic decomposition (TCD) of hydrocarbons over carbon-based catalysts in an air/water-free environment:

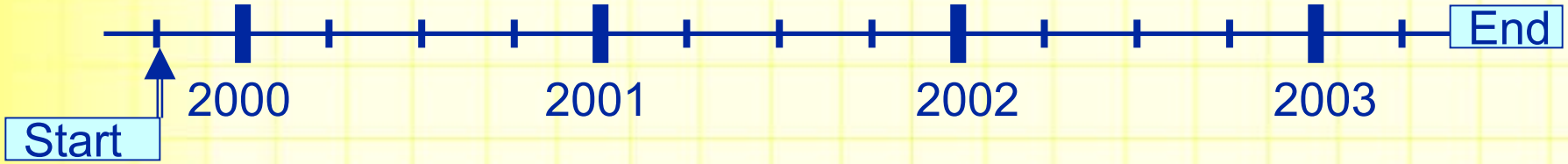
$$\mathbf{CH_4 \rightarrow C + 2H_2} \qquad (38\ \text{kJ/mol}\ H_2)$$

For comparison: $CH_4 + 2H_2O_{liq} \rightarrow CO_2 + 4H_2$ (63 kJ/mol H_2)

Advantages:

- The reaction is catalyzed by carbon particulates produced in the process (no external catalyst is required).
- No CO/CO_2 byproducts are generated during hydrocarbon decomposition stage. CO_2 emissions from the process could be drastically reduced (compared to conventional processes).
- The process produces several valuable forms of carbon that can be sold thus reducing the cost of hydrogen production.

Project Timeline



Catalyst selection

Reaction kinetics studies

Factors affecting catalyst activity

Process engineering development *

Techno-economic analysis

Testing of 1 kW reactor *

Effect of commercial hydrocarbon fuels

Process sustainability improvement

Demonstration of 3 kW thermocatalytic reactor *

Modeling and scaling up of fluidized bed reactor

*critical milestones

Accomplishments

- Catalyst activity / stability and process sustainability
  - Effect of moisture
  - Effect of sulfur
  - Carbon catalyst activation
- Demonstration of 3 kW thermocatalytic reactor
  - Effect of commercial hydrocarbon fuels
  - Testing of 3 kW reactor
- Modeling and scaling-up of fluidized bed reactor
- Assessment of market and application areas for carbon products

Effect of Moisture

- The presence of moisture ($\leq$ 2.0 v.%) in methane feedstock improves catalyst activity and stability.

- The improvement results from the increase in surface area of carbon catalyst (via surface carbon gasification)

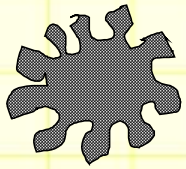
- The presence of moisture causes contamination of H_2 with carbon monoxide at the level of 0.1-0.5 v.%

- The concentration of CO could be decreased to 10 ppm level by subsequent methanation reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (Ru\text{-}0.5\%/Al_2O_3,\ 350^oC)$$

Activation of Carbon Catalyst

$+ \; H_2O, \; CO_2, \; O_2 \rightarrow$



$+ \; H_2, \; CO, \; CO_2$

carbon particle

Cyclic Activation of Carbon Catalyst with Steam, 900°C

Activation reactions:

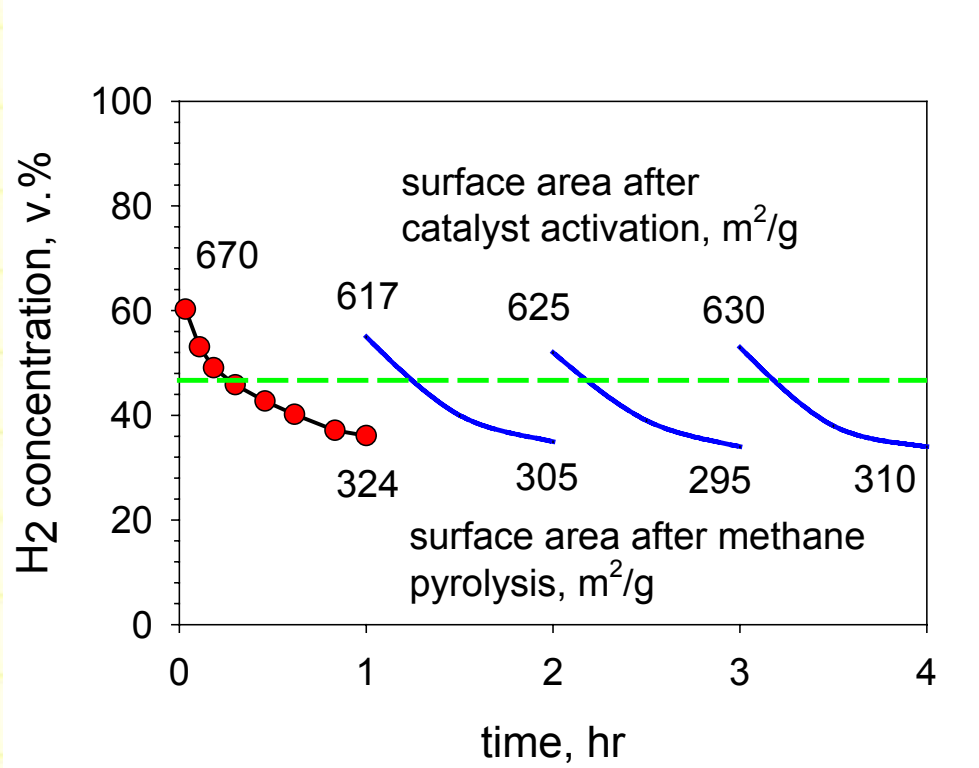
$C + H_2O \rightarrow H_2 + CO$

$C + CO_2 \rightarrow 2CO$

$C + O_2 \rightarrow CO_2$

Activating ability:

$H_2O > CO_2 > O_2$



Effect of Sulfur

- H_2S does not adversely affect the activity and stability of carbon catalysts at 800-900°C (at $[H_2S] \leq 2.5$ v.% in CH_4)

- Carbon catalyst remains free of sulfur compounds

- Reactions of H_2S in the system:

$$\left.\begin{array}{l} H_2S \rightarrow H_2 + 1/2S_2 \text{ (catalyzed)} \\ 2H_2S + C \rightarrow 2H_2 + CS_2 \end{array}\right\} H_2S \text{ conversion } 50\%$$

- Conversion of H_2S in presence of CO_2:

$$H_2S + CO_2 \rightarrow H_2, CO, S_2, H_2O \text{ (COS)} \quad (95\%)$$

Testing of 3 kW Unit Using Pipeline NG

Experimental Set-up with 3 kW Reactor

NG, v.%:

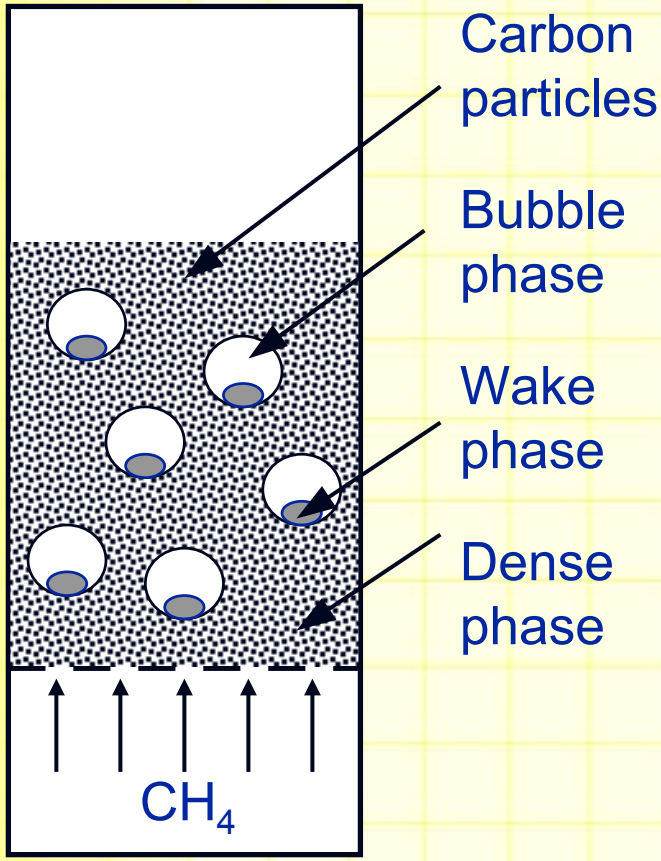
N_2- 0.9
CH_4- 93.1
C_2H_6- 4.1
C_3H_8- 0.7
C_4+- 0.3
CO_2- 0.9
CH_3SH- 4 ppm

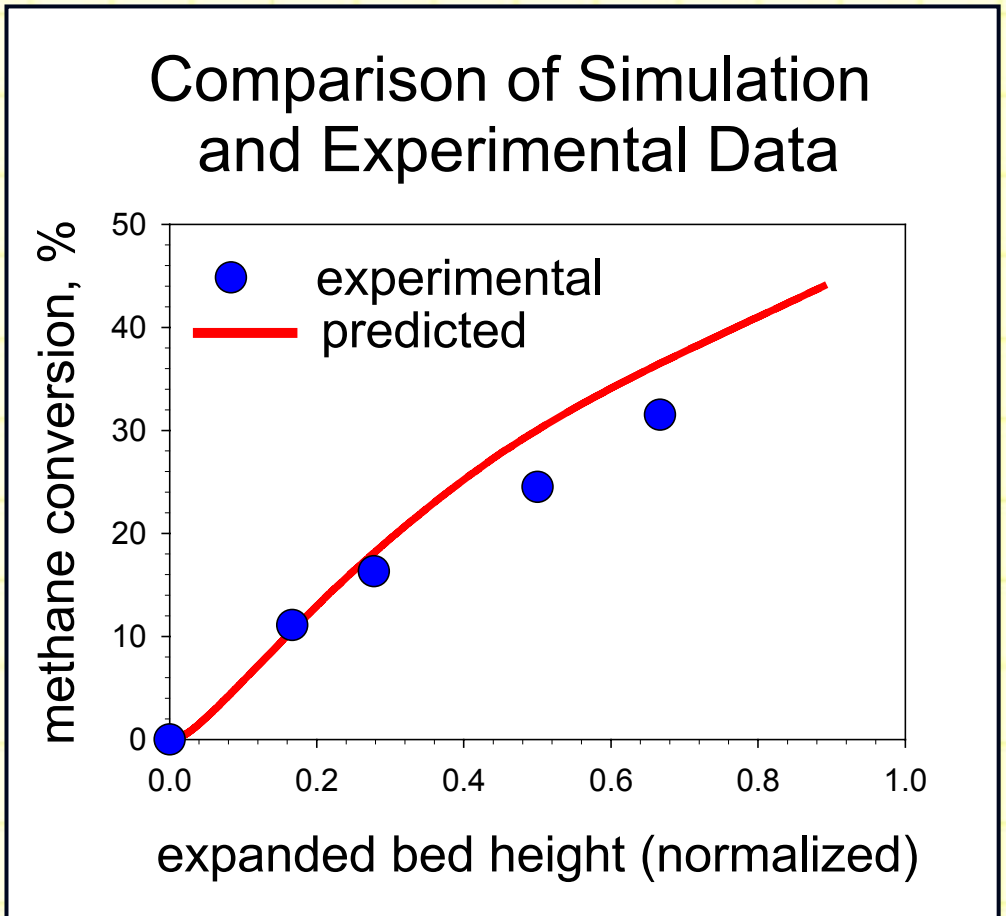
Feedstock	T, °C	Composition of gaseous products, v.%					
		H_2	CH_4	C_2H_6	C_2H_4	CO	CO_2
Pipeline Natural Gas	870	45.5	53.6	0.0	0.0	0.7	0.1
Commercial Propane	850	61.8	30.4	2.1	5.1	0.1	0.0

Modeling of Fluidized Bed Reactor (FBR) for Catalytic Decomposition of Methane

(in cooperation with REI)

Three-phase model for FBR (bubbling regime):





Modeling and Scaling-up of FBR for Catalytic Decomposition of Methane

(in cooperation with REI)

Large scale H_2 plant:

50 t/day H_2

109 t/day Carbon

FB reactor diameter:

Bubbling regime- 4.2 m

Turbulent regime- 2.1 m

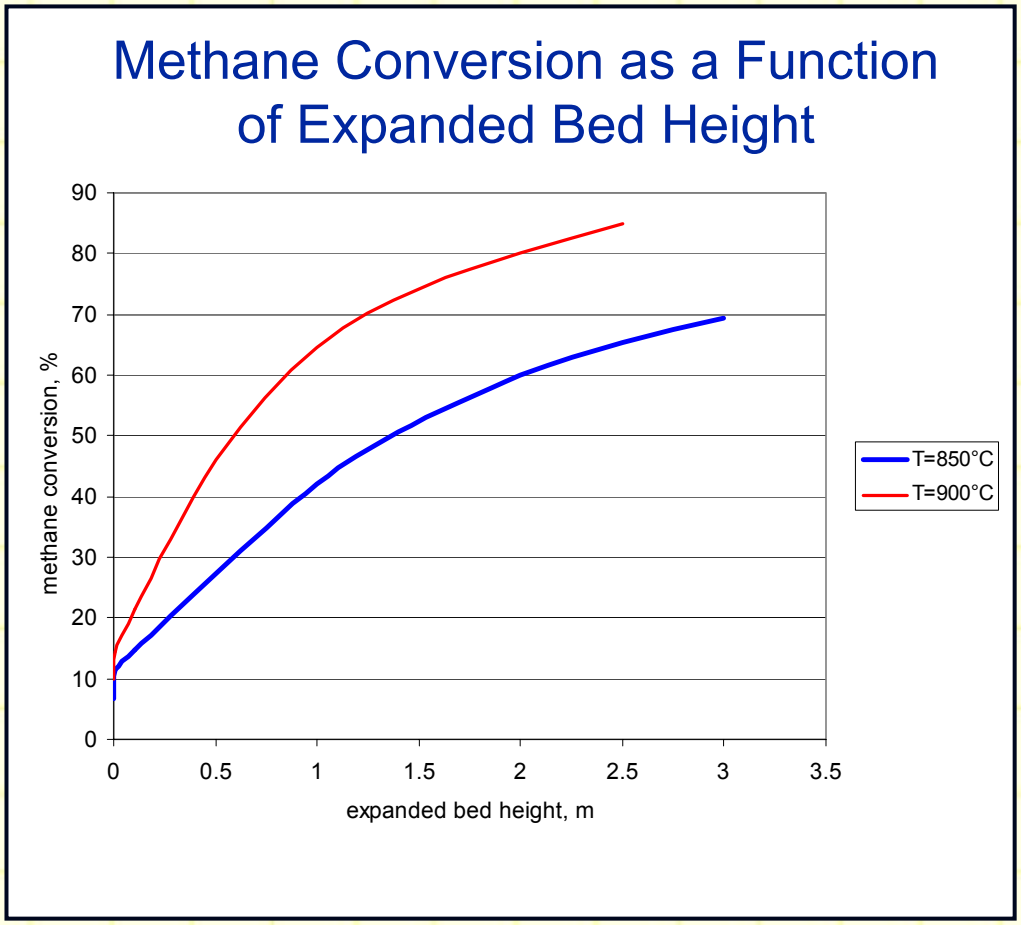
Small scale unit:

500 kg/day H_2

1090 kg/day Carbon

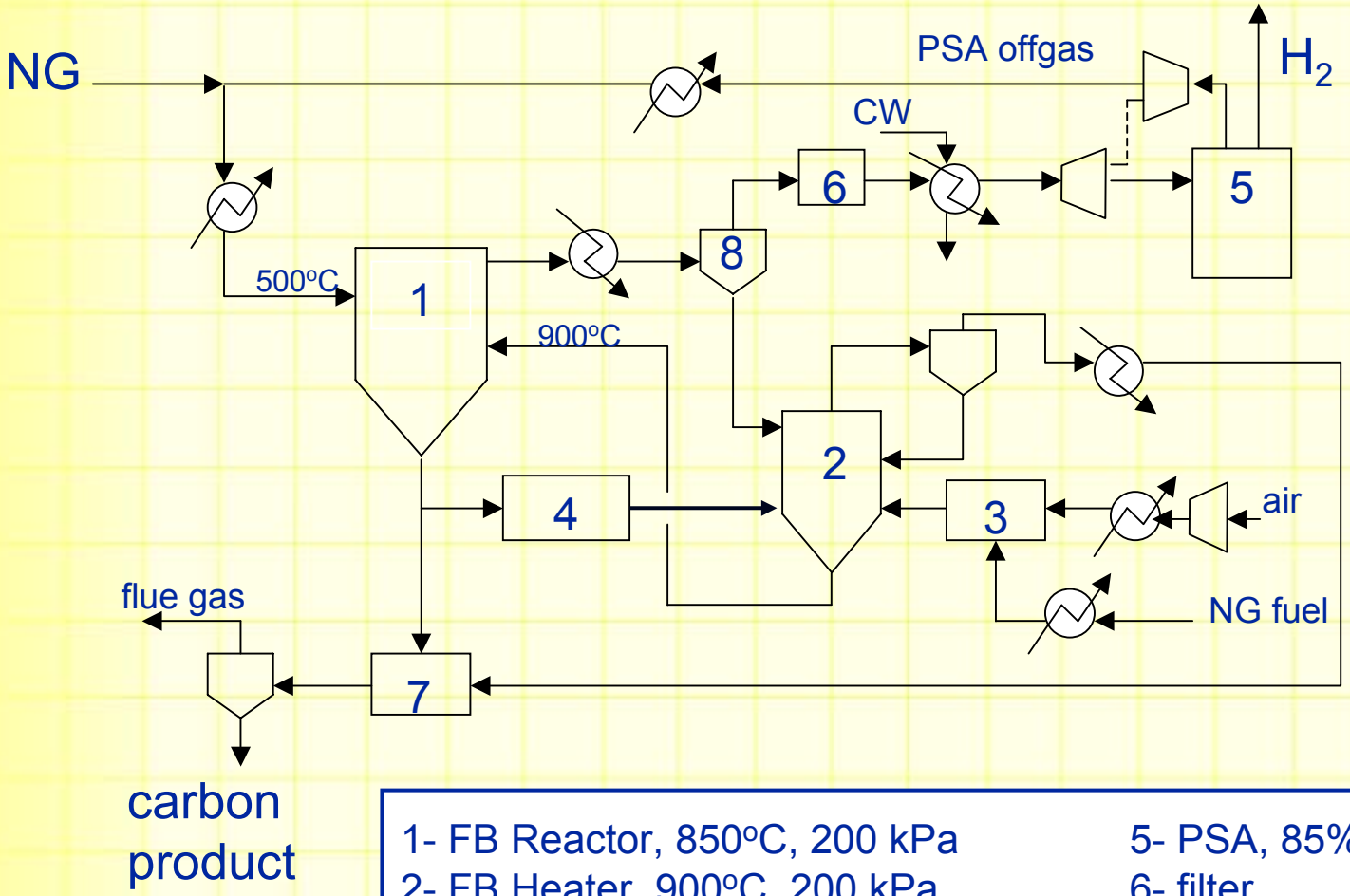
FBR diameter: 0.5 m

FBR height: 4.2 m



Process Flowsheet for Thermocatalytic Decomposition of Natural Gas

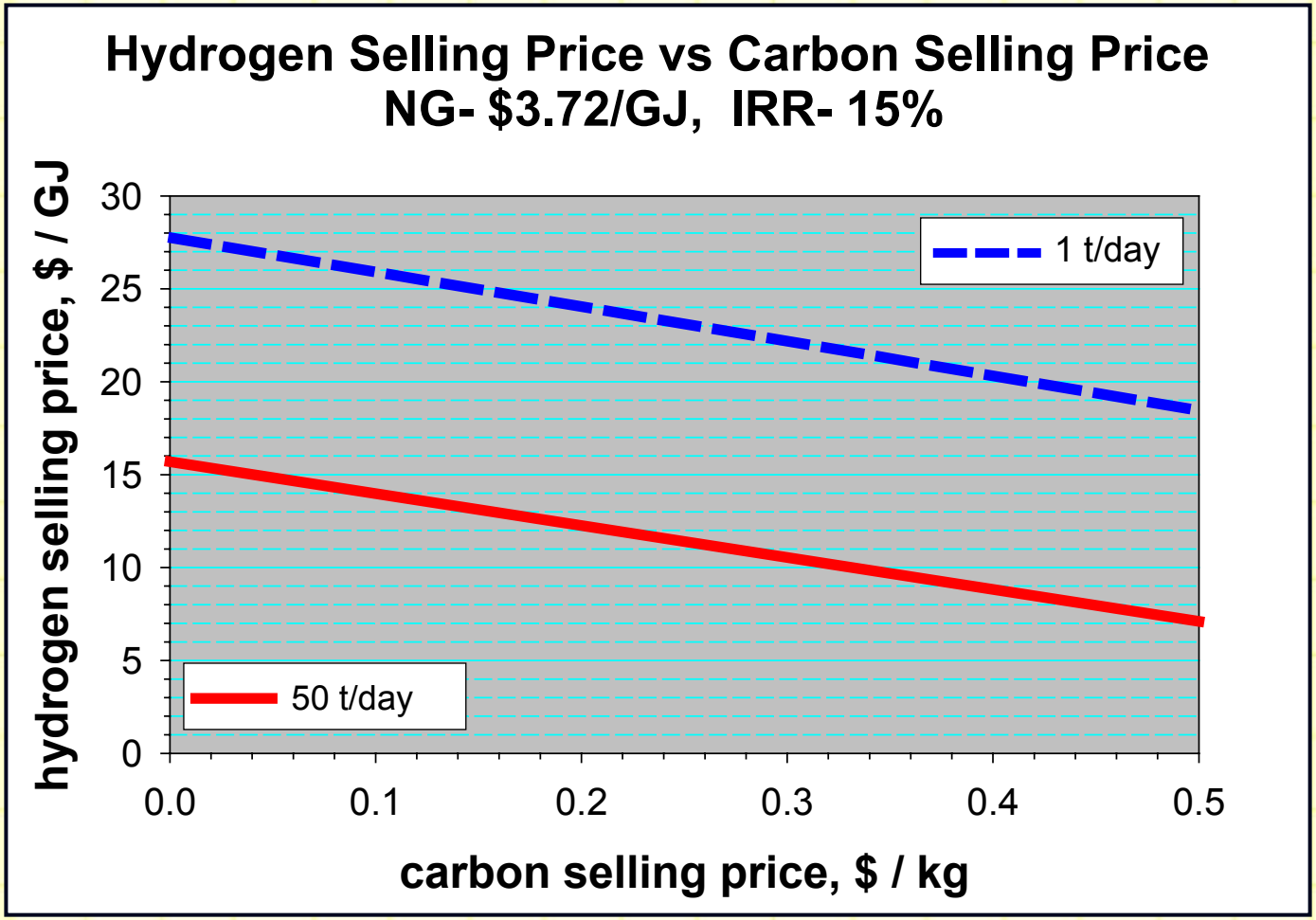
(in cooperation with NREL)



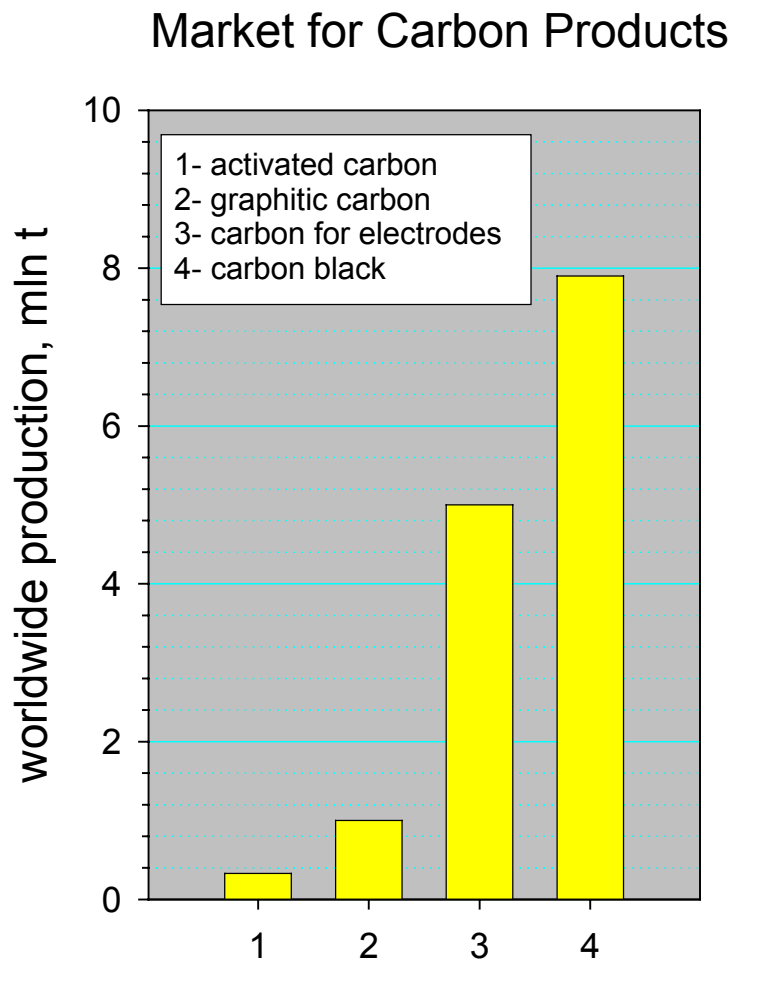
1- FB Reactor, 850°C, 200 kPa
2- FB Heater, 900°C, 200 kPa
3- combustor, 1250°C, 200 kPa
4- grinder
5- PSA, 85% H_2 recovery
6- filter
7- quencher
8- cyclones

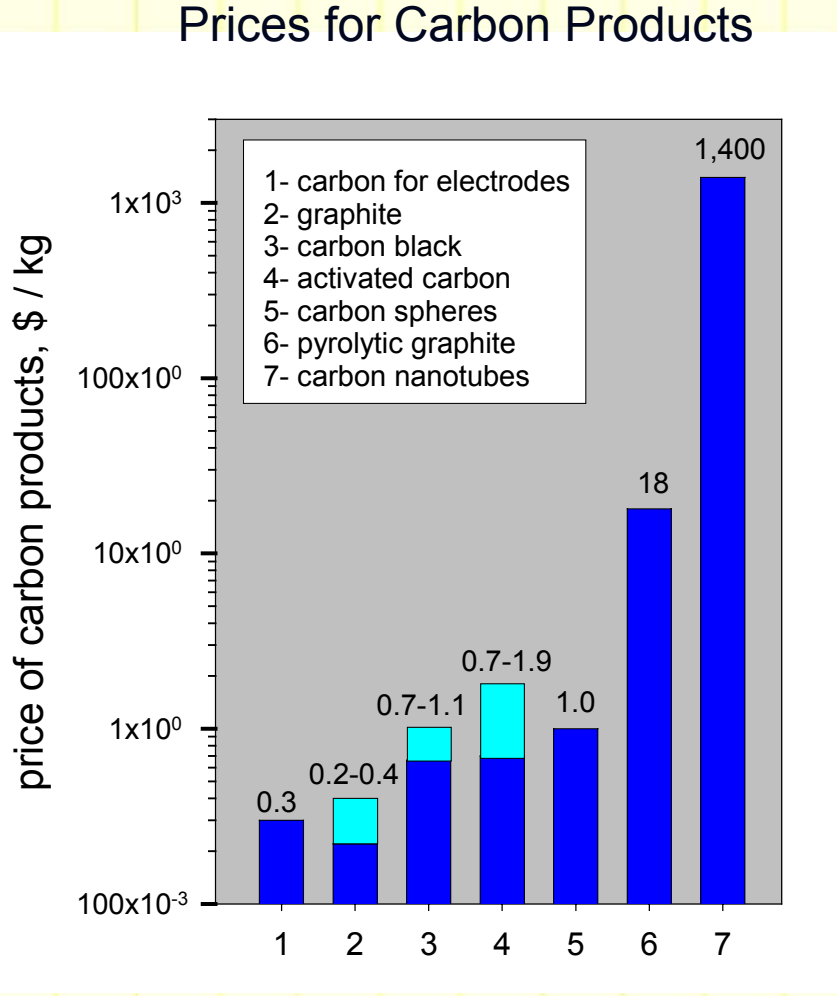
Techno-economic Analysis

(in cooperation with NREL)



Market for Carbon Products

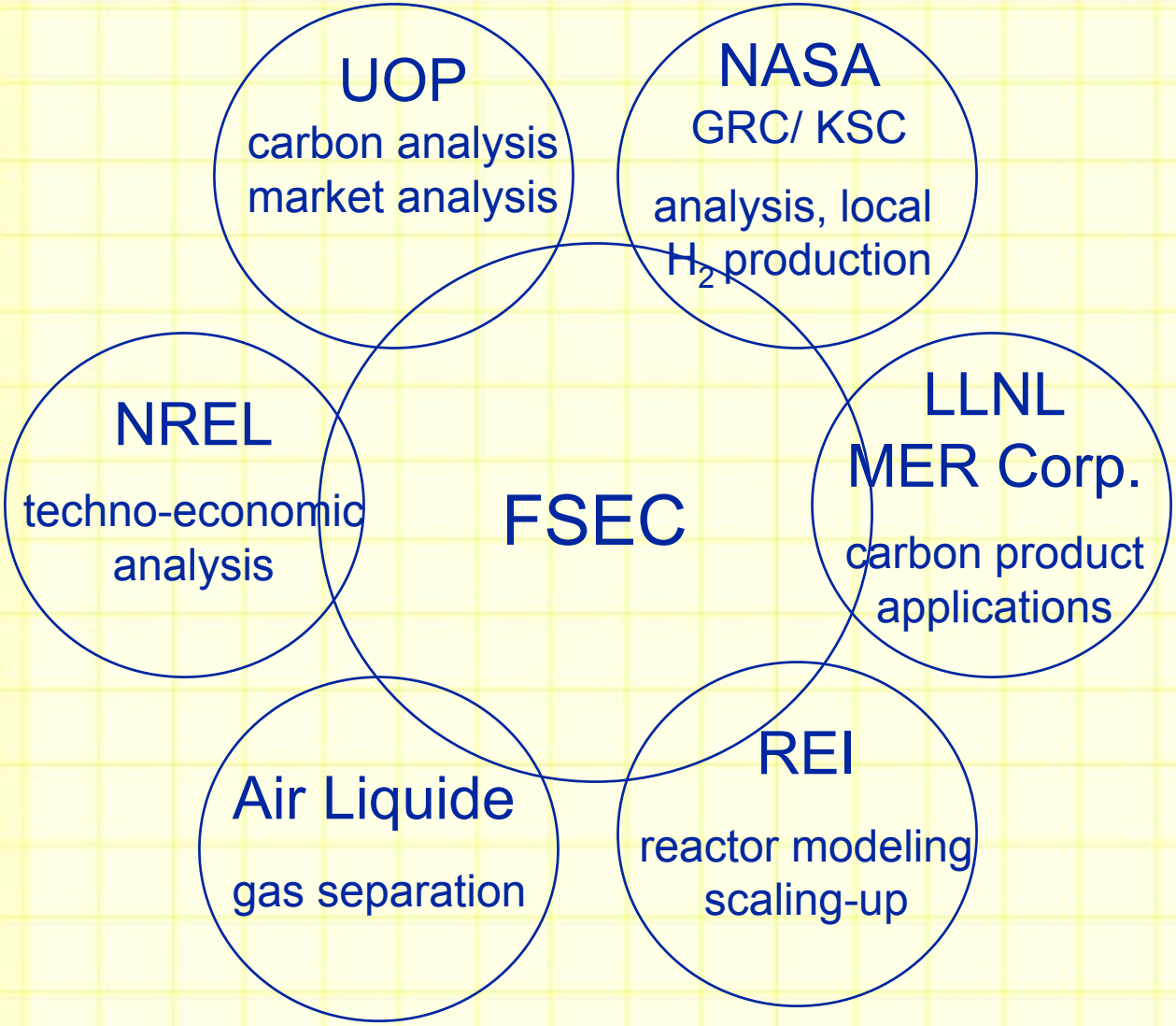




Publications, Patents

1. Muradov, N. *Journal of Power Sources,* 118, 1-2, 320 (2003)
2. Muradov, N. *Symposium: Hydrogen Energy for 21st Century, Amer. Chem. Soc. Meeting,* New Orleans, 2003
3. Muradov, N. *Symposium: Fuel Clean-up Considerations for Fuel Cells, Amer. Chem. Soc. Meeting*, *Petroleum Division*, New Orleans, 2003
4. Muradov, N., T-Raissi, A. *HYPOTHESIS-V Symposium*, Porte Conte, Italy, 2003
5. Muradov, N., Schwitter, A. *Nano Letters*, v.2, No.6, 673, 2002
6. Muradov, N. *Fuel Cells Science and Technology,* Amsterdam, Netherlands, 2002
7. Muradov, N. *14th World Hydrogen Energy Conference*, Montreal, Canada, 2002
8. Muradov, N., Noland, G., Manikowski, A. *14th World Hydrogen Energy Conference*, Montreal, Canada, 2002
9. Muradov, N. *U.S. Patent Appl. No. 60/194,828 (2002)*
10. Muradov, N. *U.S. Patent Appl. No. 60/203,370 (2002)*
11. Muradov, N. *U.S. Patent Appl. No. 60/346,548 (2003)*

Interactions / Collaborations



Plans, Future Milestones

Task	Milestones	
1	Optimize the performance of pyrolytic reformer coupled with a gas clean-up system for distributed production of hydrogen with concentration of CO and H_2S below 25 ppm	2004, Q1
2	Increase the yield of high-value carbon products (>$1/kg) (preferably, for construction materials applications)	2004, Q3
3	Determine the feasibility of using alternative feedstocks for the pyrolysis reformer (including biomass-based feedstocks)	2004, Q4
4	Optimize the reformer for the increased energy efficiency (total energy efficiency of 70%) and reduce cost of H_2 production to $2.50-3.00/kg H_2	2005, Q2

Responses to Reviewers' Comments

❖ Carbon Catalytic Activity Measurements

Catalytic activity of carbon samples toward methane decomposition was determined on the basis of both mass and surface area.

❖ Carbon Utilization Issues

Since carbon represents half of methane fuel value, carbon should be used for:

- additional hydrogen production via steam gasification, or
- power generation (as an ultra-clean coal substitute)

Determine whether the efficiency and CO_2 reduction are improved compared to conventional SMR

Responses to Reviewers' Comments (cont.)

Comparative Assessment of Three Scenarios:

(A) Steam Methane Reforming (SMR)
(B) TCD coupled with steam gasification of carbon
(C) TCD coupled with carbon combustion (power generation)

- Scenario (B) does not offer any advantages over SMR:

$$CH_4 \rightarrow C + 2H_2$$
$$C + 2H_2O \rightarrow CO_2 + 2H_2$$
Total: $$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

- Scenario (C) can be justified if TCD is coupled with direct carbon fuel cell:

$$CH_4 \rightarrow C + 2H_2$$
$$C + O_2 \rightarrow CO_2 \quad \text{(MCFC, efficiency 80\%)}$$
Total: $$CH_4 + O_2 \rightarrow CO_2 + 2H_2 + \text{electricity}$$

DOE H Program Review, May 2003

Novel Catalytic Fuel Reforming Using Micro-Technology with Advanced Separations Technology

May 2003

InnovaTek, Inc

Richland, WA

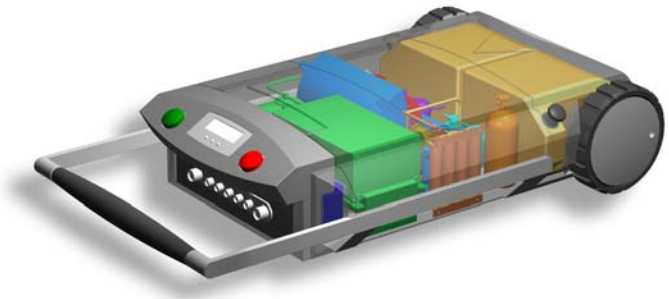
InnovaTek Program Goal

Develop fuel processors to supply clean hydrogen to fuel cells for portable and stationary power.

- **Produce H_2 for fuel cell-powered vehicle refueling stations.**
- **Provide auxiliary power units for transportation power needs.**

Industrial Design -- Use Concept

Refueling Station



Portable or Stationary APU

INNOVATEK

Development Objectives

Produce pure hydrogen from available fuels using highly efficient, micro-channel catalytic steam reforming and membrane purification technologies.

2002: Component development for 12 LPM hydrogen from natural gas and diesel with >50 ppm S (250 ppm)

2003: Component optimization and design for 60 LPM hydrogen from natural gas and diesel with >100 ppm S (500 ppm)

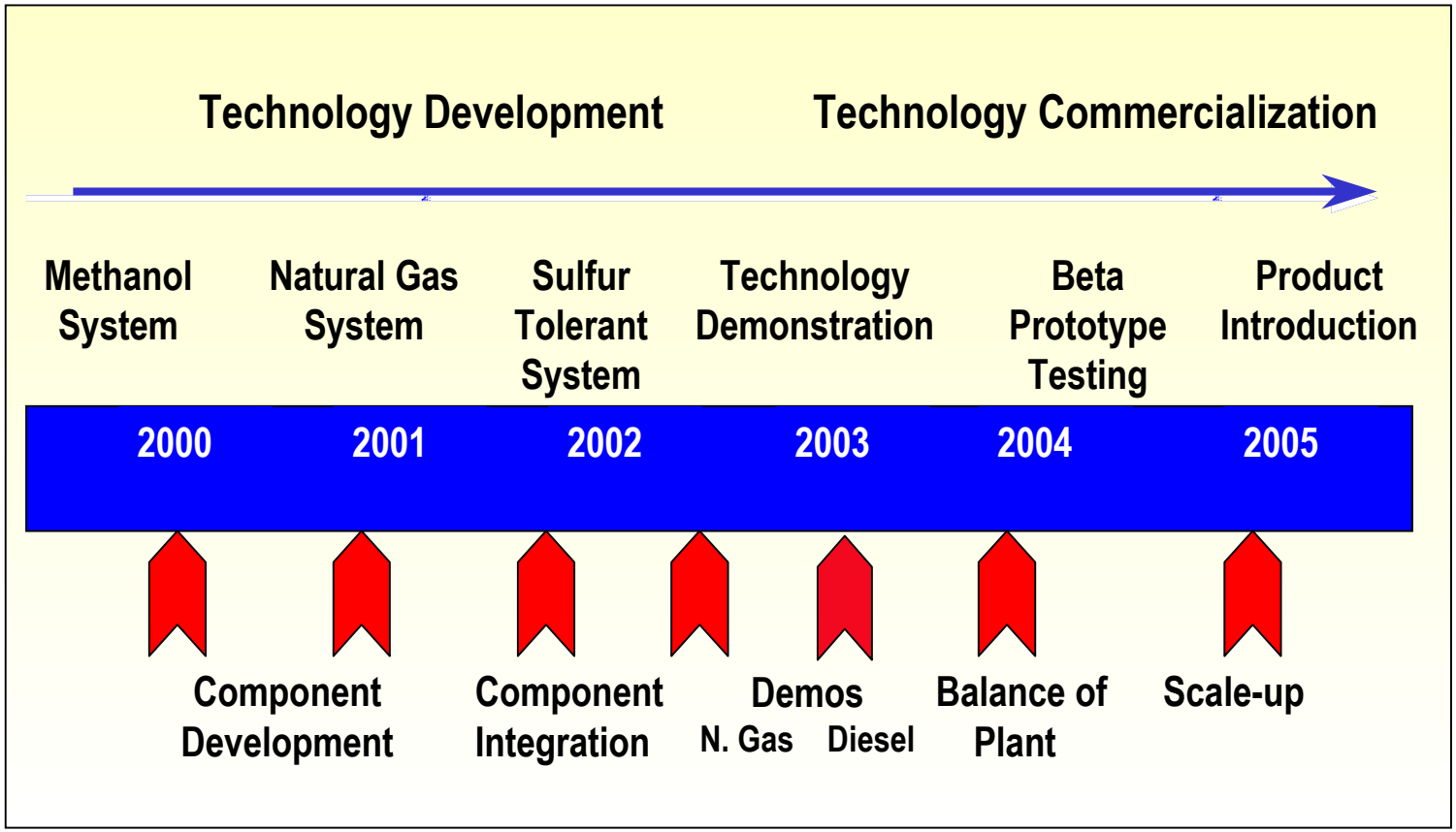
Goals and Methods

Sulfur-tolerant **steam reforming catalyst** reforms fuel without need for prior sulfur removal.

Advanced **membrane technology** produces nearly pure hydrogen output thereby enabling higher fuel cell power densities & no potential for electrode poisoning.

Micro technology for reactor, heat exchanger, combustor, and fuel vaporizer improves system efficiency through optimized thermal management and fluid dynamics.

Project Timeline



INNOVATEK

System Development Status

Develop and test core technology

Design process configurations

Evaluate configurations with model simulation

Predict component requirements with model simulation

Design and fabricate components

Conduct iterative testing of components

Demonstrate integrated system

Further development and optimization of core components

Integrated System

System design and optimization is complex

- Micro-channel heat exchangers
- Catalytic steam reformer and burner
- Hydrogen purification < 5 ppm CO
- Condensate removal and recovery
- Diesel and steam injector and mixing
- Fuel and water delivery

Integration schemes evaluated using process model

Process Simulation & Configuration Options

Developed model to track mass and enthalpy flows.

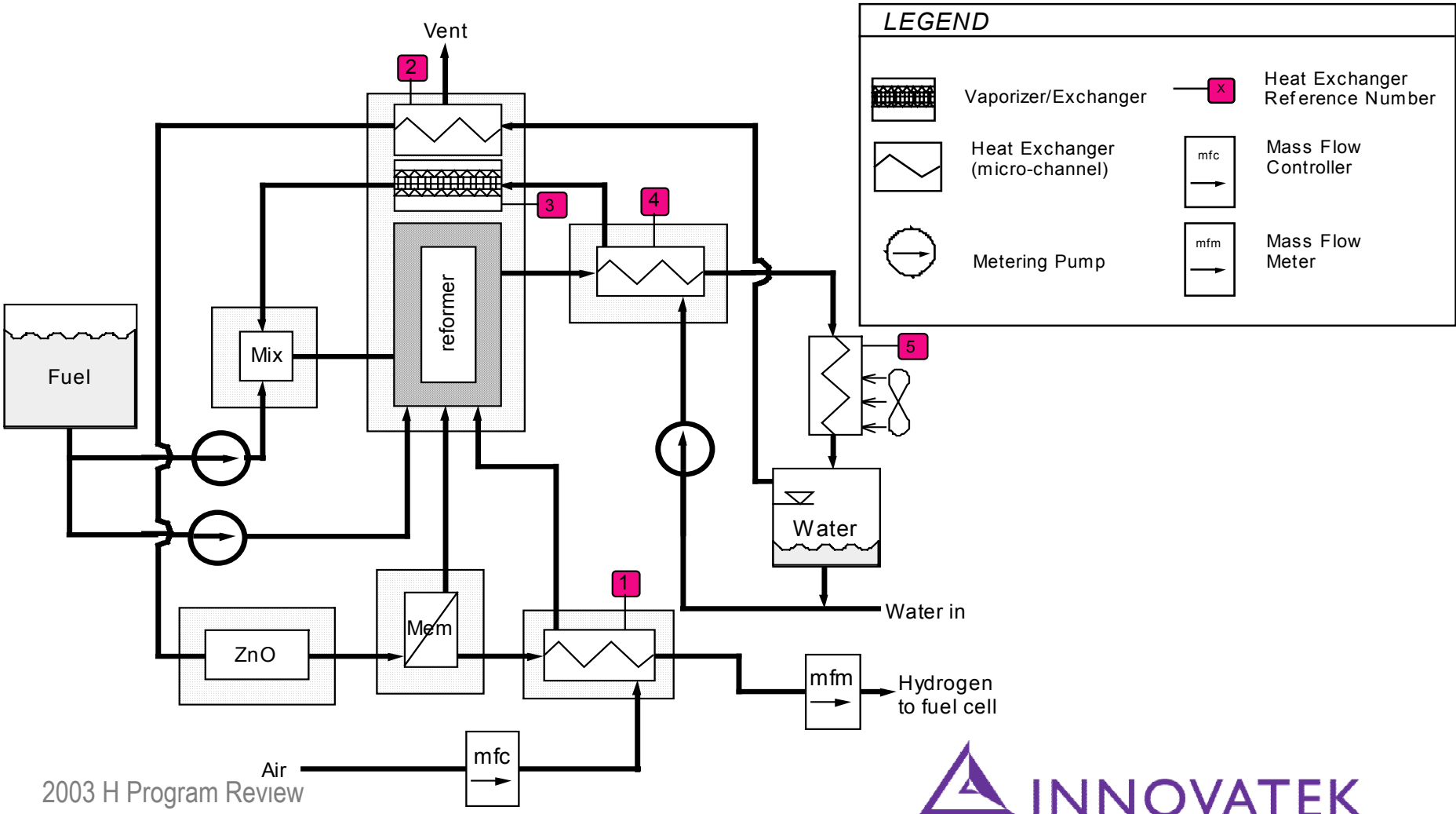
Estimates molar flows of reforming products by solving for equilibrium concentrations at given temperature and pressure.

Thermodynamic properties determine heat transfer, water removal, and air & heat required to achieve energy balance.

Model output helps size system components and select range for operating conditions.

Options for thermal management and water management – major influence on effective system operation and integration

Integrated System Schematic



INNOVATEK

Heat Exchange Components

Ref #	Description	Hot Fluid	Cold Fluid
1	H_2 Cooler	Hydrogen Product	Air Feed
2	Reformate Heater	Combustion Exhaust	Dry Reformate
3	Steam Super Heater	Combustion Exhaust	H_2O 80% Steam
4	Reformate Cooler	Wet Reformate	H_2O Feed
5	Reformate Condenser	Wet Reformate	Blower Air

InnovaGen™ Steam Reforming Catalyst

- Proprietary bi-metallic formula supported on modified Al_2O_3
- Optimized for activity, selectivity, and stability
- Tested using diesel, gasoline, and natural gas
- Determined optimized reforming conditions for diesel: reaction temp, steam/carbon, space velocity

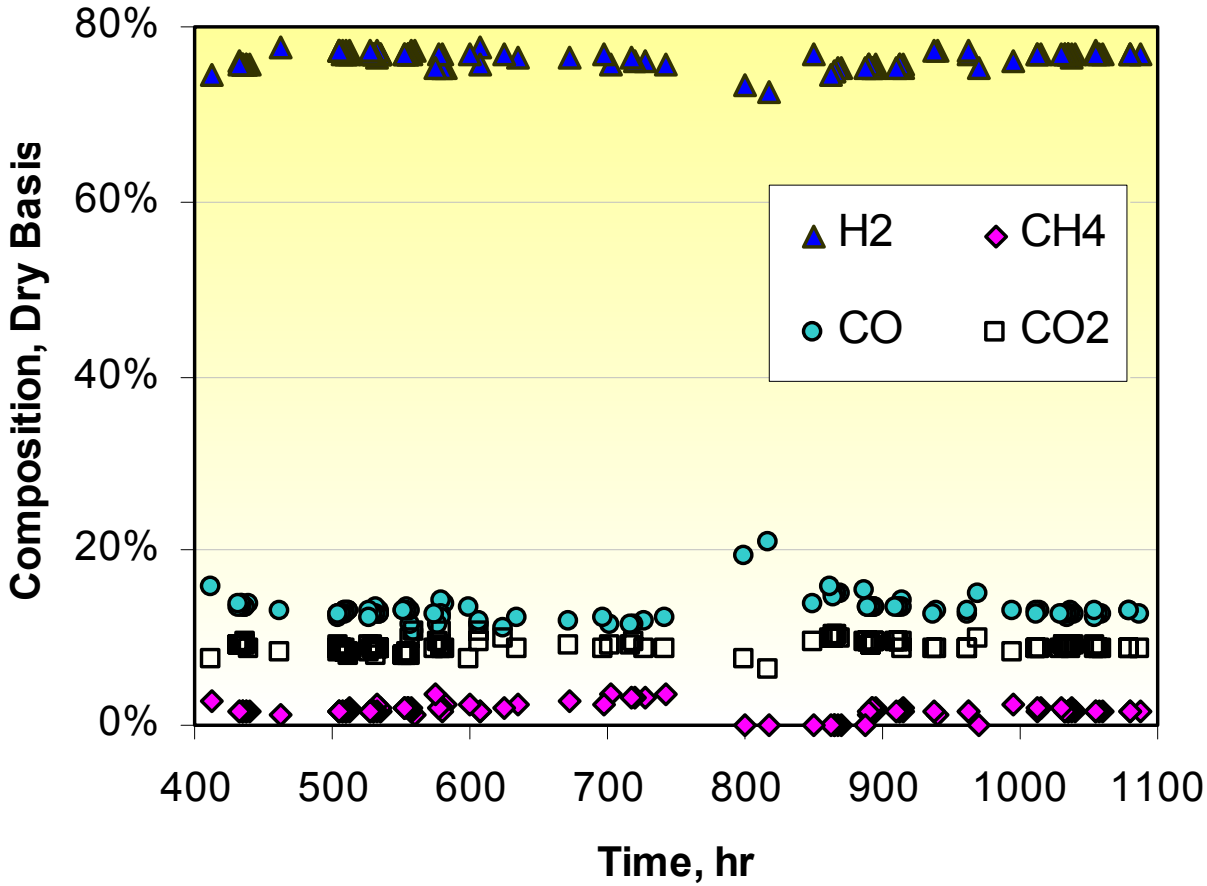
Patent pending

INNOVATEK

Catalyst Characterization

BET Surface Area:	101 m^2/gram
Metal ratio:	specific ratio produces higher sulfur resistance and low methane production
Metal loading:	High loading needed (>1 wt%) for sustained sulfur tolerance

Long-Term Natural Gas Reforming Tests

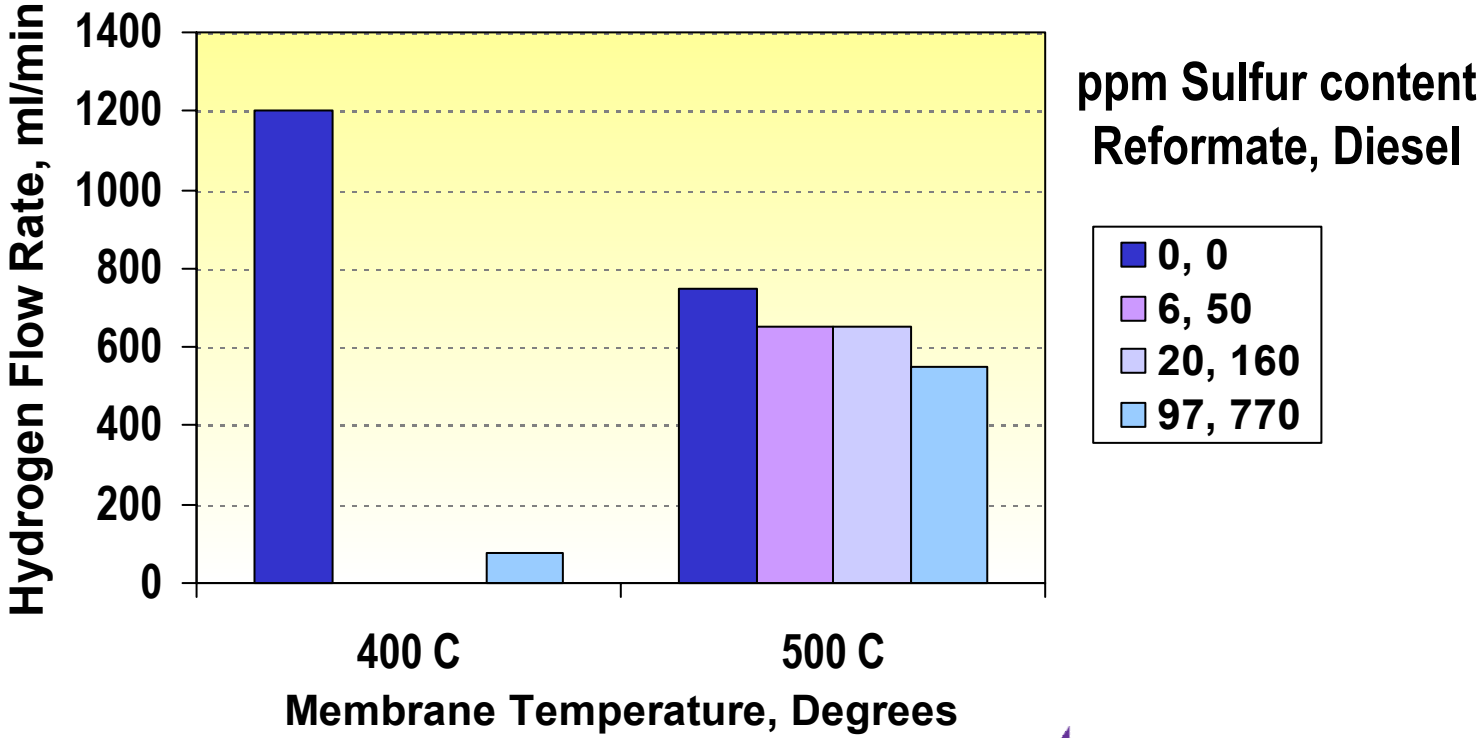


Using InnovaTek's proprietary catalyst, ITC-1148.

INNOVATEK

InnovaTek S-Tolerant Membrane Tests

H Permeation Rate as a Function of Membrane Temperature and Reformate Sulfur Content

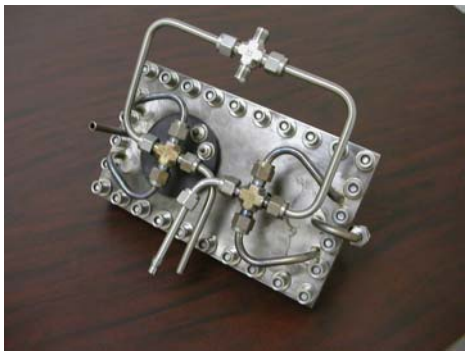


INNOVATEK

InnovaGen™ 1 kW Fuel Processor Components

Steam Reformer with Integrated Burner & Heat Exchanger

Micro-channel Heat Exchanger



H-Permeable Membrane Module

Burner Components

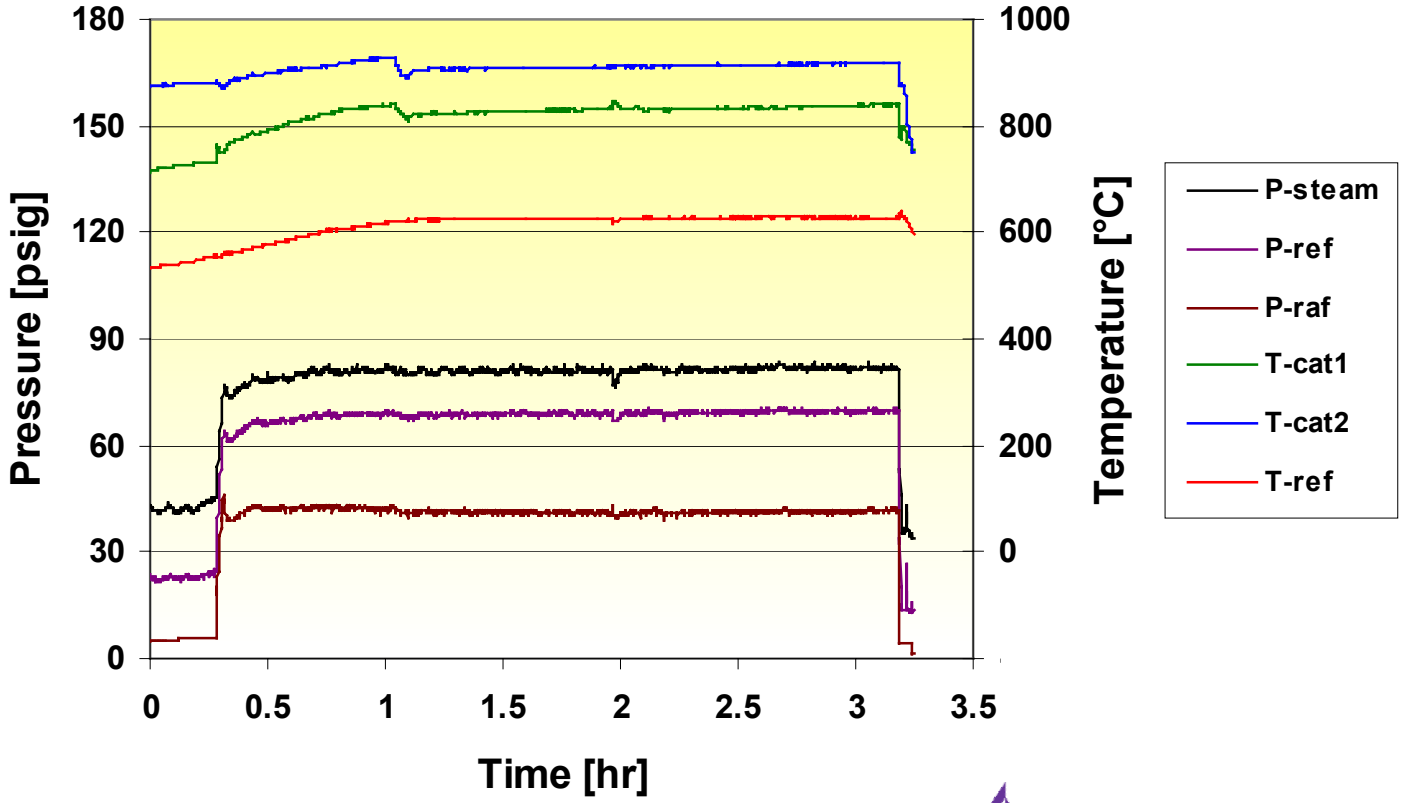
Heat Exchangers

Zinc Oxide Purifier for Sulfur Removal

INNOVATEK

System Pressures and Temperatures

Sample data from diesel test with 50 ppm sulfur.



INNOVATEK

Target Specifications and Objectives

Hydrogen Purity, CO Content	99.99%, < 5 ppm
Hydrogen Output and Temperature	12 L/min at STP, 60 °C max.
System Reliability	90% at 1,000 hours
Turn-Down Ratio	Idle and full-load only
Operating Temperature Range	1 to 40 °C
Storage Temperature Range	-20 to 50 °C
Cold Start-up to Full Output	40 minutes
System Volume, Weight (no fuel)	50 L, 30 kg
System Weight (no fuel)	30 kg
Thermal Efficiency	50% $HV_{L,hydrogen}/HV_{L,diesel}$
Diesel Fuel Sulfur Content	500 ppm by weight

Responses to 2002 Panel Review

Mass Balance	Rate, [gm/hr}
In	7,049
Diesel for reforming	218
Diesel for combustion	124
Combustion air	5,308
Feedwater	1,399
Out	7,049
Product hydrogen	59
Condensate from reformate	937
Burner exhaust	6,053

System Mass Balance:

- Based upon 1 kW electrical output.
- Process parameters calculated from system model.

Responses to 2002 Panel Review

Energy Balance	Rate, [W}
In	4,090
Diesel for reforming	2,603
Diesel for combustion	1,487
Out	4,090
Product hydrogen	1,977
Shell losses	500
Condenser heat rejection	690
Exhaust losses	632
Condensate losses	291

System Energy Balance:

- 48% thermal efficiency based upon lower heating values.
- Combustion of diesel and raffinate provides heat for reforming

INNOVATEK

Interactions & Collaborations

University of WA: Dr. Phil Malte - injector and burner design project; laser-based determinations of fuel evaporation and mixing.

WA State University: Prof. Pat Pedro - plasma catalyst deposition

PNNL: Larry Pederson - micro-channel heat exchangers; EMSL – catalyst characterization

Micro-Fabricators: working with several commercial partners

Irving, P. M., Q. Ming, and D.R. Stephens, "Development of a Fuel Processor that Generates Hydrogen from Conventional Fuels", In: Proceedings of the 14th Annual U.S. Hydrogen Meeting, March 4-6, 2003, Washington DC.

Irving, P.M., "Novel Catalytic Fuel Reforming", Global Climate Energy Project, April 14-15, 2003, Stanford University.

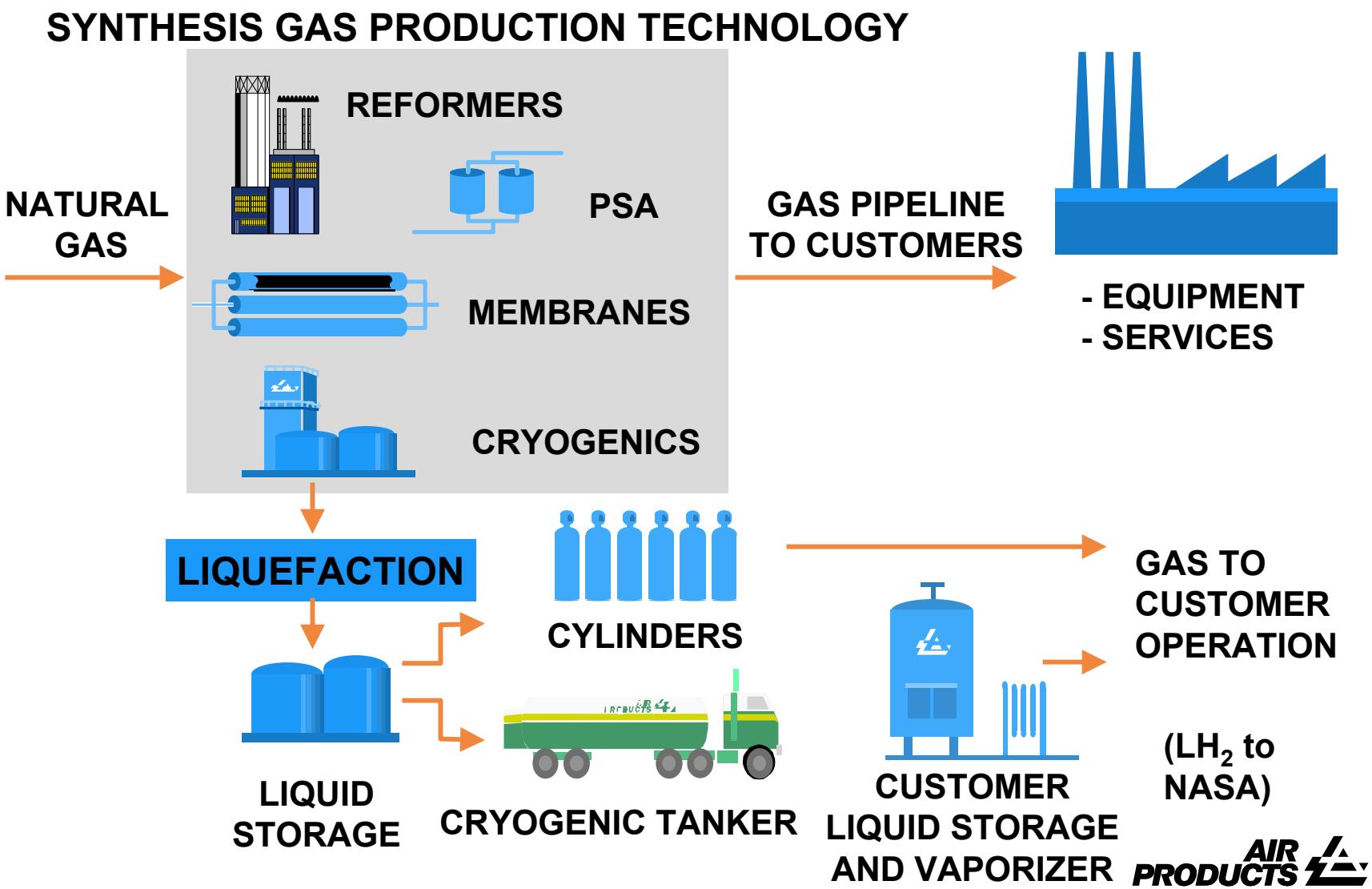
Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels (DE-FC26-97FT96052)

Christopher M. Chen
Air Products and Chemicals, Inc.

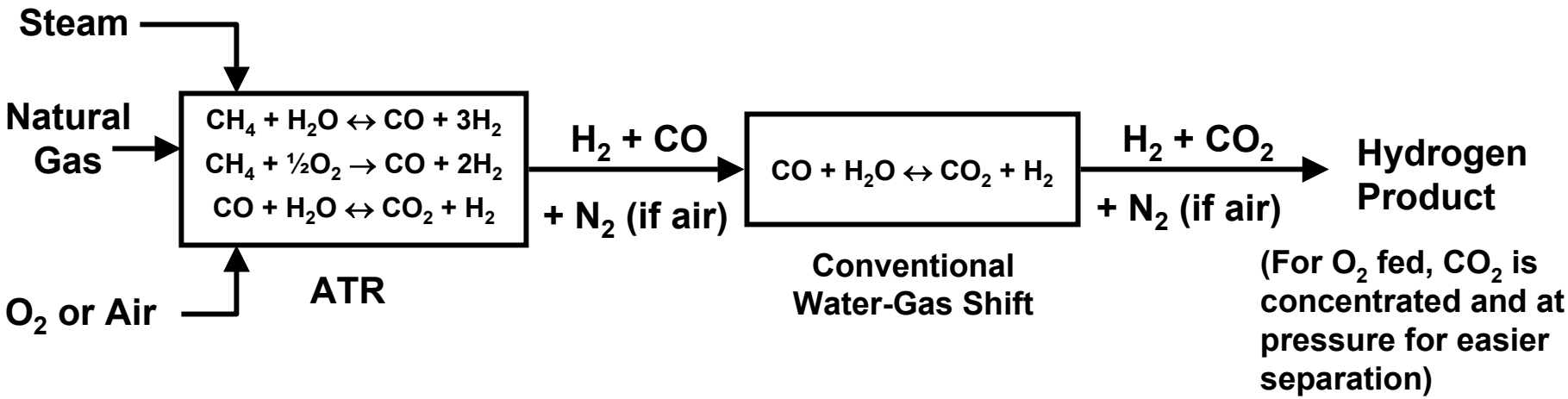
U.S. Dept. of Energy Hydrogen Program Annual Review
19 May 2003

AIR PRODUCTS

Air Products Is the Global Leader in Hydrogen Supply



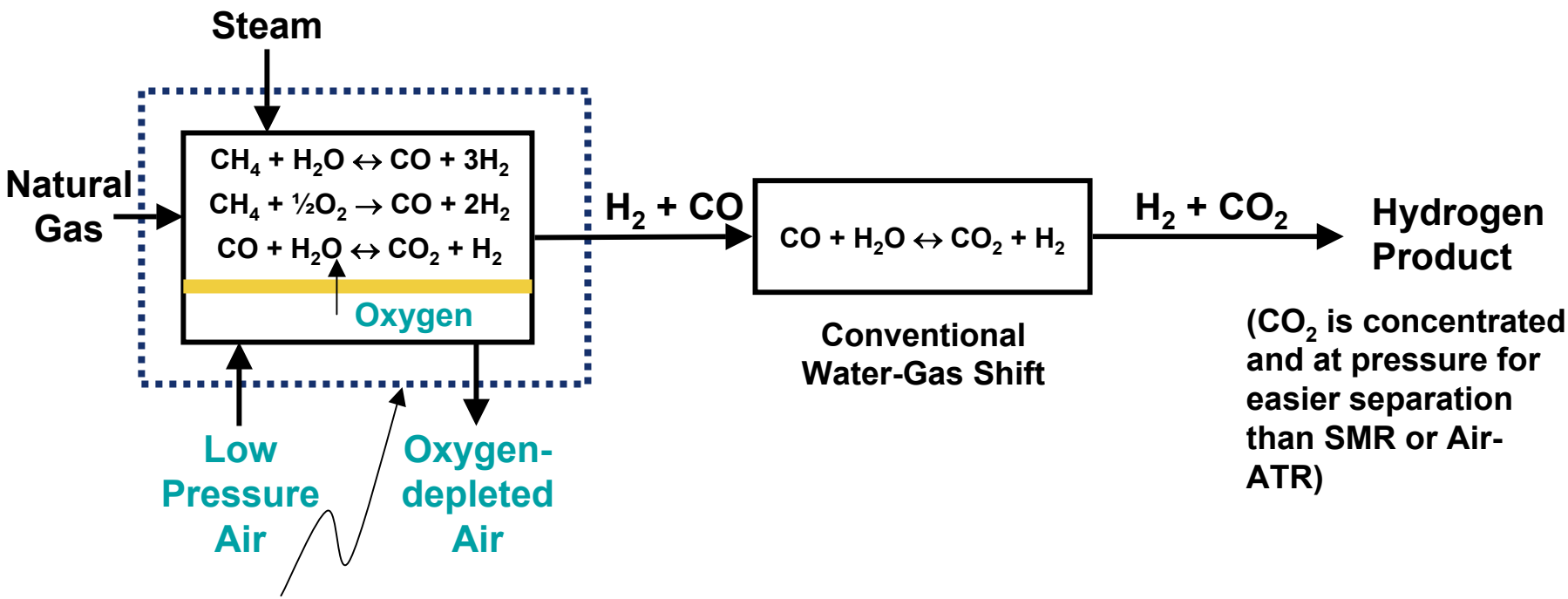
Several Companies Are Developing Autothermal Reformers for a Range of Hydrogen Plant Sizes



- Centralized hydrogen production
  - Typically use pure oxygen feed
  - Better economies of scale than SMR for large plants
  - Amenable to carbon capture
- Small stationary hydrogen production
  - Conventional pure oxygen is not economical at these small scales
  - Typically use air feed to ATR
  - N_2 dilution of synthesis gas leads to increased cost of downstream purification

AIR PRODUCTS

ITM Syngas Technology Provides the Benefits of Oxygen-Based ATR at Significantly Reduced Cost



ITM Syngas Technology

Critical Features:

- Promote steam reforming reaction
- Promote partial oxidation reaction
- Promote oxygen separation from air

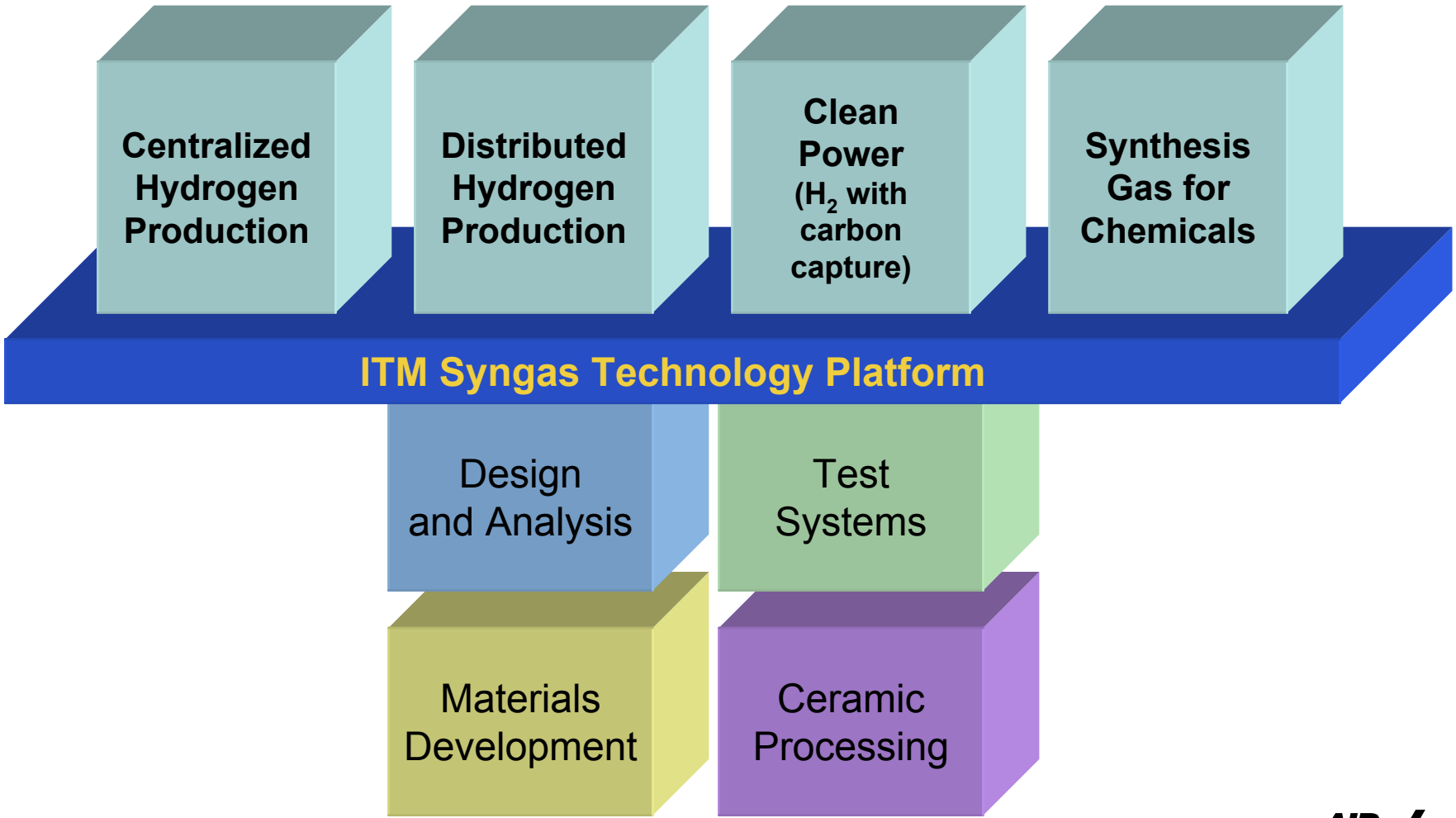
→

Achieves significant cost saving through process simplification

Combines air separation and synthesis gas production into a single reactor

AIR PRODUCTS

Project Objective: Research, develop, demonstrate ceramic Ion Transport Membrane (ITM) reactor system for low-cost conversion of natural gas to hydrogen and synthesis gas



AIR PRODUCTS

Three Phase Industry-DOE Project with Broad Development Team

Phase 1

Identified family of high-pressure membrane materials
Verified ceramic-to-metal seal performance
Selected planar membrane over tubular design

Phase 2

24,000 SCFD* Process Development Unit (PDU)
330,000 SCFD* Subscale Engineering Prototype (SEP)

Phase 3

15 million SCFD* Pre-Commercial Technology Demonstration Unit

1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007

Tested membranes at elevated pressure for over 6 months

Fabricated full planar membrane module for PDU

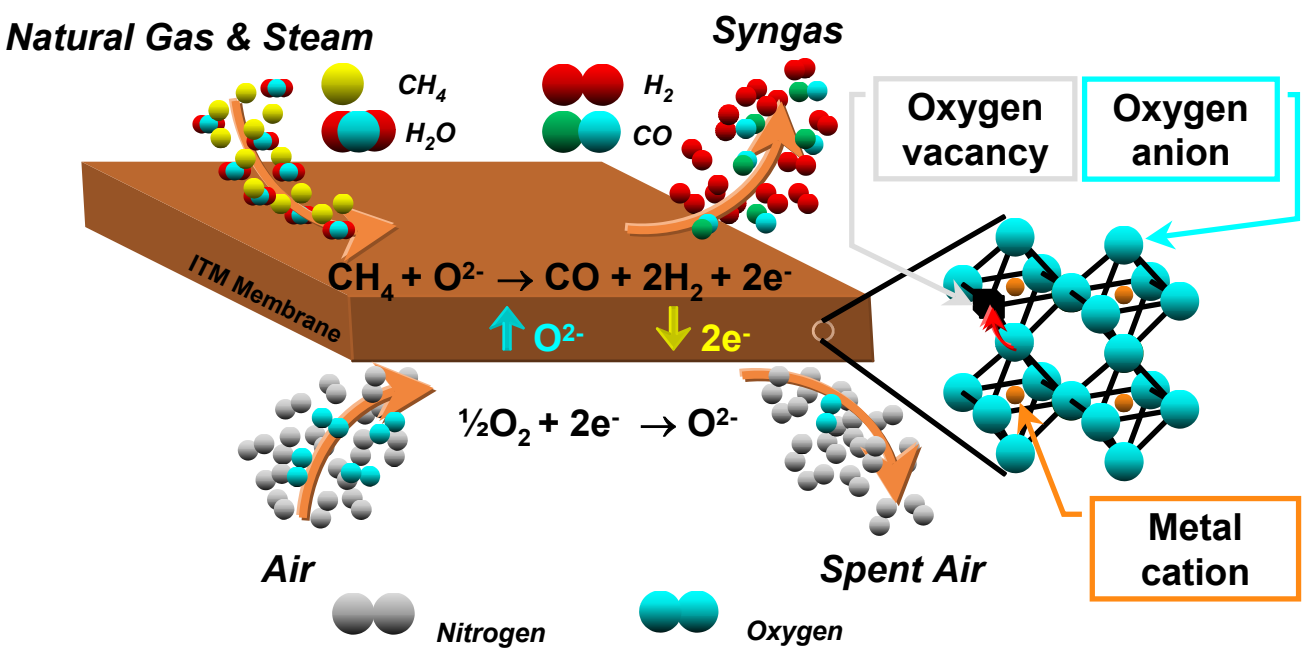
Membranes tested in PDU

Fabricated commercial-size planar membrane

* std. cu. ft. per day of synthesis gas

A Revolutionary Technology Using Ceramic Membranes

- Ion Transport Membranes (ITM)
  - Non-porous multi-component ceramic membranes
  - High oxygen flux and high selectivity for oxygen
  - Operate at high temperatures, typically over 700 °C
- ITM Syngas combines air separation and methane partial oxidation into a single unit operation, resulting in significant cost savings

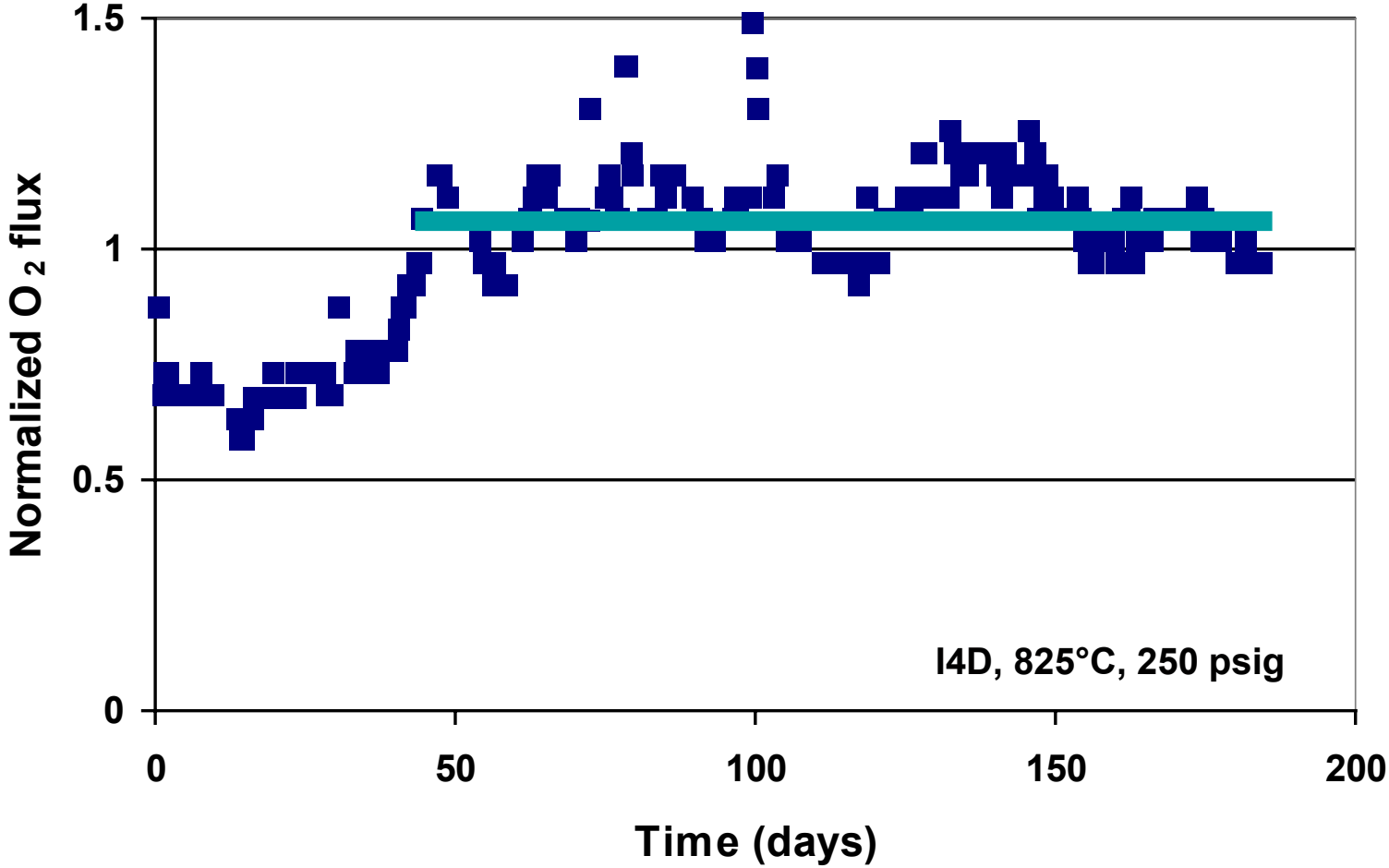


ITM Syngas Technology Challenges

- Materials
  - Stable Performance
  - Catalysis
- Reactor Design
  - Configuration (Planar vs. Tubular)
  - Seals
- Ceramic Processing Development
- Process Scaleup

AIR PRODUCTS

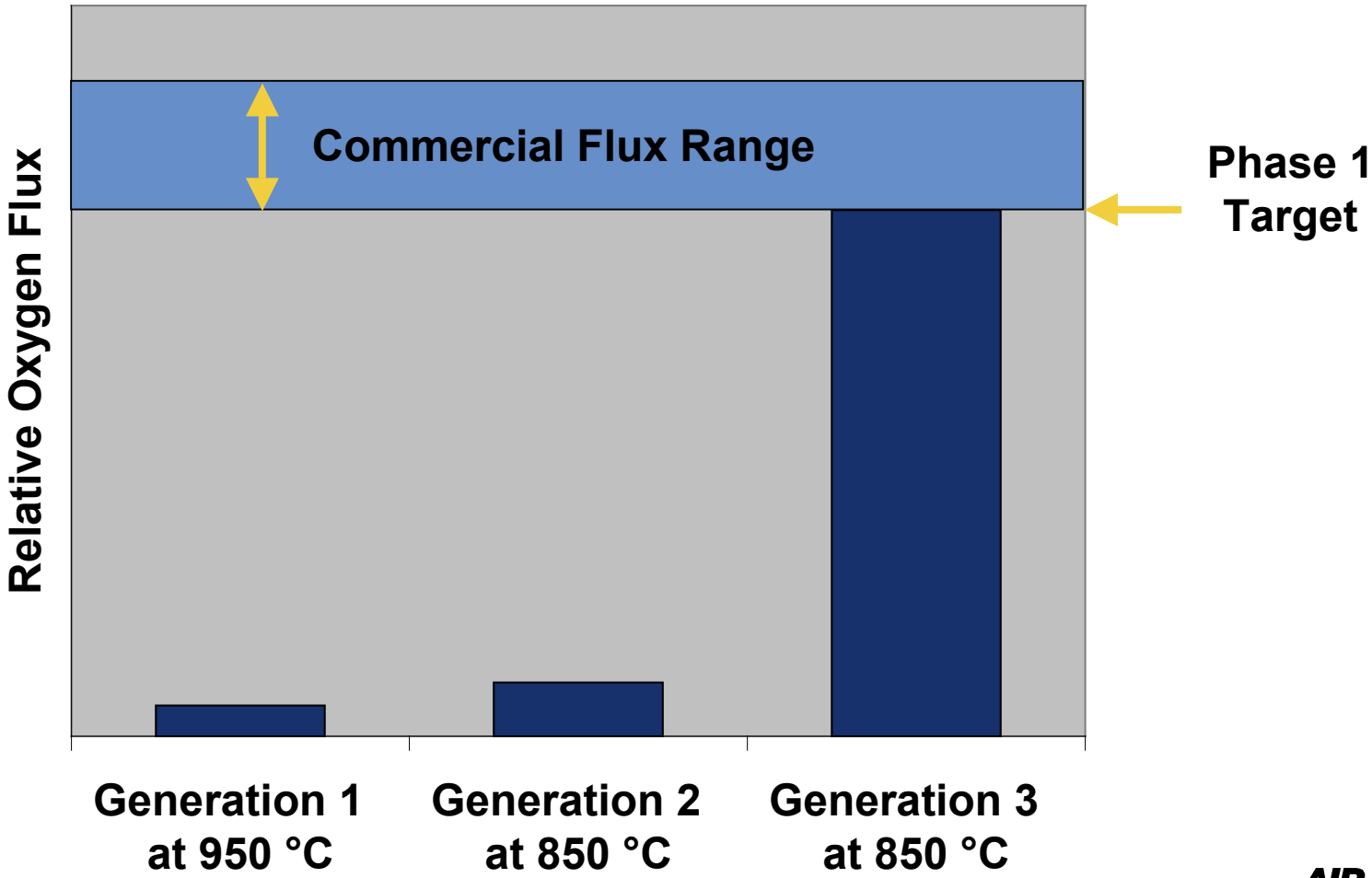
Long-Term Flux Stability Demonstrated Under High Pressure Hydrogen Production Conditions



AIR PRODUCTS

Excellent Progress in Achieving Membrane Flux Target

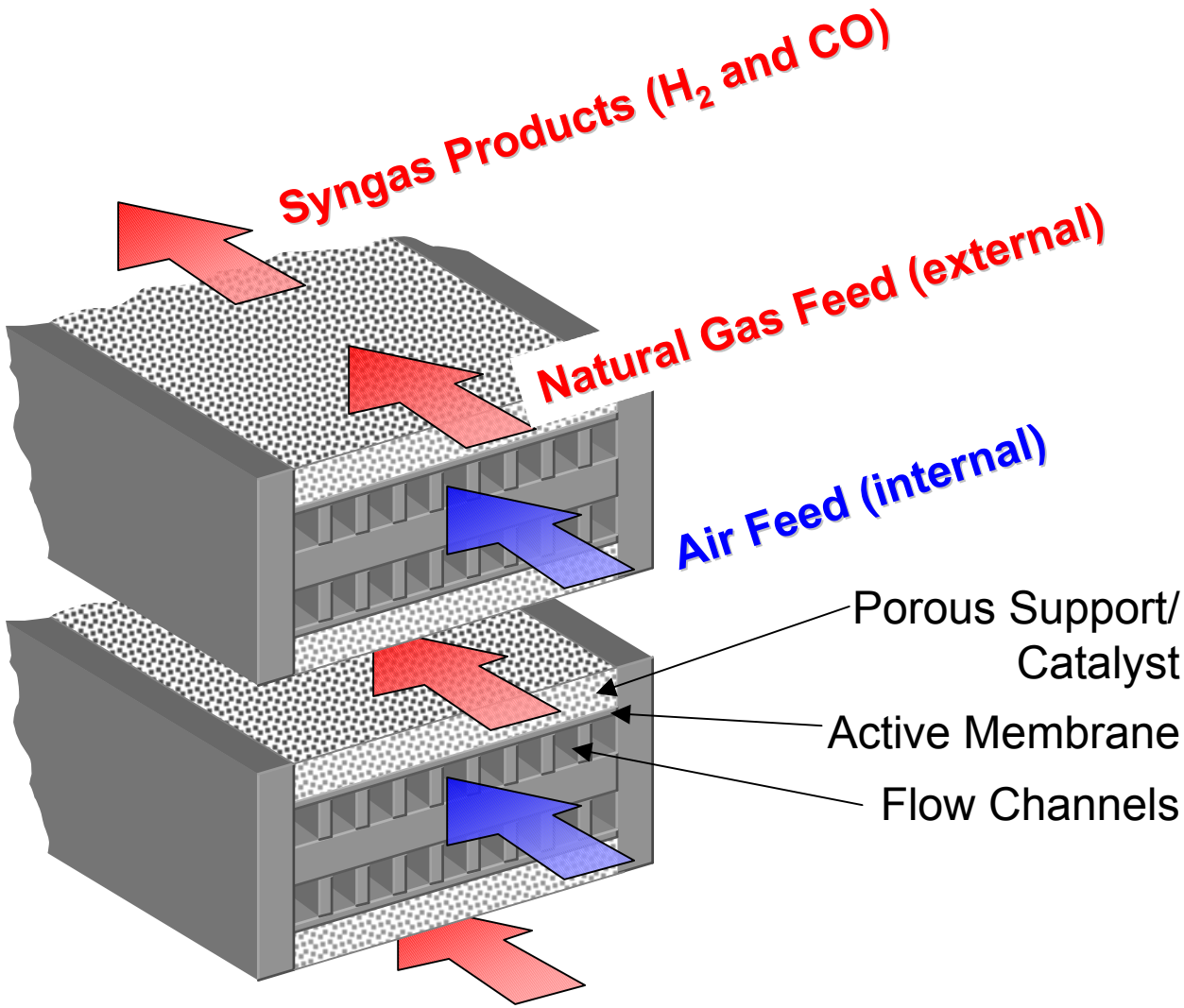
Achieved through advances in supported thin-film planar membranes and catalysts



AIR PRODUCTS

Planar Membrane Systems Have Significant Advantages

- Microchannel design
- Good mass and heat transfer
- Compactness
- Minimizes number of ceramic-to-metal seals
- Amenable to standard ceramic processing methods

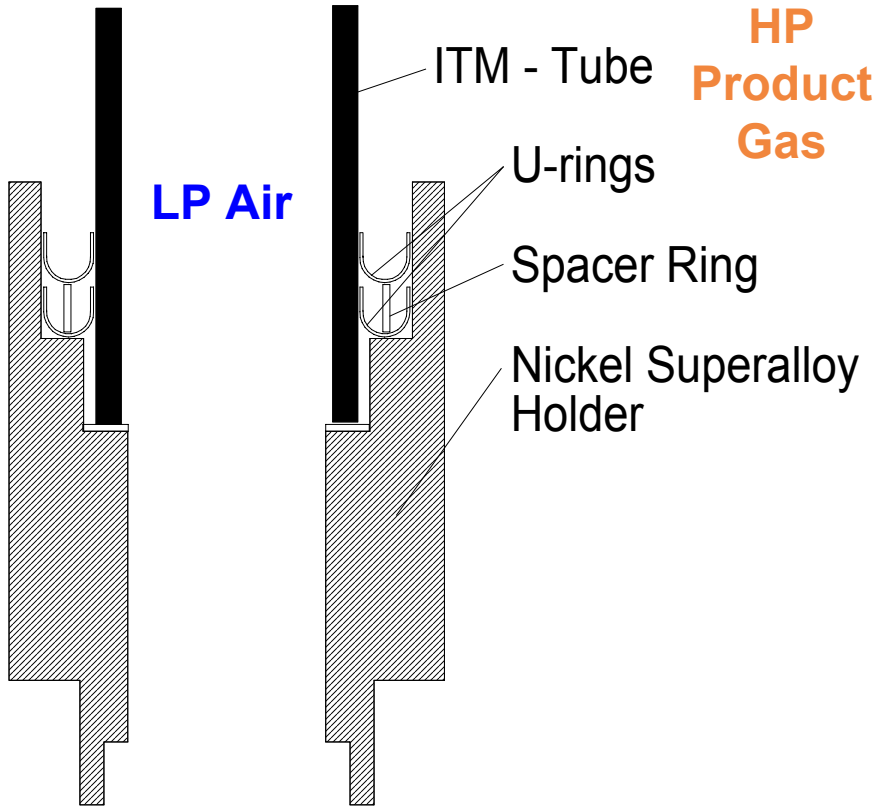


Ceramic Wafer Stack

AIR PRODUCTS

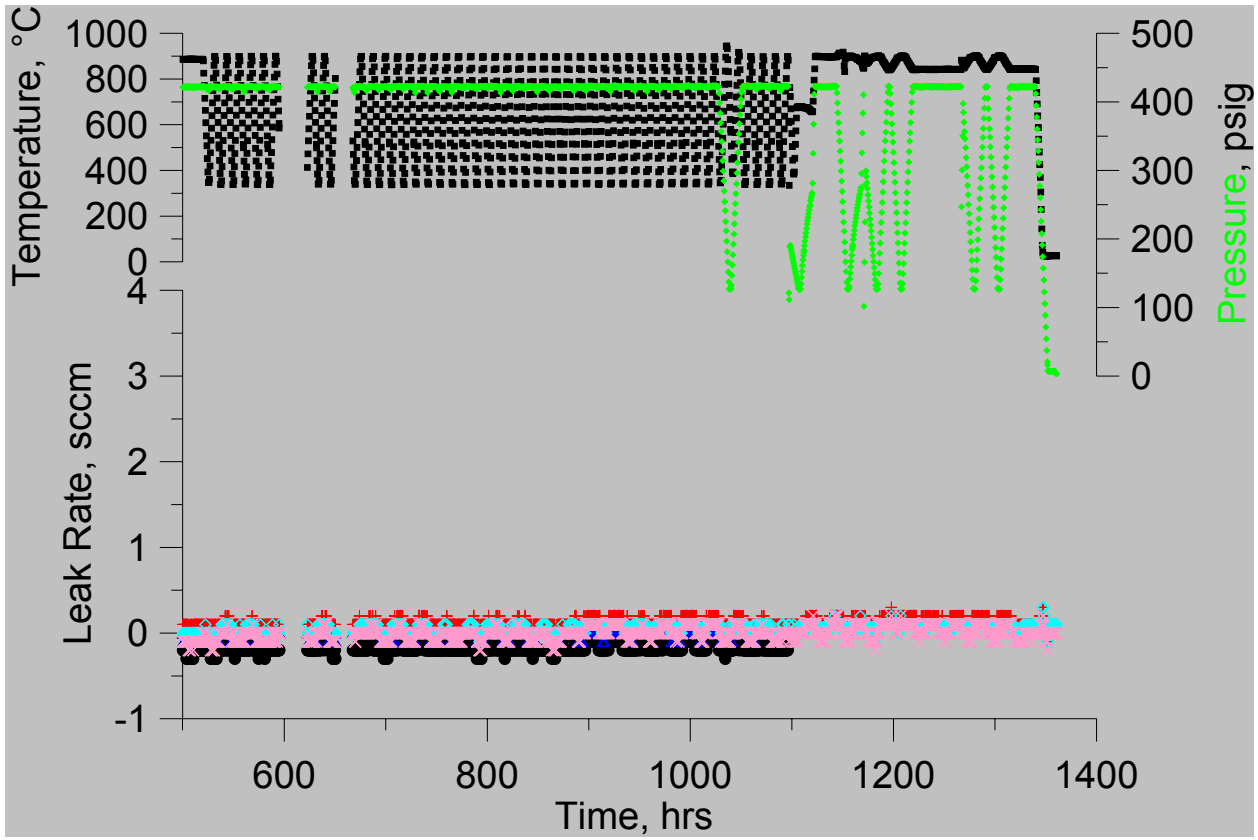
Ceramic-to-Metal Seal Designs Have Been Extended to Planar Membranes

- Successfully tested with tubular membranes during several six-month tests
- Compliant metallic sealing elements (U-rings)
- Multiple elements for improved seal and added mechanical stability
- Elements open to high pressure side to take advantage of pressure activation



U. S. Patent #6302402

PDU Module Seals Remained Leak Tight During Thermal and Pressure Cycling



Seals demonstrated leak-tight performance

- **232 days static test (900°C, 250 psig)**
- **Over 50 thermal cycles (300 to 900°C, 425 psig)**
- **8 pressure cycles (125 to 425 psig, 850-900°C)**

AIR PRODUCTS

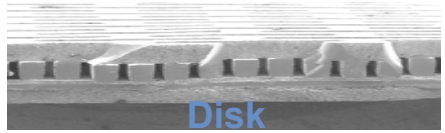
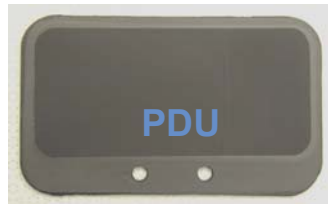
Ceramic Processing Infrastructure Is In Place

Using Conventional Processing Methods

AIR PRODUCTS

Rapid Scale Up Of Membrane Size and Function

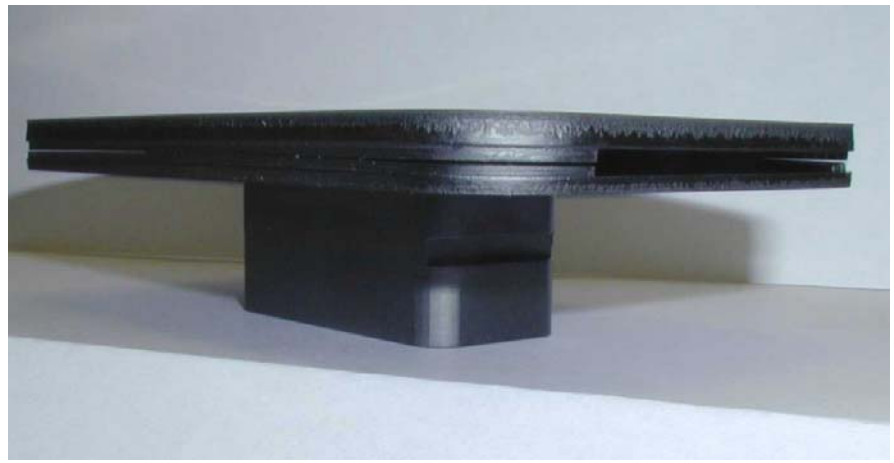
- Proof-of-concept membranes were used to develop processing methods for microchannel devices
- Functional membranes of various sizes have been successfully fabricated using standardized processes

Year	Function	Relative Area	Membrane
FY99-00	Disks * Materials * Layer Performance	1	
FY00	Prelim PDU Wafer * Fabrication * Integration	30	
FY01	PDU Wafer * Full-Featured * Operating Performance	30	
FY02	Full-Size Wafer Integration into Commercial Wafer	160	

AIR PRODUCTS

Full Planar Membrane Modules Have Been Fabricated for the PDU

- PDU ceramic membranes contain essential features of full-size commercial membranes
- Ceramic membrane internal features
  - Manifolding and air flow
  - Support greater than 400 psi pressure differential
- Membrane fabrication processes are robust and scaleable



AIR PRODUCTS

Process Development Unit (PDU) Tests Membranes at Commercial Conditions

- Objectives
  - Demonstrate performance of ITM Syngas membrane modules
  - Provide data for model validation
  - Test commercial-size wafers
- Capabilities
  - Nominal 24,000 SCFD synthesis gas
  - Pressure: 450 psig
    Temperature: 950°C
  - Residence time similar to a commercial reactor
  - Highly instrumented and PLC controlled
- Status
  - Demonstrated reliable ceramic-metal seals
  - Membrane modules have successfully undergone heat-up, pressurization and testing in syngas environment
  - Continuing to conduct performance runs

AIR PRODUCTS

Achieved All Milestones

- Task 2.1 Commercial Plant Economic Evaluation
  - ✓ Evaluate ITM Syngas process using PDU data (Q2FY03)
    - Projected hydrogen production costs* are more than 25% below draft DOE targets for 2005
- Task 2.2 Evaluate ITM Materials and Seals
  - ✓ Long-term stability tests of tubular membranes and seals at high pressure (Q1FY03)
  - ✓ Select catalysts for the SEP (Q3FY03)
- Task 2.3 ITM Syngas Membrane & Module Fabrication
  - ✓ Fabricate modules for additional PDU tests (Q3FY02)
  - ✓ Select SEP membrane module design (Q4FY02)
  - ✓ Commission the PDF (Q4FY02)
  - ✓ Initiate fabrication of SEP (full-size) membranes (Q2FY03)
- Task 2.4 Nominal 24 KSCFD ITM Syngas PDU
  - ✓ Demonstrate performance of subscale membrane modules in PDU (Q3FY02)
  - ✓ Performance test second generation sub-scale modules in PDU (Q1FY03)
- Task 2.5 Nominal 330 KSCFD ITM Syngas SEP
  - ✓ Initiate design and construction of the SEP reactor (Q3FY02) (Construction deferred due to funding delay)

* 500 KSCFD hydrogen production, 100 units/year

AIR PRODUCTS

Milestones for Next Year

- Test catalyzed planar membranes in PDU (Q4FY03)
- Fabricate balance of ceramic components for SEP module (Q2FY04)
- Conduct tests to determine kinetic parameters for membrane and catalysis performance models (Q2FY04)
- Fabricate multi-wafer membrane module for PDU test (Q3FY04)
- Initiate tests to validate full-size membrane design (Q4FY04)

AIR PRODUCTS

Response to 2002 Reviewer Questions

- Ceramic-to-metal seals have demonstrated excellent performance in long-term static tests, and in thermal and pressure cycle tests
- ITM Syngas processes to produce hydrogen range in efficiency (LHV) from 65 to 74%, depending on plant scale. Efficiency gains can be achieved with additional process integrations. (DOE 2003-2010 target is 70-75%)
- The lower capital costs associated with ITM Syngas technology will lead to lower hydrogen production costs. This will facilitate the transition to a Hydrogen Economy.

Disclaimer

A significant portion of this report was prepared by Air Products and Chemicals, Inc. pursuant to a Cooperative Agreement partially funded by the United States Department of Energy, and neither Air Products and Chemicals, Inc. nor any of its contractors or subcontractors nor the United States Department of Energy, nor any person acting on behalf of either:

1. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

2. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Department of Energy. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Department of Energy.

This paper was written with support of the U.S. Department of Energy under Contract No. DE-FC26-97FT96052. The Government reserves for itself and others acting on its behalf a royalty-free, nonexclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform this copyrighted paper.

AIR PRODUCTS

Integrated Ceramic Membrane System for H_2 Production

Cooperative Agreement: DE-FC36-00GO10534

Joseph Schwartz
Raymond Drnevich
Prasad Apte
Ashok Damle

Praxair - Tonawanda, NY
Research Triangle Institute -
Research Triangle Park, NC

DOE Annual Merit Review Meeting
May 19, 2003

Praxair Hydrogen

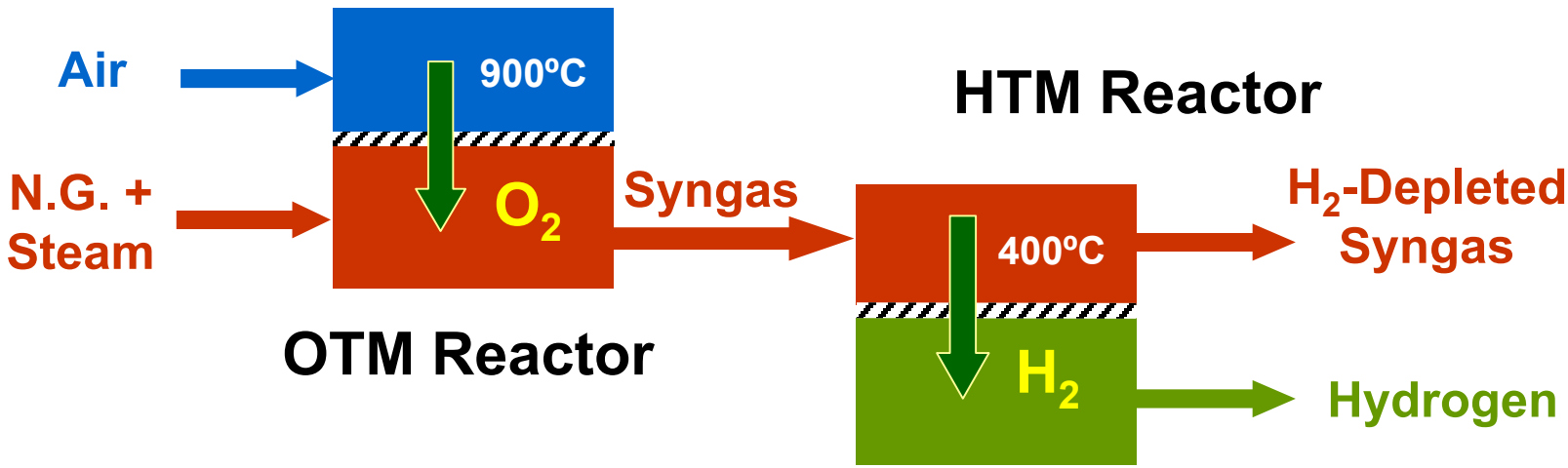
- **Only U.S. Hydrogen Supplier in All Sizes (Cylinders to Liquid to Pipelines)**
  - First industry-financed liquid hydrogen facility (1959)
  - Six large LH_2 plants designed, constructed, and operated
  - Largest capacity single-train LH_2 production system (60 t/d)
  - Four LH_2 plants currently in operation
  - Smallest industrial SMR-based product line (HGS)
- **Over 500 Million SCFD Capacity**
- **Current Distribution Network:**
  - Over 600 GH_2 and LH_2 customers
  - 50 LH_2 trailers, 16 LH_2 rail cars
  - Over 250 miles of GH_2 pipeline
  - 150 GH_2 tube trailers
- **First PSA H_2 Unit (Over 300 Designed and Built)**

Outline - Integrated Ceramic Membrane System for H_2 Production

PRAXAIR

- Concept Review
- Team Structure
- Relevance and Objectives
- Approach
- Project Timeline
- Program Plan
- Accomplishments and Progress
- Responses to 2002 Questions

OTM/HTM Concept
Preferred Process - Sequential Reactors



OTM Reactor

Synthesis gas generation

$CH_4 + ½ O_2 \rightarrow 2 H_2 + CO$

$CH_4 + H_2O \rightarrow 3 H_2 + CO$

HTM Reactor

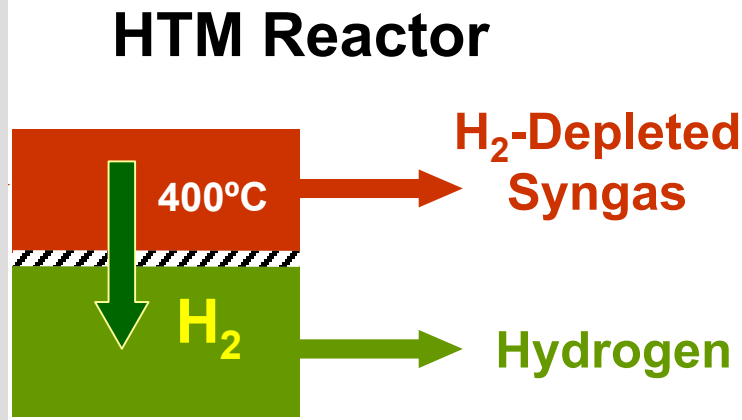
Water-gas shift reaction

$CO + H_2O \rightarrow H_2 + CO_2$

Hydrogen Separation

HTM Concept

Preferred Process - Sequential Reactors



HTM Reactor

- **Water-gas shift reaction**
- **$CO + H_2O \rightarrow H_2 + CO_2$**
- **Hydrogen Separation**

Team Structure

- **Praxair**
  - Overall Lead
  - Substrate Development
  - Process Economics
- **Research Triangle Institute**
  - Membrane Development
    - Palladium coating
  - Membrane Testing
- **Joint**
  - Membrane Production
    - Unique opportunity to integrate substrate and alloy development
    - Iterative process
  - Reactor Design

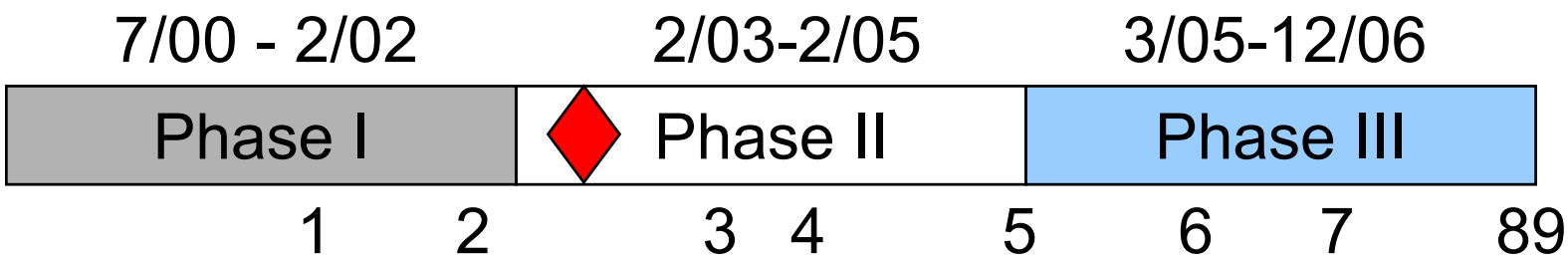
Relevance and Objectives

- **Relevance**
  - Low-Cost On-Site Hydrogen Production
    - Use existing natural gas infrastructure
    - Pd layer is thin - small component of overall cost
  - High Thermal Efficiency
  - Transportation & Industrial Markets
    - 1000 - 5000 scfh
  - Low-Cost Hydrogen Separation and Purification
- **Phase IIA Objectives**
  - Develop Cost-Effective Hydrogen Membrane
    - Supported Pd alloy
    - Syngas tolerance
    - Single-tube testing
  - Review Phase I Technoeconomic Study

Program Approach

- **Phase I**
  - Technoeconomic Feasibility Study
  - Define Development Program
- **Phase II**
  - A Develop and Test HTM Alloy and Substrate
  - B Integrate HTM and WGS in Single Tube Tests
- **Phase III**
  - Pilot Scale Demonstration
  - Define Mass Production Methods

Program Timeline



- **Phase I - Feasibility**
  1 Selected Two-Stage Process with Pd Membrane
  2 Assessed Economics Vs. Current Options
- **Phase II - Hydrogen Membrane Development**
  3 Select Alloy and Substrate
  4 Membrane Production and Testing
  5 Verify Reactor Performance and Update Process Economics
- **Phase III - System Design and Testing**
  6 Design (DFMA Focus) and Fabricate Multi-Tube Pilot Unit
  7 Operate Pilot Unit
  8 Verify System Performance and Update Process Economics
  9 Develop Commercial Offering

Phase IIA Plan

- **Select Substrate**
  - Strength, Thermal Expansion Match
  - Metal or Ceramic
- **Select Alloy**
  - Flux, Life, Cycling, Contaminant Resistance (S, CO, …)
- **Membrane Testing**
  - Confirm Performance in Simulated Syngas Environment
- **Process Economics**
  - Confirm Membrane is Cost-Effective
- **Phase IIB and Phase III Plan**

Phase IIA Tasks

- **Schedule**
  - Start: Kickoff Meeting February 2003
  - End: February 2004
- **Task 1 - Update Literature Review**
- **Task 2 - Substrate Development**
- **Task 3 - Membrane Development**
- **Task 4 - Membrane Tube Testing**
- **Task 5 - Process Economics**
- **Task 6 - Program Management**

Phase IIA Schedule

Task	Description	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan
1	Update Literature Review												
2	Substrate Development												
3	HTM Development												
4	Membrane Tubes												
5	Process Economics												
6	Program Management												

- Task 1 Complete
- Tasks 2, 3, and 4 Underway
- Task 5 Later

Phase I Review

PRAXAIR

- **Defined Optimum Process**
  - Two-stage process with OTM followed by HTM
    - Pd membrane over ceramic proton conductor
    - Higher flux
    - Lower capital cost - smaller high T reactor
    - Higher energy efficiency
    - Shorter development time
    - Better reliability
    - Lower technical risk
- **Technoeconomic Analysis**
  - Low hydrogen cost gives this process the potential to be a preferred approach compared to other small-scale methods

Accomplishments and Progress

PRAXAIR

- **Phase IIA**
  - Substrates Discovered with Suitable Thermal Expansion
    - Pd CTE = 11.9 ppm
    - CGO CTE = 12.5 ppm
    - YSZ CTE = 10 ppm
  - Alloys Identified
    - Pd-Cu, Pd-Ag, Pd-Au
  - Substrate Tubes Produced and Coated Starting in March

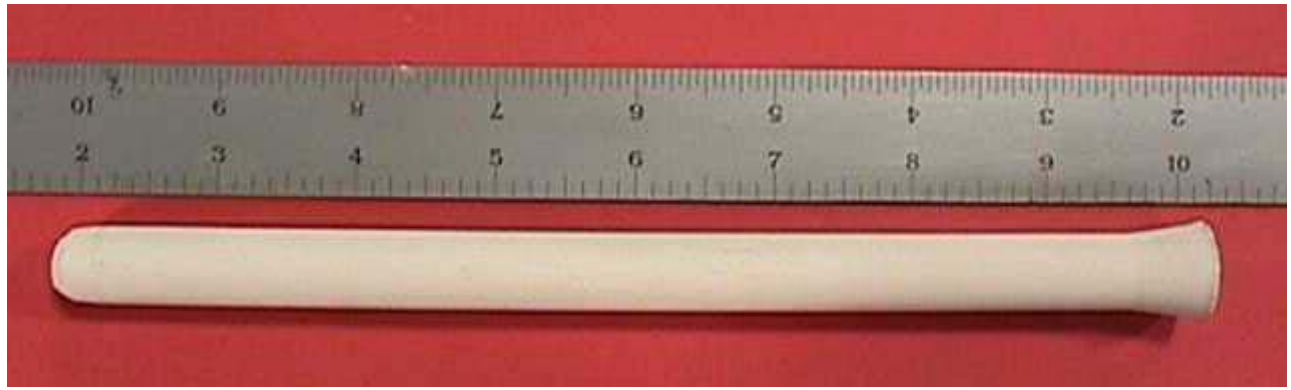
- **Progress**
  - Program is On Schedule
  - Membrane Fabrication and Testing Underway

Porous Tube Production

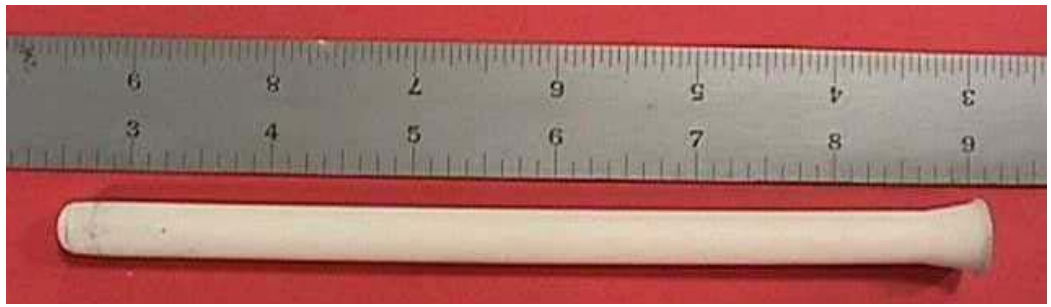
- **Tubes Made by Isostatic Pressing**
  - Isopressing Mold and Mandrel

Porous Tube Production

Green



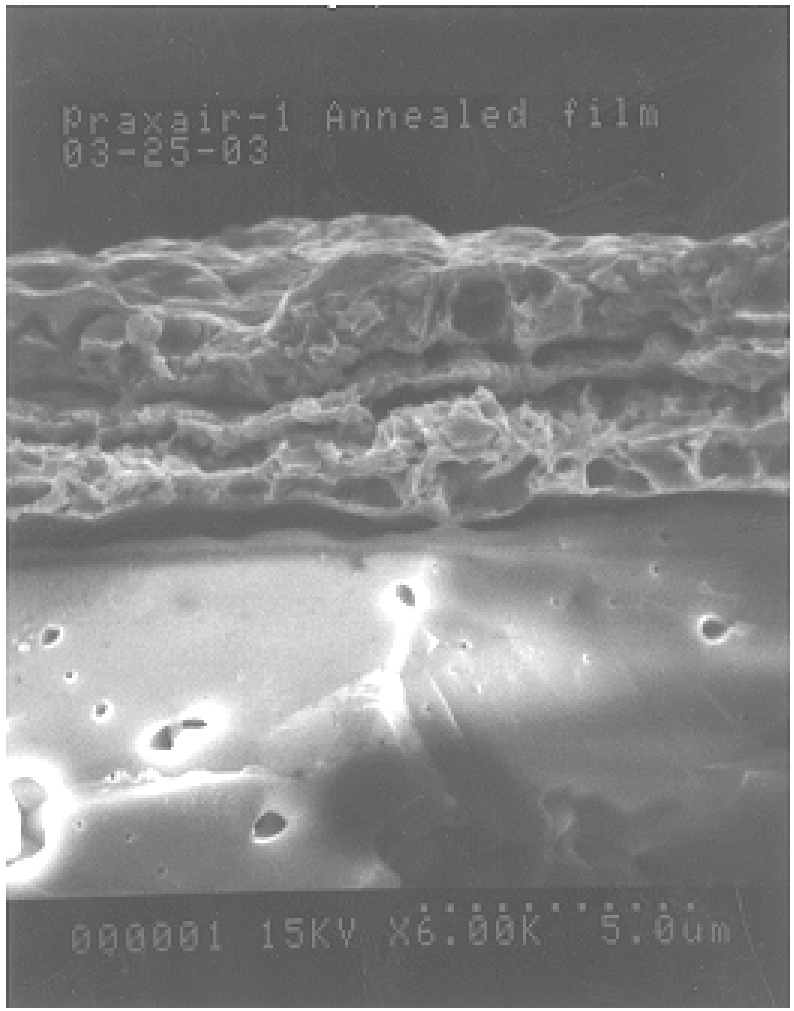
Sintered



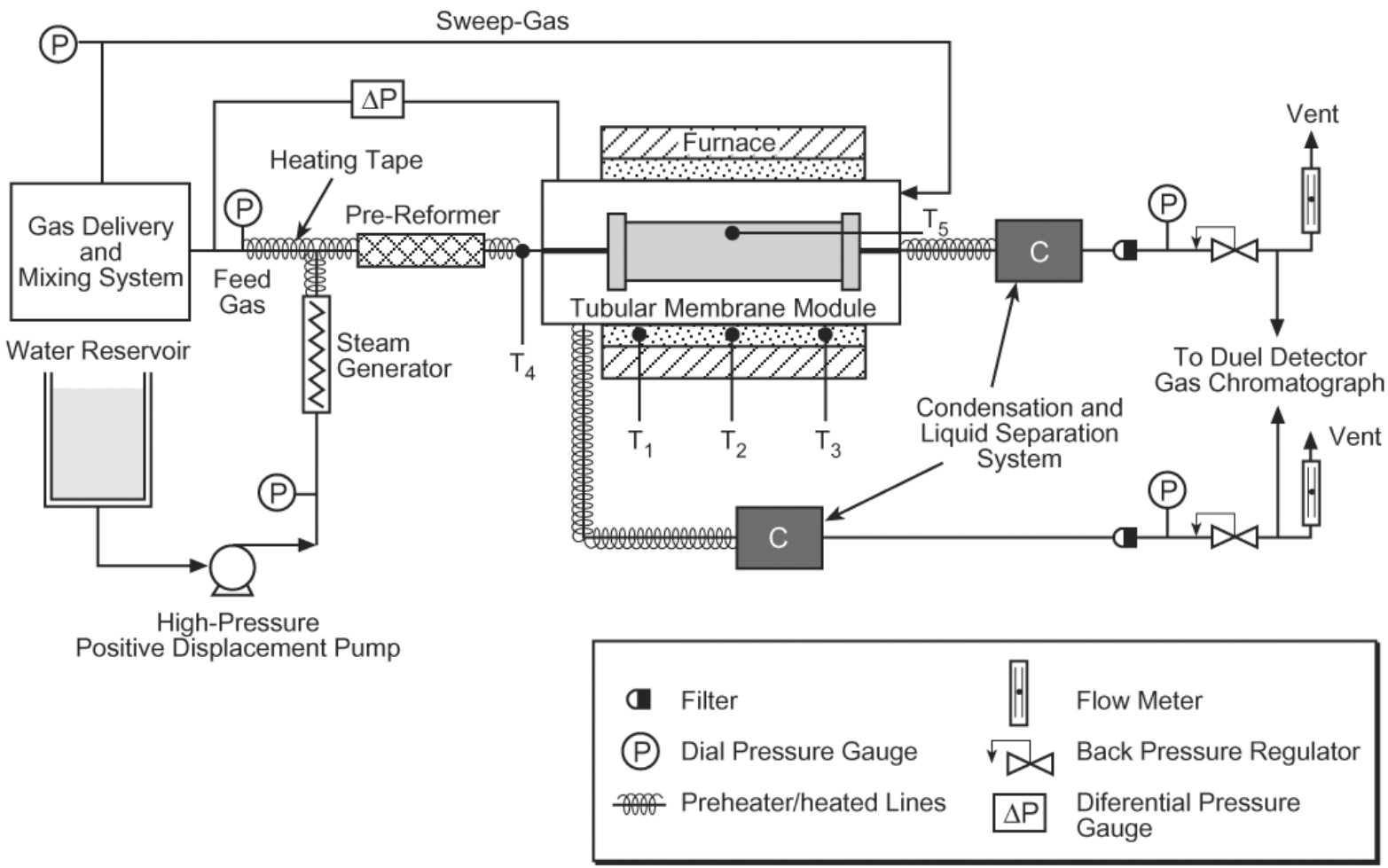
- Sintering causes shrinkage of about 20%

Tube Coating

- **Coated Tube**
  - Pd film is about 4 μm
  - Surface roughness led to holes in the film
  - Substrate needs to be smoother and more consistent
  - Pore size needs to be reduced



Test Apparatus



2002 Questions

- **Panel's Main Concern was Lack of an Experimental Program**
  - Focus of Phase I was technoeconomic evaluation and process definition
  - Focus of Phase II is membrane development and experimental validation - Began in 2003
  - Information about experimental program presented
- **Communication and Cooperation with Others**
  - RTI is an essential team member
    - No contract in place last year - could not discuss
  - Results presented in upcoming DOE reports
  - Will present external paper(s) when we have test results

Integrated Ceramic Membrane System for H_2 Production

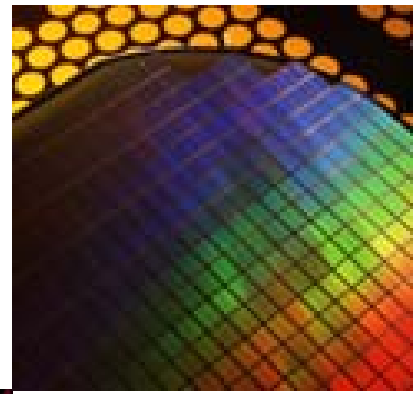
Cooperative Agreement: DE-FC36-00GO10534

Questions?

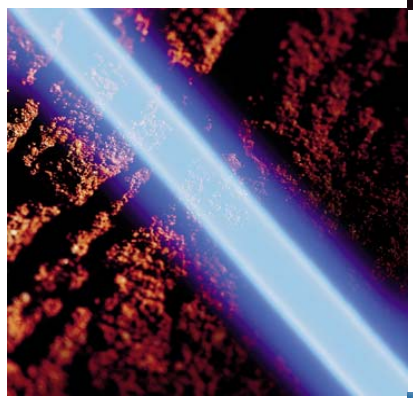
DOE Annual Merit Review Meeting
May 19, 2003

Low Cost Hydrogen Production Platform

Cooperative Agreement: DE-FC36-01GO11004



Timothy M. Aaron



Team

- Praxair - Tonawanda, NY
- Boothroyd-Dewhurst - Wakefield, RI
- Diversified Manufacturing - Lockport, NY

DOE Hydrogen Annual Review Meeting
May 19 - 22, 2003

LCHPP - Program

PRAXAIR

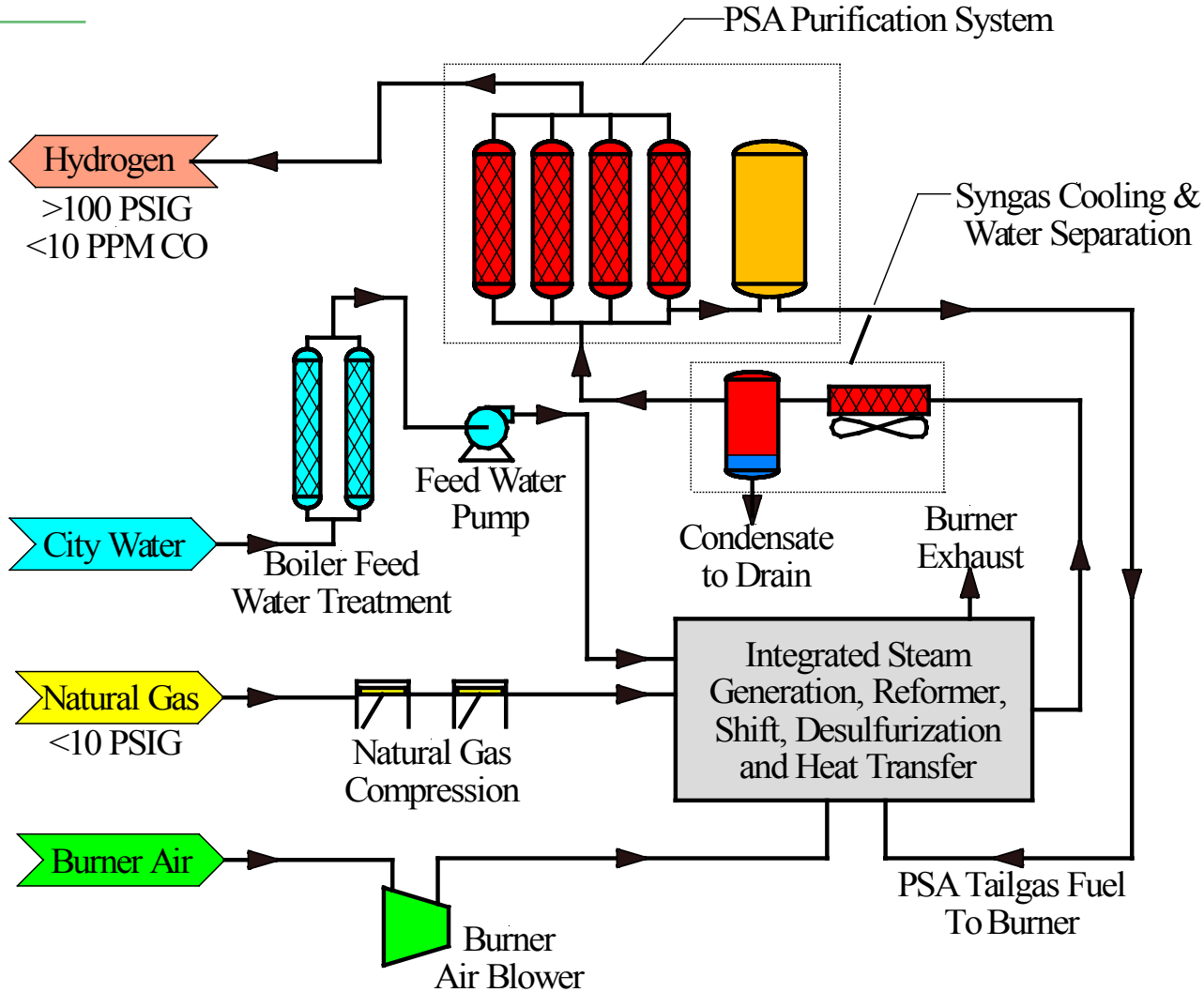
- **Goal**
  - Low Cost On-Site H_2 Production
    - Existing Technologies (SMR)
  - Transportation & Industrial (1,000 - 5,000 scfh)
    - Compression / Dispensing Not Included
    - Gas Station Capacity & Size
  - DOE Cost Target $8/MMBtu or $0.26/100 scfh H_2
    - Aggressive Target
    - 75-80% of Target Cost Required for Utilities

LCHPP - DOE Program Plan

2002	2003	2004	2005	2006
Phase I		Phase II	Phase III	

- **Phase I** ***(Completed 04/03)***
  - Preliminary Design for Transportation / Industrial
  - Assess Economics Vs. Current Supply Options
  - Business Cases
- **Phase II** ***(06/03 - 12/04)***
  - Detail / Tooling Design
  - Modeling and Simulations
  - Subsystem Prototypes and Testing
  - Update Business Model
- **Phase III** ***(01/05-06/06)***
  - Fabricate Demonstration Unit
  - Verify Performance
  - Develop Tooling Required for Manufacturing

LCHPP - Skid Process Flow

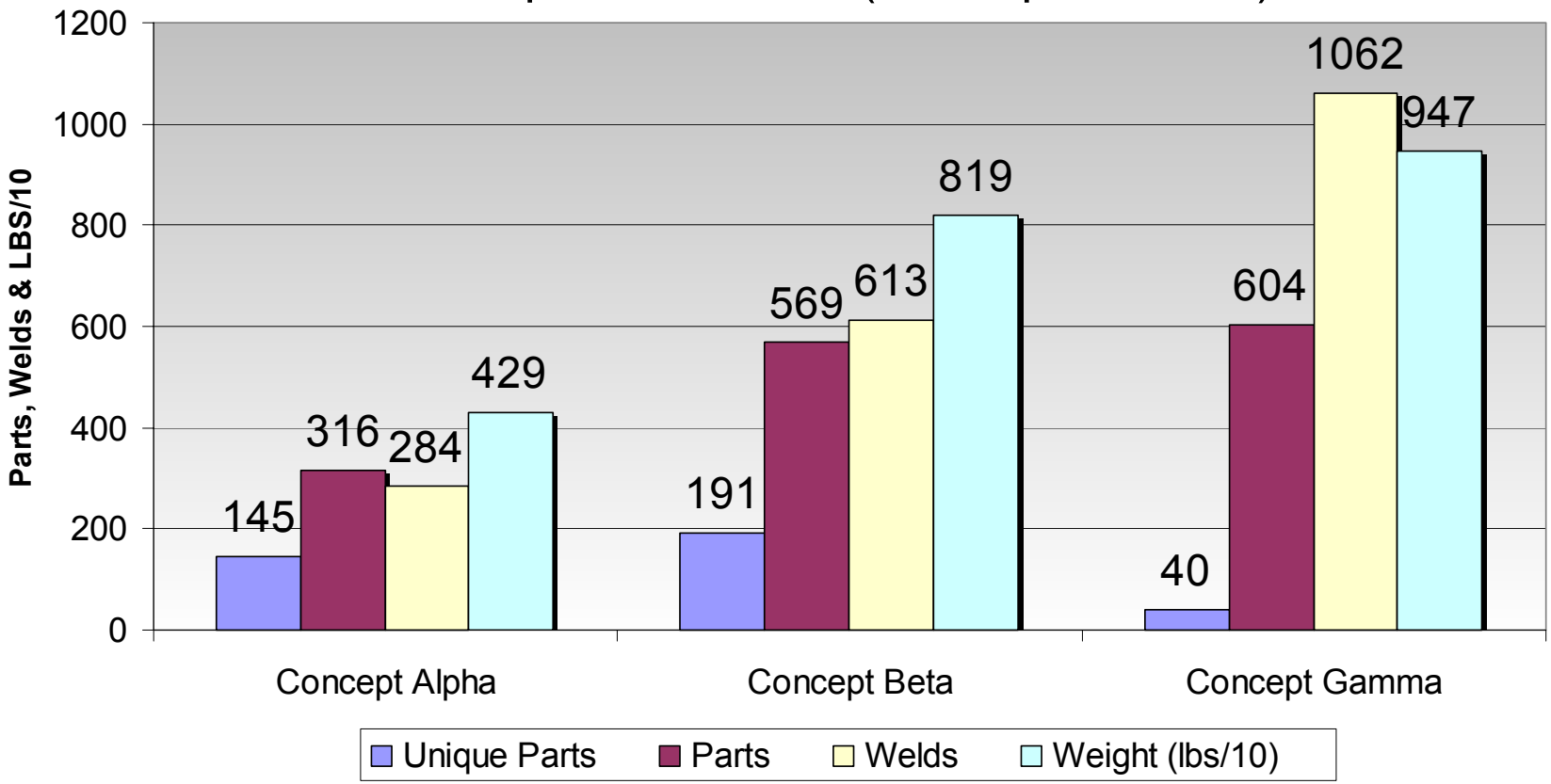


LCHPP - Phase I Accomplishments

- **Sub-System Cost Breakdown**
  - Reformer / Shift / Steam Generation >50% of Capital
- **Reformer Alternatives Evaluation**
  - Reformer Pressure
    - Syngas / Natural Gas Compression
    - Materials of Construction
  - Thermal Integration
- **System Design**
  - 6 Concepts Initially Defined
  - 3 Highest Potential Concept Selected
  - Further Refinement 3D Models / Risk Analysis / DFMA
  - PSA Purification System
  - Auxiliary Systems
  - Skid Design
- **Economic Analysis**

LCHPP - Hot Component Options

- **Approaches**
  - Minimize Part Count (Concepts Alpha & Beta)
  - Minimize Unique Part Count (Concept Gamma)



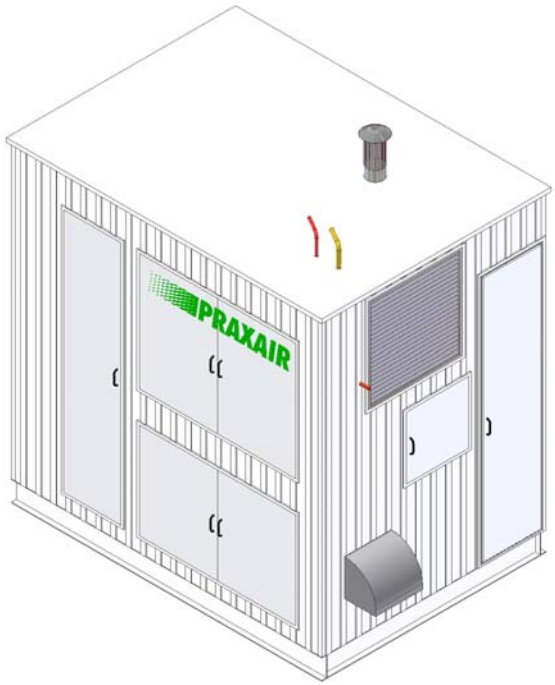
LCHPP - Hot Components DFMA Analysis

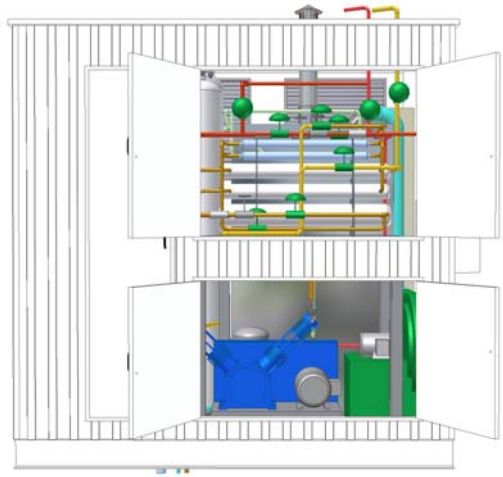
PRAXAIR

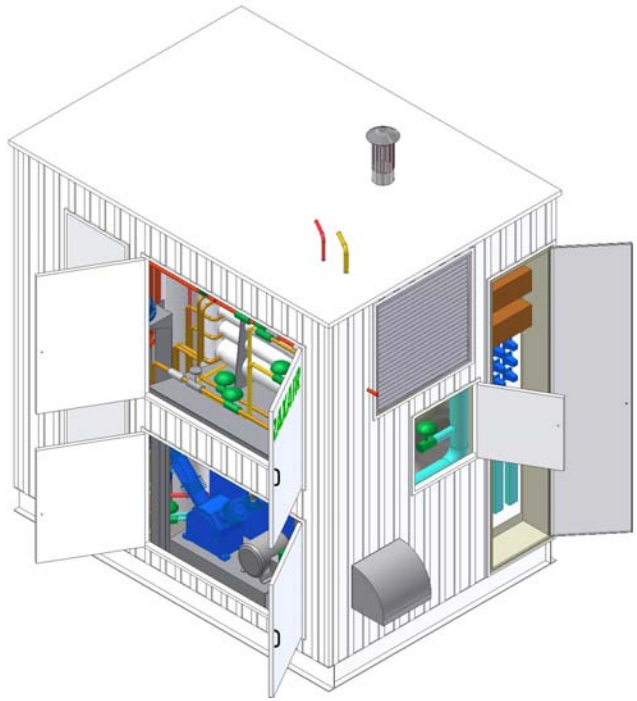
- **DFMA Summary**
  - Lower Part Count = Lower Cost
    - Integrated Concepts Chosen
  - Highest Integration = Lowest Cost Potential
    - Initial Cost Vs. Overall Cost
    - Phase II Testing
  - Material Costs Not Insignificant
    - Cost Reductions / Units Produced

LCHPP - Skid Assembly

- Safety
- Compact, Single Skid
- Easily Installed
- Welded Construction
- Highly Integrated



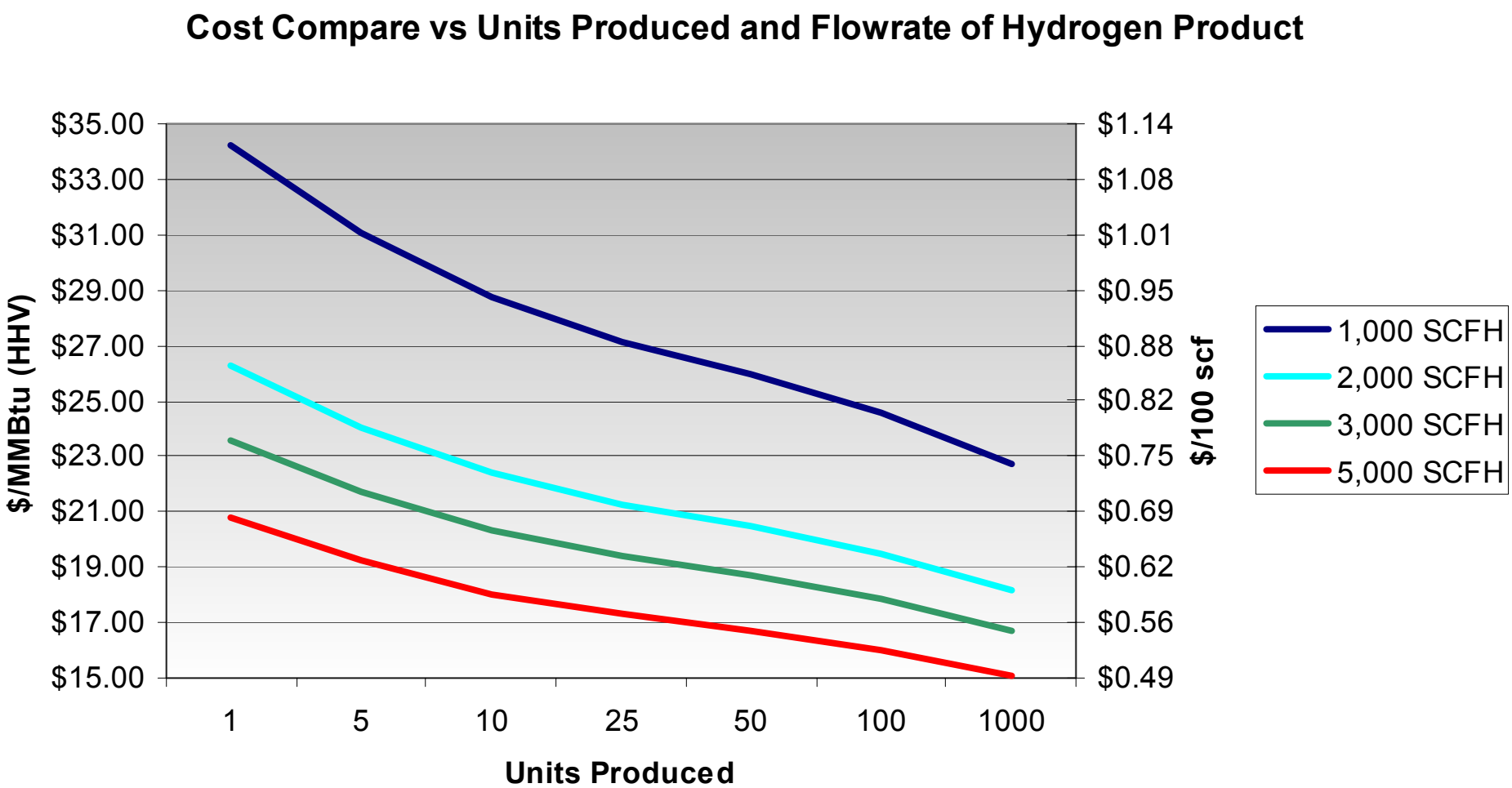




LCHPP - System Cost Summary

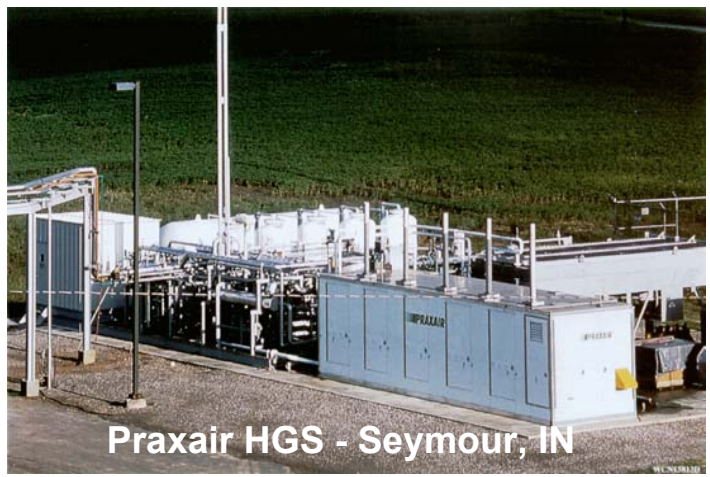
- **Cost Model Assumptions**
  - Power - $0.05 $/kWh
  - Natural Gas - $4.00 $/MMBtu, HHV
  - Water - $2.31 per 1,000 Gallon
  - Capital Recovery Factor - 15% Return, 15 Yr Life
  - On-Stream Factor - 80%
  - Contingency - 10%
  - M&R - 3% of Capital
  - Site Labor

LCHPP - System Cost Summary



LCHPP Phase I Conclusions

- **Results / Learnings**
  - Potential for Cost Competitive System
  - System Design
  - Cost / Market Analysis
  - Risk Analysis
  - Economic Study
  - DFMA Analysis (Hot Components Only)
  - Praxair HGS Comparison
    - 1/4 Capacity
    - 1/6 Physical Plant Size
    - Lower H_2 Cost
  - Recommendations
    - Phase II Development

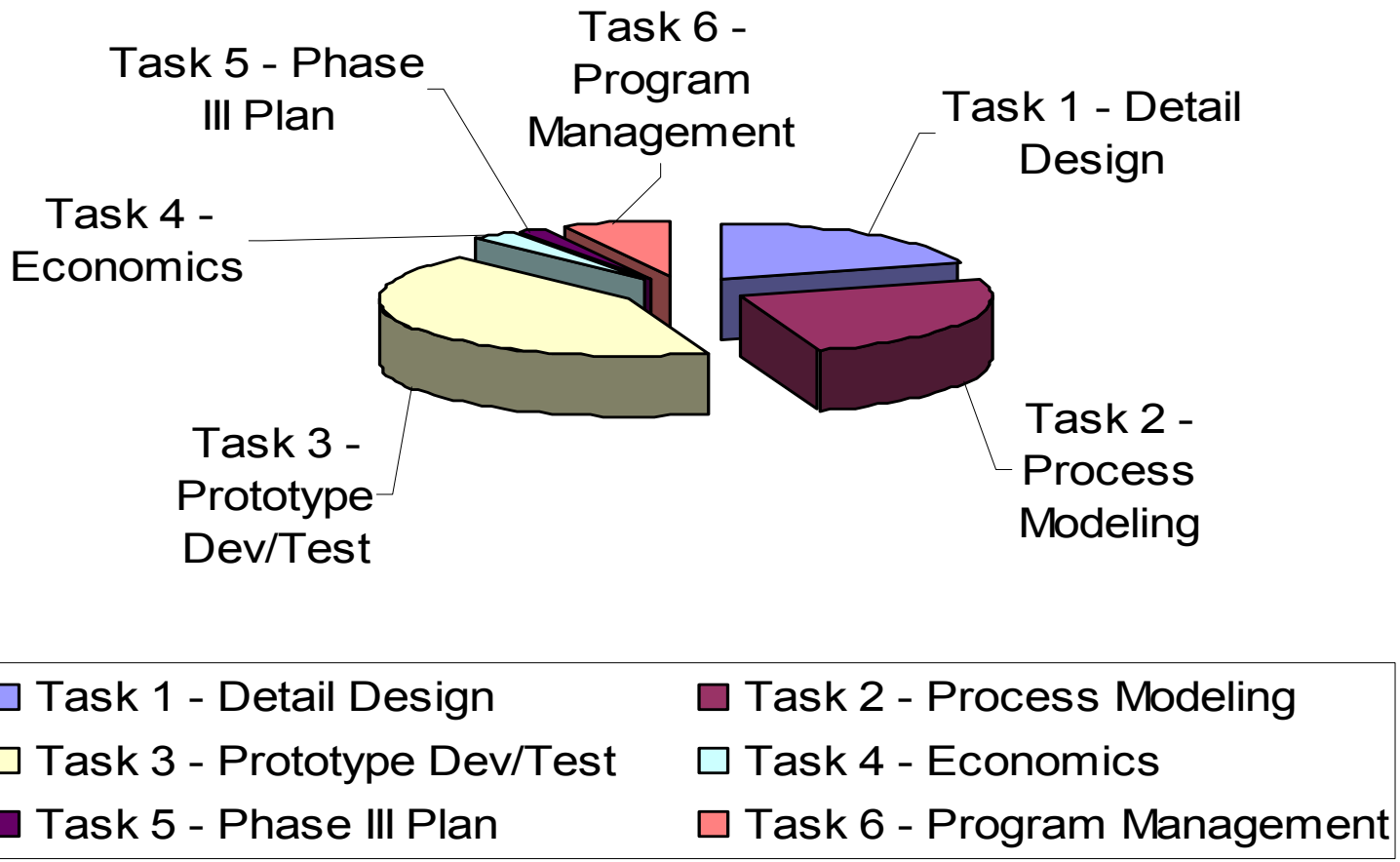


Phase II Objectives

- **Detail Design**
- **Tooling Design**
- **DFMA Analysis - System & Components**
- **Prototype Development & Testing**
  - Computer Modeling
    - Heat Transfer
    - Fluid Dynamics
    - Reaction Kinetics
  - Mitigate Risks
- **Economics / Business Case**
- **Phase III Plan**

Phase II Program Tasks & Estimated Allocation

2002	2003	2004	2005	2006
	Phase I	Phase II	Phase III	

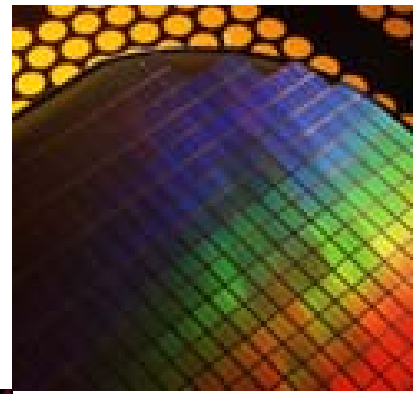


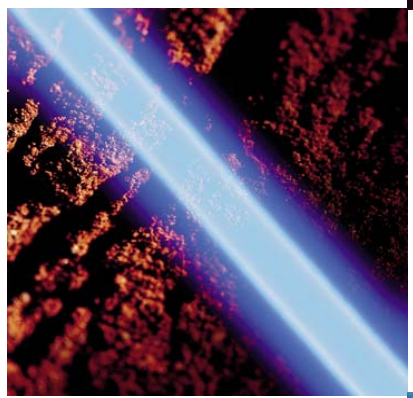
Phase II Cooperative Efforts

- **Praxair**
  - Overall Lead
- **Boothroyd-Dewhurst**
  - System Optimization
  - Cost Reduction / Estimating
- **Diversified Manufacturing**
  - Manufacturing
  - Prototype Development
- **Computer Modeling**
  - Reformer / Shift Design
  - Burner Design
  - Heat Transfer
- **Catalyst Supplier**

Low Cost Hydrogen Production Platform

Cooperative Agreement: DE-FC36-01GO11004





Questions?

Praxair Internal Review Meeting
May 19-22, 2003

Tina M. Nenoff
Distinguished Member of Technical Staff
Sandia National Laboratories
Albuquerque, NM 87185

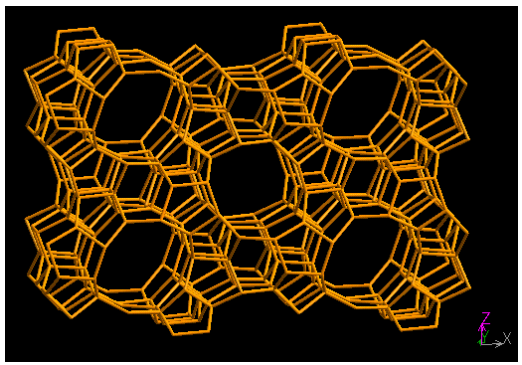
Team Members:
Margaret Welk & John Heald, SNL/NM
Martha Mitchell & Marco Gallo, Chem. Eng., NMSU
Jay Keller, Program Manager, SNL/CA

DOE/H_2, Fuel Cells and Infrastructure
Annual Review Meeting, May 19-22, 2003

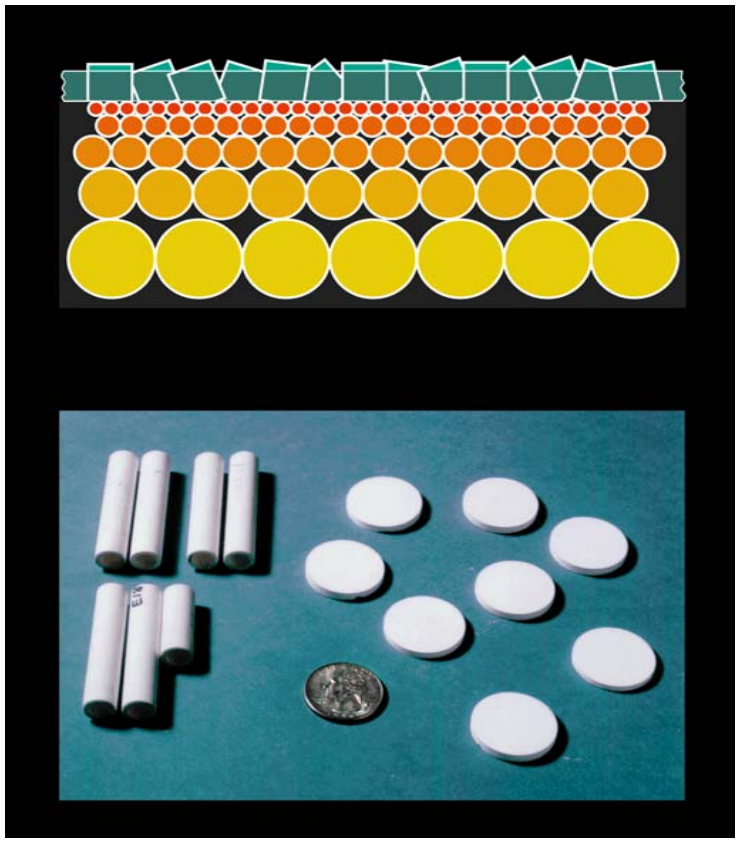
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy under Contract DE-AC04-94-AL85000

H_2 Separation Membranes: Introduction

Goal: Synthesis of robust microporous zeolite membranes to improve on H_2 separation technology of polymers of Pd alloys;
Leverage technology to syngas separations, gas purification, biomass, gas enrichment, dehydration



Pore Structure ZSM-5



Schematic: Nonselective porous membrane support w/ selective molecular sieve top layer

Actual membrane supports

H_2 Separation Membranes: Relevance

Relevance to Hydrogen:

Need to produce H_2 reliably, at low cost

Use of reforming to produce H_2

- Technical Barriers:
  - Defect-free
  - Manufacturability
- Technical Targets:
  - high permeation
  - high selectivity
  - low cost
  - high durability

Steam Reforming: $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

Dry Reforming (MCFC): $CH_4 + CO_2 \rightarrow 2CO + 2H_2$

H_2 Separation Membranes: Objectives

Objectives:

Synthesis

Defect-free Inorganic crystalline thin-film membranes:
synthesis efforts with Al/Si & Si/Ti phases (organic vs. alkali templating)
film growth on variety of supports (oxides, SS316, composite)

Permeation

Testing new membranes:
H_2, CO, CO_2, O_2, He, H_2O, CH_4 & SF_6;
mixed 50/50 CH_4/H_2 and 50/50 CO_2/H_2

Modeling and Simulation

Light gases through 1D ZSM-22 and compare to ZSM-5
Validation through permeation testing

Business Partners/Collaborations

Basic research "directed" toward commercialization
Industry (manufacturers, end-users), University

H_2 Separation Membranes: Approach (plan/milestones)

Project Method is "R&D":

Basic & Applied Research, Testing, Validation plus Business Development, Current Milestones due dates

Task 1: Thin Film and Bulk Growth:

Growth of Al/Si zeolite thin films and/or doped with other elements

Synthesis of defect-free silicotitanate (Si/Ti) thin film membranes.

Characterization of all new phases (X-ray diffraction, thermal analyses, surface area, and elemental analysis).

Membrane growth on various substrates (scale-up viability assessment).

Task 2: Modeling and Simulation:

Model separation values for pure light gases interacting with 1D channel pores compare to 3D pores (ZSM-22 vs. ZSM-5).

Model separation values for mixtures of light gases interacting with 1D channel pores compare to 3D pores (ZSM-22 vs. ZSM-5).

H_2 Separation Membranes: Approach (plan/milestones)

Task 3: Permeation Studies

Maintain unit to including repair of Residual Gas Analyzer to study selectivity to mixed gases.

Permeation studies of pure gases through membranes.

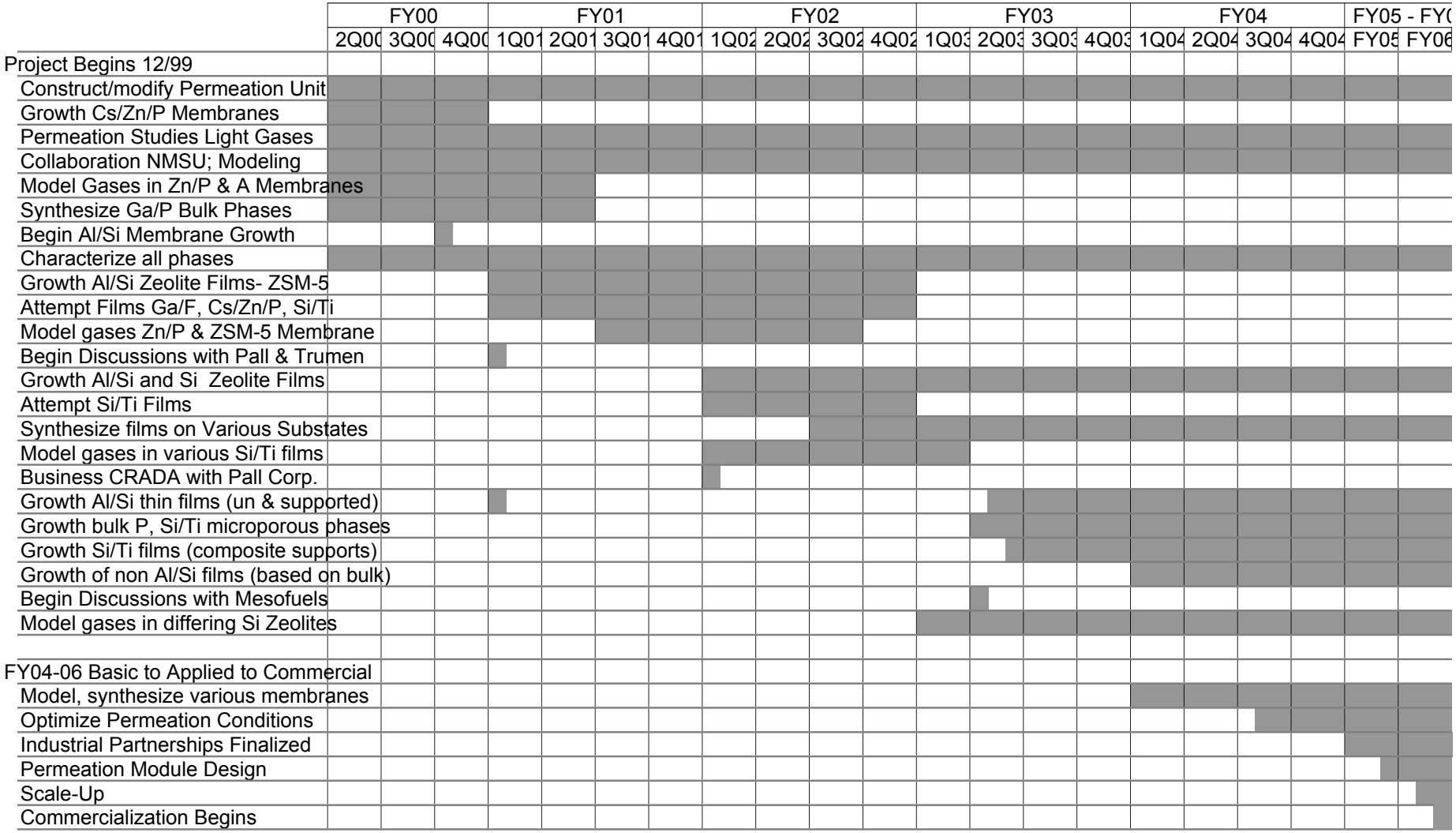
Permeation studies of mixture gases through membranes.

Task 4: Business Development:

Initiate an agreement for product development with an industrial partners.
ie., NDA, licensing or scale-up development work;
Mesofuels; Pall; Trumem.

Pursue new collaborative funding opportunities with industrial partners

H_2 Separation Membranes: Timeline



Tina M. Nenoff

H_2 Separation Membranes: (1/02 - 4/03) Accomplishments/Progress

- Permeation Unit: testing **CO and mixed gases**, RGA in repair; awaiting H_2S approval

- First evidence of **Zeolite W** (MER) membrane synthesis! 3D channel pores
  From attempted ZSM-22 growth. Secondary growth for defect-free underway

- Defect free Si/Ti membranes synthesized and permeation tested
  New Phase! Durable, Selective, Still under investigation
  To be tested versus simulation data

- All **Si ZSM-5 Silicalite** : Long lifetime and confirmed reproducible permeation
  results; growth on composite and oxide substrates;
  $CO_2 > CH_4 > H_2 > He > (N_2, CO) > O_2$

- Utilizing ceramic membrane supports: Inoceramic Alumina disks/tubes
  Trumem oxide-coated SS316 (TiO_2; SiO_2/Al_2O_3; ZrO_2 coatings)
  Pall is sending ZrO_2 coated SS316 tubes

- Modeling/Simulation: Preferential **H_2 separation** through ZSM-5 vs. ZSM-22

H_2 Separation Membranes: (1/02 - 4/03) Accomplishments/Progress

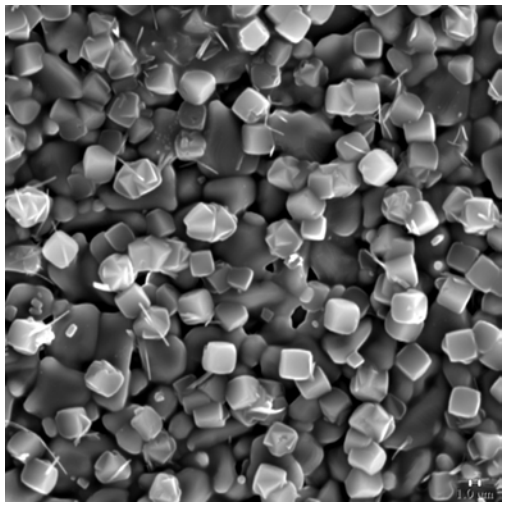
A. Thin Film and Bulk (for future films) Growth:

1. New Silicotitanate Phase grown as thin film!

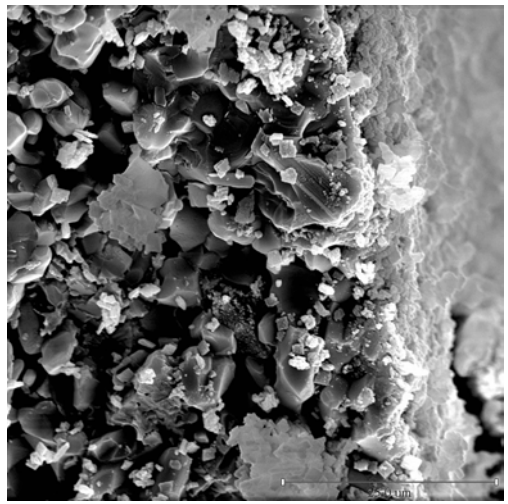
   Bulk shown to exhibit H_2 separation

   Durable, Unknown Phase, Selective (still being investigated)

   Calcination procedure being determined



Blocky silicotitanate crystals on an alumina support.



Cross section of silicotitanate crystal membrane on an alumina support.

2. **Silicalite** membranes : Lifetime studies (1+ years) show good durability; high reproducibility in procedure yielding consistent permeabilities

H_2 Separation Membranes: (1/02 - 4/03) Accomplishments/Progress

B. Modeling and Simulation:

1. Studies on Silicalite vs. ZSM-22 continuing
2. Early indication 1D pores of ZSM-22 easily blocked by gases, no good for gas separation

C. Permeation Studies for Validation - Testing pure and mixed gases

1. CO testing (ES&H approved);
2. RGA for mixed gases: in repair;
3. H_2S testing to be developed,
   working with ES&H for approval.

D. Business Development

1. Initiated interaction with Mesofuels Inc.; "Portable reforming unit"
   Non Disclosure Agreement (NDA) in progress
2. Attended HyTeP as SNL representative;
3. Invited by Sen. Jeff Bingaman (D-NM) for H_2 and Fuel Cell
   Economic Development discussions (SNL rep, industry attendees)

H_2 Separation Membranes: Interactions and Collaborations

Presentations:

M. E. Welk, T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 and CO_2 Separation and Isolation", Hydrogen and Fuel Cells 2003 Conference and Trade Show, Vancouver, BC, Canada, June 2003.

T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 and CO_2 Separation and Isolation", Spring National ACS meeting, New Orleans, LA, March 2003. *Invited Lecture*.

T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 Separation and Isolation", National Hydrogen Association Meeting, Washington DC, March 2003.

T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 Separation and Isolation", 14th World Hydrogen Energy Conference, Montreal, Canada, June 10, 2002.

Publications:

Mitchell, M.; Gallo, M.; Nenoff, T. M. "Molecular dynamics simulations of binary mixtures of methane and hydrogen in titanosilicates", *J. Phys. Chem*., **2003**, submitted.

Bonhomme, F.; Welk, M. E.; Nenoff, T. M. "CO_2 Selectivity and Lifetimes of Silicalite Membranes". *Micro. & Meso. Materials*, **2003,** in press.

Bonhomme, F.; Thoma, S. T.; Nenoff, T. M. "Two ammonium templated gallophosphates: Synthesis and structure determination from powder diffraction data of 2D and 3D-GAPON". *Micro. & Meso. Materials*, **2002**, *53*, 87.

Nenoff, T. M.; Bonhomme, F. "Defect-free thin film membranes for Hydrogen separation and isolation". 14th World Hydrogen Energy Conference Proceedings, Montreal, Canada, 2002.

Symposium:

"Modeling and Simulation in Surface and Colloid Science"; Tina M. Nenoff, Martha Mitchell, Marcus Martin, *Co-Organizers* ACS National Fall Meeting, NYC, NY Sept 7-13, 2003

H_2 Separation Membranes: Interactions and Collaborations

Cooperative Efforts:

- NDA in progress with Mesofuels Inc, Alb. NM

- Collaboration with NMSU extended to new Al/Si and Si/Ti phases

- CRADA #1596 with Pall Corporation for study of microporous materials on separation membranes; examining routes for collaboration (ie., Proposals, etc.); membrane supports, possible module design

- Cooperation with Trumem International, LLC, for oxide-coated membrane supports

- Attended HyTeP as SNL speaker/representative in Santa Fe, NM, 4/23/03

- Invited by Senator Jeff Bingaman (D-NM) for H_2 and Fuel Cell Economic Development discussions (included national lab & industry attendees), Albuquerque, NM, 4/25/03

H_2 Separation Membranes: Plans, Future Milestones (5/03-9/04)

- Synthesis and characterization:

Ion exchanged or metal doped Al/Si films

Si/Ti film growth continued

Novel bulk microporous phases, future thin films

Membrane growth on various substrates, for scale-up viability assessment (ie., SS316 vs. oxide vs. composite)

Attempt use of ALD (Atomic Layer Deposition): metal oxide layer on top of zeolite layer to catalyze H_2S

- Permeation:

Pure and mixed gases, RT and 80°C; seek ES&H approval for H_2S

- Modeling:

Simulation of gas permeation thru different Al/Si type zeolite membranes ie., ZSM-5 vs. Zeolite W

- Business Development:

Build partnerships with end-users & membrane Co. (ie.,Mesofuels; Pall; Trumem)

H_2 Separation Membranes: Responses to Panel's Questions

1. Strength/Robustness of Membranes:

   Stable in air and water.
   Durable in temperature cycling (Si/Ti >500C),
   continuous treatment and gas exposure,
   over time (1+ year Silicalite).

   mechanically durable to handling, transport and heat cycles.

2. Water and H_2S Stability of Membranes:

   Steam: Membranes are not water soluble.

   (a) a cold trap or other dehydrator could be used either up- or downstream of the membrane to remove steam.

   H_2S:

   (a) use of a Metal Oxide to remove upstream of membrane,
   (b) development of a "catalytic" membrane;
   layer of metal oxide on top of the zeolite membrane

H_2 Separation Membranes: Responses to Panel's Questions

3. Cost **Estimate** of Zeolite Membranes vs. Pd Membranes:

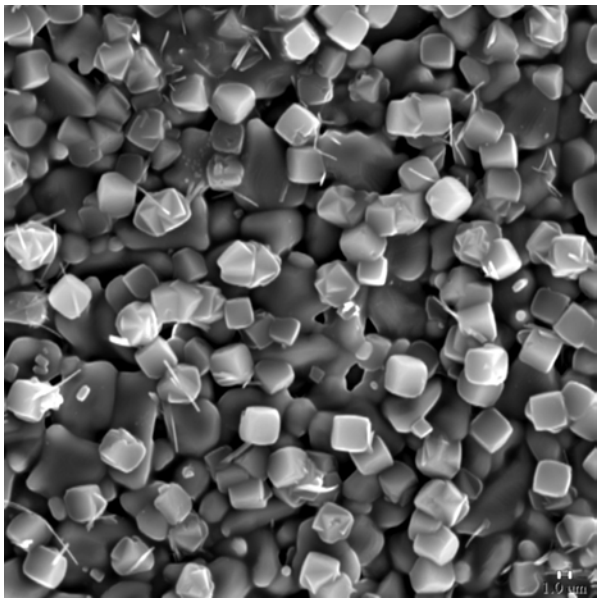
(a) Pd in limited and politically-sensitive supply for "H_2 Economy"
Currently supplied from Russia and South Africa

(b) Industry approximation of Pd film ≈ \$100/ft^2 or installed \$250/ft^2

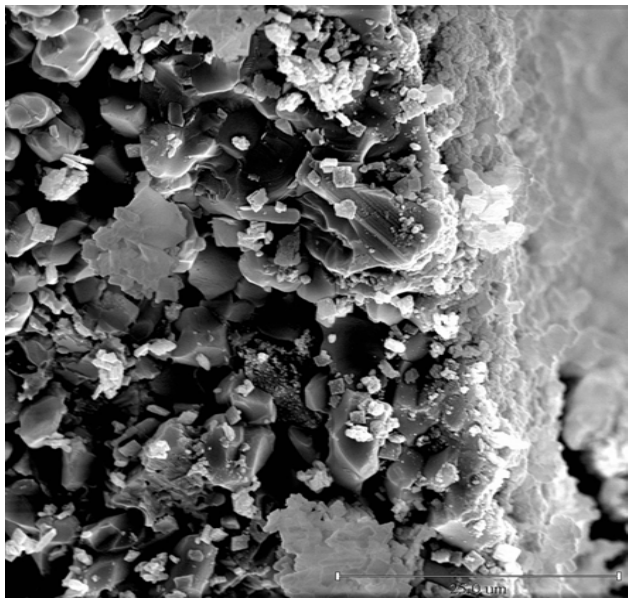
(c) Zeolite films estimated ≤ \$200/ft^2 installed
Assuming zeolite membranes will become nearly as commercially viable as Pd membranes, cost will drop!!

H_2 Separation Membranes: Current Year Highlights: Si/Ti Membranes

Unidentified/New Silicotitanate phase grown as film



Blocky silicotitanate crystals on an alumina support.



Cross section of silicotitanate crystal membrane on an alumina support.

Preliminary permeation values @ RT, SNL Si/Ti $\approx 10^{-8}$ mole/(m^2 Pa sec)

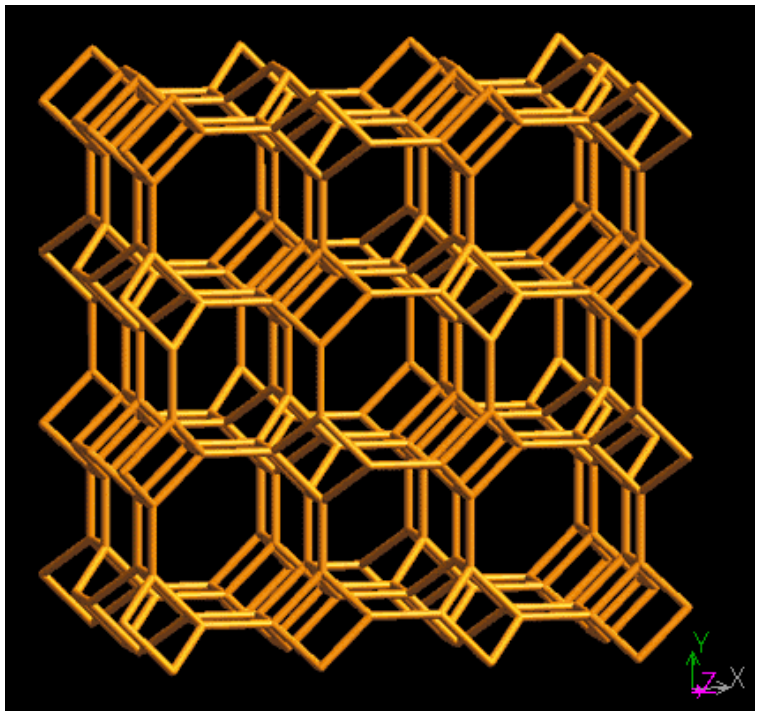
$H_2/N_2 = 2.3$
$H_2/CH_4 = 1.9$
$He/N_2 = 2.0$
$CH_4/N_2 = 1.2$
$H_2/CO_2 = 3.0$
$H_2/O_2 = 3.2$
$CH_4/CO_2 = 1.5$

Work in Progress though Selectivity Evident! Calcination procedure not perfected yet.

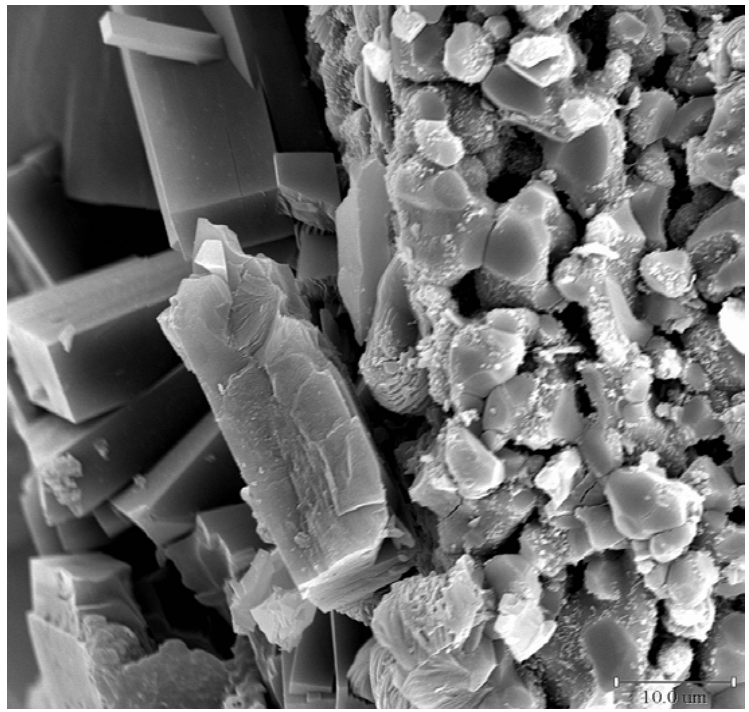
Template pore blockage still interfering with gas permeation.

H_2 Separation Membranes: Current Year Highlights: Si/Al Membranes

Zeolite W: 8 rings, 3D Pores

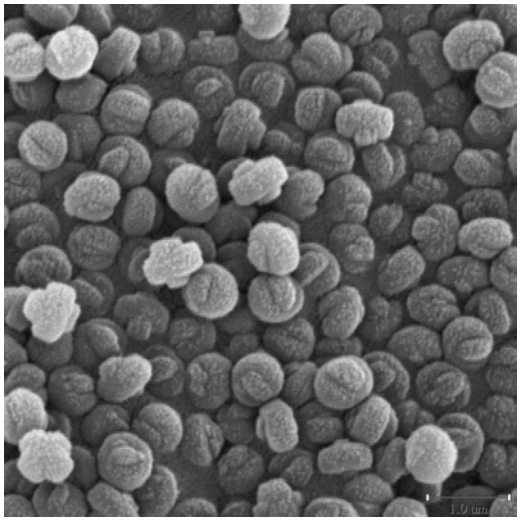


Cross Section of Zeolite W Film
On Alumina Support

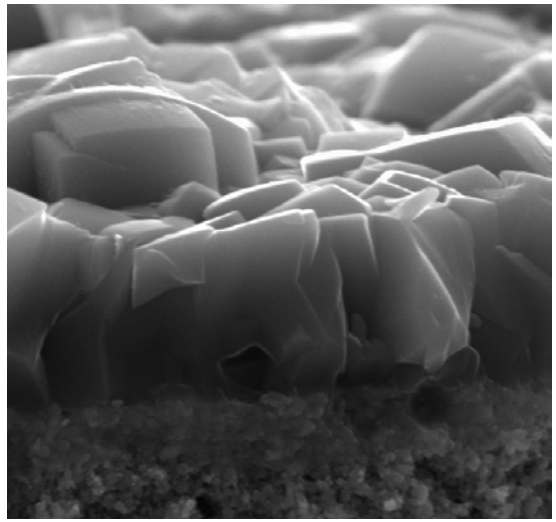


First reference of Zeolite W as a thin film membrane
Continued research needed to fill defects and study permeation

H_2 Separation Membranes: Current Year Highlights : Silicalite Films



Seed Crystals Uniform in size, 1μm



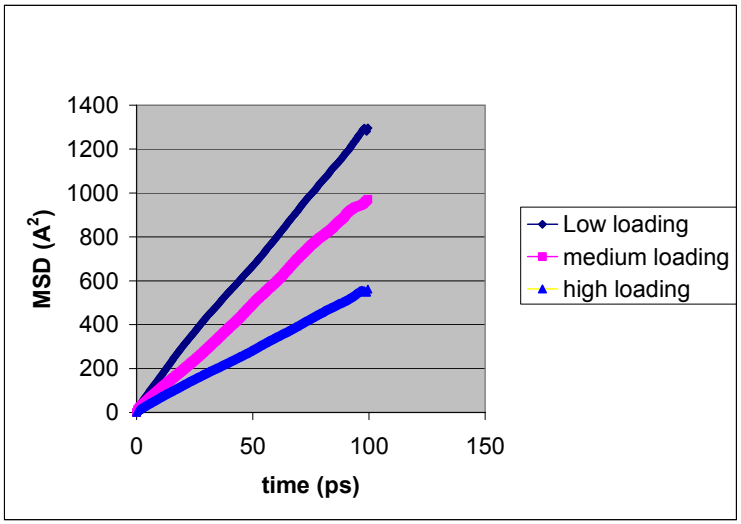
10 μm thick Silicalite Membrane on composite support

Permeation and Regenerability
Single Gas Permeance (10^{-7} mole/m^2 s Pa)
Trans-membrane pressure= 16 PSI

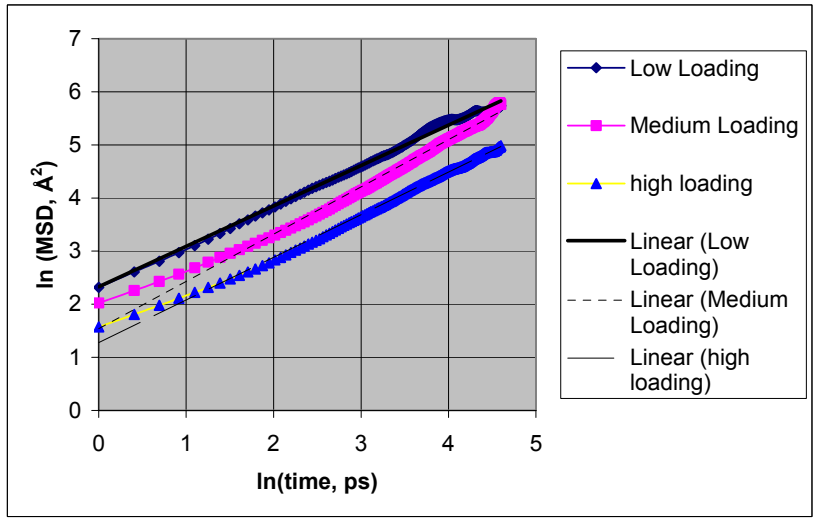
as / (Kinetic ∅ (Å)) Membrane	He (2.6)	SF_6 (5.5)	H_2 (2.8)	CO_2 (3.3)	O_2 (3.5)	CH_4 (3.8)	N_2 (3.6)	CO (3.7)
18A	1.8	< 0.05	2.4	2.9	1.4	-	-	1.6
21A	1.2	< 0.04	1.6	3.0	1.3	1.7	1.1	-
22A	1.5	< 0.02	2.0	5.9	1.2	3.2	1.4	1.4
22B	1.5	< 0.03	2.9	4.9	-	-	-	-
22B "regenerated"	1.1	-	1.4	2.9	-	-	-	-
28A	0.8	< 0.03	1.9	5.1	1.3	2.6	1.6	1.6

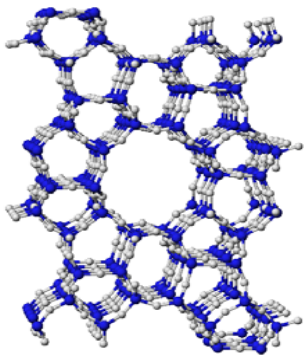
Current Simulation Studies at NMSU

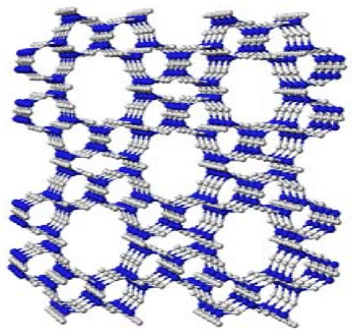
Mean-squared displacement of H_2 in Silicalite



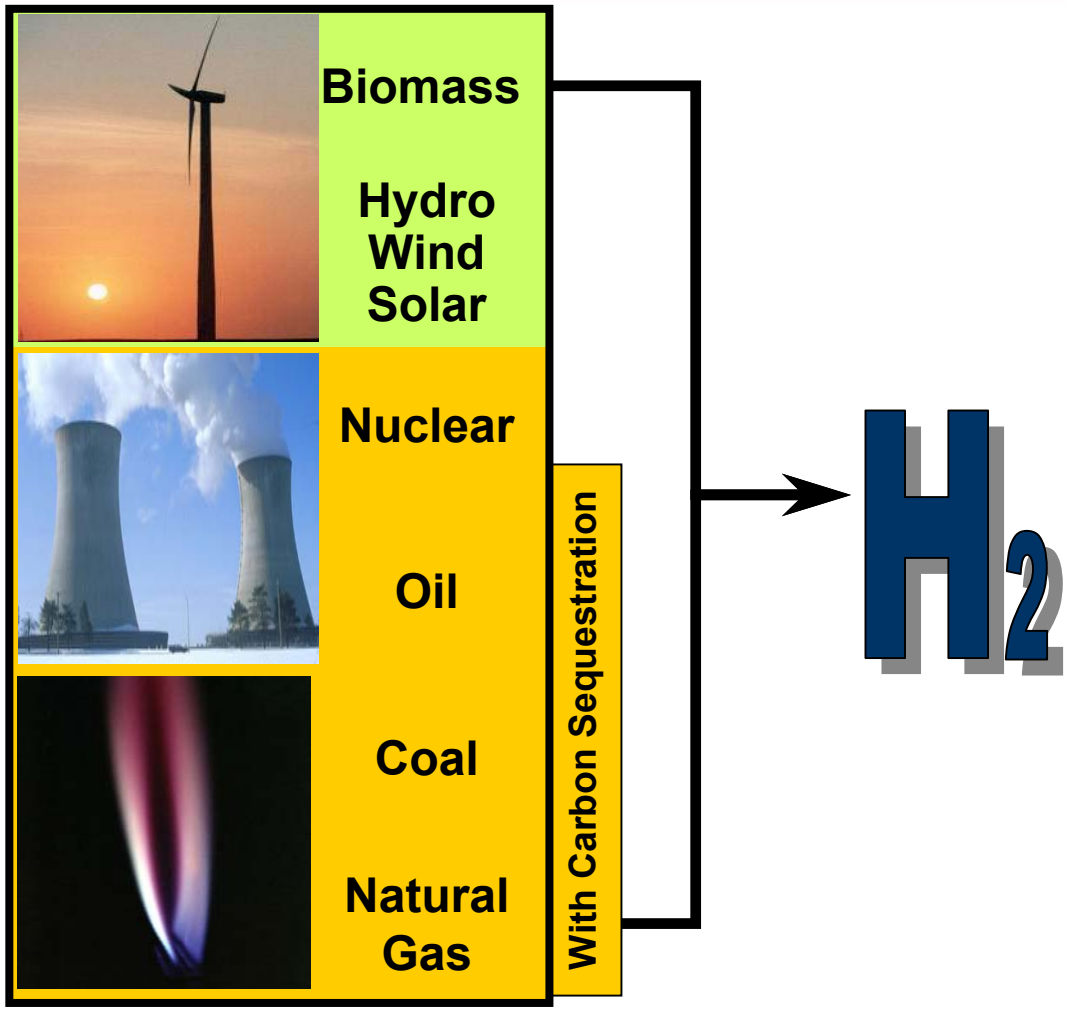
Mean-squared displacement of H_2 in ZSM-22







Simulation of Diffusion of H_2 in Silicalite vs. ZSM-22
H_2 moves much more quickly through Silicalite due to its multidimensional channels;
Gas molecules cannot "pass" each other, causing blockage in ZSM-22



Electrolytic Hydrogen Production

Matt Kauffman

Technology Barriers

- Cost
- System efficiency
- Electricity cost and emissions
- Renewable integrated systems
- Codes and standards
- Delivery (electrons vs. hydrogen)

Targets and Status

Water Electrolysis

Characteristics	Units	2003 status	2005	2010
250 kg/day refueling station 5000 psi				
Electricity cost	$/kg H_2	1.95	1.80	1.60
Total cost	$/kg H_2	4.65	3.80	2.50
Efficiency	%	60	64	73
5 kg/day refueling unit 5000 psi				
Electricity cost	$/kg H_2	4.10	3.30	2.80
Total cost	$/kg H_2	7.40	5.30	3.75
Efficiency	%	50	58	70

Current Projects
Electrolytic Hydrogen Production

• Low Cost, High Efficiency Reversible Solid Oxide System	Technology Management Inc.
• High-Efficiency Steam Electrolyzer	LLNL
• High-Temperature Solid Oxide Electrolyzer System	INEEL

2004 New Starts

Electrolytic Hydrogen Production

- High-Pressure Electrolyzer Without Downstream Compressor
- Integrated H_2 Generation System Using Wind Energy
- Electrolysis System Based on Titan HM200 Industrial Gas Generator

- Giner Electrochemical Systems
- Proton Energy Systems, Inc.
- Teledyne Energy Systems, Inc.

R&D Direction

Develop electrolysis technology for large scale production

- Analysis effort exploring large scale renewable production and delivery
- Rural hydrogen fueling stations
- Increase utilization of stranded renewable electricity sources

Develop distributed refueling technologies

- Electrochemical compression
- Plug and play, safe, modular systems
- Siting, Codes and Standards

R&D Technologies

- **Alkaline is nearer term technology for larger systems**
  - System cost reduction
  - Improve system efficiency/durability
  - Renewable integration (power conversion, storage)
- **Solid oxide electrolysis is in early development**
  - Materials and manufacturing R&D
  - Evaluate technology for power park systems
- **PEM technology geared to smaller home refueling**
  - Cost reduction and efficiency improvements needed
  - Integral compression

Low Cost, High Efficiency Reversible Fuel Cell Systems

DE-FC36-99GO-10455

POC: Doug Hooker

Dr. Robert Ruhl

Vice President, Technology

Technology Management, Inc.

9718 Lakeshore Blvd, Cleveland, OH 44108

(216) 541 -1000, tmi@stratos.net

May 19, 2003

Berkeley, CA

Outline

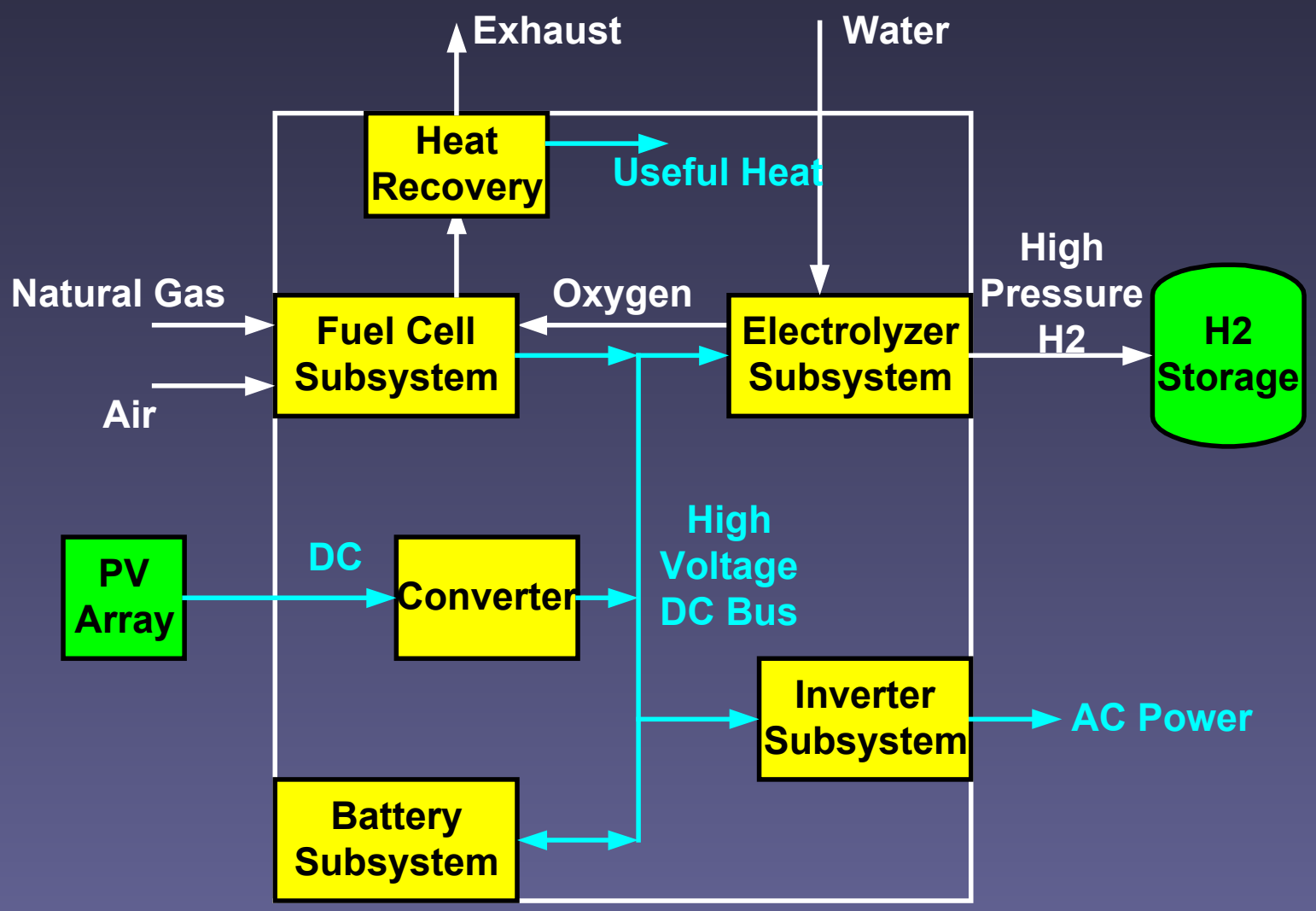
- Objectives
- Approach
- Time Line
- Accomplishments
- Interactions
- Plans

Responses to last year's reviewer comments are included throughout this presentation

Objectives

- Develop Enabling Technology for Low Cost Production of Hydrogen for Vehicles
  - natural gas
  - photovoltaic or wind power utilized when available
  - up to 80 MPa (11,600 psi)
  - residential or filling station sites
  - negligible CO and H_2O
  - negligible emissions of NO_x and other pollutants
  - cost < $1.50/kg

Approach: System Concept



Approach: Challenges

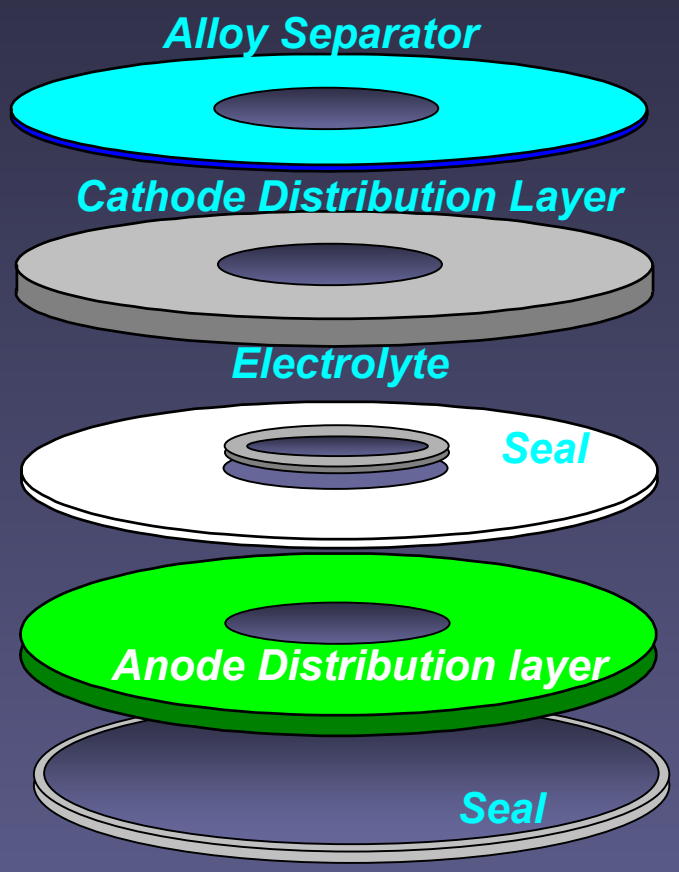
- Electrolyzer Subsystem Efficiency
- Fuel Cell Subsystem Efficiency
- Moderate Installed Capital Cost
- Other

Approach: Novel Solid Oxide Technology

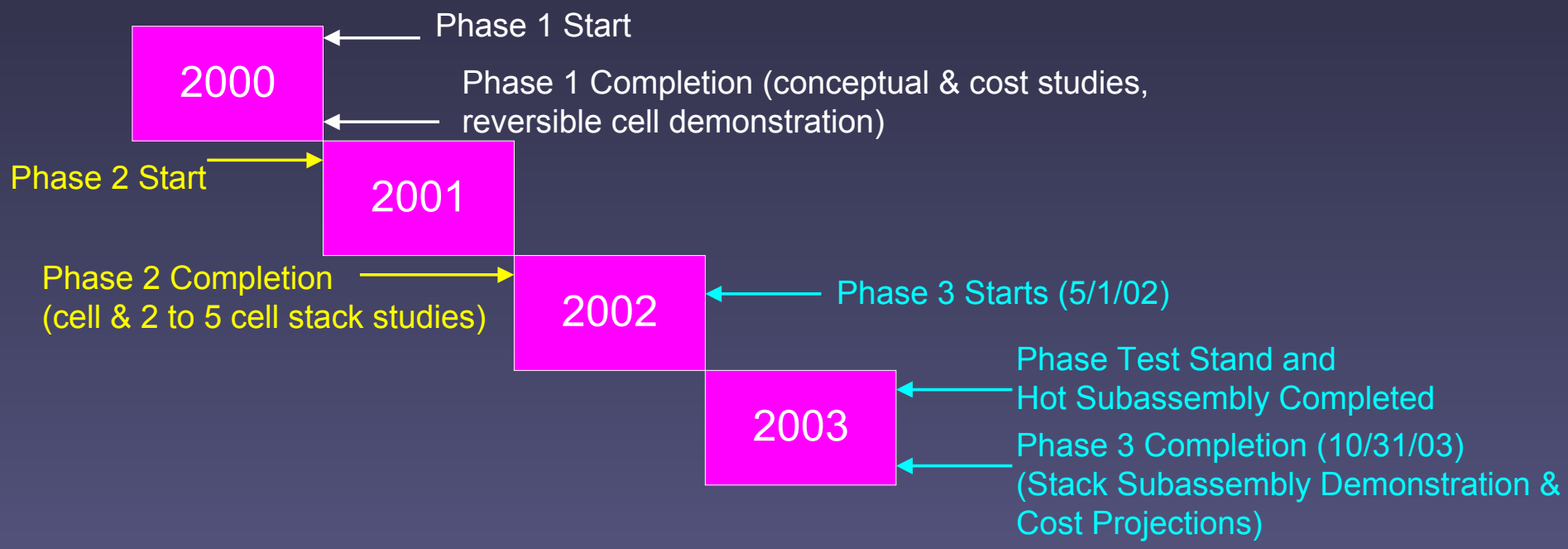
- Reversible Solid Oxide Stacks
  - target feed utilization: 100% (staged)
  - target average fuel cell voltage: 750 mV
  - target average electrolysis cell voltage: 1500 mV
- Stack Cost Target: $100./kW
- Stack Life Target: 5 years
- Integrated Subsystems

Approach - Cell Configuration

- Radial Flow
- Diffusional
- Small Diameter



Time Line

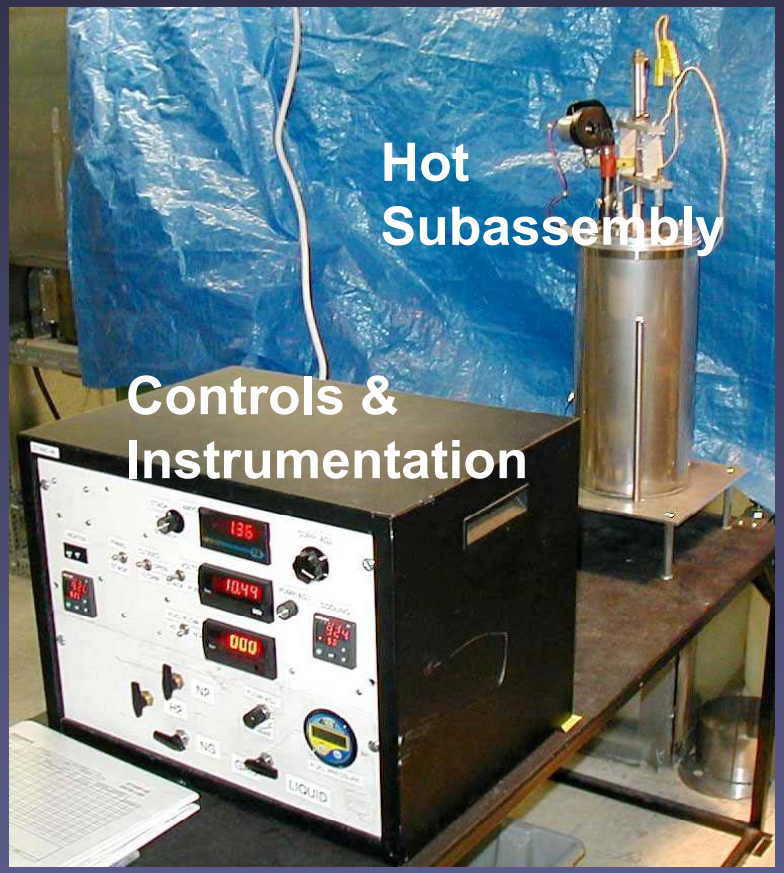

2000
Phase 1 Start
Phase 1 Completion (conceptual & cost studies, reversible cell demonstration)
2001
Phase 2 Start
Phase 2 Completion (cell & 2 to 5 cell stack studies)
2002
Phase 3 Starts (5/1/02)
2003
Phase Test Stand and Hot Subassembly Completed
Phase 3 Completion (10/31/03) (Stack Subassembly Demonstration & Cost Projections)

Cell Development Accomplishments

Parameters	Goal	Status
Seal C_v	$< 10^{-5}$	$< 10^{-6}$
Power Decline (Watts/1000 hr)	< 5%	< 5%
Area Specific Resistance (Ω - cm^2)	< 1.0	1.1 to 2.3
Cells/Stack	up to 50	up to 20

Fuel Cell System Accomplishments

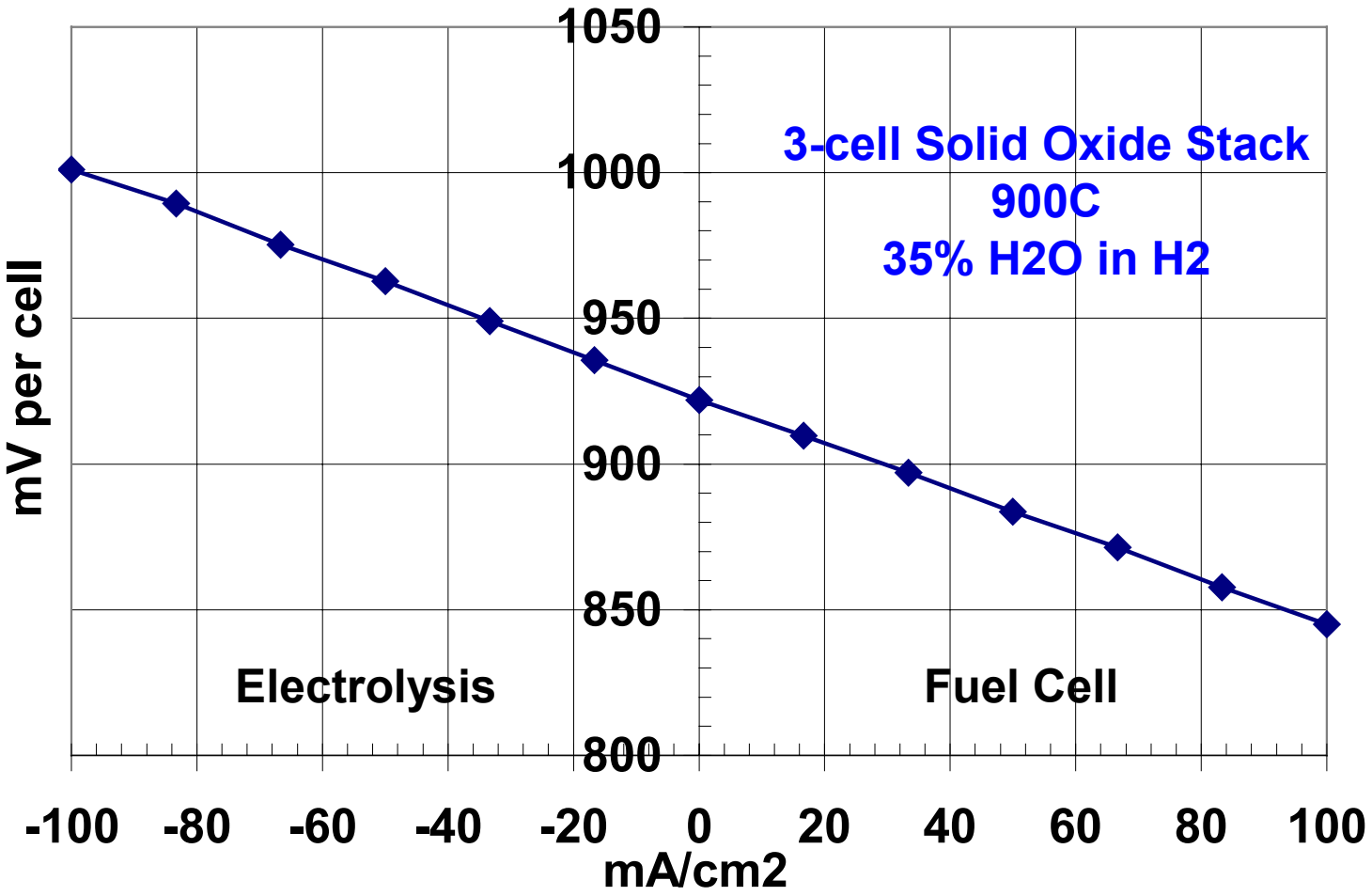
- 50 cell Reversible SOFC System Design
- Natural Gas or Water Feed



Fuel Cell System Accomplishments

- 51% Stack LHV Efficiency on natural gas
  - 20-cell stack
- less than 5% per 1000 hr power decline
  - natural gas, 19-cell stack
- additional reversible stack tests

Fuel Cell System Accomplishments



Engineering & Cost Studies Accomplishments

Example Residential System

- Annual Hydrogen 480 kg
- Annual AC 15000 kWh
- Annual Heat Recovery 18000 MJ
- Natural Gas LHV 925 BTU/scf

Engineering & Cost Studies Accomplishments

Example Residential System

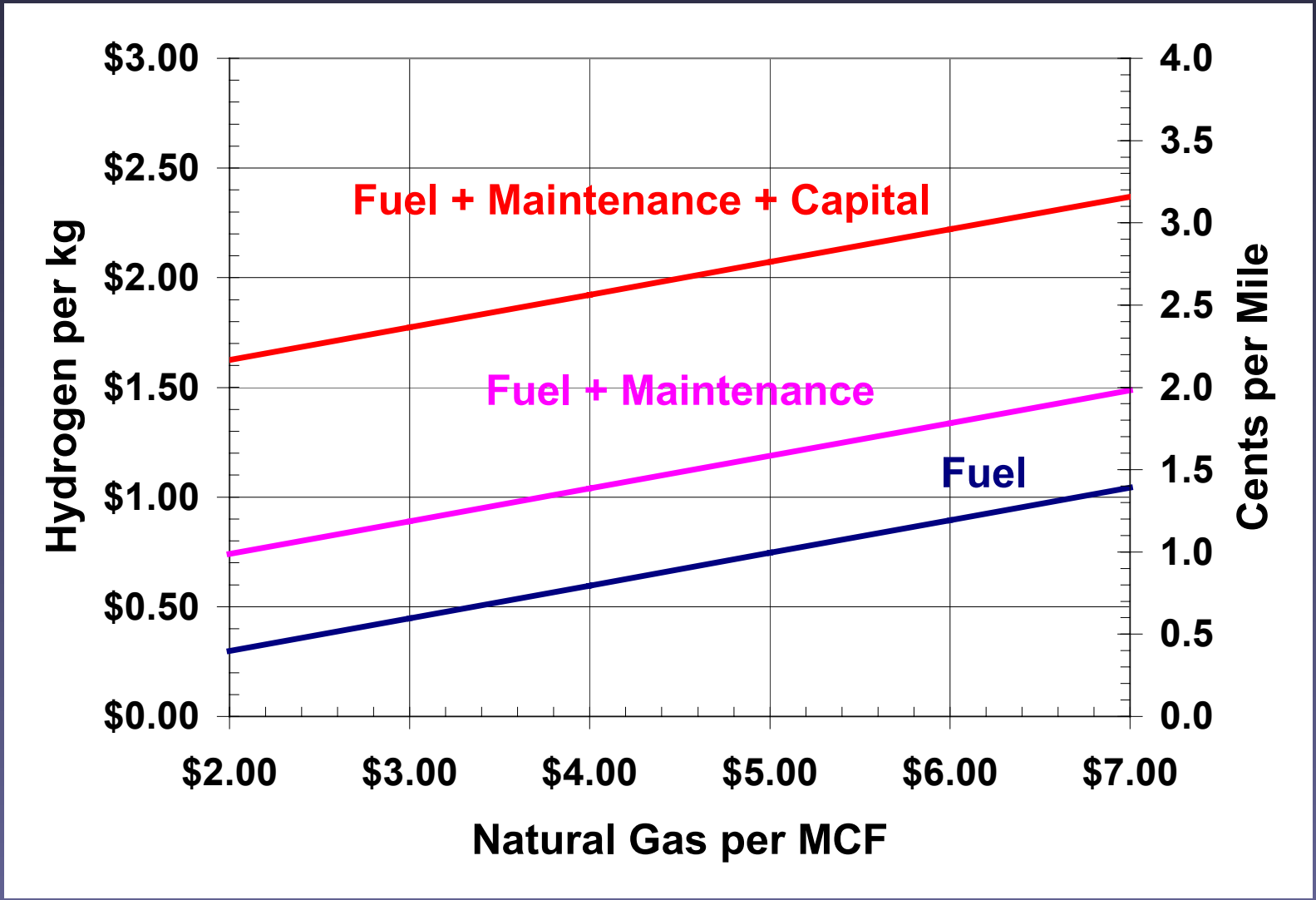
projections for large annual quantities

Fuel Cell Modules (2 x 3 kW)	$2281.
Electrolyzer Module (3 kW)	1178.
Inverter Subsystem (20 kVA surge)	317.
Battery Subsystem (20 kW surge)	388.
Photovoltaic Converter (3 kW)	49.
Heat Recovery (2 kW)	243.
Hydrogen Storage (10 kg)	261.
Total Manufacturing Costs	**$4717.**

Engineering & Cost Studies Accomplishments

Manufacturing Cost		$ 4717.
Manufacturing & Distribution Margins 75%		3538.
Installation Costs		1843.
Subtotal		$10098.
Sales Taxes 5%		505.
Total Installed Cost (end-user)		**$ 10603.**
Annual Rate (assumption)	8.0%	
Annual Capital		**$ 848.**
Annual Maintenance (20 yr. Avg.)		**$ 425.**

Engineering & Cost Studies Accomplishments



Engineering & Cost Studies Accomplishments

Example Residential System

AC Power (using Natural Gas @ $6.00/MCF)

	Cents/kWh
Fuel	2.2
Maintenance	1.4
Subtotal Cash	3.6
Capital	2.8
Total	6.4

Engineering & Cost Studies Accomplishments

H_2 and Electricity Cost Depend on:

- Fuel Cost
- Maintenance Costs
- Photovoltaic or Wind Inputs
- Sale and/or Purchase of Electricity
- Annual Capacity Factors
- Accounting Assumptions

Interactions

- NIST/ATP (Nat'l Institute of Standards & Technology - Advanced Technology) Program
  - Delco Remy International
- DoD/Air Force, Dual Use Science & Technology (DUS&T) Program
  - Electricore
  - Delco Remy International
  - NASA Glenn Research Center
- State of Ohio 3rd Frontier Action Fund
  - NASA Glenn Research Center
  - Boeing
  - Catacel

Plans

- Phase 3 completion: 10/31/03
- Cell and Stack Demonstration
  - Reduce ASR to 1.0 ohm-cm^2
  - Demonstrate Stacks up to 50 Cells
  - Preserve Power Loss < 5%/1000 hr
  - Preserve $C_v < 10^{-5}$
- Engineering and Cost Studies
  - Complete Work

High-Efficiency Steam Electrolyzer

Andrew L. Vance, John W. Trent, Ervin F. See, L. Peter Martin & Robert S. Glass
Lawrence Livermore National Laboratory

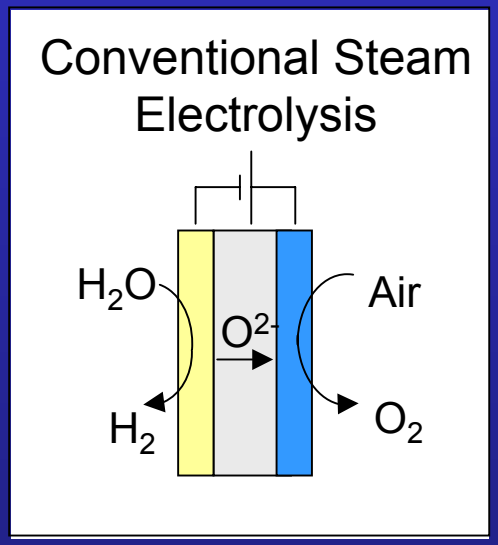
DOE Hydrogen and Fuel Cells 2003 Annual Merit Review
May 20, 2003

We are developing technology for distributed hydrogen production

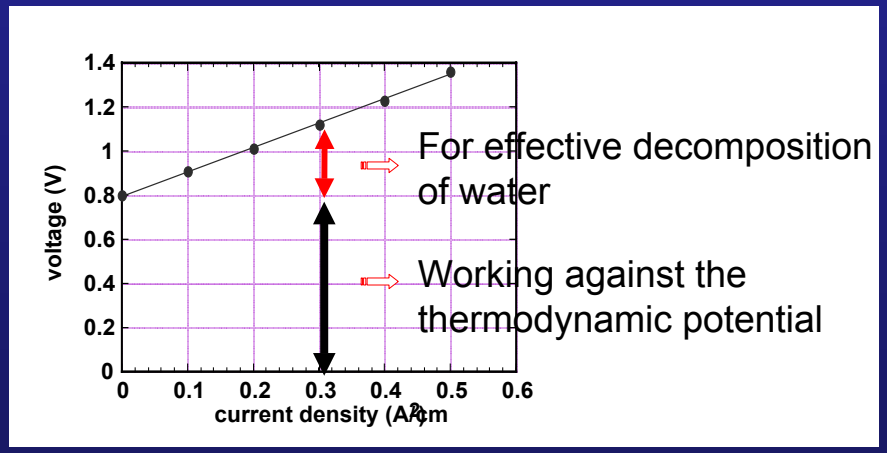
- Our goal is a hydrogen production system that is compatible with the existing, hydrocarbon-based fuel infrastructure
- We are working toward the demonstration of a 5 kW natural-gas-assisted steam electrolyzer by 2006
- For 2003, we will build and test a newly designed electrolyzer targeting 1 kW hydrogen output

There are cost and efficiency issues with conventional steam electrolysis

- In conventional systems, most of the electricity is used to overcome the thermodynamic potential
- Hydrogen production from electrolysis is expensive because of high electricity requirements



We are working toward electrolysis with reduced electricity consumption

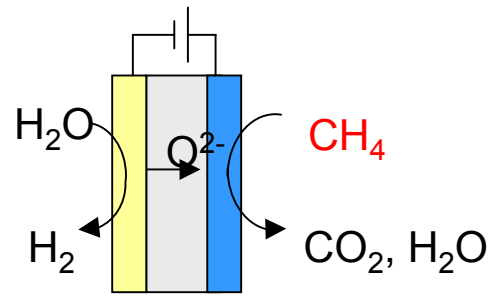


Our approach offers potential cost and efficiency advantages

Natural-Gas-Assisted Steam Electrolyzer (NGASE)

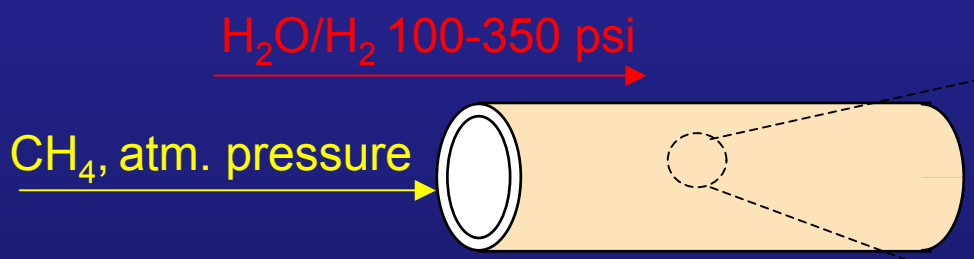
- Natural gas at the anode reduces the potential difference - lowering electricity consumption
- Hydrogen is produced at pressure at the cathode
- Current focus utilizes total oxidation mode
- Partial oxidation mode also possible, yielding additional hydrogen from methane after gas separation

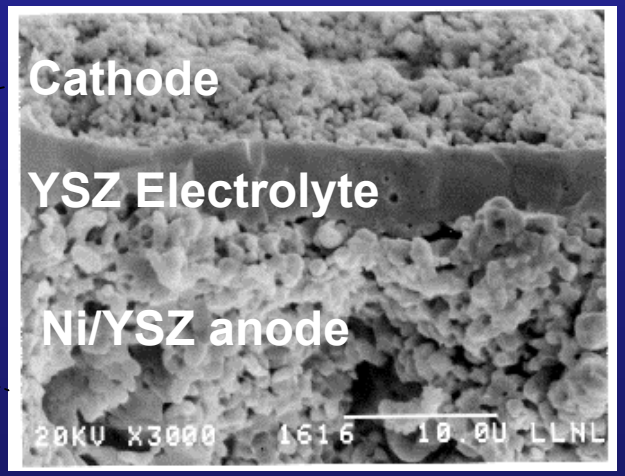
Total oxidation mode



The tubular design allows pressurized operation

- Tubes best for operation with significant pressure differentials
- Size and layer thickness controlled by fabrication technique
- Low risk of contamination of hydrogen due to pressure differential
- System provides in-situ electrochemical hydrogen compression





The project has advanced from feasibility demonstration to prototype systems

FY00 - Project initiation, feasibility demonstration of reduced electricity requirement

FY01 - Improved tube fabrication, designed multiple-tube electrolyzer, initiated industrial collaboration

FY02 - Demonstrated 200 W, 35 psi electrolyzer, improved tube performance, began design of 1 kW reactor

FY03 - Improved design of 1 kW electrolyzer, assemble and test new reactor, initiated collaboration with UConn for tube fabrication, testing improved anode materials to reduce carbon deposition

FY04-FY06 - Continued testing and refinement of 1 kW system, design and assembly of 5 kW system with field demonstration in 2006

A few challenges were encountered in the first half of FY03

- Continuing resolution limited funding levels
  - Forced cuts in manpower (loss of two technicians)
  - Delayed purchase of needed big-ticket items
- Funding difficulties for industrial partner, Solid Oxide Systems, delayed system scale-up
- PI (Quoc Pham) left LLNL for industry in February

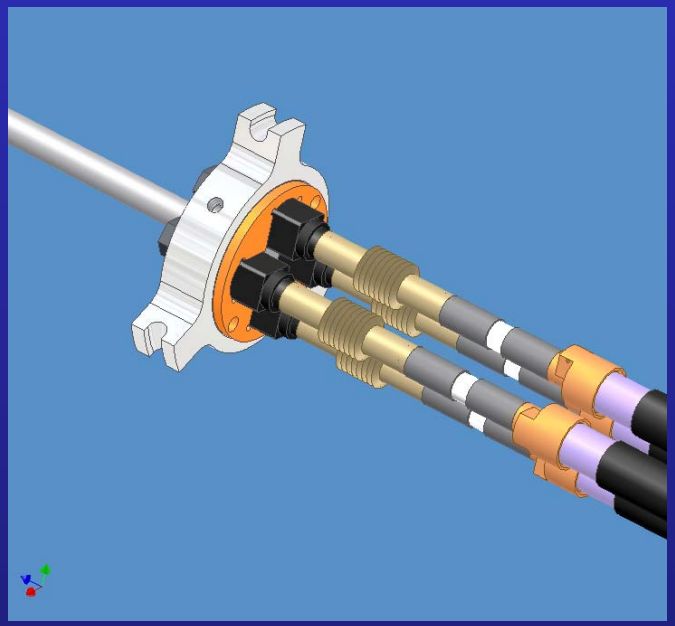
The project is back on track for FY03

We are building an improved electrolyzer and tackling materials science problems

- Significant improvements have been made in the electrolyzer design
  - Flexible and scalable to accommodate tube lengths up to 18”
  - Materials utilized to avoid problems related to operating temperature and environment
  - System will be complete in August with testing to follow
- Evaluation of potential materials for next generation systems
  - Screening of improved anode formulations
  - Materials for tube assembly (brazing alloys, interconnects, fittings)
  - Electrolyte and cathode coating methods

We are forming alliances with universities and industry

- Outsourcing for efficiency:
  - Ni-YSZ tubes to be fabricated by extrusion technique at the University of Connecticut's Global Fuel Cell Center
  - Brazing of tubes to fittings to be completed by industrial vendor
  - Industrial partner, Solid Oxide Systems, working to secure funding for manufacturing support

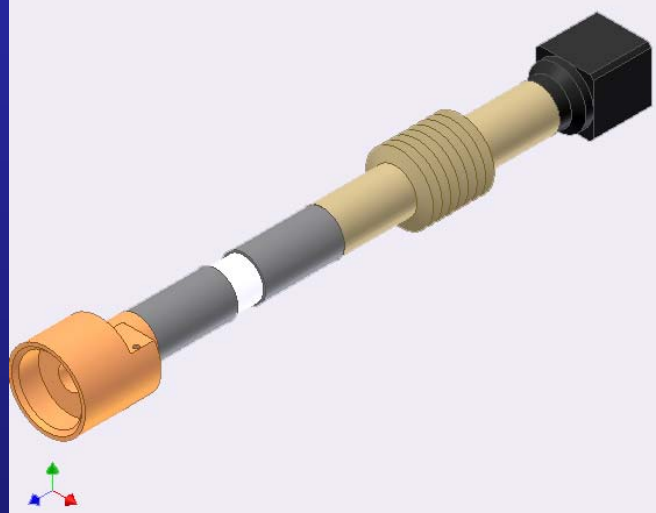


- We will focus on design, chemistry and materials issues and work to strengthen ties to other institutions (e.g. UC-Davis)

The new flexible electrical isolator design overcomes several technical issues

- CTE-matched components for 700°C
- Bellows to accommodate movement of tubes
- Insulating standoff – allows series connection
- Steam/ hydrogen environment tolerant

Electrical standoff with CTE-matched fitting for Ni-YSZ tube



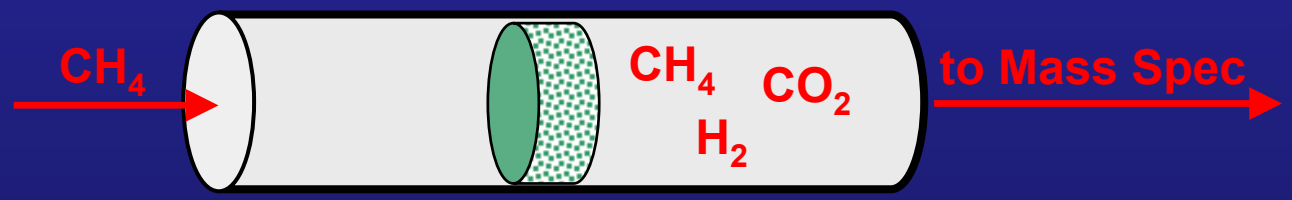
We are also addressing basic materials issues

- Carbon deposition catalyzed by nickel remains a challenge
  - Without adequate oxygen ion flow to anode, methane rapidly converts to carbon and hydrogen at operating temperature
  - Short-term solution is humidification of methane with applied potential (Liu, J.; Barnett, S.A. *Solid State Ionics*, 2003, *158*, 11)

- Long-term goal is improved material allowing use of untreated natural gas fuel
  - Processing issues must be overcome (e.g. incompatible sintering temperatures)
  - Material must be good ionic and electrical conductor

Potential anode materials are screened by temperature-programmed oxidation

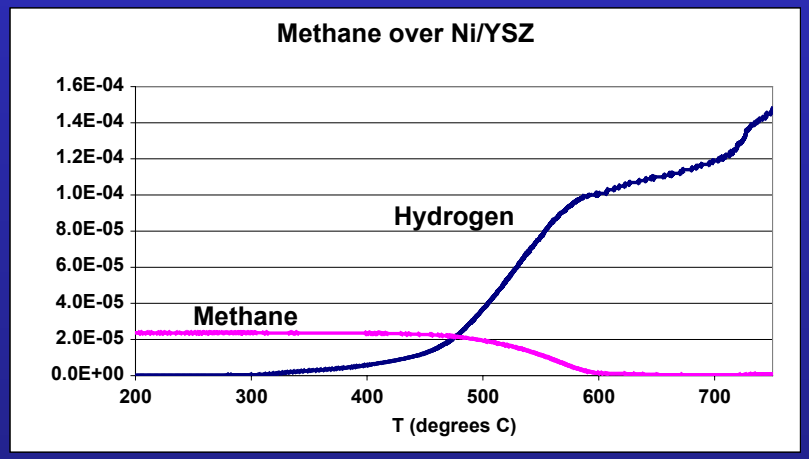
- Materials with approximate anode composition are prepared and analyzed as powder samples
- Methane flowed through heated powders in quartz tube
- Good candidates for further study will be used in single-cell testing
- Temperature-programmed oxidation-mass spectrometry (TPO-MS) useful for rapid screening of potential anode materials



TPO-MS screening reveals reaction products for powders

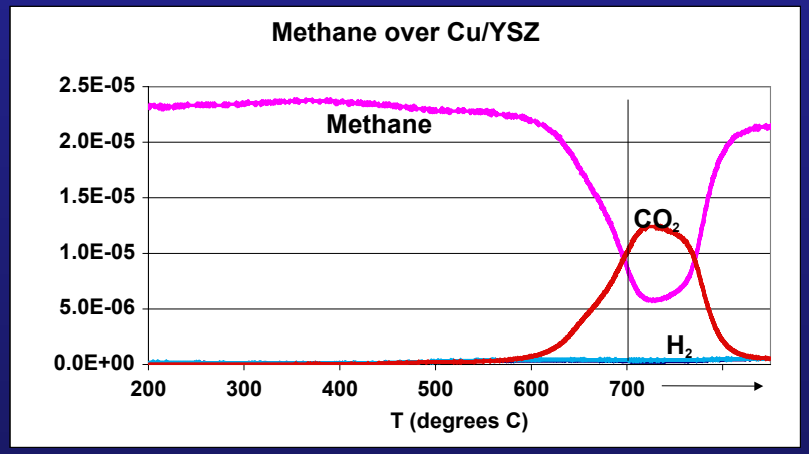
- Ni/YSZ carbon deposition shown by significant hydrogen generation

$$CH_4 \rightarrow C + 2\,H_2$$



- Cu/YSZ yields only carbon dioxide at 700°C

$$CH_4 \xrightarrow{O^{2-}} CO_2 + 2\,H_2O + 8\,e^-$$



Copper illustrative of challenges in modifying anode composition

- Well known that copper does not catalyze carbon deposition at operating temperature
  - Melting points of CuO (1326 °C) and Cu (1083 °C) below normal sintering temperature of YSZ (~1450 °C)
  - Research indicates minimization of YSZ agglomeration allows reduced sintering temperatures (Lu et al., *Solid State Ionics*, 2002, *152-153*, 393)

- Single cells will be utilized for testing of promising materials
  - Anode-supported cells for testing under electrolyzer conditions (thin electrolyte)
  - Electrolyte-supported cells to allow testing of materials without processing issues associated with anode-supported cells

Future work builds toward 5 kW system

- Remaining work for FY03
  - Complete assembly of current 1 kW system (9/03)
  - Initial testing of 1 kW system (9/03)
- FY04
  - Characterize improved anode materials (11/03)
  - Durability testing of components (1/04)
  - Long-term testing of 1 kW system (4/04)
  - Integrate interconnects and tubes (5/04)
  - Fabricate modified tubes (6/04)
  - Optimize tube composition and fabrication (8/04)
  - Define requirements for 5 kW system (9/04)

We are working toward a 1 kW electrolyzer for FY03

- After funding and personnel issues in first half of FY03, we are back on track
- We developed an improved electrolyzer design
  - Flexible, scalable system
  - Components matched to operating conditions
- Materials testing is underway
  - Exploring potential next generation tube materials
- Forming additional alliances to facilitate future work
  - Universities, industry, outside vendors

Acknowledgments

- Richard L. Landingham (LLNL) and Chris Chervin (UC-Davis) - technical advice
- Quoc Pham – previous research

- This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48

Idaho National Engineering and Environmental Laboratory

Development of a High Temperature Solid Oxide Electrolyser System

Steve Herring, Ray Anderson, Jim O'Brien, Paul Lessing, and Carl Stoots

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley, CA, May 20, 2003

1. Relevance/Objective

OHFCIT: Production Goals

Research and develop high and ultra-high temperature processes to produce hydrogen through chemical cycle-water splitting technology or other non-carbon-emitting technology utilizing heat from nuclear or solar sources.

Table 4.1.7b. Technical Targets: High Temperature Solid Oxide Water Electrolysis[1]

Characteristics		Units	2003 Status	2005 Target	2010 Target
Cell Stack	Cost	$/kg	0.64	0.46	0.27
	Efficiency[2]	%	76	85	94
Balance of Plant	Cost	$/kg	0.83	0.52	0.32
	Efficiency	%	92	93	96
Electricity[3]	Cost	$/kg	1.59	1.41	1.23
Heat[4]	Cost	$/kg	0.19	0.17	0.15
Total	Cost[5]	$/kg	3.25	2.55	1.96
	Efficiency	%	70	79	90

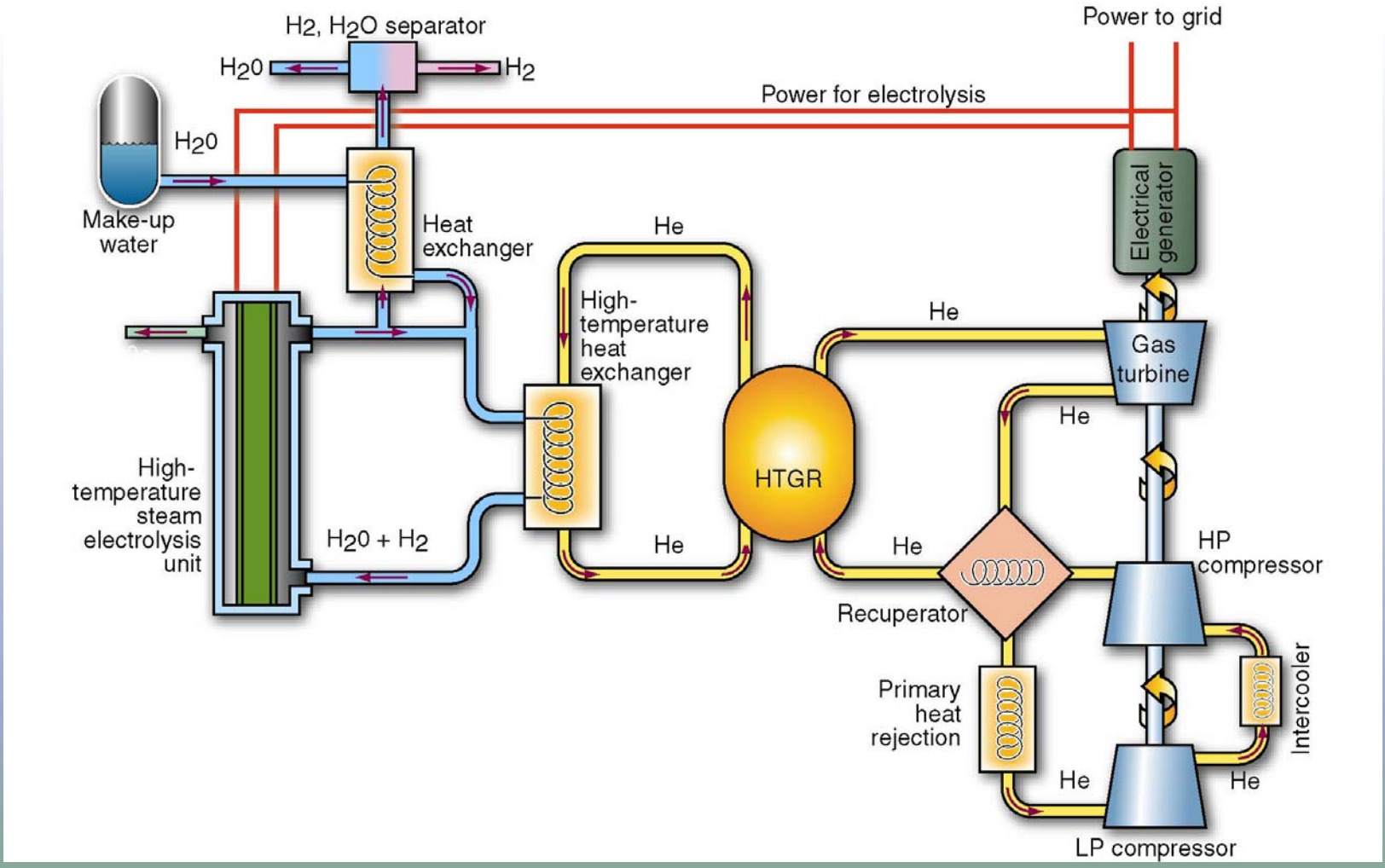
[1] Electrolyser delivering 500 kg per day (based on projected technology developments, not current system sizes).
[2] Based on total energy into electrolyzer. All calculations based on Lower Heating Value of hydrogen.
[3] Assumes electricity at $0.045 per kWh and 95% capacity factor.
[4] Heat is valued at $0.016 per kWht.
[5] Based on system capital cost of $1500, $1100, and $700. Includes O&M cost at 2% of capital charges, 15% IRR, 20 year equipment life.

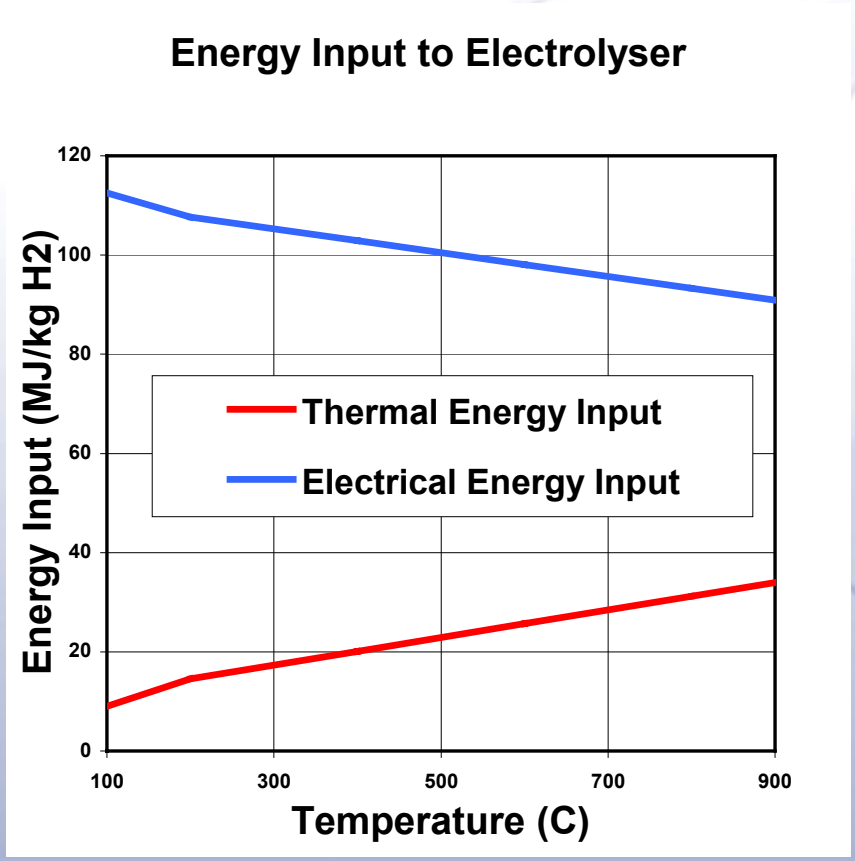
Barriers: U (scaling), V (renewable integration), W (electricity costs)

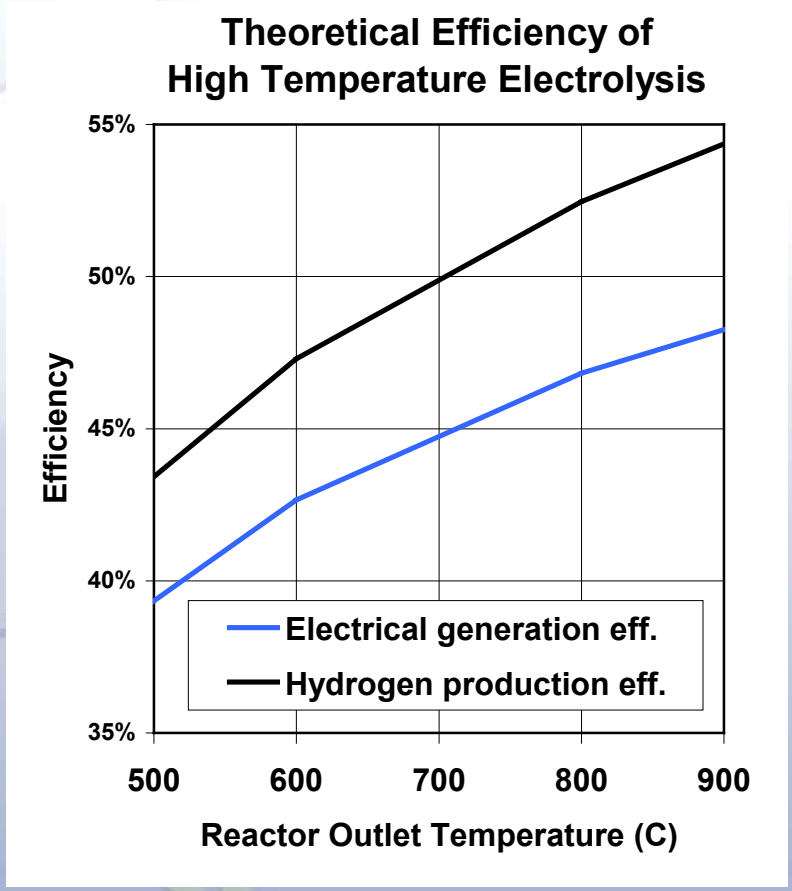
2. Approach

- Development of energy-efficient, high-temperature, regenerative, solid-oxide electrolyser cells (SOECs) for hydrogen production from steam.
  - Reduce ohmic losses to improve energy efficiency
  - increase SOEC durability and sealing with regard to thermal cycles
  - minimize electrolyte thickness
  - improve material durability in a hydrogen/oxygen/steam environment
  - Develop and test integrated SOEC stacks operating in the electrolysis mode
- Specification and testing of hydrogen-permeation-resistant materials for a high-temperature heat exchanger

2. Approach: High Temperature Electrolysis System





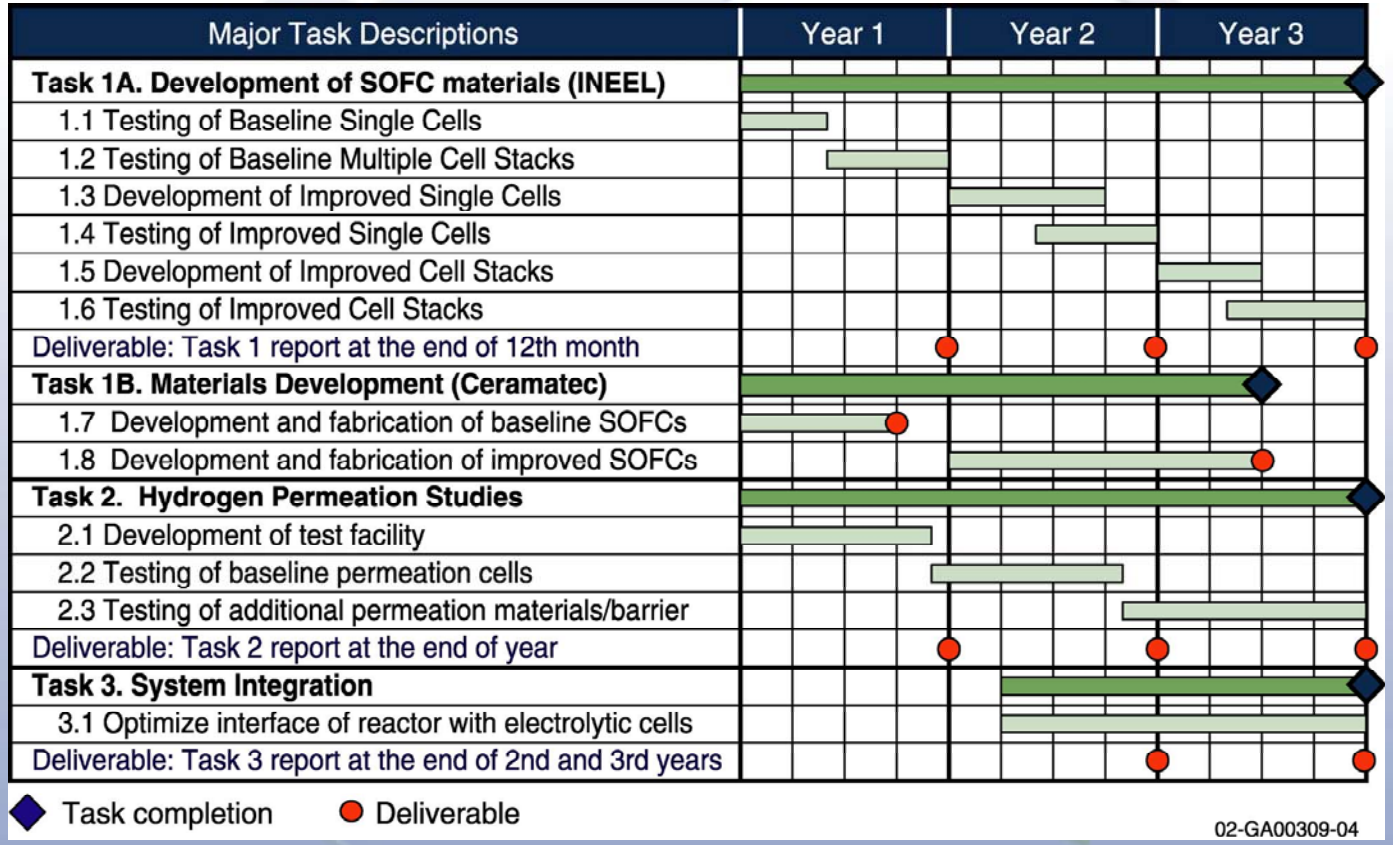


Sulfur-Iodine efficiency estimates:

0% at 670 C peak
10% at 700 C peak
35% at 800 C peak
42% at 830 C peak

3. Project Timeline / 6. Plans, future milestones

Began Jan. 2003

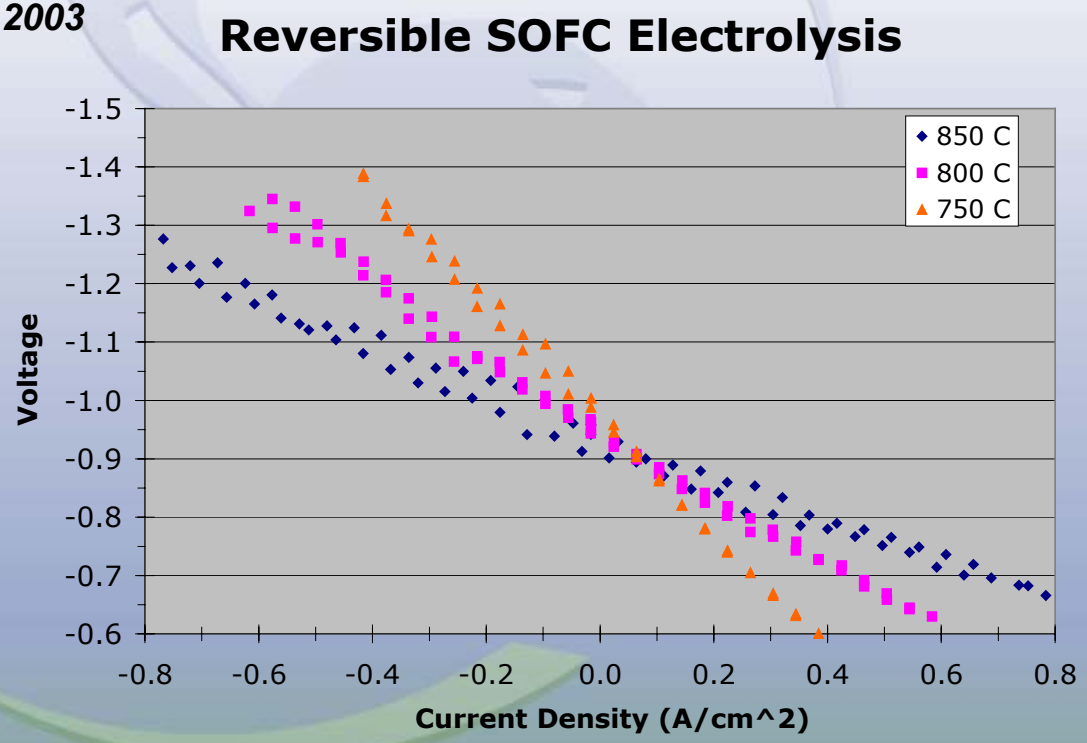


4. Accomplishments/Progress

- ***Funding began Jan. 21, 2003***
- ***Subcontract placed with Ceramatec***
- ***Initial single cell received for testing at INEEL***
- ***Tests conducted at Ceramatec***
- ***Test loop designed, passed safety review and constructed***
- ***Initial INEEL testing, May 14, 2003***

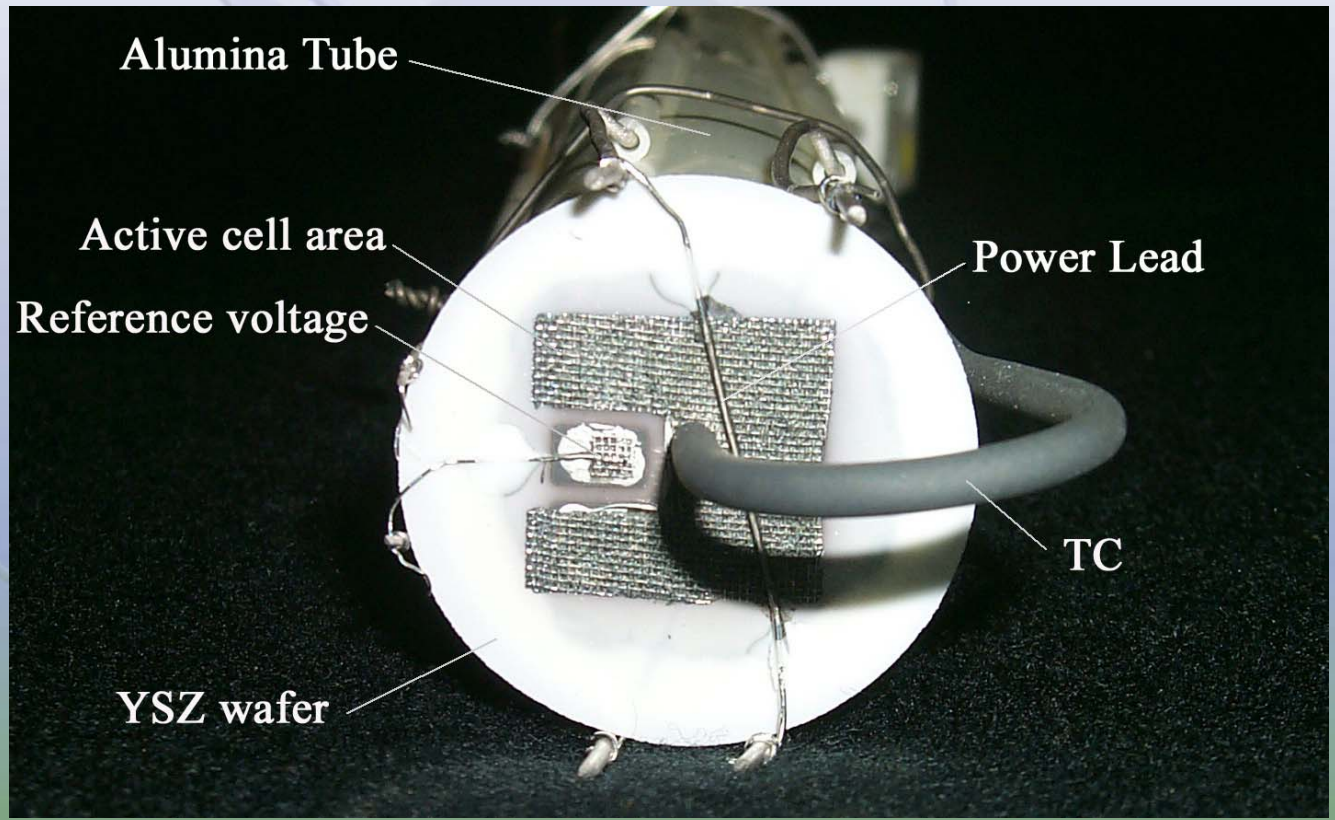
Initial Data from Ceramatec

Electrolysis portion:
ASR: 0.45 ohm-cm^2 at 850 C
0.63 at 800 C, and 0.98 at 750 C.
Bubbler temperature: 88 C
OCV: 0.94 V at 800 C
Input: 50:50 mixture steam and H2
H2 flow: 35 sccm
cell area: 2.5 cm^2
Exit mole fraction is calculated to have 73% H2 and 27% H2O using the 850 C peak current value.

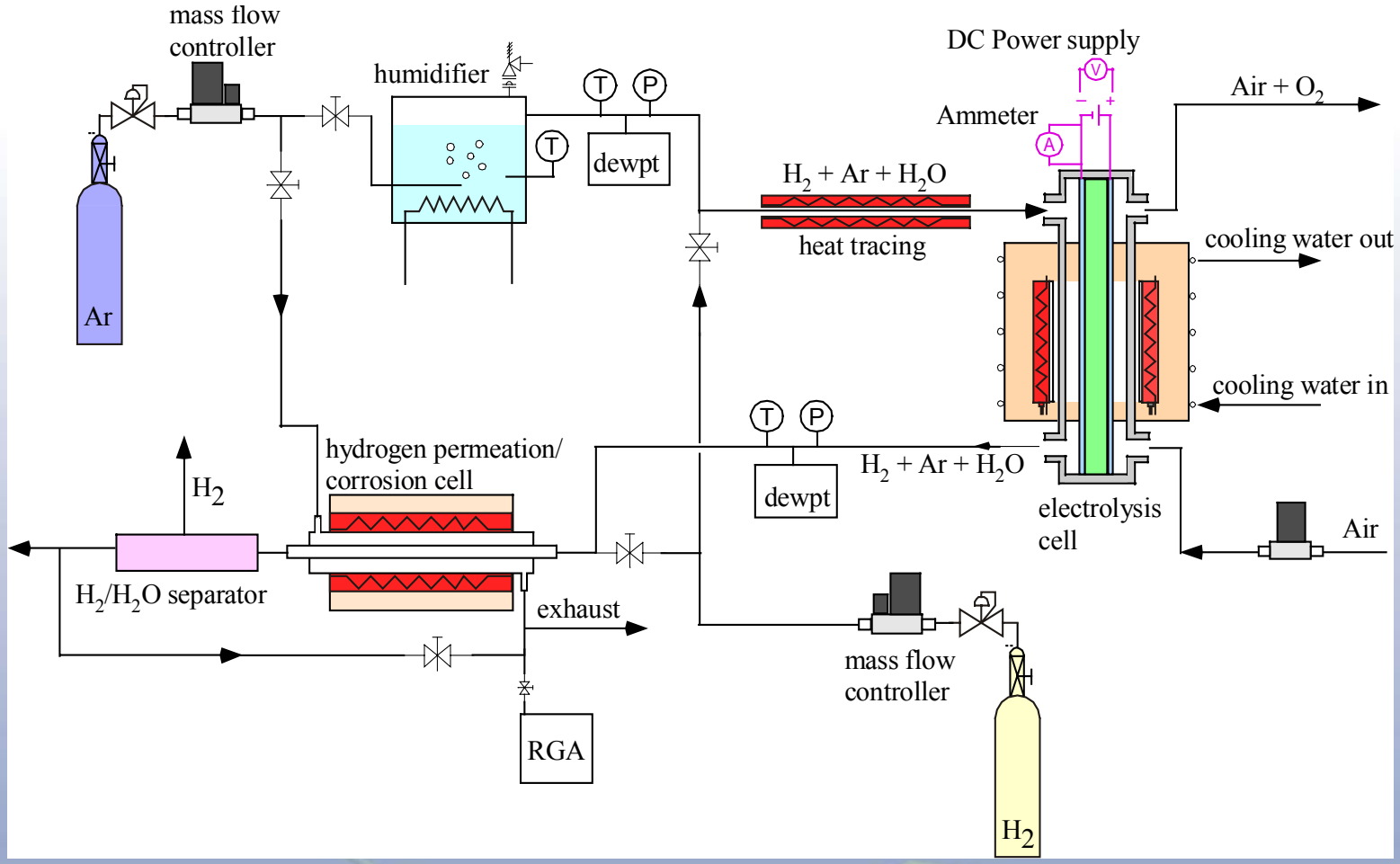


Ceramatec "button cell" for initial single-cell testing:

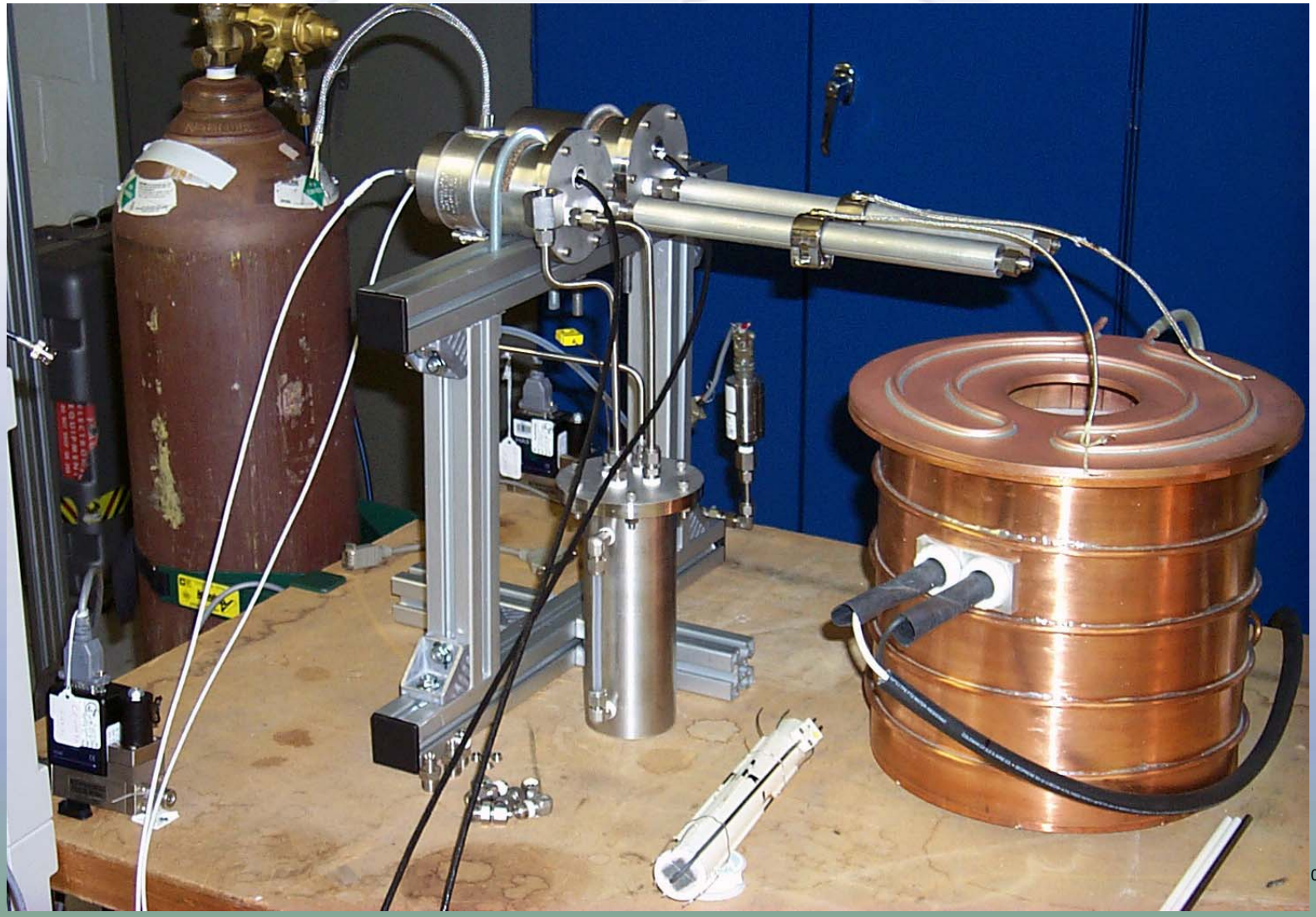
- Anode: Nickel zirconia cermet (cathode in electrolysis mode)
- Cathode: Strontium-doped lanthanum manganite (anode)
- Electrolyte: YSZ, 175 µm thickness
- Active cell area: ~ 3.2 cm^2
- Includes an electrically isolated electrode patch for monitoring of reference open-cell voltage



INEEL High-Temperature Steam Electrolysis and Hydrogen Permeation Experiment



Experimental Hardware in Assembly at INEEL



5. Significant interactions with industry

Industrial Collaborator

Ceramatec, Inc.

Salt Lake City, UT

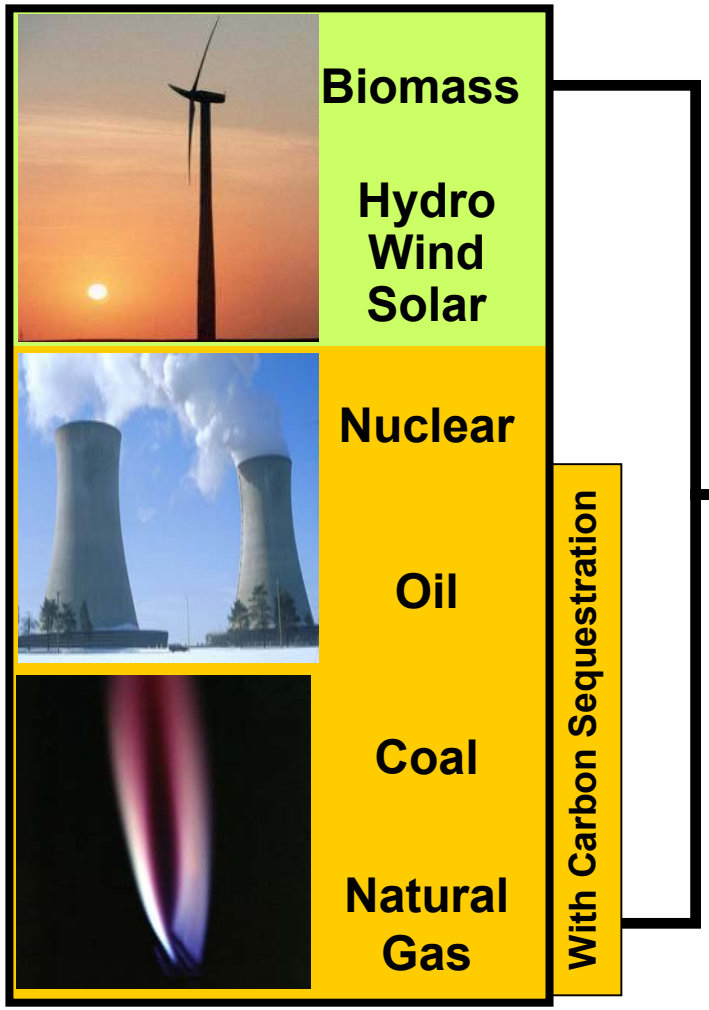
- 25+ years of contract R&D experience developing electrochemical ceramics

Responsibilities:

- Fabricate single-cell SOECs and planar cell stacks for testing at INEEL
- Collaborate in testing SOECs for High Temperature Electrolysis (HTE)
- Develop improved SOECs for the HTE application

Conclusions

- High-temperature steam electrolysis using a high temperature heat source is a viable near-term strategy for large-scale hydrogen production
- Solid-oxide cells represent a logical choice for high-temperature steam electrolysis due to their high operating temperature and high efficiency
- INEEL is initiating a research program to study materials and thermoelectric efficiency issues related to the HTE process using solid oxide electrolytes



Photolytic Hydrogen Production

H_2

Roxanne Danz

Barriers

PHOTOELECTROCHEMICAL BARRIERS

- Material durability
- Materials and system engineering
- Efficiency

PHOTOBIOLOGICAL BARRIERS

- Light utilization efficiency
- Rate of hydrogen production
- Continuity of photoproduction
- Systems engineering

Targets and Status

Photolytic Hydrogen Production

Characteristics	Units	2003 status	2005	2010
Photoelectrochemical Hydrogen Production				
Solar-to-H_2 Efficiency	%	7	7.5	9
Durability	Hours	100	1,000	10,000
Cost	\$/kg H_2	N/A	360	22
Photobiological Hydrogen Production				
Util. Eff. of Abs. Light	%	~5	10	20
Absorbed Light Energy to H_2 Efficiency	%	0.1	0.5	5
Duration of Continuous Photoproduction	Hours	240	500	1500
Cost	\$/kg H_2	200	100	30

Projects

Photolytic Hydrogen Production

• Combinatorial Chemically Derived Materials	UC Santa Barbara
• Combinatorial Discovery of Photocatalysts for Hydrogen Production	Southwest Research Institute
• Algal Hydrogen Production	**NREL**

Posters

Photolytic Hydrogen Production

• Photoelectrochemical Hydrogen Production	University of Hawaii
• Photoelectrochemical Systems for Hydrogen Production	NREL
• Maximizing Photosynthetic Efficiencies in H_2 Production in Microalgal Cultures	UC Berkeley
• Algal H_2 Production System	ORNL

Discussion Points

- These technologies are in the early stages of development
- A key to reaching a commercialization decision is for the PIs of the various projects to work together in developing each photolytic technology
- We initiated two working groups (photobiological and photoelectrochemical) made up of the current PIs and other support as necessary

Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

Eric W. McFarland (PI), University of California, Santa Barbara
DOE Hydrogen Program DE-FC36-01GO11092

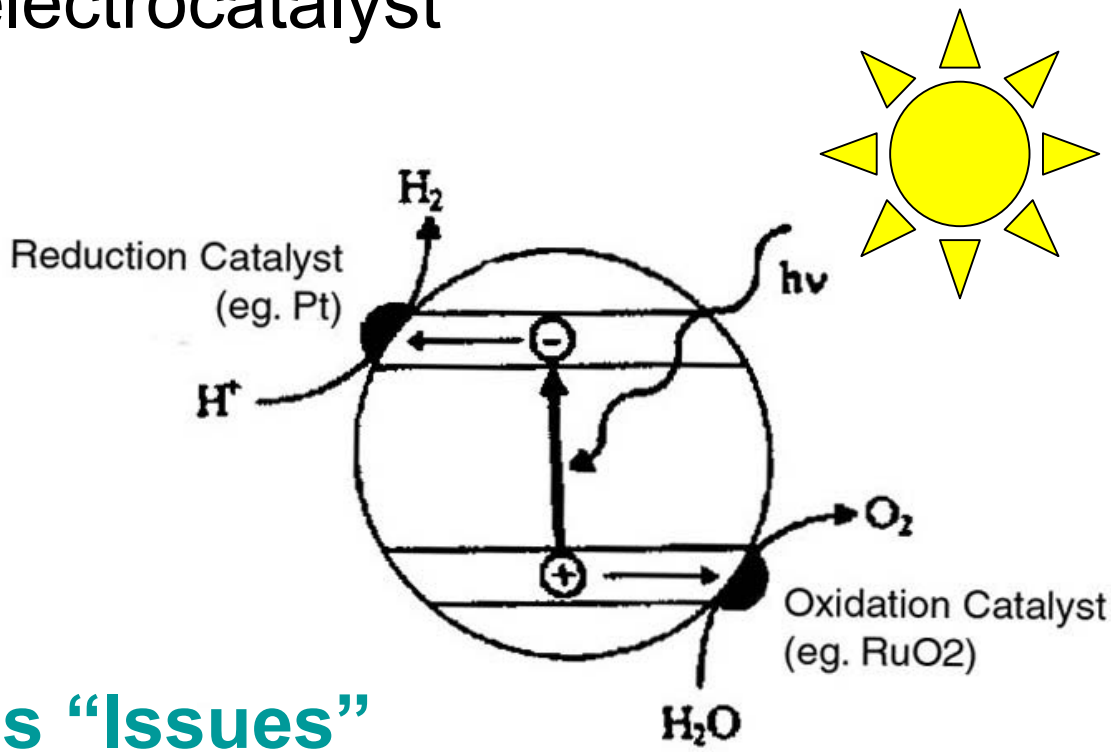
Primary Objective:

Discovery of efficient, practical, and economically sensible new materials for photoelectrochemical production of hydrogen from water and sunlight.

Methodology:

Apply combinatorial methods to complement the traditional research paradigm of serial “deductive” chemical research with a deliberate, high-speed, “inductive” exploration of the composition-structure-property relationships of new metal-oxide based solid-state materials.

Photoelectrocatalyst

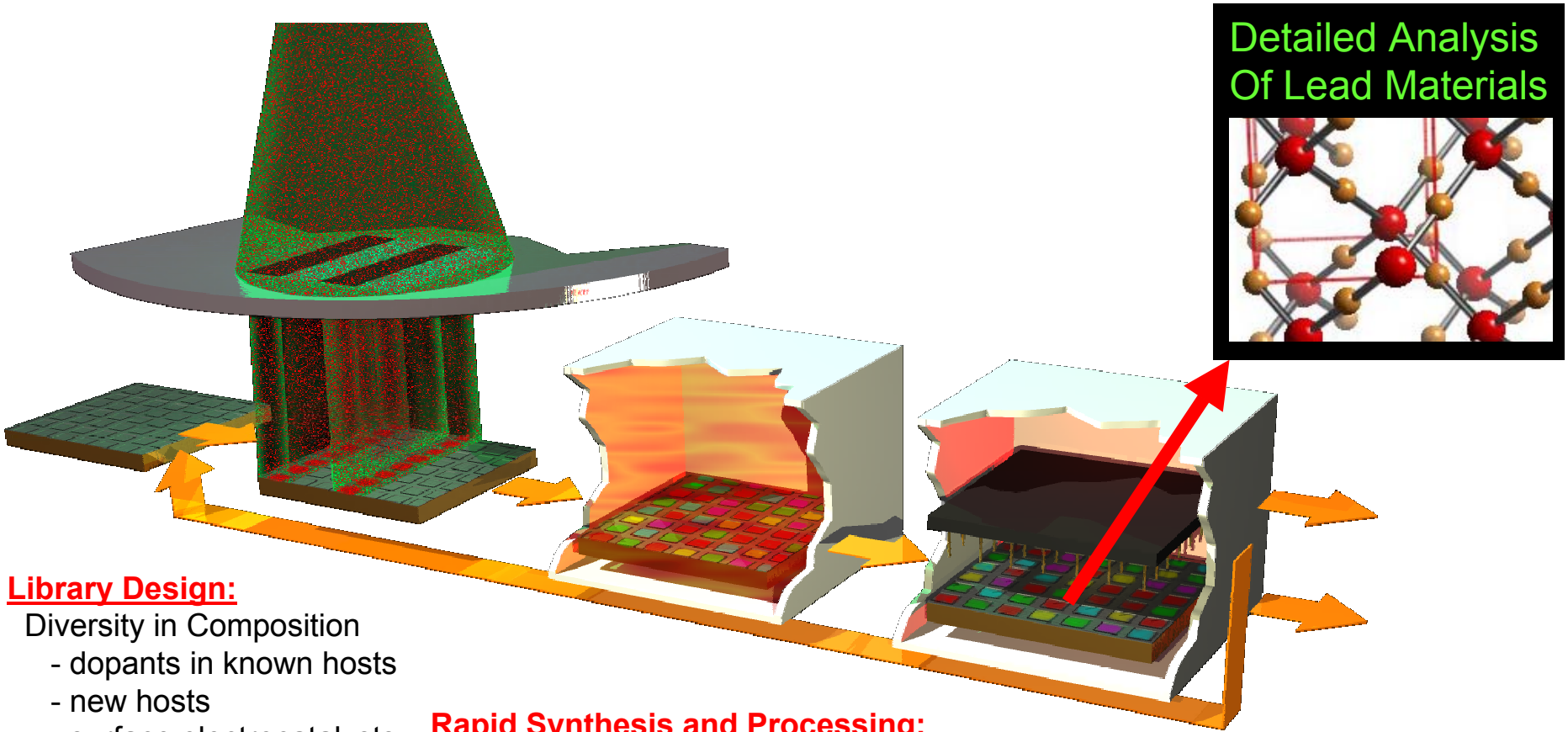


Materials "Issues"

- Absorbance
- Transport e-/h+
- Surface Electrocatalysis
- Band Structure Energetics
- **Stability and Cost**

Bulk Particulates ~ **Structural Photoelectrodes**

Combinatorial Approach: Paradigm Shift



Library Design:

Diversity in Composition
- dopants in known hosts
- new hosts
- surface electrocatalysts

Diversity in Synthesis
- structure variability
- surfactant templates

Rapid Synthesis and Processing:

Electrochemical Deposition
Electroless Deposition
Parallel Reactor Blocks
Rapid Serial Scanning Cells
Pyrolysis

High-Throughput Screening:

Photoelectrochemical
Chemo-Optical

Relevance:

- **The materials will be active electrocatalysts stable in electrolytes.**
  - *Dual use applications in electrolysers and fuel cells.*

- **They will have efficient solar spectrum absorbance and efficient electron/hole conduction properties.**
  - *Dual use in photovoltaic applications.*

- **May be economically incorporated in reactor designs using photoelectrodes or bulk slurry particulates.**
  - *Dual use in environmental photocatalysis*.

- **New metal oxide materials developed in this program will be inexpensive in bulk quantities.**

  ⇒ ***Primary Use In Cost Competitive Large Scale Hydrogen Production***

Materials Developed As Part of This Research Have Broad Applications In the US Energy Program

Project Timeline (Start Date September 2001)

Sept. 01 | Sept. 02 | Sept. 03 | Sept. 04

System(s):

- Automated Electrodeposition (Task Y1-1)
- Automated Pyrolysis
- Electro-Optical Screening (Task Y1-5)
- Electrochemical Screening (Task Y1-3)
- Optical Band Gap Screening (Y2-4)

Synthesis :

- Generalized Synthesis Chemistry (Task Y1-2)
- Validation Libraries - ZnO (Task Y1-4) | ZnO (Y2-2) | ZnO (Y3)
- AxByCzO Libraries (TaskY1- 6) | AxByCzO Libraries (Y2- 1) | AxByCzO Libraries (Y3)
- Heterostructure Libraries (Task Y2- 6)
- Mesoporous Libraries (TaskY1- 7) | Mesoporous Libraries (Y2- 7) | Mesoporous Libraries (Y3)
- Electrocatalysis Libraries (Y2-3) | Electrocatalysis Libraries (Y3)
- Electroless WOMxO

Screening and Detailed Quantitative Analysis:

- Validation Libraries (Task Y1-4, 9) | ZnO (Y2-2) | ZnO (Y3)
- AxByCzO Libraries (Task Y1-6,9) | AxByCzO Libraries (Y2- 1) | AxByCzO Libraries (Y3)
- Mesoporous Libraries (Y2- 7) | Mesoporous Libraries (Y3)
- Electrocatalysis Libraries (Y2-3) | Electrocatalysis Libraries (Y3)

Data Management:

- Database Structure (Task Y1-8)
- Software and Data Implementation

Outreach and Tech Transfer:

- Adrena Inc/SBA Materials
- IEA Annex 14
- Research Publications - 10 published papers
- 2 Patent Applications (mesoporous MOx, Pt/WO3 Fuel Cell Cat)

Significant Results To Date

- Design and fabrication of combinatorial chemistry ***systems for synthesis and screening of hydrogen producing photocatalysts.***

- Demonstrated that ***compositional and preparative modifications of known metal oxide hosts may improve their photoelectrocatalytic properties***. (WO_3 with ZB visible band photolysis, ZnO:X with improved visible band absorbance and improved stability)

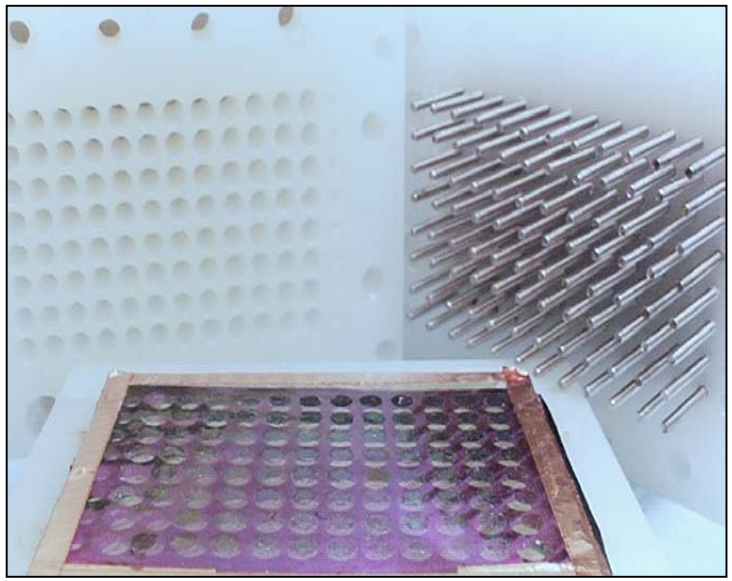
- First ***electrochemical synthesis of ordered nanoporous metal oxides*** *(Patent Assigned to SBA Materials)*

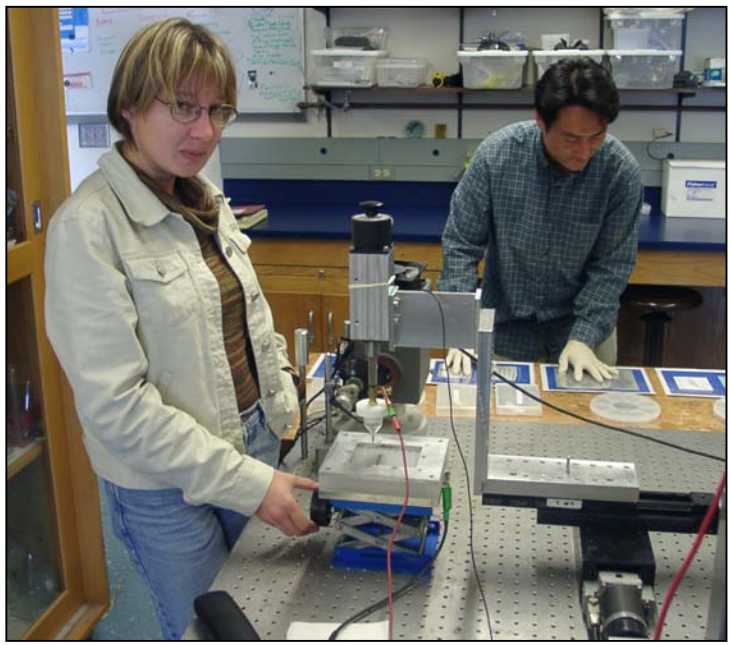
- First ***electroless synthesis of functional metal oxide*** materials and nanoporous frameworks.

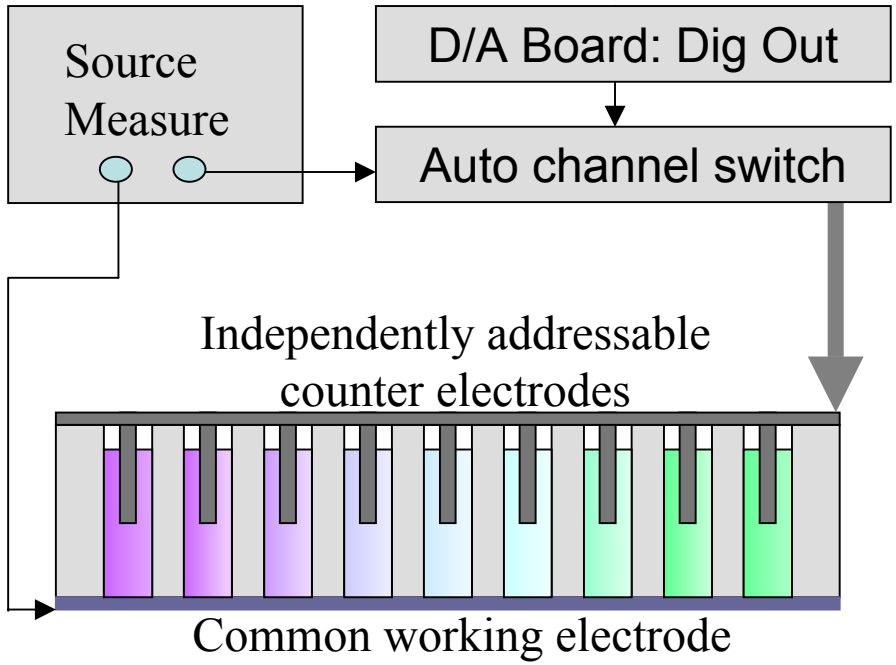
- Discovery of ***nanoparticulate Pt/WO_3 which is photoactive and resistant to CO poisoning*** and controlled electrosynthesis of high activity ***Au nanoclusters.***

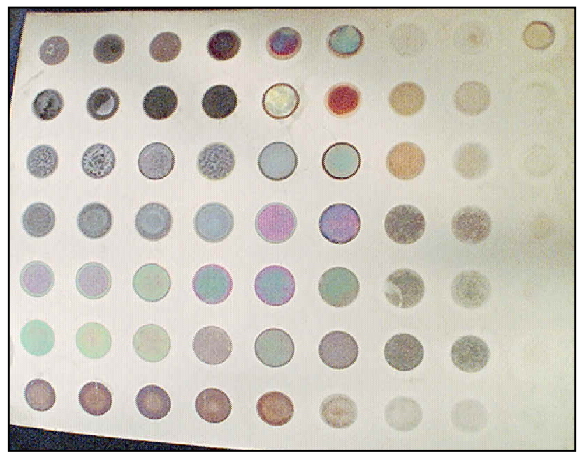
- Identification of ***H intercalation as critical component of poisoning resistance*** of metal oxide electrocatalysts.

Parallel Synthesis

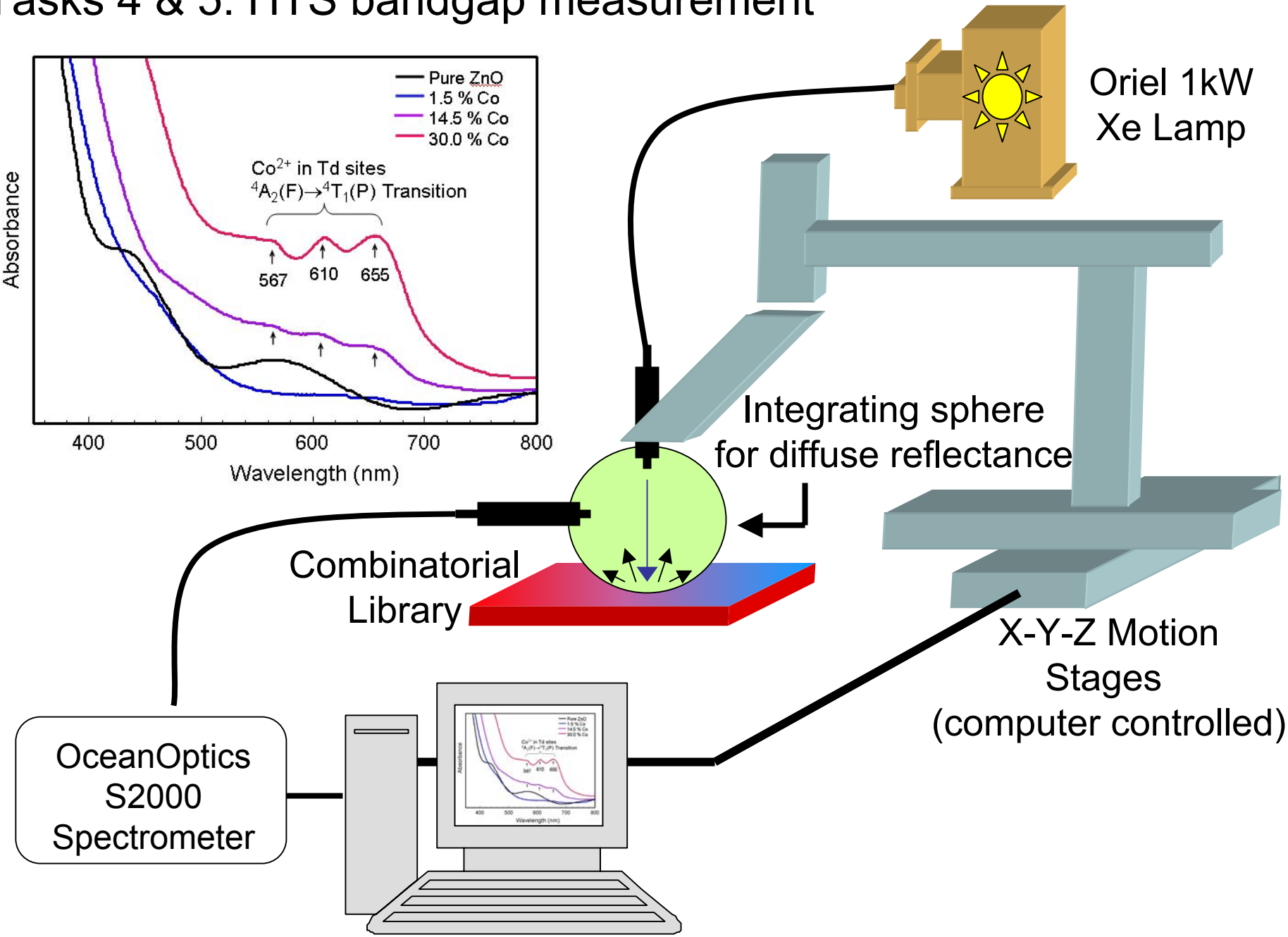








Tasks 4 & 5: HTS bandgap measurement



Generalized Synthesis Chemistries

Metal deposition/Oxidation

$M^+ \rightarrow M \rightarrow MO$

1. Metal Electrodeposition

$M^{n+} + n\,e^- \rightarrow M^o$ (Cathodic)

2. Anodization/Anneal

$M^o + H_2O \rightarrow MO + 2\,H^+ + 2\,e^-$

$M^o + O_2 \rightarrow MO$

Metal Oxide Deposition

Aqueous: $M^+ \rightarrow MOH \rightarrow MO$

1. MO Deposition

electrode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2(OH^-)_{sur}$

$[M^{n+}(\text{ligand})] + n(OH^-)_{sur} \rightarrow M(OH)_n$

ligands (acidic) = peroxide

(basic) = lactate, citrate, ethylene glycol, acetate

2. Dehydration/Anneal

$M(OH)_n \rightarrow MO_{n/2} + {}^{n}/_{2}\,H_2O$

Non-Aqueous: $M^+ + O_2 \rightarrow MO$

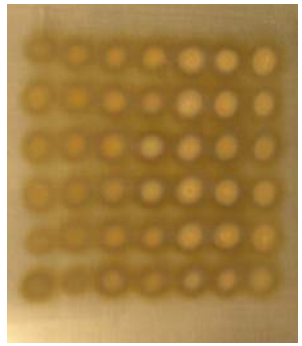
1. Direct MO Deposition

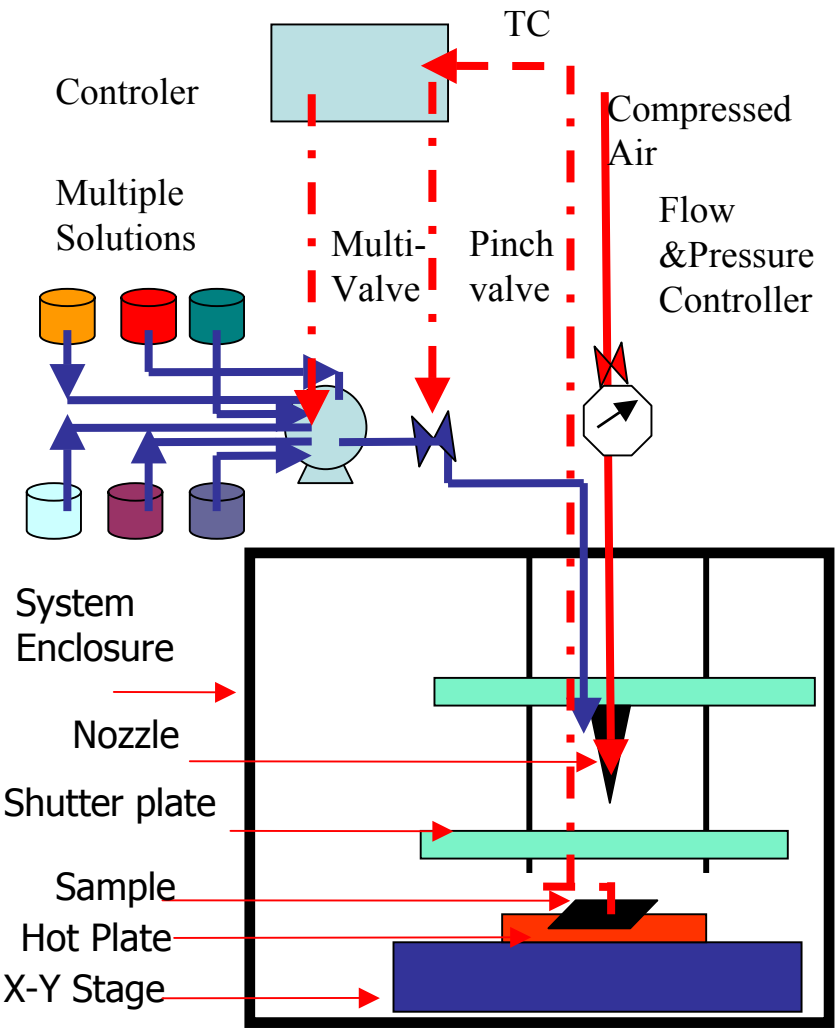
$xM^{n+} + {}^{y}/_{2}O_2 + ne- \rightarrow M_xO_y$

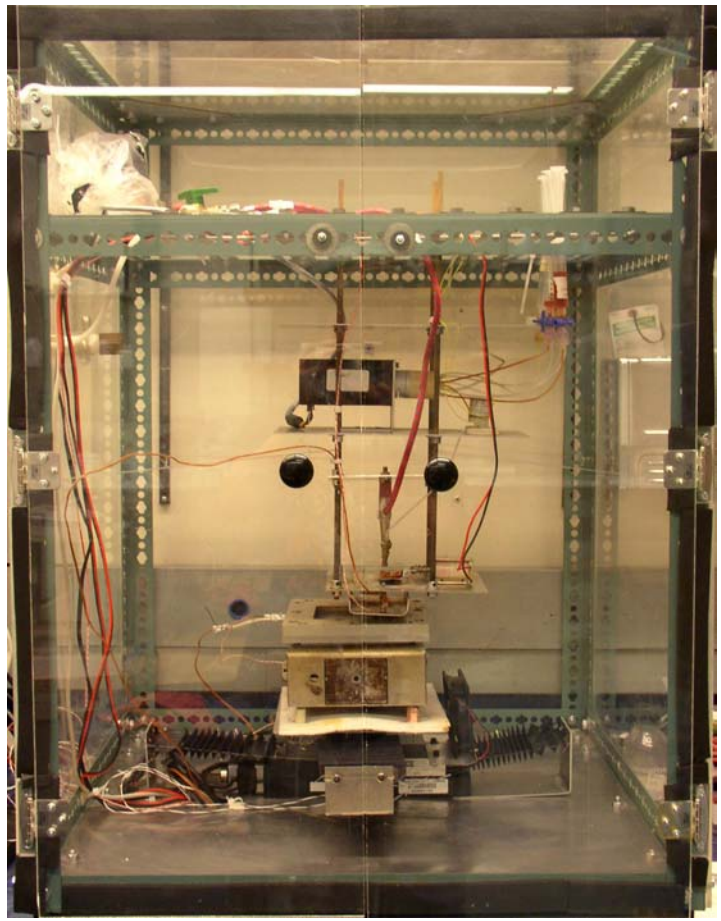
In DMSO etc

Automated Spray Pyrolysis System

Fe_2O_3 Library

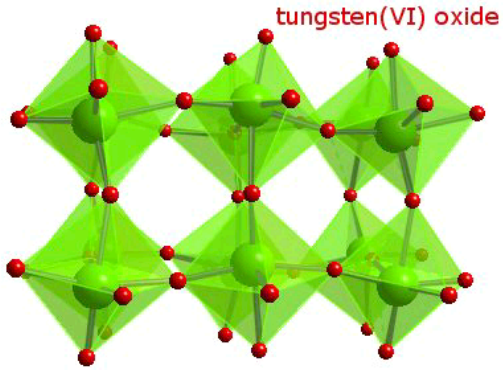


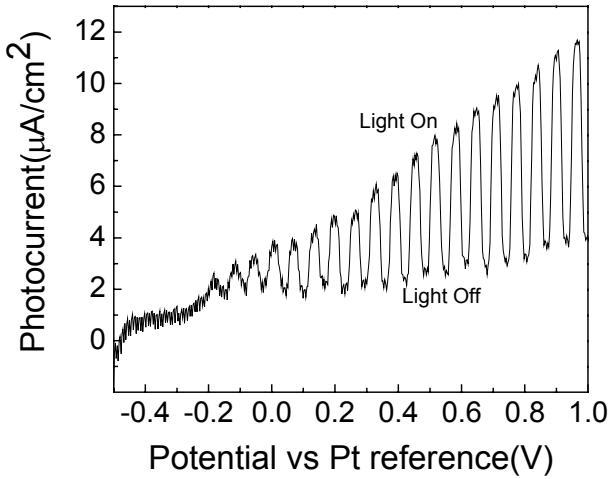


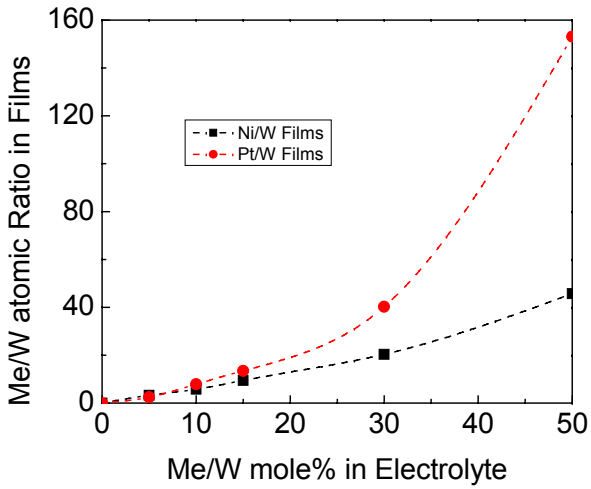


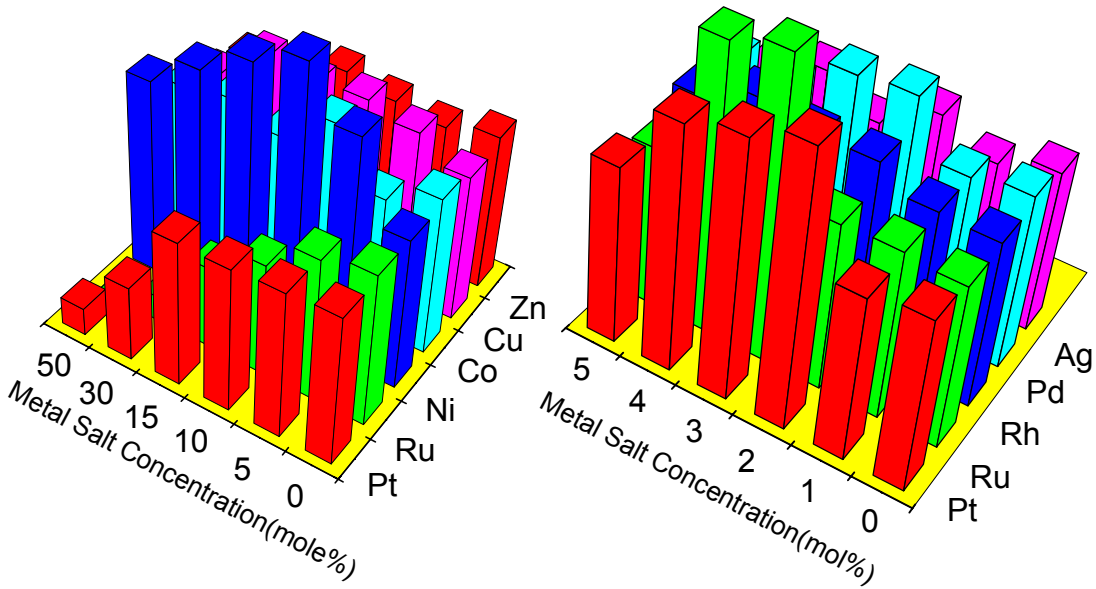
1 meter

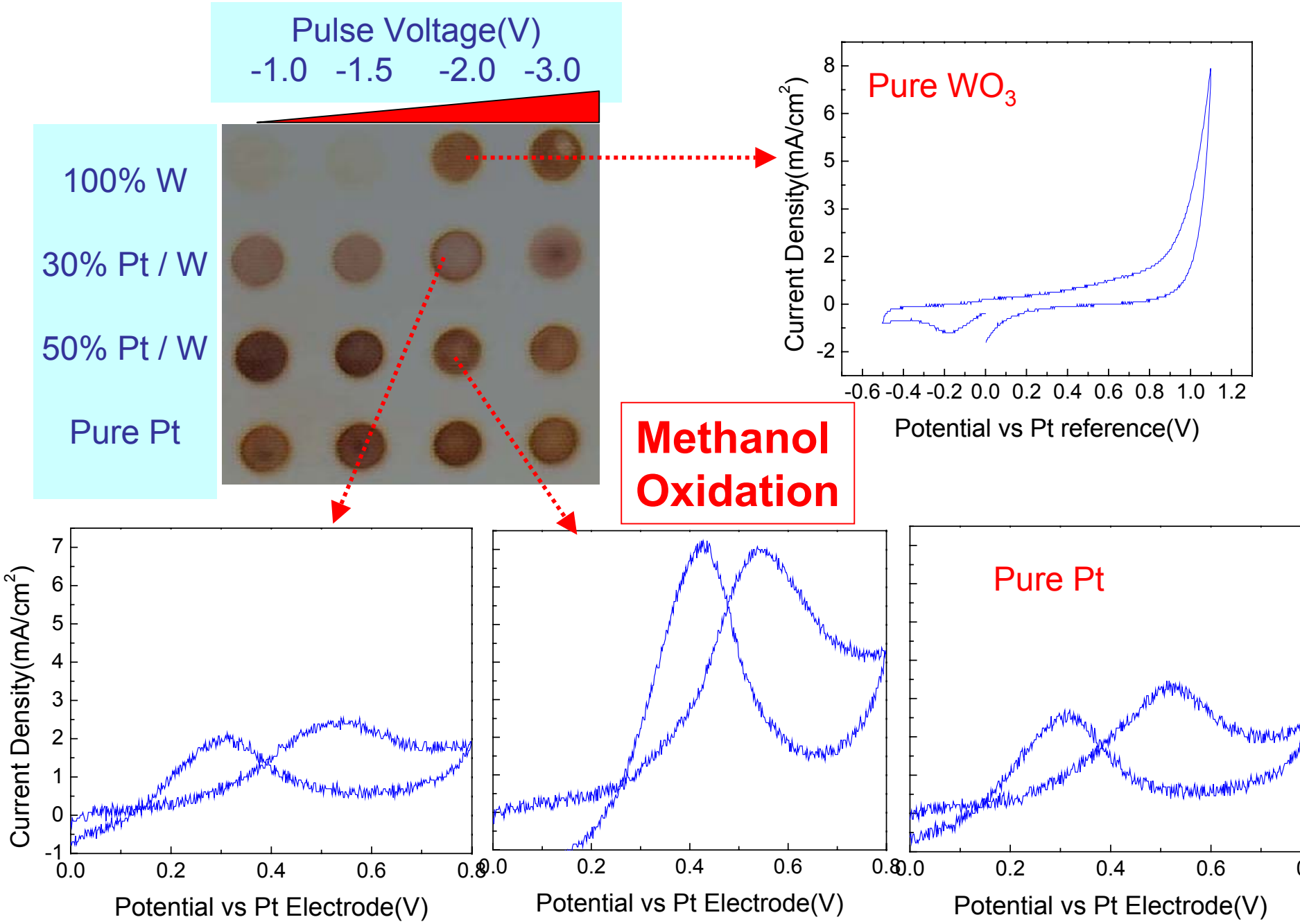
Task 1: Continue WO_3:X - stable, cost effective host



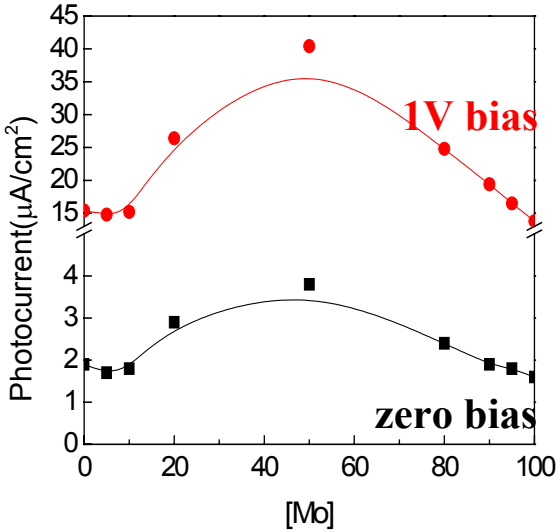




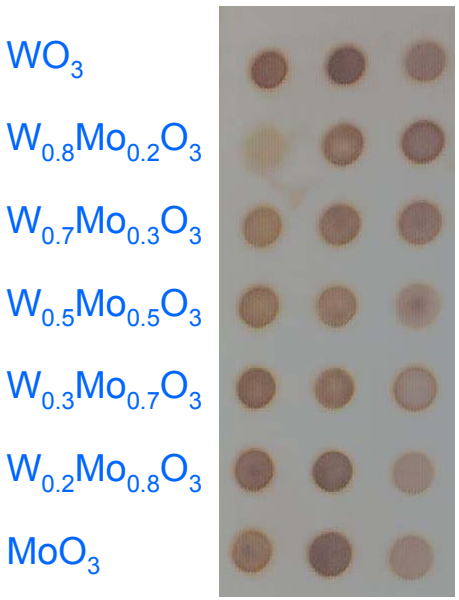



Pulse Voltage(V)
-1.0 -1.5 -2.0 -3.0
100% W
30% Pt / W
50% Pt / W
Pure Pt
Pure WO3
Current Density(mA/cm2)
Potential vs Pt reference(V)
Methanol Oxidation
Current Density(mA/cm2)
Potential vs Pt Electrode(V)
Potential vs Pt Electrode(V)
Pure Pt
Potential vs Pt Electrode(V)

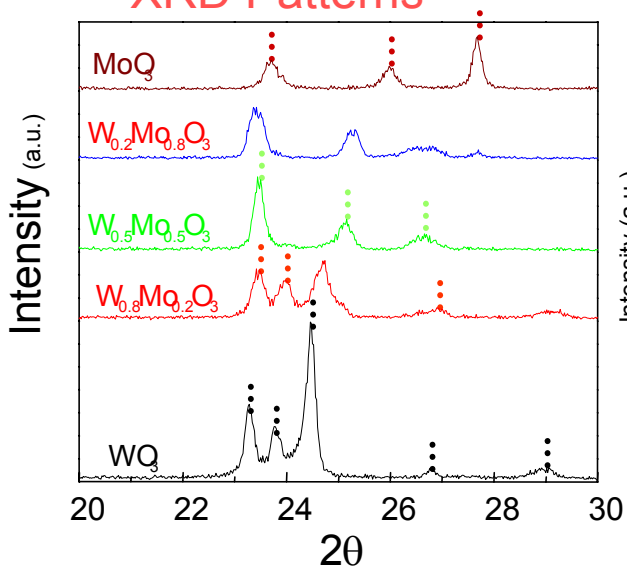
Tungsten-Molybdenum Mixed Oxides



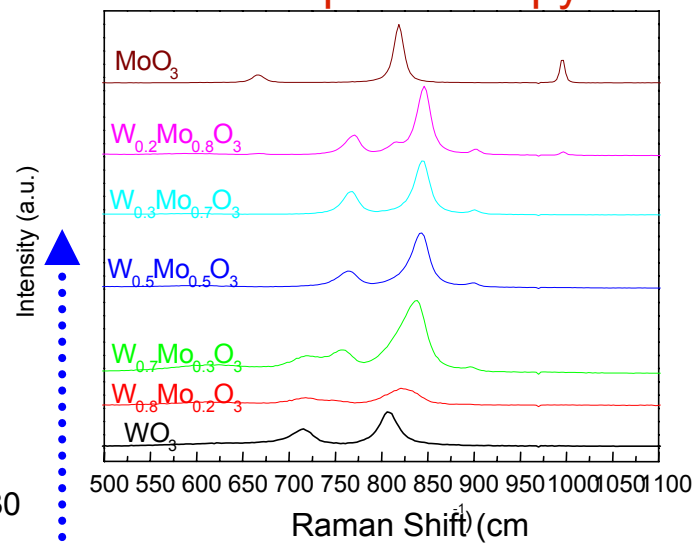
- ✓ No prior reports of zerobias hydrogen evolution from WO_3 => Defect(doping) by electrodeposition shift flatband
- ✓ New, stable, substitutional phases discovered by electrodeposition and characterized
  - ❖ Superior photocatalytic oxidation properties
  - ❖ Significantly increased cation intercalation capacity.



XRD Patterns

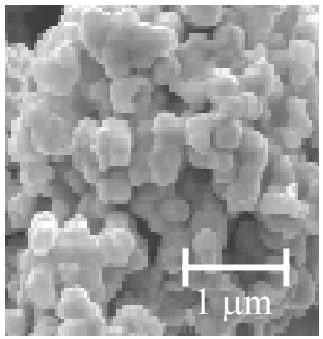


Raman Spectroscopy

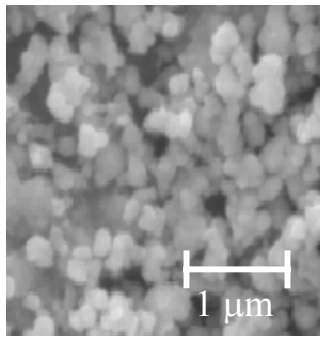


Increasing Mo Concentration

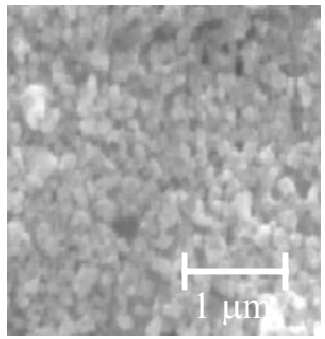
Electrodeposition of nanocrystalline WO_3 by pulsed deposition



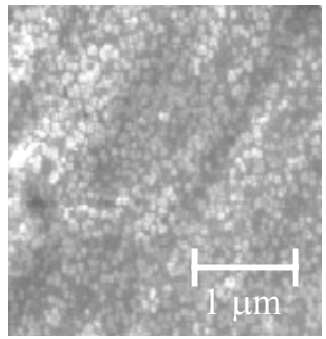
T_{pulse} =500msec



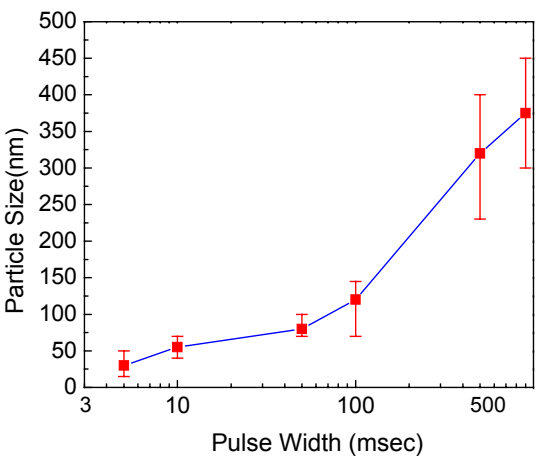
T_{pulse} =100msec

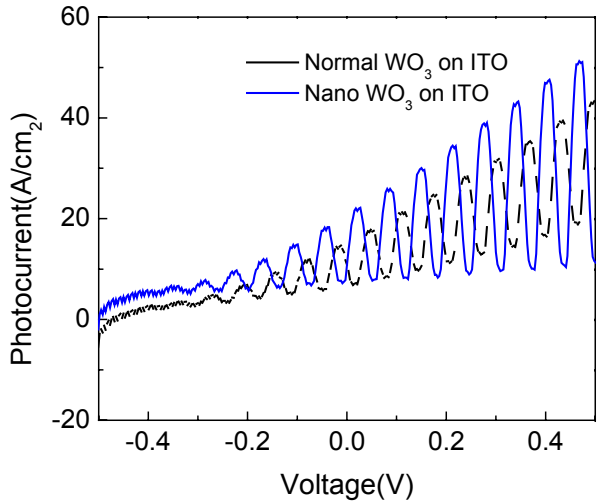


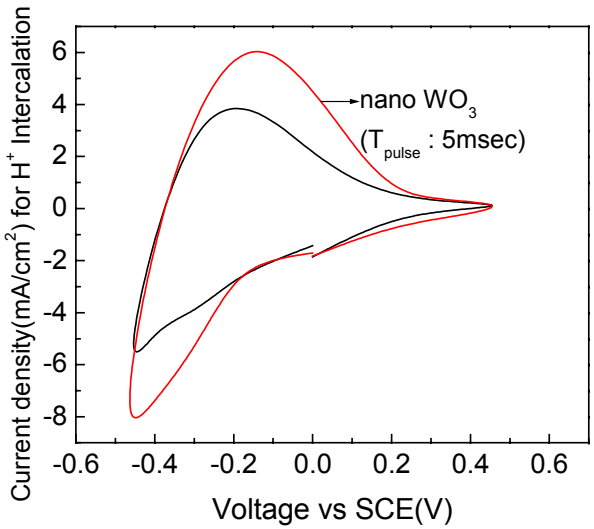
T_{pulse} =50msec



T_{pulse} =5msec





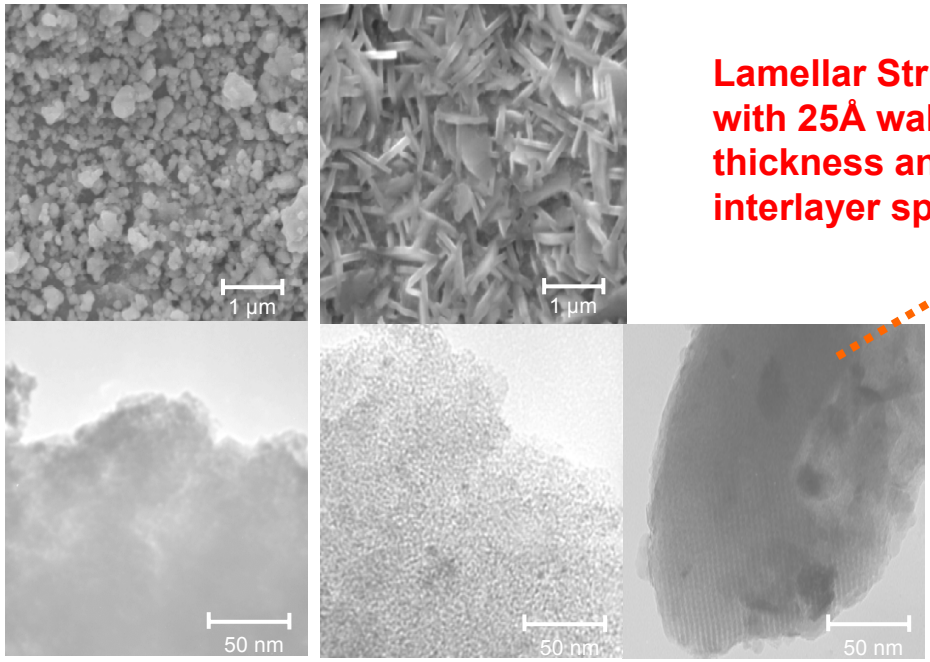


- S.H.Baeck, T. Jaramillo, G.D.Stucky, and E.W.McFarland,"Controlled Electrodeposition of Nanoparticulate Tungsten Oxide", **Nano Letters**, 2(8), 831(2002).

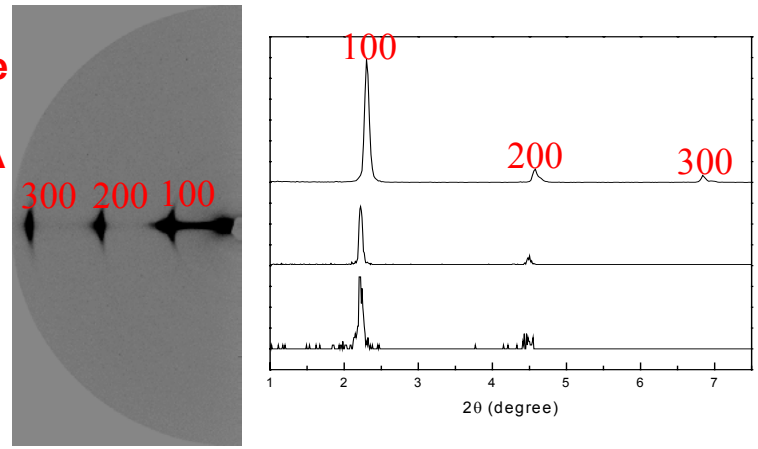
Electrodeposition of Mesoporous WO_3 Task: 7

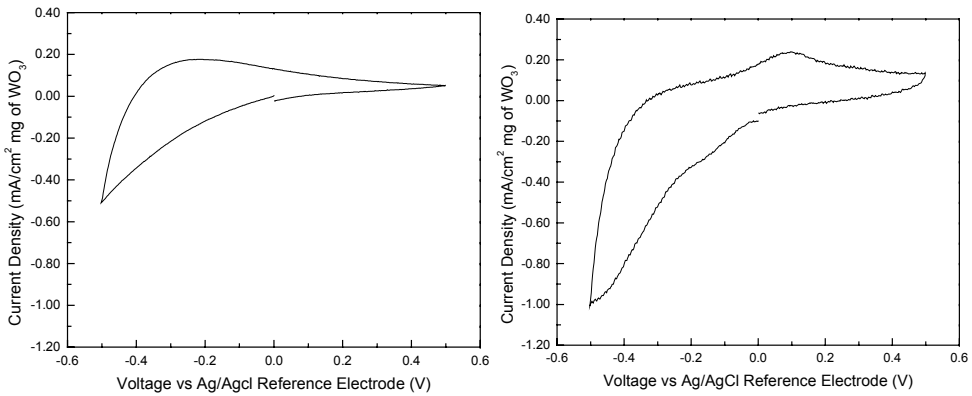
Nonporous Mesoporous

Accepted and in Pres *Adv. Materials* 2003

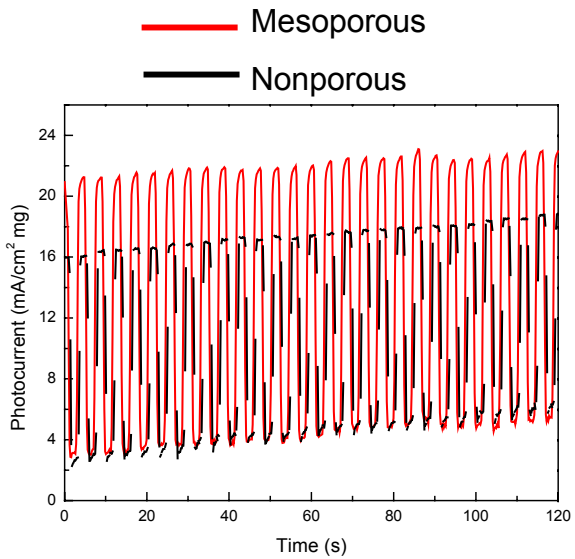


Lamellar Structure with 25Å wall thickness and 15Å interlayer spacing





Hydrogen Intercalation



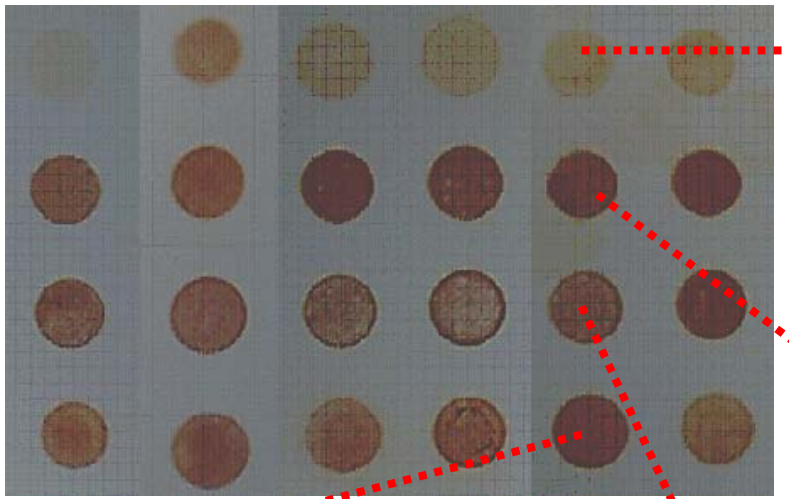
Zerobias Photocurrent

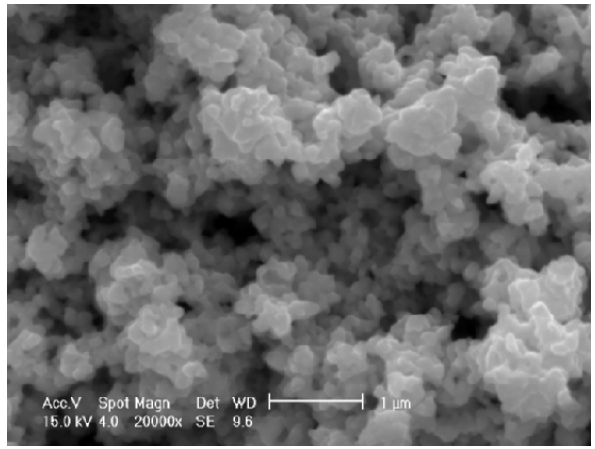
Mesoporous WO_3 Library with SDS

SDS Concentration (wt%)

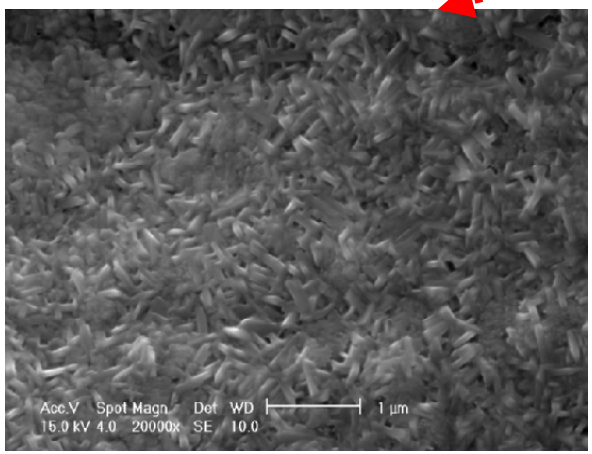
Deposition V 0 1 2 3 4 5

- 0.5
- 0.8
- 1.0
- 1.5

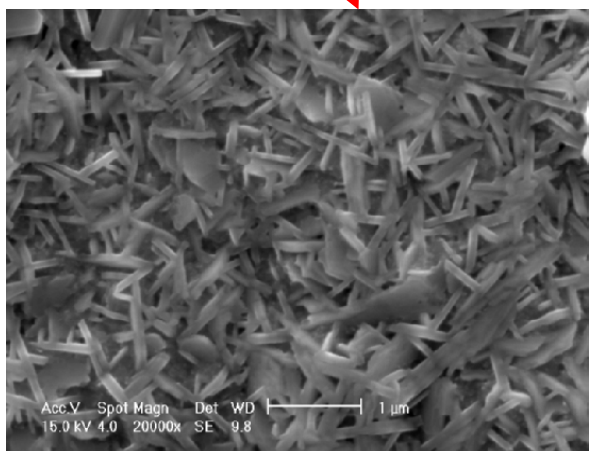




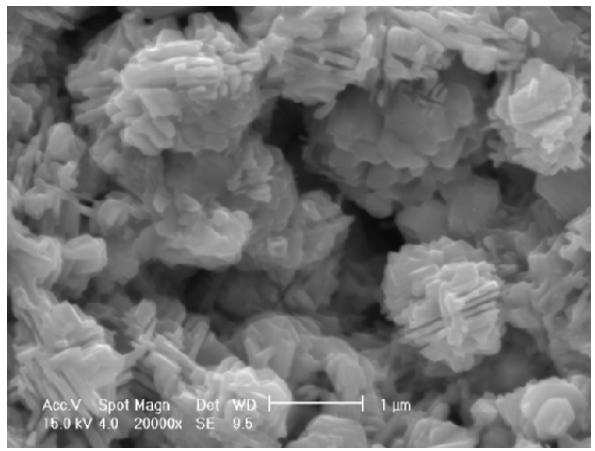
-0.5 V



-1.5 V

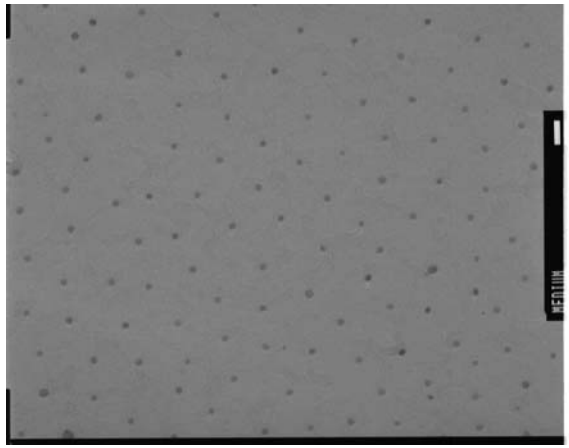


-1.0 V



-0.8 V

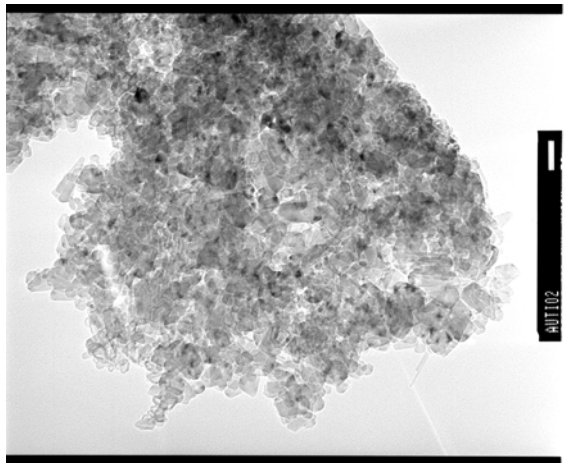
Block copolymer micelle encapsulation / Dip Coating



50nm

Thomas F. Jaramillo, S. H. Baeck, B. Roldan Cuenya, E.W.McFarland, *JACS* (2003) In Press

Electrodeposition of Nanoparticles



50nm

S. H. Baeck, Thomas F. Jaramillo, E.W.McFarland, *Proc. ACS* (2003)

Advantage

- Uniform Dispersion
- Narrow Particle size distribution
- Particle size & Density can be controlled by template

- Electrically active by design
- No requirement of post treatment
- Particle size & Density can be controlled by deposition condition

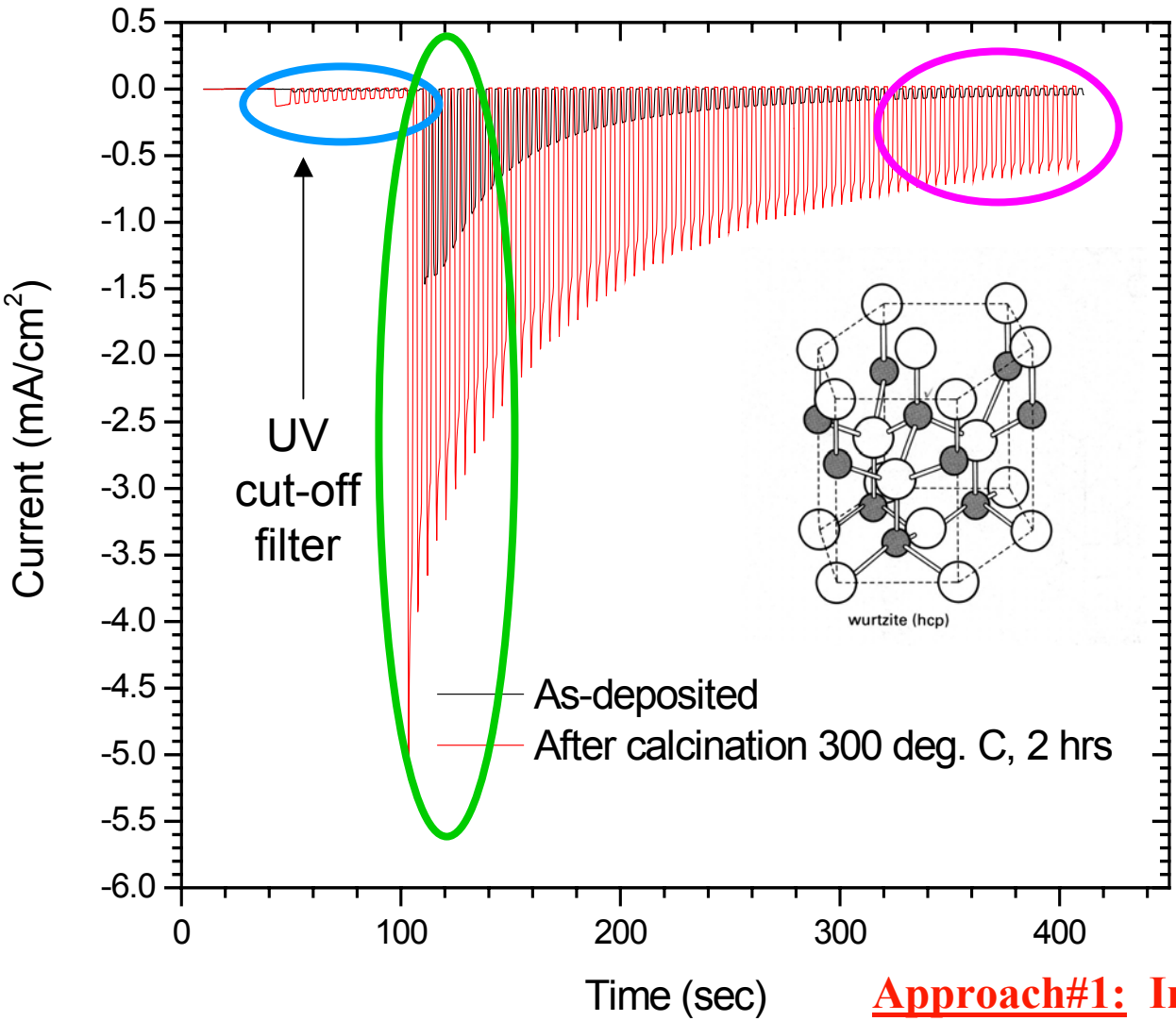
Disadvantage

- Post treatment (Removal of Polymer)
- Doping density limitation (monolayer)

- Broad particle size distribution
- Non-uniform Dispersion

Task 2: Zinc Oxide Photocatalyst Host

Inexpensive in bulk
High conductivity
High Dopant Solubility



Promising
Photocatalytically active (in the UV)

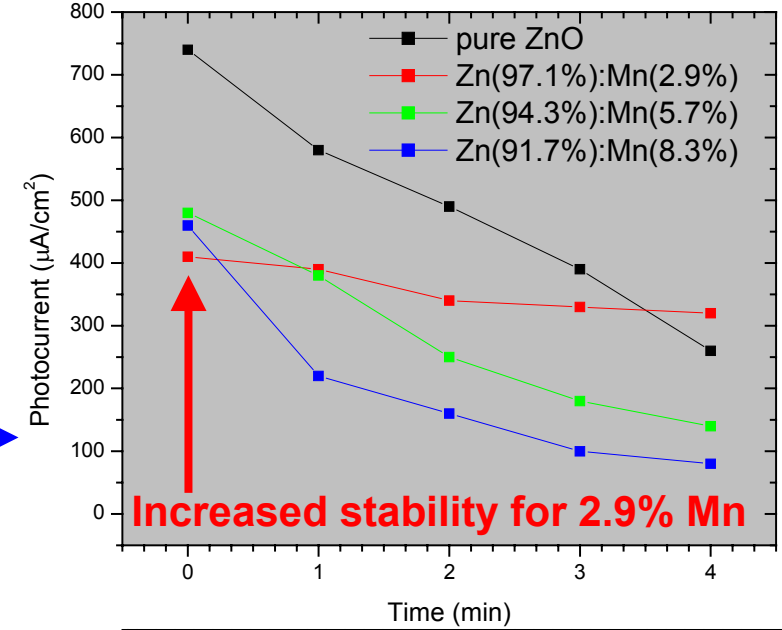
Unfortunate
3 eV Bandgap, minimal visible light photocurrent

Unacceptable
Photocurrent decay from photoanodic corrosion

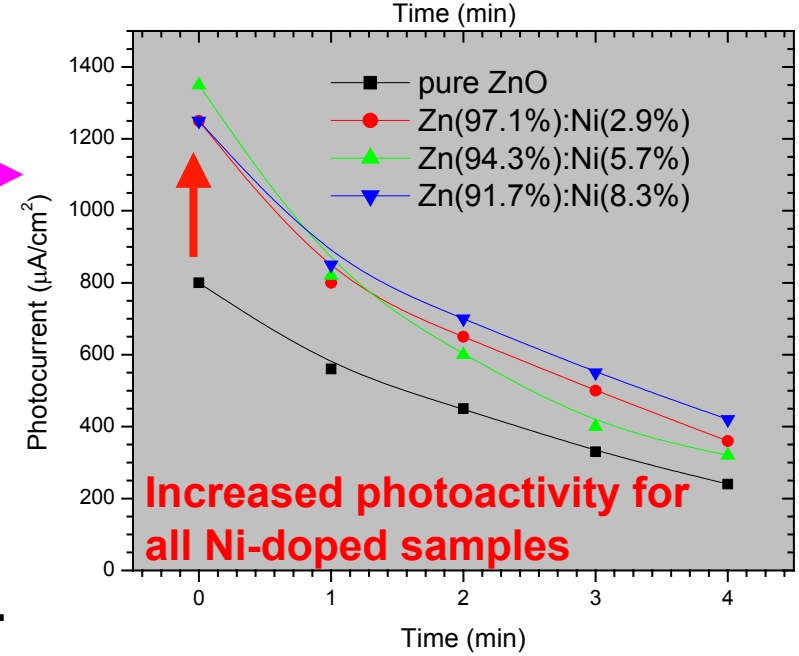
Approach#1: Introduce dopants to improve visible absorption

Other Transition metal doped ZnO library: Fe, Cr, Mn, Ni

		A	B	C	D
$Fe(NO_3)_2$	1	○ 0%	○ 0.6%	○ 1.0%	○ 1.5%
$CrCl_3$	2	○ 0%	○ 2.9%	○ 5.7%	○ 8.3%
$MnCl_2$	3	○ 0%	○ 2.9%	○ 5.7%	○ 8.3%
$NiCl_2$	4	○ 0%	○ 2.9%	○ 5.7%	○ 8.3%



All depositions:
200mM $Zn(NO_3)_2$ in DMSO (no saturated O_2)
except Fe row (100mM $ZnCl_2$)
-1.16V vs. Ag pseudo-reference (-1.0 vs. Ag/AgCl)
85 deg. C
15min deposition onto ITO-coated glass substrate



Mn improves ZnO stability.
Ni improves ZnO photoactivity in the UV
Fe may increase photoactivity in the visible
To date best is Co which improves both.

Communication and Cooperative Efforts: Task 8

Internal:

Strong collaborations with the laboratory of Professor Galen Stucky and UCSB Materials Research Laboratory (NSF)

External:

Frequent academic and industrial presentations.

Participant in the IEA Hydrogen Production Task Committee.

Cooperation with SBA Materials, Inc. and the Cycad Group, Inc. exploring issues related to process economics for commercialization of photoelectrocatalysis and photoelectroxidation. Licensing of Patents.

Publications Resulting from DOE Hydrogen Program Funding (Sept. 01-Present):

1) "High-Throughput Screening System for Catalytic Hydrogen-Producing Materials," *J. Combinatorial Chem.* 4 (1) 17-22 (2002).
2) "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-Molybdenum Mixed Oxides," *Korean J. Chem. Engin.* 19 (4) 593-596 (2002).
3) "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-based Mixed Metal Oxides," *J. Combi. Chem.* Vol 4(6) 563-568 (2002).
4) "Controlled Electrodeposition of Nanoparticulate Tungsten Oxide," *Nanoletters* 2 (8) 831-834 (2002).
5) "Influence of Composition and Morphology on Photo and Electrocatalytic Activity of Electrodeposited Pt/WO3," *Am.Chem.Soc., Abs.Pap. 224: 062-FUEL Part 1* (2002)
6) "Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials," (2002) *Proceedings of the 2002, DOE Hydrogen Program Review* NREL/CP-610-32405
7) "A Cu2O/TiO2 Heterojunction Thin Film Cathode for Photoelectrocatalysis," *Solar Energy Materials.* Vol. 77, 3,229-237 (2003).
8) "Electrochemical Synthesis of Nanostructured ZnO films Utilizing Self Assembly of Surfactant Molecules at Solid-Liquid Interfaces," *J. Am. Chem. Soc.* 124(42); 12402-12403 (2002)
9) "Electrocatalytic Properties of Thin Mesoporous Platinum Films Synthesized Utilizing Potential-Controlled Surfactant Assembly," *Advanced Materials.* (Accepted and in press 2003).
10) "Catalytic Activity of Supported Au Nanoparticles Deposited From Block Co-polymer Micelles", (Accepted and in Press 2003, *J. Am. Chem. Soc.*)
11) "Enhancement of Photocatalytic and Electrochromic Properties of Electrochemically Fabricated Mesoporous WO3 Thin Films", Submitted Adv. Materials 2003
12)"Synthesis of Tungsten Oxide on Copper Surfaces by Electroless Deposition" Submitted Chem. Mater. (2003).

Education:

Students - Tom Jaramillo, Anna Ivanovskaya, Alan Kleinman

Post-Doctoral Associates – Dr. Sung-Hyeon Baeck, Dr. Kyoung-Shin Choi

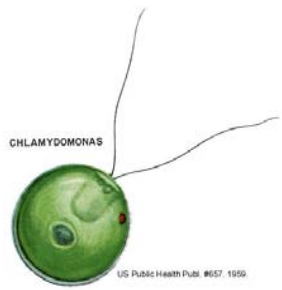
Visiting Scholars – Professor Withana Siripala

ALGAL HYDROGEN PHOTOPRODUCTION

Maria L. Ghirardi and Michael Seibert

National Renewable Energy Laboratory, Golden, CO

Program Review Meeting
Berkeley, CA
May 19-22, 2003



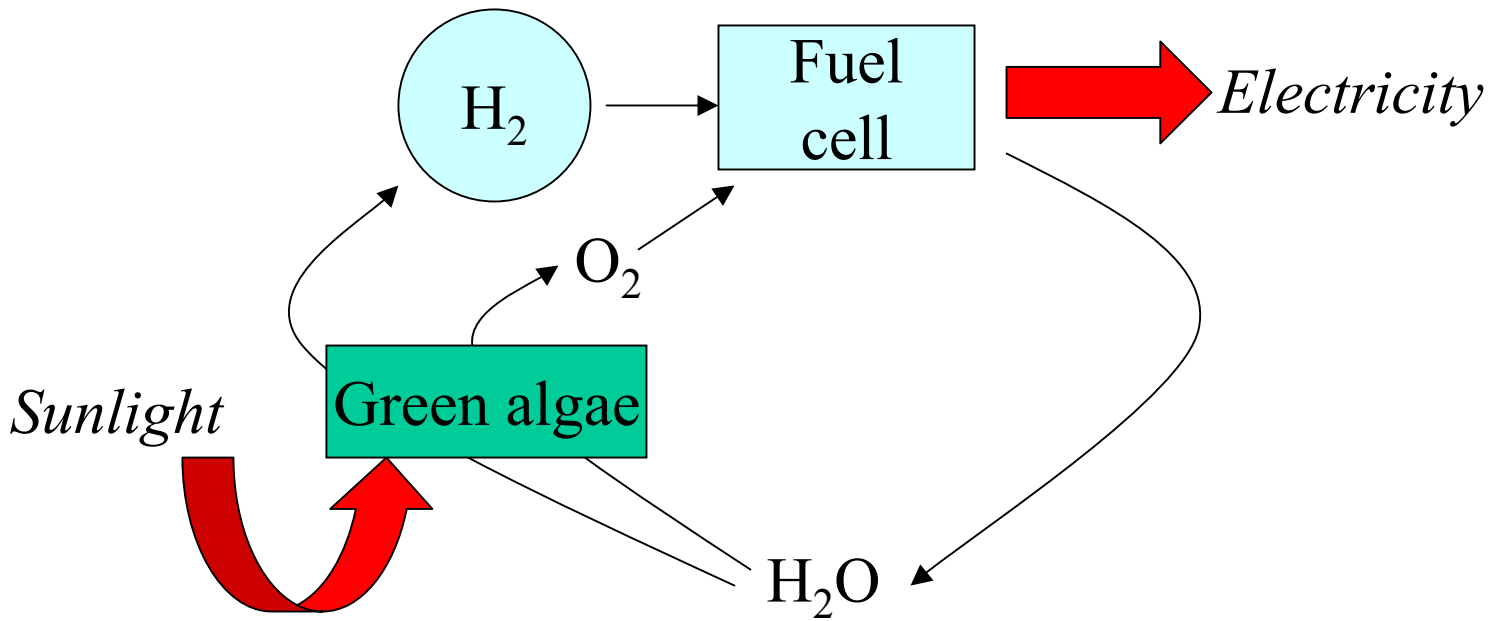
Relevance/Objectives

Develop Advanced, Renewable, Photolytic H_2-Generation Technologies Based on Algal Water-Splitting Processes

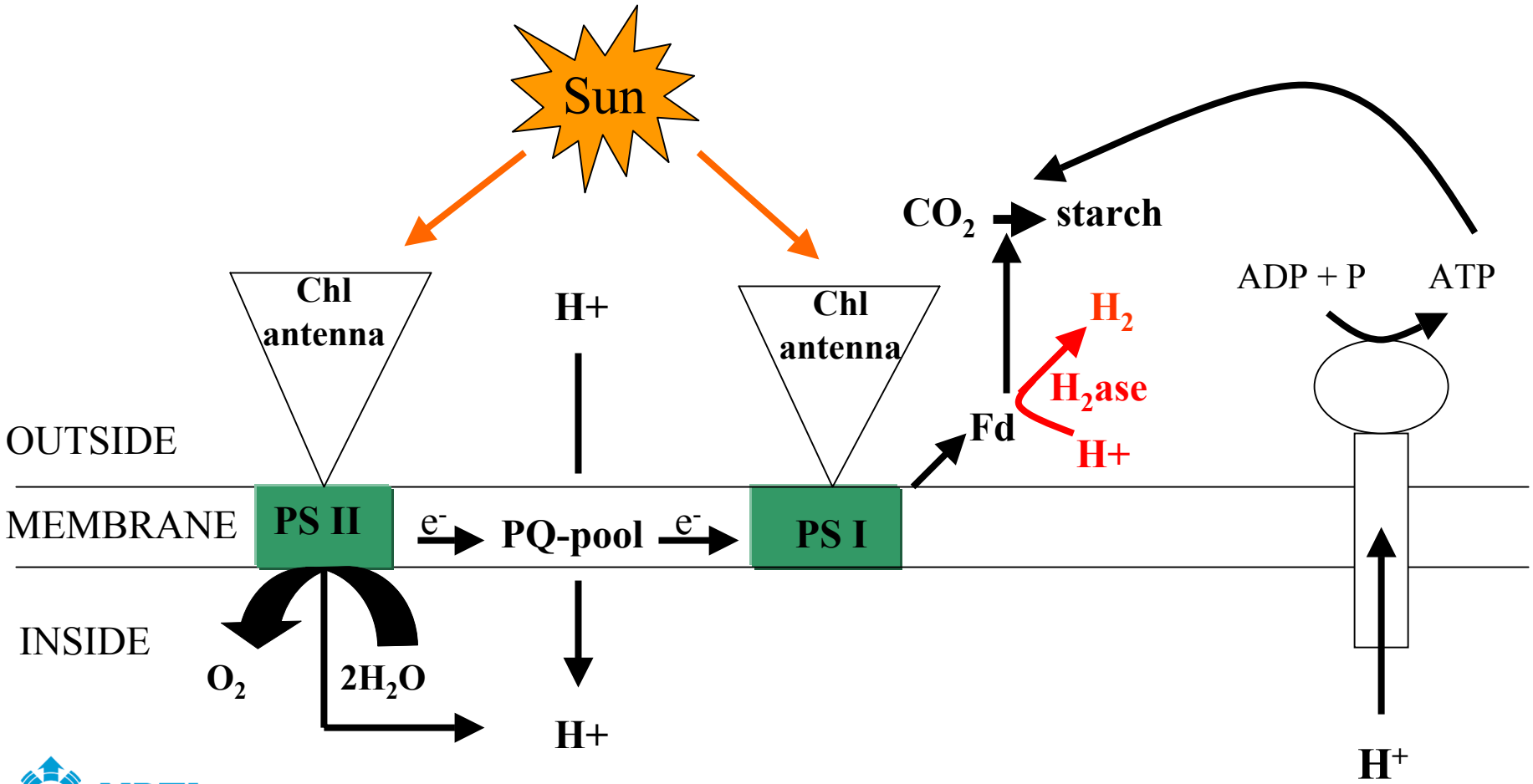
- Meet the technical challenges associated with the continuity of algal H_2-production under aerobic conditions (Technical Barrier M);

- Contribute to reaching the mid-term target of continuous H_2 photoproduction at a utilization efficiency of 20% and a cost of $30/kg by 2010 (Table 4.1.6).

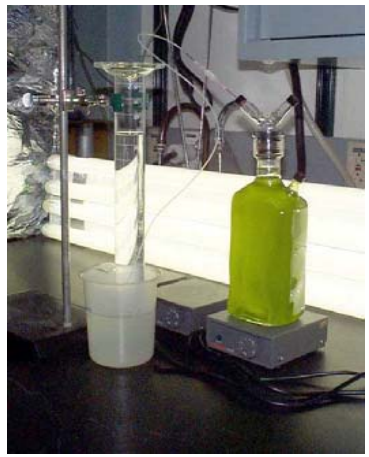
Renewable Hydrogen Production/Utilization



Biochemical Pathways (light reactions)

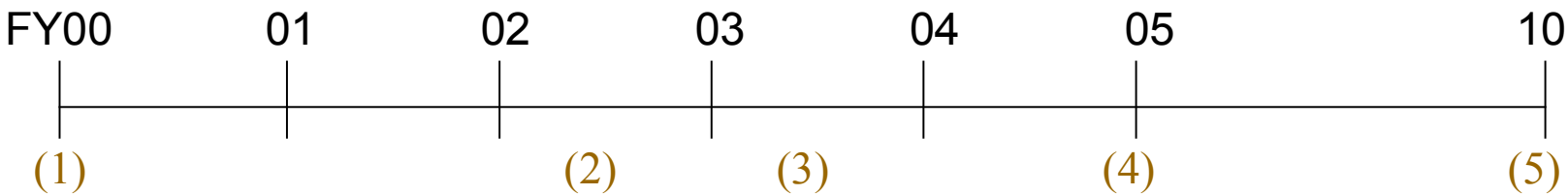


Approaches to Generate an O_2-Tolerant, Algal H_2-Producing System



1. Separate O_2 and H_2-production either temporally or physically;
2. Engineer a hydrogenase that functions in the presence of O_2.

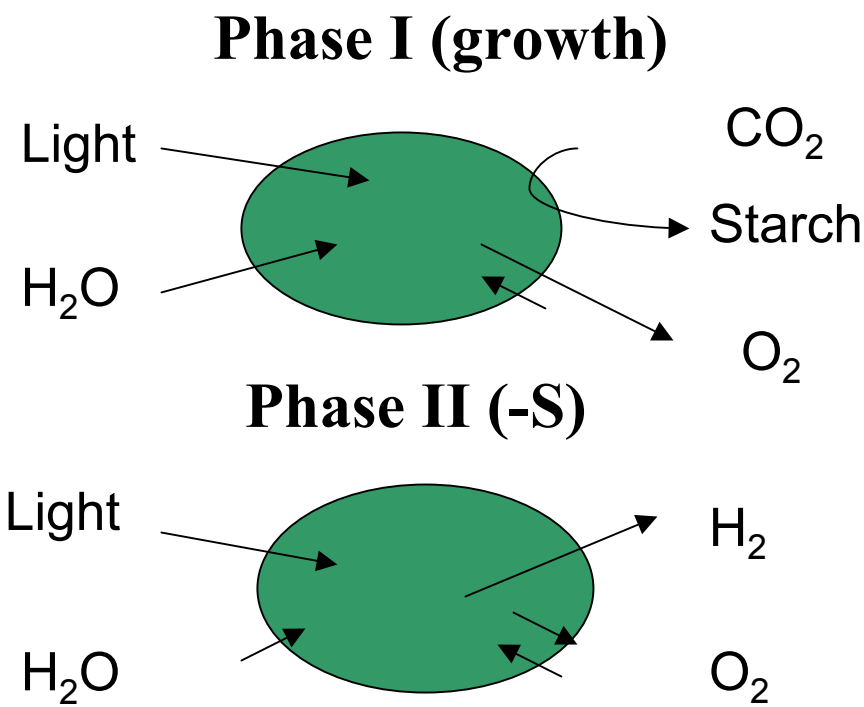
Significant Past Results and Future Milestones FY00-FY10

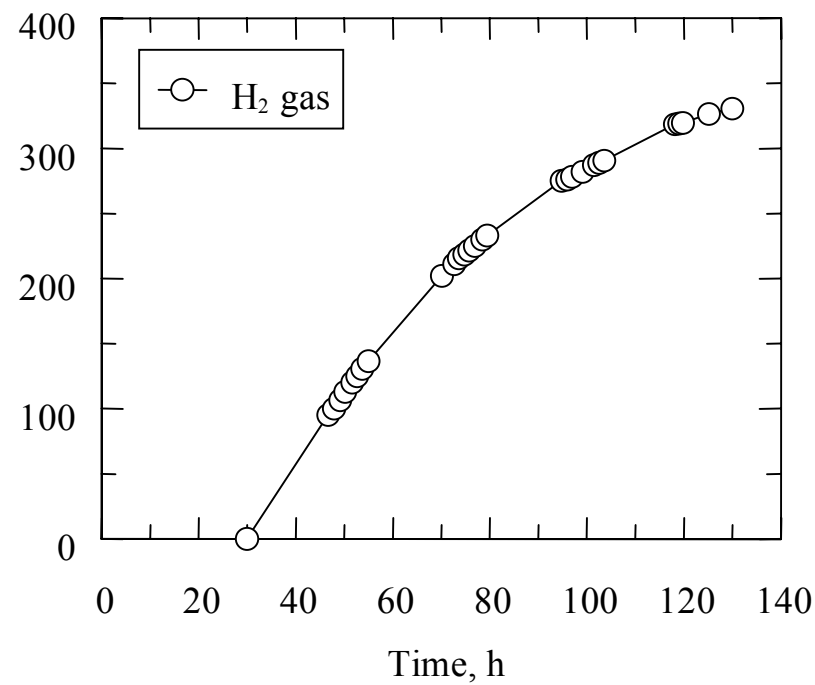


1. Separate O_2 and H_2 production

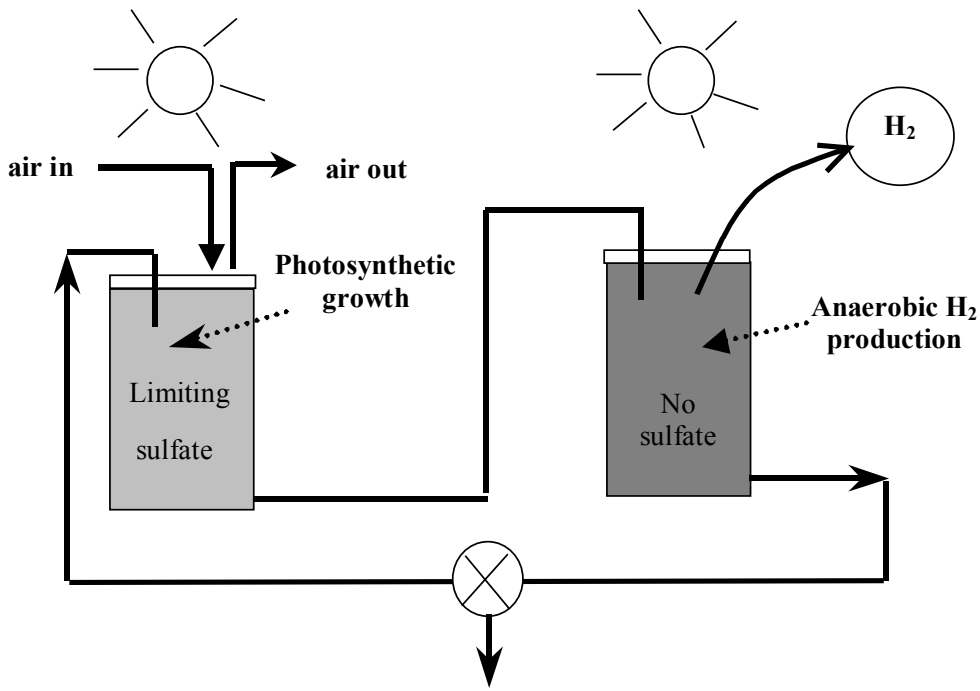
(1) 96 hours H_2-production per batch operation cycle;
(2) 240 hours of continuous H_2-production at sustained rates;
(3) 480 hours of continuous H_2-production (Milestone) but at decreased end rates;
(4) 500 hours of continuous H_2-production at sustained rates;
(5) 1500 hours of continuous H_2-production at sustained rates.

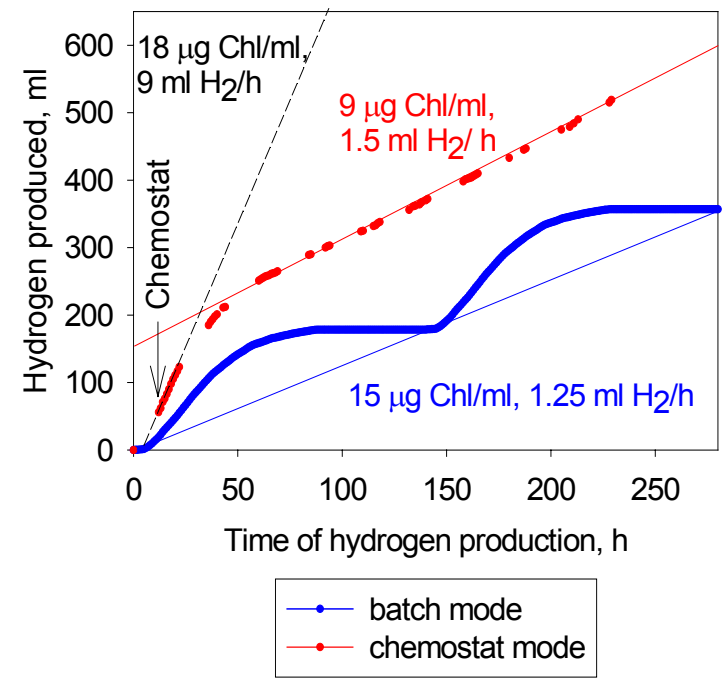
1. Temporal Separation of O_2 and H_2 Production (batch system)





Physical Separation of O_2 and H_2 Production (continuous system)





- biomass
- co-products (dyes, protein, antioxidants, nutritional supplements, pharmaceuticals, etc.)
- fermentation products (acetate, formate)

This represents a major break-through!

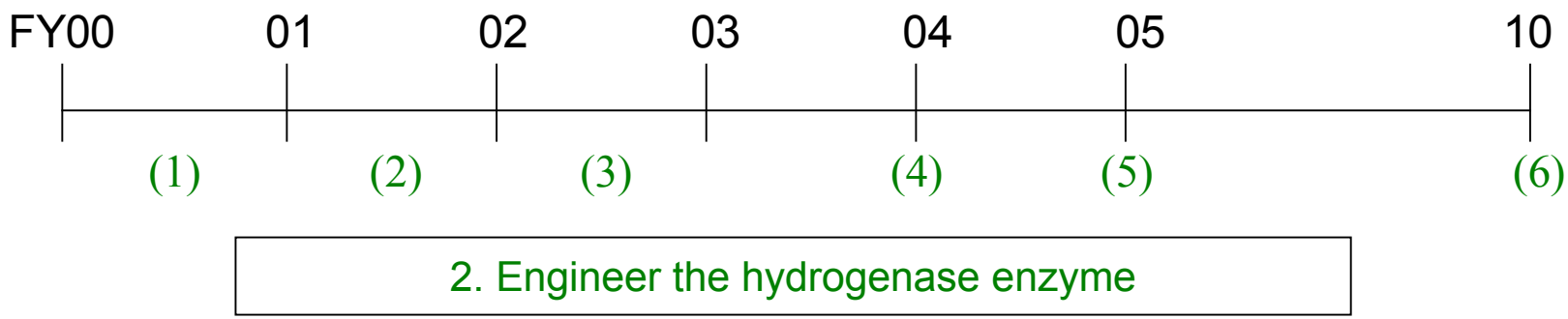
Effects of Research Progress on Projected H_2 Cost

Continuous photoproduction of pure H_2 at a rate of 1.5 ml H_2 gas/liter culture

- Current system hydrogen cost: $200/kg, down from $760/kg in FY00;
- Projected hydrogen cost: $2.34/kg (land-based system), < $1.40/kg (ocean-based system).

NREL

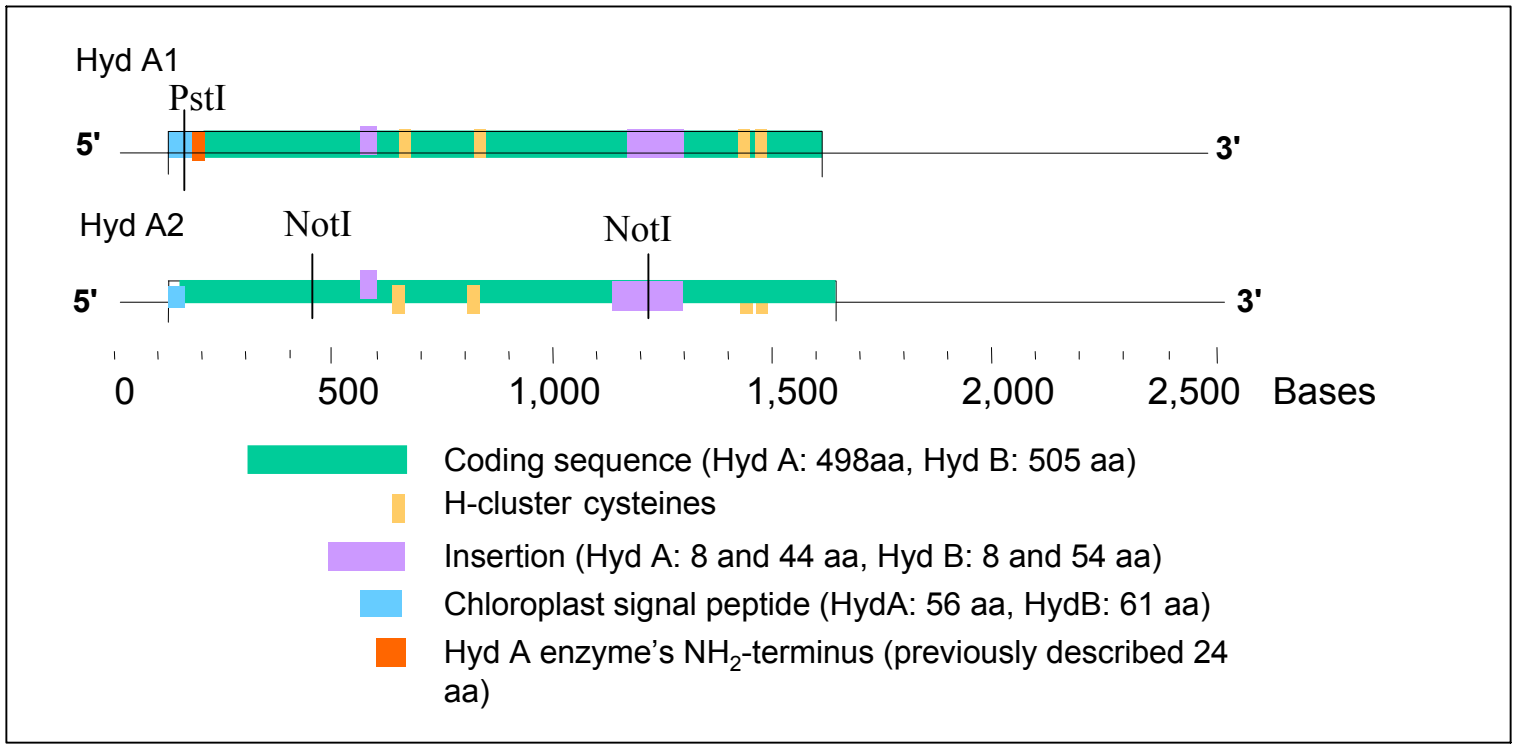
Significant Past Results and Future Milestones FY00-FY10



(1) Cloned and sequenced the catalytic site of 2 algal hydrogenases;
(2) Cloned and sequenced 2 algal hydrogenase genes;
(3) Generated our first mutant with improved O_2 tolerance (0.1% to 1% O_2);
(4) Generate 3 new mutants tolerant to O_2;
(5) Achieve 10% utilization efficiency in a theoretically integrated organism (with U.C. Berkeley and ORNL);
(6) Achieve 20% utilization efficiency in a physically integrated organism (with U.C. Berkeley and ORNL).

2. Engineering the Hydrogenase for O_2-Tolerance

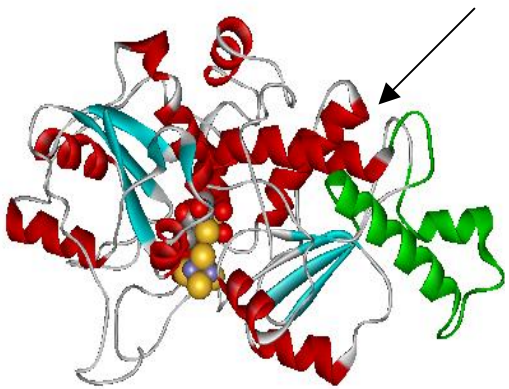
Cloning of two algal hydrogenases



Engineering the Hydrogenase for O_2-tolerance

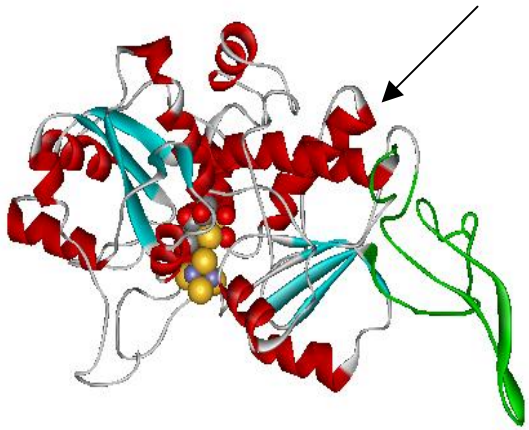
Structural modeling of the two proteins

H_2 channel



C. reinhardtii HydA1

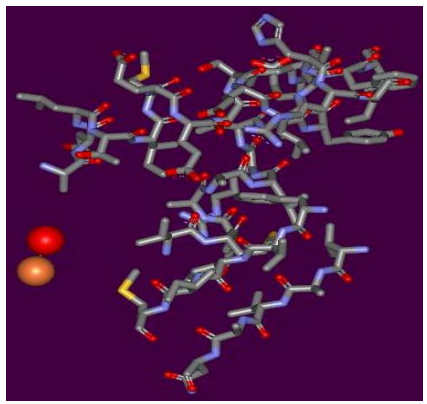
H_2 channel



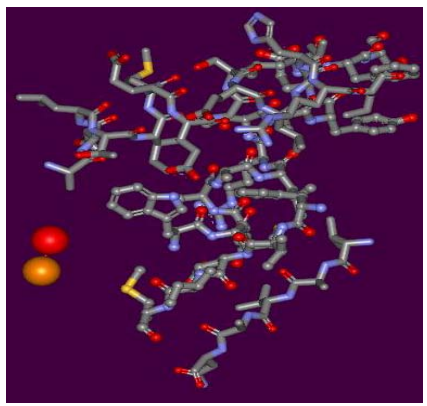
C. reinhardtii HydA2

Engineering the Hydrogenase for O_2-tolerance

Generation of a H_2-channel mutant

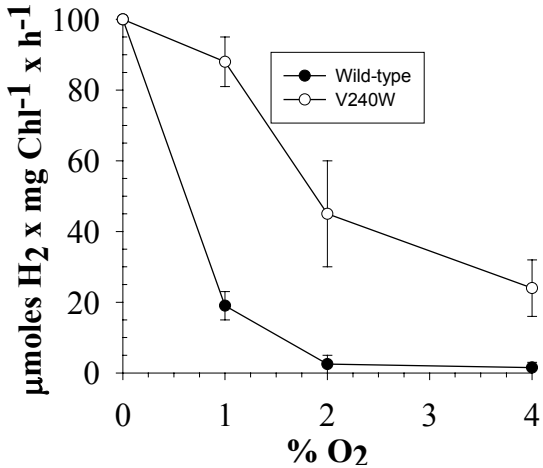


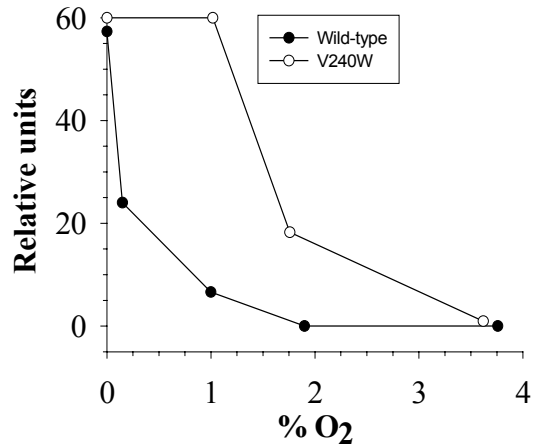
HydA1



V240W

H_2 Production Rates





This represents a major break-through!

Interactions with Others

- Papers: 7 published or in press; 3 submitted. Patents: 1 issued, 2 submitted.
- A. Melis (UC Berkeley) and J. Lee (ORNL) – Team is coordinating efforts to generate a small chlorophyll antenna mutant with non-limited rates of electron transport and an O_2-tolerant hydrogenase.
- A. Rubin (Moscow State University) and A. Tsygankov (Russian Academy of Sciences, Pushchino, Russia) – collaborating on physiological and engineering studies of algal H_2 production;
- T. Happe (U. Bochum, Germany) – collaborated on the cloning of the algal hydrogenases;
- D. Ahmann (Colorado School of Mines) – using gene shuffling techniques to generate O_2-tolerant mutants;
- R. Schulz (Christian Albrechts University, Kiel, Germany) –studying the H_2-photoproduction capability of different green algal species;
- W. Jacoby (University of Missouri) – examining photobioreactor engineering questions.

Plans and Future Milestones for FY04

- **Separate O_2 and H_2 production:**

  - maximize cell density in the continuous system to increase the volume of H_2 gas collected (May 2004);

  - improve the efficiency of H_2 photoproduction using immobilized algal cultures (July 2004).

- **Engineer the algal hydrogenases:**

  - Generate and test double mutants of the gas channel (August 2004)

  - Isolate algal hydrogenases for structural studies (September 2004)

Response to Last Year's Panel

- *"Little evidence of practicality"; "not likely to be a source of reasonably price hydrogen"; "mentions secret engineering/ economic study regarding practical (allegedly) application"; "it is difficult to know if biological hydrogen production will ever be a large scale source of hydrogen"; "see no useful purpose for this project".*

  Economic analyses done for DOE by the NREL Analysis Team (Nov. 2002) indicate that, currently, the two-stage system is not economical. However, when operated with a small antenna size mutant (U.C. Berkeley), at the maximum theoretical electron transport rates (ORNL), and at optimized productivity (NREL), **estimated prices of H_2 are about $2.34/kg**.

- *"Results are not encouraging"; "the goal is not within sight and presumably unattainable in green algae"; "the holy grail is beyond reach".*

  Our **results this year serve as definitive proof that it is indeed possible to engineer an O_2-tolerant hydrogenase** by modifying O_2 access to the catalytic site along the gas channel. This is a longer-term approach, and our milestone for the generation of an ideal organism is 2010.

Discovery of Photocatalysts for Hydrogen Production

2003 DOE Hydrogen Review
May 20th, 2003
Berkeley, CA

Theodore Mill, Albert Hirschon, Michael Coggiola and Brent MacQueen (PI)
SRI International, Menlo Park, CA
Nobi Kambe, NanoGram Corporation, Freemont, CA
Timothy Jenks, Neophotonics, San Jose, CA

SRI International

NanoGram corporation

Off We Go…

"We are at the peak of the oil age but the beginning of the hydrogen age. Anything else is an interim solution. The transition will be very messy, and will take many technological paths .....but the future will be hydrogen fuel cells."

Herman Kuipers, Manager of Exploratory Research
Royal Dutch Shell

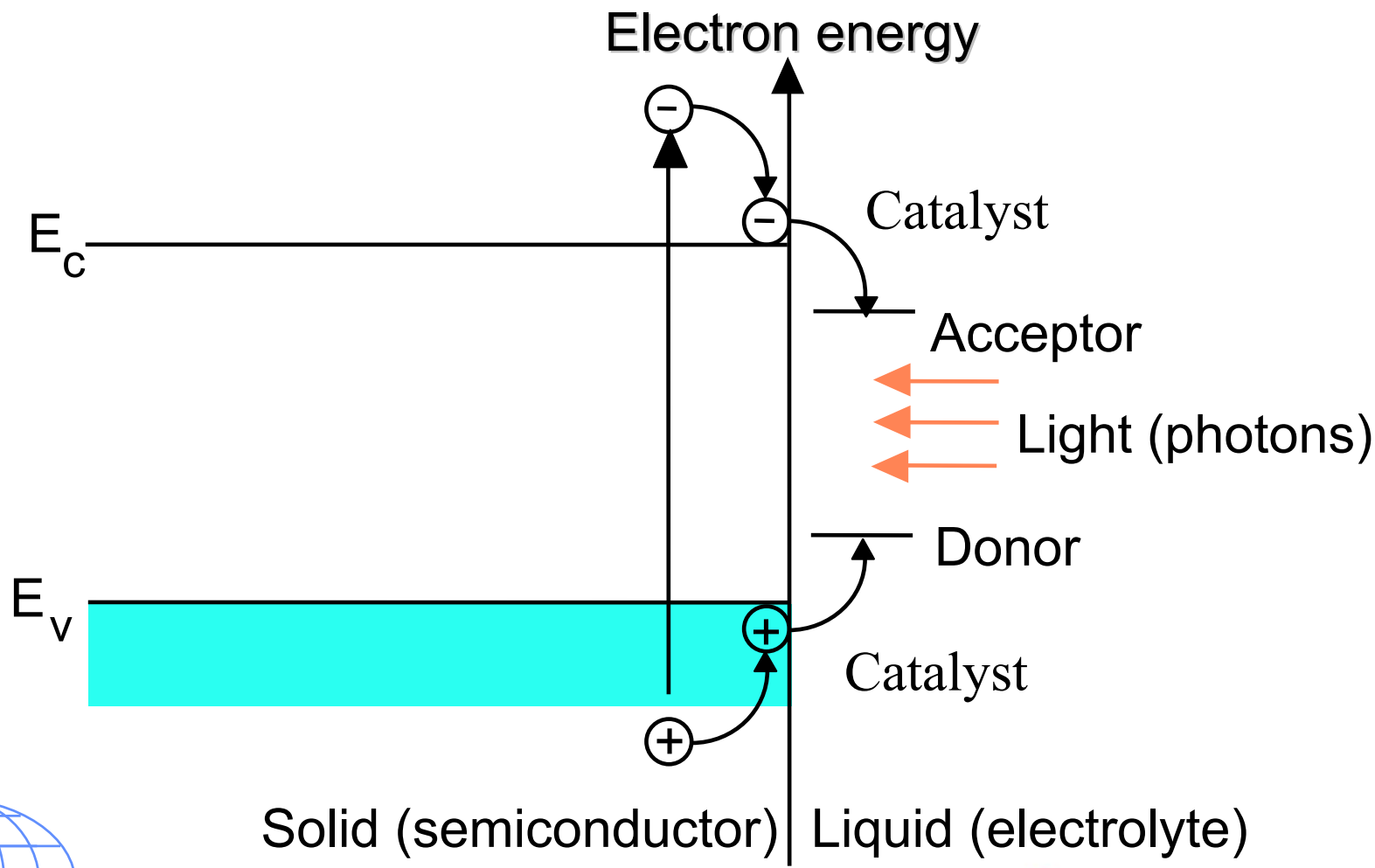
"General Motors absolutely sees the long-term future of the world being based on a hydrogen economy."

Larry Burns, Director of R&D, General Motors

SRI International

NanoGram corporation

PEC 101



SRI International

NanoGram corporation

Relevance/Objective: Technical Barriers

Key Technical Barriers are Materials and Systems Engineering Related

- **Efficiency (band gap and edges), Durability and Cost**

Materials need to be found that address these issues.

This project will assist in the identification of materials that directly address these barriers.

Specifically, the discovery of low cost materials with improved efficiency will be a driver to lower cost PEC hydrogen.

SRI International

NanoGram corporation

Relevance/Objective: Technical Targets

Characteristics	2003 Status	2005 Target	2010 Target	2015 Target
Solar-to-hydrogen Efficiency	7%	7.5%	9%	14%
Durability	100 h	1,000 h	10,000	20,000
Cost	N/a	360	22	5

Targets for 2005 and 2010 involve sequential order of magnitude improvements in durability and modest improvements in efficiency.

Meeting these targets will require improvement of efficiency of existing highly durable oxide components, systems engineering to reduce cost of efficient multi-junction designs or a combination thereof.

The materials discovery required to meet the Technical Targets will be expedited by the use of high throughput screening tools being developed in this project. Furthermore, the inclusion of a partner with the means to produce commercially relevant amounts of materials will hasten the development required to make PEC hydrogen viable.

SRI International

NanoGram corporation

Approach

The goals of this project are to:

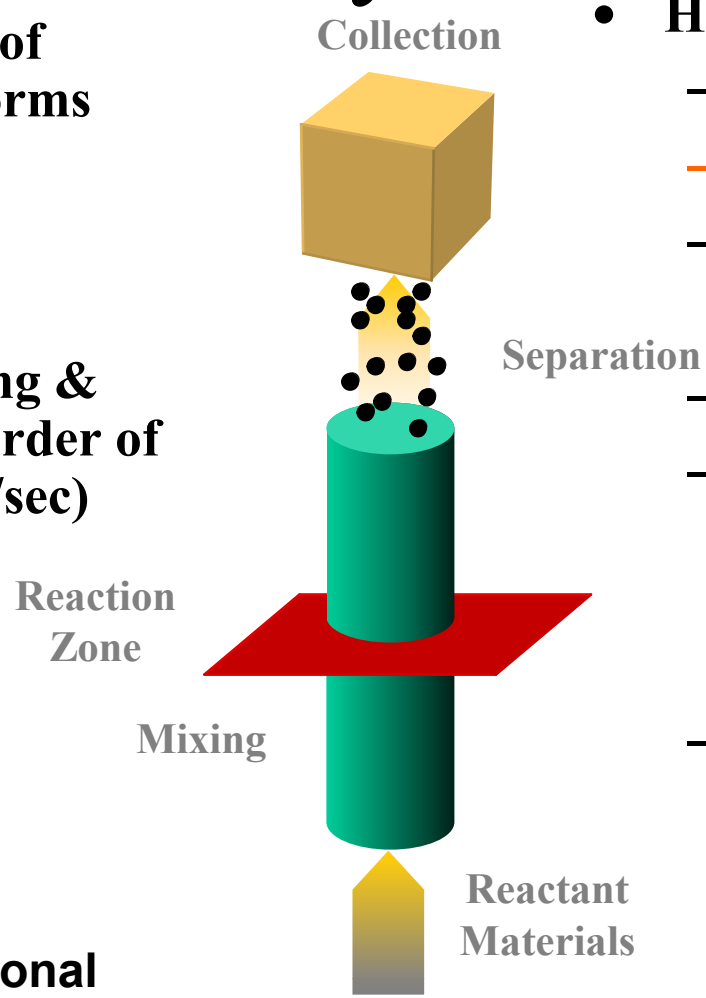
- Develop tools that will allow for the high throughput analysis of materials prepared with commercially relevant synthetic means with respect to PEC hydrogen.
- Use Neophotonics/NanoGram's laser pyrolysis to prepare new materials (composition/phase/particle size) for screening with respect to PEC hydrogen.

SRI International

NanoGram corporation

Laser-driven Nanoparticles Synthesis

- Wide range of precursor forms
  - Gas
  - Vapor
  - Aerosol
- Rapid heating & quench (at order of 10^5 degrees/sec)



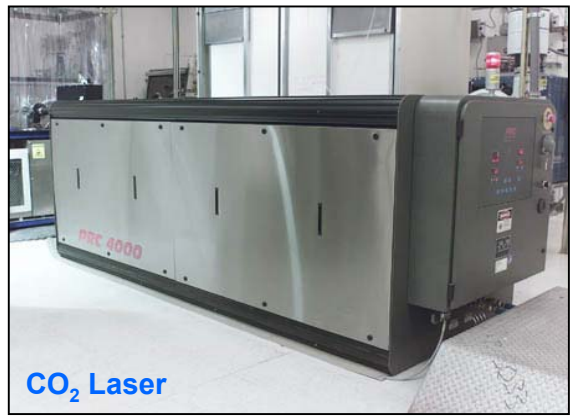
- Huge materials portfolio
  - Crystalline inorganics
  - Multi-element compounds
  - Tightly controlled size
  - High chemical purity
  - Oxide, sulfide, nitride, metal, phosphate, carbide, silicate inorganic compounds...
  - Rare earth-doping at high concentration
- Scalable over 1kg/hr per equipment

SRI International

NanoGram corporation

Scalability
High Volume Production System

LRD Reactor


CO_2 Laser

Controller

Scrubber System

Chemical Delivery System

- **Industrial; mass production**
  - **up to 10,000 wafers/year/system**
- **Fifth-generation technology**

SRI International

NanoGram corporation

Project Timeline

Project initiated in October 2001 as three year effort to develop tools and investigate new materials.

Business decisions of partner on project resulted in year 1 being 17 months. Spending to date and funding requested are summarized below:

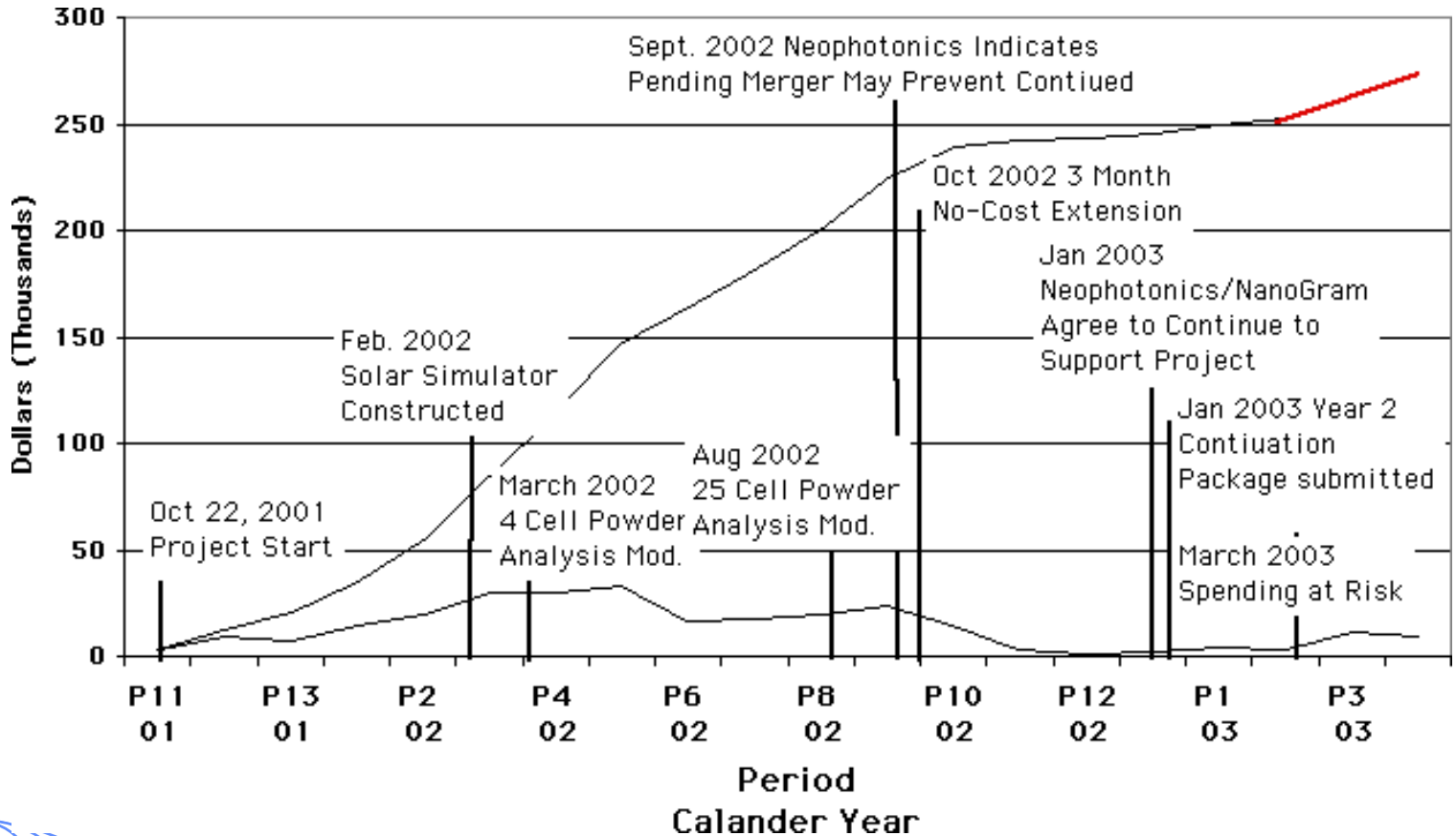
Source Year	1	2	3
DOE	250K	320K (0)	360K
Neophotonics/NanoGram	62K	80K	90K
Total	312K	400K	450K

Year 2 amount in parenthesis is funding received to date.

SRI International

NanoGram corporation

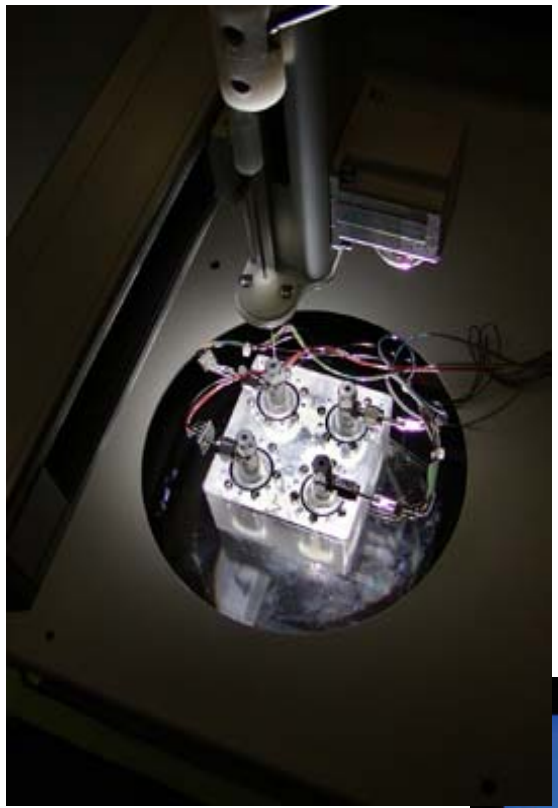
Timeline (cont..)

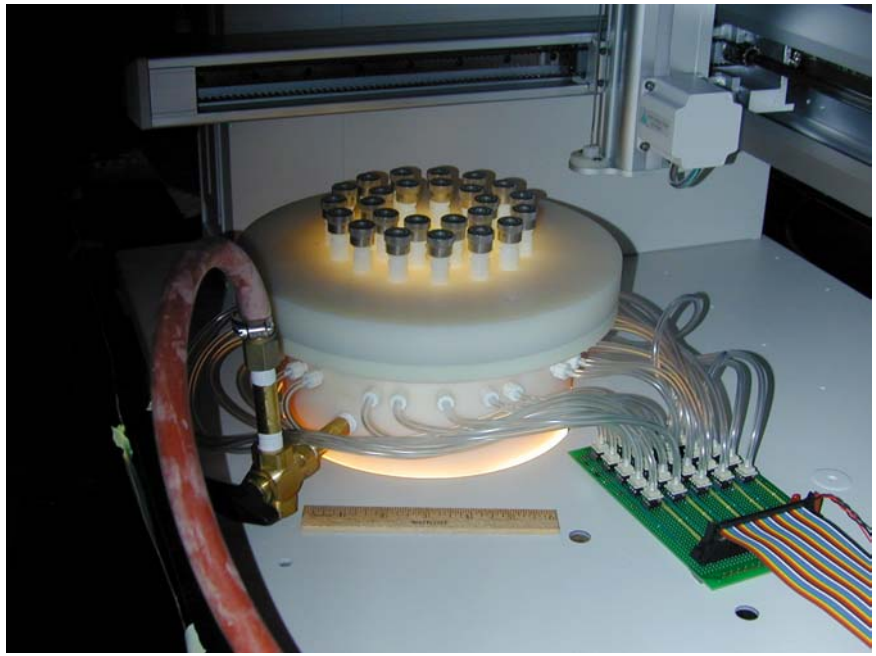


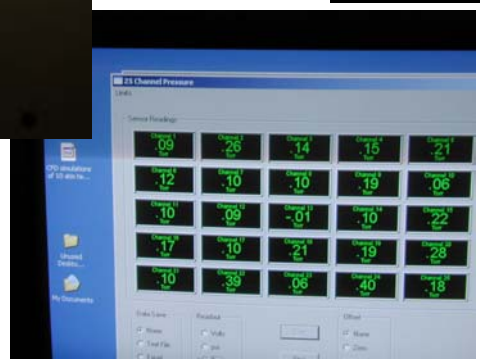
SRI International

NanoGram corporation

Accomplishments/Progress



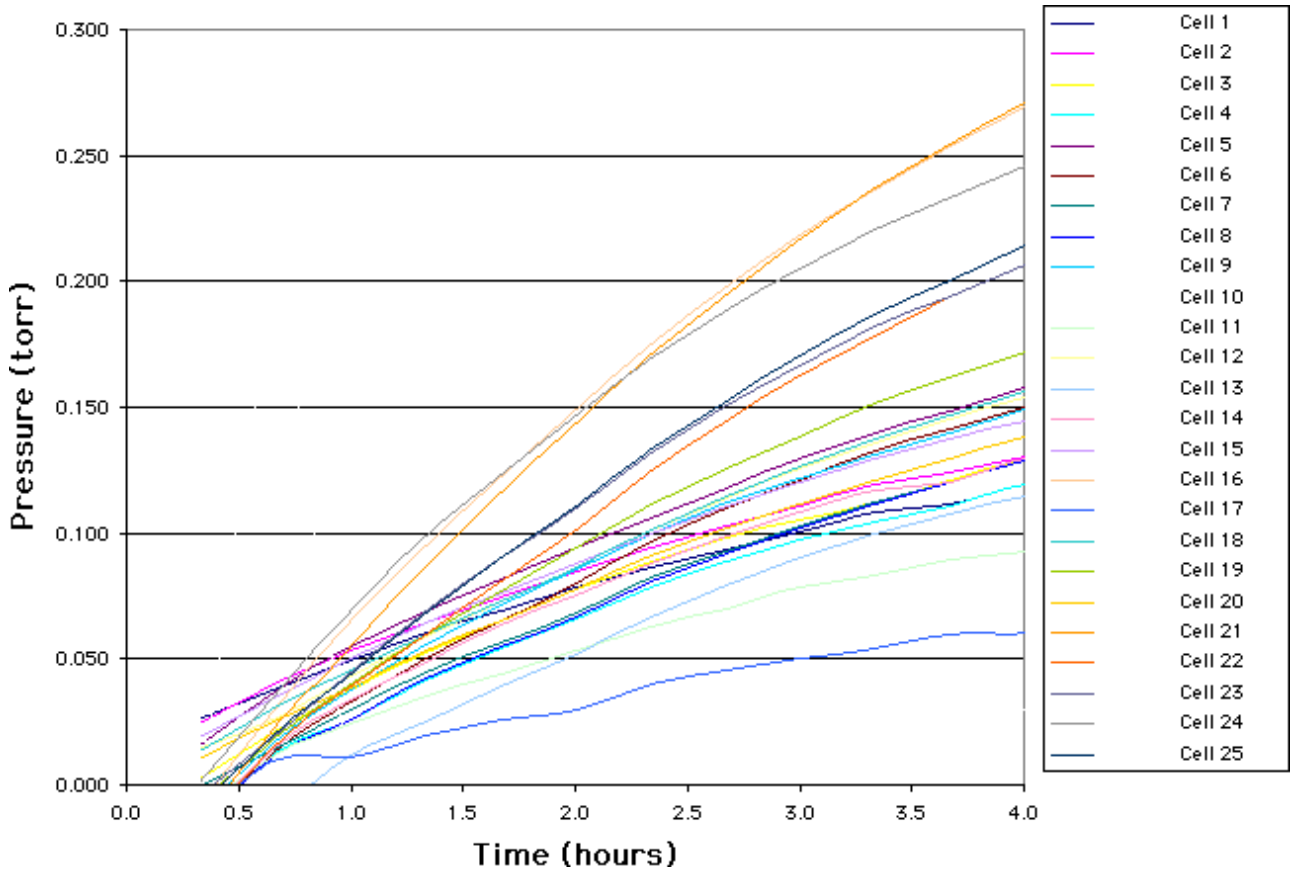




SRI International

NanoGram corporation

Accomplishments/Progress (cont.)



SRI International

NanoGram corporation

Accomplishments/Progress (cont.)

Sample	median diameter, µm	Surface area, m2/gm
TDX-25	0.11	20.9
TDX-33	0.10	20.1
TDX-30	0.08	22.8
TDX-101	0.08	27.9
TDX-37	0.07	26.2
TDX-51	0.07	25.3
DIM76	0.07	38.0
TDX-50A	0.06	29.4
TDX-55	0.06	29.0
TDX-110	0.06	33.6
TDX-24	0.05	32.8
DIM57	0.04	52.5
DIM113	<0.03	56.0
DIM82	< 0.03	55.6

SRI International

NanoGram corporation

Interactions/Collaborations

- Presentation at inaugural GCEP workshop
- Prof. Joop Schoonman, Delft University to visit SRI in early July to discuss potential collaboration
- Working on agreement with other DOE funded groups to share information and materials
- Materials transfer agreement available

SRI International

NanoGram corporation

Detailed Plans for Year 2

- Task 1 Tools Development
  - **Debug powder module software for auto sampling**
    - **Early June 2003**
  - **Electrochemistry Analysis Module**
    - **Design review: May 2003**
    - **Fabrication: August 2003**

SRI International

NanoGram corporation

Detailed Plans for Year 2 (cont.)

- Task 2. Analysis of Nanoparticulate-based PEC Systems
  - Analysis and characterization of Neophotonic (and SRI) generated materials
  - Based on results develop rationale design of future materials (elemental, phase, size)
  - Evaluate materials reported in literature
    - Synthesized at SRI
    - Submitted to SRI (Materials Transfer Agreement)

SRI International

NanoGram corporation

Detailed Plans for Year 2 (cont.)

- Task 3. Generation of Database
  - Inclusion of validated data with sufficient information for reproduction in other labs
- Task 4. Modeling Feasibility
  - Survey existing programs for suitability in modeling material stability relevant to PEC production of hydrogen

Detailed Plans for Year 2 (cont.)

Task Designation/Milestones	Year 2				Y3
	Q1	Q2	Q3	Q4	Q1
Task 1. Tools for the Development of Photoelectrochemical Systems for the Generation of Hydrogen.					
(a) Electrochemical analysis module, prototype design	▲				
(b) Prototype assembly		▲			
(c) Prototype Validation			★		
Task 2. Synthesis of Nanoparticulate-Based Photoelectrochemical Systems for Hydrogen Production Via Photolytic Water Splitting					
(a) Characterization of as received and modified materials (Y2 materials)				▲	
Task 3. Generation of Database of Experimental Results					
(a) Database setup	▲				
(b) Database implementation		★			
Task 4. Feasibility Study for the Generation of a Model to Predict Photoelectrochemical behavior of Nanoparticulate Semiconductor-Based Systems.					
(a) Survey existing modeling programs			▲		

▲ Subtask completion

★ Milestone completion

SRI International

NanoGram corporation

Reviewers Comments

- Comments were overall very positive
- “Criteria for picking candidates needs to be done”

SRI International

NanoGram corporation

Neophotonics Compositions Produced (Partial List)

Compositions Produced:

Amorphous Glass Materials

SiO_2, PSG, BPSG, GPSG

Elemental Metals

Fe, Ag, Ni, Co, Pt

Oxides

TiO_2, ZnO, VO_2, V_2O_3 , V_2O_5 , MnO, Mn_2O_3, Mn_3O_4, MoO_3, NbO_2, Nb_2O_5, Y_2O_3, SnO, SnO_2, SiO_2, Al_2O_3 , Fe_2O_3, Fe_3O_4

Complex oxides

$LiMn_2O_4$, $Li_2Mn_4O_9$, $Li_4Mn_5O_{12,}$ $LiCoO_2$, $LiNiO_2$ $LiNi_{0.8}Co_{0.2}O_{2,}$ $LiMn_{2-y}Al_yO_4$, $LiMn_{2-y}Co_yO_4$ $Li_4Ti_5O_{12}$, Y_2MoO_6, $Ag_2V_4O_{11}$, $BaMgAl_{10}O_{17}$:Eu

Carbon and Carbides

C, SiC, NbC, V_8C_7

Nitrides

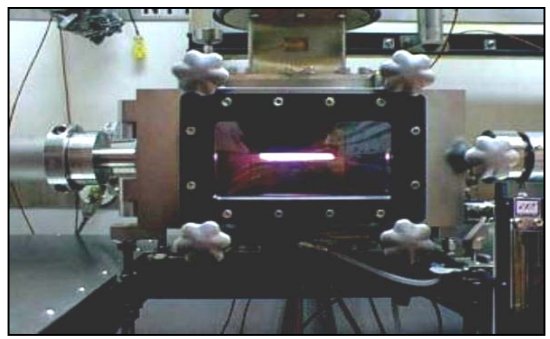
Si_3N_4

Phosphates

$LiFePO_4$

NPM™ NanoParticle Discovery System

C9000 Volume Production Module



Close-up: NanoParticle Laser Reaction Chamber

SRI International

NanoGram corporation

Thank You, Stay Tuned

Slide by R. Smalley Presented at National Nanotechnology Initiative

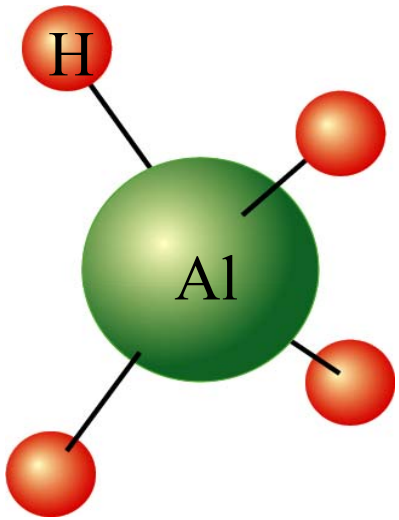
- **ENERGY**
  is the single most important problem facing humanity today.
- **WE CAN SOLVE THIS PROBLEM**
  with revolutionary breakthroughs at the frontiers of Physical Sciences & Engineering, and particularly in Nanotechnology
- We need a new APOLLO PROJECT to do this.
- The problem is huge, but it is also a magnificent opportunity.
- Success will revolutionize the largest industry in the world, Energy.
- American boys and girls will enter the physical sciences to do this, inspired by their idealism, their sense of mission, and their desire to be "where the action is".
- In the process this new Apollo Project will produce a cornucopia of new technologies, and provide the underpinnings for vast new economic prosperity for the US and the world.

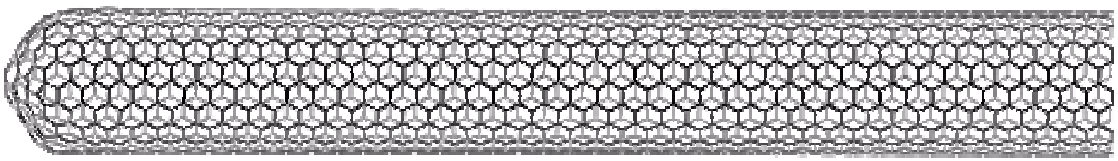
SRI International

NanoGram corporation

U.S. Department of Energy
Energy Efficiency and Renewable Energy

Hydrogen Storage





JoAnn Milliken
Lucito Cataquiz
John Petrovic
Carole Read

Objectives

Hydrogen Storage Systems

Develop and verify:

- On-board hydrogen storage systems achieving:
  - 4.5 wt%, 1.2 kWh/L, and $6/kWh by 2005
  - 6 wt%, 1.5 kWh/L, and $4/kWh by 2010
  - 9 wt%, 2.7 kWh/L, and $2/kWh by 2015

- Low cost, off-board H_2 storage systems for H_2 infrastructure needs by 2015.
- Vehicle interface technologies for fueling on-board H_2 storage systems by 2015.

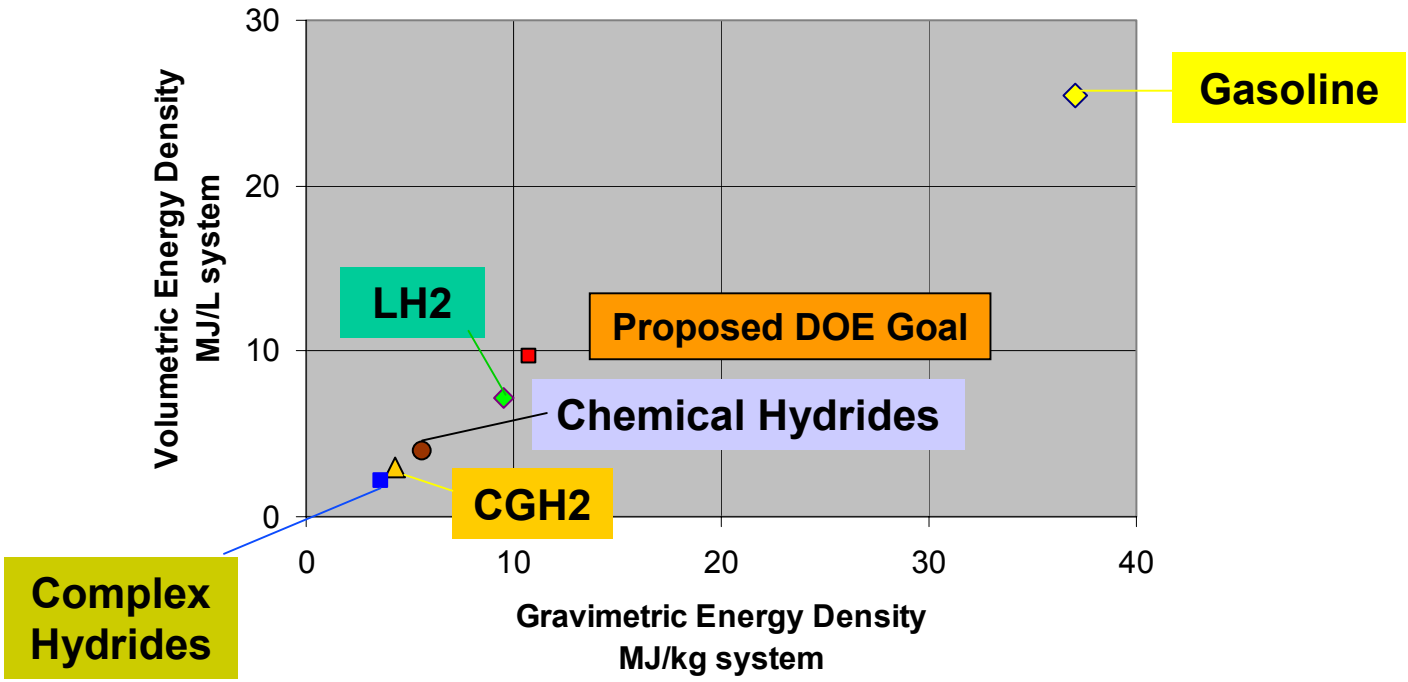
Targets

On-Board H_2 Storage Systems

Storage Parameter	Units	2005	2010	2015
Specific energy	kWh/kg	1.5	2.0	3.0
Energy density	kWh/L	1.2	1.5	2.7
Storage system cost	$/kWh	6	4	2
Cycle life (1/4 tank to full)	Cycles	500	1,000	1,500
Refueling rate	kg H_2/min	0.5	1.5	2
Loss of usable H_2	(g/hr)/kg H_2 stored	1	.1	0.05

Status vs Targets
On-Board H_2 Storage Systems

No current material or technology meets DOE/FreedomCAR targets.



Barriers

Hydrogen Storage Systems

- Cost
- Weight & volume
- Efficiency
- Durability
- Refueling time
- Codes & standards
- Life-cycle & efficiency analyses

Planning
Hydrogen Storage Systems

Identify R&D Priorities

H_2 Storage Materials Workshop
Compressed/Liquid H_2 Workshop
H_2 Storage "Think Tank" Meeting

Issue "Grand Challenge"
Build Upon Existing Work

Create Virtual Centers
Initiate New Materials R&D
Complete Compressed/Liquid H_2 R&D

Conclusions & Recommendations

Complex Metal Hydrides

- Continue fundamental studies on $NaAlH_4$ as model system
- Identify other hydride materials that have greater storage capacity

Chemical Hydrides

- Identify improved/new process chemistry for regeneration
- Complete full lifecycle analysis of $NaBH_4$

Carbon

- Conduct definitive experiments to show where and how hydrogen is stored in nanotubes
- Better understand the science to engineer carbon for hydrogen storage

Advanced Concepts

- Discuss advanced storage concepts further to refine recommendations and to resolve controversial aspects

Conclusions & Recommendations

Safety

- Understand failure modes

Economics of fibers and resins

- New materials

Smart tanks

- Sensors to detect tank health

Advanced concepts

- High pressure conformable tank structures

Manufacturing processes

- High volume production techniques

Hydrogen Storage "Think Tank" Meeting

Participants:

- Four Nobel Laureates
- Seven award-winning scientists (ACS, APS, and NSF awards; Presidential Young Investigators)

Conclusions/Recommendations

- R&D of Materials:
  - Nano-Materials
  - High Surface Area Materials, including Carbons
  - Synthetic Metals
  - Chemical and Metal Hydrides, Clathrates
- Issue a "Grand Challenge"
  - Educate the scientific community
  - Establish integrated teams (virtual centers)
  - Explore novel concepts through single investigator projects

Next Steps

National H_2 Storage R&D Project

Start Centers/ New Projects	January 2004
Selections	October 2003
Solicitation Release	June 2003
Pre-Solicitation Conference	June 2003

Projects
Hydrogen Storage Systems

Complex Metal Hydrides (UTRC, SNLL, U.Hawaii, FSEC)

- *$NaAlH_4$ System Integration*
- *Hydride Materials R&D*
- *Kinetics/Mechanistic Studies*

Chemical Hydrides (2004)

- *Aminoborane (FSEC)*
- *$NaBH_4$ Process Chemistry (TBD)*
- *Life-Cycle Analyses*
- *Other Hydrides*

Standard Test Protocols & Facilities (SwRI)

Advanced Concepts (2004)

- *TBD*

Compressed/Liquid Tanks (Quantum, JHU, LLNL, INEEL, Ergenics)

- *5,000/10,000 psi Tanks*
- *Semi-Conformal System*
- *Tank Liners/Overwrap Materials*
- *Insulated Pressure Vessels*
- *Unusual Shapes*

Carbon (NREL, CalTech, SRTC)

- *Kinetics/Mechanistic Studies*
- *Process R&D*
- *Structure/Property Analyses*

DOE Hydrogen Composite Tank Program

Dr. Neel Sirosh
DIRECTOR, FUEL STORAGE

Goals

- Optimize and validate commercially viable high performance pressure storage systems for transportation applications, in line with DOE targets

Objectives:

- Develop and validate 5,000 psi storage tanks
  - Tank efficiency: 7.5 – 8.5 wt%
- Validate 5,000 psi in-tank-pressure regulators
  - Total storage system efficiency: 5.7 wt%
- Develop and validate 10,000 psi storage tanks
  - Tank efficiency: 6 - 6.5 wt%
- Develop and validate 10,000 psi storage systems
  - Quantum Internal Program; total system efficiency: 4.5 wt%
- Optimize designs and processes to achieve the DOE cost targets

QUANTUM

DOE Storage Targets

Parameter	2005	2010	2015
Usable Specific Energy (kw hr / kg)	1.5	2	3
Usable Energy Density (kw hr / L)	1.2	1.5	2.7
Cost ($ / kw hr)	$6	$4	$2
Cycle Life (1/4 tank to full)	500	1,000	1,500
Refueling Rate (kg H_2 / min)	0.5	1.5	2
Loss of Usable Hydrogen (grams)	1	0.1	0.05

Approach

- Learn from the successful 100 yr history of pressure vessels (industrial, aerospace, CNG)
- Optimize materials, design, process to improve weight efficiency (5,000 psi tanks)
- Develop & validate volumetrically efficient storage systems (10,000 psi tanks)
- Improve system efficiency (In-tank Regulator, Balance of Plant Components)
- Validate and certify components (Codes & Standards, Regulatory approvals)
- Work towards cost reduction (Technology, Economies of Scale

Compressed Gases Have Been Around for Over 100 Years

Industrial

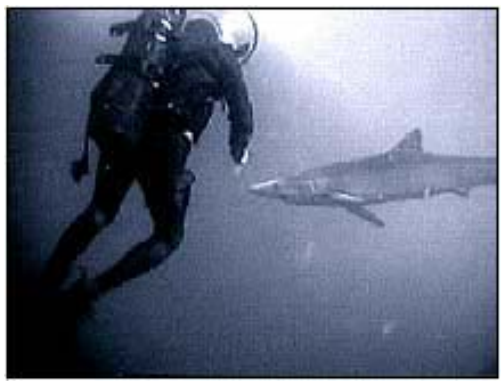
Fire Extinguishers

Life Support

Automotive

1900 1910 1920 1930 1940 1950 1960 1970 1980 1990 2000 2010

Pressures Up To 6,000 psi

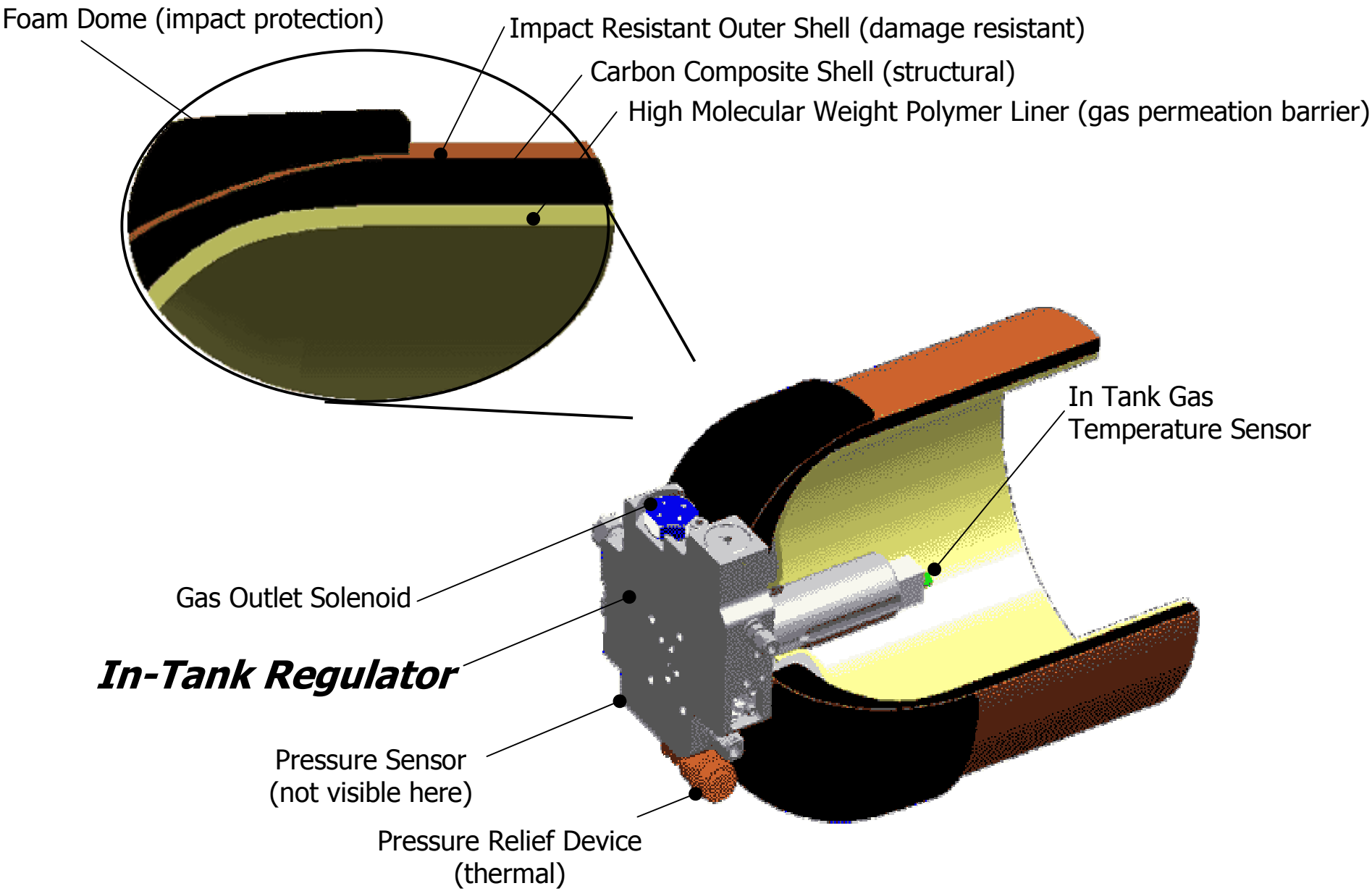


SCUBA

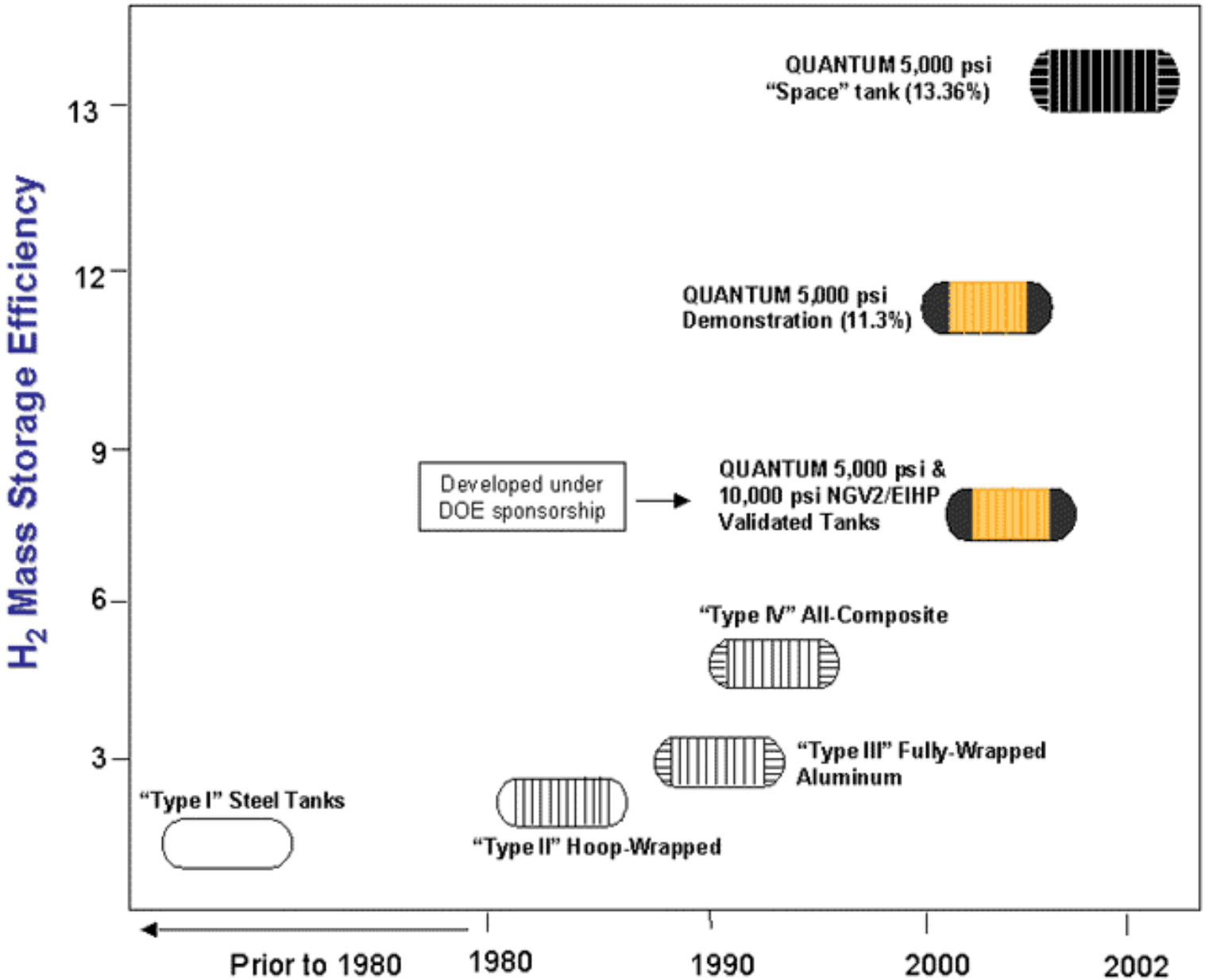
Aircraft

QUANTUM

QUANTUM Compressed Hydrogen Storage

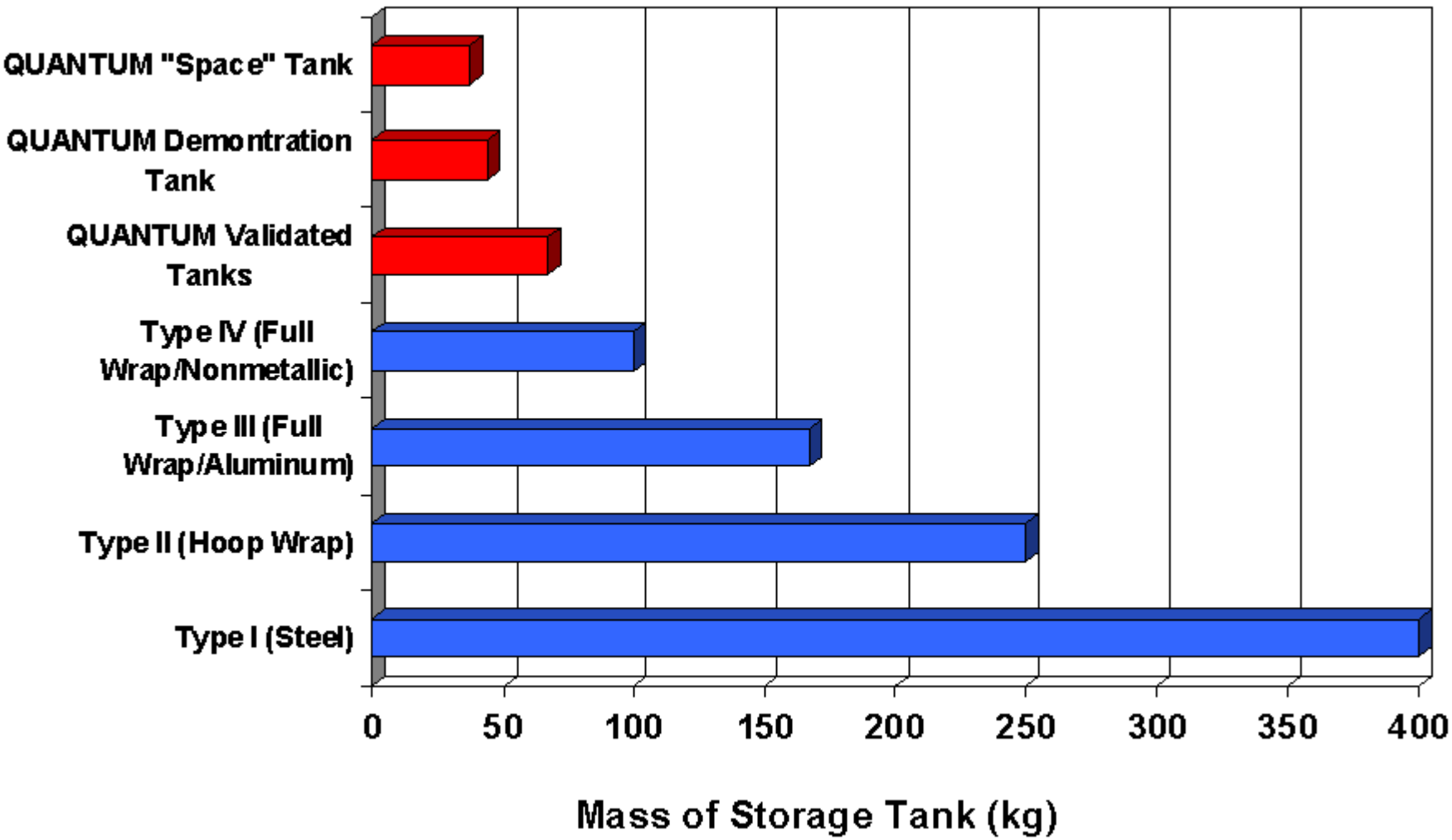


Product Benchmarking



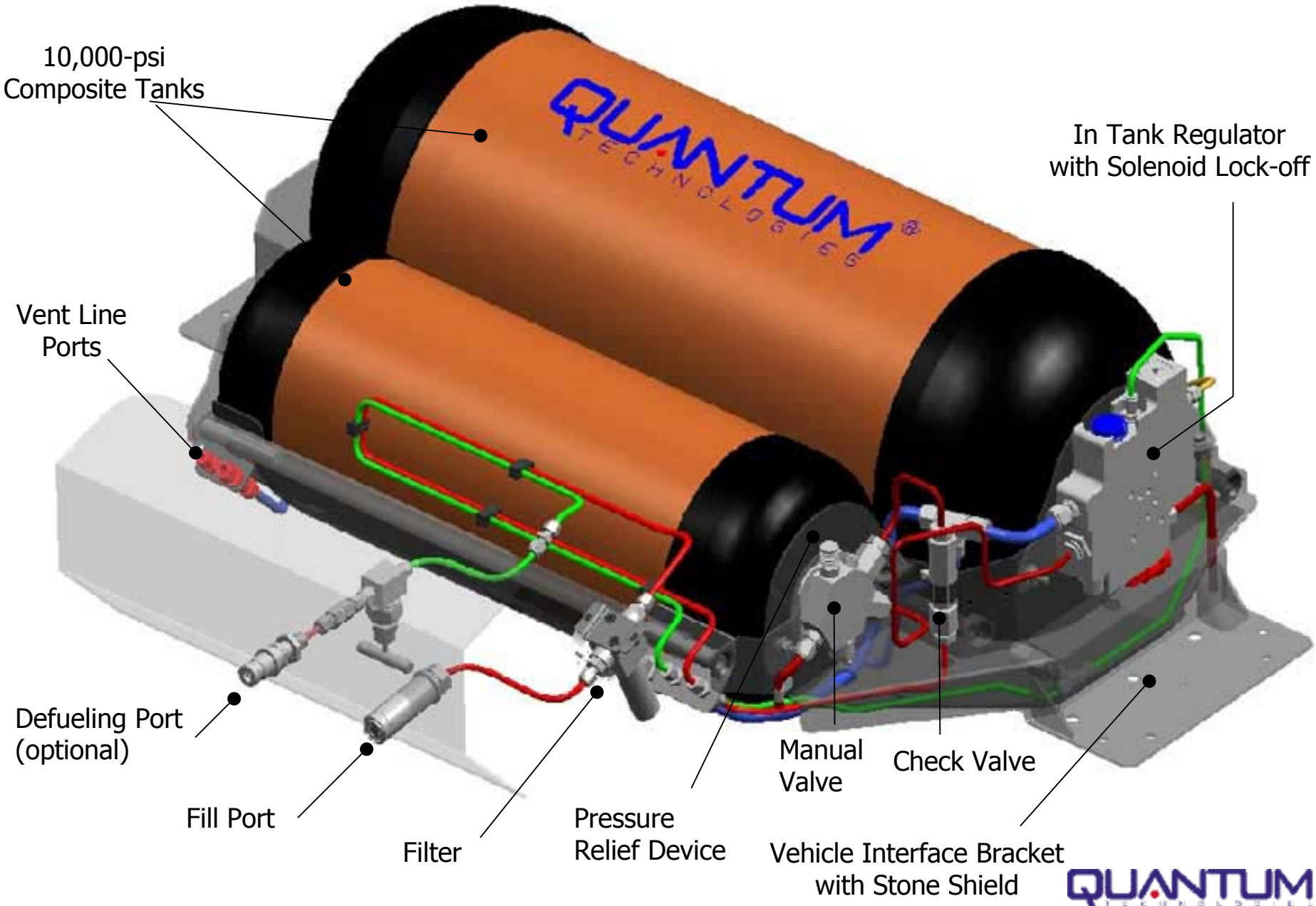
QUANTUM

Mass of Tank to Store 5 Kg of Hydrogen Gas



QUANTUM

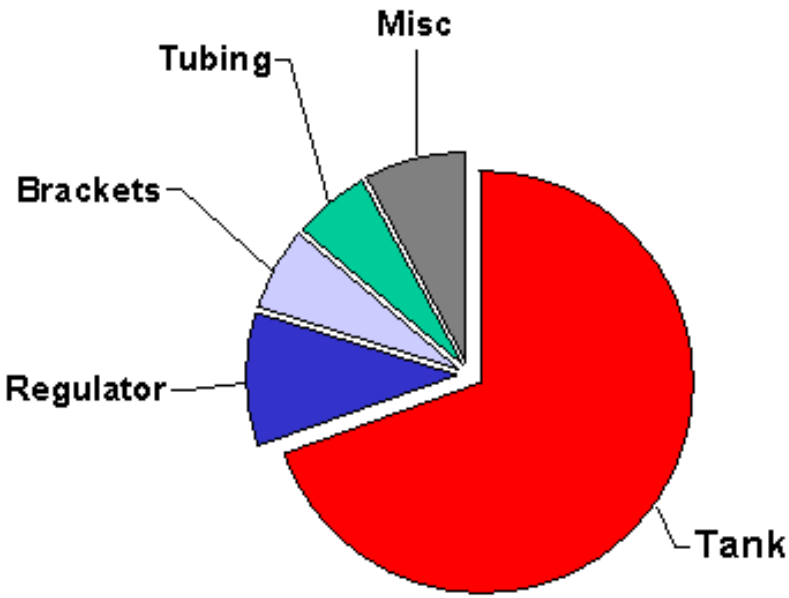
Compressed Hydrogen Storage System



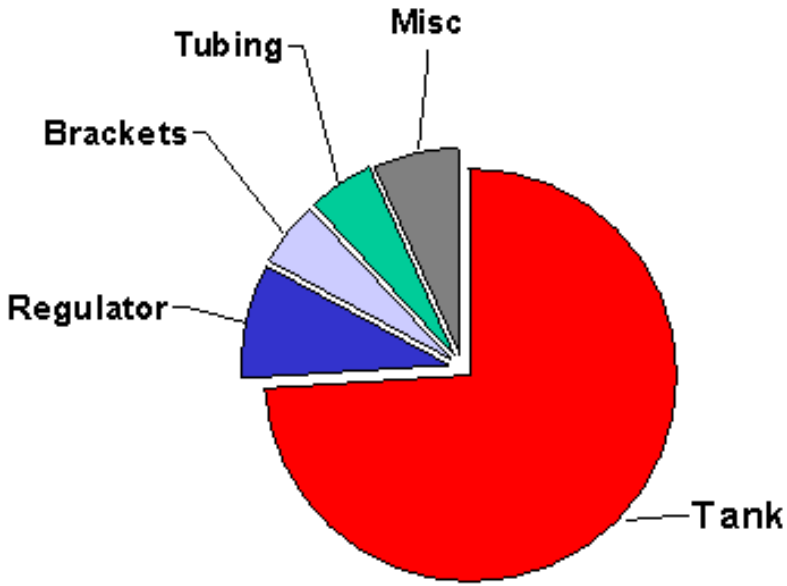
System Level Weight Efficiency

Storage of 5 kg of Hydrogen Gas (Using One Tank)

5,000 psi



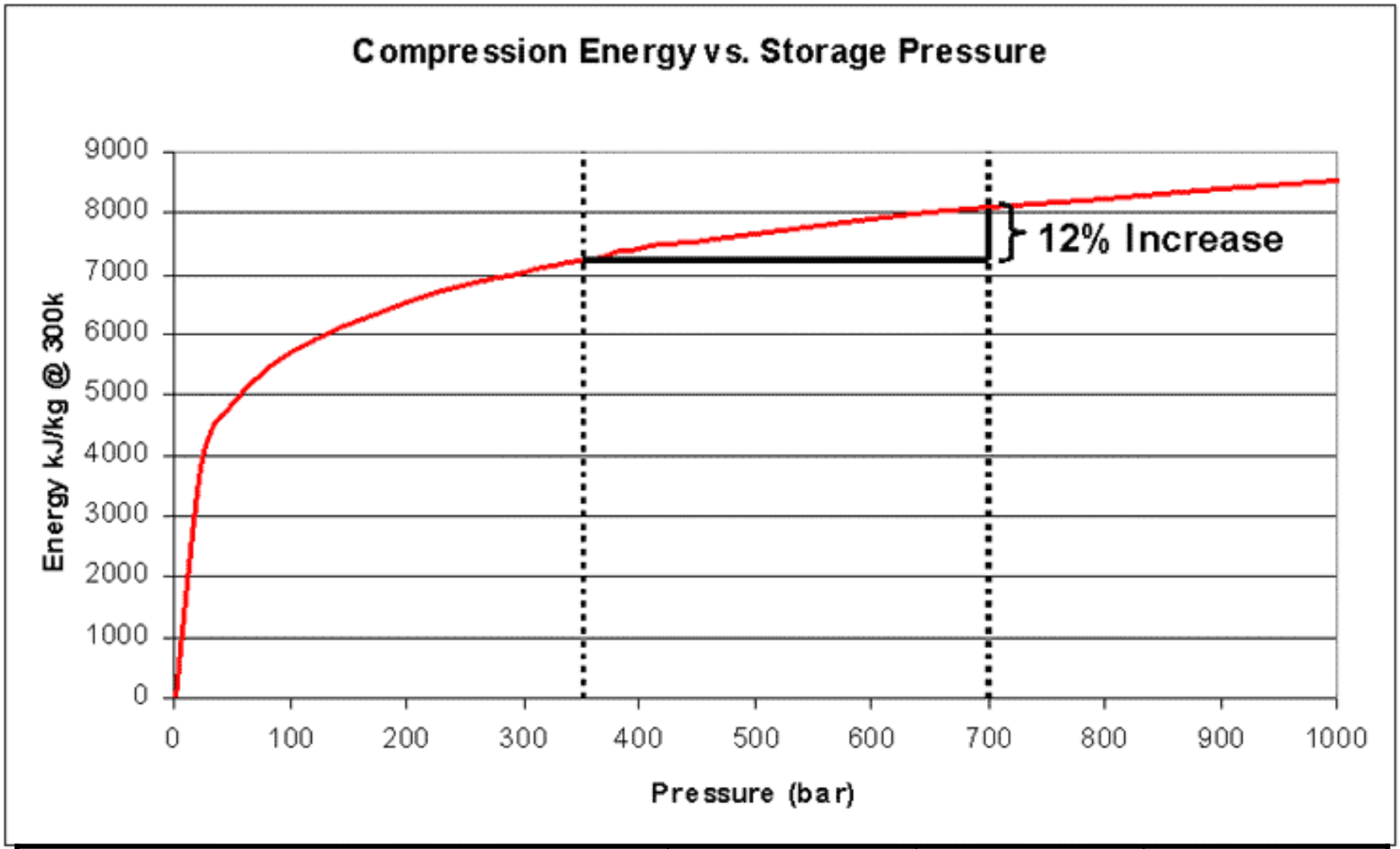
10,000 psi



Usable Specific Energy (kw hr / kg)	2005	2010	Status
5,000 psi Technology	1.5	2	1.9
10,000 psi Technology	1.5	2	1.6

QUANTUM

Volumetric Efficiency: 5,000 psi vs 10,000 psi Storage

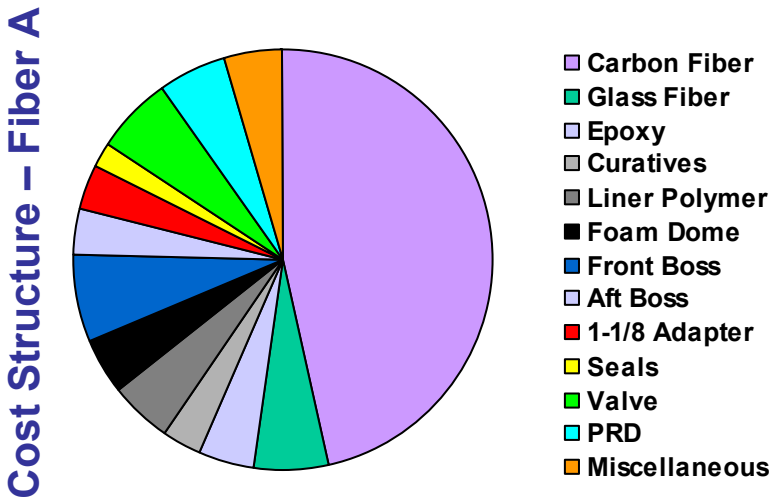


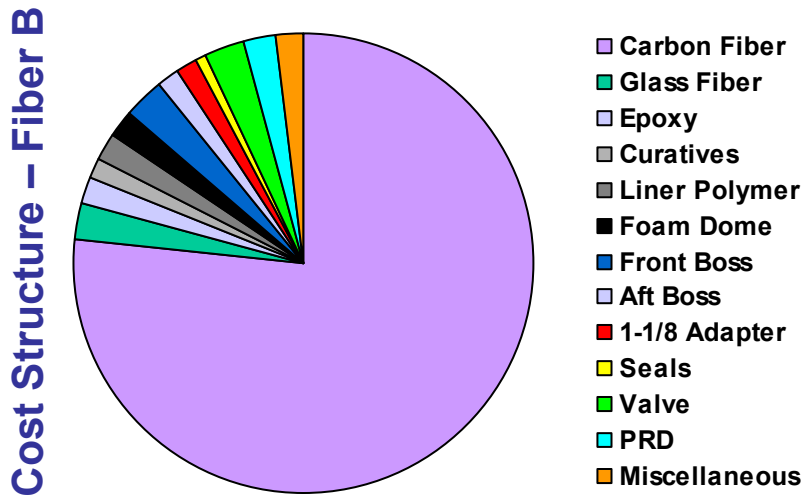
	2005	2010	Status
Usable Energy Density (kw hr / L)	1.2	1.5	1.3

QUANTUM

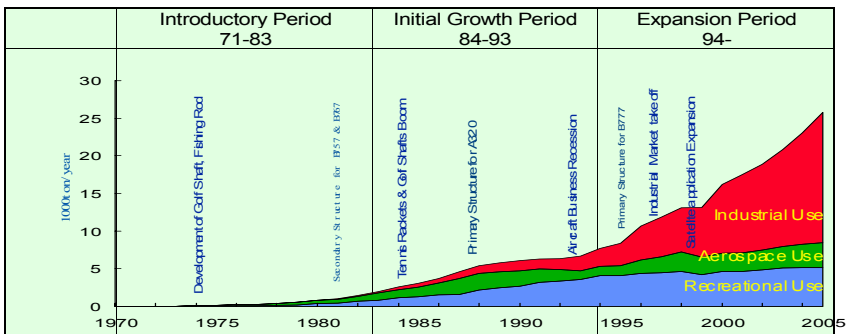
Cost Drivers

- Primary driver is material cost
  - 40 - 80% is carbon fiber cost
  - Significant opportunities for cost-reduction



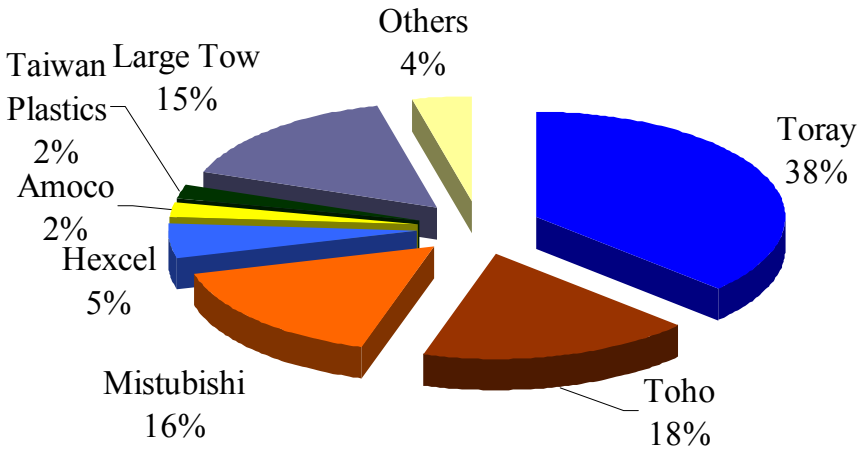


Carbon Fiber Worldwide Supply



	Introductory Period 71-83	Initial Growth Period 84-93	Expansion Period 94-
Application	Marginal Application Fishing Rod Aircraft Secondary Structure	Application Expanded Tennis Racket Golf Shaft Aircraft Primary Structure	Industrial Uses take off Energy related Transportation Civil Eng's & Construction
Remarks	High Performance	Product Grade Variety Fabrication Development	Cost Reduction Larger Scale Structure

Carbon Fiber Market Share



QUANTUM

Safety & Certification Status

Certification Status:

Storage Pressure	Approvals / Compliance
3,600 psi (250 bar)	NGV2-2000 (modified) DOT FMVSS 304 (modified)
5,000 psi (350 bar)	E.I.H.P. / German Pressure Vessel Code DBV P.18 NGV2-2000 (modified) FMVSS 304 (modified) KHK
10,000 psi (700 bar)	E.I.H.P. / German Pressure Vessel Code DBV P.18 FMVSS 304 (modified)

QUANTUM Participates in:

- E.I.H.P (European Integrated Hydrogen Project) Code Committee
- ISO Hydrogen Storage Standard Committee
- CSA – America NGV2 Hydrogen TAG

QUANTUM

Regulatory Approvals

Regulatory Agency	Validation Tests
• ISO 15869 - **International**	• Hydrostatic Burst
• NGV2 - **US/Japan/Mexico**	• Extreme Temperature Cycle
• FMVSS 304 - **United States**	• Ambient Cycle
• NFPA 52 - **United States**	• Acid Environment
• KHK - **Japan**	• Bonfire
• CSA B51 - **Canada**	• Gunfire Penetration
• TÜV - **Germany**	• Flaw Tolerance
	• Accelerated Stress
	• Drop Test
	• Permeation
	• Hydrogen Cycle
	• Softening Temperature
	• Tensile Properties
	• Resin Shear
	• Boss End Material

QUANTUM

10,000 psi Components Availability

Component	Available	Approval
Tank	✓	EIHP / TÜV
Regulator	✓	EIHP / TÜV
Check Valves	✓	EIHP / TÜV
PRD (thermal)	✓	EIHP / TÜV
Manual Tank Valves	✓	EIHP / TÜV
Pressure Transducers	✓	EIHP / TÜV
Refueling Receptacle	✓	EIHP / TÜV
Fuel Lines	✓	EIHP / TÜV
Fittings	✓	EIHP / TÜV

QUANTUM

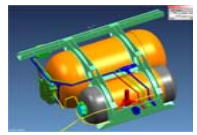
Project Timeline

PRODUCTION

250 Bar CNG

350 Bar H_2

700 Bar H_2



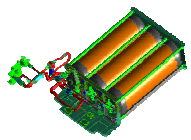
Up to 10X Cost Reduction Through Economies of Scale

PROTOTYPE

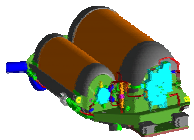
250 Bar H2

350 bar Conformable

350 Bar H_2



700 Bar H_2



Cost Reduced (30%)

700 Bar H_2

CONCEPT

250 Bar CNG

DOE Programs

350 Bar H_2

700 Bar H_2

Cost Reduced (30%)

700 Bar H_2

Cost Reduced (75%)

700 Bar H_2

Next Gen Storage

1998 2000 2002 2004 2006 2008

QUANTUM

Collaborative Work

- Alliance with Thiokol (Material, Design, Testing)
- Global alliance with GM (Fuel Cell Enabling Technologies)
- Development Program with NASA / Aerovironment (Advanced light weight systems)
- CRADA with Idaho National Labs (Enhanced Permeation Barriers)
- Collaboration with Oak Ridge National Labs (Monitoring Systems)

Accomplishments – Technical Progress

2002

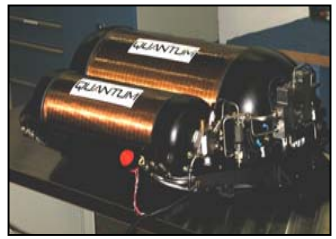
Validated & shipped 5,000psi tanks (NGV2, EIHP standards)

(7.5 & 8.5 wt %)

Validated & shipped 10,000 psi tanks (Worlds' first 10,000 psi tank; EIHP / TUV)

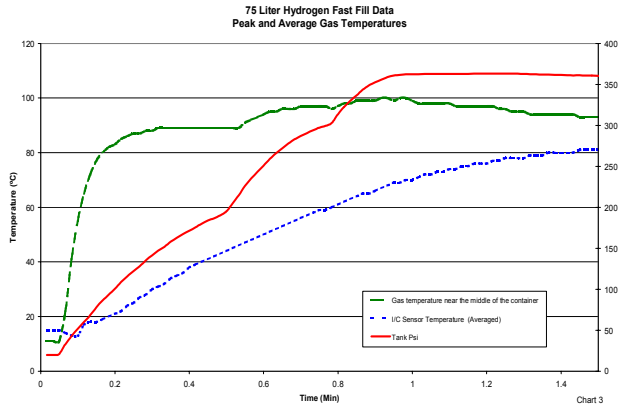
(6 wt %)

Certified complete 10,000 psi Storage System (EIHP / TUV)



(3 wt %)

Successfully demonstrated 10,000 psi fast-fill within 3 minutes



2003

Achieved 13.36 wt % tank efficiency (5,000 psi tank; aerospace)

Completed 5,000 psi tank & in-tank regulator production optimizations

Achieved >45,000 cycles fatigue life and 30% cost-reduction for 10,000 psi tanks (design, process)

QUANTUM

Accomplishments – Commercial Progress

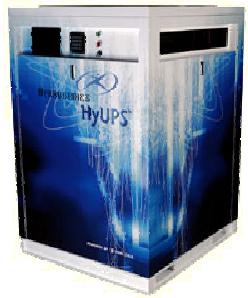
2002

Agreement with Hyundai to Jointly Develop Fuel Cell & Alt Fuel Vehicles

Texas Tech & Virginia Tech in Future Truck competition with Quantum tanks

GM's revolutionary Hy-Wire introduced with Quantum tanks

Quantum tanks used in stationary power application (NEXTEL, Hydrogenics)



2003

Ships Three Portable Refueling Systems

Production of Storage systems for Toyota

Supplies storage system to Suzuki

SUZUKI

Agreement with Sumitomo for storage systems Distribution

Sumitomo Corporation

QUANTUM

Future Plans / Milestones

- Refueling Strategy (Thermal Management with Fast-Fill) ('04)
- Structural Optimization of Tanks, Liners, Components ('04)
- Materials (Lower Cost Fibers, Strength & Cycle Life Trade-off, Liner Materials) ('05)
- Balance of Plant Components (Valves, Regulators, Filters, Relief Devices, Tubing, Fitting, Sensors, Mounting) ('05)
- Vehicle Hydrogen Safety (Impacts, Crash Statistics) ('05)
- Smart Tanks – Monitoring System to Support Lower Burst Ratio ('05)

QUANTUM

Conclusions

- 5,000 psi and 10,000 psi compressed storage systems are currently available and successfully deployed on fuel cell vehicles
- DOE 2005 performance targets are achievable
- Storage is a significant cost factor in overall fuel cell system cost
- Carbon Fiber and stainless steel hardware costs represent over 90% of the costs
- Design & process improvements to address storage tank costs are on-going

QUANTUM

Development of a Compressed Hydrogen Gas Integrated Storage System (CH2-ISS)

Peer Review Meeting

May 20, 2003

John Wozniak, Paul Wienhold, Rick Hildebrand, Mike House

The Johns Hopkins University Applied Physics Laboratory

and

Norm Newhouse

General Dynamics Advanced Technical Products

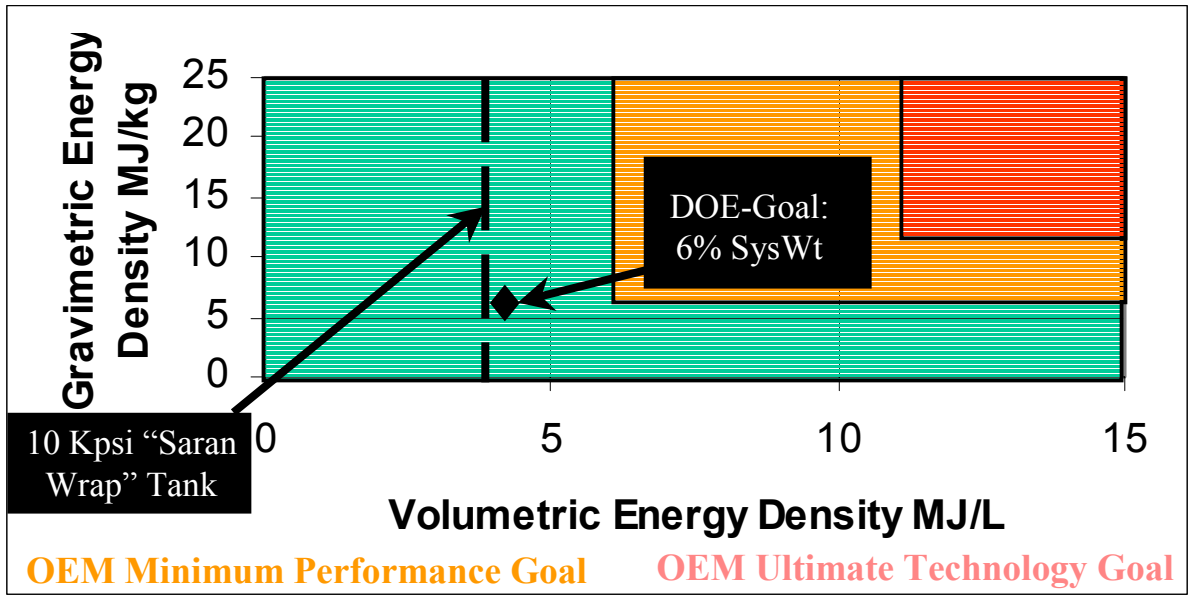
Peer Review Meeting Agenda

- Overall project relevance/objective
- Project Background
- Tasks – Goal/Approach/Accomplishment
  - Tank Technology – Overwrap/Permeation/Design
  - Shell Fabrication
  - Gas Control System
  - Vehicle Interface Technology
- Project Timeline
- Plans/Future Milestones

Project Relevance/Objective

DOE/FreedomCAR Hydrogen Storage & Vehicle Interface Technologies

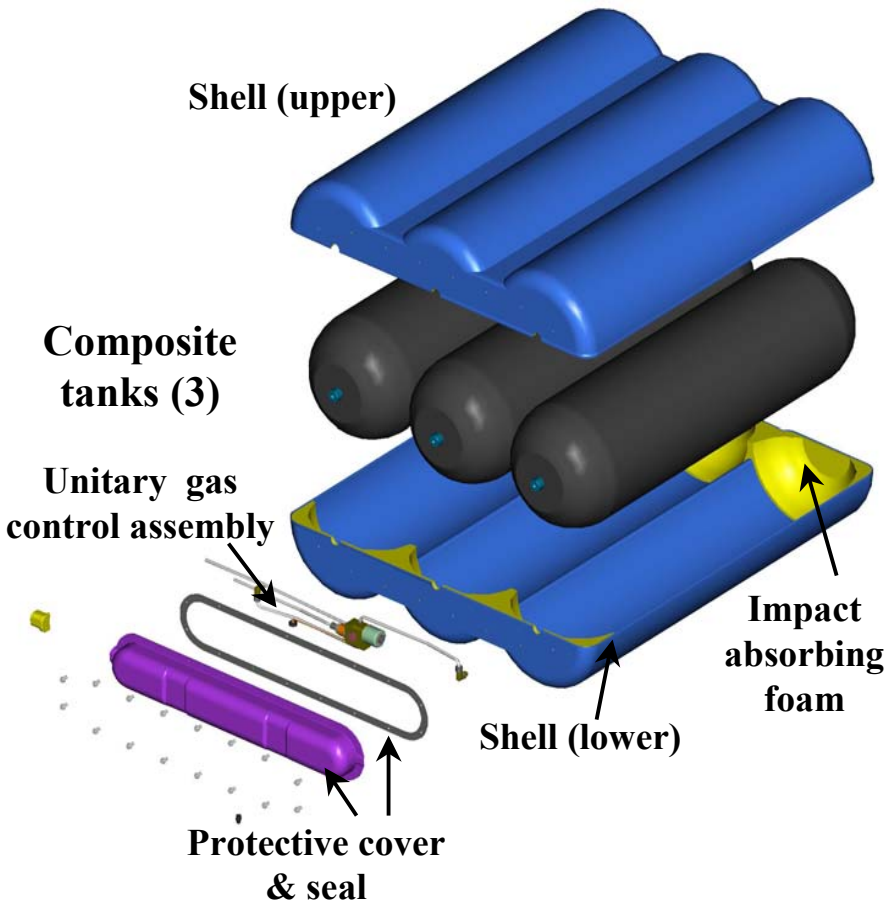
Energy Density for Hydrogen Storage Systems



" Advance the development of a cost effective, semi-conformable compressed hydrogen gas storage system and vehicle integration technology to enable FCEVs to have driving ranges comparable to conventional vehicles while not compromising passenger and cargo space or vehicle safety"

Integrated Storage System - Background

- High-pressure storage unit composed of tanks, outer shell, protective foam and gas control system all in an integrated package
- Role of pressure containment and abuse tolerance partitioned and optimized through design and materials selection
- Semi-conformable shape and lightly coupled to vehicle chassis to facilitate passenger "crumple zone"
- Protected by U.S. patents 6,257,360 (Compressed Gas Fuel Storage System, July 2001) and 6,321,775 (Gas Manifold, Nov 2001)
- NGV versions safety certified to FMVSS # 304 and undergoing long-term evaluation in experimental automobiles



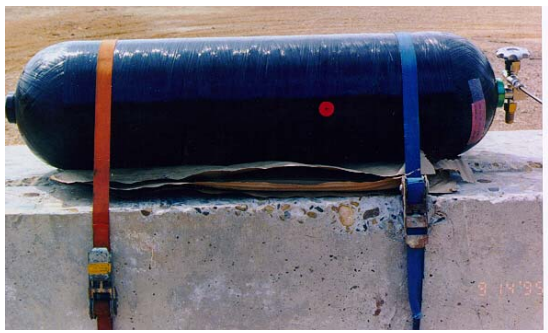
Integrated Storage System - Background Component and System Tests

Hydrostatic Burst Tests

ISS Safety Qualification Drop

ISS Guided Impact Drop

Tank Gunfire Tests



ISS Gunfire Tests

Hydrostatic Bursts

Liner Weldment Cold Impact

Liner Gas Permeation

Solenoid 50,000 Cycling

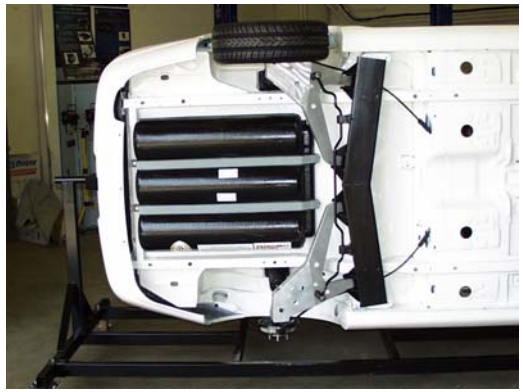
50 Cycle Manual Shut-off

Manifold 14,000 psi Safety

18,000 Cycle Pressurization

ISS Bonfire Qualification

Integrated Storage System – Background
Vehicle Application Experience



- **ANGV project supported ISS development, safety qualification and demonstrate vehicle packaging value**

- **For FCEV hydrogen gas storage, tasks are focused on :**
  - **Supporting higher service pressures (350/700 bar)**
  - **Scaling up internal volume**
  - **Satisfying hydrogen gas permeation requirements**
  - **Increasing energy density efficiency**
  - **Developing cost effective mass production design**
  - **Developing vehicle interface system design**

Toyota's FCHV

Tank Technology Task

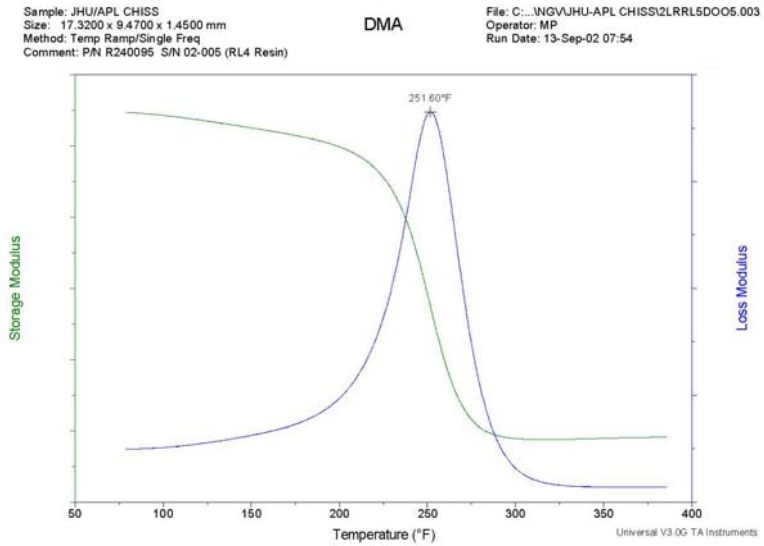
- **Goals**
  - Improve tank gravimetric energy density
  - Reduce permeation through liner
  - Optimize tank overall design for ISS application
- **Approach**
  - Establish baseline design and confirm through burst and gunfire tests
  - Revise design and conduct additional burst and gunfire tests as required
  - Conduct tests to confirm permeation in baseline tank construction
  - Evaluate materials and processes to reduce permeation
  - Develop design elements to optimize tank performance

Tank Technology-Accomplishment

(Overwrap)

- **Baseline Tank**
  - **Design**
    - » **T700 carbon fiber overwrap with high interspersed winding pattern with design FOS of 2.45**
    - » **NGV commercial tank resin system ; LRF-600**
    - » **Existing HDPE liner and bosses with 52.7 L capacity**
    - » **350 bar service pressure**
  - **Results**
    - » **Hydrostatic burst at 2.55 FOS**
    - » **Failed gunfire at 2.25 FOS**

- **Revised Tank**
  - **Design**
    - » **Similar design as baseline except for modified resin with toughness additives**
  - **Results**
    - » **Passed gunfire at 2.25 FOS**
    - » **However modified resin formulation lowered glass transition temperature and caused higher viscosity during winding**



Tank Technology-Accomplishment

(Permeation)

- **Permeation allowable per draft spec's is 1.0 scc/hr/liter at 350 bar**
  - **Represents 3% loss of gas per year from a tank**
  - **Some standards had considered reducing to 0.25 scc/hr/l**
  - **OEMs prefer further permeation reduction**
- **Permeation test results**
  - **0.91 - Baseline Untreated HDPE**
  - **0.25 - Option A – HDPE surface treatment**
  - **0.20 - Option B - Alternative liner material**
  - **Material cost, durability and manufacturability need further investigation**

Tank Technology-Accomplishment

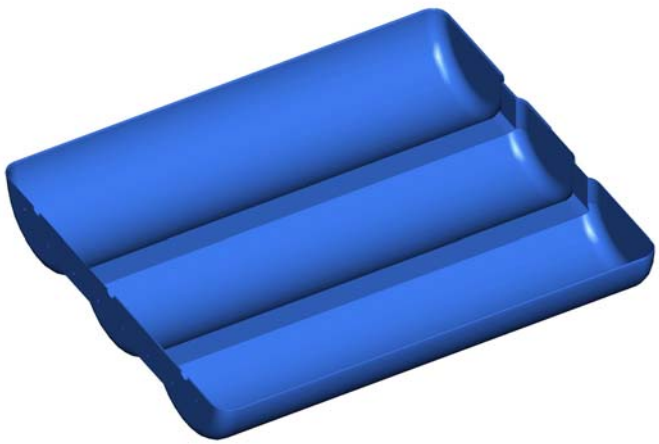
(Overall Design)

- **Design changes relative to baseline**
  - **Optimized bosses**
  - **Ultra-thin HDPE liner**
  - **All-carbon, 2.25 FOS overwrap**
  - **Maximized diameter**

- **Performance improvement over baseline**
  - **8% decrease in factor of safety**
  - **11% increase in internal volume**
  - **24% increase in gravimetric efficiency**

Shell Fabrication Task

- **Goals**
  - **Investigate appropriate fabrication processes for mass production of ISS shell and gas control system protective cover**
  - **Evaluate advantages and disadvantages of each process and material**
  - **Acquire valid estimates for non-recurring and recurring costs**
- **Approach**
  - **Develop CAD design of CH2-ISS shell and protective cover**
  - **Work with manufacturers to evaluate producibility, material recommendations, and cost estimates**
  - **Compile and compare candidate processes/materials**

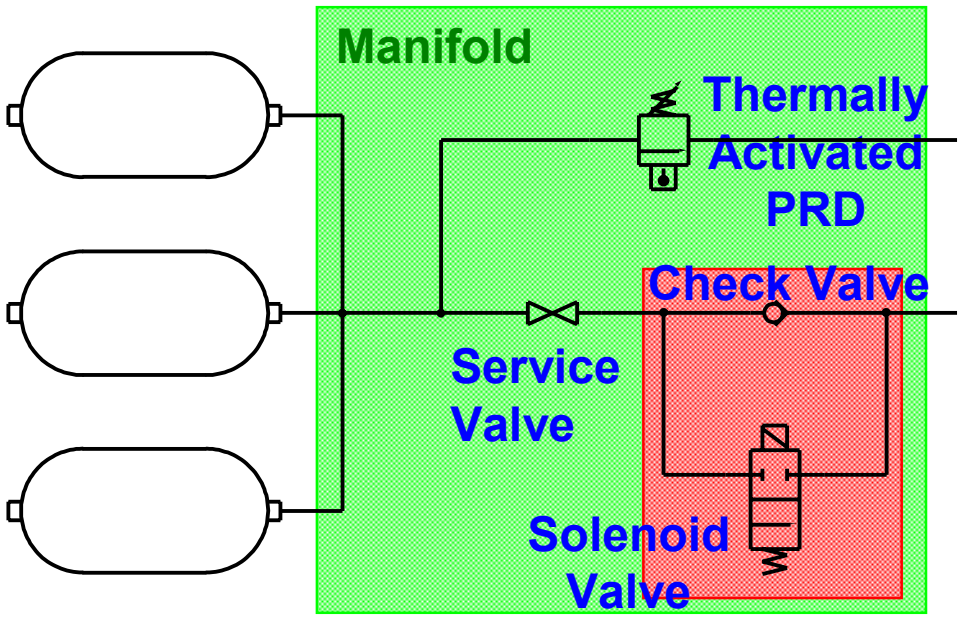


Shell Fabrication-Accomplishments

- Developed CAD solid models for composite and injection shell construction
- Performed shell manufacturing trade study
  - Provided 18 manufacturing suppliers with drawings and system requirements
    - » Part strength, roadway & environment conditions, impact strength, fire resistance
- Subcontracted National Composites Center, Kettering Ohio to evaluate Direct Fiber Preform / Structural Reaction Injection Molding (DFP/SRIM)process
- Compiled data on estimated part properties, nonrecurring cost and mass production part cost
- Downselected DFP/SRIM and compression molding with high-performance SMC as most viable alternatives
- Shell impact/fire property and "Design-for-Producibility" need further investigation

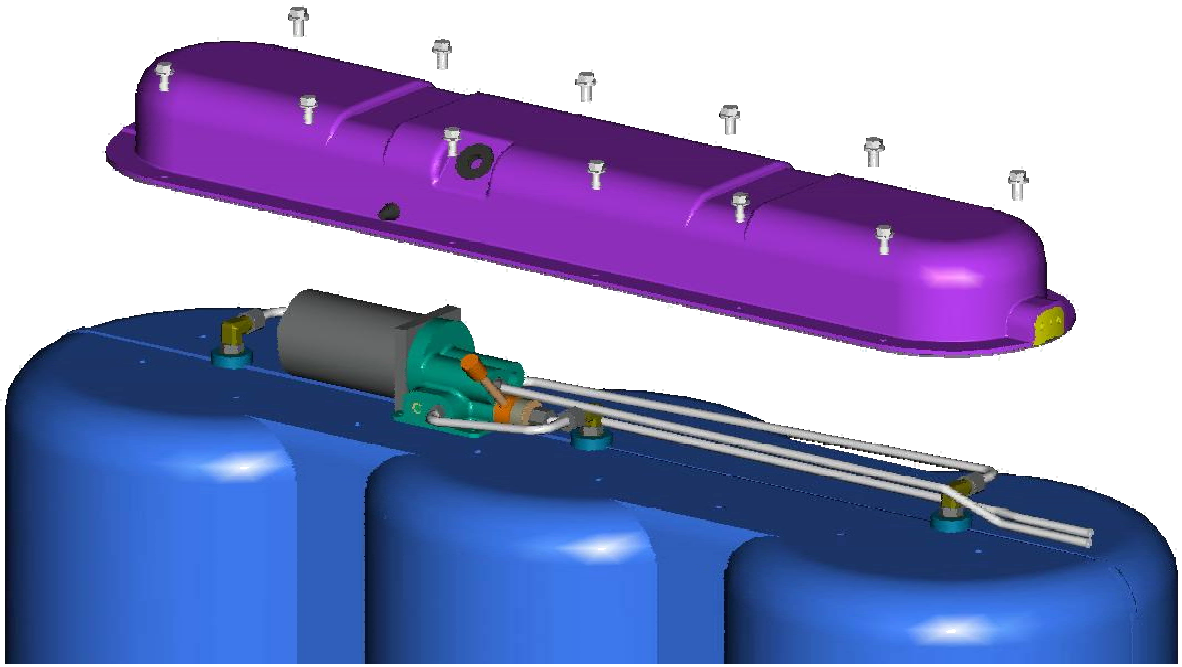
Gas Control System Task

- **Goals**
  - **Design a unitary gas control system featuring:**
    - » **Tank interconnecting manifold with single service valve, thermally activated pressure relief device and operational solenoid valve**
    - » **Low hydrogen permeation, high service cycle reliability, and tolerant to roadway vibration and temperature extremes**
- **Approach**
  - **Develop alternative designs and collaborate with valve manufacturer to support downselect to develop risk reduction prototype for test and evaluation**

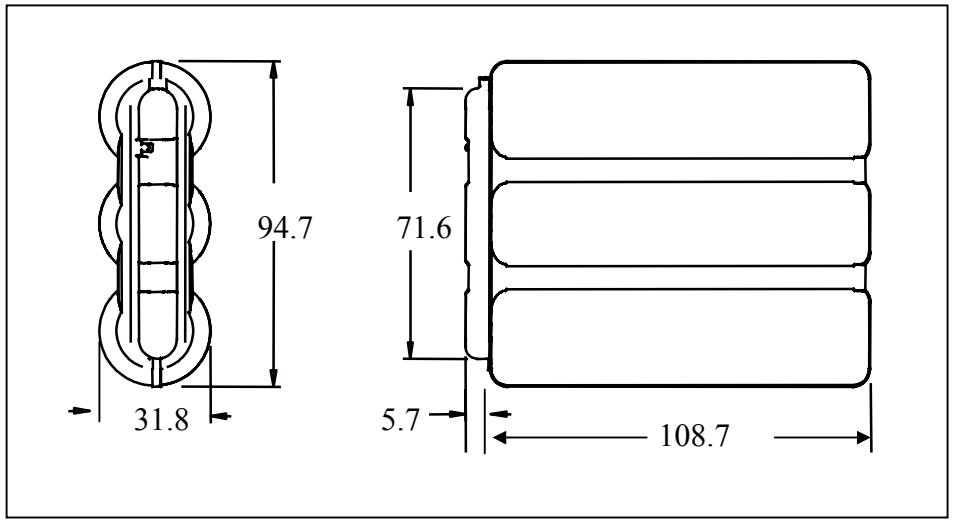


Gas Control System Task -Accomplishment

- **Accomplishments**
  - **Developed two designs using modified COTS elements and unique parts**
  - **Focused design to maximize crashworthiness protection, minimize cost of manufacture and reduce gas permeation**
    - » **Minimum number of o-rings, low permeation materials, high compression seals**
    - » **Calculate permeation rate 0.02scc/hr/liter**
  - **Partnered with Circle Seal for integration of COTS components and fabrication support**



“Current” CH2-ISS Design



ISS Interface Control Drawing (Dimensions in cm.)

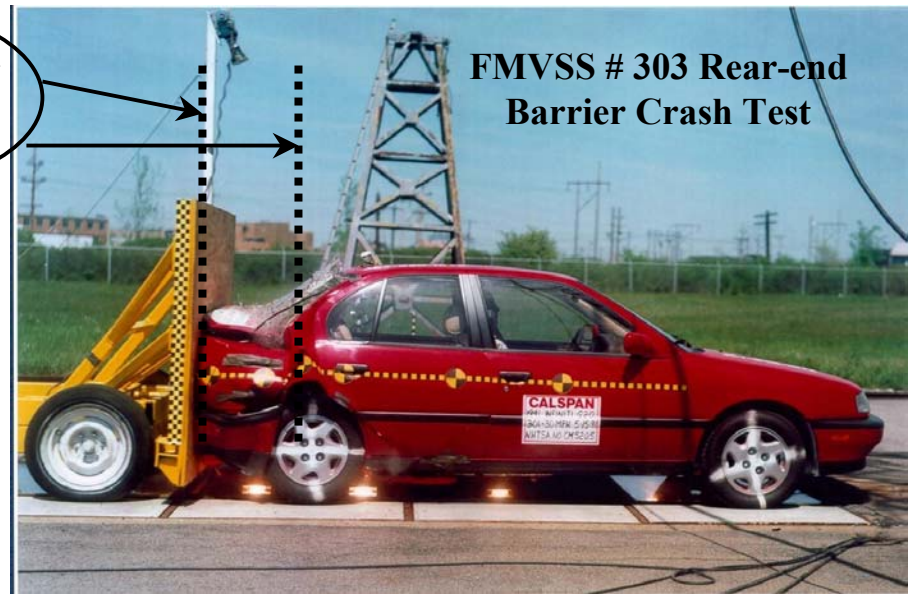
Total Empty Weight	73 Kg
Service Pressure	344 bar
Total Hydrogen Capacity	4.2 Kg
Gas/Container Mass Fraction	5.6%
External Volume	266 liter
Internal Gas Volume	166 liter

Net Volumetric Energy Density	1.9 MJ/L
Net Gravimetric Energy Density	6.7 MJ/kg
Specific Cost (Est.)	5.0 $/MJ
Hydrogen Loss	0.2 scc/hr/L
Cycle Life	> 10,000
Recoverable Capacity	> 95 %

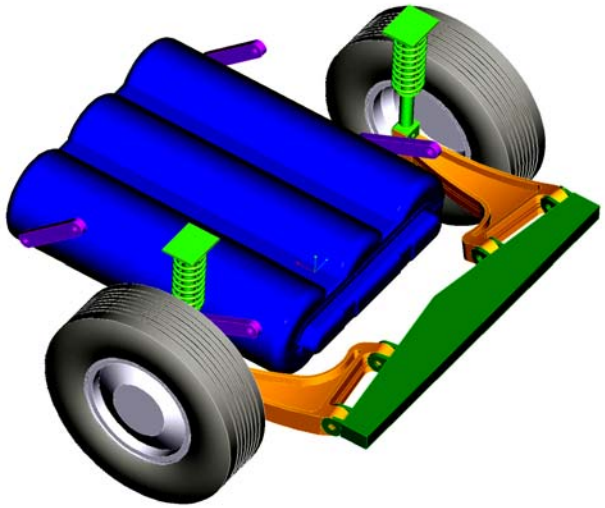
Vehicle Interface Technology Task

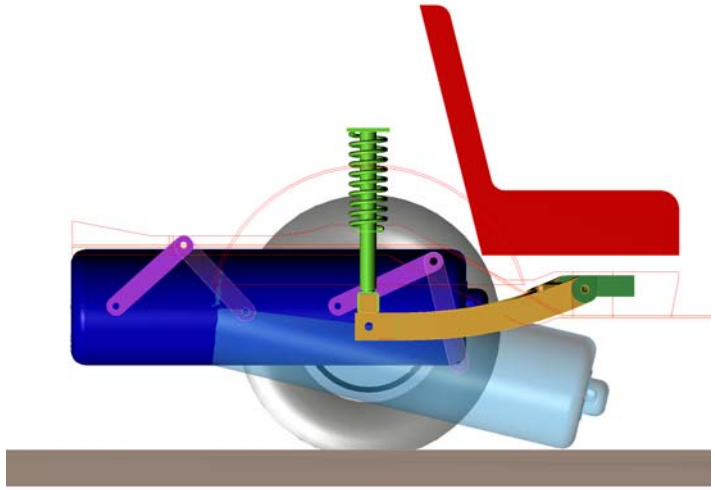
- **Goal/Approach**
  - **Develop ISS/vehicle packaging "point design" for FCEV**
  - **Storage system/vehicle interface intertwined for high pressure gas storage**
  - **Vehicle interface considerations**
    - » **Space for sufficient fuel capacity**
    - » **Preserving passenger and cargo space**
    - » **Ground clearance**
    - » **Passenger and fuel system integrity in collision**

Passenger safety "crumple zone "



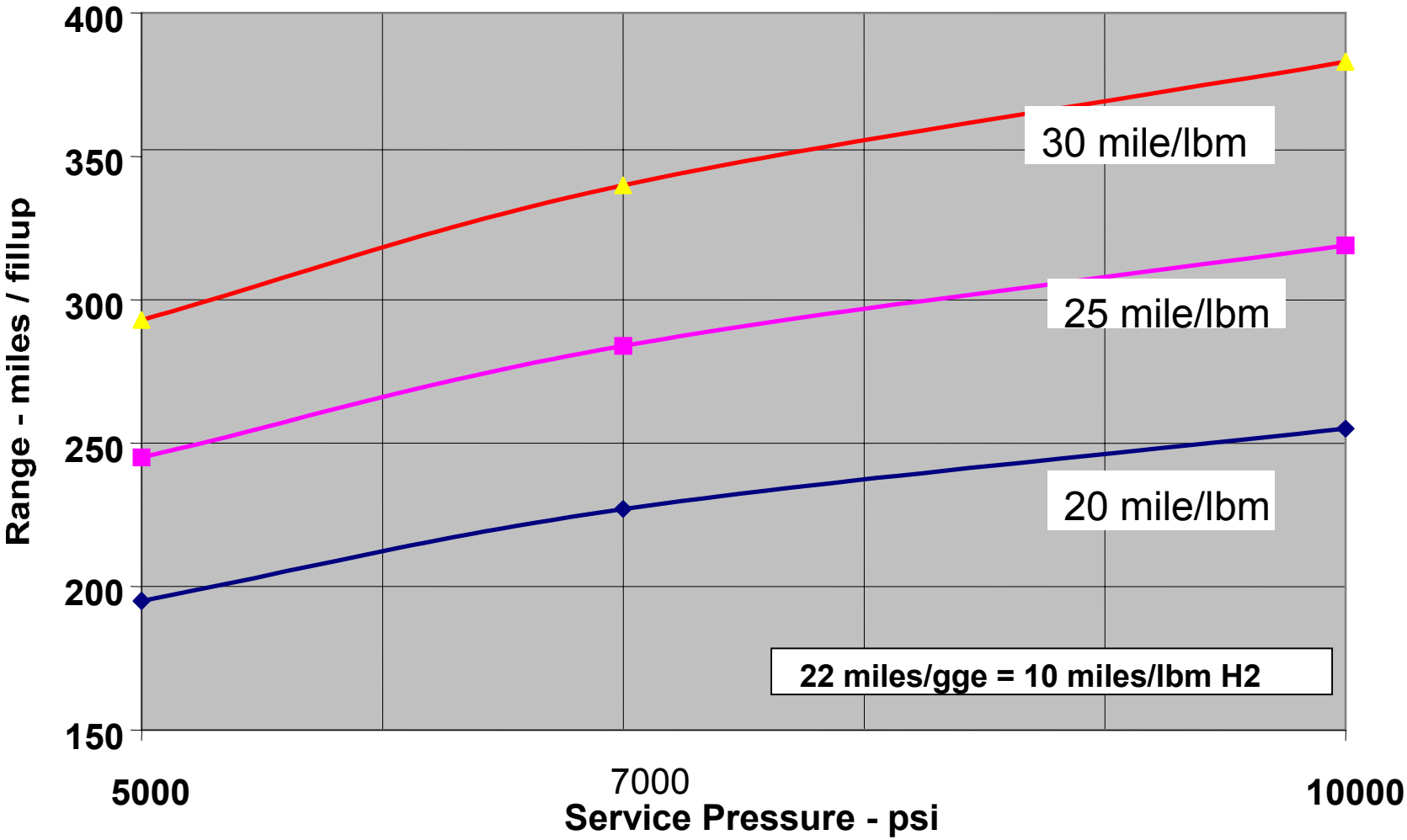
Vehicle Interface Technology-Accomplishments





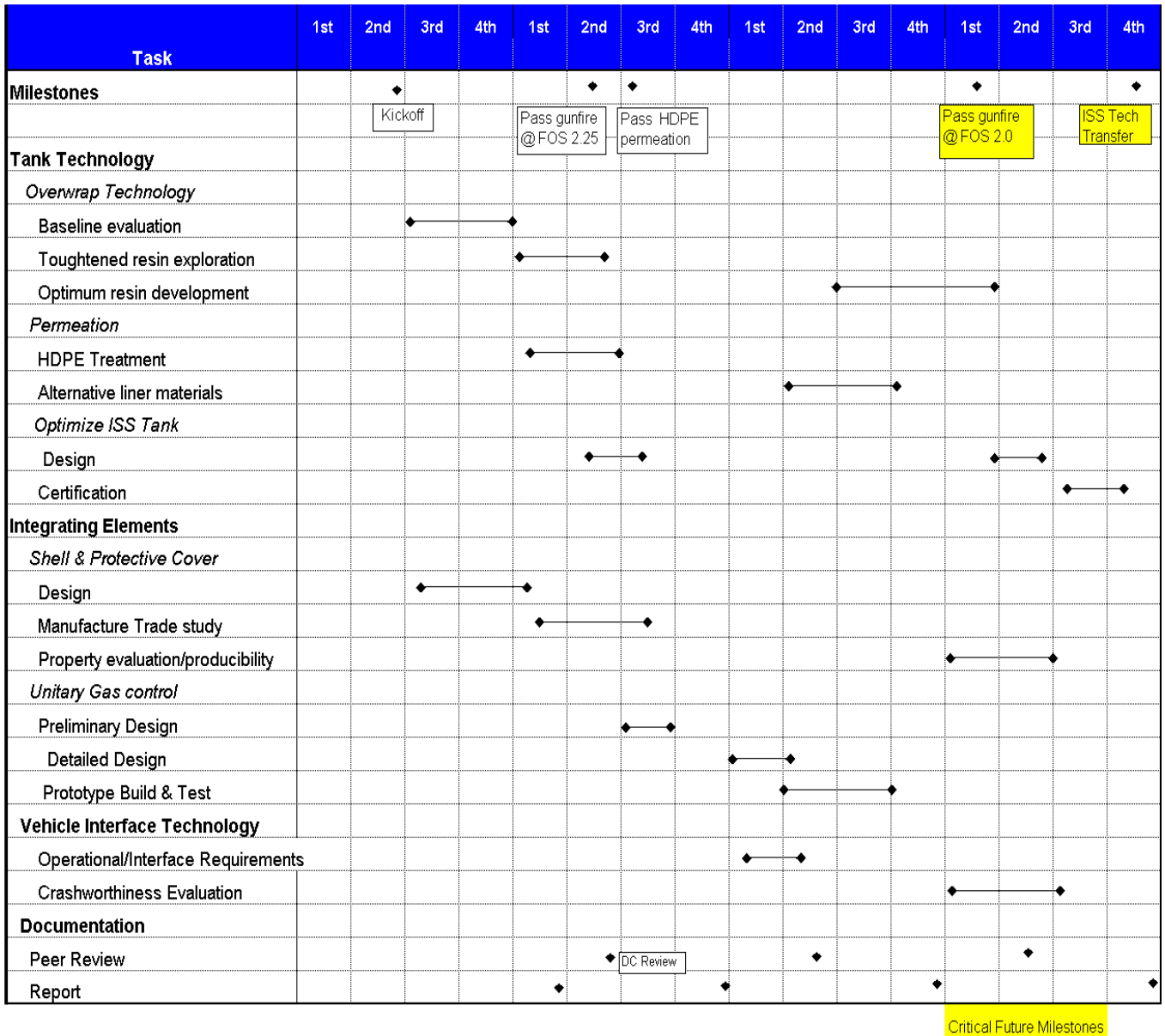
- **Developed preliminary vehicle interface/storage system packaging point design**
  - » CH2-ISS entirely in undercarriage with required ground clearances
  - » No reduction in passenger/cargo space for selected class of OEM platform
  - » Uses space tire space made possible with growing OEM "run-flat" tire trend
  - » Uses semi-trailing arm suspension designed to surround storage system while maintaining ride and handling
- **Initiated design of a "Crash Management System"**
  - » Breakaway linkage system (4-bar) to tip and guide CH2-ISS into undercarriage in high-speed, rear-end collision
  - » Controls collision energy imparted to CH2-ISS
  - » "Crumple zone' preserved to protect passengers; sensed g-impact shuts off hydrogen gas flow at the CH2-ISS

Estimated FCEV Point Design Driving Range



Based on "current" technology CH2-ISS with an external volume of 266 Liters

CH2-ISS Project Timeline



Plans/Future Milestones

- **Further increase storage energy density with optimized overwrap resin**
  - **Formulate optimized toughened epoxy resin**
    - » **Goals - Improved toughness, increased glass transition temperature, maintain processability with minor cost impact**
    - » **Approach**
      - ✓ **In collaboration with Drexel University perform parametric resin improvement study**
      - ✓ **Use optimized toughened resin(s) tanks for burst and gunfire tests with FOS < 2.25**
      - ✓ **Address issue : regulatory barriers, stress rupture reliability, blunt impact test**
    - » **Planned Milestones**
      - ✓ **Pass gunfire tests at 2.0 FOS with margin**
      - ✓ **15% increase in gravimetric energy density and 10% reduction direct material cost**
- **Finalize ISS Design**
  - **Conduct impact and fire resistance tests on shell candidate flat panel and work out design-for producibility issues**
  - **Finalize unitary gas control system design and fabricate prototype for test/evaluation**
  - **Develop CH2-ISS detailed design and cost for full development and certification**
  - **Seek commercial partner for CH2-ISS technology transfer**
- **Complete vehicle interface/packaging analysis**
  - **In collaboration with OEM or Tier I supplier support vehicle interface/packaging**
    - » **Further system design and assess characteristics**
    - » **Detail elements of Crash Management System**
    - » **Evaluate system crashworthiness via Large-Scale Deformation simulation**

Hydrogen Storage
Using Lightweight Tanks

DOE Hydrogen Program Annual Review
Berkeley, CA
May 20, 2003

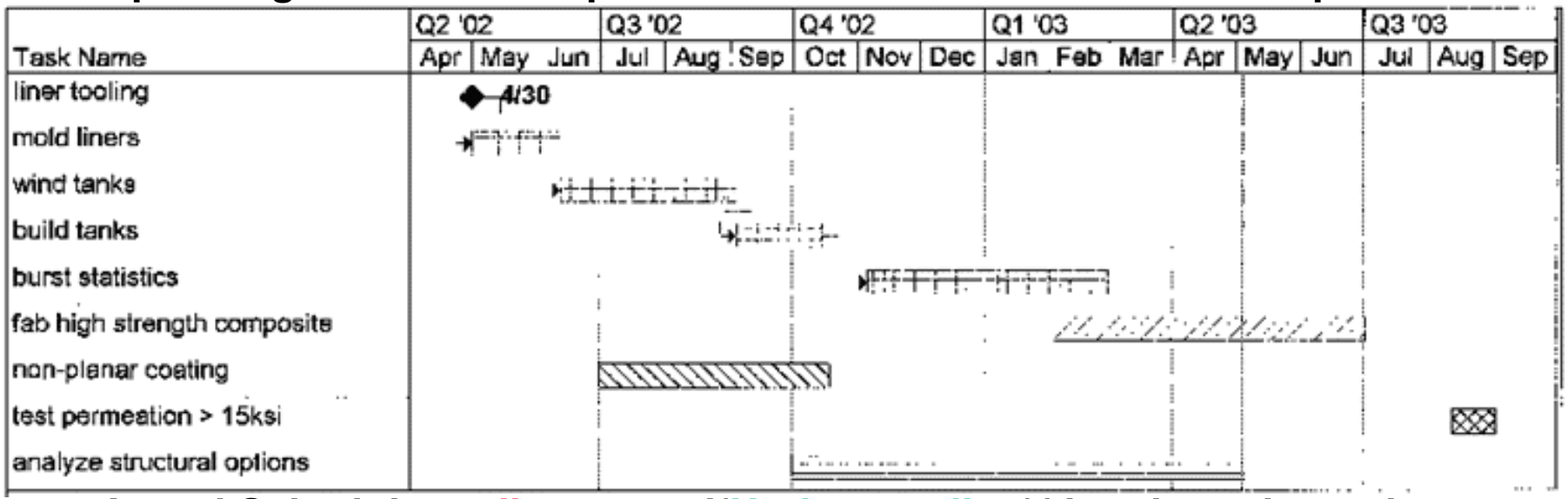
Principal Investigator: Andrew H. Weisberg
Collaborators: Blake Myers, Gene Berry

Point of Contact: Andrew Weisberg
Lawrence Livermore National Laboratory
7000 East Avenue, L-477
Livermore, California 94551-0808
(925) 422-7293, FAX: (925) 424-3731
Email: weisberg1@llnl.gov

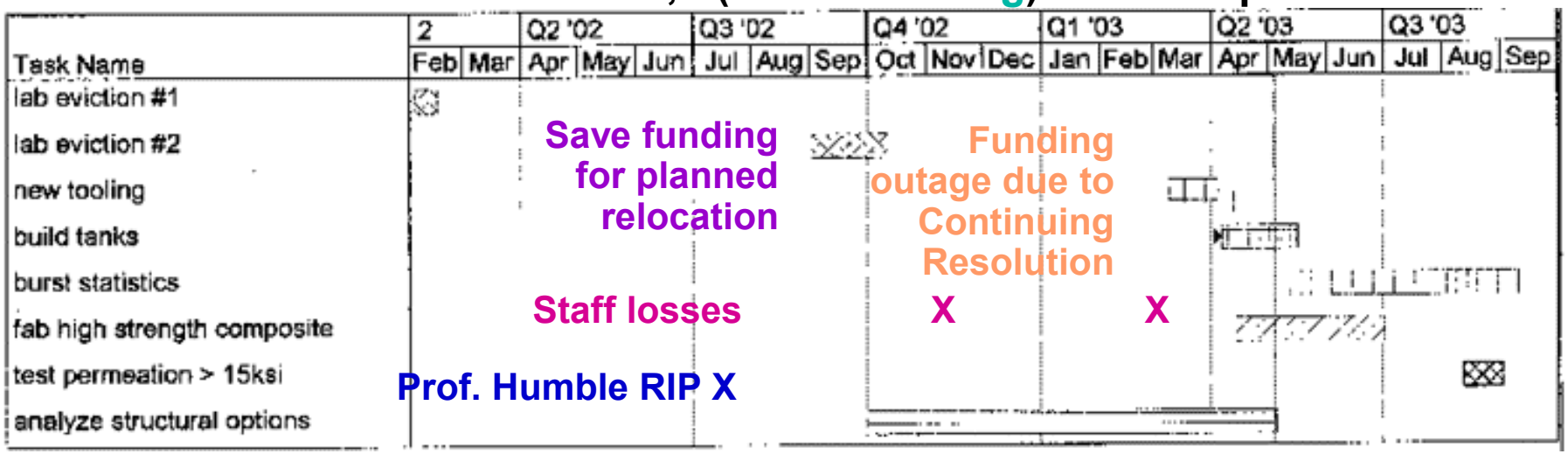
This work was performed under the auspices of the U.S. Department of Energy by University of California
Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48

Project Trajectory Through 2002 and 2003

- Tasks predicated on *predictable* funding and facilities occupancy
- Operating Plan for FY02 presumed eviction from 50% of lab space



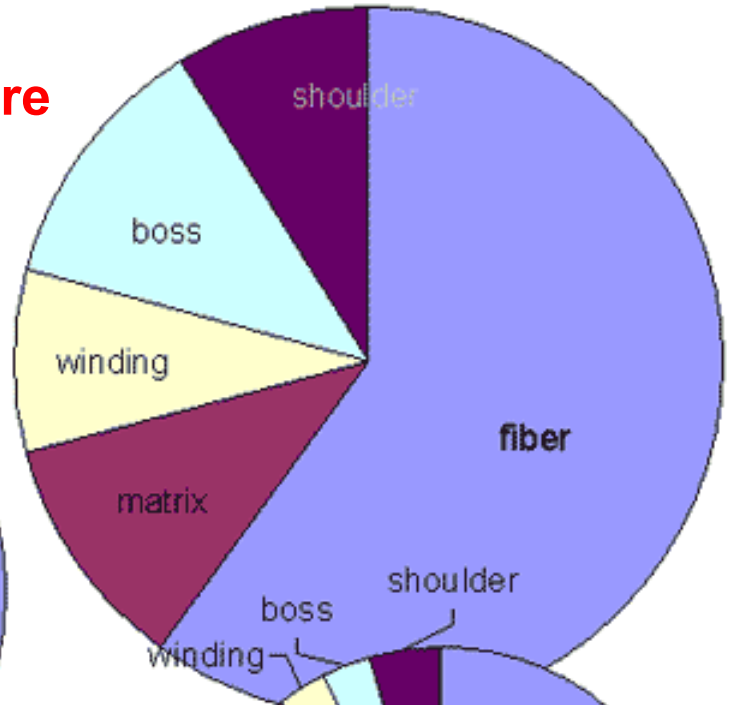
- Actual Schedule: 4 disasters, d(Understanding)/dt > than planned



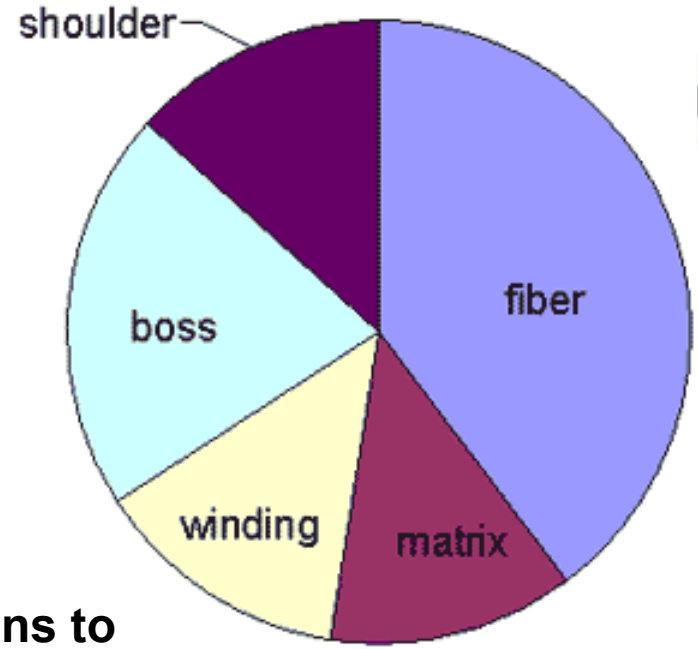
Cost Reduction Strategy (Advanced Type IV Tanks)

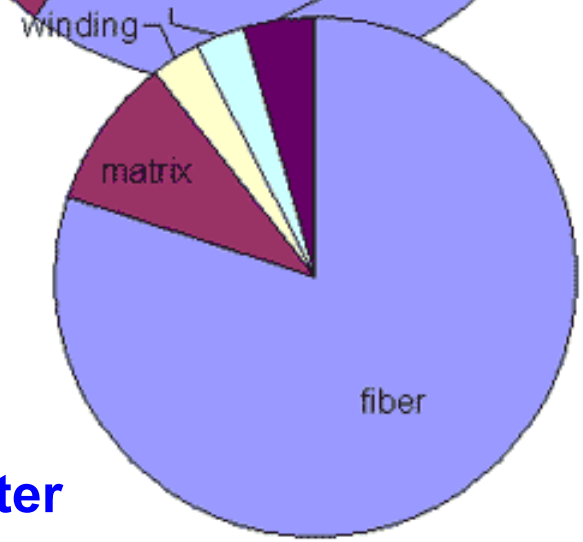
Promised approach to cutting costs of advanced compressed hydrogen tanks by factor of two

Before



Savings

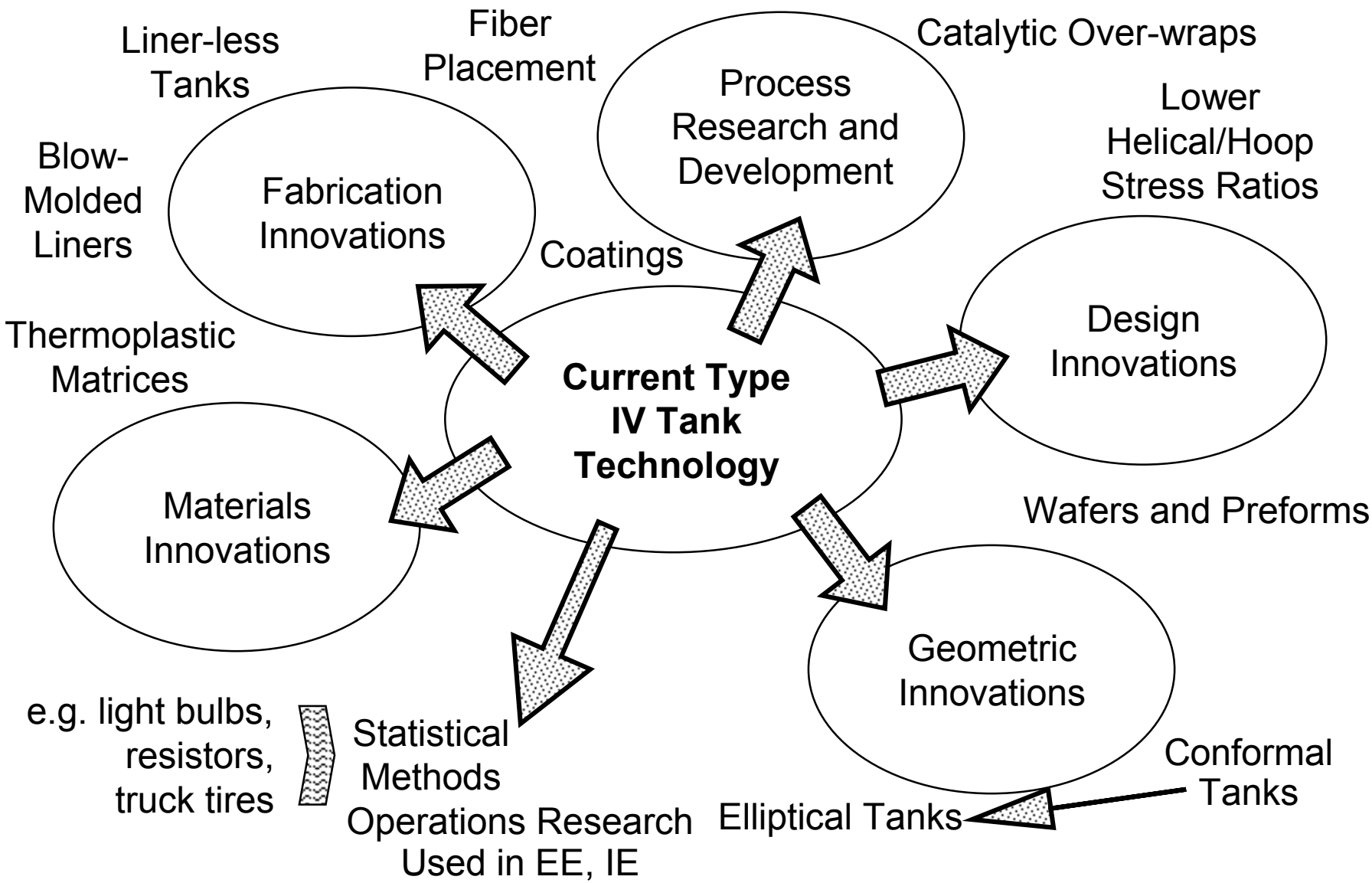




After

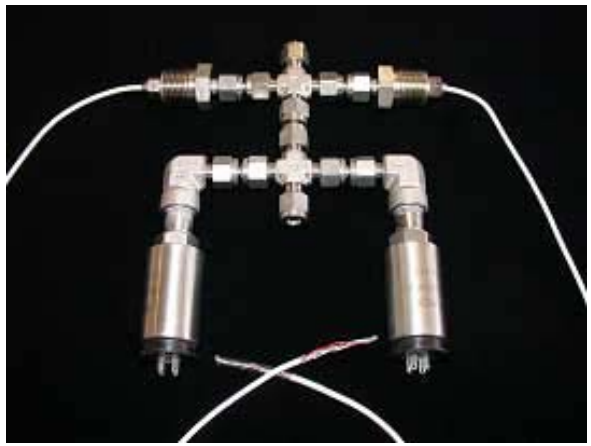
Comparisons to FY01 cost projections (confirmed in discussions with Quantum and Alliant) with updated fiber cost

Avenues for Improvement [Projected in FY01]



Statistical Experiments

- Intended to confirm utility of Statistical Process Control methods in use for many high-tech products [i.e. semiconductors, tires, light bulbs, biotech…]

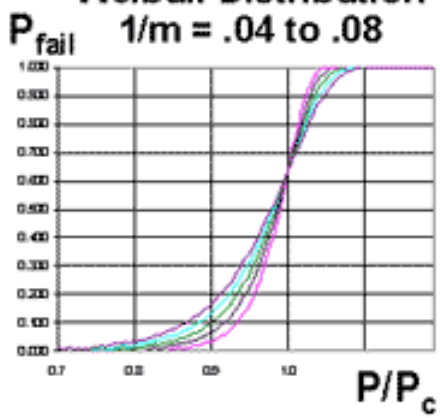


Sensors measure Pburst

Assembled Test Tank

- Method relies on samples from batch built under identical process parameters
- Parameters to Vary depend on Production method:
  - For wound tanks the most crucial parameters are cure Temperature, wind tension (affects both prepreg laminate compression and fiber pre-strain), and stress ratio (helical-to-hoop) – less crucial but potential sources of performance impairment from liner pressurization, helical angles, step back (each of which can introduce ~10 parameters)
  - For assembled tanks parameters include 2 or 3 fab temperatures, direct control of compression and pre-strain
  - Thermoplastic and metal matrix composites are affected by local heating geometry (size and timing of affected zone)

- Measurements' scatter 'identifies' Weibull Distribution 1/m = .04 to .08



Statistical Research

- Actual Failure Data collected from assembly failure forces

The first installment of structural testing wherein a nearly identical collection of samples is broken

Diameter	N	material	form	Epoxy	Shear Strength
0.840"	1	composite	tube	Vendor 1	200 psi
0.450"	4	composite	rings	Vendor 1	460-870 psi
0.335"	3	Mg	discs	Vendor 2	880-1025 psi
0.335"	5	Mg	discs	Vendor 1	380-670 psi

- Sample Size 'identifies' Weibull Disribution

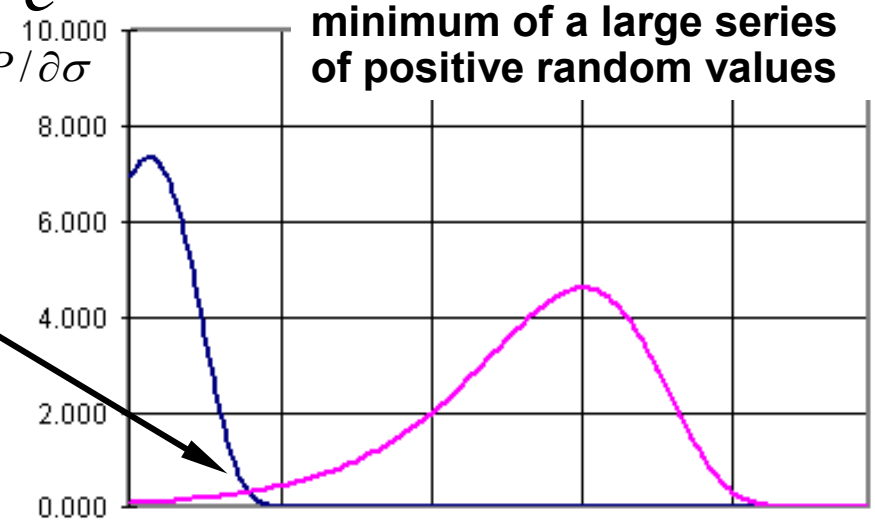
Weibull distribution

$$P(\sigma) = 1 - e^{-(\sigma/\sigma_c)^m}$$

$$p(\sigma) = \partial P / \partial \sigma$$

The other "extreme value" distribution (vs. Gaussian) correct in the limit of the minimum of a large series of positive random values

- Risk of 'suppressed' failure modes with higher variance is neglected in current safety standards – not good enough for thousands in service!

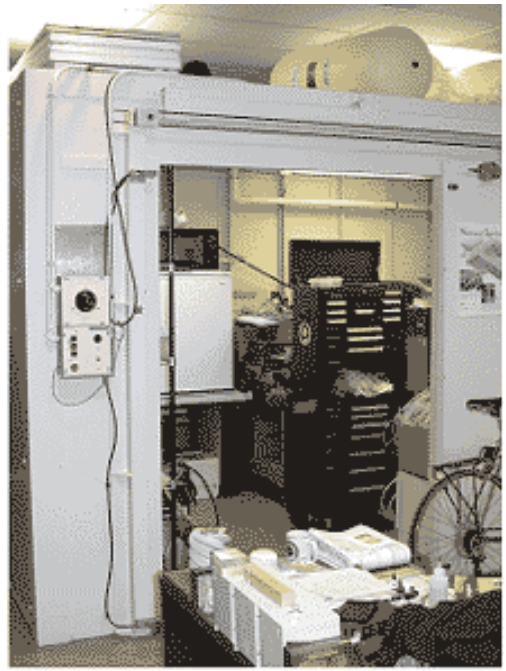


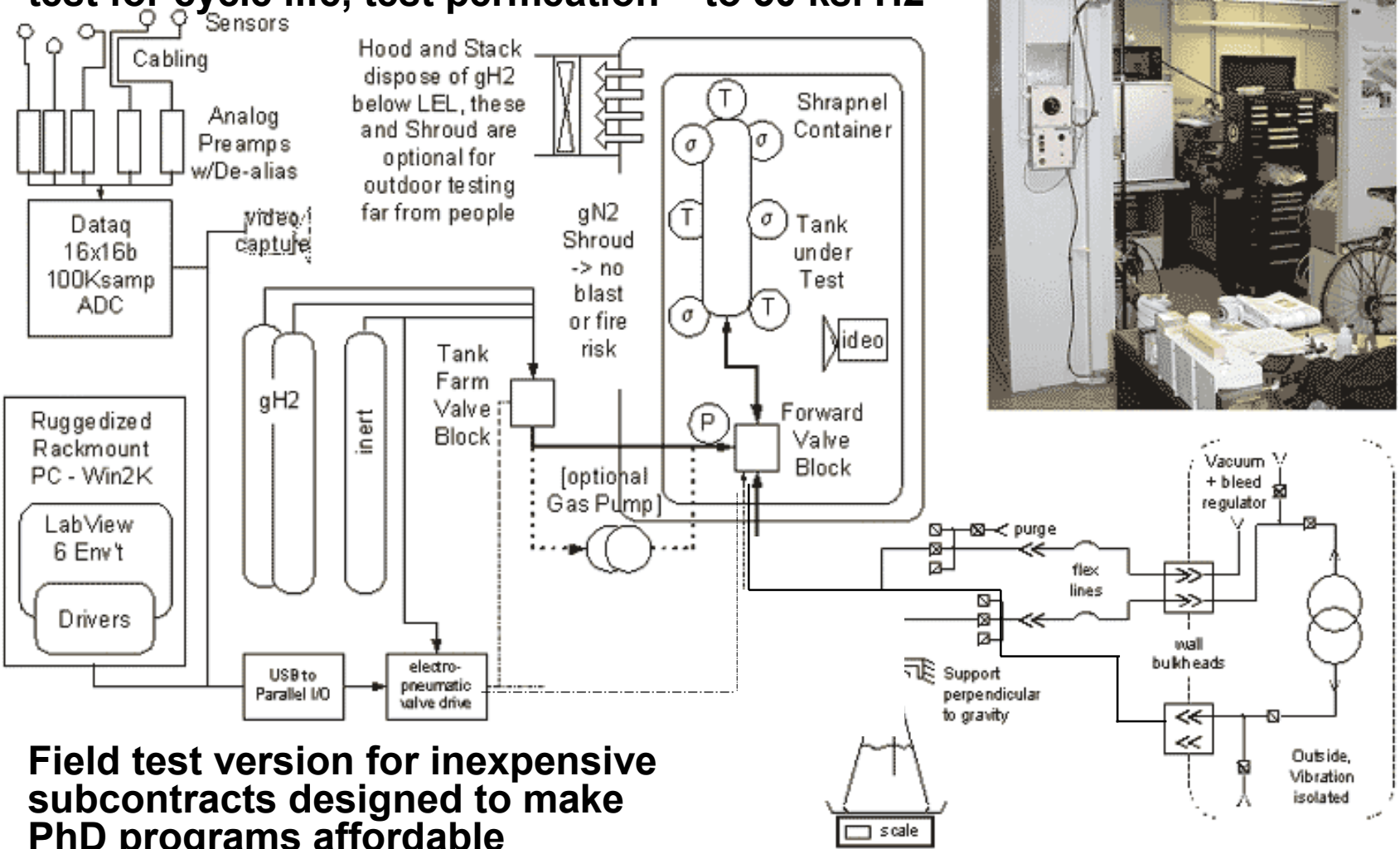
Overlap of 1/m=.05 and 1/m=.08 with "safety factor" of 1.3

- Recommend insurance requirements, European-required batch testing

High Pressure Experimental Facility

- **Experimental capabilities to burst test tanks, determine PbV/W [mass and volume efficiency] within 1%, observe fast failure phenomenology, test for cycle life, test permeation – to 50 ksi H2**





- **Field test version for inexpensive subcontracts designed to make PhD programs affordable**

Deferred Advanced Tankage Research Topics

- **Permeation – hydrogen diffuses through most materials**
  - **Curves fit to 5,000 psi (insufficient for optimal structural storage)**
    Diffuses as protons through metals, diatoms through plastics
    but what does it do in organo-metalics, densified xerogels?
  - **Cycle life of permeation = good to the end of service life?**
    No testing being done on permeation after cycling ~ "safety factor"
    As pressure ratings rise, current liners cycling above yield stress
    few plastics remain elastic beyond 10,000 psi, defects build up
- **Safety Innovations – several attractive possibilities**
  - **Strain energy in compressed storage could be advantageous**
    Megajoules stored in elasticity and PdV work are released by failure
    Compares to Gigajoules of chemical energy in stored hydrogen
  - **Sonic Disposer 'Nozzles' (hydrogen is very difficult to ignite)**
    Flame speed ~60 m/s easily exceeded by sonic jets from cracks
    Controlling how a container breaks can eliminate ~5% risk of fire
  - **Dust instead of shrapnel observed in > 3 different test programs**
- **'New' Physical Instability –> basic research + safe disassembly**
  - **Tensor 'debonding' waves presumed to dissipate strain energy**
  - **Faster than 4,000 frame/sec cameras -> arduous instrumentation**

“Turn to Dust” Failure Modes

Successful (mass record set in June 2000) tanks turned to dust in a single frame on high speed cameras

This potentially *benign* failure mode displayed almost no localized fracture, releasing fine ‘shrapnel’ that can be easily stopped by thin shielding

The “missing 7%” *may* be understood

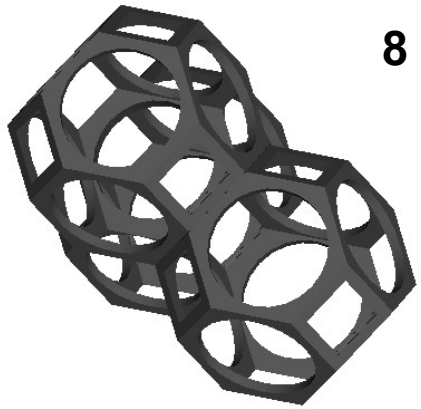
- Stress ratio (helical / hoop) “too high”
- Dome failure activated – high dispersion
- Real manufacturing problems on dome

A poor trade off : wider tows cost less but imply more severe 3D effects in dome

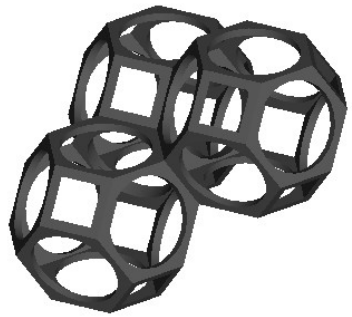
This is a repeatable class of failure modes with the potential for new Science and Engineering (designer failure modes)!

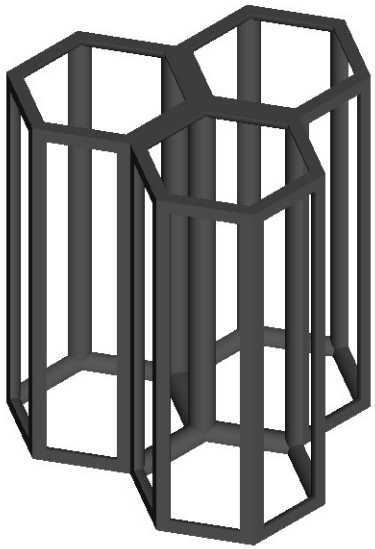
The Ultra-Conformable Zoo

- Initially believed fabrication easiest for hexagonal facets of truncated octahedral cells
- Discovered that curvature at corners of closed-trajectory faces implied excessive shear stresses that would fail matrix

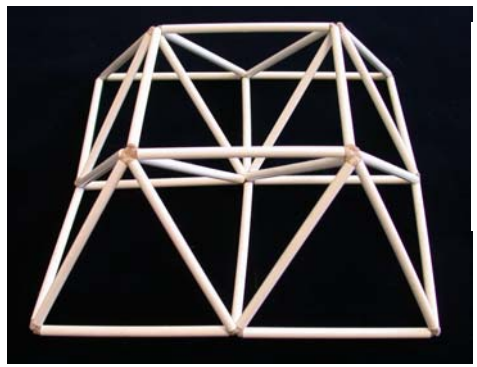


8 'wound' faces (nearly rings) can assemble to fill space

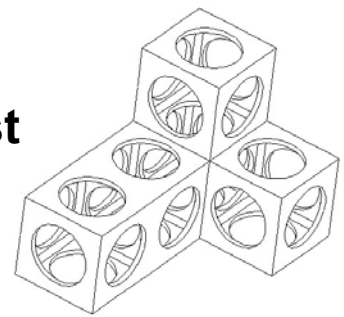




- Problems with radii of curvature are fixed by trusses whose replicated fiber struts don't cross

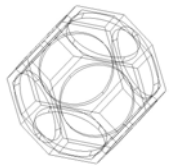


- Fuller's "Octet Truss" is strong in shear, which may or may not be a feature, compared to cubic
  - Cubic best for strong biaxial materials



- Solid modeling of replicates non-trivial, hexagonal-closed-packed cell was easiest to render, builds slabs with skins

Macrolattice Replicates



- **Mass produce identical parts**

  - **Speed down the "Learning Curve"**

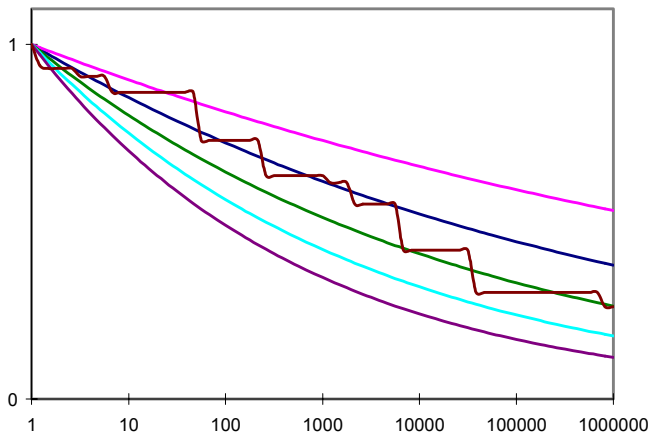
    Millions of parts for just

    hundreds of vehicles !

- **Statistical Qualification (large N)**
  - **Many container geometries**
  - **Collect data separately for**

    Each type of node, edge, face

Learning Curves



- **Metaphor = Architecture**
  - **Not many domes or arches**

compared to 'endoskeletal' structures built routinely by assembling multi-use parts

  - **A 'vocabulary' of geometries from a fixed lexicon of parts (more is richer)**

Advanced Materials = Worthwhile Frontiers

- **Metal Matrix Composites**
  - **Modification of max-strength continuous fiber = 10 Gpa failure graphite**
    - Only ~30% worse mass performance than epoxy matrix with same fiber
    - But ~3X higher shear strength reduces minimum cell size of macrolattices
  - **Whisker composites – diamond whiskers at 5 Gpa**
    - Dissolve in molten Al, but SiC coating found to allow *castable* mixtures
    - Mass performance ~50% worse than 10 GPa graphite in epoxy
      - Compares favorably to most economic 5 Gpa graphite-epoxy, lower cost!
  - **Nanocrystaline structures**
    - Some CVD and xerogel deposition methods produce spirals 20-300 nm
- **Nanolaminates – an LLNL innovation sputtered 2m meters wide**
  - **Soon to be deposited by sputtering with roll-coater (DOE funding)**
  - **Only 500 MPa failure, but strong in two axes and no matrix**
    - Comparable volume to most economic graphite-epoxy, but ~2.5X mass
    - Extremely flexible and tough -> tanks that bounce, ideal macrolattice skins
- **Nanolaminate 'Adhesives' – chemical energy fuses thin films**
  - **Likely can bond metallic thin films with >250 MPa shear strength**
- **Amorphous Metals – 2002 MRS 500 MPa, cheapest two-axes-strong**
- **Deep Compression – if prestress can be induced, Al_20_3 at –13.5 GPa**

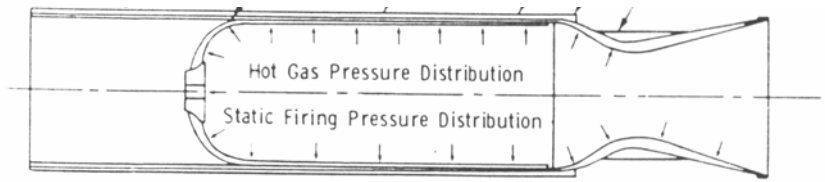
Mass-Performance Horizons

- **Potential to exceed incremental progress in physical containment**
- **No manufacturers will be harmed by funding basic research**
  - **Test articles capable of hydrogen storage are *not beyond 2012 horizon***
  - **Materials Scientists have yet to work on relevant structural performance**
    Considerable work on wear resistance, hardness, toughness, refractories
- **Factor of ~14 mass reduction (applicable at any T) is conceivable:**
  - **First factor of 1.5X comes from empirical statistics sought in this project**
    Might be pushed as high as ~1.8X for millions of units tested (macrolattices)
  - **Another factor of ~1.05X comes from several liner innovation prospects:**
    Thin liners = prestress Elgiloy –0.3%, POSS Oligomers, spin glasses and
    Linerless (e.g. DCPD matrix) and/or coatings << combined high probability
  - **Another factor of ~1.15X is available from packaging innovations:**
    Regulatory relief from incompetent installers = no shoulder pads (3 ways)
    Miniaturize bosses, pre-fab center of end-dome, smaller in-tank fluidics
  - **Process innovations that push fiber fractions above 70% -> factor 1.3X**
  - **Next factor of 1.5X comes from geometric innovations, with decrements:**
    Non-axisymmetric winding of spheres saves 1.5X but wastes > 12% volume
    Macrolattices and Hierarchical Structures tradeoff in mass overhead ~10%
  - **Factor as high as 1.9X (most fibers) available if pre-stress can be built in**
  - **Factor of Two available from materials with strength in two axes, not one**

Why Storage Mass Matters

- Range at cruise limited by drag
  - Power from fuel enthalpy ζc^2
  - Energy-per-unit-volume wins
  - Volume fraction of vehicle
- Appears to make mass irrelevant !
- Hard to reconcile with Aerospace

$$\text{Range} = \frac{2\rho_E \eta \zeta \Lambda \sqrt[3]{\text{Volume}}}{\rho_{Air} \Gamma M^2}$$



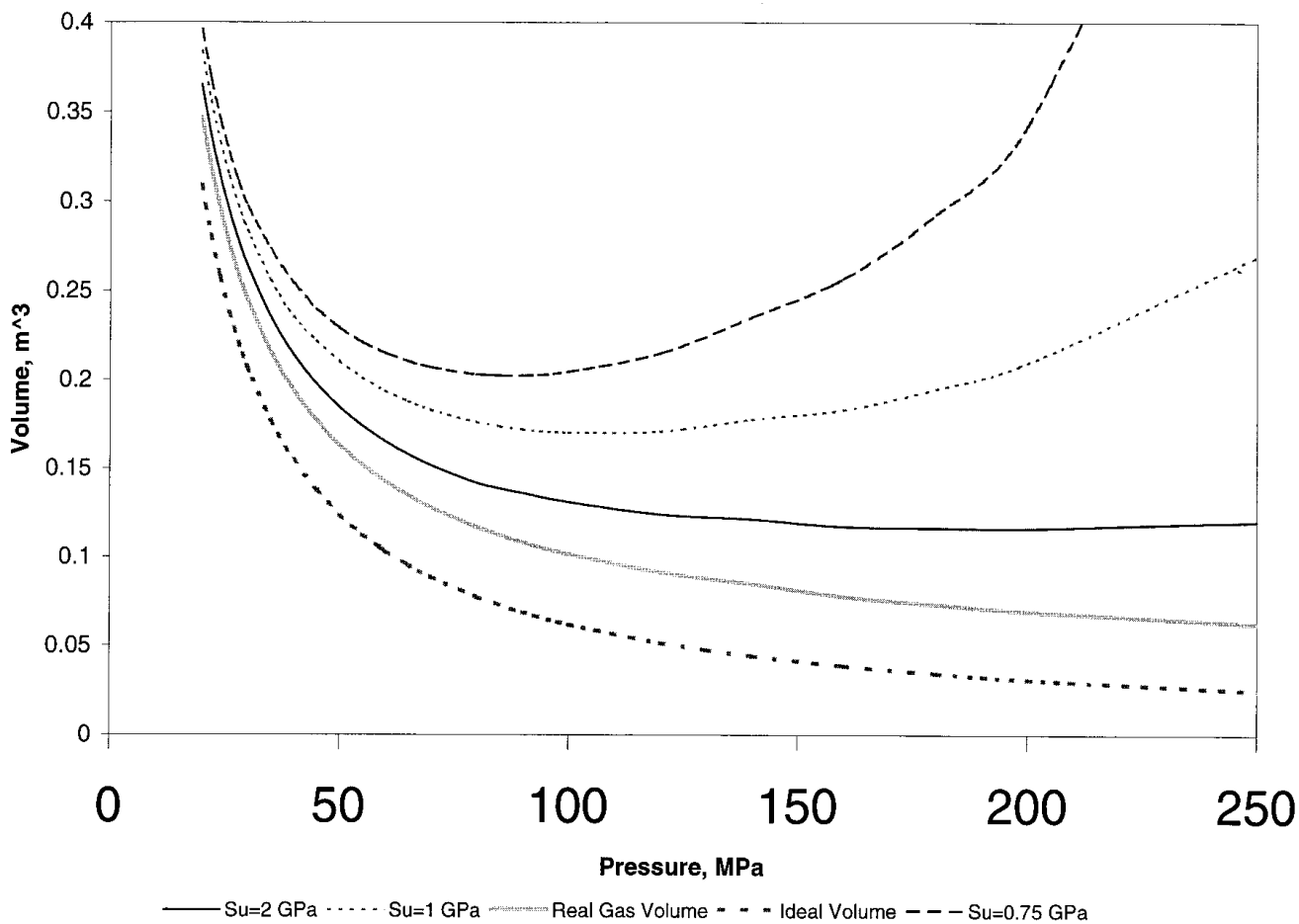
$$\text{Range} = \frac{2\eta\zeta\Lambda m_{total}}{\rho_{Air}\text{Volume}^{2/3}\Gamma M^2}$$

- drag limited range in mass fractions
  - Same role for enthalpy $h = \zeta c^2$
  - Energy-per-unit-fuel-mass here
  - Mass fraction of vehicle in fuel
- Still depends on vehicle volume but 2X stronger dependence

- Note dependence on total mass
- "Clean sheet of paper" analyses, but
  - Assumed total mass and volume were specified independent of ζ and ρ
  - Either form is only true as a perturbation that doesn't change totals
- Perturbation theories break down when mass or volume fractions -> 0.1
  - This is the case for 300 mile range with current physical and chemical hydrogen storage, but not for < 150 mile range – a "dirty sheet of paper"
  - Hydrides don't directly falsify volumetric range equation, physical does

Widely-Applicable Conclusions

Graph t (volume ratio) vs. ζ (Work to ΔG ratio) for Type IV tanks



F (mass ratio) computable from t (volume ratio) X density ratio

Dimensionless Notation

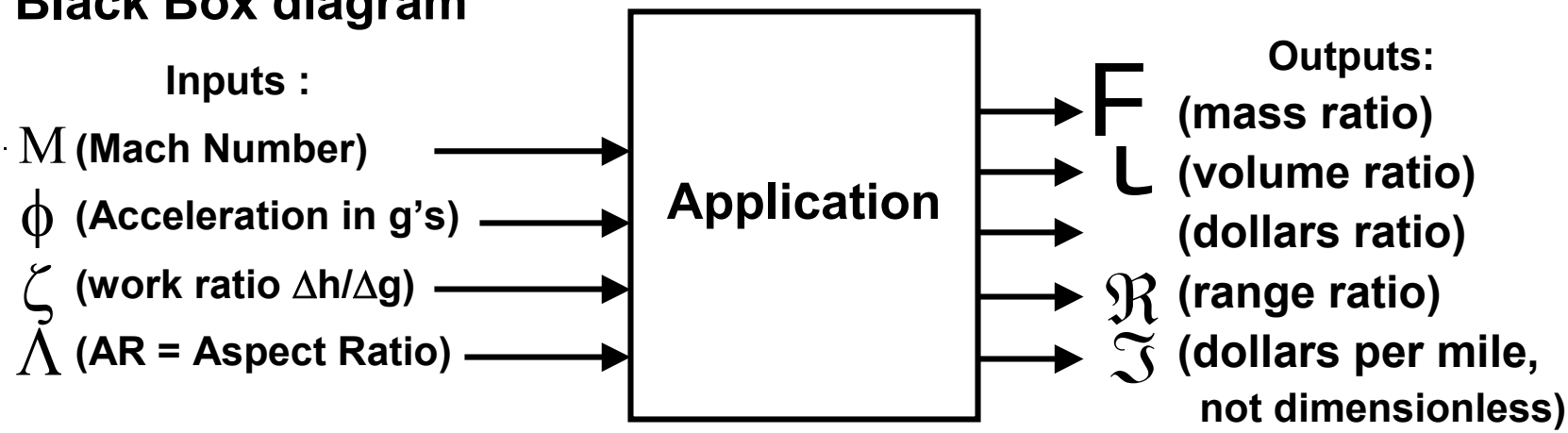
- **Symbology facilitates comprehension**
  - **Too easy to confuse volume and velocity**
  - **Subscripts don't immediately decode**
    Volume vs. mass vs. power fractions
    Which quantities are bounded < 1
  - **Show by inspection what has dimensions**
- **Use of Greek characters** →
  - **For dimensionless quantities, usually > 0**
- **Only exception is ρ, used for density**
  - **Others non-dimensionalized via c and g**
- **Use of Kannada characters**
  - **Table below shows fractions of total:**

	mass	volume	cost	power
Energy storage	gÀ	Á	o	D
fuel available	F	t	<- energy fractions	
Power Train	vÀ	9	«	P
Structure	Uï	Q	M	
Payload	£À	zÀ	—	ò

M	= Mach Number = velocity/sound-speed (c ~ 300 m/s)
Λ	= Aspect Ratio = AR = frontal-area/spherical-surface-area
Γ	= Drag Coefficient = Cd = drag-force/kinetic-pressure*front-area
Ψ	= Lift-to-Drag Ratio = L/D = lift-force/drag-force
μ	= Coeffieceint of Friction = friction-drag-force/normal-force
Ξ	= Avogadro's Number = particles/mole
ϖ	= Average Molecular Weight = grams/mole
γ	= Ratio of Specific Heats = Cp/Cv
η	= Efficeincy (power application) = power-delivered/power-consumed
ϕ	= dimensionless acceleration = Thrust/mass*g (g = 9.8 m/s2)
φ	= Mass Overhead = added-mass /functional-mass
ϑ	= Stress Coupling Ratio {at Ncycles} = shear-stress/fiber-tensile-stress
ζ	= dimensionless specific strength = Joules/kilogram*(speed-of-sound)2
ξ	= dimensionless specific power

Mixed Dimensionality Theory

Black Box diagram



Calculus of Variations for constrained optimization (e.g. min J = $/mi)

Use Lagrange Multipliers to constrain (e.g. = constant -> min J + $\lambda\Re$)

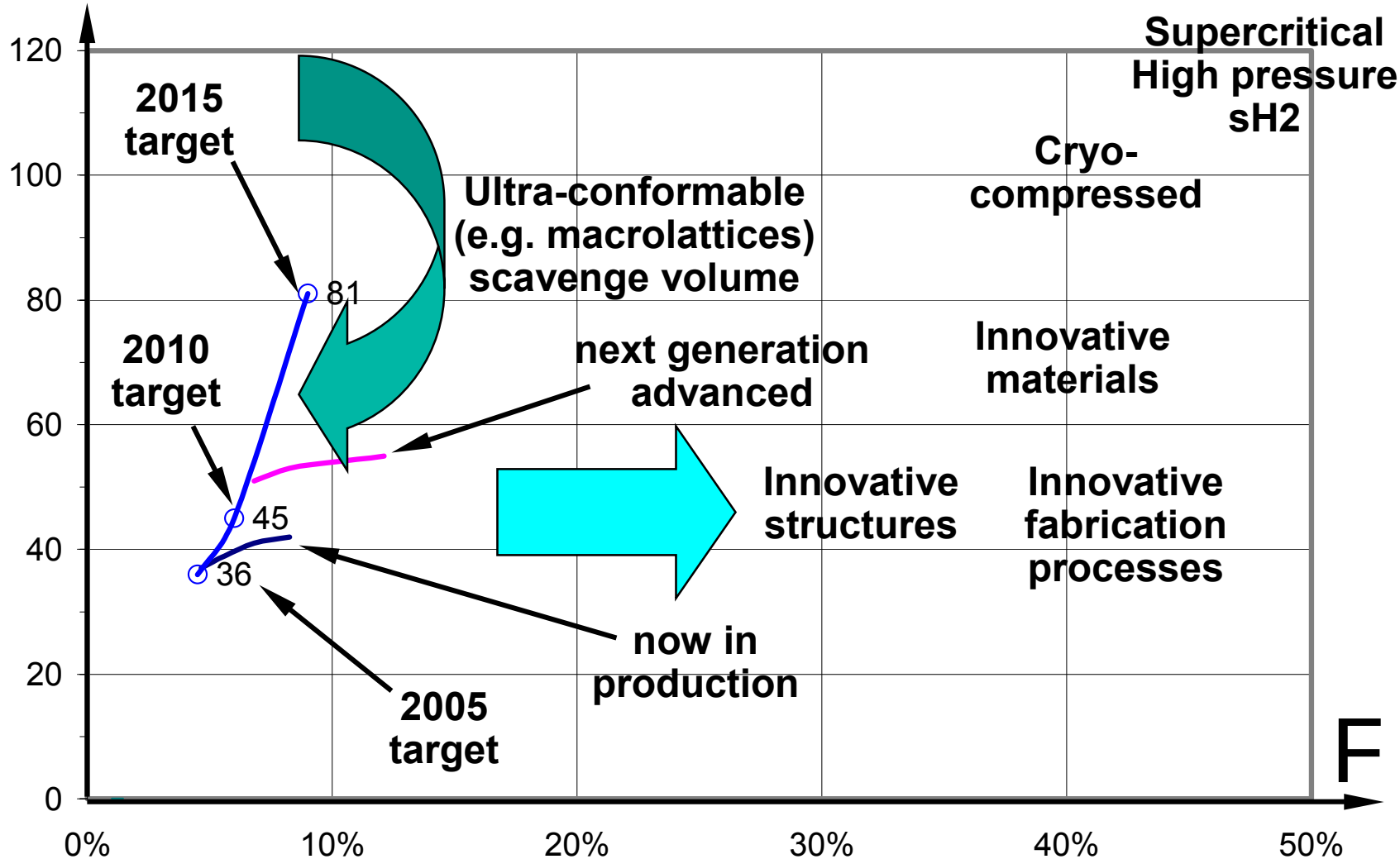
- **Mass partitioning derived from rocketry** $\pounds = 1 - q - v - U\dot{t}$
  - **The "Rocket Equation" non-dimensionalized:** $q = \exp\left(\left|M_{final} - M_{initial}\right| / M_{exhaust}\right) / F$
- **Extended to the Aircraft Range Equation:** $\Re = \text{Range} * g/c^2 = \Psi\, \eta\, \zeta \ln\left(1/1 - qF\right)$

  where ζ refers to fuel enthalpy $/^{/}c^2$ and η is thrust efficiency
- **Applies directly to vehicles whose power goes into friction** $\Psi \rightarrow \mu$
- **Solve for and eliminate Lagrange Multiplier with:**

$$\partial(J + \lambda\Re)\big/\partial V = 0 \quad \lambda = -V m_{total}\, g(\partial J / \partial[V m_{total}])\xi \big/ \zeta\eta M \qquad \Re = \frac{q}{V}\left(\frac{\zeta}{\xi}\right)\eta M$$

Strategy for Exceeding DOE Targets

- Current generations of advanced Type IV pressure vessels on track for DOE Hydrogen Storage Targets – lots of room for progress



More Economic Correlates, Collaborations

Miles-per-dollar delivered by truck in a Mobile Infrastructure = same issues

Optimal pipelines will not just re-use (add liners in) existing CNG pipelines

Using Costlier Materials makes sense for enabling applications, small scale

Laptops > Remote Power > Prostheses (cleanliness) > Small Vehicles

The PI (Principal Investigator) is under contract to DARPA to provide technical supervision of awarded Water Rocket contracts with Hamilton Sunstrand and Proton Energy; responding to renewed DARPA interest.

Three other DARPA projects have started over the past year with contributions from the PI, including the popular launch-on-demand vehicle RASCAL and 3 versions of the Eyeglass Space telescope.

Long term collaborations with academics have been underway with Stanford, Berkeley, and Purdue. The small tankage prototyping and test capability LLNL is developing is intended to re-ignite academic research into containment structures. Private sector vendors have learned to furnish liners, and entire test rigs, allowing ~one-PhD-per-$100K funding levels. These vendors have been prepared to contribute to the ONRL-managed academic outreach program, so that DOE can sponsor the most cost-efficient research into hydrogen tankage. Other sponsoring agencies besides DOE have mandates to fund advances in Mechanical Engineering, Material Sciences, and Computer Science at PhD levels.

Insulated Pressure Vessels for Vehicular Hydrogen Storage

Presented by:

Salvador M. Aceves

Lawrence Livermore National Laboratory

(925) 422-0864

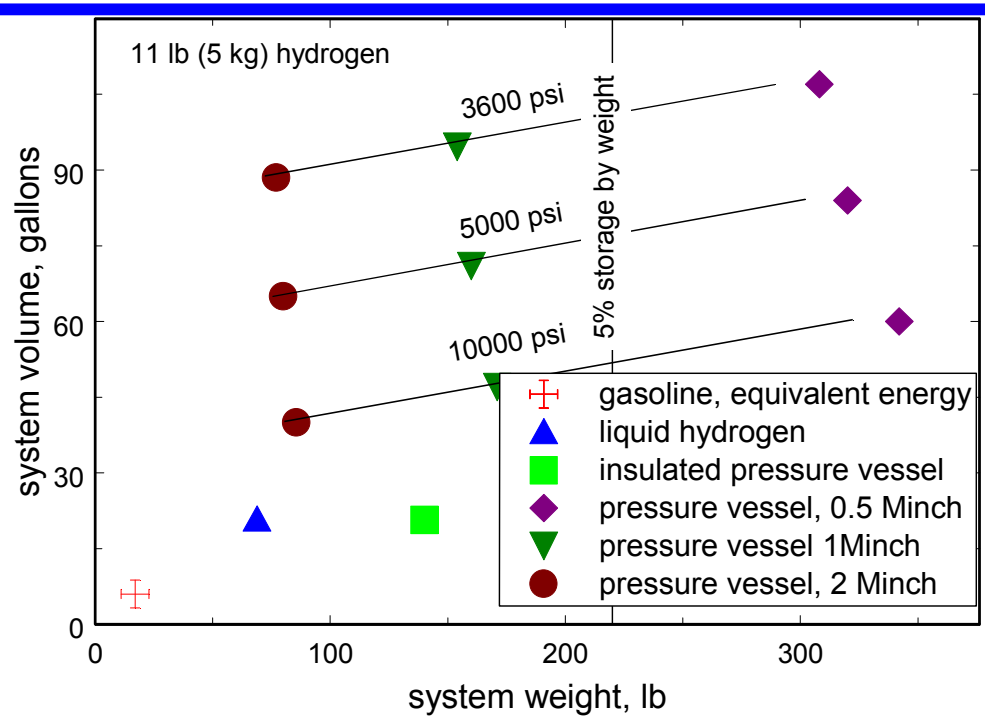
saceves@LLNL.GOV

2003 DOE Hydrogen Program Annual Review

Berkeley, CA

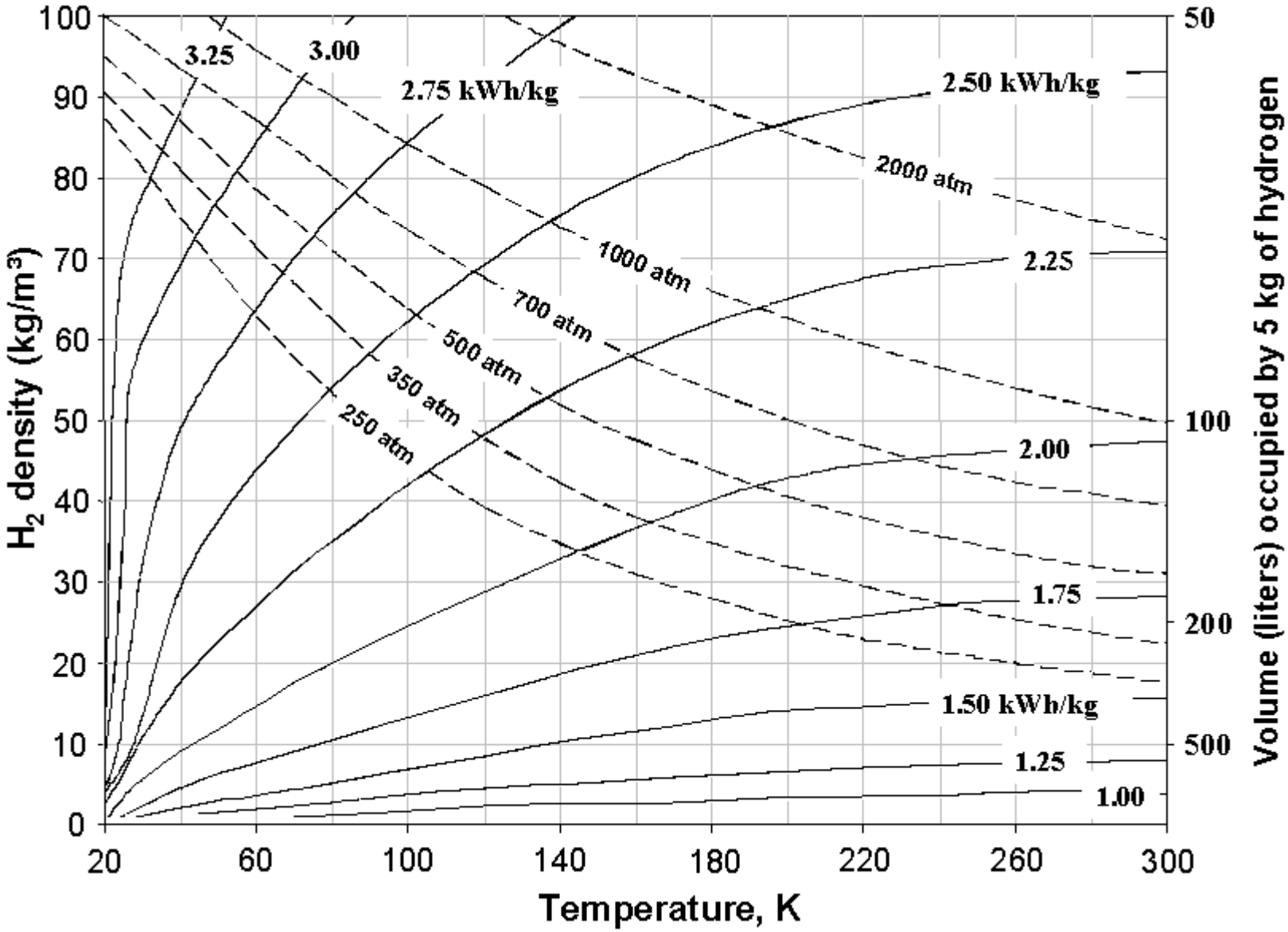
May 20, 2003

Relevance and Objective: insulated pressure vessels provide low cost, long range and infrastructure flexibility

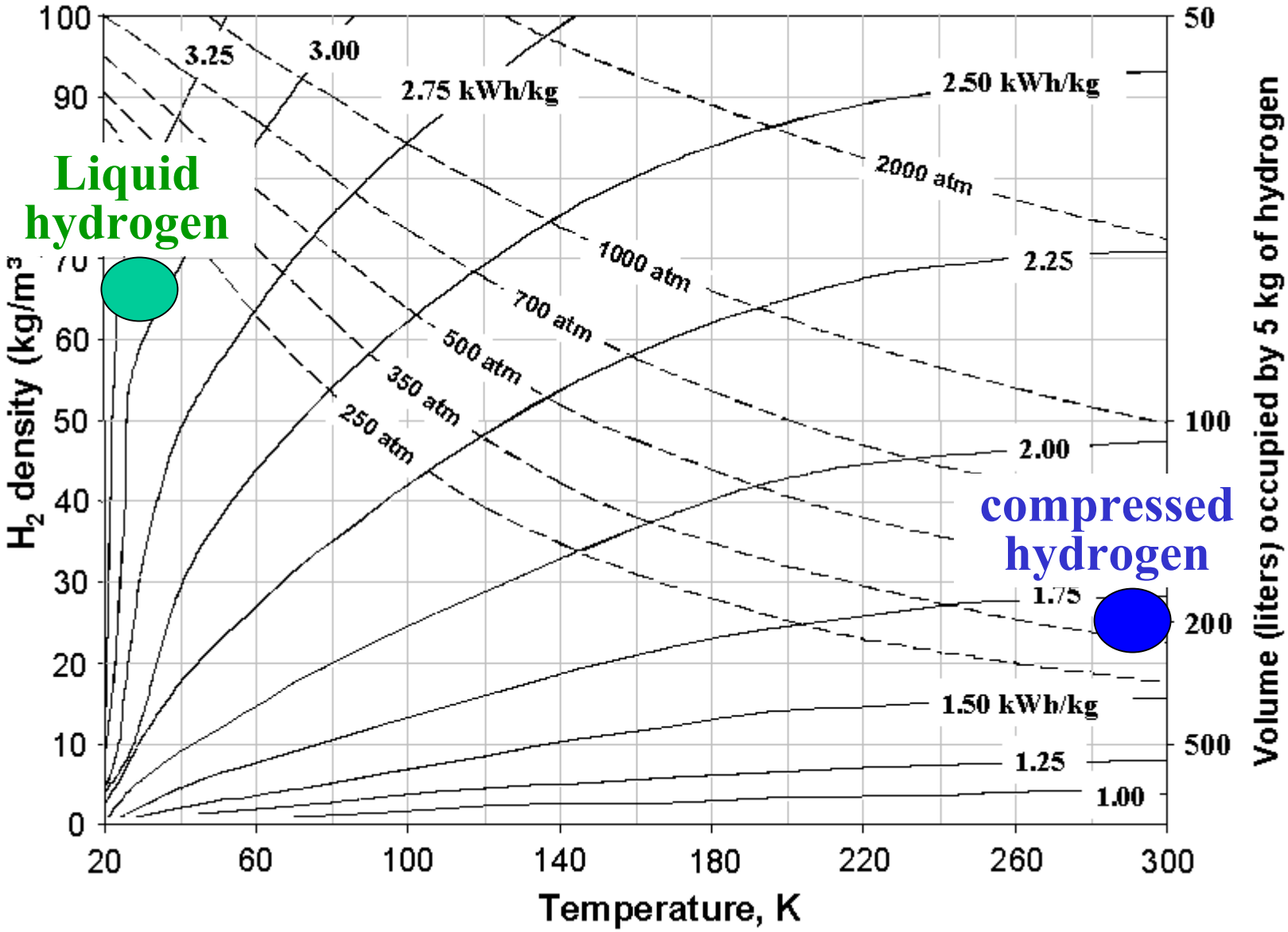


- **Insulated pressure vessels address the whole range of technical barriers from the Hydrogen Program R&D plan**
- **A. Low cost, due to lower need for fiber. B. Low volume. C. Efficient, due to the dual mode operation. D. Durable, tested over 10000 cycles. E. Short refueling time. F. We are working on codes and standards. G. We have conducted life cycle and efficiency analysis. H. Sufficient fuel storage for long range. J. We are generating tank performance data. K. Testing BOP components. L. Low venting losses.**

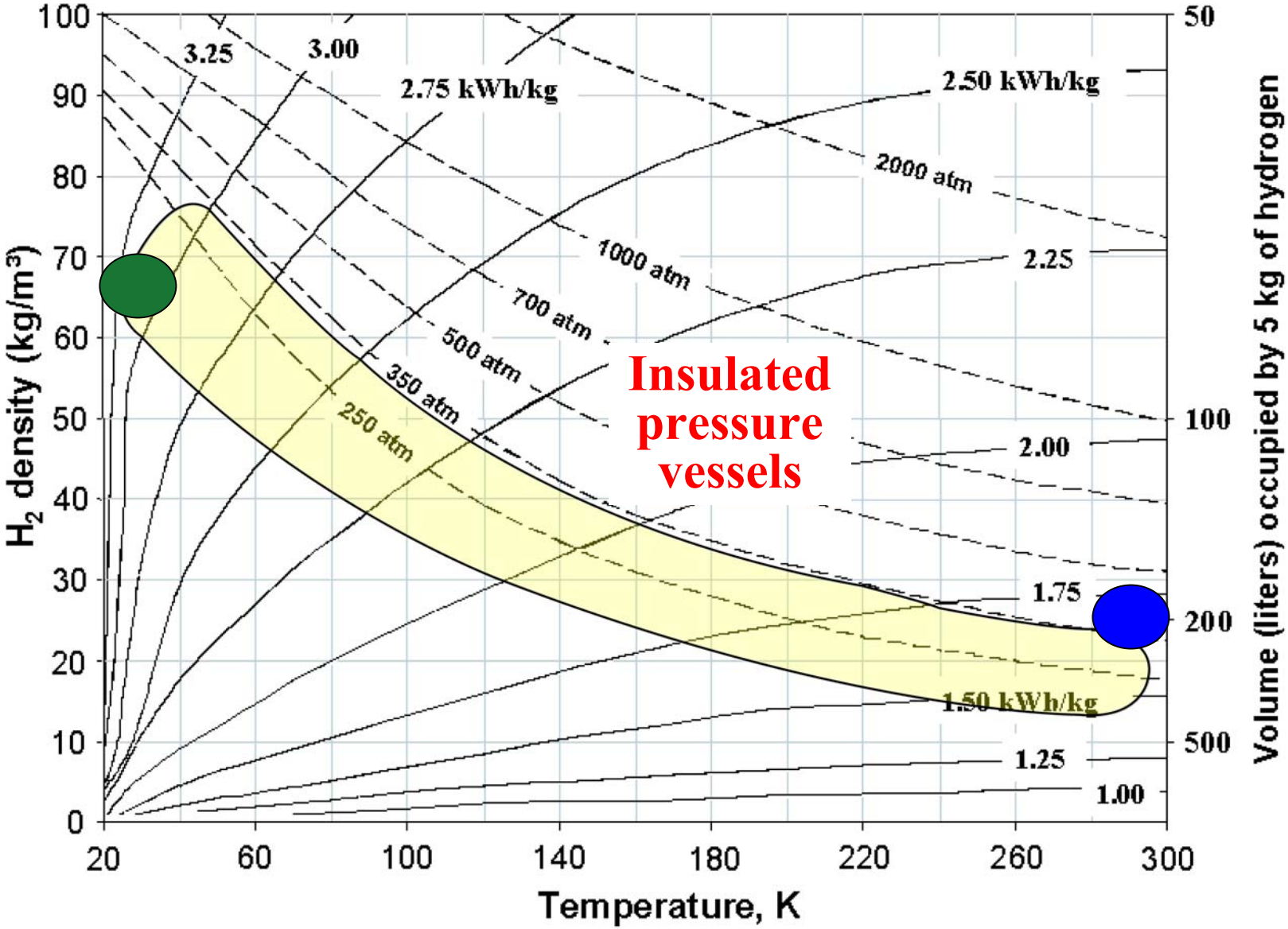
Approach: Insulated pressure vessels operate over a very wide range of operating conditions, increasing the infrastructure flexibility and saving energy



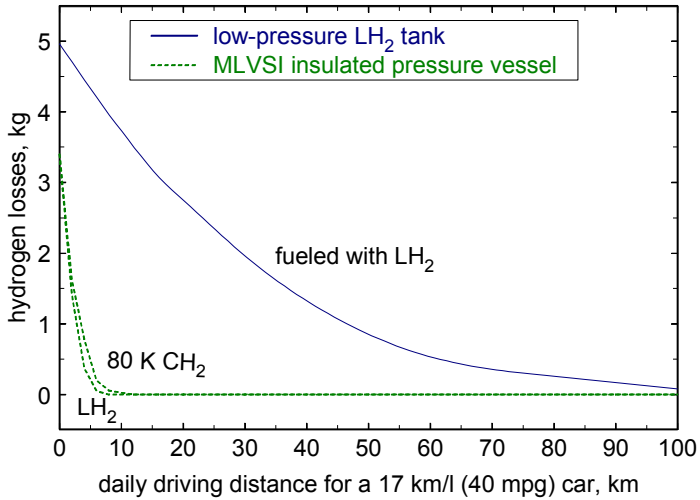
Approach: Insulated pressure vessels operate over a very wide range of operating conditions, increasing the infrastructure flexibility and saving energy



Approach: Insulated pressure vessels operate over a very wide range of operating conditions, increasing the infrastructure flexibility and saving energy



Project timeline: We have carried this project from concept to proof of principle into demonstration



1998: thermodynamic analysis

1999: cryogenic cycling

2001: DOT/ISO Tests

2003: Demonstration

Accomplishments and Progress: We are performing certification tests to demonstrate the safety of this technology

1. Perform the SAE cryogenic drop and bonfire tests. Tests complete. The insulated pressure vessels successfully passed both tests
2. Sign SCAQMD Contract. Task complete. The contract was signed and SCAQMD funding is being received
3. Study fueling system of SunLine truck. Task complete. We have generated an overall system for fueling the truck
4. Study current standards for hydrogen tanks. Task complete. We have generated a preliminary list of tests for insulated pressure vessel certification

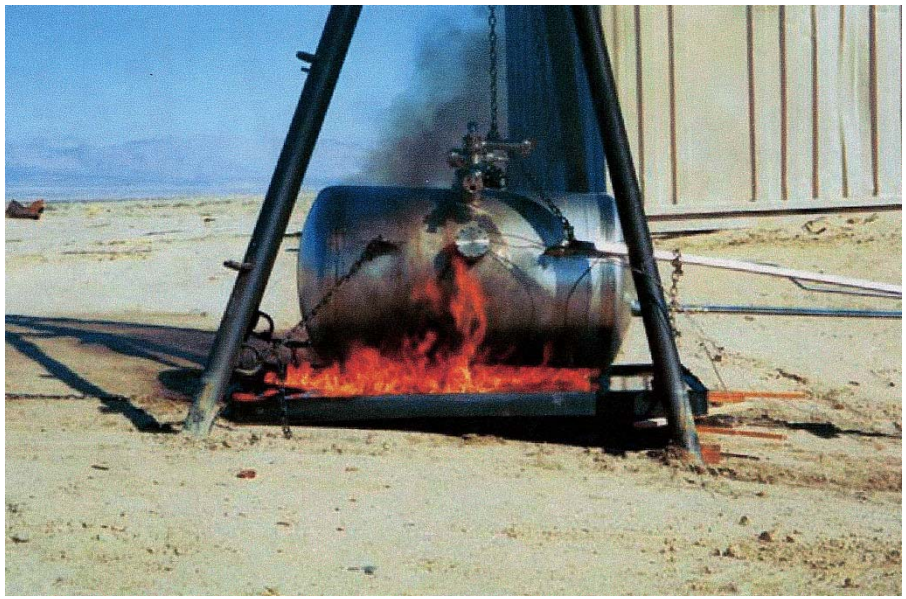
Accomplishments and Progress: We are working on demonstrating insulated pressure vessels

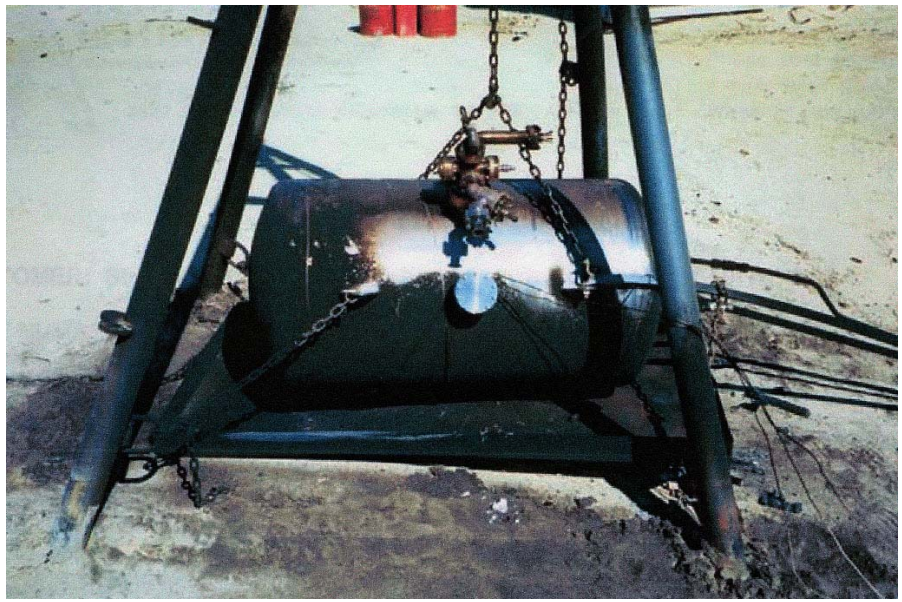
5. Test 5000-psi vessels at cryogenic temperature. Task complete. The pressure vessels were burst tested after cycling, and they met the required burst pressure criterion
6. Prepare a preliminary procedure for insulated pressure vessel certification. Task complete. We have written a certification procedure for pressure vessel certification and submitted it to SCI and the AQMD
7. Demonstration of an insulated pressure vessel in a vehicle. Task in progress. We are receiving all the required parts and we are working on the safety approvals for operation at the LLNL site.

Accomplishments and progress: We have passed the two remaining certification tests

SAE cryogenic drop test

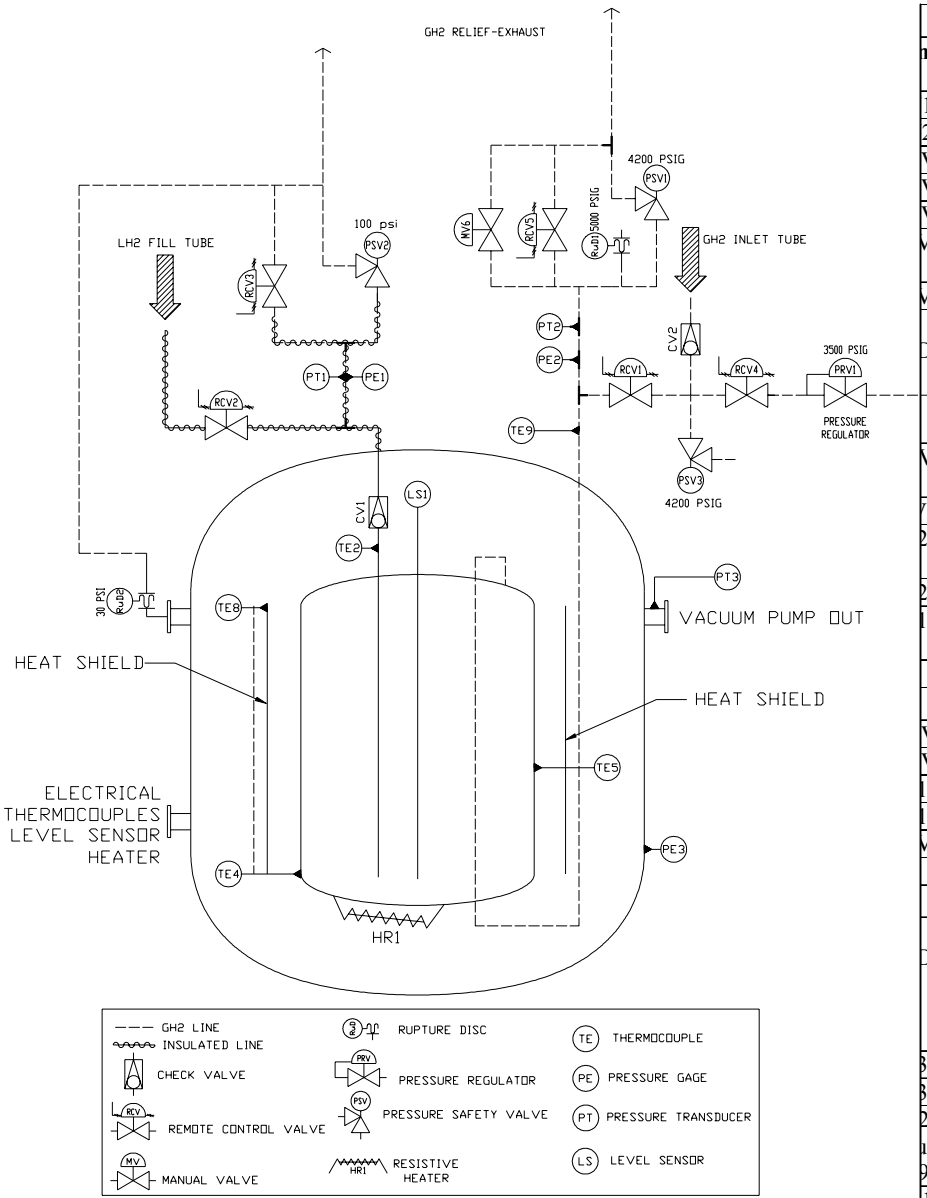
Accomplishments and progress: We have passed the two remaining certification tests





SAE cryogenic bonfire test

Accomplishments and Progress: We have designed a complete system for fueling the SunLine pickup truck



Components in the compressed hydrogen fill zone			
n #	Description	Manufacture and catalog number	M.A.W.P. (psig)
1	Check Valve	Circle Seal Controls CV04-17	6000
2	Check Valve	Circle Seal Controls CV04-17	6000
V1	Solenoid Valve	Circle Seal Controls 16304-002P1AA1C	6000
V4	Solenoid Valve	Circle Seal Controls 16304-002P1AA1C	6000
V5	Solenoid Valve	Circle Seal Controls 16304-002P1AA1C	6000
V1	Press. Relief Valve	Crosby Valve and Gage Co. # 9551118A	4200
V3	Press. Relief Valve	Swagelock SS-4R3A5	4200
D1	Rupture disc	Continental Disc Corporation Rupture Disc Standard S.S. 5000 psigg Burst Pressure With Teflon gasket, holder UT6U ½ in. Pipe, Schedule 80, 316 S.S.	5000
V1	Pressure Regulator	TESCOM Corporation # 20-1231-1405	5000
76	Manual Needle valve	Autoclave Engineers 20A-1876-6	6000
2	Pressure transducer	GP50 Corporation 242E-RV-6-AA/AA/GZ	5000
2	Pressure Gage	McMaster-Carr; #4016K1 (0-6000 psig)	6000
1	Level Sensor	American Magnetics, Level Sensor Drawing No. SKV-10819	4200
Components in the liquid hydrogen fill zone			
V2	Solenoid Valve, cryogenic	Circle Seal Controls 16300-001P4AA5C	125
V3	Solenoid Valve, cryogenic	Circle Seal Controls 16300-001P4AA5C	125
1	Pressure gage	Swagelock PG1-63C-PG200-CAQX-F	200
1	Pressure transducer	GP50 Corporation 242-RB-6-AA	300
V2	Press. Relief Valve	Circle Seal; K520T1-6MP-100	100
Components in the vacuum space			
D2	Rupture Disc	Continental Disc Corporation Rupture Disc Standard S.S. 30 psigg Burst Pressure With Teflon gasket, holder UT6U ½ in. Pipe, Schedule 80, 316 S.S.	30
3	Pressure Gage	McMaster-Carr; #4017K3 (0-15 psig)	15
3	Vacuum Press. Transducer	GP50 Corporation 242-PP-4AA	30
2 ugh 9	Thermocouple	Thermocouple type K	
1	Resistive heater	Tempresco Pancake heater	

Accomplishments and Progress: We have generated a draft certification procedure for insulated pressure vessels

- 1 tensile tests for steel and aluminum cylinders and liners
- 2 impact test for steel cylinders and steel liners
- 3 sulfide stress cracking test for steel
- 4 corrosion tests for aluminum
- 5 sustained load cracking (SLC) tests for aluminum
- 6 leak-before-break (LBB) test
- 7 extreme temperature pressure cycling
- 8 Brinell hardness test
- 9 coating tests
- 10 leak test
- 11 hydraulic test
- 12 hydrostatic pressure burst test
- 13 ambient temperature pressure cycling
- 14 acid environment test
- 15 bonfire test
- 16 penetration tests
- 17 composite flaw tolerance tests
- 18 high temperature creep test
- l9 accelerated stress rupture test
- 20 impact damage test
- 21 coating batch tests
- 22 hydrogen compatibility test
- 23 resin shear strength
- 24 hydrogen gas cycling test
- 25 Leak testing
- 26 destructive and non destructive tests of welding seams
- 27 cryogenic drop test
- 28 cryogenic flame test

Collaborations and tech transfer

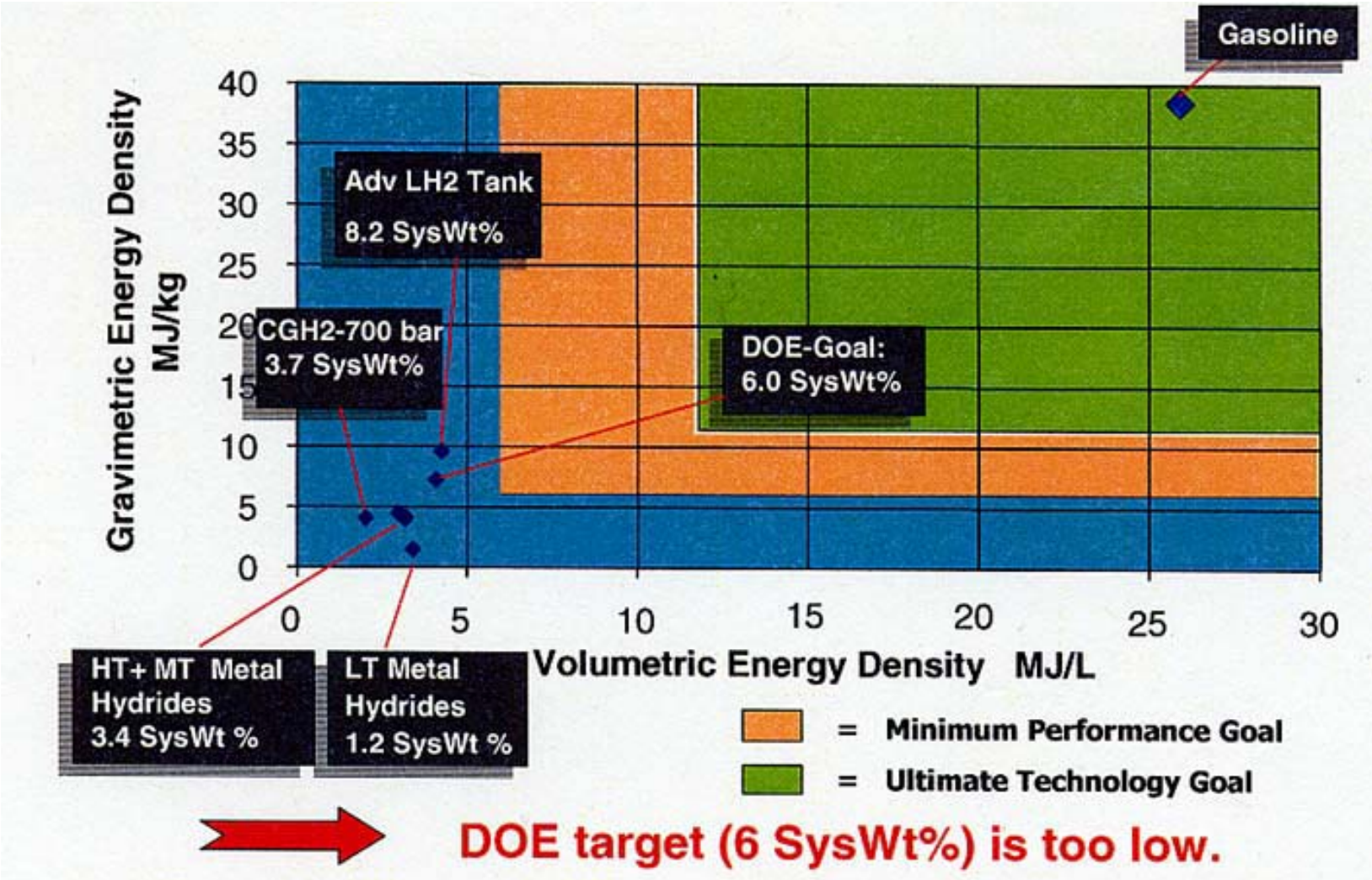
We have teamed up with SunLine and Structural Composites Industries (SCI) to do a demonstration project where the insulated pressure vessels will be installed into two of the SunLine fleet vehicles (Ford Ranger and Ford F-250).

SCI STRUCTURAL COMPOSITES INDUSTRIES

AQMD

SunLine TRANSIT AGENCY

Plans and future milestones: hydrogen energy density is limited by fundamental physics



Solution: conformable pressure vessels allow hydrogen storage in otherwise unusable space

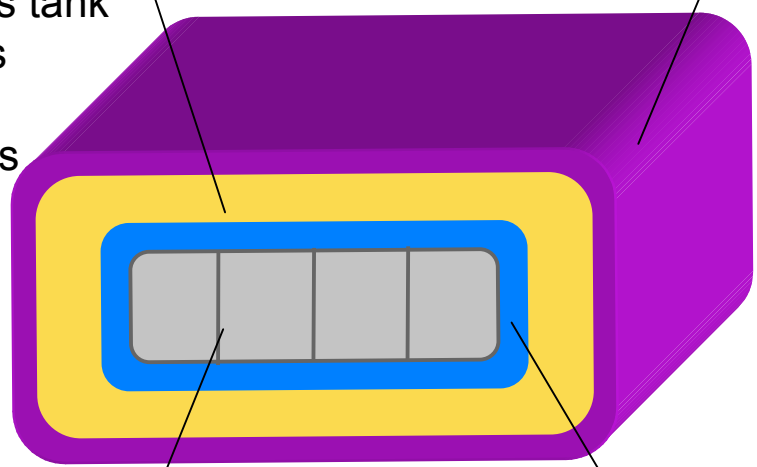
Cryogenic Conformable Tank : Components of a "Conceptual Design"

Insulation

- Supports and insulates tank
- Discrete or continuous
- Candidate materials:
  - Closed cell foams

Vacuum Shell

- Holds vacuum to insulate inner tank and provides mounting surface for external supports.



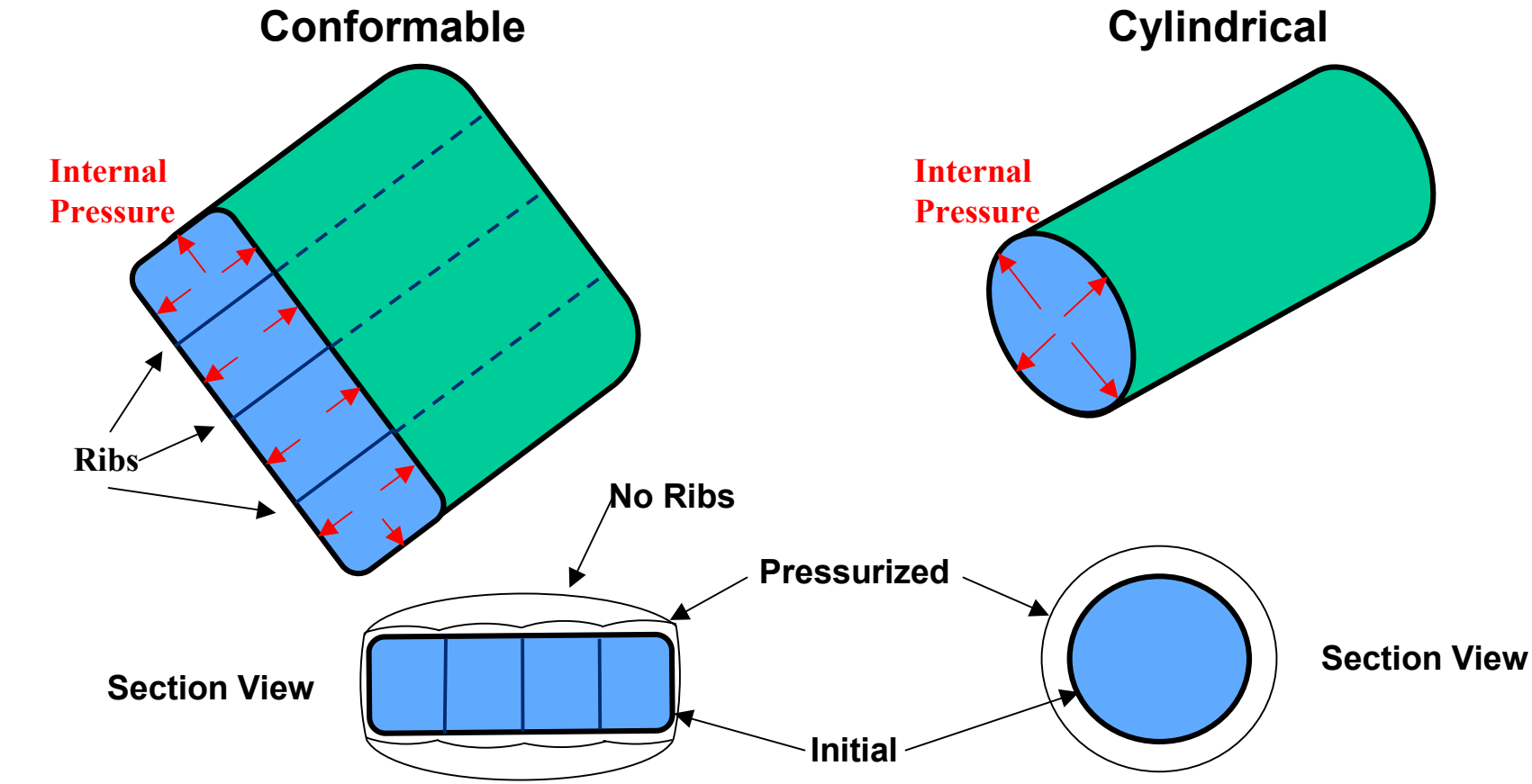
Integrated Bladder - Stiffener

- Retains hydrogen, provides "radial" support, & connects to piping
  - Integrated webbed or ribbed stiffeners (*e.g.,* metal coated composites)
- Candidate materials: formable metals

Composite Overwrap

- Structural member to "confine" internal pressure.
- Fiber: Kevlar or carbon fiber
- Manufacturing:
  - wet filament wound
  - dry textile with RTM

Conformable Tanks Require Internal Structure

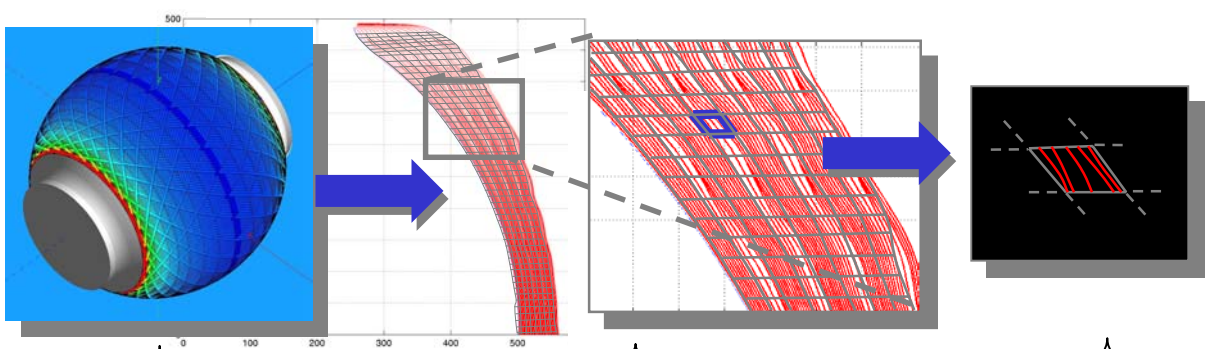


Conformable tanks require internal stiffeners to efficiently support the pressure and minimize bending stresses.

Spherical and cylindrical tanks naturally resist "bending" without internal stiffeners.

Optimized Design Requires Integrated Approach

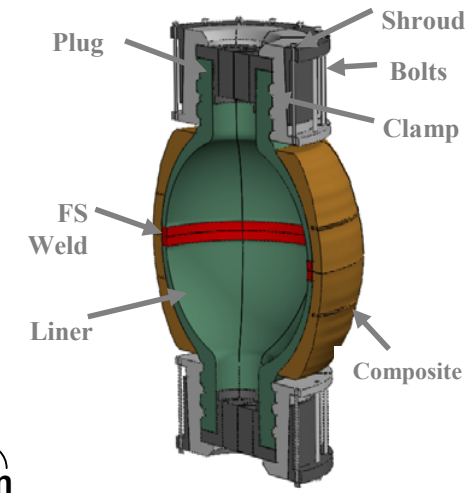
- Team with industry to design "next" generation conformable vessels for cryogenic and high pressure conditions.
- Advanced concepts will necessitate state of the art design and analysis tools.
  - e.g., New high fidelity 3-D analyses allow complex stress states to be fully characterized



Winding Simulation Tool - Cadwind©

Finite Element Model (cross section) with superimposed composite lay up

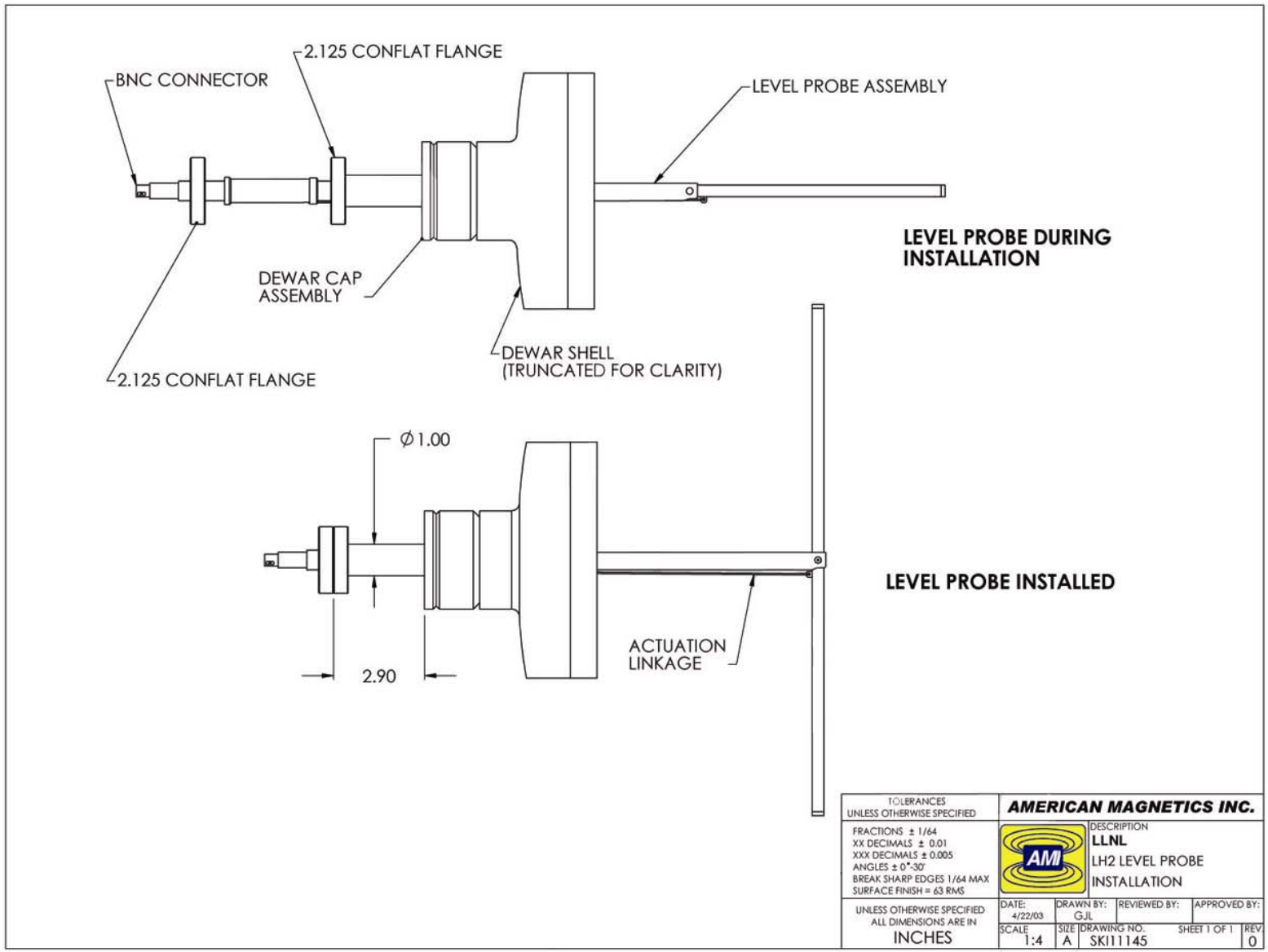
Ply representation within a single element



e.g., High Pressure Containment Vessel

Current LLNL analysis tools analyze the mechanical response of each composite ply

Responses to reviewers' comments: how to install tank in the horizontal direction



Response to reviewers' comments: Is it feasible to have both liquid and gaseous hydrogen at refueling stations? YES

Capital cost of a liquid hydrogen fueling station	$250 k
Capital cost of a compressed hydrogen fueling station:	$1250 k
A station supports	4000 cars
Cost per vehicle for a liquid hydrogen fueling station:	$ 62.5
Cost per vehicle for a compressed hydrogen fueling station:	$ 312

Cost of infrastructure is negligible compared to the cost of fuel, pressure vessels, and potential evaporative losses

Idaho National Engineering and Environmental Laboratory

Low Permeation Liner for H_2 Gas Storage Tanks

INEEL -- Dr. Paul A. Lessing

UCLA -- Prof. Y. Yang
Dr. L.P. Ma
F.C. Chen
V. Shrotriya

Quantum Fuel Systems Tech. Worldwide --
Dr. N. Sirosh
M.J. Warner

May 20,2003

Objective / Relevance

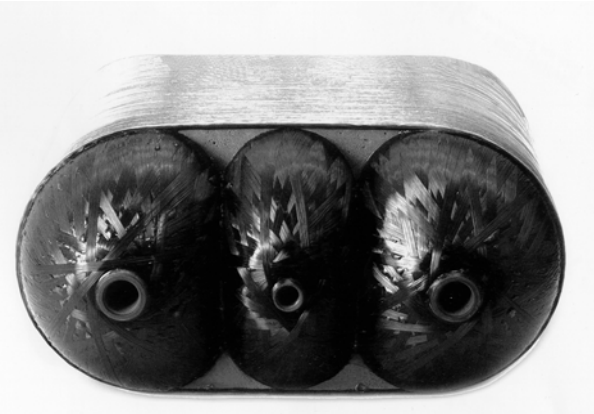
Project Objective

Greatly reduce hydrogen permeation through polymer tank liners of commercial, light-weight, composite, high-pressure hydrogen tanks.

Hydrogen Storage Relevance

Addresses On-board Storage Technical Barriers:
A. Cost B. Weight & Volume C. Durability I. Materials

Addresses Technical Targets:
1. System Cost 2. Cycle Life 3. Loss of useable hydrogen, and 4. Permeation and leakage.



"Conformable" Composite Tanks

Metric

Demonstrate measured reduction of hydrogen flux through polymer liner by a factor of 10 X as result of project.

Polymer Liners are Proposed for Composite H_2 Tanks

Examples: Nylon 6, XLPE (cross-linked polyethylene)

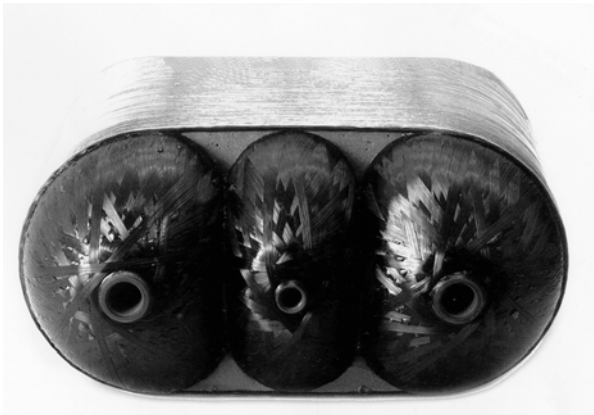
- ***Polymer liner advantages***
  - *Significant weight advantage over metal liner*
  - *Lower cost for "conformable" (non-cylindrical) geometries via blow or roto molding*
  - *Liner serves as a mandrel for winding composite wrap*
- ***Disadvantages***
  - *High permeability (compared to CH_4) for stored hydrogen*
  - *Loss of hydrogen & possible damage to structure*
  - *Sealing boss to polymer liner*
  - *Limited permeability data available*

Approach

Create Hydrogen Diffusion Barrier for Polymer Tank-liners

Requirements for Barrier:

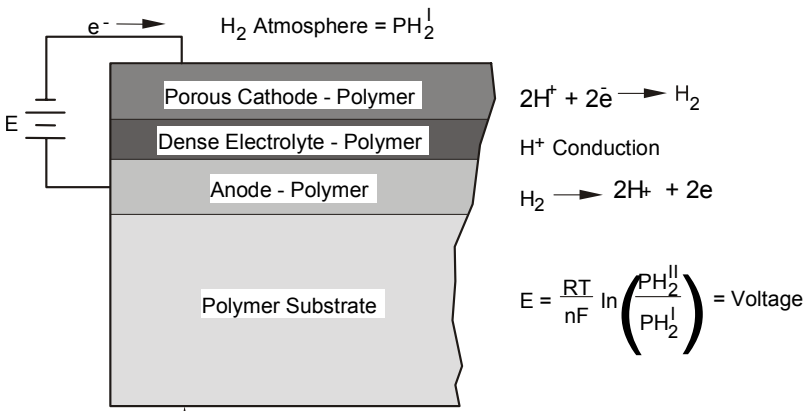
- ***Low permeability of hydrogen***
- ***Adhere well to the polymer***
- ***Modulus match to polymer to prevent cracking***
- ***Apply coating inside a tank with narrow neck***
- ***No pin-holes***
- ***Low Cost and Low Weight***

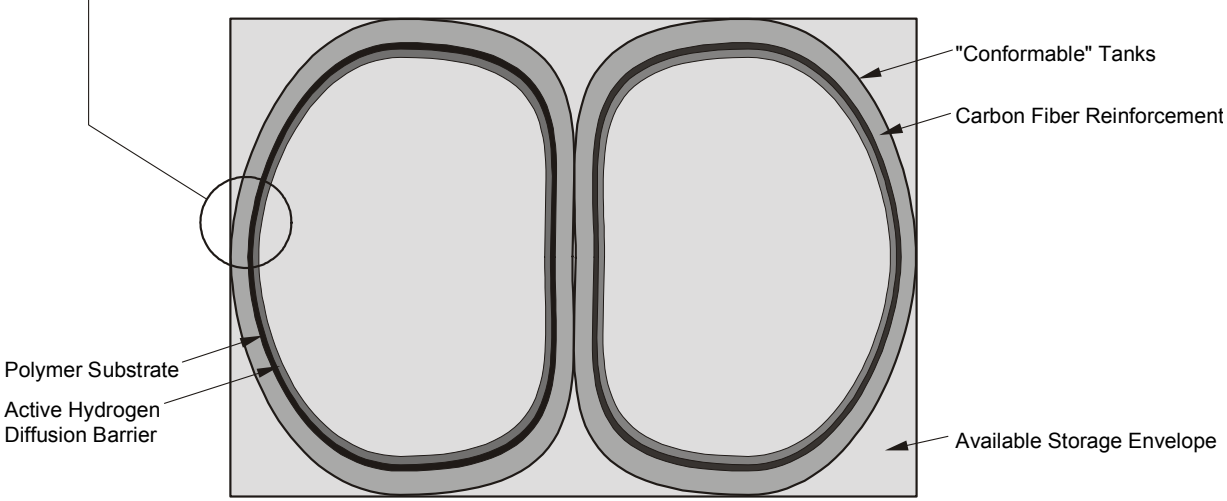


"Conformable" Composite Tanks

INEEL's Active Electrochemical Diffusion Barrier Approach

Electron-conductive polymer electrodes & proton-conductive electrolyte





Cross-section view

GA99 0062

E = -ΔG/nF = RT/nF {ln[PH_2 (ref) /PH_2 (sub)]}

The reaction of interest is:

$$H_2 \rightarrow 2\,H^+ + 2\,e^-$$

Therefore, n = 2, and for T= 300 K, and for a hydrogen pressure of 200 atm, and a postulated substrate partial pressure of hydrogen being $1x10^{-10}$ atm, the applied voltage (E) would be:

E = 0.366 volts

First Year of New Project --- On Schedule

Milestones: Δ = to be accomplished, ♦ = complete

FY03 MILESTONES	O	N	D	J	F	M	A	M	J	J	A	S
Subcontract with University signed 01/03				♦								
CRADA with Quantum signed 01/03							♦					
Task 1. Selection of Materials												
a. Electrode Candidate Polymers selected 02/03					♦							
b. Electrolyte Candidate Polymers selected 03/03						♦						
c. Catalyst Candidates selected 02/03					♦							
Task 2. Fabrication of tri-layer coatings												
a. Experiment fabrication equipment installed 04/03							♦					
b. Fabrication experiments begin 05/03								♦				
Task 3. Characterization of coating layers												
a. Determine characterization methods 06/03									Δ			
Task 4. Experiments Verification of hydrogenation protection												
a. Design of low pressure permeability device complete 02/03					♦							
b. Fabrication of low pressure permeability device complete 06/03									Δ			
c. Initial design of high pressure permeability device complete 08/03											Δ	
Report 09/03												Δ

Accomplishments/Progress

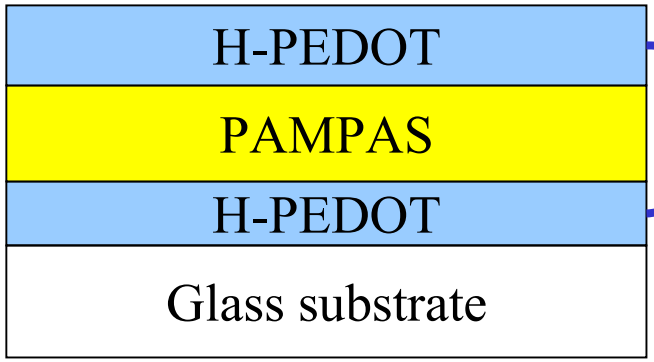
- *Filed U.S. Patent Application (# 10/253,265 in Sept. 2002)*

- *Negotiated and Signed Subcontract with UCLA (Prof. Yang's Conductive Polymers Group)*

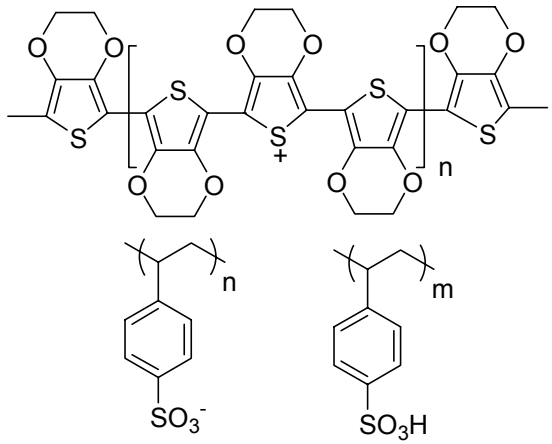
- *Negotiated and Signed CRADA (No. 03-CR-07) with Quantum Fuel Systems Technologies Worldwide, Inc. a manufacturer of composite high- pressure gas storage tanks*

- *Fabrication of tri-layer polymer coatings and fabrication of permeability measurement apparatus are well under way (see following slides)*

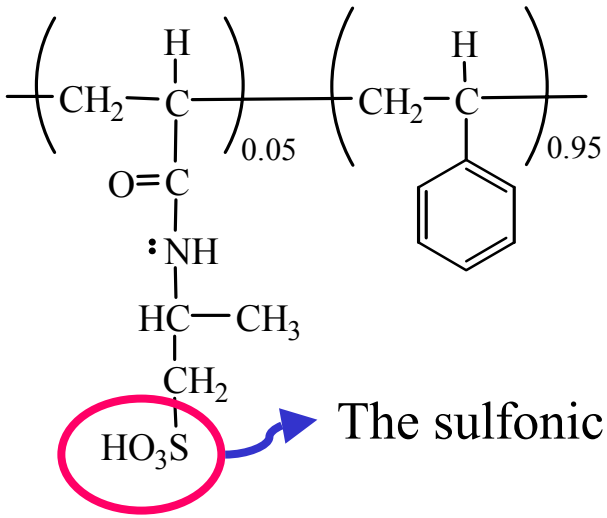
First set of candidate materials fabricated as prototype barrier



Highly-conducting PEDOT (H-PEDOT) was made by blending PEDOT with meso-Erythriol



PEDOT



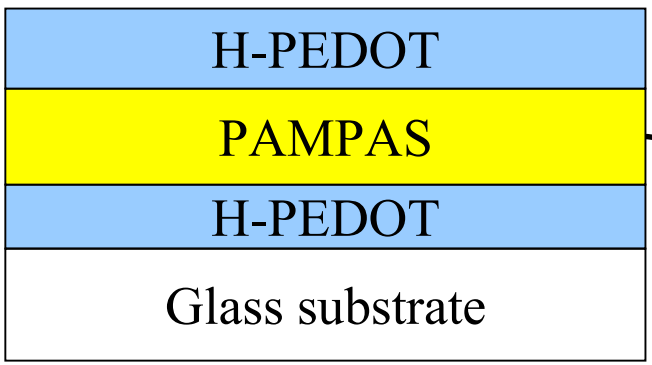
The sulfonic group here will support the proton-conductivity

Poly(2-acrylamino-2-methyl-1-propanesulfonic acid-co-styrene) (PAMPAS)

Fabrication Procedures for the Prototype Barrier

- The glass substrate was first treated by UV-ozone for 15 mins. (for surface treatment.)
- H-PEDOT was spin coated onto the substrate.
- The substrate was baked at 150°C for 2 hours.
- After cooling, 2.5wt% PAMPAS was spin coated from toluene. (because PAMPAS is transparent, a red-dye, TPP, was added to probe survive of the film)
- The substrate was then baked at 70°C for 30 mins.

Substrates under UV light



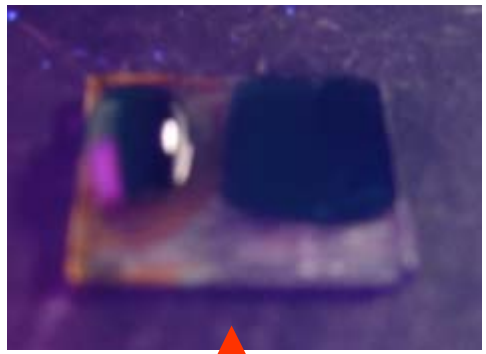
Red-dye was add to allow the probe of PAMPAS polymer film by fluorescence.

High Contact Angle Problem

- Because PAMPAS contains 95% of styrene moieties, the film can survive after washing with water-based solvent. The washing effect due to coating of the second layer of PEDOT was minimized.

- However, the non-polar surface of PAMPAS resulted in the high contact angle while spin-coating the second layer of PEDOT. The adhesion of PEDOT and PAMPAS was very poor.

- To avoid this problem, the PAMPAS film was subjected to a UV-ozone treatment to modify the surface property before spin coating the H-PEDOT layer. A good second layer of PEDOT was then obtained.



High contact angle

Low contact angle

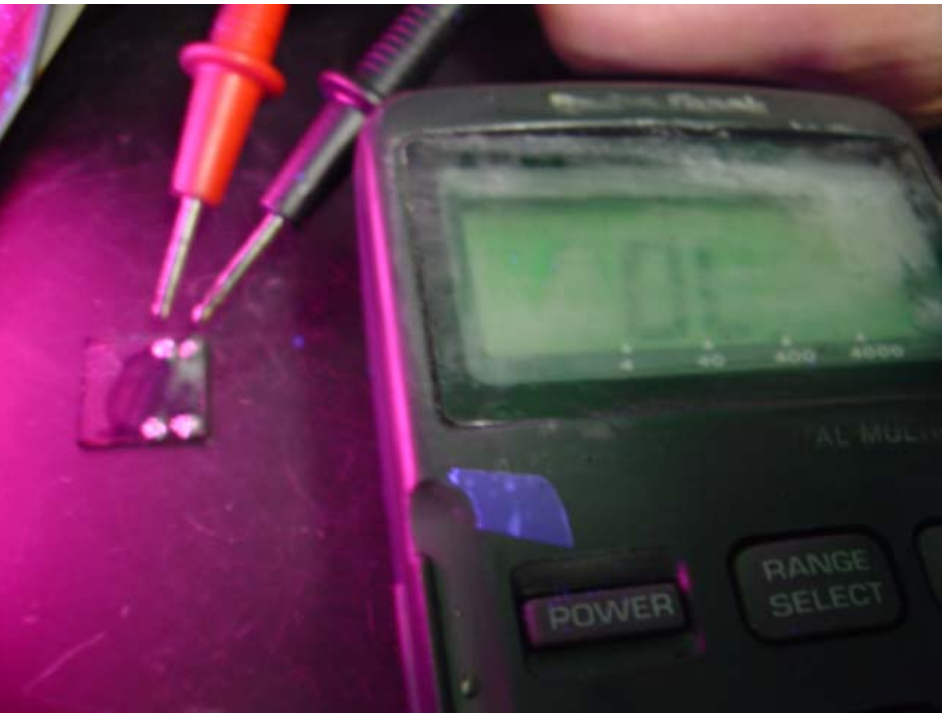
UV-Ozone Treatment Solves Contact Angle of PAMPAS Film

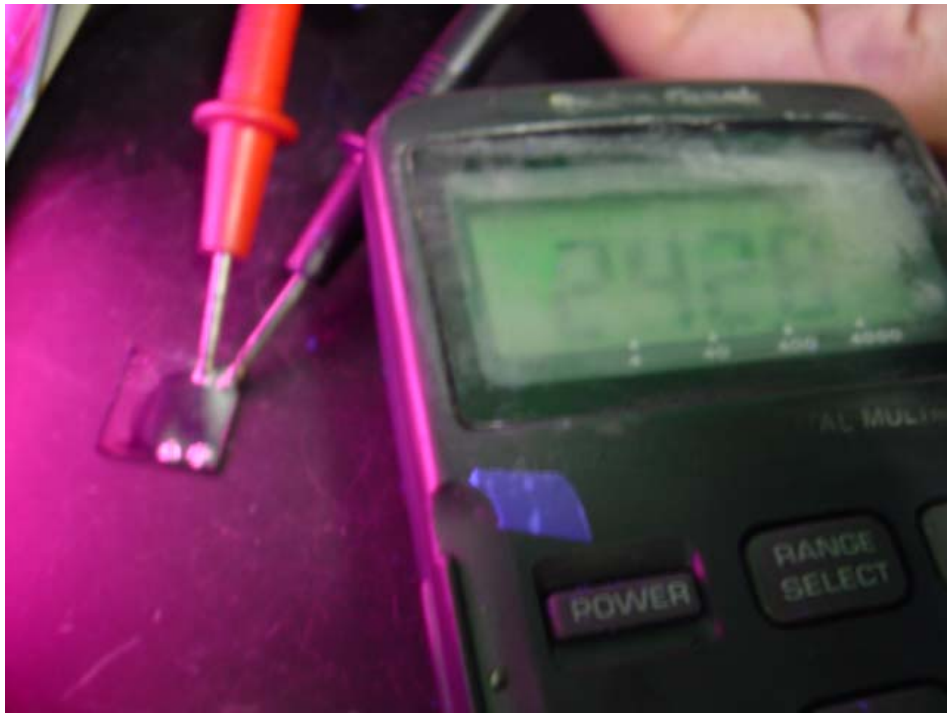
UV-Ozone Time (minutes)	Measured Contact Angle (degrees)
0.0	90.5
0.5	79.7
1.0	70.5
2.0	40.0
5.0	20.0
10.0	14.0

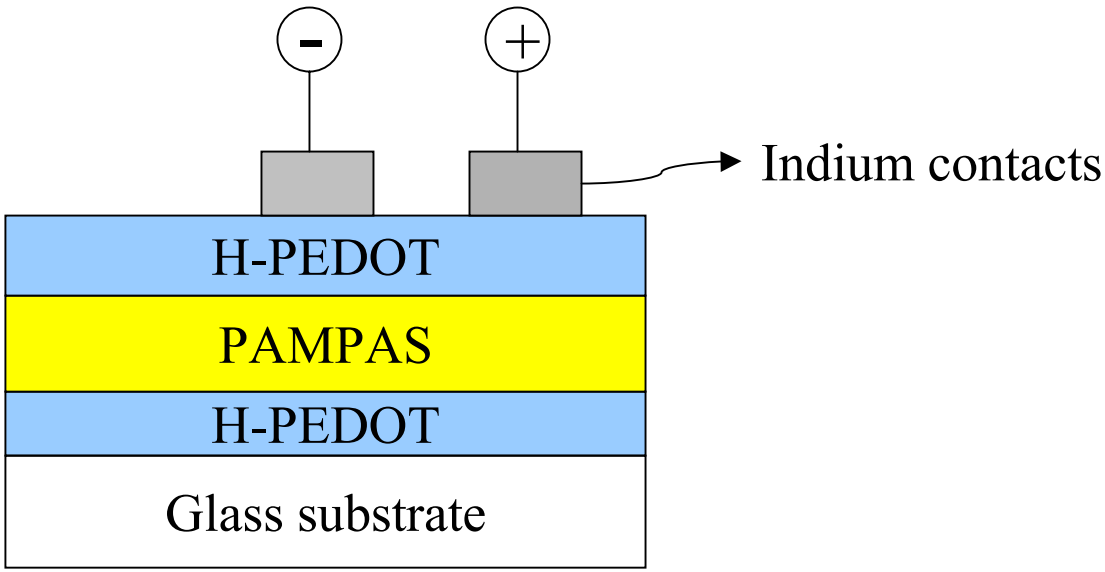
PAMPAS Solution 2.0 wt.% in Toulene Spin Coating 1500 rpm
Baking @ 70°C for 30 minutes

Contact Angle Measurement
Cam-March Contact Angle Measurement System
Droplet size: 6.0 μL
Precision: ± 2 degrees

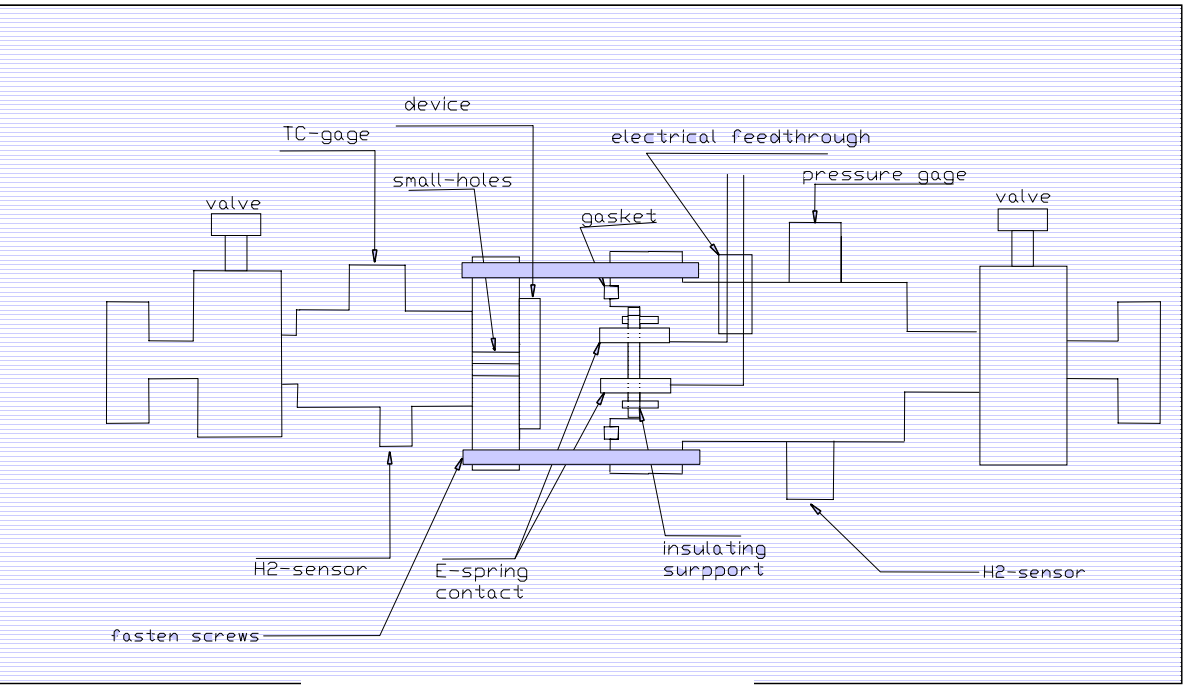
High Electronic Conductivity Demonstrated for PEDOT Electrode Layer



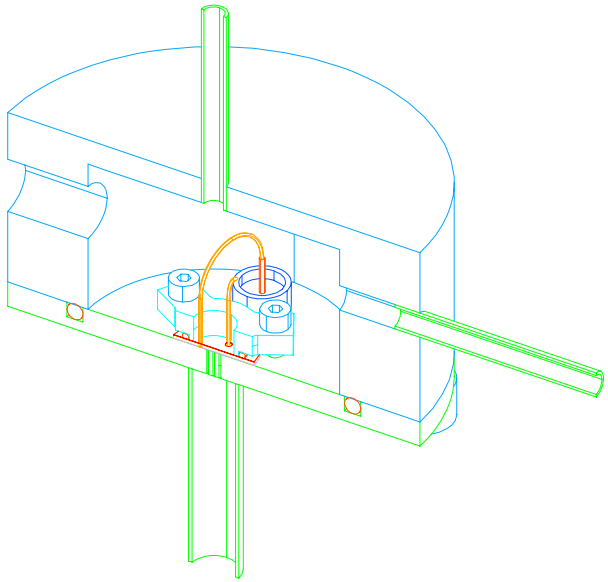




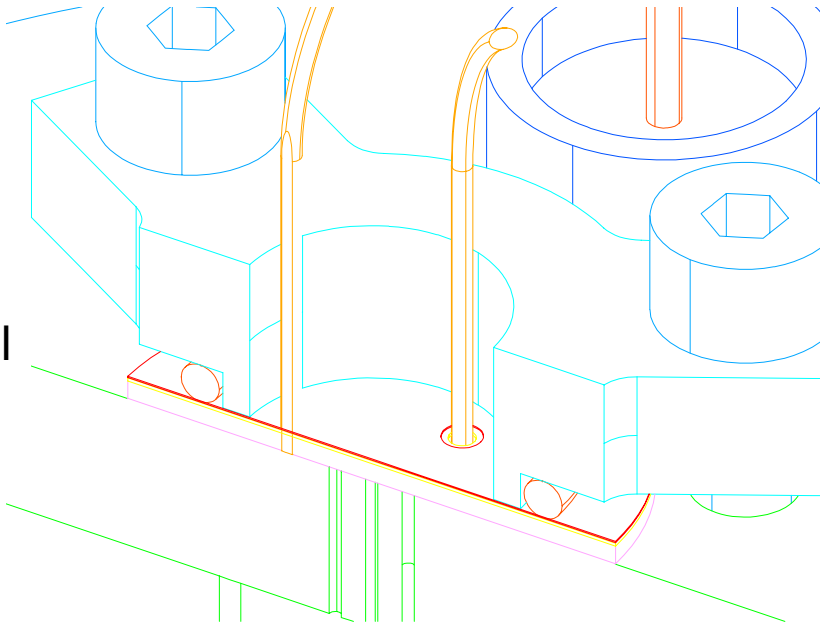
Designed a low pressure (≈100 psi) hydrogen permeability test



Schematic Drawing



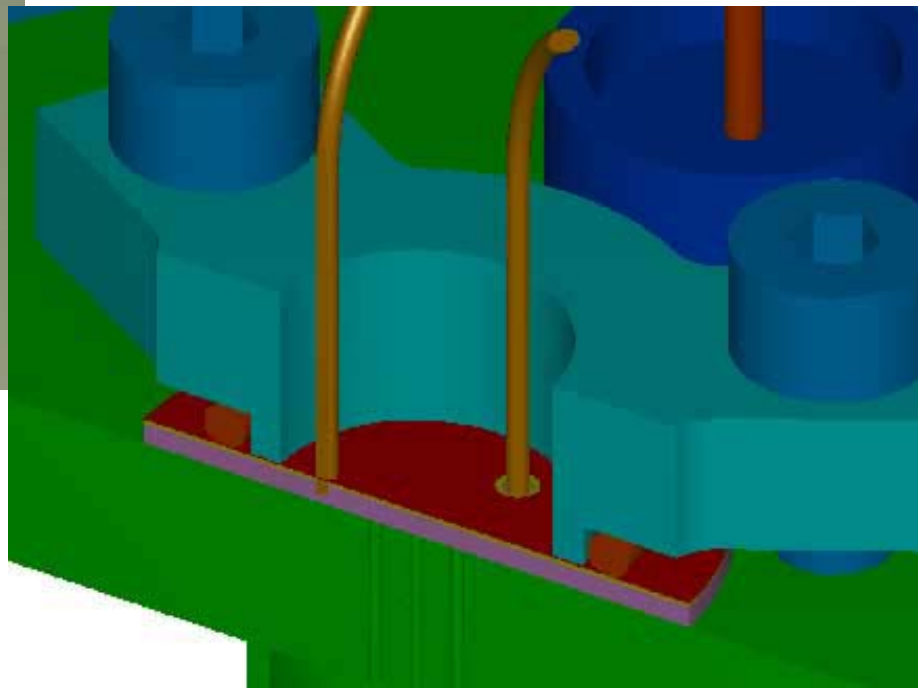
Sample Holder Detail



Fabricated the low pressure hydrogen permeability apparatus

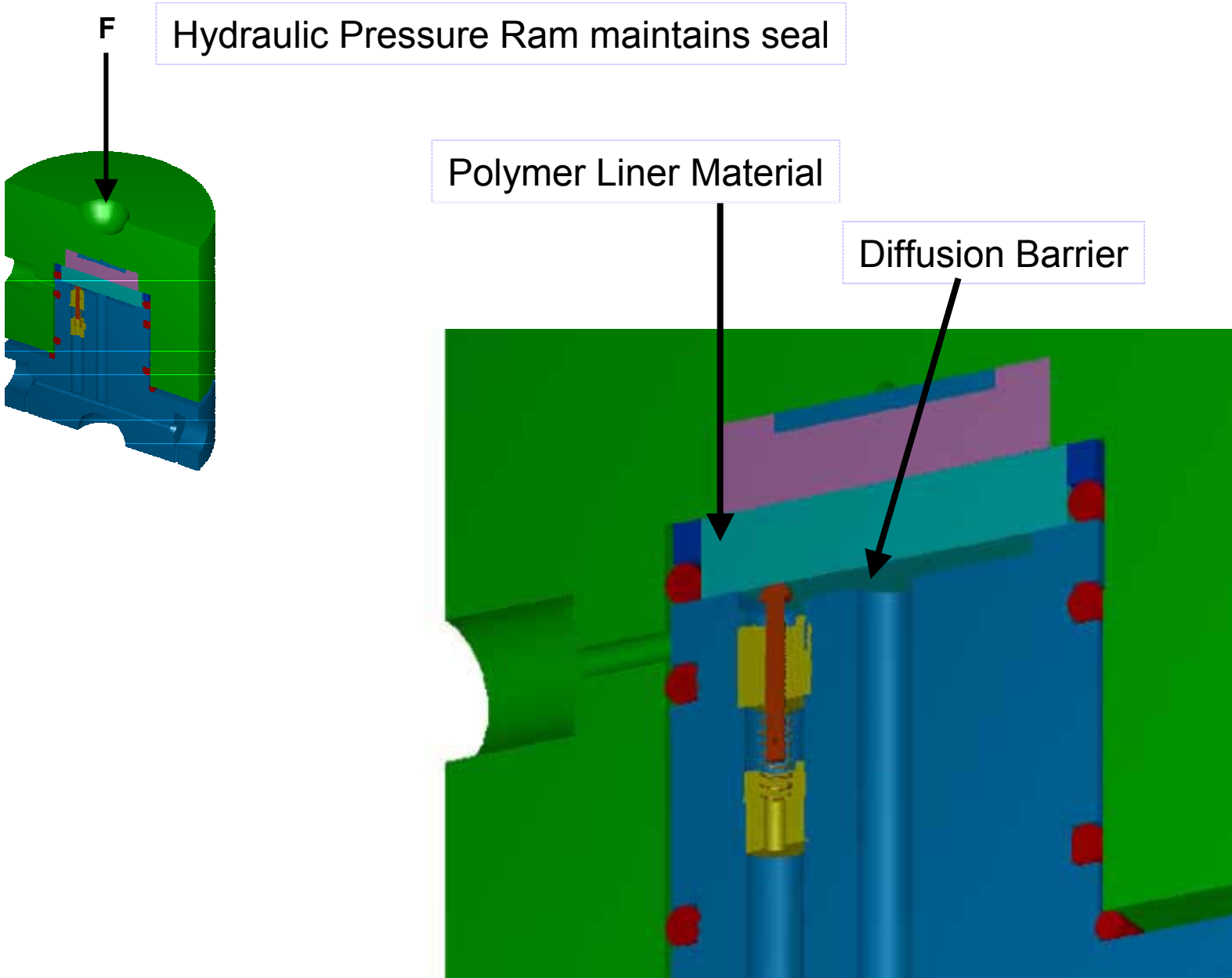
Bolts maintain chamber seal

Sample Holder with electrical connections

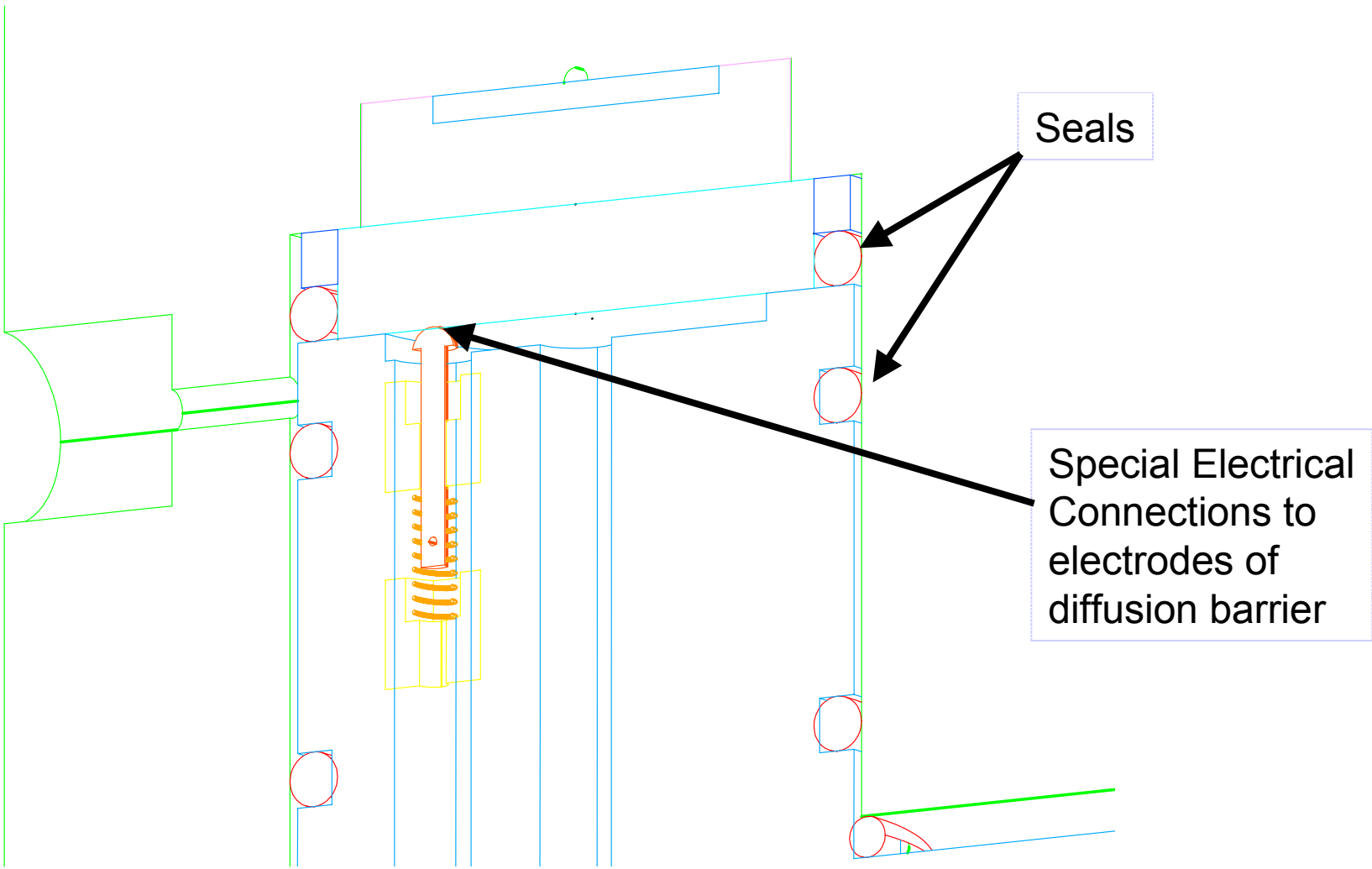


Actual Apparatus

Initial High pressure (10,000 psi) Permeability Apparatus Design



Initial High Pressure Permeability Apparatus Design



Future work

- Measure Electrical Properties of Cell Layers. **Example: Measure the current-voltage to determine the leakage current to confirm the quality of the film. (High leakage current may suggest the existing of some pin-holes or cracks of the film.)**

- Optimize Electrolyte Layer. **PAMPSA contains very few sulfonic groups, which may limit the proton conductivity. Instead of copolymer, a polymer blend system with different weight ratio of sulfonic groups and inert (insoluble in water) polymer moieties will be tested to yield both high proton conductivity and high-resistance of the washing effect from the second layer PEDOT.**

- Permeability Testing. **Complete evaluation of hydrogen sensors. Test permeability of baseline polymer materials versus same materials with tri-layer barrier coating. Evaluate effect of catalysts. Finish design and fabricate high-pressure permeability apparatus. Perform permeability tests on tanks with barrier.**

Advanced Thermal Hydrogen Compression

presented to the

US DOE Hydrogen and Fuel Cells Program

2003 Annual Merit Review

May 20, 2003

by

David H. DaCosta (presenter) and Mark Golben

Ergenics, Inc.

373 Margaret King Ave.

Ringwood, NJ 07456

(973) 728-8815

dacosta@ergenics.com

Relevance / Objective

Project Objective: Develop an advanced thermal hydrogen compressor that operates in conjunction with advanced hydrogen production technologies and improves the efficiency and economics of the compression process. Thermal hydrogen compression must offer a sustainable competitive advantage over mechanical compression for market penetration.

Relevance to National Technical Targets:

H_2 Cost: Reduce compression energy costs by an order of magnitude to meet the H_2 cost goals of:

Long Term: $1.50/gallon of gasoline equivalent (2010)

Near Term: $3.00/gallon of gasoline equivalent (2004)

Energy Density: Demonstrate pressures of 5,000 and 10,000 psi to support high pressure tank development.

H_2 Purity: Increase H_2 quality to protect both fuel cell catalyst and advanced hydrogen storage materials. (≤10 ppm CO)

Complex/Carbon: Knowledge of impurity-effects on compressor hydrides will establish a baseline for understanding impurity impact on advanced storage materials (alanates & carbon nanomaterials).

Approach

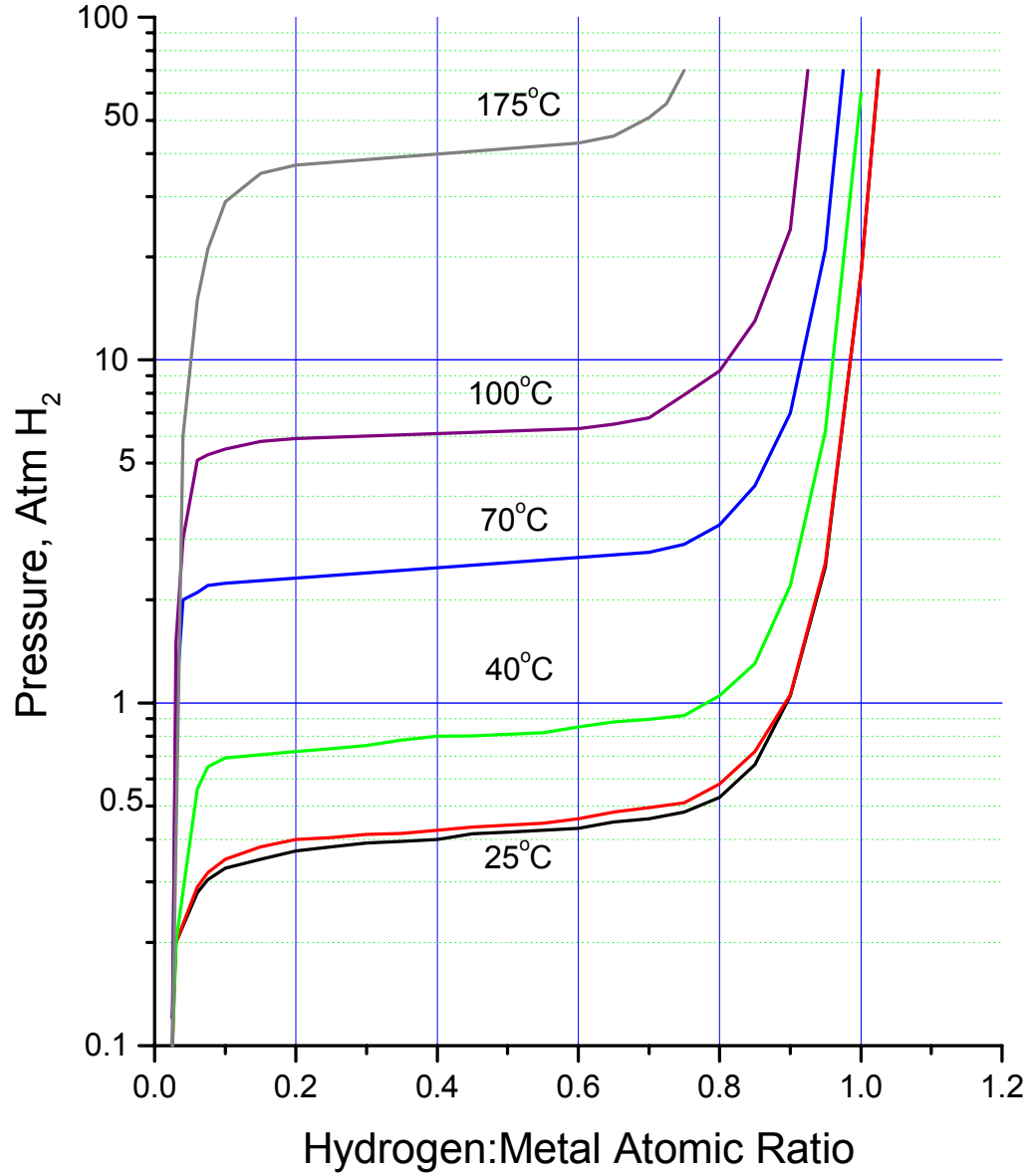
Thermal Compression with Metal Hydride Alloys

A modest increase in temperature results in a large increase in pressure.

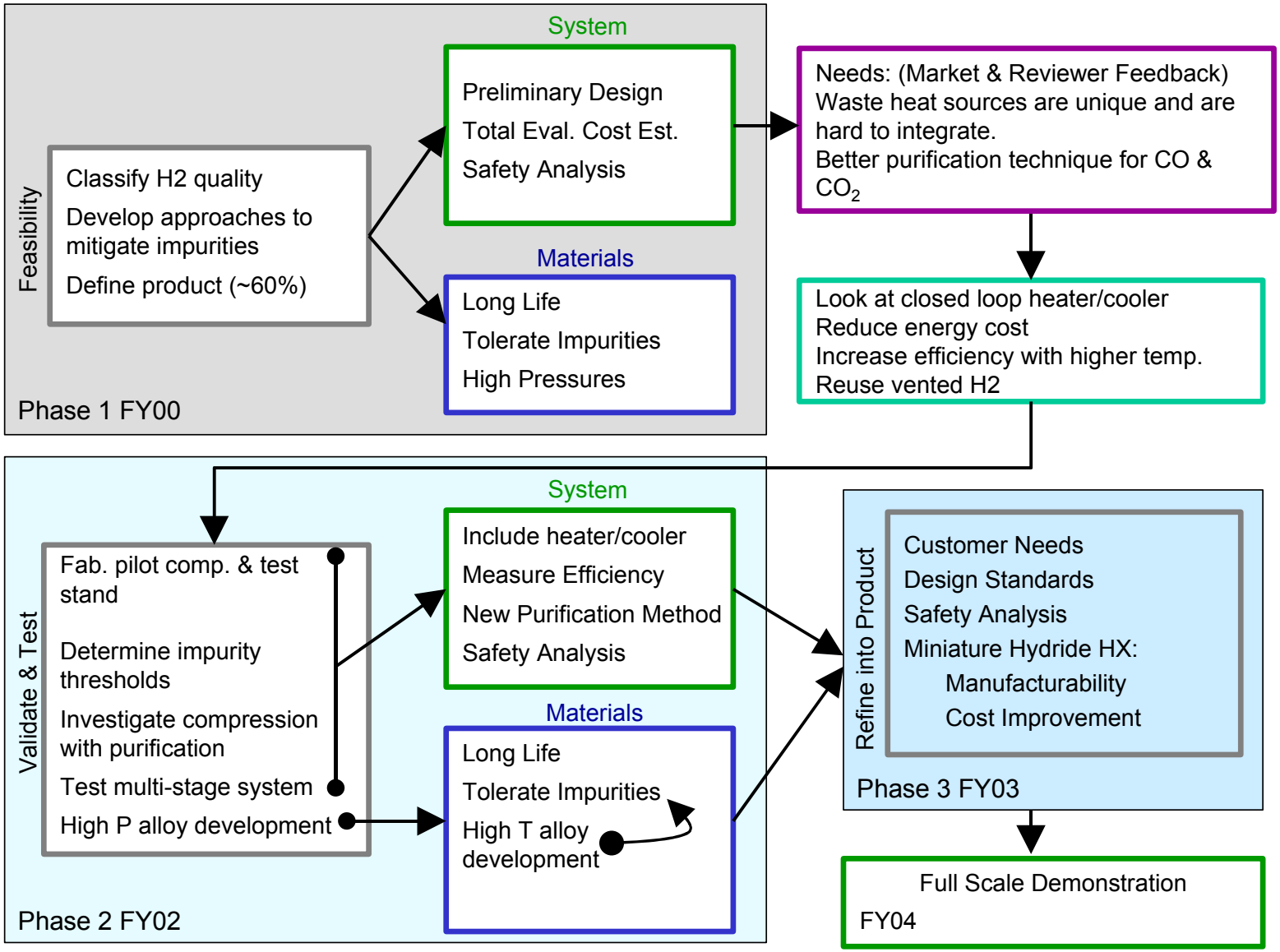
Compression energy can be provided by hot water, rather than electrical power.

High compression ratios are achieved by staging alloys with increasing plateau pressures.

Hydride alloys and systems must tolerate impurities and elevated temperatures.

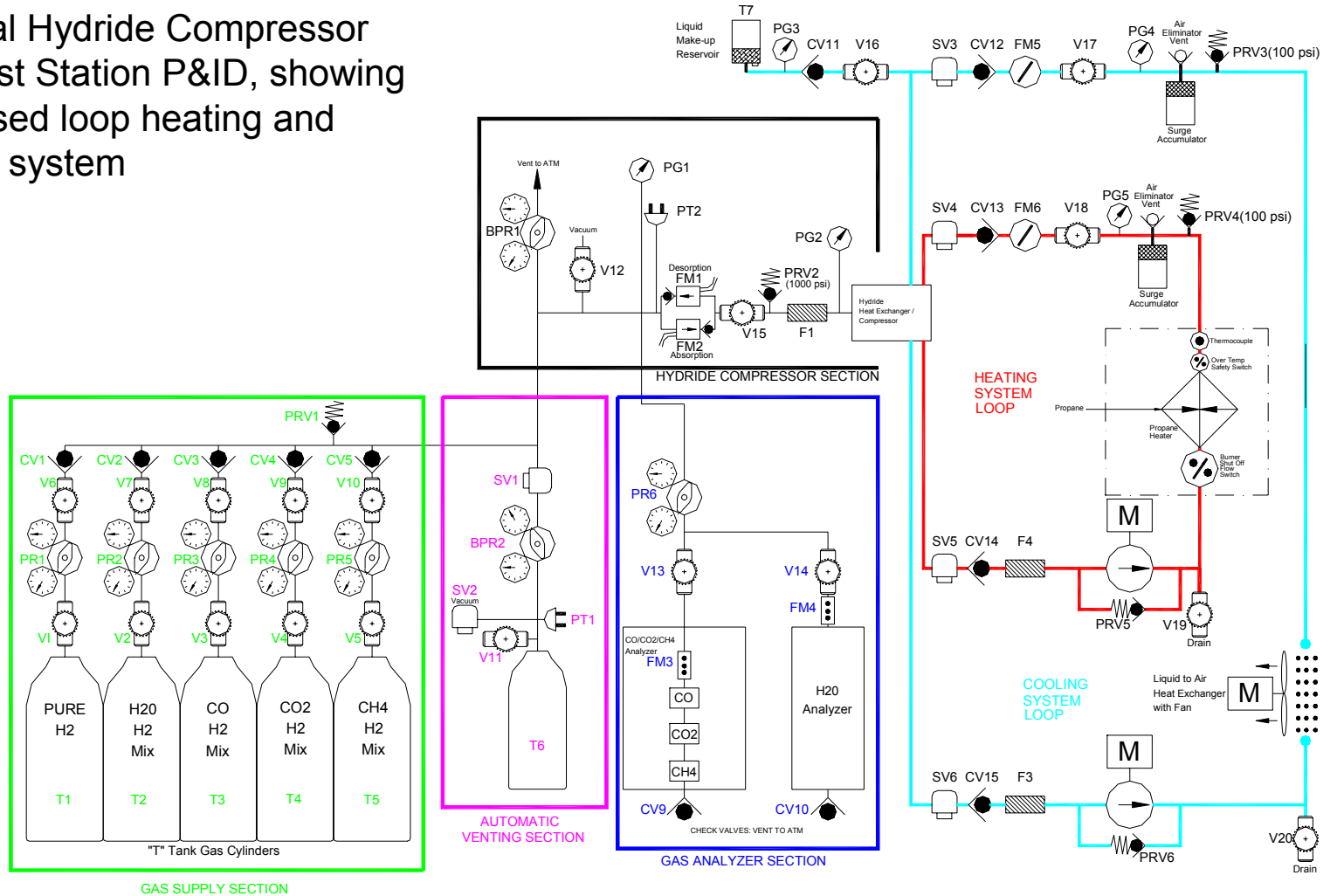


Approach


Feasibility
Classify H2 quality
Develop approaches to mitigate impurities
Define product (~60%)
System
Preliminary Design
Total Eval. Cost Est.
Safety Analysis
Materials
Long Life
Tolerate Impurities
High Pressures
Phase 1 FY00
Needs: (Market & Reviewer Feedback)
Waste heat sources are unique and are hard to integrate.
Better purification technique for CO & CO_2
Look at closed loop heater/cooler
Reduce energy cost
Increase efficiency with higher temp.
Reuse vented H2
Validate & Test
Fab. pilot comp. & test stand
Determine impurity thresholds
Investigate compression with purification
Test multi-stage system
High P alloy development
System
Include heater/cooler
Measure Efficiency
New Purification Method
Safety Analysis
Materials
Long Life
Tolerate Impurities
High T alloy development
Phase 2 FY02
Refine into Product
Customer Needs
Design Standards
Safety Analysis
Miniature Hydride HX:
Manufacturability
Cost Improvement
Phase 3 FY03
Full Scale Demonstration
FY04

Approach

Thermal Hydride Compressor and Test Station P&ID, showing the closed loop heating and cooling system



Piping & Instrumentation Diagram

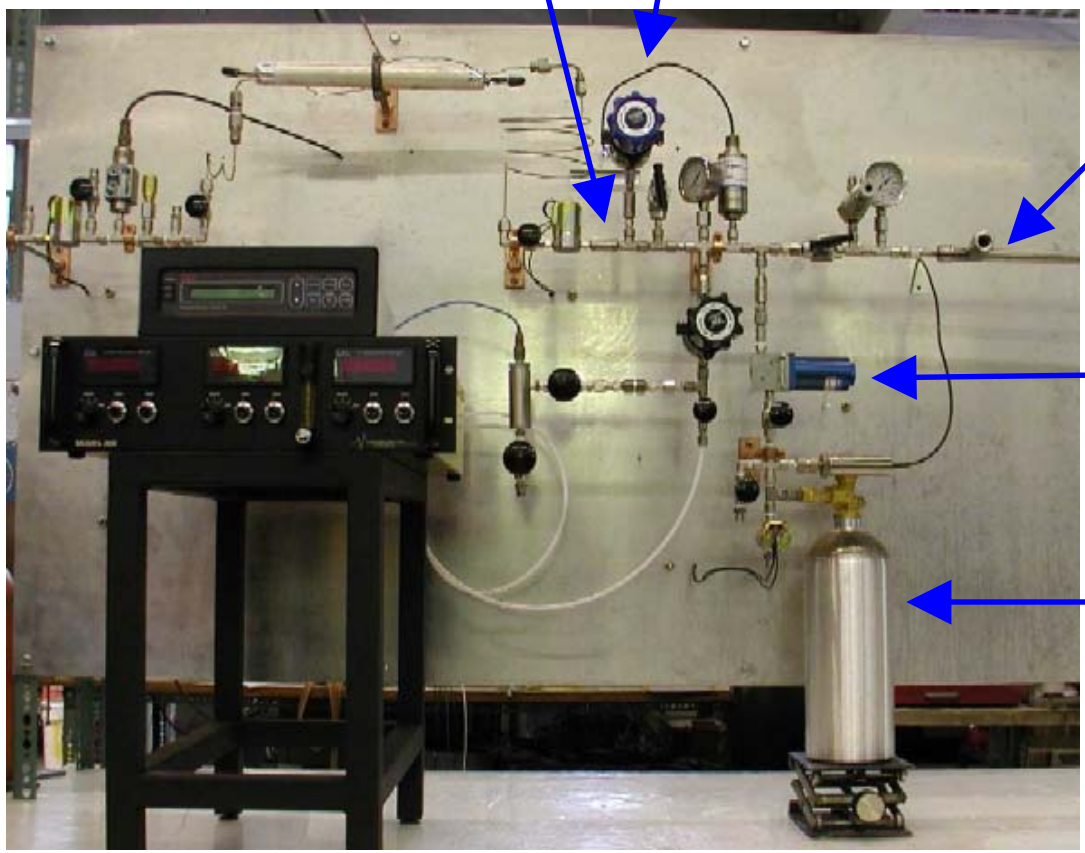
Approach

The compressor bed is a miniature hydride shell and tube heat exchanger measuring 0.75 inches in diameter by 60 inches long (19 mm D x 1524 mm L).

Hydride alloy is contained within four 0.125 inch diameter (3.2 mm) Inconnel tubes that are welded to a stainless steel tube sheet on one end and closed on the other end.

The tube “bundle” slides into the stainless steel shell, which is welded to the back side of the tube sheet. Heating/cooling fluid enters the shell via the perpendicular nozzle. The hydrogen manifold contains a filter disc to prevent alloy migration.

Approach



Hydride Compressor Test Stand

Project Timeline

Feasibility	Quantified H_2 quality anticipated from advanced and renewable production techniques. Preliminary design and Safety Analysis	FY2000
Validate and Test	Determine hydride alloys' resistance to disproportionation. Validate compressor operation at >5,000 psi. Determine hydride alloys' tolerance to impurities while cycling.	FY2001
	Test effectiveness of three purification techniques (passive purification for H_2O & O_2, **elevated temperature desorption for CO & CO_2, inert gas venting for N_2 & CH_4).**	FY2002
Refine Product Design	**Determine if compression with purification is a viable alternative for improving fuel cell performance.** **Reduce capital cost via miniature hydride heat exchangers and rapid cycling.**	FY2003
Full Scale Demonstration	**To be proposed**	FY2004

Status: Completed **In Progress** **Future**

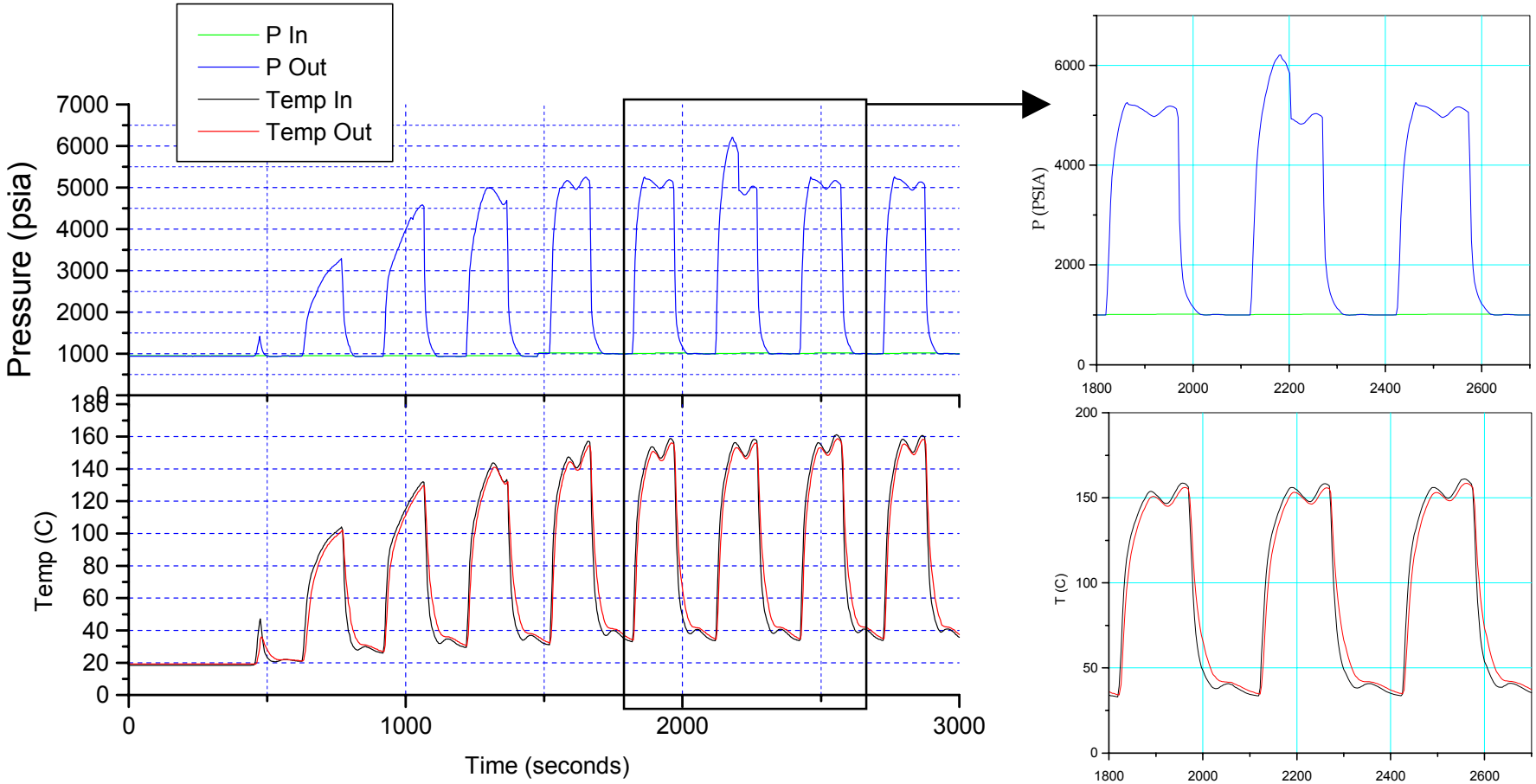
Accomplishments / Progress - H_2 Cost

Hydride Compression's Low Energy Cost Will Substantially Reduce the Cost of Hydrogen

H_2 Quantity	1 kg		1 kg	
Inlet Pressure	15 psia		15 psia	
Outlet Pressure	5,000 psia		10,000 psia	
Adiabatic Work	1,960 watt hours = 6,690 BTU		2,194 watt hours = 7,485 BTU	
Compressor Type	Mechanical	Hydride	Mechanical	Hydride
Efficiency	12%	15%	6%	10%
Fuel	Electricity at $0.05 / kWh	Natural Gas at $3 / MM BTU	Electricity at $0.05 / kWh	Natural Gas at $3 / MM BTU
Comp. Energy Cost / kg H_2	$0.82	$0.14	$1.83	$0.23
Energy Cost / H_2 Cost at $3.00/gge (2004)*	27%	5%	NA	NA
Energy Cost / H_2 Cost at $1.50/gge (2010)*	55%	9%	122%	15%

* FY 2004 Congressional Budget Request
gge = gallon of gasoline equivalent, which is ~ 1 kg H_2

Accomplishments / Progress - Energy Density



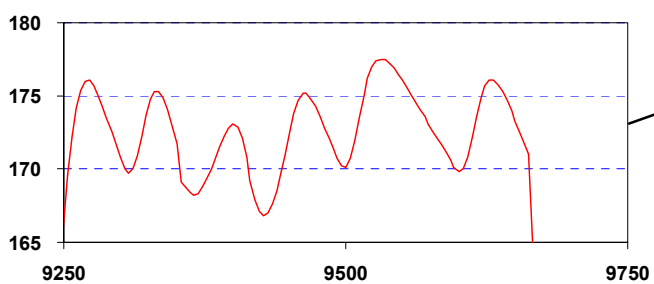
Compressed hydrogen is vented via a back-pressure regulator. The regulator was set at 5,000 psi (34 MPa) for most cycles, but was briefly increased to 6,000 psi (41 MPa) for the cycle that starts at Time = 2,000 seconds. The compressor is capable of operation to 10,000 psi (69 MPa).

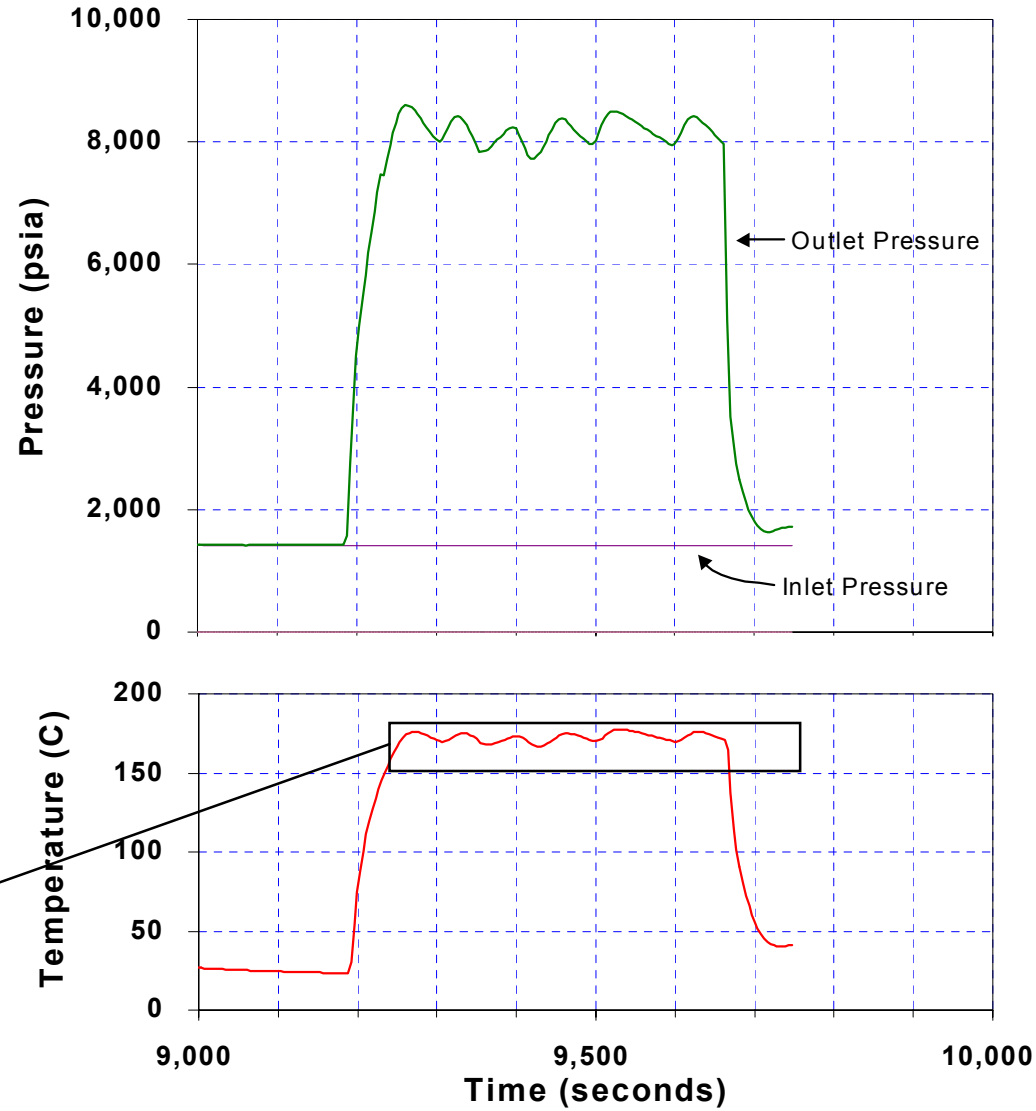
Accomplishments / Progress - Energy Density

High Outlet Pressure

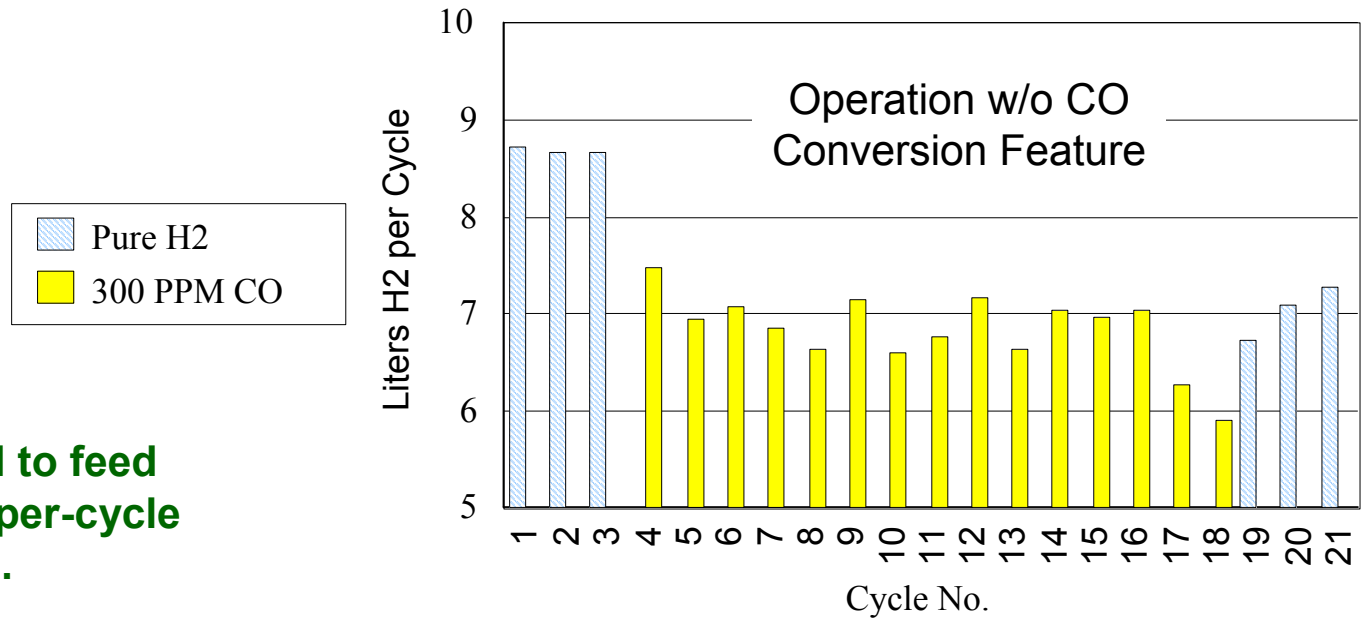
- Single Stage
- Inlet P = 1,200 psia
- Outlet P = >8,000 psia
- 10,000 psia will be achieved with elevated temperature

Pressure responds to fluctuation in water temperature as the heater cycles on and off



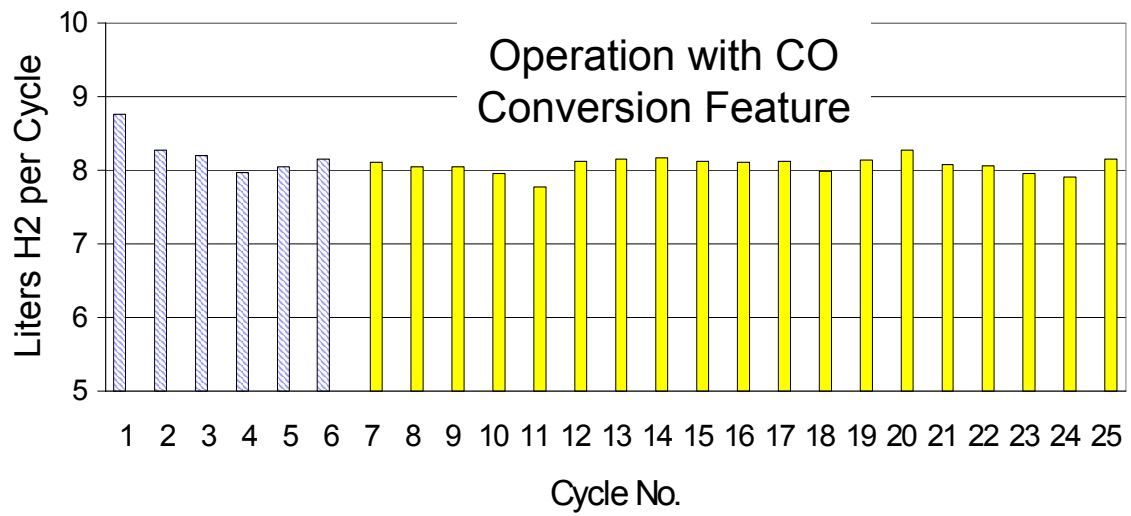


Accomplishments / Progress - H_2 Purity - Tolerating Impurities (1 of 2)



When CO is added to feed H_2, alloy capacity-per-cycle gradually declines.

A recently developed, proprietary CO conversion feature maintains alloy capacity.

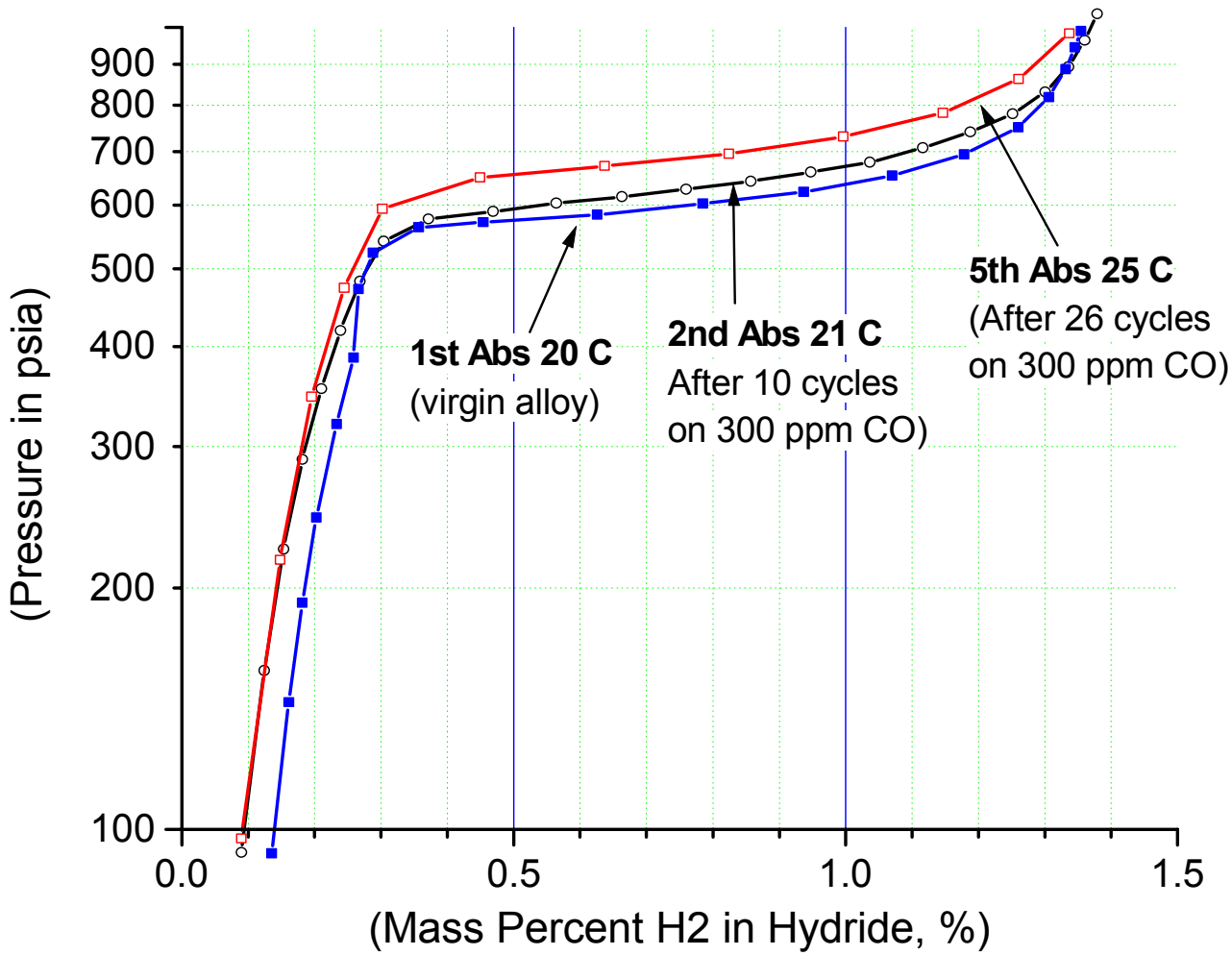


Accomplishments / Progress - H_2 Purity - Tolerating Impurities (2 of 2)

Compressor Alloy PCT Isotherms

PCT Isotherms* indicate the alloy was not damaged by CO. The differences in plateau pressures are a function of ambient temperature.

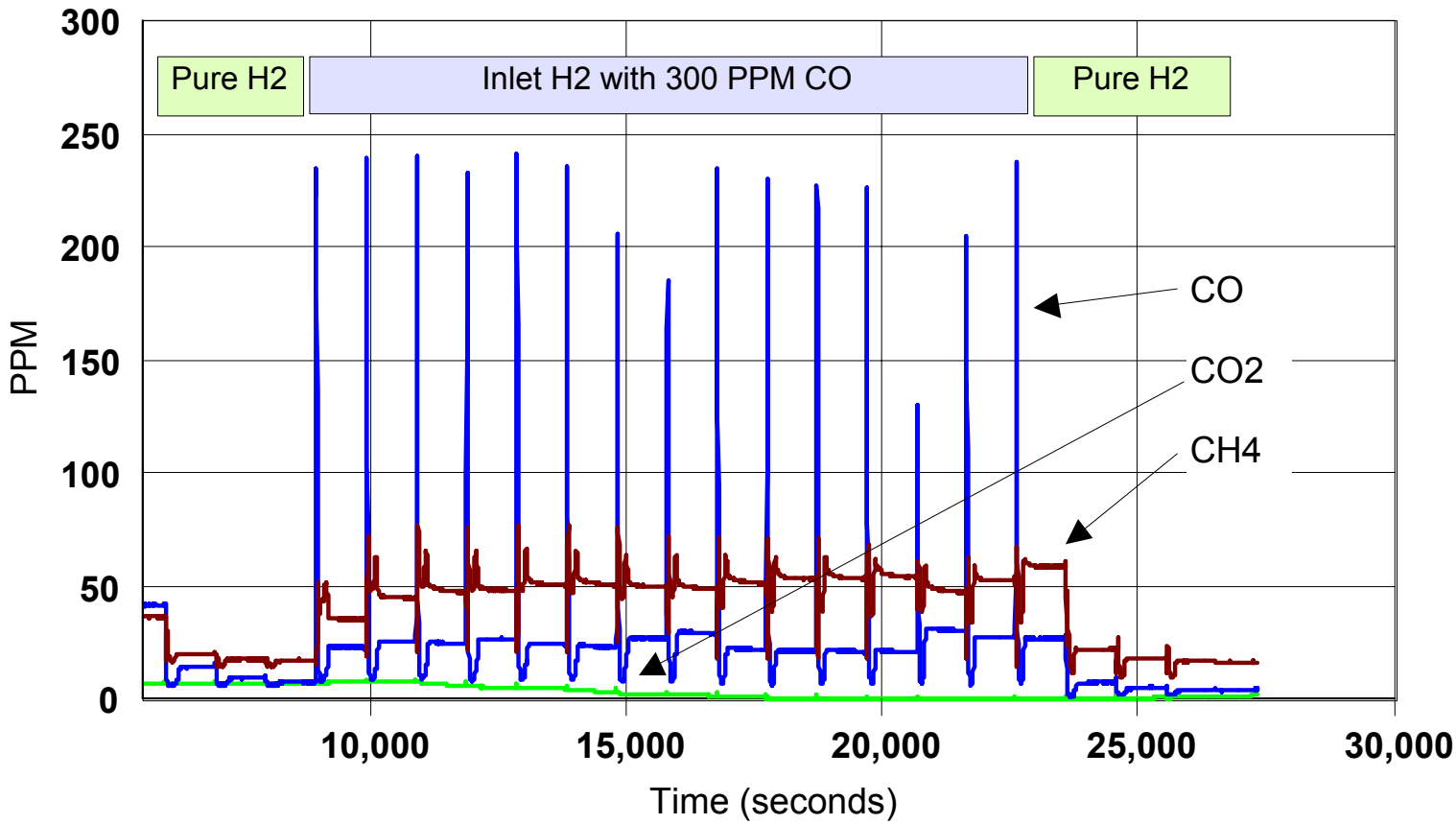
* PCT = pressure, composition, temperature



Accomplishments / Progress - H2 Purity - Removing CO (1 of 2)

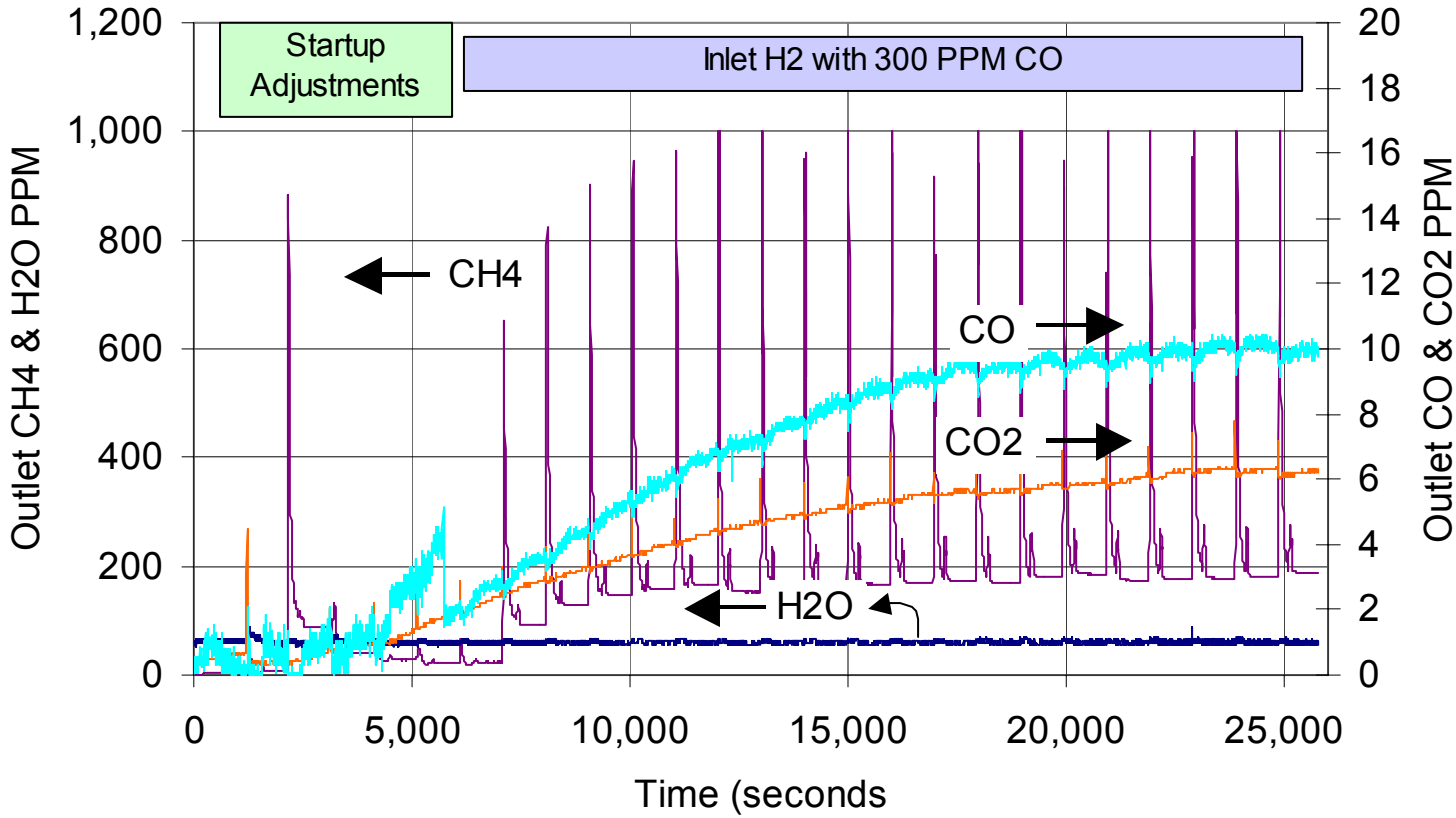
Outlet Hydrogen Composition w/o CO Conversion Feature

With 300 ppm inlet CO, CO outlet concentrations approach 250 ppm



Accomplishments / Progress H2 Purity - Removing CO (2 of 2)

Outlet Hydrogen Composition with CO Conversion Feature



300 ppm Inlet CO is reduced to 10 ppm to protect fuel cell electrode catalyst. CH4 will be removed via inert gas venting, made possible by the >1,000 ppm spike that is released at the very beginning of each desorption cycle.

Collaboration and Future Plans

Ergenics is contributing to the International Energy Agency Hydrogen Implementing Agreement for Solid and Liquid State Hydrogen Storage Materials.

Submitting patent application for CO conversion feature.

Seeking a H_2 refueling site and partners for a full scale thermal hydrogen compressor demonstration for FY2004. Are in discussions with three site operators, two hydrogen producers and a major oil company.

Catalytically Enhanced Hydrogen Storage Systems

Dalin Sun, Sesha Srinivasan, Keeley Murphy, Martin Sulic, Meredith Kuba, Alan Piwowar, and Craig M. Jensen

Department of Chemistry, University of Hawaii

Rationale

$$NaAlH_4 \Leftrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2\uparrow (3.73\ wt\ \%)$$

$$Na_3AlH_6 \Leftrightarrow 3\ NaH + Al + 1.5\ H_2\uparrow (1.87\ wt\ \%)$$

Ashby and Koberts *Inorg. Chem.* **1966**, *5*, 1615 and references therein.
Dymova, Eliseeva, and Bakum Dok. *Akad. Nauk USSR* **1974**, 215,1369.

Bogdanovic Breakthrough - 1997 The dehydrogenation process is rapid and reversible under **unprecedented**, moderate conditions upon treatment with a few mole % of selected dopant precursors.

Can doped complex hydrides be developed as hydrogen storage materials that are compatible with the Freedom CAR hydrogen storage system targets (Key parameters: cost, specific energy, and energy density).

Objectives

I. Determination of the chemical nature of the titanium species responsible for the enhanced kinetics of Ti doped $NaAlH_4$.

II. Determination of the mechanism of action of the dopants in the dehydrogenation and re-hydrogenation processes (i.e. H-H bond activation, Al-H bond activation, long-range Al atom transport?).

III. Apply fundamental insights to produce hydrides with improved hydrogen storage properties that are compatible with the Freedom CAR hydrogen storage system targets. Key parameters: cost, specific energy, and energy density.

Approach

Electron paramagnetic resonance (EPR) studies Detection of site isolated Ti^{3+}.

Magnetic susceptibility studies Quantification of the amount(s) of Ti^{3+} and Ti^{4+} present in Ti doped hydride.

X-ray diffraction Structural information (Na, Al, Ti).

Neutron diffraction Structural information (H atoms).

Approach

Solid State nuclear magnetic resonance (NMR) spectroscopy and inelastic neutron scattering (INS) Motions of the $[AlH_4]^-$ anion.

Infrared spectroscopy - Al-H bond vibrations.

Synthesis and testing of advanced alanates or other complex hydrides that are brought to light by the fundamental studies.

Timeline of Doped $NaAlH_4$ R&D Activities

Studies of doped alanates initiated at UH following Bogdanovic's "breakthrough"

Collaboration initiated with SNL for determination of engineering properties and scale-up studies.

Rate of dehydriding at 100 ˚C against 1 atm H_2 found to be 1.8 wt %/h.

Re-hydriding of >4 wt % achieved in < 0.5 h.

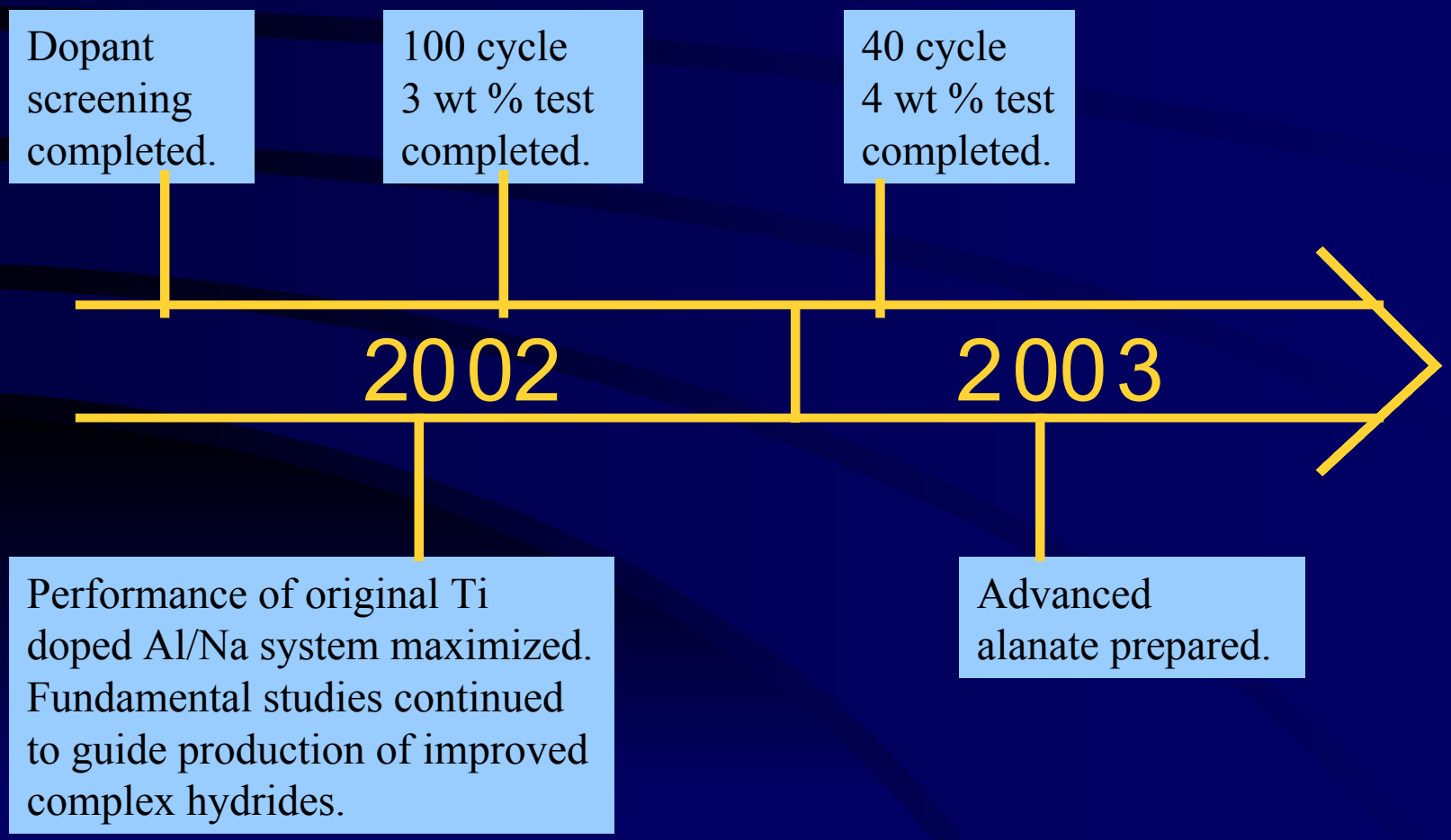
1998 1999 2000 2001

Doping of alanate by mechanical milling found to enhance kinetics and stability. Rapid dehydriding as low as 100 ˚C and 4.5 wt % reversible capacity.

Optimal conditions for dehydriding and re-hydriding determined at SNL.

XRD evidence obtained indicating that doping is a bulk phenomenon.

Timeline of Doped $NaAlH_4$ R&D Activities



Suitable Properties of Doped $NaAlH_4$ for Practical Onboard Storage of Hydrogen

- $NaAlH_4/Na_3AlH_6$ equilibrium plateau pressure: ~8 atm at 80 ˚C.
- Rate of dehydrogenation of 2 mol % Ti doped $NaAlH_4$ to Na_3AlH_6: 1.8 wt % per hour at 100 ˚C (adequate to meet the demands of an onboard PEM fuel cell).
- Rehydriding kinetics: > 4.0 wt % absorbed in 1 h (100 ˚C under 100 atm H_2).
- Stable cycling capacity for >100 cycles at 120 ˚C.

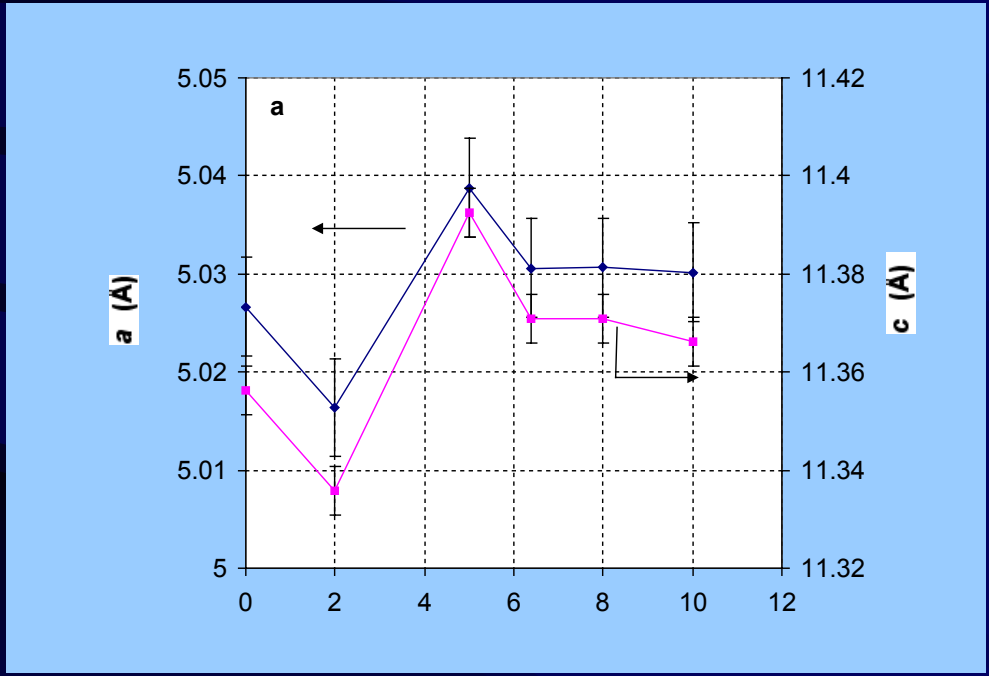
Barriers to Practicality

- Plateau pressure of the Na_3AlH_6/NaH equilibrium is less than 1 atm below 100 ˚C.
- Rate of dehydrogention of Na_3AlH_6 to NaH + Al is too slow even at 150 ˚C.
- Practical cycling capacity is (3.0 wt % at 120 ˚C and 4.0 wt % 150 ˚C) is too low.
- Search for improved dopants is exhausted.
- Dehydridng of other alanates (ie $LiAlH_4$ and $Mg(AlH_4)_2$, and alkali borohydrides (ie $NaBH_4$) irreversible under H_2 pressure.

Key question: Can the hydrogen storage properties of doped alanates or other complex hydrides be improved beyond those of the "original recipe, Ti doped Na/Al system????

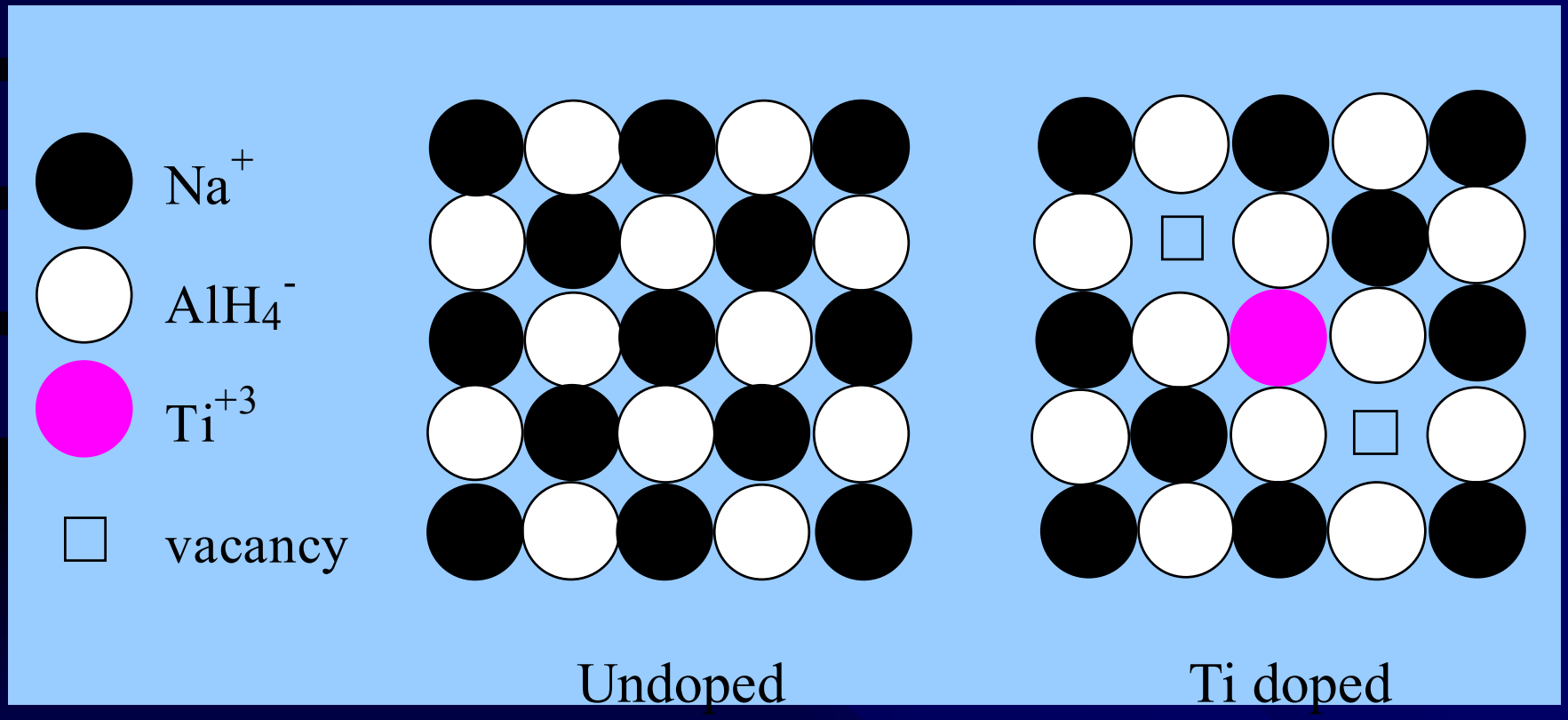
X-ray Diffraction Studies

Collaboration with the National Institute for Advanced Industrial Science and Technology, Osaka.



Lattice parameters (bulk structure) of $NaAlH_4$ vary as a function of dopant concentration.

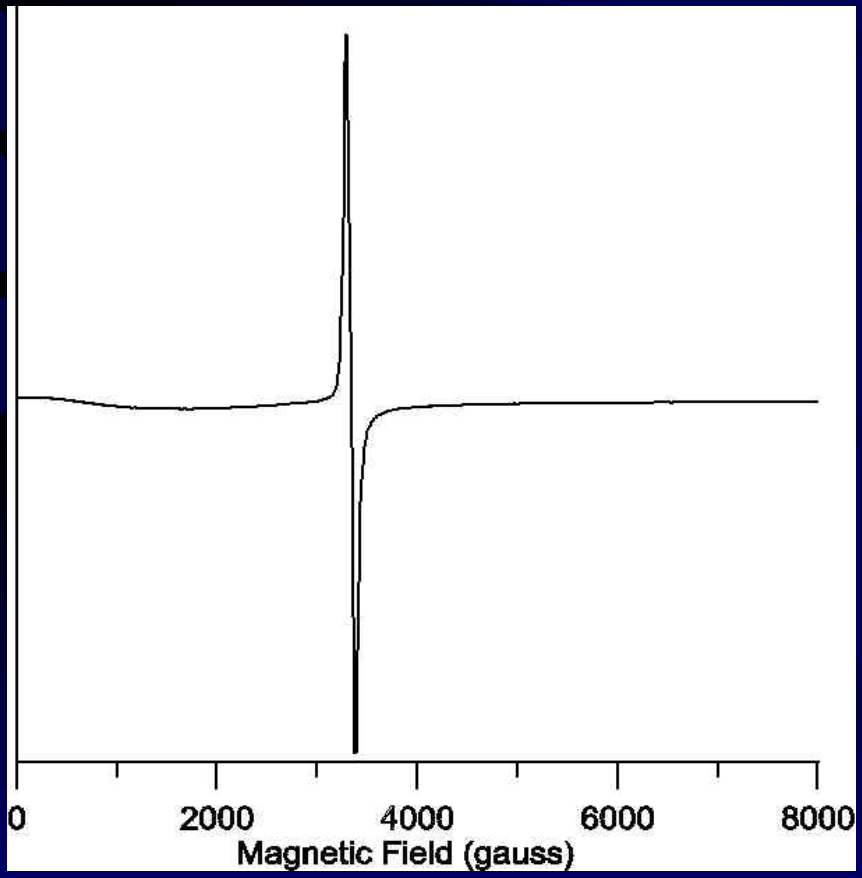
Ti^{3+}/Na^{+} substitution model of Ti doped $NaAlH_4$



D. Sun, T. Kiyobayashi, H. Takeshita, N. Kuriyama, and C. M. Jensen; *J. Alloys Compd.* **2002**, *337*, 8.

02-03 Results: EPR Studies

Collaboration with the University of Denver and Sandia National Laboratories



The EPR spectrum of $NaAlH_4$ doped with 1.5 mol % of $Ti(OBu)_4$ is dominated by a signal that is characteristic of spin isolated Ti(III). This finding is consistent with our model of the doped hydride in which Na^+ sites are substituted by Ti^{3+}.

02-03 Results
Magnetic Susceptibility

- Quantification of the amount of Ti(III) in Ti doped hydrides can be accomplished by comparison to standard curve of χ vs. moles Ti(III) loaded in inert material.

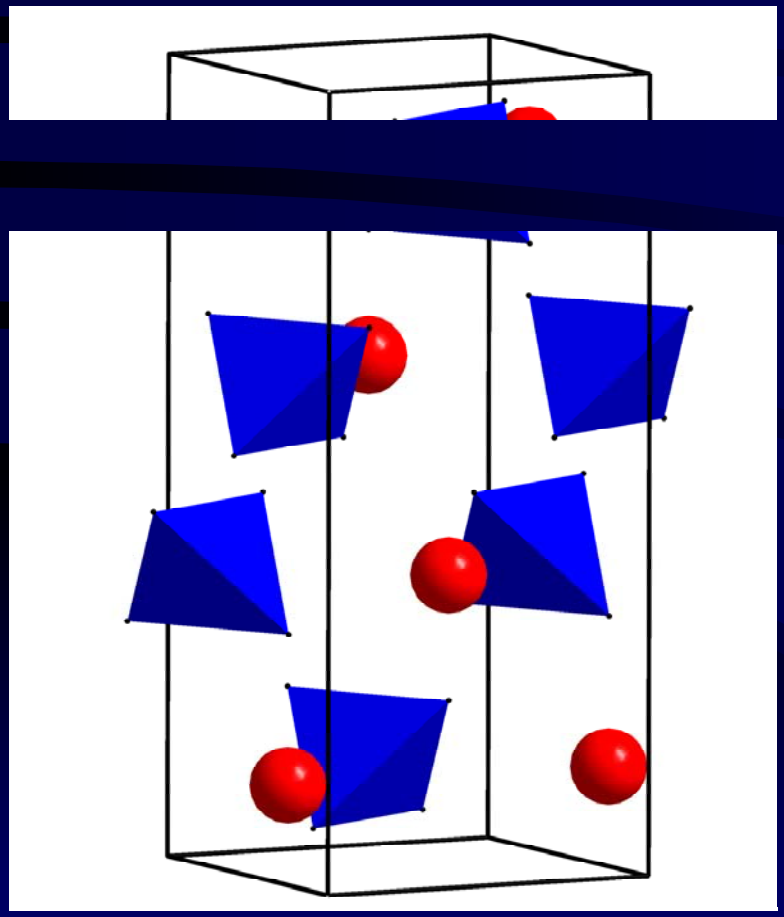
- Amount of Ti(IV) in doped hydrides can be determined by Ti_{total} - Ti(III).

- Standard curve has been generated.

Does kinetic enhancement track level of Ti(III), Ti(IV) or both?

02-03 Results
Neutron Diffraction

Collaboration with the Institute for Energy Technology, Norway



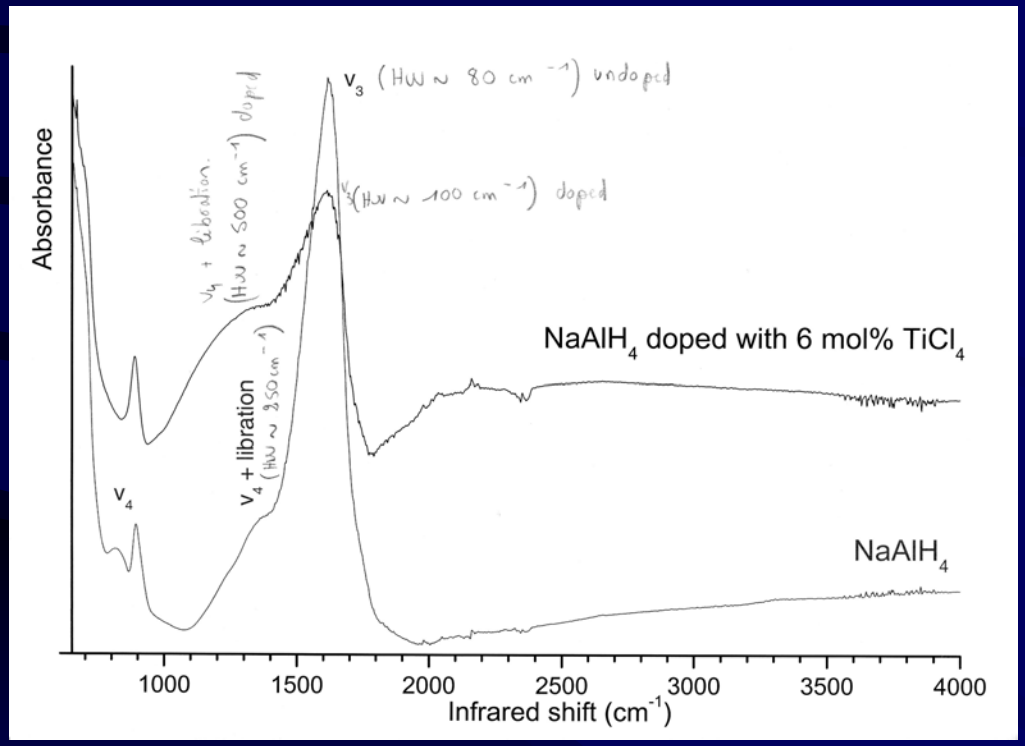
- Method developed for the synthesis of high purity $NaAlD_4$ (key to high quality neutron structure). Al-D 1.627(2), 1.626(2) Å; D-Al-D 107.30(1), 113.90(1)˚.

- No major structural differences found to arise upon doping.

B. Hauback, H. Brinks, C.M. Jensen, K. Murphy and A. Maeland; *J. Alloys Compd.* **2003,** in press.

02-03 Results
Infrared Spectroscopy

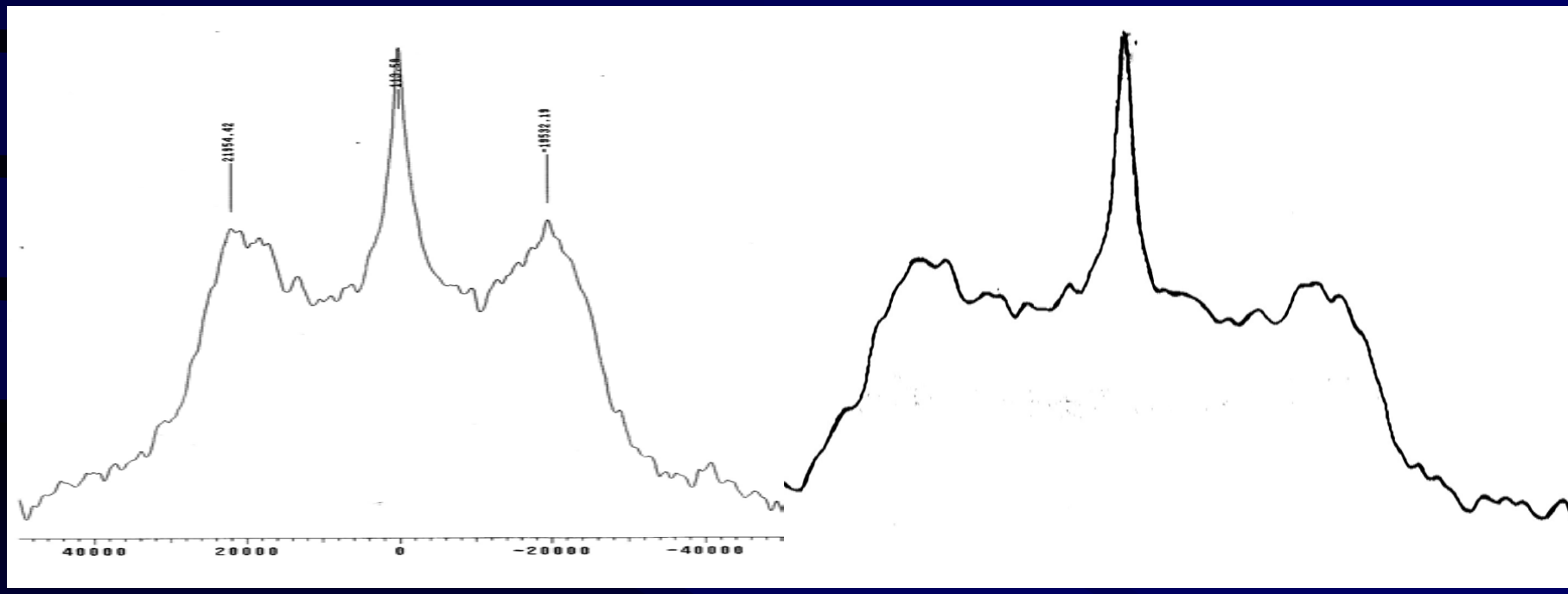
Collaboration with the University of Geneva



Broadening of Al-H upon Ti doping. ⇒ Increased distribution of Al-H vibrations.

02-03 Results: Nuclear Magnetic Resonance Spectroscopy

Collaboration with Washington University



^{2}H spectra show broadening dipolar doublet upon doping.

$\Rightarrow$ Deuterium in a wider range of environments.

02-03 Results: X-ray Diffraction and Inelastic Neutron Scattering

<u>X-ray Diffraction</u>

- "No broadening powder pattern lines upon doping"
  - University of Geneva
- "Broadening of one subset of lines upon doping"
  - IFE, Norway

<u>Inelastic Neutron Scattering</u>

- "Doped and undoped samples are very, very similar"
  - National Institute of Standards and Technology
- "Changes in relative intensities and widths of bands upon doping and new peaks in the low frequency region."
  - Los Alamos National Laboratory

Advanced Alanates

Doping $NaAlH_4$ with $TiCl_3$ or $TiCl_4$ results in the production of segregated NaCl by-product. Verified by XRD - K. Gross, G. Sandrock, G. Thomas, *J. Alloys Compd.* 2002, *330*-332, 691.

Key question: Can removal of "deadweight" NaCl lead to materials that meet program targets?

Advanced Alanates

Bogdanovic "Redox" model of doping predicts NO - Doping of $NaAlH_4$ with $TiCl_3$ thought to produce segregated AlTi alloy.

- No change in bulk thermodynamic properties
- One equivalent loss in hydrogen carrying Al
  - ⇒ 3 equivalent loss in hydrogen capacity
  - ⇒ Hydrogen capacity can not be improved over 5.60 wt % theoretical even upon removal of Na by-product.

Ti^{3+}/Na^{+} substitution model predicts YES - Doping results in bulk substitution.

- Changes in bulk thermodynamic properties.
- All Al remains available for hydrogen binding.
  - ⇒ Hydrogen capacity increases (and kinetics enhanced) upon increased doping if Na by-product is removed. Theoretical capacities of >6.00 wt %.

02-03 Results
Advanced Alanates

Effect of doping level on plateau pressure

Desorption plateau pressure of sodium aluminum hydride at 150 ºC.

Dopants and Doping Level (mol. %)		Pressure (Mpa)
$Ti(OBu)_4$	1.3	3.0(±0.2)
	1.7	3.6(±0.2)
	2.0	4.7(±0.2)
$TiCl_4$	2.0	5.7(±0.1)
TiF_3	2.0	5.5(±0.3)

Thermodynamic properties effected ⇒ Doping is a bulk phenomenon

02-03 Results
Advanced Alanates

Collaboration with the University of Milan

Proprietary method has been developed for the removal of sodium by-product.

02-03 Highlight Summary

- EPR shows high levels of spin isolated Ti(III) are present after doping in accordance with Ti^{3+}/Na^{+} model. X-ray and neutron diffraction studies show only subtle structural changes occur upon doping.

- Spectroscopic studies (IR, NMR and INS) provide evidence of increases and changes in hydrogen motions throughout the bulk of the hydride upon doping.

- Predicted changes in plateau pressures upon doping have verified.

- Proprietary method has been developed for the removal of sodium by-product.

Collaborations and Technology Transfer

National Institute for Advanced Industrial Science and Technology, Osaka, Japan - XRD; Dr. Tetsu Kiyobayashi, Dr. Nobuhiro Kuriyama.

University of Denver - EPR; Prof. Sandra Eaton.

Sandia National Laboratories - EPR; Dr. Karl Gross, Dr. Eric Majzoub.

Institute for Energy Technology, Kjeller, Norway - Neutron diffraction and XRD; Dr. Hendrik Brinks, Dr. Bjorn Hauback.

University of Geneva - Infrared; Prof. Klaus Yvon, Dr. Sandrine Gomes

Washington University- NMR; Prof. Mark Conradi

Los Alamos National Laboratories - INS; Dr. Juergen Eckert.

National Institute of Standards and Technology - INS; Dr. Terry Udovic.

University of Milan - XRD; Prof. Alberto Albinati.

International Energy Agency Annex 17.

US patent 6,471,935 licensed by the University of Hawaii to Hawaii Hydrogen Technologies.

Future Directions

Continue characterization and quantification of titanium species in Ti doped hydrides by combination of EPR and magnetic susceptibility studies and establish if the kinetic enhancement is due to Ti(III), Ti(IV), or both.

Continue infrared, NMR, and INS spectroscopic studies and obtain Raman spectra to elucidate the influence of doping on the dynamics of the $[AlH_4]^-$ anion and the relationship of these motions to the mechanism of reversible dehydrogenation of the doped hydride.

Determine the hydrogen cycling properties of doped $NaAlH_4$ following removal of the sodium by-product. Test whether this approach can be extended to $\mathbf{Na_{0.4}Ti_{0.2}AlH_4}$ $\Rightarrow$ <u>6.03 wt % available H and kinetic enhancement equal to 20 wt % Ti doping</u> and its Li and Mg analogs (6.92 and 6.60 wt % available H respectively).

Response to 02 Reviewers

THANKS!

Question 8b "….benefit the Hydrogen Program in attainment of the program goals…"
Reviewer: "will come close"

Key question: Can alanates meet the new, radically increased capacity targets or should we move on to other complex hydrides.

Response: 1) The practical improvement that can be achieved by the removal of sodium by-products needs to be determined.

Hydride Development for Hydrogen Storage

Karl Gross

Sandia National Laboratories
Livermore, California

Combining Fundamental Science,
Materials Development and Engineering Science

DOE Hydrogen and Fuel Cells Annual Merit Review
Berkeley, CA May 19-22, 2003

Sandia National Laboratories

Sandia's Hydrogen Storage R&D Objective

Practical hydrogen storage using light-weight reversible hydrides

The lack of a safe and practical means of onboard hydrogen storage is one of the biggest obstacles to the realization of hydrogen powered transportation.

Goals

- Meet or exceed US-DOE / FreedomCAR Hydrogen storage targets
- Improve performance: capacity, kinetics, thermodynamics, and cycle life
- Expand knowledge of hydrogen sorption phenomena in solid-state media

Sandia's Hydrogen Storage R&D Capabilities Strong & Expanding

People

H_2 Storage Research Team (DOE & internally funded)

- 5 Staff members
- 1 Post-doc
- 3 Technologist
- 2 Students

Facilities

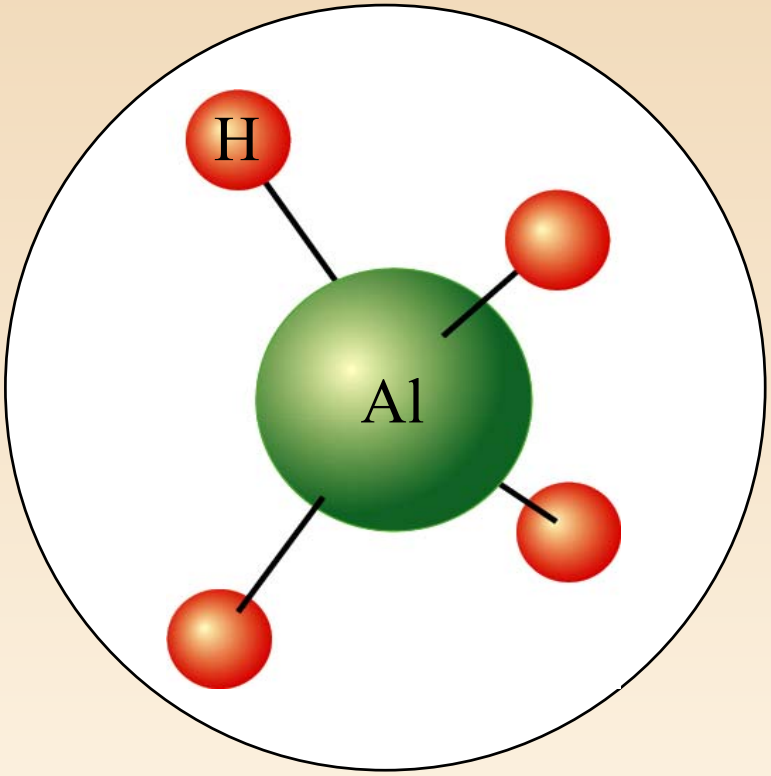
H_2 Storage Materials Synthesis & Characterization

- 1 Automated PCT instrument
- 3 Manual Kinetics instruments
- 2 Cycle-life instruments
- 2 In situ X-ray diffractometers
- 2 Inert gas prep glove boxes
- SEM, TEM, NMR, XPS, Auger...

Candidate Solid State Hydrogen Storage Media

Complex Hydrides

High Gravimetric Hydrogen Capacities !



Examples	Capacity*
$Na(AlH_4)$	5.6 wt%
$Li(AlH_4)$	7.9 wt%
$Mg(AlH_4)_2$	7.0 wt%
$Ti(AlH_4)_4$	8.1 wt%
$Fe(BH_4)_2$	9.4 wt%
$NaBH_4$	7.9 wt%
$Ca(BH_4)_2$	8.6 wt%

** Theoretical Reversible Capacities*

Sandia's Science-Based Approach

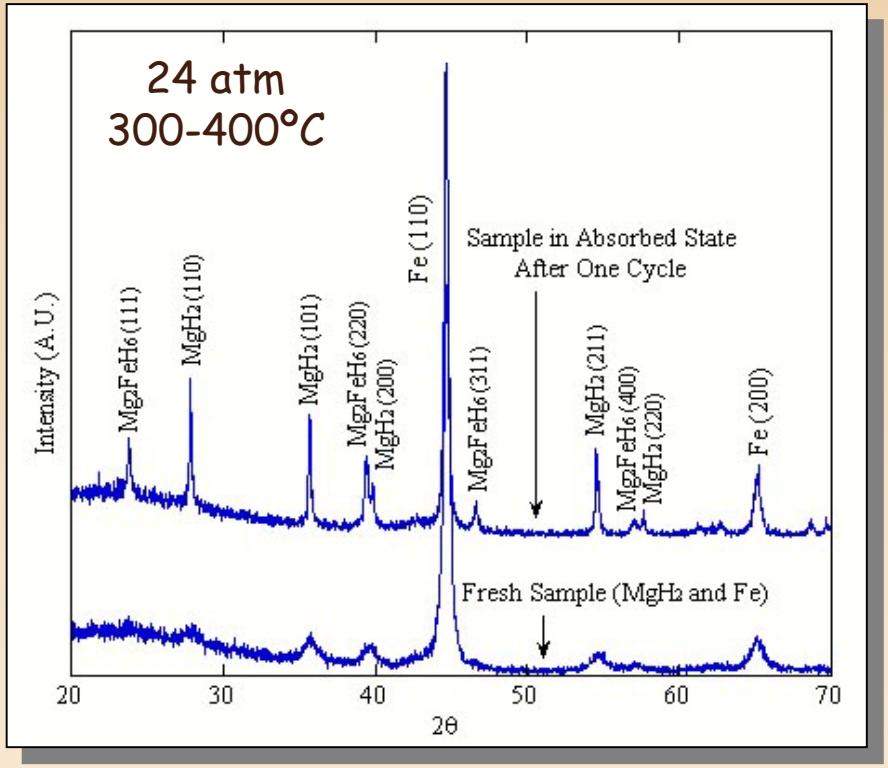
A) Advanced Complex Hydrides

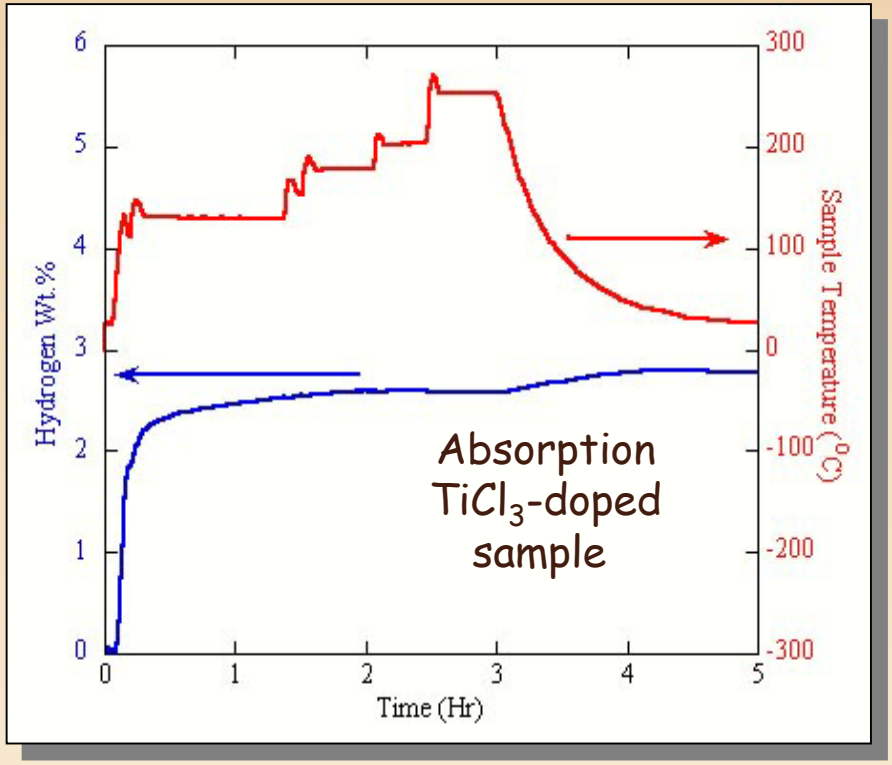
- Improve performance of alanates through modified chemistry.
- Test reversibility and stability of other complex hydrides.
- Demonstrate dopant-enhanced activity of other hydrides.

B) $NaAlH_4$ as Model System

- Develop synthesis and doping processes to:
  - Improve H_2 absorption/desorption properties.
  - Reduce cost and complexity of production.
  - Apply to development of new complex hydrides.
- Determine mechanism of Ti-enhanced Abs/Desorption through experimental analysis and modeling.
- Characterize engineering materials properties.

Reversible Complex Hydride Mg_2FeH_6





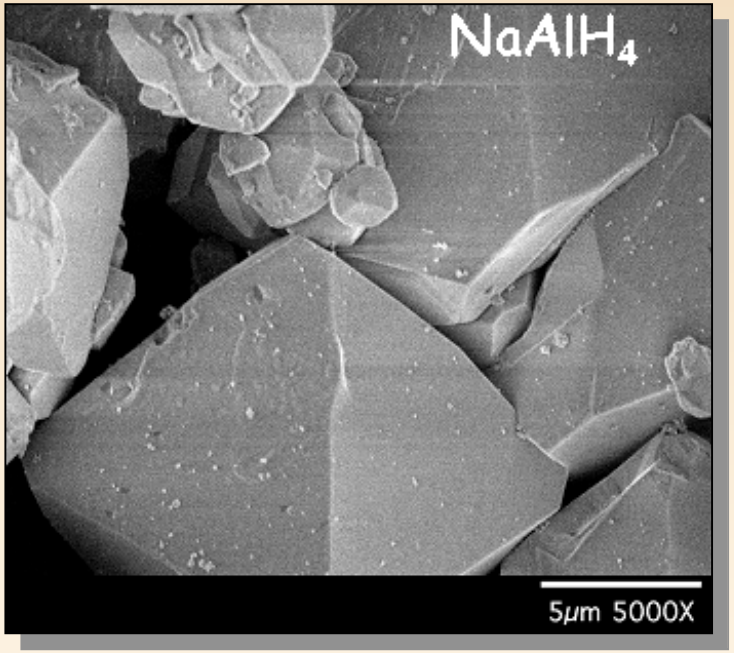
- Used direct synthesis technique starting with MgH_2 and Fe
- MgH_2 used instead of Mg for ease of milling
- Formation of Mg_2FeH_6 under milder conditions than previously reported
- Doping with $TiCl_3$ affects the rehydriding kinetics
- Notable and rapid absorption below 100°C

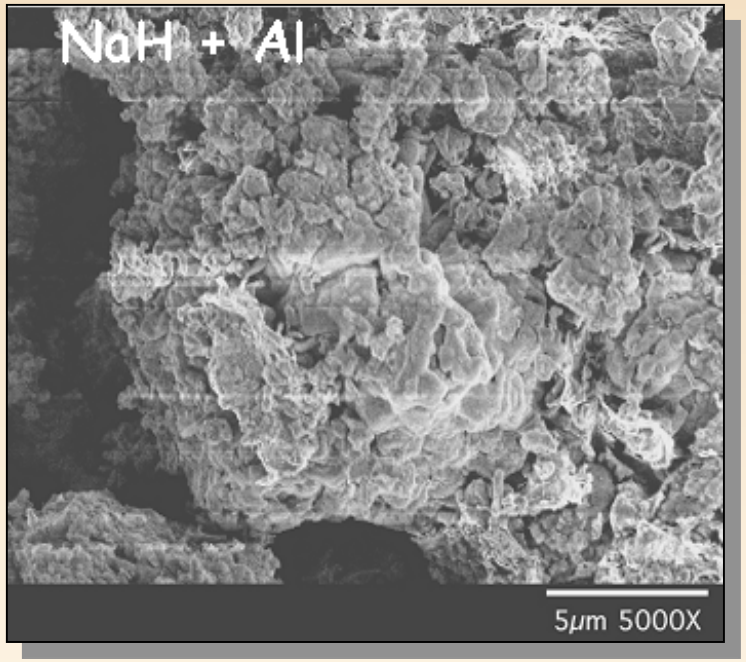
Hydrogen from Thermal Decomposition of Sodium Alanates

Total Theoretical Capacity = 5.6 wt% hydrogen

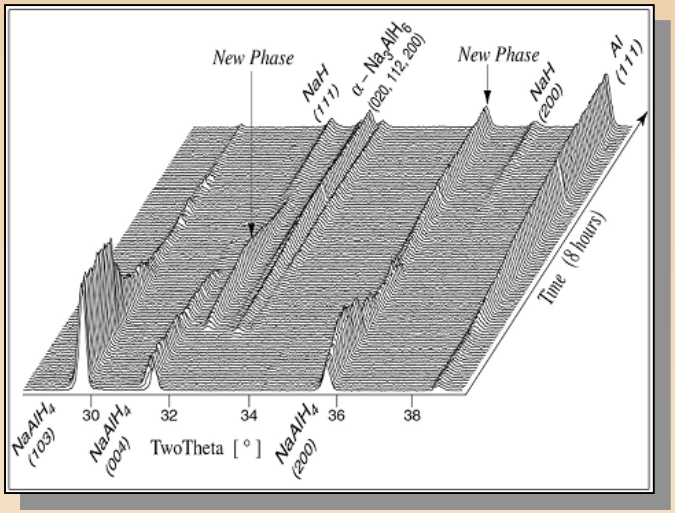
$$NaAlH_4 \Rightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \Rightarrow NaH + Al + 3/2H_2$$

3.7 wt.% 1.9 wt.%

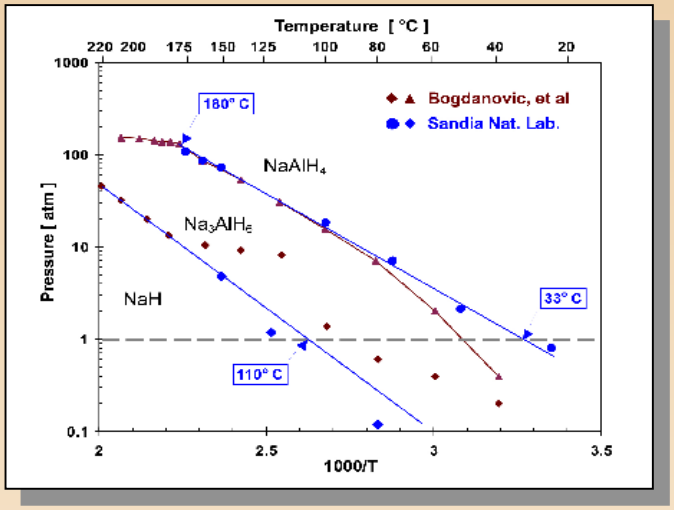




Past Accomplishments

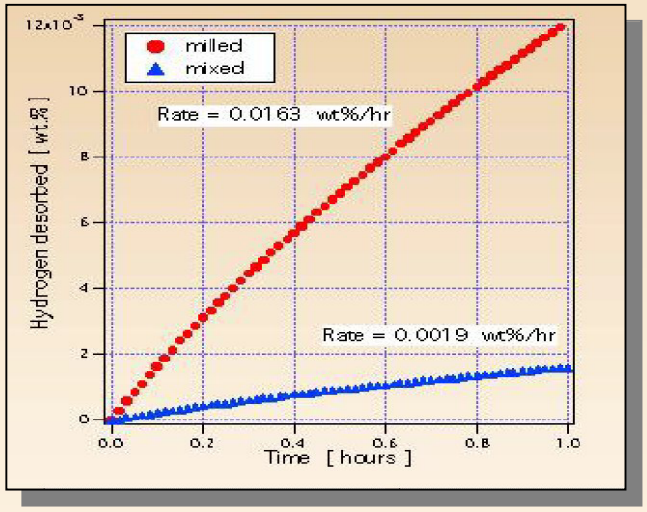


- In situ XRD - Phase Transitions



- Determined Thermodynamics

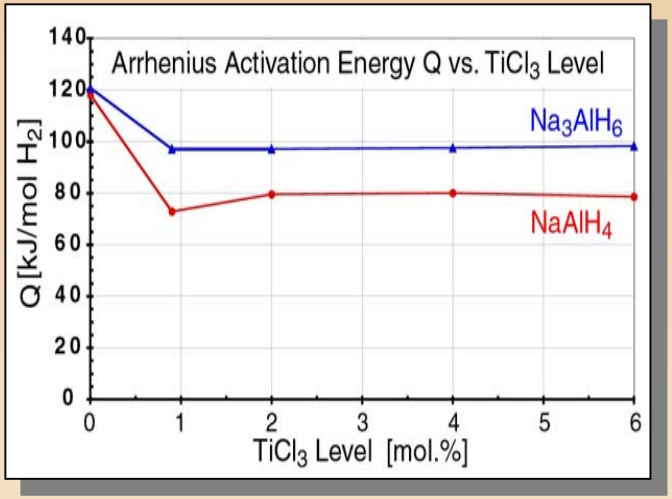
1999 → 2000

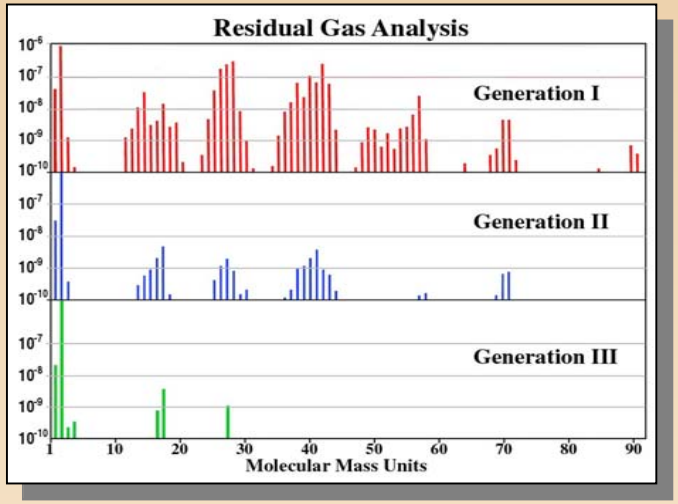


- Milling Synthesis / RT Desorption

- 1st Scaled-up Alanate Tests

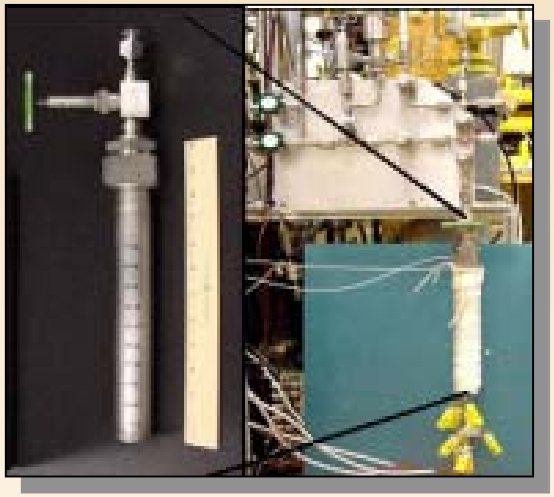
Past Accomplishments Cont.



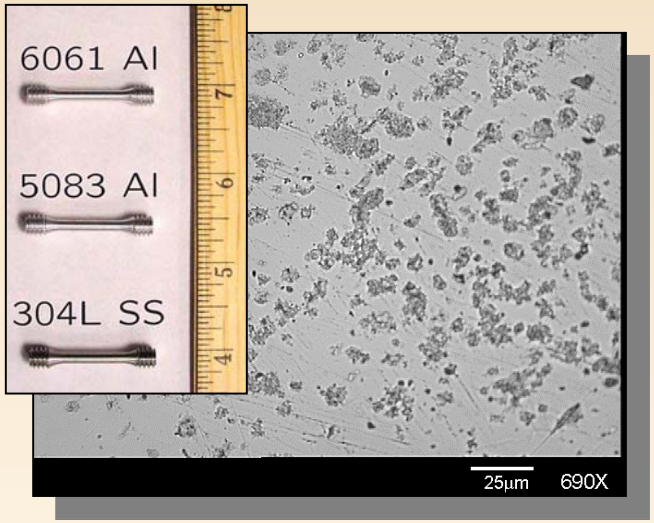


- Kinetics v.s. Level of Ti-Loading
- Direct Synthesis

2001 → 2002

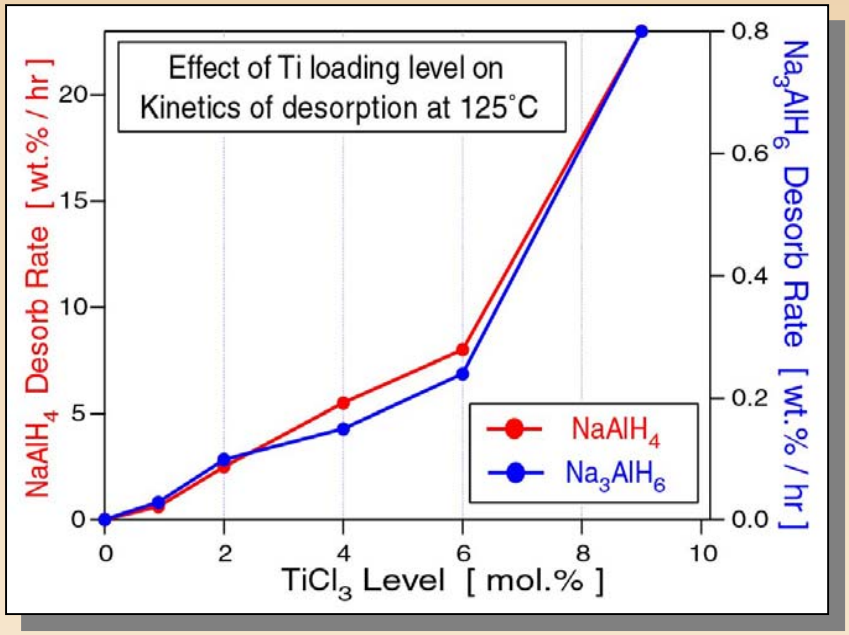


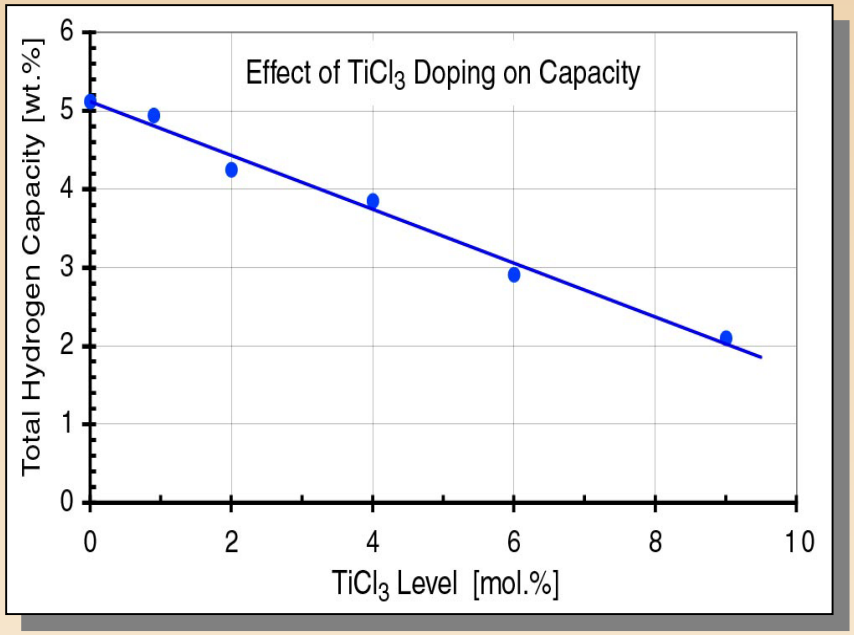
- Instrumented Test Bed



- Safety and Compatibility Testing

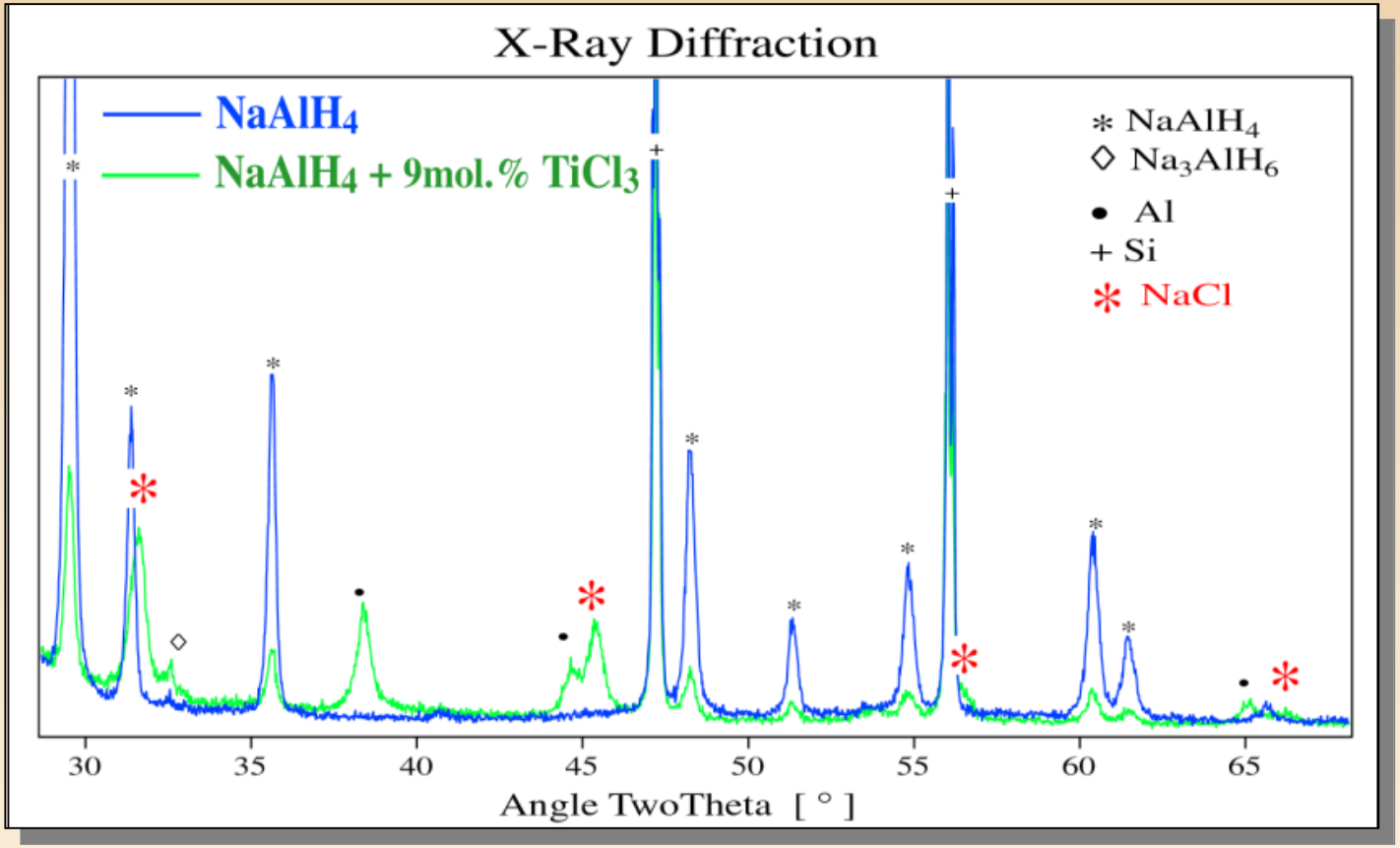
Motivation
for Understanding and Improving Doped-$NaAlH_4$





- Desorption (and Absorption) Kinetics increases with $TiCl_3$ doping level
- Reversible Hydrogen Capacity decreases with $TiCl_3$ doping level
- There is a trade-off between improved kinetics and capacity loss
- How can we improve both kinetics and capacity?
- What is the role of doping in the mechanism of enhanced kinetics?

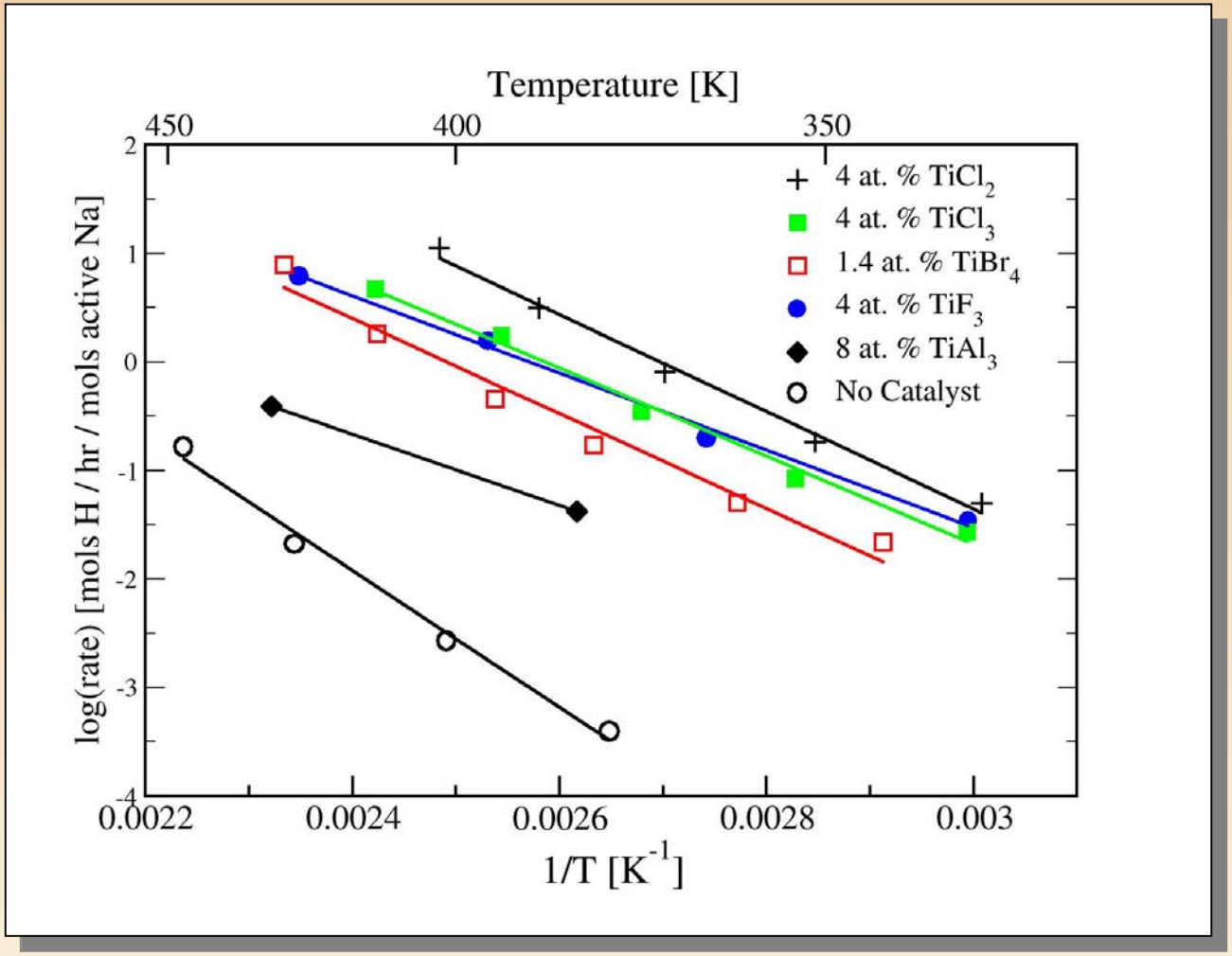
Cause of the Drop in Capacity



- XRD showed the formation of NaCl through the reaction:

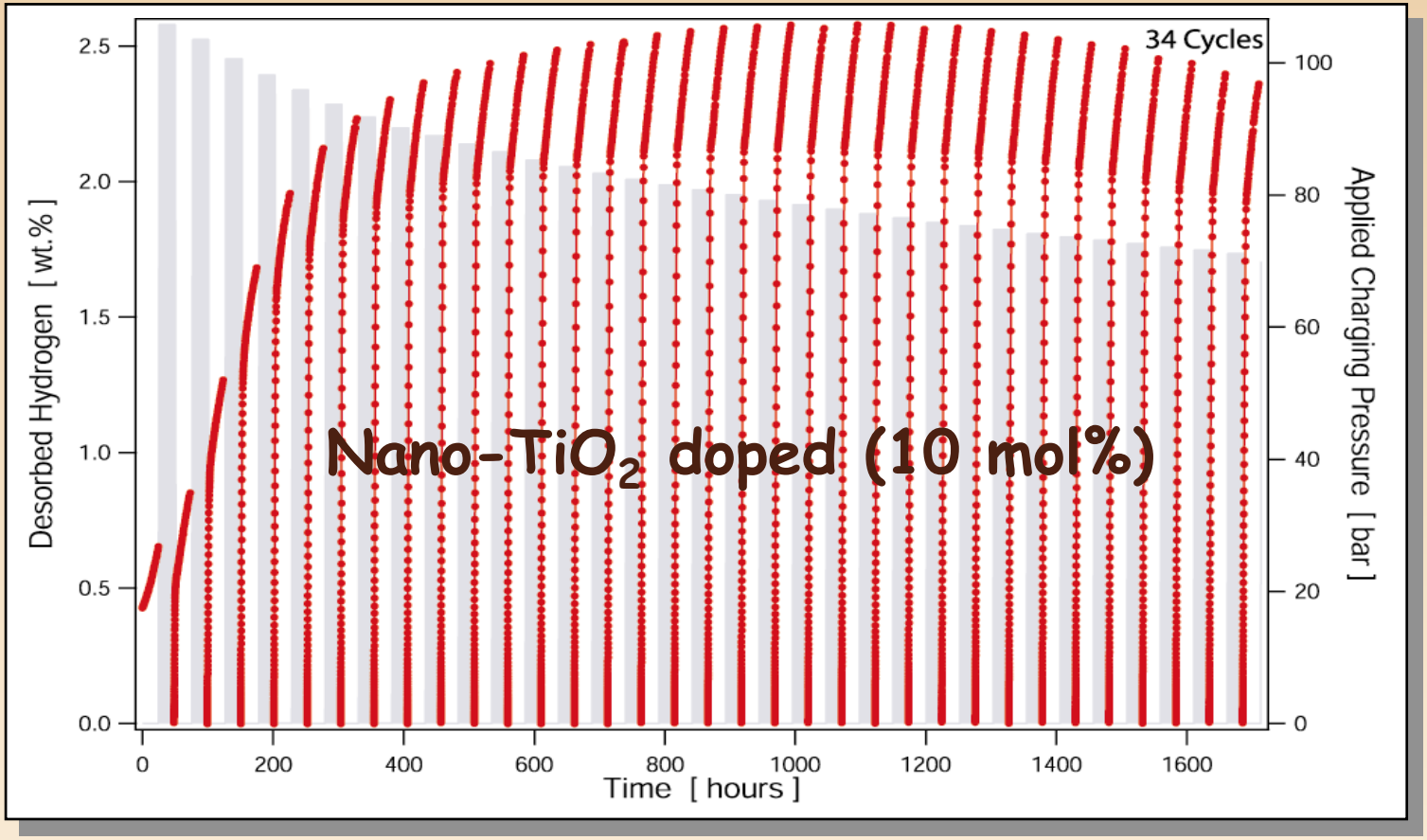
$$3NaAlH_4 + TiCl_3 \Rightarrow Ti + 3NaCl + 3Al + 6H_2$$

Doping With Other Ti-halides and Alloys



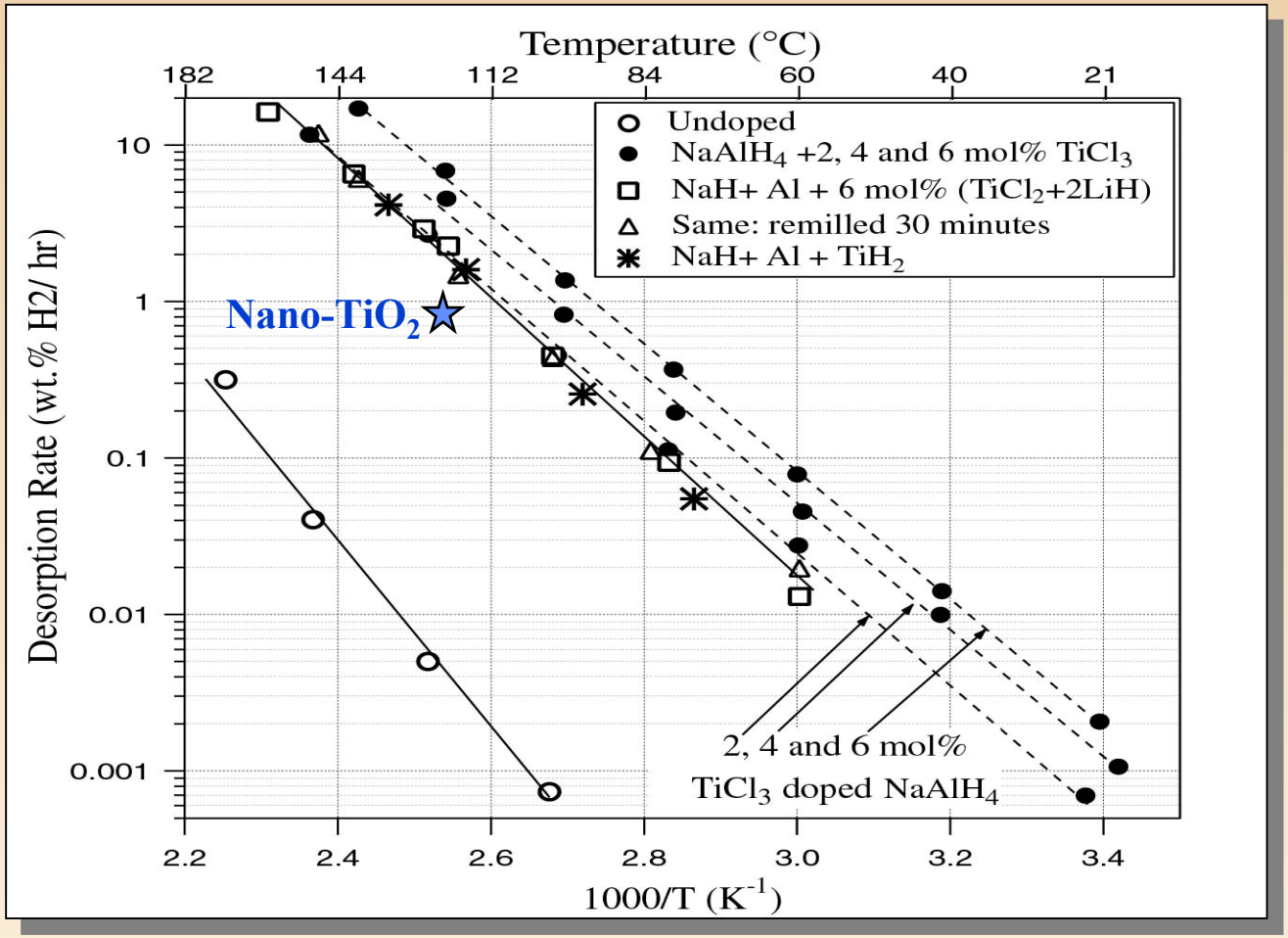
- Activation Energies are identical for $TiCl_3$ and TiF_3
- Rates are Independent of Ti-halide precursor

Reactive Halide-Doping not Required



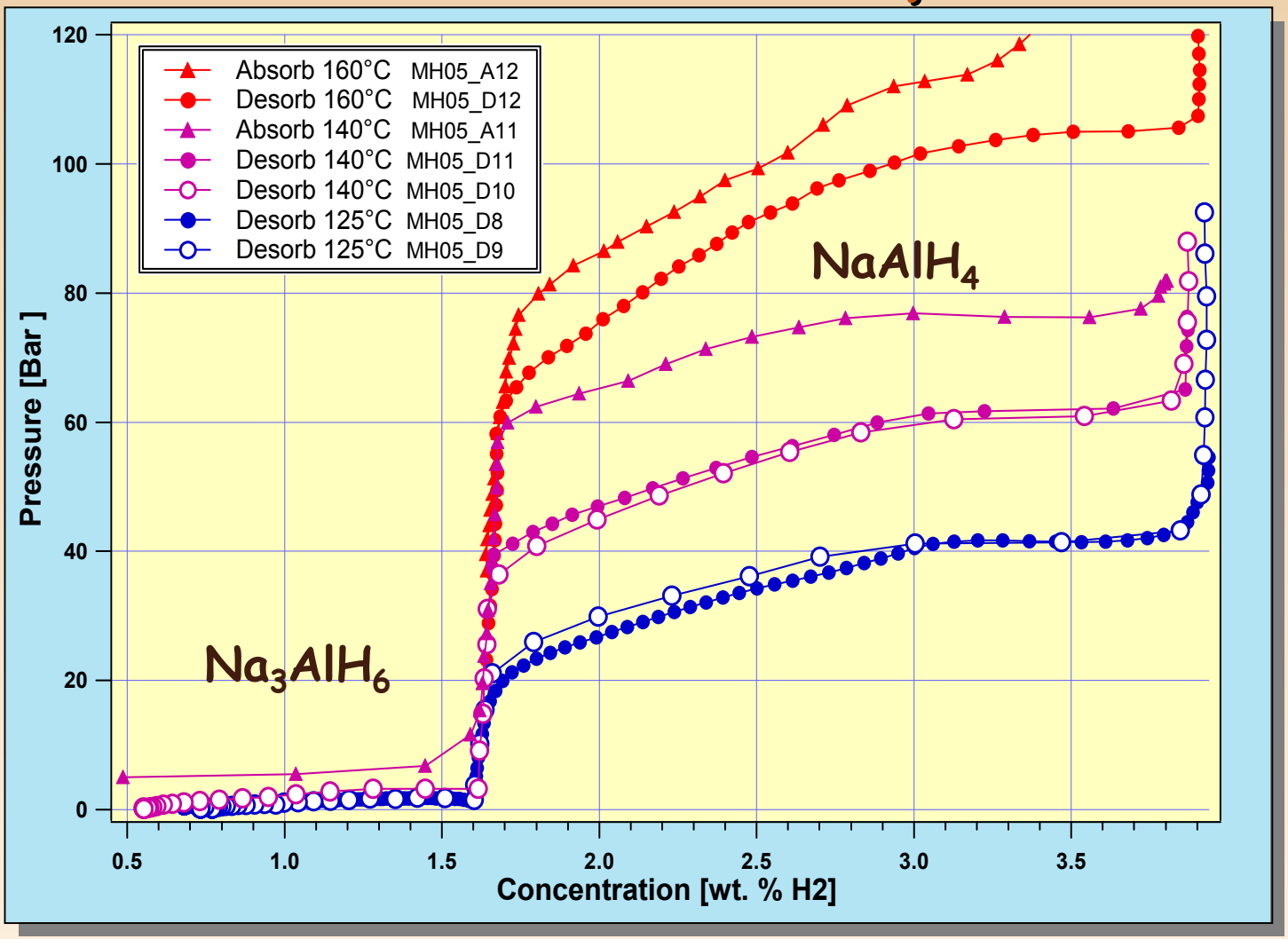
- Activation Process required ~ 8 cycles
- Rates comparable with direct doping of 1 mol% $TiCl_3$
- No capacity loss due to Na-halide reaction (nominal 4 wt.% H_2)
- Well dispersed nano-dopant may promote better kinetics

Indirect Doping Processes: TiO_2, TiH_2, PR-$TiCl_2$



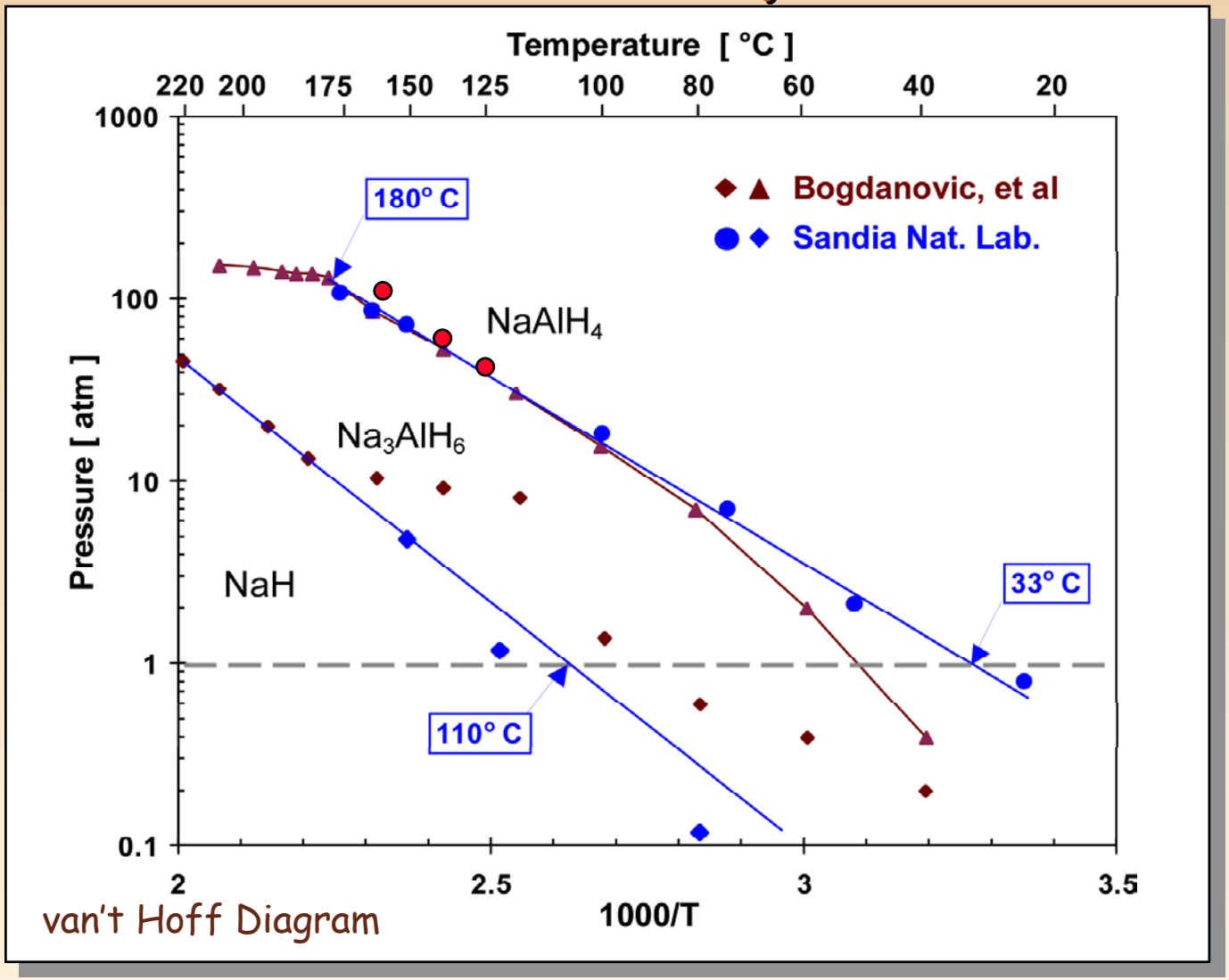
- Rates comparable with direct doping of 1-2 mol% $TiCl_3$
- Activation energies are similar to direct doping
- Potential to improve capacity

PCT Measurements: Ti-doped $NaAlH_4$



- Two separate components of $NaAlH_4$ phase (Ti distribution?)
- Combination of different kinetics and thermodynamics likely

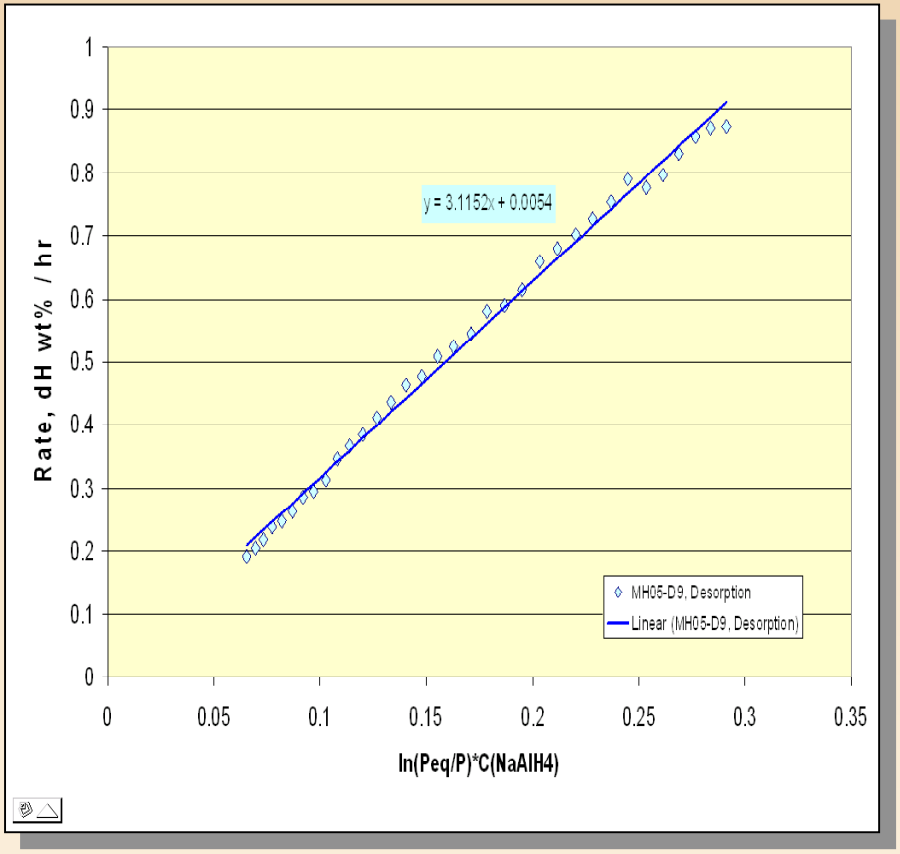
Modified Thermodynamics ?

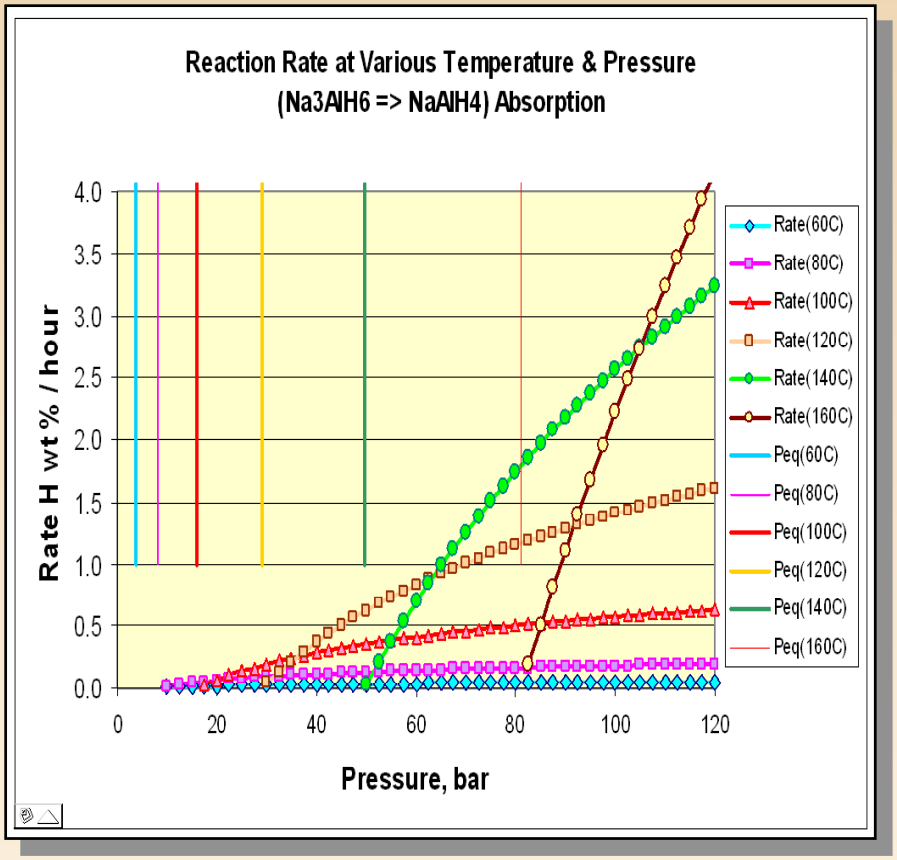


- Slightly less stable than previous data indicates

Advanced Kinetics Model ⇒ Optimum Conditions

$$dC/dt_{des} = k_o \exp(-Q/RT)\ln(P_{eq}/P)C(NaAlH_4)$$





- Rate dependent on T, ΔP, and phase content C
- Charging alanates at a lower temperature may be advantageous

Future Plans

Other Complex Hydrides

- $Mg(AlH_4)_2$ (7 wt.% theoretical)
  - Used direct synthesis technique starting with MgH_2 and Al
  - Complex hydride did not form at 100 atm and 350°C
  - Using special facilities to test high-pressure synthesis 10+kpsi
- Looking at other complex hydrides with even higher capacities

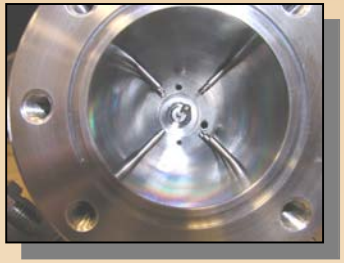
Na-Alanates

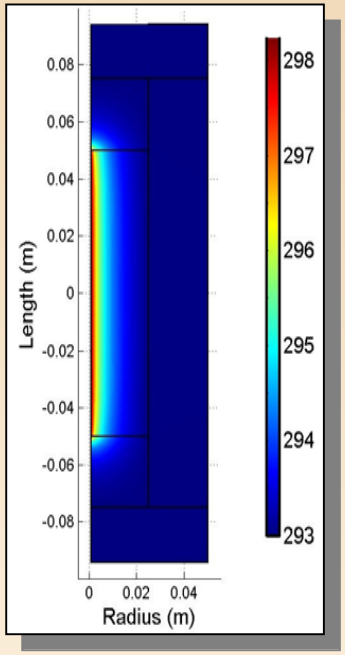
- New non-reactive dopants
- Further PCT analysis
- Structural modifications through substitution (Li,…)

Materials Engineering Properties of Complex Hydrides

- Thermal Properties
- Volume Expansion & Packing Densities
- Electrical Properties

Engineering Science: Material Properties of Sodium Alanate





Instrumented chamber to measure:

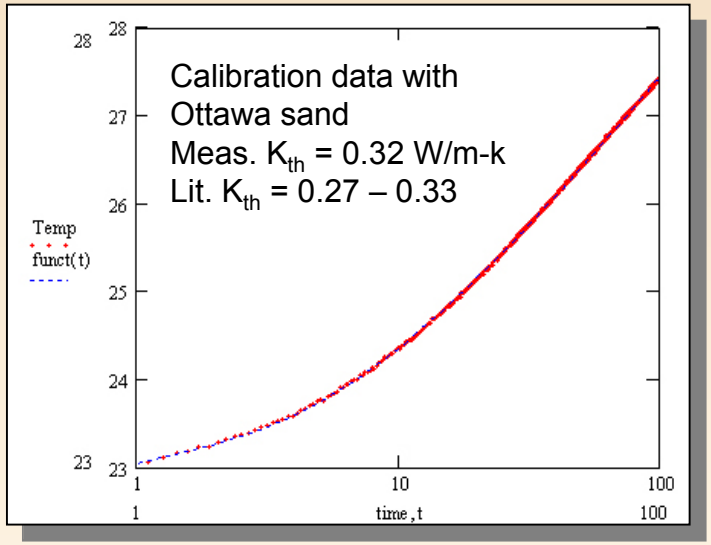
- Thermal conductivity
- Wall resistance
- Porosity

As a function of phase, temperature, cycle, morphology, and pressure.

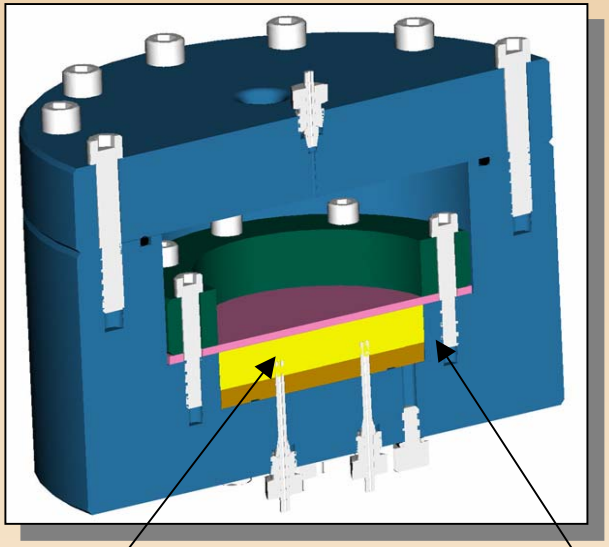
$$T(t) = A \cdot \ln t + B + C \cdot \frac{\ln t}{t} + D \cdot \frac{1}{t}$$

$$K_{th} = \frac{r_P \cdot Q'}{2 \cdot A}$$

$$h_i = \frac{1}{r_P} \cdot \left[\frac{2 \cdot K_{th}}{\frac{B}{A} - \ln\left(\frac{K_{th}}{\rho \cdot c}\right) + 2 \cdot \ln(r_p) - \ln(4) + 0.8141} \right]$$



Engineering Science: Material Properties of Sodium Alanate



Volumetric Expansion
Constrained Force

Membrane deflection measured to determine pressure exerted by phase induced volume expansion

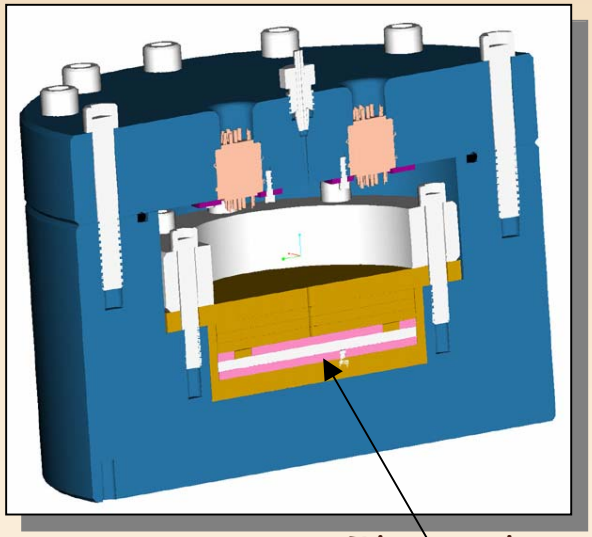
DC Electrical Properties:

- Bulk Resistivity

AC Electrical Properties:

- Capacitance (permittivity)
- Phase angle
- Power loss

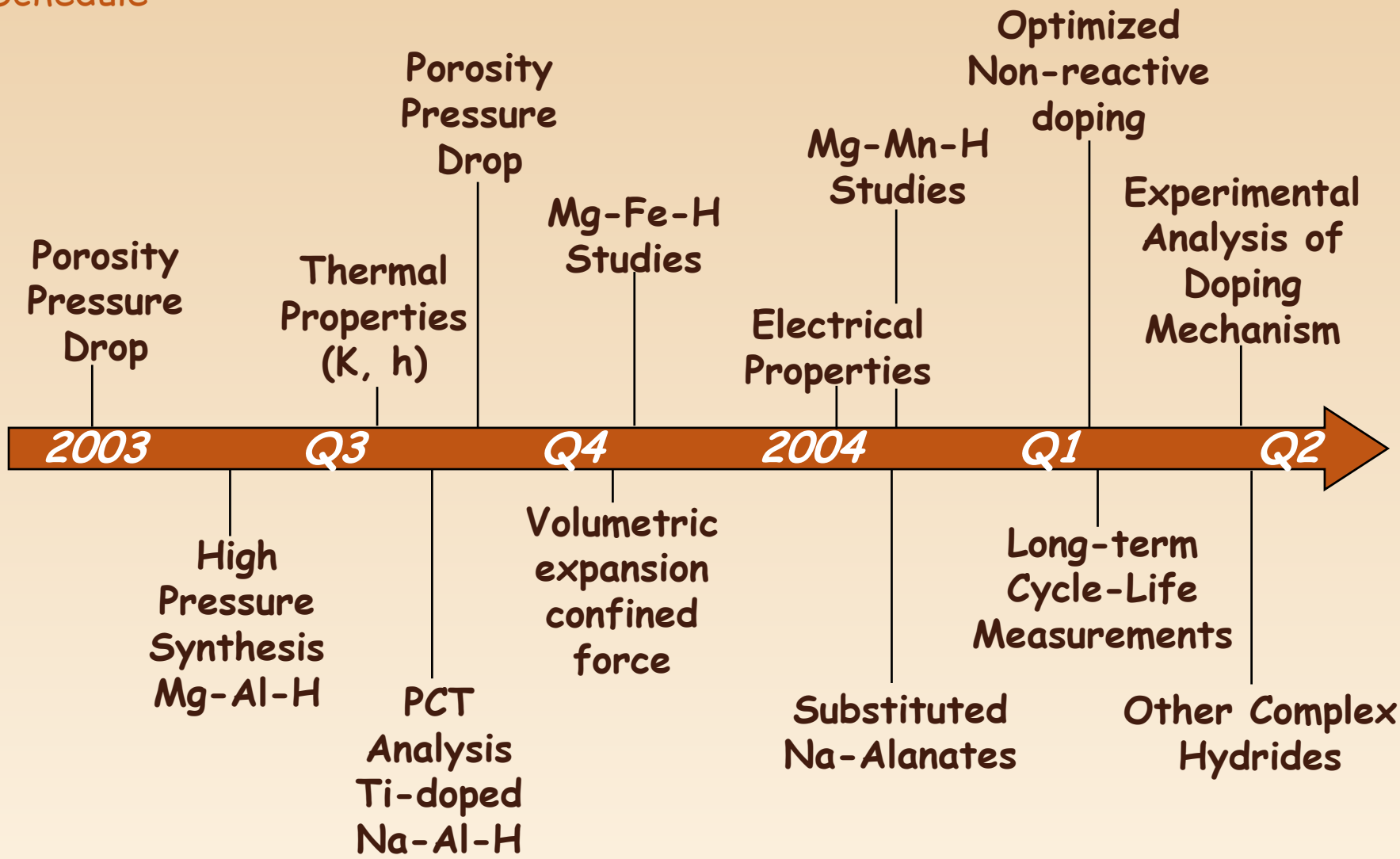
as a function of phase, AC frequency, temperature



Three electrode system, measurement plus guard

Completion Schedule

Milestones



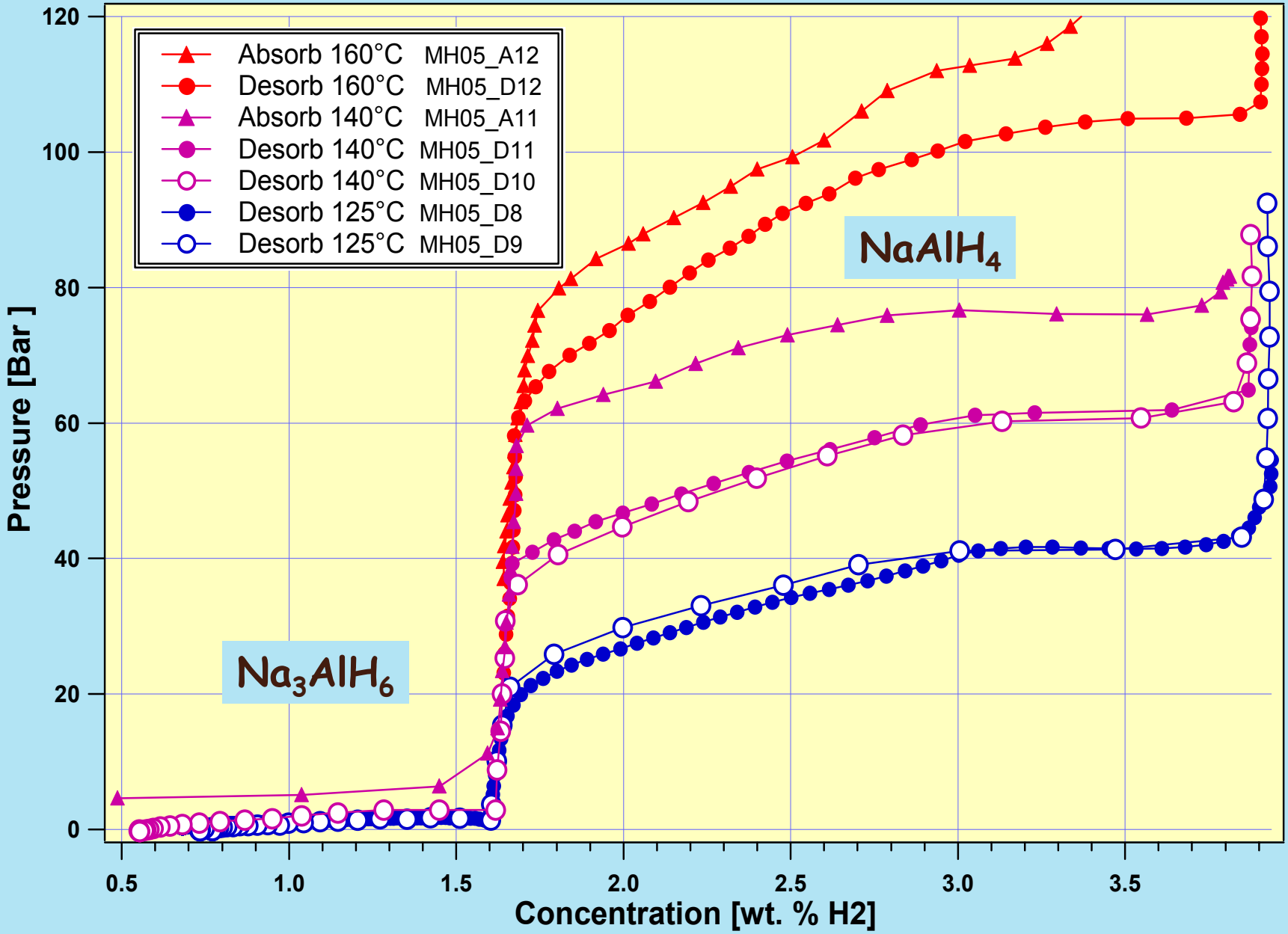
Collaborations

- University of Hawaii: Mechanisms of Ti-doping enhanced kinetics
- University of Geneva: New Complex Hydrides
- Florida Solar Energy Center: New Complex Hydrides
- Denver University: Electron Spin Resonance measurements
- NIST: Neutron Diffraction and Scattering
- UCLA: Ab Initio Calculations
- UTRC: Materials Purity Issues and Safety Testing

Publications

- "The effects of titanium precursors on hydriding properties of alanates", K.J. Gross, E.H. Majzoub, S.W. Spangler Submitted J. Alloys and Comps 2002
- "Catalyzed alanates for hydrogen storage", Gross, KJ; Thomas, GJ; Jensen, J. Alloys and Comps, 2002; v.330, p.683-690
- "Titanium-halide catalyst-precursors in sodium aluminum hydrides", E.H. Majzoub, K.J. Gross, Submitted J. Alloys and Comps 2002
- "Rietveld Refinement and Ab Initio Calculations of $NaAlD_4$", E.H. Majzoub and V. Ozolins, In preparation.
- "EPR Studies of Titanium Doped $NaAlH_4$: Fundamental Insight to a Promising New Hydrogen Storage Material", Sandra Eaton, Karl Gross, Eric Majzoub, Keeley Murphy, and Craig M. Jensen submitted Chemical Communications, 2003
- "Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates", Sandrock, G; Gross, K; Thomas, G, J. Alloys and Comps 2002; v.339, no.1-2, p.299-308
- "Microstructural characterization of catalyzed $NaAlH_4$", Thomas, GJ; Gross, KJ; Yang, NYC; Jensen, C, J. Alloys and Comps, 2002; v.330, p.702-707
- "Interactions Between Sodium Aluminum Hydride and Candidate Containment Materials", E.H. Majzoub, B.P. Somerday, S.H. Goods, K.J. Gross, Proceedings Conf."Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions, to be published.
- "Engineering considerations in the use of catalyzed sodium alanates for hydrogen storage", Sandrock, G; Gross, K; Thomas, G; Jensen, C; Meeker, D; Takara, S, J. Alloys and Comps, 2002; v.330, p.696-701
- "Dynamic in situ X-ray diffraction of catalyzed alanates", Gross, KJ; Sandrock, G; Thomas, GJ, J. Alloys and Comps, 2002; v.330, p.691

Sandia's Hydrogen Powered Data



Special Acknowledgement

Jennifer Chan	- Systems Integration
Daniel Dedrick	- Materials Engineering Properties
Terry Johnson	- Materials Engineering Properties
Steve Goods	- Hydrogen Materials interaction
Weifang Luo	- Hydrogen Storage Materials
Joshua Lamb	- Summer Student
Steve Karim	- Experimental Setup
Eric Majzoub	- Fundamental Studies
Andres Orozco	- Summer Student
Vidvuds Ozolins	- Fundamental Studies
Greg Roberts	- Hydrogen Storage Materials
Brian Somerday	- Hydrogen Materials interaction
Gary Sandrock	- Hydrogen Storage Materials
Scott Spangler	- XRD, Materials Synthesis
Ken Stewart	- Laboratory and Experimental Setup
George Thomas	- Hydrogen Storage Materials
Nancy Yang	- Microscopy

Thank you!

HYDROGEN STORAGE USING COMPLEX HYDRIDES

Darlene K. Slattery, Michael D. Hampton

FL Solar Energy Center, U. of Central FL

Objective

- Identify a hydrogen storage system that meets the DOE guidelines
  - Complex hydrides have the potential
  - $NaAlH_4$ exciting but will never have capacity
  - Other complex hydrides

Complex Hydrides

Hydride	Wt %	Hydride	Wt%
$LiAlH_4$	10.5	$Ca(BH_4)_2$	11.4
$LiBH_4$	18.2	$NaAlH_4$	7.5
$Al(BH_4)_3$	20.0	$NaBH_4$	10.5
$LiAlH_2(BH_4)_2$	15.2	$Ti(BH_4)_3$	12.9
$Mg(AlH_4)_2$	9.3	$Ti(AlH_4)_4$	9.3
$Mg(BH_4)_2$	14.8	$Zr(BH_4)_3$	8.8
$Ca(AlH_4)_2$	7.7	$Fe(BH_4)_3$	11.9

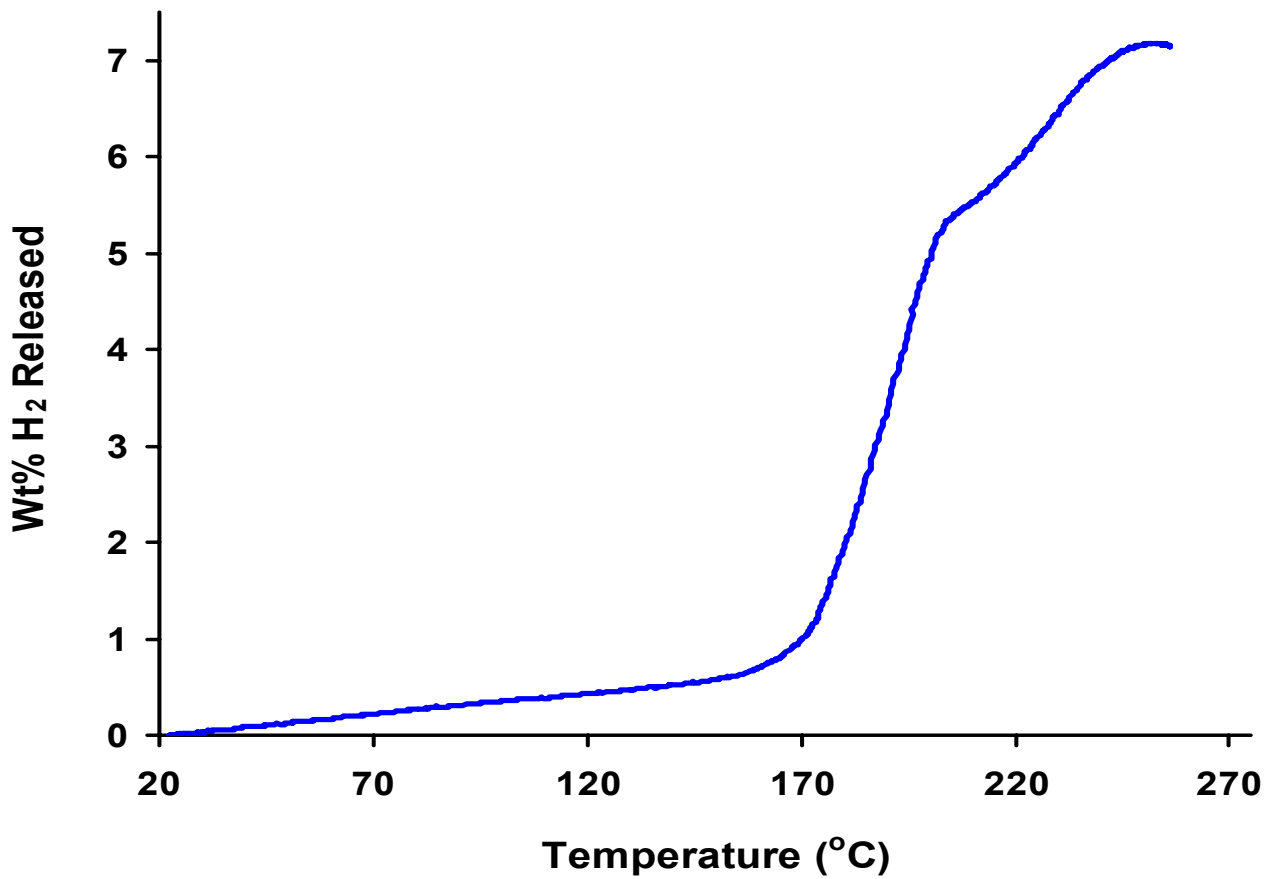
Timeline - Accomplishments

Task Designation / Milestone	FY 2002				2003
	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1
Acquire commercially available cmpds (1)		◆			
Synthesize reported cmpds (2)			◆		
Develop syntheses - unreported cmpds (3)				◆	
Det. H interaction properties of pure (1)			◆		
Det. H interaction properties of pure (2), (3)				◆	
Catalyst incorporation methods study			◆		
Determination of catalyst effects			★		
Catalyst mechanism study				★	
Propose and study other catalysts					◆

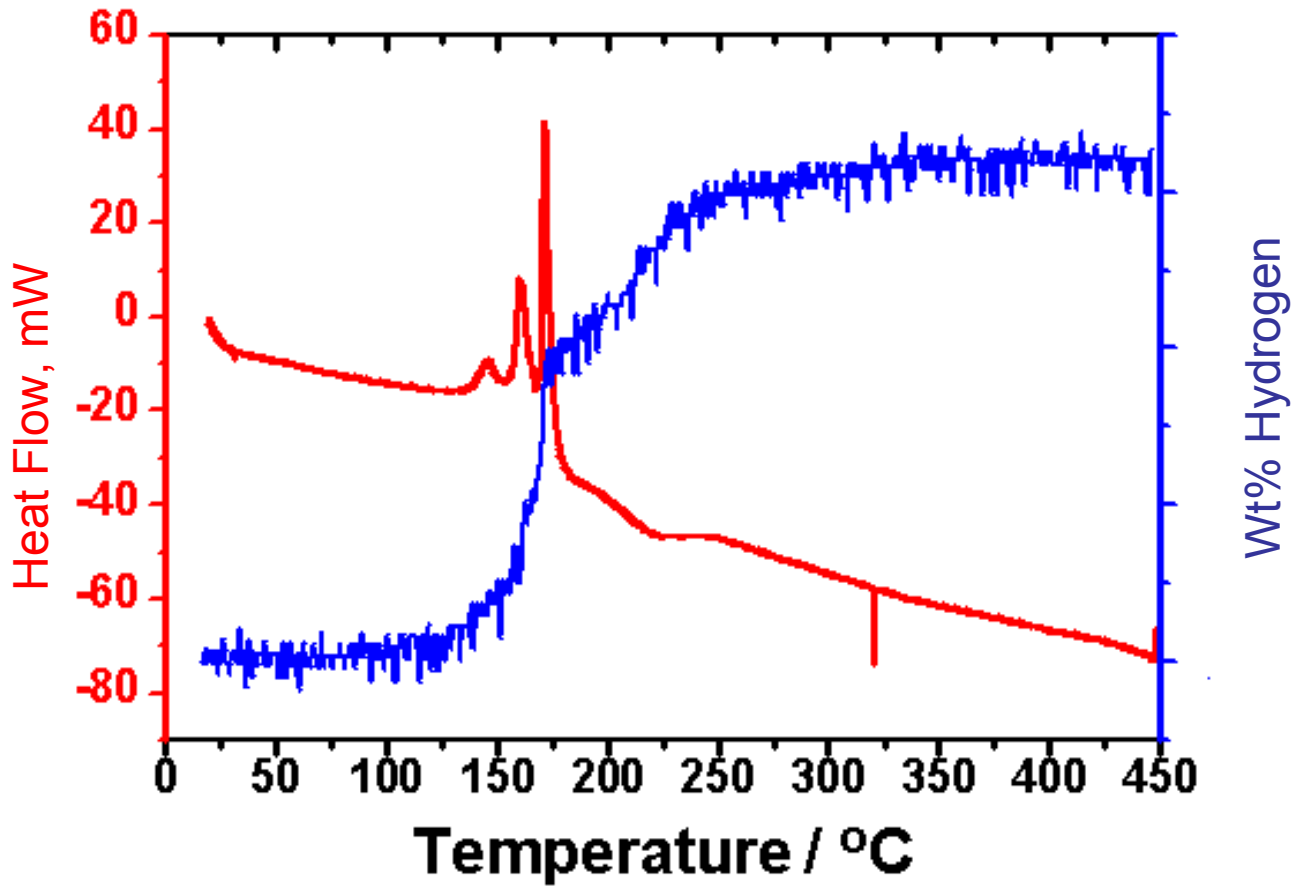
Accomplishments

- Synthesis
  - $Mg(AlH_4)_2$
  - Other cmpds via chemical and mechanical
  - $Ti(AlH_4)_4$
- Addition of elemental Ti and other catalysts
- Ball milling as an activation method

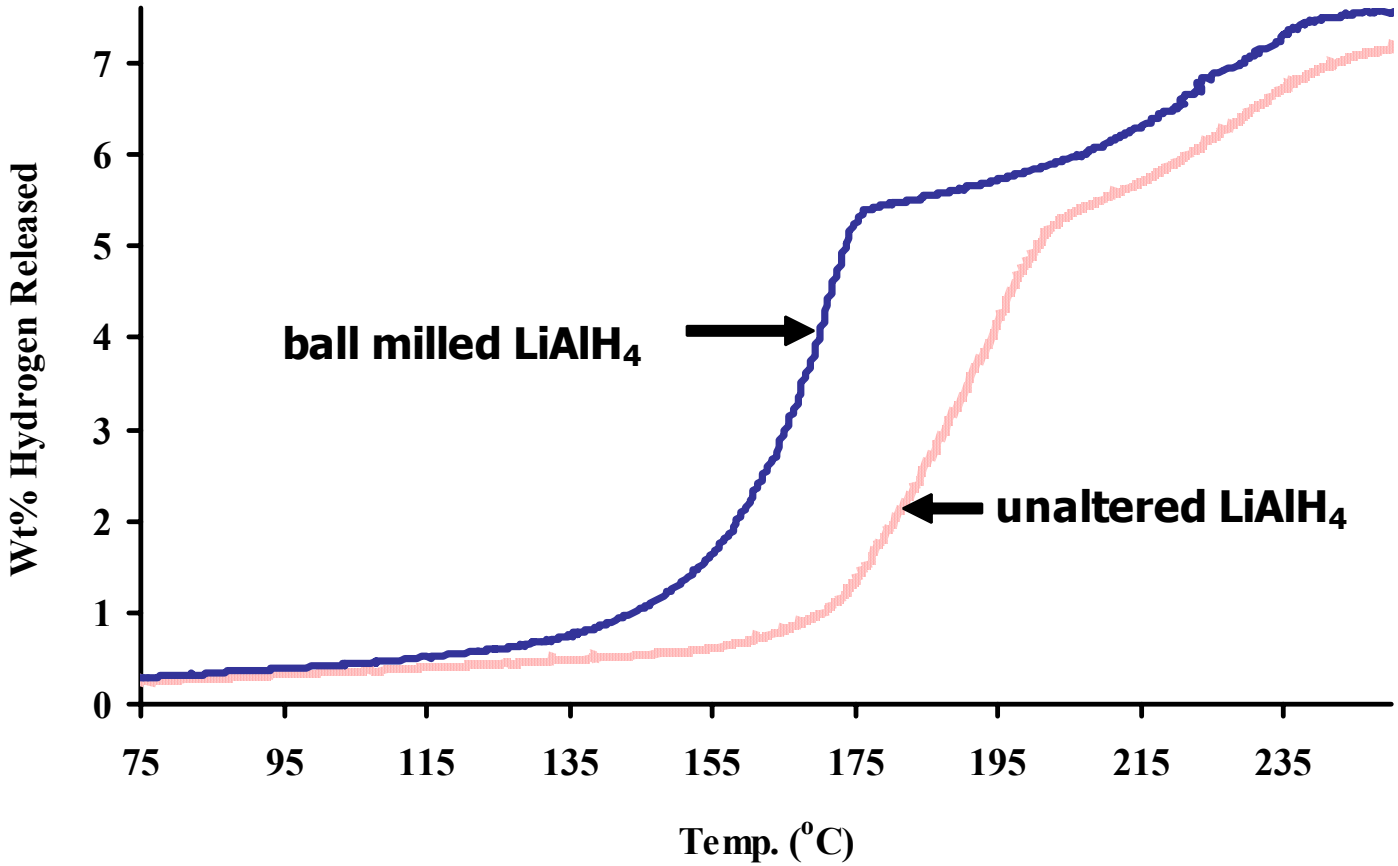
Dehydriding of $LiAlH_4$



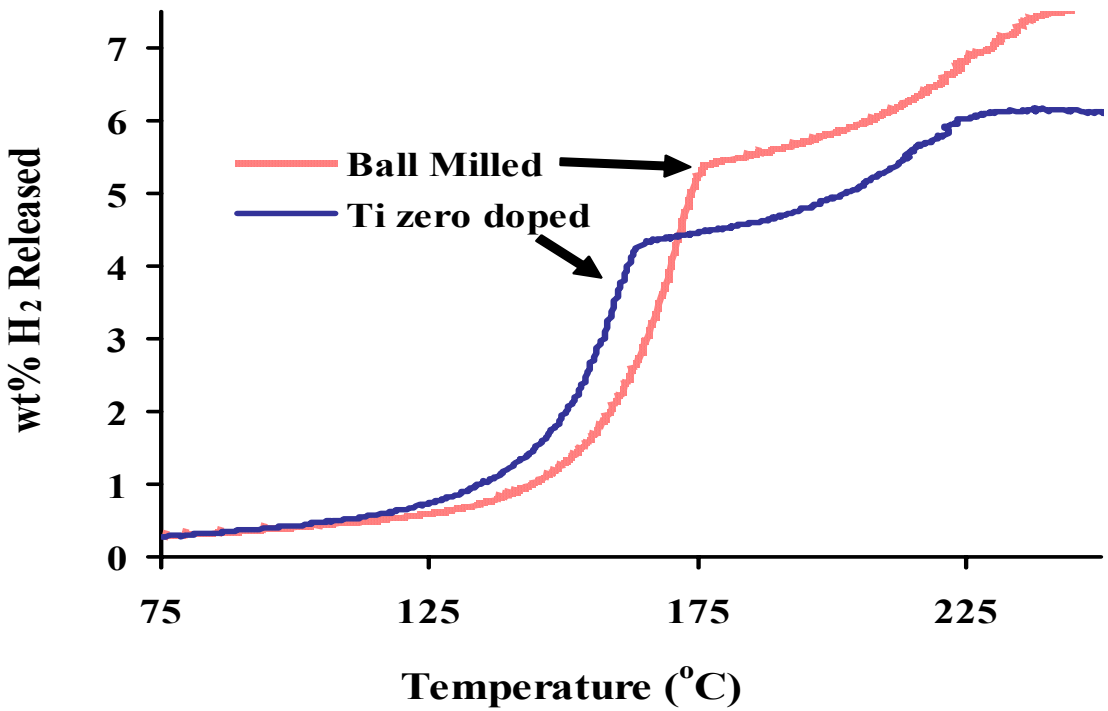
DSC Thermogram of the Dehydriding of $LiAlH_4$



Effect of Ball Milling $LiAlH_4$



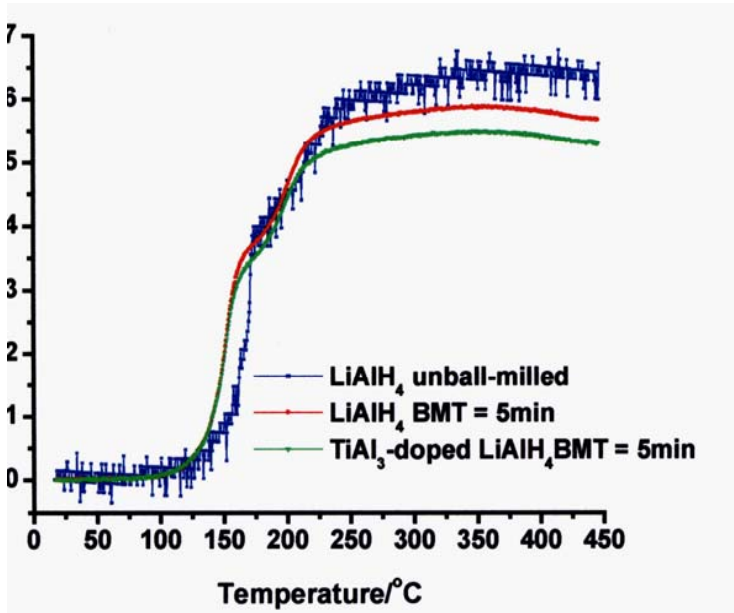
The Addition of Elemental Ti to $LiAlH_4$

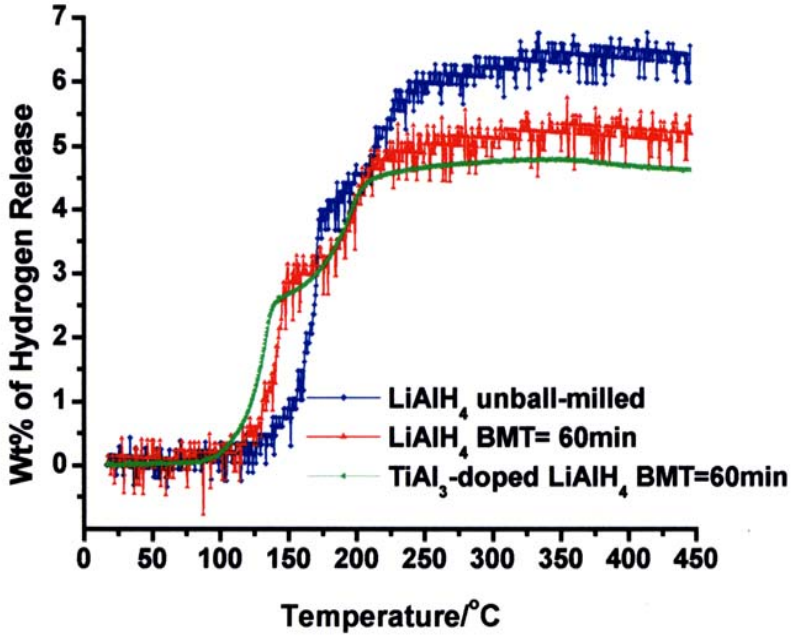


Reversibility

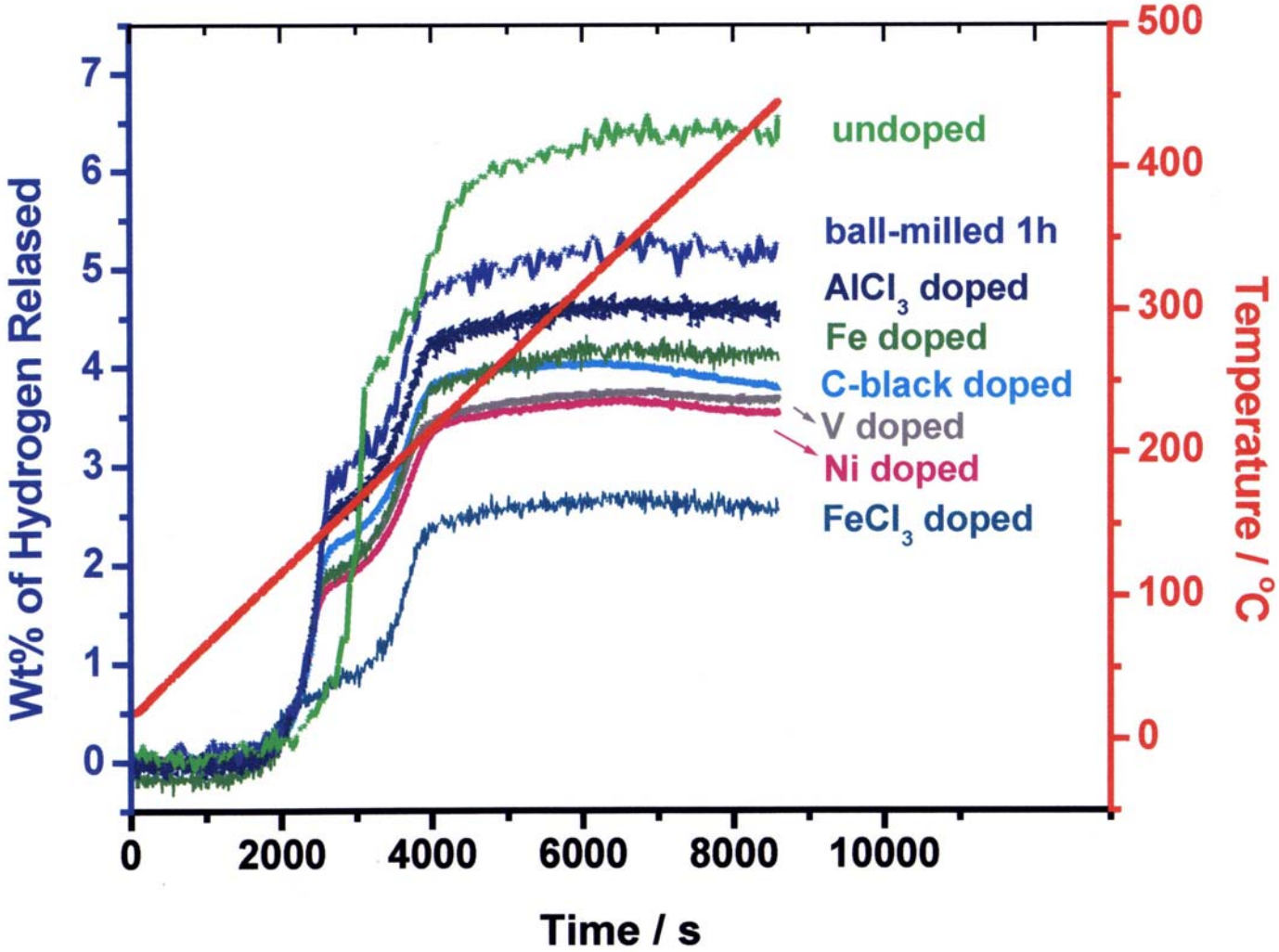
- Ti catalyzed $NaAlH_4$
- Rehydrided at 120 ^oC, 45 atm.
- Second cycle,
  - 1st decomp step at ~ 90 ^oC
  - 2nd decomp at ~ 220 ^oC
- Total hydrogen released on second cycle was 4 wt%

Additional Dopants





Additional Dopants



Reviewers Concerns

"participant has warned about unstable compounds"

Sent: Tuesday, May 14, 2002 6:21 AM

After our presentation at the Hydrogen Program Review last week, you mentioned that you had had an explosion during the heating of $LiAlH_4$… Can you tell us anything more about what happened…

Hi Darlene,

Thanks for your concern. There was no accident. We were trying to do a burn rate test according to a UN test procedure…At the DOE Review there are usually 2-3 conversations going on at the same time. I'm sorry you thought we had an accident. Thanks again for your concern.

“….fairly broad plan.”

- Narrowed scope to look at most promising materials
- Focused on experiments suggested by the research
- Limited catalyst work to using what others had already identified

Interactions & Collaborations

- Collaboration with Karl Gross – Sandia

- D.K. Slattery, M.D.Hampton, J.K.Lomness, N.Najafi-Mohajeri, M. Franjic, "Hydrogen Storage Using Complex Hydrides", Fuel Chemistry Division Preprints, **2002**, 48(1), 277.
- M. Franjic, J. Lomness, J. Gilbert, M. Hampton, D. Slattery, "Effect of Ti Catalyst on Hydrogen Storage Properties of $LiAlH_4$", 67th Annual Meeting Florida Academy of Sciences, Orlando, FL, March 21–22, 2003.
- M.D. Hampton, D.K. Slattery, N. Jafafi-Mohajeri, M.Franjic, J.K. Lomness, "Complex Hydrides as Hydrogen Storage Media", Symposium P1, "Hydrogen Electrochemistry and Generating Systems", Proceedings of the 203rd Meeting of the Electrochemical Society, Paris, France, April 27 – May 2, 2003.

Goals for Continuation Project

- Complete $LiAlH_4$ investigation
- Synthesize 5 g quantity of $Mg(AlH_4)_2$
- Investigate reversibility of borohydrides

Conclusions

- $LiAlH_4$ exhibits an exothermic decomp.
- Ball milling $LiAlH_4$ changes dehydriding characteristics
- Catalyzing with elemental Ti was shown to decrease release temp and improve kinetics without significantly decreasing capacity
- $NaAlH_4$ catalyzed with elemental Ti was shown to be reversible

Acknowledgements

Post docs:

Janice K. Lomness, Nahid Najafi-Mohajeri

Grad student:

Mirna Franjic

High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Complex Compound Hydrides

D.L. Anton
D.A. Mosher
S.M. Opalka
United Technologies Research Center
E. Hartford, CT

F.E. Lynch
HCI, Inc.
Littleton, CO

C. Qiu
G.B. Olsen
QuesTek, LLC
Evanston, IL

Merit Review
Berkeley, CA
May 19-20, 2003

Rev. B

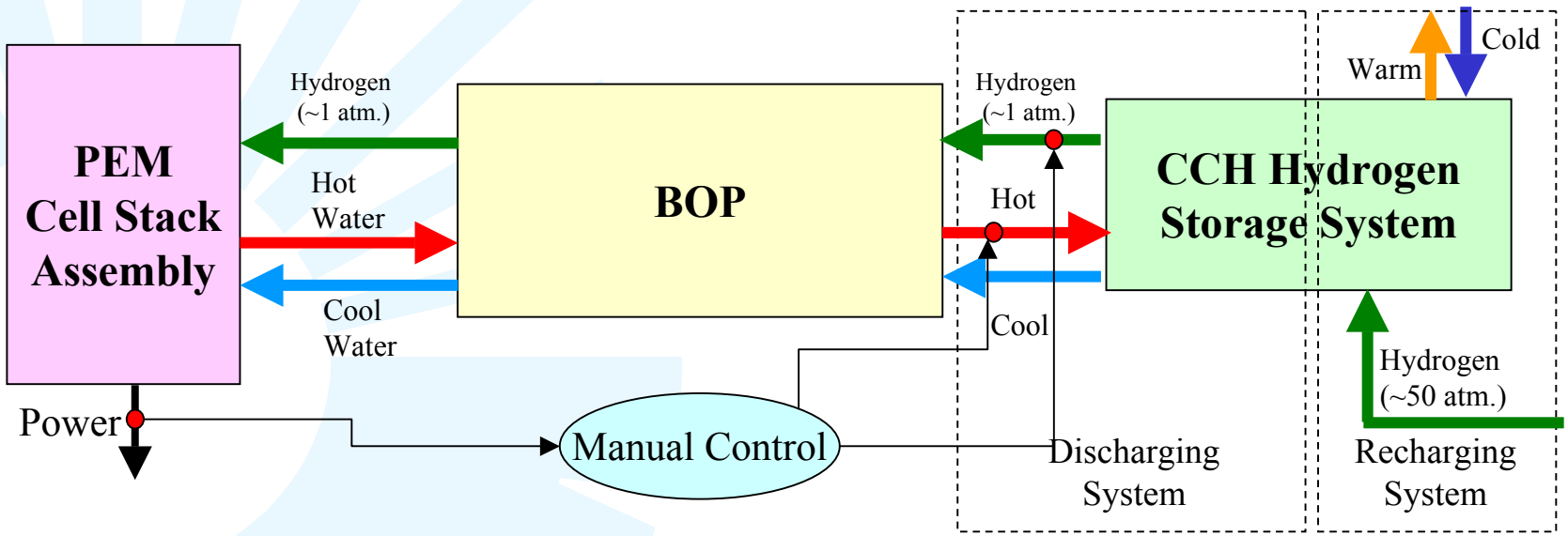
Program Specifics

Objective: Develop, build, bench demonstrate and deliver an *in-situ* rechargeable 5 kg H_2 capacity hydrogen storage system suitable for operation of a PEMFC powered mid-size auto application based.

Approach: Design a low pressure hydrogen storage system initially utilizing catalyzed **$NaAlH_4$**, but capable of being altered to use "*any*" chemical hydride having the higher gravimetric and/or volumetric hydrogen storage densities.

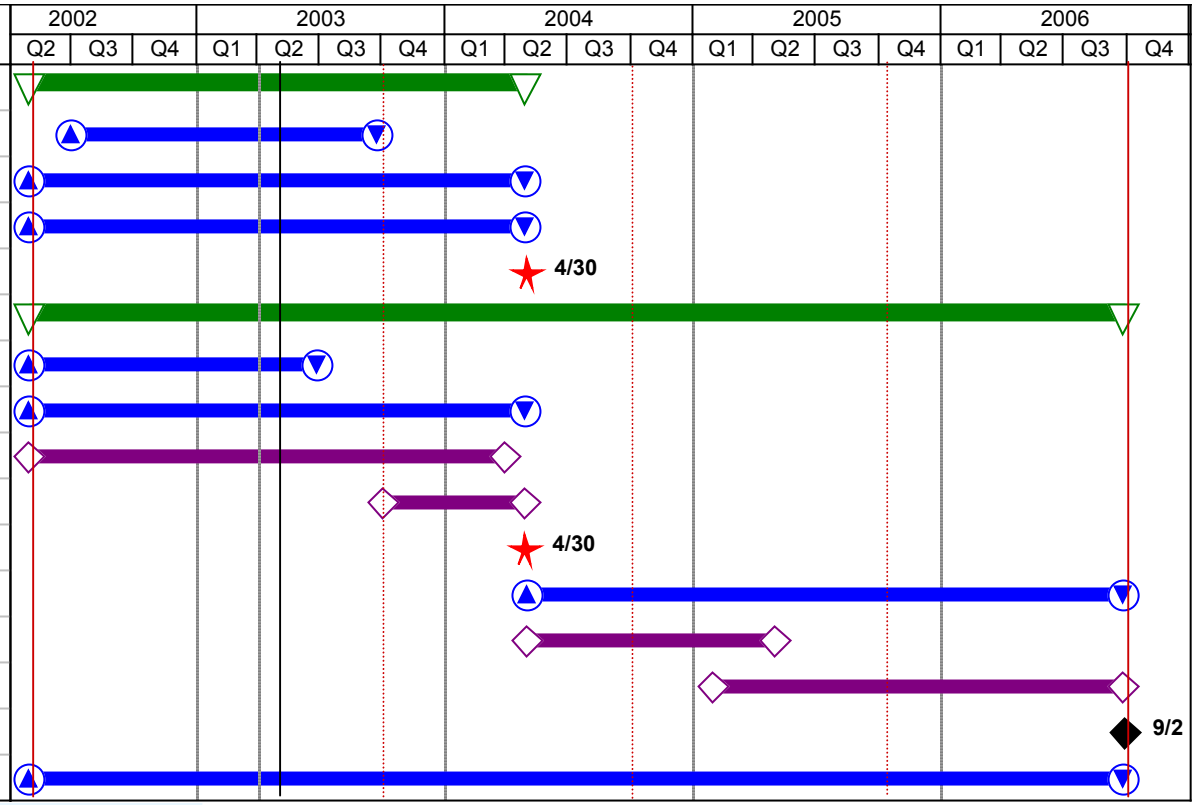
Program Outline

- Safety Analysis
- Atomistic/Thermodynamic Modeling
- 50g H_2 Prototype System
- Media Kinetic Modeling
- Heat/Mass Transfer Analysis
- 1kg H_2 Prototype/Evaluation
- 5kg H_2 Prototype/Evaluation
- 5kg Prototype Delivery



Milestone Chart

ID	WBS	Task Name
1	1	CCH Storage Media Development
2	1.1	50g H2 Sub-System Evaluations
6	1.2	50g Media Evalautions
18	1.3	NaAlH4 Thermodynamic Modeling
29	1.4	GO/NO GO Milestone
30	2	CCH Storage Sys. Demonstration
31	2.1	Safety Analysis
36	2.2	1Kg System Evaluation
37	2.2.1	Design/Fabricate CCHSS#1
45	2.2.2	CCHSS#1 Evaluation
48	2.3	GO/NO GO Milestone
49	2.4	5Kg System Evaluation
50	2.4.1	Design/Fabricate CCHSS#2
58	2.4.2	CCHSS#2 Evaluation
65	2.4.3	Ship CCHSS#2 to DoE
66	2.5	Reporting



Milestones vs. DoE 2005 & 2010 Goals

	Metric	Units	2005 DoE Goal	2010 DoE Goal	UTRC 2003 Estimate	UTRC Prop. GO/NoGo
	Capacity	kg		5		
H_2 Storage Density	Gravimetric	kWh/kg	1.5	2	0.83	1.00
	Volumetric	kWh/l	1.2	1.5	0.40	0.55
Cost	Total life cycle (15 yr/150k miles)	$(03)/kWh	6.00	4.00	16	
	Fuel (gasoline equivilent)	$(01)	3.0	1.3	TBD	
	Marginal Fuel Cost (Ref. $1/kWh for H_2)	$(03)/kg$H_2$	NA	1.5	TBD	
Operating Temperature	Min.	°C	0	-30	TBD	
	Max.	°C	50	50	50	
Cycle Life	Cycle Life (0.25-100%)	N	500	1000	TBD	
	Mean	%	N/A	90	TBD	
	Confidence	%	N/A	90	TBD	

	Metric	Units	2005 DoE Goal	2010 DoE Goal	UTRC 2003 Estimate	UTRC Prop. GO/NoGo
Hydrogen Delivery	Max. H_2 Delivery Temp.	°C	100			
	Min. H_2 Delivery Temp.	°C	-20	-30	TBD	
	Min. Full Flow	g H_2/sec.	3.0	4.0	0.31	0.30
	FC Min. Pressure	kPa/bar	250/2.5	250/2.5	TBD	
	ICE Min. Pressure	kPa/bar	1000/10	3500/35		
	Purity	% (dry)	99.9	99.9	TBD	
Transient Response	0-90% 90-0%	sec.	0.5	0.5	TBD	
	start to full flow @20°C	sec.	4.0	0.5	TBD	
	start to full flow @-20°C	sec.	8.0	4.0		
	Refueling Rate	kg H_2/min.	0.5	1.5	0.30	0.30
	Loss of Useable H_2	g/hr kg H_2	1.0	0.1	TBD	
	Permeation & Leakage	scc/hr	*Federal enclosed-area safety standard*		TBD	
	Toxicity		*Meets or exceeds applicable standards*		TBD	
	Safety		*Meets or exceeds applicable standards*		TBD	

Development Partners

Sandia National Laboratories

HCI

UTC Fuel Cells
A United Technologies Company

UNIVERSITY OF HAWAI'I

Hydrogen Storage
Task XVII
Advanced Fuel Cell Systems
Task XV

QuesTek INNOVATIONS LLC

NORTHWESTERN UNIVERSITY

SRTC
Savannah River Technology Center

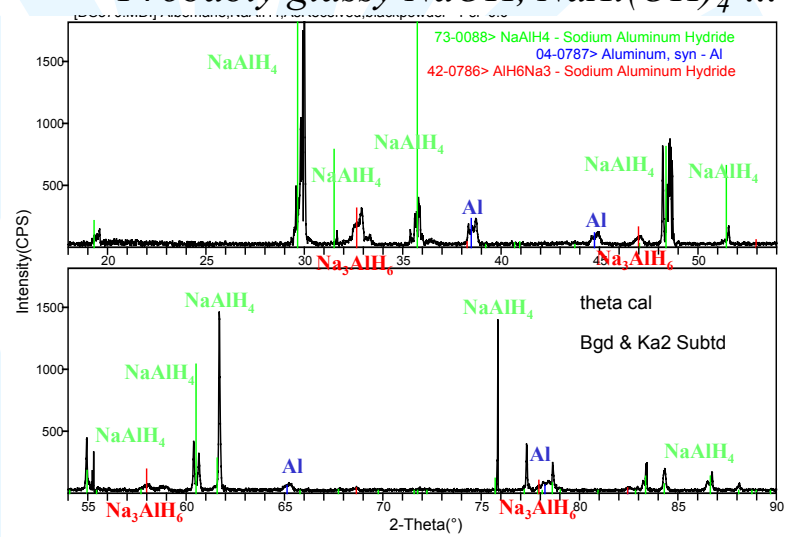
ife Institutt for energiteknikk

ALBEMARLE® CORPORATION

Commercial Materials Characterization

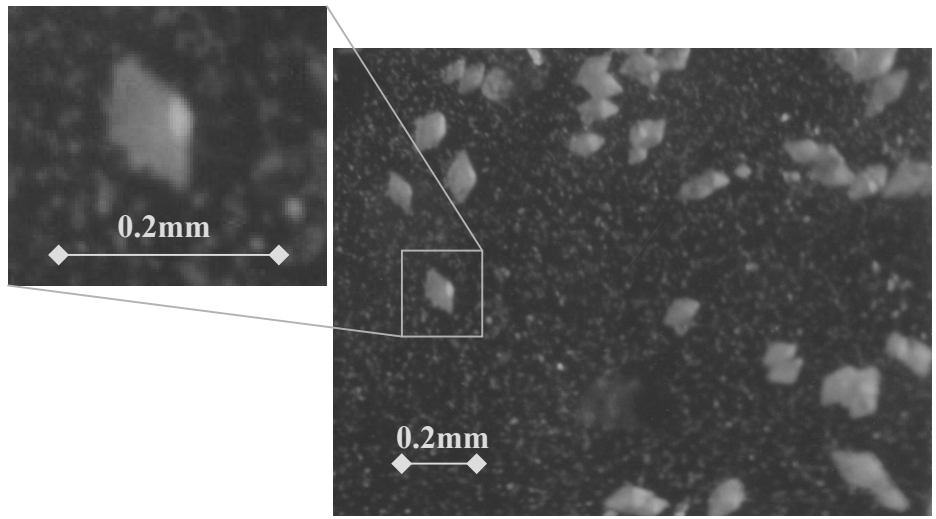
	analytical		x-ray	
	wt%	at%	wt%	at%
$NaAlH_4$	86.3	83.1	87.5	84.8
Na_3AlH_6	4.7	2.4	6.0	2.6
Al^o	7.5	14.5	6.4	12.6
Inert*	1.5			

** Probably glassy NaOH, $NaAl(OH)_4$ …*



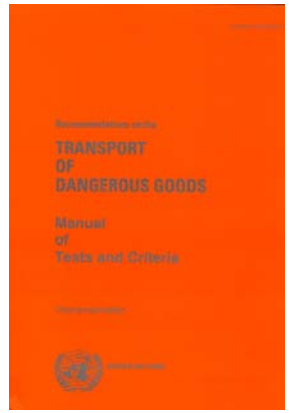
Summary

Na:Al	0.9
% Charge	94.7%
Wt%H_2	4.9
Wt% $H_{2\ th}$	5.2



Safety Analysis

DOT/UN Doc., *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 3rd Revised Ed., ISBN 92-1-139068-0, (1999).



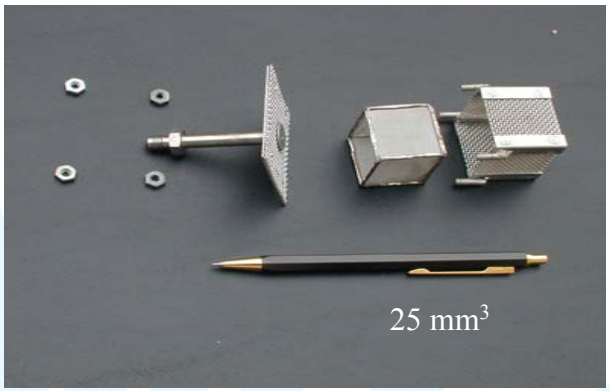
- Flammability
  - *Flammability Test*
  - *Spontaneous Ignition*
  - *Burn Rate*
- Water Contact
  - *Immersion*
  - *Surface Exposure*
  - *Water Drop*
  - *Water Injection*

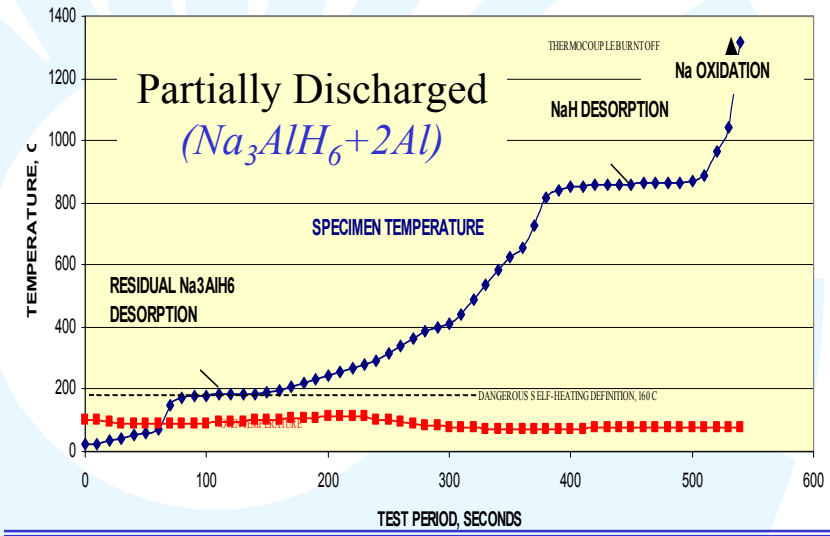
- Dust Explosion (ASTM E1226)
  - P_{max} & $(dP/Dt)_{max}$
  - *Min. Exp. Conc.*
  - *Min. Ignition Energy*
  - *Min. Ignition Temp.*
  - *Min. Dust Layer Ignition Temp.*

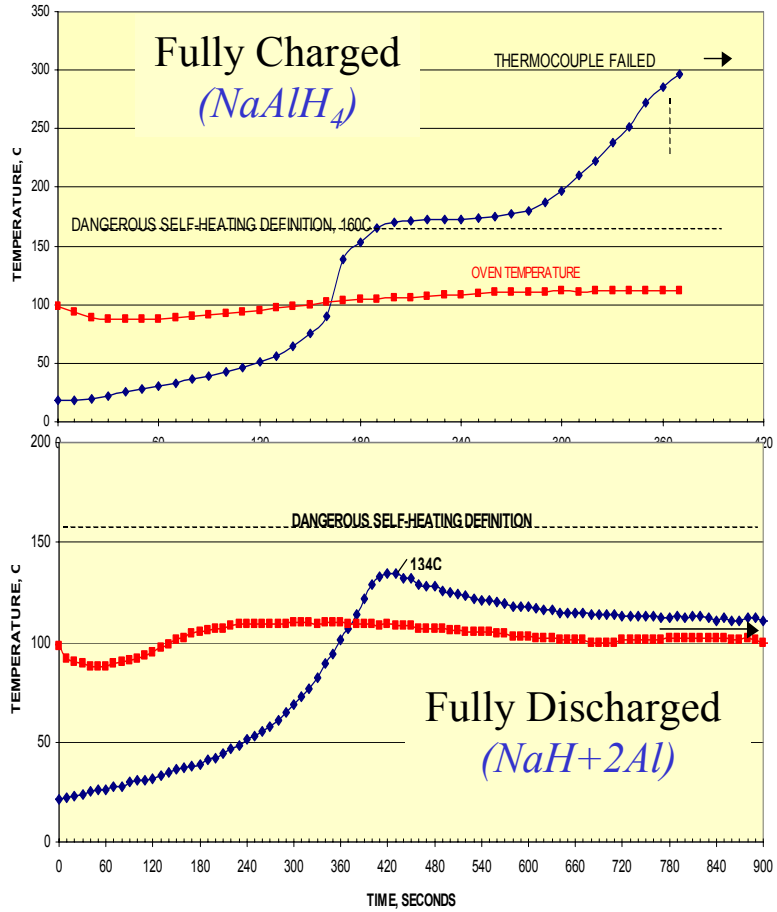
CCH#0: 2m%$TiCl_3$
Fully Charged, CCH#0-100: *($NaAlH_4$)*
Partially Discharged, CCH#0-33: *(Na_3AlH_6+2Al)*
Fully Discharged, CCH#0-0: *(NaH+Al)*

Flammability Test

Objective: To determine if material spontaneously self heats or ignites upon exposure to air at 100°C







Safety Testing Results

Class 4.3, Packing Group II:
No change from uncatalysed material.

SAFETY TESTING TABLE OF RESULTS

Test Method	Ref: UN33.	100%	33%	0%
Prelim. Screening	2.4.3.1	Yes, Flammable Solid	Yes, Flammable Solid	Yes, Flammable Solid
Burning Rate	2.4.3.2	51 mm/sec	222 mm/sec	27 mm/sec
Burning Rate, 80C	Note 1	127 mm/sec	spontanious ignition	40 mm/sec
Spontaneous Ignition, R.T.	3.1.4.3	6 Tries, Not Pyrophoric	6 Tries, Not Pyrophoric	6 Tries, Not Pyrophoric
Spontaneous Ignition, 80C	Note 1	6 Tries, No Ignition	1 Try, Ignited	6 Tries, No Ignition
Dangerous Self-Heat, 100C	3.1.3.3	Yes, Dangerous	Yes, Dangerous	Not Dangerous
Dangerous Self-Heat, 120C	3.1.3.3	Not Tested (Note 2)	Not Tested (Note 2)	Not Dangerous
Dangerous Self-Heat, 140C	3.1.3.3	Not Tested (Note 2)	Not Tested (Note 2)	Yes, Dangerous
Dangerous When Wet	4.1.4.3	Yes, Class 4.3, Pack Gp 1	Yes, Class 4.3, Pack Gp 1	Yes, Class 4.3, Pack Gp 1

Note 1: This is not a UN standard test. We want to know what happens when this material is spilled at operating temperature of 80C. All other details are per UN burn rate and spontaneous ignition test specifications.

Note 2: This test was not necessary, since this material had already shown dangerous self-heating at 100C.

Thermodynamic Modeling

Objective: Combine atomistic and thermodynamic modeling to predict: (i) quaternary phase diagrams and (ii) thermal stability of catalyzed compounds.
Approach: Atomistic calculations used to predict ΔH_f at 0K. Thermodynamic calculations to determine ΔG_f vs T & P

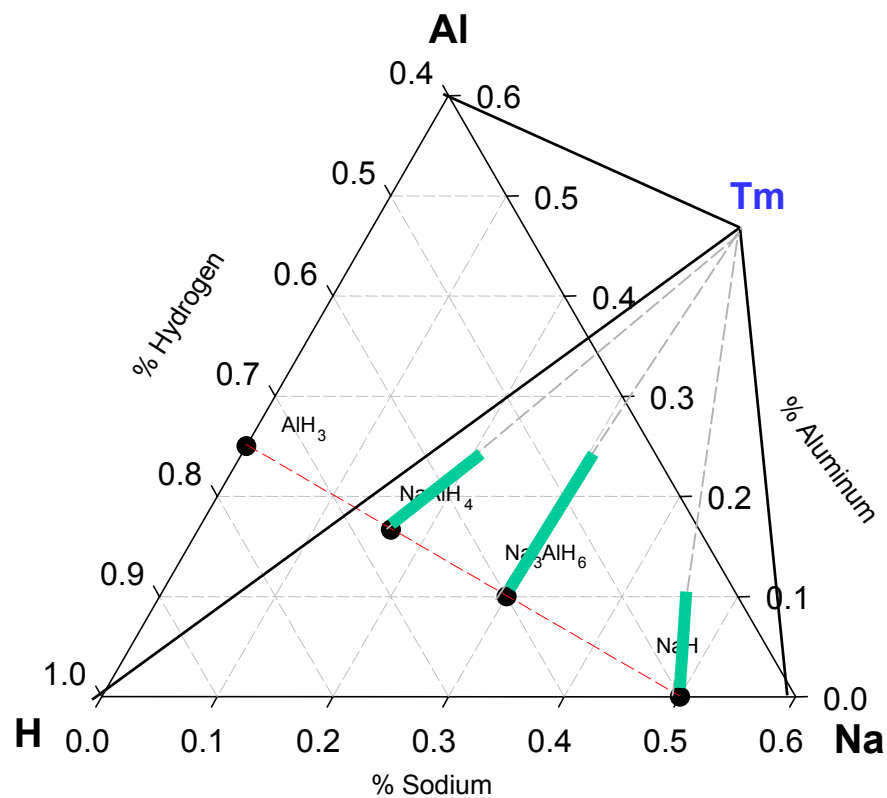
VASP

Atomistic simulations based on Density Functional Theory with pseudo-potentials for core electrons

ThermoCalc

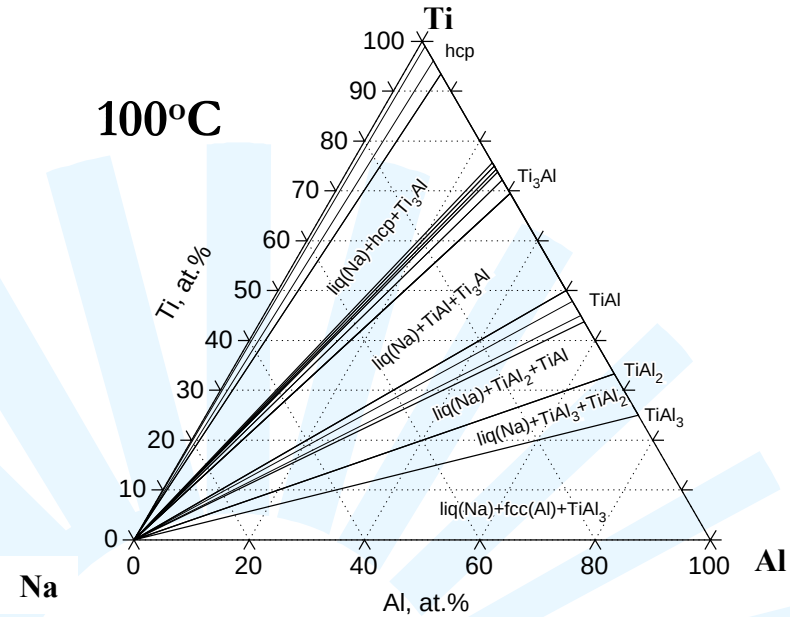
Thermodynamic Simulations of multi component phase diagrams

QUESTEK INNOVATIONS LLC

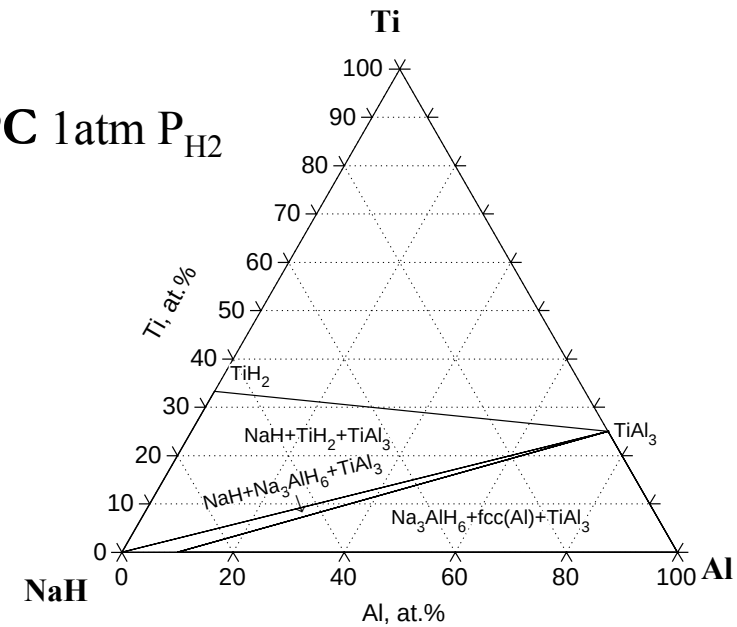


Calculated Na-Al-Ti-H Phase Diagrams

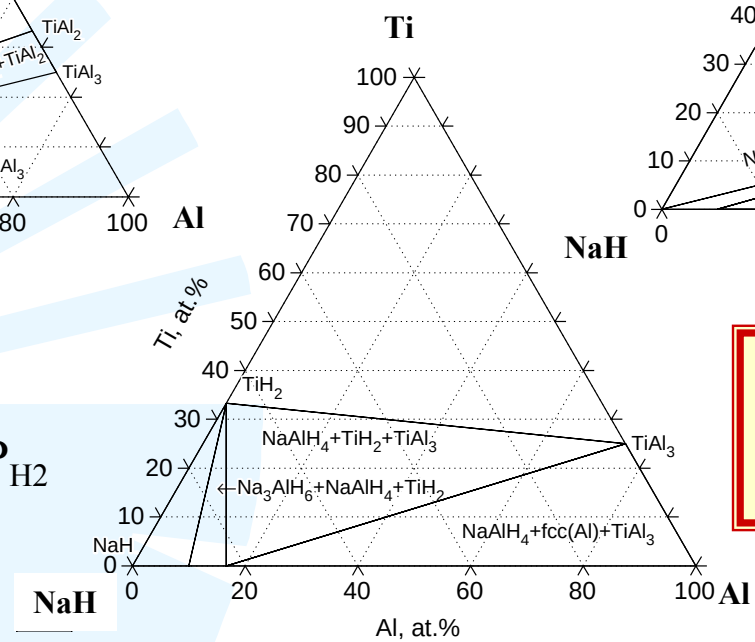
100°C



100°C 1atm P_{H2}



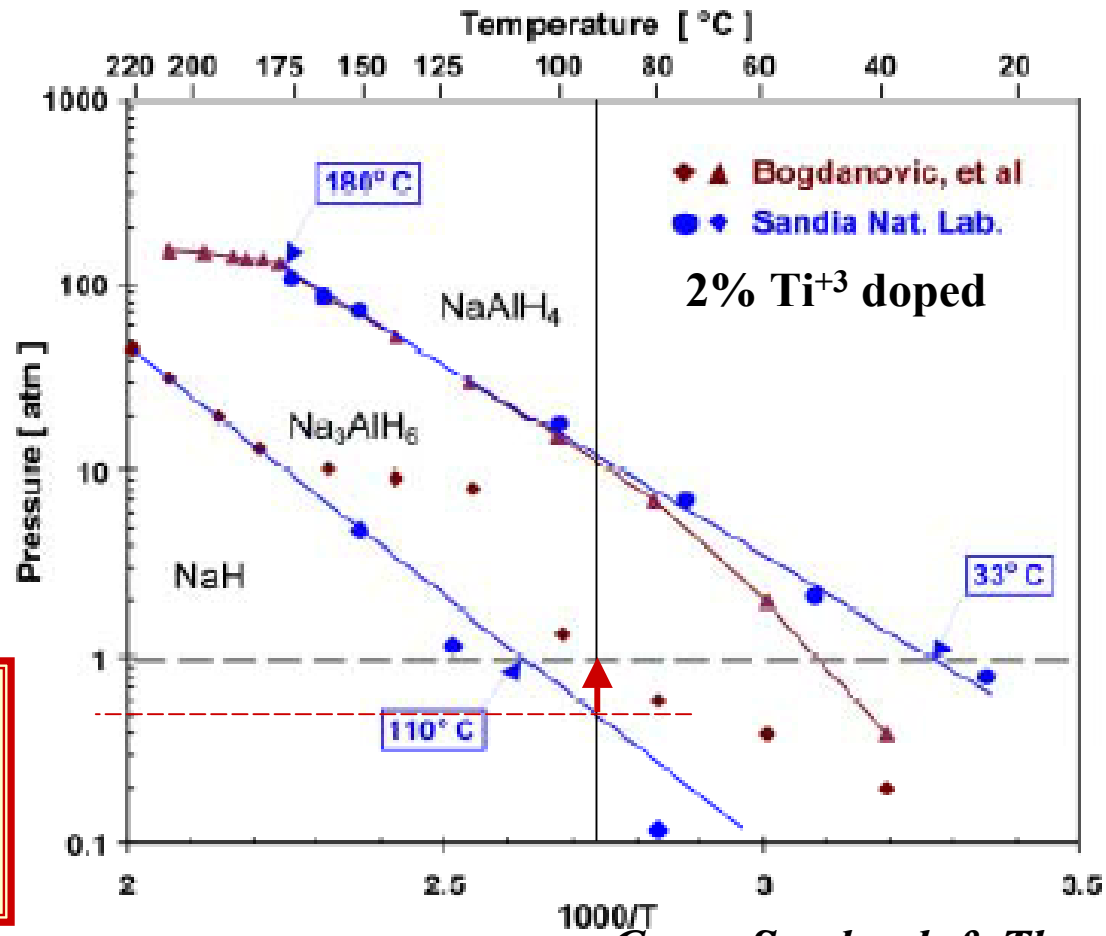
100°C 100atm P_{H2}



$Na_xAl_yH_z$-TiH_2-Al_3Ti are stable phases of interest

Is transition metal "catalytic" effect in $NaAlH_4$ catalysis or thermodynamics?

At 90°C, Na_3AlH_6 is too stable to access last % H_2
$P_e \sim 0.5$ bar



Urgent requirement to destabilize Na_3AlH_6 by 20°C (0.5bar)!!

Gross, Sandrock & Thomas

Quantum Mechanical Calculations

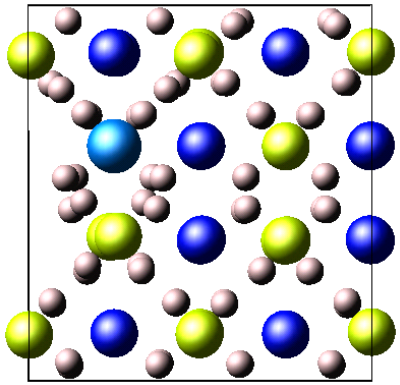
$NaAlH_4$: Enthalpy of Formation at 0K

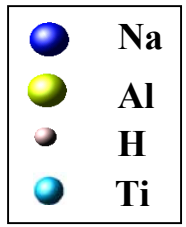
$(Na_{1-y}Am_y)(Tm_xAl_{x-1})H_4$

$(Na_{1-y}Am_y)_3(Tm_xAl_{x-1})H_6$

$Na_{16}TiAl_{15}H_{64}$ Supercell

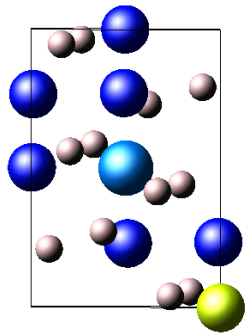
6.25 mole % $NaTiH_4$

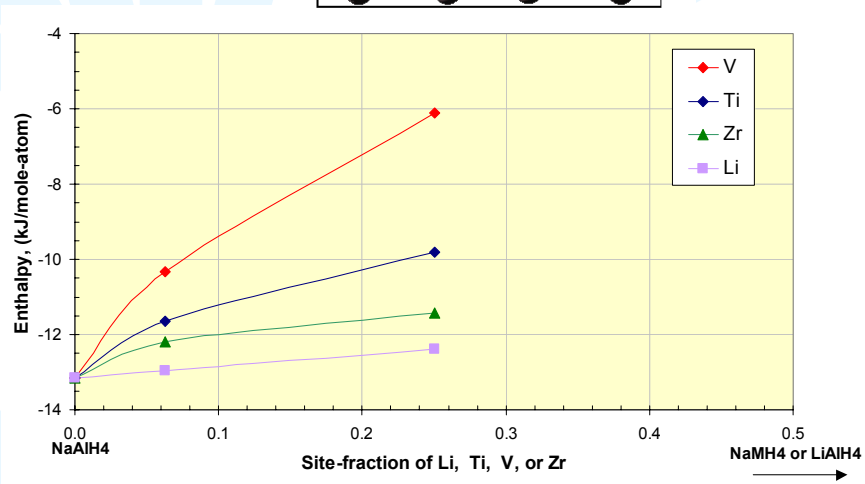


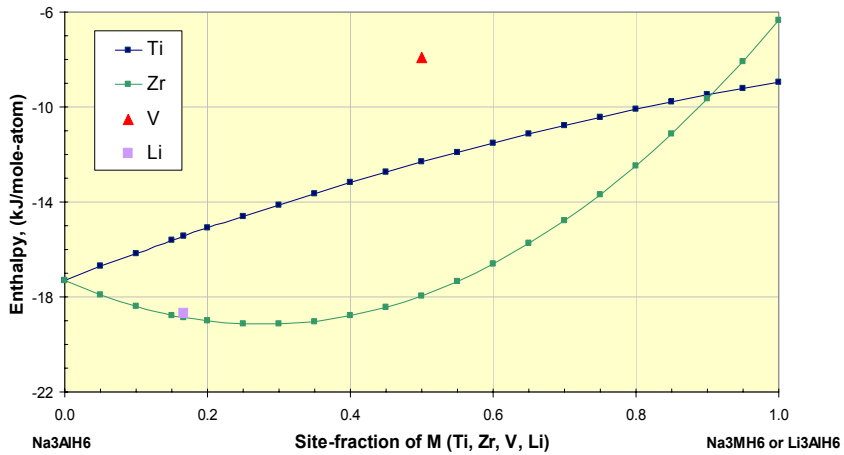


Na_6TiAlH_{12} Supercell

50 mole % Na_3TiH_6







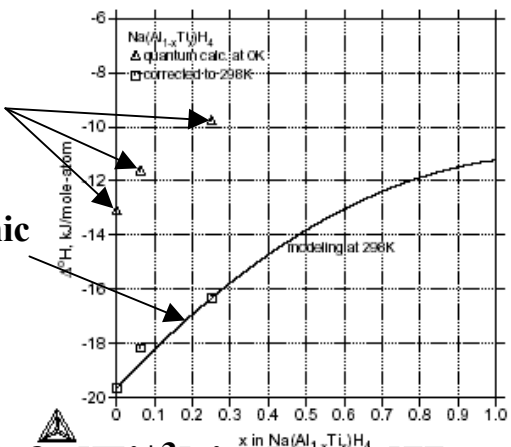
Thermodynamic Calculations

Ti^{+3} Additions

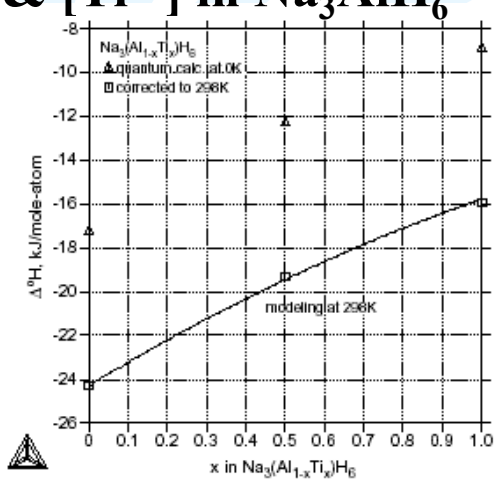
Δ^oH vs. T & $[Ti^{+3}]$ in $NaAlH_4$

Atomistic Calculations

Thermodynamic Calculations



Δ^oH vs. T & $[Ti^{+3}]$ in Na_3AlH_6

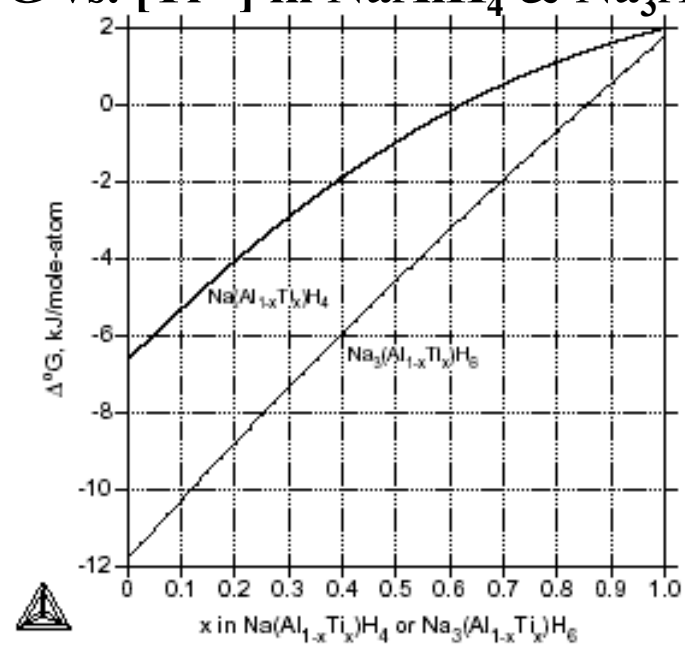


$$^oG_{NaAlH_4} = a_1 + b_1T + c_1T\ln T + {}^oG_{AlH_3} + {}^oG_{NaH}$$

$$^oG_{Na_3AlH_6} = a_2 + b_2T + c_2T\ln T + {}^oG_{AlH_3} + 3\,{}^oG_{NaH}$$

a_i, b_i, c_i—constants evaluated from experimental data (ΔH, ΔS, C_P)

Δ^oG vs. $[Ti^{+3}]$ in $NaAlH_4$ & Na_3AlH_6

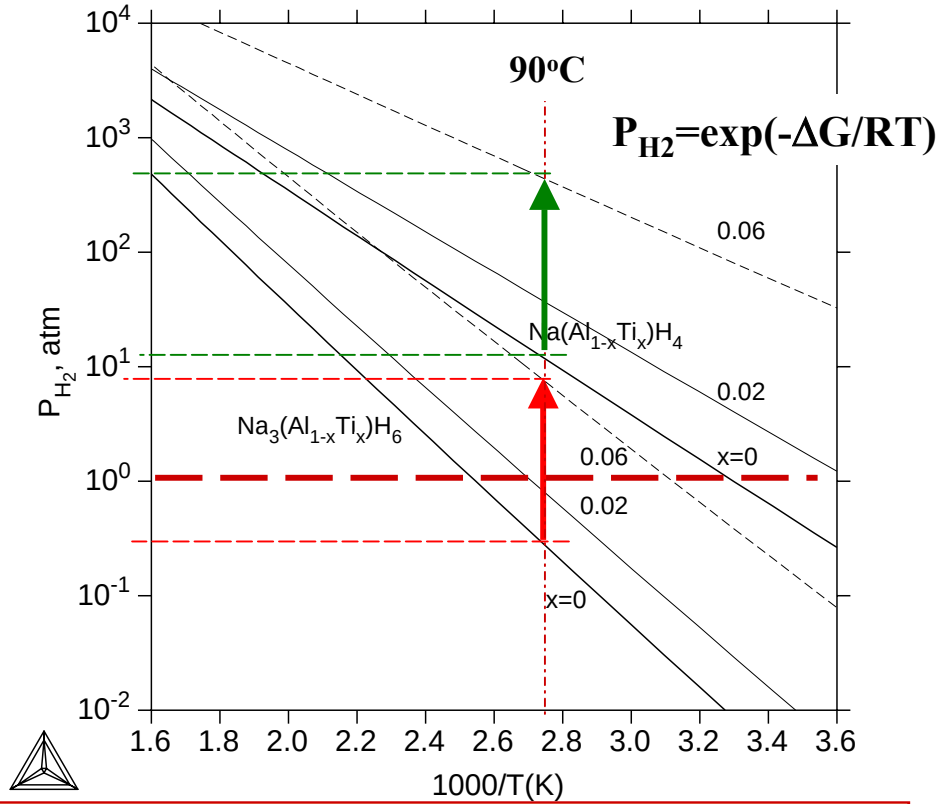


Thermal Stability of Ti^{+3} doped $NaAlH_4$ & Na_3AlH_6

- Both $NaAlH_4$ & Na_3AlH_6 destabilized with [Ti^{+3}] additions (~50°C @ [Ti^{+3}]=0.06)
- Isothermal plateau pressures predicted as a function of [Ti^{+3}]
- **$Na_3Al_{0.94}Ti_{0.06}H_6$ plateau pressure raised from 0.3 bar to 7 bar at 90°C**
- $NaAl_{0.94}Ti_{0.06}H_4$ plateau pressure raised from 10 bar to 400 bar at 90°C

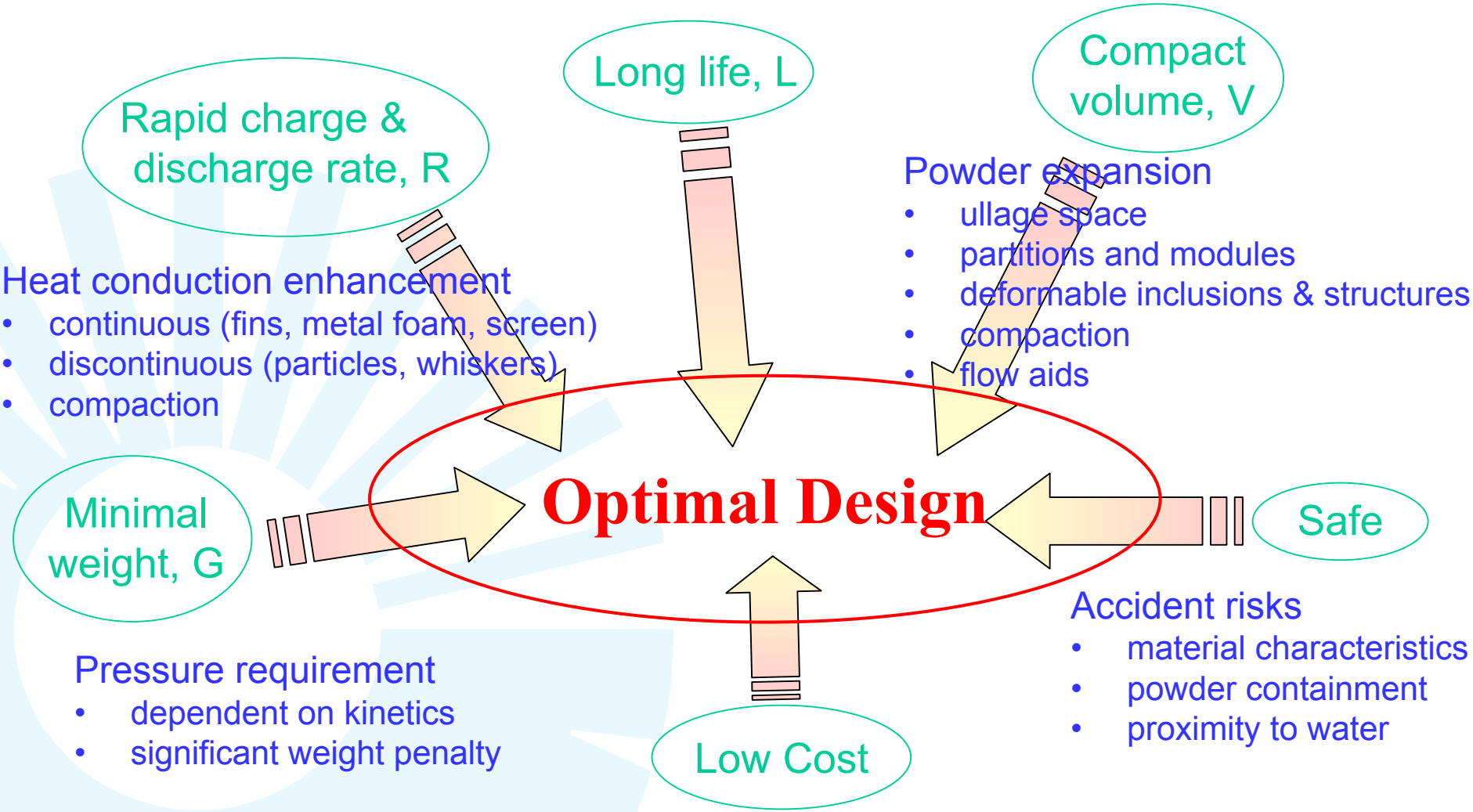
$Na(Al_{1-x}Ti_x)H_4 = 1/3Na_3AlH_6 + xTiH_2 + (2/3-x)Al + (1-x)H_2$

$Na_3(Al_{1-x}Ti_x)H_6 = 3NaH + xTiH_2 + (1-x)Al + (1.5-x)H_2$

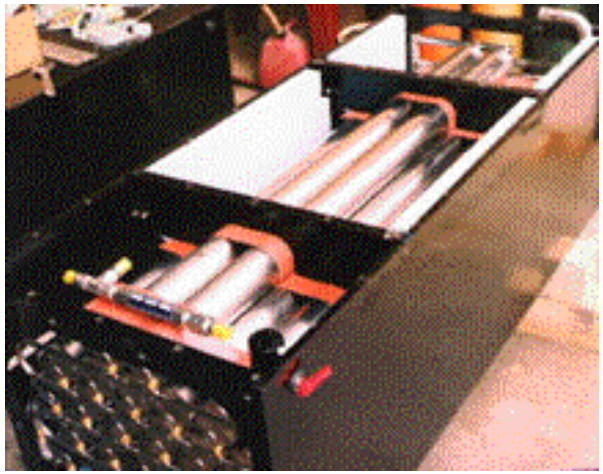


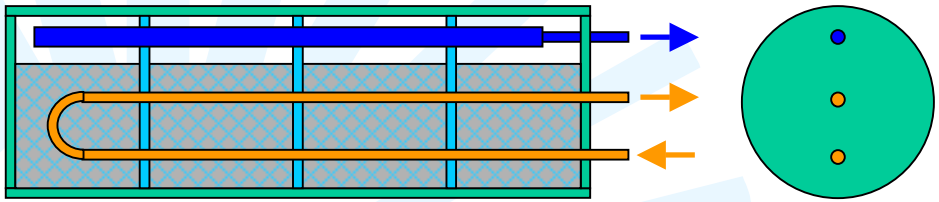
Predicts accessibility of full 5.5wt% H_2 above 1 bar pressure!!

Design Goals & System Elements



Metal Hydride Systems





- Inner pipe
- Particle filter
- Hydride material
- Heat transfer enhancement
- Partitions
- Outer pipe & end caps

SRTC design serves as a baseline

- Elements common to many designs
- Efficient pressure containment
- 280 Wh/kg (1.0 MJ / kg)
- 420 WH/L (1.5 MJ / L)

Modifications for $NaAlH_4$

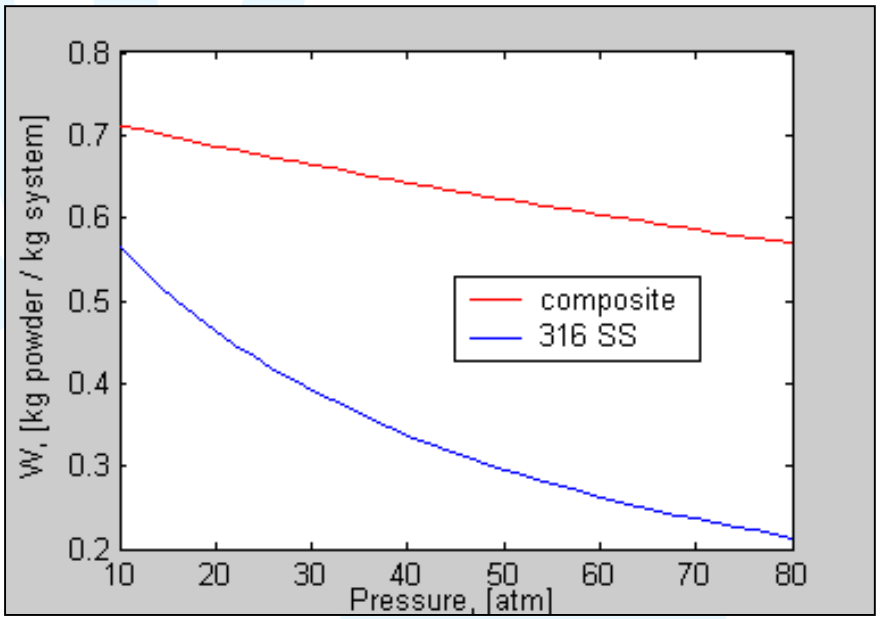
- Higher pressures
- Weight reduction
- Powder expansion differences

Design Comparisons

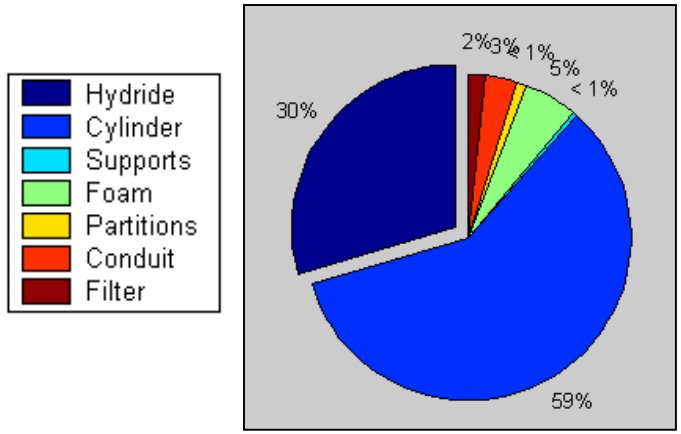
Gravimetrics vs. Pressure

System Comparison

- 4.5 wt% material
- 47% powder relative density
- 50 atm charging pressure

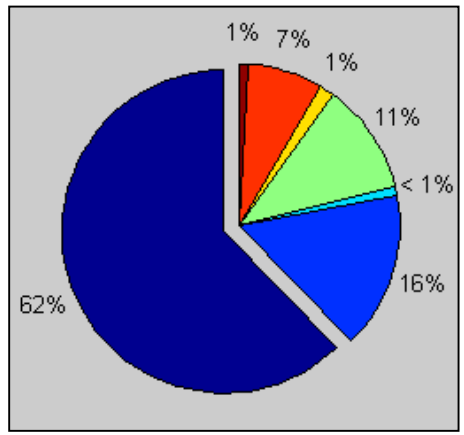


316 Stainless steel



440 Wh / kg 400 Wh / L

Carbon fiber composite



930 Wh / kg 400 Wh / L

Composite tank necessary to achieve gravimetric goals!

Kinetics Modeling

Current approach tracks weight fraction of each composition

$$\underset{C_1}{NaH + Al + 3/2\ H_2} \leftrightarrow \underset{C_2}{1/3\ Na_3AlH_6 + 2/3\ Al + H_2} \leftrightarrow \underset{C_3}{NaAlH_4}$$

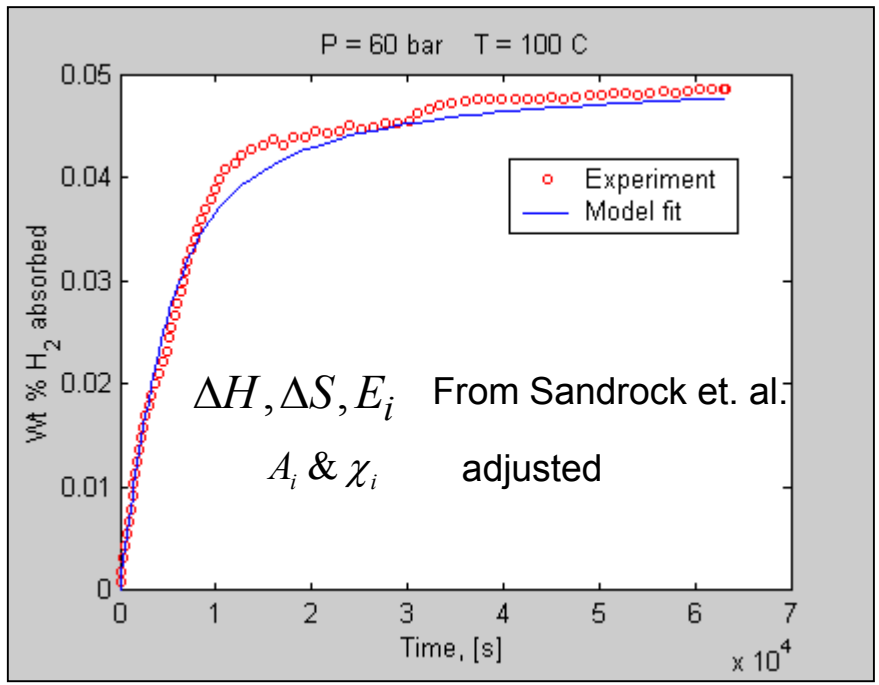
$$\left(\frac{dC_i}{dt}\right)_{ri} = f(T) * g(P) * h(C_i)$$

For C_1:

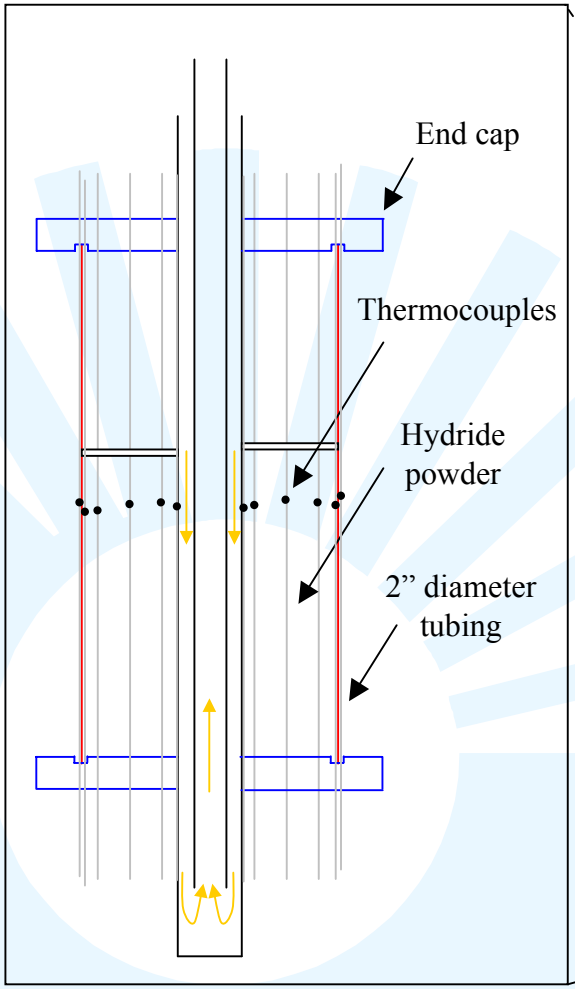
$$\left(\frac{dC_1}{dt}\right)_{r1} = A_1 \exp\left(-\frac{E_1}{RT}\right) * \left(\frac{P_{e,1} - P}{P_{e,1}}\right) * (C_2)^{\chi_1}$$

$$\left(\frac{dC_2}{dt}\right)_{r1} = -\left(\frac{dC_1}{dt}\right)_{r1}$$

El Osery, 1993

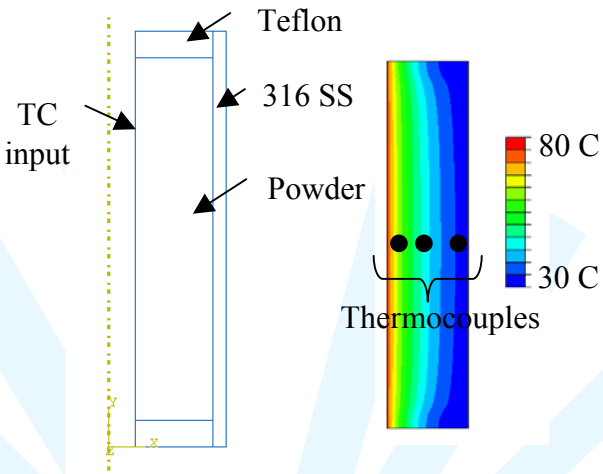


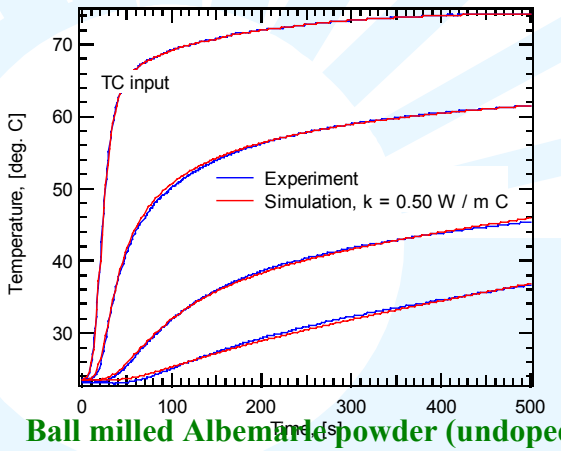
50g sub-scale system



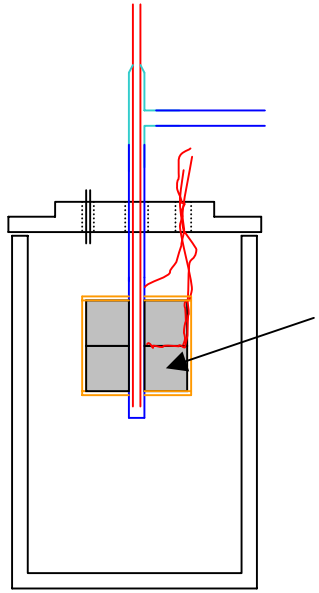
Thermal Conductivity/Enhancement

ABAQUS simulation





Ball milled Albemarle powder (undoped):
k = 0.35 to 0.50 W / m ºC



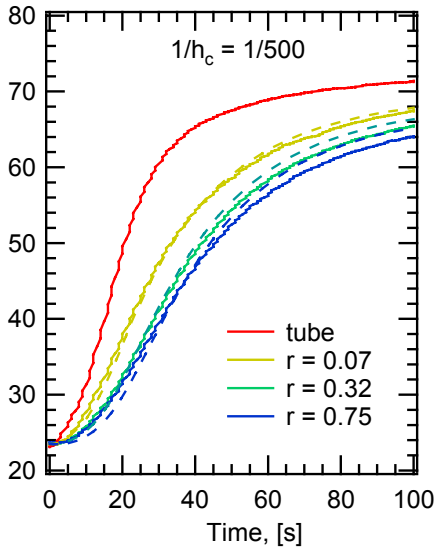
Unfilled contact resistance

$$\frac{1}{h_c} = \frac{1}{500\ \mathrm{W/m^2\ ^oC}}$$

Filled with $NaAlH_4$

$$\frac{1}{h_c} = \frac{1}{1000\ \mathrm{W/m^2\ ^oC}}$$

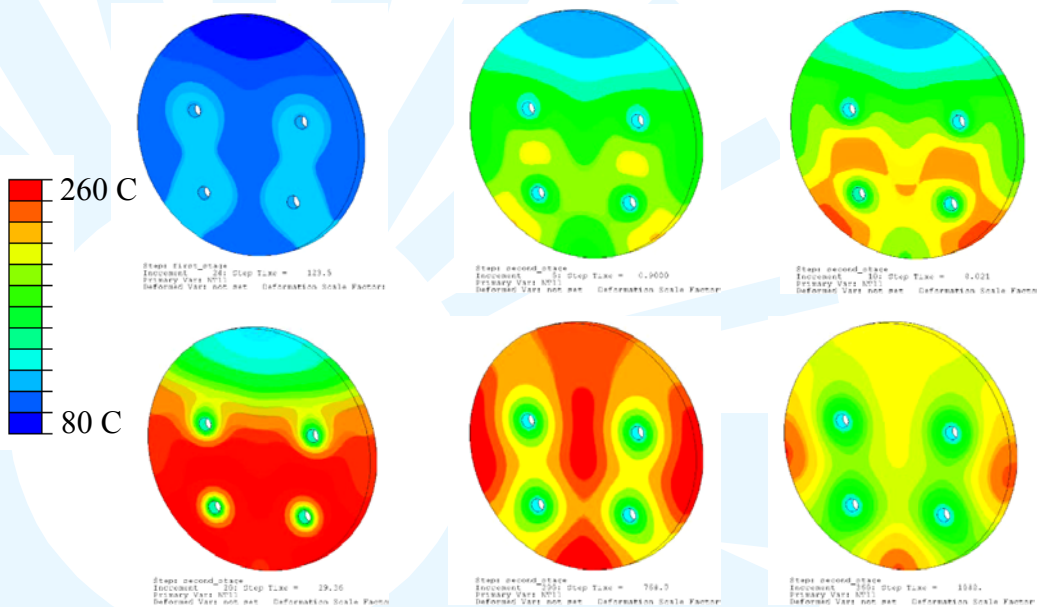
Unfilled contact resistance results

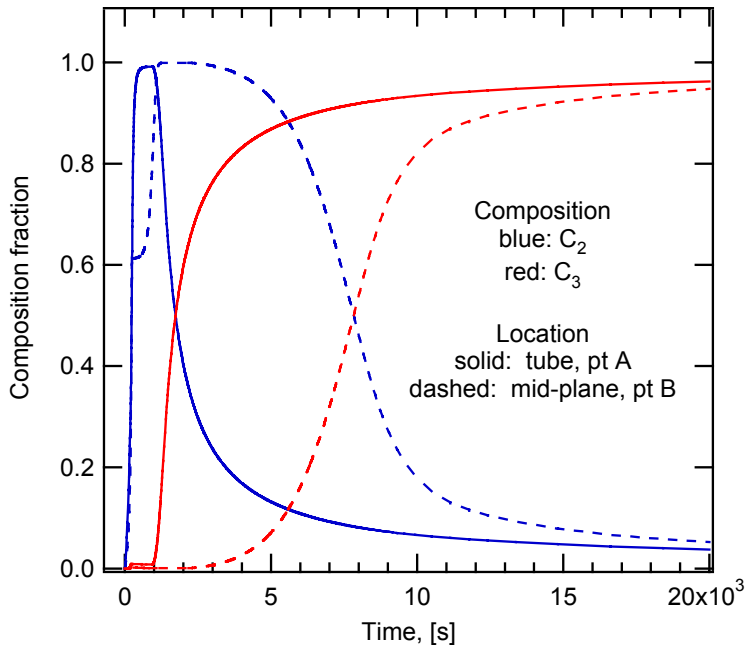


- **Thermal contact resistance is significant for interference fit**

System FEA Modeling
ABAQUS

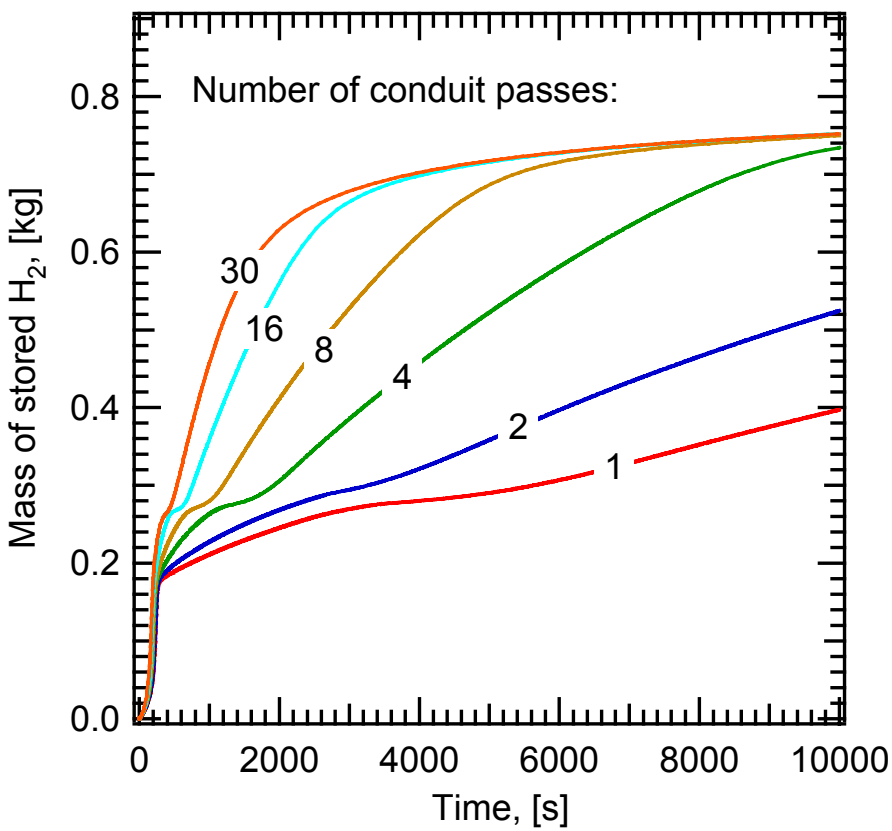
Vessel: 9” Dia. Vessel, 4 wt% Al foam, stainless steel tubing
Media: Albemarle $NaAlH_4$ + 2% Ti^{+3}
Starting state: Full discharged, 80°C
Charging state: 100 bar H_2 pressure, 120°C fluid flow

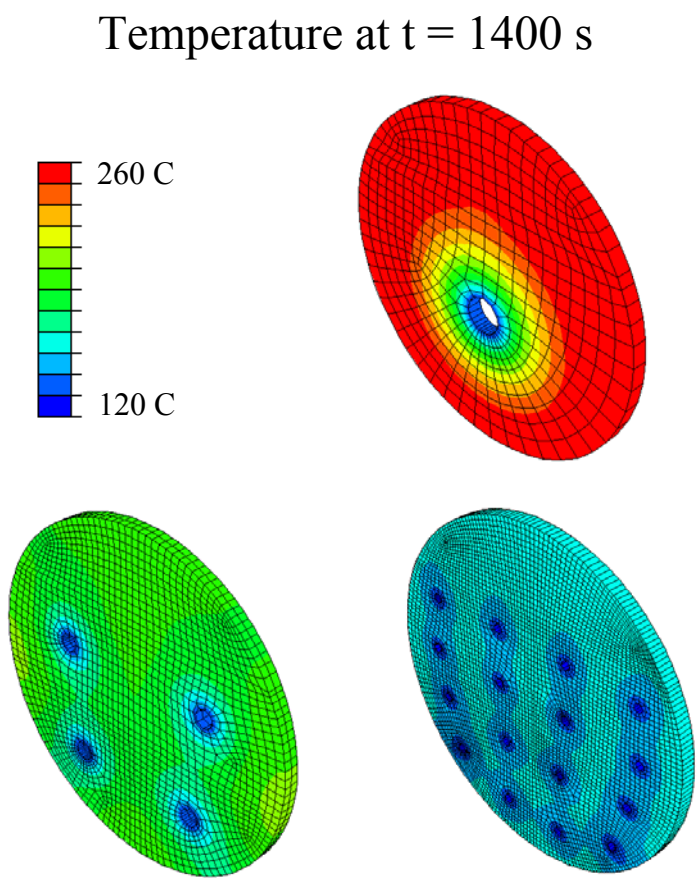




System Design Modeling

- ABAQUS subroutine calculates hydrogen mass via integration of C_i fields.
- Sensitivity study conducted for number of internal conduit passes during charging.





Future Work

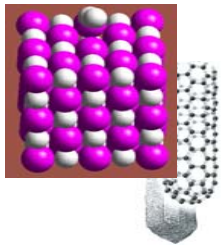
2003-04 Milestones

1. **Complete Safety Analysis**
2. **Perform 50g H_2 System Cyclic Evaluations**
3. **Assess/Complete Thermodynamic Modeling**
4. **Complete media cycling to assess durability.**
5. **Complete Prototype 1kg System Design & Fabrication**
6. **Complete Evaluation of 1kg System Prototype Capabilities to meet Go/NoGo criteria.**

Standardized Testing Program for Emergent Chemical Hydride and Carbon Storage Technologies

2003 Hydrogen and Fuel Cells Merit Review Meeting

May 19-22, 2003



Relevance/Problem Definition

- DOE's Draft Hydrogen Storage Plan sets aggressive 2005, 2010 and 2015 targets for gravimetric and volumetric efficiency and cost for on-board hydrogen storage.

- Significant R&D activity is required since no current storage material or system meets even the 2005 targets.

- Variability in adsorption/desorption measurement equipment and protocols has made it difficult to assess the potential viability of many of the new solid-state storage materials, e.g., storage capacity of SWNTs can vary by 40 to 50% when measured by TPD vs. Seiverts in the same lab.

Relevance/Need and Objectives

DOE Program Need

An ability to accurately and independently assess the performance of the wide array of solid-state storage materials and focus efforts on those that show the most promise in meeting the 2005, 2010, and 2015 performance targets.

Project Objectives

- Develop and operate a standard testing and certification program specifically aimed at assessing the performance, safety and life cycle of emergent chemical hydride and carbon adsorption/desorption hydrogen storage materials and systems.
- Work with industry and the U.S. government to develop an accepted set of performance and safety evaluation standards.

Project Team

- Southwest Research Institute
- The National Hydrogen Association
- Teledyne Energy Systems
- Energy Conversion Devices, Inc.

Technical Approach

Completed facility will contain two primary capabilities:

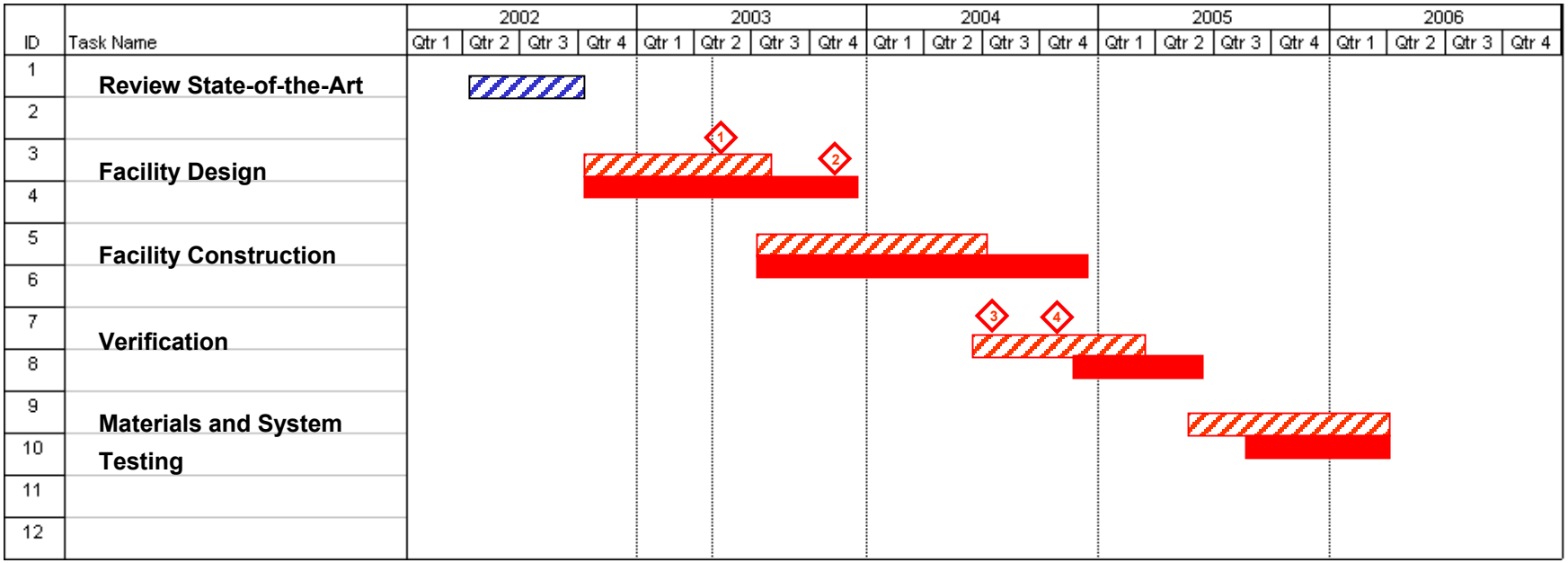
- Characterization of small quantities (milligram to gram) of candidate materials; and
- Characterization of the performance of full-size storage systems.

Completed facility will be available to all organizations involved in hydrogen storage.

Technical Approach (cont.)

- **Characterization of small quantities (milligram to gram) of candidate materials**
  - **Sorption/desorption behavior**
  - *Intrinsic thermodynamic characteristics*
  - *Elemental composition*
  - *Crystallographic properties*
- **Characterization of the performance of full-size storage systems**
  - **Sorption/desorption cyclic performance**
  - **Refueling time**
  - *Resistance to exogenous contaminates*
  - *Specific energy contained*
  - *Impact, vibration and fire resistance*

Project Timeline



Milestones

1. Submit document describing test systems for measurements of storage materials.
2. Submit document describing test systems for measurement of full-scale storage systems.
3. Initiate internal verification with standard materials.
4. Initiate round-robin verification.

Storage Material Characterization

Storage System Characterization

Project Timeline (cont.)

- The testing facility will be completed and verified (2Q, 2005) in time to provide support for Task 3: Solid-State Materials R&D and Task 4: R&D of Adv. Solid-State Materials for 2010 Targets of DOE's Draft Hydrogen Storage Plan.

- Specifically, the facility will be available in time to provide input into the go/no-go decision point on carbon nanotubes (4Q, 2005) and the downselect of complex hydride materials (4Q, 2006).

Project Timeline

Success Criteria

- Demonstrated ability to provide unbiased and accurate measurements of hydrogen storage capacities.
- Community acceptance and use of test facility.

Business Plan

- Actively solicit representative storage materials and systems for use during facility verification and benchmarking, participate in Carbon Materials Working Group round robin testing program and initiate additional round robin program.

Current Status

- Project activities initiated in April, 2002.
- Completed literature review of current measurement state-of-the-art.
- Developed preliminary facility and equipment design.
- Completed visits of leading laboratories involved in hydrogen adsorption/desorption measurements for critique of preliminary facility design.
  - GMR; 9/17/02 Air Products; 9/23/02
  - NREL; 9/30/02 Sandia; 11/18/02
- Submitted document specifying the equipment to be used for characterization of storage materials.

Current Status (cont.)

State-of-the-art Overview

- Wide range of materials results in a wide range of measurement conditions.
  - mg to g sample quantities
  - vacuum to 100 atm
- Three prominent techniques being used.
  - Gravimetric (TGA)
  - Volumetric (Sieverts)
  - Thermally programmed desorption (TPD)
- Errors develop due to indirect nature of the techniques and operating near their sensitivity limits.
- SWNTs are currently the most challenging to measure due to combination of small mass and high pressure.
- Carbon materials are being measured using gravimetric (GM), volumetric (Air Products) and TPD (NREL).

Current Status (cont.)

State-of-the-art Overview – Conclusions

- No single measurement technique will be appropriate for all of the materials that are currently being considered for hydrogen storage.
- A comprehensive testing facility will need to have multiple techniques to cover the full range of materials.
- The presence of multiple techniques will provide higher confidence in results by enabling cross checks of storage capacity using more than one technique.
- Whenever possible, gas speciation should be included in the measurement of storage capacity.

Interactions/Collaborations

- Visits have been completed with hydrogen storage research teams at GMR, NREL, Air Products and Sandia. Engaged in ongoing discussions with these teams regarding the best approaches for accurate storage measurements.

- Participating in the Carbon Materials Working Group which is initiating a round robin testing program.

Future Work and Milestones

- A testing facility equipped to perform gravimetric, volumetric and TPD measurements on small quantities of solid-state hydrogen storage materials has been defined 2Q, 2003).

- The design for the facility to test full-scale storage systems will be finalized (3Q, 2003).

- Construction of approximately 50% of the testing facility should be completed (2Q, 2004).

Future Plans (cont.)

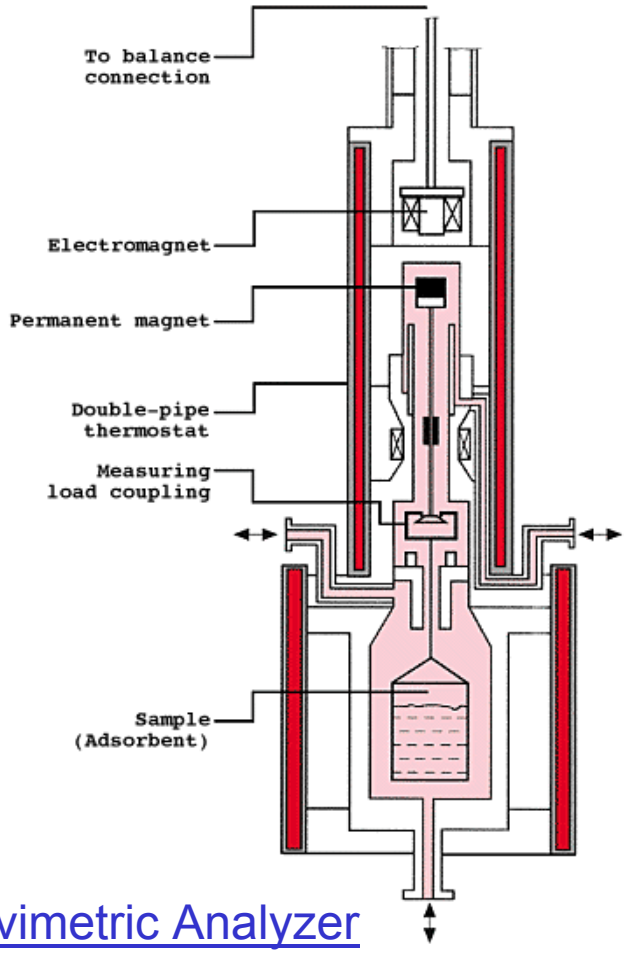
Testing Facility

- 1,000 sq ft of dedicated laboratory space
- Titan HM-200 Hydrogen Generator
  - 424 scfh
  - 99.9998% hydrogen
- Two stage hydrogen compressor for service up to 2,500psig
- Pressurized hydrogen storage vessels for 15kg hydrogen at 2,000 psi
- Source-gas manifolds with control valves and regulators
  - H_2
  - He
  - Lecture bottle source-gas manifold (CO, CO_2, H_2S)
- Electropolished supply lines and point of use purifiers
- H_2 safety sensors

Future Plans (cont.)

High-Pressure TGA

- Rubotherm magnetic suspension balance
- Mass spectroscopic desorption speciation
- Milligram – gram sample size
- 30 atm operating pressure
- Located within a glove box for air sensitive samples
- External material activation facilities
- Estimated accuracy of 3×10^{-4} wt % for 300 mg sample at 1 atm

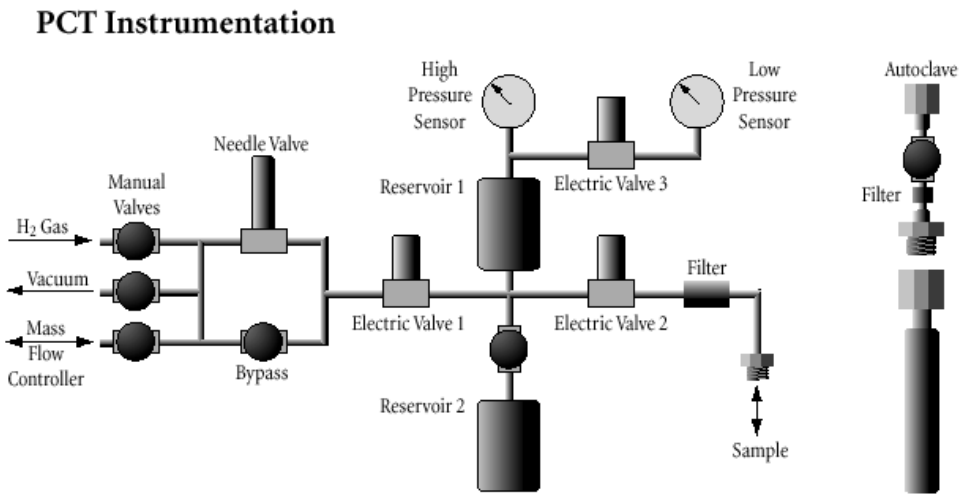


Gravimetric Analyzer

Future Plans (cont.)

Sieverts Apparatus

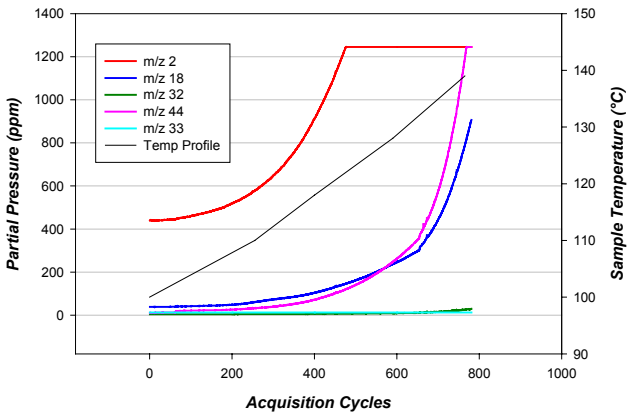
- Pressures up to 200 atm
- Sample temperatures to 400°C
- Controlled gas temperatures throughout
- Pneumatically controlled valves
- Variable sample volumes
- Estimated accuracy of 0.2 wt. % with 300 mg sample at 100 atm



Future Plans (cont.)

Thermally Programmed Desorption

- Thermal Desorption & Recoiling Mass Spectrometry (TDARMS) system developed at SwRI
  - Real- time gas-phase speciation
  - High-pressure MS interface
  - Automated leak pressurization
  - Ultra-clean components
- Real-time vibrational spectroscopy of sample (fiber optically coupled)
- TDARMS being converted to TPD
- Accuracy to be determined



Future Plans (cont.)

Volumetric Sieverts apparatus for complete system testing

- >35 atm operating pressures
- > kg sample sizes
- 5 kg delivery in < 5 min
- Calibrated reservoirs
- Mass flow controller
- Heat exchanger (point-of-service chiller)
- Control and data acquisition computer
- System containment (Hydride-bed device)
- Gravimetric backup measurement

Contact Information

Point-of-Contact/Principal Investigators:

Richard A. Page, Institute Scientist

Michael A. Miller, Manager-R&D

Southwest Research Institute

6220 Culebra Rd., San Antonio, TX 78238

Phone (210)522-3252, FAX (210)522-6220

Email rpage@swri.org

Email mmiller@swri.org

Hydrogen Storage in Carbon Nanotubes

A.C. Dillon, P.A. Parilla, K.E.H. Gilbert, J.L. Alleman, T. Gennett*, and M.J. Heben

National Renewable Energy Laboratory
*Rochester Institute of Technology

2003 DOE HFCIT Program Review Meeting

DOE Office of Energy Efficiency and Renewable Energy
DOE Office of Science, Division of Materials Science

Objective:

→ **Develop nanostructured carbon materials for vehicular H storage, focusing on carbon nanotubes**

- Reproducibly achieve 2005 DOE/FreedomCAR goals: 1.5 kWhr/kg (4.5 wt%) and 1.2 kWhr/L (0.036 kg H_2/L)

→ **Barriers:**

- Determine the hydrogen storage capacity of nanostructured carbon materials (Task 3)
- Develop cost-effective fabrication processes for promising materials (Task 3)
- Explore compressed gas/reversible storage material hybrid systems (Task 1)

→ **Permit Go/No-Go decision by 4th Quarter of FY 2005**

History & Problems with Activated Carbon (pre-1995)

- Coconut shell charcoal. (Kidnay and Hiza, 1967)
  Excess H of 2.15 wt% at 25 atm, 76 K. .
- "F12/350" carbon (Carpetis and Peshka, 1976)
  5.2 wt% for carbon at 41.5 atm, 65 K.
  Inverse relation between porosity and H wt%.
- Optimization (Schwartz, et al., 1980s, early '90s)
  Surface acidity, metal modification
  ~4.8 wt% at 59 atm and 87 K

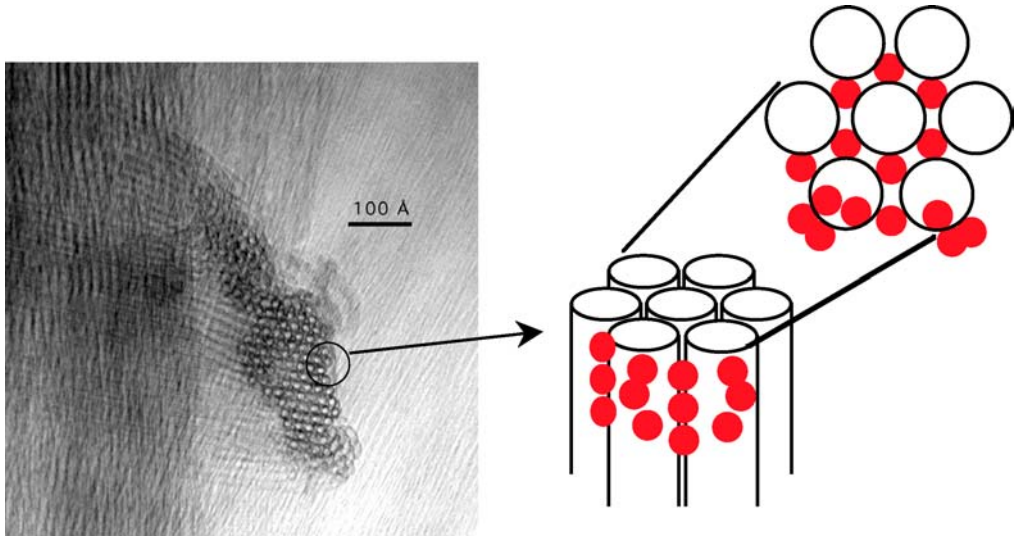
- Inaccessible volumes & heterogenous adsorption sites
- Difficult to control, study, and optimize
- Weak physisorption interactions (4-6 kJ/mol)

➔More H_2 stored in empty cylinders at T & P of interest.

A.C. Dillon and M.J. Heben, Appl. Phys. A 72, 133–142 (2001)

SWNTs: An Ideal Adsorbent for Hydrogen?

- Potential for higher binding energies, high volumetric packing, elimination of skeletal density, and maximum nanopore volume.
- SWNTs are tunable, modifiable materials, with variable electronic properties and controllable defect densities and sizes.
- Tunability offers possibility of designing P & T of operation, and capacity
- Scale-up production costs estimated to be ~ 1 $/kg



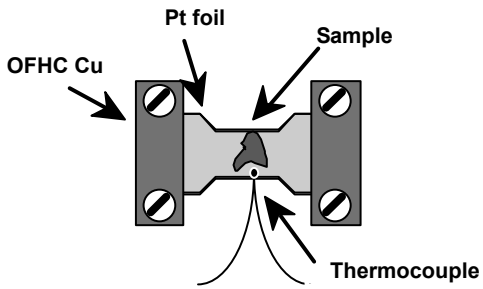
- Closed-packed crystals have densities of 1.3- 1.4 gm/cc
- 1 H:C ~ 7.7 wt%, which meets the 2005 goal
- 1 H:C in 1.3 gm/cc corresponds to ~ 0.1 kg H_2/L
- 36% of this "theoretical" maximum will meet the volumetric 2005 goal

M.J. Heben, Proc. 1993 DOE/NREL Hydrogen Program Review, 79-88, 1993.

H_2 Storage Measurement by TPD

(Temperature Programmed Desorption)

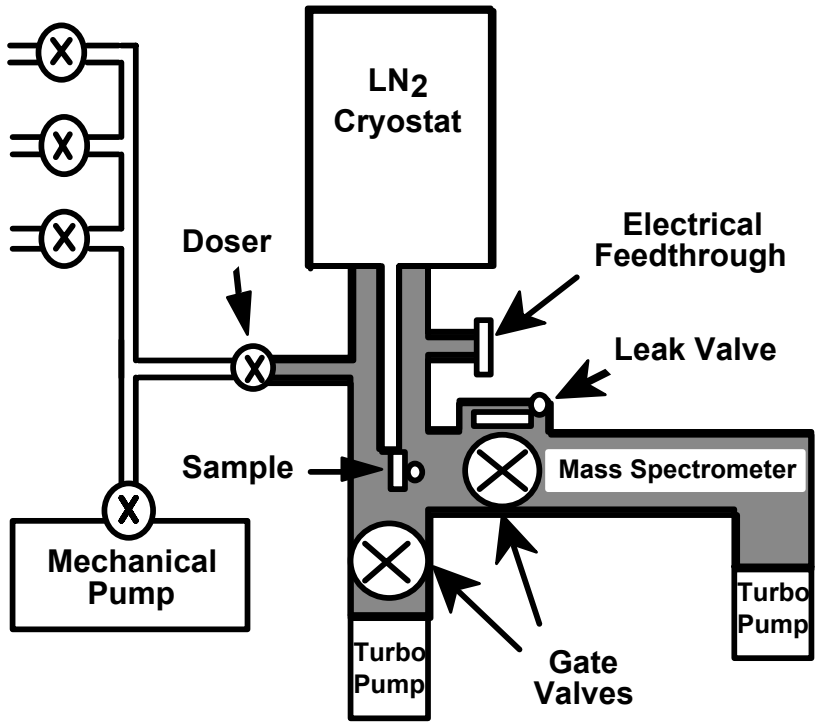
- Agrees with volumetric measurements on hydrides
- Water & gas purity detected by mass spectroscopy
- Small amounts of H are easily measured
- Cross calibration with three different standards



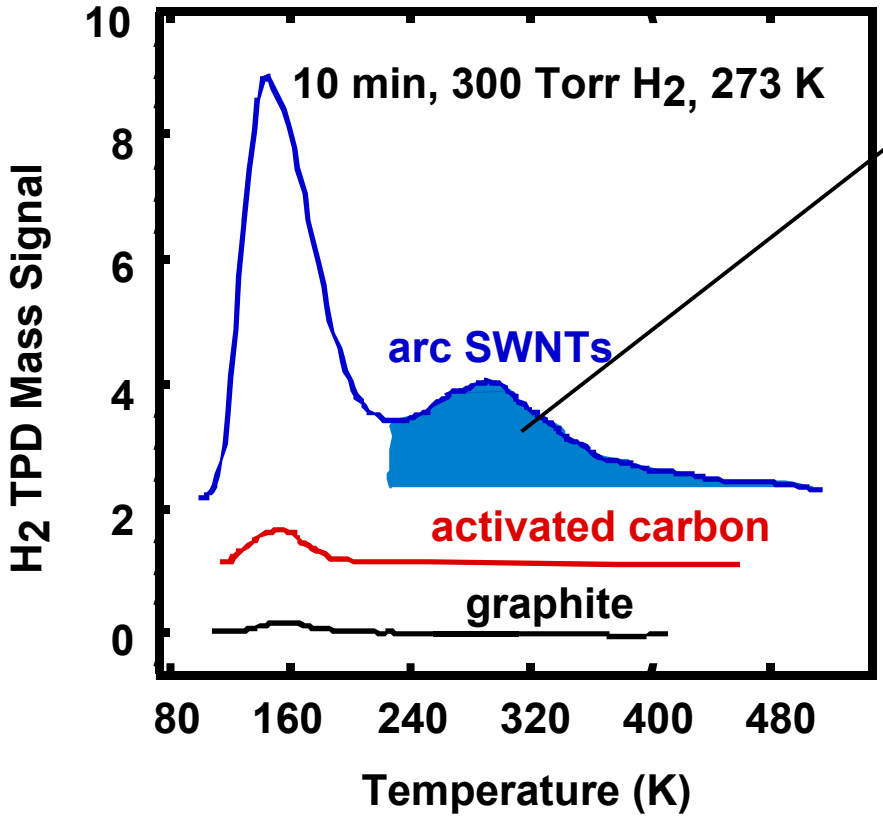
1 wt%H on 1 mg = 5 μgm H_2
≈ ΔP ~ 25 mtorr in 3 L

Capabilities:
- 90 to 1500 K
- 5 X 10^{-9} to 1000 torr
- Mass Spectra (0 - 300 amu)

1 mg samples reproducibly weighed with Mettler-Toledo UMT2 balance



Room Temperature Adsorption on Arc SWNTS



- After degassing in vacuum
- Not associated with catalytic metal particles
- Integrated H_2 ~0.01 wt% of total sample weight, between 5 and 10 wt% on SWNT basis
- 19.6 kJ/mol binding energy, higher than expectations for physical adsorption

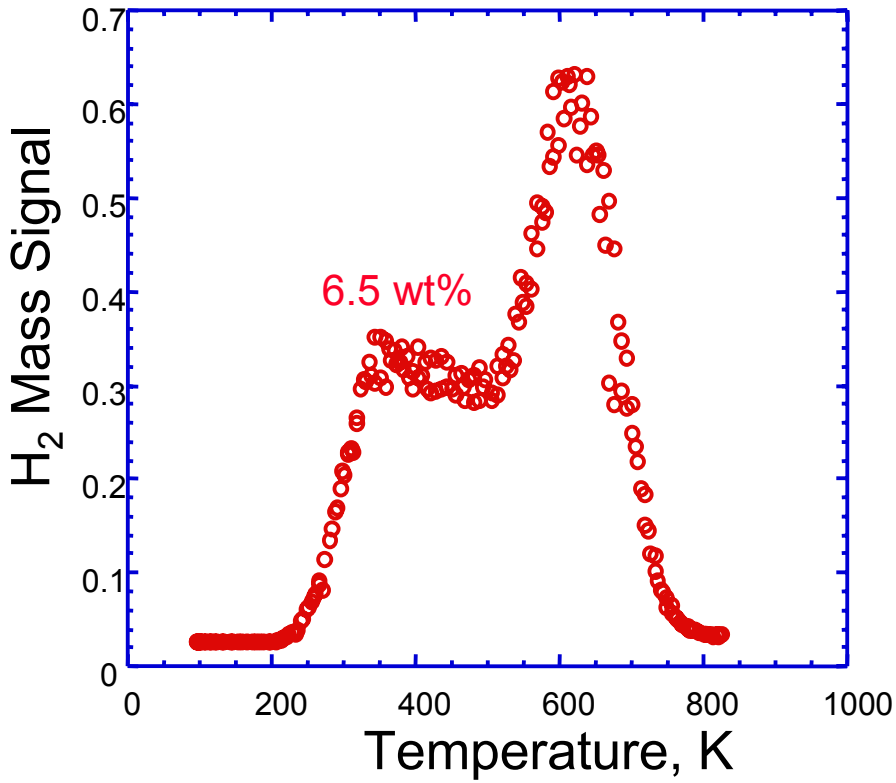
A.C. Dillon, K.M. Jones, T.A.Bekkedahl, C.H. Kiang, D.S. Bethune, & M.J. Heben, Nature (386) 377, 1997.

6.5 -7 wt% H_2 on Ultrasonically Cut Samples

Laser-generated tubes are less-defective and require aggressive cutting techniques

6.5 wt% H on total sample
Sample contains 26 wt% Ti-6Al-4V alloy (TGA)
Ti-6Al-4V alloy fraction stores < 3 wt%
Conclusion: 7 Wt% H stored on carbon fraction

Sonication:
16 hrs.
4 M HNO_3
50 W/cm^2



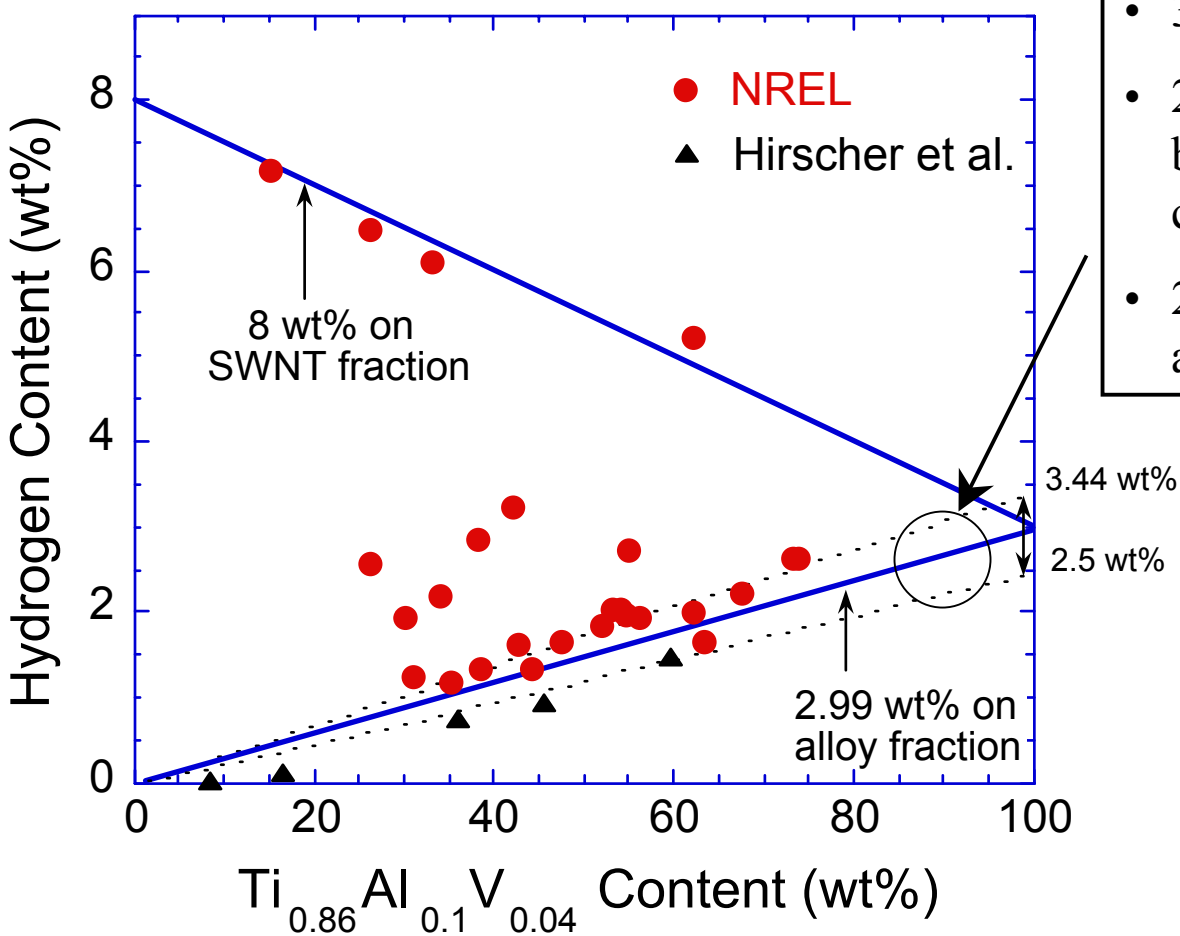
RT dose:

500 torr

Cool to 130 K prior to evacuation

Sample Prep Yields Scattered Results

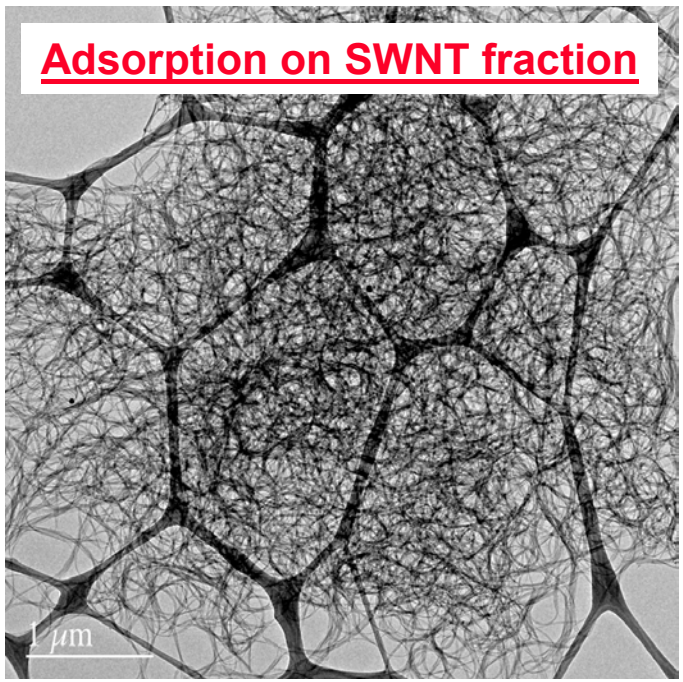
- Any data above metal hydride uptake is due to adsorption on tubes.
- ~ 50% of the data presented here shows significant SWNT uptake, up to 8 wt%.
- All of the Hirscher data falls below expectations for even alloy adsorption.

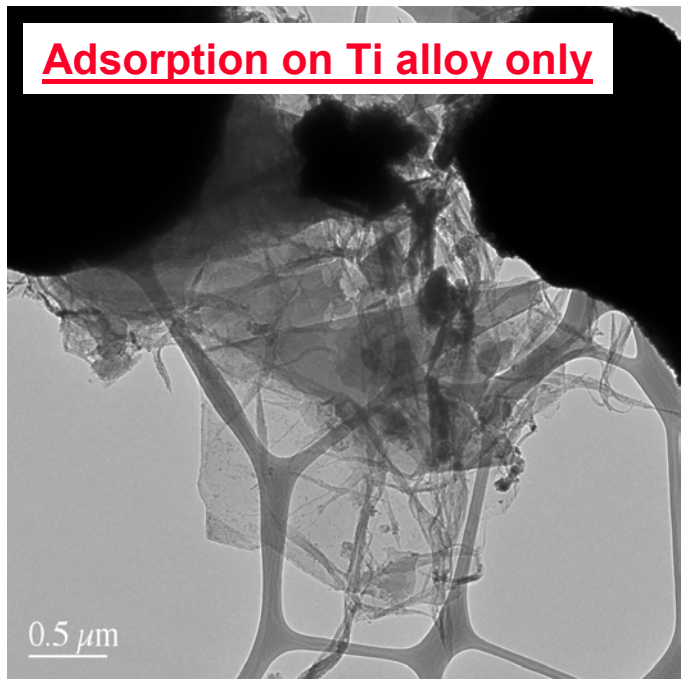


- 3.44 wt% for Ti portion to TiH_2
- 2.99 wt% on commercial alloy by volumetric method, consistent with literature.
- 2.5 wt% on probe-generated alloy by volumetric and TPD

Why is Current SWNT Activation Inconsistent?

Sonication produces differing degrees of cutting, amounts of metal, and metal particle sizes, in differing degrees of intimate contact with SWNTs, even with careful control of external parameters time such as sonication power, acid concentration, hydrodynamics.





Storage Results on Nanocarbons Vary Widely

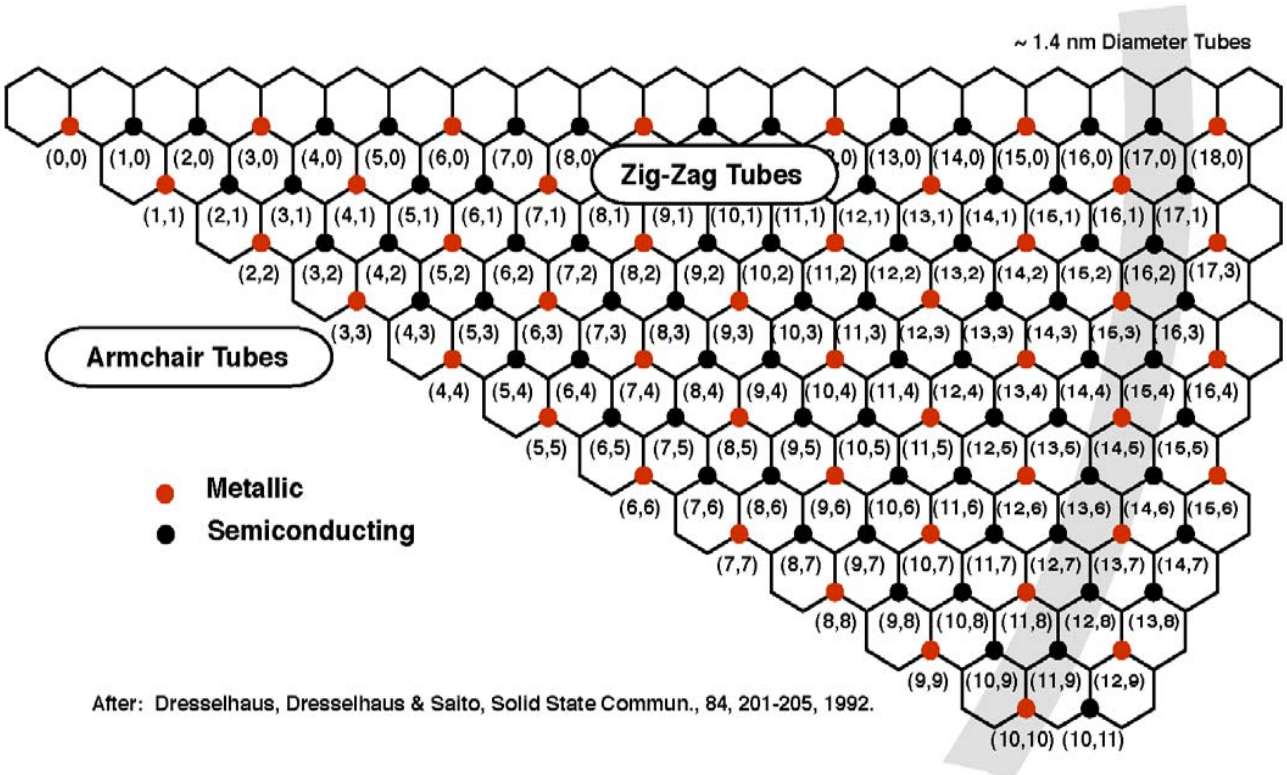
Material	Density wt%	Temp (K)	Pressure (MPa)	Reference	Year
GNFs (herring bone)	67.55	RT	11.35	Chambers	1998
GNFs (platelet)	53.68	RT	11.35	Chambers	1998
Li-MWNTs	20	~473-673	0.1	Chen	1999
K-MWNTs	14	< 313	0.1	Chen	1999
GNFs (tubular)	11.26	RT	11.35	Chambers	1998
CNFs	~10	RT	10.1	Fan	1999
Li/K-GNTs (SWNT)	~10	RT	8-12	Gupta	2000
GNFs	~10	RT	8-12	Gupta	2000
SWNTs (lo purity)	5-10	273	0.04	Dillon	1997
SWNTs (hi purity)	8.25	80	7.18	Ye	1999
CN nanobells	8	573	0.1	Bai	2001
Nano graphite	7.4	RT	1	Orimo	2000
SWNTs (hi p + Ti alloy)	6-7	~300-700	0.07	Dillon	2000
GNFs	6.5	RT	~12	Browning	2000
CNFs	~5	RT	10.1	Cheng	2000
MWNTs	~5	RT	~10	Zhu	2000
SWNTs (hi p + Ti alloy)	3.5-4.5	~300-600	0.07	Dillon	1999
SWNTs (50% purity)	4.2	RT	10.1	Liu	1999
Li-MWNTs	~2.5	~473-673	0.1	Yang	2000
SWNT (50% purity)	~2	RT	echem	Nutzenadel	1999
K-MWNTs	~1.8	< 313	0.1	Yang	2000
(9,9) array	1.8	77	10	Wang	1999
MWNTs	< 1	RT	echem	Beguin	2000
CNF	0.1-0.7	RT	0.1-10.5	Poirier	2001
(9,9) array	0.5	RT	10	Wang	1999
SWNTs	~0.1	300-520	0.1	Hirscher	2000
Various	< 0.1	RT	3.5	Tibbets	2001
SWNT (+ Ti alloy)	0	RT	0.08	Hirscher	2001

>10 wt%

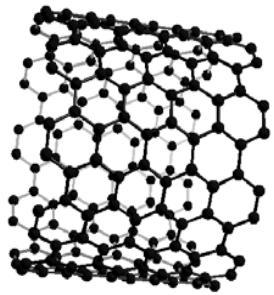
< 1 wt%

Variability Compounded by Differences in Materials

- *Only recently have methods been developed to determine the identities of tubes in a given sample (Bachilo, et al., Science, p2362, Dec. 2002)*
- *Purities and properties vary widely, especially from commercial suppliers*



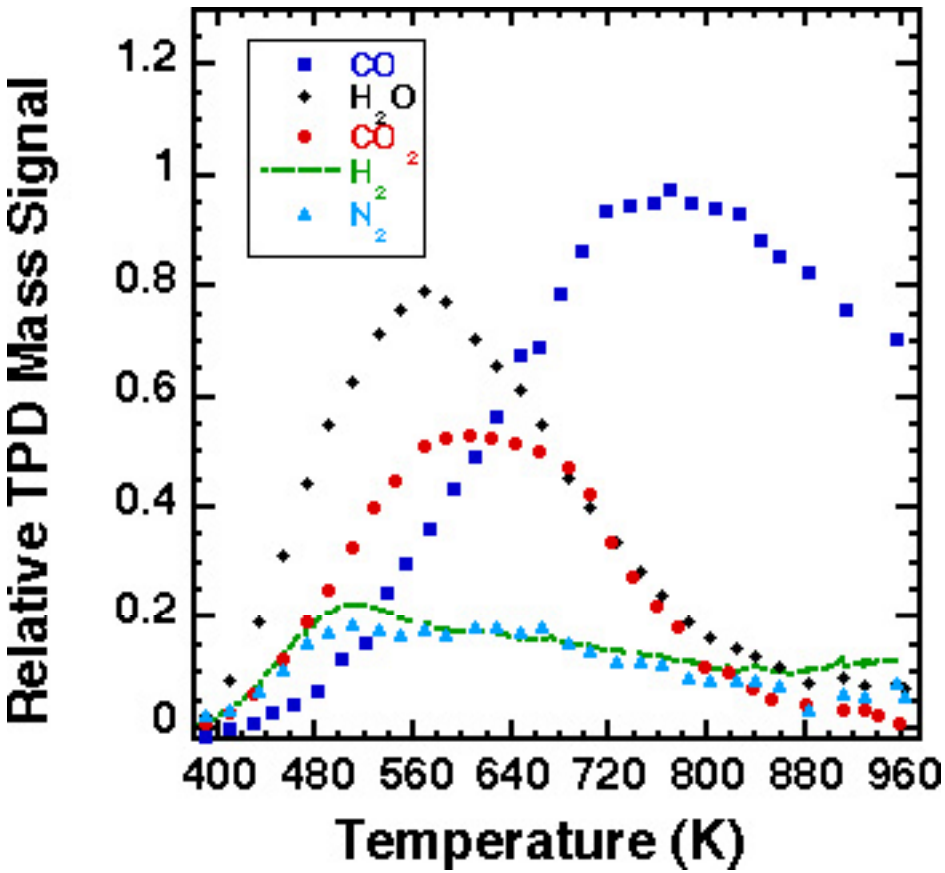
After: Dresselhaus, Dresselhaus & Saito, Solid State Commun., 84, 201-205, 1992.



(10,10) - metallic

(17,0) - semiconductor

In Most Published Work, Samples are not Cleaned in Vacuum by Degassing



A.C. Dillon, M.D. Landry, J.D. Webb, K.M. Jones and M.J. Heben
Proceedings of the Electrochemical Society, Vol. 97-4, pp. 916-929, (1997).

What is the Mechanism?

- Ti, and other metals, may assist in the addition of H either via thermal effects due to immediate contact, or by a catalytic effect
- Raman and thermopower experiments at NREL offer evidence for partial electron transfer from SWNT to H_2.
- Sp^2 bonded carbons have sp^3-like character due to curvature of tubes
  H. Cheng, et al., JACS 123, 5845 (2001); Kostov, et al., PRL 89, 146105-1(2002).
- Emerging literature on carbon / metal Hybrids

  Mechanical milling of Mg and graphite lead to enhanced physical and electrochemical properties for H adsorption.

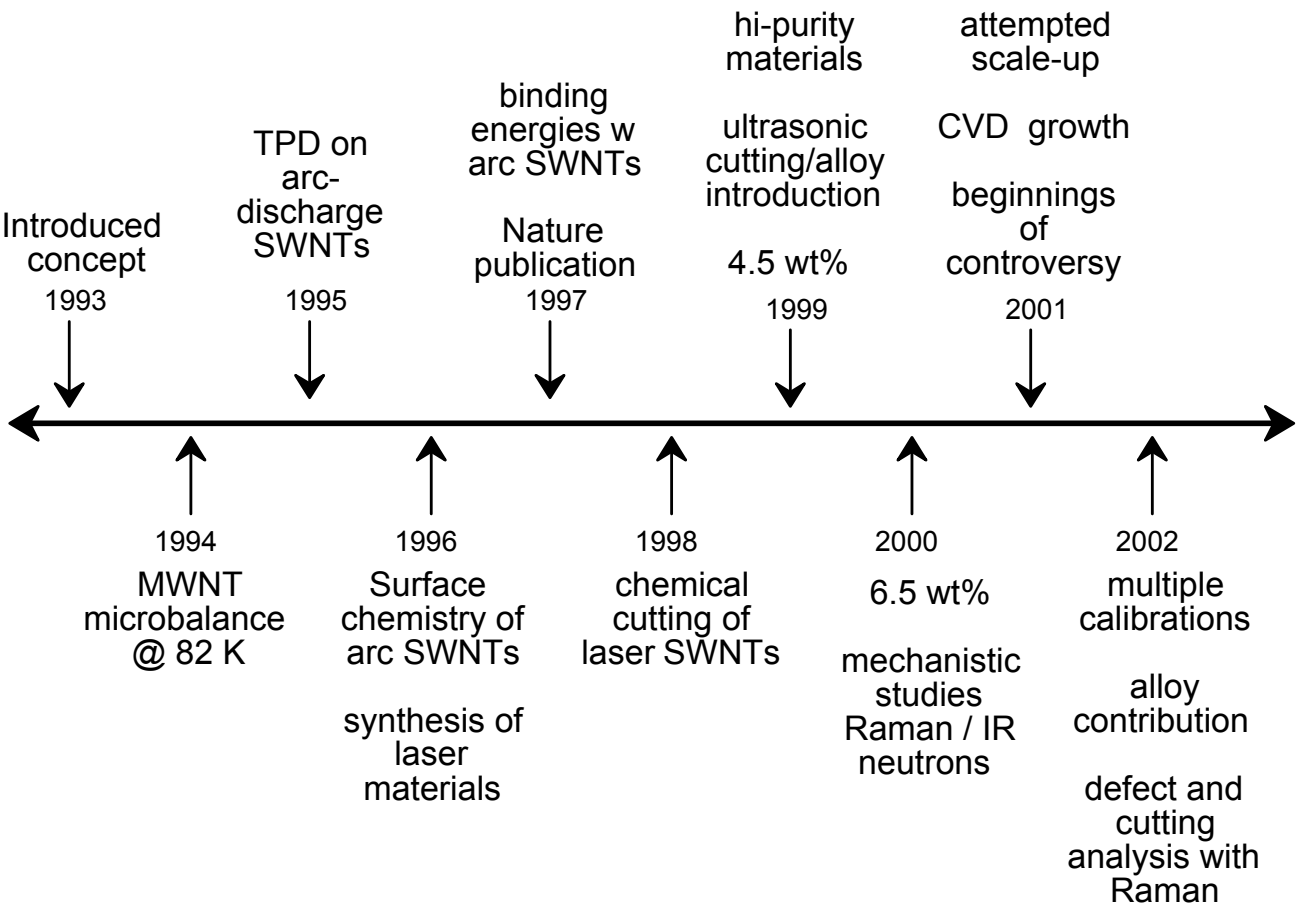
  e.g. Imamura et al., Int. J. Hydrogen Energy **25** (2000) p. 837.

  US patent publication 2002/0096048A1 (Cooper & Pez)

  "….carbon-metal hybrid materials…display an H_2 adsorption capacity that is greater than the sum of the capacities of the hybrid's individual components…"

SWNT materials may only be a special case, offering an opportunity for optimization / study through structural control.

Time-line from Beginning



Going Forward: Carbon Materials Working Group

- Bring community together to establish characterization and measurement protocols for round-robin testing and verification, discuss and vet findings

  NREL, Air Products, Caltech, HRL Laboratories, ORNL, Phillips / Conoco, U. Pittsburgh, U. Pennsylvania, Max Planck Institute, U. Quebec - Trois Rivieres, NETL, Southwest Research Institute

- 1st meeting at Argonne H_2 storage Workshop, 8/15/2002
- 2nd meeting via telecon, 1/5/03
- Worked with C. Ahn to establish plan to purify (by J. Vajo) 10 grams of commercially available material for distribution to group
- Materials will be measured at NETL, UQTR, ORNL, NREL, MPI, Air Products, HRL Labs by agreed upon protocols
- Next meeting to occur this week

Improving Understanding of Activation Process

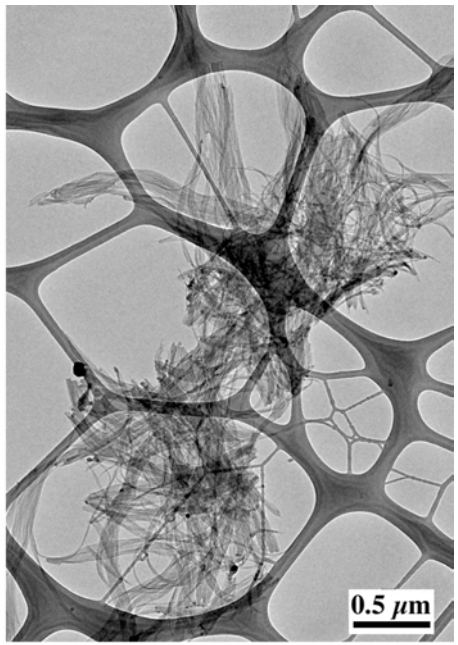
Limit the number of independent variables under study

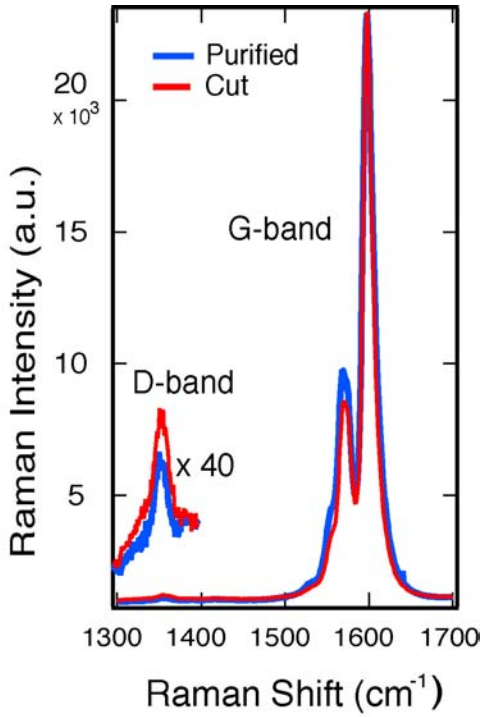
- Control tube types (chirality and diameter) during synthesis
  Chemical vapor deposition, laser growth, hot-wire deposition
- Measure tube types and defect densities
  Infrared photoluminescence excitation and Raman spectroscopies
- Develop cutting methods than do not introduce metal species
  D-band spectroscopy can assess the degree of cutting
- Introduce metals in known quantities, sizes, and locations
  Vapor transport, electrodeposition, chemical treatments, evaporation, mechanical methods

Approach to Cutting and Ti Incorporation with TiO_2

- Carbo-reduction of TiO_2 is possible at elevated temperatures and produces cutting, but the following reaction is favored:

  $TiO_2 + 3C \rightarrow TiC + 2\ CO$: Ti metal is not produced





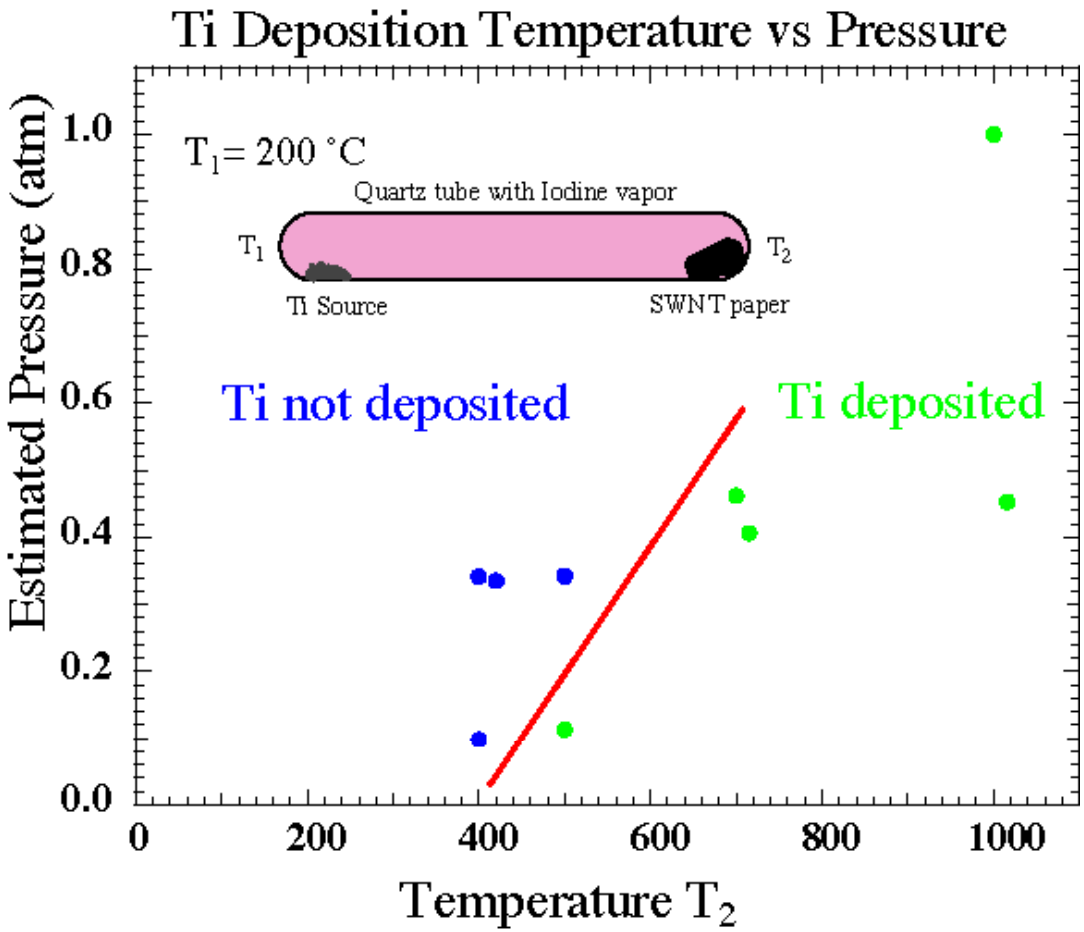
Degree of cutting can be followed by observing an increase in the D/G intensity ratio

Lower Temperature Routes to Ti Incorporation

Using well known Iodine transport reaction: $Ti + 2I_2 <-> TiI_4$

- TiC favored over Ti & C at all temps
- Kinetics inhibit formation at low temps
- At typical transport conditions, TiC will form

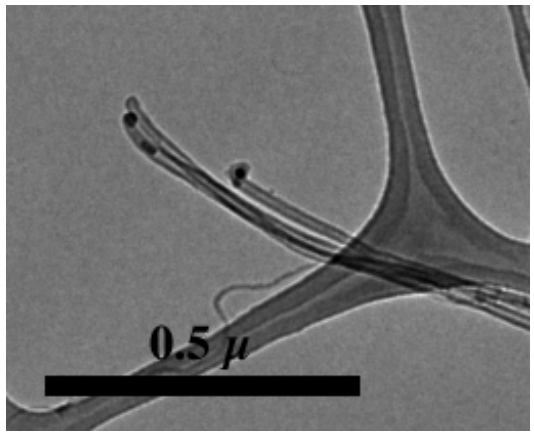
Ti metal has been incorporated by evaporation, but H adsorption has not yet been fully evaluated

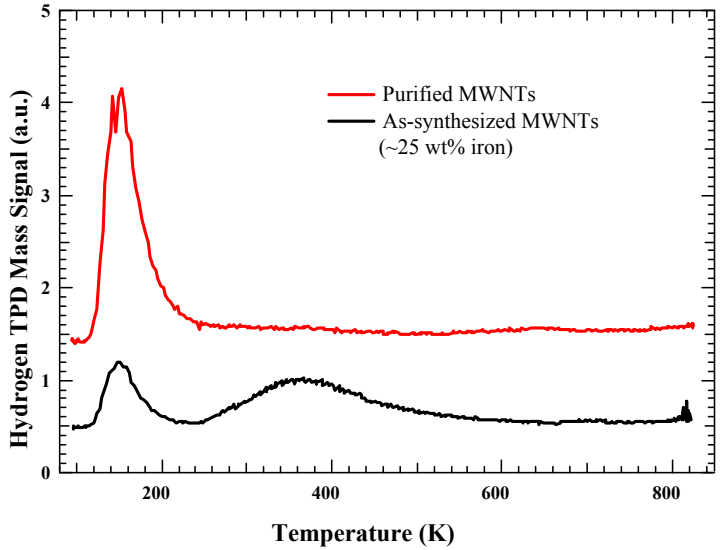


Placing Metal Particles in Specific Locations

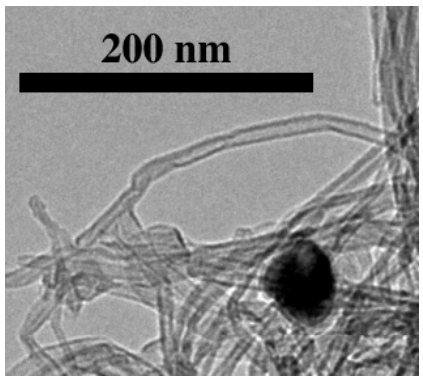
Hot-wire growth of multi-walled nanotubes with metals at tips

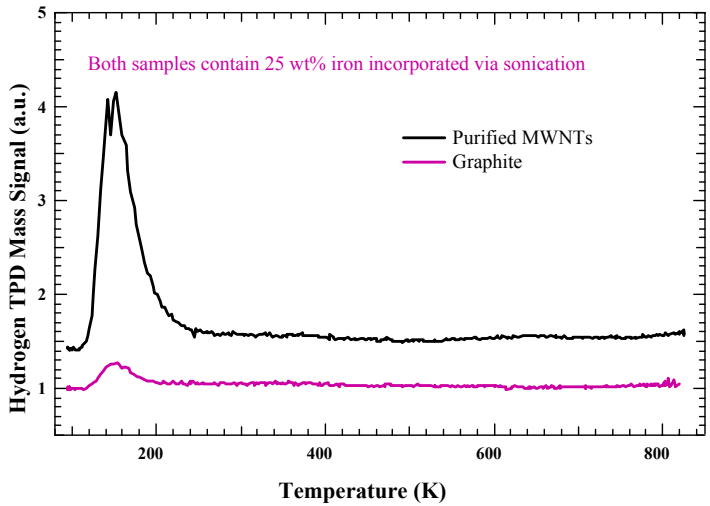
As grown, ~10-30 nm Fe particles at tube tips





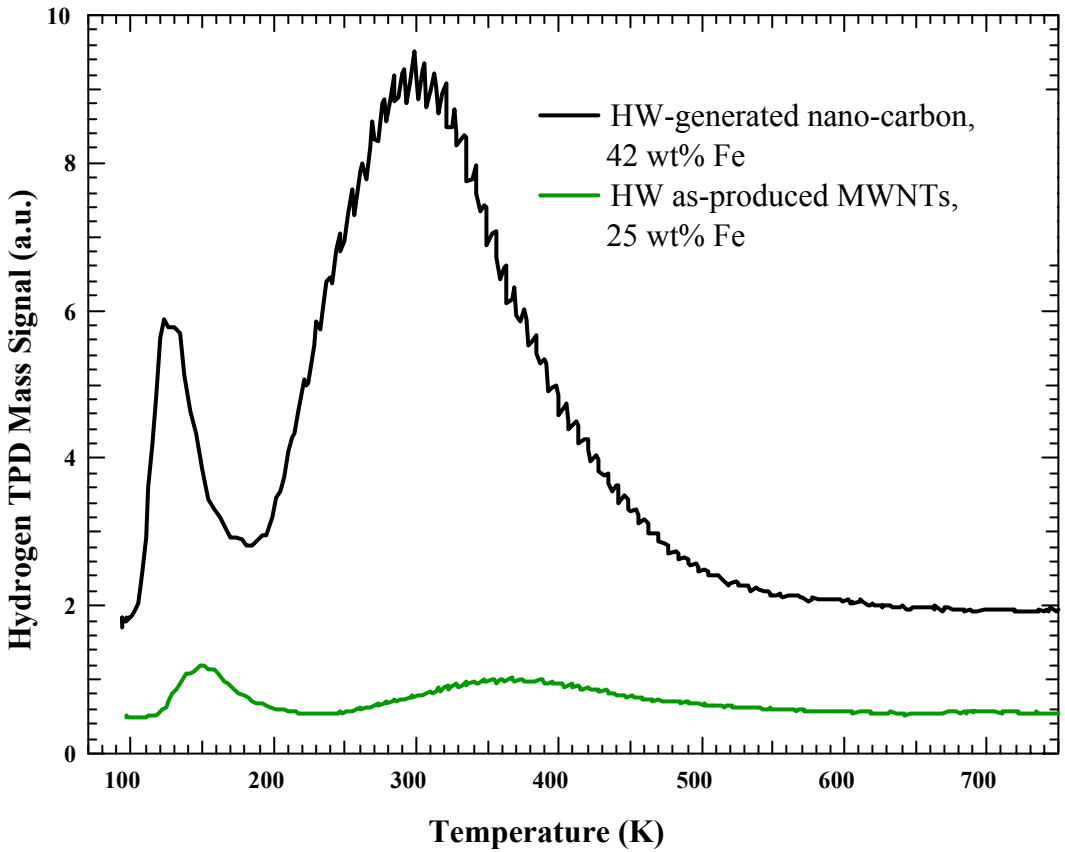
Fe particles added via sonication.

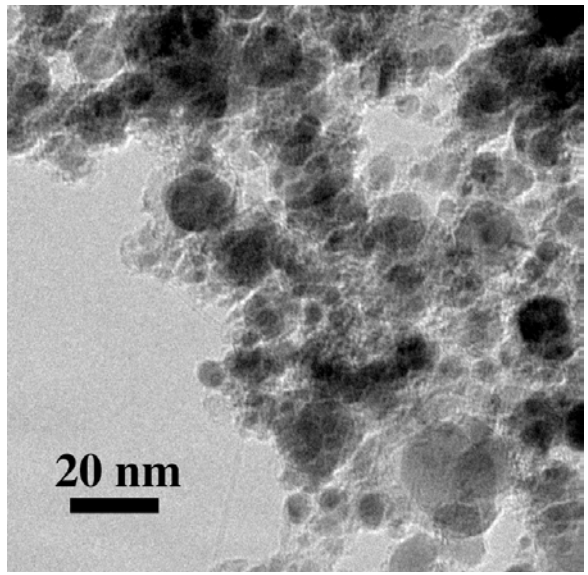




Hydrogen Storage in Nanocarbon Materials

HWCVD-generated Nano-carbon with Fe nano-particles



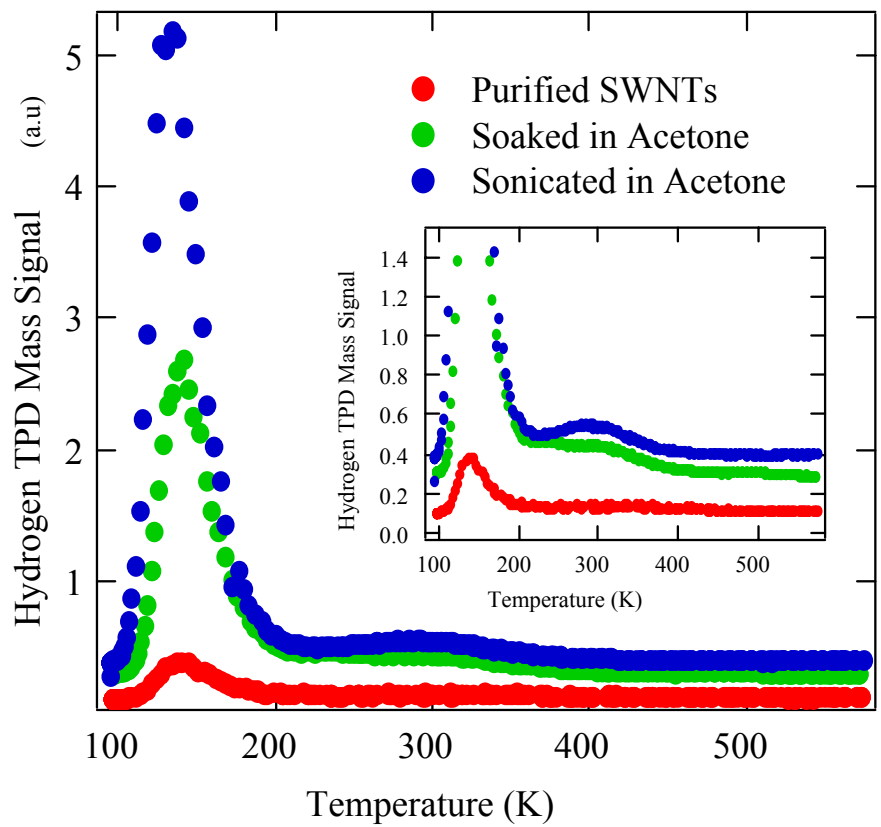


500 torr dose at room temperature

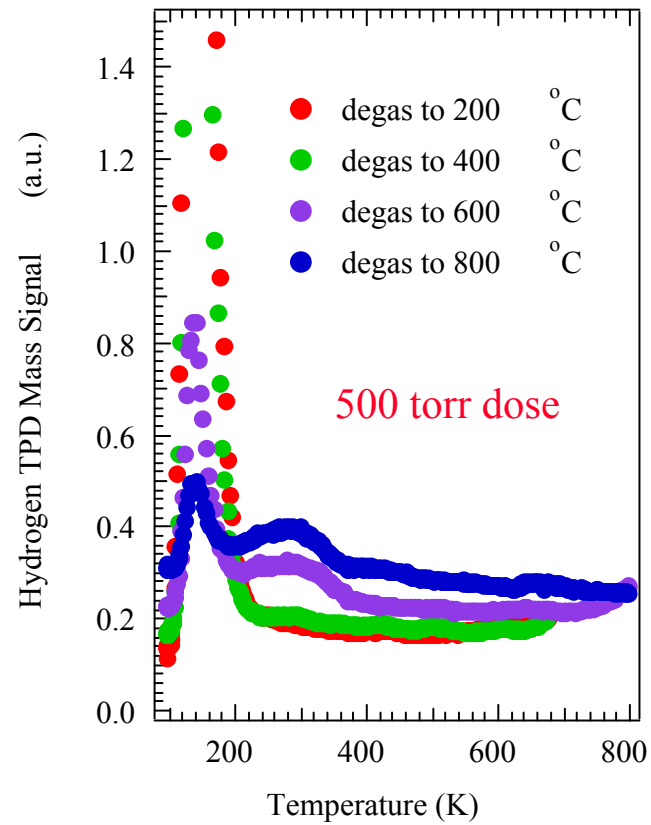
Effect of Bundle Delamination

Incorporation of acetone lowers the degas temperature needed to activated ambient hydrogen adsorption

Degas to 550 ˚C, Sonication is 1 min.



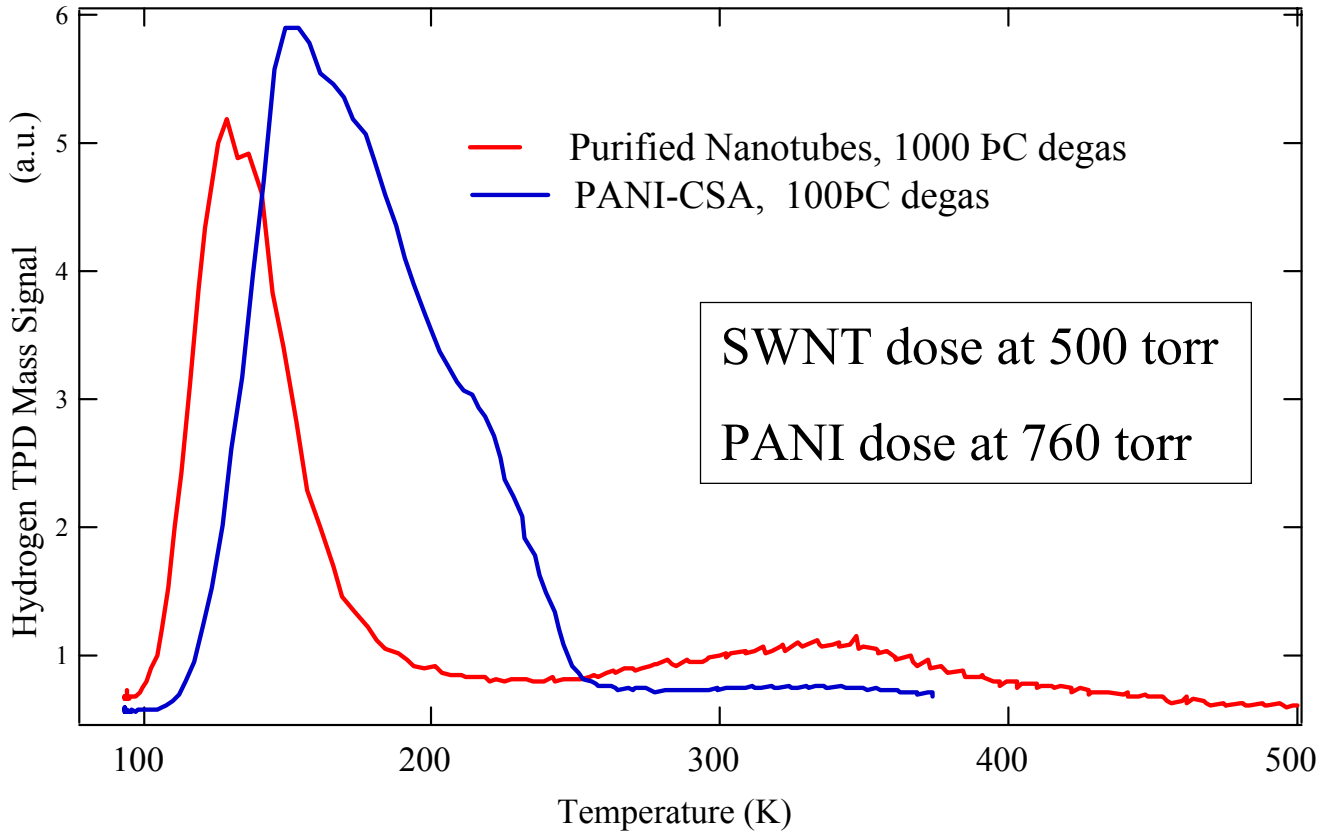
Soaked in Acetone 10 min.



Comparison of SWNTs to Conducting Polymers

Conducting polaniline samples from MacDiarmid Group (U. Penn/ UT Dallas)

Investigating the report By Cho et al. of 8 wt% storage in PANI



PANI-CSA (Camphorsulfonic Acid) one phase w/Triton X100 and stirring doped 031703

Other Interactions / Output

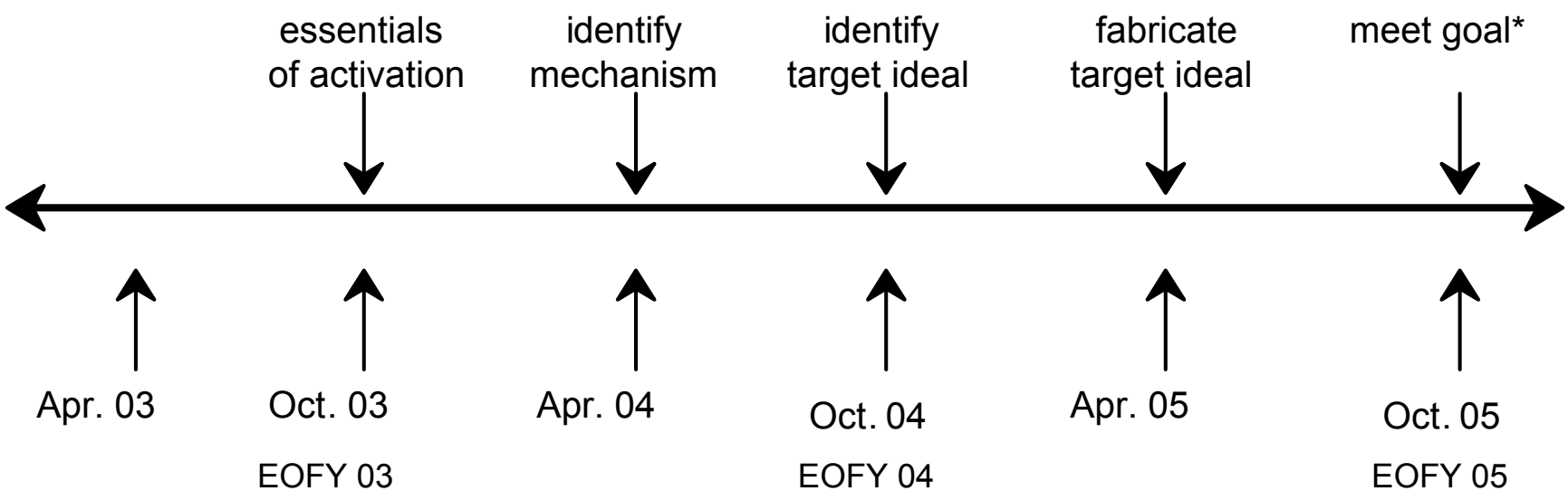
- Office of Science, Division of Materials Science: CO_2 sequestration
  - Gas transport, separation, purification in SWNT-based membranes

    CVD synthesis, dispersion in polymers, competitive adsorption & transport, impurity effects
- Office of Science, Division of Chemical Science: Nanotechnology initiative
  - Managing charge and energy transfer between semiconductor quantum dots with SWNTs.

    Cutting SWNTs, chirality and diameter selection, derivitization
- Five peer reviewed publications this year
- Several invited talks
- 1 graduate student from Colorado School of Mines (Gilbert)
- Five undergraduates researchers at NREL this summer
- Mechanical milling of nanotubes with hydrides shows that desorption temperatures can be modified

Time-line for Project

- Neutron spectroscopy: indentify site locations, first in neat materials, and then in activated
- NMR and ESR: site location, nature of bonding, role of defects, neat and activated
- Investigate "gray area" between physi- and chemisorption theoretically: optimal configurations
- Materials synthesis, purification. Chirality and diamater selection, activated materials if necessary, scale-up best to mutli-gram level
- TPD and volumetric capacities, P & T requirements, establish reproducibility, multi-lab verification
- Deconvolute activation / Is Activation necessary?
- Meas. Protocols (CMWG)



*1.5 kWhr/kg (4.5 wt%) and 1.2 kWhr/L (0.036 kg H_2/L)

U. S. DOE Hydrogen Program Annual Review May, 2003

Doped Carbon Nanotubes for Hydrogen Storage

Ragaiy Zidan

Savannah River Technology Center
Savannah River Site
Aiken, South Carolina

Objectives

Develop reversible high-capacity hydrogen storage material:

- Hydrogen capacity greater than 6 wt.%
- Favorable thermodynamic and kinetics suitable for transportaion applications
- Stable with hydriding/dehydriding cycling

(DOE goals for a H2 storage system)

SRS savannah river site ™

Savannah River Technology Center SRTC We Put Science to Work

Approach

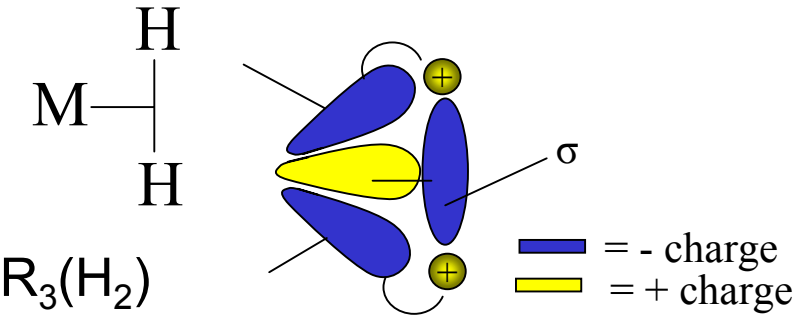
Produce large quantities of consistent structure carbon nanotube systems

- Not restricted to physisorption or chemisorption (weak covalent bond-dihydrogen is sought)
- Doped with transition metals and alloys
- Doped with other elements and metal clusters
- Material tuned for hydrogen sorption to occur at desired temperature and pressure

APPROACH Based on C-H bond

Physisorption= 2Kcal/mol, Chemisorption=17.5Kcal/mol

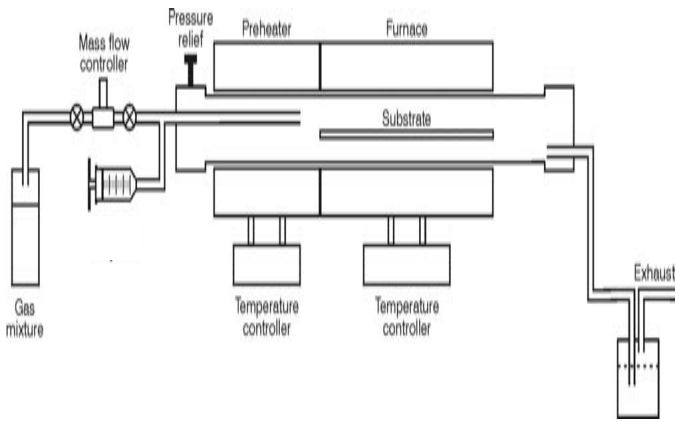
Weak covalent bond
Dihydrogen bond

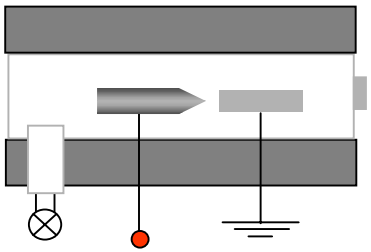


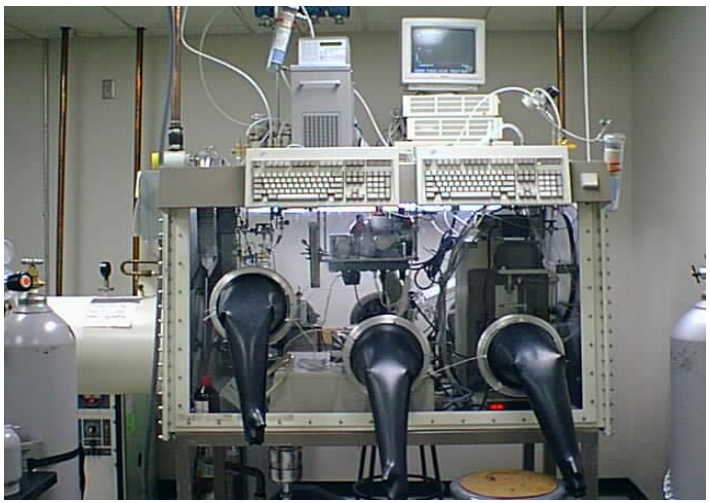
Example
$W(CO)_5RR_3(H_2)$

METHODOLOGY:

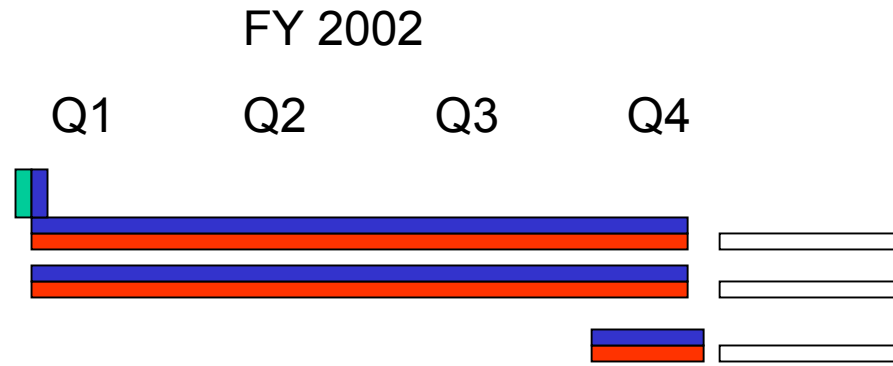
Developing a new method for producing consistent structures of doped carbon nanotubes







Status and Progress

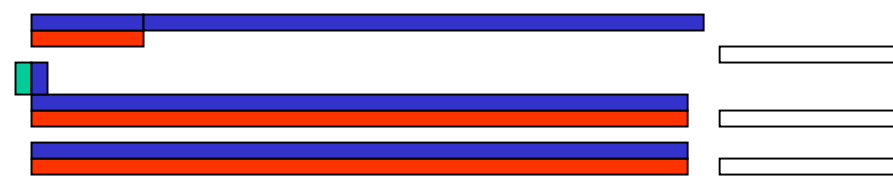


1- Synthesis of material

1a- Different dopants

1b- Different quantities of dopants

1c- Different diameters and configurations

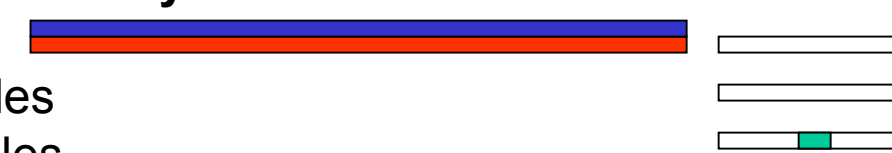


2-Thermodynamic characterization

2a. Set up a high pressure TVA system

2b. Hydriding and dehydriding

2c. Examine nanotubes with cycling



3-Material Characterization and Elemental Analysis

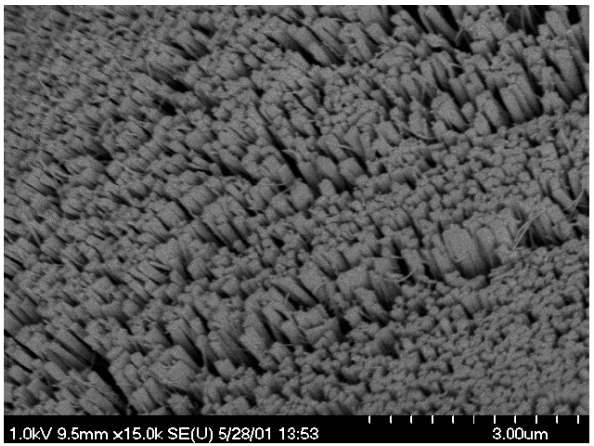
3a. Spectroscopic analysis of product

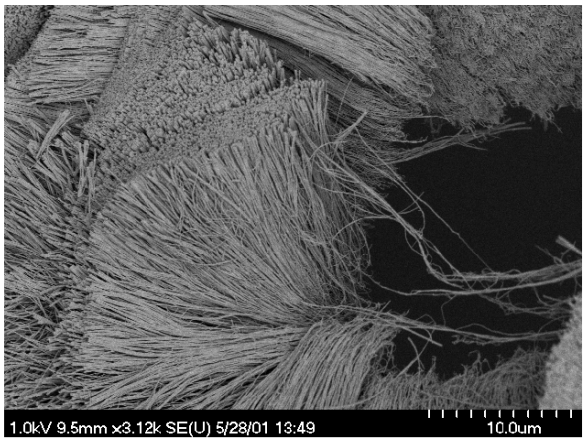
3b- Spectroscopic analysis of cycled samples

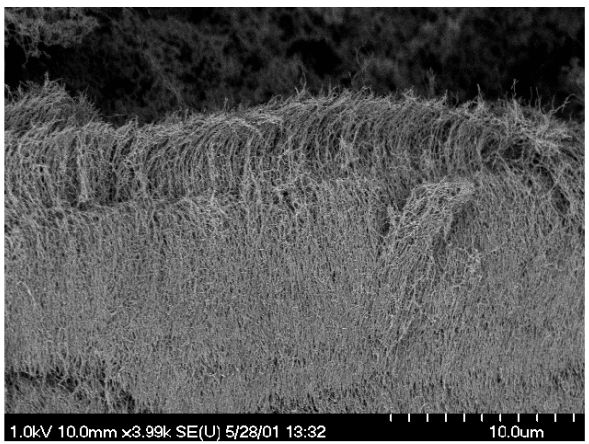
3c- Spectroscopy of H2 reaction with samples

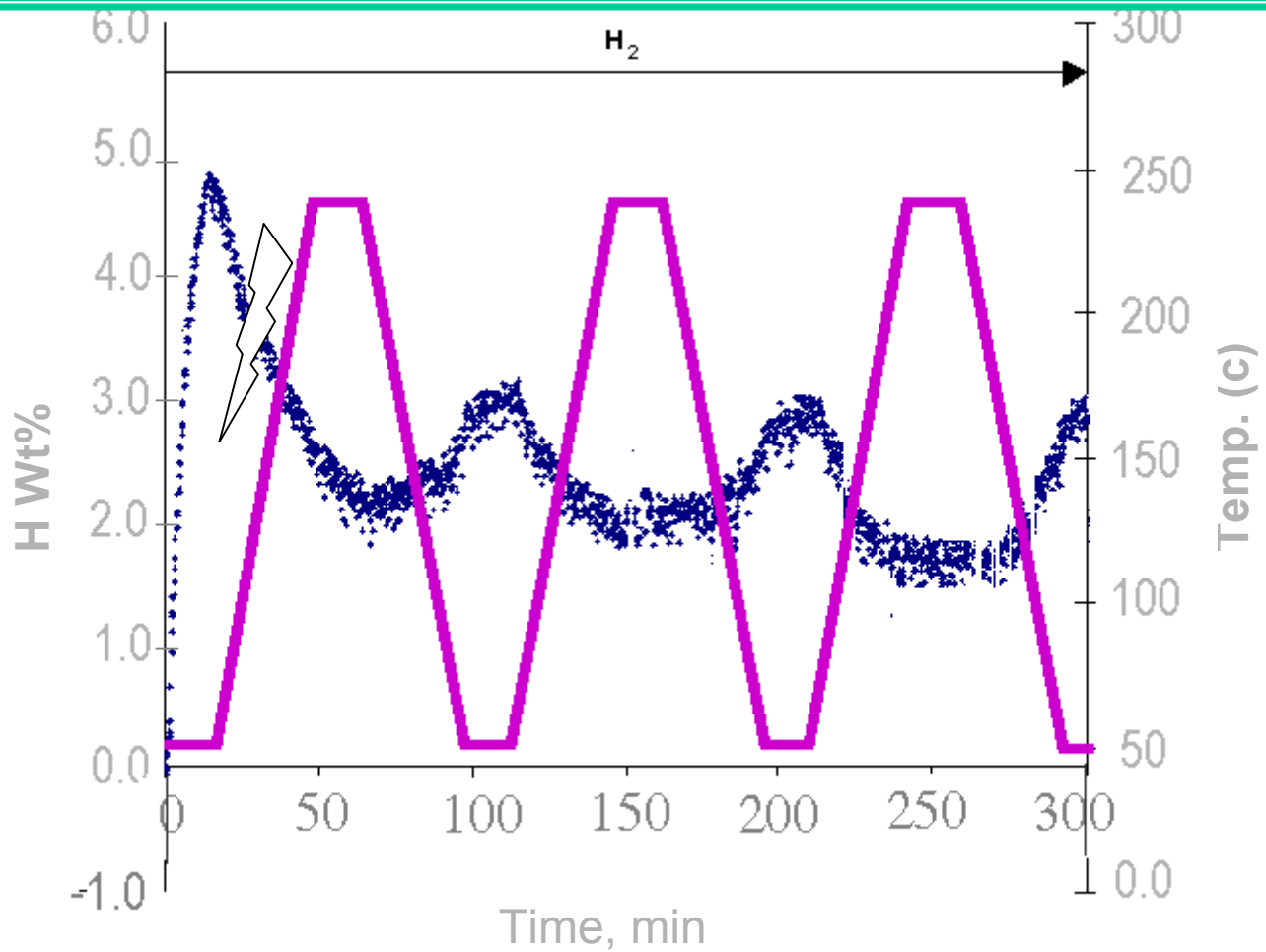
Planed Achieved Key Milestone

Consistent structure doped carbon nanotubes









Hydrogen uptake and release by doped nanotubes

Proposed Future Work

- Continue production of nanotubes with different dopants
- Determine thermodynamic characteristics of hydrogen uptake and release
- Identify the type and size of nanotubes and clusters that result in a reversible, high hydrogen capacity material (barrier)
- Tune conditions that result in a high yield of material possessing favorable characteristics
- Utilize theoretical modeling to guide the experiment
- Set up a YAG laser system for producing C-nanotubes

Leadership and Collaborations

Collaboration between the Savannah River Technology Center (SRTC) and :

- Clemson University, Dr. Apparao M. Rao,
- University of South Carolina, Dr. James Ritter

- Patent disclosure has been submitted on producing and controlling the characteristics of doped carbon nanotubes
- Effort is part of IEA
- Paper in *J. of Nanoscience and nanotechnology,*

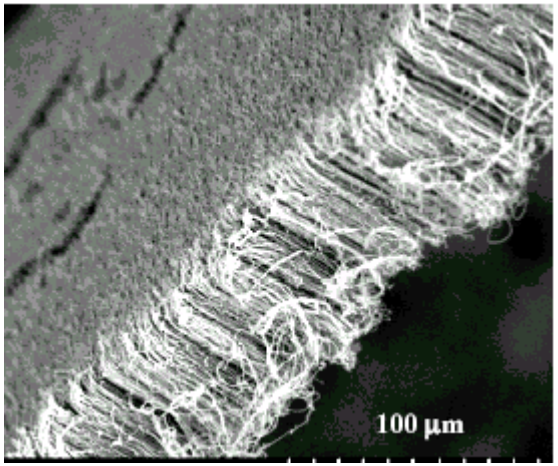
  Department of Physics and Astronomy,Clemson University, NASA Ames Research Center, Department of Materials Science and Engineering, Georgia Tech., Savannah River Technology Center

Continued work

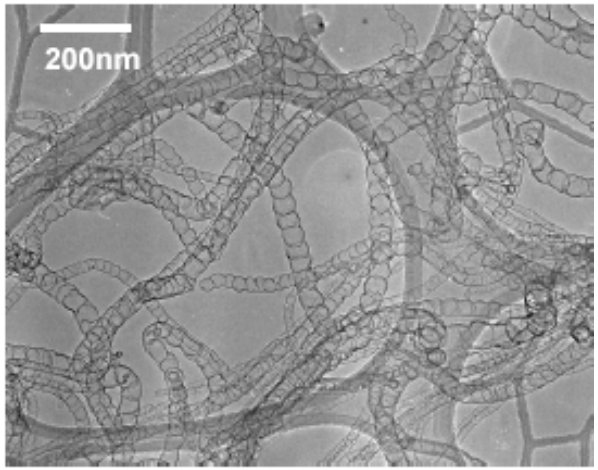
One of our goals has been to synthesize nanotubes containing other elements such as boron or nitrogen largely due to the possibility of fabricating nanotube materials with tailored electrical and mechanical properties. *

Nitrogen Doped Carbon Nanotubes, with average nitrogen content of about 5 at. %, were synthesized

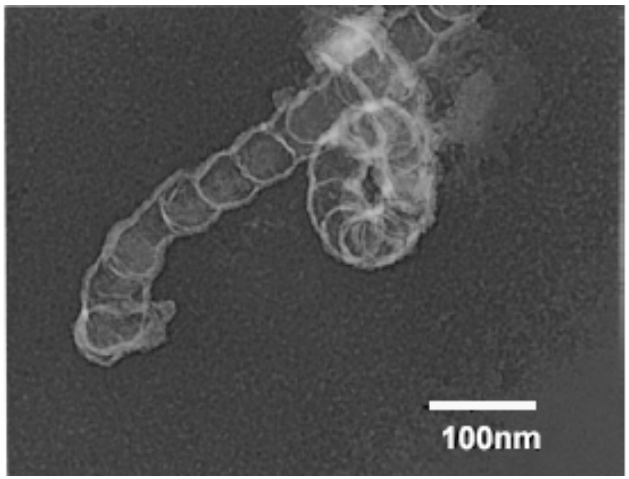
*B.Sadanadan a, T. Savage a, S. Bhattacharya a, T. Tritt a, Alan Cassell b, M. Meyyappan b, Z.R. Dai c, Z. L. Wang c, R. Zidan d and A. M. Rao a, J. nanoscience and nanotechnology accepted
"Synthesis and Thermoelectric Power of Nitrogen Doped Carbon Nanotubes"



a



b



c

(a)- SEM images of a film containing nitrogen-doped tubes

(b)& (c)- TEM images of the nanotubes prepared under identical conditions in the presence of melamine (($C_3H_6N_6$)

Nitrogen-doped nanotubes

- Individual nitrogen-doped nanotube exhibited a bamboo-like structure and comprised of 6-16 tube walls

- Electron Energy Loss Spectroscopy (EELS) measurements yielded an average nitrogen content of ~5 at % in the doped tubes.

- Thermoelectric power data of nitrogen-doped tubes remained negative even after exposure to oxygen for an extended period of time suggesting that nitrogen doping of carbon nanotubes renders them *n*-type (stable electronic structure)

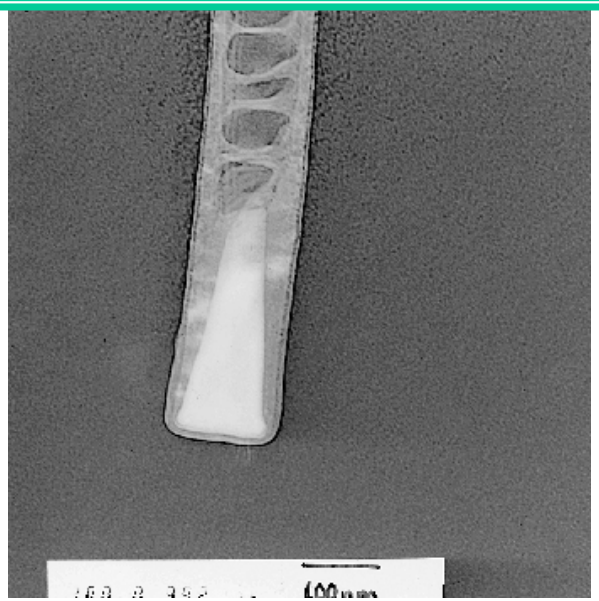
Model and Growth factors

These tubes best fit Blank *et al.* model of a spheroidal catalyst particle in which the number of inner graphene layers depends on the velocity of the particle.
These inner walls terminate when the particle slides away from the graphite sheath upon sufficient accretion of stress while the outer layer is continuous.

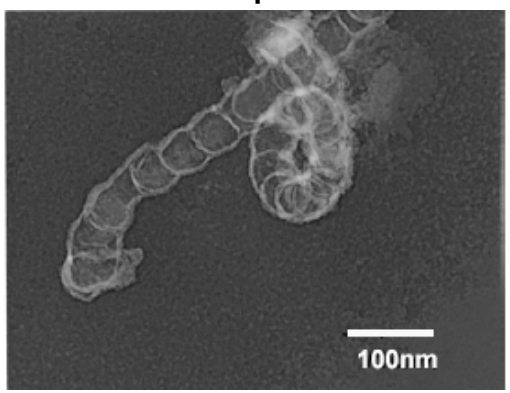
- The size and structure of an individual bamboo-like tube is largely dependent on the velocity, size, shape, and composition of the catalyst particle.

- The growth temperature influences the nanotube morphology

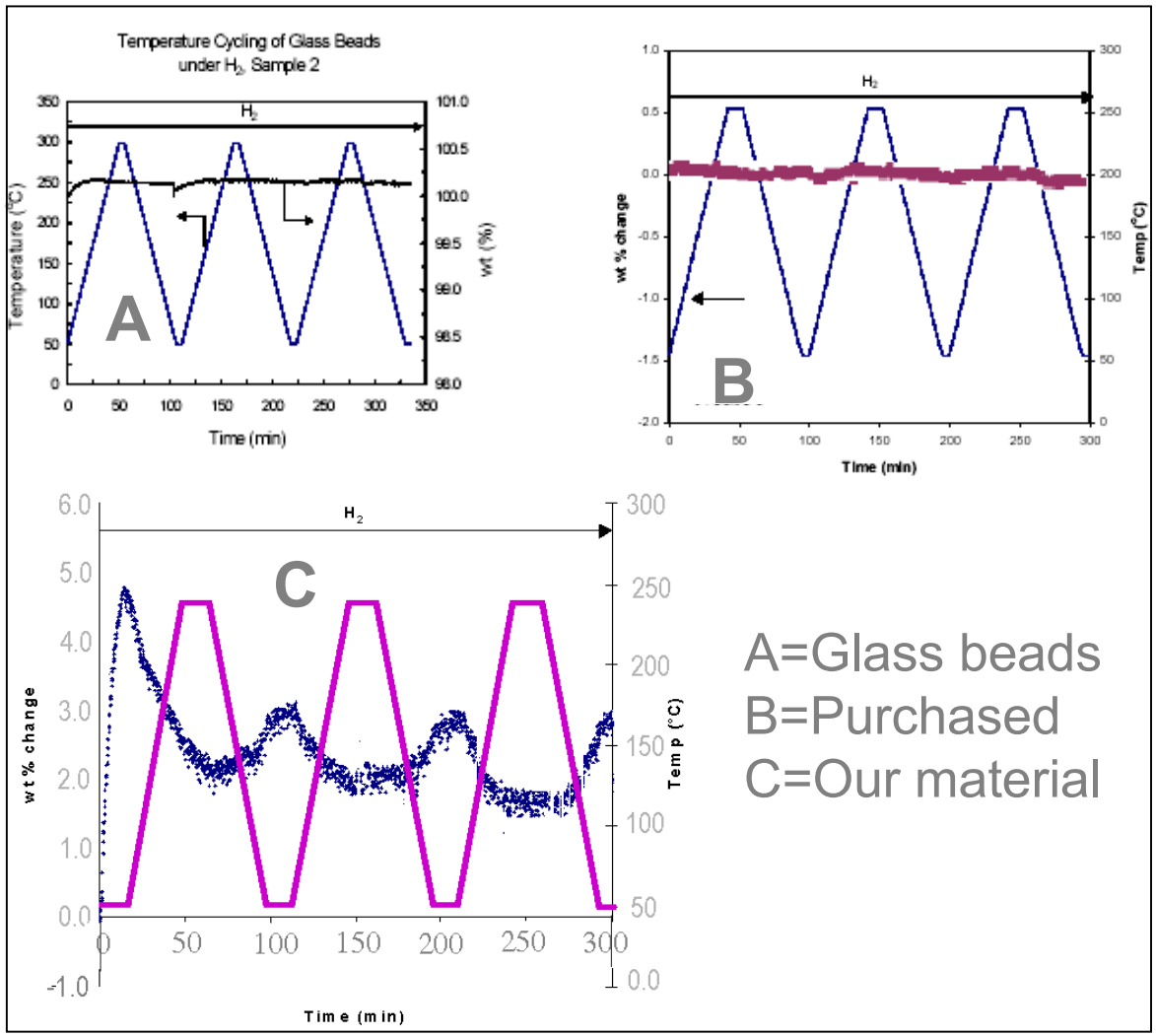
Summary



Tip of a nanotube with impeded metal particle



Nitrogen-doped tube



Conclusion

- High Risk High Reward
- Preliminary results *demonstrated* hydrogen uptake and release
- Developed a novel method of encapsulating metal, doping and controlling morphology and structure of C-nanotubes
- Further investigation of hydrogen sorption in doped C-nanotubes is needed

Reviewers 2002

- Produced large quantities of consistent structure carbon nanotubes is a good approach.
- Adopted DOE's goals for a hydrogen storage system
- Realized that neither physisorption nor chemisorption models will achieve this goal and were looking at weak covalent bond-dihydrogen as the mechanism for enhanced storage.
- Preliminary data showed only 1% wt. However their system has not been optimized and so further improvements are possible with doping.
- At the very minimum they have a model to guide their investigation. "**The Panel saw good progress and recommends continued funding**"

U. S. DOE Hydrogen Program Annual Review May, 2003

Doped Carbon Nanotubes for Hydrogen Storage

Ragaiy Zidan

Savannah River Technology Center
Savannah River Site
Aiken, South Carolina

Hydrogen Storage in Metal-Modified Single-Walled Carbon Nanotubes (start 9/15/01)

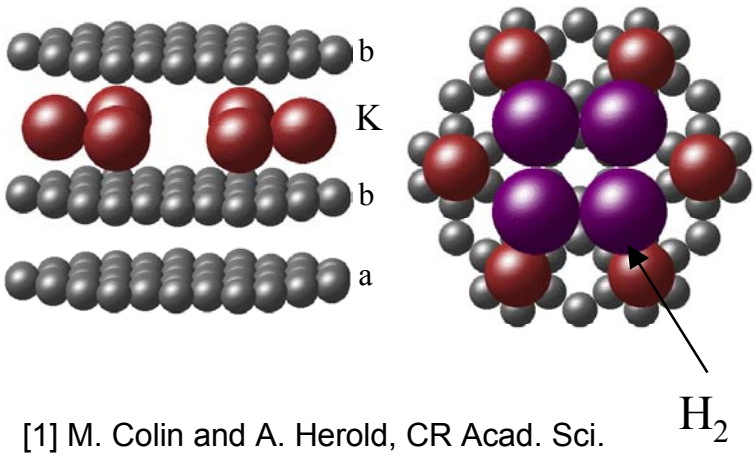
Channing Ahn, PI and Technical Contact
Division of Engineering and Applied Science, California Institute of Technology,
138-78, 1200 E. California Blvd, Pasadena, CA 91125
cca@caltech.edu

Relevance and Objectives:

- Hydrogen physisorption for reversible solid-state material storage systems.
- Investigate effect of potassium (alkal-metal) additions to single-walled nanotubes on H_2 adsorption.
  Potassium intercalated graphite long known to absorb H_2 (both physisorption, as in KC_{24} and chemisorption, as in KC_8).
- Increase effective surface area of single-walled nanotubes through intercalation.
- Understand charge redistribution mechanisms, improve temperature/pressure behavior.

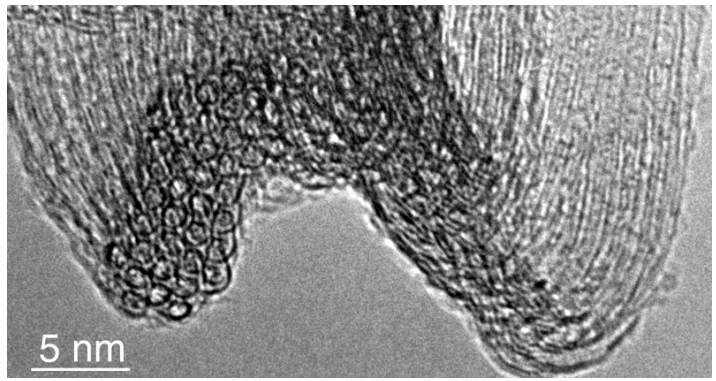
Rationale for approach

Stage 2, K-intercalated graphite (KC_{24}) accommodates H_2 through both chemisorption[1], 0.1 wt% at RT and physisorption[2] at 1.2 wt% absorption at 77K, <1 atm.

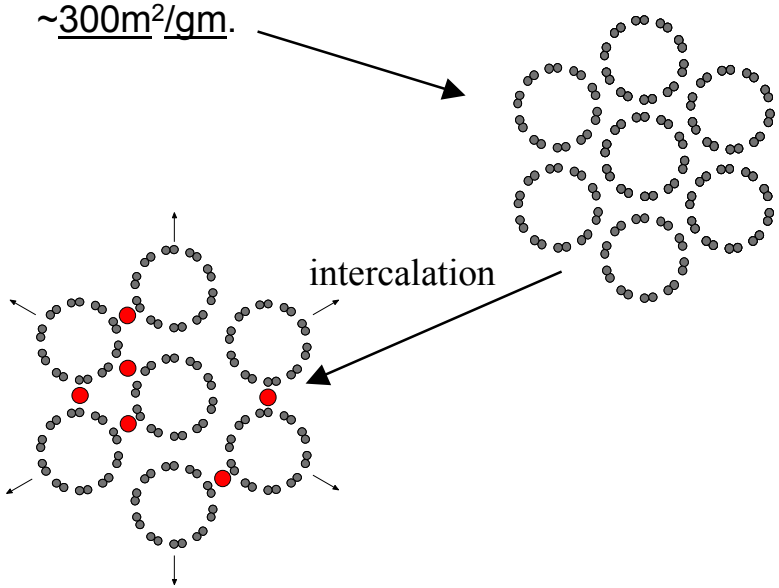


[1] M. Colin and A. Herold, CR Acad. Sci. Paris, Serie C, 269, 1302 (1969).
[2] K. Watanabe, M. Soma, T. Onishi and K Tamaru, Nature 233, 160 (1971).

Normal activated carbon dependent on surface area (# of available adsorption sites) to accommodate H_2. (Chahine criterion, 1 wt%/500m^2) at 77K.



(10,10) SWNT theoretical outer surface area 1638m^2/gm, inner surface area of 978m^2/gm (based on van der Waals diameters). But SWNTs form ropes, limiting surface area to ~<u>300m^2/gm</u>.

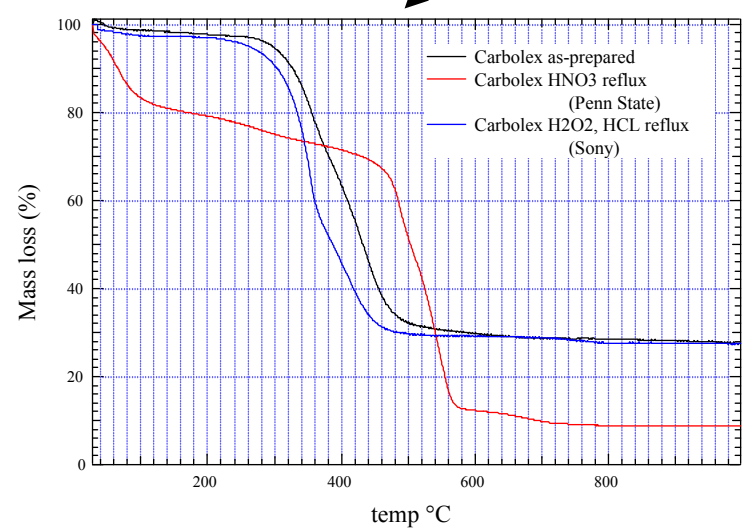


Project timeline

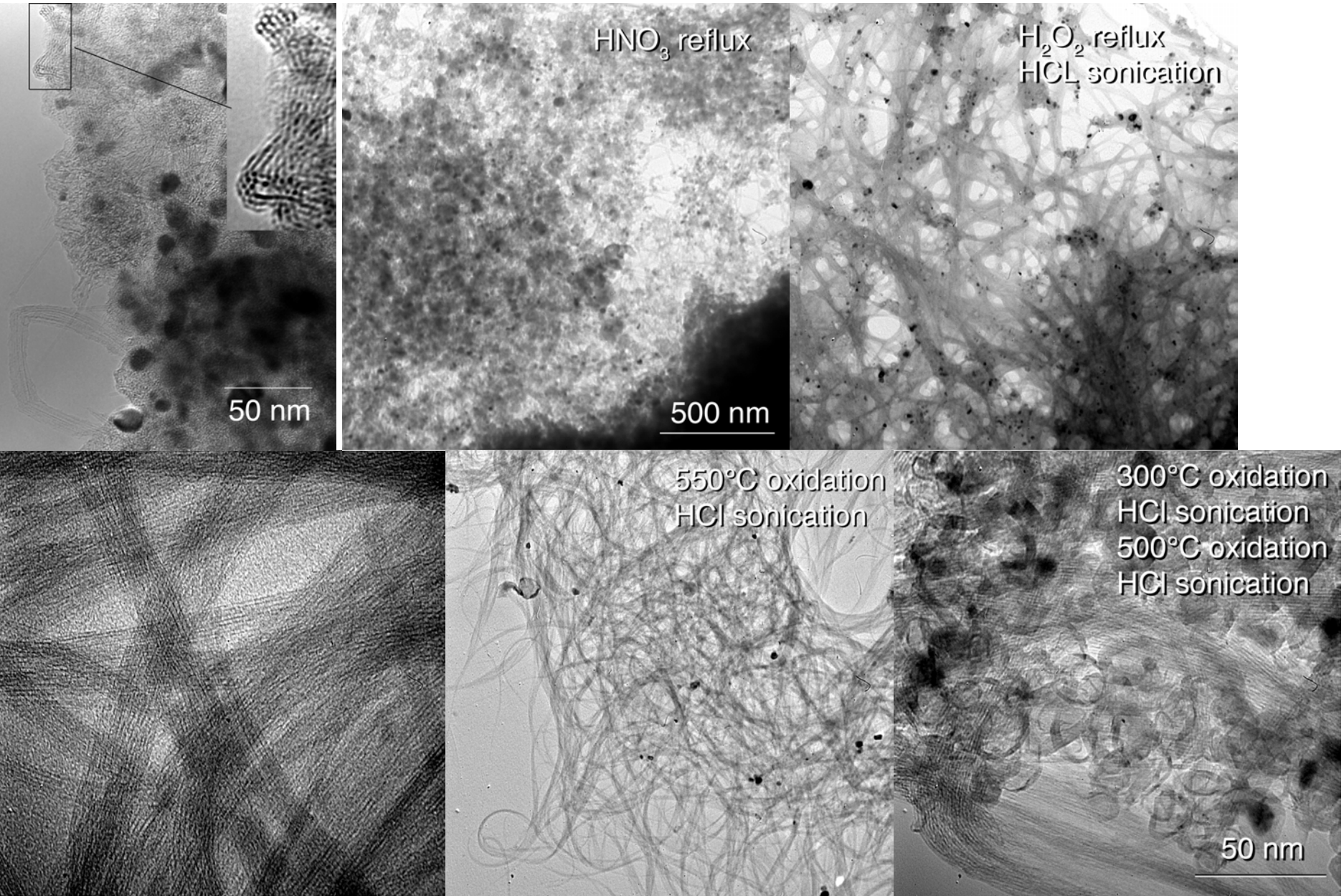
		FY2002				2003
Task Designation/Milestone		Qtr1	Qtr2	Qtr3	Qtr4	Qtr1
Single Walled Nanotube Procurement		♦				
Characterization of as-received material		♦				
Intercalation of carbons		♦	◊			
Characterization of intercalated single walled nanotubes				★		
Gravimetric and volumetric dens evaluation					☆	

Only commercial vendor of laser-oven material is Carbolex -sells as-prepared nanotubes only

Commercial Madagascar graphite provided by Superior Graphite

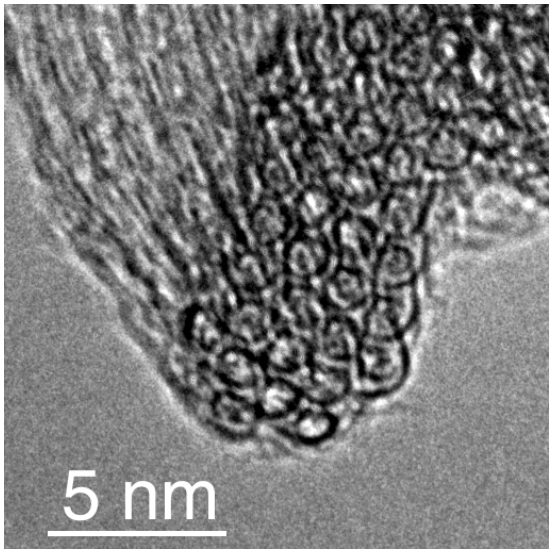


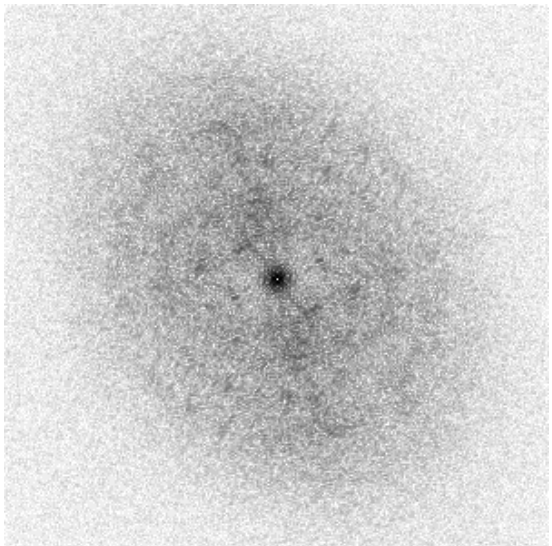
Accomplishments: Purification, microstructural evolution (Carbolex)



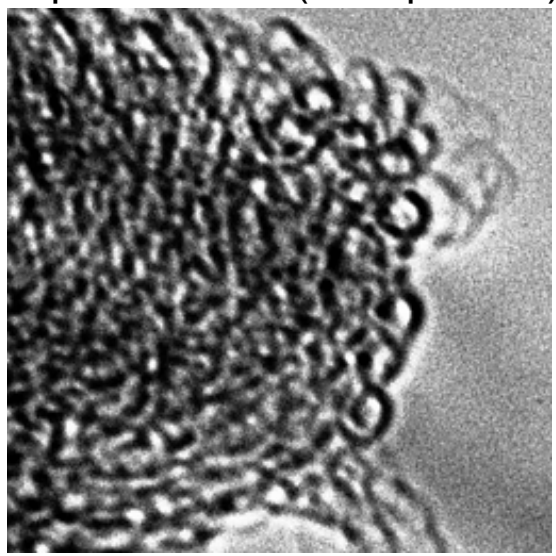
Accomplishments/Progress: Nanotube analysis Transmission Electron Microscopy

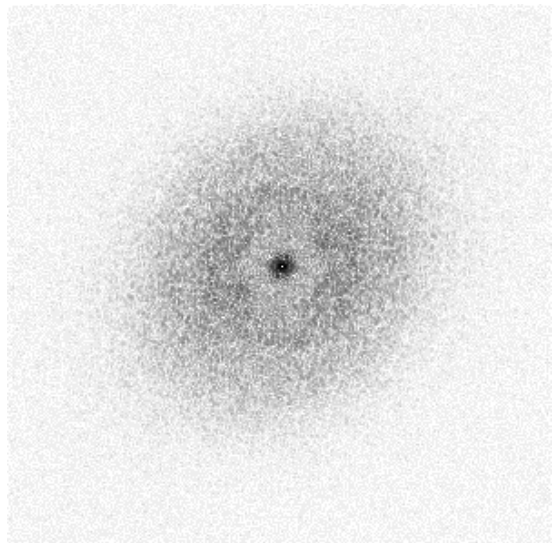
"Bucky" paper, laser-oven, Rinzler prepared



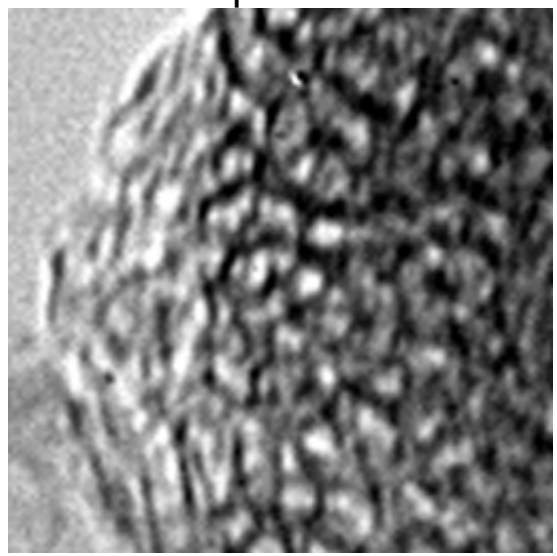


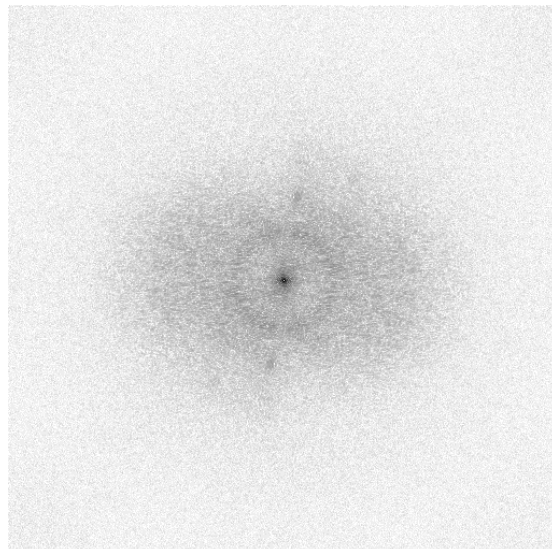
Carbon Nanotechnologies Hipco material (HRL purified)





Carbolex laser-oven Caltech purified



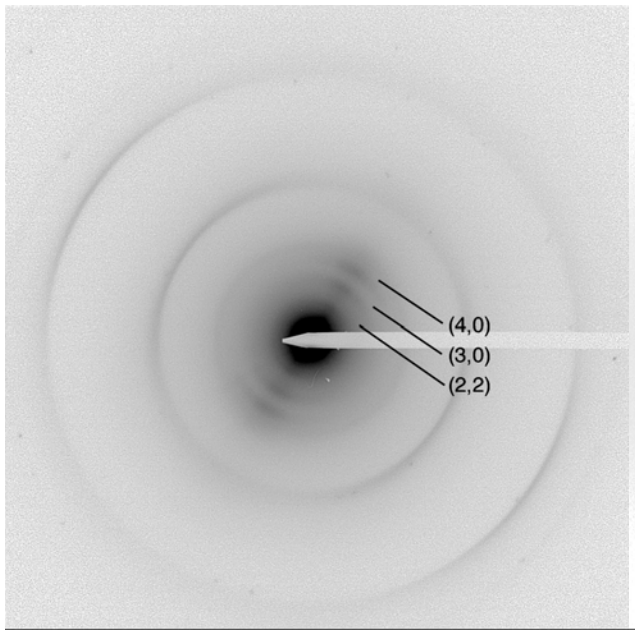


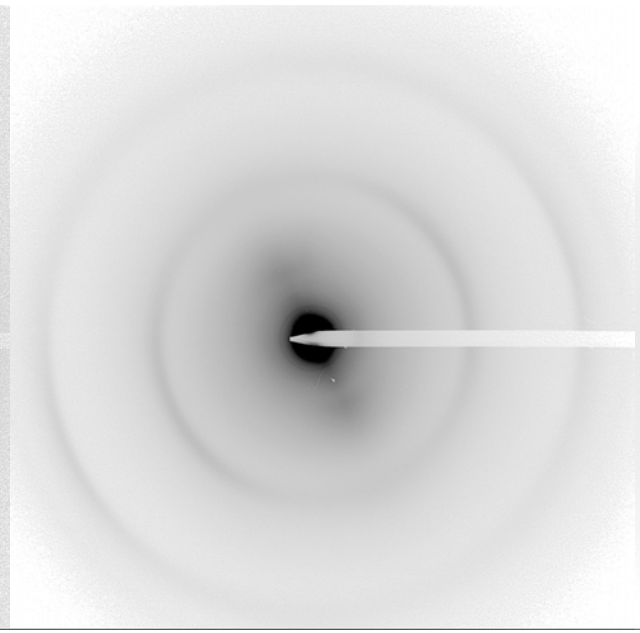
Accomplishments/Progress: Nanotube analysis Transmission Electron Microscopy (diffraction)

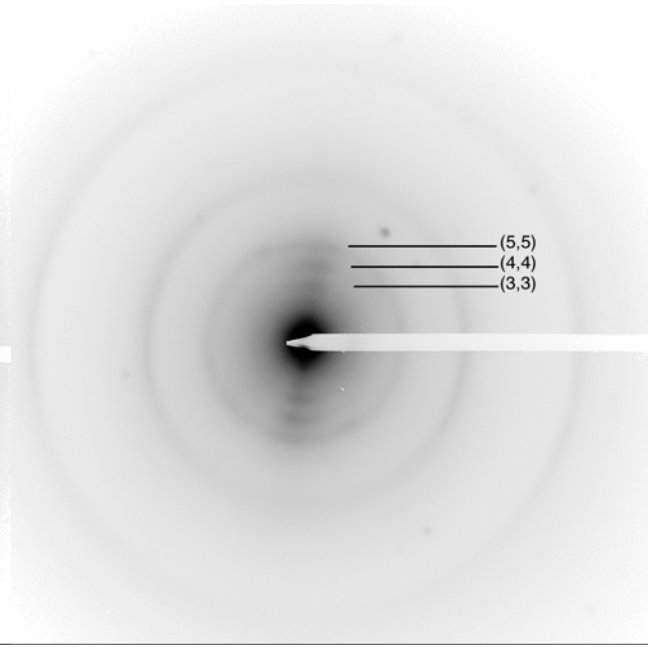
"Bucky" paper, laser-oven, Rinzler prepared

Carbon Nanotechnologies Hipco material (HRL purified)

Carbolex laser-oven Caltech purified





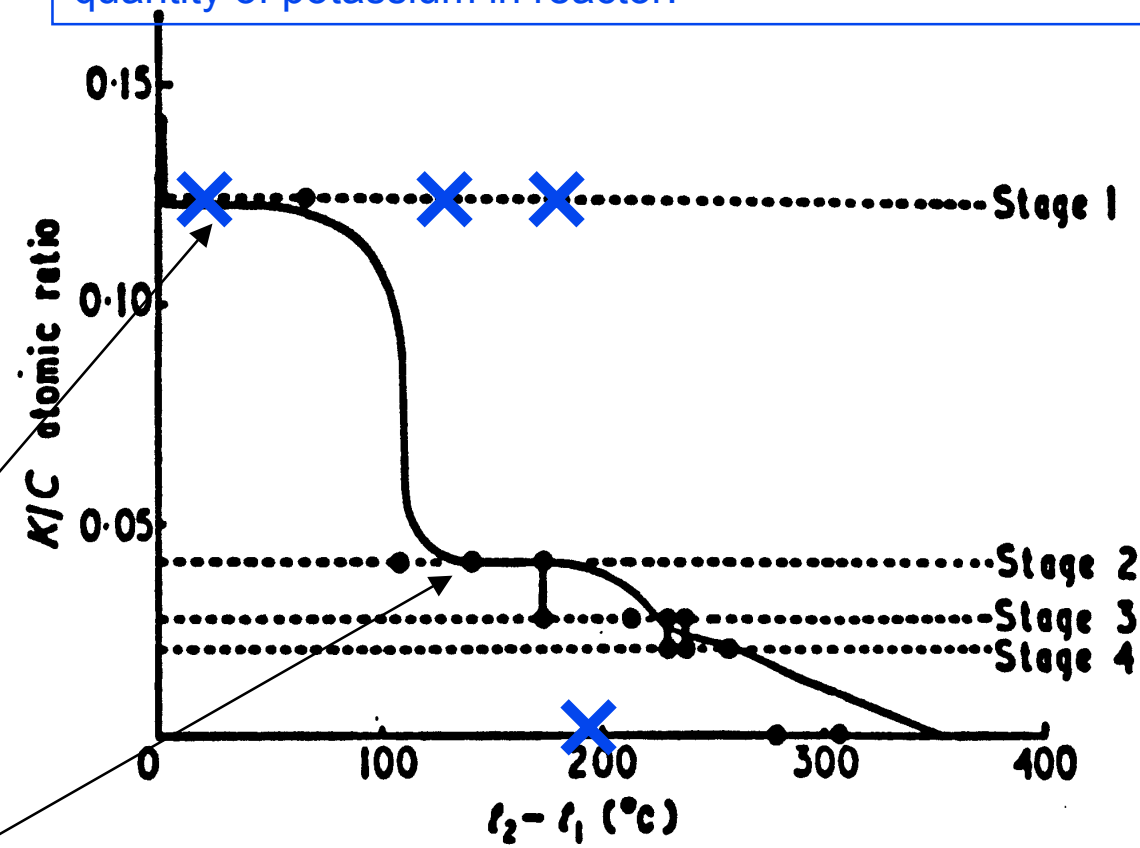


Accomplishments: Potassium intercalation synthesis routes for graphite and single walled nanotubes

Potassium interaction using any $0<\Delta t<170°C$ yields stoichiometry ~KC_8

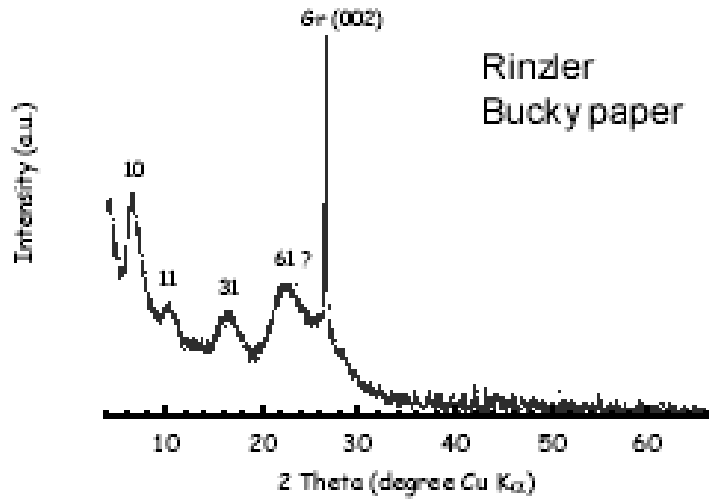
Solution for limiting nanotube stoichiometry is limiting quantity of potassium in reactor.

KC_8 KC_{24}

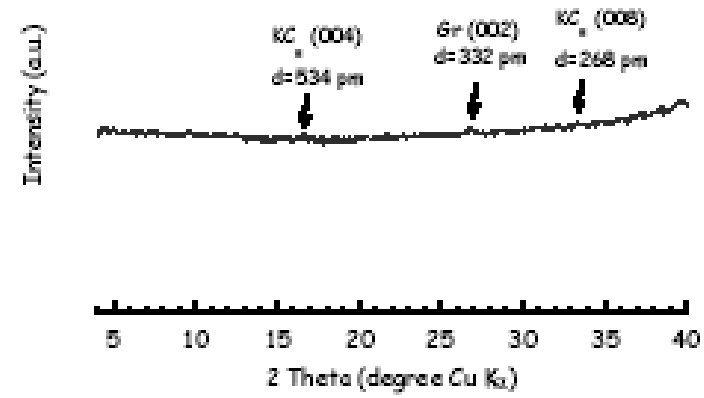


D. E. Nixon and G. S. Parry, J. Phys. D, 1, 291 (1968).

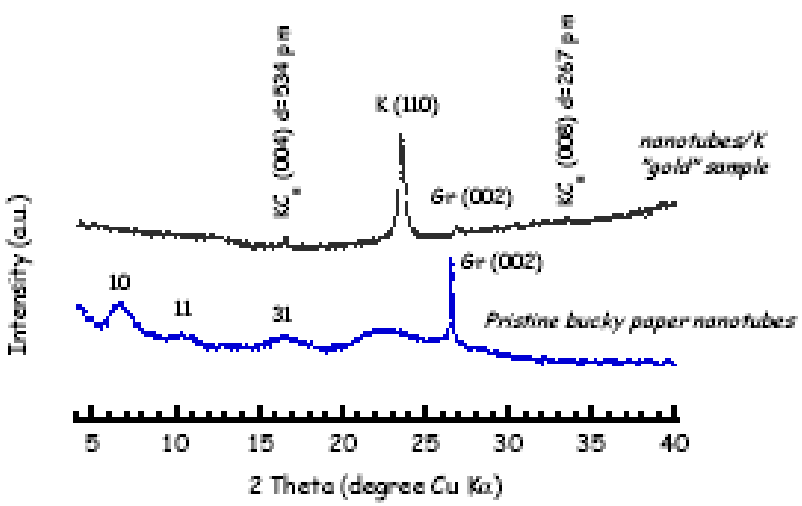
Accomplishments/Progress: Nanotube analysis, X-ray diffractometry



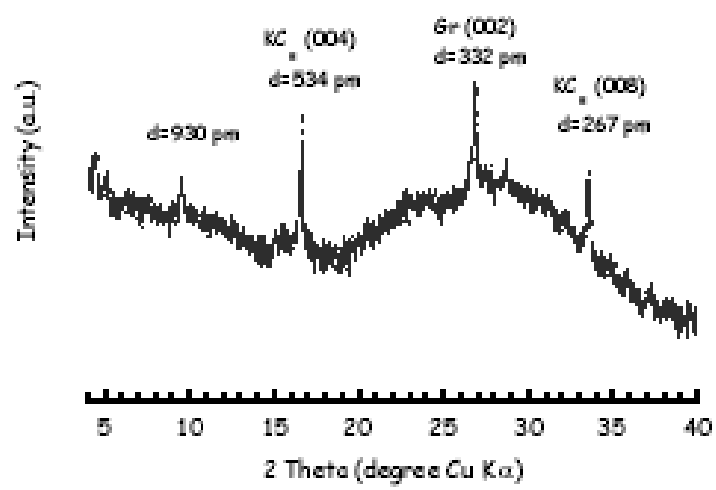
200 C, 190 C reactor temps.



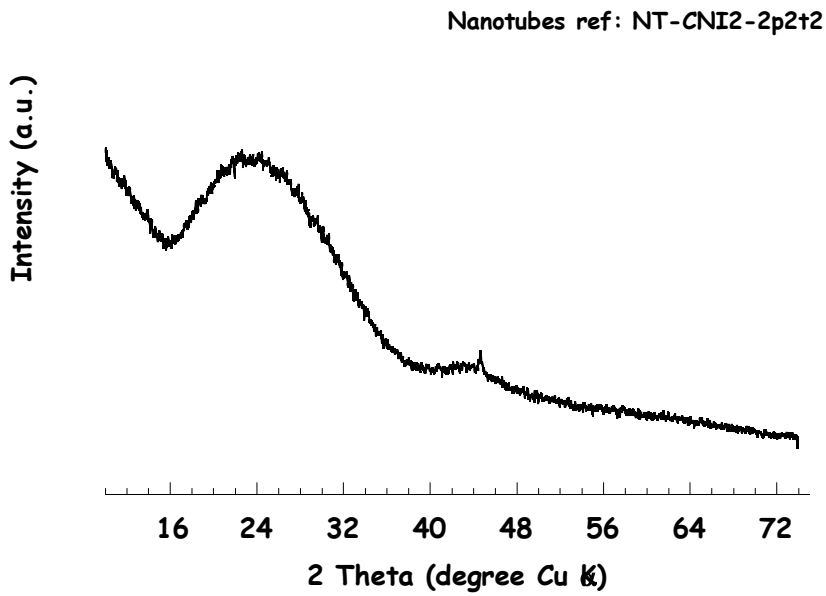
Condensed K reaction product 250 C

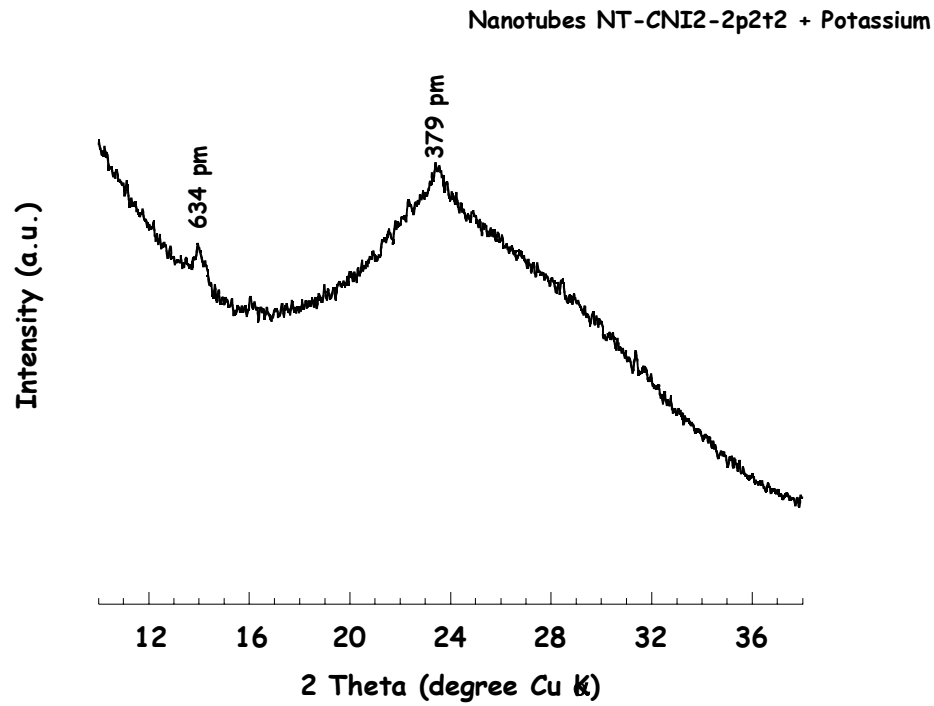


"KC19" 241 C, 248 C reverse temp.



Accomplishments/Progress: Nanotube analysis, X-ray diffractometry (cont'd)





Single point adsorption isotherm results

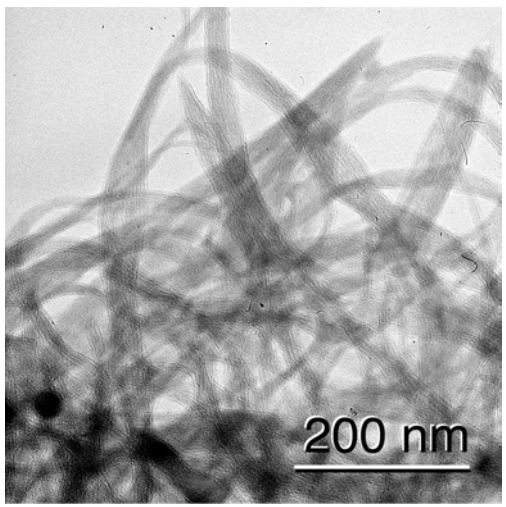
From KC_9 intercalated "Hipco" nanotube

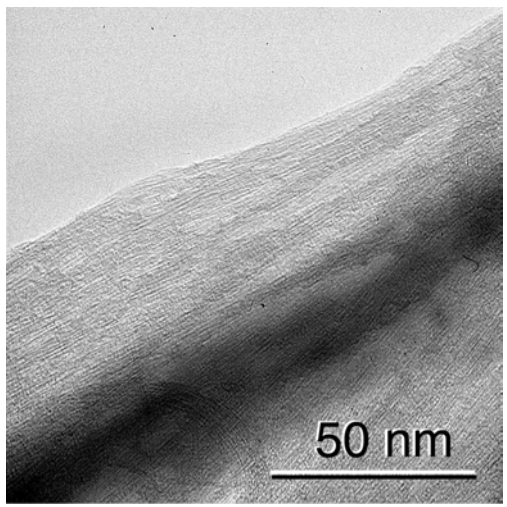
Initial introduction of H_2 at room temperature highly exothermic (dissociation reaction resulting in KH formation).
Assuming density = 2.0 g/cm^3, Capacity(25°C, 70 bar) = 0.69 wt%
Capacity (77 K, 50 bar) = 1.05 wt%
Assuming density = 2.5 g/cm3, Capacity(25°C, 70 bar) = 0.63 wt%
Capacity(77 K, 50 bar) = 0.90 wt%

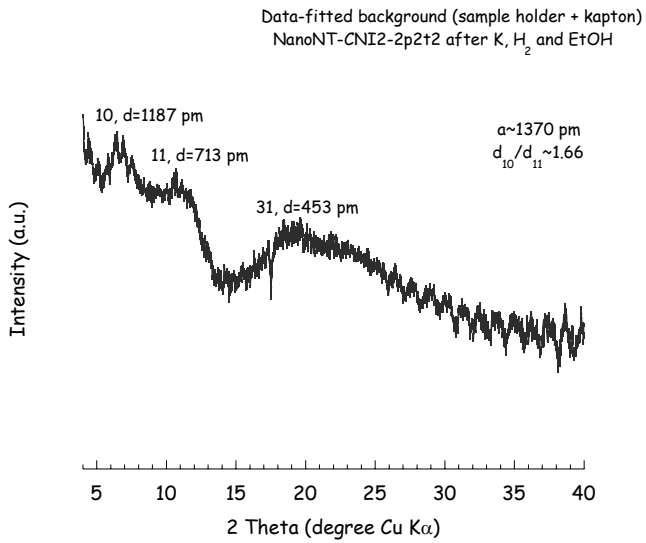
From restored KC_9 "Hipco" nanotube after K removal

0.35% at 25°C
2.36% at 77 K (90% of the as-purified results).

No unzipping from K interaction with nanotubes, (as is seen with Li)







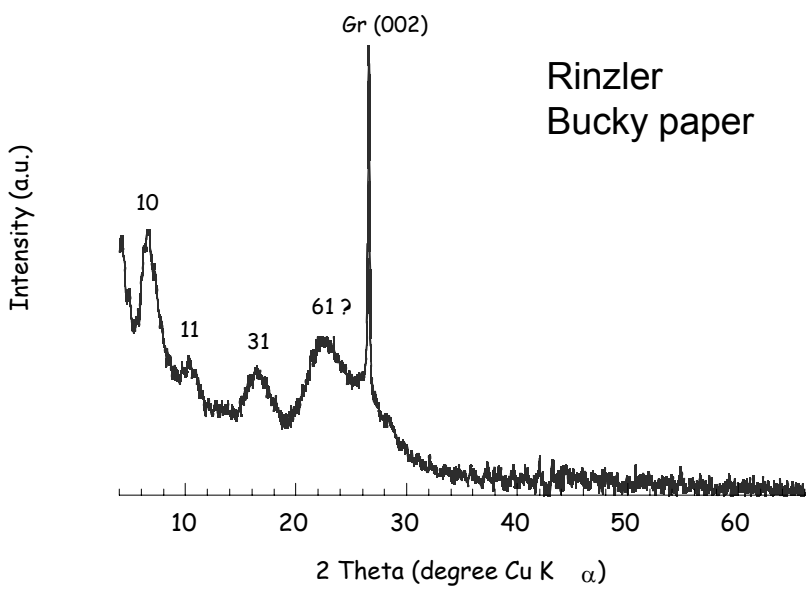
Single point adsorption isotherm results (cont'd)

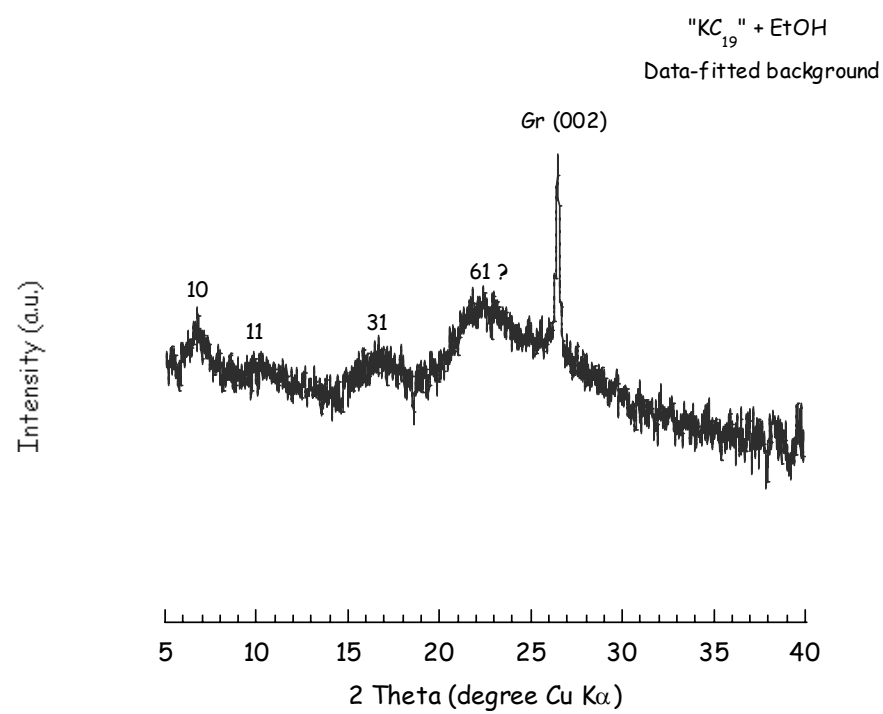
From KC_{19} intercalated "Bucky" nanotube

2.0 g/cm^3, capacity (25°C, 70 bar) = 0.06-0.11 w %
0.54-0.69 wt % at 77 K (depending on the density).

similar to results from Tubes@Rice nanotubes after recovery from the surfactant suspension purification to remove the catalyst.

No unzipping from K interaction with nanotubes.





Collaborations

J. J. Vajo, HRL Laboratories, LLC
Sievert's volumetric hydrogen sorption measurements (single point adsorption isotherms).

T. Proffen and D. W. Brown, Los Alamos National Laboratory
Neutron Diffraction measurements, pair distribution function analysis.

Igor Barsukov, Superior Graphite
Purified and milled Madagascar graphite

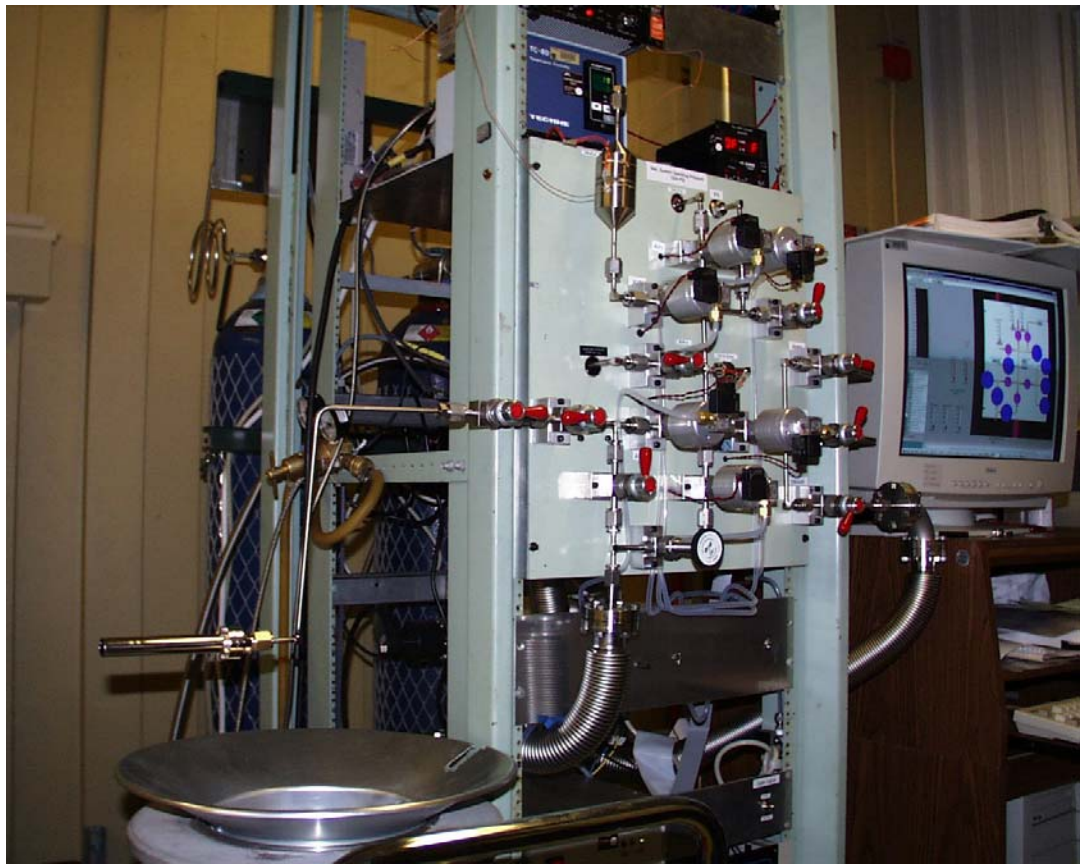
(David Eaglesham, Lawrence Livermore National Laboratory
Nanotube synthesis)

Jet Propulsion Laboratory Sieverts apparatus (R. C. Bowman, Jr.)

- New Sieverts apparatus being completed at JPL for use on Caltech campus.

- Originally intended for He cryo-cooler studies on carbons for flight detector applications (Christian Lindensmith).

Construction completion underway by Dean Johnson and Phil Wilson (JPL).



Plans/Future Milestones:

- Refinement of Intercalation procedures
  more structure analysis
- Electron Spin Resonance experiments to study charge transfer
- Sieverts apparatus set-up, testing and complete isotherm measurements
- Study other carbons (activated carbons, nanofibers).

Acknowledgements: Dept. of Energy DE-FC36-O1G011090

Caltech:
Anne Dailly, Brent Fultz, Rachid Yazami, Joanne Yim

HRL Laboratories:
John Vajo

Jet Propulsion Laboratory
Robert C. Bowman, Jr.

Hydrogen Storage in Ammonia and Aminoborane Complexes

Ali Raissi
Florida Solar Energy Center
University of Central Florida

Hydrogen Program Annual Review
Session: Hydrogen Storage – Carbon & Other
Berkeley, CA – May 21, 2002

Goals and Objectives

Analyze issues of performance, cost & safety of three hydrogen technological areas:

- Thermochemical decomposition of SQNG
- Storage in NH_3 & NH_3-based complexes
- Thermochemical cycles water splitting cycles

All Milestones

(Technical Analysis of Hydrogen Production)

Task Description	FY 2003				2004
	O N D	J F M	A M J	J A S	O N D
I. Hydrogen from Autothermal Reformation of SQNG					
a) FactSage analysis of H_2 prod^n by autothermal H_2S/CH_4 reformation					
b) ASPEN$^+$ analysis of H_2 prod^n by autothermal H_2S/CH_4 reformation					
c) ASPEN$^+$ analysis of integrated process economics					
II. Technoeconomics of NH_3-based H_2 Production					
a) Assess feasibility of autothermal reformation of NH_3					
b) Assess NH_3's potential for small-scale & fixed applications					
c) Identify cost issues, opportunities & challenges					
III. Hydrogen from Solar TCWSCs					
a) ASPEN Plus analysis of candidate solar-TCWSCs					
b) ASPEN$^+$ analysis of integrated process economics					
c) Paper at Proceedings of the 2003 Hydrogen Program Annual Review					
IV. Final Project Report					

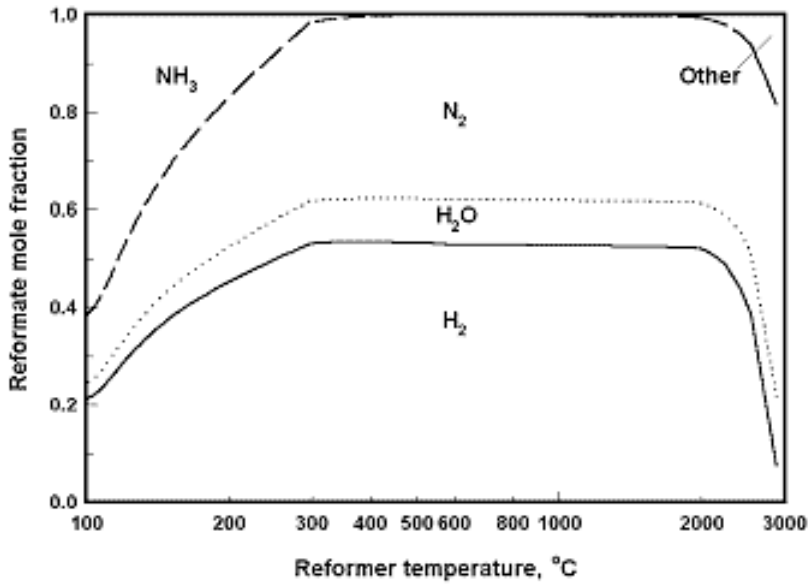
? End of the Project

Advantages of Ammonia

- Costs about $150 per short ton or less than $6.25 per million BTU of H_2 contained
- Contains17.8 wt% hydrogen
- Enjoys established infrastructure for its transportation, distribution, storage and utilization
- Stores 30% more energy by liquid volume than LH_2
- Easily reformed using 16% of the energy in the fuel
- Reformate for AFC use requires no shift converter, selective oxidizer or co-reactants
- No need for final hydrogen purification stage

Disadvantages of Ammonia

- Requires sub-ambient T and/or elevated P storage
- Safety concerns with the wide spread use as transportation fuel
- Requires some means for on-board reformation to liberate hydrogen – autothermal reformation is one approach



Chemical Hydrides (CHs) as Hydrogen & Ammonia Storers

- CHs are secondary storage methods (expendable) and their use requires:
  - Compatibility with PEMFC (no H_2S, CO or NH_3)
  - Load following capability without complex controls
- CHs fall into two classes:
  - Hydrolysis hydrides -

    H_2 is produced by reaction with H_2O, NH_3, H_2S, etc.
  - Pyrolysis hydrides -

    Decomposition by heat generates hydrogen

Hydrolysis Hydrides

Reaction	wt% H_2 Yield	Capacity Wh/kg
$LiH + H_2O \rightarrow LiOH + H_2$	7.7	1,460
$LiAlH_4 + 4\ H_2O \rightarrow LiOH + Al(OH)_3 + 4\ H_2$	7.3	1,380
$LiBH_4 + 4\ H_2O \rightarrow LiOH + H_3BO_3 + 4\ H_2$	8.6	1,630
$NaBH_4 + 4\ H_2O \rightarrow NaOH + H_3BO_3 + 4\ H_2$	7.3	1,380

Pyrolysis Hydrides

- Combination of a hydride with an ammonium halide, stabilized with polymeric binders (*e.g.* PTFE):

  $NH_4F + LiBH_4 = LiF + BN + 4\ H_2$ (~ 13.6 wt % H_2)
- NH_4X + MH formulations render compound storable, and insensitive to air & moisture
- $Mg(BH_4)_2.2NH_3/LiNO_3/PTFE$: 85/7½/7½ wt %

  - gives 12.84 wt% of 99.8% pure H_2
  - impurities include CO, NH_3 & CH_4
- $NH_3BH_3/N_2H_4.2BH_3/(NH_4)_2B_{10}H_{10}/\ NH_4NO_3$: 50/30/9.8/10.2 wt %

  - gives 16.52 wt% of >94% pure H_2
  - impurities include borazine $B_3N_3H_6$
- These reactions are highly exothermic & unstoppable

Amine-Borane Complexes

- $NH_4BH_4 = BN + 4\ H_2$ (24.5 wt % H_2)

  Unstable above -20 ^oC, unsuitable

- Ammonia borane (AB) complex:

  $NH_3BH_3 = BN + 3\ H_2$ (20 wt % H_2)

  Requires heating, decomposition at stages from ~130-450 ^oC

Pyrolysis of AB Complex

- H_3BNH_3 (l) $\rightarrow H_2BNH_2$ (s) + H_2 (g) ~137°C

  ΔH_r ~ 22 kJ/mol
- x (H_2BNH_2) (s) $\rightarrow$ $(H_2BNH_2)_x$ (s) ~125°C
- $(H_2BNH_2)_x$ (s) $\rightarrow$ $(HBNH)_x$ (s) + x H_2 (g) ~155°C
- $(HBNH)_x$ (s) $\rightarrow$ borazine + other products
- $(HBNH)_3$ $\rightarrow$ 3 BN + 3 H_2 >> 500°C
- $(H_2BNH_2)_x$ (s) $\rightarrow$ $(BN)_x$ (s) + 2x H_2 (g) ~450°C

Ref:
G. Wolf, et al., Thermochimica Acta 343(1-2): 19-25, 2000.
V. Sit, et al., Thermochimica Acta, 113, 379-82, 1987.
M.G. Hu, et al., Thermo-chimica Acta, 23(2), 249-55, 1978.
R.A. Geanangel & W.W. Wendlandt, Thermochimica Acta, 86, 375-78, 1985.

AB Complex

Property	Description
Formula	NH_3BH_3
Molecular weight	30.86
Odor	Ammonia-like
Density, g/mL	0.74
Melting point	112-114°C, slow decomp^n at approx. 70°C
Heat of formation	$\Delta H_f°$= -42.54 ± 1.4 kcal/mol
Heat of combustion	$\Delta H_c°$= -322.4 ± 0.7 kcal/mol

Drawback to AB Use

- Cost of NH_3BH_3 Production at present feedstock costs & technologies is too high

Required mass, volume and cost of chemical hydrides for specified targeted duty*

Storer	Mass, kg	Volume, l	Cost, US$
LiH [1]	1.7	3.7	109
CaH_2 [1]	4.5	4.0	104
$NaBH_4$ (35 wt% aqueous) [2]	6.21	6.21	102
H_3BNH_3	2.38	3.21	390-525

* To run a 1 kW AFC for 8 hours

1. V.C.Y. Kong, et al., Int. J. Hydrogen Energy, 24, 665-75, 1999.
2. S.C. Amendola, et al., Proceedings of the Power Sources Conference, 39th, 176-79, 2000.

Literature Search Results

- Approx. 1,450 articles related to borazine and borazine reactions of which about 50 or so related to the molecular modeling/ ab initio calculations
- About 300 articles involving borazane reactions including 50^{+} articles related to the molecular modeling/ ab initio calculations
- Only a dozen articles related to cyclotriborazane including one involving ab initio calculations (1977)
- Very few publications or studies related to the synthesis of cyclotriborazane or hydrogenation of borazine

Synthesis of AB Complex

- Indirect methods:

$$LiBH_4 + NH_4Cl \text{ — } DEE \rightarrow LiCl + H_3BNH_3 + H_2$$

$$2\ LiBH_4 + (NH_4)_2SO_4 \text{ — } DEE \rightarrow Li_2SO_4 + 2\ H_3BNH_3 + 2\ H_2$$

S.G. Shore & R.W. Parry, J. Am. Chem. Soc., 77, 6084-5, 1955
S.G. Shore & K.W. Böddeker, Inorg. Chem. 3(6): 914-15, 1964
M.G. Hu, et al., J. Inorg. Nucl. Chem. 39(12): 2147-50, 1977

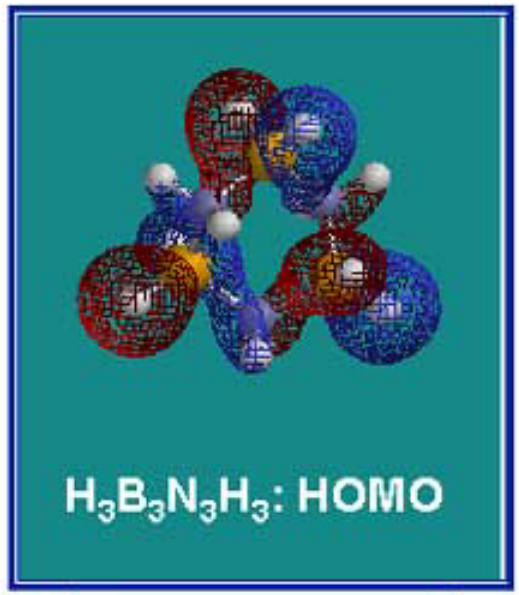
- Direct method:

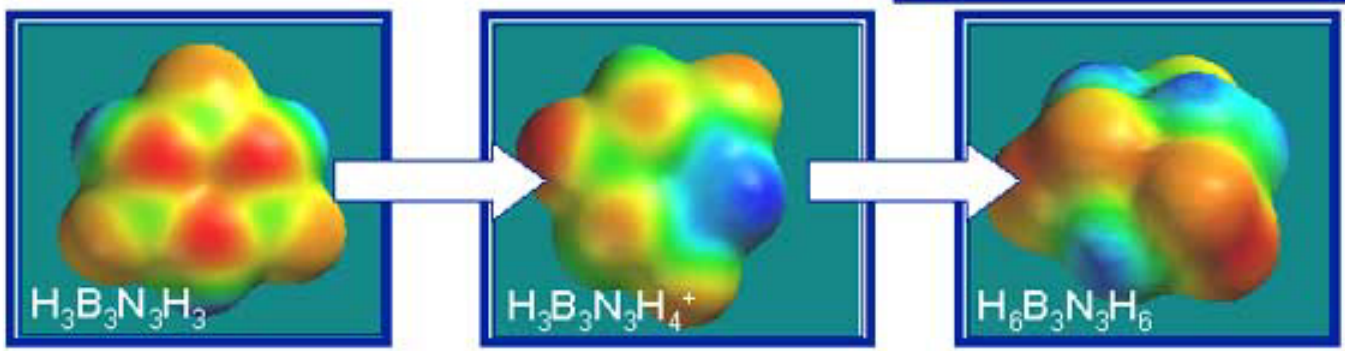
$$B_2H_6 + 2\ NH_3 \rightarrow 2\ H_3BNH_3$$

V.P. Sorokin, et al., Zh. Neorgan. Khim. 8, No. 1, 66; CA 58, 10962d, 1963
R.A. Geanangel & S.G. Shore, Prep. Inorg. React. 3: 123-238, 1966

Molecular Orbital Calculations

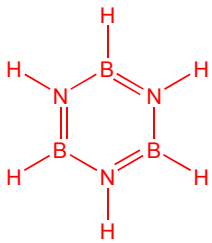
- Electrostatic potential for predicting H_2 bonding interactions
- Enthalpies of hydrogenation/dehyd.
- Potential energy surfaces
- Transition energies and structural information
- Vibrational frequencies



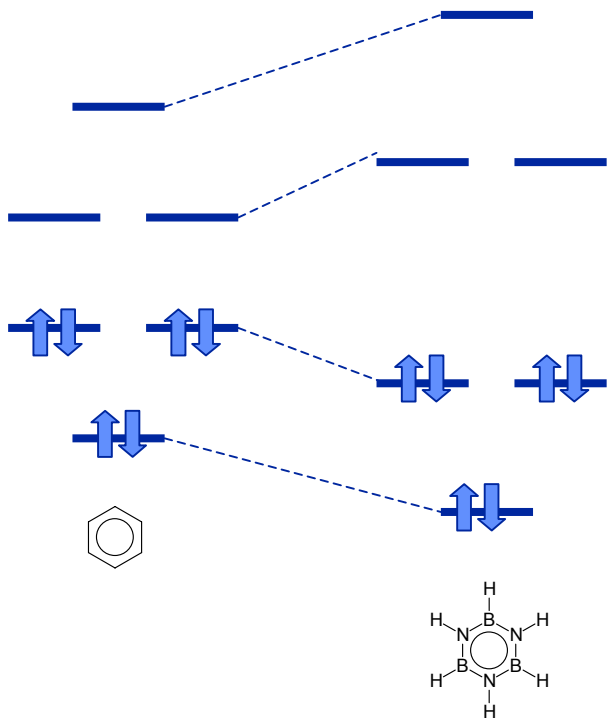


Electrostatic potential surfaces for the Isolated Molecules

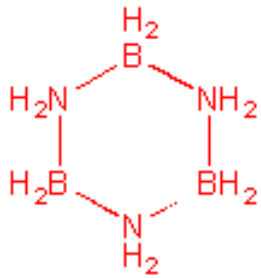
Borazine



- mp at –58°C & bp at 53°C) is stable in gas phase up to 500°C
- isoelectronic with benzene (*inorganic benzene)*
- Charge localisation on N makes borazine more susceptible to addition reactions and thus less stable than benzene



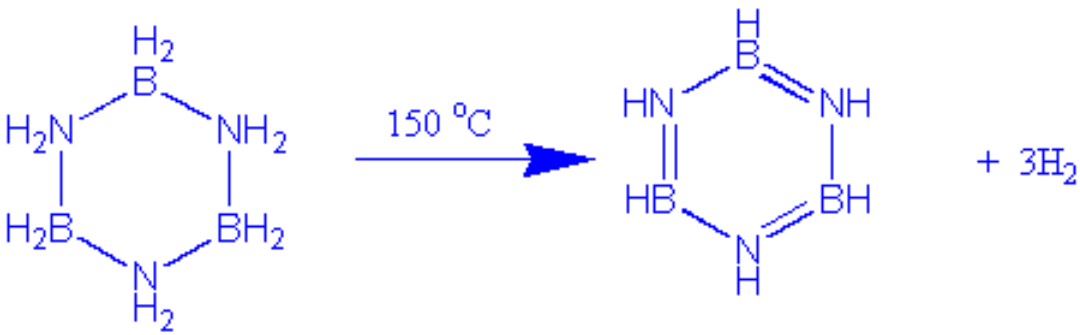
Cyclotriborazane



- Known synthesis routes:

  $2B_3N_3H_6.3HCl+6NaBH_4 \rightarrow 2B_3N_3H_{12}+6NaCl+3B_2H_6$ (1)

  $BH_2(NH_3)_2BH_4+NaC{\equiv}CH \rightarrow BH_2NH_2+NaBH_4+HC{\equiv}CH+NH_3$ (2)
- Crystalline (3)
- Does not react with water (3)
- Cylcotriborazane contains 6.47% H_2 by weight (1)

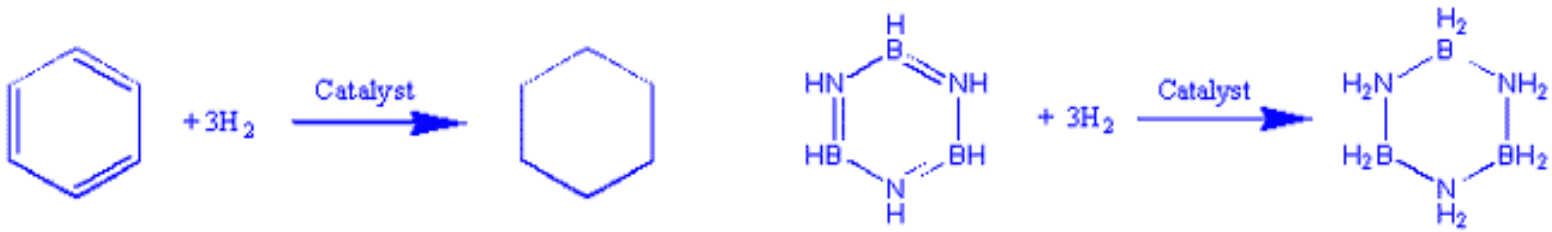


1) Dahl, G.H. & Schaeffer, R. *J. Am. Chem. Soc.* **1961**, 83, 3032.

2) Shore, S.G. & Hickam, C.W. *Inorg. Chem.* **1963**, 2, 638.

3) Boddeker, K.W., et al. *J. Am. Chem. Soc.* **1966**, 88, 4396.

Borazine Hydrogenation



Catalyst	T (°C)	P (atm)
Ni Raney (L)	150	15
Pt (G)	200	11.25

- $\Delta H_{hydrogenation}$ = 28.1 kcal/mol [1]
- Past attempts [2]
  - Ni at 70°C, 150°C & 200°C
  - Pd at 40-50°C
  - Unknown amorphous solid residue

- $\Delta H_{hydrogenation}$ = -30.1 kcal/mol [1]
- Cat. Activity: Rh>Ru>>Pt>>Pd>Ni>Co [3]

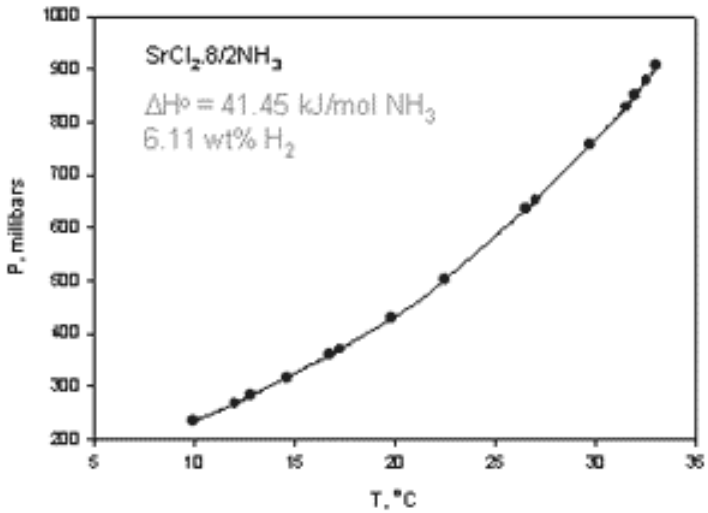
1) Gaussian 03: x86-Win32-G03RevB.01 3-Mar-2003; DFT B3LYP 6-31G.
2) Wiberg, E.; Bolz, A. *Berichte der Deutschen Chemischen* **1940**, 73B, 209.
3) Greenfiled, H. *Ann. N. Y. Acad. Sci.* **1973**, 214, 233.

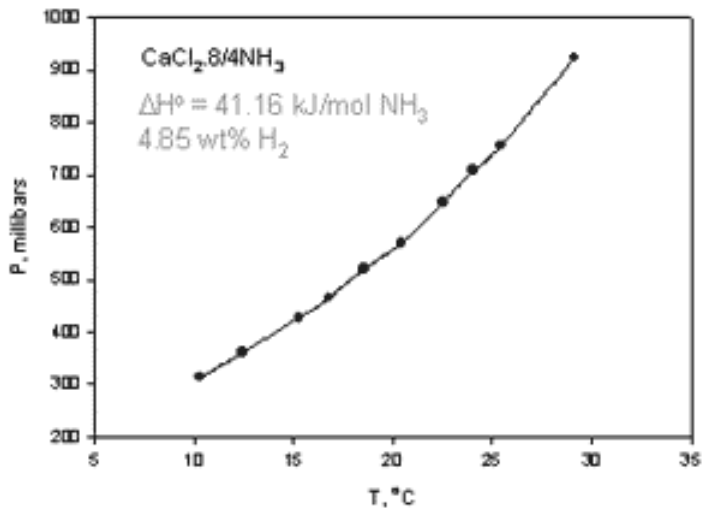
Advantageous Properties of Ammonia Complexes

- Can store large amounts of ammonia as high as the weight of the absorbing salt
- Many compounds and combinations are available
- Vapor pressure is independent of ammonia concentration, over very broad concentration ranges
- Ammonia complexes are solid state and thus not gravity sensitive

Metallic Salt Ammonia Complexes

- Solid-gas reaction pairs for chemical heat pumps [1]
- $MgCl_2$, $CaCl_2$, $CaBr_2$ & $SrBr_2$ can be used for NH_3 storage via heating to 200°C byTSA & $CaCl_2$-$CaBr_2$ mixed halides via evacuation to 10 kPa by PSA [2]

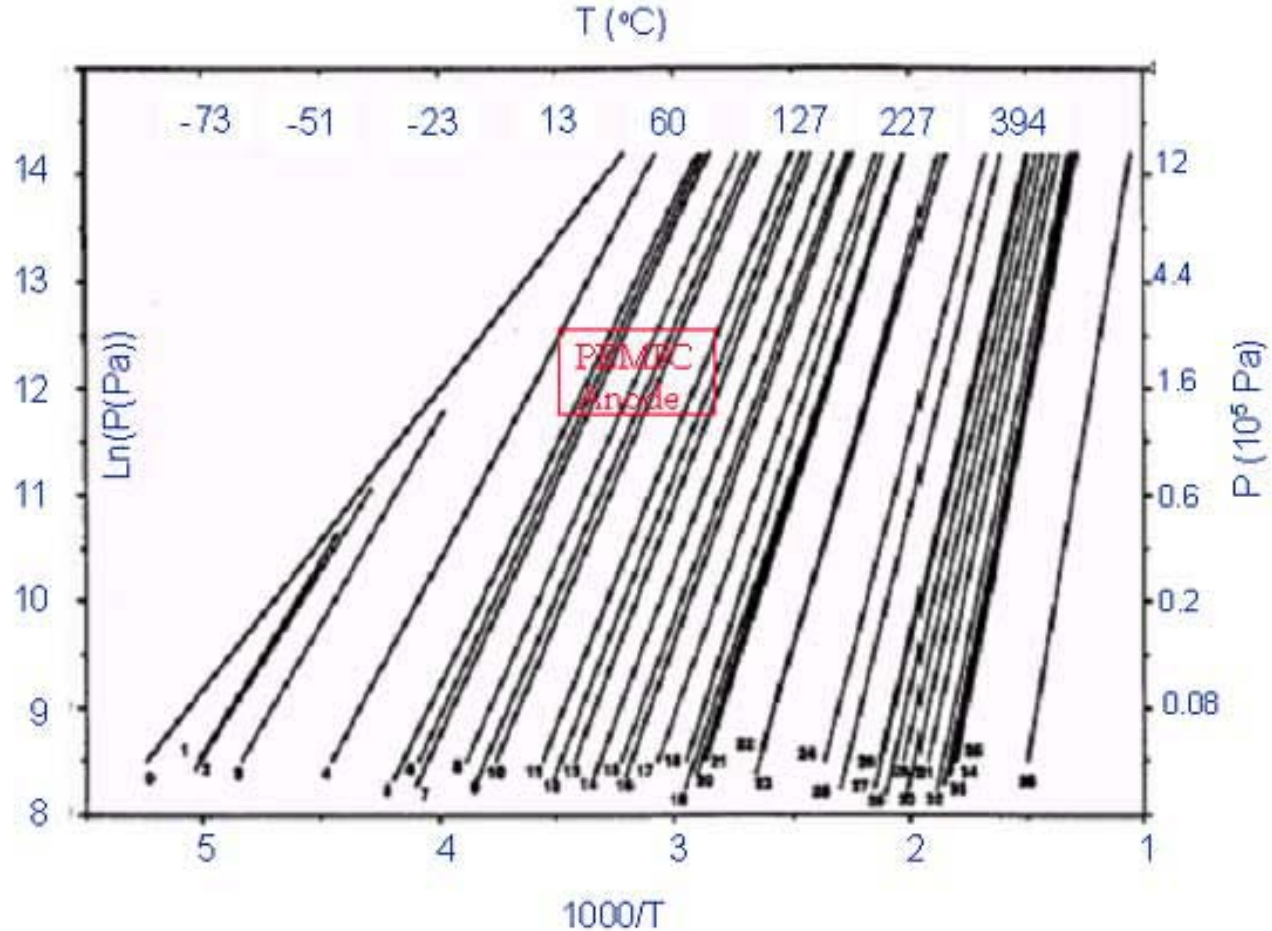




1. *Wentworth, W.E. TES Seminar, Stockholm, **1980**, 371.*
2. *Liu, C.Y. & Aika, K.-I. Chem. Lett. **2002**, 798.*

Equilibrium Lines for Various Chlorides/NH_3 Reactions

No		ΔH(J mol^{-1})
0	NH_3	23,366
1	Zn10-6	29,588
2	Ca10-6	31,387
3	Sr9-4	31,806
4	Pb8-3,25	34,317
5	Ba8-0	37,665
6	Sr4-2,5	38,920
7	Pb3,25-2	39,339
8	Ca8-4	41,013
9	Sr8-1	41,431
10	Ca4-2	42,268
11	Zn6-4	44,779
12	Pb2-1,5	46,035
13	Pb1,5-1	47,290
14	Mn6-2	47,416
15	Zn4-2	49,467
16	Cu5-3,3	50,241
17	Fe6-2	51,266
18	Cu3,3-2	56,497
19	Co6-2	53,986
20	Pb1-0	55,660
21	Mg6-2	55,660
22	Ni6-2	59,217
23	Ca2-1	63,193
24	Ca1-0	69,052
25	Mn2-1	71,019
26	Mg2-1	74,911
27	Fe2-1	76,167
28	Co2-1	78,134
29	Ni2-1	79,515
30	Zn2-1	80,352
31	Mn1-0	84,202
32	Fe1-0	86,880
33	Mg1-0	87,048
34	Co1-0	88,303
35	Ni1-0	89,810
36	Zn1-0	104,625



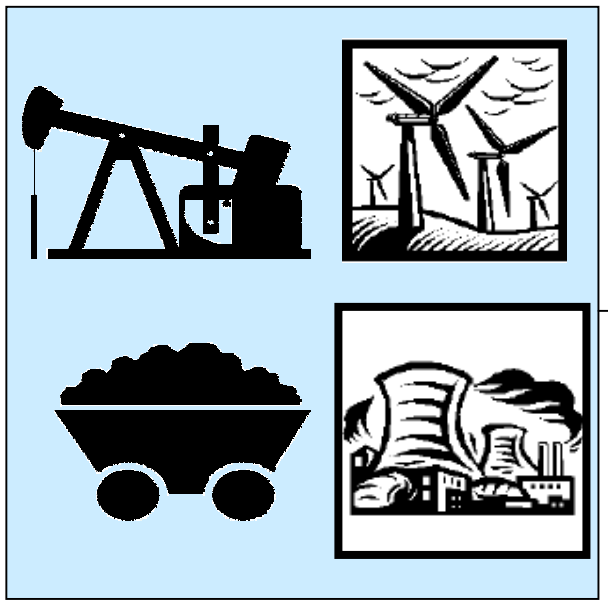
Neveu, P., Castaing, J. Heat Recovery & CHP, Vol. 13, No. 3, 1993.

Conclusions

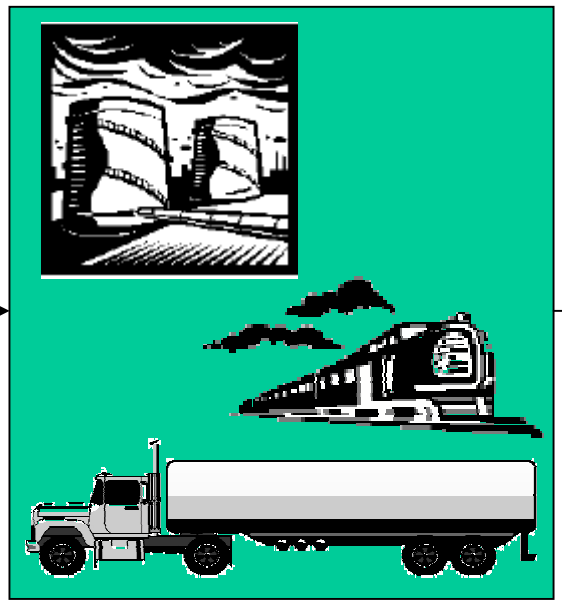
- Successful implementation of chemical hydrides for vehicular FC applications requires:
  - Substantial reduction in their production costs
  - Development of new and/or innovative synthesis routes for their preparation
- Alkali earth metal halides and/or mixed halides may provide a promising route via ammonia to reversibly store hydrogen for PEMFC applications

Hydrogen Fueling Systems and Infrastructure

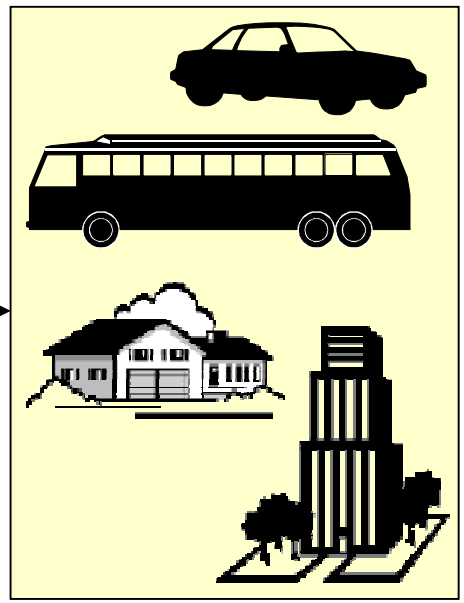
Production



Storage & Delivery



Conversion & Application



Mark Paster

Objectives

Hydrogen Production and Delivery

- Reduce the cost of distributed production of hydrogen from natural gas and/or liquid fuels to $1.50/kg (delivered, untaxed) at the pump by 2010.

- By 2015, reduce the cost of H_2 fuel delivery from the point of production to the point of use in vehicles or stationary power units to <$1.00/kg in total.

Targets and Status

Distributed H_2: Natural Gas, Liquid

Characteristics	Units	2003 Status	2005	2010
Reforming				
Natural gas cost	$/kg H_2	0.66	0.62	0.58
Other costs	$/kg H_2	3.08	1.36	0.24
Primary energy efficiency	% (LHV)	70	72	75
Total				
Total cost	$/kg H_2	5.06	3.00	1.50
Primary energy efficiency	% (LHV)	62	68	75

Barriers

Distributed Hydrogen Production

- Fuel Processor Capital Cost
- Operation and Maintenance
- Feedstock Flexibility
- GHG Emissions
- Control and Safety

Development Focus

Distributed Production Costs, Reliability, and Safety

- More robust and tolerant catalyst system
- Combining unit operations: reforming, shift, separations, heat integration
- Designing for: manufacturability, operability, low maintenance, safety, compactness

Feedstock

- GHG emissions: renewable based feedstock
- Flexibility

Targets and Status

Hydrogen Delivery

Characteristics	Units	2003 status	2005	2010
Gaseous Hydrogen Compression				
Cost	$/kg H_2	0.18	0.17	0.14
Energy efficiency	%	90	92	95
Hydrogen Liquefaction				
Cost	$/kg H_2	1.11	1.01	0.53
Energy efficiency	%	65	70	87
Hydrogen Gas Pipelines				
Trunk lines	$/mile	1.4M	1.2M	600k
Distribution lines	$/mile	600k	500k	350k
Hydrogen Carrier Technology				
Hydrogen content	% by wt	3	6.5	10
Energy efficiency	%	80	82	85

Barriers

Hydrogen Delivery

- Lack of hydrogen/carrier and infrastructure options analysis
- High costs of hydrogen compression
- High costs of hydrogen liquefaction
- High capital cost of pipelines
- Solid and liquid hydrogen carrier transport
- Transport storage costs

Projects

Hydrogen Infrastructure Development

• Turnkey Commercial Hydrogen Fueling Station	Air Products & Chemicals, Inc.
• Autothermal Cyclic Reforming-Based Fueling System	GE Energy
• Natural Gas to Hydrogen Fuel Station	Gas Technologies Institute
• Production & Delivery Analysis	NREL
• H_2 Reformer, Fuel Cell Power Plant, & Vehicle Refueling System	Air Products & Chemicals, Inc.

Projects (Continued)

Hydrogen Infrastructure Development

• Fuels Choice	TIAX
• Renewable Energy Transportation System	Sunline
• Hydrogen Storage & Compression	LAX, Praxair

Posters

Hydrogen Infrastructure Development

• Distributed Hydrogen Fueling Systems Analysis	Directed Technologies, Inc.
• Power Park Analysis	Air Products & Chemicals, Inc.
• Power Parks	State of HI
• Power Parks	Pinnacle West
• Power Parks	DTE
• Power Park System Simulation	SNL
• Filling Up With Hydrogen 2000	Stuart Energy
• Integrating a Hydrogen Energy Station into a Federal Building	TIAX

Development of a Turnkey H2 Fueling Station

David E. Guro
Air Products and Chemicals, Inc.
Allentown, PA

U.S. D.O.E. - Hydrogen Program Annual Review
May 2003

PSU Station: Goals and Objectives

- To demonstrate the economic and technical viability of a stand-alone, fully integrated H2 Fueling Station based on reforming of natural gas
  - To build on the learnings from the Las Vegas H2 Fueling Energy Station program.
  - Optimize the system. Advance the technology. Lower the cost of H_2.
- To demonstrate the operation of the fueling station at Penn State University
  - To obtain adequate operational data to provide the basis for future commercial fueling stations
- To maintain safety as the top priority in the fueling station design and operation

© Air Products & Chemicals, Inc., 2003

Three Phase Industry-DOE Project

AIR PRODUCTS

U.S. DEPT. OF ENERGY

PENNSTATE

Phase 1: Conceptual Design & Economic Evaluation

- Formulated & costed subsystem conceptual designs
- We believe we can demonstrate the roadmap to providing H2 fuel equivalent to gasoline prices
- **Completed, on-schedule.**

Phase 3: System Deployment

- Scale-up & detailed engineering
- Fabricate & install at Penn State
- Operate and Test – Vehicles Filled
- 6 Month Operations

Oct 2001 **May 2002** **June 2003** **June 2004**

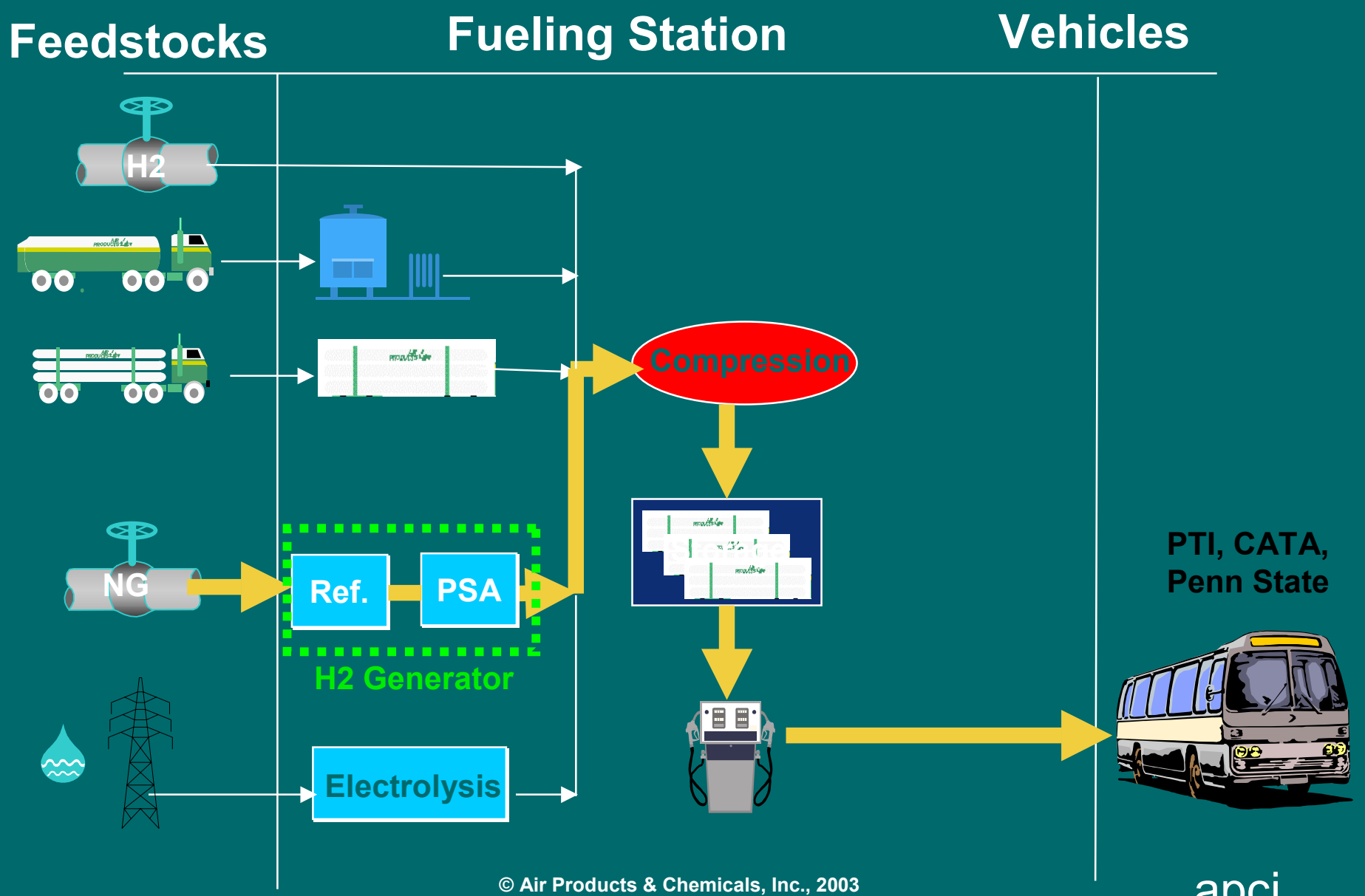
Phase 2: Subsystem Development

- Develop Subsystems and Test Components
- Advance **every** aspect of station
- Begin station aesthetics work

© Air Products & Chemicals, Inc., 2003

apci

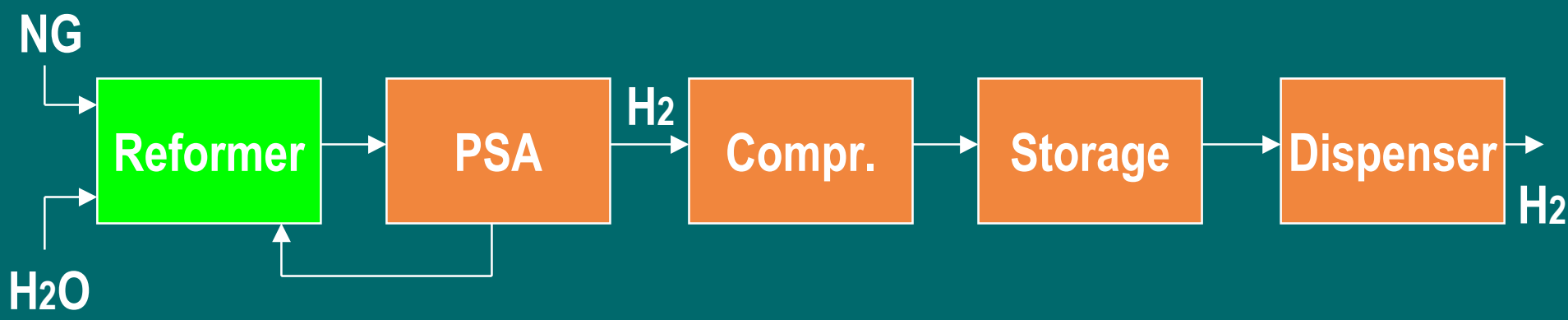
H_2 Fueling Station at Penn State



© Air Products & Chemicals, Inc., 2003

apci

Task 1.1.1. Reformer



Goals:

1. Determine the most cost effective natural gas reforming technology for fueling station applications by evaluating a range of reforming technologies.
2. Produce preliminary specifications.

© Air Products & Chemicals, Inc., 2003

apci

Reformer Evaluation

- **All reformer companies were provided the same process specification**
  - Evaluated SMR, POX, ATR, CPOX
  - Received 10 quotations for commercial or near-commercial systems
- **Not all companies responded with the same quality of information**
  - APCI adjusted quotes to get them on the same capital and maintenance basis
  - To account for uncertainty and risk, statistical bands were associated with each vendors' capital and maintenance costs
- **Cost of hydrogen from each reformer was calculated using a discounted cash flow model, using a Monte Carlo Simulation.**
- **The result of the simulation is a range of hydrogen costs for each vendor**

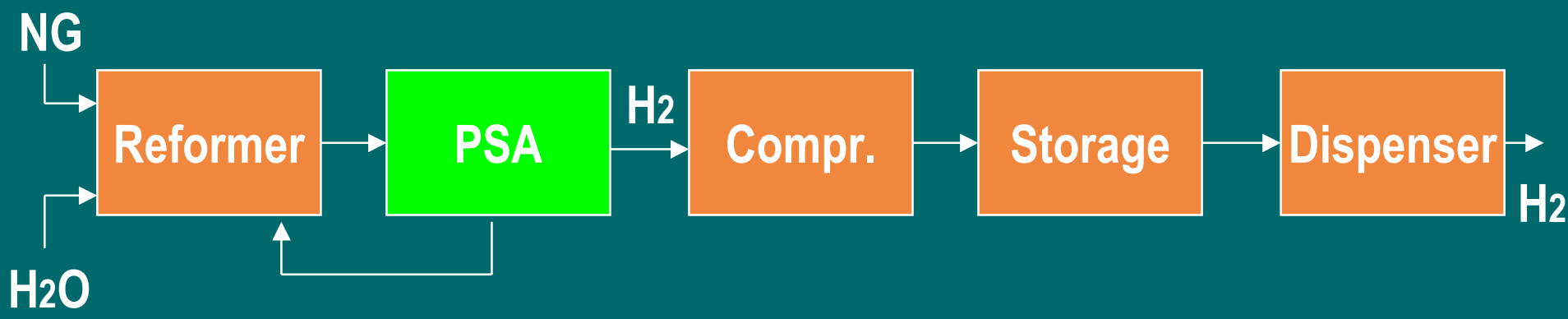
© Air Products & Chemicals, Inc., 2003

Phase 1 Reformer Study Results

- Advanced Technology SMR's are more cost competitive than the other evaluated technologies for small scale reforming applications used in hydrogen fueling stations
- SMR's tend to have lower greenhouse emissions than ATR's
  - Typically more efficient than ATR
  - Utilize less power
- Mass production of reformer, as well as building larger reforming systems, will reduce the cost of H2 produced.

© Air Products & Chemicals, Inc., 2003

Task 1.1.2. PSA Development



Goals:

1. Optimization by both Air Products and QuestAir – choose at end Phase 2
2. APCI to commence adsorbent testing
3. Conduct economic analysis of ability to hit target pricing
4. Compare with currently available technology

© Air Products & Chemicals, Inc., 2003

apci

PSA Development

- **QuestAir Engineering Services**
  - Extend Existing HyQuestor Product
  - Rotary Valve Enhancements
  - Cycle Optimization and Mechanical design

- **Air Products Development: Innovate in Multiple Areas and Functions**
  - More exotic adsorbents for higher recovery
  - Cycle optimization to reap benefits of new adsorbents
  - Valve development for rapid cycles
  - Process/Material/Mechanical integration
  - Low cost manufacturing / systems assembly
  - New adsorbent masses allow significant adsorbent size reduction & lower PSA cost, while maintaining H2 recovery
  - Lab and operating plant data collected

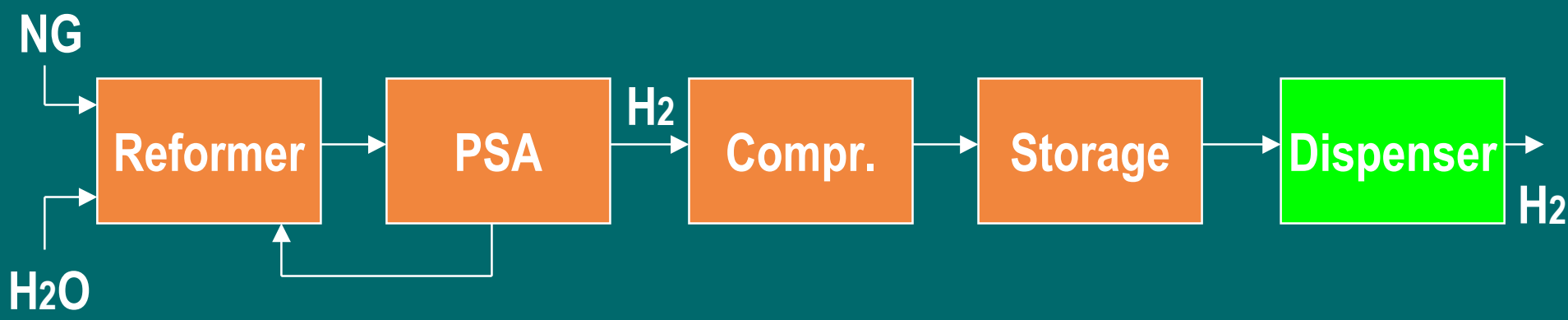
© Air Products & Chemicals, Inc., 2003

PSA Economics

- **Basis: The Adsorbent Research, Cycle Simulations, and Lab Tests That Are Underway**
  - Cycle selected
  - Process performance tested
- **Engineering Work Completed**
  - System components specified
  - Mechanical design & manufacturing improvements implemented
- **Cost Goals Met**
  - Achieved 2 – 4x reduction in cost of PSA when compared with commercially available units
  - New PSA Unit Much smaller than commercially available units
  - Evaluation of 2 Systems Underway

© Air Products & Chemicals, Inc., 2003

Task 1.1.3. Dispenser Development



Goals:

1. Use Sacramento and Las Vegas as starting point. Make dispenser less "industrial" and more aesthetic.
2. Establish cost targets and plan to achieve them.
3. Identify metering alternatives. Define test plan.
4. Canvass CNG dispenser vendors for consultation and/or supply.
5. Improve vehicle communications.

© Air Products & Chemicals, Inc., 2003

apci

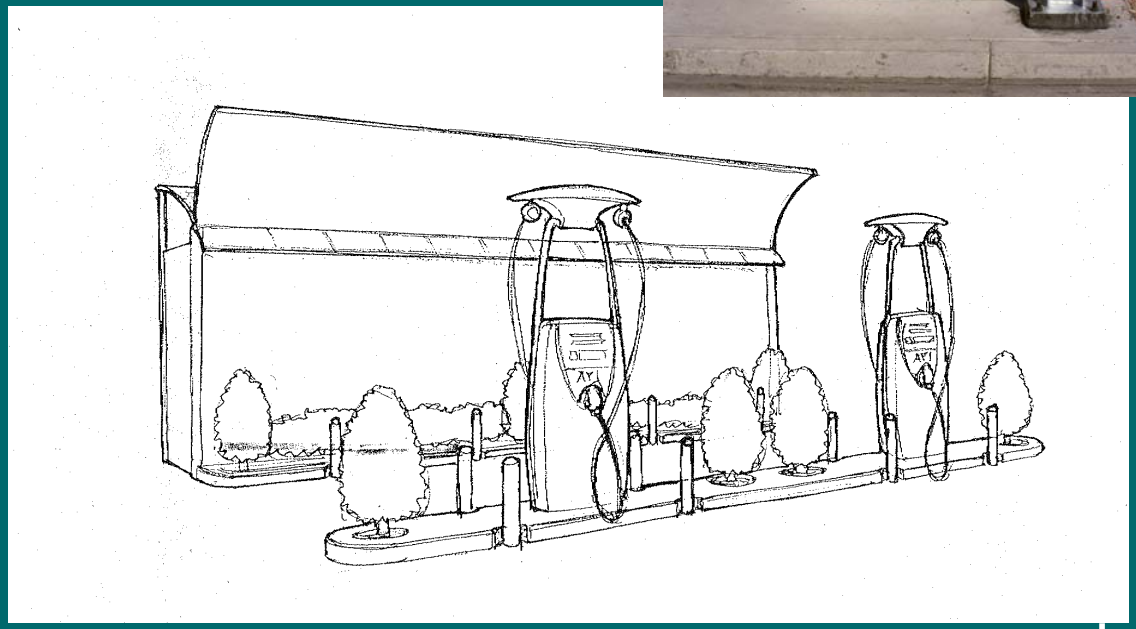
Dispenser Development

- **Design Engineering and Customer Feedback used to Improve Aesthetics & User Interface. DFMA to be performed.**
- **High Pressure Piping Components**
  - Vessels good for 7,000 psig
  - Other components selected for 14,000 psig
- **Electronics**
  - Good for classified area
  - Custom microprocessor based controller
- **Cost**
  - Factor of 2 reduction from starting point.
- **Flow Meter**
  - Test program underway
  - 3 Meters identified

© Air Products & Chemicals, Inc., 2003

Progress on the "Station"

?



© Air Products & Chemicals, Inc., 2003

apci

Task 1.1.4. Siting

- **APCI Developed Preliminary Plot Plan for Site**

- **APCI, Penn State, and PTI Chose Site**
  - Goal: Site that meets needs of PTI and PSU “H2 Institute”

  - Choice: At current CNG vehicle filling site
  - East end of PSU campus, by Beaver Stadium
    - Meets needs of PTI – for test track
    - Near ECEC where fuel cell research is done (Dr. Wang)

© Air Products & Chemicals, Inc., 2003

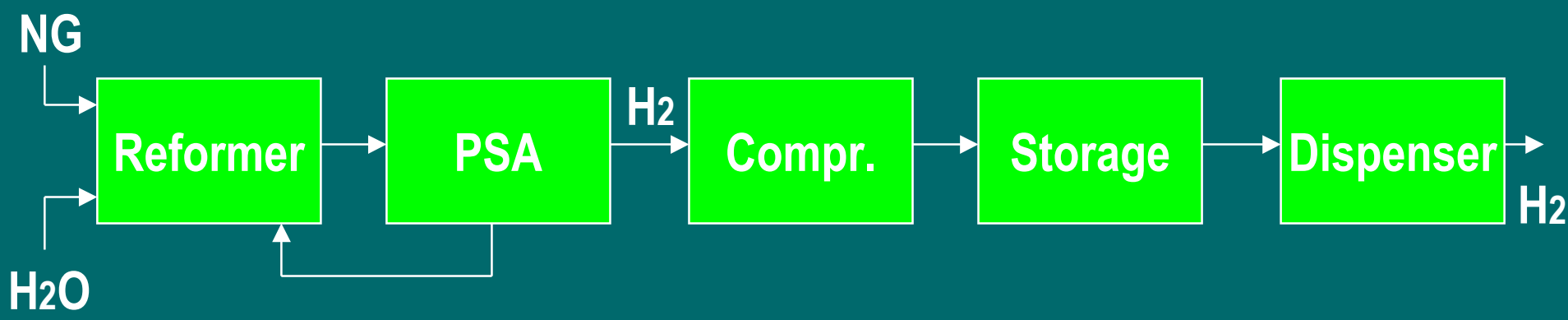
Task 1.1.5. Compression & Storage

- **Compression**
  - Cost-effective, quiet
  - Quotes obtained for H2 compression

- **Storage**
  - 7,000 psig delivery pressure current design
  - Composite materials and hydrides are being investigated
  - Current plan to use high pressure tubes

© Air Products & Chemicals, Inc., 2003

Task 1.2. System Integration



Goals:

1. Produce preliminary PFD and layout for system.
2. Determine process for turnkey system.
3. Confirm economics. Include capital, maintenance, and operating costs.

© Air Products & Chemicals, Inc., 2003

apci

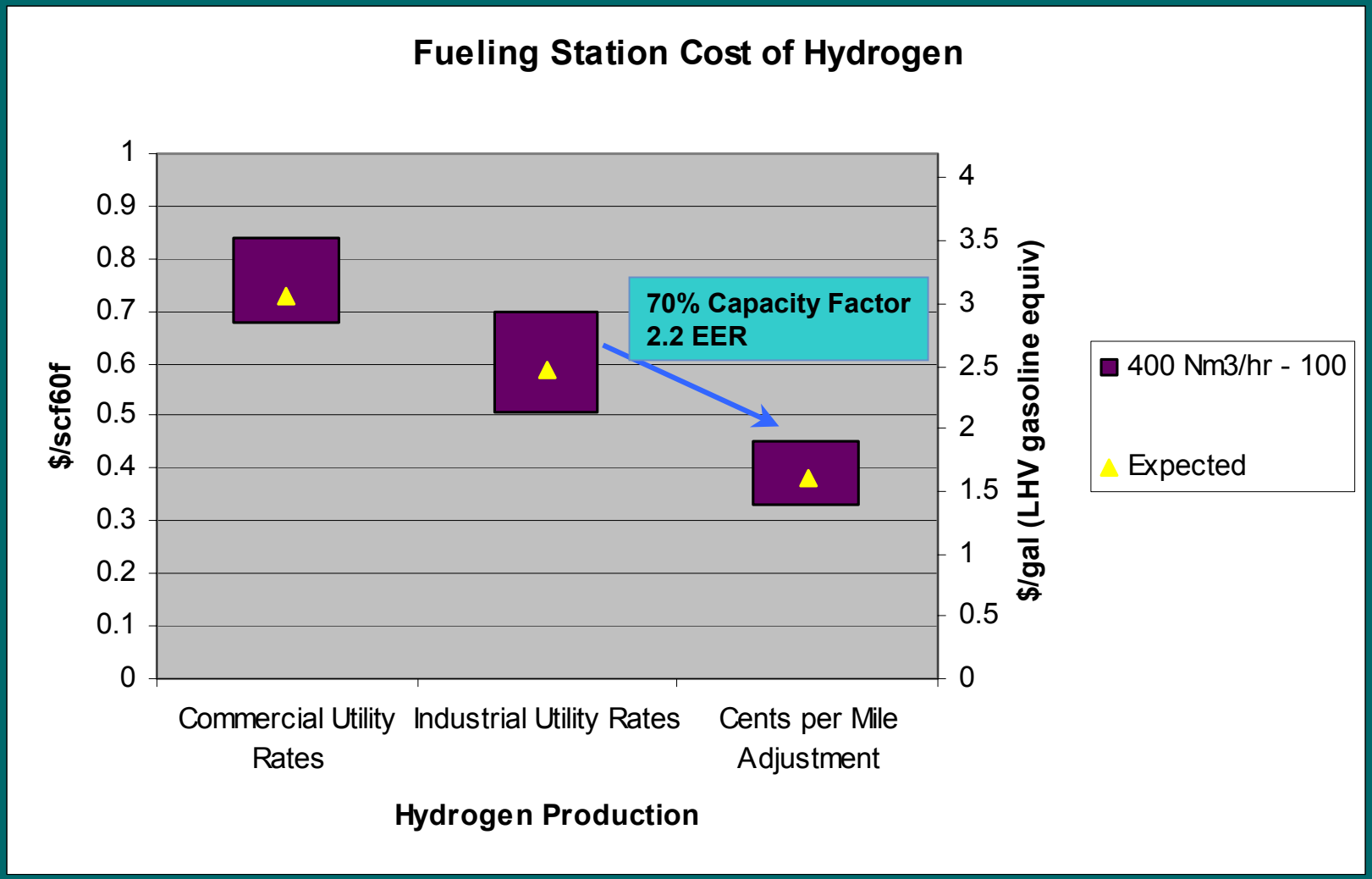
System Integration

- **PFD, Process Specs, and Plot Plan Developed**
  - Serve as basis for all work
- **Safety**
  - APCI has >40 years experience in safe design, construction, & operation of H2 plants
  - PHR: Phase 1. HAZOP: Phases 2 & 3
  - All applicable industry codes will be followed
  - APCI participates in SAE, ICC, ISO, HFPA, IETC, and EIHP2 committees
- **Fueling Station Costs**
  - Reformer Selected in Task 1.1 was used for all Fuel Station Cost and H2 Price Calculations. "Rest of Station" costs, utilities, and maintenance added.
  - Studied effect of scaling:
    - To larger H2 production per generator
    - To mass production of stations (100 units)

© Air Products & Chemicals, Inc., 2003

apci

Fueling Station Cost of H2



© Air Products & Chemicals, Inc., 2003

apci

Summary of Activities

- **Phase 1 Complete**
  - Development activities are underway
    - Reformer
    - PSA
    - Dispenser
  - Cost and schedule estimates have been updated
    - On target
  - Conclusions:
    - Cost of H2 From Stations Improves with Mass Production and Scaling to Larger Station Sizes
    - $1.50/gallon Gasoline Equivalent is a Stretch Goal, but Attainable
    - Pathway Demonstrated that a Stand-Alone H2 Station can be Technically and Economically Feasible
- **Phase 2 Work Nearly Complete**
  - Significant development work accomplished
  - Engineering work underway

© Air Products & Chemicals, Inc., 2003

Response to 2002 Questions

- **Next Generation Station**
  - **Build on learnings of Las Vegas Station**
  - **Advance technology – improve efficiency**
  - **Reduce cost of H2 produced**
- **Size of Station**
  - **Generation capacity of 50NM3/hr or 4 kg/hr H_2**
    - 100Kg/day of H2 full capacity
  - **24 car fills/day or 3-4 bus fills/day on pure H_2**
    - 170 total cars could be served
  - **80 car fills/day or 10-12 bus fills/day on 30% H2/CNG blend**
    - 600 total cars could be served with blend
- **Vehicles**
  - Sourcing of vehicles not part of this program
  - Significant effort spent with PSU and State of PA
    - Proposal has been submitted for funding vehicle conversions and stations operating costs
      - by PSU H2 Institute, PSU PTI, CATA, Air Products
  - Requested a contract change to include CNG/H2 blend dispenser and to match the timing of station start-up closer to vehicle availability.

© Air Products & Chemicals, Inc., 2003

GE

Autothermal Cyclic Reforming Based H_2 Generating & Dispensing System

Ravi Kumar, Parag Kulkarni, Court Moorefield, Shawn Barge and Vladimir Zamansky

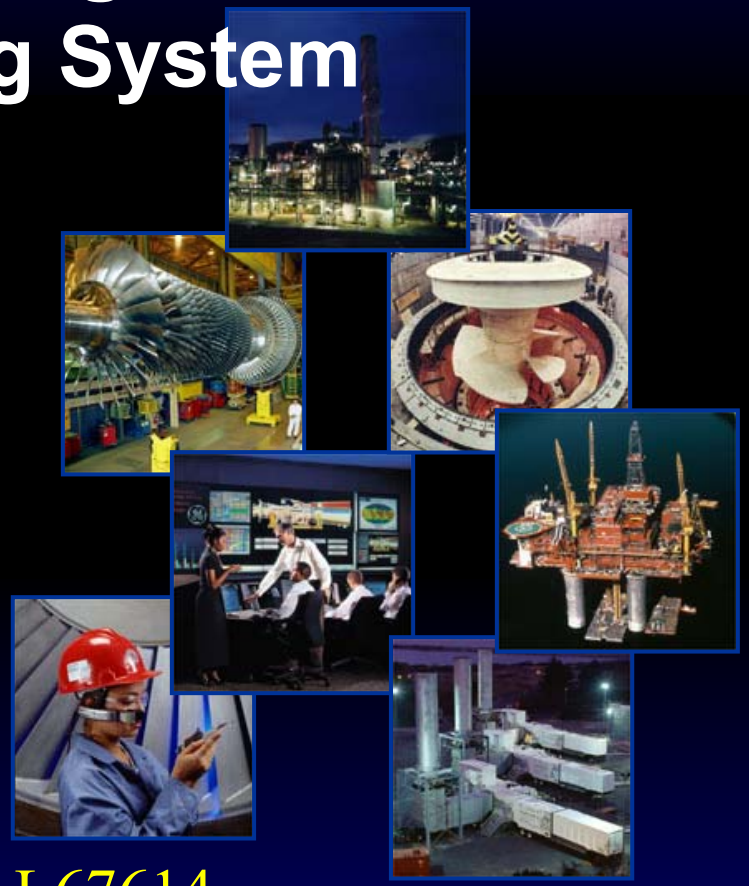
GE Energy & Environmental Research

James Smolarek and Michael Manning

Praxair

Mike Jones and Mike Flaherty

BP



Review on DOE Contract # DE-FC04-01AL67614

May 2003

Goals & Approach

DOE Goal

Cost of Delivered H_2 < $2.50/kg

Phase I (2002) – System Design

- **Design**
- **Assess the technical & economic feasibility**

Phase II (2003-4) – Sub-System Development & Integration

- **Develop the subsystems**
- **Reduce cost of components critical to achieving the economic goal**

Phase III (2004-5)– Prototype Fabrication & Demonstration

- **Fabricate, install, & operate a H_2 refueling station**
- **Verify the operational performance**
- **Verify that the cost of producing & dispensing H_2 meets the targets**

Schedule & Milestones

Praxair/ BP

ID	Task Name	2002	2003	2004	2005
1	**Phase I - Design & Analysis**				
2	Literature search				
3	Functional analysis				
4	Conceptual design				
5	Economic analysis				
6	Business plan				
7	**Phase II - Subsystem Development**				
8	Bench-scale durability testing				
9	Component Development & Testing				
10	Design of the Prototype System				
11	Economic feasibility assessment				
12	Update Business plan				
13	**Phase III - Prototype Demo.**				
14	Prototype Detailed Design				
15	Environmental health & safety				
16	Fabrication & procurement				
17	Site planning and infrastructure				
18	Unit checkout, testing & installation				
19	Operation & maintenance at user				

Design

Projected Cost of H_2

Reliability Availability Maintainability

Optimize

Design for Manufacturability

Safety

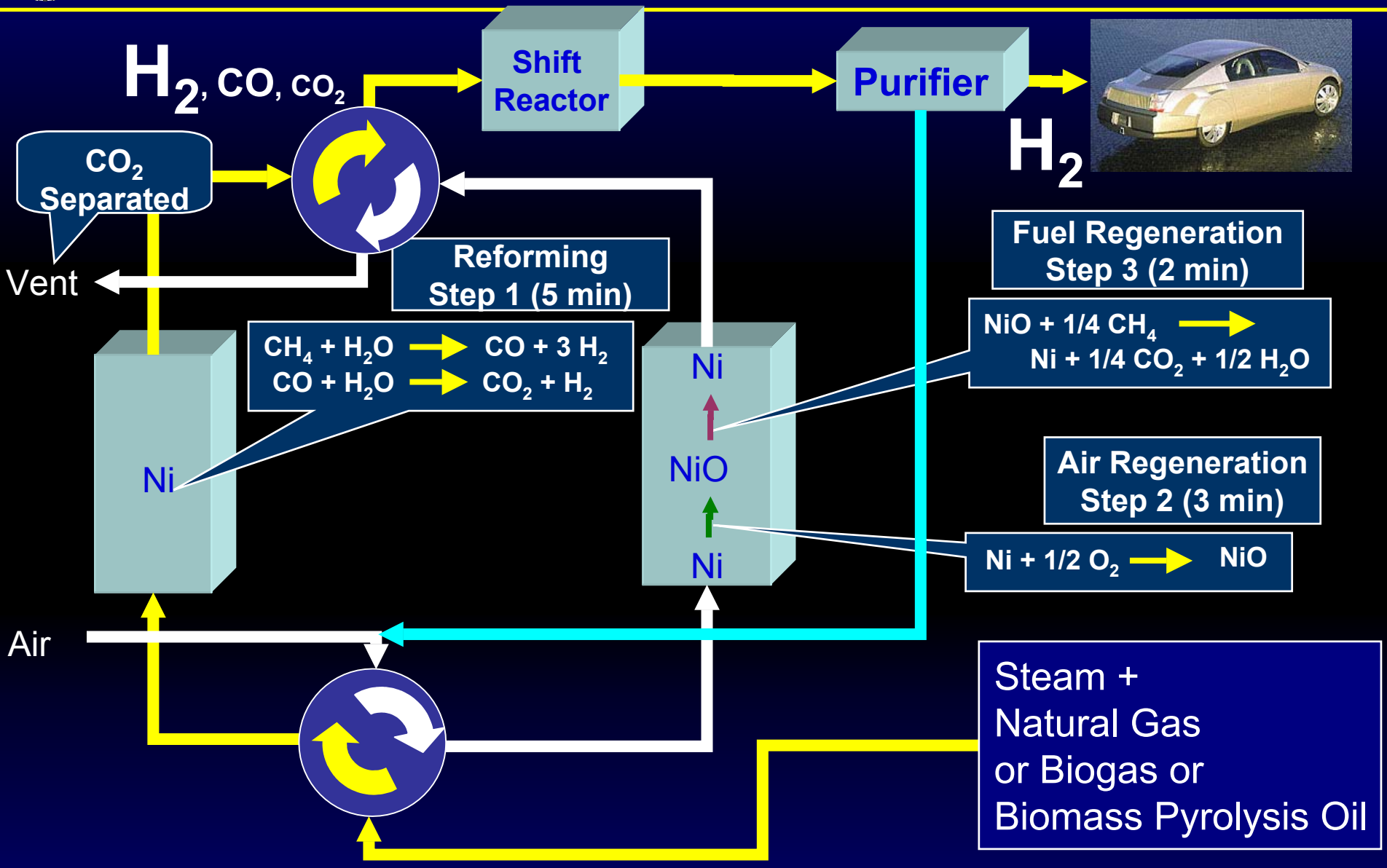
Validate

Fabrication

Installation

Autothermal Cyclic Reforming

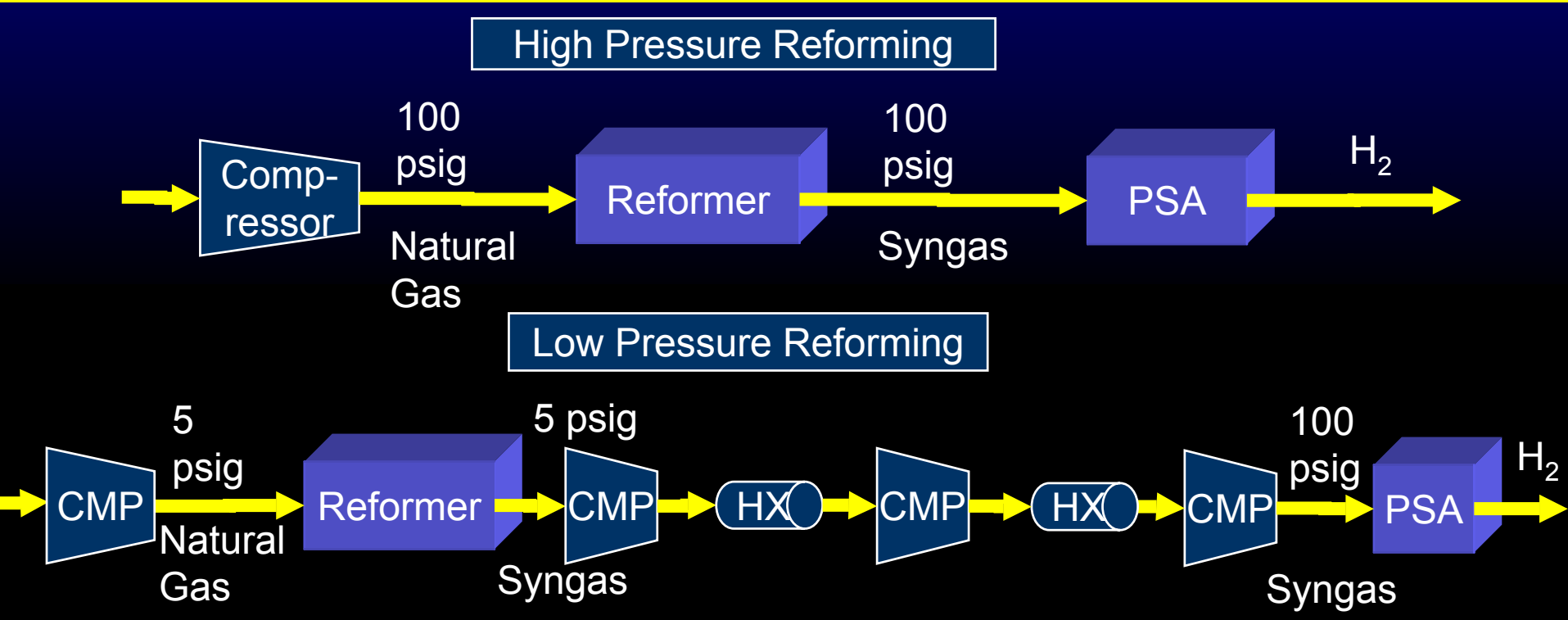
Praxair/ BP



ACR offers lower capital cost & inherent CO_2 separation

High Pressure vs. Low Pressure Reforming

Praxair/ BP



Thermal Efficiency = HHV of H_2 Produced / HHV of NG Fed

PSA – Pressure Swing Adsorption

High Pressure vs. Low Pressure Reforming Comparison

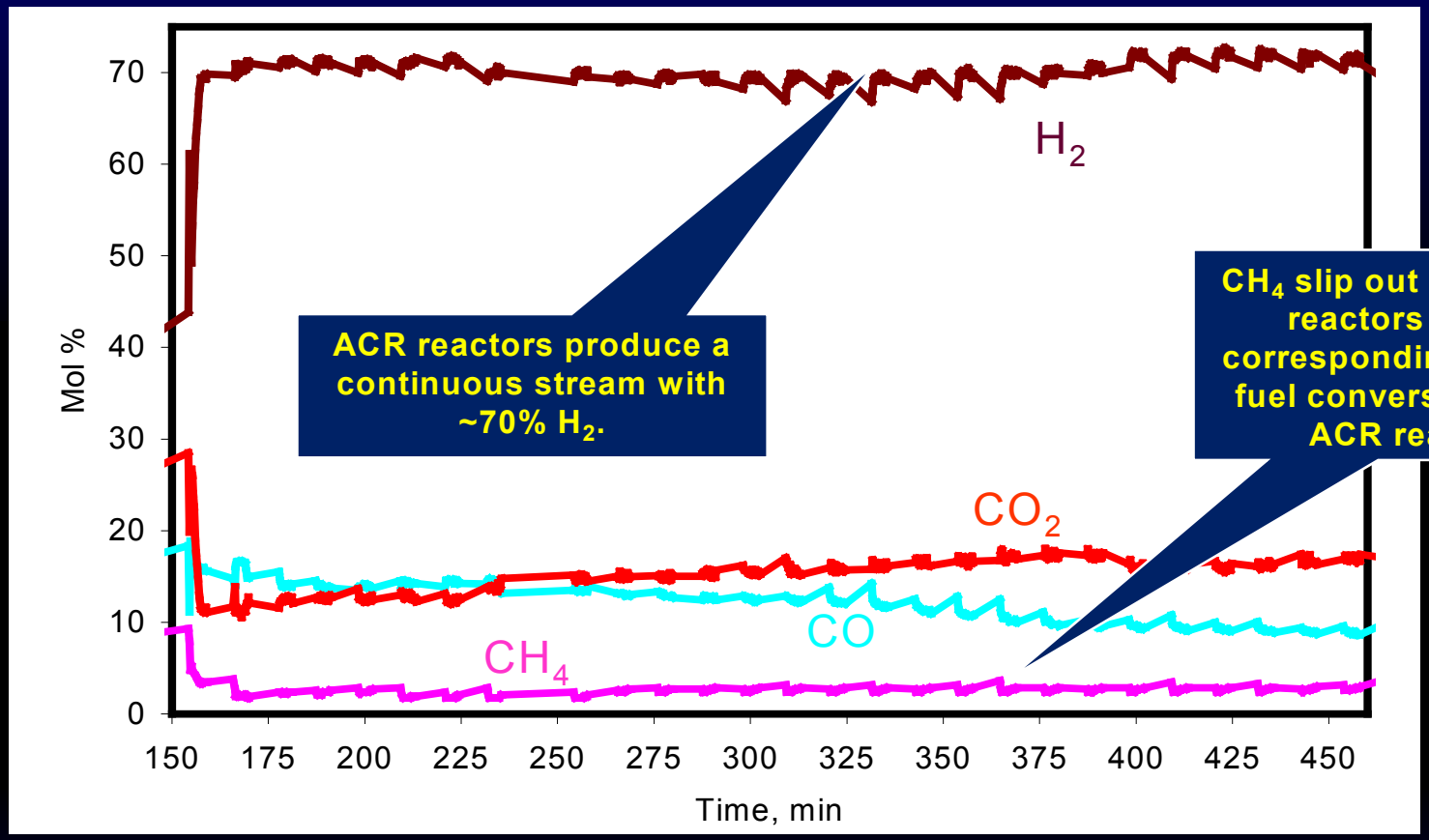
Praxair/ BP

Configuration	High-Pressure Reforming	Low-Pressure Reforming
Thermal Efficiency (Excludes Electricity) = HHV of H_2 Produced / HHV of Fuel Fed	70-80%	70-80%
Electricity Consumed / HHV of Fuel Fed	0.5-1%	3-4%
Efficiency (Includes Electricity) = HHV of H_2 Produced / (HHV of Fuel Fed + Electricity Required /Efficiency of Grid Electrical Generation-35%)	68-78%	65-74%
Advantages	❑ Higher Efficiency ❑ Lower Overall System Capital Cost ❑ Higher Reliability (Eliminates Syngas Compressor)	❑ Lower Capital Costs for Reformer Reactor Only

High Pressure ACR is more cost effective

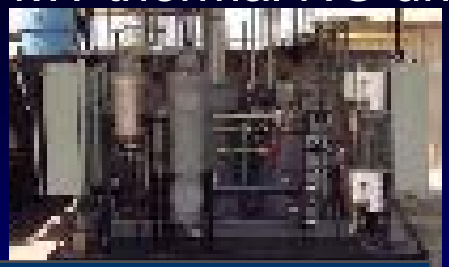
Reformer Design

Praxair/ BP



- Detailed design completed
- Low pressure reformer operated successfully
- Moving to high pressure reformer design and fabrication

150 kW thermal NG unit

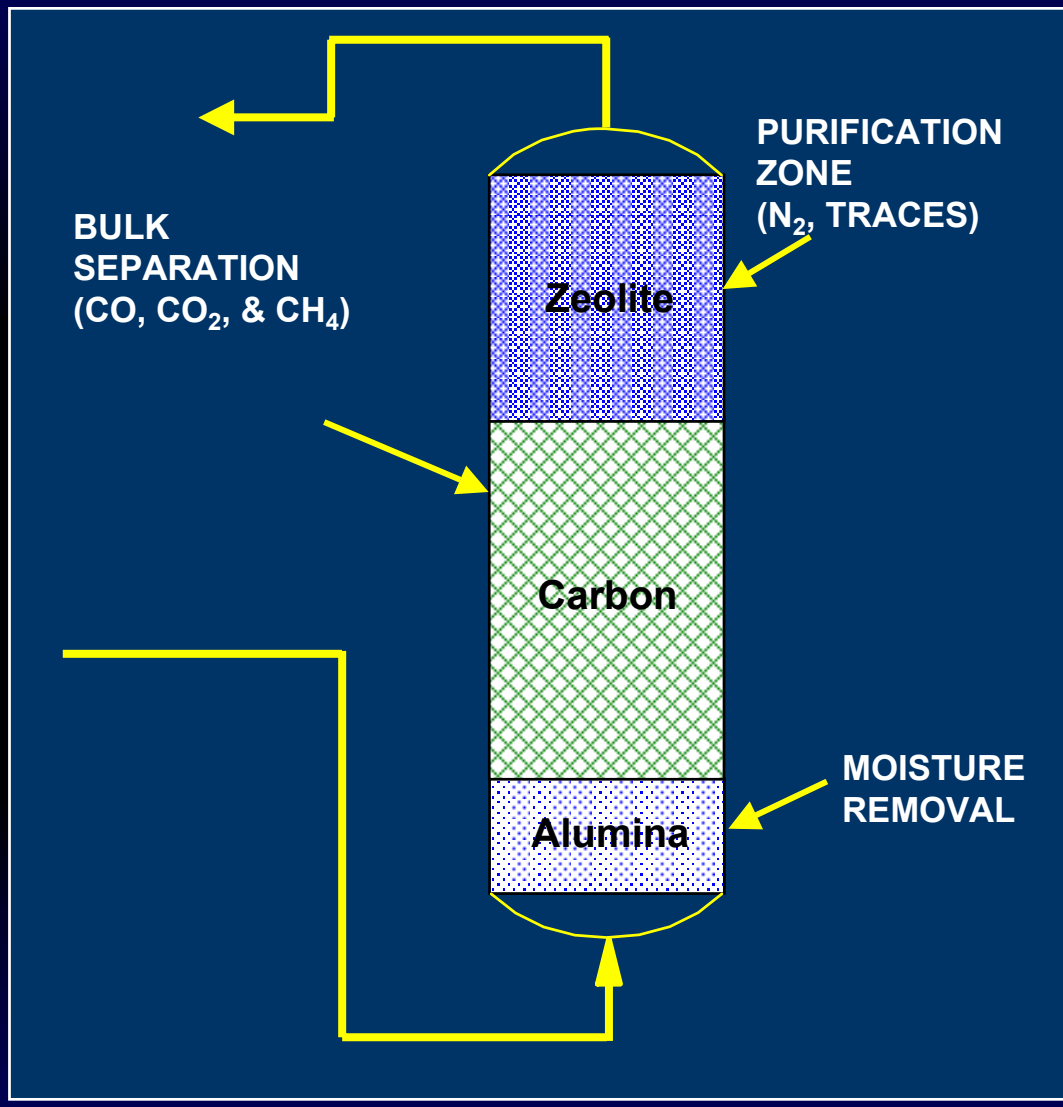


ACR was operated successfully for extended periods of time

Multi-Bed Praxair PSA Design

Praxair/ BP

- 3-bed process
- Accepts continuous feed from ACR and delivers uninterrupted hydrogen product
- Cyclic Reformer simplifies Cyclic PSA considerably, due to ease of integration by matching cycle times of Reformer and PSA
- Tail Gas from PSA can be used for fuel regeneration
- Product Hydrogen Specifications
  - » < 5 ppm CO
  - » < 10 ppm CO_2
  - » < 10 ppm CH_4
  - » < 10 ppm H_2O
  - » ~ 1,000 ppm Nitrogen
  - » ~ 99.99 % Hydrogen

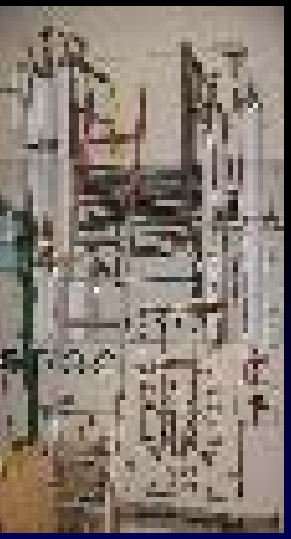


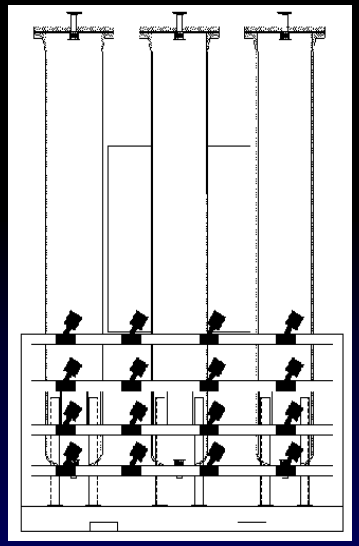
Synergy in integrating cyclic PSA with cyclic reformer

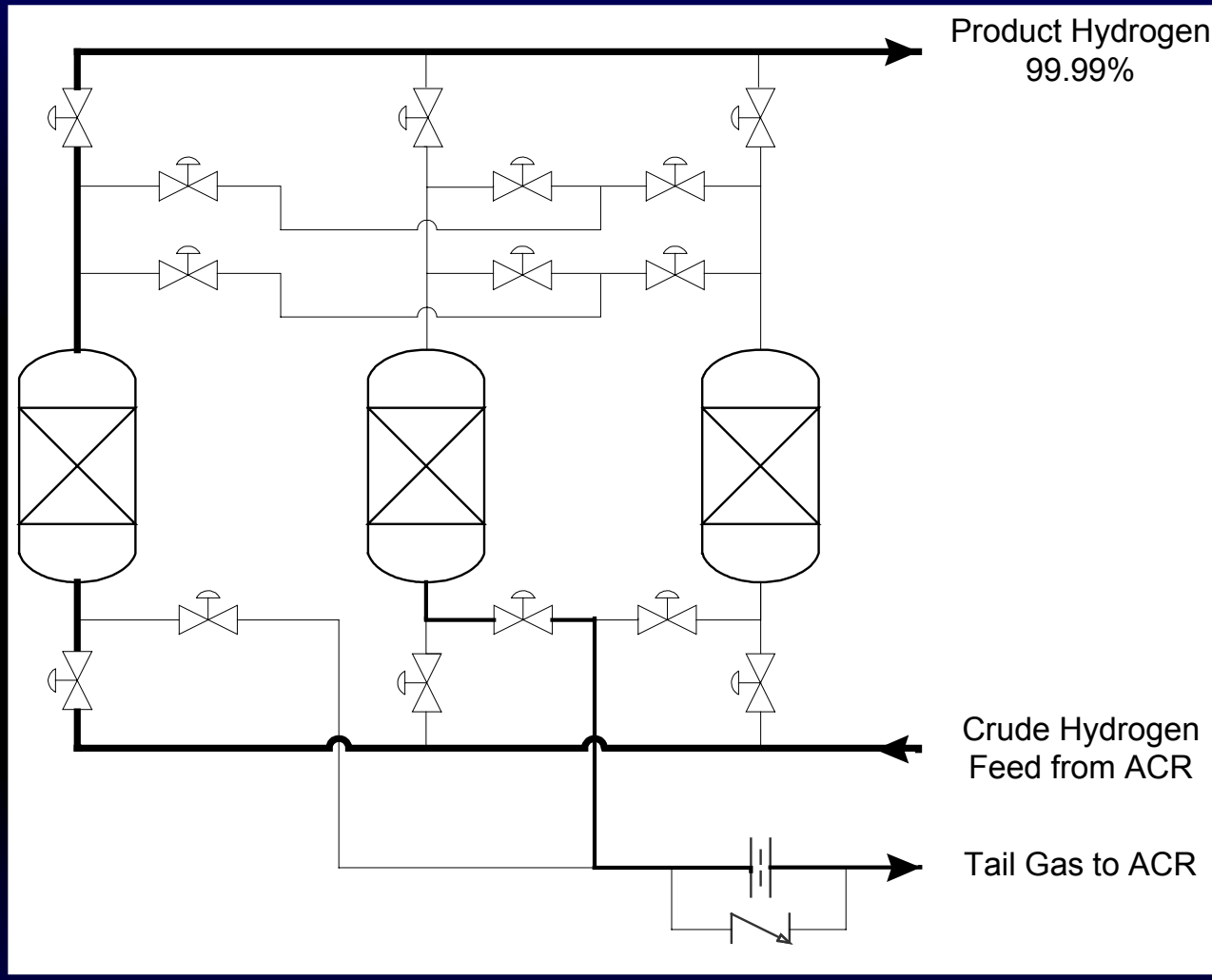
Conceptual 3-Bed PSA Skid Assembly

Praxair/ BP

- Designed for easy valve maintenance
- Employs low cost conventional components
- System costs are highly competitive





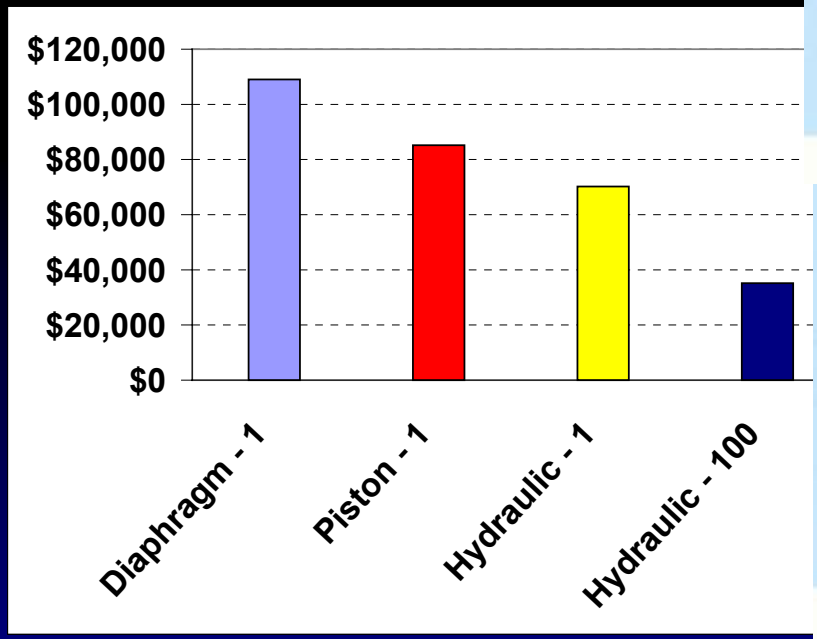


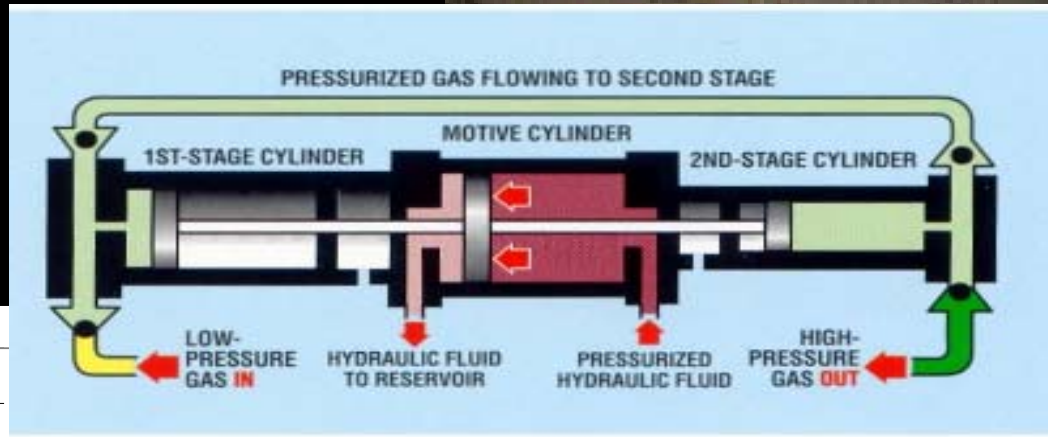
Cost Competitive Design

Hydraulically Driven H_2 Compressor

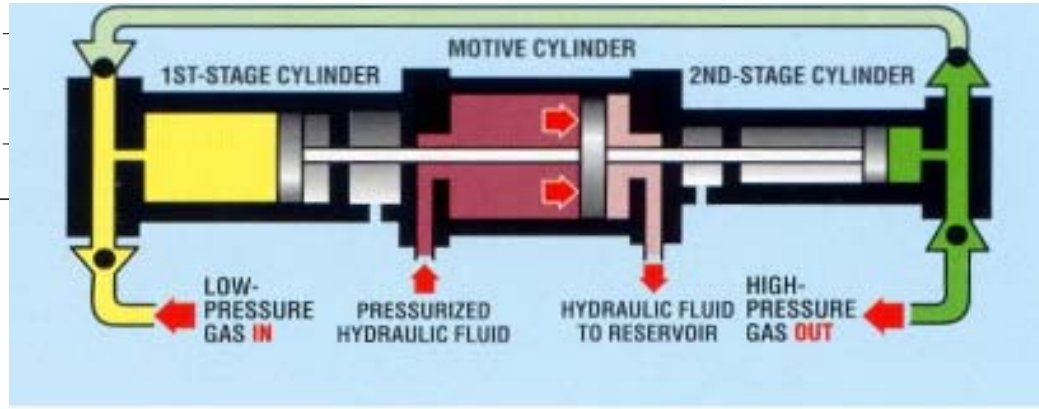
Praxair/ BP

- Oil-free nonlubricated design
- Long slow stroke results in longer packing and check valve life, and much higher compression ratios in each stage
- Piston design allows easy replacement of high pressure seals
- Variable inlet pressure capabilities
- Praxair has prior experience with Hydro-Pac in high pressure nitrogen and argon applications





STAGE I COMPRESSION

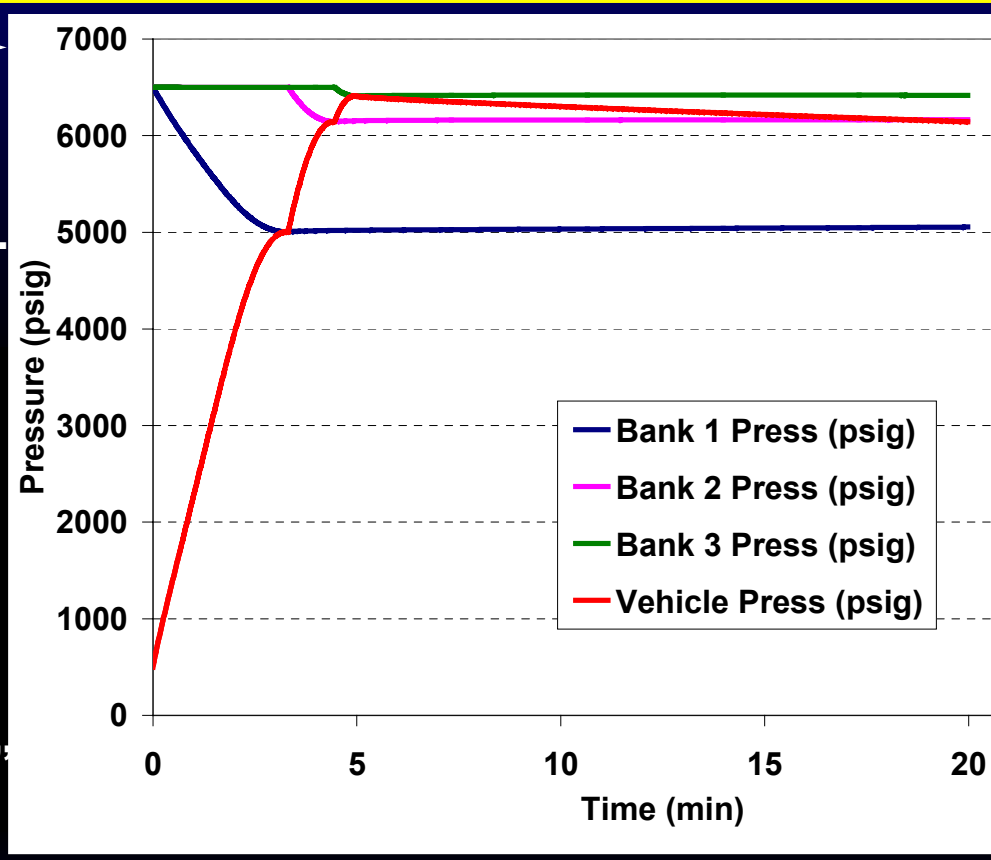


STAGE II COMPRESSION

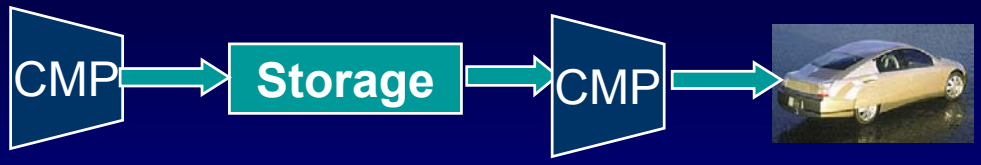
Vehicle Filling - @ 5000 psig

Praxair/ BP

- **Cascade Dispensing**
  - Direct tank to tank pressure transfer through a series of pressure transfers from 3 banks.
  - One bank may be filling while other is being emptied.

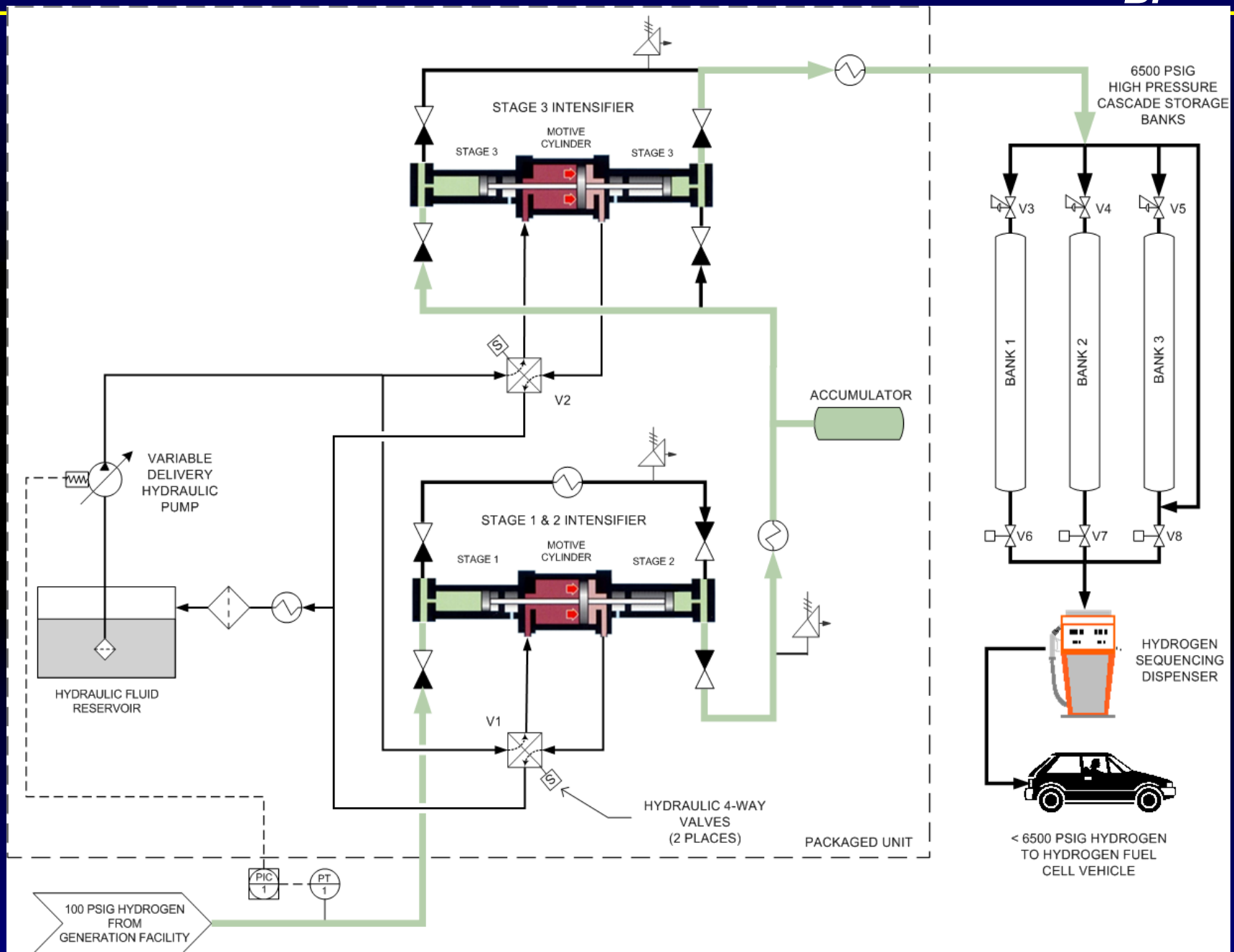


- **Fill Pump Dispensing**
  - Filling method requires 1/3 the amount of storage.
  - Each vehicle can be "topped off" to the same target pressure within 5 minutes.
  - Requires the use of two packaged compressors with low utilization on the fill pump.



Vehicle Filling - Cascade Dispensing

Praxair/ BP



Stationary Storage

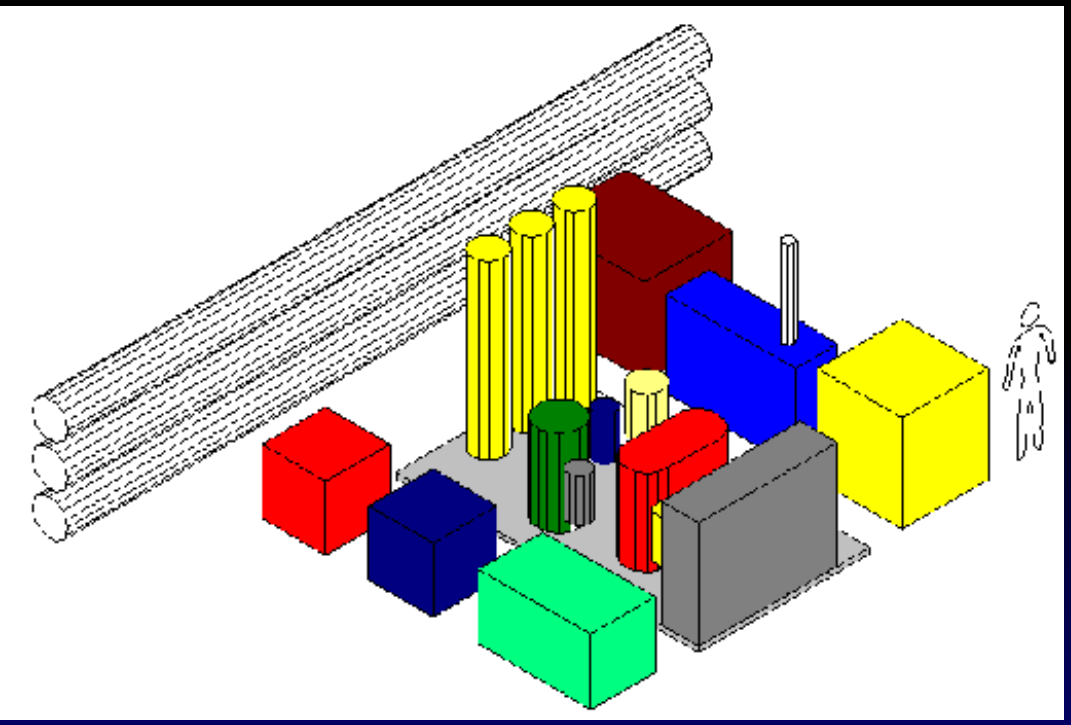
Praxair/ BP

NGV2-3 Composite Cylinders - $54,000

ASME Steel Cylinders- $51,000

Refueling Station System Footprint Summary

Praxair/ BP



60 kg H_2/day
3 consecutive fills

1

60 kg H_2/day
1 consecutive fill

2

15 kg H_2/day
3 consecutive fills

3

15 kg H_2/day
1 consecutive fill

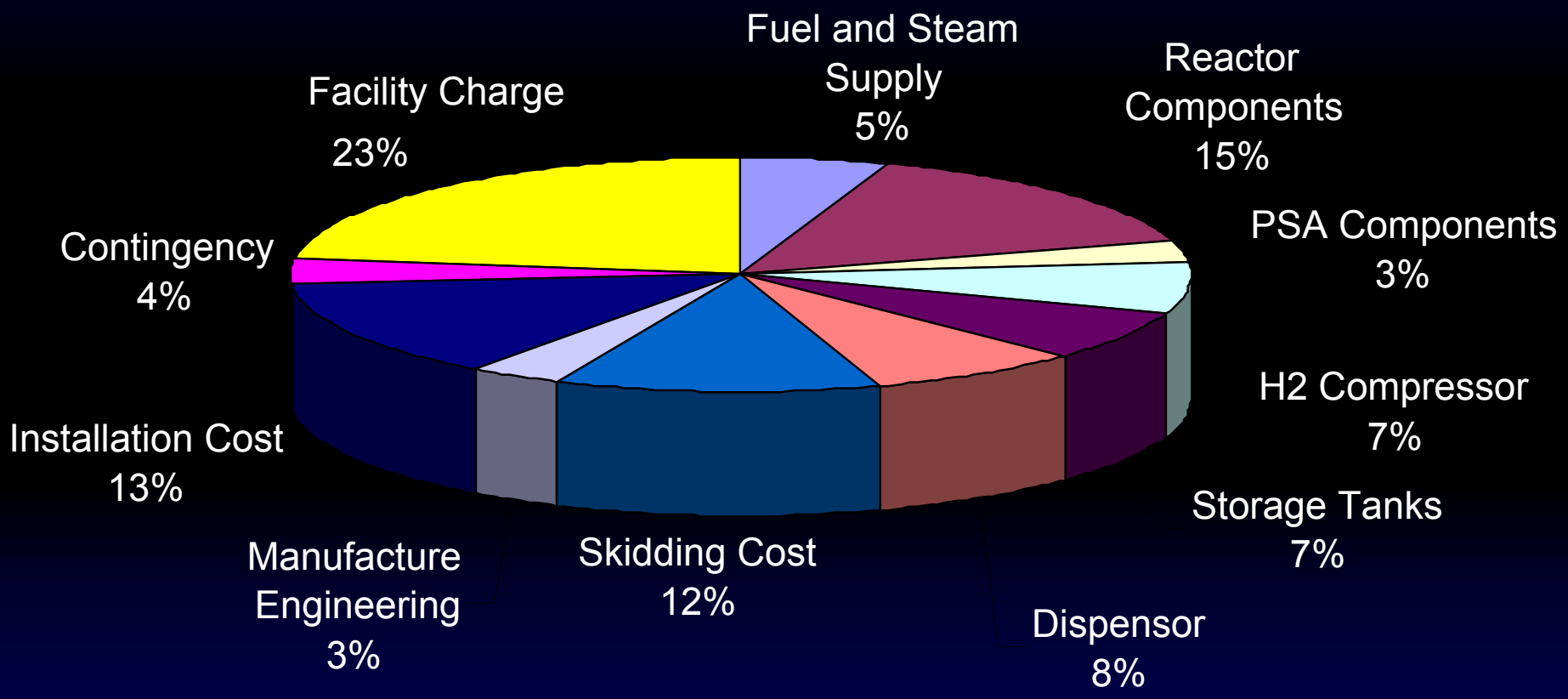
4

Hydrogen storage tanks are the largest subsystem component

Capital Cost Breakdown

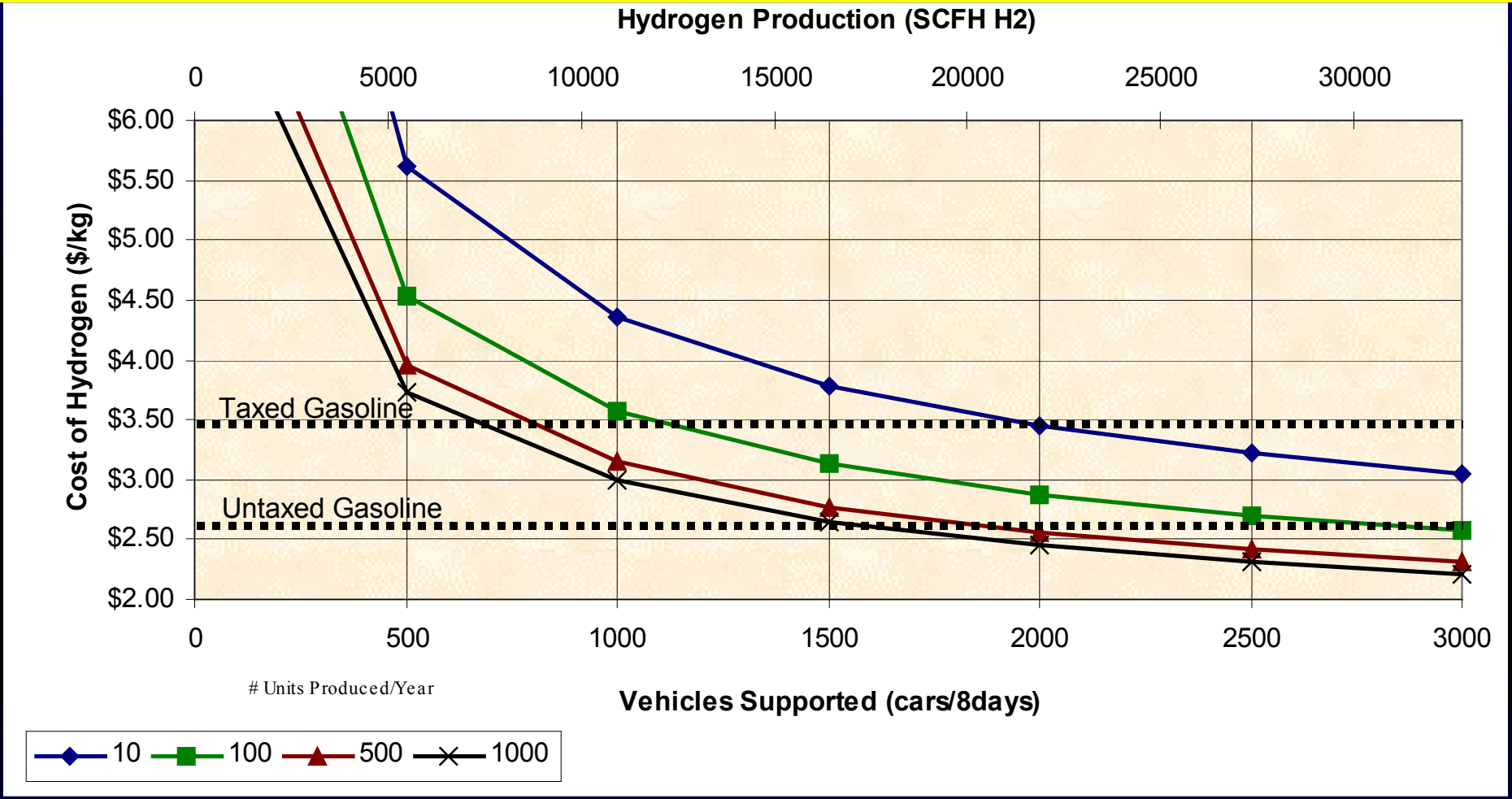
Praxair/ BP

120 kg/day H_2 Commercial @ 100 Units/year



Market Assessment - Commercial Price Targets

Praxair/ BP

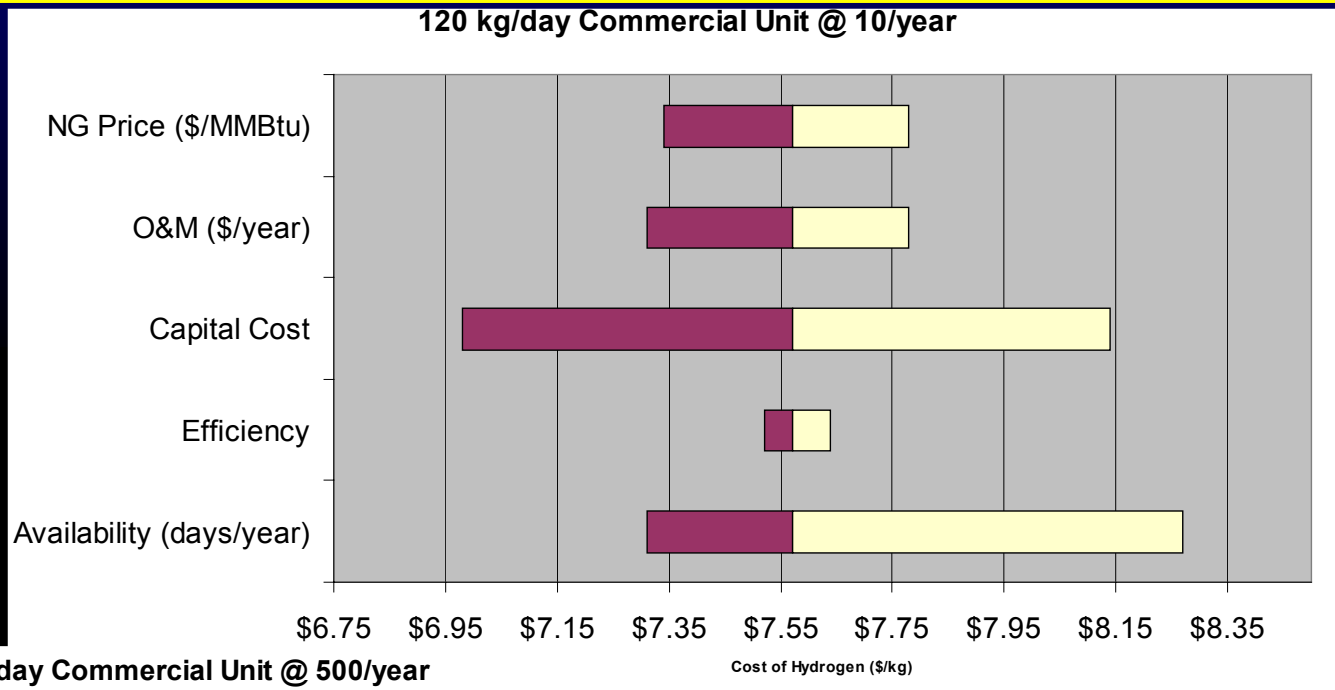


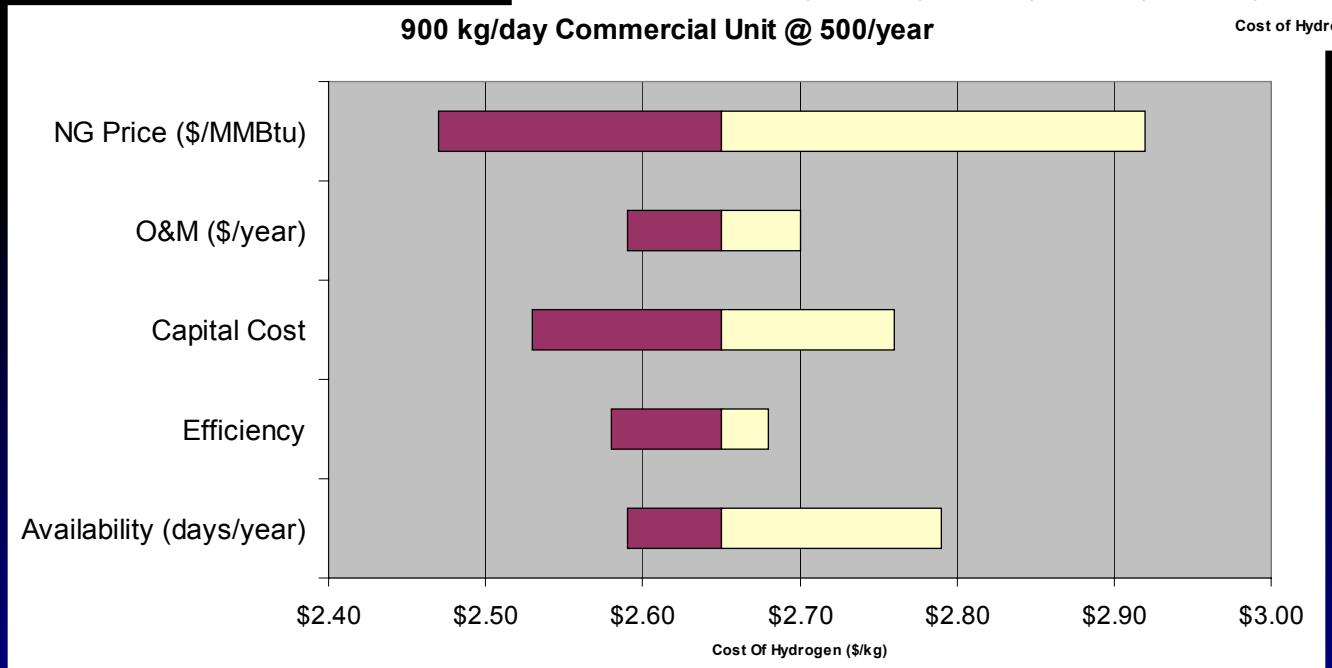
- Price Targets
  - DOE Hydrogen Targets: $2.50/kg non-taxed; $3.30/kg taxed
  - Gasoline Equivalent Price: $2.62/kg untaxed; $3.49/kg taxed
- DOE price targets Met at 15,000 scfh taxed; 5,000 scfh non-taxed
- Commercial Plants require Steady flow, High utilization, Long term contracts

Near and Long Term Market Cost Factors

Praxair/ BP

Short Term Market:
Capital Cost
Availability
O&M

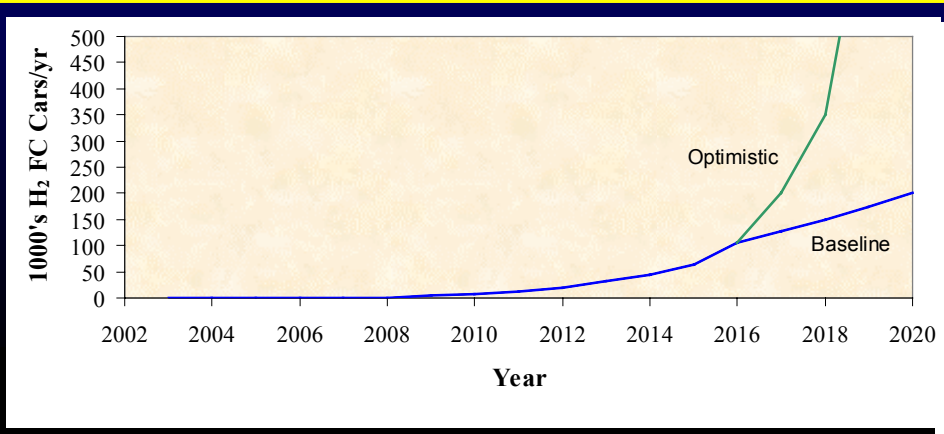


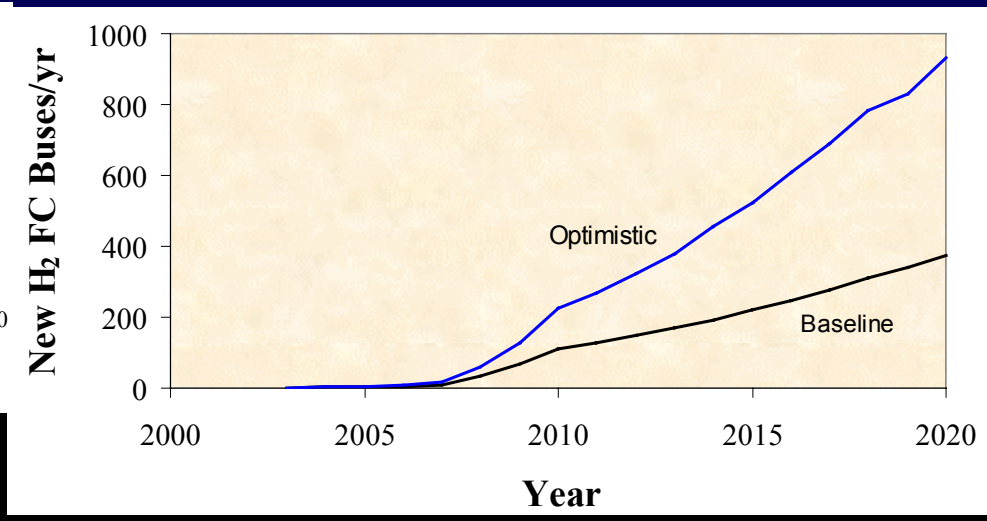


Long Term Market:
Efficiency &
NG Price

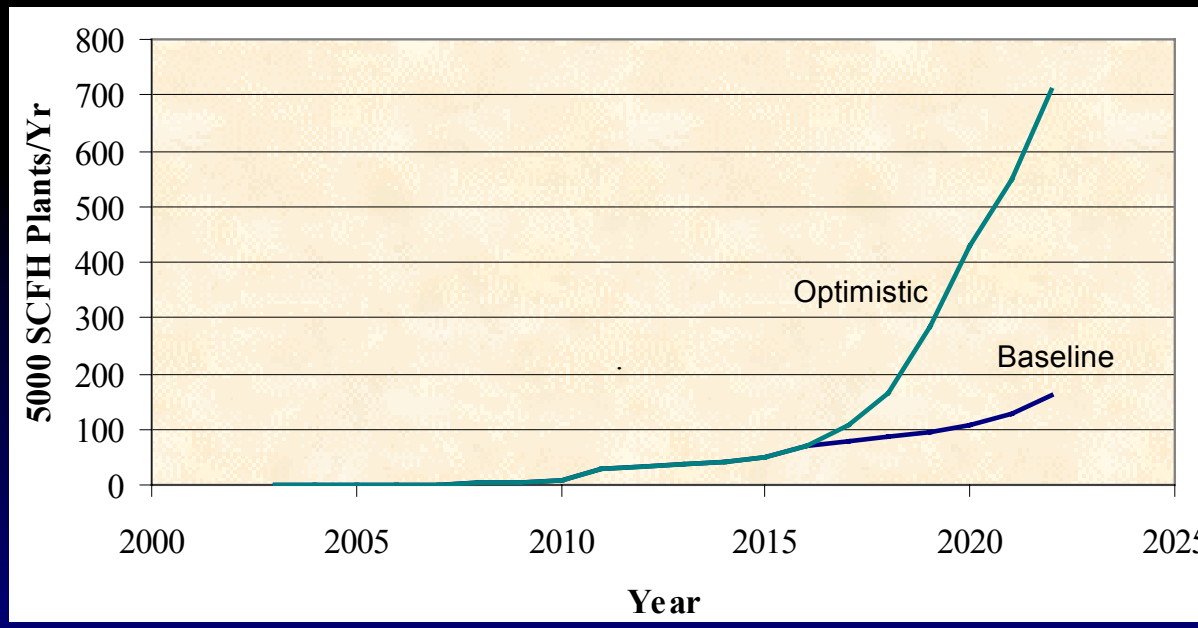
Market Projection

Praxair/ BP





- 25% market share to any one individual supplier
- Various size unit could be manufactured ranging from 1000 - 15,000 scfh
- Opportunity summary based upon an expected average size of 5,000 scfh
- Conservative estimates are used for each market sector



Business Case Analysis

- Assumed 6 year R&D Period
- Current:
  - Break even year: 17
  - NPV @10%: $6,000K
- Target:
  - 30% capital cost reduction with R&D
  - Break even year: 15
  - NPV @10%: $29,000K
- If larger hydrogen generation and dispensing units are mass produced, the $2.50/kg cost target can be met. Further R&D for 30% capital cost reduction can make the business model viable
- It is expected that it would require as long as 15 years to make the business profitable. Government legislation could help accelerate this

Further R&D & government legislation is required to make business model viable

Comments, Future Work, Acknowledgements

Last Year Reviewer Comments

- After all chemical reactions you get CO_2 16%, at 800C. However, not quite sure how this process progresses.
  - Included a slide with better explanation of chemical reactions. Data shown is with out CaO. CO_2 is lower if CaO is used.
- Is there enough data to scale up an ACR.
  - Easily scaleable. Practical experience in scaling from 30 kW to 100 kW to 150 kW

Future Work

- **Subsystem Testing: Test components on test stand & Catalysts in bench-scale**
- **Modify Economic Model to Match System Development**
- **Prototype Design**
- **Design for Reliability**

Acknowledgements

- **DOE: Mark Paster, Pete Devlin, Sig Gronich, Kathi Epping, Jill Jankouwski, Ron Fiskum**
- **CEC: Avtar Bining, Art Soinski, Mike Batham**
- **AQMD: Gary Dixon**
- **CARB: Steven Church**

Development of a Natural Gas-to-Hydrogen Fueling System

> DOE Hydrogen & Fuel Cell Merit Review

William E. Liss
Gas Technology Institute

May 2003

Cooperative Agreement DE-FC04-02AL67607

Hydrogen Fueling Systems

Problem Statement & Challenges

- Problem Statement
  - Making hydrogen competitive with gasoline on a $/vehicle mile basis
- Challenges
  - Flexible fuel reformers & systems
  - Fuel purity
  - Long-life compressors
  - Accurate dispensing
  - Capital outlay & return on investment

gti

Goals and Objectives

- Goals:
  - Distributed high-pressure hydrogen delivered at $2.50/kg or less to vehicle users
  - Avoid high costs for over-the-road hydrogen delivery
    - Leverage existing energy infrastructure
  - Leverage CNG technologies, products, and experience to extent practical
- Technical Characteristics:
  - 40-60 kg daily
  - 5000 psig fast fill system

gti

Program Participants

- Participants and Roles
  - Gas Technology Institute
    - Program manager, system integrator, fuel processing subsystem
  - FuelMaker Corporation
    - Maker of high-quality high-pressure compressors and fuel purification systems
    - Commercialization pathway
  - ANGI International
    - In-kind support on hydrogen dispensing
    - Commercialization pathway
- Cofunding from Canadian government

Project Plan and Approach

Program Duration 02/02 – 02/05	Phase I Design	Phase II Development/ Lab Test	Phase III Field Test/Dev.
	2/02-9/02	9/02–2/04	3/04–2/05
Fuel Reforming	8/2002	2/2004	2/2005
Fast Fill Testing	8/2002	2/2003	
Dispenser	8/2002	2/2004	7/2004
Compressor	8/2002	2/2004	2/2005
Purification	8/2002	2/2004	2/2005
Design/ Economics	8/2002	2/2004	2/2005

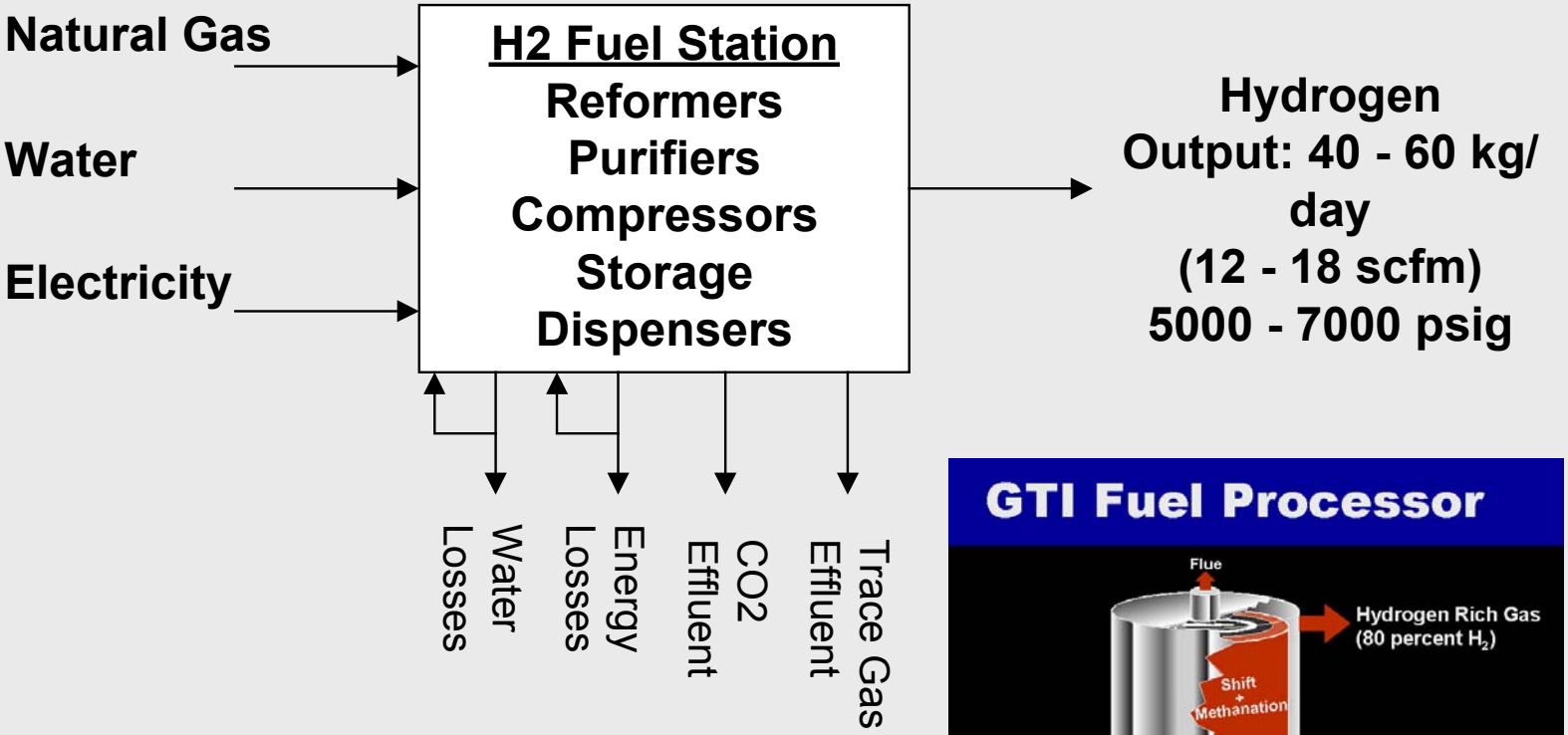
- Phase I completed and report submitted
- Fast-Fill characterization completed and reported
- Phase II development in process

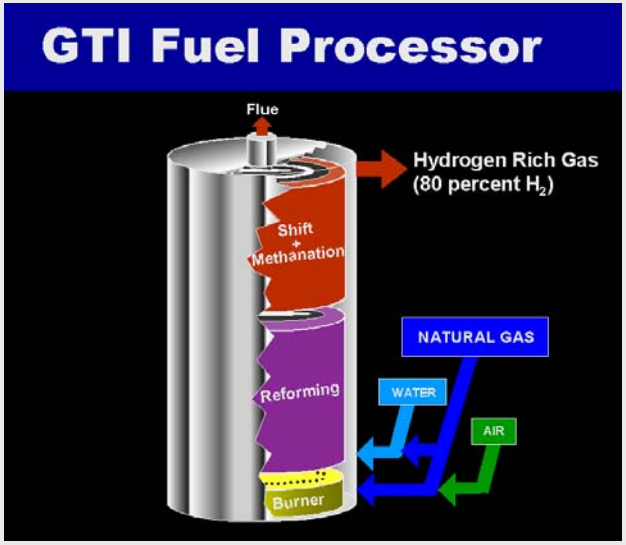
Program on schedule

Plan & Approach at a Glance

- Task 1: Fuel Reforming
  - Efficiency & turndown
  - Compressor/purifier interface
- Task 2: Fast-Fill Testing
  - Build SOA Test Facility
  - Refine CHARGE thermodynamic model
  - Conduct testing
- Task 3: H2 Dispenser
  - Component availability & cost
  - Metering and fill accuracy
  - Code & safety issues
- Task 4: H2 Compressor
  - Analytical design
  - Tribology & materials
  - Empirical testing
  - Reformer/purifier interface
- Task 5: H2 Purification
  - Adsorbent, membrane strategies
  - Reformer/compressor interface
- Task 6: Design & Economics
  - System design, model, and safety
  - System controls
  - Economic model

System Inputs & Outputs

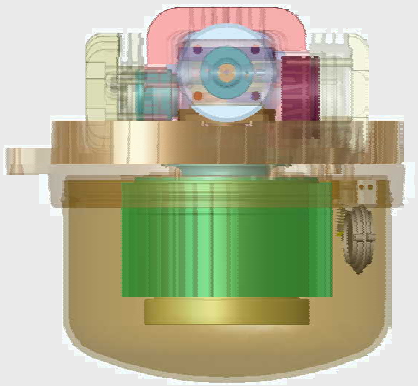




Steam Methane Reformer/Fuel Processor

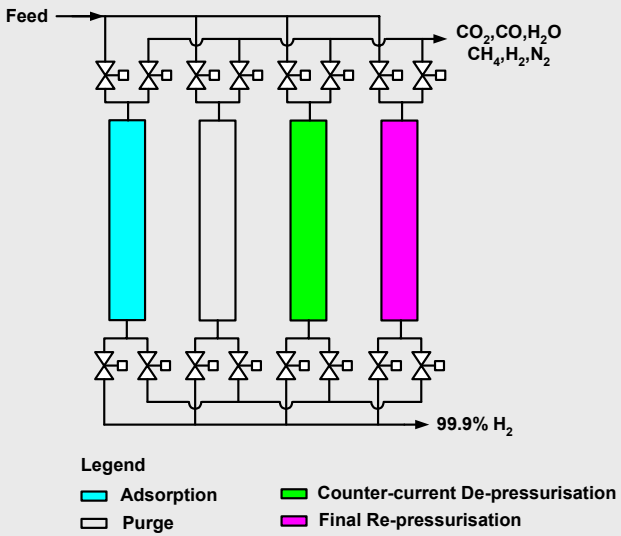
$$CH_4 + 2\,H_20 \leftarrow \rightarrow 4H_2 + CO_2$$

Some Keys to Success



Advanced oil-free high-pressure compressors

Compact fuel processing using efficient steam methane reforming process



Fuel cleanup systems that are cost effective, efficient, and meet fuel purity requirements

Reliable & cost effective hydrogen fueling system

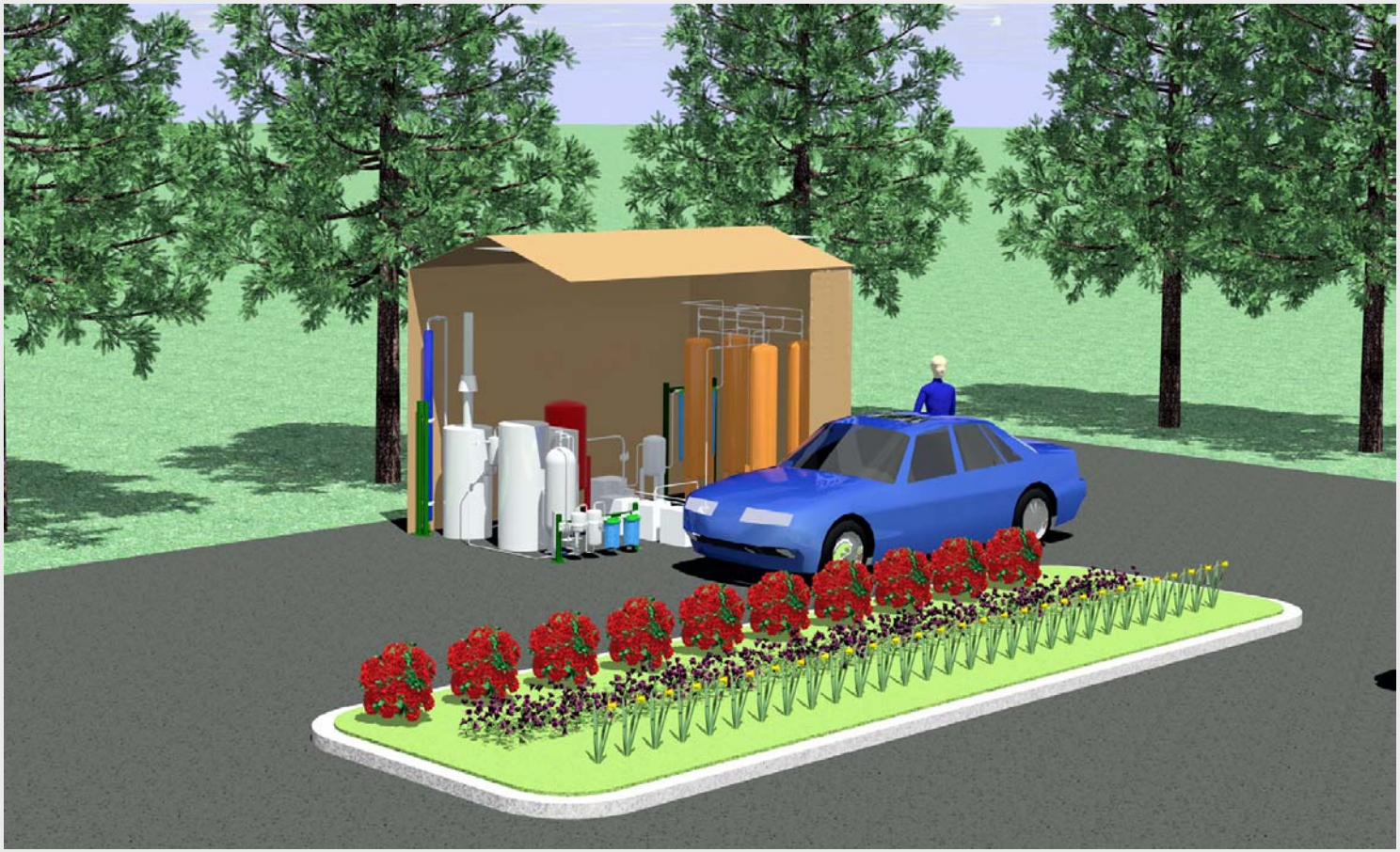
Accomplishments

- Comprehensive subsystem and system design report completed
- Lab prototype fuel processor designed and tested (alpha)
- Full-scale high-pressure hydrogen test facility constructed
- Hydrogen cylinder filling model developed (CHARGEH2)
- Comprehensive set of hydrogen fast-fill tests completed
  - Paper presented at National Hydrogen Assoc. meeting
- H2 dispenser algorithm developed (in test for validation)
- Primary hydrogen compressor designed and built (operate under 100 psig)
- Secondary compressors undergoing materials evaluation and long-term life testing (operate up to 7,000 psig)
  - Critical path item
  - Evaluating advanced metals, ceramics, and coatings
- System economic model developed
  - Paper presented at World Hydrogen Energy Conference

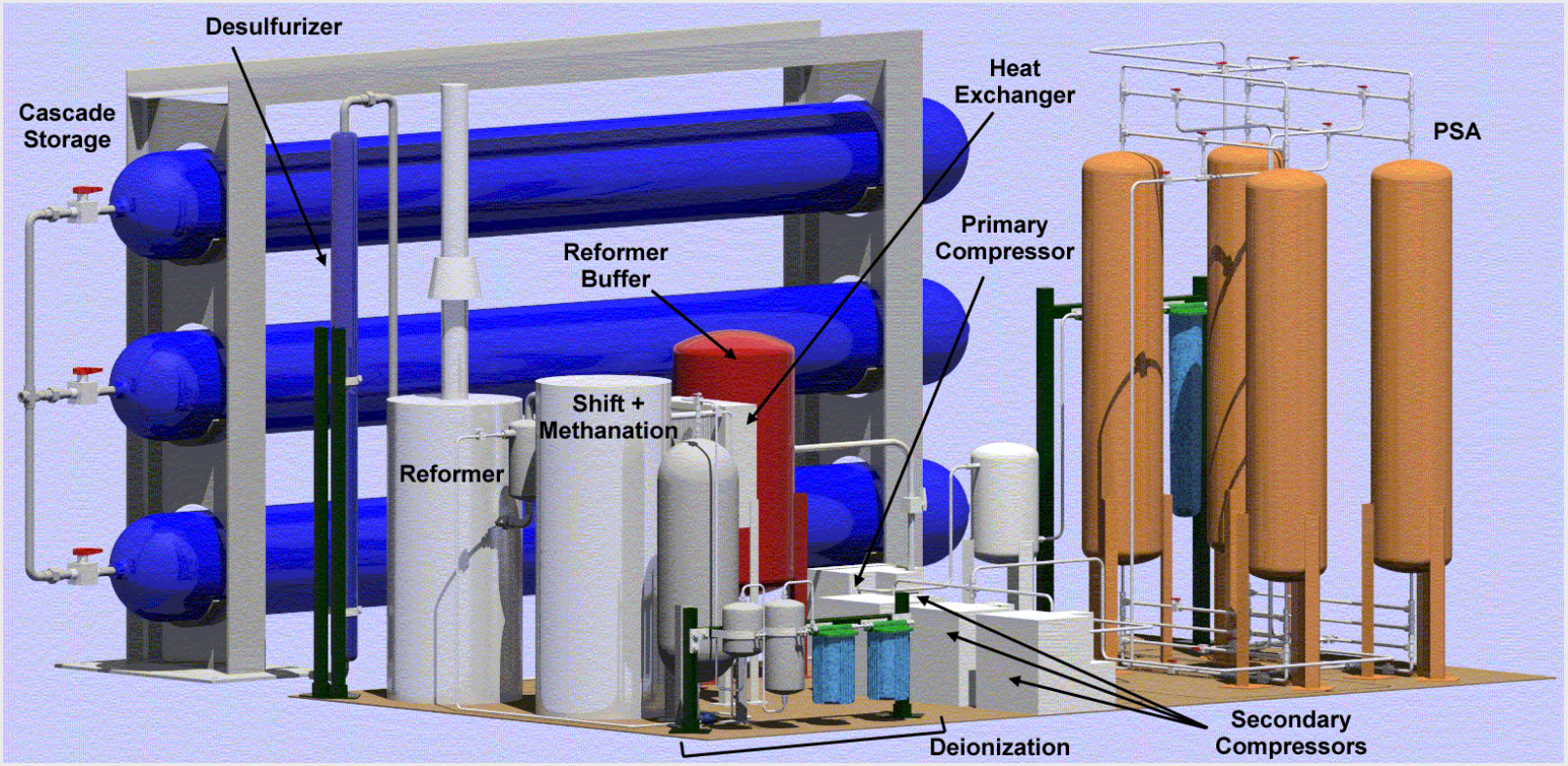
Accomplishments (cont.)

- Pressure Swing Adsorption (PSA) test facility constructed
- PSA tests underway to evaluate multi-component removal effectiveness
  - Documenting trade-offs with fuel processor in areas related to CO and methane
- Phase II Prototype - Alpha Integrated System Build
  - Building “front end” of system (“hydrogen generator”)
    - Test “front end” first, then “back end” with fuel purification and high-pressure compression
  - Steel skid procured and prepped
  - 2nd generation fuel processor subsystem procured (beta) and subsystem assembly underway
  - Natural gas & water treatment systems procured and being installed
  - Primary compressors procured and being installed
  - System controls procured

Natural Gas to Hydrogen Fueling System

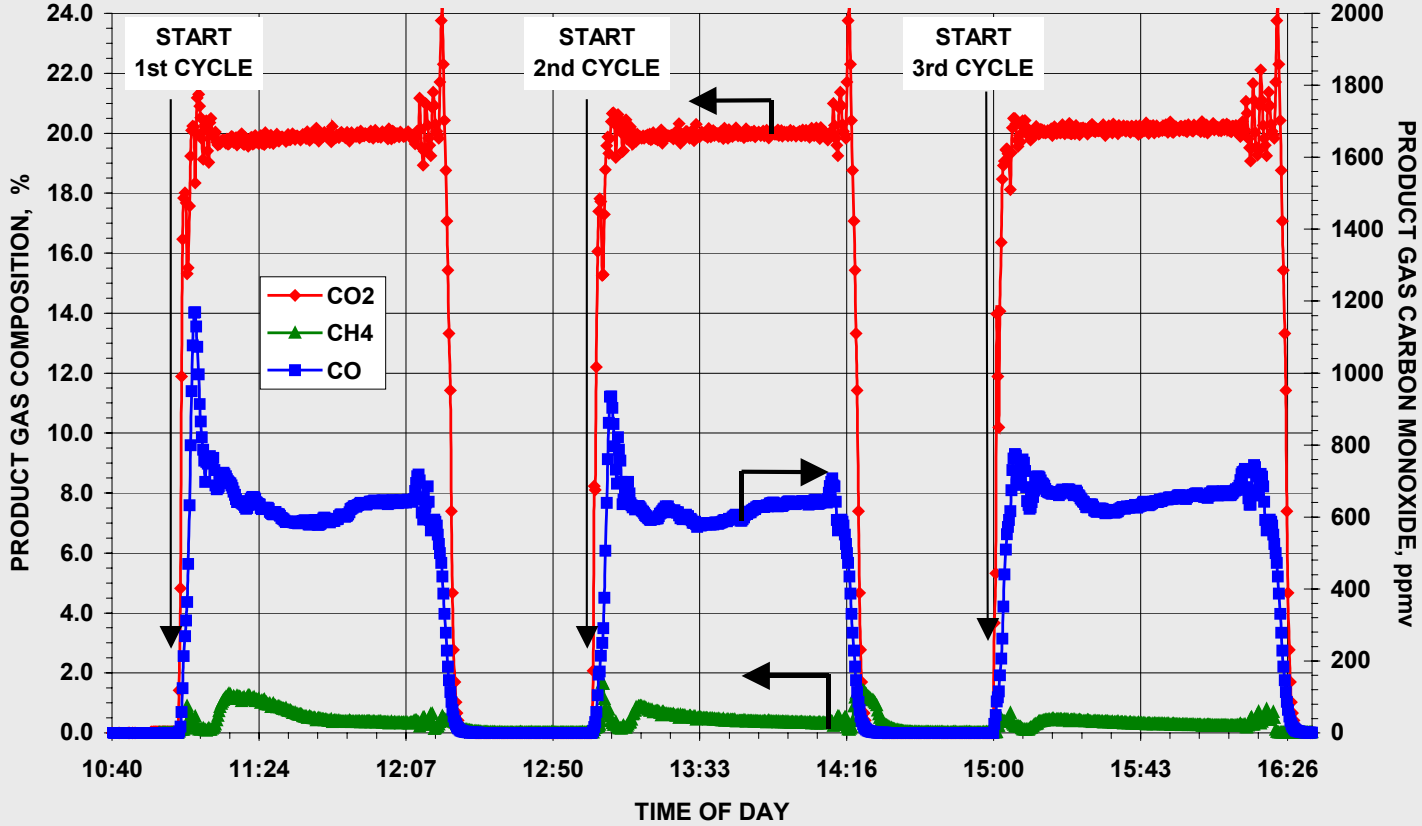


Preliminary Natural Gas to H2 Fueling Station Design



Further refinements underway to reduce size & cost

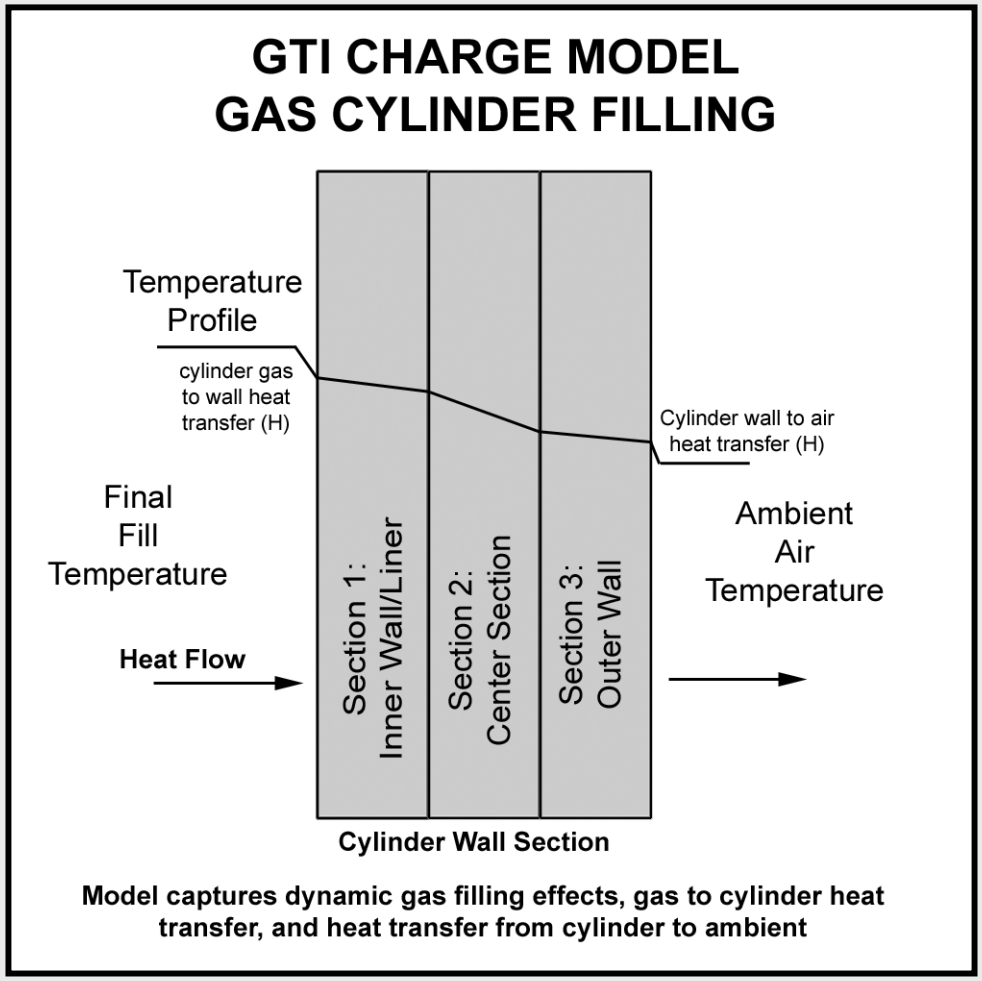
Fuel Processor Testing



Substantial testing done on start-up, ramping, shutdown testing of fuel processor to characterize dynamic response

GTI CHARGEH2 Model

- Characterizes dynamic fast-fill process
- Assess cylinders of different size & construction
- Various starting & ending fill conditions
  - Cylinders
  - Ground storage



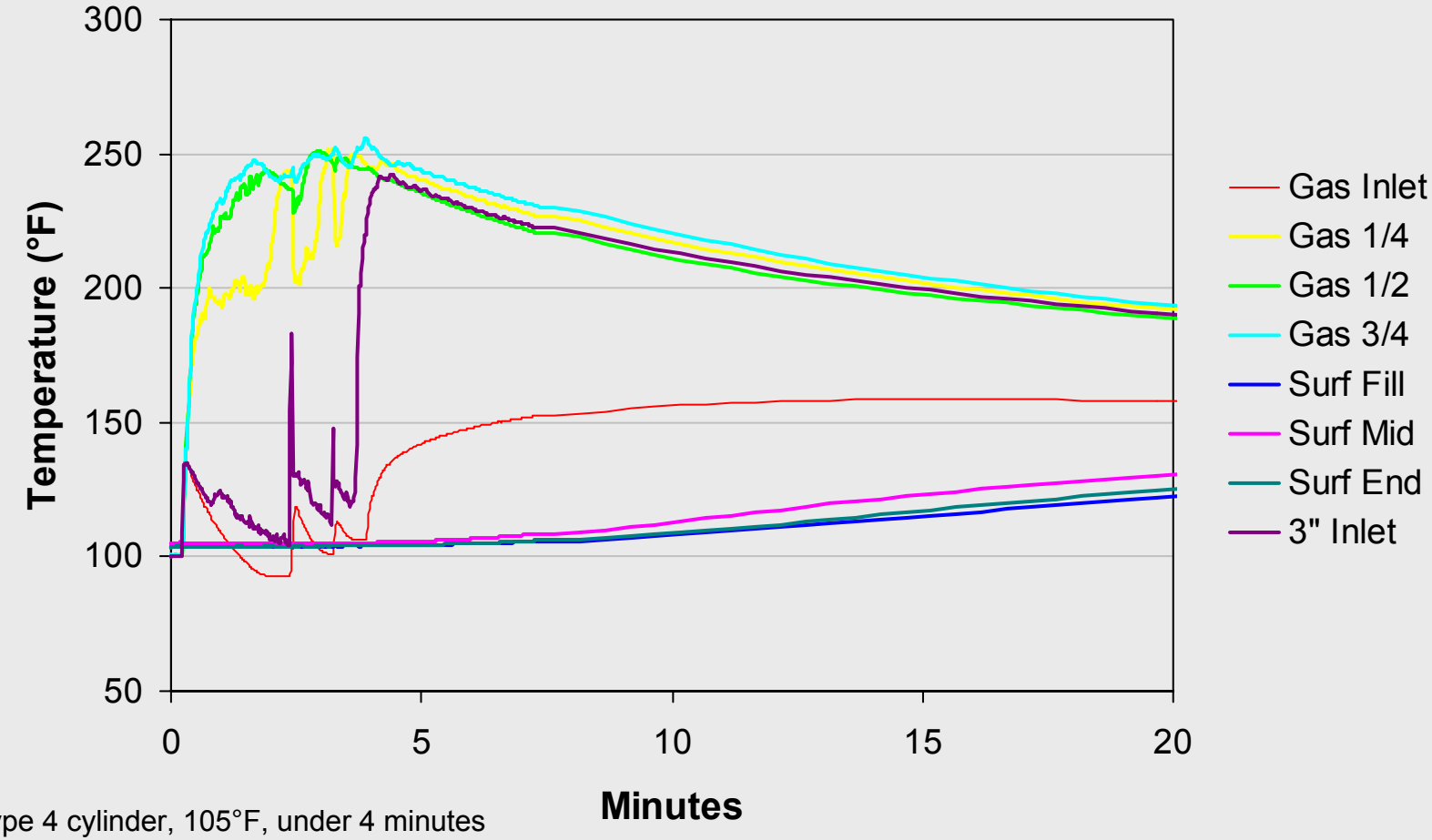
GTI High-Pressure Hydrogen Test Facility

- Full-scale, three bank, high-pressure hydrogen cascade
  - 7,000 psig
  - Expanding to 12,000 psig
- Wide temperature range
  - -50 to 160°F
- Fully instrumented with data acquisition
- Flexibility to run wide range of conditions

High-Pressure Hydrogen Environmental Chamber

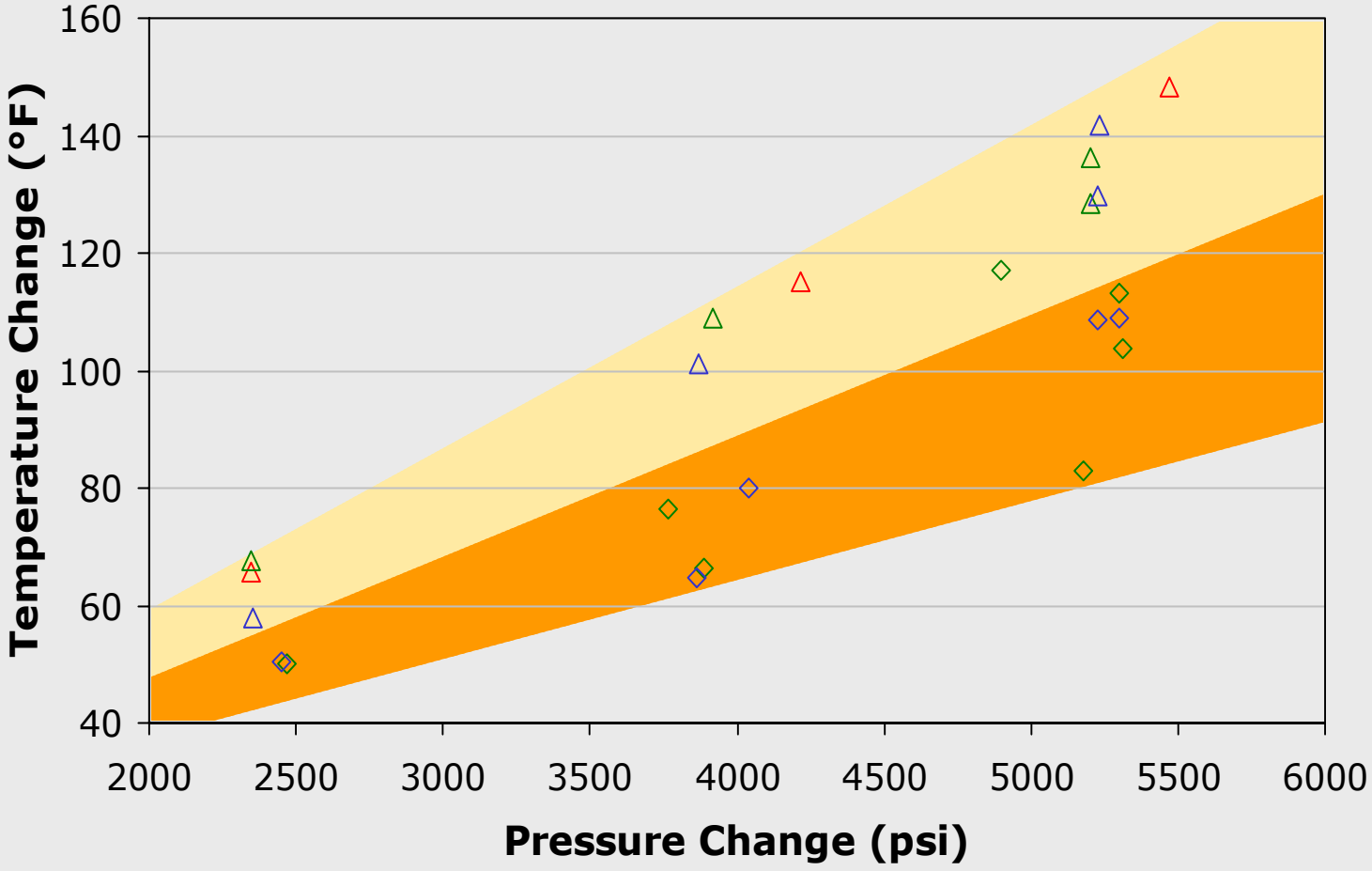
Hydrogen Cylinder Filling

> Substantial temperature variation documented



Type 4 cylinder, 105°F, under 4 minutes

Hydrogen Cylinder Filling Test Summary



Communication & Cooperation

Gas Technology Institute

- Founding Member - National Hydrogen Association
- Member - U.S. Fuel Cell Council
- DOE Executive Advisory Council for FreedomCAR
- Secretary - SAE Fuel Cell Standards Committee
  - Specific input to group on vehicle/dispenser interface
- International Code Council Ad Hoc Hydrogen Committee
- International Energy Agency Advanced Motor Fuels Annex
- U.S. TAG to ISO/TC 197 (ISO/CD 15869) and ANSI/NGV2 on hydrogen vehicle cylinder standards
- Technology exchange with several companies/organizations in U.S., Canada, Japan, China, India, and Europe
- **Presented on this work at various meetings:**
  - World Hydrogen Energy Conference (6/02), NHA Annual Meeting (3/03) SAE TOPTEC (4/03), SAE Gov-Ind Conference (5/03), others

FuelMaker Corporation

- NFPA committee on hydrogen fueling system fire safety codes

gti

Next Steps
Alpha Unit Implementation

- Complete build-up and testing of “front end” of alpha system in 2003
  - Fine tune system integration and controls
- Build “back end” of alpha system second half of 2003
- Target tests results from fully integrated alpha system by February 2004
- Identify improvements for Phase III
- Work with potential partners on field testing, commercialization, technology transfer

gti

Conclusions

- Significant thermal effects seen with hydrogen fast filling
- Meaningful variation in gas temperature exist
  - Various factors: cylinder design and materials, time of fill, ambient temperature, cascade pressure and temperature, etc.
  - Data indicate potential for large spatial internal gas temperature variation
- Intelligent pressure-based compensation algorithms are expected to be viable
  - Near 100% fill under most conditions
  - Implementation costs confined to fueling station
  - Compatible with approaches requiring additional vehicular equipment and communication

gti

National Renewable Energy Laboratory

Production and Delivery Analysis in the HFC&IT Program

Margaret K. Mann
National Renewable Energy Laboratory

Hydrogen and Fuel Cells Merit Review Meeting
May 19-22, 2003
Berkeley, California

Outline

- Market price of hydrogen today
- Purpose of analysis
- Types of analysis
- Analysis tools
- H2A
  - Objectives
  - Sub-groups
  - Activities
- Organizations

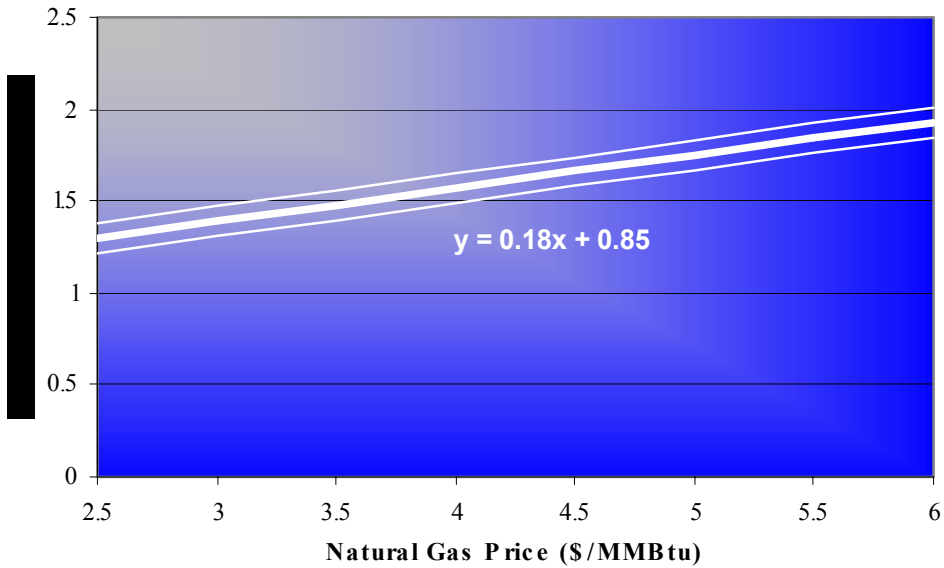
Market Value of Hydrogen Today

Source: Chemical Market Reporter, 2/24/03; Merchant H_2

- Between 1997-2002:
  - Compressed gas, tube trailer, plant-gate
  - Low: $5.3/kg (1997)
  - High: $11.0/kg (2002)
  - Steady upward trend
- Current:
  - Compressed gas, tube trailer, plant-gate: $7.2 - 11.0/kg
  - Cryogenic liquid, tanker truck, plant-gate: $4.9 - 7.6/kg
  - Compressed gas, pipeline, delivered: $0.8 - 3.4/kg

Source: SRI Chemical Economics Handbook, 2002, Captive H_2

- At $3.50/MMBtu natural gas, H_2 = $1.40 - 1.56/kg
- $0.63/kg H_2 is due to the natural gas; fixed cost = $0.77 - 0.93/kg
- At $5.00/MMBtu natural gas, H_2 = $1.67 - 1.93/kg
- No compression or storage



Analysis in the HFC&IT Program

- To support Program decision-making
- To help develop a balanced R&D portfolio
  - Part of project selection
  - Guide research toward key cost areas
  - Identify time-frames for near-, mid-, and long-term success
- To provide analytic basis for federal investment decisions
- To help quantify implications of policy
- To measure progress toward goals

Analysis Spectrum

Resource Analysis

–Where are the resources to make hydrogen and how much do they cost?

Technology Feasibility Analysis

–Which technologies have the greatest potential for economic success?

–Where should research efforts be focused?

–What are the impacts of production volume?

Environmental Analysis

–What are the environmental impacts of hydrogen technologies?

–What steps can be taken to reduce impacts?

Delivery Analysis

–What are the most economic options for delivering hydrogen?

Infrastructure Development Analysis

–What are the optimal scenarios for developing the hydrogen infrastructure?

–What will a hydrogen infrastructure cost?

Energy Market Analysis

–What is the hydrogen future?

–Which technologies are most likely to be a part of the hydrogen future, and what are the interactions between hydrogen and other energy carriers?

–What are the scenarios for hydrogen use in transportation and stationary markets

NREL

Analysis Tools

- Geographic Information Systems (GIS)
- Process modeling (e.g., ASPEN Plus)
- Fuel cell modeling (e.g., ADVISOR, PSAT)
- Cash flow analysis
- Life cycle assessment
- Delivery modeling
- Energy market modeling

Hydrogen Analysis - H2A

- Lack of transparency and consistency make comparison of the numerous studies difficult
- Collective group of analysts doing hydrogen-related work in production and delivery
- Purpose: *Improve the transparency and consistency of approach to analysis, improve the understanding of the differences among analyses, and seek better validation from industry.*
- *Two meetings: February in D.C., April in Golden*
- *Next meeting: July in D.C.*
- Lead: Mark Paster, DOE

H2A Objectives

1. Establish a **standard format for reporting** analysis results for improved transparency and ease of communicating analysis results in a short yet detailed fashion.
2. Seek better validation of public analyses: **dialog with industry**.
3. Better **demand analyses** and factoring demand into supply/ infrastructure analysis interactively.
4. Better **understanding of the differences** among current and publicly available analyses and make these differences more transparent.
5. Establish a **mechanism for facile dissemination** of all public analysis results.
6. **Improved understanding of the purpose** of hydrogen production and delivery analyses and identify analysis gaps.
7. Try to reach consensus on **specific analysis parameters** (or at least ranges, or a reference case).

H2A Sub-groups

Central production:
- Coal
- natural gas
- biomass

Forecourt production
- Dispensing
- small-scale natural gas reforming
- on-site electrolysis
- liquid carrier reforming

Other production
- central thermochemical nuclear
- central electrolysis
- wind/solar
- photobiological

Delivery
- pipelines (existing and new)
- gas truck
- liquid truck

H2A Current Activities

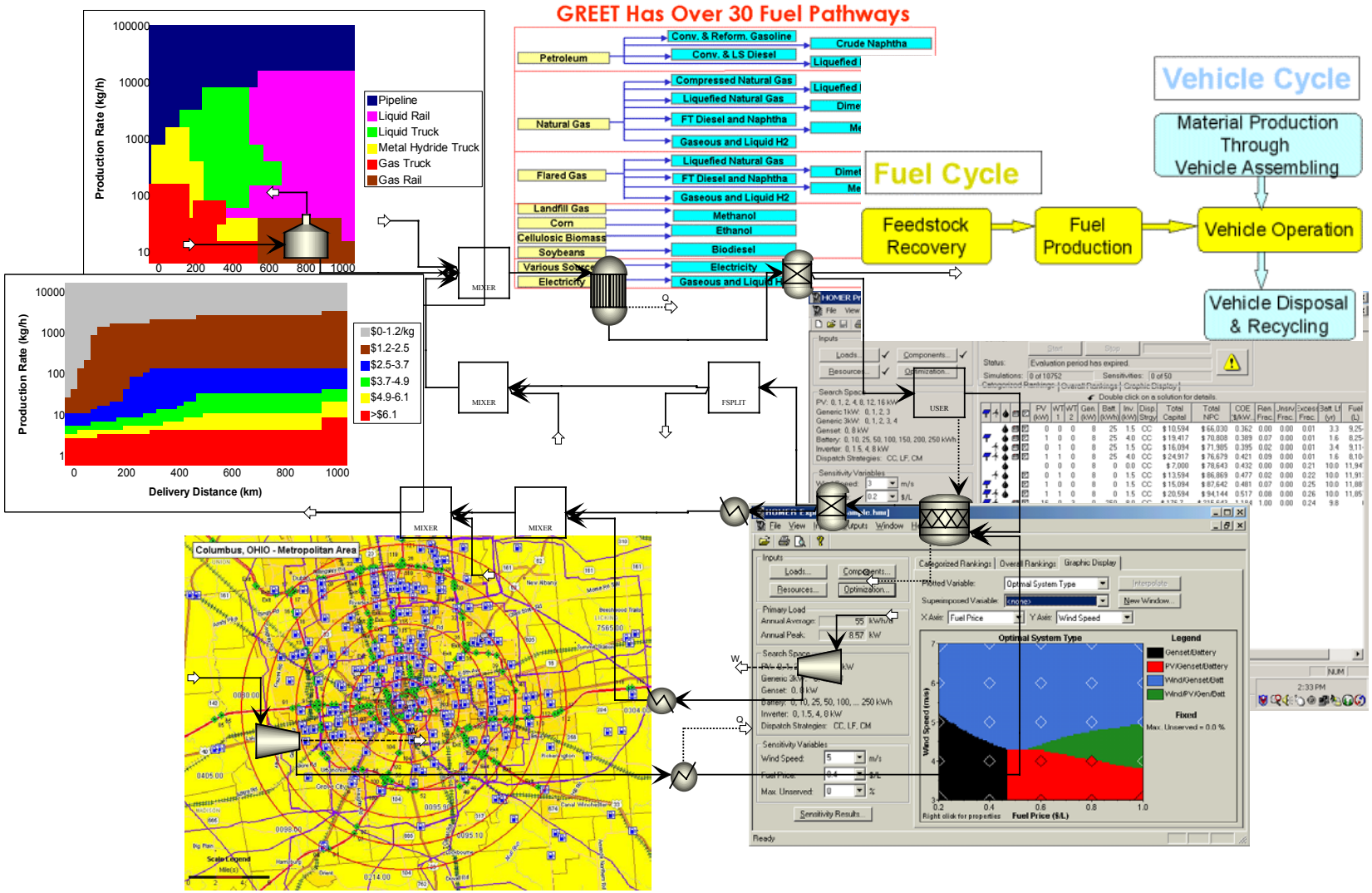
- Deliverables:
  - July: Reporting spreadsheets finalized
  - July – November: Subgroups develop case summaries
  - November: Industry comment on case summaries
  - January: Analysis conference
  - February: Publish case summaries
- Reference case parameters
  - Discount rate (internal rate of return, hurdle rate)
  - Debt / Equity and cost of debt
  - Tax
  - Plant life
  - Depreciation schedule
  - Plant decommissioning

Organizations

- Department of Energy
- Argonne National Laboratory
- Directed Technologies, Inc.
- Energetics
- Gas Technology Institute
- Industry Hydrogen Infrastructure Group (IHIG)
- Mitretek
- National Renewable Energy Laboratory, NREL
- Oak Ridge National Laboratory
- Princeton University, Joan Ogden
- Tellus Institute
- TIAX
- TMS

Seeking the involvement of industry to achieve objectives

Analysis Output Examples



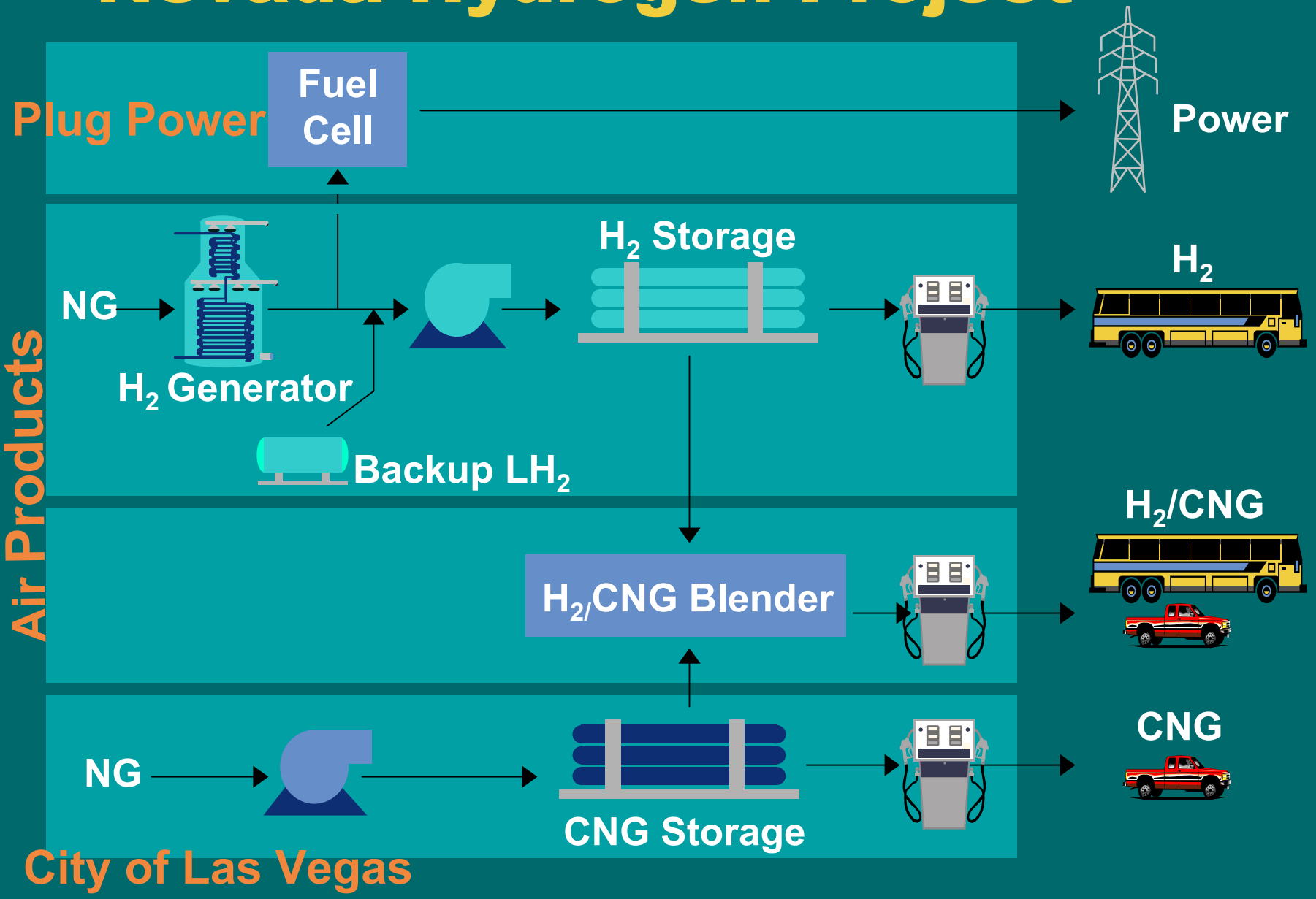
H_2 Reformer, Fuel Cell Power Plant, & Vehicle Refueling System

Venki Raman
Air Products and Chemicals Inc.
Allentown, PA

William Ernst
Plug Power Inc.
Latham, NY

2003 Hydrogen and Fuel Cells Merit Review Meeting
Berkeley, CA
May 22, 2003

Nevada Hydrogen Project



Goals and Objectives

- Develop & demonstrate small, on-site H_2 production for fuel cells and H_2 fuel stations
- Design & install multipurpose vehicle refueling station to dispense H_2/CNG blends, and pure H_2
- Develop & install H_2-fueled stationary 50kW fuel cell
- Evaluate operability/reliability/economic feasibility, of integrated power generation and vehicle refueling designs
- Expand the current facility to serve as the first commercial facility when sufficient hydrogen demand develops.

Relevant DOE Program Objectives

- Reduce dependence on foreign oil
- Promote use of diverse, domestic energy resources
  - Natural gas reformation
- Develop and demonstrate distributed hydrogen generation technology …

Milestones

LH_2-based Fuel System On stream	July 2002
Scale-up H_2 Generator On stream	Aug 2002
Initial Startup of Fuel Cell	Aug 2002
Dedication Ceremony	15 Nov 2002

(FY 2003 Major DOE program accomplishment)

H_2 Generator & Fuel Cell

Fueling Station

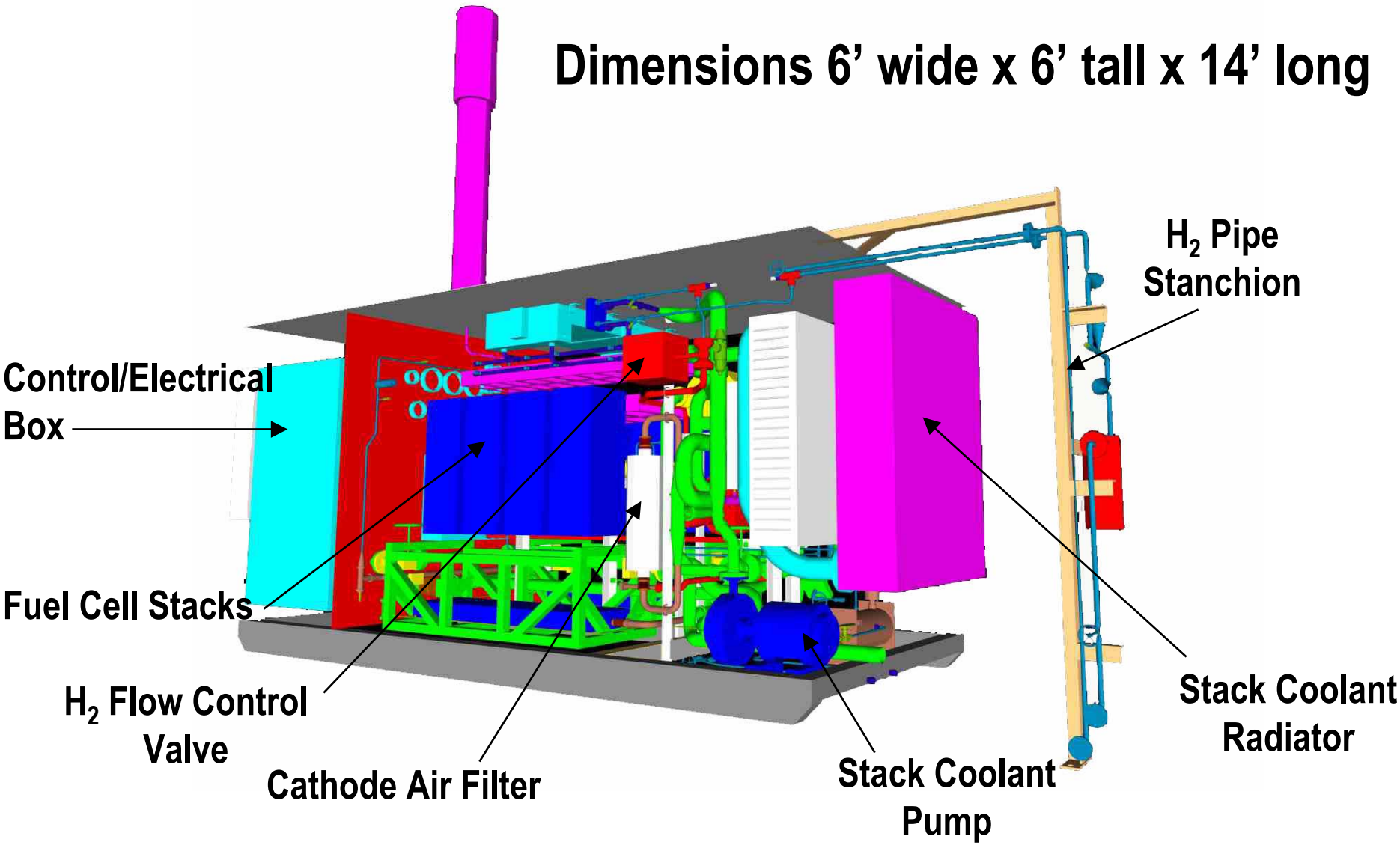
Status of Progress - H_2 Generator

- Excellent process operation and product purity of 99.95+% demonstrated
- Turn-up and turn-down of hydrogen production to accommodate varying demand by fuel cell and fuel station achieved
- Remote operation (using Enterprise remote asset monitoring) from any location
  - Currently from AP sites in Sacramento and Allentown, PA
- Performance evaluation in-progress
- Approximately 2200 total hours run time

Status of Progress - Fuel Station

- Fueling demand integrated with site wide operational controls allows for automated operation.
- CNG/H2 and H2 Fuel Dispensing successfully performed on test fill tank, CNG/H2 ICE vehicles and H2 Fuel Cell vehicles.
- Fuel dispensing integrated with City of Las Vegas fuel accounting system.
- Limited fueling demand at this time.
- CLV vehicle fleet establishment in progress; more demand for fueling expected in future.

Plug Power 50 kW Fuel Cell



Status of Progress - Fuel Cell

- Initial Startup - Aug 2002
  - Initial operational issues identified and addressed.
  - Identified two hardware design issues; scanner cards and drain valves.
- Dedication Ceremony Operation- November 2002.
- Hardware changes operational - April 2003.
  - Scanner cards redesigned and installed.
  - Water drain valve approach modified.
- Operational issues with cell voltage falloff prevented continuous operation.

Status of Progress - Fuel Cell

- Engineering team on site 4/30 to continue to evaluate root cause and develop options to place unit in operation.
- Design approach of multiple stacks with no ability to independently manage gas flows, temperature, humidity and power challenging
- Excellent list of lessons learned compiled. Additional lessons learned from PlugPower single stack 5 KW systems combined in future designs.
- Unit successfully ran 3 days with trip by reformer. Restarted successfully and ran another 3 days with trip due to low voltage stack
- Stack will be replaced week of 5/27 and restarted
- Current performance indicates near term target of 2 - 3 months operation will be met with minor tweaks.

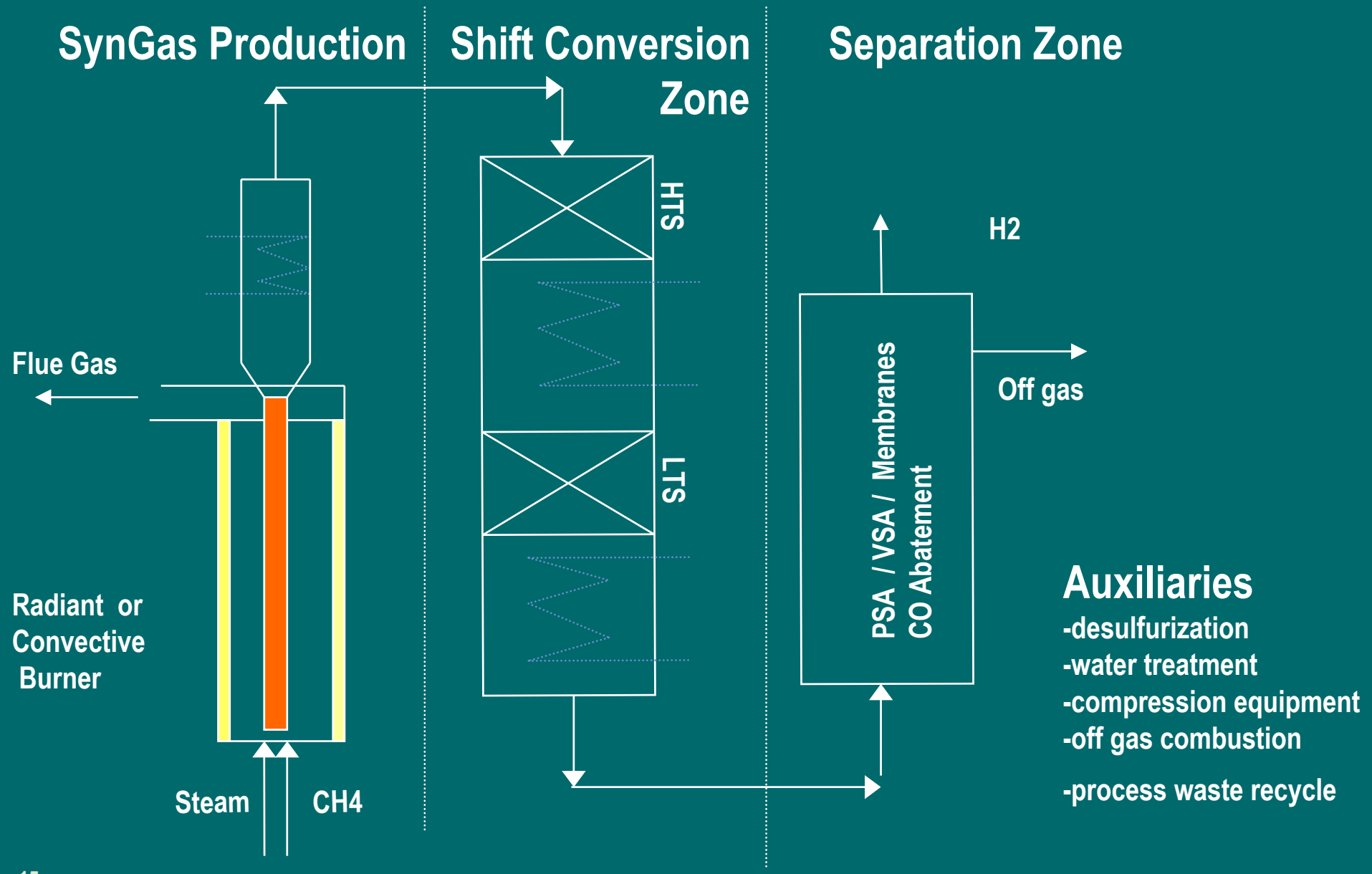
Future Work

- Begin extended unattended operation of Fuel Cell Power Generator - June 2003
- Achieve extended integrated run of H2 Generator and fuel station - June 2003
- Ongoing collection of site performance data to assess overall operation of the system - May - Nov 2003
- Vehicle fleet buildup will add 6 CLV H_2/CNG buses, and various light duty vehicles (dependent on external effort) - May 03 - May 04

Status of Business Plan & Safety Review

- Business plans to follow installation and routine operation of the integrated systems
  - Partners are interested in total integrated system as well as individual components
- Safety is top priority in design, construction and operation
  - Process & Design HAZOPs conducted on components
  - All safety and industry codes are addressed in designs
  - Air Products' 40 years of experience in commercial H_2

Traditional SMR

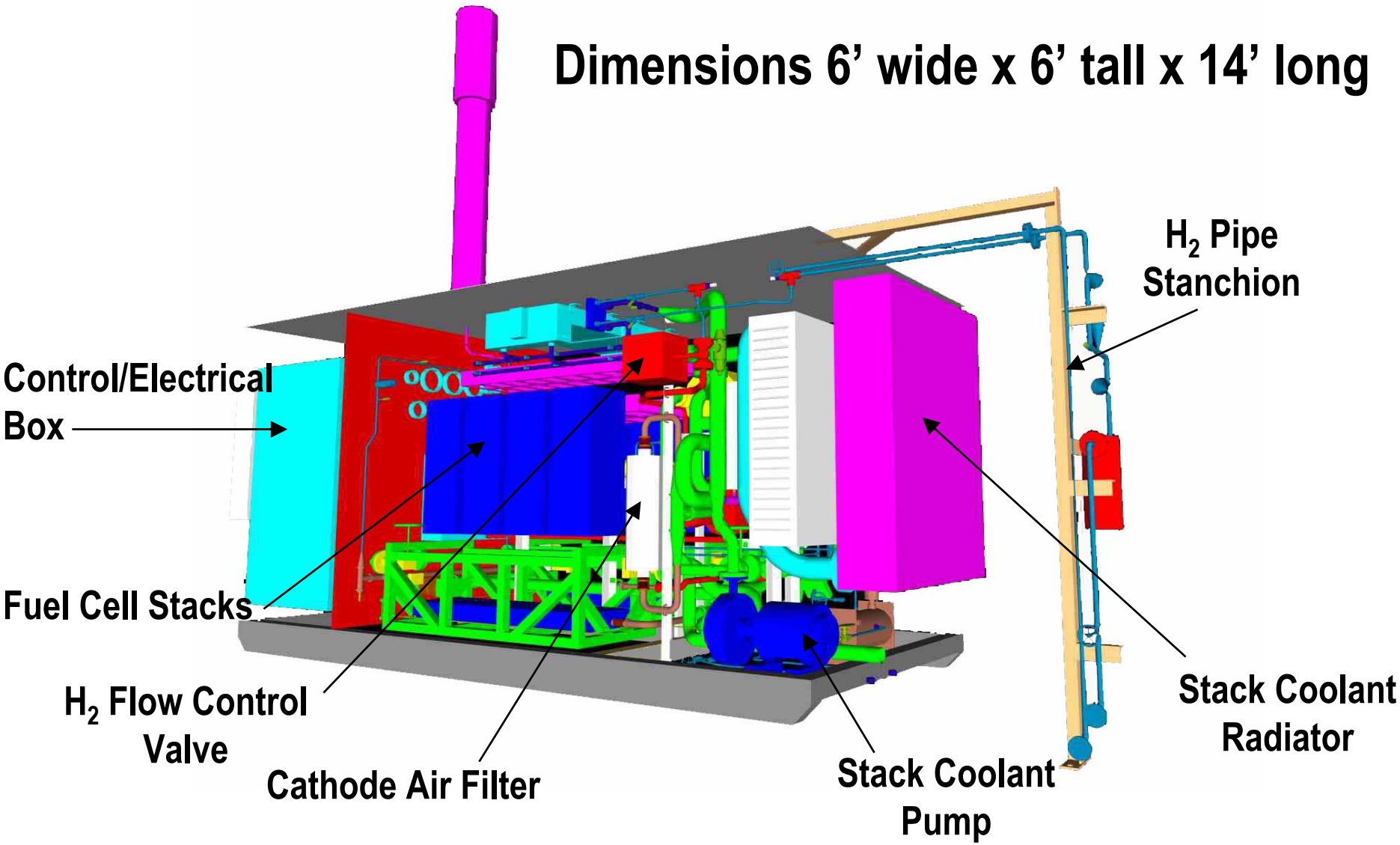


Auxiliaries

- -desulfurization
- -water treatment
- -compression equipment
- -off gas combustion
- -process waste recycle

Harvest SMR – Container Internals

Plug Power 50 kW Fuel Cell



Projected H_2 Demand

Project Phase & Date	Hydrogen Applications	H_2 Demand SCFD	Proposed Hydrogen Supply Approach
Phase 1 May 2002 - Jun 2002 Initial Fuel Station Startup	1 - 3 H_2/CNG Light Duty Vehicles (LDVs) 1 H_2 Hybrid Elec. bus 1 H_2/CNG Bus by CLV for testing beginning Jan 2001.	1,000 - 3,000	LH_2 to supply vehicle fueling initially.
Phase 2 Jun 2002 - Dec 2002 Vehicle Fleet Buildup	6 - 11 H_2/CNG LDVs 1 H_2 Hybrid Elec.bus 2 - 6 H_2/CNG Buses 50kW Fuel Cell @ 25 - 50% rate	3,000 to 15,000 3,000 to 15,000	H_2 Generator Prototype (17,000 SCFD) will supply H2; Liquid H_2 is used as backup/peak shave. Fuel Cell balances H2 Gen. Production
Phase 3 Jan 2003- Sept 2004 Full Station Operation	6 H_2/CNG Buses 11 - 20 H_2/CNG LDVs 1 H_2 Hybrid Elec Bus 50kW Fuel Cell @ full rate	54,000	Commercial H_2 Generator (65,000 SCFD) will supply H2 as bus fleet buildup achieves targets.

NV Hydrogen Program Projects Initiated in FY99

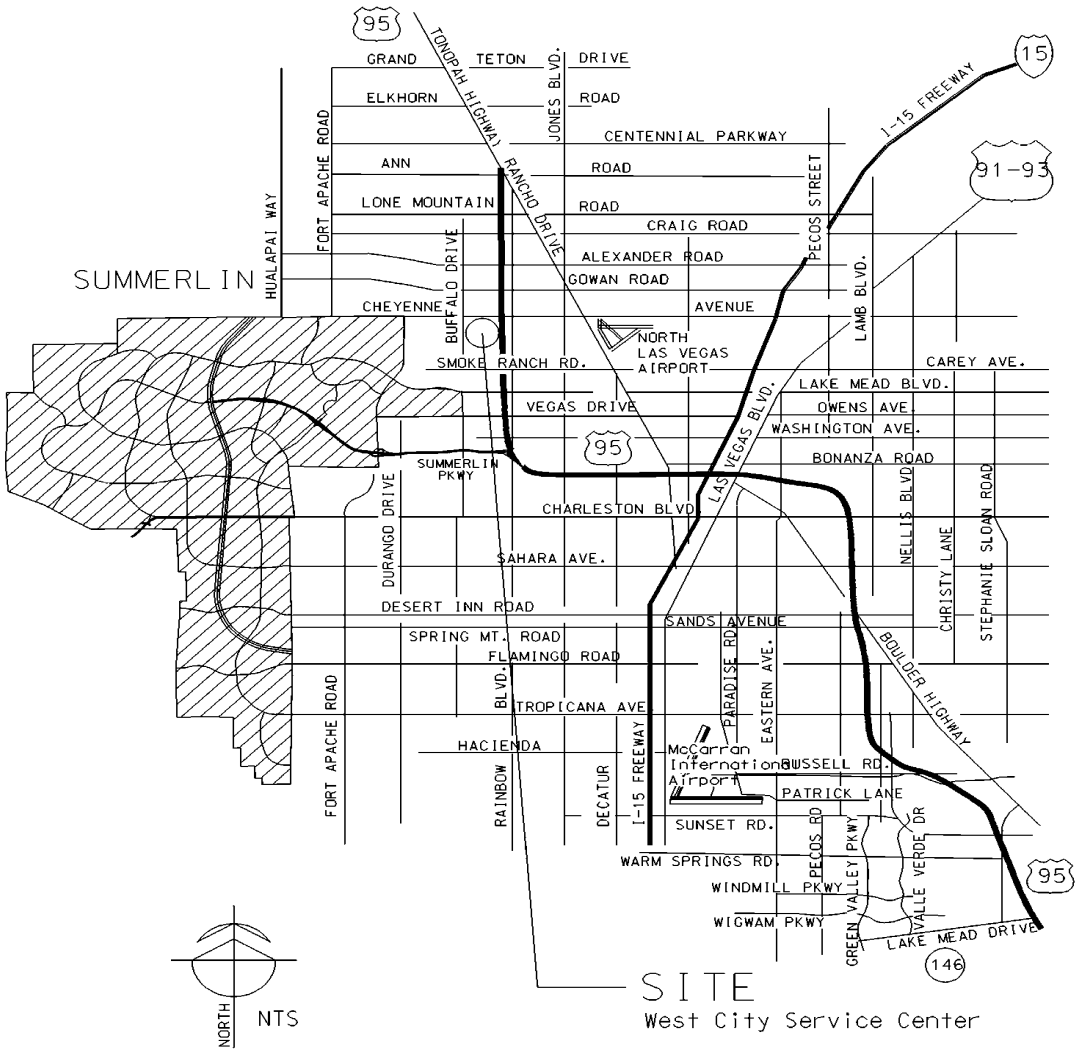
- Hydrogen Reformer, Fuel Cell Power Generator, and Vehicle Fueling System Project: Develop & demonstrate cost effective hydrogen/electricity co-production system.

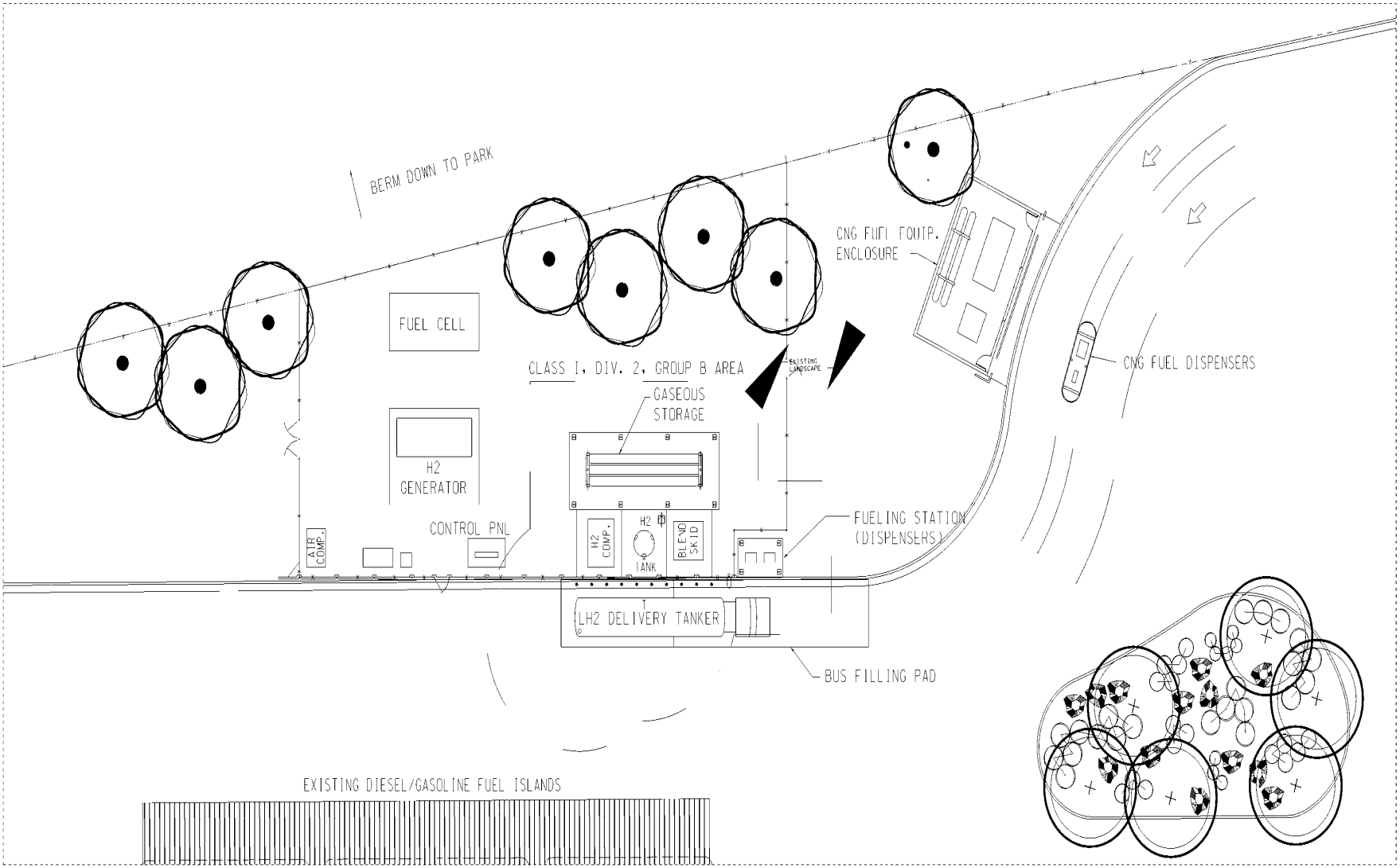
- Hydrogen-Enriched Light-Duty Vehicle Fleet Project: Achieve Equivalent Zero Emission Vehicle (EZEV) levels for combined NOx and CO.

- Hydrogen-Enriched Natural Gas City Bus Fleet Project: Demonstrate a 75% emissions reduction in heavy duty engine, mass transit application.

- UNLV H2Fuel Bus Evaluation and Upgrade Project: Develop a hydrogen transportation system demonstration platform.

VICINITY MAP – LAS VEGAS





ENLARGED PLAN - HYDROGENATED FUEL SITE & CNG FUEL SITE

Scale: 1" = 20' 0"

Hydrogen – Natural Gas Vehicles

- Heavy Duty Engine Development and Vehicle Demonstration Project
  - Retrofit up to six, 33 passenger, dedicated natural gas buses for CLV service
  - Range = 200 + miles
  - 75% reduction below EPA 1998 Heavy Duty Emission Standards

Hydrogen – Natural Gas Vehicles

- Light Duty Engine Development and Vehicle Demonstration Project
  - Convert up to 18 F-150 trucks to operate on Hydrogen enriched natural gas
  - Place in service with CLV
  - Emissions meet or exceed 2003 CARB Super Ultra Low Emission Vehicle Standards

Candidate Fuels for Vehicle Fuel Cell Power Systems: Stakeholder Risk Analysis

Work in Progress

2003 Hydrogen and Fuel Cells Merit Review Meeting

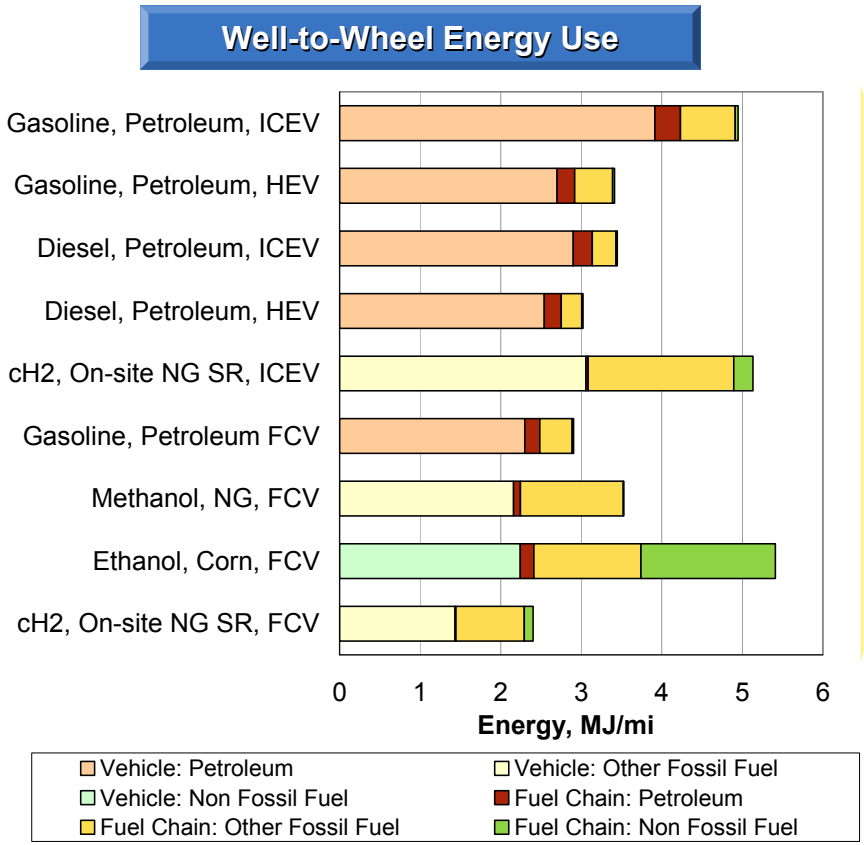
Berkeley CA

May 19-22, 2003

TIAX, LLC
Acorn Park
Cambridge, Massachusetts
02140-2390

TIAX Ref: D0035
DOE Ref: DE-FCO4-02AL67602

Fuel cell vehicles (FCV) could result in significant environmental and other benefits by way of improvements in fuel economy and energy diversity.



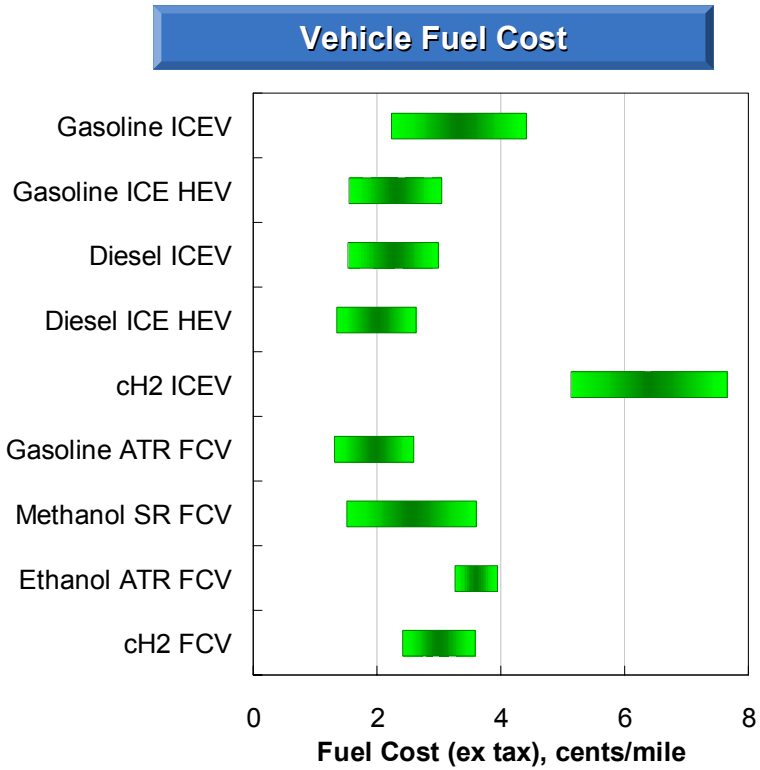
Potential Benefits

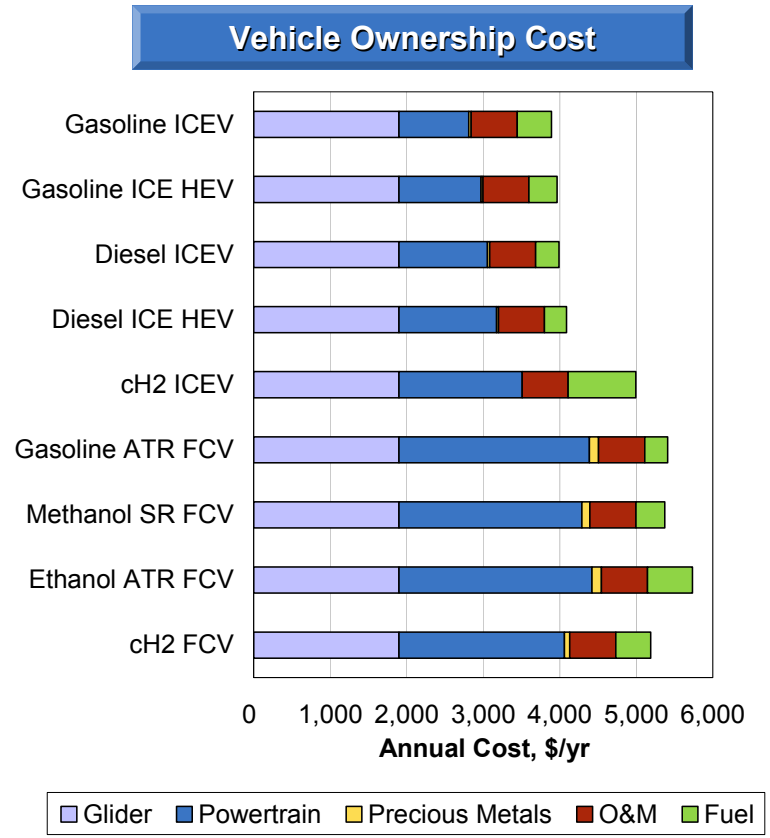
- Energy security
- Energy use reduction
- Greenhouse gas (GHG) and other emissions reductions
- Other health and environmental impacts

Legend: ICEV = internal combustion engine vehicle, HEV = hybrid (battery/ICE) electric vehicle, NG SR = natural gas steam reformer

Compressed hydrogen (cH_2) could provide the largest energy use and GHG emissions benefits of all the FCV options.

An earlier study indicated that long-term operating costs for FCVs could be competitive with conventional vehicles...





Note: sensitivity is based on historical feedstock variability, not vehicle performance (i.e. fuel economy) uncertainties

Legend: ATR = autothermal reformer, SR = steam reformer, O&M = operation and maintenance

… but that ownership costs are much higher due to high vehicle purchase costs.

In addition, there are significant technical and market uncertainties that could result in transitional risks for the introduction of FCVs.

Technical Uncertainties	Market Uncertainties
• Fuel economy • FCV and fueling equipment life • Refueling time/convenience • Performance under extreme conditions	• Fuel infrastructure development (coverage) • Future fuel prices • FCV price premium • Subsidies/taxes • Supply chain (natural gas, materials)

- Technical and market uncertainties translate into investment risk to one or more stakeholders (e.g. car manufacturers, energy companies)
- Types and magnitude of risks vary amongst fuel options
- DOE needs to understand the risk trade-offs between different fuel options in order to properly guide and support appropriate research and development

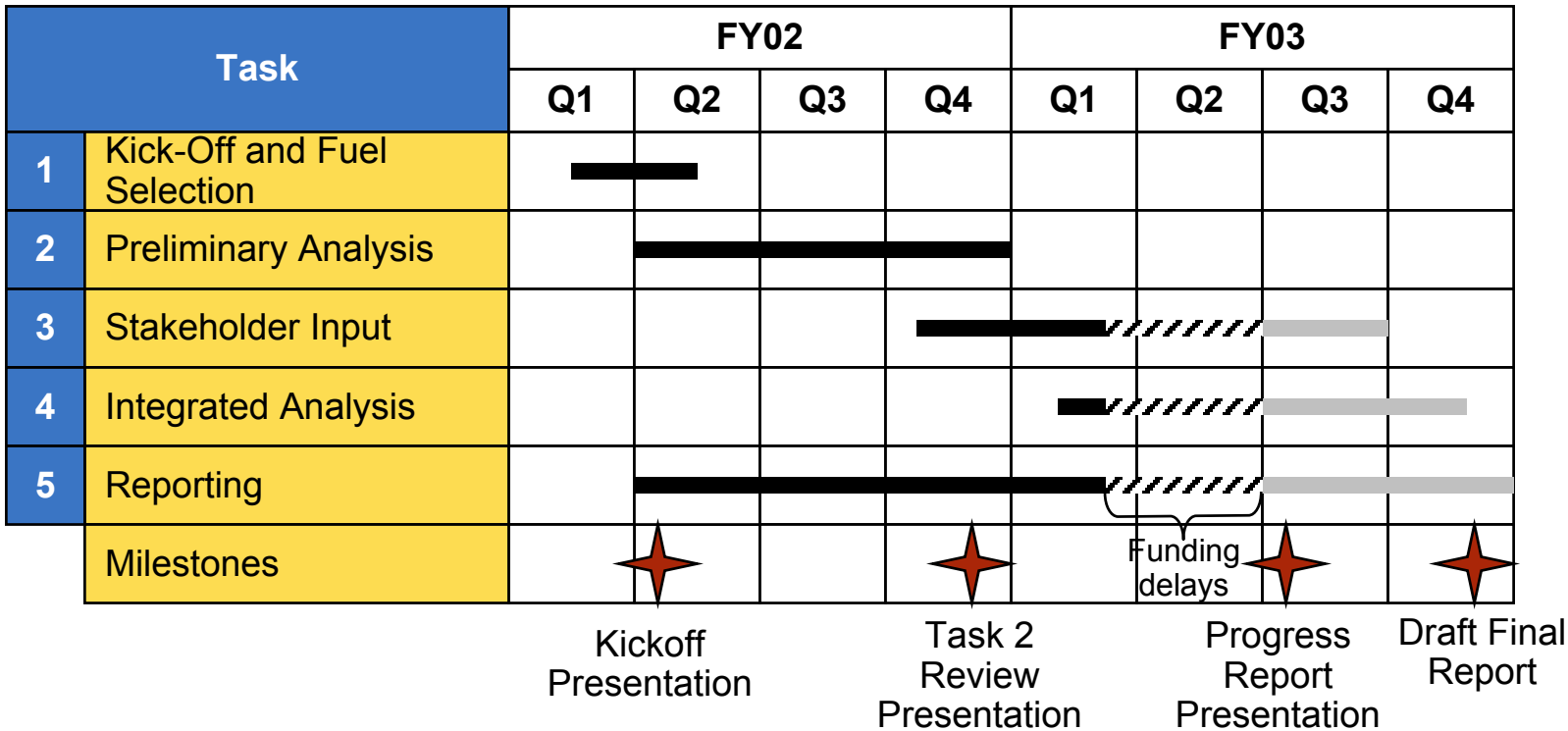
The topic of this report, and of most interest currently, is the uncertainty and risks associated with transitioning to a hydrogen infrastructure.

- Owners of alternative fueled FCVs will expect to pay about the same (or less) as fueling with gasoline today
  - Especially if they pay a premium for the vehicle
- Hydrogen will not likely be cheaper than gasoline in the early years
  - Initial costs per production plant and fueling station will be high
    - Low production volumes can't take advantage of economies of scale
  - Utilization of fueling stations (capacity factors) will be low early on - owners of hydrogen fueled vehicles will demand coverage
- FCV developers face large financial risks if they invest in fuel cell technology and the fuel infrastructure is not acceptable to FCV owners
  - Coverage must be above a minimum level - is it 10%, 50%?
- Similarly, energy companies and fuel distributors face large financial risks if they build a hydrogen fuel infrastructure and FCVs do not take off
  - Or another fuel dominates the market
  - They depend on the FCV developers to make the technology attractive (e.g. dependable, fuel efficient, competitively priced)

The motivation of this study is to facilitate the commercialization of fuel cell vehicles by understanding the risk surrounding fuel choices.

- Assess potential benefits and risks of various FCV and fuel choices, specifically compressed hydrogen
  - Compare the financial risks of direct hydrogen with onboard reforming
  - Characterization of the transition period
- Assess impact on various stakeholder and how risks could be shared and minimized
  - Identify key barriers and possible development paths
- Determine what range of factors might trigger the introduction of FCVs (e.g. oil price increase, carbon taxes, FCV cost reduction)

Prior to finalizing our analysis, we intend to obtain input from a range of potential stakeholders in both conventional and hydrogen fuel chains.



- The work to date has been slowed due to funding delays, but we are on schedule to finish by the end of this fiscal year
- We are about 60% through the total budget

We will evaluate the economic and other risks of alternative fuel introductions, particularly hydrogen.

- We will focus on financial risks due to the introduction of:
  - Hydrogen infrastructure
    - Central and local hydrogen production from natural gas (near-term)
  - The financial risks for other alternative fuel chains and the fuel cell vehicles themselves will be considered at a high level
- Perform analysis in the context of:
  - Discounted cash flows (i.e. “time value of money”)
  - Improvement of cash flow over time based on FCV introduction scenarios
- Analysis will include:
  - Characterization of financial, safety, environmental, and technical risks
  - Impact on current fuel production and distribution infrastructure
  - Feedback from stakeholders (car makers, technology developers, energy companies, fuel distributors, government)
  - Identify how risks might be shared and minimized

Likely hydrogen and FCV introduction scenarios are inputs to net present worth calculations that will be used in support of an issues analysis.

- A hydrogen infrastructure introduction analysis will be used to determine hydrogen fueling station buildup
  - Using DOE FCV introduction scenarios for hydrogen demand - not a market model
  - Regional buildup analysis to estimate station capacity factors over time
- Net Present Worth (NPW) will be used to compare financial investments for various options with business as usual (gasoline ICEVs)
  - Both FCV and fuel infrastructure investments
  - Equipment cost reduction with higher production volumes using progress ratios
  - Hydrogen revenue increase with fueling station utilization (capacity factors)
- Overall financial risk will be sum of NPW from all stakeholder groups representing net cost to the nation
  - Risks depend on volume, timing, performance assumptions, etc.
- The NPW results will be inputs to an issues analysis that we will use to obtain feedback from key stakeholder groups
  - What could go wrong by stakeholder and stage of introduction
  - Key barriers/risks

To date, we have built a time-resolved model that allows us to assess the impact of new fuel / vehicle combinations under various scenarios.

- Built time-resolved model that allows assessment of ...:
  - Economic impact of new fuel / vehicle combinations compared with conventional gasoline / ICEVs
  - Time-resolved, cumulative investment and NPW assessment
  - Triggers for implementation of alternative fuel scenarios

  … and can take into account:
  - Scenarios for the vehicle (introduction rate, performance, transitional costs)
  - Scenarios for fuel chain (pathways, introduction rate, performance, transitional cost)
  - Developments in baseline vehicle & fuel technologies
- We have evaluated a “strawman” case for the introduction of a hydrogen infrastructure using the model
  - Vehicle introduction matches DOE’s FCV introduction scenarios
  - Cost and performance assumptions are consistent with previous analysis results
- We are now seeking inputs from stakeholders to identify the most relevant alternative scenarios for analysis

A net present worth model has been developed to track vehicle and infrastructure investments on an annual basis.

Time Dependent Inputs

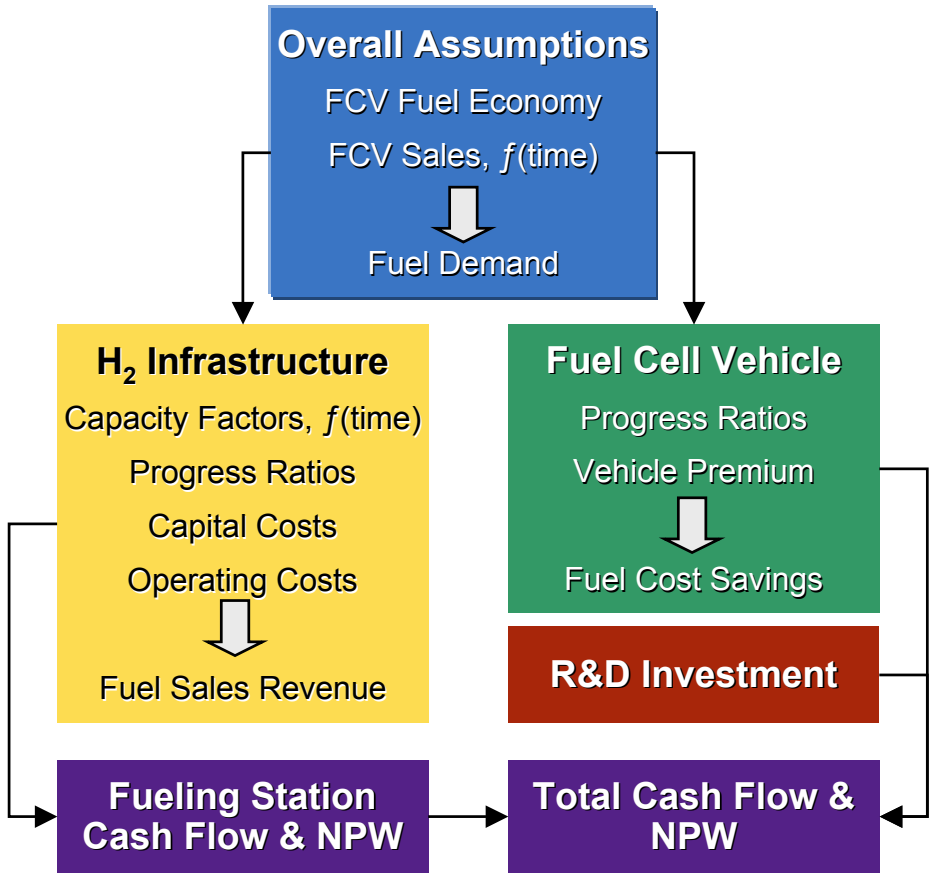
- DOE FCV introduction (sales) scenarios
- Infrastructure capacity factors
- Infrastructure pathways (central and local production, large and small stations)
- Equipment costs - based on progress ratios (infrastructure and FCV)

Time Independent Inputs

- FCV performance assumptions
- Fuel prices (e.g. gasoline, hydrogen)
- Other infrastructure costs (e.g. O&M)

Outputs

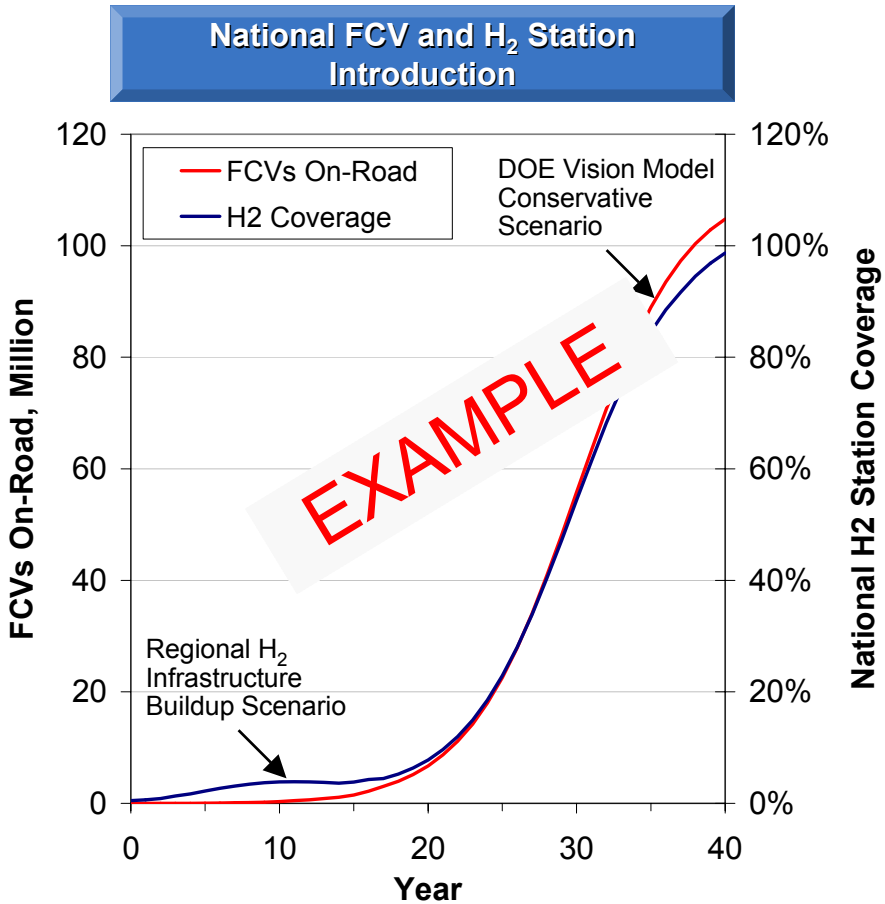
- Hydrogen revenues
- Fuel savings
- Cash flow and NPW for each stakeholder group



The model can also be used to track energy and environmental impacts over time.

We constructed a H_2 introduction scenario which proceeds from region to region so that regional coverage can be achieved cost effectively.

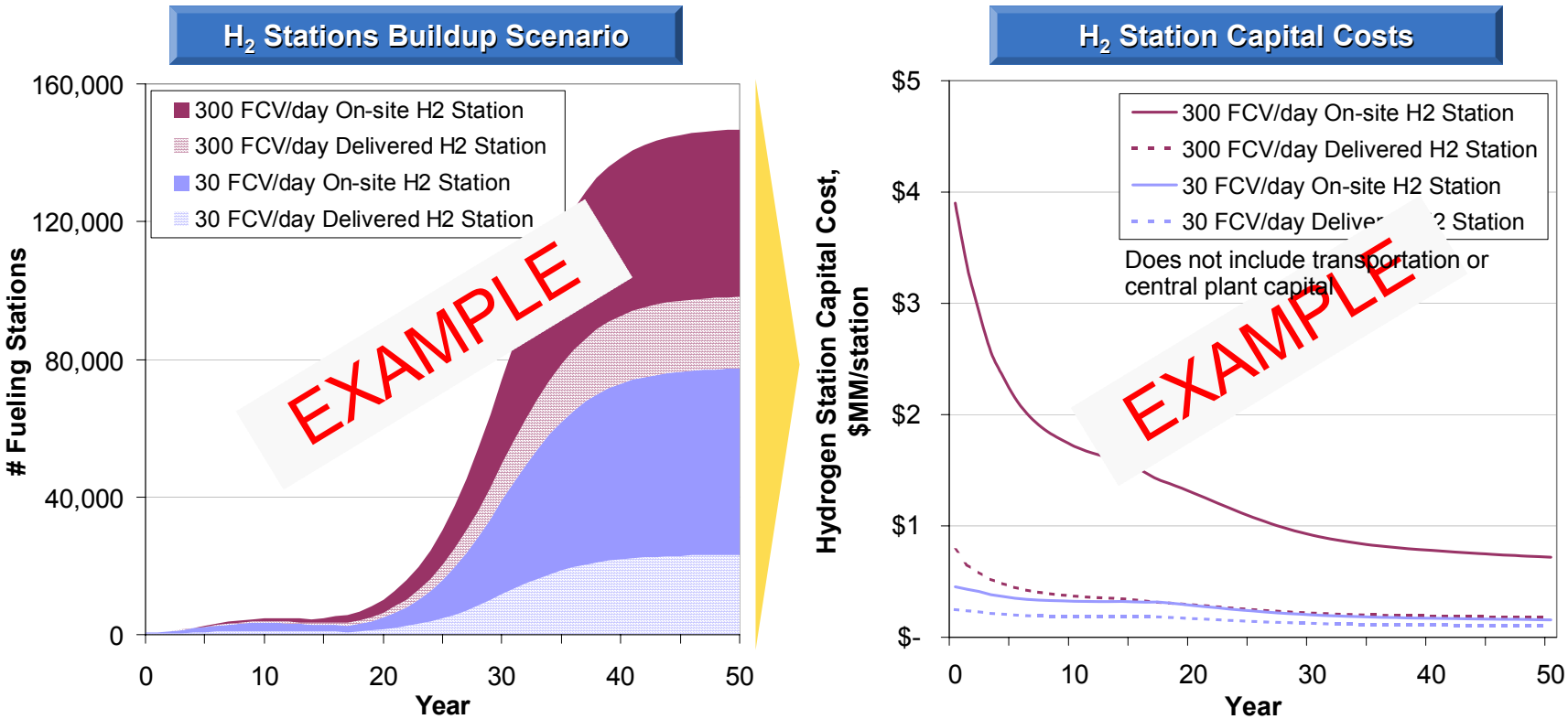
- DOE Vision Model results for the number of FCVs on-road
- Regional buildup to 10% coverage[1] in a short time (not from day 1)
  - Maximizes H_2 station capacity factors (CF)
  - CF are assumed to increase over time to 90% maximum (aggressive)
  - Region = 10 million vehicles
- National coverage takes longer and would not be uniform
  - 10% national coverage requires 12,000 new H_2 stations
- Other introduction scenarios will be constructed



[1] Assumes 0.48 gasoline stations per 1000 vehicles based on 1997 data for convenience stores/refueling stations and truck stops which have gasoline sales of at least 50% of total established sales according to US DOE Transportation Energy Data Book (TEDB) Edition 20, 2000. Note: diesel fuel coverage is about 10%.

We assume the capital cost for H_2 fueling station equipment is reduced over time with higher production volumes (i.e. economies of scale).

- Economies of scale: intensively using expensive machinery, buying supplies in bulk for a discount, developing new and better products, etc.

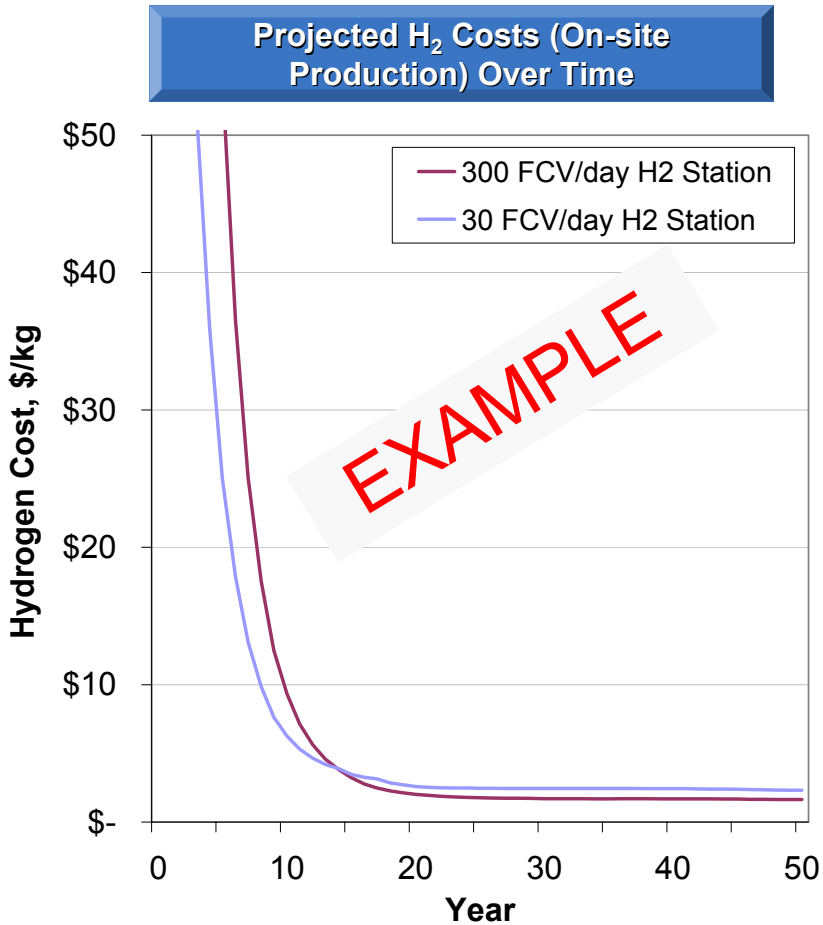


Note: On-site hydrogen production via natural gas steam reforming (SR). Delivered liquid hydrogen via tanker trucks from central SR plant. 300 FCV/day = 690 kg hydrogen per day.

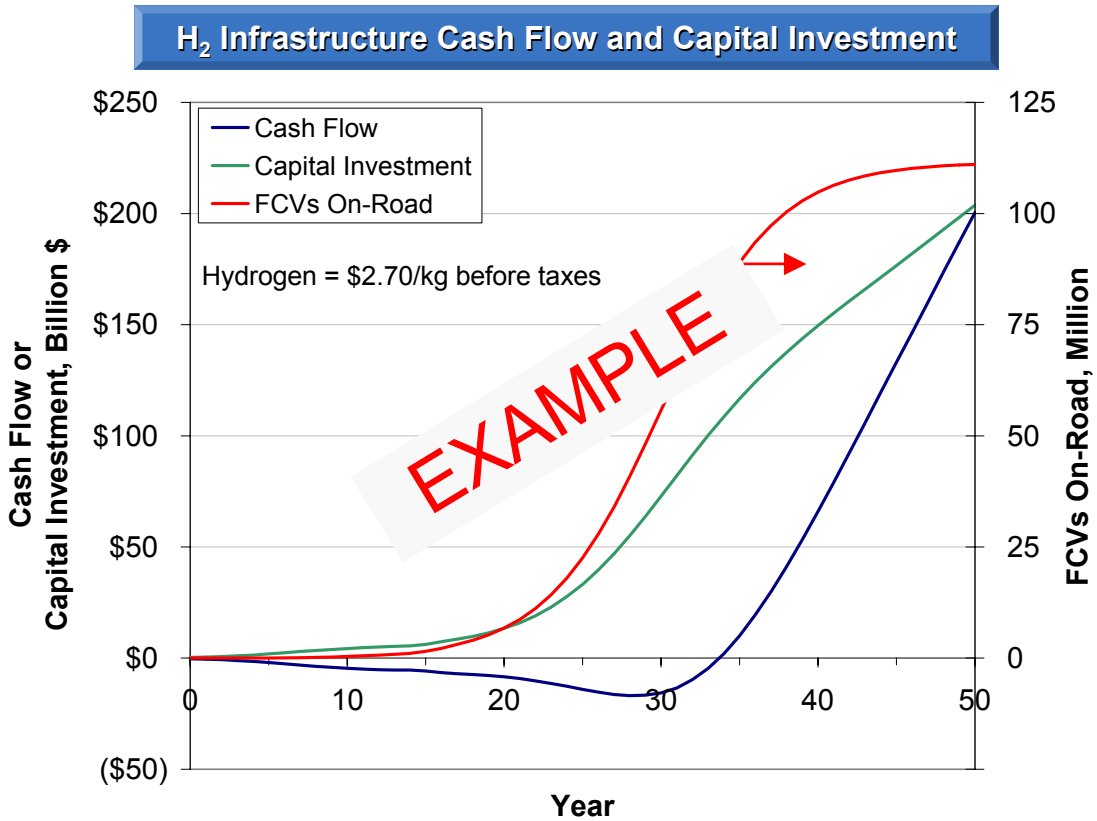
Using preliminary assumptions, H_2 production costs would ultimately reach the $2/kg projected in our previous analysis, but initial costs are high.

- Initial capital cost and utilization (capacity factors) must be improved
- A number of scenarios could help bring the initial costs down:

Utilize existing excess H_2 capacity (e.g. methanol and fertilizer plants)
FCV demonstrations and fleets (buses, government vehicles, etc)
Hydrogen ICEVs
Energy station (e.g. hydrogen for fueling and stationary power)
Alternative FCV and H_2 infrastructure introduction scenarios



Using preliminary assumptions, if H_2 were priced to provide cost-parity with conventional vehicles, break-even would be achieved in about 30 years...



In the long-run, stakeholders can turn a profit if hydrogen is sold for $2.50-$3.00/kg

- Acceptable to FCV owners if fuel economy is 2-3 times better?
- Near-term pathways are needed to improve CF and reduce capital cost

…if an initial premium of 50-100% (1.5-2x gasoline ICEV cost/mile) would be accepted, break-even may be realized in about 20 years.

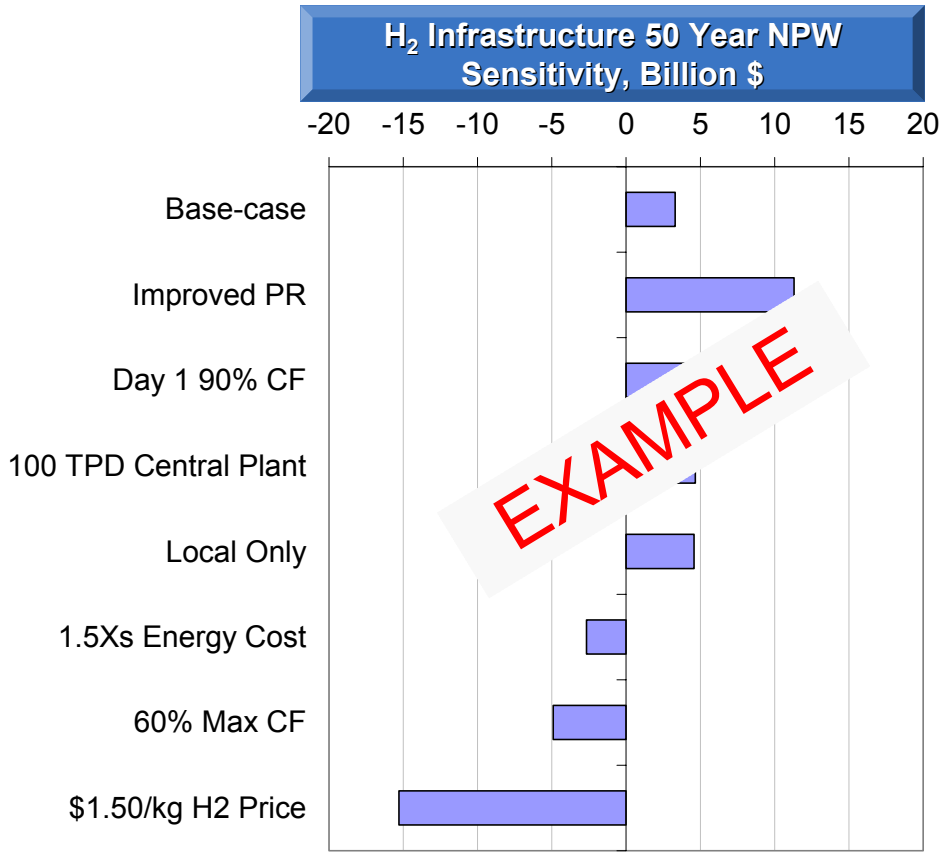
We can use the model to evaluate the sensitivity of net present worth to various input parameters.

The main drivers are:

- Hydrogen selling price - expected internal rates of return (IRR)
- Infrastructure utilization (CF)
- Production volume effects on capital cost (PR)
- Energy (i.e. natural gas) cost

Other observations:

- Local (on-site) versus central production has a smaller impact
- Tripling transportation distance negates the NPW benefits of a 3Xs larger central plant (not shown)



Once the appropriate vehicle assumptions are incorporated, we can compare the overall NPW results for various fuel and FCV types.

The preliminary assumptions used here were generated to demonstrate methodology and validate the analysis approach...

- Preliminary assumptions are based on projections of the future cost of a high efficiency hydrogen infrastructure
  - We will refine our preliminary assumptions based on discussions with stakeholders
  - Low cost pathways will be investigated in future work
- There is significant on-going work at DOE and in various industries to bring costs below those projected here
  - We did not use DOE targets
  - Using assumptions consistent with DOE target of $1.50/kg would result in a much brighter outlook
- We will conduct future work to evaluate low-cost hydrogen pathways:
  - Utilizing existing excess hydrogen capacity to reduce early capital investments, e.g. brown field expansions of ammonia and methanol plants
  - Considering the effects of FCV demos and fleets, hydrogen ICEVs, and energy stations to improve the utilization (capacity factors) of early hydrogen infrastructure

…significant additional work will be conducted to generate and vet refined assumptions for various scenarios in the final analysis.

We have meet with stakeholders and others outside of DOE to present our results/perspectives and solicit feedback on our progress.

Event	Stake-holder	Other
ASME Workshop Presentation, Rochester NY		●
Future Car Congress Presentation, Arlington VA	●	
tation, Boston MA		●
MIT Study Meeting (DOE, ANL, MIT, TAIX), Cambridge MA		●
International Hydrogen Infrastructure Group (IHIG) Presentation, Detroit MI	●	
IHIG Meeting, Cambridge MA	●	
ster, Palm Springs CA		●
	●	

We are in the process of gathering stake-holder input to define alternative introduction scenarios before evaluating overall risk for each fuel choice.

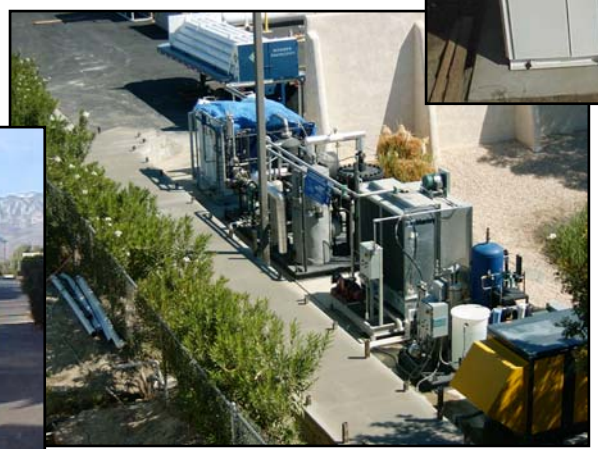
- Evaluate scenarios that could bring down the initial costs of hydrogen
  - Existing excess hydrogen, FCV demos and fleets, hydrogen ICEVs, energy stations
- Gather stakeholder input, develop additional future scenarios, and update analysis
- Validate FCV performance and cost estimates
- Evaluate the technology risk, financial exposure, and safety and regulatory risks
- Identify promising pathways to help DOE and stakeholders identify:
  - Near-term actions
  - R&D, demonstrations
  - Partnerships

Department of Energy
Merit Review and Peer Evaluation

Berkeley, California
May 19-22, 2003

SunLine 3-year Development & Demonstration Program

SunLine - DOE Peer Review



Solar System Summary and Conclusions

Summary:

218 Siemens flat panels, 1744 sq.ft, 20 kW rated capacity

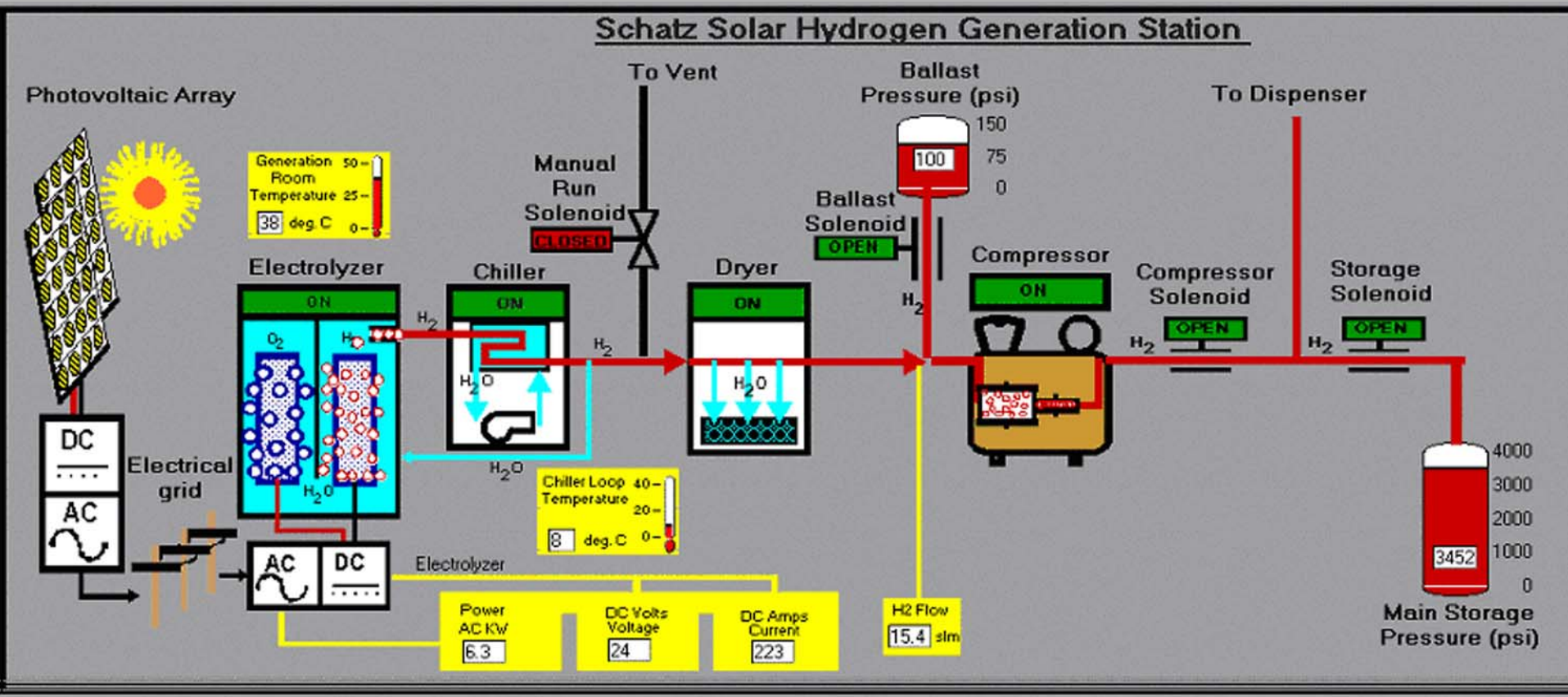
144 EcoEnergies tracking arrays, 432 sq.ft, 17 kW rated capacity

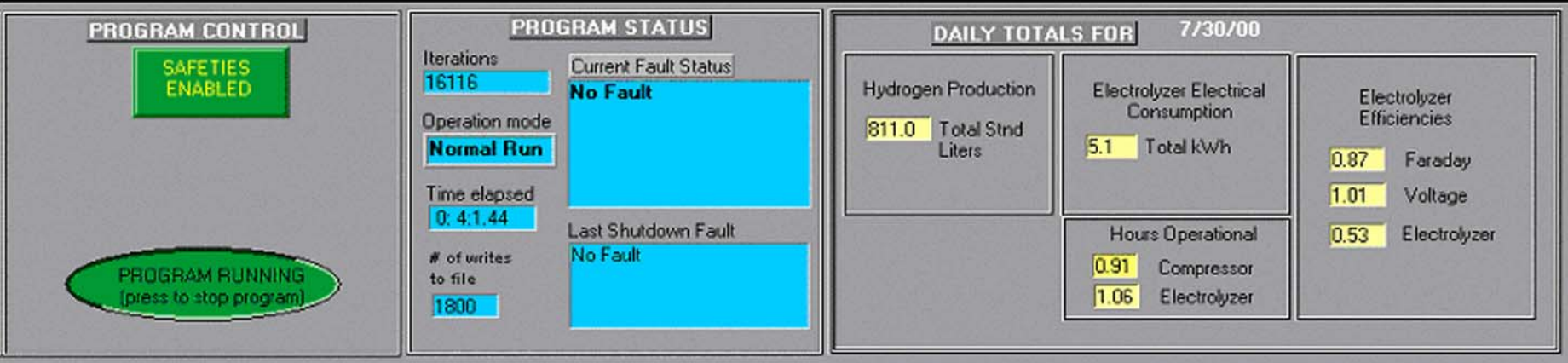
Trace DC to AC Inverter

Conclusions:

System efficiency of 7%, impacted by heat and wind blown dust

15% production lost due to system faults and limited equipment reliability


Schatz Solar Hydrogen Generation Station
Photovoltaic Array
To Vent
Ballast Pressure (psi)
To Dispenser
Generation Room Temperature
38 deg. C
Manual Run Solenoid
CLOSED
Ballast Solenoid
OPEN
Electrolyzer
ON
Chiller
ON
Dryer
ON
Compressor
ON
Compressor Solenoid
OPEN
Storage Solenoid
OPEN
DC
AC
Electrical grid
Chiller Loop Temperature
8 deg. C
Power AC KW
6.3
DC Volts Voltage
24
DC Amps Current
223
H2 Flow
15.4 slm
Main Storage Pressure (psi)
3452


PROGRAM CONTROL
SAFETIES ENABLED
PROGRAM RUNNING (press to stop program)
PROGRAM STATUS
Iterations
16116
Operation mode
Normal Run
Time elapsed
0: 4:1.44
# of writes to file
1800
Current Fault Status
No Fault
Last Shutdown Fault
No Fault
DAILY TOTALS FOR 7/30/00
Hydrogen Production
811.0 Total Stnd Liters
Electrolyzer Electrical Consumption
5.1 Total kWh
Hours Operational
0.91 Compressor
1.06 Electrolyzer
Electrolyzer Efficiencies
0.87 Faraday
1.01 Voltage
0.53 Electrolyzer

SERC/Teledyne System Conclusions

There is no substitute for instrumentation

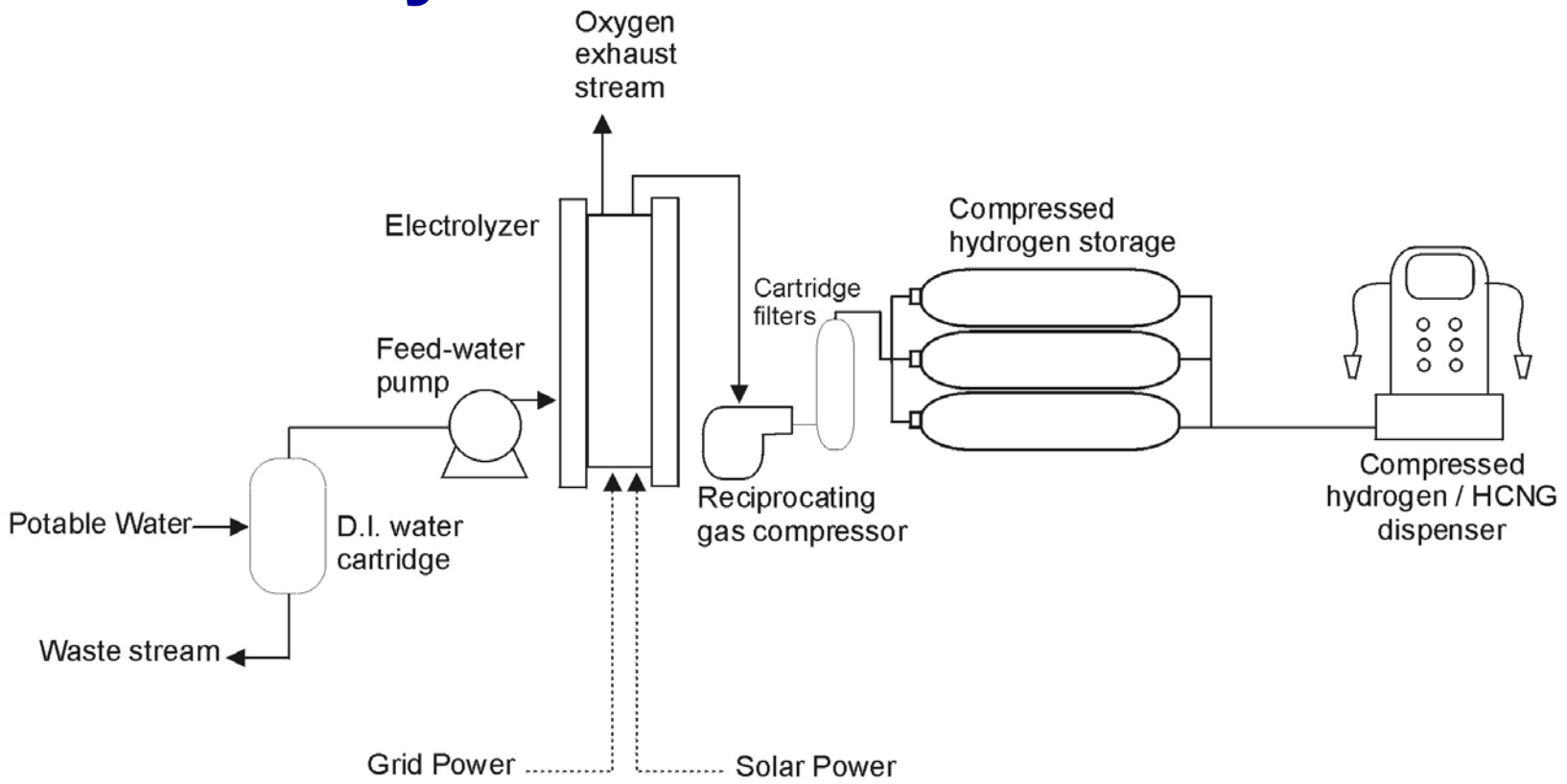
Capital cost is quite high at $110,000
(Altus 20 at $60,000, compression at $25,000, dispensing at $10,000 and installation at $15,000.)

Operating costs reasonable at $4 per gge, assuming electricity at 5 cents per kWh and no capital cost allocation

System very user-friendly and commercially available

Excellent platform for distributed generation - residential market - good fit in a two-car garage

Stuart Energy System Flow Sheet



Stuart Energy System Conclusions

There is no substitute for instrumentation

Capital cost reasonable at $625,000
CFA 1350 at $500,000, dispensing at $60,000 and installation at $65,000 (Site specific)

Operating costs reasonable at $3.25 per gge, assuming electricity at 5 cents per kWh and no capital cost allocation

System requires 65 kWh/kg

System very user-friendly and commercially available

Excellent platform for distributed generation

Turn key services available

Hythane®/HCNG Program and Conclusions

Two Hythane® fueled Nova buses used in revenue service since 2000

No engine issues, fuel consumption equivalent to CNG

Improved engine and throttle response

45% less NOx (50% plus on newer engine platforms)

Justification for the development of a hydrogen infrastructure at transit facilities

HCNG can be a bridge to hydrogen!

Hythane® fuel cost represents a 20% premium over CNG (CNG at $1.50 per gge and hydrogen at $3 per gge)

Ballard Fuel Cell Bus Program and Conclusions

13-month demonstration program

Bus traveled 8,963 miles in simulated revenue service

Last significant trip October 2001 from Fontana, CA to Las Vegas (275 miles)

Fuel consumption of 8.9 miles per gge is 2.5 times better than conventional CNG bus

Lessons learned applied to P-5 cell stack and Citarro bus

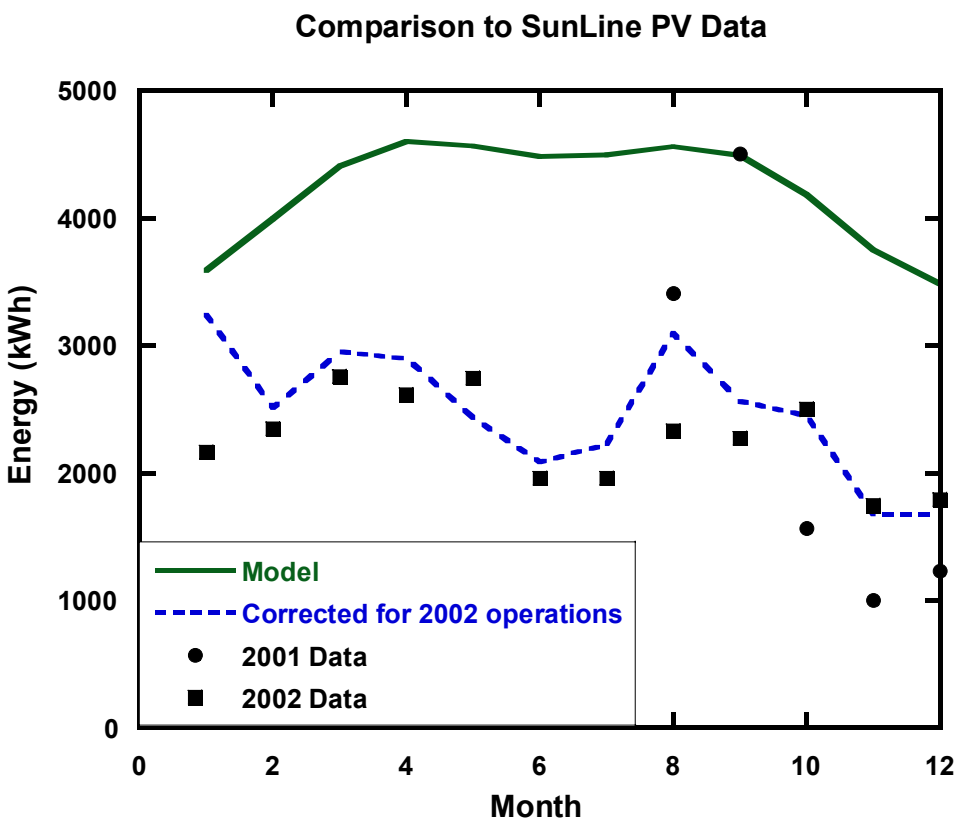
Bus still in use at SunLine for VIP use and demonstrations

Cost of recently purchased FC bus is $3.1 million plus $400k for extended warranty

Training Program

Lessons Learned

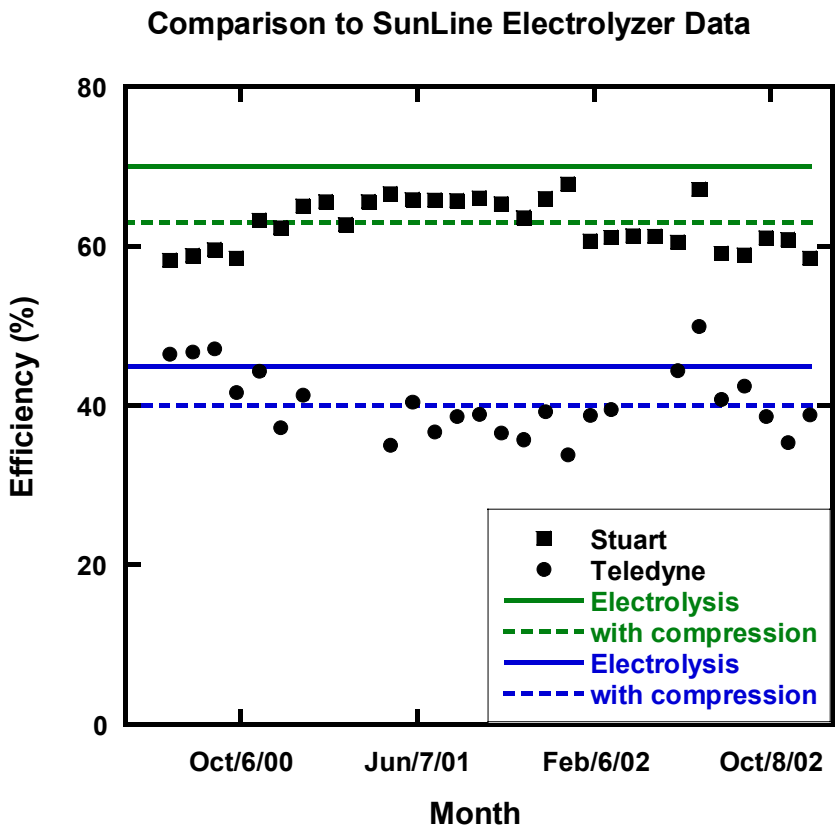
Photovoltaic collector simulation



- **Model simulation**
  - Run yearly variation
  - Integrate daily collection
  - Sum monthly to compare to SunLine data
- **Solar radiation model**
  - Analytic function of longitude, latitude, altitude
- **PV panel model**
  - Area = 360 m^2, slope 23°
  - Adjust solar-electric conversion efficiency = 7 %
- **Correct monthly sums to SunLine's operations**
  - Operating days / month
  - Sunny days / month

Lessons Learned *continued*

Electrolyzer Simulation



Model comparison

- Electrolyzer + compressor to compare with SunLine data
- Estimate efficiency of electrolysis step to match average H_2 delivery efficiency

SunLine electrolyzers:

- Stuart Energy (Phase 3 unit)
  - Low-p cell output (1 psi)
  - Compression: 4-stages at 50% efficiency to 5000 psi
- Teledyne Energy Systems
  - High-p cell output (100 psi)
  - Higher purity H_2 supply
  - Compression: 2 stages at 20% efficiency to 3600 psi

Lessons Learned *continued*

Hydrogen safety and instrumentation requirements:

- There is no substitute for instrumentation for diagnostics

Station development:

- Codes and standards, permitting issues and requirements
- Education and outreach critical

Advances in hydrogen production technology:

- Significant advances in the last few years with systems getting more efficient and user-friendly
- PLC control, data acquisition and remote access possible with web access or PC anywhere

Lessons Learned *continued*

Applications:

CNG engines run very well on HCNG blends consisting of 20% hydrogen with changes limited to engine calibration, and they can provide a demand for hydrogen production

Internal combustion engines may provide a platform for hydrogen as fuel cells are being developed and slowly introduced to the transportation and distributed power generation markets

Hydrogen fueled power generation may be required in the early stages with the deployment of natural gas reformers to address imbalances between supply and demand

Recommendations

There are no substitutes for:

<u>Experimental design</u>

DOE should provide support to all projects in this area

DOE labs should be drafted to provide in-depth technical support to industry

<u>Instrumentation and data acquisition</u>

Funds should be allocated specifically to this activity

Comprehensive comparable data is required if we are going to get an accurate picture of systems and technologies and share lessons learned.

Recommendations *continued*

Internal combustion engines:

There is a need for a consensus that comprehensive R&D with HCNG and hydrogen fueled ICE hybrids is required to provide a bridge to fuel cell technology, justify the development of a hydrogen infrastructure, and test various technologies

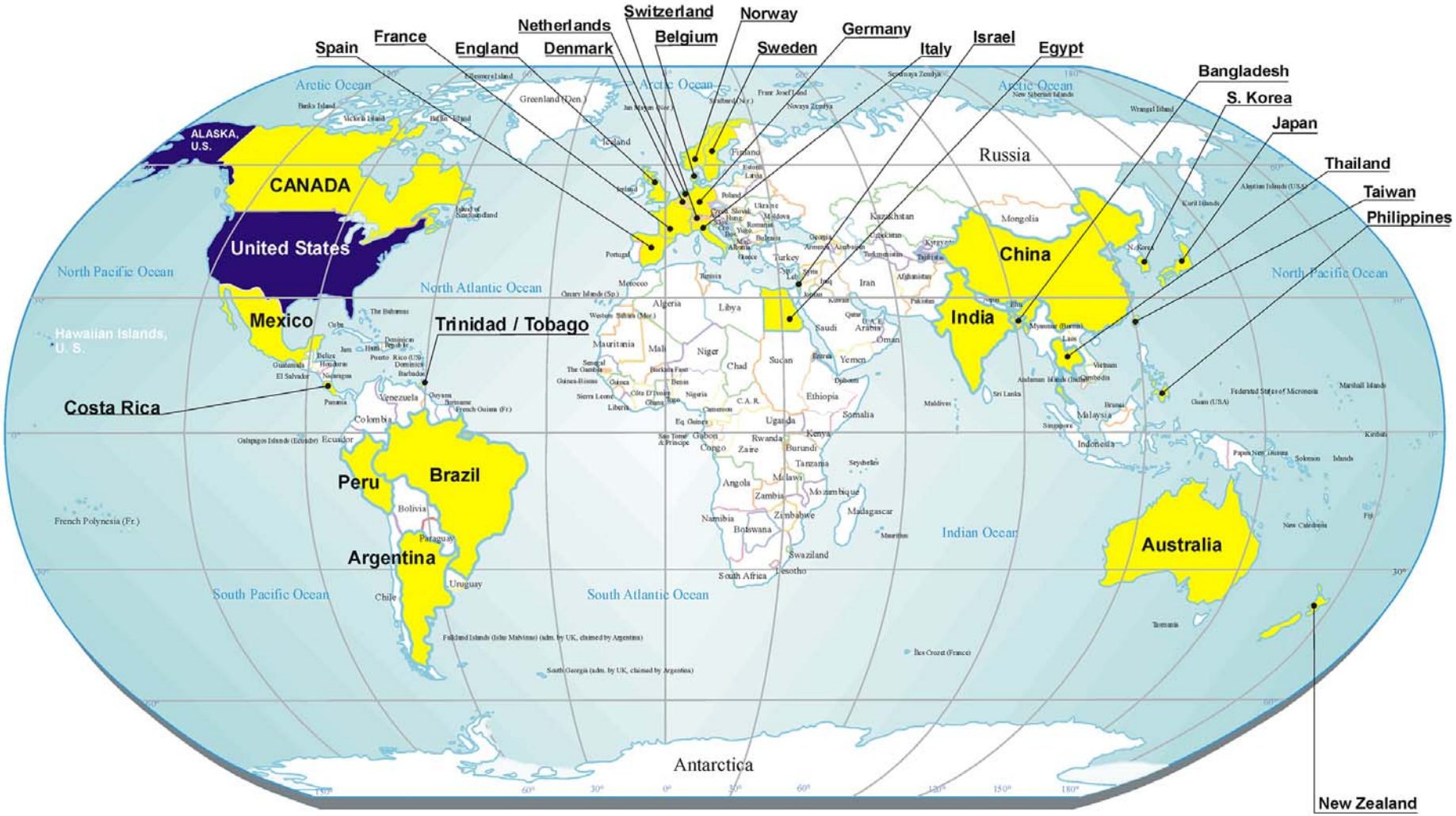
Insurance industry:

An education and outreach program to the insurance industry is required to aid industry in assessing the risks involved with hydrogen and fuel cell technology

Technology transfer:

Early adopters should be tasked to share lessons and assist with projects under development

Outreach, Collaboration and Partnerships



Future Programs

Future *continued*

Praxair
H2 Storage and Compression: LAX

State Energy Program, Special Projects

Category 6.53 Power Technologies: Compression, Storage & Dispensers (Project 67)

Mike Manning
Rob Bollinger
Aaron Rachlin

Presentation to the Department of Energy
May 22, 2003

Agenda

- Praxair Hydrogen
- Program Structure
- Program Overview
- Program Objectives
- Approach
- Schedule
- Accomplishments & Progress
- Questions

Praxair Hydrogen

PRAXAIR
H2 Fueling Station

- **Only Hydrogen Supplier in All Sizes (Cylinders to Liquid to Pipeline)**
  - First industry-financed liquid hydrogen facility (1959)
  - Six large LH_2 plants designed, constructed, and operated
  - Largest capacity single-train LH_2 production system (60 t/d)
  - Four LH_2 plants currently in operation
  - Smallest industrial SMR-based product line (HGS)
- **Over 500 Million SCFD Combined Capacity**
- **Distribution Network:**
  - Over 600 GH_2 and LH_2 customers
  - 50 LH_2 trailers, 16 LH_2 rail cars
  - Over 250 miles of GH_2 pipeline
  - 150 GH_2 tube trailers
- **First PSA H_2 Unit (Over 300 Designed and Built)**

Program Structure

- **Program Participants**
  - Praxair, as Program Leader
  - BP, as Advisor

- **Program Contributors**
  - US Department of Energy (DOE)
  - California Energy Commission (CEC)
  - South Coast Air Quality Management District (AQMD)
  - Los Angeles International Airport (LAX / City of LA)
  - Praxair

Program Overview

- **Design, Develop, Install & Operate H2 Fueling Station**
  - Integration & Packaging of Existing Technology
  - Electrolysis based On-Site Production
  - Up to Five Light-Duty Vehicles per day
  - Five Minute “Fast Fills”
  - Future Growth Flexibility to meet Demand
  - Enabled for Heavy-Duty (Bus) Fills
  - Two Year Program
- **Demonstration of Hydrogen based Fueling Infrastructure**

Objectives

- **Support a Small Fleet of Hydrogen Fueled Vehicles**
  - California Fuel Cell Partnership Goal to introduce up to 60 HFCVs by 2003
  - Compatibility with other Fueling Stations
- **Modular & Reproducible Design**
- **Station Characterization**
  - Performance
  - Maintenance
  - Operation
  - Cost of Delivered Product

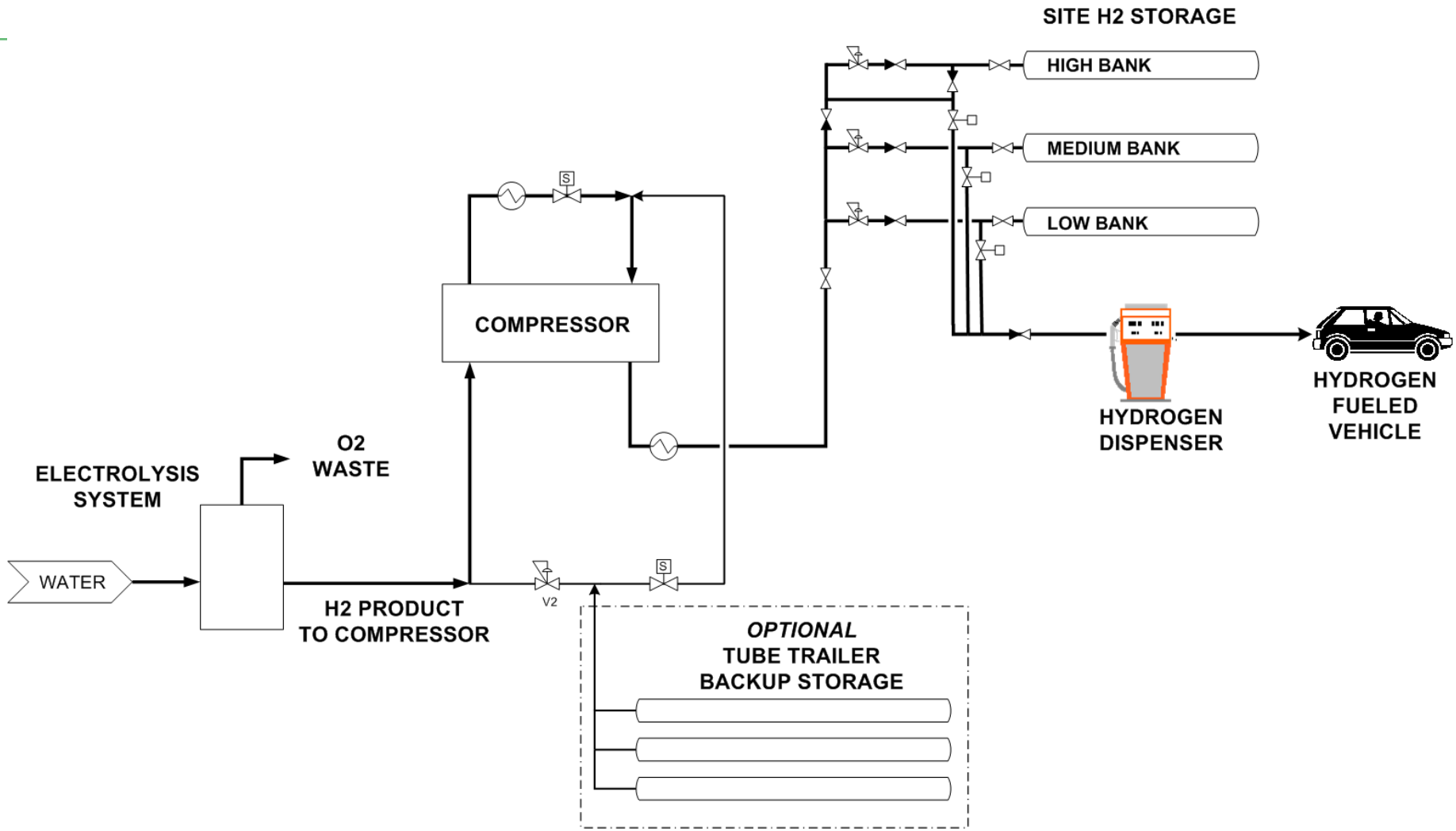
Relevance

- **Design Considerations**
  - Layout / Spacing Limitations
  - Aesthetic Appearance
  - Application of Industrial Codes to Commercial Setting
- **Modifications to Base Design**
  - Simulated Commercial Environment
  - Integrated, Aesthetic Packaging
    - Low-Profile
    - Tighter Footprint

Approach- Block Flow Diagram

PRAXAIR

H2 Fueling Station



Approach- Overview

- **Hydrogen Production**
  - Electrolysis based
  - Proven Design from Stuart Energy
  - Integrated Packaging
  - 24 kg/day Capacity

Approach- Overview

- **Compression**
  - Hydraulically Driven Reciprocating Compressor
  - Flexible Operational Modes
- **Storage**
  - Traditional ASME Coded Steel Construction
  - Cascaded Bank Configuration
  - Demonstration of Other Configurations Possible
- **Dispensing**
  - Fast Fills of Cars within 5 minutes
  - Enabled for Bus Fueling
  - BP Preferred Configuration

Schedule Overview

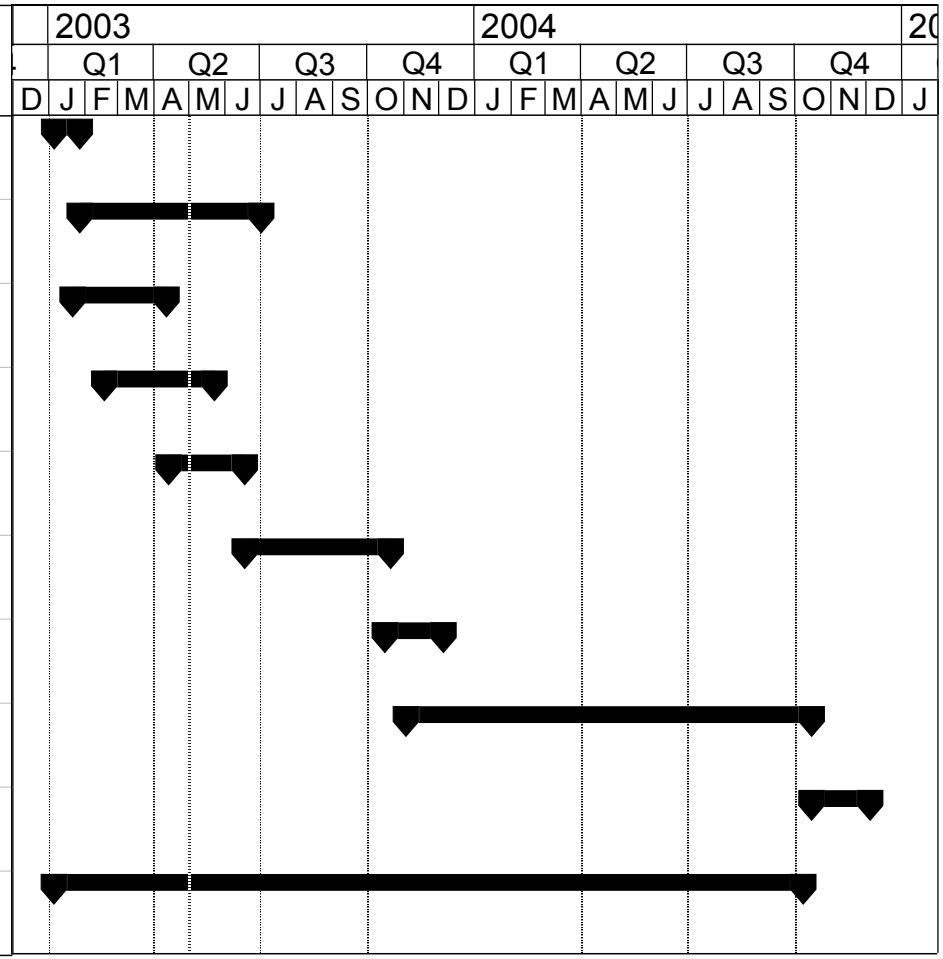
PRAXAIR
H2 Fueling Station

- **Project Milestones**
  - Planned Start — Oct 2002
  - Actual Start (Contracting Delay) — Jan 2003
  - Site Selection & Characterization — Mar 2003
  - Equipment On Order — May 2003
  - Permit Applications — Jun 2003
  - Installation — Sep 2003
  - Hydrogen Available — Nov 2003

Program Timeline

PRAXAIR
H2 Fueling Station

ID	Task Name
1	**Task 1.0 Project Scope and Definition**
6	**Task 2.0 Codes, Standards & Regulations**
12	**Task 3.0 Site Characterization and Permitting**
19	**Task 4.0 System Design**
38	**Task 5.0 Supplier Qualification, Selection, & Acquisition**
44	**Task 6.0 System Assembly & Installation**
64	**Task 7.0 System Startup & Performance Characterization**
72	**Task 8.0 System Operation**
75	**Task 9.0 Decommissioning & Relocation**
79	**Task 10.0 Project Management**



Accomplishments / Progress

PRAXAIR
H2 Fueling Station

- **Progress limited by Contracting Delay**
- **Project Status Update**
  - Permitting
    - CEQA / NEPA Review
    - Permit Applications
  - Conceptual Design Complete
  - Major Equipment Ordered
  - Preliminary Drawing Packages Complete
  - Detail Design On-Going

Praxair
H2 Storage and Compression: LAX

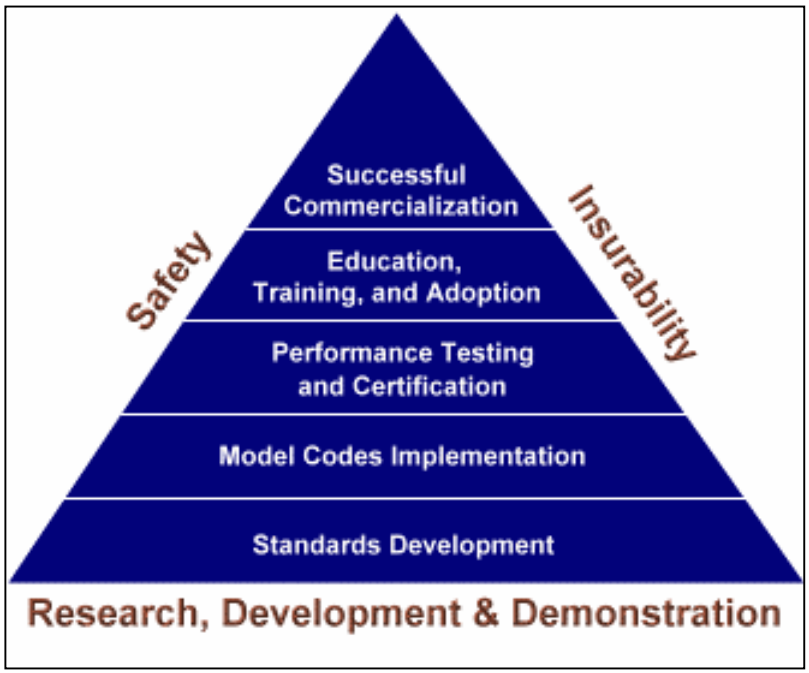
(Project 67)

Mike Manning
Rob Bollinger
Aaron Rachlin

Questions?

Presentation to the Department of Energy
May 21, 2003

Hydrogen Codes & Standards



Hydrogen Codes & Standards: Goal & Objectives

Goal : Facilitate the creation and adoption of model building codes and equipment standards for hydrogen systems in commercial, residential, and transportation applications. Provide technical resources to harmonize the development of international standards among IEC, ISO, and GRPE.

Objectives

- Complete the drafting of hydrogen building codes for NFPA's hearing cycle. Facilitate in the adoption of the ICC codes in three key regions: North East, Mid-Atlantic, and Midwest, by 2005;
- Complete the adoption of the ISO standards for hydrogen refueling and storage, by 2006;
- Complete and adopt the revised NFPA 55 standard for hydrogen storage with data from Technology Validation projects and the experimental project for underground bulk storage of hydrogen, by 2008;
- Complete U.S. adoption of a Global Technical Regulation (GTR) for hydrogen fuel cell vehicles under the Global Regulation on Pollution and Efficiency Program, by 2010.

Hydrogen Codes & Standards: Key Milestones

Milestone	Description	Date (FY)
3	Collaborate with ICC and NFPA to develop first-order continuing education for code officials.	3Q, 2004
4	Establish a coordination plan with education sub-program activity to run workshops for state and local officials.	3Q, 2004
11	Initiate negotiations with critical SDOs and develop draft generic licensing agreement and estimate of costs.	4Q, 2003
24	With industry and code officials, develop templates of commercially viable footprints for fueling stations that incorporate underground and above ground storage of liquid and gaseous hydrogen.	1Q, 2004
30	Implement analytical and experimental program to support the submittal of a comprehensive vehicular safety standard as a regulation.	4Q, 2005
32	Implement research program to support five new technical committees for the key critical standards including fueling interface, power block, and fuel storage.	4Q, 2006

Hydrogen Safety

Hydrogen Safety: Goal & Objectives

Goal : Develop and implement the practices and procedures that will ensure safety in the operation, handling and use of hydrogen and hydrogen systems for all DOE funded projects.

Objectives

- Draft a comprehensive safety plan to be completed in collaboration with industry. The plan will initiate the research necessary to fill safety information gaps and enable the formation of a Safety Review Panel, by 2004;
- Integrate safety procedures into all DOE project funding procurements. This will ensure that all projects that involve the production, handling, storage, and use of hydrogen incorporate project safety requirements into the procurements, by 2005;
- Publish a handbook of Best Management Practices for Safety. The Handbook will be a "living" document that will provide guidance for ensuring safety in future hydrogen endeavors, by 2010.

Hydrogen Safety: Key Milestones

Milestone	Description	Date (FY)
2	Develop in collaboration with NASA, DOT, Commerce, a search protocol on component and system safety.	1Q, 2004
12	Assemble panel of experts in hydrogen safety to provide expert technical guidance to funded projects.	4Q, 2003
17	Identify areas of additional study and research for failure modes scenarios.	3Q, 2004
21	Gather and review data to support the inclusion of hydrogen safety in procurements.	4Q, 2003
31	Establish annual review criteria for safety.	4Q, 2004

Codes and Standards Analysis

University of Miami

Dr. Michael Swain

Background

The lean limits of flammability currently used in safety analysis originated in the 1940's and 50's

Textbook values for flammability

- 4.1% hydrogen upward propagating lean limit of flammability
- 10% hydrogen downward propagating lean limit of flammability

The lower-limit mixture of hydrogen in air produces far too little heat to raise the mixture to it’s ignition temperature…

The tests were conducted with quiescent mixtures of hydrogen and air in containers 6 to 15 feet tall and 2 to 12 inches in cross section

Findings for 4.1% mixtures

- A ring of flame is formed initially
- Upon breaking it forms a “cloud”, a “collection of small balls of flame” or a “pencil of flame”
- The flames traveled steadily to the top of the container

Findings for 10% mixtures

The hydrogen was not completely consumed until 10% concentration was reached

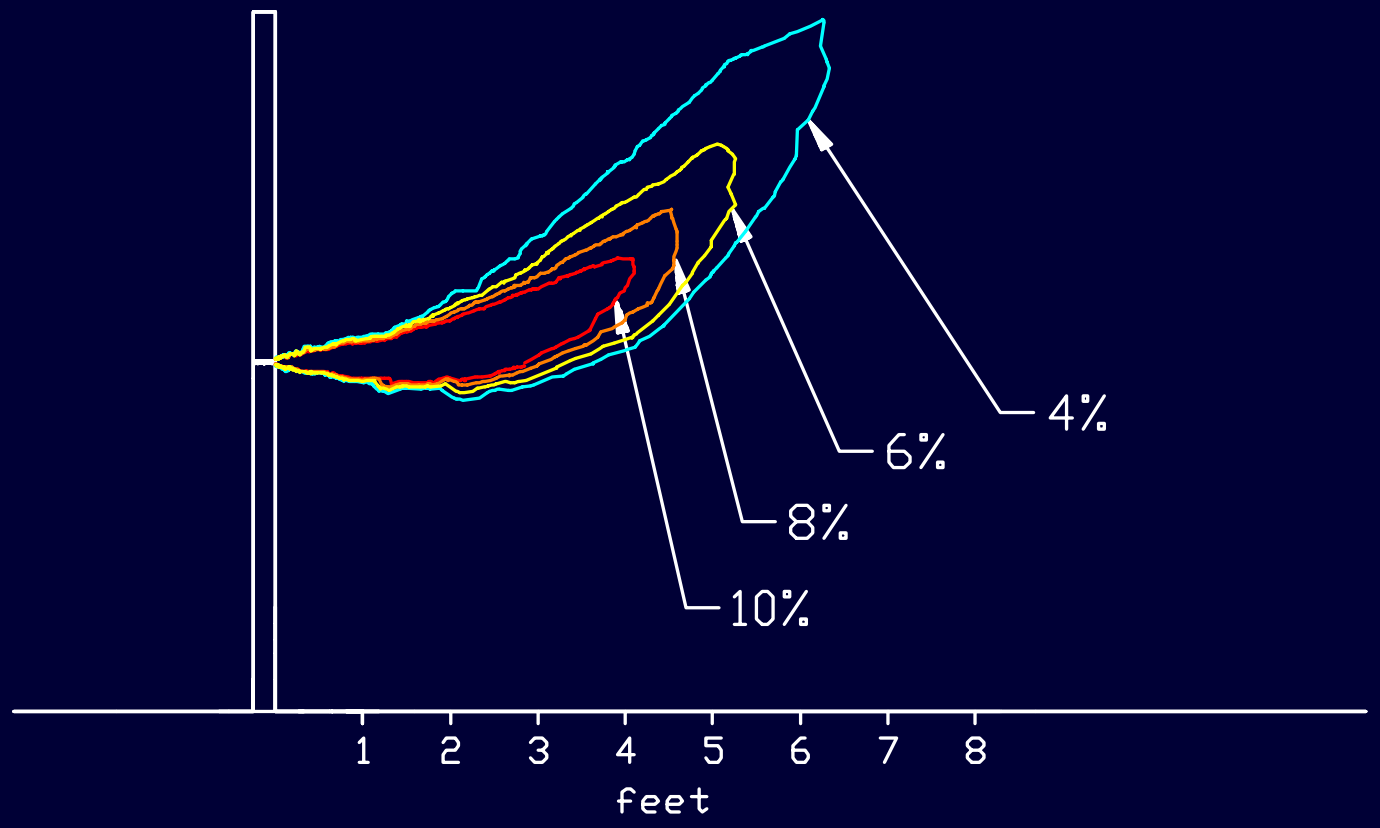
Very lean hydrogen flames are possible because of hydrogen's high diffusion rate. As the hydrogen is consumed fresh hydrogen diffuses into the flame more rapidly than other gases, richening the mixture.

The upward propagating lean limit of flammability (4.1%), in conjunction with a safety factor of 4 (yielding 1.0%), is still used in safety analyses of mixtures that cannot be quiescent

Project Description

- Task A - Analysis of lean limit of flammability for gases surrounding a hydrogen leak
- Task B - Analysis of lean limit of flammability for gases flowing in exhaust ducts
- Task C - Analysis of electrical grounding needs in a garage with an electrolyzer or fuel cell
- Task D - Analysis of hazards produced by electrical shorts in conjunction with portable fuel cells

20 SCFM Hydrogen leak



Test wall for leaks

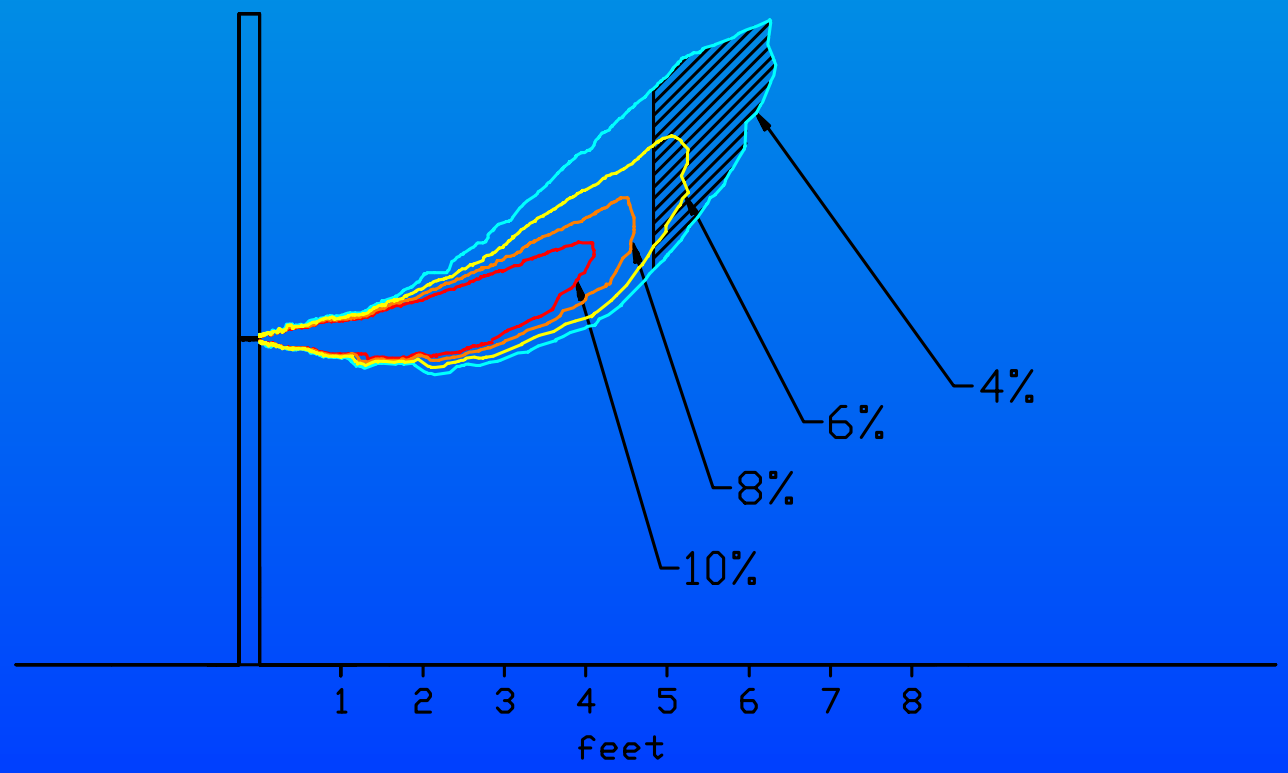
Leak test apparatus

Hydrogen sensor apparatus

Calibration apparatus

Ignition of hydrogen plume at 15%

Area tested to date – no ignition



Hydrogen Program Review

Hydrogen Codes and Standards

Jim Ohi

Russ Hewett

Cathy Grégoire Padró

National Renewable Energy Laboratory

DOE Hydrogen, Fuel Cells, and Infrastructure Technologies
Merit Review and Peer Evaluation
Berkeley, CA
May 22, 2003

Relevance/Objective

- Goals*
  - Facilitate creation and adoption of model building codes and equipment standards for hydrogen systems in commercial, residential, and transportation applications
  - Provide technical resources to harmonize development of international standards among ISO, IEC, and GRPE

*HFCIT R&D Plan

Relevance/Objective

- Key Technical Barriers*
  - Limited government leadership role
    - US consensus and self-certification process limits government role to accelerate development and harmonization of standards, codes, and regulations
  - Competition among standards/code development organizations
    - Standards and codes are valuable IP and a source of revenue
  - Large,diverse number of state/local jurisdictions
    - Up to 44,000 local jurisdictions need to adopt and enforce model codes
  - Economic competitiveness issues and national agendas
    - National and regional agendas are not always consistent with global harmonization of standards
  - Lack of technical data
    - Historically, standards and validation data have not been developed in concert

*HFCIT R&D Plan

Approach

- Key Technical Targets (addressing barriers from previous slide)*
  - Limited government leadership role
    - Create “national template” to harmonize standards, codes, regulations
  - Competition among standards/code development organizations
    - Develop generic licensing agreement for web-based access to standards
  - Large,diverse number of state/local jurisdictions
    - Develop training modules and conduct workshops with ICC and NFPA
  - Economic competitiveness issues and national agendas
    - Develop unified national agenda and support consistent representation of technical experts from industry and government at key global venues
  - Lack of technical data
    - Develop comprehensive R&D plan and program for validation of codes and standards

*HFCIT R&D Plan

Project Timeline

1994 1998 2000 2002 2004 2006 2008 2010

Standards

NHA C/S workshops

ISO work items draft standards

National template

Unified approach

ISO H_2 fueling/ storage

Codes

ICC H_2 Ad Hoc Committee

ICC approves H_2 in model codes

Regulations

Support US TAGs

Draft GTR H_2 FCV

GTR (GRPE) H_2 FCV

Publications/Training/R&D

H_2 Codes/Standards Matrix

ICC 2003 Model Codes for H_2

ICC 2006 Model Codes for H_2

Sourcebook for Hydrogen Applications

MYPP: Codes/ Standards

Accomplishments/Progress

- Overcame opposition by American Gas Association at final ICC public hearing, Ft. Worth, Oct. 1-4, 2002
  - all major changes proposed for IRC, IMC, and IFC approved
    - changes to minimum separation distances included in IFC
  - hydrogen recognized as a “fuel gas” in IFGC and proposed changes to IFGC to address hydrogen safety approved by floor vote
  - support by industry and hydrogen fuel cell exhibit key to success
- Hydrogen safety incorporated in 2003 edition of ICC model codes
  - all local chapters of major national code organizations contacted on proposed changes to model codes
- Guy Tomberlin, Commercial Inspections Supervisor, Fairfax Co., VA, and Chair, ICC H2 Ad Hoc Committee receives NHA Meritorious Service Award, March 6, 2003

Accomplishments/Progress

- August 19, 2002: national workshop to identify codes and standards needs and priorities for MYPP
- December 18, 2002: DOE workshop for MYPP targets/milestones for safety, codes and standards
- March 5, 2003: Larry Burns, VP, R&D & Planning, NHA Keynote Speech: “call to action” for federal government, included
  - “National template for codes and standards”
- March 7, 2003: DOE, NREL, and SDOs develop draft template for national standards, codes, and regulations for H_2 vehicles, fueling/service/parking facilities, vehicle/facility interface
  - Consensus by all key SDOs on lead and supporting roles to develop critical standards
  - DOE Hydrogen Codes and Standards Coordinating Committee manage implementation and updating of template

Accomplishments/Progress

National Template for Vehicle Systems and Refueling Facilities

Vehicles

Controlling Authority: NHTSA crashworthiness
EPA emissions

Fuel Cell Vehicle Systems
Fuel Delivery Systems
Containers
Reformers
Emissions
Recycling
Service/Repair

Interface

Fuel Specs
Wts/Measures
Fueling/Defueling
Sensors/Detectors
Connectors
Communications

Fuel Delivery/Storage

Controlling Authority: RSPA
Over-road Transport
Pipeline Safety

Composite Containers
Pipelines
Equipment
Fuel Transfer

Fueling, Service, Parking Facility

Controlling Authority: State, Local Government
Zoning, Building Permits

Storage Tanks
Piping
Dispensers
On-site H2 Production
Codes for the Built Environment

Accomplishments/Progress

DOE-NREL National Standards, Codes, & Regulations Harmonization Template

General Area	Controlling Authority	Functional Area	Lead SDO	Assisting Organizations
Vehicles	NHTSA	Crashworthiness	DOT	SAE
	EPA	Emissions	DOT	SAE
FC Vehicle Systems		Vehicles	SAE FC Standards Comm.	
		Containers	CSA	SAE
Fueling, Service, Parking facilities	State and local governments	Zoning and building permits	ICC, NFPA	DOE
		Stationary storage tanks	ASME	CSA, CGA, NFPA, API
		Piping standards	ASME	CSA, CGA, NFPA
		H2 Dispensers	CSA	UL, NFPA
		On-site H2 production	CSA	UL, CGA, API
Fuel Delivery and Storage	RSPA (DOT)	H2 pipelines and fuel delivery equipment	ASME	API, CGA, AGA
		Composite container standards	ASME	CSA, AGA, NFPA
		Fuel transfer standards	NFPA	API
Interface		Fuel specifications	SAE	ASTM, API
		Weights and Measures	NIST	ASME, API
		Fueling/defueling,	SAE	API, CSA
		Fueling connectors and communications	SAE	UL, CSA, API, IEEE
		Sensors/detectors	UL	NFPA, SAE, CSA

Accomplishments/Progress

- National Fire Protection Association (NFPA)
  - standards development
    - Member of Hydrogen Coordination Committee
  - training and education
    - *How to Permit A H_2 Refueling Facility Guide for Code Enforcement Officials*
- International Code Council (ICC)
  - Members of secretariat and technical advisory group to Hydrogen Ad Hoc Committee
- American Society of Mechanical Engineers (ASME)
  - Member of Hydrogen Steering Committee
- Underwriters Laboratory (UL)
  - Member of Standards Technical Panel UL2264: Hydrogen Generators
- CSA International
  - Member of Technical Advisory Group for on-board gaseous hydrogen container standard

Accomplishments/Progress

- International Hydrogen Infrastructure Group
  - Member Codes and Standards Working Group (GM, BP, Shell Hydrogen, Air Products, Praxair, ExxonMobil, DOE/NREL)
    - Working meetings with high-level managers of auto and energy industries (GM, Ford, DC, BMW, Shell, BP, ExxonMobil, ChevronTexaco, PhillipsConoco)
- California Fuel Cell Partnership
  - Member of Codes and Standards Working Group
    - Brief Steering Committee annually on codes and standards
  - Member of Working Group on Emergency Response Guide for FC Buses
- US Fuel Cell Council
  - Member of Codes and Standards Working Group
- Regional Hydrogen Infrastructure Forums
  - Co-sponsored by DOE Regional Offices and key stakeholders
    - forums held in 5 of the 6 DOE regions; 6th forum planned for Fall 03

Accomplishments/Progress

- Draft performance-based regulations for compressed and liquid hydrogen storage for vehicles completed by UN-ECE/GRPE informal group on Hydrogen/Fuel Cell Vehicles
  - Drafts will be submitted to GRPE in May 2003 under 1958 agreement (US not a signatory)
  - Depending on outcome of May meeting, signatories to1958 and/or1998 agreement (includes US) may pursue development of Global Technical Regulations for compressed and liquid hydrogen storage for vehicles
  - No further action expected until October 2003
- Partnership to Accelerate the Transition to Hydrogen (PATH) underway
  - Link mutual codes and standards interests of key Pacific Rim countries, (US, Canada, Japan, Argentina, Mexico, China, Korea)
  - Organizational meetings held, Board of Directors, organizational agreements in place

Accomplishments/Progress

- Option year subcontract in place with National Hydrogen Association to continue codes and standards workshops and US industry coordination
  - Monthly electronic hydrogen safety newsletter
  - Hydrogen codes and standards matrix on website
- Option year subcontract in place with Robert Mauro to chair ISO/TC197 TAG and to organize and manage Partnership to Accelerate the Transition to Hydrogen (PATH)
- Subcontract in place with LCC, Ltd., to continue technical support with ICC, NFPA, IEC TC105, CSA International, USFCC
- Subcontract in place with Ron Sims to continue chairing SAE Fuel Cell Electric Vehicle Standards Committee

Interactions/Collaborations

- DOE H_2 Codes/Standards Coordinating Committee
  - DOE Office of Hydrogen,Fuel Cells, and Infrastructure Technologies Program (Neil Rossmeissl, Technology Program Manager)
  - DOT, NIST, NASA, US Navy, EPA
  - ANSI, API, ASME, ASTM, CGA, CSA, ICC, NFPA, NGVC, NHA, IEEE, IHIG, SAE, UL
- Industry
  - International Hydrogen Infrastructure Group
  - California Fuel Cell Partnership
- International
  - Working Party on Pollution and Energy (GRPE)
  - European Integrated Hydrogen Project (EIHP)
  - Partnership to Accelerate the Transition to Hydrogen (PATH)

Plans, Future Milestones

- Refine overall codes and standards coordination program
  - create centralized, publicly accessible web-based data center
    - DOE license from primary standard and code development organizations
      - draft generic licensing agreement under review by DOE, NREL, and key "early adopters"
    - directory of primary contacts for information and technical assistance
    - one-stop technical assistance for hydrogen projects
- Annual safety, codes, and standards summit meeting
- Initiate comprehensive R&D plan for validation of standards
- Develop hydrogen safety training packages for local code officials with NFPA and ICC
  - Handbook of Representative Hydrogen Fueling Station Projects

Plans, Future Milestones

Standard	Content
Piping	Hydrogen specific piping design, installation, training, and certification. Replaces B31.3 reference in ICC Family of Codes
Storage	Hydrogen storage tank for portable and stationary service. Standard will be independent of adsorbent. New standard for vehicular transport of high-pressure hydrogen up to pressures of 10,000 psi. Includes supporting R&D program funded by DOE.
Materials Guide	Ensures public safety, health, and general welfare through proper selection of materials for hydrogen service. Reference for existing design and installation standards
Hydrogen Quality	Ensures safety by defining testing methods to determine the quality of the fuel independent of production technique.
MassFlow Measurement	Defines methods to quantify hydrogen mass flow rate to determine appliance efficiency
Transport	Review and modification of existing piping standards and underground storage

Plans/Future Milestones

- Leadership in development of quantifiably safe systems
  - Identify and fund appropriate experts to fully participate in development of Global Technical Regulations for on-board storage and other hydrogen-related regulations under development
    - performance requirements often set with little or no statistical data or modeling results to quantify the safety of component or system
    - only Germany provided technical expertise through TUV (German safety and vehicle certification organization)
    - opportunity for US to assert technical expertise in developing draft regulations for compressed and liquid hydrogen storage
- Global Technical Regulations for hydrogen fuel cell vehicles
  - Harmonized regulations for on-board hydrogen storage
  - Technical draft for vehicular safety standards
    - Harmonized with US Federal Motor Vehicle Safety Standards
- Harmonized standards for fuel cell power plants

1. RELEVANCE / OBJECTIVE

Project Title: Maximizing Photosynthetic Efficiencies and Hydrogen Production in Microalgal Cultures

Principal Investigator: Tasios Melis, UC Berkeley

Technical Barrier: Low Light Utilization Efficiency in Photobiological Hydrogen Production due to a Large Photosystem Chlorophyll Antenna Size (Barrier K)

Technical Target: Molecular Genetics of Organisms for Photobiological Hydrogen Production. Use DNA insertional mutagenesis and high-throughput screening methods to select organisms that have a smaller Chl antenna size and increased light conversion efficiency (Target 17)

2. APPROACH

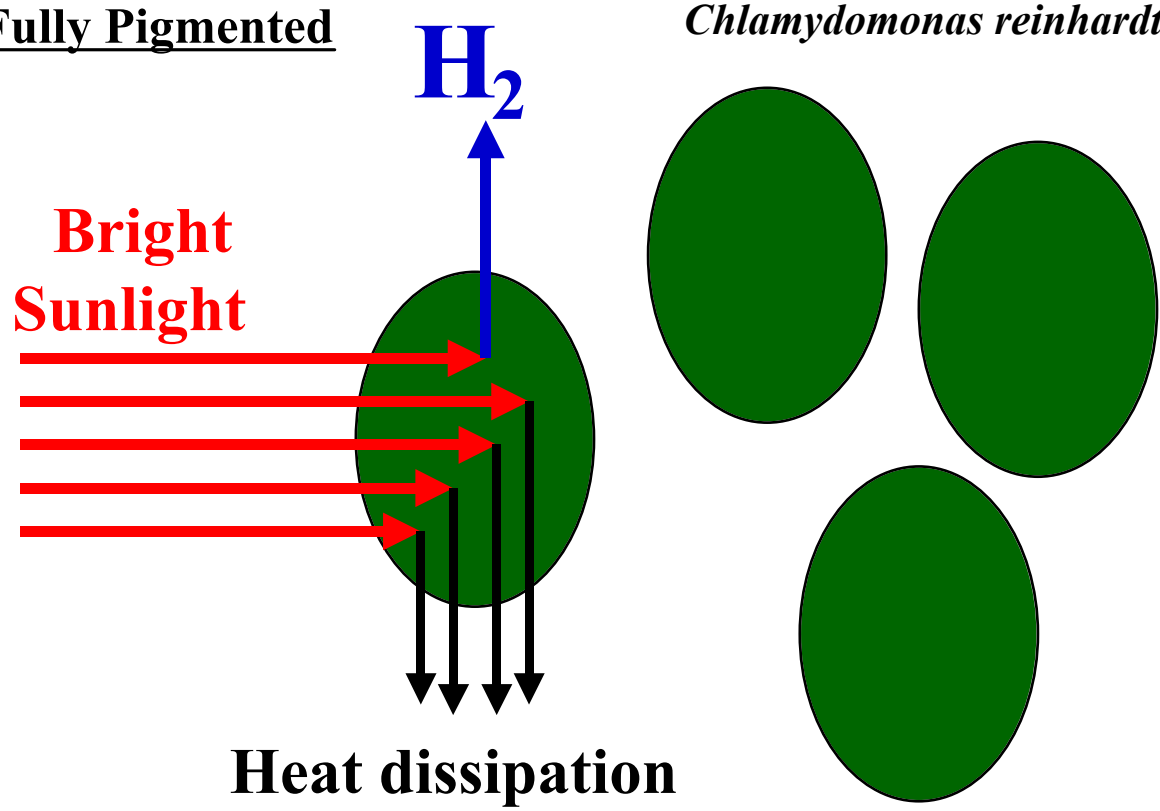
Identify and manipulate genes that attenuate, or truncate, the chlorophyll antenna size in green algae.

DNA insertional mutagenesis, screening, biochemical and molecular genetic analyses of the green alga *Chlamydomonas reinhardtii* are employed.

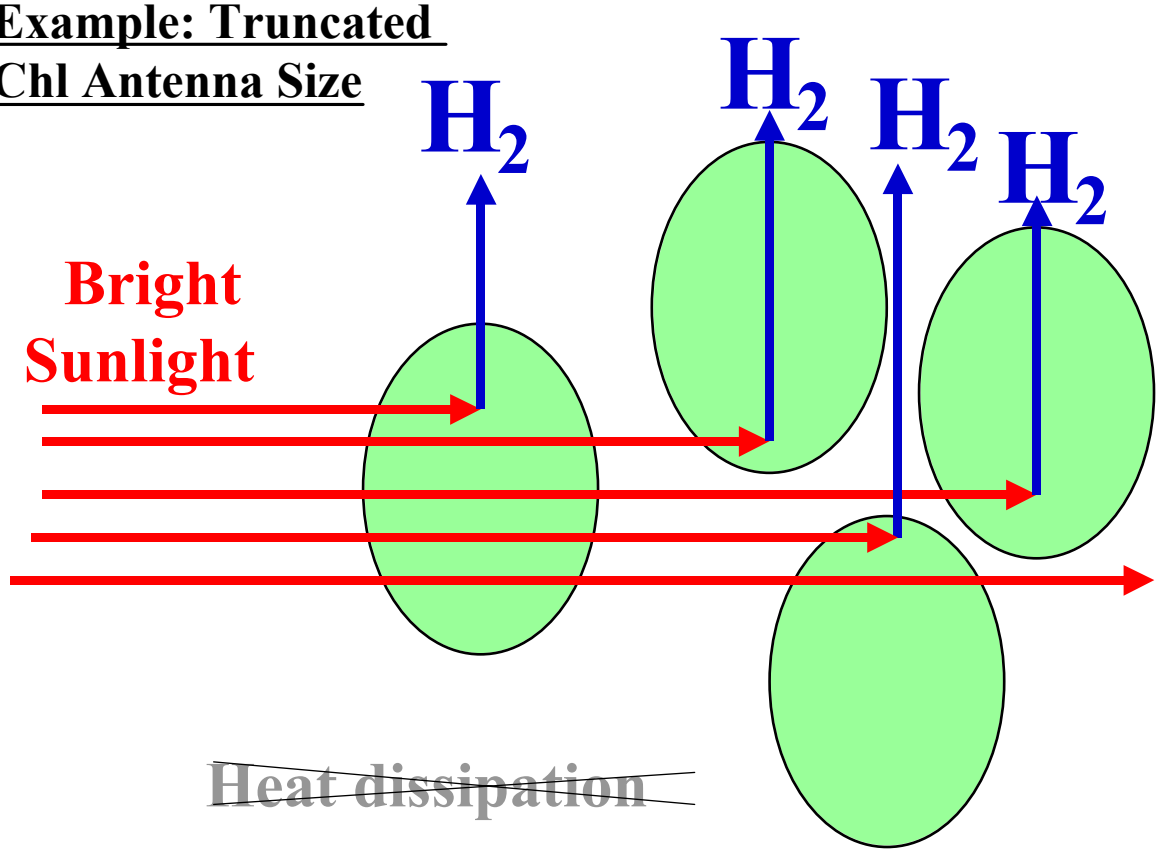
A truncated Chl antenna size would minimize absorption and wasteful dissipation of sunlight by individual cells, resulting in better light utilization efficiency and greater yield of H_2-production by the green alga culture.

Example:
Fully Pigmented

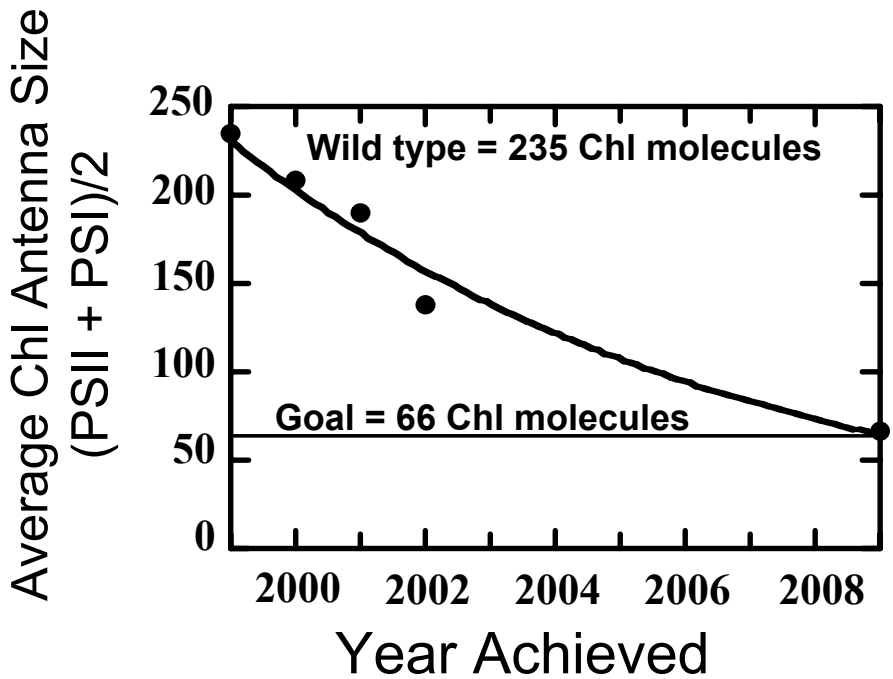
The green algae
Chlamydomonas reinhardtii



Example: Truncated
Chl Antenna Size



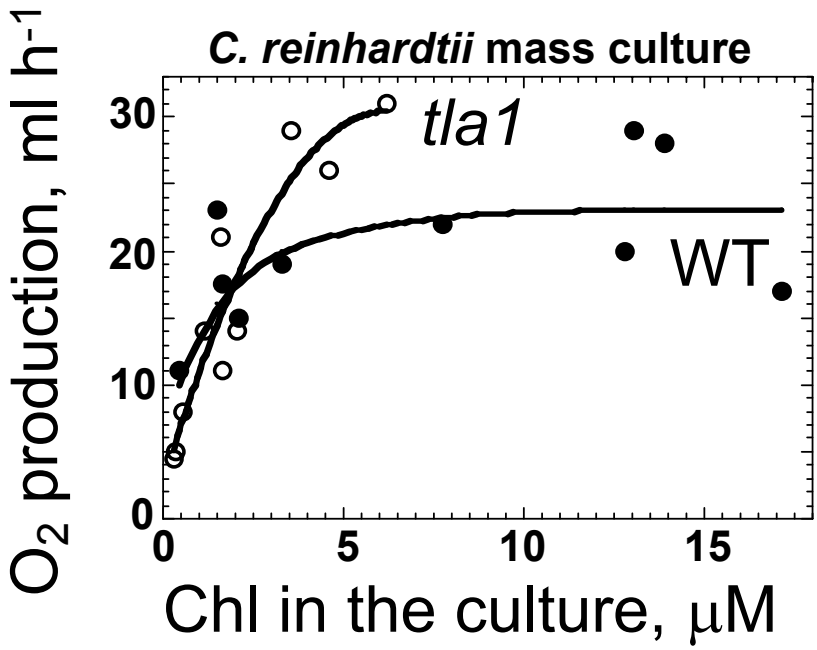
3A. Project Timeline-Graph



3B. Technical Progress - Table

	Wild type	Chl *b*-less	Lutein-less	*Tla1*	LT Goal
Chl-PSII	230	90	125	115	37
Chl-PSI	240	290	290	160	95
Average (PSII+PSI)/2	235	190	208	135	66
Year Achieved	Concept Validation	2000	2001	2002	2009

3C. Productivity in scale up cultures in the greenhouse



3D. Summary of Accomplishments

First-time cloning of *Tla1,* a 'Chl antenna size regulatory gene' (30 year breakthrough).

Genetic interference of the *Tla1* gene, resulted in a truncated PSII Chl antenna size, down to 50%, and a PSI Chl antenna size, down to 67%.

Progress toward the goal: *tla1* mutant showed enhanced productivity under mass culture conditions (see 3C).

The DOE's *Joint Genome Institute* confirmed the sequence of the *Tla1* gene (GenBank Accession No. AF534570 and AF534571) **and assigned a function on the basis of our work.**

Results from this work apply directly to green alga hydrogen-production, biomass accumulation, and carbon sequestration efforts.

Other branches of the DOE (carbon sequestration) benefited from this work (see 4A, Technology transfer).

4A. Technology Transfer

Mera Pharmaceuticals operates in Hawaii, under the auspices of the DOE, a large-scale, carbon sequestration pilot program with green algae. Mera Pharma is currently negotiating with UC Berkeley to obtain truncated chlorophyll antenna size strains of green algae from the Melis laboratory in order to enhance yields of biomass accumulation and carbon sequestration.

4B. Collaborations

In the US

- **With whom are we working?**

  NREL, ORNL as part of an integrated effort
- **Who else is working in the Chl antenna area?**

  Sole Source

Outside of the US

- **In what international collaborations do you actively participate?**

  Tokyo Institute of Technology, Hokkaido University, University of Bonn
- **Who else is working in the area?**

  Sole Source

5A. Plans, FY 2003 Milestones

A. Solar conversion efficiency (hydrogen) measurements in wild type and *tla1* mutant

B. Complementation studies of the *tla1* mutant

C. Initiate analysis of two additional DNA insertional transformants (*1A-26, 1B-2*)

D. Functional analysis of the *Tla1* gene (how does this gene work?)

E. Preparation of reports/publications in peer-reviewed journals

5B. What needs to be done beyond FY2003

Identify additional *Tla*-type genes.

Functionally characterize these genes (how do they work?)

Perform genetic crosses to combine different *tla*-type properties and phenotypes.

Establish transformation protocols w/ *Tla*-type genes (for overexpression or downregulation) in Chlamydomonas and other key green algae.

6A. Technical Challenges

Key challenge

Diminish the Chl antenna size of the photosystems, without diminishing the number of the photosystems in the green algae.

Approach being used to overcome this challenge

The existence of unique biophysical instrumentation at UCB permits independent direct measurements of photosystem concentration and PS Chl antenna size (sole source).

6B. Responses to 1-3 Questions

Question 7a: Publish the *tla1* results.

Genomic, cDNA, and protein sequences were deposited in the GenBank (Accession Nos. AF534570 and AF534571).

A first manuscript has appeared: Polle JEW, Kanakagiri S and Melis A (2003) *tla1,* a DNA insertional transformant of the green alga *Chlamydomonas reinhardtii* with a truncated light-harvesting chlorophyll antenna size. Planta DOI 10.1007/s00425-002-0968-1.

A second manuscript dealing with the molecular aspects of the *Tla1* gene is now in preparation.

Question 7b: Do H2 measurements in the greenhouse with the *tla1* strain

With the upcoming sunny season in Berkeley, efforts are under way to measure yields of H2 in wild type and truncated Chl antenna mass cultures.

7. Current FY Publications

Kanakagiri S and Melis A (2002) *Chlamydomonas reinhardtii TLA1* nuclear gene for the regulation of the photosystem chlorophyll antenna size in photosynthesis, complete cds, (bases 1 to 2181). GenBank Accession Number AF534570

Kanakagiri S and Melis A (2002) *Chlamydomonas reinhardtii* chlorophyll antenna size regulatory protein (TLA1) mRNA, complete cds GenBank Accession Number AF534571

Melis A (2002) Green alga hydrogen production: progress, challenges and prospects. Intl. J. Hydrogen Energy 27: 1217-1228

Polle JEW, Kanakagiri, S, Jin ES, Masuda, T and Melis A (2002) Truncated chlorophyll antenna size of the photosystems - a practical method to improve microalgal productivity and hydrogen production in mass culture. Intl. J. Hydrogen Energy 27: 1257-1264

Masuda T, Tanaka A and Melis A (2003) Chlorophyll antenna size adjustments by irradiance in *Dunaliella salina* involve coordinate regulation of chlorophyll *a* oxygenase (*CAO*) and *Lhcb* gene expression. Plant Mol. Biol. 51: 757-771

Polle JEW, Kanakagiri S and Melis A (2003) *tla1,* a DNA insertional transformant of the green alga *Chlamydomonas reinhardtii* with a truncated light-harvesting chlorophyll antenna size. Planta DOI 10.1007/s00425-002-0968-1

REFORMER MODEL DEVELOPMENT FOR HYDROGEN PRODUCTION

J. Bellan, N. Okong'o, K. Harstad, P. Le Clercq * and A. Leboissetier
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

May 19-22, 2003
Hydrogen and Fuel Cell Merit Review Meeting
Berkeley, CA

*Supported by a grant to J. Bellan from the Petroleum Research Fund and by A contract to J. Bellan from the Office National d'Etudes et de Rechereches Aerospatiales

TECHNICAL TASK, GOAL/RELEVANCE, OBJECTIVES AND TECHNICAL BARRIERS

- Technical task: "Advanced Fuel Reforming: Investigate other reformer improvements, including heat integration and reactor configuration"

- Relevance: address the goal "Research and develop low cost, highly efficient hydrogen production from…renewable sources

- Objectives: "Reduce the cost of distributed production of hydrogen from… liquid fuels"

- Technical barriers
  - A: "Reformer efficiencies are limited by side reactions"
  - A: "Improve performance"
  - H: "Hydrogen produced from biomass is not currently cost-competitive with gasoline due to … capital costs"
  - H: "Areas for reforming technology improvements include … reactor configuration for improved yield"

METHOD OF APPROACH

- Develop models free of empiricism, as much as possible use fundamental principles

- Sequence of the approach

  - Resolve all scales of the flow in a small domain to understand the physics (Direct Numerical Simulations (DNS)) of the drop/flow interaction, etc.

  - develop small-scale models (SGS) based on the understanding of that interaction

  - develop a model (Large Eddy Simulation (LES)) and code where we resolve only the large scales and model the small scales according to SGS

  - validate the model with experimental data

- Exercise these models to derive information directly applicable to the situation to be studied.

PROJECT TIMELINE

Reformer model; FY02

↙ ↓ ↘

1. Models of small-scale drop/turb-flow interactions for SC* drops; FY02

↓

Evaluate small-to-large scale interact. models for SC* drops; FY03

2. Test MC*-drop model robustness for drop/turb-flow interactions; FY02 (Post Doc; PRF spons. to Bellan)

↓

Develop and evaluate robust single MC*-drop model; FY03 (PRF and ONERA co-spons.)

3.New paradigm for drop injection to improve mixing;FY02 (grad. student with Egyptian fellowship)

*SC ≡ single-component

*MC ≡ multi-component mixture

SUCCESS CRITERIA AND EXPECTED COMPLETION

- Success criteria
  - validate models with experiments
  - predict the importance of various parameters
  - optimize reforming for a laboratory scale reactor
  - predict scaling up of the reactor
- Expected completion date depends on the yearly allocated funds for the project

ACCOMPLISHMENTS SINCE THE LAST REVIEW

- Analyzed the database created for temporal mixing layers laden with single-component drops and derived small-scale models of drops/flow interaction ("Consistent Large Eddy Simulation of a temporal mixing layer laden with evaporating drop. Part 1: Direct Numerical Simulation, formulation and *a priori* modeling", (N. Okong'o and J. Bellan), submitted to the *J. Fluid Mech*., 2002)

- Analyzed the database created for temporal mixing layers laden with multi-component drops ("Direct numerical simulation of a transitional temporal mixing layer laden with multicomponent-fuel evaporating drops using continuous thermodynamics", (P. C. Le Clercq and J. Bellan), submitted to the *J. Fluid Mech.*, 2002); found that the multi-component drop model is not robust at all far field conditions

- Developed a robust model for isolated multi-component drop evaporation ("A statistical model of multicomponent-fuel drop evaporation for many-droplet gas-liquid flow simulations", (K. G. Harstad, P. C. Le Clercq and J. Bellan), submitted to the *AIAA J*, 2003)

ACCOMPLISHMENTS SINCE THE LAST REVIEW, cont'd

- Completing the modeling of the coupling between small-scale models and computed large-scales for single-component evaporating drops (in preparation: "Consistent Large Eddy Simulation of a temporal mixing layer laden with evaporating drops. Part II: *a posteriori* modeling", (A. Leboissetier, N. Okong'o and J. Bellan); to be submitted to the *J. Fluid Mech.*, 2003)

- Initiated the creation of a database for studying the interaction of multi-component drops with turbulent flow in a mixing layer, using the robust multi-component drop model

SIGNIFICANT INTERACTION AND COLLABORATION WITH COLLEAGUES

- Publication: "Direct Numerical Simulations of Two-phase Laminar Jet Flows with Different Cross-Section Injection Geometries", (H. Abdel-Hameed and J. Bellan), *Phys. Fluids*, 14(10), 3655-3674, 2002; published in the NASA Tech Briefs => available to the broader community

- Three additional papers submitted for journal publication; each to be published in the NASA Tech Briefs

- Presentations (all to be published in the NASA Tech Briefs):

  - 2 papers presented at ILASS 2002, May 2002

  - 1 paper presented at the 41st Aerospace Sciences Meeting, January 2003

  - 2 papers presented at the 3rd Joint US Sections Combustion Institute Meeting, March 2003

SIGNIFICANT INTERACTION AND COLLABORATION WITH COLLEAGUES cont'd

- Proposals written with colleagues to develop additional experimental databases for model validation

  - collaboration with University of Southern California professor to develop experimental database for single-component drop sprays; submitted to NASA Microgravity Fluids, December 2002

  - collaboration with University of California Davis professor to develop experimental database for multi-component drop sprays; submitted to NASA Microgravity Combustion, March 2003

- Requests for re-prints (e.g. Prof. J. Corella from Spain, Prof. M. Papalexandris from Belgium who will visit at JPL 7/08/03)

FUTURE MILESTONES: SPRAY WITH SINGLE-COMPONENT DROPS

Spatial spray in FY04 (instead of temporal mixing layer in FY02 and FY03)

↓

1. Laminar, evaporating spray DNS runs; FY04

↓

2. Laminar, evaporating spray LES runs; FY04

↓

3. Turbulent, evaporating spray LES and experimental validation; FY04

Data of McDonell and Samuelsen, *Atomization and Sprays*, 3, 321-364, 1993; others

FUTURE MILESTONES: TEMPORAL MIXING LAYER WITH MULTI-COMPONENT DROPS

Temporal mixing layer with robust multi-component-drop model; FY04

$\downarrow$

1. Creation of the DNS database; FY04

$\downarrow$

2. Initiation of the database analysis to model the drop/small-scale interaction; FY04

ISSUE 1 FROM 2002 REVIEWERS: MODEL USEFULNESS

- Assist in resolving important challenges in reforming:
  - reduction of coke formation: the current emphasis on $\nearrow$ steam/carbon ratio is a global strategy whereas coke is formed locally
  - temperature optimization: $\nearrow T$ leads to more conversion, but it also leads to $\nearrow CO/CO_2$ ratio due to the reverse water-gas shift reaction
  - single-chemical-species diesel-surrogates or pyrolysis-oil surrogates behave differently than diesel or pyrolysis oil $\Rightarrow$ ensure that experiments are performed with diesel or pyrolysis oil instead of surrogates
  - investigate the optimal T range resulting from diesel-fuel or pyrolysis-oil composition variation
  - predict the chemical species distribution $\Rightarrow$ location of the catalyst
  - predict how reformers will scale up from the micro-reactors used in laboratories

ISSUE 2 FROM 2002 REVIEWERS: EFFORT TO MAKE THE WORK ACCESSIBLE TO THE BROAD COMMUNITY

- LES is an engineering approach supported by scientific (i.e. DNS) results: The analysis of the DNS database to

  - extract models for the interaction between evaporating drops and turbulent flow

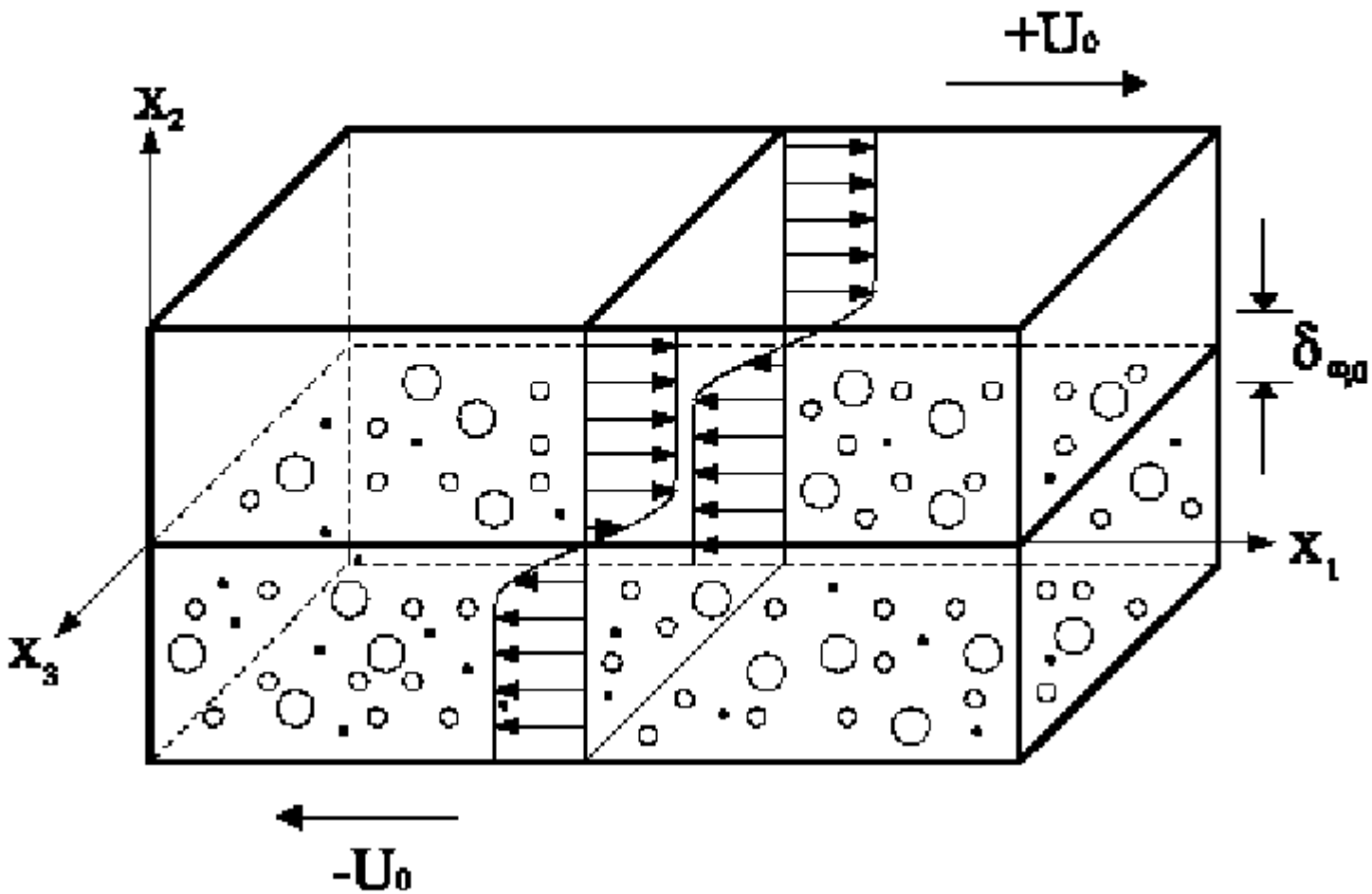
  - reduce the tracked number of drops while maintaining accuracy

make the problem computationally tractable and thus accessible to the broader community. JPL obtained a reduction by a factor of 10^2 in computational time while retaining good accuracy.

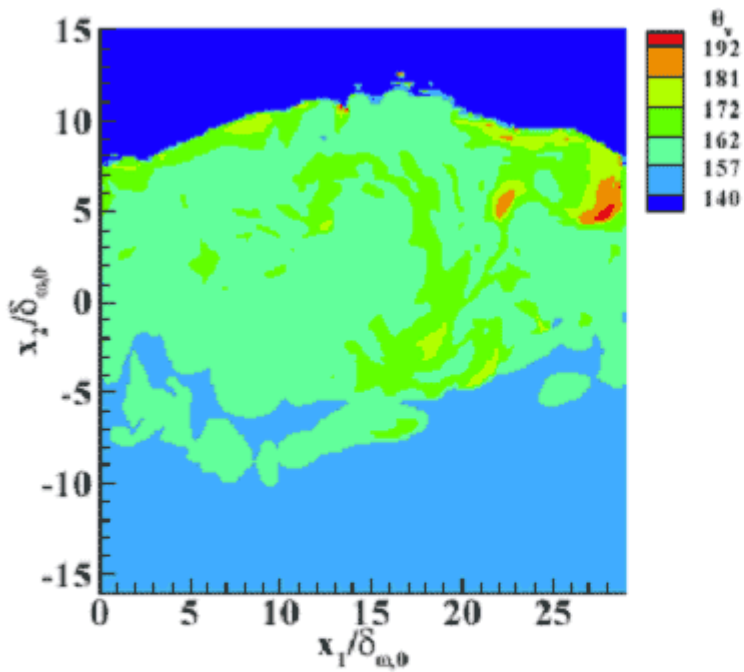
- Idea of the DNS/SGS/LES is to compute only the larger scales, and model the small scales => computational efficiency

- NASA Tech Briefs (all papers under the H_2 Program sponsorship) make the work available to the broader community

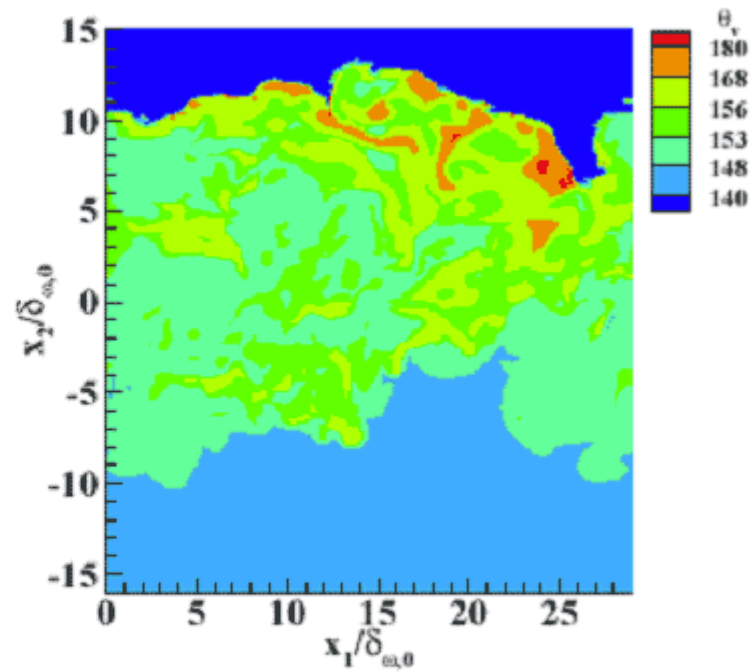
MIXING LAYER CONFIGURATION



BETWEEN-THE-BRAID PLANE CONTOURS OF THE MEAN MOLAR WIGHT FOR EVAPORATING DIESEL FUEL



$ML_0 = 0.2$



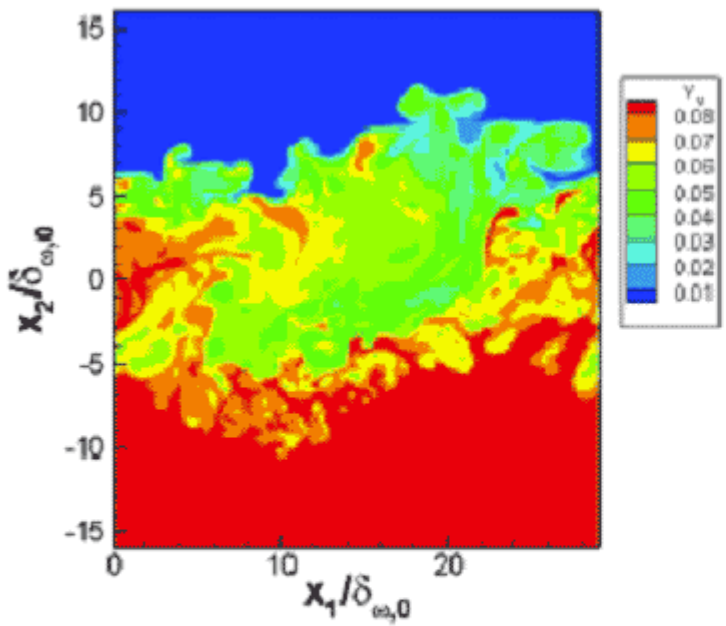
$ML_0 = 0.5$

ML_0 is the initial mass loading of the layer.

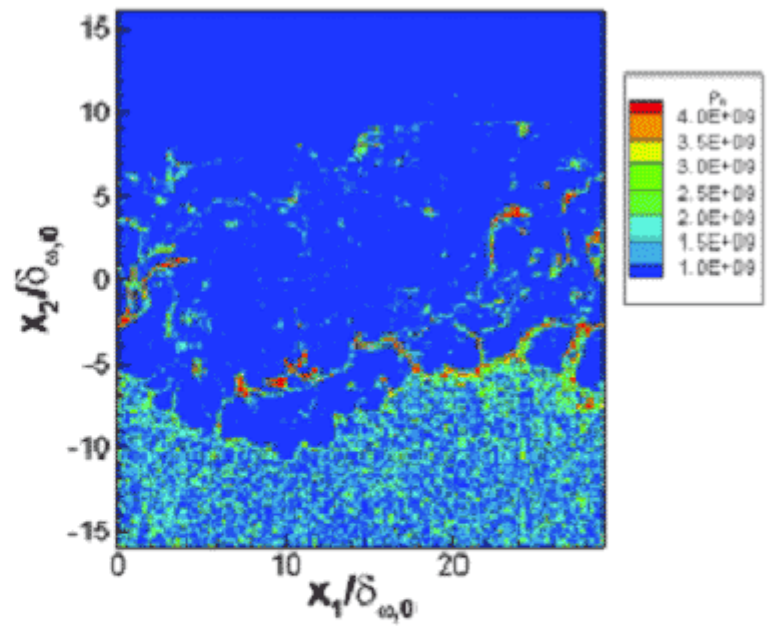
For single-component drops the mean molar weigh is uniform in the field. This shows the importance of doing experiments and performing simulations with the real fuel rather than a single-chemical-species surrogate.

BETWEEN-THE-BRAID PLANE CONTOURS OF THE VAPOR MASS FRACTION AND DROP NUMBER DENSITY

DNS WITH ALL DROPS; 2252 CPU HOURS



vapor mass fraction

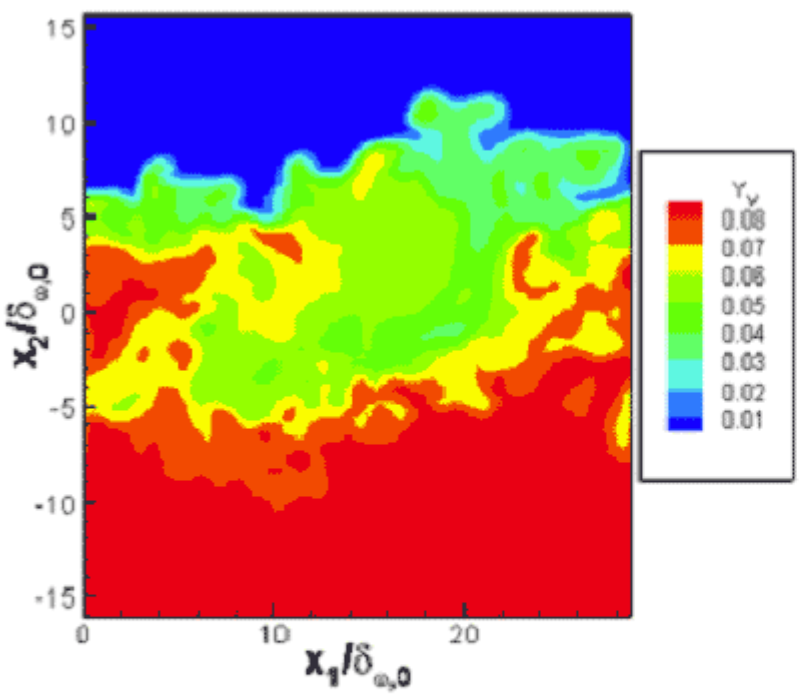


drop number density (m^{-3})

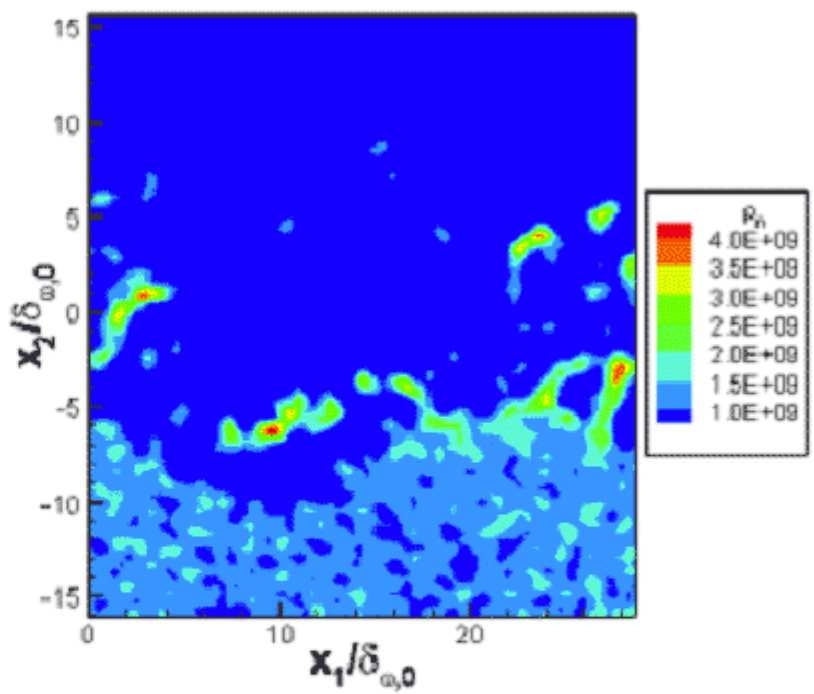
Simulation for $ML_0 = 0.2$.

BETWEEN-THE-BRAID PLANE CONTOURS OF THE VAPOR MASS FRACTION AND DROP NUMBER DENSITY

FILTERED AND COARSENED DNS AND OLY 1 OUT OF 8 DROPS PORTRAYED



vapor mass fraction

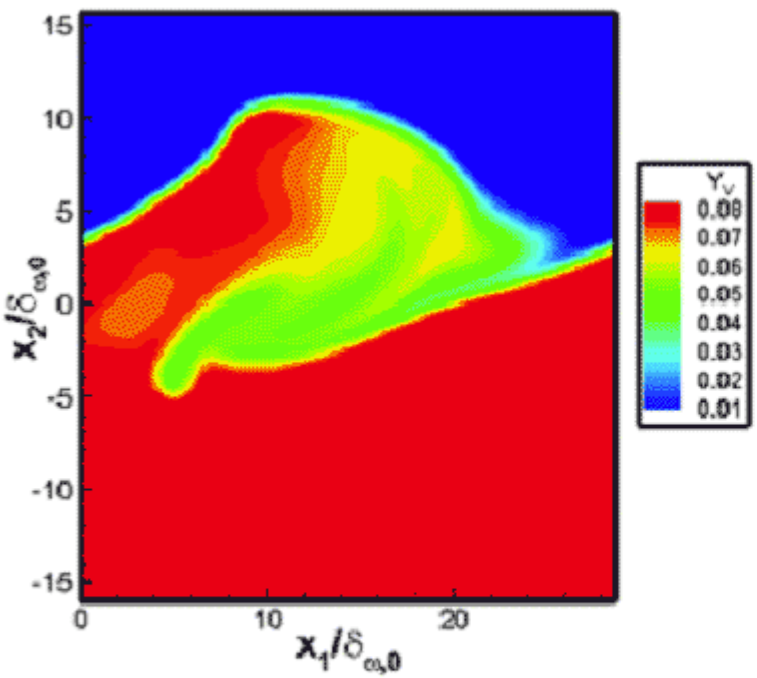


drop number density (m^{-3})

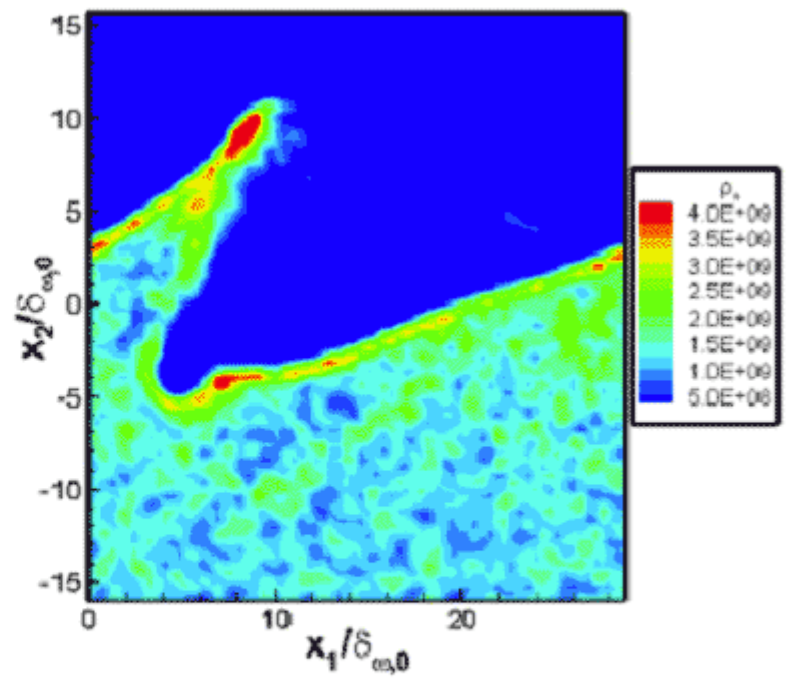
Simulation for $ML_0 = 0.2$.

BETWEEN-THE-BRAID PLANE CONTOURS OF THE VAPOR MASS FRACTION AND DROP NUMBER DENSITY, cont'd

TYPICAL SMALL-SCALE (ie MIXING LENGTH) MODEL USED IN ENGINEERING CALCUATIONS AND ONLY 1 OUT OF 8 DROPS CONSIDERED IN THE SIMULATION; 20.1 CPU HOURS



vapor mass fraction

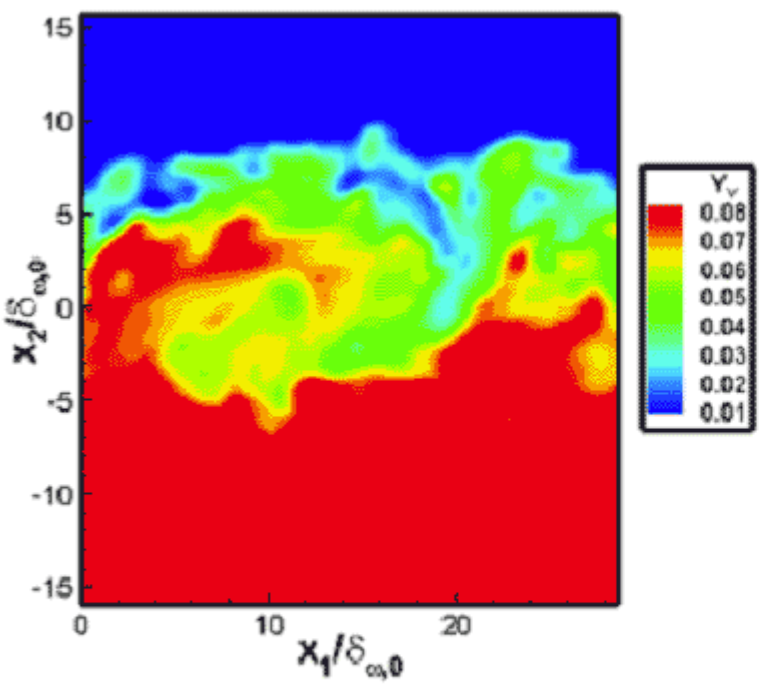


drop number density (m^{-3})

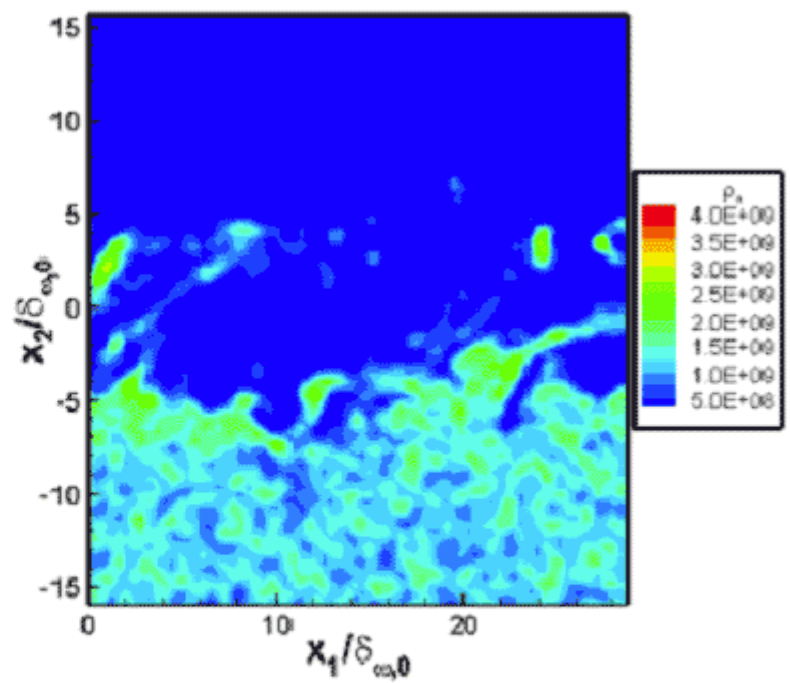
Simulation for $ML_0 = 0.2$.

BETWEEN-THE-BRAID PLANE CONTOURS OF THE VAPOR MASS FRACTION AND DROP NUMBER DENSITY, cont'd

JPL-DEVELOPED MODEL AND ONLY 1 OUT OF 8 DROPS CONSIDERED IN THE SIMULATION; 19.8 CPU HOURS



vapor mass fraction

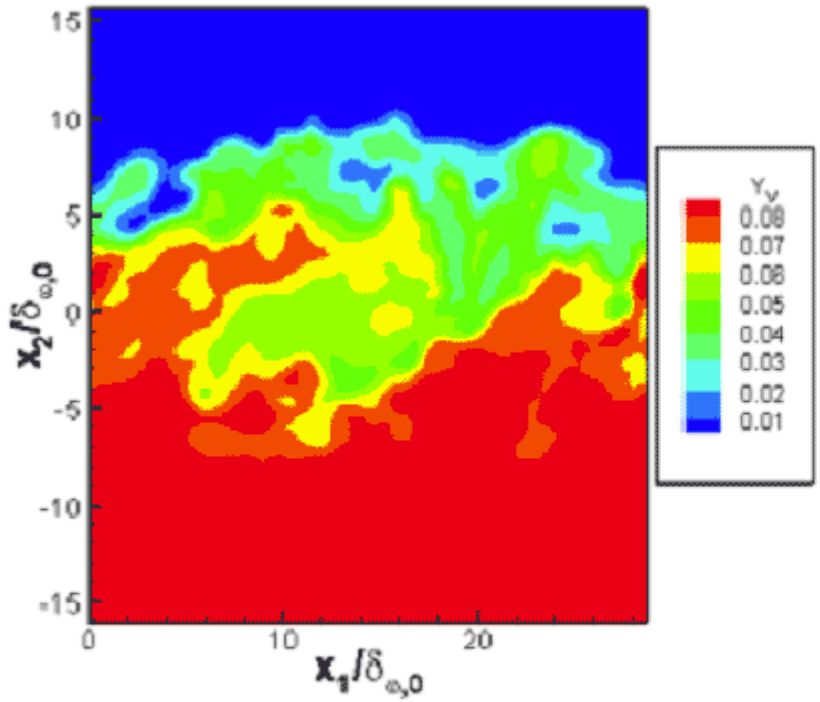


drop number density (m^{-3})

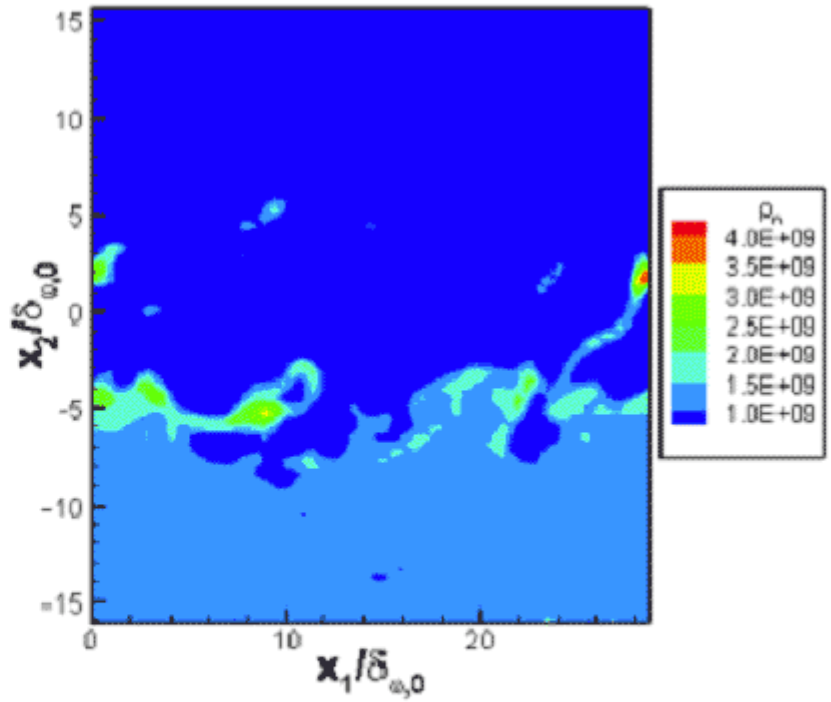
Simulation for $ML_0 = 0.2$.

EFFECT OF THE NUMBER OF DROPS

JPL-DEVELOPED MODEL WITH ALL DROPS; 113 CPU HOURS



vapor mass fraction



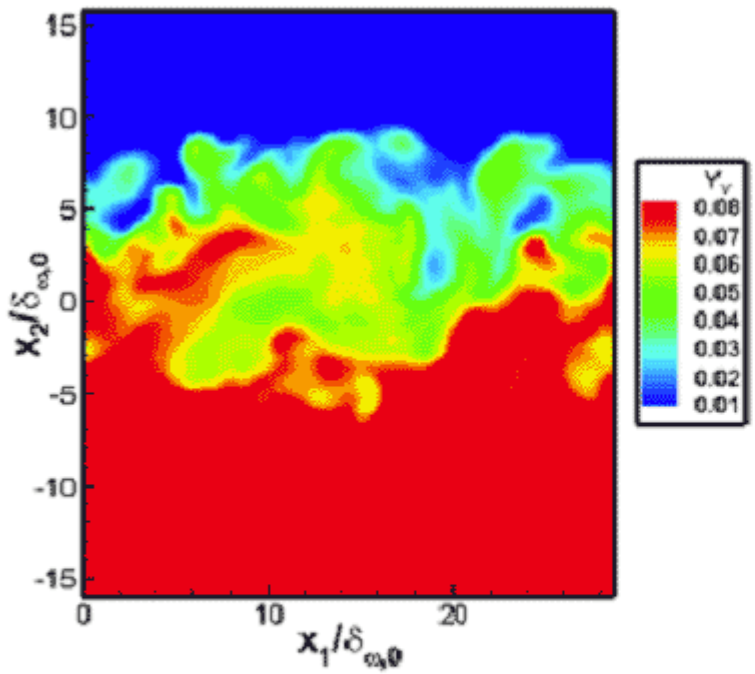
drop number density (m^{-3})

Simulation for $ML_0 = 0.2$.

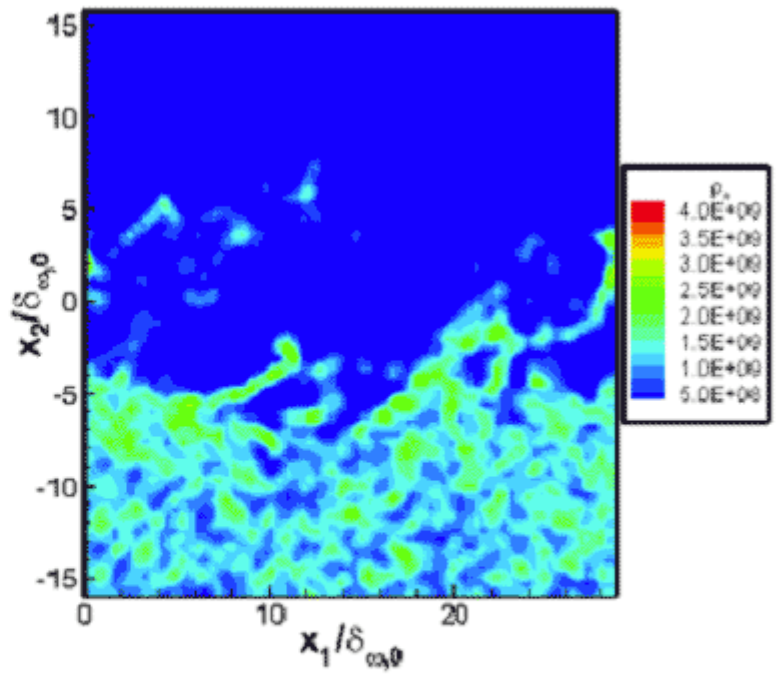
EFFECT OF THE NUMBER OF DROPS, cont'd

JPL DEVELOPED MODEL WITH ONLY 1 OUT OF 16 DROPS

12.2 CPU HOURS



vapor mass fraction



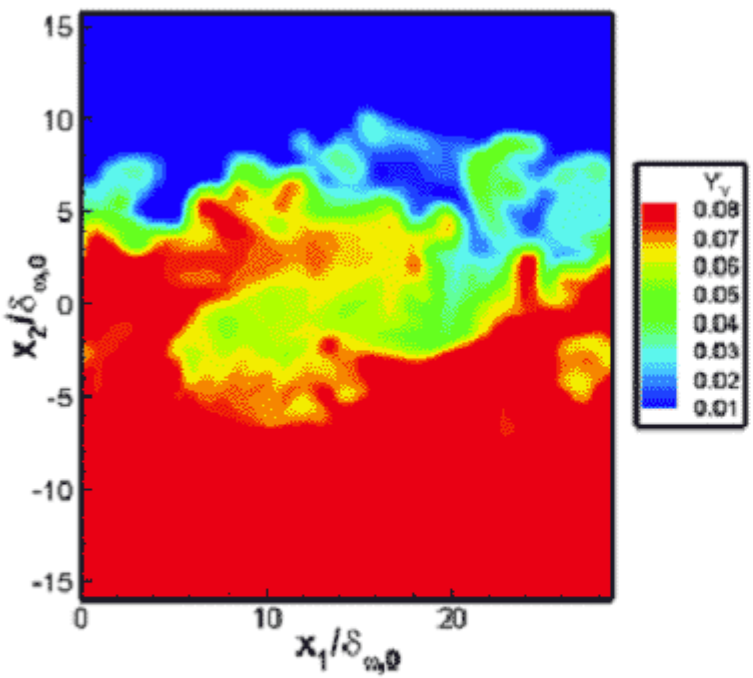
drop number density (m^{-3})

Simulation for $ML_0 = 0.2$.

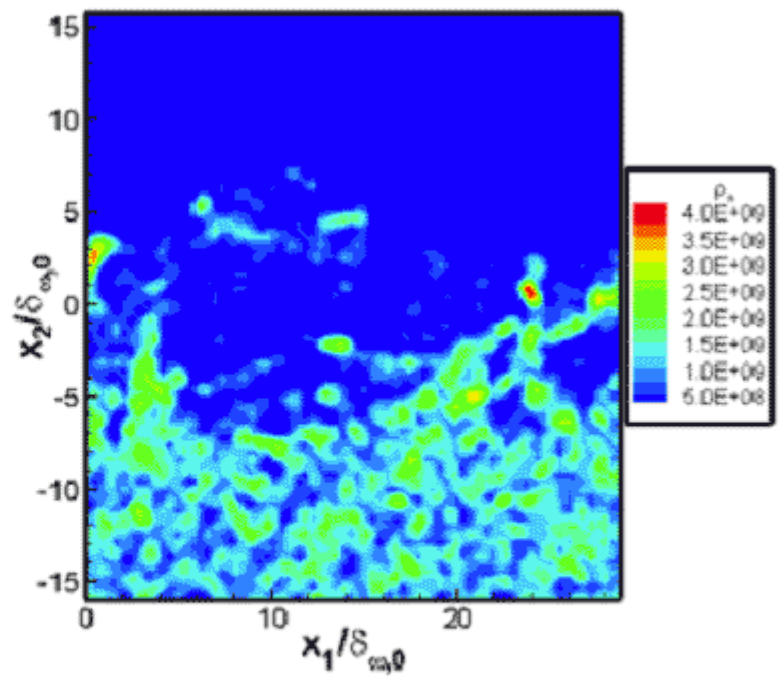
EFFECT OF THE NUMBER OF DROPS, cont'd

JPL DEVELOPED MODEL WITH ONLY 1 OUT OF 32 DROPS

9.4 CPU HOURS



vapor mass fraction



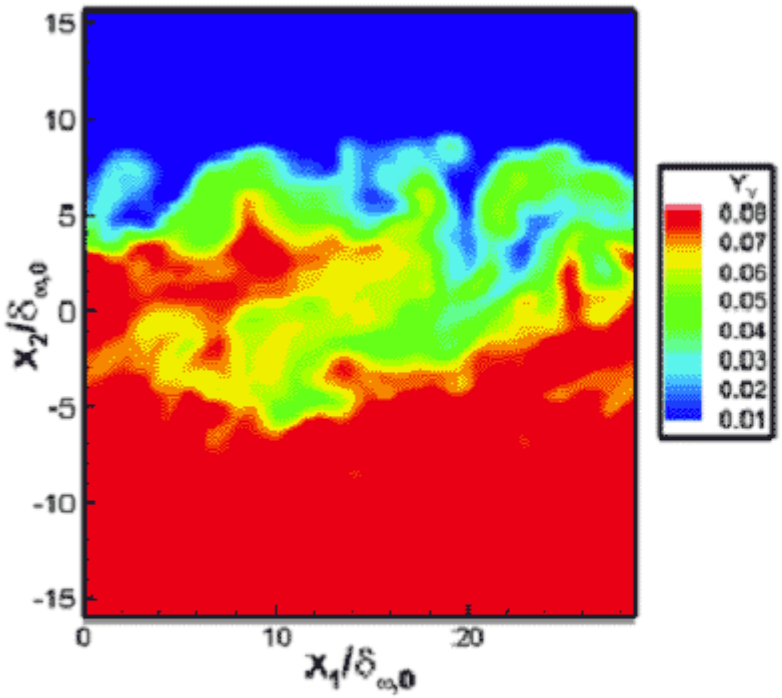
drop number density (m^{-3})

Simulation for $ML_0 = 0.2$.

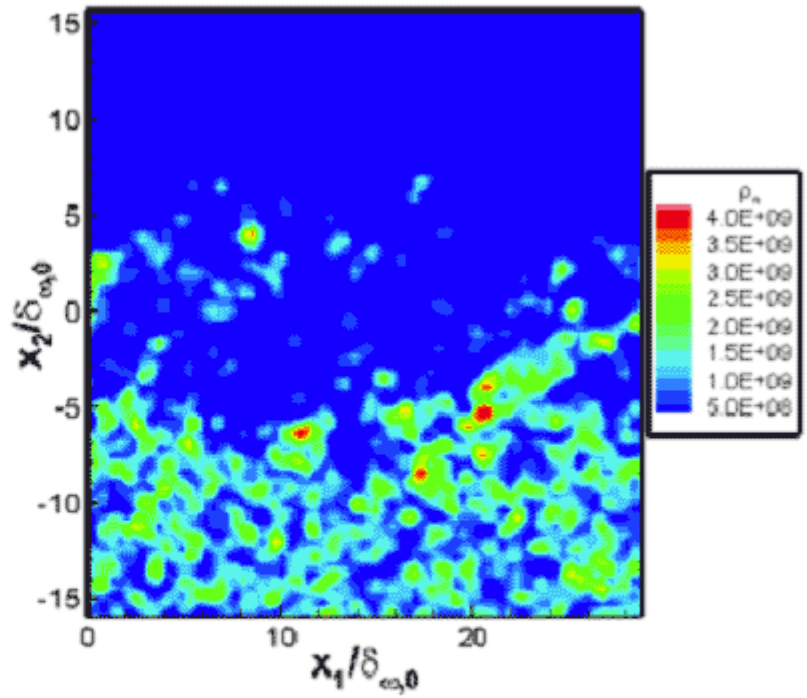
EFFECT OF THE NUMBER OF DROPS, cont'd

JPL DEVELOPED MODEL WITH ONLY 1 OUT OF 64 DROPS

8.1 CPU HOURS



vapor mass fraction



drop number density (m^{-3})

Simulation for $ML_0 = 0.2$.

Photoelectrochemical Hydrogen Production

Hawaii Natural Energy Institute

School of Ocean&Earth Science and Technology

University of Hawaii, Manoa

Eric L.Miller
Richard E. Rocheleau

ACKNOWLEDGEMENTS

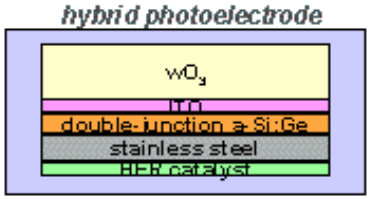
-U.S. Department of Energy for continued support of research

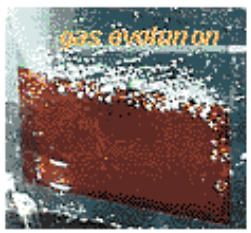
- HNEI Thin Films Lab Staff (D. Paluselli, B. Marsen, et al.) for tireless efforts

- Dr. Shahed Khan of Duquesne University

- Dr. Xunming Deng from the University of Toledo

Poster Outline



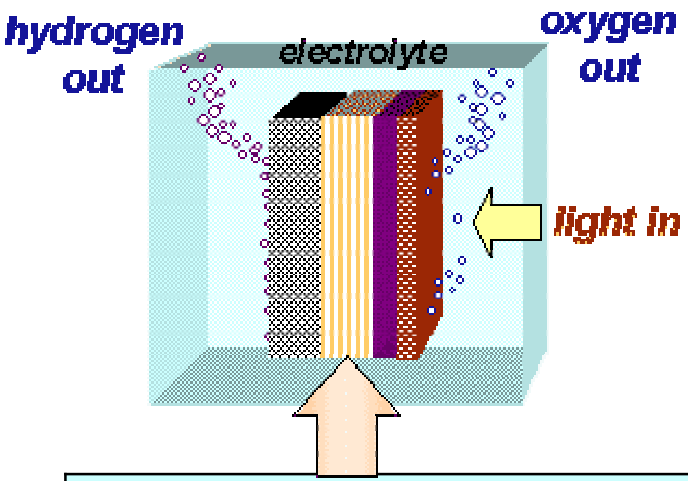


- **Approach and Goals:**
  - *Low-cost' Multijunction planar photoelectrodes for hydrogen production*
- **Hybrid Photoelectrodes**
  - *True photoelectrochemical device based on electrochemical interface at metal oxide films with integrated solid-state voltage assist*
- **Technical Barriers**
  - *General barriers to photoelectrochemical production*
  - *Hybrid photoelectrode development issues*
- **Approach to Technical Barriers**
  - *Materials research and development*
  - *Photoelectrode research and development*
  - *Advanced integrated desings*
- **Progress Status**
  - *Major milestones met*
  - *Materials: Critical metal oxides developed*
  - *Photoelectrodes: Stable hybrid demonstrated*
- **Summary and Future Directions**
- **Important Research Partnerships**

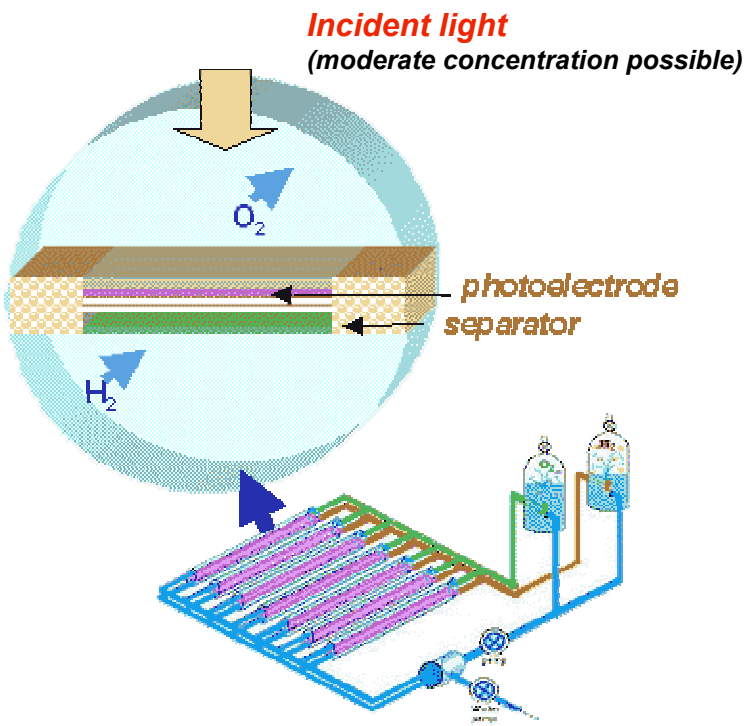
General Approach & Goals

Multi-junction Planar Photoelectrodes using Low-Cost Thin Film Materials

GOALS: 7.5% STH by 2005 @ $360/kg; 9% STH by 2010 $22 /kg



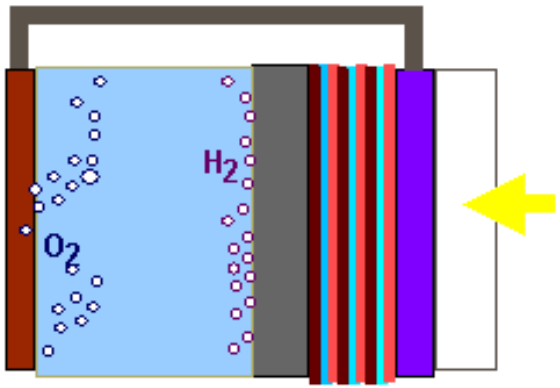
Focus Materials for Planar Photoelectrodes	
low-cost solid state semiconductor films	*amorphous Si/Ge:H*
	μ-crystalline Si
	CIS, CIGS
electrochemical metal oxide semiconductor films	*iron-oxide*
	tungsten trioxide
	titanium dioxide
catalyst films	*mixed metals (Ni, Mo, Co, etc.)*

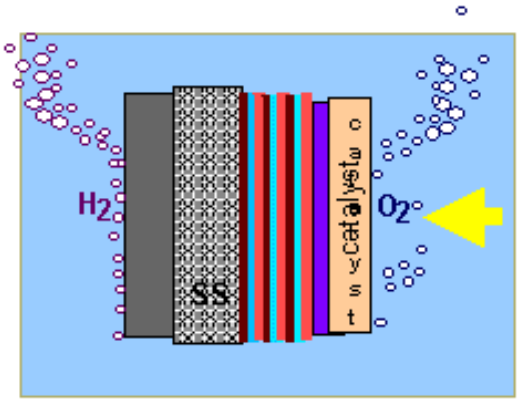


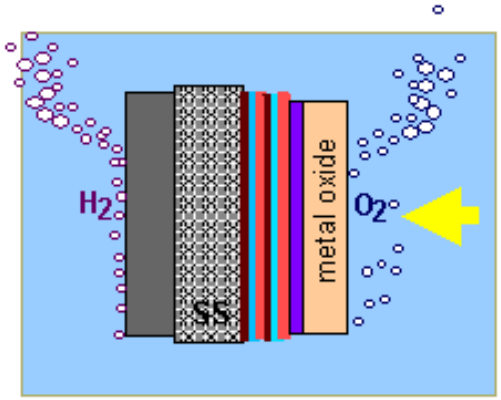
tube array with gas collectors

Multijunction Photoelectrodes

Key Finding from Analytical and Experimental Work:
Efficient utilization of sunlight for water splitting requires multi-junction systems to provide sufficient voltage and current







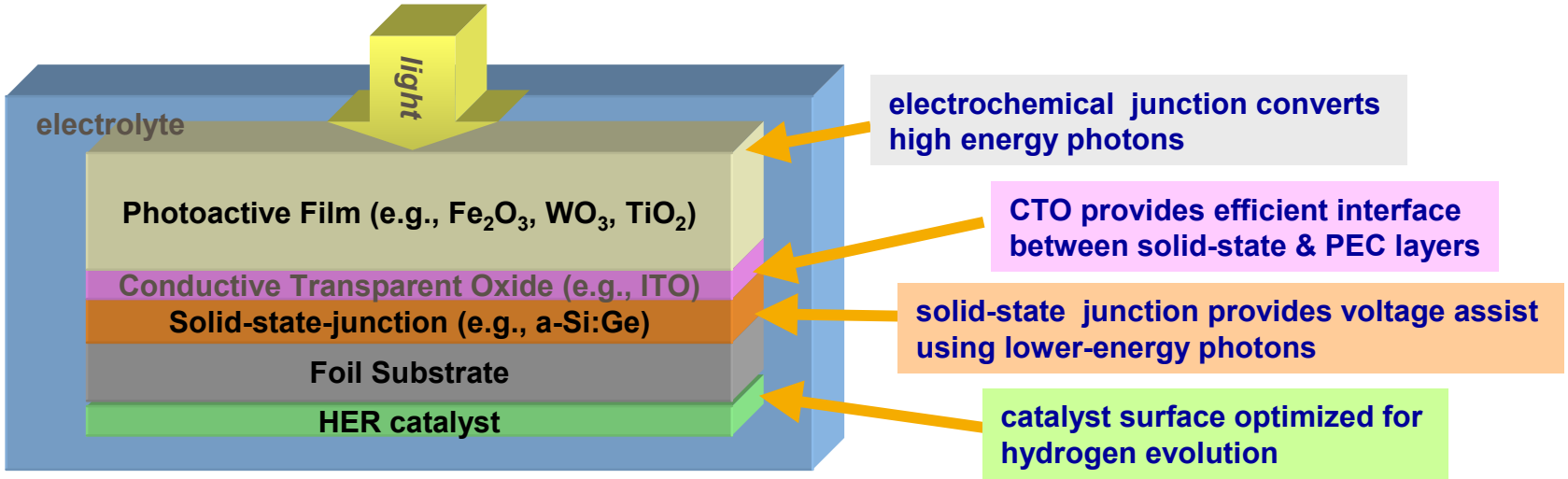
1997:
Triple junction amorhpous silicon device on glass/ITO superstrate connected to separated OER & HER electrodes demonstrates stable hydrogen production at 7.8% STH.

1999:
Triple junction amorhpous silicon device on stainless steel substrate coated with HER catalyst on back & with OER catalyst on front- operated with limited success- OER layer thin enough for transparence offered little corrosion protection

Present:
Multijunction Hybrid Photoelectrode: true electrochemical device where the front catalyst from the 1999 structure Is replaced by a photo-active oxide. The embedded solid-state junction provides a voltage assist to the metal-oxide/electrolyte junction: Hydrogen Is evolved on catalyzed back surface

Hybrid Photoelectrodes

integrated multijunction electrochemical device to provide sufficient photo-generated current & voltage for efficient water splitting *(patent in progress)*



KEY FEATURES:

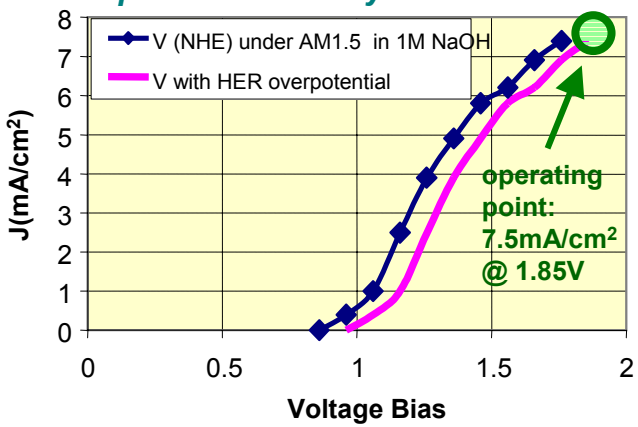
- Oxide interface provides corrosion resistance & long life
- Solid-state junction reduces metal-oxide/electrolyte interface voltage requirements
- Proven metal oxides can be used in hybrid devices for efficient, un-biased water splitting
  - Iron oxide, tungsten trioxide, modified titanium dioxide
- Simple planar structure allows easy fabrication
- Leverages DOE investments in other programs (e.g., Photovoltaics for solid-state materials)

Hybrid Photoelectrode Material Systems

➢**Initial conceptual designs based on spray-pyrolysis nano-structured oxides**

Iron Oxide Films

Duquesne University. Khan & Akikusa

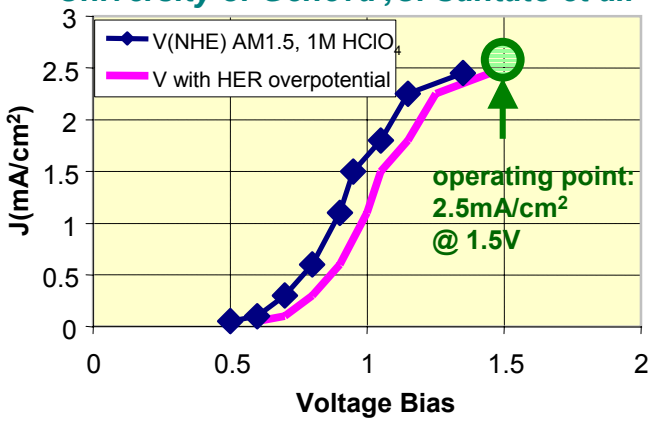


Incorporation in Hybrid Photoelectrodes

- Photojunction formed in alkaline media
- High photocurrents / low voltage

Tungsten Trioxide Films

University of Geneva ,C. Santato et al.



Incorporation in Hybrid Photoelectrodes

- Photojunction formed in acid media
- Moderate photocurrents / better voltage

TECHNICAL ISSUES:

- **Pyrolysis deposition temperatures (400-500°C) *Too High* for hybrid structure**
- **High efficiency water splitting requires modification of oxide properties**

Technical Barriers

GENERAL BARRIERS TO PEC HYDROGEN PRODUCTION

from "Multi-Year Plan (draft 3-20): Hydrogen Production"

"Durable materials with the appropriate characteristics for photoelectrochemical hydrogen production that meet the program goals have not been identified… Materials with smaller bandgaps more efficiently utilize the solar spectrum, but are often less energetically favorable for hydrogen production because of the bandedge mismatch with respect to either hydrogen or oxygen redox potentials… Hybrid designs combining multi-layers of materials could address issues of durability and efficiency. "

SPECIFIC HYBRID PHOTOELECTRODES ISSUES

- **CRITICAL ISSUE: Development of 'low-temperature' (<300ºC) processes which yield photoactive & stable metal oxide films**
- **ONGOING CONSIDERATIONS: Continued development of optimized materials and device designs are needed to meet program goals. Compatibility of semiconductor and catalytic layers, voltage tailoring, and current matching remain important considerations**

Approach to Technical Barriers

- **MATERIALS RESEARCH:** Current focus on developing low-temperature reactive sputtering process to produce photoactive & stable metal oxide films
  - Partnership Support (Duquesne University): develop further understanding of structure & composition of photoactive metal oxides for engineering new, process-compatible materials, including Fe_2O_3 , WO_3 & modified TiO_2

- **PHOTOELECTRODE RESEARCH:** Current focus on incorporating best available materials into hybrid photoelectrode structures to evaluate performance & stability
  - Partnership Support (University of Toledo): design & fabricate multi-junction amorphous-silicon alloy devices with specified voltage and current characteristics

- Continued development of optimized materials and device designs for use in high-performance / low-cost hybrid photoelectrodes

Progress: Timeline and Milestone

All Milestones ON or AHEAD of Schedule
(as of May 2003)

from "2003 Spend Plan"

start 1/1/03

TASK 1: Materials R&D	Comparative evaluation of available a-Si:Ge materials/devices	2nd quarter	*completed*
	Comparative evaluation of available Fe_2O_3 materials	2nd quarter	
	Comparative evaluation of available CIS/CIGS materials	3rd quarter	*in progress*
	Identification of alternative materials for hybrid applications	4th quarter	
TASK 2: photoelectrode R&D	Preliminary designs: a-Si:Ge/Fe_2O_3 photoelectrode test devices	1st quarter	*completed*
	Performance database of fabricated test devices	2nd quarter	
	Optimized design of a-Si:Ge/Fe_2O_3 photoelectrodes	3rd quarter	*in progress*
	Performance database of fabricated optimized devices	4th quarter	
	Design for CIGS-based high-efficiency hybrid photoelectrode	4th quarter	

end 12/31/03

Progress: Materials R&D

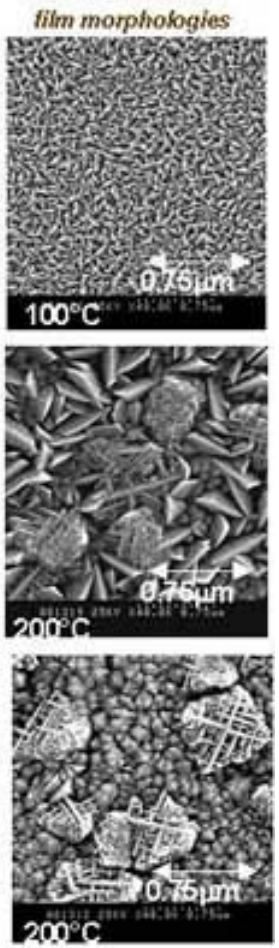
Low-Temperature Photoactive Metal Oxides

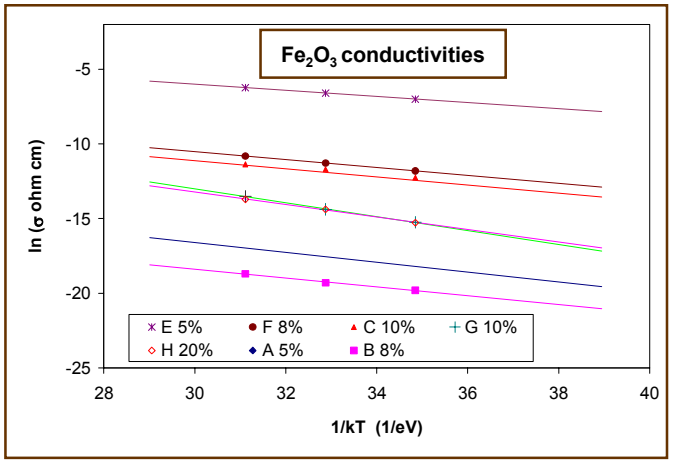
- Fe_2O_3 films successfully deposited using low temperature sputter process
  - Ability to engineer key film properties successfully demonstrated
  - Excellent film adhesion and stability in alkaline media achieved
  - Photocurrents up to 0.1 mA/cm^2 achieved under 1-sun in films deposited to date
- WO_3 films successfully deposited using low temperature sputter process
  - Ability to engineer key film properties successfully demonstrated
  - Excellent film adhesion and stability in acid media achieved
  - Photocurrents up to 0.9 mA/cm^2 achieved under 1 sun in films deposited to date

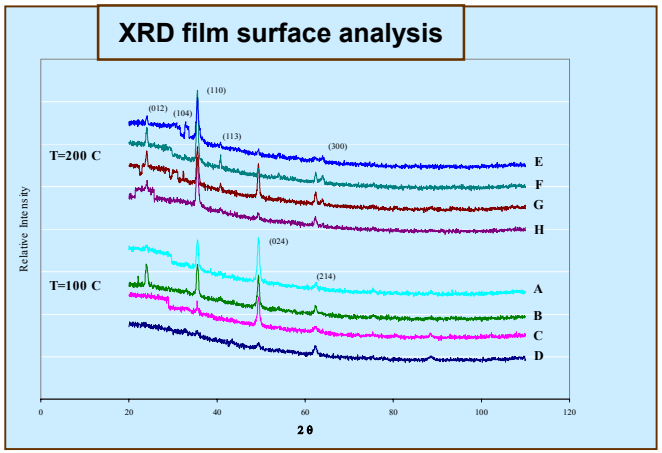
Advanced Solid-State Materials

- Amorphous silicon devices for current photoelectrode tests obtained from partners
- Micro-crystalline silicon films developed in-house (for advanced tandem cells)
- High efficiency copper-indium-gallium-diselenide (CIGS) produced in house
  - 14% efficient 4cm^2 CIGS cell on foil substrate demonstrated

Progress: Fe_2O_3 Film Research

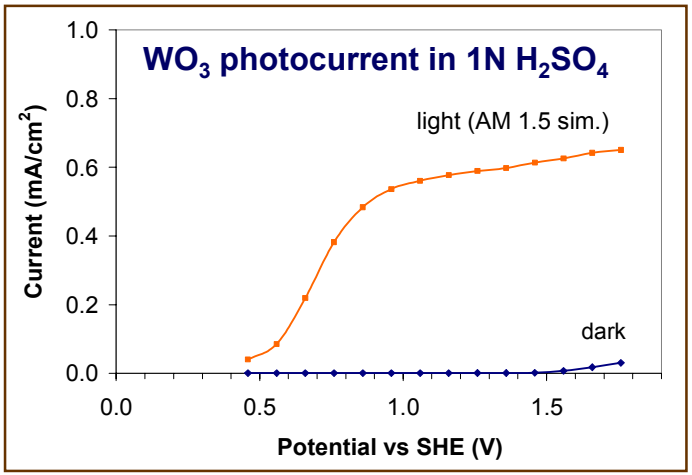


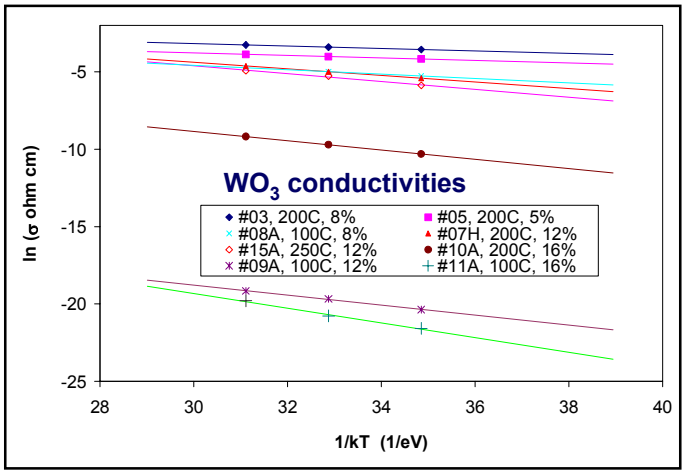




- Low temperature (<300°C) reactive sputtering from iron target
- Variable substrate temperature and oxygen partial pressure
- Structure/electronic properties vary strongly with deposition parameters
- High-purity Hematite in all films with bandgaps from 1.8 - 2.0 eV
- Film resistivities range from 10^3 - 10^9 ohm cm
- Withstands long-term exposure to 1N KOH (tested for 6 months)
- Films to date: photocurrents up to 0.1 mA/cm^2 under 1 sun in alkaline

Progress: WO_3 Film Research





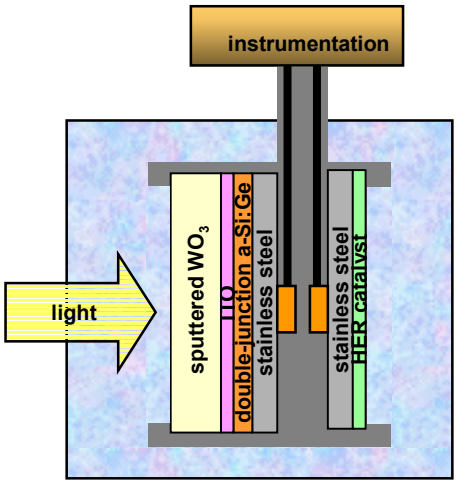
- Investigation initiated February 2003
- Low temperature (<300°C) reactive sputtering from tungsten target
- Variable temperature and oxygen partial pressure
- Measured bandgaps ranging from 3.0-3.2 eV
- Film resistivities range from 10^1 - 10^{10} ohm cm
- Excellent chemical stability in in 1Normal H_2SO_4
- Films deposited to date: photocurrents from 0.2-0.6 mA/cm^2 under 1 sun illumination in sulfuric acid

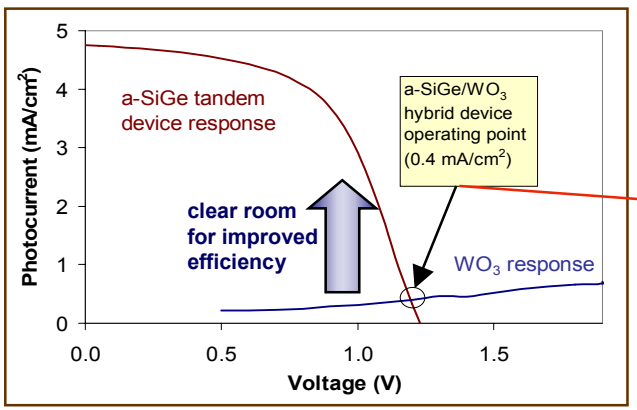
Progress: Photoelectrode Breakthrough

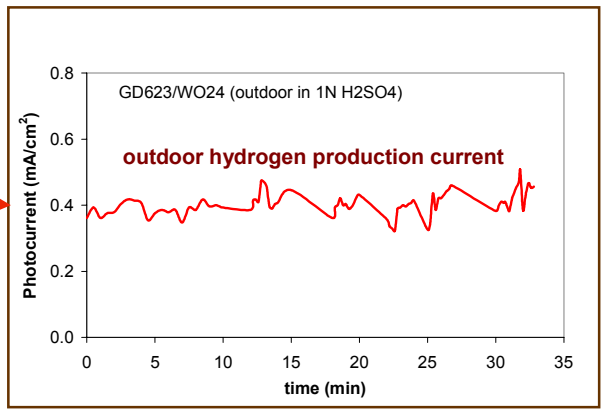
Stable Operation of Hybrid Photoelectrodes Demonstrated!

(using best low-temperature materials fabricated to date)

- **DEVICE STRUCTURE:**
  - amorphous silicon-alloy tandem (U. Toledo)
  - Low-temperature sputtered WO_3 (U. Hawaii)
  - 2.5 cm^2 area with separated counter electrode (for photocurrent measurement)
- **DEVICE PERFORMANCE:**
  - Currents up to 0.5mA/cm^2 in 1-sun outdoor tests (.7%STH)
  - Stable operation in 1N H_2SO_4 measured for over 5 hours
  - Photocurrents consistent with measured properties of the WO_3 material and the tandem silicon cell
  - Analysis indicates significant efficiency enhancement with improved metal-oxide properties







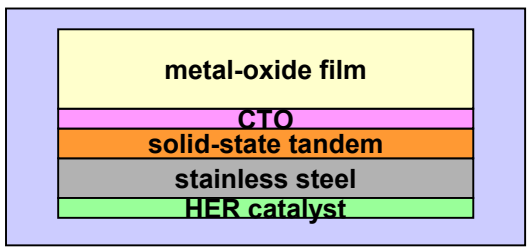
Summary & Future Directions

Status Summary

- **STABLE OPERATION of integrated thin-film Hybrid Photoelectrodes in aqueous electrolyte under 1-sun illumination has been demonstrated for the first time! This is an extremely encouraging indication that we are on a *right track* toward *commercialize-able* photoelectrochemical hydrogen production.**
- **We have identified optical/electronic properties of the present hybrid-compatible metal-oxides as the KEY limiting factor to efficiency… clearly defining the primary focus for continued research efforts.**

Future Directions

We plan to continue development of the Hybrid Photoelectrode, with expanded effort to optimize hybrid-compatible materials for efficiency and long-life. We are confident that by continuing this approach, we will be able to meet the 2005 and 2010 program goals.



Important HNEI Collaborations

CURRENT:

- Duquesne University: fabrication of nano-structured Fe_2O_3 films.
- University of Toledo: design & fabrication of a-Si:Ge multijunctions.
- "IEC" University of Delaware: design & fabrication of high efficiency CIGS.
- DayStar Technologies: design & in-house fabrication of CIGS materials.
- "UNAM" Mexico: evaluation of alternative materials, μcr-SiC corrosion studies.
- General Motors: PEC development lab for device evaluation.
- IEA Annex 14 connections: Fe_2O_3, WO_3 and TiO_2 film studies.

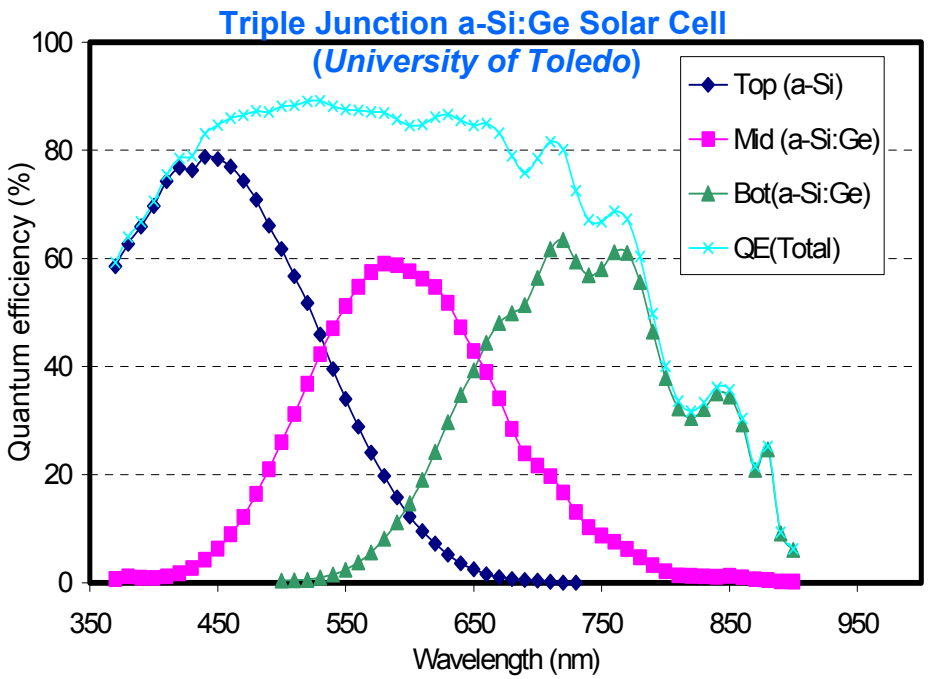
FUTURE:

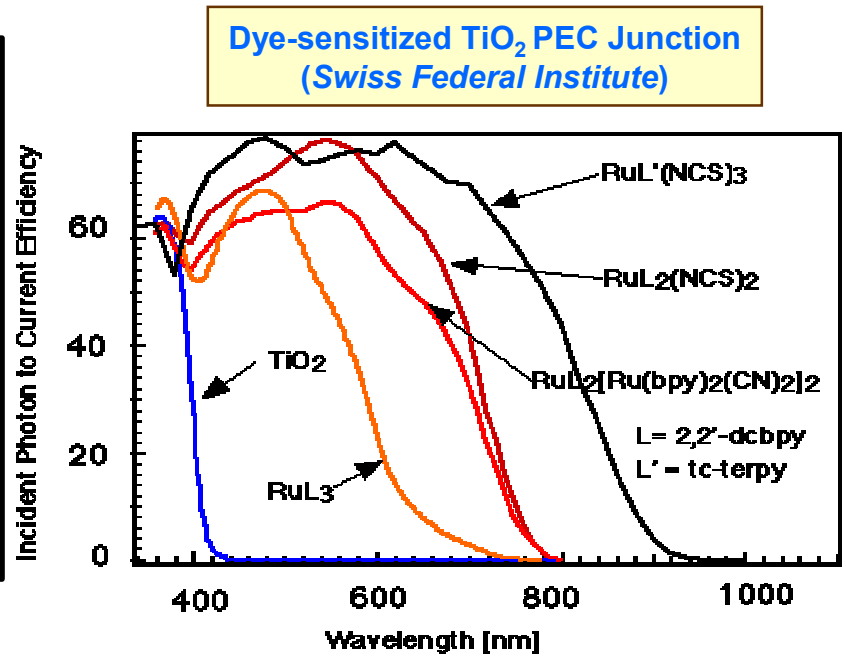
- NREL, UCSB & SRI: Fe_2O_3, WO_3 ,TiO_2 & mixed metal catalyst film screening

Supporting Information Slides…

not included in poster

Hybrid Photoelectrode Concept





- Top cell in the solid-state stack can be replaced with an electrochemical junction.
- Each junction must be current matched for high efficiency.
- Series connection of all three junctions needed to generate bias required to split water.
- Top layer must be stable under OER…. (NOT dye-sensitized TiO_2!)

Hybrid Photoelectrode Design

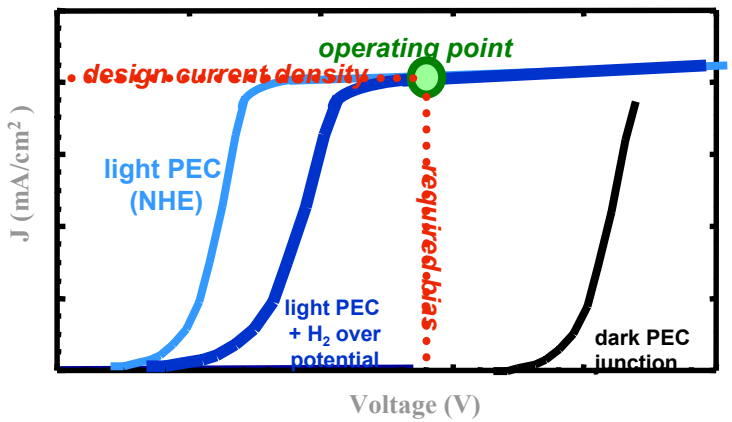
Basic Structure:

photoelectrochemical junction

photoactive semiconductor
interface layer
tandem solid-state junction
metal substrate
HER catalyst

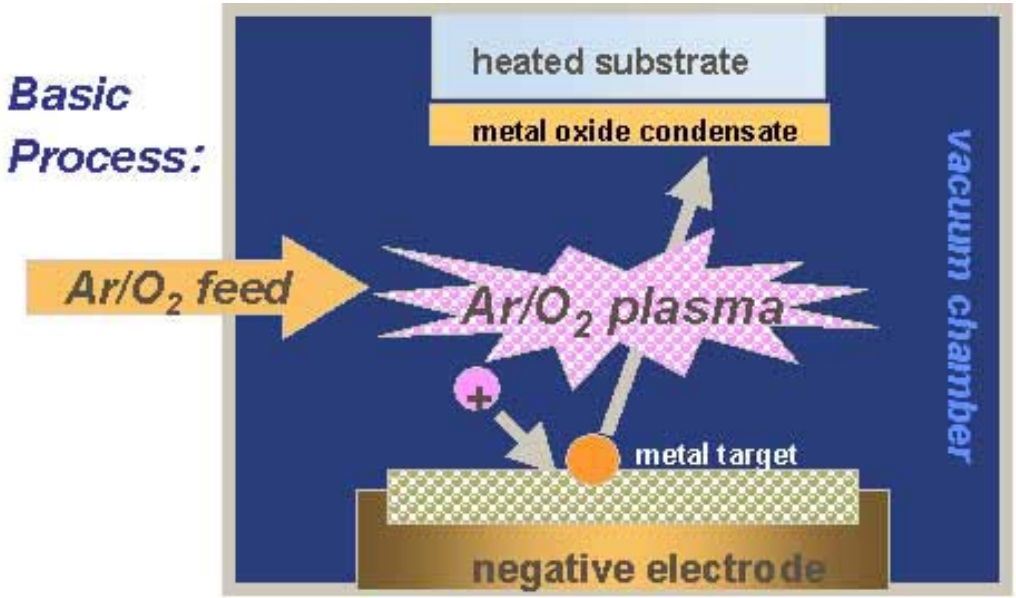
- No lateral current collection loss.
- Reduction of front surface overpotential loss.
- Back surface overpotential minimized by catalyst & texturing.
- Solid-state junctions minimized.
- Simple planar geometry for fabrication.
- Uniform stable outer layer for good chemical resistance.
- Potential for LOW COST MATERIALS

Modeling:



- Light JV and quantum efficiency for PEC junction needed.
- JV response of the PEC junction is photoshifted.
- Correction for the hydrogen overpotential loss is added.
- Intersection with the design current density establishes the necessary voltage bias.
- Tandem solid-state cell designed to drive current at the operating point using available photons.
- CURRENT MATCHING critical: efficiency limited by lowest-current cell in stack.

Reactive Sputtering of Metal Oxides



- ‘Low-temperature’ reactive r.f. sputter from metallic target
- High-purity films attainable in vacuum deposition process
- Important process parameters influencing film properties:
  - Ambient P, Oxygen PP, Substrate T, r.f. Power, Geometry, Substrate material
- Important film properties for photoelectrochemical applications:
  - Thickness, Uniformity, Composition, Morphology, Optical Bandgap, Conductivity, Chemical Stability, OER Activity, Photoactivity

Relevant Reference Material

- **Invited Lectures** (E.L. Miller)
  - International Conference on Advanced Materials (*ICAM 2001*):
  - International Materials Research Congress 2002 (*IMRC XI*)
  - International Conference on Advanced Materials (*ICAM 2003*):
- **Relevant Publications** (E.L. Miller, et al.)
  - "Design Considerations for a Hybrid Amorphous Silicon/Photoelectrochemical Multijunction Cell for Hydrogen Production", *International Journal of Hydrogen Energy*, 28 (2003) 615-623.
  - "A Hybrid Multijunction Photoelectrode for Hydrogen Production Fabricated with Amorphous Silicon/Germanium and Iron Oxide Thin FIlms", *IMRC XI Conference Proceedings.*
  - Manuscripts on sputtered Fe_2O_3 and WO_3 film research under preparation.
- **Patent Disclosure** (E.L. Miller, R. E. Rocheleau)
  - "Hybrid Solid-State/Electrochemical Photoelectrode for Hydrogen Production".

Past-Reviewers Comments

Comments from reviewers of the 2002 Program Review were generally supportive our approach and accomplishments, and indicated encouragement for continued progress.

We appreciate the support, and hope to sustain the forward momentum toward efficient solar-powered hydrogen production.

Photoelectrochemical Water Splitting

NREL Principal Investigator: John A. Turner

Current staff

Heli Wang, Postdoc
Todd Deutsch, University of Colorado (PhD Student)
John Einspahr, Colorado School of Mines (SS Student)
Jennifer Leisch, Colorado School of Mines (PhD Student)
Ken Menningen, University of Wisconsin (Sabbatical)

Recent Past

Joe Beach, Colorado School of Mines (PhD, Graduated Dec 2001)
Lara Kjeldsen, Colorado School of Mines (MS Student - graduated 2003)
Scott Warren, Whitman College (SS - now at Cornell)
Ken Varner, (SS - North Carolina State)

Others

Vladimir Aroutiounian, University of Yerevan, Armenia (CRDF, ISTC)
Arturo Fernández, Centro de Investigación en Energía-UNAM, Mexico

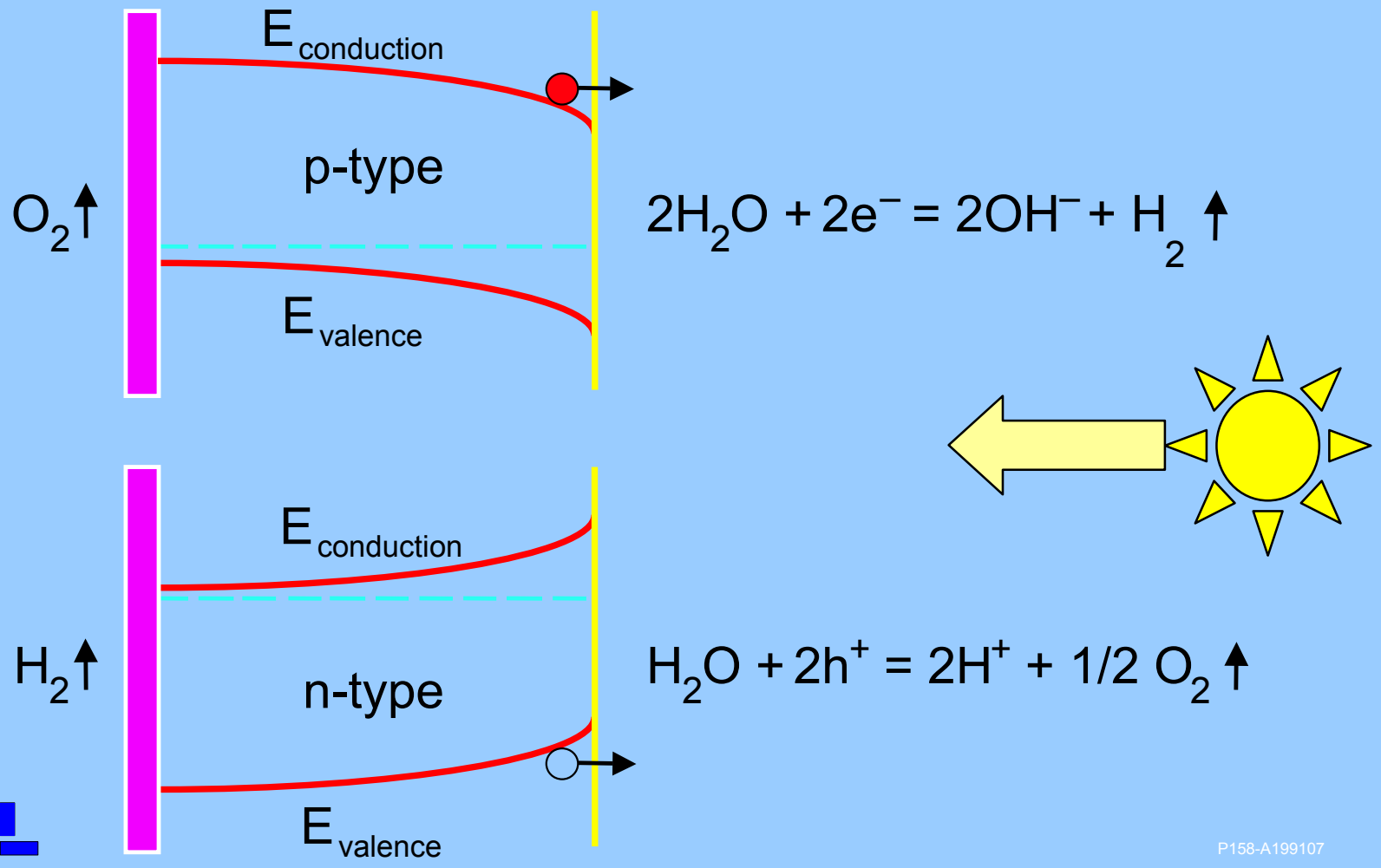
Photoelectrochemical Conversion

Goals and Objectives

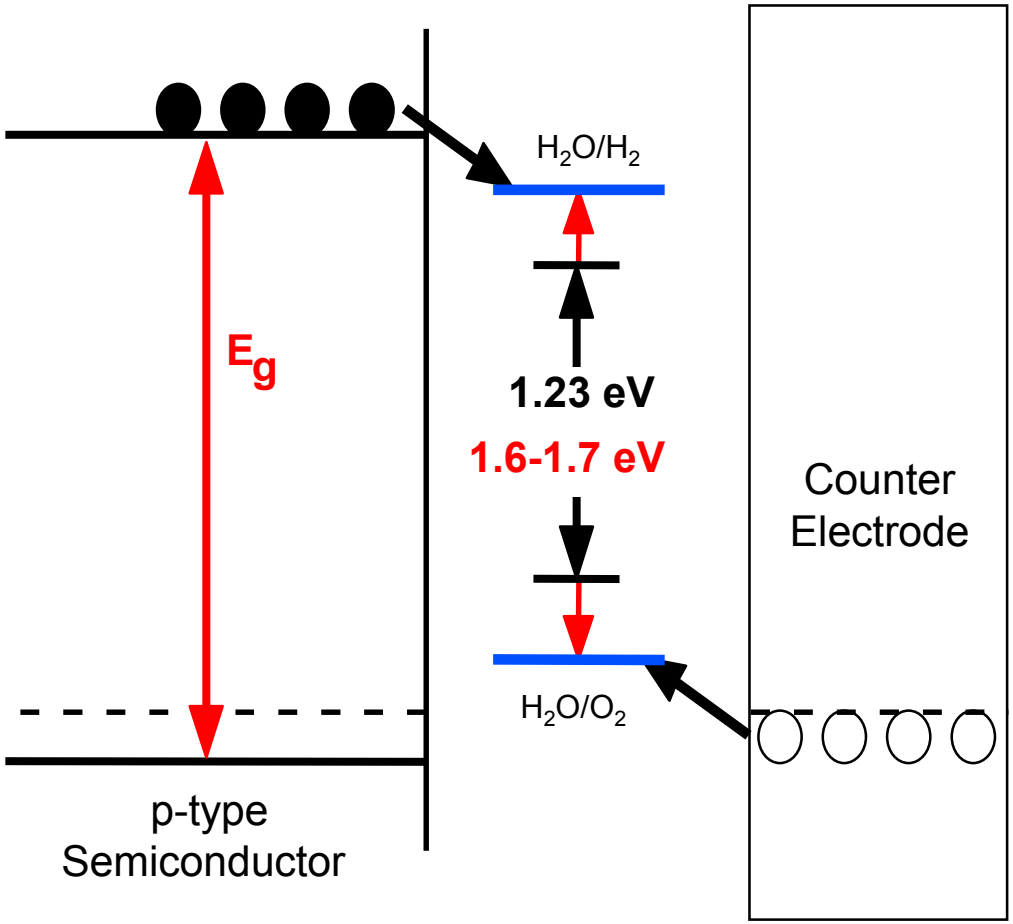
The goal of this research is to develop a stable, cost effective, photoelectrochemical based system that will split water using sunlight as the only energy input, with a solar-to-hydrogen efficiency of 10% with a 10-year lifetime. Our objectives are:

- Identify and characterize new semiconductor materials that have appropriate bandgaps and are stable in aqueous solutions.
- Study multijunction semiconductor systems for higher efficiency water splitting.
- Develop techniques for the energetic control of the semiconductor electrolyte interphase.
- Developing techniques for the preparation of transparent catalytic coatings and their application to semiconductor surfaces.
- Identify environmental factors (e.g., pH, ionic strength, solution composition, etc.) that affect the energetics of the semiconductor, the properties of the catalysts, and the stability of the semiconductor.

Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions



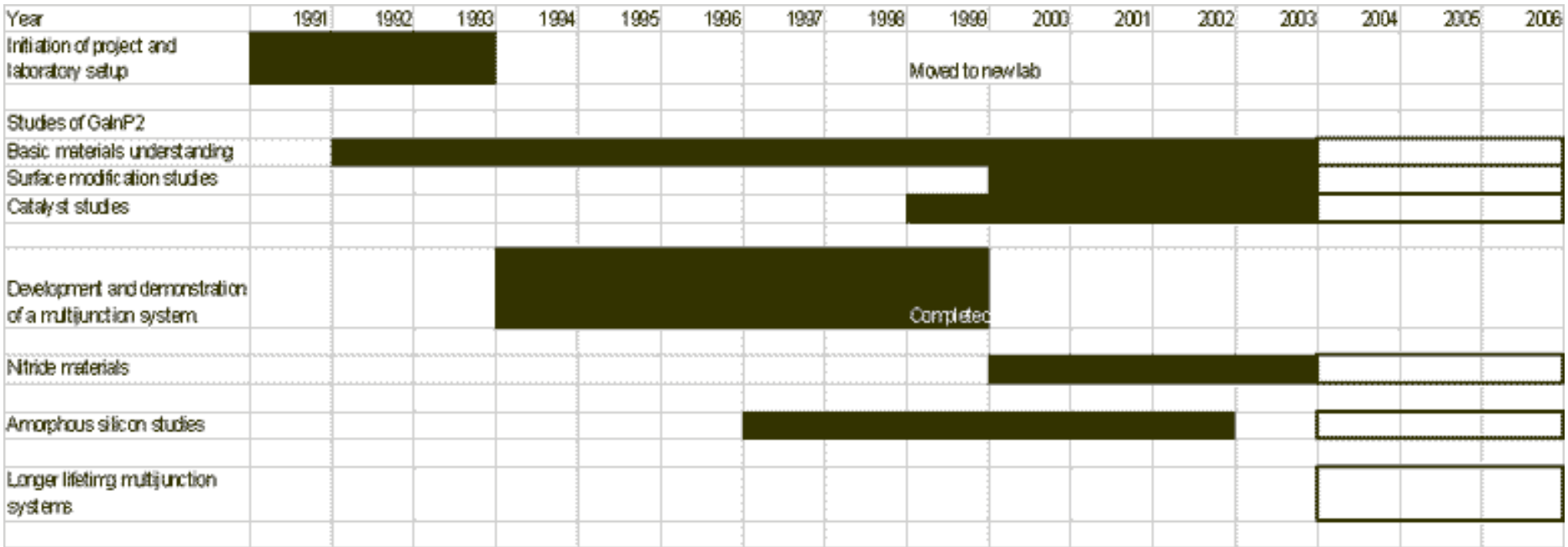
Material and Energetic Criteria



- **Band Gap** (E_g) must be at least 1.6-1.7 eV
- **Band Edges** must straddle H_2O redox potentials
- Fast charge transfer
- **Stable** in aqueous solution

All must be satisfied simultaneously

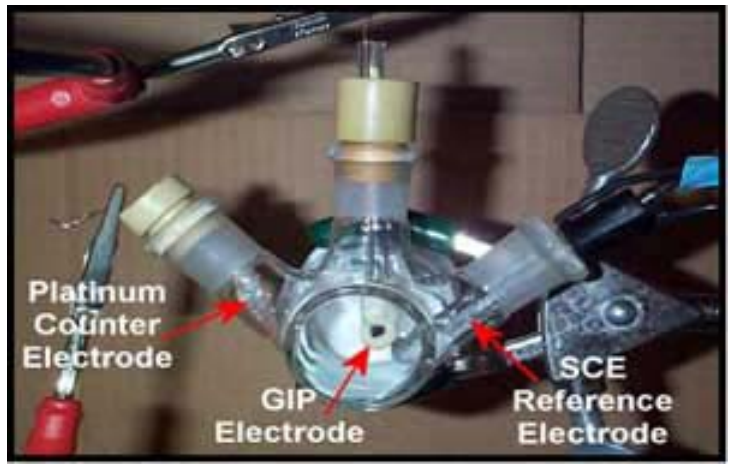
Timeline: 1991 to present



Cumulative Federal Funding: $4500K (~0.75 FTE + postdoc, average)

Project Status

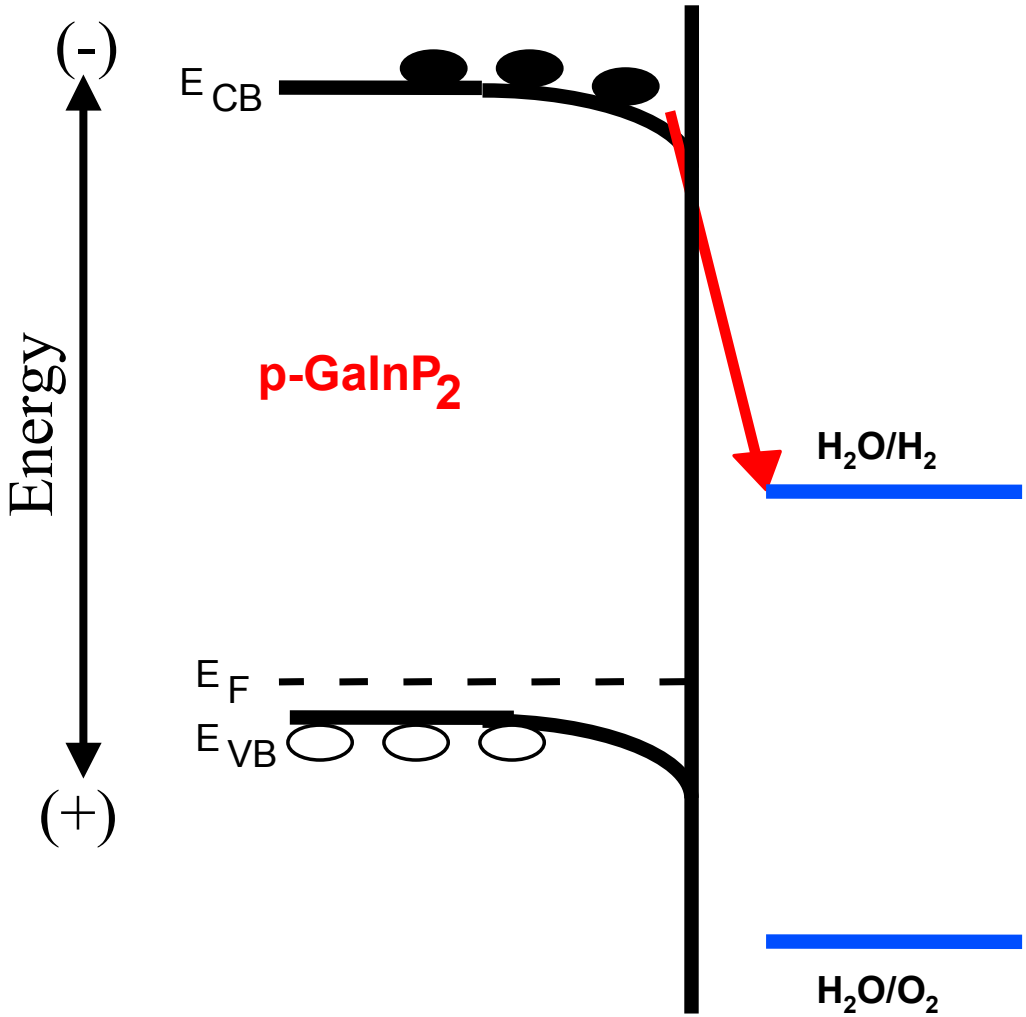
- Current status:
  - 12.4% efficiency multi-junction system, 20 hour lifetime.
  - H_2 Cost: >$13/kg



- Targets:
  - 10% solar-to-hydrogen efficiency, 10-year lifetime
  - H_2 Cost: $3/kg

Gallium Indium Phosphide/Electrolyte System

Used to gain a fundamental understanding of semiconductor/electrolyte junctions



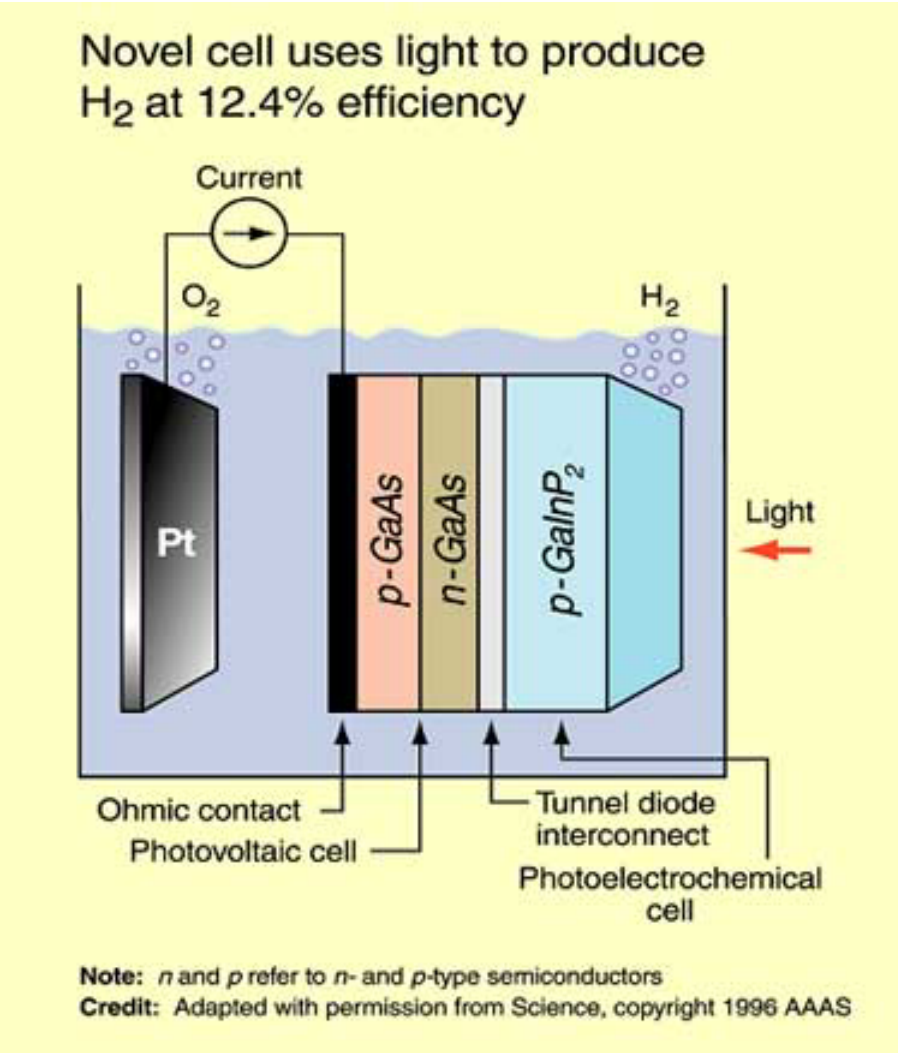
Eg = 1.83 eV

Band edges are 0.2-0.4 V too negative

Band edges are pH sensitive

World Record Photoelectrolysis Device

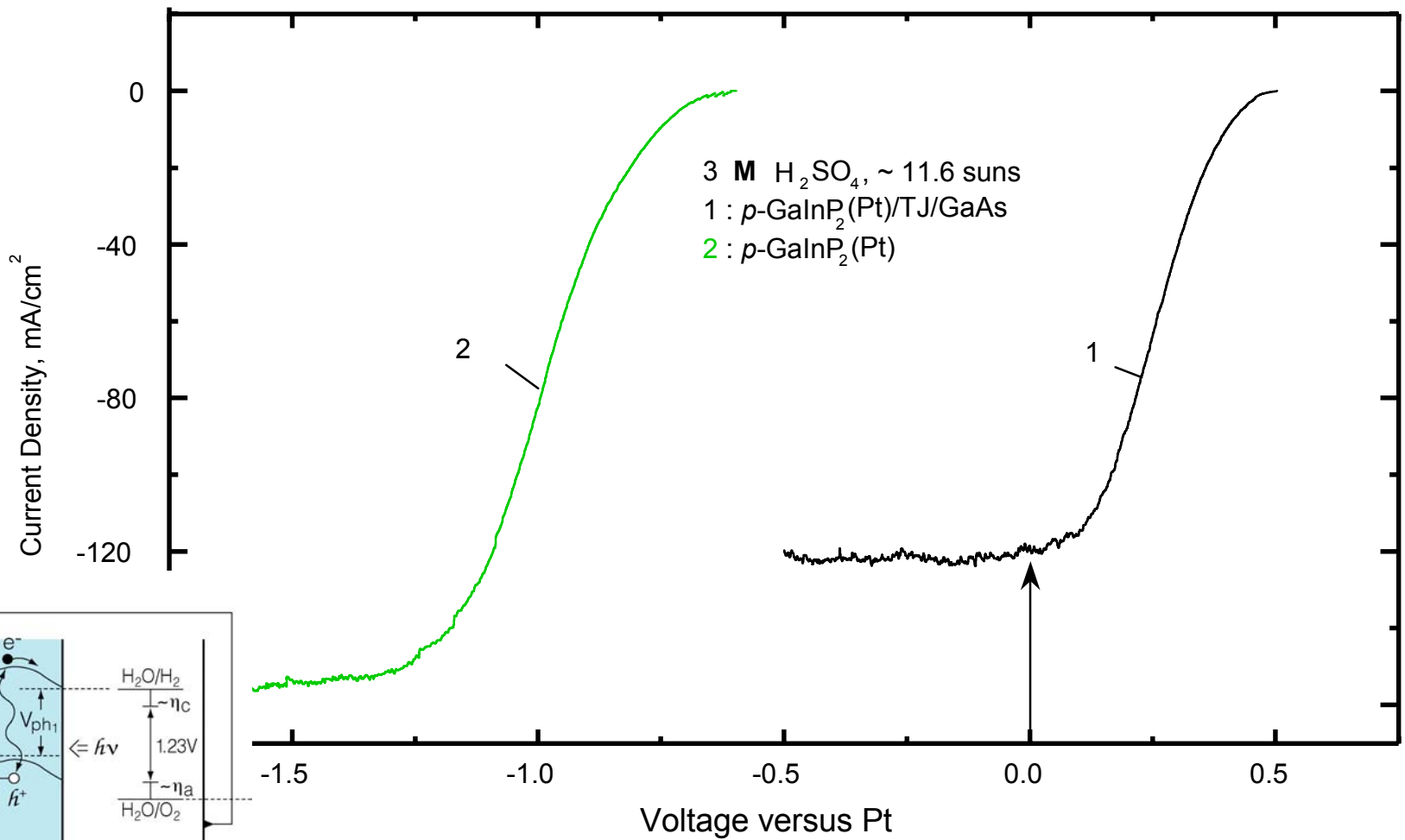
Science, April 17 1998.

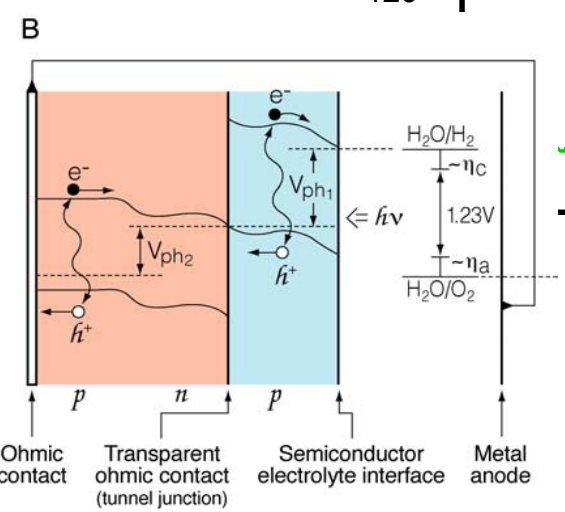


- Direct water electrolysis.
- Unique tandem (PV/PEC) design.
- 12.4% Solar-to-hydrogen

Experimental Cell

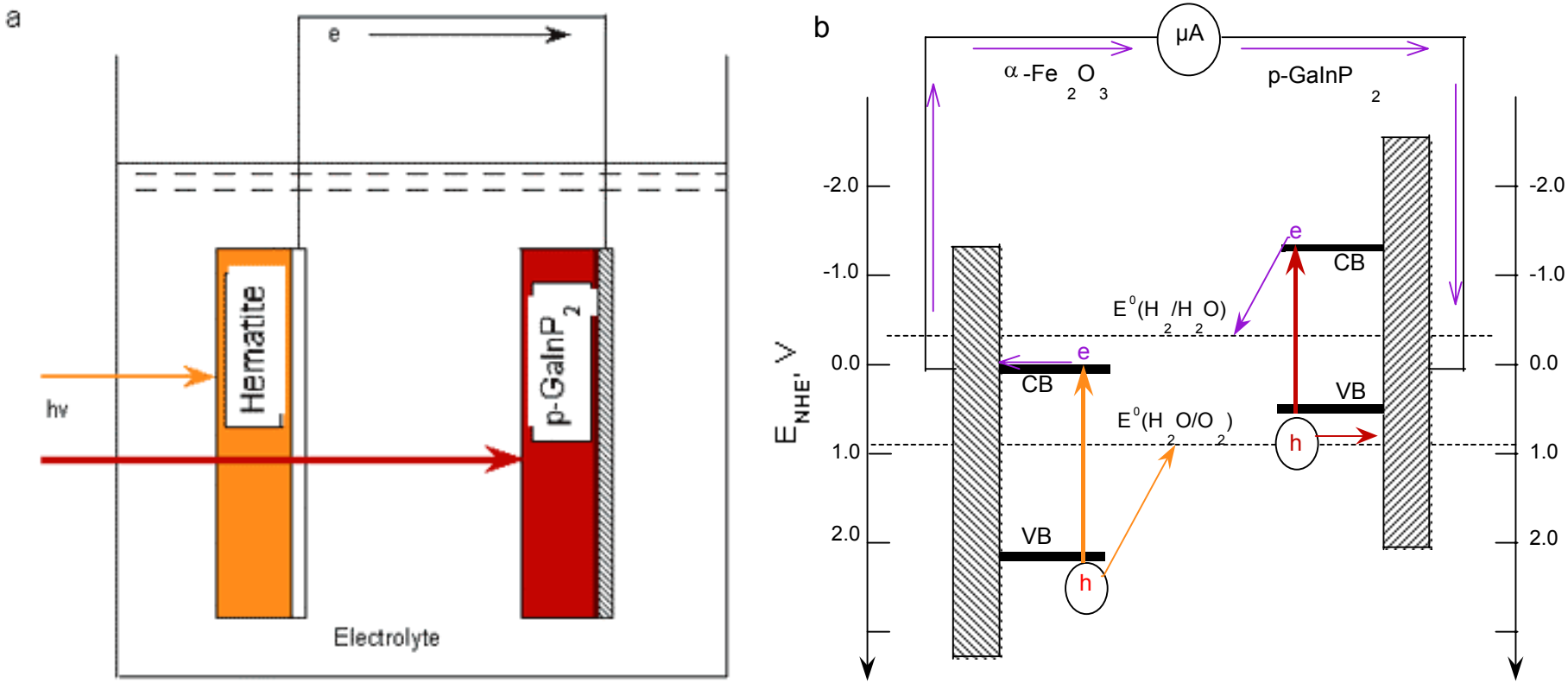
Comparison of *p*-$GaInP_2$ and PEC/PV device



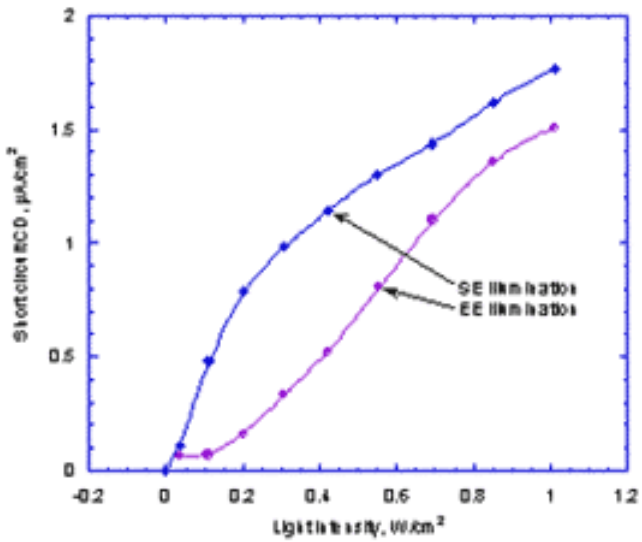


The GaAs integrated PV cell compensates for the energetic mismatch – but expensive

Additional Approaches for Bandedge Mismatch and Stability Issues

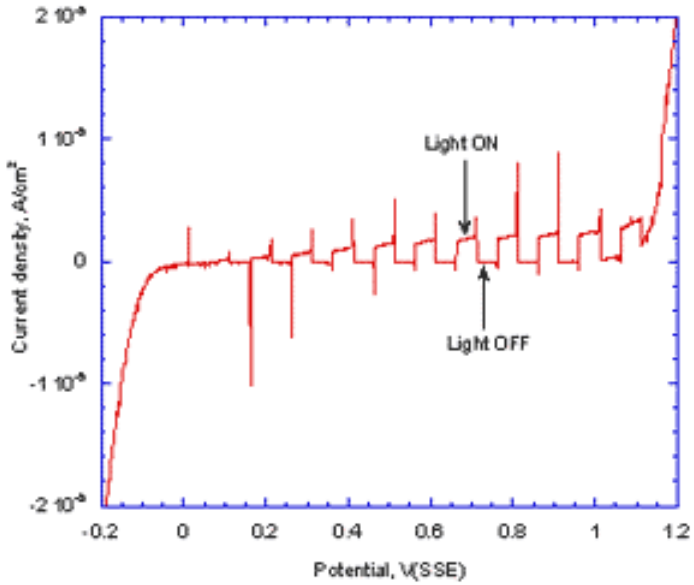


Lower cost Fe_2O_3 electrode is a possibility, but…..

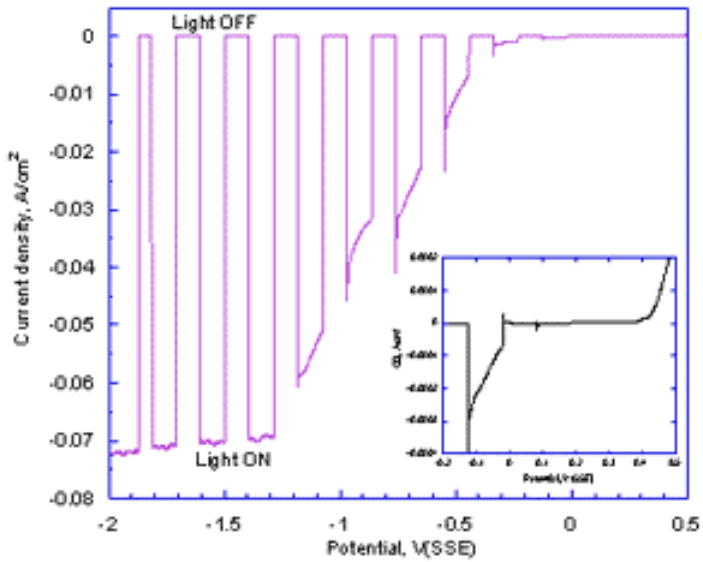


….While the System splits water, the efficiency is very low.

The photocurrent is limited by response of the iron oxide. Work is continuing in collaboration with other researchers (as part of our IEA efforts) to discover better materials.



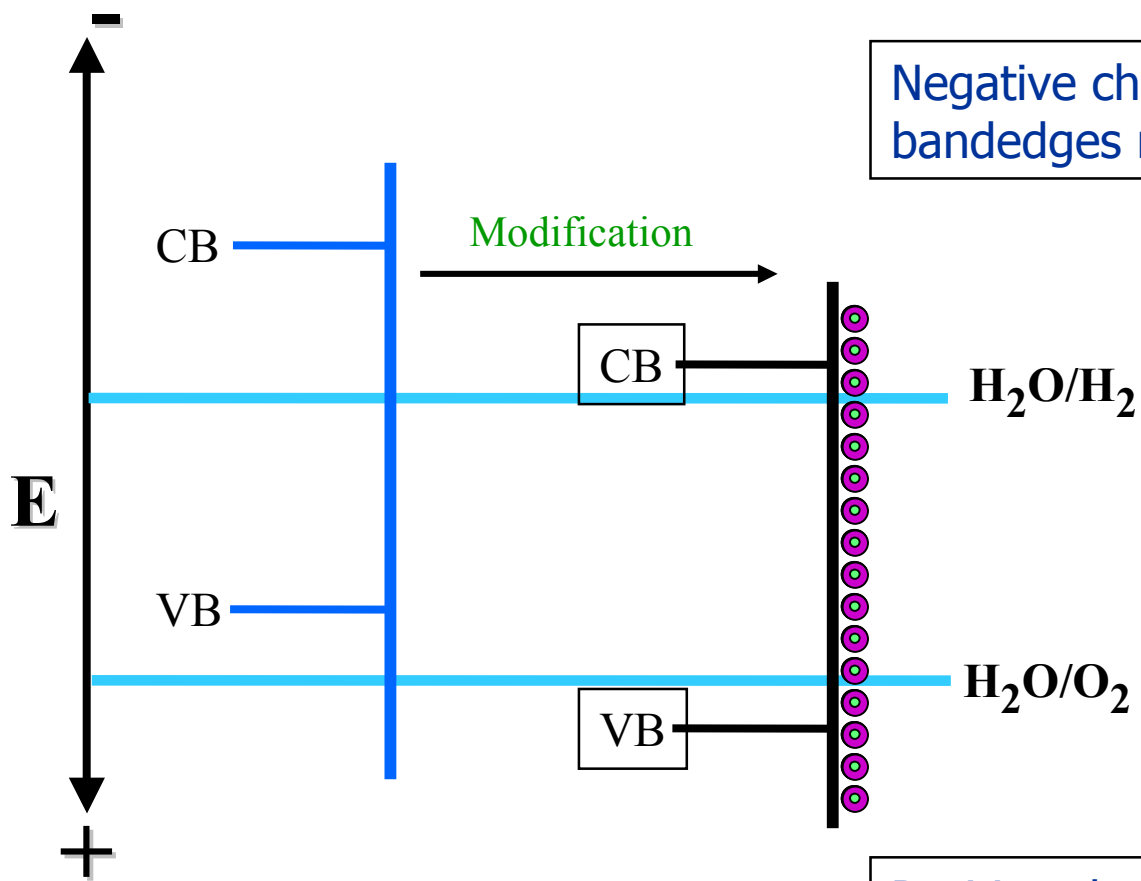
Hematite nanorods in 0.5 M KNO_3 ~1 W/cm^2



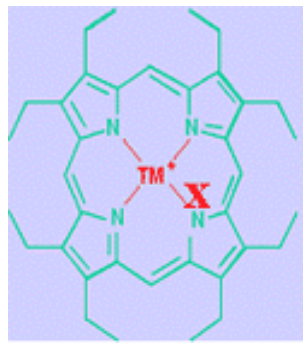
$GaInP_2$ in 0.5 M KNO_3 ~1 W/cm^2

Band Edge Engineering

The goal is to shift the band edges by surface modification to provide the proper energetic overlap.



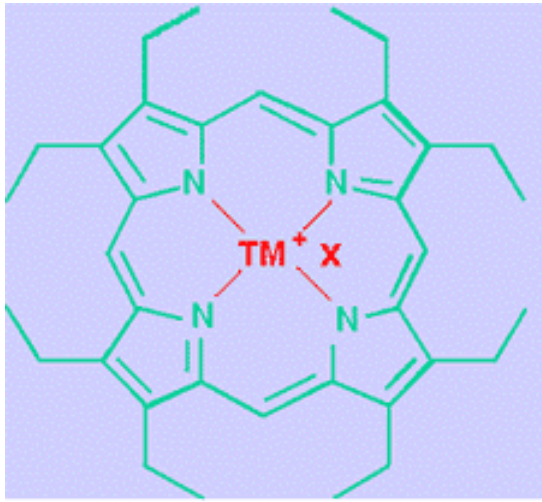
Negative charges move the bandedges negative.



Positive charges move the bandedges positive.

The work involved two series of Metallo-Porphyrins

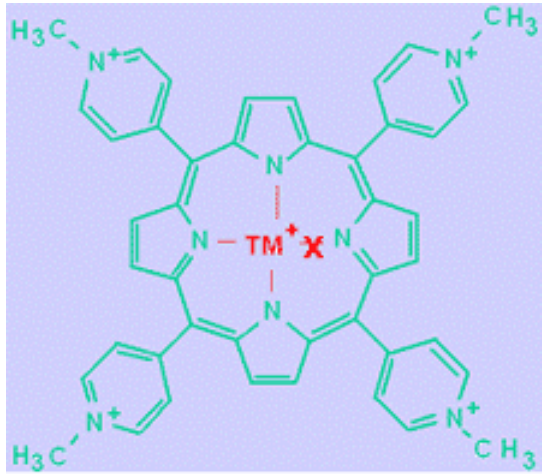
Insoluble



Octaethyl Porphyrin

~OEP~

Soluble



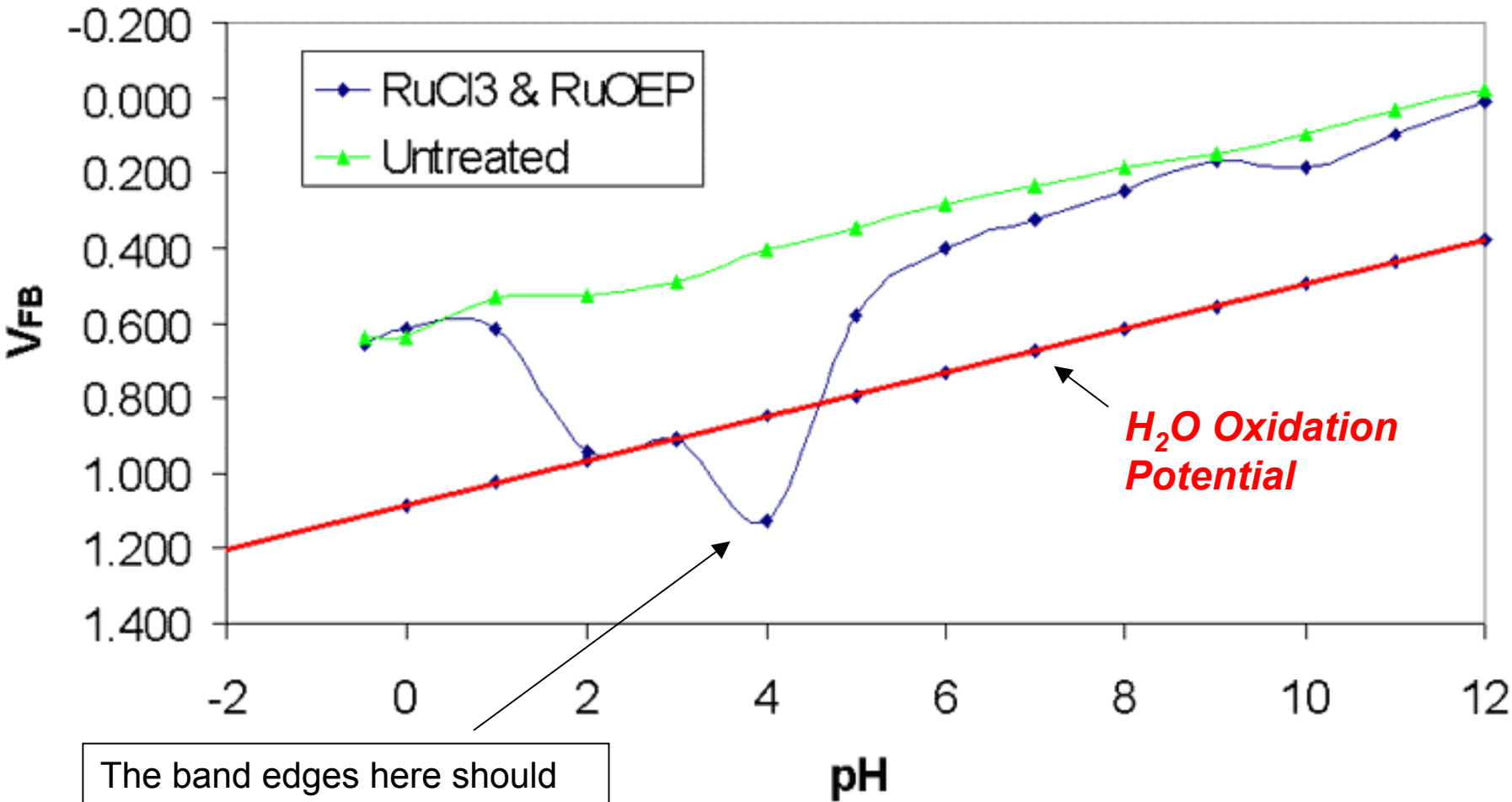
Tetra(N-Methyl-4-Pyridyl)porphyrin

~TMPyP(4)~

Transition metal in center of porphyrin *may* combine favorable properties of band edge shifting and charge transfer.

Band Edge Engineering - $GaInP_2$

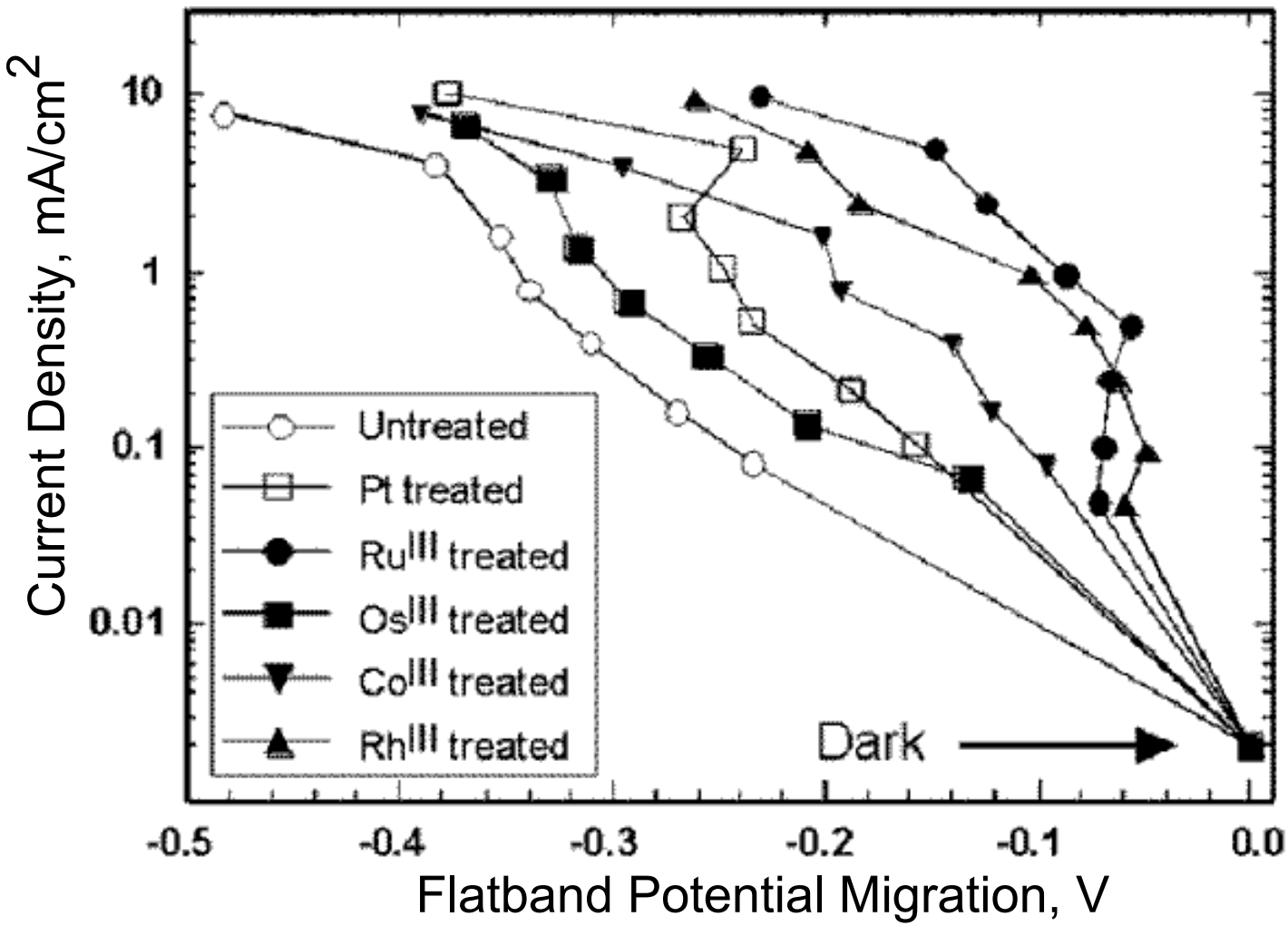
V_{FB} vs. pH for $RuCl_3$ + RuOEP Treated $GaInP_2$ Electrode



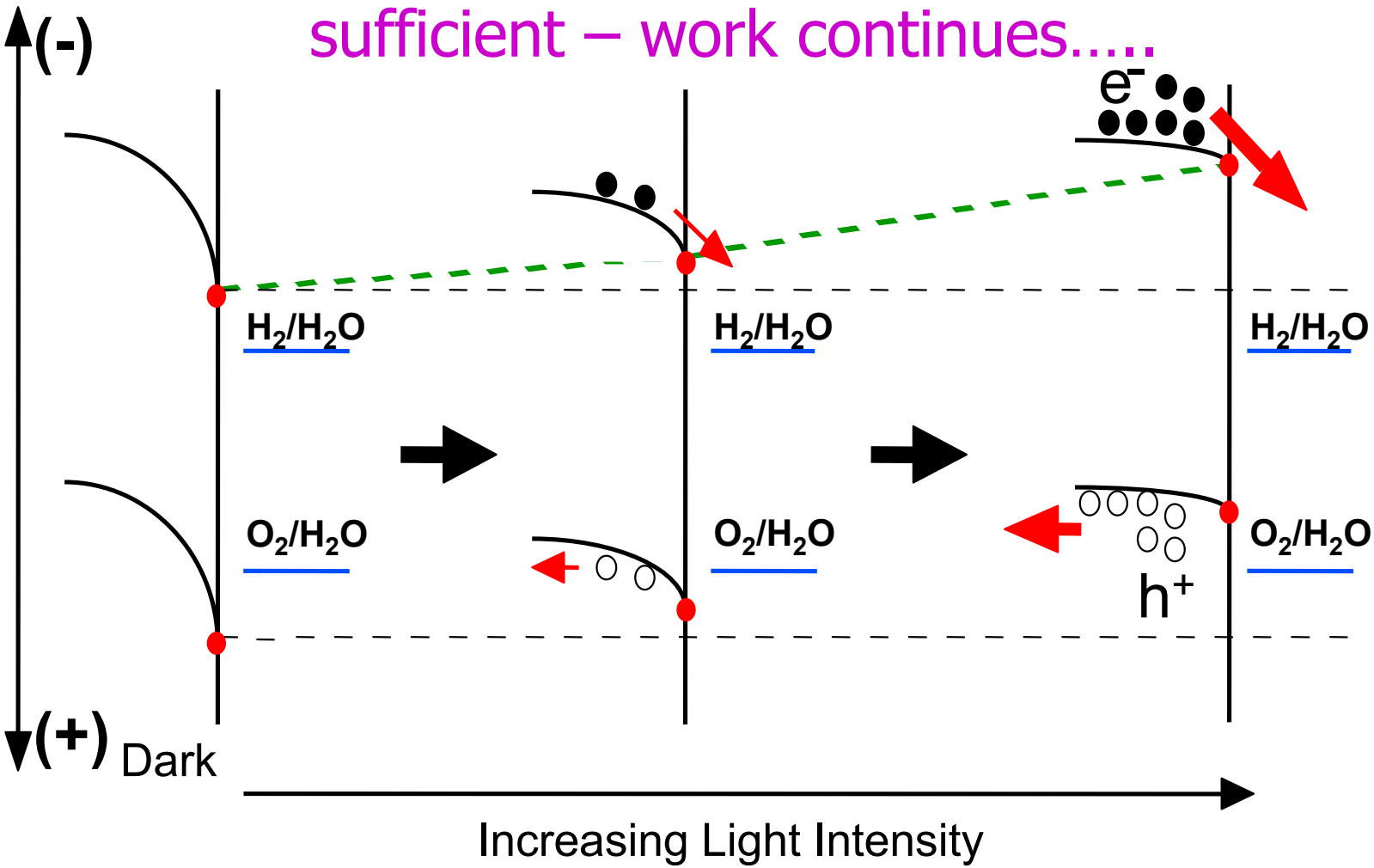
The band edges here should be able to split water…..but no water splitting observed.

Metal Ion Catalysis

All show bandedge migration

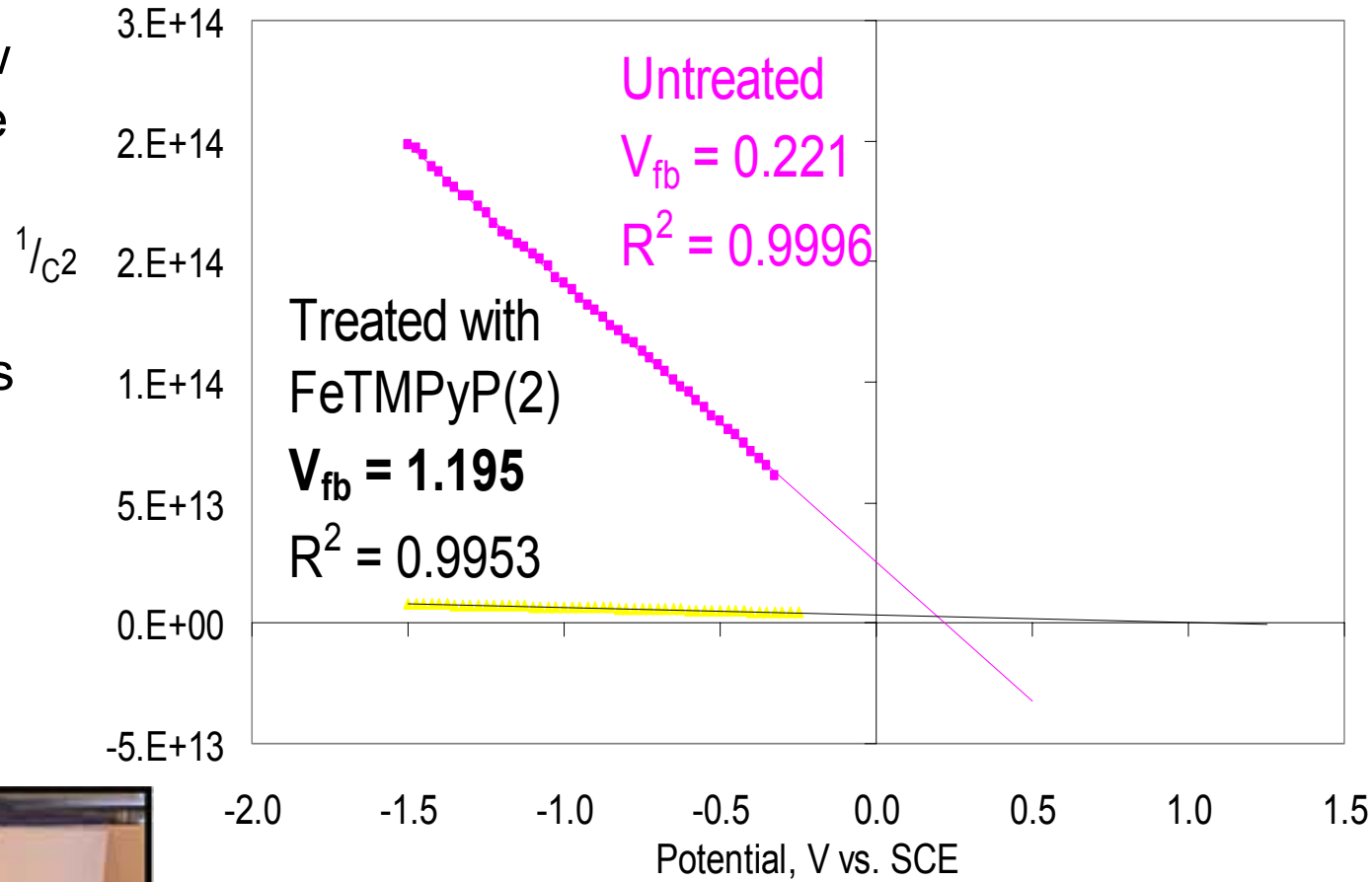


Band edge migration is due to negative charges accumulating at the surface – catalysis is not sufficient – work continues…..

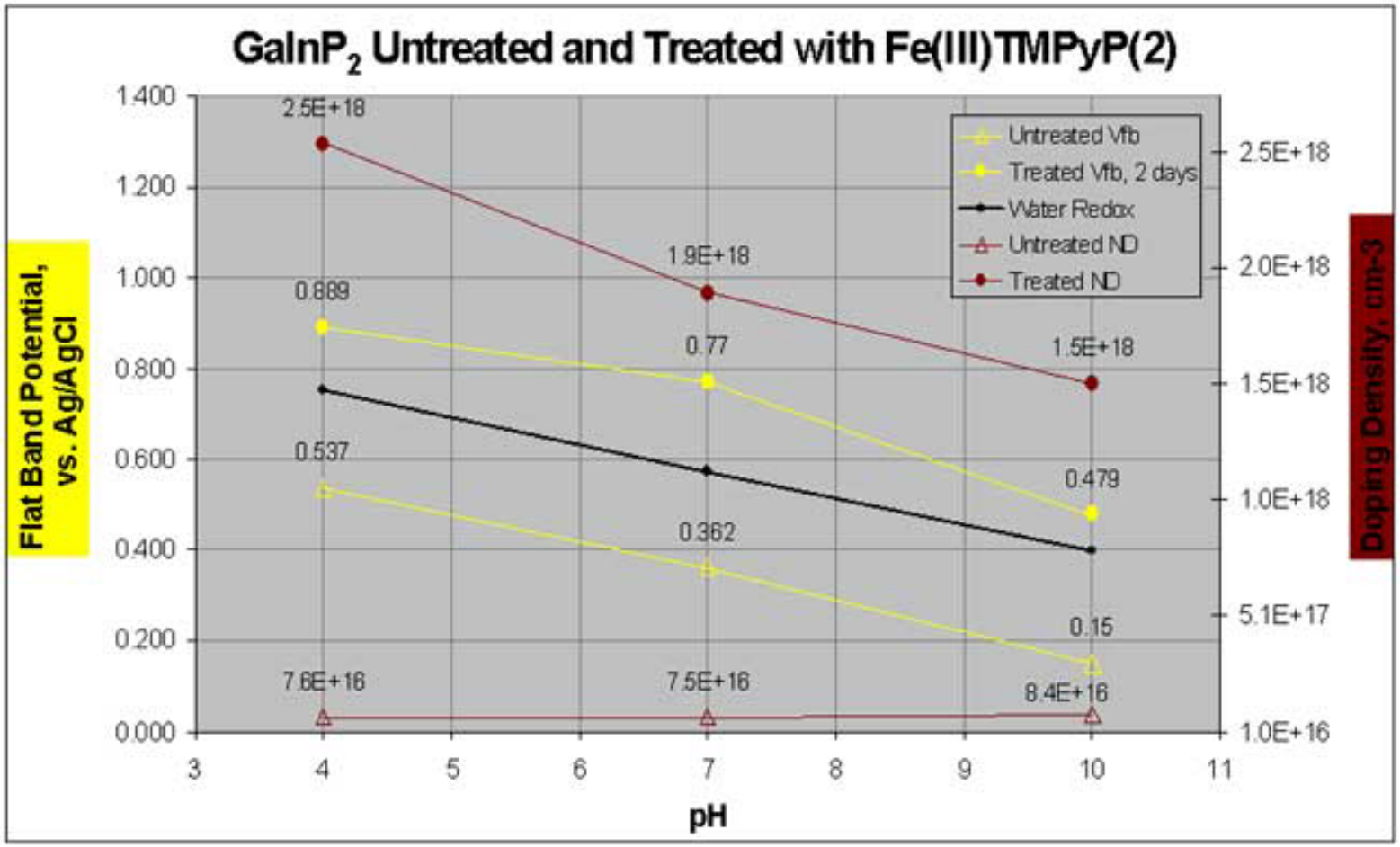


Mott-Schottky Plot of Fe(III)TMPyP(2), pH 7

The soluble porphyrins show large band edge shifts, but why the large change in slope…indicates a higher doping density…?

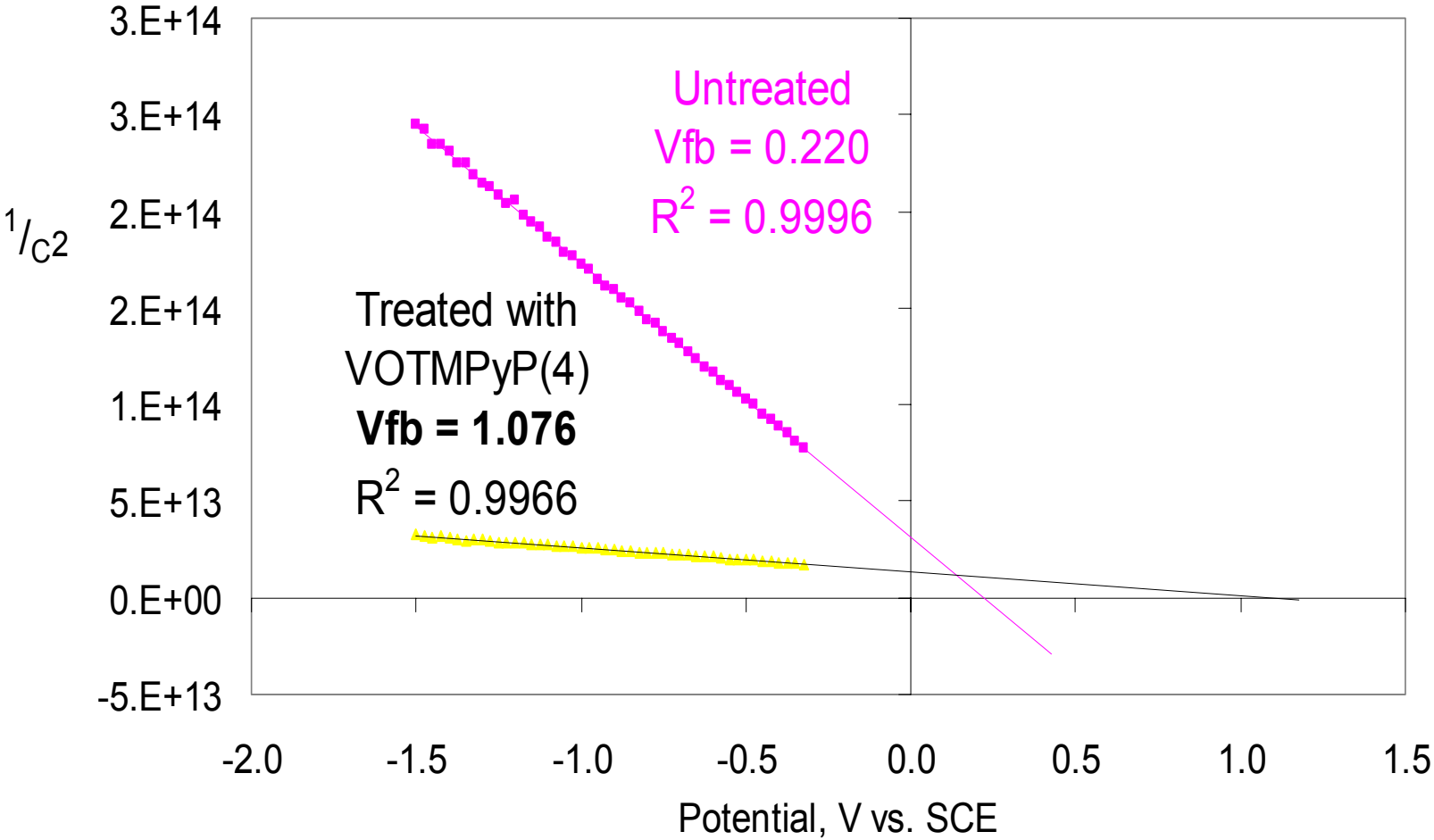


pH testing shows even more interesting behavior



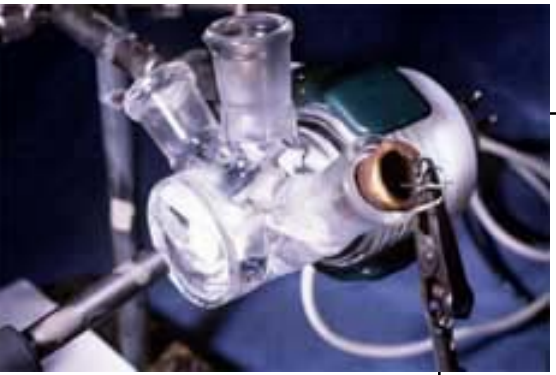
Mott-Schottky Plot for VO(IV)TMPyP(4), pH 7

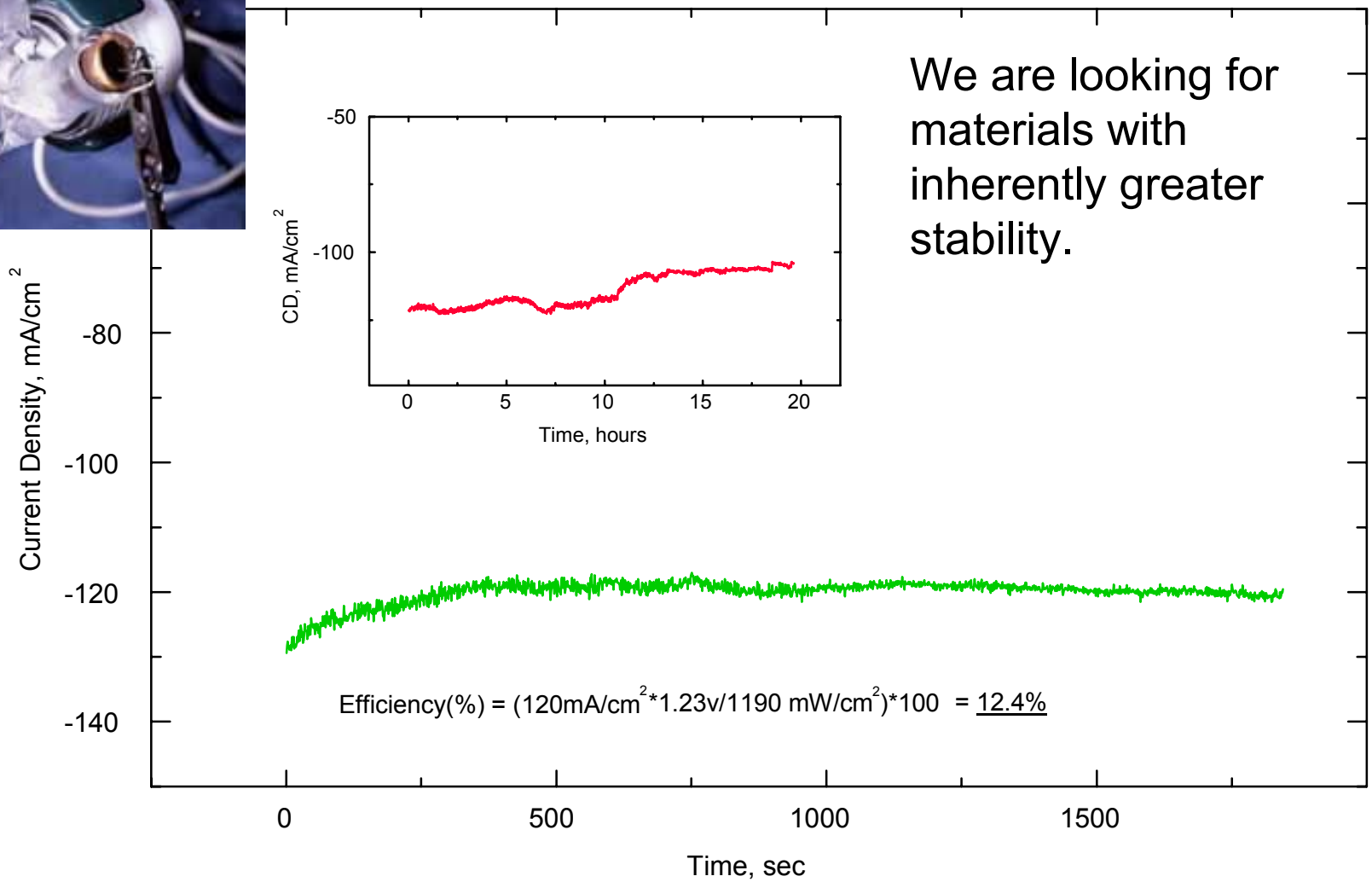
This phenomenon is not unique to the iron system.
Electron density is being drawn from the near surface of the semiconductor, but the mechanism is unclear…



National Renewable Energy Laboratory

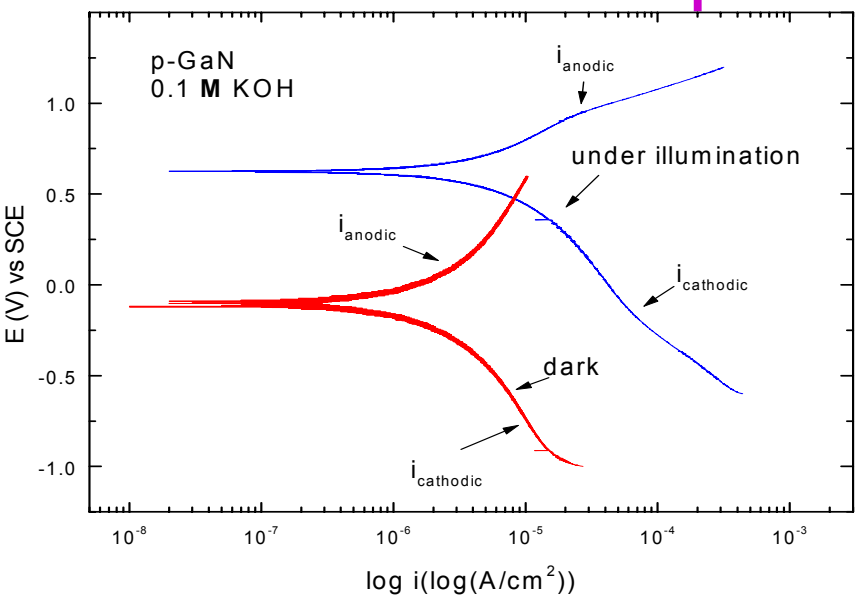
Photocurrent time profile for PEC/PV Water-Splitting device, showing current decay due to corrosion.





We are looking for materials with inherently greater stability.

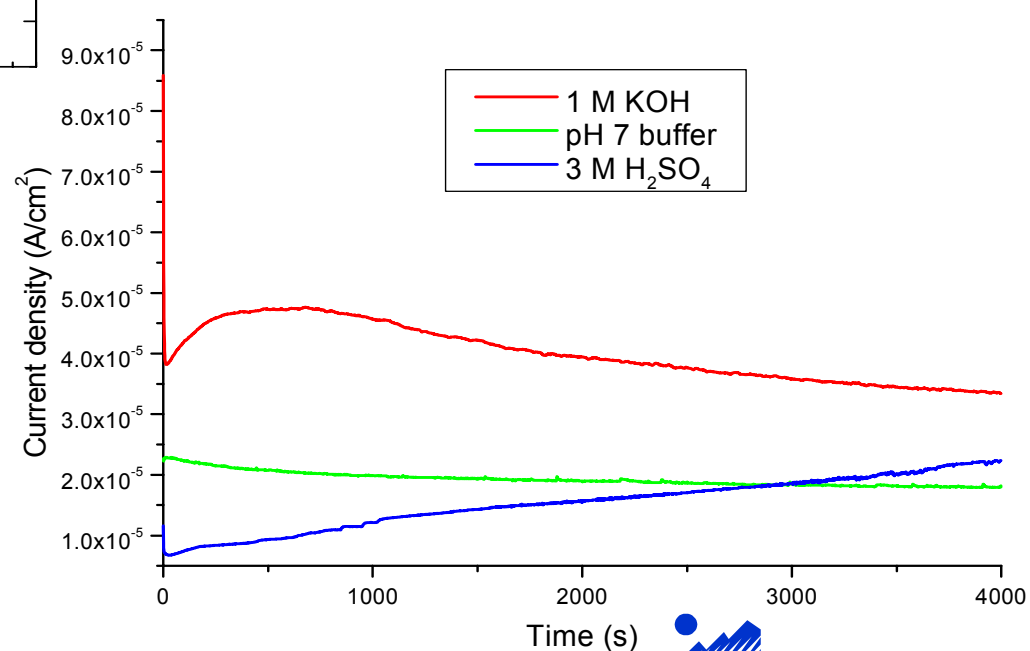
One possibility is nitride materials, an example of which is p-GaN



It shows excellent stability…

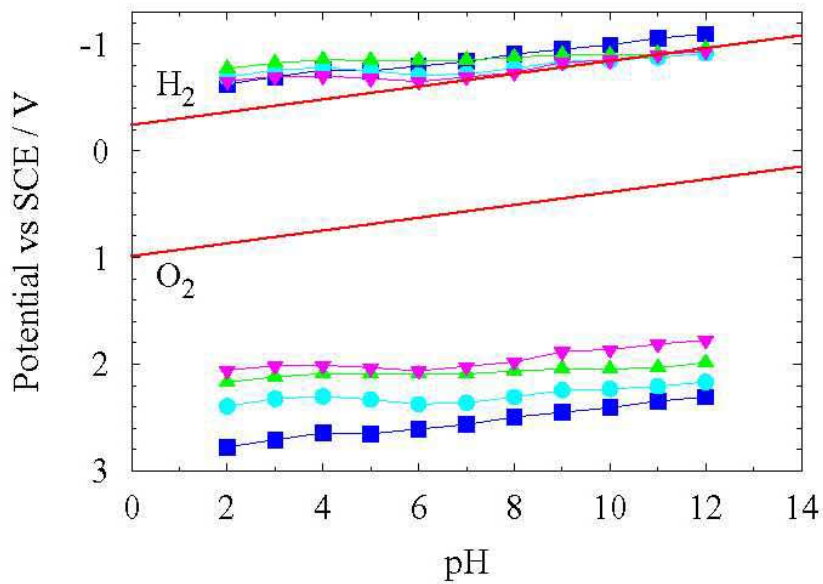
…and water splitting capability

But…3.0eV bandgap



Adding indium lowers the bandgap

The band edge potentials of n-$In_xGa_{1-x}N$



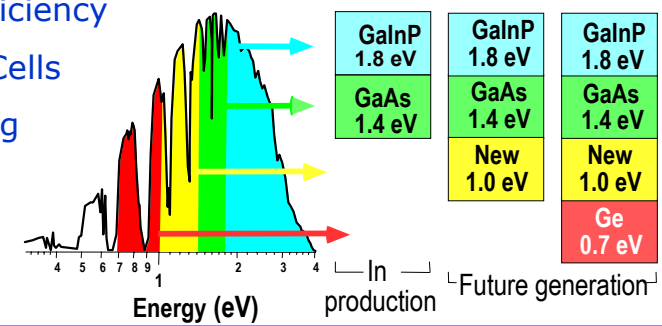
- x = 0.000, E_g = 3.40 eV
- x = 0.045, E_g = 3.08 eV
- x = 0.085, E_g = 2.94 eV
- x = 0.140, E_g = 2.71 eV

These materials are also interesting for high efficiency

- Solar Cells
- Lighting

Calculated efficiencies (ideal)

500X AM1.5D:	**36%**	**47%**	**52%**
one sun AM0:	**31%**	**38%**	**41%**

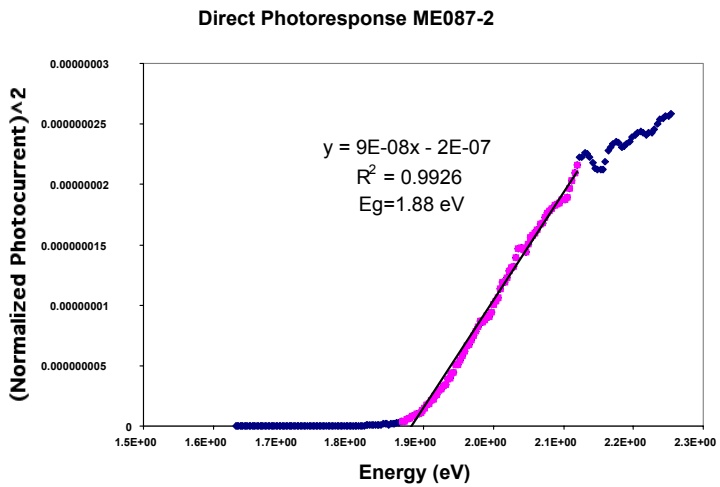


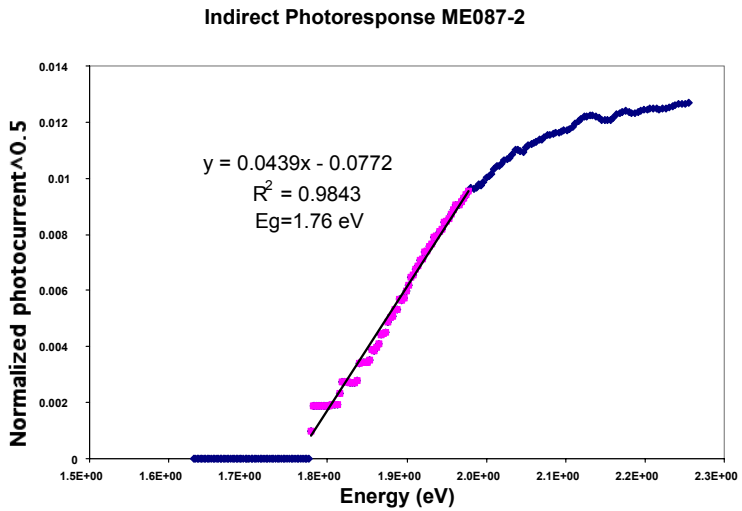
- Indium changes E_g much more than Φ_{fb}.
- Change in Φ_{fb} due to indium may be pH dependent.
- n-$In_xGa_{1-x}N$ should split water at low pH.

Other material possibilities include…..

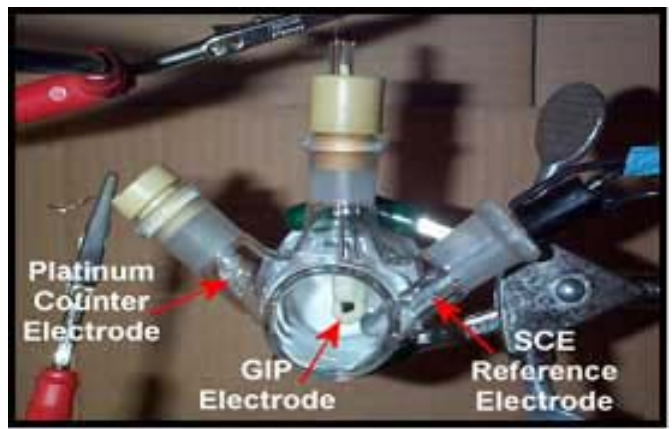
New materials - Preliminary Investigation of GaAsPN for PEC Water Splitting Systems

with Professor Carl Koval *University of Colorado at Boulder*





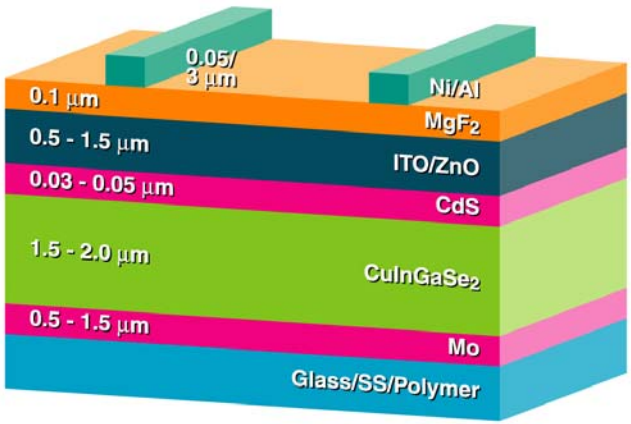
Electrode	Direct Eg	Indirect Eg
ME085-2	1.74 eV	1.69 eV
ME085-3	1.75 eV	1.67 eV
ME086-1	1.66 eV	1.59 eV
ME086-2	1.69 eV	1.58 eV
ME087-1	1.88 eV	1.75 eV
ME087-2	1.88 eV	1.76 eV

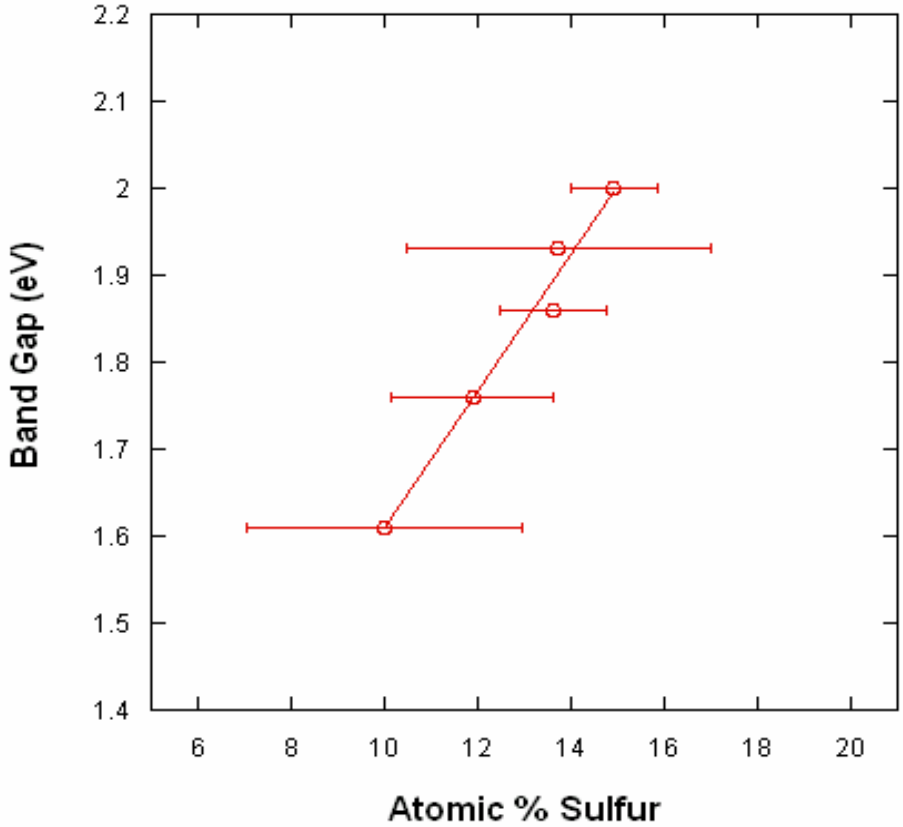


A long shot, but could be low cost….

New Materials - Band Gap Requirements for Electrodeposited CIGSSe

- Dependence on sulfur content noted.
- However, this is convoluted by varying concentrations of other elements

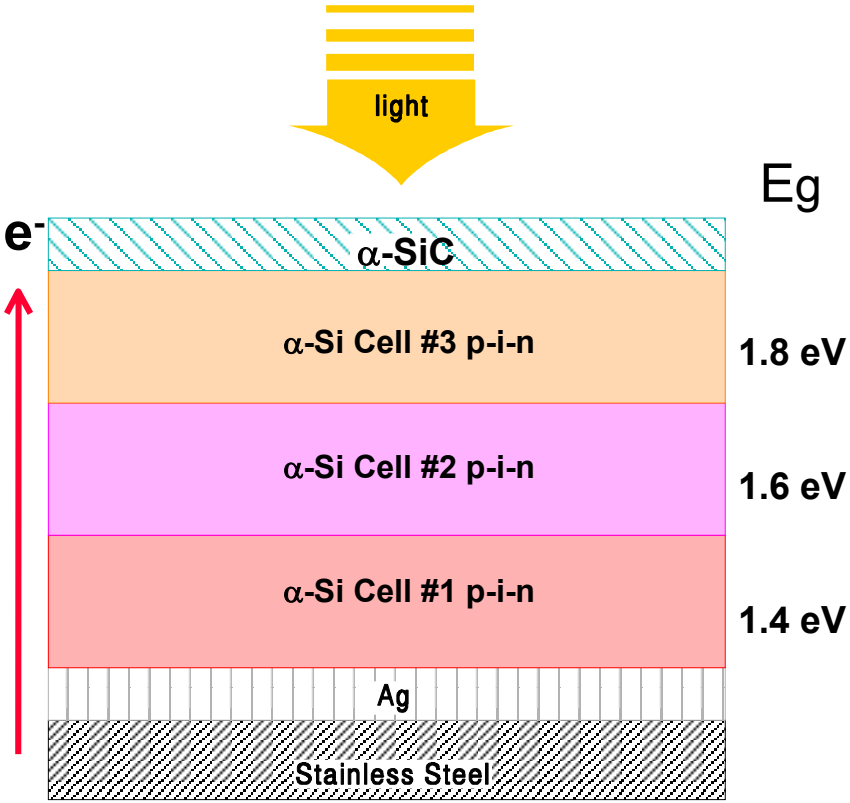


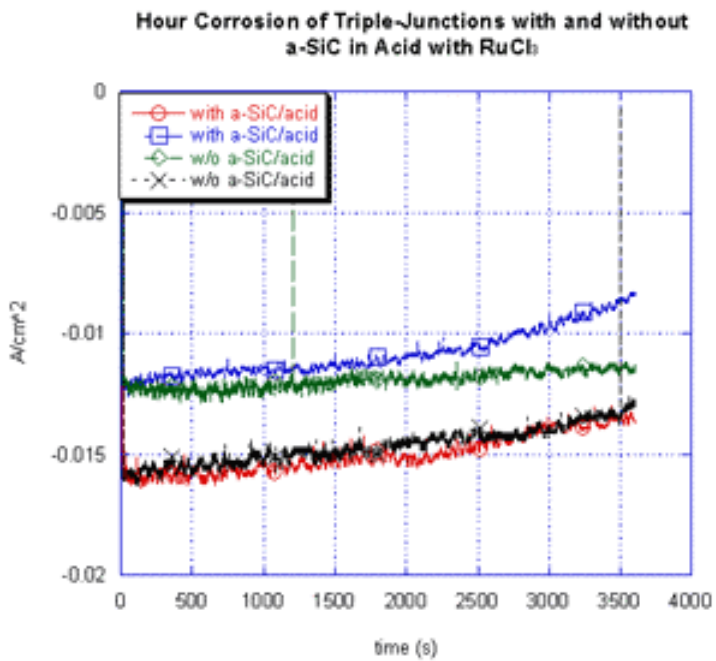


Possible low-cost thin-film material

Results for a-Si samples with Metal-ion Catalysts.

Another possible low-cost thin-film material

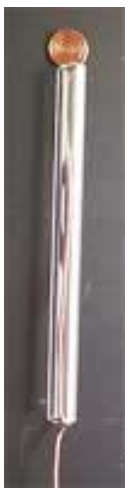




Summary of ongoing work for FY2003 in blue

- $GaInP_2$ - NREL (fundamental understanding)
- GaPN - NREL (high efficiency, stability)
- InGaN - SVT Associates, NREL, (high efficiency, stability)
- CuInGaSeS - UNAM (Mexico), NREL (Low cost)
- Multi-junction Amorphous Silicon - University of Toledo and ECD (Low cost)

- Energetics
  - Band edge control
  - Catalysis
  - Surface studies

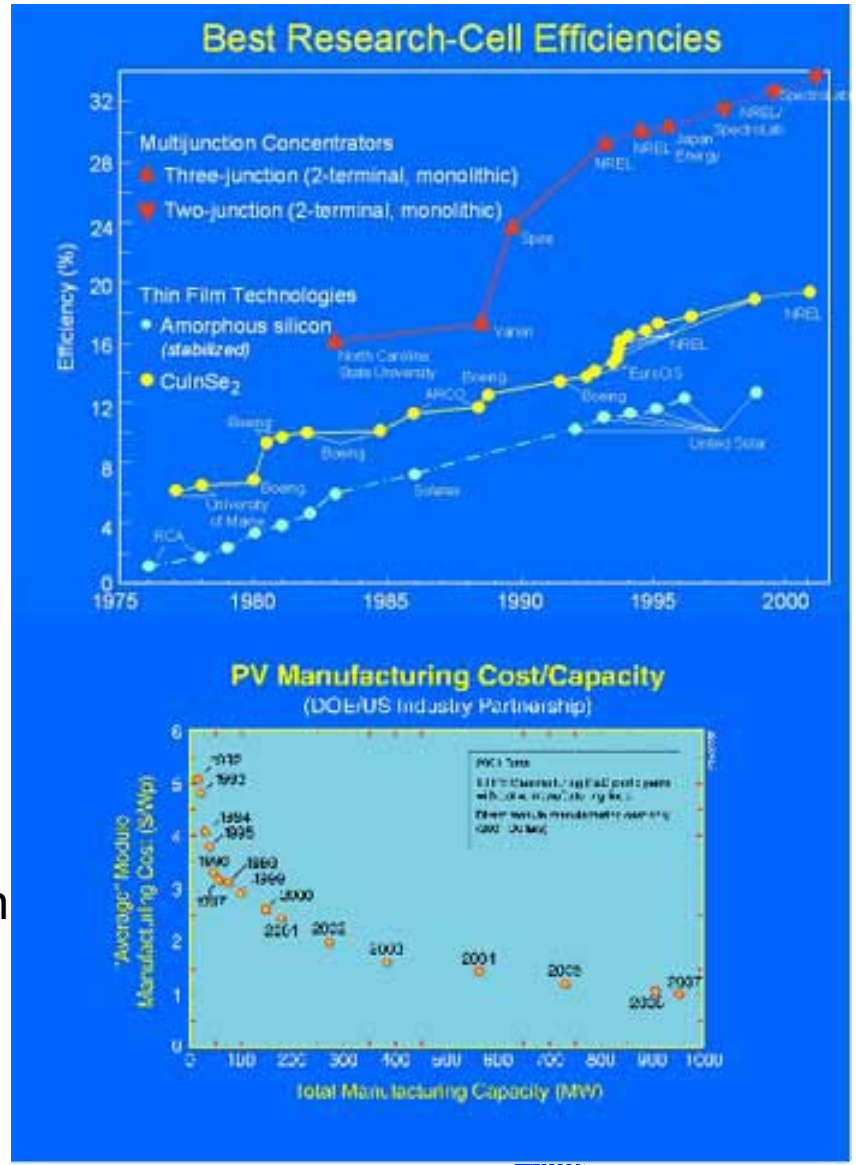


+

+

Plans for future work

- Continue materials research, discovery and development.
  - $In_xGa_{1-x}N$
  - GaPN
  - a-Si
  - CuInGaSSe
  - a-SiN (coating for stability)
  - Others…
- Energetics
  - Band-edge engineering
    - Development fundamental understanding of surface interaction
    - Try treatment on other materials
  - Catalysis
  - Surface studies



Collaborations and Interactions

In the US

Colorado School of Mines
University of Colorado
University of Wisconsin (Whitewater)
GM, Astropower (proposed)
Others working in this area: FSEC, Duquesne

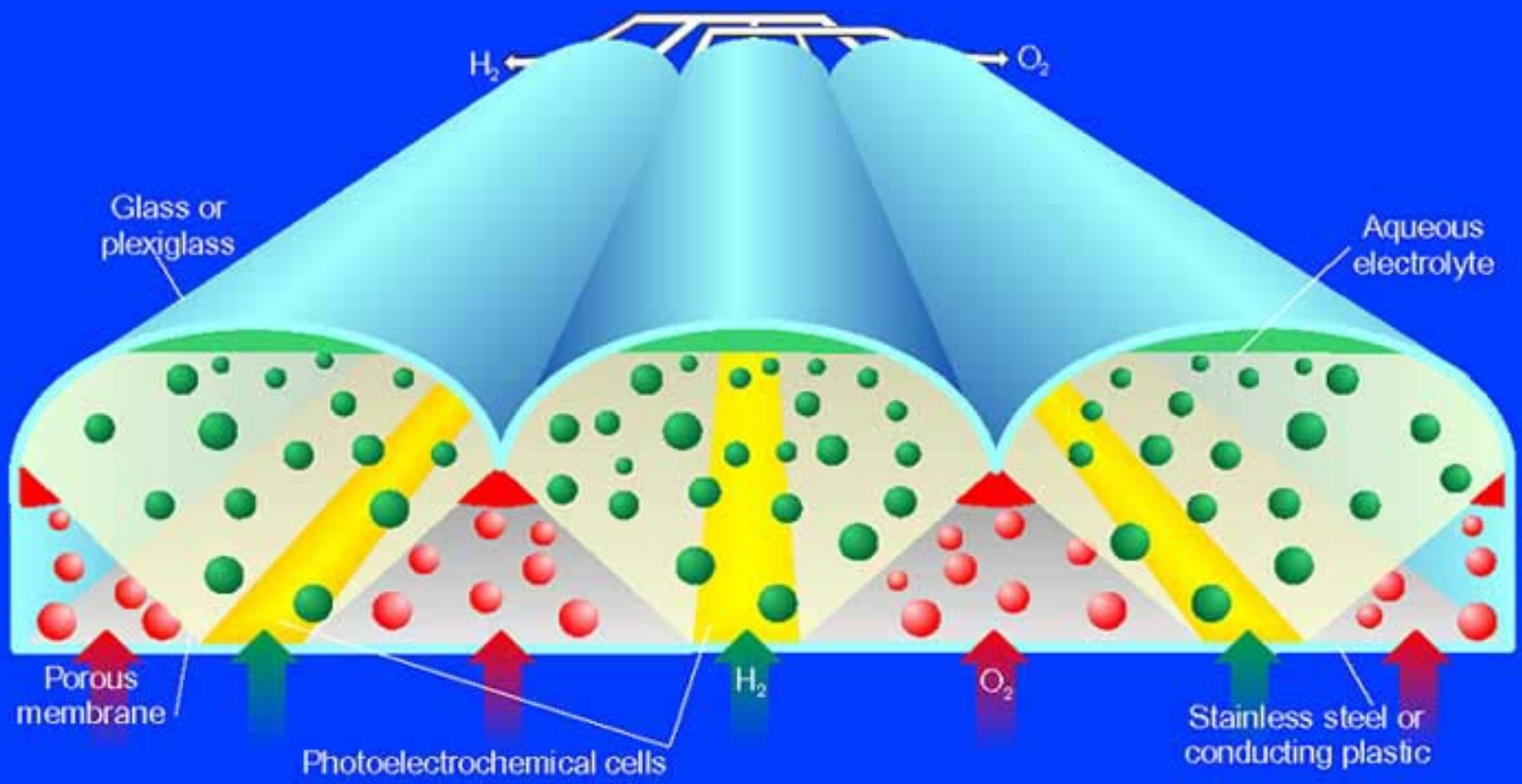
Outside of the US

Switzerland, Mexico, Armenia, Sweden, Japan

Plans

- Continue materials development.
  - Nitrides
  - CuGaInSSe
  - a-Si
- Band-edge engineering
  - Development fundamental understanding of surface interaction.
  - Try treatment on other materials
- Increase industry interactions

Conceptual Design of a Photoelectrochemical Water Splitting System with Light Concentration



LS-CD24-a376001

Encapsulated Metal Hydride for Hydrogen Separation

(Formerly Separation Membrane Development)

DOE Hydrogen Program

2003 Merit Review and Peer Evaluation

L. Kit Heung, Jim Congdon

Savannah River Technology Center

May 2003

Relevance/Objective

Relevance & Goal

- Develop a metal hydride based packing material for hydrogen separation from low concentration streams.
  - Adsorbent in present PSA process is efficient for high concentration feed stock, not for low concentration
  - Hydrogen economy will need hydrogen recovery from low concentration feed stocks

Objective

- Produce a sol-gel encapsulated metal hydride packing material that will
  - Absorb hydrogen selectively
  - Not break down to fines
  - Resistant to reactive impurities
- Evaluate the material for hydrogen absorption from low concentration streams
  - Design and fabricate experimental apparatus
  - Conduct tests with synthesized gas mixtures
- Develop separation process with the new material

Approach (1)

- Metal hydride preferentially absorbs hydrogen from gas mixtures and has high potential for hydrogen separation.
- Metal hydride particles expands when absorbing hydrogen and contracts when releasing hydrogen that causes the particle to break down to micron size fines.
- The fines self compact and plug up separation column.
- Sol-gel encapsulation technique is used to convert the fines into stable granule that is suitable for packing separation columns.
- Sol-gel process uses a liquid colloidal dispersion method to produce porous silica matrix.

Approach (2)

- Unprotected metal hydride is sensitive to reactive impurities such as oxygen and carbon monoxide.
- Silica matrix protects the metal hydride from impurities by molecular sieving.
- Different recipes are developed to encapsulate the metal hydride fines in a matrix of porous silica to improve performance of the end product.
- Batch hydrogen absorption and flow-through absorption are used to test the performance.
- Performance is evaluated in hydrogen capacity, physical stability, and resistance to impurities.
- Success is defined by a product that maintains its capacity and stability.

Project Timeline

FY98 Project started with an original objective to develop silica based membrane for hydrogen separation. Produced small samples of sol-gel coated membrane on porous support. Permeation tests showed encouraging selectivity and rate.

FY99 Attempted to produce larger membrane for gas separation evaluation. Failed to produce defect free membrane, and encountered difficulty in balancing selectivity and rate. Decided changing the approach from membrane to encapsulated metal hydride.

FY00 Developed two methods to produce silica encapsulated metal hydride. Samples of encapsulated $LaNi_{4.25}Al_{0.75}$ demonstrated hydrogen absorption and resistance to particle breakdown. Designed and fabricated apparatus for testing hydrogen absorption from gas mixtures.

FY01 Started up the hydrogen absorption test apparatus. Demonstrated hydrogen separation from nitrogen mixtures.

FY02 Demonstrated hydrogen separation from gas mixtures containing methane and carbon monoxide. But absorption kinetics and capacity are reduced by carbon monoxide.

FY03 Emphasis placed on: (1) Develop pilot scale encapsulation technique. (2) Develop fabrication conditions and formulation to improve physical strength and CO resistance of the product.

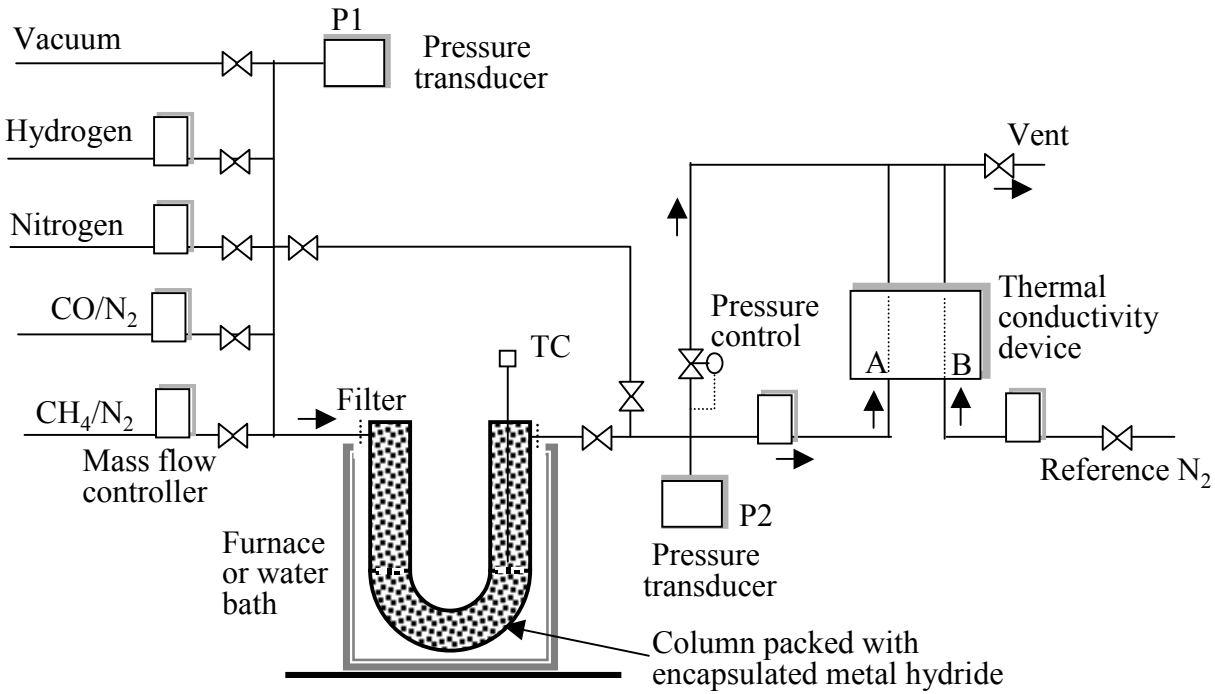
FY04 Plan: Complete pilot scale production development. Design and install pressure(and thermal) swing absorption test apparatus to develop a dual absorption hydrogen separation process combining the special properties of encapsulated metal hydride and molecular sieve. Success Criteria: Kilogram quantity "good" material produced. Hydrogen separation in a dual absorption process Demonstrated.

Accomplishments/Progress (1)

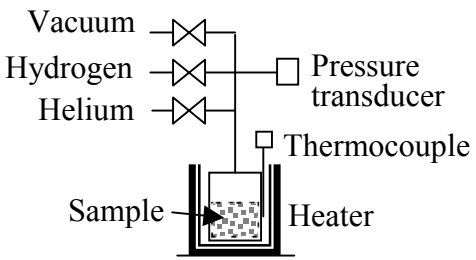
- Milestones:
  1. Begin hydrogen absorption test from mixtures containing nitrogen, methane and carbon monoxide (June 2002). - Accomplished.
  2. Develop variations of encapsulated samples for recipe optimization (March 2003). - Accomplished, 5 variations produced.
  3. Complete cost analysis (September 2003). - Delayed to next year due to insufficient funding.

Accomplishments/Progress (2)

- Apparatus for hydrogen absorption from following gas mixtures:

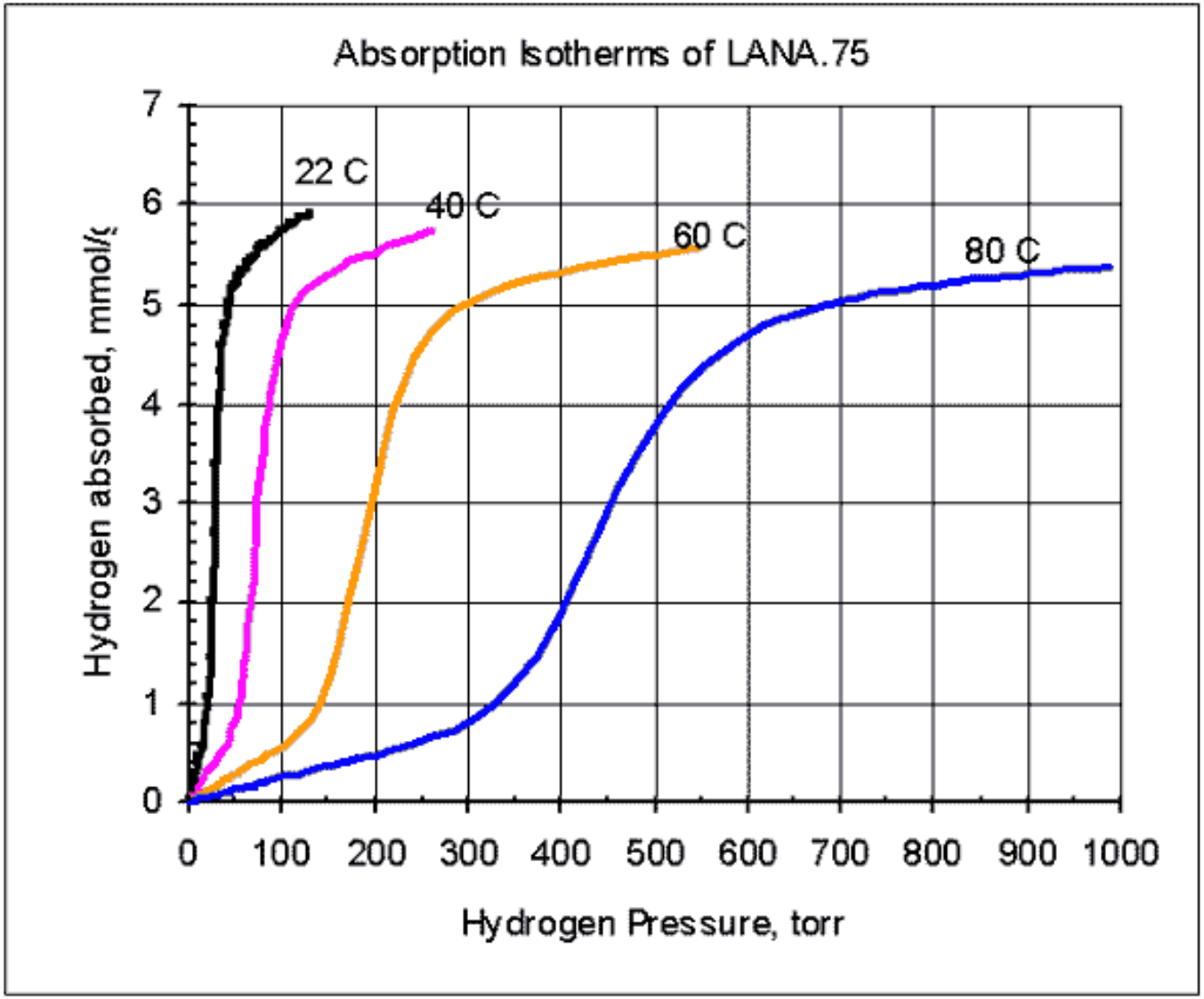


- Apparatus for batch hydrogen absorption tests



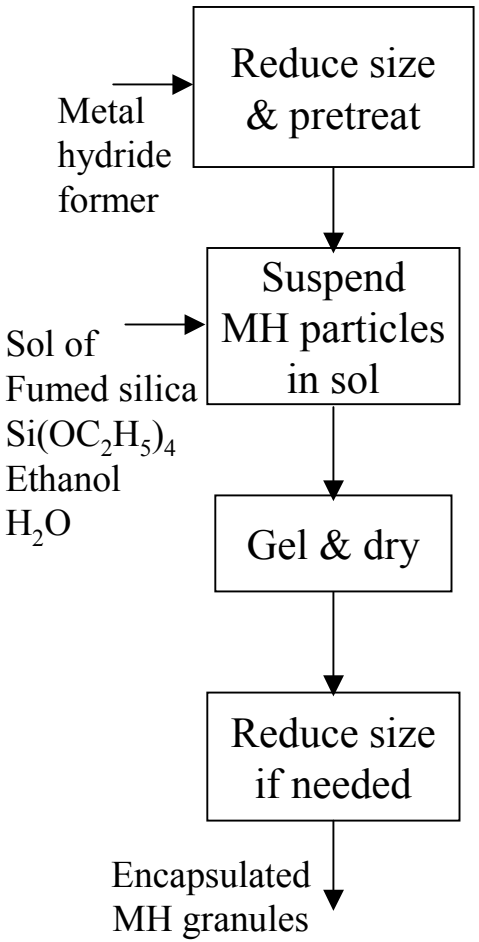
Accomplishments/Progress (3)

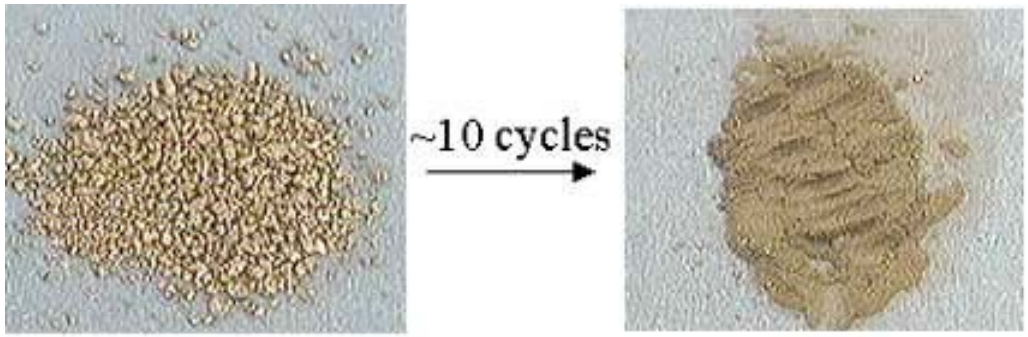
- Hydrogen Absorption Isotherms of the encapsulated metal hydride



Accomplishments/Progress (4)

- Basic steps of sol-gel encapsulation process

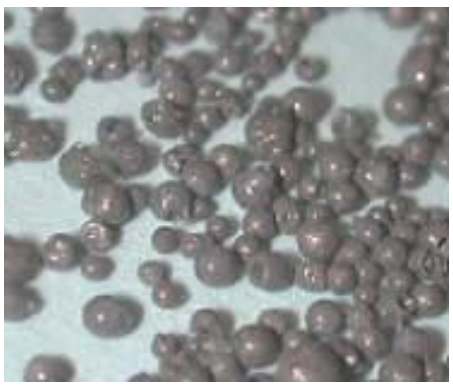




$$M + 1/2\,H_2 \rightleftharpoons MH + Heat$$

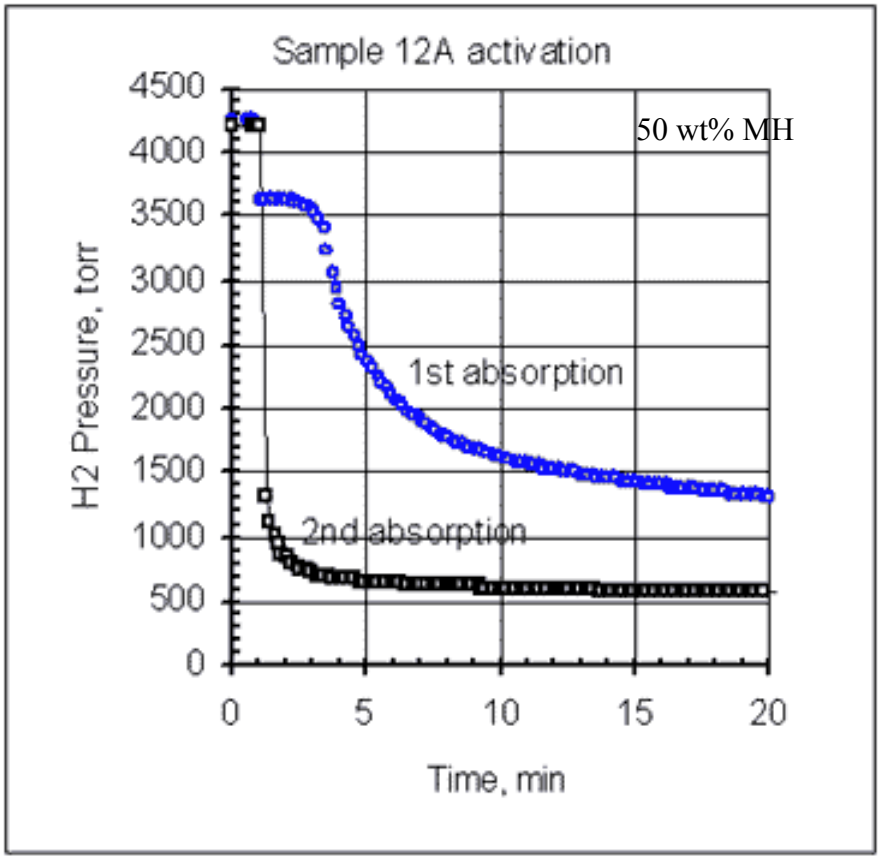
$$Si(OC_2H_5)_4 + 4\,H_2O \rightleftharpoons Si(OH)_4 + 4\,C_2H_5OH$$

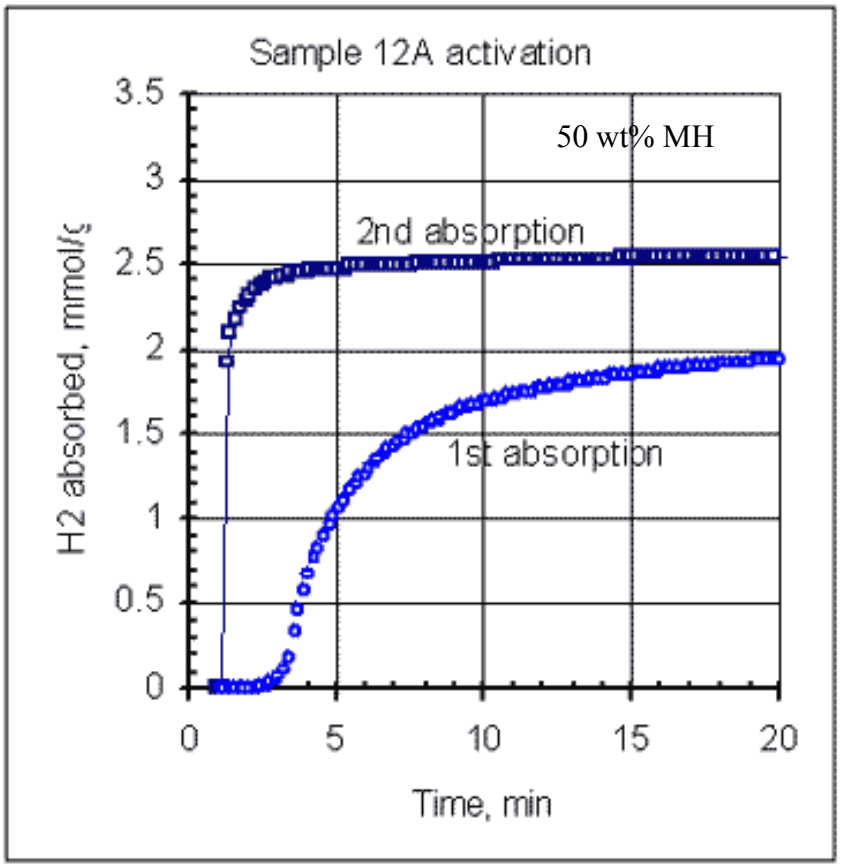
$$Si(OH)_4 \rightleftharpoons \overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - O + 2\,H_2O$$



Accomplishments/Progress (5)

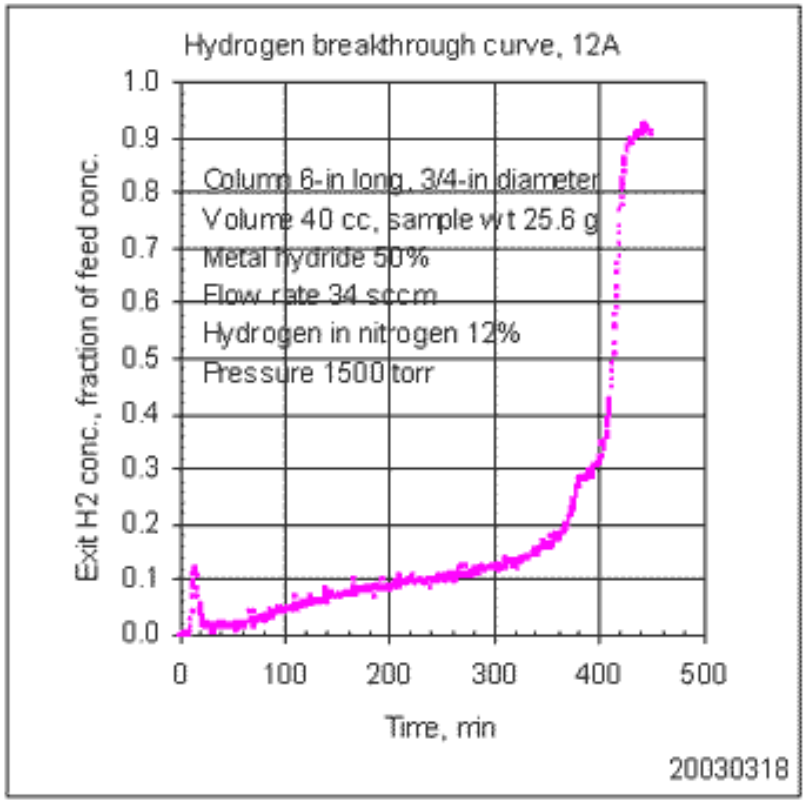
- Encapsulated metal hydride is ready to absorb hydrogen when first exposed to hydrogen

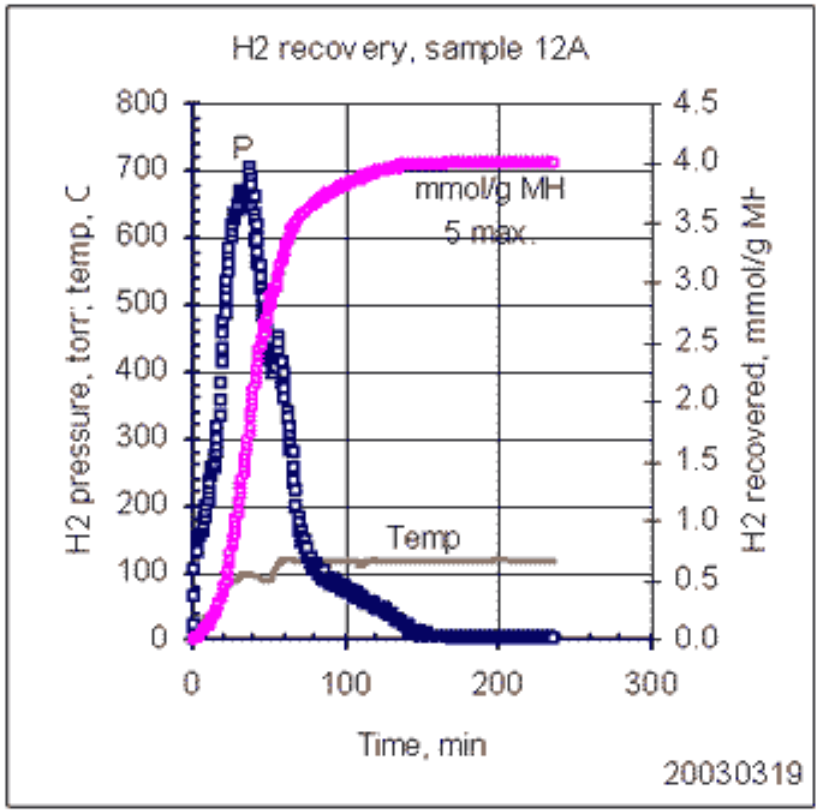




Accomplishments/Progress (6)

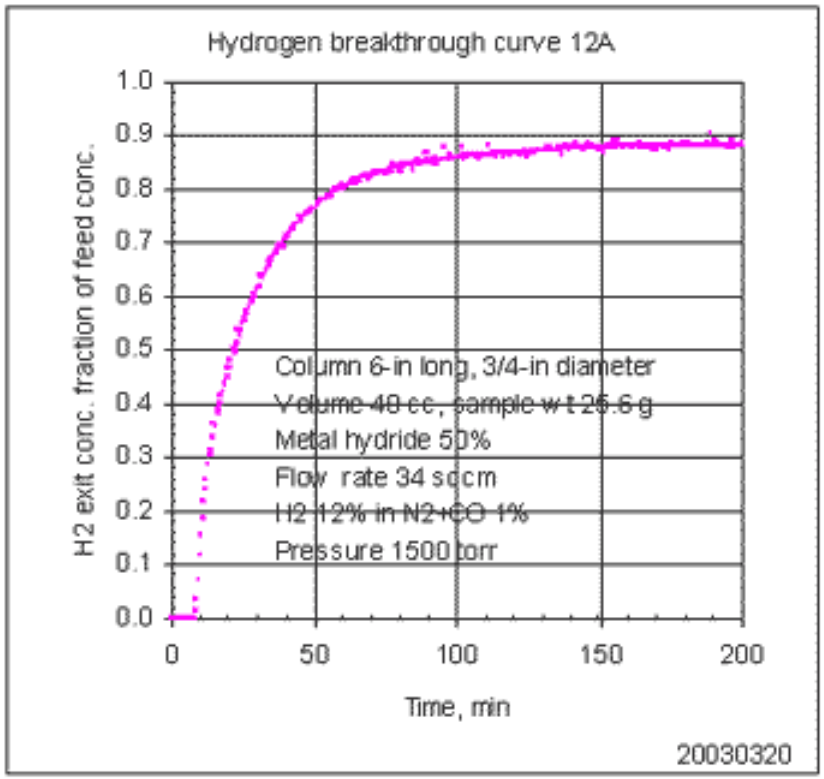
- Hydrogen separation from flowing 12% H_2 in N_2 by a 6-in long 3/4-in diameter column of encapsulated metal hydride

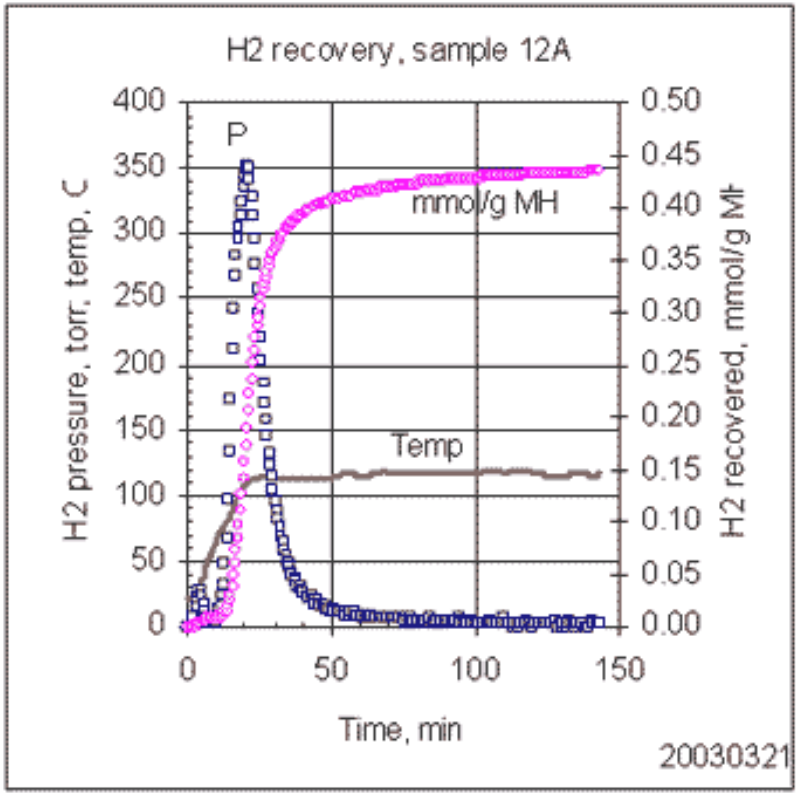




Accomplishments/Progress (6)

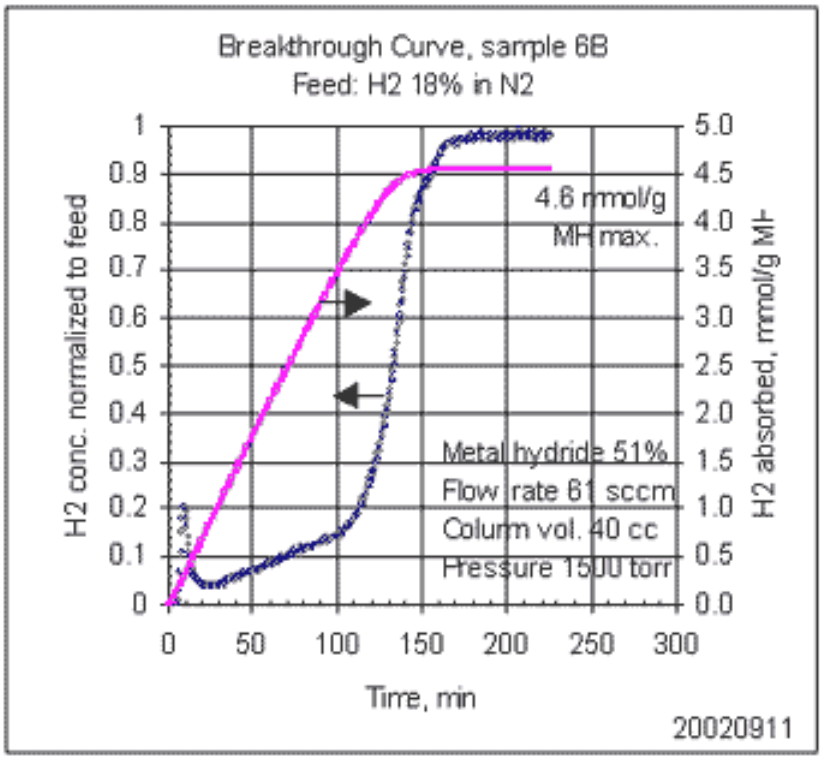
- Hydrogen separation from12% H_2 in (N_2 + 1% CO) by a 6-in long 3/4-in diameter column of encapsulated metal hydride

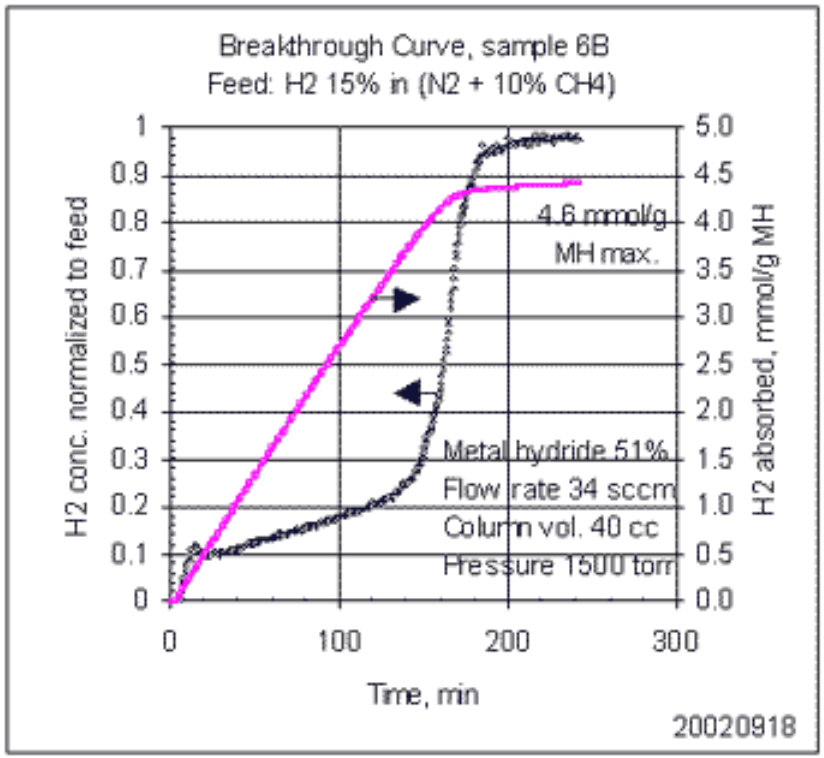




Accomplishments/Progress (6)

- Hydrogen breakthrough curve with and without CH_3 by a 6-in long 3/4-in diameter column of encapsulated metal hydride





Interaction and Collaboration

- Ongoing join effort with Clemson University via the SCUREF (South Carolina University Research & Education Foundation) program to optimize and scale-up the metal hydride/sol-gel composite fabrication process. Effort has produce two patent disclosures on gelation and pore formation methods.
- Initial discussion with University of South Carolina on using the hydrogen absorbing material to develop a dual absorbent pressure swing absorption process for recovering hydrogen from low concentration streams.

Plans and Future Milestones

Sep 03 | Dec 03 | Mar 04 | Jun 04 | Sep 04 | Dec 04

- Conduct economic analysis of the new process.
- Complete experimental testing of dual absorbent PSA.
- Startup the experimental, dual absorbent pressure swing absorption process.
- Improve the external gelation process to produce kilogram quantity encapsulated packing material
- Design and begin fabrication a pressure swing experimental apparatus to develop the dual absorbent process concept.
- Fine tune the porous matrix structure to improve its protection for the encapsulated metal hydride against impurities.

Economic Comparison of Renewable Sources for Vehicular Hydrogen in 2040

Duane B. Myers*
Greg D. Ariff
Brian D. James
Reed C. Kuhn

DIRECTED TECHNOLOGIES INC.

* Corresponding author: duane_myers@directedtechnologies.com

Project Scope

- The Challenge: *How to deliver 10 quads of H_2 from renewable sources in 2030-2050 for the U.S. transportation sector, considering*
  - Resource availability
  - Demand
  - Cost
  - Distribution pathways

10 quads H_2 ~ light-duty U.S. fleet in 2030 if converted to fuel cell vehicles

DIRECTED TECHNOLOGIES INC.

Relevance to DOE R&D Plan

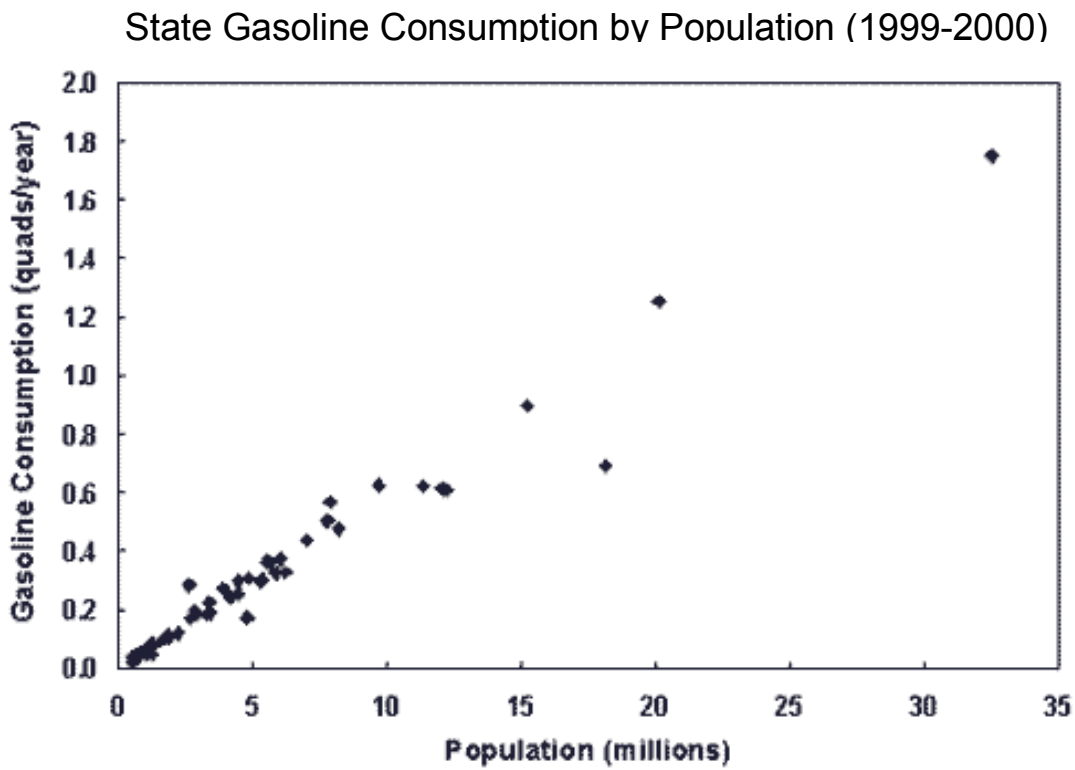
- Provides insight about a hypothetical hydrogen infrastructure for vehicles, with the hydrogen supplied from predominantly domestic resources

- Identifies cost (i.e., technical) barriers that must be overcome to achieve high utilization of renewable resources for hydrogen production

DIRECTED TECHNOLOGIES INC.

Calculation of H_2 Demand Distribution

- Calculated per capita gasoline energy use from data in chart
- Estimated population in each state for 2040 (based on Census Bureau projections)
- Estimated fraction of national fuel consumption for each state in 2040
- Allocated the 10 quads of H_2 proportional to the 2040 fractional fuel consumption



Source: EIA (gasoline usage), Census Bureau (population)

DIRECTED TECHNOLOGIES INC.

Renewable Resources Available for H_2

- Biomass availability from ORNL state-by-state analyses and EPA MSW/landfill data. (Includes dedicated energy crops, agricultural residues, wood wastes, MSW, landfill gas, and livestock manure)
- State wind totals from EPRI/DOE, state class breakdown from NREL wind map (Classes 4, 5, and 6 only)
- Solar state-by-state from 10% of BLM land with >6 kWh/m^2-day (annual average insolation)
- Geothermal from Geothermal Energy Association report
- *Nuclear was explicitly excluded*

	H_2 Potential in 2040 Quads/year
Biomass	**2.7**
Wind	**22.9**
PV Solar	**5.9**
Geothermal	**0.4**
Total	**31.9**

DIRECTED TECHNOLOGIES INC.

Biomass Cost Assumptions
115 m.t. H_2/day

Hydrogen yield	70 kg/m.t. biomass*
Plant Capital Cost	$117.3 million
Capacity factor	85%
On-stream factor	95%
Plant lifetime/payback period	25 years
Cost of capital	10.8%
Biomass cost	$44/m.t.
Annual operating and maintenance	3% of initial capital
Insurance and taxes	1% of initial capital
Operator labor (12 @ 12 hrs/shift)	$40/hour (loaded)
Corporate overhead	15% of revenues

*58 kg/m.t. for MSW

Feedstock Cost	
Energy crops	$44/m.t.
Wood & Ag Waste	$40/m.t.
Livestock Manure	$22/m.t.
MSW	$22/m.t.
Landfill gas	$1.64/Kscf

Cost of H_2 at Plant ($/kg)	
Energy crops	**1.75**
Wood & Ag Waste	**1.68**
Livestock Manure	**1.32**
MSW	**1.45**
Landfill gas	**1.98***

*** Delivered**

DIRECTED TECHNOLOGIES INC.

Wind Turbine Cost Assumptions
50 MW peak, Classes 4, 5, and 6

Plant Capital Cost ($648/kW$_{peak}$)	$32.4 million
On-stream factor	98%
Plant lifetime/payback period	25 years
Land lease rate	2.5% of revenue
Cost of capital	10.8%
Annual fixed O&M	2% of initial capital
Annual variable O&M	$0.005/kWh
Operator labor (3 @ 12 hrs/shift)	$40/hour (loaded)
Corporate overhead	15% of revenue

Capacity Factor	
Class 4	38.3%
Class 5	41.4%
Class 6	48.7%

	COE (¢/kWh)
Class 4	**4.7**
Class 5	**4.4**
Class 6	**3.8**

DIRECTED TECHNOLOGIES INC.

Forecourt Electrolysis Cost Assumptions

Plant Capital Cost ($300/kW$_e$)	$510,000
Capacity factor	69%
Plant lifetime/payback period	10 years
Cost of capital	10.8%
Annual fixed O&M	2.5% of initial capital
Water Cost	$2/1000 gal
Operator labor (1 @ 12 hrs/shift)	$20/hour (loaded)
Corporate overhead	15% of revenue

Electrolysis Cost $1.30/kg H_2

DIRECTED TECHNOLOGIES INC.

Transmission and Distribution Cost Assumptions

- Hydrogen Pipeline
  - Interstate: 40% higher (energy basis) than recent natural gas pipeline construction $\Rightarrow$ \$0.024/kg H_2-100 miles
  - Local: 40% higher (energy basis) than markup on commercial natural gas from city gate price
- Electricity $\Rightarrow$ \$0.00178/kWh-100 miles
- Compression, forecourt storage, dispensing
  - 920 kg H_2/day capacity
  - 7,000 psi storage, dispense to 5,000 psi
  - \$470,000

DIRECTED TECHNOLOGIES INC.

H_2 Pathways and Cost Factors

- All pathways deliver 5,000 psi gas to the vehicle (7,000 psi storage for fast fill)
- Cost factors were calculated from capital and operating costs using discounted cash flow method (8-11% cost of capital, 10-25 year payback)

* *Only the lowest cost pathway for each resource was selected*

  – Uneconomical pathways: liquid H_2 transport, pyrolysis oil, centralized electrolysis

- Cost of H_2 calculated from component factors

Electrolysis

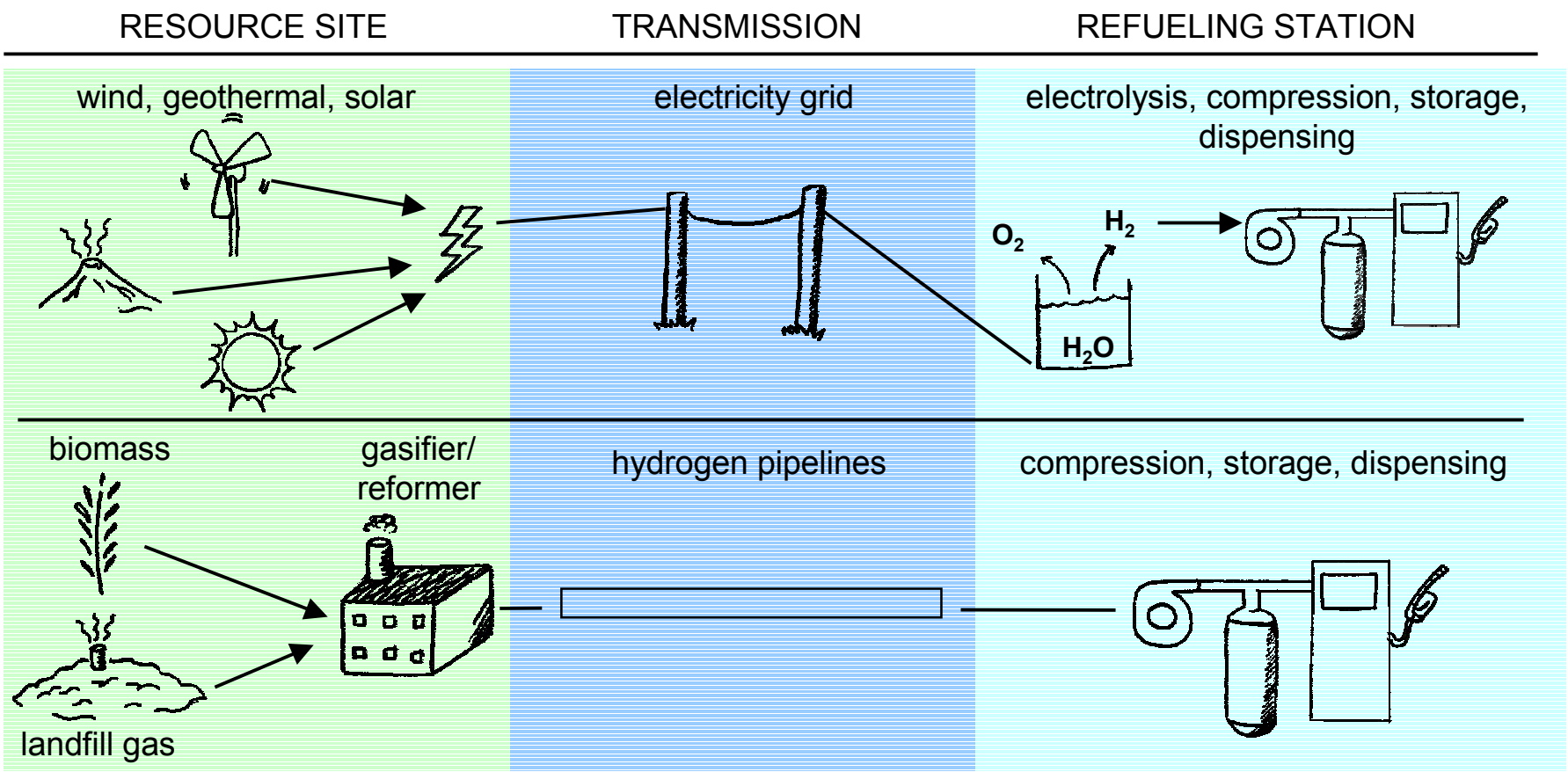
$$C_{H2} = \frac{1}{\eta_e (1 - l_T)} (C_G + C_T D) + C_E + C_{CSD}$$

Gasification

$$C_{H2} = C_G + C_{P-L} + C_{P-D} D + C_{CSD}$$

DIRECTED TECHNOLOGIES INC.

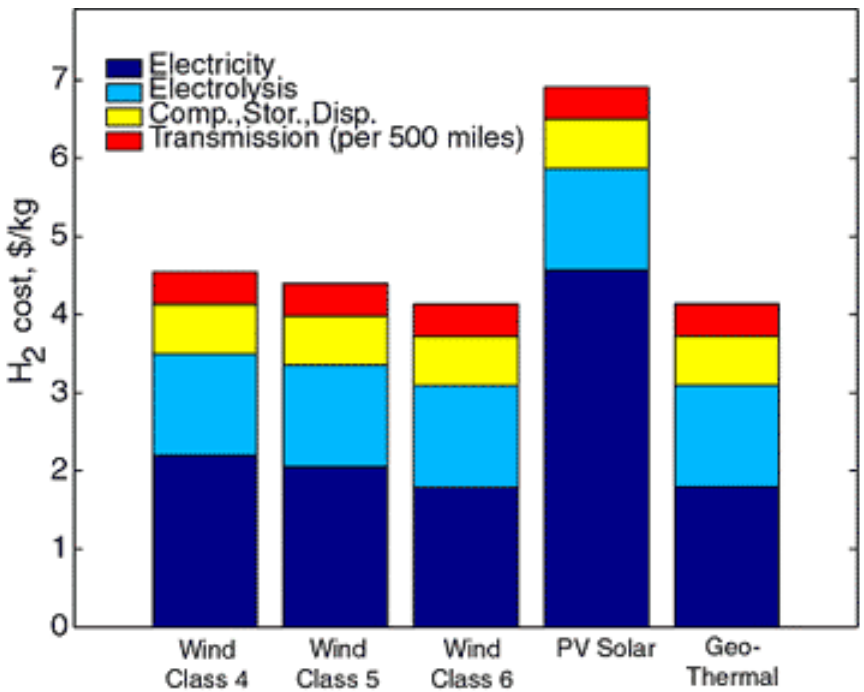
Two Categories of Hydrogen Pathways



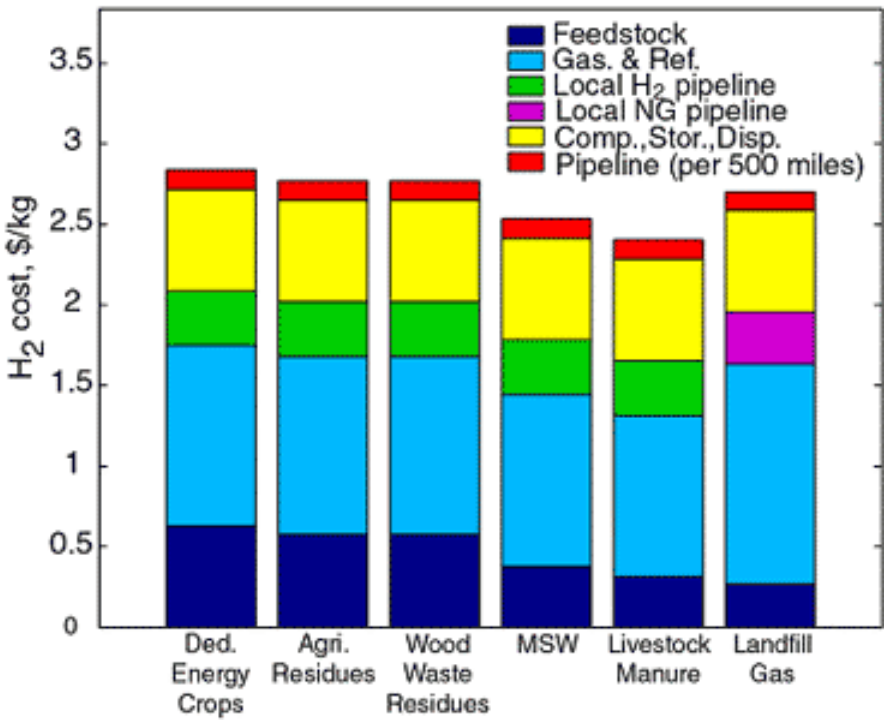
DIRECTED TECHNOLOGIES INC.

Cost of Hydrogen
(excluding sales taxes and dispensing markup)

Electrolysis Methods



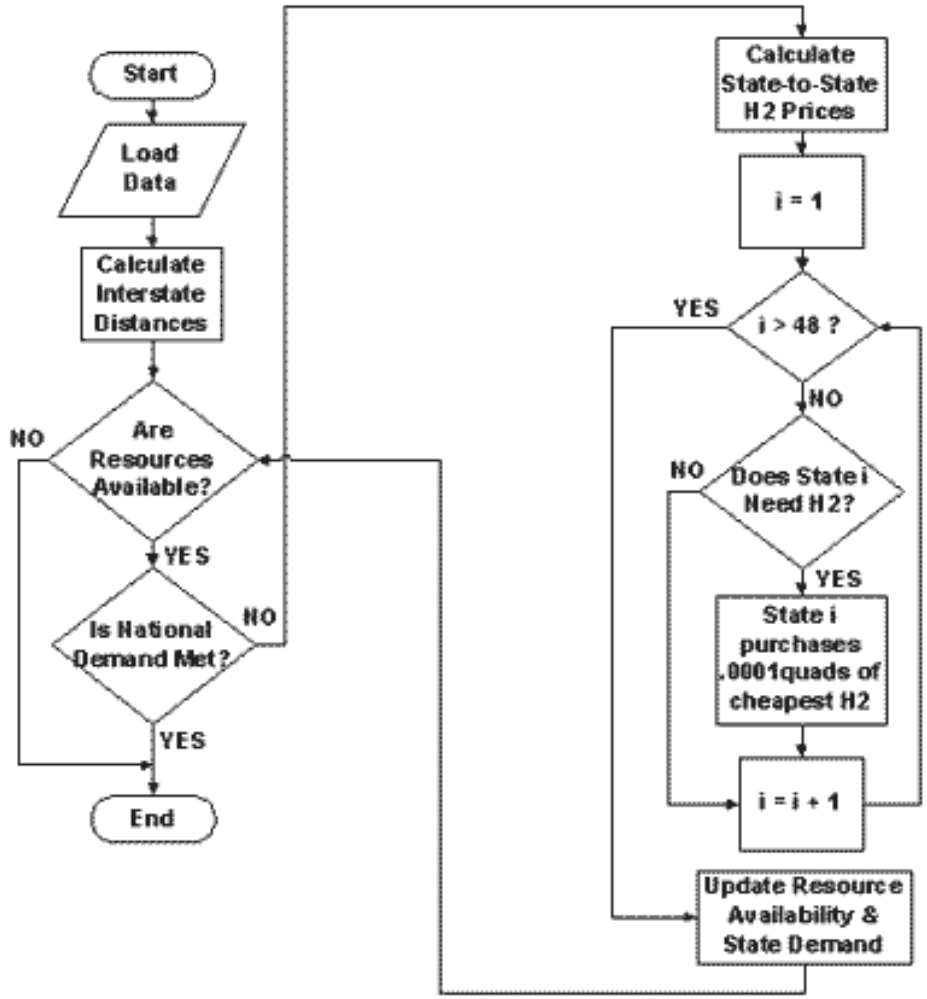
Gasification/Reformation Methods



DIRECTED TECHNOLOGIES INC.

H_2 Distribution Simulation

- Calculate cost of H_2 from each state to each state for each resource (48 contiguous states)
- States purchase H_2 in 0.0001 quad increments over multiple rounds until needs are met
- Lowest cost resources are used first
- Result ~ lowest cost for U.S.



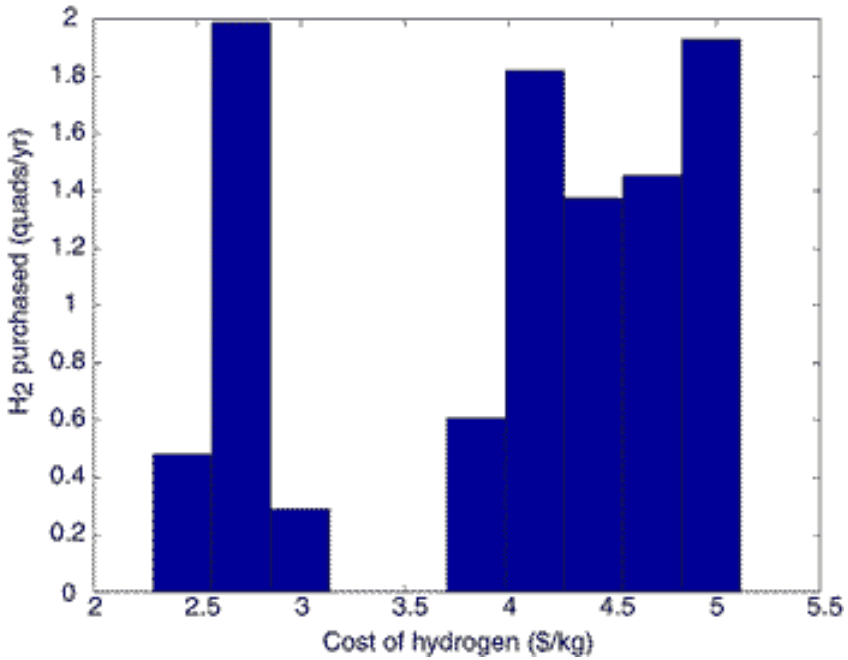
DIRECTED TECHNOLOGIES INC.

Resource Usage and Model Cost of H_2

	Potential (quads/year)	***Predicted Usage (quads/year)***
Wind Class 4	18.1	5.3 [29%]
Wind Class 5	3.1	0.48 [15%]
Wind Class 6	1.7	0.98 [58%]
Geothermal	0.43	0.43 [100%]
Biomass	2.7	2.7 [100%]
PV Solar	5.9	0 [0%]

NOTE: In general, cheapest feedstocks are used first (Biomass over Wind over Solar). Classes 5 and 6 wind are not fully utilized because of high transmission costs from remote locations.

National H_2 cost distribution



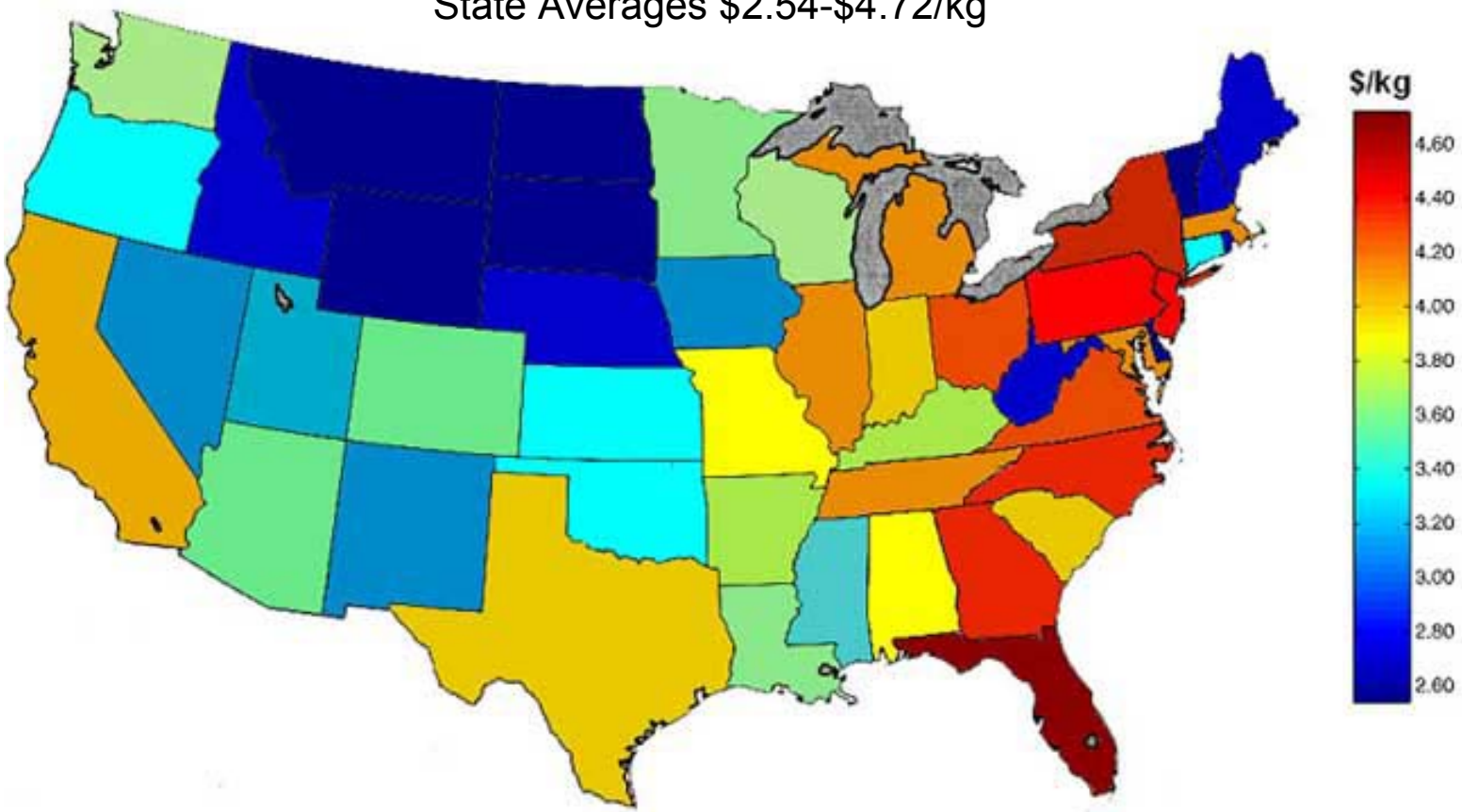
Average Cost of Hydrogen (delivered): $3.98/kg

[$33.24/GJ, $35.04/$10^6$ Btu]

DIRECTED TECHNOLOGIES INC.

Delivered H_2 Cost by State

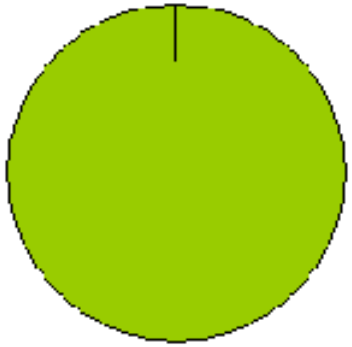
Color represents average statewide cost of H_2 without dispensing markup or sales taxes.
State Averages $2.54-$4.72/kg



DIRECTED TECHNOLOGIES INC.

Example States: Resources Used

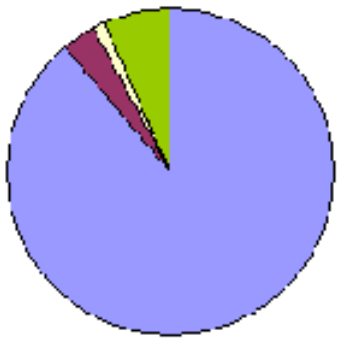
North Dakota (0.03 quads)



New Jersey (0.27 quads)

California (1.22 quads)

Texas (0.97 quads)

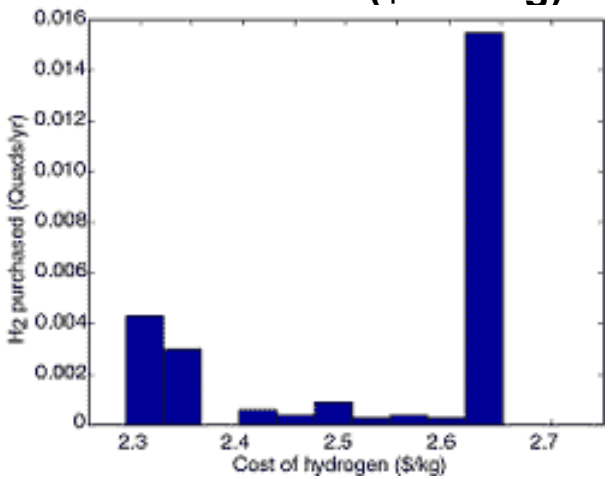


WC4 WC5 WC6 GeoT Biomass

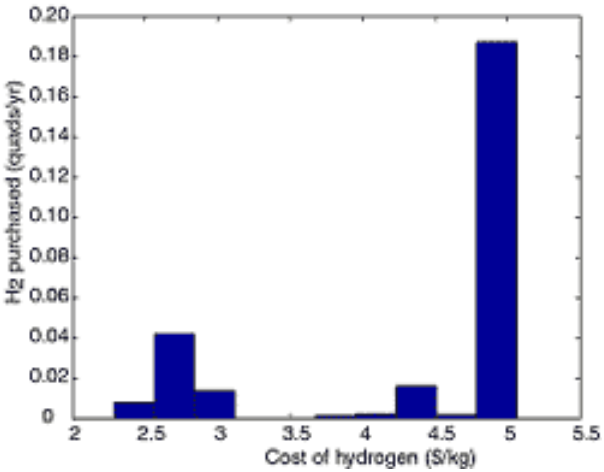
DIRECTED TECHNOLOGIES INC.

Example States: H_2 Cost

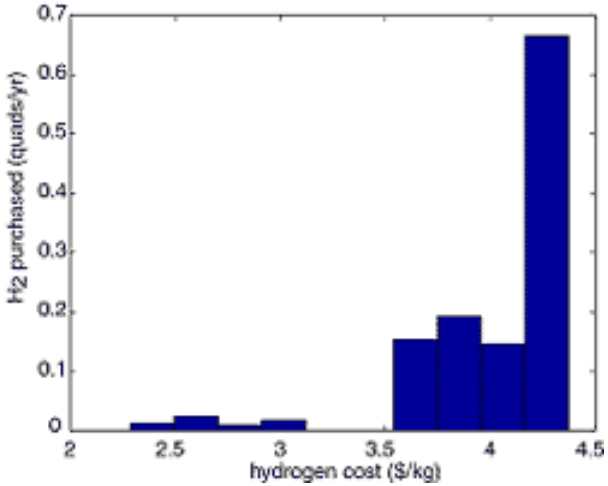
North Dakota ($2.54/kg)



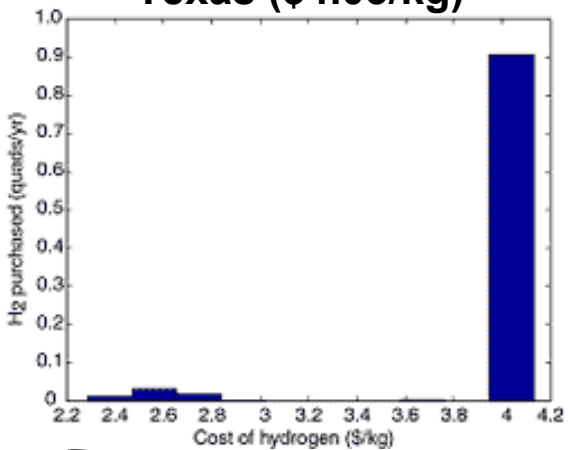
New Jersey ($4.45/kg)



California ($4.09/kg)



Texas ($4.03/kg)



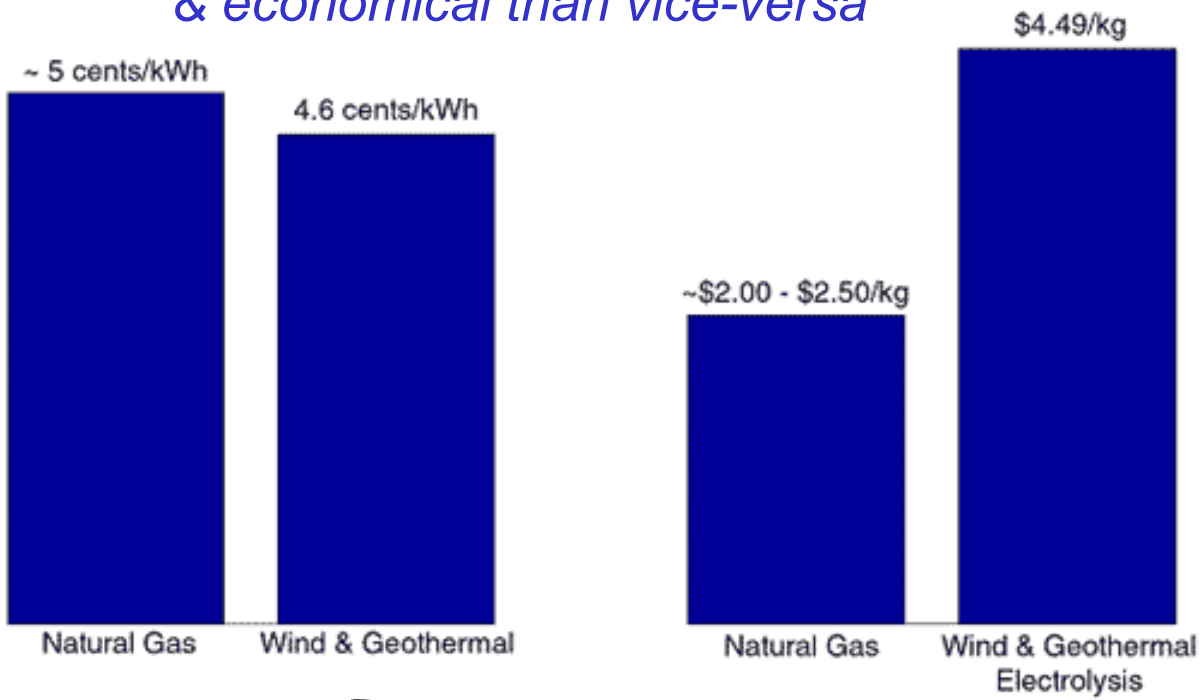
DIRECTED TECHNOLOGIES INC.

Interesting Aside: Electrolysis is an Uneconomical Use of Wind and Geothermal Electricity

- Electricity cost from wind/geothermal ≈ electricity cost from NG turbine
- H_2 cost from wind/geothermal ~85% more than H_2 cost from NG SR

∴ Natural gas → H_2 , wind/geothermal → electricity is more efficient & economical than vice-versa

Cost of electricity (generation site)



Cost of H_2 (delivered)

DIRECTED TECHNOLOGIES INC.

Conclusions

- 10 quads of H_2 from renewable sources for transportation uses is technically achievable
- Electrolysis is significantly more expensive than biomass gasification
- Relatively abundant wind resources make solar a non-factor
- Significant wind resources are “stranded” due to cost of transmission
- Alternative production and distribution methods may be used, but not on the national scale

DIRECTED TECHNOLOGIES INC.

Project Timeline

The work in the past year has been for Task 3 of a three task project.

Task	Title	Status
1	Distributed Hydrogen Fueling Systems Analysis	Complete. Report published October 2000.
2	Cost and Performance of Stationary Hydrogen Fueling Appliances	Complete. Report published April 2002.
3	Hydrogen from Renewable Energy Sources: Pathway to 10 Quads For Transportation Uses in 2030 to 2050	Draft Report issued for review February 2003.

DIRECTED TECHNOLOGIES INC.

Collaborations

- Discussed capital cost projections for solar electricity with BP Solar
- Presented results at the 14th Annual U.S. Hydrogen Conference (March 2003, Washington, D.C.)
- Draft Report submitted for review to
  - DOE H2A Working Group
  - NREL

DIRECTED TECHNOLOGIES INC.

Acknowledgements

- This work was funded by the DOE EERE Hydrogen, Fuel Cells, and Infrastructure Technologies Program

- Dr. Sig Gronich, Technology Validation Manager

DIRECTED TECHNOLOGIES INC.

Biomass-Derived Hydrogen from a Thermally Ballasted Gasifier

DOE Hydrogen Program Contractors' Review Meeting
May 18-21, 2003

Robert C. Brown
Center for Sustainable Environmental Technologies
Iowa State University

Objective

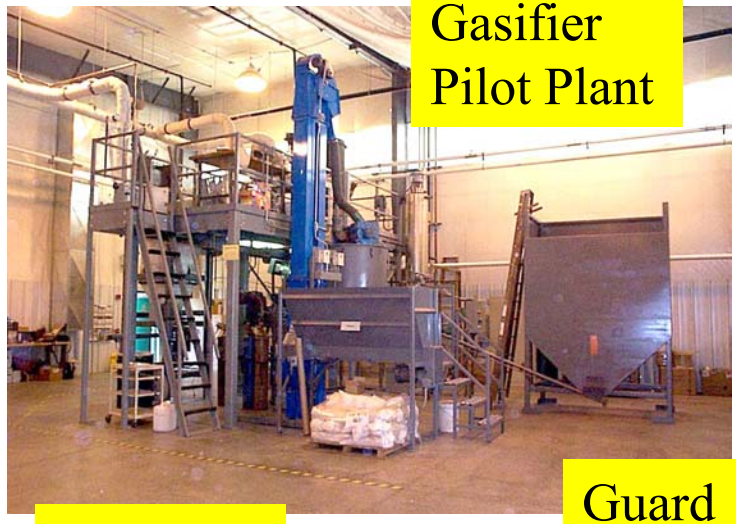
- Develop hydrogen production system based on thermal gasification of switchgrass

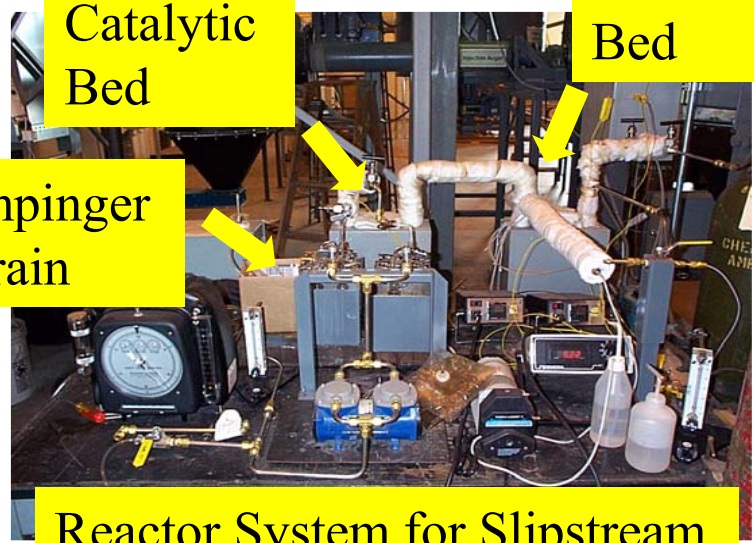
Relevance

- If successful, this project would provide a renewable source of hydrogen from biomass

Approach Outline

- Develop subsystems for the hydrogen production system:
  - Indirectly heated gasifier
  - Gas cleaning process
  - Gas conditioning system
  - Trace gas contaminant measurements
- Testing performed at two scales:
  - Pilot plants (5 tpd) for gasifier and gas cleaning system
  - Slip stream for gas conditioning system

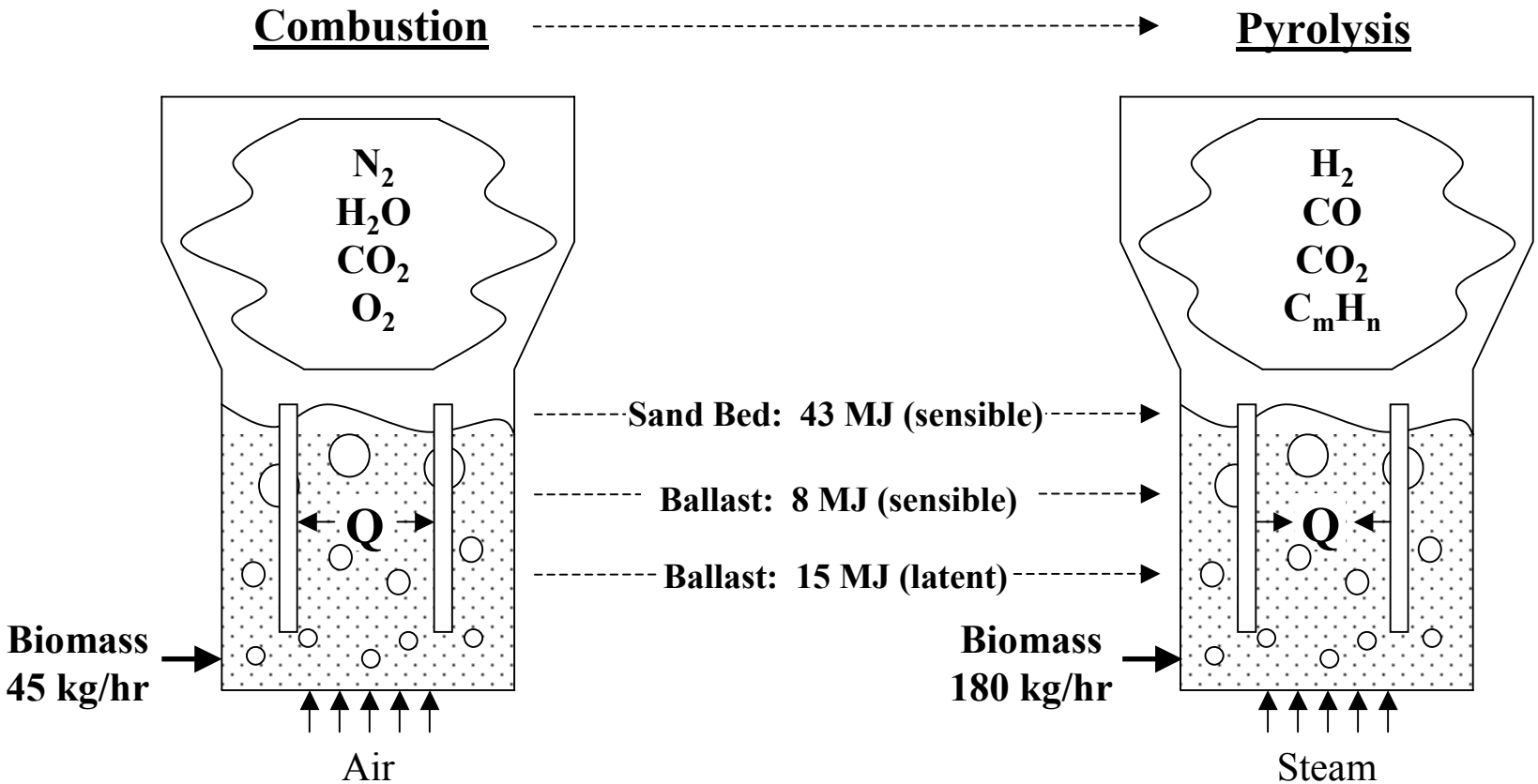




Approach: Indirectly heated gasifier

- Conventional fluidized bed gasification
  - Combustion and pyrolysis occur simultaneously in a single reactor
    - Exothermic combustion provides heat
    - Endothermic pyrolysis produces light gases and hydrocarbons
  - Products of combustion dilute product gas
- Indirectly heated gasification
  - Combustion and pyrolysis processes are separated (usually spatially)
  - No nitrogen dilution of product gas
  - Energy must be transported to the pyrolysis reactions

Approach: Indirectly heated gasifier



Combustion and Pyrolysis are Temporally Separated in the Ballasted Gasifier System

Approach: Indirectly heated gasifier

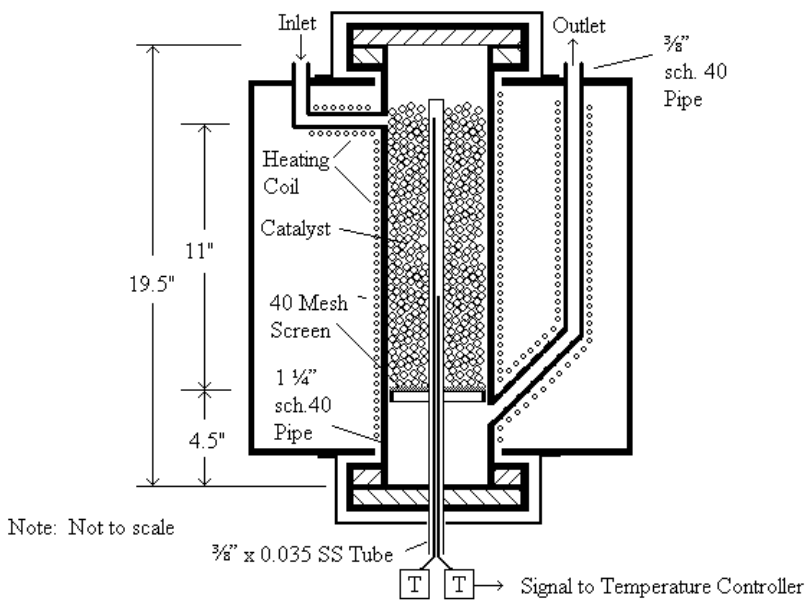
- Thermal ballast is high temperature phase-change material
  - Lithium fluoride sealed in stainless steel tubes which are immersed in fluidized bed
  - Thermal ballast consists of an array of 48 tubes
- Air fluidizes the bed during combustion
- Steam fluidizes the bed during pyrolysis
- Gasifier temperature varies between 922 K to 1172 K

Approach: Gas Conditioning

- Particulate removal
  - Required to prevent blinding of catalytic beds
  - Evaluating moving bed granular filter
- Trace contaminate removal using sorbent injection
  - H_2S and HCl removal to avoid poisoning of catalytic beds
  - Also removes some heavy tar
- Ammonia and tar removal
  - Steam reforming
- Water gas shift
  - Increases H_2 and removes CO

Approach: Gas Conditioning

- Guard bed for trace contaminant removal
  - Fixed bed of dolomite
- Steam reformer
  - Nickel catalysts
- High temperature water gas shift
  - Iron based catalyst
- Low temperature water-gas shift
  - Copper based catalyst



The four reactors are identical in construction

Approach: Gas Analysis

- Hot gas isokinetic sampling of *particulate matter*
- Impinger train using dichloromethane used for quantitative *tar* analysis
- Micro GC for periodic, *comprehensive gas* analysis
- Non-dispersive IR (CO, CO_2), thermal conductivity (H_2), and electrochemical (O_2) for *continuous gas* monitoring
- Quantitative methods developed for *trace contaminants*
    - NH_3 – collection in acid solution and analyzed at a commercial lab
    - H_2S – Draeger tubes and GC

Project Timeline (FY 03)

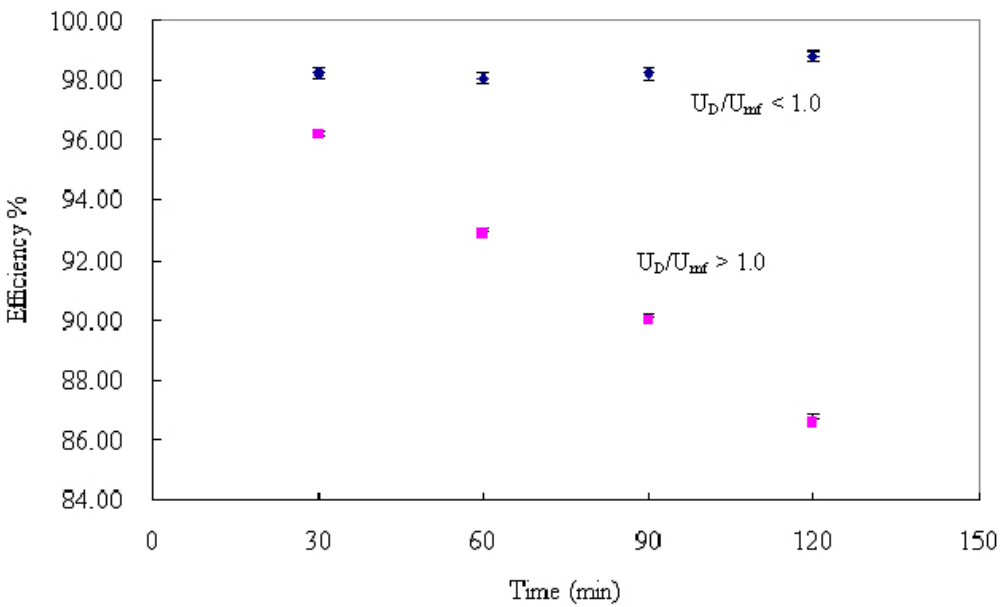
	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Task 1. Design and construct multi-contaminant control system based on sorbent injection.				
Task 2. Improve trace contaminant instrumentation.				
Task 3. Evaluate effectiveness of multi-contaminant control system.				
Task 4. Evaluate catalytic reactors for removal of tar and ammonia and enriching hydrogen				
Task 5. Identification of appropriate separation technology to purify hydrogen.				
Task 6. Thermal System and Cost Estimation Analysis				
Task 7. Project administration and reports				

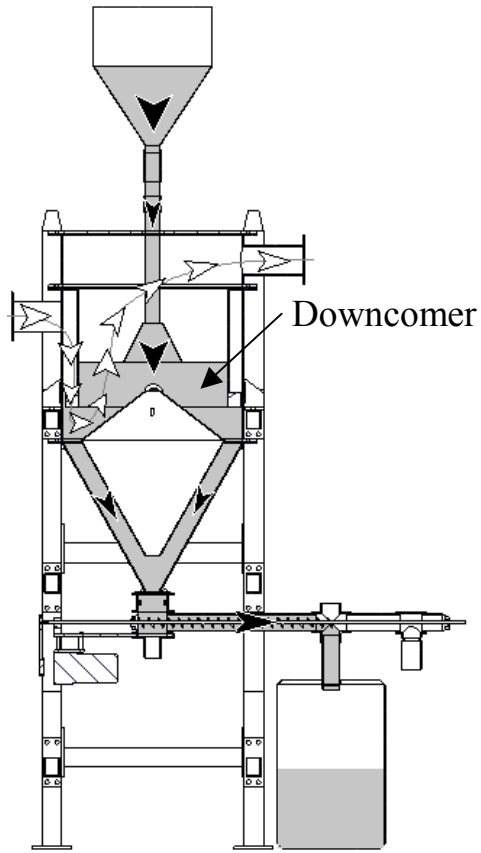
Milestone Work performed Work remaining

Accomplishments/Progress

Multi-contaminant Control

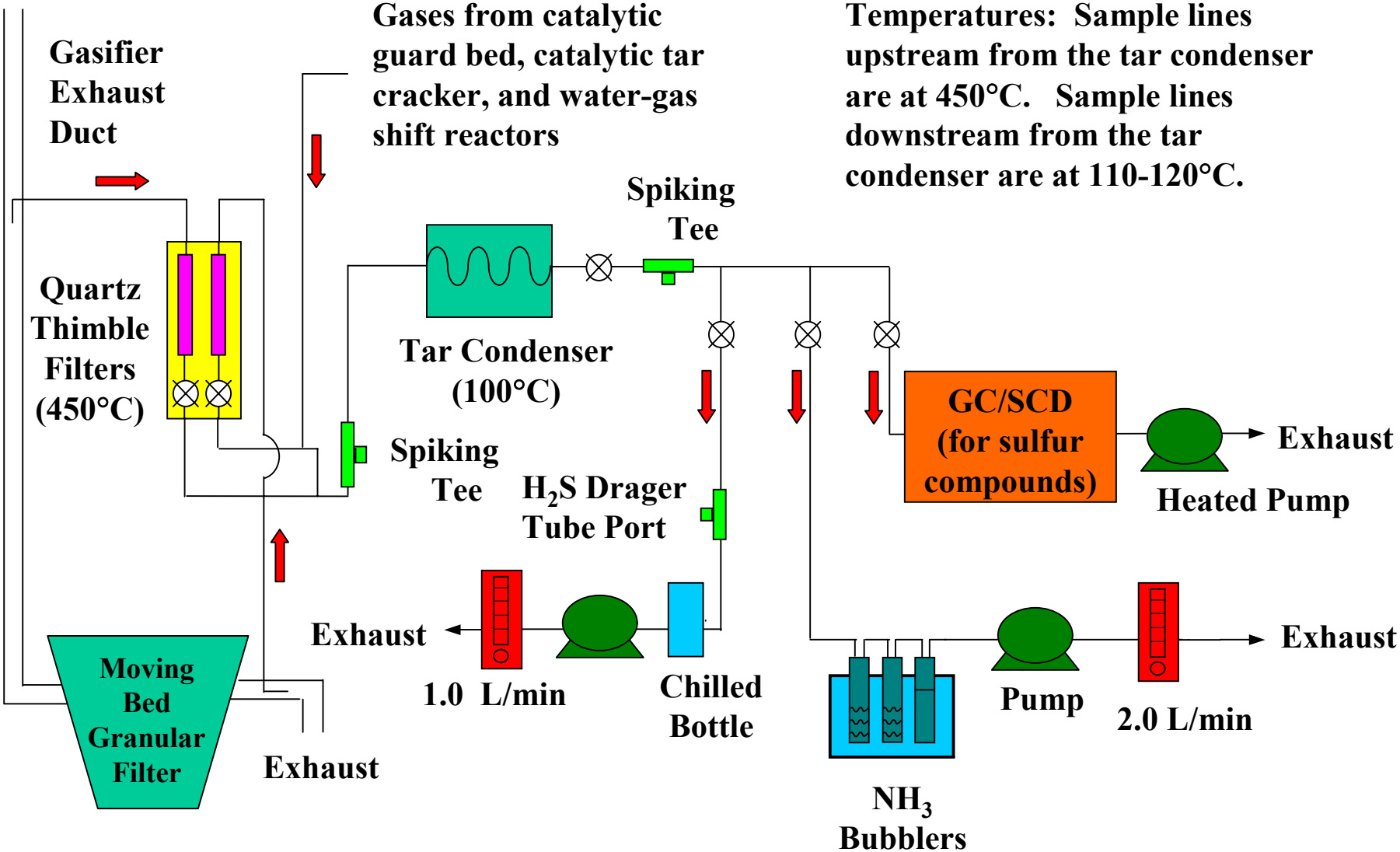
- Established ability of pilot-scale moving bed granular filter to remove fly ash
  - Efficiencies exceeding 90%
- Must keep velocity in downcomer (U_D) below the minimum fluidization velocity (U_{mf})of the granular media in the filter to keep efficiency high





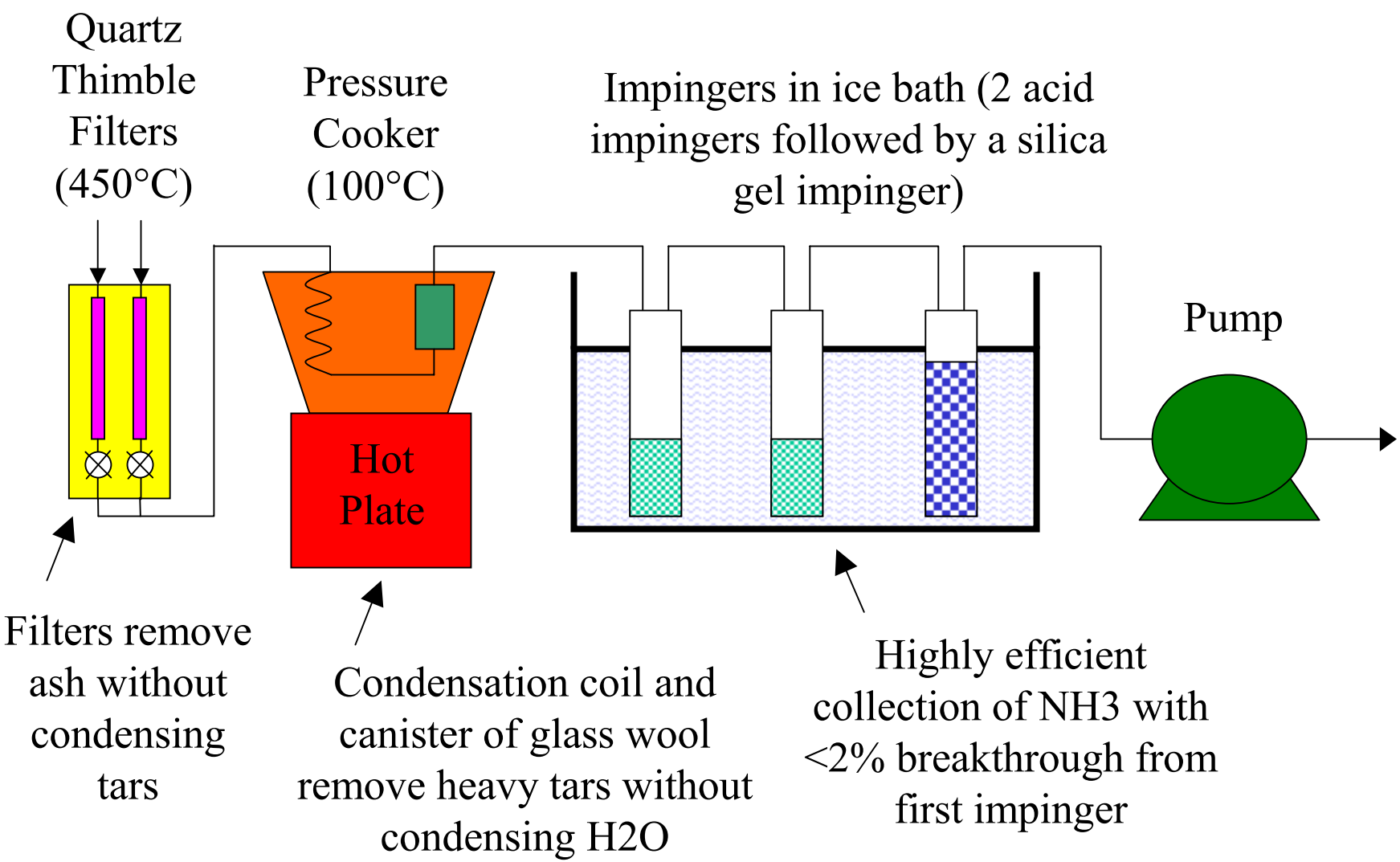
Accomplishments/Progress

Trace Contaminant Instrumentation



Accomplishments/Progress

Ammonia Sampling Procedure



Accomplishments/Progress

Gas Conditioning: Tar Cracking

Operating Conditions of Tar Cracking System

Parameter	ICI 46-1	Z409	RZ409
Calcined dolomite	120ml (132 g)	120ml (132 g)	120ml (132 g)
Ni-Based Catalyst	20 ml (22.3 g)	20 ml (23.2 g)	20 ml (23.1 g)
Inert material mixed with catalyst	20 ml (15.3 g)	20 ml (15.2 g)	20 ml (15.4 g)
Pretreatment of catalyst	No reduction	No reduction	Reduced by manufacturer
Guard bed temperature(T_{GB})	650°C	650°C	650°C
Steam reformer temperature (T_{CR})	740 - 820°C	740 - 820°C	740 - 820°C
Space Velocity (SV)	1500 – 6000 h^{-1}	1500 – 6000 h^{-1}	1500 – 6000 h^{-1}
Operating time	12 hrs	18 hrs	18 hrs

Accomplishments/Progress

Gas Conditioning: Tar Cracking

- Typical heavy tar levels in producer gas: 10 - 20 g/m^3
- All three metal catalysts proved effective
  - Greater than 99% destruction of heavy tar
  - Hydrogen increased by 6-11 vol-% (dry basis)
- Parametric effects:
  - Increasing space velocity had little effect
  - Increasing temperature boosted H2 and reduced light hydrocarbons
- Results consistent with tar destruction controlled by chemical kinetics
- Catalysts showed evidence of increasing pore size, which could lead to deactivation
- Evidence of coking and sulfur accumulation on metal catalysts

Accomplishments/Progress

Gas Conditioning: Steam Reforming & Water Gas Shift

Operating Conditions of Tar Cracking System

Items	GB	TR	HTS	LTS
Temp. of Central cat. Bed ºC	650	800	400	200
Temp. range of cat. Bed ºC	600-670	750-850	350-420	180-240
SV(h^{-1})		3000	1500	1200
Catalyst	Calcined dolomite	ICI 46-1	Fr-Cr based LB	Cu-Zn-Al based B202
Catalyst volume (ml)	200	60	120	150
Inert material (ml)	0/20	20/20	20/50	25/50
Gas Composition (%-vol)	Inlet gas	Outlet gas	Outlet gas	Outlet gas
H_2	8.5	19.44	23.7	27.1
CO	14.5	8.9	1.37	0.18
CO_2	18.1	20.1	26.8	27.2
CH_4	4.3	3.5	3.4	3.1
C_2H_4	1.5	0.27	0.31	0.13
Tar content (g/Nm^3)	19.5	-	-	-

*Volume of inert material above and below catalyst layer respectively

Accomplishments/Progress

Gas Conditioning: Steam Reforming & Water Gas Shift

Air-blown gasification of switchgrass (ballast system not operated)

Gas constituent	Raw gas	Steam reformer*	High temperature shift reactor*	Low temperature shift reactor*
H_2 (vol-%)	8.5	19.4	23.7	27.1
CO (vol-%)	14.5	8.9	1.4	0.18
CO_2 (vol-%)	18.1	20.1	26.8	27.2
CH_4 (vol-%)	4.3	3.5	3.4	3.1

*Concentration exiting the reactor

Accomplishments/Progress

Trace Gas Sampling

<u>H_2S Measured from Gasification of Waste Seed Corn</u>

- H_2S levels (Drager tubes) were consistently 190-220 ppm over a 5-hr period
- H_2S concentrations were 50-70% lower than what would be expected if ALL the sulfur remained in the gas phase
- Limestone added to the fluidized bed reactor to suppress agglomeration is the likely reason for sulfur retention

Accomplishments/Progress

Trace Gas Sampling

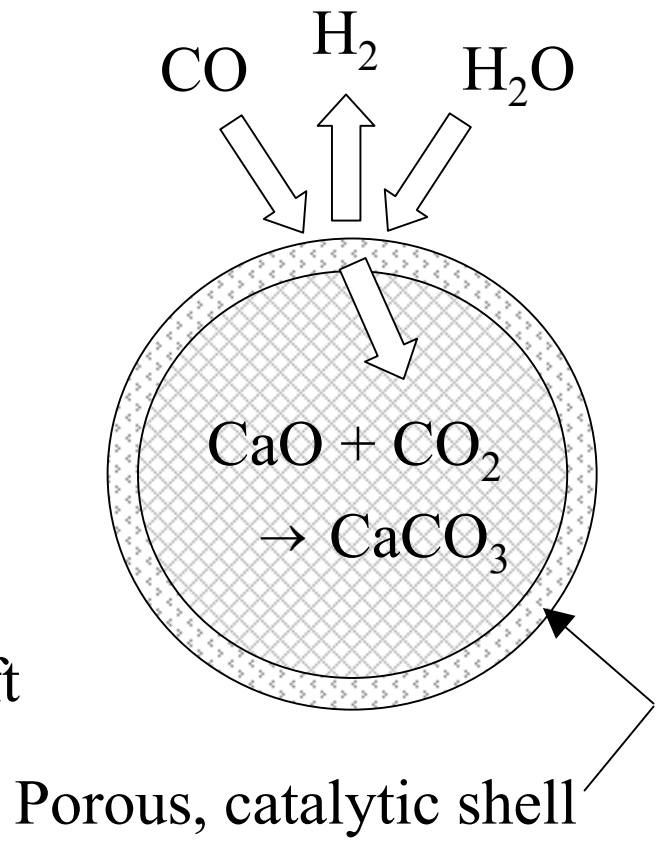
<u>NH_3 Measured from Gasification of Waste Seed Corn</u>

- NH_3 levels were about 5000 ppm; results from duplicate sample runs were within 3% of one another
- Injection of NH_3 into producer gas yielded gas stream measurements within 5% of expected values

Accomplishments/Progress

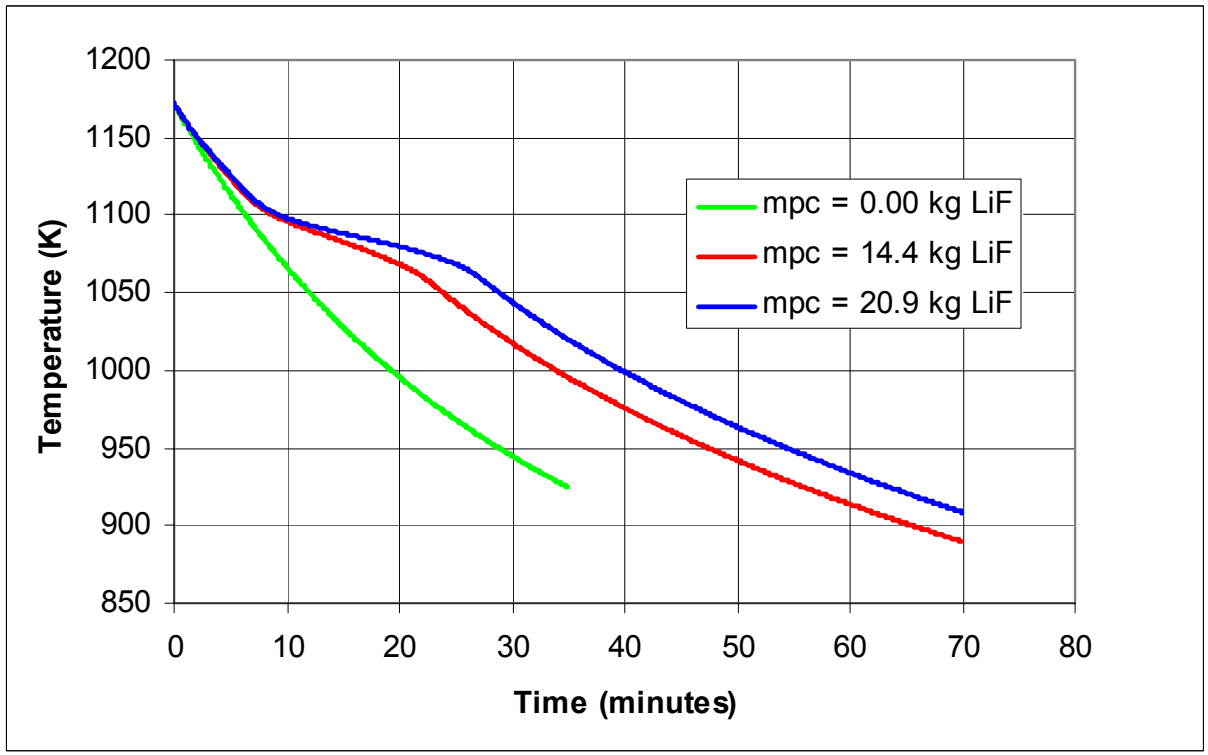
Separation Technology

- Identification of a combined water-gas shift/CO_2 removal system
- Builds upon engineered materials developed at ISU
  - Core-in-shell concept developed for gas sorption
  - Nickel catalyst in shell to promote steam reforming of methane
- This new task will explore copper and iron catalysts in shell for water-gas shift reactions



Accomplishments/Progress

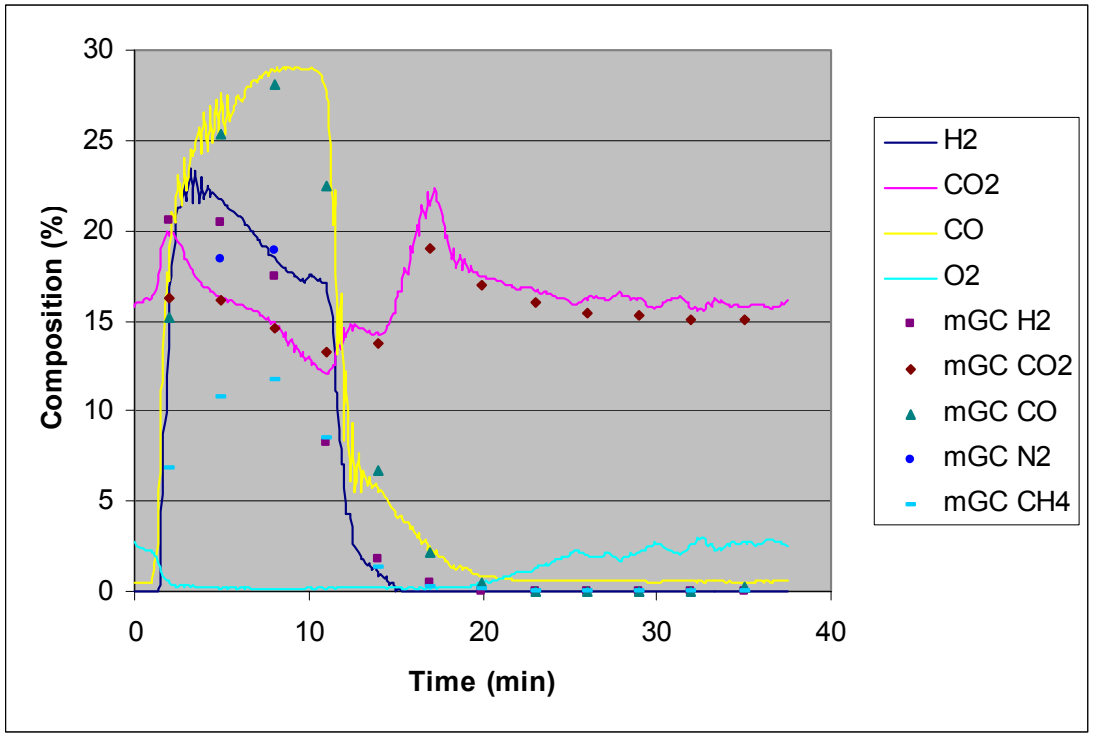
Thermal System Analysis



- Computer simulation of ballasted reactor during cooling with steam
- Phase change material plays significant role in increasing time to cool the reactor

Accomplishments/Progress

Thermal System Analysis



- Experimental data for pyrolysis phase of cycle
  - H_2 and CO_2 decrease, CO increases
  - Micro-GC data consistent with the CEM data

Interactions & Collaborations

- Energy Products of Idaho
  - Licensing technology on moving bed granular filter for control of particulate matter
- Community Power Corporation
  - Investigating use of moving bed granular filter for multi-contaminant control
- University of Victoria, University of British Columbia & National Renewable Energy Center
  - Coauthored paper on hydrogen from biomass (under review by the Int. J. Hydrogen Energy)
- Zhengzhou University, China
  - Visiting scientist working on gas conditioning catalysts

Future Plans

- Testing of multi-contaminant control system (limestone injection upstream of moving bed granular filter)
- Evaluating combined water-gas shift/CO_2 sorption concept
- Operate ballast system with gas conditioning system

Responses to FY 02 Panelist

Reviewer Comment	Investigator's Response
Gasification of switchgrass is not economical…	The ultimate advantage of hydrogen energy is replacement of polluting fossil fuels. Thus, biomass is the ultimate fuel even if not cost-effective by current economic measures.
Project is heavy on analytical methods and light on technical results…	The first year of the project was devoted to building equipment and establishing analytical methods. Significant data was collected on all phases of the project during the second year.

Acknowledgements

- Collaborators in this study include Jerod Smeenk, Andy Suby, Glenn Norton, Ruiqin Zhang, Ming Xu, Nate Brown, and Colin Brue
- This work was performed at the Iowa Energy Center's BECON facility
- This work was funded by the U.S. Department of Energy's Hydrogen Energy Program with cost-sharing from the Iowa Energy Center and Iowa State University

Hydrogen Technical Analysis: Energy Station

Work in Progress

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley CA

May 19-22, 2003

TIAX, LLC
1601 S. De Anza Blvd
Cupertino, California
95014

TIAX Ref: D0038
DOE Ref: DE-FCO4-02AL67602

Hydrogen energy stations could substantially enhance competitiveness of on-site hydrogen production in the near and long-term.

- Key hurdles to the development of a hydrogen infrastructure are:
  - Long-term cost of hydrogen
  - Transition cost to implement the minimum infrastructure
  - Efficiency of hydrogen production in on-site stations
- Combining hydrogen production with power production could provide synergy that could make both parts competitive:
  - Revenue from power sales help overall economics in early years
  - Improved economy of scale from larger systems reduces specific system cost
  - Synergy in storage system allows for cost reduction and low-cost back-up and rapid start-up for power generation system
  - Integration can increase overall efficiency slightly

The purpose of this study is to evaluate the issues surrounding the establishment of a hydrogen energy station.

- Evaluate combined fuel cell power/hydrogen Energy Stations
- Assess integration with buildings and potential for cogeneration
  - Analyze economics of energy station configurations
- Identify potential fleets for vehicle operation
- Establish partnerships for hydrogen fueling and power sales
- Identify barriers to hydrogen use

DOE Technical Targets: Integrated Stationary PEMFC Power System

Characteristics	Large (50-250 kW) Systems			
Calendar Year	Units	2003 Status	2005	2010
Electrical Energy Efficiency @ rated power	%	30	32	40
CHP Energy Efficiencyc @ rated power	%	70	75	80
Cost	$/kWe	2500	1250	750
Transient Response (time from 10% to 90% power)	msec	< 3	< 3	< 3

DOE R&D Plan

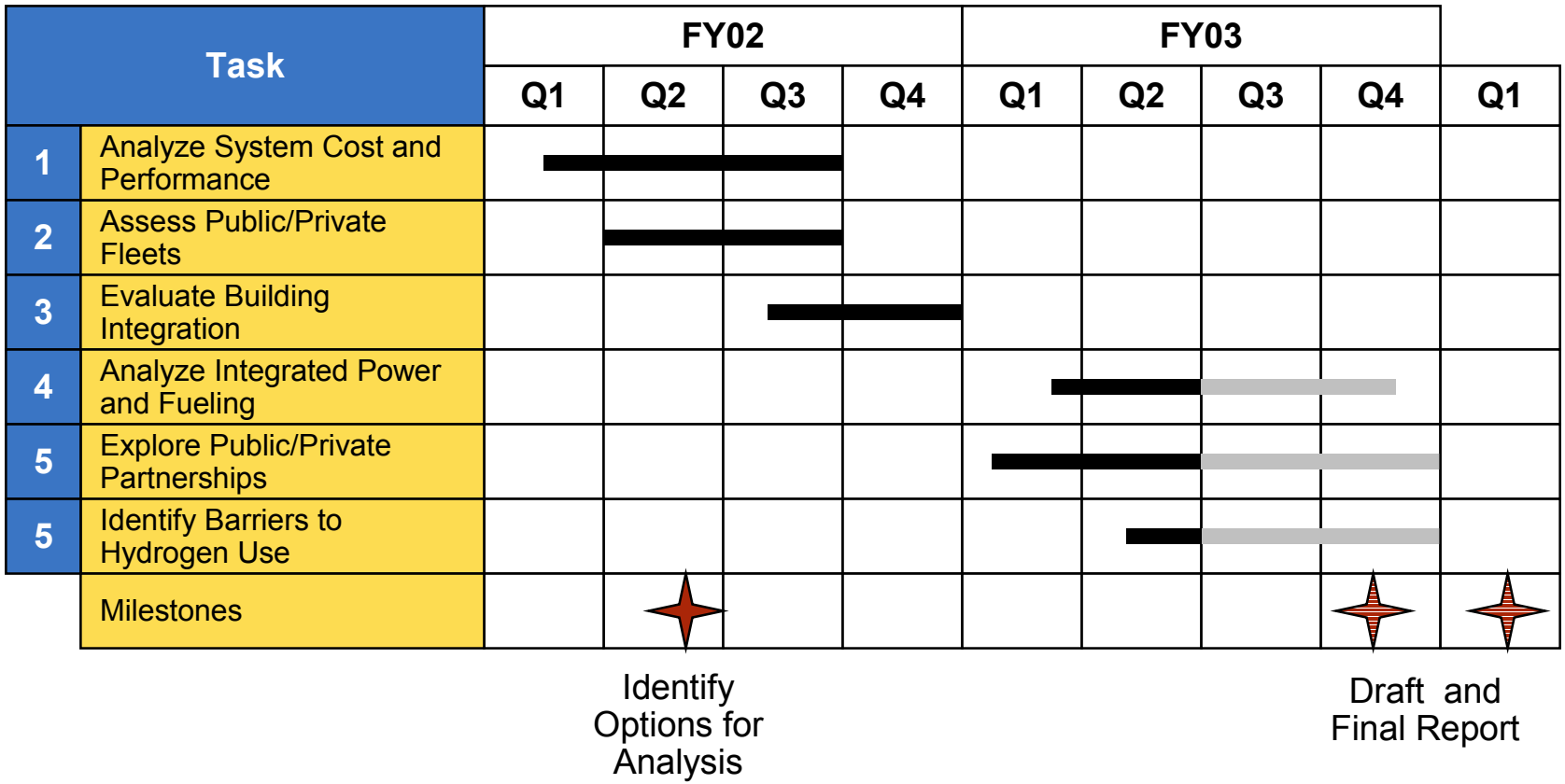
DG Technical Barrier F: Heat Utilization.

The low operating temperature of PEM fuel cell system technology limits the use of heat generated by the fuel cell, which represents approximately 50% of the energy supplied by the fuel. More efficient heat recovery systems and improved system designs and/or higher temperature operation of current systems are needed to utilize the low-grade heat and achieve the most efficient (electrical and thermal) distributed generation power systems.

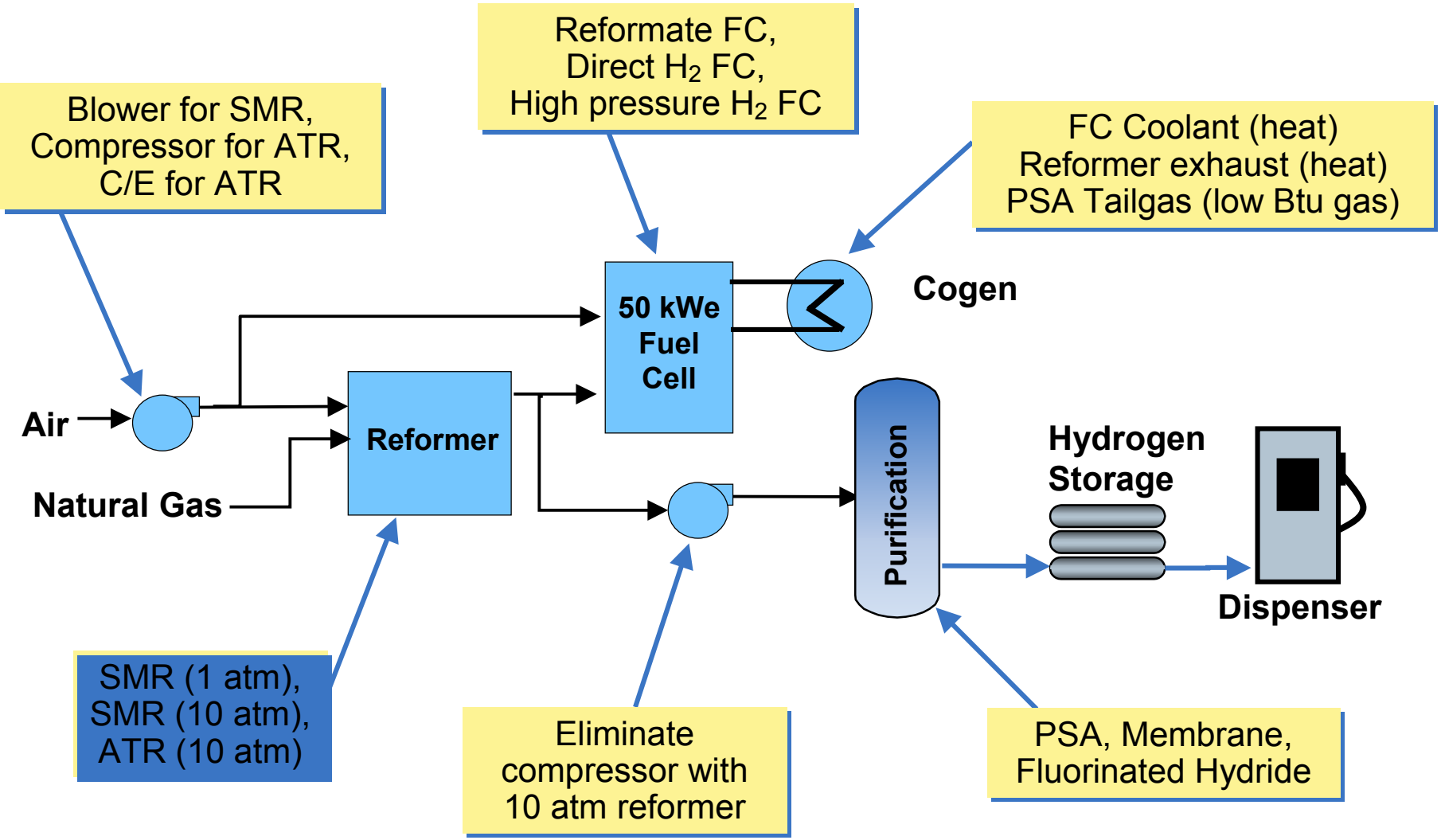
The purpose of this study is to evaluate the issues surrounding the establishment of a hydrogen energy station

- Evaluate combined fuel cell power/hydrogen Energy Stations
  - Analyze energy station systems with 50 kW PEMFCs that are suitable for installation in Federal buildings
  - Analyze options for system components including direct hydrogen and reformate fuel cells and various storage, power production, and hydrogen usage configurations
  - Determine costs and energy efficiency for different system configurations
- Assess integration with buildings and potential for cogeneration
  - Analyze potential for heat recovery from fuel cell/hydrogen production systems
  - Identify potential for cogeneration in Federal building applications
- Identify potential fleets for vehicle operation
- Establish partnerships for hydrogen fueling and power sales
- Identify barriers to hydrogen use
- *This study was supported by DOE contract DE-FC36-01GO11088*

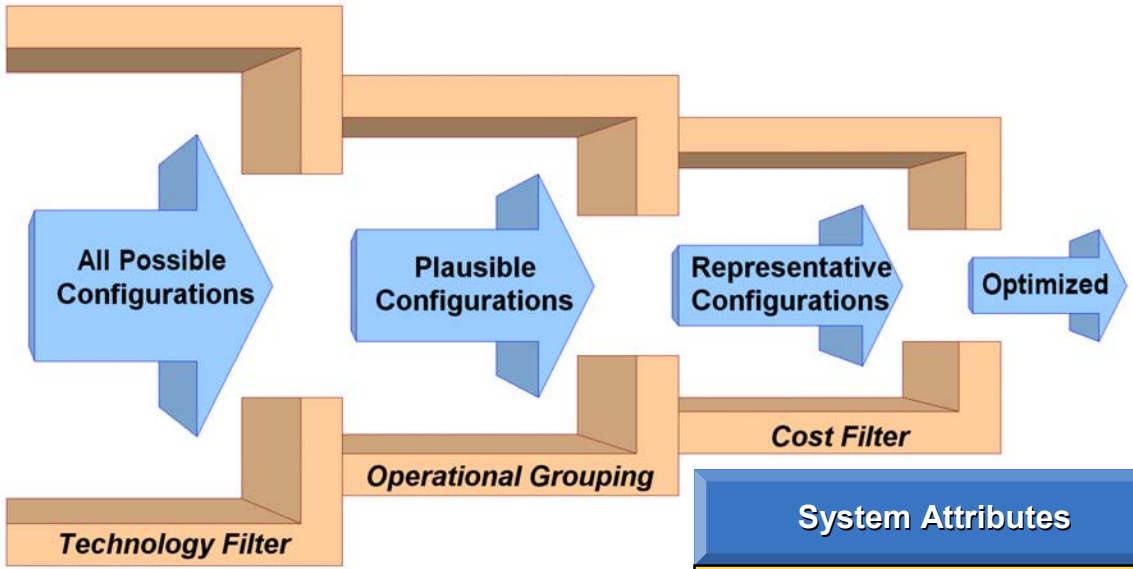
Prior to finalizing our analysis, we intend to obtain input from a range of potential stakeholders in both conventional and hydrogen fuel chains.



Several component choices are options for hydrogen production systems



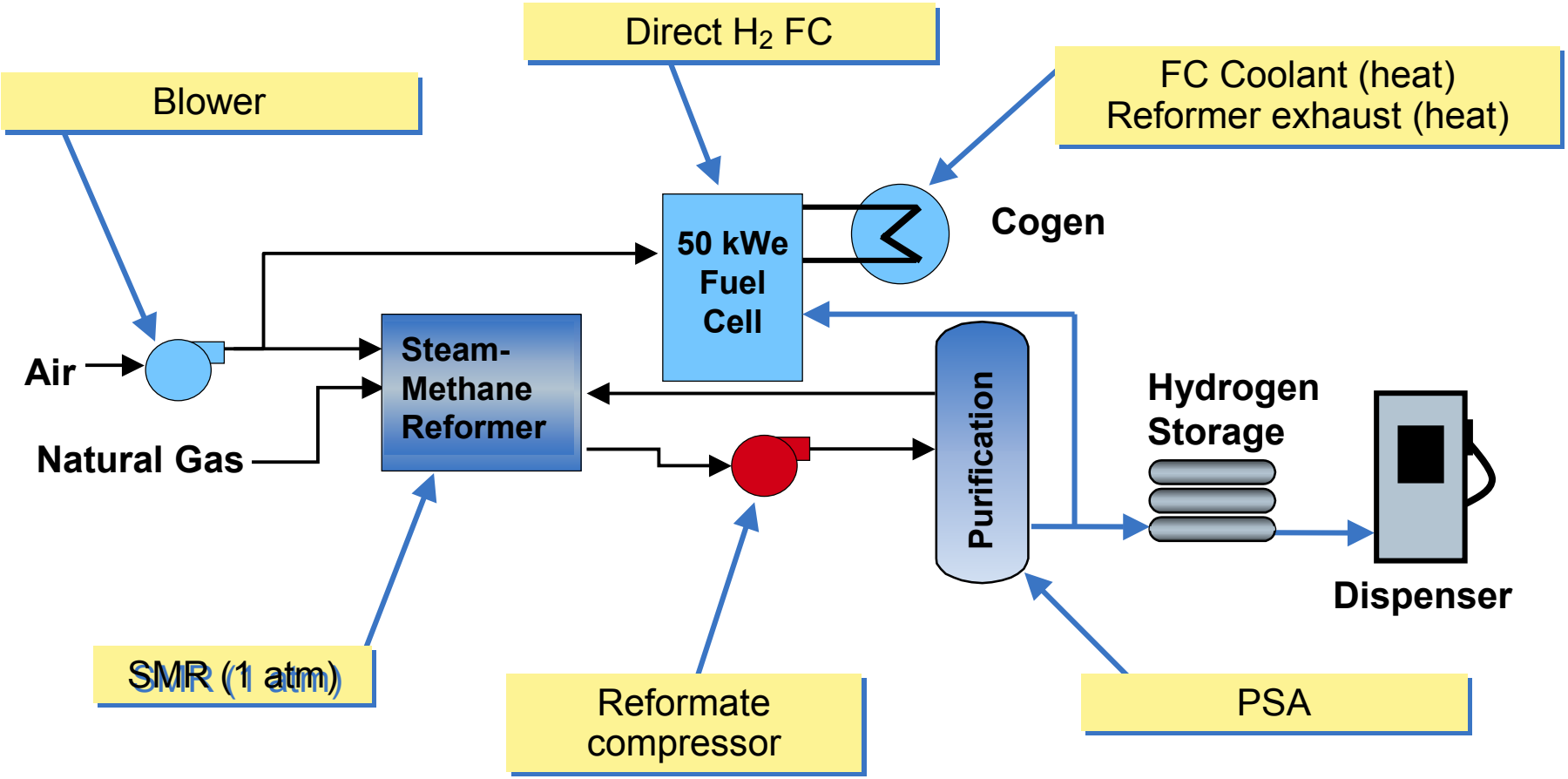
We applied filters to the matrix of possible configurations to select four promising technology combinations that meet various customer needs



System Attributes	Major Components
Conventional system	SMR, Reformate Fuel Cell, PSA
Lower cost fuel cell	SMR, PSA, Direct Hydrogen Fuel Cell
Small scale purification	SMR, Reformate Fuel Cell, Fluorinate metal hydrides
Simple cogeneration	Air Compressor, ATR, PSA, Direct Hydrogen Fuel Cell

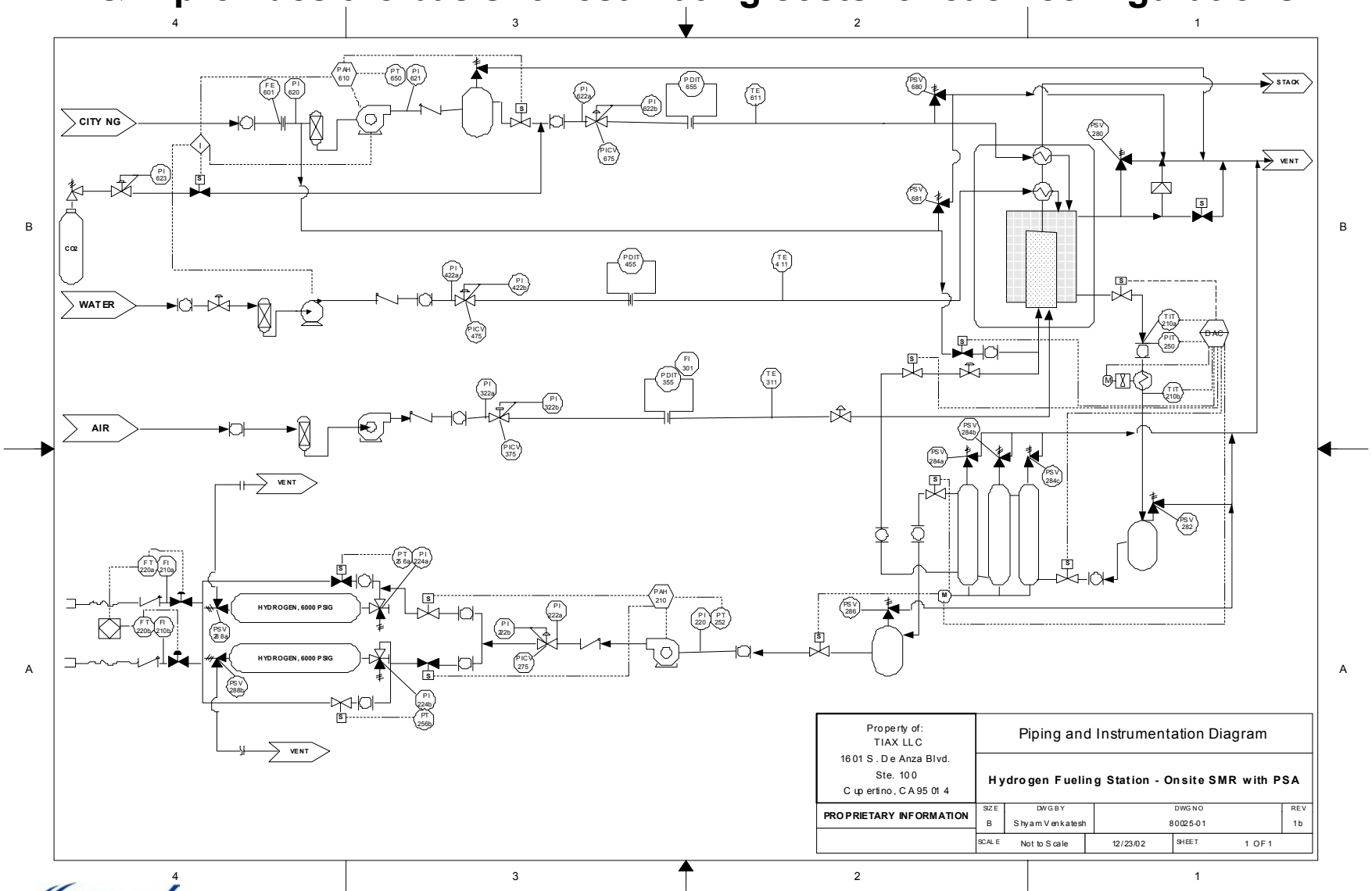
Note: Cost are for high production volumes: 1,000+ units per year.
Variations in operating profile are also being considered

A steam reformer results in higher hydrogen yield and simpler purification.



An ideal system would include a high pressure reformer and eliminate the reformate compressor.

A P&ID provides the basis for estimating costs for each configurations.

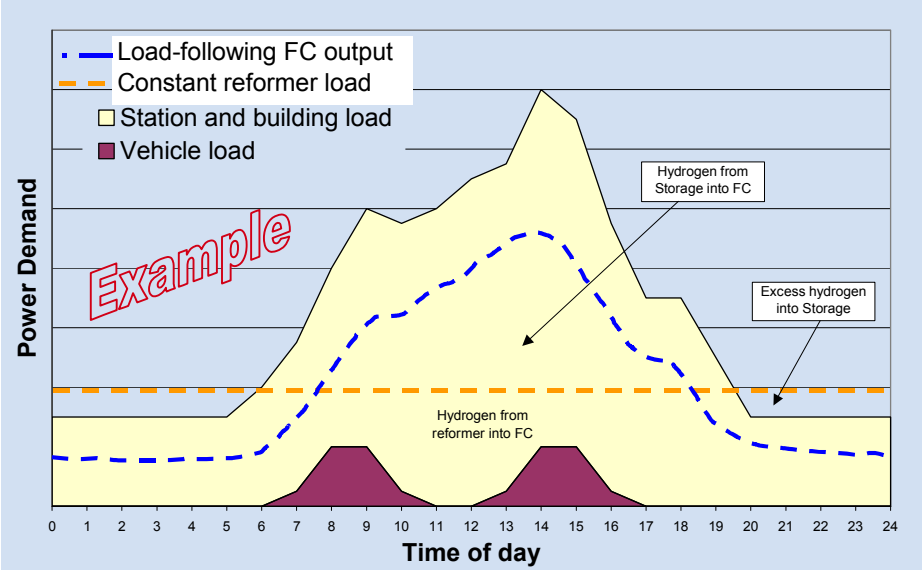


Daily operational levels for the FC and reformer will vary depending upon the target energy utilization strategy for the energy station site

Candidate Operating Strategies

- **Base-loaded**
- **Electric load-following**
- **Heat-load following co-generation**
- **Peak shaving**
- **Back-up power**
- **Tailgas Exhaust to Boiler**

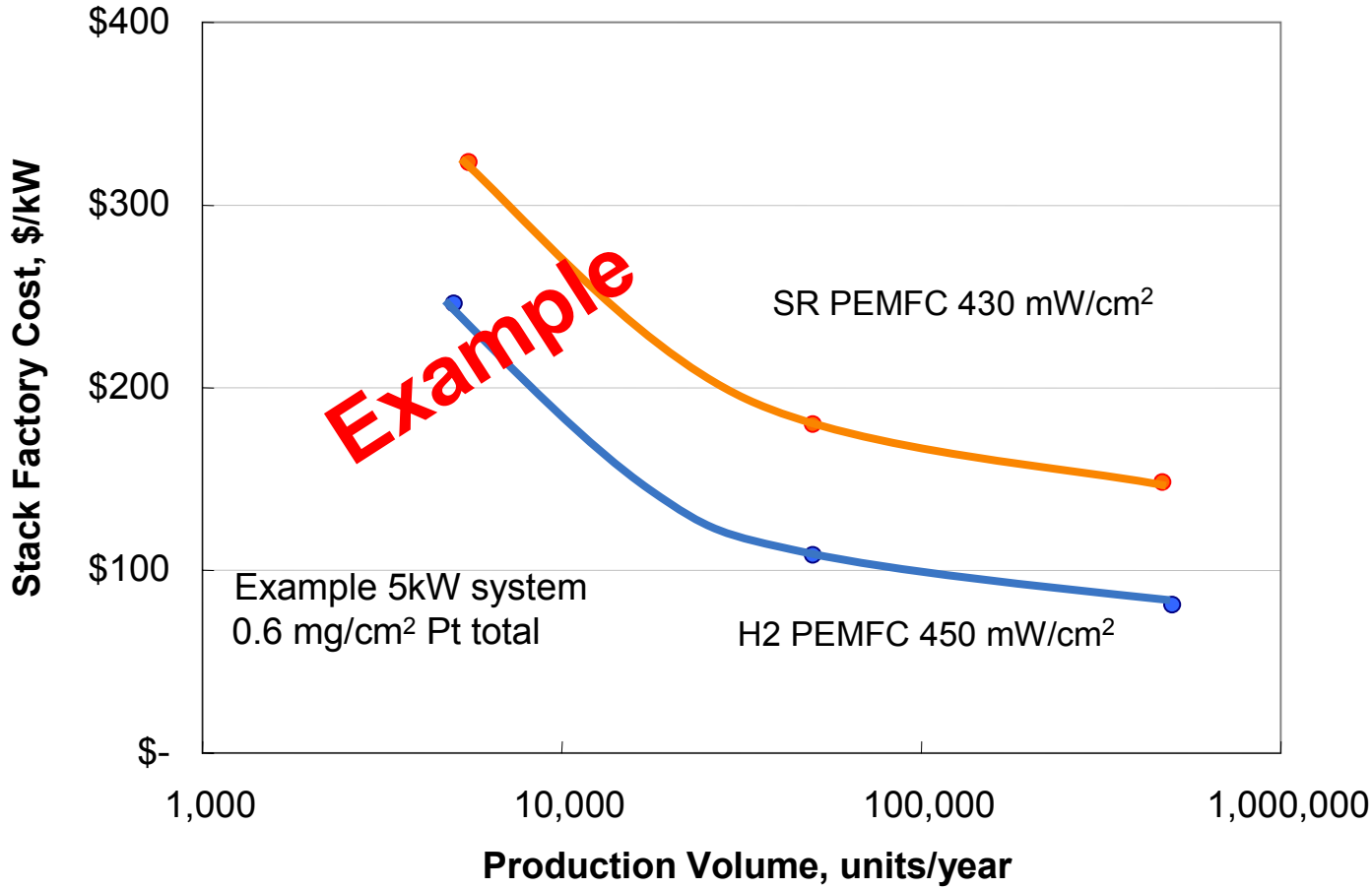
Power Demand and Fuel Cell Operating Strategies



Matching Building loads:

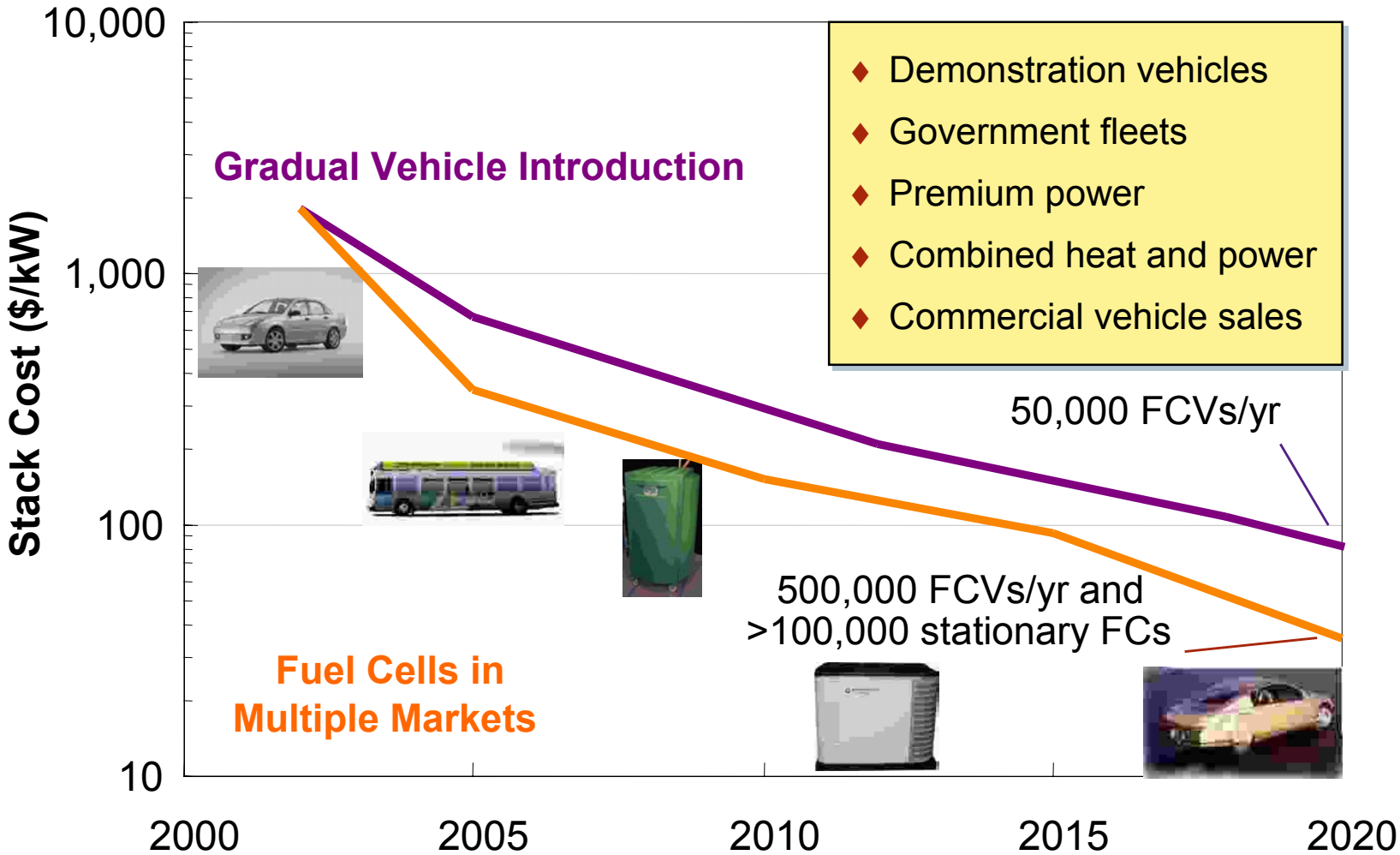
- Peak shaving: operating the fuel cell to reduce peak load on utility service
- Average load: operate the reformer and fuel cell continuously to provide power to building
- Emergency backup: operate fuel cell on stored hydrogen and/or reformer during power emergencies

In addition to technical performance parameters, the cost of components depends on production volumes.

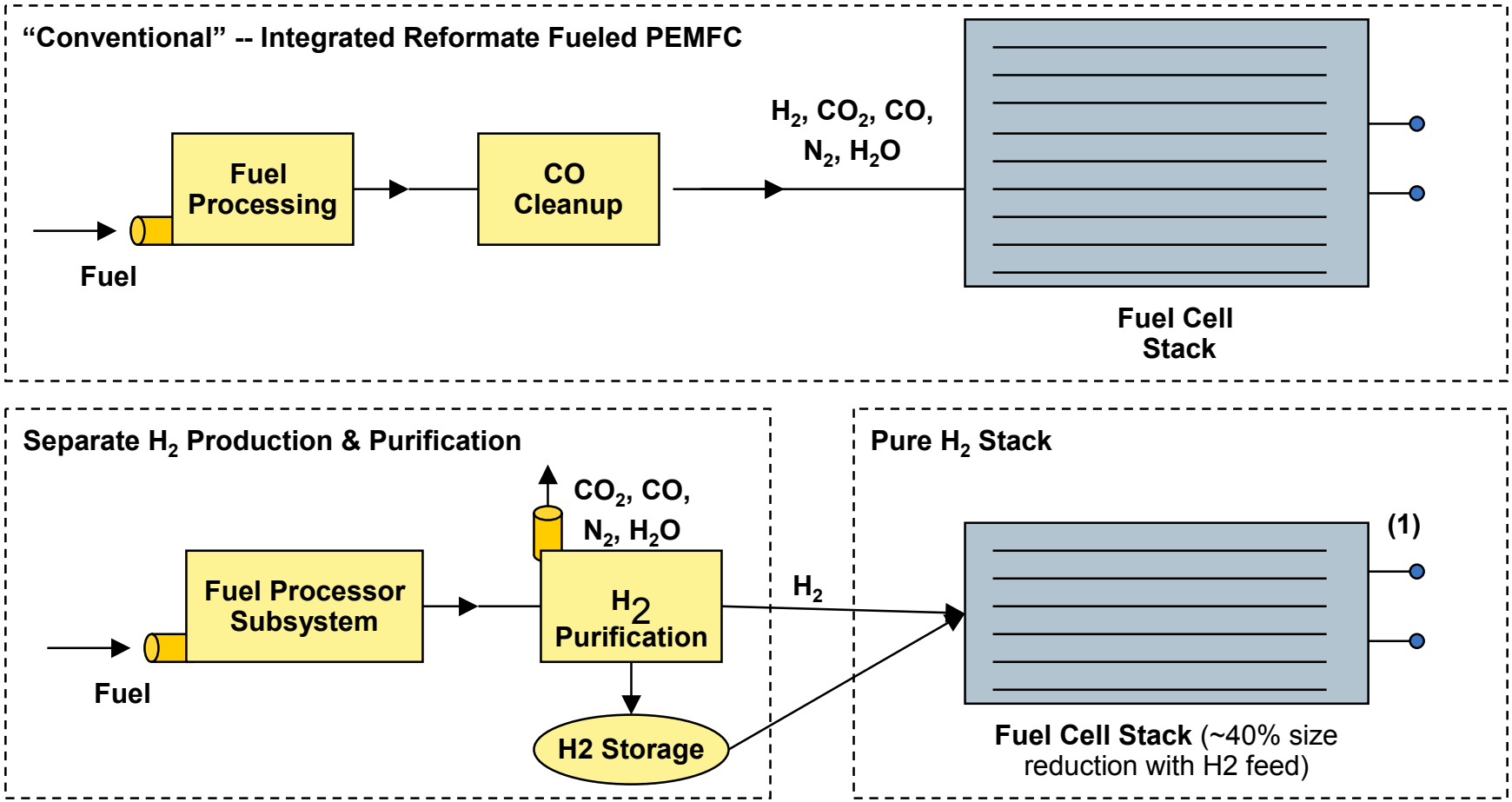


PEMFC stack components will be used in both vehicle and stationary applications while markets for steam reformers will be more limited.

The commercial success of any FCV, regardless of fuel, is tied to the cost of the fuel cell engine. Other fuel cell markets can help bring down costs.

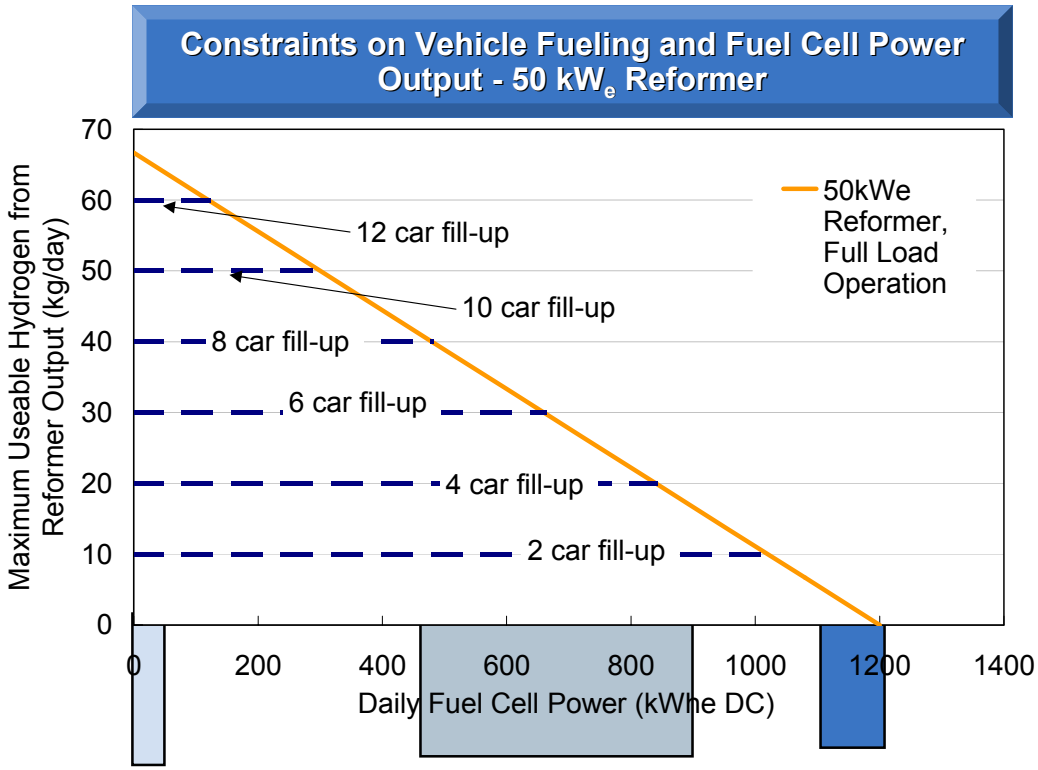


There are two basic fuel cell architectures with multiple variations thereof



This system strategy allows use of PEMFC stack technology that is likely to be available, and affordable due to early vehicle demos.

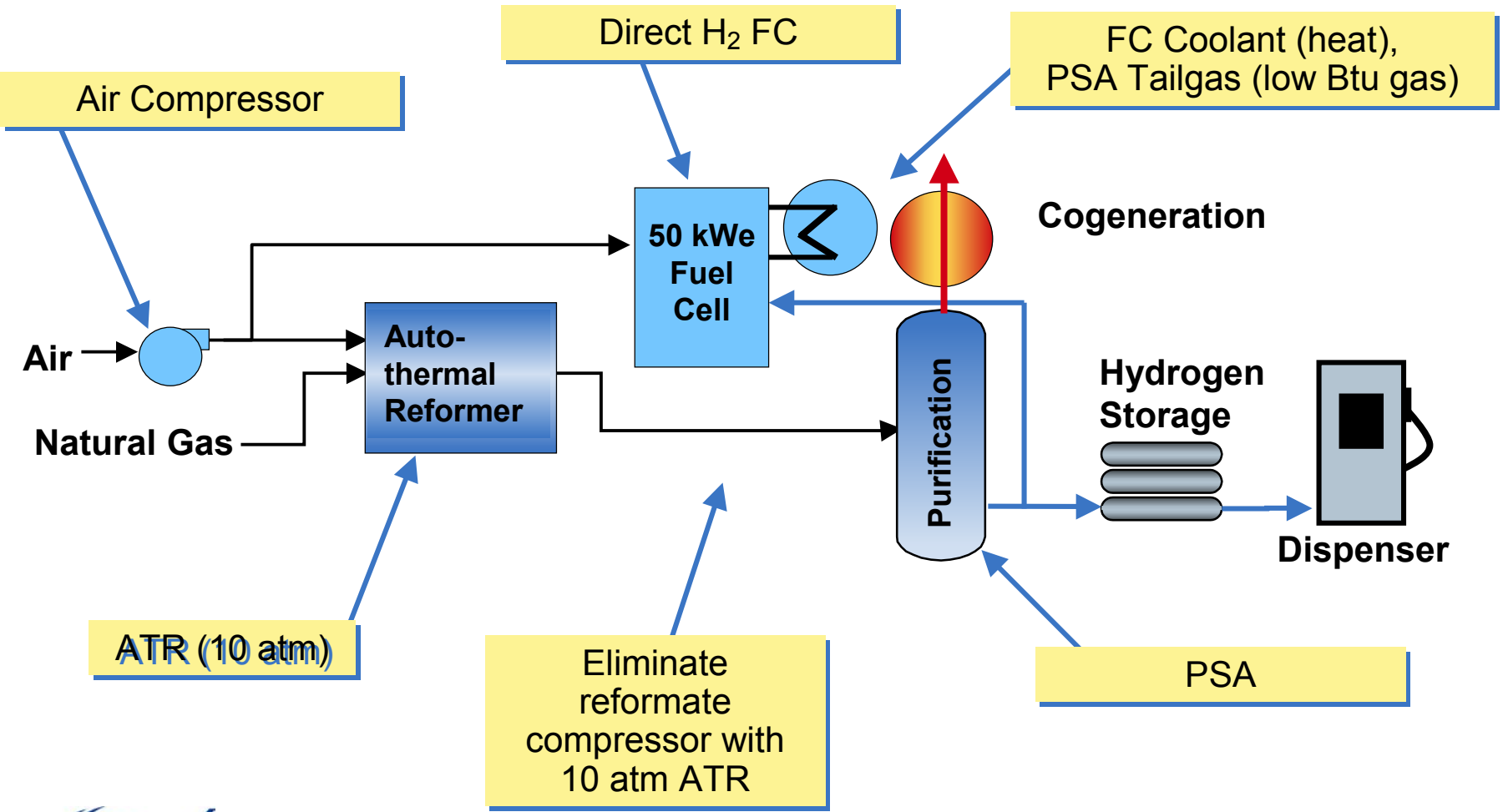
Several trade-off options available between generating FC electricity and providing sufficient hydrogen for vehicle fueling



Operating Strategies: Back up Peak Shaving Base Load

The reformer capacity, vehicle refuelings, and fuel cell can be matched for different operating strategies

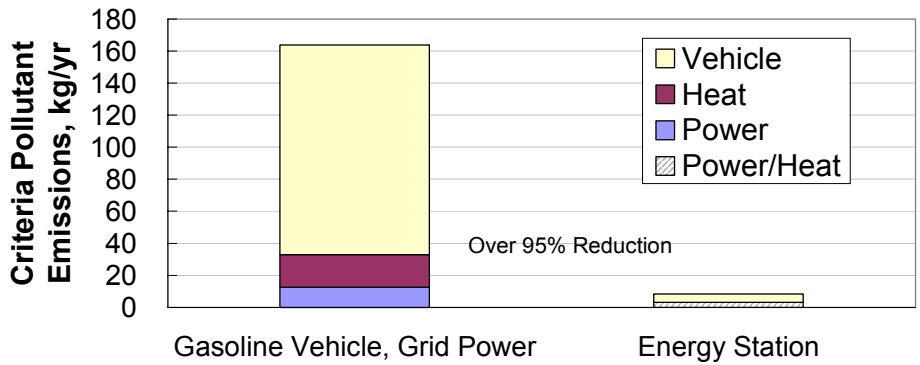
A simple cogeneration system uses the waste gas from an ATR to produce heat. Recovering the waste heat is simplified.



With an energy station, optimal use of natural resources could be combined with zero emissions and extremely high reliability.

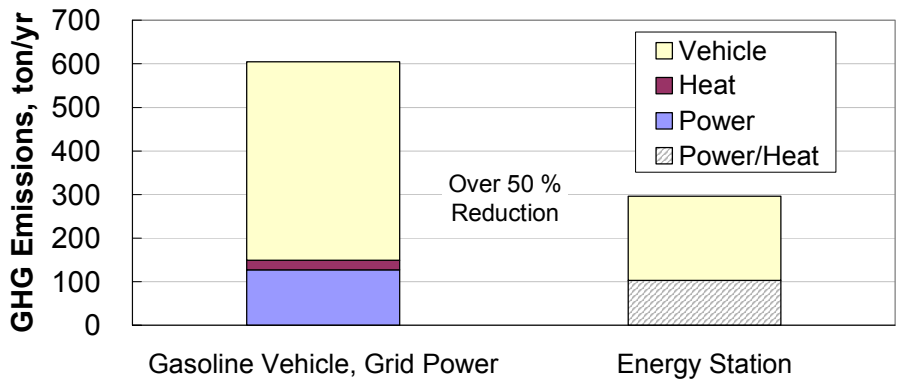
- Over 90% reduction of criteria pollutant emissions
- Enhances grid reliability through energy storage and fuel cells with few moving parts
- Reduced greenhouse gas emissions
- Managed technical risk through use of hydrogen fuel cells rather than conventional stationary fuel cell systems
- Facilitates implementation of fueling infrastructure
- Lower cost through shared components for vehicle fueling and stationary fuel cell power

Annual Criteria Pollutant Emissions



Note: criteria pollutants include NO_x, CO, and hydrocarbons

Annual Greenhouse Gas Emissions



Future energy stations need to evolve along with the vehicles.

Future Work	Challenges
Compare cost and performance to baseline technologies	• Cost depends on vehicle and stationary FC production volume
Develop a design concept for larger scale production	• Much smaller packaging would facilitate acceptance in more locations • Required stand off distances for hydrogen storage can be over 50 ft
Identify partners for commercialization	• Need to obtain better perspective of benefits to federal fleets
Evaluate barriers to hydrogen utilization	• Strained economy limits new ventures • Code requirements are evolving • Deployment of hydrogen FCVs from manufacturers presents a chicken/egg problem to potential energy station users

A number of stakeholders are being contacted to determine their requirements and interest in energy stations.

Stakeholders	Outreach Efforts	Comments
◆ Automakers ◆ Fuel cell manufacturer ◆ Electric utilities ◆ Government hospitals ◆ Military bases ◆ Government fleets ◆ EPACT fleets	◆ Attend Fuel Cell Seminar Nov '02 ◆ Made presentations on environmental impacts to CA Air Resources Board, South Coast AQMD, Blue Water Network, and others ◆ Submitted Paper to Dec '03 Fuel Cell Seminar	"This (energy station) is the only way fuel cell infrastructure will ever work" "Aren't SOFCs more efficient for stationary applications?" "We have to deal with Rule 21, for grid interconnection." "With the downturn in the economy we have to focus on our core activities." "If we could get a fuel cell car, this (energy station) would be a good idea."

Evaluation of Protected Metal Hydride Slurries in a H_2 Mini-Grid

Hydrogen Technical Analysis Phase II Work in Progress

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley CA

May 19-22, 2003

TIAX, LLC
Acorn Park
Cambridge, Massachusetts
02140-2390

TIAX Ref: D0021
DOE Ref: DE-FC36-00GO10604

The hydrogen "Energy Station" concept has been proposed by DOE and others to facilitate the development of a hydrogen fuel infrastructure.

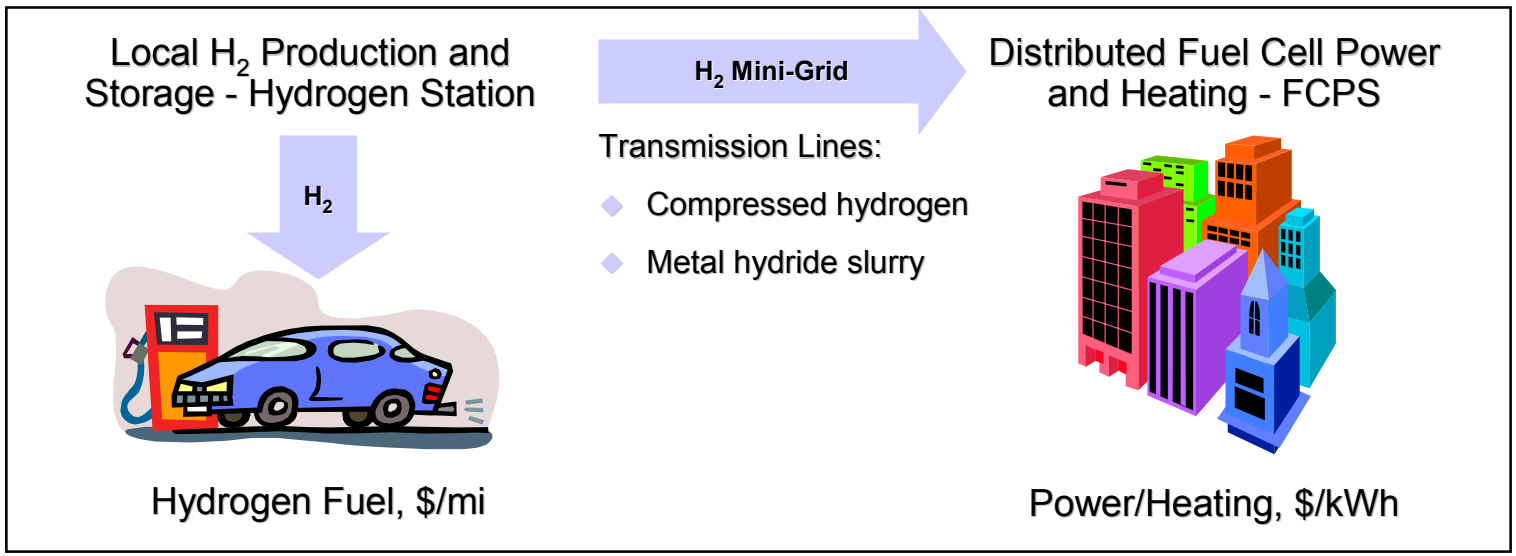
- Hydrogen is produced for stationary PEM fuel cell power systems (FCPS) and for fueling fuel cell vehicles (FCVs) at a hydrogen station
- Provides economies-of-scale and high utilization for hydrogen (H_2) production and storage equipment
- Opportunity for early revenue by supplying reliable power
- Helps solve "chicken and egg" problem for FCV/H_2 infrastructure

In addition, the Energy Station concept improves the commercialization of FCPS by lowering technical/economic risk compared to reformate-FCPS.

- Reduces risk of stack impurities poisoning
- Improves stack anode utilization
- Improves efficiency and reduces technical risk and cost of H_2 production
  - A single, larger reformer can operate base-loaded with H_2 storage
- Central hydrogen storage replaces need for battery
- Synergies with transportation developments

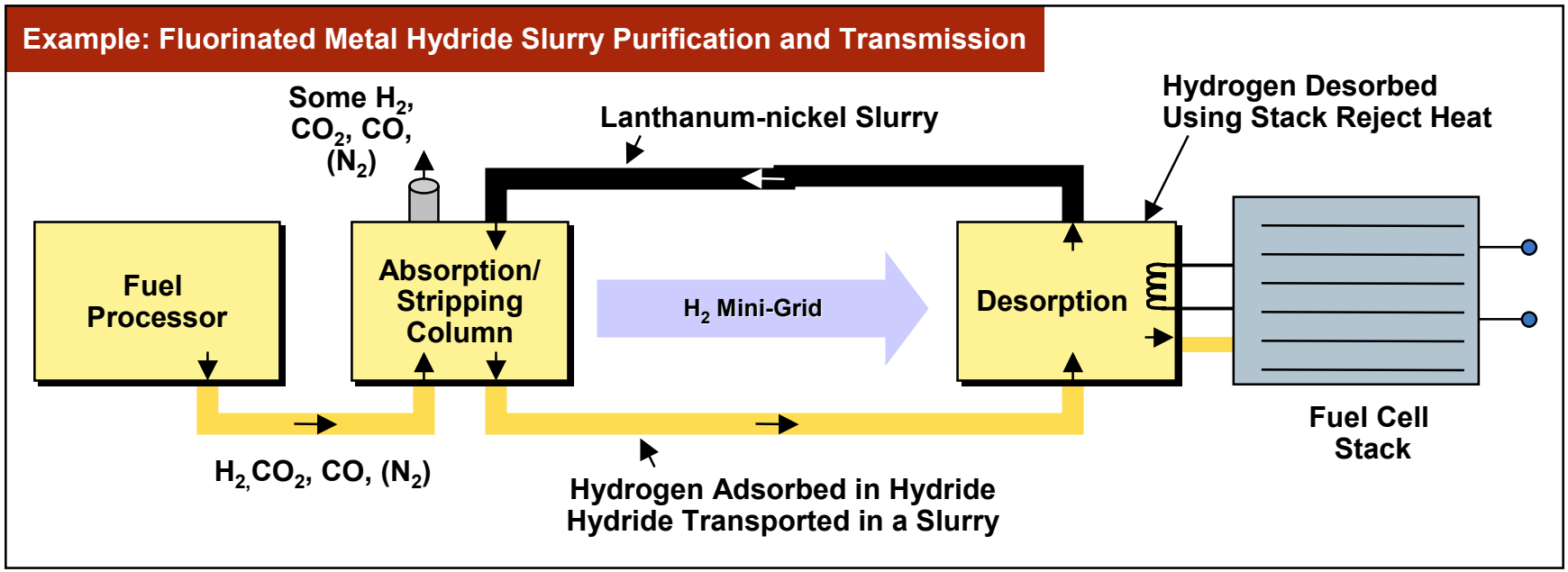
Distributed FCPS utilizing a H_2 Mini-Grid can provide all the benefits of a Hydrogen Energy Station and also provide cogen to buildings.

- Reduced technical risk and cost compared to distributed reformate-FCPS (see Energy Station Concept discussion)
- Fuel cell waste heat can be used for hot water or space heating in buildings (i.e. “cogen”)
- Distributed FCPS utilizing a H_2 Mini-Grid are quiet and emissions free



However, the perceived safety of hydrogen transmission is a major barrier to it’s implementation, especially in commercial/residential areas.

Metal hydride (MH) slurries are safer and are potentially more efficient and cheaper than compressed gas hydrogen (cH_2) transmission in pipelines.



Potential Advantages:

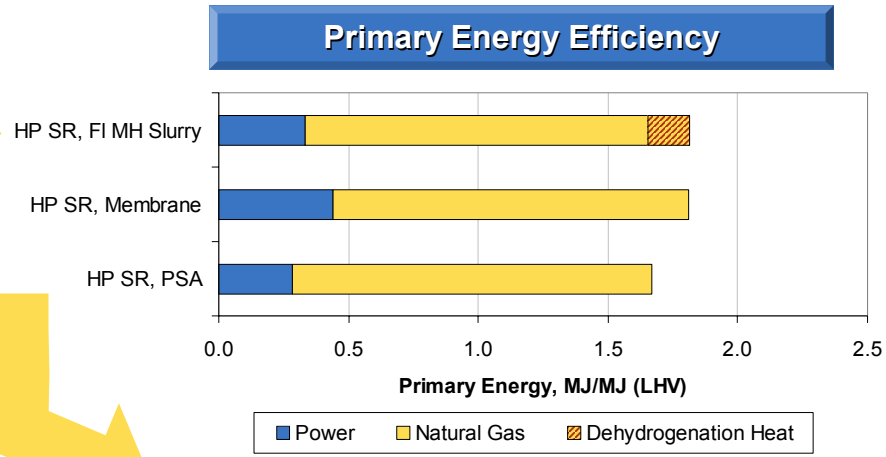
- Safer than cH_2 storage/transmission - reduced permitting and right-of-way costs
- Excellent efficiency if dehydrogenation heat can be supplied by waste heat (e.g. fuel cell)
- Requires less space than low pressure cH_2 storage/transmission
- Convenient method of combined purification, storage, and transmission
- Protected (i.e. fluorinated) MH slurries can purify reformate streams at low cost

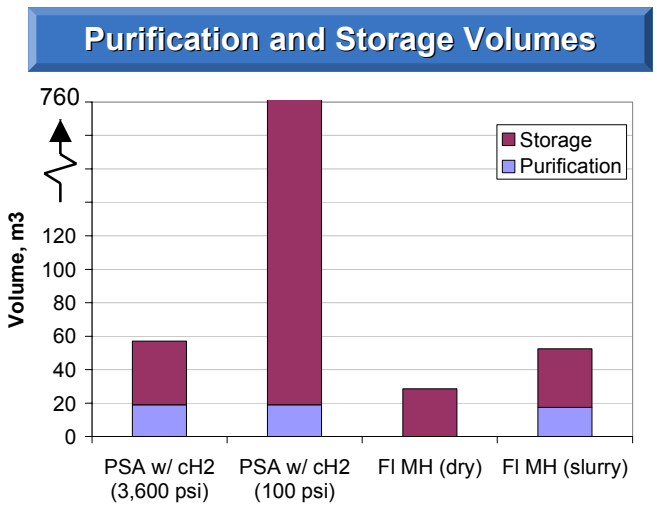
In Phase I, we identified fluorinated metal hydride (Fl MH) slurries as having potential to provide benefits as a purification and storage media.

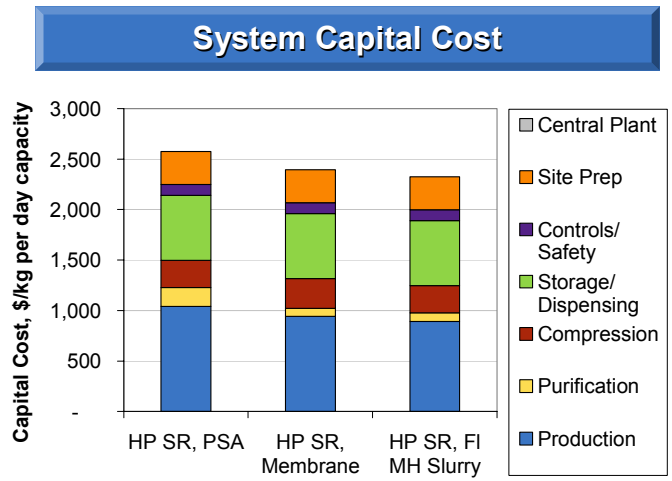
Compact Size

Excellent Efficiency

Low Capital Cost







Legend: HP SR = high pressure (10 atm) steam reformer, Membrane = Zr-Ni metal membrane, PSA = pressure swing adsorption, LHV = lower heating value

Before FI MH can be used for H_2 purification, further development will be required to prove its feasibility and optimize its implementation.

- Current MH have low tolerance to impurities typically found in reformate streams, especially oxygen and carbon monoxide
- Fluorinated (or in some other way protected) metal hydrides should be able to demonstrate high tolerance to impurities
  - Researchers in Japan have shown a fluorinated surface layer will protect the MH from multiple impurities

Compound	Impurity Threshold, vol		Comment	Reference
	Fluorinated	Untreated		
Carbon Monoxide	<100 ppm	<10 ppm		Japan Metals and Chemicals
	<3000 ppm		Was shown by applying a particular fluorination method	Kogakuin University[1]
Carbon Dioxide	< 20%	<100 ppm		Kogakuin University[1] and Japan Metals and Chemicals
Oxygen	< 20%	<10 ppm	During MH storage: no surface oxidation was found after 15 day exposure to air	X.-L. Wang, S. Suda[2]

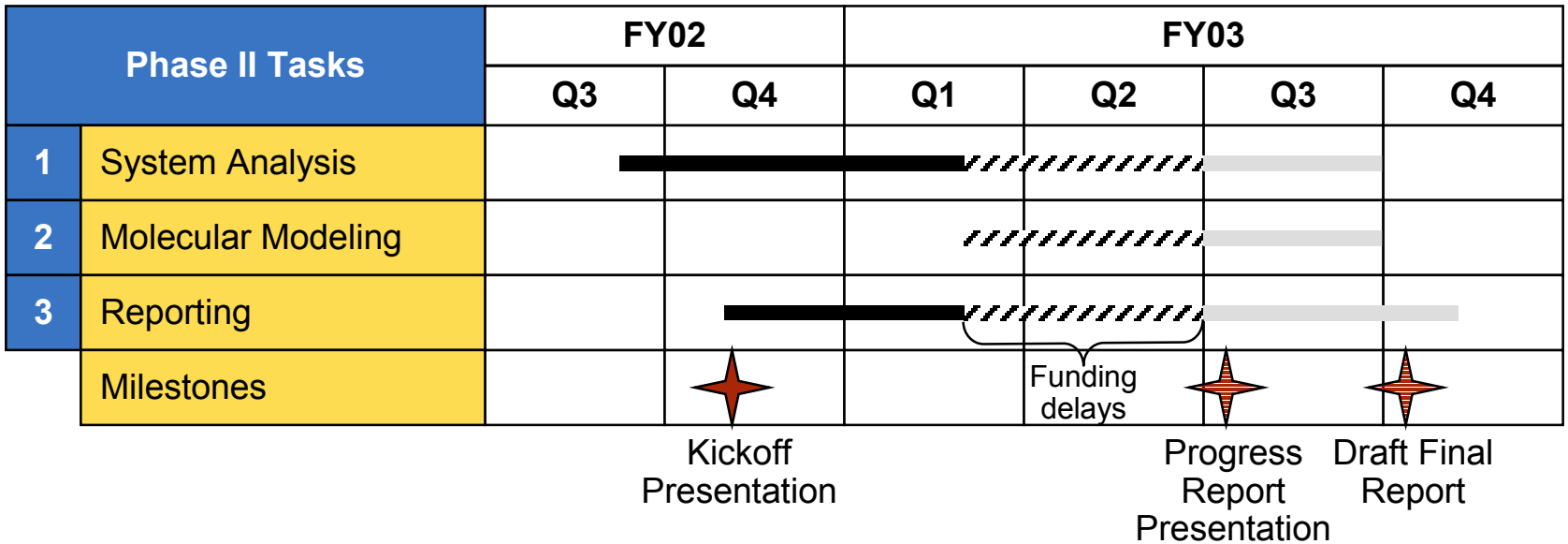
[1] Personal communication with Pr. S. Suda of Kogakuin University

[2] Stability and Tolerance to Impurities of the Fluorinated Surface go Hydrogen-Absorbing Alloys, Journal of Alloys and Compounds 227 (1995) 58-62.

The purpose of Phase II is to evaluate the feasibility of using FI MH slurries for purification and transmission in a H_2 Mini-Grid concept.

- Assess the viability of using fluorinated (or otherwise treated) metal hydrides for the purification of carbon monoxide-containing hydrogen streams
  - Using computational modeling to help fully characterize the limitations of fluorination and identify alternative technologies
- Assess the attractiveness and viability of using fluorinated metal hydride slurries in a hydrogen distribution system (H_2 Mini-Grid)
  - Including both vehicle refueling stations and building combined heat and power systems
- Establish research and development (R&D) objectives for the development of hydrogen distribution systems using fluorinated metal hydrides
  - Identify key barriers and possible development paths
  - Contingent on a positive outcome from above

We will accomplish this project's objectives in two key tasks: (1) analysis of FI MH slurries in a H_2 Mini-Grid and (2) molecular modeling of FI MHs.



- The work to date has been slowed due to funding delays, but we are on schedule to finish by the end of this fiscal year
- We are less than 40% through the total budget

In Task 1, we will analyze the potential cost and performance of H_2 Mini-Grid concepts for integrated fueling and power systems.

Subtasks to Task 1: System Analysis
Subtask 1: Evaluate metal hydride slurry purification, storage and dispensing apparatus for Integrated Systems (fueling and power)
Subtask 2: Develop hydrogen fueling system designs
Subtask 3: Develop fuel cell power system designs
Subtask 4: Determine cost of electricity (COE), hydrogen costs, energy use, and GHG* and other emissions for H_2 Mini-Grid concepts and stand-alone systems
Subtask 5: Reporting

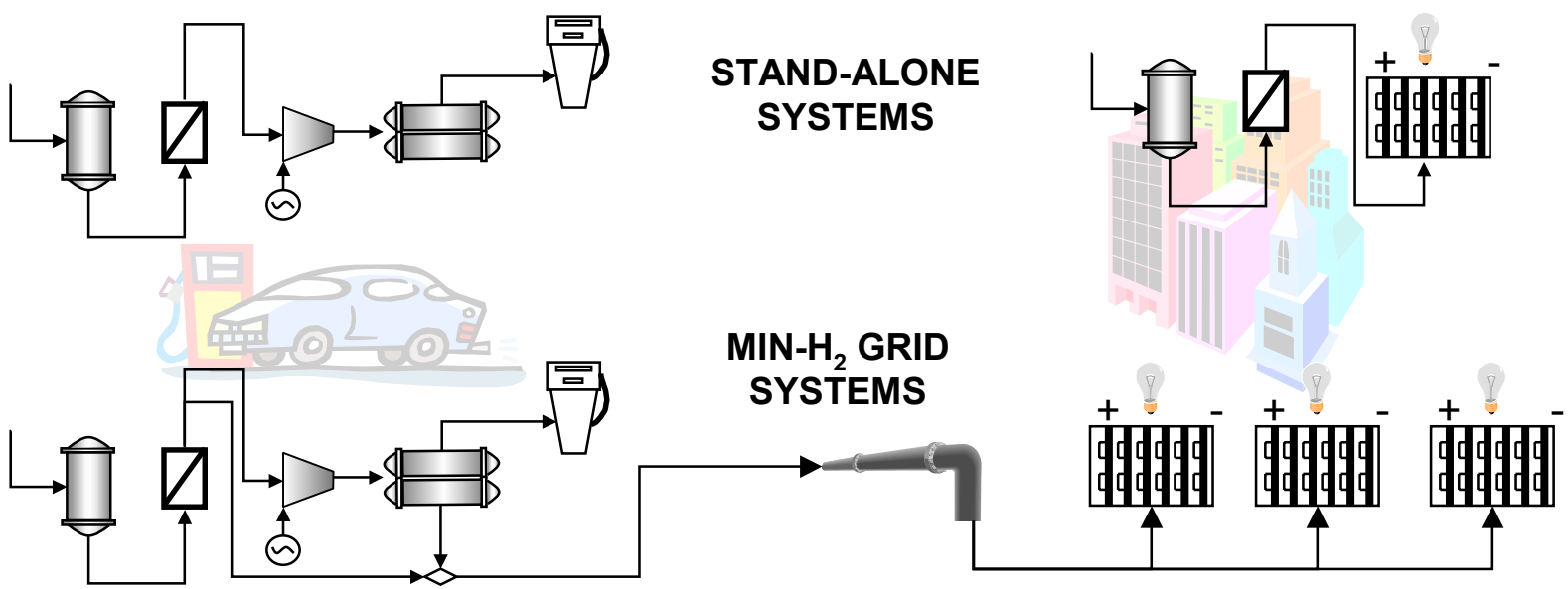
* GHG = green house gases (CO_2, CH_4, etc.)

We will investigate local hydrogen production for fueling direct-H_2 FCVs and distributed FCPS.

- <1,000 kg/day H_2 fueling capacity for compressed gas hydrogen (cH_2) FCVs
  - On-site hydrogen production via 10 atm steam reformer
    - Highest overall efficiency of the four reformer types investigated in Phase I
    - Renewables-based production is also a promising application for the H_2 Mini-Grid
  - On-site hydrogen storage via compressed gas or MH slurry
- <100 kWe PEM FCPS serving commercial and residential buildings
  - Various building load profiles - heat and power demands
  - Power and co-gen heating (conventional and high temperature PEM)
  - Grid connected for high utilization (note: load-following is possible for direct-H_2 FCPS)
  - Base-loaded during peak hours - reduces demand charges
  - Turned off when power demand drops below FCPS design power - simplest, doesn't cut into utilities' base-load and compete with cheap off-peak grid power
  - Hydrogen storage at fueling station also acts as a reliability enhancer for the FCPS

We will evaluate a number of H_2 Mini-Grid configurations and compare them to stand-alone FCPS.

- PSA with high pressure cH_2 storage and low pressure cH_2 transmission
- FI MH slurry purification and transmission and high pressure cH_2 storage
- FI MH slurry purification, transmission, and storage
- Stand-alone: (1) Reformate-FCPS and (2) distributed reformate production with FI MH slurry purification/storage



In Task 2, we will perform a molecular-level theoretical evaluation of the long-term feasibility of fluorinated metal hydride purification.

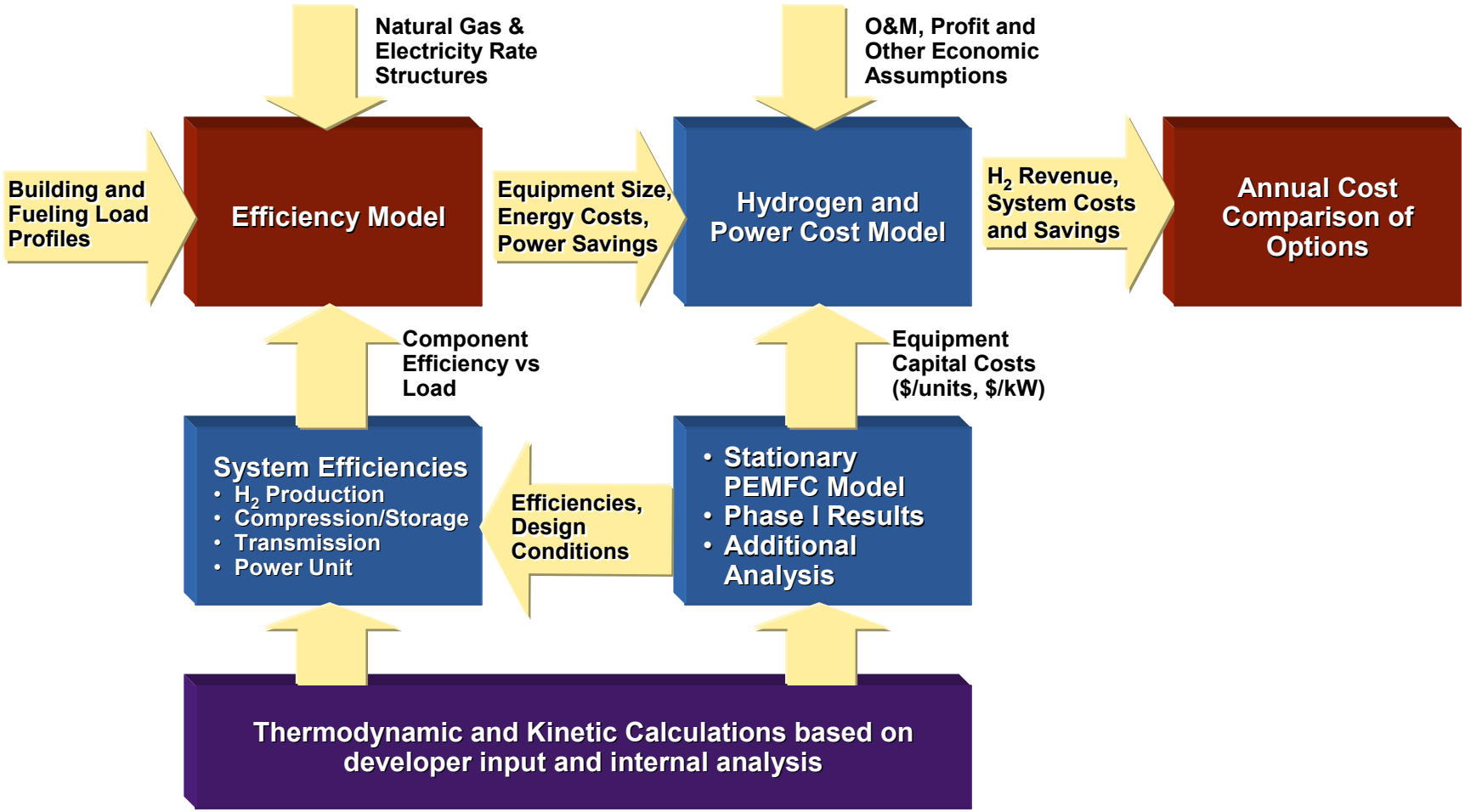
- Use first principles and quantum modeling to understand the underlying microscopic mechanism of a fluorinated metal alloy (e.g. La-Ni-Al)
- Test two main hypotheses:
  - Fluorination reduces the binding energy of undesired molecular species (e.g. O_2 and CO)
  - Diffusion barrier created by the fluorinated surface is much lower for hydrogen molecules than for undesired molecules
- Generate a general model for surface protection of metal hydrides
- Formulate general principles for protection techniques based on the general model
- Search for alternative protection methods or compounds that are even more effective in a practical application

We originally proposed to perform experimental tests to determine FI MH properties and performance, but this contract did not support lab-based R&D.

To date, we have constructed efficiency and cost models for the overall analysis and are in the process of refining the model inputs.

- An efficiency model has been developed
  - Inputs: building hourly electric and heat load profiles for the entire year, thermodynamic model results (e.g. efficiencies, cogen potential) for the FCPS and H_2 station
  - Outputs: grid power, natural gas, and FCPS hydrogen demands; GHG and other emissions
- Detailed cost calculations are being determined
  - Inputs: efficiency model results, capital cost inputs, utility rates for grid power and natural gas
  - Outputs: annual costs (electric energy and demand, natural gas, and capital cost charges)
- Preliminary design of a cH_2 Mini-Grid has been determined
  - Based on a combination of current natural gas and hydrogen distribution practices

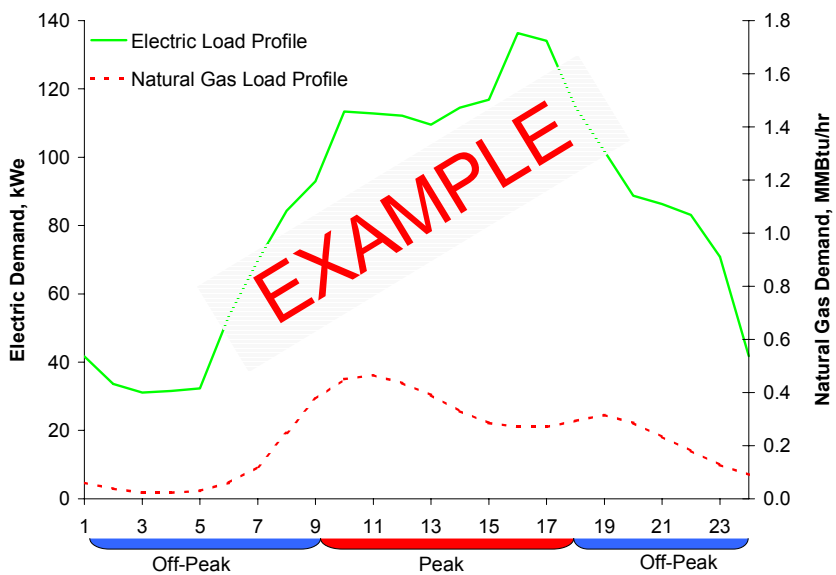
Efficiency and cost models are the backbone of the analysis to determine overall annual system costs and savings.



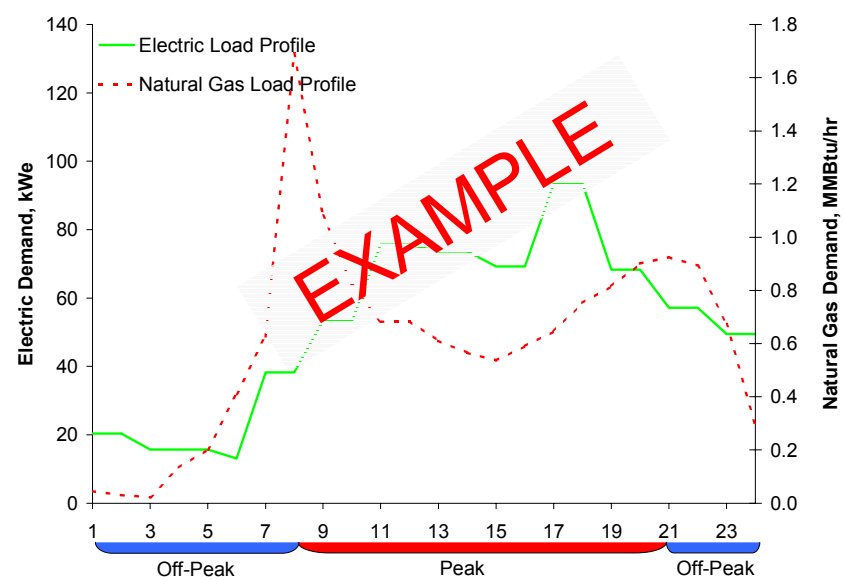
Hourly electric and heat load profiles for residential and commercial buildings have been generated for a typical meteorological year (TMY).

- Using EnergyPlus software
- Load profiles are used in the efficiency model to calculate:
  - FCPS operating times (turns on when the building demand exceeds design power)
  - Grid and FCPS monthly energy and peak power demands from the building
  - Cogen use (only when fuel cell is on and building heat is needed)

July 1 Profile for Multi-family residence in NYC



Jan 1 Profile for Multi-family residence in NYC



We constructed thermodynamic models to evaluate system parameters that can effect system efficiency and FCPS cogen capabilities.

- Using HYSYS process modeling software
- Thermodynamic results are used in the efficiency model to calculate:
  - Hydrogen (or natural gas) demand and cogen potential from the FCPS
  - Natural gas and power demand from the hydrogen station
- Models for both the FCPS and hydrogen station have been developed

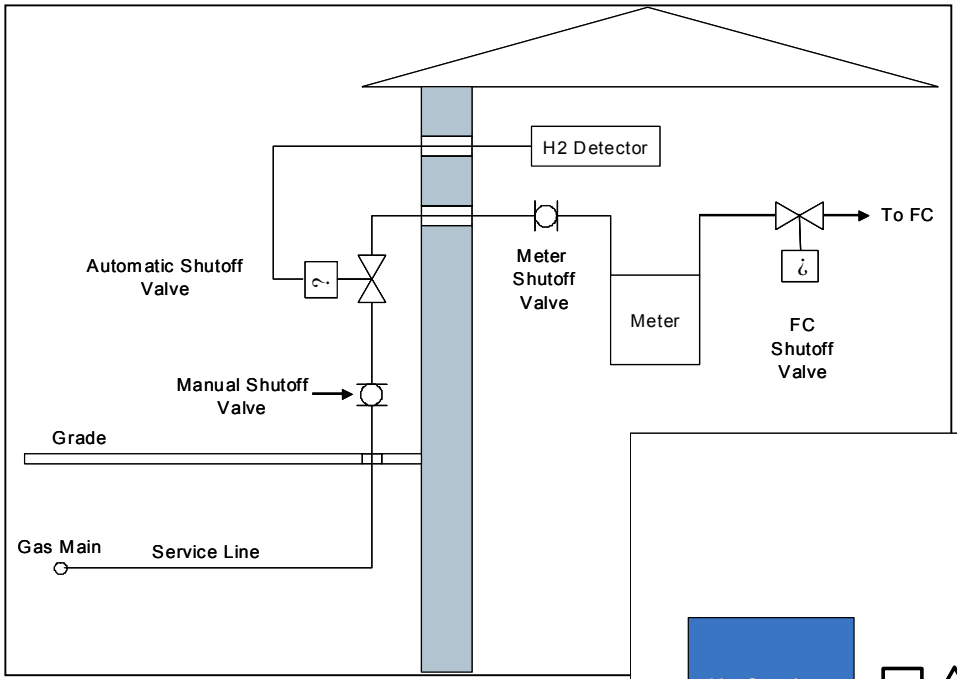
FCPS Parameters	Base Case	Low Temp.	Low Voltage	Low H_2 Util.	High Press.
Temperature, °C	80	70	80	80	80
Design Voltage, V	0.70	0.70	0.63	0.70	0.70
Hydrogen Utilization, %	95	95	95	88	95
Pressure, atm	1.2	1.2	1.2	1.2	1.5
Preliminary Results					
Cogen Capability[1], kWth/kWe	0.68	0.81	0.87	0.87	0.87
System Efficiency[2], % (LHV)	49	49	44	45	48

EXAMPLE

[1] Cogen is reduced by humidification requirements.

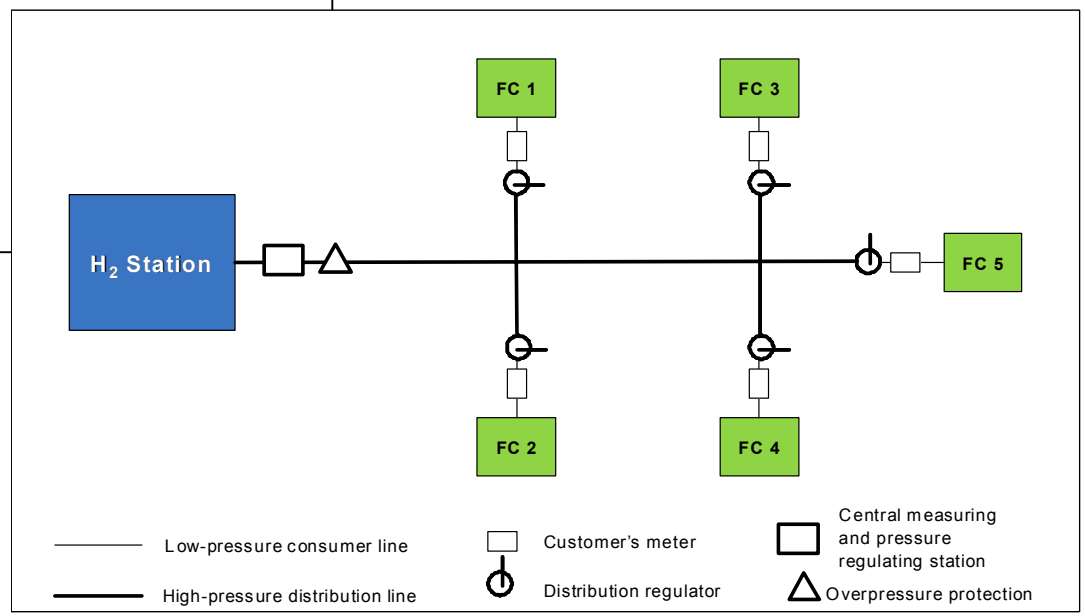
[2] Includes 95% power electronics (i.e. inverter) efficiency, 95% hydrogen utilization, and parasitic loads.

U.S. Gas Pipeline Code, NFPA, and industry experts were consulted for the design of hydrogen gas delivery systems to consumer sites.



Codes and standards incorporated in conceptual design

ASME B31.3	Pipeline design code
CGA G-5.4	H2 piping systems at consumer locations
OSHA 29 CFR 1910.103	H2
NFPA 50A	CGH2 at consumer sites
NFPA 54	Fuel gas piping systems, accessories
CSA B51	Canadian code for pressure piping containing H2
DOT RSPA 49 CFR 192	Valve spacing on gas pipelines

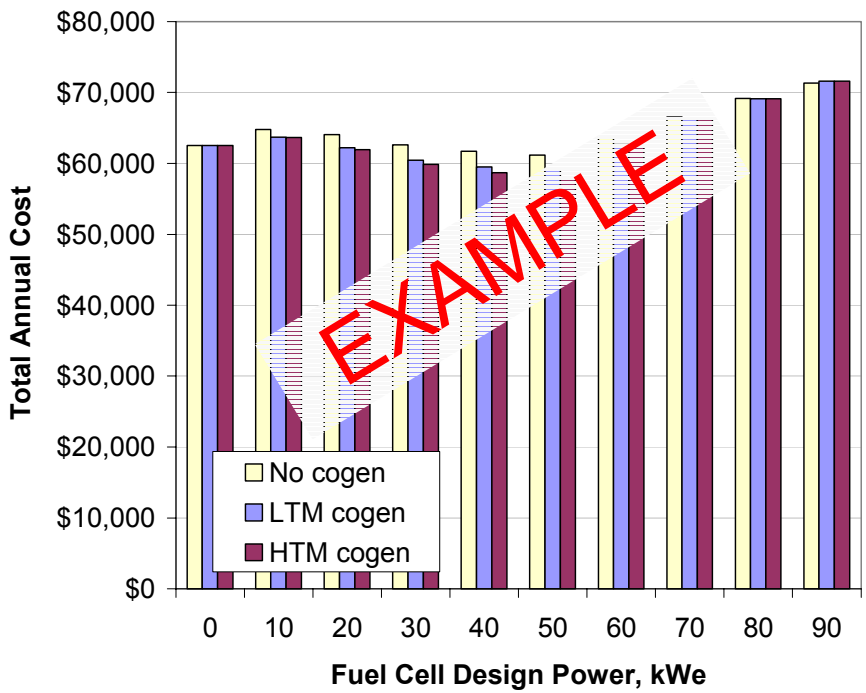


Annual costs will be determined once capital costs have been estimated (work in progress).

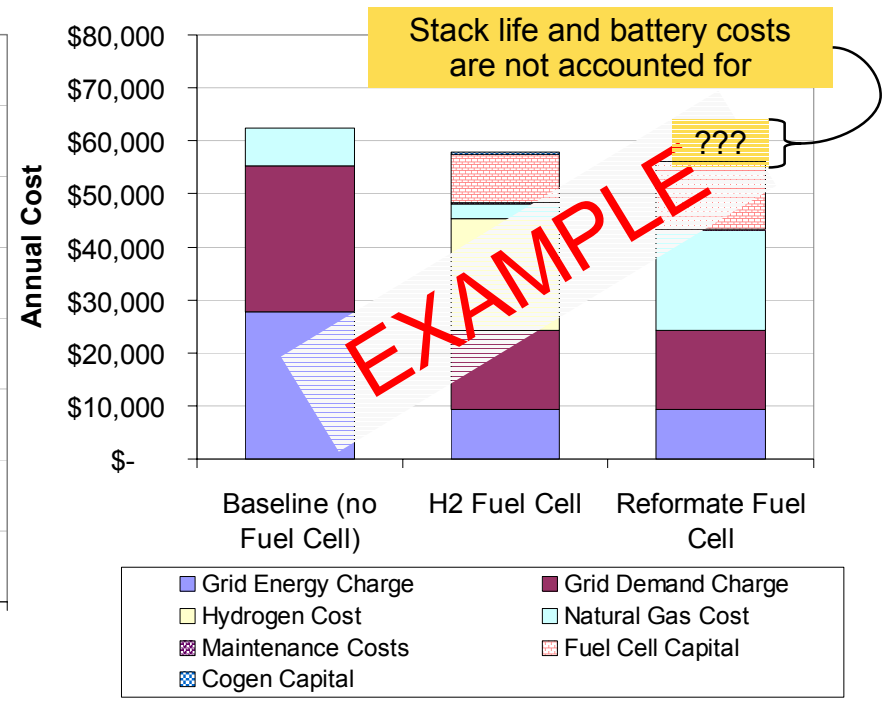
- Capital costs for the hydrogen station (production, compression, and storage equipment)
  - We are updating capital costs, scaling factors, and progress ratios
  - Based on detailed vendor quotes and internal analyses from Phase I
    - Phase I analysis assumed 100s units per year production volumes
- Hydrogen transmission cost
  - System designs have been conceptualized
  - We are estimating capital costs based on vendor quotes and additional cost assessments
  - “Right-of-way” costs dominate in most cases
- Capital costs for distributed FCPS
  - We are constructing a cost model that will automatically scale costs according to the user supplied production volume and rated power assumptions
  - Based on previous stationary PEMFC cost model

For this presentation, examples of annual costs have been generated based on assumptions for hydrogen and capital costs.

Direct-H_2 FCPS Ownership Cost



FCPS Ownership Cost Comparison



Key Assumptions:
50 kW FCPS with high temperature membrane (HTM); capital costs = $916/kW Direct H_2 and $1,253/kW Reformate-FCPS; H_2 = $1.00/kg

Using the cost model, design power and various other model inputs can be optimized to reduce total annual cost or GHG emissions.

At the end of Task 1, we will be able to assess the attractiveness and viability of using fluorinated metal hydride slurries in a H_2 Mini-Grid.

- Investigate performance of MH slurries and H_2 Mini-Grid systems:
  - Cost: hydrogen, power/heating, annual
  - Environment: energy use, GHG and other emissions
  - Other benefits: technical risk, reliability enhancement, and others
- Comparison to baseline and other systems:
  - Integrated hydrogen station concept Vs. stand-alone hydrogen station
  - MH slurry Vs. cH_2 transmission
  - FCPS (with and without cogen) Vs. conventional grid power and natural gas heating
  - FCPS utilizing a H_2 Mini-Grid Vs. stand-alone FCPS (hydrogen and reformate-based)

At the end of Task 2, we will be able to assess the long-term viability of using fluorinated (or otherwise treated) MHs for hydrogen purification.

- Establish selectivity of CO/H_2 separation based on energy surface calculation for transport through the layer
- Determine viability of fluorinated hydrides
- Develop and test hypothesis for optimization of barrier layer
- Establish R&D objectives for MH slurries based on Task 1 and 2 results
  - Identify key barriers and possible development paths
  - Contingent on a positive outcome from above

AIR PRODUCTS

Validation of an Integrated System for a Hydrogen-Fueled Power Park

Merit Review and Peer Evaluation
May 19, 2003
Berkeley, Ca

Phase I Program Goals

Central Question:

Is it Economically Feasible ($0.10/kWh) to Produce Power with a PEM Fuel Cell From Natural Gas?

Investigate:

- Natural Gas and PEM Fuel Cells
- Combined Heat and Power
- Distribute Electrons or Protons?
- Residential (multiple dwellings), Commercial, and Light Industrial (50 kW- 250 kW)

AIR PRODUCTS

Tools and Techniques

- ASPEN PLUS process simulation
  - Efficiency
  - Waste heat availability
- Develop cost of operation models
  - Capital
  - Fuel costs
  - Installation
  - Operation
  - Maintenance
- Operating mode study (load-following or baseload)
- Today's costs
- Gap analysis

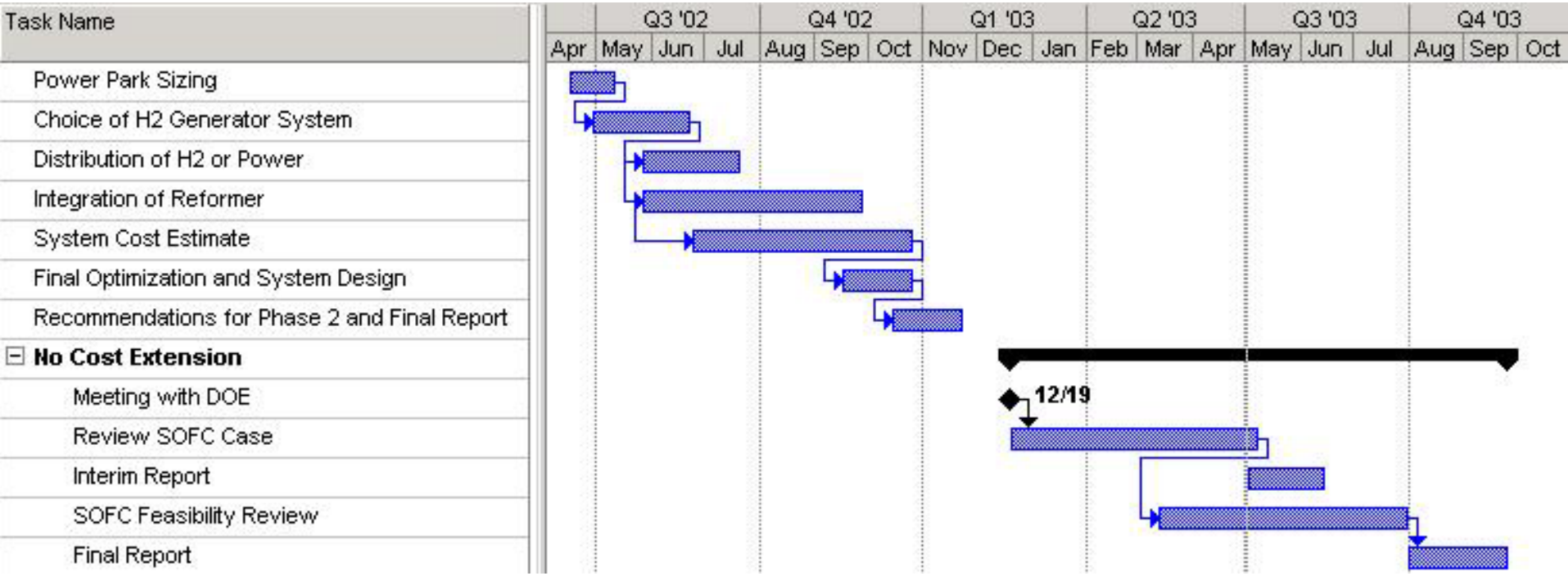
AIR PRODUCTS

Base System

- 50-200 kW reformer system
  - 100 kW system chosen for base case
  - Steam Methane Reforming
  - Pressure swing adsorption
  - PEM fuel cells
- 3 buildings located 200 yards each from the central reformer with equal loads
- All waste heat can be utilized
- 3-5 kW commercially available PEM fuel cells (linearly scaled to system size)
- Penn State campus assumed for construction estimates

AIR PRODUCTS

Timeline


Task Name
Q3 '02
Q4 '02
Q1 '03
Q2 '03
Q3 '03
Q4 '03
Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct
Power Park Sizing
Choice of H2 Generator System
Distribution of H2 or Power
Integration of Reformer
System Cost Estimate
Final Optimization and System Design
Recommendations for Phase 2 and Final Report
No Cost Extension
Meeting with DOE
Review SOFC Case
Interim Report
SOFC Feasibility Review
Final Report
12/19

Summary of Phase I

- **Findings**
  - **Natural Gas to Electricity using Distributed Reformer and PEM**
    - SMR with PSA Purification
      - Most efficient, 25-33% Overall Efficiency
      - Lower impurities, protect highest cost component
    - Cost is $0.45/kWh (Today) and $0.14/kWh (Future) – 10 year term
  - **Distribute Protons or Electrons?**
    - Electrons Lowest Cost – run electric wires vs. hydrogen pipe
    - Electrons ($50K), Protons ($100k)
  - **Combined Heat and Power Has the Potential to Lower Power Cost by ~$0.01/kWh**
    - CHP Requires Reformer and Fuel Cell Close to Heating Load
    - Large Local Reformer with Local PEM is The Most Viable Case (>250kW)
- **Conclusions**
  - **Small Reformer/PEM System has Low Potential for Distributed Power Generation with Natural Gas Feedstock**
  - **Potential Uses of PEM in Distributed Power Applications**
    - **Hydrogen Pipeline or Low Cost Hydrogen Offgas**
    - **Hybrid Energy Station**
      - Higher Efficiency & Capital Utilization
      - Potential For Cost Competitive Power Generation and Fueling
      - Peak (Electrical Generation), Off-peak (Hydrogen Generation)

AIR PRODUCTS

Further findings

- Sizing
  - Ideal size would be greater than 800 kW
    - Obtain lower fuel costs (industrial rates)
    - Lower cost per kW for fuel cell and reformer (economies of scale)
- Amenable building types
  - Hospitals
  - Apartments
  - 24 hour store (Wal-Mart)
  - Prison
  - Dormitory
  - Warehouses with cooling requirements

AIR PRODUCTS

Natural Gas to Electricity Efficiencies

Subsystem	Today	Future	FC Company 1 1-250 kW	FC Company 2 1-250 kW	FC Company 3 1-250 kW
Reformer + Purification	75%	80%	75%	76%	75%
Balance of Plant	90%	90%	100%	100%	90%
Anode Eff	100%	100%	85%	78%	100%
PEM	52%	62%	52%	52%	53%
Electrical Conversion	90%	90%	81%	92%	85%
Total Efficiency	31.59%	40.18%	26.85%	28.36%	30.41%
Total Cost	$14,000/kW	$3,300/kW			

	NG Recip >200kW	Micro turbine 30-500kW	Stirling 30-60kW	Small Turbine >500kW	CCGT >20MW
Efficiency	38%	27%	30%	35%	40%
Cost	$1,000/kW	$3,000/kW	$3,000/kW	$1,200/kW	$850/kW

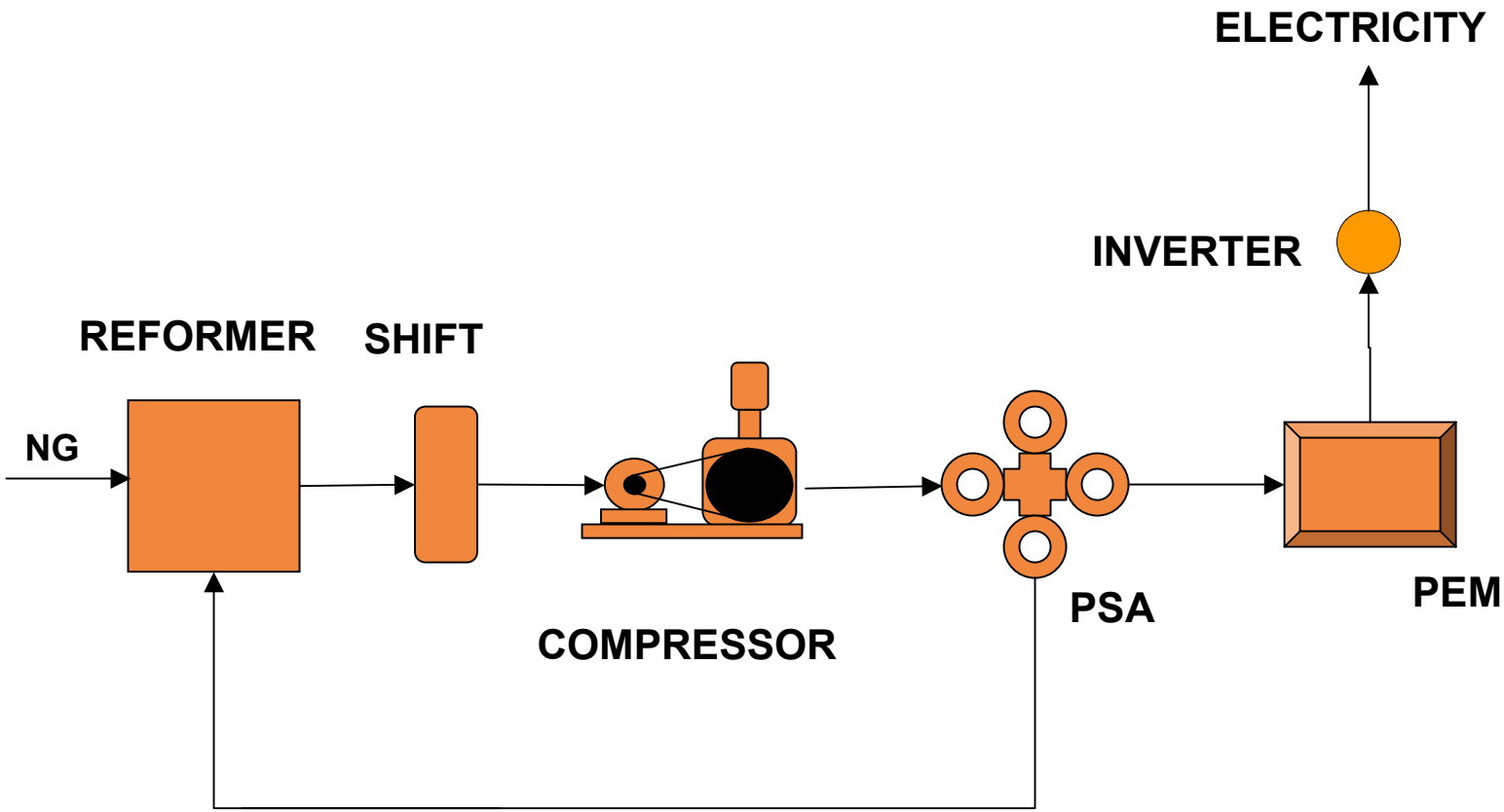
AIR PRODUCTS

Combined Heat and Power

- **CHP Requires Reformer and Fuel Cell Close to Heating Load**
  - Hot Water Distribution is Cost Prohibitive
  - Large Local Reformer with Local PEM is Most Viable Case
- **Integrated Heat Recovery (Minimal HVAC Tie-In Costs)**
  - Building HVAC System
    - Hot Water Boiler/Adsorptive Chiller System for HVAC
    - Constant Load - Year Round ~80% efficiency
  - Available Excess Heat is ~90% of the Electrical Output (kW)
  - 70% of Excess Heat can be Recovered
  - Savings Primarily from Fuel Reduction
- **Credit**
  - $0.013/kWh Commercial Utility Rates
  - $0.008/kWh Industrial Utility Rates

AIR PRODUCTS

Integrated System



Overall Efficiency (LHV): 25-33%

Efficiency = Electricity/Natural Gas (LHV)

Modeling Assumptions

- **Non-Load Following, Baseload System (95% Utilization)**
- **After Tax Return: 10% (DCF basis)**
- **Overhead: 20% of capital**
- **Insurance and Property Taxes: 2.5% of capital**
- **Taxes: 35% Federal, 3% State and Local**
- **Inflation: 2.5%**
- **Book and Economic Life: 10 Years**
- **Capital, Utilities, and Maintenance: per vendor quotation**
- **Utilities (10 year avg commercial rate - 2000 dollars)**
  - Natural Gas $5.65/MMBTU (HHV)
  - Electricity $0.0822/kWh

AIR PRODUCTS

Effect of Technology Advancement on Cost of Power

Cost of Power	Today $14,000/kW	Future* $3,300/kW
Capital Recovery	$0.349	$0.083
Ops and Maintenance	$0.008	$0.008
Fuel and Power	$0.093	$0.075
Total Cost	**$ 0.45**	**$ 0.17**

***10,000 units/year and 40%Efficiency**

AIR PRODUCTS

Similar Findings

- **DTI - Cost Analysis of Stationary Fuel Cell Systems Including Hydrogen Co-Generation-1999**
  - $0.44/kWh @ 36% efficiency@ 20% part load
  - $7,011/kW at 100 units production
  - $3,230/kW at 10,000 units production

- **Idatech – 2002 AICHE Spring Session**
  - >$0.36/kWh @ 30.4% efficiency
  - >$10,000/kW Cost

AIR PRODUCTS

Modeling Cost Sensitivities

Base Price $0.67/kWh

Variable	Basis	Sensitivities	Cost Adjustment	Future Cost
Natural Gas Price	$5.65/MMBTU	$3.37/MMBTU	-$0.032	$0.64
Life	5 Year	10 Year	-$0.221	$0.42
		15 Year	-$0.290	
Reformer Cost	$11,000/kW	$6,000/kW	-$0.124	
		$4000/kW	-$0.174	
		$2,800/kW	-$0.204	$0.22
Fuel Cell Cost	$3,000/kW	$1,000/kW	-$0.050	
		$500/kW	-$0.062	$0.16
		$200/kW	-$0.069	
		$50/kW	-$0.073	
Efficiency	33%	40%	-$0.021	$0.14

AIR PRODUCTS

What's Needed To Achieve The Goal of Competitive Power ($0.10/kWh)?

- **25% Increase in Overall Efficiency**

AND

- **4000% Increase in Fuel Cell Life**
  - 3,000 hr Guarantee Today
  - Fifteen Year Term

AND

- **500% Increase In Power Output**
  - Near Term 150kW
  - Larger Systems (>800kW for Industrial Gas Rates)
  - Natural gas utilities will not typically combine smaller accounts to achieve higher volume lower cost gas. Many of the costs incurred are based on distribution, metering, etc.

AND

- **95% Reduction in Cost of PEM Fuel Cell and 75% Reduction in Cost of Reformer System**
  - Mass Production (>10,000 units/year)
  - Must be driven by : Government Credits, Rebates, Military, Government Buildings, Emissions Legislation, Automobiles, Buses, or other Transportation

AIR PRODUCTS

Does PEM Have A Place in Distributed Generation?

- **Low Cost Existing Hydrogen Source**
  - Pipeline
  - Offgas Hydrogen

- **Energy Station**
  - Reformer/Dispenser/PEM
  - Other

AIR PRODUCTS

Conclusions and Recommendations

- **Small Reformer/PEM System**
  - Low Potential for Distributed Power Generation with Natural Gas Feedstock
  - Intangible Benefits
    - Low Noise & Emissions
    - Solid State
    - Utility infrastructure reduction
  - Don't Recommend a Phase II Demonstration
- **Pipeline/Offgas PEM System**
  - Economic in Limited Geographic Region
  - Potential H_2 Pipeline Demonstration
- **Hybrids**
  - Distributed Generation
  - Energy Station
  - Recommended further Phase I Review

AIR PRODUCTS

Collaboration

- Reformer Vendors
  - Various Vendors
  - Provided heat and material balance information and cost information
- Purification System Vendors
  - Various Vendors
  - Provided recovery, operating reqts, and cost
- Fuel Cell Vendors
  - Various Vendors
  - Provided efficiency, life, and cost information
- University
  - Penn State, Dr. Wang
  - Princeton, Dr. Ogden and Dr. Kreutz
- LBNL – Joe Huang (building load profiles)

AIR PRODUCTS

tell me more

www.airproducts.com

AIR PRODUCTS

Novel Compression and Fueling Apparatus to Meet Hydrogen Vehicle Range Requirements

Merit Review and Peer Evaluation
May 19, 2003
Berkeley, CA

Phase I Program Goals

Central Issue:

- There is no cost-effective, proven method for fast filling (10 minutes or less) vehicles to 700 barg

Investigate:

- Novel "Isothermal" Compressor
- High pressure automatic valves
- 900 barg storage vessels for cascade
- Flowmeter and other instruments
- Dispensing equipment

AIR PRODUCTS

Method

- Design, simulate, and test a novel compressor concept involving compression of hydrogen with a “liquid piston” with little temperature rise
  - ASPEN heat and material balance
  - ASPEN dynamics
  - Design spreadsheets for various system components
- Develop valves, instruments, storage systems, and dispensing components for 700 barg with industry partners

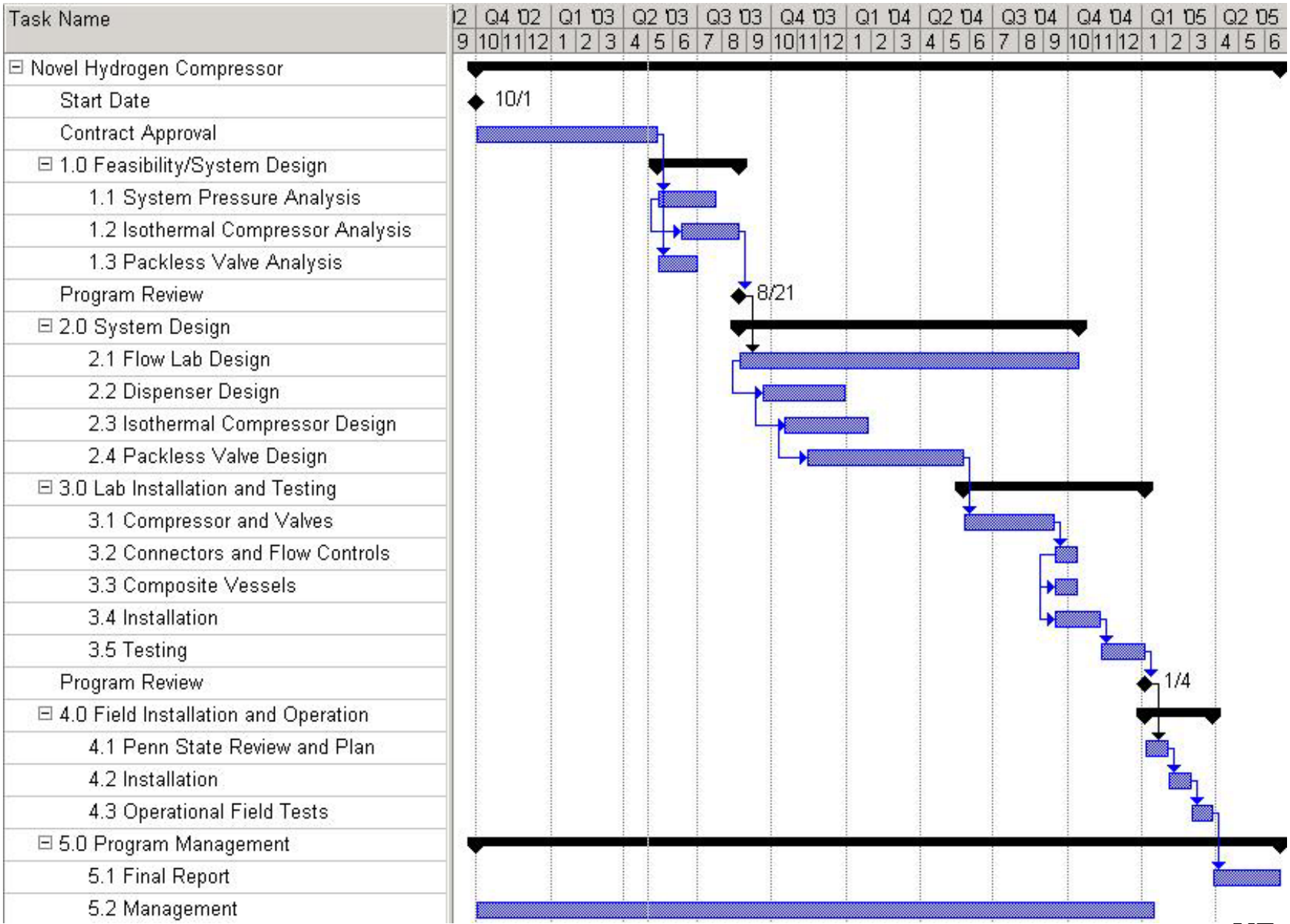
AIR PRODUCTS

Technology Status

- Fast fill (<3 minutes) at 350 barg
  - Issues
    - Tank heating
    - Communications
    - Flow control and measurement
    - Codes not in place yet
    - Storage costs
- Systems up to 75 nm3/hr available, but most systems are 1-20 nm3/hr
- Automobile ranges are under 200 miles
- Industry moving to 700 barg to address range issues

AIR PRODUCTS

Timeline



AIR PRODUCTS

System Pressure Analysis

- Intermediate pressures will not meet the automotive range requirements, so 700 barg fill will be the system design basis
- Automotive companies are beginning to request 700 barg systems
- Most components have higher pressure alternatives that are available commercially
- Cost increases, but cost per kg of delivered hydrogen decreases slightly
- 700 barg delivers 71% more hydrogen for a similar sized vehicle tank

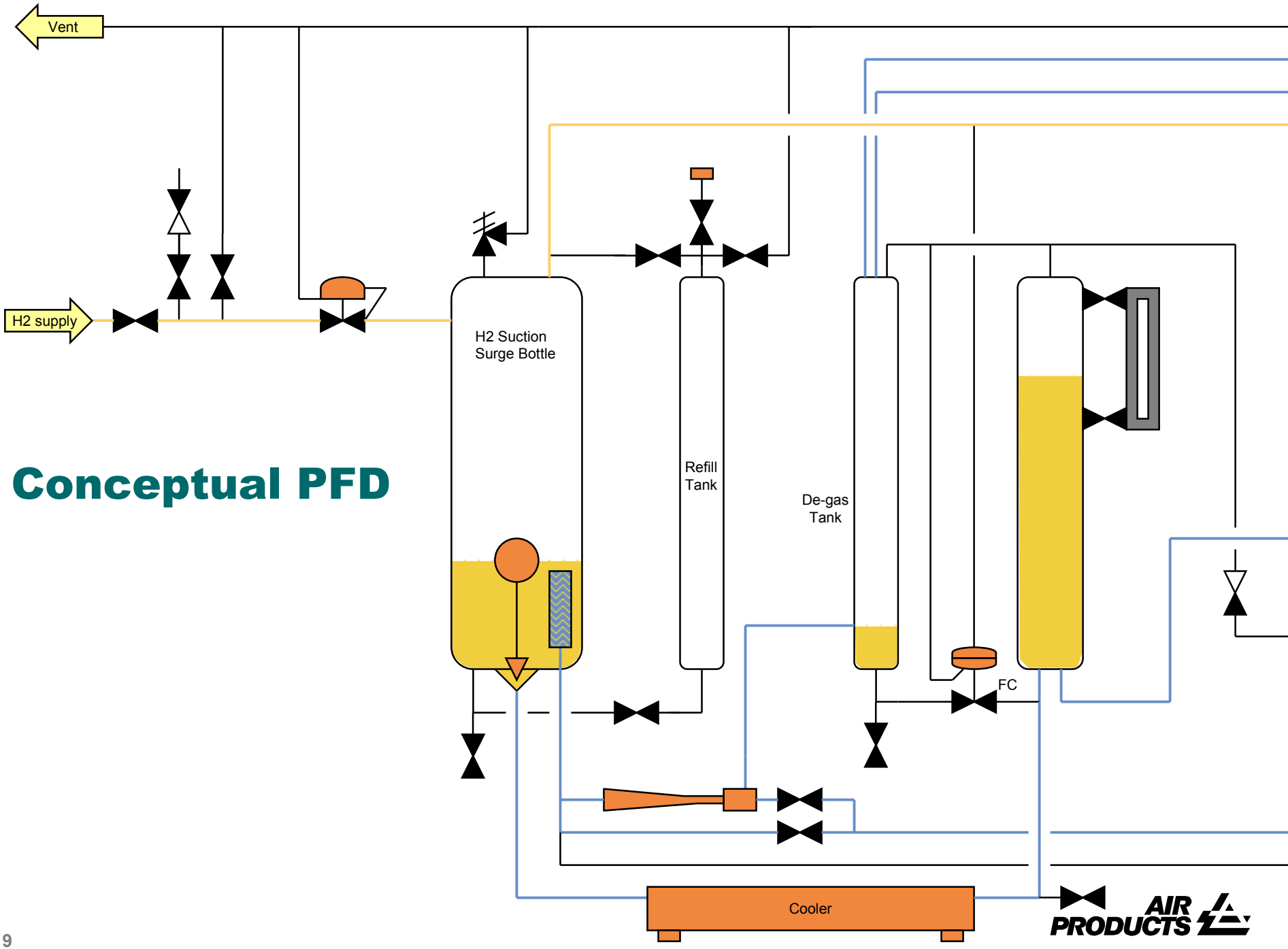
AIR PRODUCTS

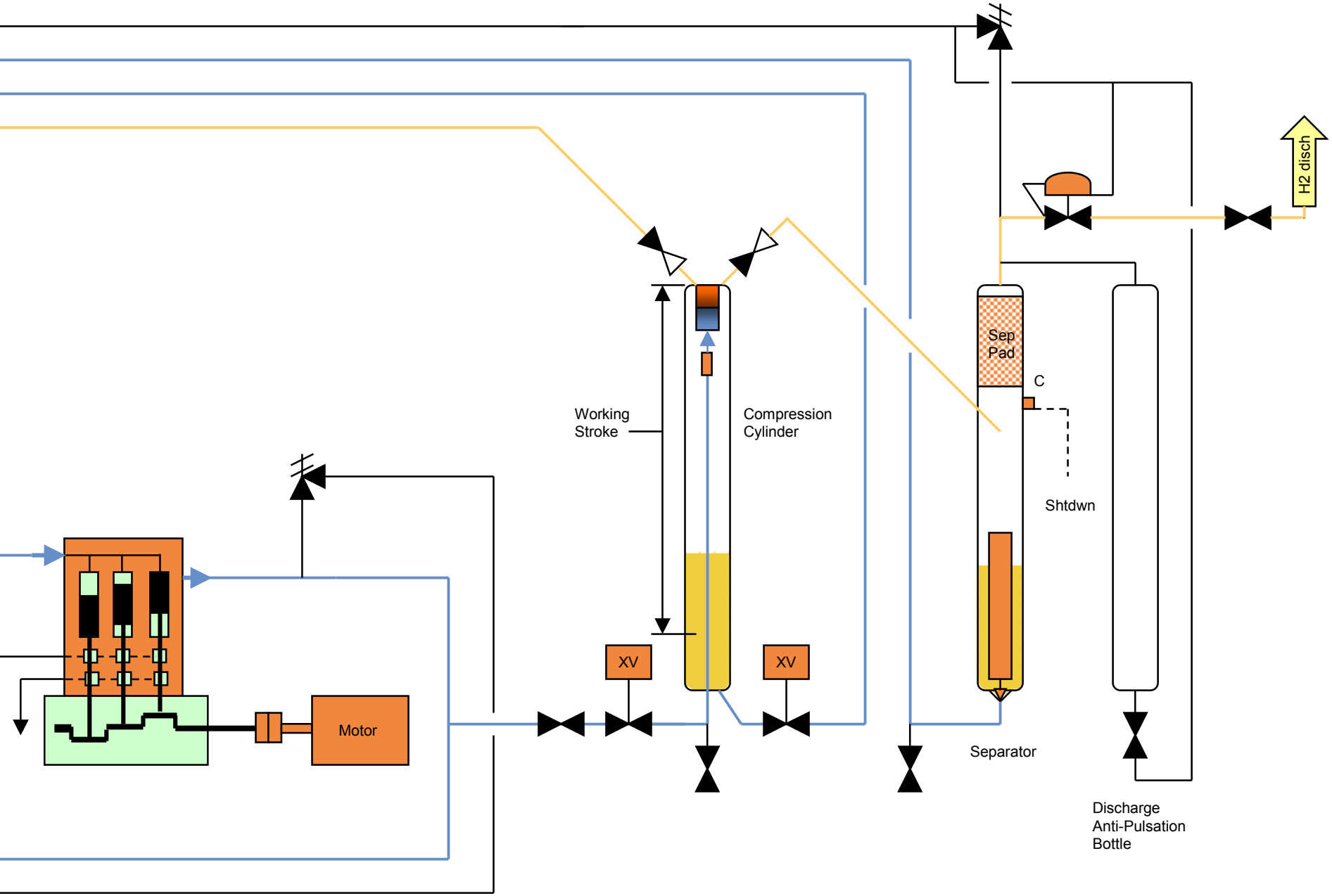
Novel Compressor

- Targets:
  - Prototype flow rate ~ 1 nm3/hr (2 kg/day)
  - Output pressure 12000-14000 psig
  - Cost < $15,000
  - Less than 5 Hp
- First pass
  - Water-based with pump and eductor set
  - Separation and surge volumes
  - Issues
    - Hydrogen solubility
    - High pressure water lubricity
- Further work - Other fluids

AIR PRODUCTS

Conceptual PFD





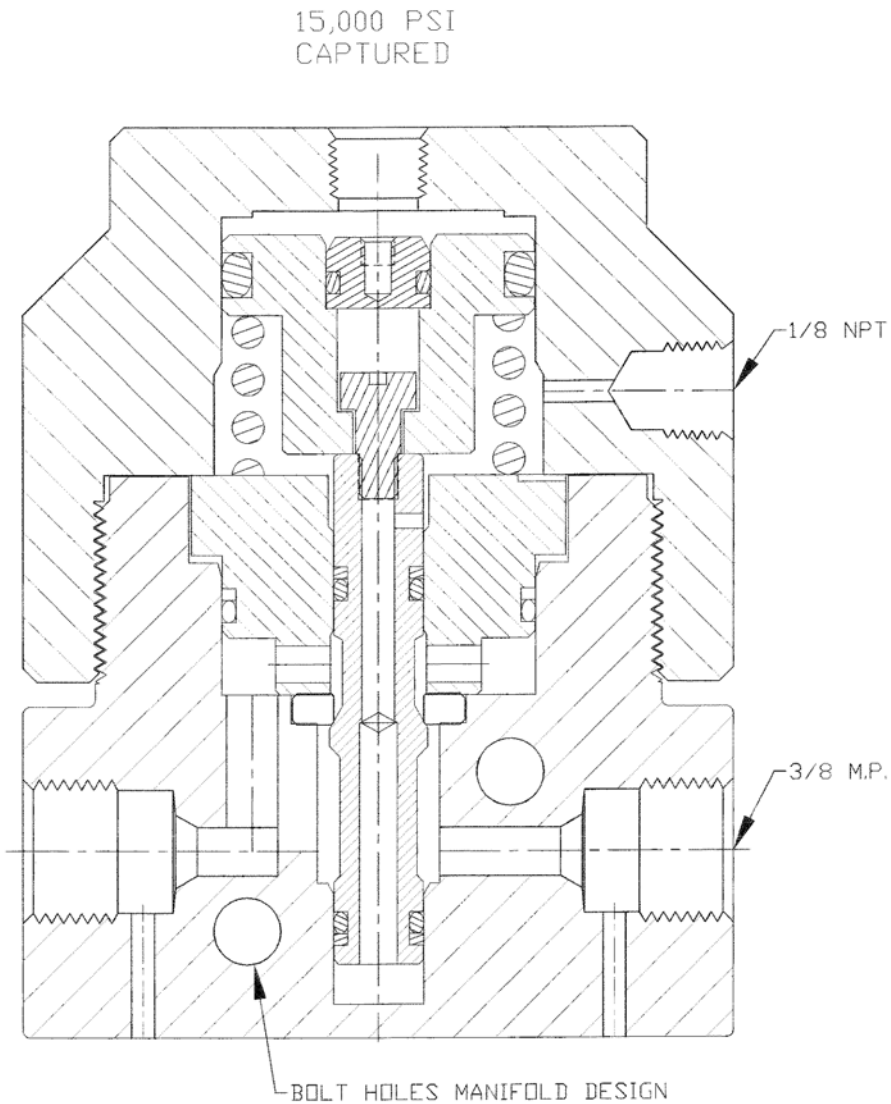
AIR PRODUCTS

High Pressure Automatic Valves

- Developed with a valve supplier
- Unique, balanced-piston design
- Actuated with process gas
- Packless
- Captured vent
- Rated to 15,000 psig
- Small size and footprint (3” dia x 3.5” height)
- Able to manifold multiple valves together
- Cost can be reduced with moderate volumes to around 50% of single item cost today

AIR PRODUCTS

High Pressure Automatic Valves



AIR PRODUCTS

900 Barg Storage

- Investigating many options
  - Cascade to 350 barg and use booster to direct compress into vehicle at 700 barg
    - Upgrade to existing stations
  - Composite cylinders
    - Not ASME-approved
    - High cost
  - Steel cylinders at 900 barg
    - Not mass produced
    - Custom designed

AIR PRODUCTS

Instrumentation and Flowmeter

- Flowmeter
  - Testing 350 barg flowmeter types in another DOE program
  - Work with successful vendors from the first program to increase the pressure capability to 900 barg
- Instruments
  - End connections must be robust and reliable
  - High pressure hydrogen concerns
  - Some devices are not currently available to 900 barg
  - Work with vendors to utilize appropriate end connections and raise pressure capability

AIR PRODUCTS

Dispensing Equipment

- Working with fueling vendor (OPW) and other industry partners to develop a standard for nozzle and breakaway
  - Existing nozzles and breakaways are not SAE J2600 compliant
  - SAE and ISO standards are not approved yet
  - Communications even more important at higher pressures
  - No existing true nozzle or breakaway available at 700 barg
  - High pressure hose quick-connects typically used for 700 barg systems today

AIR PRODUCTS

Progress and Milestones

- May 15, 2003 – Final Contract approved and in hand to allow material purchases
- June 1, 2003 – Testing of compressor subassemblies, Construction of 700 barg fueling system
- August 1, 2003 – Testing of custom compressor machined devices
- August 21, 2003 – Go/No Go decision for Phase II

AIR PRODUCTS

350 Barg Fueling System

AIR PRODUCTS

Collaboration

- OPW/Shearex
- California Fuel Cell Partnership
- Major valve manufacturer
- Fluid manufacturer
- Pump manufacturer
- Custom machine shops
- A number of potential demonstration sites

AIR PRODUCTS

tell me more

www.airproducts.com

Hawaii Hydrogen Power Park

2003 Hydrogen & Fuel Cells Merit Review Meeting

19-22 May 2003

Maurice Kaya, PI, State of Hawaii
Dr. Rick Rocheleau, PI, University of Hawaii
Mitch Ewan, Project Manager, University of Hawaii

DBEDT The Department of Business, Economic Development & Tourism

Hawaii hydrogen power park

HNEI Hawai'i Natural Energy Institute University of Hawai'i at Mānoa

Objectives

- Demonstrate an integrated Hydrogen Power Park comprised of the following:
  - Electrolyzer powered by a renewable energy source. (Barrier V-Renewable Integration)
  - Hydrogen storage & distribution system. (Barrier V-Renewable Integration)
  - PEM fuel cell connected to grid & building. (Barrier V-Renewable Integration)
  - Optional hydrogen fueled vehicle hydrogen dispensing system.
- Demonstrate hydrogen as an energy carrier.
- Investigate interface issues with grid and buildings. (Barrier S–Siting)
- ID codes & standards required to site a Power Park. (Barrier S–Siting)
- ID barriers to a hydrogen infrastructure.
- Educate local authorities on hydrogen technologies. (Barrier S–Siting)
- Economic analysis of hydrogen infrastructure using actual data. (Barrier R – Cost)
- Generate public interest & support. (Barrier S–Siting)

Benefits to Hawaii

- Supports the “Hawaii Hydrogen Mission” plan.
- First step in building a Hawaii hydrogen infrastructure.
- Leverages other Hawaii-based (DoD) hydrogen programs.
- Stimulate creation of a hydrogen high tech industry in Hawaii.
- Help make Hawaii “hydrogen friendly” - Identify & overcome institutional barriers.
- Inform State policy & decision makers.
- Create environment to mitigate financial risk for investors.
- Attract private sector strategic partners for Asia Pacific markets.
- Instill a “sense of wonder” in our students.

Approach

- Leverage Hawaii Fuel Cell Test Facility (HFCTF):
  - Mitigate technical, schedule and financial risk.
  - Accelerate implementation.
- Work with industry technology leaders such as UTC Fuel Cells, Stuart Energy Systems and SunLine to transfer technology & “lessons learned”.
- Multi-phase project development to limit technical & project risk:
  - Provide off-ramps.
  - Program flexibility.
- Integrate a modular Hydrogen Power Park system that can be easily transported & demonstrated inter-island:
  - Promote Pacific Rim market opportunities.
- Utilize commercial off-the-shelf components whenever possible to mitigate risk.
- Develop & implement innovative public outreach program:
  - Utilize web & learning channel cable TV.

Technology Transfer/Collaborations

California Energy Commission

stuartenergy

THE GAS COMPANY
Citizens Energy Services

Hawaiian Electric Light Company

State of Hawaii
Principal Investigator

HNEI

Implementing Partner

SENTECH, INC.

UTC Fuel Cells
A United Technologies Company

Hawaiian Electric Company, Inc.

SunLine
TRANSIT AGENCY

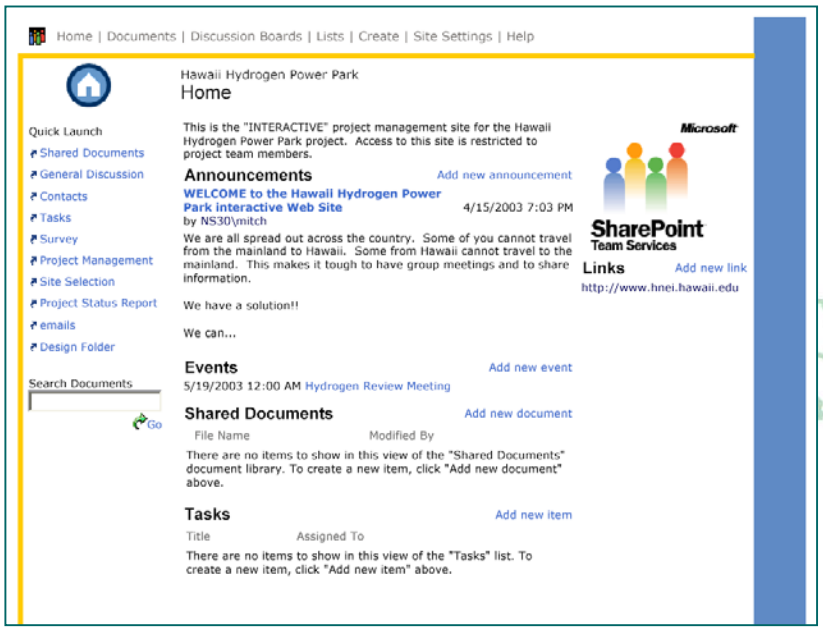
DBEDT
The Department of Business, Economic Development & Tourism

Hawaii hydrogen power park

HNEI
Hawai'i Natural Energy Institute
University of Hawai'i at Mānoa

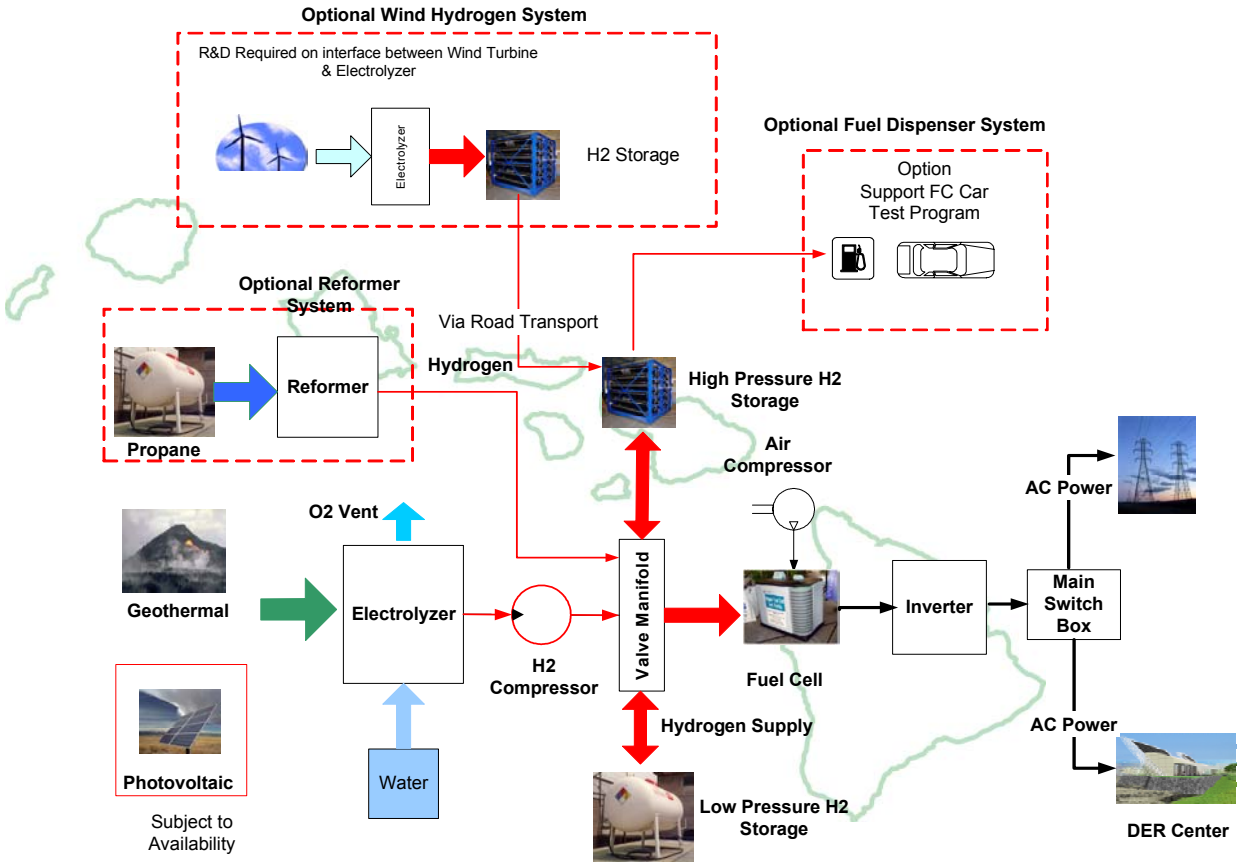
Collaboration & Coordination

Management Website Initiated – www.H2PP.com



- Interactive project management web site promotes close coordination with our partners.
- Automated notice of new information sent to partners.
- Rapid exchange of information & technical specifications.

Power Park Conceptual Design



DBEDT The Department of Business, Economic Development & Tourism

Hawaii hydrogen power park

HNEI Hawai'i Natural Energy Institute University of Hawai'i at Mānoa

Conceptual Design Features

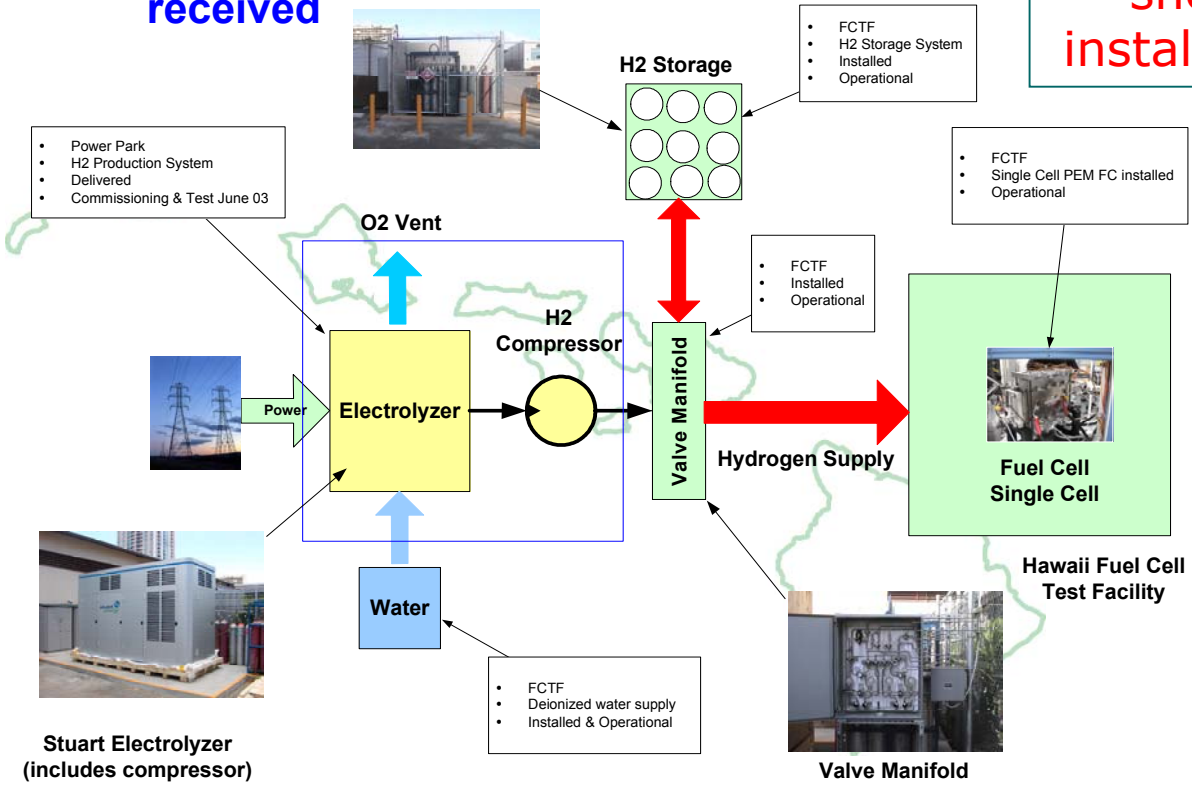
- Modular design provides for flexibility in siting, matching components & addition of optional subsystems.
- Low pressure hydrogen storage utilizing propane tanks.
- High pressure storage using lightweight, modular composite tanks.
- Modular fuel cell power system based on UTFC 5kW units.
- Geothermal energy delivered by HELCO grid.
- Desired options:
  - Wind-hydrogen production system to demonstrate renewable energy derived hydrogen.
  - Propane reformer.
  - Hydrogen vehicle gas dispenser system to support transportation demonstration projects.

Technical Accomplishments

Oahu 1 status as of 01 May 03

Oahu site permit received

All components shown are installed on site



FCTF leveraged assets

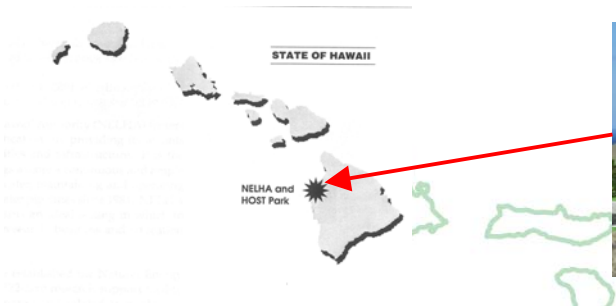
DBEDT The Department of Business, Economic Development & Tourism

Hawaii hydrogen power park

HNEI Hawai'i Natural Energy Institute University of Hawai'i at Mānoa

Progress Summary

- Overall project approximately 3 months ahead of schedule.
- Site Selected – NELHA Gateway DER Center.



- Permits for Oahu system development site issued.

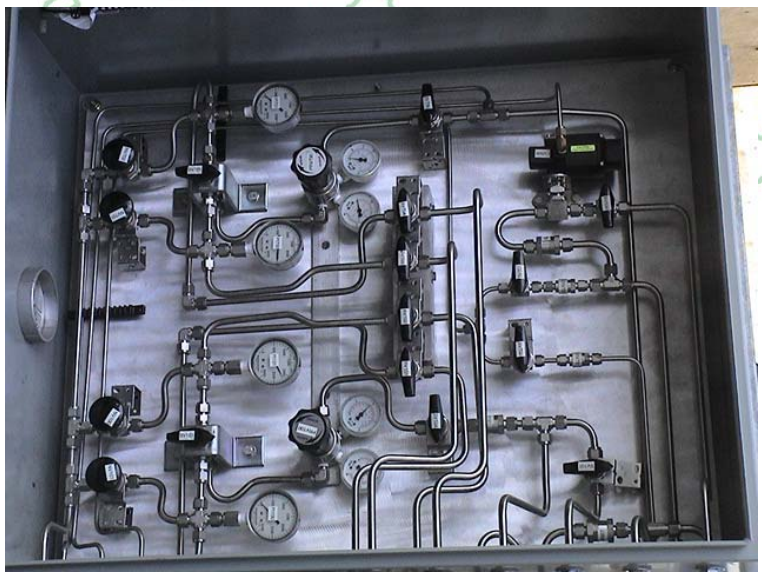
Leverages Hawaii Fuel Cell Test Facility to accelerate program.

Progress Summary

- Stuart Electrolyzer Delivered.
  - Installation & commissioning underway.
  - Projected to be fully operational mid June 03.

Progress Summary

- Prototype gas distribution panels installed & operated.
  - To be tested with electrolyzer.
  - To be modified as required for Power Park.



Leverages Hawaii Fuel Cell Test Facility to accelerate program.

Progress Summary

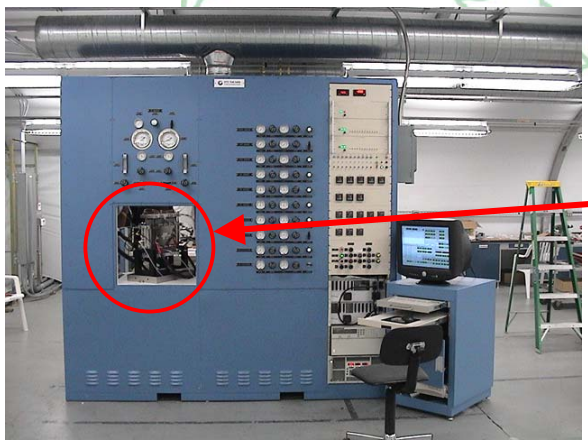
- Hawaii Fuel Cell Test Facility High Pressure Hydrogen Storage System installed and operated.
- Utilized to test Electrolyzer.

Leverages Hawaii Fuel Cell Test Facility to accelerate program.

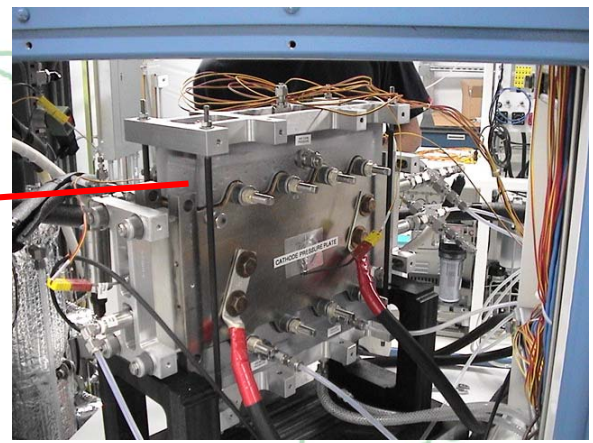
Progress Summary

- UTC Fuel Cell (UTCFC) single-cell PEM fuel cell available for initial testing of electrolyzer output utilizing Hawaii FCTF capabilities.

Leverages Hawaii Fuel Cell Test Facility to accelerate program



UTFC PEM fuel cell test stand



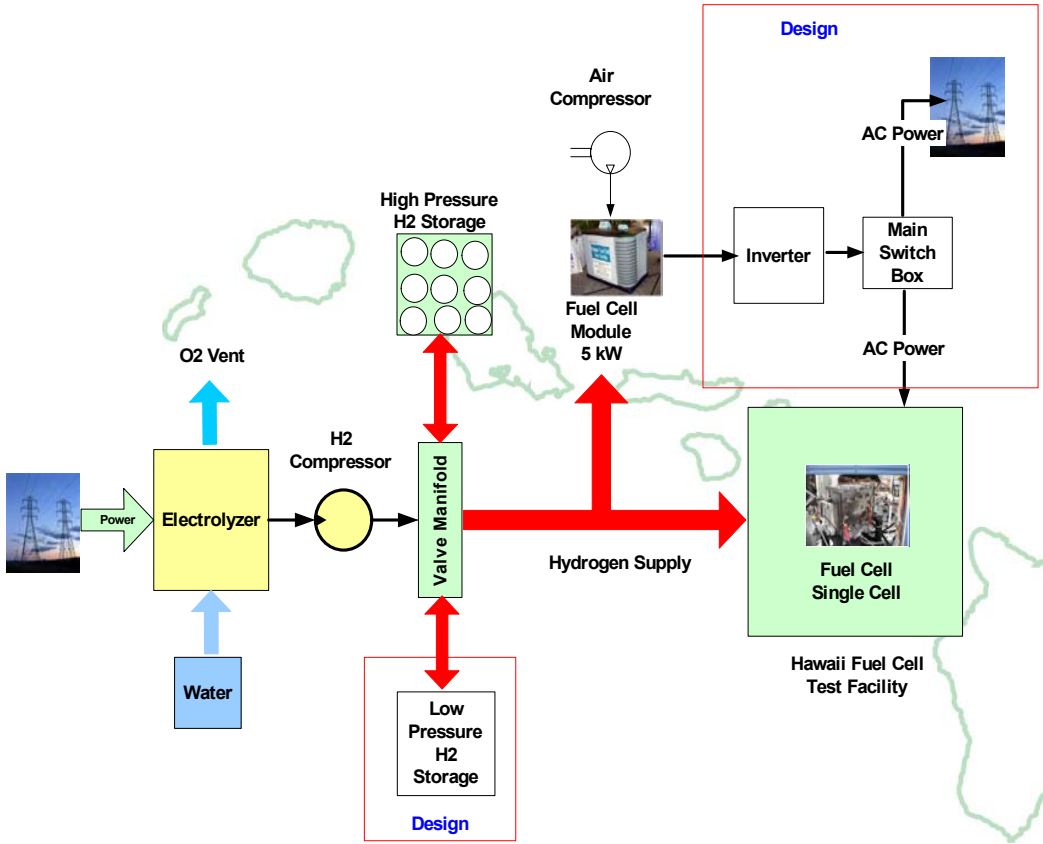
UTFC single-cell PEM fuel cell

Project Progress – Bottom Line

- System integration significantly accelerated by leveraging DoD-funded Hawaii FCTF.
- 3 months ahead of schedule.
- Key hardware on site.
- Site selected.
- Oahu permit issued.

Future Work Plans

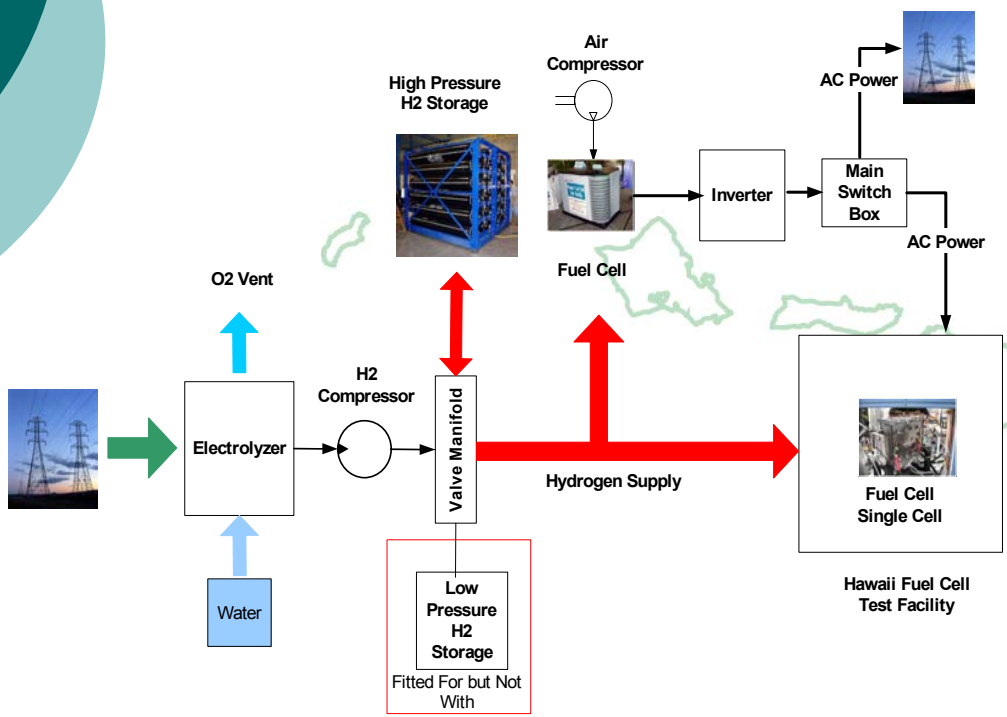
Oahu 2: Projected status as of 31 Dec 03



- Integrate 5kW fuel cell module.
- Design FC utility & building interfaces.
- Design Low Pressure Hydrogen Storage System.
- Design Data Acquisition System.
- Design Remote Control System.

Future Work Plans

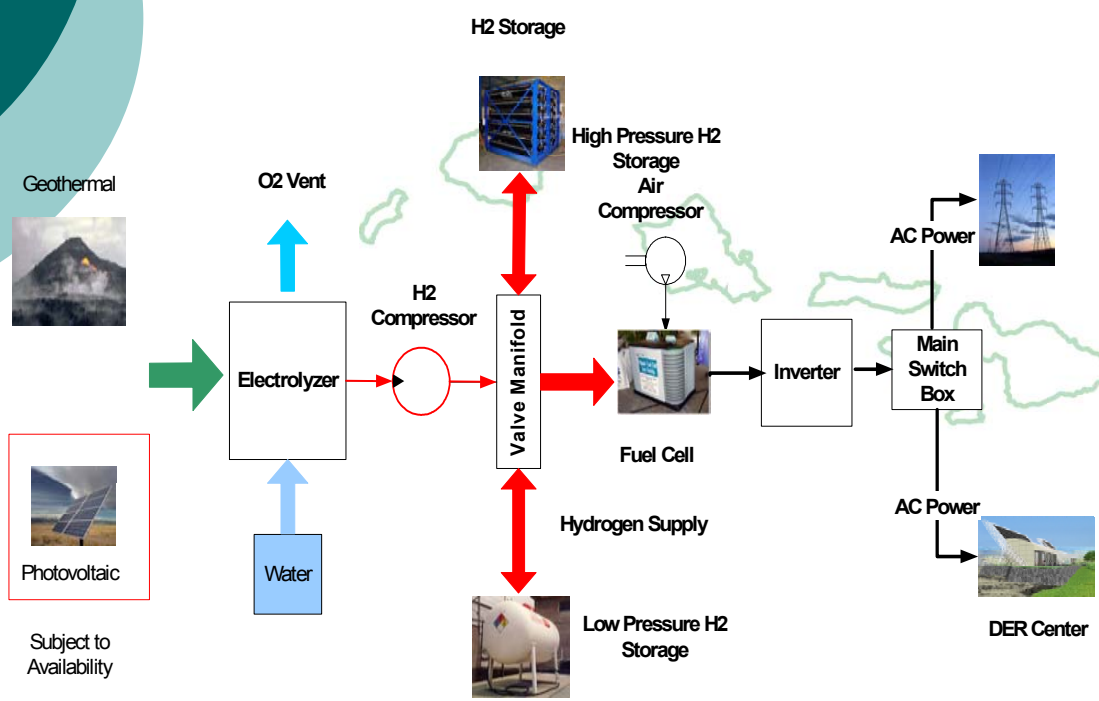
Oahu 3: Projected status as of 31 March 04
Test full system before shipping to NELHA



- Fully test system prior to shipping to NELHA test site.
- Integrate FC utility & building interfaces.
- Integrate NELHA High Pressure H2 Storage System.
- Integrate Low Pressure Hydrogen Storage System less storage tank.
- Integrate Data Acquisition System.
- Integrate Remote Control System.

Future Work Plans

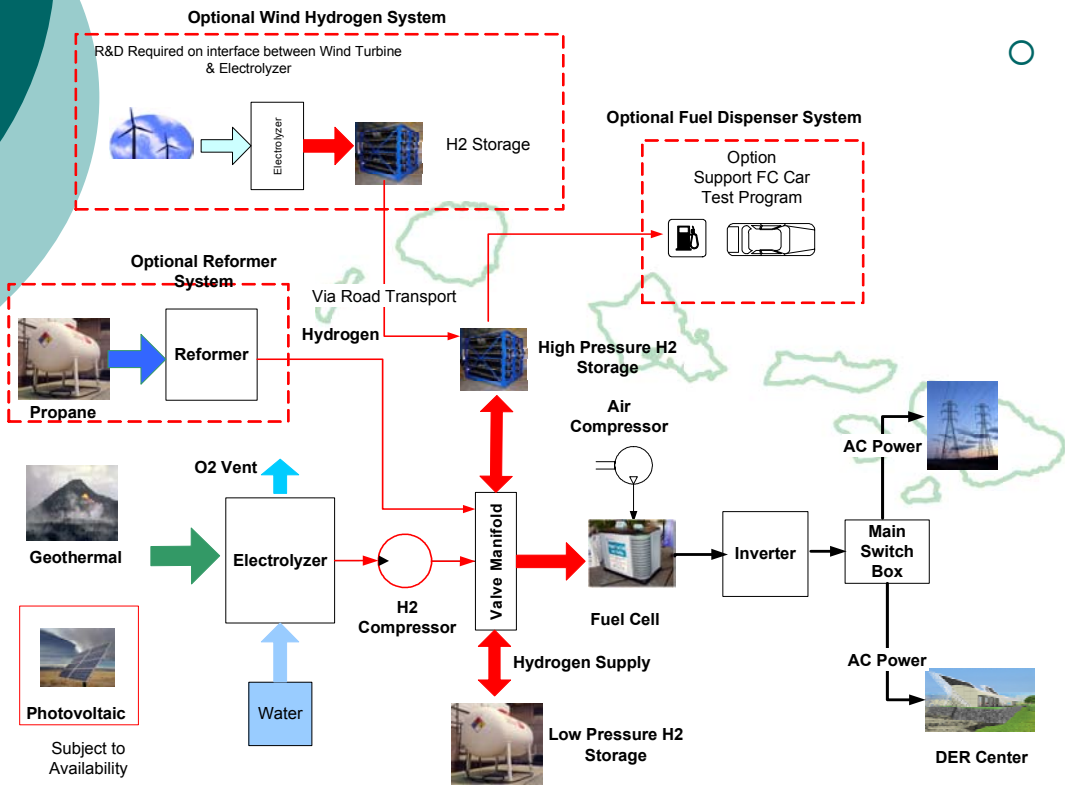
NELHA 1: Projected status as of 30 June 04
Ship & install system at NELHA



- Obtain Hawaii County permits.
- Complete NELHA site preparation.
- Deliver & install system.
- Install Low Pressure H2 Storage System.
- Install Remote Data Acquisition & Control systems.
- Train local system operators.
- Commence experiments.
- Collect data.
- Analyze & report results.
- Conduct public outreach activities.

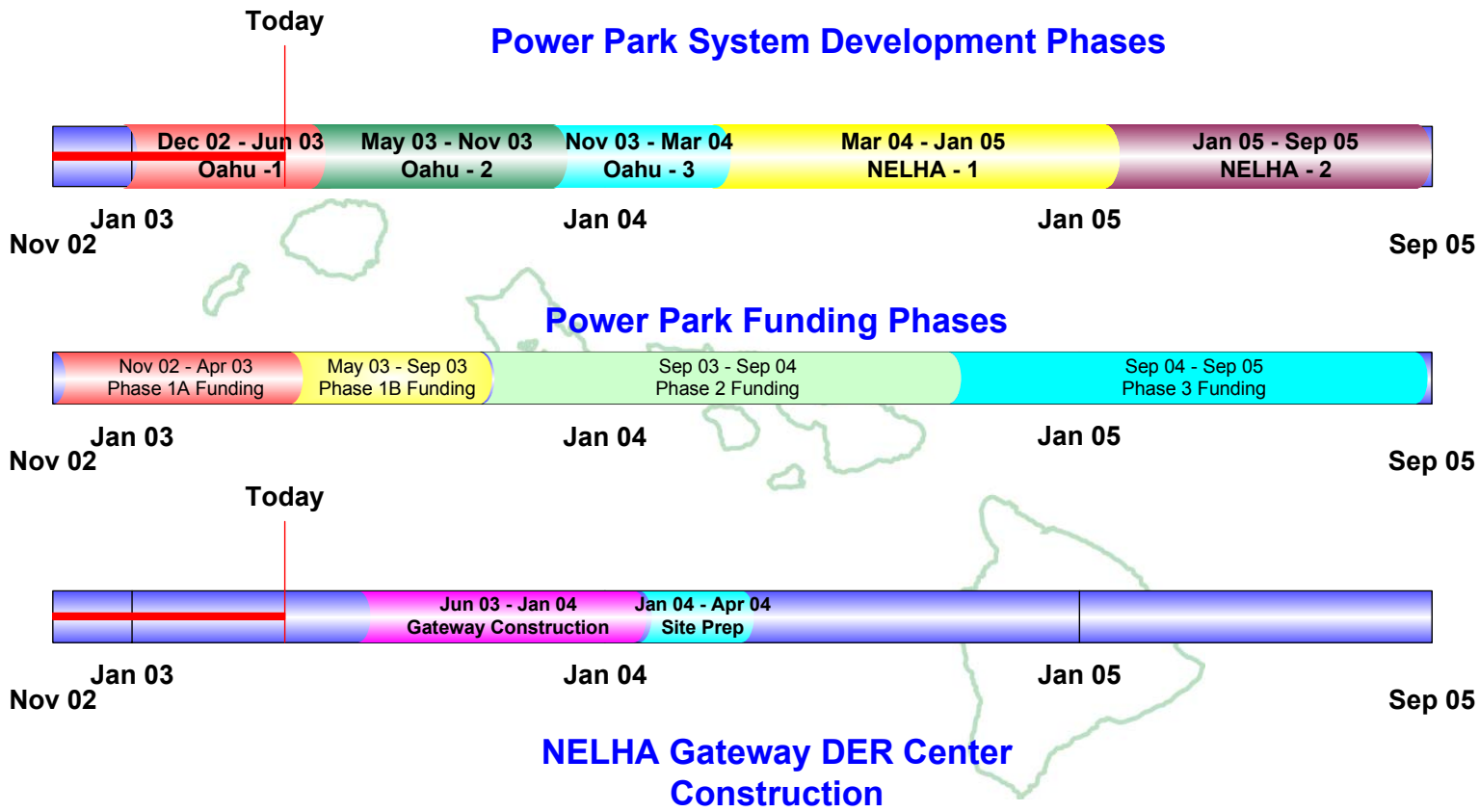
Future Work Plans

NELHA 2: Projected status as of 31 Dec 04
Ongoing testing & evaluation at NELHA



- Desired Options
  - Install Wind Hydrogen Production System to support President's Hydrogen Fuel Initiative.
  - Transport H2 to NELHA.
  - Install H2 Dispensing System to support Freedom Car Program.

Timelines


Today
Power Park System Development Phases
Dec 02 - Jun 03
Oahu -1
May 03 - Nov 03
Oahu - 2
Nov 03 - Mar 04
Oahu - 3
Mar 04 - Jan 05
NELHA - 1
Jan 05 - Sep 05
NELHA - 2
Jan 03
Nov 02
Jan 04
Jan 05
Sep 05
Power Park Funding Phases
Nov 02 - Apr 03
Phase 1A Funding
May 03 - Sep 03
Phase 1B Funding
Sep 03 - Sep 04
Phase 2 Funding
Sep 04 - Sep 05
Phase 3 Funding
Jan 03
Nov 02
Jan 04
Jan 05
Sep 05
Today
Jun 03 - Jan 04
Gateway Construction
Jan 04 - Apr 04
Site Prep
Jan 03
Nov 02
Jan 04
Jan 05
Sep 05
NELHA Gateway DER Center
Construction

Power Park

Pinnacle West Capital Corporation

Objectives

- *Economic hydrogen production*
- *Renewable Energy Opportunities*
- *Integration of distributed generation and transportation fuel production*
- *Incorporation with existing Energy Assets*
- *Scalability (small, medium, large)*
- *Integrated Business Opportunities*
- *Identification of technical barriers*
- *Identification of market opportunities*

Approach

- Safety & Economics
  - Deflagration & detonation of hydrogen
  - Codes, engineering, modeling, fabrication
  - Building block design
- Economic new technology
  - Solar reforming of natural gas
  - Low cost electrolysis opportunities
  - Identify hydrogen purity requirement
  - Heat energy recovery
  - Chemical by-products

Approach (continued)

- Subsystem test & development
  - Zero emission Genset
  - 55 % thermal efficiency with Genset system
  - Vehicle refueling model
  - Low hazard compression & storage model
  - Electrolysis & compression model
  - Integration with host site models
  - Hydrogen storage models
  - Chemical by-product management model
  - Pilot Solar reforming of natural gas model

Approach (continued)

- Operational analysis of system elements
- Integration of system elements
- Marketing Opportunity
- Economics of Market Opportunity
- Summary of Barriers
  - **Technical**
  - **Code**
  - **Zoning**
  - **Other**

Project Timeline

- Get Contract in Place

Accomplishments to Date

- Pilot hydrogen production and motor vehicle refueling facility in place and operating.
- Solar Panels in place & operating.
- 100 KW Genset unloaded operation on hydrogen.
- Prototype methane solar reformer operating.
- Refueling Motor vehicles with hydrogen & blends.

Collaborations

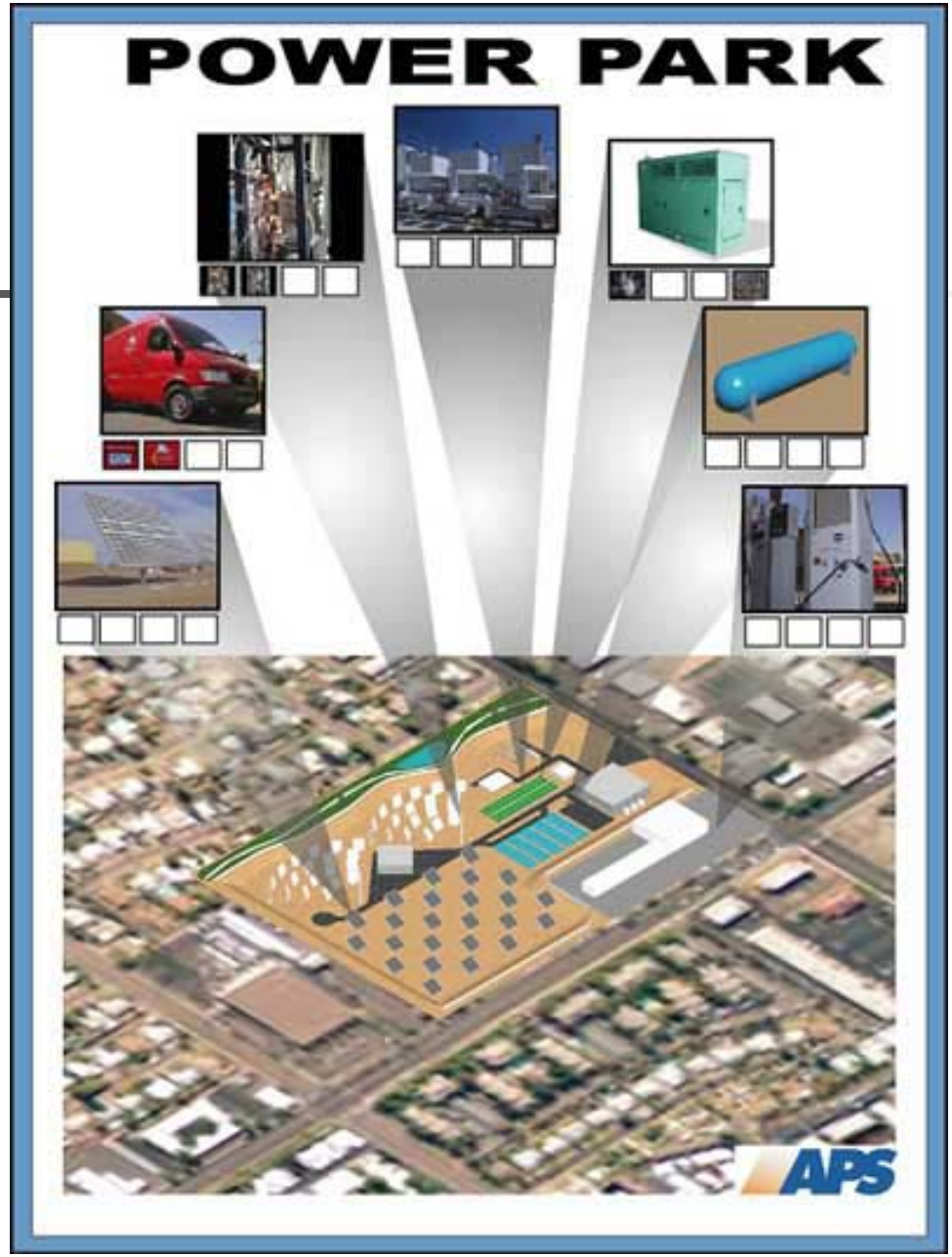
- APS (Arizona Public Service)
- Collier Technologies
- ETEC
- Energy CS
- Boyle & Associates
- Distributed Utility Associated
- University of Colorado
- INTEL

Plans Future Milestones

- Minimize Genset Emissions (NO_x).
- Genset Thermal Efficiency to 55% including heat recovery.
- Quantification of chemical by-products
- Perform heat balance on modeled integrated facility.
- Motor vehicle refueling beyond test fleet.
- Market opportunities

HYDROGEN

FLAMMABLE


POWER PARK
APS

DTE Hydrogen Power Park

DOE Merit Review

May 19-22, 2003

DTE Energy

Project Rationale

Given the potential for the commercialization of hydrogen as a replacement energy carrier for fossil fuels, DTE Energy will develop and test a working prototype of a hydrogen-based energy system.

The company believes this demonstration project, which models a complete renewable hydrogen system, from biomass/solar power to hydrogen generation and storage to electrical generation and vehicle fueling, will provide meaningful information into the technical and economic challenges of realizing a hydrogen-based economy.

Approach

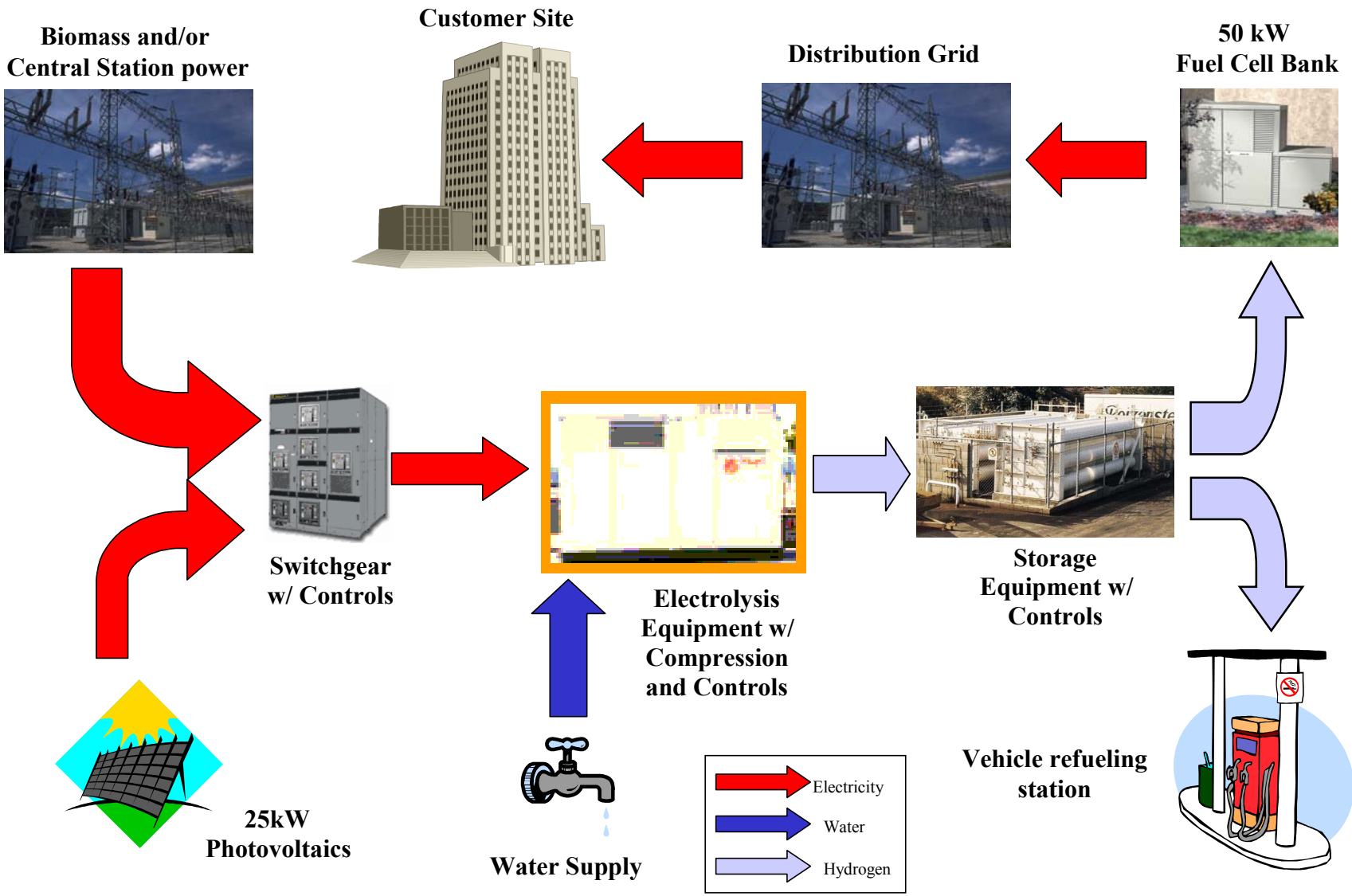
Approach

DTE Energy continues its commitment to integrating clean and renewable technologies into its portfolio.

This project will be the first of its kind to integrate renewable energy into an end-to-end hydrogen energy station concept that utilizes solar & biomass power combined with electrolysis and stationary PEM fuel cell technology to take advantage of low-cost power during off-peak hours to generate hydrogen for on-peak power generation and vehicle fuelling.

Using state-of-the-art hydrogen generation, storage, regeneration and control technologies, the project will evaluate opportunities to reduce overall system cost and maximize performance through optimization of system design & operation, practical approaches to permitting, and integration of power and transportation applications using a common hydrogen infrastructure.

Approach


Biomass and/or
Central Station power
Customer Site
Distribution Grid
50 kW
Fuel Cell Bank
Switchgear
w/ Controls
Electrolysis
Equipment w/
Compression
and Controls
Storage
Equipment w/
Controls
25kW
Photovoltaics
Water Supply
Vehicle refueling
station
Electricity
Water
Hydrogen

Approach

Enterprise wide initiative for DTE Energy, employing a diverse group of business units with relevant and complementary capabilities:

- Edison Development Corporation –Technology Investments
- DTE Energy Technologies – Integrated DG solutions
- Detroit Edison – Electric utility
- Michigan Consolidated Gas – Gas utility
- DTE Biomass Energy – Non-regulated renewable energy provider

Develops, installs, and operates a multi-use compressed gas hydrogen system capable of delivering approximately 500 kWh/day of on-site electricity and vehicle fuel using:

- On-site renewable energy source (demonstrating zero emission pathway)
- ~170 kW electrolyzer (effective for low volume on-site hydrogen requirements)
- Compressed gas storage at +5,000 psi (proven, safe, relatively cost effective)
- 25 – 75 kW fuel cell bank (quiet, clean, efficient)
- Hydrogen vehicle fueling at up to 5,000 psi (state of the art)

Approach

Integrates and installs system on-site

- Simplifies design and construction
- Minimizes footprint
- Reduces cost
- Mitigates execution risk

Uses installed infrastructure base

- Solar panels (from existing Detroit Edison renewable energy program)
- Electrical substation (power supply to / from system)
- Multiple generation sources – solar / grid
- Water supply (potable – purification part of electrolysis system)

Relevance

Technology Validation Aspect

Demonstrates a complete, integrated hydrogen system using representative commercial units in a real-world application under realistic operating scenarios

Can provide data necessary to validate component technical targets

Can provide feedback for efficient Department of Energy R&D program management

Barriers Addressed

Hydrogen Refueling Infrastructure: provide information on early penetration barriers, including high cost of hydrogen production, low availability of hydrogen production systems, and safety issues

Project Objectives	DOE Technical Barrier
Build knowledge and experience in hydrogen infrastructure design and implementation, including safety requirements and applicable codes	Hydrogen Refueling Infrastructure
Determine conditions for system optimization and cost reduction, including design footprint and multi-use energy stations	
Evaluate peak shaving potential, scaling potential, and competitiveness of electrolysis-based hydrogen systems with other on-site production technologies	

Barriers Addressed

Market assessment and economic analysis: based on project learnings and system performance data, assess market potential and develop business plan for commercialization of hydrogen energy systems

Project Objectives	DOE Barrier
Identify the key drivers of economic performance for integrated hydrogen-based power systems, including fuel sources, capital costs, O&M expenses, safety codes & standards, and emissions Benchmark use of central station power for hydrogen production against DG technologies, including renewable	Market and economic assessments

Barriers Addressed

Hydrogen from Renewable Resources: provide operational, durability, and efficiency information on renewable/electrolyzer systems in distributed applications, including integration of biomass and solar

Project Objectives

Develop, install, and operate a compressed gas hydrogen system capable of delivering approximately 500 kWh/day of on-site electricity and fuel for vehicle refueling

Integrate system with on-site renewable (solar) power and carbon-neutral biomass power via the grid

Evaluate operational, durability, and efficiency information of a renewable/electrolyzer system

DOE Technical Barrier

Hydrogen from Renewable Resources

Barriers Addressed

Codes & Standards: contribute real-world information needed to develop codes and standards that will permit deployment of integrated distributed generation and refueling applications in a cost-effective, timely manner

Project Objectives	DOE Technical Barrier
Permit and install electrolytic hydrogen production and storage facility in the State of Michigan	Codes & Standards
Permit and install hydrogen refueling facility in the State of Michigan	
Permit and install hydrogen DG application in the State of Michigan	

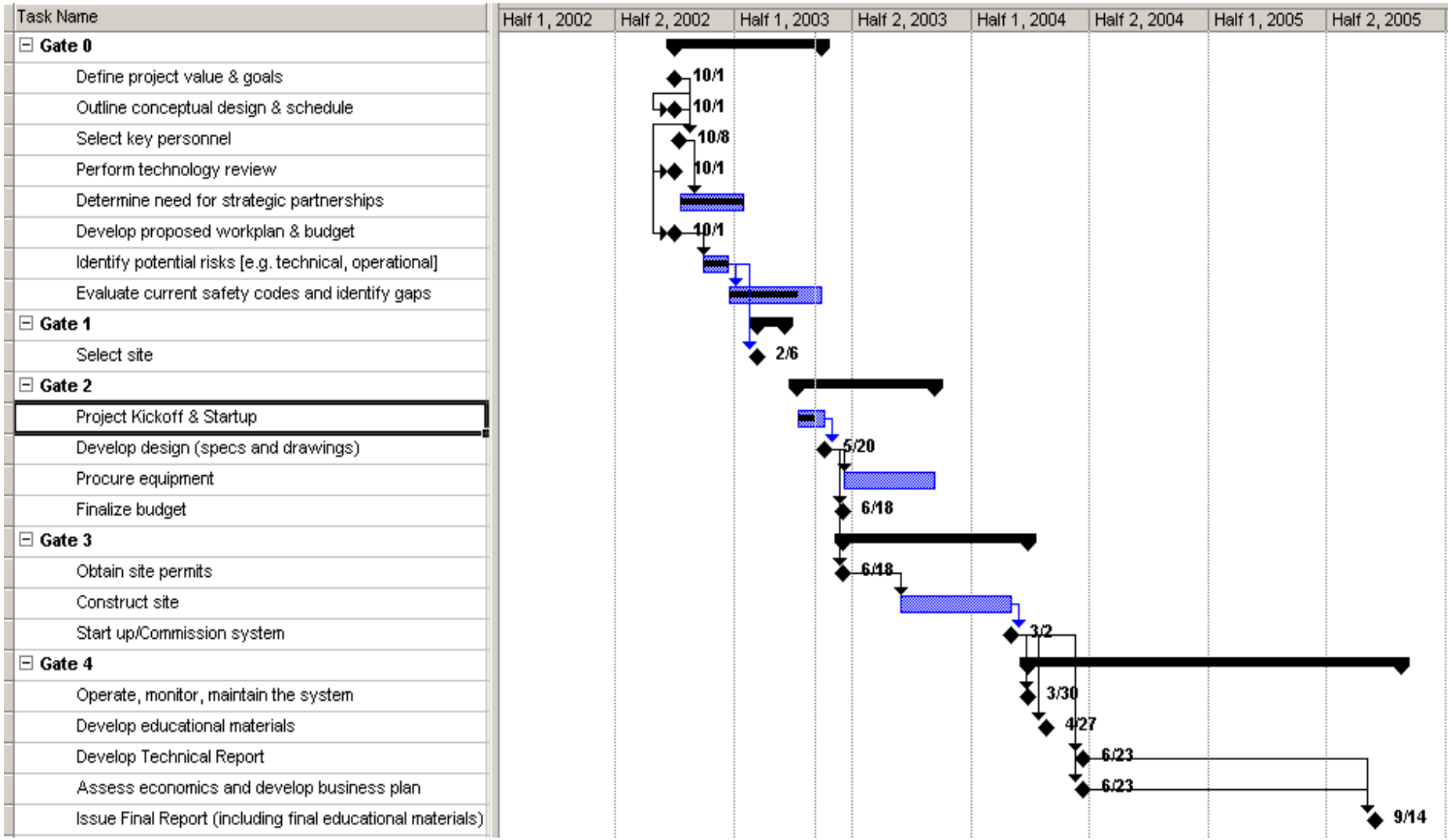
Barriers Addressed

Co-production of hydrogen & electricity: contribute to understanding the economic viability of clean technology systems that co-produce hydrogen fuel and electricity

Project Objectives	DOE Technical Barrier
Identify the characteristics of an economically viable hydrogen-based energy system for peak shaving applications and its potential for use in fuelling applications	Co-production of hydrogen and electricity
Evaluate impact of multi-use energy station design on the economics of hydrogen-based infrastructures	

Timeline

Project Timeline



Project Timeline

Phase I (First 6 months)

- Select Team
- Establish optimal technologies and sources
- Develop workplan & budget
- Establish codes & standards framework
- Site system

Phase II (months 7-18)

- Design system & obtain permits
- Procure equipment
- Install, commission and operate system
- Develop educational program

Phase III (months 19-36)

- Operate, monitor, and maintain system
- Develop technical report
- Assess economics and develop business plan
- Document and publish project results

Accomplishments

Accomplishments

Phase I (First 6 months)

Select Team - **complete**

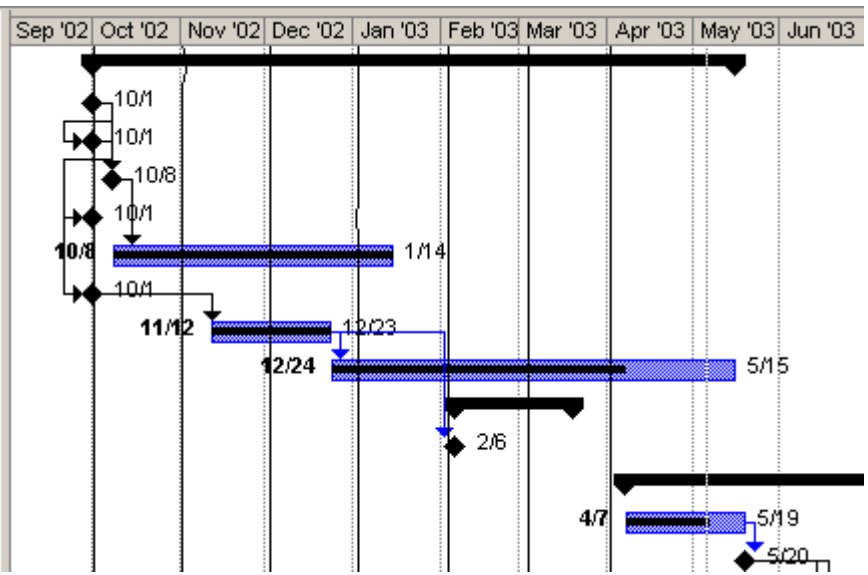
Establish optimal technologies and sources - **complete**

Develop workplan & budget - **complete**

Establish codes & standards framework - **in progress**

Site system - **complete**

	Task Name
	Gate 0
✓	Define project value & goals
✓	Outline conceptual design & schedule
✓	Select team
✓	Perform technology review
✓	Determine need for strategic partnerships
✓	Develop proposed workplan & budget
✓	Identify potential risks [e.g. technical, operational]
	Evaluate current safety codes and identify gaps
✓	**Gate 1**
✓	Select site
	Gate 2
	Project Kickoff & Startup
	Develop design (specs and drawings)



Collaborations

Significant Interactions

Internal

- Edison Development Corp (EDC) – Project Sponsor
- DTE Energy Technologies (DTech) – Project Manager
- Detroit Edison (DeCo) – Site owner & operator
- Michigan Consolidated Gas (MichCon) – NGV expertise
- DTE Biomass Energy – renewable energy supplier

External

- Private Sector
  - Working with third party firms and equipment suppliers to source optimal system designs and technologies
- Government Sector
  - Coordinating efforts with State alternative energy technology development programs to leverage resources and information exchange
- Academic
  - Collaborating with cross-disciplinary university programs to match project opportunities with educational needs

Current Plan

Plan with milestones

Phase II (months 7-18)

[in progress]

Design system & obtain permits

Procure equipment

Install, commission and operate system

Develop educational program

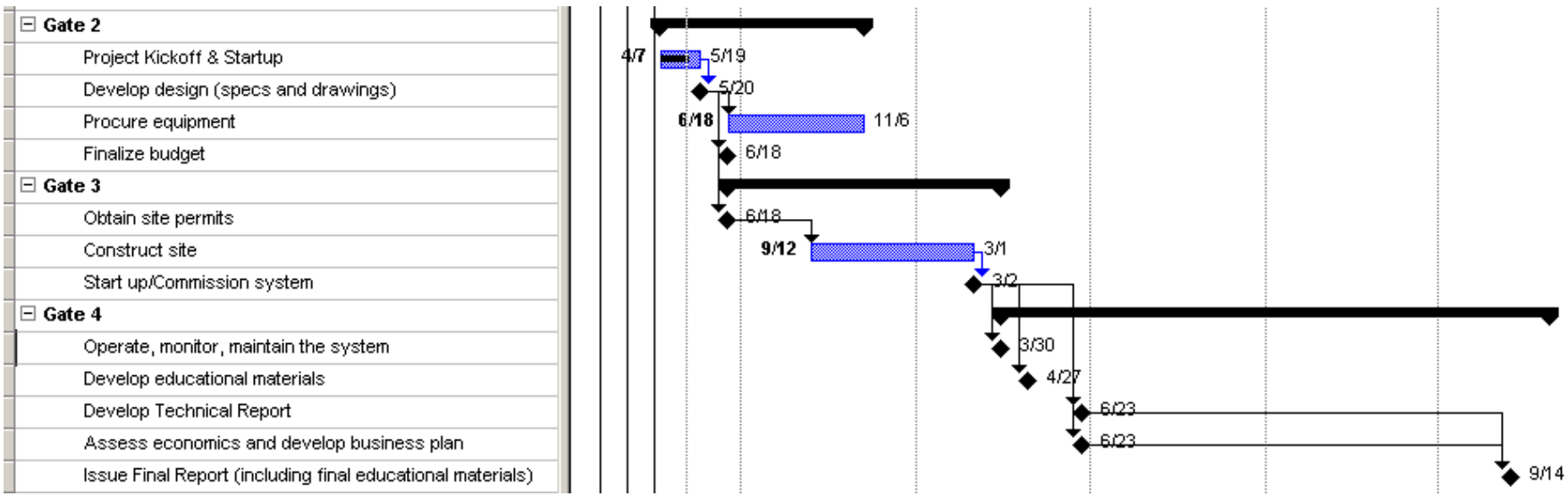
Phase III (months 19-36)

Operate, monitor, and maintain system

Develop technical report

Assess economics and develop business plan

Document and publish project results



stuart energy

the power of hydrogen

Filling Up With Hydrogen 2000

Matthew J. Fairlie & Paul Scott

Stuart Energy USA

Technical Barriers Electrolysis

- Cost
- Siting System (emissions, codes and standards)
- Efficiency
- Grid Emissions + Connection to Renewable Power

General Goals

- Validate Stuart Fuel Appliance approach:
  - Appliances convert existing electricity infrastructure to hydrogen fuel – on-site production avoids fuel distribution costs and “scale up costs” ;ideal for fleet application
  - “Zero emission” Hydrogen Fuel Infrastructure is Near-term Option – achievable through emission mitigation at power plant
- Demonstrate superiority of Stuart electrolytic method:
  - Appliances of any size/“fill fuel needs anywhere”;
  - Compact: footprint less than 10% of vehicle;
  - Emission-free: only O_2 and H_20 vapour;
  - Can achieve hydrogen fuel cost in car of $2.50/kg.

Specific Objectives

- Prove Stuart CST cell stack technology in large scale systems (> 1 Nm3/h) – key to cost reduction strategy;
- Introduce Personal Fuel Appliance (PFA) to broad audience – "change the way people think about hydrogen";
- Validate goals:
  - Cost: Manufacturing pathway $300/kW
  - Footprint: Less than 10% of vehicle
  - "Plug and Produce": Automation/Reliability (8000 h service interval)

Methodology

- Prototyping development approach to product development:
  - Educate users - “change thinking”
  - Learn from customer experience and system reliability
  - Develop strategic positions for future commercialization
  - Five steps in “prototyping” product development process:
    - ✓ Design, Build, Test, Customer Evaluation and Post Mortem

1999

2003

Plan for Personal Fuel Appliance

D = Design | B = Built | T = Testing | CE = Customer Evaluation | PM = Post Mortem

Prototype	Cell Type	Capacity (SCFH)	Pressure (psig)	Test Site	D	B	T	CE	PM
Model 10	Single Stack	20	3000	Selected Demo	Q3 98	Q4 99	Q3 99	Q1 00	Q3 99
Model 25	Single Stack	40	3600	Ford Motor Co.	Q2 99	Q3 99	Q2 00	Q2 01	Q2 04
Deca	Single Stack	40	3600	Numerous Demos	Q2 00	Q2 00	Q3 00	Q3 00	Q4 02

psig: pounds per sq. in.

SCFH: std. cu. ft. per h

Plan for Fleet Fuel Appliances

D = Design | B = Built | T = Testing | CE = Customer Evaluation | PM = Post Mortem

Prototype	Cell Type	Capacity (SCFH)	Pressure (psig)	Test Site	D	B	T	CE	PM
P3-1A	Multi Stack	1500	4000 psig	SunLine Transit	Q3 98	Q1 99	Q3 99	Q1 00	Q2 03
P3-1B HP	Single Stack	400	5000 psig	Powertech Labs CFCP	Q1 00	Q2 00	Q4 00	Q2 01	Q3 03
P3-1B LP	Single Stack	400	220 psig	Factory Tested to be delivered to FCPI Q4-2002	Q2 99	Q4 99	Q1 00	Q4 02	Q2 03
P3-5	Multi Stack	10000	N/A	Design Only	Q1 01	—	—	—	—
P4-1A	Single Stack	500	6000 psig	Internal	Q2 01	Q3 01	Q2 02	—	Q3 02
P4-1B	Single Stack	1000	6000 psig	AQMD	Q3 01	Q1 02	Q2 02	Q3 03	Q1 05
Mark 1	Single Stack	400	5000 psig	Bus Transit	Q1 02	Q1 03	Q2 03	Q3 03	Q4 04

CFCP: California Fuel Cell Partnership,

FCPI: Fuel Cell Propulsion Institute

AQMD: South Coast Air Quality Management District

P3 Fleet Appliances Progress

P3-1A: SunLine Transit (4,000 psig) - 3100 h over 3.5 million SCF

- Demonstrate stack performance: 49 kWh/kg
- Gas purity has been demonstrated: Unit has fueled Ballard and UTC bus engines
- Leak detected in stack (Q1 03) due to electrode connection

P3-1B HP: PowerTech Labs (5,000 psig) – 5,000 h over 2 million SCF

- Dispenses H_2 and 51% H_2/CNG mix at 6000 psig
- Demonstrate pushbutton operation/ basis for 10000 psi development
- Similar unit built for CFCP in Richmond, California

P3 Fleet Appliances Progress

P31B LP: FCPI - factory tested for 2500 h / 150 h in field

- Appliance Performance: 65 kWh/kg
- Low pressure (200 psig) fuel dispensing for metal hydride converted to high pressure for field trial
- Unit delivered on mobile fueling deck to Fuel Cell Propulsion Institute (FCPI)

P3-5: Cell Block Design & Demonstration Only - 1,250 h over 4.5 million SCF

- Stack Performance: 47.5 kWh/kg
- Cost target achieved $150/kW
- Material manufacturing quality control problems identified – quality control improved

P4 Fleet Appliances Progress

P4 - 1A: Internal Testing

- 10,000h pressurized CST cell stack test successful
- Problems with instrumentation/contamination
- Pressure insufficient to achieve economy in compression
- Design approach of pressurized CST stack abandoned in favour of acquisition of Vandenborre Hydrogen Systems

P4 – 1B: South Coast Air Quality Management District – 250 h test

- Unit deployed at South West Research Institute to supply fuel to H_2 ICE Motor/generator set (Ford Power Products)
- Unit will test CST integration with renewable power/ unit will “follow generator”

P4 Fleet Appliances Progress

Mark I : SunLine Transit

- 450 SCFH @6000 psig
- 65 kWh per kg
- Delivery June 2003

Personal Fuel Appliance Progress

White Box | 200 Series | Deca

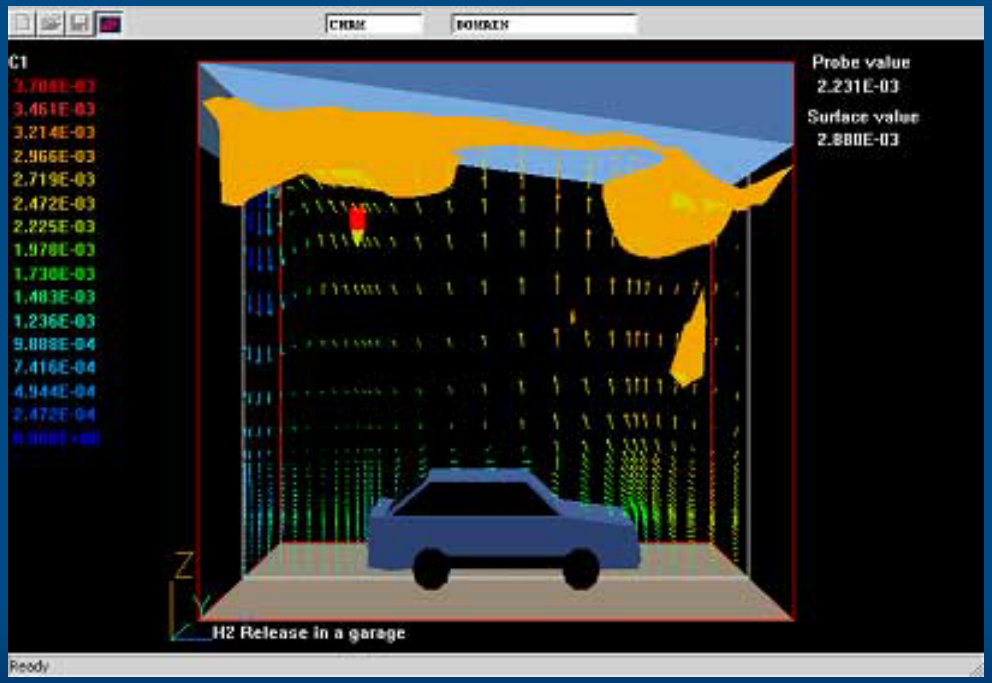
Three design Generations

- reduction in size of 80%
- U/L (Underwriters Laboratories) certification
- unit widely demonstrated
- Technical tasks complete, final report submitted for approval

Joint Evaluation with Ford Motor Company

Safety Update

- PFA received ULC Special Inspection Label;
- Larger appliance have met requirements of approval agencies; (UL,CSA, CE)
- Developing CFD mathematical models of leak scenarios



Business Plan Update

- Adjust to delays in bringing fuel cell vehicles to market & slower than expected introduction of fuel cell buses in North America:
  - Smaller fuelers for small fleet fuel applications
  - Market intro for PFA delayed (2008)
- "Energy Station" near term focus :
  - Evolve "dual role" Infrastructure backup power and vehicle refueling
  - Promote hydrogen ICE as low cost way to develop infrastructure

ICE: Internal Combustion Engines

Challenges

- Achieving Emissions:
  - Easier to deal with large sources
  - Realize regional opportunities where power is clean
  - Long-term will help finance renewable energy
- Fuel cost margins tight
  - Monetize emission benefits ($100 per ton for CO_2) results in $1 credit per kg ($3.50 per kg)
- Fuel cell gap – no cars until 2010
  - Bridge gap with ICE – building infrastructure, testing components will accelerate fuel cell commercialization

Cost Model

- Hydrogen costs of $3.50 per kg are achievable
  - Appliance cost : $300 per kW
  - o/m + CRF = $60 per kW per y (20%) or .75¢/kWh (assuming 40% capacity factor)
  - Electricity cost: $2.20 /kg @ .04¢/kWh
  - Total: $3.14/kg

Next Steps

Commercialization:

- System available in two sizes: 450 SCFH & 1350 SCFH
- Offer "turn-key" solution:
  - complete station design including back-up power option
  - fuel appliance, storage, dispenser
  - safety analysis
  - service contract

Mixtures of Hydrogen and Natural Gas (HCNG) for Heavy-Duty Applications

Dr. Kirk Collier
Collier Technologies

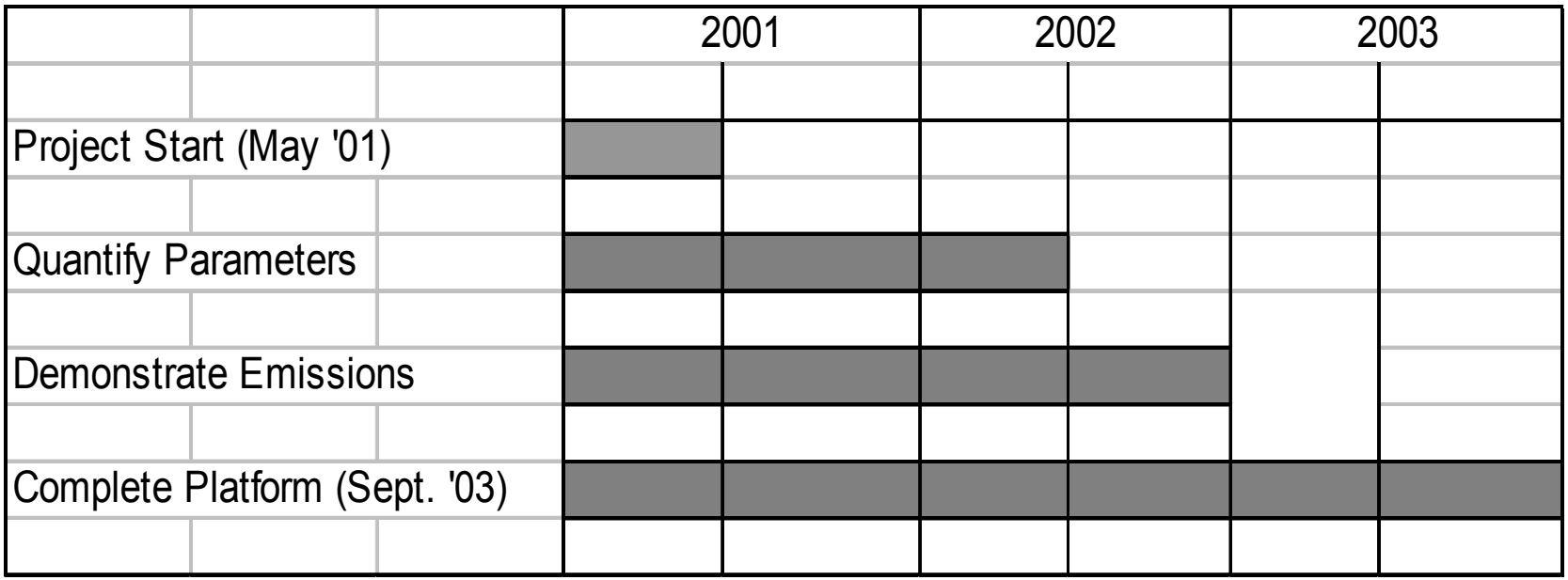
Relevance/Objectives

- Accelerate Hydrogen Refueling Infrastructure
  - Creating cost-effective applications for hydrogen
- Influence on Codes and Standards
  - Operation of vehicles will provide important data base for developing regulations.
- Enhance the Development of Electricity-Hydrogen Co-Production
  - Partnerships with electric utilities

Approach

- Use Hydrogen as an Additive to Natural Gas.
  - Reduces exhaust emissions dramatically
  - Improves engine efficiency
  - Utilizes existing engine technology
    - No new technology development required
    - No new repair and maintenance infrastructure required

Project Timeline



Accomplishments/Progress

Emissions from Las Vegas Bus Engine

Individual Modes	NOx (g/bhp-hr)	THC (g/bhp-hr)	NMHC (g/bhp-hr)	CO (g/bhp-hr)	Weighting Factor
1800 rpm - 100% Load	0.15	3.70	0.11	0.00	0.15
- 75% Load	0.12	3.86	0.12	0.00	0.15
- 50% Load	0.09	4.86	0.15	0.00	0.15
10% Load	0.13	8.82	0.26	0.00	0.1
2800 rpm - 100% Load	0.21	3.31	0.10	0.00	0.1
- 75% Load	0.15	3.77	0.11	0.00	0.1
- 50% Load	0.10	5.75	0.17	0.00	0.1
- Idle	0.22	7.21	0.22	0.00	0.15
Weighted 8 Mode (g/bhp-hr)	0.15	5.11	0.15		
Weighted 8 Mode (g/kw-hr)	0.20	6.85	0.21		

Collaborations

- City of Las Vegas
- Hess Microgen (subsidiary of Hess Oil)
- University of California-Davis
- Air Products and Chemicals
- British Columbia Hydroelectric
- Arizona Public Service Company
- Penn State University

Future Plans

- Will License Engine Design and Controls for Powering and Repowering Heavy-Duty Vehicles
  - Diesel bus repowering seen as large market
  - Natural gas bus repowering also a market
  - Cut-Away vans are viable market
  - Fleets that do not currently comply with future emissions regulations.

Previous Q&A

- Previous Work Has Not Used Conventional Heavy-Duty Engine Bases
  - Our previous work has used racing engine platforms because we could purchase components compatible with hydrogen fuel.
  - Our latest work has focused on existing heavy-duty engine platforms with components and controls designed specifically for hydrogen.

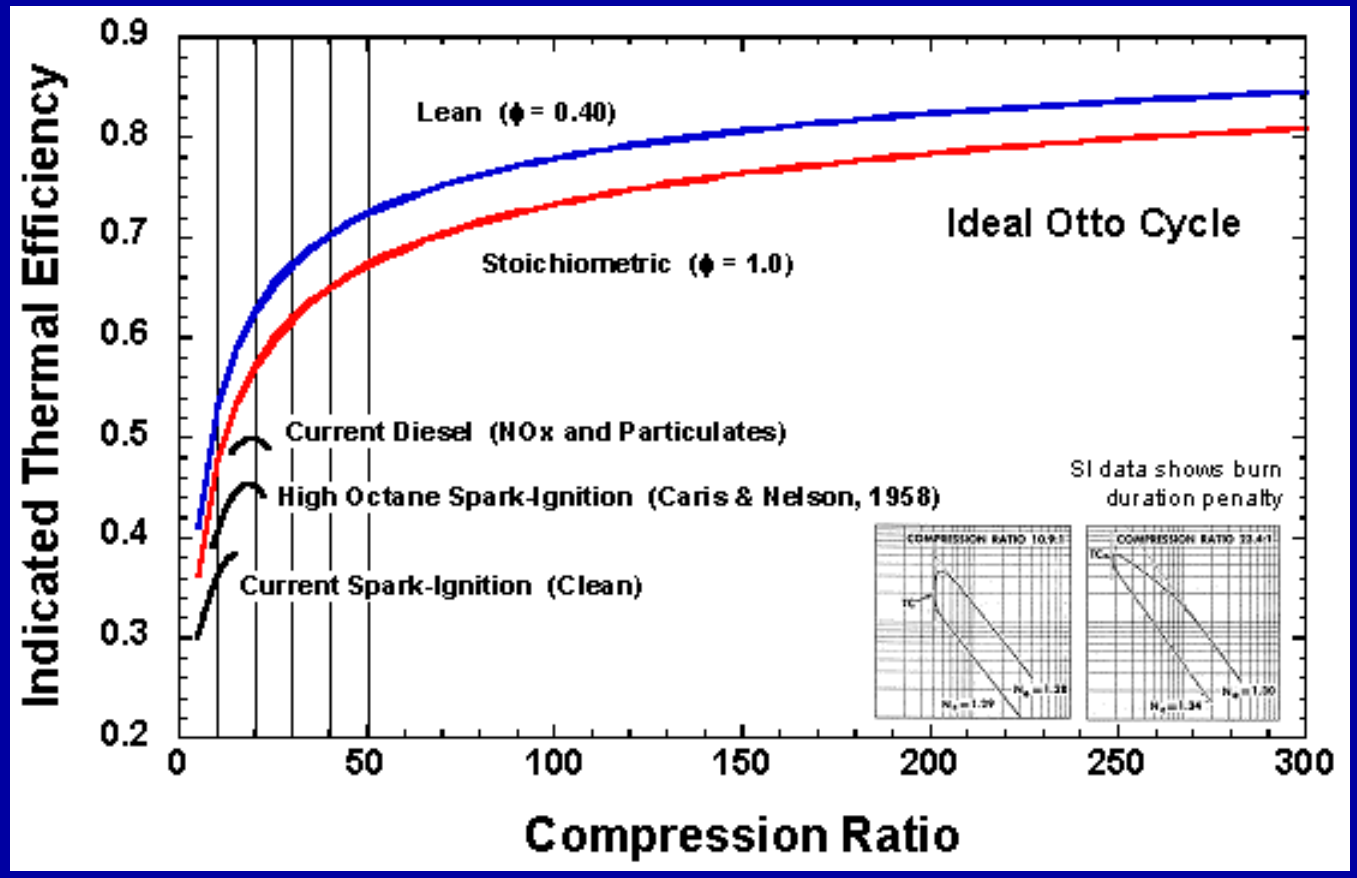
Toward the Development of a Thermodynamic Fuel Cell

Peter Van Blarigan
Scott Goldsborough
Sandia National Laboratories

Hydrogen, Fuel Cells & Infrastructure Technologies Program
Merit Review and Peer Evaluation
May 19-22, 2003

Goal

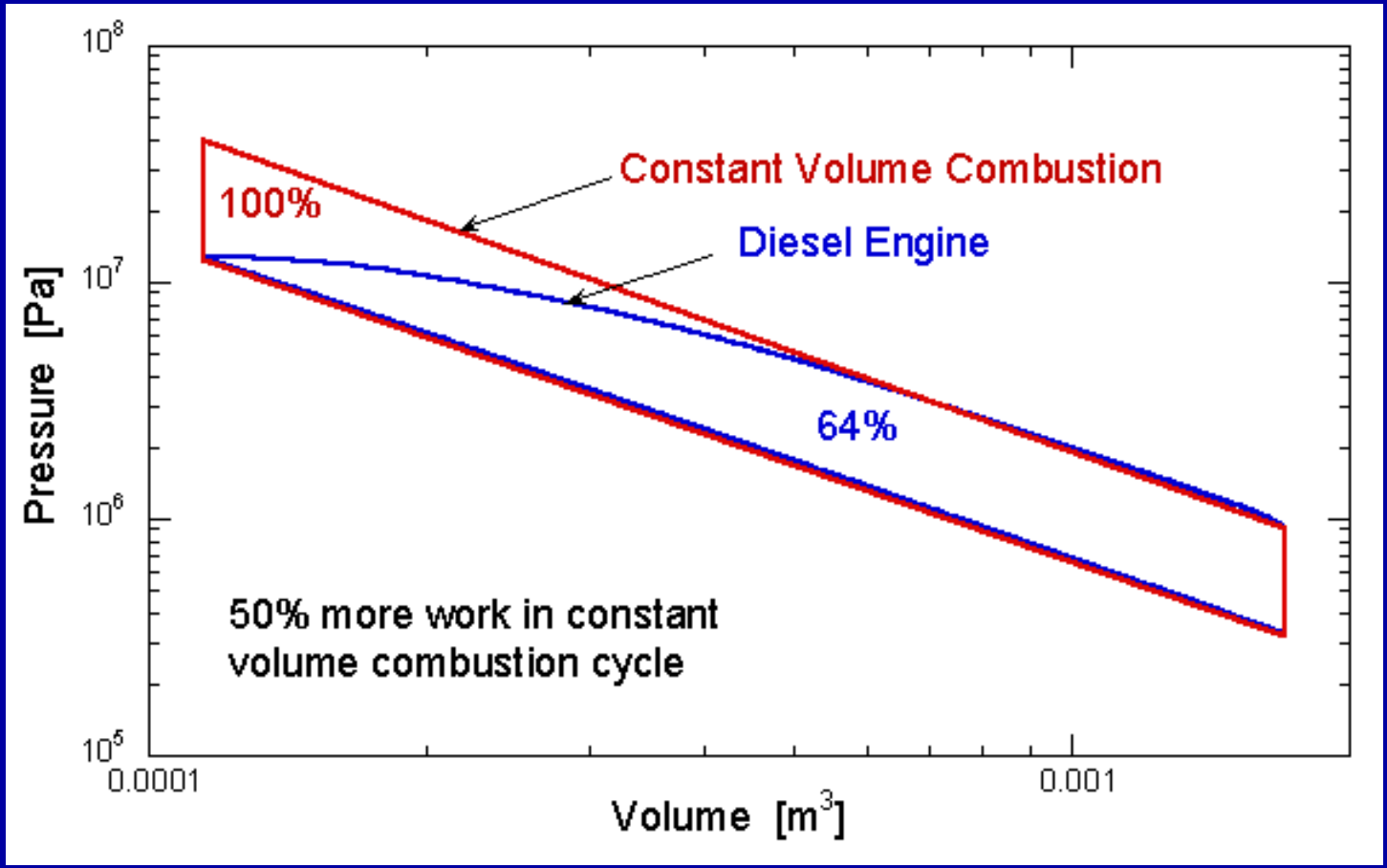
Develop an ideal, thermodynamic cycle based electrical generator.



→ Otto cycle is fundamentally capable of high (>80%) conversion efficiency.

Sandia National Laboratories

Illustration of burn duration penalty



➜ **Modern 4 stroke Diesel is extreme case, pressure limitations control design.**

Ideal, thermodynamic (Otto) cycle is constant-volume combustion

Possible approaches

Spark-Ignition /Diesel

Homogeneous Charge Compression Ignition (HCCI)

Piston stops and waits for combustion to finish.

Combustion is so fast that piston is stationary during burn.

Details

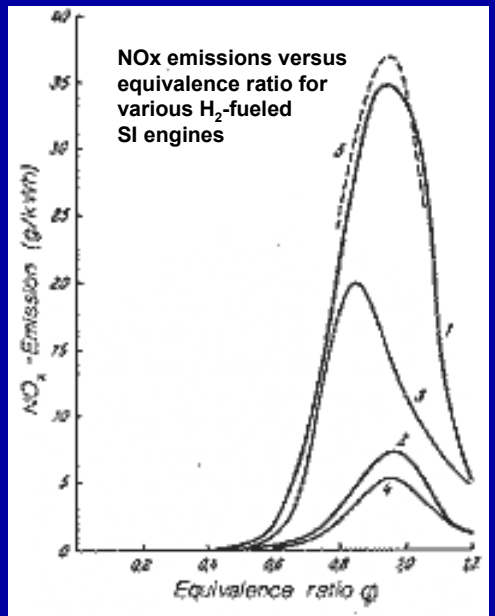
- Mechanically complex.
- Greater heat loss.
- Compression ratio limited by knock (SI).

- Loss of timing control.

Sandia National Laboratories

Homogeneous Charge Compression Ignition

- Fuel / air premixed.
- Charge combusts due to compression heating.
  - No flame propagation / diffusion mixing required
  - Chemical kinetics dominate (VERY FAST!)
- Can achieve constant-volume combustion.
- Multi-fuel capable → no flammability limits.
- NOx control by dilution.
  - → limits combustion temperatures



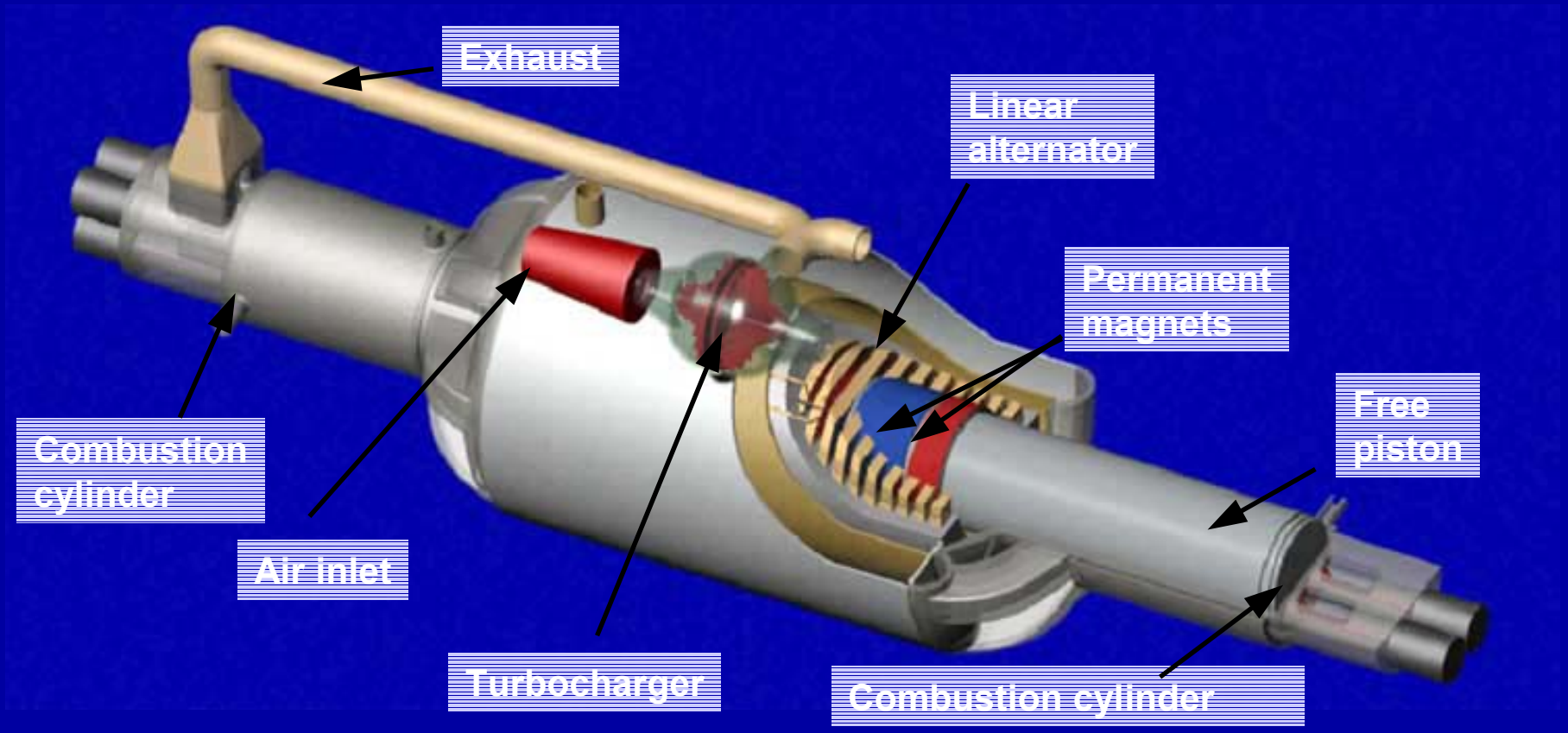
Sandia National Laboratories

Device utilizing HCCI to its full potential will:

- Compress the fuel / air mixture rapidly to reach high compression ratio at ignition.
- Electronically control compression ratio.
- Be capable of surviving high peak, short duration pressure pulse.
- Have mechanical simplicity for high reliability / low cost potential.

Sandia National Laboratories

Thermodynamic Fuel Cell

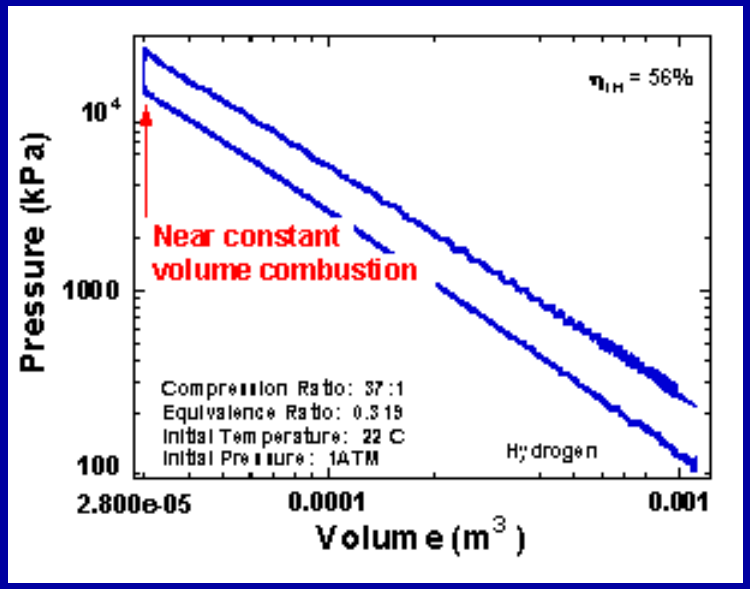


- Free piston → rapid compression
- HCCI combustion driven
- Direct electrical output

Sandia National Laboratories

Characteristics of Thermodynamic Fuel Cell

- Optimizes thermodynamic cycle with free piston, rapid compression.
- Combustion experiments show high compression ratio and high efficiency, with near 0 NOx emissions.
- Utilizes linear alternator for compression ratio control and mechanical simplicity.



Typical pressure – volume data from a free piston, Rapid Compression Expansion Machine

- Compression is developed inertially – no heavy support components required.
- Linear alternator is electromagnetic equivalent of brushless, direct-current permanent magnet generator, +96% efficient.

Sandia National Laboratories

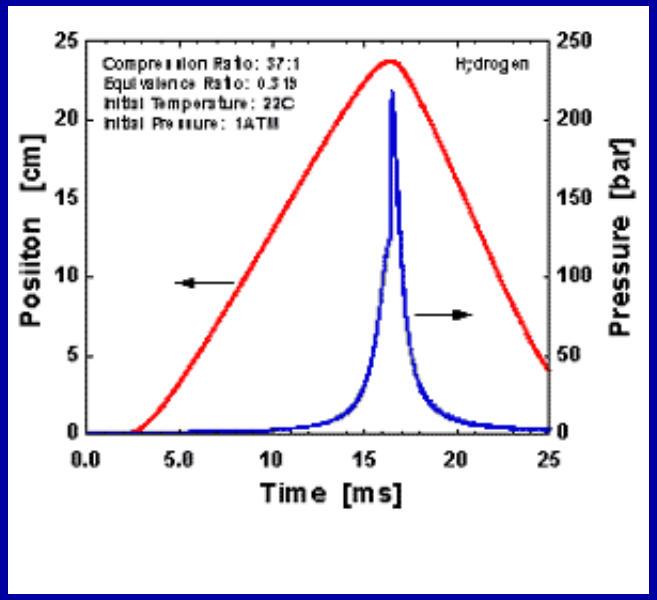
Approach to Development

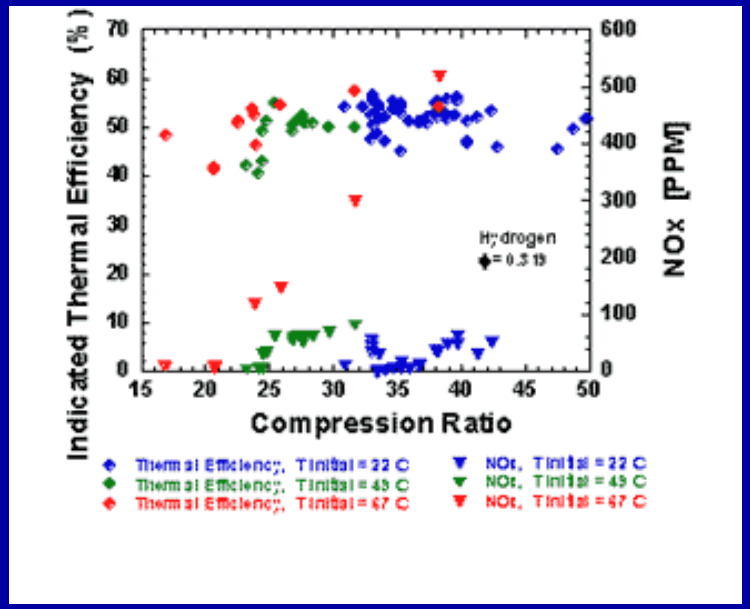
- Demonstrate HCCI combustion potential.
- Develop linear alternator.
- Develop inlet / exhaust process.

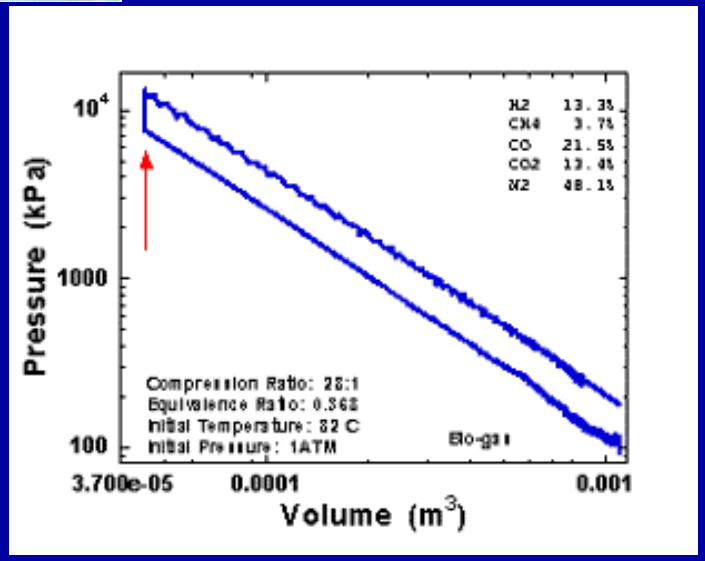
∴ Combine critical components into 30kW prototype research engine.

Sandia National Laboratories

RCEM Combustion Experiment







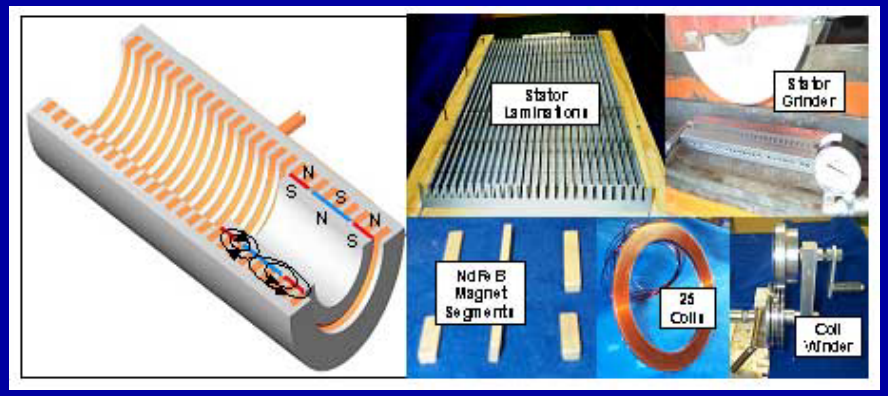
Pressure – volume data using low BTU bio-gas

Sandia National Laboratories

Linear Alternator

Parallel development plan

- **In-house (Sandia / Magsoft)**
  - Electromagnetic modeling (FLUX2D)
    - Describe velocity profile, anisotropic materials. Calculate I^2R losses.
  - Parametric variations to focus on optimal configuration.



- **Magnequench International**
  - Design, fabricate and supply at no cost.

Experimental verification

Alternator Test Rig

Sandia National Laboratories

Intake / Exhaust System

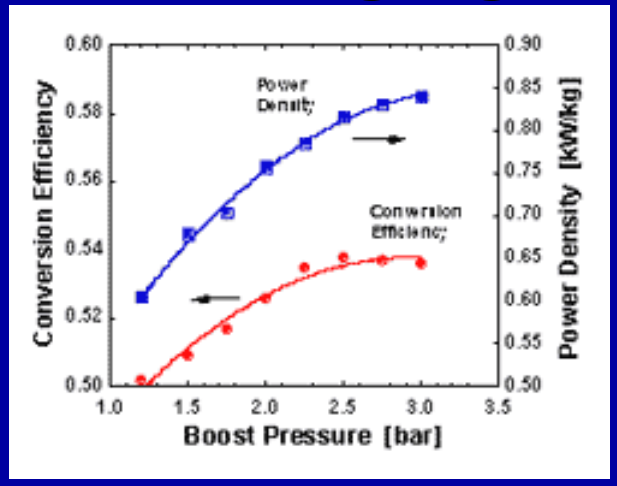
Critical for efficiency / emissions goals

- Charge preparation for HCCI combustion.
- Control of short-circuiting (fuel loss, HC emissions).
- Limit pumping power.

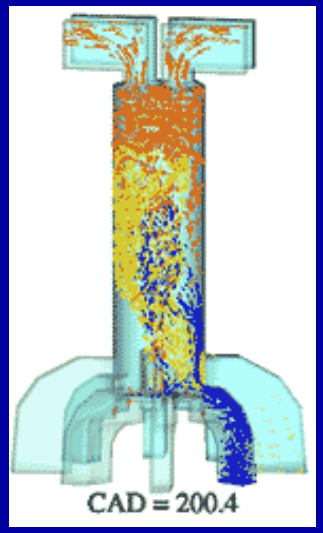
CFD modeling and visualization

- KIVA3V / Ensight.
- Parametric optimization.

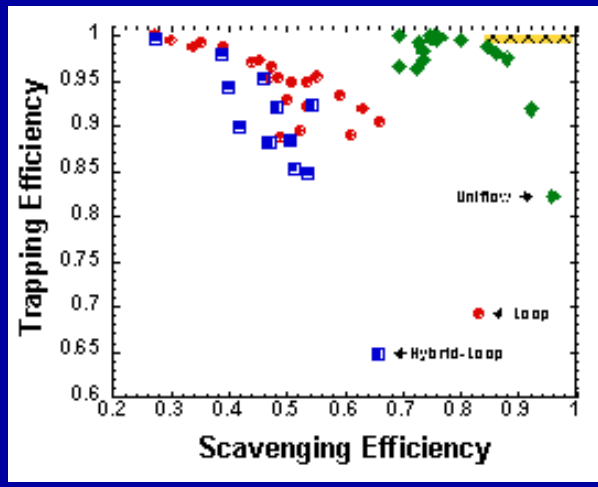
Turbocharging



Increase in fuel-to-electricity conversion efficiency, and power density with increasing boost pressures



Stratified Scavenging, uniflow design



Scavenging performance for various charge delivery methods; desired operating region illustrated

Sandia National Laboratories

Relevance

- Thermodynamic fuel cell provides electrochemical fuel cell like performance.
- Utilizes highly developed reciprocating engine technology.
- Near term cost will be low.
- Multi-fuel capability important.
- Provides an alternative, competitive path for hydrogen conversion.
- Meets FreedomCAR 2010 goals for internal combustion systems operating on hydrogen or hydrocarbons.

	GOAL	Thermodynamic fuel cell
Efficiency	45%	50%
Cost	$30 / kW	$20 / kW
Emissions	Meet Standards	≈ 0

Sandia National Laboratories

FY 2003 Progress

- Scott Goldsborough, PhD completed.
- Investigation of turbocharging / hybrid gas turbine systems performance.
- Preliminary 4kW gas compressor design.
- Hans Aichlmayr joins group, postdoc appointee.
- Magnequench linear alternator testing.
- 5 presentations.
- 2 publications.

Sandia National Laboratories

Interactions / Partnerships

Caterpillar – Inlet / exhaust process, free piston technology

Magnequench – Permanent magnet / linear alternator

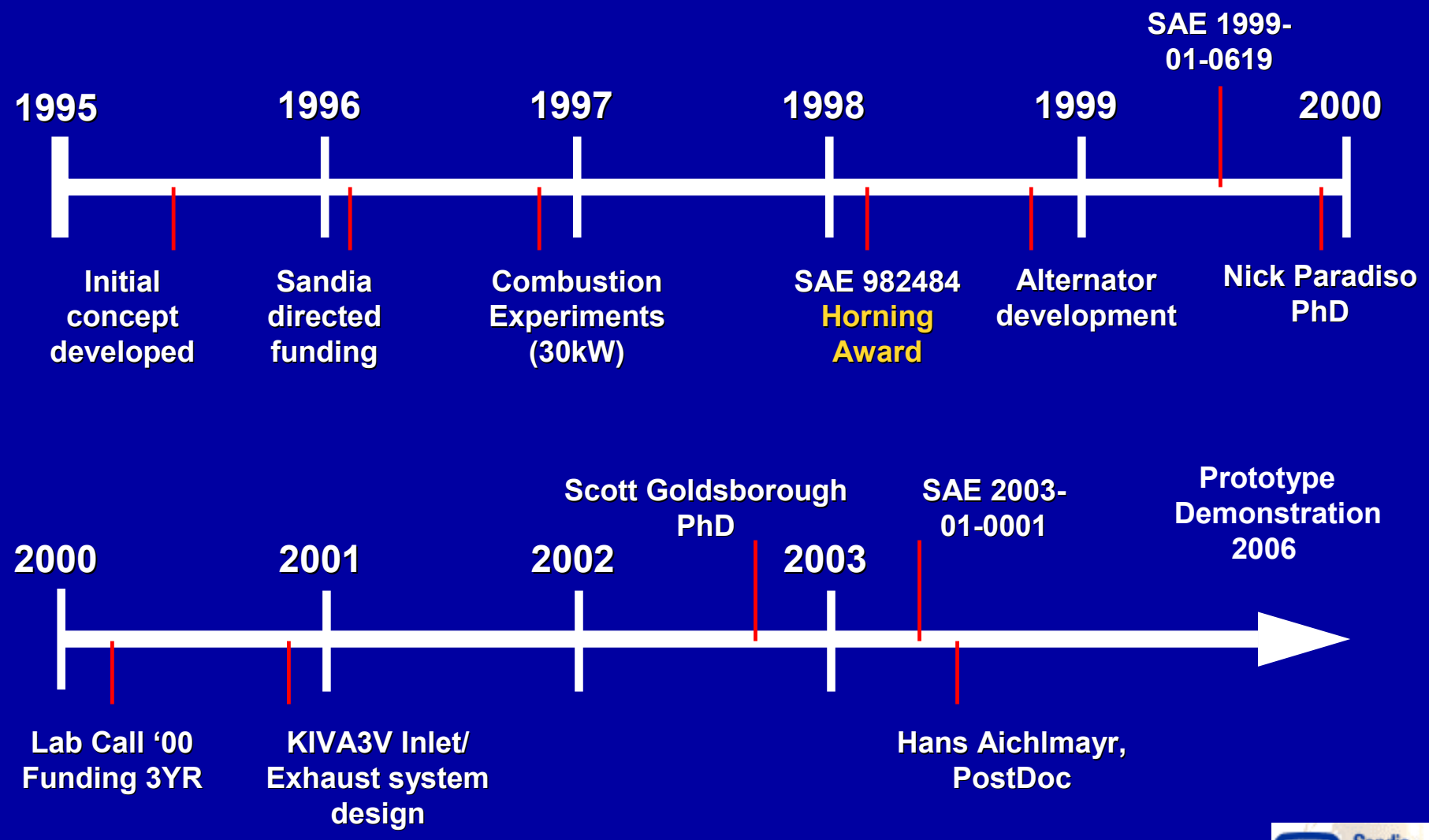
Magsoft – Alternator modeling

Lotus Engineering – Piston engine design

DOE
- Office of Distributed Energy and Electricity Reliability
  Distributed Energy Resources
- Office of FreedomCAR and Vehicle Technologies
  Engine and Emissions Control Technologies

Sandia National Laboratories

Timeline


SAE 1999-01-0619
1995
1996
1997
1998
1999
2000
Initial concept developed
Sandia directed funding
Combustion Experiments (30kW)
SAE 982484 Horning Award
Alternator development
Nick Paradiso PhD
Scott Goldsborough PhD
SAE 2003-01-0001
Prototype Demonstration 2006
2000
2001
2002
2003
Lab Call '00 Funding 3YR
KIVA3V Inlet/ Exhaust system design
Hans Aichlmayr, PostDoc

Reduced Turbine Emissions Using Hydrogen-Enriched Fuels

Robert W. Schefer
Joseph C. Oefelein
Jay O. Keller

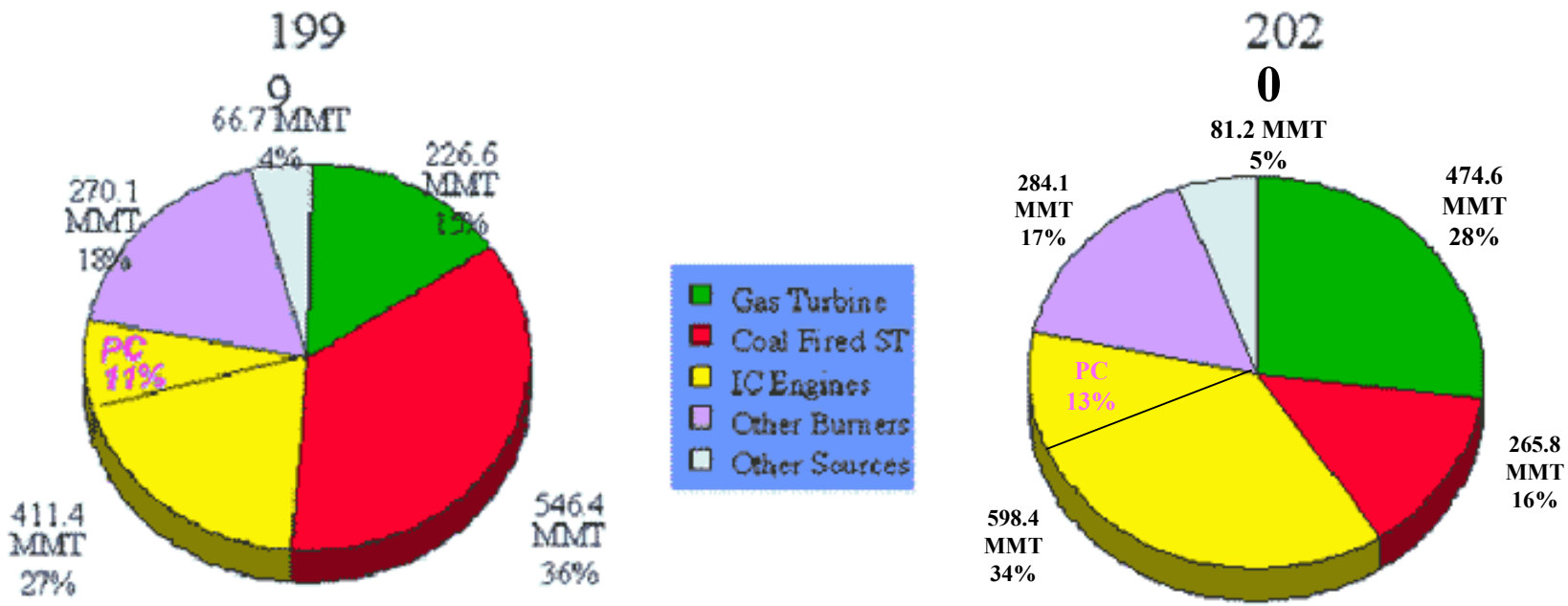
Combustion Research Facility
Sandia National Laboratories
Livermore CA 94551

2003 Hydrogen and Fuel Cells Merit Review Meeting
May 19-22, Berkeley, CA

Relevance to DOE, FreedomCAR, and Hydrogen Technical Barriers and Targets

- Use of hydrogen in gas turbines provides a driver for increased hydrogen production and infrastructure development
  - Mechanism for near-term utilization of hydrogen
  - Relaxes more stringent and costly requirements of feed stock purity for fuel cell utilization
  - Field testing of emerging production technologies (approached by a major oil company to use H_2-enriched turbines as market pull for their developing H_2 production hardware)
- Added Environmental Benefits
  - Hydrogen-burning gas turbines enable optimal use of fuel lean combustion for NO_x control
  - Replaces hydrocarbon fuels for reduced CO_2 emissions
- Aids in the attainment of energy independence from foreign sources
  - Low-heating and medium-heating value fuels containing H_2 can provide significant source of cost-effective fuels for gas turbines
  - Enables use of domestically-produced H_2

U.S. CO_2 Emissions

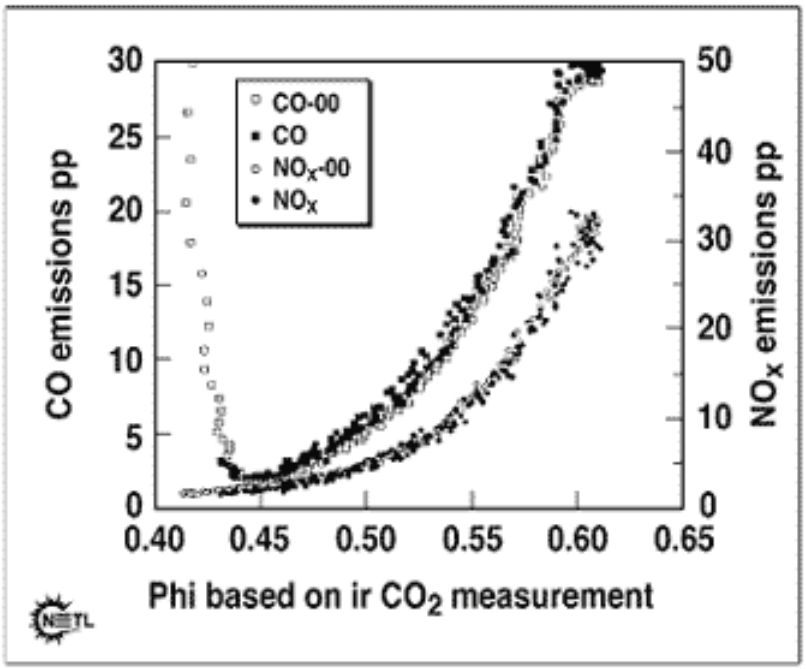


- Gas turbines are the fastest growing power production technology
- Passenger cars account for only a small fraction of total CO_2 emissions

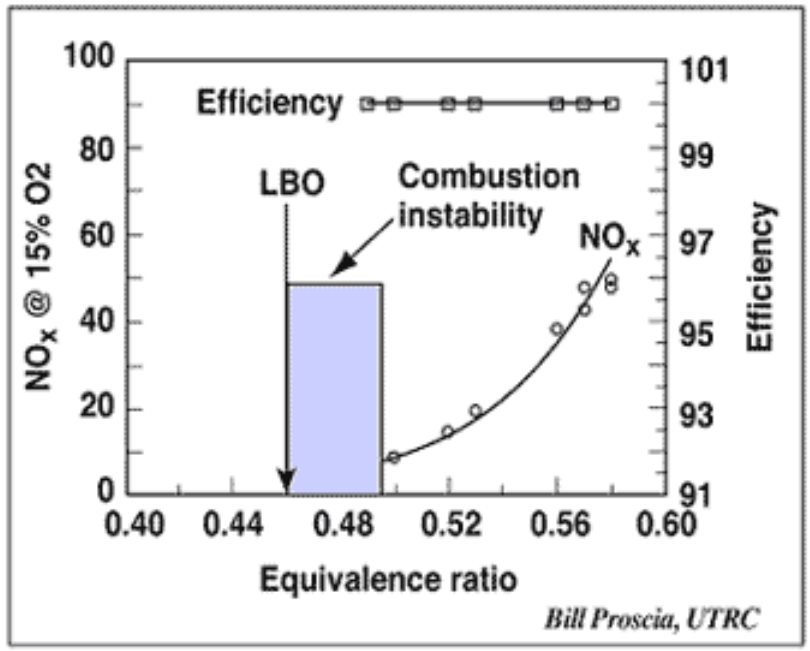
Source: Analysis of Strategies for Reducing Multiple Emissions from Power Plants: Sulfur Dioxide, Nitrogen Oxides, and Carbon Dioxide, EIA, Dec 2000

Trade-offs Associated with Lean Premixed Combustion Systems

- Lean Premixed Combustion (LPC) is method of choice for NO_x control in Gas Turbines



At ultra lean conditions a tradeoff exists between NOx and CO emissions



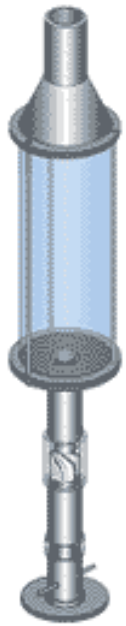
Ultimately, lean operation is limited by the onset of flame instability and blowout

- ***Hydrogen-enrichment extends the lean flammability limit and reduces CO emissions***

Approach

Lean Premixed Swirl Burner Experiments

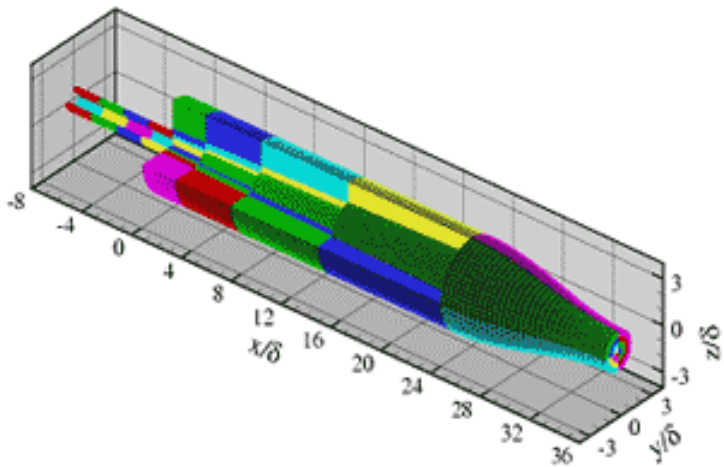
- Establish scientific data base for lean premixed swirl burners typical of Dry Low NO_x gas turbine burners
- Emphasize H_2-enriched fuels over wide range of pressures
- Design and fabricate a lean premixed swirl burner with well-characterized boundary and flow conditions
- Quantify effects of H_2 addition on flame stability and emissions
- Leverage existing Sandia expertise in experimental diagnostics development



Sandia CRF
Confined
Flow Burner

Large Eddy Simulation Model Development

- Parallel development of next generation simulation capability based on Large Eddy Simulation (LES)
- Detailed model development and validation at atmospheric pressure
- Extended validation at realistic operating pressures and temperatures
- Bridge gap between laboratory and gas turbine environment through collaborations with industry



Sandia National Laboratories
Combustion Research Facility

Project Timeline

Task Name / Milestone	2001				2002				2003				2004				2005			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Lean Premixed Swirl Burner																				
Fabricate & characterize CFB burner operation																				
Obtain nonreacting & reacting flow databases																				
LES model development & validation																				
Obtain low-pressure database in SimVal burner																				
Obtain high-pressure database in SimVal burner																				
Hydrogen Burner Collaboration (NASA)																				
Characterize burner operation																				
Identify design improvements & implement																				
Industrial Collaboration																				
Implement hardware & develop test matrix																				
Identify problem areas for potential H_2 use																				
Demonstrate merits of H_2 addition																				
Economic Analysis																				
Establish base case cost & emissions																				
Evaluate economics of H_2 addition for NO_x control																				
Extend cost analysis to include carbon credits																				
International Collaborations																				
Parse off program areas & solicit funding																				
Develop hierarchy of test burners																				
Obtain experimental databases for chosen flames																				
Collaborative model validation and development																				

Current Status

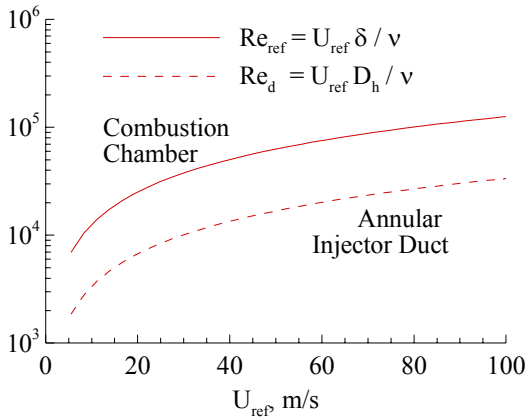
- **Comprehensive experimental-computational program focused on *hydrogen-enriched* lean premixed gas turbines established**
  - **Detailed diagnostics being applied in swirling-flow dump-combustor configurations**
  - **Benchmark experimental databases under development**
- **Comprehensive simulation capability based on the Large Eddy Simulation (LES) technique in place**
  - **Massively-parallel high-fidelity simulations of key target flames being performed**
  - **Device relevant issues related to transient combustion being systematically treated**
- **Hierarchy of laboratory-scale burners and target flames identified and at various stages of development**
  - **Emphasis placed on complex phenomena associated with *hydrogen-enriched* lean premixed combustion**
  - **Detailed subgrid-scale model development and collaborative model comparisons underway**

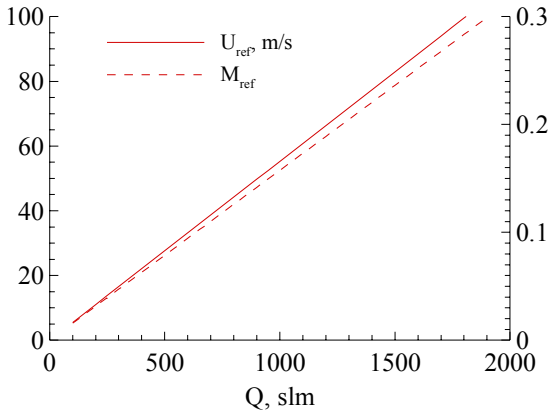
CRF Confined Flow Burner

- *Established as test bed for all working groups*

- **Design provides well-defined non-ambiguous boundary conditions for LES**
- **Makes optimal use of advanced laboratory and diagnostic capabilities at CRF**

- **Injector Section (Note $D_h = D_o - D_i$)**
  - **D_i = 20 mm (centerbody diameter)**
  - **D_o/D_i = 1.4**
  - **L = 320 mm (16 D_i)**
  - **Choked at inlet, houses premixing-, swirler-, and wake-mixing sections**
- **Burner Section**
  - **D_b = 115 mm (5.75 D_i)**
  - **L_b = 485 mm (24.25 D_i)**
  - **Ceramic face plate, quartz outer wall**
- **Nozzle Section**
  - **D_e = 50 mm (2.5 D_i)**
  - **L_n = 230 mm (11.5 D_i)**
  - **High Mach number flow at exit**



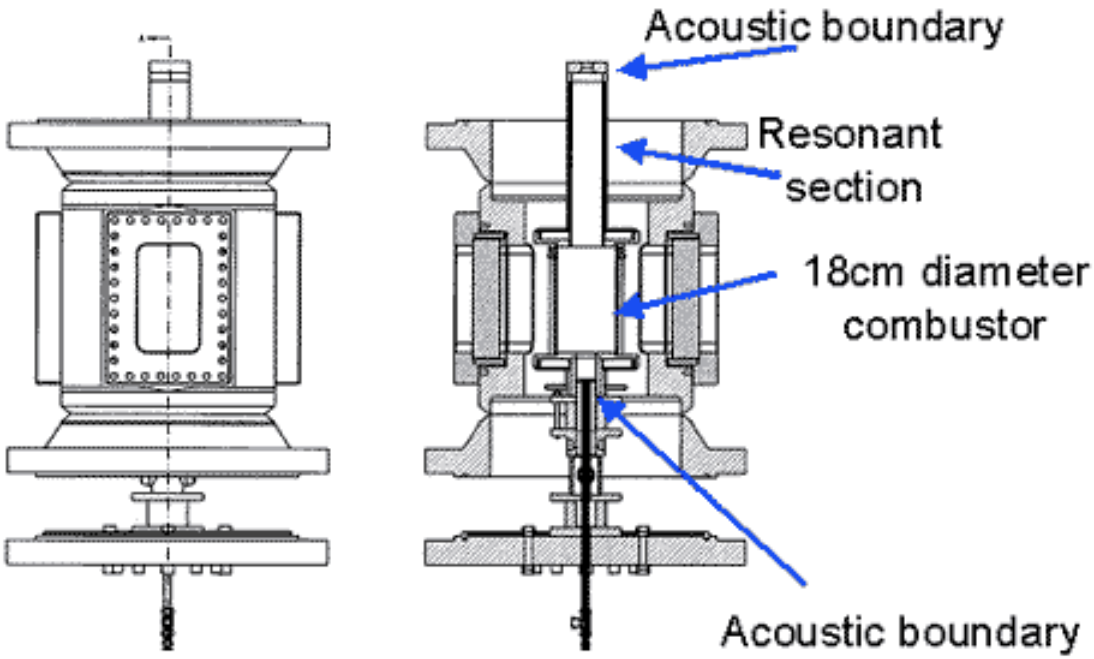


Sandia National Laboratories
Combustion Research Facility

Complimentary to NETL SimVal Burner

SimVal Combustor

Pressure:
30 atm max.
Inlet temperature:
800 K max.
Air flow:
1.4 kg/s max
Fuel:
Natural Gas



- **CRF burner will be used to provide complete high-fidelity validation datasets at 1 atmosphere**
- **NETL burner will facilitate investigations at device relevant pressures.**
- **NETL has delivered SimVal hardware to CRF**

Experimental Capabilities

Diagnostic	Quantity	Comments
Particle Image Velocimetry	Instantaneous velocity field	Velocity, vorticity and strain fields.
OH and CH PLIF	Instantaneous OH/CH distributions	Flame zone structure and characteristics (thickness, local extinction).
Simultaneous OH & CH PLIF/PIV	Simultaneous velocity/OH/CH fields	Turbulence/flame interactions. Flame stability/extinction
Simultaneous OH and CO PLIF	Forward reaction rate of $CO+OH=CO_2+H$	Characterize CO production and burnout
Simultaneous Raman/Rayleigh/LIF	N_2, O_2, CH_4, H_2, H_2O, CO_2, CO, OH, NO and Temperature	Turbulent mixing, flame structure and chemistry. Validation of flame chemistry models.

LES Capabilities

- **Theoretical Framework**
  - Fully-coupled compressible conservation equations of mass, momentum, total energy, species (multicomponent, mixture-average)
  - Generalized treatment of equation of state, thermodynamics and transport (high-pressure, real-gas, liquid, cryogenic fluids …)
  - Dynamic modeling for treatment of subgrid-scale turbulence and scalar mixing
  - Full treatment of multiple-scalar mixing, finite-rate chemical kinetics
  - Full treatment of multiphase phenomena, particulates, sprays
- **Numerical Framework**
  - Implicit multistage scheme using dual-time stepping with generalized all-Mach-number preconditioning (Eulerian-Lagrangian formulation)
  - Fully-conservative, staggered, finite-volume differencing in generalized curvilinear coordinates, time-varying mesh capability
  - Highly scalable, massively parallel with general distributed multi-block domain decomposition

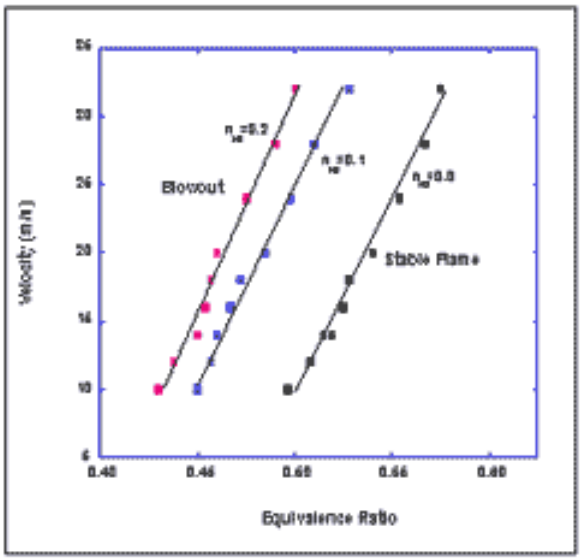
Validation Sequence for Target Flames

- **Cold-flow PIV, LDV measurements**
  - Time-averaged characterization of burner inlet conditions
  - Instantaneous, time-averaged structure of planar velocity field
  - Time-averaged profiles of mean, rms, cross-stress terms
- **Reacting PIV, LDV, PLIF measurements**
  - Companion datasets analogous to cold-flow measurements above
  - Instantaneous, time-averaged characterization of minor species fields
  - Time-averaged profiles of simultaneous velocity-scalar correlations
  - Instantaneous, time-averaged flame zone structure
- **Raman-Rayleigh-LIF point/line measurements**
  - Instantaneous, time-averaged characterization major species, temperature
  - Instantaneous reaction-rate imaging

CRF Burner : *Experimental Progress*

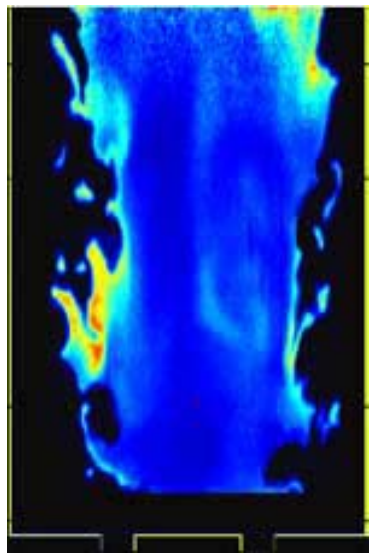
- Burner operation characterized over a range of conditions ✓

- Quantified effect of H_2 addition on lean flame stability ✓

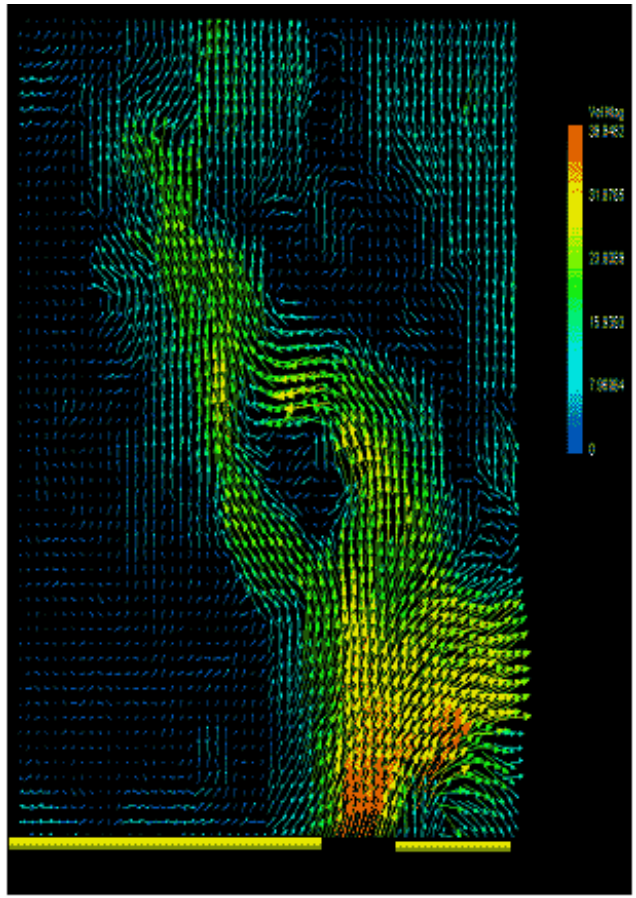


- Flame structure characterized using OH imaging ✓

OH PLIF Image



Particle Image Velocimetry



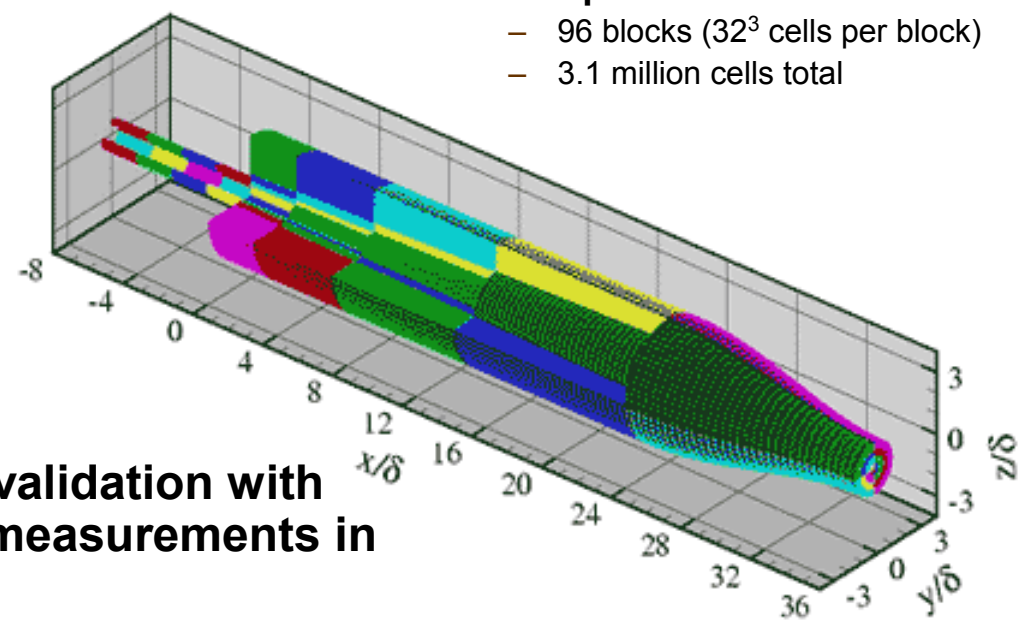
- Velocity field characterized in nonreacting flow ✓

Sandia National Laboratories
Combustion Research Facility

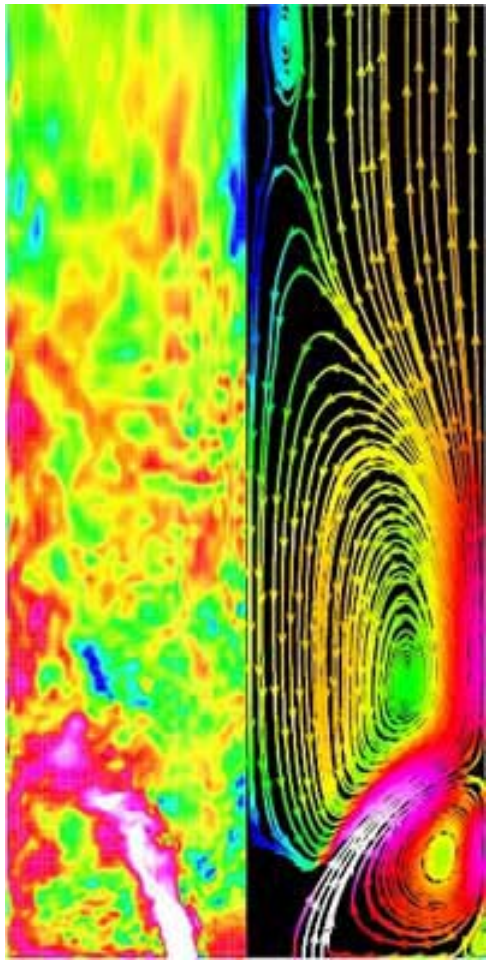
CRF Burner: *Model Progress*

- Baseline operating conditions, target cases, and corresponding grid configuration established ✓
- Grid resolution requirements for high-fidelity (wall-resolved) simulations of target cases established ✓
- First high-fidelity simulations for validation with Particle-Image-Velocimetry (PIV) measurements in progress
- Development of multiple-scalar combustion closure based on approximate deconvolution methodology in progress

- **Generalized multi-block decomposition**
  - 96 blocks (32^3 cells per block)
  - 3.1 million cells total



Instantaneous and Mean Flow Characteristics Established

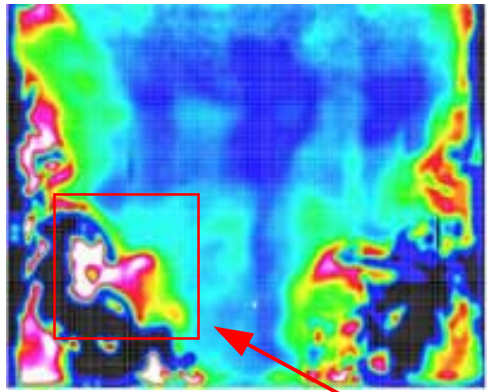


Flame structure:

- Premixed flame fronts
- Local quenching.
- Extinction, re-ignition
- Strained and freely propagating

Flow structure:

- Primary toroidal recirculation zone
- Unsteady stagnation point
- Flow separation and reattachment
- Secondary, tertiary recirculation zones



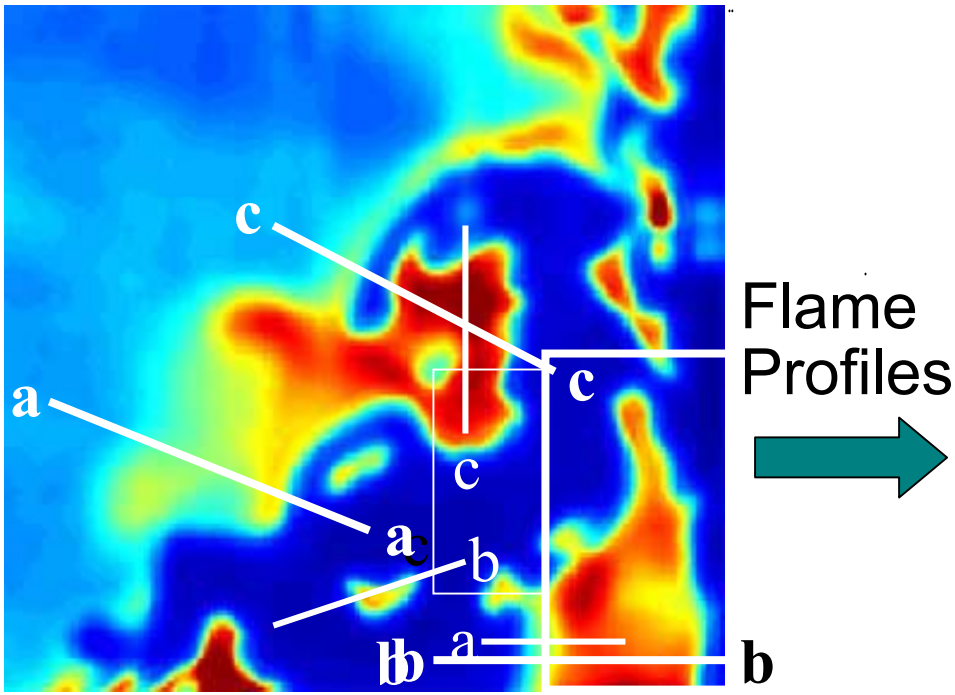
OH measurements highlight local flame characteristics

LES calculations highlight complex fluid dynamic interactions

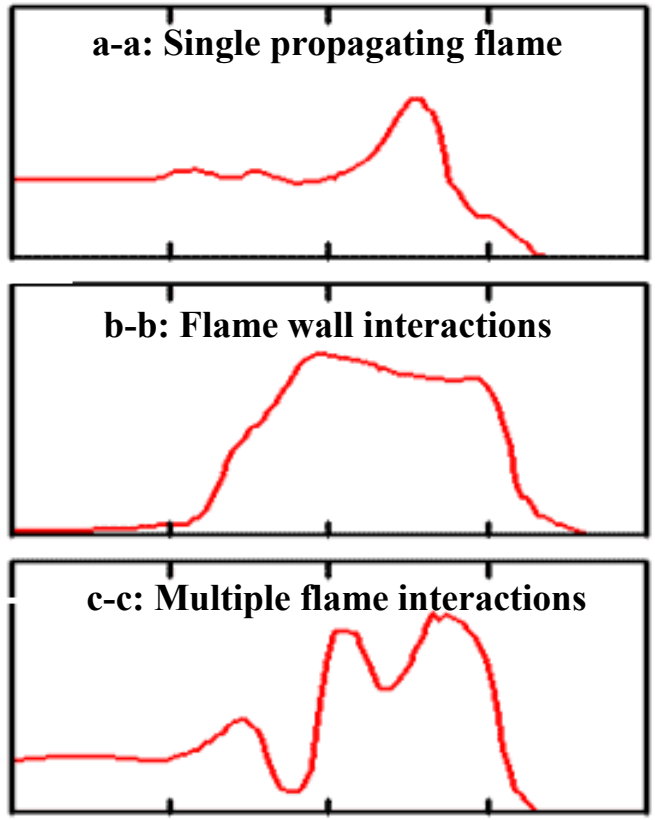
- **Turbulent combustion involves strong interaction between flow and chemistry**
- **Plots left show turbulent velocity field obtained using LES**
- **Plots above show corresponding OH PLIF image and flame luminosity**

Local Flame Characteristics Established

Instantaneous OH Field

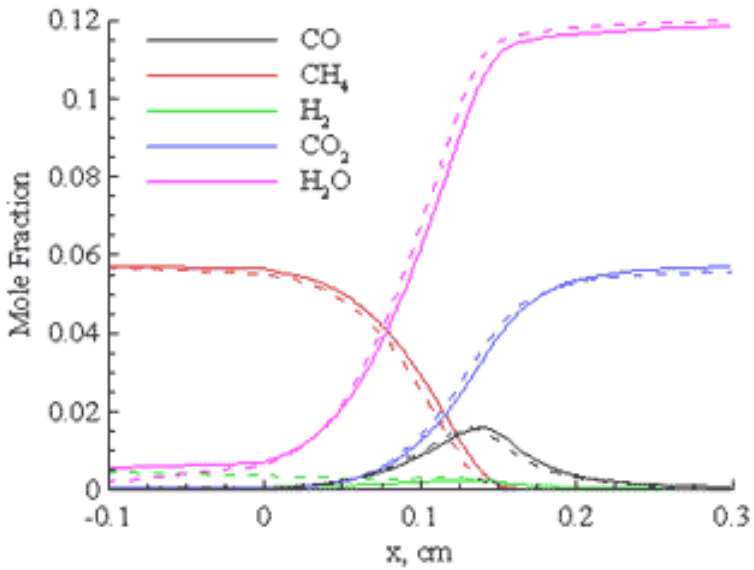


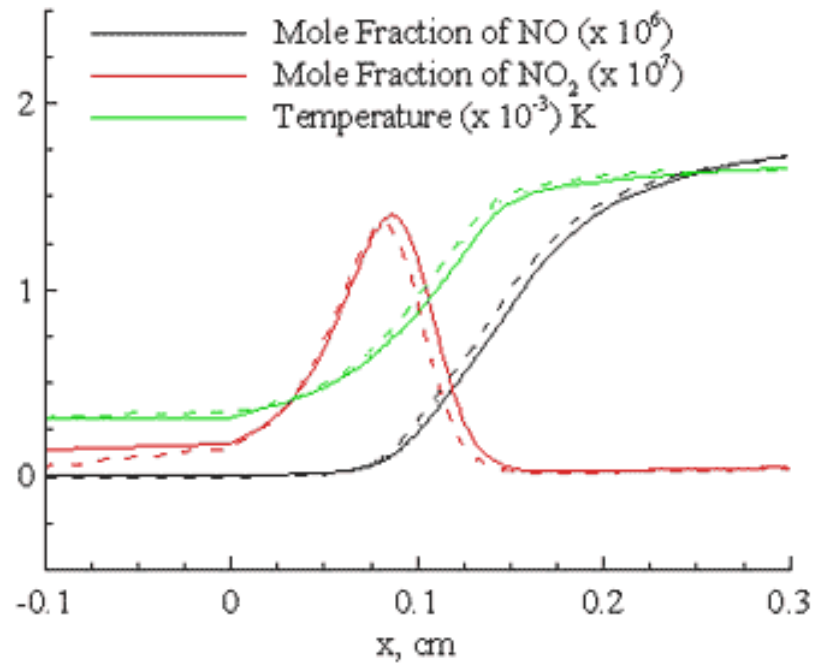
Flame Profiles



Flame structure changes locally with mixture properties and fluid dynamics

Ideal Flame Structure With Detailed Chemical Kinetics Analyzed





- **Solid lines represent pure CH_4-Air flame (Φ_{Global} = 0.6)**
- **Dashed lines represent CH_4-Air flame enriched with 10 % H_2**

Current Collaborations

University

Vanderbuilt (Diagnostics)
Heidelberg (Kinetics)
Darmstadt (LES Development)
Lund Technical (Diagnostics)
Cranfield (Diagostics)
U. Oklahoma (LES Validation)
Cornell (Diagnostics)
U. London (LES Validation)
Toronto (Diagnostics)

Government

Sandia (LES Development & Validation, Diagnostics)
NETL(LES Validation, Diagnostics)
WPAFB (LES Validation, Diagnostics)
AFOSR (LES Validation, Diagnostics)
NASA (Diagnostics, LES Validation)

Industrial

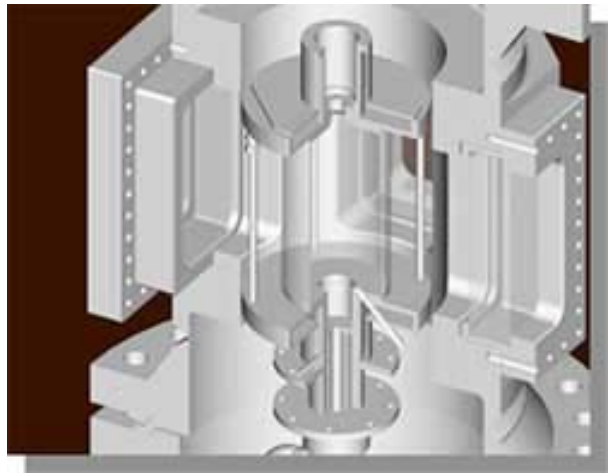
General Electric (LES Development)
Pratt & Whitney (LES Development)
Rolls Royce (LES Development)
Praxair (H_2 Utilization)
Pinnacle West (H_2 Utilization)

NETL Collaboration: *Approach & Progress*

Approach

- Extend data base for lean premixed swirl burners to realistic pressures and temperature. Emphasis on H_2-enriched fuels
- Atmospheric-pressure tests in SimVal burner at Sandia; high-pressure tests at NETL
- Utilize Sandia's diagnostic expertise for the development of high pressure diagnostics in realistic gas turbine environments

SimVal Burner



Progress

Sandia Burner Completed ✓

- Atmospheric pressure operation
- Design optimized for Sandia CRF laboratory facilities
- Full optical access for optimal use
- Of advanced diagnostics

NETL Burner Completed ✓

- Operation to 30 atmospheres
- Inlet temperature to 800 K
- Optical access
- Limited datasets at elevated pressure

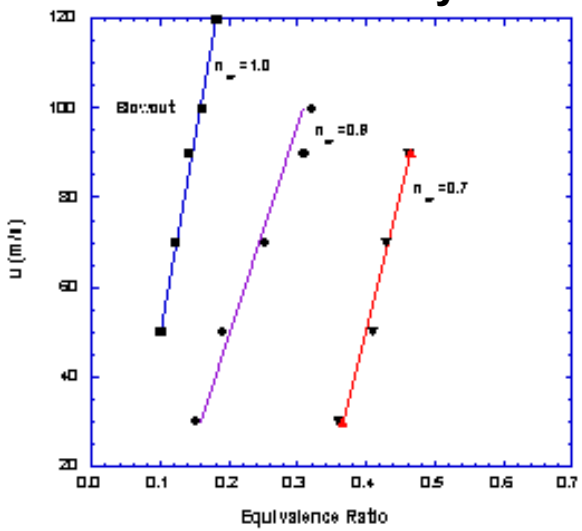
NASA Collaboration: *Approach & Progress*

Approach

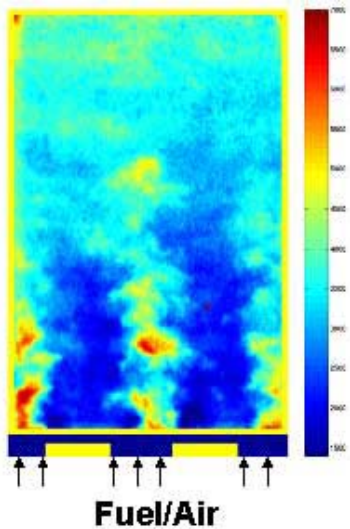
- Program focuses on the development of H_2-fueled burner for aircraft application
- Atmospheric- pressure testing at Sandia high-pressure tests at NASA GRC

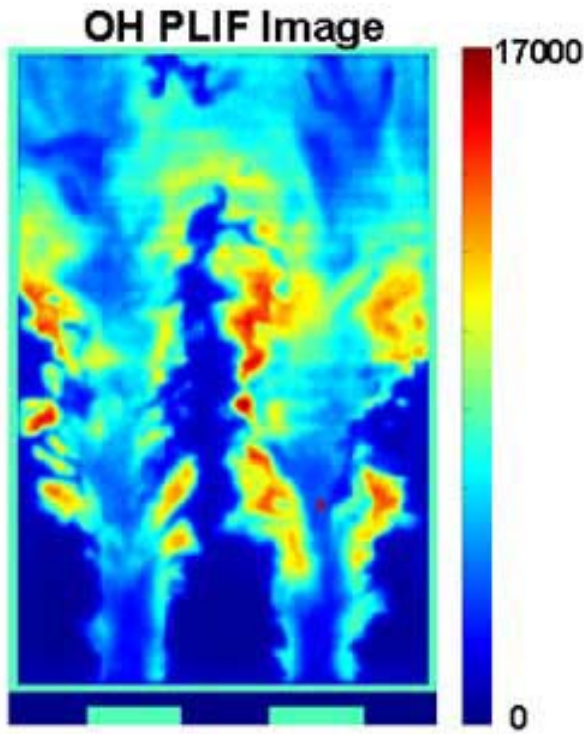
- Burner operation characterized ✓

- Quantified effect of H_2 addition on lean flame stability ✓



- Acetone PLIF used to quantify fuel/air mixing ✓





- Flame structure characterized using OH imaging ✓

Sandia National Laboratories
Combustion Research Facility

GEAE Collaboration: *Approach & Progress*

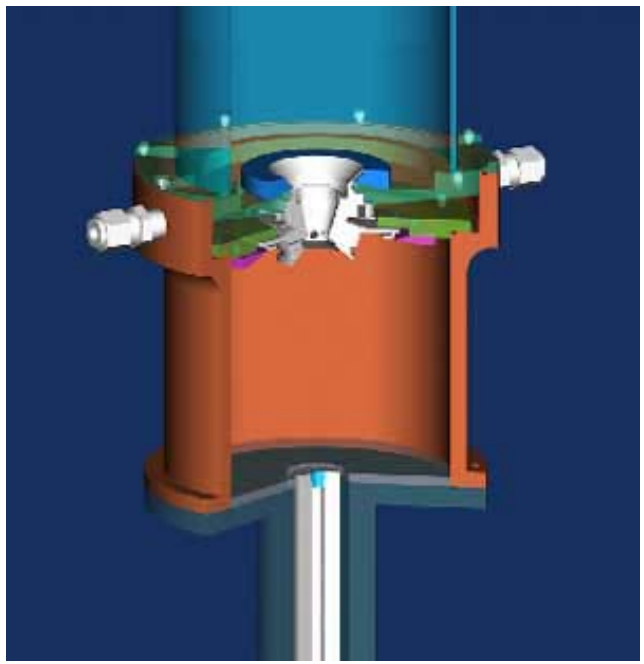
Approach

- Select fuel injector for lean premixed operation
- Apply advanced diagnostics and LES to understand problematic areas related to industrial gas turbines
- Identify problem areas where hydrogen addition could be beneficial and demonstrate merits of H_2 enrichment

- Diagnostics implemented ✓
  - PIV, OH and CO PLIF
  - Raman Scattering

- Design issues identified ✓
  - Lean blowout limits
  - Lean emissions (NO_x, CO)
  - Fuel-air mixing
  - Combustion instabilities

- Completed hardware for swirlcup installation in Confined Flow Burner ✓



GEAE Swirlcup Injector

International Efforts

IEA Technical Working Group on Modeling

- **Develop an international effort to address fundamental and applied aspects of H_2-enriched fuels for lean premixed gas turbine combustion**
- **Define program research areas**
- **Establish a validated simulation capability based on the LES technique**
- **Establish a complementary experimental capability for database acquisition**

Group Members

- Sandia
- University of Heidelberg
- Darmstadt University
- Lund University
- Cranfield University
- National Energy Technology Laboratory
- University of Toronto
- NASA Glenn

Progress

- **Primary program focus is the *use of gas turbines in "zero-emission" H_2 applications* ✓**
- **Administrative framework established. Technical and Strategy Committee members selected with Sandia co-chairs on each ✓**
- **Technical and Strategy groups met in Fall, 2002 to discuss procedures related to multi-nation tasks and to review technical progress ✓**
- **Working group meeting was held in Spring, 2003 ✓**

Related Efforts

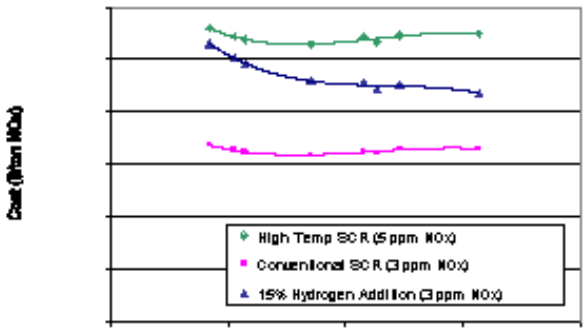
International Workshop on Modeling and Validation of Combustion in Gas Turbines

- Objective is to establish a collaborative validation capability based on the LES technique
- Focused on turbulent, swirl-stabilized flames and the complex flow dynamics in gas turbine combustors
- Construct database repository on Web for selected flames to be used for model validation ✓

Workshop home page:
www.ca.sandia.gov/CGT

Economic Analysis

- Energetics Inc. performed technical cost analysis ✓
- Cost comparisons with Dry Low NO_x combustors and Selective Catalytic Reduction showed 20% H_2 addition is cost competitive ✓
- H_2 addition up to 20% offers NO_x levels below 1 ppm and reduced CO_2 emissions ✓
- Extended analysis showed up to 60% H_2 addition is cost competitive when carbon credits are included ✓



Cost to retrofit Gas Turbines with NO_x Control

Sandia National Laboratories
Combustion Research Facility

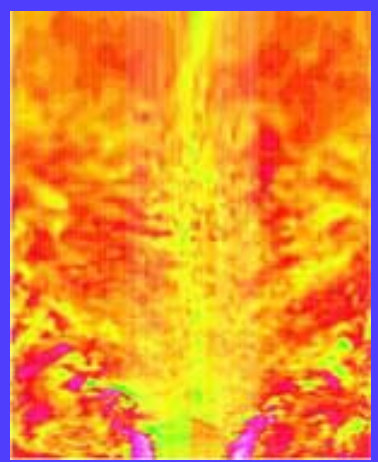
Working Groups

IEA Technical Working Group on Modeling

- Primary program focus is the *use of gas turbines in "zero-emission" H_2 applications* ✓
- An administrative framework has been established. Technical and Strategy Committee members were selected with Sandia co-chairs on each ✓
- The Technical and Strategy groups met in Fall, 2002 to discuss procedures related to multi-nation tasks and to review technical progress ✓
- A working group meeting was held in Spring, 2003 ✓

Project	Organization
H_2 Enrichment / Diagnostics	Sandia
LES Development	Sandia
Kinetics	Heidelberg
Hydrogen Burner	NASA Glenn
LES Development	Darmstadt
Diagnostics	Lund Technical
Diagnostics	Cranfield
High Pressure Experiments	NETL
Diagnostics	Toronto

LES of swirl burner

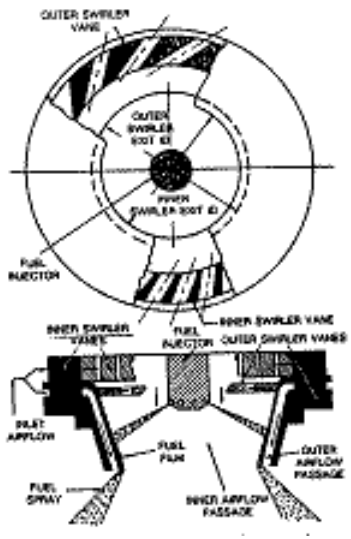


AIAA Fluid Dynamics Technical LES Working Group

- Goal is development of predictive design tools for next generation aerospace and industrial applications
- Group focus is joint LES/laboratory investigations on prototypical configurations with industrial impact
- Participants are NRL, GEAE, Pratt & Whitney, WPAFB, U. Cinncinati, FOI-Stockholm, NCSU, Rolls-Royce, Alstom, SNL, U. Poitiers & CNRS, CTR and GATECH

New Collaborations

Swirl Injector



Pratt and Whitney

- P & W will supply fuel injector to emphasize different aspects of practical gas turbine combustors (flow and flame dynamics)
- Fundamental data needed for LES model development
- Sandia will apply advanced diagnostics and LES to characterize combustion process and obtain detailed datasets
- Identify problem areas where hydrogen addition could be beneficial

Wright Patterson Air Force Base (emerging)

- WPAFB has extensive high-pressure diagnostic capabilities that complement Sandia capabilities
- Available high-pressure test facilities for realistic combustion pressures and temperatures

Proposed Future Work and Milestones

- Obtain detailed measurements of the velocity, temperature and species concentration fields in atmospheric pressure burner at Sandia (swirl burner)
- Establish LES model validity through comparisons with experimental database (swirl burner)
- Develop laser diagnostics for high pressure application (NETL)
- Complete evaluation of fuel/air mixing and implement improvements in hydrogen burner (NASA)
- Obtain NO_X and CO emissions data in hydrogen burner (NASA)
- Explore issues surrounding the use of H_2 as an alternative gas turbine fuel (NASA)
- Complete experimental measurements in production injector (GEAE)
- Identify areas where H_2 addition could prove beneficial and demonstrate potential merits of H_2-enrichment in these areas (GEAE)
- Explore potential use of H_2 addition as a "control knob" to eliminate instabilities related to fuel lean operation in practical gas turbines (GEAE)

Responses From 2002 Review Panel

- **Panel strongly endorsed continuation of this project**
  - No criticisms or questions, continued funding recommended
  - Score 95 (rank 2 in session, highest score was 96)
- **Goals and objectives being addressed properly**
  - Cost competitive even at 15% H_2 due to avoided cost of NO_x removal
  - Goal to use hydrogen to reduce NO_x emissions deemed solid
- **Approach viable and project well planned and on track**
  - Strong project management and research tools
  - Good use of laboratory resources and capability
- **Significant progress being made with reasonable milestones**
  - All milestones met or exceeded, significant results produced
  - Strong commercial collaboration in place and growing
- **Excellent communication, collaborations and publication record**

Publications

- Schefer, R. W., "Hydrogen Enrichment for Improved Lean Flame Stability, " International Journal of Hydrogen Energy, 2003 (to appear).
- Wicksall, D. M., Schefer, R. W., Agrawal, A. K. and Keller, J. O., "Simultaneous PIV-OH PLIF Measurements in a Lean Premixed Swirl-Stabilized Burner Operated on H2/CH4/Air, "Proceedings of the Third Joint Meeting of the U.S. Sections of the Combustion Institute, March 17-19, Chicago, IL (2003).
- Wicksall, D. M., Schefer, R. W., Agrawal, A. K. and Keller, J. O., "Fuel Composition Effects on the Velocity Field in a Lean Premixed Swirl-Stabilized Burner, " Proceedings of ASME Turbo Expo 2003: 48th ASME International Gas Turbine and Aero Engine Technical Congress and Exposition, June 16-19, Atlanta, GA (2003),
- Schefer, R. W., Smith, T. D. and Marek, C. J., "Evaluation of NASA Lean Premixed Hydrogen Burner, " Sandia Report SAND2002-8609, January, 2003 (submitted to Combustion Science and Technology).
- Schefer, R. W., Wicksall, D. M. and Agrawal, A. J., "Combustion of Hydrogen-Enriched Methane in a Lean Premixed Swirl-Stabilized Burner," Twenty-Ninth Symposium (International) on Combustion, Sapporo, Japan, July 21-26, 2002 (to appear).
- Vagelopoulos, C. M., Oefelein, J. C. and Schefer, R. W., "Response of Lean Premixed methane Flames to Hydrogen Enrichment, " Proceedings of the Third Joint Meeting of the U.S. Sections of the Combustion Institute, March 17-19, Chicago, IL (2003).
- Vagelopoulos, C. M., Oefelein, J. C. and Schefer, R. W., "Effects of Hydrogen Enrichment on Lean Premixed Methane Flames, " 14th Annual U.S. Hydrogen Conference and Hydrogen Expo USA, March 4-6, Washington, D.C. (2003).
- Towns, B., Skolnik, E., Miller, J., Keller, J. and R. Schefer, "Analysis of the Benefits of Carbon Credits to the Hydrogen Addition to Midsize Gas Turbine Feedstocks, " 14th Annual U.S. Hydrogen Conference and Hydrogen Expo USA, March 4-6, Washington, D.C. (2003).
- TherMaath, C., Skolnik, E., Keller, J. and Schefer, R., "Emissions Reduction Benefits from H2 Addition to Midsize Gas Turbine Feedstocks," 14th World H2 Energy Conference, Montreal, Quebec, Canada, June 19-13, 2002.
- Schefer, R.W., "Reduced Turbine Emissions using Hydrogen-Enriched Fuel," 14th World Energy Conference, Montreal, Quebec, Canada, June 9-13, 2002.
- J. C. Oefelein and R. W. Schefer. Modeling and validation of lean premixed combustion for ultra-low emission gas turbine combustors. Proceedings of the 1st International SFB568 Workshop on Trends in Numerical and Physical Modelling for Turbulent Processes in Gas Turbine Combustors, Darmstadt University of Technology, Darmstadt, Germany, November 14-15 2002.
- J. C. Oefelein. Progress on the large eddy simulation of gas turbine spray combustion processes (invited). Proceedings of the 11th Annual Symposium on Propulsion, The Pennsylvania State University, University Park, Pennsylvania, November 18-19 1999. The Pennsylvania State University, Propulsion Engineering Research Center.

A Techno-Economic Assessment of Hydrogen Production by Gasification of Biomass

> Poster Presented By:
David A. Bowen
Gas Technology Institute

2003 DOE Hydrogen and Fuel Cells Merit Review and Peer Evaluation

Berkeley, California
May 19-22, 2003

Project Team

- Project sponsored by U.S. Dept. of Energy (EERE), Hawaii Electric, Gas Technology Institute (GTI), Electric Power Research Institute (EPRI), and the University of Hawaii.
- DOE Program Manager: Mr. Douglas Hooker

- **GTI Team Members**
  - Francis S. Lau
  - David A. Bowen
  - Remon J. Dihu
  - Shain J. Doong
  - Robert J. Remick
  - Rachid B. Slimane
  - Robert F. Zabransky

- **Other Team Members**
  - Scott Q. Turn, HNEI
  - Evan E. Hughes, EPRI

gti

Project Objectives

- Determine the technical and economic potential of producing hydrogen from biomass with an end-use in PEM fuel cells
- Project outline:
  - Develop a biomass resource assessment
  - Collect information on feeding systems
  - Simulate gasification with biomass
  - Determine gas cleaning requirements
  - Determine hydrogen production costs
  - Assess public programs and initiatives
  - Determine barriers to commercialization

gti

Project Timeline

Task		Task Name	Months From Start of Project														
			01	02	03	04	05	06	07	08	09	10	11	12	13	14	15
1.0		Resource Assessment of Biomass Feedstocks															
	1.1	Bagasse, Switch Grass, and Nut Shell Availability and Cost															
	1.2	Process Scale Determination															
2.0		Hydrogen Production via Gasification/Pyrolysis of Biomass															
	2.1	Identification/Evaluation of Solids Handling Systems															
	2.2	Modeling for Gasification of Three Feedstocks and Analysis															
	2.3	Gas Purification/Cleanup Requirements															
3.0		Cost of Hydrogen Production and Cost Sensitivity Analysis															
4.0		Assessment of Public Programs and New Policy Initiatives															
5.0		Market Barries and Commercial Opportunites															
6.0		Final Report															

Figure 2. Project Schedule (Start Date: September 15, 2001 / End Date: December 15, 2002)

gti

Project Relevance

- Biomass represents an alternative, low cost fuel source that has potential to produce a high value end product, hydrogen.
- Biomass gasification is a source of non-fossil based energy and chemical production.
- Hydrogen production from domestic biomass resources can alleviate foreign dependence on fossil fuels while producing a clean fuel for PEM fuel cells.

Technical Approach

- A resource assessment was performed to determine plant size capacities
- A GTI proprietary, empirical model was used to simulate gasification of biomass
- A HYSYS® design and simulation package was used to simulate hydrogen production
- The economic analysis was performed utilizing data from EPRI's existing database

Project Assumptions

Technical Assumptions for Gas Purification

- Fuel gas can be cleaned at gasifier temperature
- Reformer Requirements
  - H_2S less than 100 ppmv
- PEM Fuel Cell Requirements
  - H_2S less than 1 ppmv
  - NH_3 less than 1 ppmv
  - CO less than 10 ppmv
- 80% recovery in PSA with 99.9% purity H_2

Economic Assumptions

- Power law scaling for increased capacity
- Linear hydrogen production with increased plant size capacity

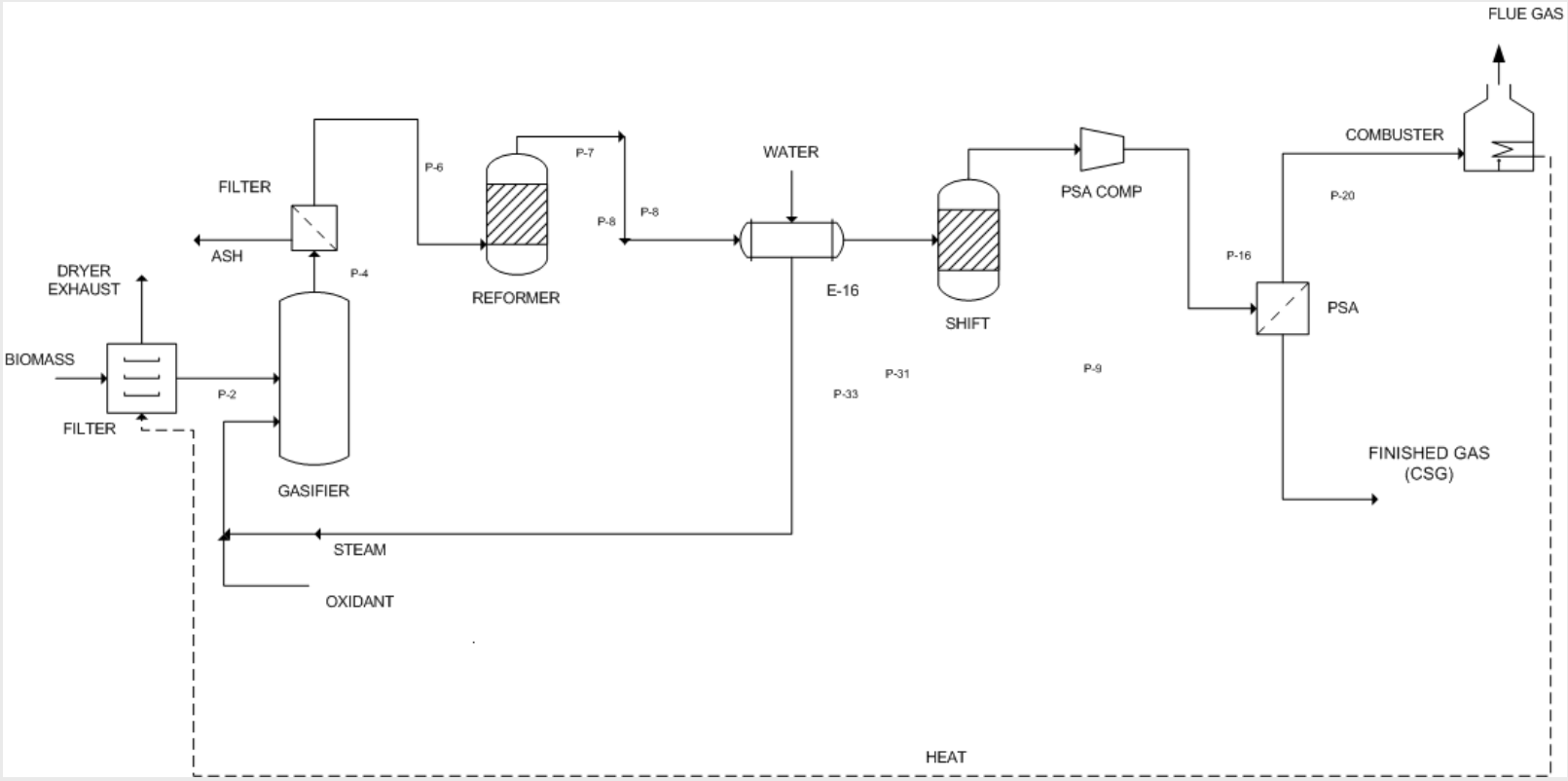
gti

Resource Assessment

- Three Feedstocks Selected:
  - Bagasse, Switchgrass, and a Nutshell Mix
- Bagasse
  - Delivered cost of $30 - 40 / tonne
  - Potential availability of 700 – 5200 tonnes / day
- Switchgrass
  - Delivered cost of $27 – 46 / tonne
  - Availability undetermined
- Nutshell Mix
  - 40% almond shell, 40% prunings, 20% walnut shells
  - Delivered cost of $12 – 44 / tonne
  - Potential availability of 500 tonnes / day

gti

Process Flow Diagram



Bagasse Process Flow Diagram

Simulation Results

	Bagasse	Switchgrass	Nutshell Mix
Heat Used in Reformer [GJ/h]	24.8	25.7	24.2
Heat Used in Dryer [GJ/h]	45.8	0	0
Heat Recovered from PSA Reject [GJ/h]	60.0	80.5	89.0
Heat Recovered from Reformer Stream [GJ/h]	19.1	8.1	5.3
Net Heat from the system [GJ/h]	8.5	62.9	70.1
Power Used in PSA Compressor [GJ/h]	6.97	8.20	8.45
Power Used for Air Separation [GJ/h]	5.90	5.10	4.10
Total Heating Value of H_2 Product [GJ/h]	186	220	230
Total Heating Value of Dry Biomass Feed [GJ/h]	297	342	361
Cold Efficiency	0.628	0.644	0.637
Effective Thermal Efficiency	0.583	0.744	0.756
H_2 / Dry Biomass [g/kg]	78.1	84.1	88.3

BASIS: 500 tonnes / day at gasifier fed moisture content

gti

Economic Results

	Gasifier Feed Rate	Hydrogen Produced		Feedstock Cost	Capital Cost	H_2 Cost 15% IRR
Feedstock	Dry Tonnes / Day	Tonnes / Day	Nm^3 / Day	US $ / GJ	US $ Million	US $ / GJ
Bagasse	400	31.2	347,000	1.50	37.0	9.13
	800	62.5	695,000	1.50	61.1	7.64
	1600	125	1,390,000	1.50	100.9	6.57
Switchgrass	440	37.0	412,000	1.50	36.5	7.95
	880	74.0	824,000	1.50	60.6	6.73
	1760	148	1,648,000	1.50	100.9	5.86
Nutshell Mix	438	38.7	488,000	1.50	36.3	7.72

gti

Commercialization Barriers

- Technical Barriers
  - Materials handling
  - Cleaning and purification
- Economic Barriers
  - Hydrogen infrastructure (chicken and egg)
  - Supply and demand of waste crops
  - High cost fuel compared to available sources
- Psychological Barriers
  - Hindenburg and Challenger disasters
  - Educational programs

gti

Conclusions

- Hydrogen Can Be Produced Economically From Biomass
  - Costs are competitive with SMR and potentially better with lowered fuel costs through the inception of public programs
- Areas Deserving Further Research
  - Gas Clean Up
  - Membrane Separation
  - Feeding Systems
  - Development of a Hydrogen Infrastructure

gti

Future Plans

- Address the technical issues found in the conclusion of this report
- Build on the expertise gained in this paper study and apply it to an experimental study of hydrogen production from biomass
- Commercialize the process of hydrogen production from biomass gasification using GTI's fluidized bed, RENUGAS technology

gti

2002 Merit Review Responses

- Comment:
  - Would it make more sense to take a low-tech approach to crop residue? If burning it to make steam and generate electricity is not profitable, then trying to make hydrogen will not be either.
- Response:
  - Electricity production is more efficient using gasification than combustion. Energy is also not the only use for hydrogen. Hydrogen produced from biomass for other processes may prove more cost effective.

gti

SUPERCRITICAL WATER PARTIAL OXIDATION

Presentation to the

Department of Energy
Hydrogen Program Annual Review
Berkeley, CA

May 19-22, 2003

PI: Mike Spritzer

Research Lead: Glenn Hong

GENERAL ATOMICS

OBJECTIVES

- Develop a gasification technology that can convert biomass wastes of all types into hydrogen and other high-value products.
- Verify that high-pressure supercritical water is an ideal medium for gasification of biomass.
- Show that high hydrogen yields and gasification efficiencies can be reliably achieved with Supercritical Water Partial Oxidation (SWPO).
- Confirm competitive hydrogen production costs of ~$3/GJ can be achieved with small-size SWPO gasifiers.
- Demonstrate a 5-tpd reduced-scale gasifier at a small municipal POTW.
- Construct a 40-tpd commercial biomass gasifier at a large municipal POTW.

APPROACH

- Build on 20 yrs experience with Supercritical Water Oxidation (SCWO) of hazardous wastes.
- Exploit the inherent characteristics of supercritical water (SCW) to convert wet biomass into hydrogen
  - SCW quickly gasifies all organics with minimum char
  - Water-gas shift contributes significantly to hydrogen yields
  - SCW scrubs particulates and acids from hydrogen-rich gaseous products
  - High pressures aid in separation/storage of hydrogen
- Develop Supercritical Water Gasification System in a four-step program:
  - Phase I: Pilot scale testing / feasibility studies (complete)
  - Phase II: Technology development (expect recompete/award in 2003)
  - Phase III: System integration and design
  - Phase IV: Reduced scale demonstration of 5-tpd system
- Following DOE cost-share program:
  - Design and construct 40-tpd commercial demonstration system

GENERAL ATOMICS

PROJECT TIMELINE

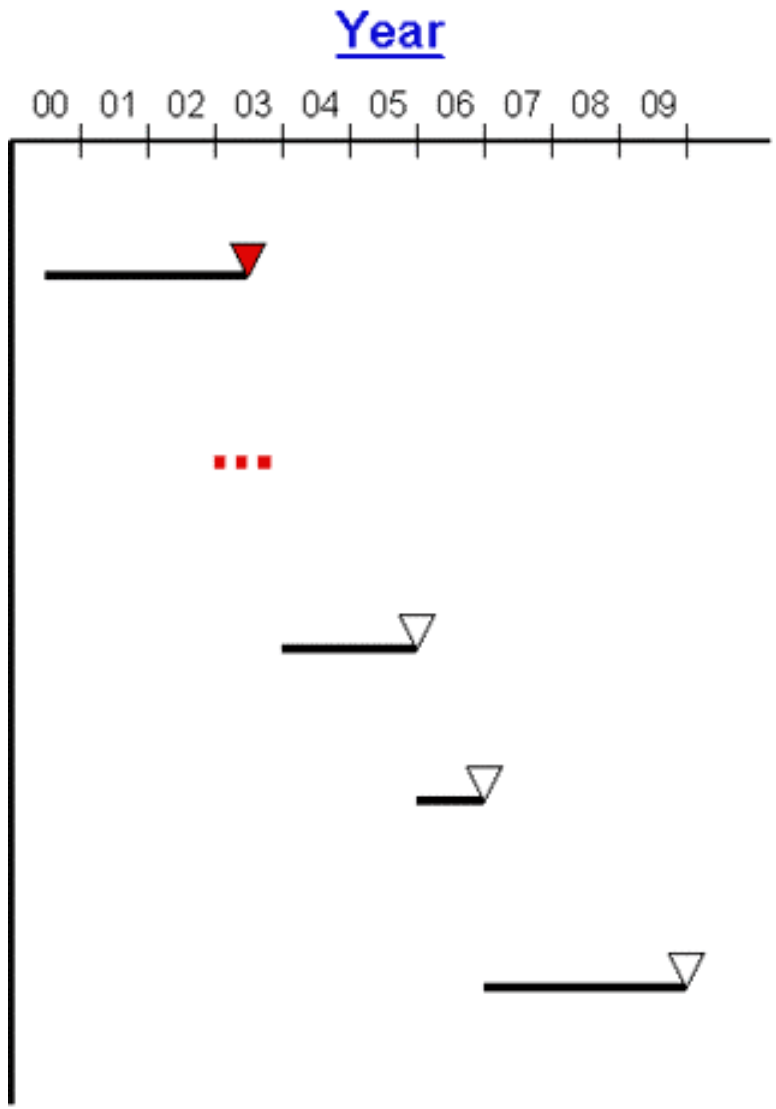
Phase I: Pilot scale testing / feasibility studies (complete) (5/00 – 6/03)

Recompete for H_2 program participation (1/03 – 12/03)

Phase II: Technology development (1/04 – 12/05)

Phase III: System integration and design (1/06 – 12/06)

Phase IV: Reduced scale demonstration of 5-tpd system (1/07 – 12/09)



GENERAL ATOMICS

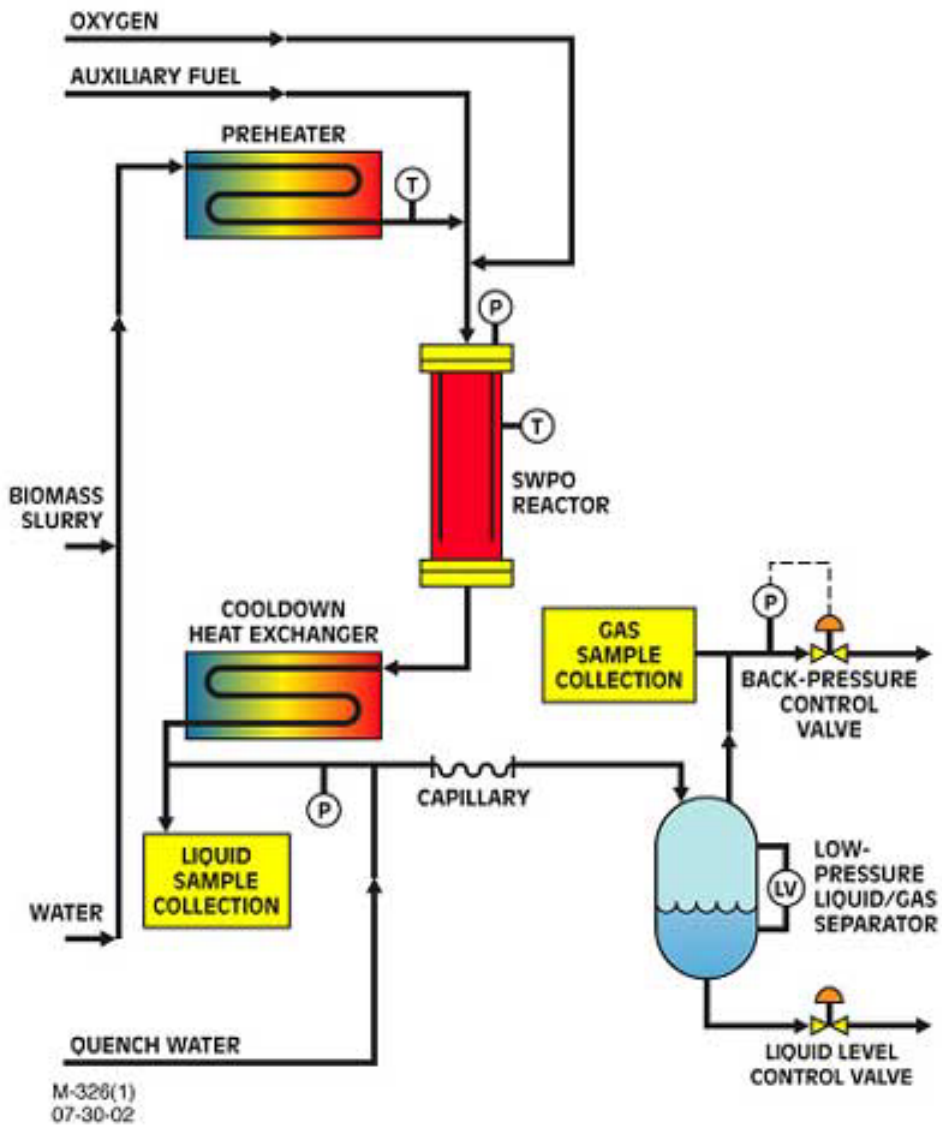
PHASE-I MILESTONES

PILOT-SCALE TESTING/FEASIBILITY STUDIES

- 5/02 – Complete Pilot-Scale SWPO Tests (Complete)
- 6/02 - Perform pilot-scale design concept for Phase II (Complete)
- 6/02 - Perform analysis to predict when/how H_2 production goals can be met (Complete)
- 8/02 - Prepare a SWPO Development Plan with cost and schedule estimates (Complete)
- 8/02 - Prepare a Business Plan to identify SWPO market potential (Complete)
- 12/02 - Define follow-on Phase II Technology Development activities and a follow-on Phase II Proposal (Complete)
- 12/02 – Issue Phase I Final Report (Complete)

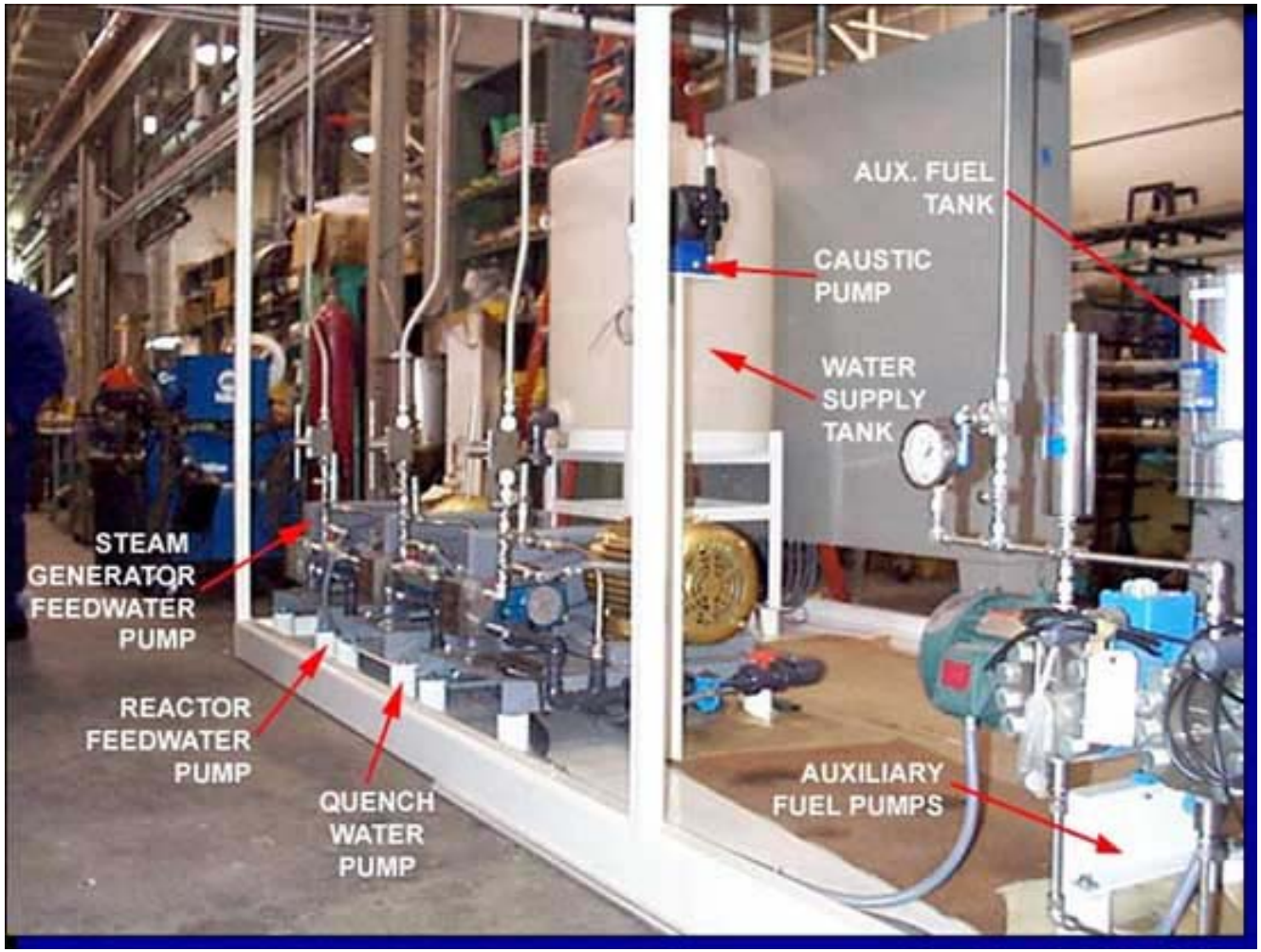
GENERAL ATOMICS

SIMPLIFIED SWPO PROCESS FLOW DIAGRAM



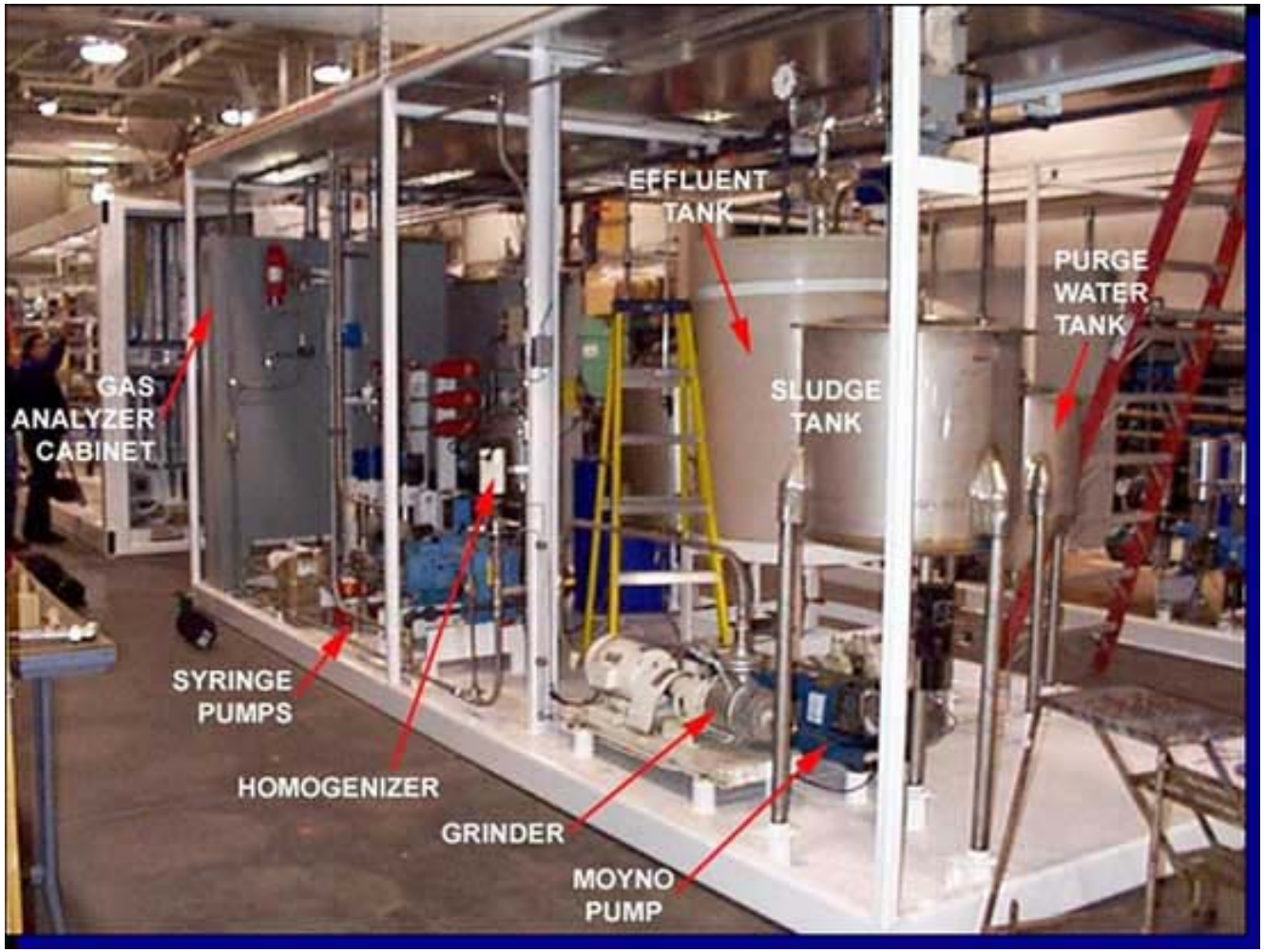
GENERAL ATOMICS

SWPO PILOT-PLANT PUMP SKID



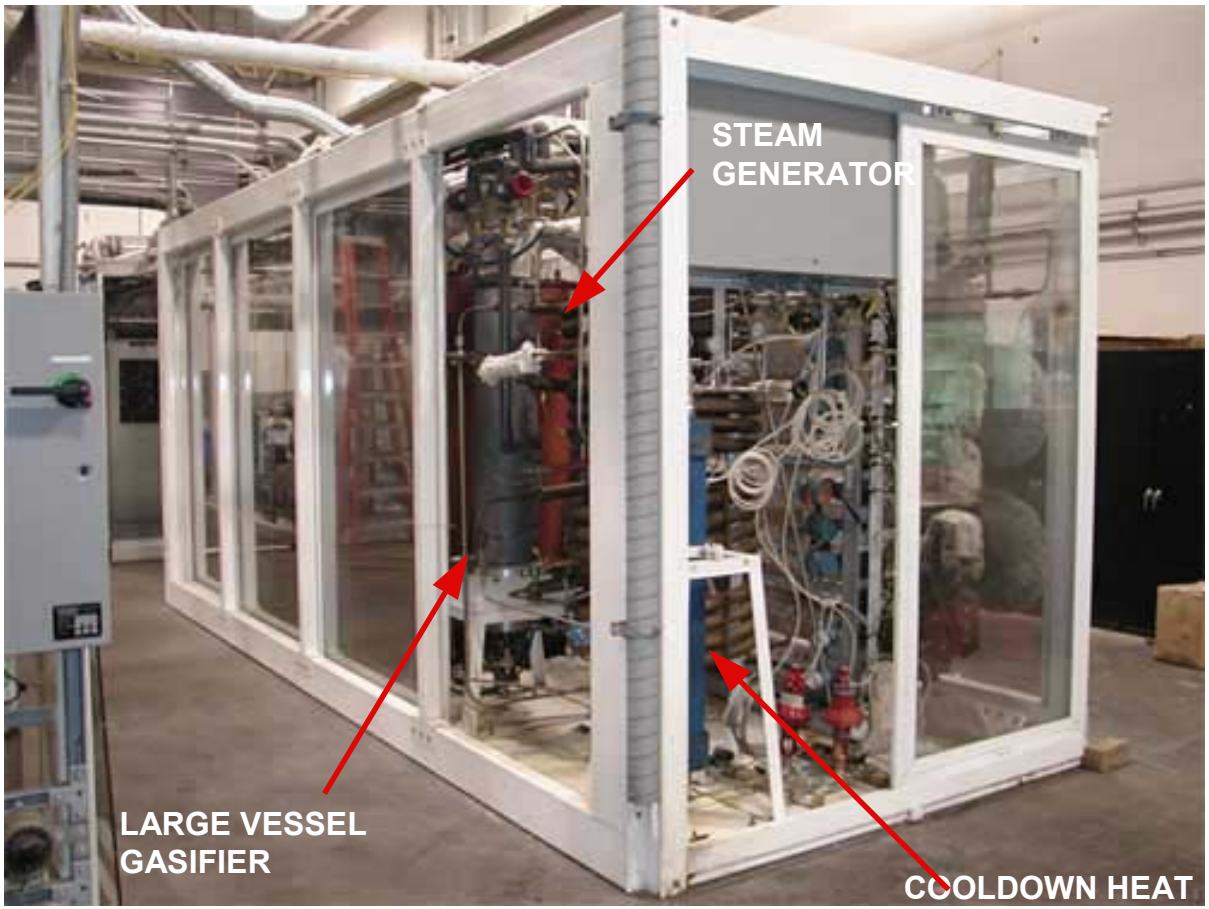
GENERAL ATOMICS

SWPO PILOT-PLANT SLURRY AND EFFLUENT SKID



GENERAL ATOMICS

SWPO PILOT- PLANT REACTOR SKID WITH LARGE VESSEL GASIFIER



GENERAL ATOMICS

SWPO LARGE VESSEL GASIFIER

GENERAL ATOMICS

ACCOMPLISHMENTS

Key findings during Phase I testing:

1. Pumping tests indicate that a biomass slurry feed concentration of about 12 wt% solids is a practical maximum.
2. Feed preheat should be limited to 260°C to avoid char formation and plugging.
3. A high-heating value waste must be coprocessed with biomass in order to attain the desired gasifier temperature and still have sufficient feedstock for gasification. Suitable high-heating value wastes are trap grease, plastics, rubber, or coal.
4. A vessel-type gasifier is required to achieve higher gasifier operating temperatures and minimize heat losses.
5. A catalyst-free gasifier is required to enable long-term operation with dirty feed materials without plugging.
6. A high-energy nozzle is required for high dispersion of the incoming feed to improve mixing and attain high gasification yields.
7. A methane-steam reformer is required on the clean SWPO product gas to reform the methane-rich gas to hydrogen.

SUMMARY OF WOODY BIOMASS GASIFICATION TESTS

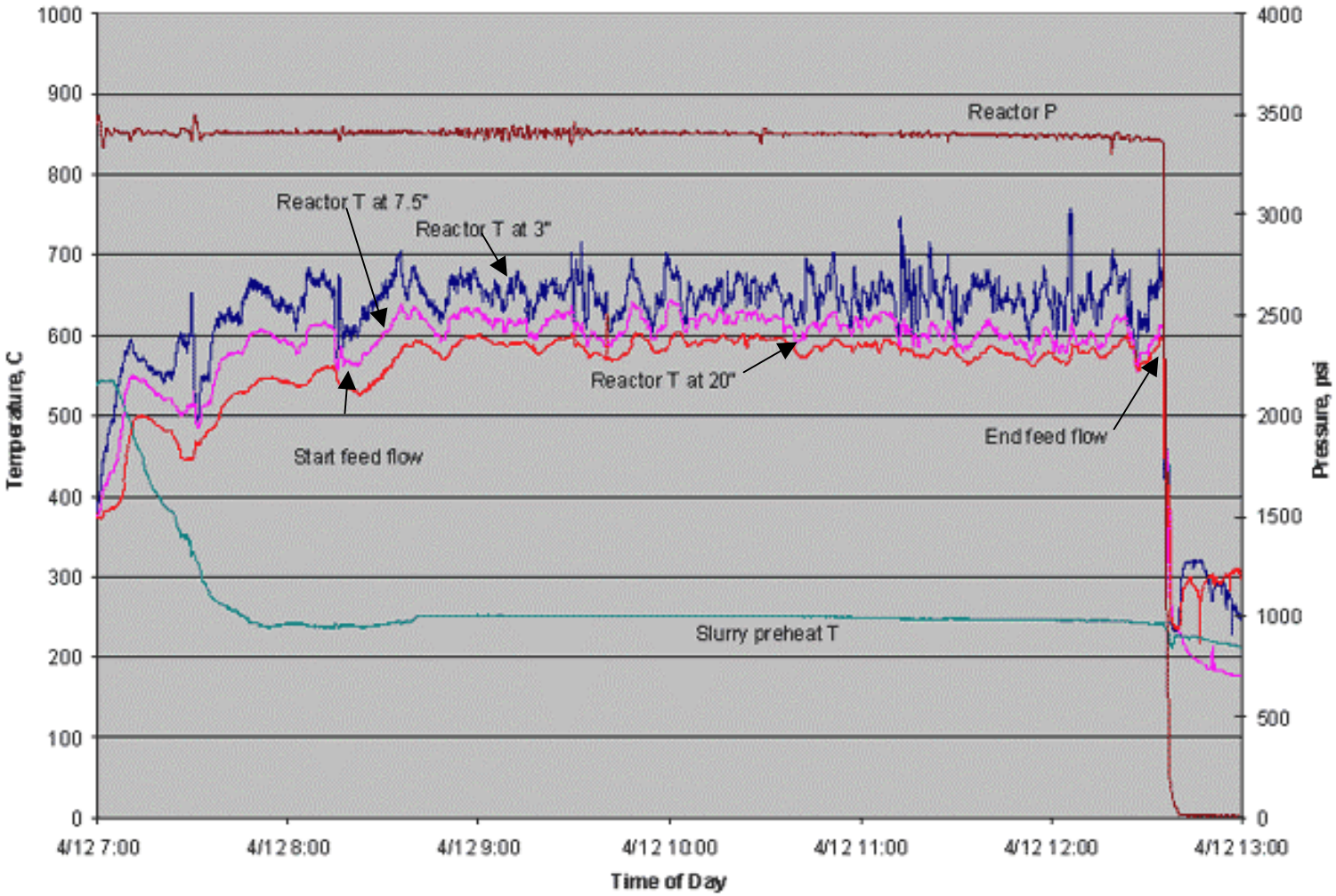
Run Date:	**4/10/2002**	**4/12/2002**	**4/17/2002**	**4/18/2002**	**4/23/2002**	**4/24/2002**
Feed (dry basis)	9% wood	9% wood	9% wood	9% wood	9% wood	9% wood
Gasifier T, C	650	650	800	800	650	800
Input						
Run time min	105	250	242	195	128	132
Oxygen g/min	109	104	110	112	86	113
Stoich. EtOH g/min	52.2	49.8	52.7	53.7	41.2	54.1
Excess EtOH g/min	16.8	22.2	10.3	3.3	17.8	7.4
Feed g/min	367	345	350	336	330	347
CMC %(1)	2.5	2.5	2.5	2.5	2.5	2.5
Output						
Gas SCFM	4.5	5.1	4.6	4.7	4.3	4.9
H_2 %	18.6	21.1	17.0	18.8	25.3	16.9
CH_4 %	16.3	16.7	13.6	14.9	15.7	13.3
C_2H_6 %	0.1	0.1	0.1	0.1	0.2	0.1
CO %	2.7	2.9	1.9	2.2	4.1	1.7
CO_2 %	48.6	48.6	54.5	48.7	43.7	54.9
N_2 %	10.4	8.0	9.5	11.2	8.1	9.7
O_2 %	3.5	2.7	3.5	4.1	3.0	3.5
% Feed C in solid (char)	6.9	2.7	3.5	2.7	0.5	0.2
% Feed C in liquid (tar)	2.3	2.9	6.0	0.0	8.7	5.0
Carbon balance %	79	88	90	90	83	94

Notes:

(1) – CMC is a suspension agent to prevent settling in the feed slurry.

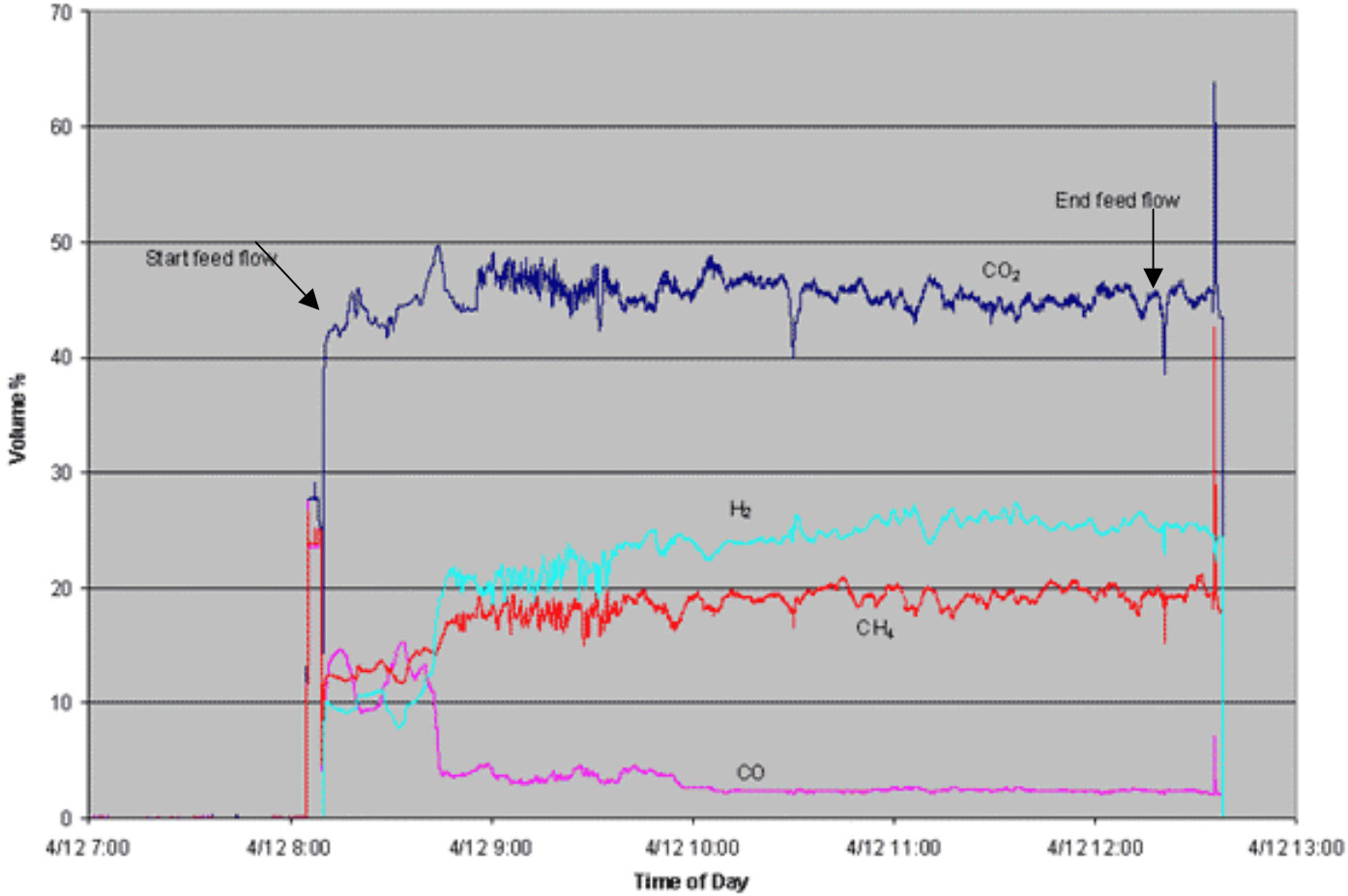
GENERAL ATOMICS

SWPO T-P DATA AT 650°C



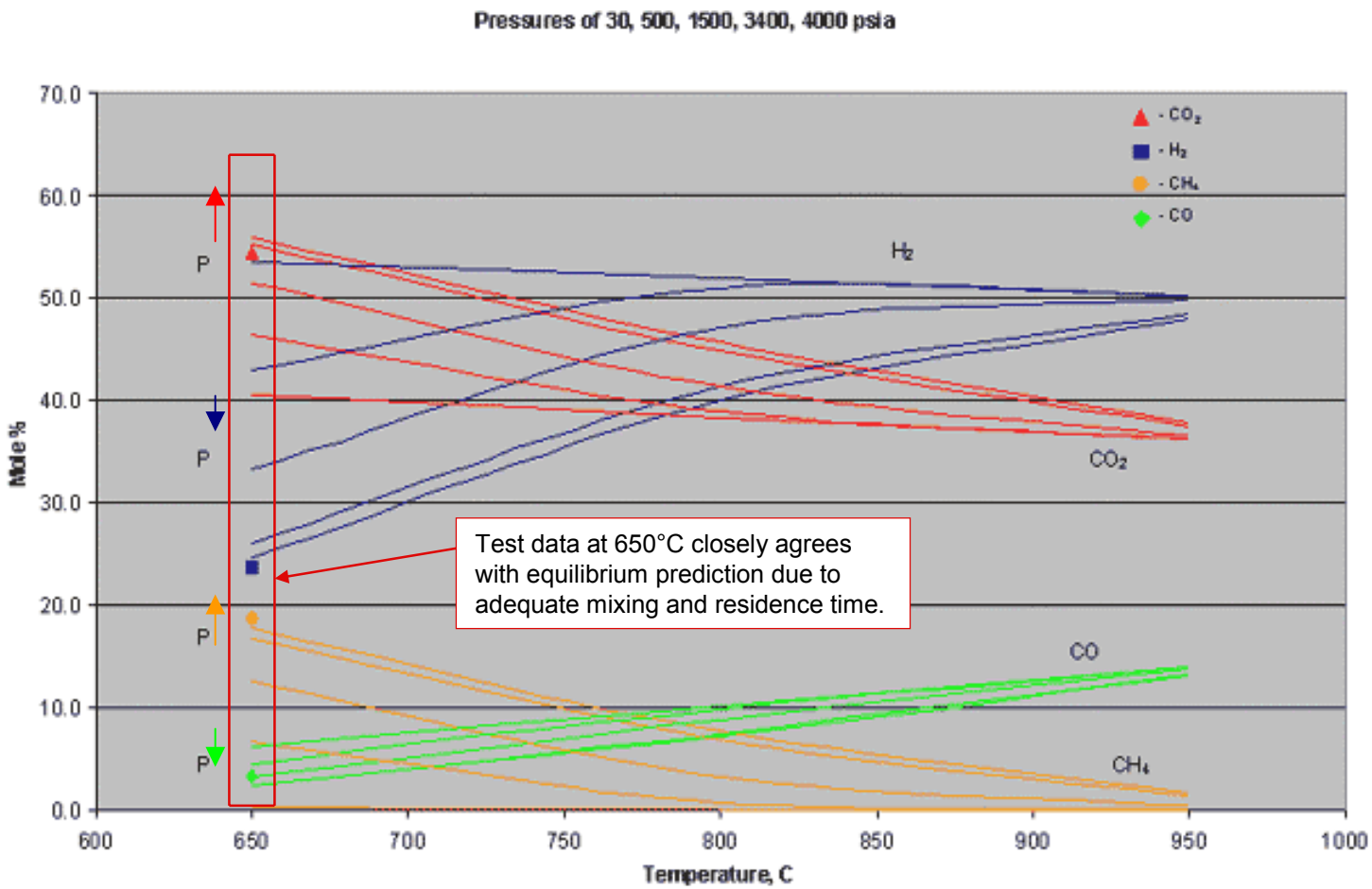
GENERAL ATOMICS

SWPO GAS ANALYZER DATA AT 650°C



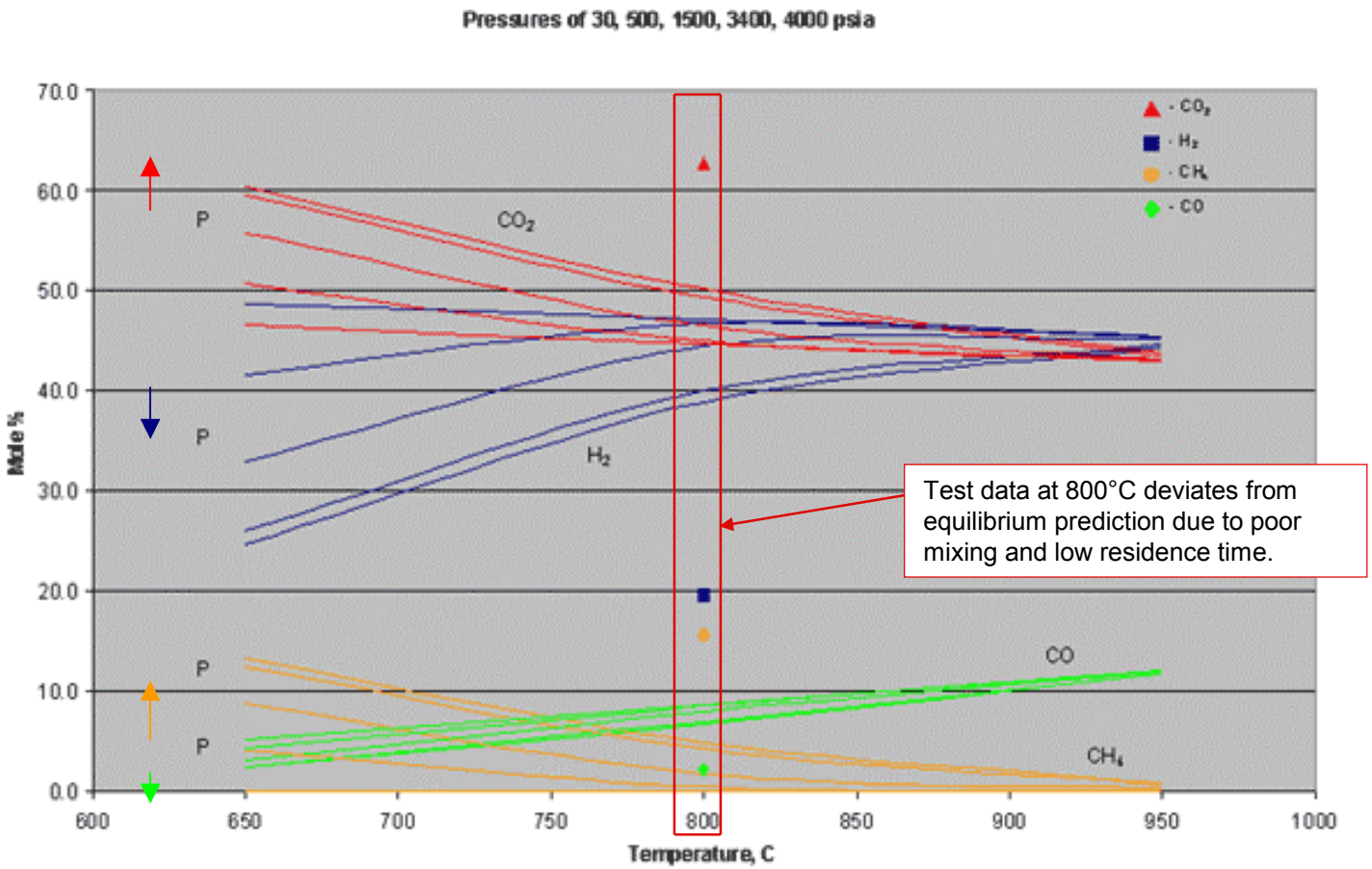
GENERAL ATOMICS

SWPO DATA AT 650°C COMPARED TO EQUILIBRIA PREDICTIONS



GENERAL ATOMICS

SWPO DATA AT 800°C COMPARED TO EQUILIBRIA PREDICTIONS



GENERAL ATOMICS

COMPARISON OF SWPO GAS PRODUCTION WITH INDIRECTLY-HEATED GASIFIERS

Organization	Feed	T °C	P psi	H_2O: C ratio	Product gas mol%					Max possible H_2 yield, g/100g feed		Max possible gasification efficiency, %	Notes
					H_2	CH_4	C_2+	CO	CO_2	Feed	Product gas		
GA	9% wood + 2.5% CMC[1]	650	3400	7.5	43.6	38.3	0.2	6.3	11.5	19.4	15.3	79	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	650	3400	6.7	40.0	31.6	0.3	5.6	22.5	20.1	17.5	87	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	800	3400	8.4	38.5	30.8	0.2	4.3	26.2	18.6	15.6	84	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	800	3400	9.9	44.7	35.4	0.2	5.2	14.5	17.5	21.1	121	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	650	3400	7.1	47.4	29.5	0.4	7.7	15.0	19.7	16.8	85	Yields based on unoxidized organic
GA	9% wood + 2.5% CMC[1]	800	3400	9.0	37.6	29.6	0.2	3.8	28.8	18.2	17.2	94	Yields based on unoxidized organic
UHM	10.4% CS[2]	650	4061	14.0	45	14	0.0	2	35	13.7	14.5	105	UHM, 1997a
UHM	5% wood + 5.5% CS[2]	650	4061	12.6	34	23	0.2	3	45	15.2	13.3	87	UHM, 1997a
UHM	5% wood + 5.6% CS[2]	650	4061	12.6	50	10	0.0	4	39	15.2	15.5	102	UHM, 1997a
UHM	5% wood + 6.1% CS[2]	650	4061	11.9	43	14	0.2	3	37	15.1	13.5	89	UHM, 1997a
UHM	11.5% wood + 4.2% CS[2]	650	4061	7.6	57	6	0.0	4	33	15.9	15.2	95	UHM, 1997b
TNO	Waste biomass	600	4351	NA	54	9	NA	3	34	NA	NA	NA	TNO, 1998
Battelle	Wood	826	25	0.8	21	16	5.8	43	13	18.0	12.5	70	Craig and Mann, 1996
Battelle	Wood	927	15	0.6	21	15	6.0	47	11	18.5	13.2	72	Katofsky, 1993
Wright-Malta	Wood	600	218	1.1	21	35	0.0	7	38	17.2	17.3	101	Katofsky, 1993
MTCI	Wood	697	15	2.6	50	8	0.4	22	19	17.8	14.9	84	Katofsky, 1993

Notes:
1.CMC is carboxymethylcellulose suspension agent.
2.Activated carbon catalyst. CS is corn starch.

GENERAL ATOMICS

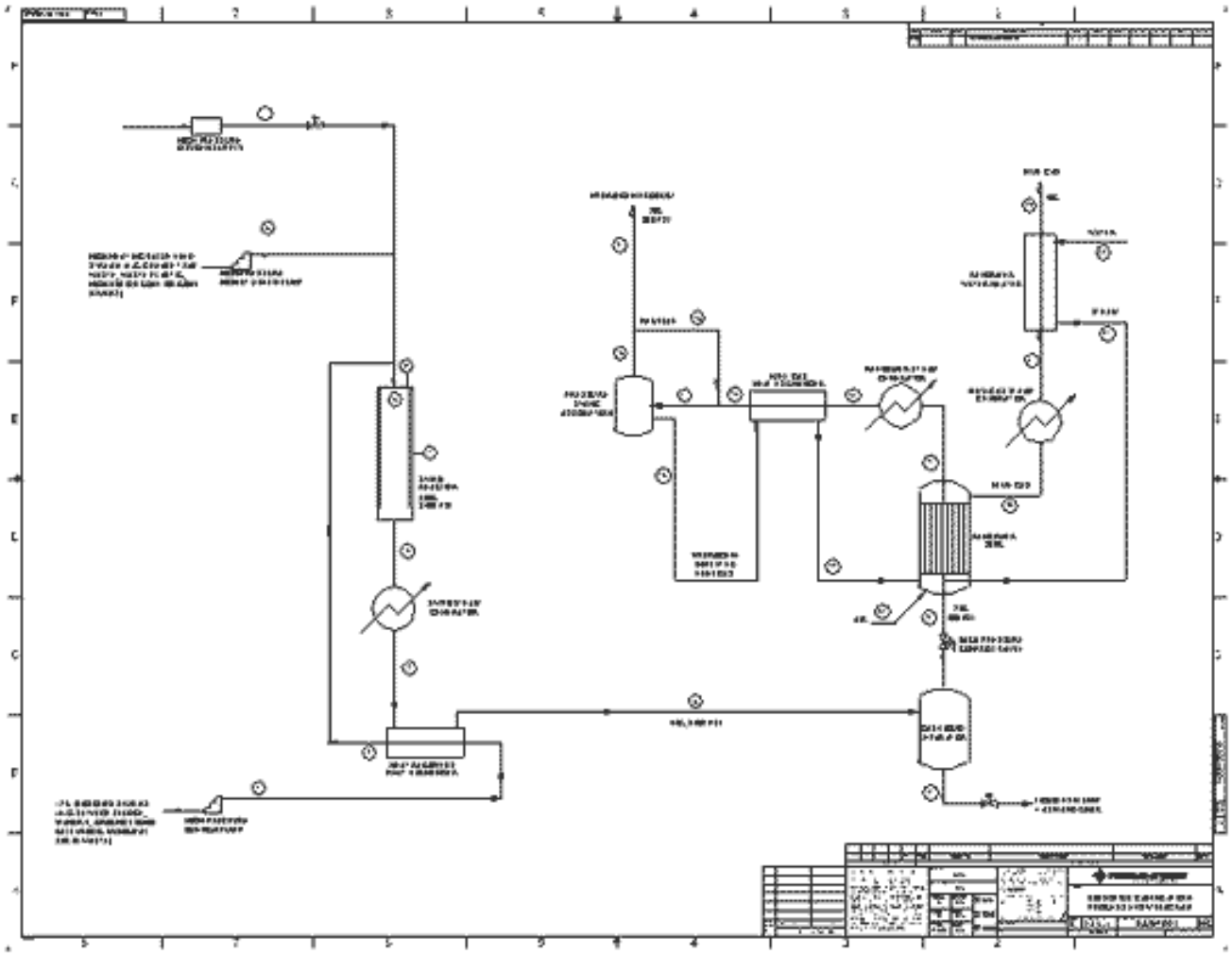
COMPARISON OF SWPO GAS PRODUCTION WITH DIRECTLY-HEATED GASIFIERS

Organization	Feed	T °C	P psi	H_2O: C ratio	O_2:Feed mass ratio	Product gas mol%					Max possible H_2 yield, g/100g feed		Max possible gasification efficiency, %	Notes
						H_2	CH_4	C_2+	CO	CO_2	Feed	Product gas		
GA	9% wood + 2.5% CMC[1,2]	650	3400	3.9	1.0	21.5	18.9	0.1	3.1	56.3	21.9	8.1	37	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	650	3400	3.6	0.9	23.6	18.6	0.2	3.3	54.3	21.9	9.7	44	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	800	3400	4.0	1.1	19.5	15.6	0.1	2.2	62.5	22.0	7.7	35	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	800	3400	4.1	1.2	22.2	17.6	0.1	2.6	57.5	22.2	9.3	42	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	650	3400	4.0	0.9	28.4	17.7	0.2	4.6	49.1	21.6	9.7	45	Yields based on all organic
GA	9% wood + 2.5% CMC[1,2]	800	3400	4.0	1.1	19.4	15.3	0.1	2.0	63.2	22.1	8.0	36	Yields based on all organic
IGT	Wood, air-blown[3]	830	460	0.7	0.3	25	18	0.2	19	38	17.3	10.6	62	Craig and Mann, 1996
IGT	Wood, O_2-blown	982	500	0.7	0.3	31	12	0.5	22	35	17.0	11.6	68	Katofsky, 1993
TPS	Wood, air-blown[3]	870	20	0.3	0.5	37	0	0	46	16	17.3	11.1	64	Craig and Mann, 1996
Shell-bio	Wood O_2-blown	1085	352	0.2	0.5	38	0	0	48	14	17.0	11.1	65	Katofsky, 1993

Notes:
1.CMC is carboxymethylcellulose suspension agent.
2.Nitrogen- and oxygen-free basis used for product gas.
3.Nitrogen-free basis used for product gas.

GENERAL ATOMICS

SWPO COMMERCIAL GASIFIER PROCESS FLOW DIAGRAM



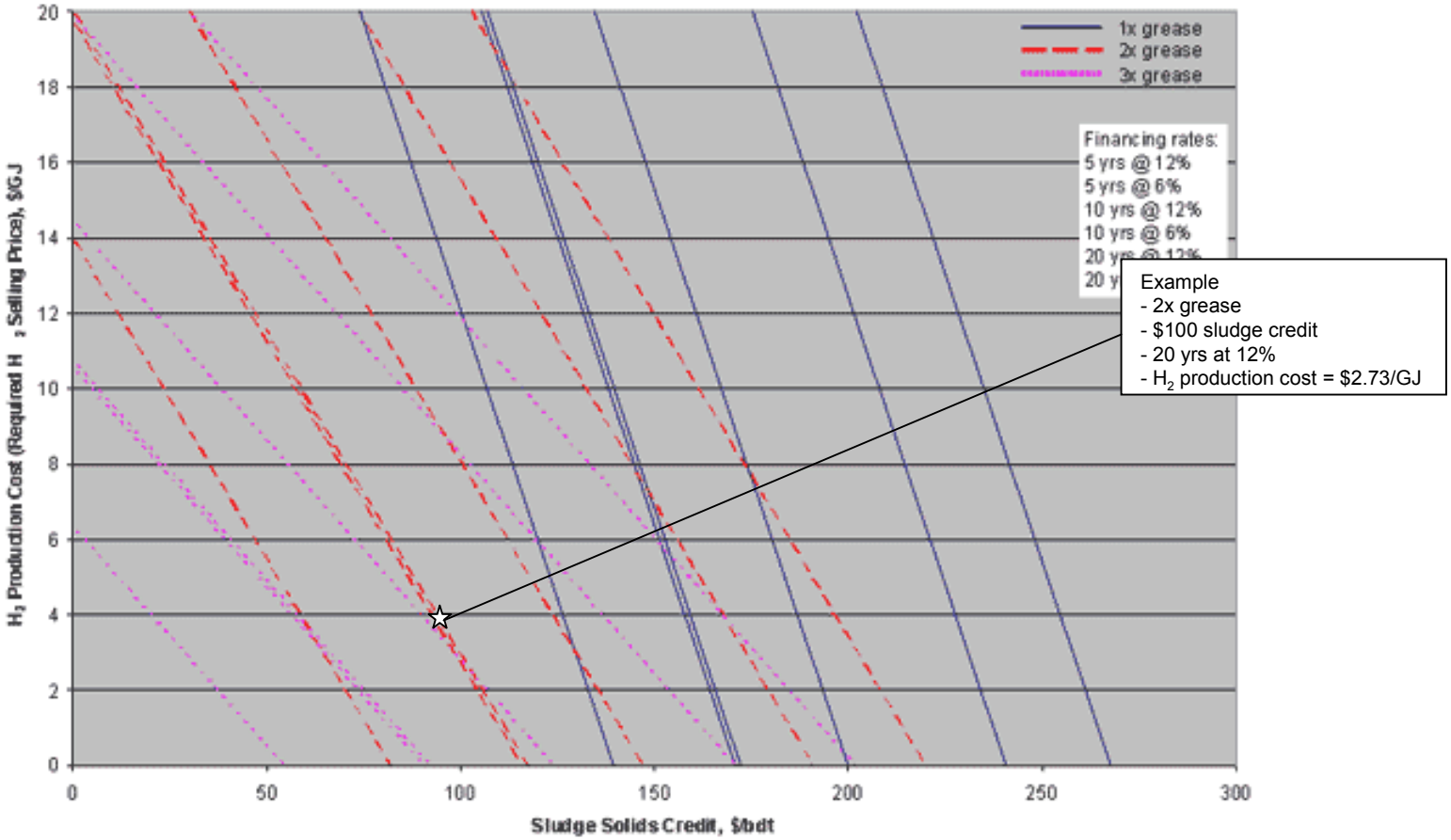
GENERAL ATOMICS

SWPO ECONOMIC ANALYSIS BASES

Description	Assumption	Reference
Plant size	40 tpd total solids, 30 tons/day organic sludge solids (not grease)	Numerous plants of this size in the US and worldwide
Sludge solids credit	$0-300 per dry ton	SDSU survey (Appendix D)
Gasifier residence time	20 seconds	15 seconds for UHM, 1998a
Trap grease credit	$0.08 per gallon	Darling/Al Max telecons
Steam credit	$3.50 per MMBtu (≈ 1000 lb)	Yeboah et al., 2002
Cost of liquid oxygen (LOX)	$0.04 per pound	Vendor discussions
Financing rate	6 to 12%	Current prime interest rate is below 5%
Financing period	Up to 20 years	City of San Diego methane contract is a 20-yr term

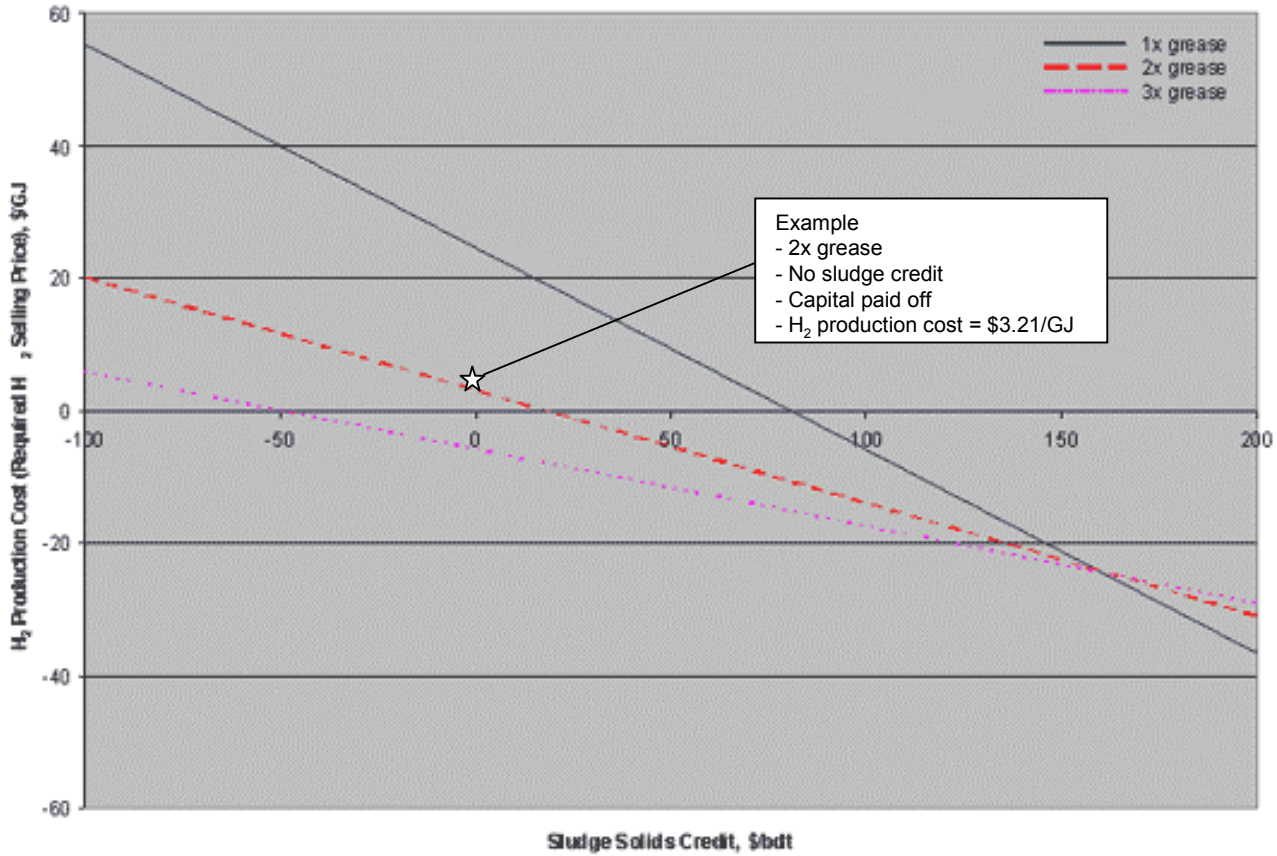
GENERAL ATOMICS

HYDROGEN PRODUCTION COST FOR SEWAGE SLUDGE WITH TRAP GREASE



GENERAL ATOMICS

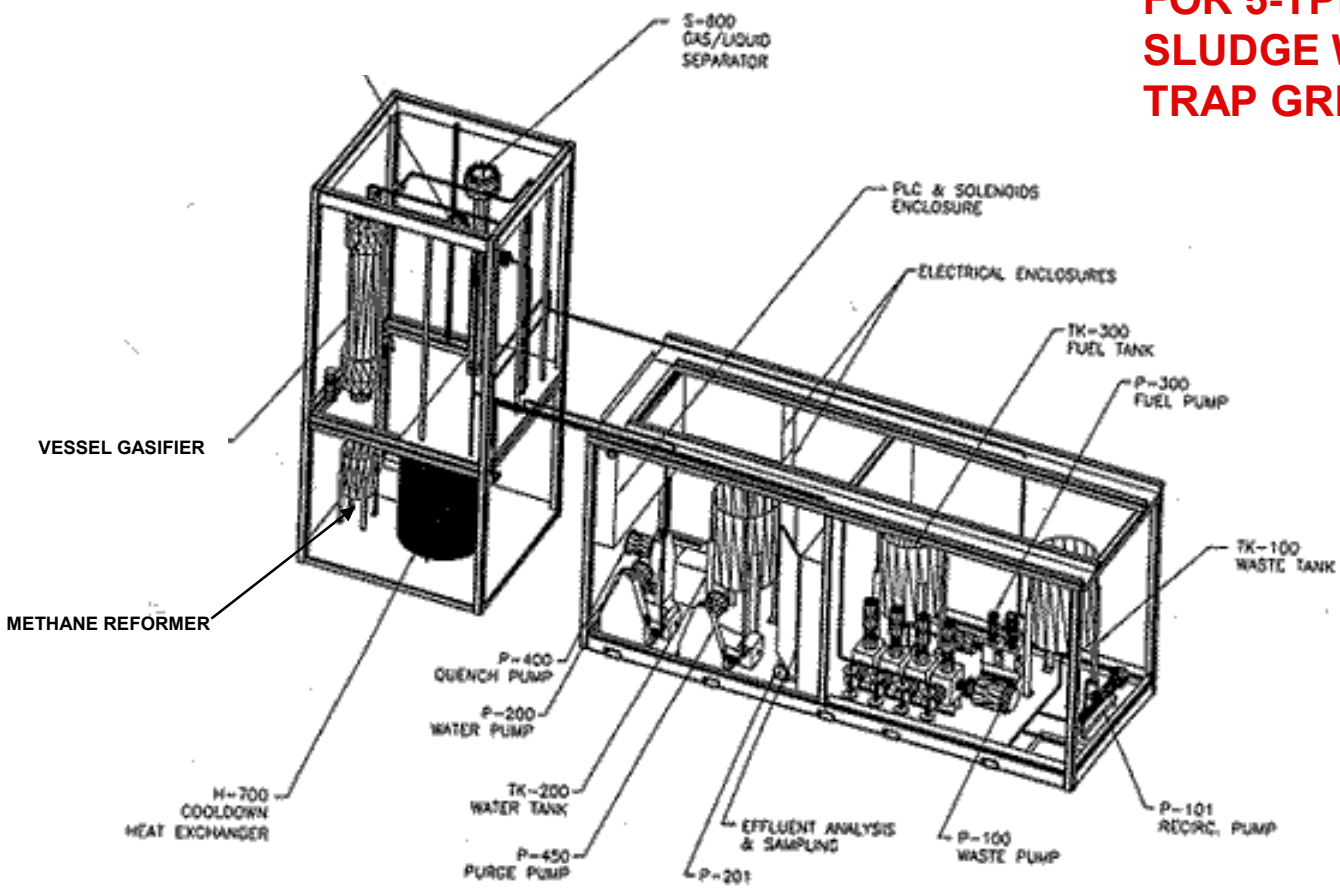
HYDROGEN PRODUCTION COST FOLLOWING CAPITAL RECOVERY



GENERAL ATOMICS

SWPO REDUCED-SCALE DEMONSTRATION SYSTEM

FOR 5-TPD SEWAGE SLUDGE WITH TRAP GREASE



GENERAL ATOMICS

COLLABORATIONS

- GA SWPO pilot plant is supporting multiple project sponsors with synergistic goals – DOE H_2 Program, U.S. Air Force waste gasification, DOE Mixed Waste Focus Area, other projects.
- In contact with the International Energy Agreement (IEA) Hydrogen Programme.
- Sponsored MBA study of U.S. and Canada waste water treatment plants for potential opportunities for SWPO gasification.
- Identified two new collaborations – Regional Economic Research (RER) and University of California, Riverside (UCR) who are doing related research for the California Energy Commission.
- Pursuing related programs with City of Los Angeles.

GENERAL ATOMICS

PLANS, FUTURE MILESTONES

- Phase II: Technology Development: (1/04 to 12/05)
  - Design, fabricate and test advanced pilot-scale SWPO reactor
  - Optimize SWPO operating parameters and H_2 yields during extended-duration tests
  - Revise market, economic and life cycle cost assessments and define scale-up requirements.
- Phase III: System Integration & Design: (1/06 to 12/06)
  - Perform safety, RAM, and permitting studies
  - Perform process design and long-lead procurement for Phase IV
  - Update development plan for Phase IV
- Phase IV: Reduced-scale Demonstration of 5-tpd System: (1/07 to 12/09)
  - Implement requirements defined during Phase III studies
  - Match reduced-scale SWPO system to industrial H_2 separation and storage systems

GENERAL ATOMICS

PEER REVIEW QUESTION #1 – WHY SWPO AS OPPOSED TO TRADITIONAL STEAM GASIFICATION?

- SWPO utilizes negative value feedstocks with high water content (sewage sludge, yard wastes, etc.).
- SWPO gasifier operates efficiently at much higher steam/carbon ratios than traditional gasifiers (no need for feedstock drying).
- Less energy required to vaporize water at supercritical pressures.
- High water content in SWPO reduces CO in product gas and reduces or eliminates the need for shift reactors.
- SWPO gasifiers are more compact than traditional gasifiers, with less surface area for heat loss.
- While supercritical pressures tend to reduce hydrogen yields and increase methane yields, the effects are virtually eliminated at gasification temperatures of about 950°C (see equilibria plots).
- GA's proprietary SWPO gasifier can operate at temperatures of 800°C, or higher.
- SWPO is expected to perform as well as traditional steam gasifiers, but with dirty, wet biomass feedstocks – a fundamental improvement.

PEER REVIEW QUESTION #2 – WHY USE INTERNAL FUEL HEATING FOR PRODUCTION OF DELICATE GASES?

- Most traditional coal gasifiers (Texaco, Shell) and some biomass gasifiers (IGT) are directly fired by partial oxidation of the feed.
- Partial oxidation is beneficial in SWPO by:
  - minimizing heat transfer across surfaces that are easily fouled with low-value, dirty biomass feeds (tar, char, mineral salts, etc.)
  - rapidly heating the biomass feed through the char-formation temperature range thus minimizing char formation
  - allowing gasification temperatures above 800°C to be internally generated without overheating the high-pressure alloy vessel
- While partial oxidation reduces the amount of hydrogen generated, it greatly simplifies the heating process – a worthwhile tradeoff, especially with low-grade, dirty biomass feedstreams.

PEER REVIEW QUESTION #3 – CAN ENOUGH HYDROGEN BE PRODUCED AT ANY ONE TREATMENT FACILITY TO BE WORTH COLLECTING?

- Commercial-scale 40-tpd sewage sludge gasifier is ideal size for distributed hydrogen generation at hundreds of municipal waste-water treatment plants throughout the U.S.
- A 40-tpd Publicly Owned Treatment Works serves a population of about 200,000.
- Economic analysis of a 40-tpd SWPO gasifier predicts hydrogen generation of ~80,000 GJ/year at a cost of ~$3/GJ.
- This is sufficient hydrogen to power about 1200 households or 600 automobiles for a year, about 0.5 - 5% of the population requirement.
- Additional 40-tpd (or larger) SWPO plants for MSW can add further to the municipal energy requirements for urban centers.
- Based on the above, we believe SWPO of municipal biomass wastes is an economically viable distributed hydrogen production technology.

GENERAL ATOMICS

DEVELOPMENT OF EFFICIENT AND ROBUST ALGAL H_2-PRODUCTION SYSTEMS

Part A: Creation of Designer Alga for Efficient and Robust Production of H_2

James W. Lee,[1]* Laurens Mets,[2] Dong Xu, [1] Barbara R. Evans, [1] and Jizhong Zhou[1]

*[1]Oak Ridge National Laboratory and [2]University of Chicago *Corresponding email: Leejw@ornl.gov, Telephone: 865-574-1208, Fax: 865-574-1275*

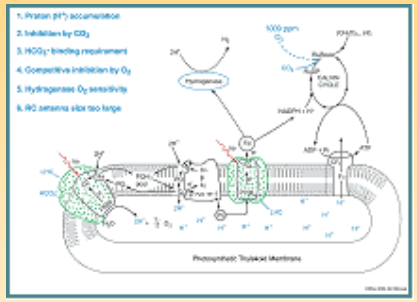
Abstract

Algal photosynthetic hydrogen (H_2) production is a potentially clean energy resource. However, there are a number of technical issues that must be addressed before algal H_2 production can become practical. In this paper, we will discuss the following six physiological problems that currently challenge researchers and investors in the field of photosynthetic H_2 production.

These problems are: *(1)* restriction of photosynthetic H_2 production by accumulation of a proton gradient, *(2)* competitive inhibition of photosynthetic H_2 production by CO_2, *(3)* requirement for bicarbonate binding at photosystem II (PSII) for efficient photosynthetic activity, *(4)* competitive inhibition by O_2, *(5)* classic O_2 sensitivity of the hydrogenase enzyme, and *(6)* light-saturation phenomenon due to large antenna size.

Potential solutions to overcome these roadblocks to photosynthetic H_2 production will also be presented. The solutions are based on a novel approach that has recently been developed at Oak Ridge National Laboratory (2001 ORNL Invention Disclosure). In this approach, a "designer alga" for efficient and robust H_2 production will be created by genetic insertion of hydrogenase promoter–programmed polypeptide proton channels in photosynthetic thylakoid membranes. This designer alga will be integrated also with the benefits of an O_2-tolerant hydrogenase that will be created by NREL and a smaller chlorophyll antenna size that will be created by UC Berkeley. Therefore, this ORNL effort is complementary with those of NREL and UC Berkeley, and will contribute jointly with the sister NREL and UC projects to achieving a common goal of effective photobiological H_2 production. By use of this approach, we will be able to simultaneously solve the six physiological problems for efficient and robust production of H_2 through photosynthetic water splitting.

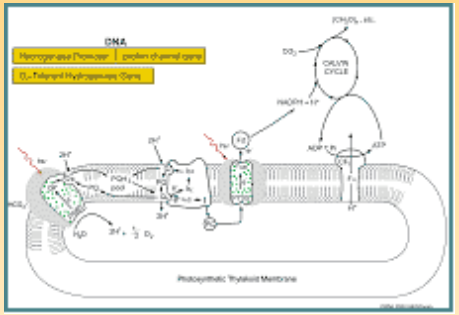
ORNL 2003-02121/gss



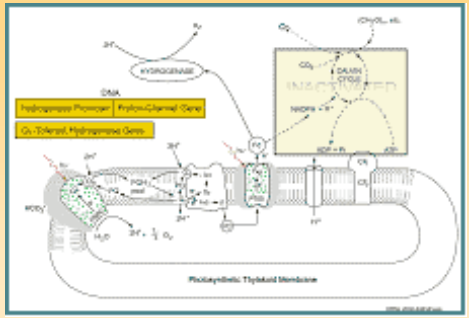
Objective: Overcoming nation's roadblocks to photosynthetic H_2 production by creation of designer alga

To meet DOE H_2 Program goal ($10/MMBtu), our proposed work will solve the six problems in algal H_2 production

Approach: Creation of designer alga for efficient and robust production of H_2 through genetic insertion of a proton channel into thylakoid membrane



*ORNL-invented concept: designer alga performing normal photosynthesis under **aerobic** conditions*



*Solution: designer alga becomes an efficient and robust H_2-production system under **anaerobic** conditions*

Project Timeline: If DOE can provide funding support of this 3.0 FTE effort, the project objective can be achieved within 4 years with the following milestones.

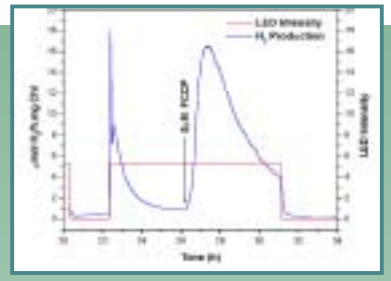
Path Forward—Milestones

Creation of designer alga for efficient and robust production of H_2

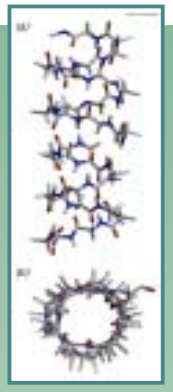
[3.0 FTE effort by Lee, Mets, Xu, Evans, Zhou, and a postdoctor]

	Year 1	Year 2	Year 3	Year 4
Year 1—Design and construction of DNA sequence coding for polypeptide proton channel	→			
Year 2—Genetic transfer of hydrogenase promoter-linked polypeptide proton-channel DNA into DS521		→		
Year 3—Characterization and optimization of the polypeptide proton-channel gene expression			→	
Year 4—Demonstration of efficient and robust production of H_2 in designer alga (ready for next phase: scale up and commercialization)				→

Accomplishment/progress: This is a new project. Because of the Congress and DOE budget situation under the "Continuing Resolution," this project has not received any funding until last month (April 2003). It was last month that DOE H_2 Program office authorized $50K for J. Lee:
(1) to attend this H_2 Review meeting, and
(2) to make preparation for a full start of the project on October 1, 2003. So, the following are the results of our preliminary studies.



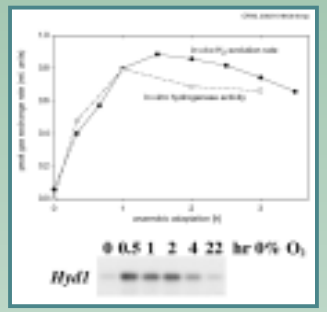
Proof of principle demonstrated by proton uncoupler FCCP experiments in wild-type algal H_2 production with 1000 ppm O_2



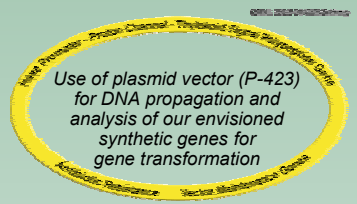
A preliminary design of polypeptide proton channel achieved by computer simulations at ORNL

The transformants will be screened and cultured for a number of assays to test for the predicted features of the designer alga

Our customer-designed state-of-the-art OLIS Photospectrometer system can be used to measure the activity of our envisioned polypeptide-proton channels in the designer alga at ORNL

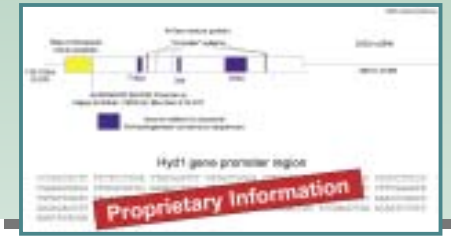


Anaerobic hydrogenase-induction studies demonstrated the potential of Hyd1 Promoter to serve as our envisioned genetic switch

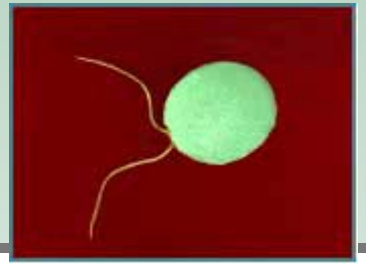


DNA analyzers at ORNL

Our dual-reactor-flow detection system can be used for both H_2-production and recyclable-growth assays

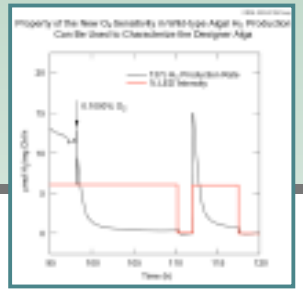


DNA map of the hydrogenase gene (Hyd1) cloned by one of us (L. Mets) and ready for construction of our envisioned genetic switch



We can deliver the genes (DNA) into our Chlamydomonas host cells by use of a biolistic gene gun (PDS-1000/He system)

Microarray equipment for mRNA assays at ORNL



Property of our newly discovered O_2 sensitivity in wild-type (C. reinhardtii 137c) algal H_2 production can be used as a reference to test the designer alga

Significant interactions or collaborations with others: This is an multi-disciplinary R&D team with scientist from three ORNL divisions and University of Chicago. We also collaborate with the teams of NREL and UC Berkeley in a complementary way to achieve the common objective for the DOE Photobiological H_2 Program.

Plans and future milestone: Presented in Project Timeline.

ORNL 2003-02134/gss

HYDROGEN FROM BIOMASS FOR URBAN TRANSPORTATION

Collaborating Project Team

Y. Yeboah (PI) and K. Bota (**Clark Atlanta University, Atlanta, GA**)

D. Day (**Eprida Scientific Carbons Inc., Blakely, GA**)

D. McGee (**Enviro-Tech Enterprises Inc., Matthews, NC**)

M. Realff (**Georgia Institute of Technology, Atlanta, GA**)

R. Evans, E. Chornet, S. Czernik, C. Feik, R. French, S. Phillips, J. Patrick (**National Renewable Energy Lab, Golden, CO**)

Hydrogen, Fuel Cells and Infrastructure Technologies Program Review Meeting

Berkeley, CA

May 18-22, 2003

ABSTRACT

Hydrocarbon fuels produce emissions during combustion that cause pollution. From the standpoint of heating value per unit mass and emissions, hydrogen is the best fuel producing only water when combusted. However, hydrogen does not occur naturally in appreciable quantities and the current cost of producing it makes it less economical than other fuels for most applications. This poster summarizes the progress on the DOE funded pilot-scale project aimed at producing 25 kg/day hydrogen from biomass, such as peanut shells, for urban transportation. The process involves pyrolysis of the biomass followed by catalytic steam reforming of the gas and bio-oil products to produce H_2 at \$2.90/kg H_2 by 2010 and \$2.30 by 2015.

Successful operation for 100 hours demonstrated technical feasibility of the process, discovered agricultural uses of the carbon product, and identified economical co-product options for the bio-oils. Use of the reformer gas in an engine resulted in significant reduction of NO_X. Further R & D over 1,000 hours process operation and higher hydrogen production rate could lead to a viable hydrogen and integrated bioconversion process to fulfill the President's FreedomCAR and Hydrogen Fuel Initiative goals.

BACKGROUND

- **There is a need for clean fuels to address global climate change.**
- **Hydrogen is the most environmentally friendly and highest energy per mass fuel.**
- **FreedomCAR and Hydrogen Fuel Initiative are now national energy priorities.**
- **There is a need to produce and deliver economically competitive hydrogen (e.g., $1.50 by 2010 vs. $6 per gasoline gallon equivalent in 2003 from natural gas and liquid fuels)**
- **Potential sources of hydrogen include biomass, natural gas and other fossil fuels.**

BACKGROUND (Contd)

- **Biomass offers several advantages:**
  - Renewable, zero-net CO_2 impact.
  - Target costs of \$3.80/kg H_2 (2003), \$2.90 (2010) and \$2.30 (2015)
- **Agriculture is Georgia's largest industry and will provide biomass feedstock.**
  - Peanut shells are a start, other forms of biomass will be investigated.
- **Hydrogen can be used for transportation and stationary fuel cell power generation.**
- **Integrated biomass conversion process can revitalize rural economy.**

Reforming Reactions

- $C_nH_m + nH_2O = nCO + (n + m/2)\,H_2$

$$(-\Delta H^\circ_{298} < 0)$$

- $CO + H_2O = CO_2 + H_2$

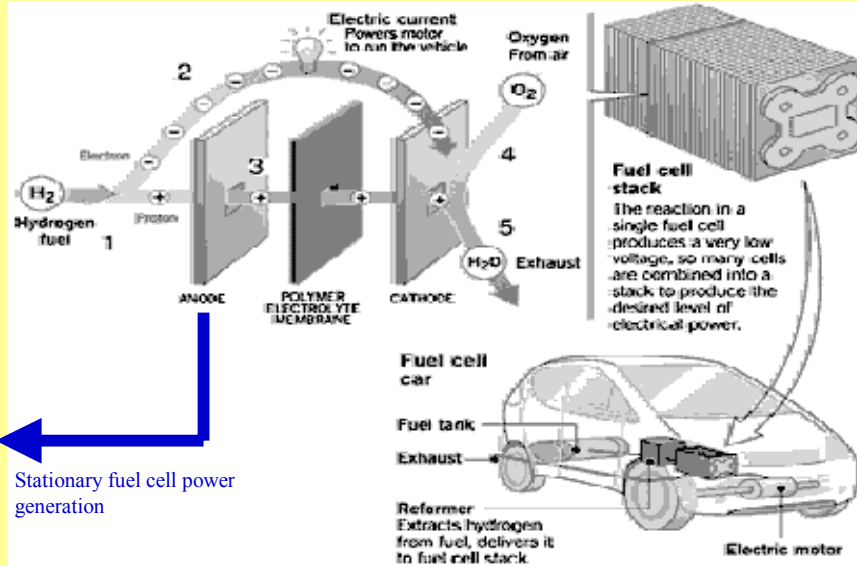
$$(-\Delta H^\circ_{298} = 9.48 kcal/mol)$$

- $CO + 3H_2 = CH_4 + H_2O$

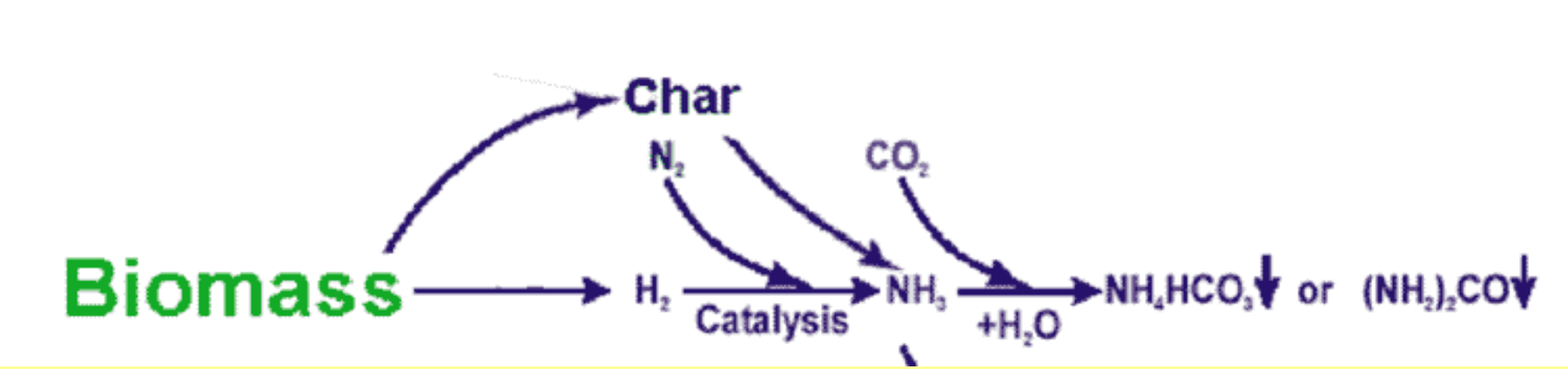
$$(-\Delta H^\circ_{298} = 49.27\ kcal/mol)$$

The Peanut Shell to Hydrogen Cycle

Stationary fuel cell power generation



Biocarbon-Based Fertilizers



Courtesy
D. Day,
Eprida/
Scientific Carbons
Inc.

Relevance to DOE, FreedomCAR, and Hydrogen Initiative

- Project is developing technology (pyrolysis-reformer process) that will:
  - Produce hydrogen from biomass (e.g., peanut shells)
  - Utilize the biomass hydrogen for transportation and/or stationary power generation
  - Reduce cost, and develop improved technologies
- Project addresses national and global issues related to:
  - Improvement in America's energy security by reducing the need for imported oil
  - Improving air quality and reducing greenhouse gas emissions
  - Revitalization of rural economy (e.g., Georgia)
  - The four E's: Energy, Environment, Economy, and Education

OBJECTIVES

- Undertake the engineering research and pilot scale process development studies relating to:
  - Production of hydrogen from biomass (e.g., agricultural residues) for $2.90/kg H_2 by 2010; $2.30 by 2015
  - Separation, safe storage and utilization of the hydrogen
  - Production and identification of uses of the co-products
- Increase diversity of the Nation's workforce and the broader impact of the project through the education and training of underrepresented minorities.

APPROACH

- **Develop process based on biomass pyrolysis and steam reforming of pyrolysis vapors (bio-oils and gases).**
- **Perform catalytic steam reforming in a fluidized-bed (25-250 kg/day H_2 production)**
- **Conduct pyrolysis at: T: 500°C; P: 10 psig; Feed Rate: 50-500 kg/hr pelletized peanut shells.**
- **Study reforming at: T: 850°C; P: 6 psig; $H_2O/C = 5$, Catalyst: nickel-based (300-500 microns)**

APPROACH/ PROJECT TASKS

- **Task 1: Feedstock supply, process economics and deployment strategies (modeling, extraction, and property estimation)**
- **Task 2: Process modifications, integration, and shakedown**
- **Task 3: Long term (1,000 hours) catalyst and process testing**
- **Task 4: Hydrogen separation, storage, and utilization**
- **Task 5: Environmental and technical evaluation**
- **Task 6: Partnership building and outreach**

PROJECT TIMELINE

TASK/ACTIVITY	YEAR				
	9/2000	2001	2002	2003	3/2004
Task 1: Modeling and Extraction Studies					
- Develop model of network steps	----------→				
- Solubility & Parameters Estimations		----------→			
Task 2: Design, Construction and Shakedown					
- Reformer Design, Construction, and Testing	-------→				
- Integration of Pyrolyzer- Reformer Unit		------→			
- Modifications for 1,000 hours run			------→		
Task 3: Long-term Catalyst Testing					
- 100 hour Testing of Unit			---→		
- 1000-hour testing of catalyst and unit				--------→	

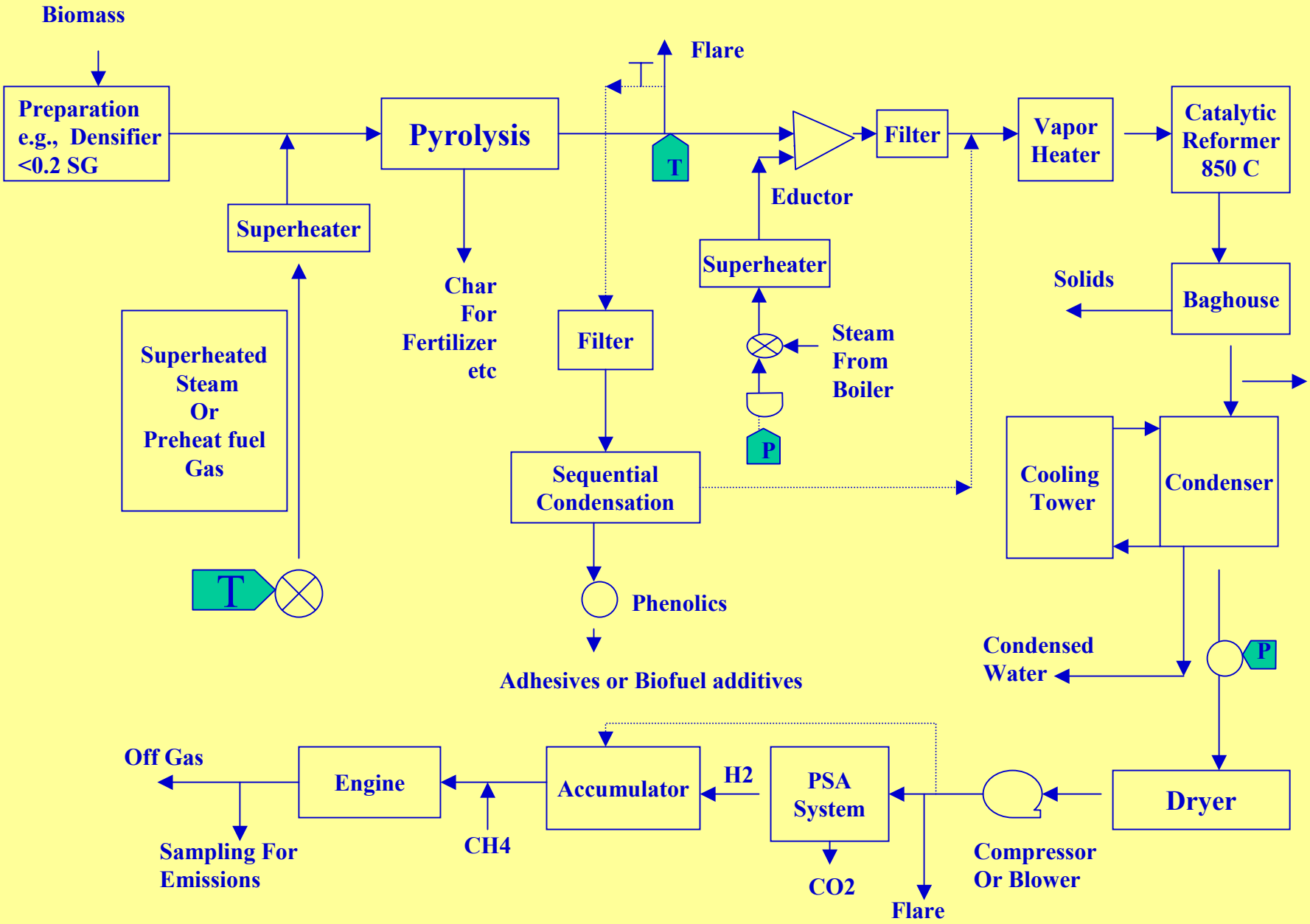
PROJECT TIMELINE(contd.)

TASK/ACTIVITY	YEAR				
	9/2000	2001	2002	2003	3/2004
Task 4: Hydrogen Separation					
- Design and acquisition of PSA			----→		
- Installation and testing of PSA				----→	
Task 5: Environmental and Technical Evaluation					
- Acquisition of analytical instruments		------→			
- Development of methods and procedures			--------→		
- Analysis and monitoring of process streams			---------→		
Task 6: Partnership and Outreach					
- Partnerships and collaborations			----------→		
- Education and training of students			----------→		

ACCOMPLISHMENTS/PROGRESS

- **Completed design, construction and testing of reformer (Phase 1)**
- **Completed integration of reformer with pyrolyzer (Phase 2)**
- **Completed 100 hours of successful operation of pilot unit (Phase 2)**
- **Identified modifications for 1,000 hours operation run**
- **Identified potential co-products options**
- **Developed partnership and collaboration with potential companies/ organizations**
- **Educated and trained several underrepresented minorities on project**
- **Planning on 1000-hour run in 2003**

Schematic Flow Diagram of the Biomass Refinery for Hydrogen, Char and Chemicals



PICTURES OF PILOT PLANT

PICTURES OF PILOT PLANT

Blakely, Georgia Site

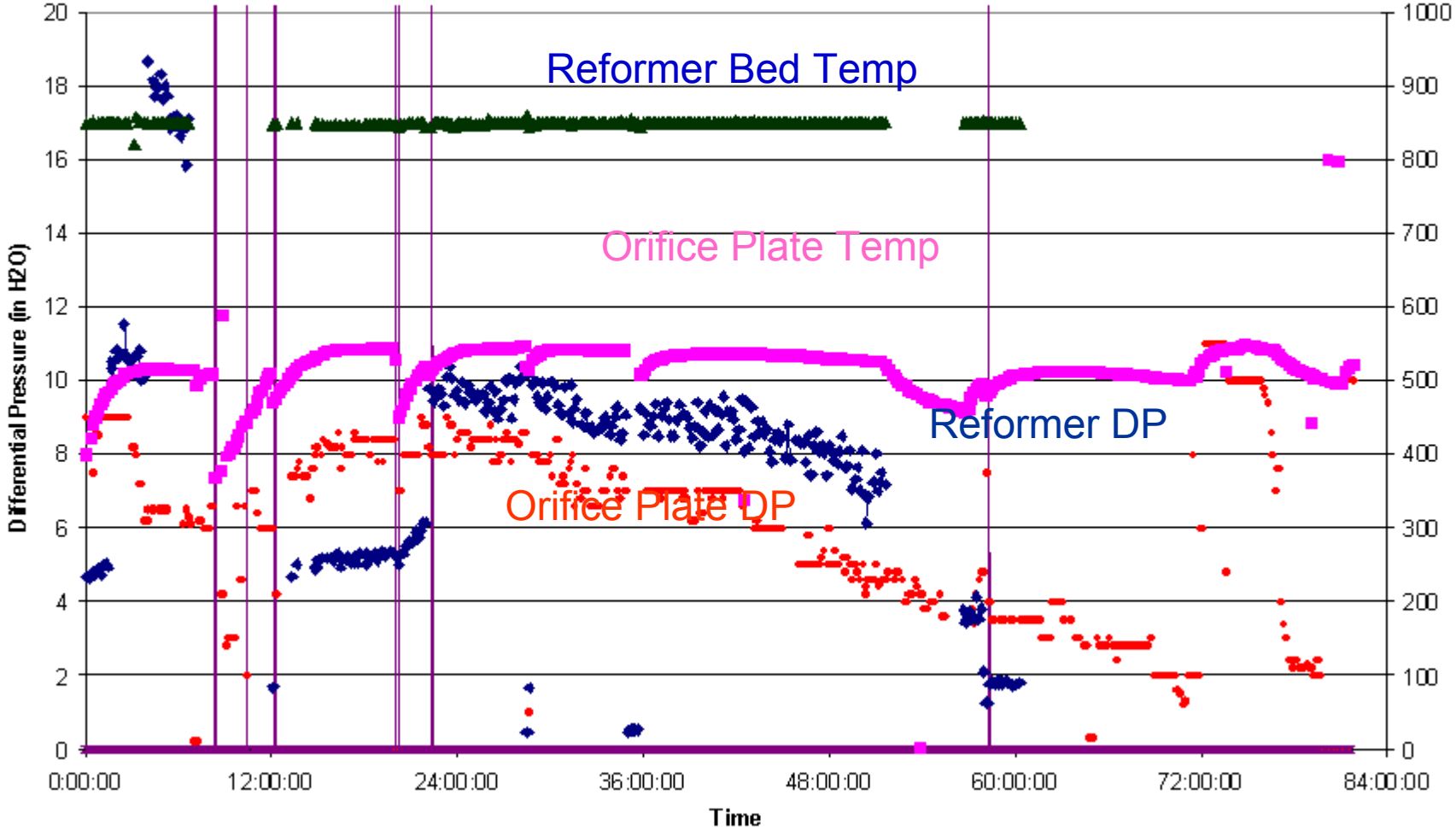
Typical Analysis of Peanut Shell Feedstock

- **Component** **%**
  - Lignin ---------- **34.8**
  - Glucan ---------- **21.1**
  - Extractives ---------- **14.2**
  - Protein ---------- **11.1**
  - Xylan ---------- **7.9**
  - Ash ---------- **3.4**
  - Arabinan ---------- **0.7**
  - Galactan ---------- **0.2**
  - Mannan ---------- **0.1**
  - Others (e.g., free carbohydrates) ---------- **6.5**

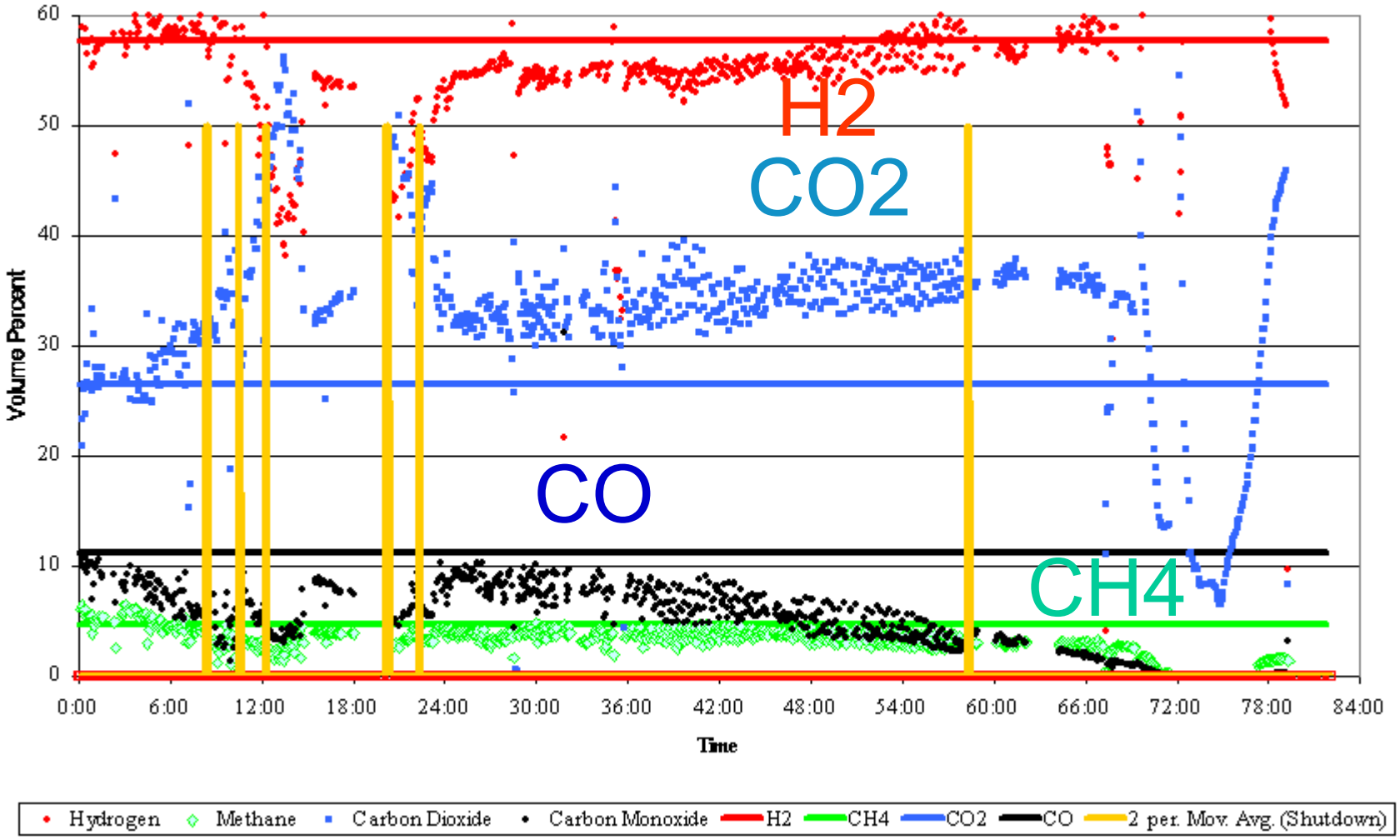
RESULTS: TYPICAL PRODUCT COMPOSITION/ YIELD

Pyrolyzer (Yields)		Reformer (Gas product composition, on dry N_2-free basis)	
Char	32%	Hydrogen	57%
Water	32%	Carbon Dioxide	26%
Bio-Oils	31%	Carbon Monoxide	12%
Gases	5%	Methane	5%

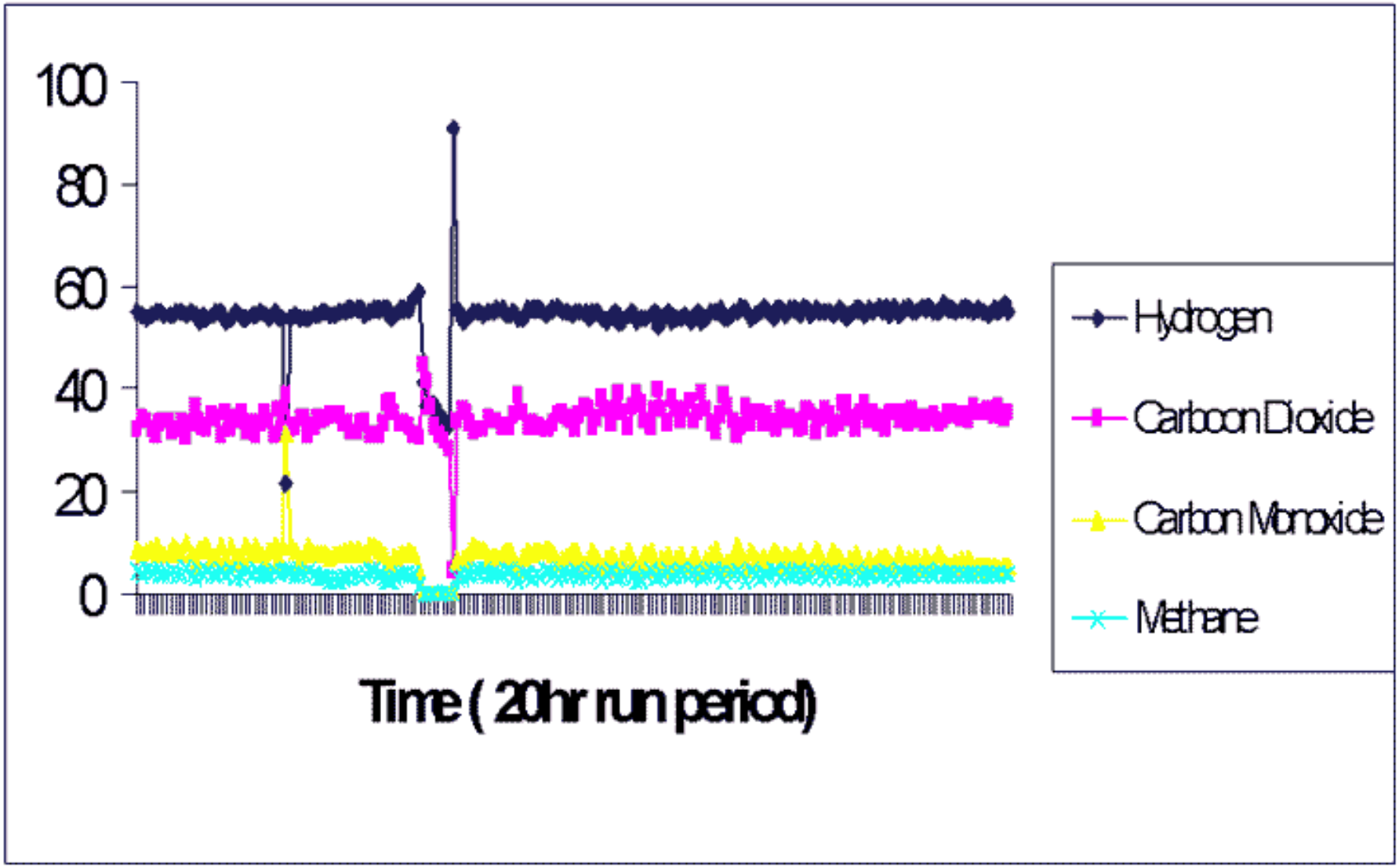
Reformer Performance



Gas Composition



Plot of Gas Composition Vs.Time (hrs)



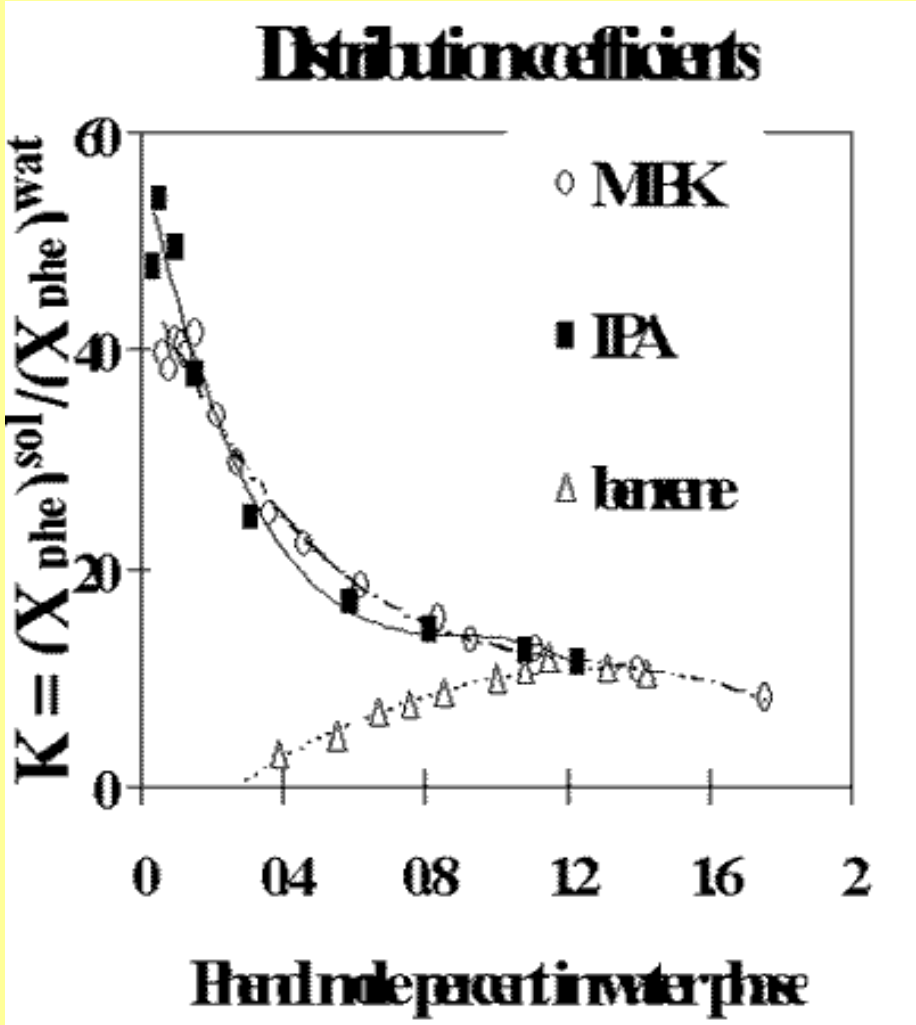
Pyrolysis Bio-Oil Product

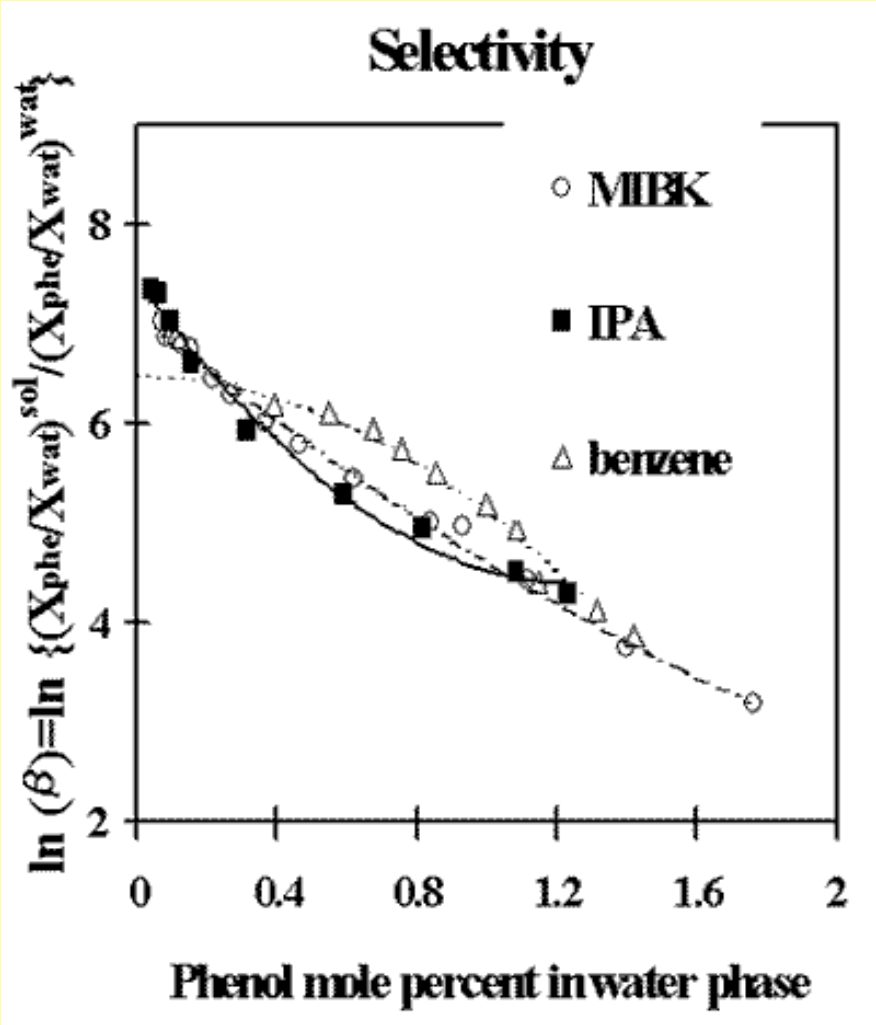
- **Empirical Formula: $CH_{1.9}O_{0.7}$**
- **Water: 15 – 25%**
- **Organics: 75 – 85%**
  - Aldehydes, alcohols and acids from carbohydrate fraction
  - Phenolics from lignin fraction

- **Representative Compounds**

Water	Ethanol	Methanol
Cyclohexanol	Formic Acid	Acetic Acid
Glucose	Phenol	O-cresol
2-Butanone	Dodecanoic acid	Tannin

Selectivity / Distribution Plot





SIGNIFICANT INTERACTIONS AND COLLABORATIONS

- **The project has resulted in significant interactions and collaborations between the following organizations:**

  - Clark Atlanta University, Atlanta, GA
  - Eprida Scientific Carbons Inc., Blakely, GA
  - Enviro-Tech Enterprises Inc., Matthews, NC
  - Georgia Institute of Technology, Atlanta, GA
  - National Renewable Energy Lab, Golden, CO
  - Oak Ridge National Lab, Oak Ridge, TN
  - Southern Company, Atlanta, GA
  - University of Georgia, Athens, GA

FUTURE PLANS

- **Demonstrate process control and operability for 1,000 hours of operation (Phase 3).**
- **Undertake further research and development studies in a larger scale pilot plant (250 kg H_2/day).**
- **Develop process models for scale up and process optimization.**
- **Perform detailed techno-economic analysis based on pilot results.**
- **Identify and evaluate integrated bioconversion process for different feed stocks and product options.**

PLANS AND FUTURE MILESTONES (Phase 3)

ACTIVITY	COMPLETE BY
• **Modeling and solubility studies**	**September 2003**
• **Evaluation of co-products options**	**December 2003**
• **Modifications and installation of controls**	**August 2003**
• **Integration of analytical systems**	**September 2003**
• **Shakedown runs before 1,000 hr run**	**September 2003**
• **1,000 hours of operation of pilot unit**	**November 2003**
• **Engine tests with reformer gas**	**November 2003**
• **Installation and testing of PSA unit**	**September 2003**
• **Education and training of students**	**March 2004**

RESPONSE TO SIGNIFICANT QUESTIONS/ CRITICISMS

- **Reviewers recommended appropriate safety reviews and operational readiness inspection prior to start-up of the pilot plant demonstration unit.**

  - Safety has always been of top priority in this project
  - It has been incorporated in all designs, operations and phases of this study based on input from safety experts from NREL.
  - Safety reviews and operational readiness inspections will be undertaken by safety experts from NREL, University of Georgia, and the project team prior to start-up of the pilot demonstration unit.

CONCLUSIONS

- **Demonstrated successfully pyrolysis-reformer concept for 100 hours operation**
- **Discovered agricultural uses and carbon sequestration strategy: Novel carbon slow release sequestered fertilizer.**
- **Identified economical co-product options for bio-oils: Adhesives.**
- **Run successfully the product gas in an engine with significant reduction of NO_x**
- **Further R & D over 1,000 hours operation and higher hydrogen production rate could lead to economically competitive hydrogen and a viable integrated bioconversion process.**

ACKNOWLEDGEMENTS

- **Support of Department of Energy under Grant # DE-FC36-00GO10528**.
  - Doug Hooker, James Alkire, Beth Dwyer
  - Chris Bordeaux, Sigmund Gronich, Neil Rossmeissl
- **Support of the Partner Institutions**
  - Clark Atlanta University
  - Eprida Scientific Carbons Inc.
  - Enviro-Tech Enterprises Inc.
  - Georgia Institute of Technology
  - National Renewable Energy Laboratory

Water-Gas Shift Membrane Reactor Studies

Richard Killmeyer, Kurt Rothenberger, and Bret Howard
US DOE, NETL

Michael Ciocco and Bryan Morreale
NETL Site Support Contractors,
Parsons Project Services

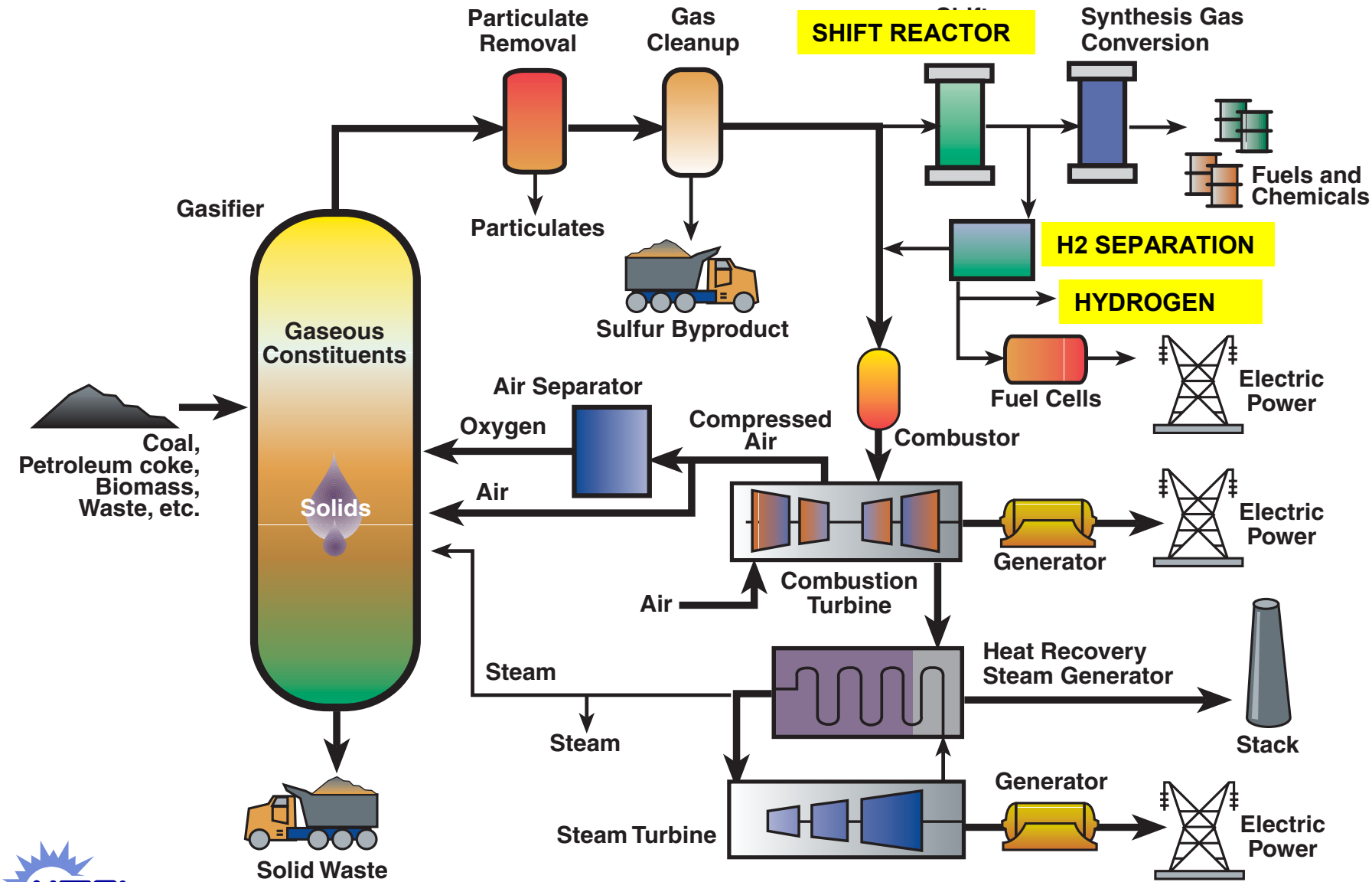
Prof. Robert Enick and Felipe Bustamante
NETL Research Associates
University of Pittsburgh

National Energy Technology Laboratory
Office of Science & Technology
Fuels and Process Chemistry Division

NETL's Hydrogen Program

- **Vision**
  - Fossil fuel resources are the transition feedstocks for the production of hydrogen for broad-based applications in the "Hydrogen Economy"
- **Mission**
  - Develop and demonstrate technology to produce and to separate hydrogen for downstream uses, both in advanced energy plant applications and in off-site applications
- **Program Directions**
  - Clean hydrogen for downstream processes
  - Transition to the Hydrogen Economy
  - CO_2 capture and sequestration

Coal Gasification Technology Options

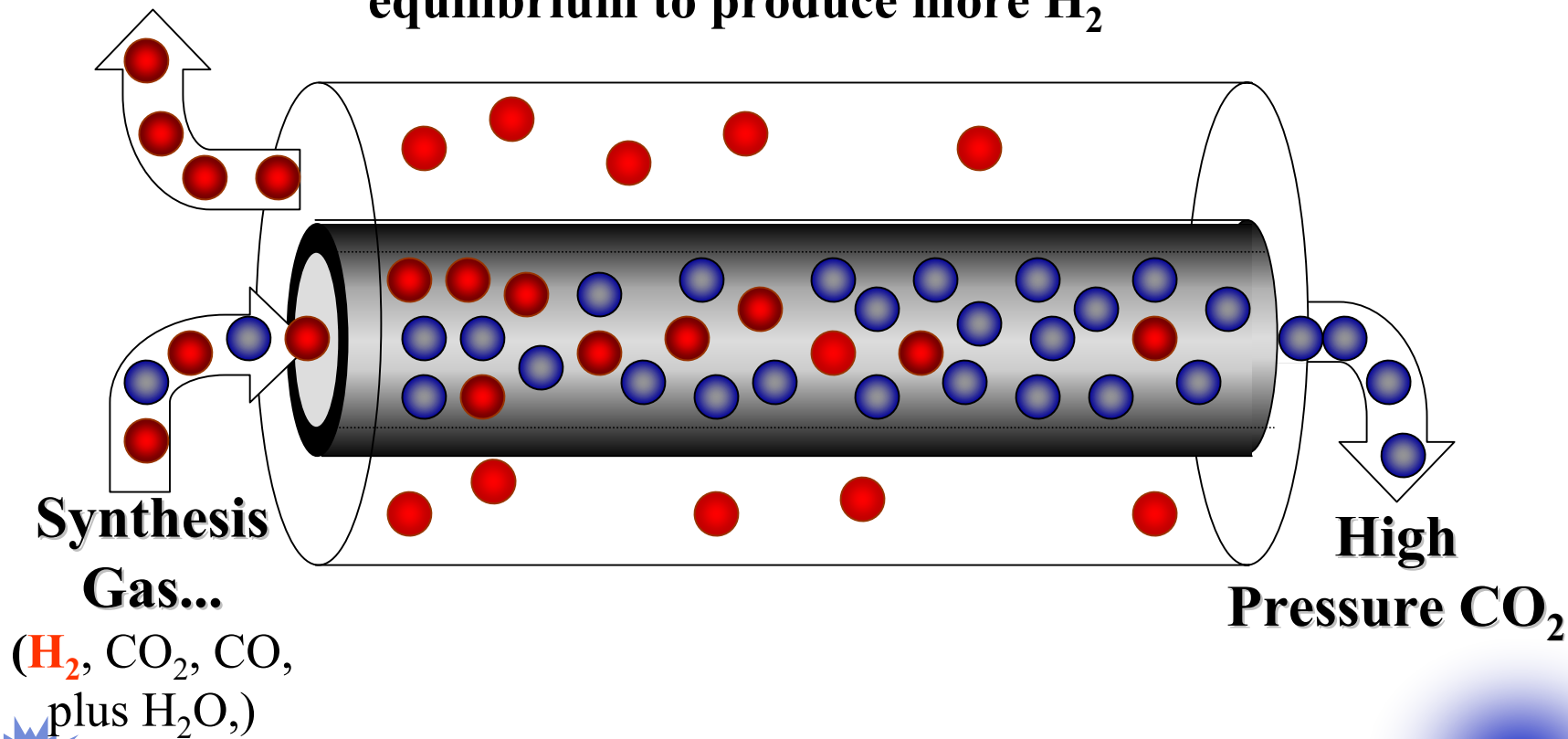


H_2 Membrane Reactor Concept

*WGS Reaction: $CO + H_2O \Rightarrow CO_2 + H_2$

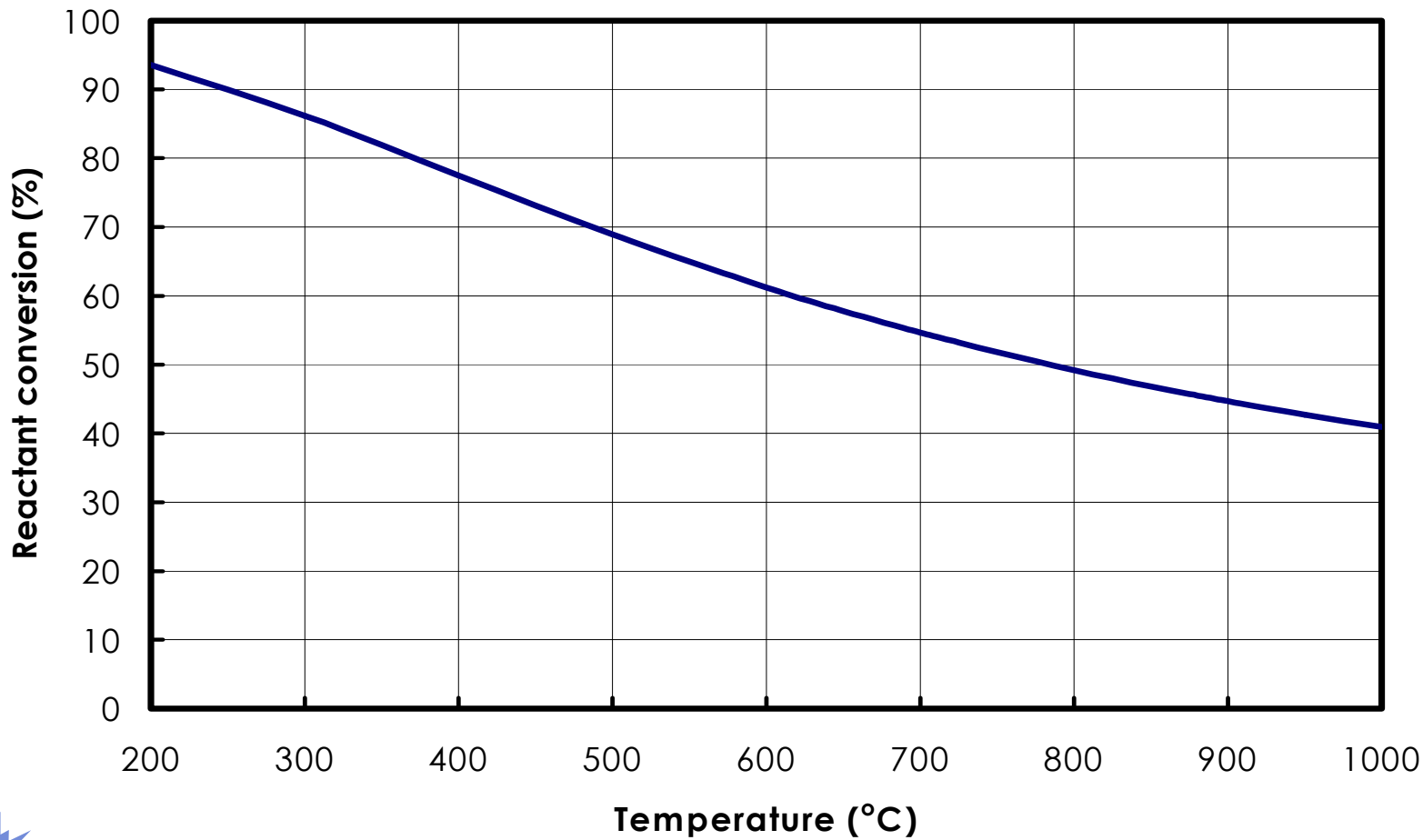
*High-T for favorable kinetics

*Membrane removes H_2 to "shift" unfavorable equilibrium to produce more H_2



Equilibrium Conversion for the Water Gas Shift Reaction

$[CO]_0=[H_2O]_0$, $[CO_2]_0=[H_2]_0=0$



Project Rationale

- **Designing WGS Membrane Reactors Requires the Consideration of Reaction Kinetics and Mass Transport Phenomena**
  - Forward Water-Gas Shift Kinetics
  - Reverse Water-Gas Shift Kinetics
  - Catalytic Effect of Reactor Materials, Membrane Materials & Heterogeneous Catalyst Particles
  - Heterogeneous Catalysis May Not Be Needed
  - Hydrogen Flux Through Membrane
  - Hydrogen Selectivity of Membrane
  - Durability of Membrane in Extreme Environments

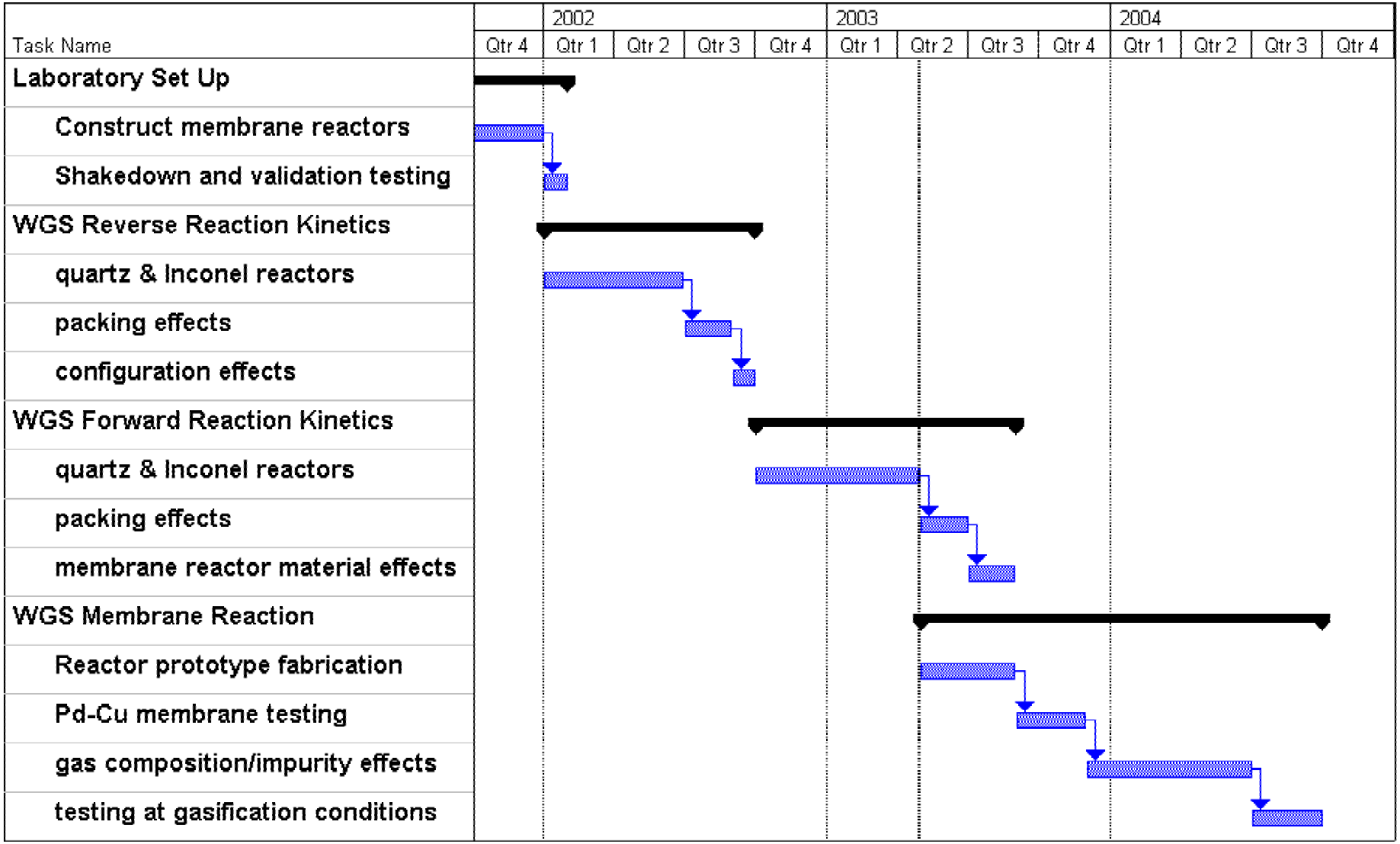
Relevance to EE H2 Production R&D Plan

- Project falls within the Technical Objective to develop technology to produce pure H_2 from coal using a 600ºC membrane system at a cost of $0.79/kg by 2015
- Related Technical Targets are based on use of a membrane water-gas shift reactor in the system
- Project addresses Technical Task 4 on "Alternative and Improvements to Conventional Water-Gas Shift" and related technical barriers

FY03 Approach

- **Goal: evaluate WGS kinetics and membrane flux using industrial gas mixtures and conditions**
  - complete reverse kinetics and CFD modeling to optimize reactor geometry for forward reaction
  - measure forward kinetics in quartz & Inconel reactors to determine reactor wall catalysis
  - measure forward kinetics in reactor lined with membrane material to determine catalytic activity
  - measure membrane H_2 permeability in presence of clean syngas components (CO_2, H_2O, CO)
  - conduct forward WGS using a membrane reactor at favorable conditions

Project Timeline

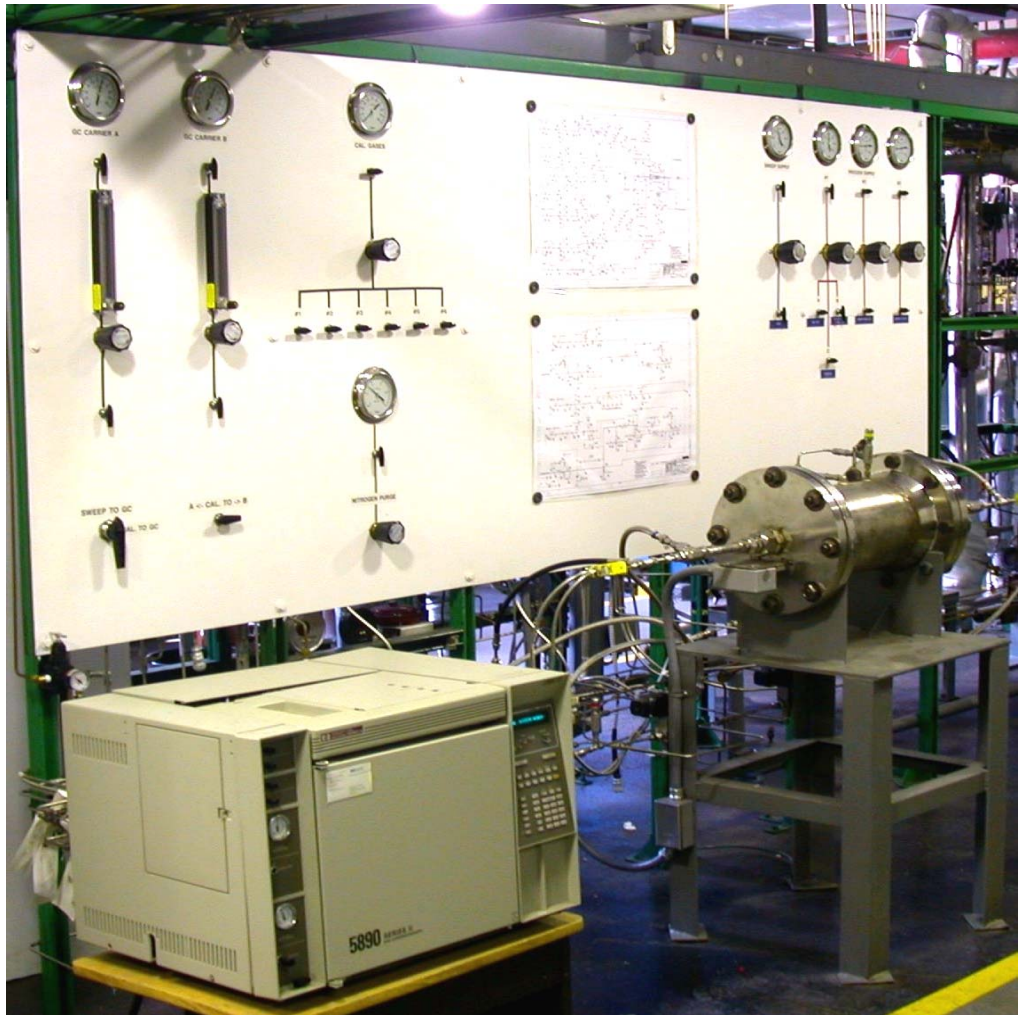


FY02 & FY03 Accomplishments

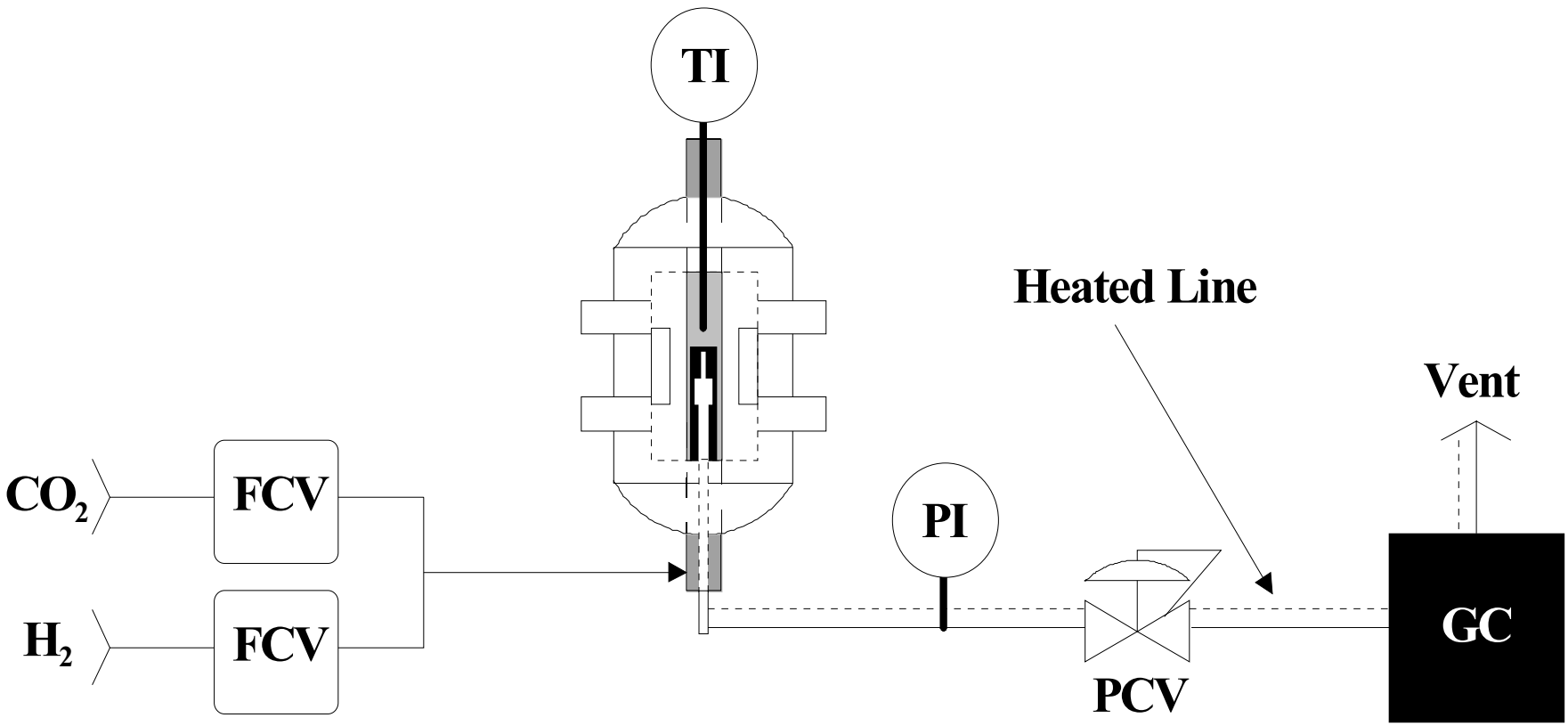
- **High-T water-gas-shift (WGS) reaction concept:**
  - conducted first-ever hi-T and hi-P reverse WGS reaction kinetics study
  - reverse WGS significantly catalyzed by Inconel reactor wall
  - conducted CFD simulations for effect of reactor geometry on kinetics
  - completed intrinsic kinetics testing of forward WGS reaction
- **Designed & constructed HMT3 unit with enhanced features for membrane reactor testing**
- **F. Bustamante et al., "Very High-T, High-P Homogeneous WGS Reaction Kinetics," AIChE Mtg., Reno NV, 11/01**
- **F. Bustamante et al., "Kinetic Study of the Reverse WGSR in Hi-T, Hi-P Systems," ACS H_2 Symp., Boston MA, 08/02**
- **F. Bustamante et al., "Kinetics of the Homogeneous WGS Reverse Reaction at Elevated Temp.," AIChEJ (in press, 2003)**

NETL Hydrogen Separation Facilities

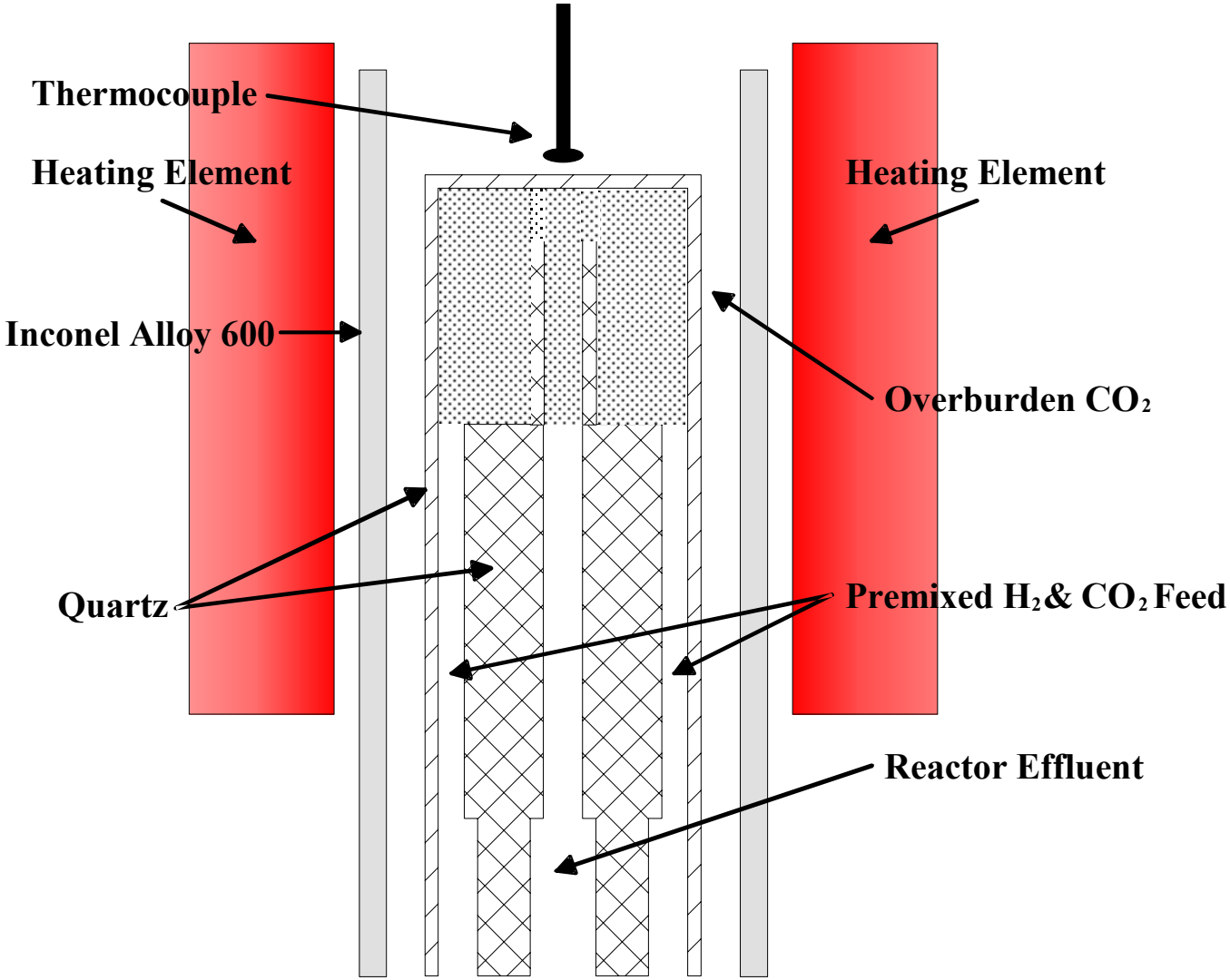
- 3 H_2 Membrane Test Units
- Constructed FY99 to FY02
- Temperatures to 900°C
- Pressures to 400 psi
- Disk & tubular membranes
- 1/4” to 1/2” membranes
- Feed gas flexibility
- Membrane separation & reactor configurations
- “Clean” and “sulfur-laden” gas feedstocks
- Online analysis of products by GC



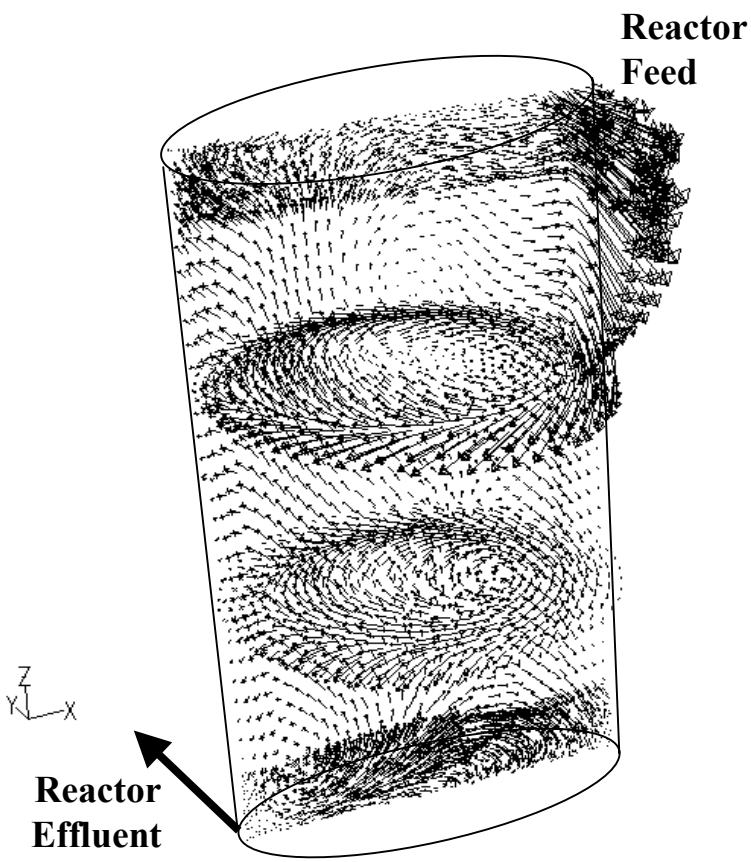
Experimental Setup



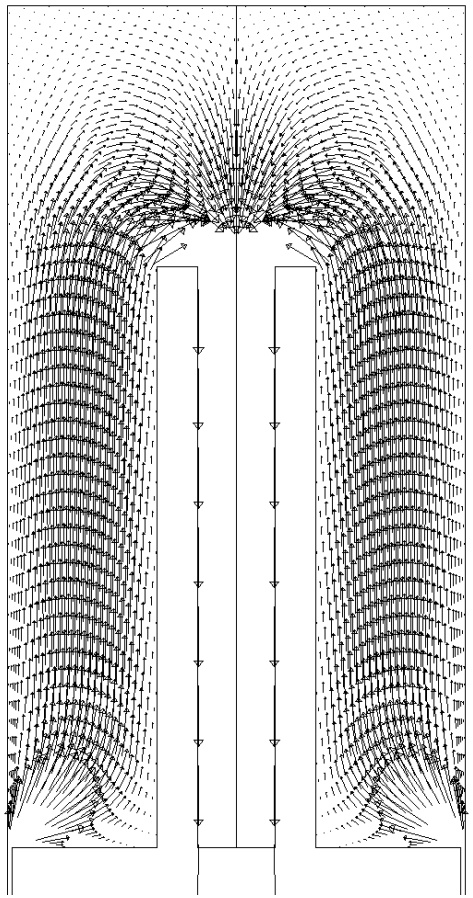
Quartz Reactor



High-T, Low-P Reverse WGS Kinetics CFD Modeling of Flow Patterns in Reactor



Graven & Long, 1954



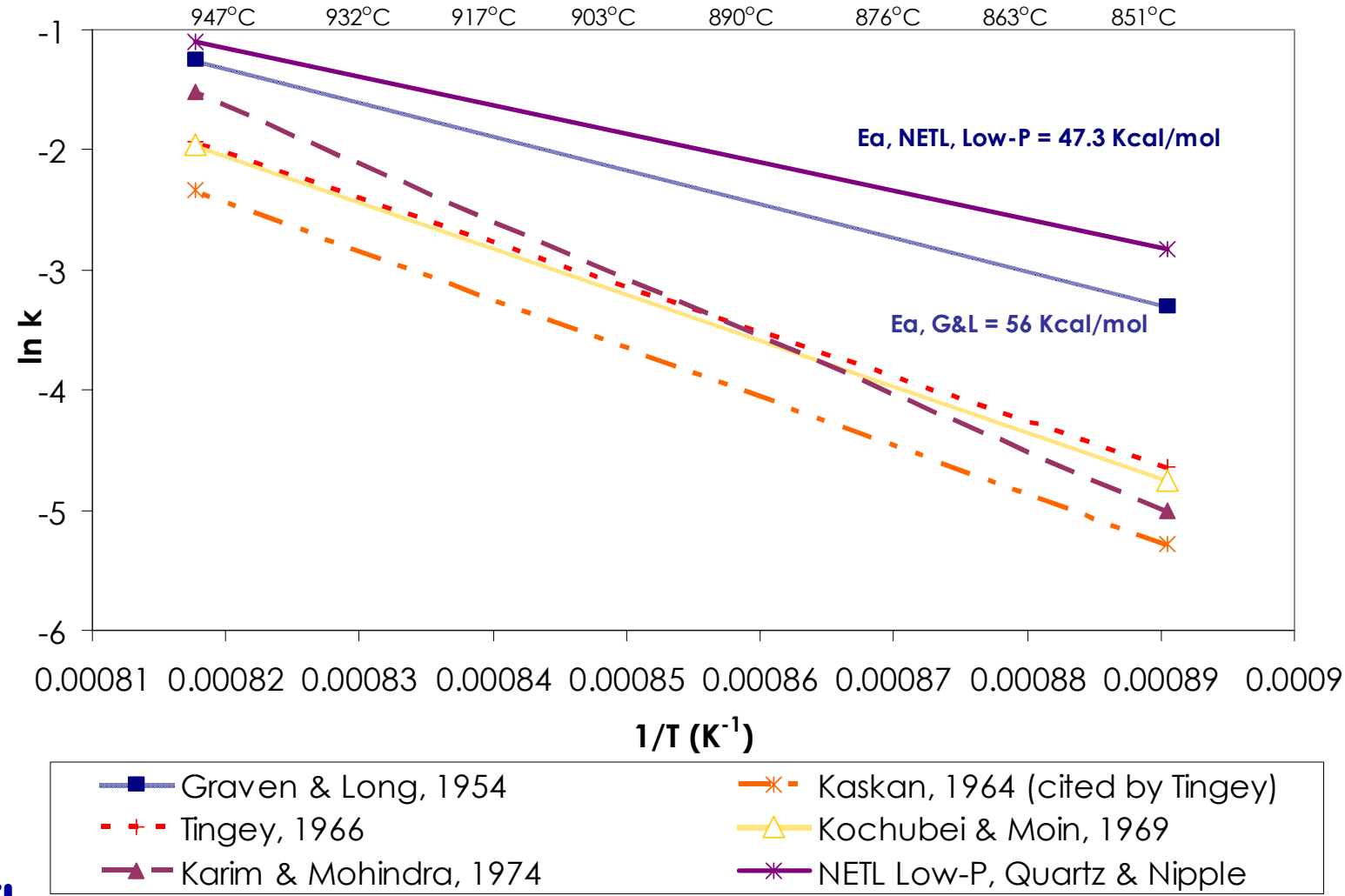
NETL, 2002

Simulations performed by S. Shi (Fluent) and B. Rodgers (NETL)

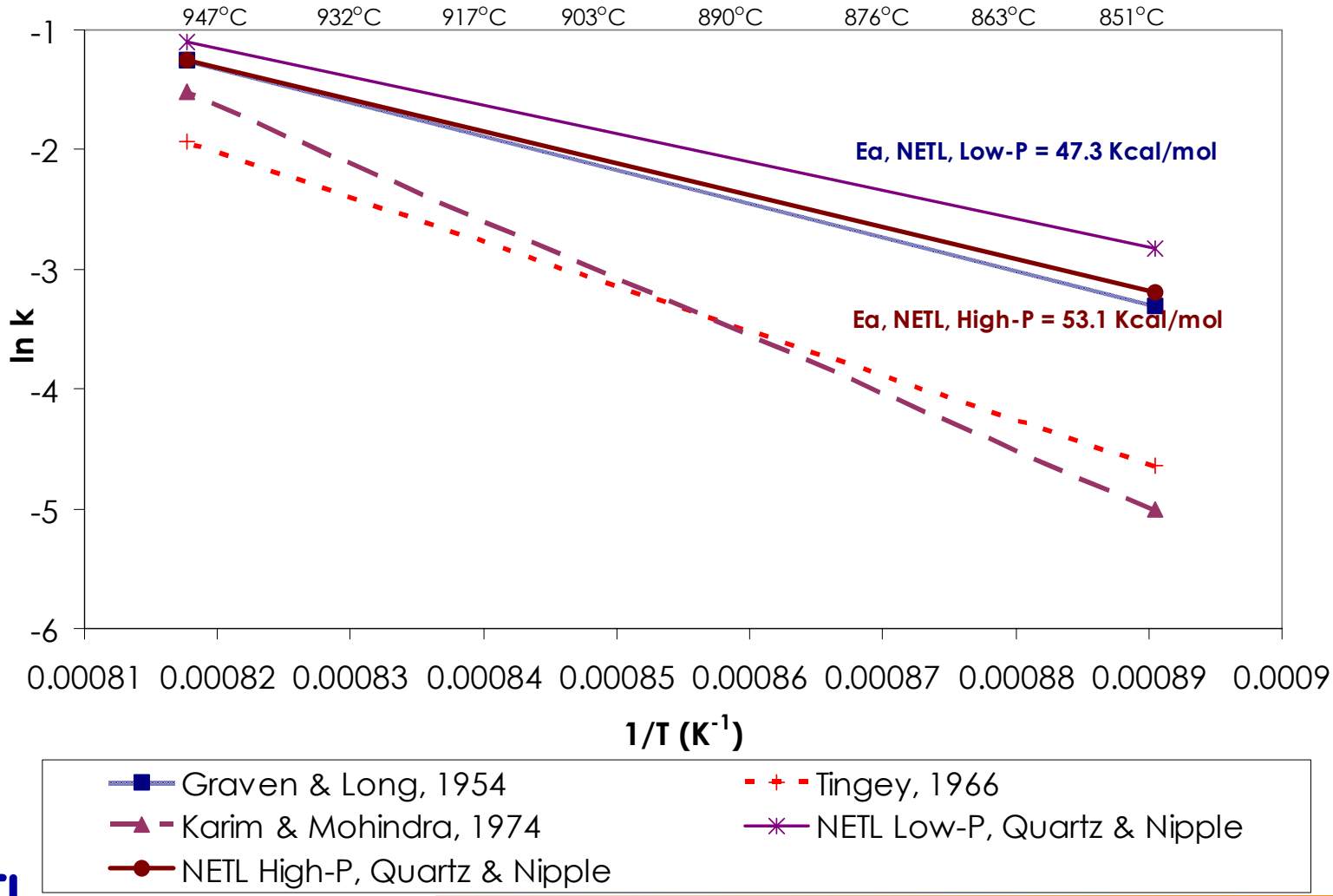
Kinetic Expression for the Reverse WGS Reaction Based on the Bradford Mechanism

- ***Reverse** Reaction*
- $CO_2 + H_2 \longrightarrow H_2O + CO$
- $r = - k_r [H_2]^{0.5}[CO]^1$
- $k_r = k_{ro} \exp(-E_a/RT)$

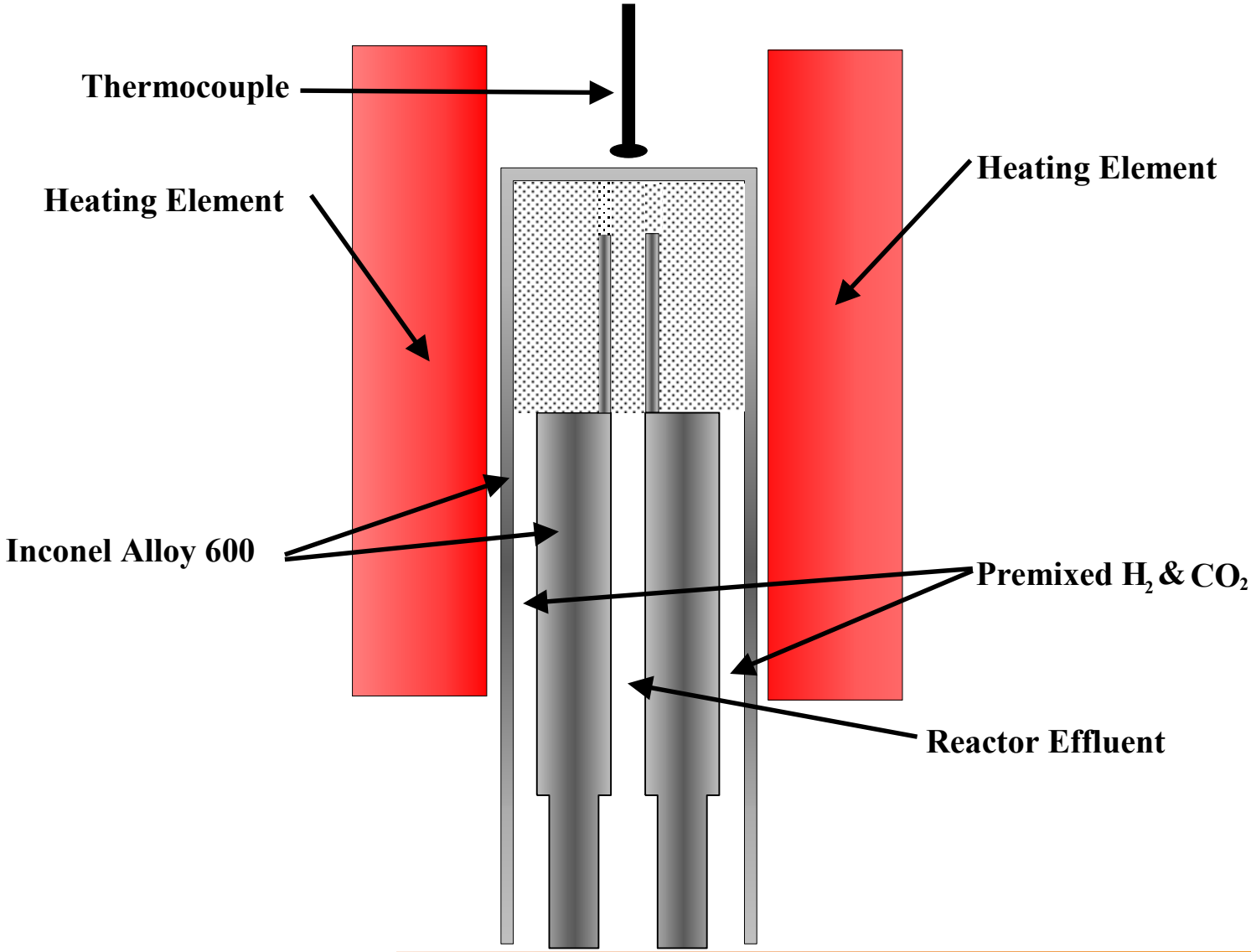
High-Temperature (>850°C), *Low-Pressure* (1 atm) Reverse WGS Quartz Reactor



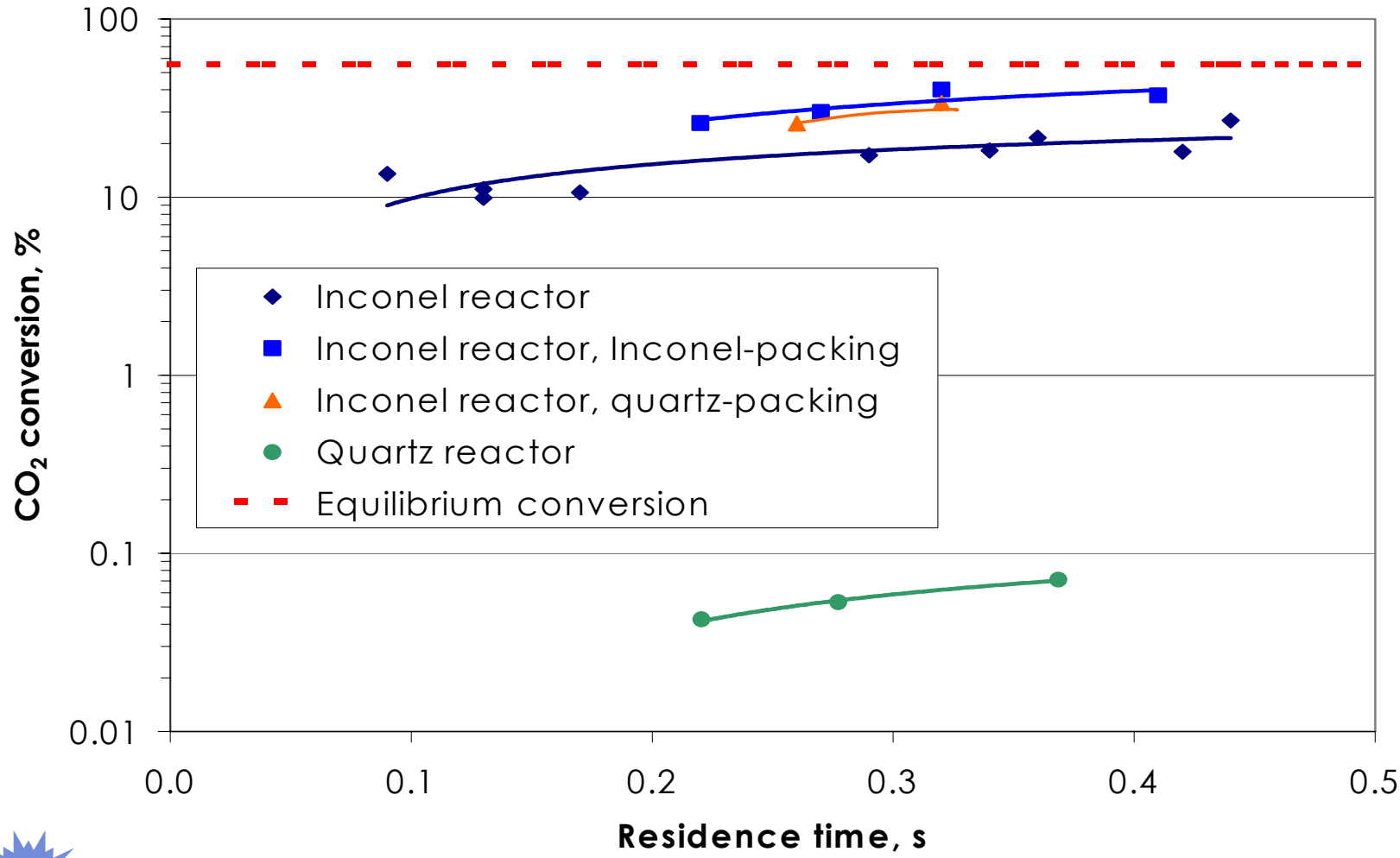
High-Temperature (>850°C), *High-Pressure* (16 atm) Reverse WGS in a Quartz Reactor



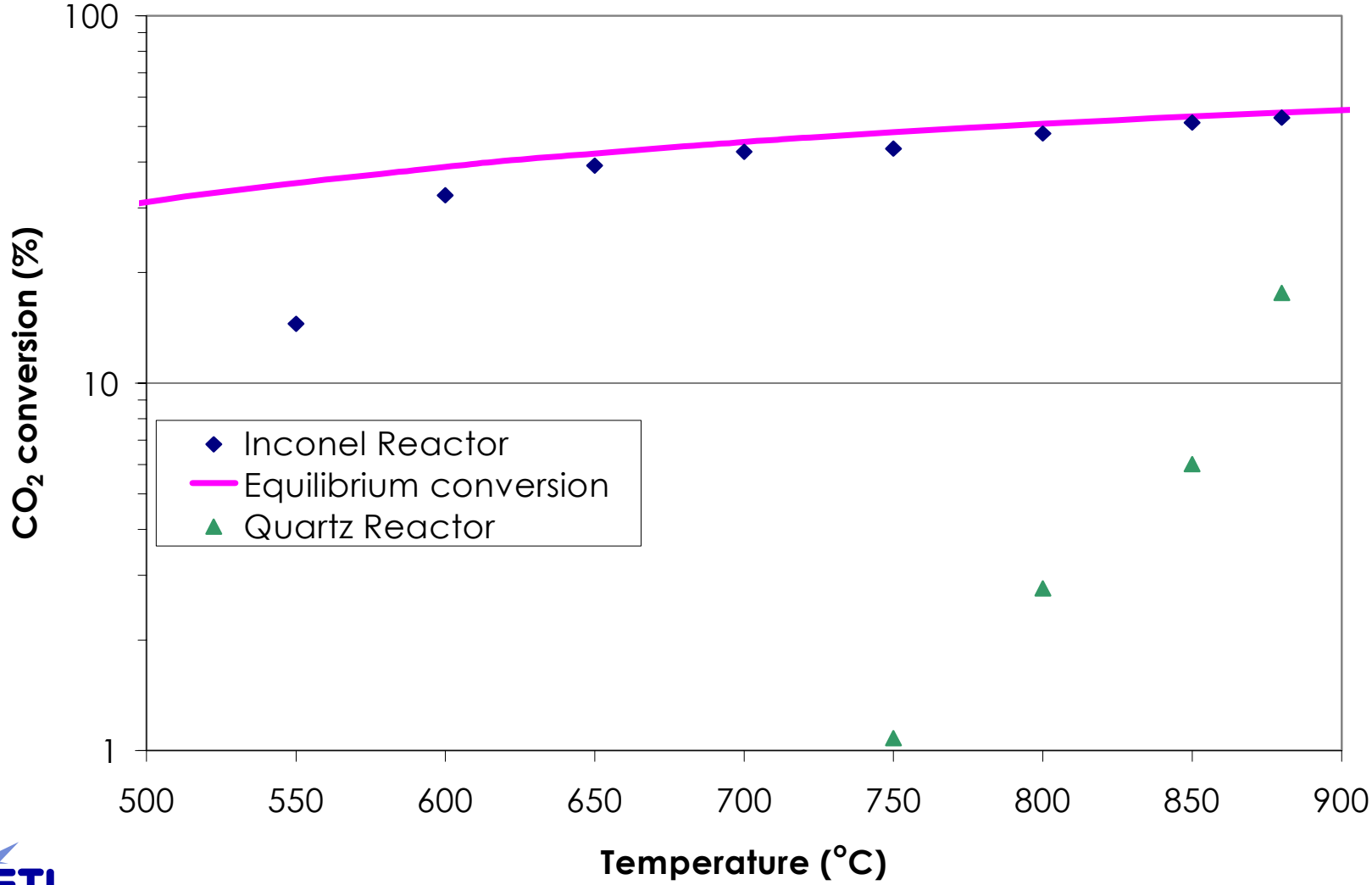
Inconel Reactor



WGS Reverse Reaction Test Data (Inconel reactor, 900°C, 101.3 kPa, Equimolar H_2 and CO_2 feed)



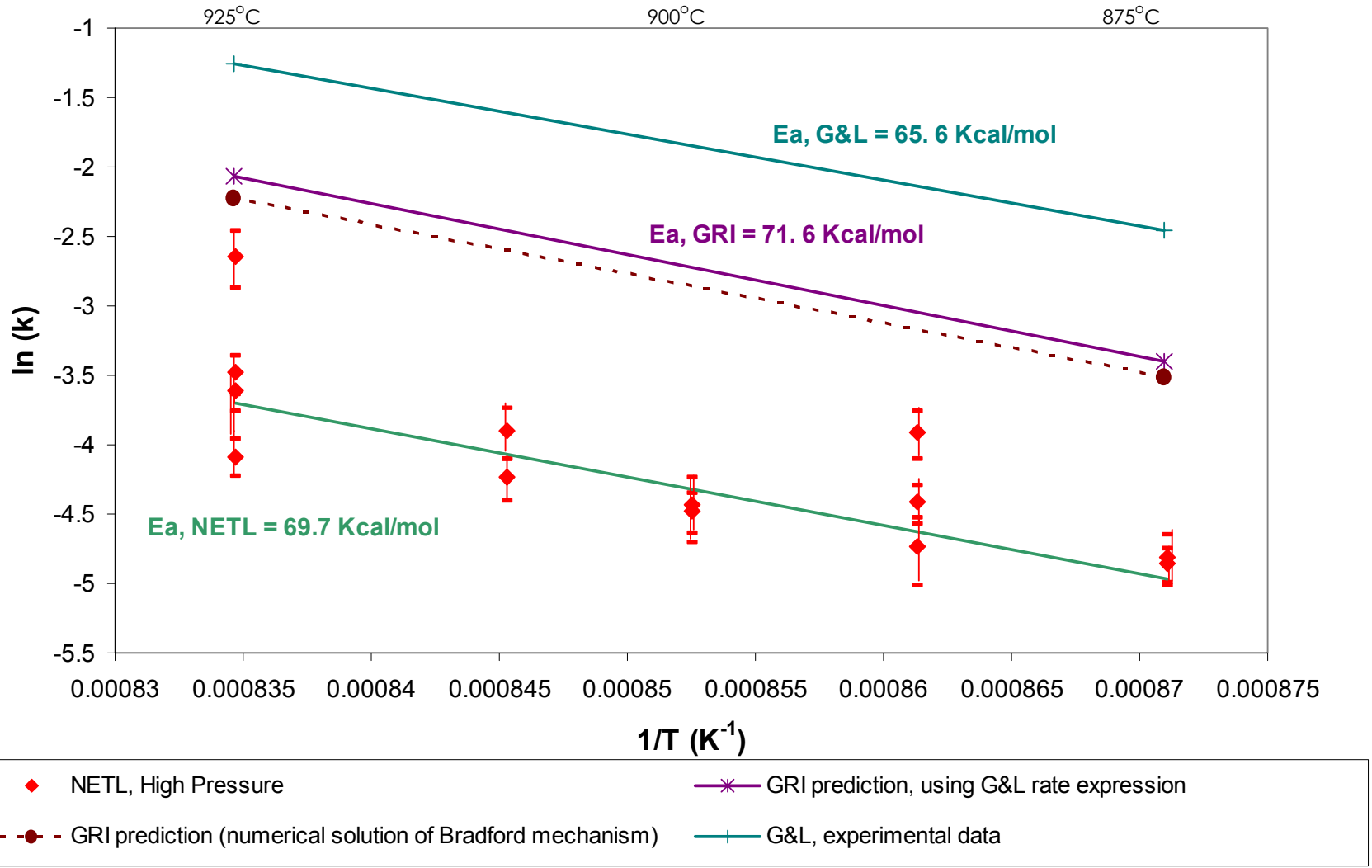
High-Pressure (16 atm), High-Temperature <u>Reverse</u> WGS in an Inconel Reactor



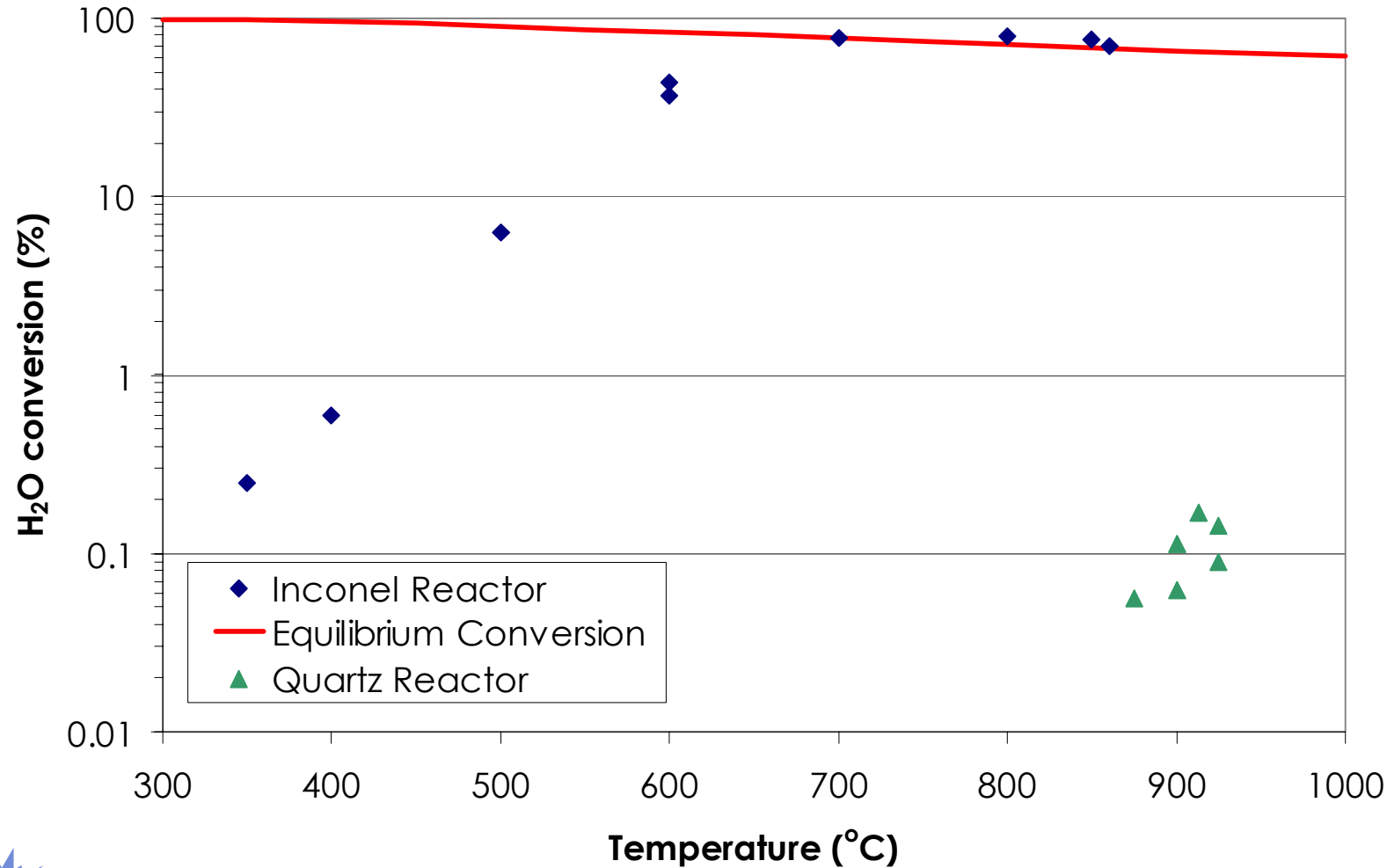
Kinetic Expression for the Forward WGS Reaction Based on the Bradford Mechanism

- *Forward Reaction*
- $H_2O + CO \longrightarrow CO_2 + H_2$
- $r = -k_f [H_2O]^1[CO]^{0.5}$
- $k_f = k_{fo} \exp(-E_a/RT)$
- Exponents of 1 and 0.5 verified
- Boudouard reaction produces C
- 2CO = C + CO2
- Suppress C deposits via short reaction runs
- Removal of C deposits via overnight O_2 purge to produce CO_2

High-Temperature (>850°C), *High-Pressure* (16 atm) Forward WGS in a Quartz Reactor



Ambient-P, *Forward* WGS – Inconel Reactor Wall Effects

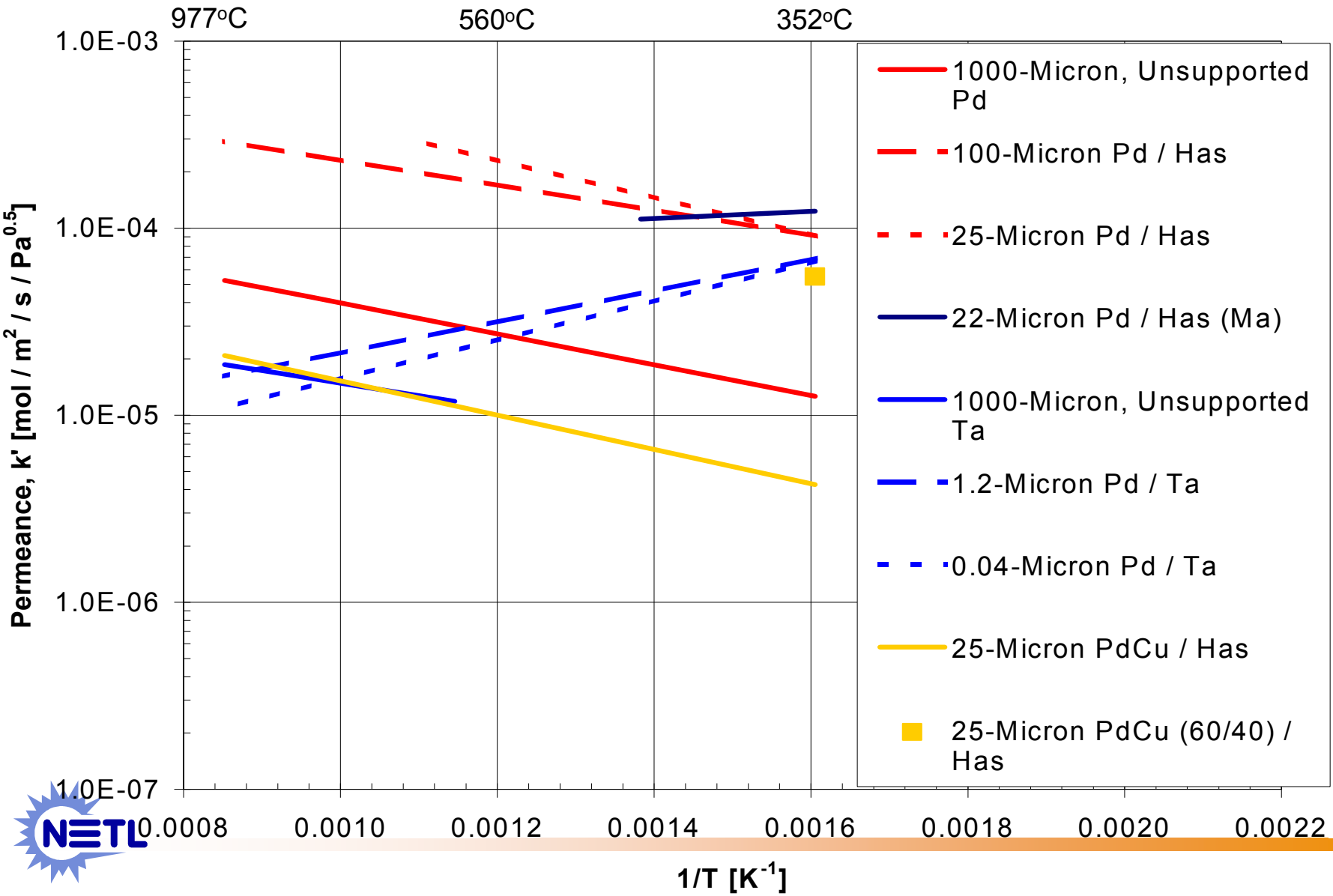


$(x_{CO})_0 = 0.72$, $(x_{H2O})_0 = 0.28$, $(x_{CO2})_0 = (x_{H2})_0$, $\tau \sim 0.5 - 1$ s

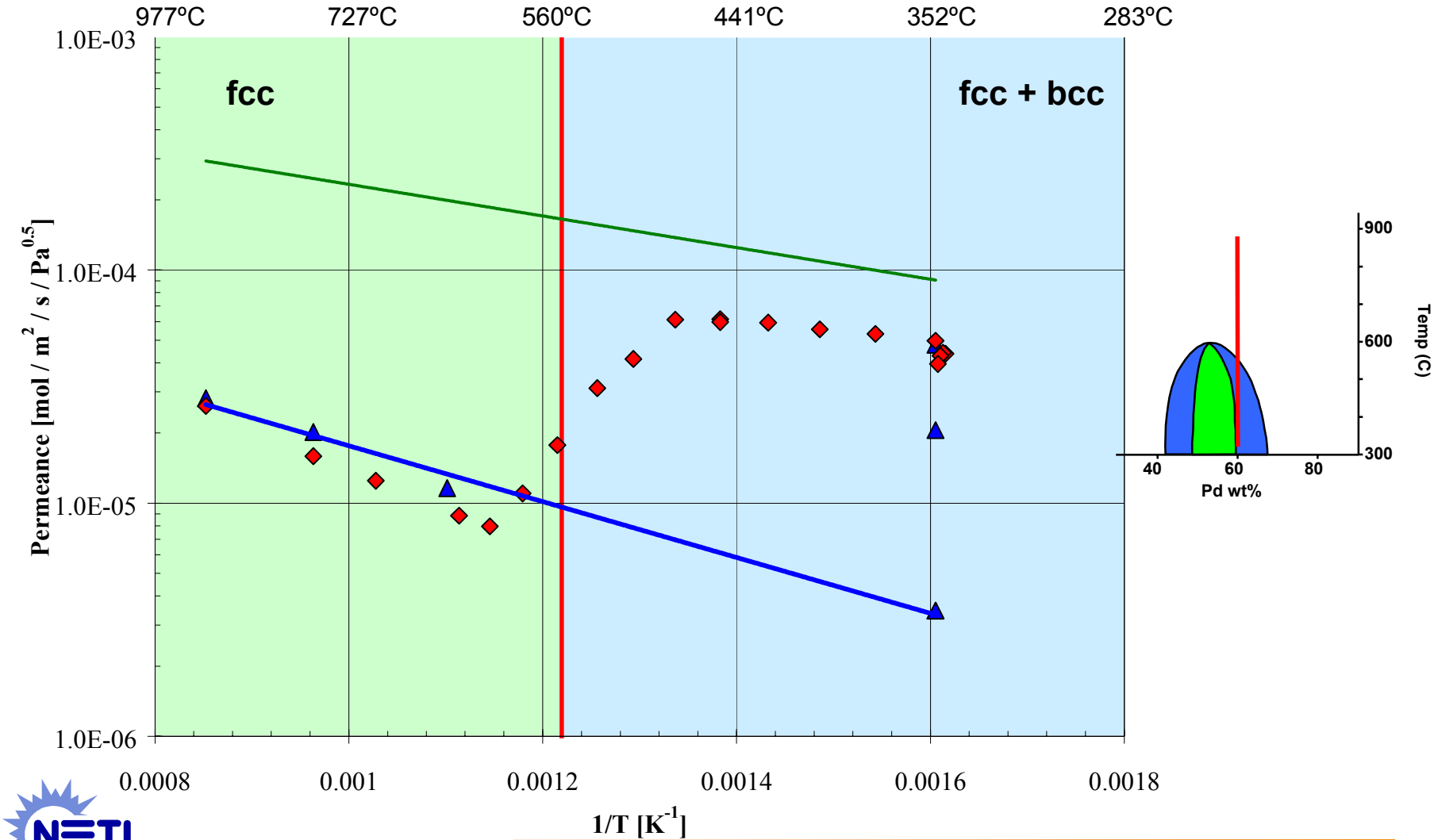
Related Project Activities Funded by DOE-FE

- Development of membrane reactors requires knowledge of both reaction kinetics and membrane performance
- Membranes will be evaluated over a wide range of T (up to 900° C) and P (up to 400 psia)
- The H_2 permeance and selectivity of dense membranes and porous membranes will be investigated
- The effect of CO_2, H_2O and CO on permeance and selectivity will be determined
- The effect of gaseous contaminants (e.g. H_2S) on membrane performance will be evaluated

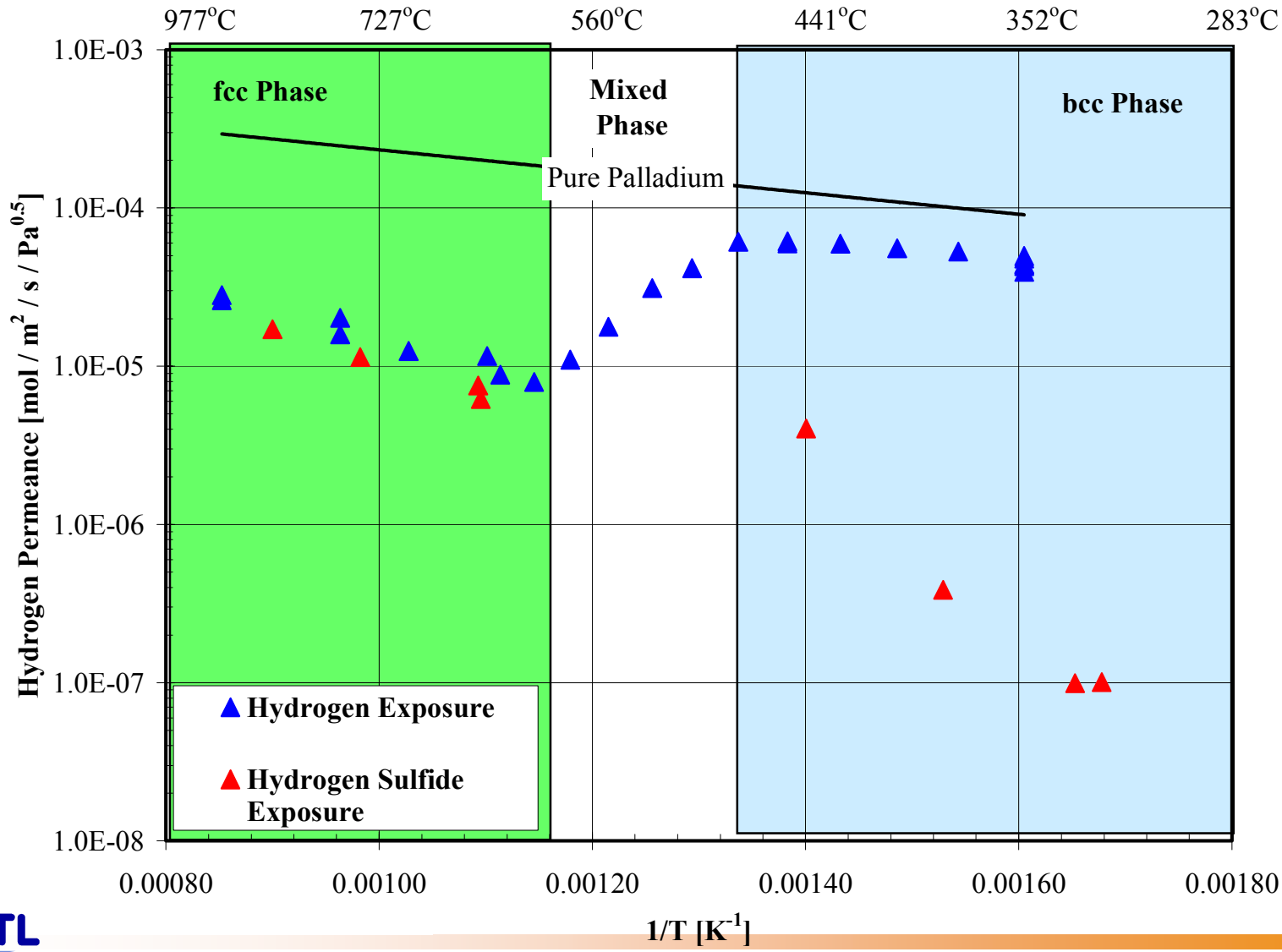
Summary of Membrane Permeability Test Data



60%Pd-40%Cu Alloy Permeance Through Phase Transition



Sulfur Tolerance of 60/40 Pd-Cu



Future Plans

- Kinetics studies of the forward WGS reaction
- Effect of membrane materials on reaction kinetics, e.g. Pd, PdCu alloys
- Effect of sulfur poisoning on catalytic reactor materials, membrane materials, or heterogeneous catalyst particles
- Construction of a sulfur-resistant membrane reactor for the forward water-gas shift reaction
- Incorporation of all reaction kinetics results and permeability results into a high T, high P WGS membrane reactor model

High Temperature Solar Splitting of Methane to Hydrogen and Carbon

Allan Lewandowski (NREL)
Alan Weimer (University of Colorado, Boulder)
Team Members:
CU: Jaimee Dahl, Karen Buechler, Chris Perkins
NREL: Carl Bingham, Judy Netter

2003 Hydrogen and Fuel Cells Merit Review Meeting
May 19-22, Berkeley, CA

Thermal Decomposition of Methane

- Demonstrated by Thagard in late 70's
  - electrically heated, porous wall reactor
- Simple in concept
  - essentially single step to end products
- Extremely high reaction rates at 1600-2000°C
- Various end-product configurations possible
- Co-products both have economic value

$\Delta H_{1800°C}$ = -76 kJ/mole

-394 kJ/mol C

$$CH_4 + \text{☀} \rightarrow C + 2H_2$$

-890 kJ/mol CH_4

-572 kJ/2mol H_2

Project Goals

- Near term
  - Current status:
    - 70-95% CH_4 conversion to H_2 @ 1850°C
    - $0 -12/kg depending on process configuration and co-product value
  - Targets:
    - 70% conversion on a continuous basis
    - $3/kg for fleet fueling station with carbon black at tire market price
- Long-term
  - < $2/kg for water-splitting cycles

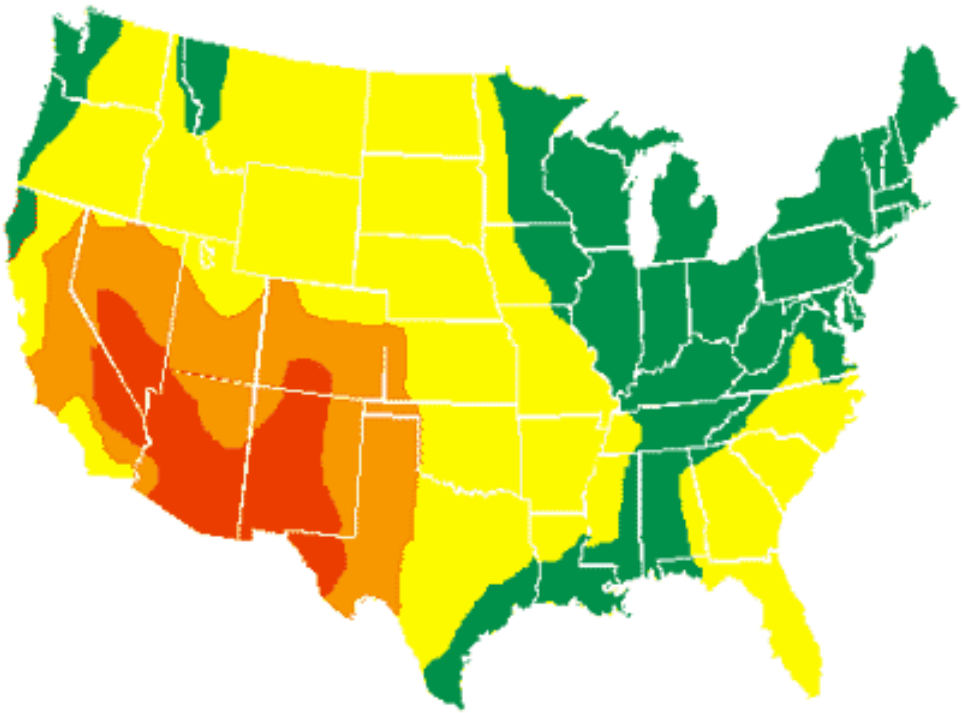
Historical Perspective

- Initiation of Project: FY2000
  - University of Colorado awarded competitive DOE GO subcontract
- Significant Results:
  - FY00: demonstrated proof-of-concept at HFSF
  - FY01: achieved 80% conversion in new reactor
  - FY02: demonstrated fluid-wall (aerosol) reactor
  - FY03: achieved 94% conversion
    - Limited funding to complete Ph.D. thesis experimental work
  - Overall:
    - very high reaction rates demonstrated
    - no technical showstoppers
    - near-term commercialization opportunities

Why Use Solar Energy?

- Environmentally benign energy source
  - little or no CO_2 emissions (depending on process)
- High concentrations possible (>1000 W/cm^2)
  - high temperatures easily achieved (>3000 ^oC)
  - reduced reactor size; low thermal mass
- Rapid heating rates (>>1000 ^oC/s)
  - quick start/stop operation
- Abundant resource (both US and worldwide)
  - Sufficient to power the world (if we choose to)
- Advantages tradeoff against collection area
  - this is true for all technologies using sunlight
  - heliostat costs are significant fraction of capital
    - importance depends on overall process efficiency

World Class Direct Resource in US



Solar Intensity

- Good
- Excellent
- Outstanding
- Premier (World Class)

- World Class area in US: $5.8*10^5$ km^2
  - >6 kWh/m^2/day
- Annual US Energy Usage: $2.9*10^{13}$ kWh (Year 2000 EIA data)
  - At η=10%, area required: $1.3*10^5$ km^2 (50% of Arizona)
- Annual World Energy Usage: $1.2*10^{14}$ kWh
  - At η=10%, area required: $5.5*10^5$ km^2 (95% of Arizona +Nevada)

Vision for Solar Thermal Processing

- Apply advantages to a clean hydrogen economy producing hydrogen from water
- Near-term (0-5 years): Methane as transition fuel
  - Identify/develop promising processes
    - e.g. NG dissociation, dry reforming
  - Develop aerosol flow reactor and process understanding
    - technical and economic
  - Introduce solar technology on small scale in appropriate markets/locations (SW United States)
    - HCNG fleet fueling stations
- Longer-term (3-15 years): Move to water as the fuel
  - Initially through thermochemical cycles
    - e.g. 2-step metal oxide reduction, others as identified
  - Eventually to direct, high-temperature splitting/separation
    - significant materials separation issues need to be overcome
  - If renewable electric power is ever cheap enough: electrolyzers

Potential Application Areas

- Bulk Hydrogen
  - large-scale systems, pipeline feeds
- Distributed Fleets
  - fueling stations
  - HCNG a near-term possibility
- Industrial User/Supplier
  - Semiconductor industry
- Syngas
  - add reformer to system
- Utility plants
  - power and hydrogen
- Carbon black plant
- Stranded gas/capped wells

Technical Challenges

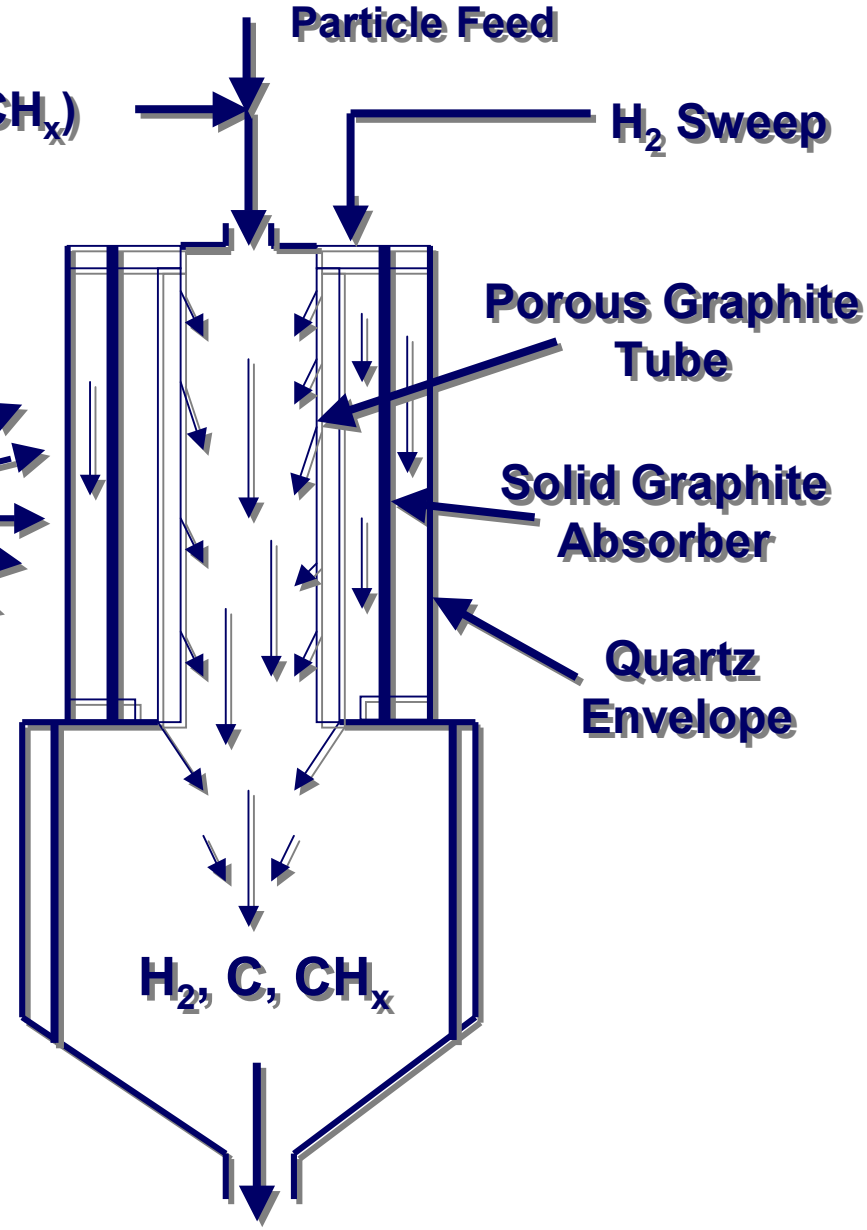
- Compatibility with on/off nature of sunlight
  - short start-up & shut-down times
  - semi-continuous operation
- High efficiency reactor design for high temperature
- Materials of construction
- Thermophoretic deposition of carbon black

Non-technical Challenges

- Co-product marketing (outlet for carbon black)
- Poor fit to a single business

Aerosol Flow Reactor Concept

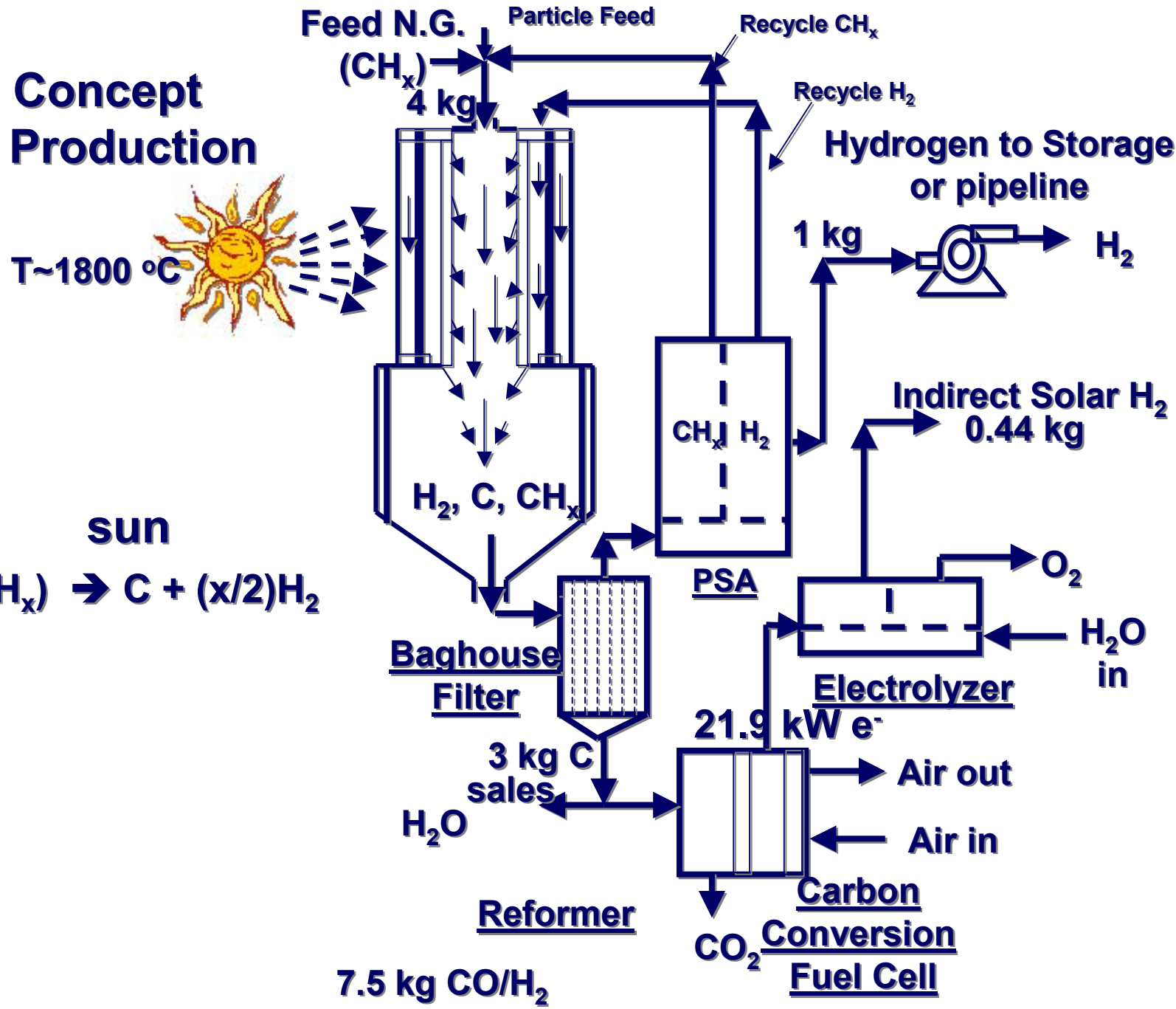
T~1800 °C



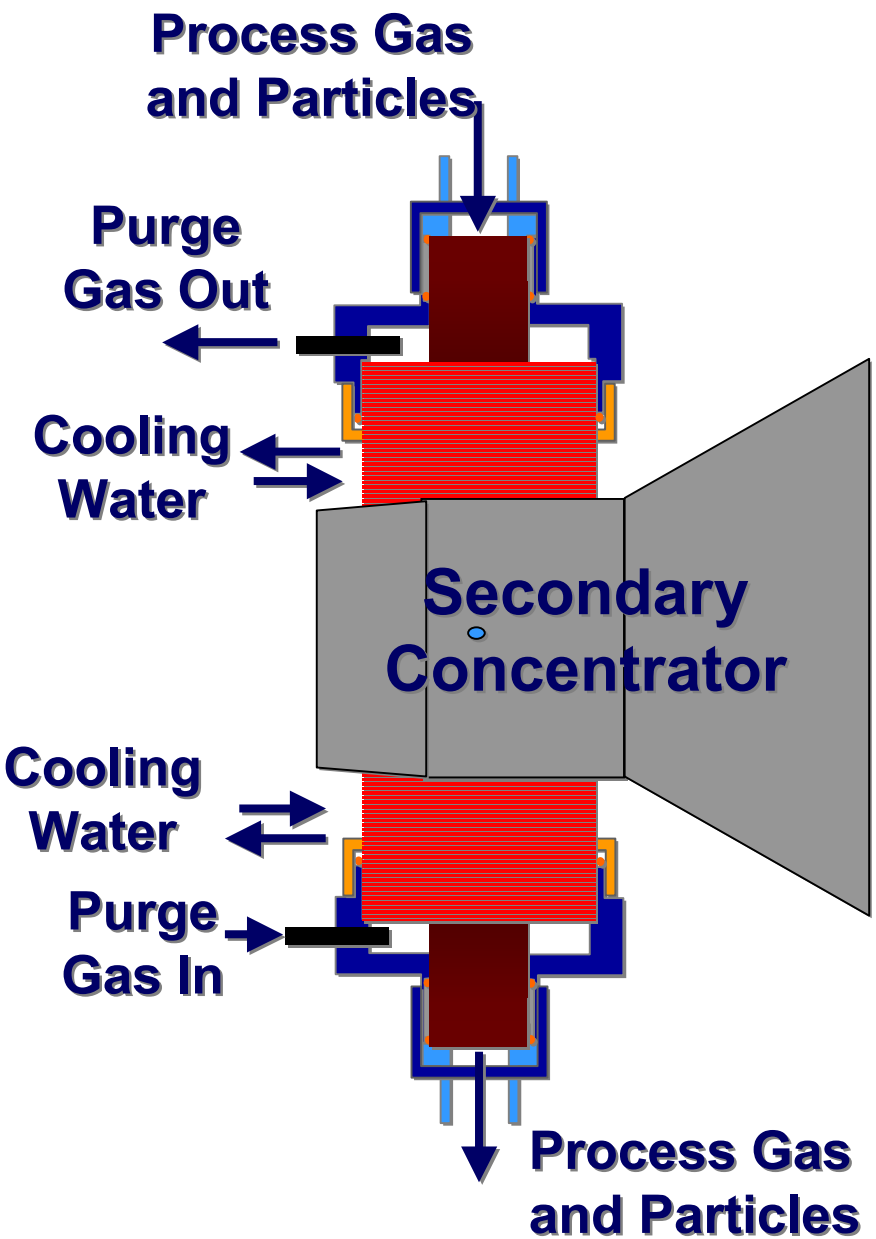
Sun

$$N.G.(CH_x) \rightarrow C + (x/2)H_2$$

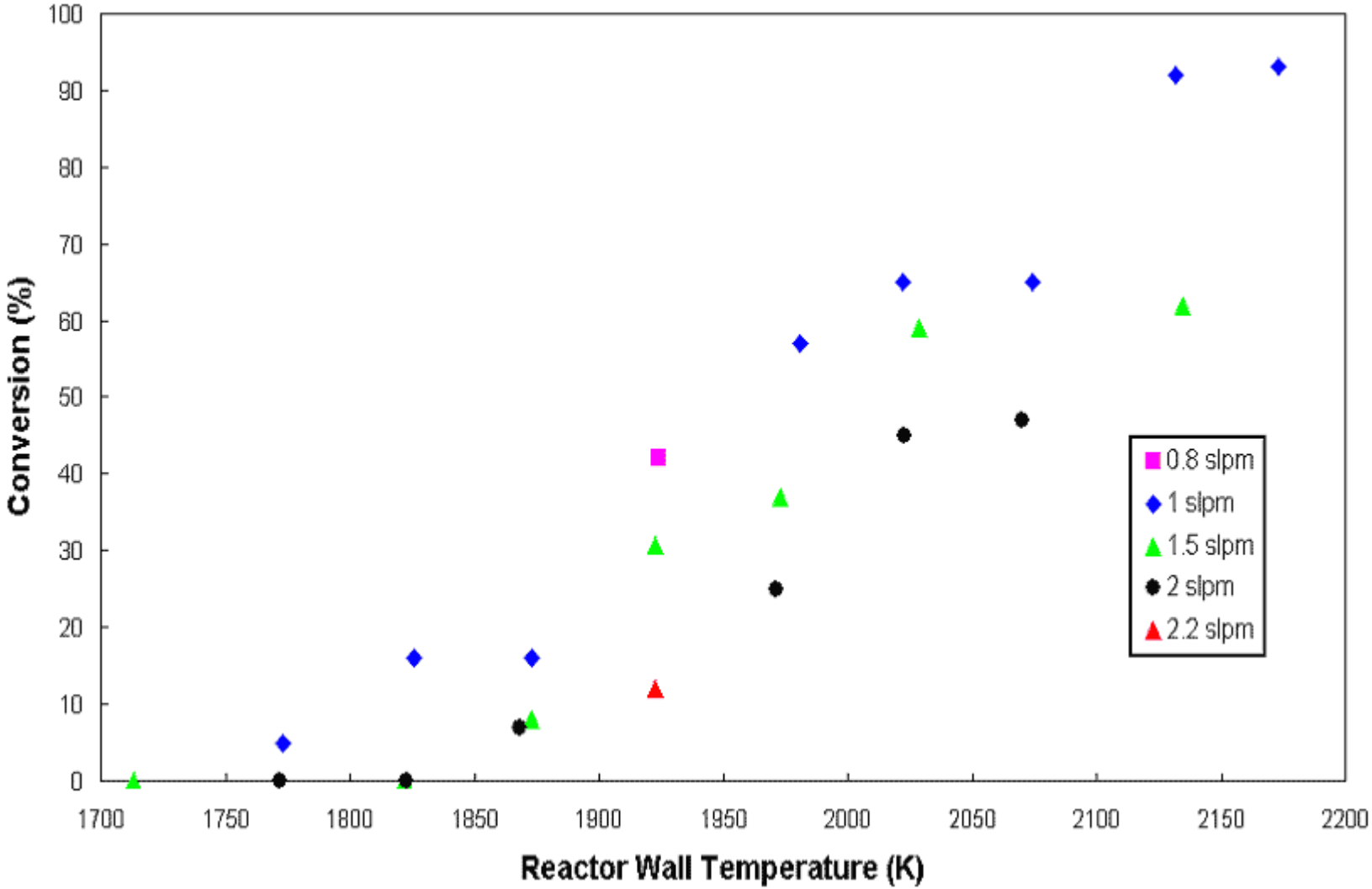
System Concept
Hydrogen Production



Reactor System



Conversion as a Function of Reactor Wall Temperature for Various Initial Methane Flow Rates



Energy use and GHG Emissions

(H_2 Supplied as High-pressure Gas)

Steam-reforming Plant + Liquid H_2 + Transport

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

+310 MJ/kg of H_2
+20.42 kg CO_2-eq/kg H_2

(Spath and Amos, 2002)

Solar-thermal NG Dissociation Distributed Plant

$$CH_4 \rightarrow C + 2H_2$$

(carbon is sold)

+38 MJ/kg of H_2
+3.46 kg CO_2-eq/kg H_2

Fossil fuel avoided = 272 MJ/kg H_2
CO_2 avoided = 17 kg CO_2/kg H_2

(carbon is converted to H_2)

+218 MJ/kg of H_2
+14.2 kg CO_2-eq/kg H_2

Fossil fuel avoided = 82 MJ/kg H_2
CO_2 avoided = 6.22 kg CO_2/kg H_2

Economic Studies

(Spath and Amos 2002)

Fueling Stations

(H_2 @ 3000psig; $0.66/kg C)

Collector Area (m^2)	Capital Cost ($M)	H_2 Selling Price ($/kg) "Out the Gate"	H_2 Selling Price ($/kg) Compressed/Stored
2,188 (1.8 acres)	4.42	-----	12.30 (250 kg/day)
	2.15	3.35 (462 kg/day)	-----
8,750 (7 acres)	8.93	-----	8.04 (750 kg/day)
	4.34	2.61 (1141 kg/day)	-----

Basis: $3.92/1000 scf NG; 15% IRR, 20 yr life, Equity funded

Economic Studies

(CU analysis)

Semi-conductor Plant

(300 psig, $4.35/kg current contract price)

Collector Area (m^2)	Capital Cost ($M)	H_2 Selling Price ($/kg)
985 (0.8 acre)	**$ 1.46**	**3.92 (240 kg/day total; 75 kg/day stored)**

Small Utility

(co-gen 1.6 MW electricity & H_2 out the gate)

Collector Area (m^2)	Capital Cost ($M)	H_2 Selling Price ($/kg)
7,800 (6.2 acres)	**$ 4.96**	**3.22 (1743 kg/day; electricity @ 5 ¢/kWh)**

Basis: $3.92/1000 scf NG; 15% IRR, 20 yr life, Equity funded

Collaborations

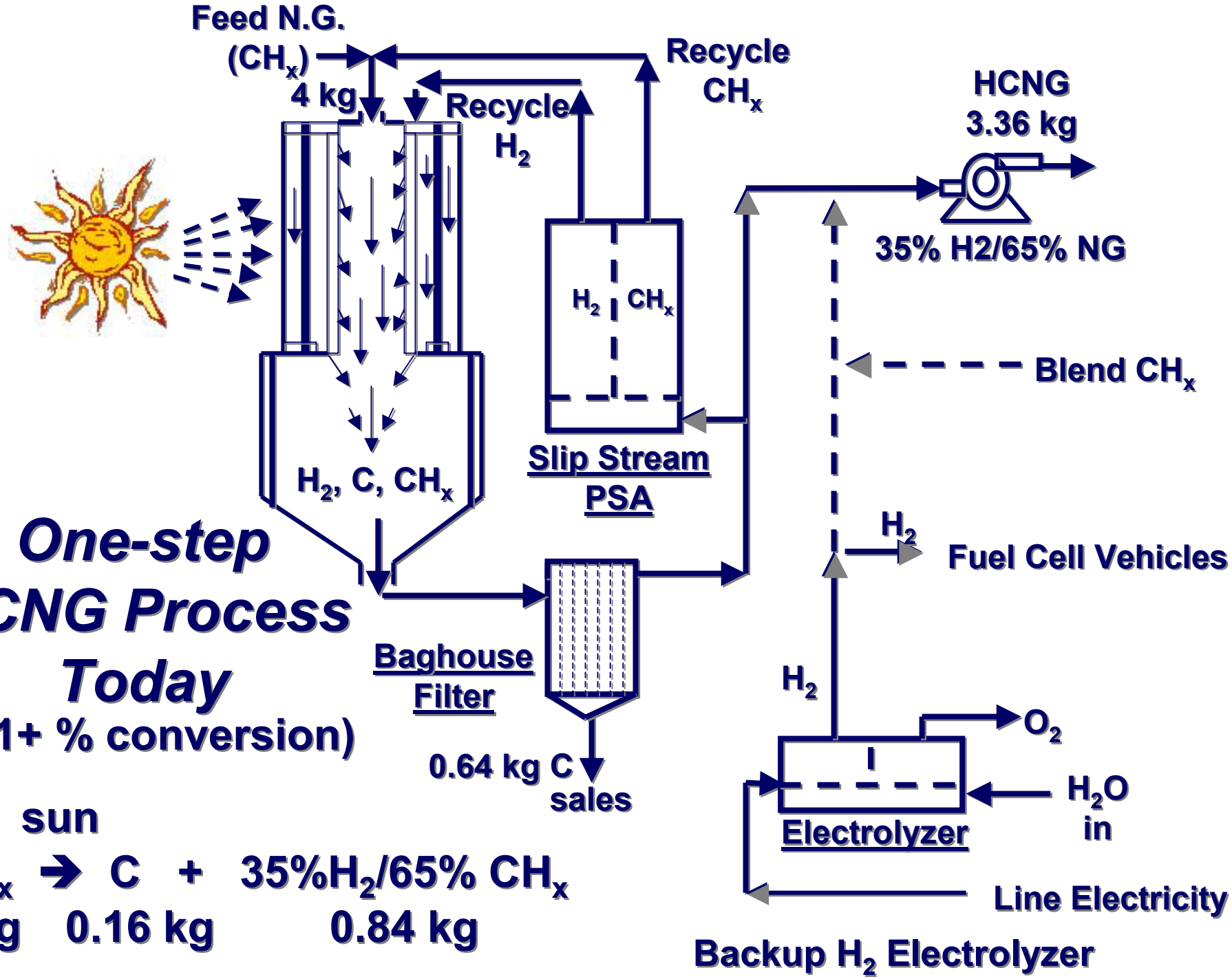
- In the US
  - 10 industrial partners (in-kind cost share)
  - BP, ChevronPhillips, GM, EPRI, Harper International, Siemens, Pinnacle West, ChevronTexaco, Plug Power
- Outside of the US
  - IEA SolarPACES, Task II, Solar Chemistry (AL is US Coordinator)
  - Paul Scherrer Institute, Switzerland
  - Swiss Federal Institute of Technology (ETH), Zurich

2002 Review Panel Comments

- Team took exception to the use of a carbon fuel cell to extend hydrogen production into dark hours
  - Response: the carbon fuel cell is a long-term technology that was considered as an option for use of the carbon byproduct and is not essential to the overall concept technically or economically.
- "…inclusion…in the hydrogen program portfolio is important in that it keeps the technology area broad, maximizes options for commercial use, and complements other dissociation technologies."

HCNG Fleet Opportunity in Desert SW United States

- First Fueling Station: Phoenix Area
  - Pinnacle West is already in business
    - HCNG, NG, H_2; H_2 by electrolysis w/off-line e^-
  - Arizona Public Service, Municipal Vehicles, Taxis, Bus Lines, …
- Combined Fleet Facility with Industrial H_2 users
  - Intel & Motorola are heavy users
  - Tucson, Albuquerque, Las Vegas, Denver, Colorado Springs, Salt Lake City, …
- Potential scale-up scenario
  - H_2 Enriched NG (HCNG) (20 – 35% H_2) for Fleets
  - Increased H_2 Content HCNG (50% or more)
  - Fuel Cell Vehicles (100% H_2) or IC engines running on H_2
    - Carbon Conversion Fuel Cell Marketed



One-step HCNG Process Today

(21+ % conversion)

sun

$CH_x \rightarrow C + 35\%H_2/65\%\ CH_x$

1 kg 0.16 kg 0.84 kg

Economic Impact of Fleet Station Development

Number of 327 fill-up HCNG Fleet Stations	*Total Annual Revenue ($M)**	*% North American Carbon Black Market*
40	141	1%
200	706	5%
400	1,413	10%
1600	5,648	40%

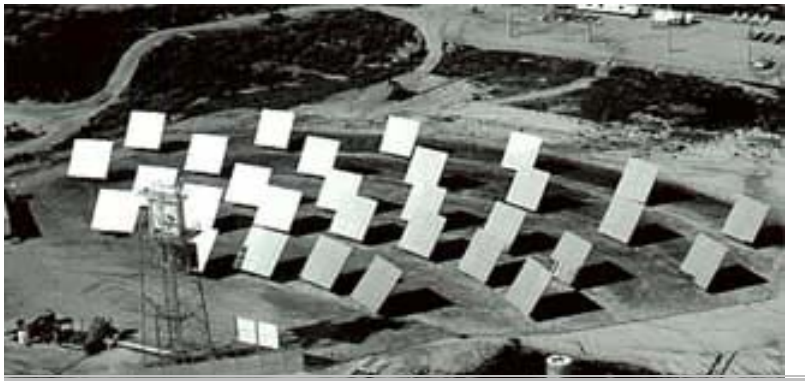
*based on capital cost of $3.2M per station and operating costs of $2.3M/year

Carbon Black Market

- World Market: ~ 8 billion kg/year
- Tire & industrial rubber: 92%of World Market
  - 7.3 billion kg/yr
- North American Market: 25% of World Market
  - 1.8 billion kg/year

Al's Quik Serv
Hydrogen
HCNG
NG
STT

Solar Examples



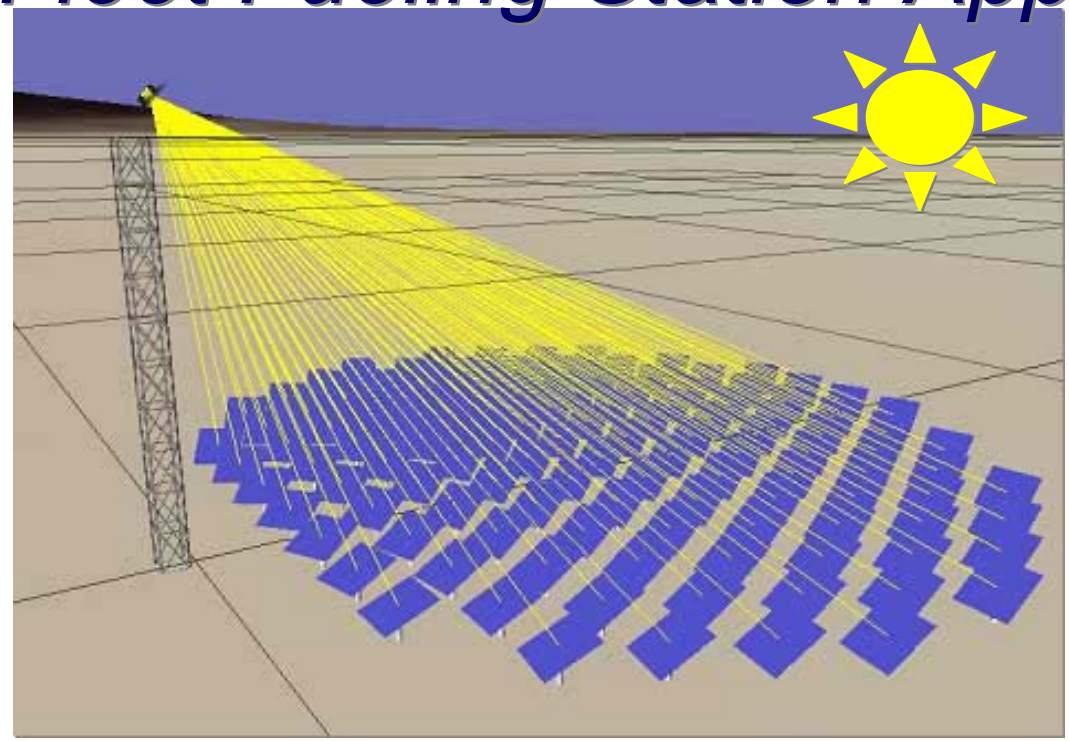
Enhanced oil recovery, early 80's

Large solar furnace, France

Small central receiver, Israel

30 MW_{th} Solar Plant, CA

Preliminary HCNG Field Design for Fleet Fueling Station Application



- Phoenix Area
- ~ 6,546 kg/day HCNG
- ~ 327 fill-ups/day
  (@ 20 kg/fill-up)
- ~ 1250 kg C/day
- ~ 0.57 hectares (1.4 acres)

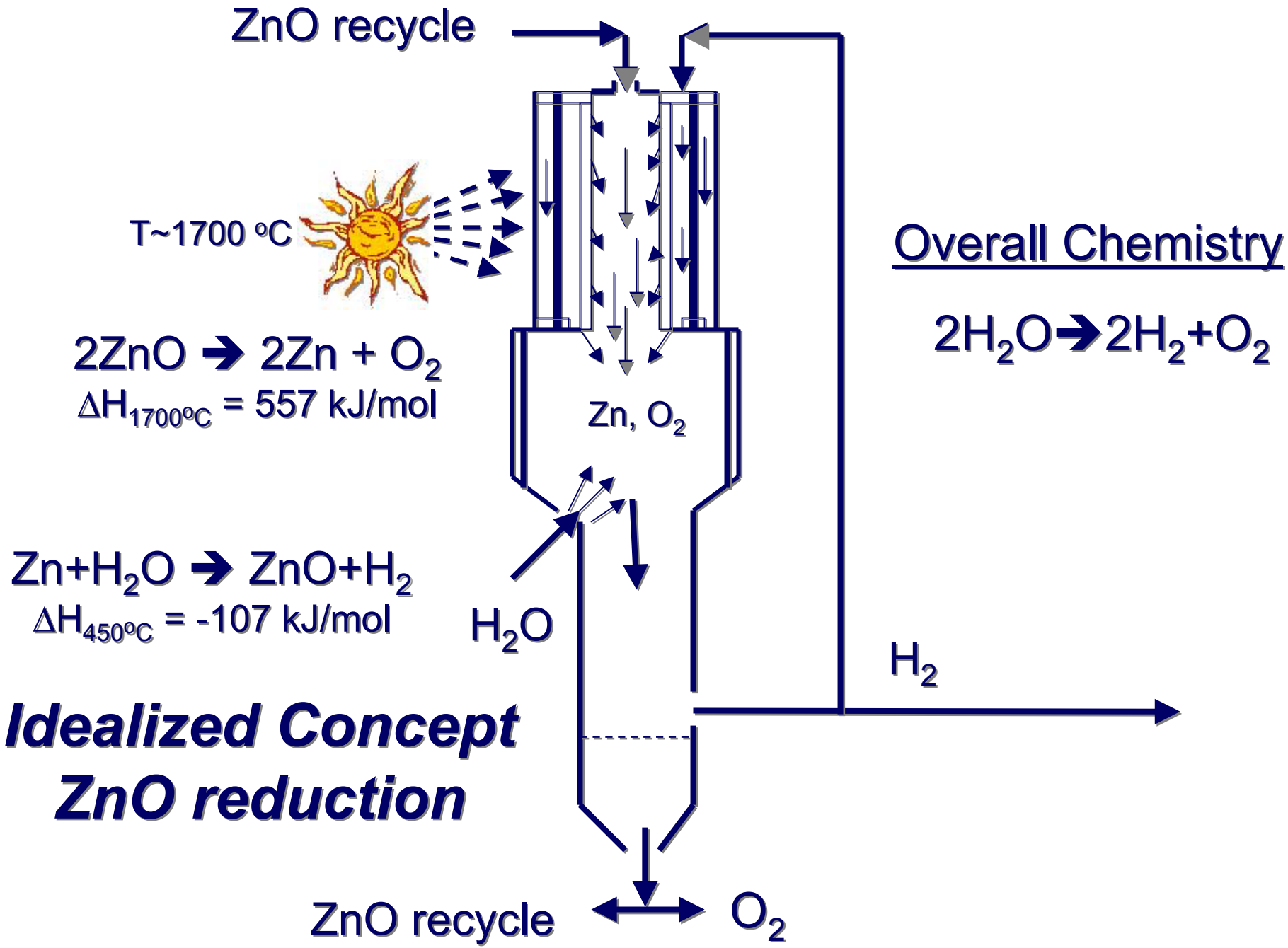
- ~ 1.1 MW_{th}
- ~ 5 cm ID x 48 cm reactor
- ~ 122 heliostats (~1770 m^2)
- Overall optical η~70%
  - peak flux >3000 suns

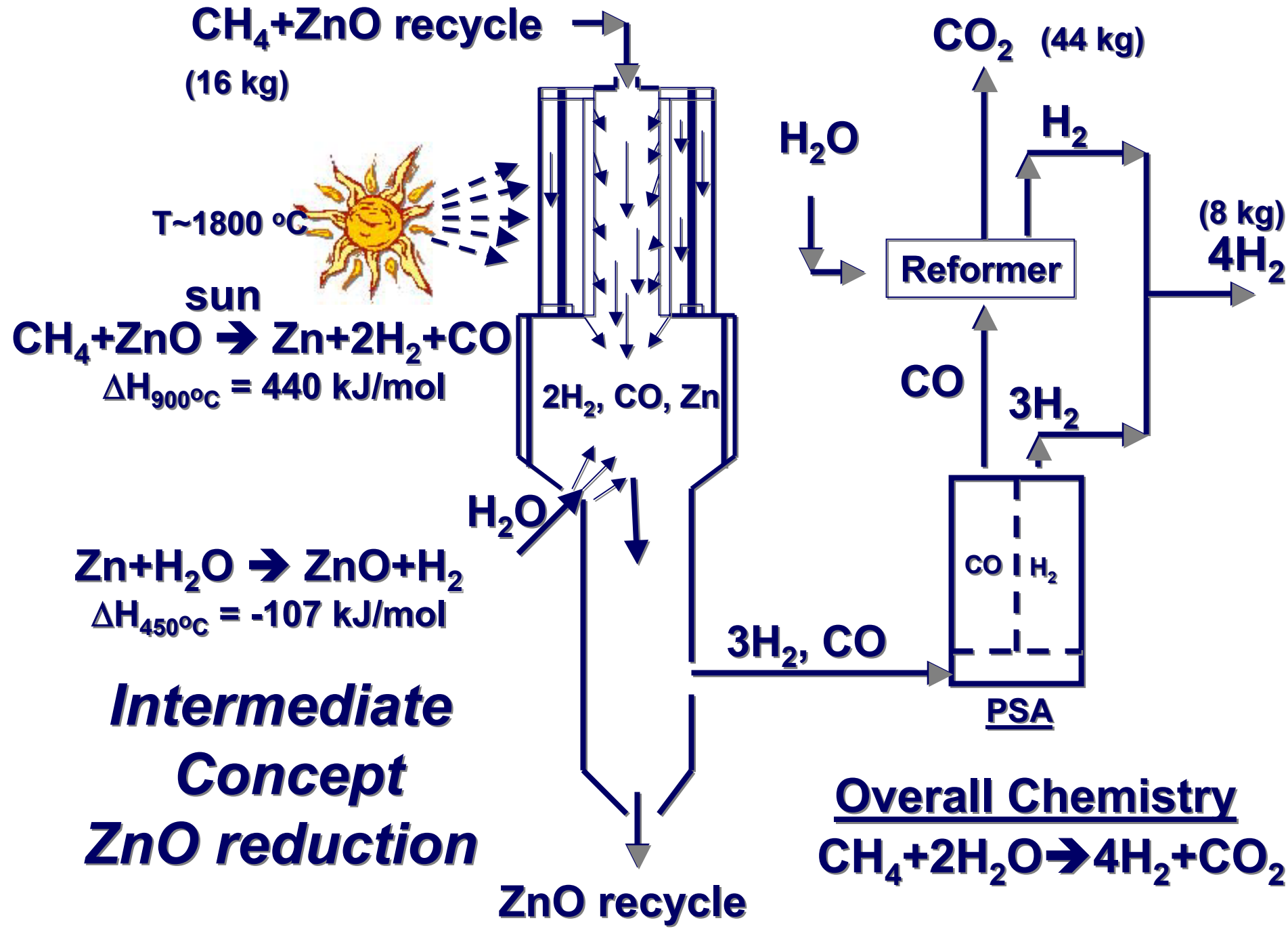
Next Step Applications/Options

- Industrial H_2 to Semi-conductor Plants in SW, etc.
- Co-generating Utilities
  - H_2 and electricity
- Coal Bed Methane Conversion
  - largest reserves in the world are in the Four Corners Region of the desert SW United States)
- Biogas Conversion
  - waste landfill biogas, etc.
- Dry Reforming of CO_2 Contaminated Gas Wells
- Water-splitting cycles

Water-splitting Cycles

- 2 Step metal oxide reduction
  - high temperature endothermic reduction
  - lower temperature exothermic reaction with water
  - Ongoing European solar projects
- Thermochemical cycles
  - originally studied with nuclear reactors in mind
  - recent General Atomics study identified 2 candidates
    - adiabatic UT-3
    - Sulfur – iodine
  - GA proposing to identify others with higher temperature operation using solar thermal power
- Direct water splitting
  - requires T>2500°C, high temperature separation
  - $\Delta H_{2500^{o}C}$ = 238 kJ/mole


ZnO recycle
T~1700 °C
2ZnO → 2Zn + O2
ΔH1700°C = 557 kJ/mol
Zn, O2
Zn+H2O → ZnO+H2
ΔH450°C = -107 kJ/mol
H2O
H2
Overall Chemistry
2H2O→2H2+O2
Idealized Concept
ZnO reduction
ZnO recycle
O2


CH_4+ZnO recycle
(16 kg)
T~1800 °C
sun
CH_4+ZnO → Zn+2H_2+CO
$\Delta H_{900°C}$ = 440 kJ/mol
2H_2, CO, Zn
H_2O
Zn+H_2O → ZnO+H_2
$\Delta H_{450°C}$ = -107 kJ/mol
Intermediate Concept ZnO reduction
ZnO recycle
CO_2 (44 kg)
H_2O
H_2
Reformer
(8 kg)
4H_2
CO
3H_2
CO
H_2
3H_2, CO
PSA
Overall Chemistry
CH_4+2H_2O→4H_2+CO_2

Dry Reforming Experiments

- **Application to high CO_2 containing gas wells and landfill gas processing**

$$CO_2 + 2CH_4 \rightarrow C + 2CO + 4H_2$$

Feed Gas: 0.90% CH_4; 0.45% CO_2

Flux (kW/m^2)	% CO_2	% CH_4	% CO	% H_2
none	0.45	0.84	0	0
1500	0.23	0.20	0.35	1.55
2000	0.11	0.07	0.62	1.60

Chemically-assisted Solar-thermal Water Splitting

$$CH_4 + ZnO \rightarrow Zn + 2H_2 + CO$$

$$\Delta H@900^oC = 440\ kJ/mol$$

$$Zn + H_2O \rightarrow ZnO + H_2$$

$$\Delta H@450^oC = -107\ kJ/mol$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

- -

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$$

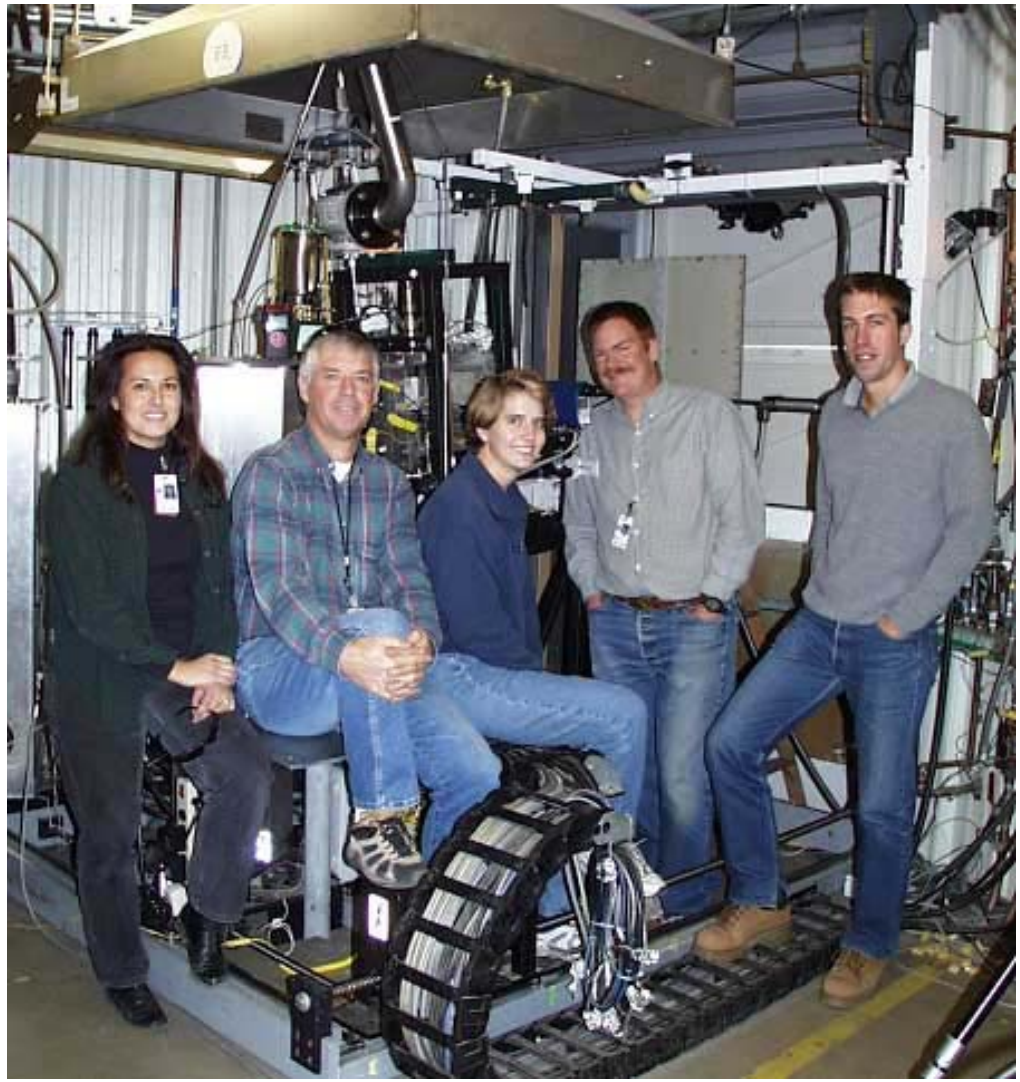
Summary

- Splitting methane using concentrated sunlight is technically feasible
- Various system configurations and applications have economic potential
- Technical concept can be extrapolated to other chemical reactions and to water splitting
- A near-term application, business opportunity and path forward have been identified
- Continued funding is warranted

Project Team

Al, Karen

Sarah



Judy, Al, Jaimee, Carl, Fabian

Power Parks System Simulation

A. E. Lutz and J. O. Keller
Combustion Research Facility
Sandia National Laboratories
Livermore CA 94551

Hydrogen Program Annual Review
May 19, 2003

Objectives and Relevance

Objective

- Develop a flexible system model to simulate distributed power generation in power parks that use H_2 as an energy carrier

Power parks combine power generation co-located with a business, an industrial energy user, or a domestic village

- H2 generators -- reformers, electrolyzers
- H2 storage -- high-pressure vessels, hydrides,
- Electricity generation -- fuel cells, H2-engine, micro-turbine
- Renewable sources -- Photovoltaic, wind turbine, biomass gasification
- Vehicle refueling

Deliverable

- Tool to construct simulations of H_2 systems, including power parks, to analyze performance (thermodynamic efficiency and cost)

Method of Approach, Milestones

Software Design

Use Simulink software as platform for transient simulations

- Simulink provides:
  - Graphical workspace for block diagram construction
  - ODE solvers for integration of system in time (not quasi-steady approximation)
  - Quick-look output from simulation
  - Control strategies and iterative loop solutions

Create a library of Simulink modules to represent components

- Component models based on fundamental physics to the extent practical
- Example:
  - Coupled Chemkin software routines as Simulink functions
  - Thermodynamic properties of gas mixtures used in energy balances
  - Equilibrium composition used for catalytic reforming and combustion burners
- Library components can be quickly re-configured for new system concepts
- Generic components from library can be customized using data on the performance of specific unit

Method of Approach, Milestones

Project Plan for FY03:

		FY2003				FY2004			
Item	Task	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
1.	Develop additional modules for power park components.	*	*	*	*	*	♦		
2.	Configure systems to model existing power park sites			*	*	*	*	♦	
3.	Evaluate system performance of the power park.			*	*	*	*	*	♦
4.	Implement a control algorithm to optimize power park.					*	*	*	♦

* Continuous development
♦ Milestone for completion

Simulink library modules, *Progress*

Library of Simulink modules includes:

- **Reformers: steam methane and autothermal (partial oxidation)**
- **Fuel cell system**
- **Compressor (mechanical)**
- **High-pressure storage vessel**
- **Electrolyzer**
- **Photovoltaic Solar Collector**

Module descriptions:

- **Steam-methane reformer (SMR)**
  - **Reformer T determined by balance of heat transfer from combustion of reformate stream after H_2 separation**
  - **SMR module uses several sub-modules that call Chemkin**
- **Fuel cell system**
  - **Module uses H_2 flow rate and requested electric power**
  - **Sub-module uses data table for efficiency-power relation**

Simulink library modules, *Progress*

Module descriptions (con't):

- **Compressor**
  - **Raises pressure of H_2 to fill storage vessel**
  - **Computes power required for ideal multi-stage compression**
- **High-pressure storage vessel**
  - **Accepts H_2 flow rate and integrates H_2 stored**
  - **Computes pressure using Sandia's real-gas equation-of-state for H_2**
- **Photovoltaic Solar Collector**
  - **Model for average solar radiation**
    - **Flux is analytic function of longitude, latitude, altitude, and time**
  - **PV module uses a solar-electric conversion efficiency**
    - **Function of panel area and slope or tracking capability**
    - **Can be adjusted to match a specific collector design**
- **Electrolyzer**
  - **Convert electric power into flow of H_2 using efficiency**
    - **Initial model specifies efficiency consistent with SunLine data**

Simulation of power systems, *Progress*

PV system simulates H_2 production at SunLine Transit

- Solar radiation modeled over calendar year
- PV arrays produce power to run electrolyzers
- H2 stored for vehicle refueling

Power system modeled after City of Las Vegas refueling facility

- SMR operates at steady state – sized to supply fuel cell and vehicles
- Fuel cell stack uses H_2 to generate power to utility grid
- H_2 is compressed and stored in high-pressure vessel for vehicles
- Vehicle usage model depletes storage tanks

Transient simulation evaluates:

- Local efficiencies of individual components
- System thermal efficiency includes
  - H2 generated (and stored for use by vehicles or fuel cell)
  - Electric power from fuel cell (or other power conversion devices)
  - Compressor power required to store H_2

Simulink provides:

- Solution variables displayed numerically & graphically
- Numerical output stored in Matlab vectors for post-processing

Proposed Future Work and Milestones

Task 1

Continue to add and refine components to Simulink library

- **Battery, H2 storage as liquid or metal hydride, wind turbines**

Task 2

Collaborate with researchers at existing power parks

- **SunLine Transit, City of Las Vegas, and other DOE sites**

Task 3

Perform long-term studies of distributed H_2 production

- **Include economics of generating H_2 and power**
- **Expand existing analysis to examine thermodynamic *availability***

Task 4

Implement a control system to optimize performance

- **Direct power flow and size components to minimize H_2 cost**

Cooperative Efforts

Collaborations:

- U C Berkeley – Energy and Resources Group (ERG) – Tim Lipman, Carl Mas
  - economic analysis of H_2 systems
- SunLine Transit Agency – Using data for PV energy and electrolyzer performance
- City of Las Vegas Refueling Station – Will use data from reformer and fuel cell
- University of Alaska, Fairbanks -- Dennis Witmer (Remote Area Power Program)

Publications:

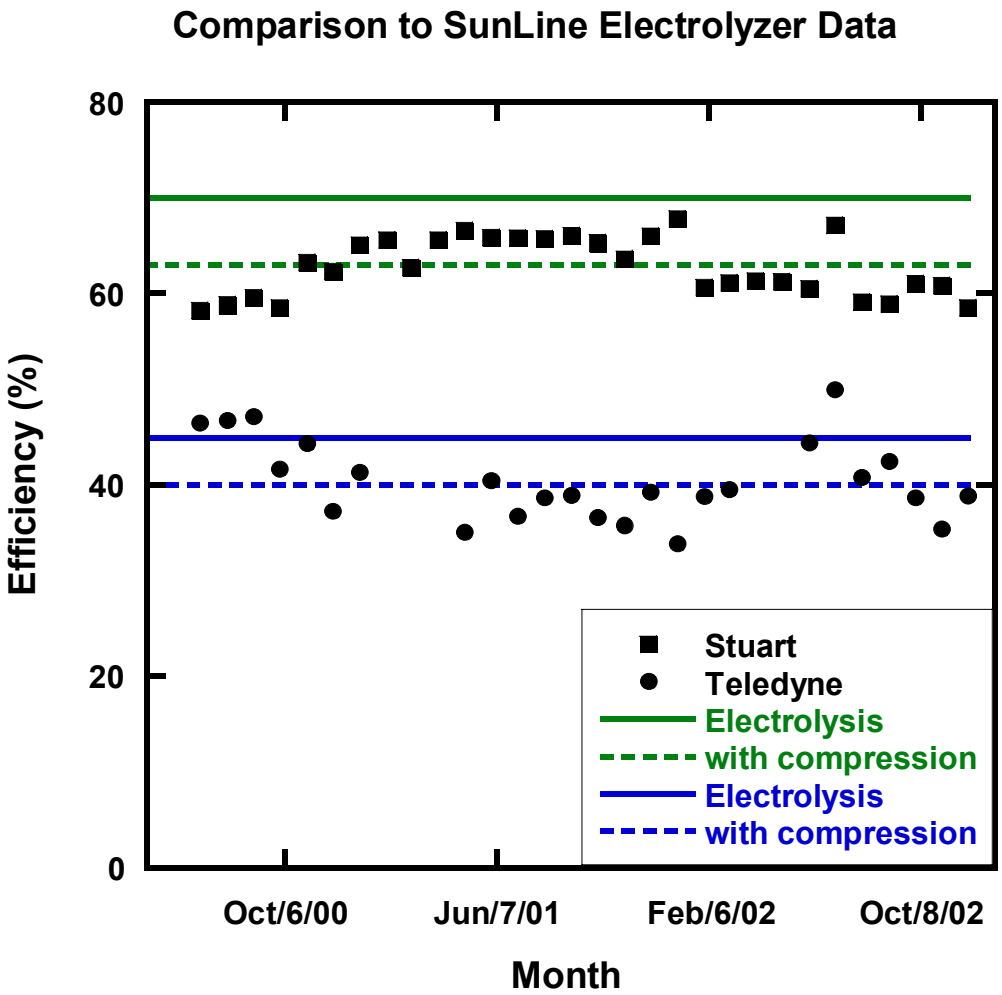
- Lutz, A E, Bradshaw, R W, Keller, J O, and Witmer, D E, "Thermodynamic Analysis of Hydrogen Production by Steam Reforming," *Int J of Hyd Engy*, 28 (2003) 159-167.
- Lutz, A E, Bradshaw, R W, Bromberg, L and Rabinovich, A, "Thermodynamic Analysis of Hydrogen Production by Partial Oxidation Reforming," submitted to *Int J of Hyd Engy*, 2003.
- Lutz, A E, Larson, R S, and Keller, J O, "Thermodynamic Comparison of Fuel Cells to the Carnot Cycle," *Int J of Hyd Engy*, 27 (2002) 1103-1111.

Response to FY 2002 review

- **FY2002 Ranking**
  - **Project ranked tied for 5th place in category with score 91/100**
    (Storage, Utilization, Safety, Analysis and Technology Transfer)
- **Reviewer's suggestion:**

  "We encourage further collaborations and modeling of actual power park sites such as Las Vegas, SunLine, etc."
- **Collaborations with power park sites:**
  1. **Established collaboration with SunLine transit**
     - **Using performance data on electrolyzers and PV collectors**
     - **Model comparison appears on following slides**
  2. **Continuing to participate on teleconferences with City of Las Vegas, Air Products, Plug Power, and DOE to follow progress**
     - **Attended opening of facility in November**
     - **Will use reformer and fuel cell performance data when it becomes available**

Electrolyzer Simulation



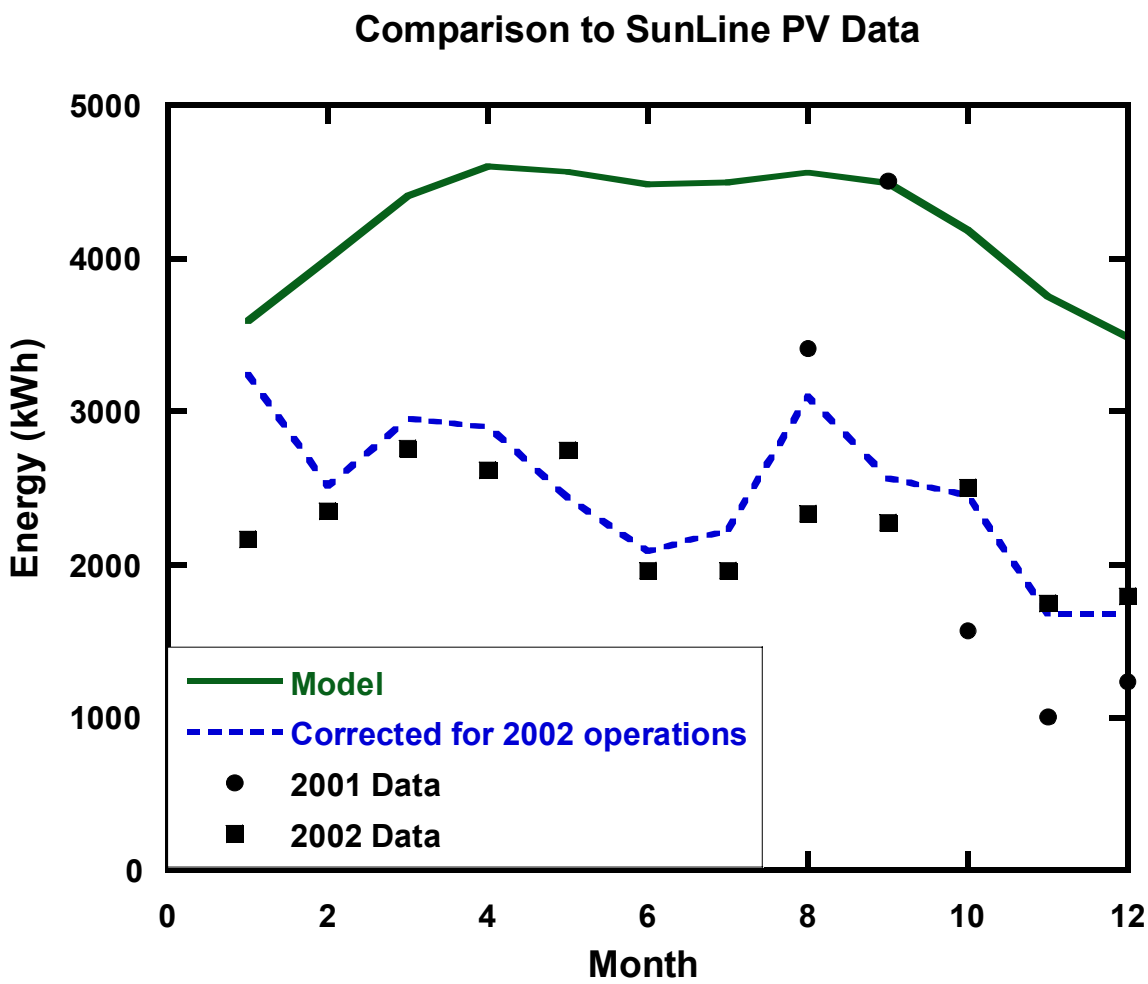
Model comparison

- Electrolyzer + compressor to compare with SunLine data
- Estimate efficiency of electrolysis step to match average H_2 delivery efficiency

SunLine electrolyzers:

- Stuart Energy (Phase 3 unit)
  - Low-p cell output (1 psig)
  - Compression: 4-stages at 50% efficiency to 5000 psi
- Teledyne Energy Systems
  - High-p cell output (100 psig)
  - Higher purity H_2 supply
  - Compression: 2 stages at 20% efficiency to 3600 psi

Photovoltaic collector simulation



- **Model simulation**
  - Run yearly variation
  - Integrate daily collection
  - Sum monthly to compare to SunLine data
- **Solar radiation model**
  - Analytic function of longitude, latitude, altitude
- **PV panel model**
  - Area = 360 m^2, slope 23°
  - Adjust solar-electric conversion efficiency = 7 %
- **Correct monthly sums to SunLine's operations**
  - Operating days / month
  - Sunny days / month

Vehicle H_2 consumption survey

Vehicle	Storage Mode	Internal Volume (l)	H_2 (kg)	Mileage (mpgge)	Range (miles)
Ford Model U	**10,000 psi**	180	**7**	**45**	**300**
Ford P2000 – ICE	**3600 psi**	**87**	**1.5**	**31.4/46.7**	70
BMW 750hL – ICE	**Liquid**	**140**	9.9	22	**218**
Ford Focus FCV	**5000 psi**	**186**	4.3	47	**200**
Toyota FCHV	**3600 psi**	**136**	**3.2**	57	**182**
Honda FCX	**5000 psi**	**157**	**3.8**	45/58	**170/220**
Chrysler Natrium	**$NaBH_4$**	**200**	10	**30**	**300**
GM HydroGen3	**Liquid**	**68**	**4.5**	55	**250**
GM HydroGen3	**10,000 psi**	86	**3.1**	55	**170**
GM Hy-wire	**5000 psi**	88	**2**	40	**80**

- **Data collected from journals, press releases, and private communication**
- **Bold font indicates data that is specified, other values are computed**
- **Gaseous storage values computed using Sandia's real-gas equation-of-state**
- **External volume of container depends on storage mode and design**

HYRADIX™

HYDROGEN GENERATION SYSTEMS

SunLine TRANSIT AGENCY

On-Site Hydrogen Generation & Refueling Station

South Coast Air Quality Management District

AQMD

the clean air people

Project Objective

Demonstration of Auto Thermal Reforming based refueling station

DOE Objectives

Demonstrate hydrogen fueling station
On-site Auto Thermal Reforming of natural gas
Cost analysis vs. target of $3/gge in 2008
Evaluation of FC vehicles under real-world conditions
Public education on hydrogen and fuel cells

HYRADIX™
HYDROGEN GENERATION SYSTEMS

Performance goals

	Design
Hydrogen Purity	>99%
Flow Rate	100 nm3/hr
Compression & Storage	6200-6500 psi
Dispensing	5000 psi
Refueling rate	15 min per bus 3-5 min per car

HYRADIX™
HYDROGEN GENERATION SYSTEMS

Approach

- On-site Natural Gas reforming with Catalytic Auto Thermal Reforming (ATR) technology
- Advanced sulfur removal technology
- Purification through Pressure Swing Adsorption (PSA)
  - Producing 100 nm^3/hr of high purity hydrogen
- Compression & Storage for 5000 psi Dispensing
- Close integration of hydrogen production and CS&D
- Demonstration
  - Refueling fuel cell & HCNG busses in commercial operation
  - Refueling fuel cell & HCNG street sweepers and cars
- Collaboration with SunLine Services Group for CS&D, education and demonstration

HYRADIX™
HYDROGEN GENERATION SYSTEMS

Accomplishments to Date

- Project start date January 2003
- Prototype built & installed with testing on-going
- Demonstration unit design complete March 2003
- Demo unit fabrication in progress May 2003
- Compression, storage & dispensing system designed with equipment on order May 2003

Project remains ahead of schedule and on-track to meet technical and operational goals

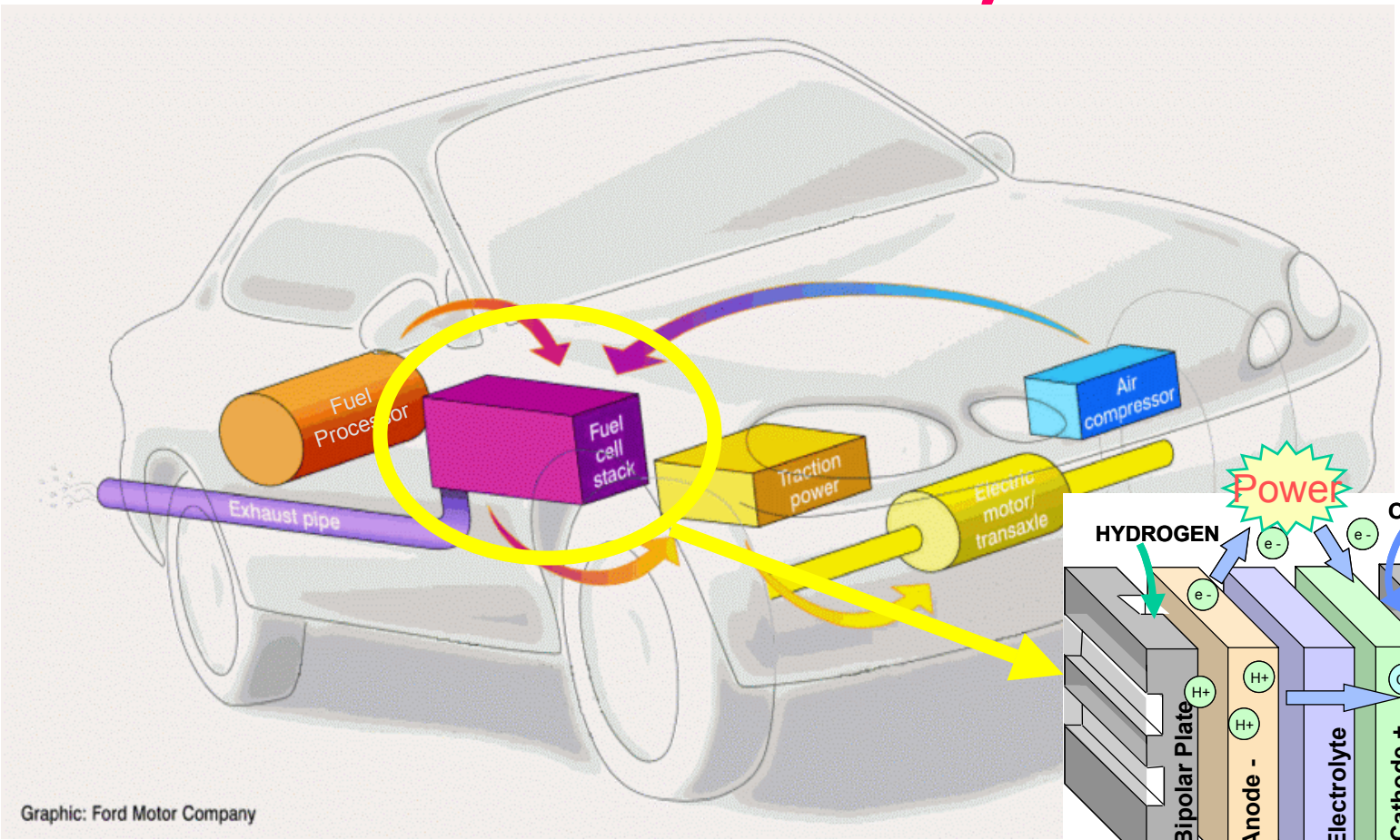
HYRADIX™
HYDROGEN GENERATION SYSTEMS

Future Milestones

- Permitting complete June 2003
- Demonstration unit delivered to SunLine July 2003
- Refueling station operational August 2003
- Demonstration August – October 2003
- Post-project plans:
  - Continued use of refueling station at SunLine for fuel cell and HCNG busses and vehicles
  - Leveraging technology for industrial applications
  - Continued public education at SunLine's facility

HYRADIX™
HYDROGEN GENERATION SYSTEMS

Fuel Cell Stack Components



Graphic: Ford Motor Company

Example shown is for acidic electrolytes

Nancy Garland

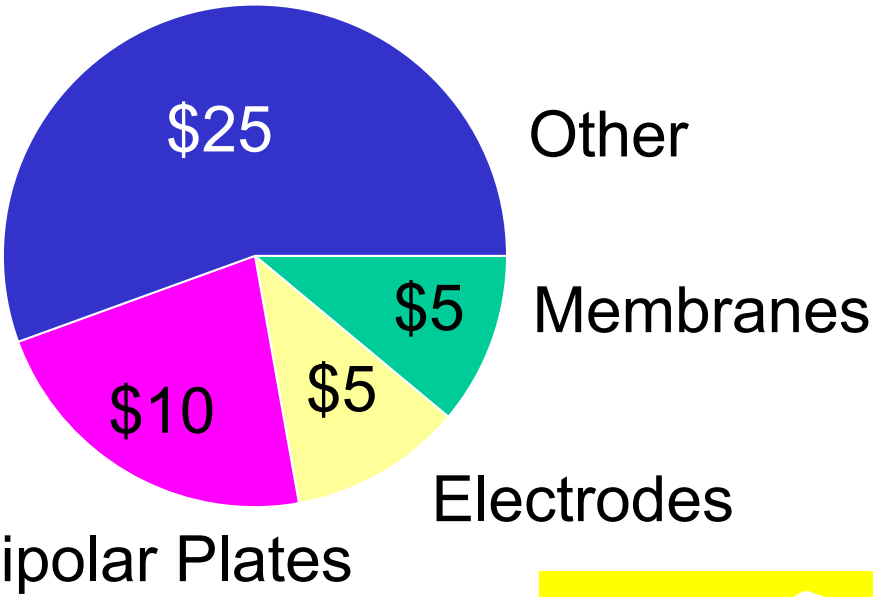
Targets

Fuel Cell Stack Components

Component	Characteristics	Units	Target
Membranes	Cost	$/kW	5
	H_2 Crossover	mA/cm^2	<1
	O_2 Crossover	mA/cm^2	<3
Electrodes	Cost	$/kW	5
	CO Tolerance (steady state)	ppm	500
	CO Tolerance (transient)	ppm	1000
	Durability	hours	5000
MEA	Cost	$/kW	10
	Performance on H_2	mA/cm^2	400 @ 0.8 V
	Performance on O_2	mA/cm^2	500 @ 0.75 V

Barriers
Stack Components

Fuel Cell Power Systems
$45/kW



BARRIERS

- Stack material cost/manufacturing
- Durability
- Electrode performance
- Thermal and water management

Stack Component Projects (oral)

• High Temperature Membranes	CWRU
• Microstructural Characterization of PEMFCs	ORNL
• Electrodes for PEMFC Operation on H_2/Air or Reformate/Air	LANL
• New Electrocatalysts for Fuel Cells	LBNL
• Low-Platinum and Platinum-Free Catalysts for Oxygen Reduction at PEM Fuel Cell Cathodes	Naval Research Laboratory
• Low-Platinum-Loading Catalysts for Fuel Cells	Brookhaven National Lab
• Scale-Up of Carbon/Carbon Composite Bipolar Plates	Porvair Corp.

Stack Component Projects (oral, continued)

• Integrated Manufacturing for Advanced MEAs	De Nora North America, Inc.
• Advanced MEAs for Enhanced Operating Conditions	3M
• High-Temperature Polymeric Membranes and Improved Cathode Catalysts	UTC Fuel Cells
• High-Performance, Low-Pt Cathodes with New Catalyst and Layer Structure	Superior MicroPowders
• Ultra-Thin Composite Membrane for High-Temp. Operation in PEMFCs	Fuel Cell Energy
• Design and Installation of a Pilot Plant for High-Volume Electrode Production	Southwest Research Inst.

Stack Component Projects (Posters)

• Carbon Composite Bipolar Plates	ORNL
• Cost-Effective Surface Modification for Metallic Bipolar Plates	ORNL
• Carbon Foam for Fuel Cell Humidification	ORNL
• High Temperature Proton Exchange Membranes	Virginia Polytechnic Institute
• Inorganic Solid State Proton Conducting Systems	Colorado School of Mines

Discussion Points

- High Temperature Membrane Working Group
- Non-Platinum Catalysts – workshop/future work
- Cost Reduction (Pt and membrane)
- Possible interest in expanding bipolar plate work for cost reduction

E-TEK

DOE Cooperative Agreement
"Integrated Manufacturing for Advanced MEAs"

Topics 1.A.1 and 1.A.2

January '02 through May '03

DE-FC04-02AL67606

National Laboratory Review
Lawrence Berkeley National Laboratories
May 2003

DUPONT The miracles of science™

Northeastern UNIVERSITY

DE NORA NORTH AMERICA, Inc.
GRUPPO DE NORA
Durantes Vincunt

Objectives

1A1

- New cathode alloys and ELAT structures that allow an overall cell performance of greater or equal to 0.4A/cm^2 at 0.8V or 0.1A/cm^2 at 0.85V operating on hydrogen/air with precious metal loadings of 0.3mg/cm^2 or less and scales to mass manufacturing technology.
- Support 1A2 with high temp interface and/or GDL structure.

1A2

- Develop membrane which operates at 120 °C and 25% RH
  - Water vapor pressure of 7 psi
- Membrane resistance ≤ 0.1 ohm cm^2
  - Nafion N112 has 0.7 ohm cm^2 @ 120 C, 25% RH
- Hydrolytic, oxidative, mechanical stability in FC at 120 °C
  - 5K/40K hrs auto/stationary
- No leachable components
- H_2 (or MeOH if DMFC) fuel permeation ≤ than 5 mA/cm2
- Cost ≤ Nafion®

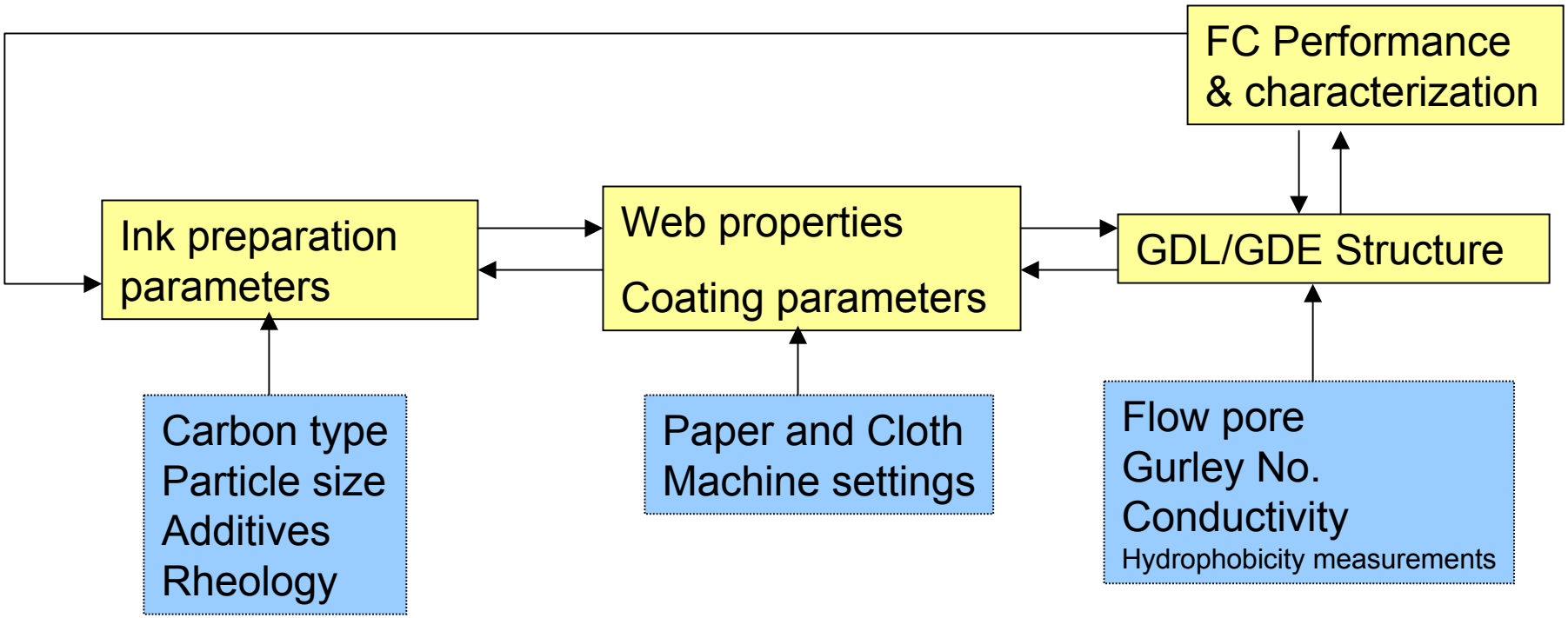
"Success" in 1A1 or 1A2 leads to 1A3: Advanced MEA Fabrication, and further reduction of metal load

Approach: Catalyst

- Technical Approach is to explore new methods of catalyst formation, identify those methods capable of controlling relative crystal face population, and using that method to create an abundance of the desired faces
- We will explore four new areas for manipulating catalyst formation chemistry : “organic precursors”, “controlled environment,” “low temperature formation,” “new carbon supports”: with NU evaluate structure with Reitveld analysis of XRD, XAFS, and XANES
- In general, the goal is to create catalysts that combine the high specific activity of highly loaded preparations (~40-50% Pt/C) with the very high surface area of low loaded preparations (~10% Pt/C).

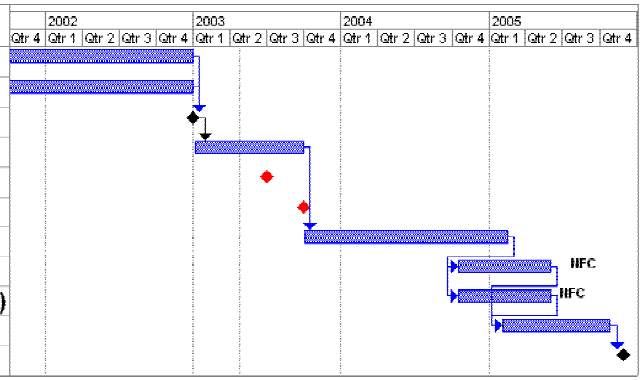
Approach: Fine Gradient ELAT®

- Develop a new ELAT gas diffusion structure based on fine gradients of hydrophobicity and porosity using developmental coating machine
- Methodology:



Project Timeline: Milestones and Success Criteria

ID	Task Name
1	Identify catalyst prep. approach that is a pathway for highly active Pt or alloy
2	demonstrate proof of principle for the fine gradient ELAT® ("fg-ELAT")
3	Criteria: show FC Single Cell incr. power and/or decr. PM over standard
4	Create a fg-ELAT/ catalyst system that is a pathway to interim Program targets
5	Go/No Go:cat./ fg-ELAT that approaches DOE Power/PM targets-0.4mg PM/sq cm
6	Go/No Go: Scale Best System to 225 cm^2 and validate performance at NFC
7	Program (1A3):MEA Fab. with PM loading decrease (to 0.3mg/sq cm total PM)
8	Scale-up/Validate: MEA fg-ELAT/catalyst(>4 stack elements,225 sq cm)
9	Scale-up/Validate: MEA Hi Temp. fg-ELAT/membrane (>4 stack elements,225 sq cm)
10	Pilot manuf./optimized components either <100 deg C and/or >120 deg C
11	*Deliverable: Stack(s) w Performance validated 1-10KW (Hi T and/or Cathode)*



Key Success Criteria is short stack verification of improvements by team partner Nuvera Fuel Cell

Final Deliverable (1A3): 1-10KW NFC Stack with successful MEA From either Program 1A1 or 1A2

New Method for Pt/C

Comparison *Crystallite Size* (XRD, nm) on Vulcan XC-72

%Pt/C	Stnd	New
10	2.0	-
20	2.5	2.2
30	3.2	2.5
40	3.9	2.8
60	8.8	3.7
80	25	4.9

Comparison *ECSA* (CO stripping, m^2/g)

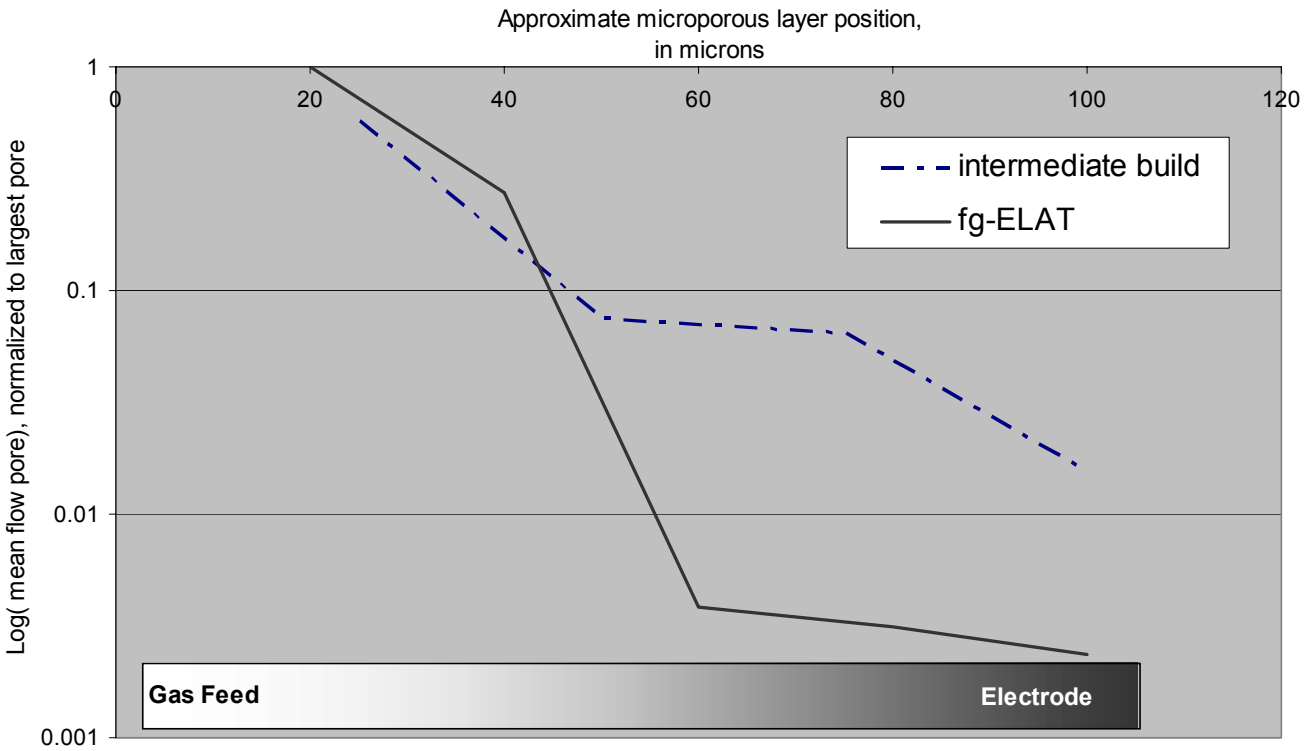
%Pt/C	Stnd	New
30	32	53
40	-	39
60	-	28
60*	-	52

*(new carbon)

- New chemistry/ reduced sulfur levels – no Cl^-
- Lower Processing Costs
- Have scaled 30%Pt/C to 2Kg batch

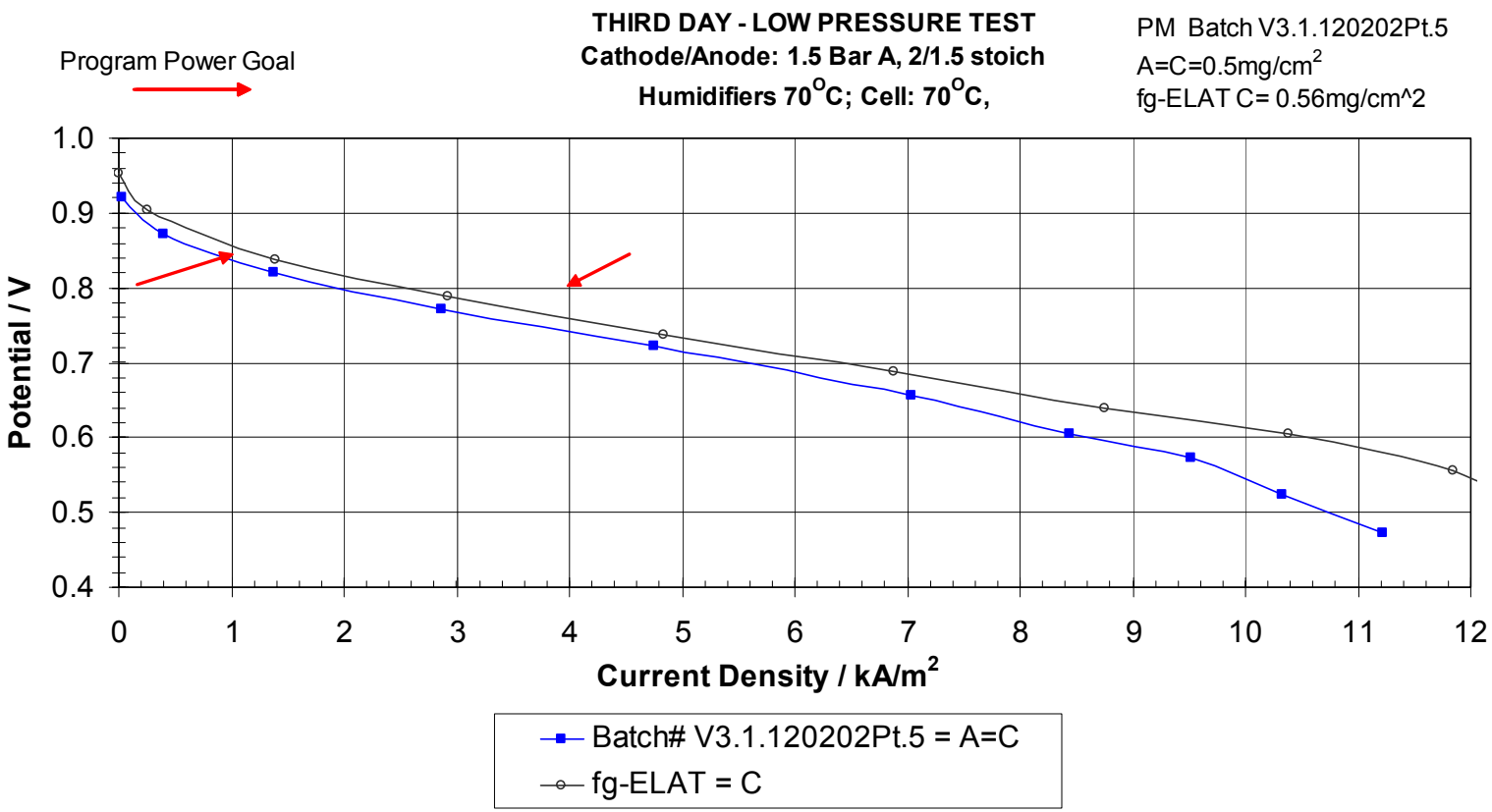
Porosity Gradient: Mean Flow Pore Comparison

Capillary Flow Porometry



The equivalent plot for hydrophobicity is missing

fg-ELAT: Proof-of-Concept



Impact of Web and More Facile Control of Gradient

Platinum Power Density

	Cathode	Cathode	Total PM	Total PM
	$1kA/m^2$	$4kA/m^2$	2005	2010
Cloth Web	g/Kw	g/Kw	g/Kw	g/Kw
Standard (st. Pt/C)	6.40	1.80	0.6	0.2
Type 1 (st. Pt/C)	3.73	1.29		
Type 2 (new Pt/C)	3.11	0.89		
Type 3 (st. Pt/C)	6.69	2.50		

(70°C, 1.5B A ,A/C 1.5/2 stoich. Nafion® 112)

Accomplishments/Progress

- *Met Dec milestone for both catalyst prep and fg-ELAT: achieved 50% reduction in platinum power density*
- *Have submitted samples to NFC for verification (ahead of schedule)*
- *Have created low temperature process (<200 deg c) for alloy formation: scaled best Pt/C prep to 2Kg (ahead of schedule)*
- *NU high temperature simulations (RDE) indicate that there may not be an "alloy effect" under low water conditions (Introduced at Asilomar Conf 2/03, ECS Paris 4/03)*
- *"High temperature" GDE interface evaluated at Du Pont: at NU Inorganic gel additives can improve conductivity at lower RH in the reaction layer*

Other Notable Progress

Patents

- Two Patent Applications pertaining to fg-ELAT
- Two Patent Applications on new catalyst preparation methods (low temp Alloys, new Platinum prep)

Publications

- A systematic investigation of the shift in water binding energy and its effects on the on-set Oxygen Reduction. (in preparation; Andrea F. Gullá, Robert J. Allen and Sanjeev Mukerjee)
- Electrocatalysis and Charge Transfer in Proton Conducting Membranes Operating at Elevated Temperatures. (in preparation; Sanjeev Mukerjee, R. Craig Urian, Chengsong Ma, Lei Zhang and Andrea F. Gullá)
- Investigation on the kinetics of Pt based alloys using Rotating disk (RDE) and Fuel Cell data; effect of synthesis procedures and the effect of water binding. (in preparation; Andrea F. Gullá, Robert J. Allen, Vivek Srinivasamurthy and Sanjeev Mukerjee)

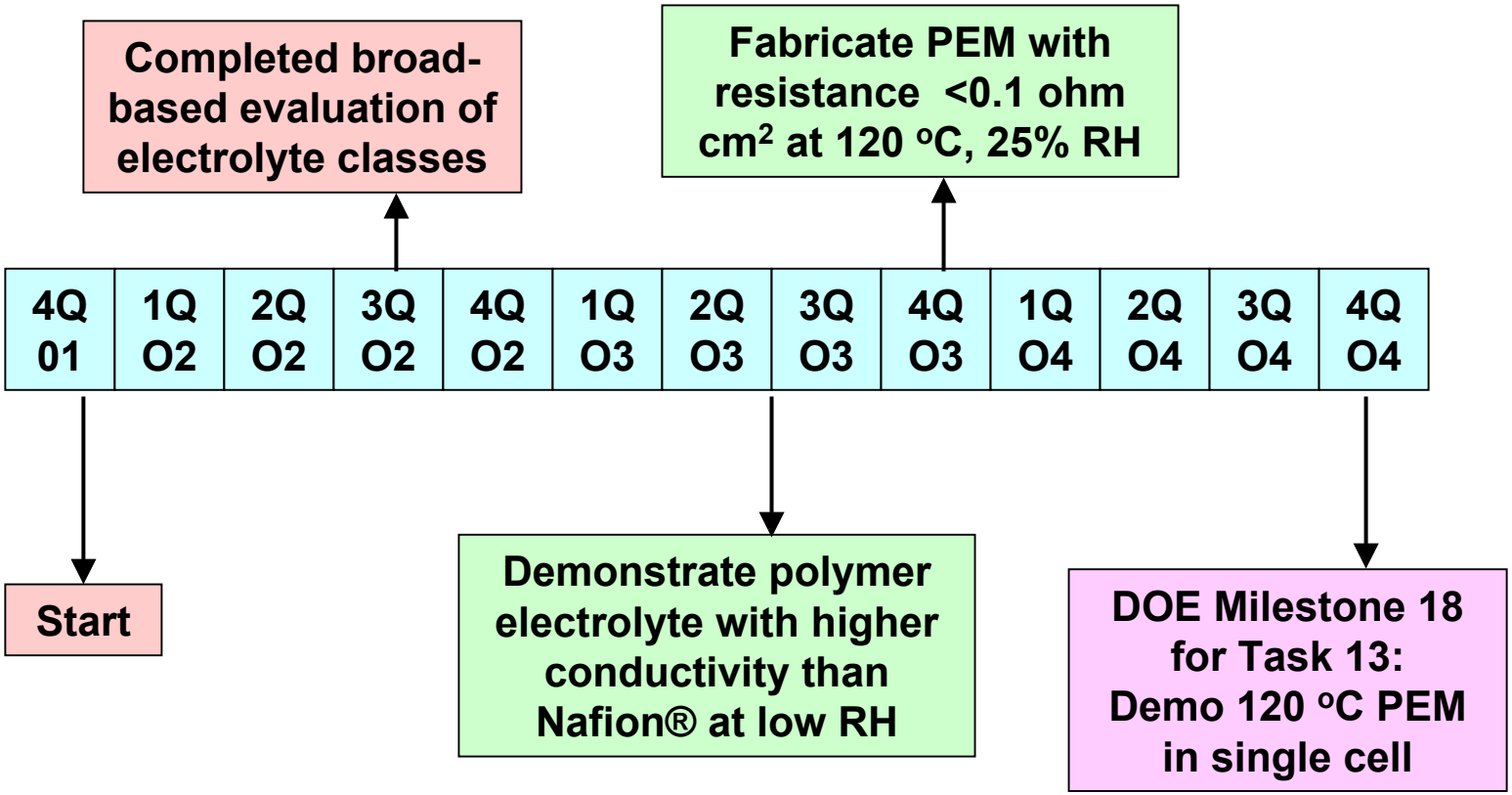
Going Forward

- Achieve lower total PM loadings by "jump-starting" limited Ion Beam Assisted Deposition (IBAD) on membrane for low loaded anodes (Program 1A3)
- Use increased coating control to lower metal load in GDE: continue with improvements in Nafion/GDE structure
- Use morphological characteristics of carbon cloth/paper and different carbon gas diffusion layers ("fg-ELAT") to build structure of GDE to designed for DOE power targets
- Develop quantitative methods to measure hydrophobicity during builds (will pursue with CWRU)

Higher Temperature Membranes: DuPont's Approach

- Synthesize model compounds and monomers
  - Evaluate conductivity at low RH
- Make ionomers
  - Thermally, hydrolytically, oxidatively stable
  - Incorporate best functionality from model compound studies.
    - With and without additional groups supporting ionization
- Fabricate Membranes
  - Optimize equivalent weight
  - Control swelling & provide mechanical properties
    - Composite membranes
    - Crosslinking
- Examine new electrolyte functional group
- Explore ionomers with uncollapsible hydrophilic domains
  - With CWRU
- Make MEA's and test in single cells

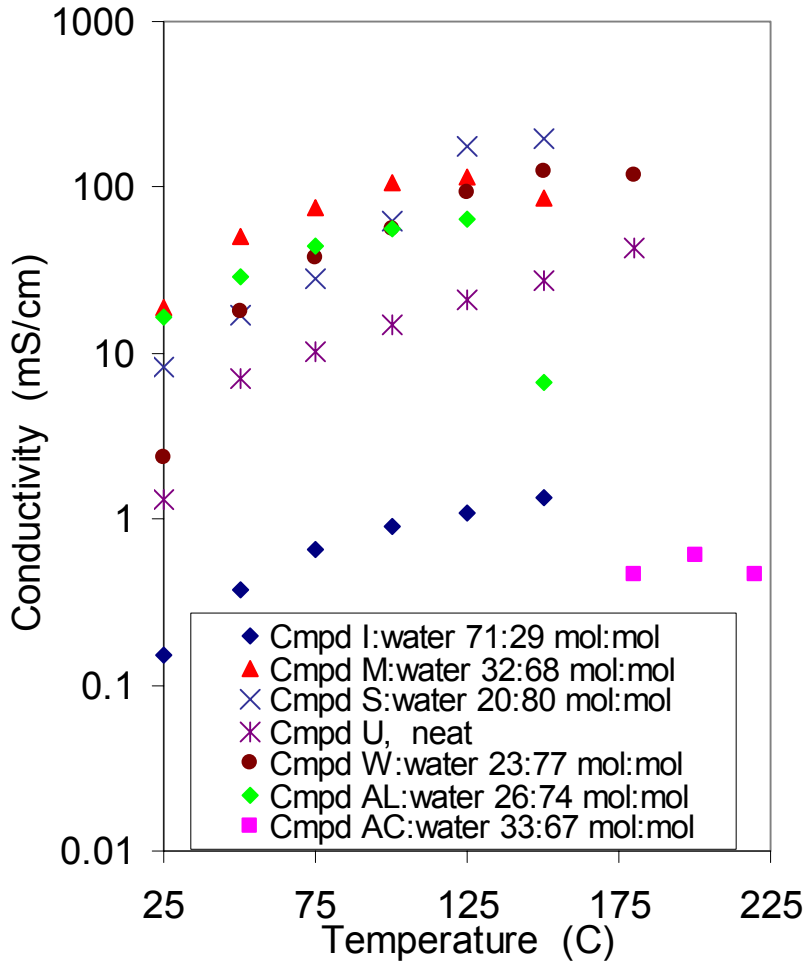
HT Membrane Timeline



Conductivity of Liquids

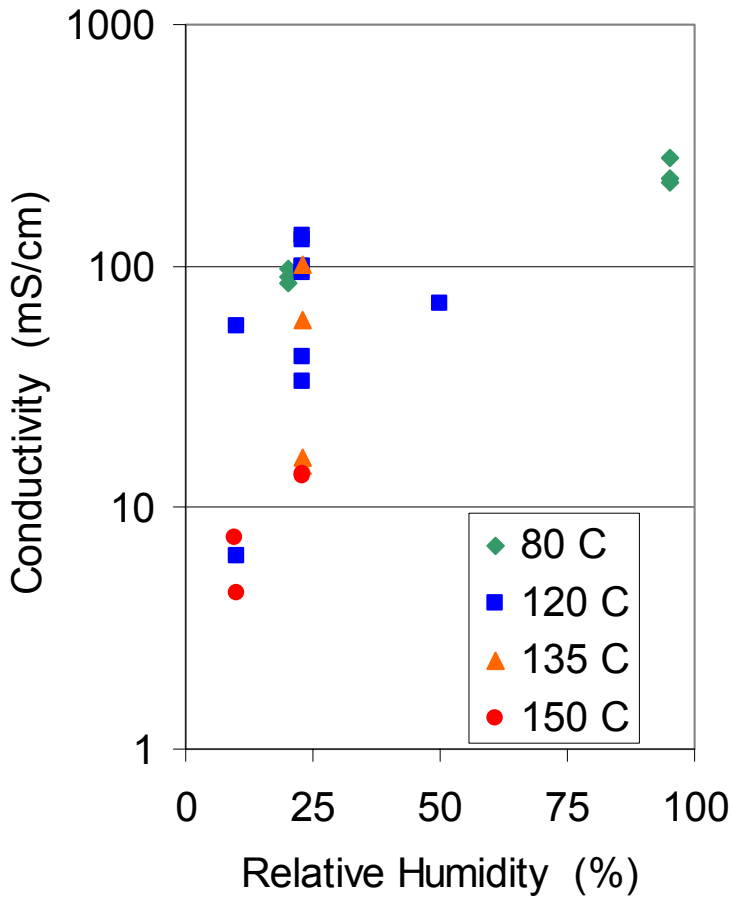
- More than 25 model electrolyte compounds and monomers synthesized
  - Which functionalities can engender conductivity at low RH?
- The water contents used are lower than required by Nafion®.
  - Cell was not pressurized.
  - Water vapor partial pressure was less than 1 atm.
- Compound U requires no water!
- Compound M is a monomer.

- Now pursuing ionomers based on the best functionalities from this study.



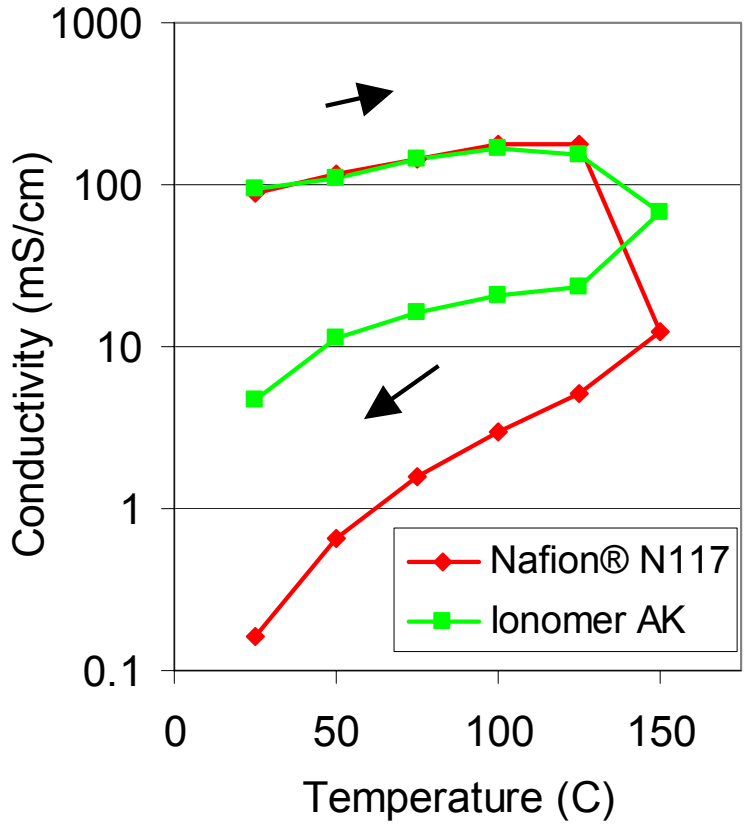
Conductivity for New Electrolyte X

- X is a small molecule model liquid compound
  - Sample for conductivity made by soaking X into ceramic paper
- Measured under controlled RH
  - Several different samples plotted with different loadings on paper
- Maintains conductivity at low RH better than several other electrolytes that have been examined



Conductivity of Polymeric Version

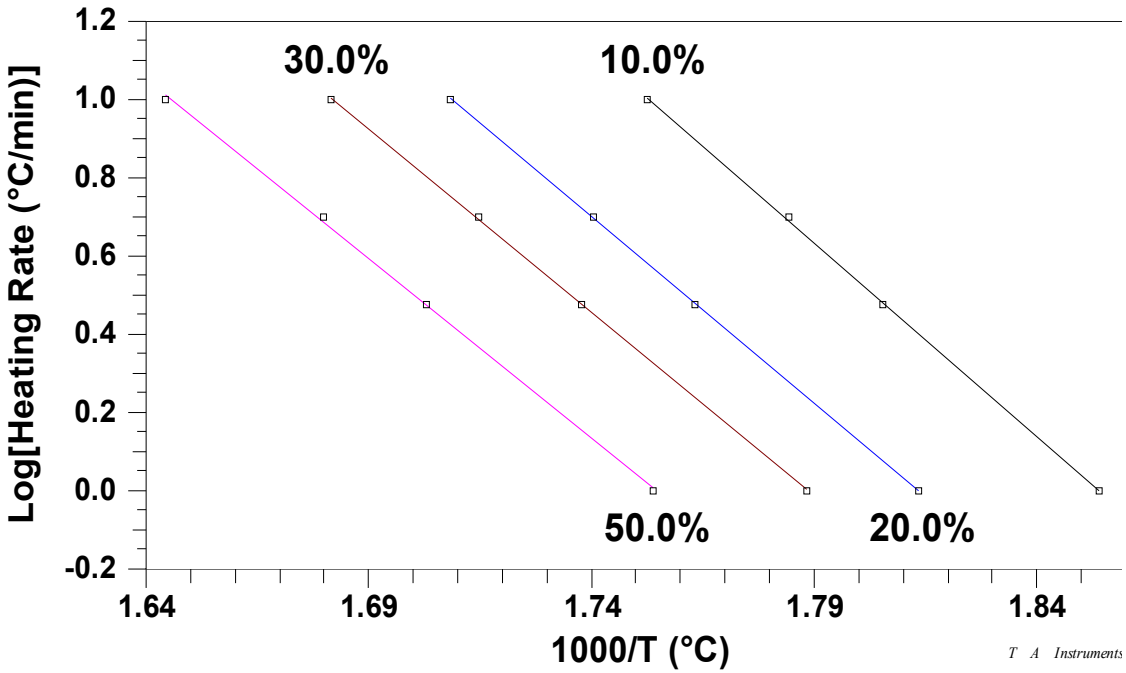
- Candidate ionomer AK
  - Polymer based on model compound X
  - Porous sample suitable for conductivity testing
- Through-plane Conductivity
  - Samples fully-hydrated at start
  - Samples dehydrate during measurement (no water added to cell)
  - Total pressure is 1 atm
  - RH ~ 25% @ 150 °C
- Maintains higher conductivity after exposure to low RH than does N117 benchmark
- Further work required to achieve thin impermeable membrane suitable for FC testing



Thermal Stability

- Will the ionomers be even thermally stable for the required lifetimes at 120 °C?
- Assessing with accelerated test using Kinetic TGA Method.
  - Measure TGA at different heating rates under slightly-wet air.
  - Plot log(heating rate) *vs* 1/T for different levels of weight loss.
  - Parallel lines indicate 1st-order decomposition and give E_a.

Sample	Activation Energy E_a (kJ/mol)	Lifetime limit due to thermal decomposition @ 120 °C (khr)
Candidate AE	265	>1,000
Nafion® 1100 EW benchmark	166	260 (±70 gage repeatability)
Candidate AM	178	27
Candidate AF	180	0.42

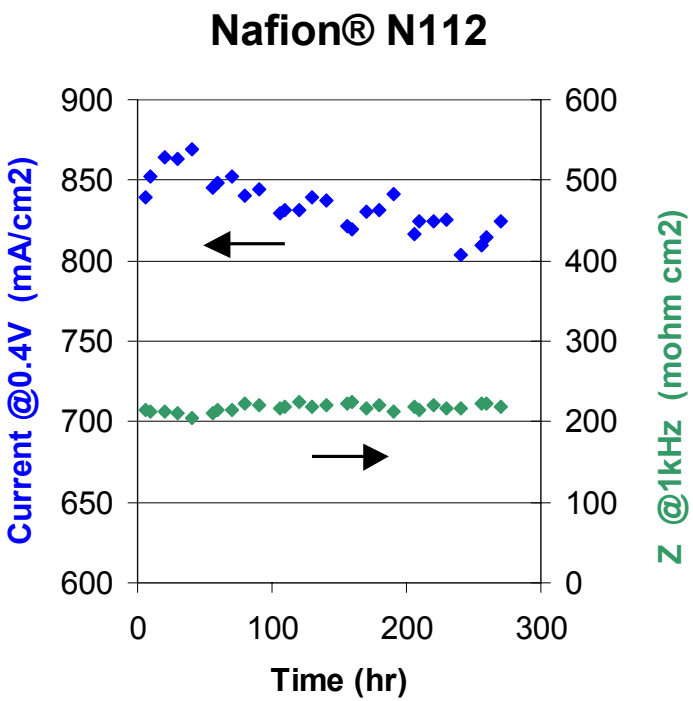


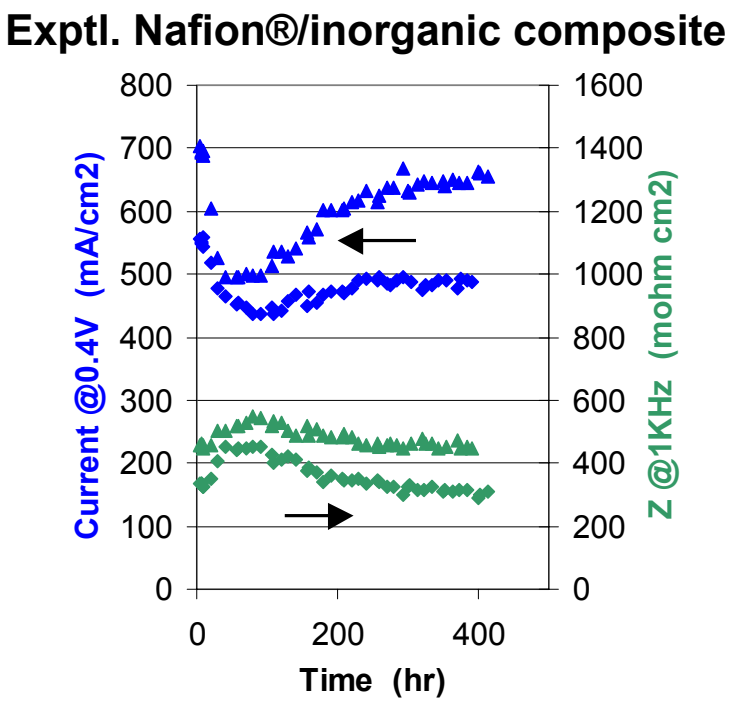
Question from the July 2002 Freedom Car Review of HT Memb. sub-Program

- Q: You have shown some preliminary results on new membranes operating at higher temperature for short periods of times. What happens after 3-5 days?
  - A: FC testing has now been carried out which shows significant degradation of performance, at least partly attributable to the membrane, after 400 hr for benchmark Nafion® and Nafion®/inorganic composite membranes.

Benchmarking 120 °C FC Lifetime

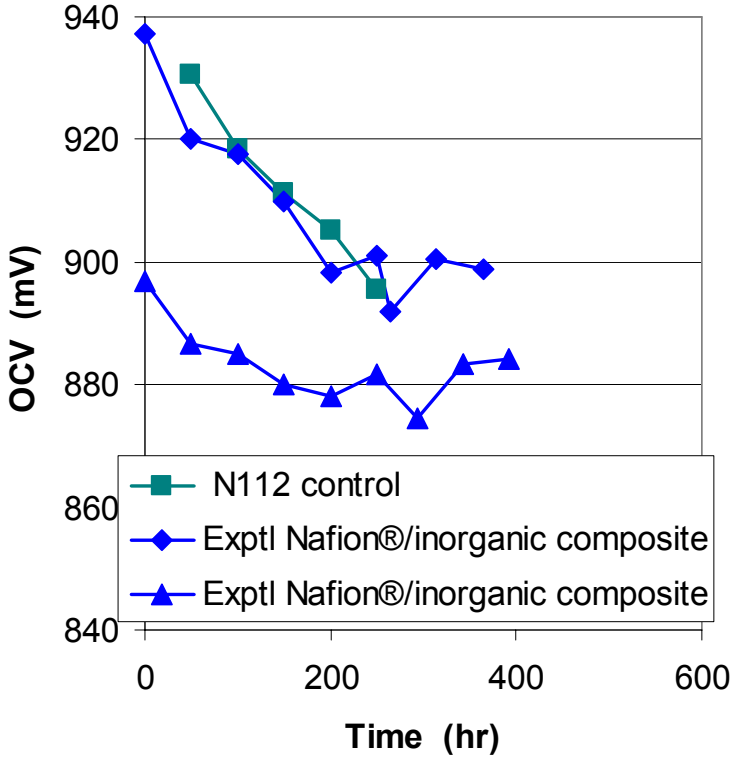
- MEA's prepared using ELAT® GDE's
- Conditions: HFC, const. 0.4 V, 120 °C, cathode/anode feeds 50% RH, 15 psig, stoic. 1.5/1.5 @1.6A/cm^2
- N112 lost 5% of current in first 250 hr; reasonably stable resistance
- Exptl. composite memb. shows higher resistance and instability in current and resistance attributed to decomposition of the inorganic component.





Open Circuit Voltage

- Cycle at 120 °C, 50% RH feeds
  - 49.5 hrs at 0.4 V
  - 0.5 hrs at open circuit
- Decay in OCV is believed due to increase in hydrogen crossover (membrane failure)
- Hydrogen crossover increase confirmed with voltammetric measurements on cells with feed switched to N_2 anode-side / H_2 cathode-side
- Further studies to determine causes
  - Chemical degradation
  - Mechanical failure



Responses to two Questions from the July 2002 Freedom Car Review of HT Memb. sub-Program

- Q: In designing your membranes, FreedomCAR is not only interested in high temperature membranes but those with acceptable performance over a wide range: automobiles will still have to start at sub freezing temperatures.
  - A: We have measured the temperature dependence of conductivity and acknowledge that, at constant low RH, some of our new electrolytes have a higher activation energy than Nafion® (larger decrease at lower temp.) However, at lower temperatures the FC pressure budget allows higher RH, which strongly increases the conductivity. We can only commit to keeping this requirement in mind as it is balanced against the other requirements.

Going Forward

- Develop further work on ionomer "AK" to achieve thin impermeable membrane suitable for FC testing
- Explore ionomers with uncollapsible hydrophilic domains
- Make ionomers
  - Thermally, hydrolytically, oxidatively stable
  - Carry strong acid groups
  - With and without additional basic groups supporting self-ionization
- Optimize equivalent wt., control swelling, and provide mechanical properties
  - Composite membranes
  - Crosslinking
- Continue to examine new electrolyte functional groups

Acknowledgements

De Nora N.A. E-TEK *div*

- Yu-Min Tsou, Ph.D.
- Lixin Cao, Ph.D.
- Guy Havet, Ph.D.
- Hua Deng, MS, ChE
- Michael Schneider
- Maria Cayetano
- Jeffrey Morse
- Laura Bellamy

Northeastern University

- Prof. Sanjeev Mukerjee
- Andrea F. Gullá (DNNA.), Ph.D.
- Robert J. Allen (DNNA) Distinguished Visiting Scientist
- Vivek Srinivasamurthy (Graduate Student)
- Lei Zhang (Graduate Student)
- Jillian Goldfarb (Undergraduate)

DuPont

- Mark G. Roelofs, Ph.D (Project Leader)
- Mark Teasly, Ph.D.
- Zhenyu Yang, Ph.D.
- Hongli Dai, Ph.D.
- Jayson Bauman, Ph.D.
- John J. Borowski
- Ruping Wang
- Robin Blackburn
- James I. Johnson

DE NORA NORTH AMERICA, Inc.
GRUPPO DE NORA
Durantes Vincunt

Northeastern UNIVERSITY

DUPONT
The miracles of science™

Development of High Temperature Membranes and Improved Cathode Catalysts

DOE contract DE-FC04C-02-Al-67608

2003 DOE Funds: 2.7 M$

DOE Merit Review

Sathya Motupally and Mike Perry

UTC Fuel Cells

UTC Fuel Cells
A United Technologies Company

May 19, 2003

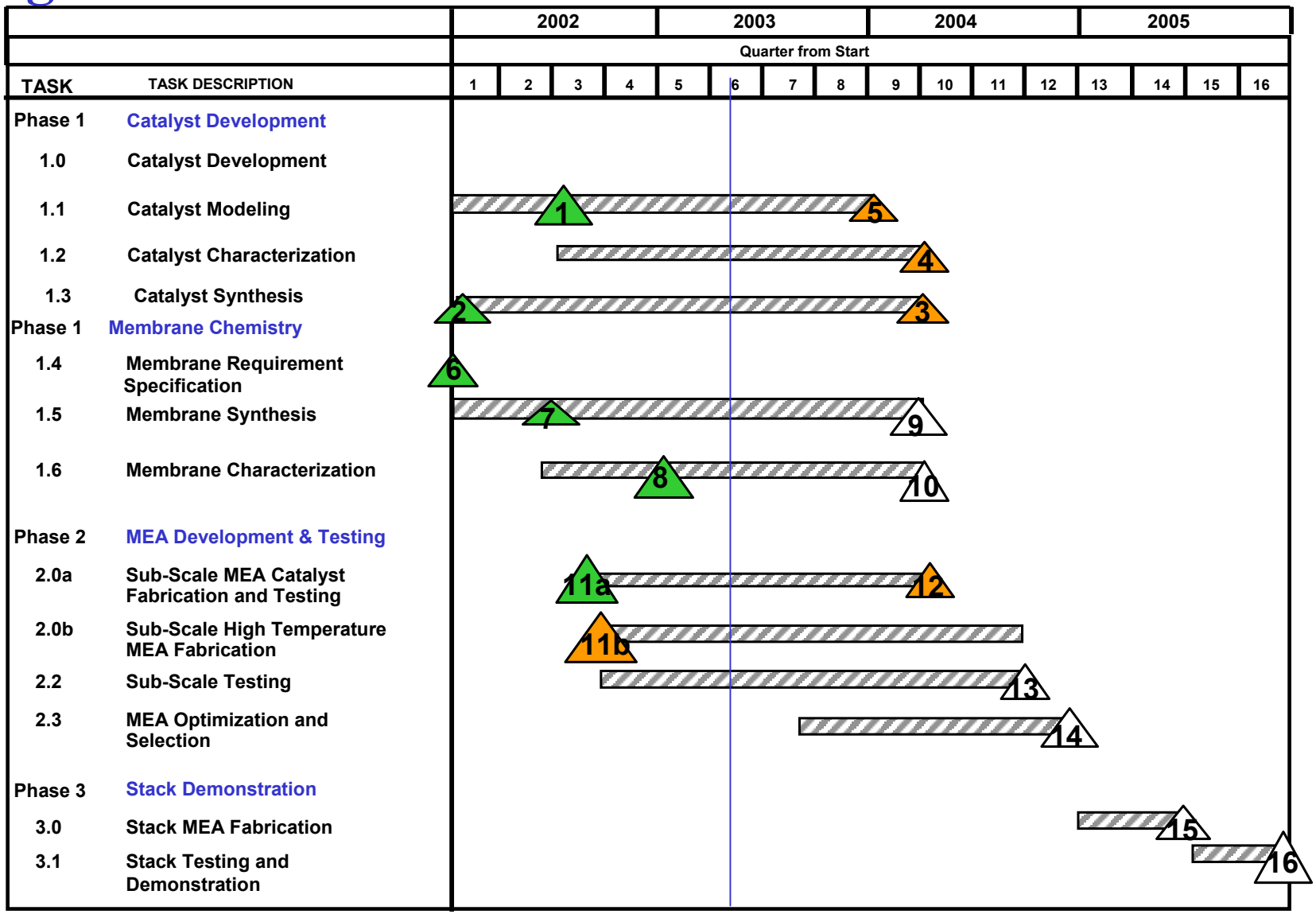
Outline

- Objectives
- Approach
- Project timeline
- Technical highlights:
  - High-temperature membrane (HTM)
  - Advanced cathode catalysts
- Future work

Objectives and Approach

- **High temperature proton exchange membranes**
  - Develop membranes capable of satisfying DOE targets. Operating conditions: *120*°C -150°C and 1.0-1.5 atm.
  - Collaboration with leading polymer chemists to develop new membrane systems.
- **Advanced cathode catalysts**
  - Develop high concentration Pt-alloy catalyst systems with improved activity.
  - Utilize the higher activity, reduce catalyst-layer thickness and achieve reduced precious-metal loading (DOE goal of 0.05 mg/cm^2).

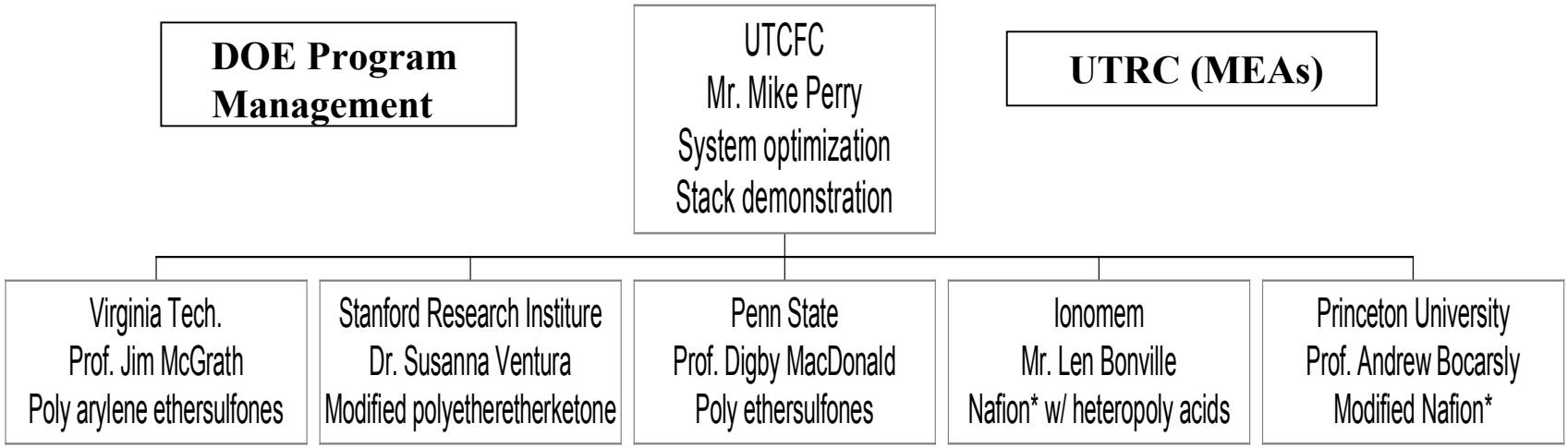
Program Timeline



Milestone Schedule

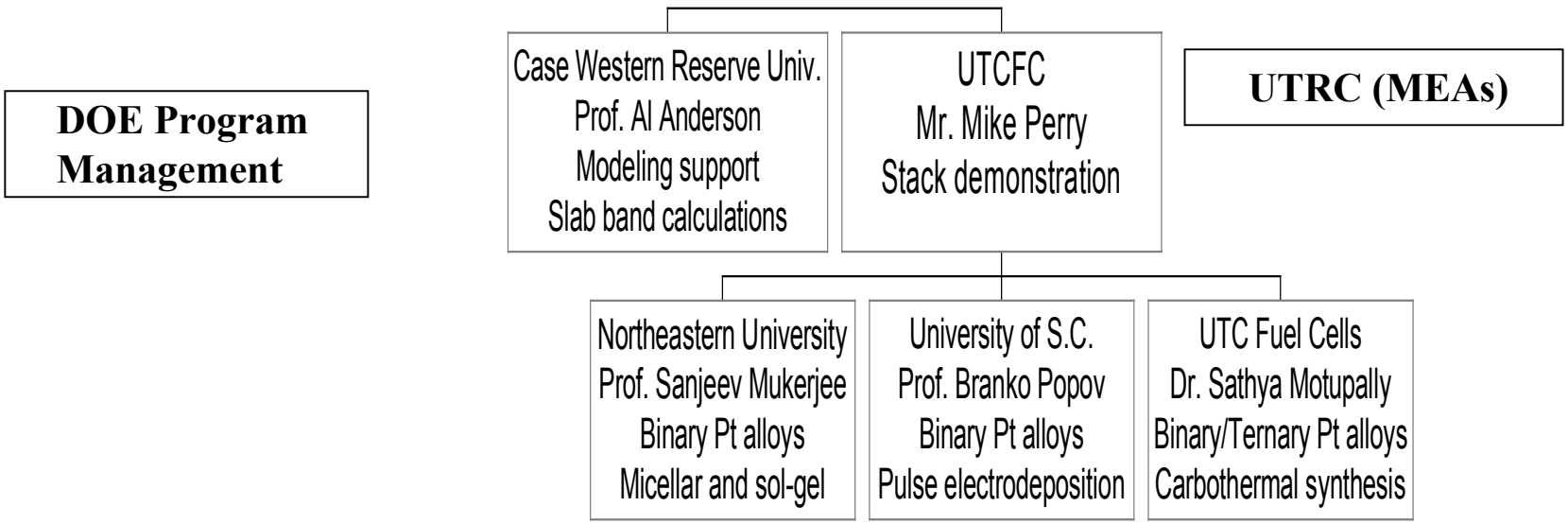
PHASE	MILESTONE #	MILESTONE
Phase 1 Membrane Chemistry and Catalyst Development	1	Preliminary model completed
	2	Begin alloy synthesis
	3	Complete alloy synthesis
	4	Complete characterization and down-selection
	5	Complete modeling + correlation
	6	Membrane specification to team members
	7	Initial sample membrane
	8	Characterization of initial membrane samples
	9	Synthesis of final membrane samples
	10	Select membrane for Phase 2
Phase 2 MEA Development and Testing	11a	Initial electrode fabrication (catalyst)
	11b	Initial electrode fabrication (HTM)
	12	Complete subscale testing for cathode catalyst and down-select catalysts
	13	Complete subscale testing for membranes and down-select membrane(s)
	14	Select optimum catalyst-membrane combination for Phase 3
Phase 3 Stack Demonstration	15	Complete test and assembly of 2-20 cell stacks.
	16	Complete stack verification test

High-Temperature Membrane Team



- Collaboration with leading polymer chemists to develop new membrane systems.
- Systems include non-Nafion® and also modified-Nafion® membranes.

Advanced Cathode Catalyst Team



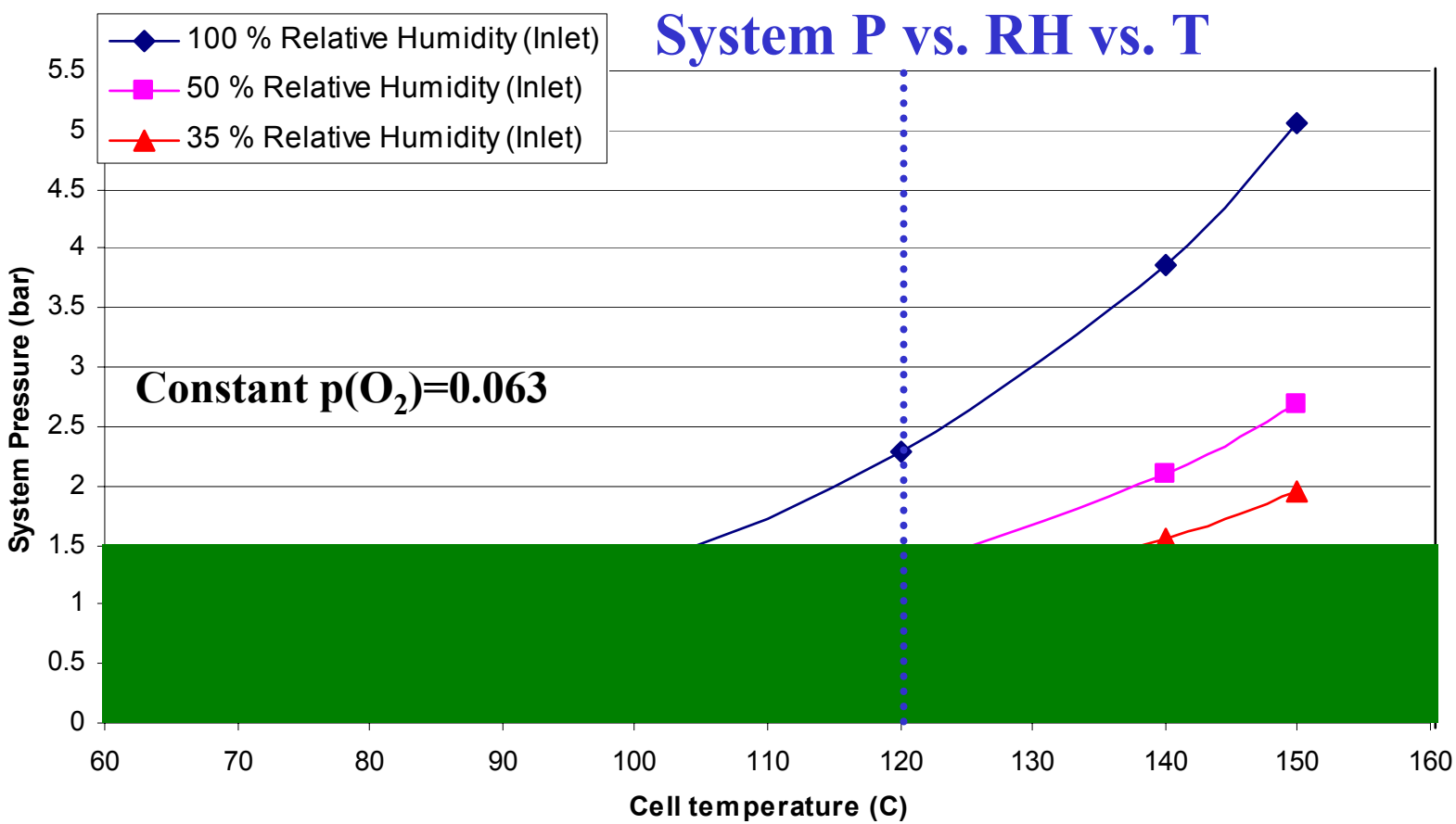
- Collaboration with leading electrochemists to develop higher activity catalyst systems.
- Systems include binary and ternary Pt alloys.
- Various deposition routes being investigated.

High-Temperature Membranes

Summary of Technical Achievements

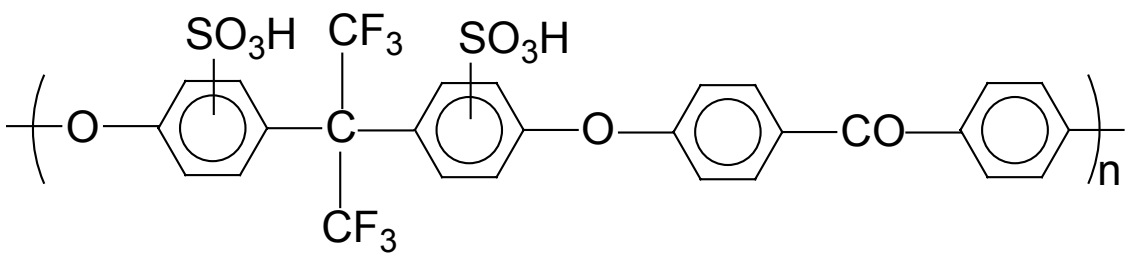
- 4 membrane systems with proton conductivity on the order of 10 mS/cm at 120 C and 50% RH synthesized.
  - BPSH from Va. Tech
  - Modified S-PEEK from SRI
  - FPES from Penn State and
  - HPA filled Nafion® from IONOMEM
- Majority of membranes synthesized date on the program require hydrophilic fillers to conduct at reduced RH.
- IONOMEM has established a baseline for HTM performance of 0.6 V at 0.4 A/cm^2 (120 C, 30% RH).

System Pressure Requirements



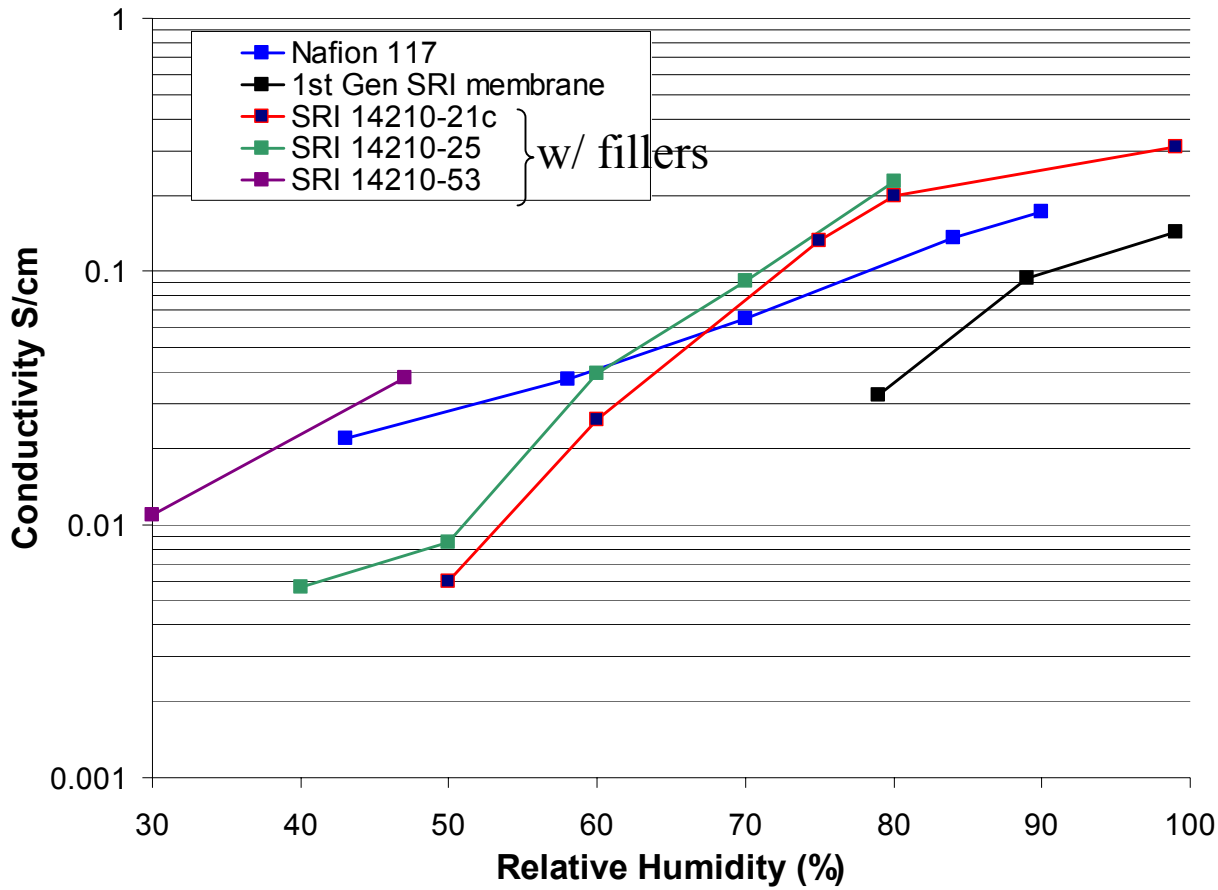
SRI Approach

- SRI polymer membrane is based on sulfonated liquid crystalline polymers crosslinked to produce dimensionally stable and flexible membranes.



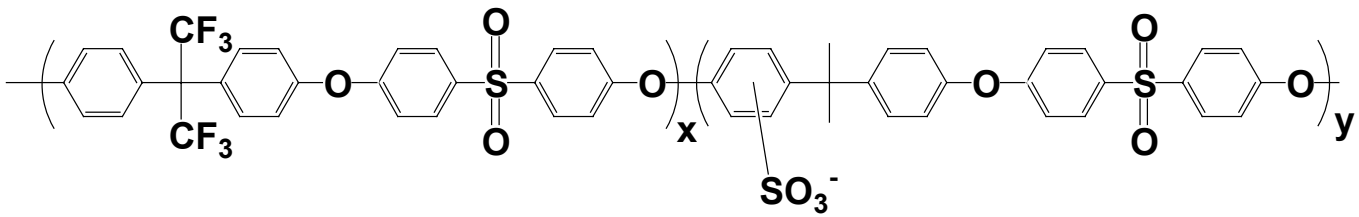
  – Hydrophilic polymers designed to retain water of hydration are added to the membrane to aid in conductivity at reduced RH.

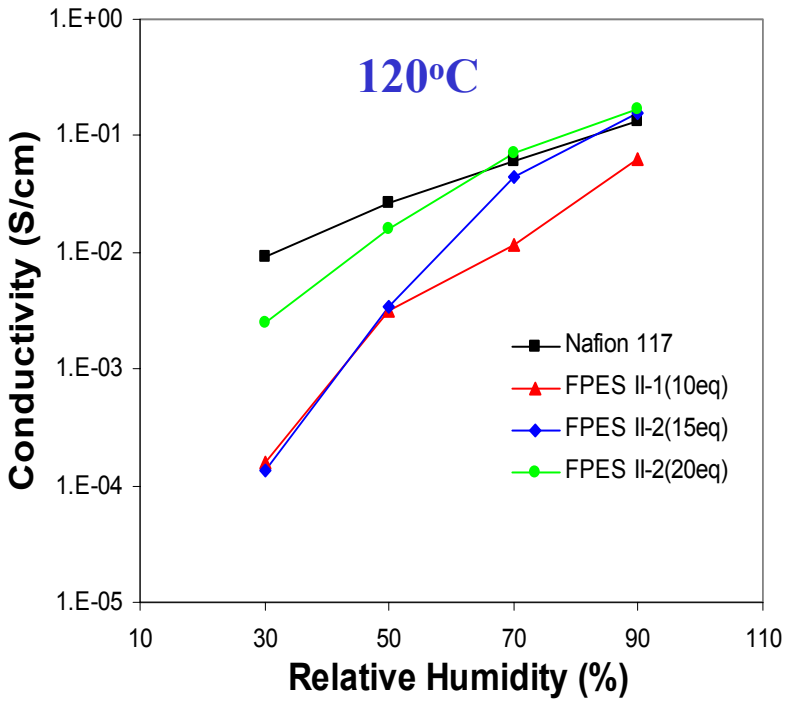
Membrane Conductivity at 120°C vs. RH

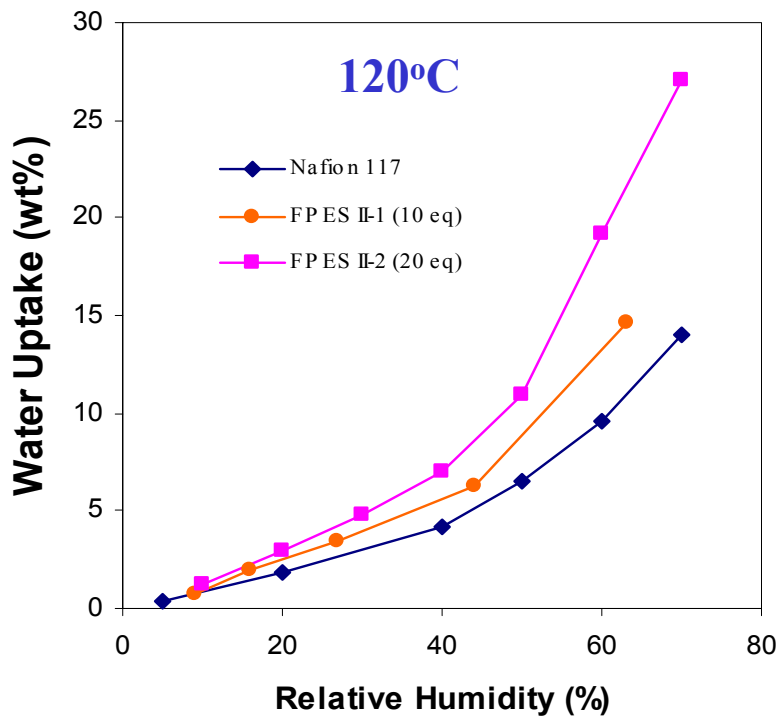


- Conductivity of 0.011 S/cm at 120°C@ 30% relative humidity and 0.038 S/cm at 120°C@ 47% relative humidity.

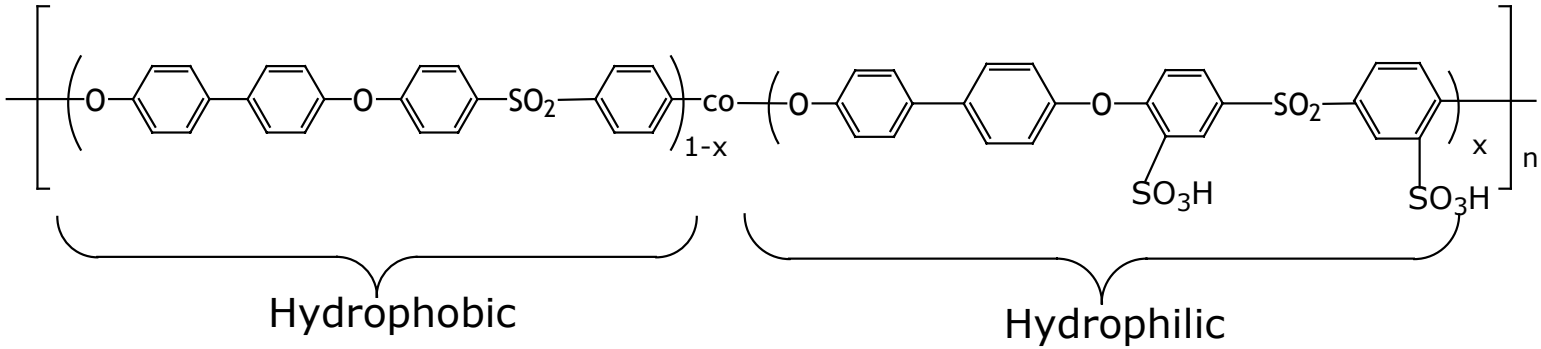
F-PES Membrane (Penn State)



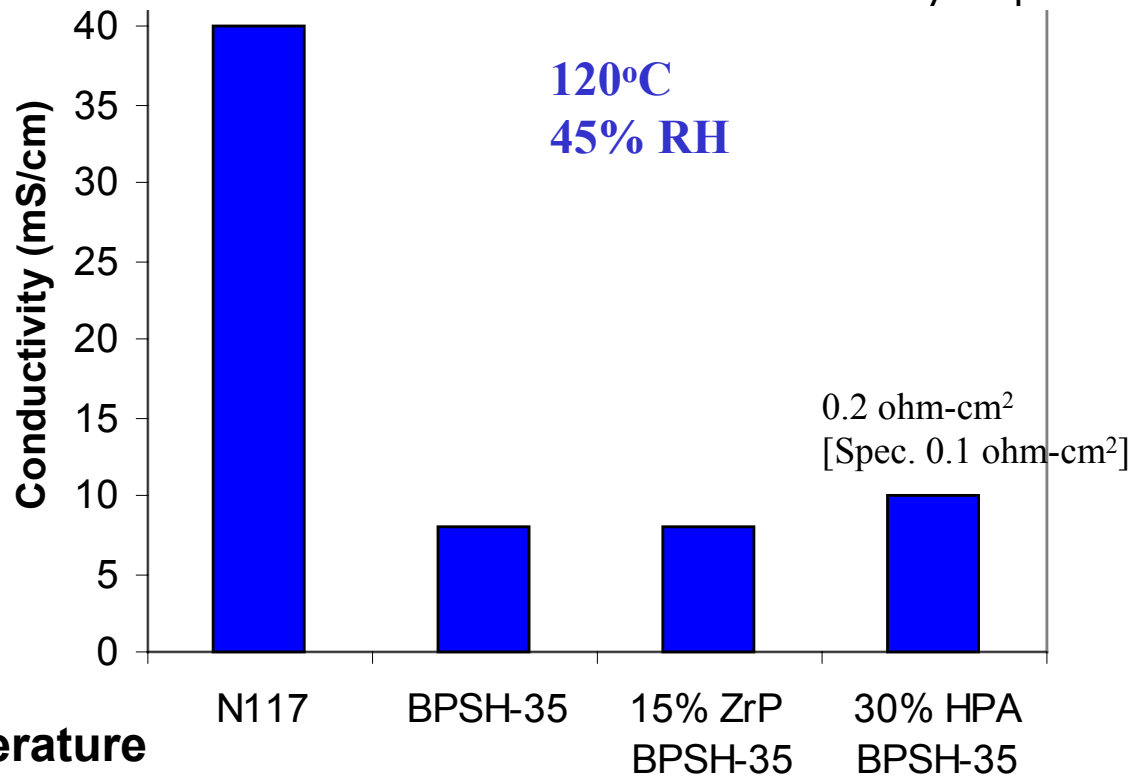




BPSH Membrane Virginia Tech



Bi-phenyl sulfones

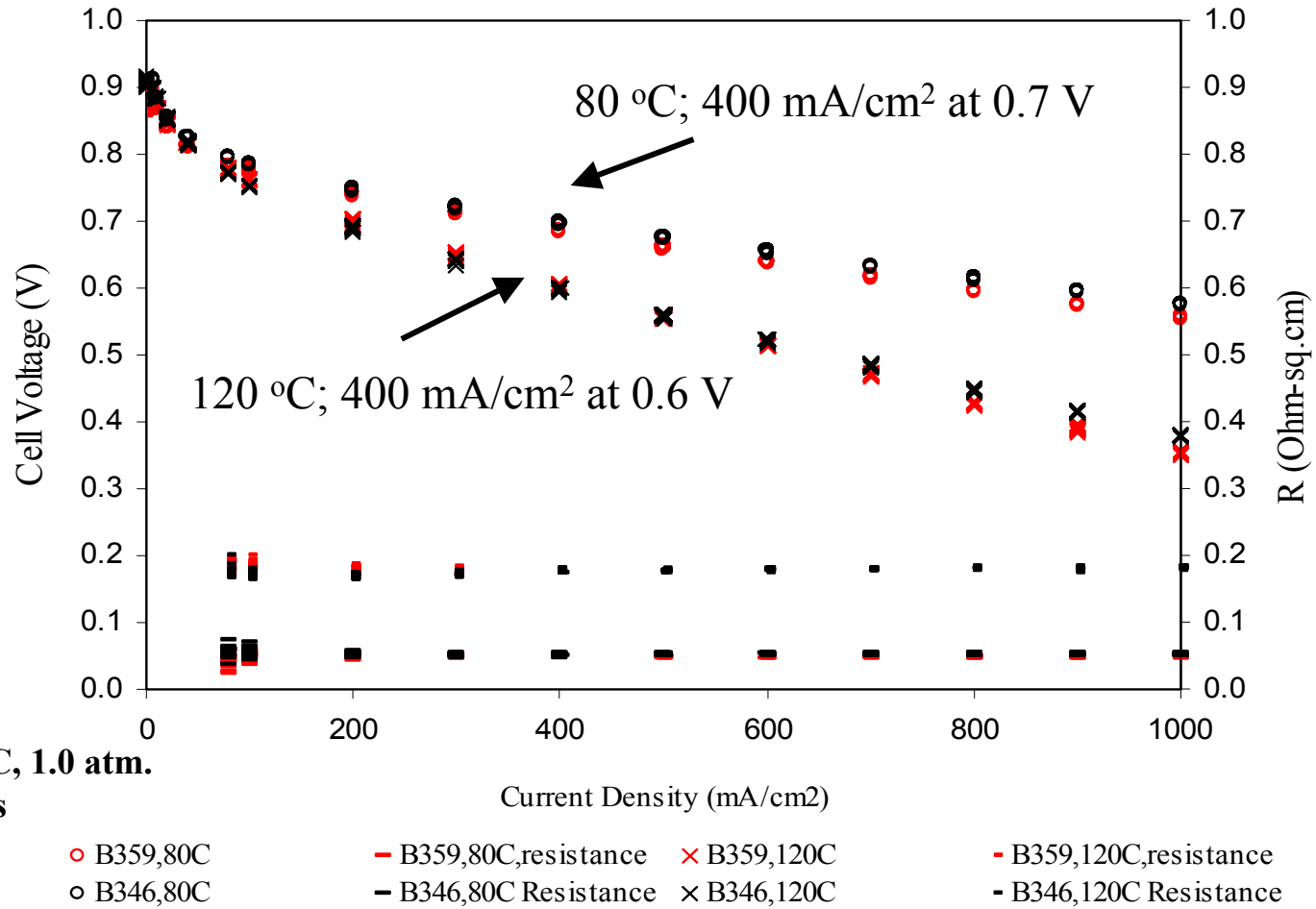


Upper use temperature fully - hydrated T_g

99°C **135°C**

Nafion®-HPA Composite Membranes (IONOMEM)

Nafion®-Teflon®-phosphotungstic acid (HPA)



80 °C and 120°C, 1.0 atm.
H_2/air reactants
3.3/4.0 Stoich.

Future Work (2003)

- Further optimization of membrane systems and/or fillers required to improve conductivity at practical RH.
- Develop a generalized stability template for HTMs.
- Initiate HTM down-select process.
- Initiate HTMEA fabrication and optimization.

Advanced Cathode Catalyst

Summary of Technical Achievements

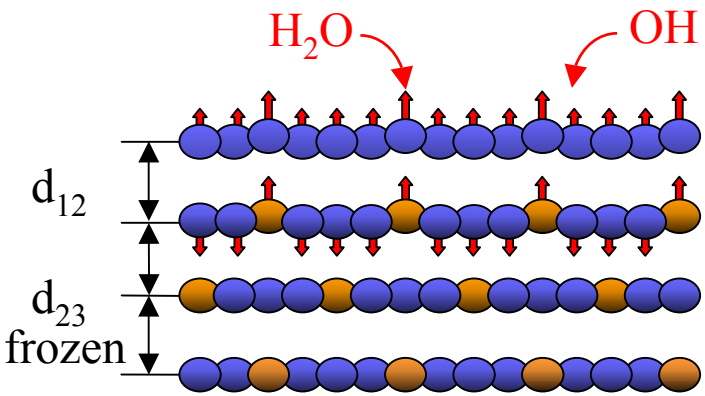
- Slab band calculations using VASP program have provided insight into binary alloy skin effect.
- Higher activity and more stable binary Pt alloys synthesized using the colloidal-sol, carbothermal, and pulse electrodeposition routes.
- Reproducible and SOA CCMs fabricated using the decal transfer process.

VASP Modeling (Case Western)

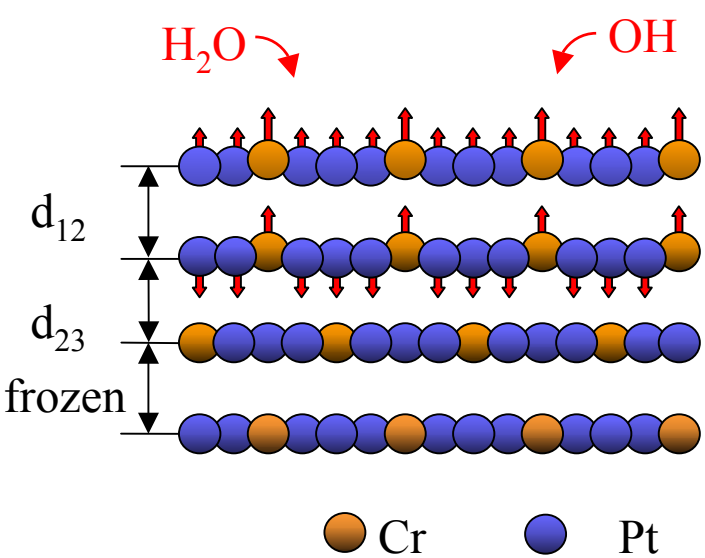
$\Delta U^o = U^o(\text{alloy}) - U^o(\text{Pt}) =$

$[\,(D_0(OH)_{Pt} - D_0(OH_2)_{Pt}\,] - [D_0(OH)_{alloy} - D_0(OH_2)_{alloy}\,]$

Pt(111)-skin on Pt_3Cr



Mixed metal surface on Pt_3Cr

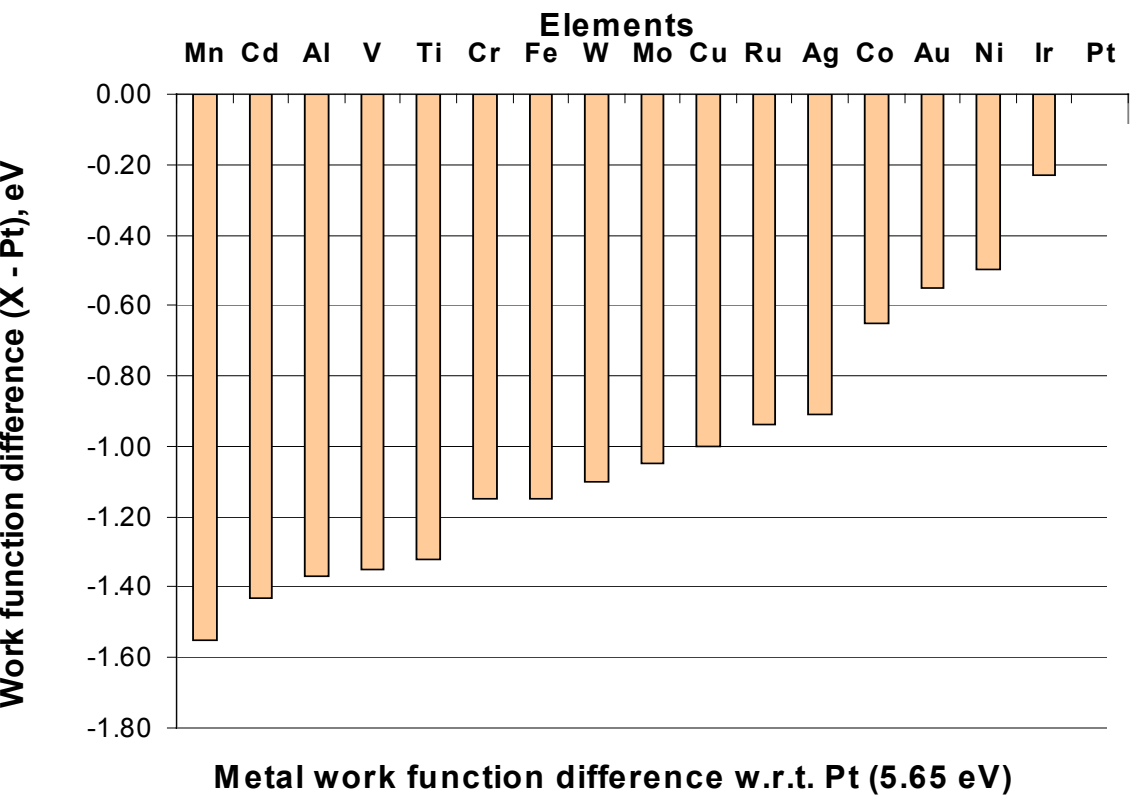


Catalyst surface	D_0(Surface-OH) eV	D_0(Surface-OH_2) eV	ΔU^o eV
Pt(111) (θ = 0 ML)	2.371	0.231	0
Pt(111)-skin on Pt_3Cr (θ = 0 ML)	2.241	0.210	0.11
Pt_3Cr mixed metal surface (θ =0 ML)	3.316 on Cr 2.516 on Pt	0.628 on Cr 0.204 on Pt	-0.55 -0.17

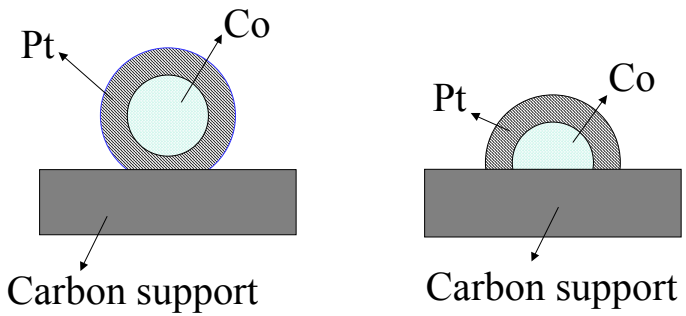
- On Pt-skin, model model predicts that charge transfers from Cr to Pt skin.

Shell-Core Structures (UTCFC)

- The model studies support the following model structures for composite catalysts based on the work-function differences.
- Current effort is focused on verifying this core-shell concept experimentally in conjunction with the theoretical modeling.

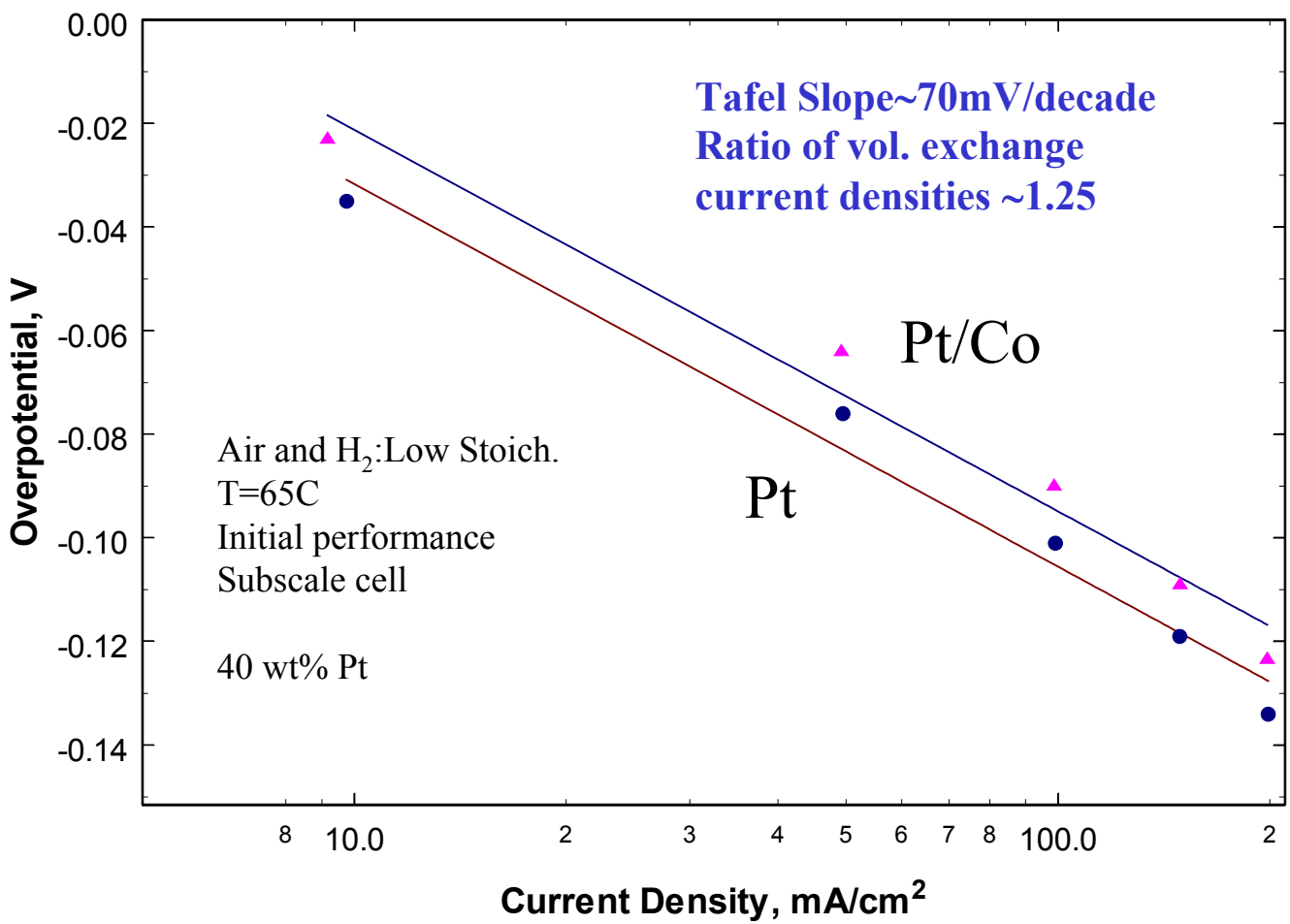


Supported $Metal_{core}$– Pt_{shell} nanoparticles



Kinetic Enhancement with Pt-Co Binary Alloy (UTCFC)

- True catalyst activity of Pt-Co is approximately 2.2 X Pt.



$$i = p_{O_2}\, a.i_0 e^{-\alpha \frac{F}{RT}\eta}$$

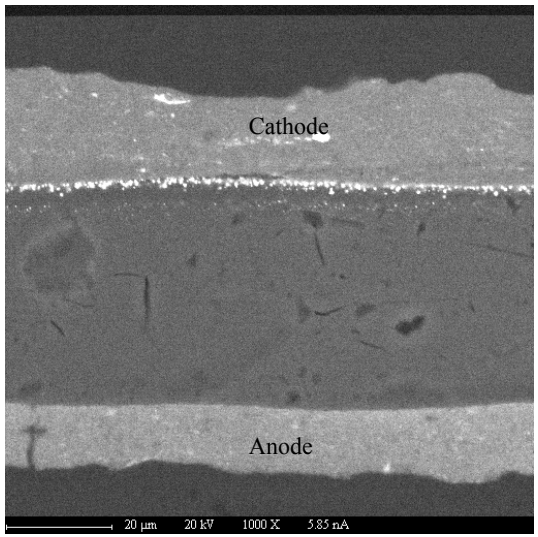
η=A+B log(i)

η=overpotential
i=current density
$a.i_0$=Exchange current density

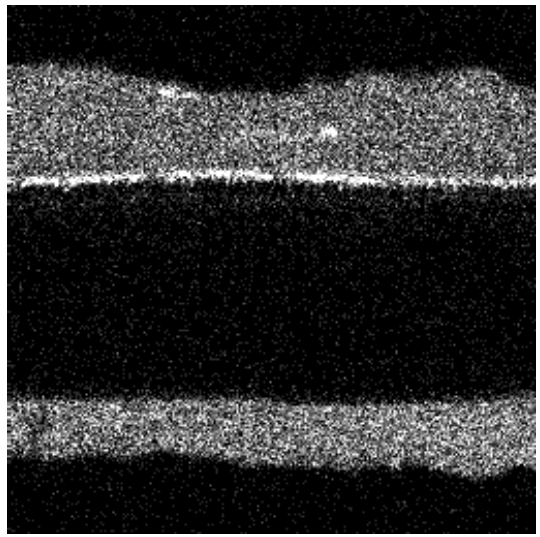
Cycling Stability with Pt-Co

(a) PtCo CCM

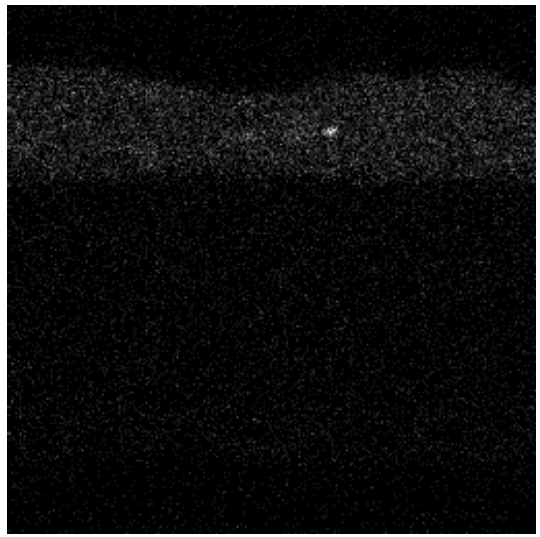
4000 Cycles
1.3 V-0.9 V



B.S.E.

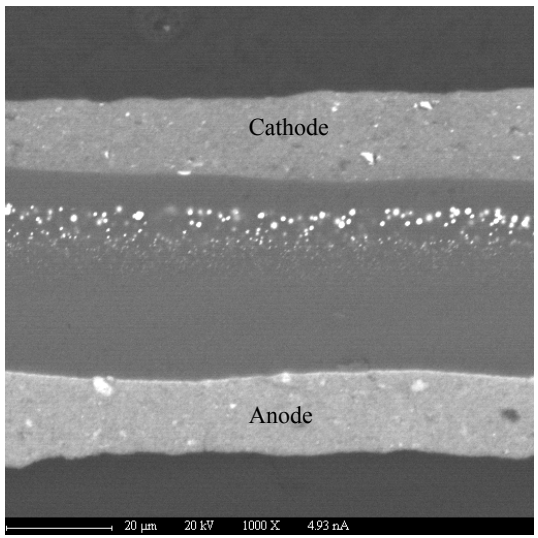


Platinum

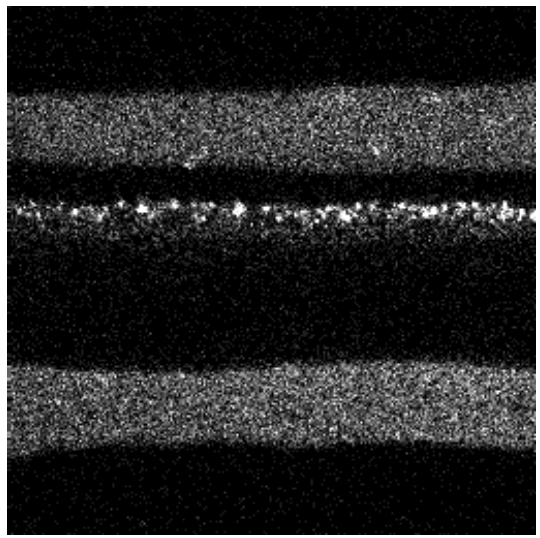


Cobalt

(b) Pt CCM



B.S.E.

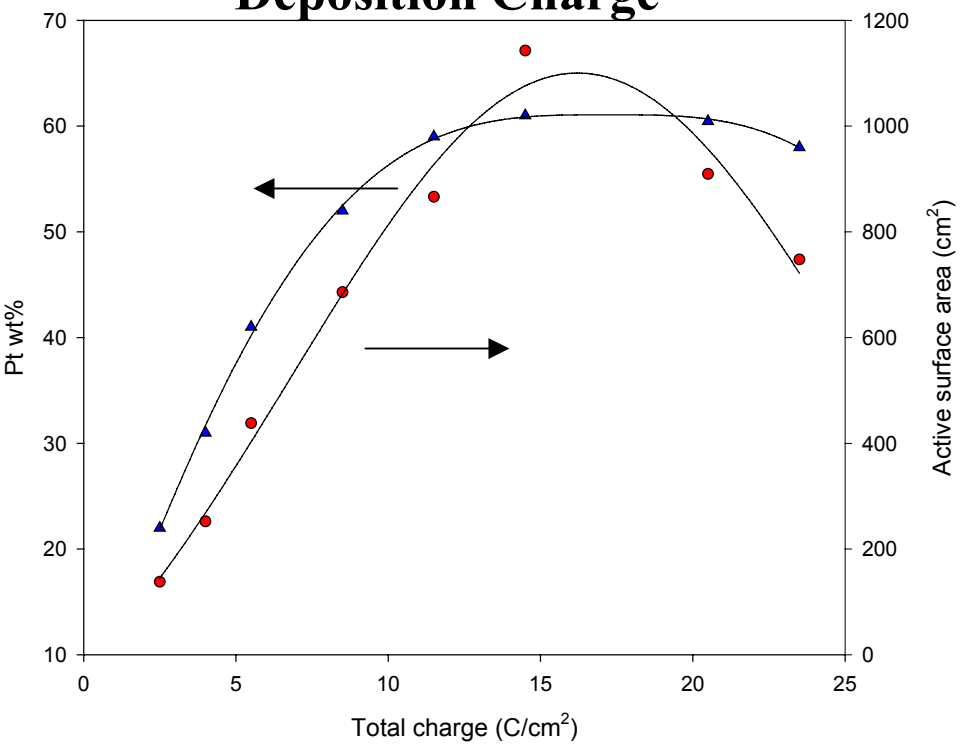


Platinum

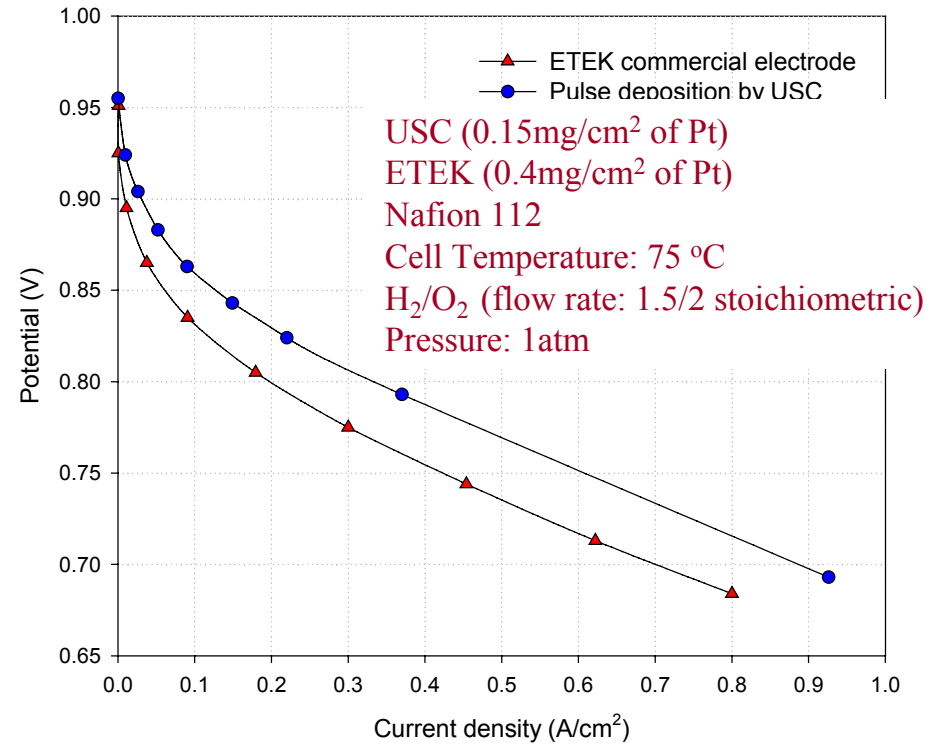
- The electron microprobe analysis shows no evidence of Co in the membrane and/or anode.
- The absence of Co migration is a strong benefit for the Pt/Co alloy system.

Pt Pulse Electrodeposition (USC)

Pt wt% vs. Surface area vs. Deposition Charge



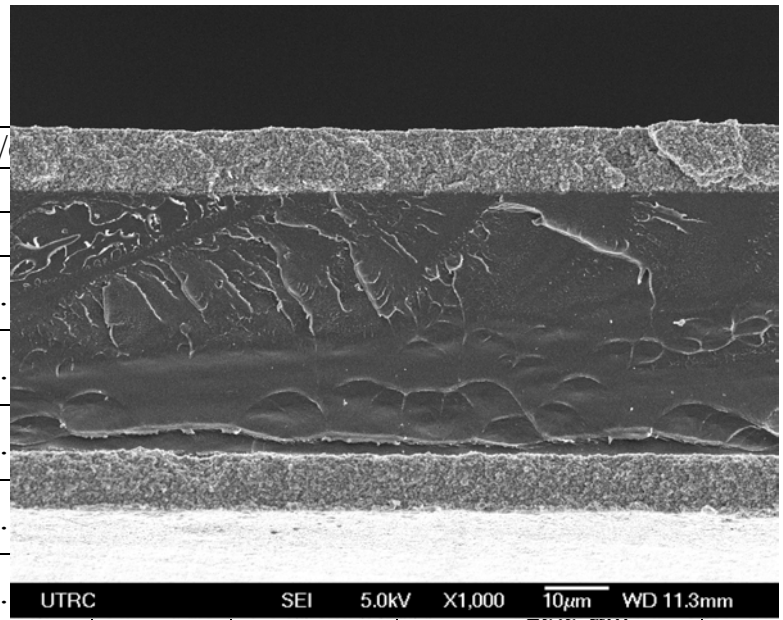
Sample Performance Curve



CCM Fabrication (UTRC)

- Reproducible and SOA CCMs currently being fabricated with decal transfer process.

HRSEM of a Freeze Fracture



CCM ID	V, mV @ 400 mA/cm		V, mV @ 100 mA/				
	H_2/O_2	H_2/Air	H_2/O_2	H_2/Air			
DOE target**	0.80		0.85				
Commercial → PEM 411***	0.824	0.786	0.885	0.			
PEM 404	0.800	0.760	0.875	0.			
PEM 413	0.795	0.757	0.879	0.			
PEM 414	0.790	0.748	0.880	0.			
PEM 415	0.810	0.767	0.887	0.			
PEM 416	0.798	0.756	0.886	0.854	69	44	Membrane thickness

Relatively Uniform Cathode Thickness, ~10 μm

** DOE targets are specified for 85%H_2/60%O_2 utilization;
*** Pt Loading on cathode side=0.4g/cm^2;

Future Work (2003)

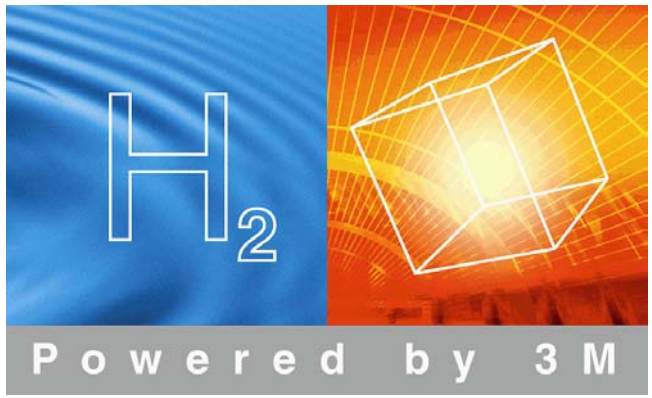
- Investigate the feasibility of Pt/X skin effect.
- Continue Pt-alloy synthesis using the various routes and optimize for activity and stability.
- Initiate catalyst down-select process.
- Investigate several methodologies to reduce Pt loading (e.g., ionomer gradient, etc.)

2003 DOE HYDROGEN, FUEL CELLS, AND INFRASTRUCTURE TECHNOLOGIES PROGRAM REVIEW MEETING

May 19-22, 2003

Berkeley, CA

Advanced MEA's for Enhanced Operating Conditions, Amenable to High Volume Manufacture



3M/DOE Cooperative Agreement

No. DE-FC04-02AL67621

Technical Goals and Objectives

3M/DOE Cooperative Agreement No. DE-FC04-02AL67621

Development of high performance, lower cost membrane electrode assemblies (MEA's) qualified to meet demanding system operating conditions of higher temperature and little or no humidification, with less precious metal catalysts, and higher durability membranes than current state-of-the-art constructions.

Technical goals include development of:

- Durable MEA's at 85 < T < ~ 120ºC, operating on low humidification with PFSA based ionomer and lower cost materials and catalysts
- Development of MEA's for 120 < T < 150ºC, based on non-aqueous proton conduction mechanism, lower cost materials and fabrication processes
- Matched MEA materials and processes scaleable to high volumes

Work Plan Summary

Task 1 is directed at advancing the state-of-the-art in cathode structures and durable PFSA based membranes to stretch the limits of current MEA technology toward more stability at hotter, drier operating conditions (85 < T < 120ºC) with lower cost materials and high volume compatible processes.

Subtasks include:

- Development of advanced cathode catalysts: Pt ternaries, combinatorial methods, others
- Modified membranes based on 3M's non-Nafion™, PFSA ionomers
- Matching 3M MEA and air management operating conditions
- Advanced modeling for flow field and gas diffuser optimization
- Optimization of catalyst coated membrane assemblies and GDL's
- Short stack testing

Work Plan Summary (continued)

Task 2 focuses on development of very high temperature PEM membranes that do not rely on water for H^+ transport, stable catalysts and supports with matching gas diffusion and flow field components to take the MEA into an operating range of $120 < T < 150°C$ and nearly dry operation.

Subtasks include:

- Development of a high temperature electrolyte membrane and appropriate catalysts;
- Optimization of the catalyst membrane interfaces;
- Advanced materials characterization and modeling with subcontractors; and
- Short stack testing

Task 3 is directed at the scale-up and optimization of MEA component fabrication processes amenable to high volume, high quality, low cost production for selected components from Tasks 1 or 2.

Subtasks include:

- Scale-up and optimization of the fabrication processes for membrane, catalyst, CCM, GDL
- MEA's characterized in full-scale short stacks.

Relevance to Overall DOE Objectives, Technical Challenges, Commercialization Barriers

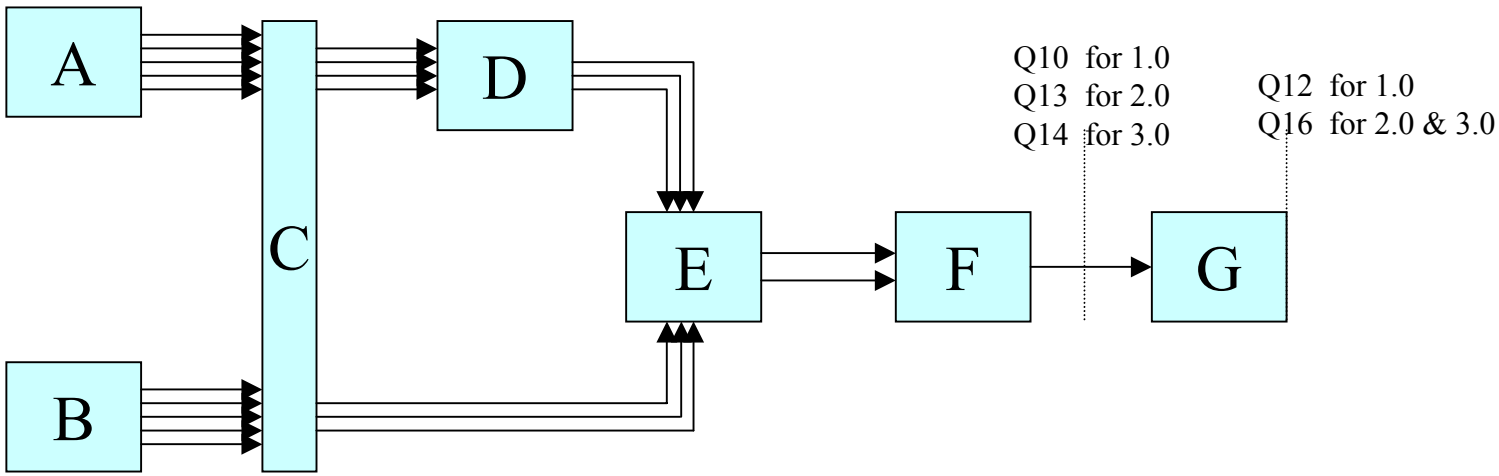
Transportation and/or Stationary Issue:	Contributing Solution from 3M Approach
Thermal management, size and weight	Higher T(C) operation giving - more effective heat transfer - smaller radiators, condensers, coolant flow rates
Water management	Sub-saturation operation for T < 120ºC Dry operation for T > 120ºC
Lower cost	Less precious metal catalysts Lower cost membrane and GDL materials High volume manufacturable MEA's Simpler balance of plant from high T(C) and reduced humidification requirements
High volume capacity	Roll-good manufactured MEA components

Relevance to Overall DOE objectives, Technical Challenges, Commercialization Barriers

Transportation / Stationary Issue:	Contributing Solution from 3M Approach
Durability	Improved membrane durability (lower F^- at T < 120ºC) More stable catalysts (less loss of catalyst performance, surface area) More oxidation-stable catalyst supports Optimized electrode structures (uniformity of current density) Flow field/GDL optimized for uniformity of mass flow Integrated MEA seals/gaskets
Impurity tolerance	High temperature operation
Efficiency	Higher activity cathode catalysts, i.e. higher operational voltage Higher performance from matched component MEA's Reduced balance of plant parasitic power loss from - flow field/GDL optimized for lower stoichiometric flow - improved thermal management

Approach - General

MEA and Component Development Path



A = PEM new materials
B = Catalyst new materials
C = Critical property measurements of new materials
D = Membrane formation, treatment methods
E = CCM/MEA fabrication with integrated components and fuel cell screening
F = Full high temperature testing of selected MEA's w/comprehensive diagnostics
G = Stack development and testing

Approach – A: New PEM Materials, 85ºC < T < 120ºC

* Based on 3M's non-Nafion perfluorinated sulfonic acid ionomeric membranes
  - less fluoride generation than Nafion
  - longer lifetimes in accelerated durability testing than Nafion
  - improved mechanical properties
  - existing scaled-up processing

* Incorporation of functionalized additives to 3M membrane:
  - facilitate peroxide decomposition for better oxidative stability
  - enhance water retention for higher conductivity under low humidification
  - powders, nanoparticles, polyoximetallates, sol-gels, acid modification

Target: Develop an advanced membrane which can operate stably for > 2000 hours under sub-saturation at 85 < T< 120ºC and provide excellent catalyst interfacial kinetics.

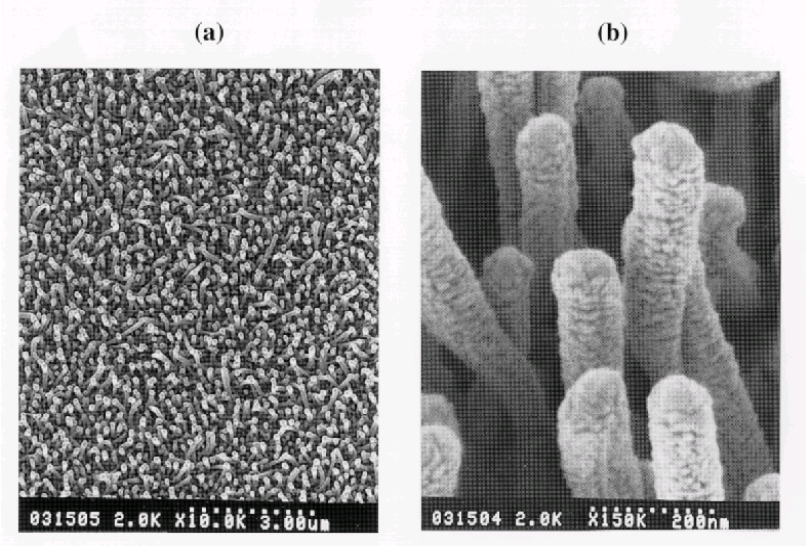
Approach – A: New PEM Materials, T > 120ºC

* Replace liquid water as the proton conductor
  - 3M fluorinated liquids as proton conducting components
  - inorganic proton conductors
* Incorporation into polymer matrices
  - casting mixed dispersions of polymer with dispersions of the inorganic, or
  - *in situ* synthesis of the inorganic phase in the polymer film
  - incorporation into microporous media
* New polymer matrices
  - acid functional polymer, such as 3M ionomer, or
  - non acid containing polymer (such as PBI)
  - incorporation of inorganics or fluorinated liquids
  - microporous film technology

Target: Develop an advanced membrane which can operate stably for > 2000 hours under dry conditions at 120 < T< 150ºC and provide good catalyst interfacial kinetics.

Approach – B: New Catalysts

* **Extension of 3M nanostructured thin film multi-element catalyst development: PtABC**
  - Unique electronic features, increased surface area,
  - catalyst specific activity is 2x pure Pt
  - roll-good processing established
  - enhanced oxidative stability of support whiskers



Pt coated nanostructured whisker supports (0.25 mg/cm^2), at 10,000 X plan view (left) and 150,000 X 45° view (right).

* **Combinatorial approach (w/ Dalhousie U.)**
  - same catalyst deposition processes employed
  - wide latitude of PtAB material compositions over 50-cm^2 areas
  - full materials fabrication and spatial characterization (XRD, e-µProbe)
  - novel 3M combinatorial screening methods for catalyst activity
  - most promising combinations reproduced for fuel cell evaluations

* **Conventional dispersed catalysts**
  - improved oxidatively stable carbon supports

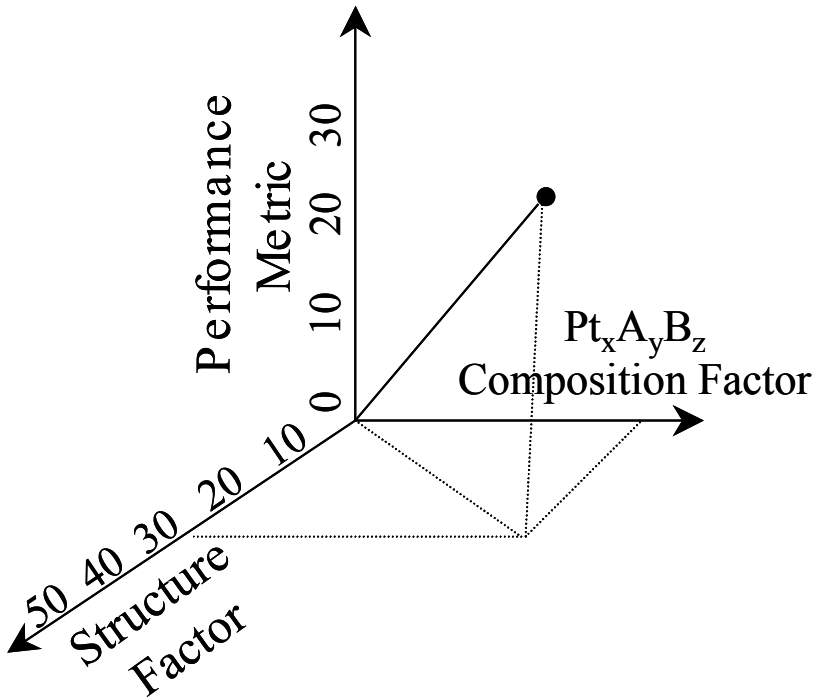
Approach – B: New Catalysts

Material Variation :
- PtCB,
- PtDB,
- PtABC, and
- relative amount of element B.

Structural Variation:
- atomic element ratios,
- physical structure, process conditions
- surface finish

Fabrication methods:
- roll-good based
- high volume manufacturability

Exploration Grid for PtAB Ternary Catalysts

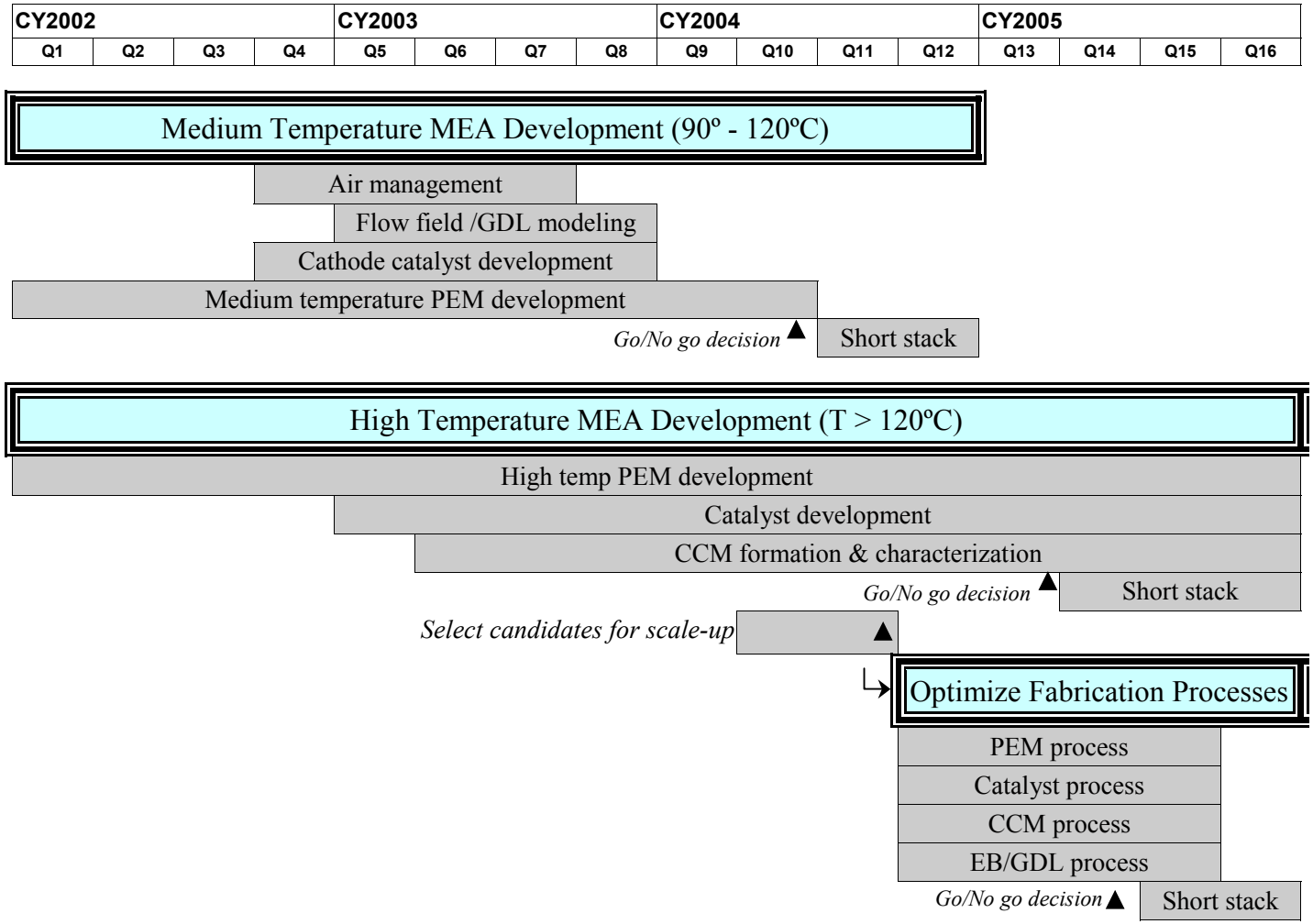


Target: Develop cathode catalysts/supports requiring < 0.6 g of precious metal catalysts total per rated kW, and which are stable under enhanced operating conditions for > 2000 hours.

Approach – C: Critical Property Measurements

- **PEM, Ionomer Conductivity**
  - In-plane 4 point probe
    EIS up to 80ºC, 20 % to 95% RH or up to 200ºC, dry, ambient pressure.
  - Through-plane 5-cm^2 fuel cell
    EIS, DC (H_2/H_2) up to 200ºC, 0% to 100% RH, up to 60 psig.
  - DC conductivity – H^+ versus ionic
- **Permeability**
  - H_2O- "cup test" or fuel cell.
  - H_2- crossover (cyclic voltammetry).
  - O_2 – fuel cell test under development.
- **Chemical Stability**
  - Water boil – leachable components
  - Peroxide boil – 50 ppm Fe
  - Fluoride ion generation
- **Water Absorption**
- **PEM Physical/Mechanical Properties**
  - Puncture resistance
  - Tensile, Creep (controlled RH up to 90ºC, dry up to 150ºC)
- **Catalyst Properties**
  - Electrochemical surface area
  - Specific activity
  - PtA_xB_y composition
  - PtA_xB_y structure
  - Loadings
- **Fuel Cell Characterization**
  - Continuous H-pump
  - Fourier Transform Electrochemical Impedance Spectroscopy under load
  - Tafel plots for catalyst activity
  - Standard polarization type scanning

Timeline


CY2002
CY2003
CY2004
CY2005
Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q8 Q9 Q10 Q11 Q12 Q13 Q14 Q15 Q16
Medium Temperature MEA Development (90º - 120ºC)
Air management
Flow field /GDL modeling
Cathode catalyst development
Medium temperature PEM development
Go/No go decision
Short stack
High Temperature MEA Development (T > 120ºC)
High temp PEM development
Catalyst development
CCM formation & characterization
Go/No go decision
Short stack
Select candidates for scale-up
Optimize Fabrication Processes
PEM process
Catalyst process
CCM process
EB/GDL process
Go/No go decision
Short stack

Accomplishments – Membranes, 85 < T < 120ºC

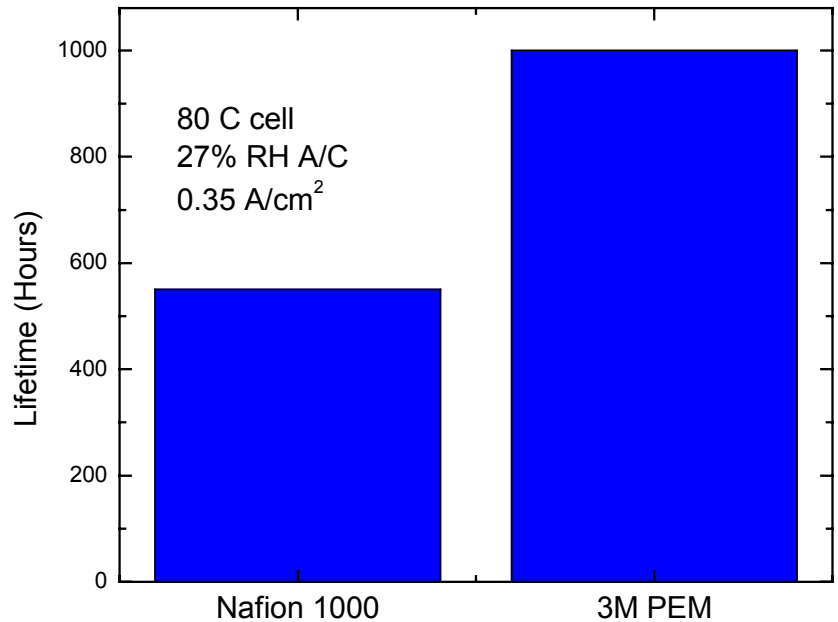
3M's non-Nafion perfluorinated sulfonic acid ionomeric membrane shows reduced F^- ion generation and longer lifetime under accelerated testing:

* 80% lifetime increase for 30 µm membrane at 80ºC, 60%/60% RH

* 5 to 10 fold decrease in F^- ion in effluent under several temperatures (up to 120ºC) and different operating conditions

* Improved mechanical properties

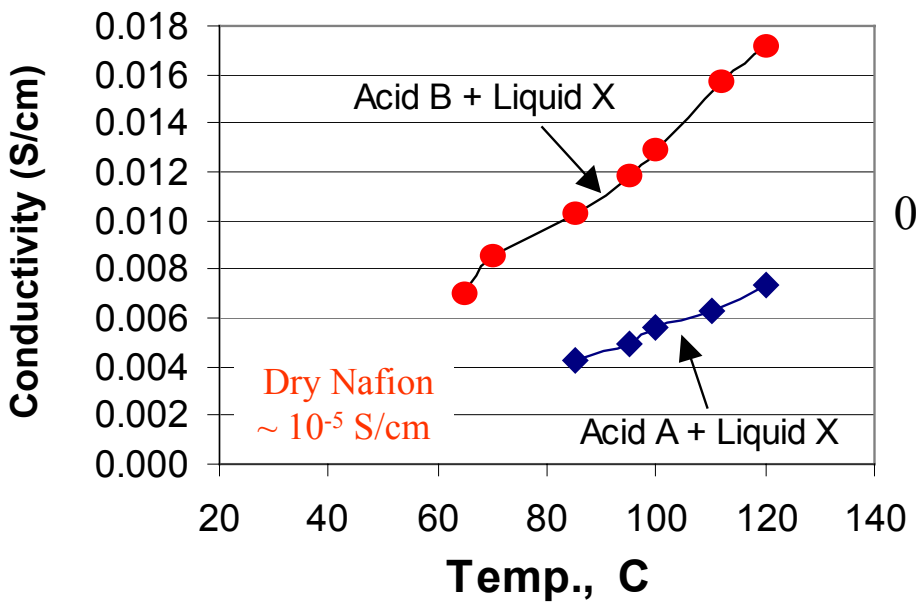
Incorporation of functionalized additives to the 3M membrane should further enhance these properties.



Accomplishments – Membranes, 120 < T < 150ºC

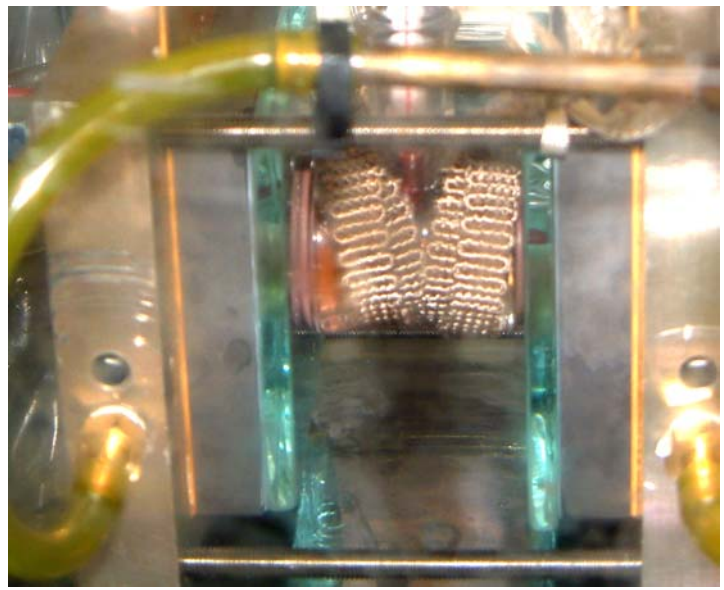
* Technique developed to measure the proton conductivity of ionic liquids and acids:
  - in addition to ionic conductivity from AC impedance
  - a "liquid H-pump" technique
* 3M proprietary perfluorinated acids plus liquid additives show proton conductivities with 0 mole % water strongly dependent on acid type and temperature.

Proton Conductivity of Acids + Liquids as a Function of Temperature under H_2



0 % H_2O

Liquid, Proton Conductivity Cell

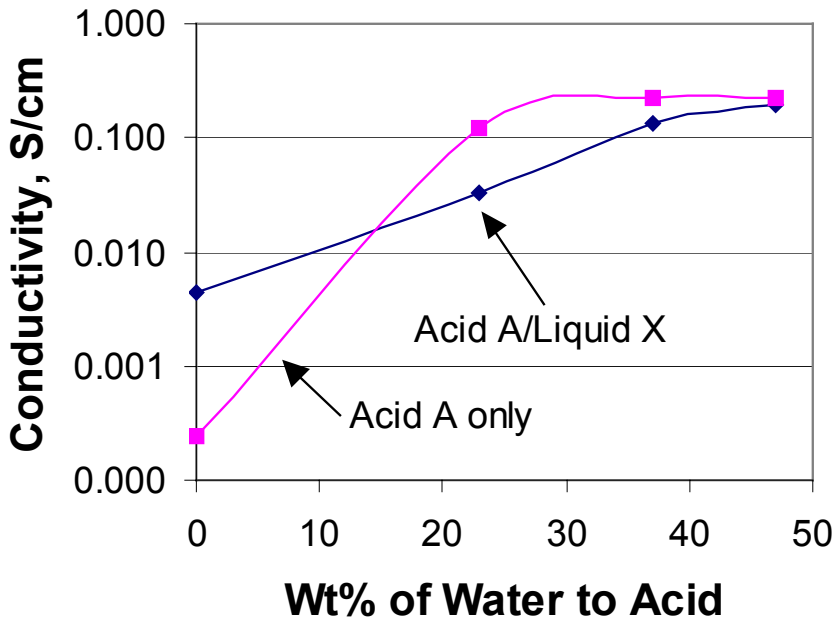


Accomplishments – Membranes, 120 < T < 150°C)

* With very small weight % of water, the combined acid A and liquid additive show significant increase in proton conductivity.

* Acid B plus Liquid X to be measured yet. Could increase proton conductivity to target range of 0.025 to 0.1 S/cm.

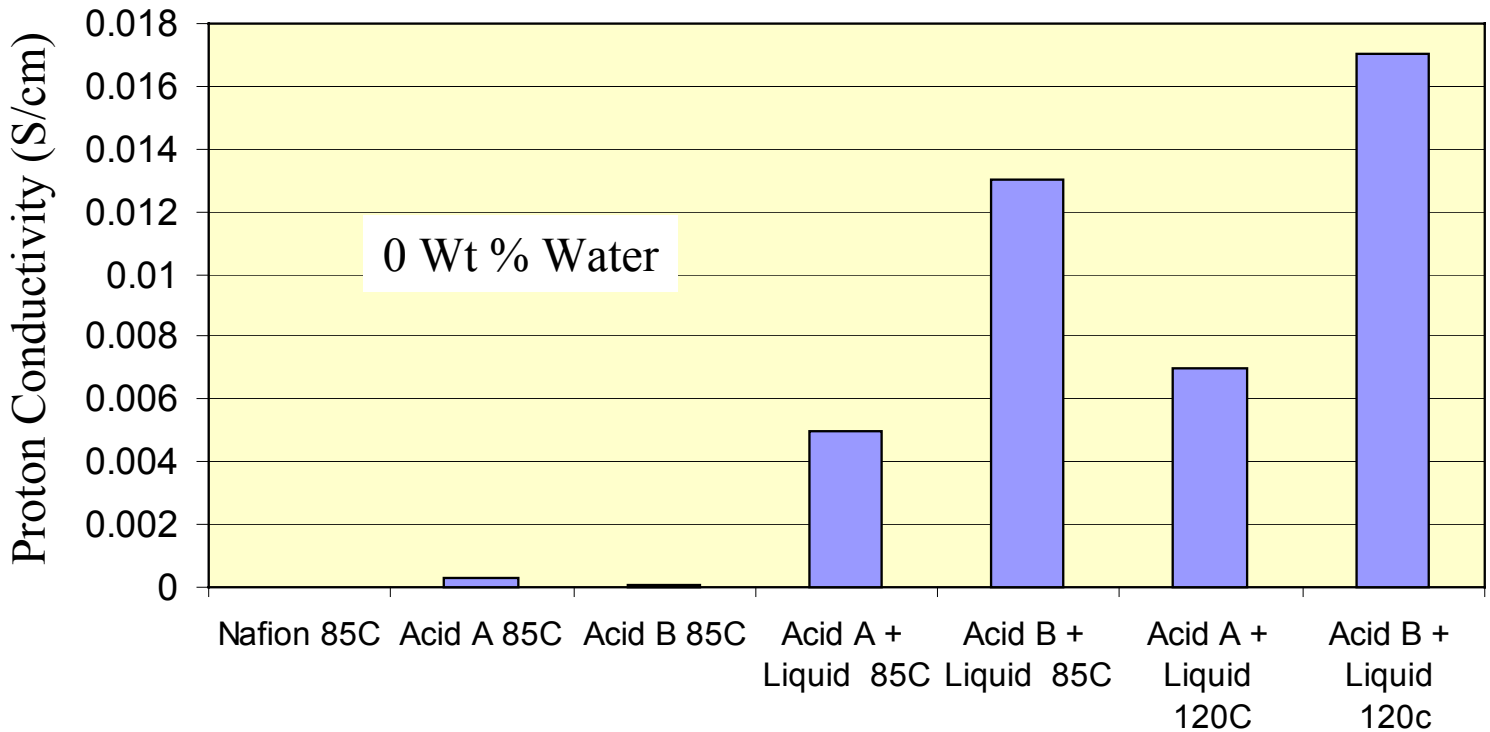
Proton Conductivity of Acid A vs. Acid A / Liquid X as a function of water conc. at 70°C / H_2



Accomplishments – Membranes, 120 < T < 150ºC

* DC method of proton conductivity in liquid form of mixed proprietary 3M perfluorinated acids and liquids

* Liquid mixtures show increased proton conductivity over anhydrous acids by factors of 100-1000 times with no added water.



Accomplishments – Advanced Cathode Catalysts - Background

Previous 3M/DOE Contract (12/02): Final stack testing of 3M roll-good fabricated MEA's with 3M nanostructured thin film catalysts:

*** Utilized roll-good fabricated Nano-MEA's with ~ 0.34 mg Pt/cm^2 total.**
*** 14 cells, 200 cm^2**

*** Demonstrated operation at automotive conditions for H_2/air):**

- within 11 mV of target of 680 mV at 0.8 A/cm^2
- pressurized per automotive compressor curve
- sub-saturation (dry cathode) operation
- excellent cell-to-cell uniformity (23 mV spread, 6 mV std. dev. @ 1 A/cm^2
- excellent fuel and air utilization (max of 95% H_2 and 77% air at 0 psig)
- 400 hours of operation with no substantial change in performance

*** Exceeded peak power design specifications:**

- Obtained - 1.9 kWe + 2.25 kW heat at 62% air utilization
- Targeted - 1.4 kWe + 1.9 kW heat at 45% air utilization

*** 0.34 mg Pt/cm^2 and 1.9 kW meets DOE 2005 target of 0.6 g Pt/peak kW**

Accomplishments – Advanced Cathode Catalysts

* 46 PtM_1M_2 ternary catalyst compositions and structures fabricated and evaluated
  - All have constant loading of Pt of 0.1 mg/cm^2
* High pressure oxygen performance (Tafel) metric
  - Most ternaries are significantly better than the Pt control
  - Improvements over PtAB used in previous 3M/DOE contract.

Mixed Metal Catalysts Evaluated

Previous 3M/Contract :

PtM binaries – numerous

PtAB – 16 compositions/structures

This contract to date :

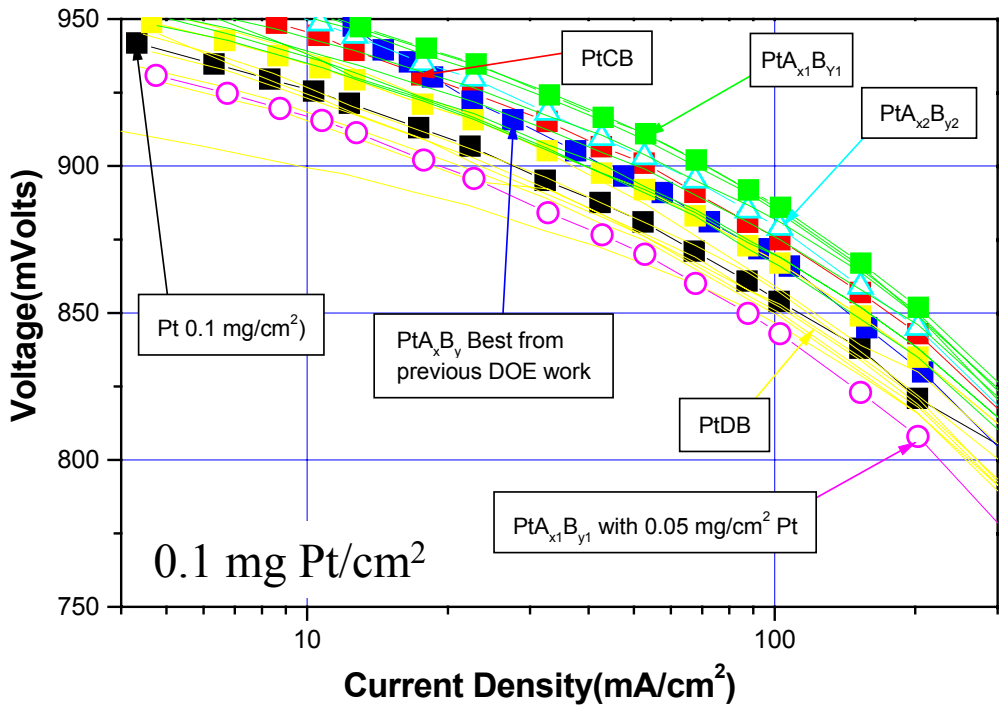
PtDB – 10

PtCB – 12

$PtAx_1By_1$ – 12

$PtAx_2By_2$ – 10

O_2 Metric: 75C, 200% RH, 30 psig H_2/O_2, 1200/600 sccm



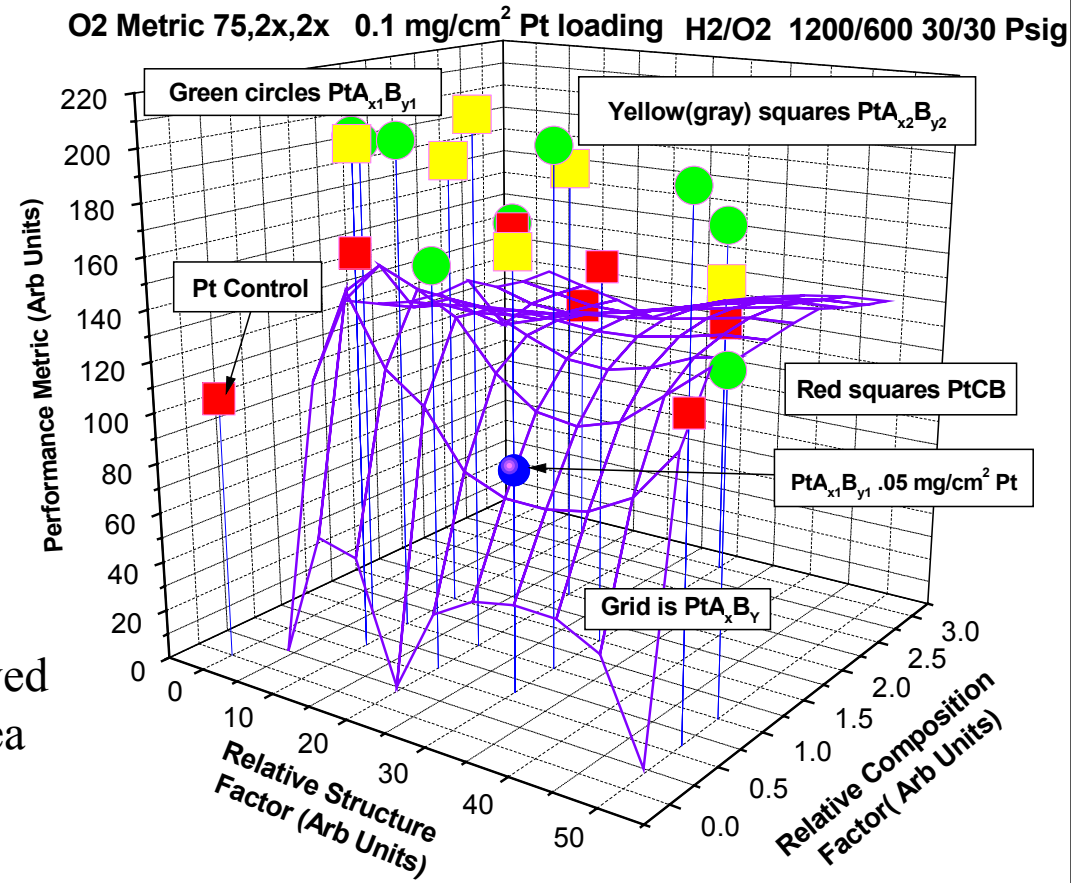
Accomplishments - Advanced Cathode Catalysts

Comparison of activities of $PtA_{x1}B_{y1}$ and PtC_xB_y ternaries against the grid of original PtA_xB_y (previous 3M/DOE contract) ternary samples.

* 3M process controls the relative metallic composition and structure of the catalysts

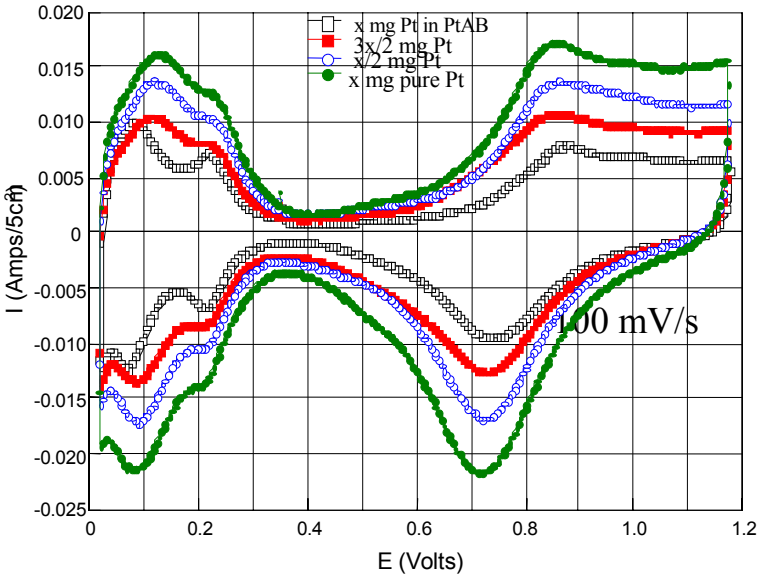
* Catalyst performance depends on the composition and structure factors

* Ternary compositions give improved performance from both surface area increases and electronic effects

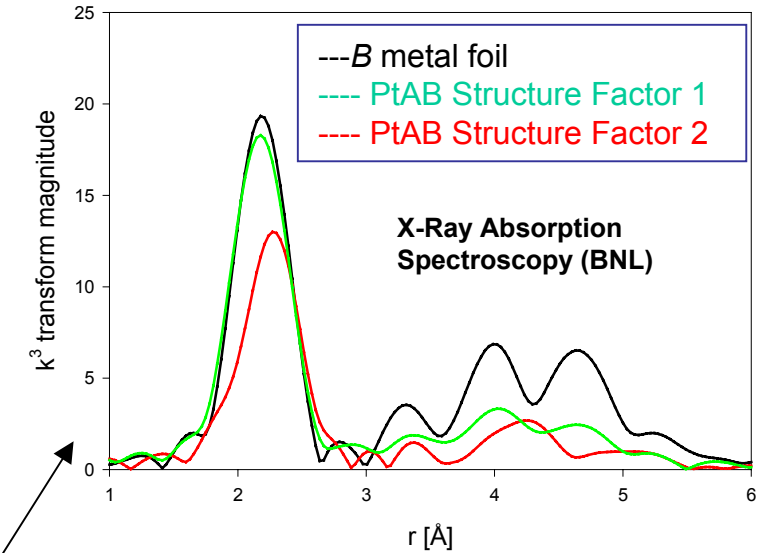


Accomplishments – Advanced Cathode Catalysts – Fundamental Properties

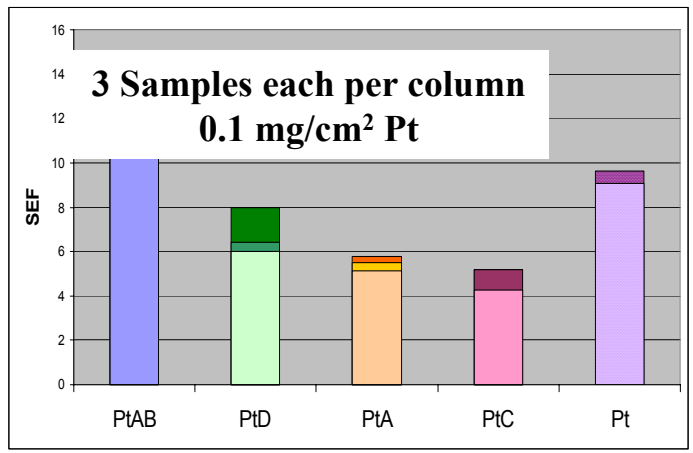
- Enhanced surface area as measured by Hydrogen adsorption over pure Pt or Pt binary catalysts.
- A shift of ~30 mV of the weakly adsorbed H compared to pure Pt.
- Local atomic environment by XAS of the noble and non-noble components depends on structure factor.



Cyclic voltammograms of Pt and PtAB show a 30 mV shift of weakly adsorbed H on PtAB, indicating a stronger adsorption than on pure Pt, => electronic structure effects.



Fourier transform at *B*-edge. The number of nearest non-Pt neighboring atoms to Pt changes from 3.5 to 6.3 in going from the Structure Factor 1 to 2.



Electrochemical surface area enhancement factor (SEF) is higher for the ternary catalyst over pure Pt and various binaries compared to Pt.

Accomplishments - Advanced Cathode Catalyst Support Stability

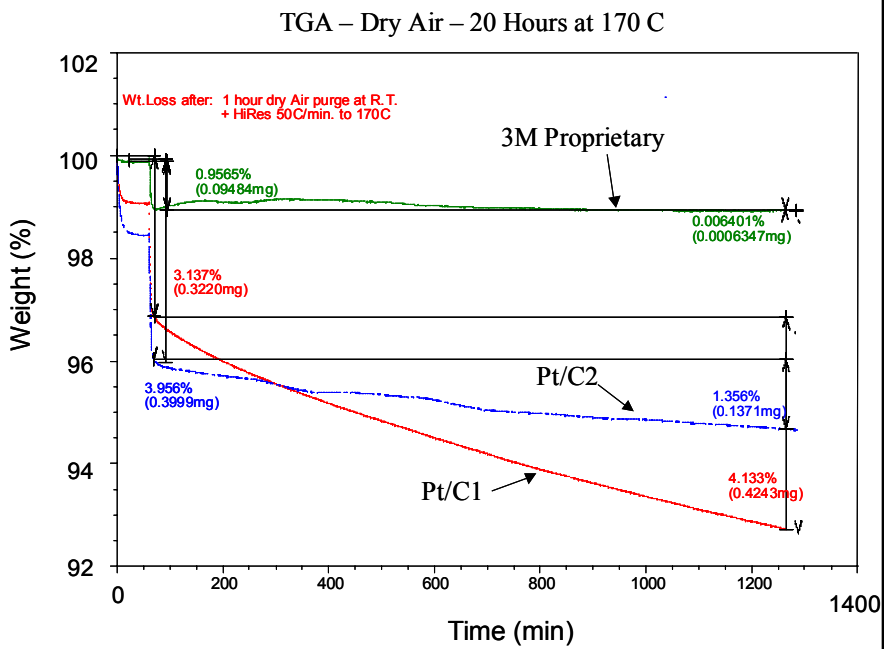
* Oxidative chemical stability of 3M proprietary catalysts and supports are much improved over commercial carbon black supported Pt catalysts.

* Highly sensitive TGA weight-loss profiles over 20 hrs at 170ºC air
  Corrected for water desorption mass loss
  Mass loss of two Pt/C commercial catalysts vs
  3M proprietary catalyst and support system

Pt/C1: wt % loss = 4.133 %
Pt/C2: wt % loss = 1.356 %
versus
3M catalyst/support: wt % loss = 0.0064%

* 3M catalyst support appears more stable for hot (120 - 150ºC), dry operating conditions

* Fuel cell tests at 120 ºC show no loss in surface area over 90 hours of test.



Subcontractors and National Laboratory Interactions

Advanced Catalysts: Fundamental Understanding and Characterization

- **U. of Illinois, Urbana (A. Wieckowski) - Subcontractor**
  Use electrochemical, isotope labeling, NMR and infrared spectroscopy
- **Brookhaven National Laboratories (J. McBreen)**
  EXAFS, XANES characterization of 3M PtAB catalysts
- **Lawrence Berkeley National Labs (P. Ross, N. Markovic)**
  Catalyst-anion interaction effects

Advanced Catalysts: Combinatorial Fabrication

- **Dalhousie University (J. Dahn) – Subcontractor**
  Utilize existing combinatorial materials science capability at Dalhousie University to produce and characterize a wide spectrum of ternary metals for use as electrocatalysts.

Advanced Membranes: Fundamentals

- **U. of Minnesota (W. Halley) – Subcontractor**
  Theory and simulation studies for non-aqueous membrane based proton conduction
- **CWRU (T. Zawodinski) – Subcontract being established**
  Fundamental experimental studies of proton transport in liquid and solid proton conductors

MEA Modeling:

- U. of Miami (H. Liu) - Subcontractor

Extend existing 3M/U. of Miami developed MEA model to determine electrode, gas diffusion and flow field properties required for durable operation under enhanced operating conditions.

Air Management:

- Vairex, Inc. – Subcontractor

Understanding and development of an air management system designed for optimized performance of MEA's operating under hot, dry conditions.

Plans and Future Milestones (through 2003)

* Continue to execute the current plans for Tasks 1, 2 and 3 as discussed;
  - continue materials development and screening
  - incorporate into integrated catalyst coated membranes
  - robust fuel cell testing and evaluation
  - optimization of gas diffusion layers, flow fields and operating conditions

* Accelerate interactions with subcontractors

POWERING A CLEANER FUTURE

R&D on an Ultra-Thin Composite Membrane for High-Temperature Operation in PEMFCs

Chao-Yi Yuh

(DE-FC02-99EE27567)

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley, CA
May 19-22, 2003

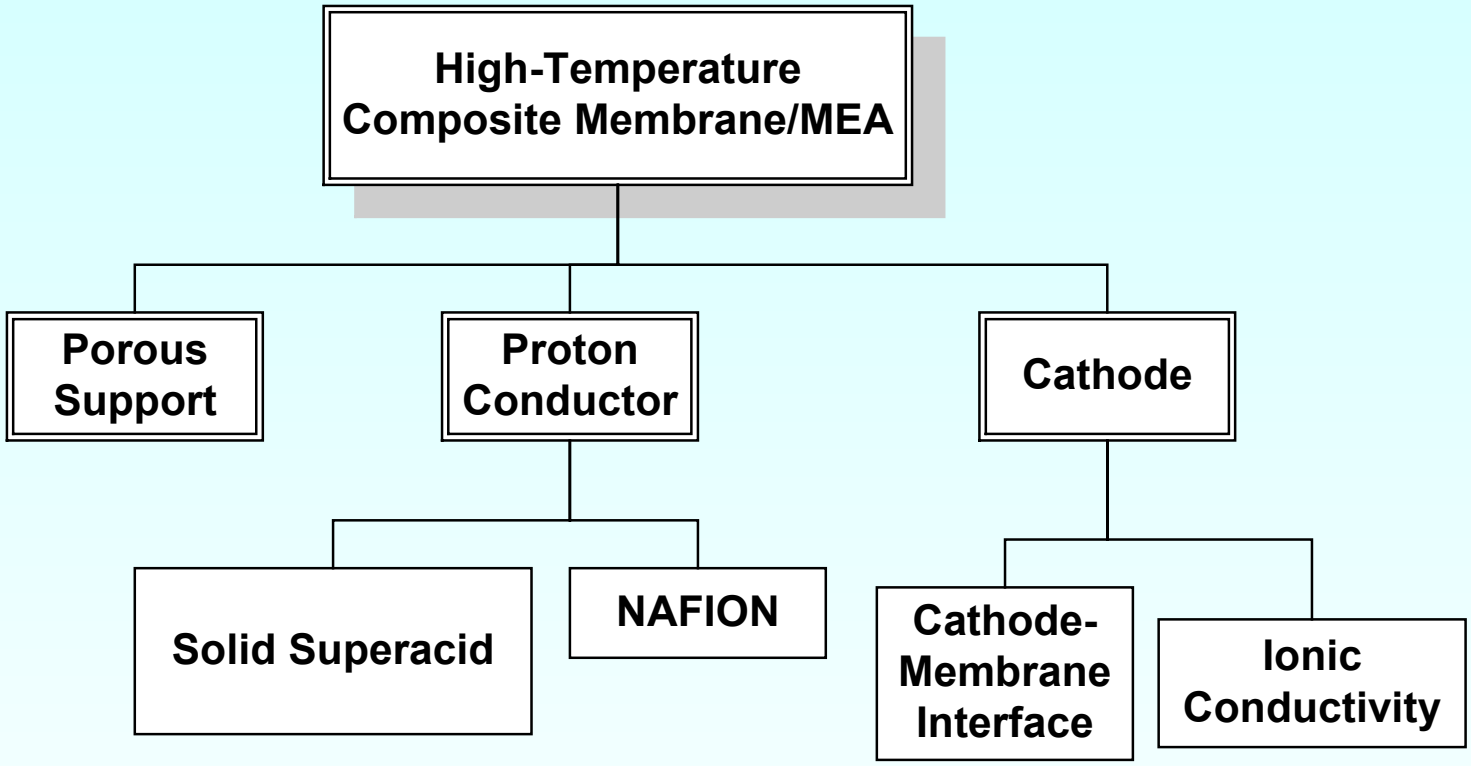
FuelCell Energy

HIGH-TEMPERATURE MEA (STATIONARY SYSTEM)

- **Advantages:**
  - Easier CO Management
  - Accelerated Electrochemical Reaction Kinetics
  - Easier Water & Thermal Managements
- **Issues:**
  - Dehydration
    - Ohmic Resistance Increase (Membrane and Electrode)
    - Electrode Polarization Increase (Slower ORR)
    - Reduced durability
- **DOE Ultimate Goal:**
  - >100°C (120-150°C) Membrane
  - 0.32 W/cm^2 at 0.8V (at 400mA/cm^2)
  - Membrane ASR <100 mΩ•cm^2; < 1% Cross-Over
  - Atmospheric Pressure Operation
  - >40,000h Life and <$1500/kW System Cost

FuelCell Energy

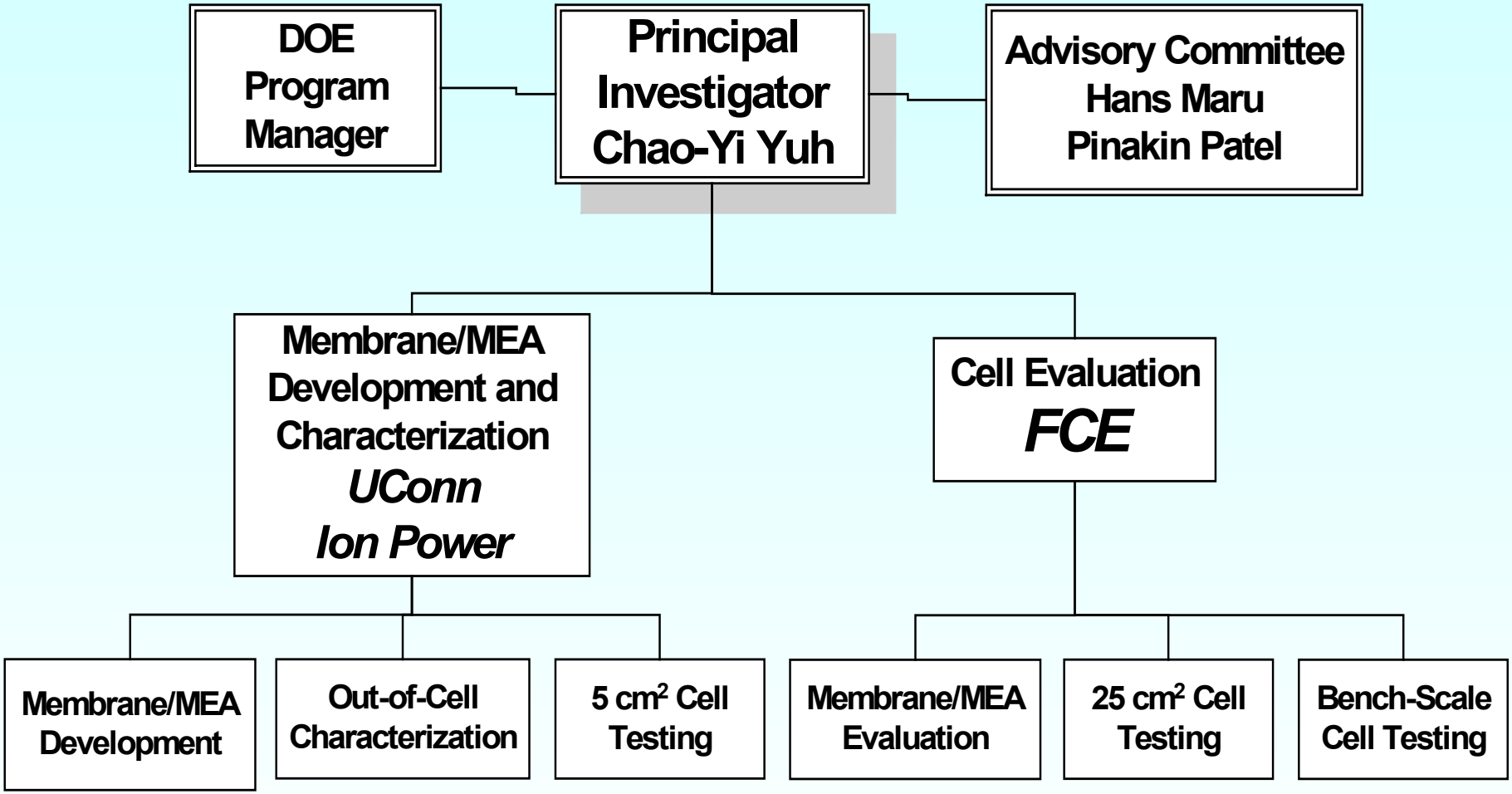
MEMBRANE/MEA TECHNICAL APPROACHES



GOAL: ULTRA-THIN, DURABLE, >100°C HIGH-TEMPERATURE COMPOSITE MEMBRANE/MEA

FuelCell Energy

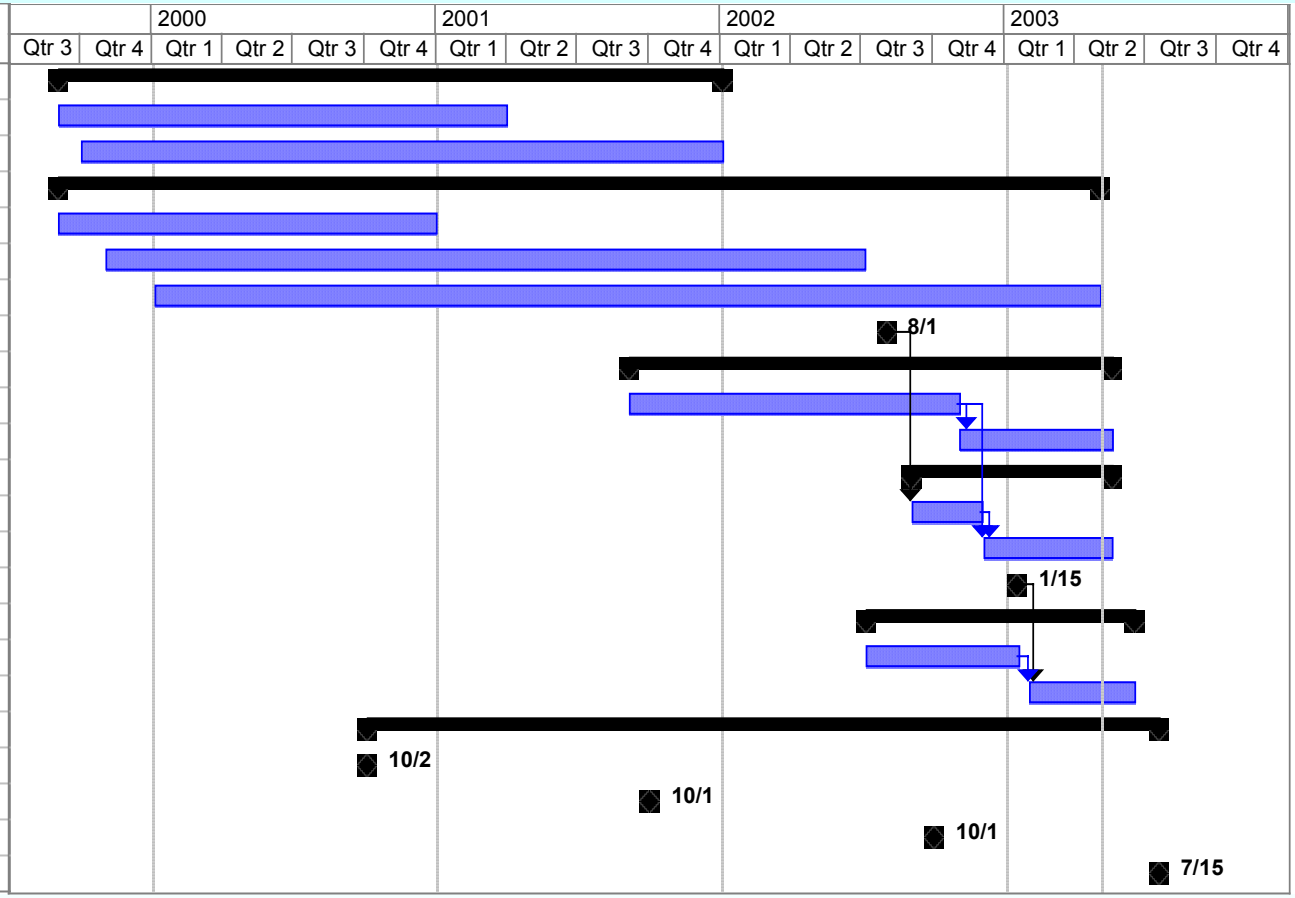
PROJECT ORGANIZATION



FuelCell Energy

Project Schedule

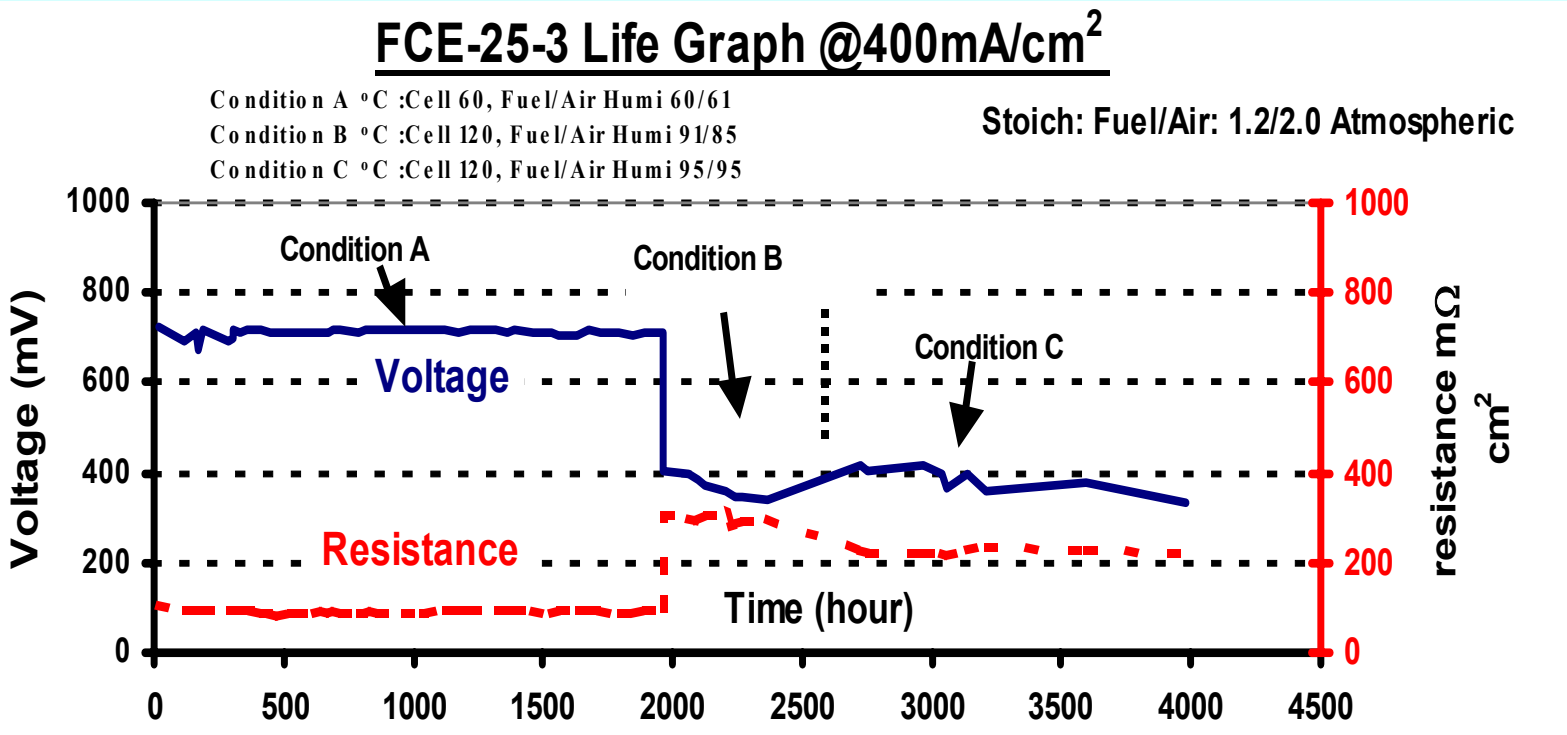
ID	Task Name
1	**1. Membrane Development**
2	Composite Membrane Development
3	Membrane Characterization
4	**2. MEA Development**
5	Commercial MEA performance/endurance
6	MEA development
7	Lab-scale cell testing
8	Achieve 600mV 120C performance
9	**3. Fabrication of Bench-scale Membrane**
10	Membrane scale-up to 300cm2
11	Membrane Fabrication
12	**4. Fabrication of Bench-scale MEA**
13	MEA scale-up to 300cm2
14	300cm2 MEA fabrication
15	300cm2 MEA for cell testing
16	**5. Bench-scale Cell Testing**
17	Bench-scale cell design and fabrication
18	Bench-scale cell testing
19	**6. Analysis and Reporting**
20	2000 Annual Report
21	2001 Annual Report
22	2002 Auunal Report
23	Final Report



The Program to Be Completed in June, 2003

FuelCell Energy

BASELINE NAFION MEA WITH 25μm MEMBRANE

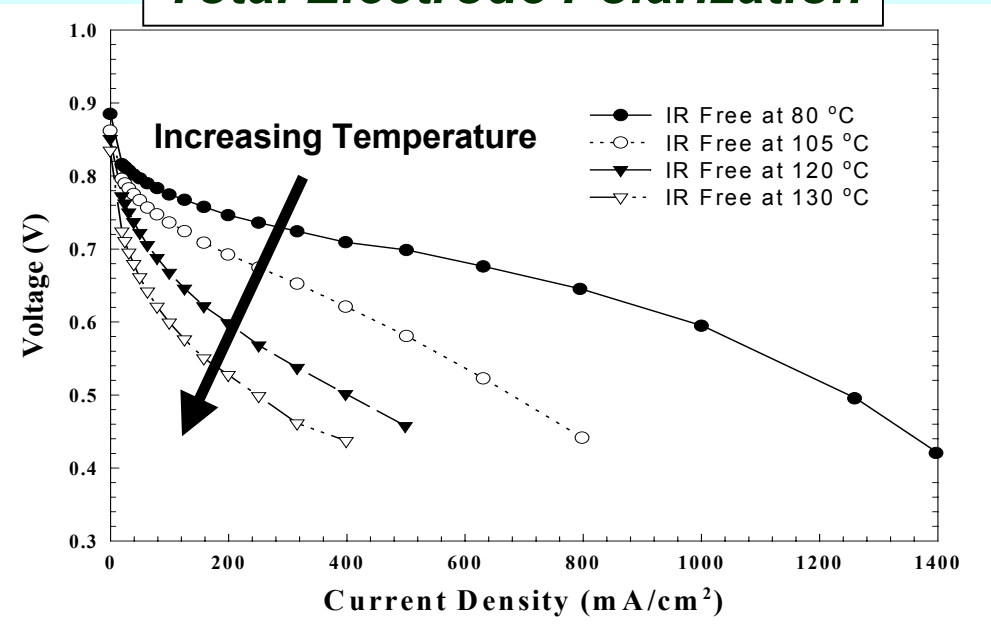


- Stable > 700mV Performance at 60°C for 2,000 Hours
- Significant Performance Loss and decay at 120°C
  - >300 mV Additional Loss (40-80mV Ohmic, >250mV Electrode Polarization); Steady Membrane Ohmic Loss

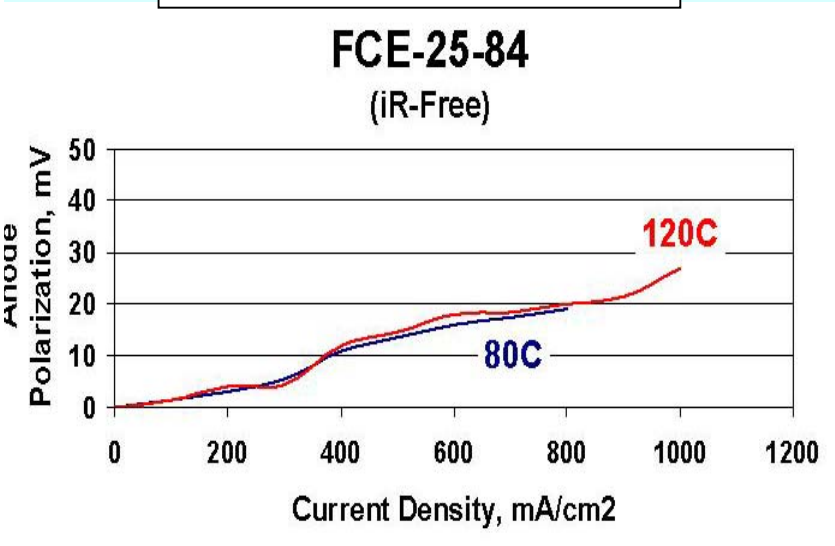
FuelCell Energy

ELECTRODE POLARIZATION

Total Electrode Polarization



Anode Polarization



- **Total Electrode Polarization Increases Significantly with Temperature, but Negligible Anode Polarization Increase**
- **Majority (>60%) of Cell Performance Loss Attributed to Cathode ⇒ *High-Temperature Cathode Needed***

FuelCell Energy

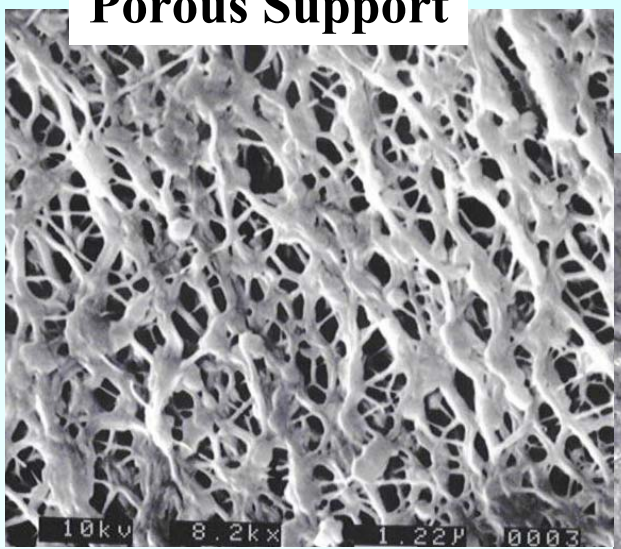
COMPOSITE MEA AND TEST CONDITIONS

- 25cm^2 Cell Area
- Pt Loading (0.4 mg/cm^2 Each Electrode)
- Ultra-Thin Membrane (<25μm)
- High-Temperature Proton Conducting Additives: in Membrane and/or Cathode
  - Phosphotungstic Acid (PTA), Zeolite, Nano sulfated Oxide, Zirconium Hydrogen Phosphate (ZHP)
  - Low EW Ionomer
- Atmospheric Pressure, 60-120°C
- Neat H_2 Fuel, 1.2 Stoich; Air Oxidant, 2.0 Stoich
- Humidification:
  - Cell 60, 80°C: 100% R.H.
  - Cell 120°C: R.H.<40% (90-95°C Humidification)

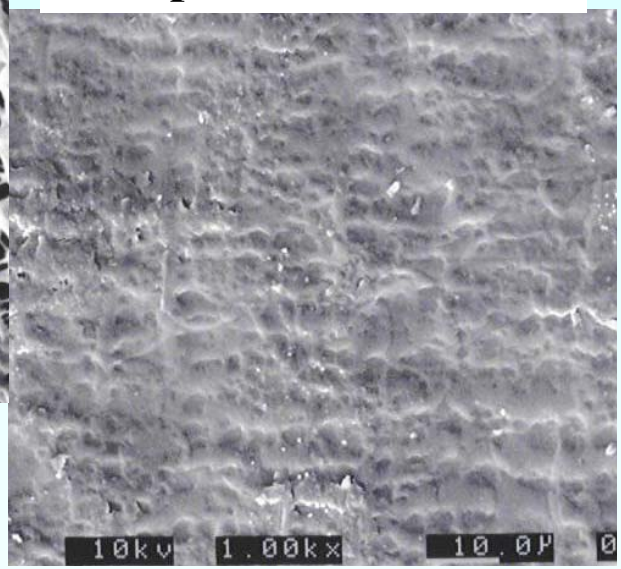
FuelCell Energy

COMPOSITE MEMBRANE/MEA FABRICATED

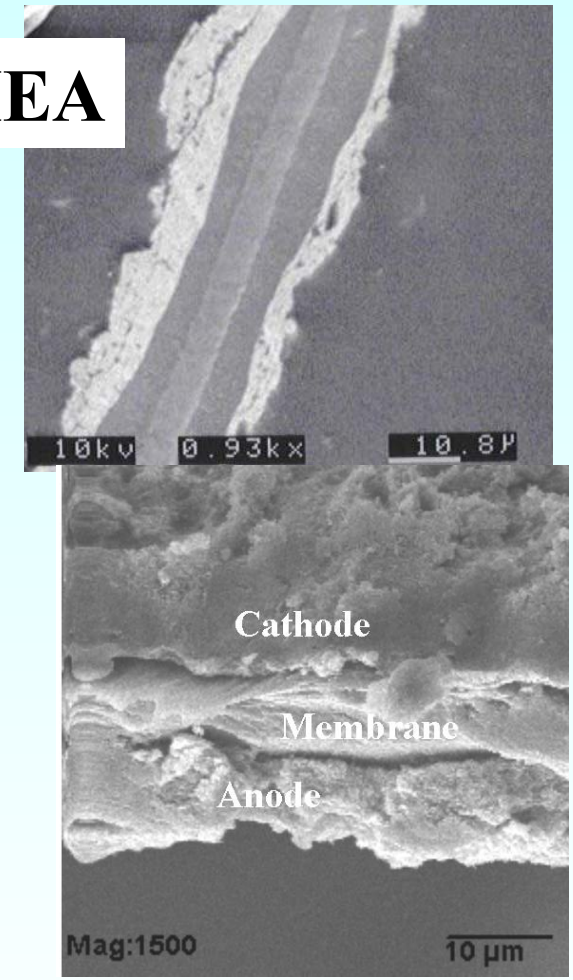
Porous Support



Composite Membrane



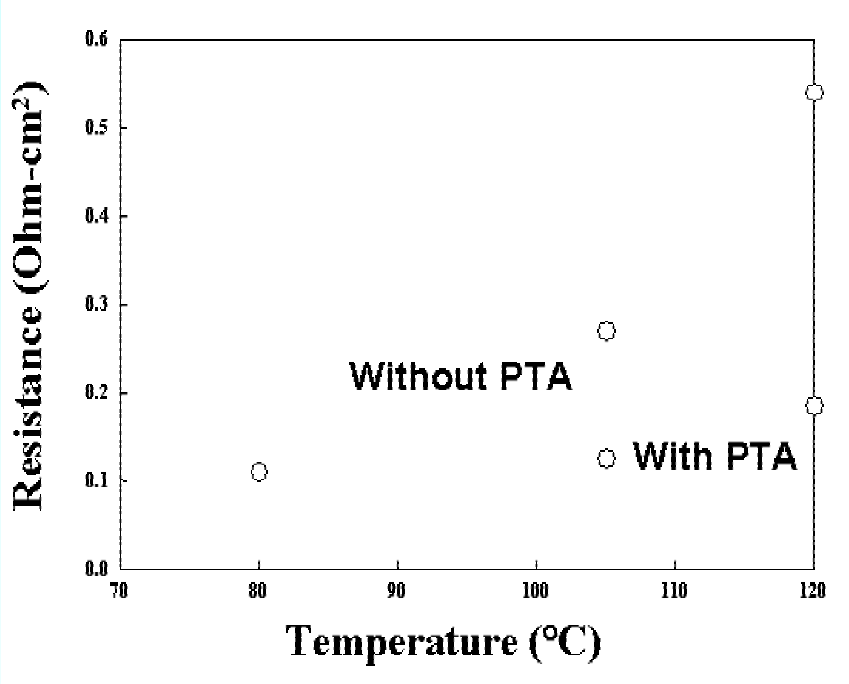
MEA

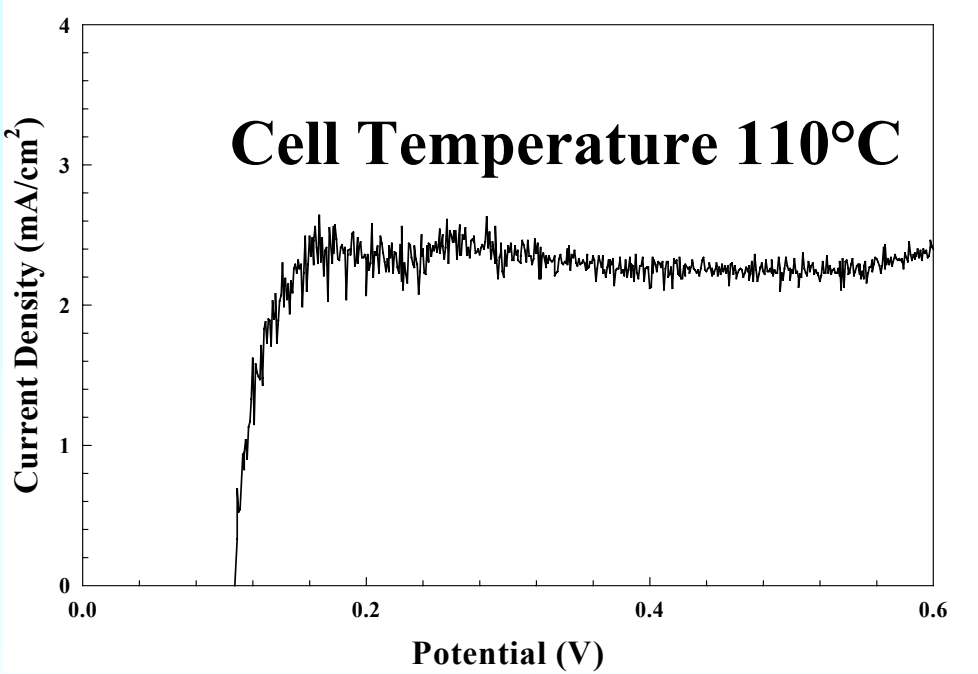


- Pore-free membrane/MEA successfully fabricated

FuelCell Energy

PTA IMPREGNATION IN SUPPORTED NAFION MEMBRANE



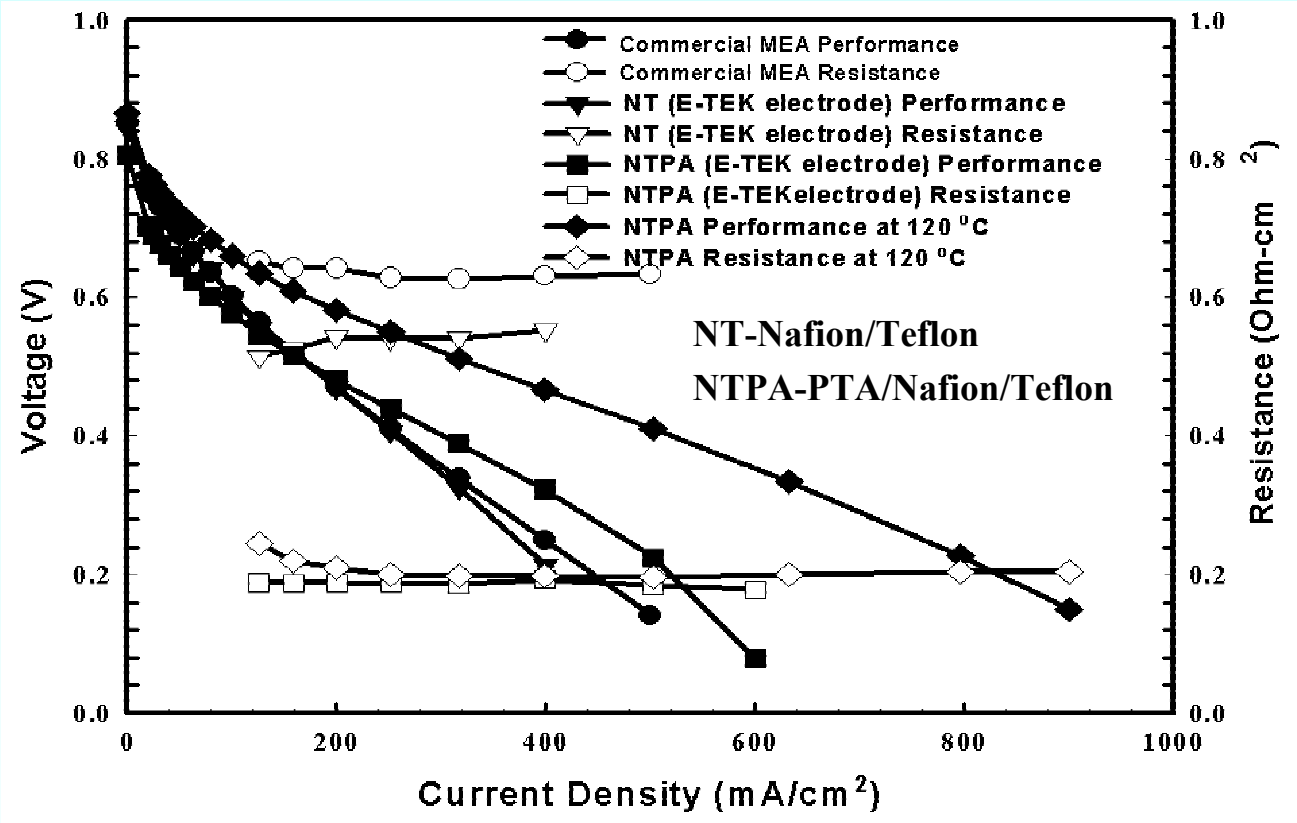


PTA Impregnation Reduces Ohmic Resistance Significantly at 120°C; However, Resistance Still Higher Than Well-Humidified Nafion® at 80°C

Low Membrane Cross-Over Achieved

FuelCell Energy

Improvements Achieved to 2001

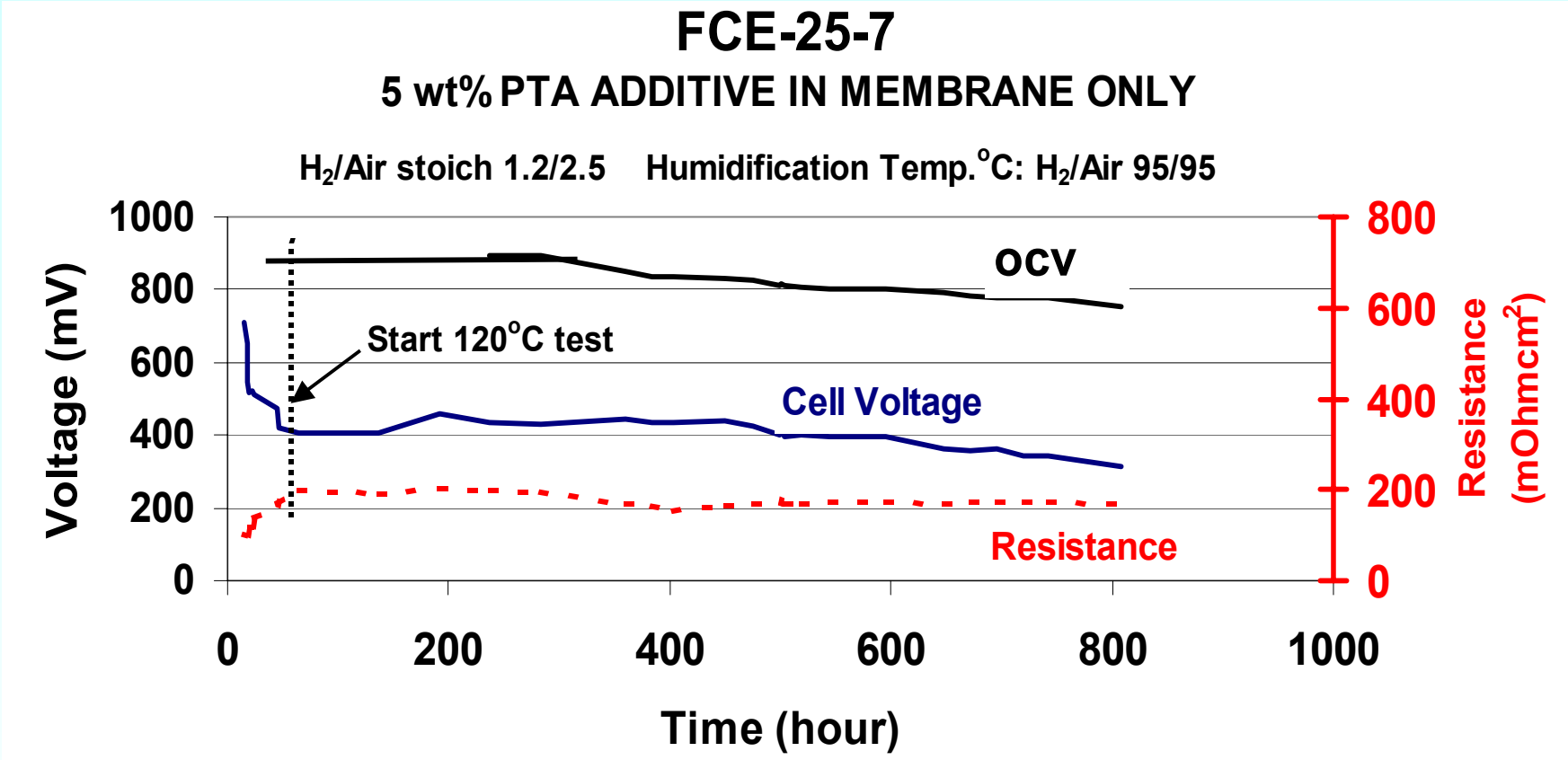


0

- **ACHIEVED SIGNIFICANT RESISTANCE REDUCTION AND PERFORMANCE INCREASE**

FuelCell Energy

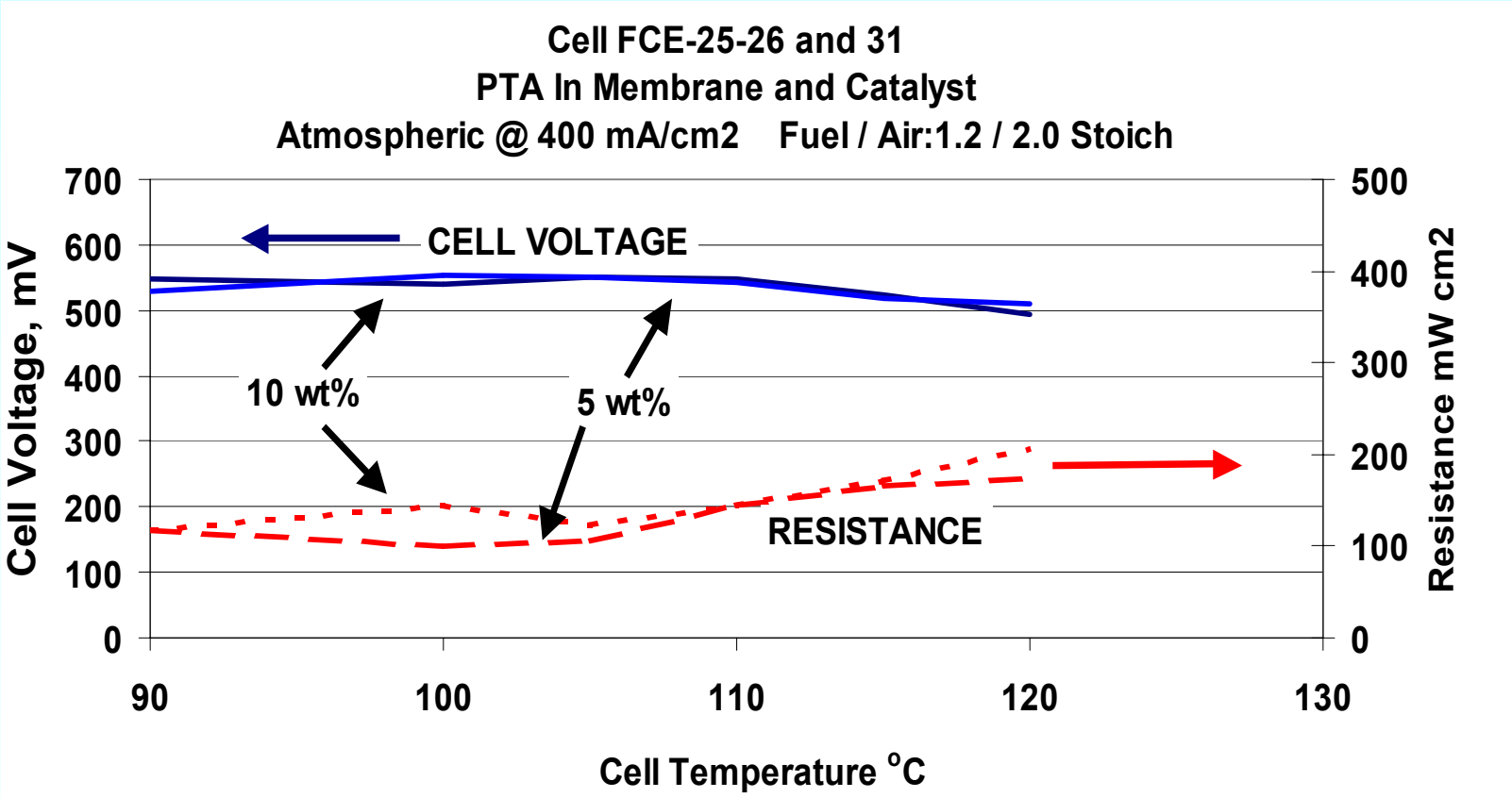
120°C ENDURANCE OF PTA MEA



- ~400mV 120°C Performance (at 400mA/cm^2)
- Cell Voltage Decay due to Membrane Cross-Over increase

FuelCell Energy

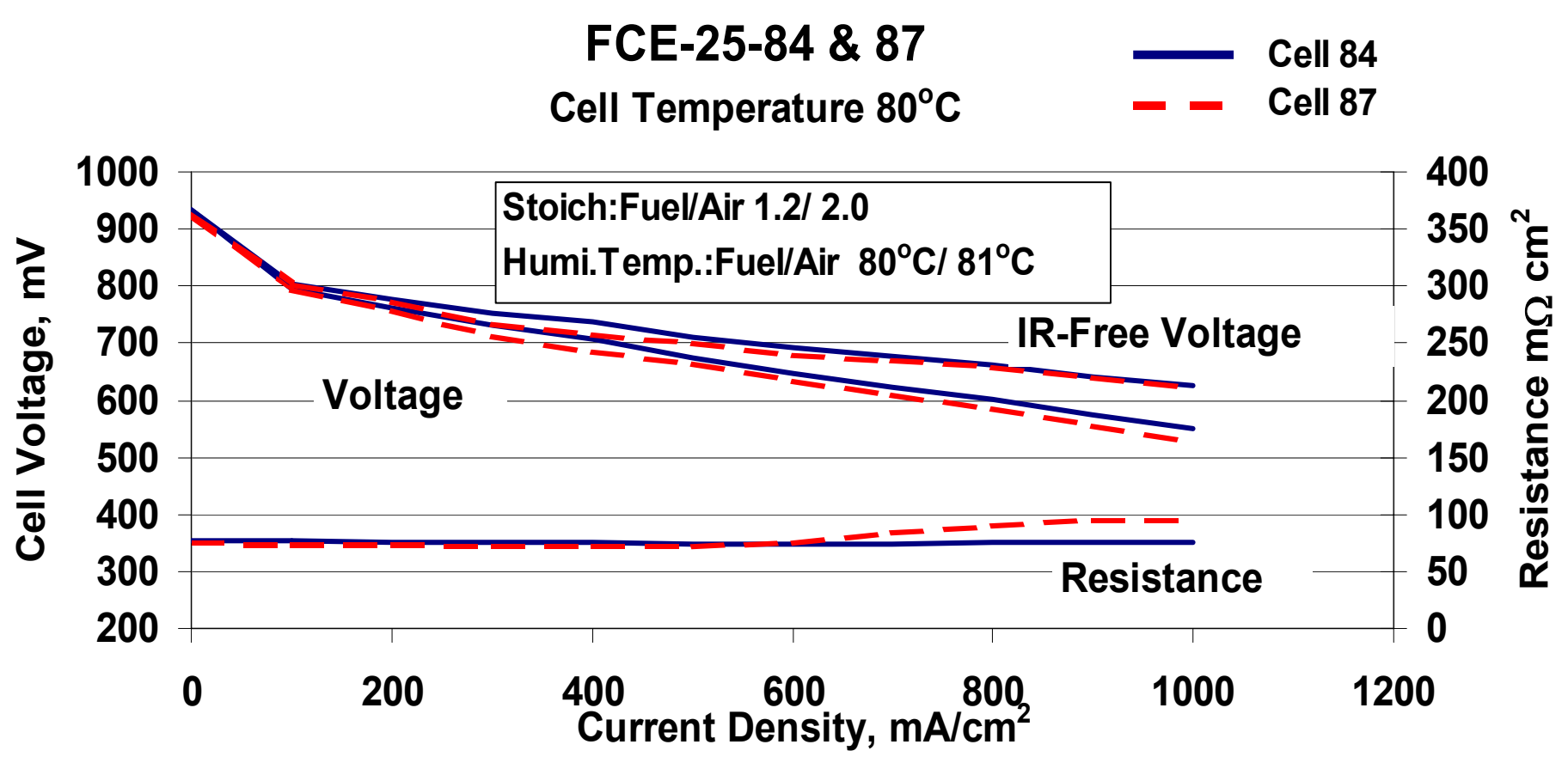
EFFECT OF TEMPERATURE (PTA ADDITIVE in Membrane and Catalyst)



Achieved 500mV Performance and 200mΩcm^2 Resistance at 400mA/cm^2 and 120°C

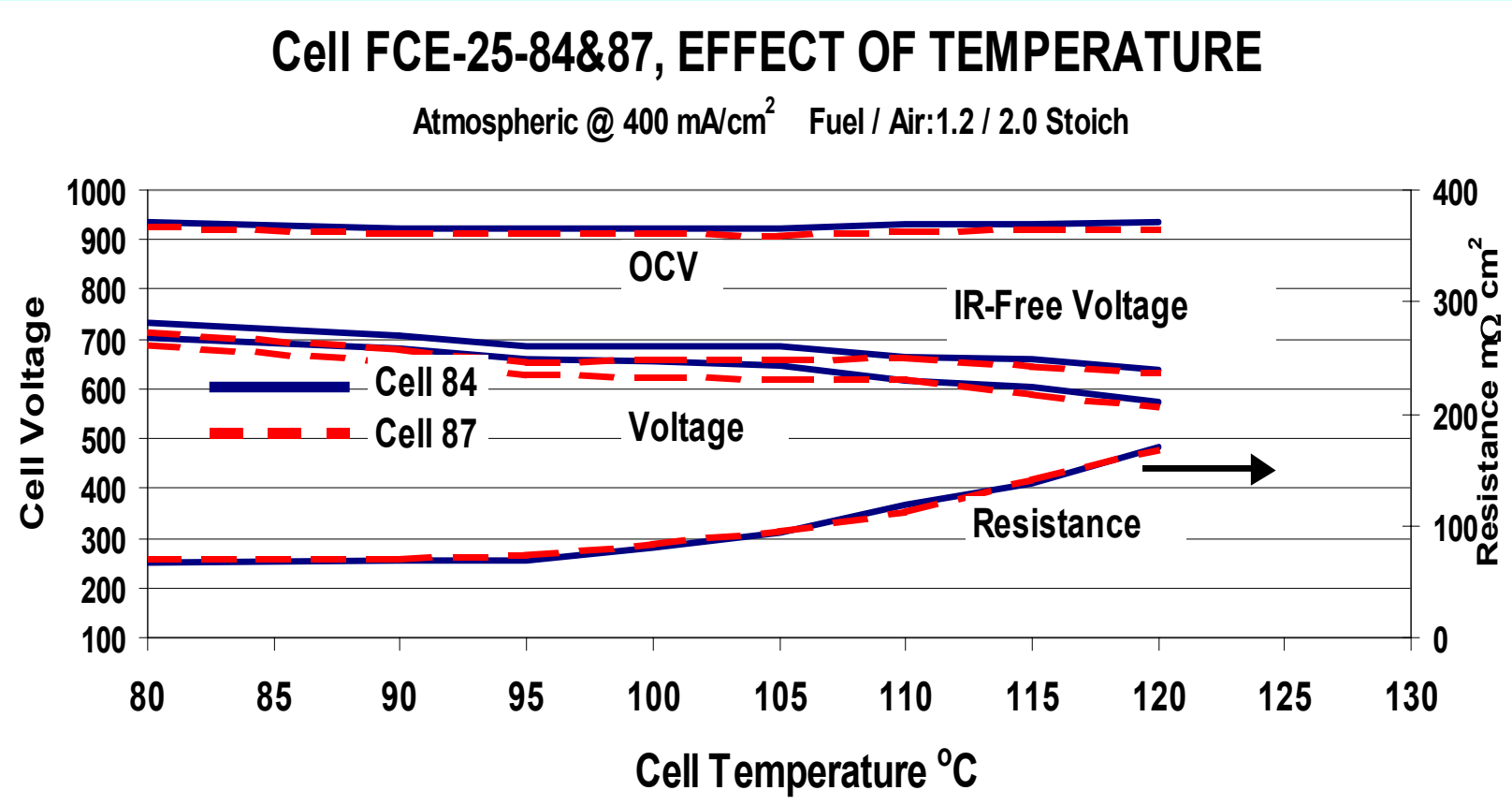
FuelCell Energy

~700mV Performance at 80°C with Alternative Proton Conducting Additive



FuelCell Energy

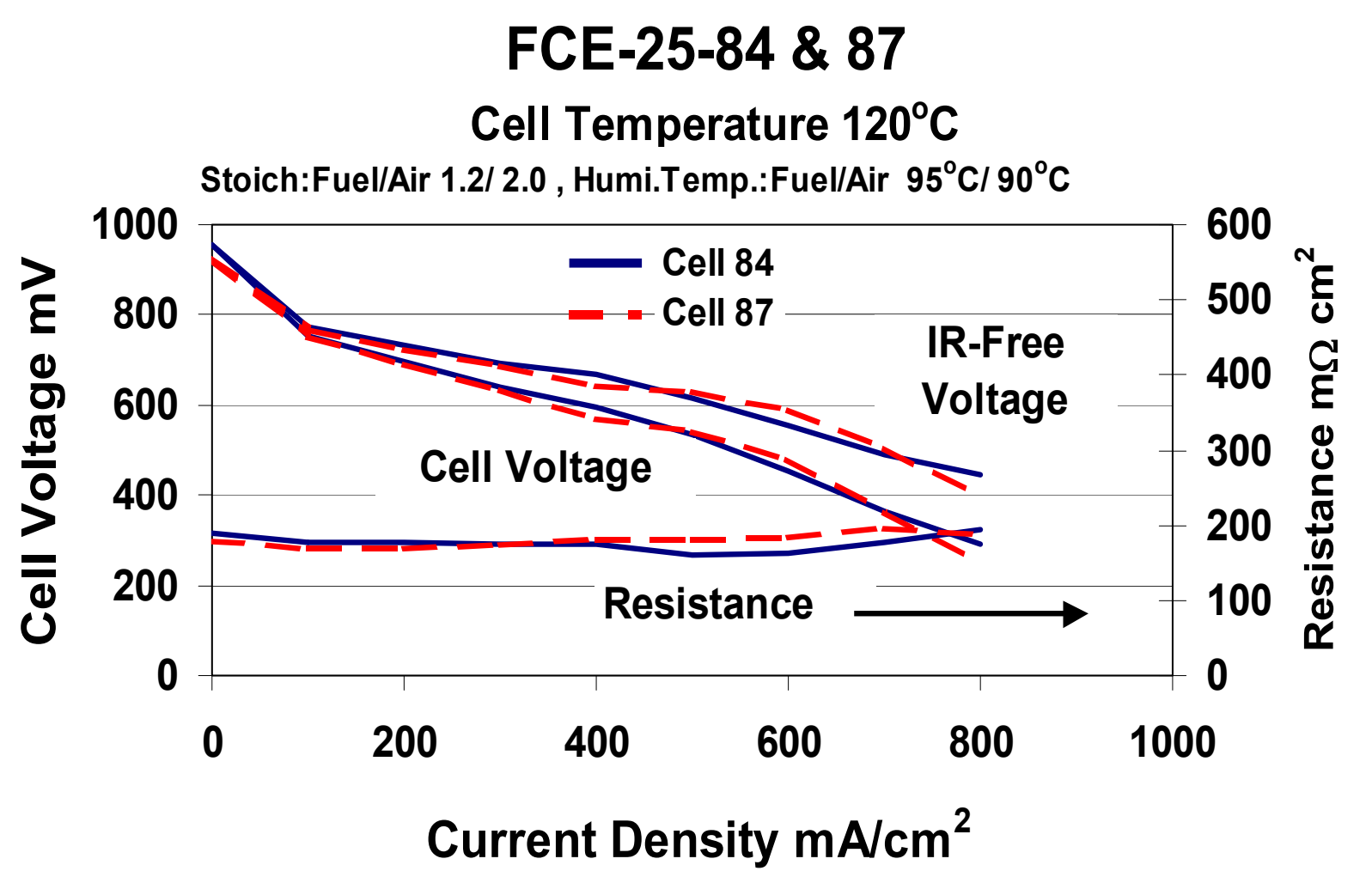
EFFECT OF TEMPERATURE



~600mV and 160mΩcm² at 120°C

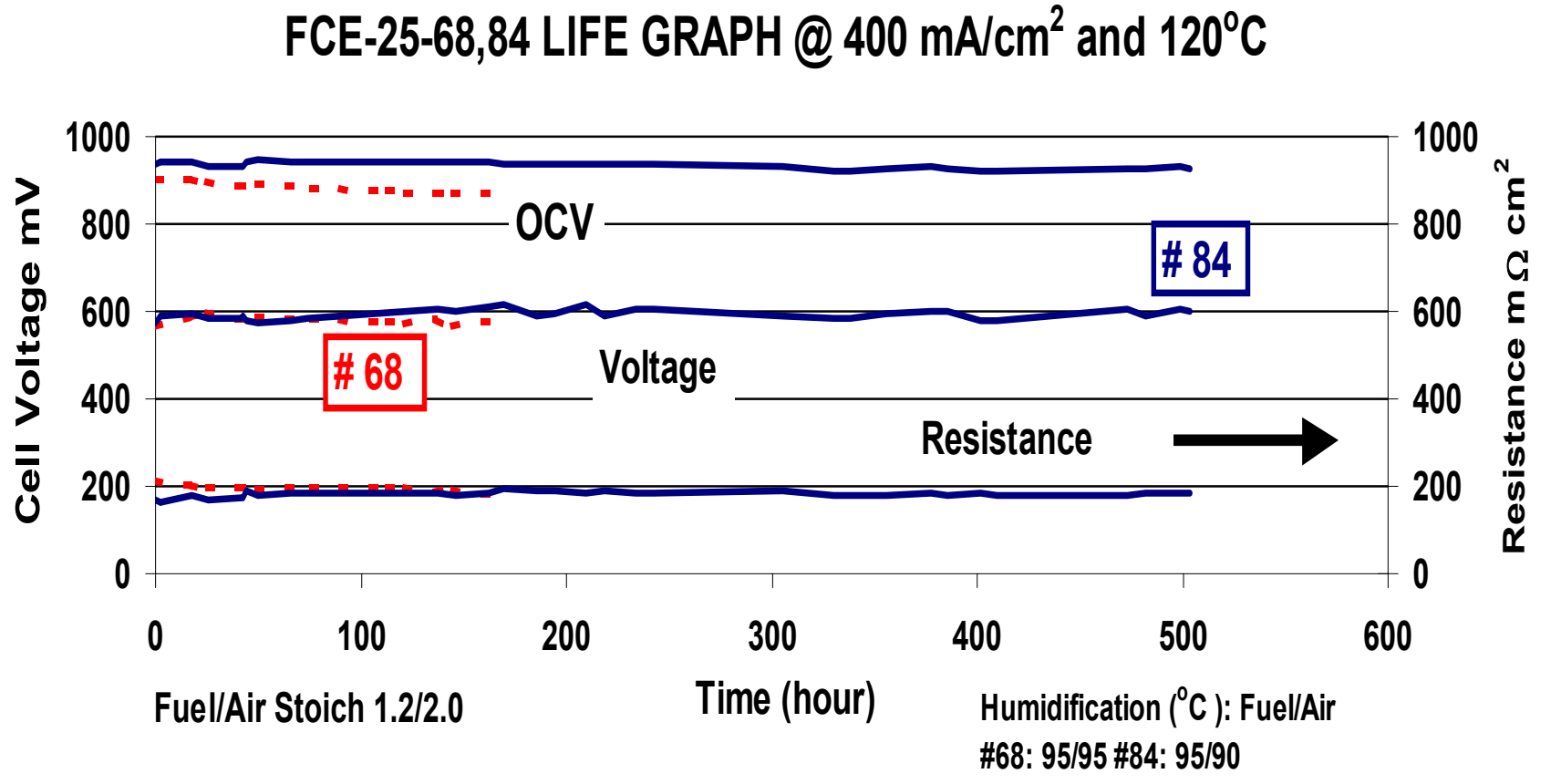
FuelCell Energy

600mV Achieved at 120°C and 400mA/cm²



FuelCell Energy

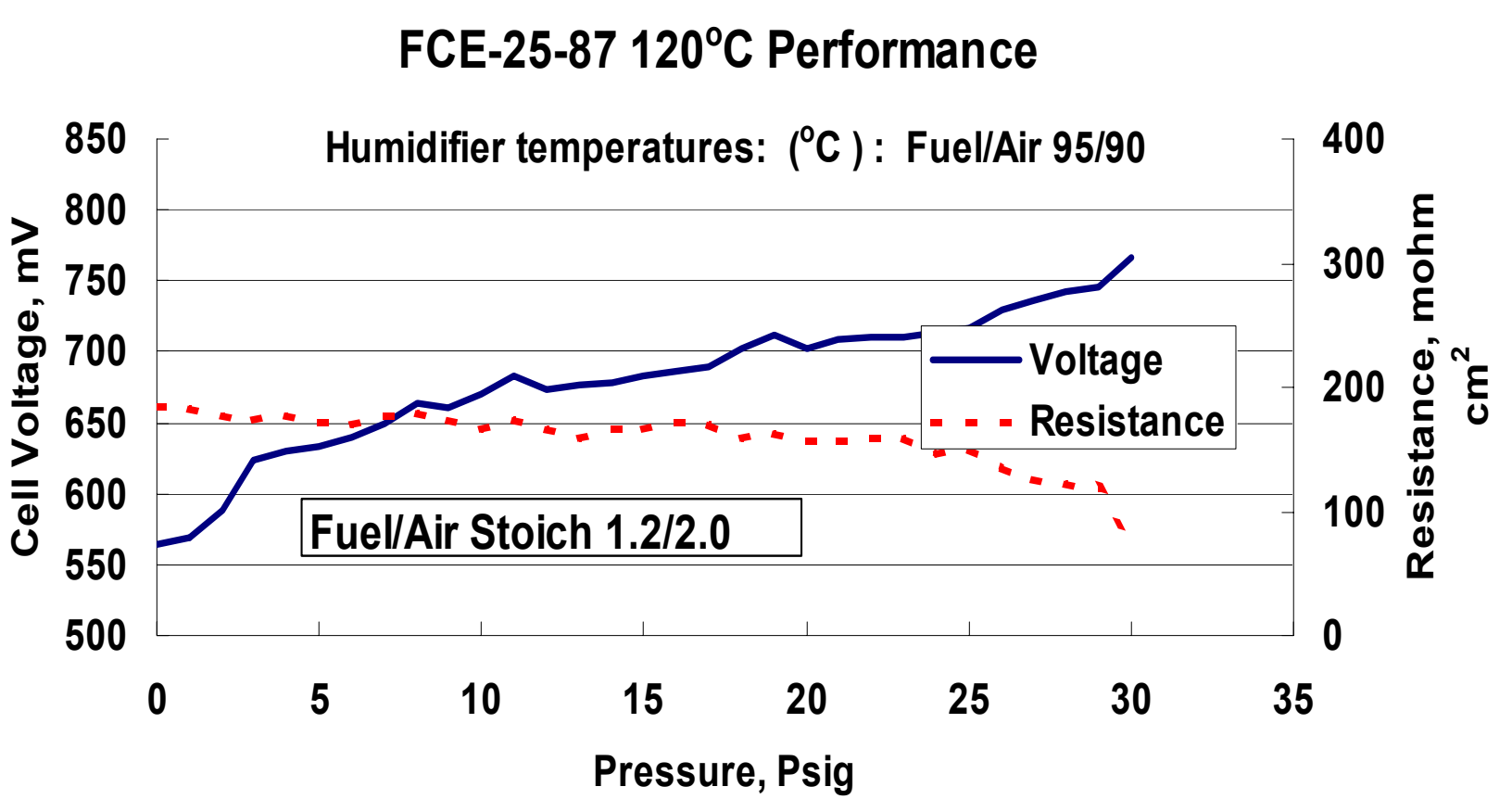
MEA ENDURANCE AT 120°C



Stable 600mV 500h Endurance

FuelCell Energy

EFFECT OF PRESSURE

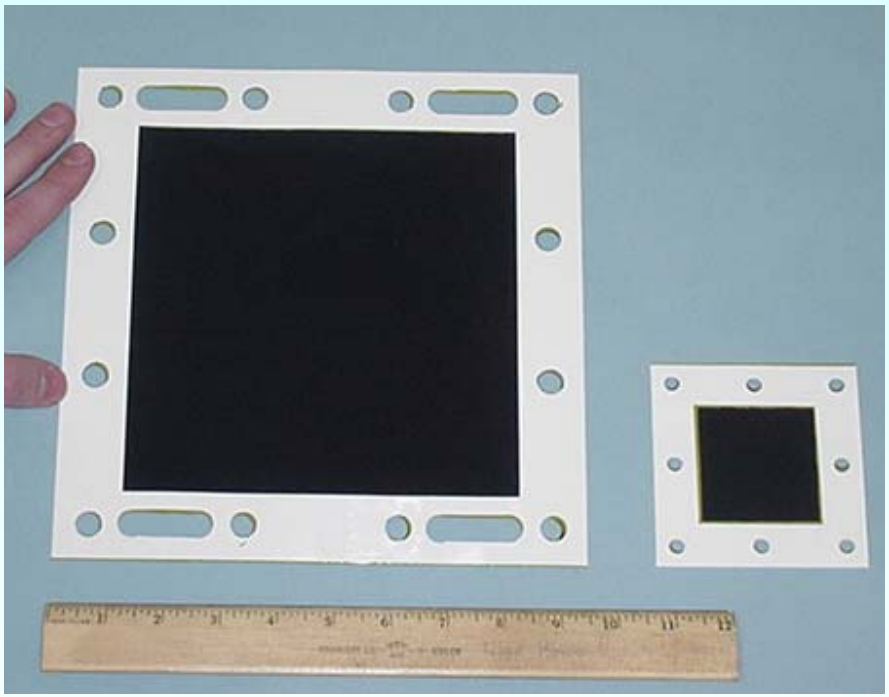


>750V at 400 mA/cm^2 at 30 Psig

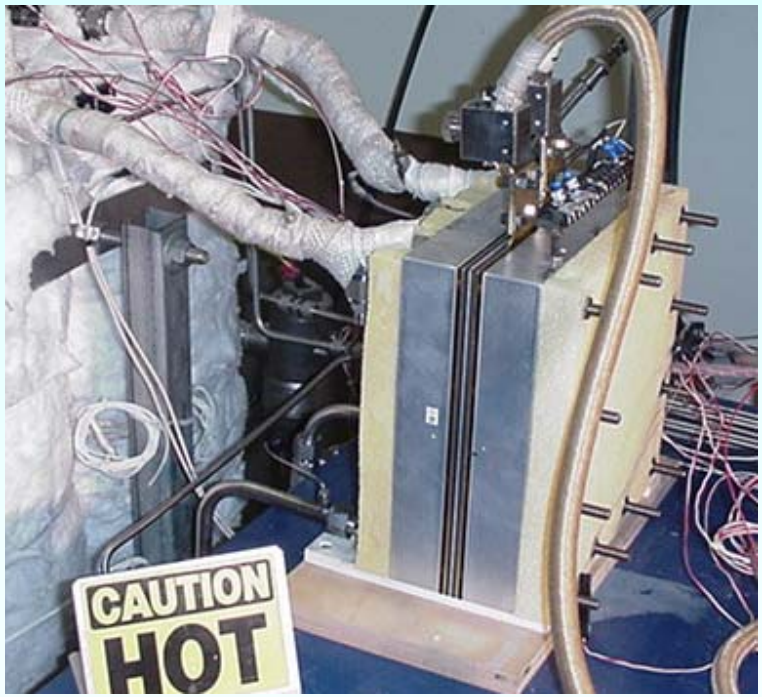
FuelCell Energy

300cm² MEA Fabricated

MEA



300cm² Cell



FuelCell Energy

CONCLUSIONS

FABRICATED ULTRA-THIN COMPOSITE MEA:

- WITH CONSISTENT LOW OHMIC RESISTANCE ($\leq$200 mΩ-cm^2) AND LOW CROSS-OVER AT 120°C
- STABLE 600mV ATMOSPHERIC-PRESSURE PERFORMANCE FOR 500 HOURS (>200mV IMPROVEMENT OVER BASELINE)

REQUIRE FURTHER EFFORT TO ACHIEVE ADDITIONAL PERFORMANCE AND ENDURANCE IMPROVEMENTS

- ENHANCE PROTON CONDUCTIVITY IN CATHODE
- INCREASE CATALYST UTILIZATION
- UNDERSTAND DECAY MECHANISMS

FuelCell Energy

2003 DOE Hydrogen and Fuel Cells Merit Review Meeting, May 19-22, 2003

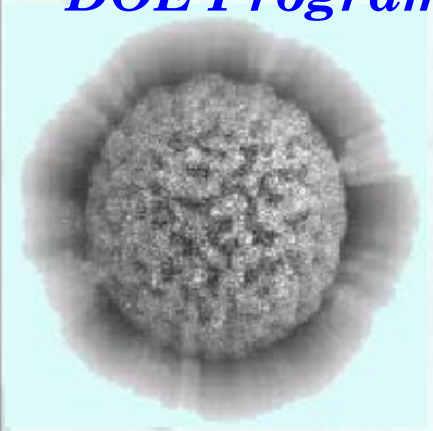
Title of Project: Development of High-Performance, Low-Pt Cathodes Containing New Catalysts and Layer Structure

Contractor: Superior MicroPowders, LLC

Duration: 4 years, September 2001- September 2005

Award: March 28th, 2002; DE-FC0402AL67620, Topic 1A1

DOE Program Manager: Valri Lightner



Subcontractors: DuPont Fuel Cells, CFDRC

Stack Testing: GM

Principal Investigator: Paolina Atanassova, Ph.D.
phone: (505) 342-1492, ext. 52
e-mail: paolina@smp1.com

SUPERIOR MicroPowders

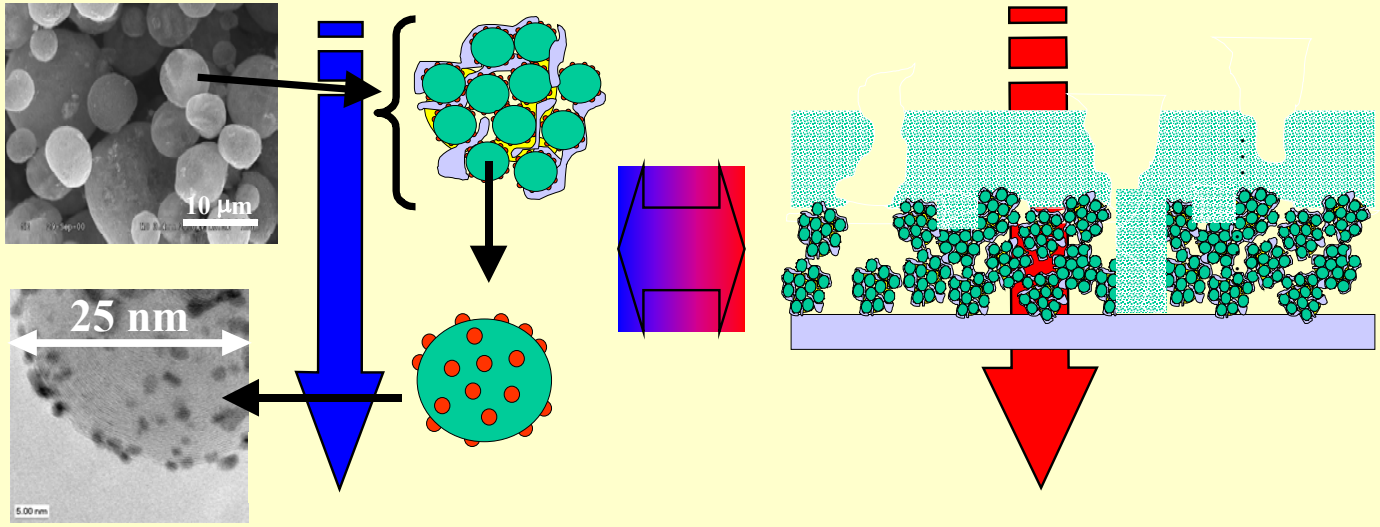
Approach - Technical Concept

Effort 1

Discovery of new, low Pt catalyst compositions and particle microstructures

Effort 2

Modeling and deposition of engineered cathode layers

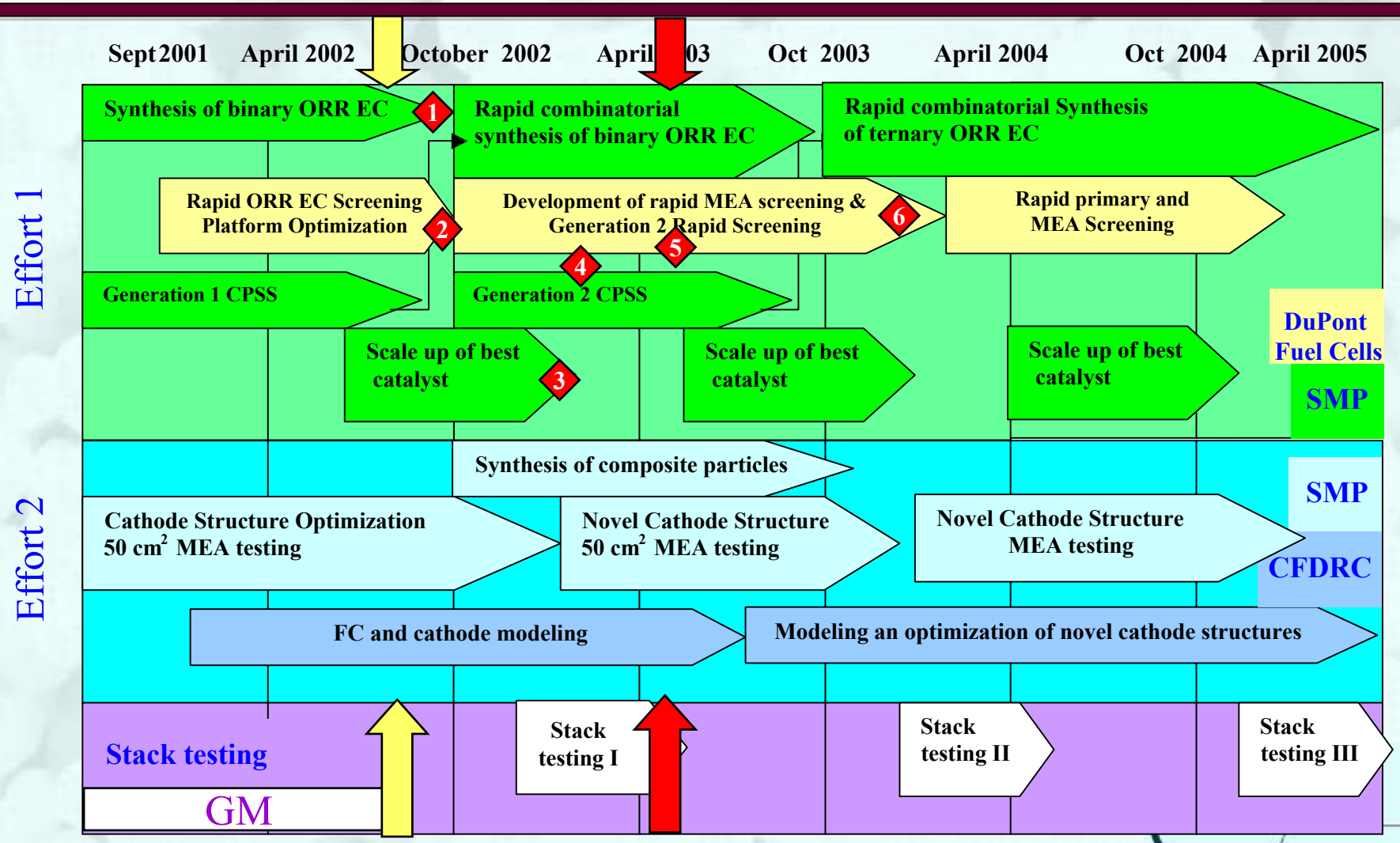


High Performance Low-Cost MEA

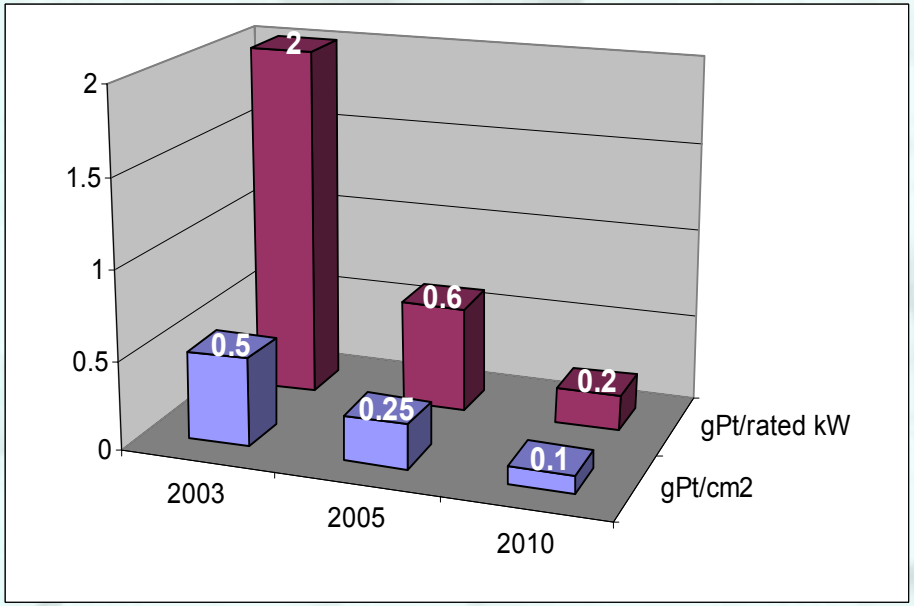
- **Effort 1:**
  - » *SMP*
  - » *DuPont Fuel Cells*
- **Effort 2:**
  - » *SMP*
  - » *CFDRC*
- **Short Stack Testing:**
  - » *GM*

SUPERIOR MicroPowders

Project Timeline and Milestones



Relevance and Objectives



- Technical targets
- Technical Task 14:

MEA Materials, Components, Processes

- Relevance to DOE Freedom CAR barriers and technical targets:

  Component technical barriers:

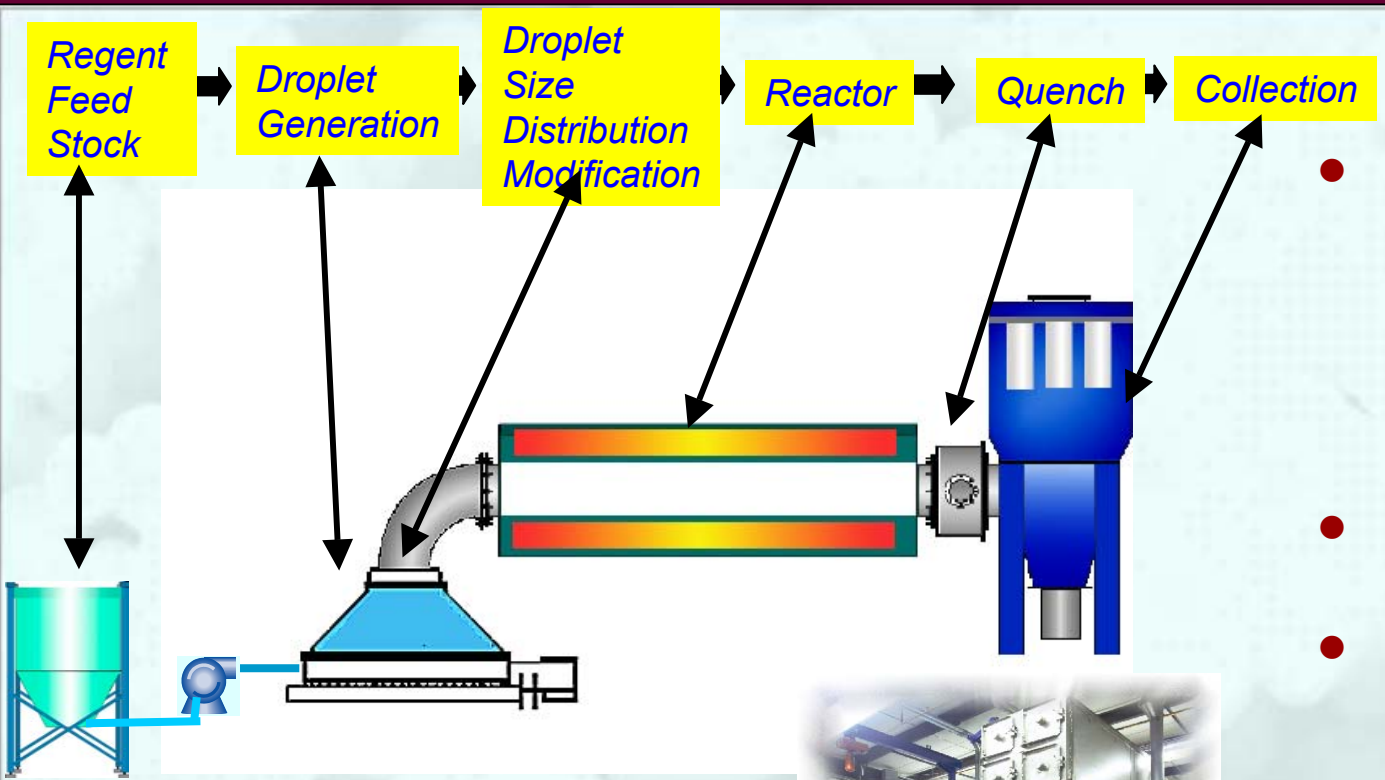
  » Barrier O. Stack Material and Manufacturing Costs: low-cost, high-performance alternative oxygen reduction electrocatalysts

  » Barrier Q. Electrode Performance: cathode voltage losses and higher power densities at higher voltages

  » Barrier P. Durability: catalyst agglomeration and stability

SUPERIOR MicroPowders

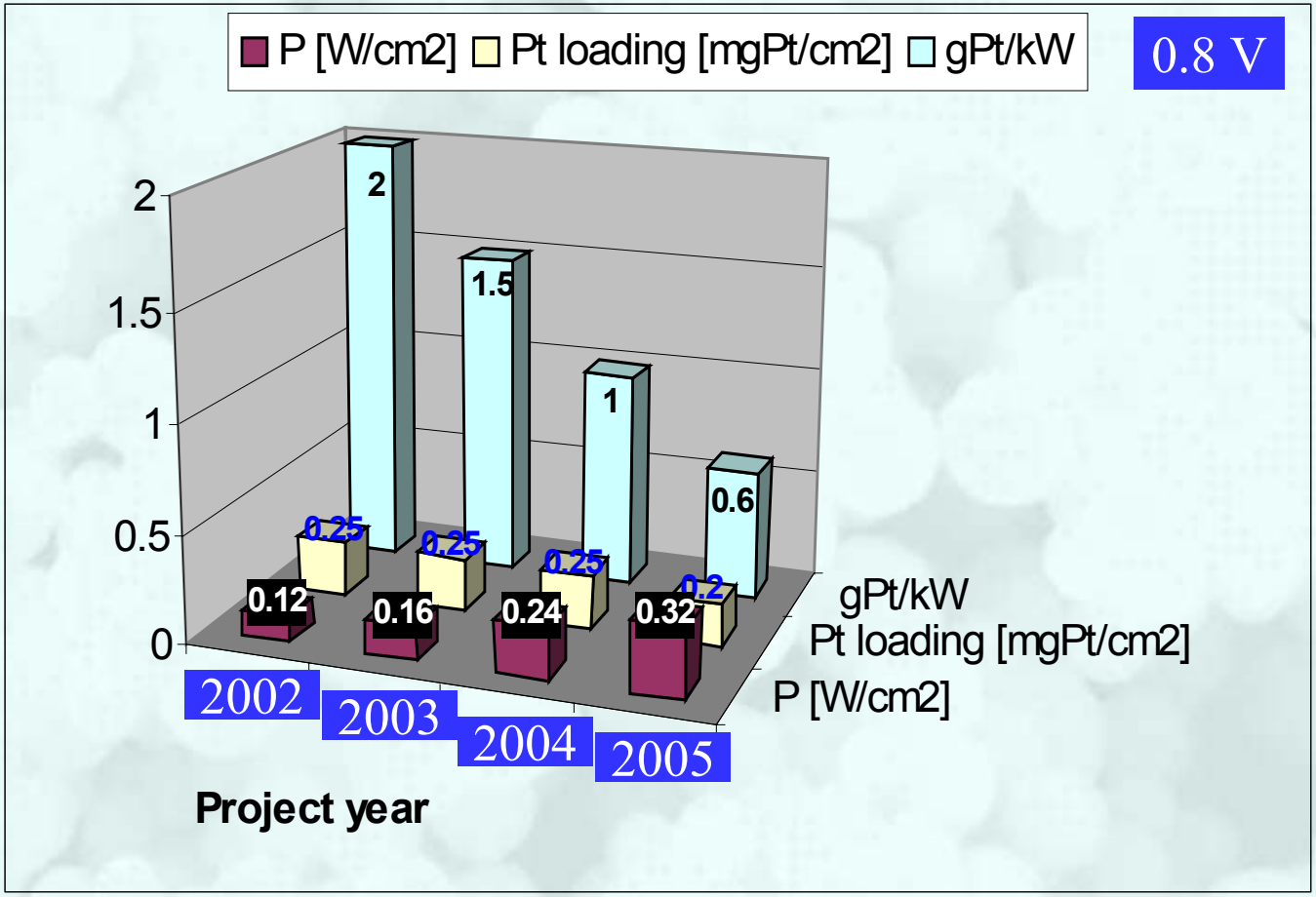
Technology Platform: SMP's Spray Based Manufacturing



- Low cost manufacturing
  - » Single step processing
  - » Highly controllable and reproducible
  - » "Green" process with minimal waste streams
- Agile platform
  - » Complex compositions
- Ability to engineer critical properties
  - » Particle morphologies and size distributions
  - » Dispersion, crystallinity and size distribution of catalytically active phase

SUPERIOR MicroPowders

Project Performance Targets



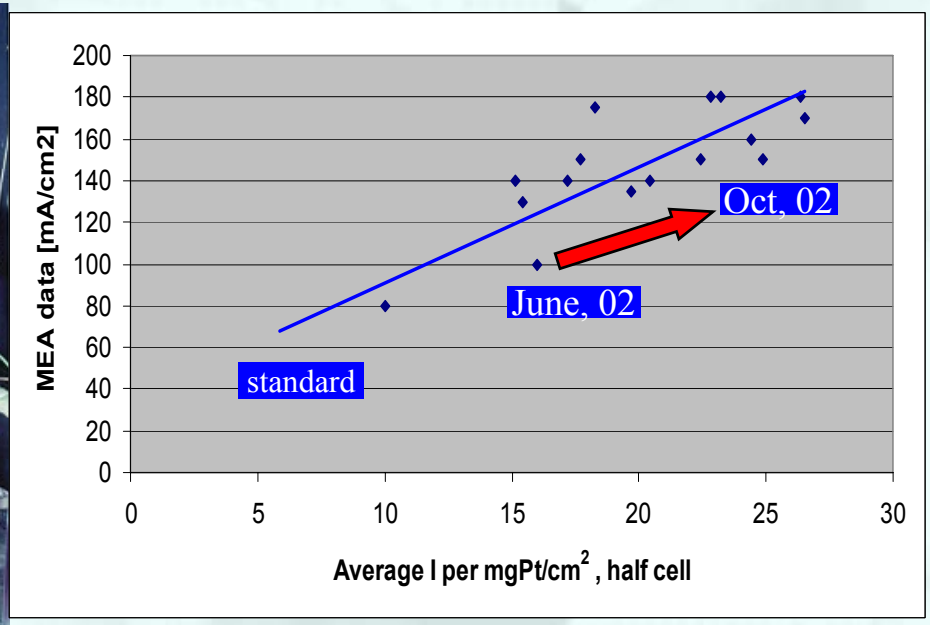
- *Single MEA 50 cm² test cell, Nafion 112*
- *Cell temperature 80C*
- *Anode/cathode constant flow rates = 510/2060 mL/min H_2/air (1.5H_2/ 2.5 air stoich at 1 A/cm²)*
- *30 psig pressure on both anode and cathode*
- *100% humidification of gases, 80 C dew points*
- *Galvanostatic, mode, 15 min per*

Summary of Achievements Effort 1 Combinatorial Approach

Milestone	Description	Achievement	Timing	Status
1	Synthesis of benchmark alloy catalysts by spray pyrolysis	Ability of spray approach to generate complex alloy catalysts with improved performance	October 2002	Up to 40 % improvement in terms of lower gPt/kW for $Pt_xNi_yCo_z$ ternary alloy system
2	Half-cell rapid screening approach optimization and benchmarking at DuPont	Correlation between ranking of catalysts and MEA performance and go-no-go decision criteria established	October 2002	Rapid screening used exclusively for initial screening of new catalysts

SUPERIOR MicroPowders

Summary of Achievements Effort 1 Milestone 2



Correlation of Half Cell Screening Data and MEA Performance

DuPont Fuel Cells

". . . powered by DuPont"

DUPONT The miracles of science

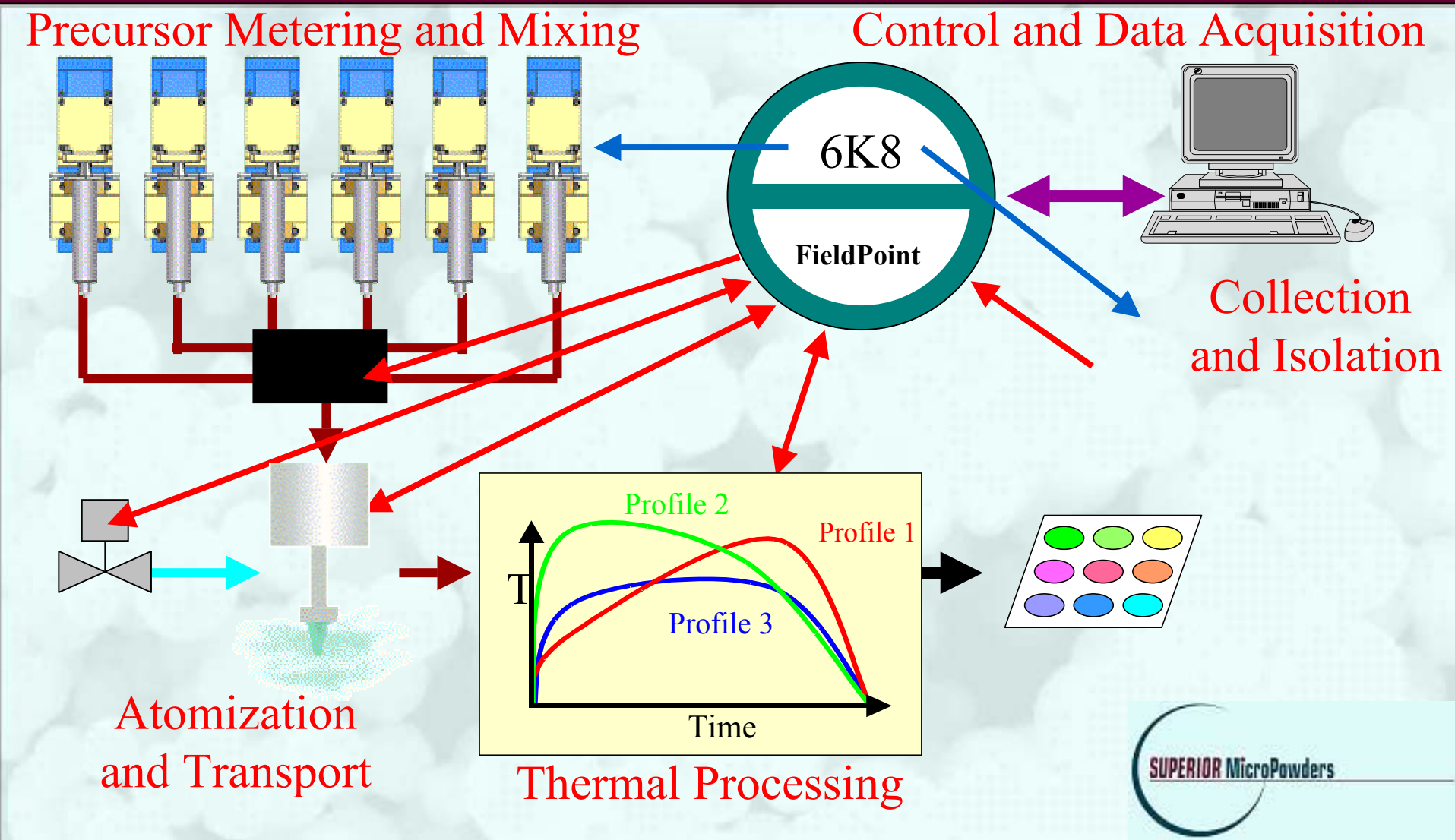
SUPERIOR MicroPowders

Summary of Achievements Effort 1 Combinatorial Approach

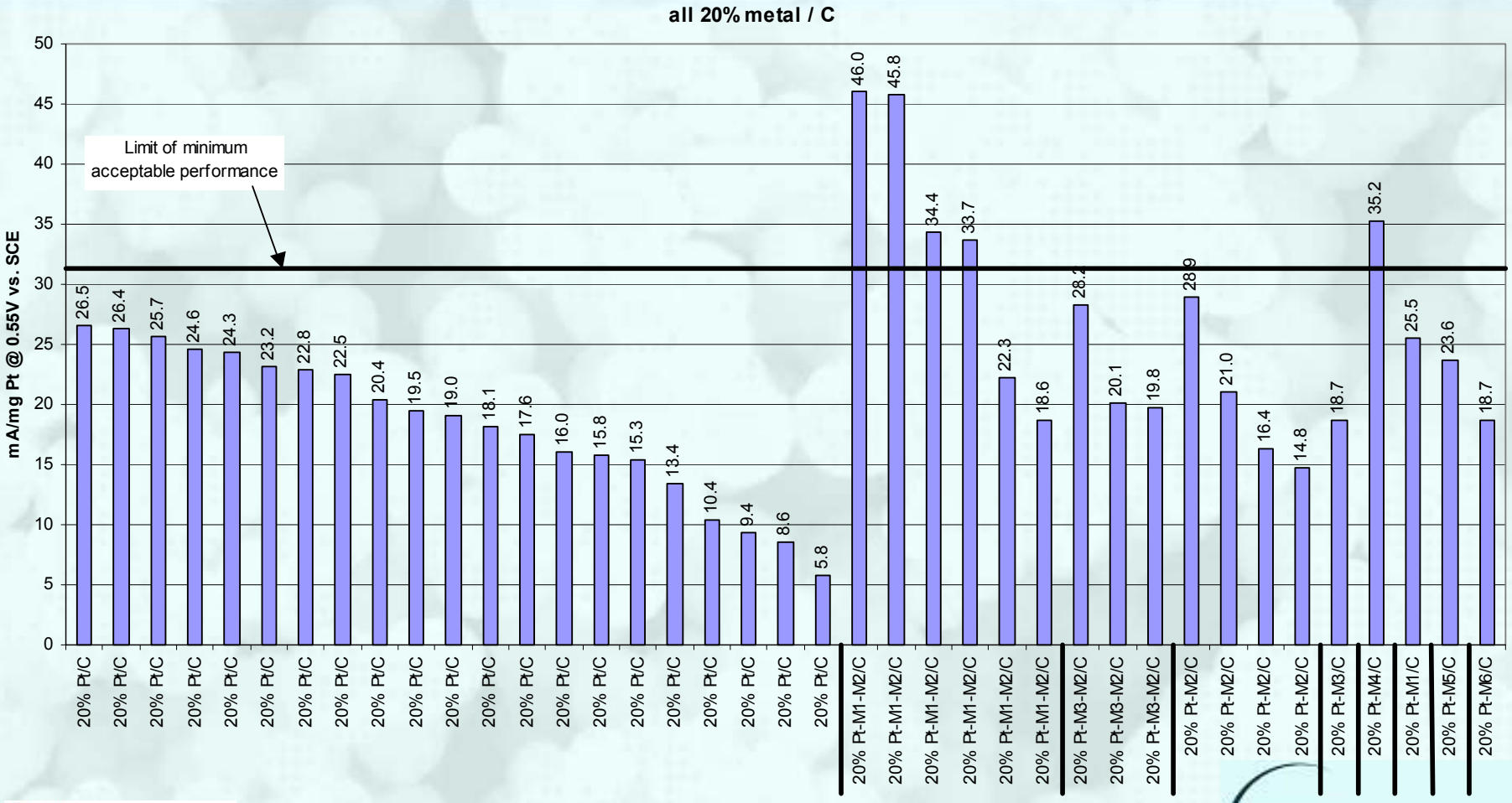
Milestone	Description	Achievement	Timing	Status
3	Scale up of best performing catalysts	High surface area Pt/carbon and Pt ternary alloy/carbon catalysts scaled up	January 2003	Performance of scaled up materials at least equal to small scale ones
4	Complete assembly of Combinatorial Powder Synthesis System (CPSS) and optimize parameters	System fully integrated and automated, target production rates achieved, Pt/C catalysts benchmarked	March 2003	100 samples per week at 0.25 g achievable, start to investigate broad number of alloy compositions and microstructures
5	Complete assembly of rapid ink formulation equipment at DuPont	System assembled, testing of baseline catalysts in progress	May 2003	75-150 samples per week testing rate achievable

SUPERIOR MicroPowders

Milestone 4: From Design to Functional Equipment



Summary of Achievements Effort 1 Milestone 5: High Throughput Screening



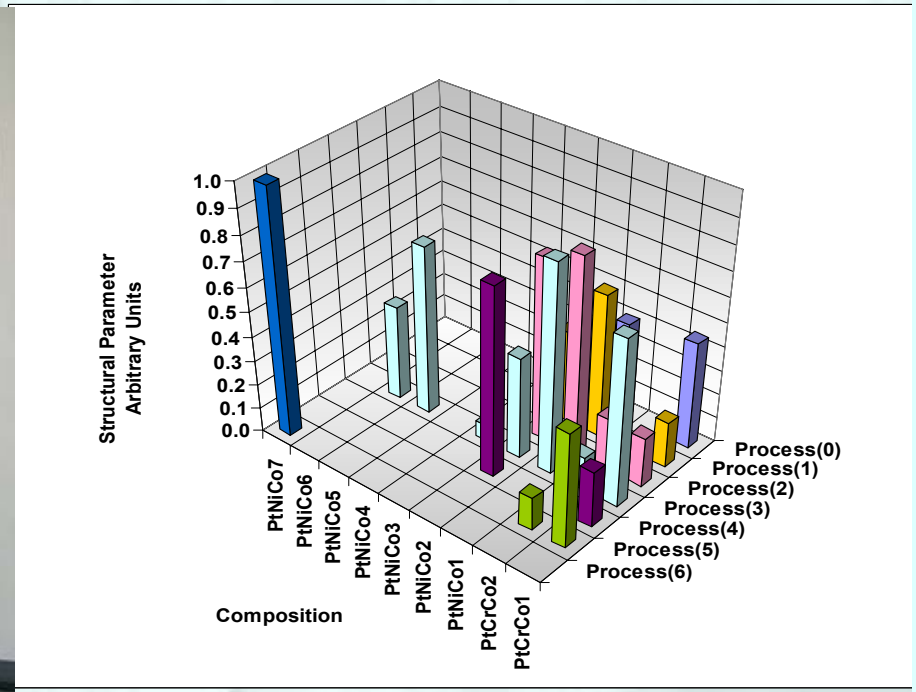
The miracles of science

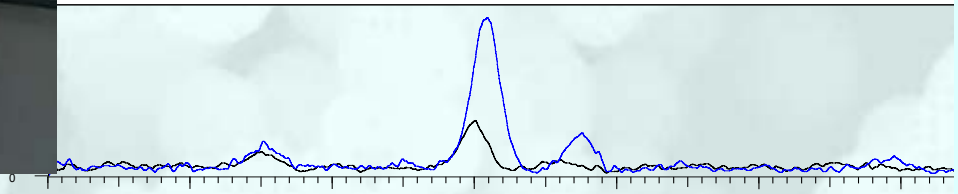
DuPont Fuel Cells

". . . powered by DuPont"

SUPERIOR MicroPowders

Characterization of Pt-alloy Electrocatalysts



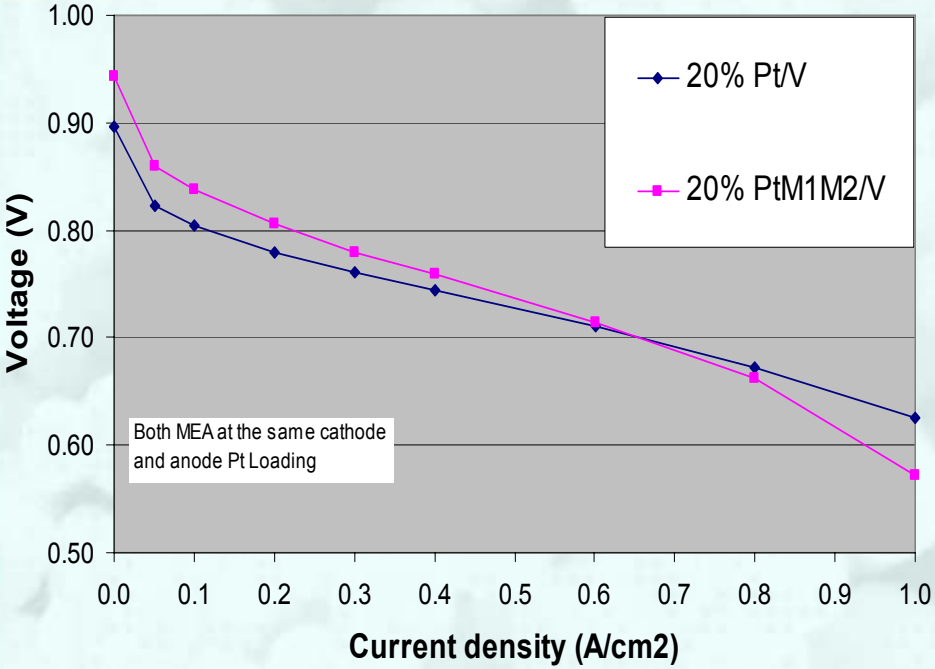


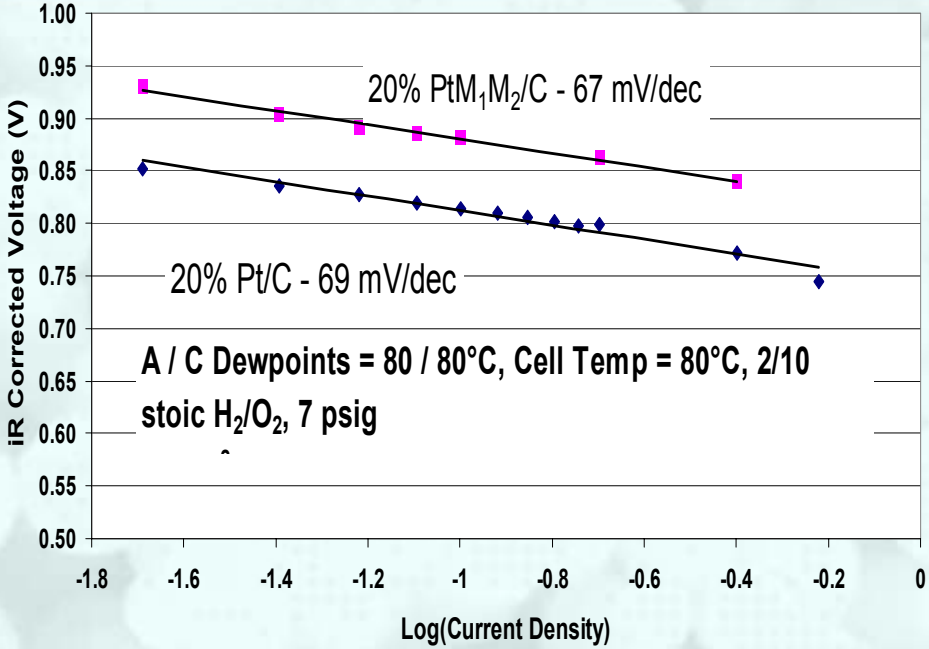
20 wt.% $Pt_xNi_yCo_z/C$

- *Degree of alloying dependant on spray processing parameters and post-processing conditions*

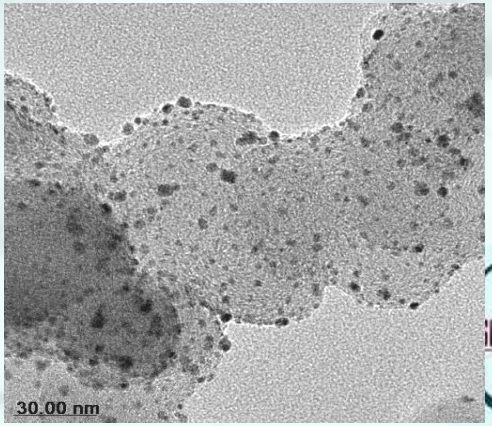
PERIOR MicroPowders

Characterization of Pt-alloy Electrocatalysts



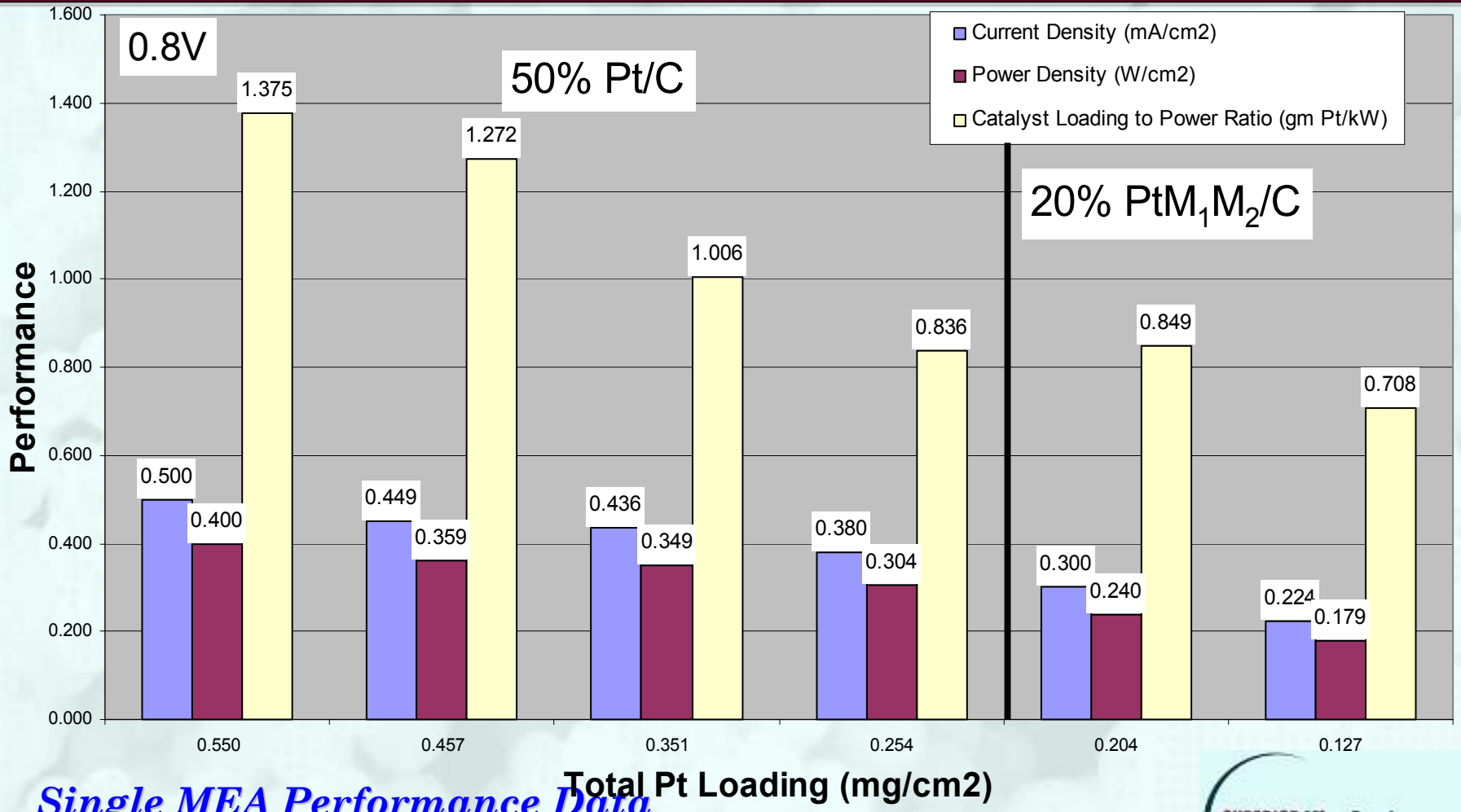


Single MEA Performance Data
80 C, 1.5H_2/2.5air at 1A/cm^2, 100% RH, 30 psig, 15 min/point



SUPERIOR MicroPowders

Summary of Achievements Effort 2
MEA Structure Optimization



Single MEA Performance Data
80 C, 1.5H_2/2.5air at 1A/cm^2, 100% RH, 30 psig, 15 min/point

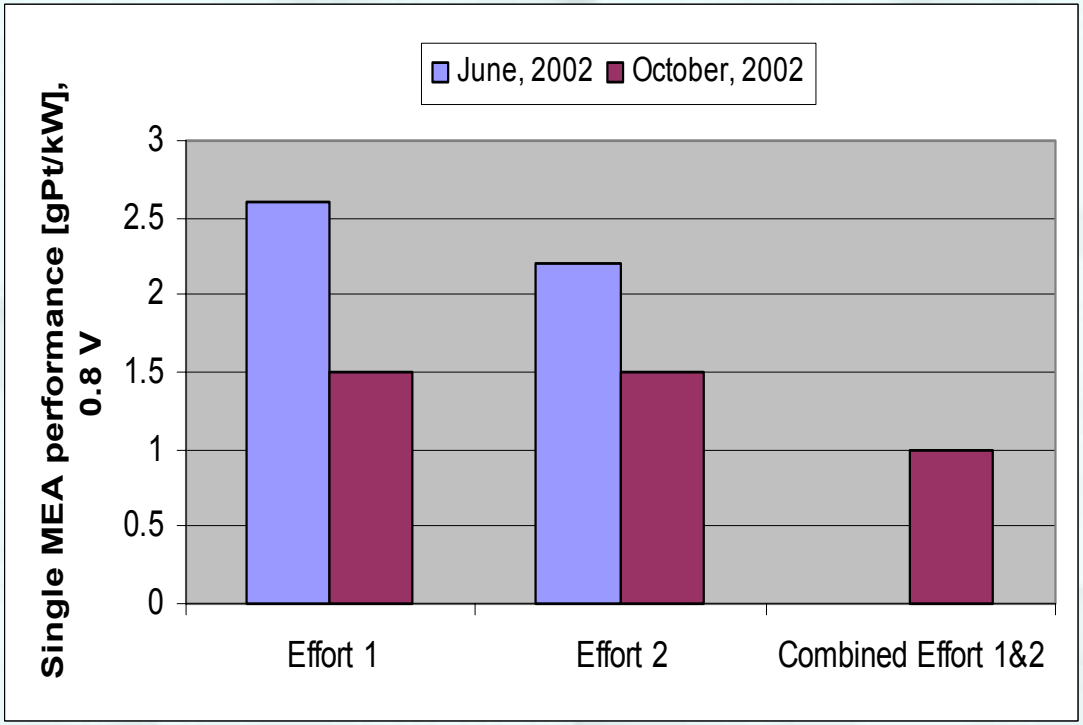
SUPERIOR MicroPowders

Significant Interactions

- ***Los Alamos National Laboratory***
  - » Knowledge/experience transfer for alloy ORR catalysts
  - » Pt alloys characterization by XRD (Fernando Garzon)
  - » Validation testing (Francisco Uribe)
- ***General Motors, Fuel Cell Activities***
  - » Testing criteria (Hubert Gasteiger)
  - » Validation testing (Susan Yan)
- ***Other Fuel Cell Developers***

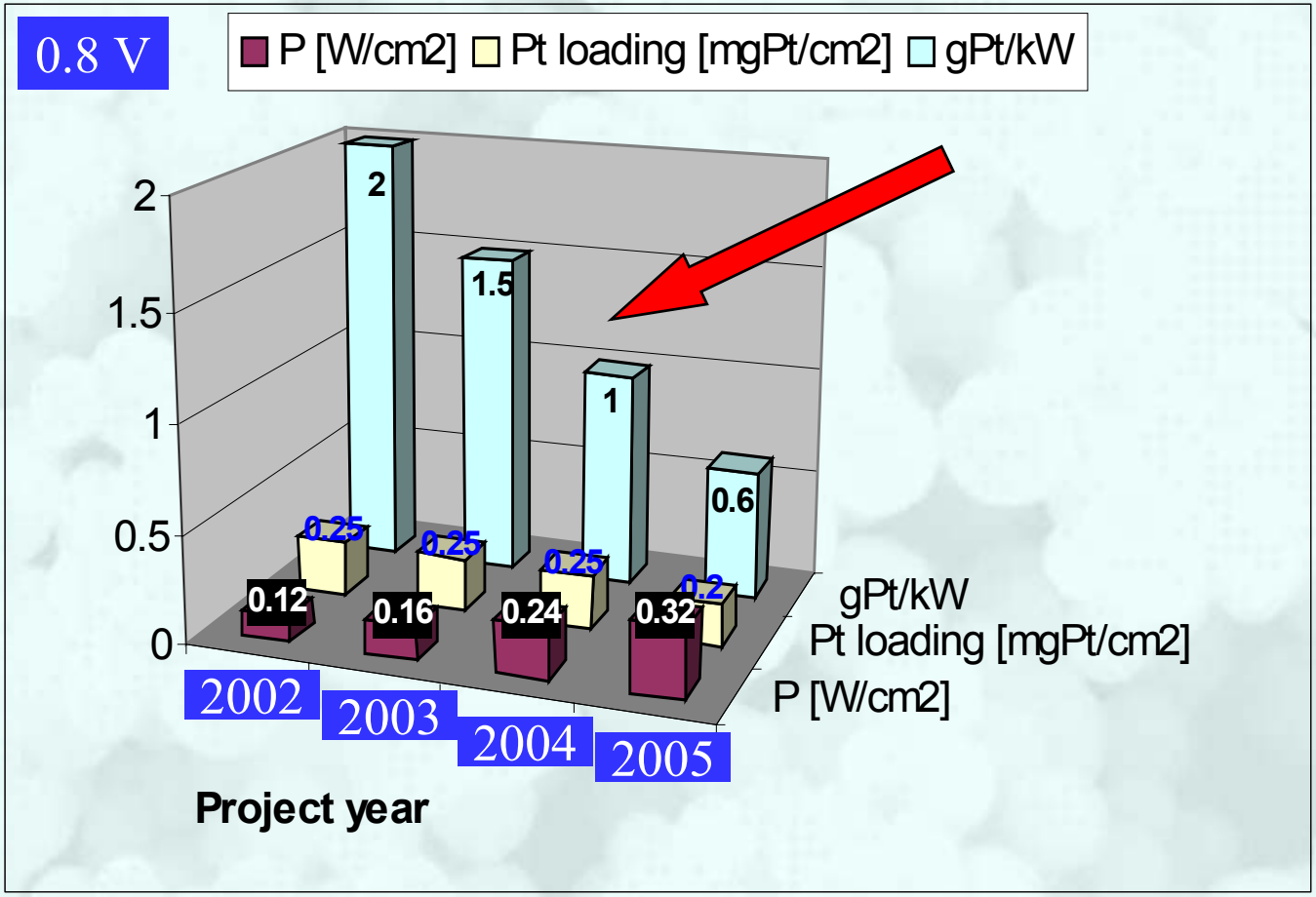
SUPERIOR MicroPowders

Summary of Achievements Combined Effort 1 and Effort 2



- **Effort 1:** Ternary alloy catalyst performance improved from 2.6 gPt/kW to <1.5 gPt/kW
- **Effort 2:** MEA structure development yields improvement from 2.2 gPt/kW to <1.5 gPt/kW
- Combined best alloy catalyst and best MEA structure result in performance of <1 gPt/kW

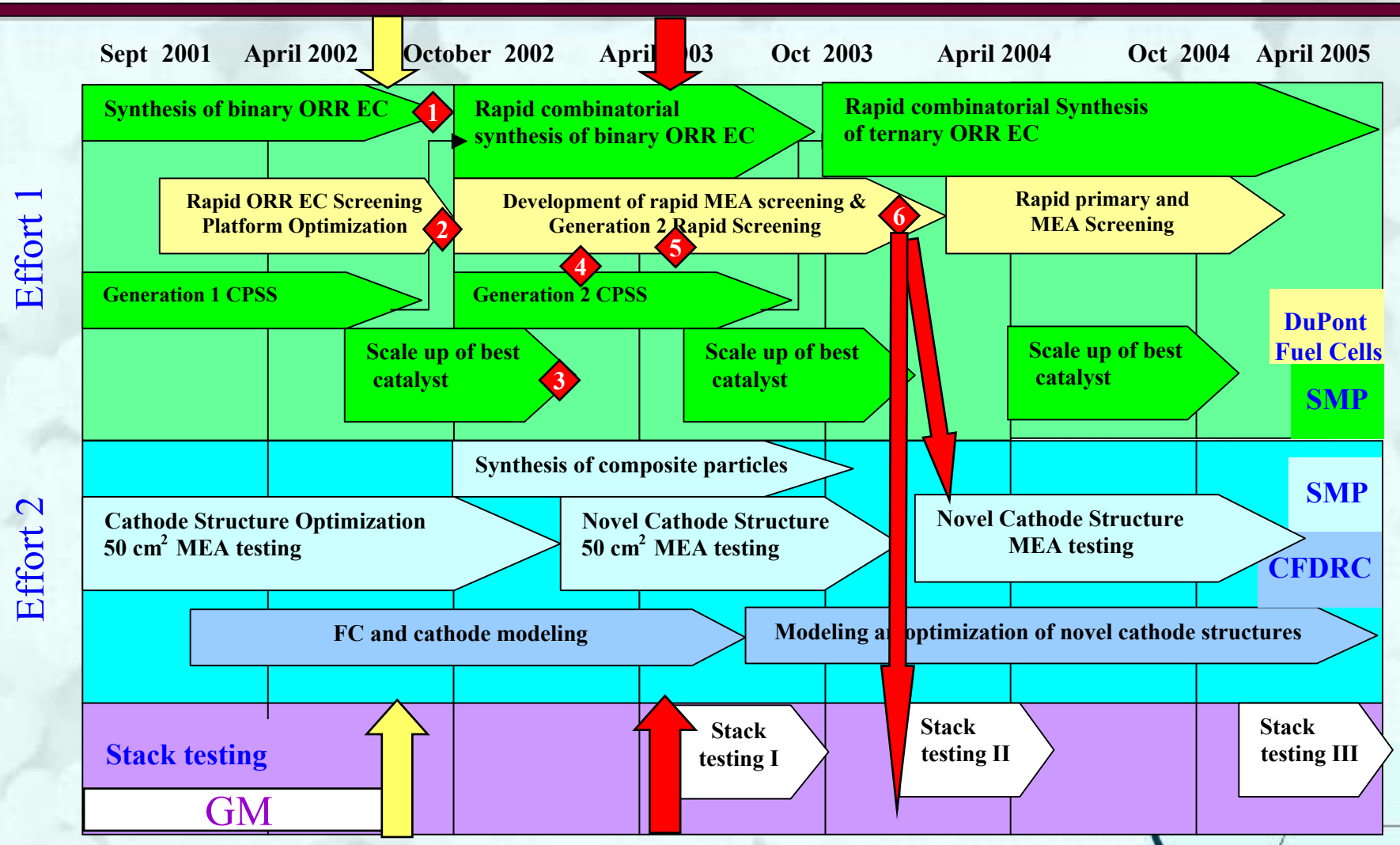
Status vs. Project Performance Targets



- *Currently in a single MEA 50 cm² test cell, Nafion 112*
- *Testing at fixed lower stoich conditions*
- *Need to validate results in stack*
- *Need to address long term stability*
- *Further improvements can be derived also from a thinner membrane*

SUPERIOR MicroPowders

Plans and Future Milestones

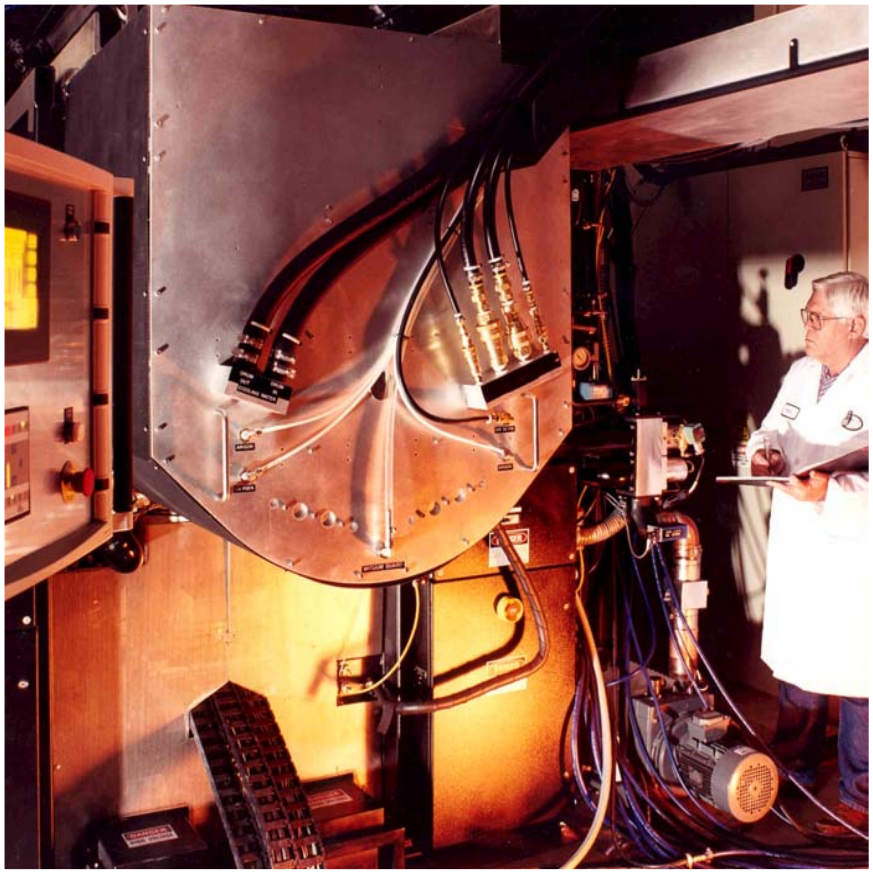


Acknowledgements

- *DOE OTT, Award DE-FC0402AL67620, Topic 1A1*
- *JoAnn Milliken, Valri Lightner*
- *SMP, DuPont Fuel Cells and CFDRC for cost share funding*
- *The whole SMP team and especially:*

  Mark Hampden-Smith, David Dericotte, Paul Napolitano, Bogdan Gurau, Rimple Bhatia, Jim Brewster, Jenny Plakio, Heath Quiggle , Tomas Wood, Bryan Apodaca, Henry Romero
- *DuPont Fuel Cells: JoAnn Schwartz, Lin Wang,Keith Tomey, John Gantzhorn, Richard Okine*
- *CFDRC: Sandip Mazumder, Sam Lowry*

SUPERIOR MicroPowders



Design and Installation of a Pilot Plant for High-Volume Electrode Production

James H. Arps, Manager

Surface Engineering Section

Southwest Research Institute

DOE Hydrogen and Fuel Cells Merit Review Meeting

May 19, 2003

Key Contributors

- SwRI
  - Bruce Lanning
  - Walt Machowski
  - Forrest Campbell
  - Jim Riggs
- W.L. Gore and Associates
  - Jeff Kolde
  - Dave Lane
  - Simon Cleghorn
  - Nick Sisofo
- General Motors
  - Julie Wang
  - Matt Fay
  - Mark Mathias

Overview

- Introduction/relevance to DOE objectives
- Program goals
- Technical accomplishments
- Future plans

MEAs-The Heart of the Fuel Cell

Fuel Cell Catalyst Issues

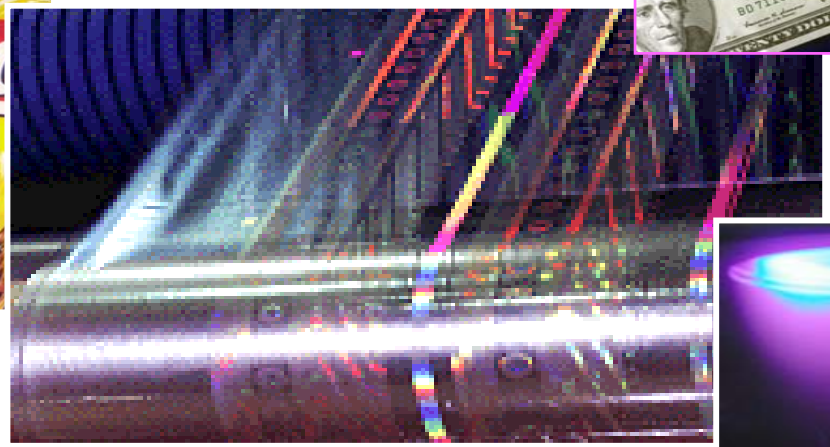
Deposition Approaches

- Rolling/spraying
- Screen printing
- Solution casting/hot pressing
- Other emerging methods

Challenges

- Uniformity
- Achieving low Pt loadings (AND good performance)
- Volatile organic species
- Process can be labor intensive
- Cost

Vacuum Web Coating



- A preferred method for high-volume treatment of polymeric materials
- Advantages
  - Highly Controllable Deposition
  - Ultra-Thin Layers
- Applications
  - Packaging
  - Anti-Counterfeit

Relevance to DOE Objectives

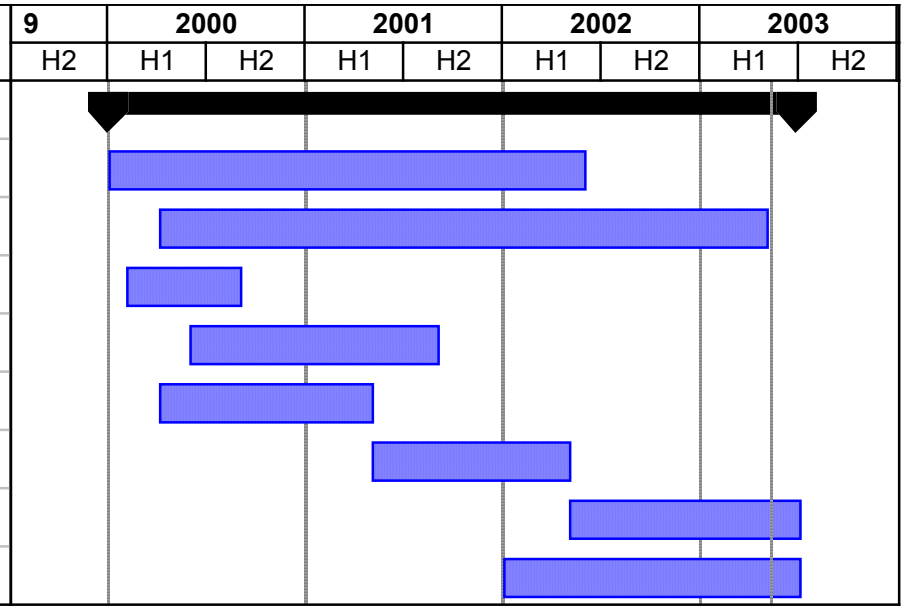
- Significantly reduce overall MEA cost by developing low precious metal loading vacuum catalyzation methods (0.2 g/rated kW by 2010).
- Improve prospects for practical implementation of FC technology in high-volume applications by demonstrating scalable, high-throughput manufacturing technology.
- Evaluate performance of materials under relevant fuel cell operating conditions to confirm process viability.

Primary Project Objectives

- Design, install, and demonstrate pilot manufacturing equipment capable of catalyzing up to 100,000 m^2 of electrode materials per year.
- Optimize loading, uniformity, composition, and throughput of catalyzed materials.
- Produce MEAs and benchmark against commercially available products.
- Incorporate MEAs into 2 “short” stacks and deliver to ANL for test and evaluation.

Timeline

ID	Task Name
1	**SwRI timeline**
2	Catalyst Optimization
3	MEA and Materials Testing
4	Process Cost Analysis
5	Large Area Proof of Concept
6	System Design and Specifications
7	System Construction and Installation
8	Pilot Trials and System Optimization
9	Stack Development and Testing

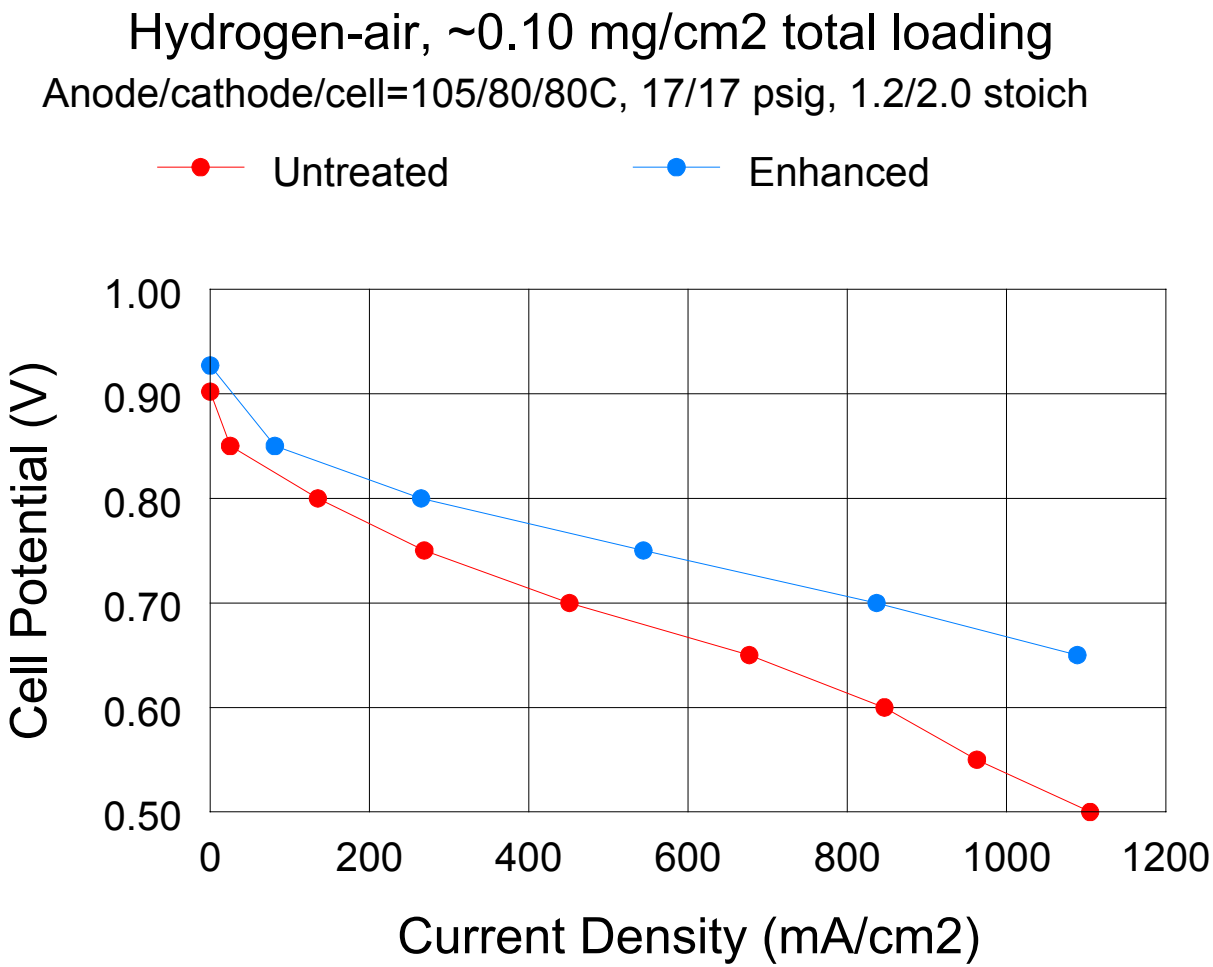


- **Major Milestones**
  - **Validated MEA fab/test methods**
  - **Completed MEA catalyzation cost analysis (go/no-go)**
  - **Pilot system complete and on-line**
  - **MEAs delivered to Gore and GM for testing and evaluation**

Sample Electrode Material

- Several thousand linear feet of material supplied by W.L. Gore and Associates for use in pilot manufacturing trials .

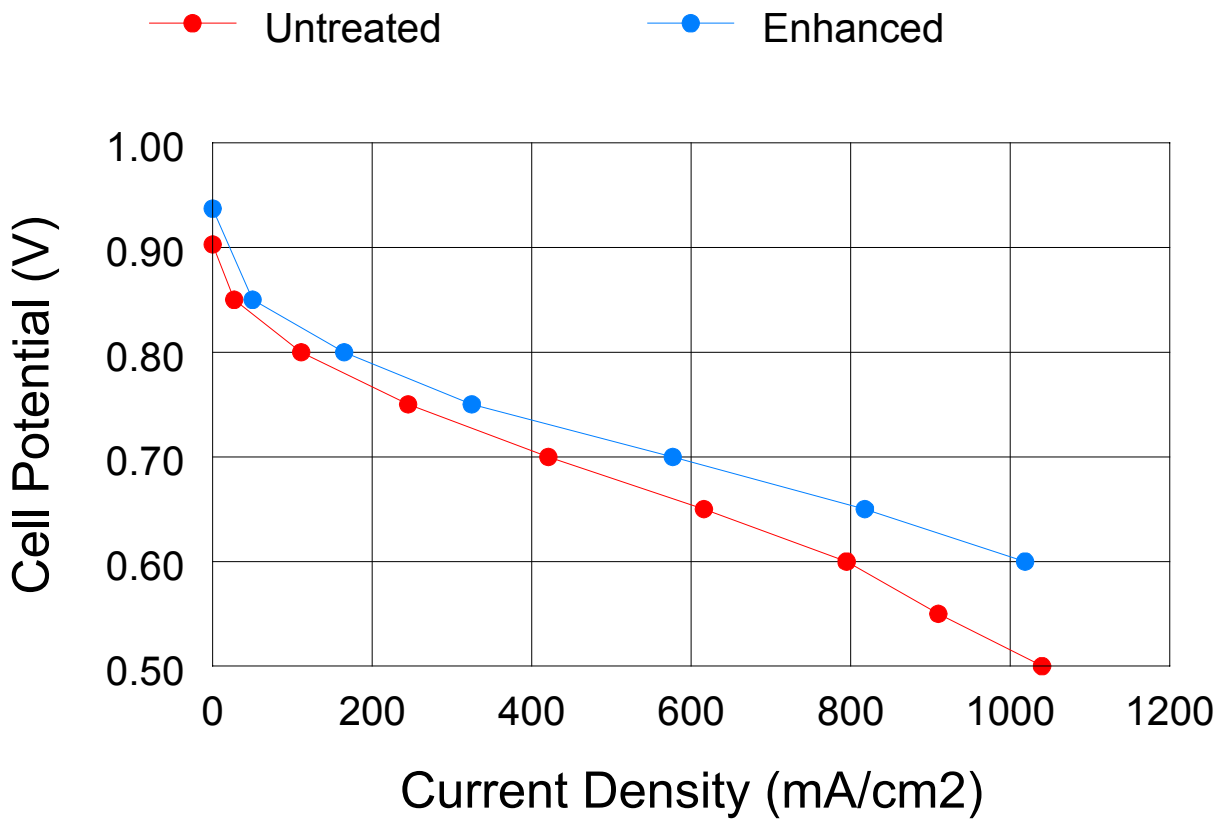
Sample MEA Performance H2-Air



MEA Performance Reformate-Air

Reformate-air(10ppm CO), ~0.15 mg/cm2 total loading

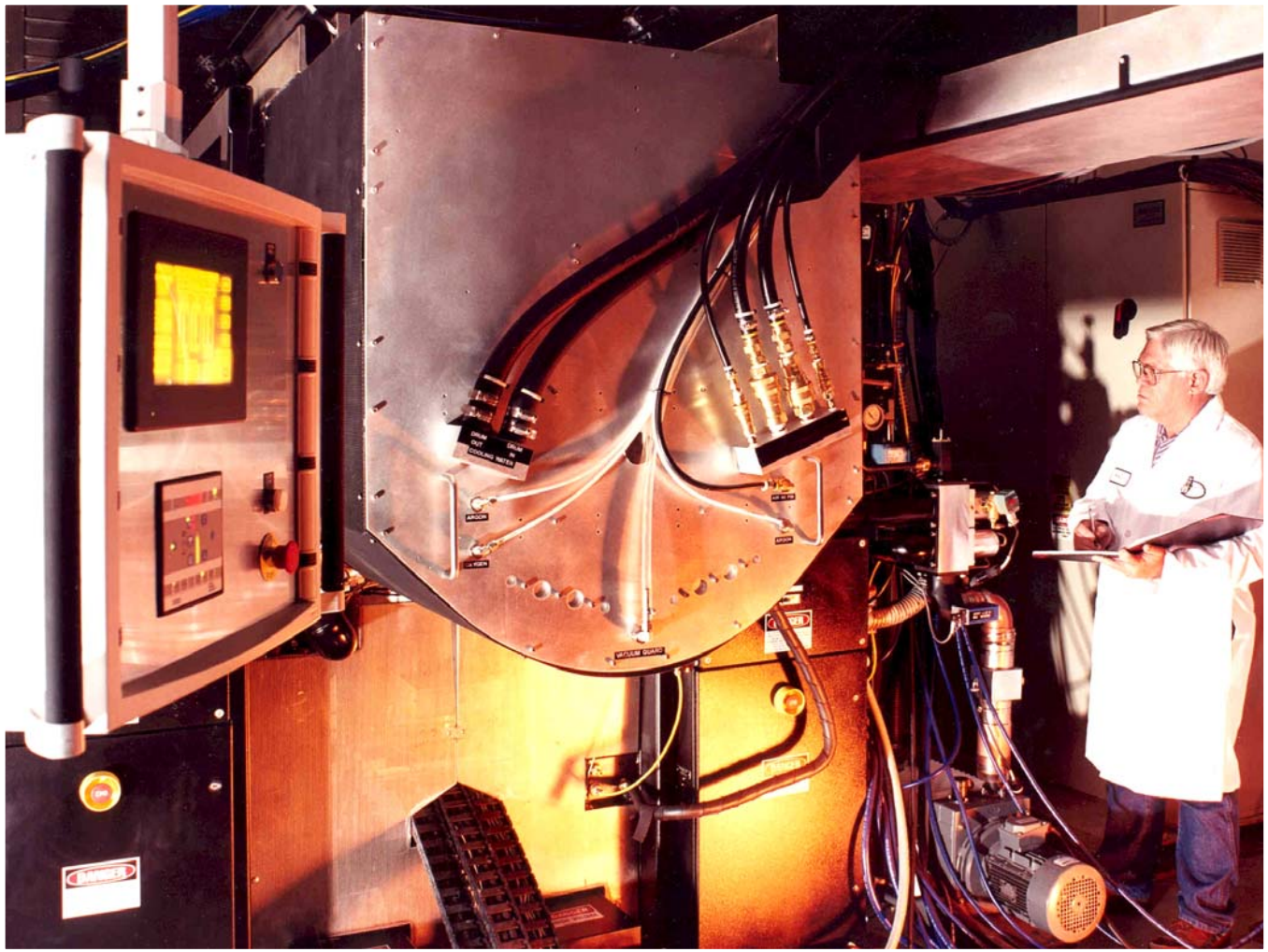
Anode/cathode/cell=105/80/80C, 17/17 psig, 1.2/2.0 stoich



SwRI Fuel Cell Material Manufacturing Facility

- Fully automated, touch-screen control
- Data logging of critical process parameters
- Real-time closed-loop control of catalyst deposition rate
- Estimated ability to catalyze enough electrode materials to make ~10,000 fuel cell “engines” each year

Virtual Tour of Facility



Accomplishments in Past Year

- Catalyzed over 3000 linear feet of electrode material as part of ongoing system optimization and production yield studies.
- Demonstrated >85% recovery of unused catalyst from shielded areas.
- Investigated effects of cell assembly, GDM, and test conditions on performance of vacuum catalyzed materials in conjunction with Gore and GM.
- Fabricated and delivered sufficient full scale (800 cm^2) MEAs for short stack evaluation at GM on reformate and H_2/air.

Remaining Tasks

- Completion of small cell durability testing at Gore.
- Conduct additional electrochemical impedance testing in concert with Gore to further investigate effects of certain key pilot system parameters.
- Final testing and delivery of stacks to ANL.

Directions for Future Research

- Large area, ultra-thin Pd alloy membranes for hydrogen purification.
- Catalysts for unitized reversible fuel cells.
- Non-precious metal fuel cell catalysts.

porvair

fuel cell technology

porvair
fuel cell technology

SCALE-UP OF CARBON /CARBON BIPOLAR PLATES

Quarterly Report to the Department of Energy, May 19-22, 2003

Cooperative Agreement DE-FC04-02AL67627

David P. Haack

Ken Butcher

porvair
fuel cell technology

ABOUT PORVAIR FUEL CELL TECHNOLOGY

A Division of the Porvair Advanced Materials Group

Core Technology in Advanced Porous Materials

porvair
fuel cell technology

DOE PROGRAM OVERALL OBJECTIVES

Scale-up of Carbon/Carbon Bipolar Plates

- **Project Objectives**
  - Build and demonstrate a pilot facility capable of producing 300 bipolar plates per hour
  - Develop a quality assurance plan for the facility
  - Demonstrate plate properties that meet or exceed performance requirements over an extended period of use
  - Perform cost analysis on plates produced with this facility and project costs to higher volume production

porvair
fuel cell technology

DOE PROGRAM OBJECTIVES

Scale-up of Carbon/Carbon Bipolar Plates

- **Phase I – Technology Development**
  - Develop materials to meet/exceed DOE and customer target specifications
  - Demonstrate plate performance in fuel cell testing at customers site
  - Investigate and develop processes having high production rate potential
  - Build a pre-pilot line capable of manufacturing 5-10 plates per hour

porvair
fuel cell technology

DOE PROGRAM OBJECTIVES

Scale-up of Carbon/Carbon Bipolar Plates

- **Phase II – Process Development and Demonstration**
  - Design and Build 300 plate/hour production line
  - Develop comprehensive quality assurance program
  - Demonstrate line capability through production metrics
  - Demonstrate 5000 hour plate operation with minimal performance degredation
  - Document product costs and project to higher volumes

porvair
fuel cell technology

PHASE I SUMMARY

Scale-up of Carbon/Carbon Bipolar Plates

- **Excellent Material Properties Achieved**
  - Electrical conductivity (thru-plane) 600 S/cm (DOE target > 100 S/cm)
  - Flexural strength (3-point bend) 4200 psi (DOE target > 610 psi crush)
  - H_2 permeability < $2x10^{-6}$ cm^2/sec (DOE target met)

porvair
fuel cell technology

PHASE I SUMMARY

Scale-up of Carbon/Carbon Bipolar Plates

- **Pre-Pilot line built and functioning**
  - Expanded line beyond scope of project to accommodate demand for plates in near-term
- **Extensive fuel cell testing performed**
  - Both single and multiple cell testing on regular basis since June 2002
  - Testing initially focused upon product demonstration
  - Recent tests performed to demonstrate new designs in transition to low cost bipolar plate products

porvair
fuel cell technology

PHASE I SUMMARY

Scale-up of Carbon/Carbon Bipolar Plates

- **High volume rate production processes investigated (on-going) in preparation for Phase II**
  - Methods for high speed material forming, pattern forming and thermal treatment investigated (some on-going)
  - Investigation yielded equipment specifications for Phase II expansion

Lawton

THERMAL TECHNOLOGY INC

porvair
fuel cell technology

PHASE II ACTIVITIES AND STATUS

Scale-up of Carbon/Carbon Bipolar Plates

- **Phase II Production Line Technology**
  - High production rate processes in concept trials
- **Phase II Line Design**
  - Concept block diagram complete
  - Cross-functional teams set-up to design line
  - Detailed schedule being generated
  - Detailed cost estimate being generated

porvair
fuel cell technology

PHASE II ACTIVITIES AND STATUS

Scale-up of Carbon/Carbon Bipolar Plates

- **Quality Assurance Program**
  - Generated and customer-audited during Phase I program
  - All documents and procedures generated to yield fully integrated quality system
    - SOP's, FMEA's, process control plan, etc.
  - System of continuous improvement installed
    - Examines process metrics
    - Utilizes cross-functional teams to generate process improvement activities

porvair
fuel cell technology

PHASE II ACTIVITIES AND STATUS

Scale-up of Carbon/Carbon Bipolar Plates

- **Quality Assurance Program (Cont.)**
  - Back-bone in place, but QA program will require modification in Phase II
    - New Control Plan, SOP's and FMEA's will be requried to match high speed process
    - Updated customer audit will be required prior to Phase II line production

porvair
fuel cell technology

PHASE II ACTIVITIES AND TIMELINE

Scale-up of Carbon/Carbon Bipolar Plates

- **Overview of Phase II Line Schedule**
  - Project Planning – May 2003
  - Process Development – Complete by July 2003
  - Facility Demolition – Complete by August 2003
  - Set-up Equipment – Complete by October 2003
  - Commissioning – October to December 2003
  - Fully Functional – mid December 2003

porvair
fuel cell technology

SUMMARY

Scale-up of Carbon/Carbon Bipolar Plates

- Phase I Activities Complete
- Phase I Process Expanded to Meet Near-Term Product Demand
- Phase II Activities for Line Expansion Underway
- Expect Phase II Line Functional by December 2003

porvair
fuel cell technology

CONCLUSIONS

Scale-up of Carbon/Carbon Bipolar Plates

- PFCT is excited about bipolar plate opportunities and future markets
- PFCT is committed to bringing the technology to a profitable business in the next two years
- PFCT's believes our bipolar plate product will be superior to the competition in properties and competitive in cost, enabling fuel cell transportation technologies to enter the market in the coming years.

High Temperature Polymer Membranes for Fuel Cells

Thomas A. Zawodzinski Jr.

Case Advanced Power Institute

Dept. of Chemical Engineering

Case Western Reserve University

Cleveland, OH

DOE Technical Barriers for Components

O. Stack Material and Manufacturing Cost

P. Durability

Q. Electrode Performance

R. Thermal and Water Management

DOE Technical Target for Fuel Cell Stack System for 2010

Cost $35/kW

Durability 5000 hours

High Temperature Membranes Participating Partners

- ⇩CWRU
- ⇩UT/Dallas
- ⇩Arizona State
- ⇩JPL
- ⇩Virginia Commonwealth
- ⇩Northeastern
- ⇩UConn
- ⇩LANL
- ⇩LBNL
- ⇩Foster-Miller

Rationale

Operation at Elevated Temperature: substantial system benefits for both automotive and stationary applications

- Auto: smaller radiator size
- Stationary: simpler reformate clean-up

- A High Temperature membrane is an enabling technology for hydrogen-based fuel cells in automotive applications!

This Effort

- Calls for development of systems for both:
  - 120°C: maybe we can use hydrated polymers
    - Focus on new polymers and other scaffolds carrying sulfonic acids or other superacids
    - 25% RH at operating temperature suggested by GM, based on system requirements
    - Need improved durability
  - >150°C: need to replace water with 'proton mobility facilitator'
    - Focus on different conduction modes, non-volatile molecules to effect proton transfer
    - Durability of any polymeric components also a must

Barriers to Overcome

1. Adequate conductivity from start-up to T > 100°C

2. Adequate polymer stability

3. Ability to fabricate MEAs with new polymers

4. Electrode performance at high T

High T Membrane/MEA Development: Organizational Approach

- ⇩ Develop team of innovative researchers in polymer synthesis, physical chemistry of electrolytes, MEA development, fuel cell testing; team assembled through proposal process

- ⇩ Work the problem from fundamentals to implementation in fuel cells

- ⇩ Seed funding provided (administered by LANL); after ~2 years, we hope to see transitions to other funding sources based on promising results

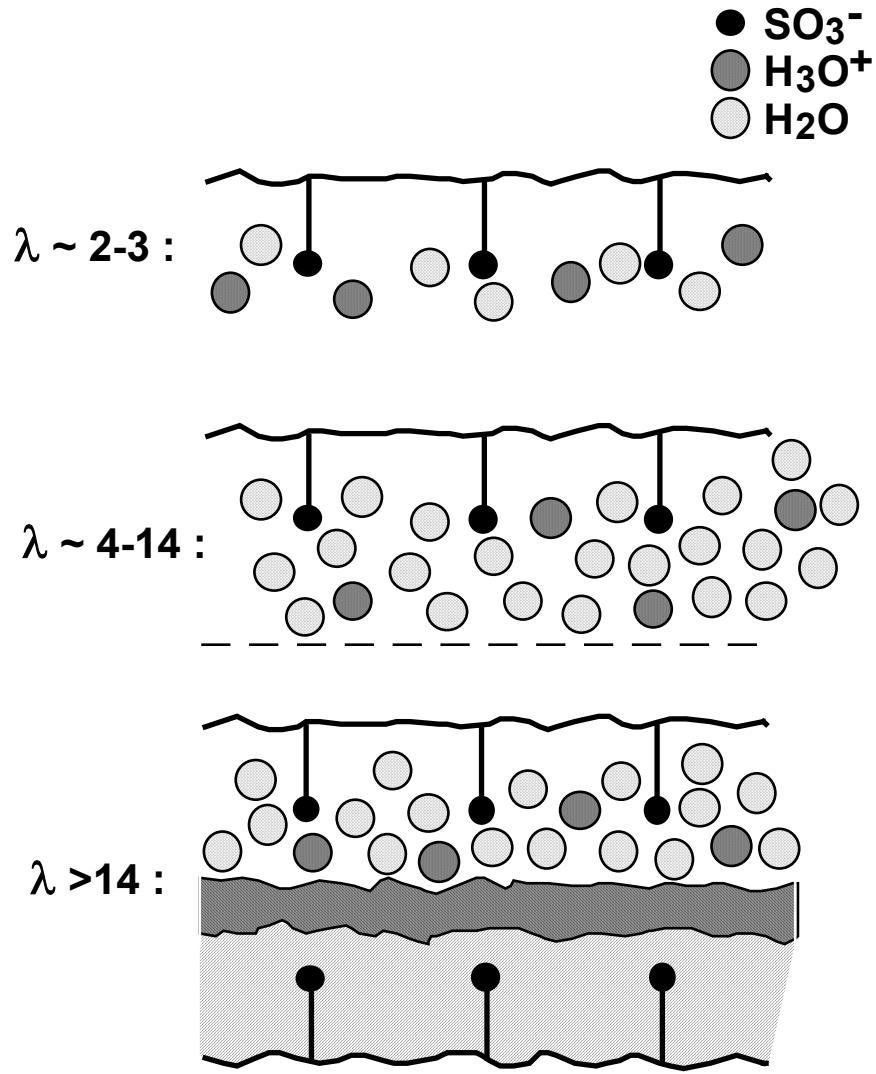
High T Membrane/MEA Development: Technical Approach

- ⇩ Synthesis based on new 'scaffolds': (different polymers, inorganic hosts etc.)
- ⇩ Using 'additives' to enhance conductivity
- ⇩ Physical chemistry and computational Studies: guiding synthetic approach
- ⇩ MEAs/Electrodes:
  - ⇩ ORR at higher temperature
  - ⇩ Electrode structure: buried interfaces within electrodes
  - ⇩ MEA fabrication for new membranes
- ⇩ Scale-up: polymers, film-making and MEA production

Proton Conduction in PEMs: A Qualitative Picture

Steps in the Process

- Dissociate
- Escape and 'Bridge the Gap'
- Plasticize



A General Approach

- Acid moieties on polymer or other support (‘scaffold’) must be connected to some type of structure

- Transport of protons require ‘extended structures’---> water or additives (ProMoFacs)

‘Scaffolds’, ProMoFacs, Acids Under Investigation in this Project

- Polymeric scaffolds
  - Poly(phosphazene), Poly(benzimidazole), Poly(phenylenes), Poly(sulfone), Poly(imide), Functionalized poly(arylene ether)
- Inorganic scaffolds
  - Silica, Alumina, Alumino-silicates
- ProMoFacs
  - Water!!
  - Imidazole, Phosphoric Acid
  - Molten Salts/Ionic Liquids
  - Solid acids
- Strong acids
  - Fluorosulfonates attached to phenyl
  - Bis(sulfonimides)

High Temperature Membranes Approaches by research group

⇩CWRU: inorganic/organic hybrid systems; new polymers; strong acid groups; electrode studies at high T; MEA making; polymer scale-up and film processing; computational studies; FC testing. (working on both temperature ranges)

⇩UT/Dallas: inorganic scaffolds with added conducting polymers (primarily high temperature range)

⇩Arizona State: molten salts (primarily high temperature range)

⇩JPL: proton conducting salts (primarily high temperature range)

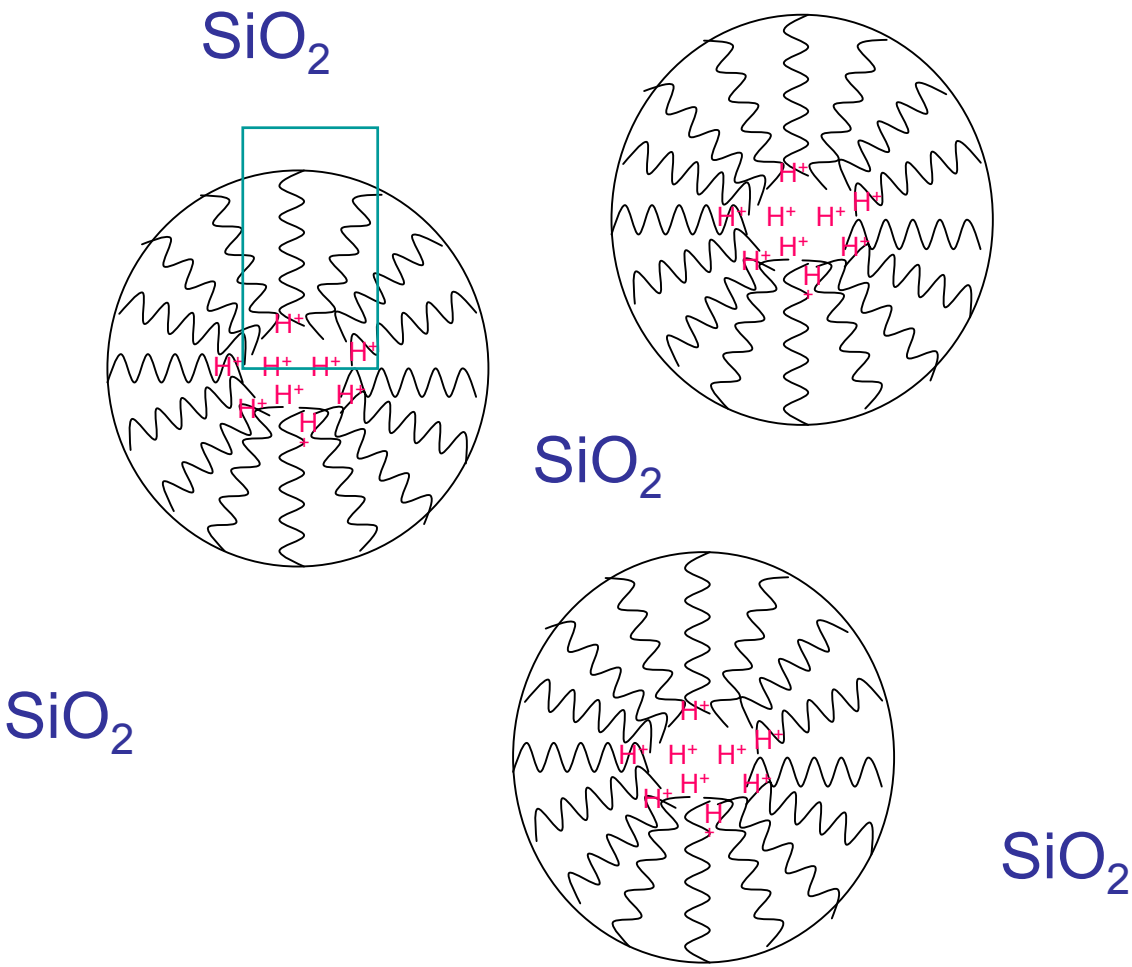
⇩Virginia Commonwealth: strong acid groups; * advanced MEA processing method (primarily low temperature range)

High Temperature Membranes Approaches by research group

⇩Northeastern: electrode studies
⇩UConn: polymer blends
⇩LANL: imidazoles, molten salts
⇩LBNL: imidazoles immobilized on polymers; composite electrode studies
⇩Foster-Miller: novel matrix loaded with imbibed ionomer

Progress and Results to Date

Attach acid moieties to nanoporous materials, Al_2O_3 or SiO_2 membranes



Concept: very close spacing of sulfonates leads to extended network of tightly bonded water leading to conducting pathway in insoluble matrix

Result:
RT conductivity ~10^{-2} S/cm; Membrane too brittle

Next steps: hybrid membranes with better physical properties

Computational Studies
A guide to development

- ⇩ Target 1: Understand proton transfer in polymer systems: studies of solvation of different types of acids extended

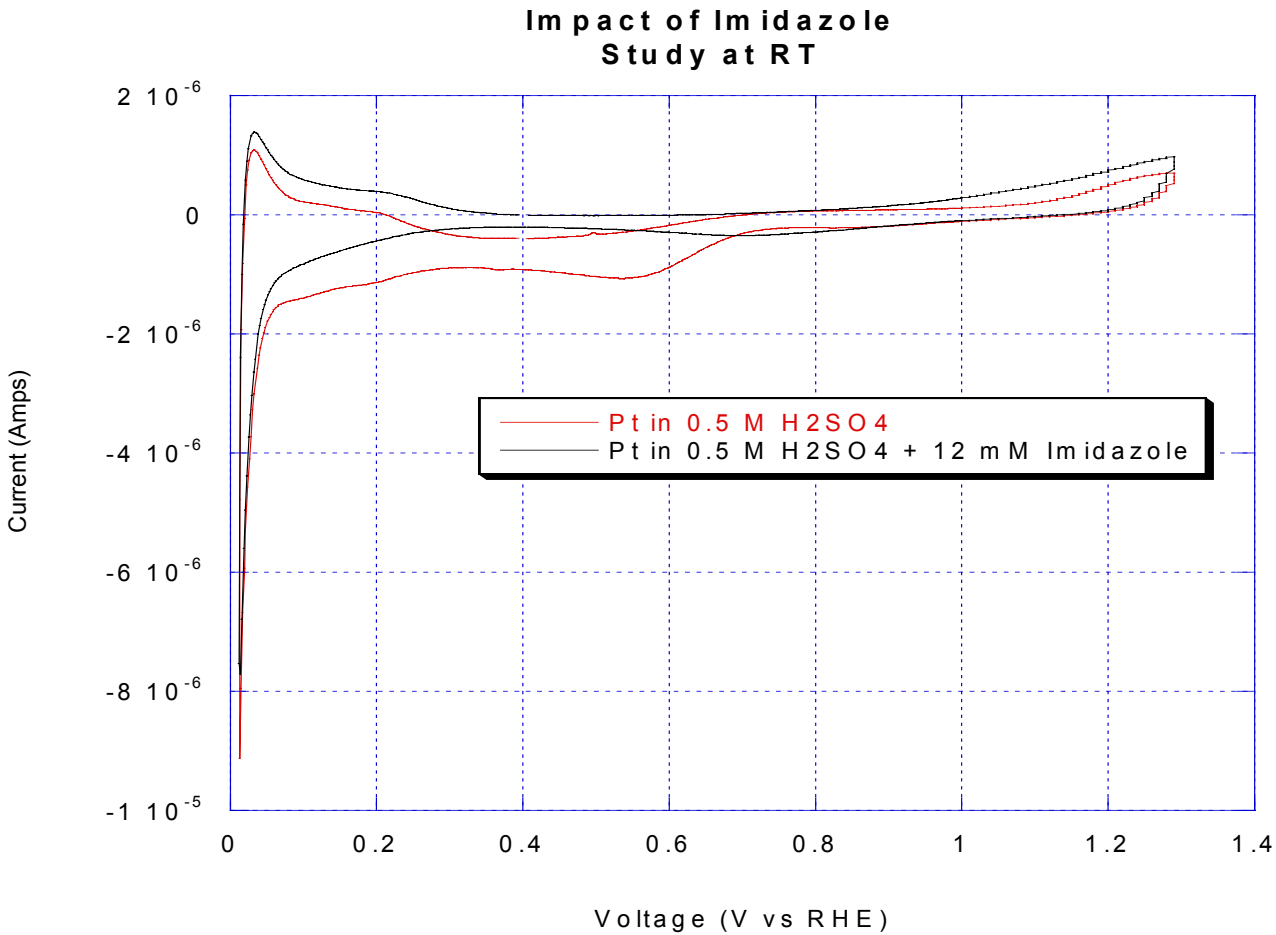
- ⇩ Target 2: Tailor bases to mimic water: electronic structure calculations to estimate pK's of appropriate bases (esp. substituted imidazoles)

Imidazole – Electrode Interaction

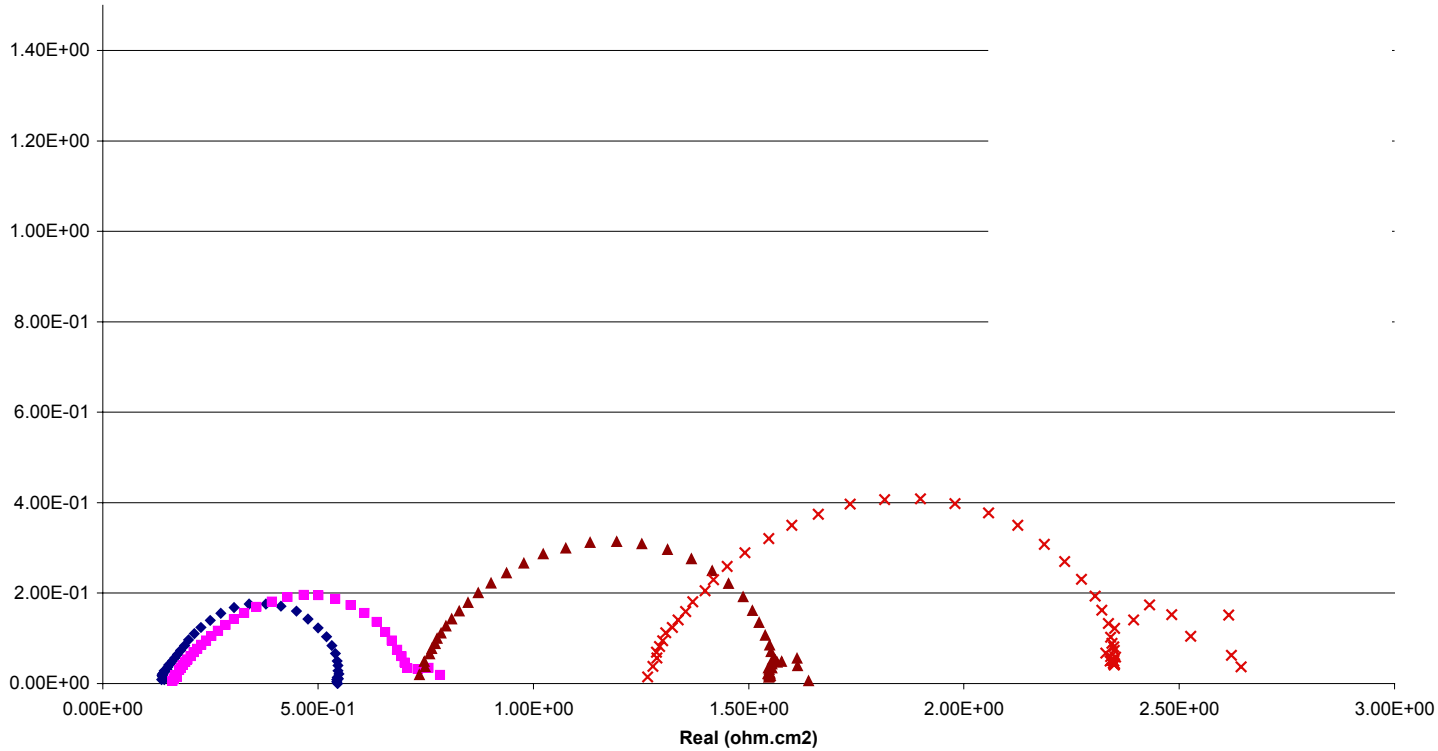
What impact does Imidazole and its derivatives have on the hydrogen oxidation and oxygen reduction ?

- Cyclic Voltammetry – adsorption – qualitative
- RDE studies – Hydrogen Oxidation, Oxygen Reduction
- Computational – looking at charge distribution

Imidazole – Electrode Interaction



Impedance Studies of Cathode under sub saturated conditions

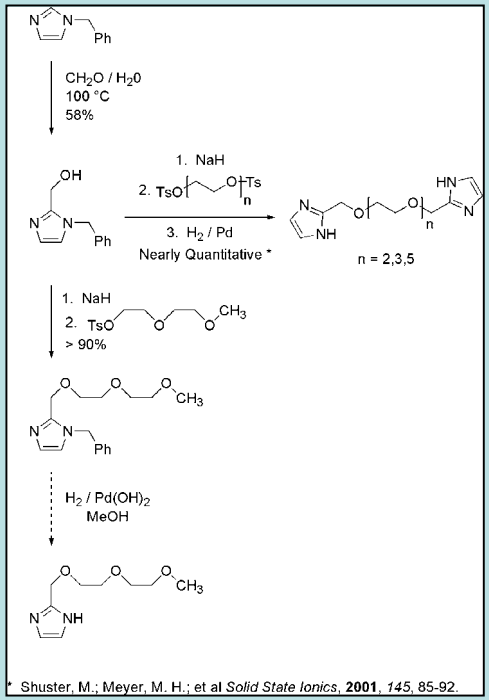


<u>Operating conditions:</u> Current density : 0.1 A/cm^2 Pressure: Ambient; Fuel: H_2; Oxidant: Oxygen; Gas utilization: 10% Cell tempr. 70 C to 100 C; Dew Point : 70 C;

LANL HTMWG Synthesis

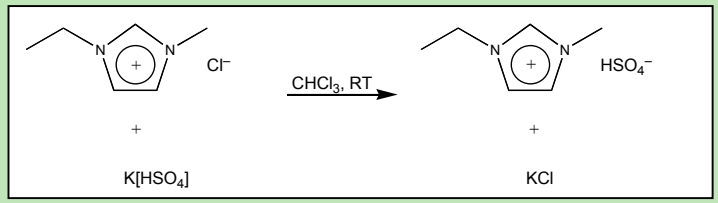
Synthesis and characterization of imidazole based materials has already yielded some initial results.
Our approach is to find materials with needed conduction properties and then incorporate into membranes.

Functionalized Imidazoles

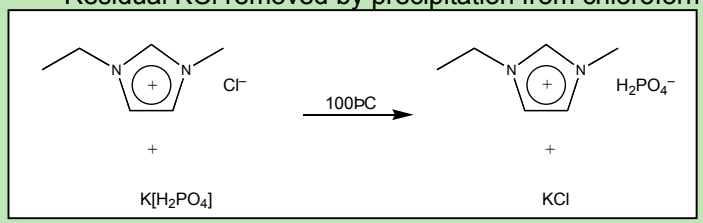


We have synthesized functionalized imidazole groups with a chemistry that could be used to tether them to polymer backbones or other porous substrates.

Ionic Liquids



- Mixture is filtered to eliminate bulk of KCl
- Residual KCl removed by precipitation from chloroform



- Solid reaction product is extracted into methanol and filtered
- Methanol is removed under vacuum and residual KCl removed by precipitation from $CHCl_3$

Ethyl Methyl Imidazolium (EMI) Salts

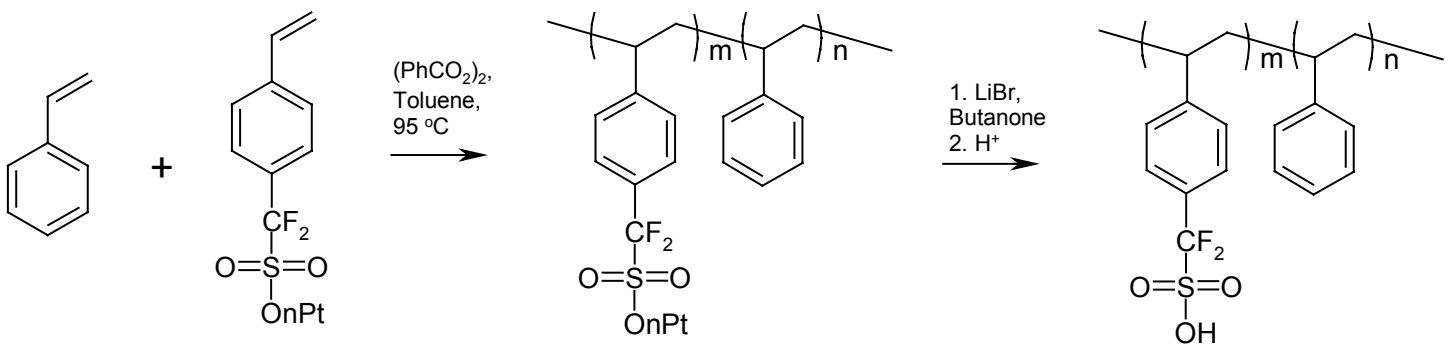
We have successfully synthesized these two proton containing imidazolium molten salts.

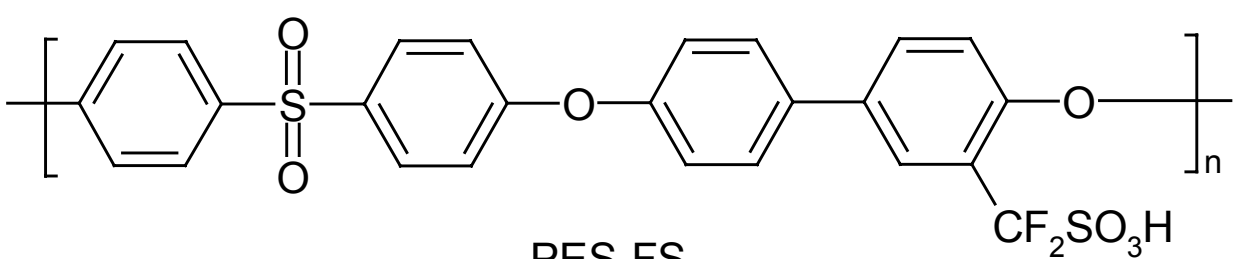
DOE High-T Membrane Program

Gary Wnek
Department of Chemical Engineering
Virginia Commonwealth University

1. Toward Routes to Functionalize Monomers and Polymers with $–CF_2SO_3H$ Units

Motivation: lower pK_a ('Nafion-like'); higher conductivity at lower water content due to lower basicity of difluorosulfonate anion; desulfonation reactions at high-T minimized.



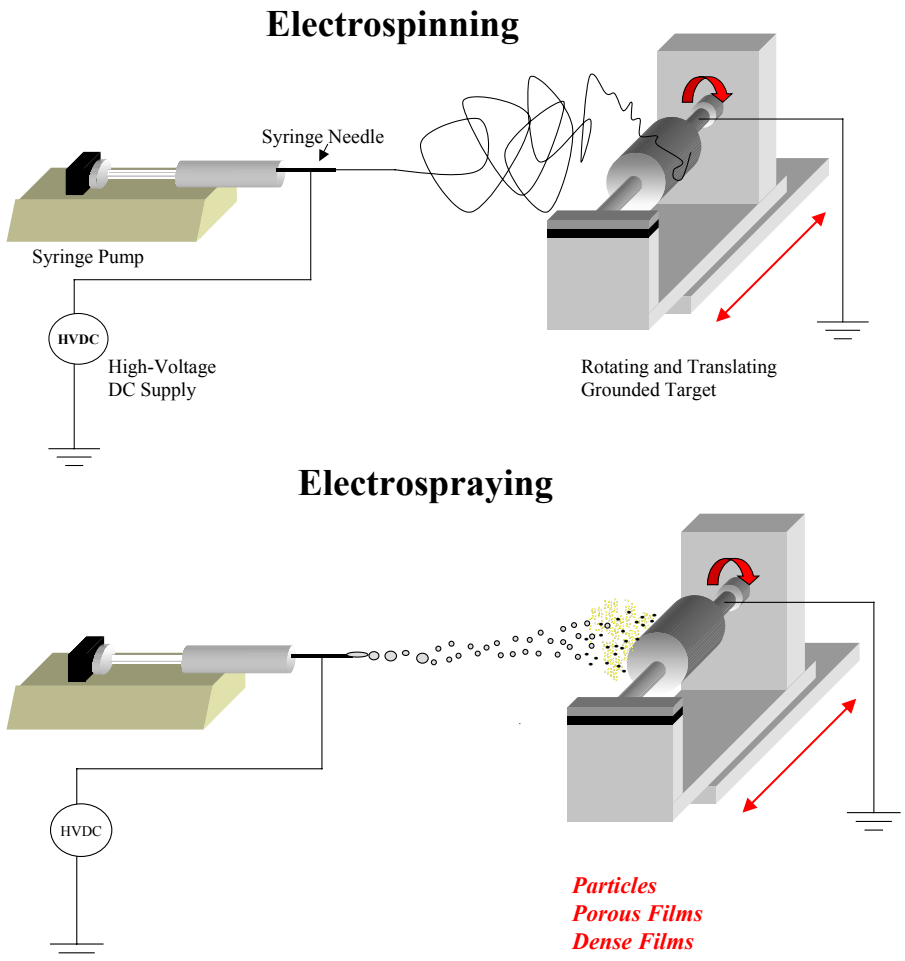


PES-FS

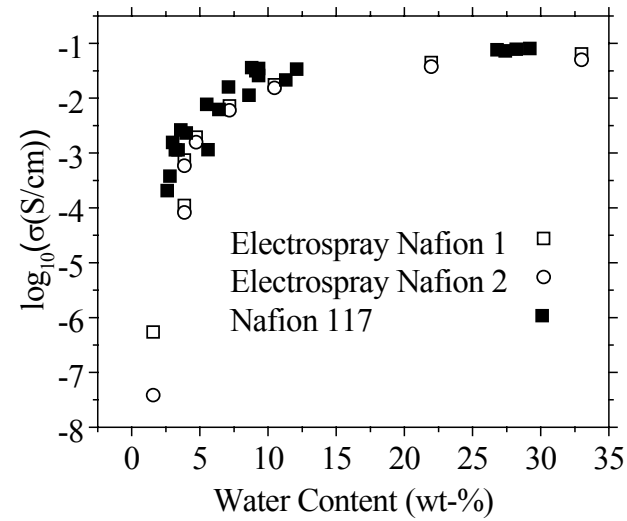
Optimization of reaction conditions and characterization of polymers are in progress

2. Electrostatic Processing (Electrospraying, Electrospinning) of PEM Components

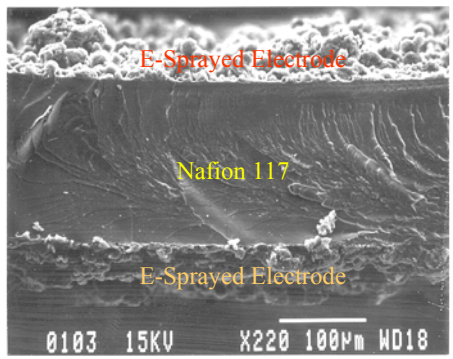
Motivation: potentially general and broad approach to tailoring PEM, electrocatalyst, and gas diffusion layer properties.



Sanders et al., in "*Advances in Materials for Proton Exchange Membrane Fuel Cell Systems,*" poster presentation abstract, Asilomar, CA, Feb. 2003.

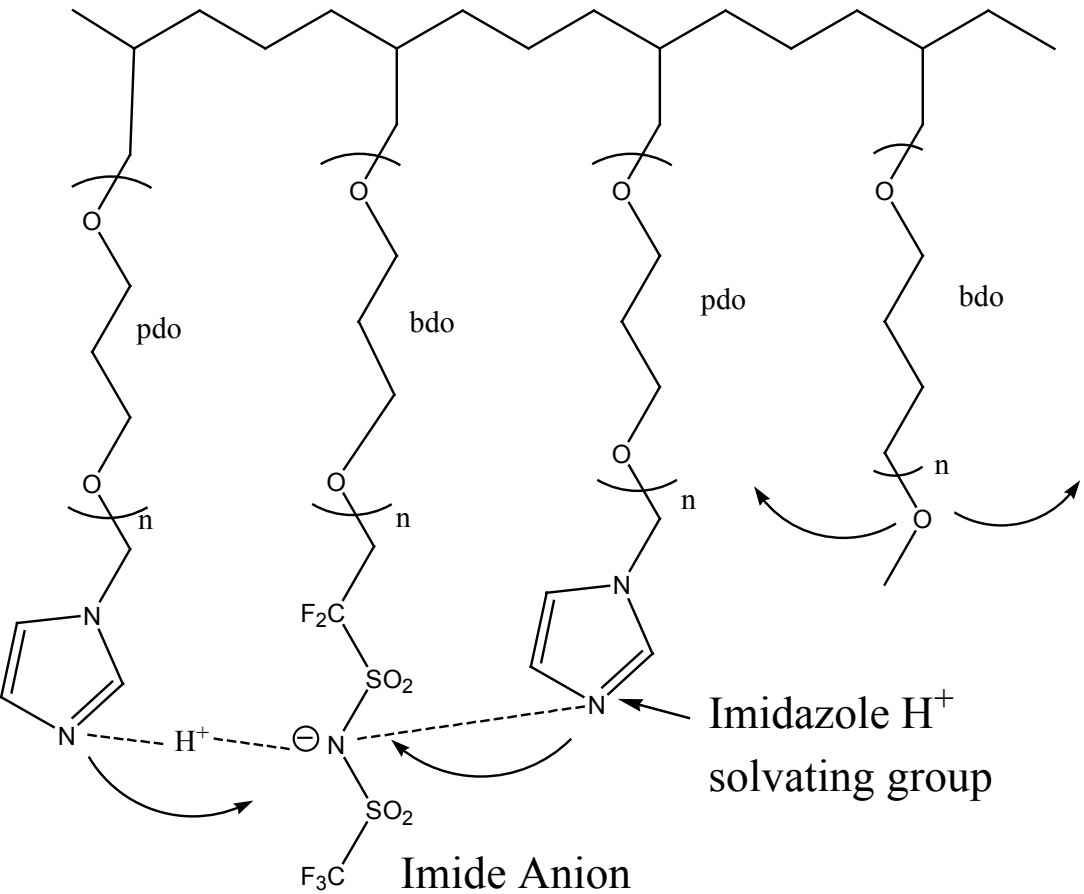


Conductivity vs. water content for 2 electrosprayed Nafion films compared w/ Nafion 117. Data from John Fontanella and Charles Edmonson, USNA



SEM of fracture surface of electrosprayed electrodes (Nafion + Pt/C) on Nafion 117 showing good adhesion between electrode and PEM

LBNL: New Polymer Architectures for Imidazole Solvating groups, Anion Mobility and Flexibility



- Attach anions and solvating groups by grafting –control nature and concentration.
- Use nature (pdo/bdo) and length of side chain to control chain mobility.
- Backbone (PE, polystyrene, polysiloxane) and cross-link density to control mechanical & morphological properties.
- Degradation results in Release of small fragments - facilitates failure analysis.

ARIZONA STATE UNIVERSITY

1. Liquids for ambient-to-high-temperature applications are provided by **ATMS** (Ambient Temperature Molten Salts). These are vapor-free.
2. ATMS with exchangeable protons can be prepared by using anhydrous Brönsted acid-base reactions

CHARACTERIZATION DATA:

1. **Vapor pressure**
We can correlate the depression of vapor pressure over these liquids with the difference in pKa values of the reacting pair, using aqueous solution data and plotting against excess boiling point (see Fig. 1). Some liquids are stable against boiling to >300ºC (Tb estimated for propylammonium triflate is ≈700ºC, far exceeding the decomposition temperature)

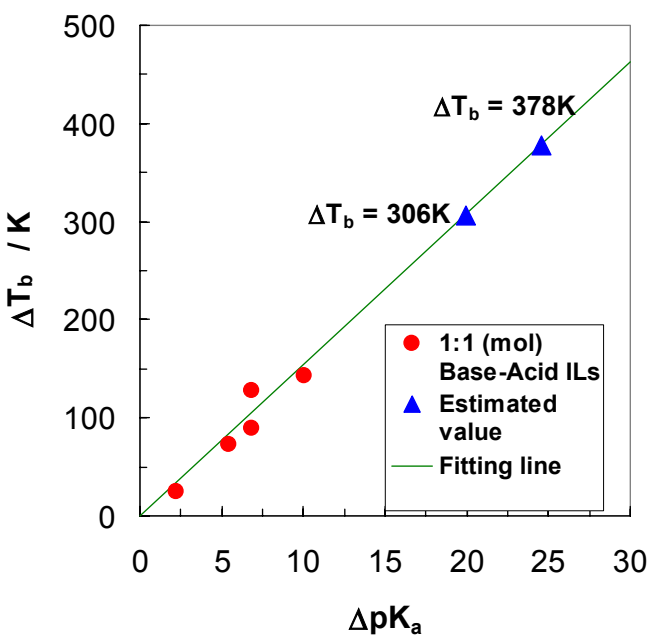


Figure 1. Relationship of ΔT_b and ΔpK_a

2. **Conductivity.**
Some of these proton transfer ionic liquids in their neutral state can have extremely high ionic conductivities, rivaling aqueous solutions. They also support formation of dianion complexes, which have even higher conductances.

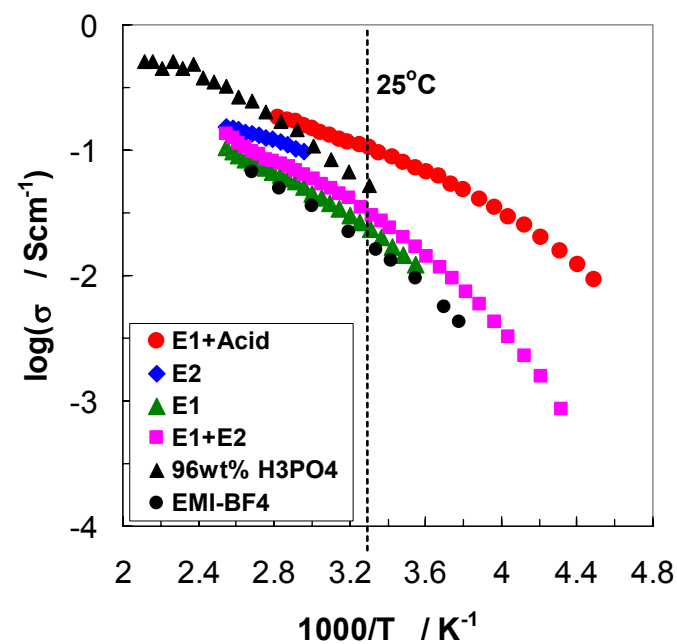


Figure 2. Temperature Dependence of the Conductivity

Nanostructured Hybrid Membranes for High Temperature Fuel Cells

Performer: Dr. John P. Ferraris and Dr. Kenneth J. Balkus, Jr.
Department of Chemistry
The University of Texas at Dallas

Objective:

- The design and experimental demonstration of polymer/molecular sieve composite membranes with high proton conductivity.

Payoffs:

- Mesoporous molecular sieves
  - Thermal stability
  - Chemical stability
  - Proton conductivity
  - Water-retention
- Organic/polymer
  - Proton conducting
  - Flexible
  - Less fuel crossover
- Polymer/molecular sieve composites:
  - Proton conducting
  - Thermal/chemical stability

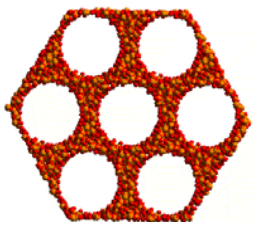
Approach:

- Proton conducting mesoporous molecular sieves.
  - Sulfonic acid functionalized mesoporous silica
  - Sulfonated mesoporous benzene silica (MBS)
  - Tungsten silicates and tungsten phosphate molecular sieves
  - Mesoporous silica filled with polyaniline (PANI)
  - Free standing molecular sieve films
- Prepare and investigate proton conductivity of acid doped free standing *meta*-PANI films.
- Prepare and investigate proton conductivity of sol-gel hybrid acid doped polyethyleneimine (PEI).
- Prepare and investigate sulfonated PEI.
- Investigate proton conductivity of acid doped polymer/molecular sieve composite.

Nanostructured Hybrid Membranes for High Temperature Fuel Cells

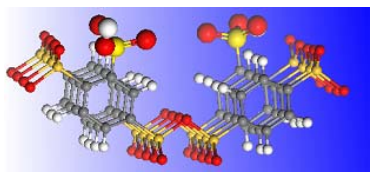
Accomplishments:

- Functionalized mesoporous molecular sieves:
  - PANI filled SBA-15 was prepared
  - MBS was prepared, and ~15% of phenyl rings were sulfonated.
  - Sulfonic acid functionalized SBA-15 was prepared
  - Tungsten silicates and tungsten phosphate molecular sieves are under development.
- Proton conductivity of H_3PO_4-doped *meta*-PANI was investigated.
- Sol-gel/PEI hybrid membrane doped using different acids and proton conductivity are under investigation.
- Polymer/molecular sieve composites are under development.

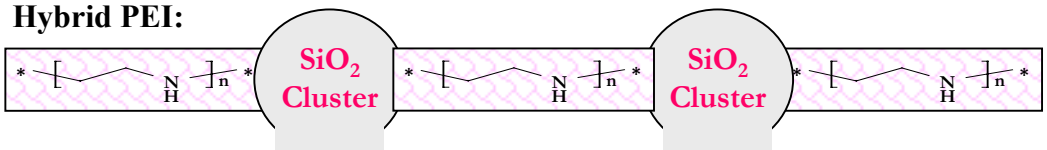


SBA-15

Sulfonated MBS



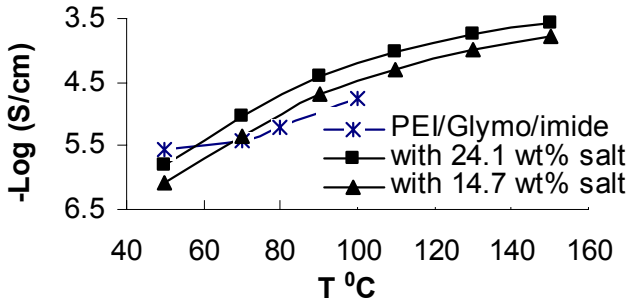
Hybrid PEI:



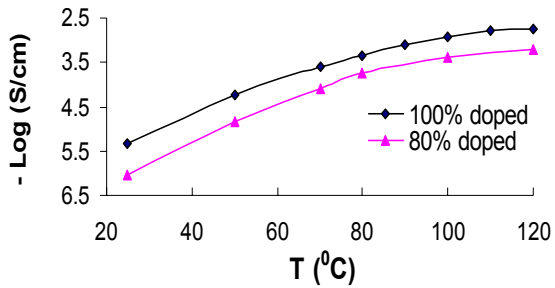
(a) σ of molecular sieves

Materials	Water content (wt%)	- Log σ (S/cm)
Sulfonated MBS	64.9	1.61
Sulfonated SBA-15	55.5	1.85
W-MCM-41 (W/Si=0.025)	42.4	1.75
W-MCM-41 (W/Si=15)	20.6	1.48
Si-MCM-41	21.5	1.30

(b) σ of PEI films under dry conditions, with or without Trifluoromethyl sulfonimide-dipropylamine salt



(c) σ of H_3PO_4-doped *m*-PANI



High Temperature Membrane Working Group

- ⇩ Meeting bi-annually (typically associated with ECS meetings)
- ⇩ Representatives from a variety of industry, academic and national lab groups
- ⇩ Recent briefings and guidance from GM, 3M, UTC, WL Gore, DuPont etc.

Roadmap: Research Topics

Priority	Approach/Research Topic	Approx. Timeframe
High	New polymers with improved thermal stability (non-Nafion systems)	To 2008
Medium	Polymers with hydrophilic additives or improved hydrophilicity	To 2004
Medium	Polymers with added acids	To 2004
Low	Water-dependent inorganic conductors	To 2003
Medium	Phosphoric acid-based systems	To 2006
High	Non-aqueous proton conducting phases as additives	To 2008
Medium	Inorganic conductors	To 2008
High	Adhesion between polymer membrane and catalyst layer	To 2008
Medium	Materials properties of catalyst layers	To 2008
High	Understanding of proton dissociation, conduction in non-aqueous systems	To 2008
High	Non-adsorbing ionic conducting phases	To 2008
High	Understanding, Improving local structure in catalyst layers and its relation to function	To 2008

Roadmap dates in process of updating!

Summary/Future Directions

•We feel that this program is finally 'launched'; mix of funded players emphasizes synthesis

•Continue directions described above

- •Start developing MEAs from new materials (CWRU)
- •Begin to distribute 'lessons learned' info via website

•Next round of new start funding: increased emphasis on 120°C solutions

•Continue to streamline funding process

Electrodes for PEMFC Operation on H_2 and Reformate

Los Alamos National Laboratory
Materials Science Division

Peter Adcock
Guido Bender
Eric Brosha
Fernando Garzon
George Havrilla
Kirsten Norman
Tommy Rockward
Judith Valerio
Andrew Saab
Wayne Smith
Francisco Uribe (presenter)
Mahlon Wilson
Jian Xie

DOE Program Manager: Nancy Garland
LANL Program Manager: Ken Stroh

Hydrogen, Fuel Cells and Infrastructure Technologies Program
Annual Review, Berkeley, CA, May 2003

Los Alamos
NATIONAL LABORATORY

Response to Comments from 2002 Review

* **Investigate long term stability of the Adzic catalyst.**

  → ***A 500 hr FC test with this catalyst (1 wt%Pt-10 wt%Ru) is currently in progress. New improved catalyst will be tested.***

* **Should focus on development of evaluation "tools" to identify better electrodes.**

  → ***In addition to traditional electrochemical methods, fundamental relationships between electrode structure and properties were studied with newly developed methods such as scanning XRF imaging, simultaneous measurement of catalyst layer electronic and ionic conductivities and catalyst layer porosity measurements.***

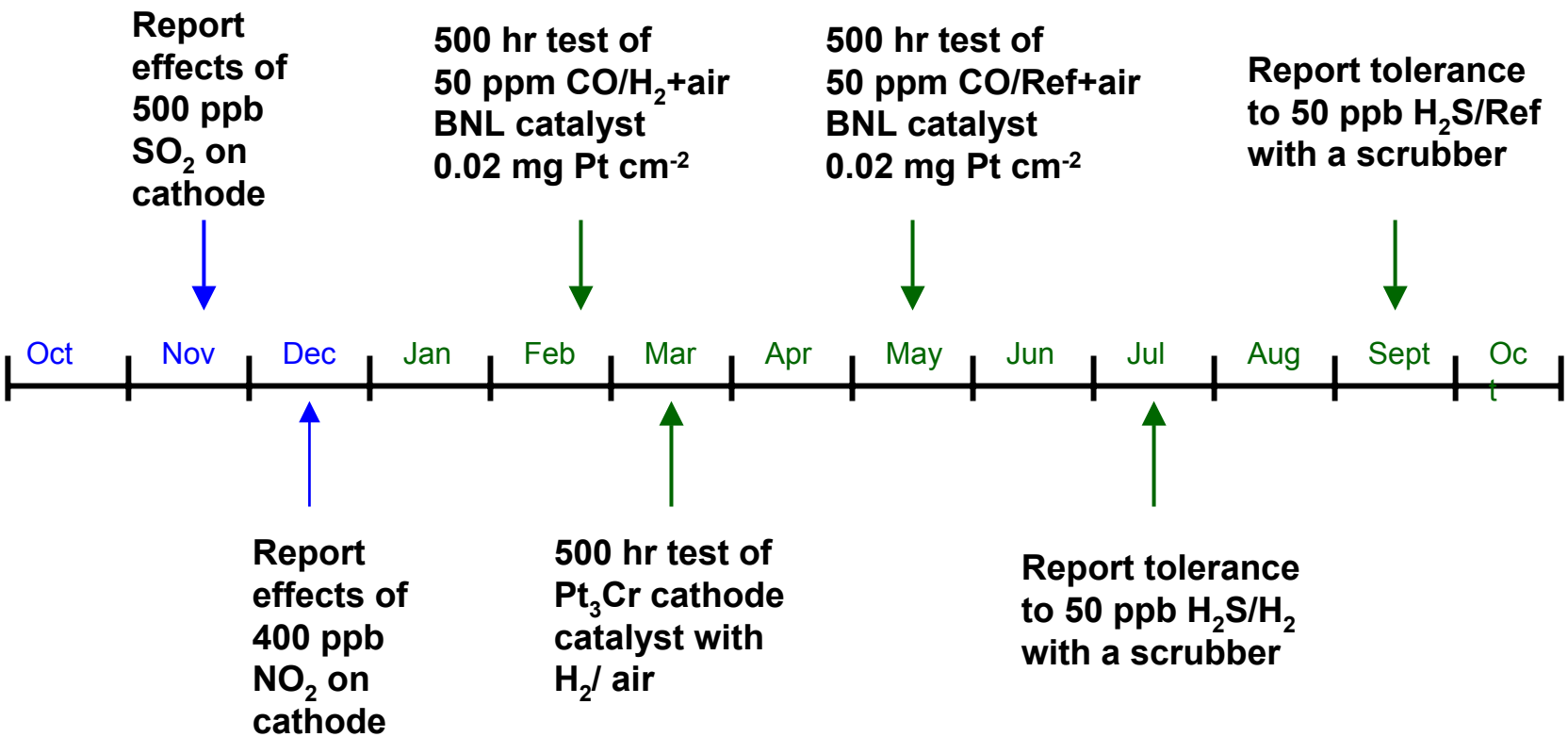
* **Emphasize interactions that develop more fundamental understanding of catalyst and electrodes.**

  → ***On going collaborations with ORNL and BNL for studying MEA structure and low Pt content catalysts.***

* **Appropriate project for national laboratory to develop tools and criteria to evaluate catalyst and electrode performance from a neutral perspective.**

  → ***LANL is a key participant in developing and performing the "single cell test protocol", implemented by the U.S.Fuel Cell Council in collaboration with private industry.***

Work Timeline



Collaborations and Outreach Activities

Donaldson (E. Stenersen) **: Ambient air impurities** (CRADA)

DuPont: MEA evaluation (CRADA)

SMP (P. Atanasova)**: Catalyst Testing**

OMG: Catalyst Testing

TKK: Catalyst Testing

Brookhaven NL (R. Adzic)**: Evaluation of low Pt content catalysts**

Navy Research Laboratory: LANL hosted researchers

USA Fuel Cell Council: Single cell test protocol

Presentations at: ACS Asilomar Meeting, ECS Mtg., FC Seminar, FreedomCar Technical Team Mtg., Alabama EPSCOR workshop.

Anode Work: Goals and Approach

Overall Goal: Improve CO Tolerance and study the effects of other impurities on FC performance

* Improve tolerance to CO using reconfigured anodes (RCA) while optimizing air bleed

* Develop and test new materials for reconfigured anodes

* GC measurements for understanding RCA operation

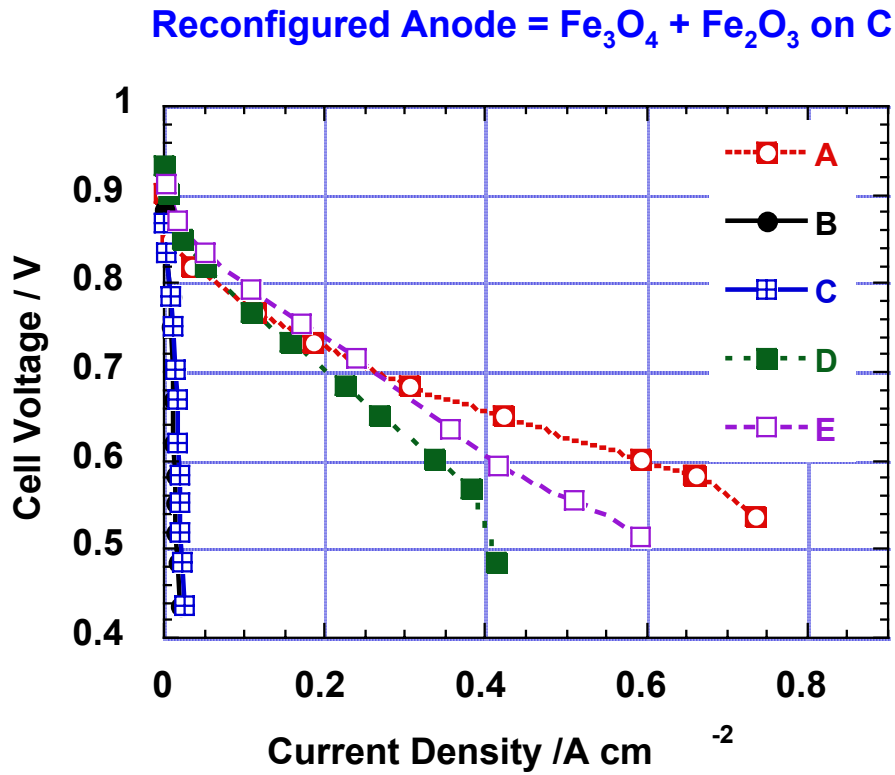
* Evaluate low Pt content catalysts (R. Adzic, BNL)

* Study effects of impurities on electronic and ionic conductivity of the catalyst layer

* Model various " poisoning mechanisms"

* Diagnostic Tools:
  Advanced Segmented Cell
  Method for measuring ionic and electronic conductivities in the catalyst layer

Incomplete Tolerance to 500 ppm CO in Synthetic Reformate



A RCA, Pt (0.2 mg cm^{-2}), No CO and No Air
B RCA, Pt (0.2 mg cm^{-2}), 500 ppm CO, No air
C RCA, Pt (0.2 mg cm^{-2}), 500 ppm CO + 6% air
D No RCA, Pt-Ru (0.1 mg Pt cm^{-2}), 500 ppm CO + 6% air
E RCA, Pt-Ru (0.1 mg Pt cm^{-2}), 500 ppm CO + 6% air

Even 6% air-bleed makes practically no difference with a Pt anode.

The RCA layer improves CO tolerance of Pt-Ru anode in the presence of 6% air. However, above about 0.35 A cm^{-2}, tolerance is incomplete.

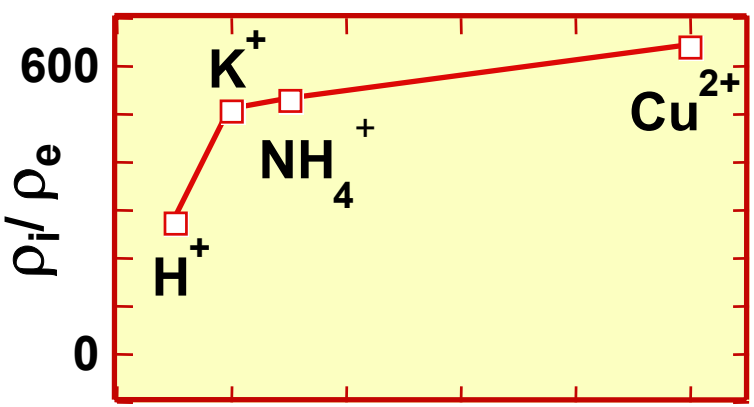
Full tolerance in synthetic reformate has been demonstrated for up to 250 ppm CO.

Effect of contaminant ions on catalyst layer ionic resistivity

Nafion Form	$\frac{\rho_{ionic}}{\rho_{electronic}}$
H^+	273
K^+	504
NH_4^+	528
Cu^{2+}	640

$\rho_{electronic} \approx 1\ \Omega\cdot cm$ all cases

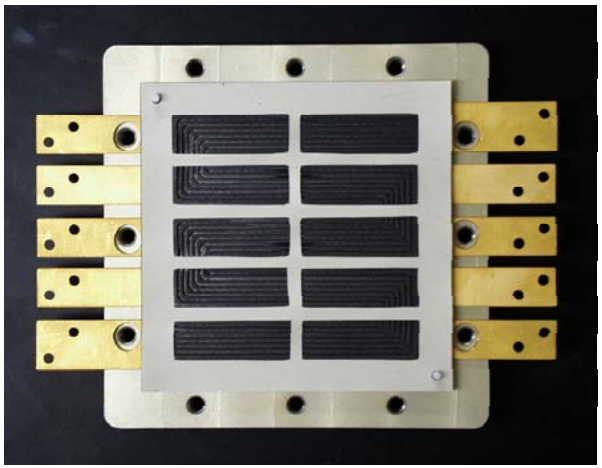
- When H^+ in catalyst layers containing acid-form Nafion is exchanged for other ions, an increase in ionic resistivity results



Relative Ion Exchange Selectivity for Sulfonated Polystyrene (Arb. Units)

- The increase in resistivity parallels the trend in ion exchange selectivity of sulfonate ionomer

Advanced Segmented Cell Hardware and Test



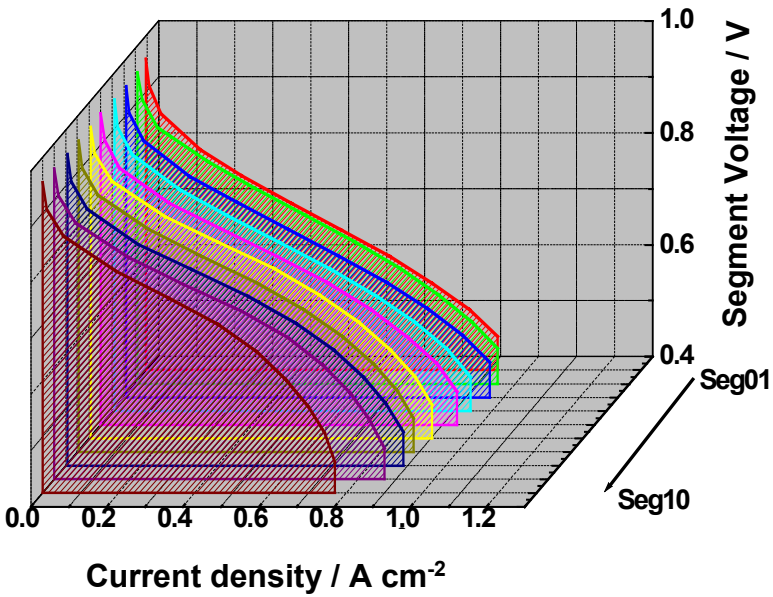
Segment area: 7.71 cm^2

New characteristics of cell hardware:

* Faster time resolution (10 samples/sec)
* AC Impedance measurements possible
* Highly reproducible segmented MEA electrodes

Objectives:

* measure current, voltage, HFR distribution
* study spatial CO and CO coverage
* optimize flow-field design and water management



Observations

* current distribution not homogeneous
* downstream effects along the flow channel
* water management issues
* performance enhancement possible

Anode: 810 sccm H_2, T_A=105°C, p=30psig

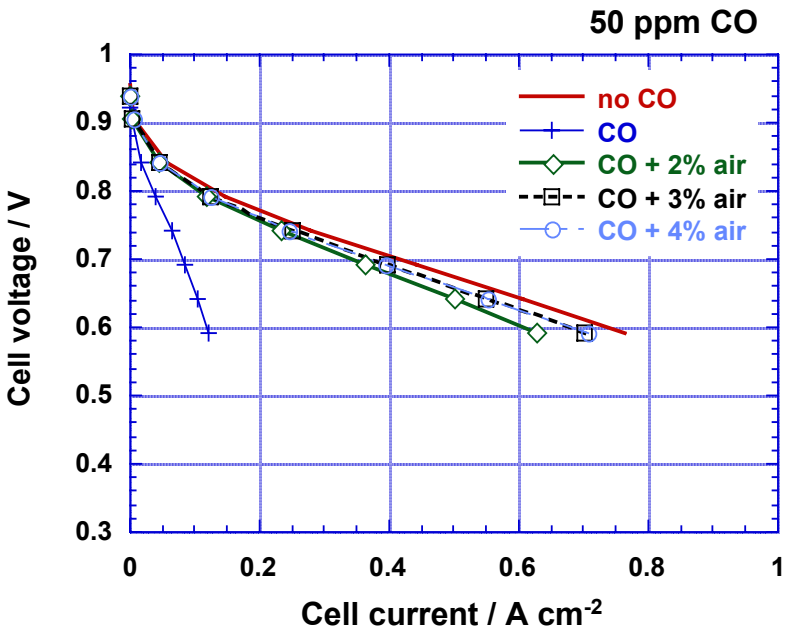
Cathode: 4000 sccm Air, T_C=80°C, p=30psig

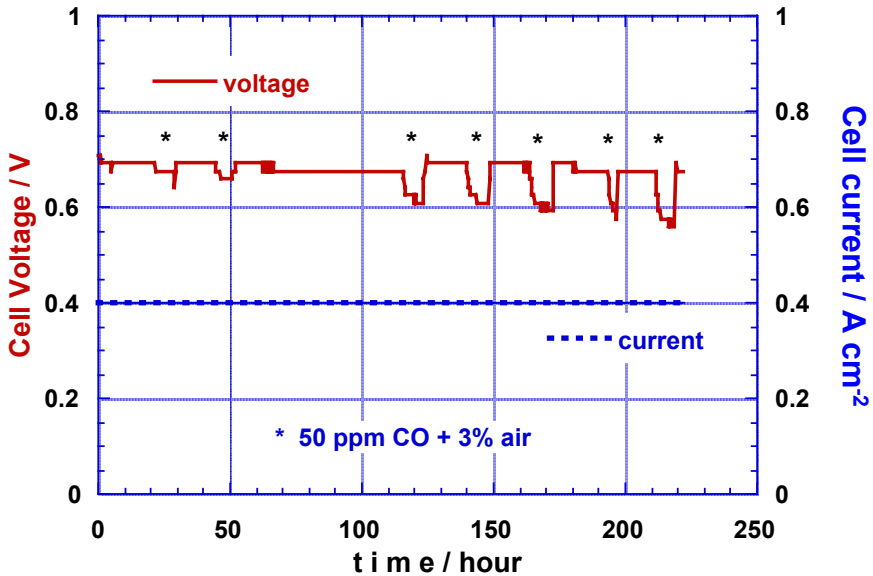
Cell temp. = 80°C, 0.2 mg Pt/cm^2 at each electrode

Low Pt Content Catalyst Long Term Test

Carbon supported 1 wt% Pt - 10 wt%Ru catalyst (R. Adzic, BNL)

Anode Pt Loading: 19 µg/cm^{-2}





50 cm^2 H_2/Air cell at 80 ^oC
A: 0.21 mg total metal/cm^2
C: 0.20 mg Pt/ cm^2
1.5 H_2 stoich

* **48.5 hrs operation with 50 ppm CO + 3% air**
* **Performance loss of 100 mV after 222 hr of operation at 0.4 A/cm^2**

Cathode Work: Goals and Approach

Goals : Improve cathode performance at high voltages
New catalyst development
Investigate effects of air impurities

* Work with catalyst suppliers to develop improved cathode catalysts

* Evaluate catalysts with high Pt content but small particle size

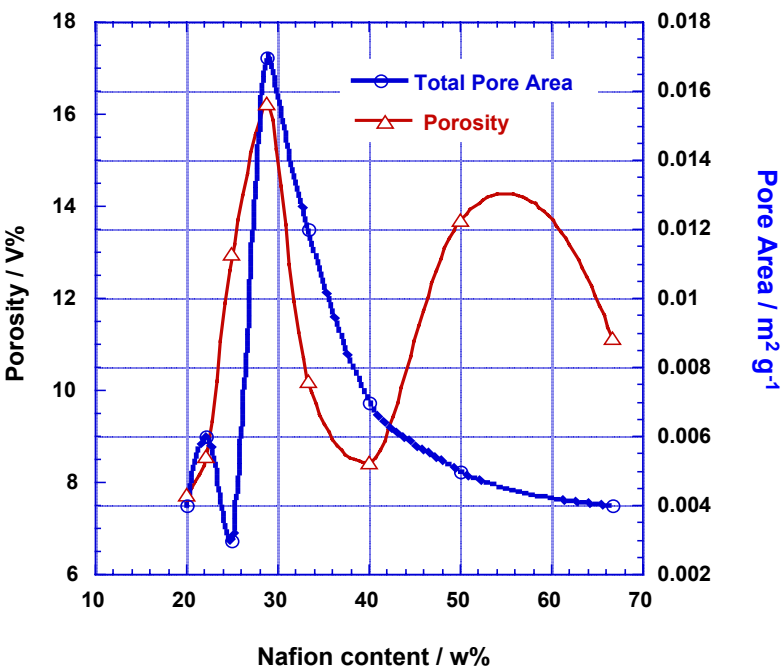
* Study cathode structure and performance relationship: New diagnostic tools (Porosimetry studies, XRF imaging)

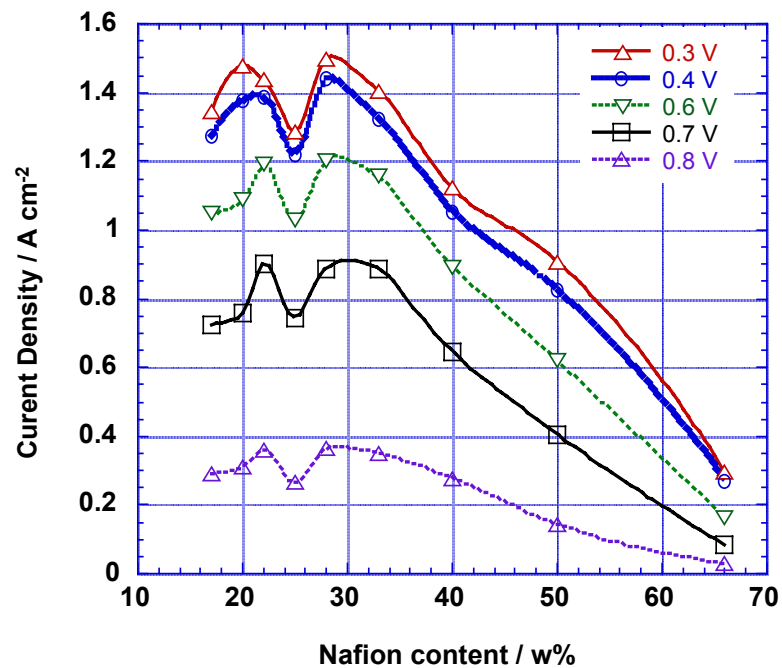
* Evaluate long term performance of Pt-Alloys

* Plan for non-precious metals catalysts development

* Study the effect of ambient air impurities on cathode performance (SO_2, NO_2, sea water, diesel soot, hydrocarbons)

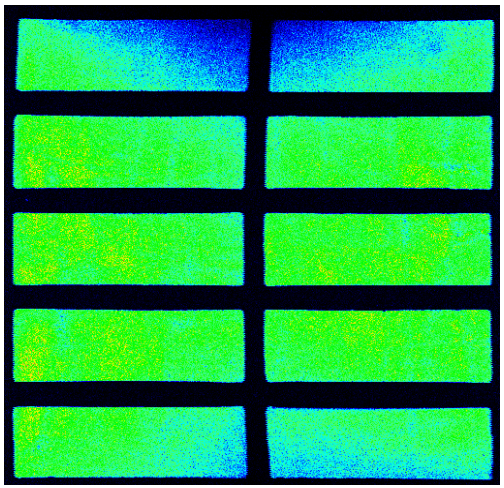
Pt_3Cr Catalyst Layer Porosimetry Data and Cathode Performance as a Function of Nafion Content



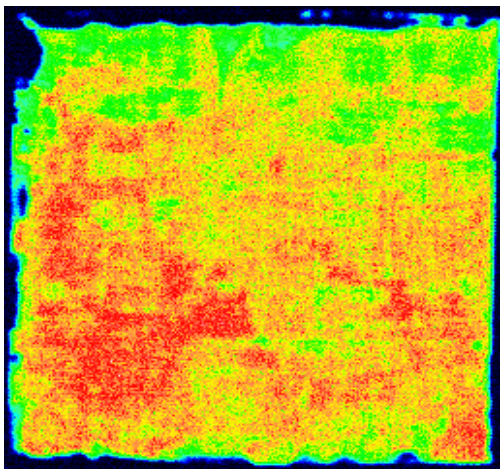


- **Porosimetry data demonstrates good correlation between MEA Nafion content and current density**

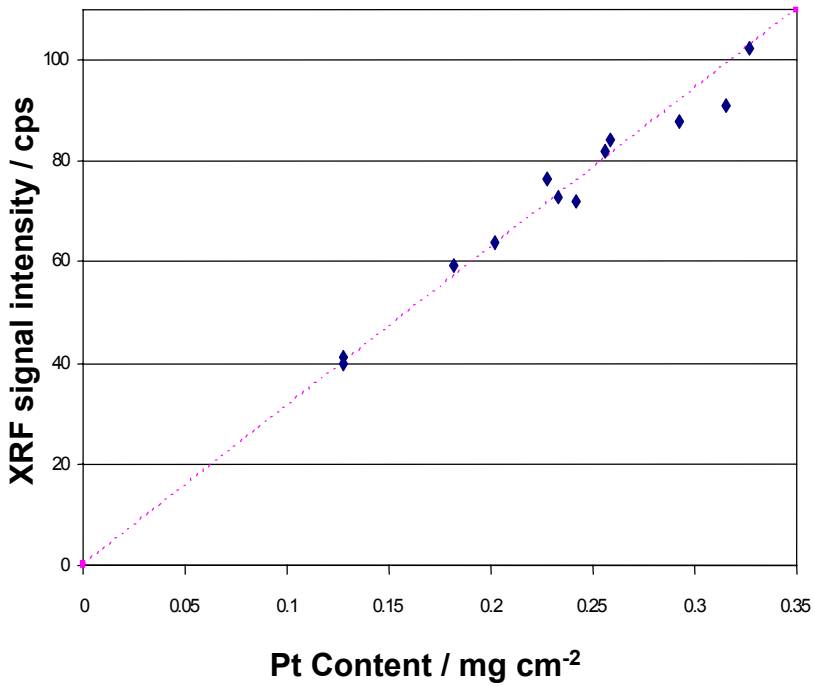
XRF Imaging and Pt Content



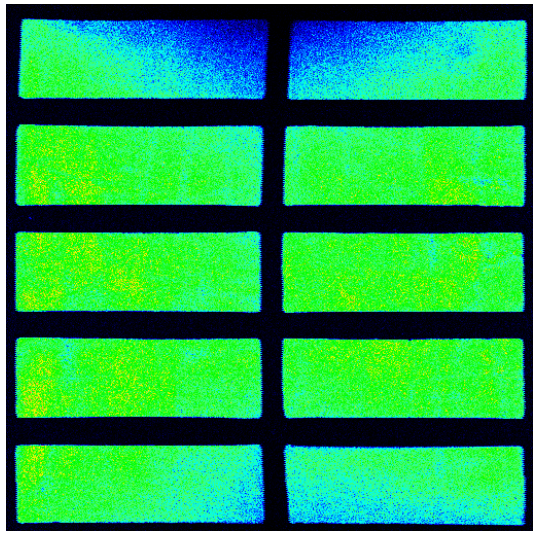
Anode side
Pt M-Line
(doctor bladed)

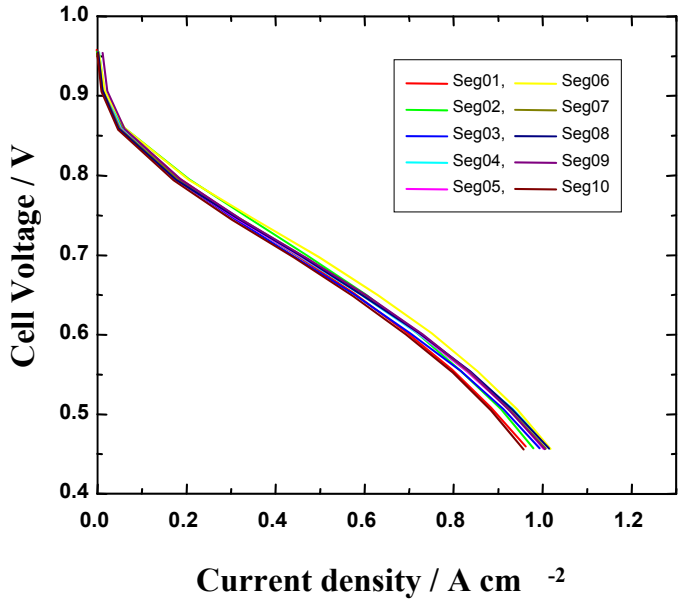


Cathode side
Pt M-Line
(hand painted)



XRF Imaging and Segment Performance in the Segmented Cell





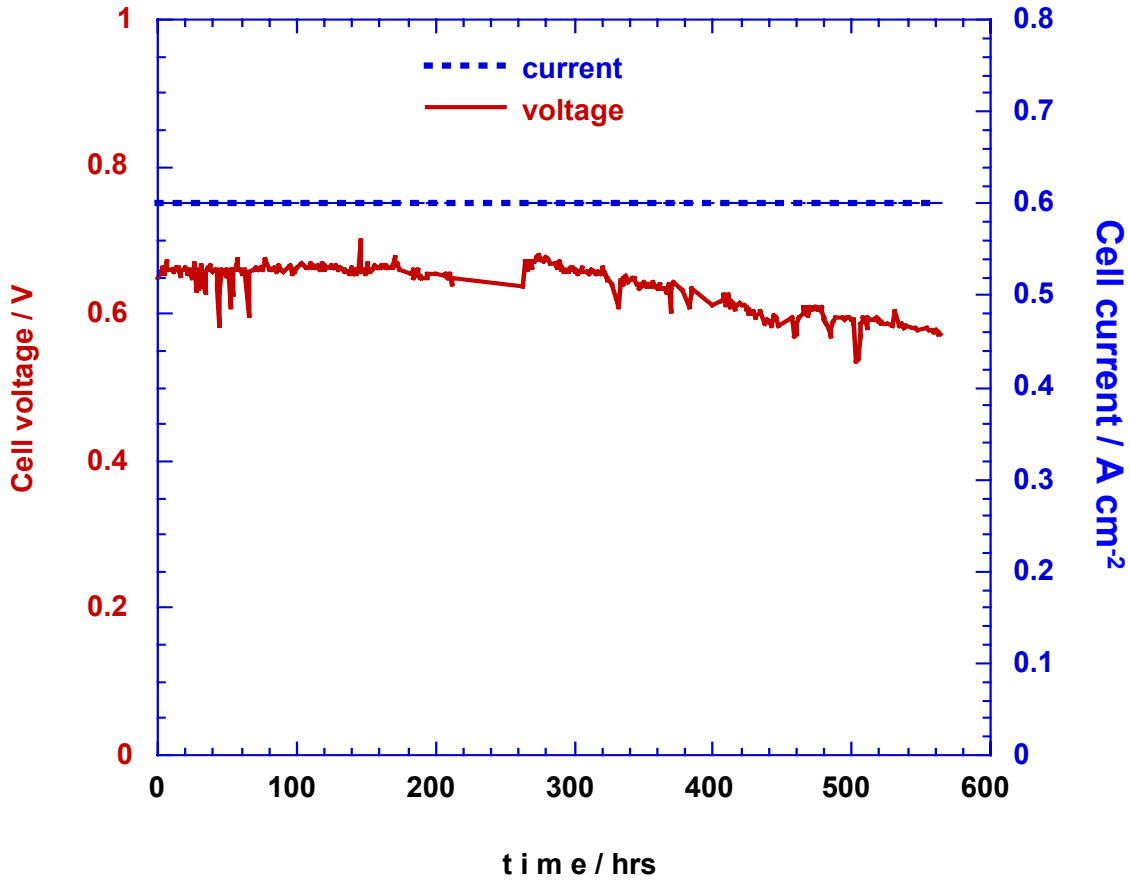
- Image shows even Pt distribution in all segments
- Even Pt distribution generates equivalent currents in all segments

Anode: 810 sccm H_2 , T_A=105°C, p=30psig

Cathode: 4000 sccm Air, T_C=80°C, p=30psig

Cell temp. = 80°C, 0.2 mg Pt/cm^2 at each electrode

Pt:Cr / 3:1 alloy cathode catalyst performance and stability



Pt/Cr mass ratio changes (from XRF data)

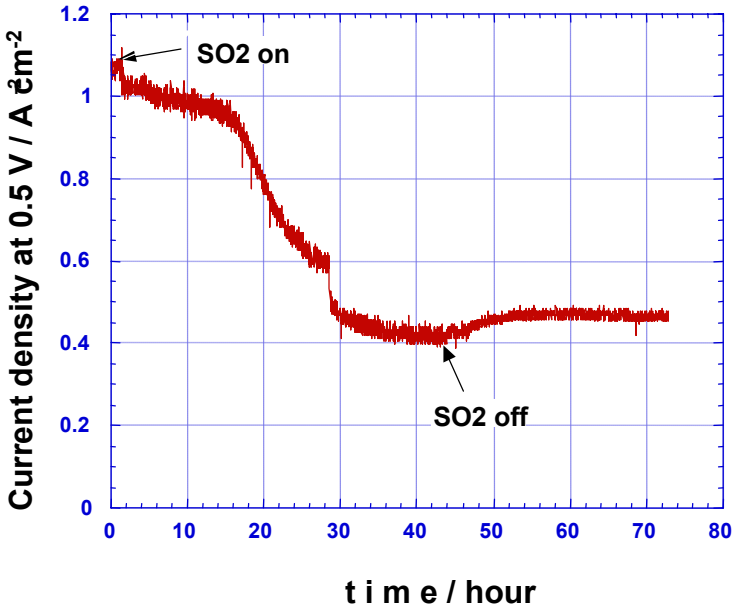
Initial: 0.053
Final: 0.042

Performance losses: 90 mV

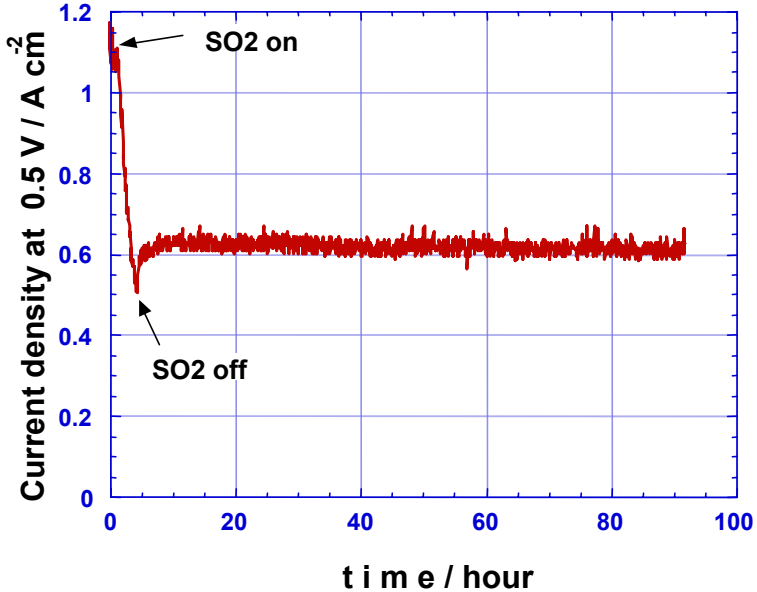
50 cm^2 , 80 ^oC
A: 0.17 mg Pt cm^{-2} ;
C: 0.17 mg Pt/cm^{-2} (Pt_3Cr)
H_2:1.3 stoich; Air:2.0 stoich

FC Performance on cathode exposure to SO_2

1 ppm SO_2



5 ppm SO_2



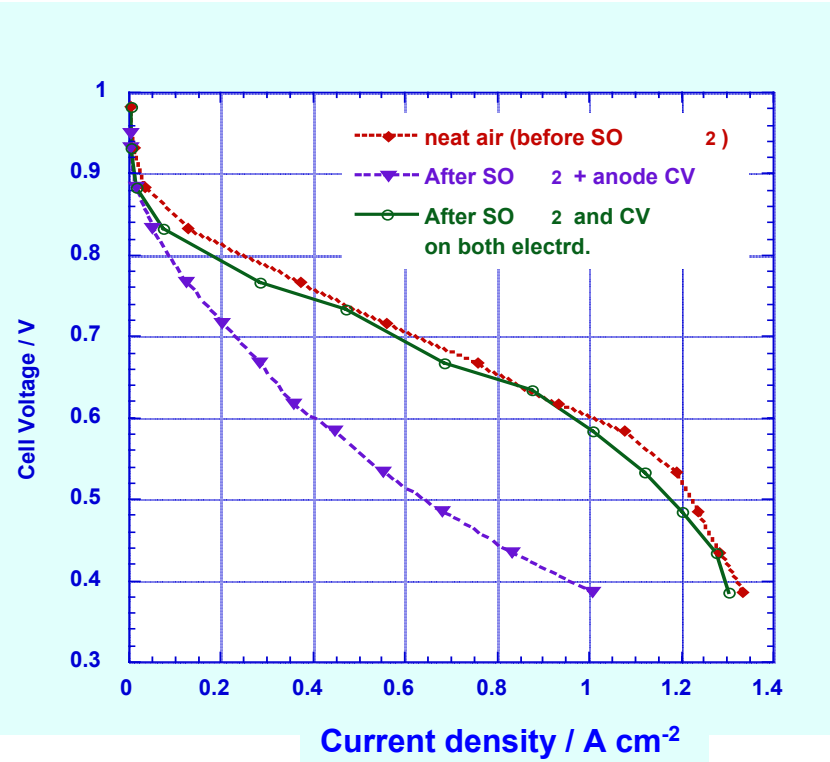
- **Current became stable after 40 hr of operation**
- **FC performance did not recover much after SO_2 was shut off and cell run on clean air.**

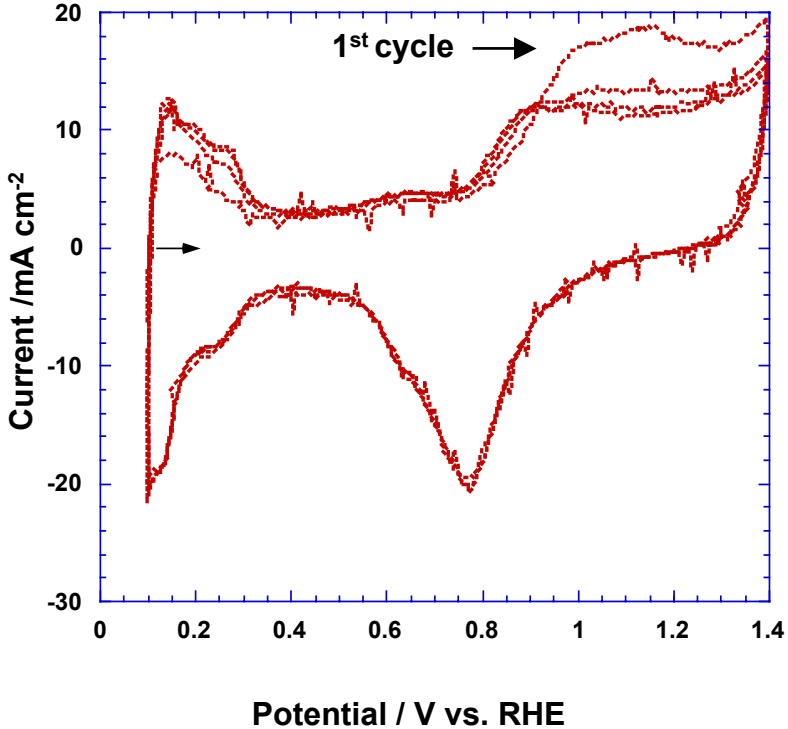
5 cm^2 H_2/air cell , T= 80 °C
A: 0.17 mg Pt/cm^{-2}
C: 0.18 mg Pt/cm^{-2}

- **Cathode was exposed to SO_2 for 3.4 hr**
- **FC performance did not recover after SO_2 was shut off and cell run on clean air for 87 hr**
- **Degradation appears to be irreversible**
- **Exposure to SO_2 must be avoided**

SO_2 Effect on FC Performance at 60° C and Cyclic Voltammetry at the cathode after poisoning

5 ppm SO_2 injected at the cathode

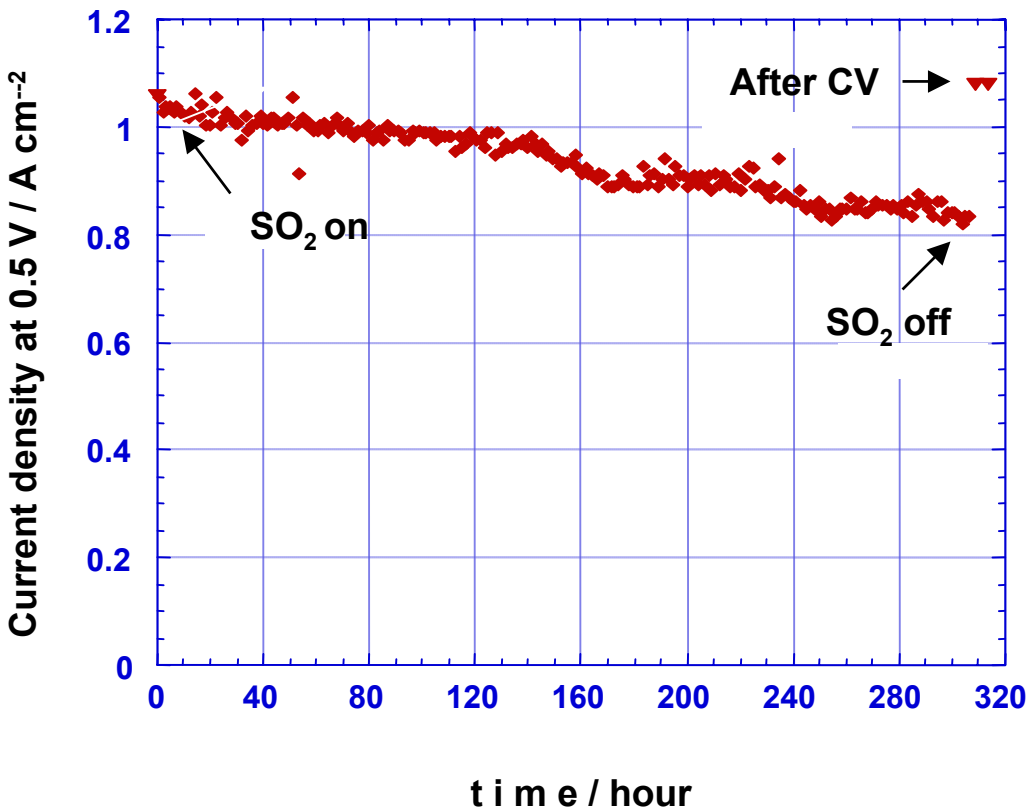




* **5 ppm SO_2 injected at the cathode for 17.6 hrs**
* **Decreased H_{ads} peaks reveals partial Pt surface poisoning by SO_2**
* **High potentials (>1 V) are required for cleaning the Pt surface**
* **After CV at the cathode, the cell recovered full performance**

5 cm^2 H_2/air cell , T= 60 °C
A :0.16 mg Pt/cm-^{2}
C: 0.19 mg Pt/cm^{-2}

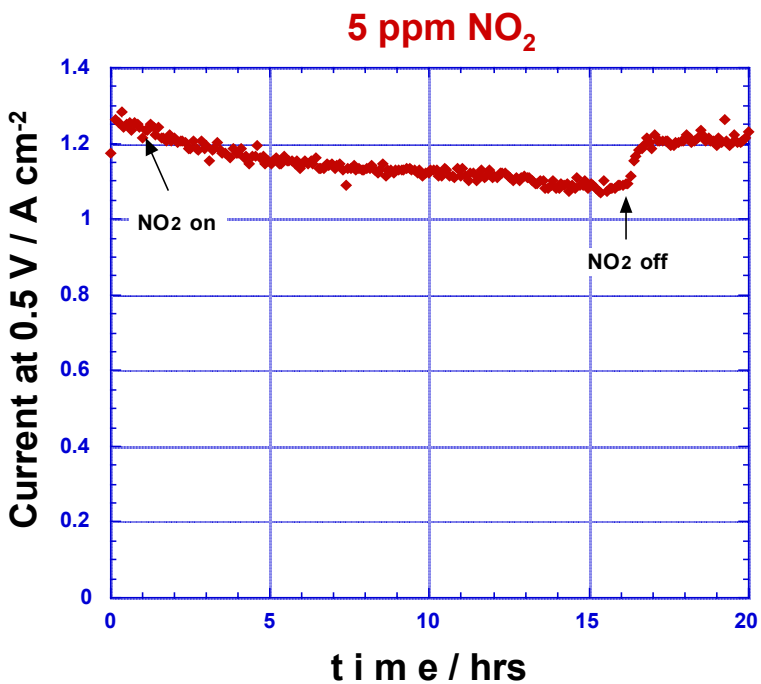
Milestone: Life Test with 500 ppb SO_2 on the Cathode

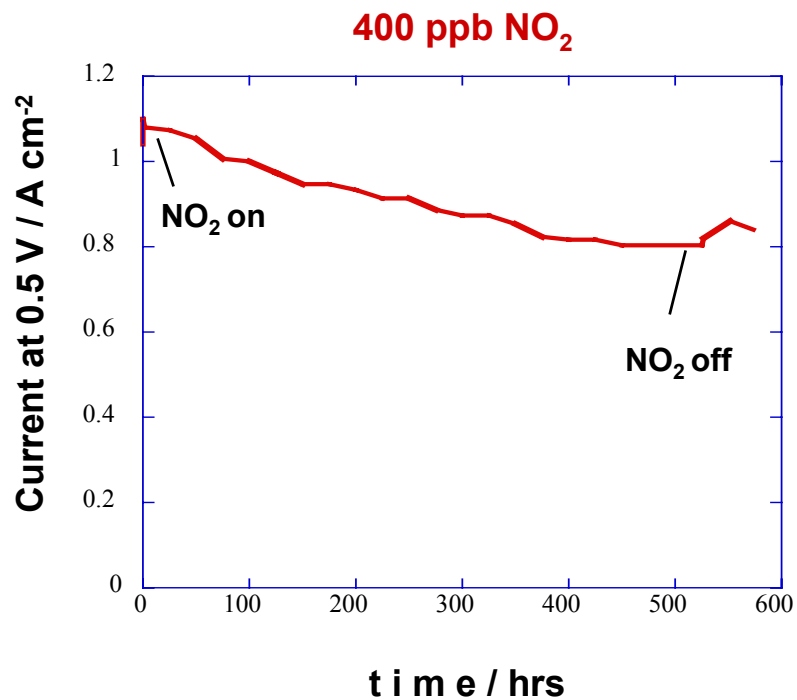


- Cell current dropped about 20 % during 300 hrs of exposure to SO_2
- Cell performance recovered after CV

5 cm^2 H_2/air cell , T= 80 °C
A: 0.18 mg Pt/cm^2; 1.3 H_2 stoich
C: 0.22 mg Pt/cm^2; 2.5 air stoich
20% Pt/C ETEK, N1135

Effect of NO_2 on Cathode FC Performance





* 5 ppm NO_2 injected at the cathode along with the air
* NO_2 has a detrimental effect on FC performance
* The cell fully recovered on operation with clean air

* NO_2 injected at the cathode for 500 hr.
- Cell did not recover performance after NO_2 was turned off and operated on clean air for approximately 70 hrs

5 cm^2 H_2/air cell , T= 80 °C
A: 0.23 mg Pt/cm^2
C: 0.23 mg Pt/cm^2

Technical Progress Summary/Findings

General

* FC performance and catalyst layer porosity correlates with Nafion content.
* Pt catalyst contents and distribution in the MEA can be determined by XRF imaging.

Anode

* Modest progress to CO tolerance with RCA, but 500 ppm CO target not achieved yet.
* Low Pt content BNL catalyst tested for 222 hours. Performance decreased with time.
* Foreign cations decrease the ionic conductivity of the catalyst layer.

Cathode

* Operation at high voltages degrades performance due to Pt surface oxidation.
* PPB levels of SO_2 and NO_2 in the air stream degrades cathode performance.
* Negative effects of SO_2 are irreversible under normal FC operating conditions.
* A SO_2-poisoned catalyst cannot be reactivated with neat air.
* Cell recovery on exposure to NO_2 depends on concentration and time of exposure.
* Short term (1 hr) cathode exposure to NaCl solutions only affect air transport (flooding).

Future Work

General

1. **Develop methods for cleaning or reactivating poisoned catalysts** (e.g. H_2S and SO_2) **under standard operating conditions**
2. **Initiate studies on effects of impurities and conditions on gas diffusion layer**

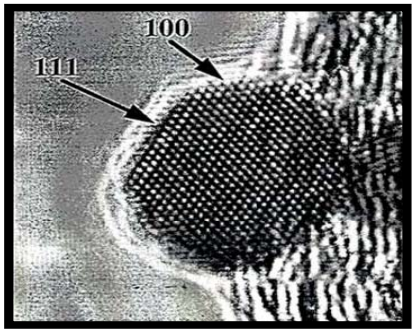
Anode

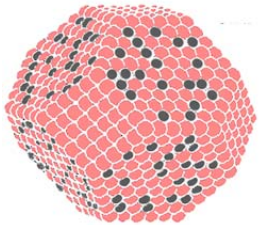
1. **Test new BNL catalyst** (2% Pt / 20% Ru/C)
2. **Examine CO tolerance of BNL catalysts in reconfigured anodes** (RCA)
3. **Elucidate CO oxidation mechanism in RCA**
4. **Model impurity effects**

Cathode

1. **Evaluate new catalyst materials** (high Pt content)
2. **Study tolerance to SO_2 and NO_2 with filters**
3. **Determine poisoning mechanism by NO_2**
4. **Study simultaneous tolerance to SO_2 and NO_2 with filter**
5. **Investigate the effect of NaCl and $CaCl_2$ on cathode performance**
6. **Study the effect of particulate matter from the air on FC performance**
7. **Initiate non-precious metal based catalysts studies**

New Electrocatalysts For Fuel Cells





Objective: Reduction of precious metal loading

Principal Investigator: Philip N. Ross, Jr.

Staff Scientist: Nenad M. Markovic

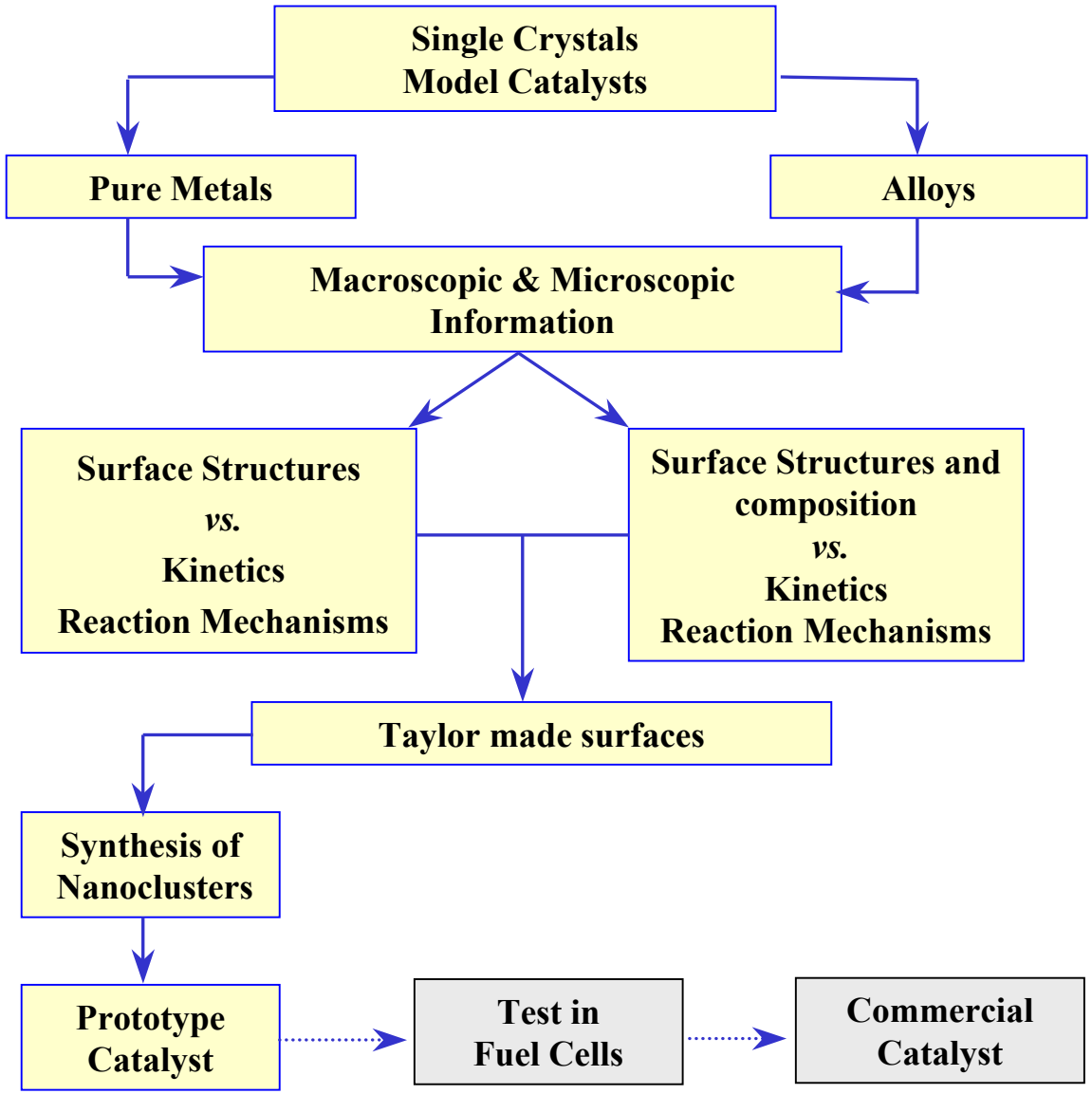
Post Doctoral Fellow: Vojislav Stamenkovic

Visiting Scientists: Matthias Arenz (Humboldt Fellow)

Berislav Blizanac (Belgrade)

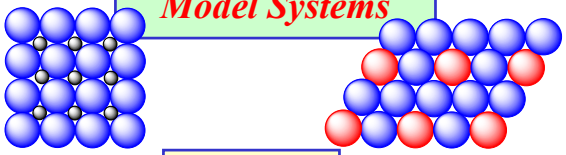
A research program conducted at the Lawrence Berkeley National Laboratory for the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Advanced Transportation Technologies of the U.S. Department of Energy under contract No. DE-AC03-76SF00098

LBNL *Materials-by-Design Approach*



Methodologies

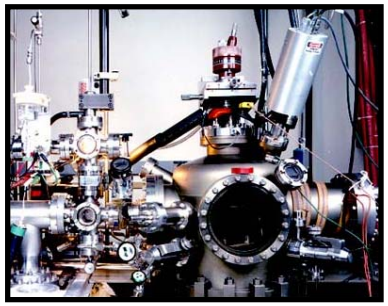
Model Systems



Ex-Situ

XPS

AES

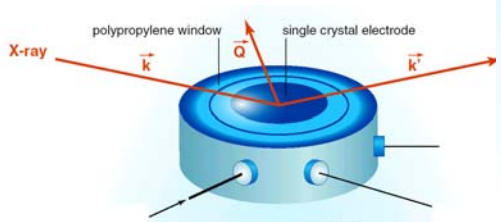


LEIS

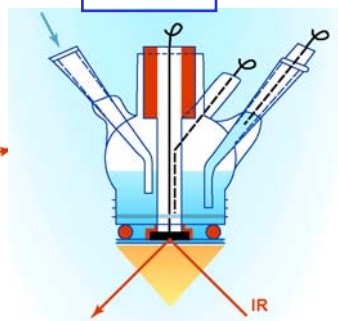
LEED

In-Situ

SXS

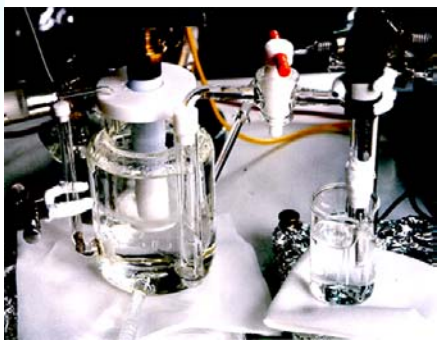


FTIR



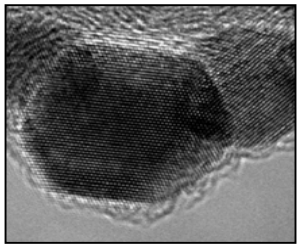
RRDE

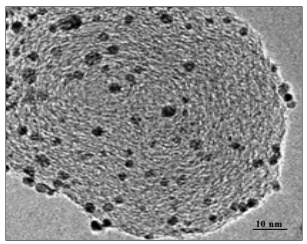
Kinetics

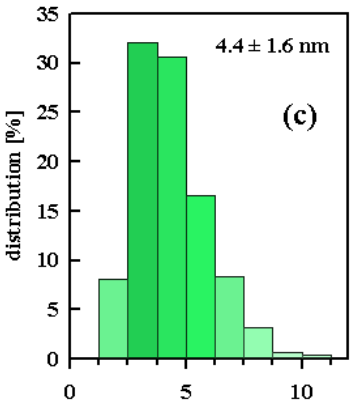


Real Catalysts

TEM



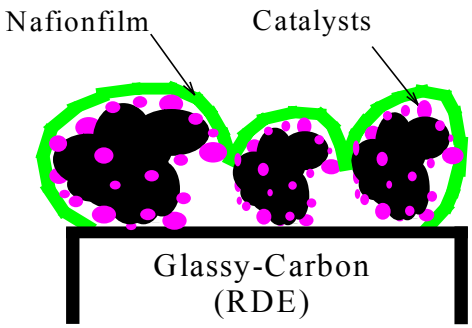




Collaborations

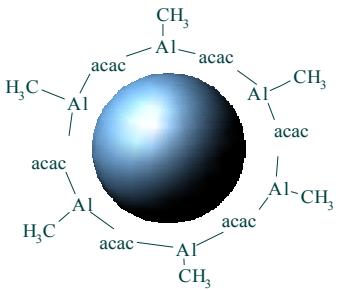
Industry

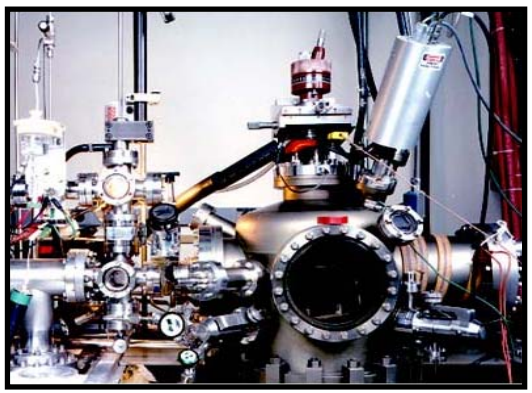
- GM, Rochester, NY, USA
- IFC, South Windsor, CT, USA
- 3M, Minneapolis, MN, USA



Universities and Institutes

- Max-Planck-Institut fuer Kohlenforschung, Muelheim/Ruhr, Germany
- Texas Tech University, Lubbock, TX, USA
- University of Eindhoven, Holland
- University of Wales, UK
- University of Bonn, Germany
- University of Liverpool, UK





Publications (Since 10/2001)

Refereed Journals and Refereed Conference Proceedings:

1. U.A. Paulus, A. Wokaun, G.G. Scherer, T.J. Schmidt, V. Stamenkovic, V. Radmilovic, N.M. Markovic, and P.N. Ross, "Oxygen Reduction on Carbon Supported Pt-Ni and Pt-Co Alloy Catalysts", *J. Phys. Chem. B* 106 (2002) 4181.
2. Stamenkovic V. Schmidt TJ. Ross PN. Markovic NM. "Surface composition effects in electrocatalysis: Kinetics of oxygen reduction on well-defined PtNi and PtCo alloy surfaces." *Journal of Physical Chemistry B*. 106(46):11970-11979, 2002 Nov 21.
3. Tripkovic AV. Popovic KD. Grgur BN. Blizanac B. Ross PN. Markovic NM. "Methanol electrooxidation on supported Pt and PtRu catalysts in acid and alkaline solutions." *Electrochimica Acta*. 47(22-23):3707-3714, 2002 Aug 30.
4. Schmidt TJ. Stamenkovic V. Arenz M. Markovic NM. Ross PN. "Oxygen electrocatalysis in alkaline electrolyte: Pt(hkl), Au(hkl) and the effect of Pd-modification." *Electrochimica Acta*. 47(22-23):3765-3776, 2002 Aug 30.
5. Paulus UA. Wokaun A. Scherer GG. Schmidt TJ. Stamenkovic V. Markovic NM. Ross PN. "Oxygen reduction on high surface area Pt-based alloy catalysts in comparison to well defined smooth bulk alloy electrodes." *Electrochimica Acta*. 47(22-23):3787-3798, 2002 Aug 30.
6. Schmidt TJ. Markovic NM. Stamenkovic V. Ross PN. "Surface characterization and electrochemical behavior of well-defined Pt-Pd{111} single-crystal surfaces: A comparative study using Pt{111} and palladium-modified Pt{111} electrodes." *Langmuir*. 18(18):6969-6975, 2002 Sep 3.
7. Schmidt TJ. Ross PN. Markovic NM. "Temperature dependent surface electrochemistry on Pt single crystals in alkaline electrolytes Part 2. The hydrogen evolution/oxidation reaction." *Journal of Electroanalytical Chemistry*. 524(Special Issue):252-260, 2002 May 3.
8. Arenz M. Stamenkovic V. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. "CO adsorption and kinetics on well-characterized Pd films on Pt(111) in alkaline solutions." *Surface Science*. 506(3):287-296, 2002 May 20.
9. Paulus UA. Wokaun A. Scherer GG. Schmidt TJ. Stamenkovic V. Radmilovic V. Markovic NM. Ross PN. "Oxygen reduction on carbon-supported Pt-Ni and Pt-Co alloy catalysts." *Journal of Physical Chemistry B*. 106(16):4181-4191, 2002 Apr 25.
10. Schmidt TJ. Ross PN. Markovic NM. "Temperature-dependent surface electrochemistry on Pt single crystals in alkaline electrolyte: Part 1: CO oxidation." *Journal of Physical Chemistry B*. 105(48):12082-12086, 2001 Dec 6.
11. Schmidt TJ. Stamenkovic V. Attard GA. Markovic NM. Ross PN. "On the behavior of Pt(111)-Bi in acid and alkaline electrolytes." *Langmuir*.17(24):7613-7619, 2001 Nov 27.

Research Plan: 2002

- **Unified concept for both anode and cathode catalysts utilizing PGM-based bimetallic nanoparticles with "grape" structure (PGM skin with base metal core)**

  Choice of skin and core metals different for anode and cathode
  PGM/base metal combinations selected based on existing electronic theory and synthesized in UHV

- **Pursue new synthetic chemistry to synthesize nanoparticles with the "grape" structure**

  Currently focusing on Re as metal core with Pt and Pd as PGM

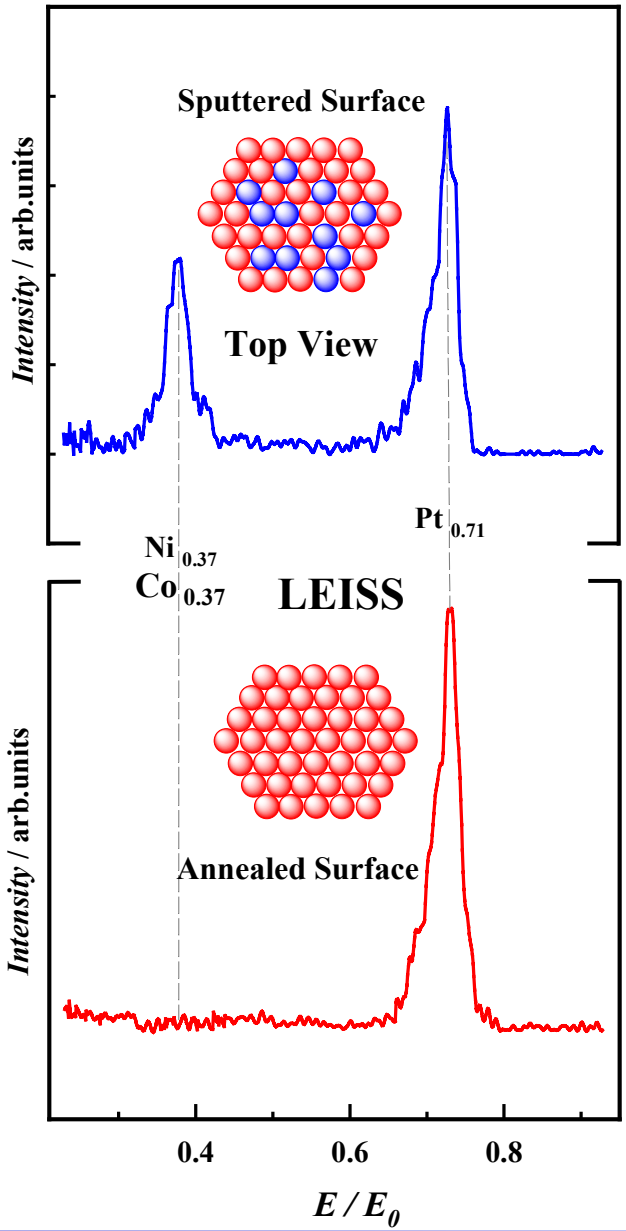
  Pt and Pd monolayers on Re(0001) model system

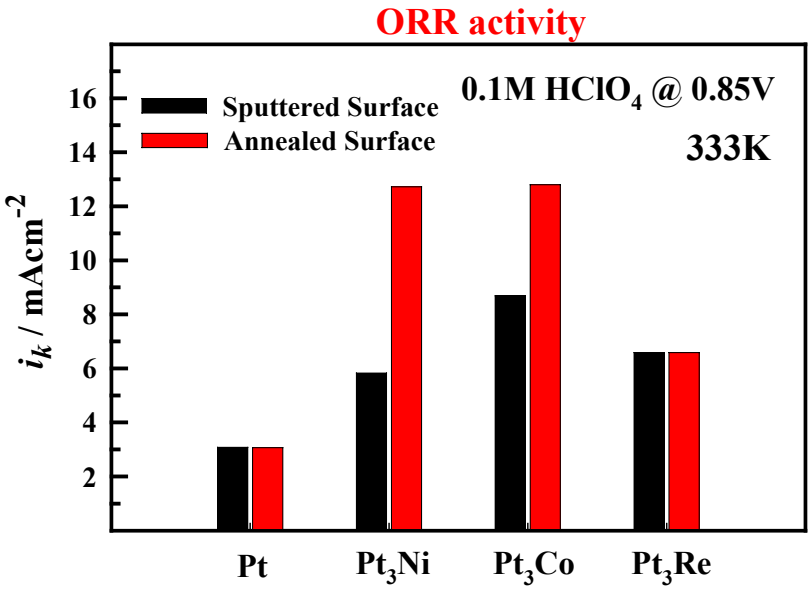
  Re colloidal chemistry

- **Optimization of AuPd anode catalyst for HT membranes**

- **Computational screening of non-PGM catalyst concepts using newly developed (under BES funding) *ab initio* theory of the ORR**

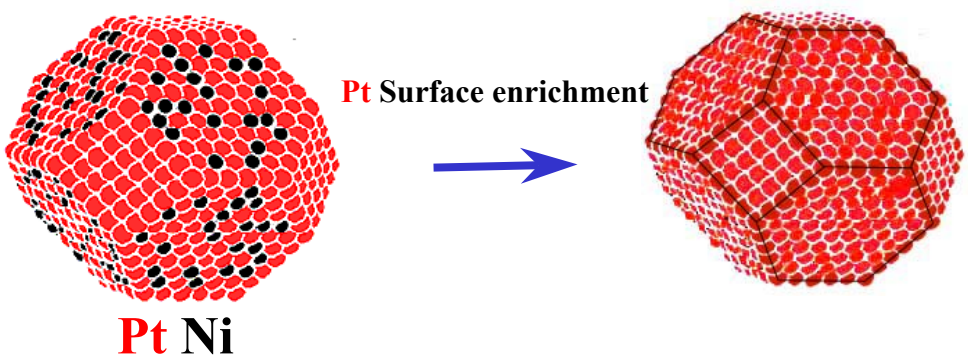
Segregation Effect: Platinum Skin vs. Bulk Alloy Surfaces





Platinum Skin Effect: Bimetallic Nanoparticle

- Higher intrinsic activity (per unit area)
- Substitution of "buried" Pt atoms in particle core by base metal atoms



Stability: Pt_3Co and Pt_3Ni Surfaces

Experimental Procedure

Pt_3Co ; Pt_3Ni
Sputtered Surfaces

298K

CV stability
Before Treatment
0.0<E<1.0V

ORR : stability
activity
Before Treatment
0.0<E<1.0V

Hold @ 1.0V; 30 min

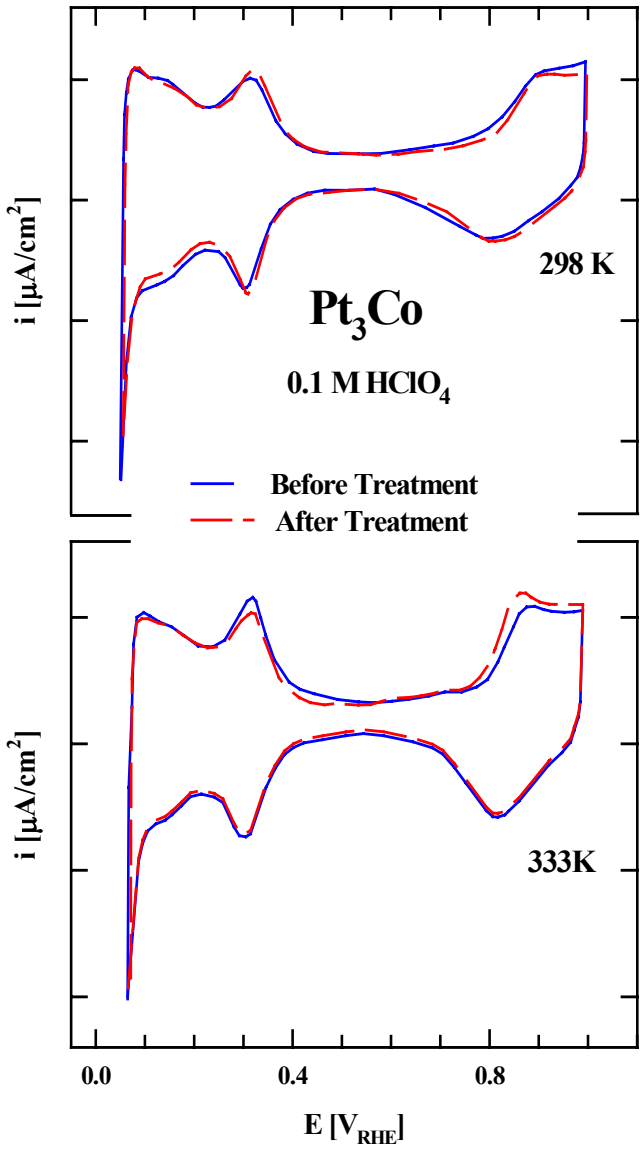
ORR : stability
activity
0.0<E<1.0V

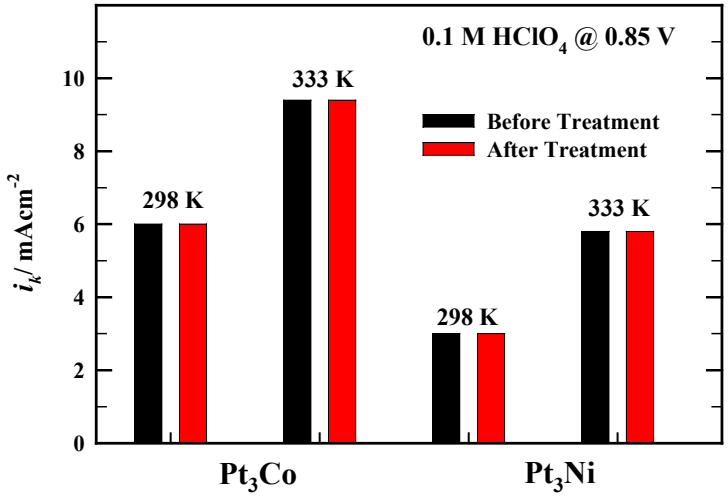
Hold @ 1.2V; 60 min

ORR : stability
activity
After Treatment
0.0<E<1.2V

CV stability
After Treatment
0.0<E<1.2V

333K



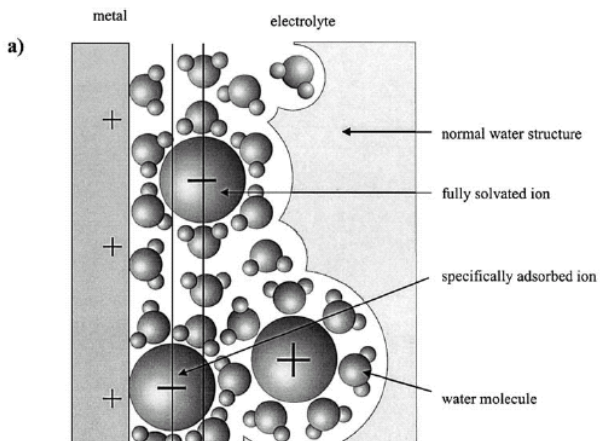


Conclusions

Surface composition is stable between 0.0 < E< 1.2 V !

ORR activity remains the same between 0.0 < E< 1.2 V !

Mechanism of the ORR at metal electrodes

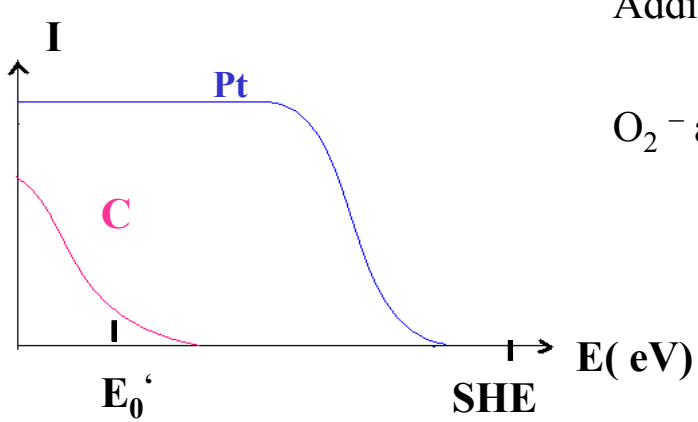


Rate limiting step in electrochemical reduction of O_2 is 1st electron transfer

$O_2 + 1\,e^- \rightarrow (O_2^-)_{sol}$ Outer Sphere ($\mathbf{E_0' = -0.3\ V}$)

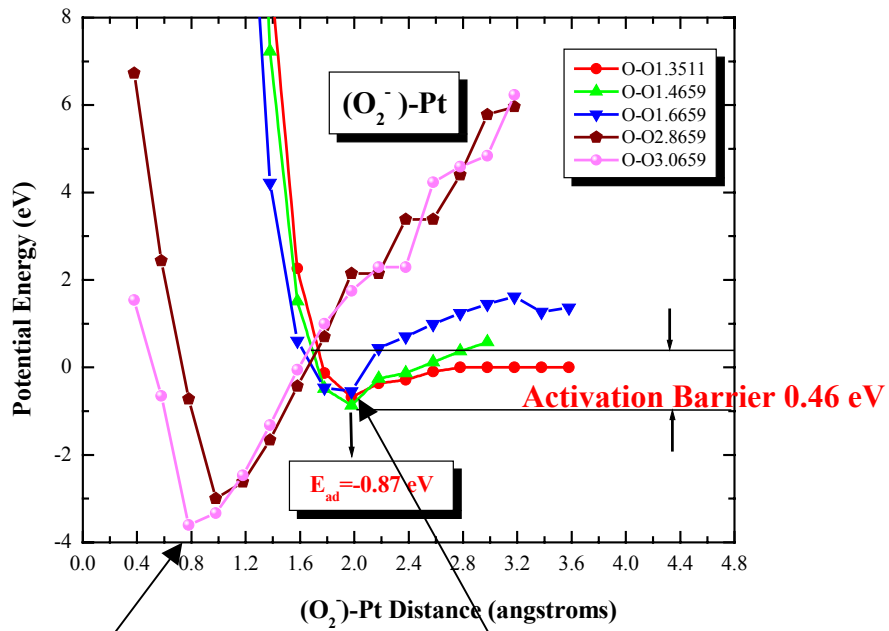
$O_2 + 1\,e^- \rightarrow (O_2^-)_{ads}$ Inner Sphere ($\mathbf{E_0' + \Delta G_{ad}/F}$)

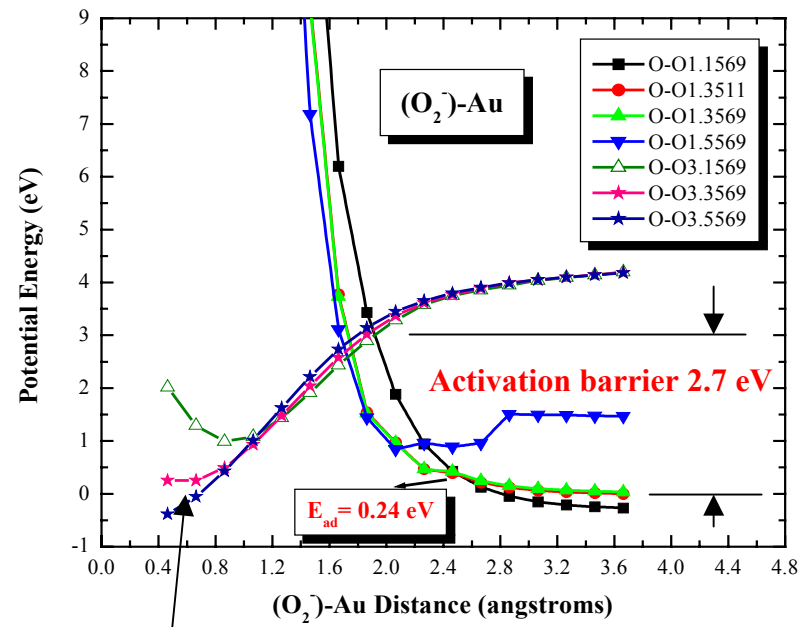
Addition of first electron needed to break O-O bond

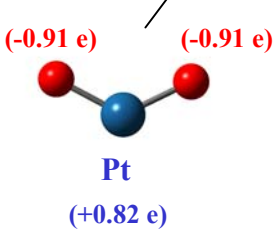


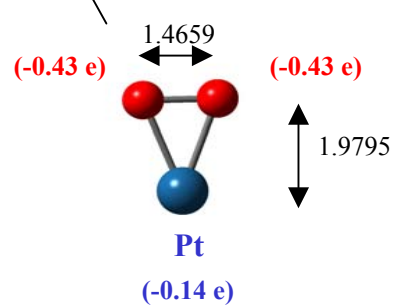
O_2^- adsorption strength related to the electronic properties of the electrode material

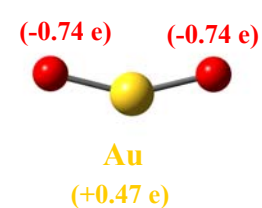
(O_2^-)–Me Potential Energy Curves vs. O-O bond length





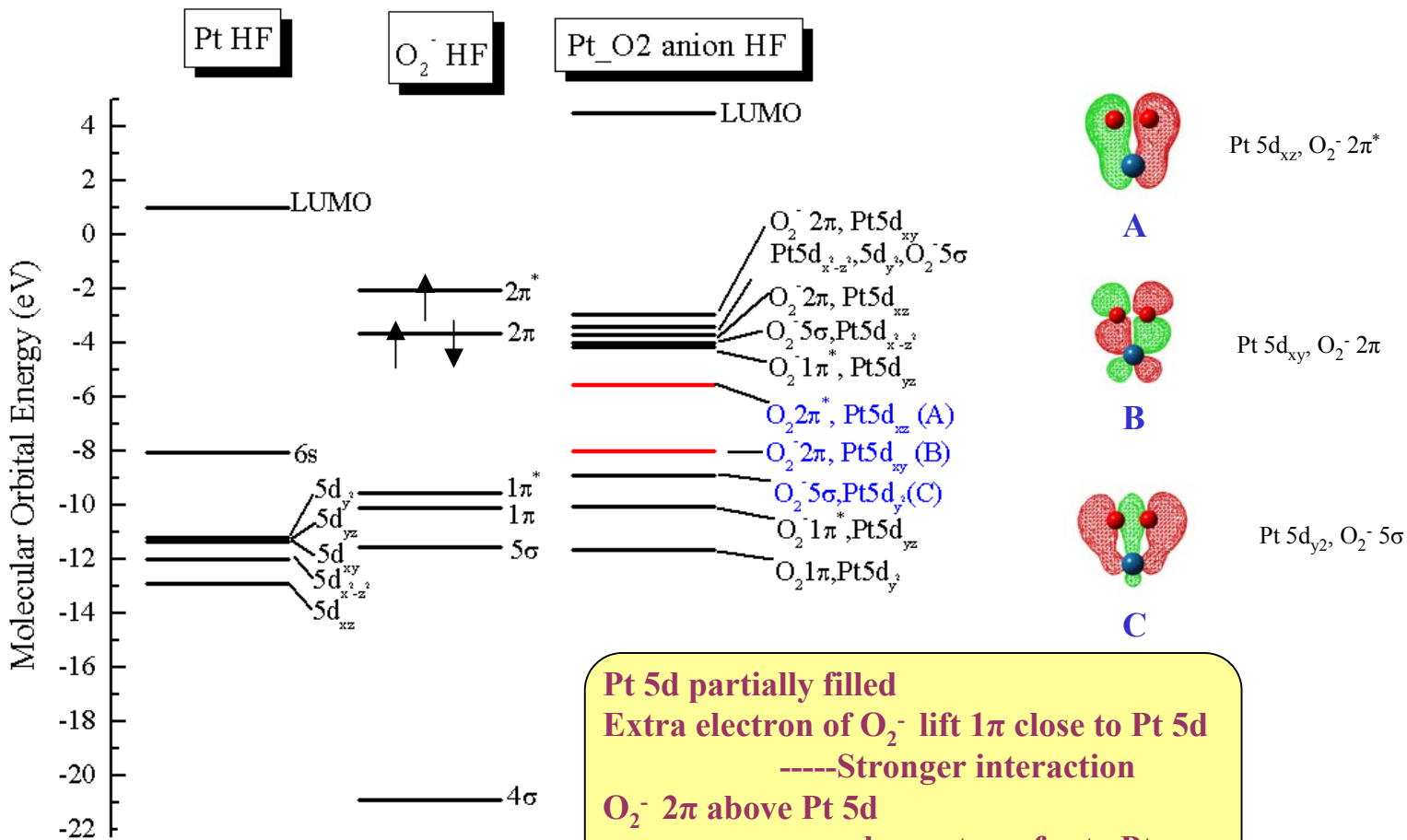






➢No bound state of O_2^-

Correlation Diagram of the Molecular Orbitals of (O_2^-)-Pt



Pt 5d partially filled

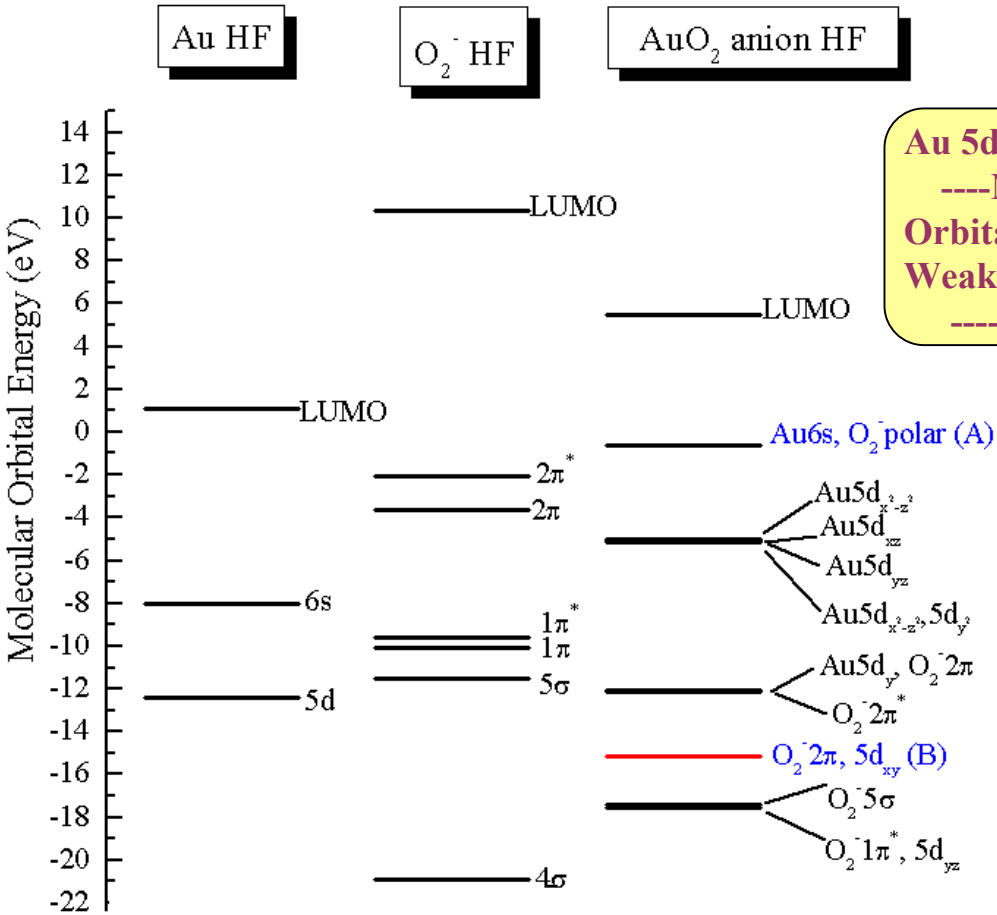
Extra electron of O_2^- lift 1π close to Pt 5d

-----Stronger interaction

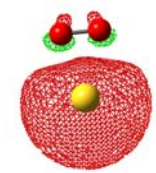
O_2^- 2π above Pt 5d

------charge transfer to Pt

Correlation Diagram of Molecular Orbitals of (O_2^-)-Au



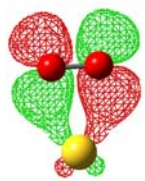
Au 5d completely filled
----No charge transfer between Pt and (O_2^-)
Orbital with different symmetry do not interact
Weak Interaction due to polarization
----Au6s and (O_2^-) π levels



A

Au 6s, O_2^- 2π

Polarization effect

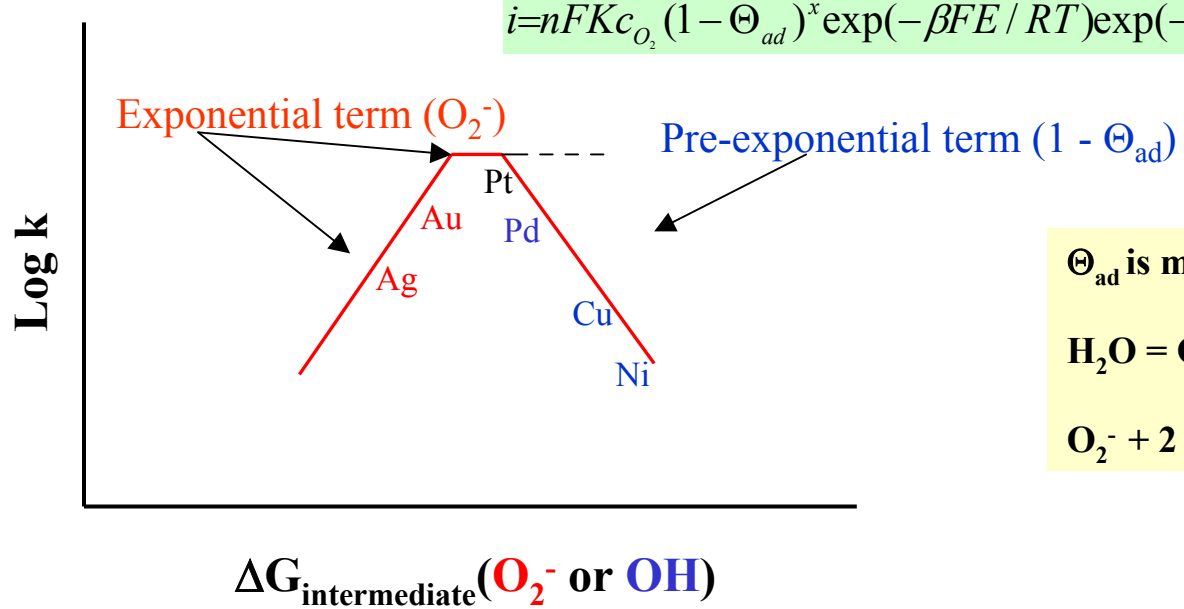


B

Au $5d_{xy}$, O_2^- 2π

The Volcano Relation in ORR Kinetics

$$i = nFKc_{O_2}(1-\Theta_{ad})^x \exp(-\beta FE/RT)\exp(-\Delta G^*_\Theta/RT)$$



Θ_{ad} is mostly OH_{ad} not $(O_2^-)_{ad}$

$H_2O = OH_{ad} + H^+ + e^-$

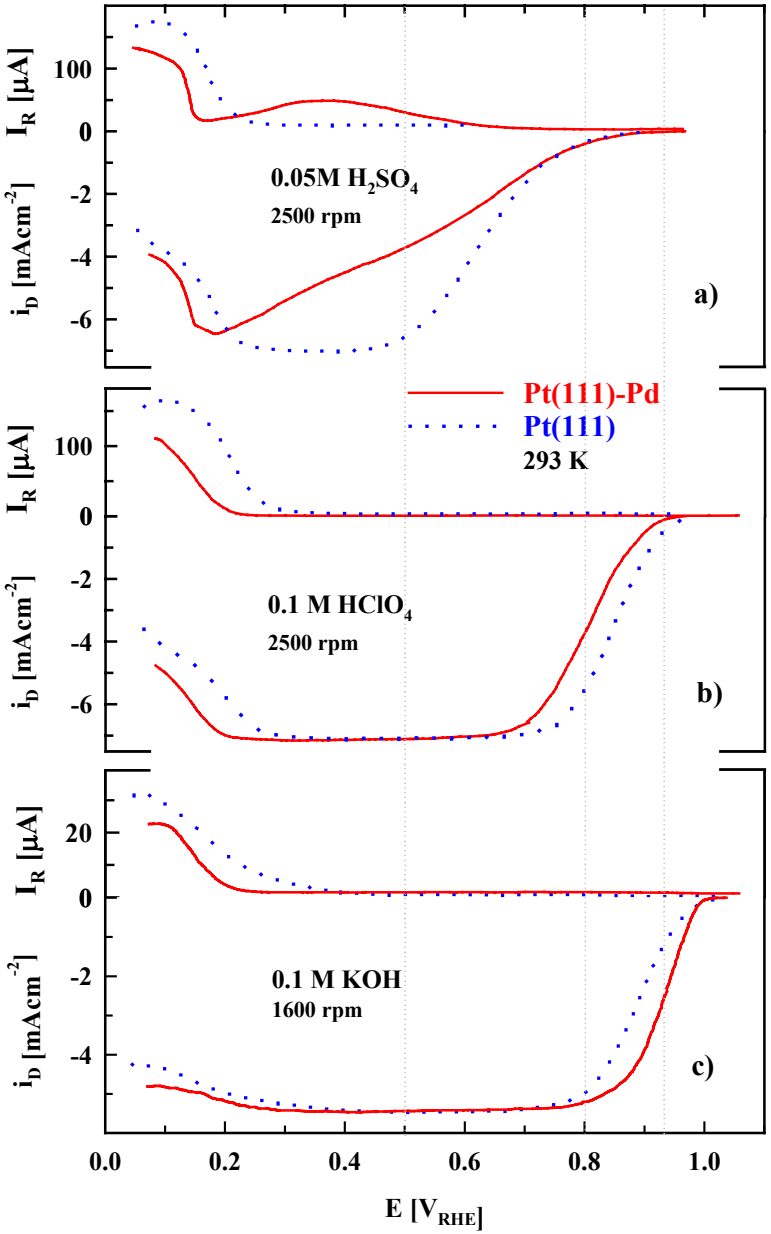
or

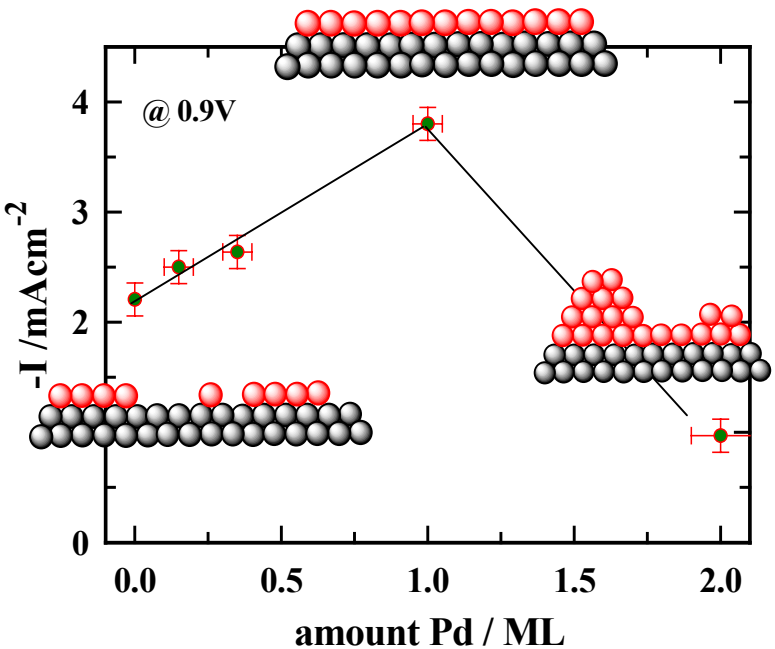
$O_2^- + 2\,H^+ + e^- = 2\,OH_{ad}$

Pt at the Top of the Volcano

- **Interaction of the electrode with O_2^- requires partially filled d-orbitals with large radial extent**
  - **Group 1B, 2B, 3B etc. metals have closed d-shells**
  - **Of Group VIII metals, d-orbitals in first row ($3d^{9-n}$)**
    - **do not have sufficient radial extent**
  - **The $5d^{9-n}$ orbitals are the best for forming long bonds**
- **Interaction of the electrode with OH_{ad} must be relatively weak of the Group VII metals, Pt has the weakest interaction with OH_{ad}**

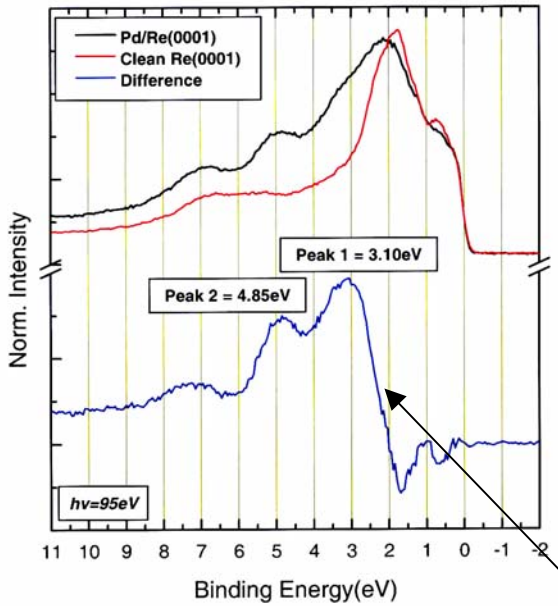
ORR: Pt(111)-Pd

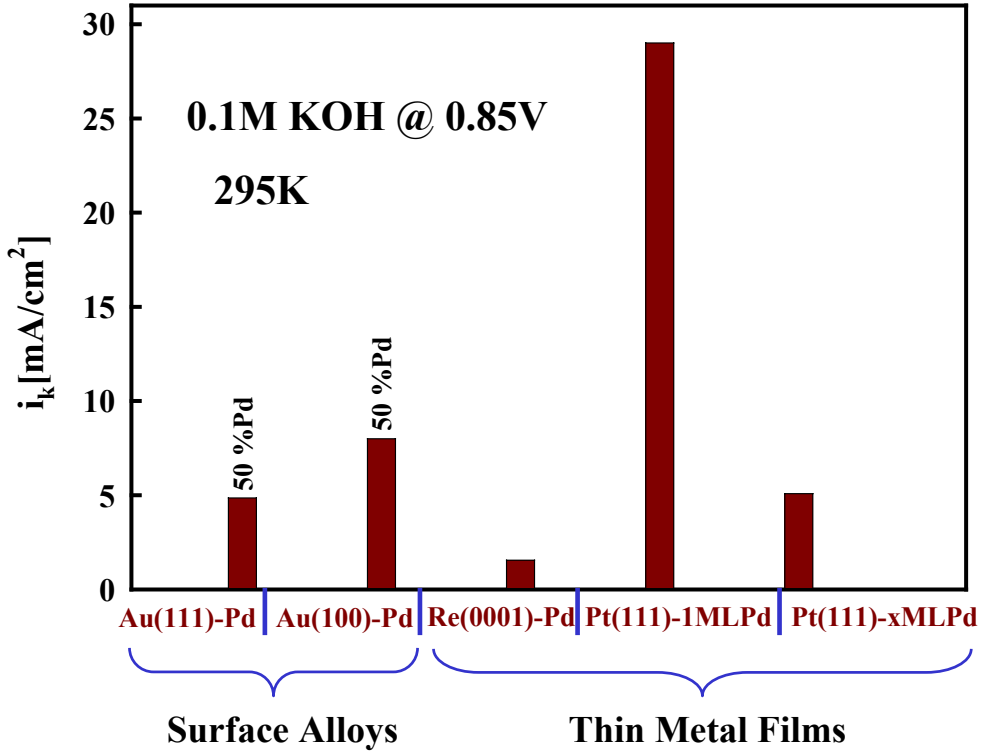


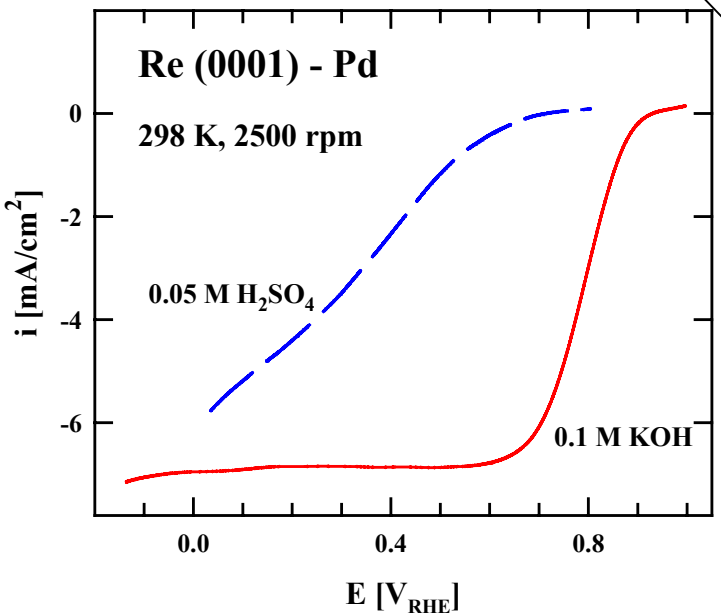


- "Vulcano Plot"
- Electronic Effect

ORR: Re(0001)-Pd





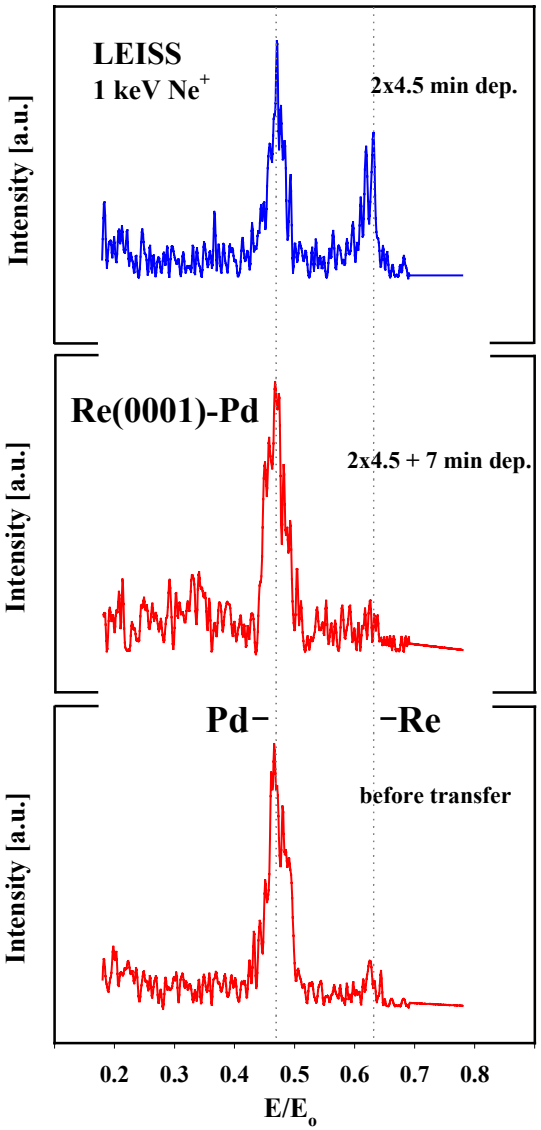


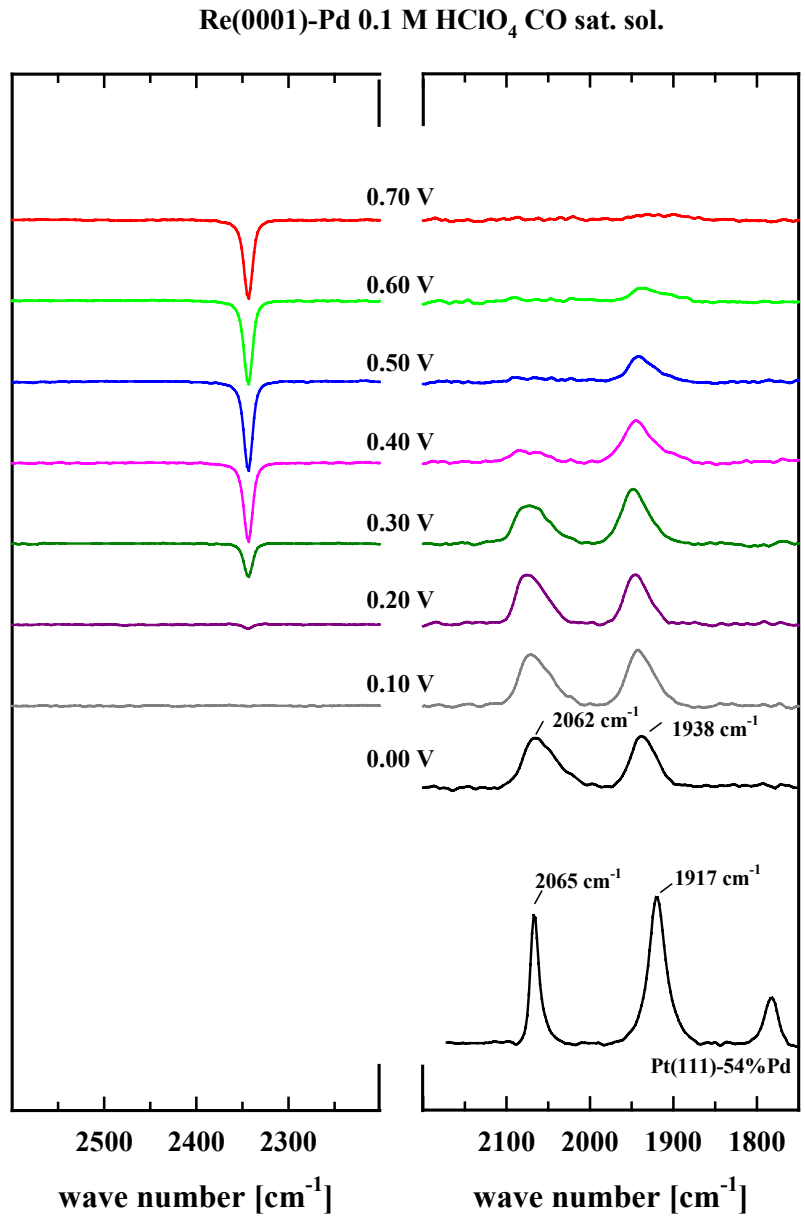
Pd ML film on Re(0001) has Ag-like d-band Density of States (DOS)

and

Activity for ORR is shifted towards that for Ag(111)

CO oxidation: Pt(111)-Pd vs. Re(0001)-Pd





In situ FTIR:

- **two adsorption bands**
- **electronic modification shifts frequency**
- **preferential oxidation of high frequency band**
- **electronic modification shifts oxidation potential by ca. – 0.2 V**

Research Plan: 2003-2004

- **Unified concept for both anode and cathode catalysts utilizing PGM-based bimetallic nanoparticles with "grape" structure (PGM skin with base metal core)**

  Choice of skin and core metals different for anode and cathode PGM/base metal combinations selected based on existing electronic theory and synthesized in UHV

- **Pursue new synthetic chemistry to synthesize nanoparticles with the "grape" structure**

  Continue focus on Re as metal core with Pt and Pd as PGM

  Pt and Pd monolayers on Re(0001) as model systems

  Begin evaluation of Re-rich supported Pt-Re catalyst for ORR (if stable this catalyst could reduce Pt loading by a factor of 4)

- **Optimization of AuPd anode catalyst for HT membranes**

- **Computational screening of non-PGM catalyst concepts using newly developed (under BES funding) *ab initio* theory of the ORR**

Low-platinum hydrous metal oxides for PEMFC cathodes

Karen Swider-Lyons, Peter Bouwman, Norma Ugarte
Naval Research Laboratory

Wojtek Dmowski
University of Pennsylvania

DOE review 19 May 03
Berkeley, CA

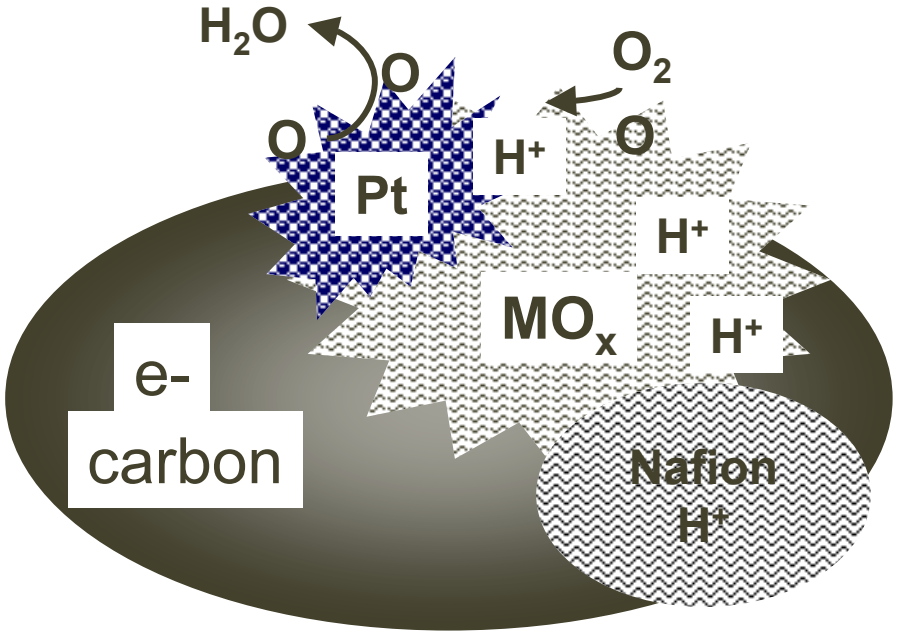
Objective and Approach

- Meet DOE goals to achieve 0.02 g Pt/rated kW before 2010.
- Focus on lowering Pt in fuel cell cathode
- Cathode has most Pt because
  - slow oxygen reduction kinetics
  - poor Pt stability and ripening over time.

NRL approach is to support Pt on a metal oxide

improve opportunity for

* proton mobility to Pt sites
* chem/phys attraction of O_2
* metal-support interactions with Pt



Pt supported on $MO_x \cdot H_2O$ supported on carbon

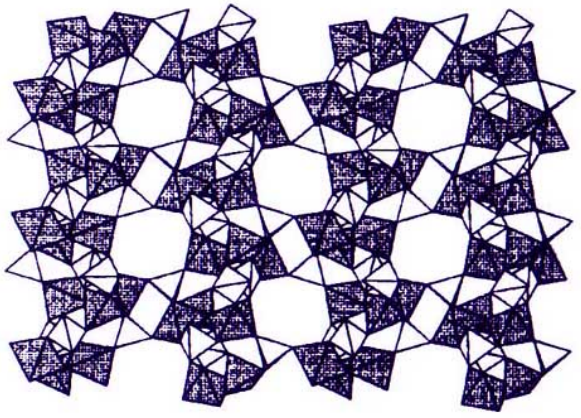
$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$

Catalyst development via electrochemical and structural analysis

Pt-MO_x systems

1. Pt-$FePO_x$•xH_2O - hydrous iron phosphate
   - Iron phosphate used as an anti-corrosion additive in paint
   - $FePO_x$ is a partial oxidation catalyst
2. Pt-SnO_x•xH_2O - hydrous tin oxide
   - Prior ORR literature shows promise for anhydrous Pt-SnO_x
   - Tin hydrates are corrosion resistant
3. Pt-$NbPO_x$•xH_2O - hydrous niobium phosphate
   - Niobium is ultra resistant to corrosion - used in electrolysis.
   - $NbPO_x$ is a partial oxidation catalyst

"Open Framework Inorganic Materials"
A. K. Cheetham G. Férey, T. Loiseau,
Angew. Chem. 1999, v. 38 p. 3286.



Example:
Microporous $AlPO_4$

✓Hydrous oxides are excellent for proton conduction

✓Selected oxides have other ideal catalytic properties (e.g. partial oxidation)

✓Materials have open framework structures

Progress to date (2 years)

April 01 Start Program

FY01 Lab review

FY02 Lab review

FY03 Lab review

Observe 20× catalytic activity of Pt-$FePO_x$ compounds

Receive LANL test results for Pt-$FePO_x$ catalyst performance in a PEMFC - poor performance

Identify structure of active Pt-$FePO_x$ compounds

Observe high catalytic activity of Pt-$NbPO_x$ compounds

Pt-SnOx catalyst activity improved

Positive results for Pt-SnO_x MEAs in ambient fuel cell

Acquire fuel cell test station - ONR

Fe, Nb and Sn catalysts shown to be stable in acid at 90 °C
New stable Pt-$FePO_x$ phase resolved

Positive results for Pt-SnO_x MEAs at 60 °C

Catalyst stability evaluation

Method: *recommended by H. Gasteiger and S. Kocha of GM*

- ✓ Stir catalyst in sulfuric acid and/or phosphoric acid for 12 h at 90 °C
- ✓ Test catalyst performance in RDEs before and after acid wash
- ✓ Test acid solution for evidence of metal leaching with ICP

RESULTS

Pt-$FePO_x$

- Portion of catalyst dissolve in acid, leaving an acid-stable, phosphate-rich compound with 9.5 % Pt
- RDE of acid stable Pt-$FePO_x$ phase is better than that of the original material

Pt-SnO_x

- Compound is insoluble in sulfuric acid
- RDE evaluation underway

Pt-$NbPO_x$

- Compound is insoluble in sulfuric acid and phosphoric acid
- RDEs are unaffected by acid treatment

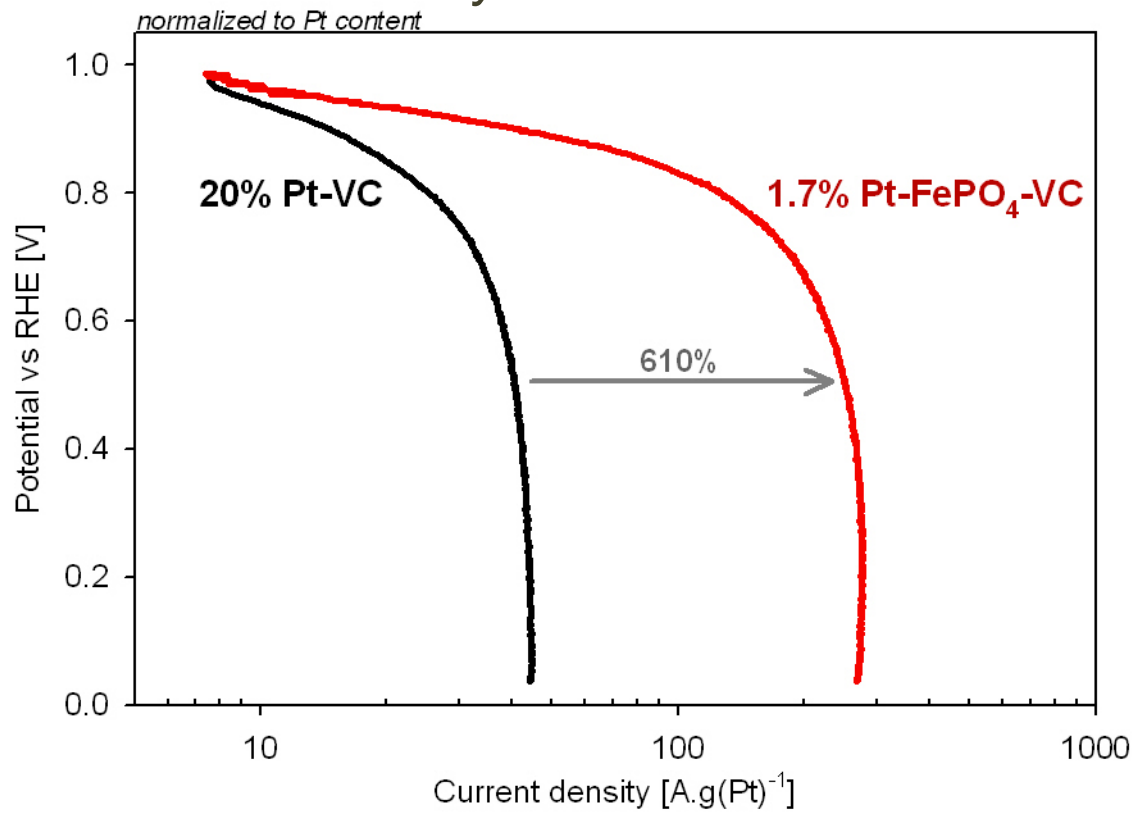
Evaluation of catalyst leaching with ICP still underway

All materials dissolve in aqua regia (like Pt metal)

RDE results for acid-stable Pt-$FePO_x$

Tafel plot:
1.7% Pt-$FePO_x$- 80% Vulcan carbon vs. 20% Pt-VC standard

Rotating disk electrode of catalyst ink in Nafion ionomer:

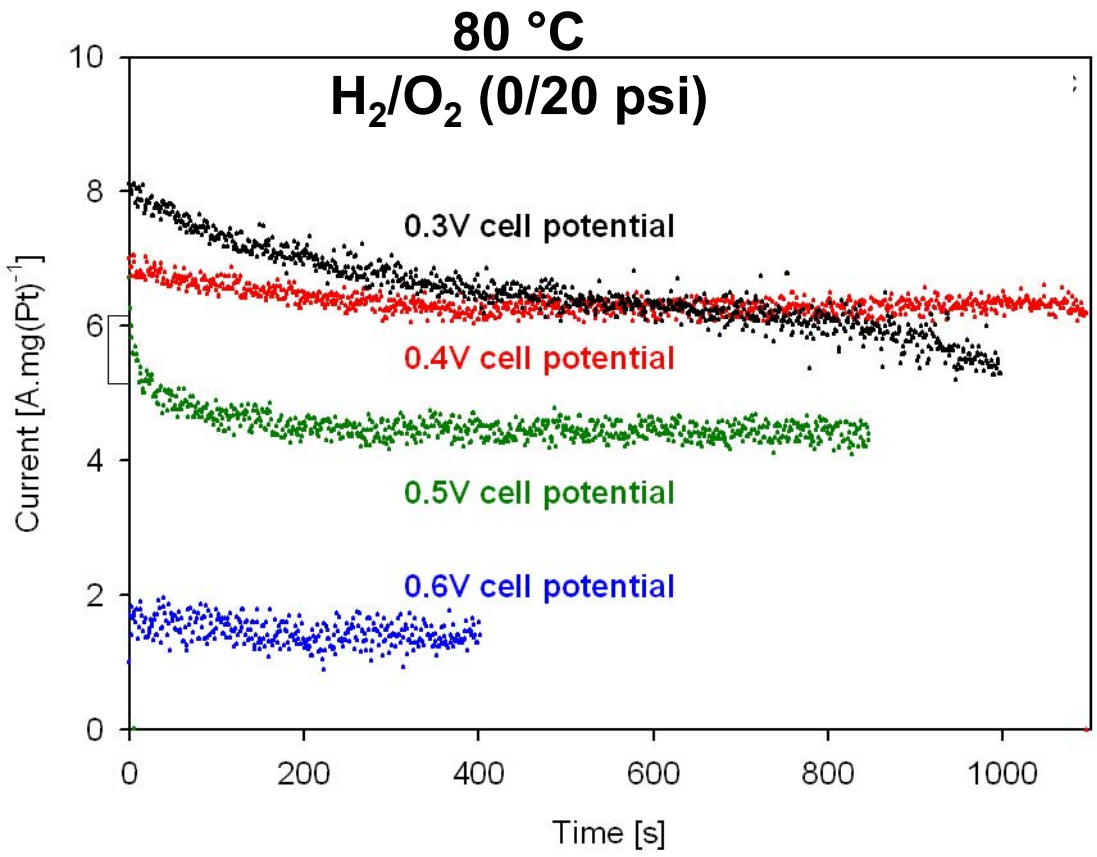


Normalized to Pt content: Pt-$FePO_x$ has >6× activity of 20%Pt-VC

60 °C 5 mV/s
0.1 M $HClO_4$
1600 rpm 100 ccpm O_2 flow
Tafel plots calculated from the difference of scans run under Ar and O_2 compared to 20% Pt/VC standard

Performance of Pt-$FePO_x$ MEAs

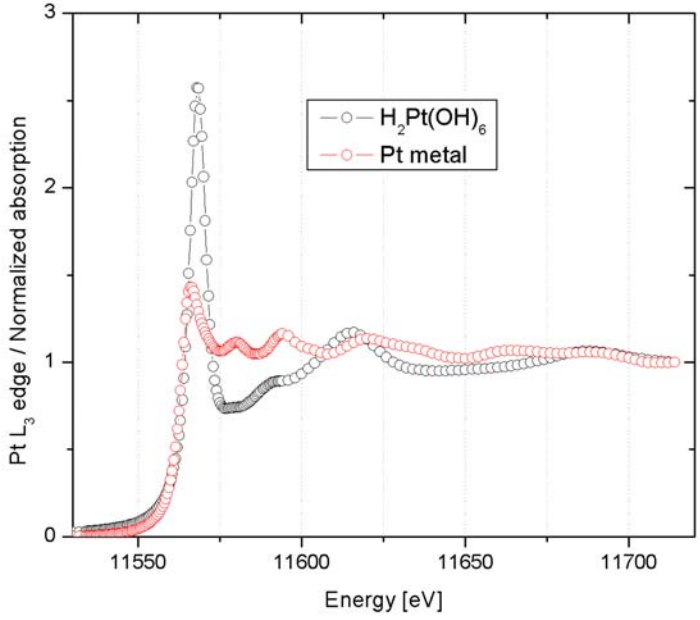
- Pt-$FePO_x$ compound holds a steady potential from 0.6 V to 0.4V - degrades at 0.3 V
- Note that this fuel cell had a low OCP
- Preparation of MEAs need optimization

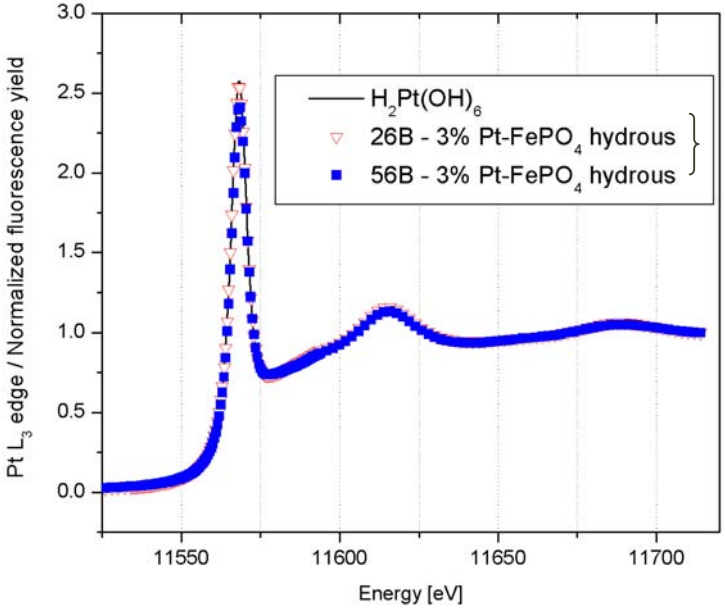


1.7% Pt-$FePO_x$- 80% VC cathode 0.013 mg Pt/cm^2
20% Pt-VC anode 0.08 mg Pt/cm^2

Oxidation state of Pt

Pt XANES measurements at the NSLS/X18B





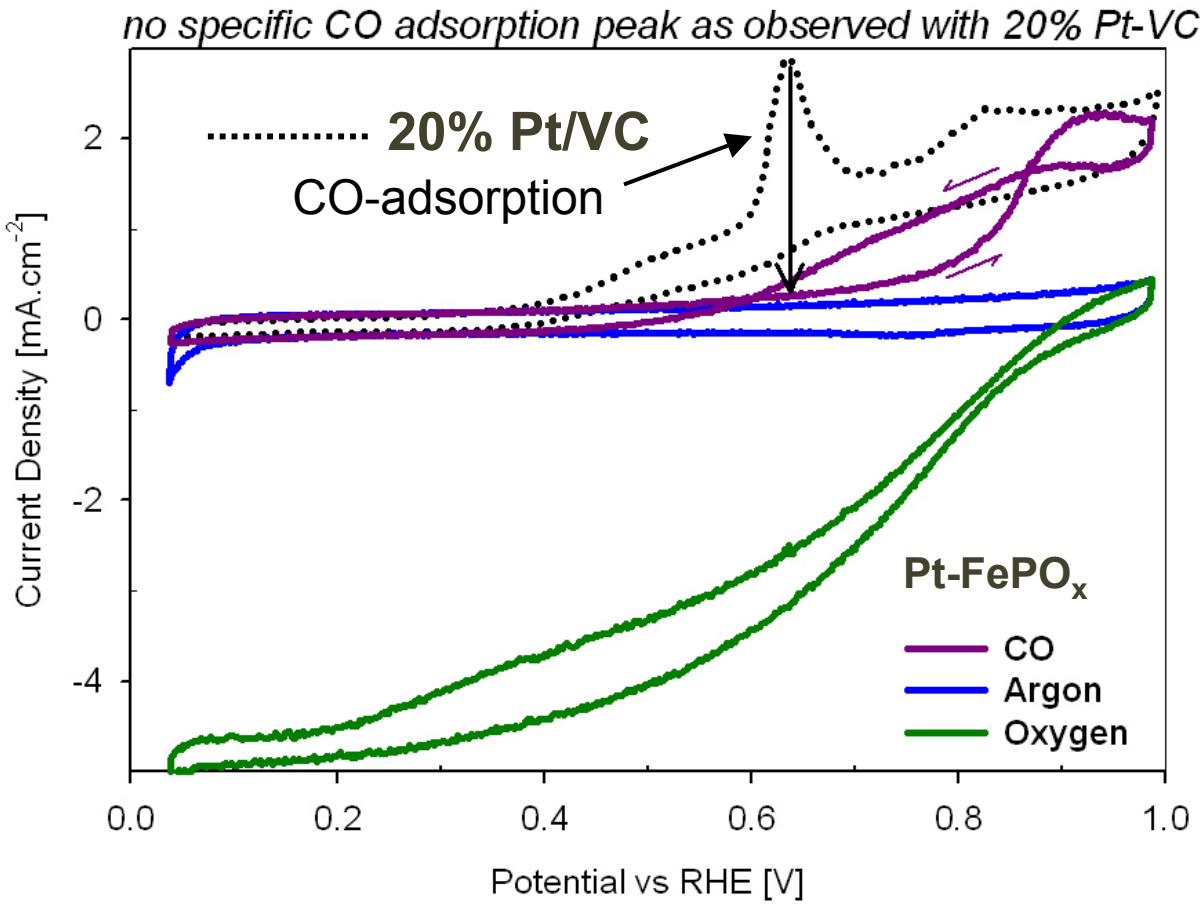
Active Pt-$FePO_x$ catalysts

Pt is oxidized (~Pt^{4+}) and not metallic in Pt-$FePO_x$

$FePO_x$ environment compresses metal-metal bond lengths, thereby changing the electronic states of the Pt and possibly making it a better catalyst

d-p bonding - occupied states at Pt modified

CO stripping of Pt-$FePO_x$



- Pt-$FePO_x$ phase shows no evidence of CO adsorption
- Pt be less susceptible to poisoning in the phosphate structure

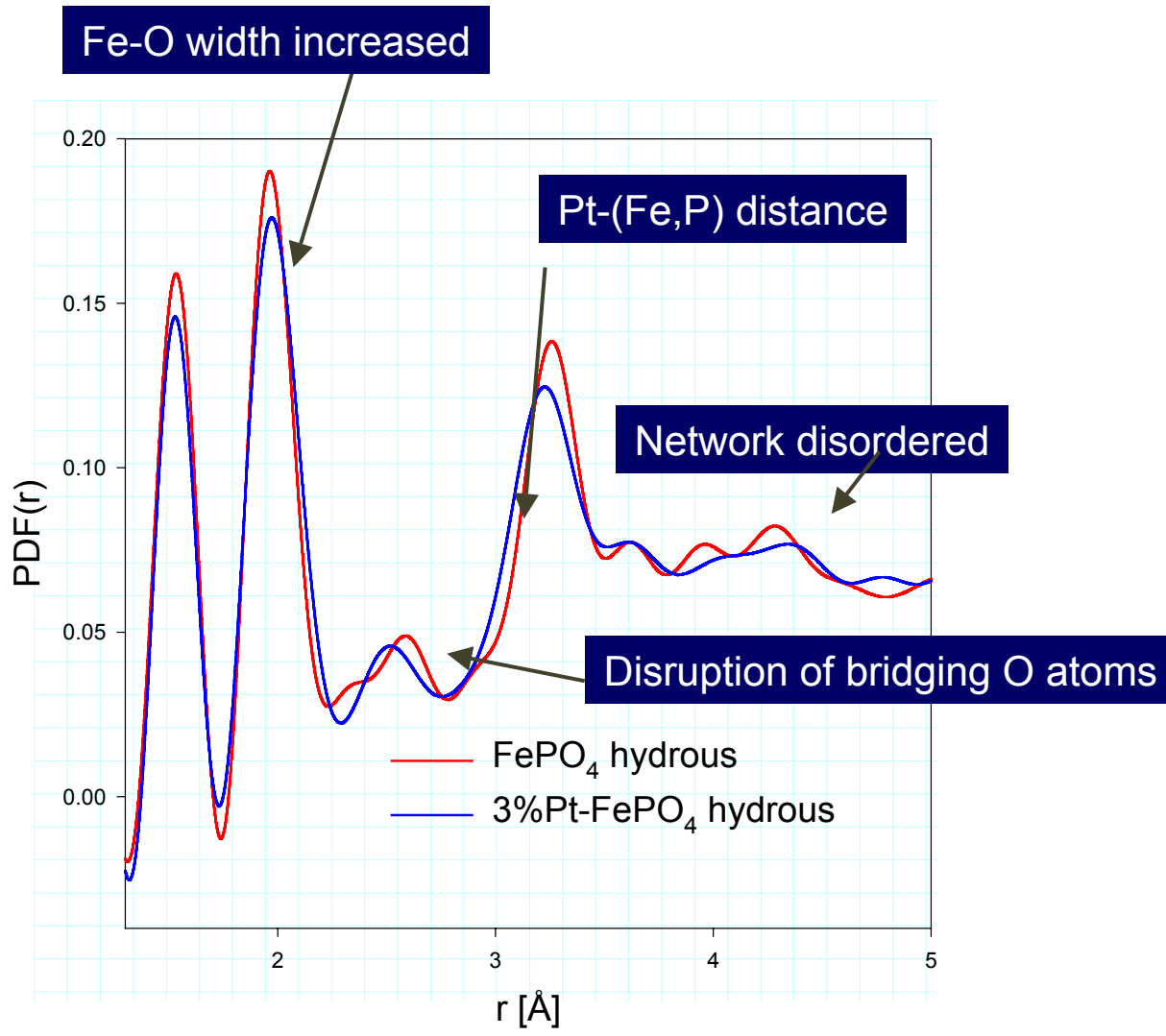
New results on acid stable Pt-$FePO_x$ phase

1.7% Pt-$FePO_x$- 80% Vulcan carbon

Structural analysis of Pt-$FePO_x$

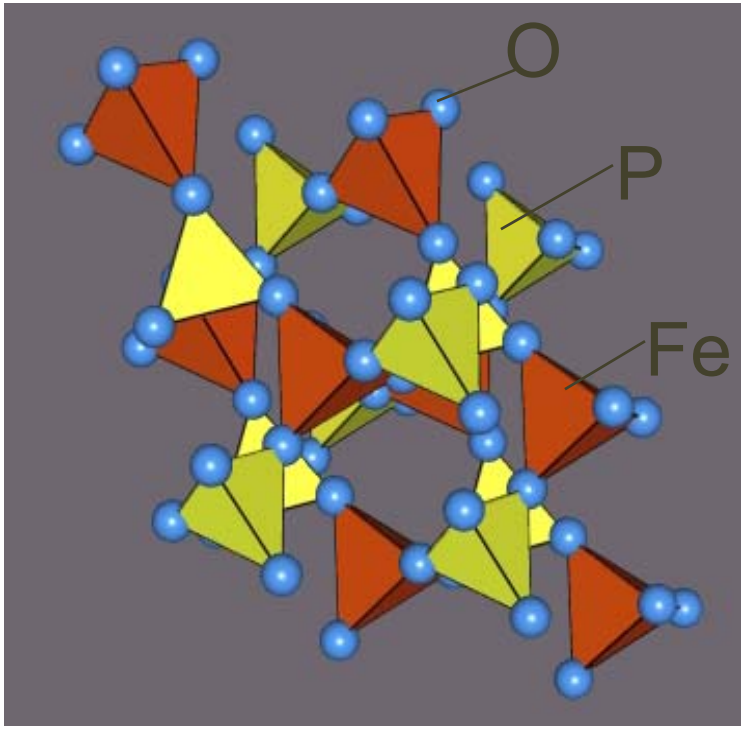
Key structural elements of active material:

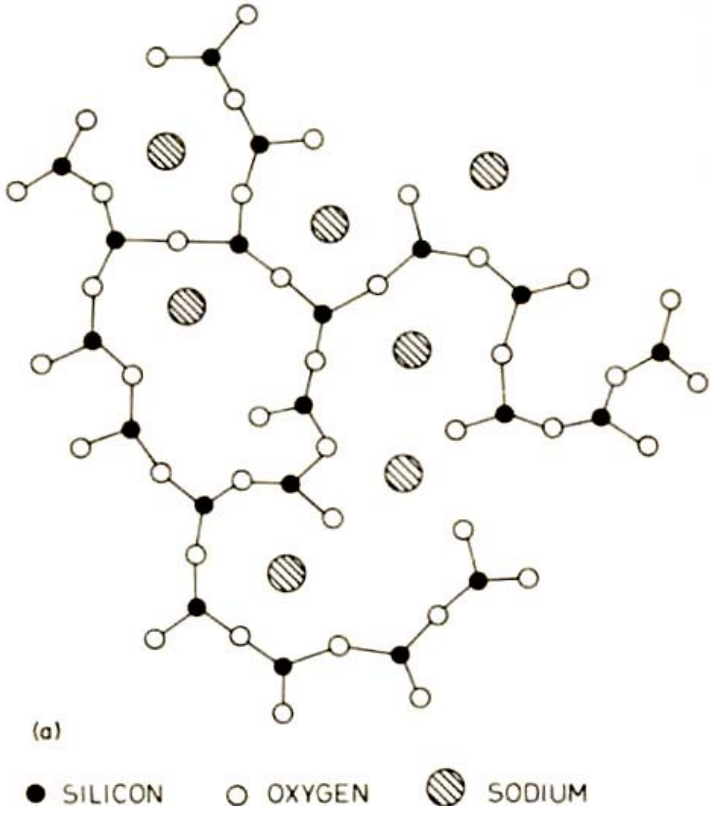
- Glassy network of FeO and PO tetrahedra – disordered α-quartz structure
- Fe is mixed valence
- Pt built-in as a "glass modifier"



Atomic pair density analysis (PDF) of high energy X-ray scattering reveals key structural elements of active material

Pt as a glass modifier

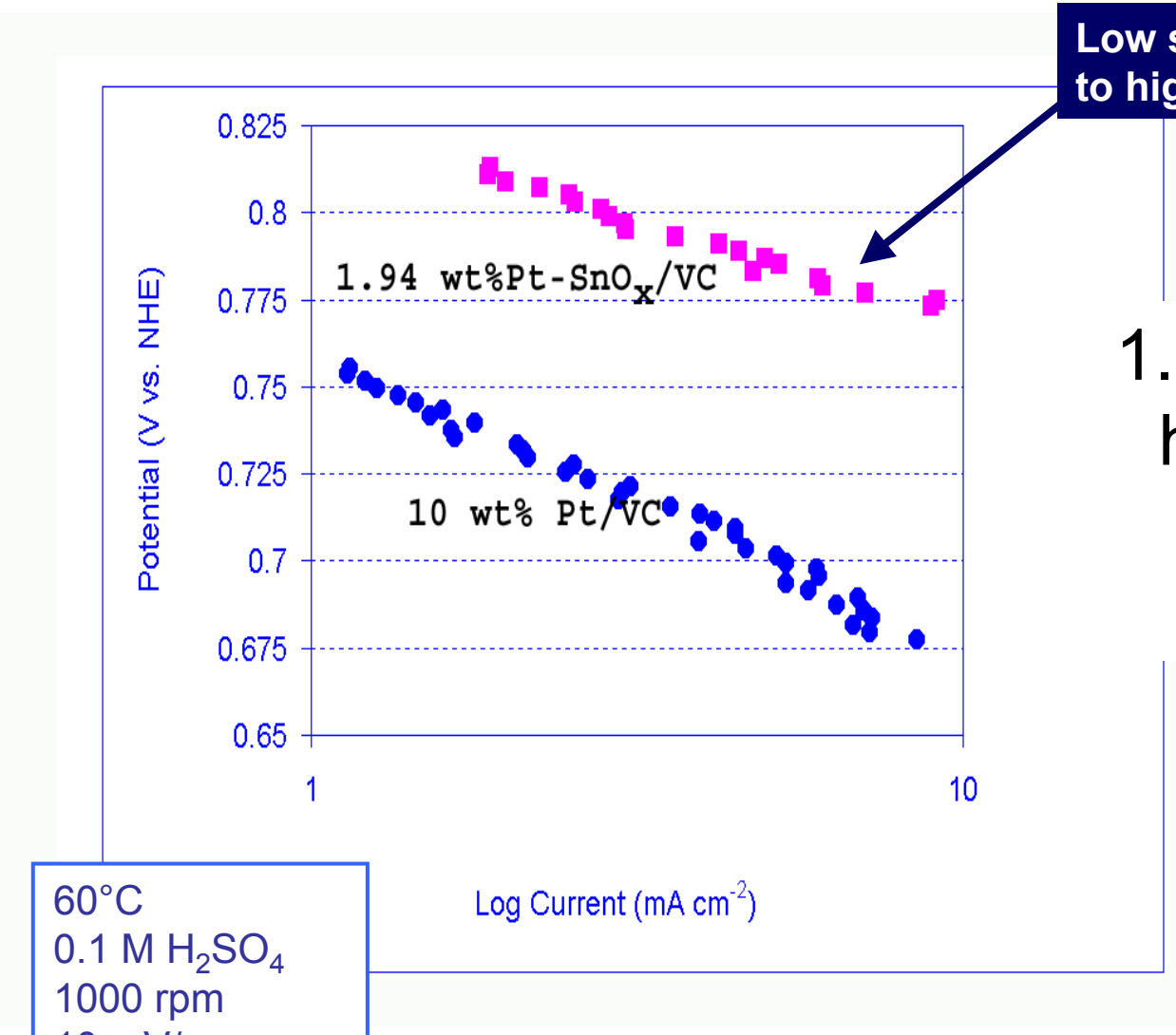




- Iron phosphate
  (*berlinite*) – *α-quartz structure*
- Pt modifies micropore sizes and long-range order

Example: Na modifies the structure of silicon oxide to form a glass

RDE performance of Pt-SnO_x



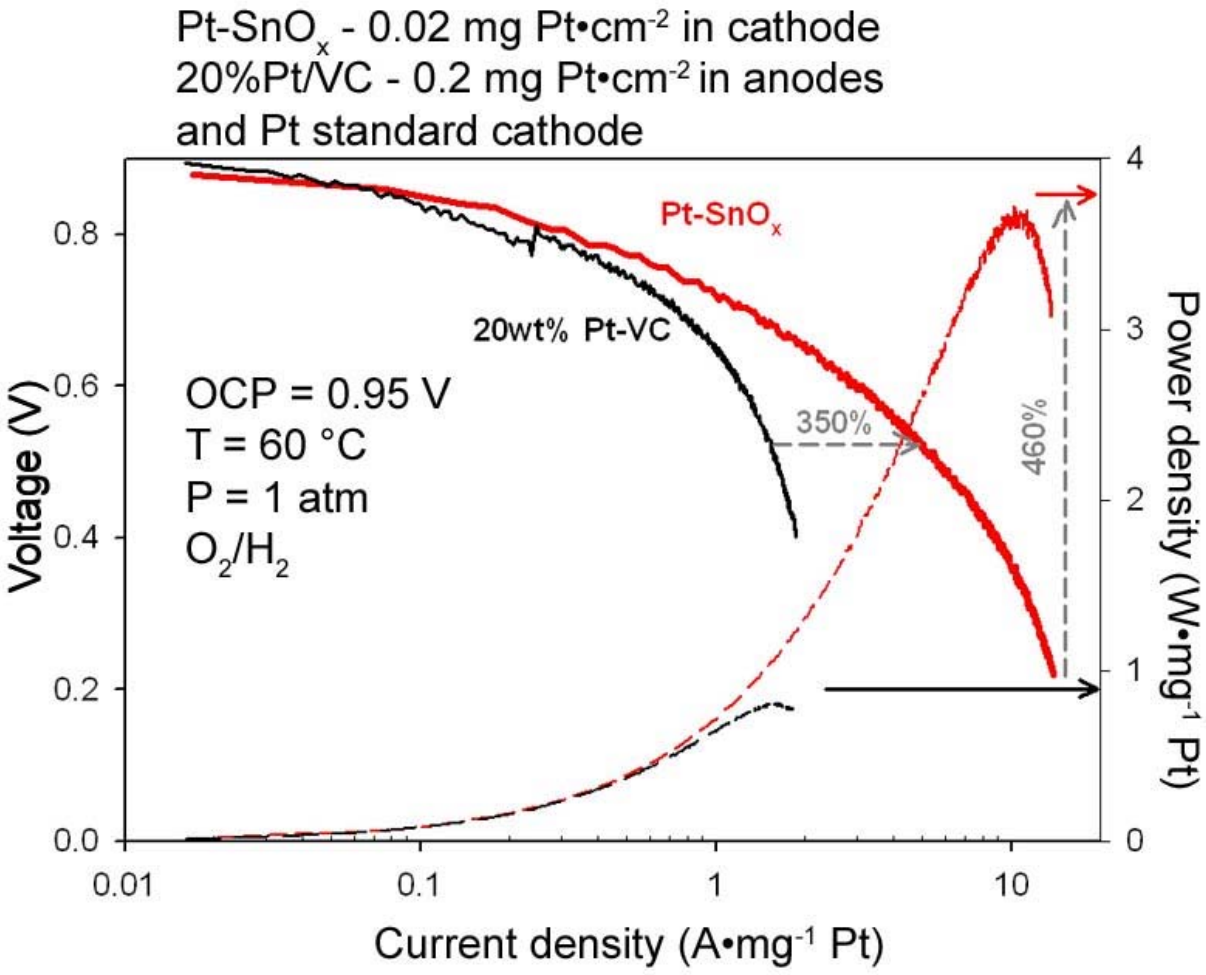
Low slope at high currents due to high H^+ conduction??

60°C
0.1 M H_2SO_4
1000 rpm
10 mV/sec

1.9 wt% Pt in SnO_x-VC has higher ORR activity than 10 wt%Pt-VC
Despite ~5x lower Pt

Pt-SnO_x cathode performance in a PEMFC

- Fuel cell performance of Pt-SnO_x is 3.5× better per wt% Pt in first-generation MEAs
- Improvements needed in MEAs (e.g., thinner catalysts layers)
- Performance at 80°C same as that at 60°C - under investigation



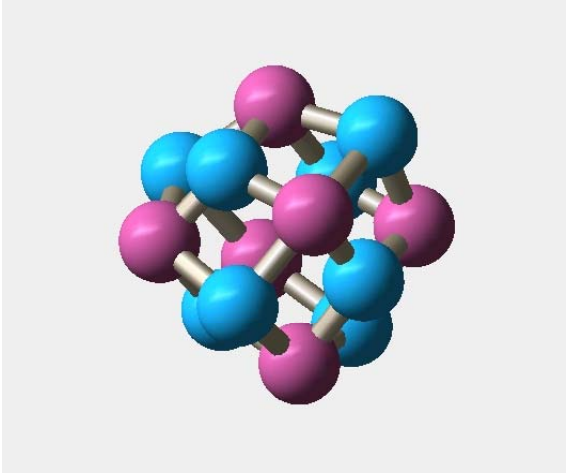
Structural analysis of Pt-SnO_x

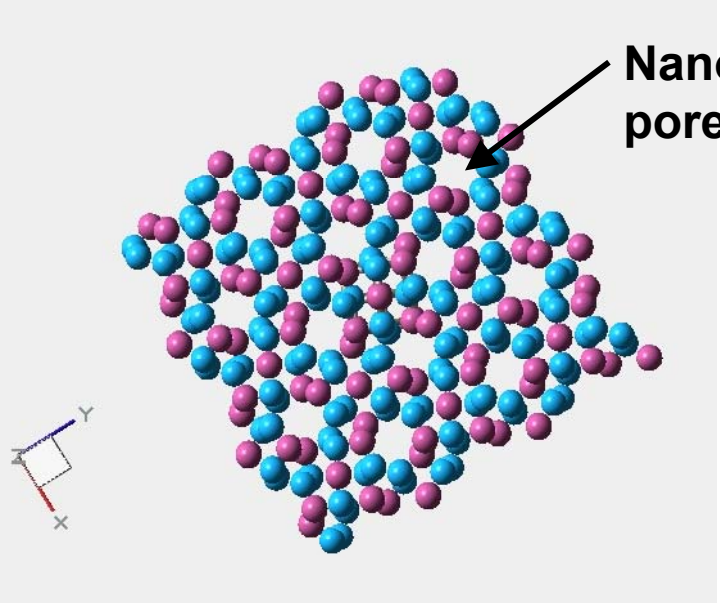
with conventional XRD and high energy XRD/PDF analysis

hydrous SnO_x - as prep is crystalline - $Sn_6O_4(OH)_4$ *(BCC packing of Sn_6O_8 clusters)*

⇒Hydrous SnO_x heated to 150 °C is amorphous

⇒Hydrous Pt-SnO_x heated to 150 °C has short-range order

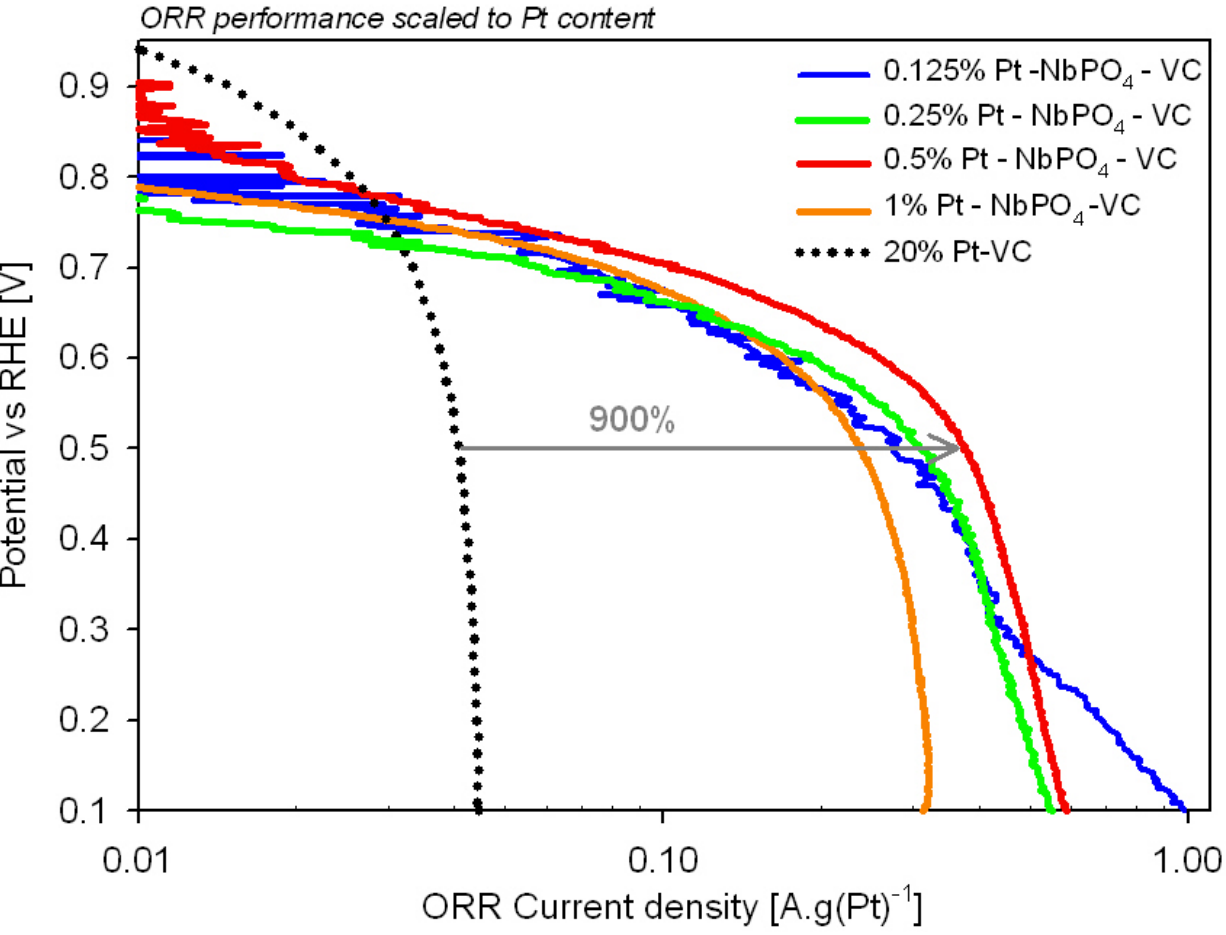




Addition of Pt and 150 °C heat treatment results in changes both within cluster and inter cluster arrangements, but the microporous structure is retained

TEM indicates that Pt distribution is non-uniform

RDEs of Pt-$NbPO_x$



- $NbPO_x$ doped with various levels of Pt - best *relative* performance from 0.5 wt% Pt in $NbPO_x$
- 9× improvement in activity per mass Pt
- OCP of Pt-$NbPO_x$ materials is lower than expected ~0.8 V vs H
- MEAs have not yet been made successfully

60 °C 10 mV/s
1600 rpm 0.1 M H_2SO_4
100 ccpm O_2 gas flow

Collaborations

- LANL - NU and PB traveled to LANL to make state-of-the-art Pt/Vulcan carbon MEAs
- General Motors - H. Gasteiger and S. Kocha traveled to NRL and shared expertise in fuel cell and RDE evaluation. KSL, PB and NU will travel to GM in late May.

Materials transfer agreements being signed with:

- ✓ GM
- ✓ E-TEK
- ✓ RPI - Benicewicz (PBI membrane fuel cells)

Response to DOE Tech Barriers

Metal	Relative costs
Pt	100%
Fe	0.12
Nb	2.4
Sn	0.14

estimated based on costs of metals in Alfa-JM 2003 catalog

Can these catalysts be useful for high T MEAs??

O: Stack materials cost (Electrode goal = $5/kW)

0.02 mg Pt/cm^2 and 3.7 W/mg Pt (for Pt-SnO_x)

Assume $15/g Pt

--> $4/kW for Pt-$SnO_x$ cathode

P: Durability (5000 h)

Catalysts are stable in sulfuric and phosphoric acid

Pt distributed in oxides will be less prone to ripening than metallic particles, so there is opportunity for longer lifetime

Q: Electrode performance (reduce high overpotentials at cathode)

Under investigation

Goals for 2003-2004

- Isolate active Pt-phosphate and/or Pt-oxide phases
- Improve MEA development via internal research and collaborations
  - ✓ Modify catlyst morphology (surface area & particle size)
  - ✓ Identify optimal deposition methods and processing conditions
- Improve electronic transport in metal oxides via doping with appropriate metals
  - ✓ $FePO_x$ doped with Mo
  - ✓ $NbPO_x$ doped with W
  - ✓ SnO_x doped with In or Sb
- Understand structure of active catalyst
  - ✓ In situ XANES and PDF-XRD studies
- Investigate carbon-support interactions
  - ✓ Nitrogen functionalities on carbon may enhance Pt-iron phosphate activity
- Continue stability evaluation of catalysts in acids and in fuel cells

Response to reviewers

A lot of constructive criticism from last year - we responded to all practical suggestions

- ✓ Validate results from RDE measurements by testing materials in MEAs in fuel cells
  - Our RDE and MEA results correlate to the ORR (but not for HOR)
  - MEA development needed to maximize benefits of new materials
- ✓ Justify approach to work on iron oxides
  - Iron phosphates have unique properties and are stable in acid with Pt
- ✓ Evaluate materials' stability
  - Preliminary stability studies have been completed and stability must be evaluated in a fuel cell
- ✓ Expand collaborations with industry
  - Collaborations with industry will expedite progress in 2003 - 2004

Summary

- Low-Pt catalysts can be prepared by dispersing Pt in metal oxide supports
- Choice of metal-oxide support is critical

  naturally-forming microporous oxides have good attributes for fuel cells
- Pt-impregnated oxides and phosphates can be stable under the acidic conditions of fuel cells
- Pt present as ~Pt^{4+} and may be less easily poisoned
- Oxidized Pt atoms can be active catalytic sites with the appropriate oxide environment (electronic and ionic effects)
- Structural analysis of new catalysts performed EARLY

  PDF of XRD is an excellent tool for analysis of materials with nanoscale features
- "Amorphous" can be a function of your analytical method

Project: LOW Pt LOADING ELECTROCATALYSTS

Principal Investigator: Radoslav Adzic

Research Associates: Kotaro Sasaki and Miomir Vukmirovic (since Jan. 2003)

With contribution from: Yibo Mo, Jia Wang, Junliang Zhang (graduate student at SUSB)

Materials Science Department,
Brookhaven National Laboratory, Upton, NY 11973-5000

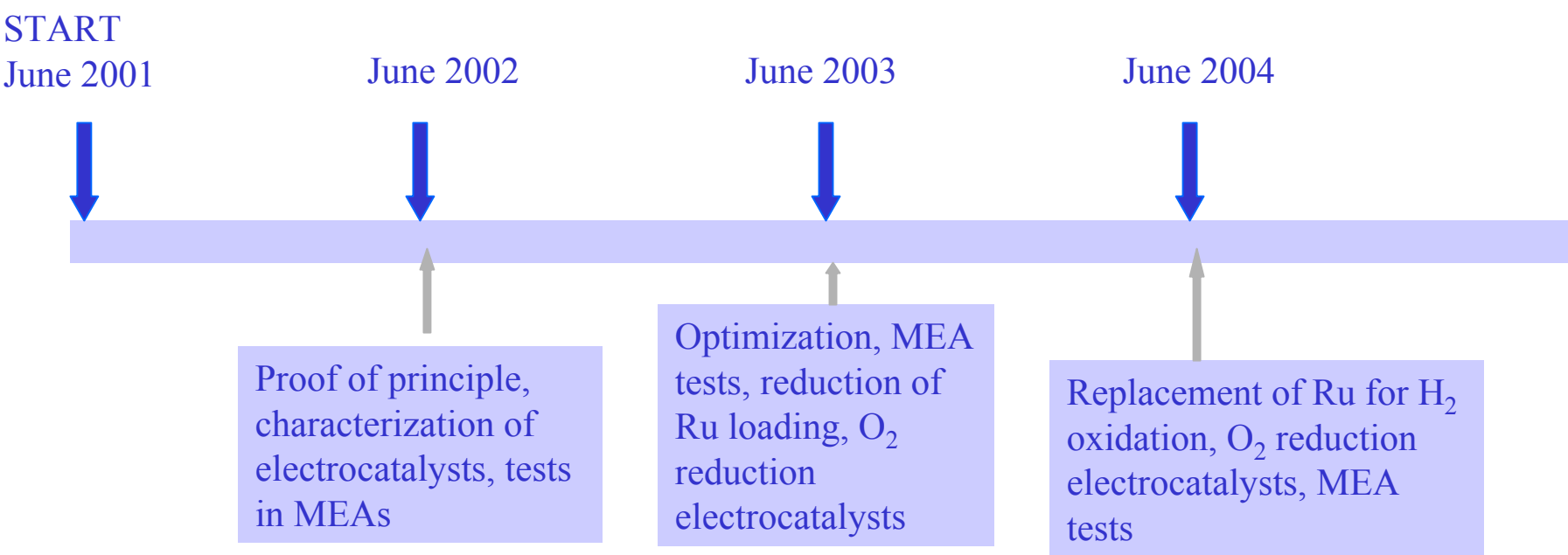
WHY Pt MONOLAYER ELECTROCATALYSTS ?

- ultimate reduction of Pt loading
- complete Pt utilization – every Pt atom counts
- low coordination of Pt atoms should enhance their activity
- strained overlayer - enhanced activity
- compressed overlayer - decreased activity
- coverage dependent electronic properties

OBJECTIVES

1. Development of novel electrocatalysts with a monolayer level Pt loadings.
2. Elucidation of their catalytic action.

PROJECT TIMELINE



ACCOMPLISHMENTS

BROOKHAVEN NATIONAL LABORATORY

- The (√19 x √19)6CO phase determined by SXS on Pt(111) and a fast (2 x 2) ↔ (√19 x √19) phase transition found. H_2 oxidation less inhibited by this phase than by the (2 x 2) adlayer.

- A considerable improvement of the 1%Pt /10%Ru/C catalyst has been achieved. The "life" for the oxidation of 1000 ppm CO/H_2 at 2500 rpm extended from <3h to >6h. Stability tests at LANL show a good activity after 222h of combined CO/H_2 and H_2 operation.

Loadings in anode: 18μg Pt/cm^2 + 180 μg Ru/cm^2
DOE Target for 2004: 300 μg/cm^2 for anode and cathode

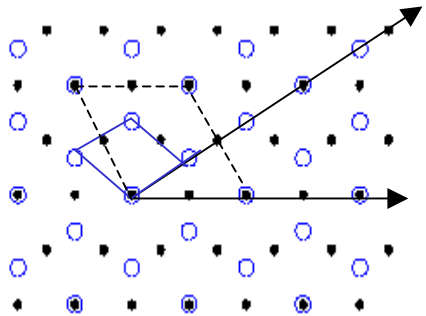
- Pt on C-supported Au nanoparticles can be an efficient catalyst for O_2 reduction. The Pt mass specific activity 2.5 times higher than that of Pt10%/C achieved. Stability needs to be investigated.

- Pt on C-supported W nanoparticles (synthesized by D. Mahajan, BNL) appear promising as a catalyst for H_2 oxidation.

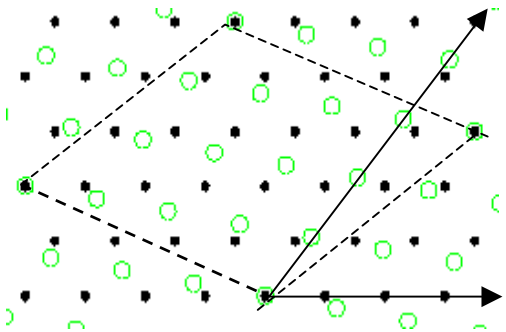
CO ADSORPTION AND H_2 OXIDATION ACTIVITY ON Pt(111)

New insights into the structure and phase behavior from *in situ* SXS

(2x2)-3CO, θ=0.75

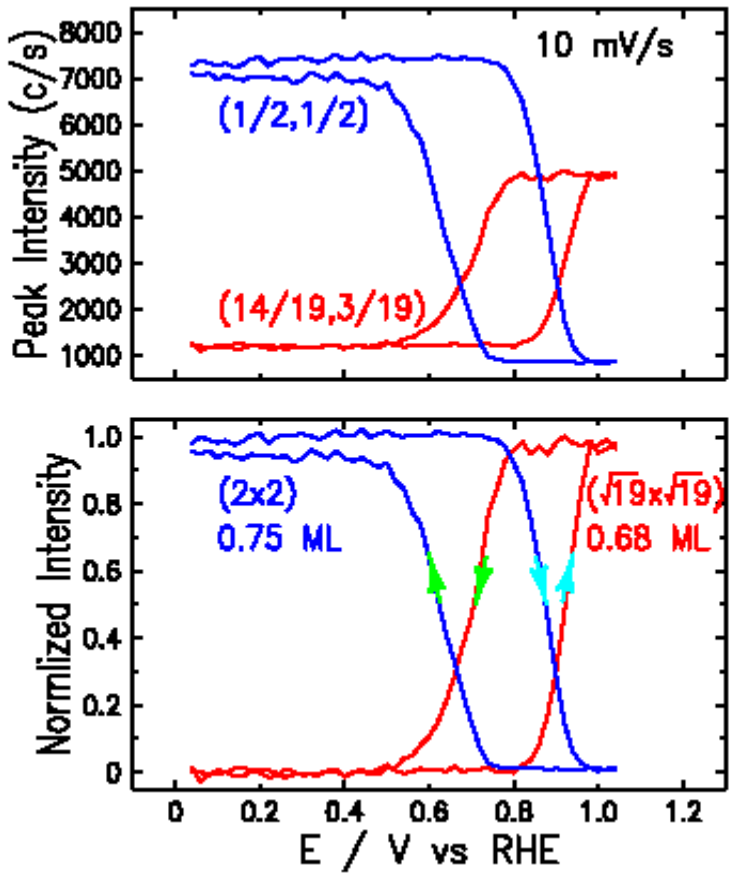


(√19x√19)-13CO θ=0.68



CO 1 atop, 6 near-atop, 6 near-bridge. The near-atops prefer to surround the atop.

(2x2)-3CO ↔ (√19x√19)-13CO phase transition

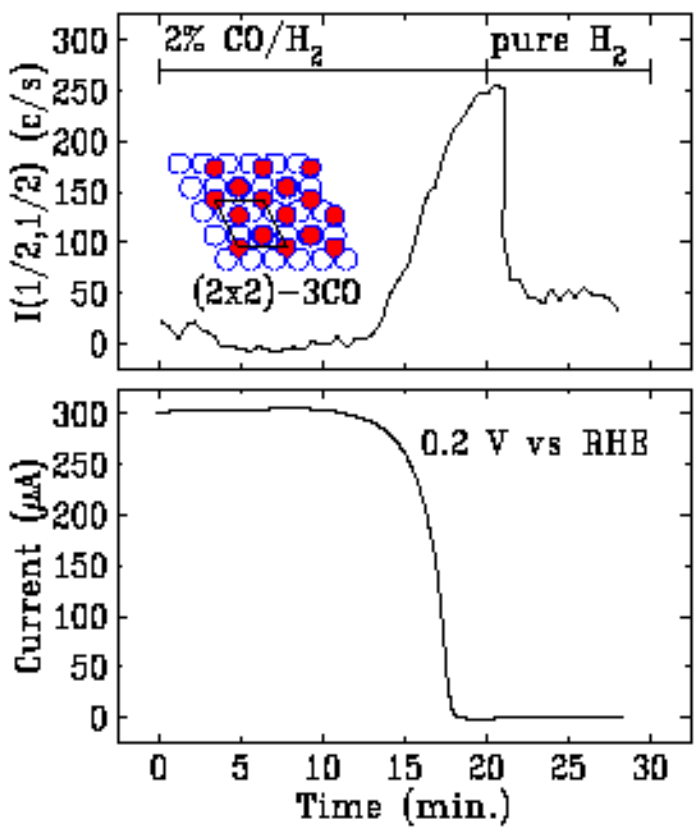


Both phases can exist over wide potential region depending on CO concentration

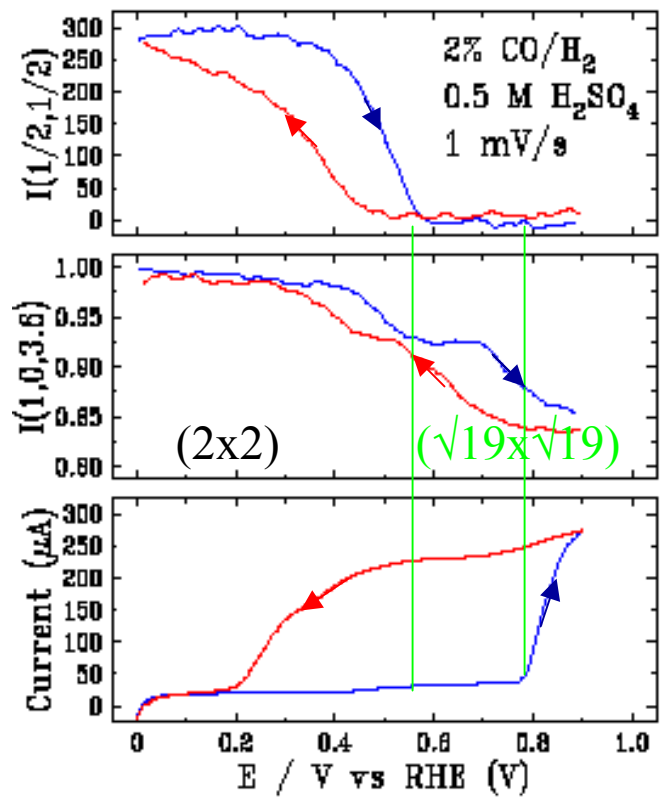
Fast phase transition – small energy barrier between different sites

CO ADSORPTION AND H_2 OXIDATION ACTIVITY ON Pt(111)

Phase behavior in 2% CO/H_2 in sulfuric acid solution



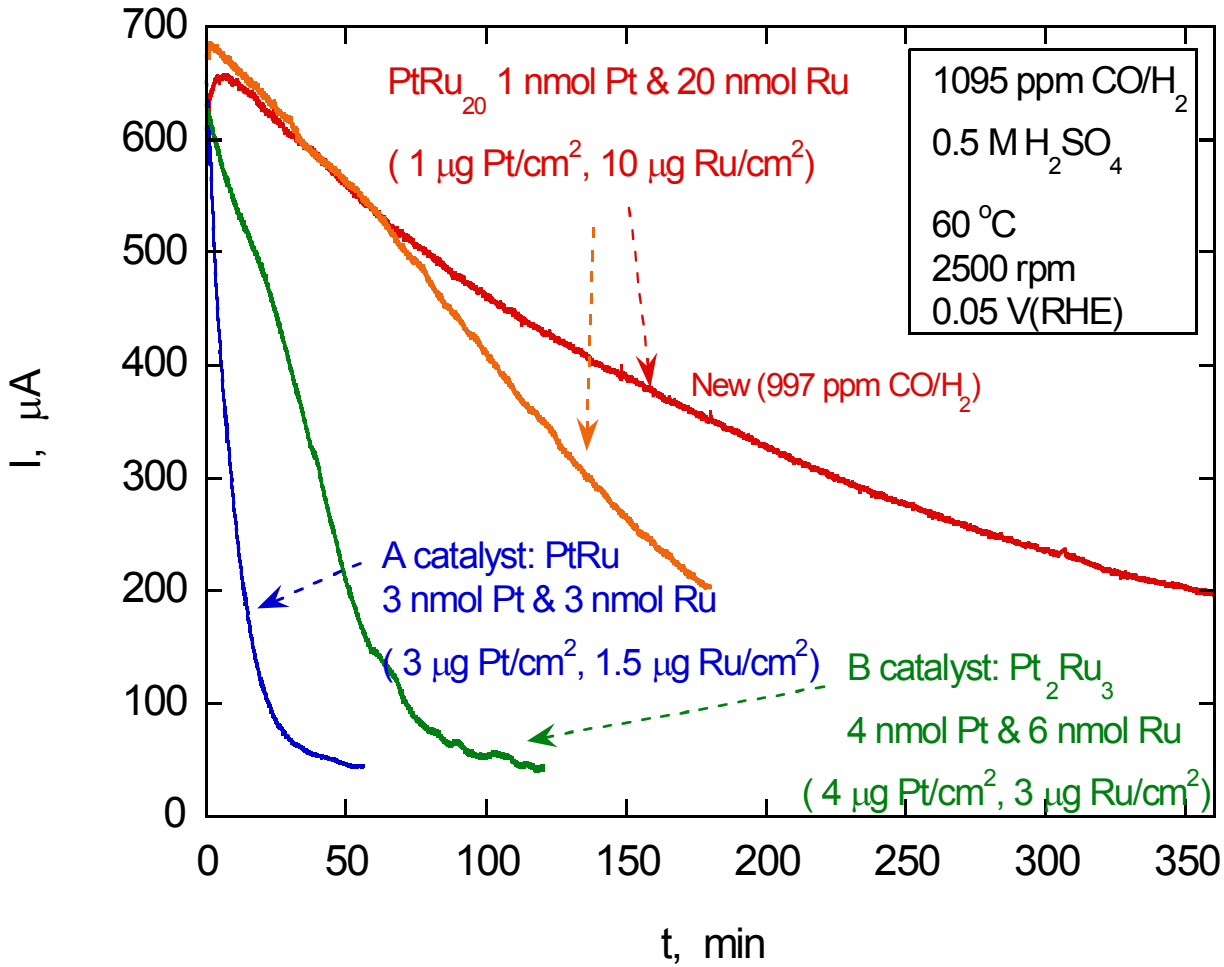
The (2x2) phase forms in small patches, which completely inhibit H_2 oxidation.



Larger hysteresis in activity than in CO phase transitions. Smaller inhibition by the low-coverage (√19x√19) phase.

IMPROVEMENT OF A $PtRu_{20}$ ELECTROCATALYST

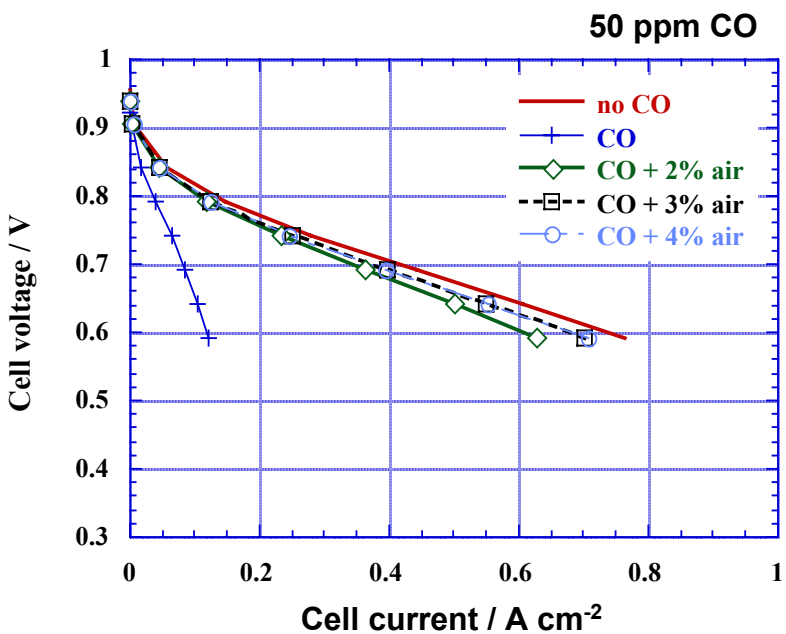
- Mixed Pt-other noble metal (Os, Re, Ir) adlayers on Ru are not better than $PtRu_{20}$
- Optimization of the preparation procedure resulted in an improved CO tolerance of $PtRu_{20}$

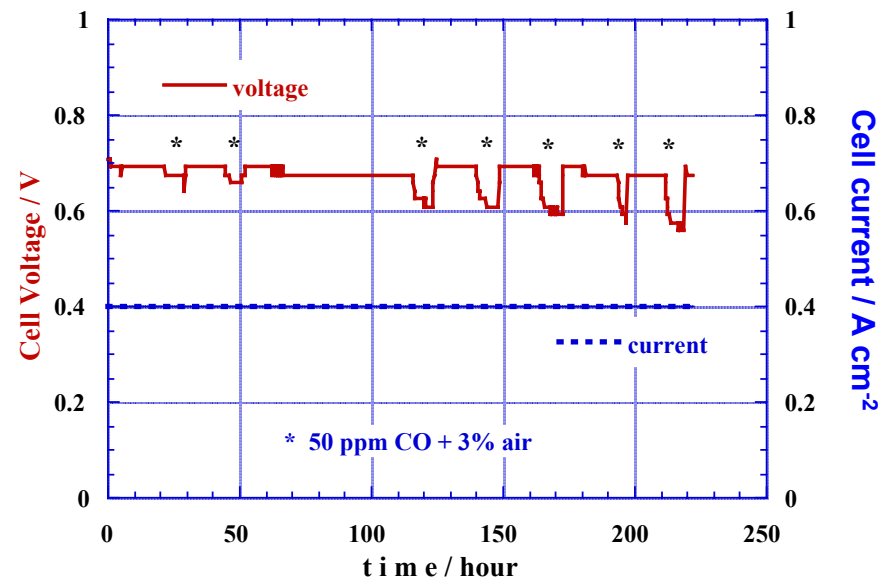


Low Pt Content Catalyst Long Term Test*

Carbon supported 1 w% Pt - 10 w%Ru catalyst (BNL)

Anode Pt Loading: 19 μg/cm^{-2}





50 cm^2 H_2/Air cell at 80 ^oC
A: 0.21 mg total metal/cm^2
C: 0.20 mg Pt/ cm^2
1.5 H_2 stoich

*** 48.5 hrs operation with 50 ppm + 3% air CO**

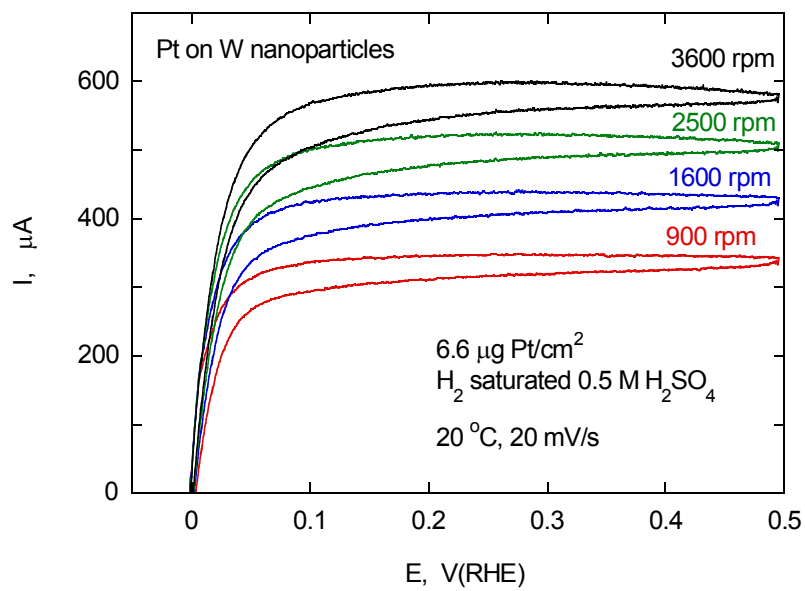
*** Performance losses of 100 mV after 222 hr of operation at 0.4 A/cm^2 or 17 mV for H_2.**

*The results obtained by Francisco Uribe and coworkers, LANL

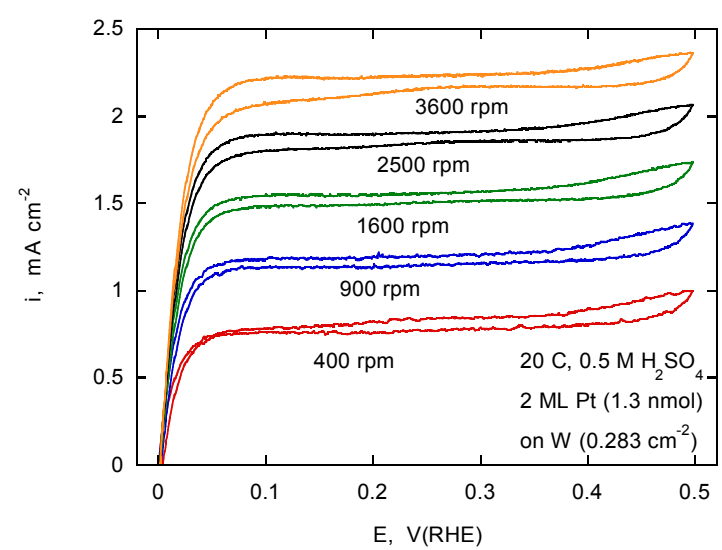
REDUCTION OF Ru CONTENT IN Pt/Ru ELECTROCATALYSTS

- RuNi, RuCo nanoparticles were deposited on XC-72 by wet impregnation and then Pt was deposited spontaneously. Compositions determined by EDX after Pt deposition. Activity of these catalysts is somewhat lower than that of Pt/Ru, CO tolerance similar.
- Pt/Wpoly and Pt/W/C have a good activity for H_2 oxidation but poor CO tolerance.

H_2 oxidation on Pt/W/C



H_2 oxidation on Pt_{2ML}/Wpoly

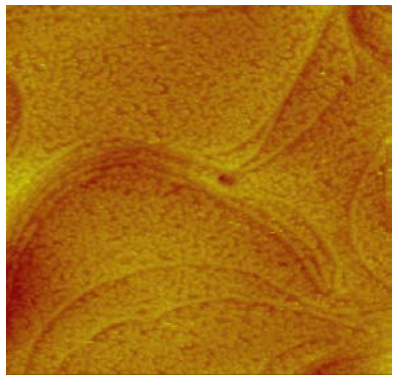


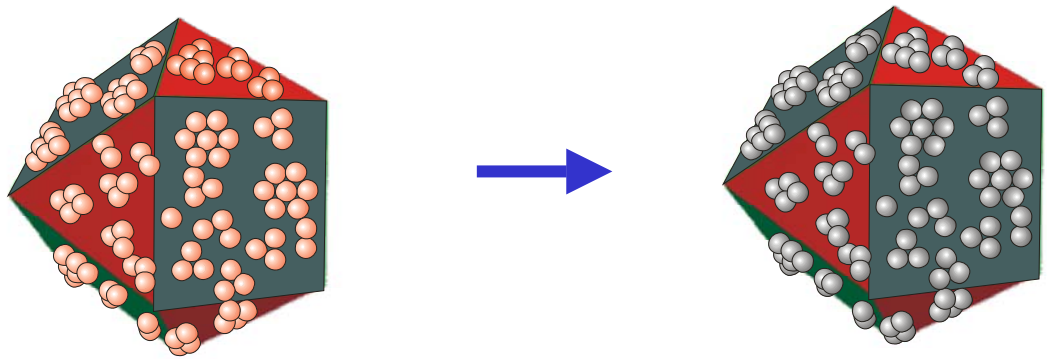
O_2 REDUCTION ON Pt MONOLAYERS on C-SUPPORTED METAL NANOPARTICLES

Pt MONOLAYER ON Au(111) BY REPLACING A Cu UPD ADLAYER

$Cu_{UPD}/Au + Pt^{2+} \rightarrow Pt/Au + Cu^{2+}$

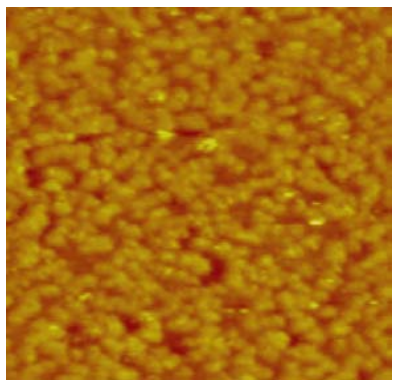
320x320nm

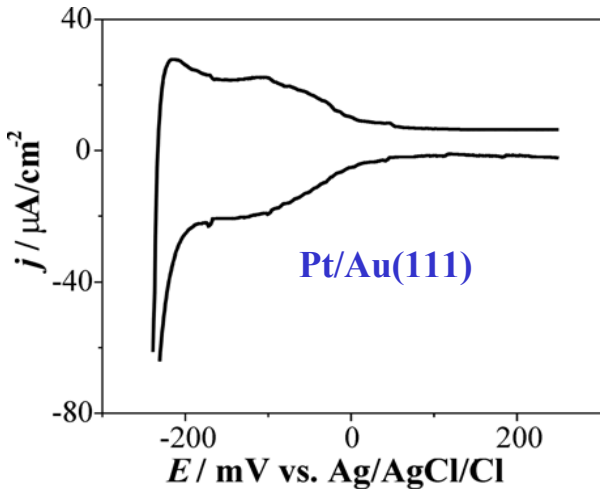


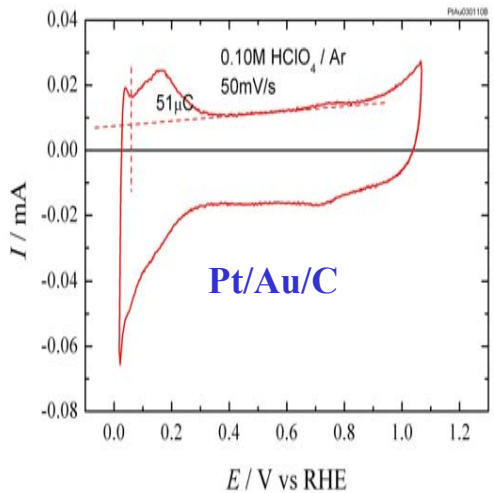


No step edge effects

105x105nm

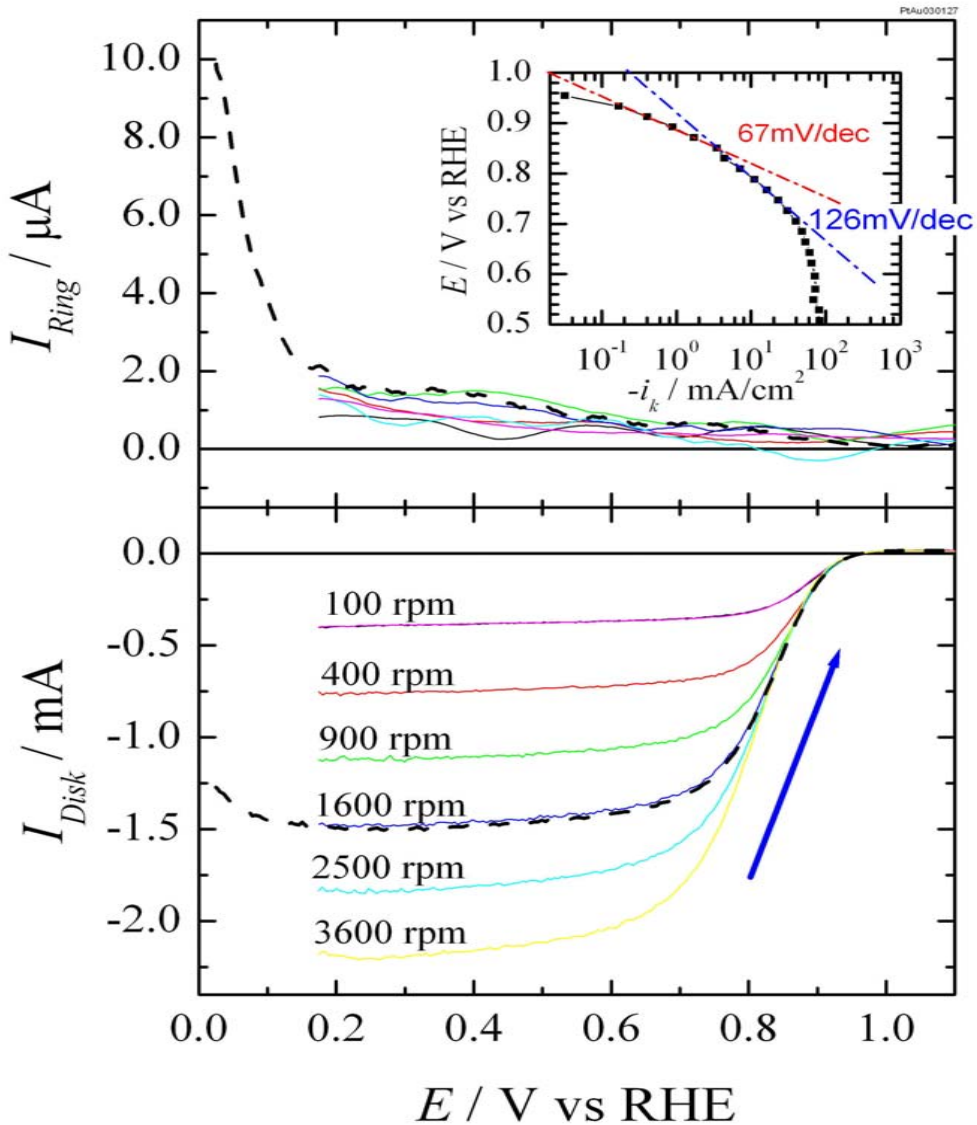


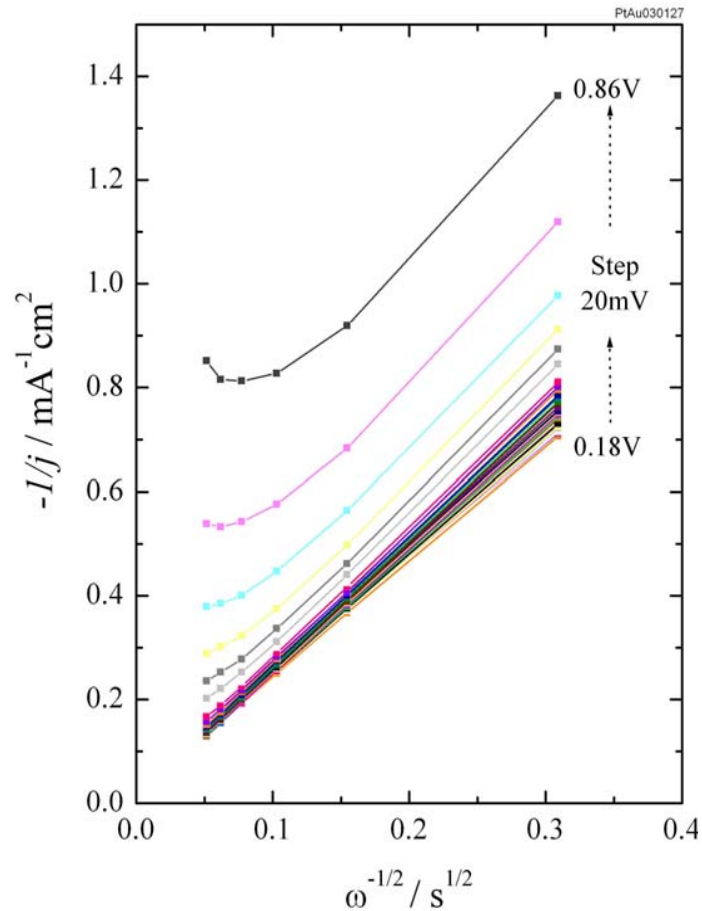




Low coordination of Pt atoms

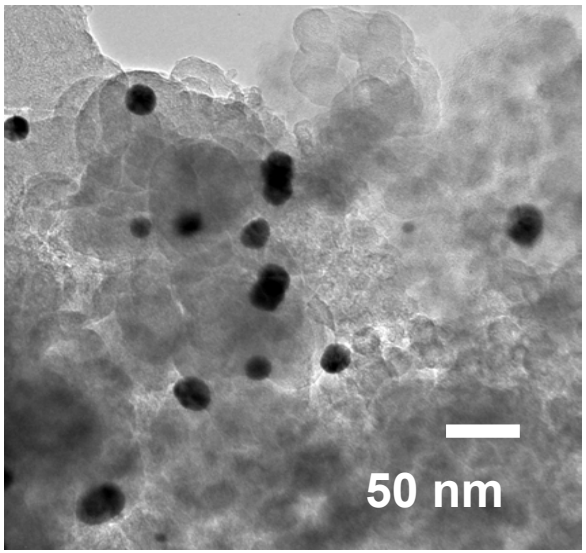
O_2 REDUCTION ON $Pt_{1ML}/Au(111)$

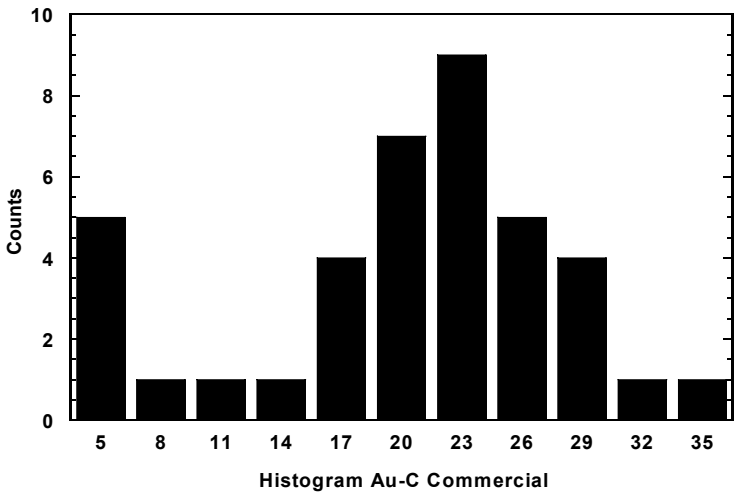


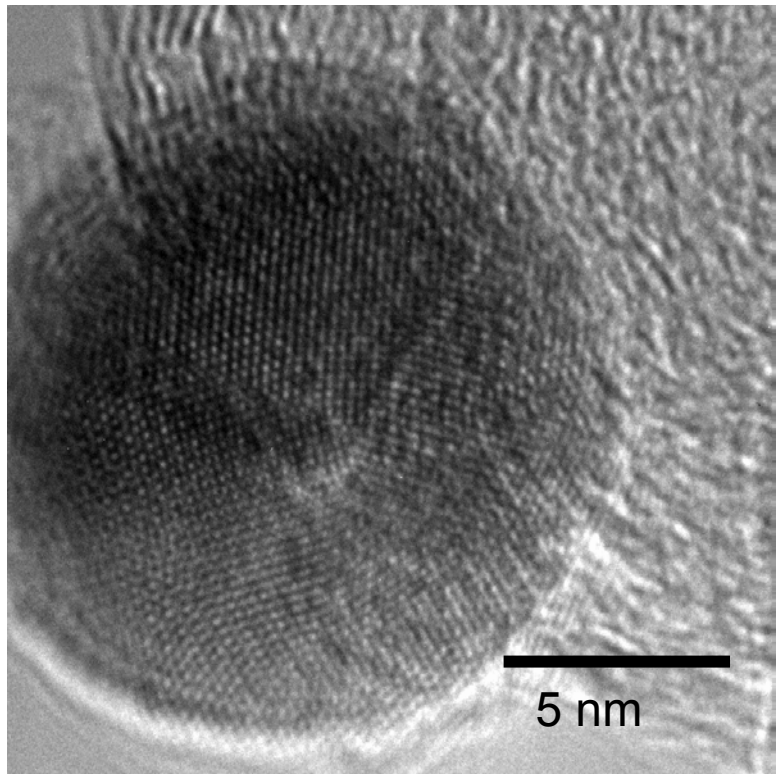


HRTEM OF Au NANOPARTICLES ON C

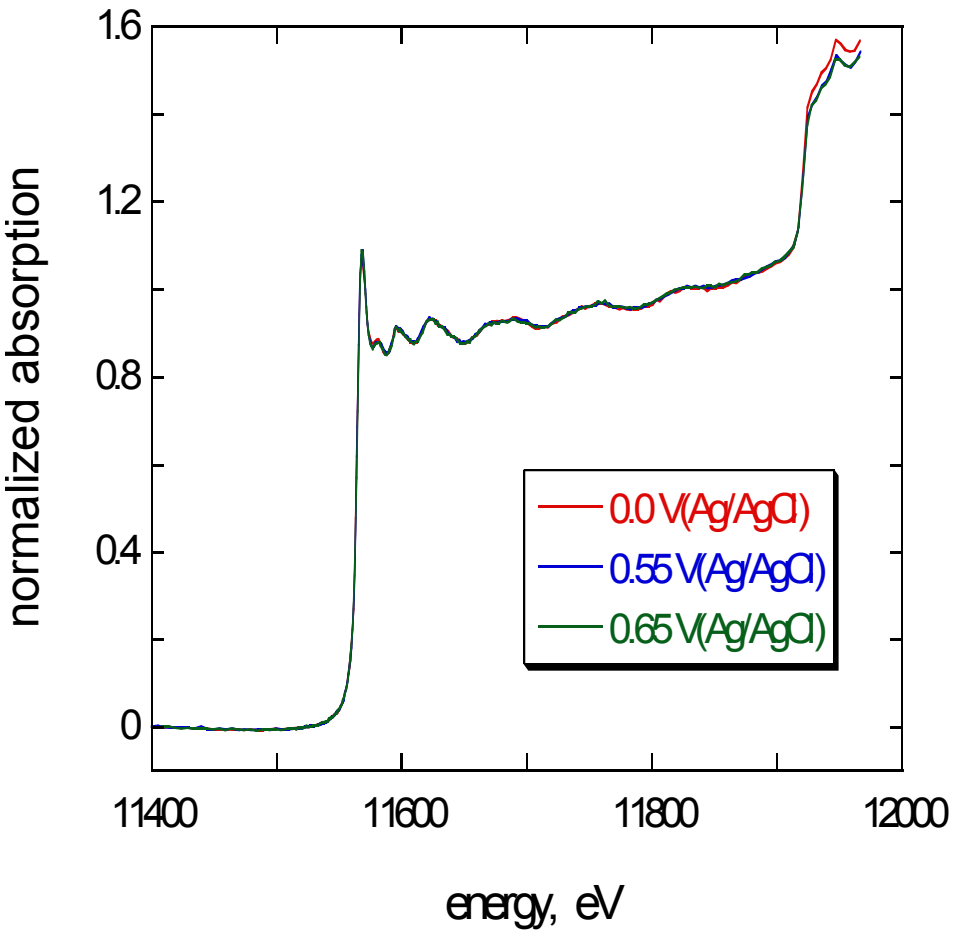
Au(10%) / Vulcan XC-72 commercial

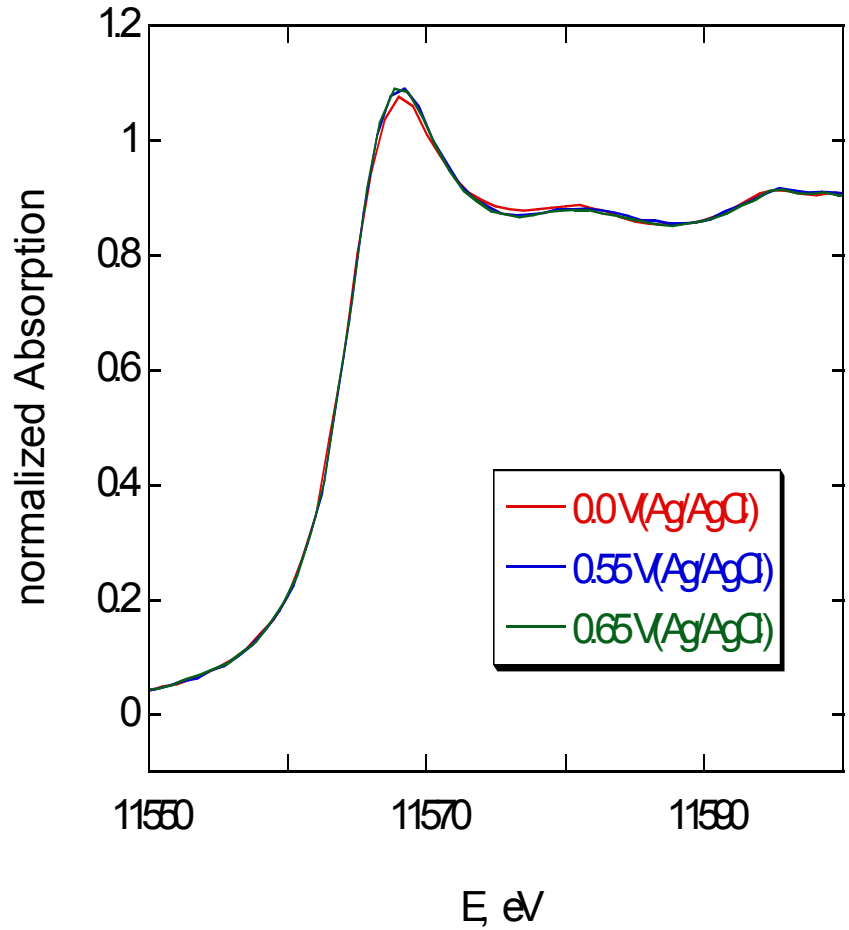






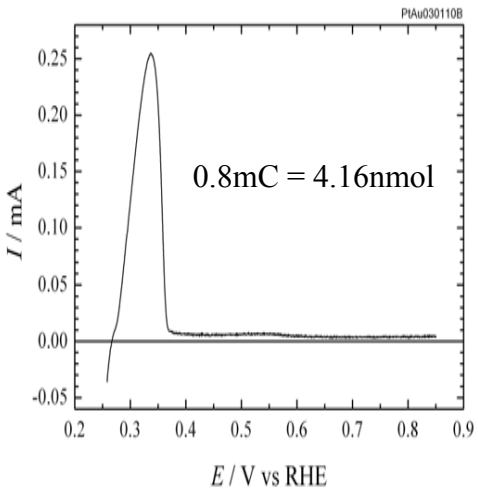
IN SITU XAS OF Pt/Au/C

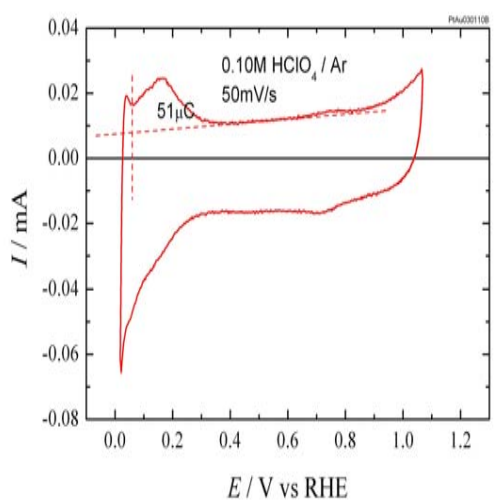




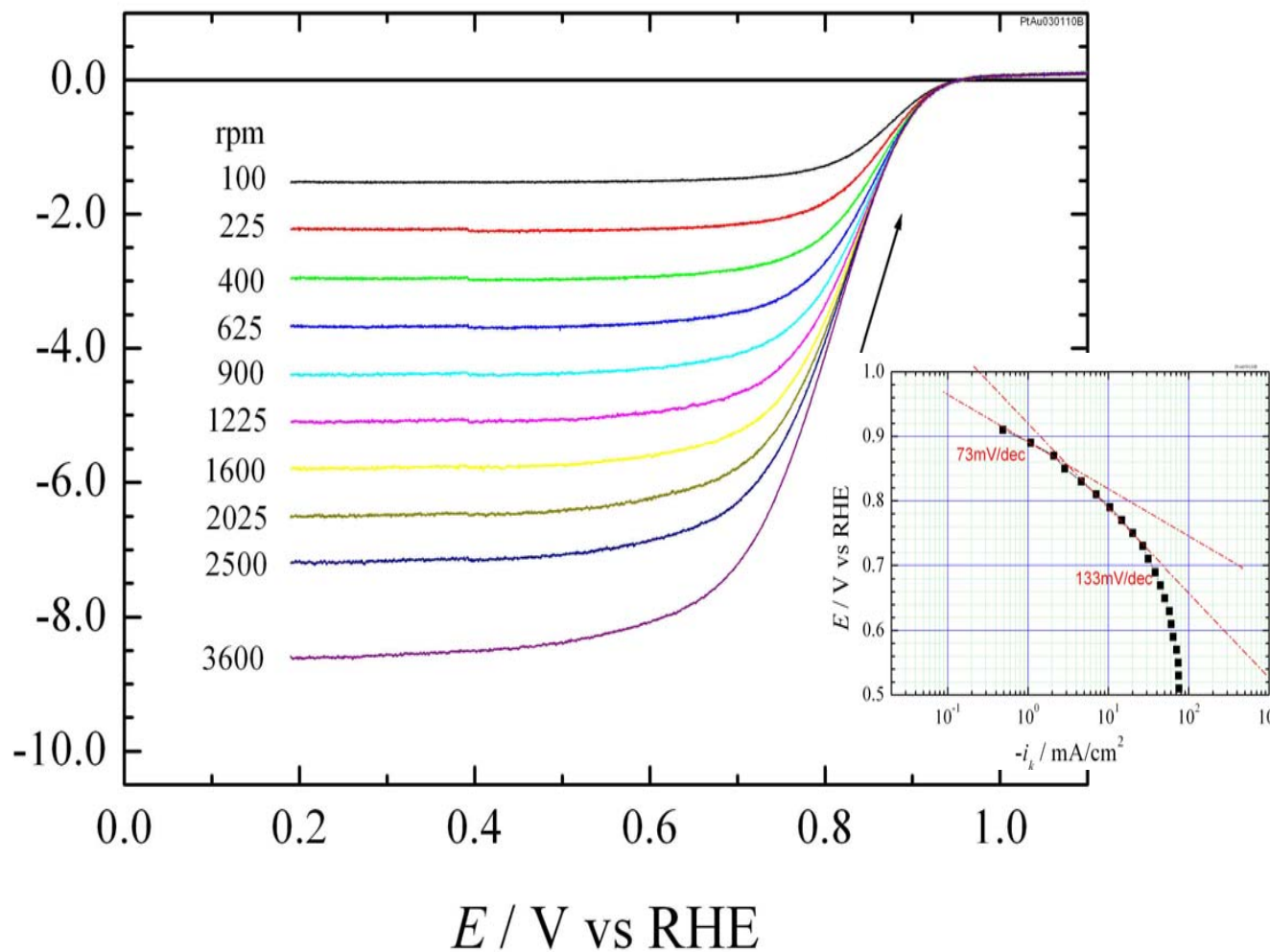
O_2 REDUCTION ON Pt/Au/C

Stripping Cu from Au nanoparticles

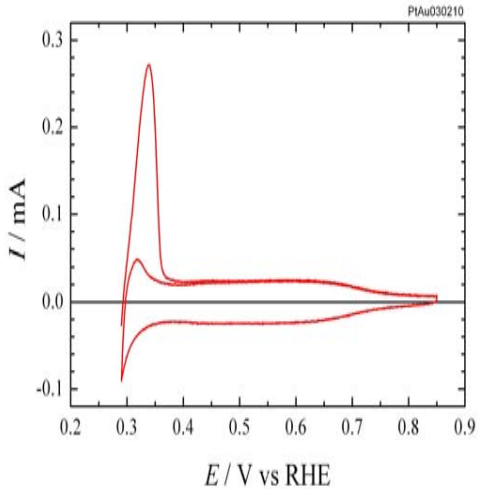


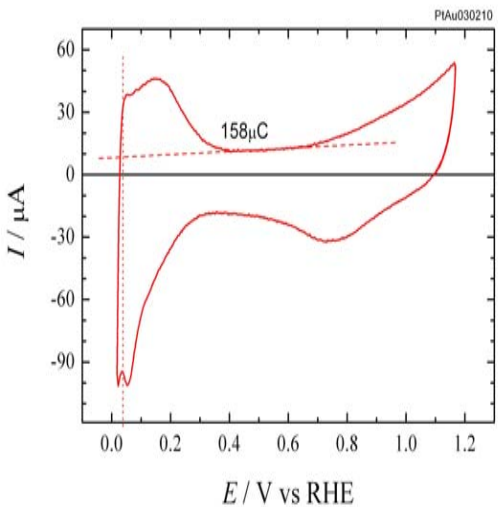


0.1M $HClO_4$; 10mV/s **Pt loading ~ 9 μg/cm²**



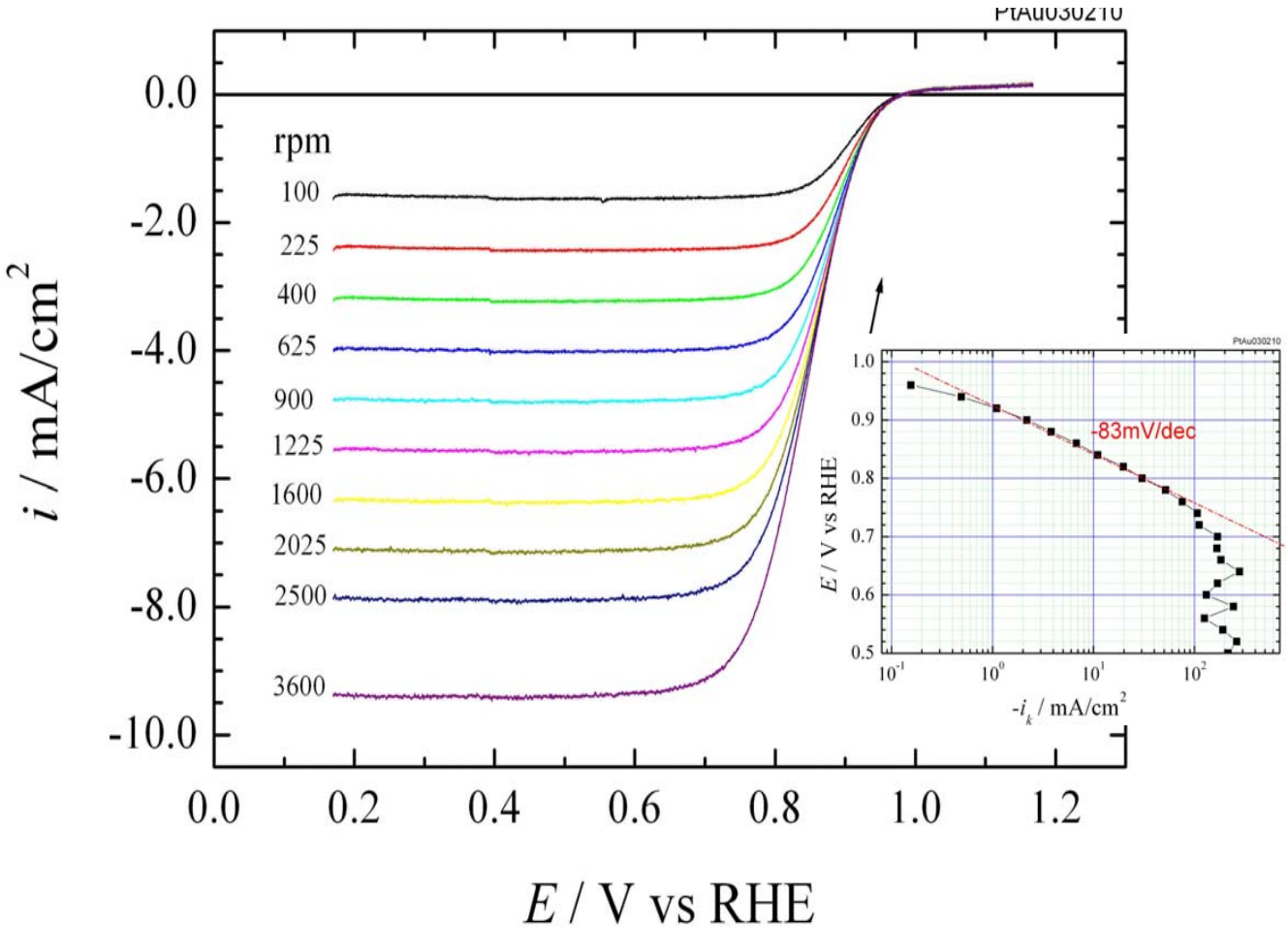
O_2 REDUCTION ON Pt/Au/C



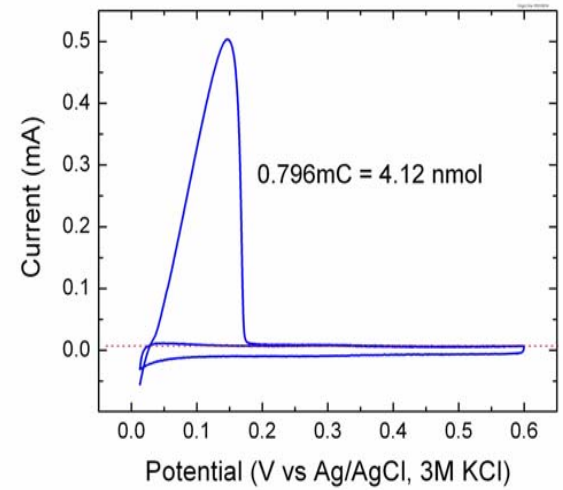


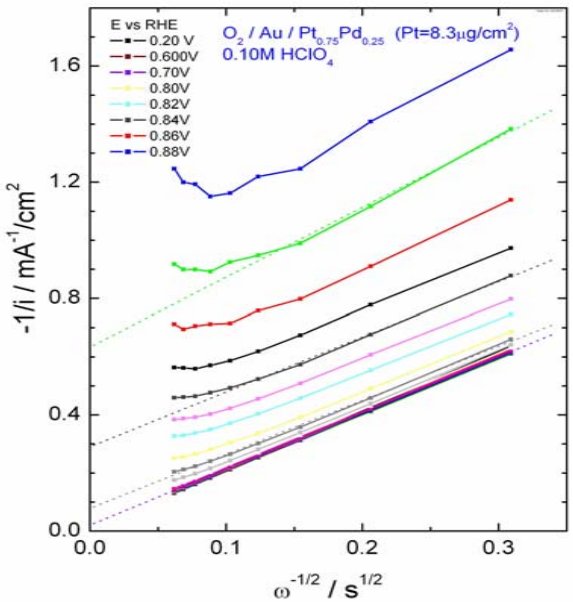
0.1M $HClO_4$ 10mV/s

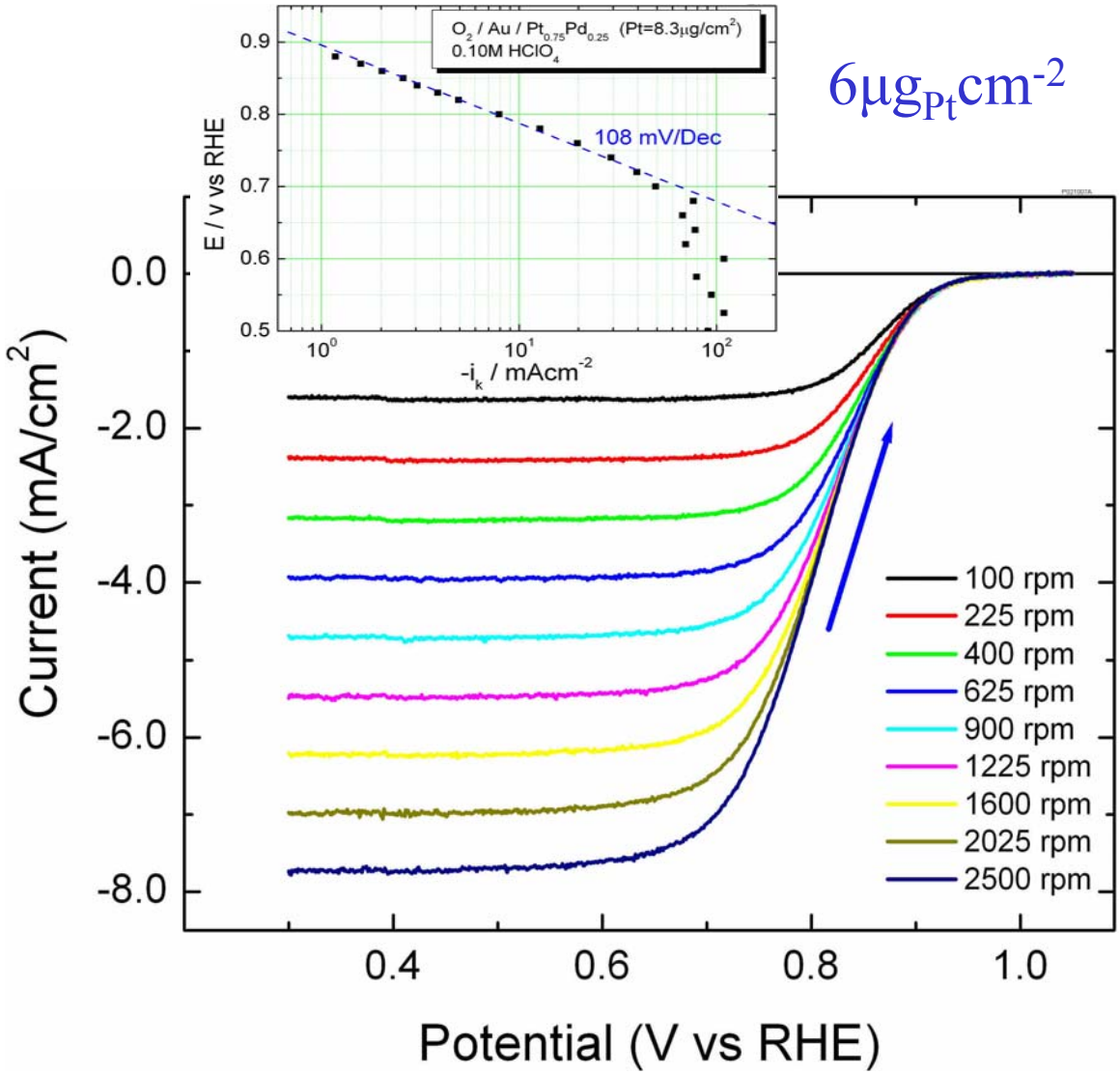
Pt loading ~ 18 μg/cm2



O_2 REDUCTION ON $Pt_{0.75}Pd_{0.25}$/Au/C





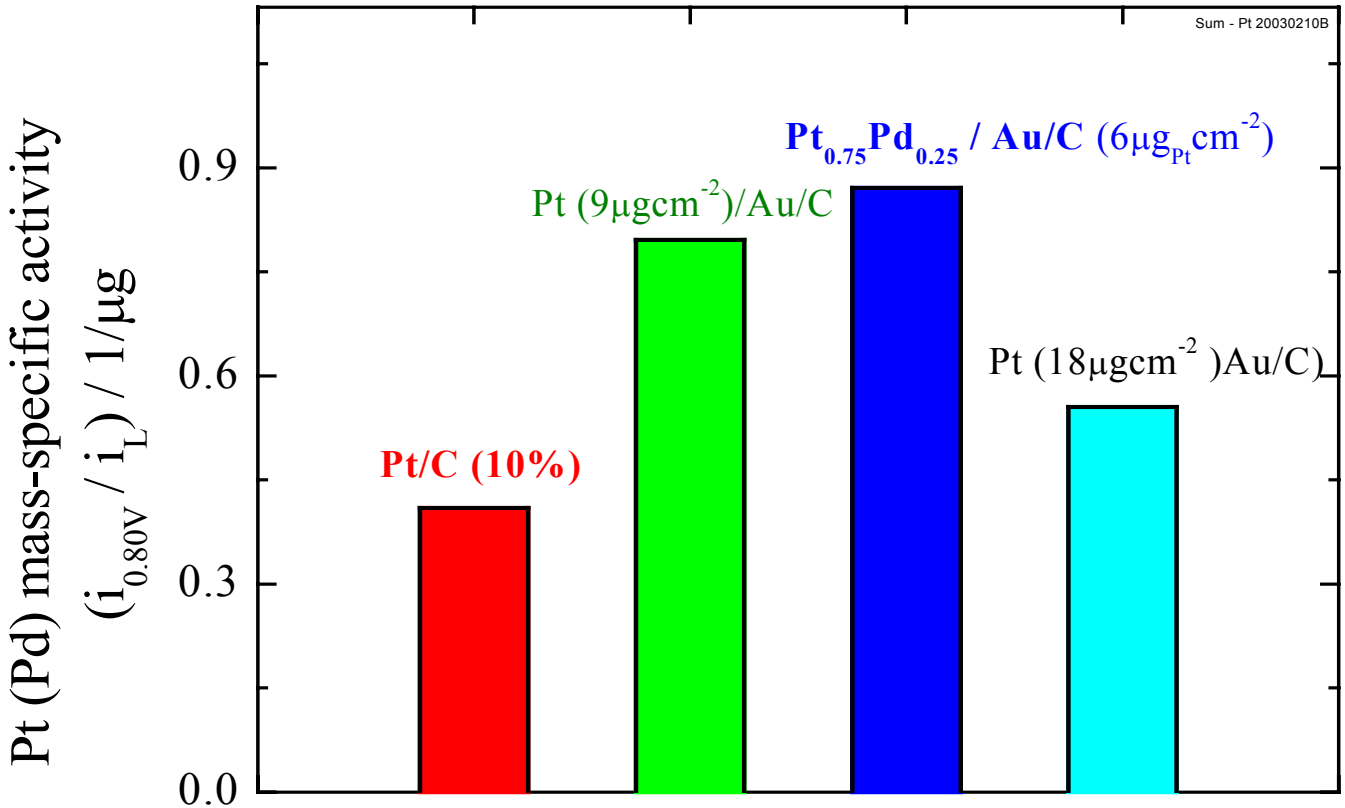


Tafel slopes and half-wave potentials for O_2 reduction on Pt adlayer electrocatalysts

Electrocatalyst/electrode	Tafel slopes / mv(dec)$^{-1}$		$E_{½}$ / V
	l.c.d	h.c.d.	
$Pt_{0.5}$ML/Au(111)	80	188	0.780
Pt_{1ML}/Au(111)	67	126	0.830
Pt(10%)/C	63	122	0.820
Pt_1/Au/C	71	133	0.820
$Pt_{0.75}Pd_{0.25}$/Au/C	65	88	0.817
Pt/Pd/Au/C	54	86	0.853
Pt_2/ Au/C	83	-	0.863
Pt(111) (Markovic et al.)	85	120	0.830

1-(9μgcm-2); 2-(18μgcm-2)

MASS-SPECIFIC ACTIVITIES OF SEVERAL ELECTROCATALYSTS



Interaction with Catalysts Manufacturers :

FCC & I Inc., and Plug Power; renewed contacts with E-TEK

Other Collaboration:

Los Alamos National Laboratory

Answers to the previous review:

Sintering of nanoparticles, stability, rearrangement of Pt?

Sintering is expected to be a lesser problem for Pt(1%)/Ru(10%) (a predominantly Ru particle) than for PtRu (1:1) alloy nanoparticles.

A Pt on Ru system is a strongly segregated case and Pt is expected to remain on a Ru nanoparticle surface. Entropy factors that favor mixing should be small for small nanoparticles.

Reactivation at positive potentials after prolonged tests indicates that Pt dissolution is not significant.

O_2 reduction is more important… - research commenced

FUTURE WORK

H_2/CO and H_2 oxidation

1. Optimization of a Pt/Ru electrocatalyst and final tests at LANL and industrial laboratories.

2. Pt or PtRu on W (W has a d-band vacancy smaller than other valve metals and the Pt/W system is strongly segregated). A 3D growth of Pt has to be suppressed.

O_2 reduction

1. Further development of Pt/Au/C electrocatalyst. Tests at LANL.
2. Investigations of Au-nonoble metal alloy nanoparticles as support for Pt.
3. Pt/Pd/C (initial results very good).

Microstructural Characterization of PEM Fuel Cells

Doug Blom

Larry Allard

ORNL

Objective

- DOE technical targets: Precious metal loading and cost
  - Use TEM characterization techniques to provide information necessary to optimize the distribution of precious metal catalyst for **increased efficiency and reduced catalyst loading** leading to cost reductions.
- DOE Technical target: durability
  - Characterize/quantify microstructural changes and relation to the **performance loss** in PEMFCs upon use in a fuel cell system to understand issues relating to durability and lifetime.

Approach

- Develop special techniques and procedures to prepare cross-sectional samples suitable for TEM observation from the cathode to the anode, to facilitate the ability to understand the entire cell as a unit. These samples must maintain the spatial relationships among the constituents of the cell in order to achieve insight into the operation of the real system.

Approach

- Characterize the microstructure and chemical composition of PEM cells before and after use to correlate performance to the microstructure down to the nm level.
- Characterize the role of processing in the development of the PEM electrode microstructure: e.g. Nafion content, catalyst particle type, catalyst ink application, etc.

Project Timeline

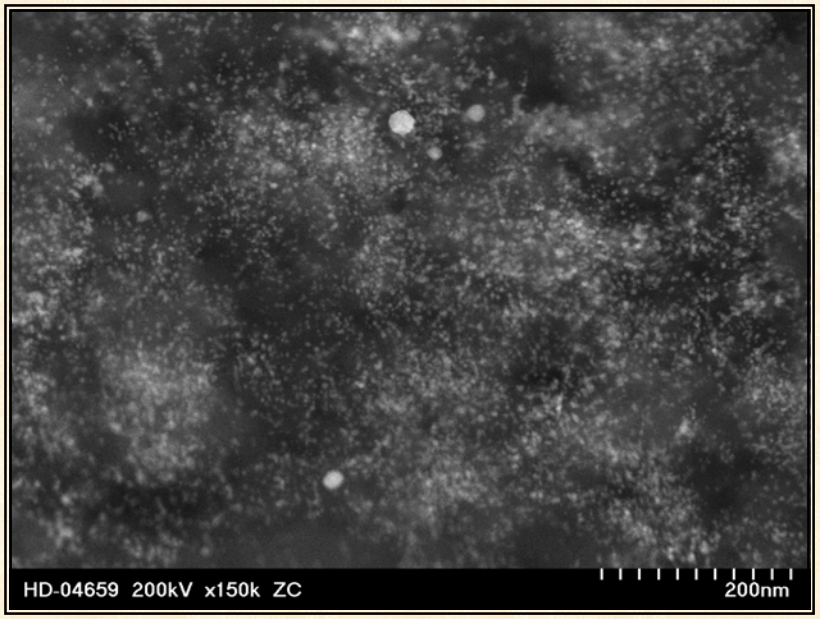
- Start of project **September, 1999**
- First successful cross-section **January, 2000**
- First fresh vs. aged microstructural comparison **June, 2000**
- Pt catalyst size distributions and microchemical changes at PEM/electrode interfaces **June, 2001**
- Establish new cryo-ultramicrotomy facility **October, 2001**
- Successful room-temperature ultramicrotomy **January, 2002**
- Analysis of failed MEA **June, 2002**
- Microstructural changes occurring during MEA assembly (with LANL) **June, 2003**
- Cryo-ultramicrotomy for thinner samples **October, 2003**
- Feedback aging changes to MEA designers **June, 2004**

Highlights for Fiscal Year 2003

- Room temperature ultramicrotomy successful at sub-100 nm thick sections
  - Eases overlap/projection problem
- Secured funding for acquisition of Hitachi HD-2000 STEM
  - Powerful analytical electron microscope well suited for characterization of PEM fuel cell cross-sections
- Examined a number of LANL produced PEM fuel cells to understand the processing-microstructure-performance relations in PEM fuel cells

Thinner is better – advances in room temperature ultramicrotomy

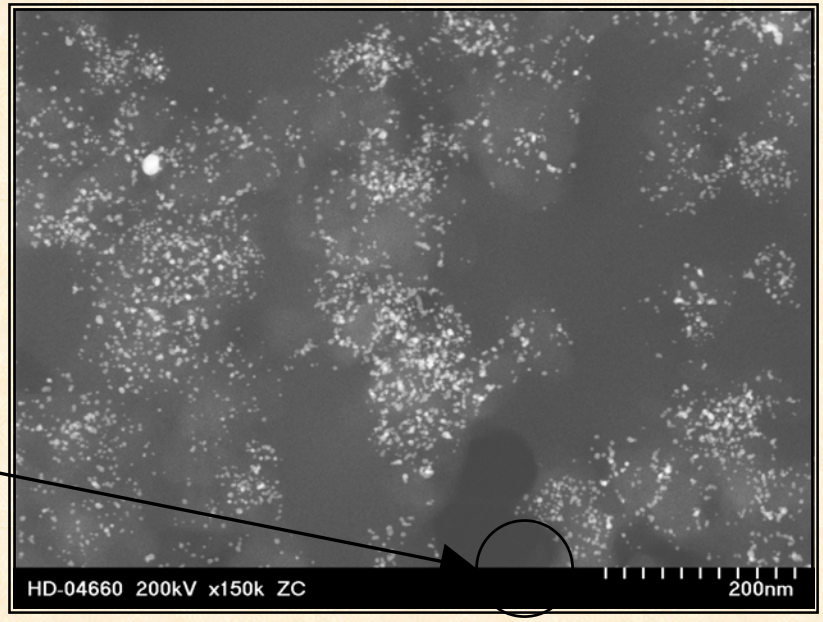
- Initial sectioning produced samples 300 nm thick
- Can see catalyst particles, but not porosity and support phases – catalyst coarsening is NOT the whole story



300 nm

Thinner is better – advances in room temperature ultramicrotomy

- Improved technique provides more information about ALL components
- Porosity visible at bottom
- Catalyst particles and their relation to support visible – 3 phase boundary is where active material lies

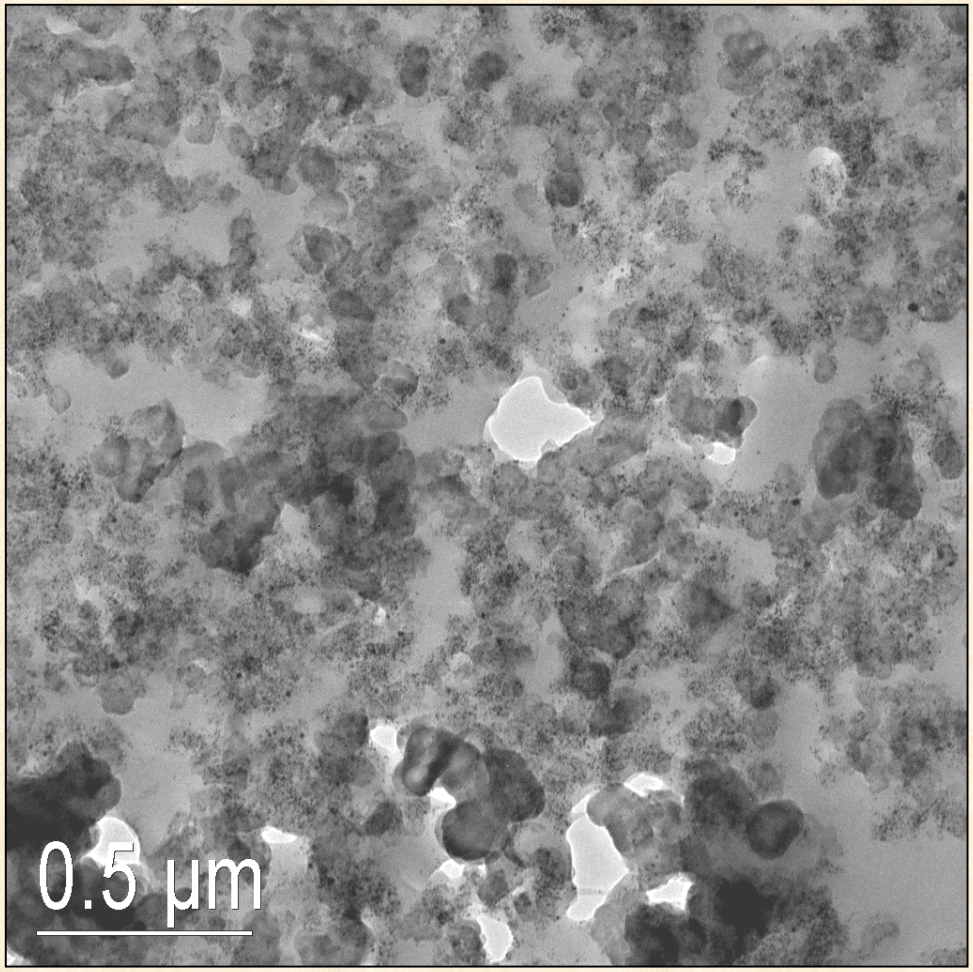


50 nm

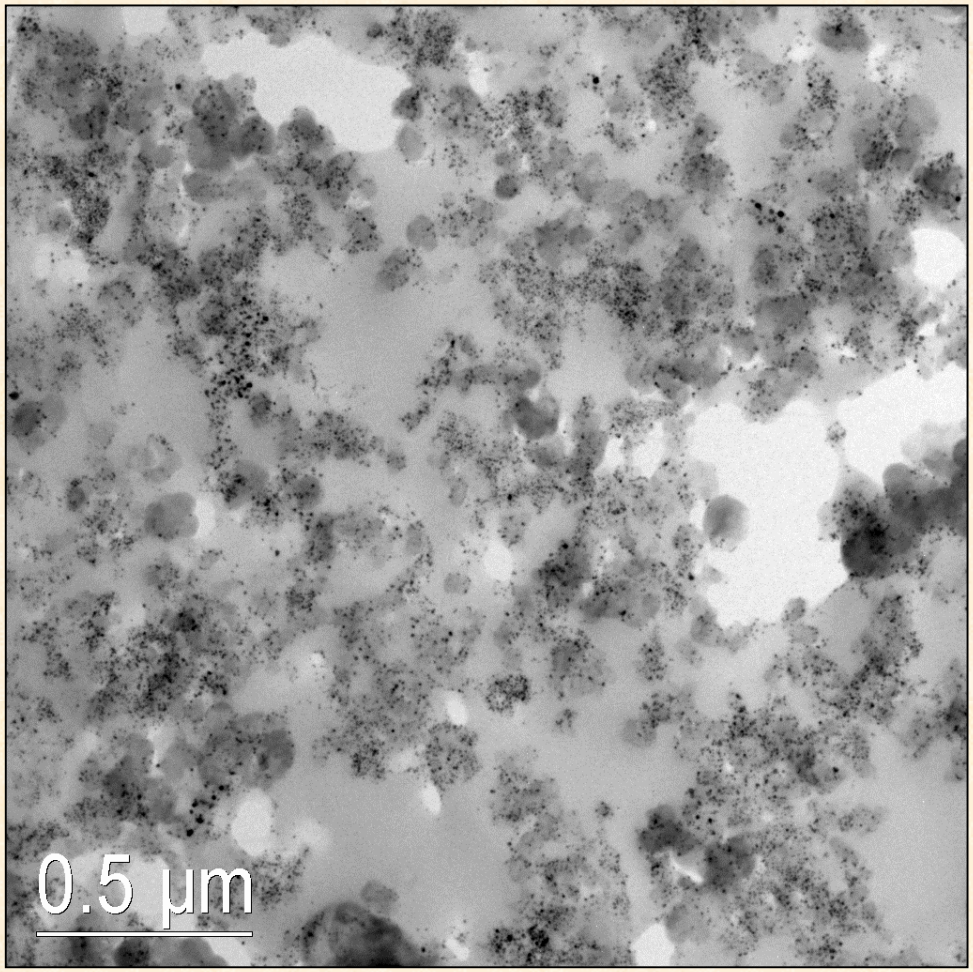
HD-2000 STEM on order

- 0.3 sr solid angle EDX detector – fast, accurate elemental analysis
- Z-contrast detector – ideal for imaging Pt (or other heavy elements) on C
- 2D composition maps easily achieved

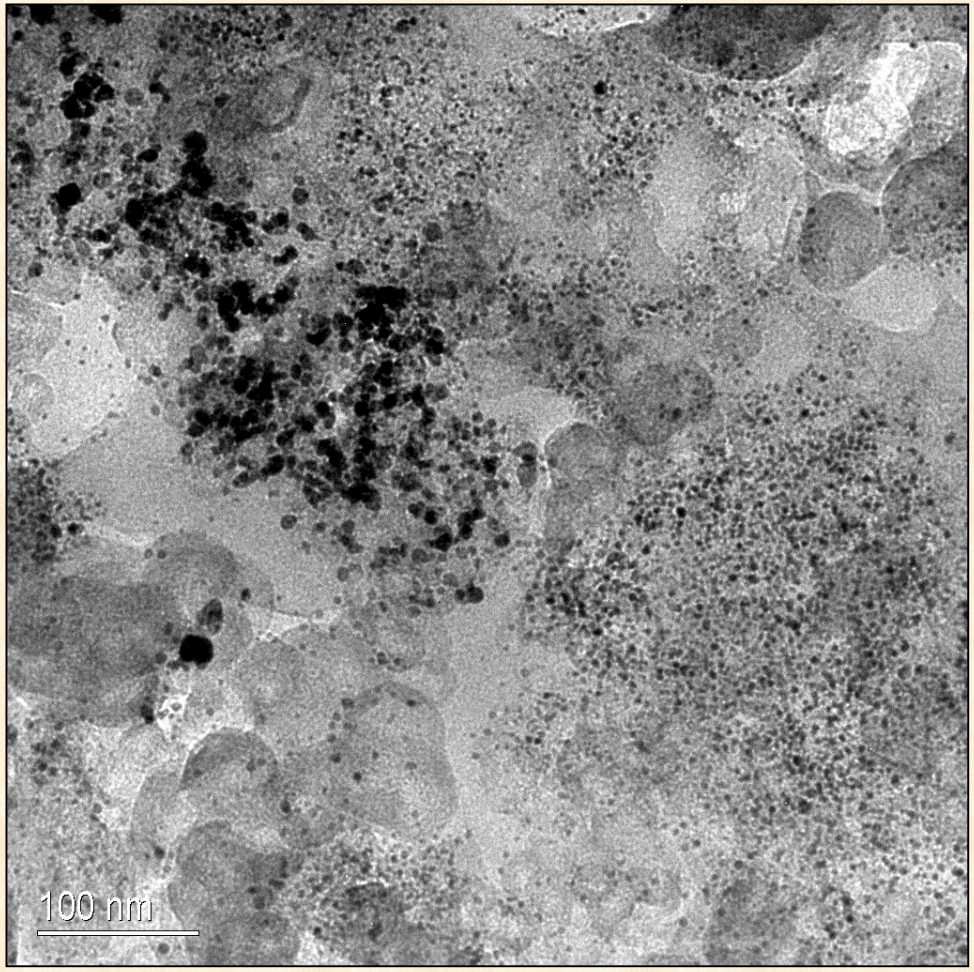
LANL PEMFC without sulfuric acid boiling step



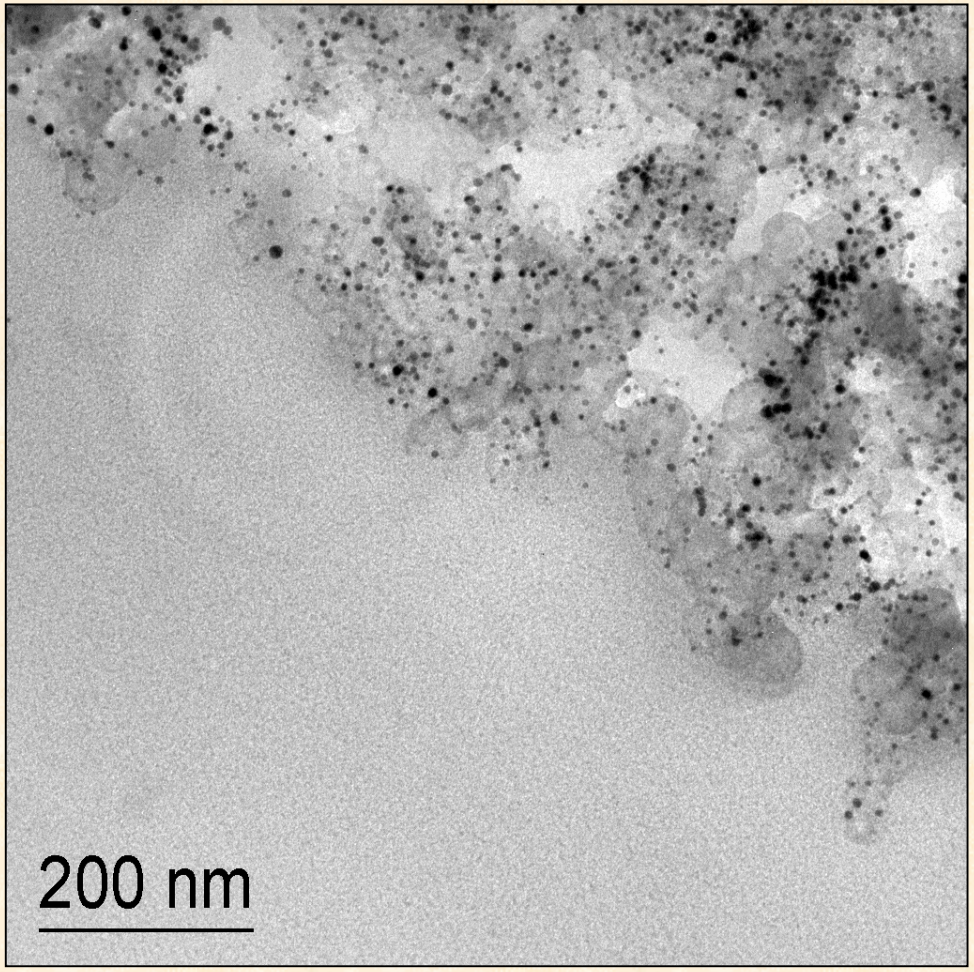
With boiling step



Spatial distribution of particle size distribution for fresh LANL MEA



400 hour life tested LANL MEA



Collaborations

- LANL providing a series of PEM fuel cells with varying initial processing.

Plans and Future Milestones

- Improve cryo-ultramicrotomy technique for preparation of ultra-thin (<<100nm) to achieve improved analytical results
- Continue collaboration with LANL on the microstructural changes which occur during the MEA preparation process and report on results

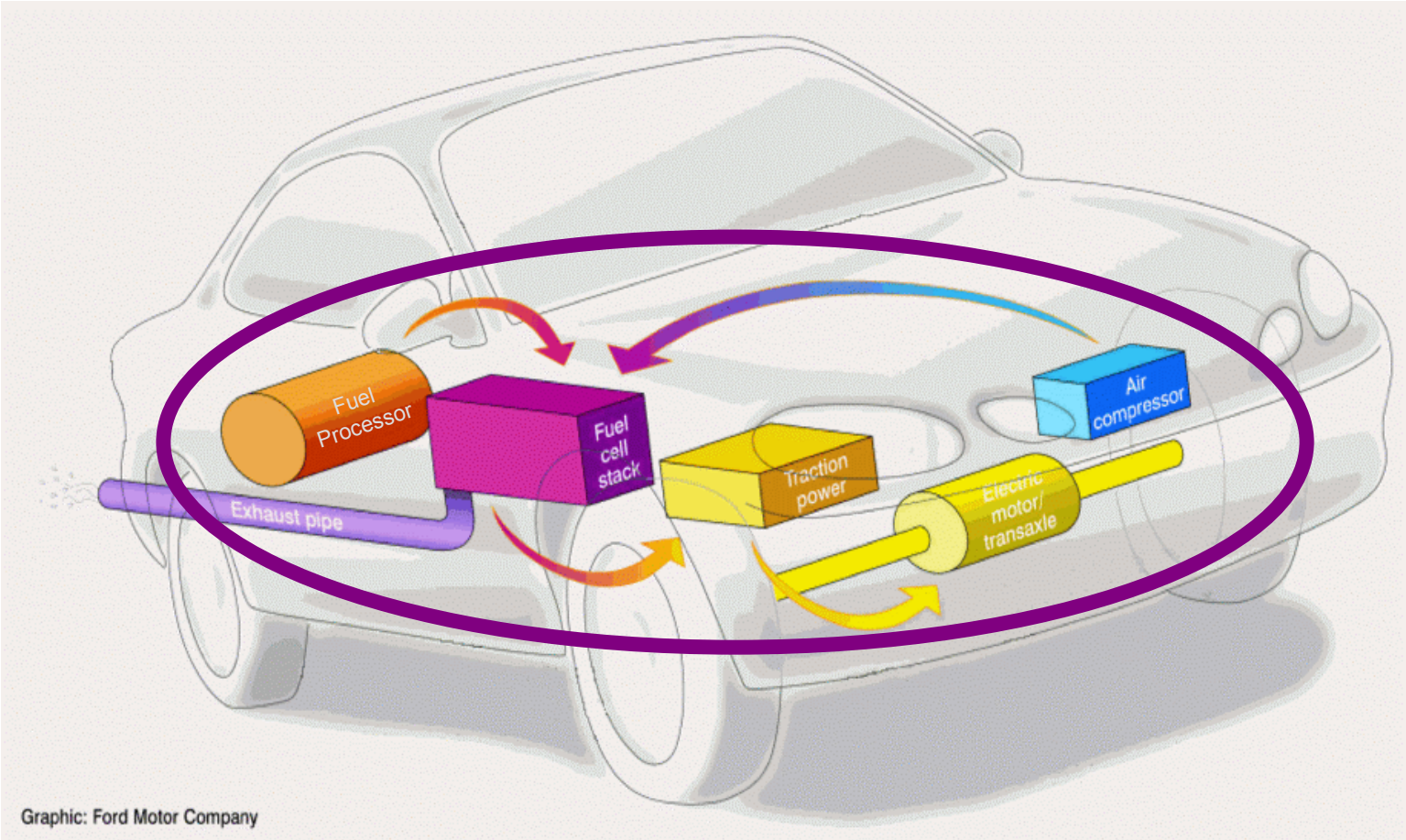
Response to Comments from 2002 Review

- Cyro-ultramicryotomy sample preparation should work to generate <100 nm thick samples – the technique would be valuable if this could become the "routine" sectioning method
  - Work in progress to improve cryo-sectioning capability

Response to Comments from 2002 Review

- More effort to establish more routine EDX data capability if the full advantages for understanding of MEA structural and chemical changes are to be realized
  - New instrumentation acquisition underway to integrate analytical information fully into characterization

Fuel Cell Power Systems Analysis



Graphic: Ford Motor Company

Patrick Davis

Barriers

Integrated Power Systems

- Balance-of-plant (compressors, humidifiers, heat exchangers, sensors, controls)
- Cost reduction
- Integrated modeling activities

Targets and Status

50 kWe (net) Integrated Fuel Cell Power System

Characteristics	Units	2003 status	2005	2010
Operating on Tier 2 gasoline containing 30 ppm sulfur, average				
Power density	W/L	140	250	325
Cost	$/kW	325	125	45
Durability	Hours	1000	2000	5000
Operating on direct hydrogen				
Power density	W/L	400	500	650
Cost	$/kW	275	125	45
Durability	Hours	1000	2000	5000

Projects

Fuel Cell Power Systems Analysis

• Fuel Cell Systems Analysis	ANL
• Fuel Cell Vehicle Systems Analysis	NREL
• Cost Analyses of Fuel Cell Stacks/ Systems	TIAX
• DFMA Cost Estimates of Fuel Cell/ Reformer Systems at Low, Medium, & High Production Rates	Directed Technologies, Inc.
• Assessment of Fuel Cell Auxiliary Power Systems for On Road Transportation Applications	TIAX
• Precious Metal Availability & Cost Analysis for PEMFC Commercialization	TIAX

Posters

• Non-Destructive Study of H_2O Transport Mechanism Inside Operating PEMFCs Using Neutron Imaging Techniques	NIST
• Advanced Underground Vehicle Power & Control Fuel Cell Mine Locomotive	Vehicle Projects LLC

Discussion Points

- Program focus on component development
- Continued importance of modeling
- Benchmarking will be used to measure progress
- Air management will continue as a major focus area

Fuel Cell Systems Analysis

R. K. Ahluwalia, X. Wang, and R. Kumar
Argonne National Laboratory

2003 USDOE Hydrogen and Fuel Cell
Merit Review Meeting
Berkeley, CA
May 19-22, 2003

Objective

Develop a validated system model and periodically update it to assess the technology status.

Technical Barriers Addressed

A. Compressors/Expanders
B. Thermal Management
C. Fuel Cell Power System Benchmarking
D. Heat Utilization
H. Start-up Time
I. Fuel Processor Start-up/Transient Operation
K. H_2 Purification/CO Cleanup
M. Fuel Processor System Integration and Efficiency
R. Thermal and Water Management

Approach

Develop, document & make available versatile system design and analysis tool.

- GCtool: Stand-alone code on PC platform
- GCtool_ENG: Coupled to PSAT (MATLAB/SIMULINK)

Validate the models against data obtained in laboratory and at Argonne's Fuel Cell Test Facility.

Apply models to issues of current interest.

- Work with FreedomCAR Technical Teams.
- Assist DOE contractors as requested by DOE.

Project Milestones

Milestone	*Date*	
Support setting of CEMM targets.	Oct. 2002	✓
Support setting of H_2 storage targets.	Jan. 2003	✓
Build models for components and systems.	Apr. 2003	✓
Propose and analyze FC systems for hybrid vehicles.	May 2003	✓
Analyze Nuvera data.	Jul. 2003	
Evaluate FC systems for combined heat and power.	Sep 2003	

Reviewers' Comments

Focus on dynamic model development and issues of transients, turndown ratio, start-up.

- Will present results on transient response & cold-start of H_2 FC systems
- Assisted project on fast start of gasoline fuel processors
- Filed a patent on load-following fuel processors

More interactions with FreedomCAR Fuel Cell, Systems Analysis, and Energy Storage Tech Teams.

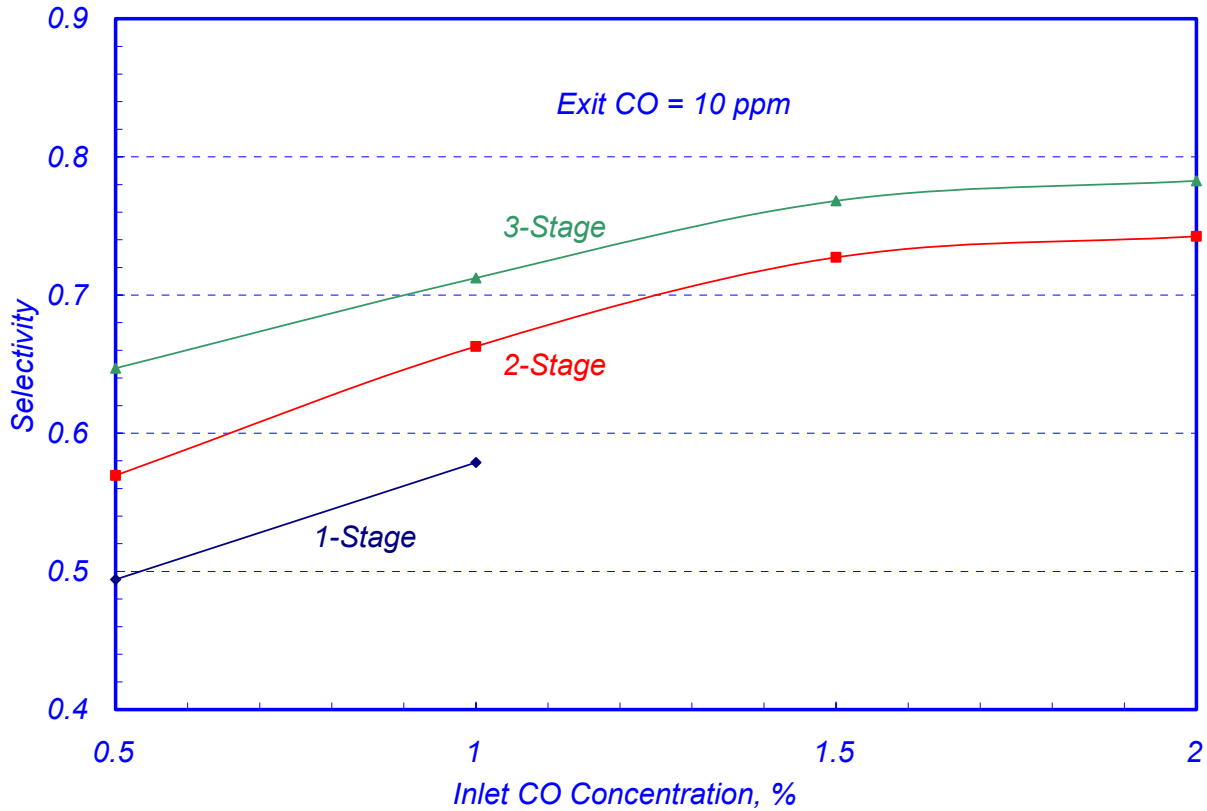
- Supported setting of targets for air management system.
- Supported setting of H_2 storage targets
- Participating in hybridization study.

Emphasize code development.

- Developed dynamic models of catalytic reactors, CEMM, heat rejection system, water management system …….

Code Development in FY2003

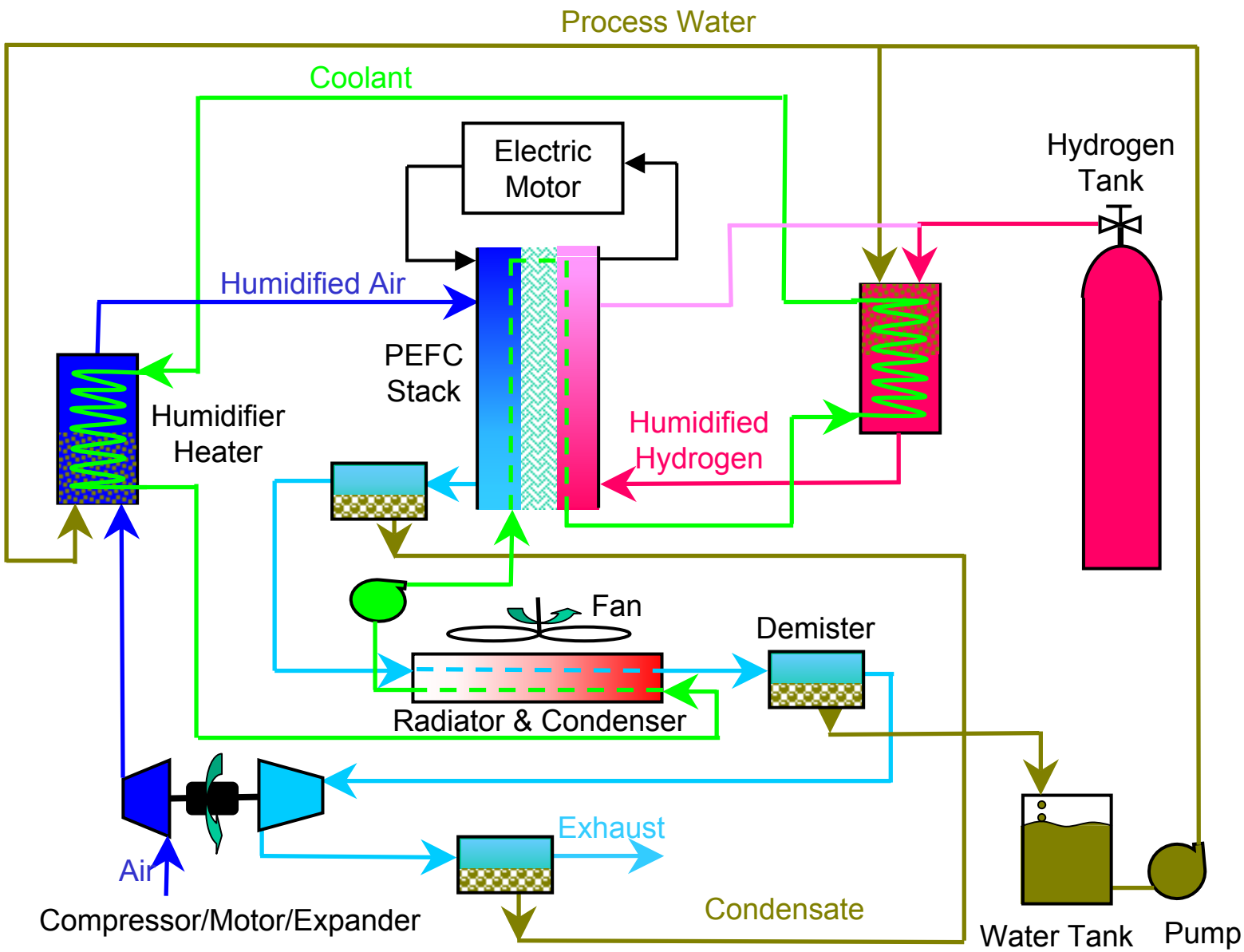
- Dynamic model of compressor, expander & motor on single shaft.
- Ram-air cooled condenser and radiator.
- Catalytic WGS and ATR on microlith supports
- Monolith – supported PROx (data from LANL)



Hydrogen Storage Targets
Fuel Economy of H_2 Fuel-Cell Vehicles

		Cavalier		Taurus		Explorer	
		ICE	H_2-FC	ICE	H_2-FC	ICE	H_2-FC
Weight (kg)		1214	1400	1693	1850	2055	2320
Drag Coefficient		0.38		0.32		0.41	
Frontal Area (m^2)		1.8		2.2		2.46	
Coeff. Roll. Friction		0.009		0.009		0.0084	
Engine Power (kW)		86	90	116	120	160	160
TIM (kW)			**58/90**		**78/120**		**100/160**
Fuel Economy (mpgge)	FUDS	25	73	20	58	18	47
	FHDS	32	75	29	69	23	54
	Comb	27.6	73.8	23.2	62.4	19.8	49.7
H_2 / ICE mpgge		1.0	2.7	1.0	2.7	1.0	2.5
EPA Fuel Economy Combined (mpgge)		26.0		23.7		18.4	

Pressurized Direct H_2 Fuel Cell System



FC Systems for Hybrid Vehicles

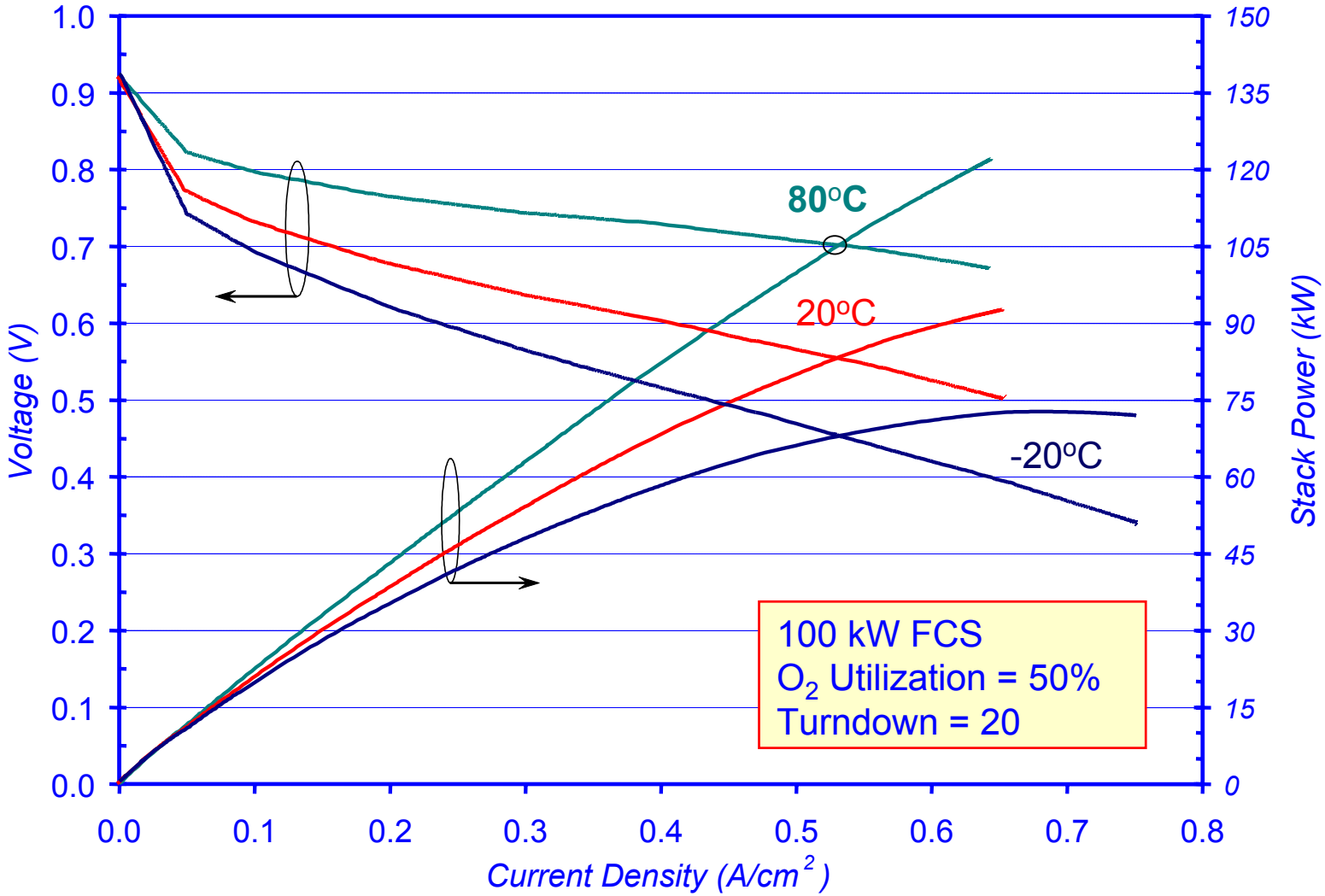
Requirement	Approach
FCS alone meets vehicle power demand at top sustained speed.	Defines mimimum FCS rating.
FCS alone maintains the vehicle at 55 mph at 6.5% grade for 20 min.	Heat rejection system sized for top speed or gradeability at T_{amb} = 42°C.
0 to 60 mph in 10 s with battery assist.	Defines the size of energy storage system.
50% FCS efficiency at rated power.	0.7 V cell voltage at rated power.
15-s cold start time at T_{amb} = 20°C.	Oversize the air management system.
30-s cold start time at T_{amb} = -20°C.	
1-s transient response time for 10 to 90% power.	Overload motor & let O_2 utilization exceed 50% during fast acceleration.
FCS is self sufficient in water.	Balance water management system for all loads at 50% O_2 utilization and T_{amb}<42°C.

FCS For Hybrid Mid-Size SUV

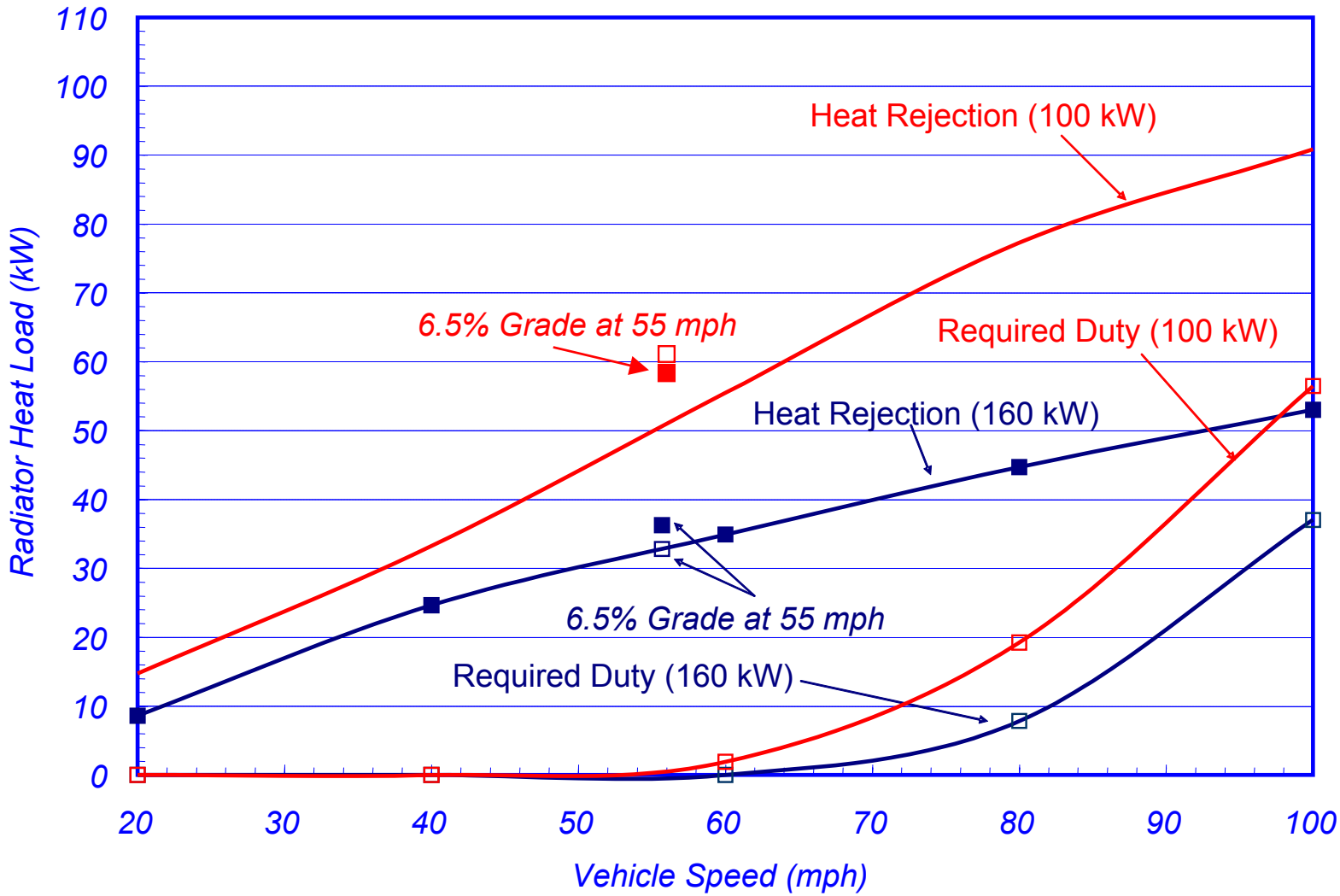
	Mid-Size AWD SUV		
GVW with FCS	2400 kg	Frontal Area	2.46 m^2
Coefficient Rolling Fraction	0.0084	Drag Coefficient	0.41
	Traction Power Requirement		
Z-60	160 kWe		
Top Speed (110 mph)	80 kWe		
6.5% Grade (55 mph)	60 kWe		
	FCS - 1	FCS - 2	FCS - 3
Rated Power at 0.7 V	100 kWe	100 kWe	160 kWe
Air Management System	CMM	CEMM	CEMM
CEMM / CEM M/C Power	27.3 kW	9.5 kW	15.1 kW
FCS Efficiency			
@ Rated Power	47.2%	53.6%	53.6%
@ 25% of Rated Power	61.3%	62.3%	62.8%
@ 80 kWe	52.0%	55.7%	59.2%
@ 20 kWe	61.6%	63.0%	63.9%

Stack Behavior with Oversized CEMM

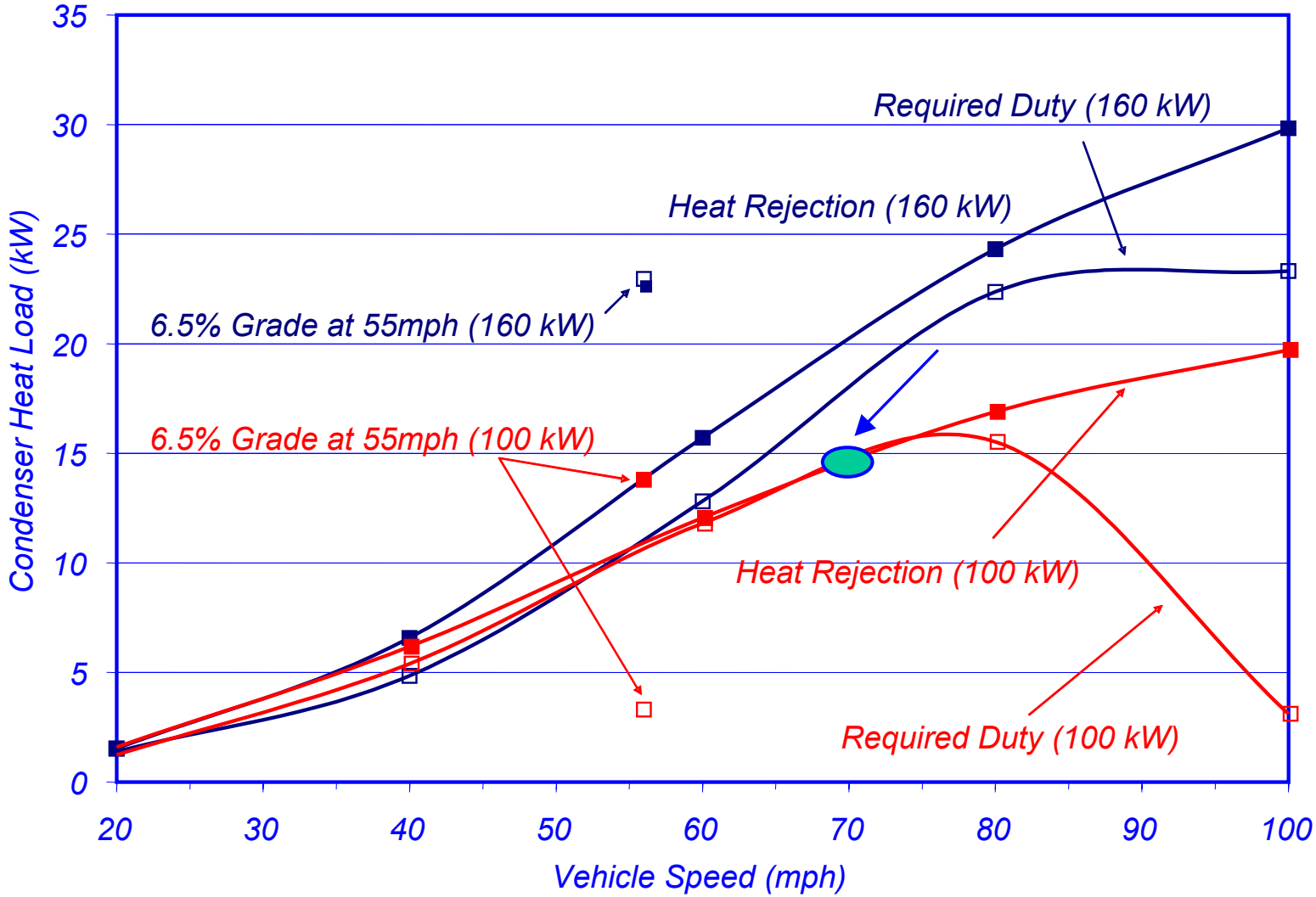
- At 80°C, stack can produce 20% more than rated power.
- Stack derated by 20% at 20°C and 35% at -20°C.



Radiator sized for 6.5% grade at 55 mph can reject heat at all operating conditions.



Condenser is challenged most at 6.5% grade in FCV and at intermediate speed in hybrid FCV.



CEMM Idle Speed

Minimum idle speed is the rpm at which the CEMM can provide sufficient cathode air to enable FCS to generate the power needed by the overloaded CEMM/CMM.

Idle speed may be determined by

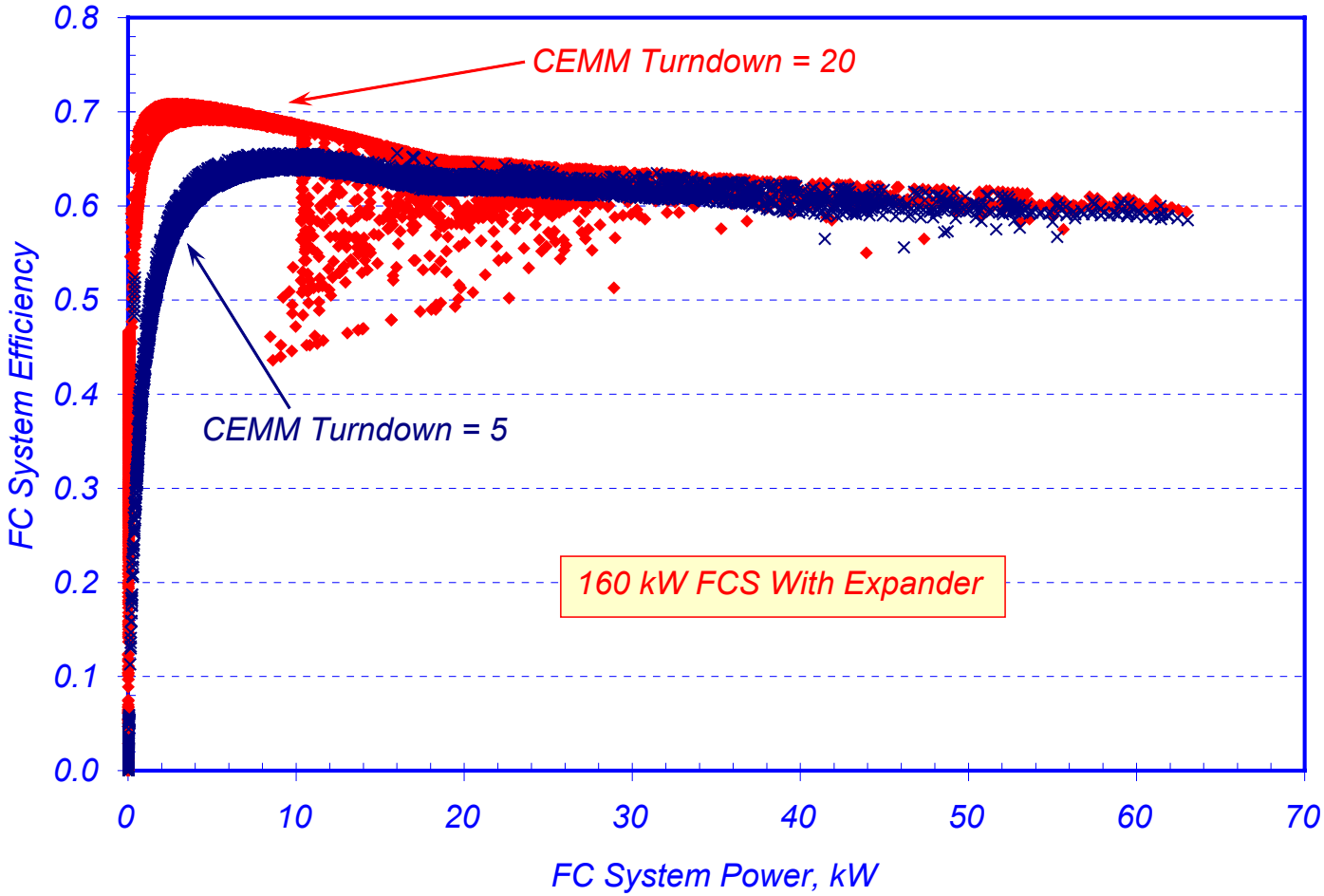
- Motor power and M/C.
- Maximum turndown available with a given CEMM configuration.

Idle Speed for a Turbocompressor/Expander Module

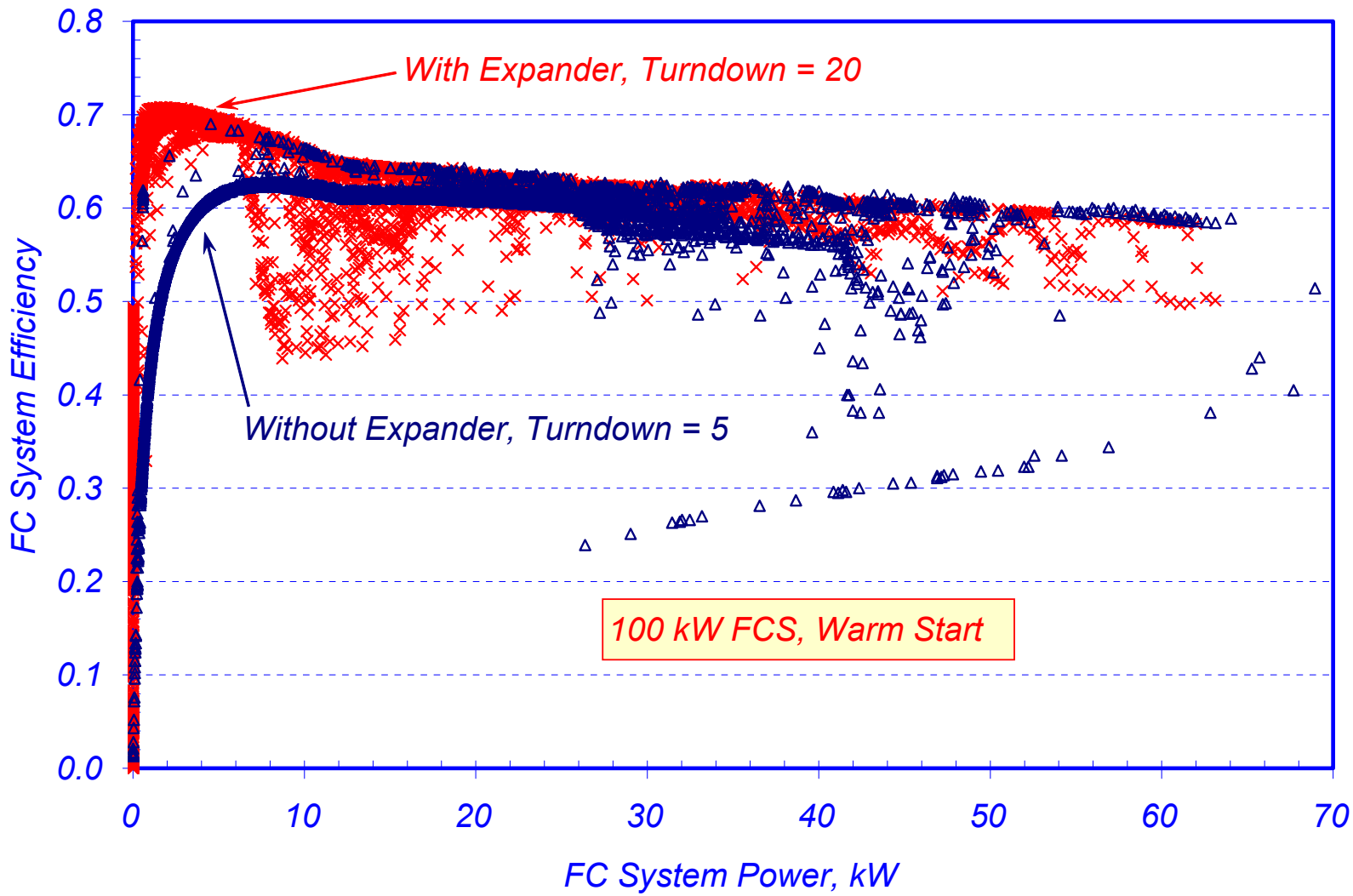
	Idle rpm	Maximum Turndown
CEMM: System with Expander	42,500	20
CEM: System without Expander	46,000	12

CEMM turndown affects FCS efficiency at low loads.

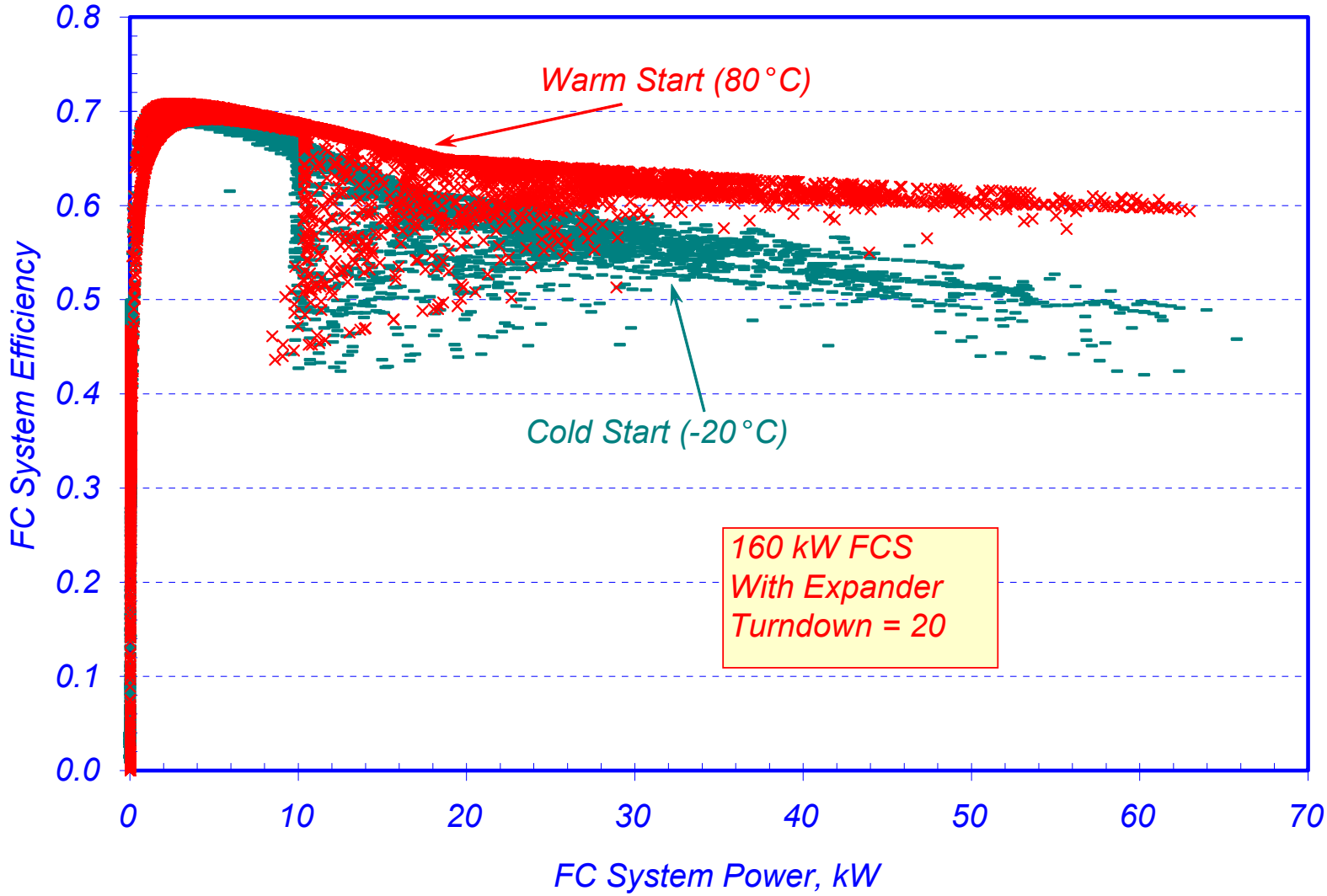
- Efficiency depends on power demand, dynamic variation in load, and maximum CEMM turndown.



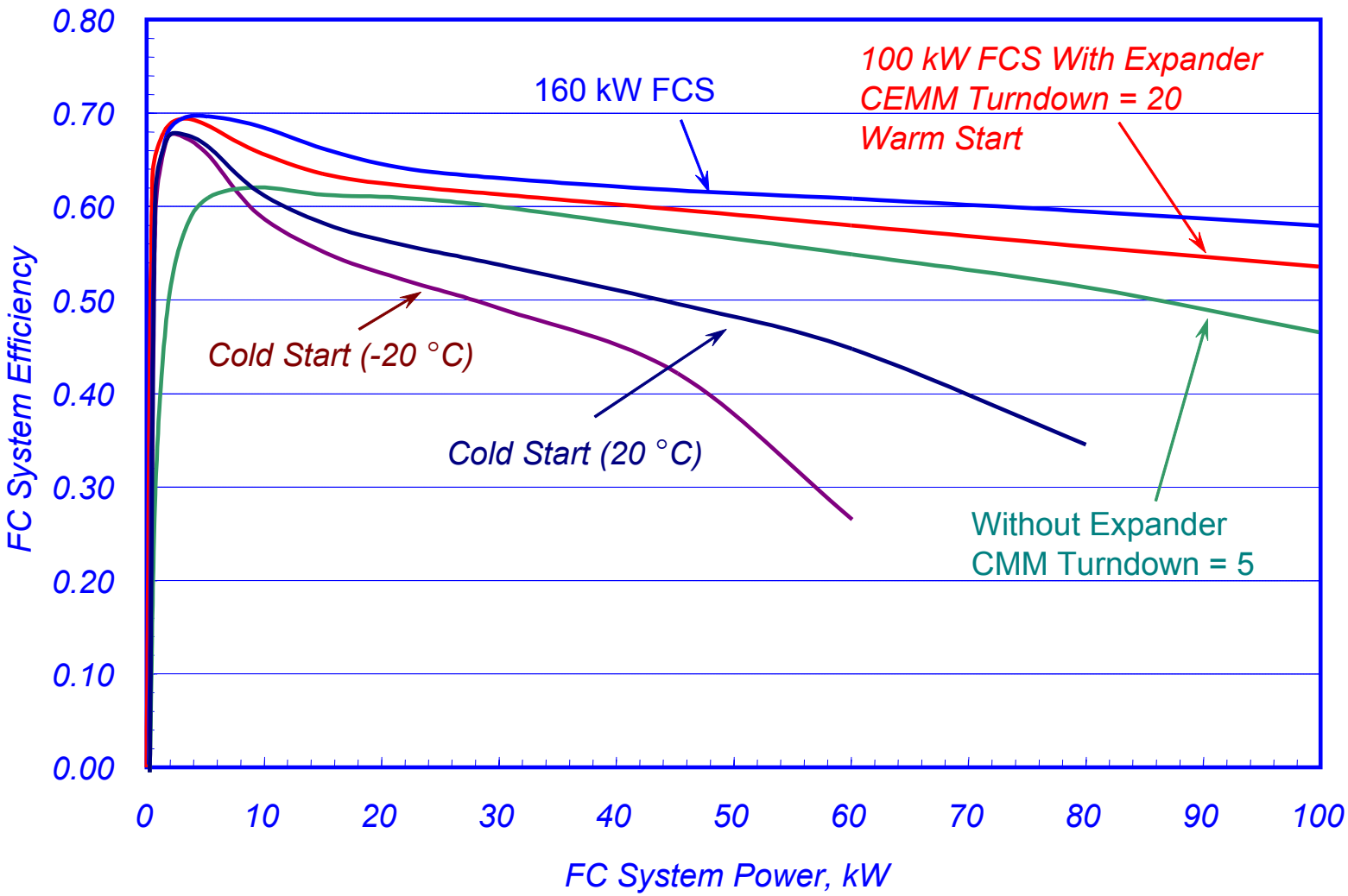
Effect of Expander on FCS Efficiency (FUDS)



FCS Efficiency on FUDS
Warm vs. Cold Start



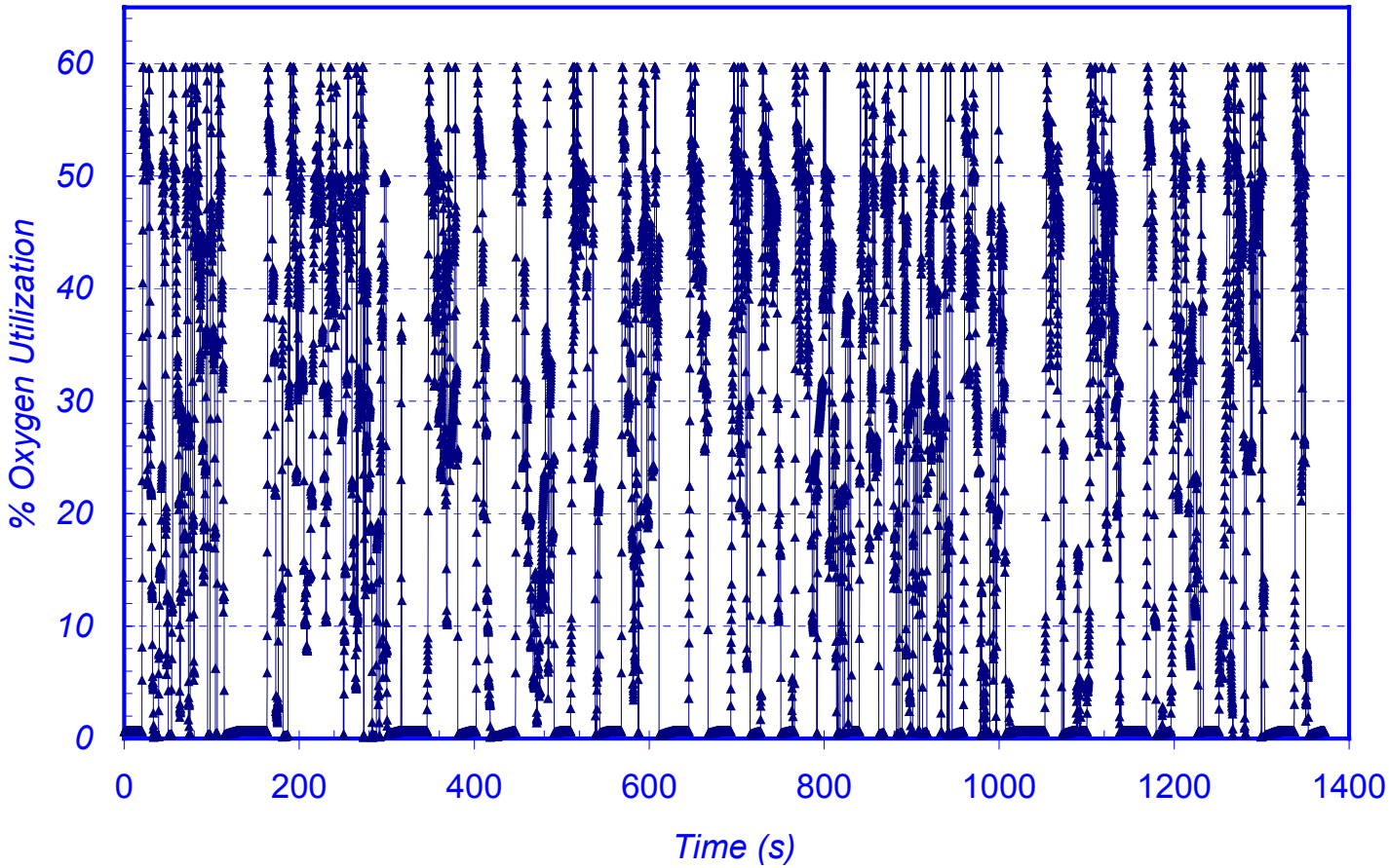
FCS Efficiency at Constant Load



Oxygen Utilization over Urban Cycle

- O_2 utilization cannot be held constant over drive cycle.
- Low utilization during idling conditions and deceleration.

100 kW FCS With Expander CEMM Turndown = 20



Technology Transfer and Collaborations

Licensed GCtool to >50 domestic and international private enterprises, universities, national labs, and government affiliated organizations.

Collaborations and Interactions

- Joint IEA Annex XV Tank-to-Wheel Study (Canada, Germany, Italy, Korea, Netherlands, Sweden, and U.S.)
- FreedomCAR Fuel Cell Tech Team
- Joint Battery, Fuel Cell and SEAT Tech Team
- FASTER Program: LANL, PNNL, ORNL, PCI
- Nuvera Fuel Cells: Fuel Reforming and HiQ
- Mechanology, LLC: Flow Leakage in TIVM

Proposed Future Work

- Fuel Cell – Battery Hybridization study with Joint Tech Team
- Drive cycle analysis of direct hydrogen and reformed liquid fuel systems
- International Tank-to-Wheel Study (IEA Annex XV)
- Fuel cell systems for combined heat and power
- Support fuel processor engineering projects at ANL
- Continue to support DOE/FreedomCAR development efforts

Fuel Cell Vehicle Systems Analysis

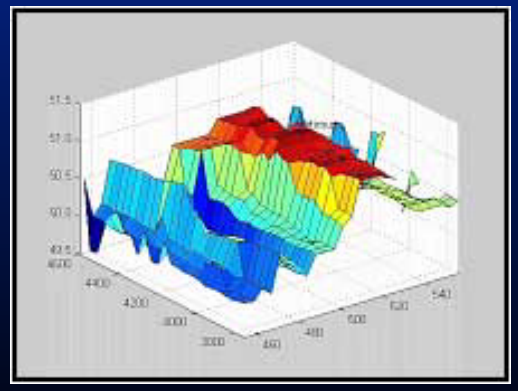
Tony Markel, Keith Wipke, Kristina Haraldsson,
Ken Kelly, Andreas Vlahinos
National Renewable Energy Laboratory

May 20, 2003

DOE Hydrogen and Fuel Cell 2003 Annual Merit Review
Berkeley, California

Outline

- Objectives
- Approach
- Timeline of Highlights
- Accomplishments
- Addressing Reviewer Comments
- Industry Interactions
- Future Plans
- Summary

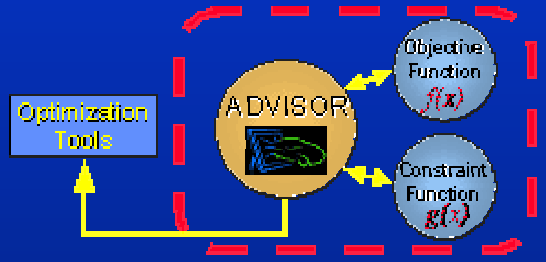


Objectives

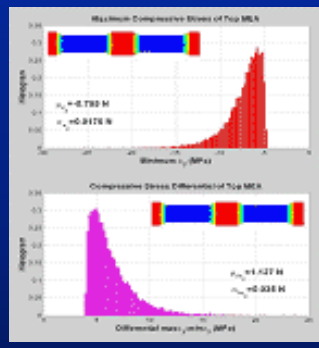
- Provide DOE and industry with technical solutions and modeling tools that accelerate the introduction of robust fuel cell technologies
- Quantify benefits and impacts of HFC&IT development efforts at the vehicle level (current status evaluation)
- Understand sensitivity of fuel cell technical target values and provide recommendations to DOE program managers (future goal evaluation)

Approach

- Develop and link to existing component and vehicle models to enhance systems analysis capabilities



- Work with industry to apply robust design techniques, optimization tools, and CAE tools to overcome technical barriers



- Study benefits of fuel cell system and vehicle design scenarios and transfer to industry

- Assess impact of various technical team targets at component level

Highlights and Milestones

Planned
Completed
* = milestone

6/02	Presented FC response time study results at FutureCar Congress
10/02	Presented fuel cell system model evaluation study at 202nd Electrochemical Society Meeting
10/02	Incorporated two detailed fuel cell system models into ADVISOR vehicle simulation program
11/02	Presented the Technical Targets Tool to DOE
3/03	Developed FEA models of fuel cell components and successfully demonstrated the application of robust design techniques
4/03	Presented results of 4 fuel cell system studies at ASME/RIT Fuel Cell Technology Conference
6/03	Results of gasoline reformer warm-up fuel economy impacts study to be presented at 2003 Future Transportation Technology Conference
7/03*	Expand database of fuel cell components
9/03*	Summarize the influence of key fuel cell program technical targets on fuel consumption reduction
9/03	Complete initial applications on reformer, end-plate design, stack pressure profile and high-temperature stack design
9/03*	Publish technical report on methodology for applying robust design techniques to fuel cell components

Accomplishments

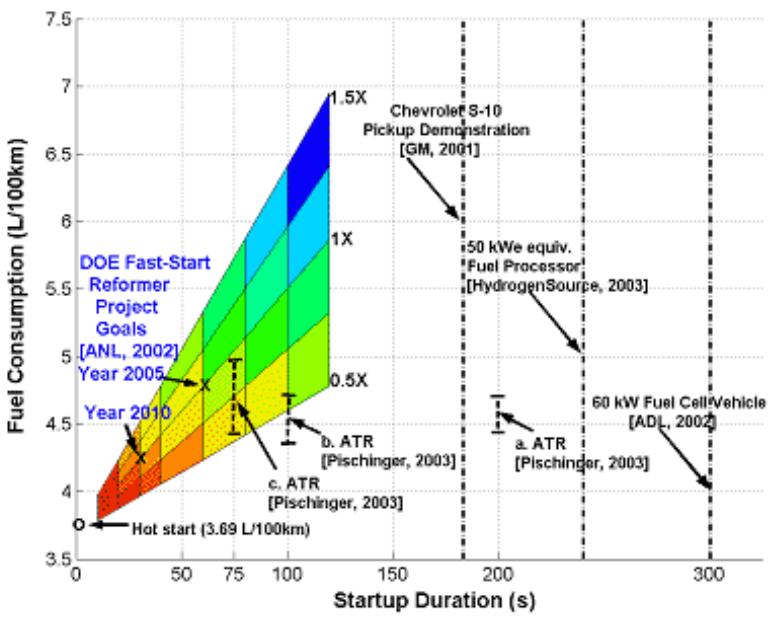
Analyzed Fuel Economy Impacts of Gasoline Reformer Warm-up

A. Allow warm-up period before FTP starts

B. Design reformer and fuel cell system to provide minimum power requirements for FTP cycle with no energy storage

C. Hybridize to balance out drive cycle requirements with achieving reasonable/efficient reformer startup time

Reformer Warmup Time (s)	Power (kW)	Cum. Raw Energy [Usable] (Wh)	SOC Window (%)	Nom. Battery Pack Total Energy (Wh)
30 s	13.5	15	20	75
60 s	13.5	45	20	225
195 s	25.7	158	20	790
10 min	25.7	658	20	3290
Toyota Prius	25	--	~5	1781
Honda Insight	6	--	~10	936
Honda Civic	n/a	--	n/a	864

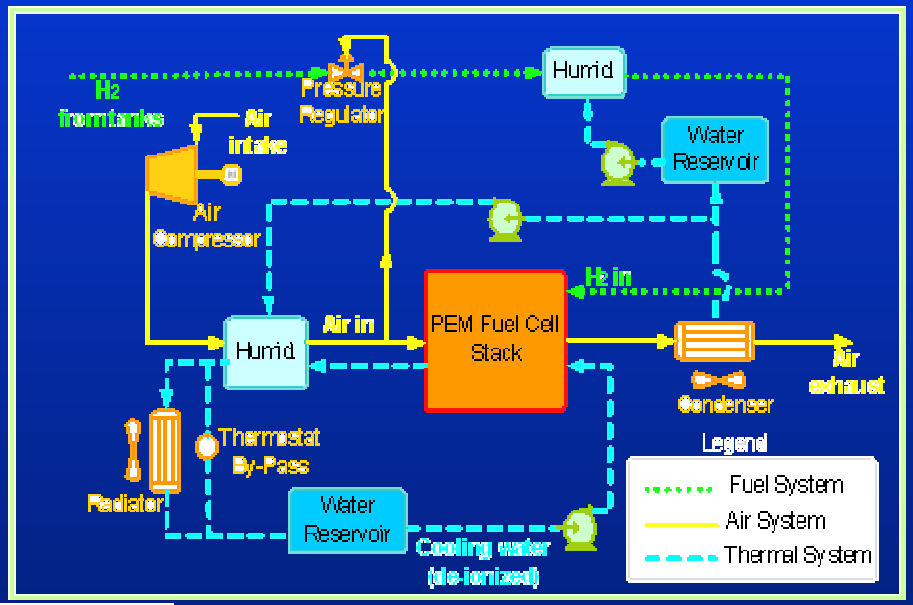


- **Drive cycle traction power and energy demands satisfied with relatively small battery**

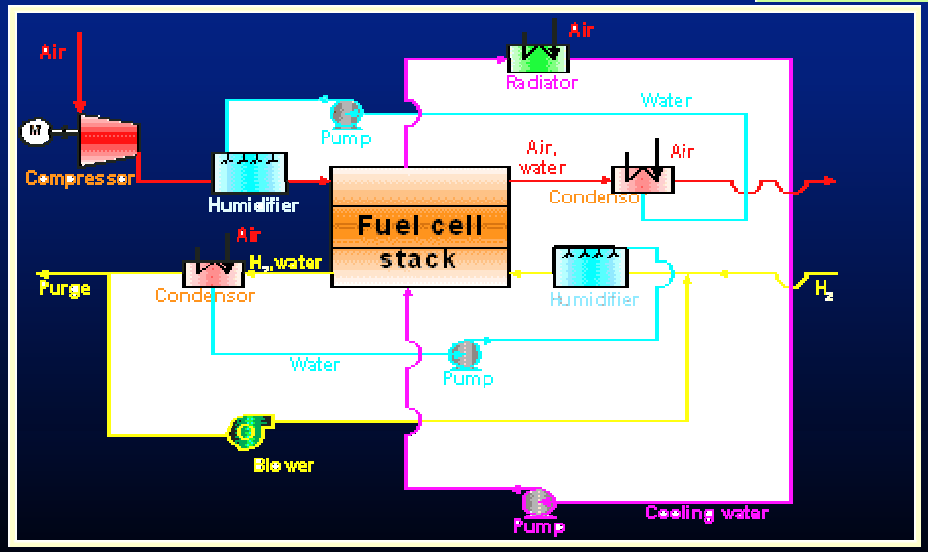
- **Fuel economy penalty significant if duration is long or fuel rate is high**

Accomplishments

Two Detailed Fuel Cell System Models in ADVISOR



the Virginia Tech Model



the KTH Model

Accomplishments
Range of Model Complexity in ADVISOR

More Detail

KTH Model
- Springer et. al. fuel cell model
- thermodynamic library
- balance of plant components
- water transport in MEA

*** User-defined model ***
- configurable subsystem structure
- ability to link to fuel cell models in other tools (e.g. Saber, Simplorer,…)

VT Model
- parametric polarization curve
- system thermal model
- balance of plant components
- variable operating pressure

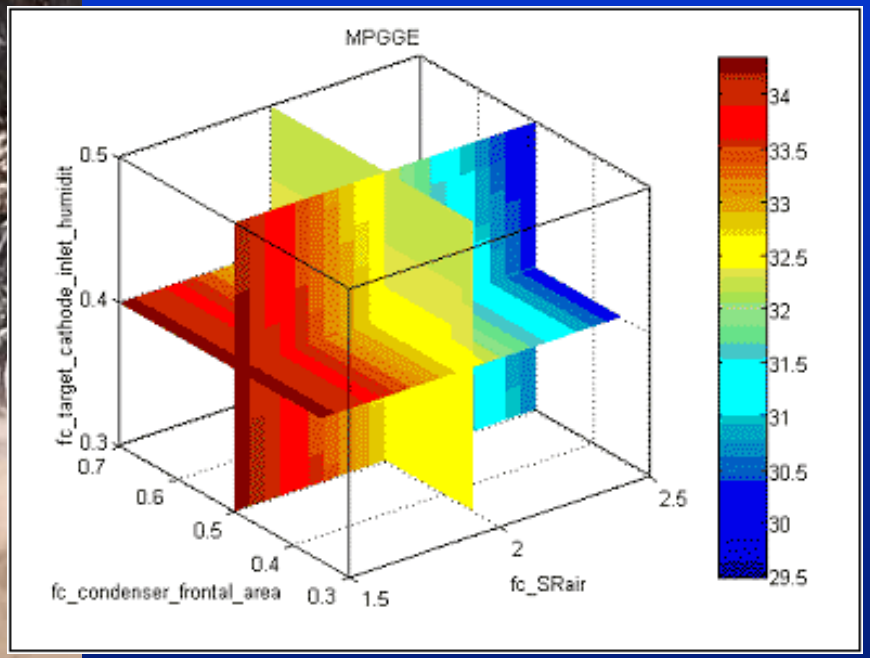
Less Detail

Simple Polarization Curve
- defined current and voltage
- simplified balance of plant

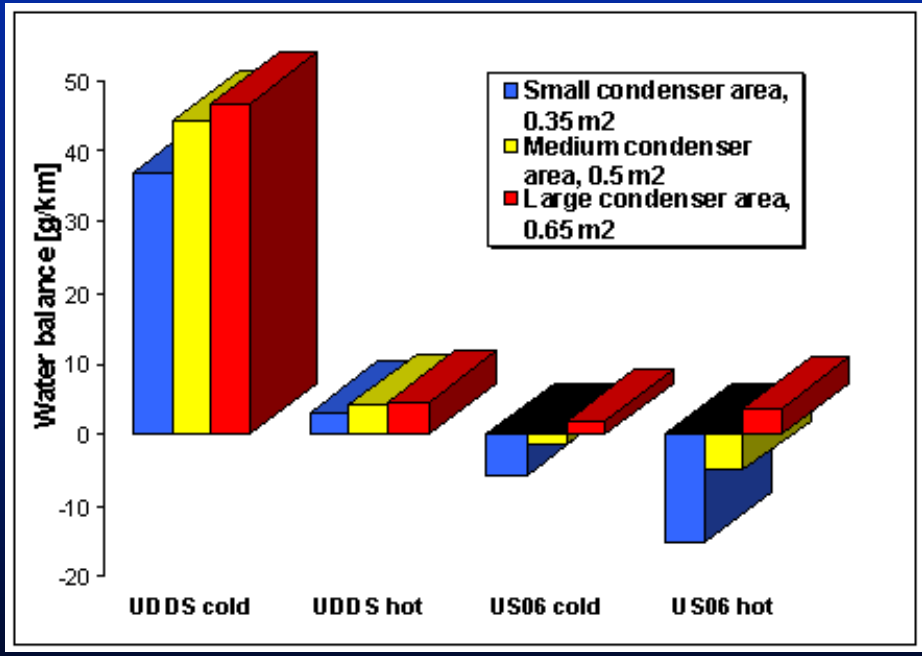
Net Power vs. Efficiency
- single curve
- scalability

ADVISOR 2002
Advanced Vehicle Simulator

Accomplishments
Water Balance Sensitivities Assessed



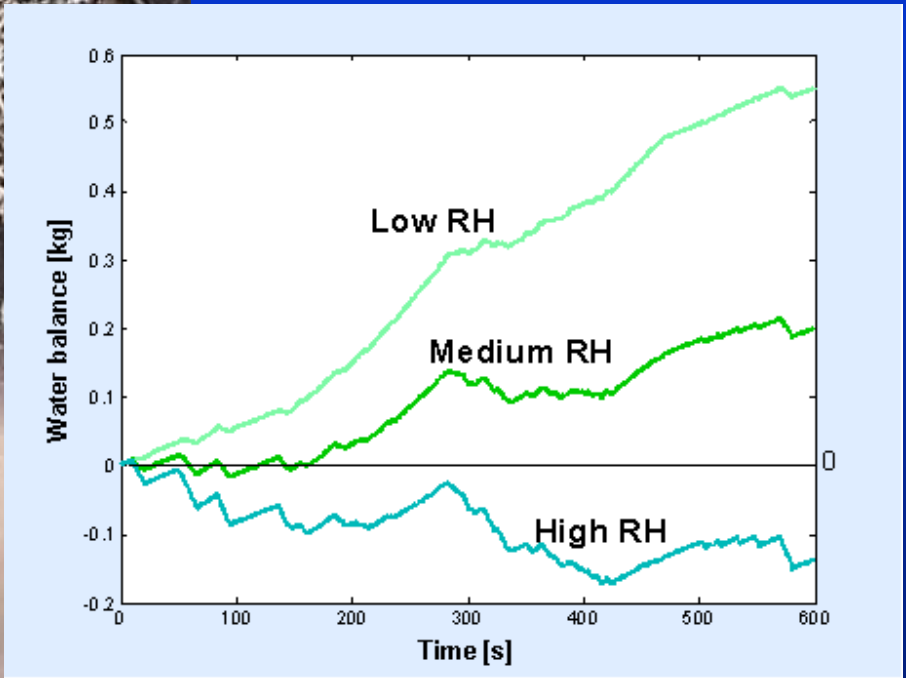
- Assessed water balance sensitivity in vehicle environment (drive cycles)
- Impact of condenser size and startup conditions quantified



UDDS:
sensitive to cold/hot start

US06:
sensitive to condenser size

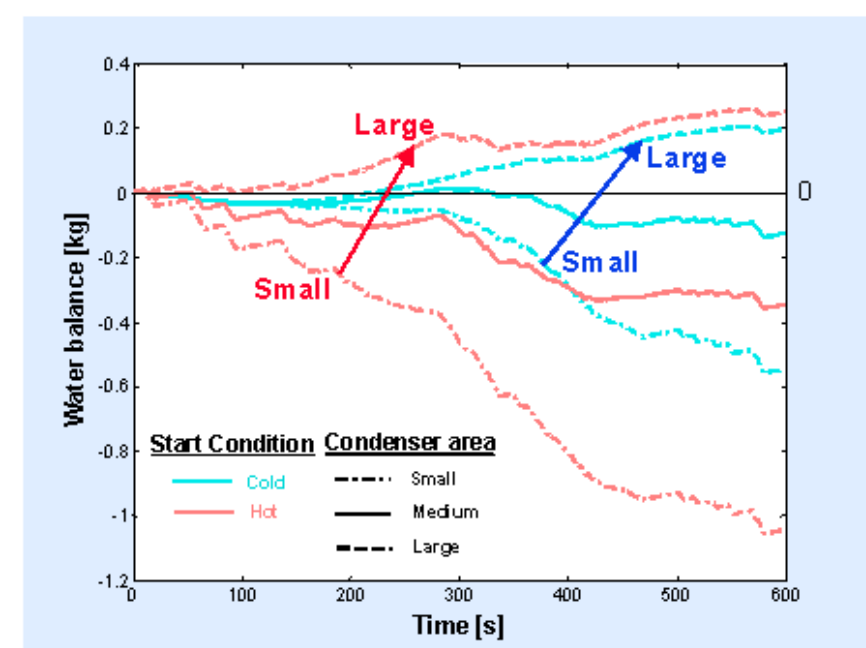
Accomplishments
Water Balance Variability on the US06 Drive Cycle



Positive WB at low relative humidity requirements

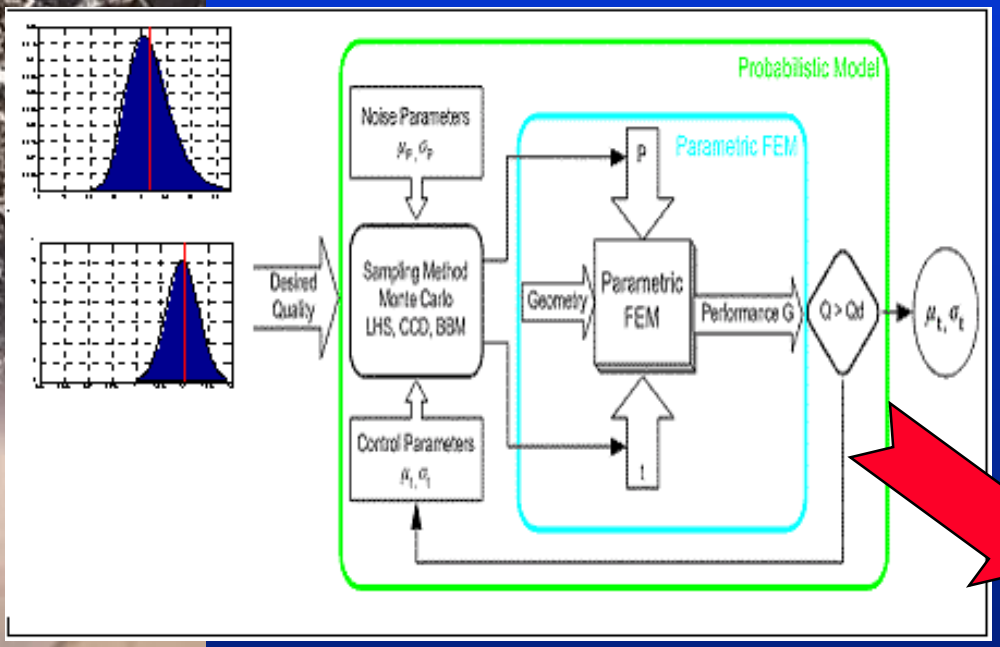
Cathode Rel. Humidity Requirements

Condenser Area



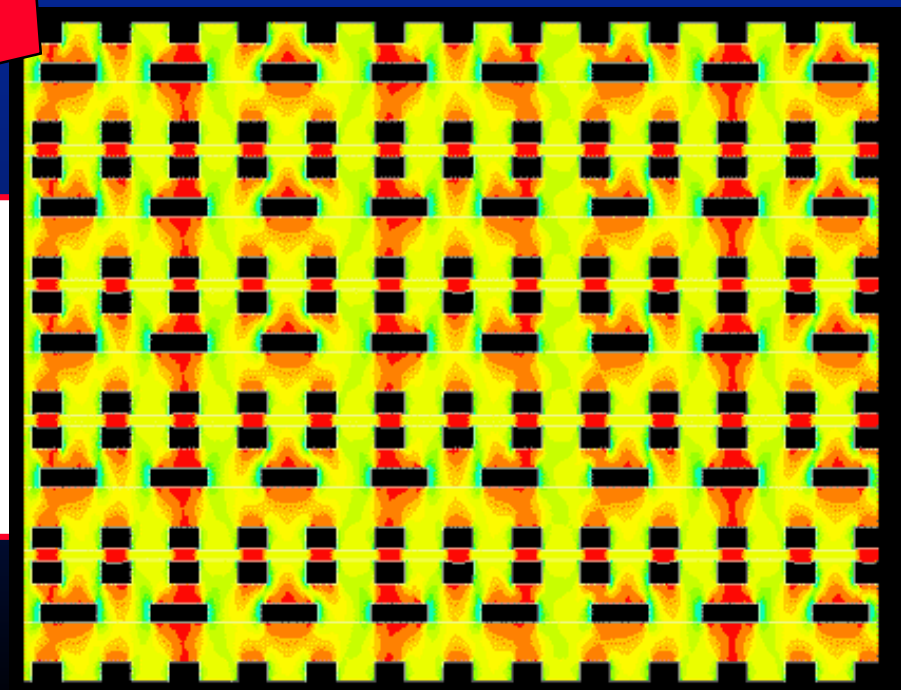
Better WB at low temperature operation

Accomplishments
Robust Designs of Fuel Cell Components



Collaborative effort with industry to apply <u>robust design</u> techniques to fuel cell components:

- Parametric FEA modeling
- Probabilistic design and optimization techniques integrated with FEA
- Topology optimization for reduced mass and improved pressure profiles

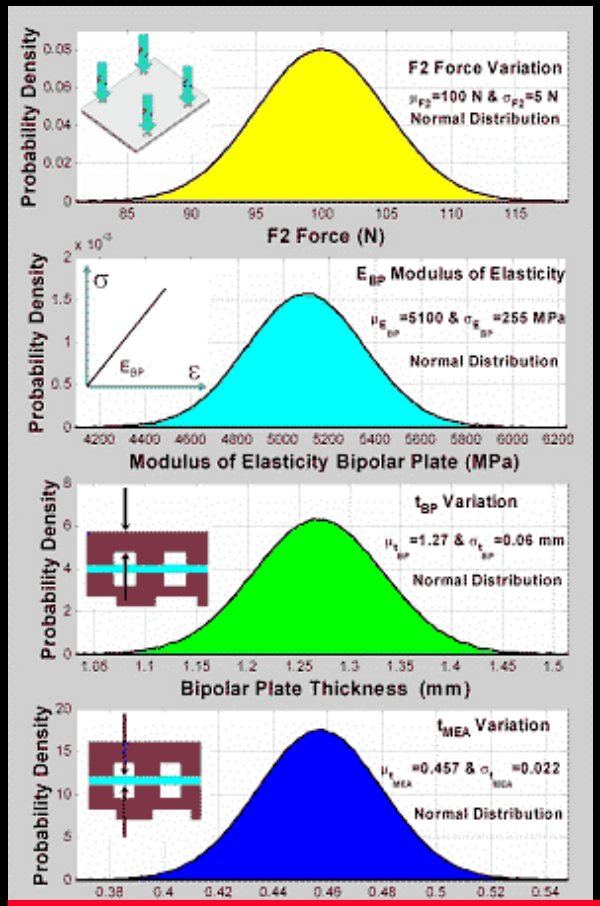


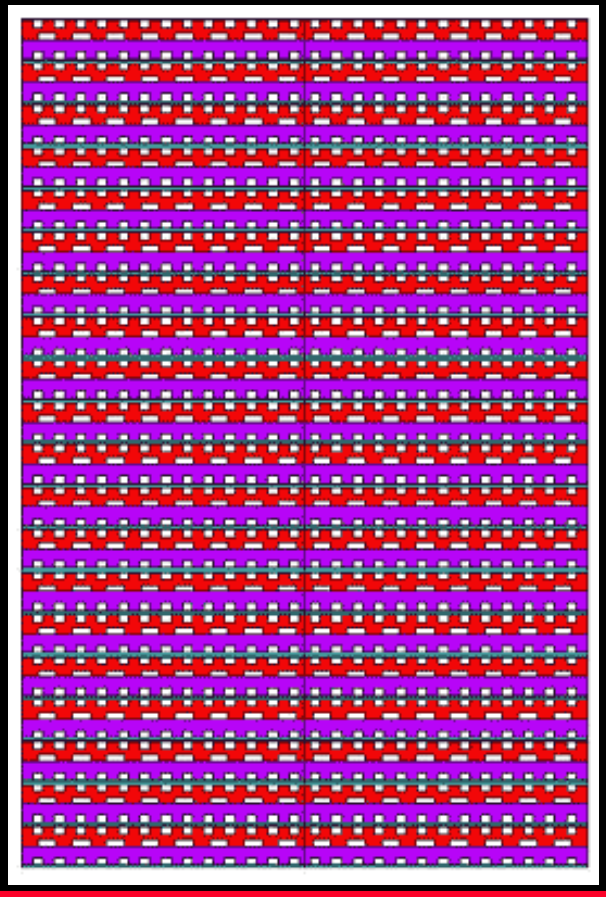
Solutions to real-world technical issues:

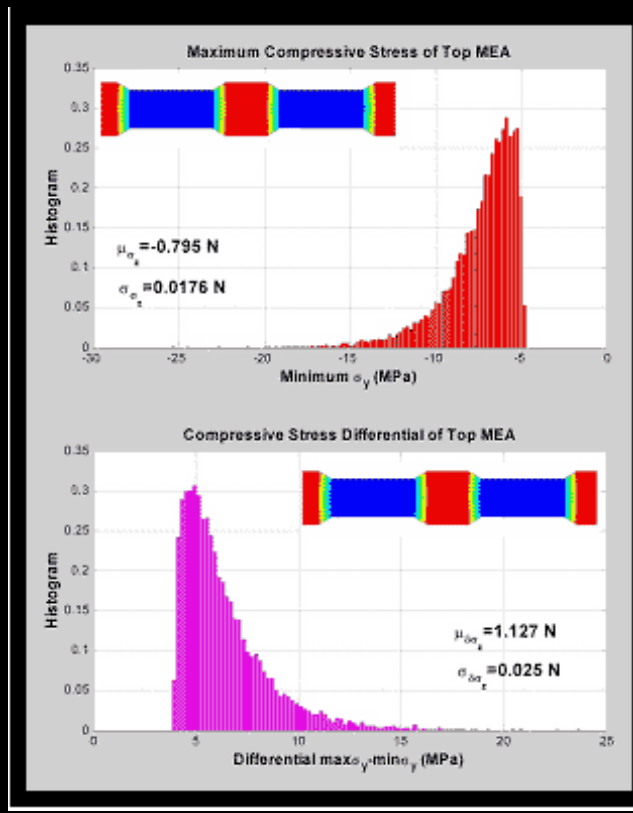
- improved thermal mechanical fatigue of ATR
- analyzed thermal efficiency of ATR
- improved pressure distribution within stack
- quantified sensitivity of design factors to non-uniform MEA pressure distribution

Accomplishments
Robust Designs of Fuel Cell Components

Statistical Distribution of Material and Manufacturing Variations → **Parametric FEA Model of Fuel Cell Stack** → **Statistical Distribution of Output Performance Measures**



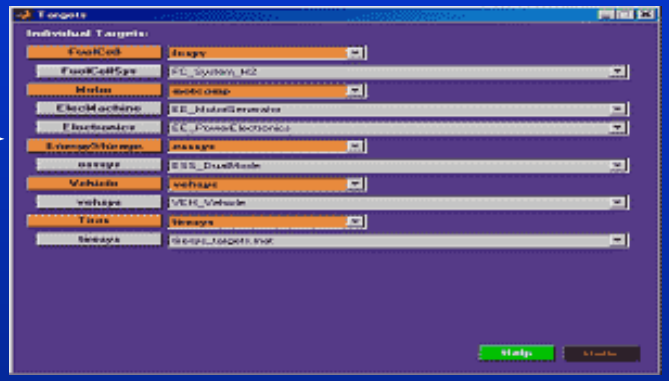




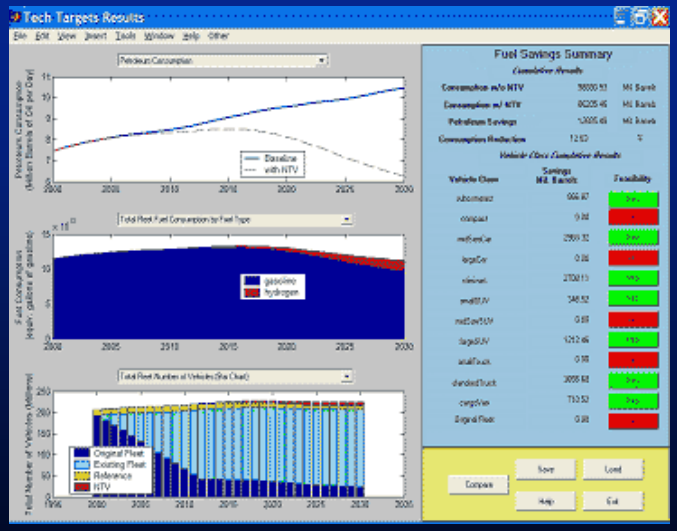
Published methodology for assessing the "Effect of Material and Manufacturing Variations on MEA pressure Distribution" ***(co-authored with Plug Power)***

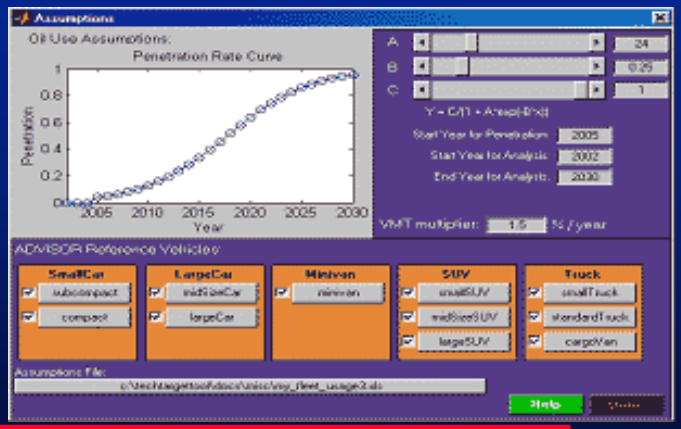
Accomplishments
Technical Targets Tool Developed

Target Values



Model Parameters

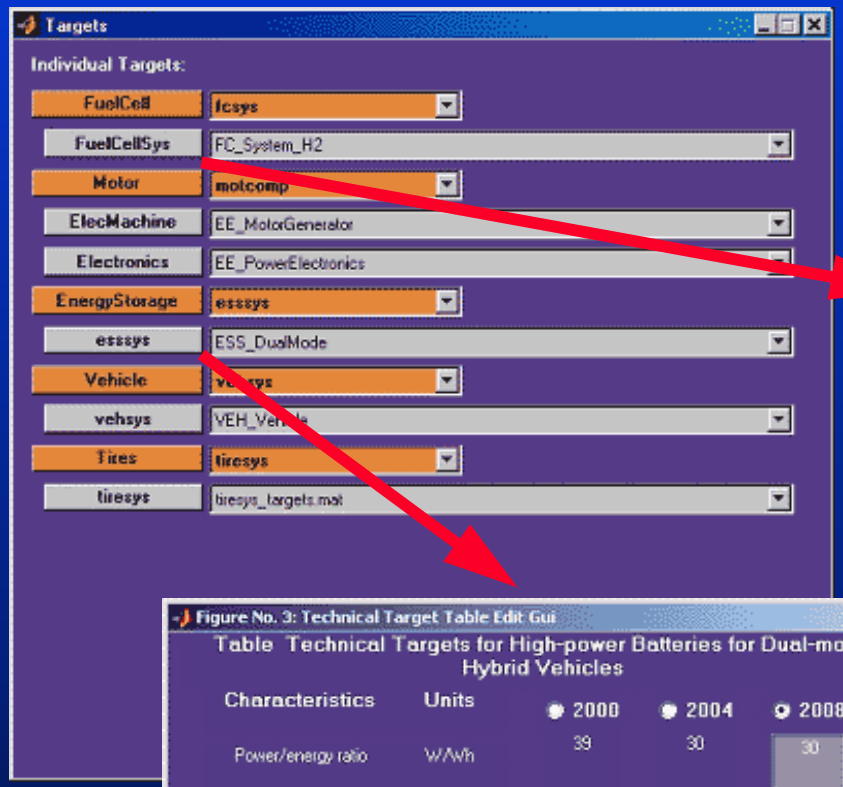


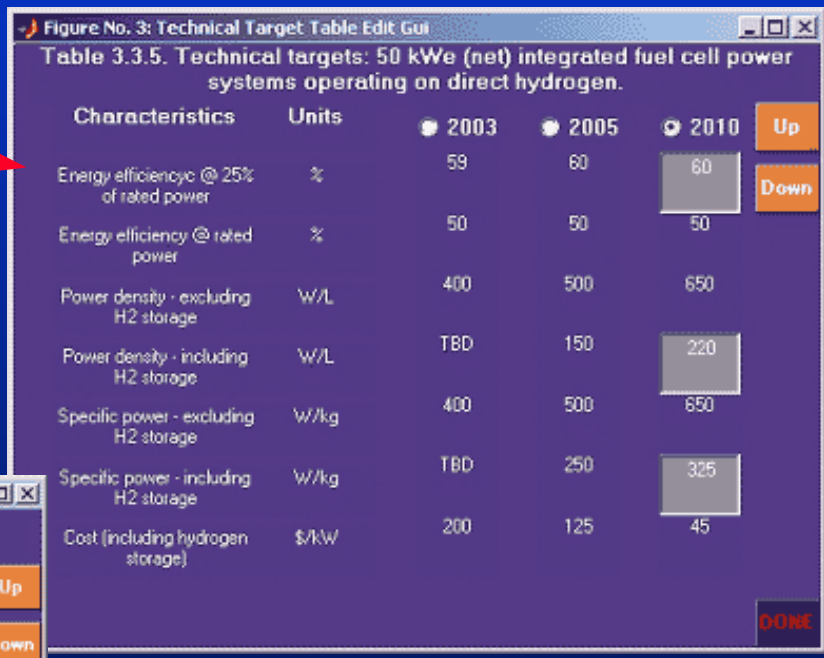


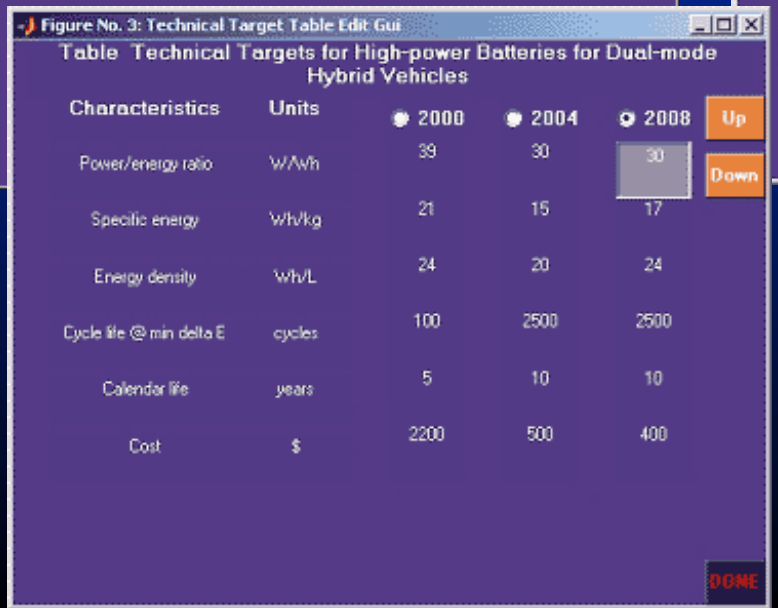
Quantifies potential impact of DOE programs.

Accomplishments

T^3 - A Repository for Component Targets



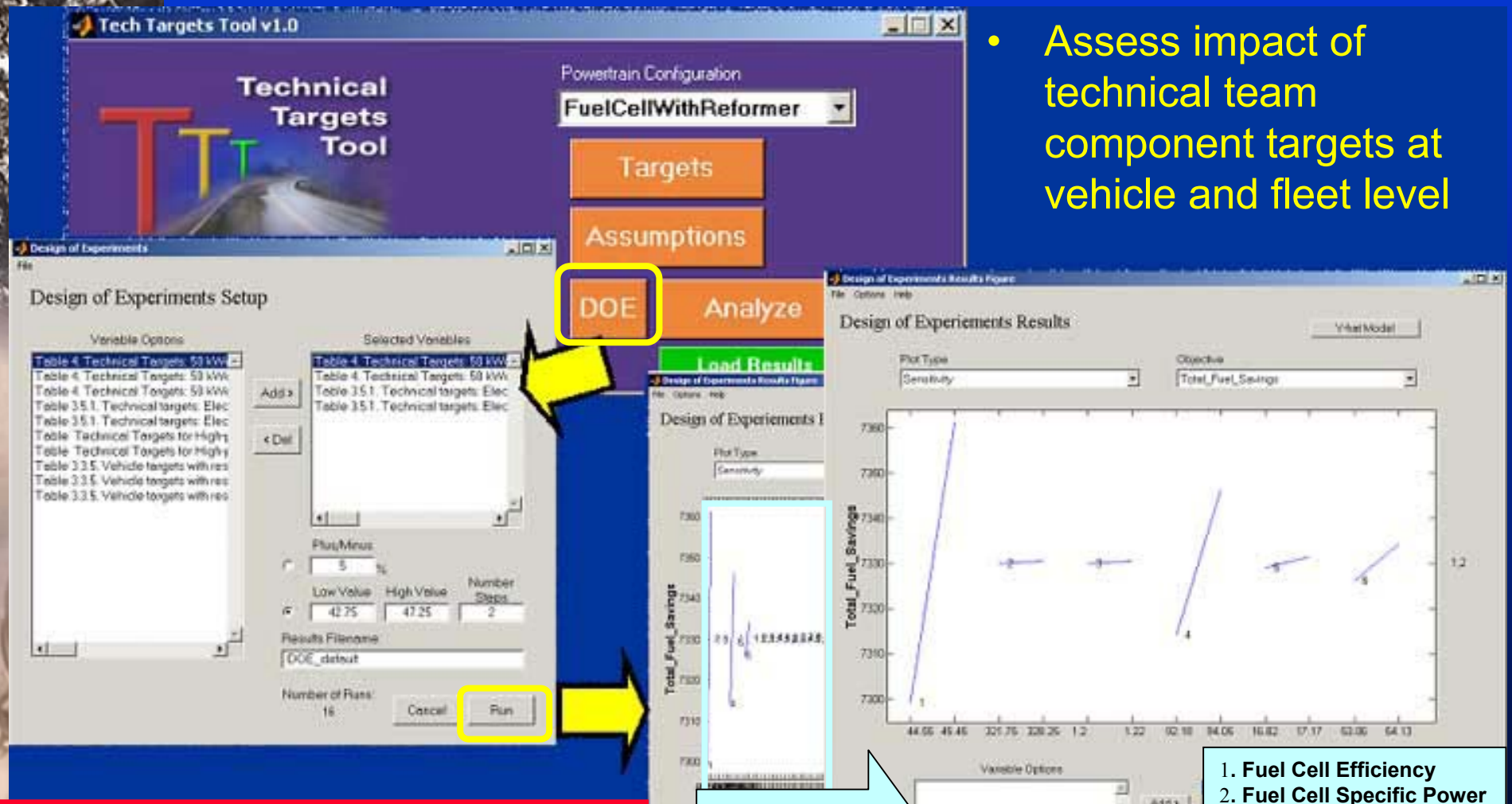




Accomplishments

Fuel Cell Targets Analyzed Using Technical Targets Tool

- Assess impact of technical team component targets at vehicle and fleet level

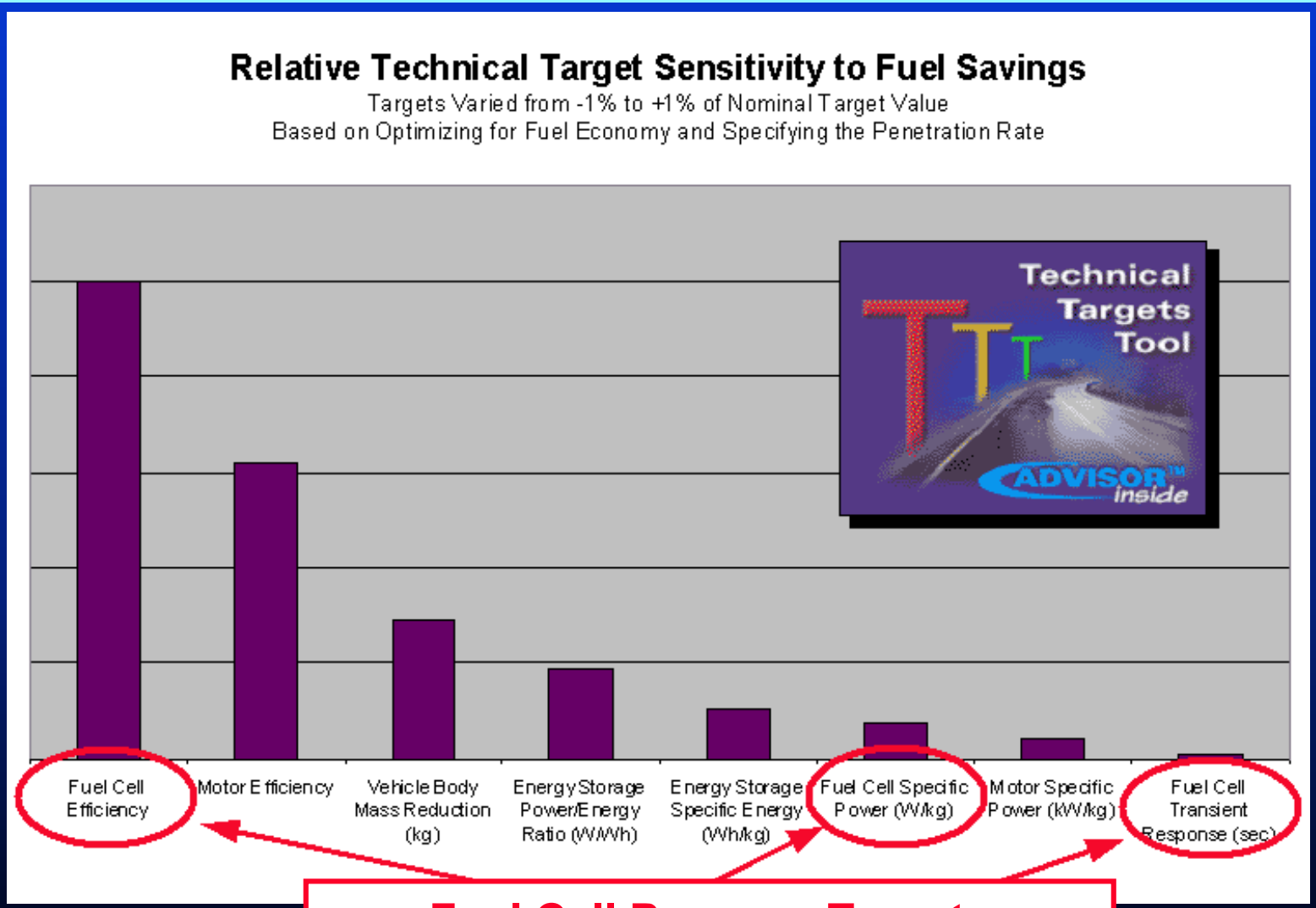


1. Fuel Cell Efficiency
2. Fuel Cell Specific Power
3. Motor Specific Power
4. Motor Efficiency
5. Battery Specific Energy
6. Body Mass Reduction

Technical target variation leads to sensitivity in total fuel savings

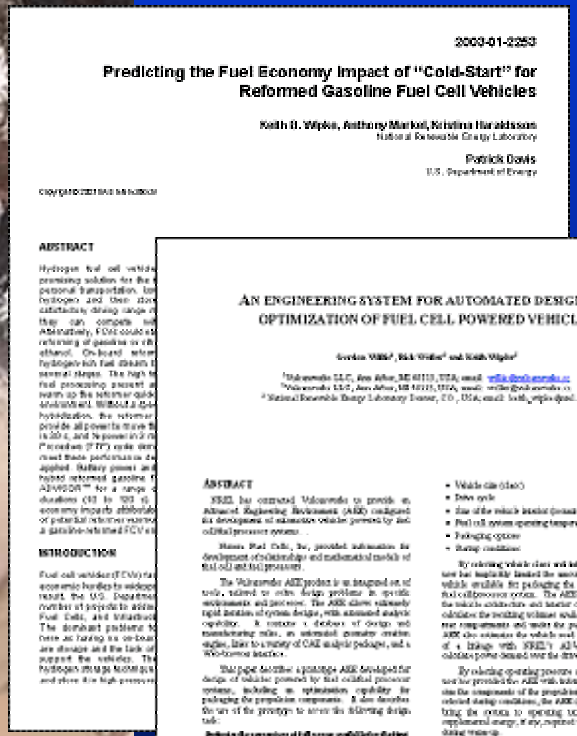
Accomplishments

T^3 and DOE Highlight Relative Sensitivity of Fuel Economy



Fuel Cell Program Targets

High Visibility of NREL's Vehicle Systems Analysis Activity Through Publications


2003-01-2253

Predicting the Fuel Economy Impact of "Cold-Start" for Reformed Gasoline Fuel Cell Vehicles

Keith B. Wipke, Anthony Markel, Kristina Haraldsson
National Renewable Energy Laboratory

Patrick Davis
U.S. Department of Energy

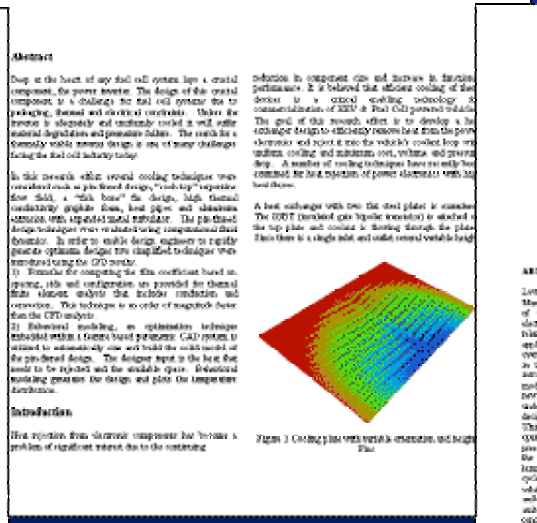
ABSTRACT

INTRODUCTION

AN ENGINEERING SYSTEM FOR AUTOMATED DESIGN AND OPTIMIZATION OF FUEL CELL POWERED VEHICLES

ABSTRACT

INTRODUCTION


First International Conference on Fuel Cell Science, Engineering and Technology
April 21-23, 2003, Rochester, New York, USA

INNOVATIVE THERMAL MANAGEMENT OF FUEL CELL POWER ELECTRONICS

Abstract

Introduction

First International Conference on Fuel Cell Science, Engineering and Technology
April 21-23, 2003, Rochester, New York, USA

EFFECT OF MATERIAL AND MANUFACTURING VARIATIONS ON MEMBRANE ELECTRODE ASSEMBLY PRESSURE DISTRIBUTION

AN ANALYSIS OF WATER MANAGEMENT FOR A PEM FUEL CELL SYSTEM IN AUTOMOTIVE DRIVE CYCLES

ABSTRACT

INTRODUCTION

ADVISOR 2002
Advanced Vehicle Simulator

ADVISOR™ inside

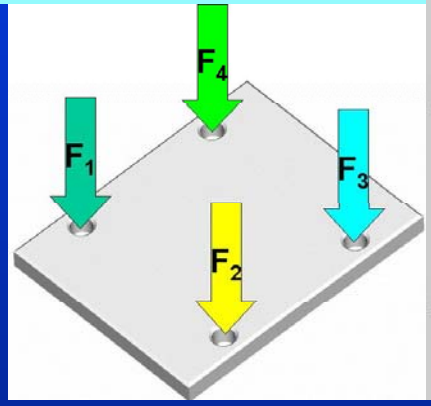
Addressing Reviewer Comments

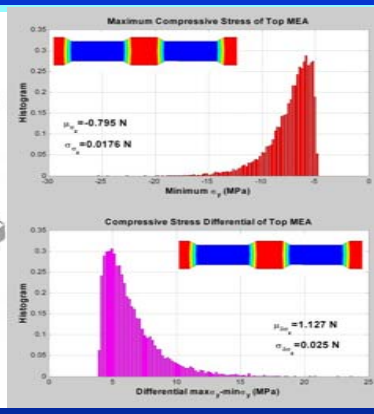
- System cost estimates should be included in analyses
  - System costs estimated within Technical Targets Tool and recent Energy Storage System Requirements study
- Computer models should be used to evaluate fuel cell program technical targets
  - Technical Targets Tool developed and applied
- Need to accommodate fuel cell and subsystem design trade-offs
  - 2 parametric detailed fuel cell system models integrated with ADVISOR vehicle simulation tool
- Review of assumptions by industry
  - working with fuel cell, hydrogen, energy storage, and vehicle systems technical teams
  - collection of peer reviewed papers published

Recent Collaborative Projects with Industry

Plug Power:

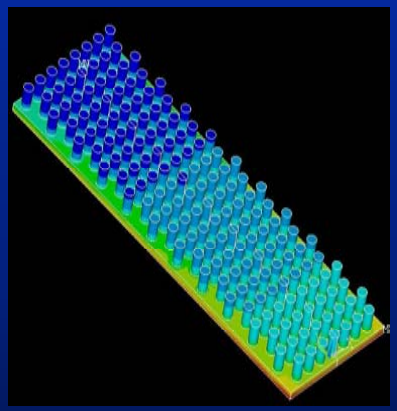
- ATR thermal analysis
- Analysis of MEA pressure profiles
- End plate topology optimization
- Robust high temp. stack design

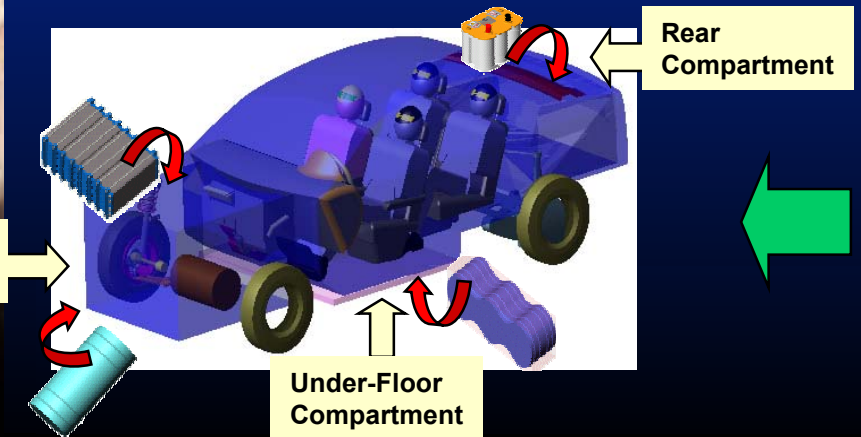




Ballard Power Systems:

- Thermal management of fuel cell power electronics





VulcanWorks/Nuvera:

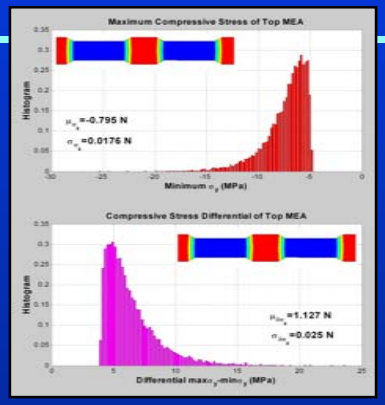
- Design and optimization of fuel cell vehicle packaging solutions

Plans and Future Milestones

- Fuel cell hybrid vehicle system optimization – working with fuel cell, energy storage, vehicle systems teams on energy storage targets for fuel cell vehicles **(9/03)**
- Technical Targets Tool study on sensitivity of fuel cell technical targets applied to multiple vehicle platforms **(9/03)**
- Complete water and thermal management analysis for fuel cell vehicles under real driving conditions **(11/03)**
- Validation of fuel cell models with industry partners **(2/04)**
- Robust design process transferred to industry to address fuel cell stack cost and durability technical barriers **(9/04)**

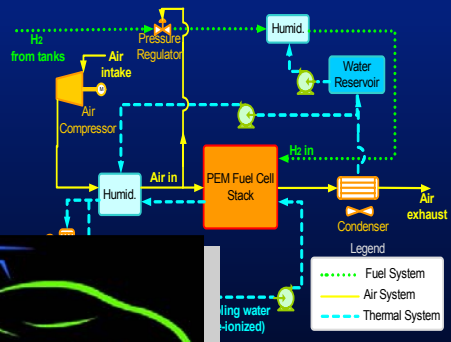
Summary

- Vehicle systems tools coupled with optimization and robust design methods are being applied to address cost and durability technical barriers



- Technical Targets Tool introduced and applied to understand sensitivity of fuel consumption to the fuel cell program technical targets

- Enhanced fuel cell system models incorporated into vehicle model to analyze thermal and water management technical barriers



Cost Analyses of Fuel Cell Stacks/Systems

DE-FC02-99EE50587

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley, CA

May 19-22

TIAX LLC
Acorn Park
Cambridge, Massachusetts
02140-2390

Reference: D0006

In the initial tasks of the project, Argonne National Laboratory provided modeling support.

Program Manager: Nancy Garland
ANL Technical Advisor: Robert Sutton

TIAX Team

Primary Contact: Eric J. Carlson

Core Team:
Dr. Suresh Sriramulu
Stephen Lasher
Rebeca Hwang

Argonne National Laboratory
System Thermodynamic Model

Primary Contact: Dr. Romesh Kumar

For PEMFC powertrains to be viable in the market place, they must have attractive performance and cost attributes.

Technical Targets

System	Efficiency	Cost ($/kW) 2010	Cost ($/kW) 2015
Direct Hydrogen Fuel Cell Power System (including hydrogen storage)	60%	45	30
Reformer-based Fuel Cell Power System • clean hydrocarbon or alcohol based fuel • 30 second start-up • satisfies emissions standards	45%		

Barriers

N. Cost (Fuel-Flexible Fuel Processor)
O. Stack Material and Manufacturing Cost

PEMFC powertrains are competing with mature but still evolving internal combustion engine (spark or compression ignition) technology.

Project Objectives

To assist DOE in the development of fuel cell system technologies by providing cost and manufacturing analysis.

- To develop an independent cost estimate of PEMFC system costs including a sensitivity analysis to:
  - Operating parameters
  - Materials of construction
  - Manufacturing processes
- To identify opportunities for system cost reduction through breakthroughs in component and manufacturing technology
- To provide annual updates to the cost estimate for the duration of the project

Project Approach

In this multi-year program, we developed a baseline system configuration and cost and then looked at various system scenarios and the impact of future technology developments.

Task 1: PEMFC System Technology Synopsis

- Develop baseline system specification
- Project technology developments
- Assess impact on system performance
- Identify manufacturing processes

Task 2: Develop Cost Model and Baseline Estimates

- Develop cost model
- Specify manufacturing processes and materials
- Develop production scenarios
- Baseline cost estimate

Task 3: Identify Opportunities for System Cost Reduction

- Perform sensitivity analysis to key parameters
- Evaluate the impact of design parameters and potential technology breakthroughs on subsystem and overall system costs
- Identify and prioritize opportunities for cost reduction in transportation PEMFC systems
- Obtain industry feedback

Tasks 4, 5, 6 & 7: Annual Updates

- Assess technology evolution
- Update baseline cost estimate based on technology developments

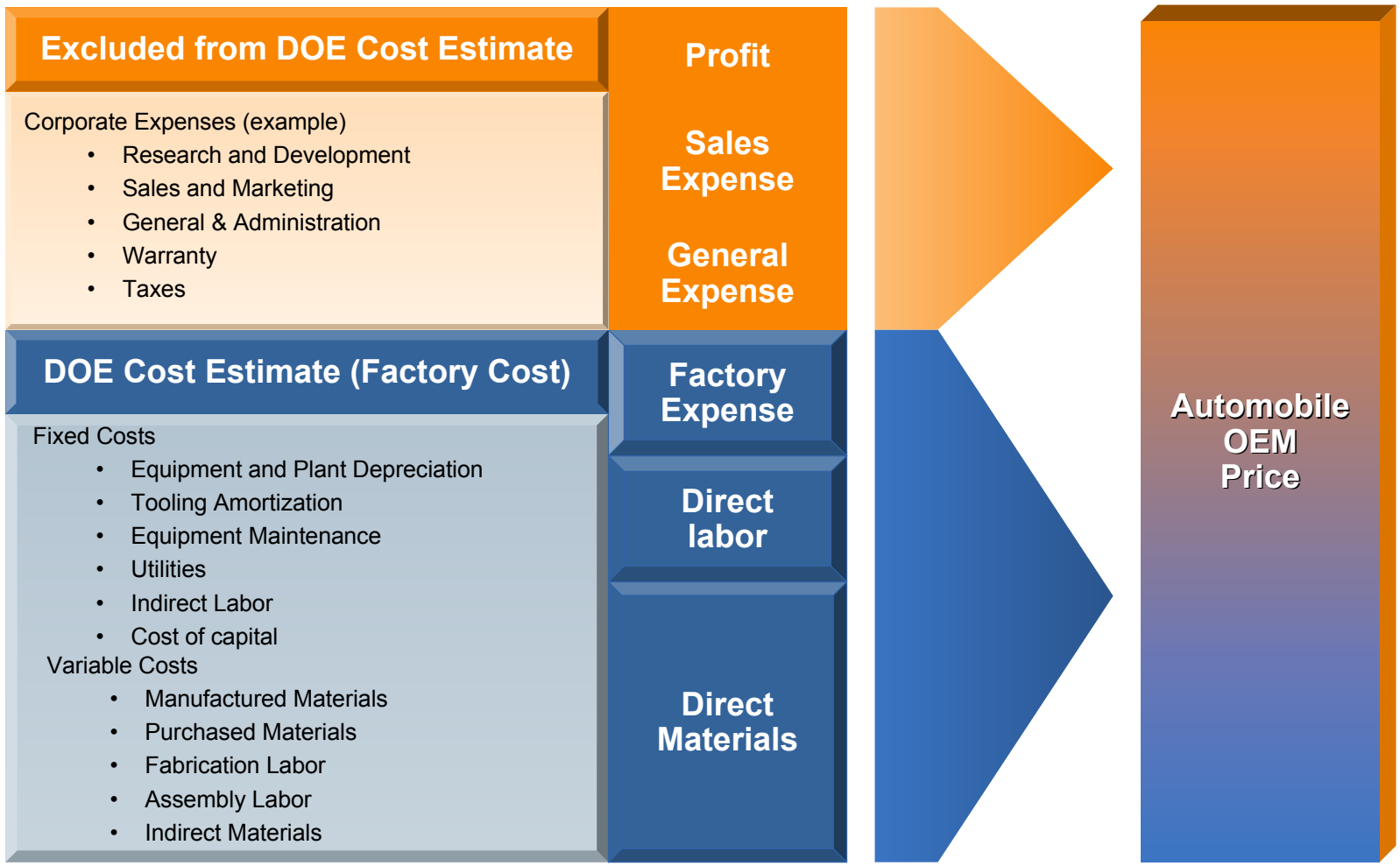
Year 1 (1999)) — *Year 2 (2000)* — *Years 3, 4, and 5*

Ends 3/04

Project Accomplishments

- Developed comprehensive system configuration and activities-based cost estimate for this system produced in high volume with near term available technology
  - Presented results to the fuel cell industry for feedback and incorporated this into a revised baseline cost estimate
  - Presented results to National Research Council review
  - Identified key cost drivers and development areas
- Provided program support to OATT by evaluation of system operating and future scenarios
  - High efficiency versus High Power
  - Hybrid scenarios ($/kW versus rated power)
  - Future reformer and direct hydrogen scenarios
- Program support in development of hydrogen cost targets
- Support for other DOE efforts including Full Choice Project, Report to Congress, and Annex XV
- Fundamental analysis of stack cost versus platinum loading

We have estimated the system cost up to and including factory costs for annual production volumes of 500,000.

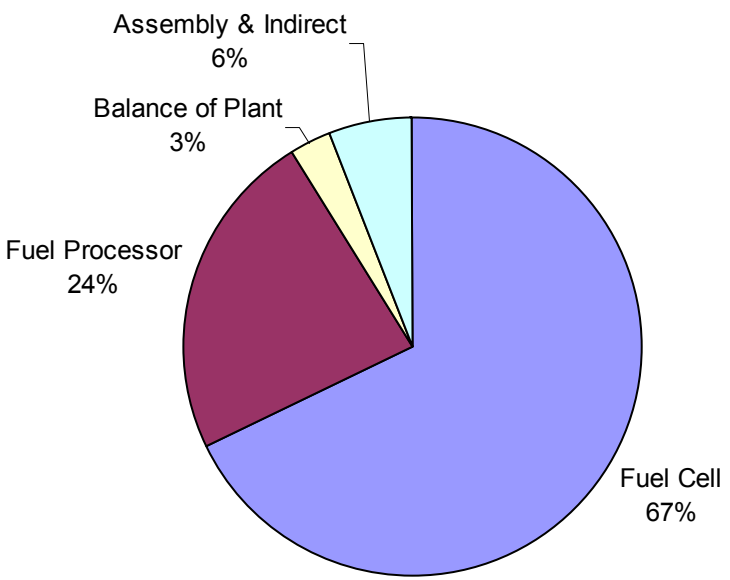


Individual components have been distributed between the major sub-systems as shown below.

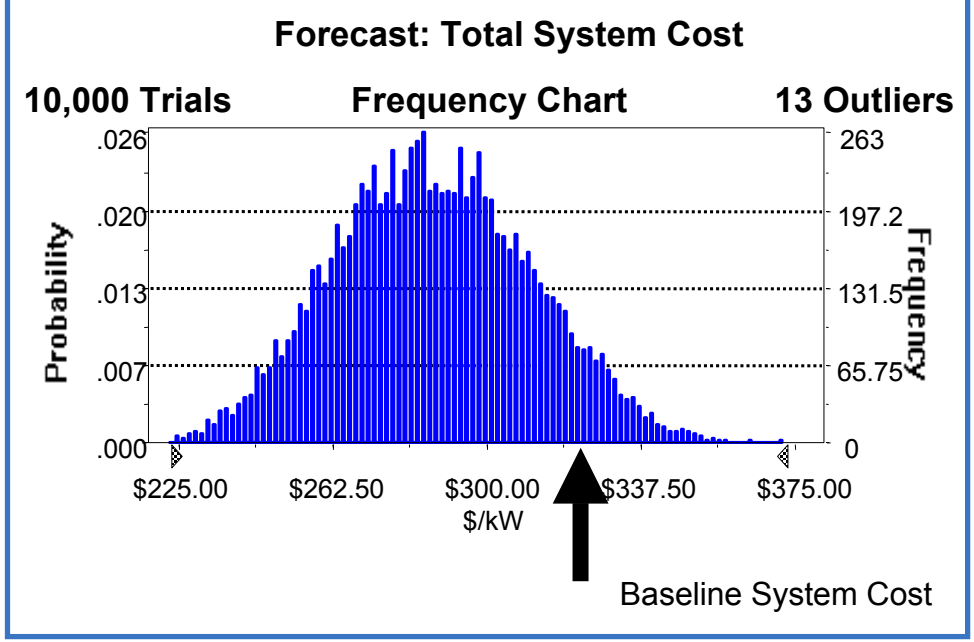
Fuel Processor Sub-System		Fuel Cell Sub-System	Balance-of-Plant
◆ **Reformate Generator** ◆ ATR ◆ HTS ◆ Sulfur Removal ◆ LTS ◆ Steam Generator ◆ Air Preheater ◆ Steam Superheater ◆ Reformate Humidifier	◆ **Fuel Supply** ◆ Fuel Pump ◆ Fuel Vaporizer	◆ Fuel Cell Stack (Unit Cells) ◆ Stack Hardware ◆ Fuel Cell Heat Exchanger ◆ Compressor/Expander ◆ Anode Tailgas Burner ◆ Sensors & Control Valves	◆ Startup Battery ◆ System Controller ◆ System Packaging ◆ Electrical ◆ Safety
◆ **Reformate Conditioner** ◆ NH_3 Removal ◆ PROX ◆ Anode Gas Cooler ◆ Economizers (2) ◆ Anode Inlet Knockout Drum	◆ **Water Supply** ◆ Water Separators (2) ◆ Heat Exchanger ◆ Steam Drum ◆ Process Water Reservoir		
◆ Sensors & Control Valves for each section			

The fuel cell subsystem dominates the cost of the reformate system based on near-term technology but produced at high volume.

Yr 2001 Cost Breakdown by Sub-System (Total Cost: $324/kW)

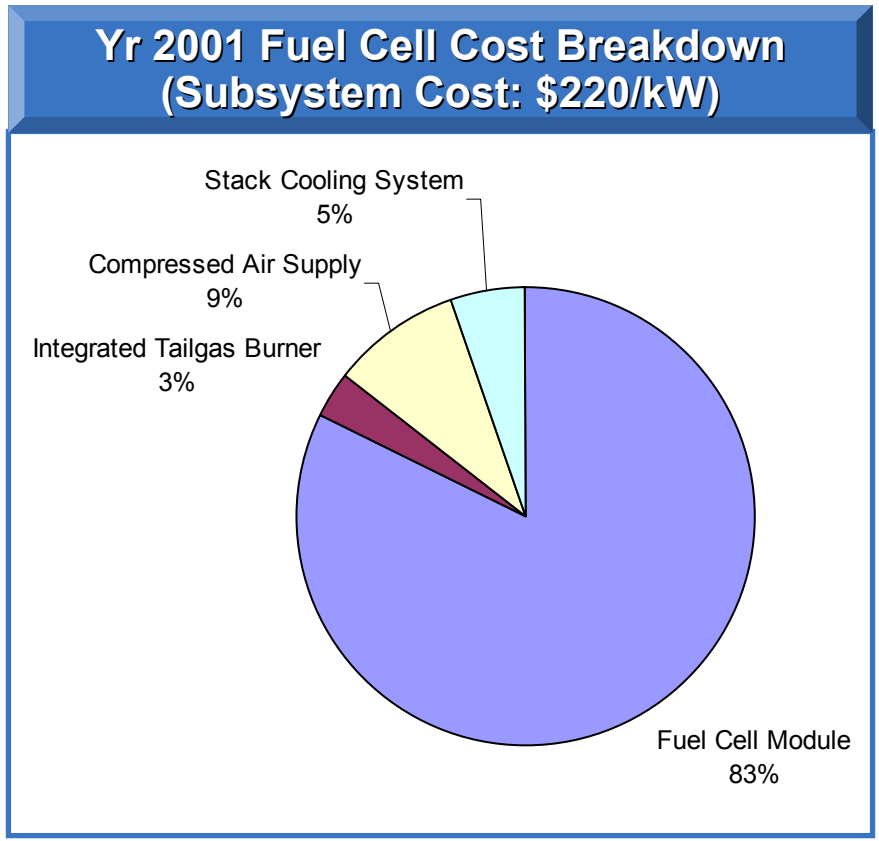


Monte Carlo Simulation of Model



Consideration of uncertainty in the baseline model assumptions still leads to a cost over $200/kW.

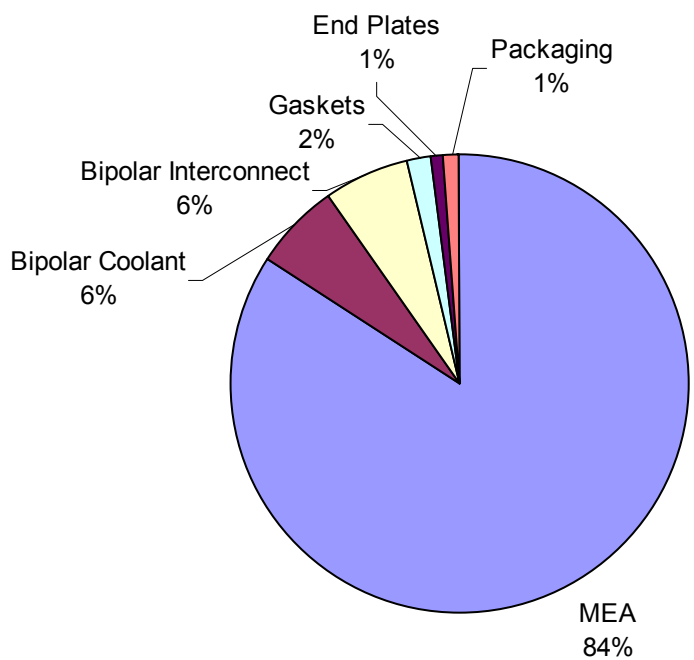
The fuel cell stack dominates cost of the fuel cell subsystem, however, thermal management is critical to system size.



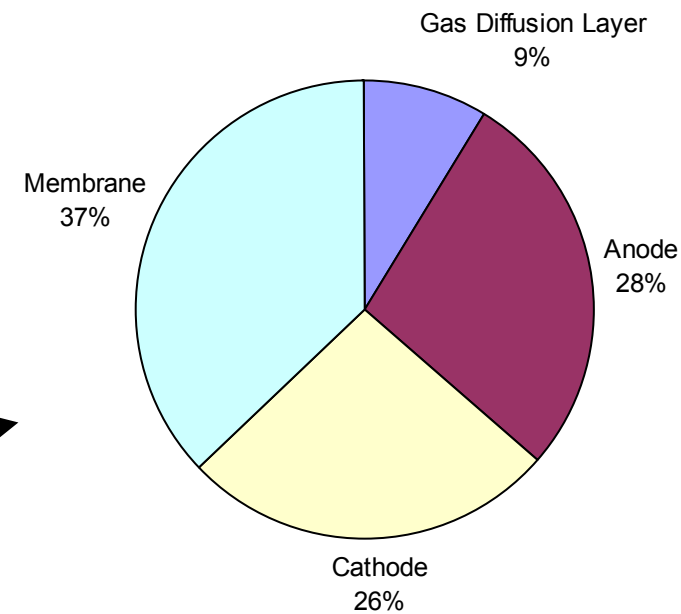
Basis: 50 kWe net, 500,000 units/yr. Not complete without assumptions.

Platinum and the electrolyte membrane are the major contributors to the stack cost.

Yr 2001 Fuel Cell Stack Cost Breakdown (Stack Cost: $181/kW)



Yr 2001 MEA Cost Breakdown (MEA Cost: $152/kW)



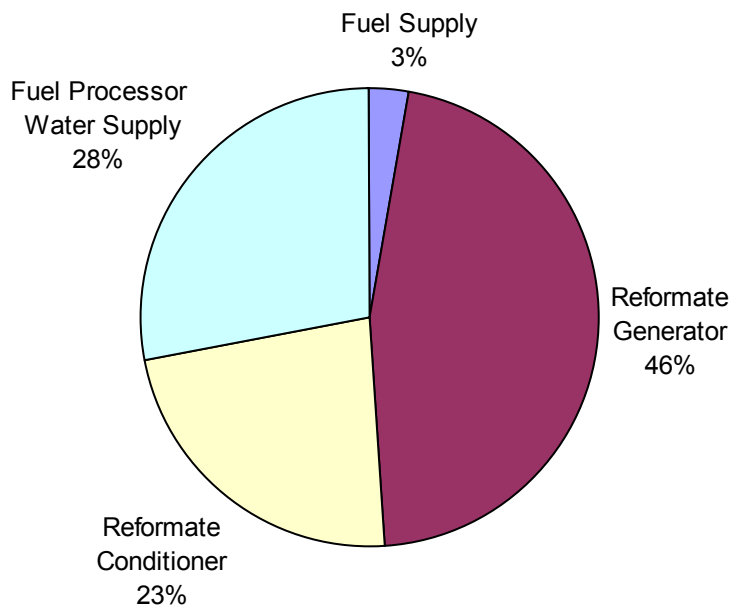
180 grams Pt (0.8 mg/cm^2) for 0.8V @ 250 mW/cm^2

*Basis: 50 kWe net, 500,000 units/yr. Not complete without assumptions.

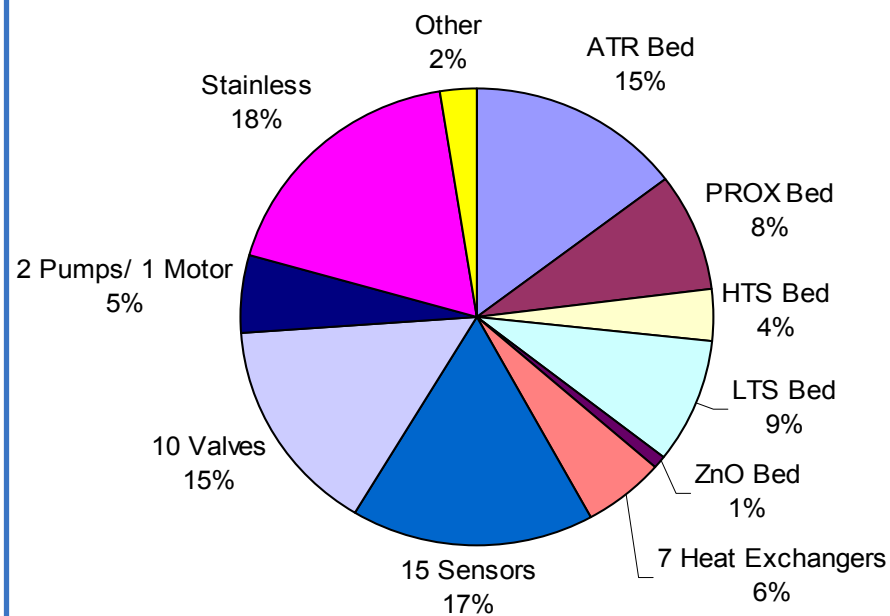
While power density determines the actual amount of material in the system. Parasitic power losses further increase size and cost.

System simplification and cost reduction of components will be needed to reduce the cost of non-catalytic materials and components.

Yr 2001 Fuel Processor Cost Breakdown (Cost: $76/kW)

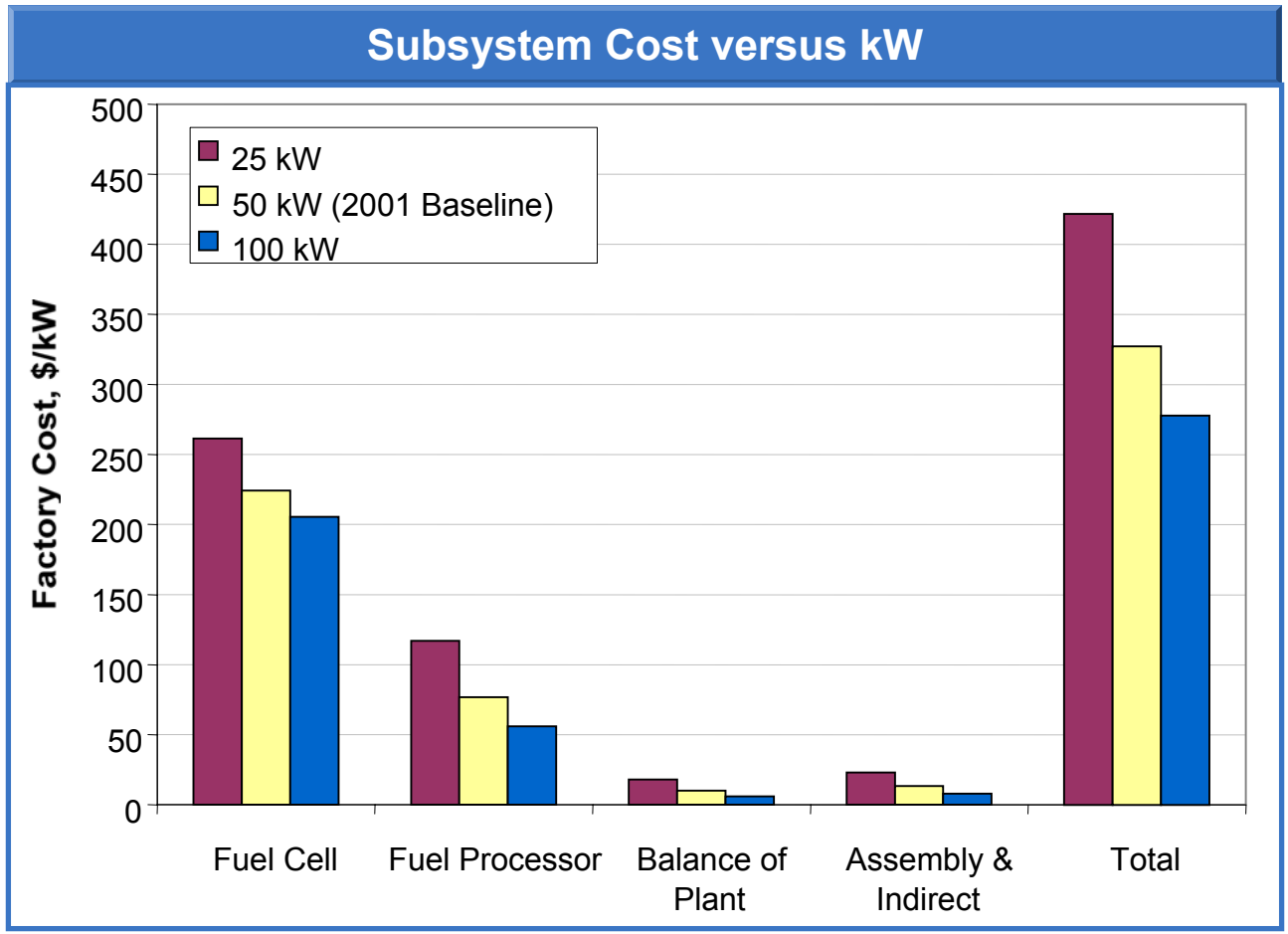


Yr 2001 Fuel Processor Cost Breakdown by Material



*Basis: 50 kWe net, 500,000 units/yr. Not complete without assumptions.

Some of the cost benefits of reducing total rated power in a hybrid system will be offset by increased cost per kW arising from fixed costs.



*Basis: 50 kWe net, 500,000 units/yr. Not complete without assumptions.

The potential for reduction in platinum loading was estimated by calculating 'best-case' cathode polarization curves for various operating conditions.

$$V^{cell} = V^{OC} - J\,R_{total} - \eta_c - \eta_a$$

Baseline experimental activity data (h_c Vs. *i*)
- 60 C
- 1 atm O_2
- Aqueous electrolyte
- 3.5 nm Pt

→

Correct data for :
Temperature (T) Partial pressure (P_{O2})
- Solubility of O_2 in the electrolyte
- Alloy catalyst activity

→

Account for:
Loading
- Area utilization
- Particle size effects

→

h_c Vs. J for any T, P, Loading

Tafel Kinetics

$$i = \gamma i_0 \exp\left[\frac{\eta}{b}\right]$$

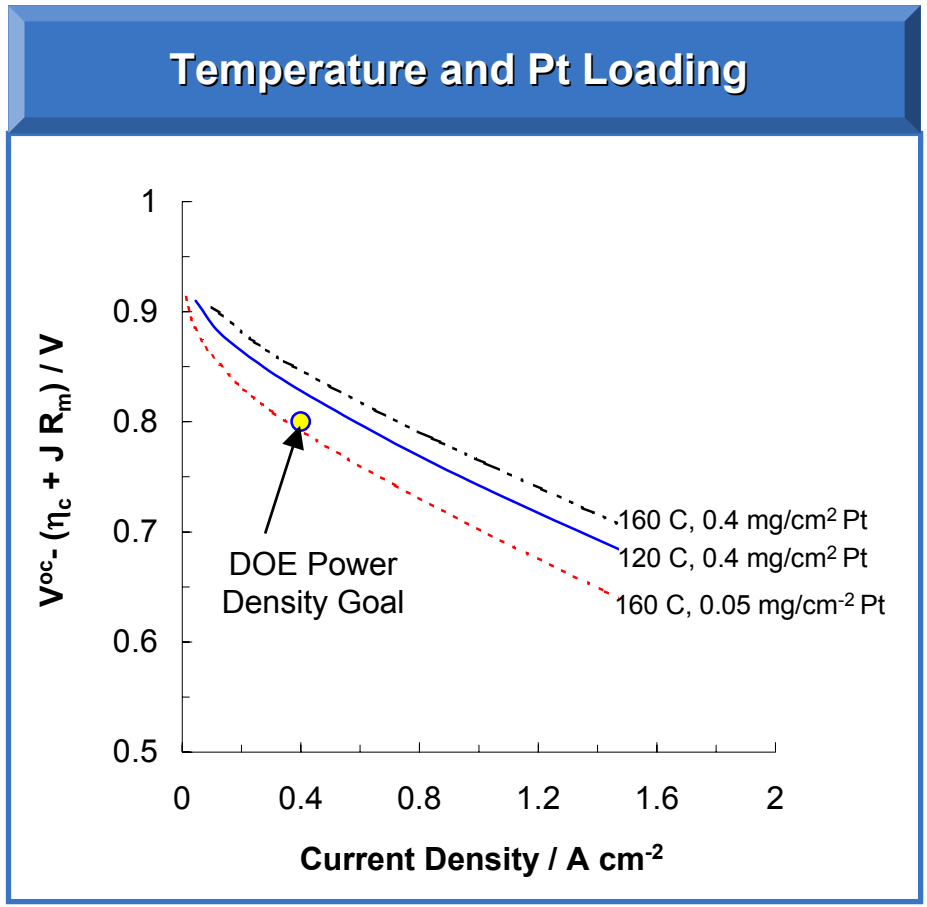
$$i_0 = k\left(sP_{O_2}\right)^n \exp\left[-\frac{E_a}{RT}\right]$$

Parameter	Value
i_0 - Exchange current density	Experimental data[1]
b - Tafel Slope	Experimental data[1]
k - pre-exponential factor	2 x Pt activity (Pt:Ni)[2]
n - Reaction order	1 (Exp. data)[1]
s - O_2 solubility	3 x that in water (Exp.)[3]
E_a - Activation energy	28 kJ/mol (Exp.)[1]

1 U. Paulus, T. J. Schmidt, H. A. Gasteiger, R. J. Behm, J. Electroanal. Chem., 495 (2000) 134.
2 P. N. Ross, N., Markovic, T. J. Schmidt, V. Stamenkovic, in DOE 2001 Review, OTT Fuel Cells program, ORNL (2001)
3 S. Gottesfeld and T. Zawodzinski in R. C Alkire, H. Gerischer, D. M. Kolb, C. W. Tobias (Eds.), Adv. Electrochem. Sci. Eng. V 5, Wiley-VCH, Weinhem (1997).

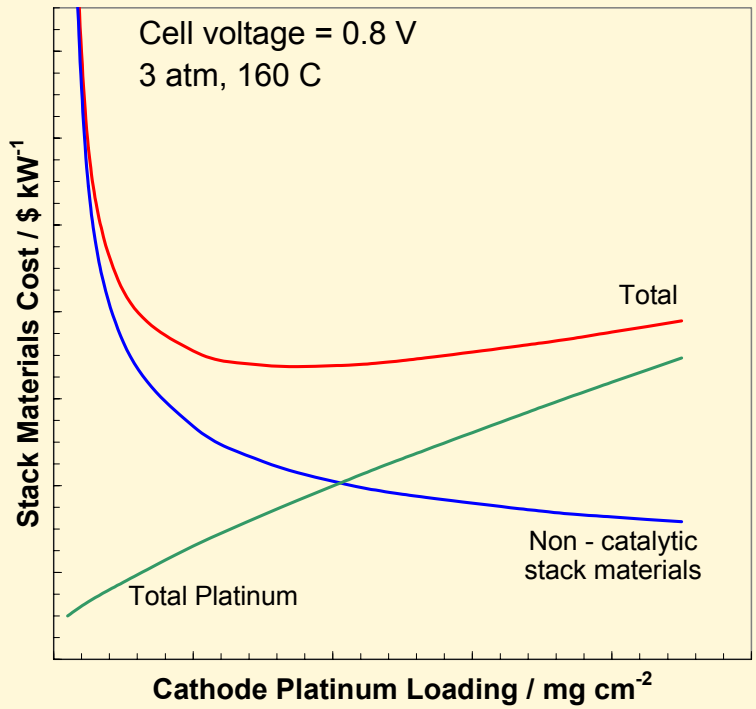
A minimum platinum loading of 0.2 - 0.4 mg/cm2 is needed to achieve DOE power density goals (0.4 A/cm^2 @ 0.8 V) at 120 C.

Operating Conditions:
3 atm, 2x Pt activity, R_t = 0.1 Ω cm^{-2}, 3.5 nm catalyst diameter



Voltage losses at the anode will lower the estimated curves.

Increasing stack costs due to non-catalytic materials limits the benefit of reducing platinum loading below a certain value.



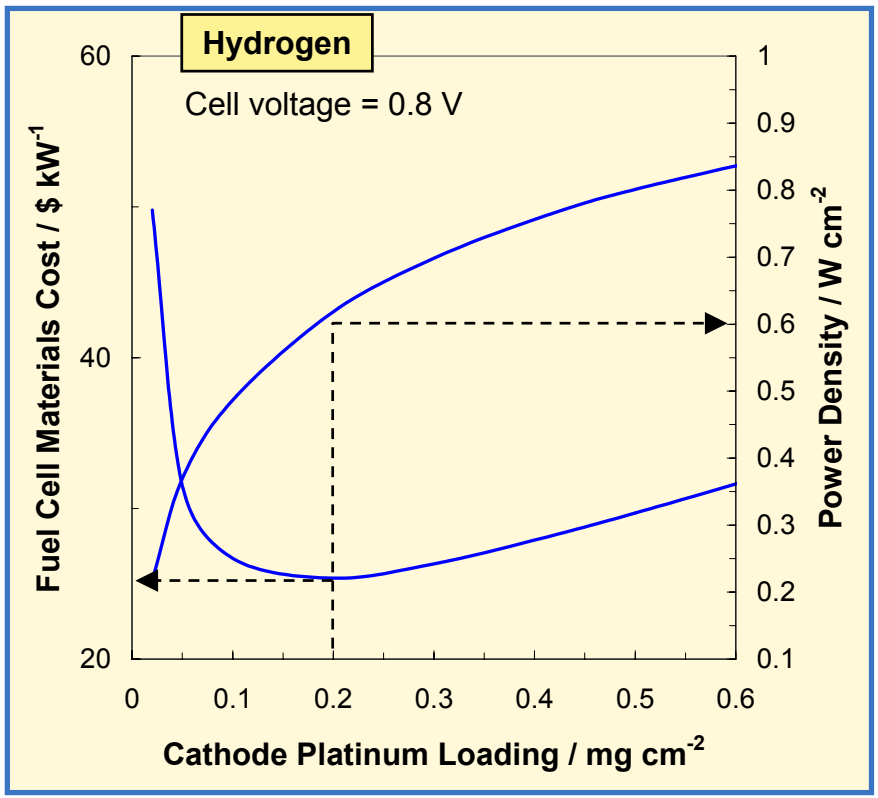
Non-catalytic materials dominate cost

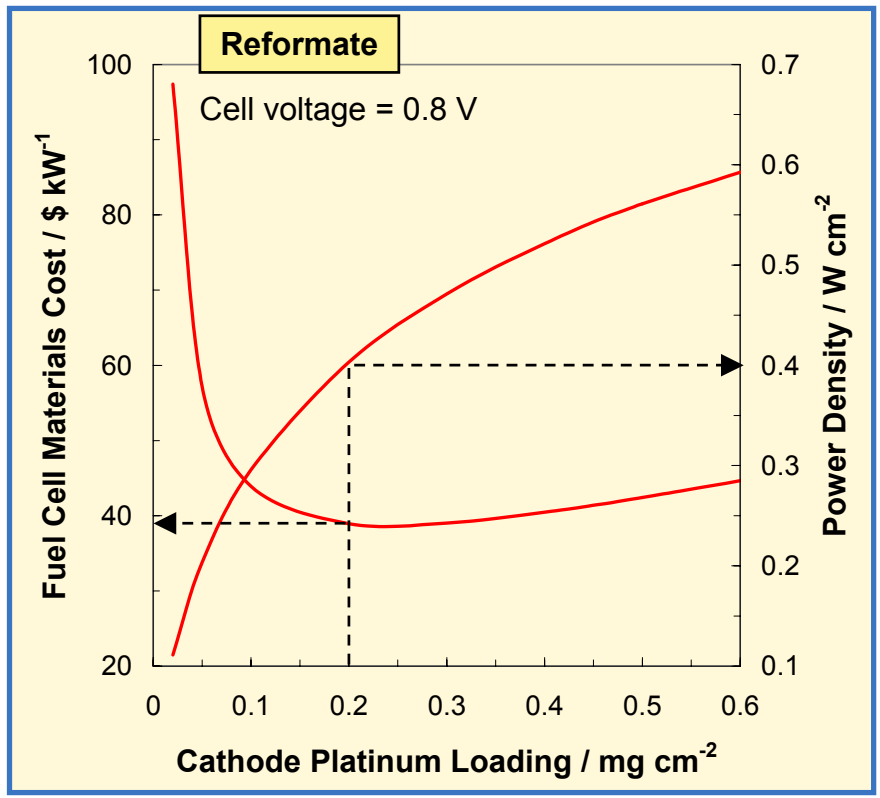
Similar contribution of Pt and non-active materials

Pt costs dominate

Ohmic losses limit the benefit of higher Pt loading

In both reformate and direct hydrogen cases, the minimum in stack material costs occurs around cathode platinum loadings of 0.2 mg/cm^2.

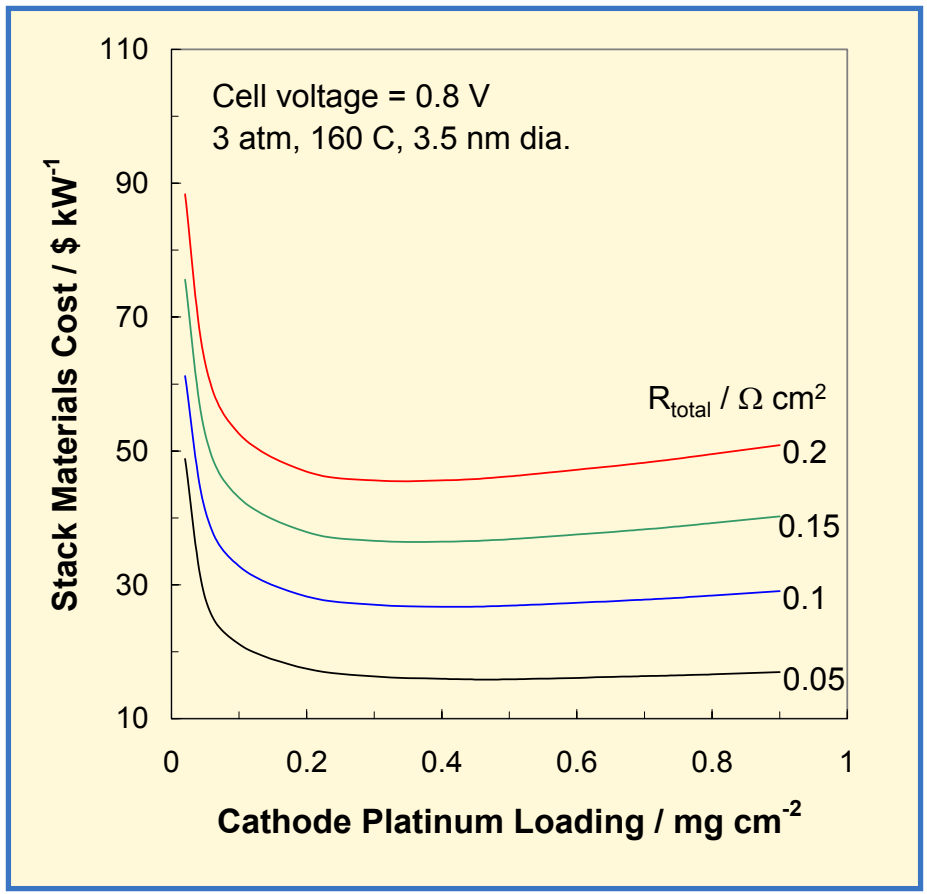




Assumptions	Hydrogen	Reformate
Anode overpotential (mV)	0	30
Membrane Resistance (mΩ cm^2)	50	50
Electronic Reisistance (mΩ cm^2)	20	20

Operating Conditions:
0.8 V, 3 atm, 160 C, 3.5 nm Particles, 2x Pt activity

The cell resistance (ionic + electronic) has a significant influence on the cost-effectiveness of platinum usage in the stack.



Assumptions: Anode Pt loading = 50 % of that of the cathode, Platinum cost = 18,000 $/kg, Membrane cost = 50 $/m^2, Bipolar + coolant plate = 22 $/m^2, GDL = 31 $/m^2
Operating Conditions: 0.8 V, 3 atm, 160 C, 3.5 nm Particles, 2x Pt activity

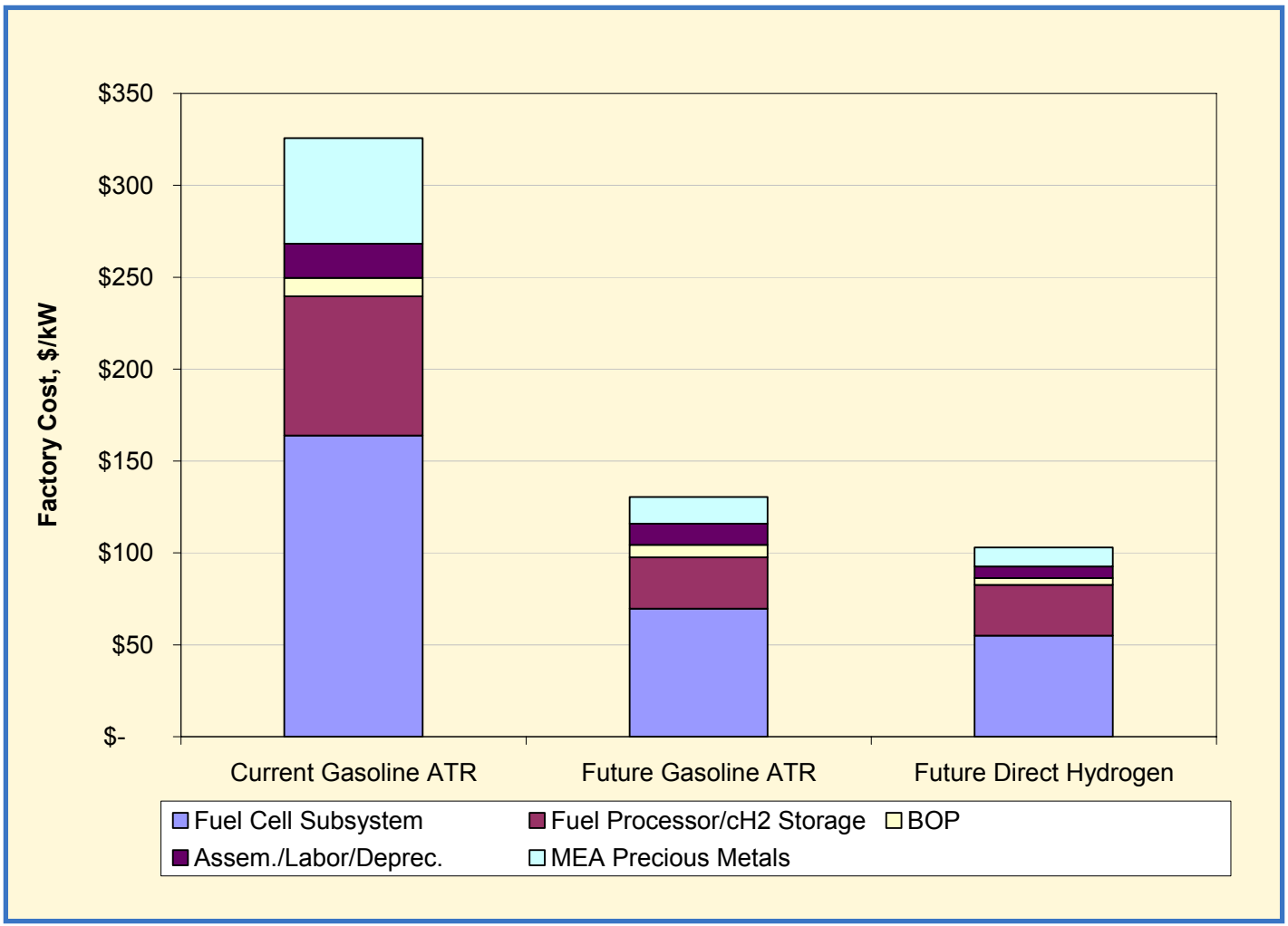
The platinum content for the DOE Goals scenario is much lower than the other cases due to its very aggressive cathode loading assumption.

MEA Precious Metal Calculation	Current Reformate	Future Reformate	Future Hydrogen	DOE Goals Reformate
Cathode Pt Loading, mg/cm²	0.4	0.2	0.2	0.05
Anode Pt Loading, mg/cm²	0.4	0.1	0.1	0.025
Power Density, mW/cm²	248	400	600	320
Gross System Power, kW	56	53	53	56
Cathode Pt, g	90	26	18	8.8
Anode Pt, g	90	13	8.8	4.4
Anode Ru, g	45	6.6	0	2.2
Stack Precious Metals, g	**225**	**46**	**27**	**15**

Projection of future system costs were made by assuming higher power densities, advances in reformer technology, and compressed hydrogen storage.

Parameter	Baseline	Future Reformate	Future Hydrogen
Stack Improvements ◆ Current Density (mA/cm^2) ◆ Power Density (mW/cm^2) ◆ Cathode Pt (mg/cm^2) ◆ Anode Pt (mg/cm^2) ◆ Anode Ru (mg/cm^2)	310 250 0.4 0.4 0.2	500 400 0.2 0.2 0.0	760 610 0.2 0.1 0.0
Fuel Processor Improvements		◆ Short contact time reactor ◆ Improved shift catalysts ◆ No sulfur bed ◆ No PrOX	◆ No Fuel Processor ◆ Compressed H_2 storage ◆ Simpler tailgas burner
System and Material Cost Reduction		Reduced Sensor, CEM, and Membrane costs	

One can project significant cost reductions due to advances in technology, however, further improvements are required to achieve DOE goals.



Next Steps

- Provide 2003/2004 Cost Update
- Provide program support as required

Precious Metal Availability and Cost Analysis for PEMFC Commercialization

DE-FC04-01AL67601 Topic 6.A

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley, CA

May 19-22

TIAX LLC
Acorn Park
Cambridge, Massachusetts
02140-2390

Reference: D0034

Project Team

Program Manager: Arlene Anderson
ANL Technical Advisor: Bill Cleary

TIAX Team

Primary Contact: Eric J. Carlson

Core Team:
Peter Teagan
Dr. Yueqiu Huang
Margot Noordzij

The availability and pricing of platinum group metals (PGMs) is critical to the commercialization of fuel cells.

- Critical to achieving the required levels of performance (power density and efficiency)
- In the stack, primarily platinum and some ruthenium essential to catalysis of anodic and cathodic reactions
- In the fuel processor, important for catalysis of reforming and shift reactions
- Fuel cell stack dominates the demand

PGMs also represent a significant contribution to the overall system cost.

Barriers

N. Cost (Fuel-Flexible Fuel Processor)
O. Stack Material and Manufacturing Cost

Technical Targets

	gPt/kW
Reformate Based-System	0.2

Will the successful adoption of fuel cells in transportation applications be threatened by platinum price increases and limitations in platinum supply in the long-term?

- Given various demand scenarios, can the industry keep supply and demand in balance?
  - What are the factors influencing increases in supply?
  - How fast can supply increase?
- Are resources sufficient to satisfy potential demand?
  - Recycling scenarios?
  - New ore bodies?
  - Technology developments to economically recover deeper deposits?
  - How can recycling reduce demand for primary platinum?

Project Objectives

TIAX LLC is assessing the potential impact of PEM fuel cell commercialization on platinum pricing and availability for the DOE.

- Assess current and projected demand for PGMs exclusive of fuel cell applications
- Estimate the relationships between price and supply/demand for PGMs
- Simulate the impact of fuel cell market growth scenarios on PGM supply and pricing
- Perform sensitivity analysis to critical parameters in the model related to fuel cell markets and technology advances
- Obtain critical feedback from the important participants in the PGM value chain on the model assumptions and projections
- Develop cost projections for the economics of recycling of PGMs from fuel cells and the impact on PGM supply and price

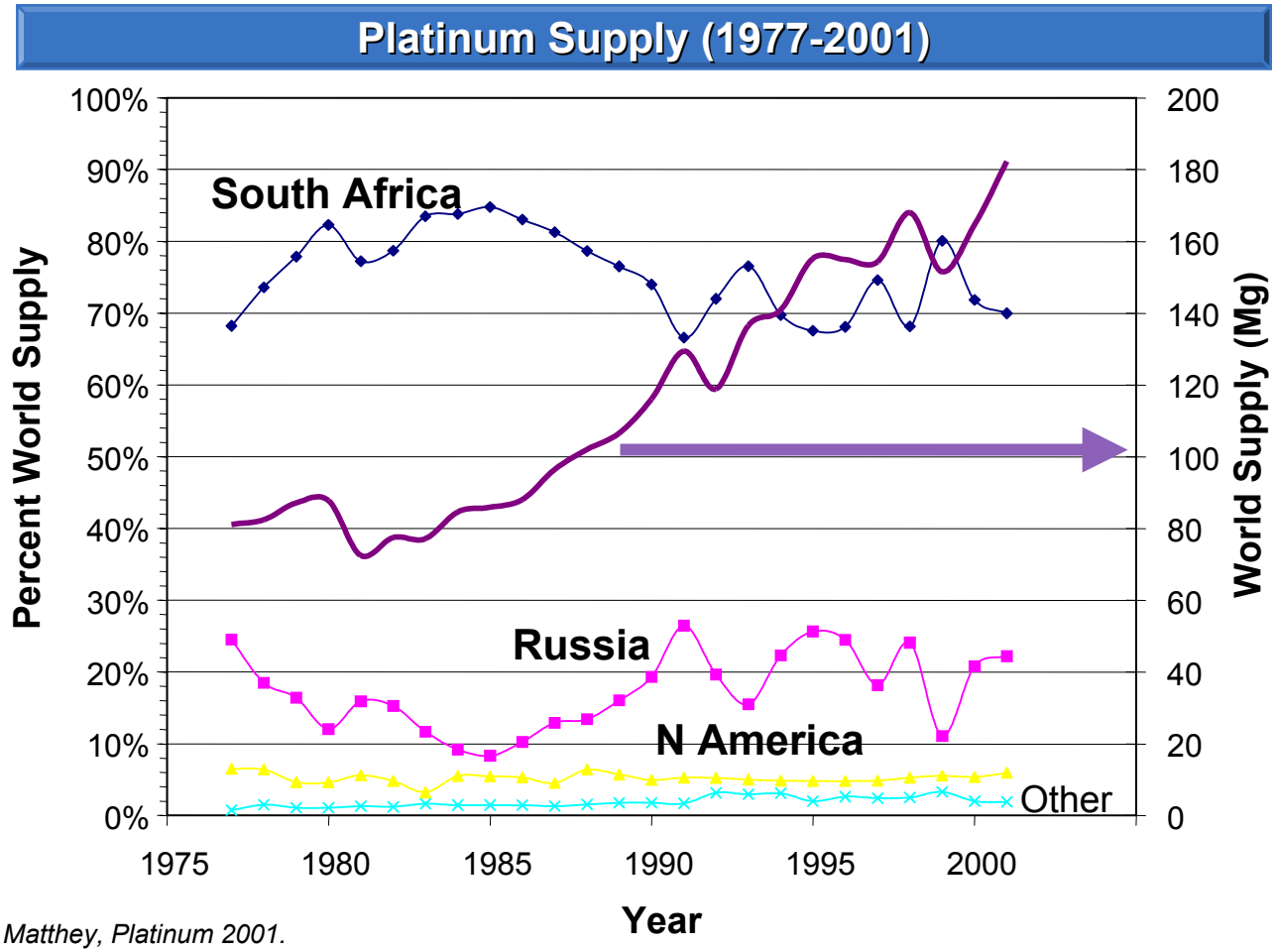
We are approximately 90% through the project and currently focussing on Task 5.

Task 1 PGM Data	*Task 2* Fuel Cell Market Projections	*Task 3* PGM Value Chain	*Task 4* Econometric Model	*Task 5* Industry Feedback
• Annual PGM Statistics: - Pricing Data - Supply Data - Demand by Application - Reserve Data	• Develop projections for stationary, transportation, and portable applications • Develop segmentation for each market • Scenario-based forecasting model	• Description of value chain (mine to market) • Recycling value chain process scenario • Development of high level PGM PEMFC recycling cost model	• Market factor assessment • Model development • Model validation • Projection of Pt supply, demand, and price for FCV commercialization scenarios	• Solicit feedback from the PGM industry and automotive OEMs • Factor feedback into the model, database, PGM market projections, and conclusions
Completed 12/02	**Results Ready for Industry Feedback**	**Results Ready for Industry Feedback**	**Historic Data Analysis Complete 12/02 Analysis of Future Scenarios Awaits Industry Feedback (May/June)**	**(May/June)**

Project Accomplishments

- Econometric analysis of historical platinum price, supply, and demand data
- Compiled platinum resource and market data
- Presented results to Johnson-Matthey and International Platinum Association (IPA) for feedback
- Developed demand scenarios and projection of platinum demand to 2050
  - Will present to South African mining companies and IPA to obtain feedback on potential supply responses, resource projections, and technology assumptions
  - Will present to automotive OEMs for feedback

South Africa's superior ore deposits have led to its domination of platinum supply.

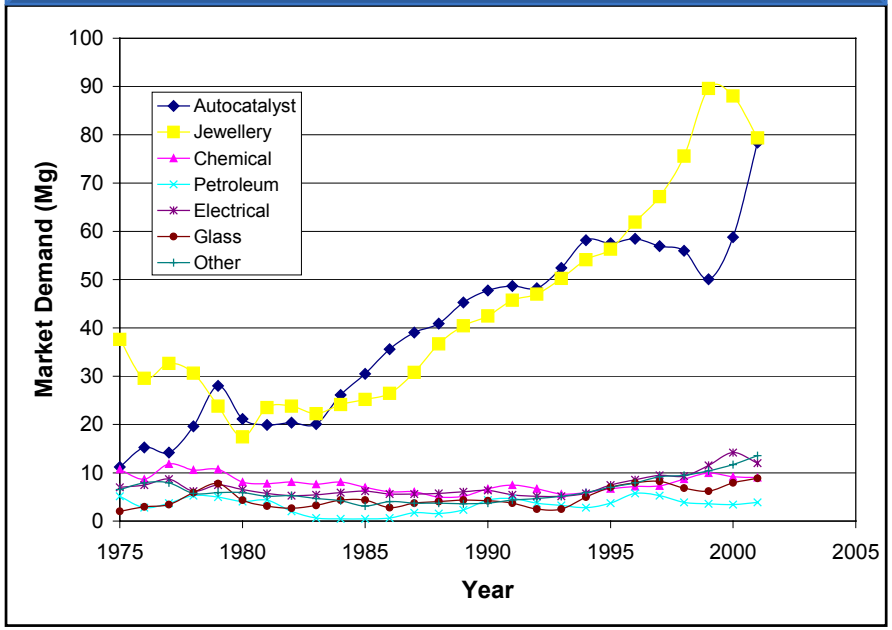


Source: Johnson Matthey, Platinum 2001.

Russian supplies fluctuated during the 1990s.

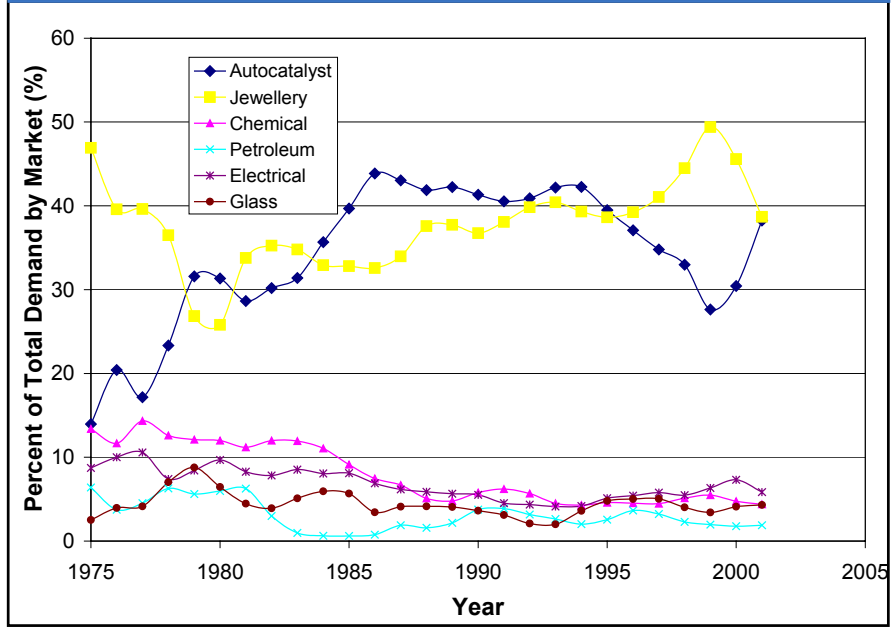
Autocatalyst and jewelry applications now dominate both market share (80%) and growth in demand for platinum.

Demand for Platinum by Application (Mg)*



Source: Johnson Matthey, Platinum 2001.

Market Share by Application (%)*



Source: Johnson Matthey, Platinum 2001.

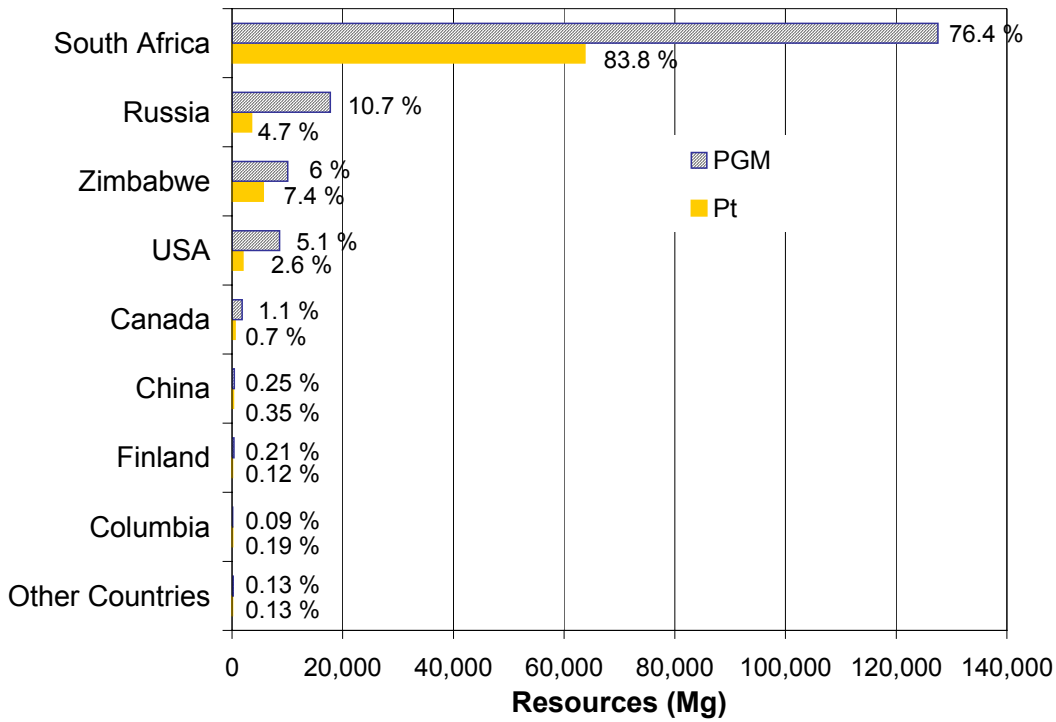
Demand from other applications including chemicals, petroleum, electronics, and glass has been relatively stable.

Resource data is reported on a geological basis and was used in our study for the assessment of potential long-term platinum availability.

- The platinum resource projection is based on geological information:
  - Significant platinum deposits are located in dense formations and can be detected by aerial magnetic surveys.
  - South African ores are located in well defined layers—the depth of these layers can be accurately estimated.
  - South African resource data is now reported to a depth of 2 km (reported resource data for gold is based on a greater depth).

Reserve data which focuses on near-term available ores, (i.e., 3-5 years), was not used to characterize future platinum availability.

In the long run stable prices will depend on the amount of economically recoverable platinum resources relative to cumulative demand.

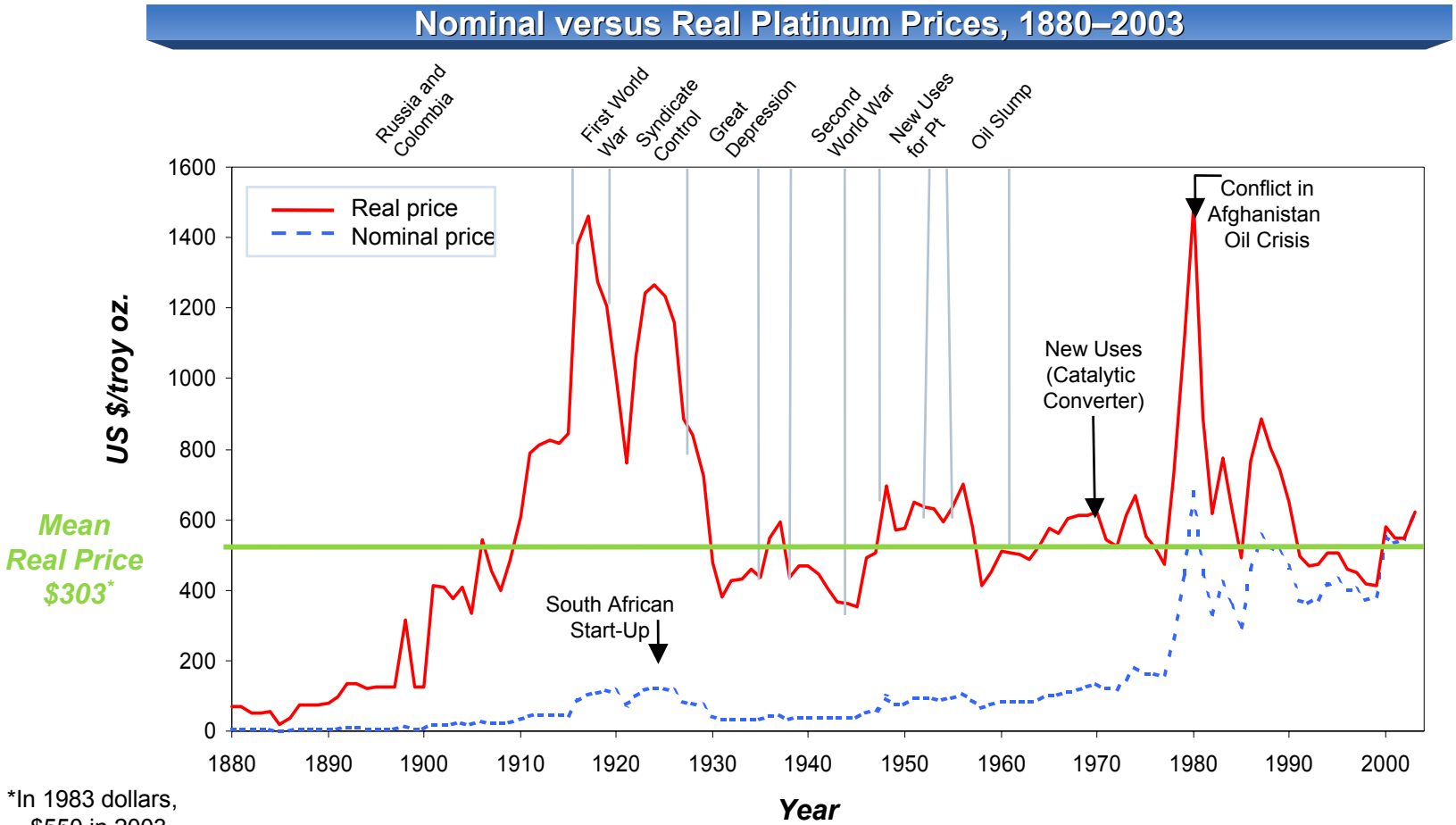


Compiled from a variety of sources, including Cawthorn, Vermaak, Page, Mining Weekly, and Stribyn

Total Platinum Resource: 76,000 Mg

@ 30 grams per vehicle equals 2.8 billion vehicles

Statistical tests have shown that historically, real prices have remained at a constant level.



*In 1983 dollars, $550 in 2003 dollars

Data Sources: U.S. Geological Survey, Vermaak, C.F., *"The Platinum-Group Metals,"* pp. 110

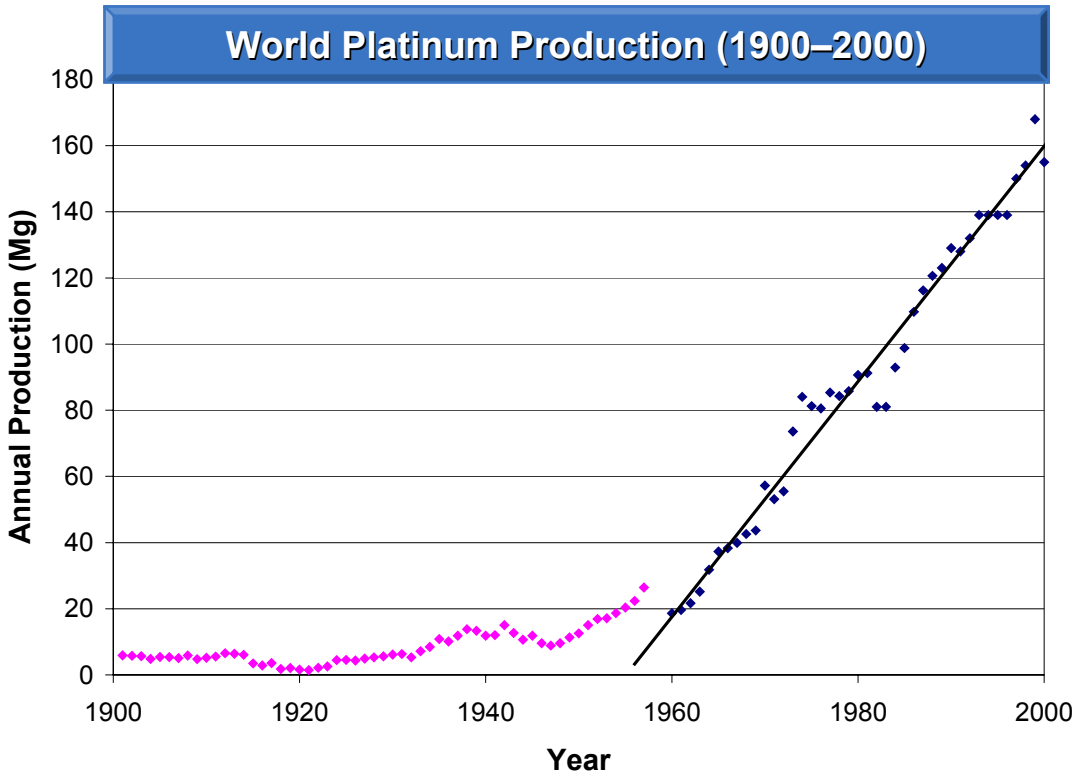
Our statistical tests support a stationary real platinum price over the last century- particularly since South African supply started.

- Interviews with Englehard and Johnson Matthey confirmed our tests and observation of a stationary real platinum price: it is in the best interest of mines to maintain a stable price to prevent end users from substituting other metals for platinum and ultimately destroying the platinum market.

Test	Finding	
Visual Inspection	• The real price of platinum appears constant (i.e., there is no trend). • The price spiked during WW I (due to military demand for platinum), introduction of catalytic converters for cars, and the oil crisis. • Following each spike, the real price returned to its long-run mean.	
Slade's Hypothesis	• The results for platinum are quite different from those found by Slade for other commodities. There is no evidence of a U-shaped pattern and virtually no support for an upward trend in real platinum price.	
Stationarity Test	• 1880–1998	Not conclusive about stationarity of real platinum price series
	• 1910-1998	Some support that platinum real price is stationary
	• 1925–1998	Strong evidence that platinum real price is stationary

Steadily increasing supply since the 1950s, i.e. at approximately 3.5 Mg per year, has been critical to price stability.

- In anticipation of the introduction of catalytic converters in the 1970s in the United States and the 1980s in Europe, South Africa mines expanded production to meet demand.
- In 1980-1990s, South African mines continued to increase supply to meet increasing demand for platinum jewelry from Japan and China.



Data Sources: 1901-1957 Die Metallischen Rohstoffe Heinrich Quiring, pp 98-99
1963 -1983 Mineral Facts and Problems, U.S. Bureau of Mines
1986-2000 Mineral Yearbook, U.S. Geological Survey

Based on this analysis, we have several key expectations for the impact of fuel cell commercialization on platinum pricing:

Shorter Timeframes

Over short periods, prices can be volatile—increasing with the introduction of fuel cell technology or other spikes in demand.

"Longer" Timeframe

The real platinum price will tend to return to its long-term mean as additional supply and material substitution combine to restore prices.

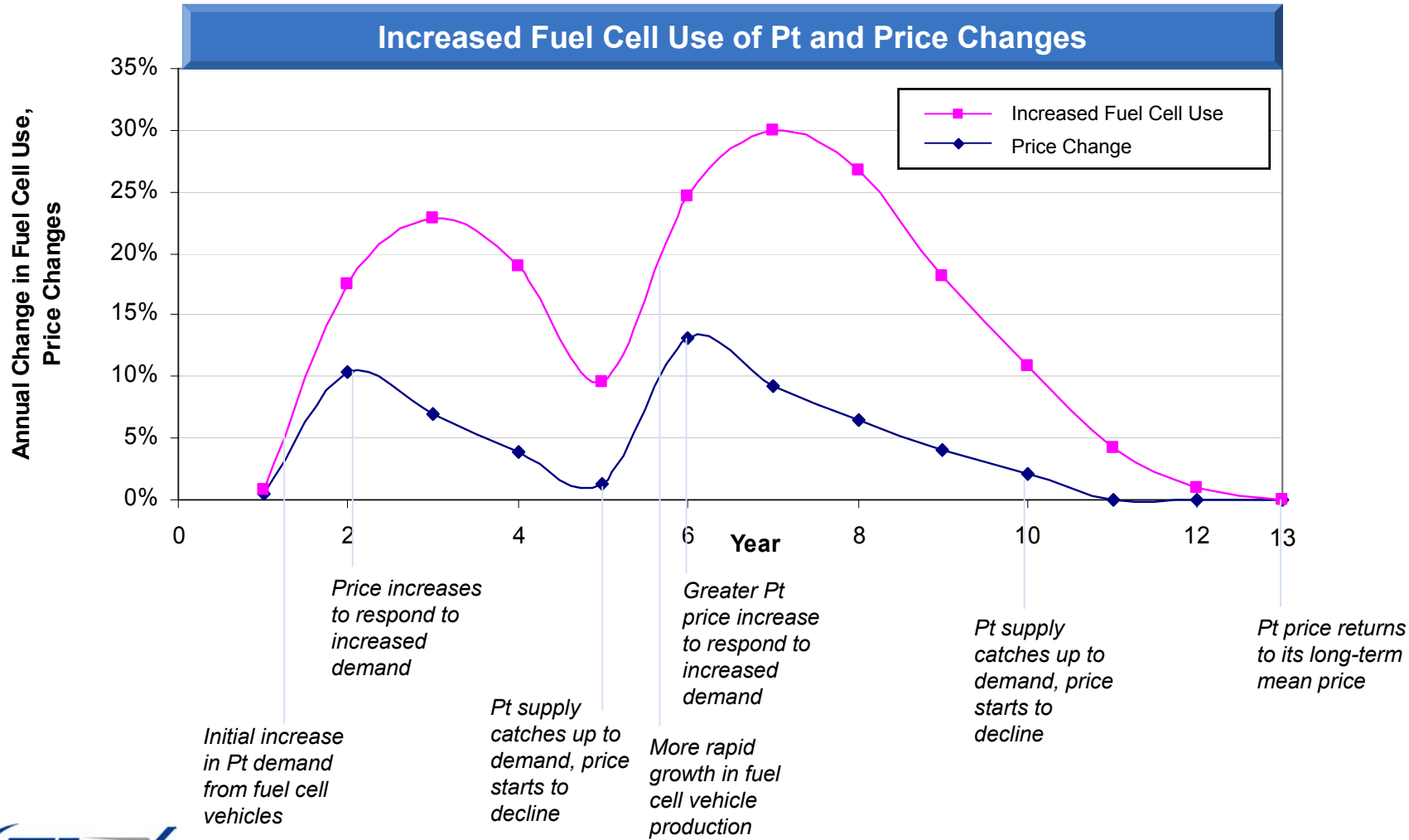
While anticipated fuel cell demand for platinum may drive higher platinum prices in the short-run, the price will likely return to its long-term mean.

An increase in demand for platinum from fuel cell technology will increase the platinum price in the short-run.

- Based on the estimated parameters from our econometric models of platinum supply and demand and information from automobile industry, we simulated the impact of an increased platinum demand from fuel cell technology on the short-run platinum prices.

Year of fuel cell vehicles introduced	Fuel cell vehicle production (million)	Pt demand (g)/vehicle	Fuel cell use of Pt (millions Troy oz)	Increased fuel cell use of Pt in total Pt consumption	Pt price changes
1	0.01	100	0.03215	0.50%	0.81%
2	0.25	88	0.7034	10.35%	17.46%
3	0.50	75	1.206	7.02%	22.89%
4	0.75	63	1.507	3.94%	18.90%
5	1.00	50	1.608	1.26%	9.63%
6	1.80	46	2.662	13.09%	24.61%
7	2.60	42	3.511	9.32%	29.94%
8	3.40	38	4.154	6.46%	26.78%
9	4.20	34	4.592	4.12%	18.10%
10	5.00	30	4.823	2.10%	10.92%
11	5.00	30	4.823	0.00%	4.21%
12	5.00	30	4.823	0.00%	0.99%
13	5.00	30	4.823	0.00%	0.00%

An increase in demand for platinum from fuel cell vehicles will increase the platinum price in the short-run (continued).



We have developed vehicle sales estimates based on projected population growth and different vehicle per capita scenarios, but will report these results after we have obtained feedback from industry.

Population Projection

- UN Forecast for
  - United States
  - Europe
  - Japan
  - China
  - India

Total Vehicle Forecast

- Replacement factor
- New demand
- Vehicle per capita trends
  - US maximum
  - Versus GDP

Fuel Cell Vehicle Projection

- Use diffusion model to simulate market penetration
- Define Scenarios
  - Commercialization start date
  - Time to rapid growth
  - Ultimate market penetration
  - Pick delay between developed and developing countries
- IC vehicle market by difference

Fuel Cell and IC Powertrain Pt Requirements

- Fuel Cell - g Pt/kW
- IC vehicle - grams per vehicle
- Timeframe

Pt Demand vs Time

Next Steps

- Incorporate information and feedback from International Platinum Association (visit to South Africa) into our assessment
  - May
- Present assessment to automobile companies and incorporate their comments
  - June
- Reporting (June/July)
  - Prepare draft final report and supporting appendices for review by concerned parties
  - Prepare Final Report

During our visit, we would like to obtain feedback on preliminary findings and receive critical inputs on supply and resources.

- Discuss project findings to-date with the mining companies
- Develop improved understanding of production processes for platinum group metals
- Obtain platinum industry inputs on supply responses to potential demand scenarios
- Obtain industry inputs on the projection of PGM resources

DFMA Cost Estimates of Fuel-Cell/Reformer Systems at Low/Medium/High Production Rates

Brian D. James, Greg D. Ariff, Reed C. Kuhn, Duane B. Myers

2003 Hydrogen and Fuel Cells Annual Merit Review Meeting
Berkeley, California
20 May 2003

Directed Technologies, Inc.
3601 Wilson Blvd, Suite 650
Arlington, VA 22201
(703) 243-3383 voice
(703) 243-2724 fax

DIRECTED TECHNOLOGIES INC.

Project Relevance/Objective

Freedom Car Technical Barriers Addressed:

Fuel Flexible Processors Technical Barriers

N: Cost ←

Component Technical Barriers

O: Stack Materials and Manufacturing Cost ←

Objective:

Prepare technology-based cost estimates of complete fuel cell-reformer systems at low/medium/high manufacturing rates to assess the current status and identify the most pressing cost barriers.

Project Approach

1. **Prepare designs of complete automotive FC power systems:**
   - Onboard gasoline fuel processor and PEM fuel cell system
   - Direct hydrogen fuel cell system (with 5kpsi H_2 storage)

2. **Determine costs for system production rates using DFMA* methodology:**
   - DFMA= Design for Manufacturing & Assembly
   - 500/10,000/30,000/500,000 vehicles per year

3. **Consider Current Year Technology** (i.e. no dramatic forward projections)

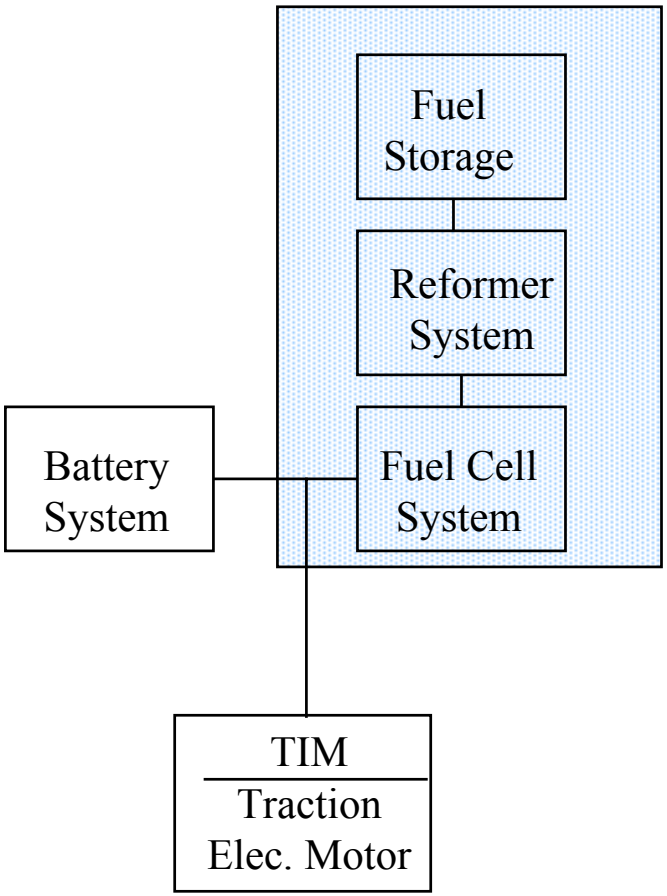
4. **Perform Annual Cost Updates**

5. **Conduct Investigations on Selected Topics**

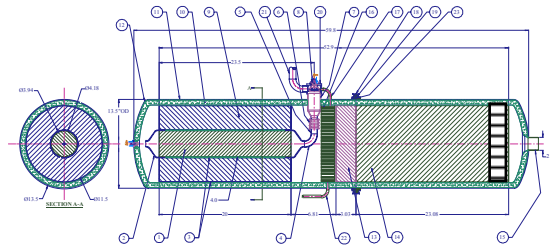
* DFMA is a registered trademark of Boothroyd Dewhurst Inc.

DIRECTED TECHNOLOGIES INC.

Scope of Project



What is included in Project:



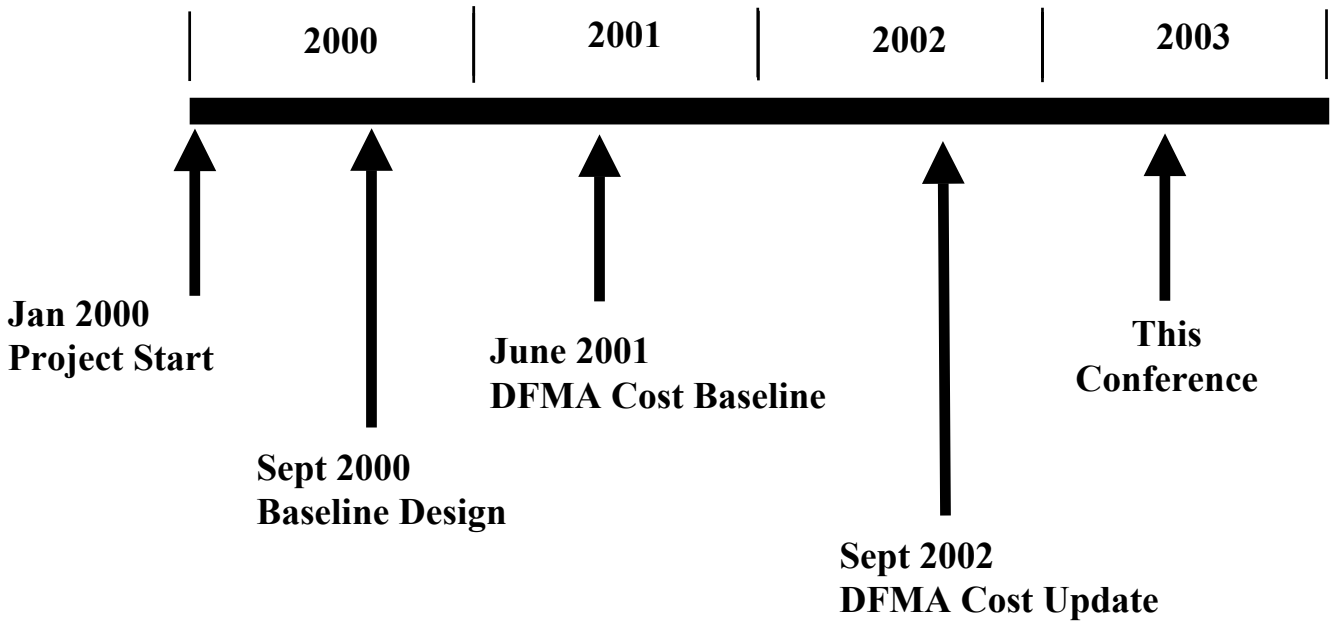
- Reformer
  - Fuel vaporizer
  - Burner
  - Reformer
  - Shift beds
  - Gas cleanup
- Fuel Cell System
  - Fuel cell stacks
  - Air supply and humidification
  - Thermal management
  - Water management
- Fuel Supply System
- Power conditioning and electronics (for FC/Ref. Only)
- Electrical System
- Control System
- Sensors
- Safety Systems

What is <u>not</u> included in Project:

- Traction Inverter Module (TIM)
- Traction Electric Motor
- Peak-Power/Start-Up Battery

DIRECTED TECHNOLOGIES INC.

Project Timeline



Presentations/Reports

July 2001 OATT Report
Sept 2001 Program Review Presen.
June 2002 OATT Report

August 2002 SAE Future Car Congress Presentation
Sept 2002 FreedomCar FC Tech Team Presentation
March 2003 SAE Congress Presentation

DIRECTED TECHNOLOGIES INC.

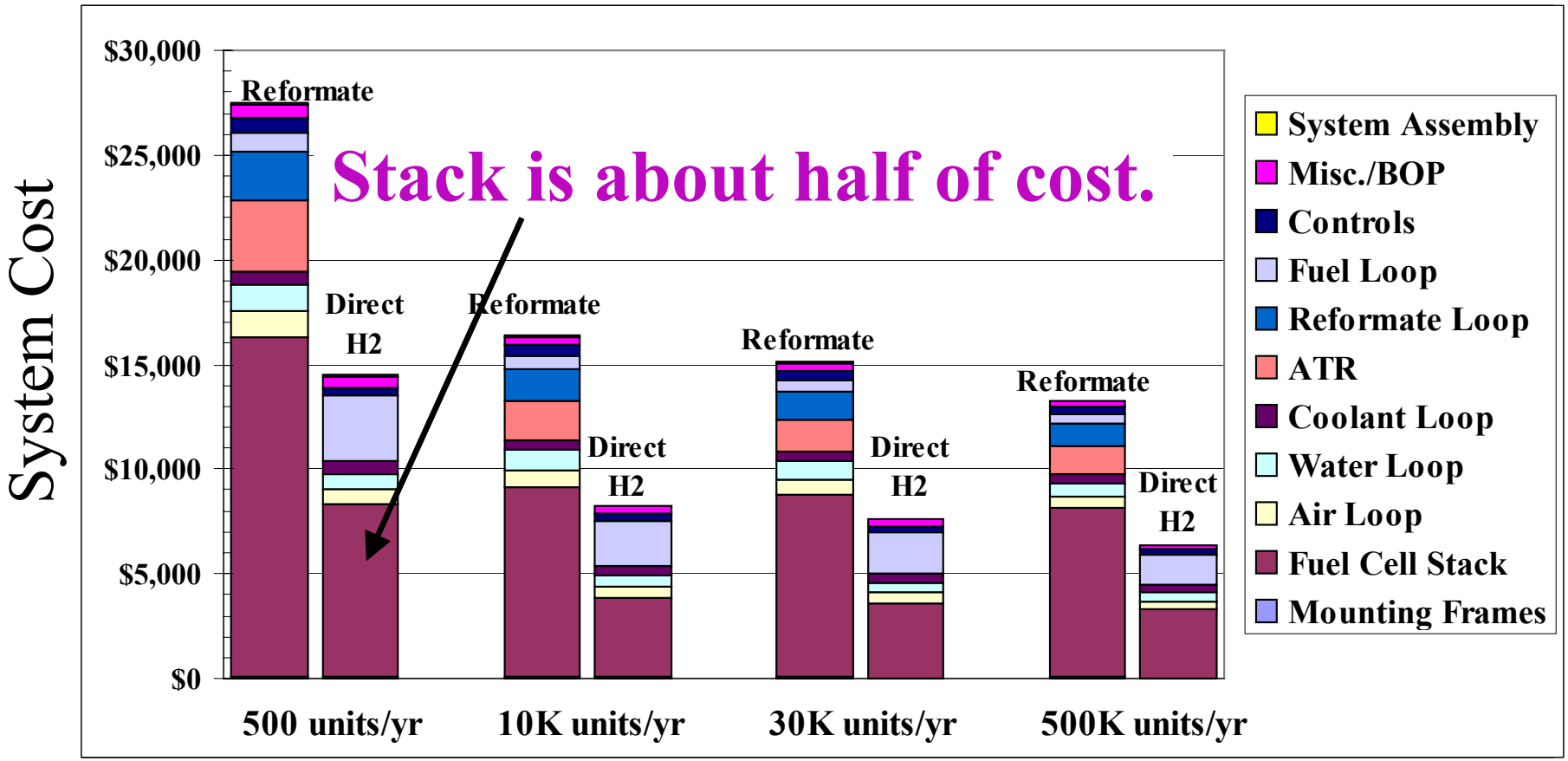
Accomplishments/Progress

- **2002 DFMA System costing update**
- **Sensitivity Analysis of Power Density and Material Costs**
- **Microchannel reformers & HX to reduce cost- In Progress**
- **Generation of "Roadmap to Lower System Cost"- In Progress**

System Comparison

Reformate System vs. Direct H_2 System

(both at 0.7volts/cell)

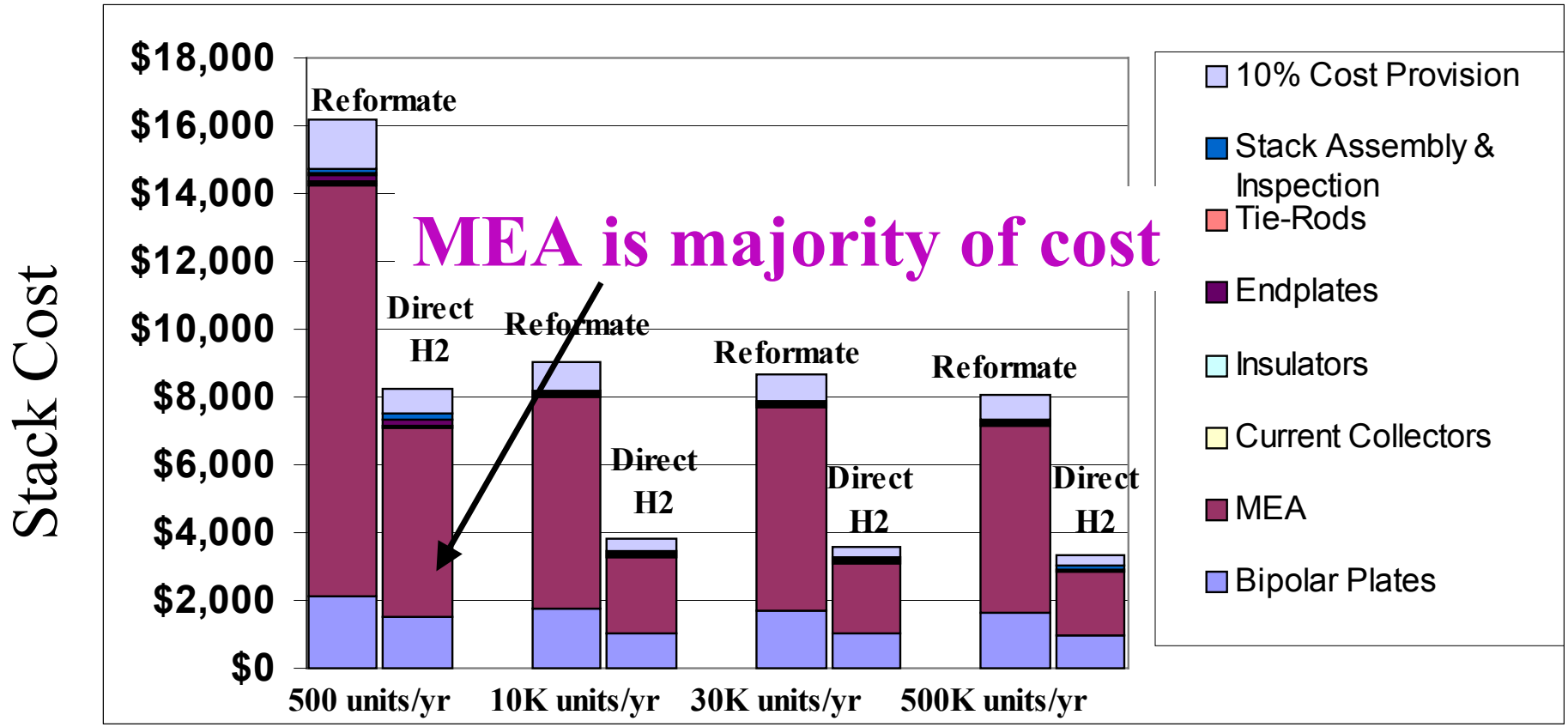


DIRECTED TECHNOLOGIES INC.

Stack Comparison

Reformate System vs. Direct H_2 System

(both at 0.7volts/cell)

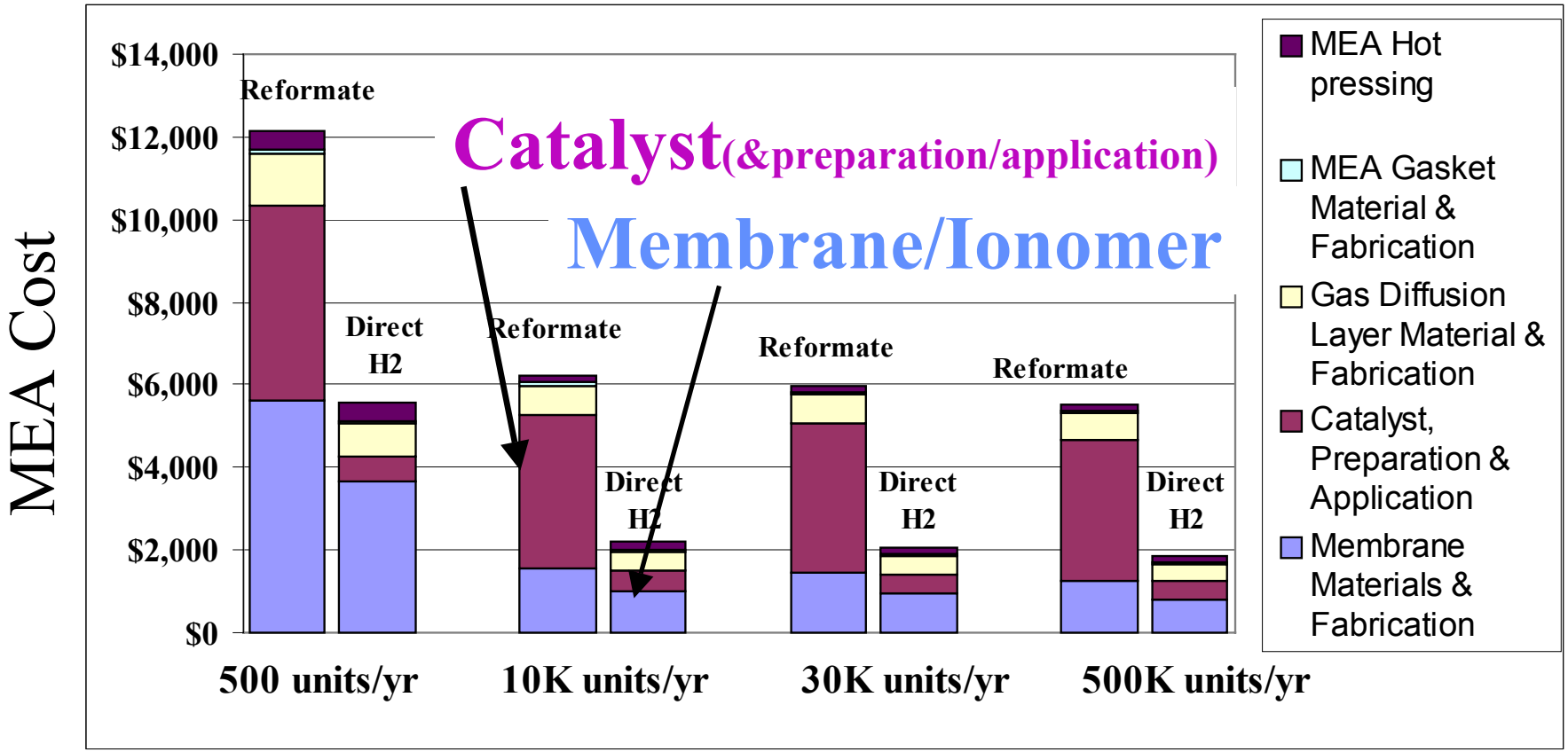


DIRECTED TECHNOLOGIES INC.

MEA Comparison

Reformate System vs. Direct H2 System

(both at 0.7volts/cell)



DIRECTED TECHNOLOGIES INC.

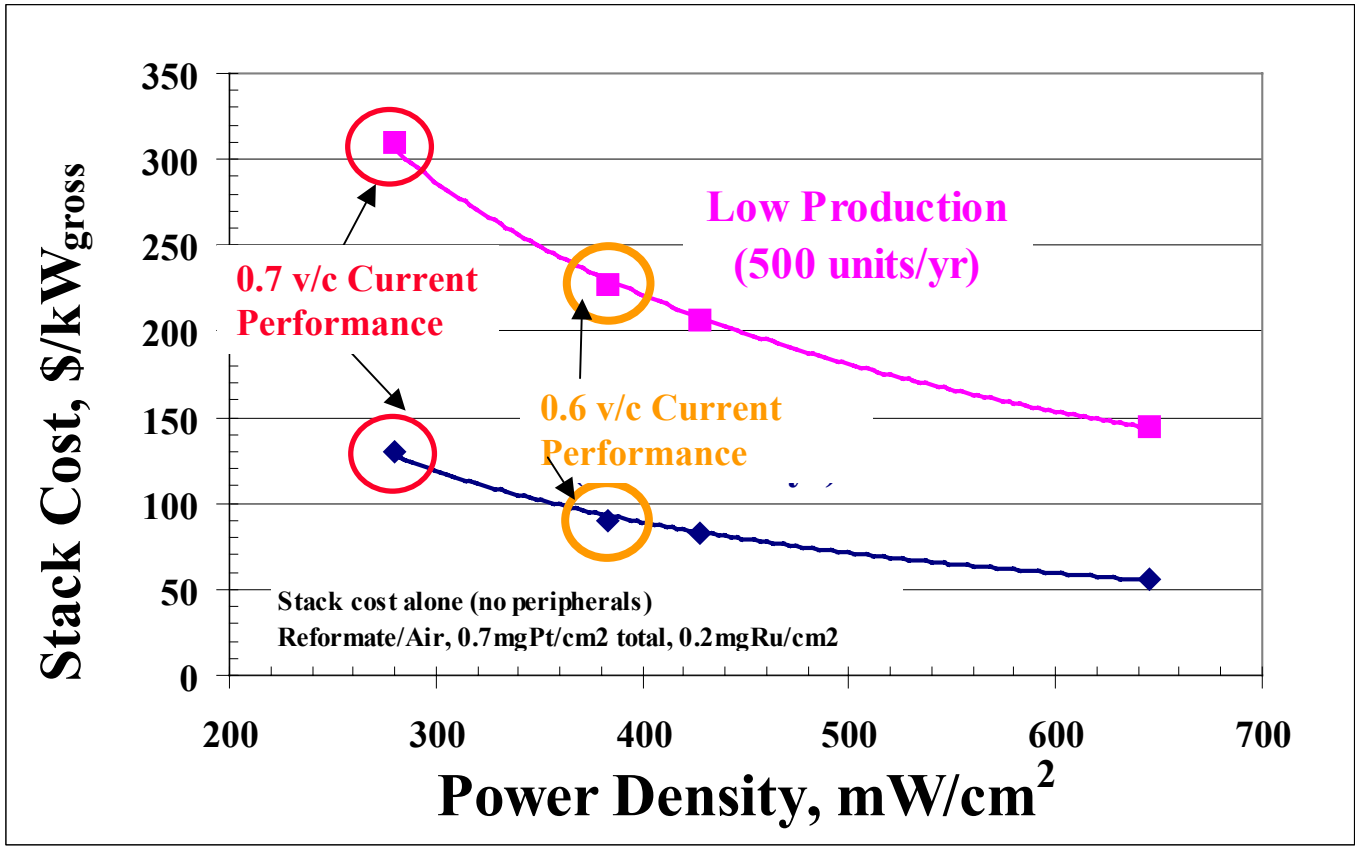
Technical Target Comparison

		FC-Reformer on Tier 2 Gasoline				Direct Hydrogen			
			DOE Technical Targets				DOE Technical Targets		
		DTI 2002 Estimates	2003 Status	2005	2010	DTI 2002 Estimates	2003 Status	2005	2010
Fuel Cell Stack includes stack peripherals	$/kW$_{net}$	$193	$200	$100	$35	$88	-	-	-
Reformer System includes reformer peripherals	$/kW$_{net}$	$65	$65	$25	$10	-	-	-	-
Total System includes final assembly, BOP	$/kW$_{net}$	$266	$300	$125	$45	$157	$200	$125	$45
							includes hydrogen storage		

- **50kW$_{net}$ Systems at 500,000 units per year production volume.**

DIRECTED TECHNOLOGIES INC.

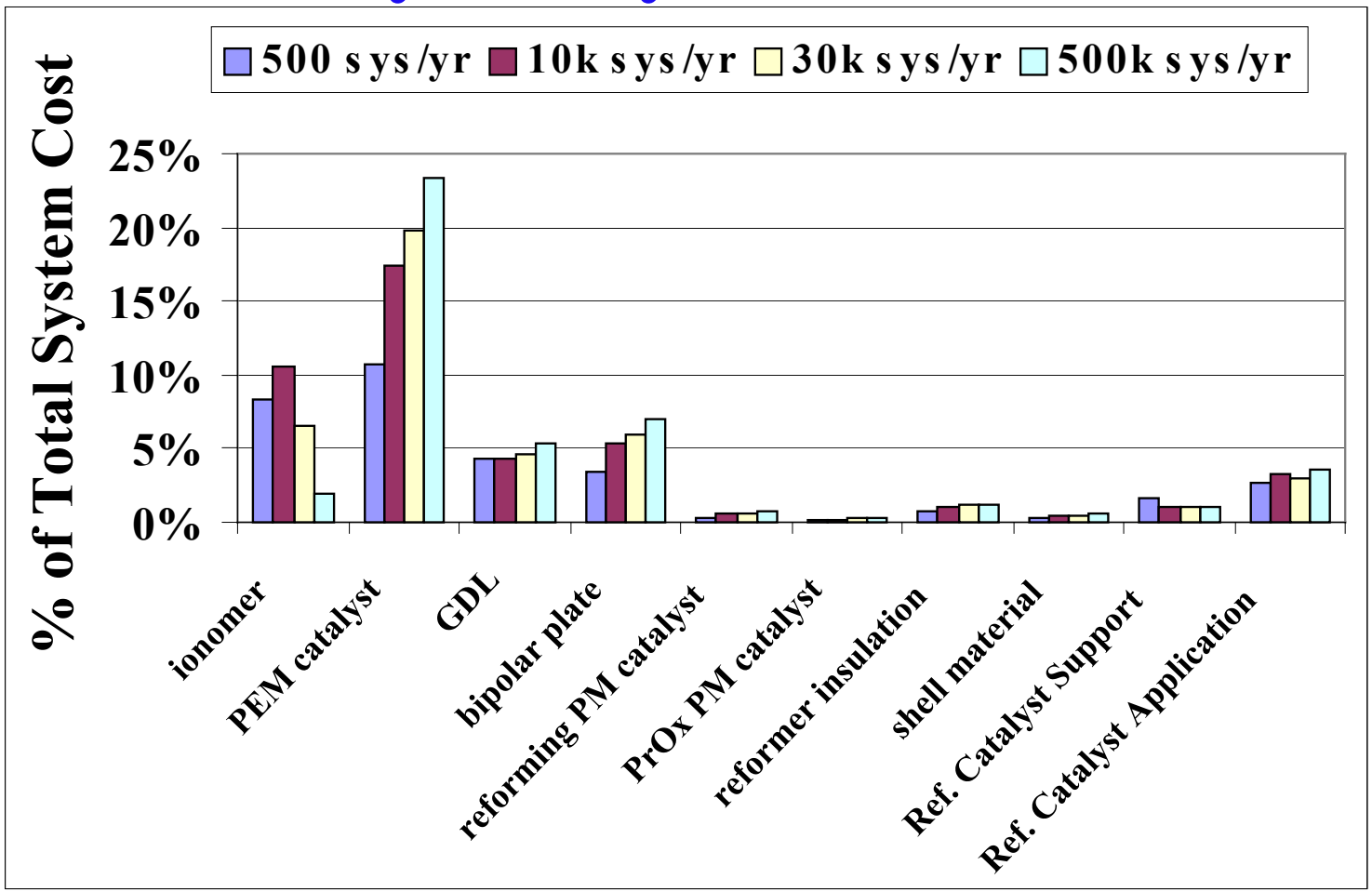
Sensitivity Analysis- Stack Power Density



- Stack resized to maintain constant power
- Stack scaling only slightly off linear
- Power density increase best way to decrease stack cost

DIRECTED TECHNOLOGIES INC.

Sensitivity Analysis- Material Cost



- PEM catalyst cost becomes large cost fraction
- Ionomer cost becomes a lesser cost fraction
- Reformate catalyst cost appears not to be significant

DIRECTED TECHNOLOGIES INC.

Microchannel Heat Exchangers and Reactors

- **Technology Description**
  - Flow channels with a characteristic dimension of <1 mm
  - High specific heat transfer area
  - Scalable manufacturing processes

- **Why are we considering microchannel components for the fuel processor?** ***Potential for significant improvements over conventional technology***
  - Mass--*Weight reduction could benefit entire system*
  - Volume--*Microchannel architecture allows dense construction*
  - Cost--*Mass manufacturability is possible*

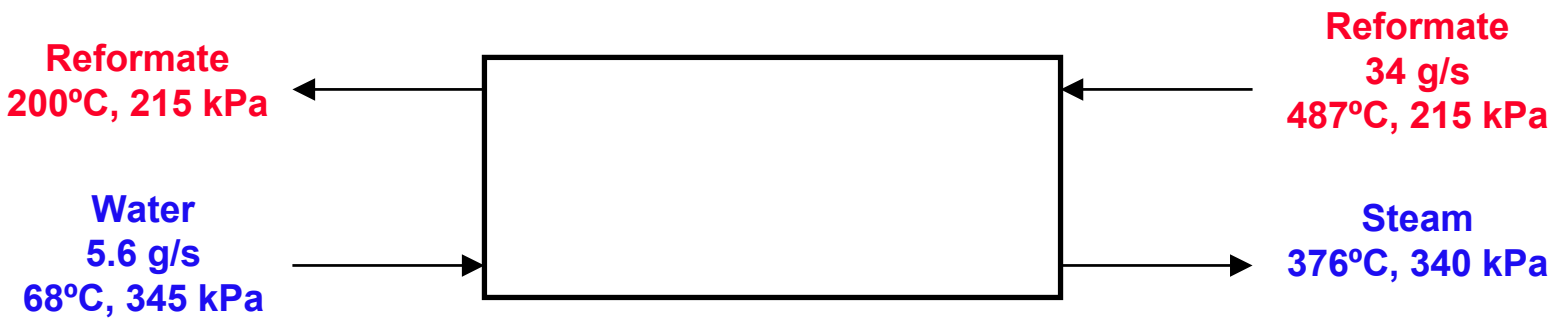
- **Options for microchannel design in fuel processor**
  - Heat exchanger only: *Water vaporizer/boiler*
  - Reactor only: *ATR/SR, WGS*
  - HEX/Reactor: *PROX*

Microchannel Patent Resources

Organization	Patent(s)	Technology
PNNL	6,200,536 6,503,298 5,811,062 6,352,577	Active microchannel heat exchanger; Hydrogen separation/purification utilizing rapidly cycled thermal swing sorption; Microcomponent chemical process sheet architecture; Microchannel laminated mass exchanger
PNNL pending	Applications 20020194990 20020114762 20030072699	Method and apparatus for thermal swing adsorption and thermally-enhanced pressure swing adsorption (Wegeng); Catalysts, reactors and methods of producing hydrogen via the water-gas shift reaction (Tonkovich); Integrated reactors, methods of conducting simultaneous exothermic and endothermic reactions (Tonkovich)
Precision Combustion	6,394,791	Method and apparatus for a fuel-rich catalytic reactor

*InnovaTek is developing microchannel reformers but has not patented the microchannel aspects.

Microchannel Water Vaporizer:
Heat Exchange



- Current design is a finned tube
- Microchannel vaporizer design criteria
  - Reformate ΔP <1 kPa
  - Considered to be a stand-alone component (i.e., it was not designed to fit into the Baseline fuel processor)
  - Size based on film coefficient calculations for reformate and water, with 5% design allowance

DIRECTED TECHNOLOGIES INC.

Water Vaporizer Summary

Heat Duty 16.6 kW

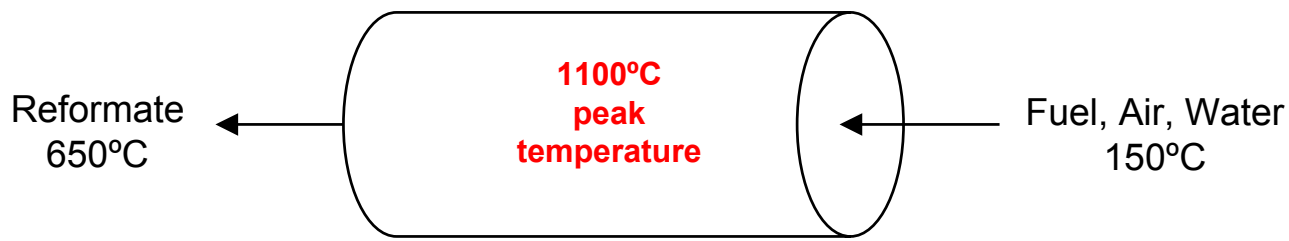
	Heat Transfer Area (cm^2)	Volume (cm^3)	Heat Transfer Coefficient (W/m^2-ºC)	Mass (grams)	Cost
Existing Finned-Tube Design	15,600	707	91	2,588	$613 (500/yr); $151 (500k/yr)
Microchannel Design (core only)	6,775	171	359	537	in progress
Microchannel Design (system)	--	669	--	905	in progress

- Microchannel heat exchanger provides mass advantage over finned-tube exchanger
- When system integration components are added, volume advantage of microchannels is slight

DIRECTED TECHNOLOGIES INC.

Autothermal Reformer:

Reaction



- Current design is a washcoated monolith
  - Monolith has some attributes of microchannel (~1 mm channels) but lacks the heat exchange capability
  - Washcoat does not appear to be diffusion limited ⇒ pores account for only ~10% of resistance to diffusion
- ATR temperatures are prohibitively high for microchannel construction
  - Corrosion allowance (5,000 hours, 980ºC) for the most oxidation resistant alloys is ~75 μm per side, or 150 μm total (Inconel 601 is 375 μm per side)
  - PNNL patent examples at <750ºC use 125 μm plates
- *Adiabatic reactions are not a good application for microchannel components*

DIRECTED TECHNOLOGIES INC.

Microchannel Summary & Future Tasks

- Largest gains will be for integrated systems- not discreet component substitutions (baseline design already integrated)
- The water vaporizer could realize mass reduction if it were changed to microchannel configuration
  - 0.9 kg for microchannel vs. 2.6 kg for finned tube
  - *Action item: Calculate cost for mass manufacturing of vaporizer*
- Adiabatic operations (ATR and WGS) would have little or no advantage as microchannels
  - *Action item: Examine WGS with integrated heat transfer—may eliminate one of the WGS stages*
- *Action Item: Consider PROX with integrated reaction/heat exchange*
  - Mass in current design ~7 kg
  - Cost in current design $505 @ 500/year, $175 @ 500,000/year

Plans & Future Milestones

Remainder of 2003

- **2003 DFMA System costing update**
  - Updates to cell performance, catalyst loading, ionomer cost
- **Complete Analysis of Microchannel reactors to reduce cost**
  - component replacement
  - complete microchannel system
  - investigate onboard steam reforming
- **Complete "Roadmap to Lower Cost"**
  - focus on reformer redesign/simplification
  - stack power density
- **Gas Separation for Enhanced Stack Performance**
  - compact Pressure Swing Adsorption (PSA)
  - compact Thermal Swing Adsorption (TSA)

Plans & Future Milestones

2004

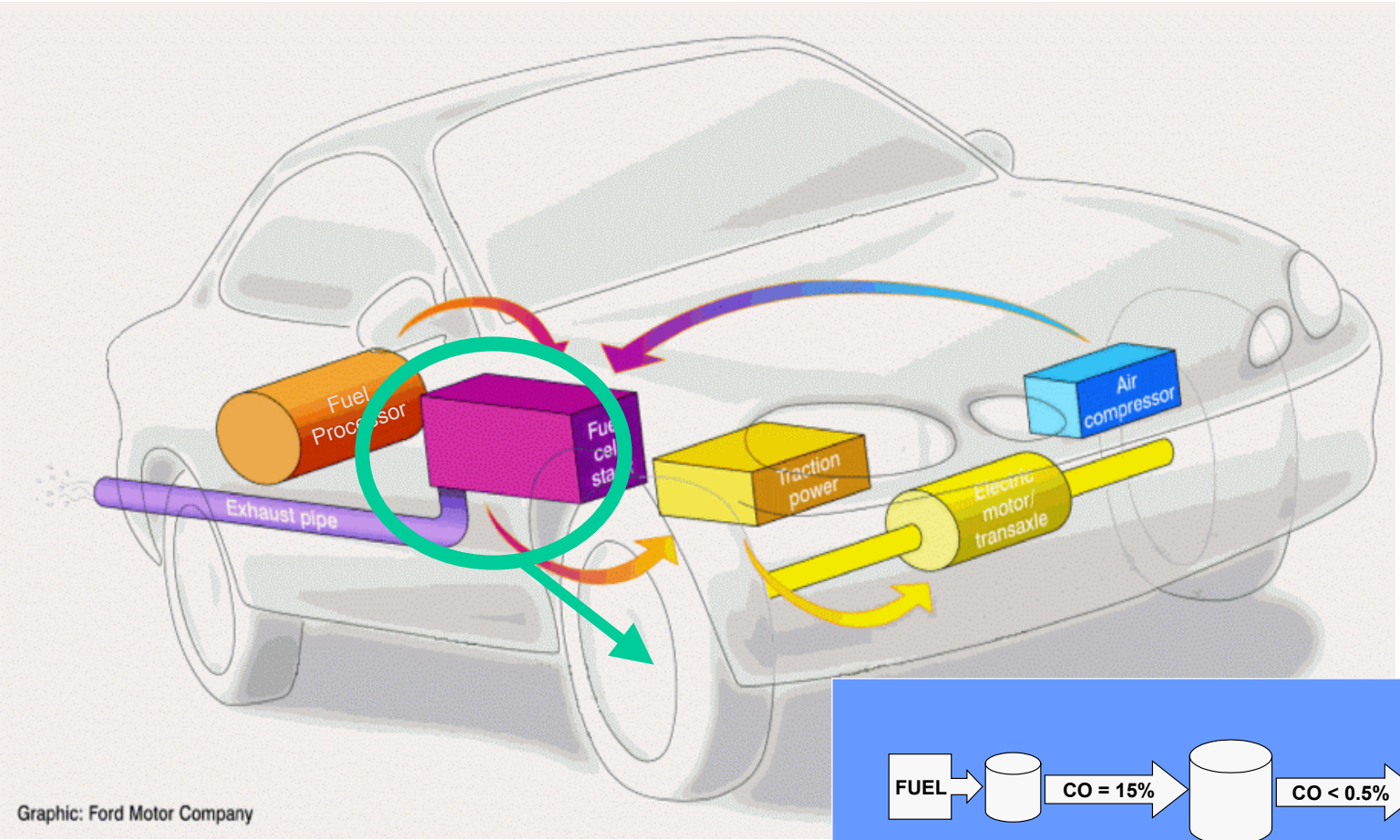
- **Ambient vs. Pressurized Operation Analysis**
- **High Temperature Operation Analysis**
- **Hydrogen Membrane Purification Analysis**
- **Alternate PEM Fuel Cell Approaches**
  - Alternate stack construtuion
  - Fuel Cell Pulsing
  - Alternate Air Compression Approaches

Collaboration/Interactions

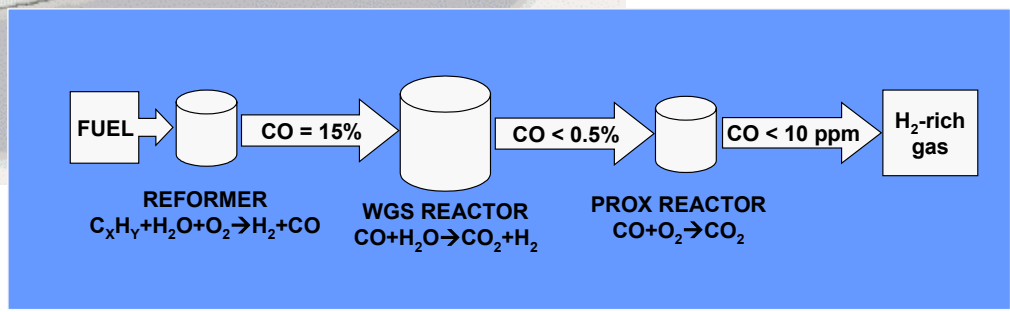
- **Argonne National Lab - reactor design parameters/space velocities**
- **Oak Ridge National Lab - reactor design**
- **PNNL - microchannel performance & design**

- **W.L. Gore & Associates - catalyst loading/FC performance**
- **DuPont - catalyst loading/FC performance**

Fuel Processing



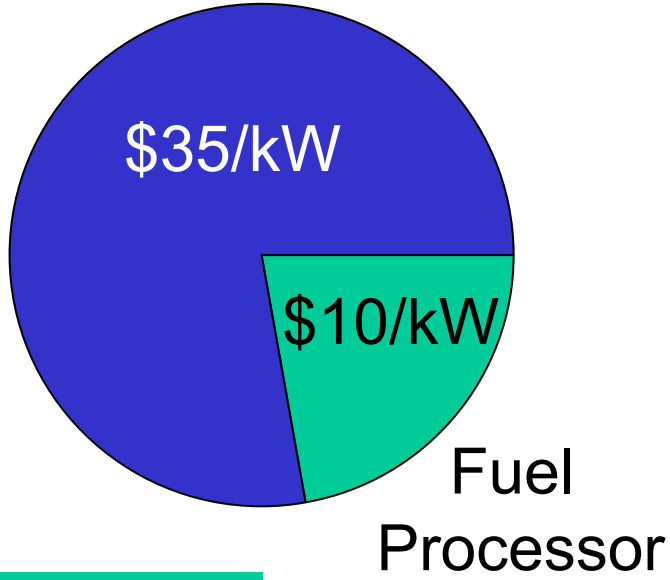
Graphic: Ford Motor Company



Valri Lightner

On-Board Fuel Processing Barriers

Fuel Cell Power Systems
$45/kW by 2010



BARRIERS

- Fuel processor start-up/ transient operation
- Durability
- Cost
- Emissions and environmental issues
- H_2 purification/CO cleanup
- Fuel processor system integration and efficiency

On-Board Targets and Status

Fuel Processor for 50 kWe (net) Fuel Cell Systems

Fuel processor generating hydrogen-containing fuel gas from reformulated gasoline containing 30 ppm sulfur, average

Characteristics	Units	2003 status	2005	2010
Energy efficiency	%	78	78	80
Power density	W/L	700	700	800
Cost	$/kW	65	25	10
Durability	Hours	2000	4000	5000
Cold start-up time to max power @ +20ºC ambient temp.	Min	<10	<1	<0.5

Fuel Processing Posters

• Fuel Processing of Diesel Fuel for APUs	NETL
• Sulfur Removal from Reformate	ANL
• Evaluation of Partial Oxidation Fuel Cell Reformer Emissions	TIAX, LLC
• Diesel Reforming	ANL
• Fast Start Reformer Components	LANL, ORNL, and PNNL
• Selective Catalytic Oxidation of Hydrogen Sulfide	ORNL

Discussion Points

- Go/No-Go review in late 2004 to determine the future course of on-board vehicle fuel processing activities. Review will focus on ability to meet <0.5 minute start up time to minimize the energy penalty and other critical technical target.
- Emphasis on stationary reforming, auxiliary power, and improved water gas shift catalysts.

Fuel Processing Projects

• Water-Gas Shift Catalysis	ANL
• Catalysts for Autothermal Reforming	ANL
• Water-Gas-Shift Membrane Reactor	Ohio State University
• Hydrogen Enhancement	UTRC

Fuel Processing Projects
Continued

• Advanced High Efficiency Quick Start Fuel Processor for Transportation Applications	Nuvera Fuel Cells, Inc.
• Fuel Cell Distributed Power Package Unit: Fuel Processing Based on Autothermal Cyclic Reforming	GE
• Plate-Based Fuel Processing System	Catalytica
• Quick-Start Fuel Processor	ANL
• Microchannel Steam Reformation of Hydrogen	PNNL
• Fuel Processors for PEM Fuel Cells	University of Michigan

Water-gas shift catalysis

Sara Yu Choung, John Krebs, Magali Ferrandon,
Razima Souleimanova, Deborah Myers,
and Theodore Krause

Chemical Engineering Division
Argonne National Laboratory

Hydrogen, Fuel Cells, and
Infrastructure Technologies
2003 Merit Review
Berkeley, CA
May 19-22, 2003

Objective is to develop water-gas shift catalysts for on-board fuel processing

- Meet the DOE technical targets of
  - ✓ gas-hourly space velocity (GHSV) ≥ 30,000 h^{-1}
  - ✓ CO conversion of ≥ 90%
  - ✓ selectivity of ≥ 99%
  - ✓ lifetime of > 5000 h
  - ✓ cost of <\$1/kW_e
- Address issues with commercial CuZn catalysts
  - ✓ Eliminate the need for well-controlled *in situ* preactivation
  - ✓ Improve tolerance to temperature excursions
  - ✓ Eliminate the need to sequester during shutdown

This work addresses technical barriers J, L, and N.

Approach

- Explore metal/support combinations that exhibit the bifunctional mechanism.

$* + CO \rightleftharpoons *\text{-}CO_{ad}$ — * = metal surface site, adsorbs CO

$2MO_2 + *\text{-}CO_{ad} \rightleftharpoons M_2O_3 + CO_2 + *$ — oxidation of CO via oxygen transfer from support

$M_2O_3 + H_2O \rightleftharpoons 2MO_2 + H_2$ — reoxidation of support via dissociation of water

- Metals (Pt, Ru, Co, Cu) that have CO adsorption energies between 20-50 kcal/mol.
- Metal oxides that exhibit redox activity under WGS reaction conditions.

Industrial collaborations/interactions

- Work For Others (WFO) contract with Toyota Motor Corporation to develop WGS catalysts.

- Cu/oxide and Pt/mixed oxide samples are being evaluated by
  - ✓ Nissan Motor Corporation
  - ✓ Aspen Systems
  - ✓ H2Gen Innovations

Reviewers' comments from FY2002 Annual Review

- Activities too low to meet DOE target for GHSV.

  Increased the activity of our Pt catalyst with a bimetallic formulation.

- More emphasis on deactivation is needed.

  Investigated the effects of temperature, H_2S, and CO_2 on the rate of deactivation of our Pt catalyst resulting in decreased deactivation with a bimetallic formulation.

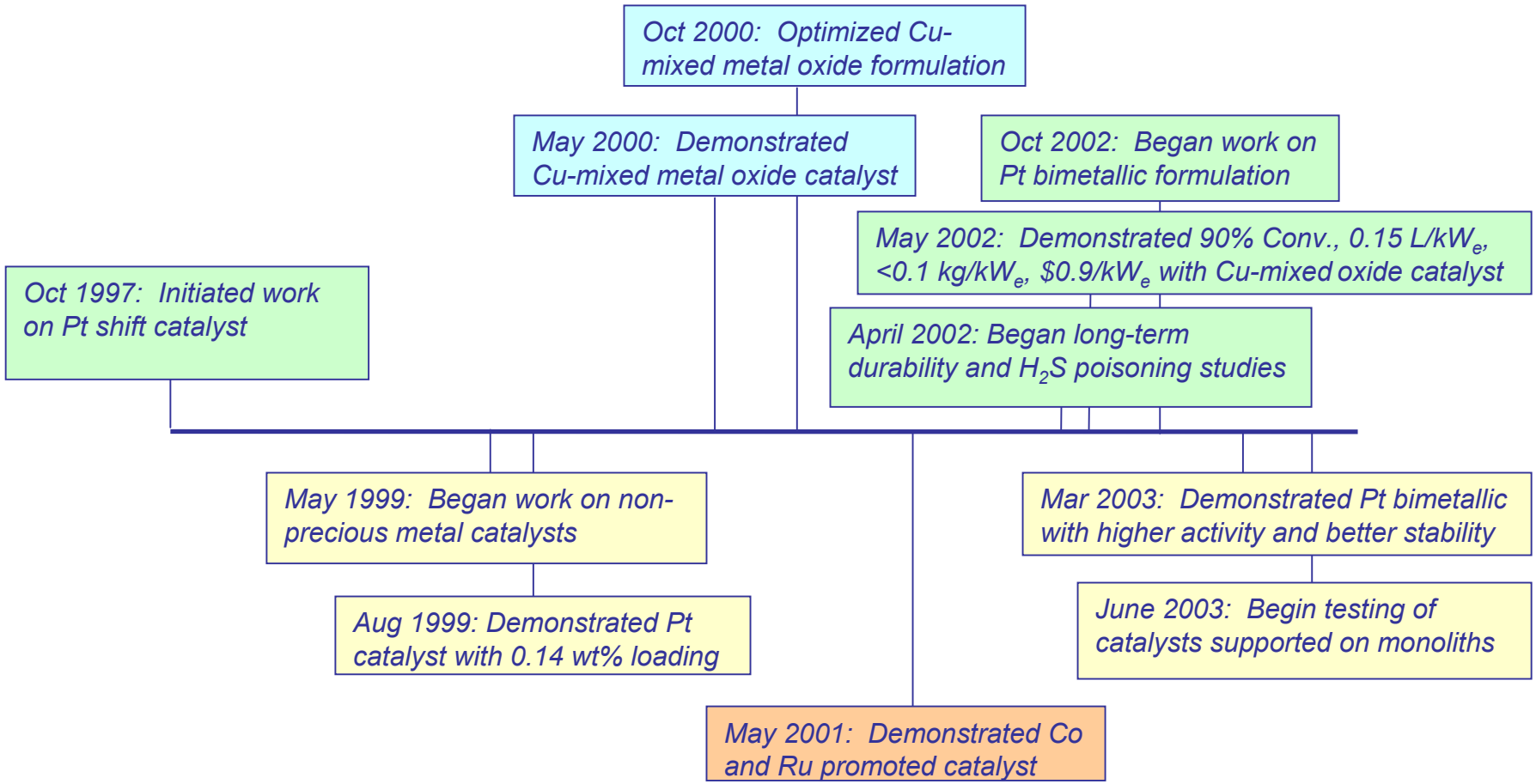
- Select additional mixed-oxide systems for study to improve activity and durability.

  Investigated the effect of dopants to increase the activity of Ce-based catalysts. Also investigated other oxide promoters.

- More emphasis on sulfur tolerance.

  Working on it with some interesting results.

Project timeline



FY2003 accomplishments

- Pt catalysts
  - ✓ Improved the activity and stability of the Pt-Ce catalysts with a bimetallic formulation.
  - ✓ Identified Zr and Gd as dopants for ceria that can improve shift activity at temperatures >300°C compared to undoped Pt-Ce.
  - ✓ Demonstrated that 5 ppm H_2S does not contribute to deactivation of Pt-Ce catalyst at 300°C but does promote deactivation at 400°C.
- Non-Pt catalysts
  - ✓ Identified Cu sintering and oxide agglomeration as modes of deactivation for Cu/mixed oxide catalyst.
  - ✓ Investigated Re, Ni-Re, and Mn as promoters to enhance the activity of Cu catalysts.

Use of modeling helps define our goals

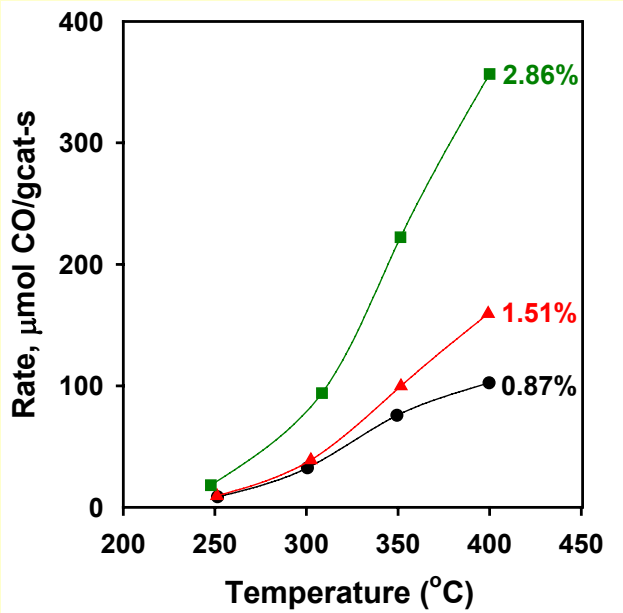
- The shift reaction is under kinetic control over the temperature range of 280-375°C.
- The activity of precious metal catalysts must be increased by a factor of 4 to achieve the GHSV target of 30,000 h^{-1}.
- The merit of increasing the water content to improve the kinetics and to raise the temperature of the low temperature shift reactor is being evaluated.

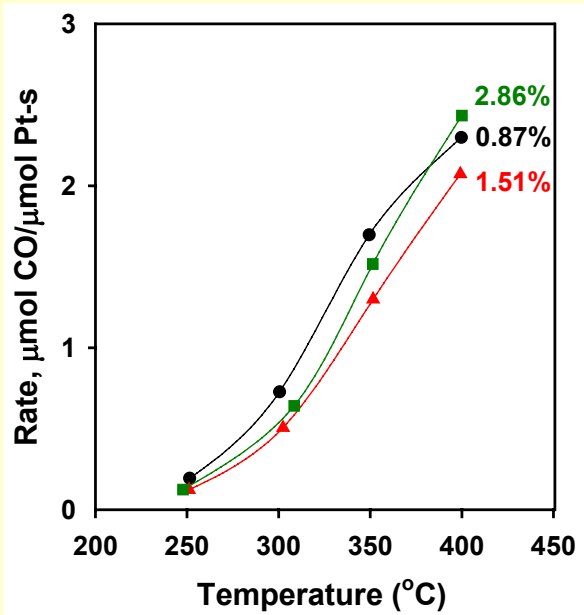
For Pt-CeO_2, our effort is directed to improve H_2O dissociation and oxygen transfer rates

- Kinetic studies* show that the rate is zeroth order in CO and half-order in H_2O (rate α P_{CO}^{0} $P_{H_2O}^{0.5}$)
  - ✓ Metal surface is saturated with CO
  - ✓ Reaction may be controlled by
    - rate of reoxidation of ceria by water
    - rate of oxygen transfer from ceria to metal interface
    - metal dispersion and surface area
- Improve ceria redox/oxygen transfer rates by cation doping
- Improve water dissociation on Pt surface by addition of a second metal
- Stabilize Pt against sintering

* Bunluesin et al., *Appl. Catal. B* **15** (1998) 107-114; Hilaire et al., *Appl. Catal. A* **215** (2001), 271-278; Wang et al., *J. Catal.* **212** (2002) 213-230.

CO conversion per mole of Pt was independent of Pt loading from 0.87-2.86 wt%

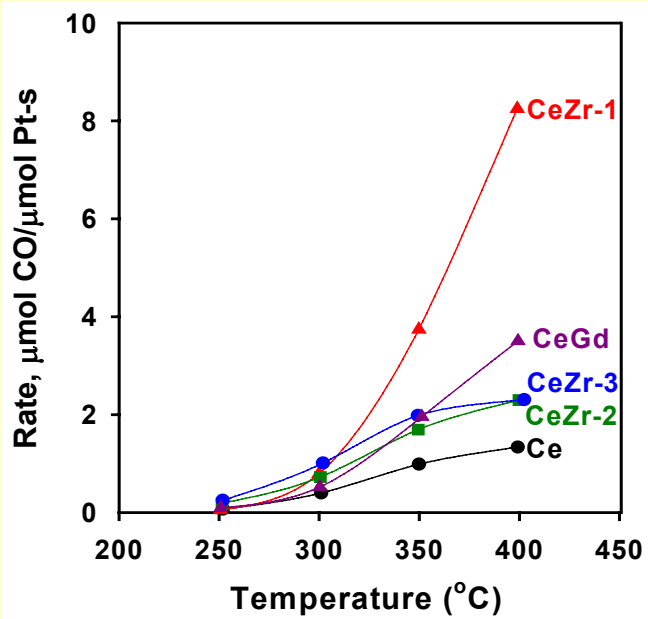




Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 600,000-1,800,000 h^{-1}, 0.05-0.1 ml catalyst diluted with α-Al_2O_3

- By increasing the Pt loading, the CO conversion per unit volume of reactor can be increased.
- Increasing the Pt loading will make it difficult to achieve the cost target of \$1/kW_e.

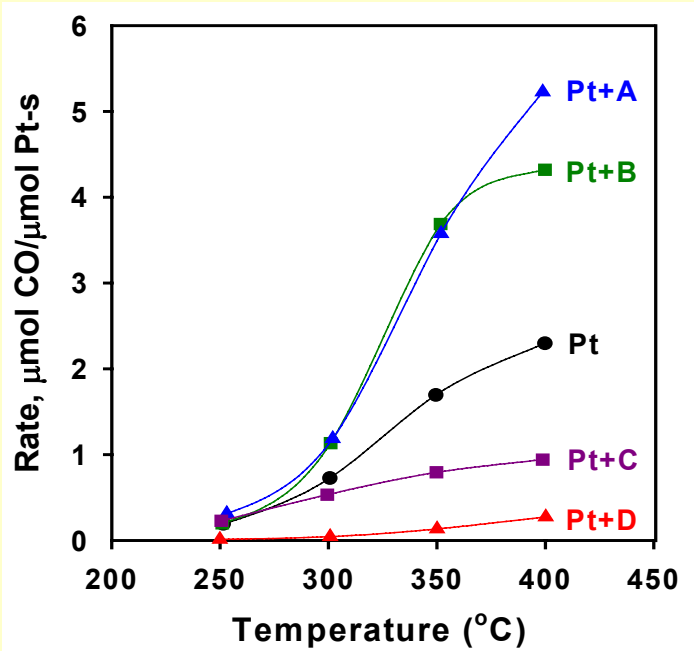
Doping CeO_2 with Gd or Zr increased activity at temperatures above 300°C



Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 600,000 h^{-1}, 0.1 ml catalyst diluted with 0.4 ml α-Al_2O_3

- Doping CeO_2 is known to lower the temperature at which Ce^{4+} reduction occurs and to increase oxygen release rates.
- Our results suggest that doping Ce will not significantly improve its activity below 300°C.

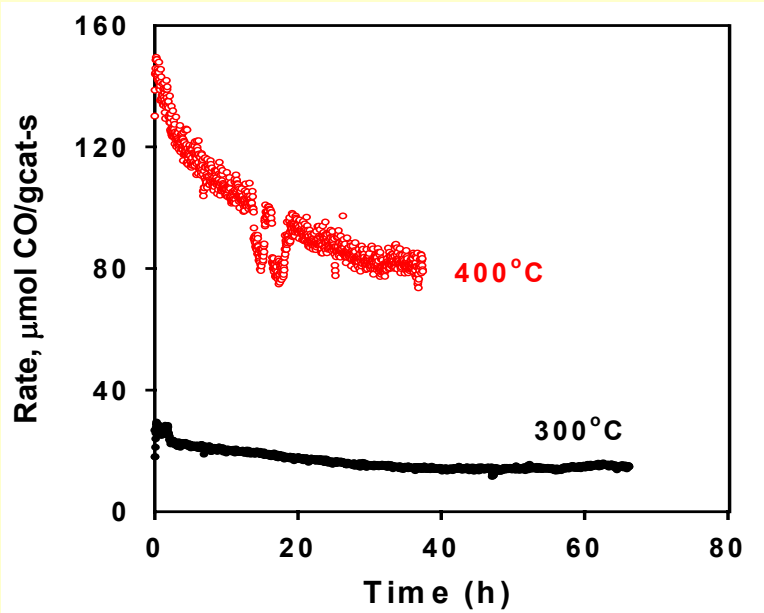
Increased the activity by a factor ~2 with certain Pt bimetallic formulations

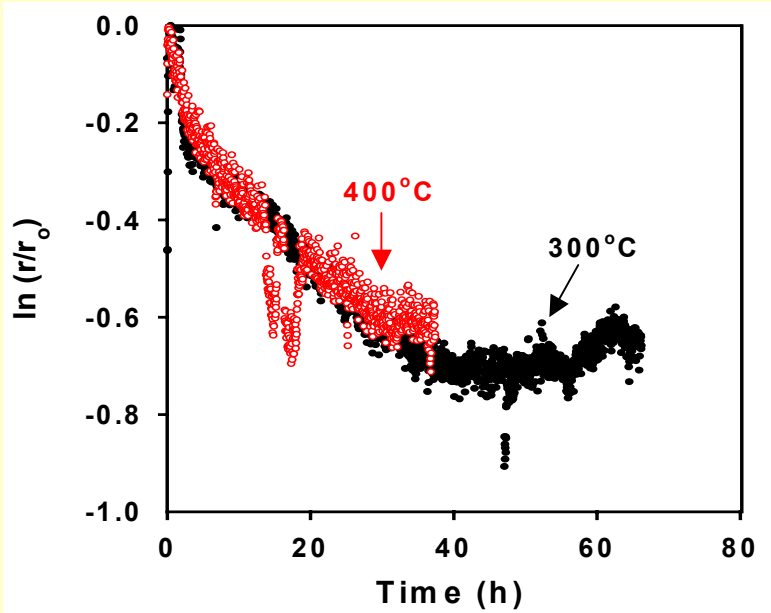


Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 200,000-1,500,000 h^{-1}, 0.05-0.4 ml catalyst diluted with α-Al_2O_3

- Selection of bimetallic formulation based on theoretical studies of the energetics of H_2O dissociation and reaction between CO_{ads} + OH_{ads} on Pt-mixed metal clusters (Ishikawa et al., *Surface Science* **513** (2002) 98-110).

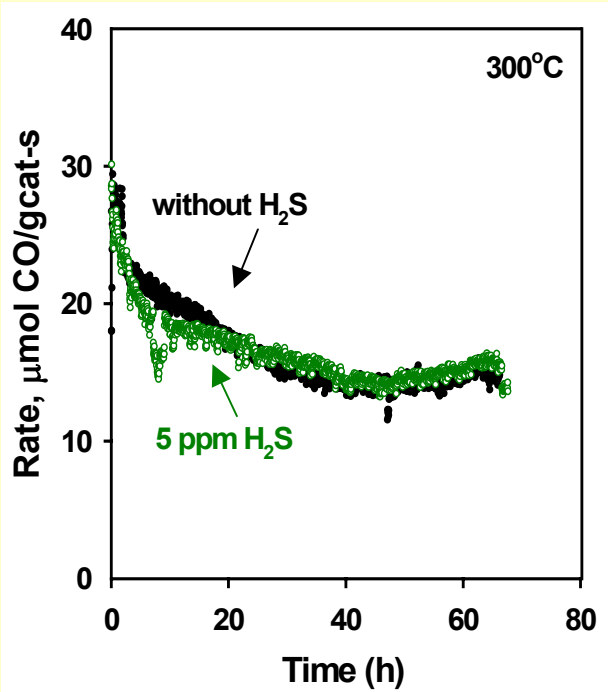
~50% loss of activity was observed over 40 h at both 300 and 400°C with Pt catalyst

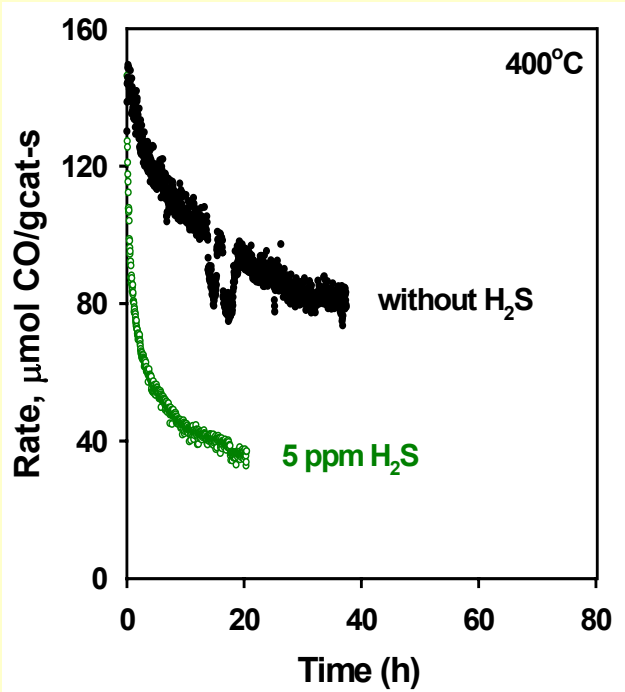




Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 300,000-1,200,000 h^{-1}, 0.03-0.1 ml catalyst diluted with α-Al_2O_3

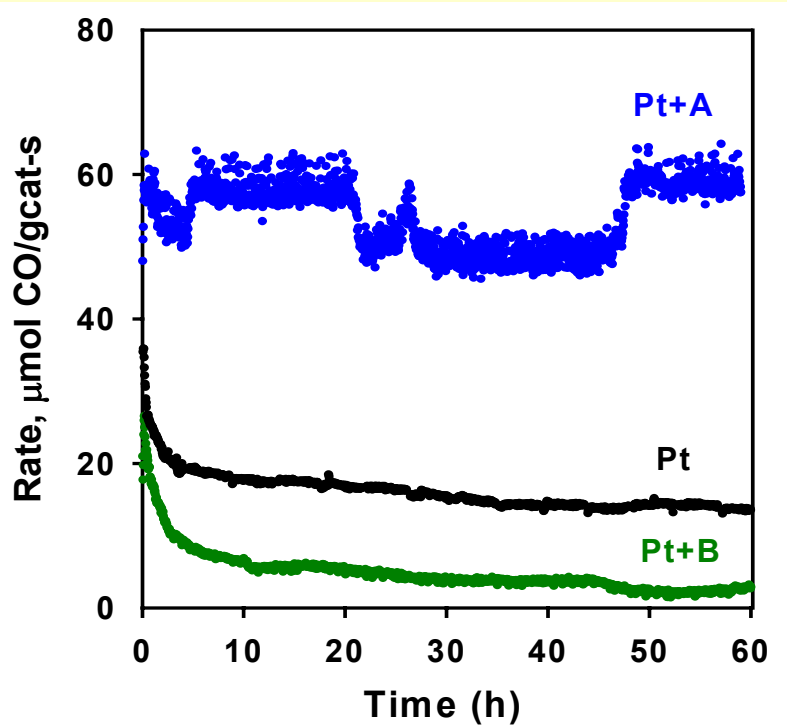
5 ppm H_2S increased the rate of deactivation at 400°C, but not at 300°C with Pt catalyst





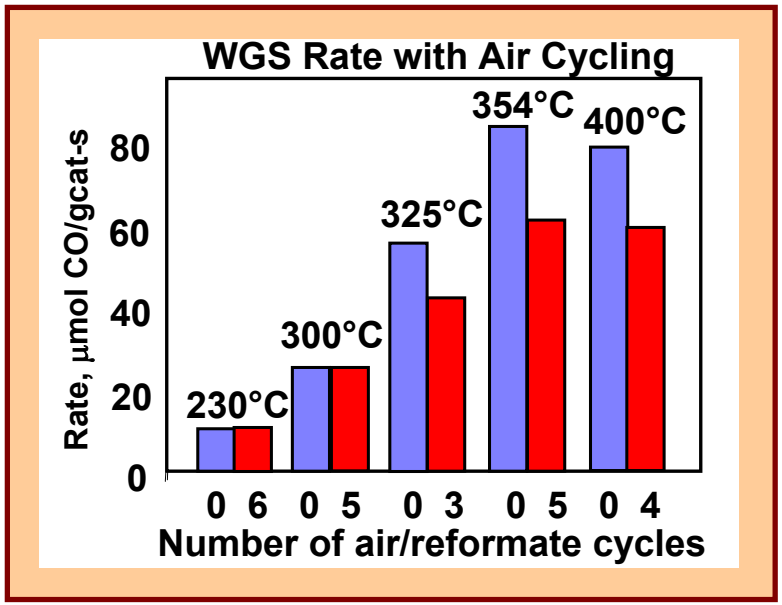
Conditions: 5 ppm H_2S, 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 300,000-1,200,000 h^{-1}, 0.03-0.1 ml catalyst diluted with α-Al_2O_3

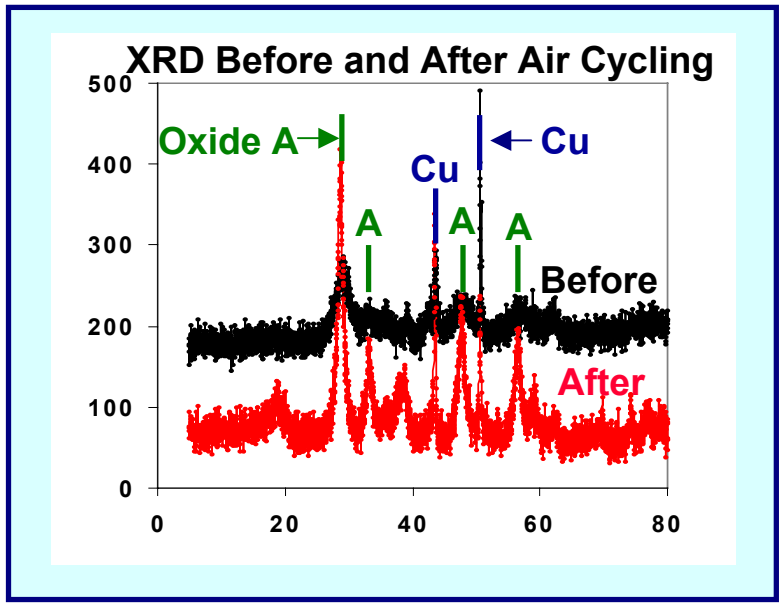
Pt+A bimetallic was more stable than Pt at 300°C



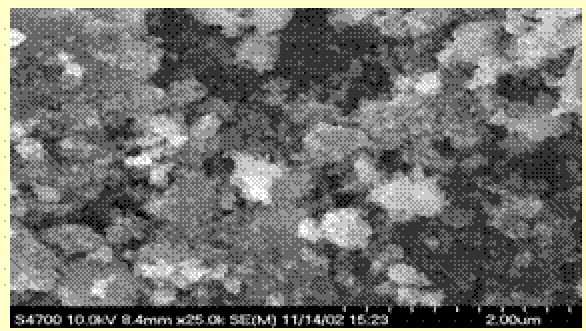
Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O
GHSV = 300,000-400,000 h^{-1}, 0.10-0.12 ml catalyst diluted with α-Al_2O_3

Deactivation of Cu/mixed oxide at >300°C likely caused by sintering of Cu and agglomeration of oxide

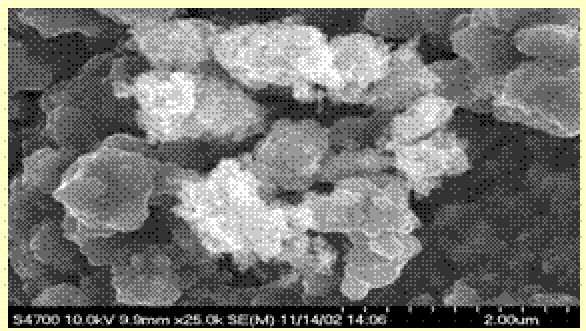




Fresh Sample



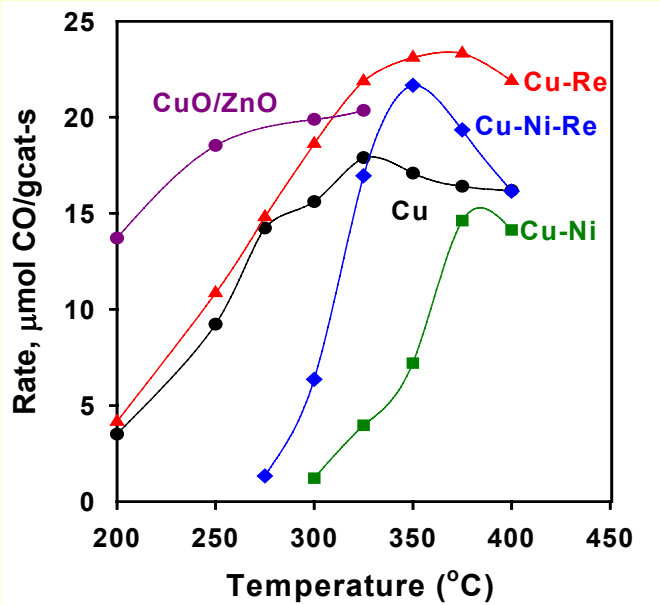
S E M (25k)



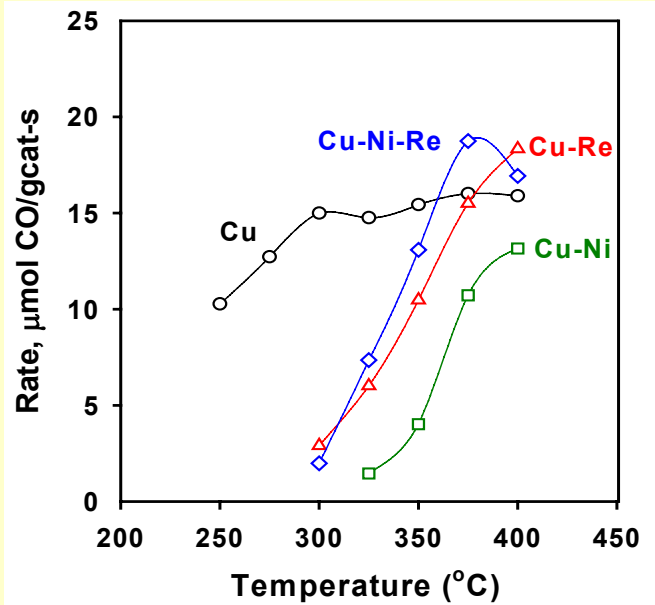
After WGS at 325°C for 167 h

Investigated Ni and Re as promoters for improving activity and stability of Cu catalysts operating at 250-400°C

Rate observed with fresh sample



Rate after air exposure

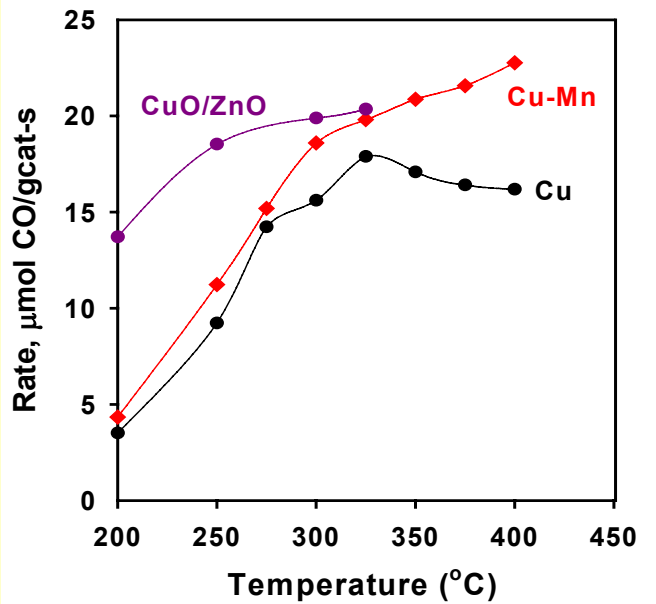


Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O, GHSV = ~40,000 h^{-1}

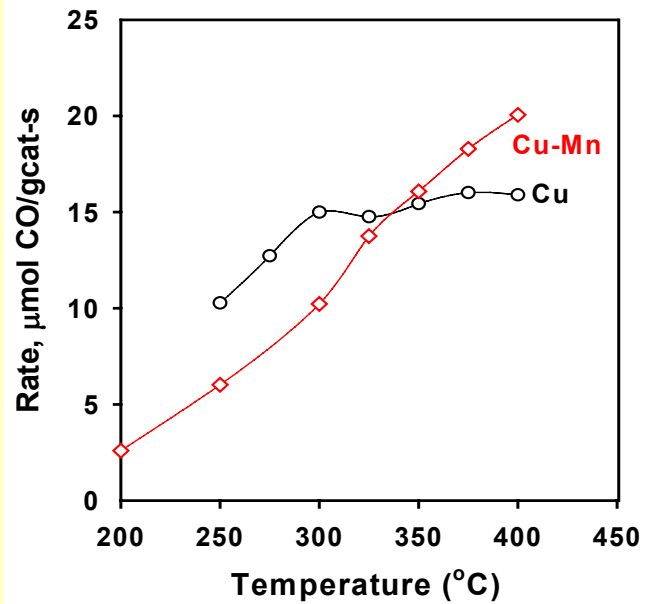
- Our previous work has shown that Re stabilizes Co-based catalysts.
- Ni and Cu form a solid solution that can accommodate ~10 atom% Re.

Investigated Mn as a promoter for improving activity and stability of Cu catalysts operating at 250-400°C

Rate observed with fresh sample



Rate after air exposure



Conditions: 6.9% CO, 10.35% CO_2, 20.7% N_2, 31.05% H_2, 31.0% H_2O, GHSV = ~40,000 h^{-1}

- Mn enhances Cu activity as observed with Re and Ni-Re.
- Cu-Mn is more active than Cu after air exposure at >350°C.

FY2003 milestones

Milestone	Date
Improve low-temperature (<250°C) activity of catalyst to >9 μmoles CO g^{-1} s^{-1}.	02/03
We have developed a Cu that yields 10 μmoles CO g^{-1} s^{-1} at 250°C. Long-term stability is still an issue.	
Complete 1000 h test of catalyst using sulfur-free synthetic reformate.	02/03
We have completed a 250 h test of Pt-Ce that we have extrapolated to 1000 h.	
Improve sulfur tolerance of non-precious metal catalyst in reformate containing 3 ppm H_2S.	06/03
Work in progress – has proven to be challenging.	
Demonstrate $\leq$1% CO out using a structured form of the catalyst(s).	09/03
Coating of monoliths is in progress. Testing to begin 6/03.	

Future work

- Pt-Ce catalysts
  - ✓ Optimize bimetallic formulation to increase activity while decreasing Pt loading to achieve DOE cost target
  - ✓ Retard Pt sintering
  - ✓ Address H_2S poisoning at temperature of 400°C
  - ✓ Evaluate catalyst performance on monolith
- Cu catalysts
  - ✓ Increase low temperature (230-300°C) activity
  - ✓ Reduce Cu sintering through the addition of promoters to improve stability
  - ✓ Improve sulfur tolerance
- Conduct characterization studies (SEM/TEM and EXAFS/XANES) to improve activity and reduce deactivation.

Catalysts for autothermal reforming

Jennifer Mawdsley, Magali Ferrandon,
Cécile Rossignol, James Ralph, Laura Miller,
John Kopasz, and Theodore Krause

Chemical Engineering Division
Argonne National Laboratory

Hydrogen, Fuel Cells, and
Infrastructure Technologies
2003 Merit Review
Berkeley, CA
May 19-22, 2003

Objectives

- Develop advanced autothermal reforming (ATR) catalysts that meet DOE targets for the Fast Start reformer
  - ✓ gas-hourly space velocity (GHSV) ≥ 200,000 h^{-1}
  - ✓ efficiency of ≥ 99.9% with H_2 selectivity of 80%
  - ✓ durability of ≥ 5000 h
  - ✓ cost of ≤ $5/kwe
- Develop a better understanding of reaction mechanisms to
  - ✓ increase catalytic activity
  - ✓ reduce deactivation
  - ✓ improve sulfur tolerance

This work addresses technical barriers I, J, K, and N.

Approach

- Building on past ANL experience, we are investigating two classes of materials.
  - ✓ Transition metal(s) supported on mixed oxide substrates
  - ✓ Perovskites, with no precious metals
- Determine catalyst performance (H_2, CO, CO_2, and CH_4) as a function of:
  - ✓ catalyst composition
  - ✓ fuel composition and sulfur content
  - ✓ operating parameters: O_2:C and H_2O:C ratios, temperature, GHSV
- Conduct catalyst characterization and mechanistic studies to gain insight into reaction pathways.
- Work with catalyst manufacturers to optimize catalyst structure and performance.

Industry and University collaborations

- Industry
  - ✓ Süd-Chemie, Inc.
    - Manufactures catalyst under a non-exclusive licensing agreement
    - ANL and Süd-Chemie working jointly to improve catalyst structure and performance
- Universities
  - ✓ University of Alabama (Profs. Ramana Reddy and Alan Lane)
    - Characterization studies (SEM, TEM, XPS) of ATR catalysts
    - Kinetic and mechanistic studies of ATR catalysts
  - ✓ University of Puerto Rico, Mayagüez (Prof. José Colucci)
    - Determine reaction condition boundaries for carbon formation

Reviewer's comments from FY2002 Annual Review

- Space velocities are still low.

  We have increased the GHSV by a factor of ~4 compared to data presented at last year's review.

- Non-CH_4 hydrocarbon outlet levels seem high.

  Hydrocarbon slip has been significantly reduced. We are investigating the effect of support geometry (cell density for monoliths and monolith vs. foam) to further reduce slip.

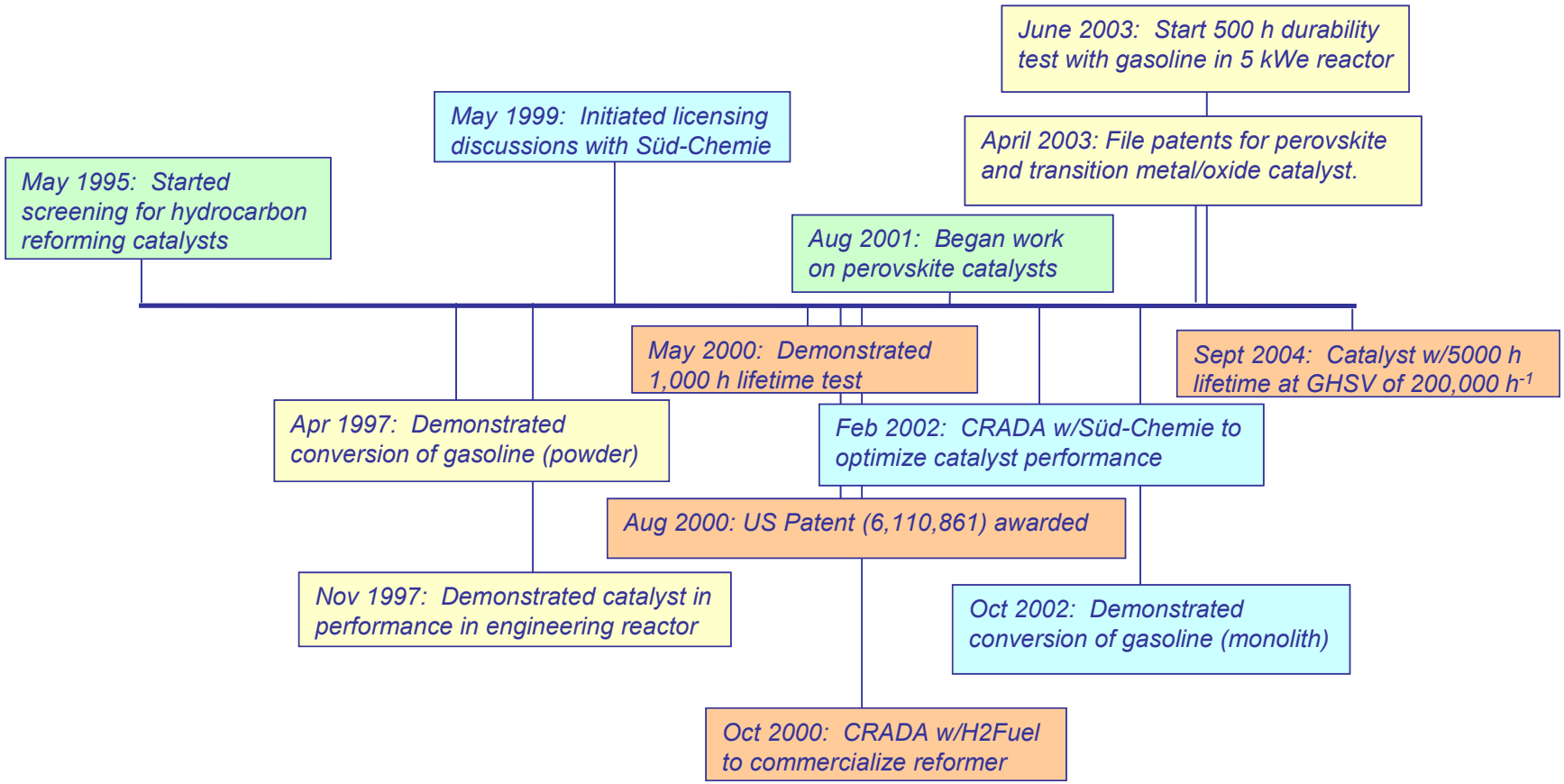
- Demonstrating sulfur tolerance is key.

  Has proven to be challenging. Deactivation but not complete loss of activity has been observed over 100-150 h.

- Detailed knowledge of reaction process would be helpful.

  Using the Advanced Photon Source at ANL, we are studying reaction and catalyst deactivation mechanisms. Through university collaboration, catalyst characterization and kinetic/mechanistic studies are being conducted.

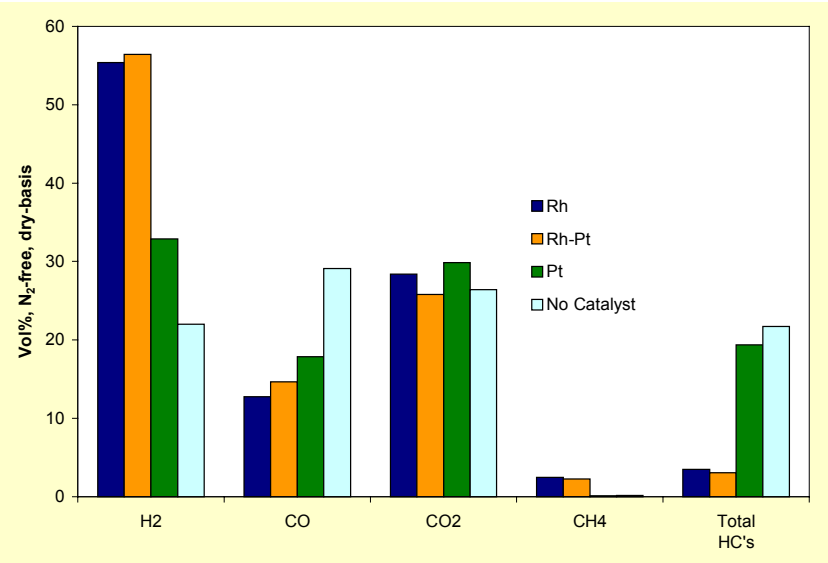
Project timeline



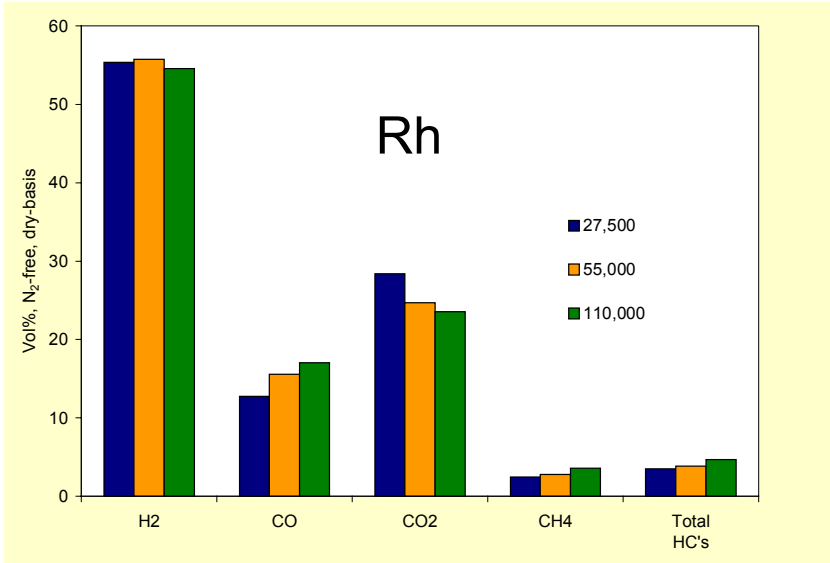
FY2003 accomplishments

- For transition metal on mixed oxide supports
  - ✓ Began testing monoliths with commercial grade gasoline
  - ✓ Demonstrated 55% H_2 (dry, N_2-free) from sulfur-free (<450 ppb S) gasoline at GHSV of 110,000 h^{-1}
  - ✓ Identified mechanisms for catalyst deactivation
  - ✓ Identified new oxide substrate that is more stable than ceria under reforming conditions
- For the Ni-based perovskites
  - ✓ Began testing powders with commercial grade gasoline
  - ✓ Optimized composition to improve structural stability while maintaining high activity
  - ✓ Demonstrated <50% loss in activity with benchmark fuel w/50 ppm S
- Filed two patent applications

Rh catalysts produced reformate with high H_2 concentration from sulfur-free gasoline



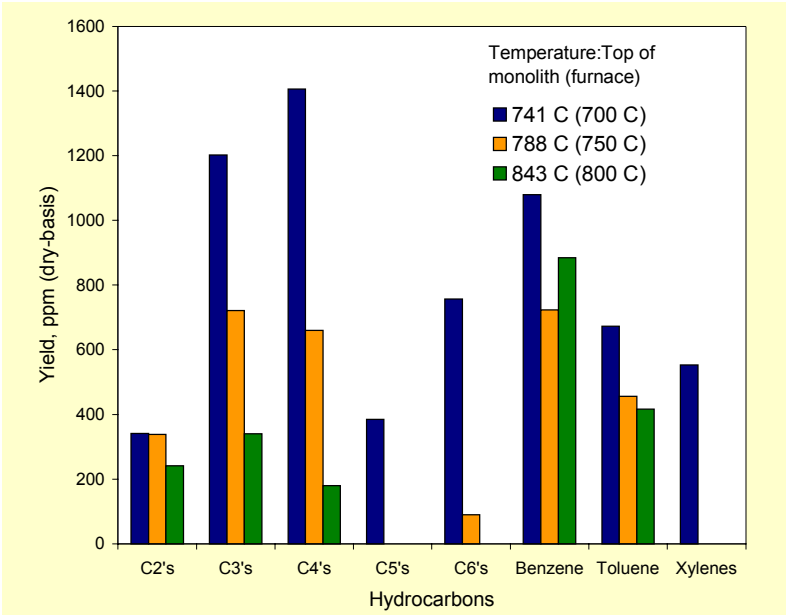
Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)
Feed ratio: O_2:C = 0.5, H_2O:C = 1.8, GHSV = 27,000 h^{-1}, Furnace Temperature is 700°C.



Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)
Feed ratio: O_2:C = 0.5, H_2O:C = 1.8, Furnace Temperature is 700°C.

- Rh and Rh-Pt catalysts produced a reformate containing ≥55% H_2 (N_2-free, dry-basis) at a GHSV of 27,000 h^{-1}.
- 55% H_2 concentration was maintained at a GHSV of 110,000 h^{-1} for Rh.

For Rh, non-CH_4 hydrocarbon slip decreased with increasing temperature (gasoline)

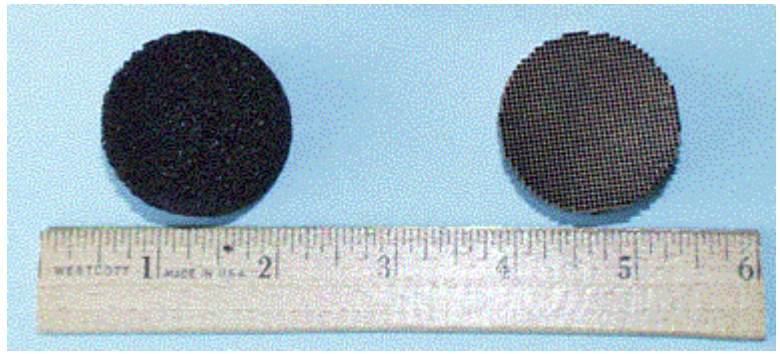


Fuel: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)
Feed ratio: O_2:C = 0.5, H_2O:C = 1.8, GHSV = 55,000 h^{-1}

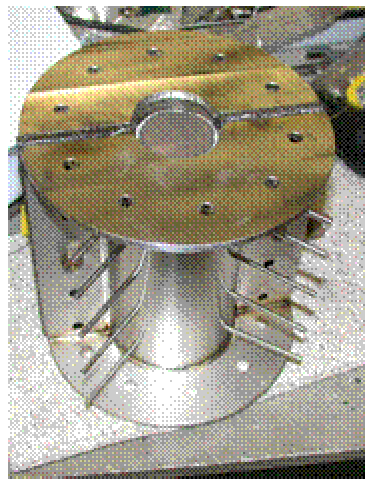
- Increasing the O_2:C ratio to increase the reaction temperature results in a decrease in the H_2 yield.
- Raising the reaction temperature accelerates the rate of catalyst deactivation.

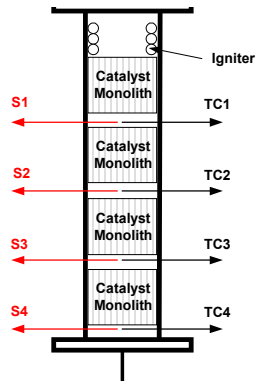
Tests are in progress to determine the optimal geometry for the structured support to improve fuel efficiency

- High mass transfer rates will be crucial in operating at a GHSV of 200,000 h^{-1}
- We are evaluating the performance of the catalyst supported on different structured forms
  - ✓ monoliths with 600, 900, and 1200 cpsi
  - ✓ metal foams
- Testing is being done in a kWe reactor system under adiabatic conditions



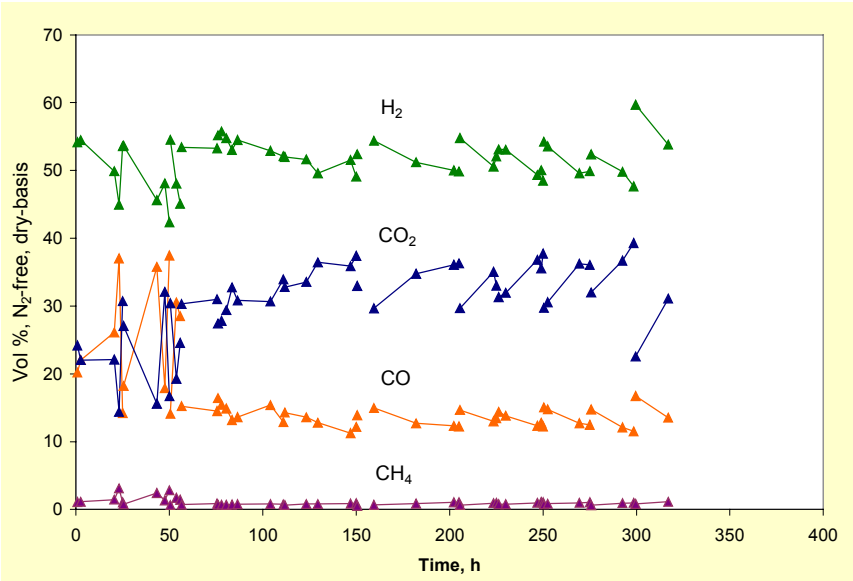
Metal foam (left) and 600 cpsi monolith

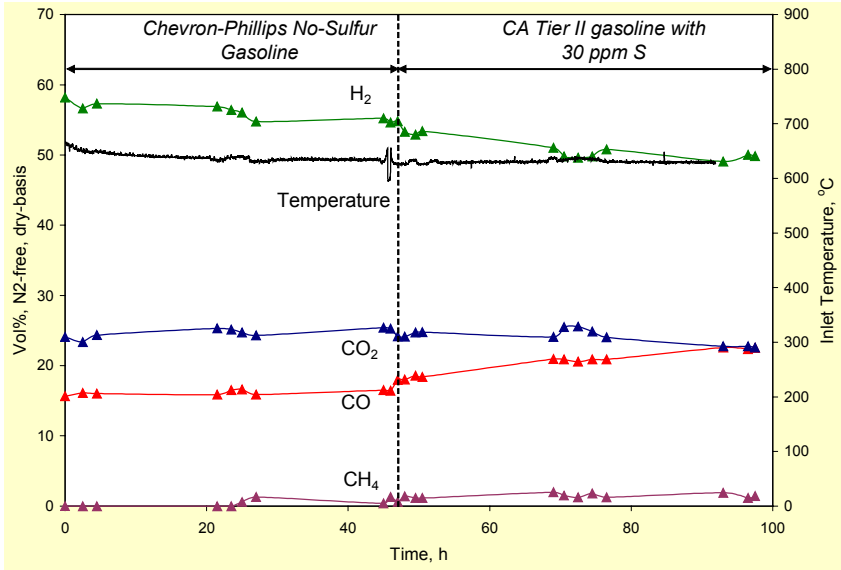




kW_e Reactor System

Deactivation and sulfur poisoning observed in long-term tests with Pt-Rh catalyst





Periodic Shutdown/Restart

Fuel: Sulfur-free benchmark fuel (75 vol% isooctane, 19 vol% xylenes, 5 vol% methylcyclohexane, x% 1-pentene)
Feed ratio: O_2:C = 0.41, H_2O:C = 1.6, GHSV = 9,000 h^{-1}

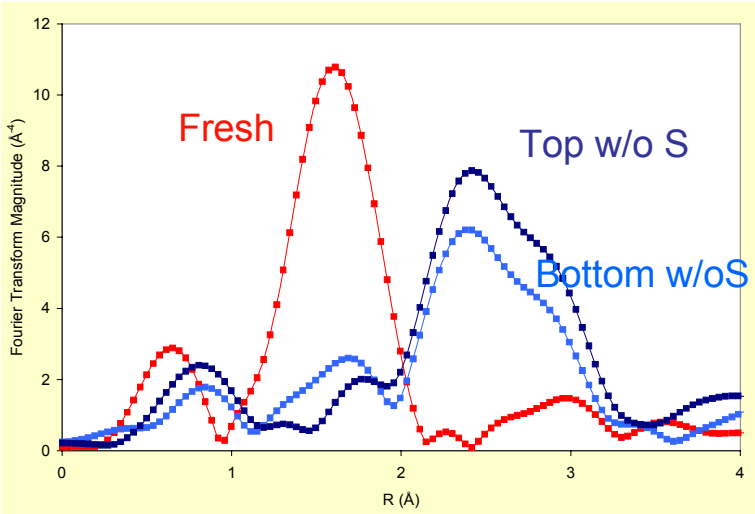
Continuous Operation

Fuels: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S), CA Tier II w/30 ppm S
Feed ratio: O_2:C = 0.45, H_2O:C = 1.6, GHSV = 57,000 h^{-1}

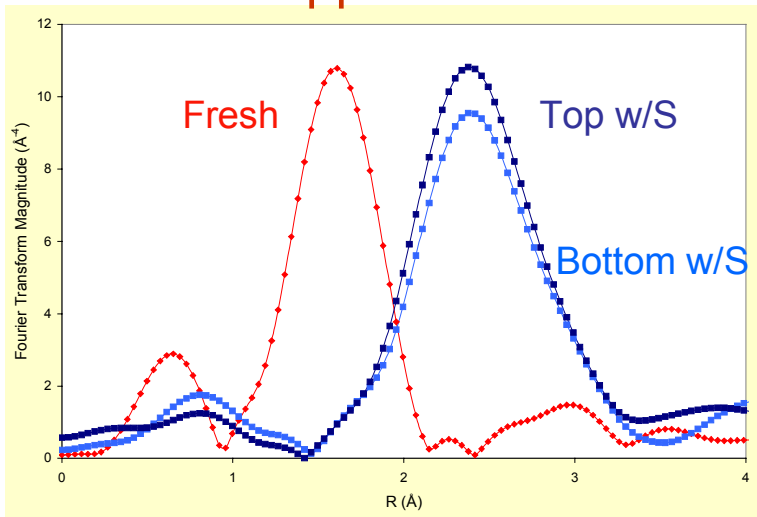
- Activity loss during operating cycle was mostly recovered on restart for testing involving periodic shutdown.
- Greater loss of activity due to sulfur poisoning than deactivation for testing involving continuous operation.

EXAFS showed that Pt sinters during reforming and that sulfur may further promote sintering

No Sulfur



50 ppm Sulfur



Sample	Shell	N	$\Delta s^2 \times 10^4$ (Å^2)	R (Å)	ΔE (eV)	ρ (%)
Fresh	Pt-O	6.0	0.0	2.07	0.1	2.3
Bottom - w/o S	Pt-O	1.7	0.3	2.10	0.0	6.2
	Pt-Pt	7.3	0.0	2.78	0.0	
Top - w/o S	Pt-O	1.0	0.2	2.14	0.4	3.8
	Pt-Pt	9.6	0.0	2.78	0.0	
Bottom - w/S	Pt-O	1.5	0.0	2.29	11.3	3.9
	Pt-Pt	10.5	0.1	2.76	0.0	
Top - w/S	Pt-O	1.4	0.0	2.29	10.8	6.3
	Pt-Pt	12.0	0.0	2.76	0.2	

- EXAFS analysis is on going for Rh and Pt-Rh catalysts.

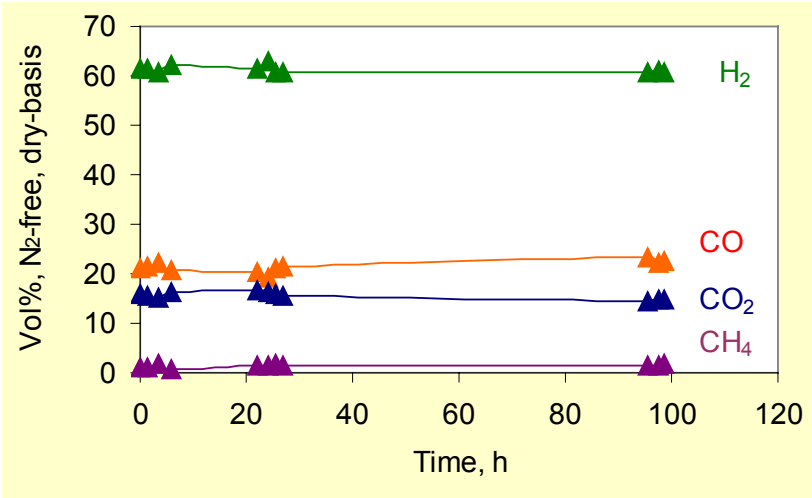
Sintering of ceria substrate shows need for more stable substrates

- Because of concern over loss of activity due to sintering of the ceria, we are investigating more thermally-stable supports.

	Surface Area (m^2/g)		
	As prepared	ATR (150 h)	Thermal Treatment*
Rh/doped -CeO_2	36	17	3
Rh/MO	37	33	33

* 24-h at 900°C in 33% H_2, 17% H_20, bal N_2

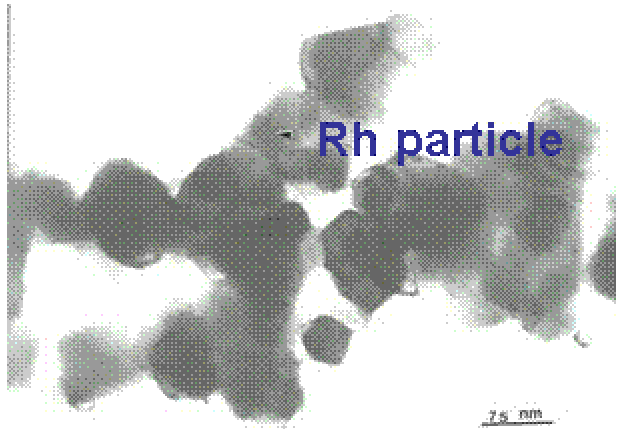
- Rh/MO showed stable yields of H_2, CO, CO_2, and CH_4 over 100 h reforming sulfur-free benchmark fuel.



Conditions: Benchmark fuel, O_2:C = 0.45, H_2O:C = 1.6, GHSV = 82,000 h^{-1}

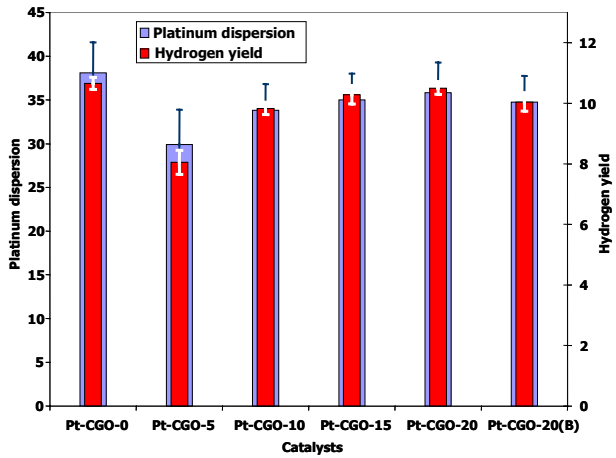
Some highlights from our collaborations with the University of Alabama

- TEM study to determine the effect of H_2 reduction on Rh particles and ceria grains.
  - ✓ Significant increase in ceria grain size after reduction
  - ✓ Sharp interface between Rh and ceria observed on calcined samples becomes diffuse after reduction suggesting poorer interaction between metal and ceria



2 wt% Rh-CGO after reduction

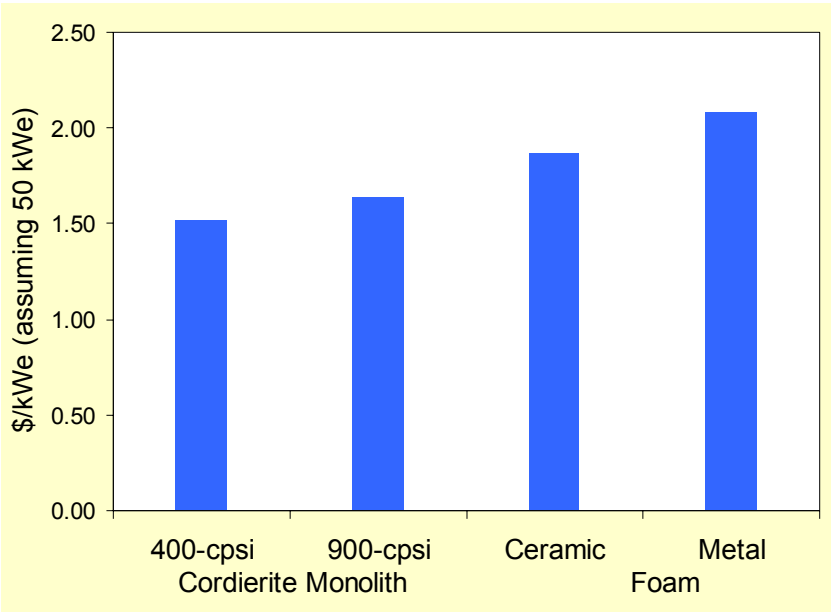
- Kinetic study of isobutane steam reforming catalyzed by $PtCe_{1-x}Gd_xO_{2-(x/2)}$
  - ✓ Rate is proportional to Pt dispersion
  - ✓ Effect of Gd concentration over the range of $0 \leq x \leq 0.2$ is minimal
  - ✓ A rate equation based on the Langmuir-Hinshelwood-Watson kinetic model has been developed



Relationship between Pt dispersion and H_2 yield for Pt-CGO at different Gd concentrations

Cost targets can be achieved

- With a GHSV of 200,000 h^{-1}, the cost target of ≤ $5/kWe is achievable, even with a precious metal catalyst.
- The estimated materials cost (structure, oxide substrate, precious metal), not including manufacturing cost, is $1.50-$2.50/kWe.

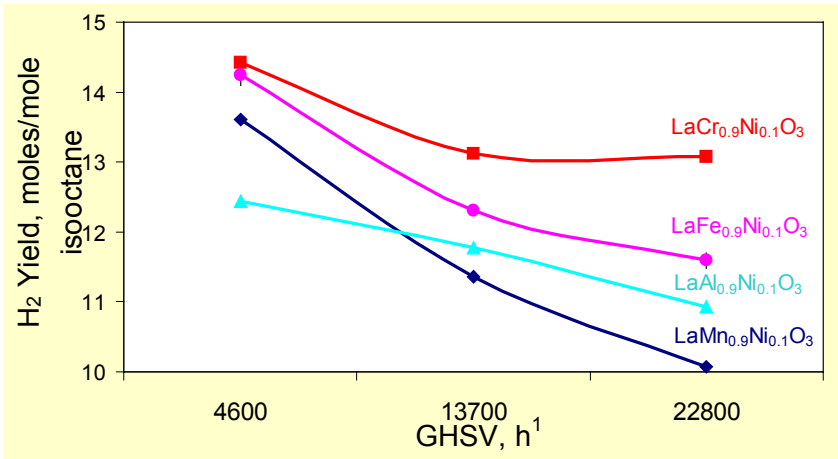


We have focused on increasing the stability of Ni-based perovskites

- Lanthanum on the A-site of $ACr_{0.9}Ni_{0.1}O_3$ gave the best performance in terms of H_2 yield, fuel conversion, and avoiding coke formation.

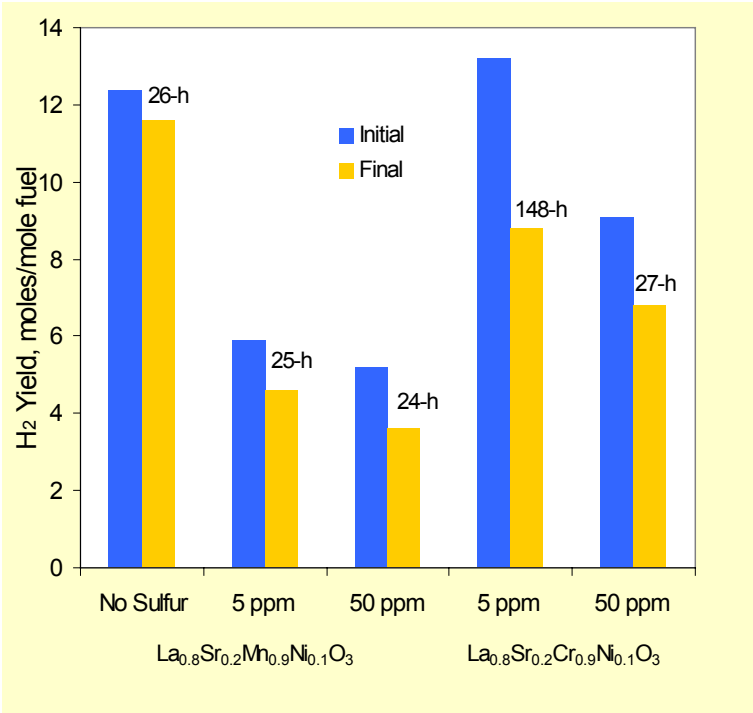
A-site	H_2 Yield*	Conv., %	C, Wt%
La	13.1	96.9	0.63
Pr	11.3	87.6	2.2
Nd	11.9	97.0	6.3
Gd	13.3	99.9	5.1
Er	13.9	97.7	8.0

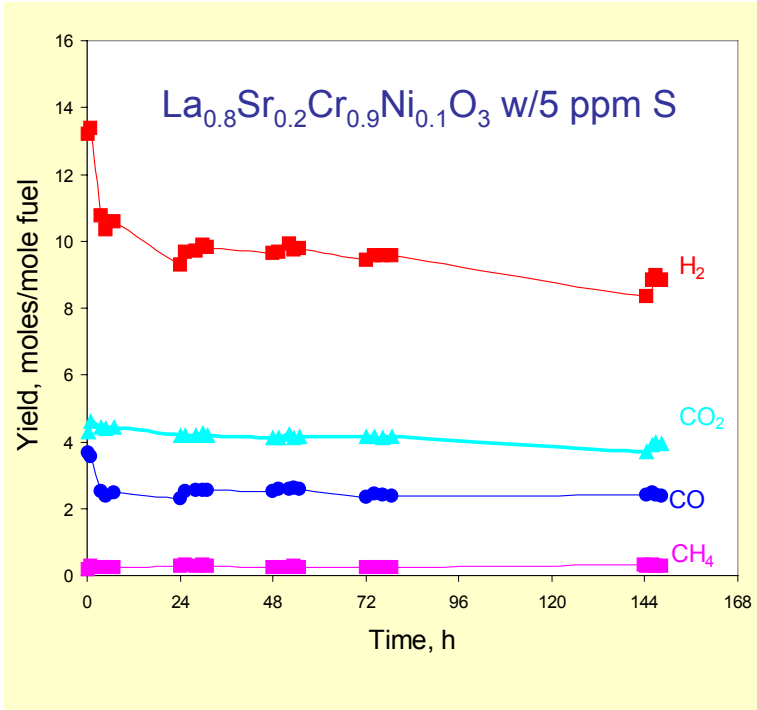
- Cr was the best dopant on the B-site of $LaB_{0.9}Ni_{0.1}O_3$ for stabilizing the perovskite structure while maintaining high reforming activity.



Fuel: Isooctane, Feed ratio: Temperature = 700°C, O_2:C = 0.37, H_2O:C = 1.15, GHSV = 22,800 h^{-1}

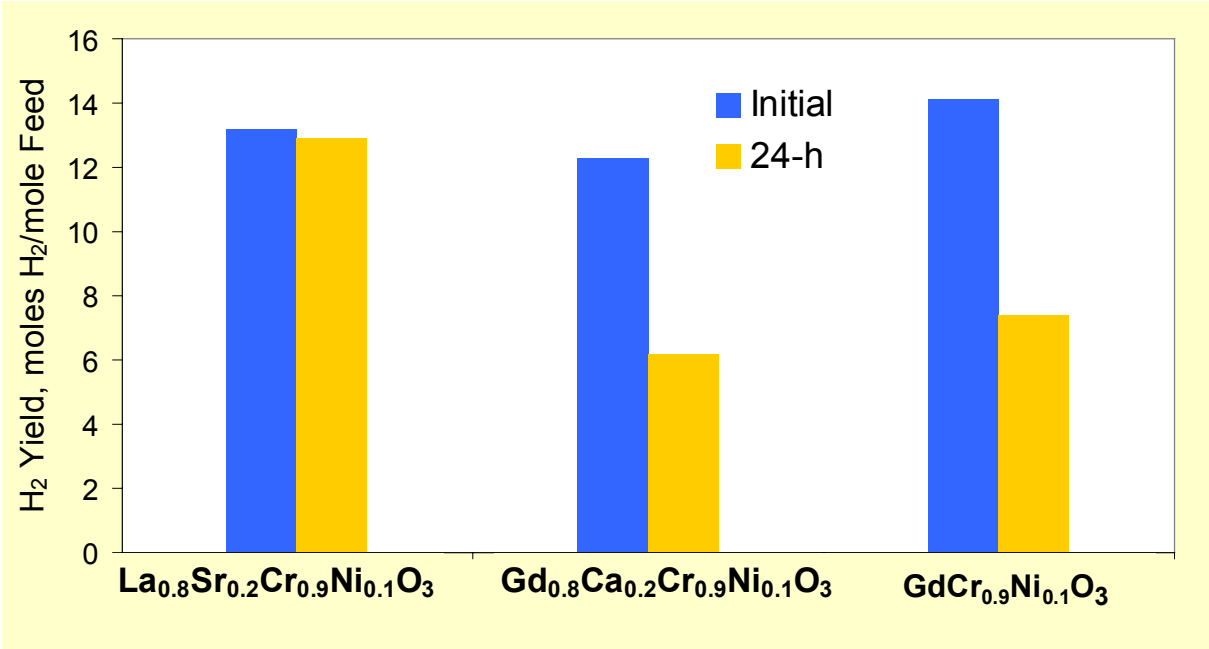
Perovskites are susceptible to sulfur poisoning with most activity lost during the first 10 h





Fuel: Benchmark fuel (78 vol% isooctane, 16 vol% xylenes, 5 vol% methylcyclohexane, 1% 1-pentene) with sulfur added as benzothiophene
Feed ratio: Temperature = 700°C, O_2:C = 0.45, H_2O:C = 1.6, GHSV = 25,000 h^{-1}

$La_{0.8}Sr_{0.2}Cr_{0.9}Ni_{0.1}O_3$ exhibited <5% loss in H_2 yield over 24-h in test with sulfur-free gasoline



Fuels: Chevron-Phillips No-Sulfur Gasoline (<450 ppb S)
Feed ratio: O_2:C = 0.45, H_2O:C = 1.6, GHSV = 25,000 h^{-1}

FY2003 milestones

Milestone	Date
Demonstrate 60% H_2 from California Tier II low sulfur gasoline at 700-800ºC and a space velocity of 100,000 h^{-1} with structured form of metal-doped ceria or perovskite catalyst (N_2, H_2O-free basis).	02/03

Demonstrated 55% H_2 from no sulfur gasoline at 110,00h h^{-1} in a microreactor. Testing with gasoline with 30 ppm sulfur to be conducted in 5-kWe adiabatic reactor.

Demonstrate improved sulfur tolerance of non-Pt catalysts with benchmark fuel containing 30 ppm S (less than 50% loss in activity over a 100-h period compared to activity measured with sulfur-free benchmark fuel.)	06/03

In progress – Less than 50% loss in H_2 yield over 24-h.

Future work

- Evaluate catalyst performance on a larger scale using 1-5 kWe adiabatic reactors.
  - ✓ Confirm microreactor results
  - ✓ Better evaluate long-term performance
  - ✓ Determine optimal geometry for structured support
- Work to decrease precious metal loading while improving catalyst stability and sulfur tolerance.
- Work to improve catalyst activity and sulfur tolerance of perovskite catalysts.
- Address the effect of rapid startup on catalyst stability.
- Increase our fundamental understanding of reaction processes and mechanisms for deactivation and sulfur poisoning.

Development of Novel Water-Gas-Shift Membrane Reactor

Addressing

Barrier L: H_2 Purification/CO Clean-up

Target: <10 ppm CO in Product Stream

W.S. Winston Ho

The Ohio State University, Columbus, OH

DOE Hydrogen & Fuel Cells 2003 Annual Merit Review

Claremont Resort Hotel, Berkeley, CA, May 19-22, 2003

Water-Gas-Shift Membrane Reactor

- **Relevance/Objectives**
  - Produce Enhanced H_2 Product with <10 ppm CO at High Pressure Used for Reforming
  - Overcome Barrier L: H_2 Purification/CO Clean-up
  - Achieve Target: <10 ppm CO in Product Stream

- **Approach: CO_2-Selective Membrane**
  - Remove CO_2 for H_2 Enhancement
  - Drive WGS Reaction to Product Side

$$CO + H_2O \rightarrow H_2 + CO_2 \uparrow$$

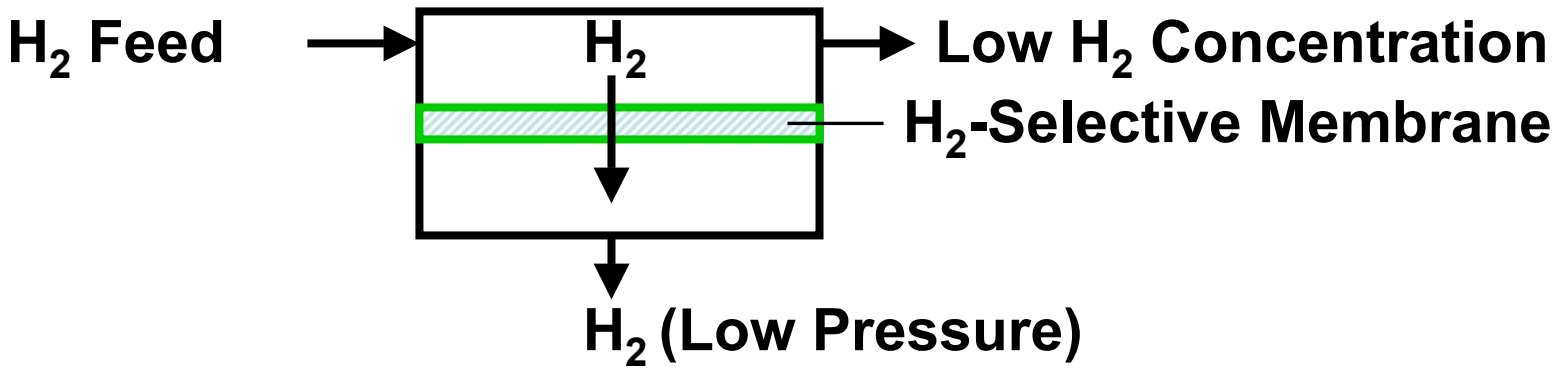
  - Decrease CO to <10 ppm

On-Board/Off-Board Purification of Reformed Gas with Membrane

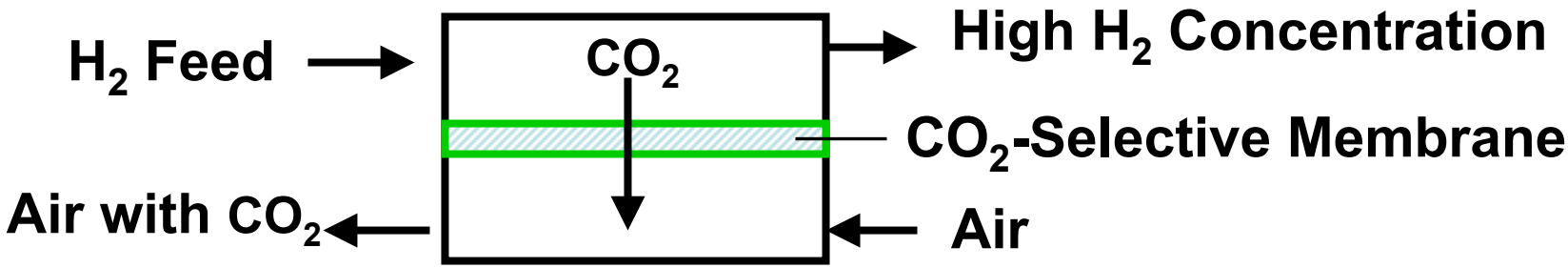
- Light Weight
- Compact – Membrane Module
- Simple Operation
  - Pressure Differential
  - No Moving Parts

Novel Membrane Process for H_2 Purification

- **Conventional / Commercial Membrane Process**



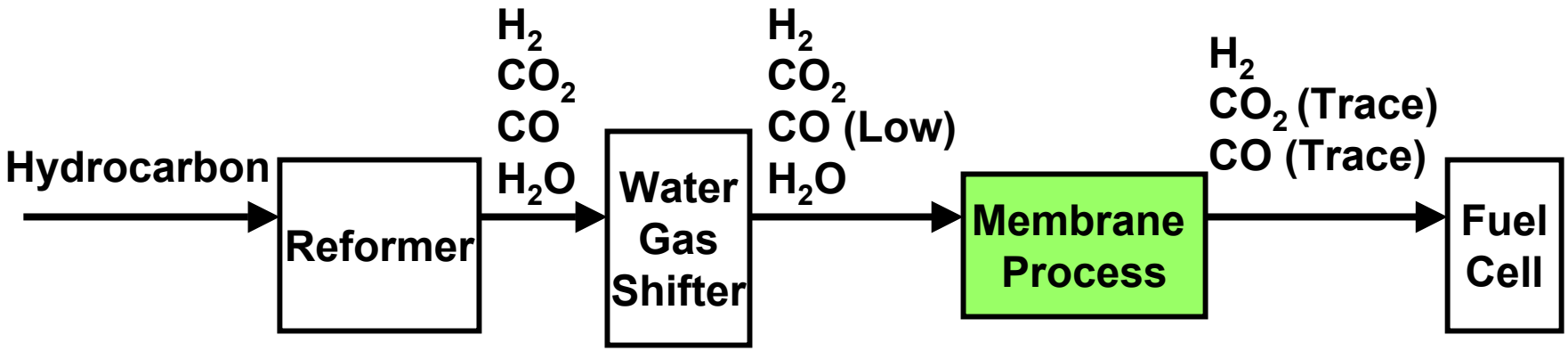
- **Novel Membrane Process**



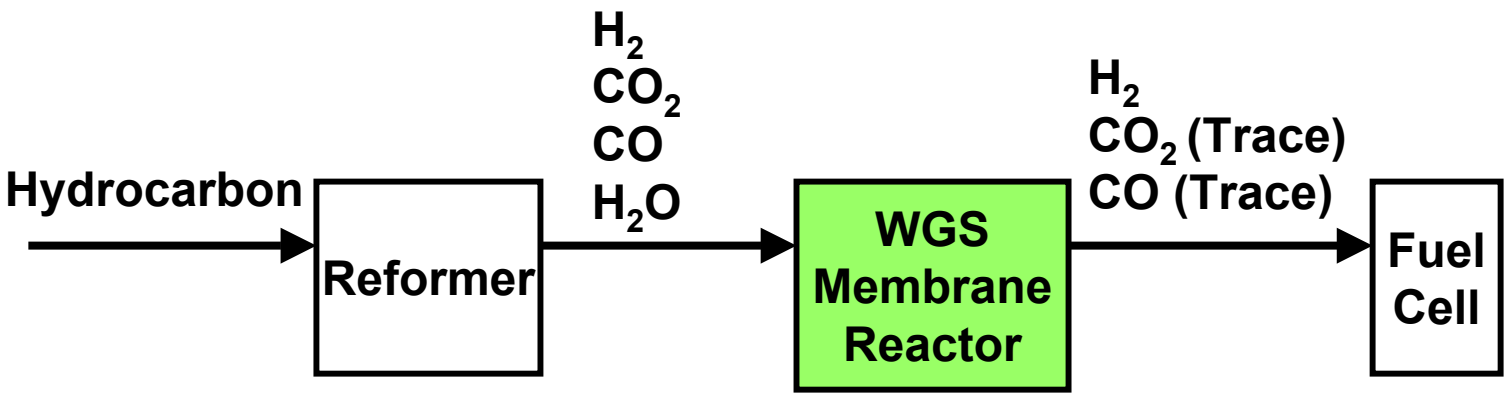
- High-purity H_2 Recovered at High Pressure
- High-purity H_2 Product without CO_2 Desirable
  + CO_2 acts as diluent / produces CO via reverse WGS reaction
- High H_2 Purity/Recovery via High Driving Force from Air Sweep
- Minimal Parasitic Power Required for Air Blown Separation

Fuel-Cell Fuel Processing with CO_2-Selective Membranes

- **Low Temperature CO_2-Selective Membrane**

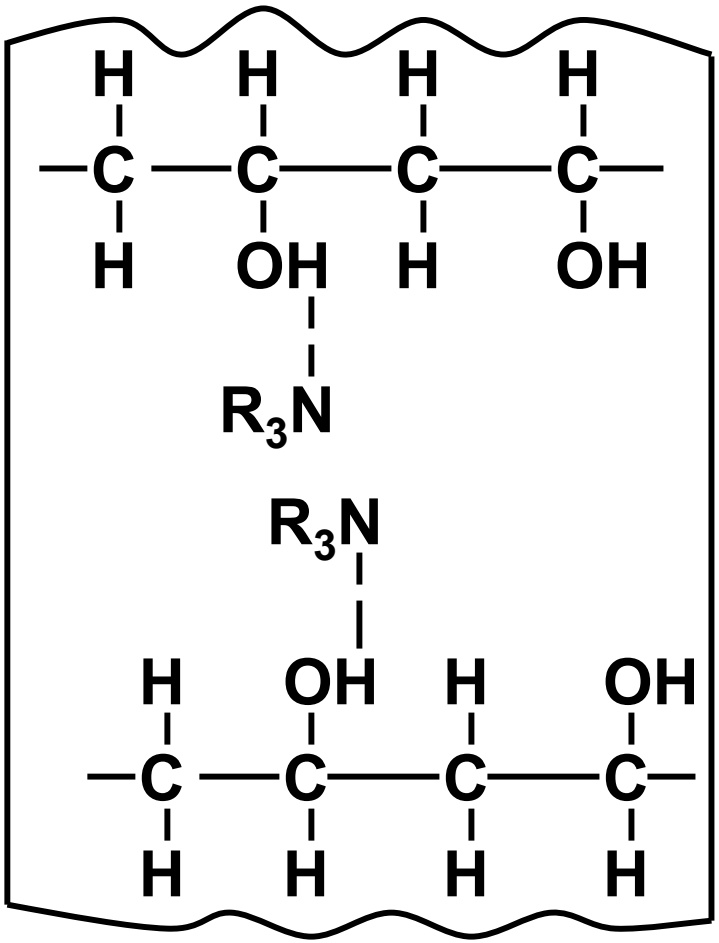


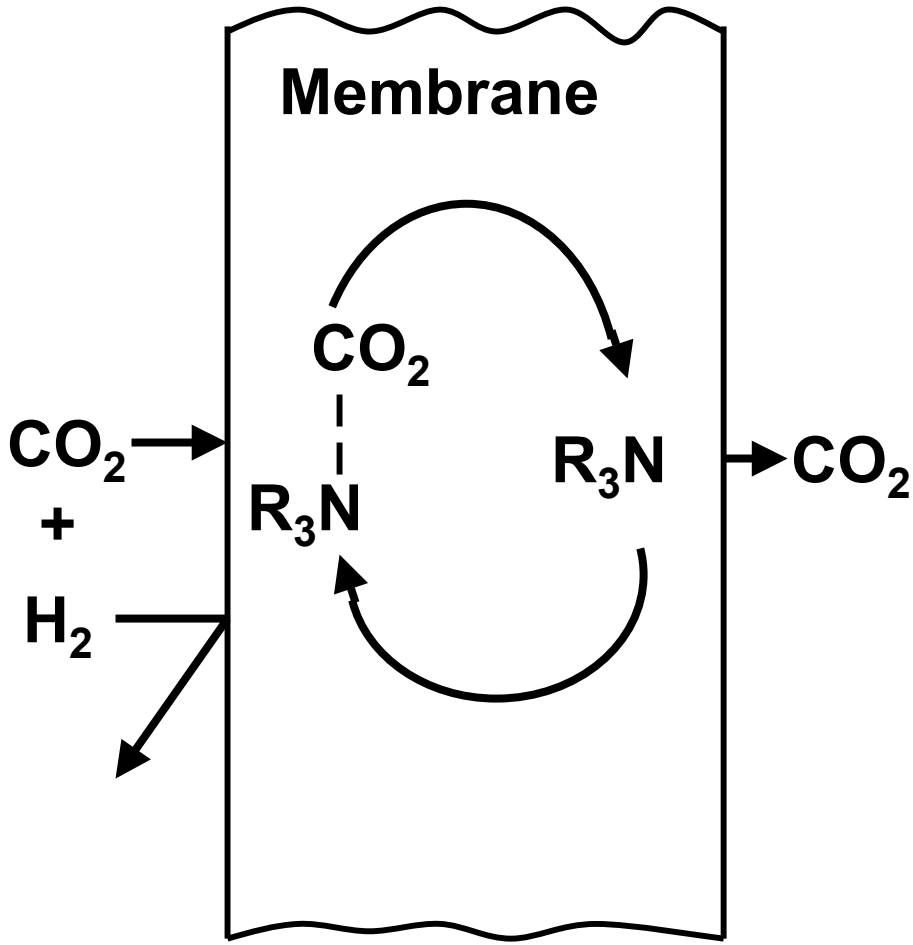
- **High Temperature CO_2-Selective Membrane**



CO_2-Selective Membranes by Incorporating Amines in Polymer Networks … Facilitated Transport

Example: Polyvinylalcohol-Containing Amine Membrane

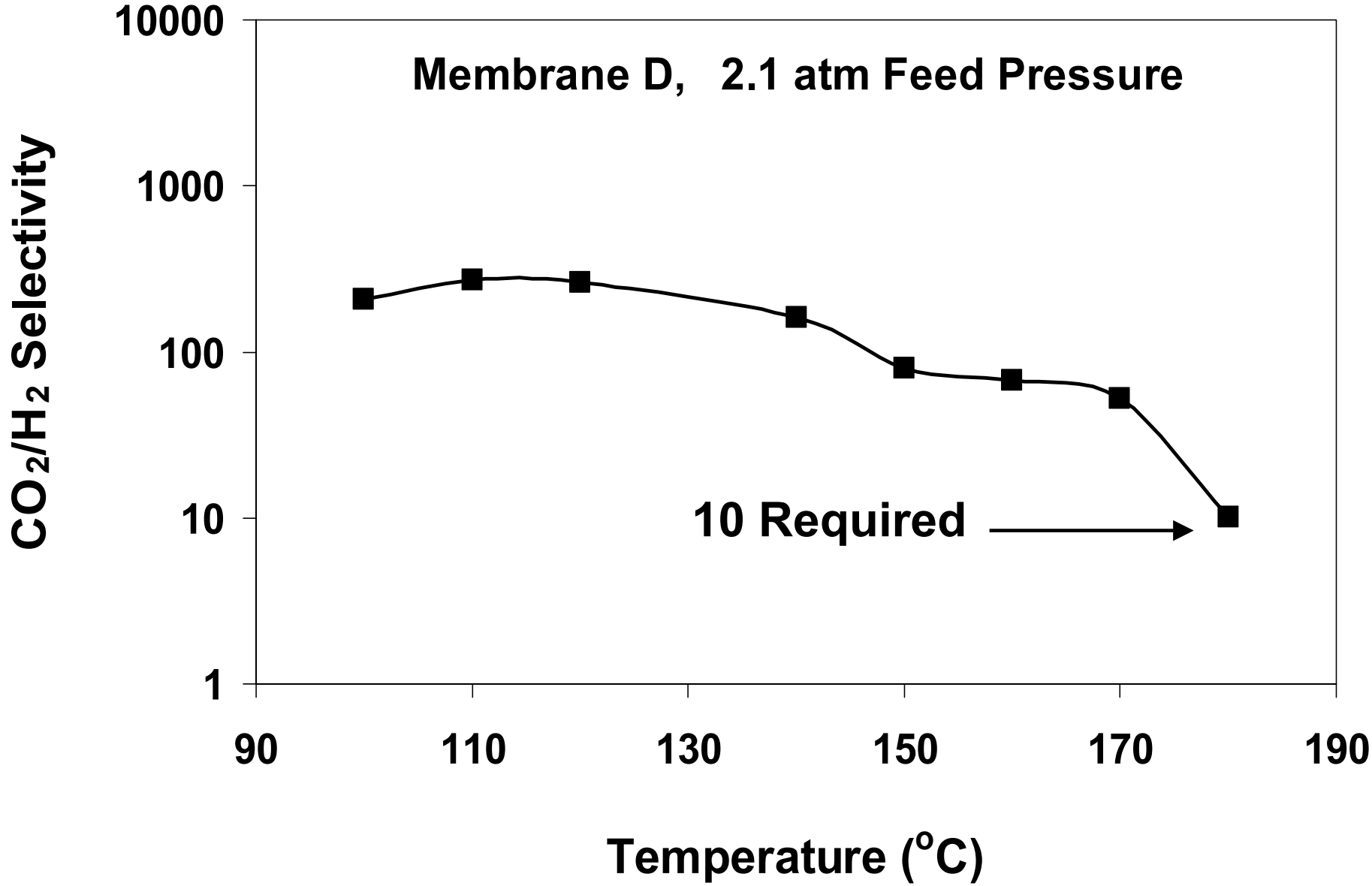




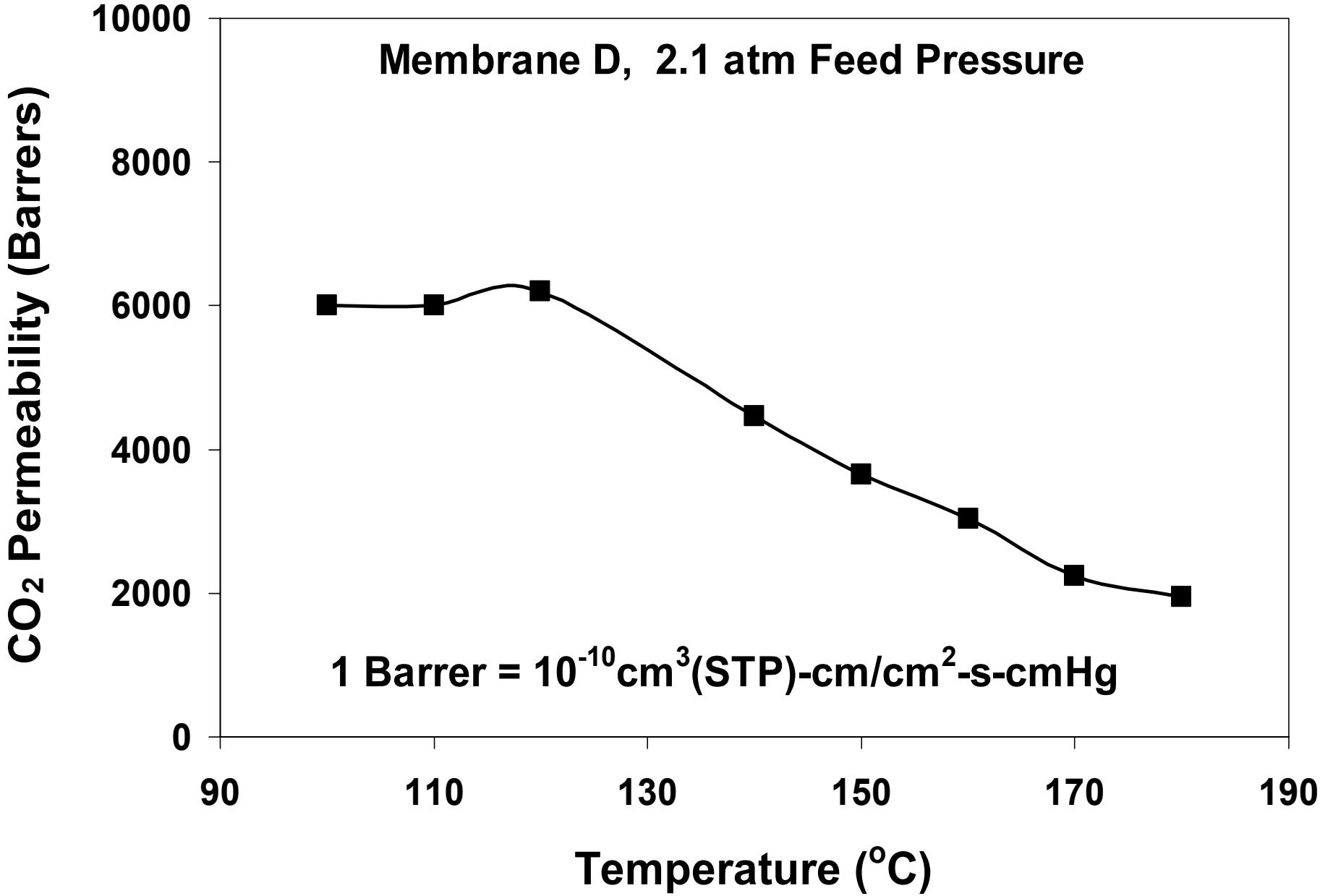
Project Timeline

Task	2001 4Q	2002 1Q	2002 2Q	2002 3Q	2002 4Q	2003 1Q	2003 2Q	2003 3Q	2003 4Q	2004 1Q	2004 2Q	2004 3Q
Phase 1												
1. Modeling Study to Show <10 ppm CO Feasible					Δ							
2. Synthesis of Novel Membranes												
Phase 2												
3. Characterization of Membranes												
4. Set-up of Lab Reactor												
5. Membrane Fabrication												
6. Proof-of-Concept Demo									Δ			
Phase 3												
7. Set-up of Membr. Reactor												
8. Fabrication of Prototype Membrane Module												
9. Prototype Reactor Demo												Δ

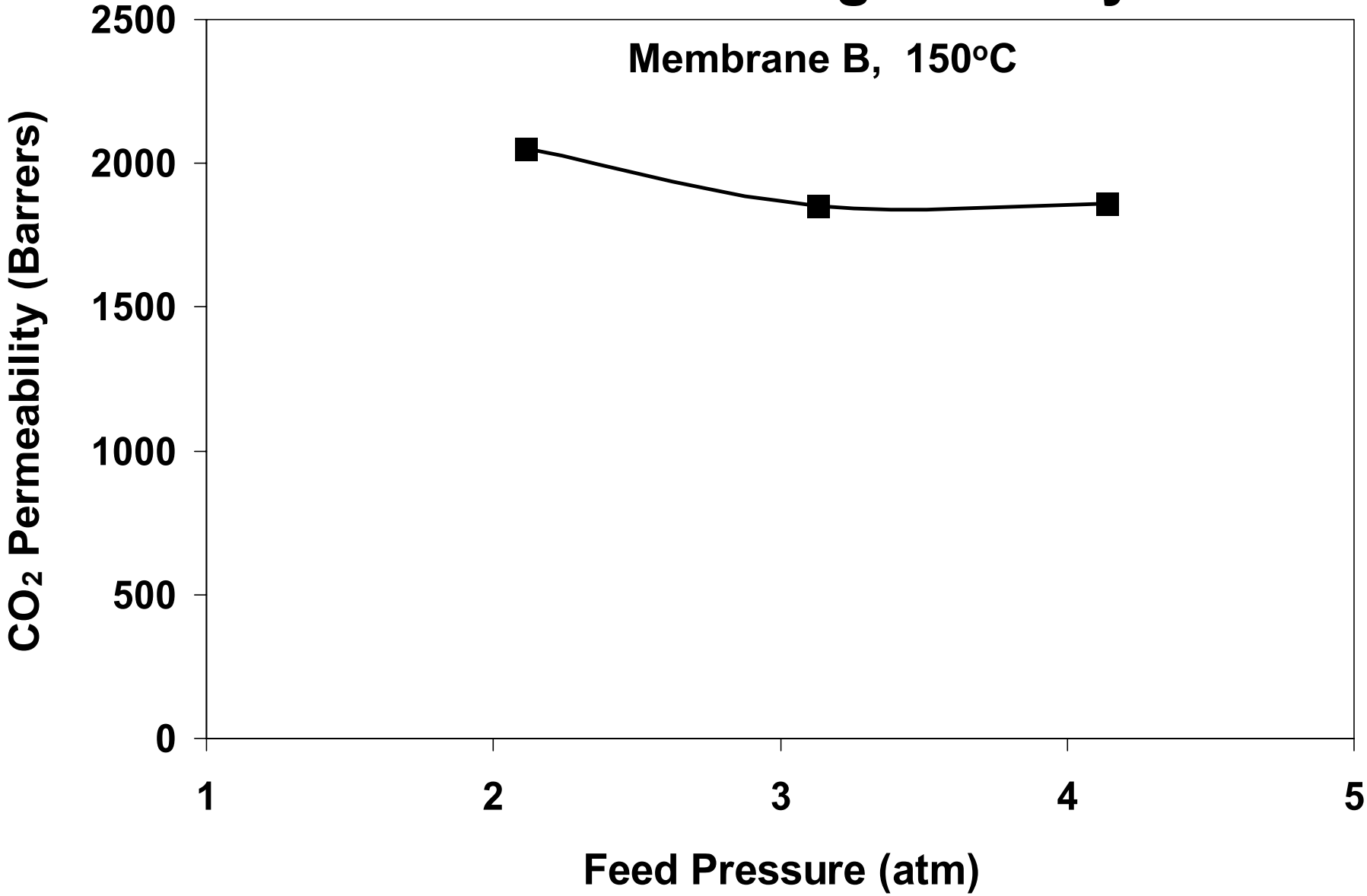
High CO_2/H_2 Selectivity Obtained



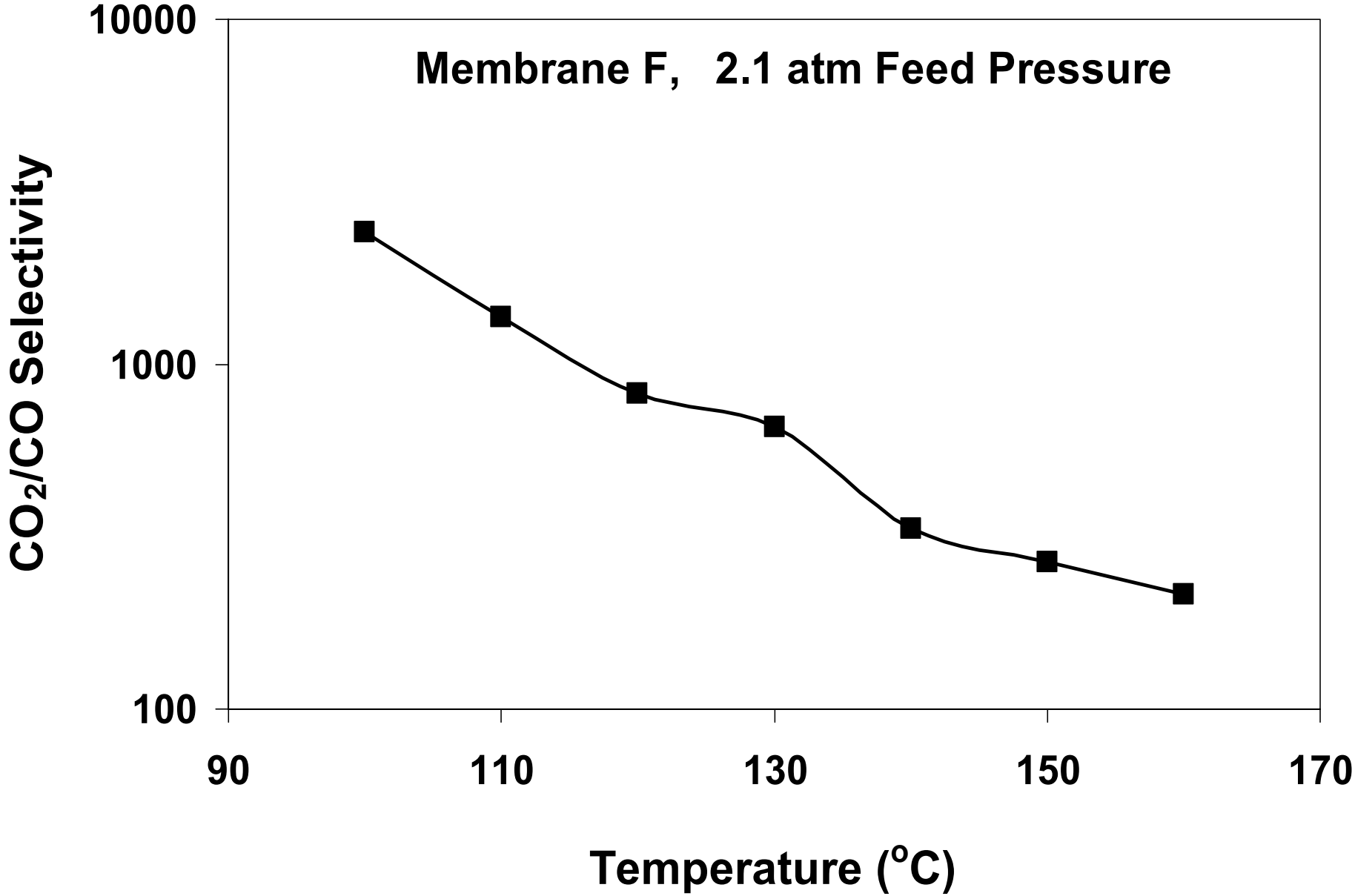
High CO_2 Permeability Obtained



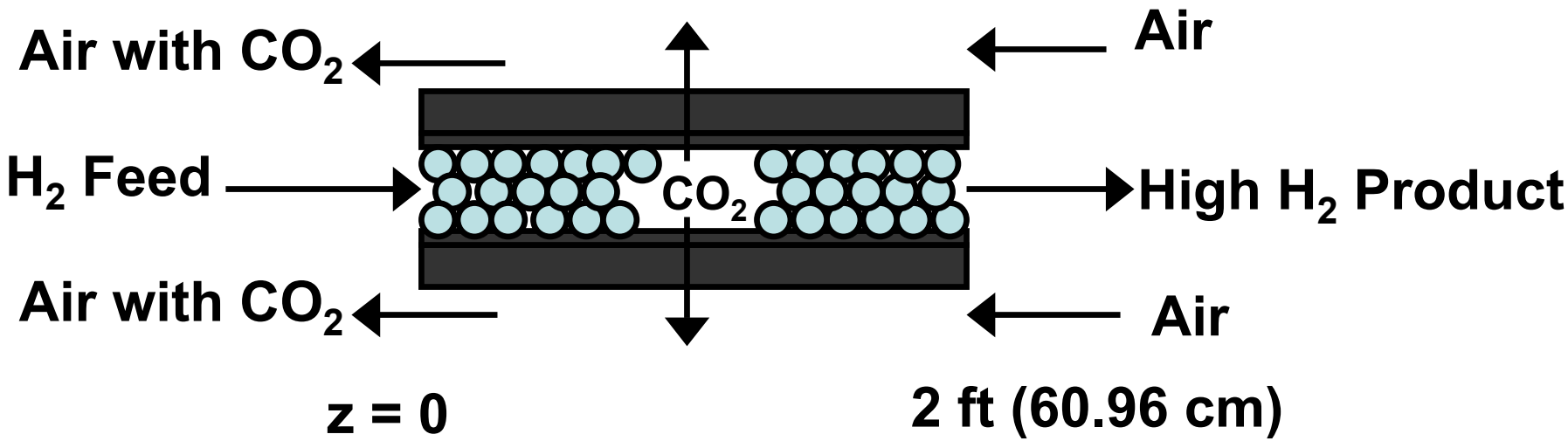
CO_2 Permeability Did Not Change with Pressure Significantly



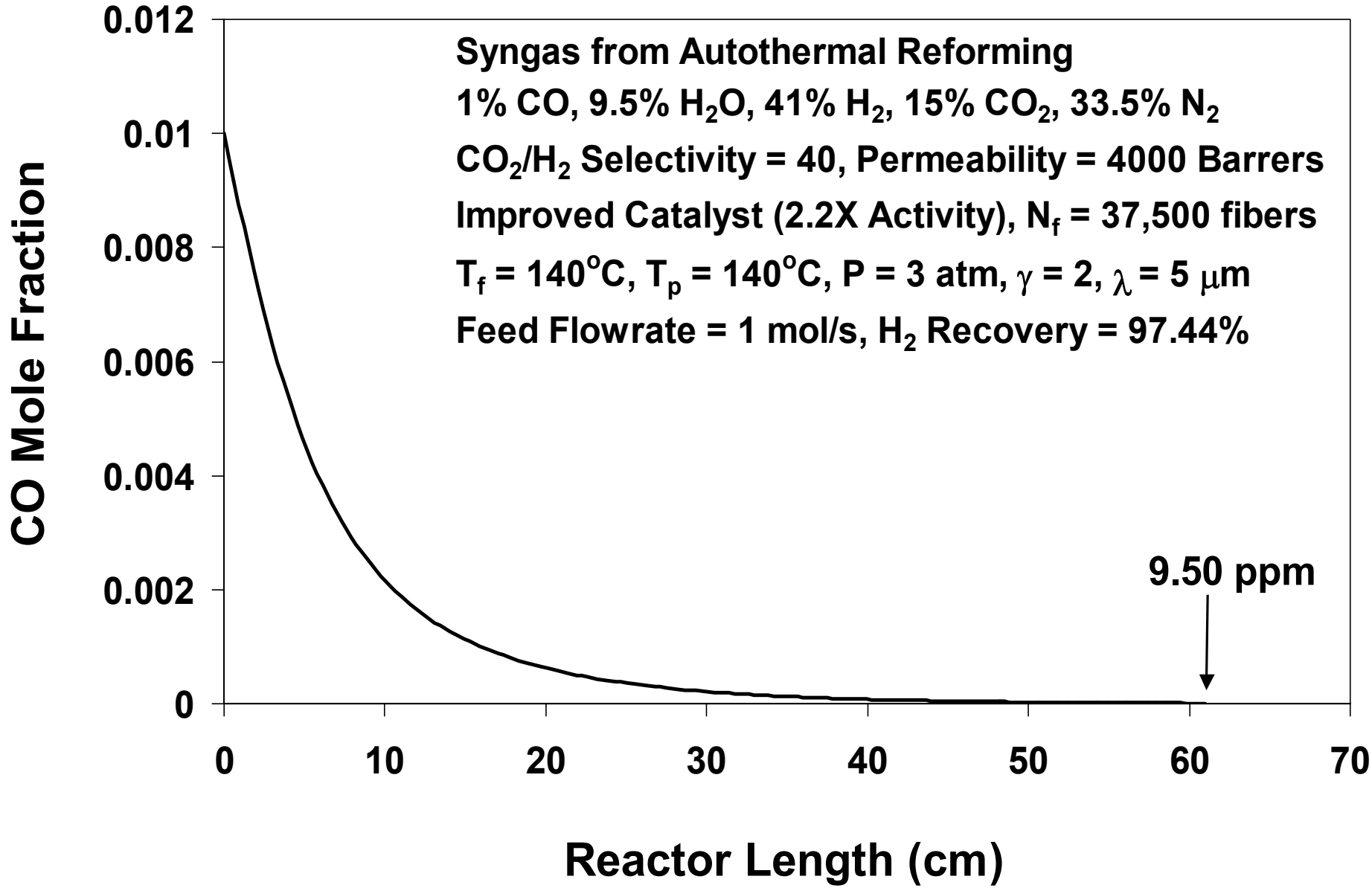
High CO_2/CO Selectivity Obtained



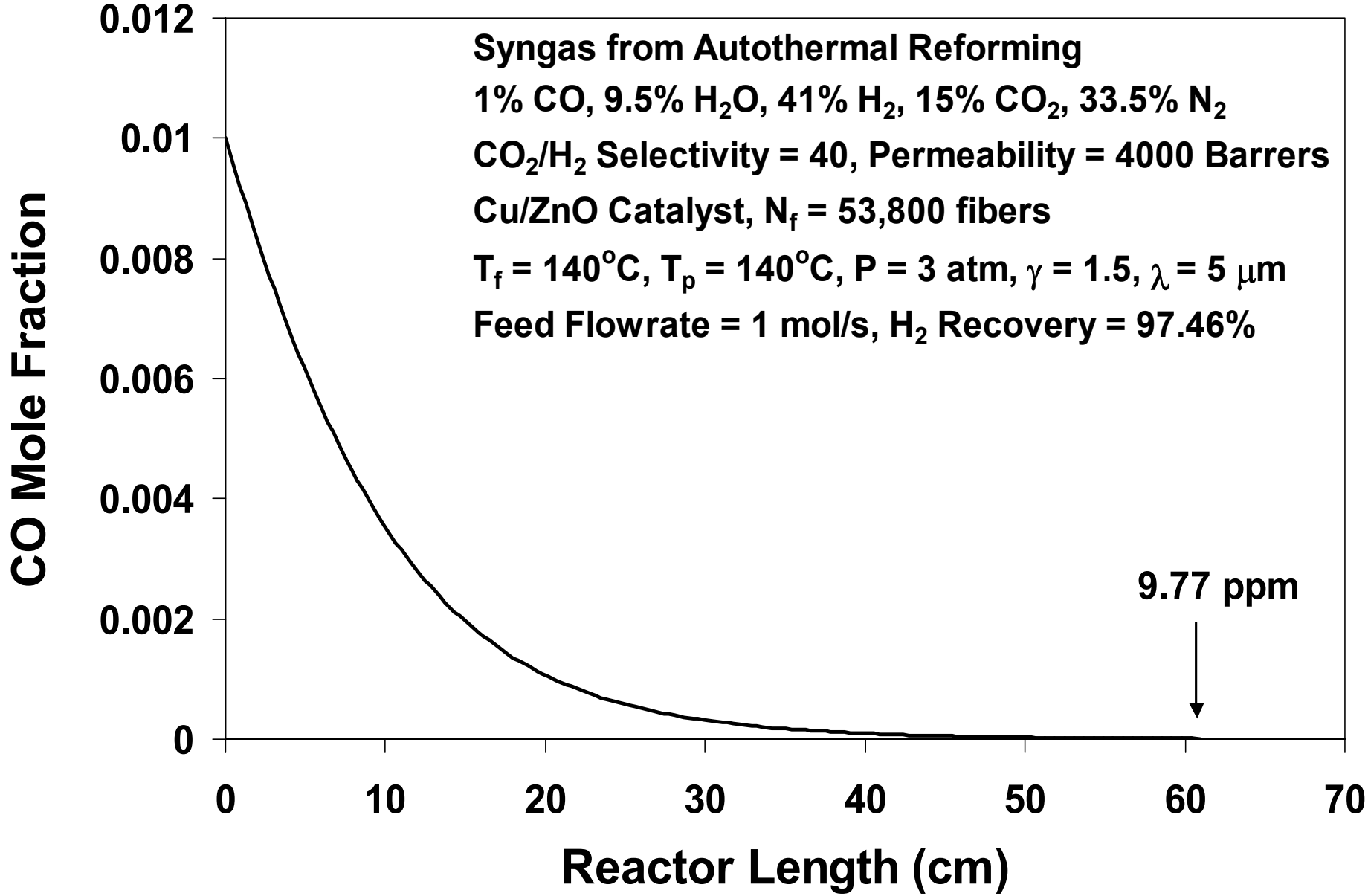
CO_2-Selective Membrane Reactor



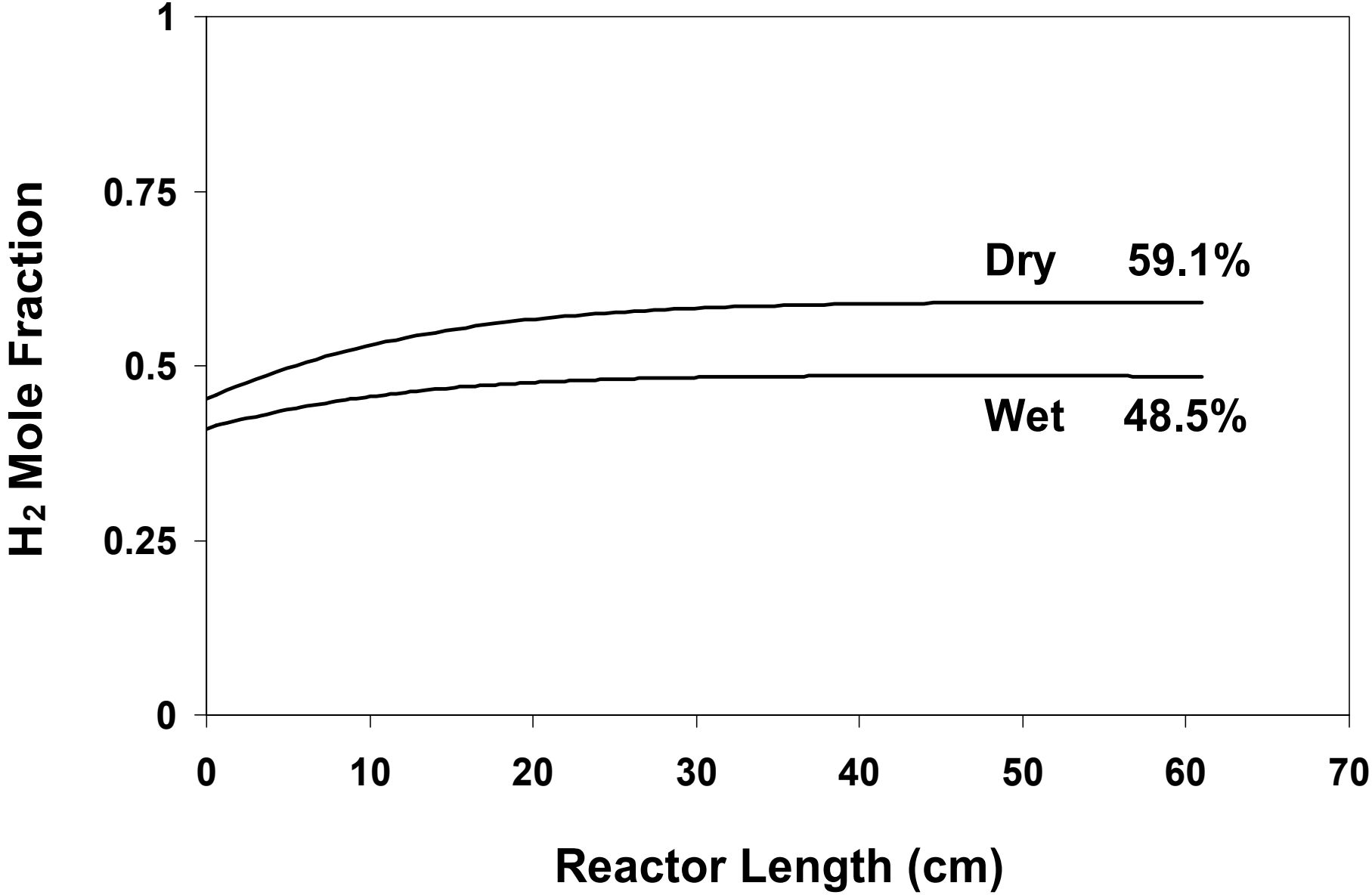
Modeling of Water Gas Shift Membrane Reactor Shows < 10 ppm CO Achievable



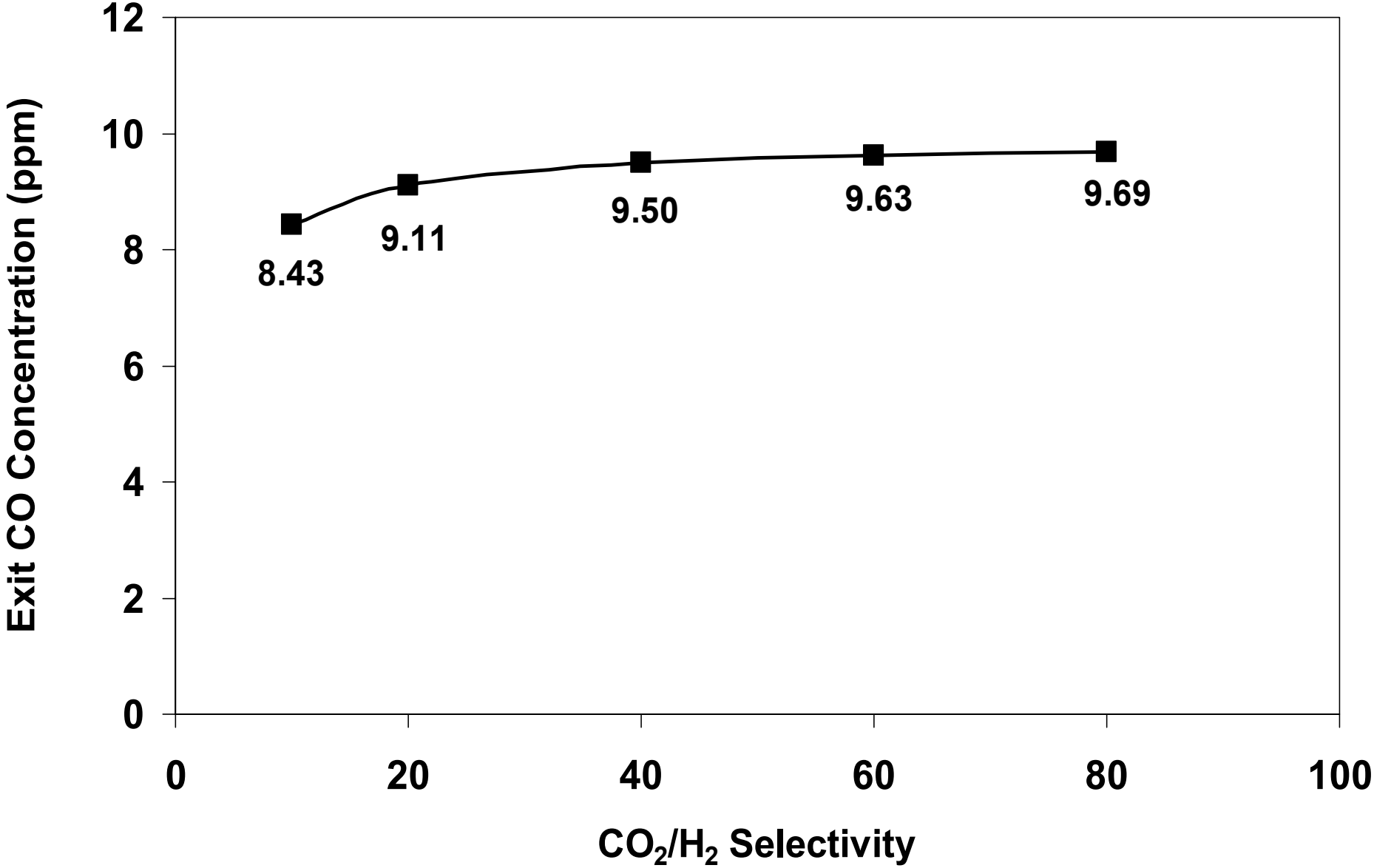
Modeling of WGS Membrane Reactor Shows <10 ppm CO Achievable with Cu/ZnO Catalyst



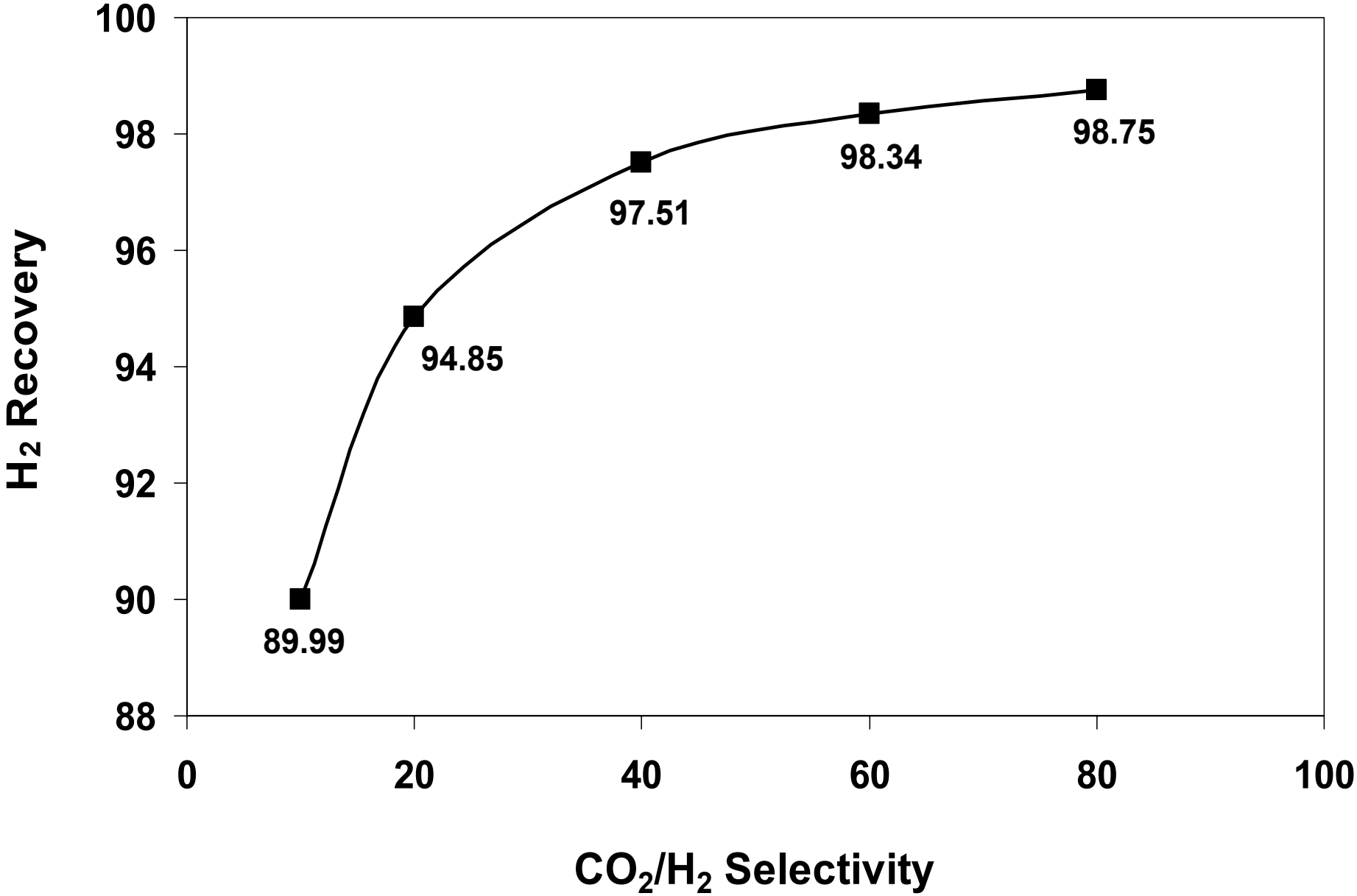
High H_2 Enhancement Achievable



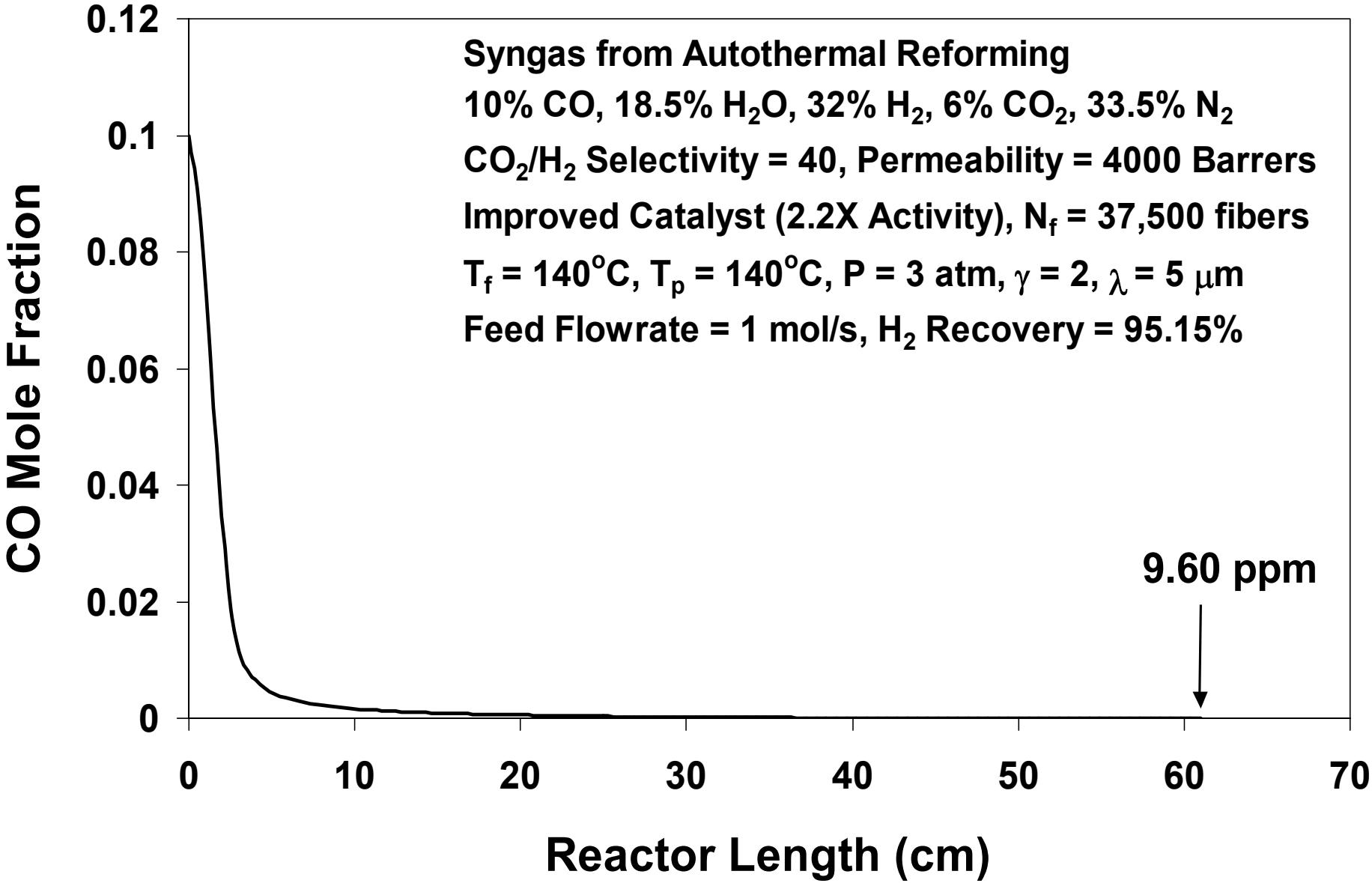
CO_2/H_2 Selectivity Does Not Affect Exit CO Concentration Significantly



CO_2/H_2 Selectivity Affects H_2 Recovery



Modeling Shows < 10 ppm CO Also Achievable for 10% CO Feed



Significant Interactions/Collaborations

- Work with H2fuel / Unitel Technologies / Avista Labs on Membrane Scale-up
  - Successful Scale-up to 40 Inches Wide by ~500 ft Long
  - Membrane Evaluation by Auto Company

- Two Presentations to Freedom CAR Fuel Cell Tech Team

Summary

- **Membranes with High CO_2/H_2 & CO_2/CO Selectivities & CO_2 Flux Synthesized**
- **Modeling Results for Synthesis Gases from Autothermal Reforming Show:**
  - **< 10 ppm CO Achievable**
  - **High CO Conversion Achievable**
  - **High H_2 Enhancement Achievable**
  - **High H_2 Recovery Achievable**

Future Plans

- **Continue to Synthesize / Characterize Membranes with Improved Permeability**
- **Conduct Proof-of-Concept Demonstration**
- **Carry out Prototype Membrane Reactor for Fuel Cell (50 kW)**

On-Board Vehicle, Cost Effective Hydrogen Enhancement Technology for Transportation PEM Fuel Cells DE-FC04-02AL67628

Merit Review and Peer Evaluation
May 19-22, 2003
Berkeley, CA

Mallika Gummalla, Benoit Olsommer, Zissis Dardas, Ying She, T.H. Vanderspurt

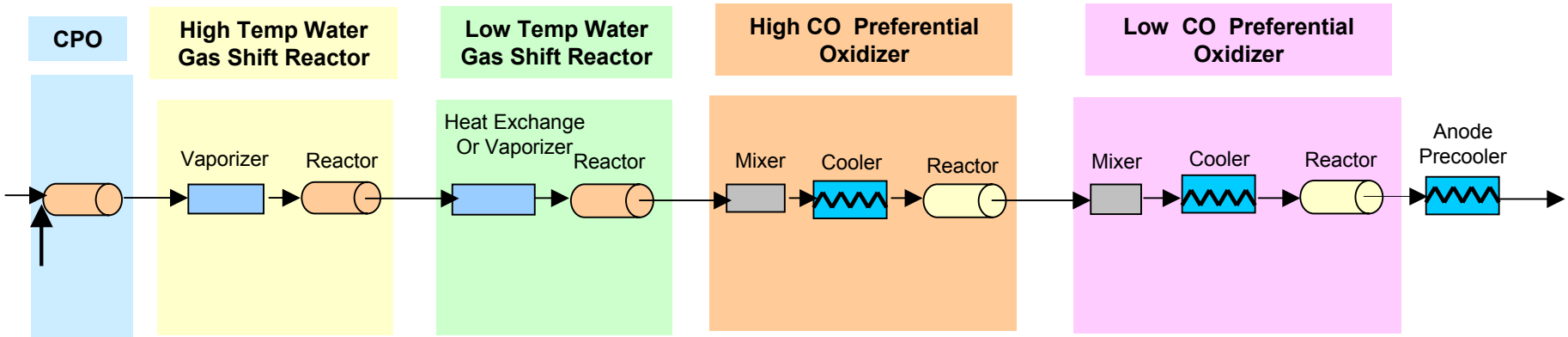
United Technologies Research Center

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe any privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

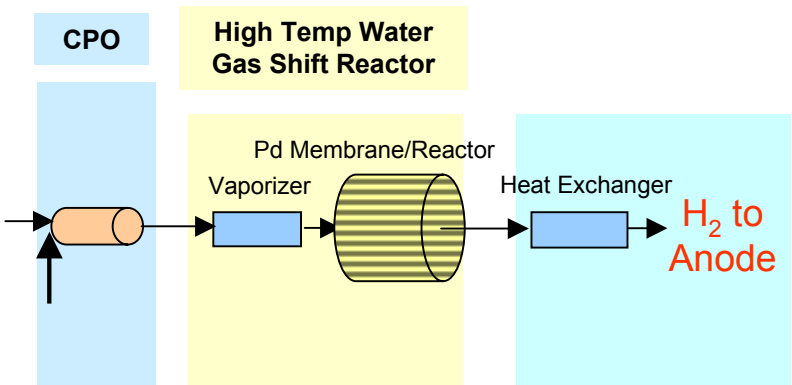
Integrated Pd Membrane Water Gas Shift Reactor

System simplification for size and cost reduction

Non Pd membrane FPS

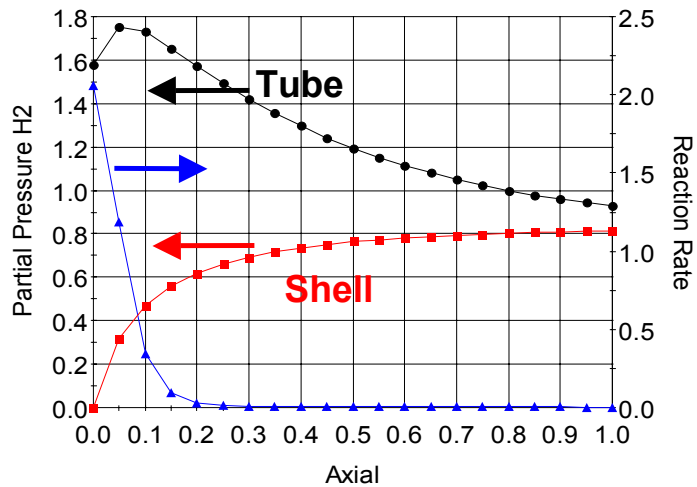


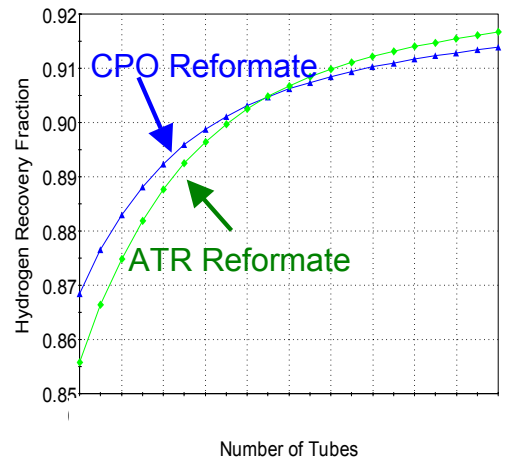
Simplified system

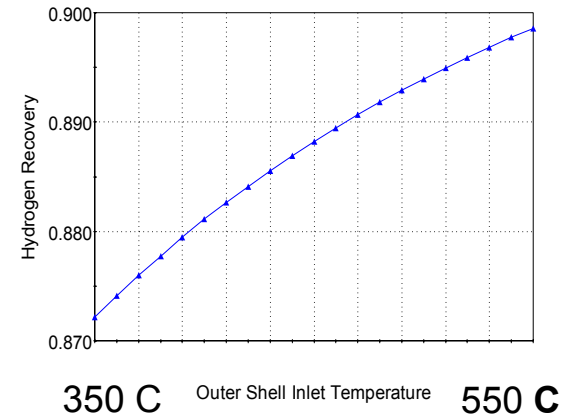


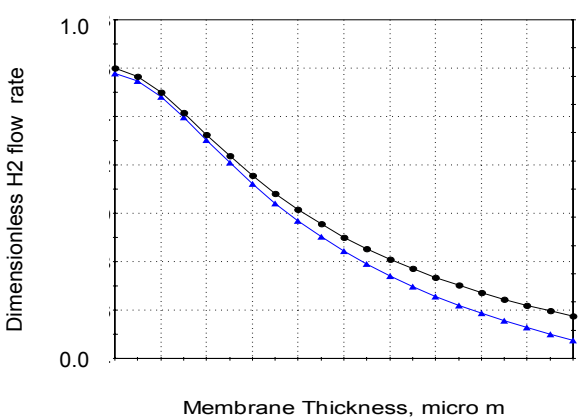
FPS and Membrane Reactor Modeling & Analysis

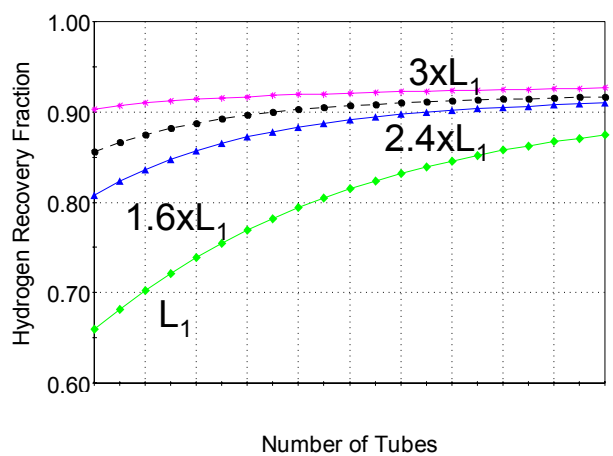
Reactor volume & efficiency is a trade off between differential pressure, membrane area (number of tubes, length) and permeance (Pd thickness)

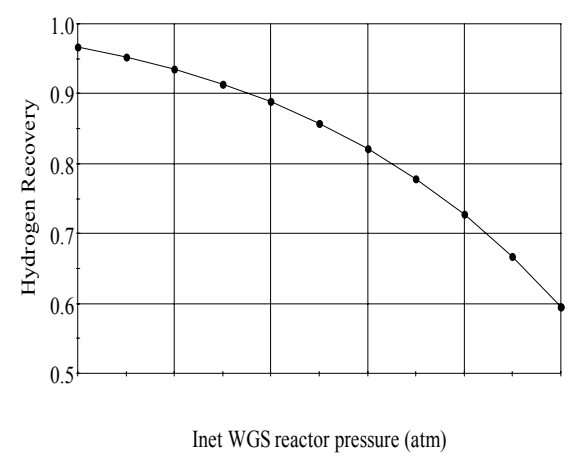






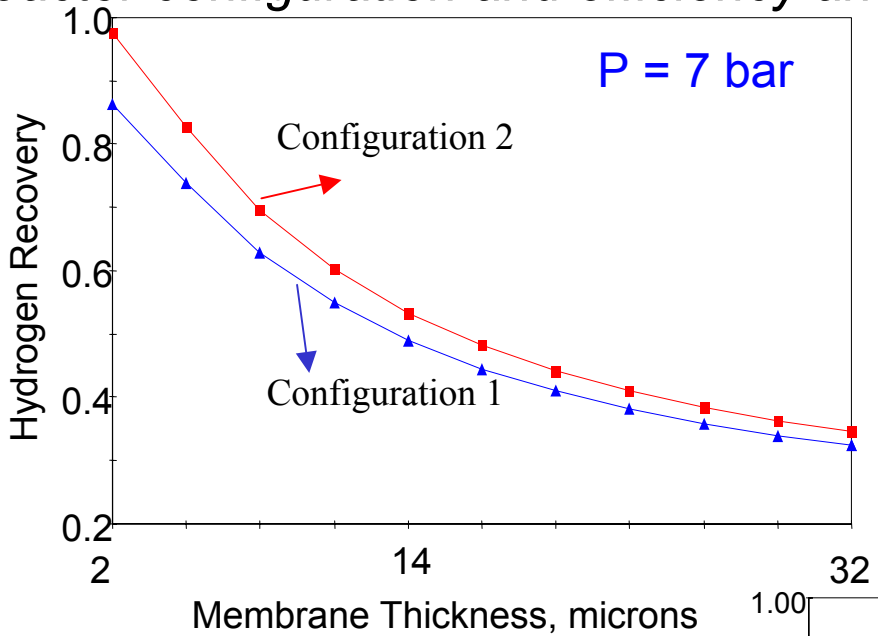






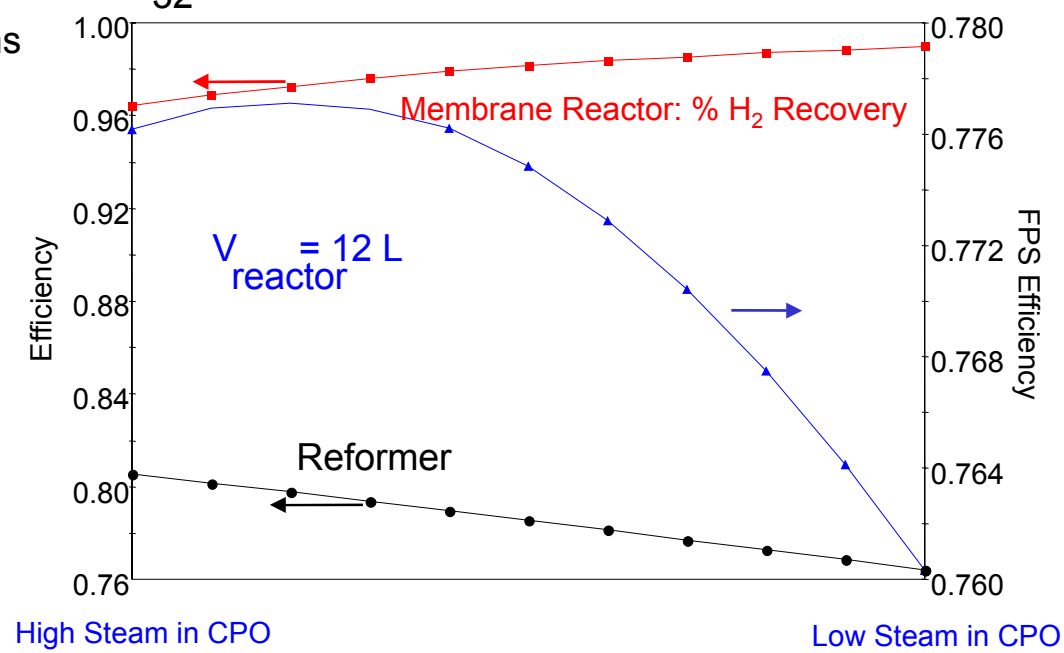
FPS and Membrane Reactor Modeling & Analysis

Reactor configuration and efficiency and FPS efficiency optimized



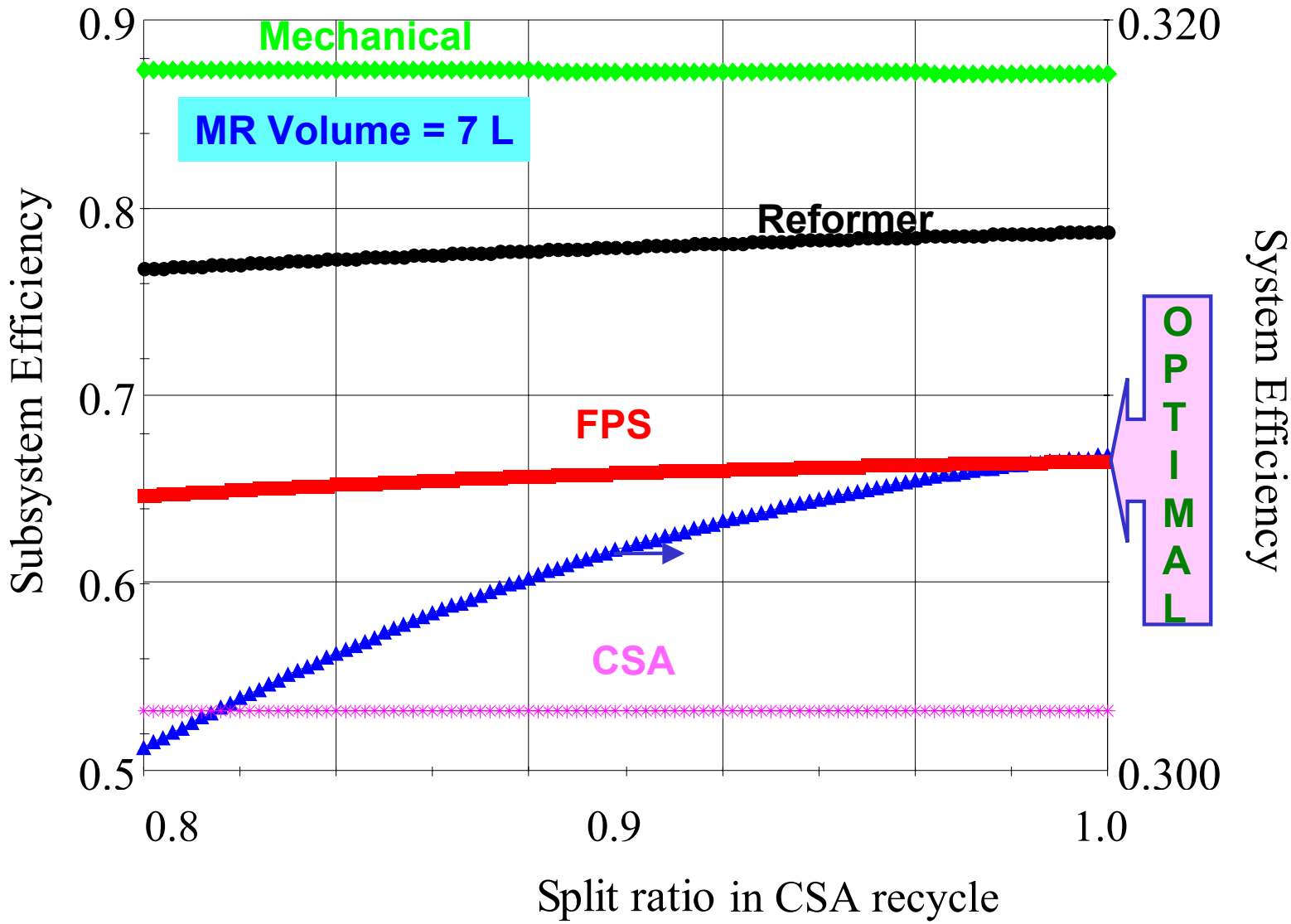
Configuration 2 provides better hydrogen recovery over configuration 1 for similar operating conditions and membrane thickness

For specified reactor volume, maximum reformer efficiency does not translate to optimal FPS efficiency



FPS and Membrane Reactor Modeling & Analysis

Optimum fuel cell system efficiency of 30.8% with ~68% FPS efficiency



FPS and Membrane Reactor Modeling & Analysis

Key Findings

- Adding an expander to the exit of the retentate gas stream from the membrane reactor to drive the air compressor improves mechanical efficiency dramatically (increases by 15 %)

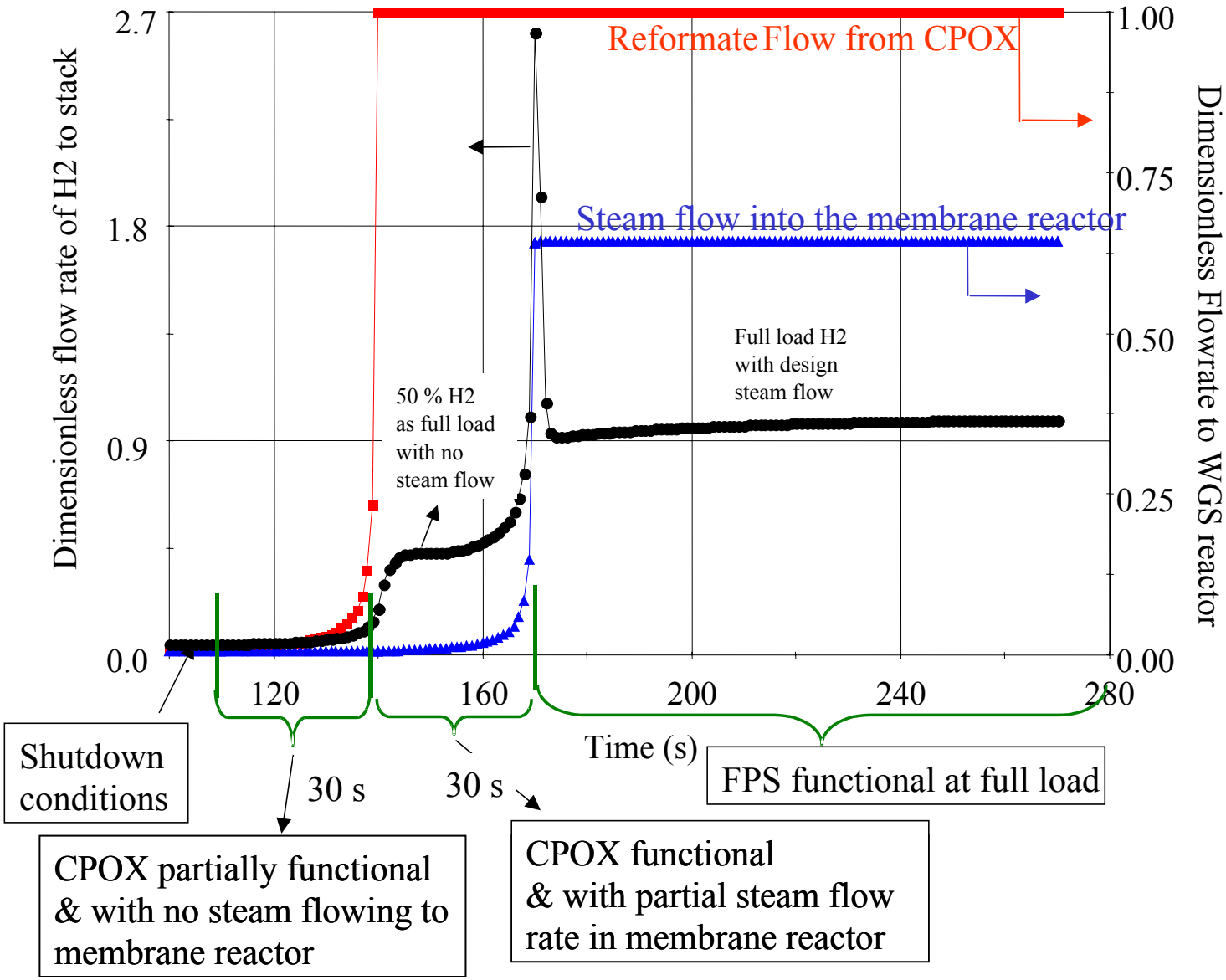
- Optimizing the membrane reactor configuration provides considerable membrane reactor volume reduction (to 7 L) in the system level model when operated “near optimal efficiency” (~30.8%). In order to sustain the power plant, the membrane reactor is forced to operate at lower efficiency (85 %)

- Maximum FPS efficiency does not necessarily imply maximum FC efficiency

- The overall FC system efficiency rather than FPS efficiency should be maximized

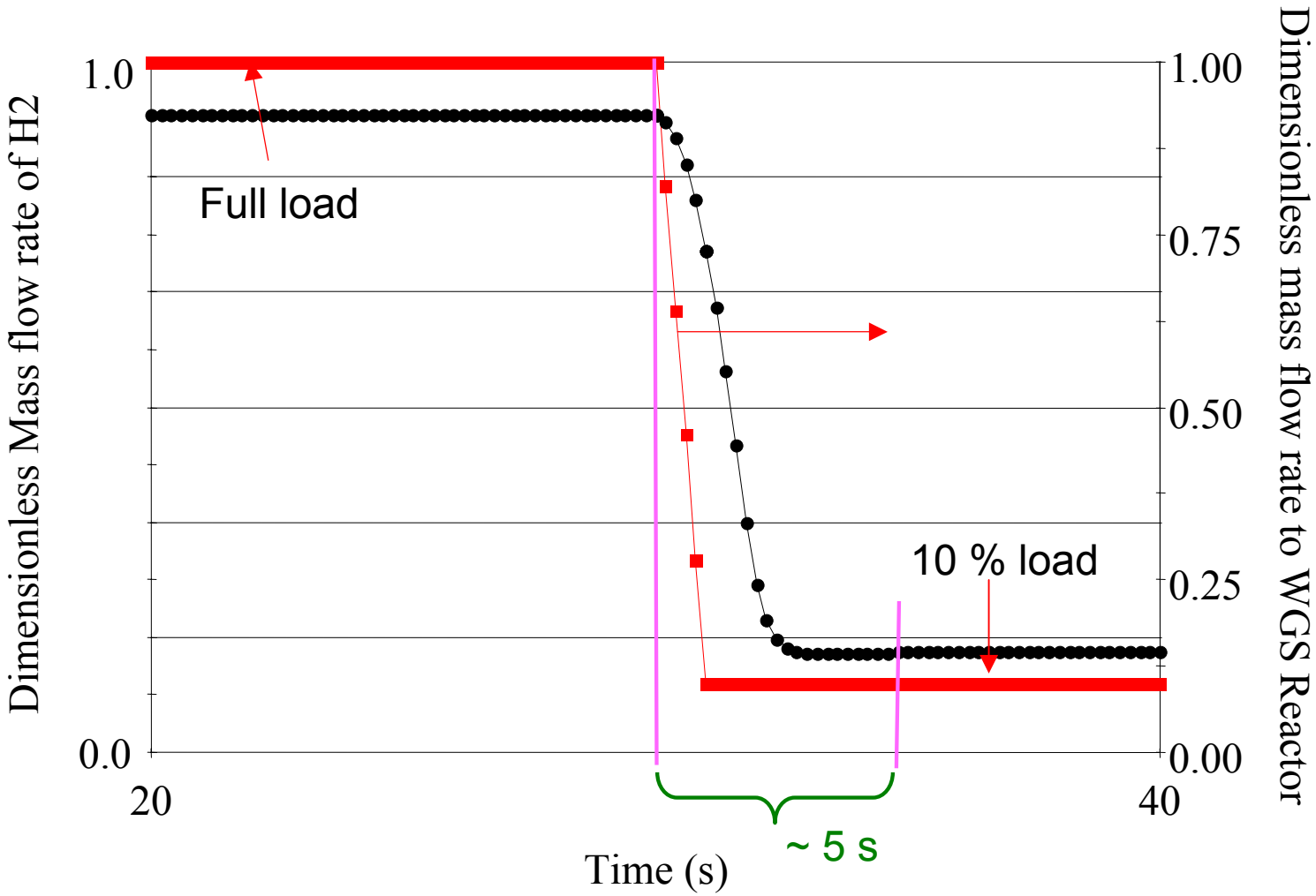
FPS and Membrane Reactor Modeling & Analysis

Startup time of less than 1 min for 50 % of FPS full power



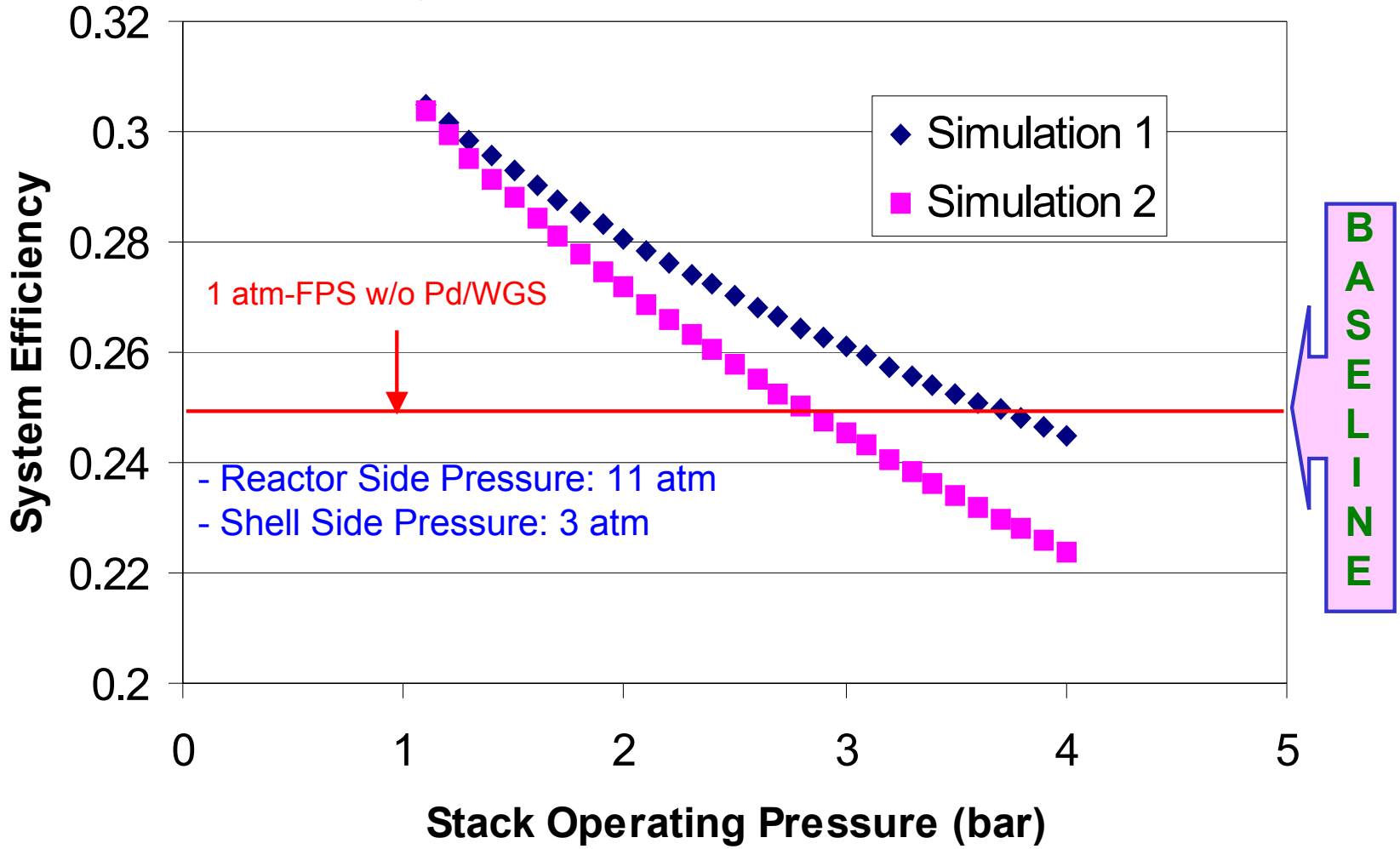
FPS and Membrane Reactor Modeling & Analysis

< 5 sec 90% to 10% down transient for the membrane reactor



FPS and Membrane Reactor Modeling & Analysis

Fuel cell system efficiency is reduced at 3 atm of operating pressure

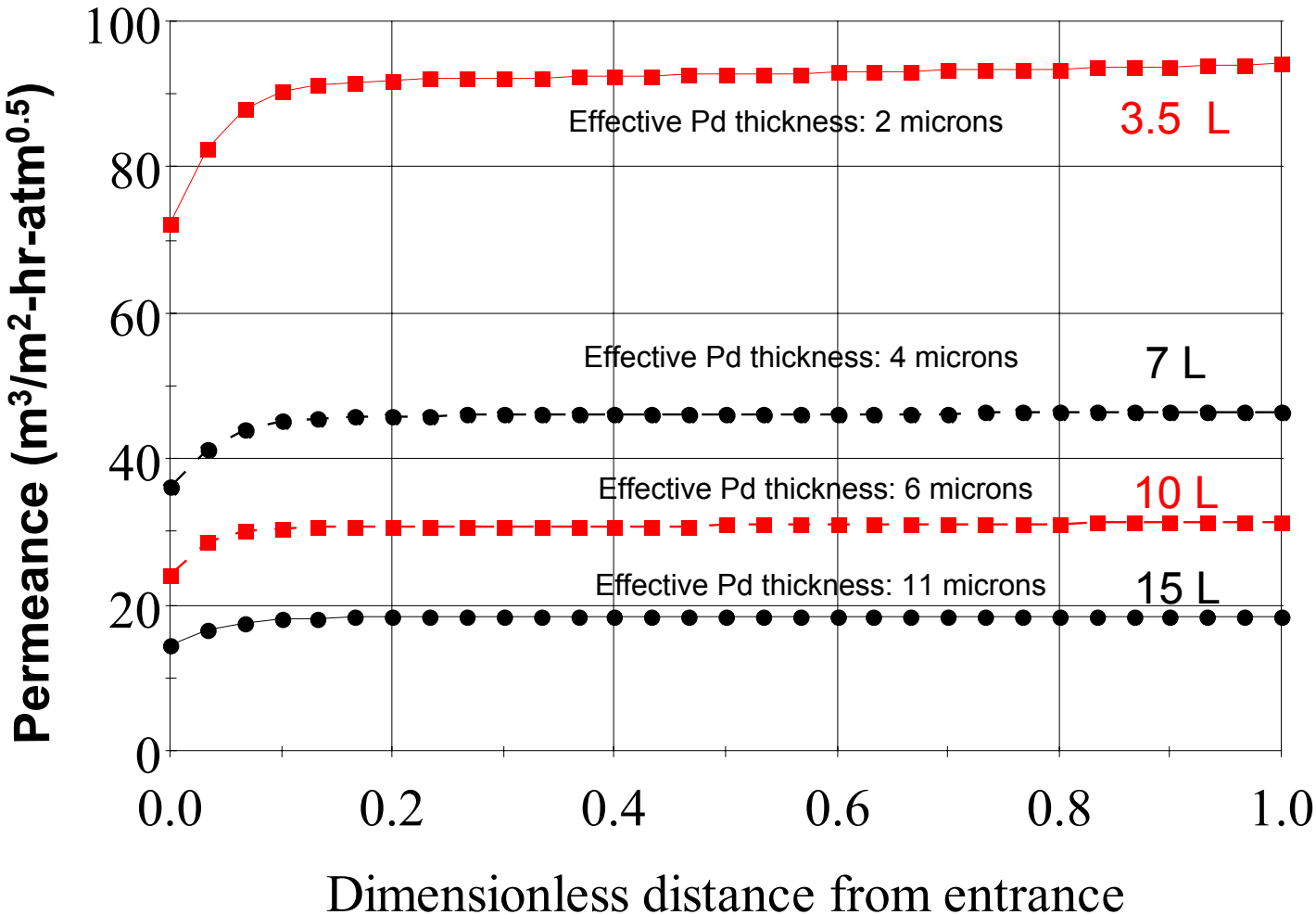


Simulation 1: Very Good compressor/Expander efficiency (0.8)

Simulation 2: Reasonable compressor/Expander efficiency (0.7)

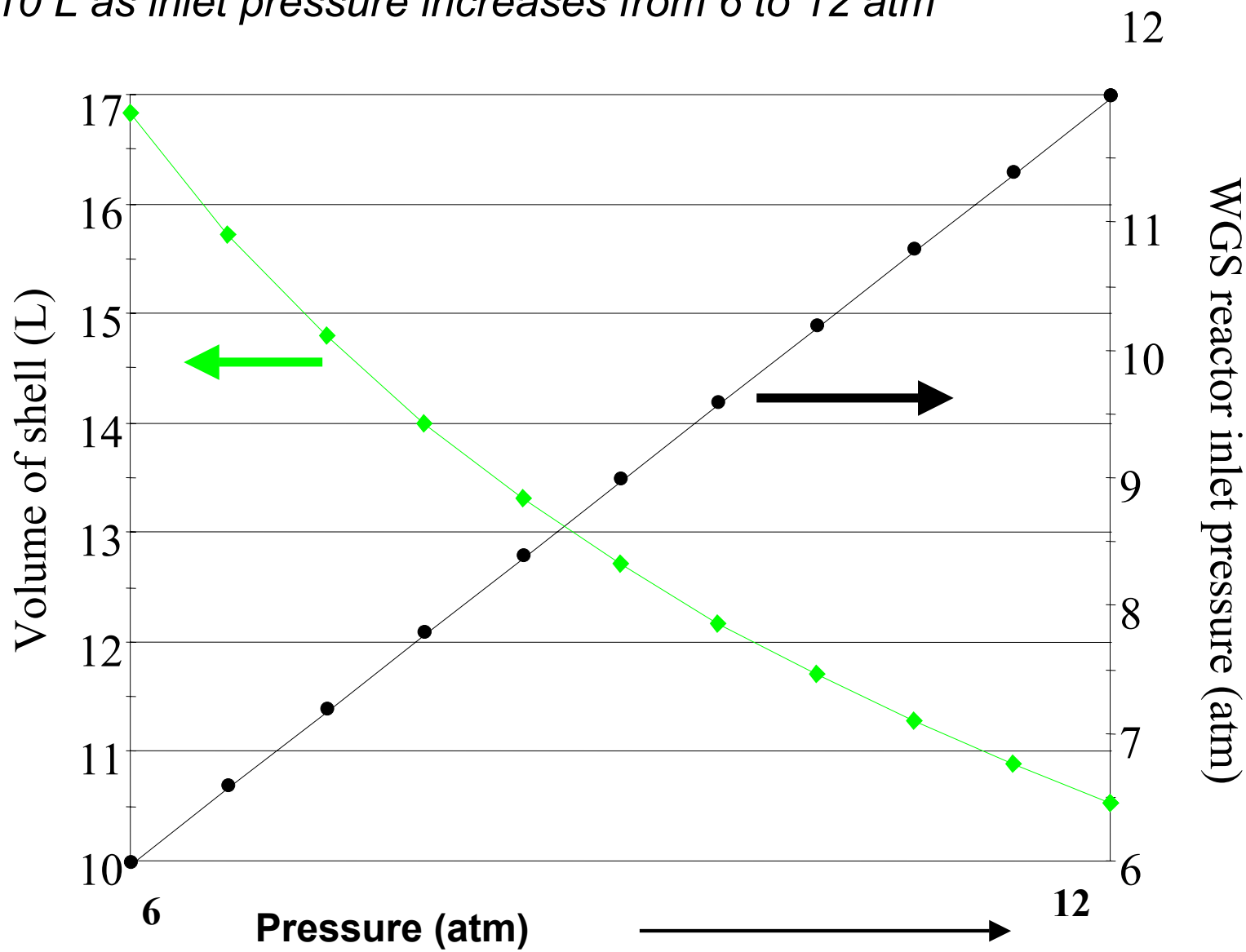
FPS and Membrane Reactor Modeling & Analysis

< 10 L reactor volume with $\eta_{FC\ power\ plant}$=30.8%, η_{FPS}=68% for 6 atm inlet pressure and < 6 microns Pd thickness (> 30 m^3/m^2-hr-$atm^{0.5}$ permeance)



FPS and Membrane Reactor Modeling & Analysis

For permeance of 20 m^3/m^2-hr-$atm^{0.5}$, the reactor volume decreases from 17 L to 10 L as inlet pressure increases from 6 to 12 atm



FPS and Membrane Reactor Modeling & Analysis

Excellent progress made towards DOE system targets

Metric	DOE Target	Non Membrane FPS	Status (04/03)
FPS Efficiency	78%	67%	77.7%
FPS Power Density (with insulation)	> 700 W/L	570 W/L	1100 W/L
H_2 Recovered in Pd WGS Reactor	-	N/A	96%
FPS Cost ($/KW)	25	C	0.4xC + $16/KW
FPS Start Up Time	< 1 min for 33% Full Power (FP)	~ 3 min for < 50% FP (non optimized)	< 1min (~30 sec for Pd/ WGS) for 50% of FP
FPS 10%-90% Transient Response Time	≤ 5 sec	-	< 5 sec for Pd WGS Reactor
PEM Fuel Cell System Efficiency (ambient P)	-	24.7%	30.8%

Based on FPS subsystem

Based on power plant system

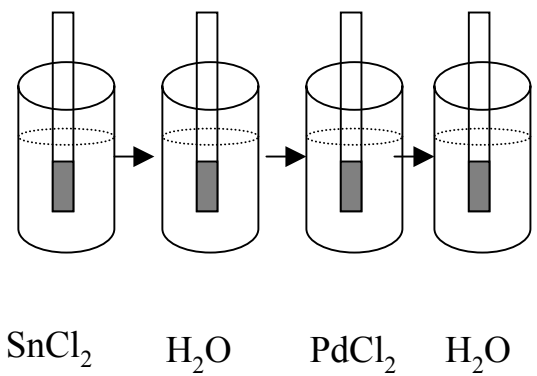
Pd Membranes Synthesis

Electroless plating process (current state of the art)

Activation of the support

Surface of the support seeded with Pd nuclei

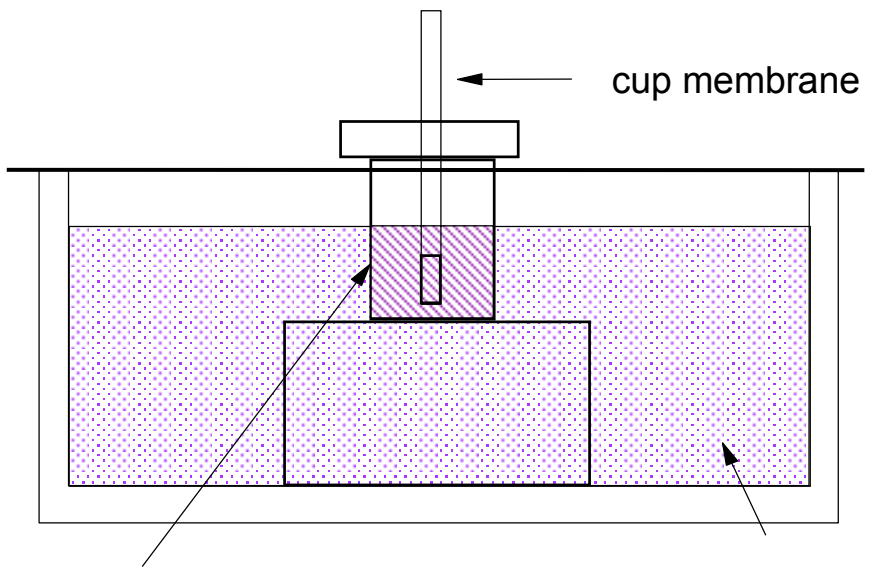
$$Pd^{2+} + Sn^{2+} = Pd^{0} + Sn^{4+}$$



Electroless plating

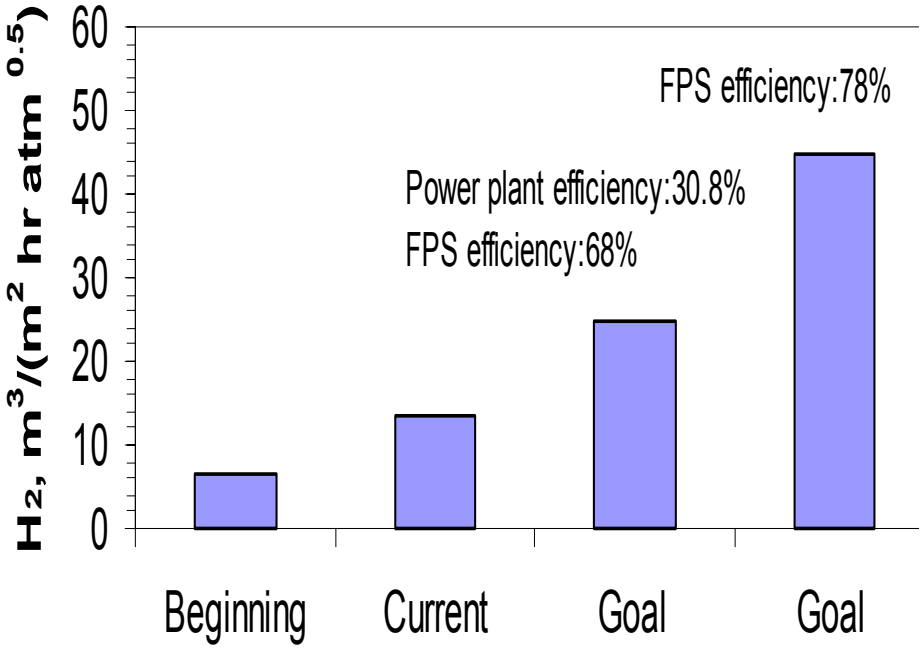
Autocatalyzed reduction of complex on target surface

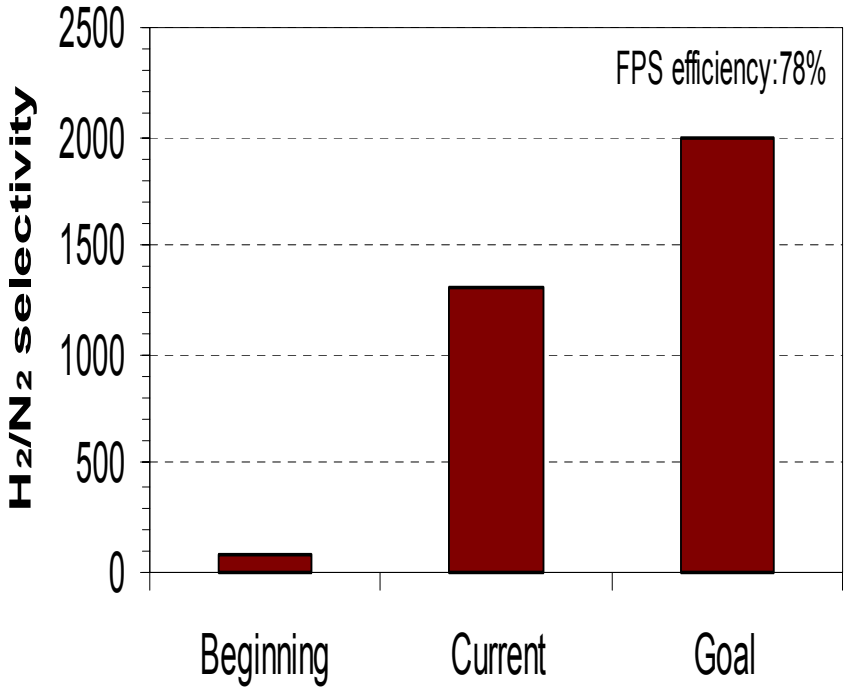
$$2Pd^{2+} + H_2NNH_2 + 4OH^- = 2Pd^0 + N_2 + 4H_2O$$



Pd Membranes Synthesis

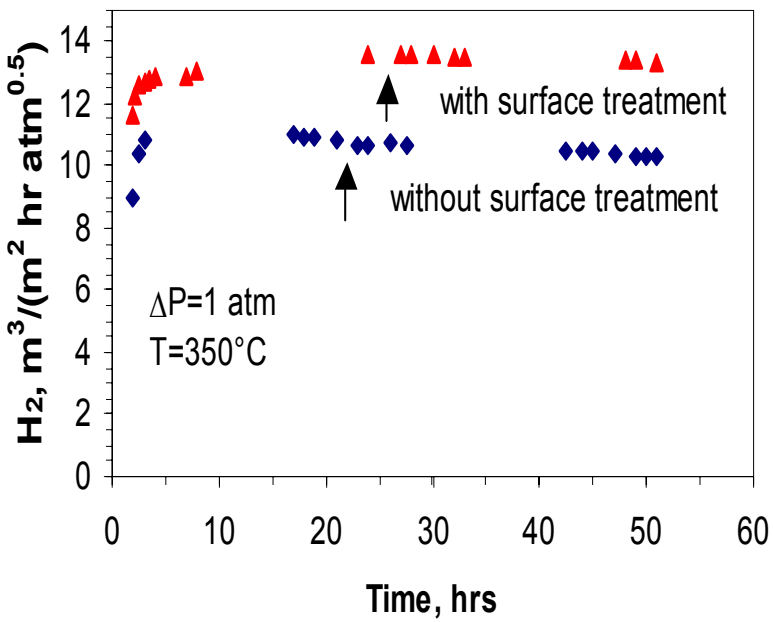
Significant progress made on both permeance and selectivity. On trajectory to achieve project goals

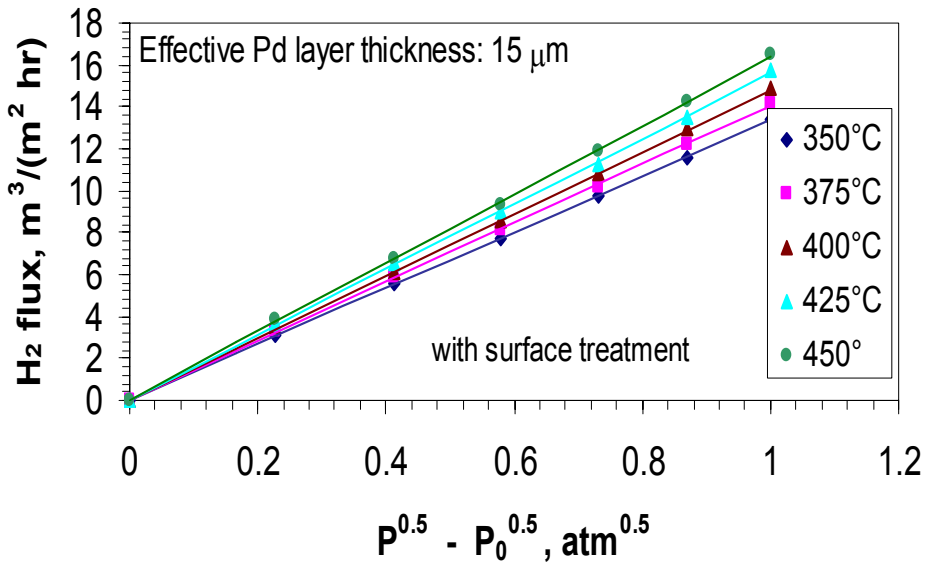




Pd Membranes Synthesis

Surface treatment enhances Pd membrane H_2 permeance. Process not optimized



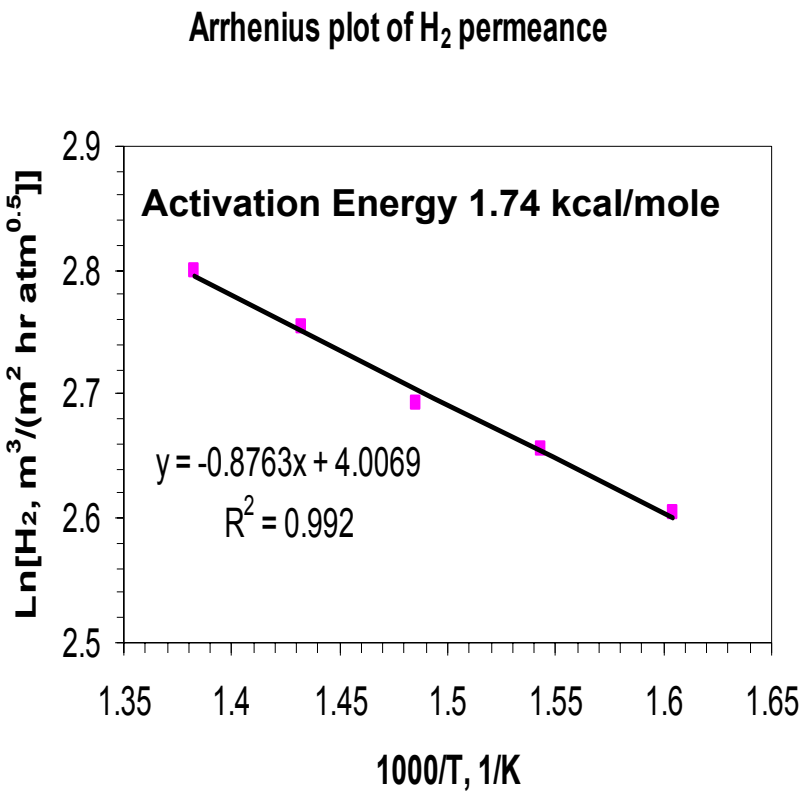


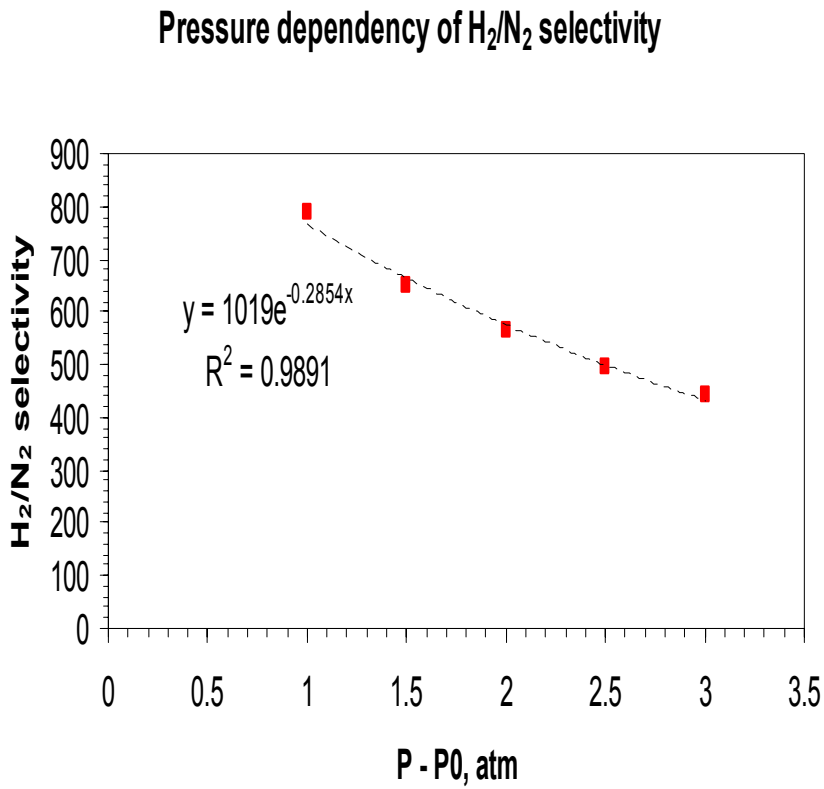
<u>H_2/N_2 selectivity:</u>

- 1100 without surface treatment
- 800 with surface treatment

Pd Membranes Synthesis

Temperature has a weak effect on permeance but pressure has an adverse effect on selectivity





Summary of Accomplishments

- Pd membrane WGS reactor optimized for H_2 recovery efficiencies between 85-96%

- Optimum FPS (77.7%) and PEM fuel cell power plant system efficiency (30.8%) identified

- Excellent progress made towards DOE FPS volume, start up, transient response and cost targets

  - ❑ Simulated Pd Membrane/WGS FPS: 1100 W/L, < 1 min for 50% full power, 5 sec 10%-90% transient response and $16/kW +0.4x(Cost of FPS w/o Pd) projected cost

- Optimum FPS efficiency does not correspond to optimum PEM FC power plant efficiency

- Significant progress made on synthesis of Pd membranes on both H_2 permeance and Selectivity

  - ❑ Current Status: 13.5 m^3/m^2-hr-$atm^{0.5}$ H2 permeance @ 350 ^oC & 800 selectivity at 1 atm of differential operating pressure

- On track to achieve the aggressive project goals with a Pd alloy: 2x-3x increase in permeance, 2,000 selectivity at 1 atm of differential operating pressure

Future Work

Targeted to increase membrane H_2 permeance by 2x-3x and selectivity by > 2x on a Pd alloy membrane

- Synthesize Pd membranes on internal surface of PSS substrate
- Synthesize Pd membranes on smoother external surface of PSS substrate.
- Seek PSS substrates with narrow pore size distribution
- Seek a PSS substrate tube coated on the internal surface with a ceramic-coated layer of 0.02 – 0.1μm pore size
- Alternative intra-pore Pd deposition process development
    - ❑ Decision point: Select best approach (10/30/03)
- Synthesize Pd alloy membranes (Start: 05/15/03)

2003 Milestones

Stated milestones represent significant stretch

Requirement	Project Goals	Calendar Year 2003 Goals (12/20/03)	Current Status
H_2 Permeance at 350 ^oC (in m^3/m^2-hr-$atm^{0.5}$) with a Pd Alloy	25-45	25	13.5 with pure Pd
Maximum Equivalent Pd Phase Thickness	< 5 microns	< 8 microns	15 microns
H_2/N_2 Selectivity at 350 ^oC and differential operating pressure of: - 1 atm - 6 atm	2,000 500	1,000 250	~200 (Projected from Data between 1-3 atm) ~ 800 ~ 180 (Projected from Data between 1-3 atm)
Membrane Module Life Testing under HT WGS Conditions	5% Performance loss for 400 hrs & 100 Start Up/Shut Down cycles	10% Performance loss for 150 hrs & 10 Start Up/Shut Down cycles	

Key Technical Barriers

Significant technical barriers must be overcome to demonstrate (critical risk reduction) and commercialize this technology

- Achieving a pin hole -“free”, thin (< 5 microns) Pd alloy, metal-supported membrane that will withstand up to 1,000 start up/shut down cycles for 4,000 hrs with < 25% performance deterioration in a reformate (high CO) gas environment

- Identification of a cost-effective route to commercialize Pd alloy metal supported membranes for mass production

NUVERA
FUEL CELLS

Advanced High Efficiency, Quick Start Fuel Processors for Transportation Application

Prashant S. Chintawar and Christopher O'Brien
Nuvera Fuel Cells, Inc.
35 Acorn Park
Cambridge, MA 02140

Agenda

- STAR™ (1999-2003)
  - Substrate based Transportation application Autothermal Reformer
- HiQ (2001-2005)
  - High Efficiency Quick Start Transportation Fuel Processor

STAR Program Overview

Mission Statement

Building on Nuvera's past experience, develop an automotive multi-fuel processor which will meet or exceed FreedomCAR targets (efficiency, power density, durability, etc.)

Technical Approach

Replace conventional pelleted catalysts and heat exchangers with compact and low thermal mass substrate (monolith, foam, reticulate) based media

Program Overview

- Four year R&D program (1999-2003)
- Subcontractors: SudChemie, Inc.; Corning, Inc.; STC Catalysts, Inc.
- Deliverables: STAR automotive fuel processor to Argonne National Lab

STAR Program Activities

Period	Activities	Accomplishment
1999-2001	Component R&D -Substrates -Monolithic catalysts -Compact heat exchangers -Desulfurization technology	All substrate-based catalysts - ATR, HTS, LTS, PROX, TGC
2001-now	Integrated FP and FCPS -Design of STAR fuel processors -Fuel processor construction and gasoline testing -Integration of STAR FP and Nuvera's PEM FC -Controls development	Over 10X reduction over previous design fuel processor

STAR Fuel Processor

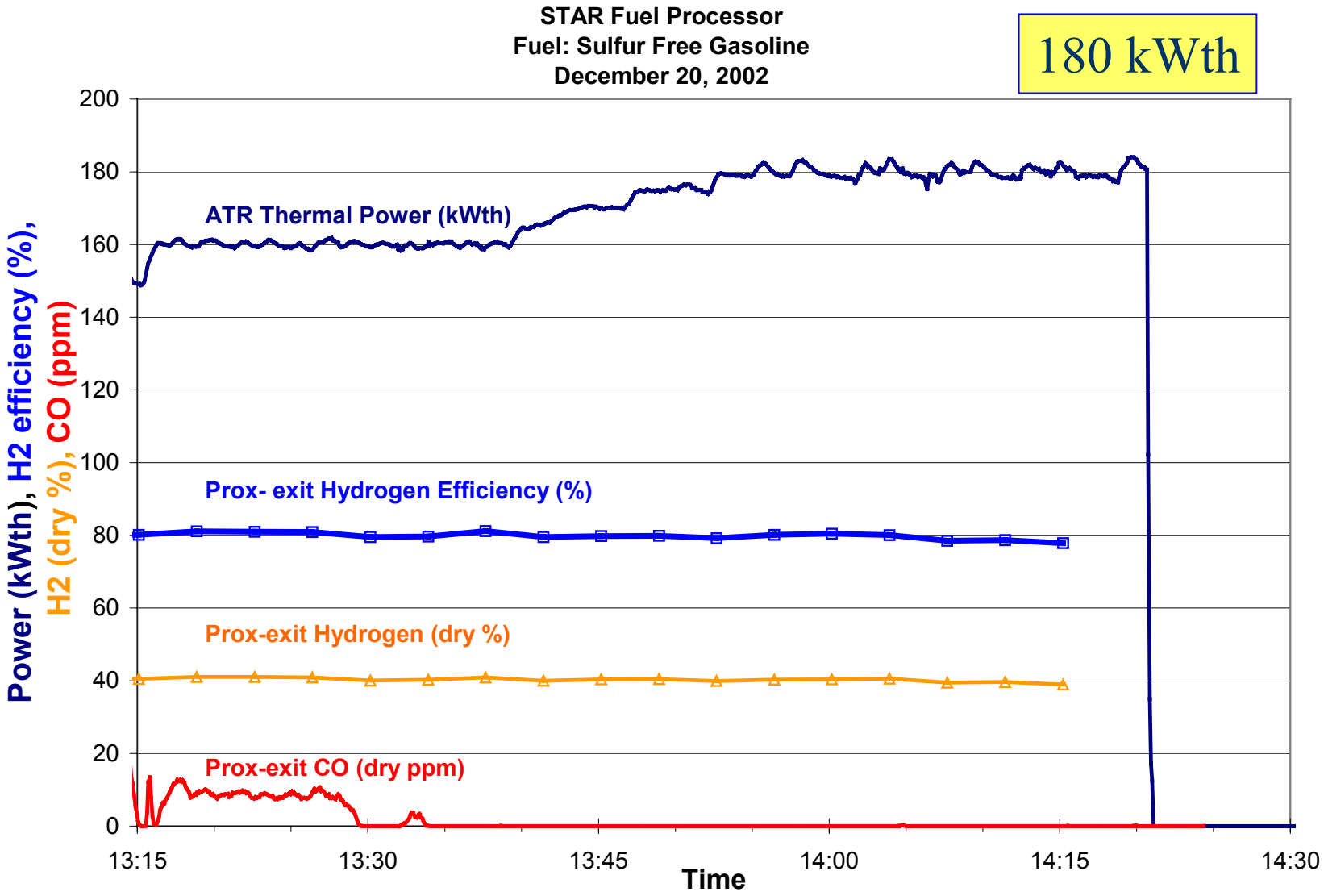
- Autothermal reformer
- Substrate-based catalysts (no pellets)
- 200 kWth input
- Automotive volume (~75 liters)
- Design focus on gasoline
- Under-vehicle “flat” aspect ratio
- Modular, serviceable design

STAR Program Highlights

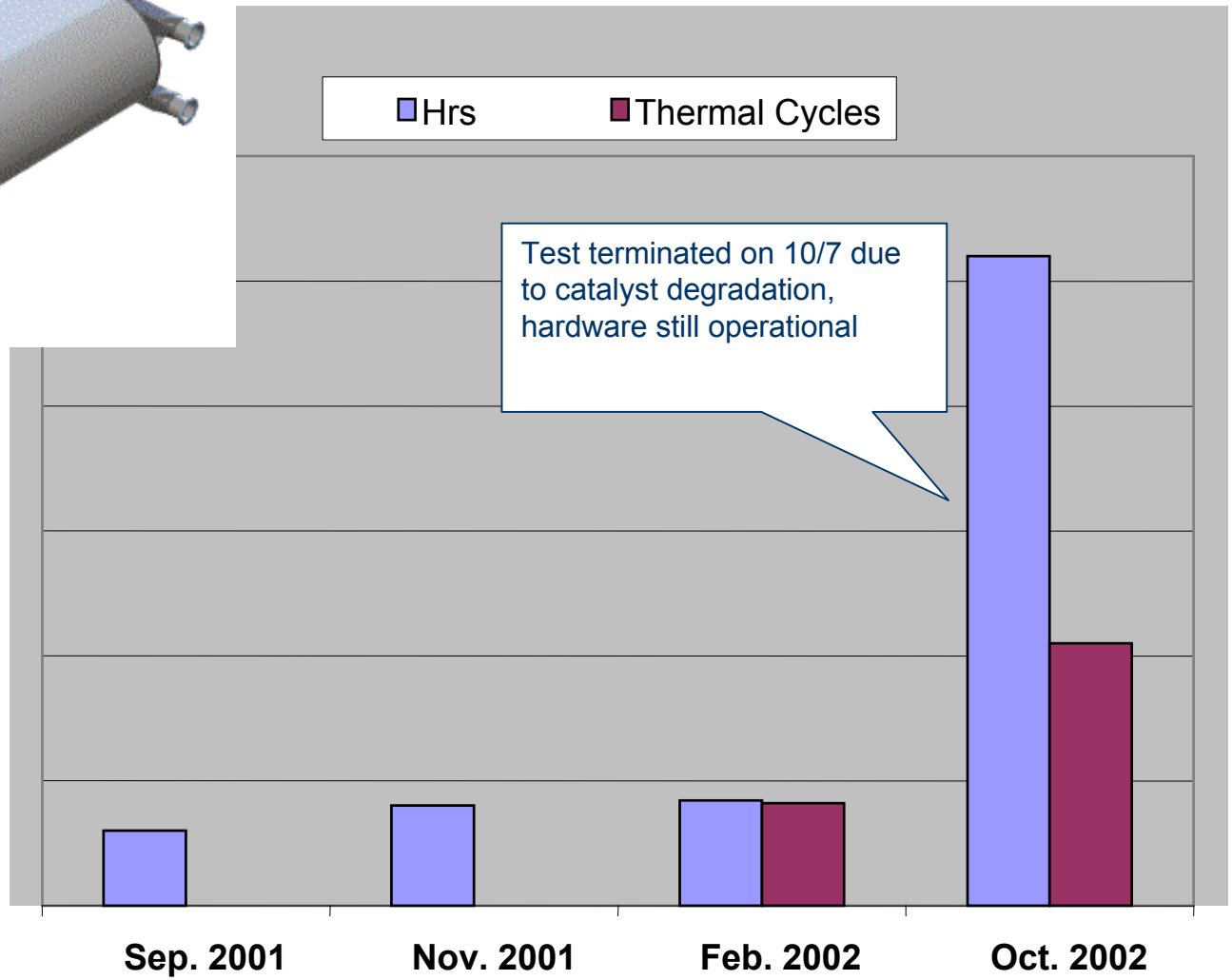
- **Meets or exceeds several fuel processor targets**
  - High power density -75 liters and 200 kWth gasoline feed rate
  - Efficiency - 80% hydrogen efficiency
  - Reformate quality - undetectable ammonia, CO < 10 ppm
  - Packaged for auto application

- **Successfully integrated with Nuvera's PEM fuel cell**

STAR Test Data (Gasoline)



Durability Improvement



Other STAR Highlights

- **Rapid development process**
  - Built and tested six design iterations
- **Design improvements in many areas**
  - Thermal Stress
  - Serviceability
  - Mixing
  - Heat Exchange
  - Thermal Integration
- **Controls Development**
  - Automated Startup
  - Custom Control System

STAR Status in 2003

Specification	2005 Target	STAR
Energy Efficiency	78%	80%
Power Density	700 W/L	➡
Specific Power	700 W/kg	640
Cost	25 $/kWe	TBD (➡)
Start-up Time	<1.0 min	➜
Transient Response	5 sec	TBD
Emissions	< Tier II	➡
Durability	4000 h	TBD
CO in Product	<10 ppm	➡
H2S in Product	<50 ppb	➡
NH3 in Product	<0.5 ppm	➡

2003 STAR Plans

- Continue characterization on gasoline - Q2
- Demonstrate multi fuel capability (ethanol and natural gas) – Q3
- Prepare system for Argonne National Laboratory delivery – Q3
- Support operation at ANL – Q4
- Submit Final Report – Q4

HiQ Program Overview

Mission Statement

- Design, develop and test a high power density, multi-fuel fuel processor system that enables high efficiency and quick start operation of an integrated fuel cell power system for automotive applications

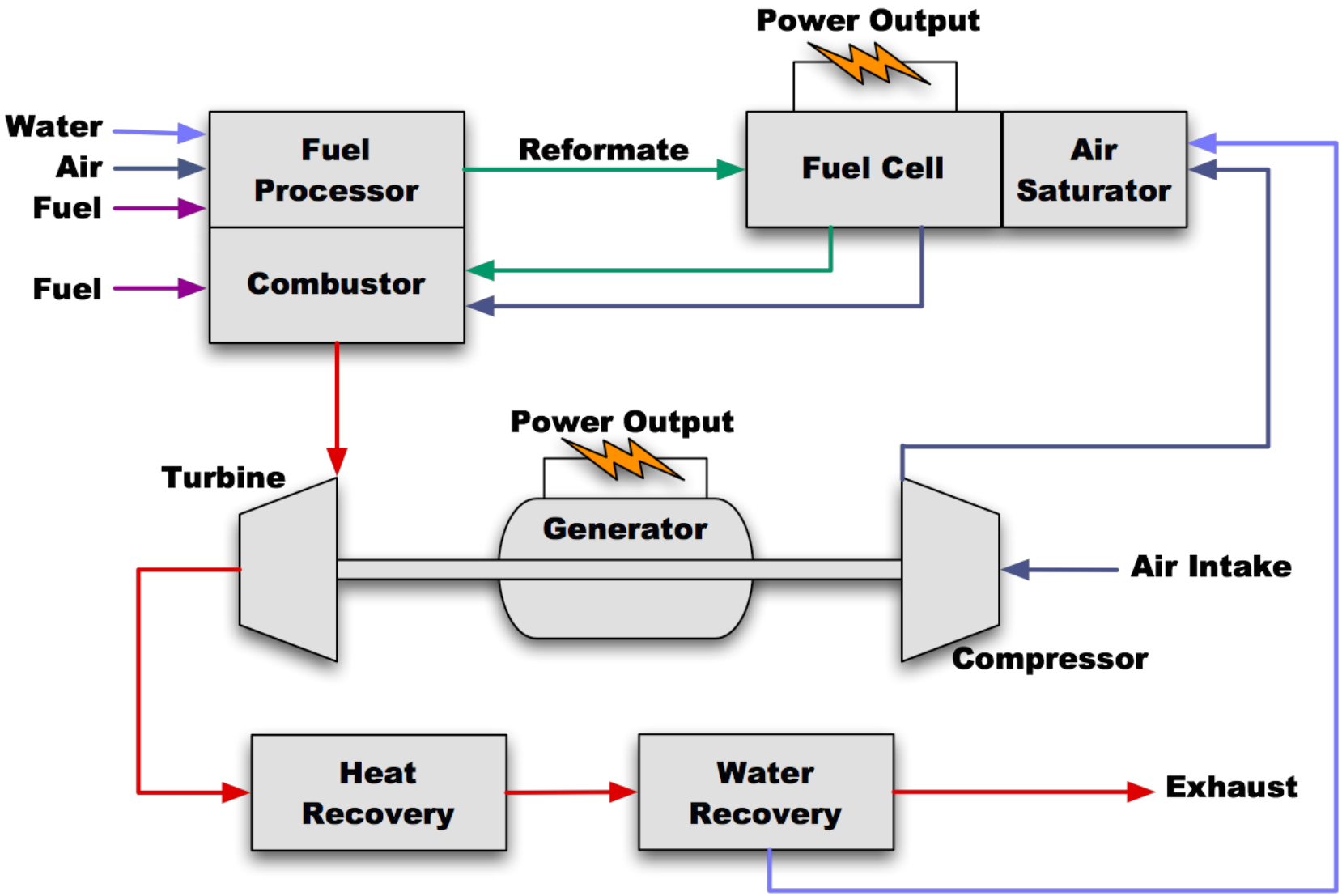
Technical Approach

- Integrate fuel processor with a turbo-generator system to recover waste energy from stack and provide capability for rapid start to low power levels

Program Overview

- Four year R&D program (Oct. 2001 - Oct. 2005)
- Subcontractors: Engelhard Corp. (catalyst and membrane development)
  Worcester Polytechnic Institute (catalyst kinetics)
- Deliverables: Complete automotive fuel processor to Argonne National Lab

HiQ System Concept



Main Advantages of Hybrid Design

- **Significantly higher net system efficiencies**
  - Stack "waste heat" is converted into useful work
  - Rankine cycle adds sufficient power to turbine to create net power output from turbine - compressor system
  - Brayton cycle is also made more effective via turbine
  - Best performance with elevated stack temperatures (~90 °C)
- **Use of existing automotive-type compressor-expander**
  - Higher efficiency than reciprocating or low-T compressor-expanders
  - Low cost, proven durability
  - Limits system size to > 50 kW_e (smallest available turbines)
- **Reduced radiator size**
  - Lower heat duty due to efficiency improvement
  - Higher LMTD due to high exhaust dew point
- **"Instant" startup to low power output**
  - Turbo-generator / burner can produce power very quickly without stack

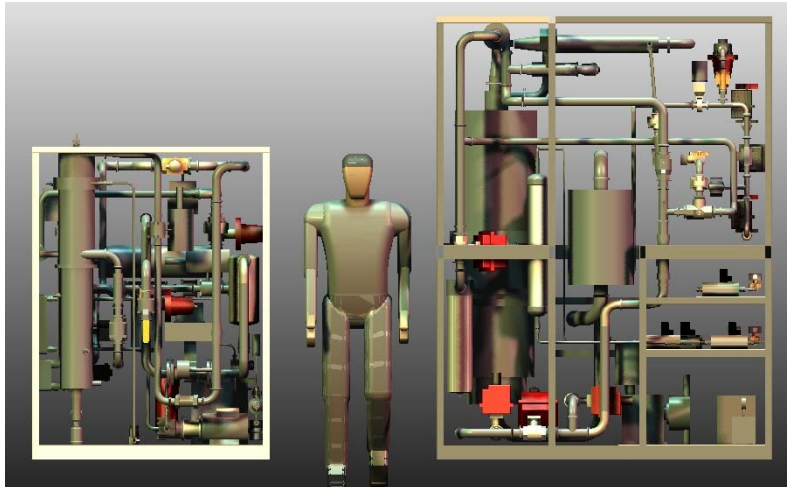
Major Milestone Demonstrations

Milestone	Date	Equipment	Purpose
Proof of Concept	1/31/2003	FP 1 Turbocharger Stack Simulator (80 - 90 °C)	▪ Support modeling results ▪ Startup demo (<60 s) ▪ Burner demo
Turbo - Generator Integration	12/31/2003	FP 1 Turbocompressor / Motor-Generator Stack Simulator (80 - 90 °C)	▪ Motor-driven startup (30 s) ▪ Show generator power output (= high efficiency)
Automotive FP Demo	3/31/2005	HiQ Automotive FP Turbocompressor / Motor-Generator Stack Simulator (90 - 110 °C)	▪ High power density FP ▪ 30 second startup ▪ High system efficiency
ANL Delivery	10/31/2005	HiQ Automotive FP Turbocompressor / Motor-Generator	▪ System automation ▪ Test unit at ANL

Proof of Concept System Testing

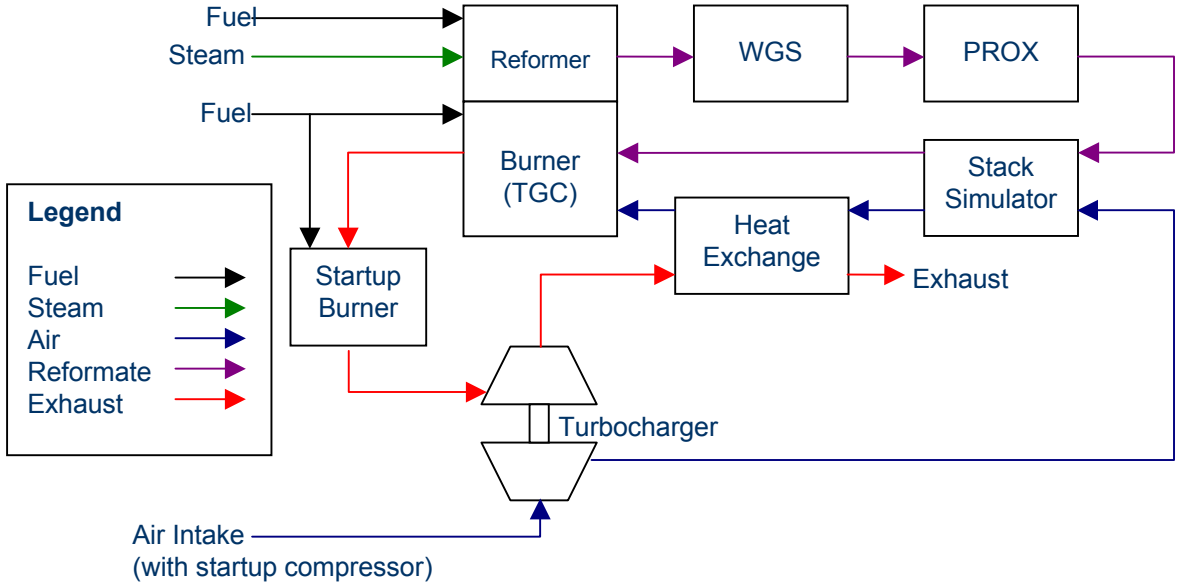
Stack simulator

- Accurate simulation of anode / cathode returns
- Low cost



Proof-of-concept fuel processor

- Low-cost, durable catalysts
- Focus is new cycle, not power density



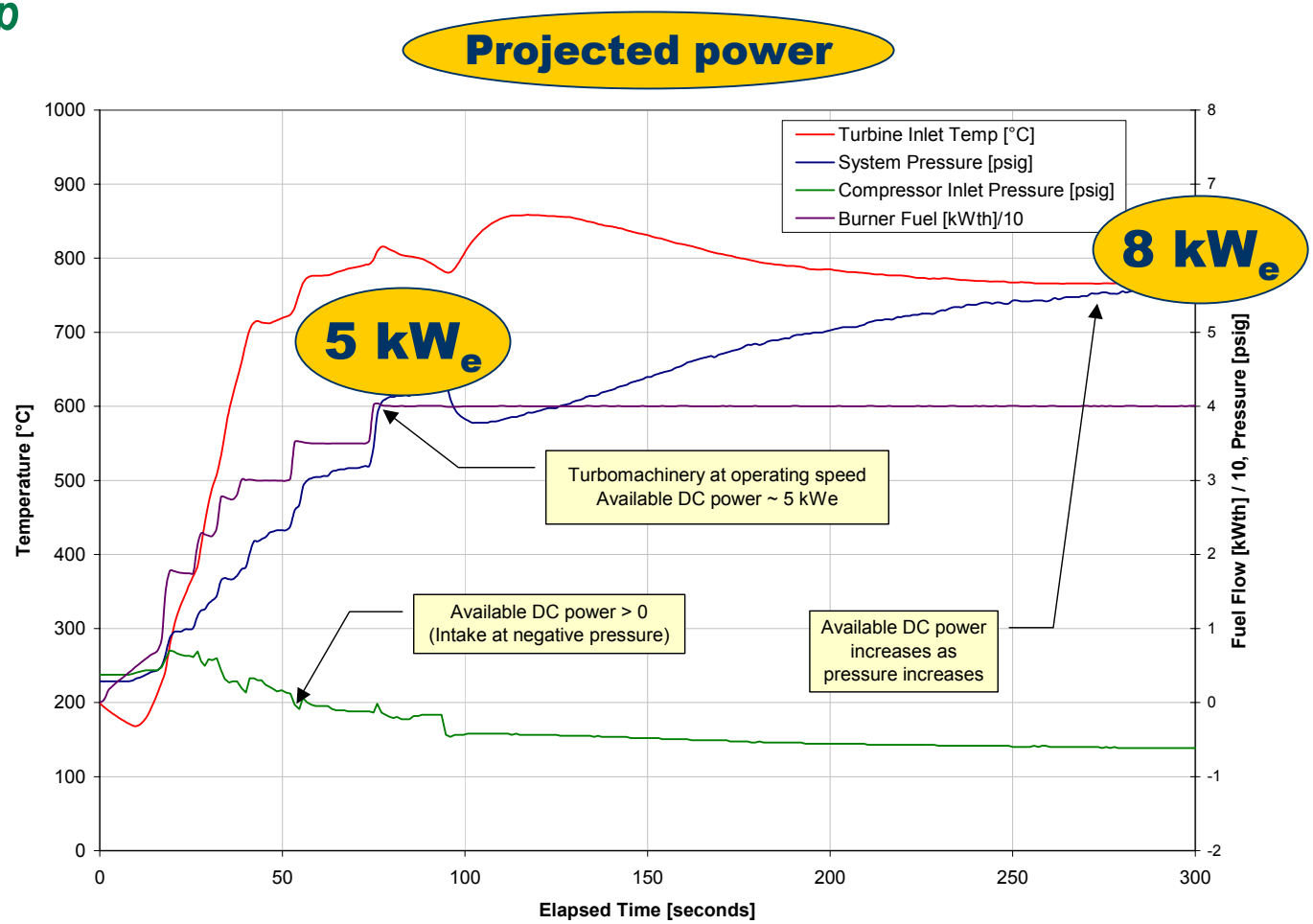
Proof of Concept vs. HiQ Fuel Processor

Proof of Concept System	Automotive HiQ FP
▪ **Low Power Density Fuel Processor** – Use proven, durable reforming technology – Keep focus on system concept	▪ **Gasoline / Multi Fuel Substrate-Based Fuel Processor** – Incorporate high power density STAR technology – HiQ system configuration
▪ **Turbocharger** – Avoid motor-generator complications and development times – Vent excess compressor air / bypass turbine flow to simulate generator load	▪ **Turbocompressor / Integrated Motor-Generator** – Show actual power < 30 sec after startup
▪ **Stack Simulator** – Provide realistic return streams for stack at elevated temperature – Important for developing burner that runs on cathode return air	▪ **Compatible with 50 kW_e elevated temperature stack** – Fuel processor will not depend on any one stack technology, only on general operating conditions

Startup Time Demonstration

At startup, the HiQ fuel processor system can operate in a Brayton cycle (gas-turbine) mode to provide partial power while the fuel processor catalysts are still warming up

- Automotive turbocharger is used to simulate turbogenerator
- External compressor drives turbocharger to simulate motor
- Net power is available when intake pressure is less than atmospheric
- About 25% power available at start-up in optimized system from turbo



HiQ Projections

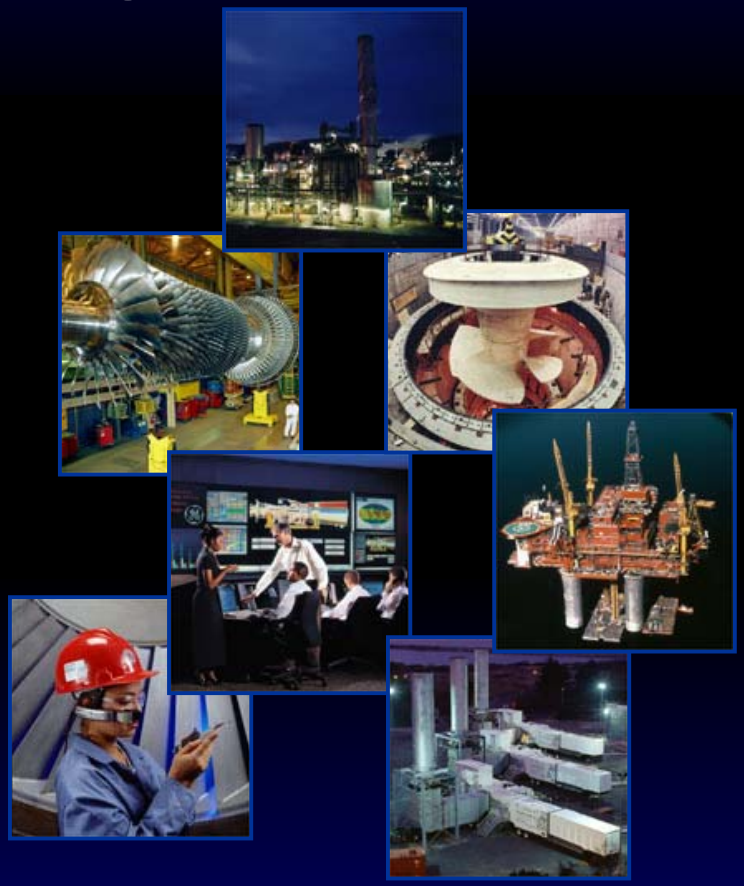
Specification	2005 Target	STAR	HiQ
Energy Efficiency	78%	80%	80%
Power Density	700 W/L	➡	➡
Specific Power	700 W/kg	640	➡
Cost	25 $/kWe	TBD (➡)	➡
Start-up Time	<1.0 min	➜	➡
Transient Response	5 sec	TBD	➡
Emissions	< Tier II	➡	➡
Durability	4000 h	TBD	➡
CO in Product	<10 ppm	➡	➡
H2S in Product	<50 ppb	➡	➡
NH3 in Product	<0.5 ppm	➡	➡

Future Plans

- **Proof-of-concept fuel processor testing** **Q2-Q3 2003**
  - Startup optimization
  - Emissions testing
  - Control development and optimization
- **High-power density fuel processor development** **Q2-Q4 2003**
  - Incorporate STAR technology developments
  - New design based on proven HiQ cycle
  - Build on results of new subscale catalyst testing and development
- **Turbo-generator system development** **Q2-Q4 2003**
  - Joint development program with vendor
  - Testing with proof-of-concept reformer in Q4 2003
- **Construction of HiQ fuel processor** **Q1 2004**
  - Testing in early 2004
  - Automotive power density targets

Fuel Cell Distributed Power Package Unit: Fuel Processing Based On Autothermal Cyclic Reforming

Parag Kulkarni, Court Moorefield, Shawn Barge,
Ravi Kumar and Vladimir Zamansky
GE Energy & Environmental Research



Review on
DOE Contract # DE-FC02-97EE50488

May 2003

Objectives & Approach

DOE Targets

- Reduce cost of fuel processor
- Improve reliability of fuel processor
- Improve efficiency of fuel processor

DOE (1999-2000) Bread-Board Fuel Processor Development

- Design, fabricate & operate breadboard fuel processor
- Assess the technical & economic feasibility of the design

DOE (2001-3) Integrated Fuel Processor Development

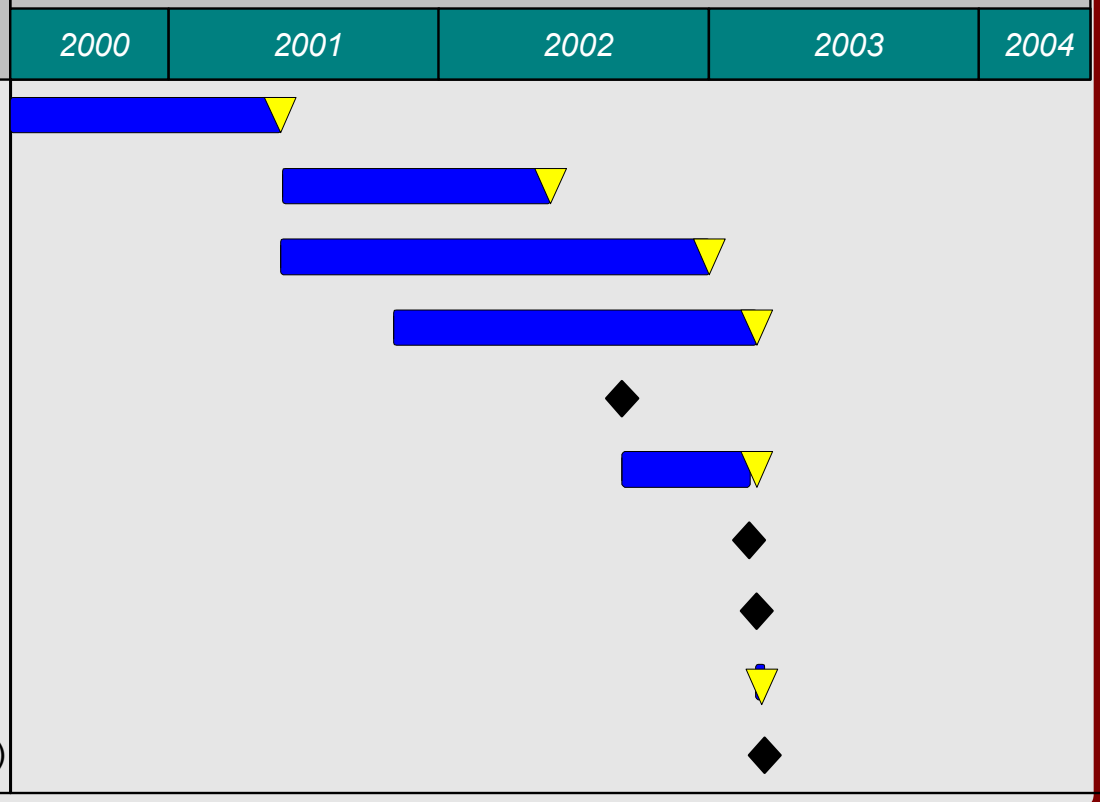
- Design, fabricate and operate an integrated fuel processor
- Assess the reliability, cost and performance of the fuel processor

CEC/ARB (2002-4) Integration of ACR Fuel processor with PEM Fuel Cell

- Integrate fuel processor with the fuel cell
- Improve efficiency & reliability of the fuel processor
- CEC – California Energy Commission
- ARB – California Air Resources Board

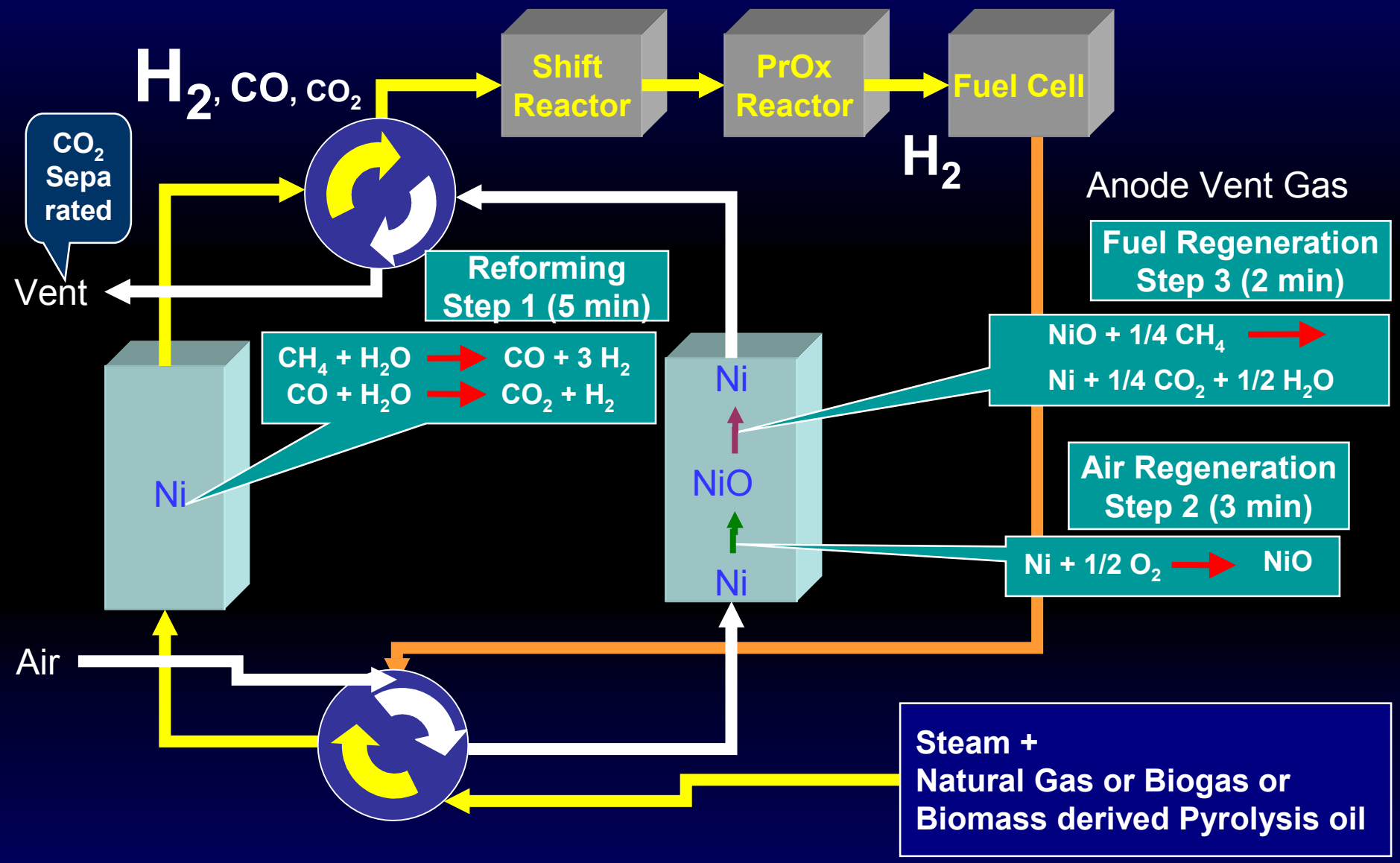
Schedule and Milestones

ID	Task Name
1	Operation of Breadboard ACR Reformer
2	Design of Integrated Fuel Processor Unit
3	Economic Feasibility Analysis
4	Fabrication of Integrated Unit
5	Operation of ACR Reactors
6	Optimization of ACR Reactor Operation
7	Production of Continuous H_2 Stream
8	Shift and PrOx Reactor Operation
9	Integrated operation of ACR Fuel Processor
10	Continuous production of H_2 stream (<50 ppm CO)



All milestones have been met

Autothermal Cyclic Reforming for PEM Fuel Cell



In-situ heat generation on catalyst lowers capital cost

Advantages of ACR Process for PEM Fuel Cell

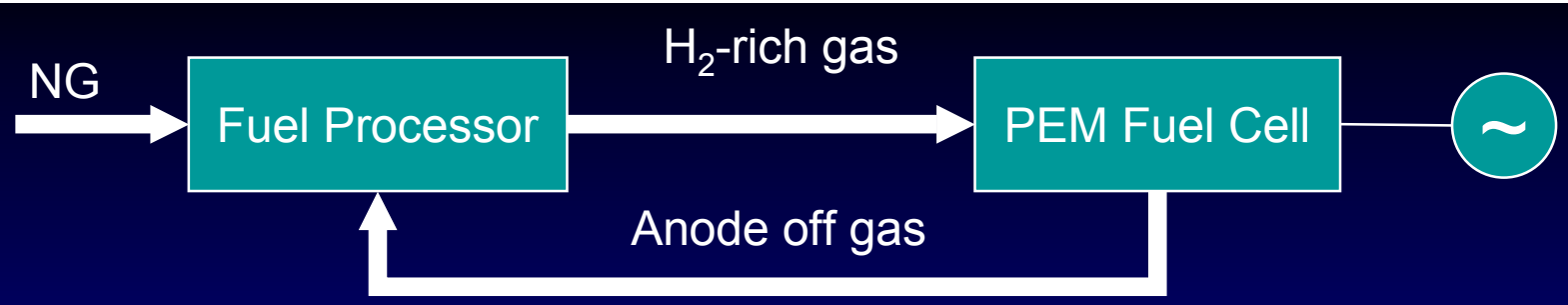
Metric	Autothermal Cyclic Reformer (ACR)	Advantages
High H_2 Purity from Reformer	70-80%	• Air is not mixed with fuel
High Efficiency (HHV)	70-80%	• Better system integration leads to higher efficiency, since anode off gas is used for fuel regeneration
Capital Cost	Low	• In-situ heat generation lowers metal temperatures and thus lowers capital costs (< 600C)
Fuel Flexibility	Diesel, NG, Propane, Biogas, Biomass Pyrolysis Oil	• Coke is burnt off during regeneration
Inherent CO_2 Separation	Yes	• Fuel regeneration step
Sulfur Tolerance	Yes	• Catalyst is sulfur tolerant
Turndown/ On-Off Cycling	Yes	• Lower metal temperature allows turndown & on-off cycling

ACR has advantages over competing technologies

Process Analysis & System Efficiencies

- **Several process configurations were analyzed for the desired performance targets using process model**

Fuel Processor Conversion Efficiency	(HHV of H_2-rich gas – HHV of Anode off gas)/ HHV of NG Fed	70-80%
Fuel Cell Efficiency	Electricity Generated/ (HHV of H_2-rich gas – HHV of Anode off gas)	45-55%
Net Electrical Efficiency	Electricity Generated/ HHV of NG Fed	30-40%
Total System Efficiency (includes cogeneration benefit)	(Electricity Generated + Cogeneration Credit)/ HHV of NG Fed	60-85%



Efficiencies depend on system size

ACR Reactor Design

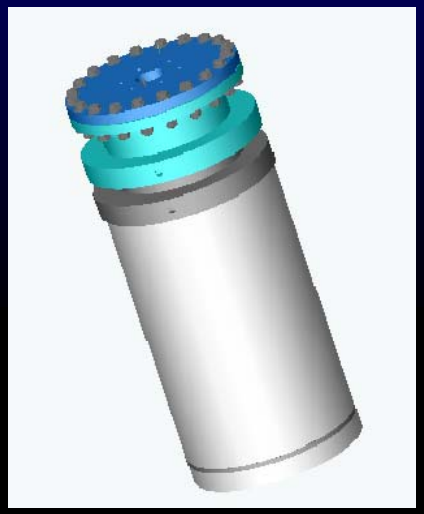
Performance Metric	Bread-Board Design	Integrated Design A	Integrated Design B
CH_4 Conversion	> 90%	> 95%	> 95%
Pressure drop (psig)	< 1	< 1	< 1

- Several reactor design configurations were analyzed for the desired performance targets and two integrated designs were chosen
- Both the selected integrated ACR reactor designs showed better performance than the bread-board design. Both the designs were implemented.
- Dynamic process model was used to optimize the process conditions.

Reformer Reactor Design Met all of the Performance Metrics

Design of System Components

ACR Reactor:
Single Catalyst Bed



Shift Reactor:
Single Catalyst Bed

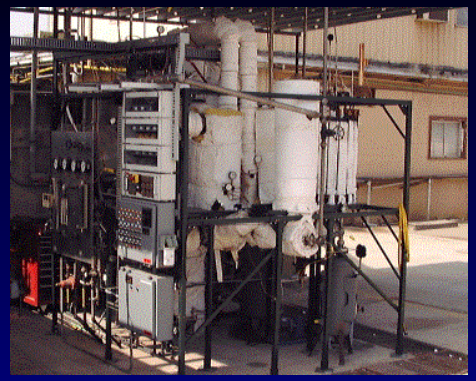
PrOx Reactor:
Multi-bed reactor with
multiple air injection ports

Program Status

- 10 kWe Diesel unit was operated
- 35 kWe Bread-board natural gas (NG) unit was operated
- 50 kWe Integrated NG unit was operated

10 kWe Diesel Unit

35 kWe Bread-Board NG Unit

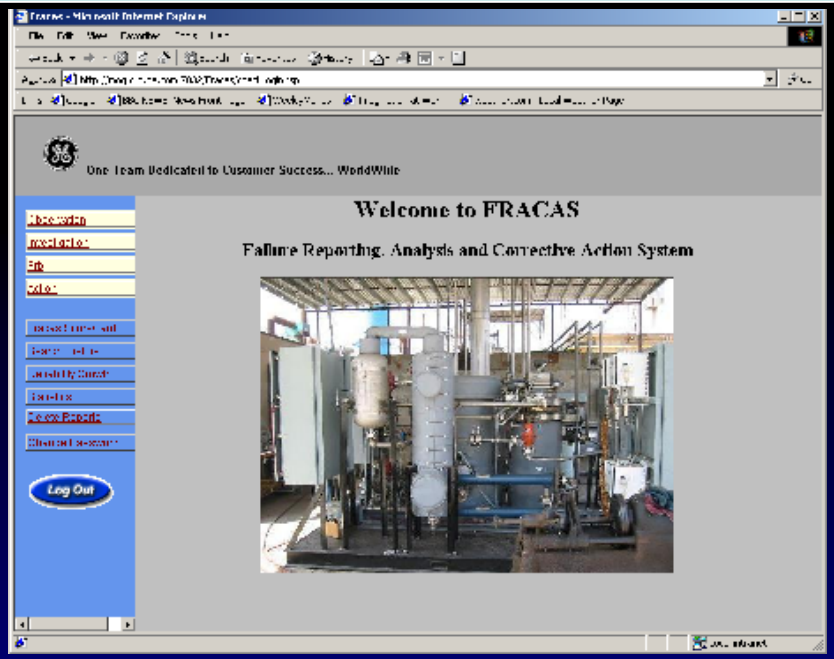


50 kWe Integrated NG Unit

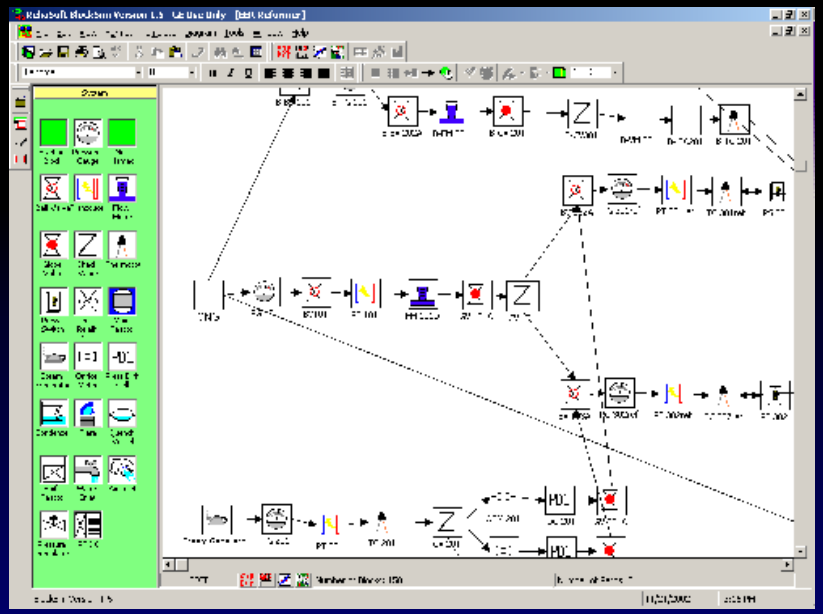
Reliability of ACR-based Fuel Processor

- Reliability Tracking:
  - FRACAS (Failure Reporting, Analysis and Corrective Action System) web-based tool has been developed for the ACR fuel processor. This system is being populated to calculate reliability information.
- Calculation of System Reliability:
  - Reliasoft block diagram is being used for quantification of reliability

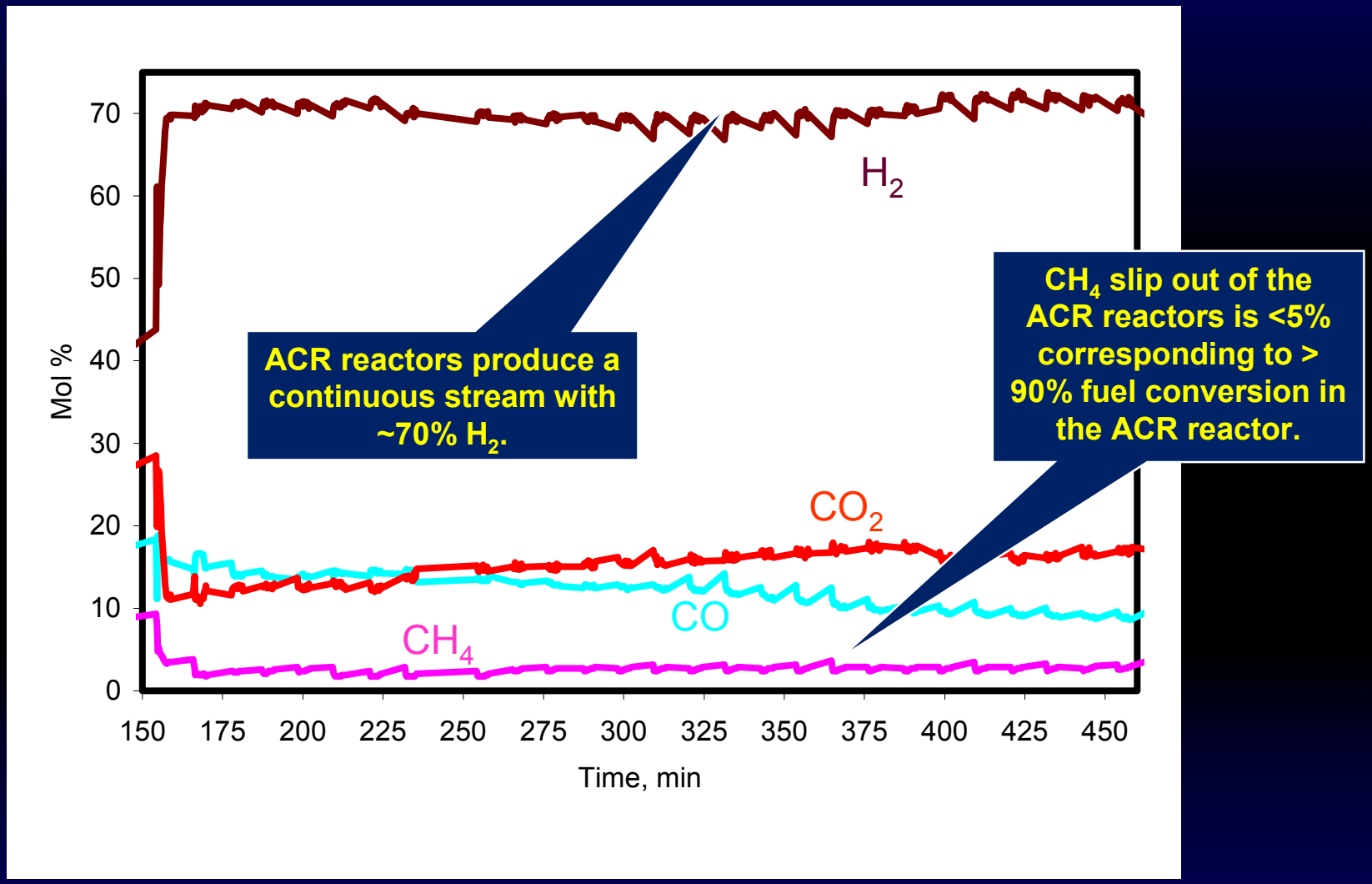
FRACAS Tool for Reliability Tracking



Reliasoft Block Diagram

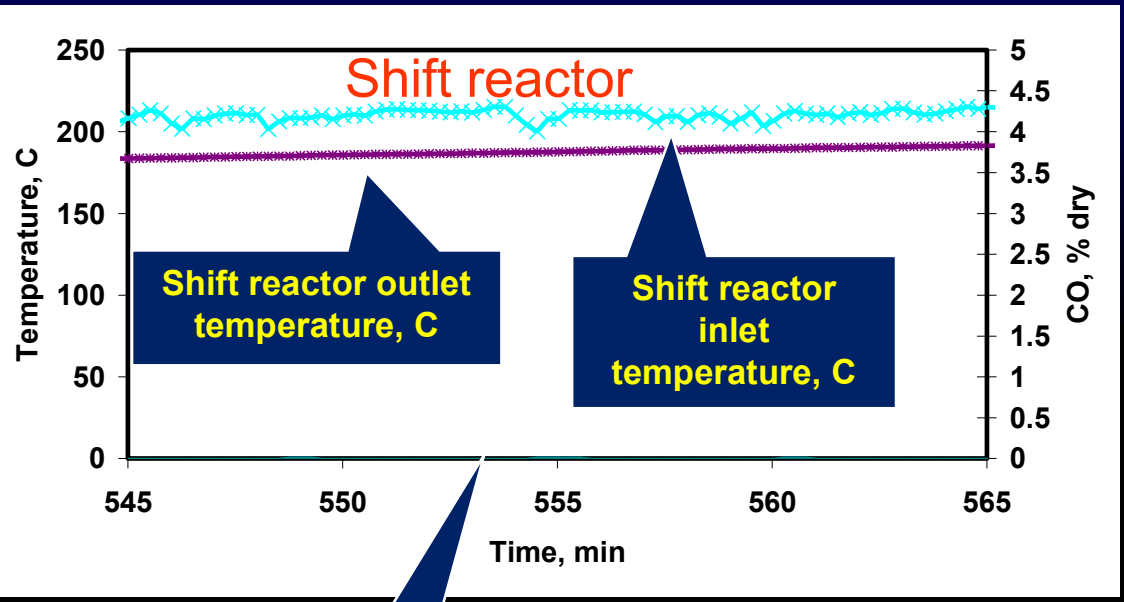


Performance of ACR Reactor



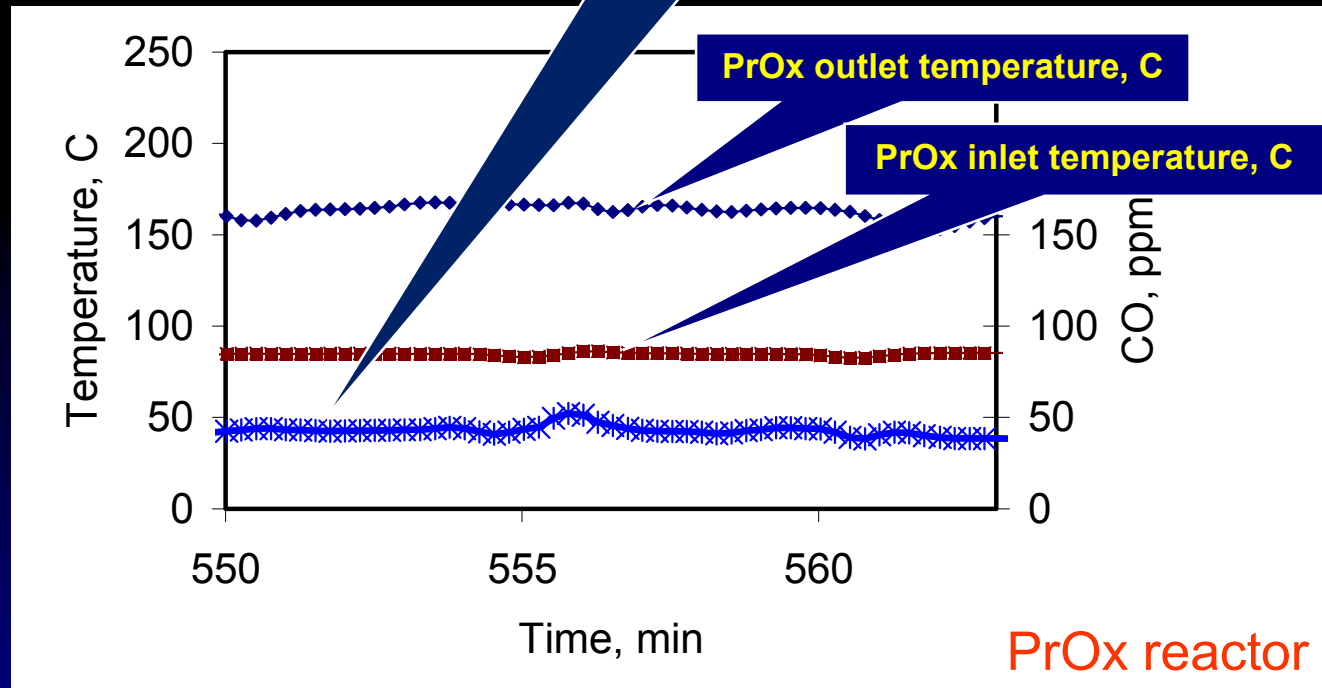
Shift reactor dampens fluctuations from ACR reactor

Performance of Shift and PrOx Reactors

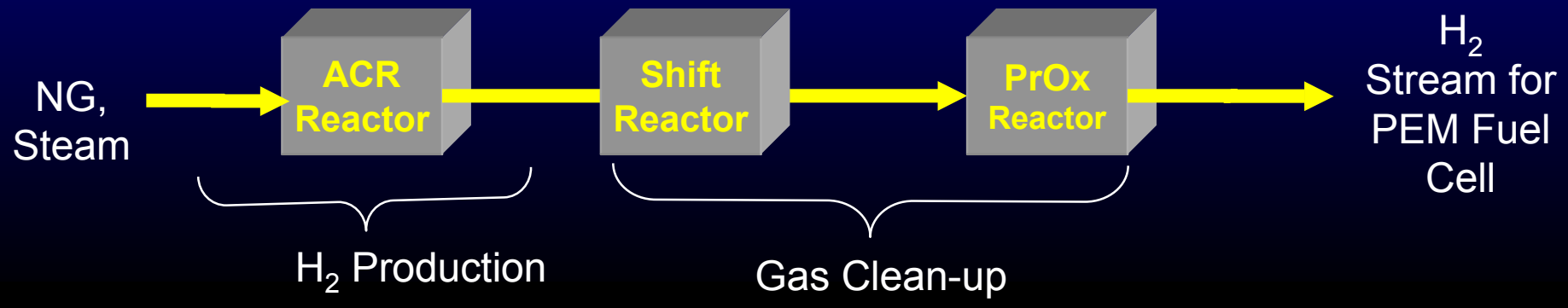


Shift reactor reduced the CO to < 0.5%

PrOx reactor reduced CO to < 50 ppm. Further optimization is being performed to reduce CO to < 10 ppm



Purity of Hydrogen Stream in the ACR Fuel Processor



	H_2	CO	CO_2	CH_4
ACR Reactor Outlet	69%	9%	19%	3%
Shift Outlet	73%	0.6%	23%	3%
PrOx Outlet	72%	< 50 ppm	25%	3%

ACR Fuel Processor produces a continuous H_2 stream with < 50 ppm CO

ACR Catalyst Development

ACR catalyst development is being carried out in a bench scale test stand.

- 30 commercial and custom made reforming catalysts have been tested.
- A reforming catalyst durable for 2000 hrs has been developed using accelerated durability testing techniques.
- Current tests are targeted toward developing an active and durable catalyst for >5000 hrs.

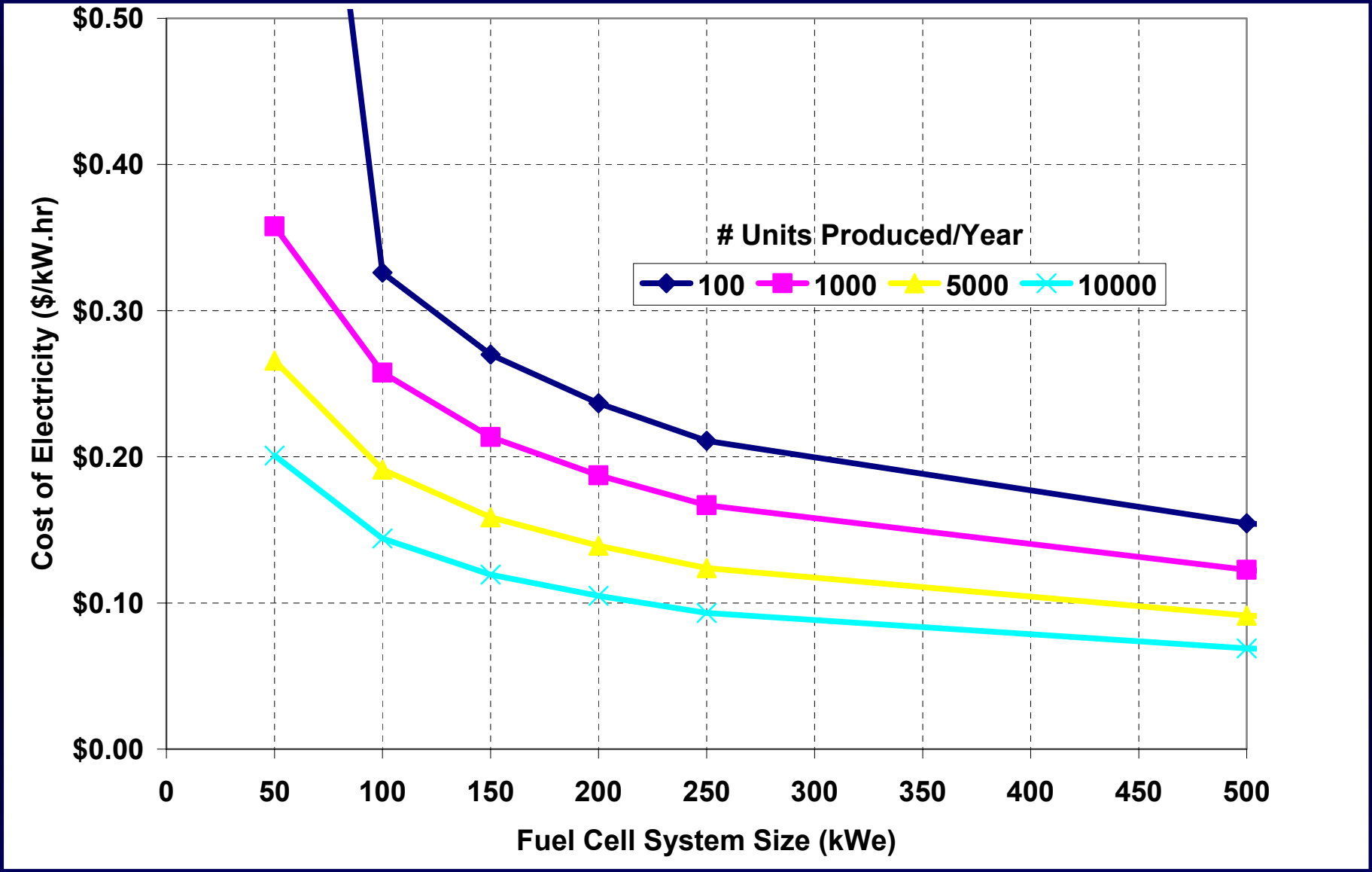
Stationary Fuel Cell System Economic Model

- Detailed Cost Estimates
  - Prototype Hardware Costs
  - Subsystem Quotes
  - Mechanical and Electrical Fabrication Cost
- Scaling Laws
  - System Sizing
  - Mass Production Factors

- O&M
- Consumables
- Annualized Capital Cost
- Facility Charge

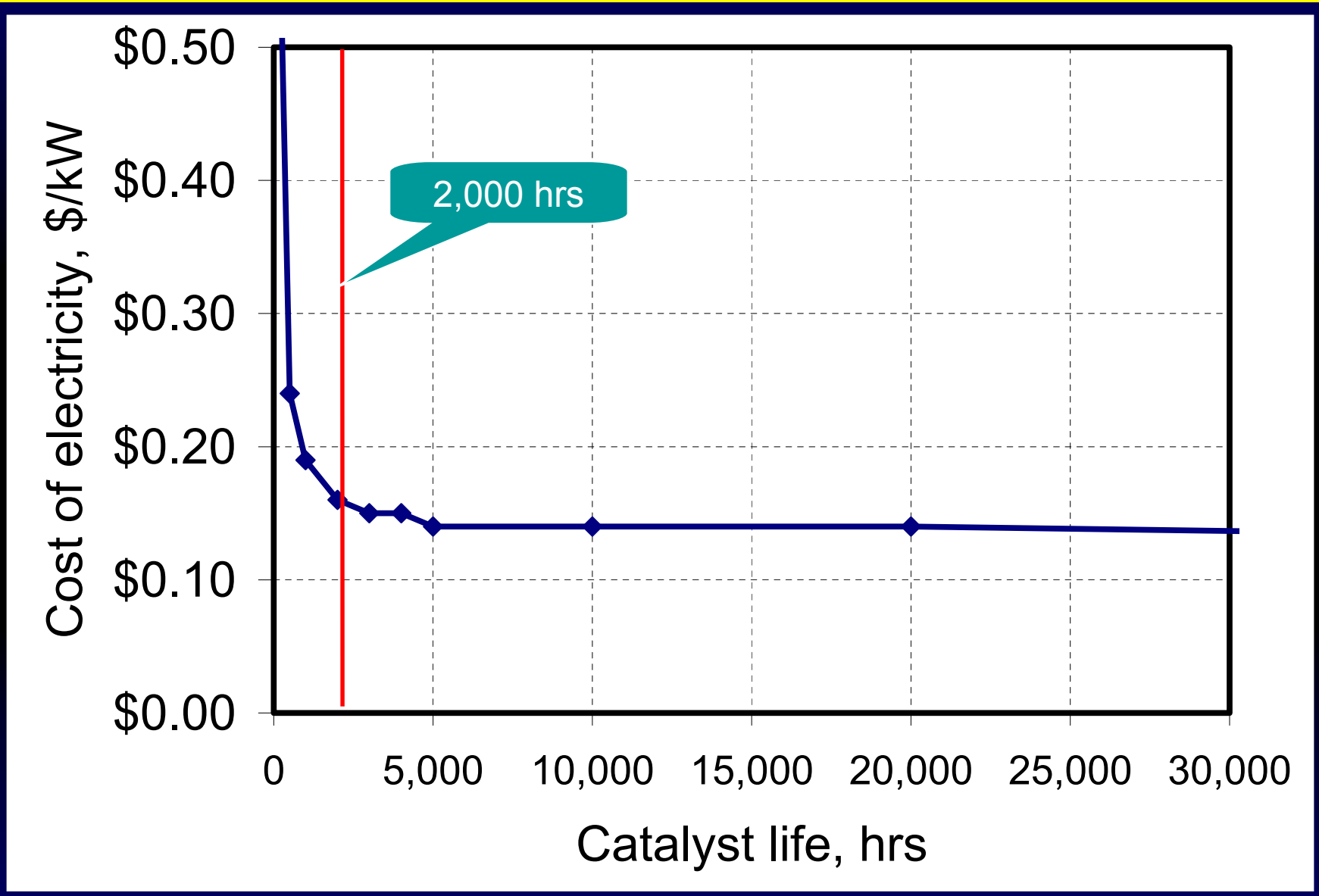
Model is based on actual experience

Stationary Fuel Cell System Economics



Fuel cell system cost competitive at large scales and when mass-produced
Further Technology Advances Can Reduce Costs

Impact of Catalyst Life on the Cost of Electricity



ACR catalyst should have at least 2,000 hr life

Future Work: CEC and ARB Project

- ACR Based Fuel Processor Prototype optimization
  - **Optimization of CO clean-up system to lower the CO concentration from 50 to < 10 ppm in the product stream.**
- Integration of the Fuel Processor with PEM Fuel Cell in partnership with National Fuel Cell Research Center (NFCRC) which is run by University of California at Irvine (UCI).
- Improve Reliability

Acknowledgements

- DOE: Kathi Epping, Jill Jankouwski, Ron Fiskum, Mark Paster, Pete Devlin, Sig Gronich
- CEC: Avtar Bining, Art Soinski, Mike Batham
- AQMD: Gary Dixon
- CARB: Steve Church

Catalytica ENERGY SYSTEMS

2003 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting

Plate Based Fuel Processing System

DOE ID# DE-FC04-01AL67605

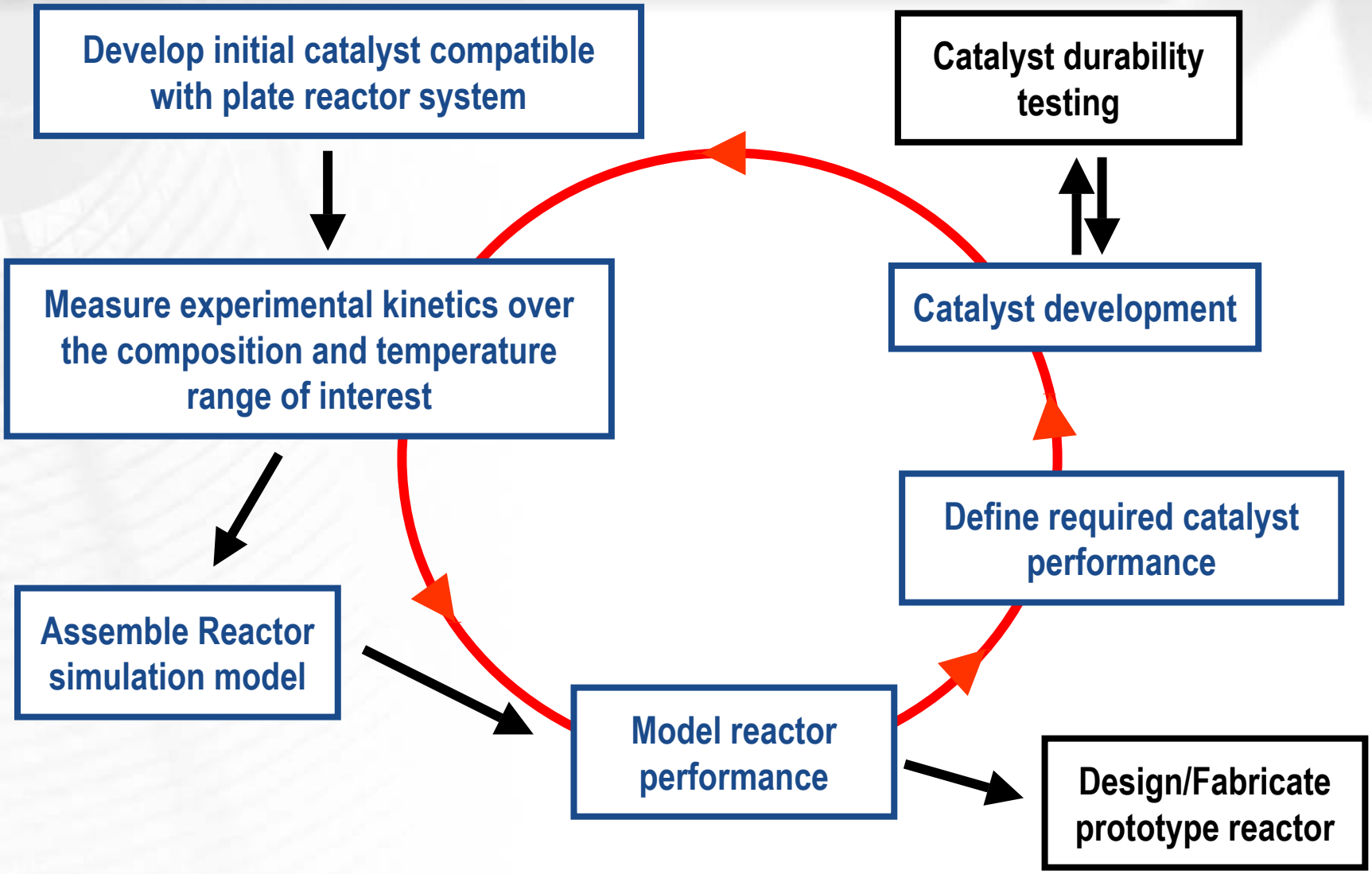
May 19-22, 2003

DEDICATED TO INNOVATIVE SOLUTIONS FOR CLEAN ENERGY PRODUCTION

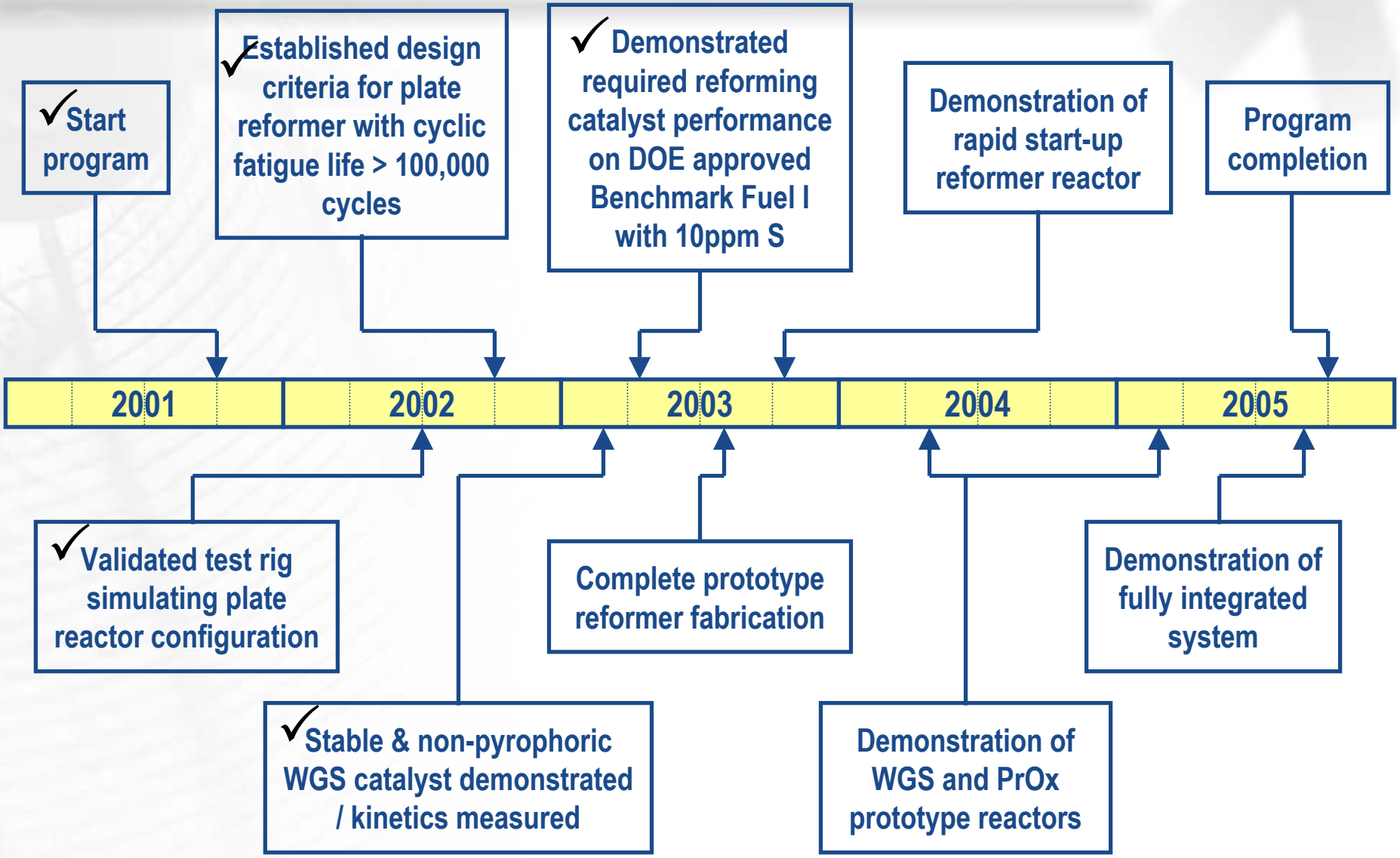
Project Objectives

- Develop new catalytic reactor designs and reactor technology for processing gasoline to PEM quality H_2
  - Develop improved catalyst materials compatible with these reactor systems
- Design and fabricate prototype units for each reactor at the 2 to 10kW(e) scale
  - Demonstrate steady state and transient performance
  - Evaluate rapid start up performance
- Integrate component reactors in a fuel processor system taking gasoline to PEM quality H_2 (specific objective being refined)

Approach


Develop initial catalyst compatible with plate reactor system
Measure experimental kinetics over the composition and temperature range of interest
Assemble Reactor simulation model
Model reactor performance
Design/Fabricate prototype reactor
Define required catalyst performance
Catalyst development
Catalyst durability testing

Project Timeline



12 month milestones: Success Criteria

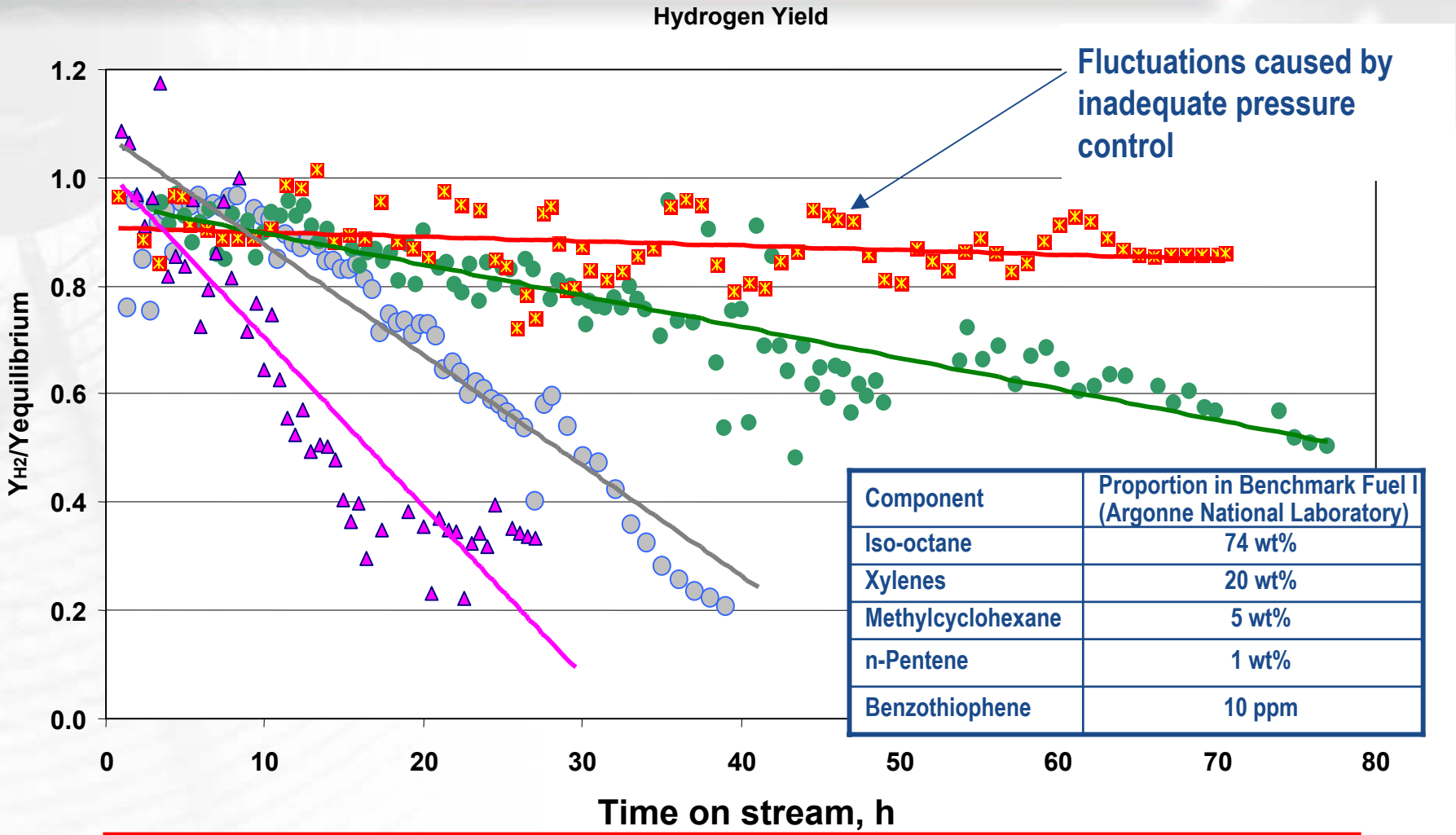
- Demonstration of rapid startup prototype reformer
  - 2 to 5 kW(e) prototype reformer "brass board" unit designed to required critical performance aspects
  - Rapid start up and rapid cycling tests run under realistic conditions
  - Start up to full reformer output in < 30s

  Technical Barriers: Reduced thermal mass, low light-off catalysts, rapid heat/start strategy

- Demonstration of WGS and/or PrOx prototype reactors
  - 2 to 5 kW(e) prototype reactor "brass board" unit
  - Steady state and rapid cycle testing

  Technical Barriers: Reactor design strategy that reduces WGS reactor weight and volume
  Establish durability of PrOx catalyst and integrate into plate configuration

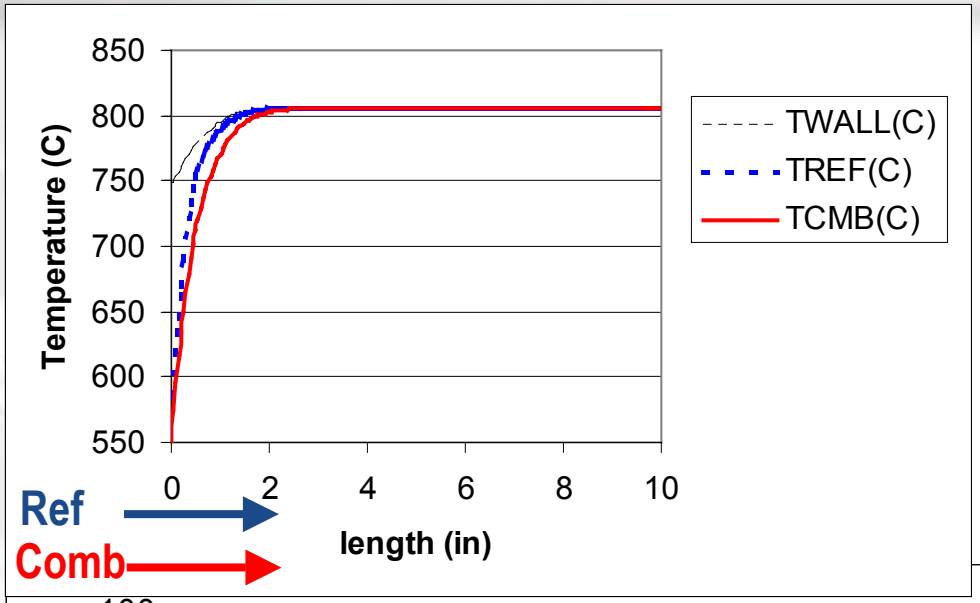
Improved Reformer Stability

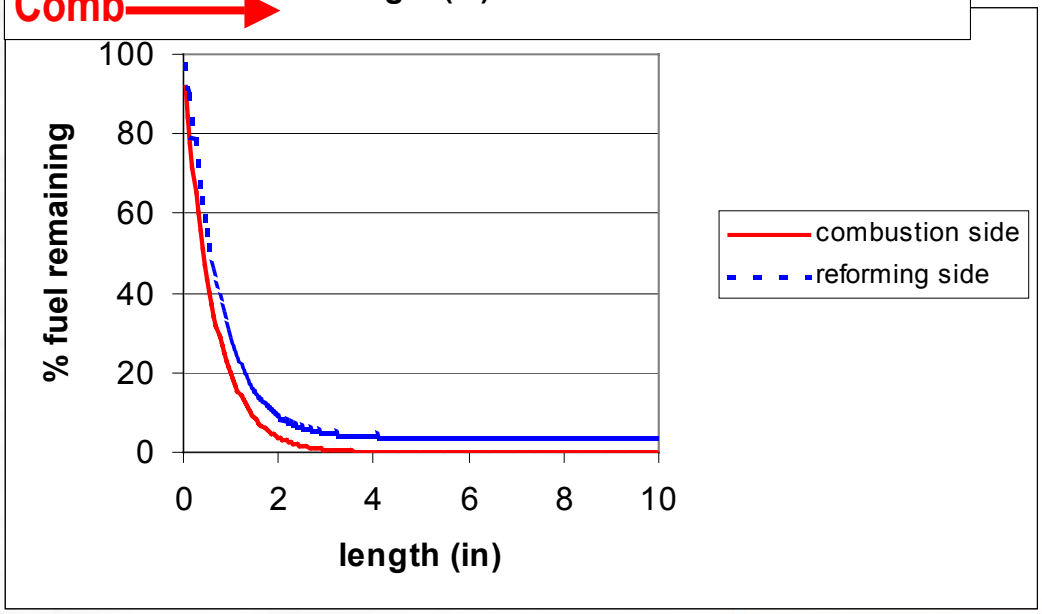


Component	Proportion in Benchmark Fuel I (Argonne National Laboratory)
Iso-octane	74 wt%
Xylenes	20 wt%
Methylcyclohexane	5 wt%
n-Pentene	1 wt%
Benzothiophene	10 ppm

High stability achieved with Benchmark Fuel I with 10ppm S

Co-Current Reformer Design



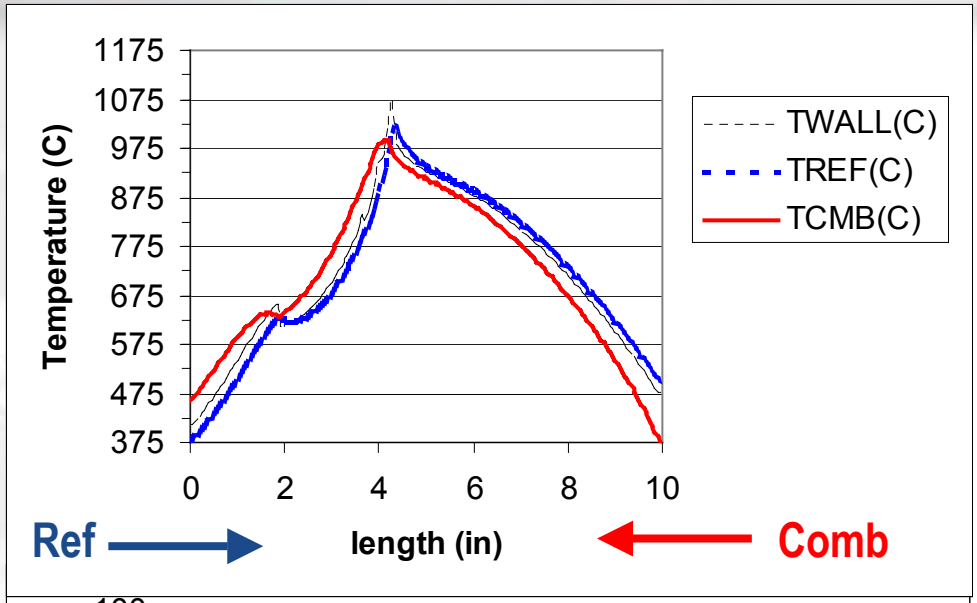


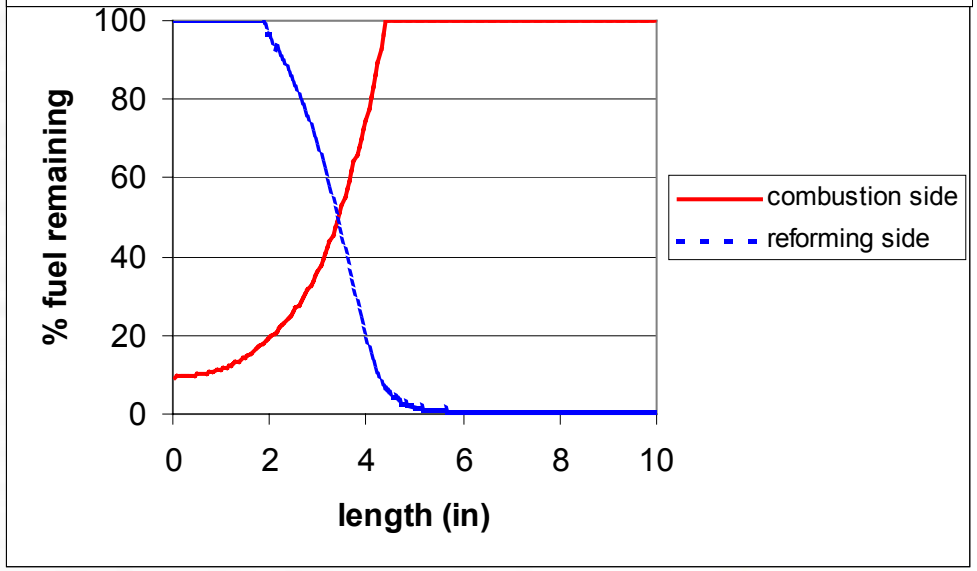
Reactor model of plate reformer using hypothetical kinetics

Conclusions:

- Exothermic and endothermic reaction well matched for this test case
- Reactor volume requirements and space velocities are reasonable
- Robustness studies (load from 25% to 100%, deactivation, poisoning) show good performance

Counter-Current Reformer Design





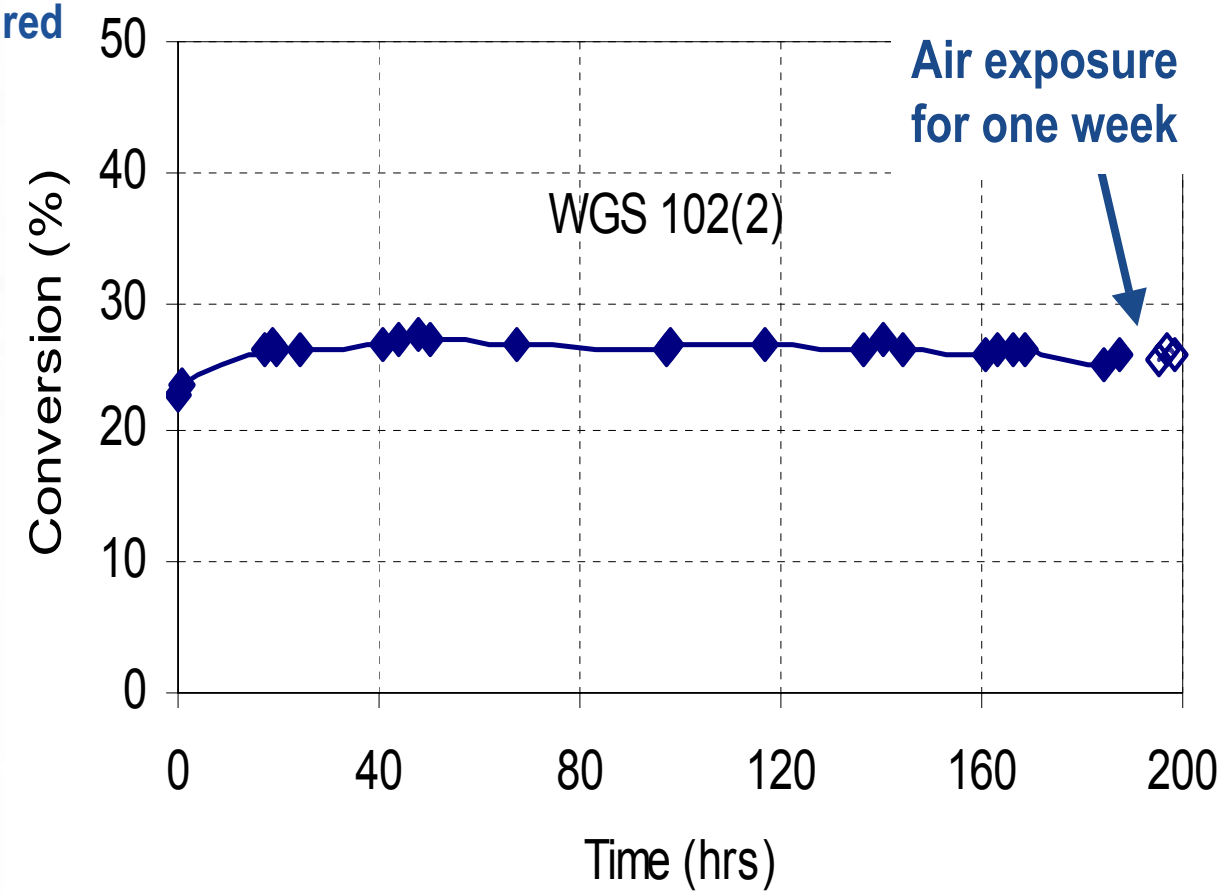
Reactor model of plate reformer using hypothetical kinetics

Conclusions

- Design of reactor and catalytic coating is very critical to performance
- Can achieve outlet temperatures that integrate well with upstream and downstream processes
- Robustness studies (load from 25% to 100%, deactivation, poisoning) show good performance

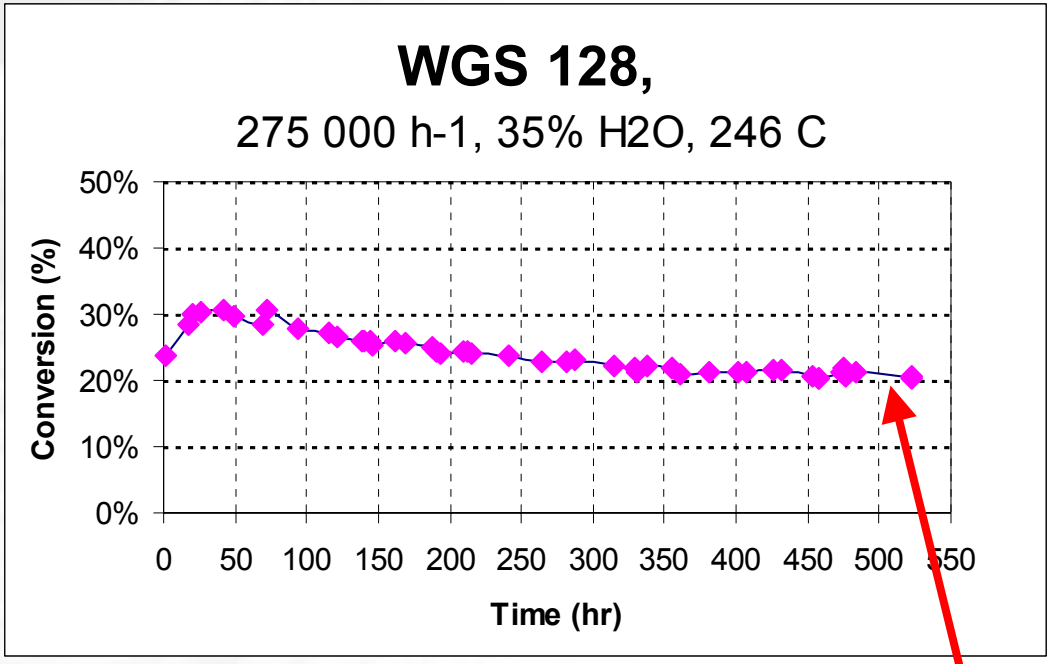
Effect of Air Exposure

- Water gas shift catalyst development
  - Base metal nano-particle structure
  - Non-pyrophoric
  - No pre-reduction required
  - Air stable



Catalyst Durability

Long term reactor runs show good durability



To obtain 5000 hour durability data

Have developed a static aging system

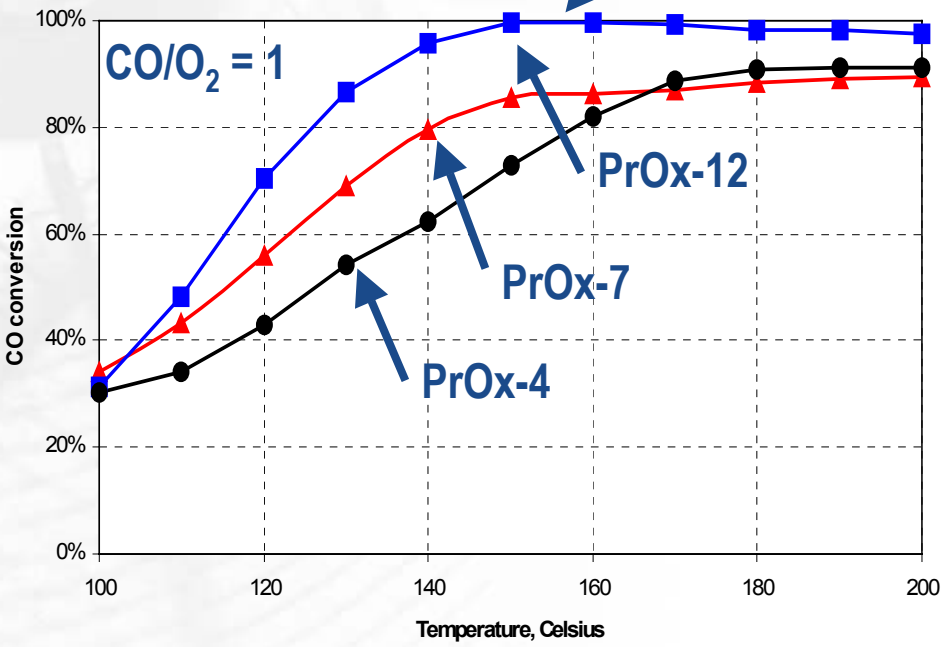
- Age multiple samples
- Low operating cost
- Can run to 5000+ hours
- Have demonstrated correlation with on-line reactor aging data

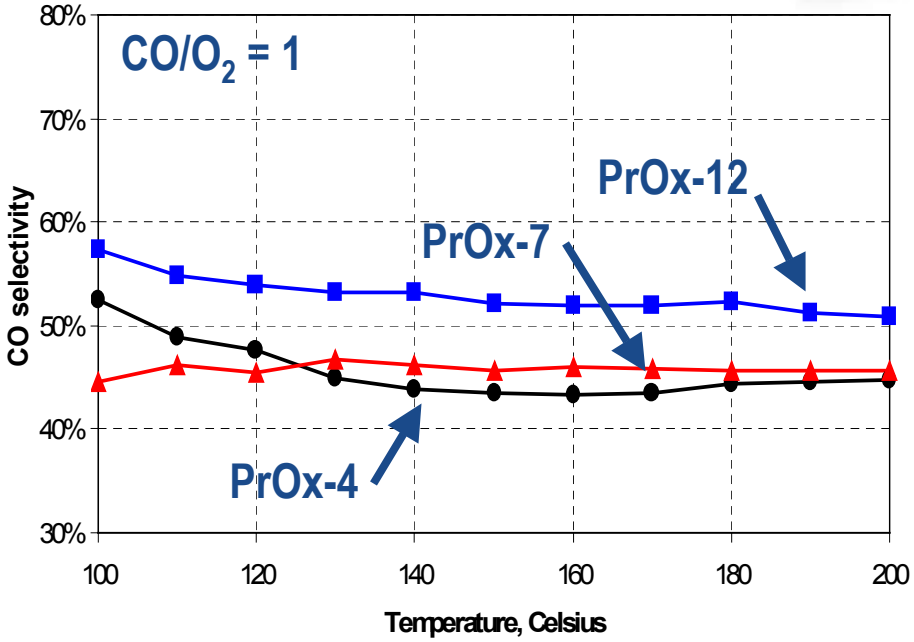
At this activity, 5 kg of catalyst required for 50kW(e) plate reformer

→ Meets DOE WGS catalyst performance target

Improved PrOx Performance

Conversion near target performance





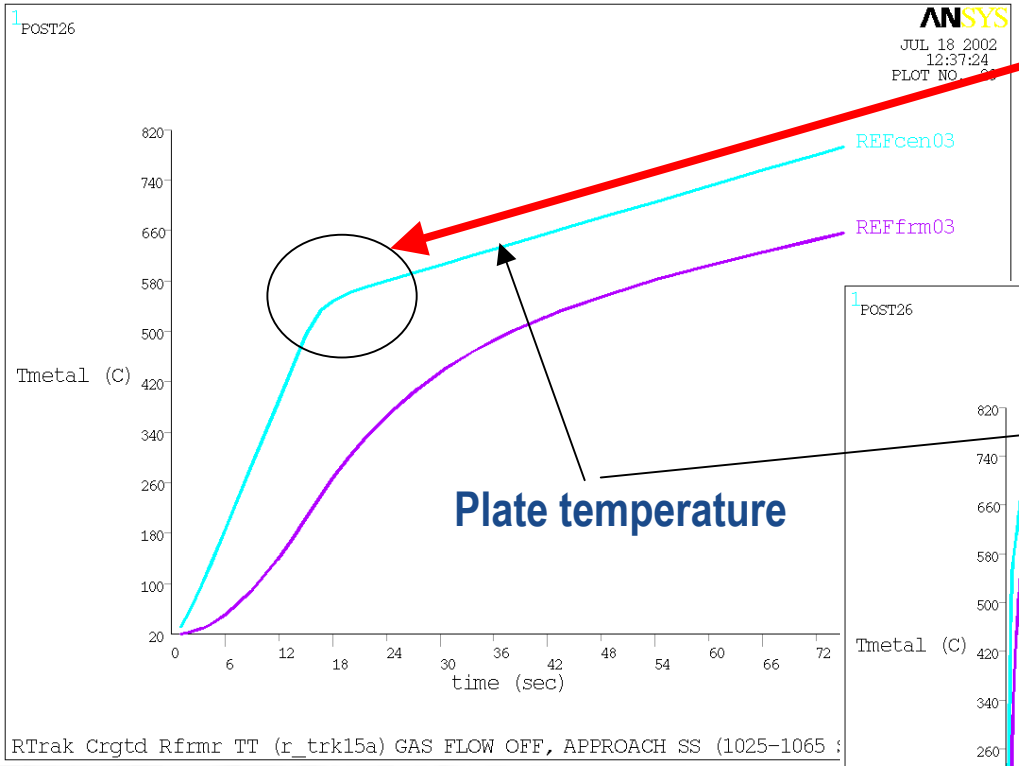
At this activity, 0.6 kg of catalyst required for 50kW(e) PrOx reactor in plate configuration

Transient Thermal Stress Analysis

- Transient thermal stress
  - Expected to limit mechanical durability due to the spatial temperature variation throughout time.
- Low cycle fatigue life target
  - 100,000 to 250,000 start/load transient cycles
- Numerous configurations have been analyzed

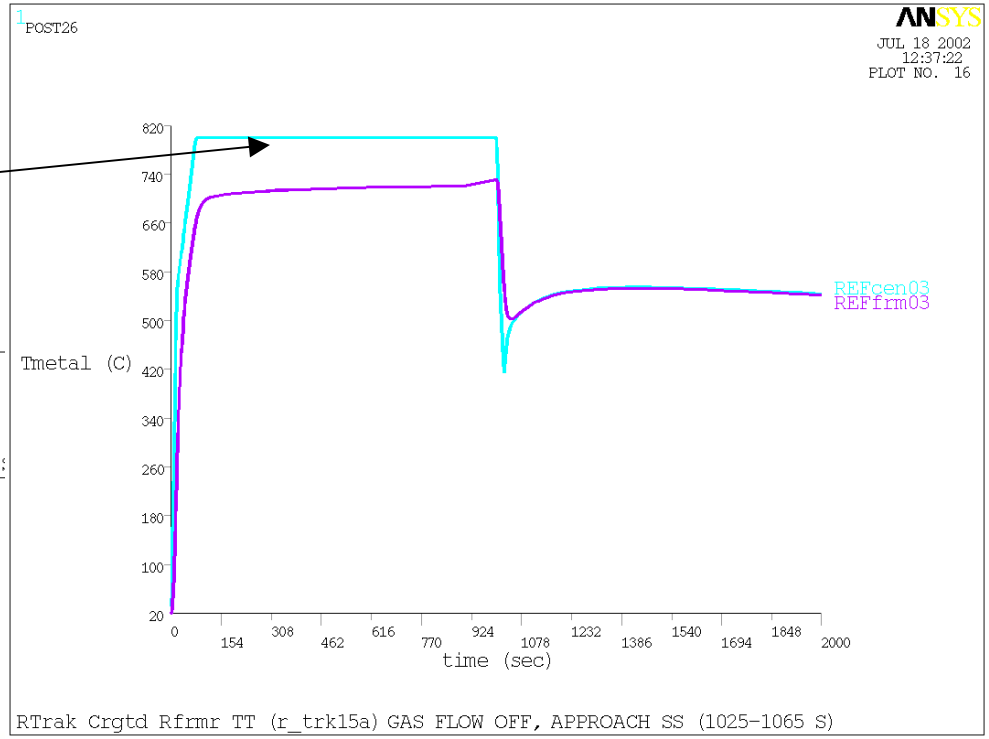
Plate Temperature vs. Time

Close up of early time shows largest gradient between 15 and 20 seconds where limiting strain condition occurs.



For most designs, the highest stress was in the 15 to 25 second period

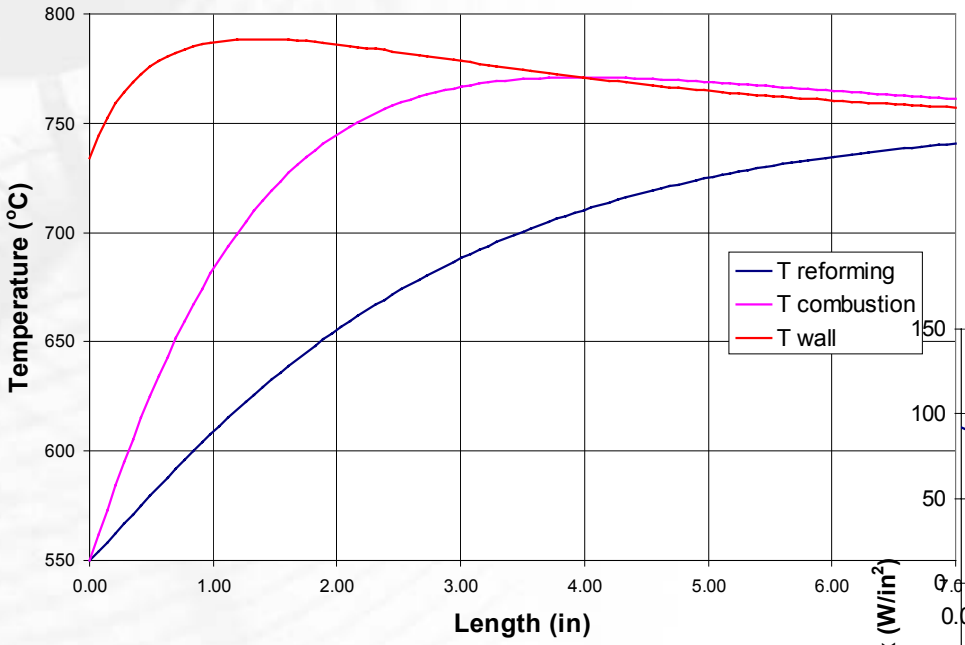
Plate temperature



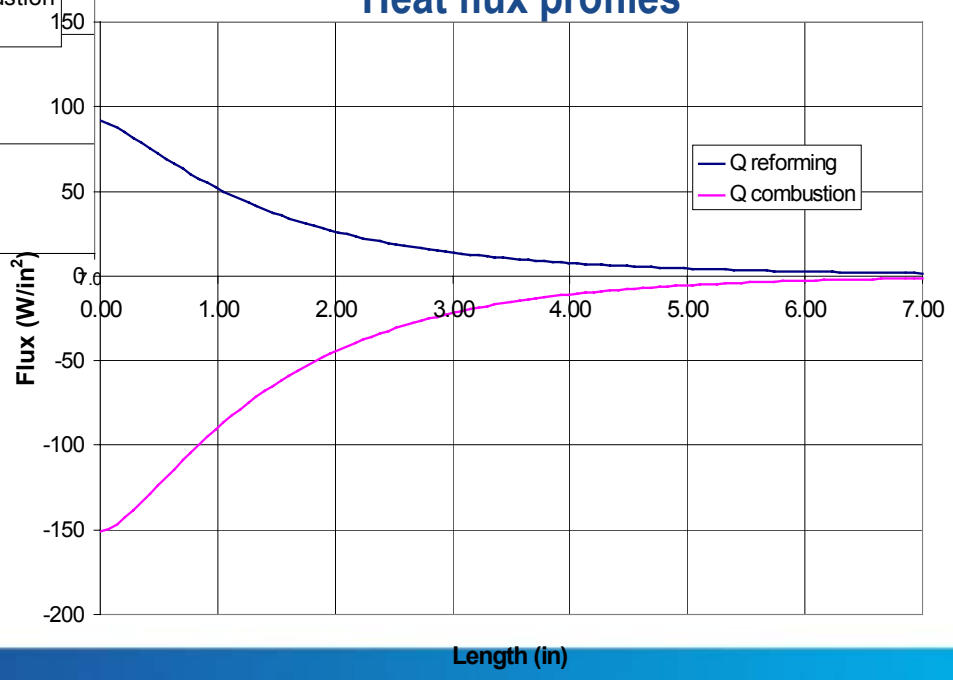
Boundary Conditions

Boundary conditions for reactor plate provided by reactor simulation model of the steam reformer

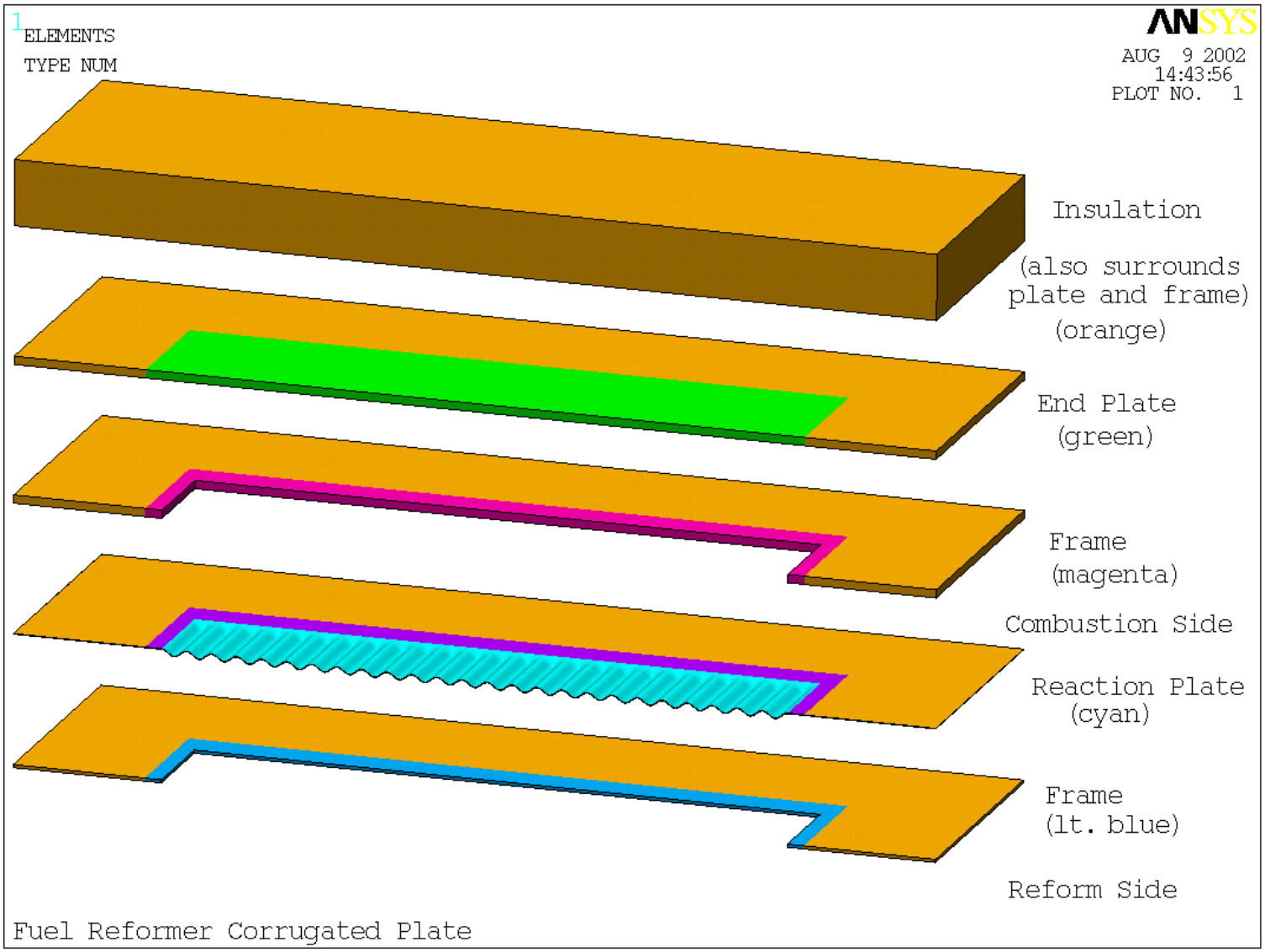
Gas temperature profiles



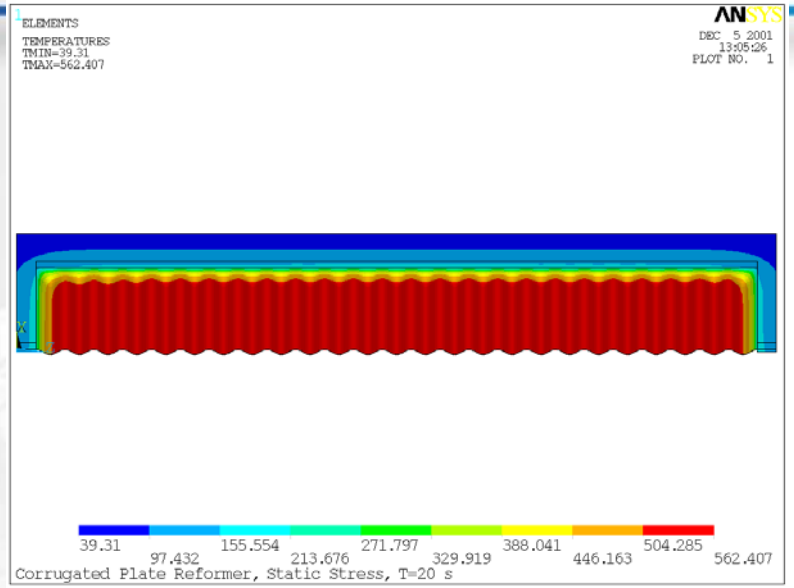
Heat flux profiles

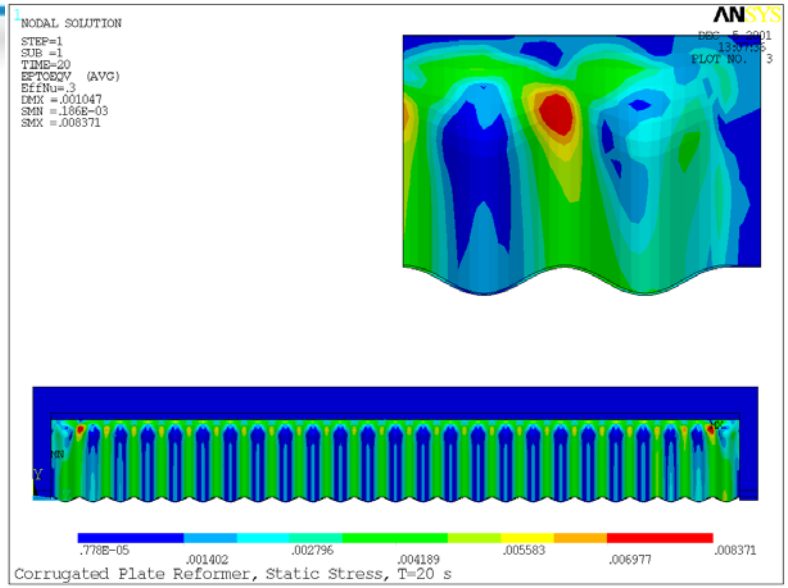


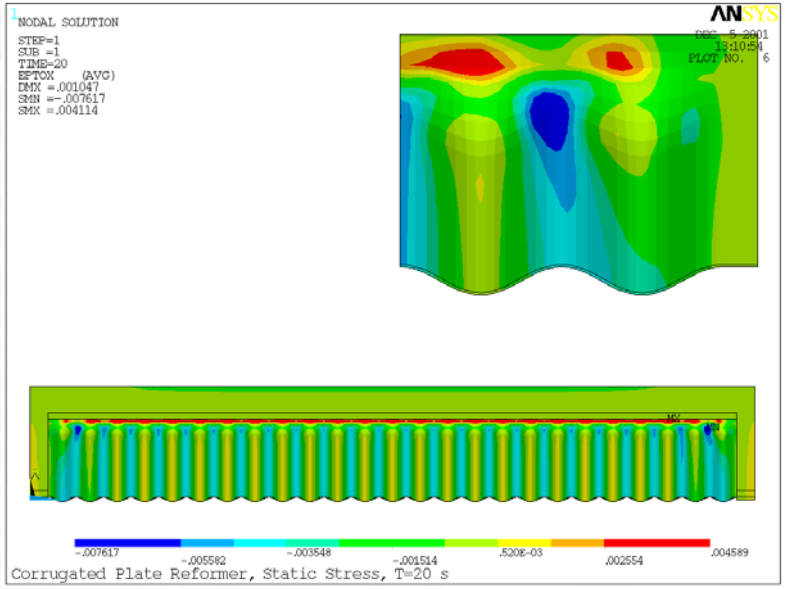
Finite Element Model

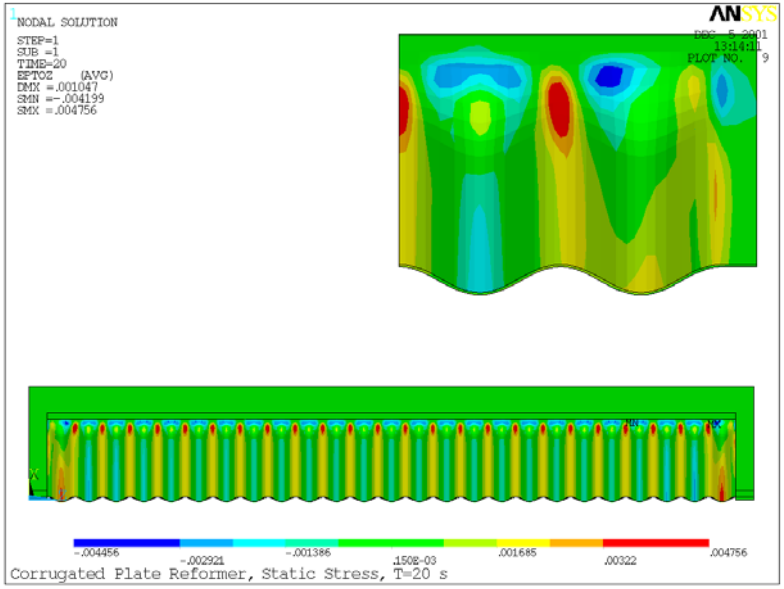


Finite Element Model









Prototype Design

- Have developed design strategy for plate reactor
  - Cyclic fatigue life > 150,000 cycles
  - Potential for very rapid startup
- Mechanical design in progress
  - Prototype unit for laboratory demonstration
  - 2 to 10 kW size with applicability to the reforming, WGS and PrOx reactors
  - Identifying vendors with required fabrication capability, initial fabrication in progress

Prototype Testing Plan

- Will fabricate several prototype reactors
  - Will contain > 10 layer segments for adequate simulation of full scale system
- Demonstration objectives
  - Basic gasoline reforming demonstration at required (high) temperature
  - Fast transient startup
  - Durability studies including cyclic durability (100s of cycles) and long term operation
- Laboratory facilities being upgraded to handle larger flow volume and rapid startup design
  - Gasoline feed system
  - Disposal of product reformate stream

Reactor Components Sizing—Status

Based on plate reactor design strategy

➔ Preliminary estimate of reactor size and volume
(not including system piping, heat exchangers or controls)

		Weight (kg)	Volume (liters)
Steam Reformer		3.7	4.0
WGS		25.3	30.6
PrOx		3.6	3.9
Total		**32.7**	**38.5**
DOE Targets	2005	71.4	71.4
	2010	62.6	62.5

➔ The WGS reactor offers best potential for weight and volume reduction

➔ Other components appear adequate—need confirmation of input data

Future Plans: next 12 months

Prototype plate reactor demonstration

- Design and fabricate prototype reactor
- Upgrade test rig to handle prototype reformer testing
  - Demonstrate steady state performance
  - Demonstrate rapid startup of the gasoline reformer

Reformer reactor

- Establish global kinetics for gasoline reforming
  - Best catalyst system
  - ANL Benchmark Fuel I with 10ppm S
- Complete design studies of plate reformer

Future Plans: next 12 months

WGS reactor

- Continue catalyst development – low level effort
  - Evaluate outside catalyst systems (vendors, Nat'l Labs)
  - Durability testing to 5000 hours – static test rig
- Reactor design/modeling studies to reduce weight and volume

PrOx reactor

- Establish kinetics over working range
- Model plate reactor systems to achieve <10ppm CO
- Initial durability studies

Los Alamos
NATIONAL LABORATORY

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Quick-Starting Fuel Processors

2003 Hydrogen and Fuel Cells Merit Review Meeting

May 19-22, 2003, Berkeley, CA

ornl
OAK RIDGE NATIONAL LABORATORY

Objective

- Study feasibility of fast-starting a fuel processor
  - To meet DOE targets for on-board fuel processing
    - 60 seconds (2005); 30 seconds (2010) from 20°C

Relevance : On-board fuel processing will ease the transition to the hydrogen economy

Addresses Technical Barriers

I: FP Startup, Transient Operation

L: CO Clean-up

M: FP Efficiency

Feasibility of **A**cceptable **S**tart-**T**ime **E**xperimental **R**eformer

Reviewer Comments

- Demonstrate a fast-start strategy
- Focus on a specific design
- Solicit guidance from industry on practicality of design changes

- ✓ A fast-start strategy has been developed
- ✓ A specific design which can implement the strategy has been defined
  - Industrial partners interested in outcome of specific design are providing input
- ✓ The strategy will be tested in Oct.'03 - Jan.'04

Program Approach

- Consortium of DOE laboratories, universities, and private enterprise
  - National Labs contribute core technologies
  - Private industry contributes components, expertise
  - University resources provide support
    - Faculty members contribute expertise
    - Students participate in experimental activity
  - Information exchange through multiparty NDA
  - Project Duration: October 2002 – June 2004

Technical Approach

- Design a "ATR/Shift/PrOx" fuel processor
  - Capable of implementing a start-up strategy
  - Consistent with application-specific constraints
    - e.g. efficiency, etc.
- Set up in the laboratory as a learning tool
  - Build and test experimental hardware, apparatus
  - Analyticals, balance-of-plant, PC-based data acq./control
- Supported by modeling and small experiments
  - GCTool, CFD
  - Experiments to confirm expectations
    - e.g., ignition of liquid gasoline in the ATR at start-up

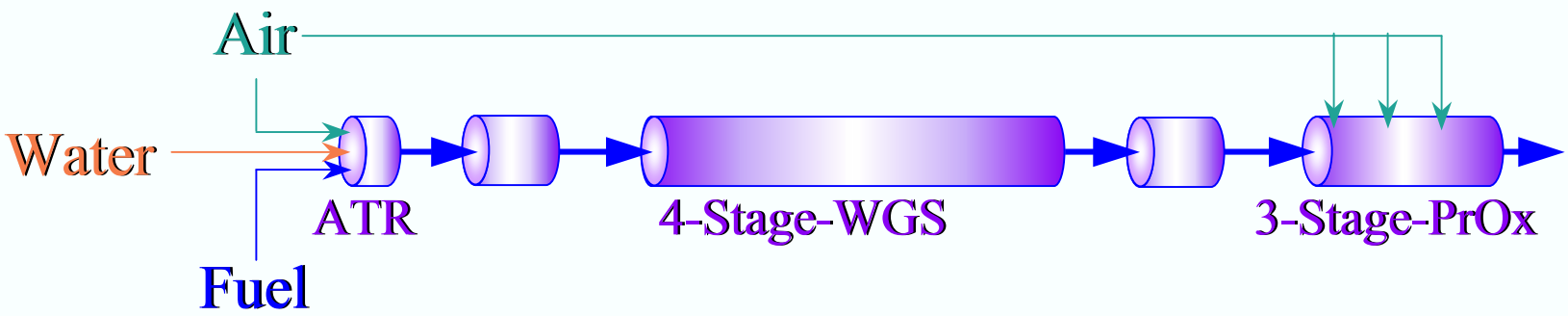
Demonstrate fuel processor generating reformate gas at 90% capacity (9 kWe)

Start-up Time	60 seconds
FP Max. Capacity	10 kWe
Start-up Capacity	9 kWe (145 SLPM of H_2)
Fuel	Gasoline
Reformate @ 61 sec.	$H_2 > 30\%$; $CO < 50$ ppm
Demonstration	Jan. 2004

Project Milestones

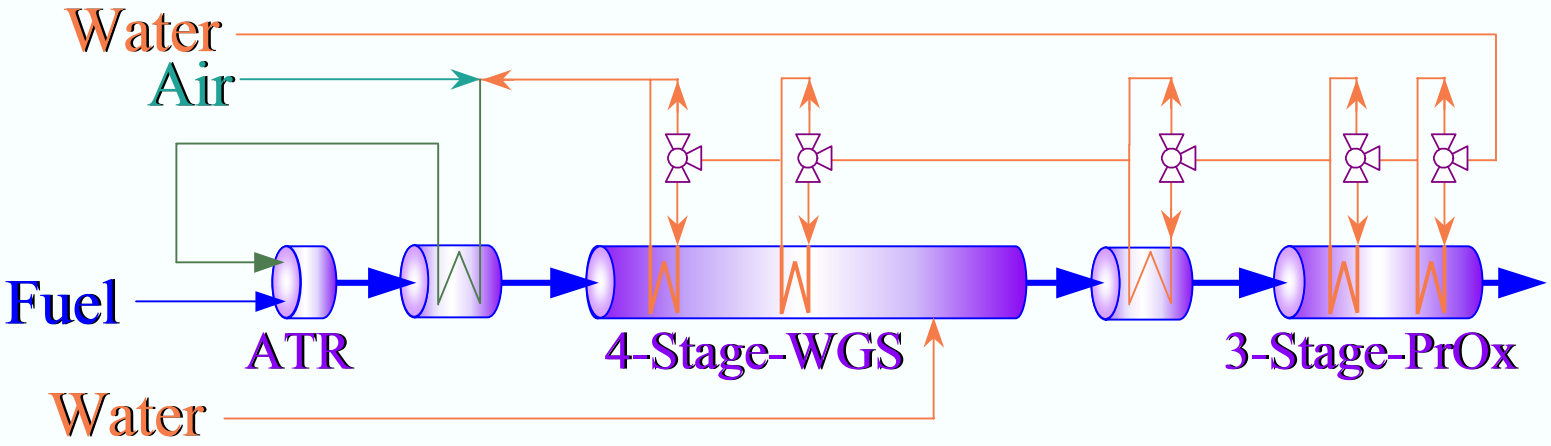
Milestone	*Date*	
FP Defined	Dec. '02	✓
FP Component Sizes Specified	Mar. '03	✓
Components Received at ANL	Jun. '03	
FP System Assembled	Aug. '03	
FP Tests Begin	Oct. '03	
Demonstrate Performance	Jan. '04	
Conclusions to DOE	May '04	

Fuel processor is based on ATR, followed by WGS and PrOx



- 4-stage water gas shift reactor
- 3-stage preferential oxidation reactor
- Thermally integrated unit

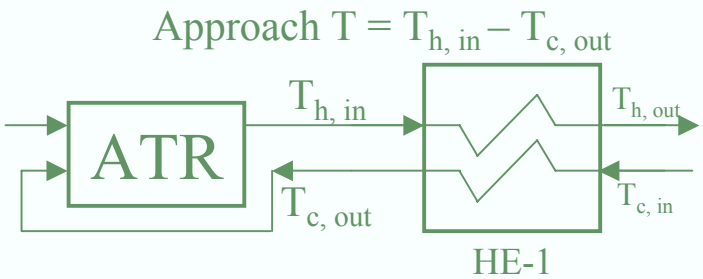
Temperature control features prominently in system definition



- Heat removal in WGS and PrOx units are on-demand only
- Liquid water injected before WG4
  - Heat exchanger not meaningful at low heat duty
  - Higher [H_2O] favors shift reaction

O/C, S/C, and $T_{Approach}$ significantly impact the design

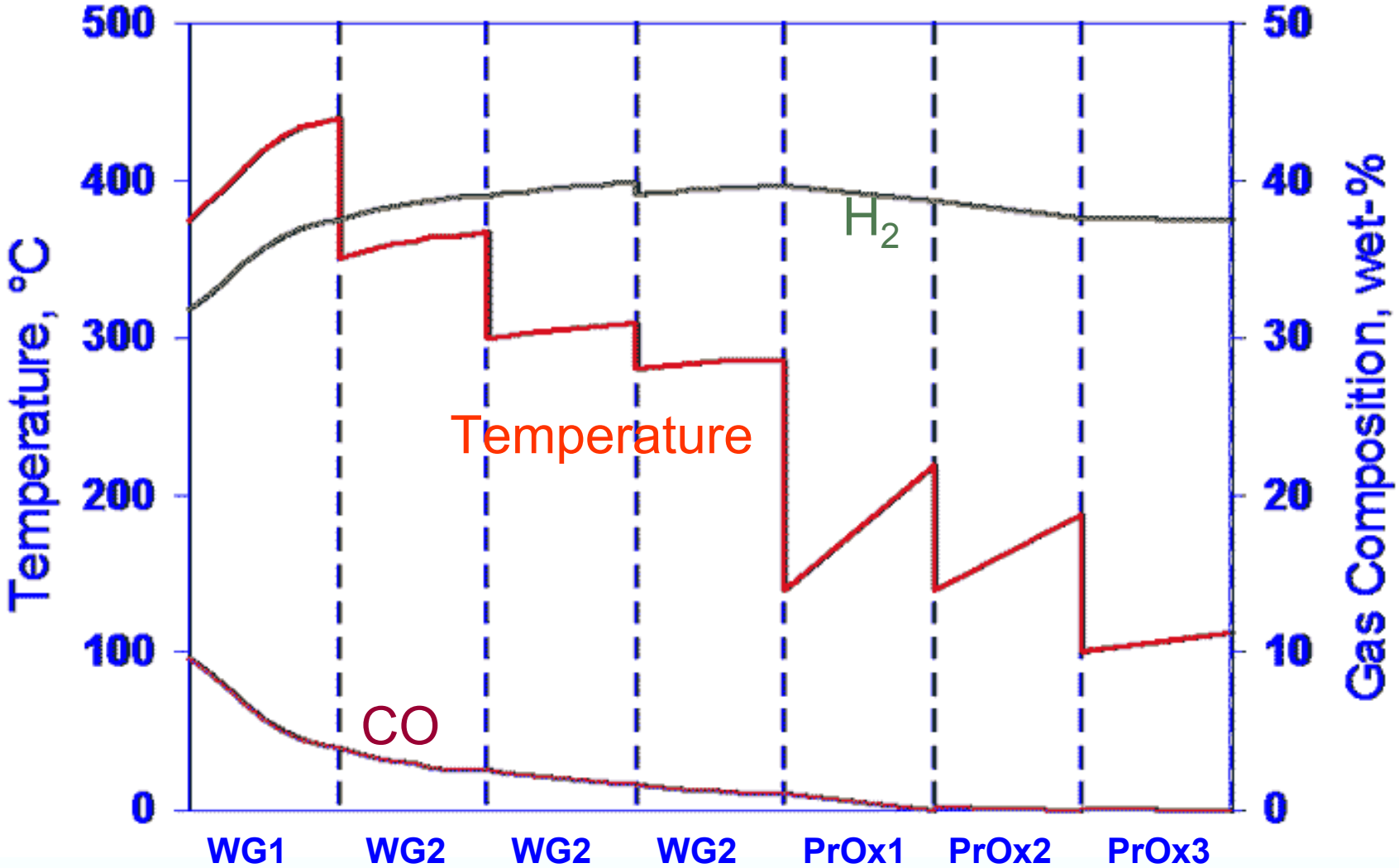
- Higher O/C
  - Raises ATR temperature
    - Reduces CH_4 slip, improves H_2+CO yield
    - Increases CO/CO_2 ratio, increases WGS load
    - Increases heat loads on HEx (more shift rxn, mass flows)
    - Material durability (catalyst, housing, post-ATR HEx)
  - May reduce H_2 concentration in reformate
  - May reduce H_2 yields, lowering FP efficiency
- Higher S/C
  - Lowers ATR temperature
  - Lowers CO/CO_2 ratio, reduces WGS load
  - Shrinks WGS size significantly
  - Reduces fuel processor efficiency
- Higher approach temperature in HEx-1
  - Smaller and lighter heat exchanger
  - Increases (slightly) heat load of heat exchangers
  - Requires more O/C to achieve desired ATR temperature
  - Permits higher S/C



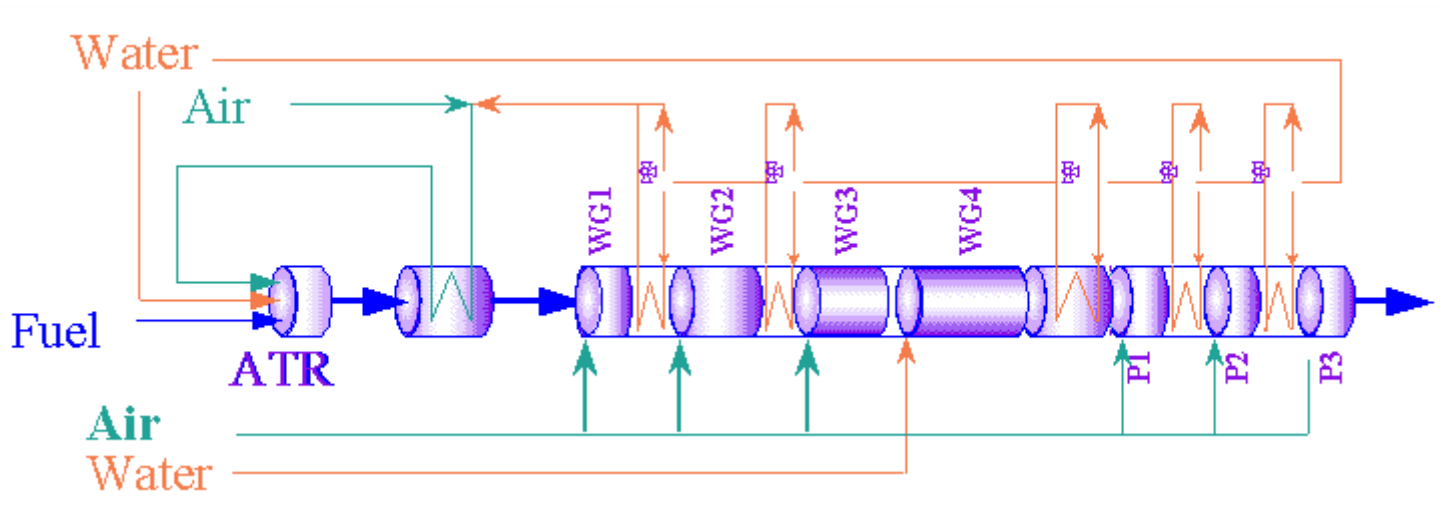
Model predicts 84% efficiency at design point

	ATR	WG1	WG2	WG3	WG4	P1	P2	P3
GHSV, per hr	74K	66K	41K	22K	13K	37K	37K	37K
Catalyst Weight, kg	0.15	0.24 (9%)	0.38 (16%)	0.69 (28%)	1.15 (47%)	0.29	0.29	0.29
Inlet Temperature, °C		375	350	300	280	140	140	100
Exit Temperature, °C	775	440	367	310	287	220	188	113
O/C Ratio (at Inlet)	0.75							
S/C Ratio (at Inlet)	2.1				2.3			
H_2 at Exit, %-wet	31.8	37.5	39.1	39.9	39.7	38.7	37.7	37.5
CO at Exit, %-wet	9.7	4.0	2.5	1.6	1.0	0.3	0.1	10 ppm
H_2O at Exit, %-wet	23.9	18.1	16.6	15.8	16.9	16.9	17.2	17.2

Heat removal stages are arranged to approximate a preferred temperature profile



Start-up: Produce (H_2+CO) in ATR, oxidize downstream to generate heat



- Bring ATR to temperature in 10 seconds
  - Liquid fuel and water injected into ATR
- Hydrogen produced in ATR is catalytically oxidized in the shift reactor to generate heat
  - Heat up first three stages only during start-up
- PrOx catalysts are active at room temperature
  - Sized to handle 4% CO

More than 9-g of gasoline will be needed to heat the catalysts in 60 seconds (10 kWe)

- **For start-up, only the catalyst zones need to be at temperature**

	ATR	WG1	WG2	WG3	WG4	P1	P2	P3
Catalyst Weight, g	150	235	375	690	1,150	290	290	290
Min. Temperature, °C	500	300	300	250	25	75	75	75
Min. Fuel Required*	9-g (13-mL)							

- **Superheated steam and preheated air will be available after heat exchangers are hot**

	HE-1	HE-2	HE-3	HE-4	HE-5	HE-6
Ht. Exchanger Weight, g	1100	586	586	943	943	943
Avg. Temperature, °C	570	400	330	225	180	140
Min. Fuel Required†	15-g (21-mL)					

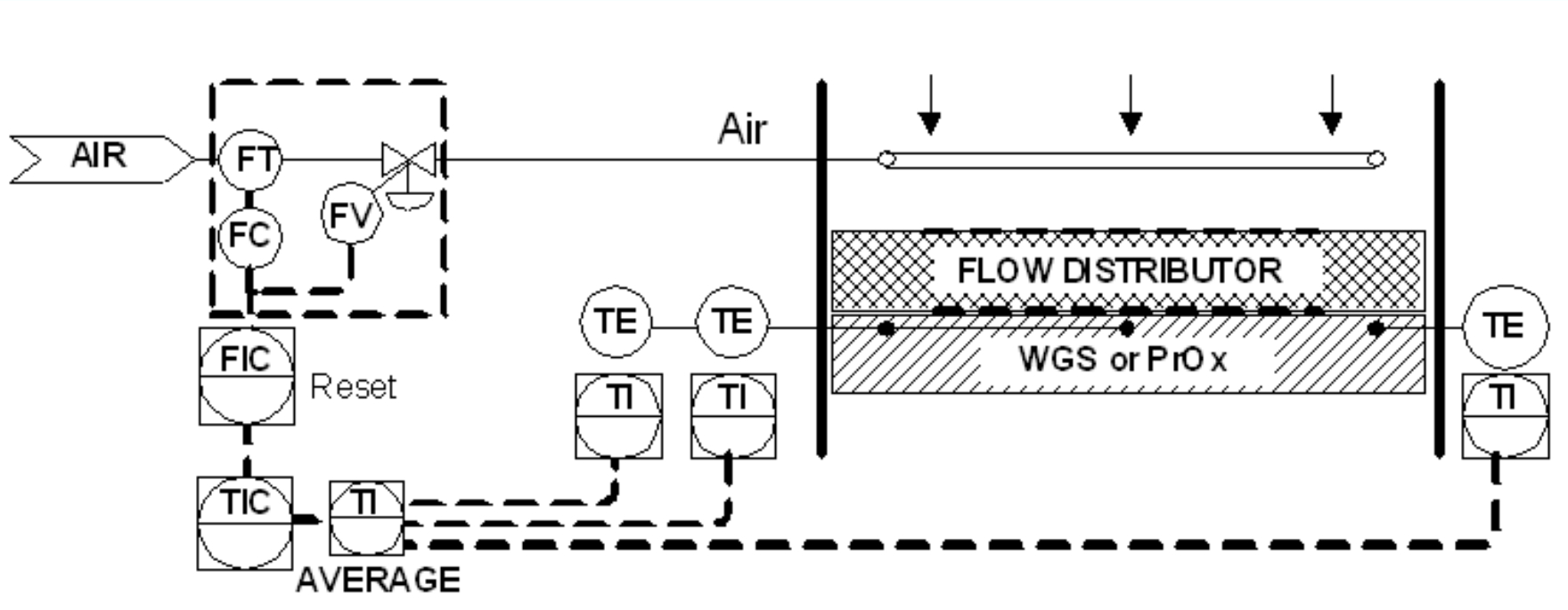
- **For steady state, catalysts will need to be at design temperature**
- **Minimum 34-g of gasoline will be needed per start**
  - **For 50 kWe : 0.07 gals or 1.5 MJ of fuel per start**

*Fuel Rate at 10 kWe □ 42 g/min

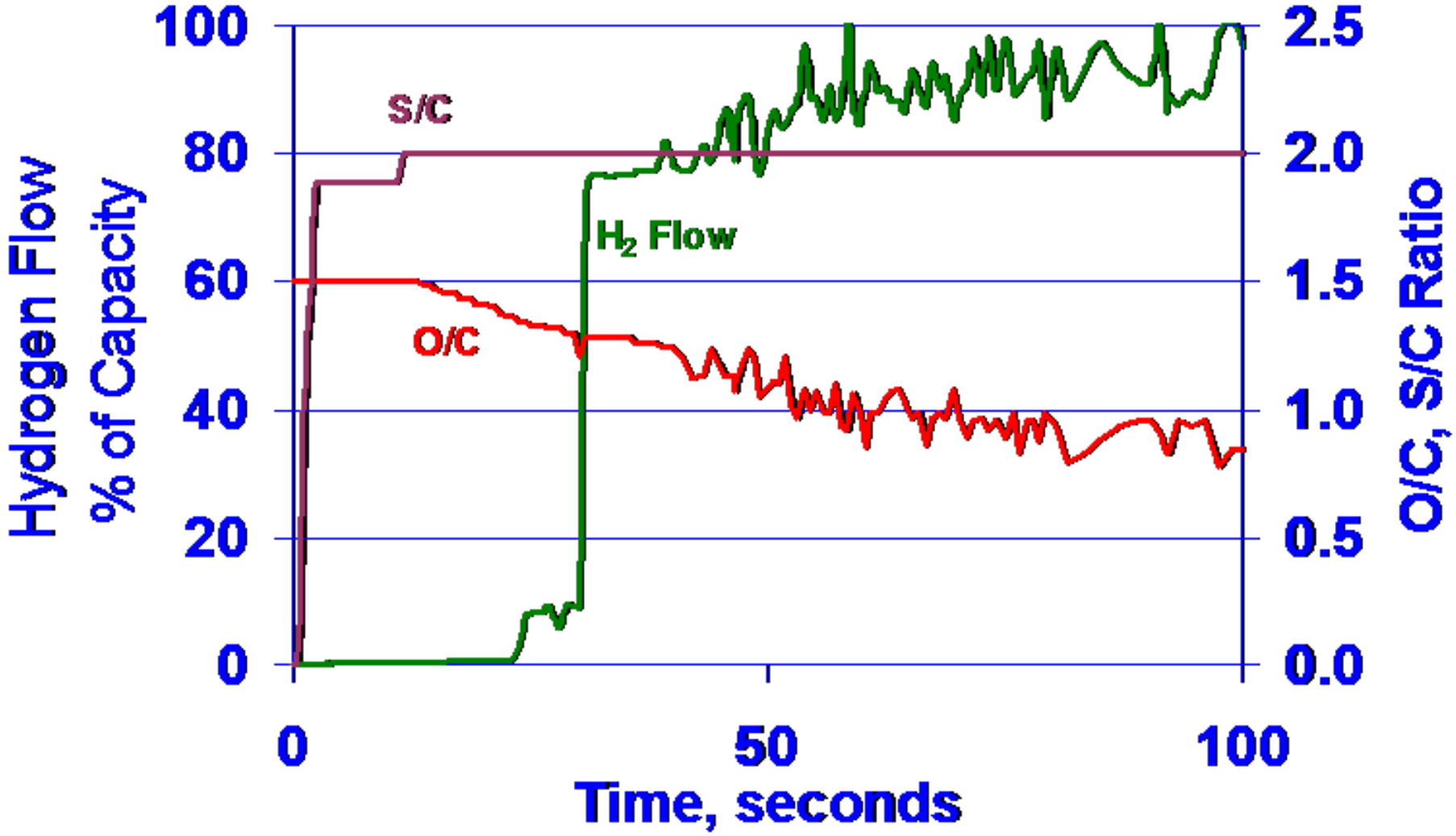
†At 100% heat transfer effectiveness

Start-up performance will rely on timely execution of control algorithm

- Cascade control
  - Field instruments – MFCs, thermocouples, signal averaging, etc.
  - Hardware - Opto22, National Instruments, etc.
  - PC-based software - direct digital control (DDC) - LabView, iFix-Intellution, etc.
- Hardware based control for loops requiring fast response

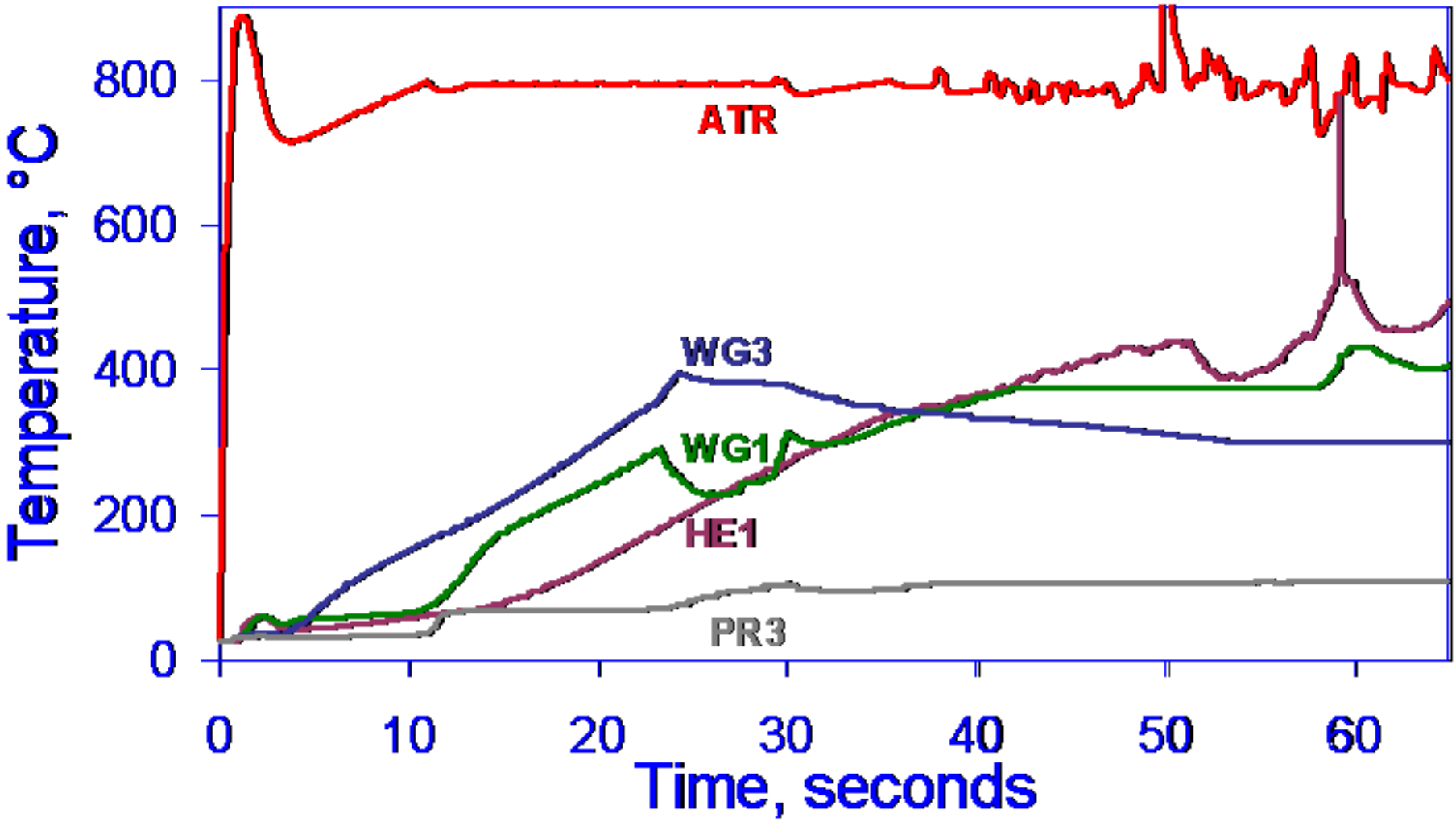


Model: O/C and S/C ratios are adjusted to yield 90% of H_2 capacity in 60s



The critical catalyst zones can be heated quickly

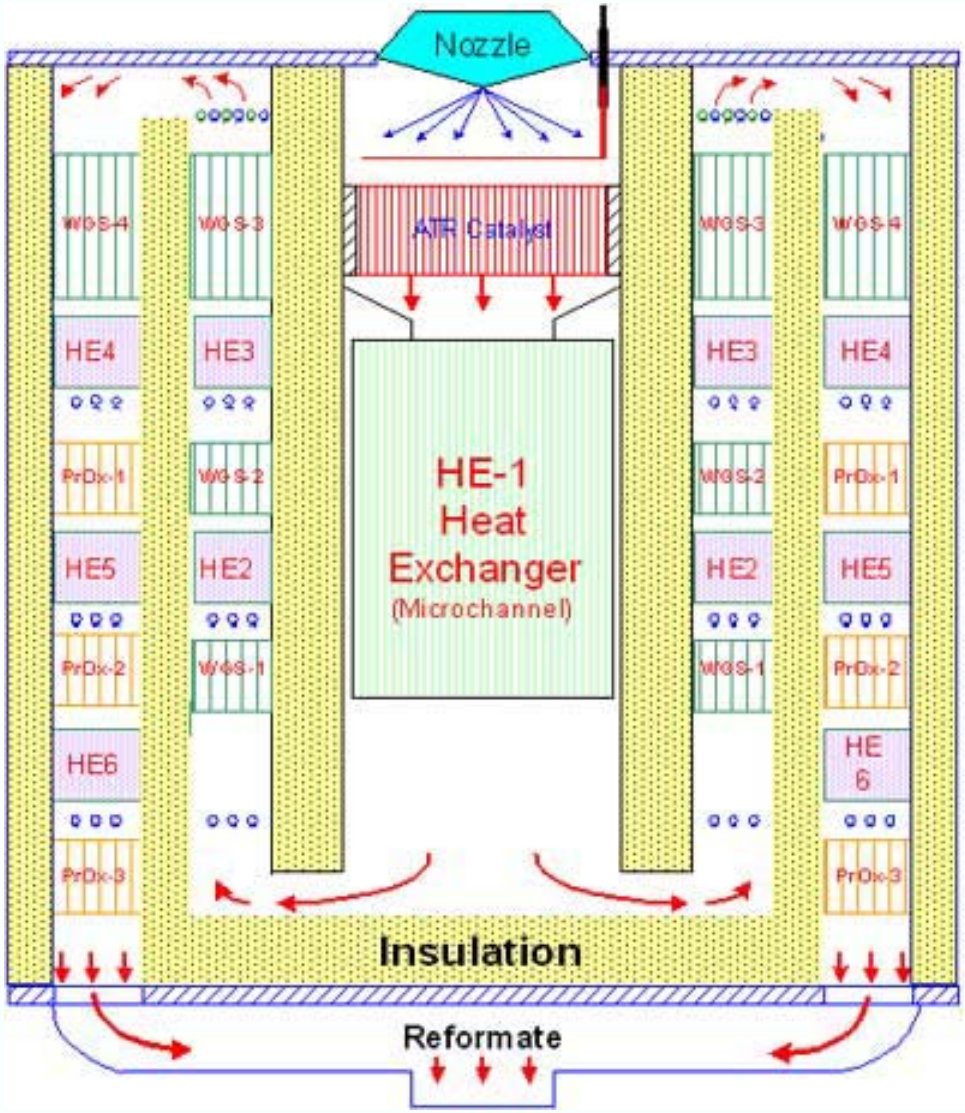
- Catalyst durability will depend on controlling temperature rise

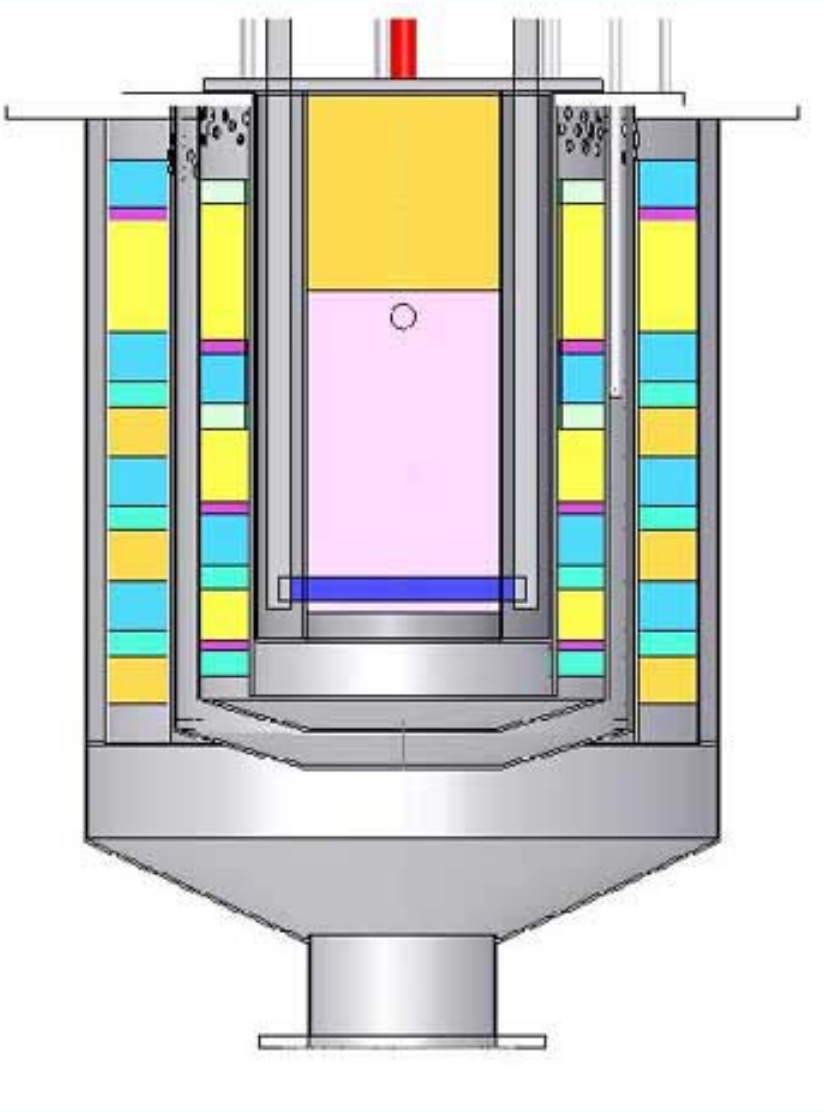


When the fuel processor is better than the sum of its parts

- Precision Combustion Inc.
  - Microlith™ -based ATR and WGS catalyst assemblies
- ArvinMeritor
  - Reactor Fabrication and Prototyping
- Quantum Group Inc.
  - CO sorbent
- Los Alamos National Laboratory
  - PrOx technology and catalyst assemblies
- Oak Ridge National Laboratory
  - Carbon Foam heat exchangers for WGS, PrOx cooling
- Pacific Northwest National Laboratory
  - Microchannel heat exchanger between ATR & WGS-1
- University contributions
  - Sensors (IIT), Controls (Purdue-Calumet, IIT)
- Argonne National Laboratory
  - Modeling, system assembly, control, testing, analysis

Layout of the Fuel Processor Components

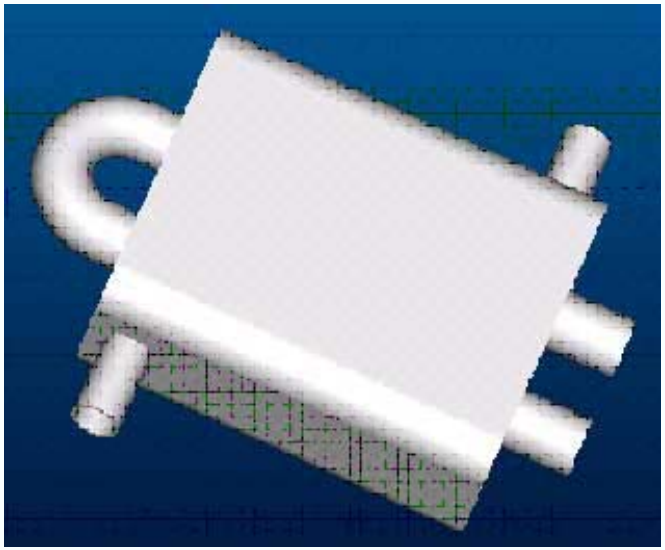




Custom fuel vaporizer and nozzle should enhance reformer performance

- Compact vaporizer
- Heated with gas from spent-gas burner
- Electrically heated during start-up

L=98 mm; W=48 mm; H=120 mm



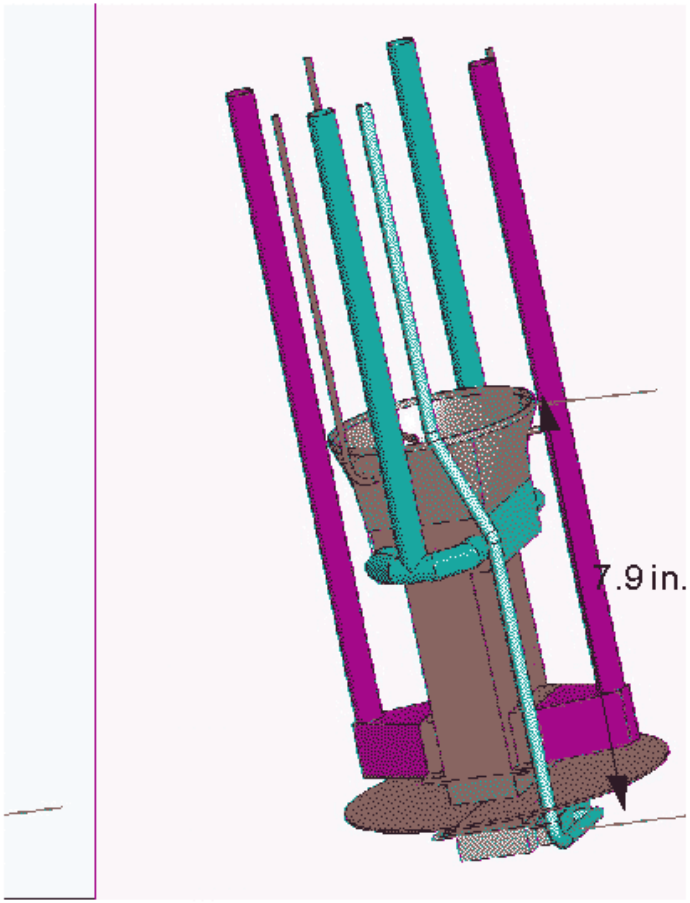
- Nebulize liquids (fuel, water) during start-up
- Spray vaporized fuel, steam, preheated air during normal operations

D=70 mm; H=24 mm

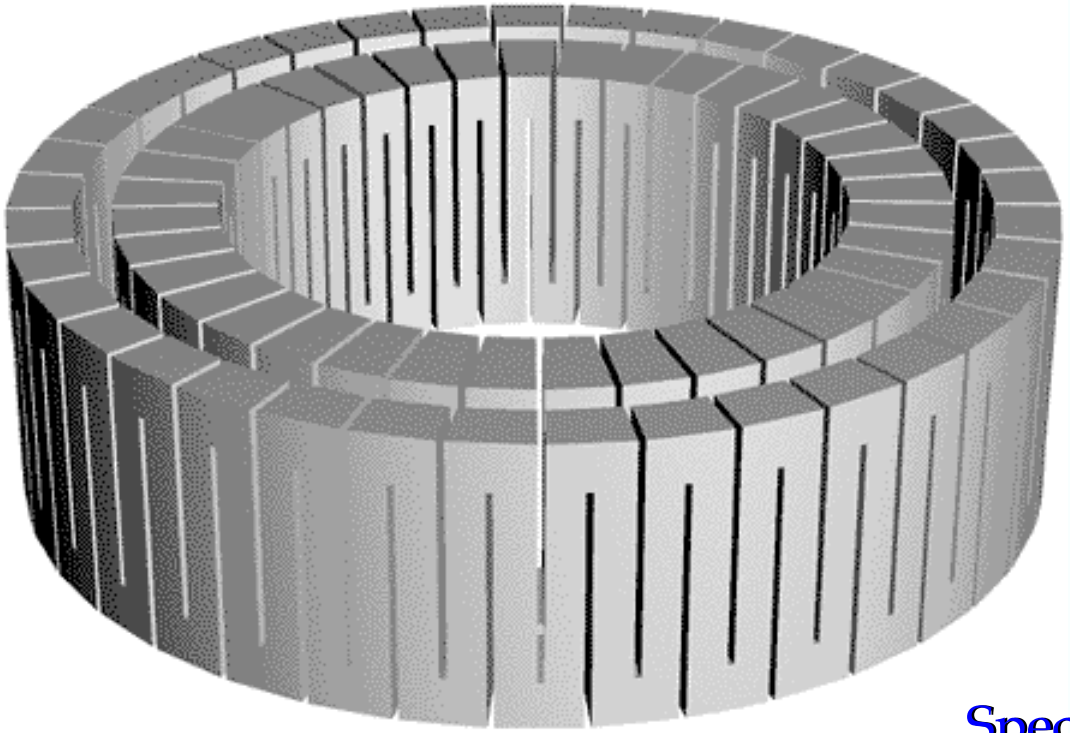
Microchannel Recuperator fits below ATR in the central cylinder

Microchannel Recuperator

- 100°C hot end approach
- 3.6 kW duty
- Approx 1.1 kg
- $\Delta P_{cold} + \Delta P_{hot} < 0.4$ psi total
- Uniform outlet temperature



Annular heat exchangers were designed to match heat load and pressure drop constraints

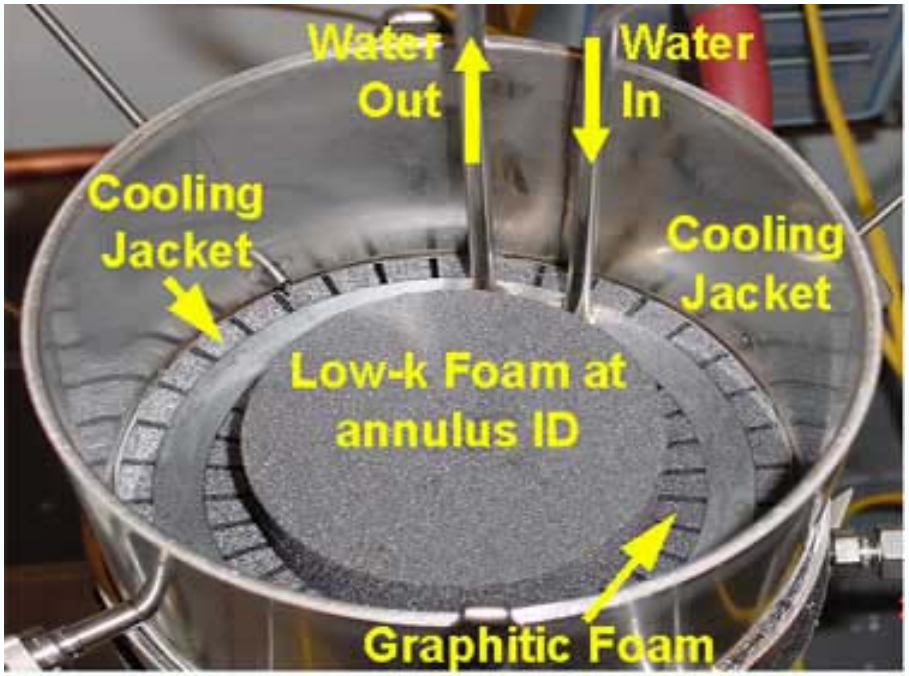


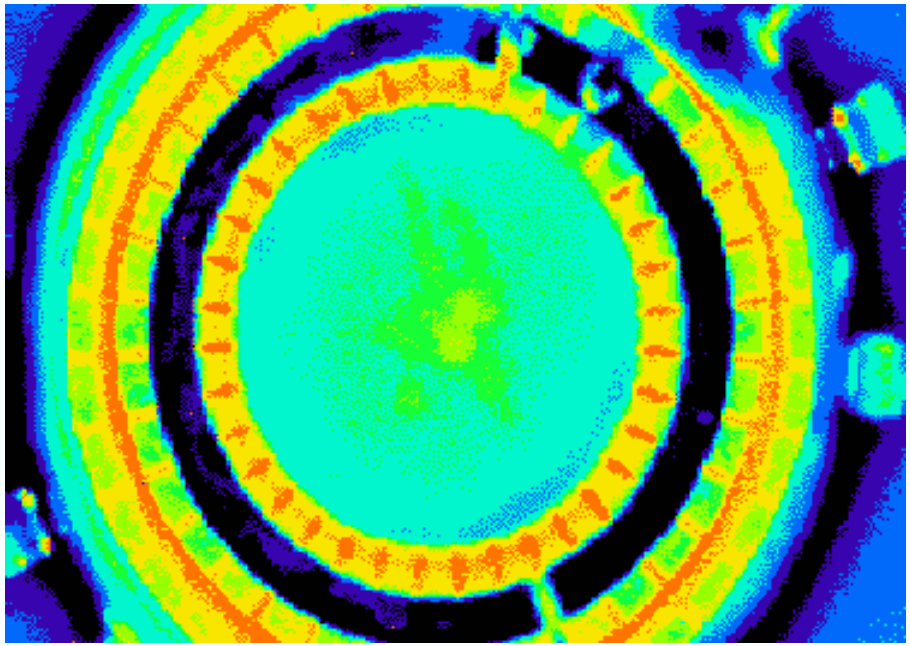
<u>Specifications</u>

- Hot Gas : Flow = 300 slpm
  $\Delta T > 100°C$ (symmetric)
  $\Delta P < 0.1$ psi
- Coolant : Water, 2-phase

OAK RIDGE NATIONAL LABORATORY

Tests indicate rapid, symmetric cooling and low pressure drop





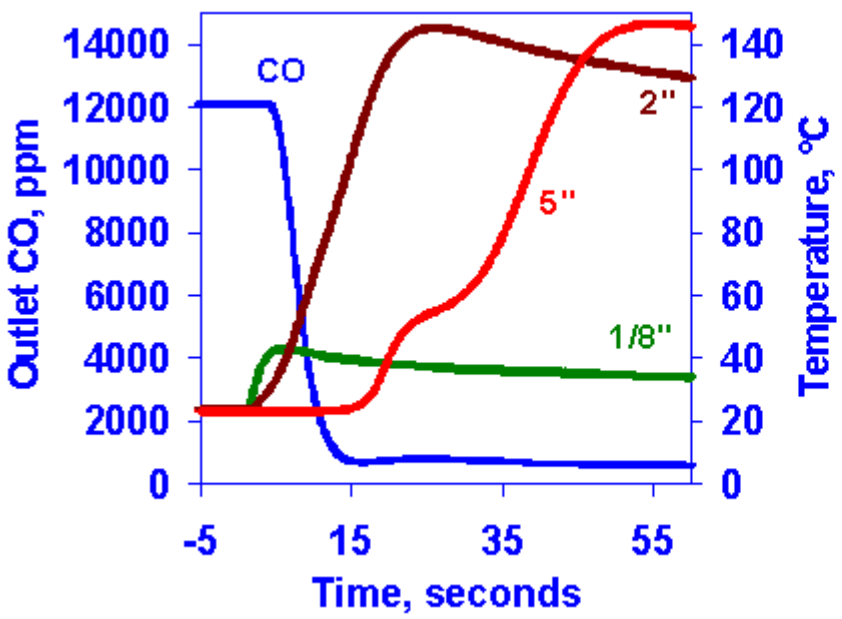
<u>Test Data</u>

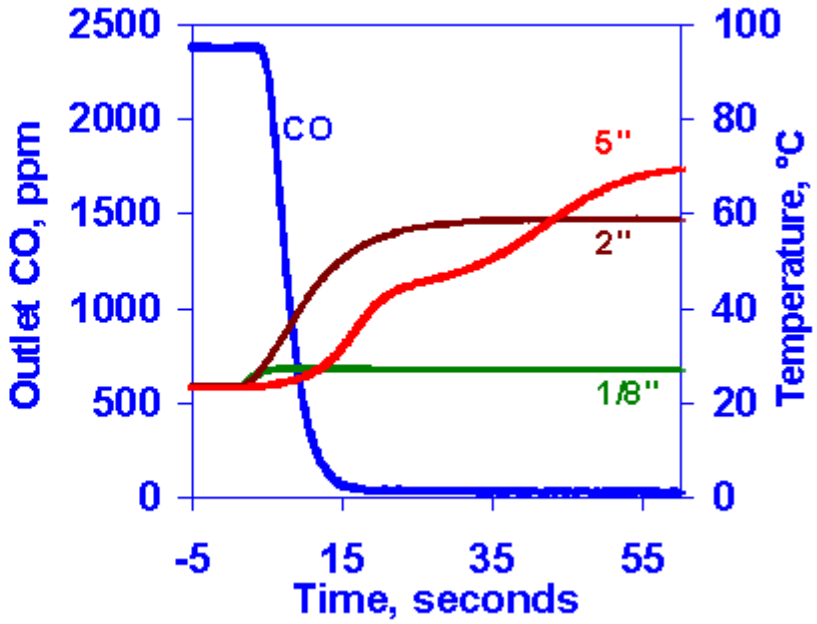
- Hot Gas: Flow = 307 slpm
  - $\Delta T \sim 200°C$ (symmetric)
  - $\Delta P < 0.04$ psi

OAK RIDGE NATIONAL LABORATORY

PrOx is designed to oxidize up to 4% CO at start-up

- Defined catalysts and supports with low thermal mass
  - GHSV = 13,000 /hr, Wt. = 0.87 kg
- Experiments indicate 1.2% CO can be converted in 2-stages
  - 4% CO conversion in 3-stages to be confirmed





Los Alamos NATIONAL LABORATORY

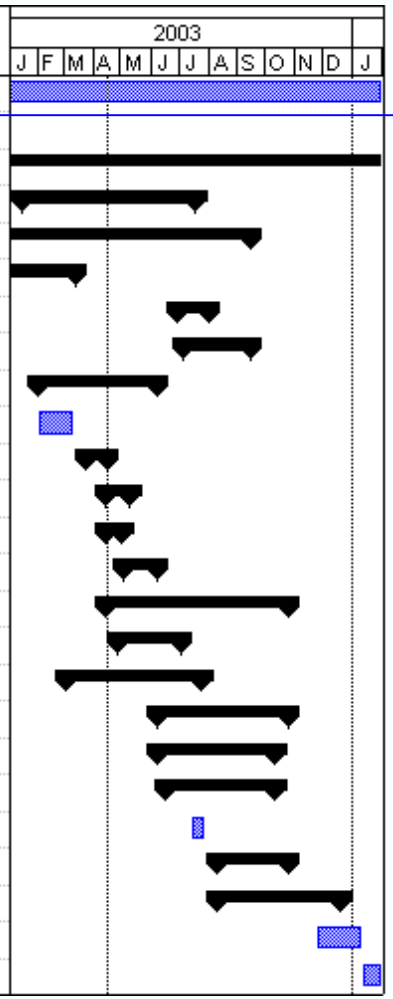
Argonne Electrochemical Technology Program

Progress and Accomplishments

- Determined kinetics of ATR, WGS, PrOx catalysts
- Modeled FP system to define design point
- P&ID complete
- Modeled to establish mixing characteristics
- Reactor design completed
  - DFM in progress
- Designed nozzle and vaporizer
- Studying ignition and catalytic oxidation rates of reformate gas
- PNNL : Designed micro-channel heat exchanger to fit below ATR
- ORNL : Designed foam heat exchangers for annular geometry
  - Experiments in progress to confirm projections
- LANL : Verified PrOx activity and response at room temperature

Project Schedule

ID	Task Name	Finish
1	Project Duration	Fri 1/30/04
2	System Definition	Fri 9/27/02
3	Modeling	Fri 1/30/04
7	R&D Solutions	Fri 7/18/03
13	Reactor - Spec to Assembly	Mon 9/15/03
14	Component Specs	Wed 3/12/03
17	Receive Components	Thu 7/31/03
25	Assembly	Mon 9/15/03
28	FP System Engineering	Fri 6/6/03
29	Develop Block Flow Diagram	Fri 3/7/03
30	P&ID	Wed 4/16/03
35	Bill of Materials	Fri 5/9/03
40	Long Lead Items	Fri 5/2/03
43	System Layout	Fri 6/6/03
48	Control System and EE	Fri 10/24/03
60	Procurement	Thu 7/3/03
73	Lab Set-up	Fri 7/25/03
82	System Fabrication	Thu 10/23/03
83	Process and Mechanical	Fri 10/10/03
91	Electrical and Control	Fri 10/10/03
97	Analytical	Fri 7/25/03
98	Safety Review	Thu 10/23/03
101	Testing	Fri 12/19/03
116	Total System Testing	Fri 1/9/04
117	Demonstration	Fri 1/30/04



- Reformate Ignition
- Fuel Vaporizer
- Nozzle evaluation
- Ignition w/ liquid fuel
- ATR Catalyst

Test Plan

Focus on reliable control to execute start-up strategy

- Confirm ATR start-up and control — *Jul.*
  - From manual to automated
- Add next component and confirm performance — *Sep.*
- Execute start-up strategy in slow mode — *Dec.*
- Accelerate start-up process incrementally — *Jan.*
- Benchmark start-up, steady-state performance — *Jan.*
- Report progress and recommendations to DOE — *May*

Can on-board fuel processors meet the start-up target?

- Time and fuel needed to reach rated efficiency
- Rate limiting step
- Failure modes and solution
- Core R&D needs and priority

Summary

- A collaborative effort is underway to study fast-start feasibility of on-board fuel processors
- A laboratory-scale fuel processor has been defined
- Models predict start-up in 60 seconds is feasible
- The study contributes to state of fuel processing technology and promotes technology transfer

Contributors

- ANL
  - Rajesh Ahluwalia
  - Sheldon Lee
  - Stephen Lottes
  - Dennis Papadias
  - Daniel Applegate
  - Kai Liao
  - Todd Harvey
  - Steve Calderone
  - Akram Hossain
  - Vince Novick
  - Xiaohua Wang
  - Shabbir Ahmed
- LANL
  - Michael Inbody
- ORNL
  - April McMillan
  - James Klett
  - Glenn Romanoski
- PNNL
  - Greg Whyatt
  - Larry Pederson

Progress in Microchannel Steam Reformation of Hydrocarbon Fuels

2003 Hydrogen and Fuel Cells Merit Review

May 19-21, 2003

Greg A. Whyatt

Team Members: Kriston Brooks, Jim Davis, Chris Fischer, Dave King, Larry Pederson, Susie Stenkamp,Ward Tegrotenhuis, Bob Wegeng

Pacific Northwest National Laboratory

Approach –2003

- Confirm benefits of operating steam reformer at higher temperature.
  - Productivity for benchmark fuel increased 3X between 650°C and 850°C.
  - Sulfur tolerance significantly increased.
  - Higher productivity reduces thermal mass → less air and fuel required for startup, reduced losses associated with cycling thermal mass on startup.
- Operate a low dP steam reformer capable of fast startup
  - Design/build system to achieve fast start while maintaining capability to achieve 78% efficiency during steady-state operation.
  - Fast start to be achieved by maintaining pressure drops low and using large flow of combustion gas. Initial work based on a 650°C reformer in stainless steel.
- Integrate reformer with WGS and PROX at 2 kWe scale.

Objectives

- Develop a prototype microchannel-steam reforming based fuel processor at 2 kWe scale that will meet DOE performance targets when scaled up to 50 kWe.

Performance Criteria	2003 Projected Performance	2005 DOE Target
Power Density	1191 W/liter	700
Specific Power	376 W/kg	700
Efficiency	78.7%	78.0%
Durability	>1000 hr[(a)]	4000 hr
Transient (10% to 90%)	~5 sec[(a)]	5 sec
Cold Start, 20C	30 sec[(a)]	< 1min

(a) Durability and transient demonstrated for reformer and associated HX only. Cold start estimate is for reformer and HX only.

- Engage industrial partner(s) to facilitate development of full-scale fuel processing system.
- Develop reactors, vaporizers, recuperative heat exchangers, and condensers broadly applicable to other fuel processing options.

Project Timeline

FY 1998
Full-size gasoline vaporizer/combustor
R&D100 Award

FY 1999
Fast SR kinetics observed in a microchannel reactor

FY 2000
Designed and built 10 kWe SR with integrated HX network

FY2001
10 kWe reactor testing
First "low dP" vaporizers
Modular test stand established

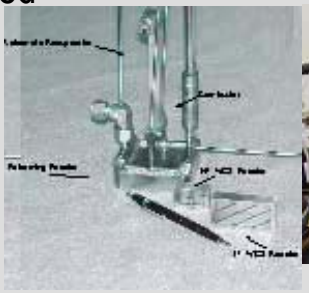
FY 2002
SR fuel flexibility, durability testing
WGS/PROX catalyst studies
Differential temperature reactor concept
SR/WGS/PROX initial integration
Full-scale low dP vaporizers delivered

Engineered catalyst, reactor development

Feasibility of rapid start capability

Sulfur management

Integrated reformer/fuel cell at ~2 kWe



FY 2003
Investigate improved steam reforming kinetics and sulfur tolerance at high temperatures. Fast start. WGS and PROX integration.

Collaborate with industrial partner(s) on manufacturing, field testing, lifetime, controls

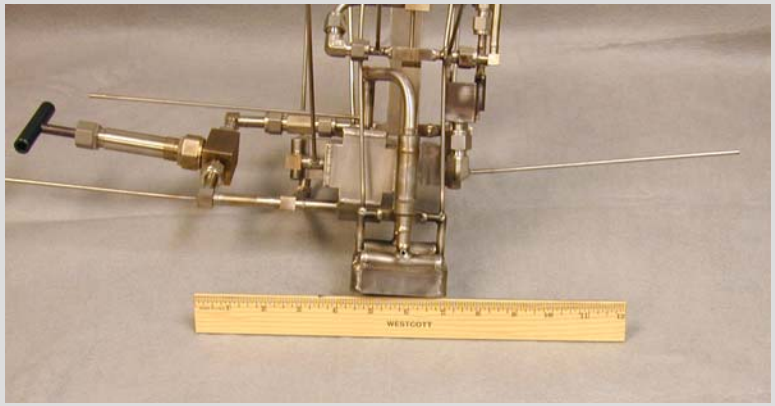
2003 — 2004 — 2005 — 2006 — 2007 — 2008

High Temperature Steam Reforming

Motivation for Investigation

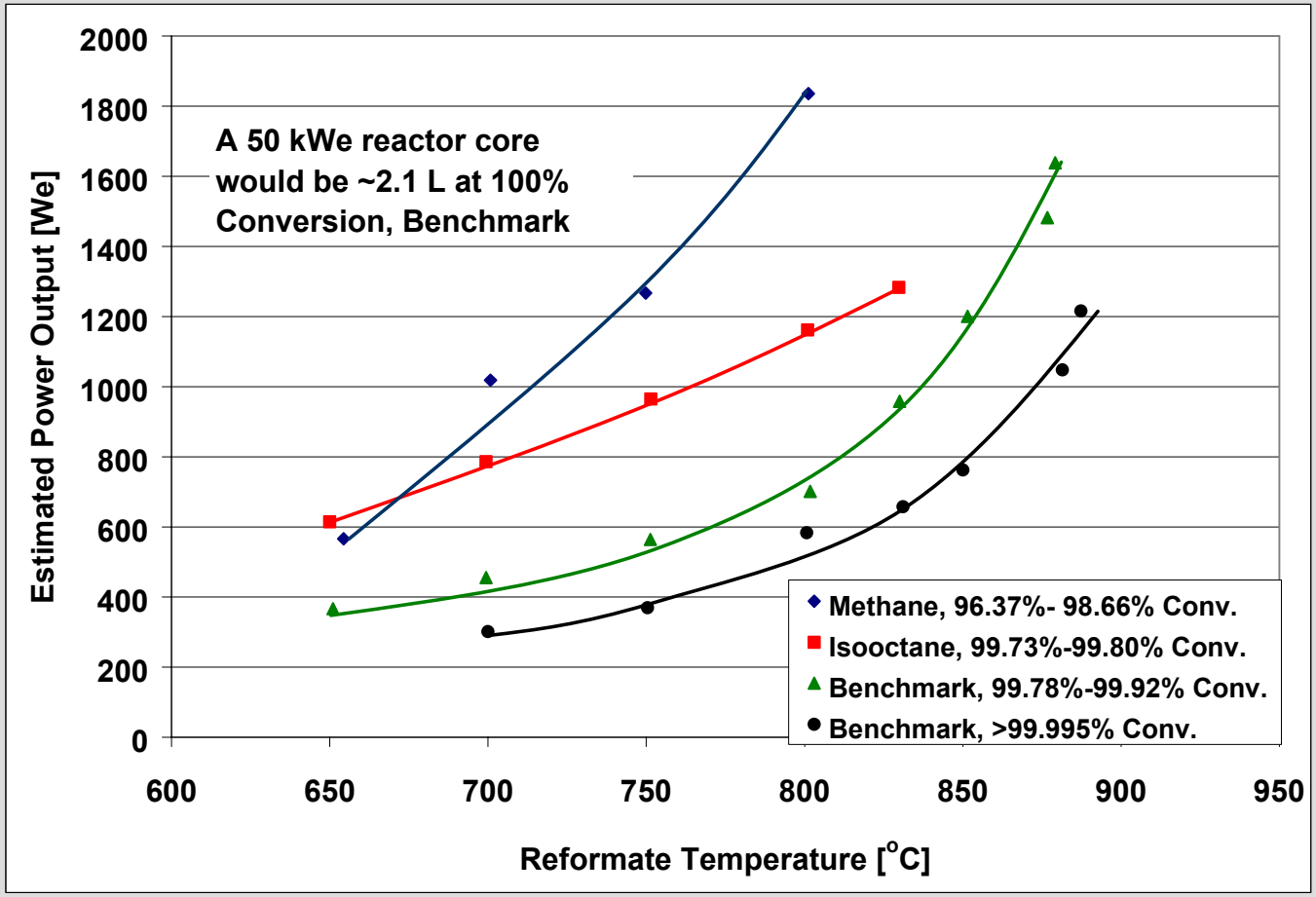
- Reduce Reactor Size - exponential productivity increase with temperature
- Reduce Catalyst Quantity - higher productivity results in less catalyst
- Reduce Reactor Startup Mass – reduction in mass results in less fuel and air compression required during startup. Losses associated with cycling of thermal mass are reduced.
- Improve Sulfur Tolerance – Improve sulfur tolerance may allow sulfur cleanup to be performed on reformate rather than on liquid fuel.
- Evaluate Carbon Deposition Potential - High temperatures increase potential to deposit carbon by cracking of hydrocarbons at inlet (even if not an equilibrium condition).

Inconel 625 Reformer



Reformer Productivity vs Temperature

(All fuels at 3:1 S:C, CH_4 conv. is % approach to equil., Inconel 625 reformer)



Stability of catalyst productivity verified by measuring the conversion at a reference condition before and after generation of the data for each curve.

Characterization of Sulfur Sensitivity

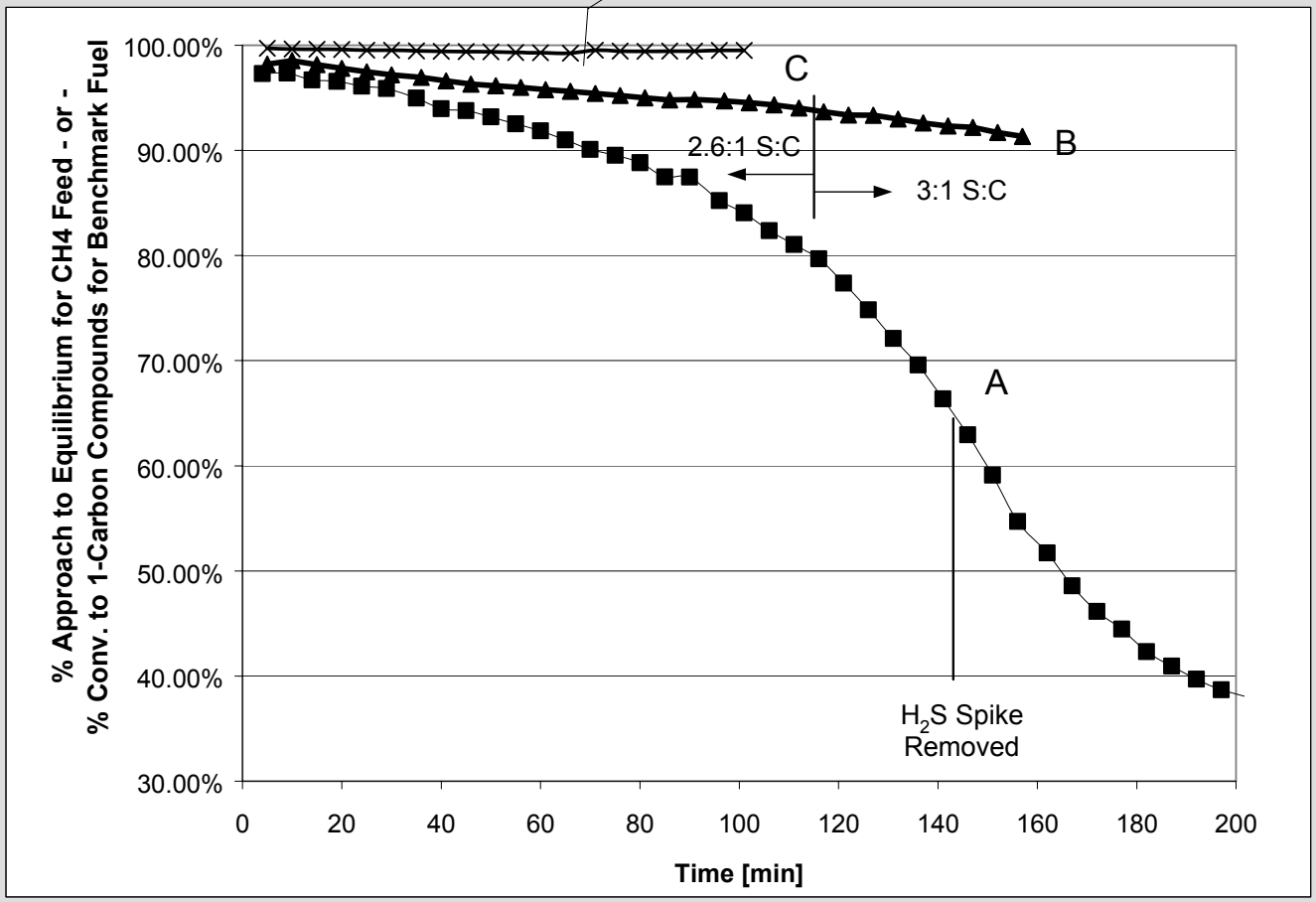
Sulfur Added as H_2S Spike in Methane

(3:1 S:C, Inconel 625 reformer)

A – Reformate outlet at 650°C. CH_4 with H_2S at 5.4 ppmv (10 ppmw benchmark equivalent)

B – Reformate outlet 650°C. Benchmark Fuel w/estimated 10 ppmw S plus CH_4/H_2S spike at 10 ppmw S equivalent.

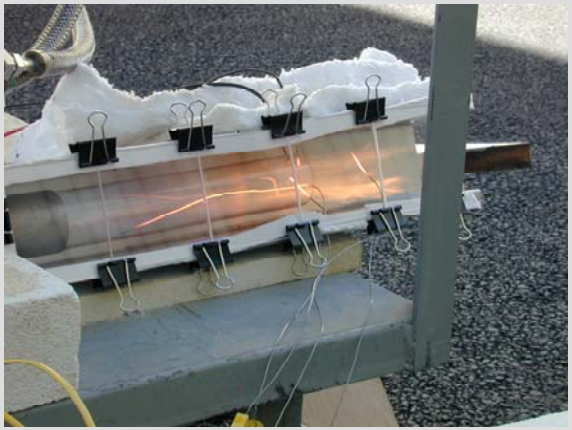
C – Reformate outlet 800°C. Benchmark Fuel w/estimated 10 ppmw S plus CH_4/H_2S spike at 10 ppmw S equivalent. Sulfur from previous test (B) not removed prior to test.



Benchmark Fuel Composition, wt%: 74% Isooctane, 20% Xylenes, 5% methylcyclohexane, 1% 1-Pentene

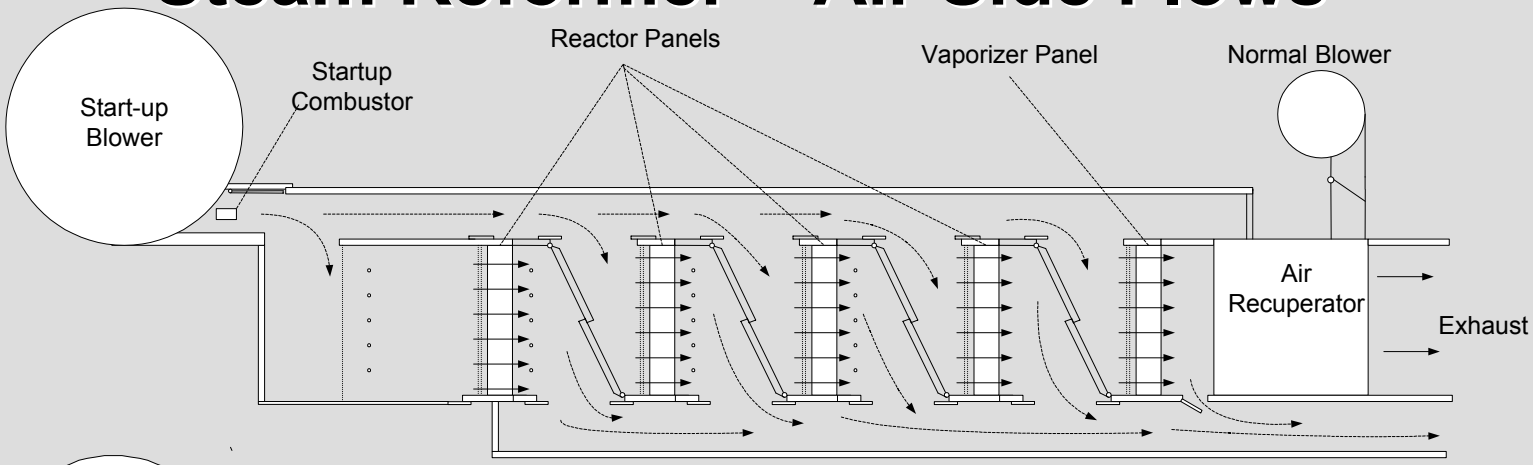
Fast Start Approach

- Focus initially on steam reformer, vaporizer, and air and reformate recuperators. Incorporate WGS and PROX in system as development continues.
- Current system designed to 2 kWe at 650°C reformer temp.
- High combustion gas flows at low pressure drop heat the reformer, vaporizer and air recuperator.
- Reformate recuperator is heated via steam from vaporizer.
- Combustion gas at startup generated by non-catalytic atomized fuel combustion. Combustor tested for isooctane and regular gasoline. Provides 800°C gas in as little as 2 seconds.

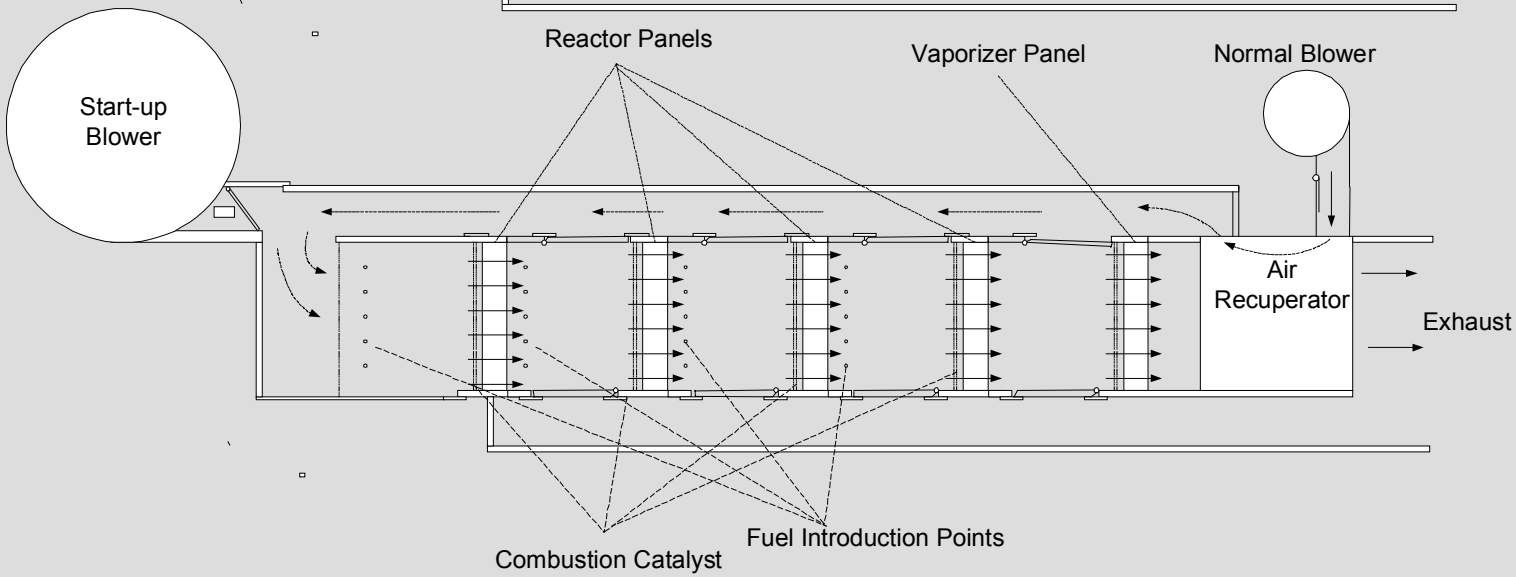


Concept for Low Pressure Drop, Rapid-Start Steam Reformer – Air Side Flows

Startup



Operation



2 kWe Reactor System – Predicted Air Side Pressure Drops

	2 kWe, Steady State Output Condition		30-Second Startup Condition	
Device	**Flow [slpm]**	**ΔP [inches H_2O]**	**Flow [slpm]**	**ΔP [inches H_2O]**
Steam Reformer Panel	100	0.65/panel 2.6 total for 4	800	5.2
Water Vaporizer Panel	100	0.28	800	2.2
Air Recuperator	100	1.5 cold side 1.6 hot side	200 (vap exhaust)	3.0
Total	**100**	**6.0**	**4000**	**5.2**

<u>50kWe-Scale Air Compression Power Implications</u>:

During operation theoretical compressor power is very low (~63W)

During 30 second startup, theoretical compressor power is ~2.2 kW

Fast Start/Low dP Reforming System Components

Reformer

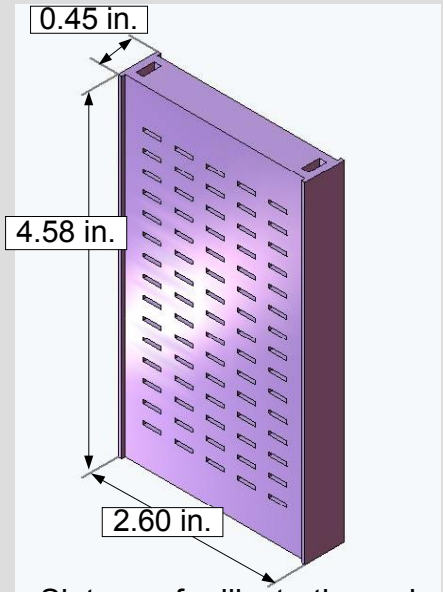
- 4X, ~500 We panels for 2 kWe total at 650°C.
- Air side ΔP ~0.65 inches water at 500 We output.
- uniform temperature for all reaction pathways.
- Stainless construction, ~1534 g for 4 panels.

Water Vaporizer

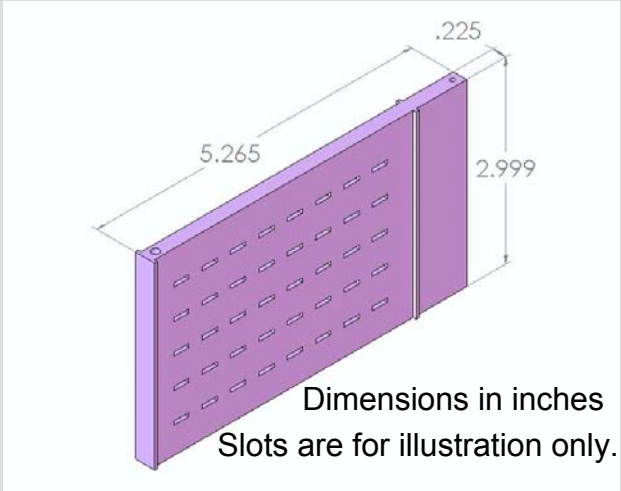
- Low gas side ΔP, <0.28 in. water
- Utilizes reactor exhaust
- Gas inlet/outlet 633°C/146°C
- Steam outlet 293°C
- ~400g

Air Recuperator

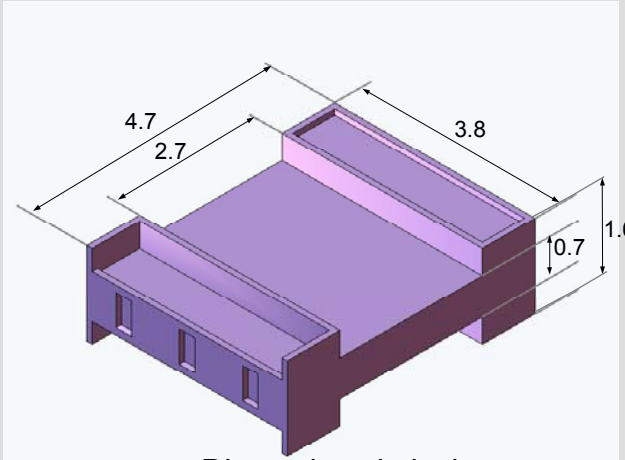
- Low ΔP, <2 in. water per pass
- 87% effective, ~50°C outlet
- Excellent Turndown
- ~876 g



Slots are for illustration only.



Dimensions in inches
Slots are for illustration only.



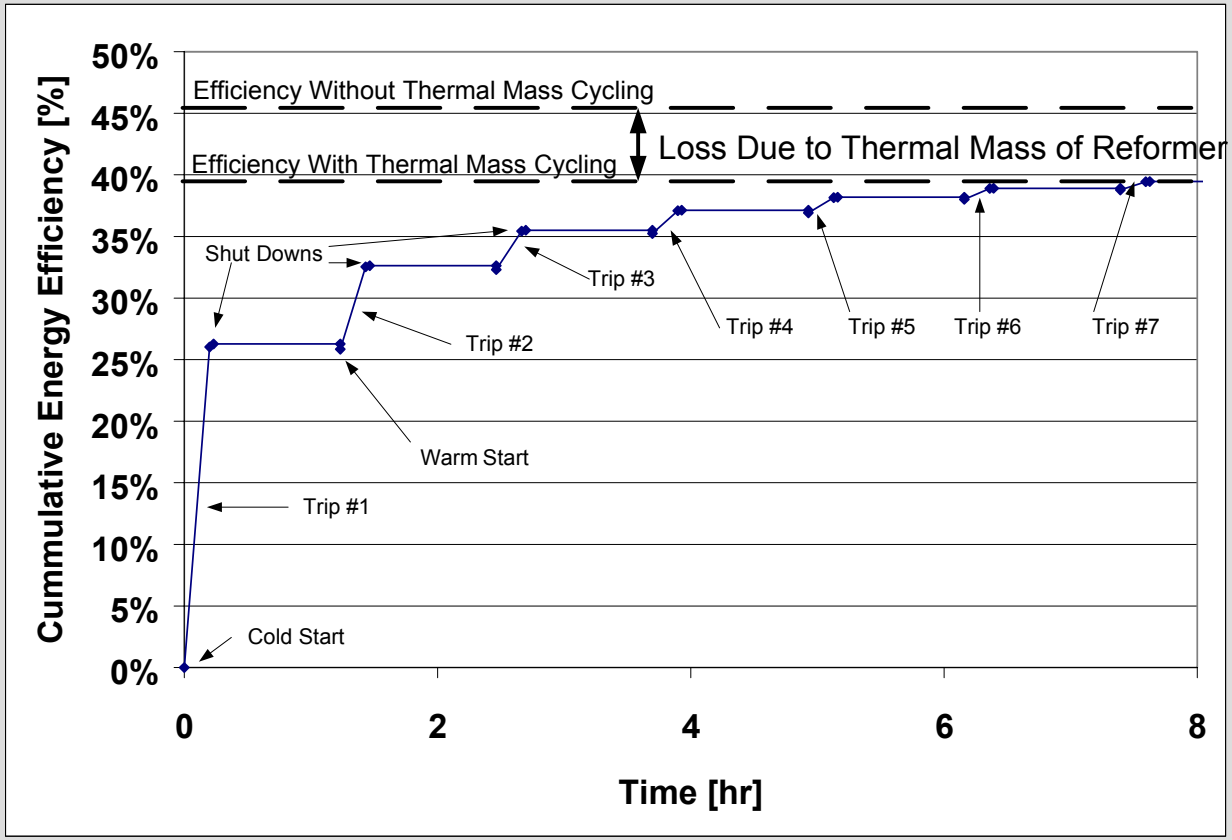
Dimensions in inches

Preliminary Estimate of Efficiency Loss Due to Cycling Thermal Mass of Reformer on Startup/Shutdown Cycles

- Objective – Assure that the thermal mass associated with the fuel reformer does not impose a severe efficiency penalty when thermally cycled in an automotive application.
- California Air Resources Board (CARB) real-world study
  - 6.7 Trips per day
  - 61% of cold soaks <1 hour
  - 24.8 mph (average per trip)
  - 46 miles per day
- Various Assumptions →7 trips/day separated by 1 hour shutdowns, each trip having 12 minutes at 37% output and 1.9 minutes at 5% output.
- Estimated masses of components with 3.5 inches conventional insulation, neglect connections.
- Calculation addresses only thermal mass effect, does not include electrical consumption and exhaust heat losses during startup.

Thermal Mass Startup Penalty

- Efficiency penalty ~5.2% for one day, ~4.5% for 7 day cycle.
- At 650°C reformer temperature, reactor is over half the thermal mass.
- Higher temperature reformer will reduce startup penalty



Plans 2003

- Sulfur Testing - Continue high-temperature sulfur testing to include longer-term testing, with liquid S spikes up to ~30 ppmw.
- Improved Catalyst – Improved catalyst is now available. It is expected to have similar activity at lower cost with increased mechanical and high-temperature durability.
- Fast Start Low-dP System
  - Complete fabrication of stainless reactors and components
  - Conduct initial testing of panel reformer with new catalyst.
  - Generate design input for high-temperature low-dP reformer.
  - Conduct 30-second start tests. Initial tests will not include WGS and PROX.
- Move to High-Temperature System - Revise fast start system design to incorporate high temperature low-dP reformer.
- Integrate with WGS and PROX at 2 kWe scale.

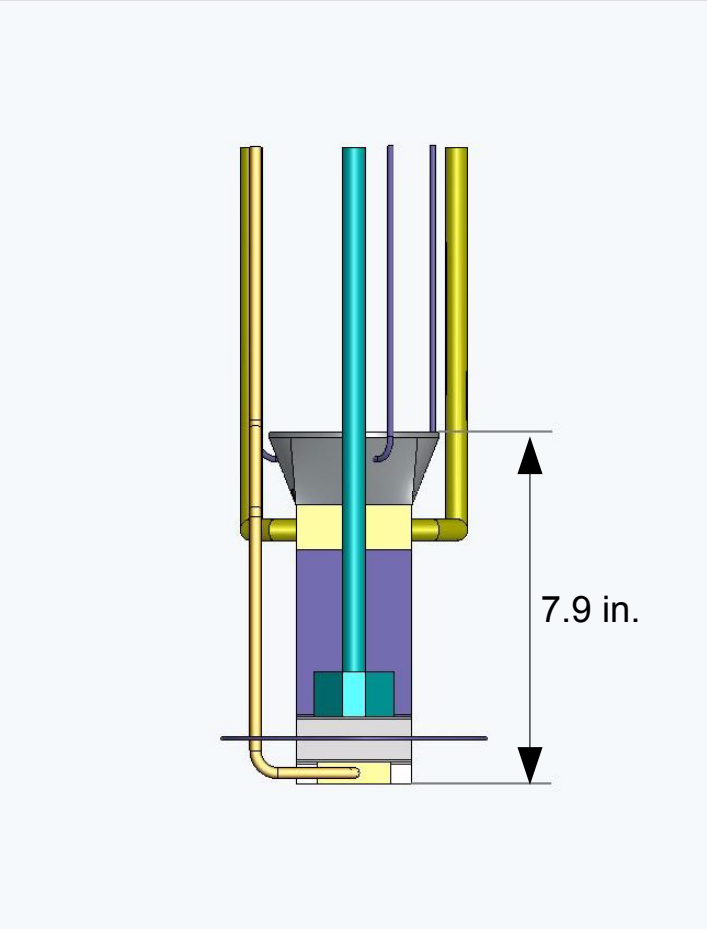
Interactions –
Microchannel Recuperator and Mixer Assembly for FASTER Project

Microchannel Recuperator

- -100°C hot end approach
- -3.6 kW duty
- -Approx 1.1 kg w/o mixer
- -$\Delta P_{cold} + \Delta P_{hot} < 0.4$ psi total
- -Uniform outlet temperature

Microchannel Mixer

- -Uniform outlet temp
- -Uniform air-reformate mixture



Interactions, continued

- Posting on the Federal Business Opportunity Website for *Microchannel Fuel Reformation for Fuel Cell Applications*. – The quality and quantity of responses led to a decision to license intellectual property on a non-exclusive basis.
- Testing of a microchannel water vaporizer designed for a 50 kWe fuel processor was concluded at McDermott. Similar testing concluded at GTI for boiler application.
- Finalizing contract with the Gas Technology Institute (GTI) to work with Cleaver-Brooks and GTI to provide a prototype micro-channel economizer for a highly efficient boiler.

Conclusions

- High Temperature Reforming Benefits
  - >3X productivity when increasing from 650°C to >850°C.
  - Significantly increased sulfur tolerance at 800°C vs 650°C.
  - Reductions in reformer thermal mass
  - Less air and fuel required during startup
  - Penalty associated with cycling thermal mass reduced
- A low pressure drop steam reformer that can start in 30 seconds appears feasible.
- Penalty associated with thermal mass of fuel processor is non-negligible. Penalty is reduced significantly by considering multiple restarts in a single day.

Responses to Comments

- *"Given the ...thermal masses, startup energies need to be …considered, not just start-up times":* **Calculation performed to assess impact of thermal mass on system efficiency.**
- *"Steam reformer needs to operate at higher temperature thus transition from stainless steel higher-temperature alloys needs to be completed"*: **High-temperature Inconel 625 reactor tested up to 887°C.**
- *"Hydrocarbon conversion levels for liquid fuels are higher than earlier 90% but significant additional improvement is needed"* -and- *"High temperature reformer operation and demonstration of >99.9% conversion of non-methane hydrocarbons are critical to further progress"*: **Reformer was operated on Benchmark Fuel over a range of temperatures to generate a curve of productivity possible while producing no detectable non-methane hydrocarbons**.

Reformate Cleanup: The Case for Microchannel Architecture

DOE Hydrogen and Fuel Cells
2003 Annual Merit Review

May 19-22, 2003

W.E. TeGrotenhuis

K.P. Brooks, J.M. Davis, C.M. Fischer, D.L. King,
L.R. Pederson, G.C. Rawlings, V.S. Stenkamp,
R.S. Wegeng, G.A. Whyatt

Pacific Northwest National Laboratory

Overview

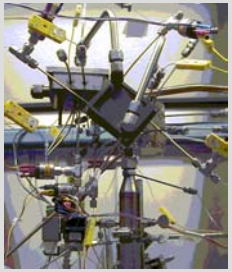
- Reformate Cleanup
  - Water Gas Shift (WGS)
  - Preferential Oxidation (PROX)
  - Desulfurization
- Balance of Plant
  - Water Management - Partial Condenser / Phase Separator

Objectives and Relevance

- Overall Objective
  - Apply microchannel architectures where appropriate in fuel processing for transportation, stationary, and portable applications to reduce size and weight, improve fuel efficiency, and enhance operation.
- Technical Challenges – Approaches
  - Compact size and weight to meet packaging requirements – rapid heat and mass transfer for high hardware productivity
  - Thermal management – high heat transfer effectiveness in heat exchangers and reactors for maximum heat utilization and high fuel efficiency
  - Water management – compact and efficient air-cooled partial condensers
  - Rapid start-up – imbedded heat transfer in reactors facilitates rapid heating
  - Cost – improved productivity of precious metal catalysts

Project Timeline

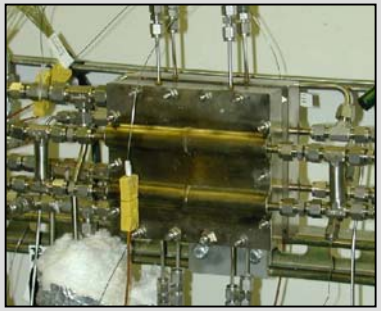
FY 1998
Full-size gasoline vaporizer/combustor
R&D100 Award



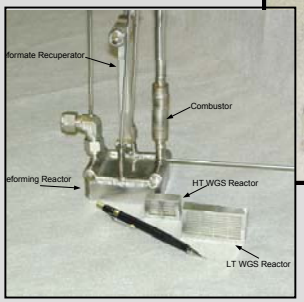
FY 1999
Fast SR kinetics observed in a microchannel reactor

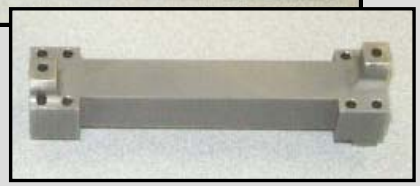
FY 2000
10 kWe SR system
Invented phase separator concept

FY2001
10 kWe reactor testing
First "low dP" vaporizers
Demonstrated partial condenser



FY 2003
2 kWe WGS and PROX reactors.
Improve SR kinetics and sulfur tolerance.





FY 2002
WGS/PROX catalyst studies
Differential temperature reactor concept
SR/WGS/PROX initial integration
Air-cooled partial condenser

Engineered catalyst, reactor development

Demonstrate rapid start capability

Sulfur management

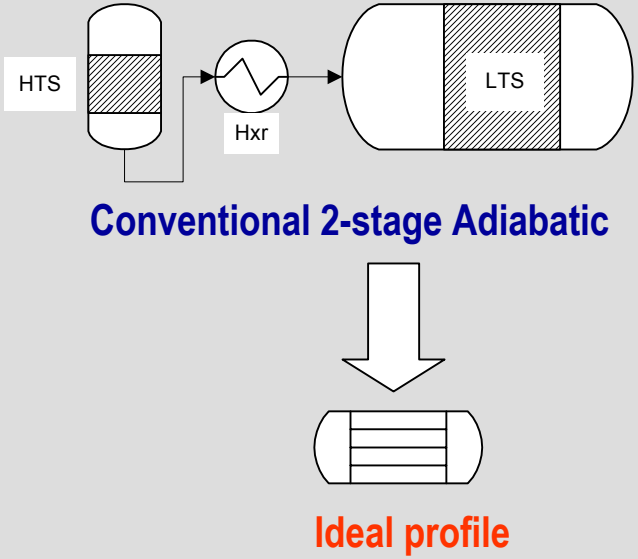
Integrated reformer/fuel cell demonstration at ~2 kWe

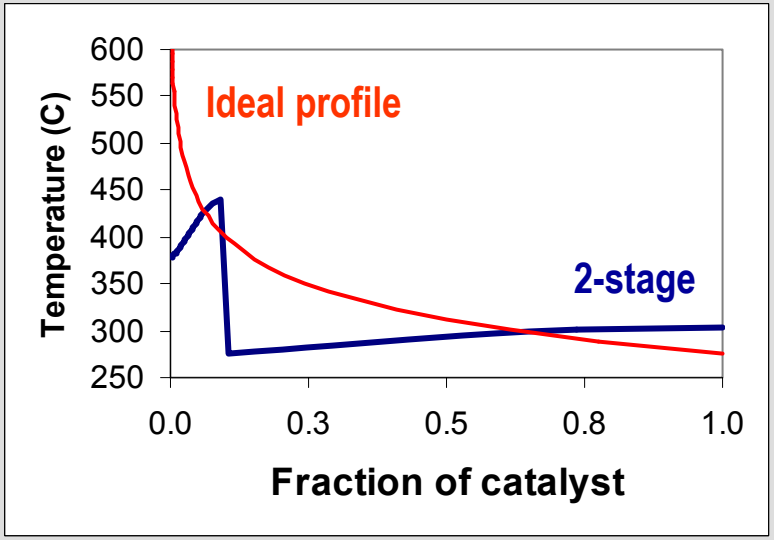
Collaborate with industrial partner(s) on manufacturing, field testing, lifetime, controls

2002 2003 2004 2005 2006 2007 2008

Differential Temperature Water Gas Shift Reactor
Objective/Approach

- Objective:
  - 90% Conversion single-stage WGS reactor < 3 liters at full-scale
- Approach:
  - Precious metal catalyst for high activity
  - Integrate microchannel heat exchange for temperature control
  - Optimize thermal profile
  - Reduce catalyst loading by up to 1/2
- Relevance
  - Smaller size – higher power density and specific power
  - Reduced cost
    - Improved catalyst efficiency
    - 3 devices collapsed into 1
  - Potential of higher energy efficiency



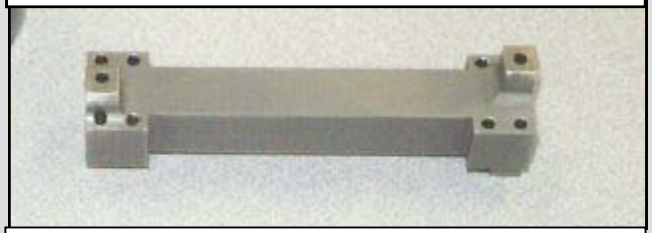


Battelle

Differential Temperature Water-Gas Shift

Progress: Multi-channel Reactor Testing

Prototype 7-channel Reactor

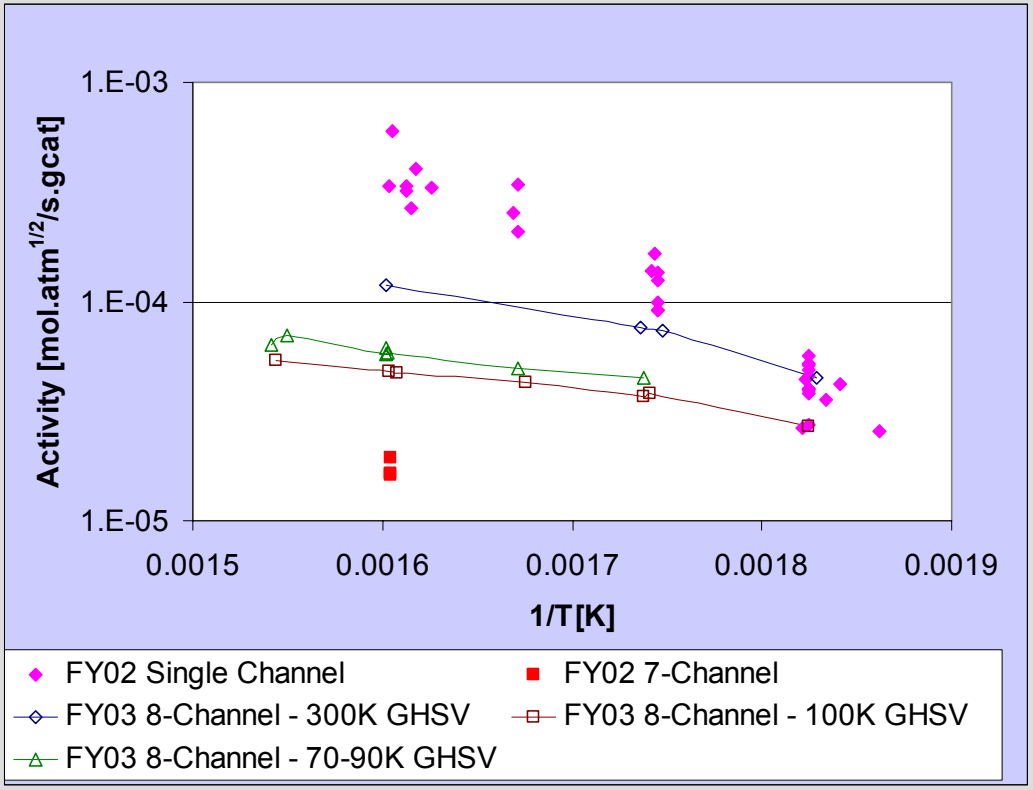


Reactor can be operated isothermally or with a temperature gradient

- PROGRESS:
  - Catalytic activity improved in multi-channel prototype reactor
  - Up to 79% CO conversion (12.4% to 2.6% dry CO) in single stage at 100,000 GHSV and 0.65 steam:gas.
- ISSUES:
  - Activity diminishes at lower GHSV
  - Loss of temperature dependence

Activity coefficients from isothermal reactor FEA model:

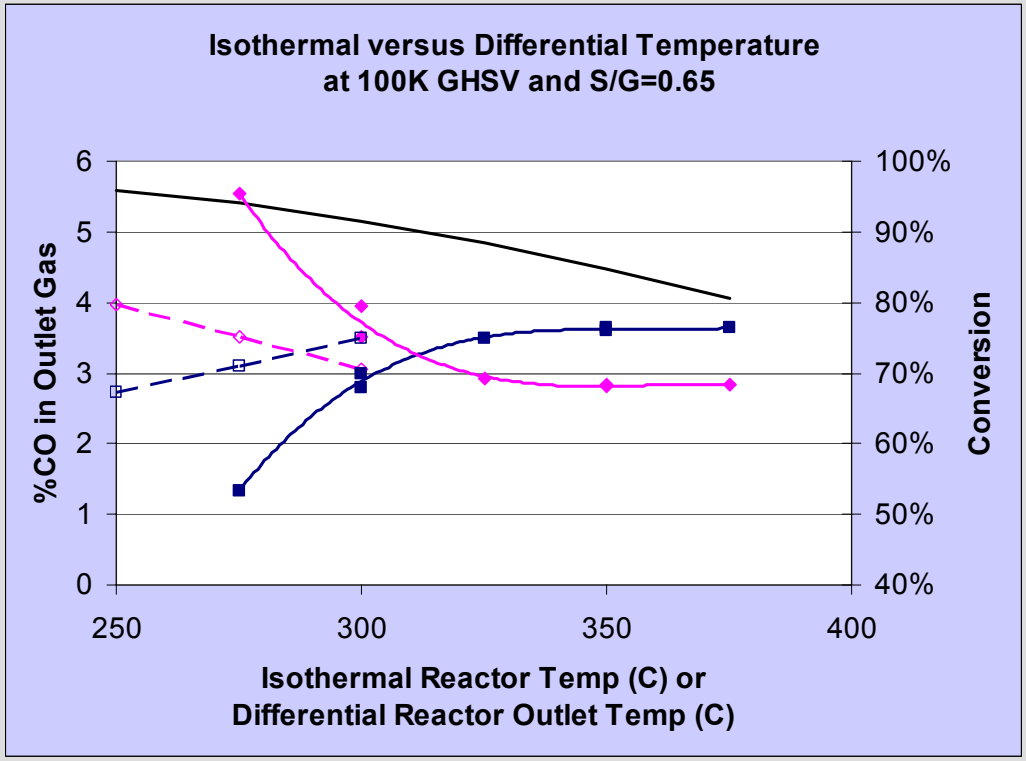
$$r_{CO} = \rho_B \, k_{CO}(T) \, p_{CO}^{-1} \, p_{H_2}^{-1} \, p_{CO_2}^{-1/2} \left(p_{H_2O} \, p_{CO} - \frac{p_{H_2} \, p_{CO_2}}{K_{eq}(T)} \right)$$



Battelle

Differential Temperature Water-Gas Shift

Progress: Differential Mode Testing



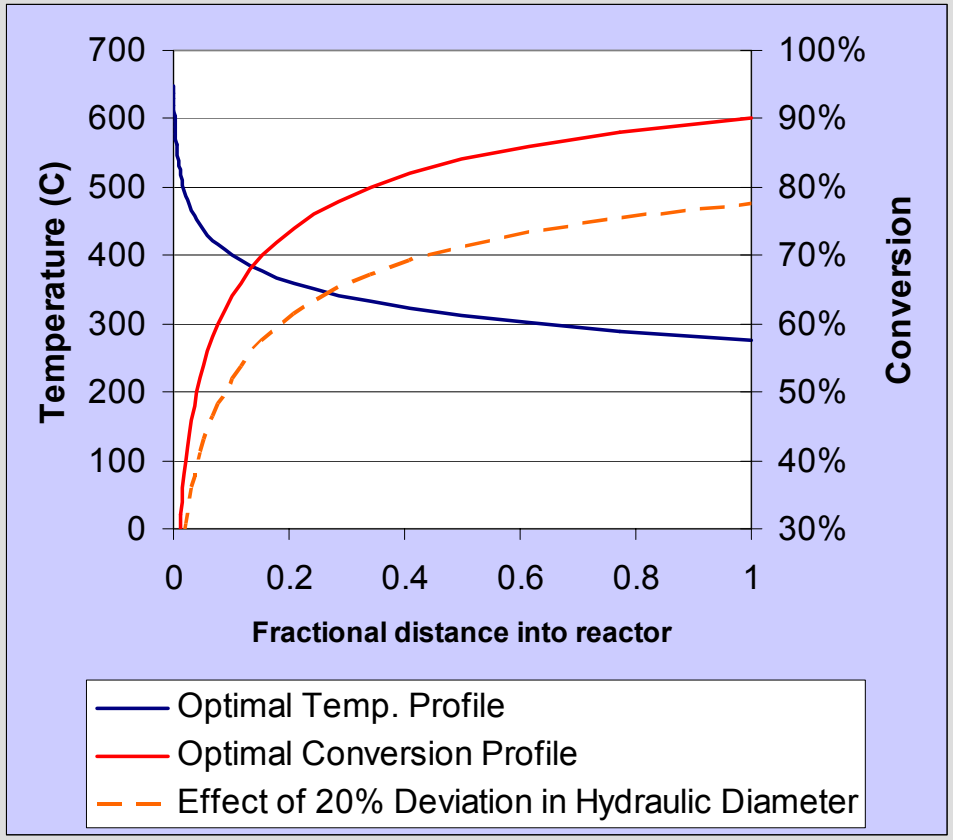
- Isothermal Operation - Outlet Gas CO%
- Differential Temperature Operation - Outlet Gas CO%
- Isothermal Operation – CO Conversion
- Differential Temperature – CO Conversion
- Equilibrium Conversion

- Conditions
  - Steam Reformate Feed
    - 12.4% dry CO
    - 14.3% dry CO_2
    - 0.65 Steam:Gas
  - 100K GHSV
  - Isothermal operation at high heat exchange flow
  - Differential temperature operation
    - Feed at 350C
    - 2 SLPM air coolant fed at outlet temperature

Differential Temperature Water-Gas Shift

Issue: Flow Maldistribution

- Flow maldistribution between channels is an important issue
  - Flow rate $\alpha\ d_h^3$
  - Compounded by increased heat and mass transfer resistance
- Example
  - Impact of 20% distribution in hydraulic diameter on optimal conversion profile
  - Does not account for heat and mass transfer effects
  - Does not account for catalyst loading maldistribution



Differential Temperature Water-Gas Shift

Future Plans

- Continue catalyst development
  - Long-term testing
  - Start-up/shutdown and temperature cycling
  - Evaluate new formulations
    - Improved activity
    - Better activity maintenance
  - Sulfur sensitivity
  - Optimization of geometry and loading
- Multi-channel Improvements
  - Apply improved design and fabrication techniques to improve channel consistency
  - Demonstrate >90% conversion in single stage with integral heat exchange
- Develop WGS Reactor at 2 kWe-scale
  - Optimize catalyst productivity
  - Thermally integrate with 2 kWe-scale reformer system

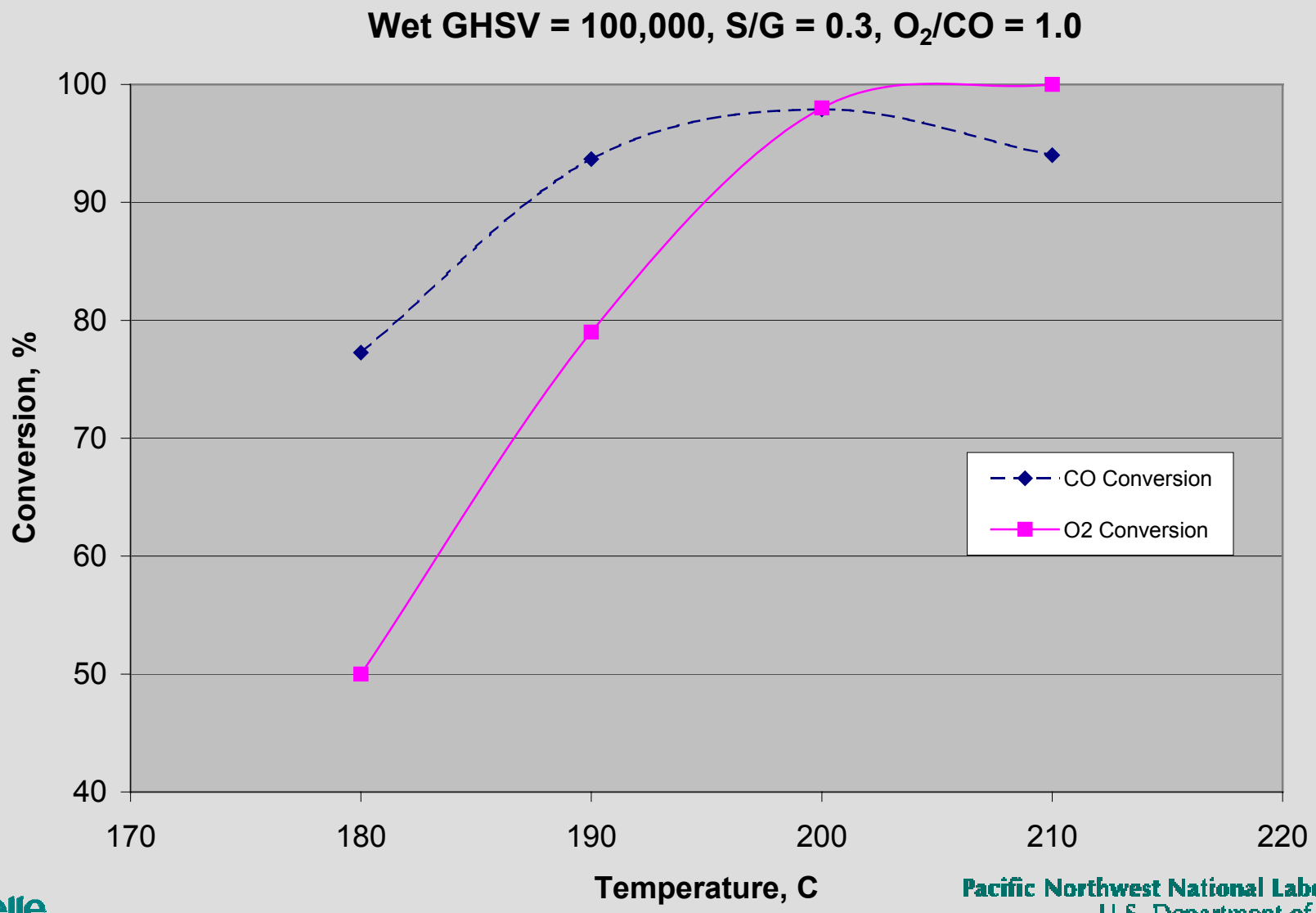
Microchannel PROX Reactor Investigations

- Objective: Determine whether microchannel architecture provides opportunities for size, weight reduction for PROX reactor.
- Approach:
  - Single-channel catalyst tests – evaluate industrial PROX catalysts for fast kinetics
  - Design & test 2 kWe PROX reactor unit; confirm favorable operational characteristics
  - Investigate weight reductions through use of low-density alloys (e.g., alloys of aluminum and titanium)
  - Investigate transient and startup characteristics
- Progress:
  - 1st Stage PROX microchannel reactor demonstrated at 2 kWe scale – exhibits high productivity due to internal microchannel heat exchangers providing temperature control

Preliminary Single Channel Catalyst Tests Used to Down-select for 2kW PROX Unit

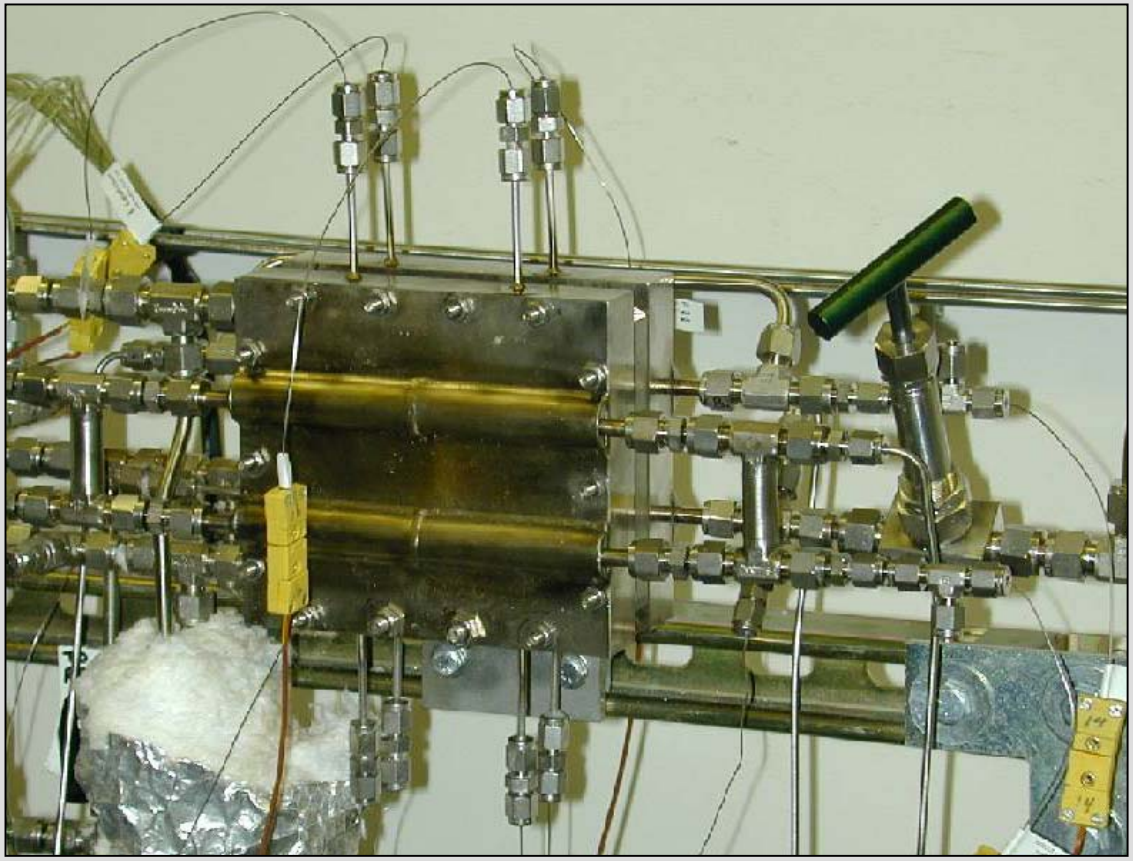
- At 1% CO in reformate, both precious metal and non-precious metal catalysts can be employed for PROX
  - Both catalysts show maximum CO conversion around 200°C
  - Adiabatic operation must be avoided (excessive temperature rise)
- At 0.1% CO in reformate, precious metal catalyst are required
  - Higher CO activity at lower temperatures (~100°C)
    - Lower activation energy
    - Different dependence on CO concentration (analogous to wgs)
  - Adiabatic operation may be possible
- Non-precious metal catalyst was selected for 2kW PROX test in microchannel hardware
  - CO ~1%, input from wgs reactor
  - Lower catalyst cost
  - Higher CO oxidation selectivity (lower H_2 consumption and O_2 requirements)

Selective CO Oxidation (PROX) With Non-Precious Metal Catalyst

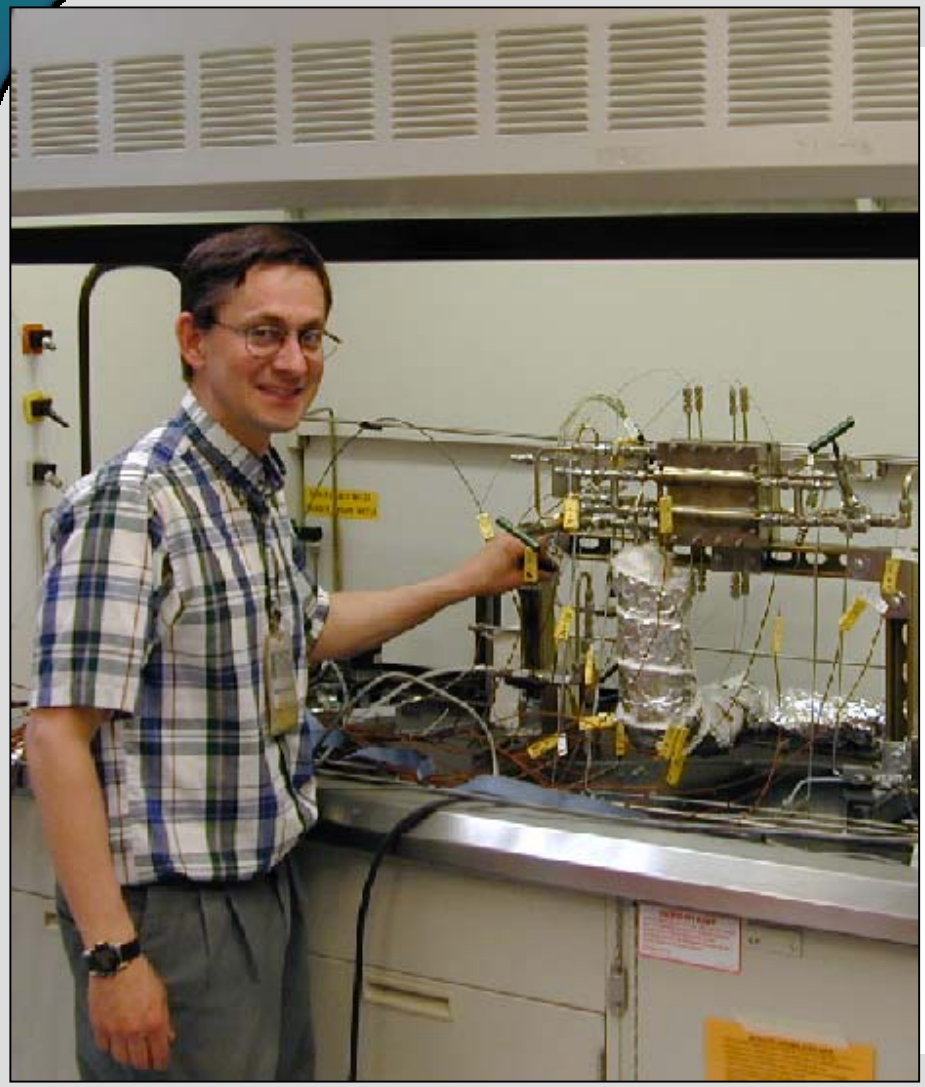


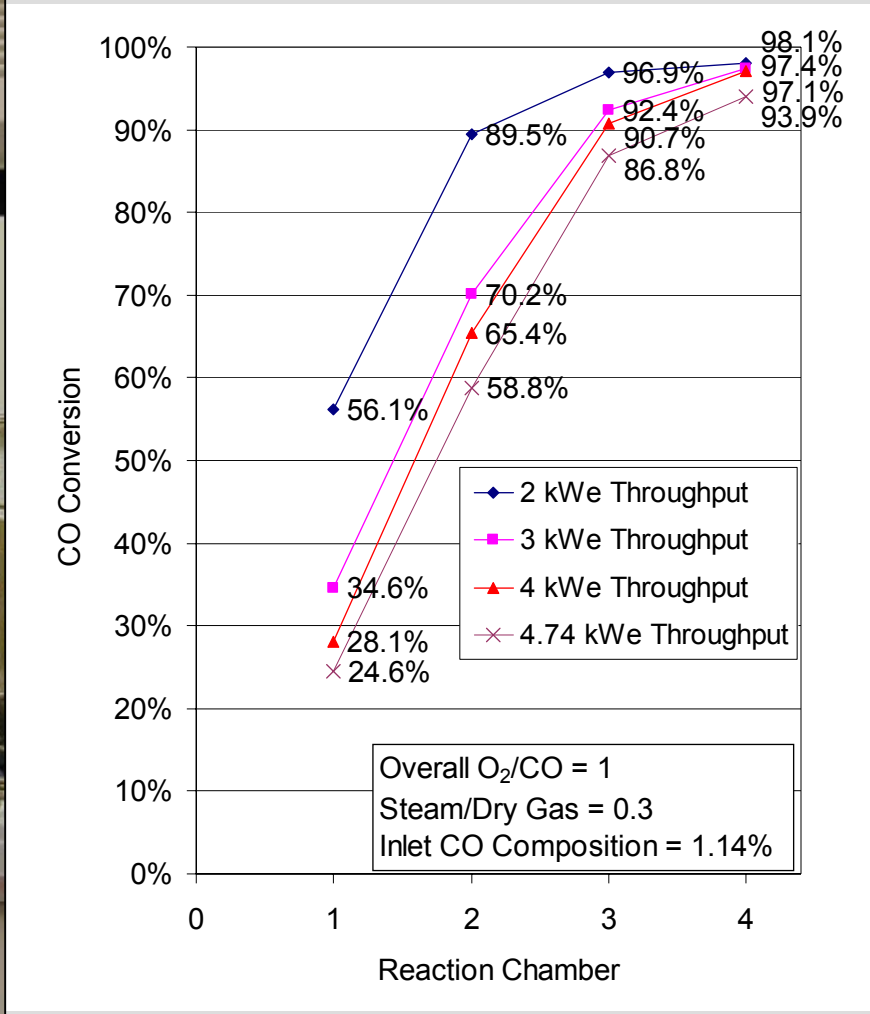
Demonstration of Microchannel PROX Unit

- Designed as 1st Stage PROX for 2 kWe operation
- Operates as a quasi-isothermal reactor
  - Incorporates microchannel heat exchange
- Employs non-precious metal catalyst
- Allow multi-compartment bleed-in of air



Operation of First Stage Microchannel PROX





Future PROX Work

- Continue to evaluate industrial PROX catalysts for use in microchannel reactors
- Evaluate aluminum and titanium alloys for microchannel PROX reactor
  - Potential weight reduction
- Integration of 1st and 2nd Stages
  - Investigate differential-temperature operation
- Test as part of integrated fuel processor with steam reformer, water-gas-shift reactors and heat exchangers
  - Evaluate fast startup, rapid transient potential
  - Evaluate thermal recuperation of PROX heat

Reformate Desulfurization Using Microchannel Devices

- Concept: microchannel absorbers can provide compact units for H_2S removal from reformate
  - ZnO absorption:
    - Fast uptake kinetics at $T \geq 400^oC$ but relatively high equilibrium H_2S concentration in high steam environments
    - Slower kinetics at $T \leq 300^oC$ but lower equilibrium H_2S concentration
  - Differential temperature microchannel absorber can provide more effective H_2S removal by operating over temperature range 300-400^oC
- Challenge: absorber bed capacity in microchannel configuration
- Approach and status
  - Carry out initial studies (underway) to quantify ZnO uptake kinetics vs. T
  - Calculate optimal temperature profile for differential temperature absorber
  - Construct microchannel unit and obtain experimental performance data under differential temperature conditions
  - Compare results with isothermal operation

Balance-of-Plant
Partial Condenser / Phase Separator

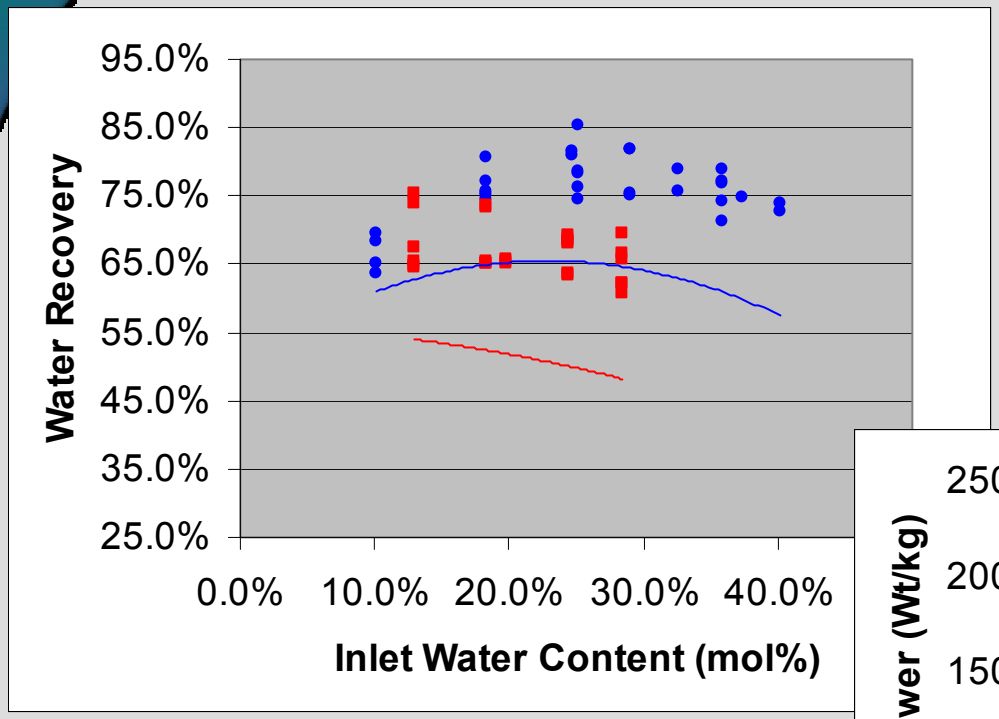
- Objective: Develop compact microchannel heat exchange technology for the recovery and recycle of water in fuel processor / fuel cell systems.

- Designed for water recovery from PEM fuel cell cathode effluent
- Condenses and separates water
- Aluminum for light weight
- Air-cooled
- Cross-flow for low coolant-air pressure drop
- 1.5-kWe-scale cathode condenser
  - Air coolant - 30 °C
  - Air pressure drop - 2.2 in. H2O
  - Weight - 260 g
  - Volume - 170 mL
  - Est. Fan Power - 14 W full-scale

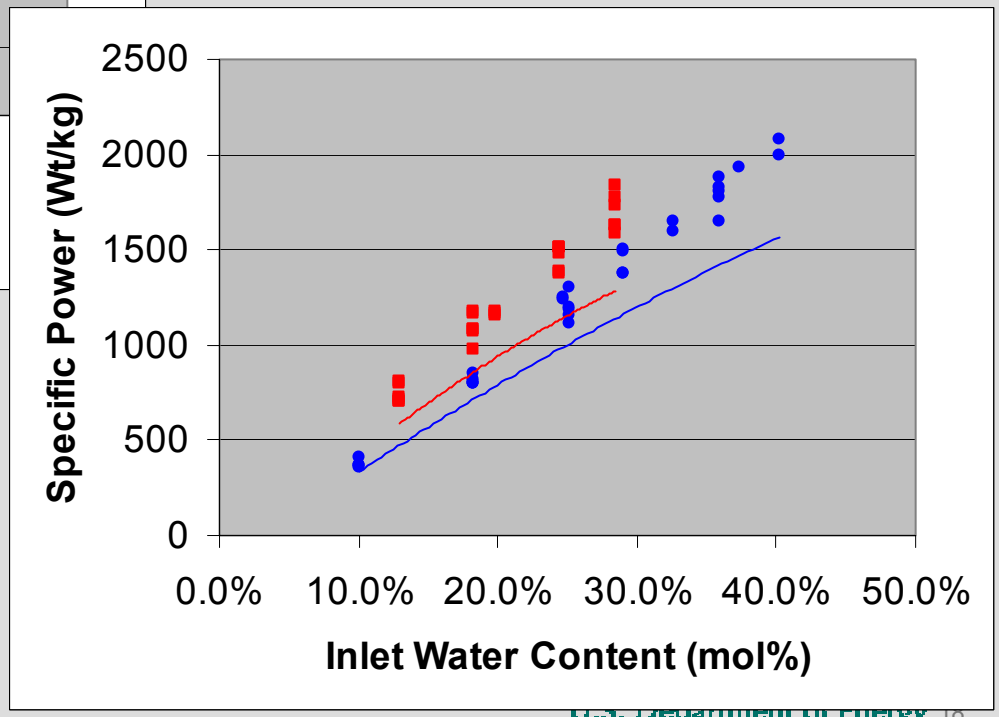
3 condensing channels (left to right)
4 cooling channels with fins

Vapor-Liquid Separator

Measured versus Predicted Performance



32 std Liter/min air flow
48 std Liter/min air flow
Average model prediction



CONCLUSIONS

- Actual performance exceeds predicted performance.
- 2000 W_t/kg specific power at 74% water recovery.
- Water separation efficiency 90-100%.
- Coolant side pressure drop about 2X design ~ 4 in. H_2O.

Interactions

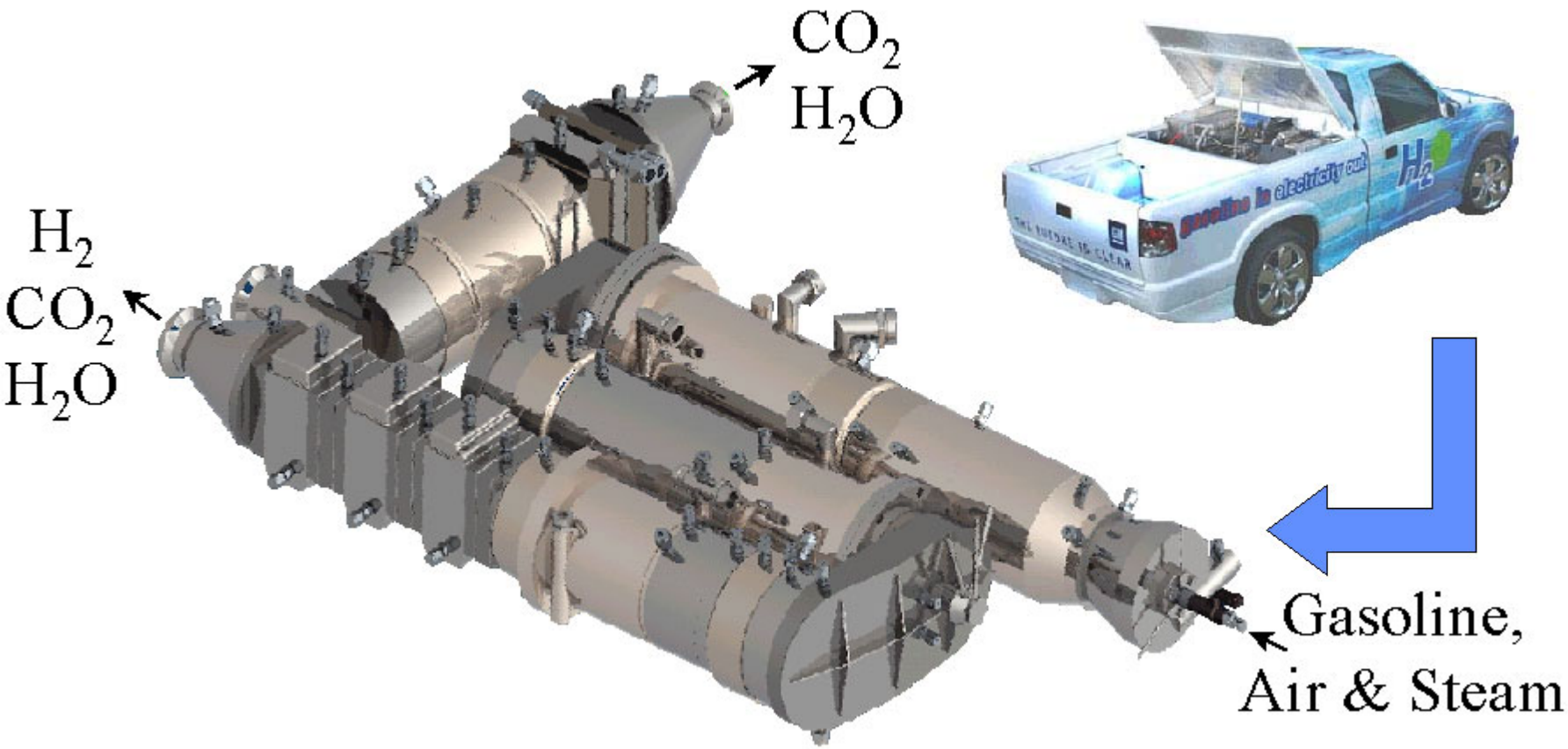
- Catalyst Development
  - Sud-Chemie, Inc. – WGS, PROX, Desulfurization
  - Engelhard - PROX
- Technology Transfer
  - Interest expressed by SOFCo for a 50-kWe-scale Differential Temperature Water Gas Shift reactor.
- Technology Spin-off
  - Microchannel Partial Condenser / Phase Separator successfully tested in zero gravity onboard NASA's KC-135 aircraft.
  - Microchannel Phase Separator is a candidate technology for NASA's Space Plane for water recovery from cathode of PEM FC power system.

Responses to Comments

- *"WGS durability may be a significant challenge…" and "Lack of WGS durability data"*
  - Catalyst deactivation has been a challenge, particularly with thermal cycles and restarts, and is under investigation.
  - A single catalyst piece has been on stream for 100 hours with nominal initial deactivation; ~ 10-20%.

- *"Little of proposed work is related to advancing fundamental understanding, which should be of high importance"*
  - WGS work is pursuing a fundamental understanding, including:
    - Kinetic model development in an engineered form
    - Finite element heat and mass transfer models of reactors for analysis and design
    - Scale-up from single channel to multi-channel reactors to understand the issues associated with scale-up, such as flow maldistribution

Challenge: Decrease Size and Cost of Fuel Processor



MichiganEngineering

DoE Fuel Processor Targets

(Excludes fuel storage)

Characteristics	Units	Current Status	Project Goal	Long-Term Goal
Energy efficiency	%	78	78	80
Power density	W/L	300	700	800
Specific power	W/kg	300	700	800
Cost	$/kW	85	25	10
Cold Startup @ -20 °C to Maximum Power	min	10.0	2.0	1.0
Cold Startup @ 20 °C to Maximum Power	min	<5	<1	<0.5
Transient Response (10 to 90 % power)	sec	15	5	1
Emissions		<Tier 2	<Tier 2	<Tier 2
Durability	hours	2000	4000	5000
Survivability	°C	-20	-30	-40
CO content steady state	ppm	10	10	10
CO content transient	ppm	500	100	100
H_2S content in product stream	ppm	<0.3	<0.2	<0.1
NH_3 content in product stream	ppm	<10	<5	<1

MichiganEngineering

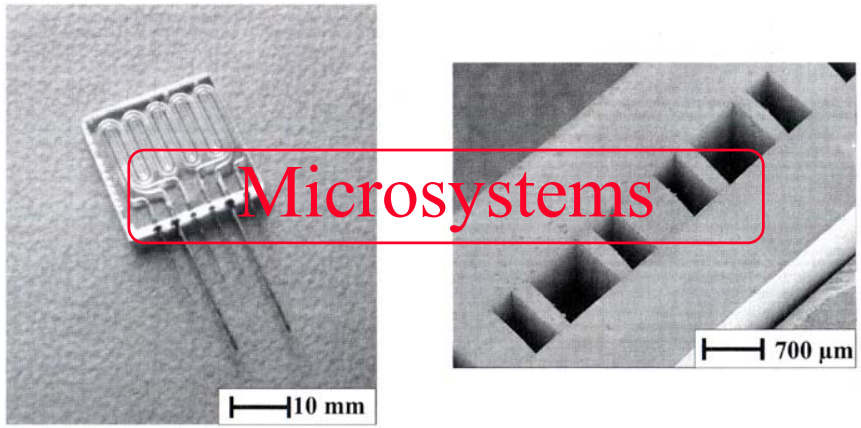
Fuel Processors for PEM Fuel Cells

High Performance Materials

+

High Degree of Integration

+



Project Director: Levi Thompson (ltt@umich.edu)

Co-PIs: Gulari, Savage, Schwank & Yang (ChE); Assanis, Im, Ni & Wooldridge (ME); Dahm & Powell (Aero)

Subcontractors: MesoFuel (NM); Ricardo, Inc. (MI); *IMM (Germany)**

Funding: $5,937,184

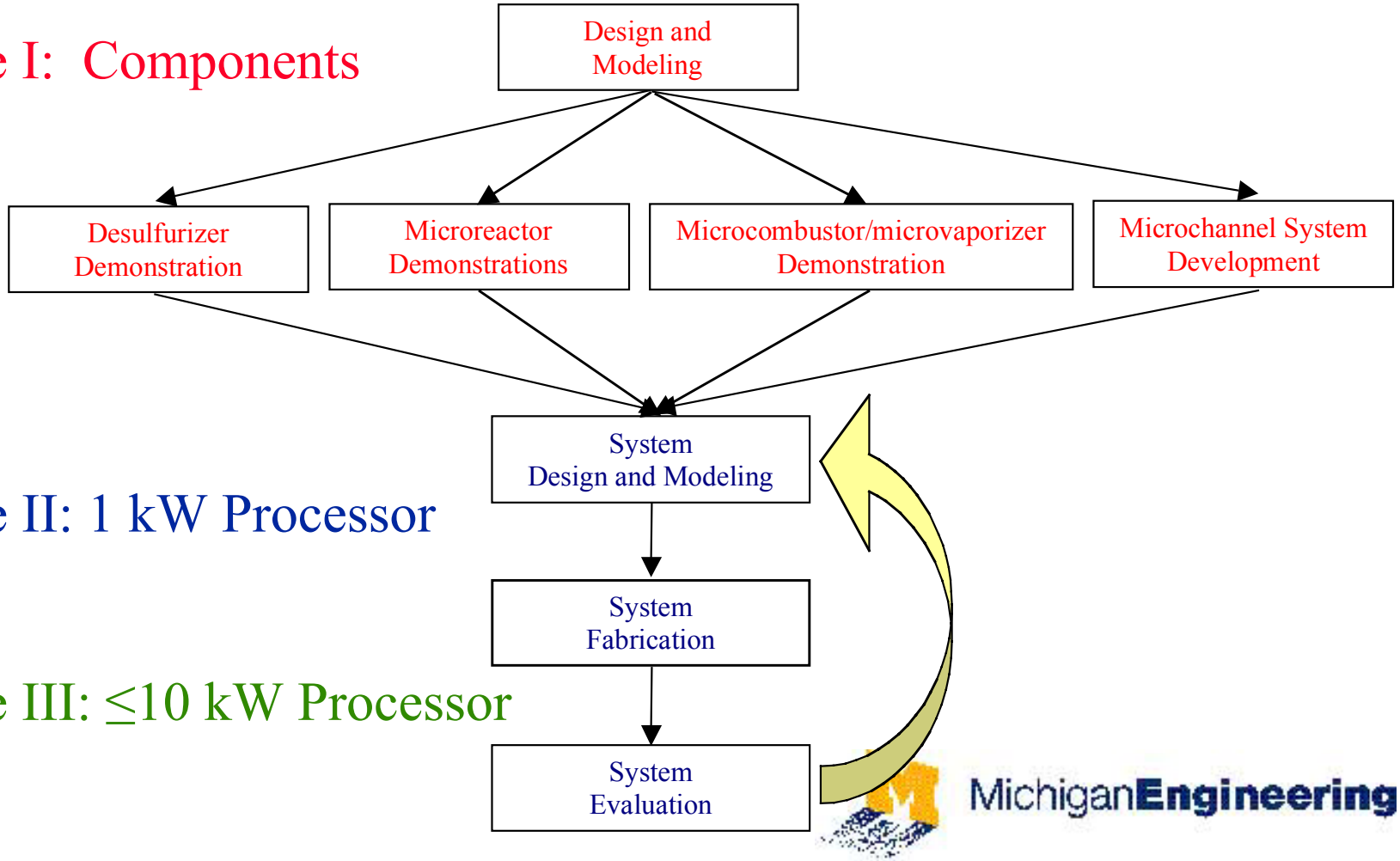
Project Duration: 4 years (Go/No-Go after 3 years)

* Not yet engaged

MichiganEngineering

Technical Approach

Phase I: Components



Phase II: 1 kW Processor

Phase III: ≤10 kW Processor

MichiganEngineering

Major Tasks/Milestones

Task	Quarter															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Component design and modeling																
Sorbent development																
Catalyst development																
Microcombustor/-vaporizer developmt.																
Microchannel system development																
Component evaluations																
1 kW Fuel processor design /modeling																
1 kW Fuel processor fabrication																
1 kW Fuel processor evaluation																
10 kW Fuel processor design /modeling																
10 kW Fuel processor fabrication																
10 kW Fuel processor evaluation																
Cost Analysis																

11/01 $

MichiganEngineering

Thrust Areas

- Materials
  - Sulfur Adsorbents (Yang)
  - ATR Catalysts (Schwank)
  - WGS Catalysts (Thompson)
  - PrOx Catalysts (Gulari)
- Hardware
  - Micro-Reactors (Gulari, Ni, Thompson)
  - Micro-Combustor/Vaporizer (Dahm)
- Modelling (Savage, Assanis, Im, Powell)

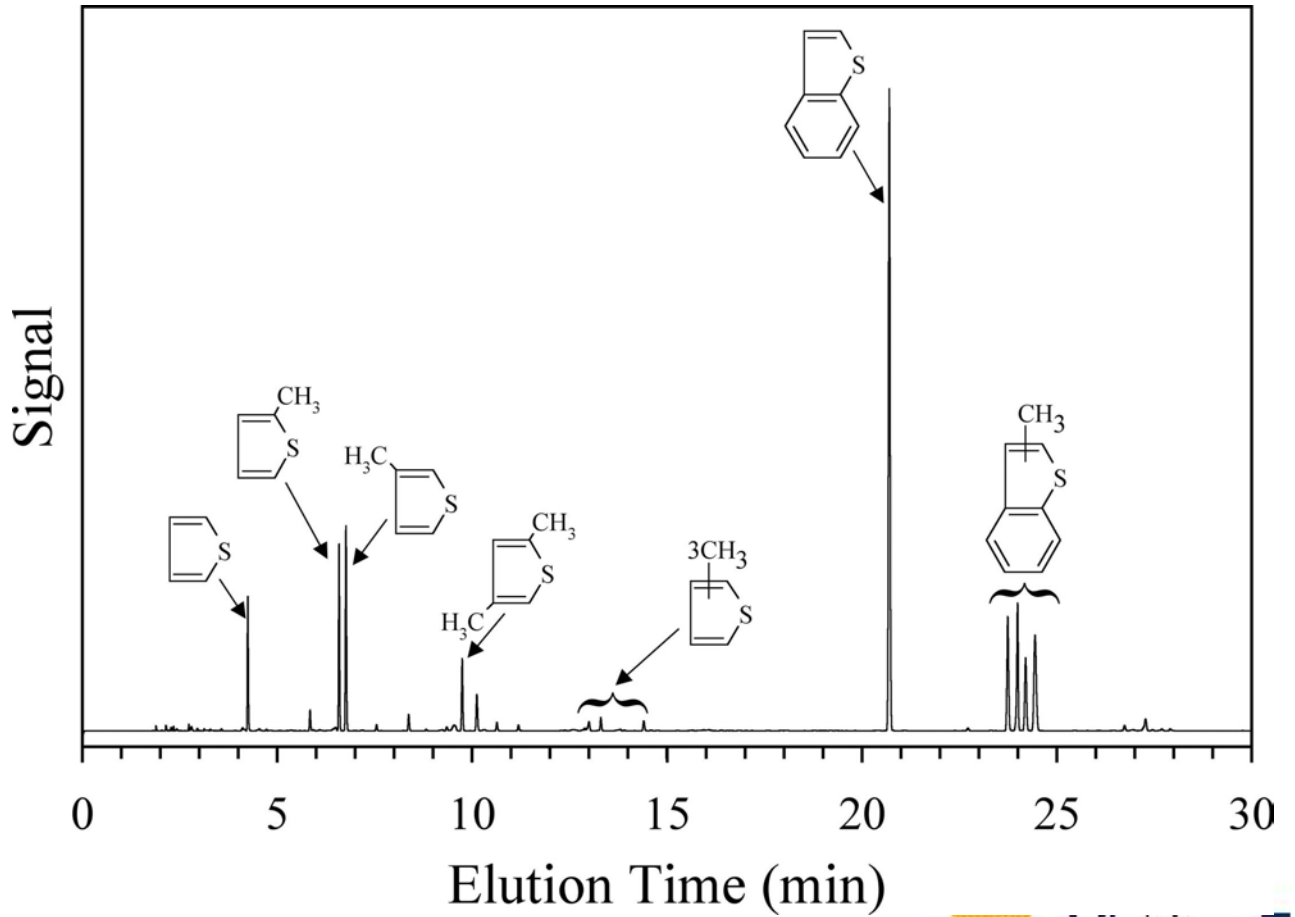
MichiganEngineering

If We Are Successful: 10 kW Fuel Processor

Component Weights (kg)	Current	Reduction Goal	Proposed Prototype	Comment
Fuel pump	0.45	50%	0.23	capillary action in microcombustor
Desulfurizer	2.42	35%	1.57	higher capacity liquid sorbents
Water tank	3.63	50%	1.81	better integration
Water pump	0.91	50%	0.45	capillary action in microcombustor
Fuel/water preheater	2.56	90%	0.26	microcombustor/microvaporizer
Reformer heat	4.40	90%	0.44	better thermal integration
Reformer	2.90	67%	0.96	better catalysts/microreactors
Shift reactors	11.88	67%	3.96	better catalysts/microreactors
Intercooler	2.27	90%	0.23	better thermal integration
Air compressor	0.60	0%	0.60	
Preferential oxidizer	3.30	67%	1.10	better catalysts/microreactors
Fuel cell air cooler	2.27	90%	0.23	better thermal integration
Fuel cell exhaust drier	0.23	50%	0.11	
Burner	3.40	50%	1.70	microcombustor/microvaporizer
Thermal insulation	0.91	50%	0.45	better thermal integration
Valves	0.28	0%	0.28	
Starter Battery	0.22	0%	0.22	
Instrumentation/controls	2.27	50%	1.13	novel strategies/sensors
Sub-total	44.9		15.74	
Component integration		10%	-1.57	
Total	44.9		14.17	Specific energy of 704 W/kg

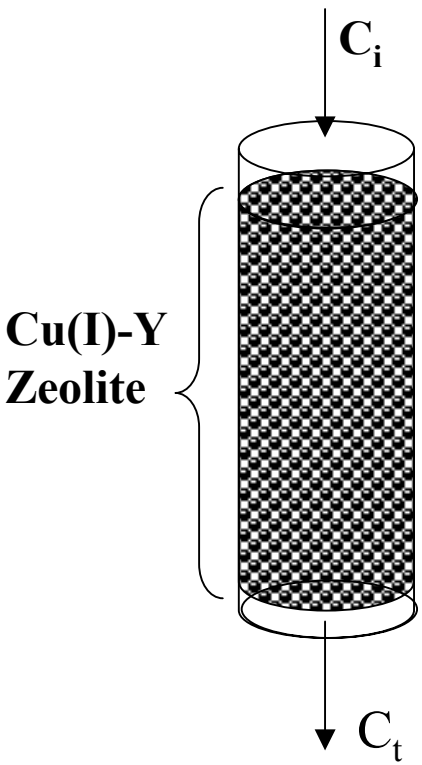
MichiganEngineering

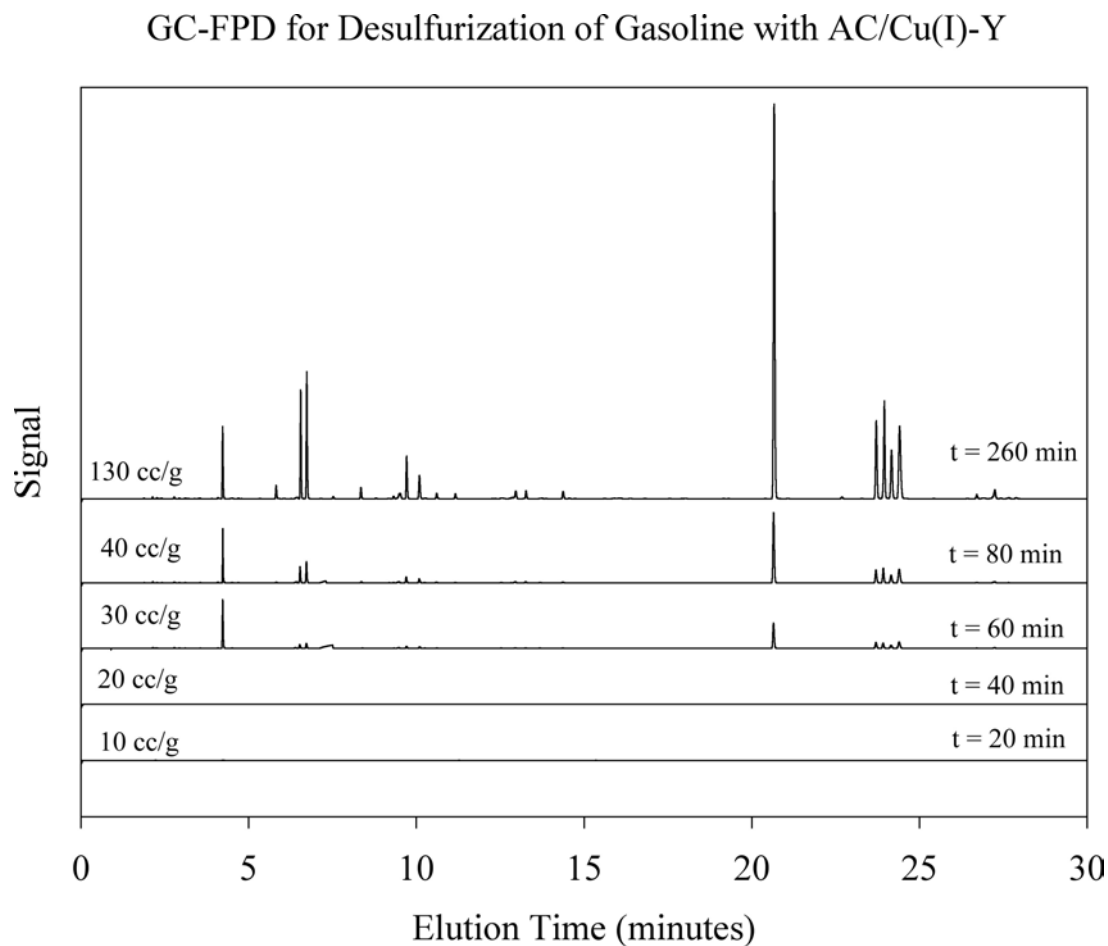
GC-FPD of Regular Gasoline



MichiganEngineering

Desulfurization of Gasoline and Diesel by Adsorption

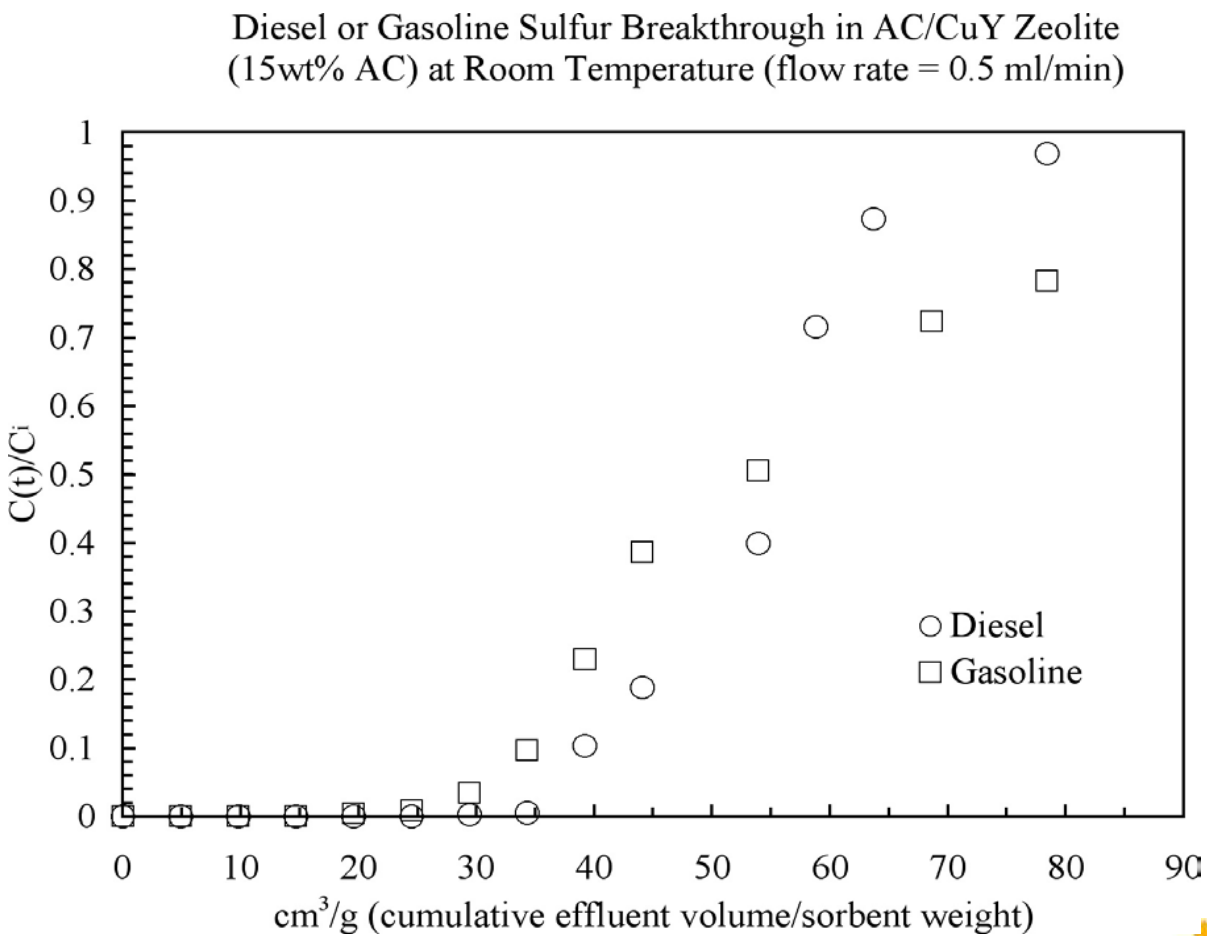




A. J. Hernandez-Maldonado and R. T. Yang, to be published.
Yang et al., U.S. and foreign patents applied.

MichiganEngineering

Desulfurization of Gasoline and Diesel by Adsorption



- 5 kg sorbent produces 170 L sulfur-free diesel, or 2,500 mile driving range (assumes 60 miles/gal)
- Order of magnitude better than others (Ma et al., *Catalysis Today*, **77**, 107 (2002))

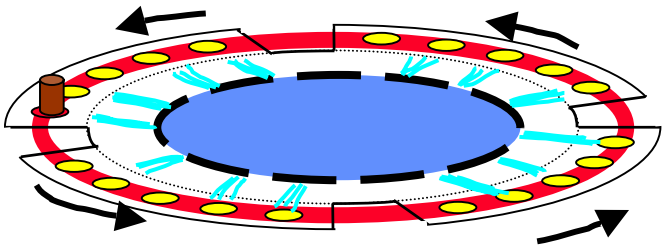
MichiganEngineering

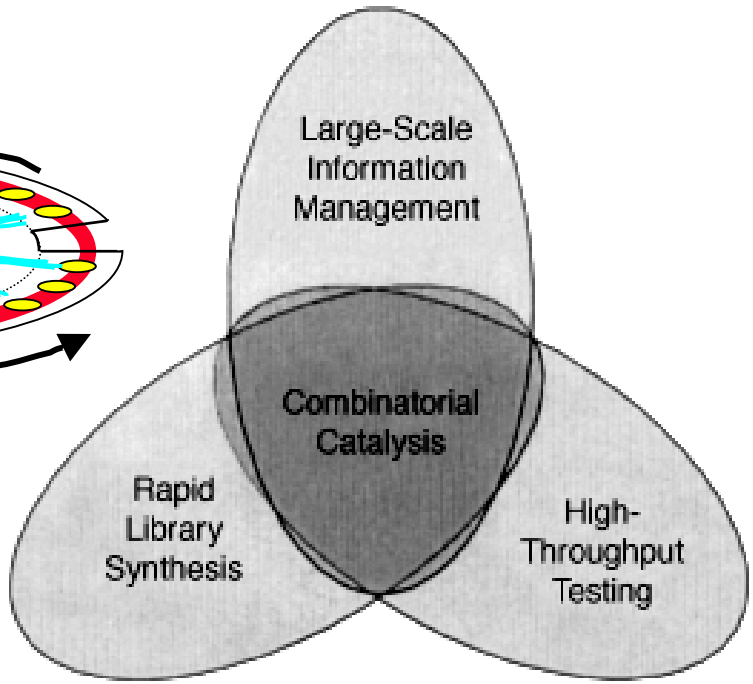
Combinatorial Catalysis

1000's of guesses

several candidates

a couple of leads





MichiganEngineering

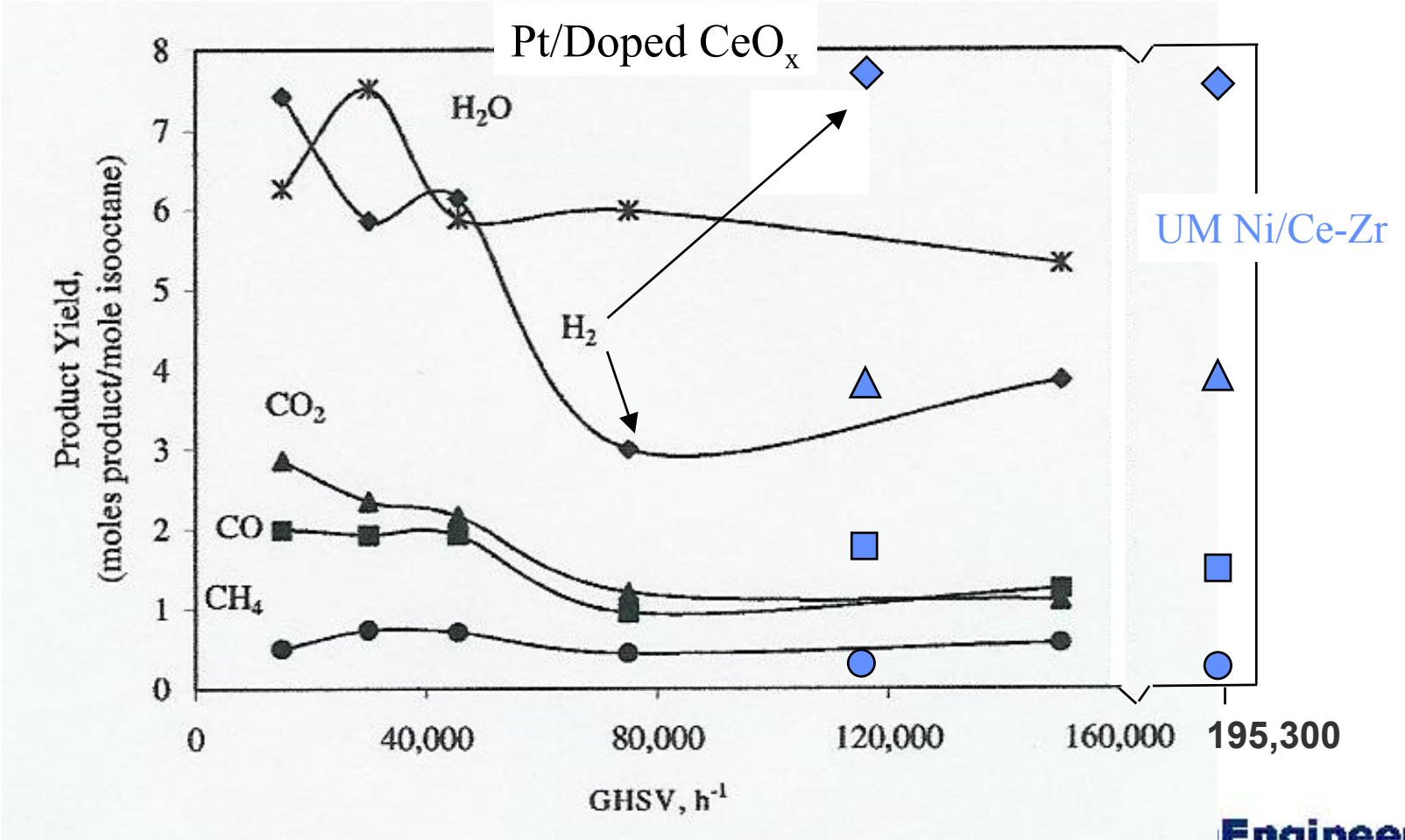
Novel ATR Catalyst Formulations

- Ni-Ce/Zr mixed oxide
  - Prepared by sol-gel technique (urea hydrolysis) and impregnation
    - Effect of varying Ce:Zr molar ratios (optimum: $Ce_{0.75}Zr_{0.25}$)
    - Ni loading (5-15%)
- Ni/β”-alumina (material with high Na^+ ion mobility)
  - Prepared by conventional impregnation and flame spray pyrolysis
- Ni/yttria stabilized zirconia, Ni/CeO_2 , Ni/TiO_2
- Supported Pt and Pt-Ni

MichiganEngineering

ATR of Isooctane

M. Krumpelt et al. , Catal. Today 77 (2002) 3-16



Engineering

Novel Water Gas Shift Catalysts

Au/Ag/Ru on Reducible Oxides

- Au/MO_x highly active — Stephanopoulus et al., 2001
- Questions about stability — Löffler et al., 2002

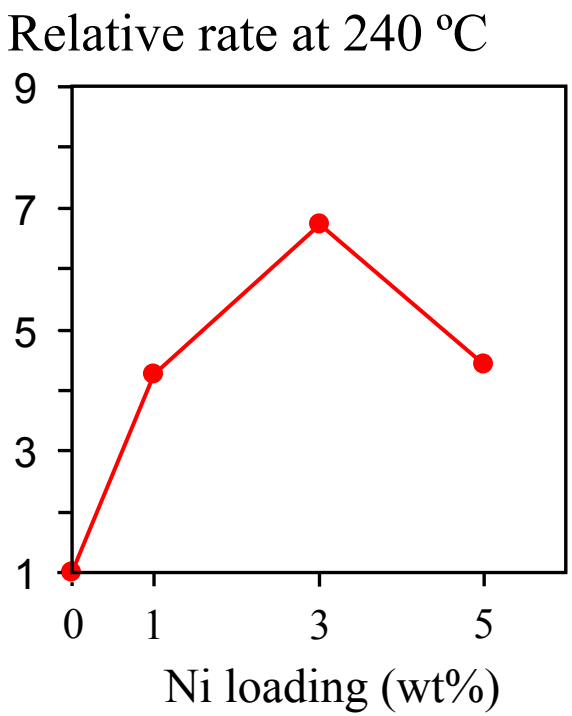
Early Transition Metal Carbides

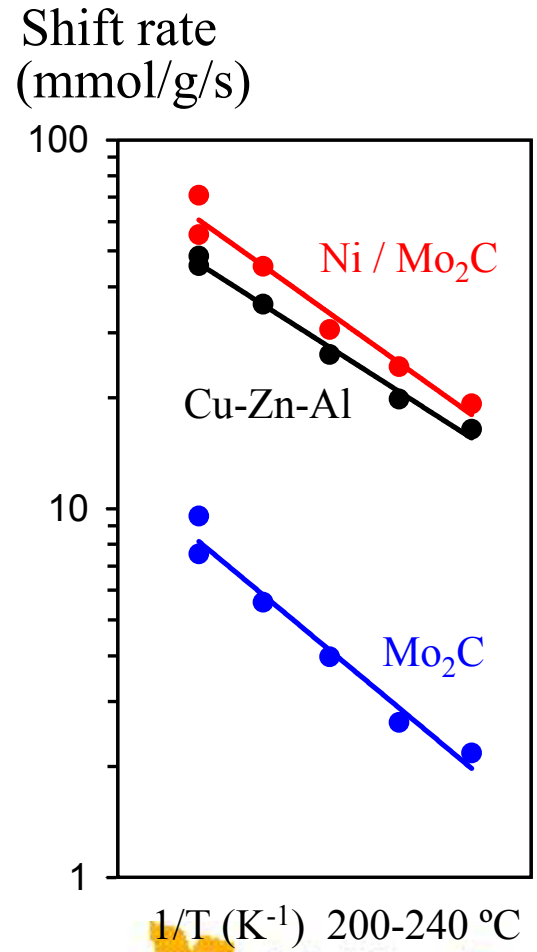
- Catalytic properties similar to Pt-group — Levy and Boudart, 1973; Oyama, 1992
- Highly active for WGS — Thompson et al., 2000
- Tolerant to sulfur — Manoli et al., 2001

MichiganEngineering

Mo_2C Supported Ni

- Effect of metal loading:





- No methanation

MichiganEngineering

DoE Targets: Water Gas Shift Catalysts

Characteristics	Target	Cu-Zn-Al†	UM Catal.
GHSV (hr^{-1})	30,000	30,800	>78,000
Conversion (%)*	>90	76	89
H_2 Selectivity (%)	>99	>99	>99
Volume (L/kW_e)	<0.1		
Weight (kg/kW_e)	<0.1		
Durability (Hrs.)	5000		
Cost ($\$/kW_e$)	<1		

* 38 % H_2, 16% N_2, 10% CO, 6% CO_2 and 30% H_2O: T=240 °C: X_{eq}=96.5%
† Tested at the UM.

MichiganEngineering

Comparison of PrOx Catalysts

Catalyst	3%Au/Fe_2O_3	0.5%Pt/Al_2O_3	2%Pt/Al_2O_3	5%Pt/Al_2O_3-Fe_2O_3 (Engelhard)
SV (hr^{-1})	60,000	60,000	60,000	120,000
Conversion No H_2O, No CO_2	100% @ 50 °C		80% @175 °C	90% @90°C (1000 ppm CO, 10% H_2O, 20% H_2)
Selectivity	55-65%	45-55%	45-55%	~50-65%
Conversion 10% H_2O, 25% CO_2	92% @ 50 °C	100% @150 °C (CO < 5 ppm)	100% @130-160 °C (CO < 5 ppm)	~70%@100°C (North Carolina 30,000 hr^{-1})

Space velocity in units of L/hr•$kg_{catalyst}$

40-50% H_2, 20-25% CO_2, 10% H_2O, 1%CO, 1%O_2 and He

MichiganEngineering

Micro-Systems

Reactors:

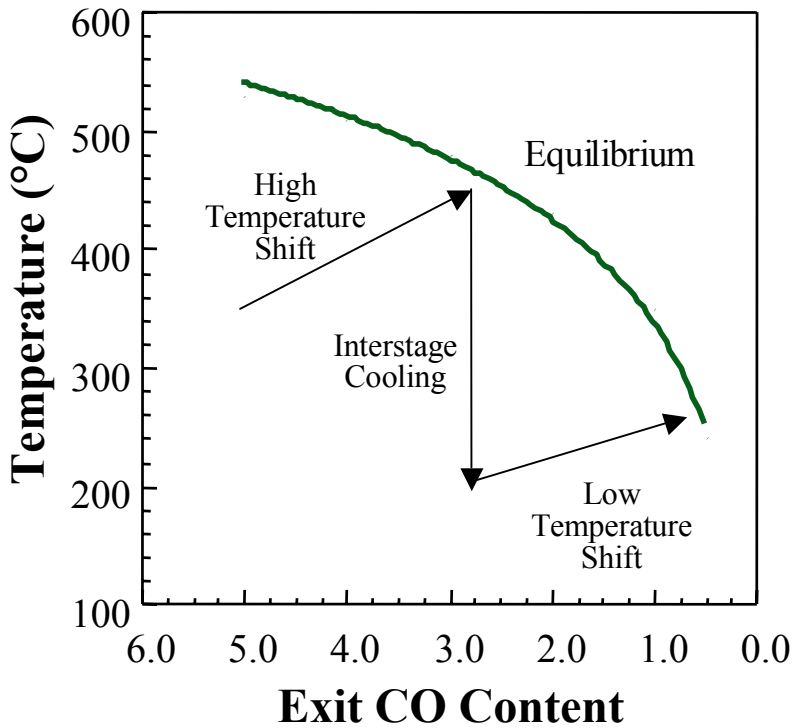
- Silicon Microfabrication
- Micromachined Metals
- Low Temperature Co-Fired Ceramics (LTCC)

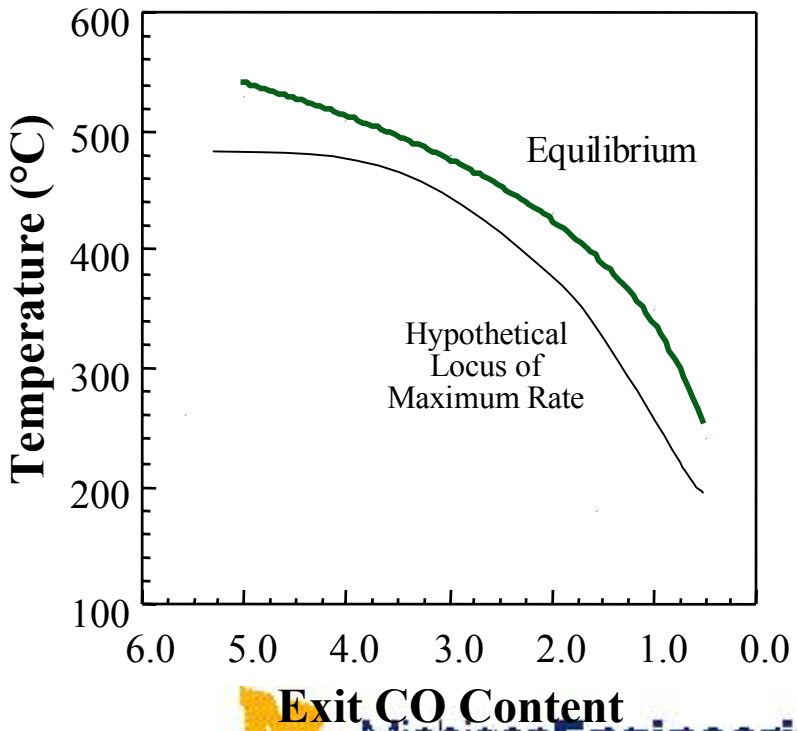
Microcombustors/vaporizers

MichiganEngineering

Micro-Systems

(1) Active cooling





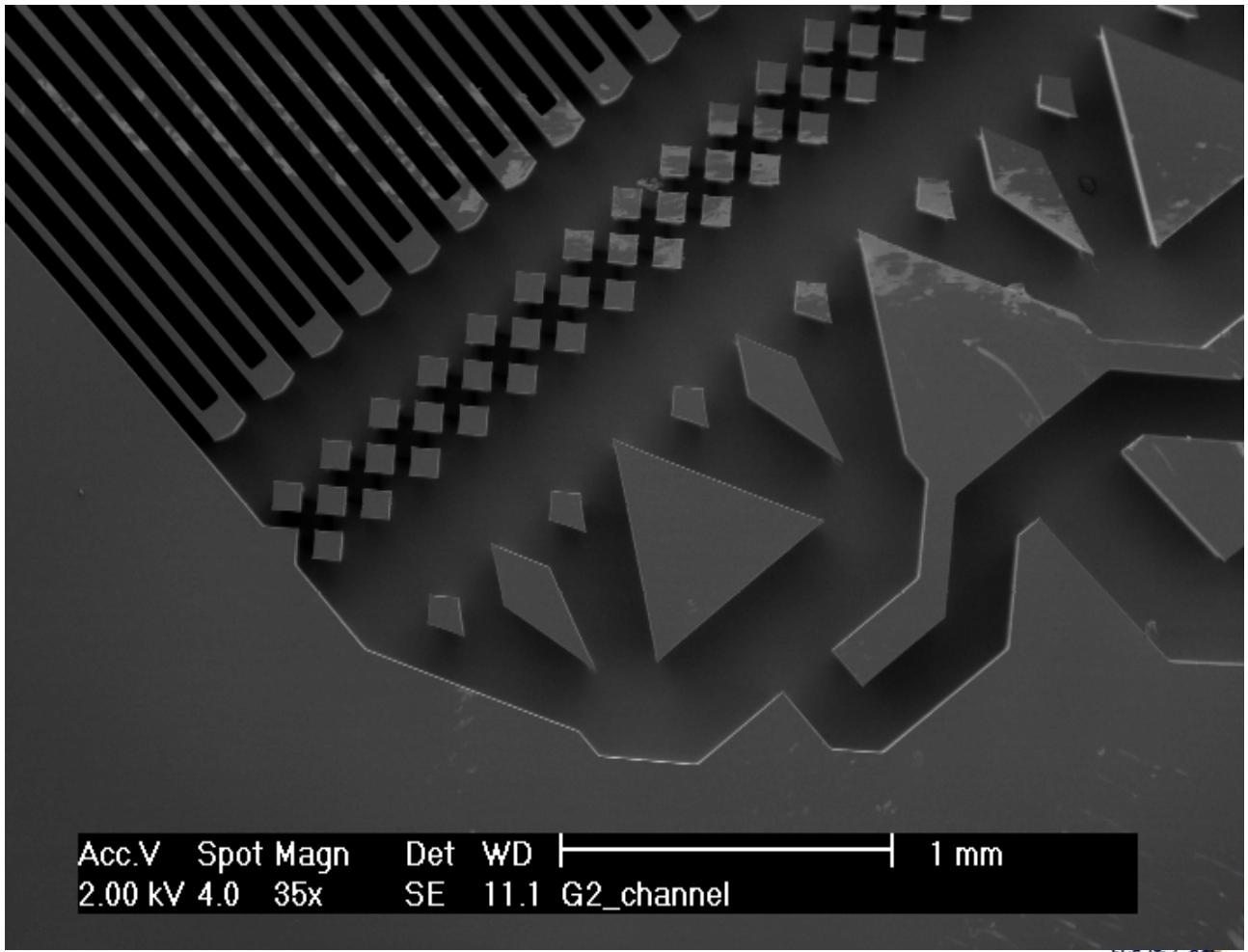
MichiganEngineering

Micro-Systems

(1) Active cooling
(2) Reduced heat and mass transport resistances
(3) More efficient thermal coupling
(4) Better cold start and transient responses

MichiganEngineering

Silicon Microchannel Reactors



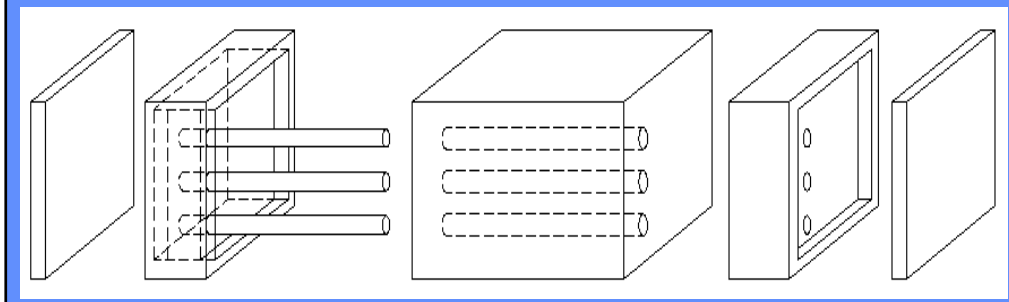
Micro-reactor showing flow distribution manifold

Very low pressure drop but catalyst loading was very low

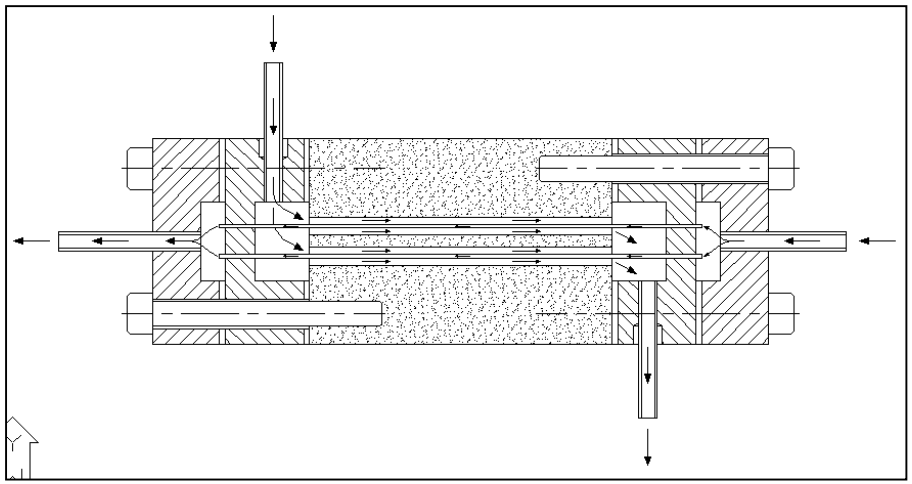
MichiganEngineering

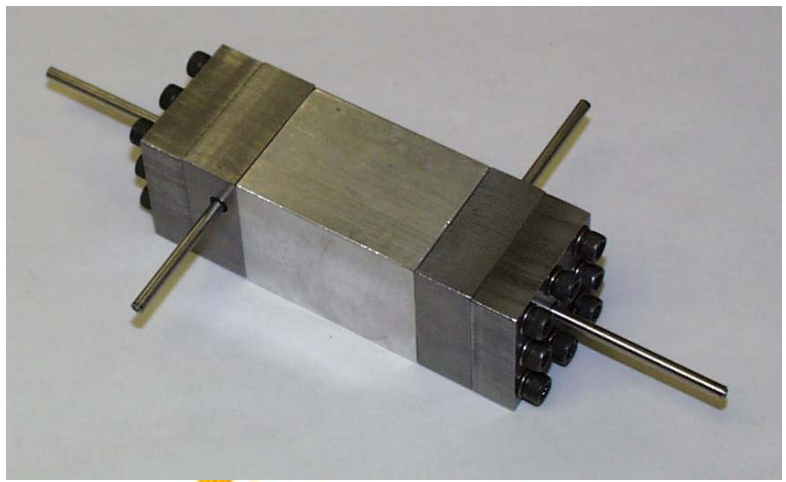
Microtube Prototype Design

- **Initial prototype used available microtube technology**
- **Concentric channels to enhance heat exchange**



Prototype Assembly



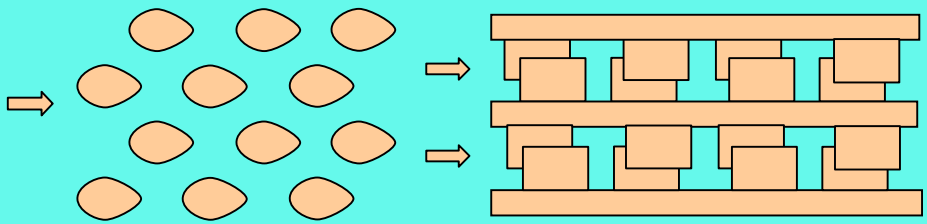


Difficult to integrate catalysts

MichiganEngineering

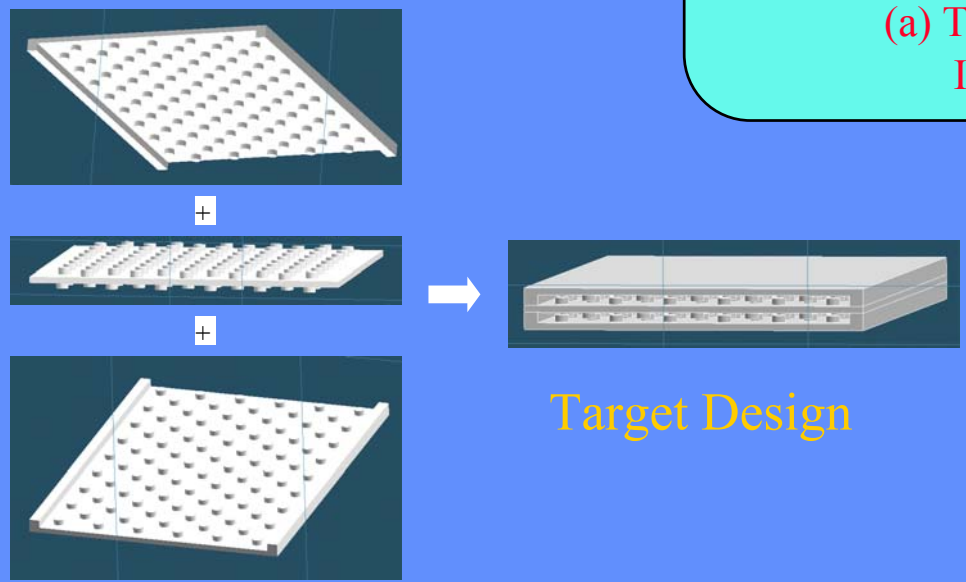
Target Design

The design goal is to achieve large surface area to volume ratio with minimum pressure drop.



(a) Top view (b) Side view

Illustration of design concept



Target Design

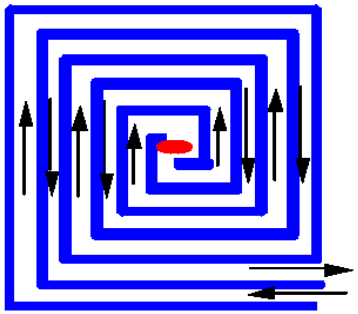
Dimensions:

- Size: 35x25x7 mm
- Pin: ϕ1 x 1 mm

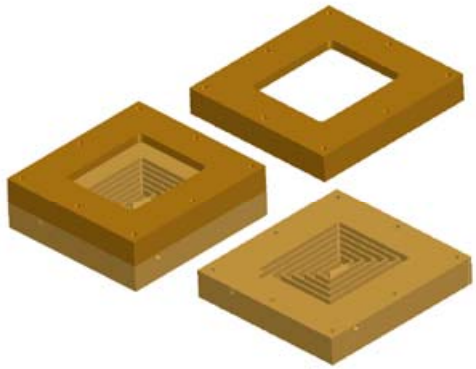
MichiganEngineering

Combustor Approaches

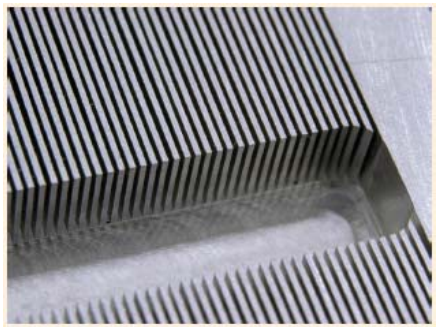
- Swiss roll, highly recuperative self-stabilizing "excess enthalpy combustors"

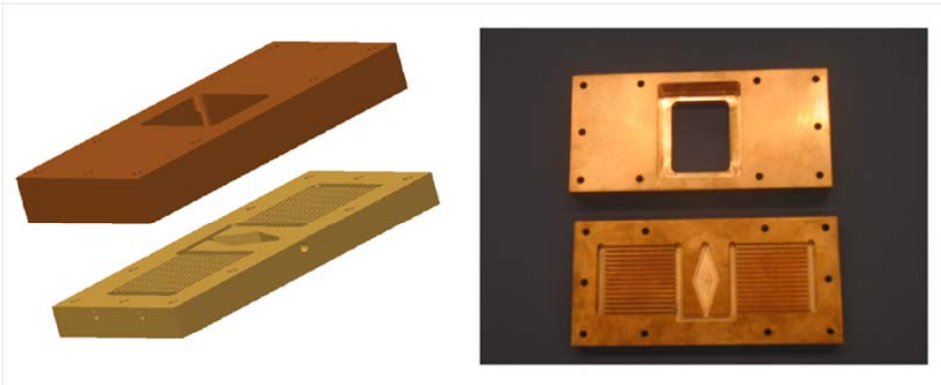


Swiss Roll Concept



- Microchannel combustors

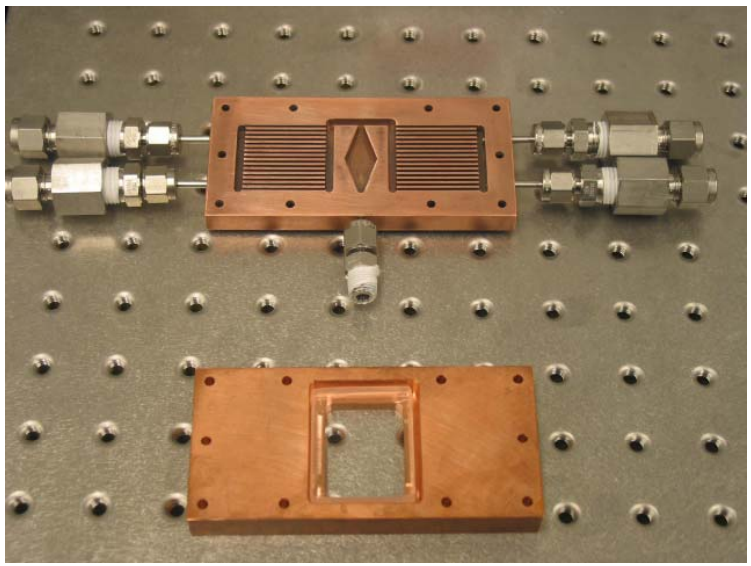




Combustor Test Hardware

- F-Burner scaled for i-octane vaporization on tailgas combustion
- W-Burner scaled for water vaporization on iso-octane vapor combustion
- Scaling model allows for design, initial sizing and optimization

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.



- Well-defined chamber designed for high turndown; “micro” channels provide heat extraction to surface-mated vaporizer
- Channel size set by heat transfer, oxidation, and mass considerations

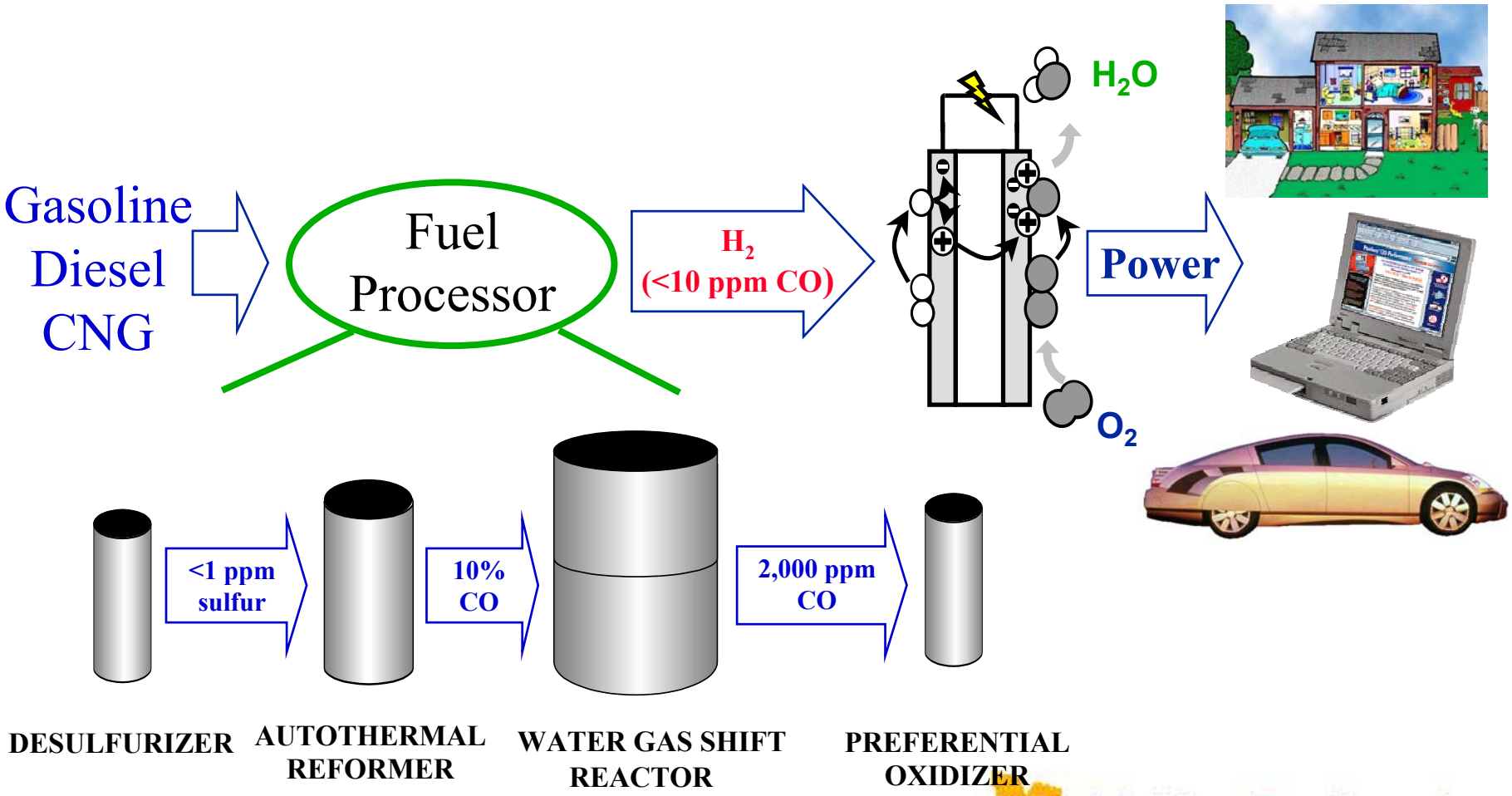
MichiganEngineering

Other Issues

- Significant interactions or collaborations with others:
  - Program partners (MesoFuel; IMM)
  - Osram Sylvania
  - Working to exchange catalysts with ANL
- Plans and future milestones
- Challenges

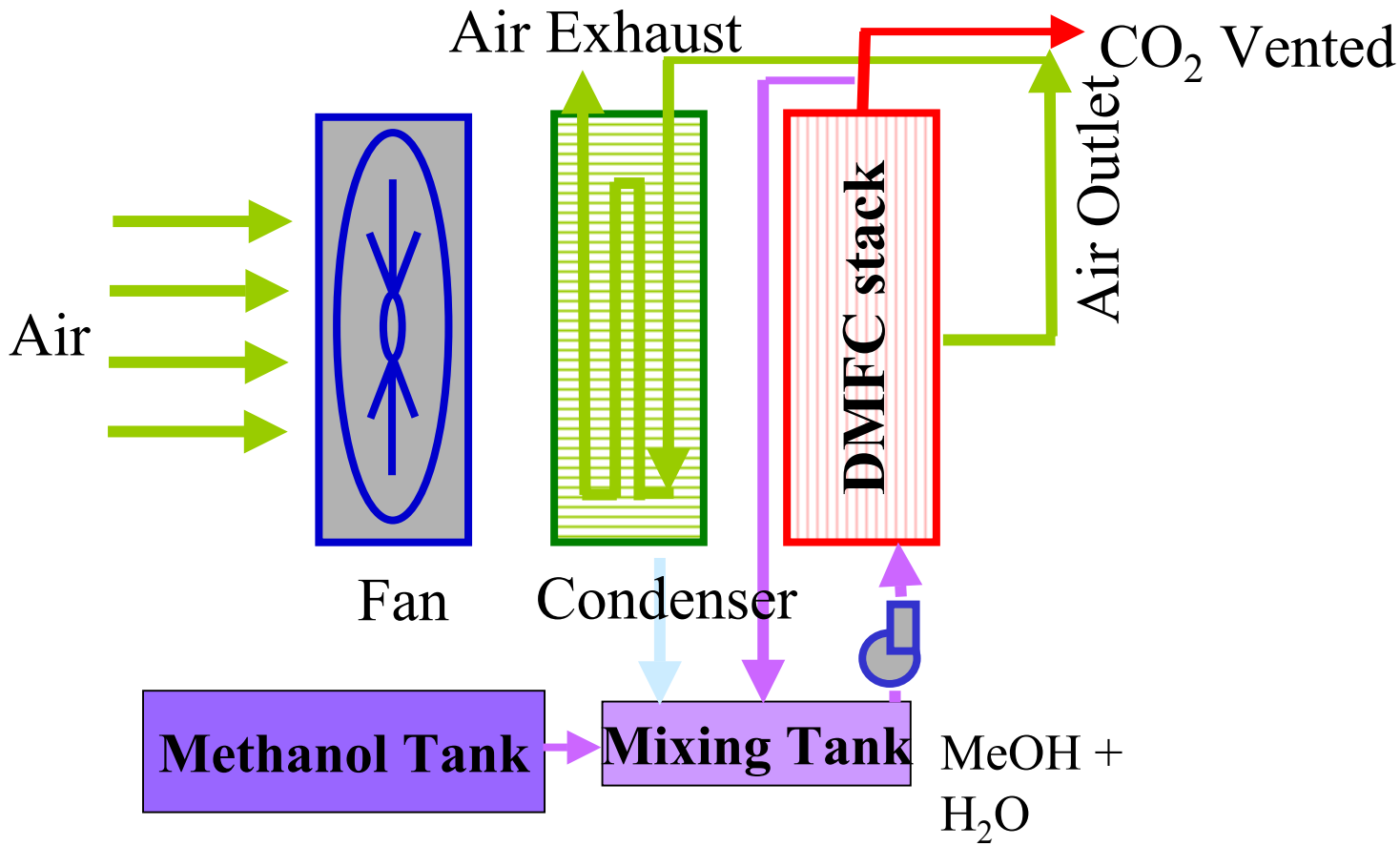
MichiganEngineering

Thank You!



MichiganEngineering

Direct Methanol Fuel Cells



Nancy Garland

Projects

Direct Methanol Fuel Cells

• Direct Methanol Fuel Cells	LANL
• Advanced Catalysts for Direct Methanol Fuel Cells	NASA Jet Propulsion Laboratory

Direct Methanol Fuel Cells

Piotr Zelenay

Los Alamos National Laboratory, Los Alamos, New Mexico

Status by the End of FY 2002 *(Highlights)*

- **Promising performance and low methanol crossover demonstrated with BPSH MEAs in single cell testing**
- **Three-fold improvement in selectivity over Nafion achieved with alternative membranes in short stacks**
- **New binary Pt-X/C cathode catalyst identified (patent pending); composition of carbon-supported Pt cathodes optimized; respectable performance shown with 1.2 $mg_{Pt}\,cm^{-2}$ (total cell)**
- **Atomic composition of Pt-Ru blacks for DMFC anodes optimized**
- **First generation 22 W DMFC stack for portable power applications designed, fabricated, optimized, tested and delivered to Ball Aerospace for system integration**
- **Several key components for 500 W stack for auxiliary power applications developed, fabricated and demonstrated with very good results in single cell operation**

FY 2002: Reviewers' Comments (R)

Comments

- *"Good progress on all fronts – cathode, anode and membrane as well as stack development." "Astonishing productivity on variety of topics."*
- *"Probably the most successfully integrated program of those presented this year."*
- *"Funding DMFCs for portable power applications is good approach." "Performance improvement is […] very encouraging and hold promise for transportation applications."*

Recommendations

- *"Membrane work less advanced." "Solid plan – consider evaluation of other membranes."*
- *"Need preliminary durability data." "Conduct durability testing."*
- *"Use stack characterization to enhance DMFC technology."*

Response to Selected Reviewers' Comments

R

"V-I sweeps should be done under conditions of constant or controlled air-stoich ratios and not under conditions of constant flow. Also for methanol flow at the anode."

Constant air-stoich operation, only sporadically used a year ago, has been since introduced into all stack DMFC R&D at LANL, i.e. into all system-relevant testing. Constant air flow is still used in electrocatalysis and membrane research, which does not involve full DMFC testing.

Because of re-circulation of methanol, constant stoich operation of the DMFC anode is not very important. It is methanol concentration, not the flow rate or stoich ratio as such, that impacts anode/cell performance the most (especially at high currents). Unlike at the gas-fed cathode, high MeOH flow to the anode does not lead to significant power losses."

R

"Why is testing at 30 psi?"

Some testing with back-pressurized cathode (up to 30 psig) has been done for performance-vs.-pressure characteristics of larger systems, which potentially could afford a compressor (if performance warranted). No such testing is performed in research for portable power."

Major Collaborations & Commercial Interactions (c)

- **Ball Aerospace**
  - ✓ Palm Power research project continued in FY 2003 with significant effort in catalysis, membrane and MEA as well as stack development;
  - ✓ Four generations of stacks for 20 W portable system developed;
  - ✓ Four 11 W DMFC stacks delivered to Ball in January 2003 for integration in two demonstration units for DARPA.
  - ✓ Technology transfer from LANL to Ball in the final stage of negotiations
- **Motorola**
  - ✓ CRADA re-instated in the area of DMFC technology for portable electronics.

Major Collaborations & Commercial Interactions (II)

- **Catalyst research:**
  - ✓ **Johnson Matthey – effect of atomic composition, morphology and crystallography of Pt-Ru blacks on DMFC anode activity;**
  - ✓ **OMG – development of novel cathode catalysts;**
  - ✓ **Superior MicroPowders – carbon-supported anode and cathode catalysts, MEAs for direct methanol fuel cells;**
  - ✓ **University of Illinois, Urbana-Champaign – fundamental research in electrocatalysis.**
  - ✓ **TKK Tanaka – carbon-supported catalysts.**
- **Membrane/MEA research & development:**
  - ✓ **Virginia Tech – development of alternative polymers and MEAs with significantly improved selectivity and duarbility;**
  - ✓ **W.L. Gore – new membranes and MEAs with improved performance and methanol selectivity.**

September 2003 DMFC Milestones

(1) Determine optimum cathode operating conditions in the backpressure range from 0 to 30 psig

(2) Reduce air stoichiometry to no more than 3×

(3) Demonstrate DMFC cathode catalyst with performance by 15% better and long-term stability for 200 hours at least as good as a corresponding reference Pt catalyst

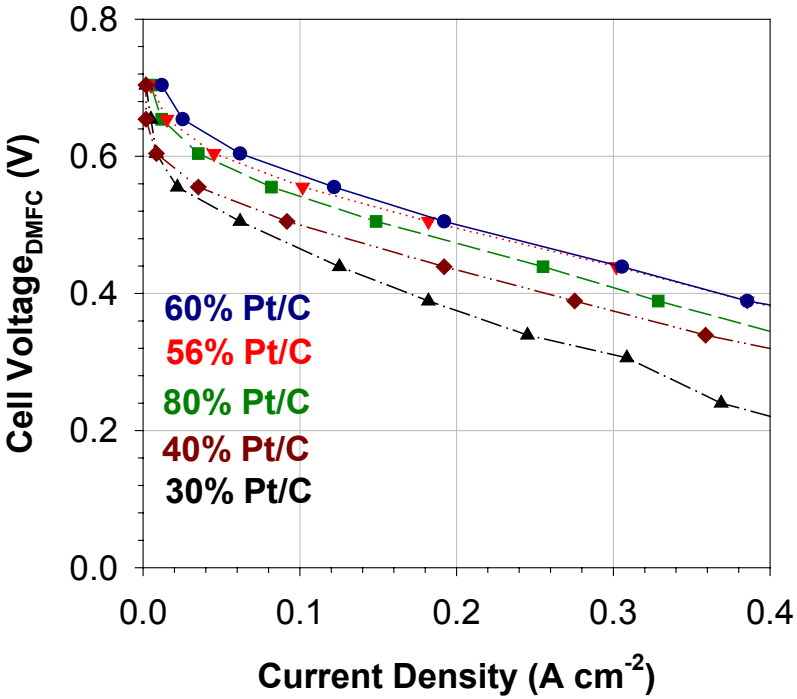
(4) Identify main routes of DMFC performance degradation

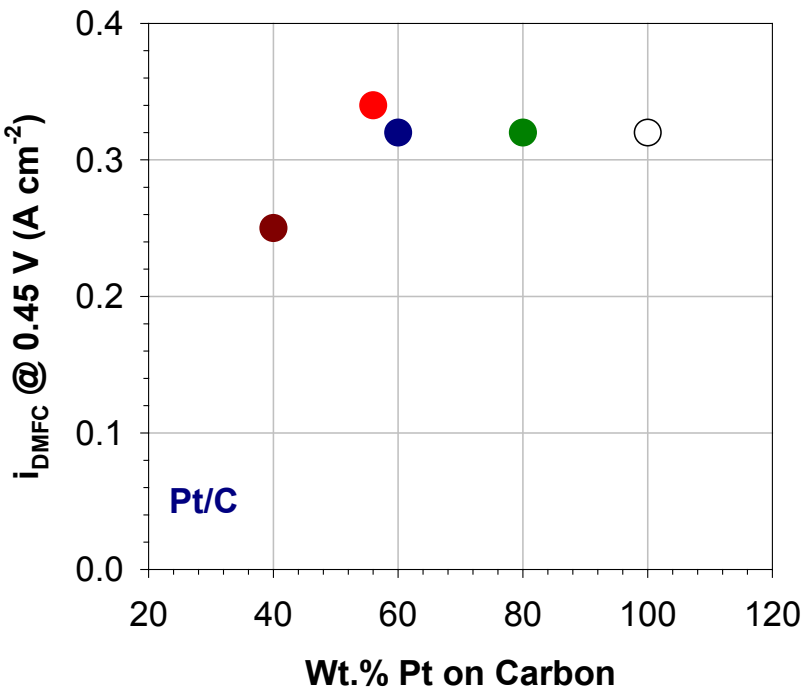
(5) Lower by a factor of two the rate of performance degradation for membranes with significantly higher selectivity than Nafion; demonstrate such membrane(s) in a cell operating for no less than 100 hours

(6) Design and build a 500 W DMFC stack

Cathode Research

Optimization of Cathode Composition at Ultra-Low Pt Loading (0.6 mg cm^{-2})



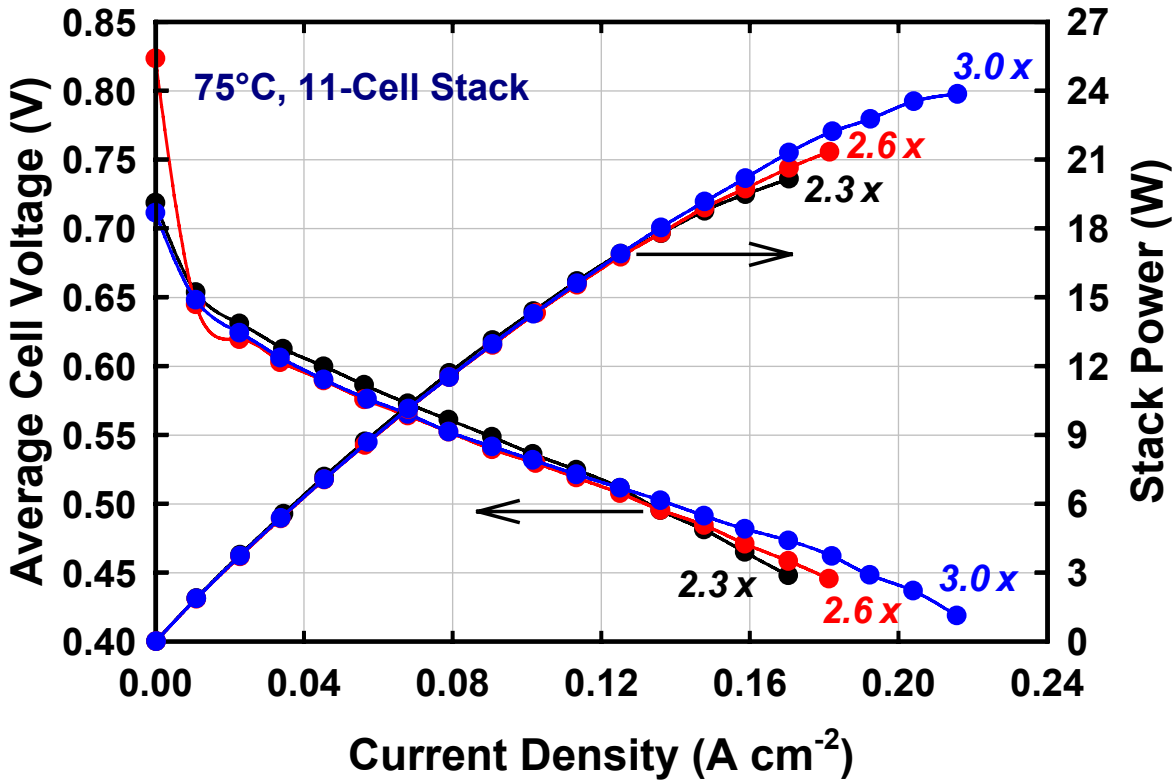


When low catalyst loading is required, such as 0.6 mg cm^{-2}, carbon-supported cathode catalysts containing between 50% and 60 wt% of Pt are best suited for DMFC operation. Two main factors determining catalyst performance are: (i) ability to handle methanol crossover and (ii) catalyst utilization.

C ***Collaboration with Superior MicroPowders and TKK Tanaka***

Cathode Research

Cathode Optimization and Reduction in Air Stoichiometry



(1) ***Good performance achieved with low air stoich ratios in single cells an stacks***

(2) ***High efficiency demonstrated independently of air flow***

2003 Milestones #1 & #2 Accomplished

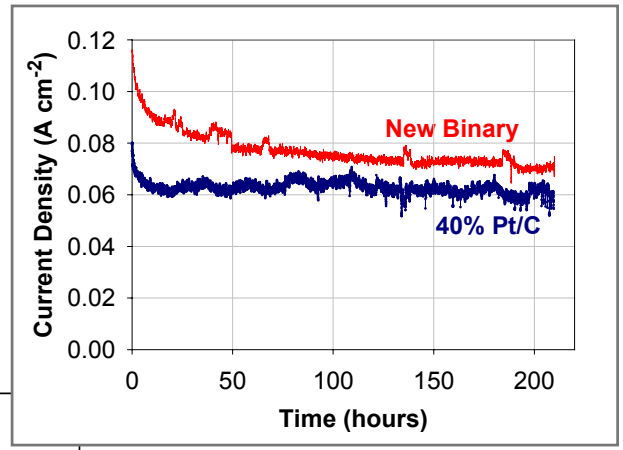
(data above relevant to Milestone #2)

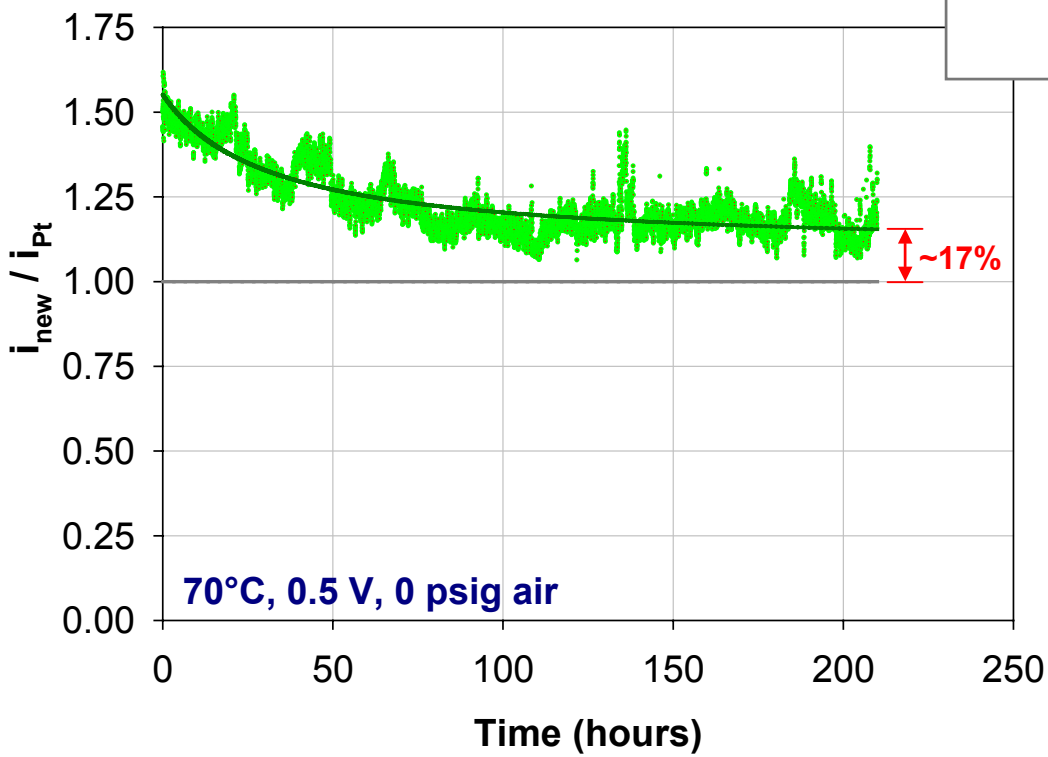
Cathode Research

200-Hour Life Test of Carbon-Supported Cathode Catalysts

Demonstrated binary carbon-supported cathode catalyst with 200-hour performance significantly better than that of corresponding 40% Pt/C catalyst.

2003 Milestone #3 Accomplished





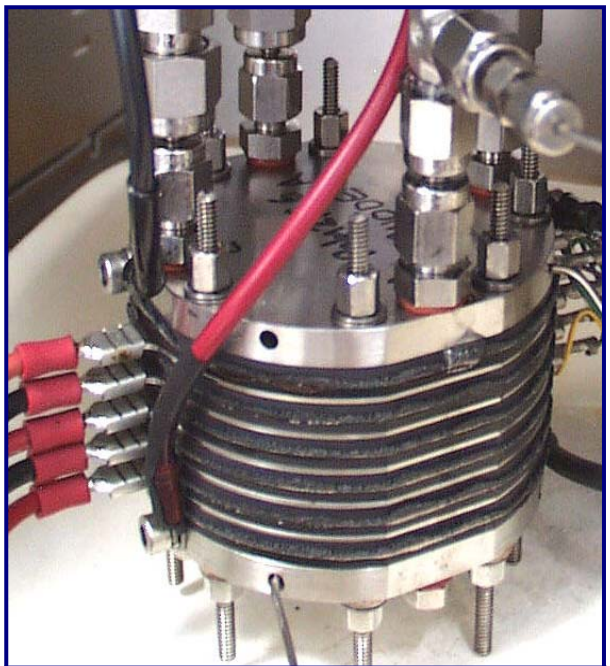
Future Research

(i) Improvement in long-term stability of the binary catalyst

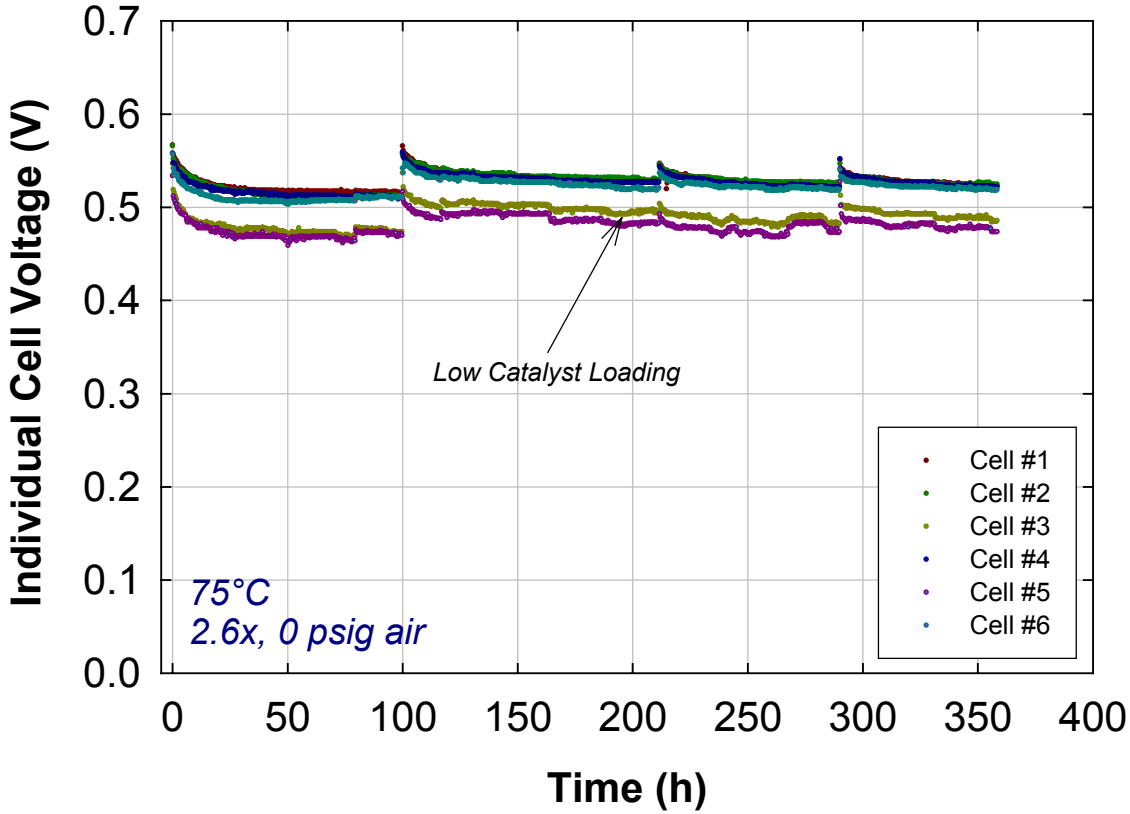
(ii) Synthesis and optimization of the unsupported binary catalyst.

Durability Research

DMFC Life Test Using Six-Cell Setup (75°C, Ambient Air)



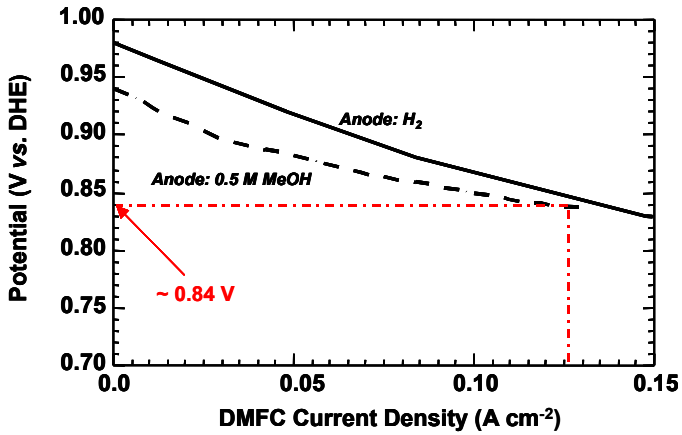
Six-Cell Setup for MEA Durability Testing

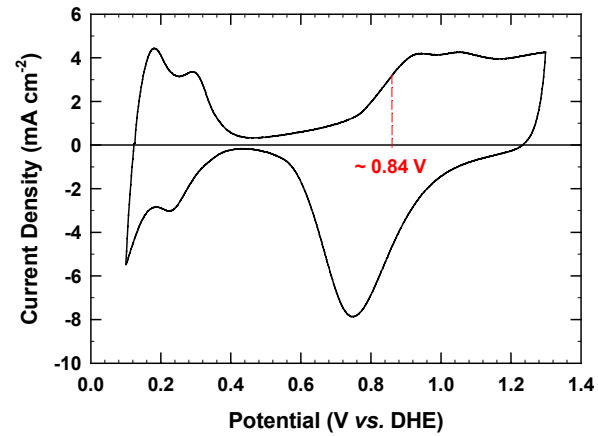


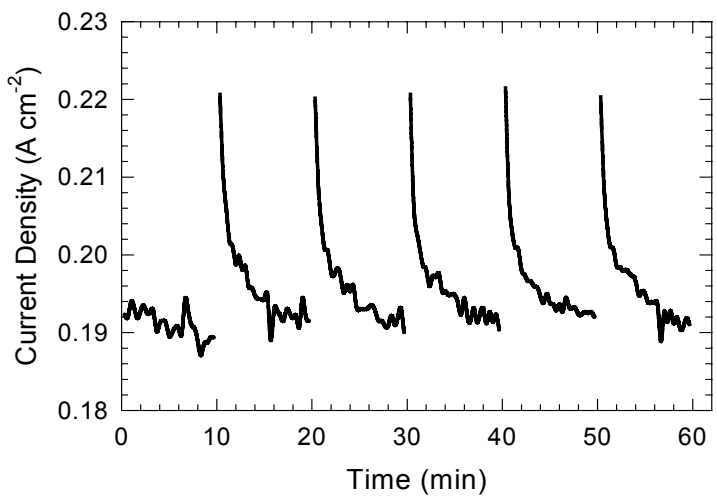
There is up to ~40 mV/cell, reversible performance loss early in the life test of "standard" MEAs operated under <u>high-efficiency conditions</u> (0.55 V/cell).

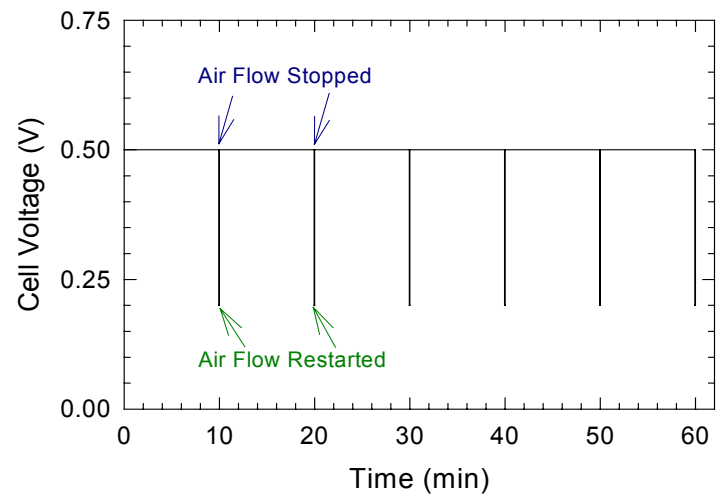
Durability Research

Short -Term Performance Loss: Why & What to Do About It?







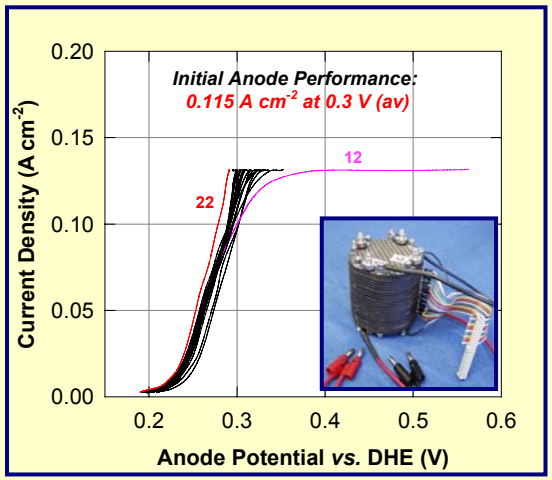


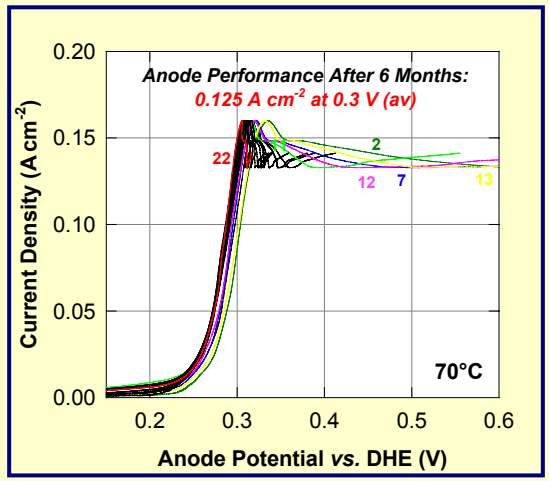
Short-term performance loss due to <u>surface oxidation of the Pt cathode</u> can be regained by voltage (cathode potential) "pulsing", e.g. via cathode air break (system-friendly approach).

Durability Research

Long-Term Performance Loss

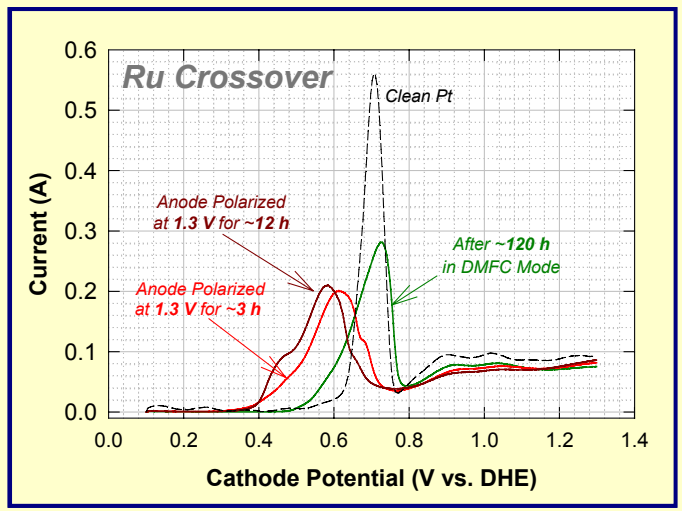
- ***There is little or no Pt-Ru anode performance loss in single-cells or stacks***





- ***Possible cathode losses:***
  - ✓ ***Ru crossover (electronic effects, blocking of O_2 reduction sites)***
  - ✓ ***Diminishing GDL hydrophobicity***
  - ✓ ***Nafion leaching & resulting loss of electrode integrity***

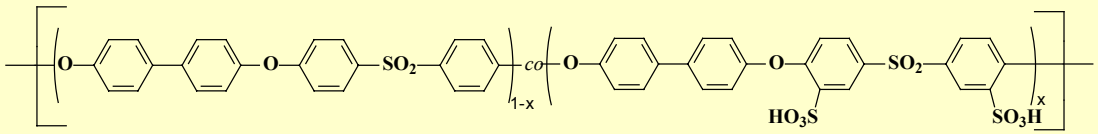
Milestone #4 on Schedule



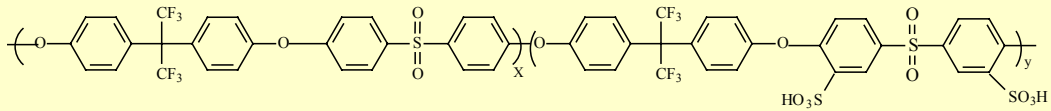
Membrane / MEA Research

Three Poly(Arylene Ether Sulfones)

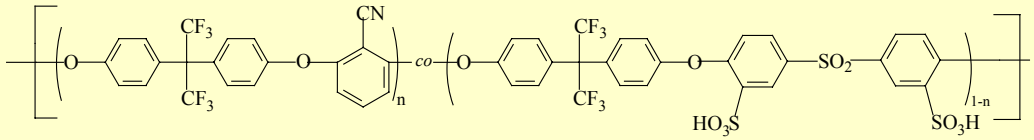
BPSH-XX



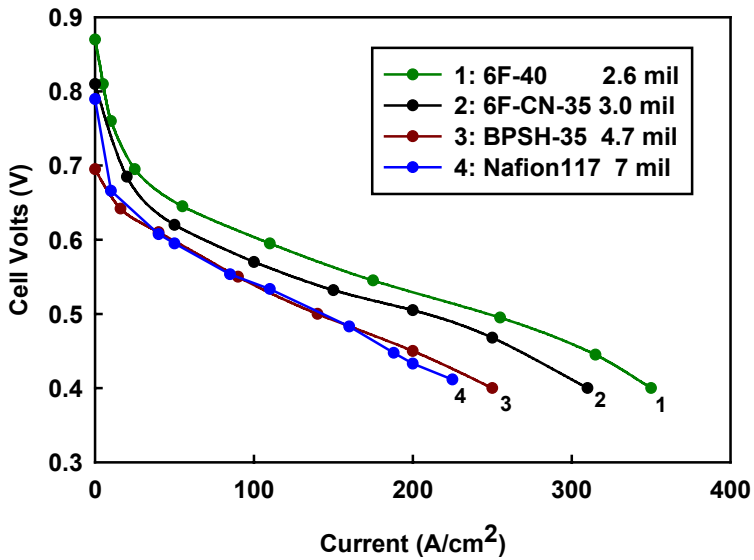
6F-XX



6F-CN-XX



XX - percentage of disulfonated monomer units

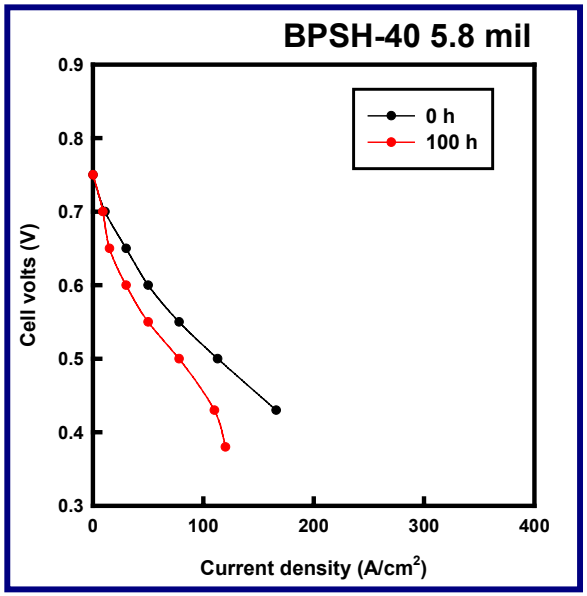


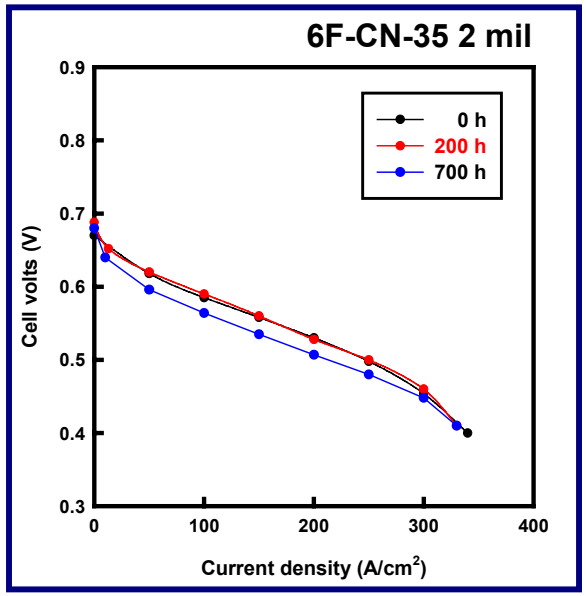
C *Collaboration with Virginia Tech*

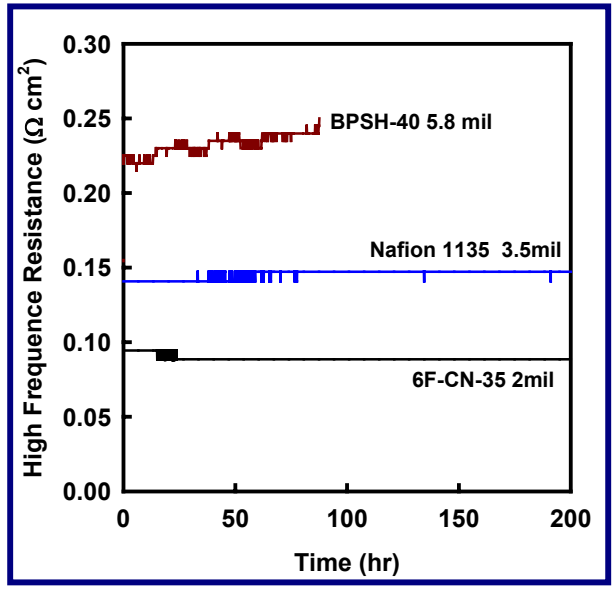
Poly(arylene ether sulfones) exhibit either better or similar initial DMFC performance to that measured with Nafion 117.

Membrane / MEA Research

DMFC Performance of Poly(Arylene Ether Sulfones) (80°C, 0.5 V)





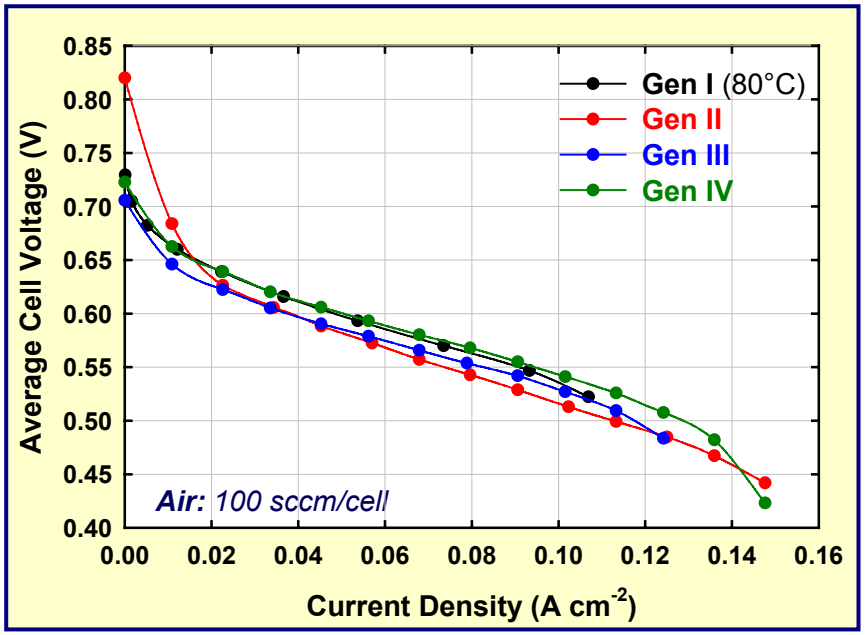


Unlike BPSH, which suffers irreversibly reduced performance after 100 hours, 6F-CN shows no degradation in the first 200 hours and only slight performance drop after 700 hours. Like Nafion (but not BPSH), 6F-CN shows no signs of resistance increase, suggesting good membrane/electrode interface. This represents a <u>significant achievement</u> in alternative DMFC membrane research.

<u>2003 Milestone #5 on Schedule</u>

DMFC Stack Prototypes for Portable Power

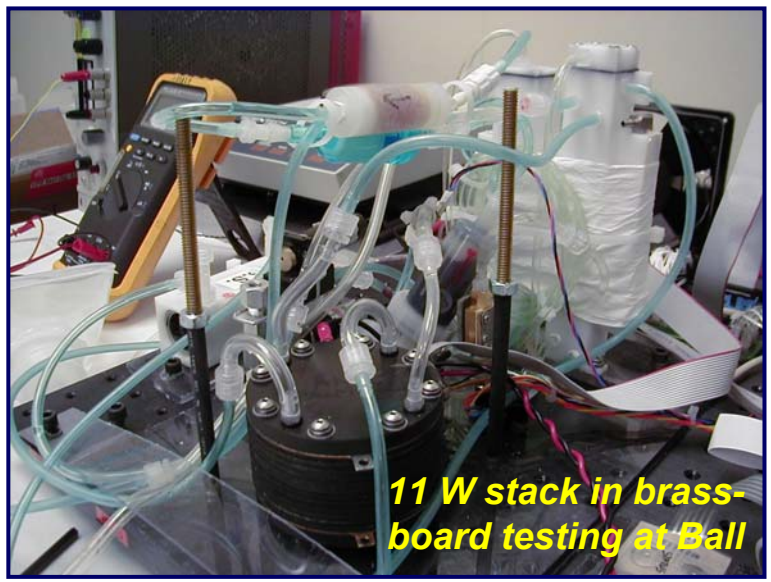
Three Generations of Portable 11 W Stacks



(1) Generations II, III and IV of 11 W stacks designed, built and successfully tested in FY03

(2) Four Generation IV 11 W stacks delivered to Ball Aerospace in January 2003 for integration in two 20 W demo systems

(3) Palm Power hardware solutions extensively used in the 500 W APU stack design



C *Collaboration with Ball Aerospace*

500 W APU Stack

Improvements to Hardware & Six-Cell Short Stack

Relative to the original design:

- *Compressive forces reduced and cell-to-cell distribution improved thanks to better gas-diffusion layer design and modified sealing*
- *Individual cell thickness lowered to as little as 0.055" (1.4 mm) due to new hardware used*
- *Mass-per-cell further reduced following footprint optimization*
- *Part count lowered thanks to combining functionality of various stack components*

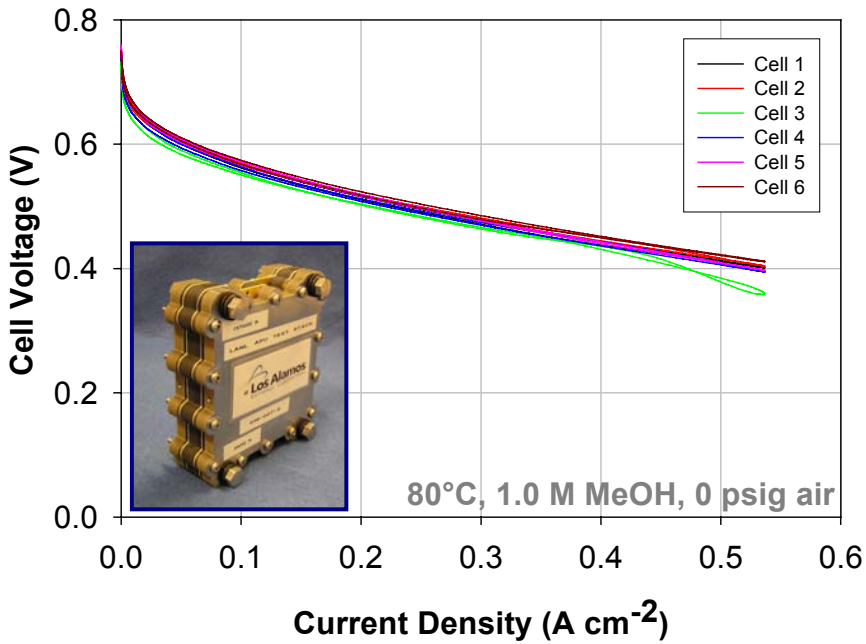
- *Predicted mass of APU stack operating with ~40% total efficiency:* ***3.2 kg***

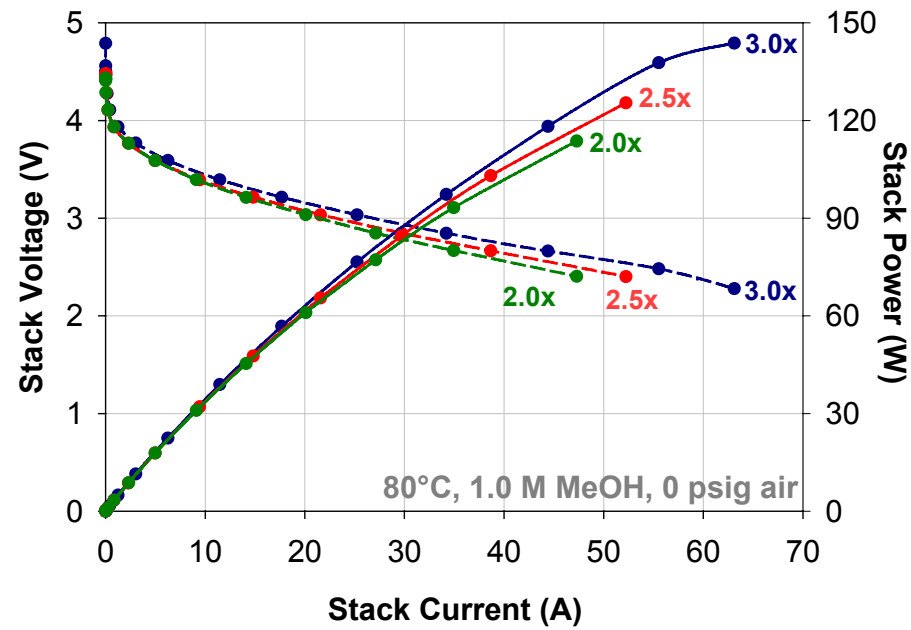
500 W Stack Model

Six-Cell Short Stack

500 W APU Stack

Short Six-Cell Stack Testing





Demonstrated uniform performance of individual cells, high power of 140 W (at 3.0x stoich & zero cathode backpressure) and negligible scale-up penalty from single cell to short stack. Expected maximum power of the full-size stack: 900 W – 1000 W (can be scaled up to 2,000 W, if required).

***2003 Milestone #6 on Schedule** (full-size stack to be built in September)*

2003 DMFC Research at Los Alamos

Summary

Cathode Research:

- ✓ **Cathode operating conditions tested for optimum air back-pressure and flow rate**
- ✓ **Composition of carbon-supported Pt catalysts optimized for good performance at a very low loading of 0.6 mg cm^{-2}**
- ✓ **Low-stoich operation of cathodes in single cells and stacks achieved**

Electrocatalysis:

- ✓ **Alternative carbon-supported cathode catalyst demonstrated for over 200 hours with performance by ~17% better than corresponding Pt catalyst**
- ✓ **Study of the effect of Pt-to-Ru atomic ratio on anode performance continued using, among others, CO probing of active catalyst sites**

Performance Durability:

- ✓ **Effect of Pt oxide formation on short-term DMFC performance shown; a method for recovering cathode activity developed and demonstrated**
- ✓ **Possible reasons for long-term MEA degradation identified; Ru crossover through Nafion membrane shown for the first time**

2003 DMFC Research at Los Alamos

Summary (II)

Membrane Research:

- ✓ **Novel polymers from the group of sulfonated poly(arylene ether sulfones) used in DMFCs for the first time**
- ✓ **6F and 6F-CN demonstrated to have reduced interfacial resistance relative to "regular" BPSH and superior properties to Nafion in terms of resistance and selectivity**
- ✓ **Extended DMFC lifetime shown with the 6F-CN membrane**

Stack R&D:

- ✓ **Three generations of 11 W stacks for 20 W DMFC system for portable power applications designed, built and tested; four *Generation IV* stacks delivered to Ball Aerospace in January 2003 for integration in two systems**
- ✓ **Design of all components for the 500 W - 900 W APU stack completed; six-cell 100-cm^2 stack built and found to deliver 140 W maximum power at zero cathode back-pressure and air stoich ratio not exceeding three**
- ✓ **Virtually no scale-up penalty from a single cell to six-cell stack detected**

2004 Research Plans

- Investigate mechanisms and design methods for controlling degradation of the Nafion and non-Nafion membrane-electrode assemblies
- Optimize performance and improve durability of systems based on novel alternative membranes, such as 6F and 6F-CN
- Perform theoretical and practical study of the impact of catalyst layer structure on the rate of methanol oxidation and oxygen reduction
- Investigate novel carbon-supported catalysts for low-loading DMFC operation
- Improve DMFC performance by understanding and optimizing hydrophilic/hydrophobic properties of the cathode
- Demonstrate for at least 100 hours sustained operation of a large-surface area stack with air-stoich ratio below two

JPL

DEVELOPMENT OF ADVANCED CATALYSTS FOR DIRECT METHANOL FUEL CELLS

S. R.Narayanan
C. K. Witham and Jay Whitacre
Jet Propulsion Laboratory
Contract : DE-AI01-01EE50659

DoE 2003 Merit Review, Berkeley, CA
May 19-23, 2003

JPL

Program Objectives

Overall Objective:

- Reduce catalyst cost for direct methanol fuel cells

Specific objectives:

- Reduce noble metal loading below 0.5 mg/cm^2
- Develop a new method of fabrication of MEAs
- Develop anode catalysts with enhanced activity
- Develop non-noble metal anode catalysts

JPL

Milestones/Accomplishments

2000-2002 (Effort level: 1.75 FTE total)

- Co-sputtering can provide active thin film catalysts

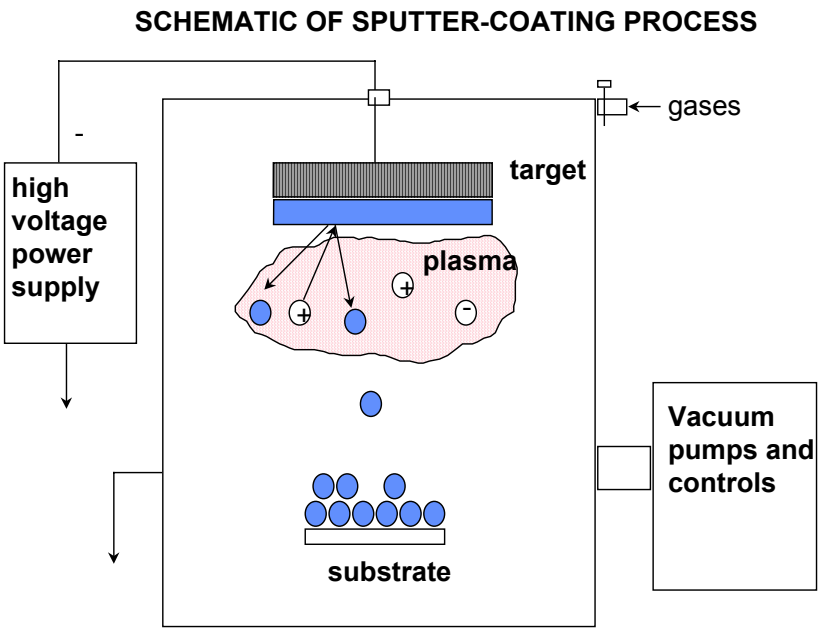
- Thin film Pt_xRu_{1-x} alloys were prepared and characterized for electrochemical activity

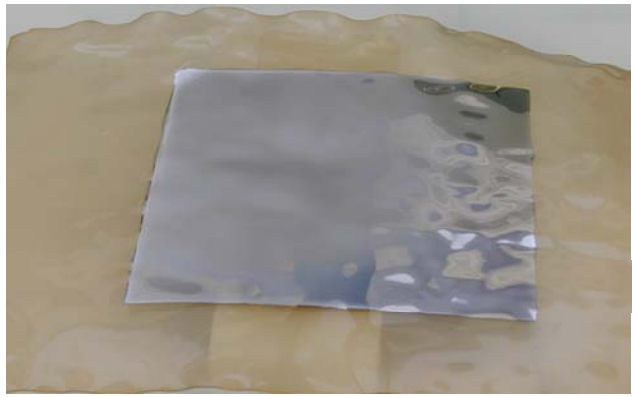
- Thin film catalysts demonstrated in Nafion MEAs

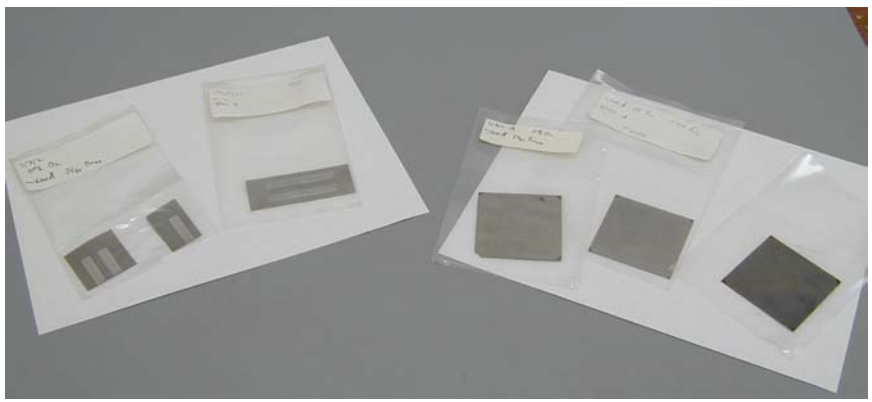
- Anode activity of 800 mW/mg at 0.1 mg/cm^2 with sputtered thin films and 2000 mW/mg at 0.03 mg/cm^2 (as opposed to 40 mW/mg with conventional ink method)

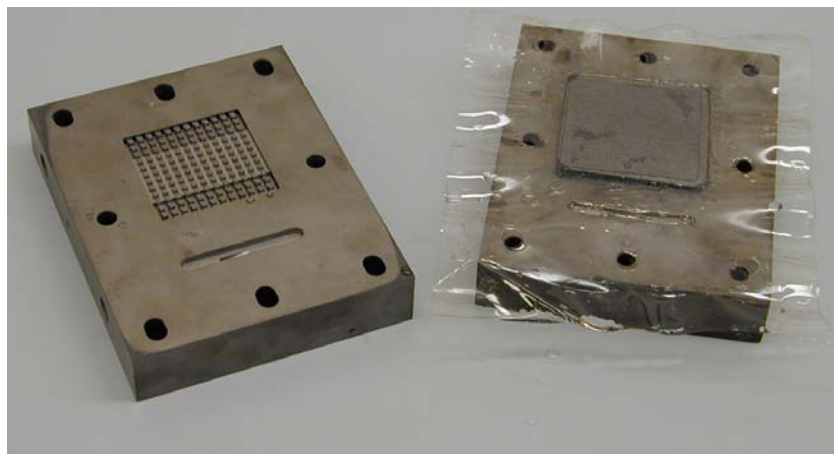
- Sputter-deposition and characterization of Pt-RuO_x layers and unique high surface area structures

Sputtered thin film catalyst layers



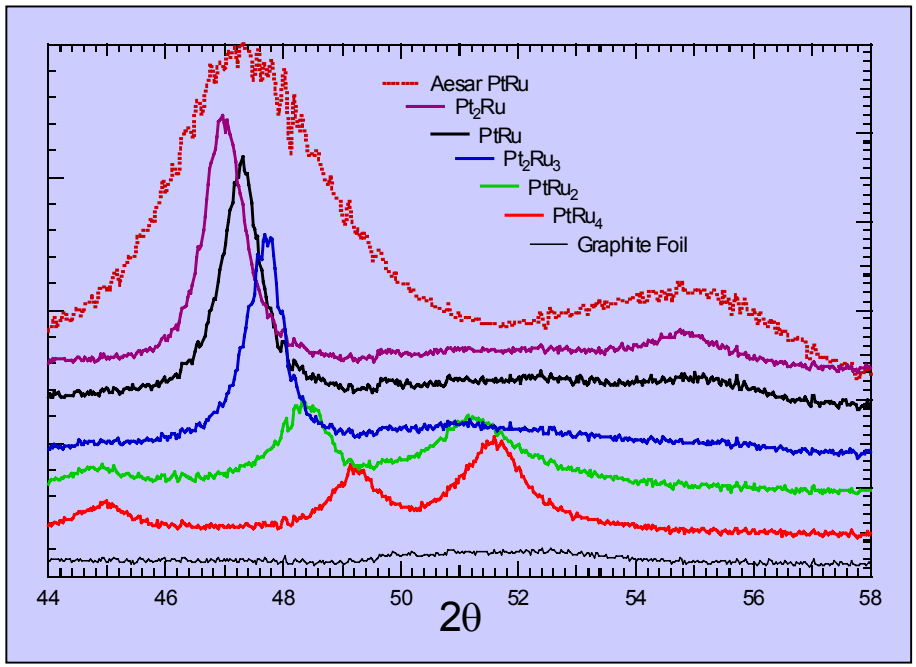




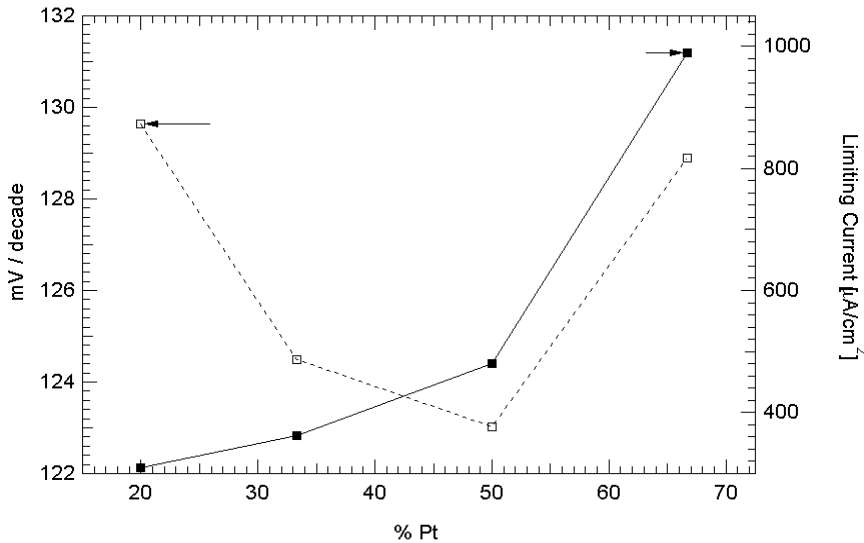


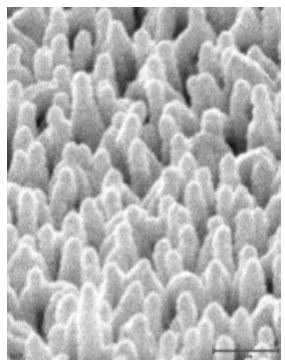
Properties of sputtered Pt-Ru films

XRD of sputtered films of Pt_xRu_{1-x}



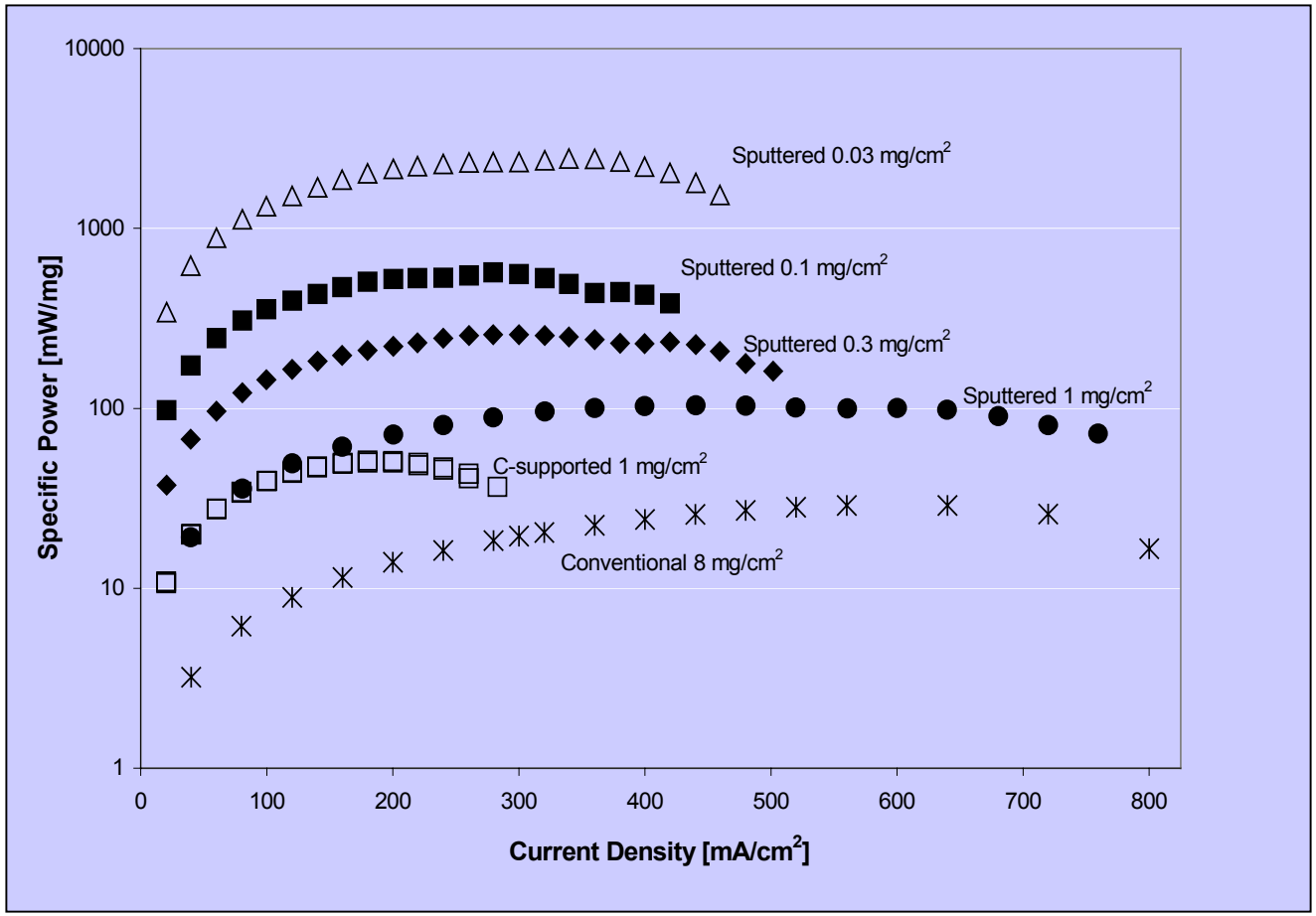
Electrochemical Activity





Unique microstructures

Utilization with thin film catalysts



800 mW/mg at 0.1 mg/cm^2, and 2000 mW/mg at 0.03 mg/cm^2

Milestones and Accomplishments

<u>2003</u> (Effort level 0.5 FTE total)

- Identification of novel corrosion-resistant non-noble nanophase thin film catalyst layers

- Sputterdeposition of electrodes and characterization under fuel cell conditions

Non-Noble Metal Thin Film Catalyst layers

Motivation

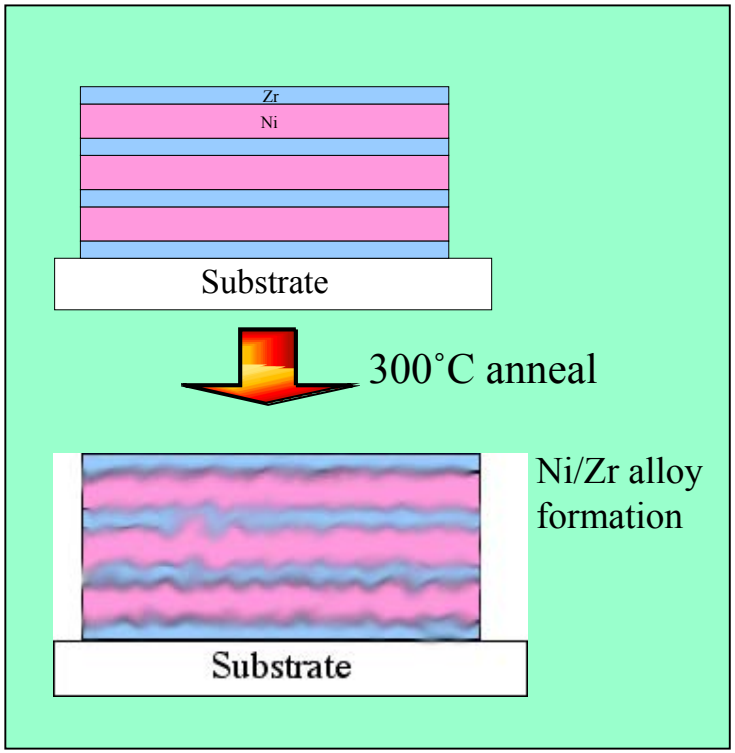
- Identifying alternates to precious metal catalysts
- Developing noble metal and non-noble metal combinations to reduce precious metal loading and enhance activity

Approach

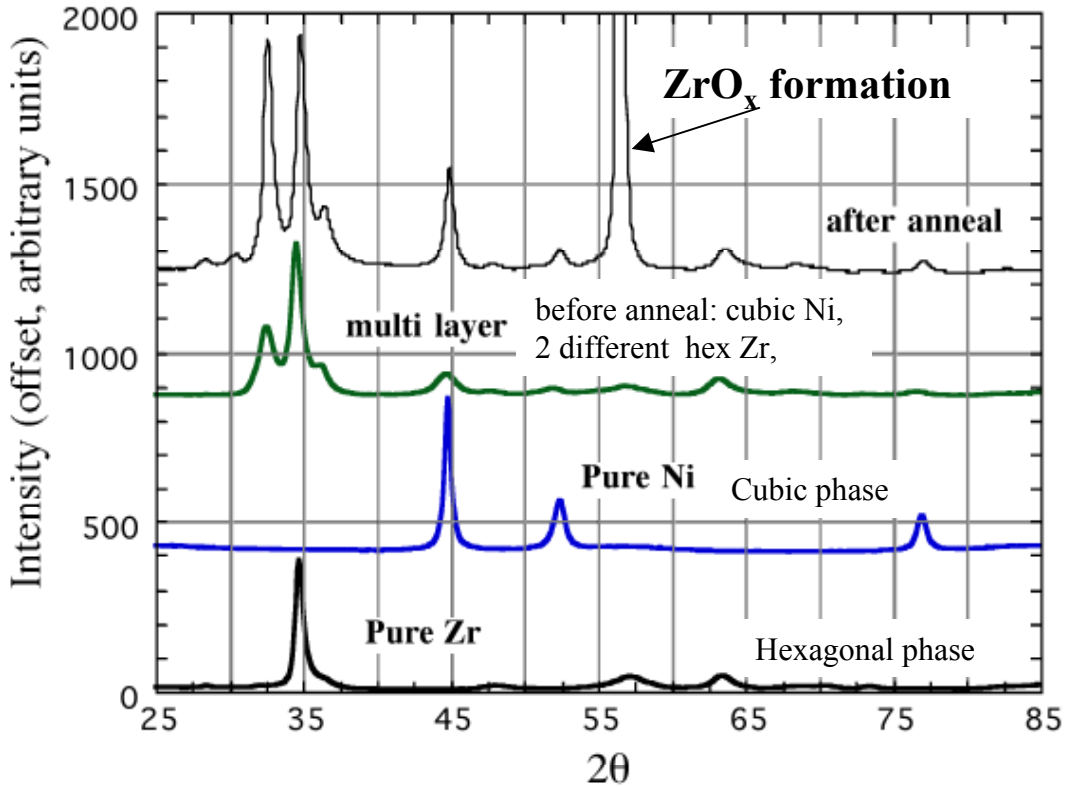
- Take advantage of sputter-depositon to identify a corrosion resistant non-noble metal system
  - non-equilibrium phases, unique nanophase structure, morphology and electronic properties.
- Ni/Zr system as proof-of-concept
- Characterization:
  - Corrosion studies in sulfuric acid, XRD,SEM
  - Fuel Cell studies with Ni-Zr/Pt-Ru catalyst layers

Multilayer Ni/Zr films

Concept

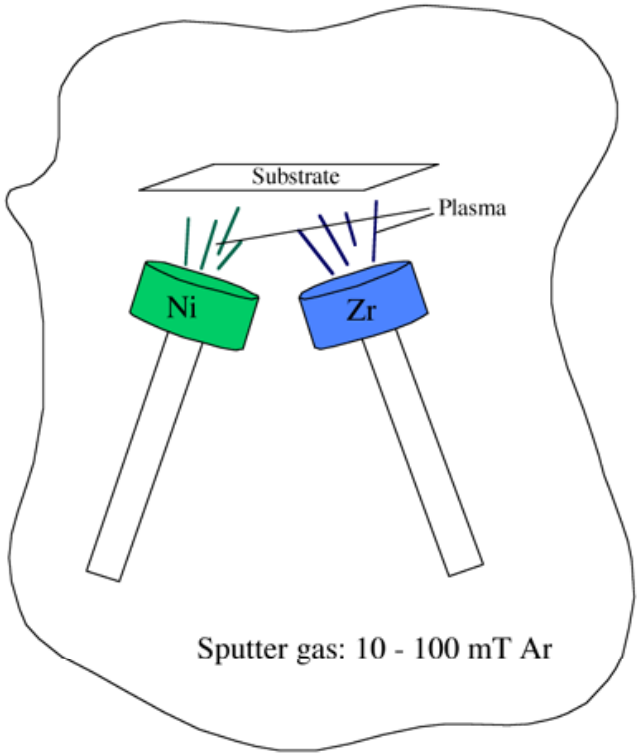


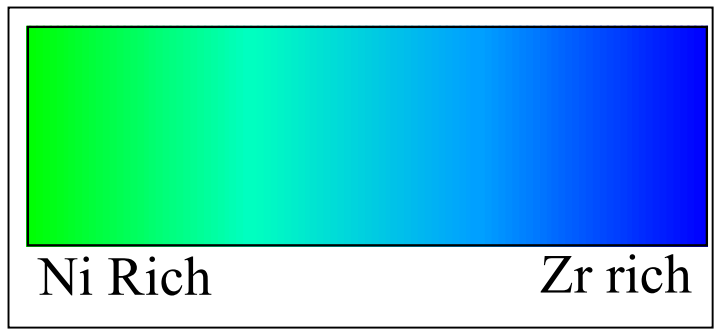
XRD of 50/50 NiZr films



- Polycrystalline films with grain diameters of ~50 nm
- 300°C annealing produces secondary phases: ZrO_x and Ni
- Multiphase composition not ideal for corrosion resistance

Co-sputtering of Ni/Zr

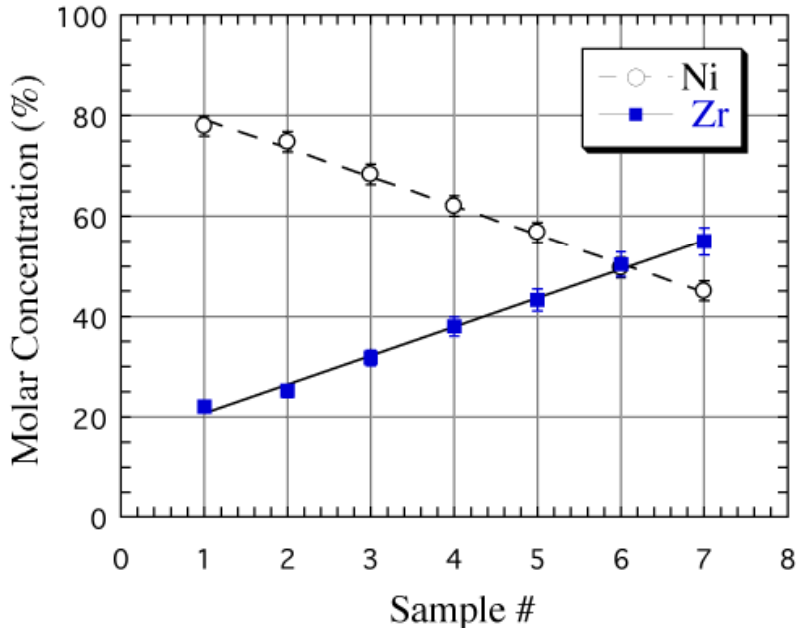




- Simultaneously use two sources
- Create a compositional gradient
- Produce multiple samples in one deposition experiment

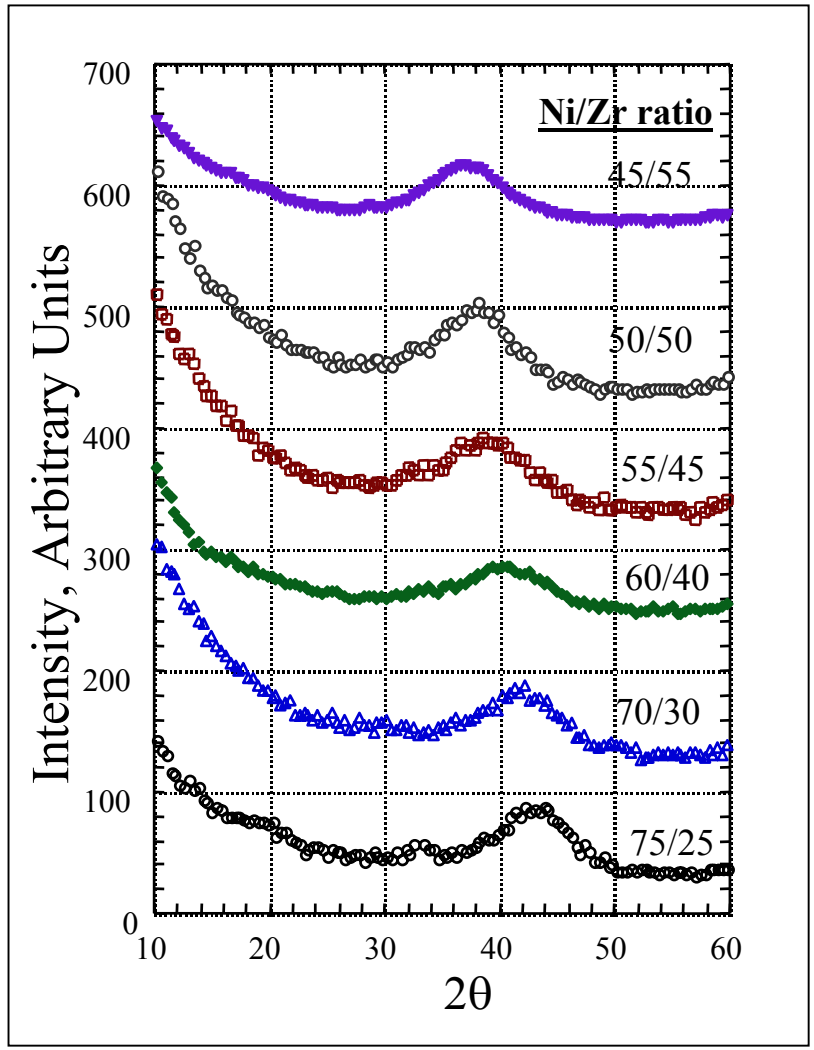
Composition and Structure of co-sputtered Ni/Zr films

EDAX Results of composition



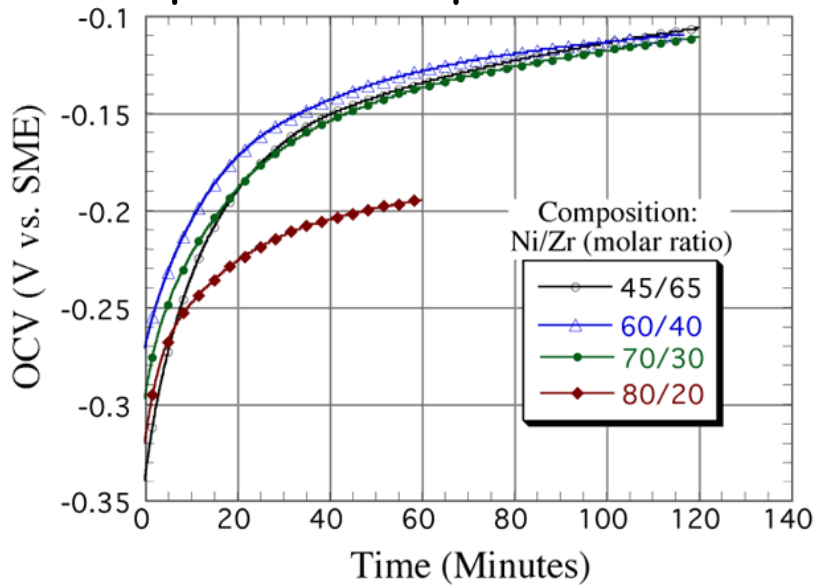
- Ni/Zr 45/55 to 75/25
- Amorphous to nanocrystalline
- Grain diameter 1.5 nm

XRD Results

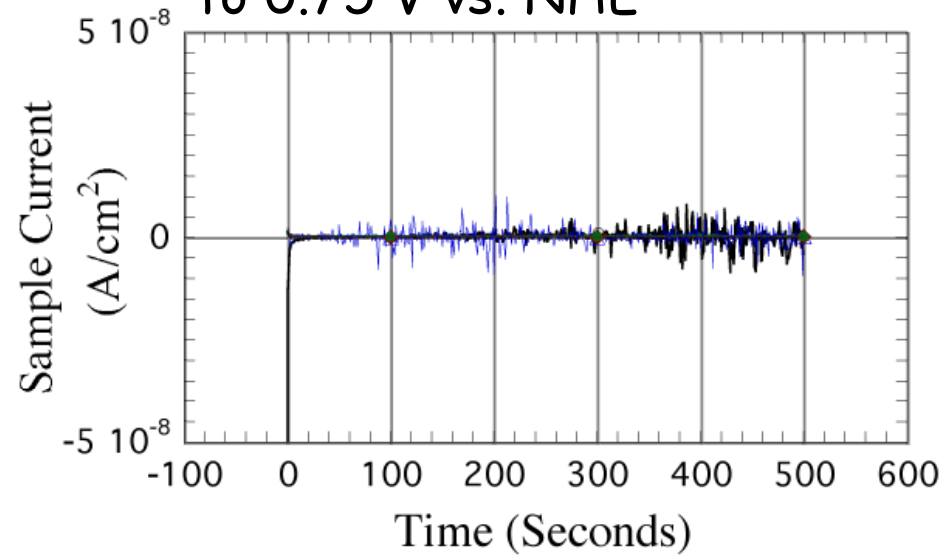


Polarization Studies in sulfuric acid solution

Open circuit potential



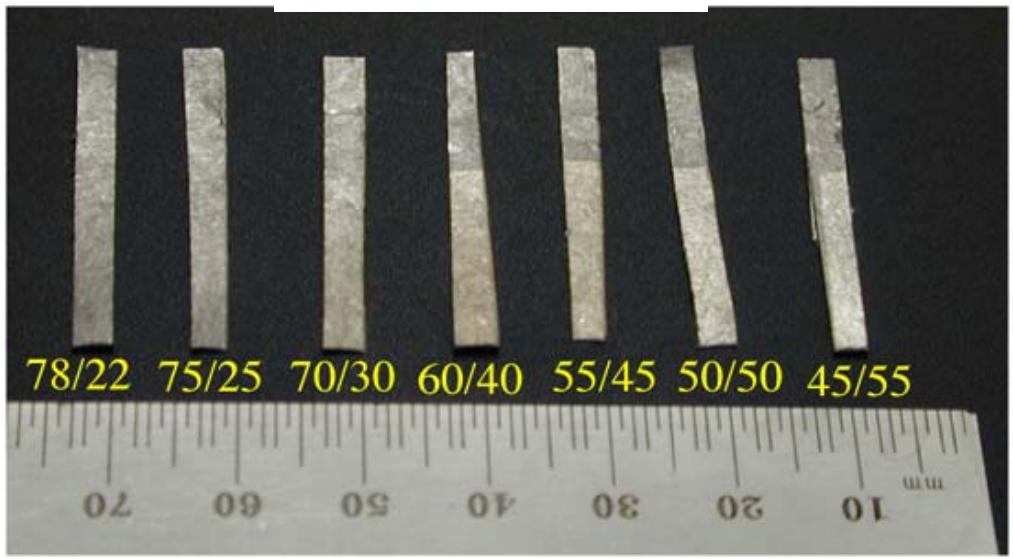
Potential scanned from 0.05 to 0.75 V vs. NHE



- Films with < 70% Ni had similar high open circuit potential of about +0.55V vs. NHE, indicative of passivation.
- Faradaic current of the order of 1 nanoampere/cm^2 over wide potential window: Good corrosion resistance

Corrosion Resistance of Ni/Zr samples in sulfuric acid

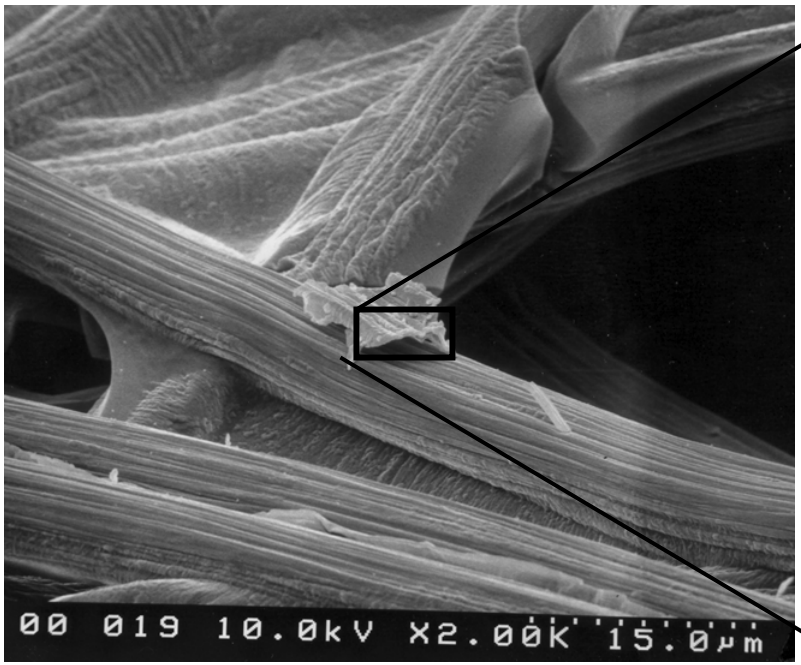
Samples with different Ni/Zr ratio



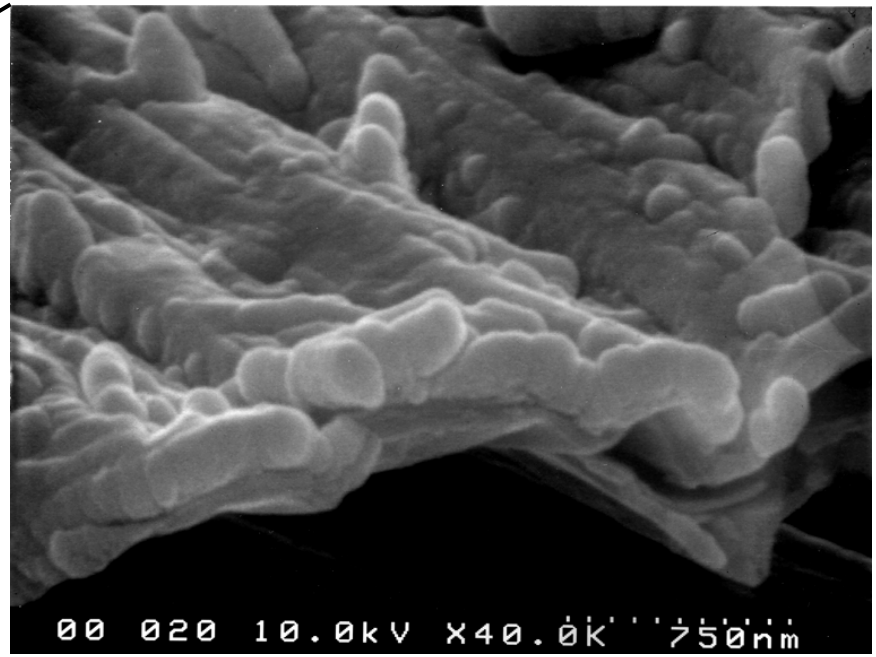
- Samples with nickel content <70% show no visible evidence of corrosion
- Samples with nickel content >70% tend to dissolve in sulfuric acid over extended period of time
- Consistent with positive open circuit potential values.

Nanoscale Morphology of Ni/Zr films

Ni-Zr films on Toray paper

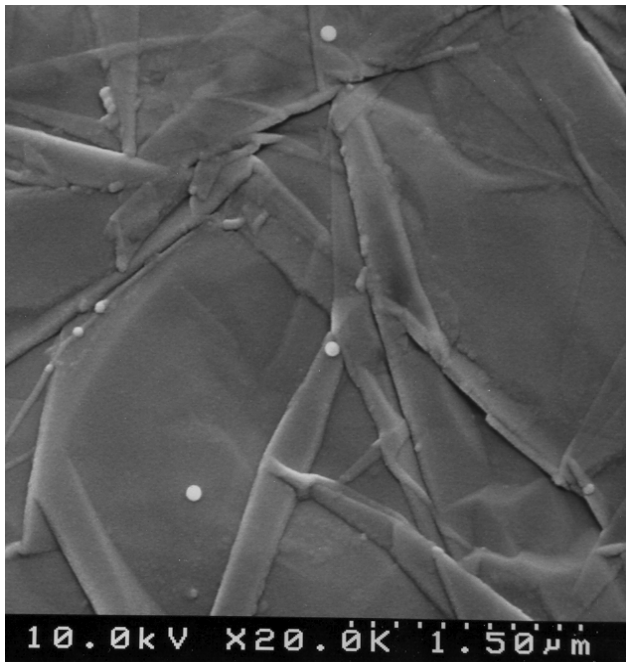


Magnified view of film



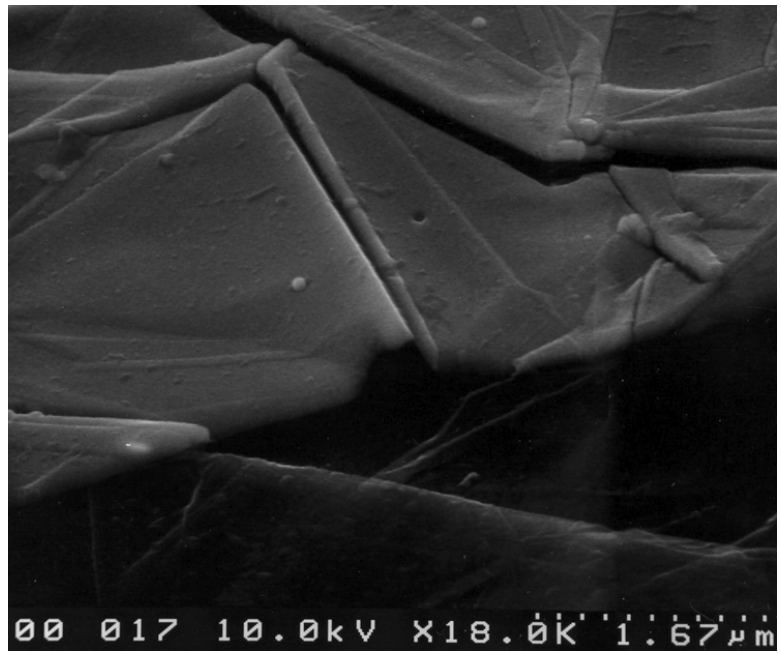
Rough nano-scale morphology can result in high surface area and active sites for catalysis

Morphology of films after exposure to 2 M sulfuric acid



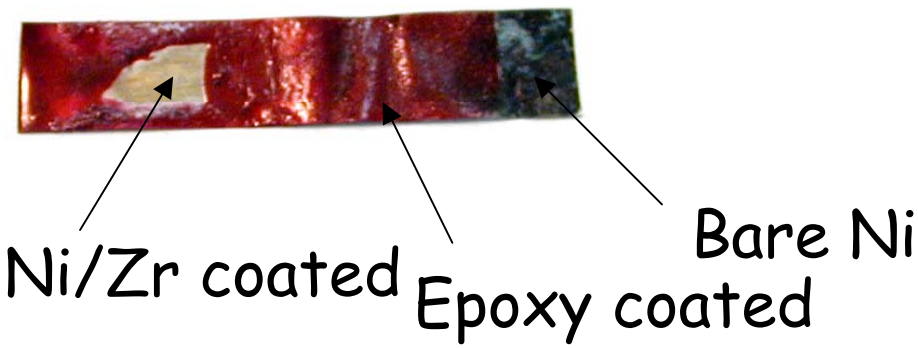
- Smooth films that conform to graphite foil substrate before acid exposure

Ni/Zr 50/50

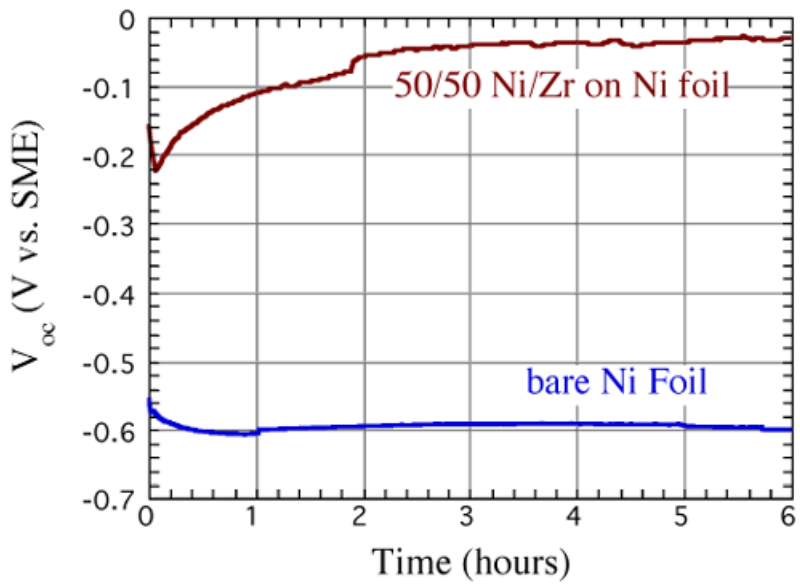


After 48 hours of exposure
Pristine surface, no visible change

Coated Ni Foil exposed to sulfuric acid



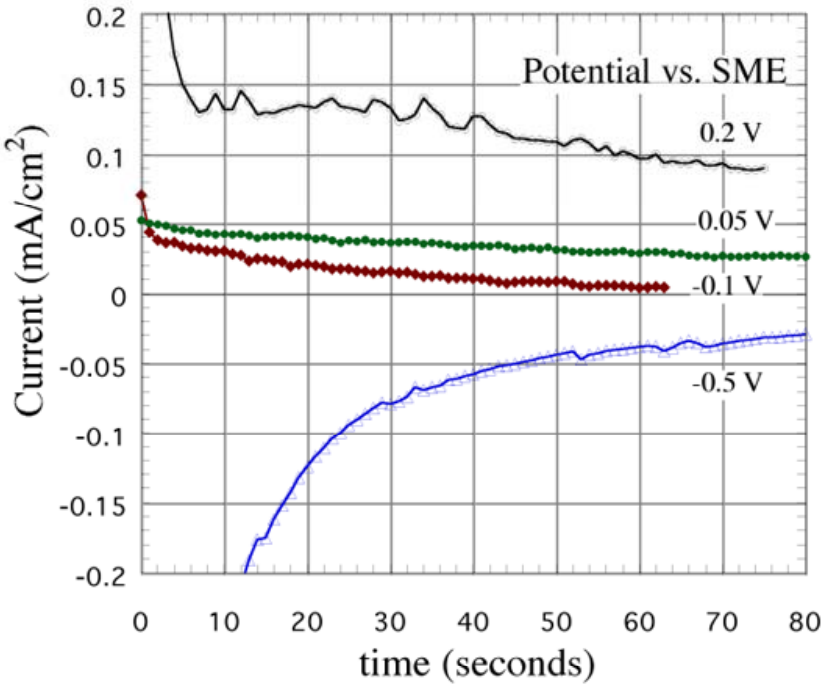
Open circuit potential measurements



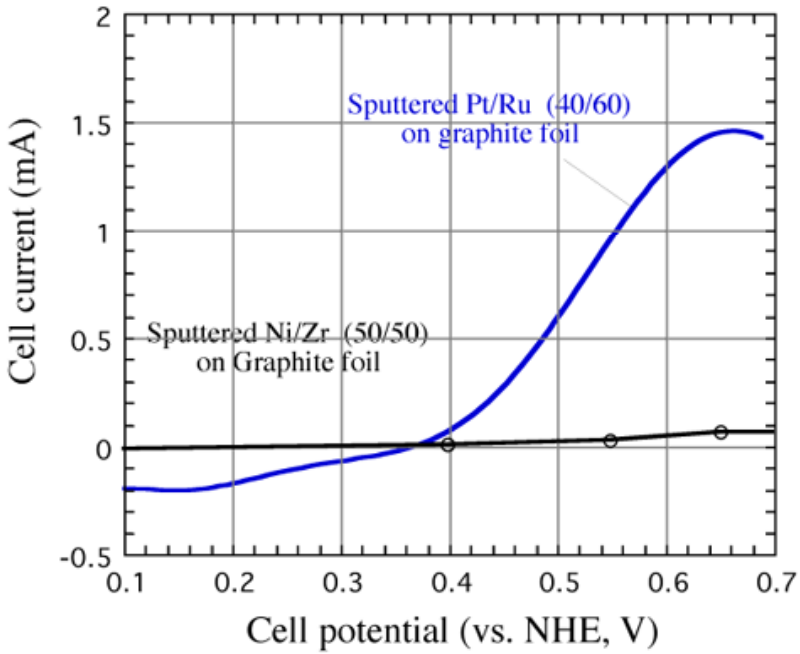
- Ni/Zr is a corrosion resistant coating for base metals.
- Protective coating for metal biplates and fuel cell hardware

Methanol oxidation activity of Ni/Zr (Preliminary Studies)

Ni/Zr 50/50

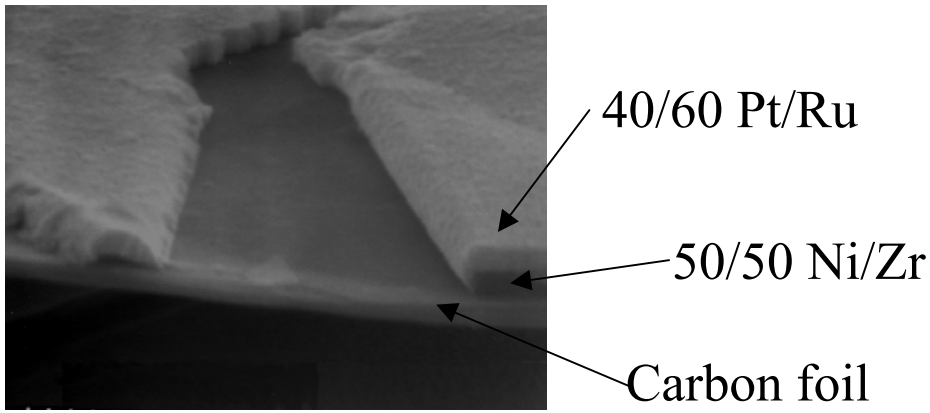


Polarization in 1M methanol/ 1M sulfuric acid, 25°C.

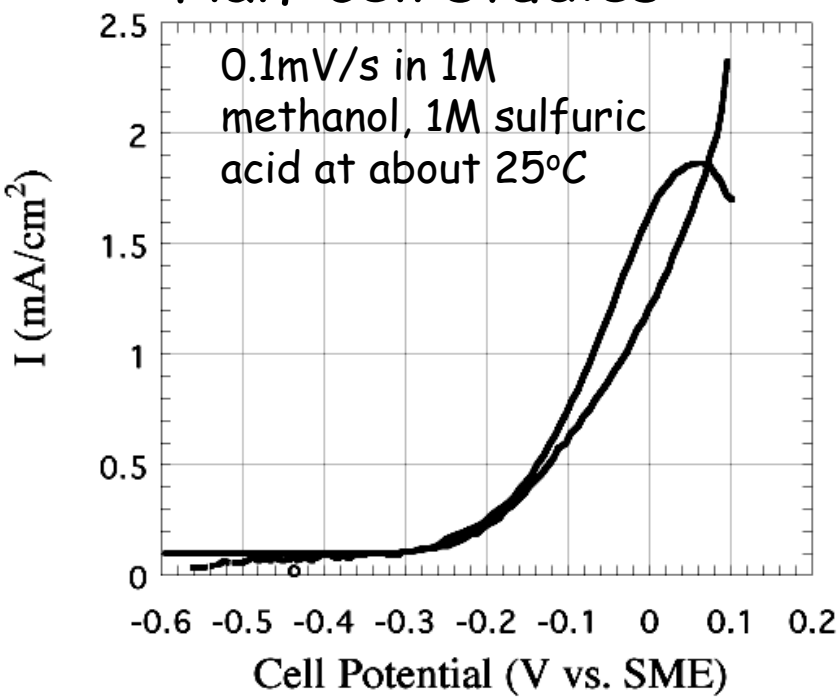


Methanol oxidation on NiZr(50/50) about 1 order-of-magnitude lower than sputtered Pt-Ru

Pt-Ru coatings on Ni/Zr

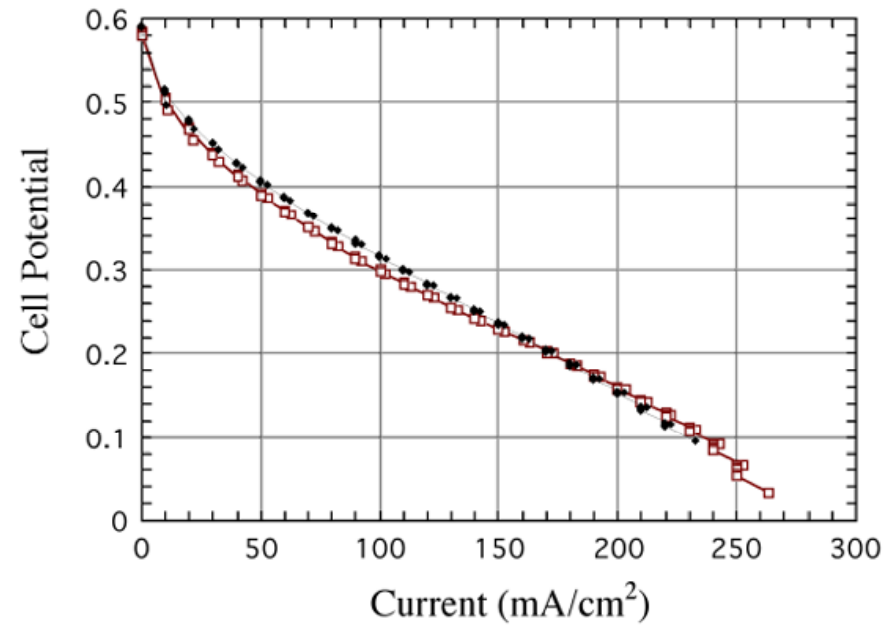


Half cell studies



Fuel Cell Studies:

0.1 mg/cm² PtRu/NiZr Nafion 117, Standard Pt cathode, 1 M methanol, 90°C



Stable operation during 4 days of testing;Ni/Zr underlayer is stable in fuel cell environment

JPL

Summary of 2003 Progress

- A non-noble metal system with corrosion resistance with potential catalytic activity has been produced
- Sputter-deposition has been demonstrated to provide unique non-equilibrium nanophase materials for fuel cell applications
- Co-sputtered Ni/Zr coatings with Ni content less than 70% have desirable properties for fuel cells.
- Ni/Zr underlayer with Pt/Ru catalyst layer has shown stable performance in fuel cells.
- Ni/Zr coatings have demonstrated to protect base metals such as Ni.
- Quaternary compositions based on Ni-Zr-Pt-Ru have been prepared.

JPL

Future Studies

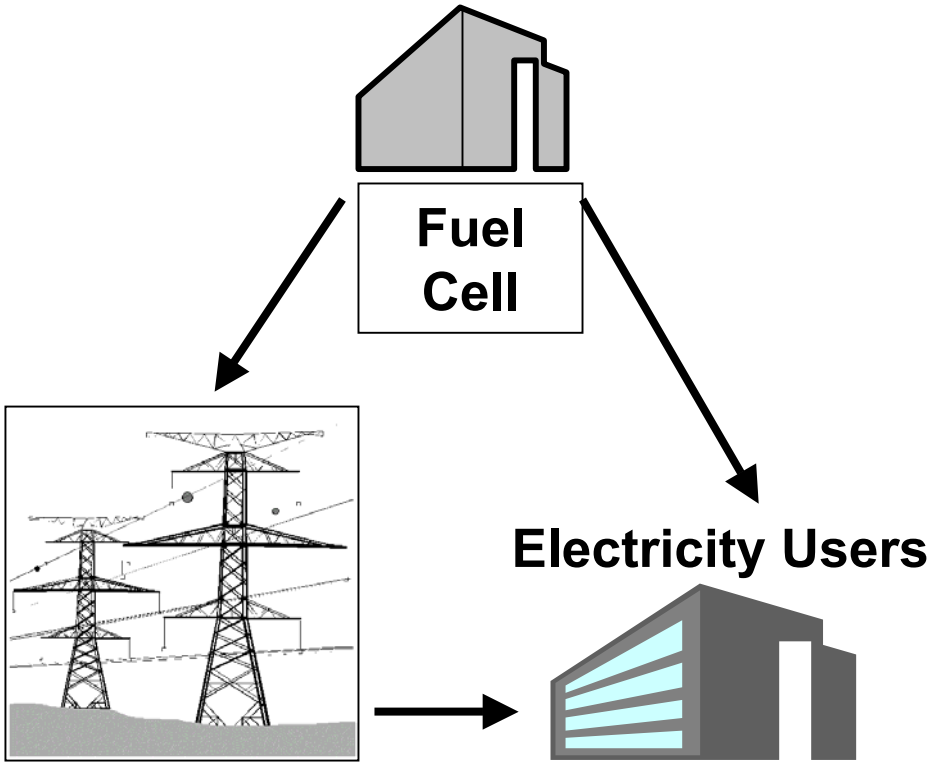
- Continue to study composition, morphology and electrochemical performance Ni/Zr coatings.

- Evaluate quaternary compositions of Ni-Zr-Pt-Ru; potentially lower the amount of Pt-Ru and provide opportunity for tuning electronic interactions

- Evaluate Co-Zr sputtered layers for methanol oxidation activity ; Co has higher catalytic activity compared to Ni for many organic transformations

- Correlate electronic properties of materials from EXAFS and XPS with catalytic properties.

Distributed Energy Fuel Cells



Kathi Epping

Objectives & Barriers

Distributed Energy

OBJECTIVES

- Develop a distributed generation PEM fuel cell system operating on natural gas or propane that achieves 40% electrical efficiency and 40,000 hours durability at $400-750/kW by 2010.

BARRIERS

- Durability
- Heat Utilization
- Power Electronics
- Start-Up Time

Targets and Status

Integrated Stationary PEMFC Power Systems

Operating on Natural Gas or Propane Containing 6 ppm Sulfur

Characteristics	Units	2003 status	2005	2010
Small (3-25 kW) Systems				
Electrical Efficiency	%	30	32	35
Cost	$/kWe	3,000	1,500	1,000
Durability	Hours	>6,000	30,000	40,000
Large (50-250 kW) Systems				
Electrical Efficiency	%	30	32	40
Cost	$/kWe	2,500	1,250	750
Durability	Hours	15,000	30,000	40,000

Projects
Distributed Energy

• Proton Exchange Membrane Fuel Cell Power System on Ethanol	Caterpillar
• Ultra-thin Composite Membrane for High Temperature Operation in PEMFCs	Fuel Cell Energy
• Fuel Cell Distributed Power Package Unit: Fuel Processing Based On Autothermal Cyclic Reforming	General Electric
• Proton Conducting Membranes	Iowa State University

Solicitation Status

Solicitation for "Research and Development for Fuel Cells for Stationary and Automotive Applications"

- Solicitation issued on 24 January 03, closed on 27 Mar 03
- Solicitation focuses stationary fuel cell R, D, and D, including cross-cutting stationary and automotive R&D.
- Selection of up to 20 awards is expected Summer 03
- Awards will have a term up to 5 years
- Total Estimated government funding is approximately $70M
- Cost Share varies from 20-50%, depending on the topic, based on risk (with the exception Economic Analysis Topic)

Future Direction/ Discussion Topics

SOLICITATION TOPICS

- Development of Stationary PEM Fuel Cell Power System
- Development of Back-up Fuel Cell Power System
- Development of Materials for High Temperature Membranes and PEM Stack Durability for Stationary & Transportation Applications
- Fuel Processing Technology for Stationary Applications
- Stationary Fuel Cell Demonstration
- Platinum Recycling Technology Development
- Non-Precious Metal Catalyst Development
- Water and Thermal Management
- Economic Analysis of PEM Fuel Cell Systems

Fuel Cell Power System
for
Transportation – Gasoline Reformer

May 21, 2003

Michael Tosca
Program Manager, Automotive

UTC Power
A United Technologies Company

UTC Fuel Cells
A United Technologies Company

Agenda

- Technical Goals and Objectives
- Organization and Team Structure
- Background and Program Overview
- Timeline
- Testing Status and Results
- Summary

DOE Technical Goals and Objectives

"Develop a 45% efficient reformer-based fuel cell power system for transportation operating on clean hydrocarbon or alcohol-based fuel that meets emissions standards, a start-up time of 30 seconds, and a projected manufactured cost of $45/kW by 2010 and $30/kW by 2015."

- Transportation Technical Barrier D-Fuel Cell Power System benchmarking, being addressed with reformer based integrated fuel cell power system program

UTC OVERVIEW

UTC Power
A United Technologies Company

UTC Fuel Cells
A United Technologies Company

Utilities / Commercial / Industrial

CA1451

Fuel Cell

CA1807

Microturbine

CA1832

Organic Rankine Cycle

Transportation

CA1622

Fleet Vehicles

CA0815

Space

CA1569

Automotive

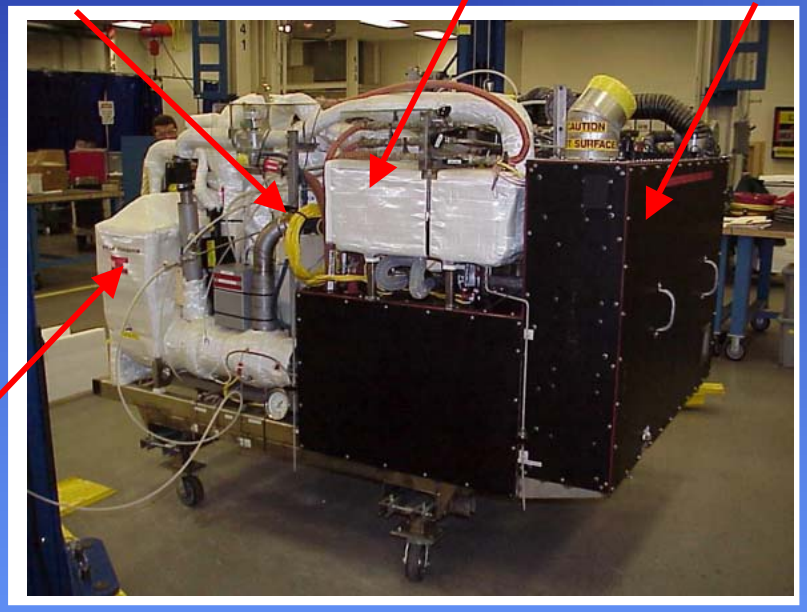
Program Team

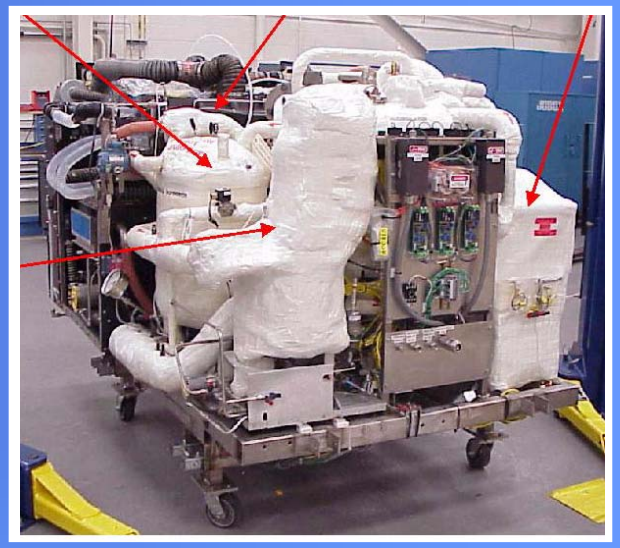
UTC Fuel Cells
A United Technologies Company

HYDROGENSOURCE

Develop, manufacture and sell Fuel Processors for the fuel cell and hydrogen fuel markets.

Background - Series 200 ATR Based FPS

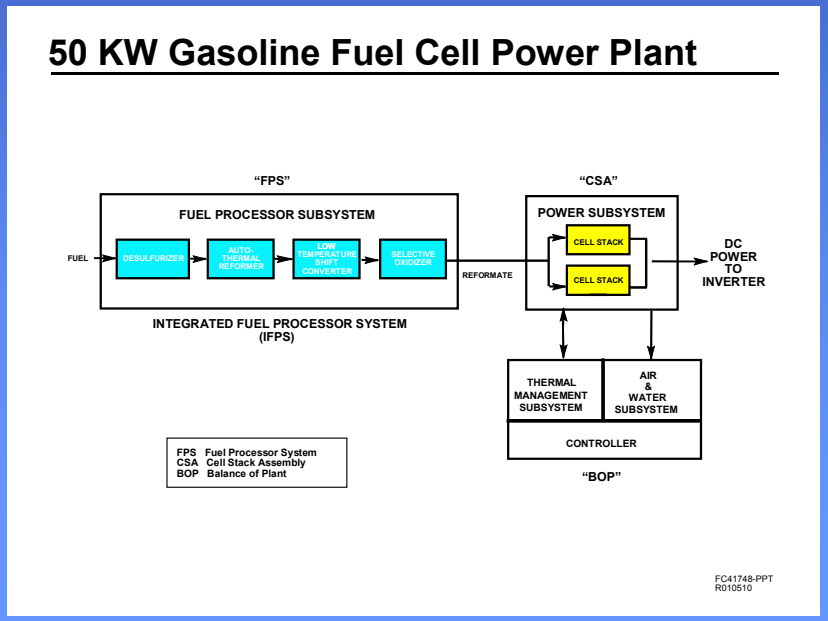


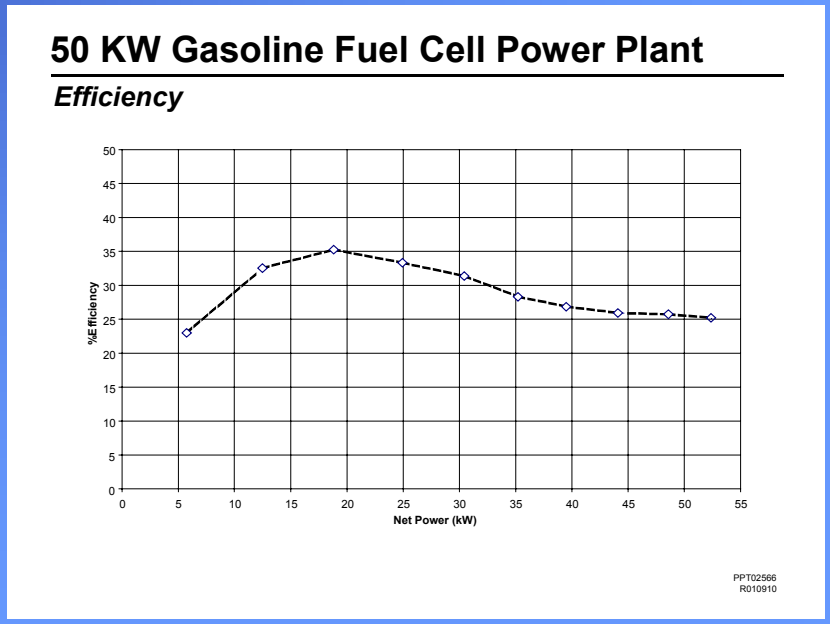


- Fully integrated system
- Ambient pressure

Series 200 Data

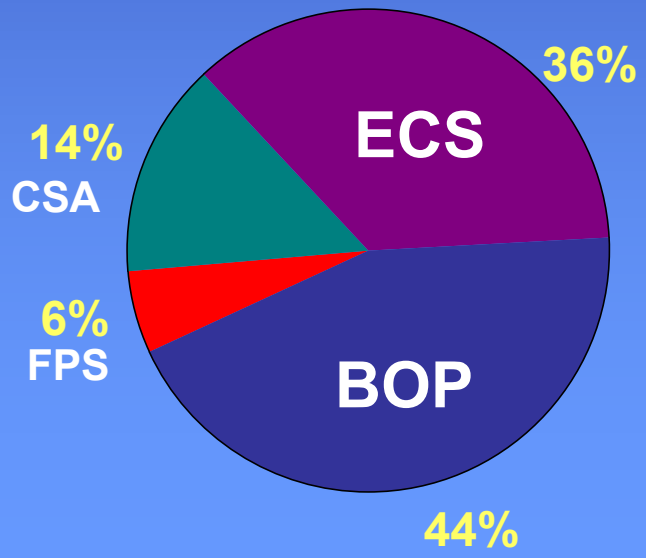
- ~45 minute start time
- Efficiency 25% at full power (53 kW)
- Volume ~ 870L





Next Generation Series 300

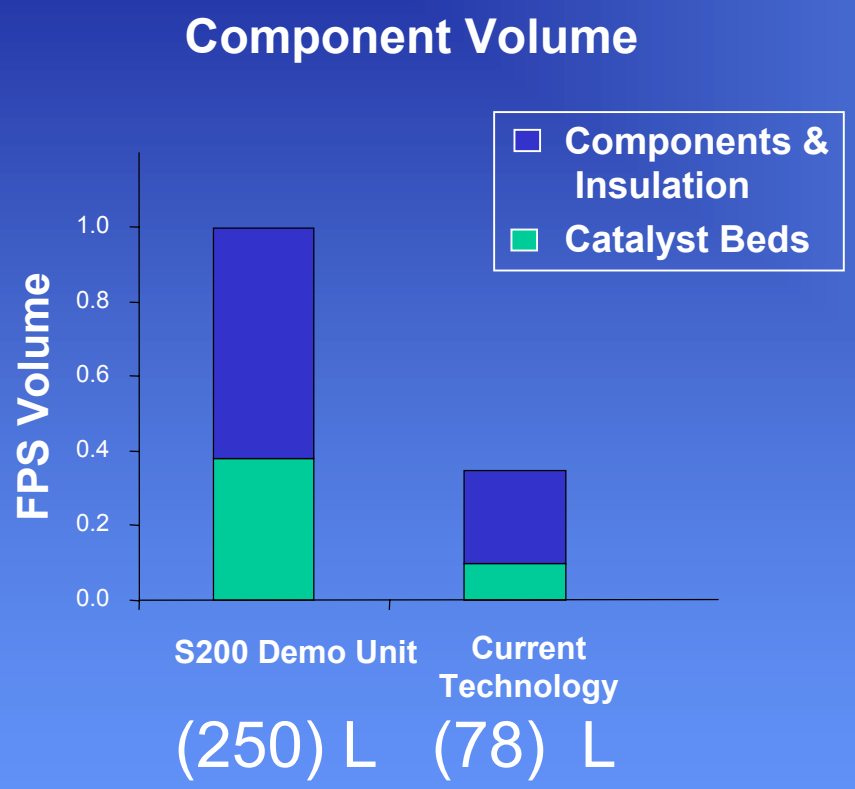
- Focus on Fuel Processor System (FPS) technology, catalyst development
- Start time
- FPS volume
- Two step approach, Integrated FPS (FP1) and Integrated power plant (PP1R)

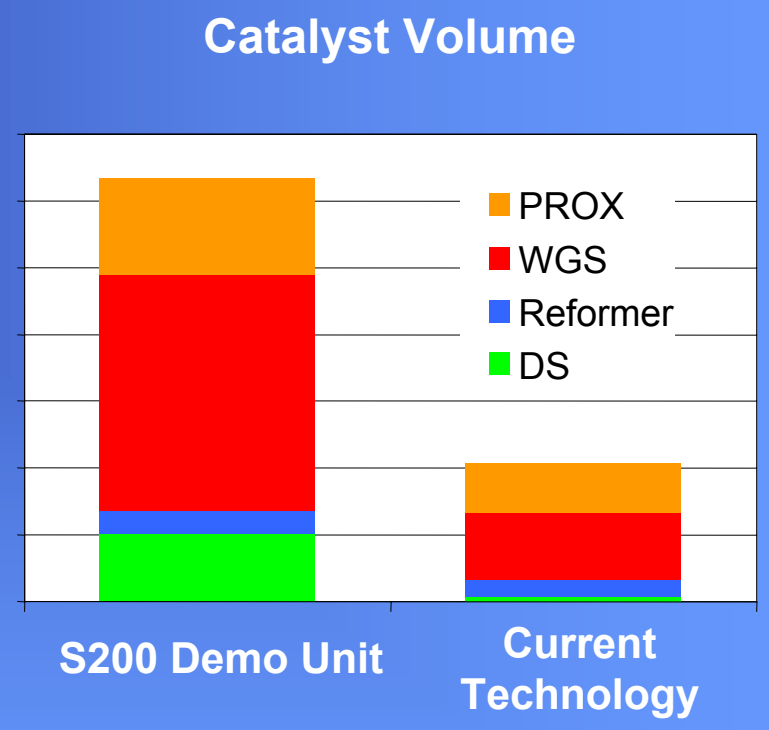


FP1

FPS

Improvements in FPS Volume



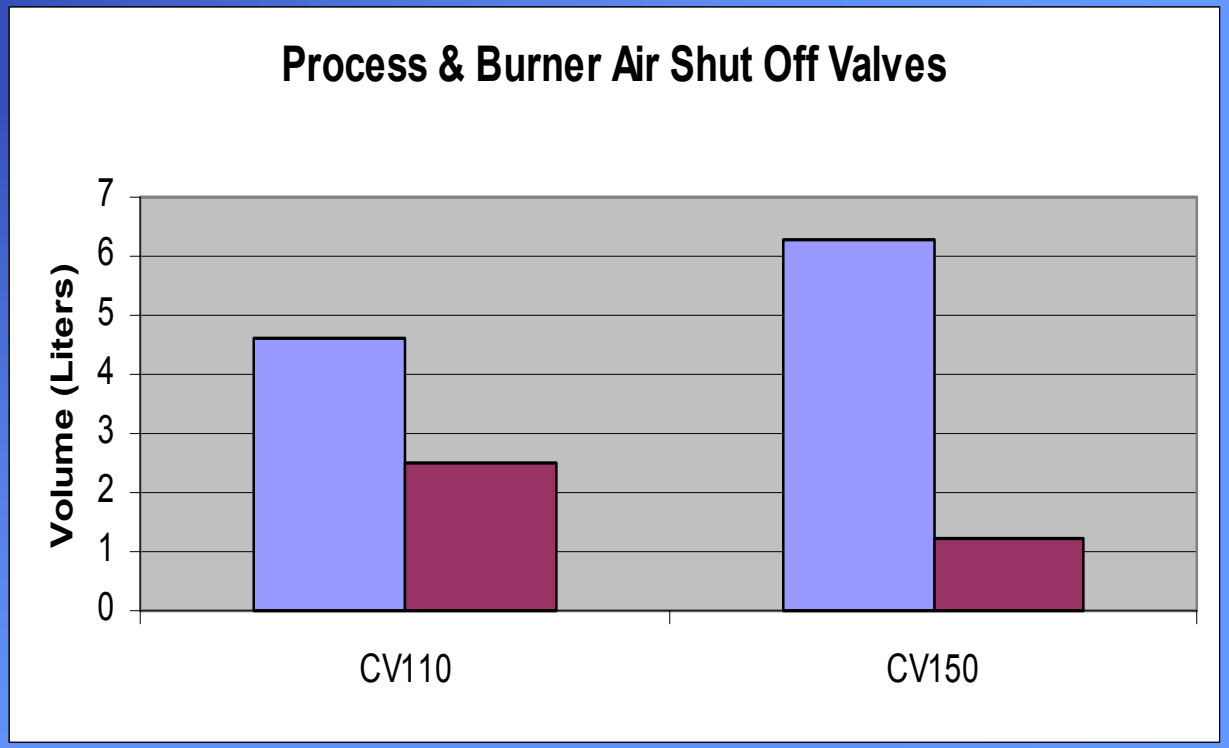


CPO Based FPS

- Benefits
  - No steam generator (smaller)
  - Fuel flexibility (Low sulfur gasoline, naphtha, diesel, F-T diesel, CNG, ethanol…)
  - Reformer durability on CA RFG II / III gasoline (desulfurized by UTC FC)
  - Faster start (lower mass) than ATR

- Start Time: 10 sec CPO, ~ 5 min FPS
- Volume: 78L Packaged (150 kW H2)
- Emissions: SULEV
- H_2 Production efficiency: 75% FPS, >80% CPO

BOP Volume Reduction Opportunities



Series 300 Schedule

FPS Delivery 9/16

Start FP1Test 12/4

Complete FP1 Test 5/30

Complete PPIR Power Plant

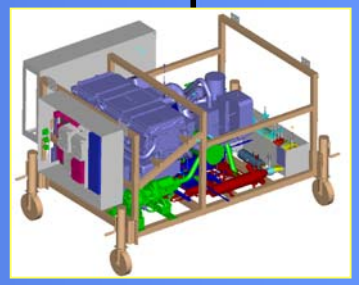
PPIR Test 10/1

Complete Teardown

2002

2003

2004



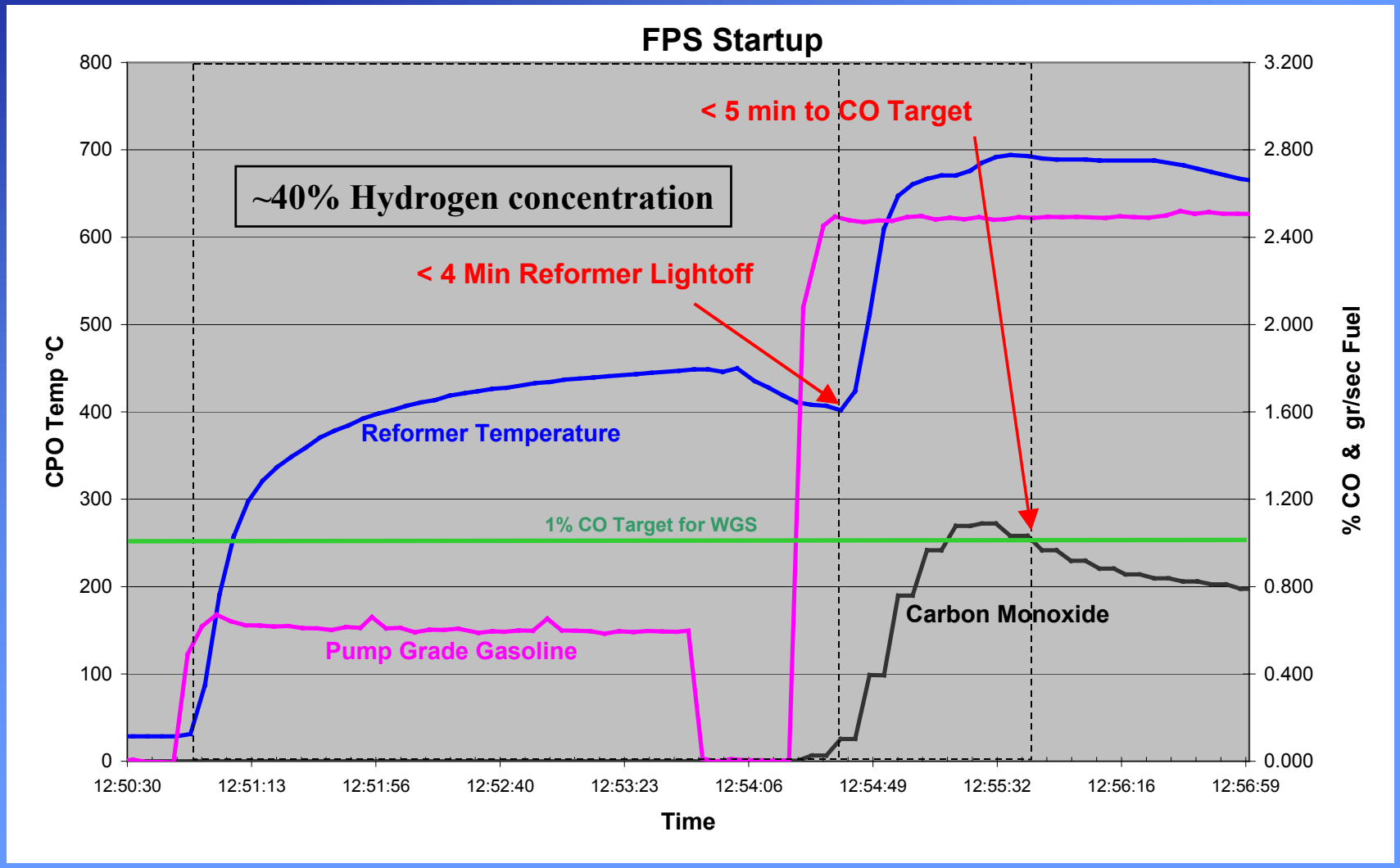
Program Goals

2001	Down select optimum system
2002/2003	FP1-Start Time, Controllability & Volume
2003/2004	PP1R-Weight & Volume, Start Time Controllability, Emissions & Efficiency

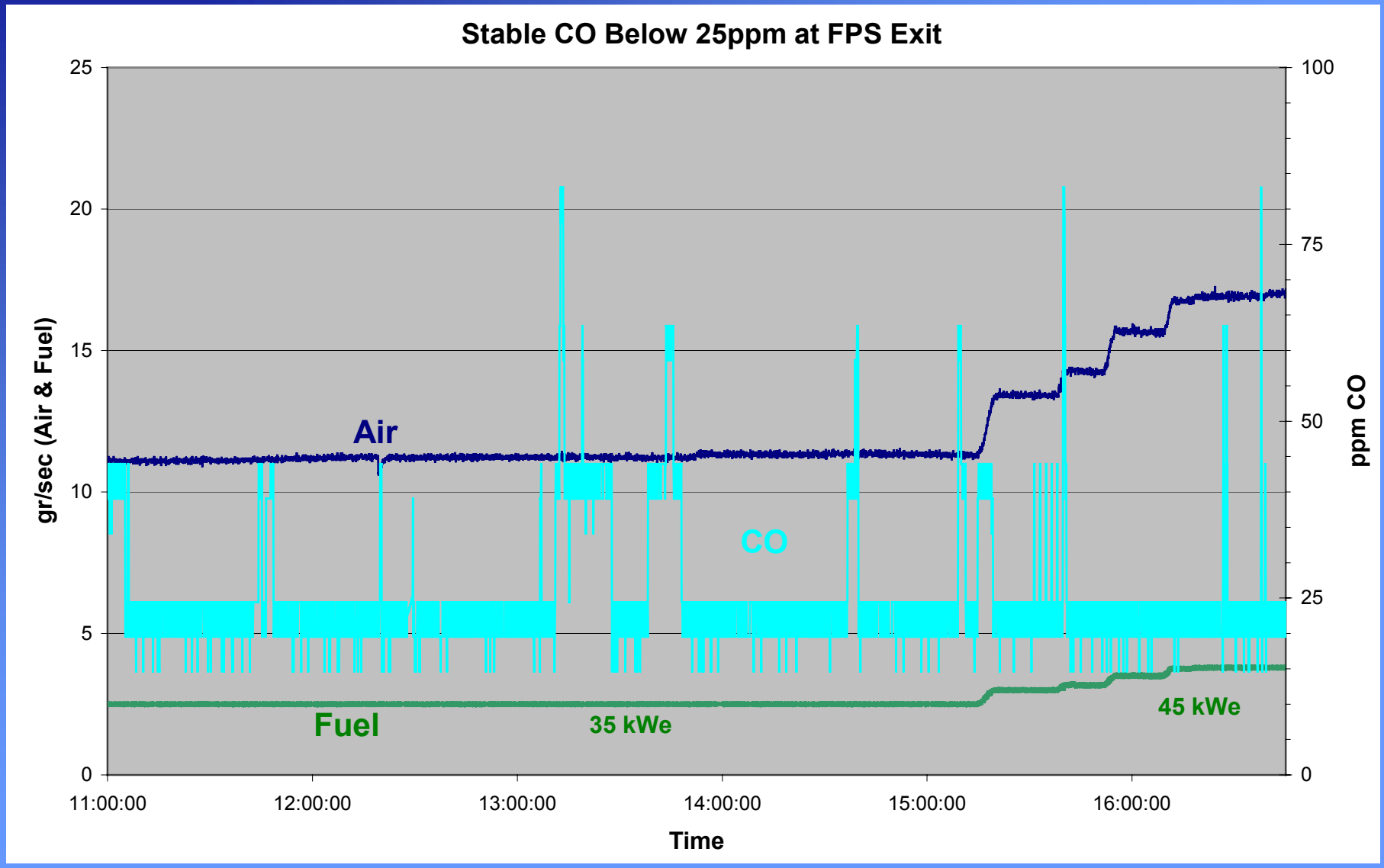
Summary of FP1 Performance Data vs. Target

	Target	Test Data
• FPS Volume, liters	75	78
• Heat up time, s	165	290
• Transient (s for 20-90%)	10	200 (prelim)
• Number of start/stops	500	55
• Duration of operation (total hrs)	2000	150 hrs
– Longest single run, hrs		10 hrs
• Range of equivalent power, kWe	10-50	24-45
• LHV efficiency, % at rated	≥75	TBD
LHV efficiency, % below rated	≥70	TBD
• Emissions (ppmvw)		
– Start (NMHC, CO, NOx)	< 34, 1791, 21	TBD
– Run (NMHC, CO, NOx, CH4)	< 22, 15, 1.6, 700	TBD
– Transient (CO, NH4, Aromatics)	< 100	TBD

FP1 Startup Data



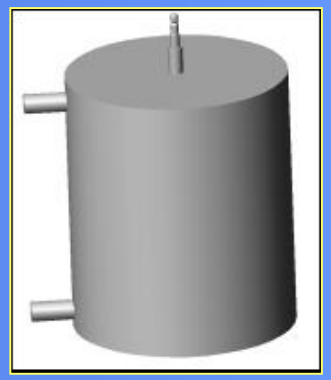
FP1 CO Data


Stable CO Below 25ppm at FPS Exit
gr/sec (Air & Fuel)
ppm CO
Air
CO
Fuel
35 kWe
45 kWe
Time
25
20
15
10
5
0
100
75
50
25
0
11:00:00
12:00:00
13:00:00
14:00:00
15:00:00
16:00:00

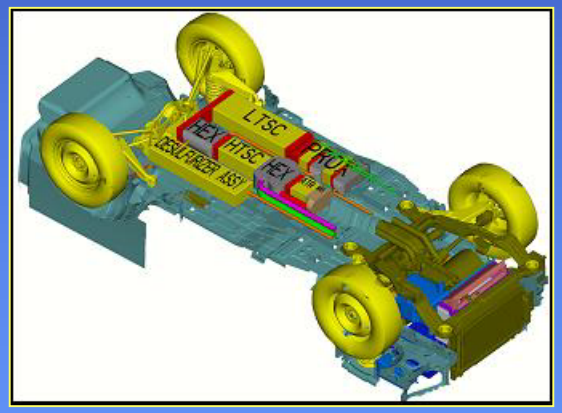
Fuel Cell Power System for Transportation – Gasoline Reformer

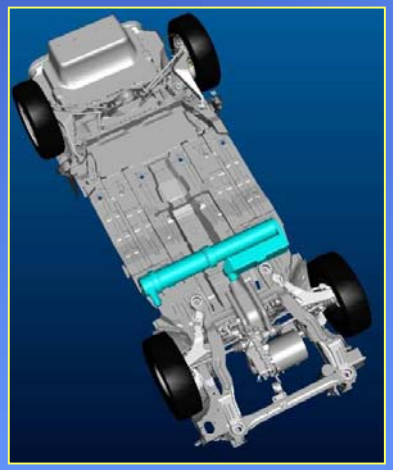
ATR

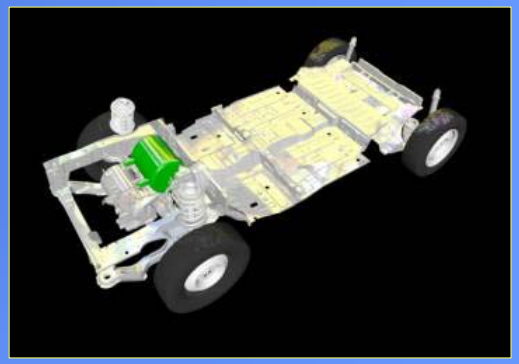
Current FPS



Next generation FPS







- 250 L
- 45 min start

- 78 L
- 4 min start

Goal

- 35 L
- 30 sec start

Summary

- Encouraging results achieved to date
- Complete testing of FP1 to document baseline
- Build FP1 into full power plant with UTC FC PEM Fuel Cell
- Test Power Plant

For More Information

Michael G. Tosca
Program Manager, Automotive

UTC Fuel Cells
A United Technologies Company

UTC Fuel Cells
195 Governor's Highway
South Windsor, Connecticut 06074
(860) 727-7324 Fax: (860) 727-2750
E-mail: Mike.Tosca@UTCFuelCells.com
www.utcfuelcells.com

UTC Power
A United Technologies Company

CATERPILLAR®

WHERE THE WORLD TURNS FOR POWER

PEMFC Power System on Ethanol

Caterpillar Inc.

Thomas J. Richards

CATERPILLAR®

WHERE THE WORLD TURNS FOR POWER

NUVERA FUEL CELLS

PEM ETHANOL FUEL CELL

DOE Hydrogen & Fuel Cells 2003 Annual Merit Review

21 May 2003

CAT®

Williams

PEM ETHANOL FUEL CELL

In 2003, a 10-15 kW stationary PEM fuel cell system will be field tested for 4000 hours at the Williams Bioenergy's ethanol production facility in Pekin, Illinois.

The unit will be powered by corn-based ethanol and will produce AC power for the local grid.

The program examines the durability of a PEM based fuel cell system while operating on ethanol - a renewable fuel.

The program is a consortium among Nuvera, Caterpillar, and Williams Bioenergy with funding from DOE and the State of Illinois.

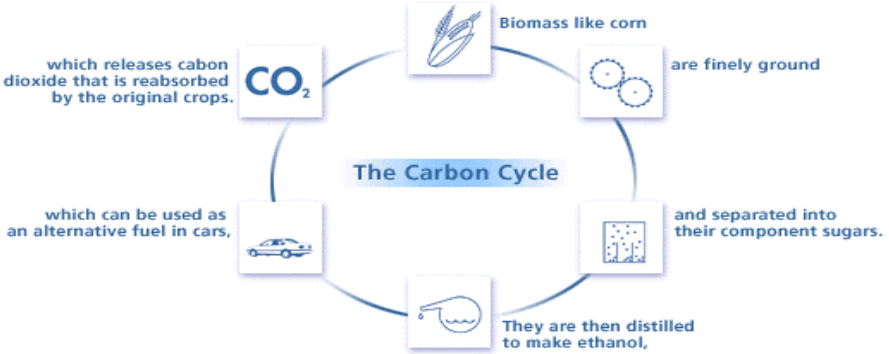
Ethanol: A Renewable

Economy

The U.S. ethanol industry has grown to over 2.3 billion gallons of production capacity, with plants located in 19 states.

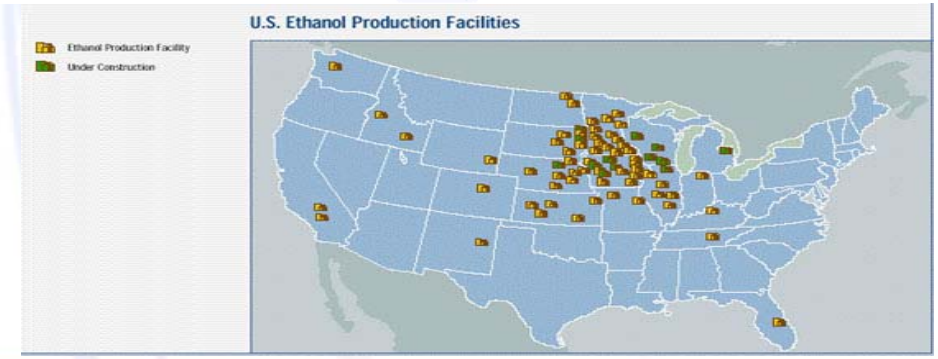
Emission

The ethanol production process represents a carbon cycle, where plants absorb carbon dioxide during growth, "recycling" the carbon released during fuel combustion.



Other Reasons

- Helping the US Energy Balance
- Fighting the Carbon Cycle creation
- Economy boost to Rural America
- State Visibility (Midwest)
- Fuel Choice for Fuel Cells???



Program Overview

Program Partners

- Nuvera Fuel Cells
- Williams Bio-Energy

Program Sponsors

- Department of Energy
- IL Department of Commerce & Community Affairs

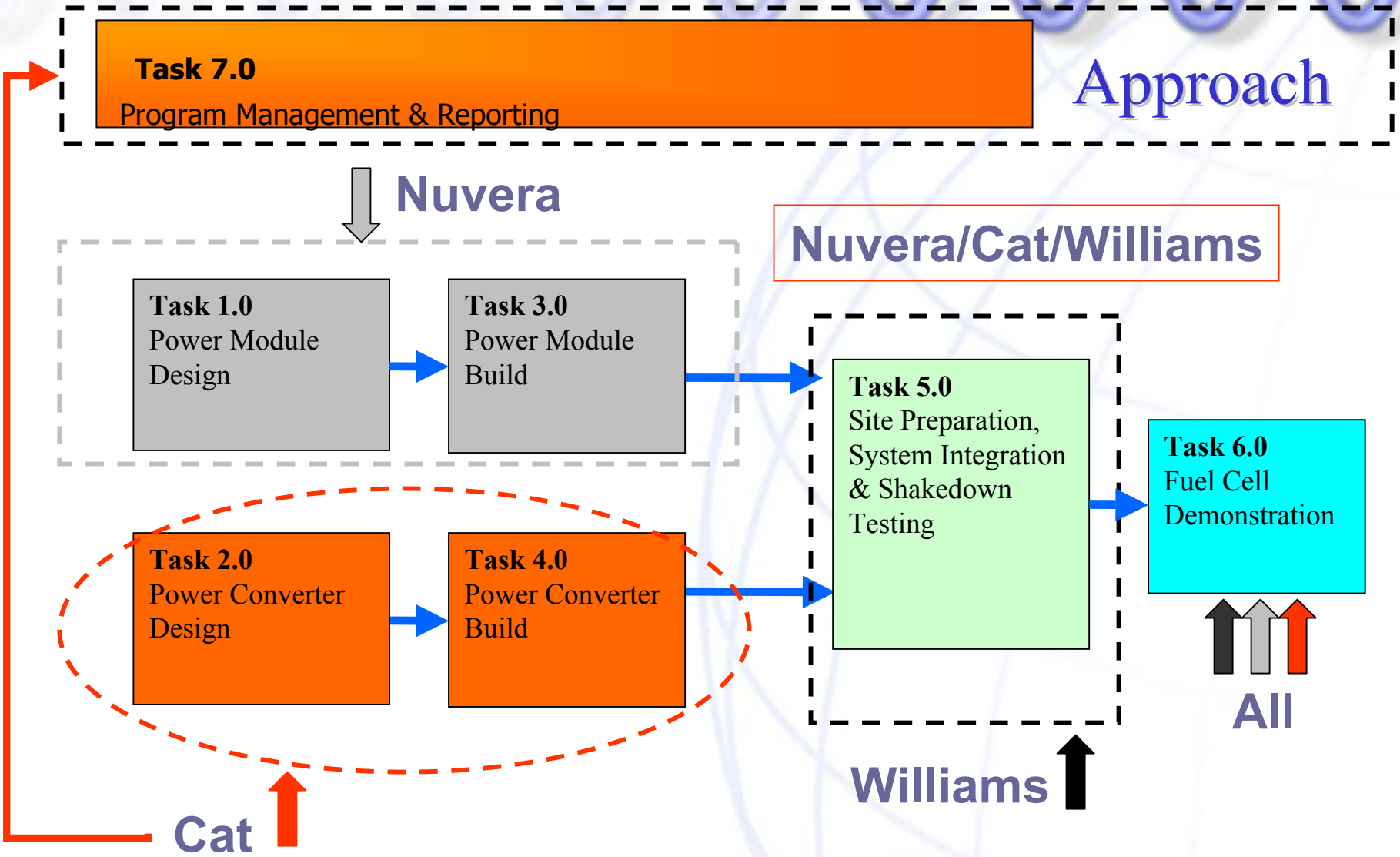
Program Objectives

- 2-Year Cooperative Program to:
  - Design/Fabricate/Test an Ethanol-based PEM Fuel Cell
  - Demonstrate Performance and Durability: 4000 hours
  - Remove Technical Uncertainties
  - Understand Correlation and Reduce Gaps between Stationary and Transportation Application
  - Data Collection to Evaluate Economic Feasibility
  - Assess Commercial Viability of Total System

Program Objectives

- Integrated PEM Fuel Cell System
  - Ethanol based Power Plant
  - 10-15 kW
  - 3-Phase 120/208 V_{AC} @ 60 Hz
  - Greater than 25% Target Efficiency
  - Operability & Performance
- <u>Demonstrate 4,000 Durability</u>
- Data Gathering as Baseline for Feasibility
  - Economic Study
  - Transportation & Stationary Correlation

Approach


Task 7.0
Program Management & Reporting
Nuvera
Nuvera/Cat/Williams
Task 1.0
Power Module
Design
Task 3.0
Power Module
Build
Task 5.0
Site Preparation,
System Integration
& Shakedown
Testing
Task 6.0
Fuel Cell
Demonstration
Task 2.0
Power Converter
Design
Task 4.0
Power Converter
Build
All
Williams
Cat

Program Timeline (2 Years) June 2002 to June 2004

Description	1Q 02	2Q 02	3Q 02	4Q 02	1Q 03	2Q 03	3Q 03	4Q 03	1Q 04	2Q 04	3Q 04	4Q 04
PEM Ethanol Fuel Cell		√	√	√	√	→	→	→	→	→		
Power Converter Design	√	√	√	√	√							
Power Convert Procurement		√	√	√								
Assemble / Development			√	√	√							
Validate				√	√	→						
Power Module Concept	√	√										
Pow Module System Design		√	√									
Pow Mod System Build			√	√	√	→						
Site Preparation		√	√	√	√							
Field Demonstration							→	→	→			
Program Management & Reporting	√	√	√	√	√	→	→	→	→	→		
Milestones				Δ1		Δ2	Δ3		Δ4	Δ5		

Major Milestones

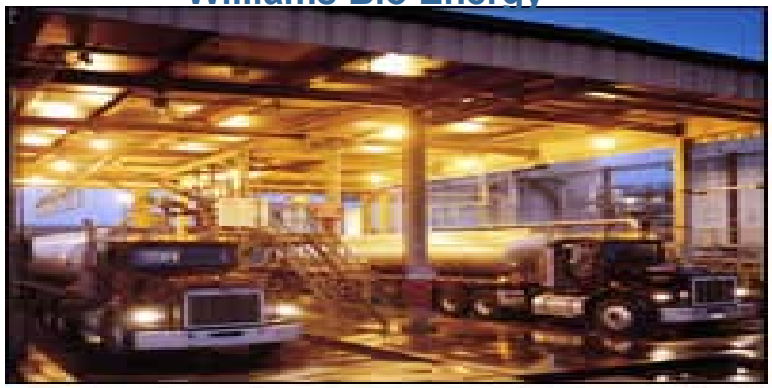
Milestone	Description	Date / Status
Δ1	Final Design Review	November 02 / Complete
Δ2	Component Testing at Rated Power / Site Prep	April 03 / Complete
Δ3	Commence field demo	Q3-03
Δ4	4000 hour Utility Interactive Durability Test	March 04
Δ5	Final Analysis & Report	May 04

Durability Program

- 2-Year Cooperative Program:
  - Design/Fabricate/Test 10-15 kW Ethanol-based PEM Fuel Cell
  - Demonstrate Performance and Durability: 4000 hours
  - Technology and Economic Feasibility Assessment
- Ready to test in June 03

CATERPILLAR

Williams Bio Energy



NUVERA

Ethanol Power Module (Field Unit)

Ethanol Power Module (Field Unit)

Williams' New Demo Facility

- Dimensions (mm):
  - 1321 H x 1372 W x 762 D (Power Module)
  - 304 H X 610 W X 914 D (Power Converter)
- DC Output Voltage (V): 55 to 100
- Startup Time (minutes): 20-40
- 25 to 90 % Load Response (s): 60

Cat Power Electronics

Accomplishments: Power Module

- ✓ Designed and built a fully integrated power system based on Model B fuel processor for ethanol operation
- ✓ Achieved afterburner free startup
- ✓ Eliminated need for reformate cleanup by eliminating ammonia formation
- ✓ Created new, robust control strategy for both reformer and fuel cell sub-systems
- ✓ Field unit demonstrated @ 11 kWe continuous output
- ✓ About 40 hr continuous run on integrated system; 125 hours total power in the laboratory

Power Converter Accomplishments

Item	Target	Actual
Resistive load	15 kW	16 kW
Line interactive	15 KW input	15 kW input
Acceptance test	100 hour	24 hours
Efficiency	93%	90%

Accomplishments: Test Site

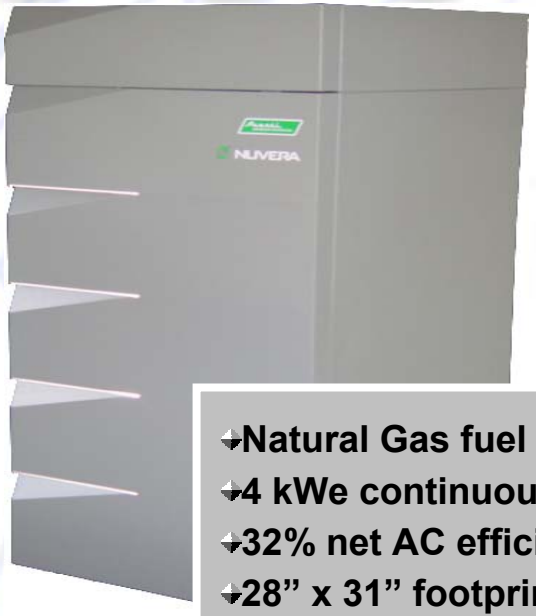
- ✓ Utility interactive
- ✓ Ethanol availability
- ✓ Data acquisition system
- ✓ Remote monitoring, data backup & internet view
- ✓ Visitor parking & observation amenities
- ✓ Hazardous operations procedures in place

Acceptance Test Criteria

Test Duration	Condition	Hardware	Test Type / Location
1 x 24 hour continuous	≥15 kWe	Cat power converter	Factory acceptance test/ Caterpillar
3 x 24 hour continuous	≥10 kWe	Nuvera power module	Factory acceptance test/ Nuvera
500 hour combined continuous + interrupted	Any power	Nuvera power module	Factory acceptance test/ Nuvera
24 hour continuous	≥10 kWe	Power module + power converter	Factory acceptance test/ Nuvera
1 x 8 hour continuous	Max flows	Williams Utilities (fuel / water / air)	Factory acceptance test/ Williams
24 hour continuous	≥10 kWe	Power module + power converter	Site acceptance test / Williams

Interactions

- ✓ Leverage Cat's Fuel cell commercial program in power electronics/packaging
- ✓ Leverage underground mining machine fuel cell program
- ✓ Improved Cat electronics platforms and common design to DG equipment
- ✓ Extracting lessons and processes used for New Product Introduction (NPI) in commercial applications
- ✓ Cat's life cycle cost analysis pro-format will be used in economic feasibility
- ✓ Constant communication with Nuvera's commercial 4kW natural gas power system program and individuals



- Natural Gas fuel
- 4 kWe continuous
- 32% net AC efficiency
- 28" x 31" footprint

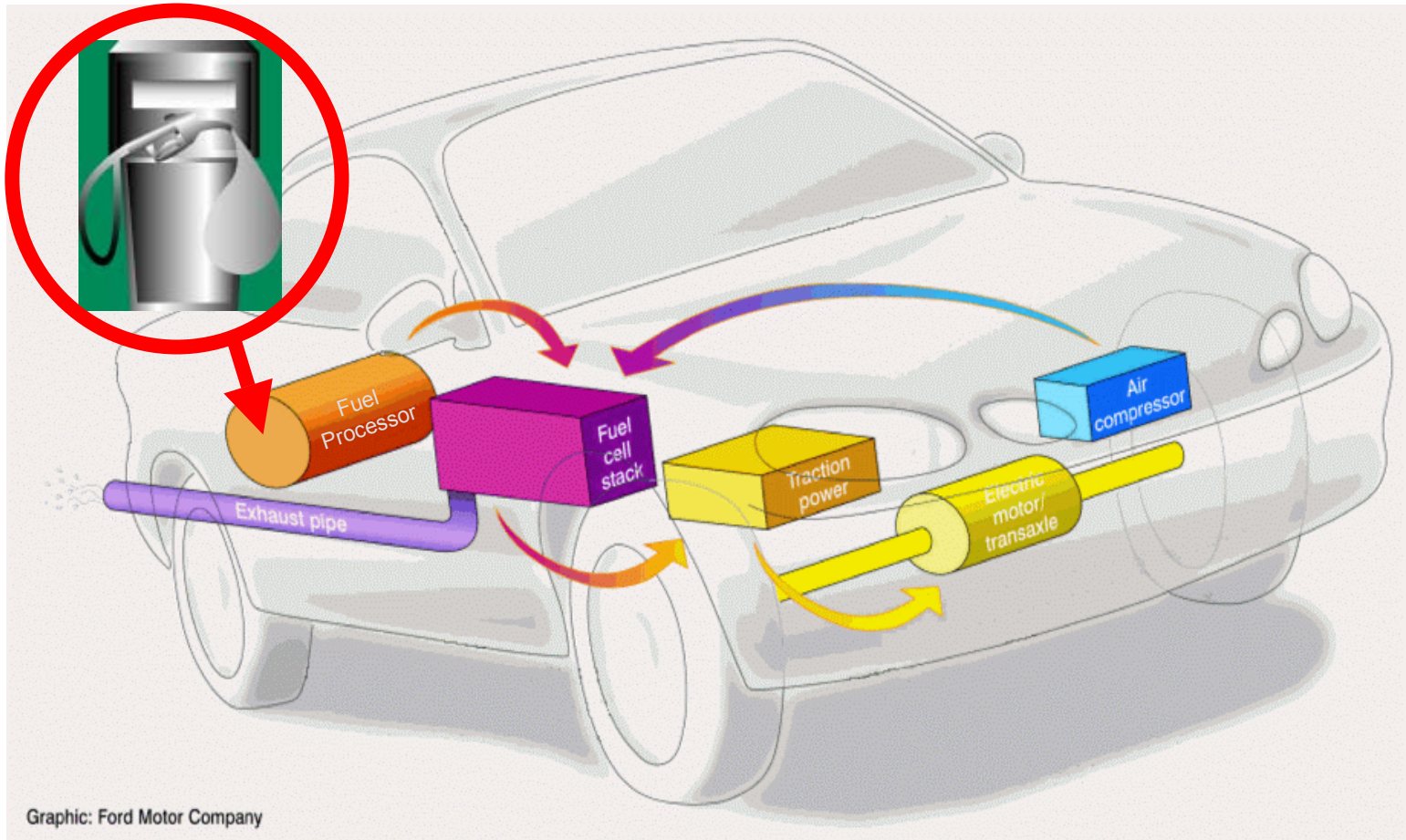
Contacts

Ahmed Amrani (Primary Contact), Thomas Richards
Caterpillar Inc.
Technical Center, P.O. Box 1875
Peoria, Illinois 61656 – 1875
(309) 578 3913, Fax: (309) 578 6113, E-mail: Amrani_Ahmed@cat.com

DOE Technology Development Manager: Kathi Epping
(202) 586 4725, Fax (202) 586 9811, E-mail: Kathi.Epping@ee.doe.gov

ANL Technical Advisor: William M. Swift
(630) 252-5964, Fax: (630) 972 4473, E-mail: Swift@cmt.anl.Gov

Fuels Effects



Nancy Garland

Fuel Effects Projects

- Effects of Fuels Constituents on Fuel Processing Catalysts — ANL
- Testing of Fuels in Fuel Cell Reformers — LANL

Effects of Fuel Composition on Fuel Processing

J.P. Kopasz, D. Applegate, L. Miller,
Cecille Rossignol
Argonne National Laboratory

Annual Review

The Hydrogen, Fuel Cells & Infrastructure

Technologies Program

May 19-22, 2003

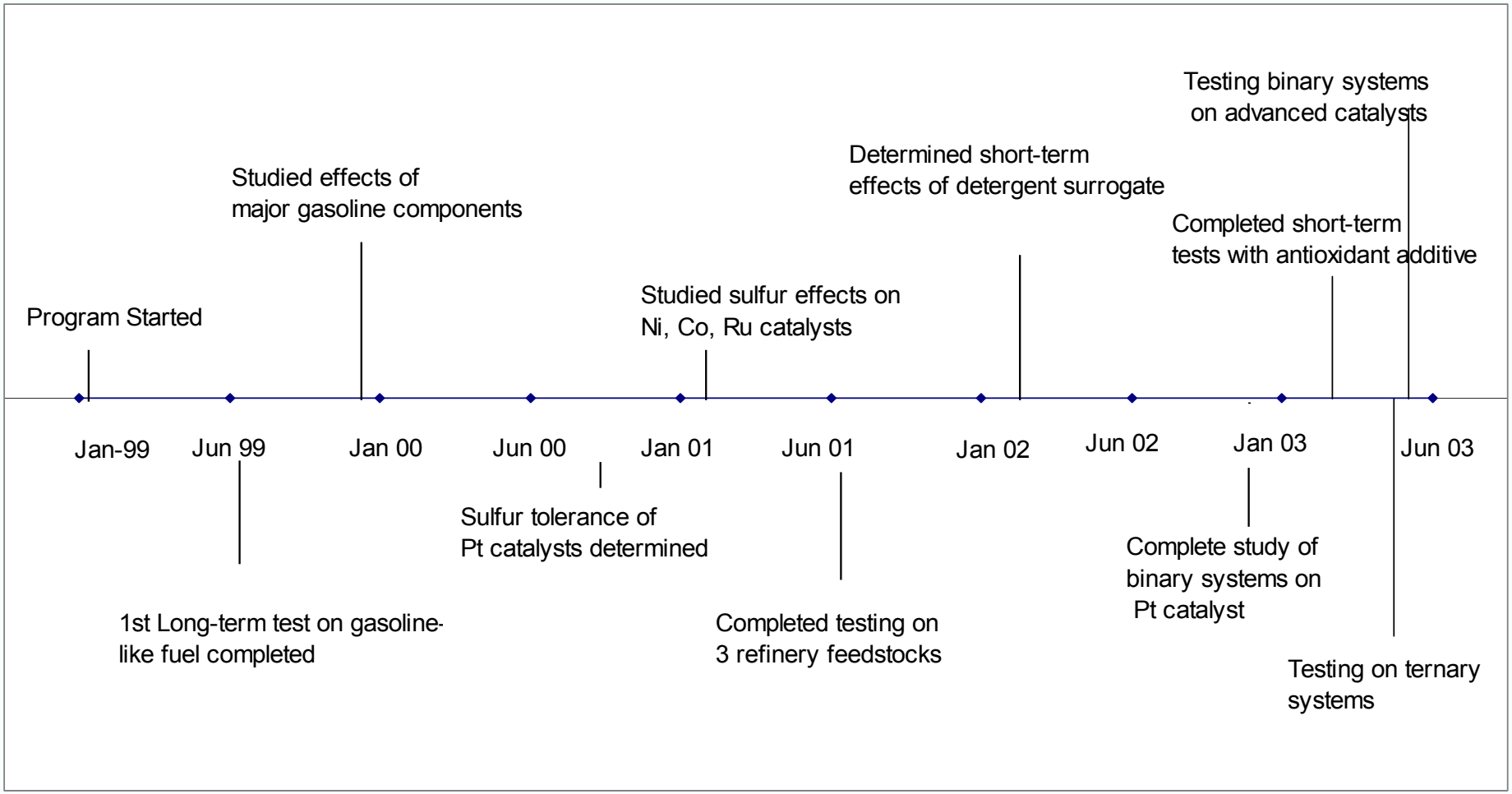
Objective: Evaluate effect of the fuel composition on H_2 yield

- Determine effects of major constituents, additives, and impurities in petroleum fuels on fuel processor performance and durability
- Collaborate with major oil companies for development of future fuels for fuel cells

Fuel composition affects many technical targets/barriers

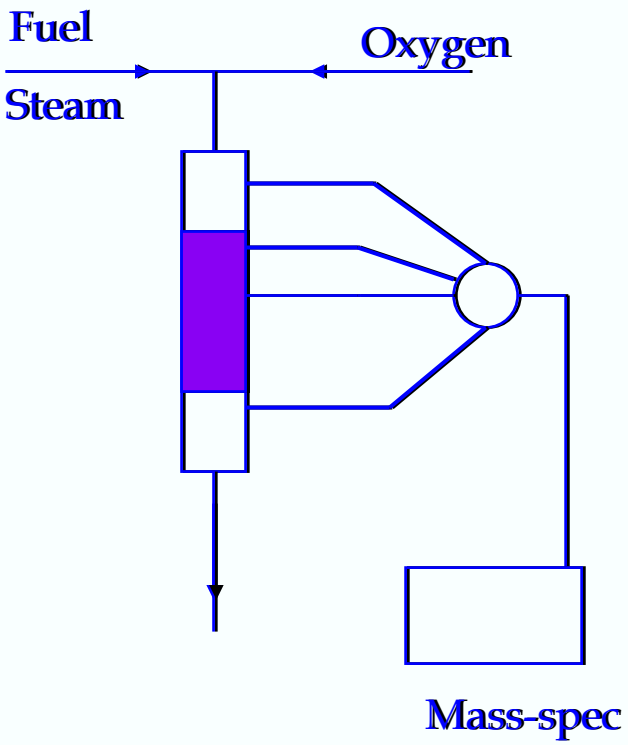
- Fuel processor efficiency (barrier M)
- Processor durability (barrier J)
- Power density
  - Catalyst volume
  - Catalyst weight
- Costs (barrier N)
- Emissions (barrier K)

Timeline


Program Started
Studied effects of
major gasoline components
Studied sulfur effects on
Ni, Co, Ru catalysts
Determined short-term
effects of detergent surrogate
Completed short-term
tests with antioxidant additive
Testing binary systems
on advanced catalysts
Jan-99
Jun 99
Jan 00
Jun 00
Jan 01
Jun 01
Jan 02
Jun 02
Jan 03
Jun 03
1st Long-term test on gasoline-
like fuel completed
Sulfur tolerance of
Pt catalysts determined
Completed testing on
3 refinery feedstocks
Complete study of
binary systems on
Pt catalyst
Testing on ternary
systems

Experimental approach

- Determine product gas composition dependence on temperature and space velocity using a microreactor (relates to targets for reforming efficiency, and GHSV)
  - test minor components, additives, and impurities as isooctane solutions
  - test blends of fuel components
  - test real-world fuels from refineries
- Long-term testing (1000h)
  - determine poisoning, long-term degradation effects

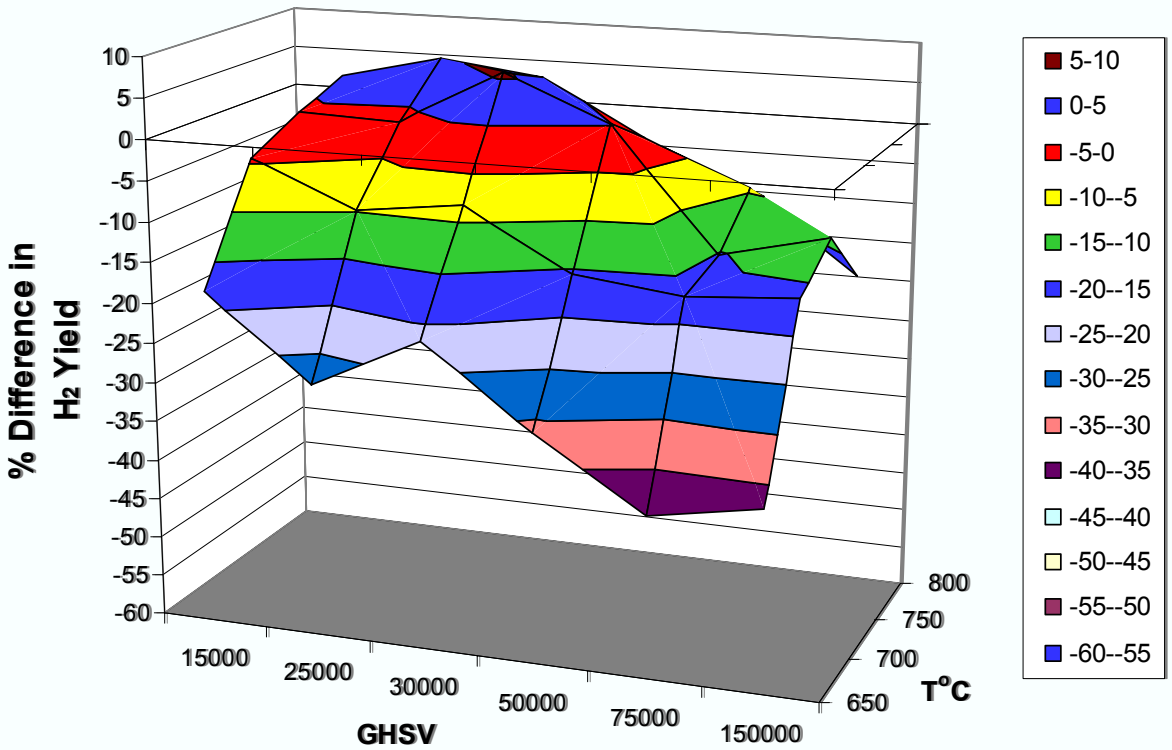


Additive and impurity studies

- Phenol used as surrogate for hindered-phenol class of antioxidants
- Ethanol used as oxygenate additive
- Pyridine used to investigate effects of N-containing heterocyclic impurities
- Benzothiophene used to investigate S effects
- Held O_2:C ratios constant at 0.42
- Held H_2O:C ratios constant at 1.4
- Varied temperature and GHSV

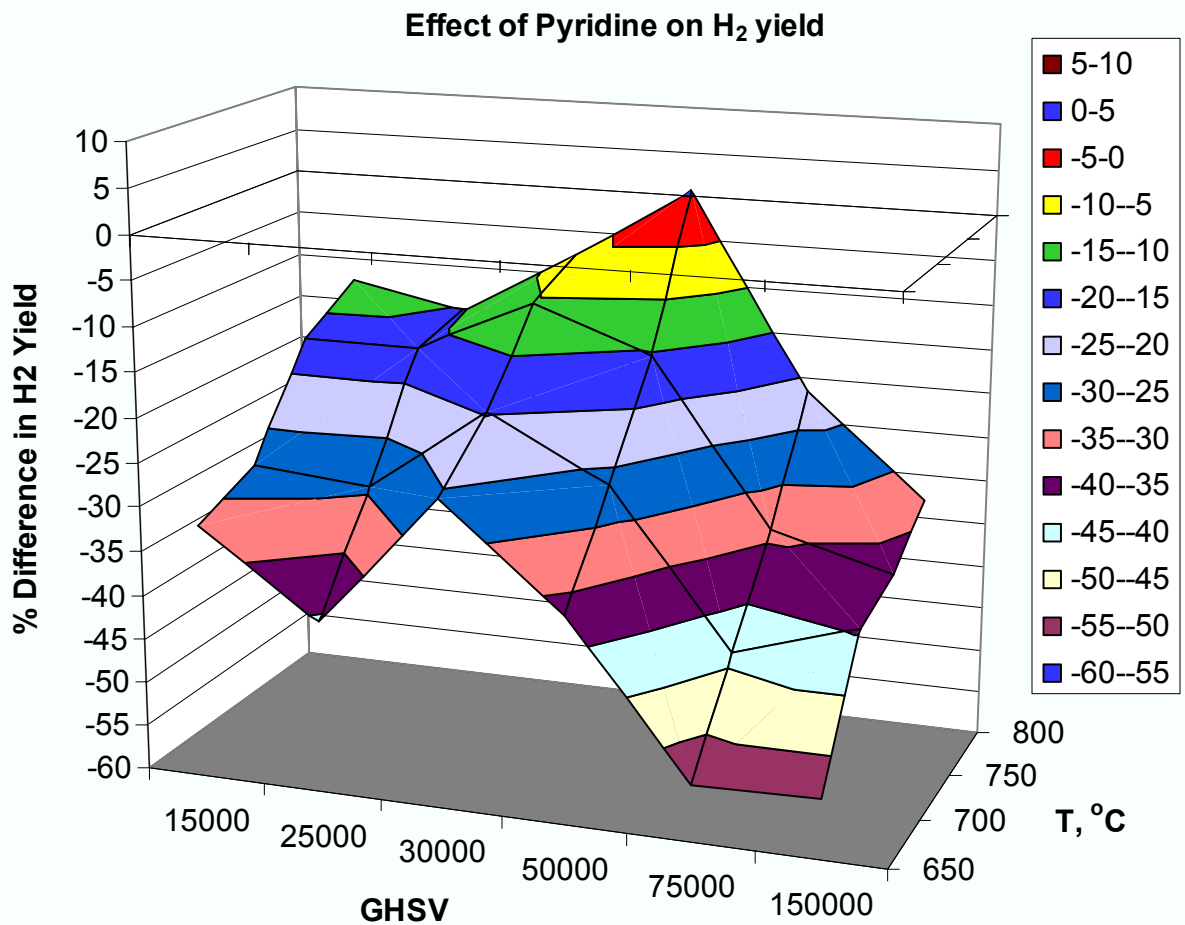
Antioxidant had little effect on H_2 yield from isooctane reforming at high temperature and GHSV < 50,000 h^{-1}

- H_2 yields decreased at high GHSV or low temperature
- Poorer H_2 yields due to increased breakthrough of heavier cracking products



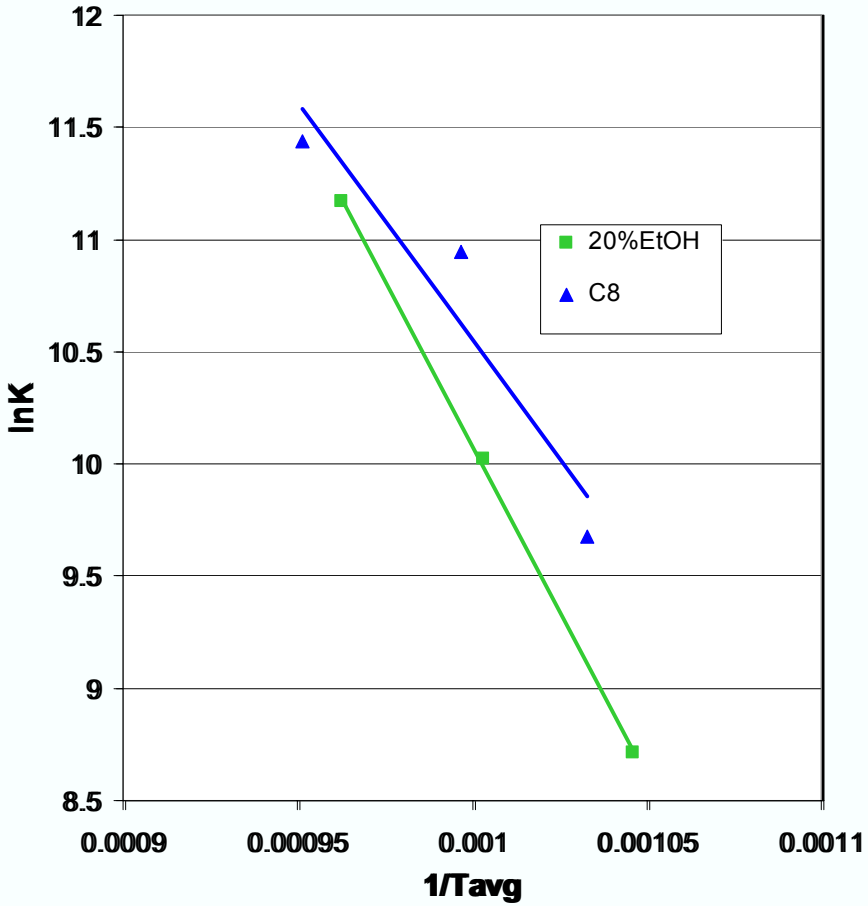
Pyridine decreased H_2 yields substantially under most conditions

- 50 ppm pyridine decreased H_2 yield from isooctane by >10% over most of the parameter space investigated



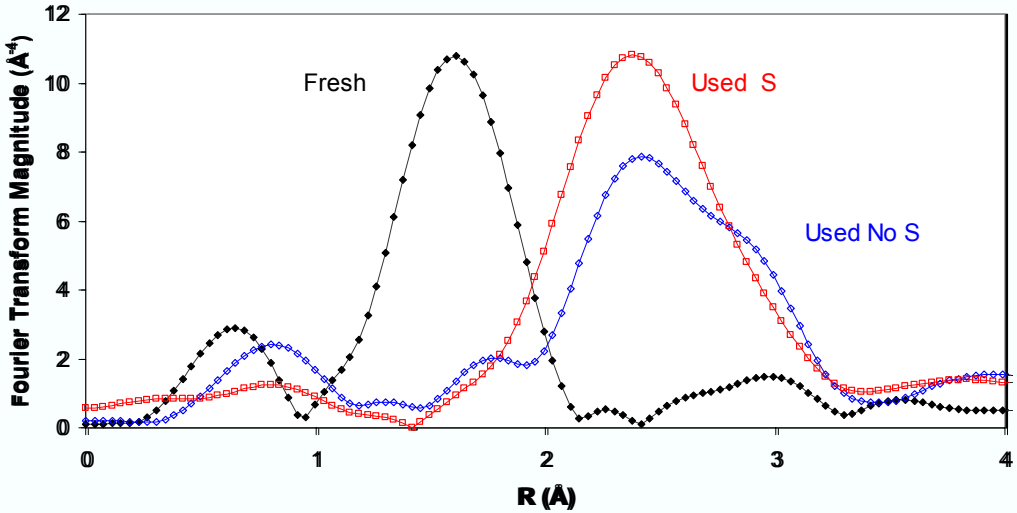
Ethanol decreased the rate of reforming of isooctane at low temperature

- First-order rate constants for decay of C4 species for isooctane-ethanol mixtures are less than those for pure isooctane when corrected to the average catalyst temperature



Long-term tests suggest sulfur affects Pt sintering

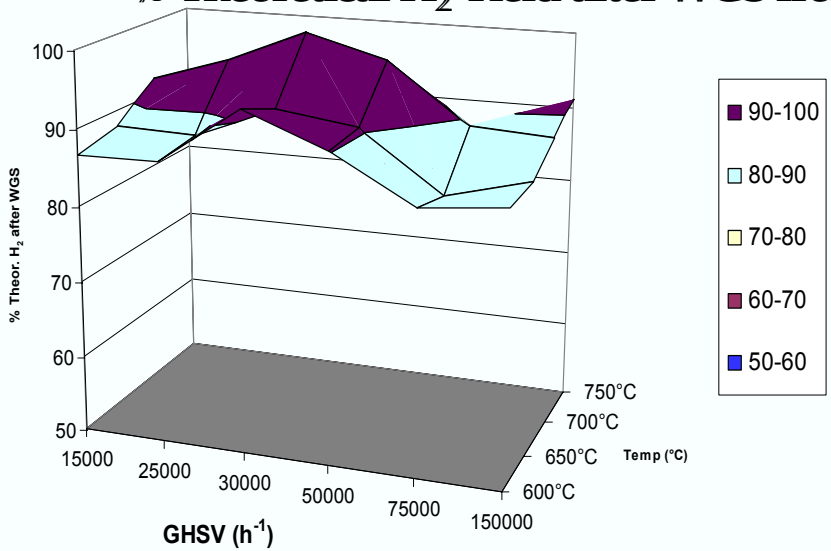
- EXAFS analysis of catalysts after reforming suggests sintering is more prevalent when S is present
  - Fresh sample Pt-O distance and adsorption energy match that for PtO_2
  - Large shift in adsorption energy and Pt-O distance for sample with S indicates no PtO_2 present.
  - Sample with S indicates larger Pt-Pt coordination number



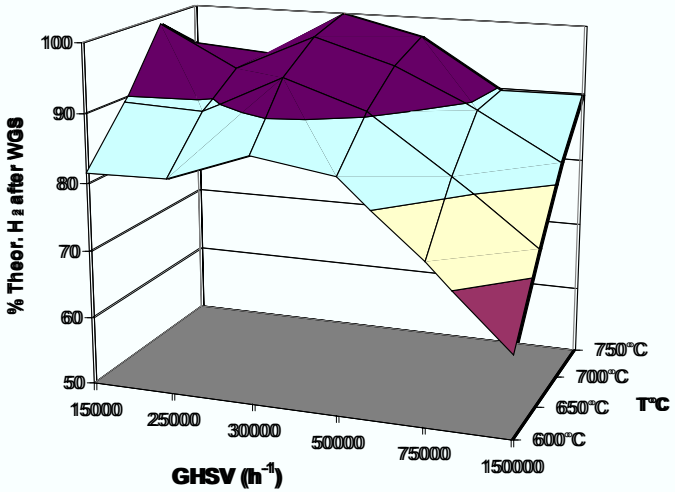
Sample	Shell	N	R (Å)	ΔE (eV)
Fresh	Pt-O	6.0	2.07	0.1
Used - no S	Pt-O	1.0	2.14	0.4
	Pt-Pt	9.6	2.78	0.0
Used - S	Pt-O	1.4	2.29	10.8
	Pt-Pt	12.0	2.76	0.2

Aromatic or naphthenic components decreased H_2 production at high GHSV or low temperature regardless of catalyst

% Theoretical H_2 Yield after WGS from Reforming over Bimetallic Catalyst



Isooctane

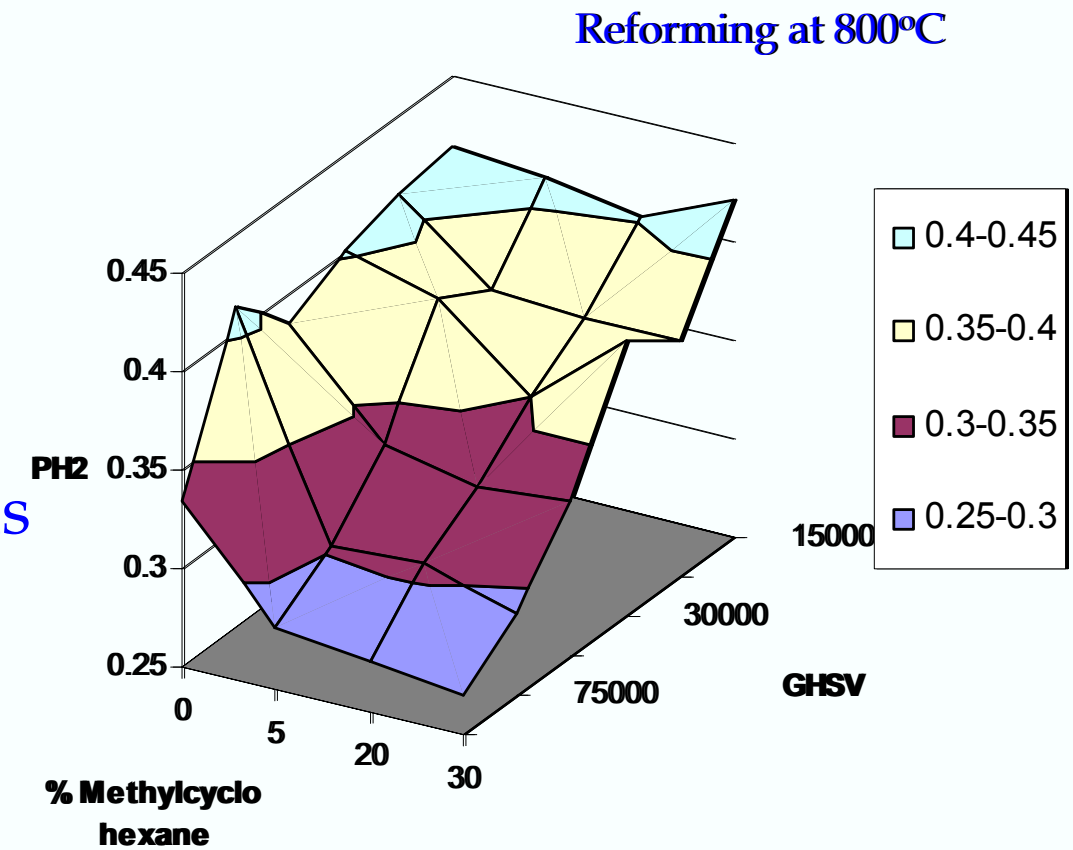


Isooctane+20% Xylene

- Observe decreased H_2 production at low temperature and high GHSV due to slower kinetics for paraffin reforming with mixtures for Pt catalyst and bimetallic catalyst
- Effects are reduced in magnitude and shifted to lower temperature for more active catalysts

Ternary blends indicate complex relationship between composition and performance

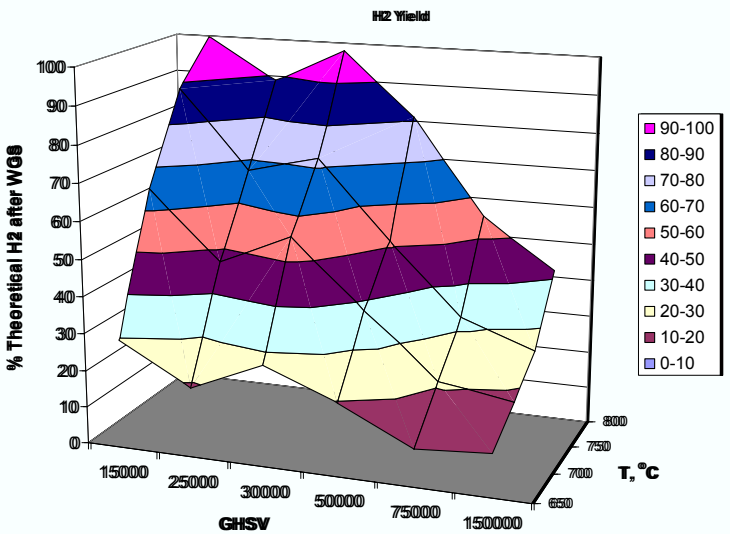
- Dependence of hydrogen yield on methylcyclohexane content in blends of isooctane, xylene, and methylcyclohexane was found to be highly nonlinear



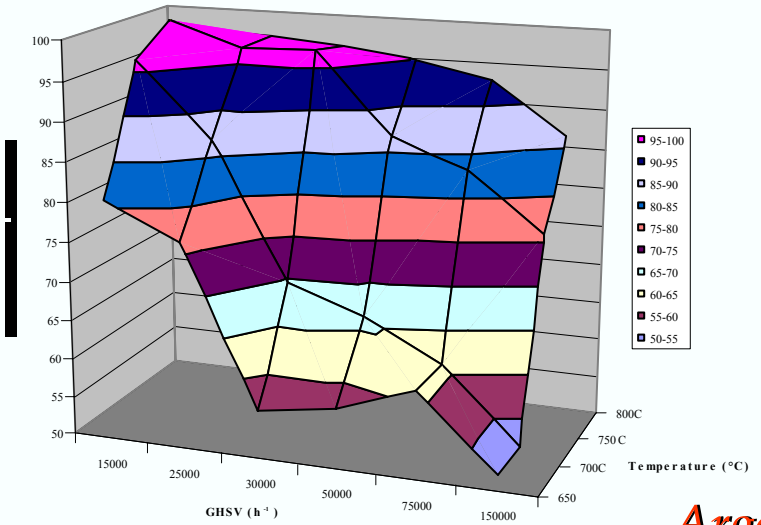
Refinery streams high in naphthenic components reformed poorly

- Naphthenic fuel reforms poorly except at high temperature and low GHSV

Naphthenic Fuel

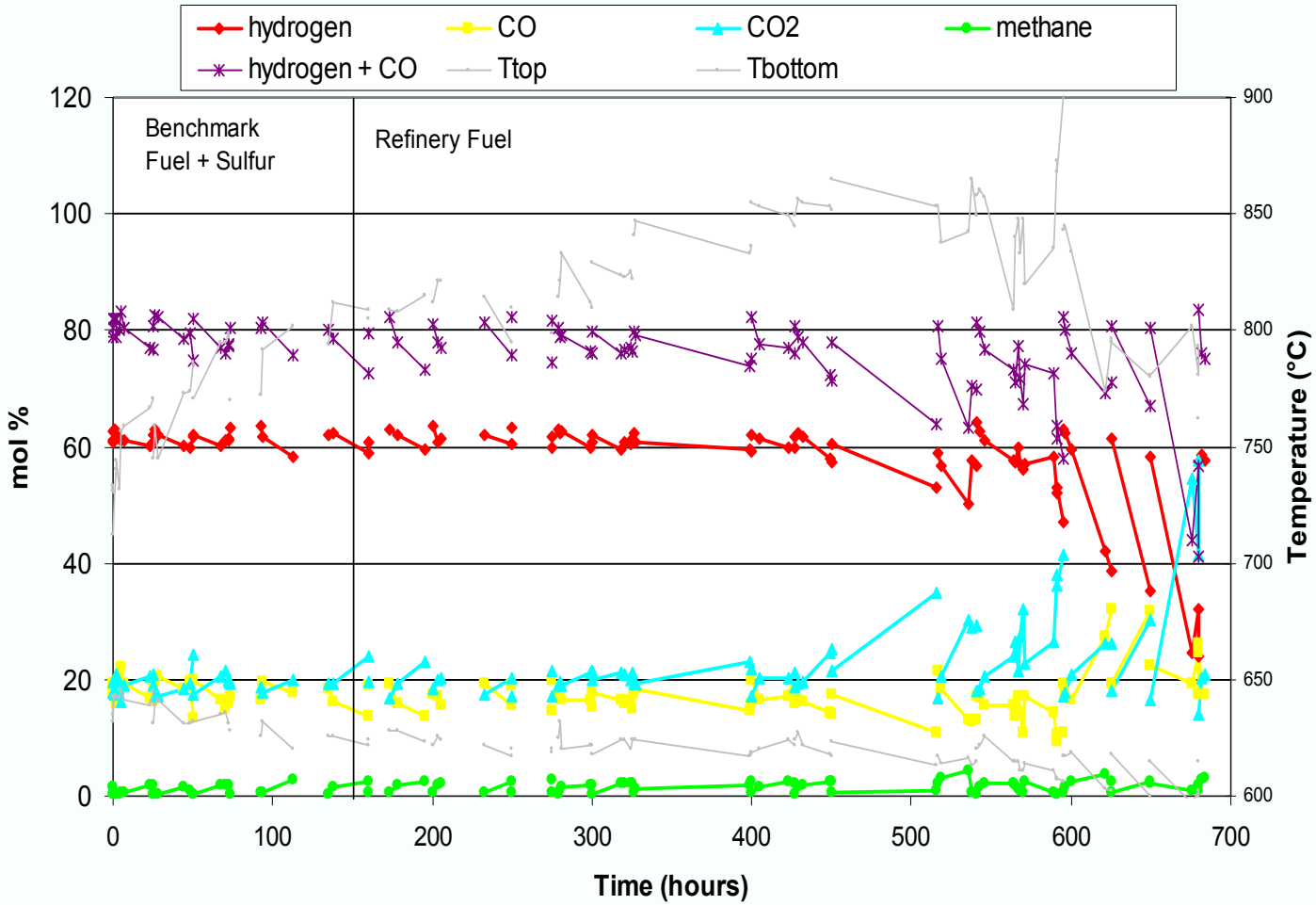


Paraffinic Fuel

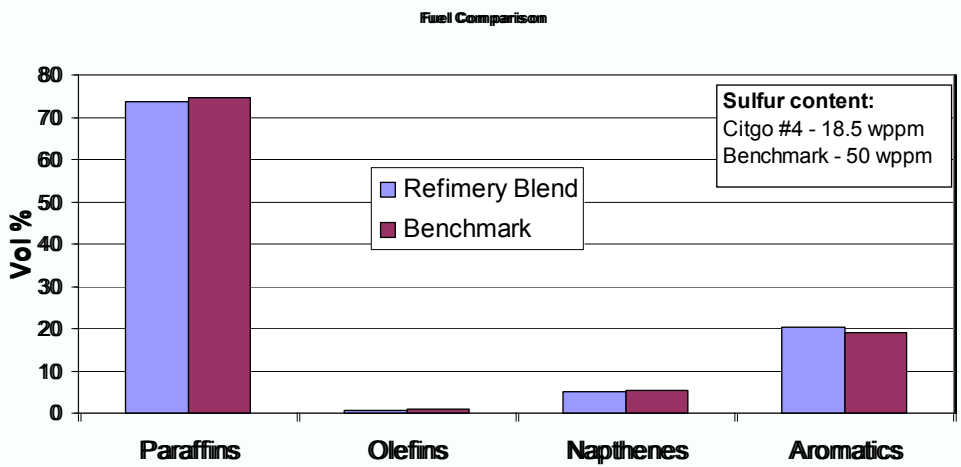


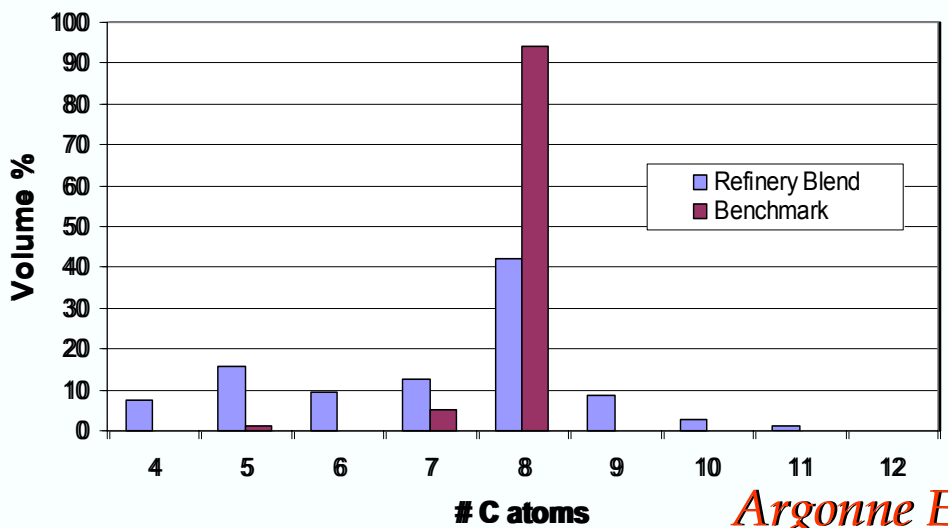
Paraffinic fuel provides good H_2 yield over a wider range of temperature and GHSV

Long-term testing of gasoline shows problems developed after ~600h on-line



Main difference between Refinery blend and benchmark fuel is the size of the chains/rings





Results suggests chain length may affect reforming

Size also impacts transport properties

We are investigating mass transfer effects

Conclusions

- Fuel composition can have substantial effects on reforming
- Fuel components compete for reaction at catalyst sites
- Kinetic rates decreased when more strongly adsorbing species are present

Future Work

- Have initiated testing of gasoline plus commercial additives in engineering scale reactor
  - Liquid injection capability which allows for delivery of high molecular weight polymeric additives
- Investigate reforming of binary/ternary mixtures with advanced catalysts
- Investigate effects of additives with advanced catalysts
- Investigate long-term effects of antioxidant additives and heterocyclic impurities
- Modeling reforming of complex fuel mixtures

Milestones

- Complete long-term testing on detergent surrogates 12/02
  - Completed long-term test using secbutyl amine
- Complete short-term testing of oxygenate and antioxidant additive/surrogate 2/03
  - Completed testing using phenol as antioxidant surrogate
  - Completed testing using ethanol as oxygenate
- Complete testing of binary mixtures on 2 different catalysts 6/03
  - Completed testing on Pt based catalyst
  - Testing on bimetallic catalyst underway

Reviewers Comments

- … final resolution of the detergent issue will require real chemistry and direct injection of liquid fuel into the fuel processor to prevent fractionation and gum formation within vaporizer
  - Have initiated tests in reactor with direct liquid injection capability to test commercial detergent additive package
- Focus on development of fuel additives/compositions that can enhance fuel processor performance
  - We are investigating optimizing fuel composition with our industrial collaborators

Collaborations

- Industrial collaborations with major oil companies
  - PDVSA/Citgo
  - Shell
- Collaborations with catalyst producers
  - Süd-Chemie
- University collaborations
  - Royal Military College of Canada

Testing of Fuels in Fuel Cell Reformers

2003 Hydrogen and Fuel Cells Merit Review Meeting

Rod Borup, Michael Inbody, Jose Tafoya, Dennis Guidry, Will Vigil and Troy Semelsberger

Los Alamos National Laboratory

FY2003: Funding: $1200k (Program Manager Nancy Garland)

divided between:

Fuels (Gasoline Component) Testing - (FY2002 $300k)

Gasoline Reformate and H_2 PEM Durability

Diesel Reforming (SECA program)

Technical Objectives:

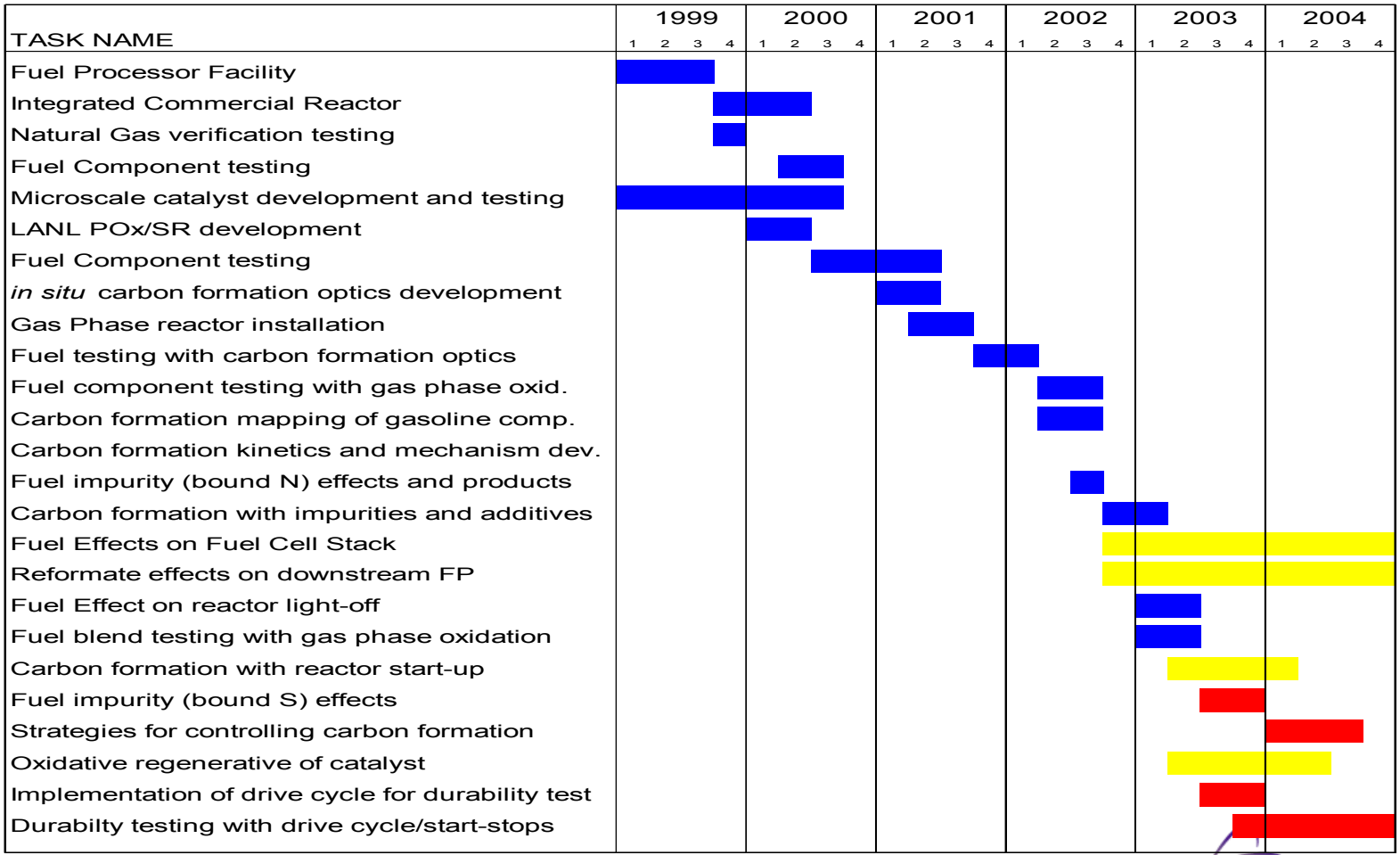
Examine Fuel Effects on Fuel Processor Performance and Durability

- Quantify fuel effects on performance and durability.
  - Fuel component, impurity, additive effects
- Examine fuel effects on fuel processor start-up
- Understand parameters that affect fuel processor and stack lifetime and durability.
  - Fuel processor catalyst stability and activity
  - Evaluate fuel effect and start-up effect on carbon formation
  - Identify chemical species limiting durability
  - Durability testing to evaluate long term performance

- Fuel Processor (& System) Targets:
  - Power density, specific power, cost (catalyst performance and loading)
  - Cycle capability (light-off, durability testing)
  - Start-up Time (Barrier I) (light-off temperature and performance)
  - Energy efficiency (Barrier M) (fuel performance)
- Fuel Processor Barriers:
  - Durability. (Barrier J) (durability and carbon formation studies)
  - Fuel Pr. Start-up/Transient (fuel effect on light-off)
  - Cost. (Barrier N) (effect on catalyst loading and durability)

Fuels Testing Timeline

Project initiated in 1999 / Fuels testing initiated 2000
Part of Multi-year-program-plan Fuels for Fuel Cells (5 yr) program

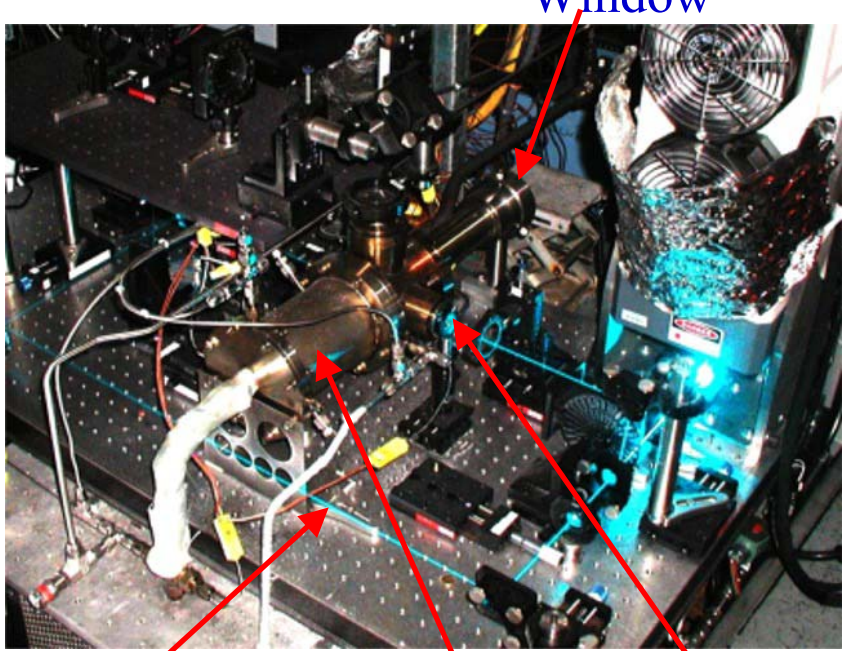


Approach to Fuels Testing

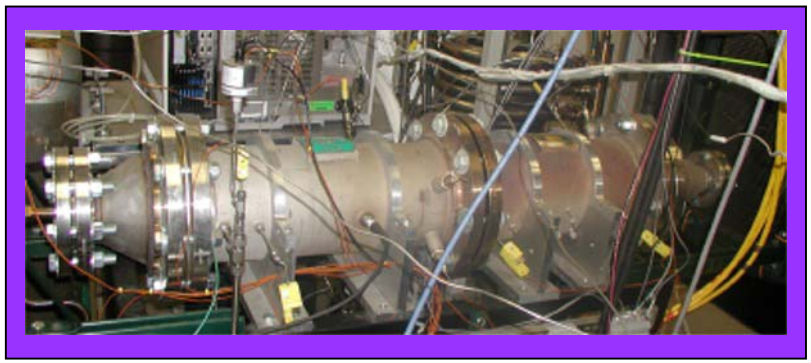
- Measure fuels effects in fuel reformers
  - Adiabatic, vehicle scale reformers
    - Catalytic partial oxidation / steam reforming
    - Gas phase partial oxidation / catalytic steam reforming
- Fuel reforming kinetics
  - Ease of partial oxidation / steam reforming
    - Fuel components, fuel impurities, fuel additives
  - Effect on light-off (fuel processor start-up)
- Measure Carbon formation
  - Fuel effect on steady state, startup and transient carbon formation
- Effect on fuel processor durability
  - Measure carbon formation
  - Hydrocarbon breakthrough

Adiabatic Reactor Testing / 'Vehicle' Scale

Catalytic
Partial Oxidation/Steam Reforming
in situ Carbon Formation Laser Optics



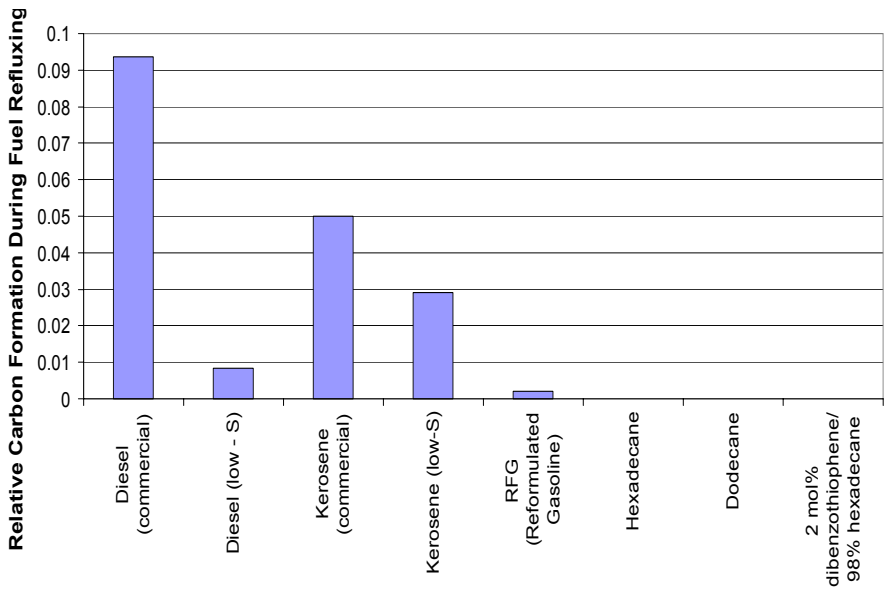
Gas phase partial oxidation



Fuel components testing with gas phase partial oxidation / catalytic steam reforming

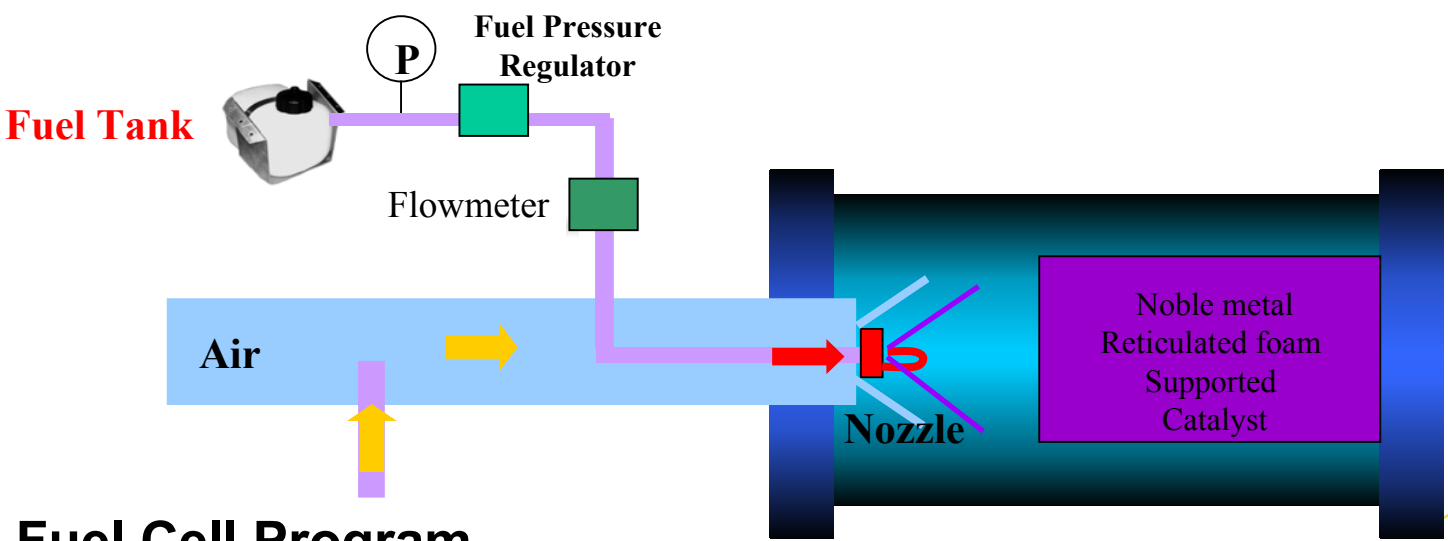
(provided by Nuvera)

Relative Carbon Formation from Fuel Vaporization



Diesel fuel shows pyrolysis upon vaporization

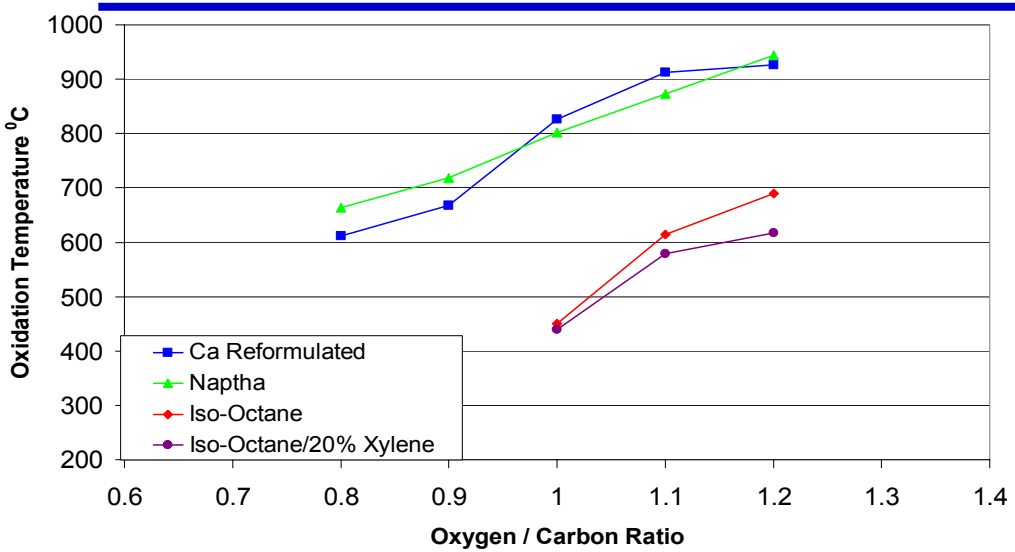
- Diesel fuel reformers require
  - Direct fuel injection
  - Water to suppress carbon formation
- Directly inject fuel to reforming catalyst
  - Commercial fuel nozzle
  - Limited preheating of fuel/air
    - Prevents fuel vaporization/particulate formation
  - Carbon formation experiments under real conditions



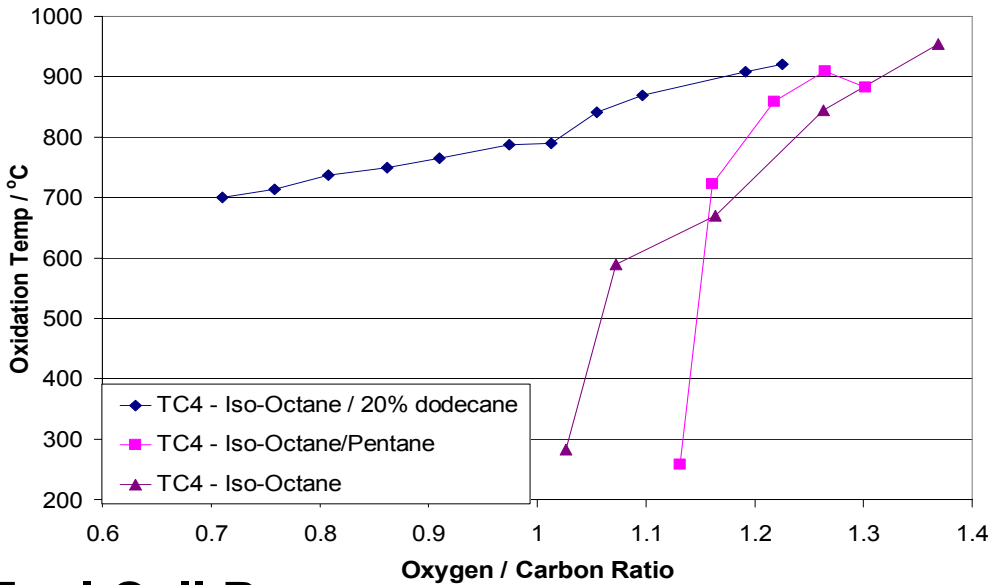
POx/SR

Los Alamos

Fuels During Gas Phase Oxidation



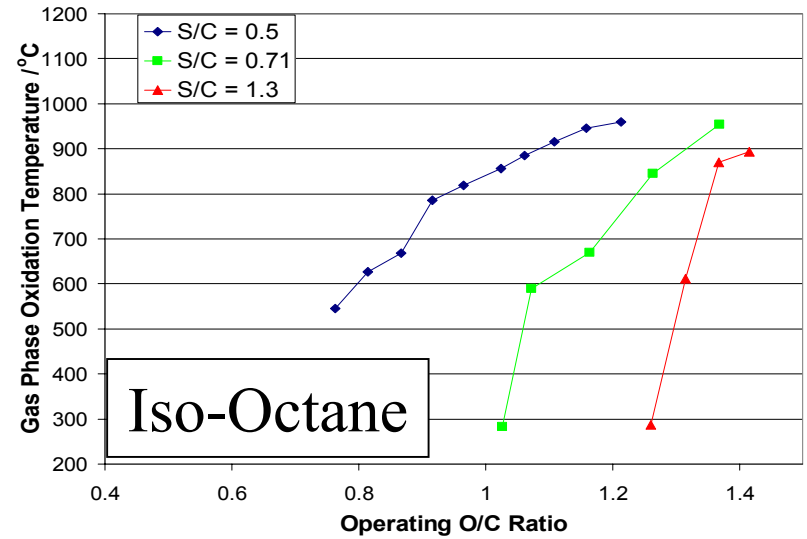
- Gas phase oxidation was easier with 'real' fuels
- Difficult to keep combustion with pure components iso-octane and iso-octane/xylene

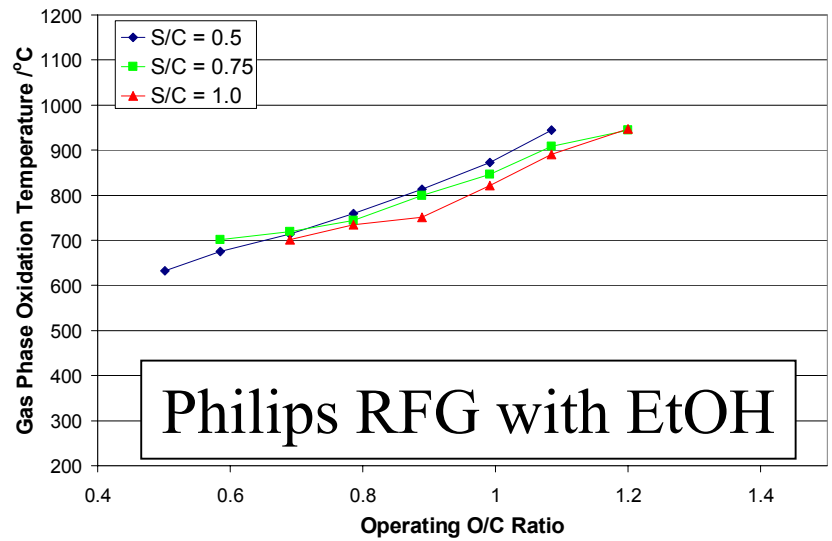


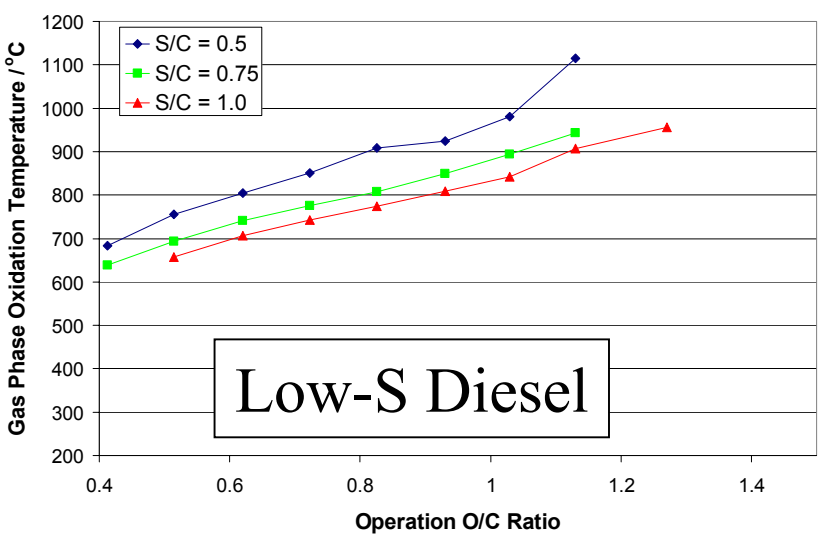
- Adding dodecane to iso-octane simulated oxidation of fuel blends.
- Addition of pentane shows essentially same results as iso-octane.
- Addition of heavier hydrocarbons provides easier gas phase oxidation

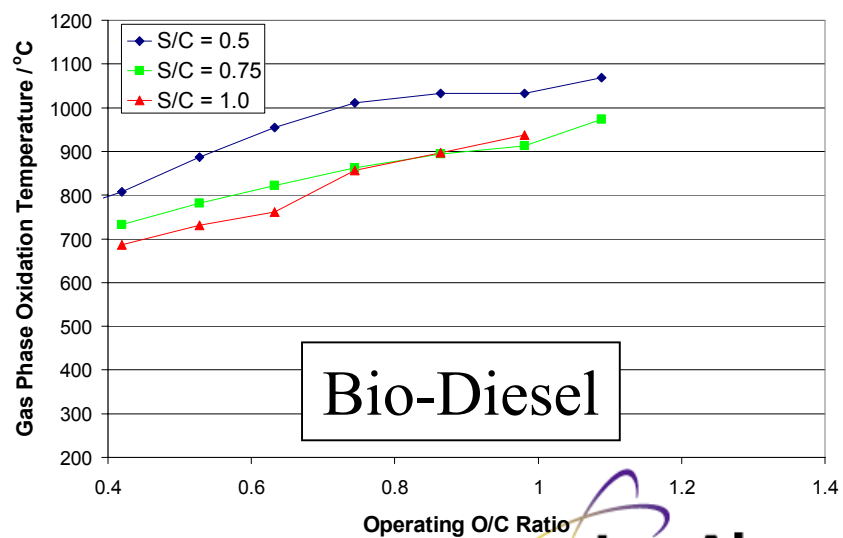
Gas Phase Partial Oxidation of Fuels

Steam/carbon effect on fuel oxidation

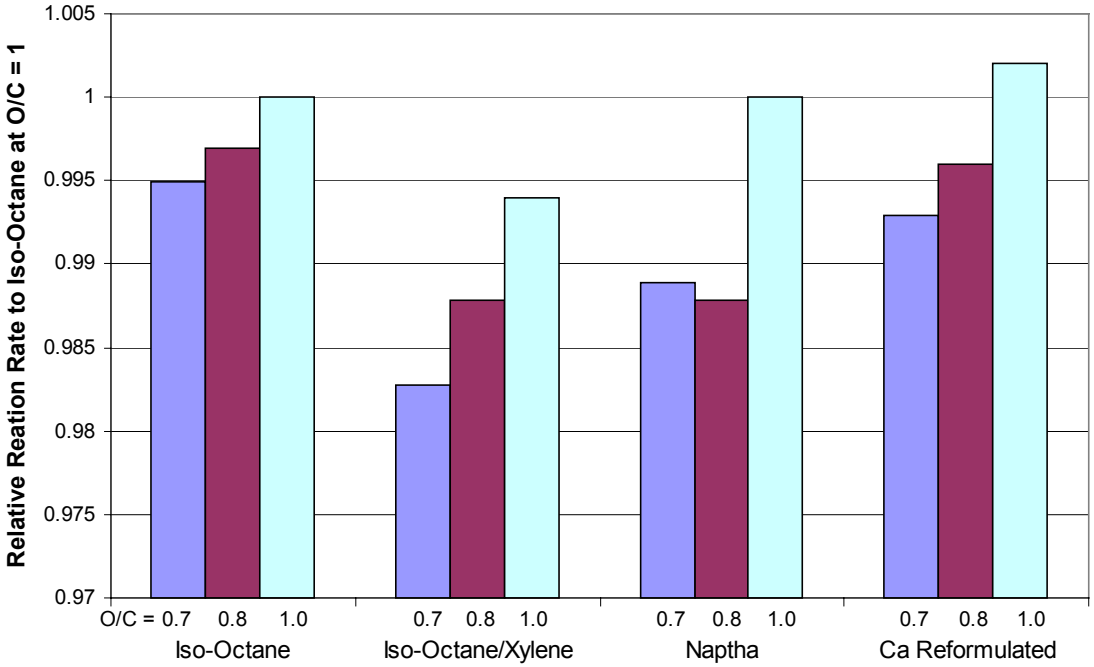








Catalytic Partial Oxidation Stage



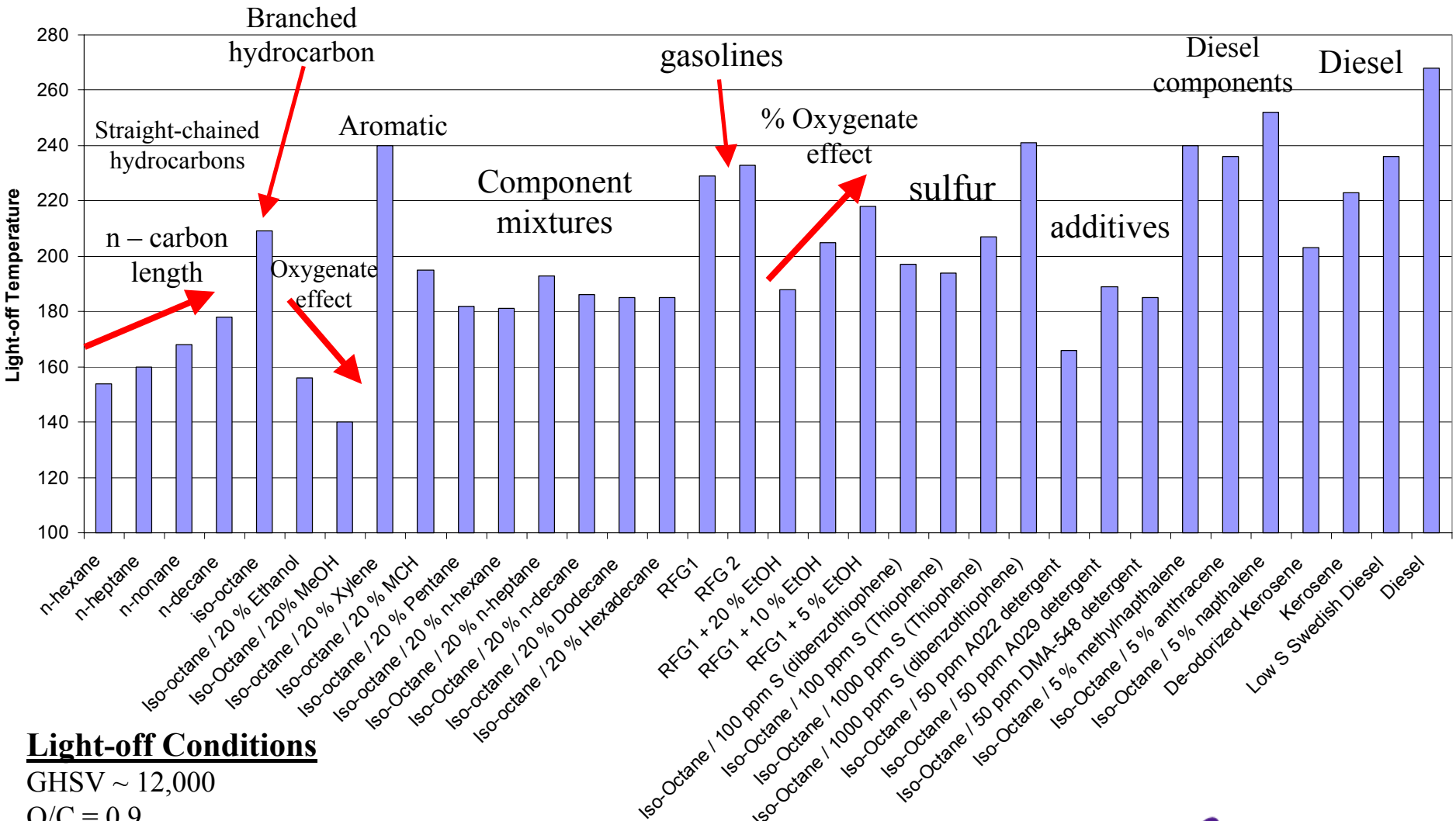
Aromatics slow oxidation and reforming

Longer Chained hydrocarbons also slow reforming kinetics

Higher Temperatures (O/C ratio's) are required for long chained hydrocarbon conversion for similar residence times – leads to H_2 dilution

- **For full conversion of hydrocarbon fuels which include long chains, aromatic:**
  - **Either longer residence times required for similar conversion**
    - **leads to bigger reactor, more catalyst**
  - **Higher Temperature → O/C, which leads to inefficiency**

Fuel Effect on Catalyst Light-off



Light-off Conditions

GHSV ~ 12,000

O/C = 0.9

S/C = 1.0

Fuel Effect on Reactor Light-off

Fuel Effect on Gas Phase Reactor Light-off

Reactor light-off (ignition) can vary with fuel and fuel components:

For Gas Phase oxidation reactor ignition requires:

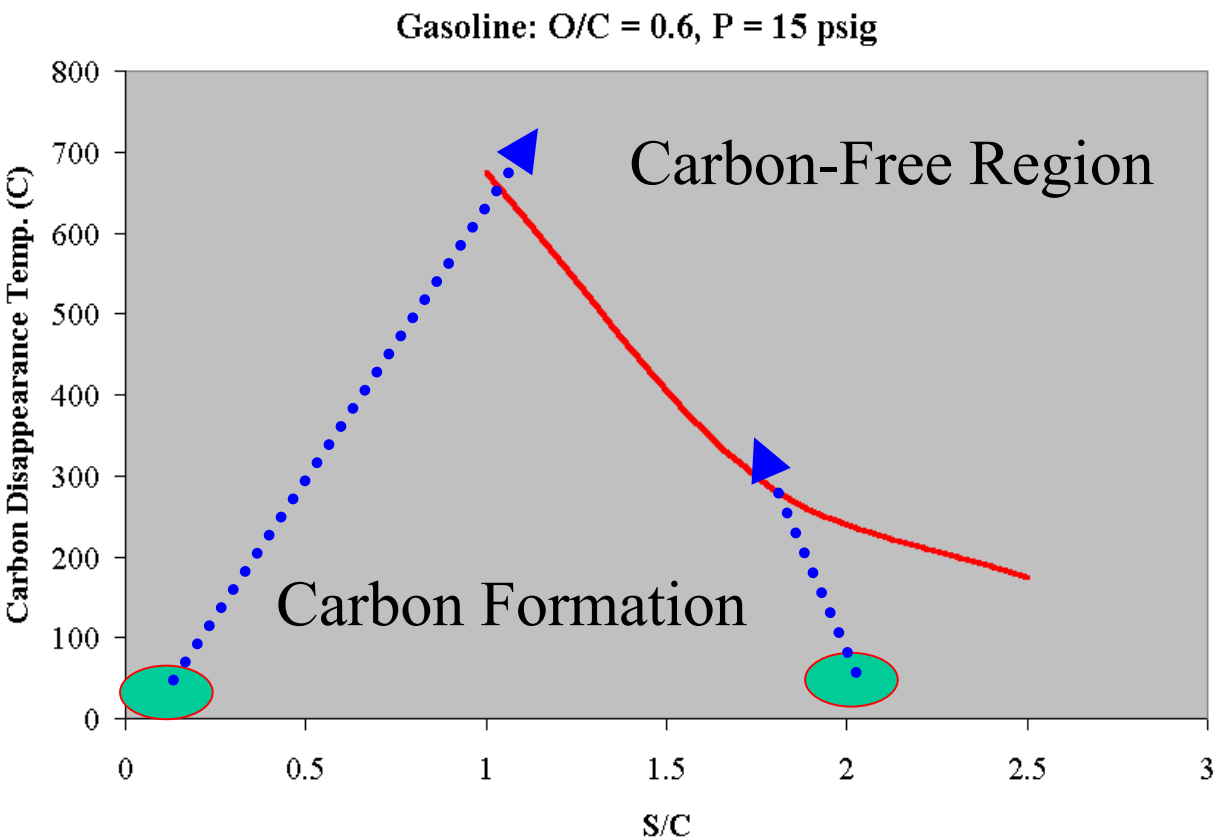
Iso-Octane: O/C = 1.2, at S/C ~ 0.5

RFG (gasoline): O/C = 1.0, at S/C ~ 0.5

Fuel Effect on Catalytic Reactor Light-off

- Fuel Composition Effects on fuel processor operation
  - Gas phase oxidation prefer high long-chained hydrocarbons
  - Catalyst oxidation prefer shorter chained hydrocarbons
- Light-off
  - oxygenated compounds speed light-off
  - straight-chained hydrocarbons ease light-off compared with branched
  - aromatics slow kinetic light-off
  - long chained hydrocarbons (diesel) slow light-off
- Light-off Temp. corresponds inversely to C-H or C-C Bond dissociation energy

Equilibrium Modeling



Equilibrium defines fuel processor operating conditions

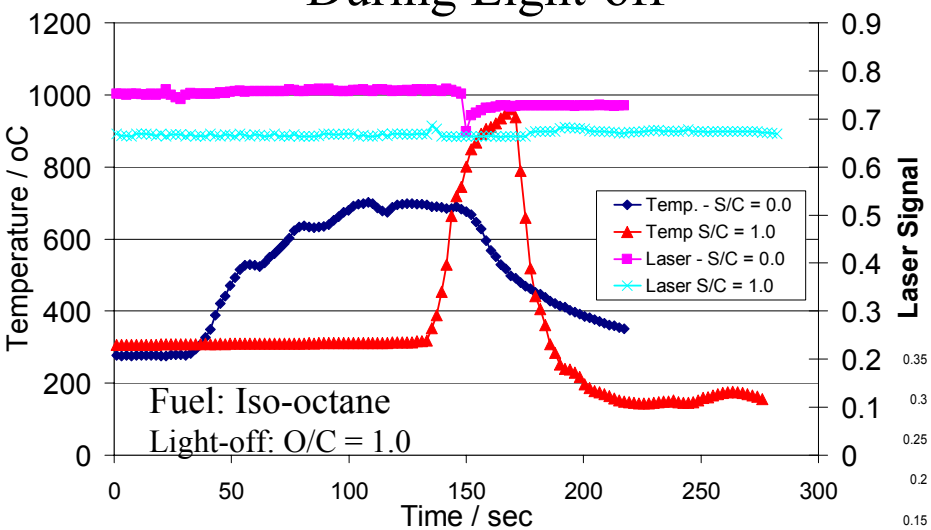
At start-up of fuel processor, water availability is questionable (freezing conditions)

Avoiding zero equilibrium carbon will be difficult whether water is available or not.

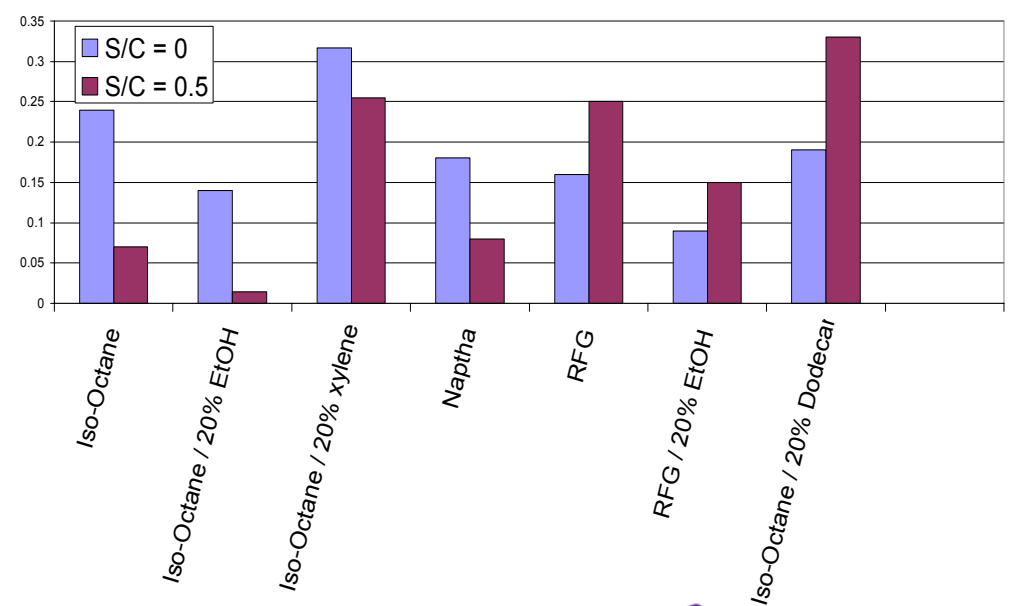
At high S/C during start-up, during transition to carbon-free region - carbon formation kinetics appear low

Carbon formation during reactor light-off

Carbon Formation Measurements During Light-off



In situ laser measurement during light-off of fuel conducted at S/C = 0.0, and S/C = 0.5 for fuels including iso-octane, iso-octane/xylene, iso-octane/ethanol, iso-octane/dodecane, naptha, reformulated gasolines (RFG), RFG/ethanol, Iso-octane /dodecane and Iso-octane/pentane.



Quantitative carbon measurements indicate carbon made during start-up for all fuels.
Water during start-up suppresses some carbon formation, but carbon is still formed, in smaller quantities.
Ethanol suppresses carbon formation, while aromatics shower high carbon formation.

Carbon Formation Effect on Durability

- Carbon formation during operation and start-up
  - function of fuel composition, also O/C and S/C

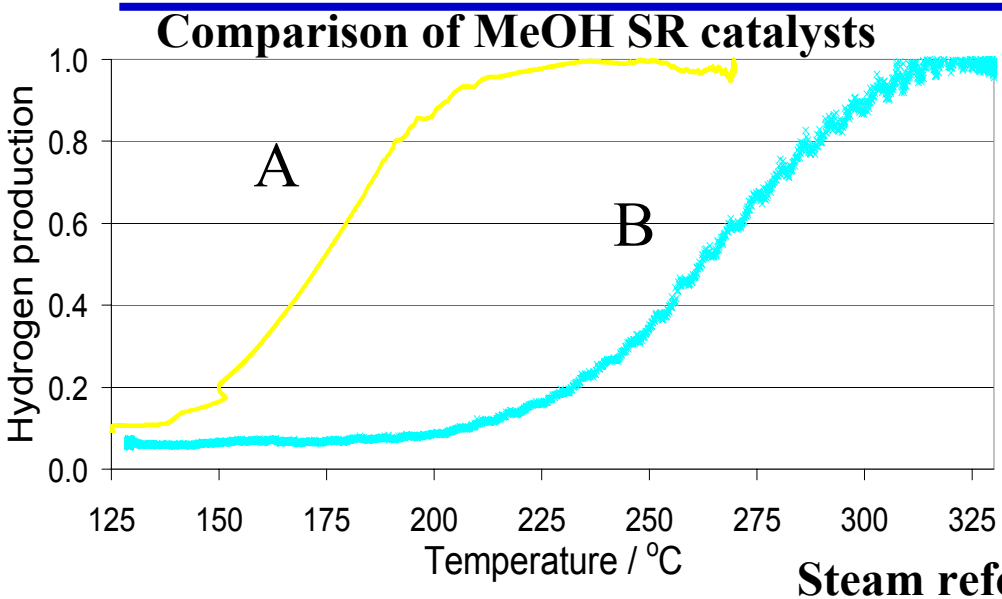
- Carbon formed during start-up ~ 0.5 % to 3 % of carbon from fuel (for 30 sec)
- Normal operation at O/C = 0.75, S/C => 1.0, no measurable carbon

- Ethanol addition decreases carbon formation: 40 % (RFG) to 80% (Iso-Octane)

- Durability targets 5000 hrs. (# start-ups 4,000 – 10,000 cycles (drive cycle))
  - RFG (4,000 cycles) forms 1.0 kg carbon
  - RFG (10,000 cycles) forms 2.5 kg carbon

- Post-catalyst analysis does not show carbon poisoning noble metal catalysts
  - carbon typically moves down stream in system
- Carbon formation with nickel catalyst tends to remain in ATR

Low Temperature Reforming Fuels
Support of portable power



MeOH (Methanol)

H_2O/MeOH = 1.5

Space Time = 0.5 sec

DME (DiMethylEther)

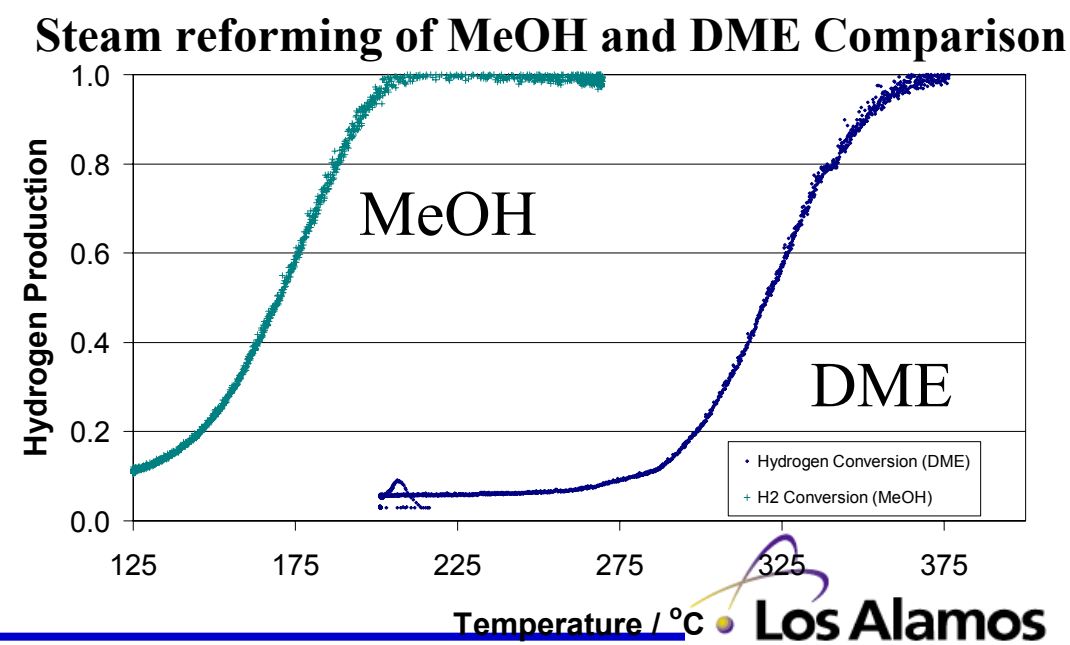
S/C = 2.5

Space Time = 0.5 sec

Full conversion of MeOH at ~ 200 – 220 °C (~ 10,000 GHSV)

TON at ~ 220 °C 8.5 per min
(based on CO adsorption sites)

Full conversion of DME at 360 – 380 °C



2002 Fuel Cell Review Comments

–Not clear that results show 'durability' – instead appear to provide valuable insight into transient response. Can effect of shut-down overshadow long-term 'normal' ATR Operation?

Believe that the short term effects are durability effects – these 'transient' effects can be significant during start-up, shut-down and potentially overshadow long-term operation.

– Unclear how iso-octane can provide knowledge addressing durability issues – why is 'normal' gasoline not used for tests?

– Important to address issues of effect of normal gasoline on whole system

– Use 'real' reformate & publish results

We are using various components, including gasoline

– In-situ method is an excellent approach – however work presented appears to provide durability during transient behavior, not necessarily long-term operation.

We use in situ measurements define short term fuel effects to extrapolate to durability. We also do long-term operation to define durability. Durability system operates with adiabatic reactor, with HTS/LTS, PrOx and slip stream to PEM cells. Hydrocarbon breakthrough in ATR limits durability

Interactions/Collaborations

- National Technical Presentations/Publications
  - AIChE, ACS, SAE
- Delphi Automotive
  - discussions (~ reactor design, testing, diesel)
- CRADA Interactions
  - Motorola (MeOH SR)
- Haynes International (reformer materials)
- Phillips Petroleum
  - providing fuel for testing, additives, fuel formulations
- Catalysts (for fuel reforming (gasoline, diesel, MeOH), Durability)
  - Univ. Alabama, Engelhard, Delphi, Süd-Chemie, Johnson Matthey

2002 - 2003 Milestones

	Gasoline
May 2002	500 - 1000 hrs of operation durability in adiabatic reactor
September 2002	Carbon formation with detergent additives
June 2003	Comparison Measurements of carbon formation effect at start-up and light-off for 4 fuel components and 2 fuel
September 2003	Measurement of sulfur effect on carbon formation
	Methanol
December 2002	Relative reaction rate evaluation of 4 existing methanol steam reforming catalysts
July 2003	Kinetic rate expression development for Methanol steam reforming catalyst
	Diesel (SECA Program)
December 2002	Direct Fuel Injection/Air Mixing Demonstration
March 2003	Multiple Regeneration Cycles Removing Carbon From Catalytic Partial Oxidation
September 2003	Carbon Formation Kinetics Rate Expression Development

Summary/Findings

- ATR of Fuel Components
  - Catalytic vs. gas-phase
    - gas-phase oxidation favors 'real' fuel mixtures and higher hydrocarbons
      - Steam input has large effect on gas phase oxidation, small on catalytic
    - Catalytic oxidation favors short-chained aliphatic hydrocarbons
      - Aromatics/long-chained HC's have lower catalytic kinetics

- Fuel Effect on Reactor Light-off
  - Homogeneous
    - high steam content slows light-off
  - Catalytic
    - oxygenated, straight-chained HCs speed light-off
    - aromatics, branched chained slow light-off

- Carbon Formation
  - Monitoring carbon formation during the start-up transient
    - Aromatics show highest tendency for carbon formation
    - Oxygenates help suppress carbon formation during light-off

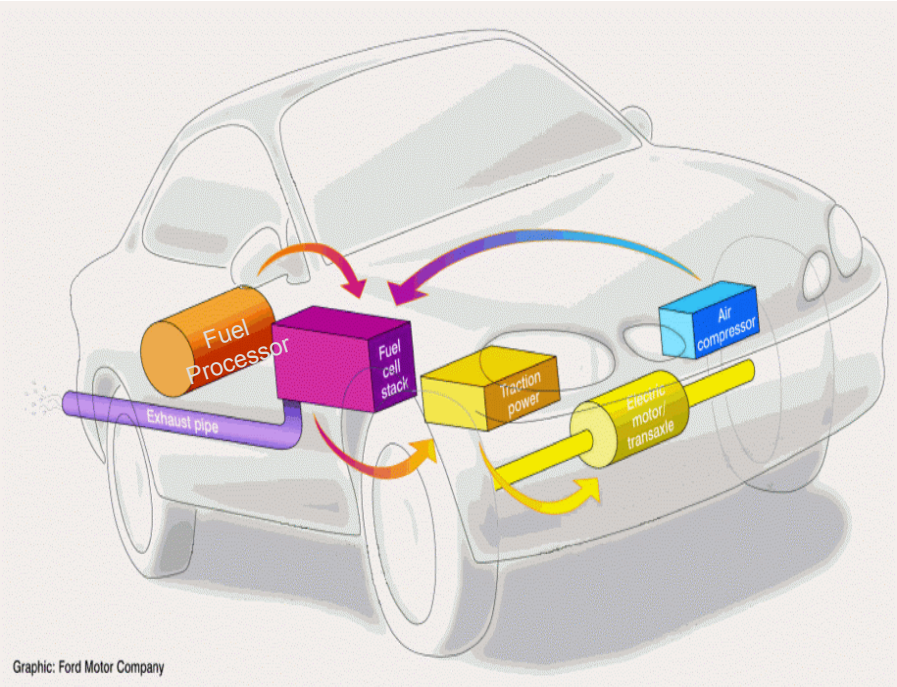
Future Plans

- Remainder of FY 2003:
  - Carbon formation:
    - Sulfur effect on carbon formation
    - Oxidative regenerative of catalyst
  - Fuel reforming and hydrogen fuel cell durability testing
    - Implement drive cycle testing into durability testing

- FY 2004:
  - Hydrogen / gasoline reformate durability comparison
    - Implementation of drive cycle including start-up cycling on fuel processor
  - Carbon formation fundamentals
    - Kinetic expressions and mechanistic studies of carbon formation
  - Strategies for controlling carbon formation
    - Avoidance and minimization of carbon formation
    - Oxidative regeneration of catalyst
  - Characterization of start-up emissions
    - Contaminant and hydrocarbon breakthrough

Sensors for Safety & Performance

Vehicles



Stationary Systems

Neil Rossmeissl

Targets and Status

Sensors for Automotive Fuel Cell Systems

Sensor	Op. Temp.	Response Time	Accuracy
CO: 1-100 ppm reformate pre-stack sensor 100-1000 ppm CO 0.1-2% CO sensor	 <150 °C 250 °C 250-800 °C	 0.1-1 sec 0.1-1 sec 0.1-1 sec	 1-10% full scale (fs) 1-10% fs 1-10% fs
H2 in fuel processor output	70-150 °C	0.1-1 sec for 90% response to step change	1-10% fs
H2 in ambient air	-30-80 °C	Under 1 sec	5%
Sulfur compounds	Up to 400 °C	<1 min @ 0.05 ppm	N/A

Targets and Status

Sensors for Hydrogen and Fuel Cell Systems

Sensor	Op. Temp.	Response Time	Accuracy
CO: 1-100 ppm reformate 100-1000 ppm CO 0.1-2% CO sensor	 <150 °C 250 °C 250-800 °C	 0.1-1 sec 0.1-2 sec 0.1-3 sec	 1-10% full scale (fs) 1-10% fs 1-10% fs
H2 in processor output	70-250 °C	0.1-3 sec for 95% response to step change	1-10% fs
H2 in ambient air	-30-80 °C	Under 1 sec	5%

Sensor Types

- CO
- H_2 in Fuel Processor Output
- H_2 in Ambient Air
- Sulfur Compounds (H_2S, SO_2, organic sulfur)
- Flow Rate of Fuel Processor Output
- Ammonia
- Temperature
- Relative Humidity for Cathode and Anode Gas Streams
- O_2 in Fuel Processor and at Cathode Exit
- Differential Pressure in Fuel Cell Stack

Sensor Requirements

- Must perform within required ambient and process conditions
- Fast response time
- Acceptable accuracy
- Must conform to size, weight, and cost constraints of automotive applications
- Acceptable lifetime (durability)
- Must measure properties within the required range

Sensor Projects

• Carbon Monoxide Sensors for Reformate-Powered Fuel Cells	LANL
• Electrochemical Sensors for PEM Fuel Cell Vehicles	LLNL
• Interfacial Stability of Thin Film H2 Sensors	NREL
• Sensors for Automotive Fuel Cell Systems	UTC Fuel Cell
• Micro-Machined Thin Film H2 Gas Sensors	Advanced Technology Materials, Inc.
• Sensor Development for PEM Fuel Cell Systems	Honeywell Sensing and Controls

Sensor Posters

• Gallium Nitride Integrated Gas/ Temperature Sensors for Fuel Cell Systems Monitoring for Hydrogen & Carbon Monoxide	Peterson Ridge LLC
• Robust Fiber-Optic Temperature Sensor for Fuel Cell Monitoring	ORNL

Discussion Points

Barriers

- Cost
- Application
- Lifetime
- Flexibility
- Public Perception

CO Sensors for Reformate Powered Fuel Cells

Rangachary (Mukund) Mukundan
Eric Brosha
Roger Lujan
Fernando Garzon (Sensor Team Leader)
MST-11
Los Alamos National Laboratory
Los Alamos NM 87545 USA

May 22, 2003

DOE Hydrogen and Fuel Cells
2003 Annual Merit Review

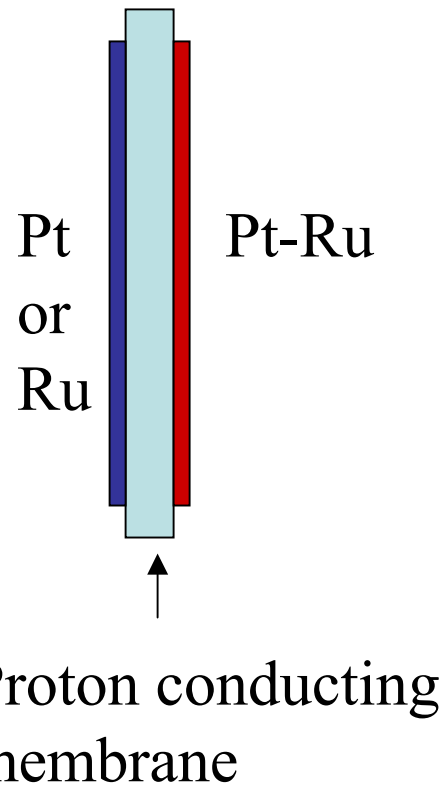
Los Alamos
NATIONAL LABORATORY

Objectives

- Reformate gas powered fuel cell systems require sensors for carbon monoxide level monitoring and feedback control
  - A high temperature sensor (>200°C) is required for measurement of 0.1 to 2% CO in reformate gas for PROX reactor control
    - The reformate gas could either be from a low temperature WGS reactor or methanol reformer
  - A low temperature sensor for measuring 10-100 ppm CO concentrations for stack poisoning control
    - This sensor can be used to control the air bleed into the fuel cell anode
    - This sensor could also be used to control the oxygen input of the PROX reactor

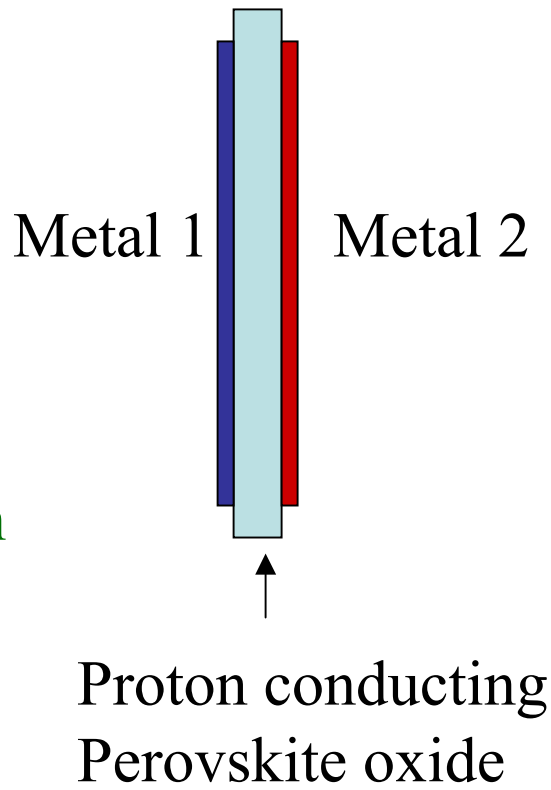
Approach (Low Temperature)

- Low temperature amperometric device based on CO inhibition of hydrogen oxidation kinetics
  - Use Nafion® as the proton conducting membrane
  - Use Pt or Ru electrode as working electrode
    - Electrode is sensitive to CO poisoning
  - Use Pt-Ru electrode as a counter electrode
    - Electrode is tolerant to the presence of CO



Approach (High Temperature)

- High Temperature device based on the differential inhibition of the hydrogen oxidation reaction at an oxide/metal interface
  - Use high temperature proton-conducting oxides like strontium and barium cerate or calcium and strontium zirconate
    - Commercially available H_2 sensor (NOTORP, TYK America)
    - Modify electrode configurations to study CO poisoning effects



Approach (High Temperature)

- Potentiometric CO sensor based on the mixed-potential developed at an oxide electrolyte/metal electrode interface

$$V_O^{\cdot\cdot} + \tfrac{1}{2}O_2 + 2e^- \rightarrow O_O$$

CO sensor in air

$$CO + O_O \rightarrow CO_2 + V_O^{\cdot\cdot} + 2e^-$$

$$H_2 + O_O \rightarrow H_2O + V_O^{\cdot\cdot} + 2e^-$$

CO sensor in H_2

- Use YSZ(zirconia) and CGO(Ceria) electrolytes
- Use various (Pt, Pd, Au, Ni) metal electrode combinations

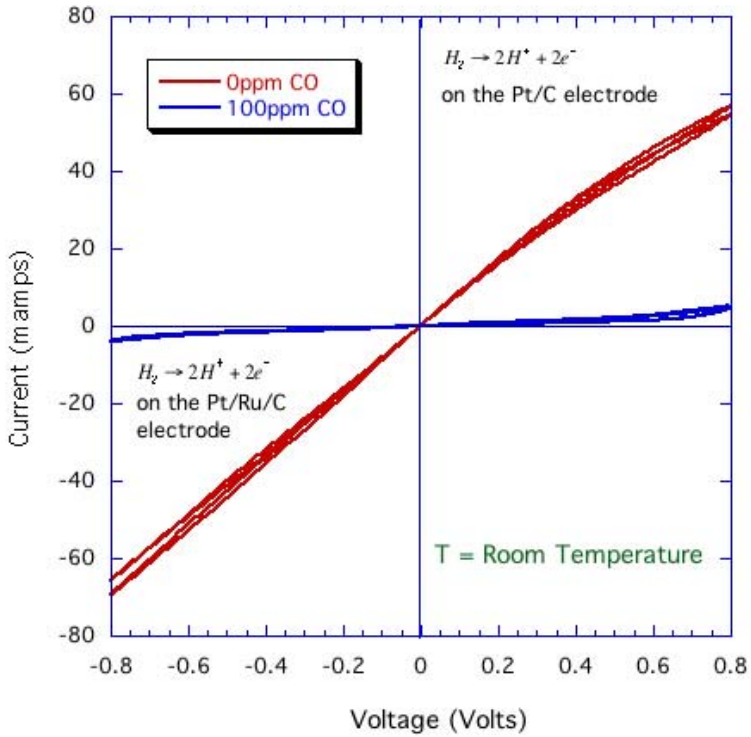
A. Hashimoto et al. *Electrochem. and Solid State Letters*, **5(1)** H1-H3 (2002)

Accomplishments (Low temperature)

- Working Electrode
  - Pt/C/Nafion : 0.22mg/cm^2 of Pt
- Counter Electrode
  - Pt/Ru/C/Nafion : 0.25mg/cm^2 of Pt/Ru(50/50)alloy
- Electrolyte
  - Nafion 1135

- Both the Pt/C and the Pt/Ru/C electrodes are good at hydrogen oxidation and both of them get poisoned by the CO

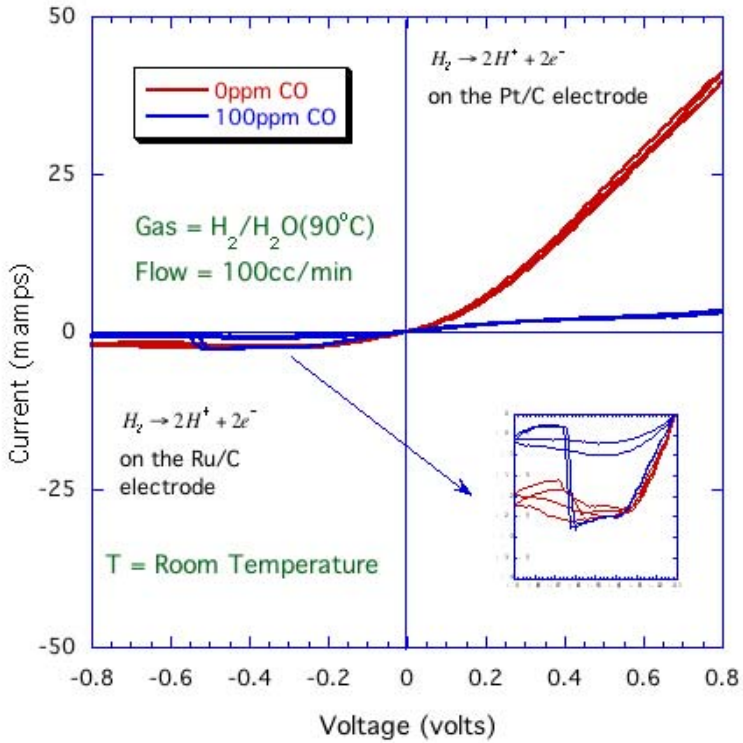
- The CO poisoning is not easily reversible
  - Recovery takes hours without air bleeding



Accomplishments (Low temperature)

- Working Electrode
  - Pt/C/Nafion : 0.22mg/cm^2 of Pt
- Counter Electrode
  - Ru/C/Nafion : 0.12mg/cm^2 of Ru
- Electrolyte
  - Nafion 1135

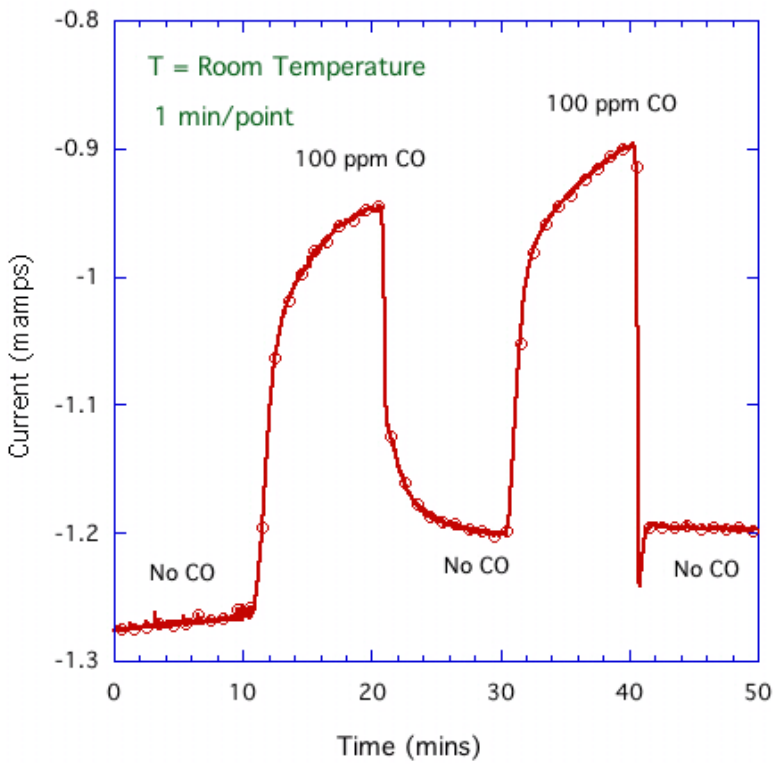
- The Ru/C electrode is not very efficient at H_2 oxidation
- Both the electrodes get poisoned by the CO, the Ru/C electrode to a lesser extent
- The CO from the Ru/C electrode can be easily stripped at voltages <-0.5V (see inset)



Accomplishments (Low temperature)

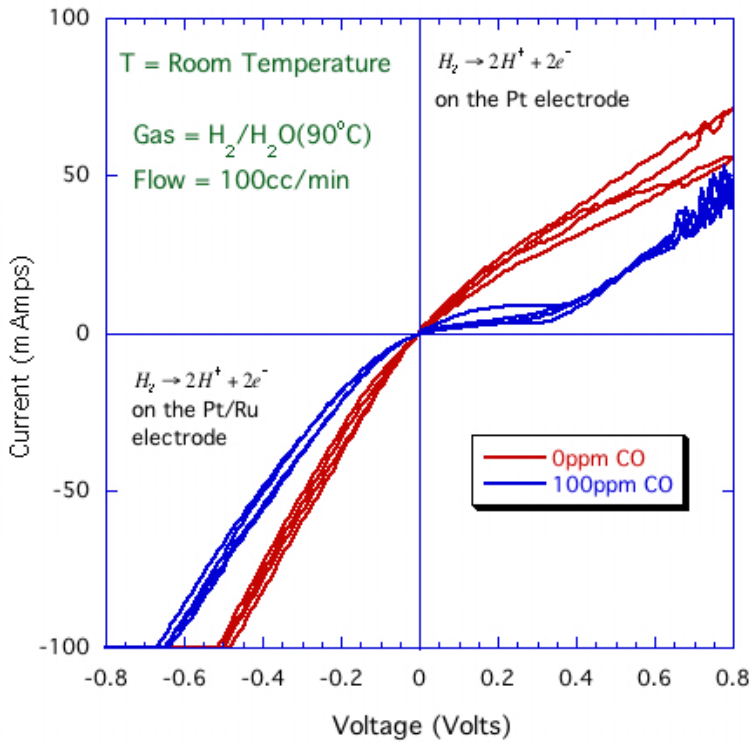
- Working Electrode
  - Pt/C/Nafion : 0.22mg/cm^2 of Pt
- Counter Electrode
  - Ru/C/Nafion : 0.12mg/cm^2 of Ru
- Electrolyte
  - Nafion 1135

- Reproducible sensor signal was attainable when sensor was operated at -0.7V
- Sensor is slow, almost 10 mins to 90% of response level
- Sensitivity is low, < 0.3mamps change for 100 ppm CO



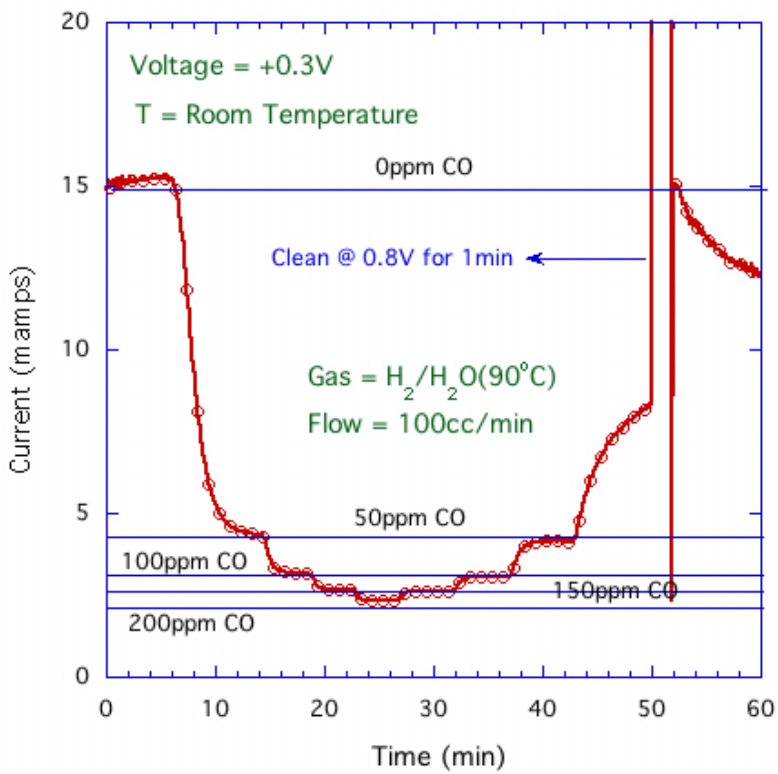
Accomplishments (Low temperature)

- Working Electrode
  - Pt/Nafion : 10mg/cm^2 of Pt
- Counter Electrode
  - Pt-Ru/Nafion : 10mg/cm^2 of Pt-Ru (50/50) alloy
- Electrolyte
  - Nafion 117
- Both the Pt and Pt/Ru alloy electrodes are good for H_2 oxidation
- There is very little effect of CO on the Pt/Ru alloy electrode.
  - This electrode could serve as a pseudo-reference electrode
- The Pt electrode gets poisoned by the CO which can easily be cleaned at voltages > 0.4V



Accomplishments (Low temperature)

- The extent of poisoning on the Pt electrode can be used to give a useful sensor response
- The current at 0.3V decreases from 15mamps to <5mamps when the CO content in the H_2 stream is increased from 0 to 50ppm.
- The final CO can be cleaned by applying a 0.8V potential for approx. one minute
- Slow Response time (>5 mins) when CO is introduced

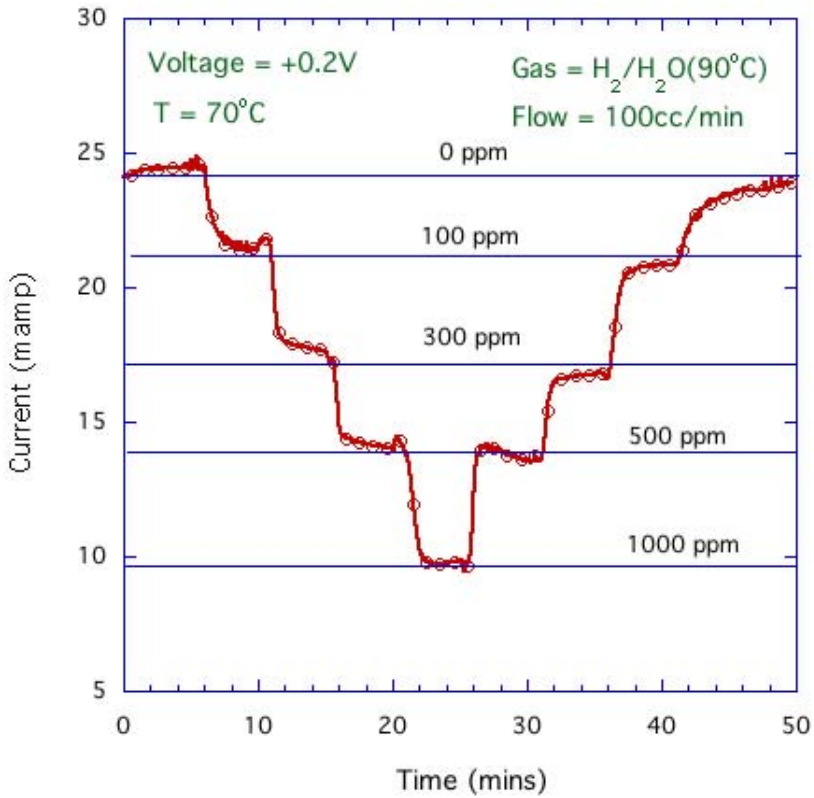


Milestone :Operation at 70°C

- Stable response obtained at 70°C
- Elevated temperature improves the response of the sensor
- No CO cleanup is required
- Response time : 1 - 2mins
- Sensor sensitivity is greatly reduced
  - 100 ppm of CO

  80% change at room temperature

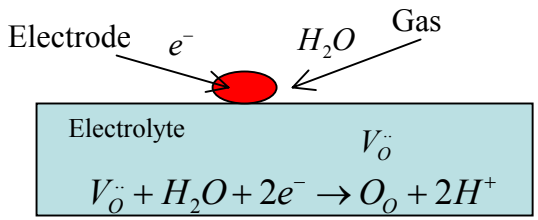
  16% change at 70°C
- Baseline recovery is still slow



Useful to protect fuel cell from spikes

Proton Conductors (High Temperature)

- Electrolyte
  - $SrZr_{0.9}Y_{0.1}O_{2.95}$, $SrCe_{0.95}Yb_{0.05}O_{2.975}$ and $BaCe_{0.8}Gd_{0.2}O_{2.9}$
- Electrodes
  - Pt, Au, Ni and Pd
- Negligible response to CO
  - CO adsorption at temperatures >250°C is not significant to affect the hydrogen oxidation reaction

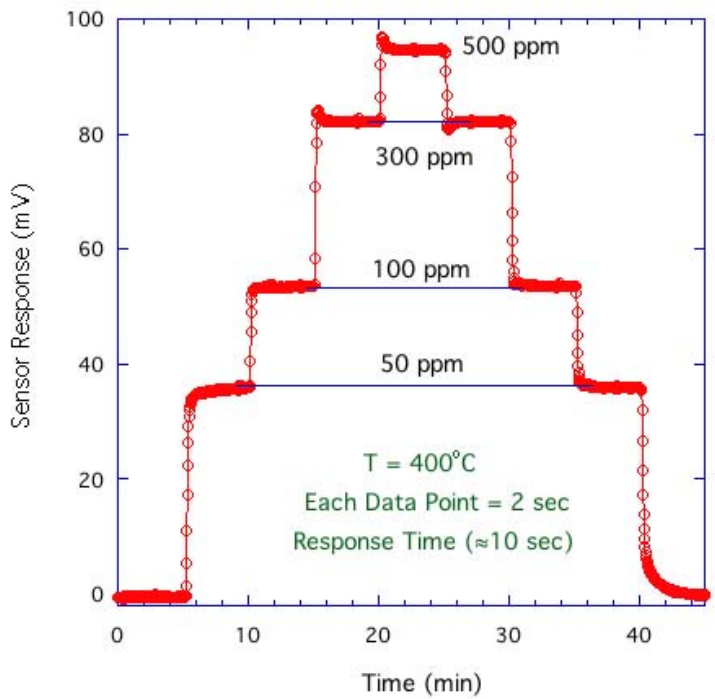


$$H_2 \rightarrow 2H^+ + 2e^-$$

Oxygen Conductors (High Temperature)

- Electrolyte
  - 8mole%YSZ ($Zr_{0.85}Y_{0.15}O_{1.93}$) or 20mole%CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$) or
  - 20mole%EBO($Bi_{0.8}Er_{0.2}O_{1.9-\delta}$)
- Electrodes
  - Pt, Au
- Kinetic Control (Electrode morphology)
- Stable CO response in Air (tested for up to 2 months)
- Response time < 10sec
- Reproducible results from multiple sensors

Pt / $Ce_{0.8}Gd_{0.2}O_{1.9}$ / Au



Patent application filed

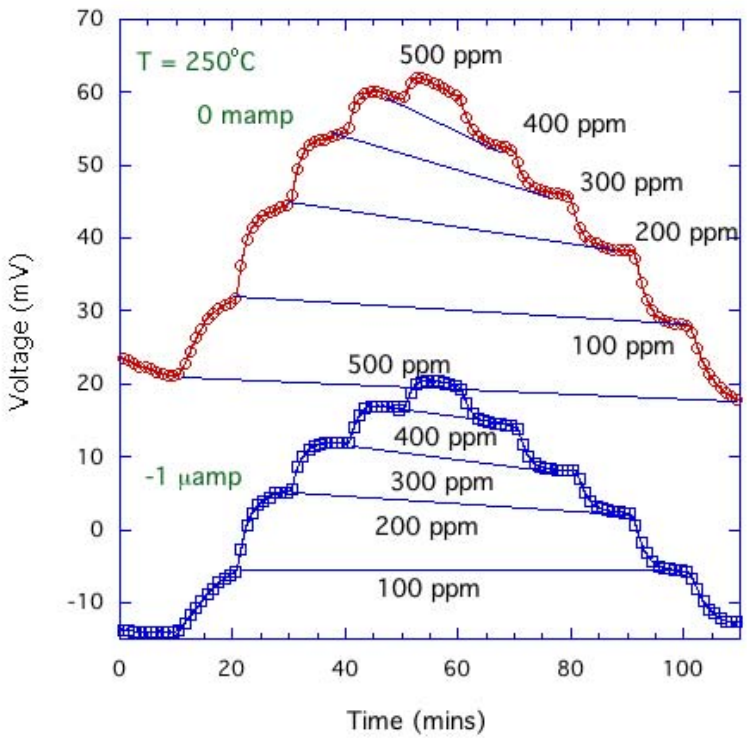
Accomplishments (High temperature)

- Electrolyte
  - 20mole%CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$)
- Electrode
  - Pt and Ni (1 μm sputtered)
- Lower operating temperature (250°C)
- Response of 35mV @ 500ppm CO
- Response decay with time
- Improvement under -ve bias

$$CO_{Ni} + O_O \rightarrow CO_2 + V_{\ddot{O}} + 2e^-$$

- The potential of the pseudo reference electrode (Ni) may be changing with time

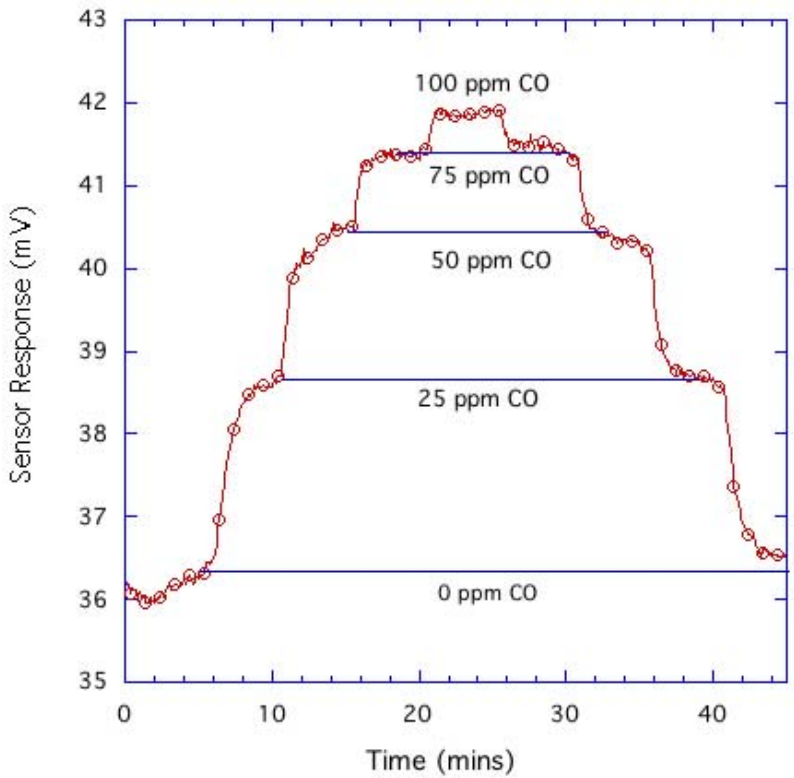
Base Gas = 70%H_2/30%CO_2(H_2O)



Milestone : Ceria based sensor

- Electrolyte
  - 20mole%CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$)
- Electrode
  - Pt and Ni (1 µm sputtered)
- Lower operating temperature (240°C)
- Response of 6mV @ 100ppm CO
- Response was stable over a period of 2 days
- Approx. 1-2 minute response time
- Unstable baseline

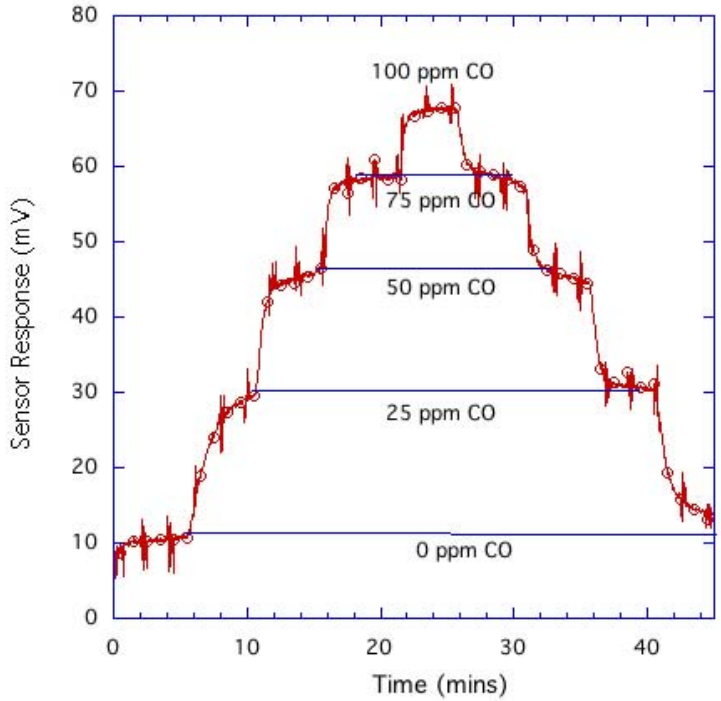
Base Gas = 70%H_2/30%CO_2(H_2O)



Improvement?

- Electrolyte
  - 3mole%YSZ
- Electrode
  - Pd paint and Ni (1 μm sputtered)
- Lowered operating temperature (185°C)
- Response of 60mV @ 100ppm CO (10 fold increase)
- Stable baseline
- Approx. 1 minute response time
- High noise (need to average)
- Stability and Reproducibility?

Base Gas = 70%H_2/30%CO_2(H_2O)



Reviewer's Questions

- How is Oxygen replaced in YSZ based sensor? Stable?

$$H_2O + V_O^{\cdot\cdot} + 2e^- \rightarrow H_2 + O_O$$

  - Ceramic can operate under reformate conditions for extended periods
- Hydration, high loadings, stability of PEM assembly?
  - Novel oxide based sensor to sense 25-100ppm CO for stack control. Stable operating temperature of 200-300°C should be achievable by self heated sensor positioned between PROX reactor and Fuel Cell
- <1 minute response time?
  - Demonstrated in oxide based sensor in air. Should be achievable under reformate conditions when the sensor is optimized

Project Timeline

Fy01 Fy02 Fy03 Fy04

Project begins

Low temp CO sensor prototype developed
Sense 100-1000ppm CO in H_2
Oxide proton conductor thin film technology developed

Elucidated the working principle of these low temperature sensors

Improved Low Temperature sensor
Works at Room Temperature
Stable response to 10-200ppm CO in H_2

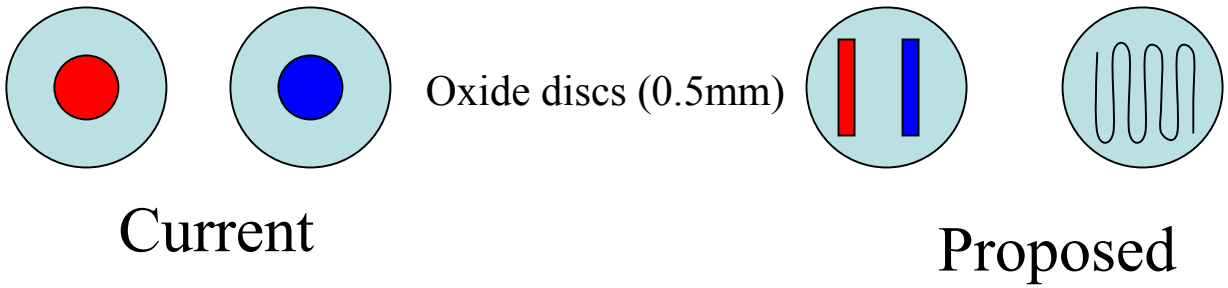
Oxide based amperometric sensors do not have sensitivity to CO and Oxide based mixed-potential sensors do not operate stabily in the presence of H_2

Demonstrate low temperature CO sensor
Stable operation at 70°C

Demonstrate higher temperature CO sensor
25-100ppm CO @ 200-300°C

Future Work (FY 04)

- Optimize Sensor : Ru and Pd sputtered electrodes
- Study response of sensors to high CO contents at 300°C
- Self heated sensor



- Test in durability test stand after PROX (Mike Inbody)

Collaborations

- Look for partners to develop CO sensor

- Worked with USCAR on DOE CRADA for hydrocarbon sensor development
- Working with ARES and University of Florida on development of NO_X sensor

Conclusions

- PEM based CO sensor has stable reproducible response to 50-200ppm of CO at room temperature
- Elevated temperatures decrease the sensitivity of the sensor while improving response time (Useful sensor to protect fuel cell from excessive CO)
- Oxide based sensors can be used to measure 25-100ppm CO in $H_2/CO_2/H_2O$ mixtures
- Stability and response time need improvement
- Oxide based sensors could be used for air(oxygen) injection control of both PROX reactor and fuel cell stack

Acknowledgements

- Bryan Pivovar and Piotr Zelenay for help with unsupported MEAs with high catalyst loadings
- Judith Valerio for help with the carbon supported MEAs with low catalyst loadings
- Francisco Uribe for help with the I-Vs

Electrochemical Sensors for PEMFC Vehicles

L. Peter Martin and Robert S. Glass
Lawrence Livermore National Laboratory

presented to:

The DOE National Laboratory Fuel Cells for Transportation Program Review
May 22, 2003

This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

There is an emerging need for hydrogen sensors for PEMFC vehicles*

- **Improvements are needed in:**
  - **Size**
  - **Cost**
  - **Reliability, lifetime**
- ***Safety sensor:* Monitors for leaks at strategic locations in FC vehicle**
  - **Passenger compartment, wheel wells, hydrogen storage tanks**
- ***Fuel sensor:* Monitors fuel gas quality at reformer output**
  - **Most existing sensor technologies are not designed to operate in the fuel cell environment**

*** From:** ***Sensor Needs and Requirements for Proton Exchange Membrane Fuel Cell Systems and Direct-Injection Engines*****, U.S. DOE, Office of Transportation Technologies, UCRL-ID-137767, May, 2000.**

The objective is to develop solid-state electrochemical sensors for safety and fuel monitoring applications

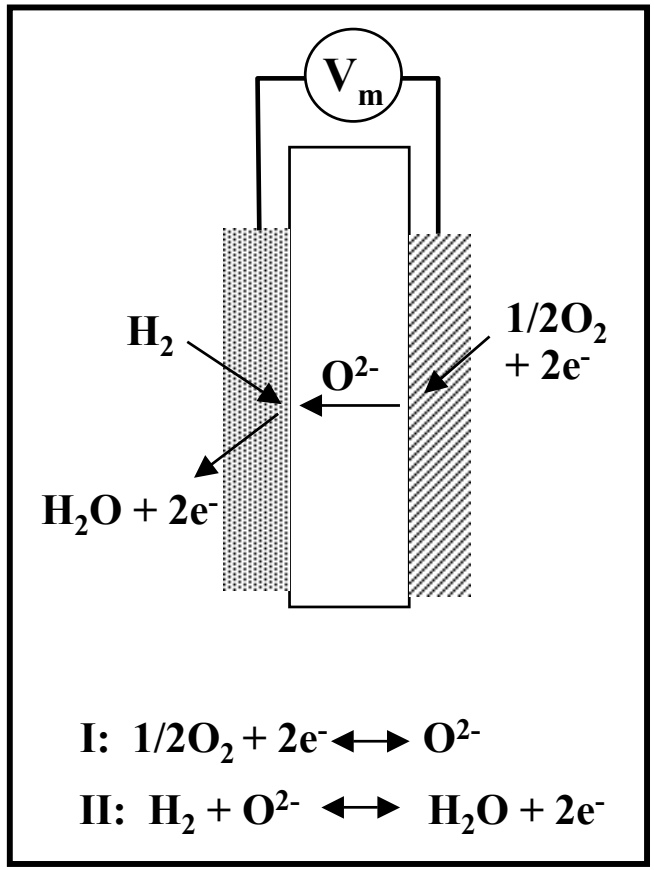
- ***Hydrogen Safety Sensor*** **performance targets*:**
  - **0.1 to 10% hydrogen in ambient air (10 – 98% relative humidity)**
  - **Response time under 1 second**
  - **Selectivity versus hydrocarbons, humidity**
  - **Operating temperature: - 30 to 80 ^{o}C**
- ***Hydrogen Fuel Sensor*** **performance targets*:**
  - **1 to 100% hydrogen concentration**
  - **10 - 30 mol% water, ~15% CO_2, <1% CO and CH_4**
  - **90% response time of 0.1 to 1 second**
  - **Operating Environment : 70-150 ^{o}C, 1-3 atm**

*** From:** ***Sensor Needs and Requirements for Proton Exchange Membrane Fuel Cell Systems and Direct-Injection Engines*****, U.S. DOE, Office of Transportation Technologies, UCRL-ID-137767, May, 2000.**

Safety Sensor: The approach is to apply new electrode materials to well-known oxygen conducting ceramics

- H_2 concentration is determined from the measured potential difference (V_m) between two electrodes
- The electrode potentials result from simultaneous, competing redox reactions
- Electrodes with different catalytic properties will have different steady-state potentials
- In principal, both reactions happen at both electrodes but…
- Electrode materials can be chosen so that:
  - Reaction I dominates @ reference electrode
  - Reaction II dominates @ sensing electrode

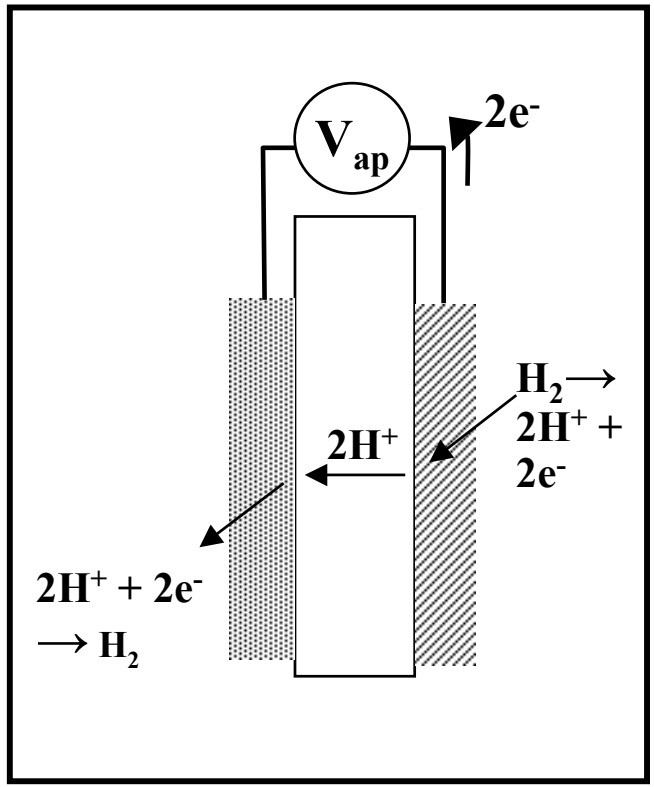
Potentiometric Safety Sensor



Fuel Sensor: The approach is to adapt novel proton conducting ceramics to a traditional sensor concept

- An applied potential (V_{ap}) 'pumps' H^+ ions through the electrolyte
- The resultant current is related to the H_2 concentration
- Most well known proton conducting ceramics either:
  - Are unstable at required H_2O/CO_2 levels
  - Do not have sufficient H^+ conductivity
  - Have unacceptable O^{2-} or e^- conductivity
- Initial efforts are to identify suitable electrolyte/electrode materials

Amperometric Fuel Sensor



A laboratory prototype for the *Safety Sensor* was reported last year

- A non-integrated sensor
  - Tested in furnace hot-zone (not self-heated)
- 2-3 second response time at 500 ^{o}C
  - Response benchmark is 0.2% H_2 in flowing air
- Selectivity to H_2 vs. CH_4 was 10x at 500 ^{o}C
- Sensor stability was excellent for 110 hours at 500 ^{o}C
  - Response to 0.2% H_2: 165±5 mV
  - Baseline in flowing air: 4±4 mV
- Lower temperature resulted in severe overshooting

The 2003 milestones specify completion of the *Safety Sensor* and initiation of the *Fuel Sensor* development

- **Reduce *Safety Sensor* operating temperature below 500 ^{o}C (12/02)**
  - **Sensor operating temperature of 500 ^{o}C is compatible with requirements, but…**
  - **Lower operating temperature reduces power consumption**
- **Complete *Safety Sensor* development (5/03)**
  - **Develop self-heated safety sensor (6/02)**
  - **Characterize response and power consumption (5/03)**
  - **Package for sending out for independent testing (Ford) (5/03)**
- **Evaluate designs for the H_2 *Fuel Sensor* (7/03)**
- **Fabricate first prototype *Fuel Sensor* (9/03)**

Current status: The *Safety Sensor* is nearing completion and the *Fuel Sensor* has been started

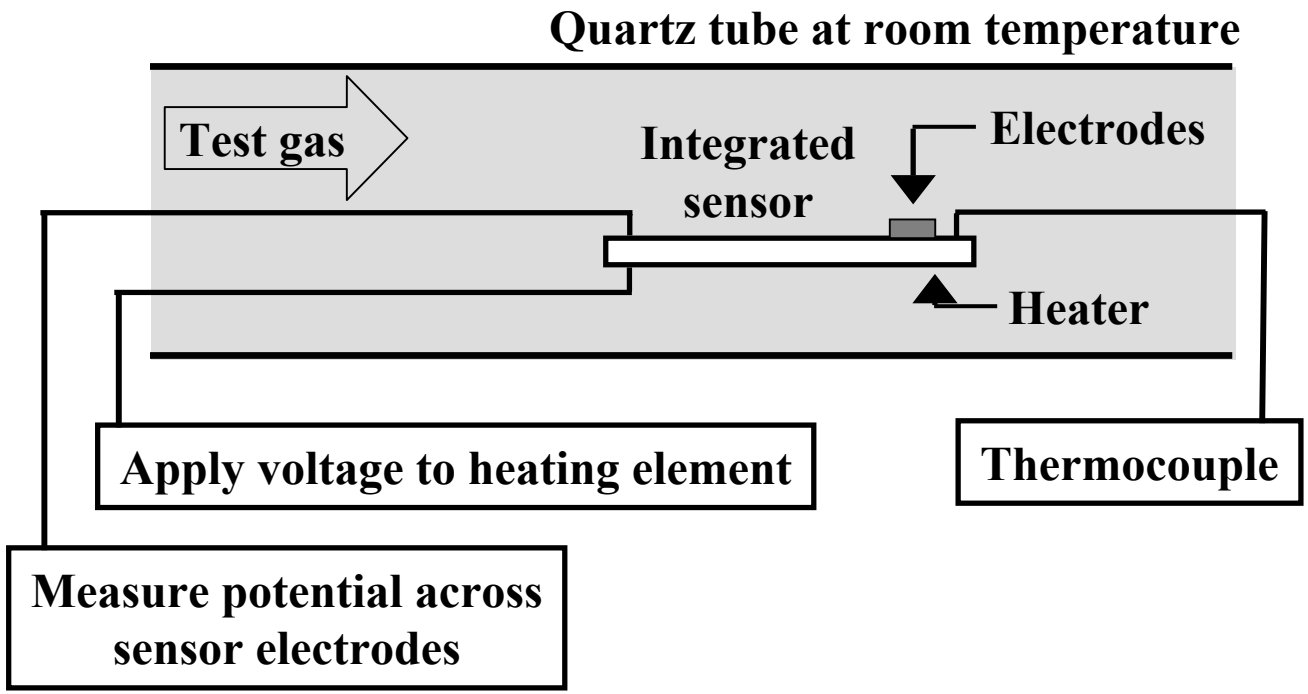
- ***Safety Sensor* development:**
  - **Electrode/electrolyte compositions have been finalized**
  - **Operating temperature has been reduced to 440 ^{o}C**
  - **An integrated, planar heater/sensor design has been established (heated substrates supplied by Ford)**
  - **A packaging concept has been implemented**
  - **External collaborators interested in testing/commercialization are being explored (Ford is currently testing)**

- ***Fuel Sensor* development:**
  - **A candidate electrolyte material has been selected**
  - **Processing techniques have been developed for the electrolyte**
  - **Preliminary laboratory prototypes have been fabricated and are being tested**

The project timeline indicates that we are on schedule…

Task	Year			
	FY 01	FY 02	FY 03	FY 04
H_2 Safety Sensor				
- Select approach/materials	▲			
- Integrated (heated) sensor		▲		
- Complete development			▲	
H_2 Fuel Sensor				
- Select approach/materials			▲	
- Fabricate 1st prototype			▲	
- Complete development				▲

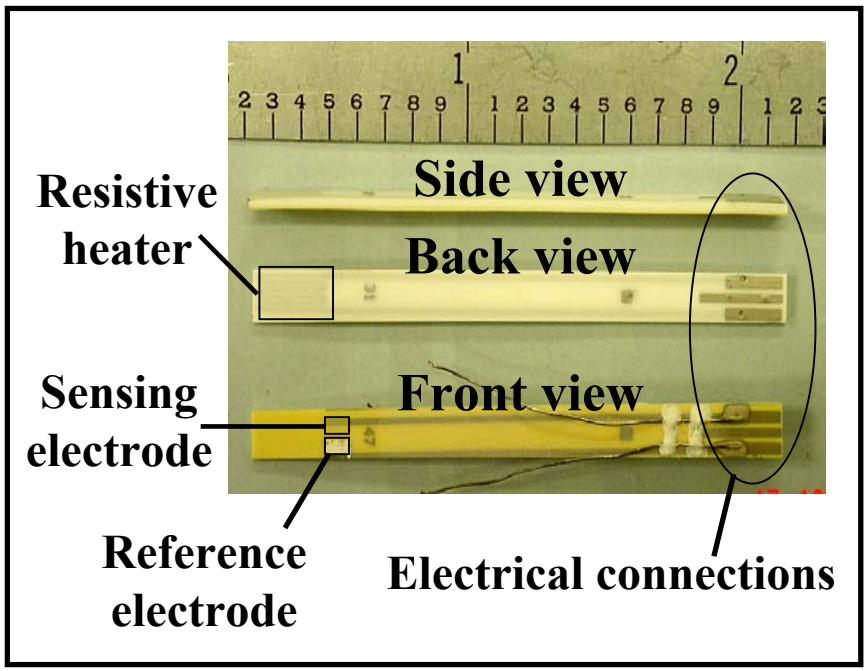
Integrated safety sensors are tested on the bench top by applying a voltage to the heating element



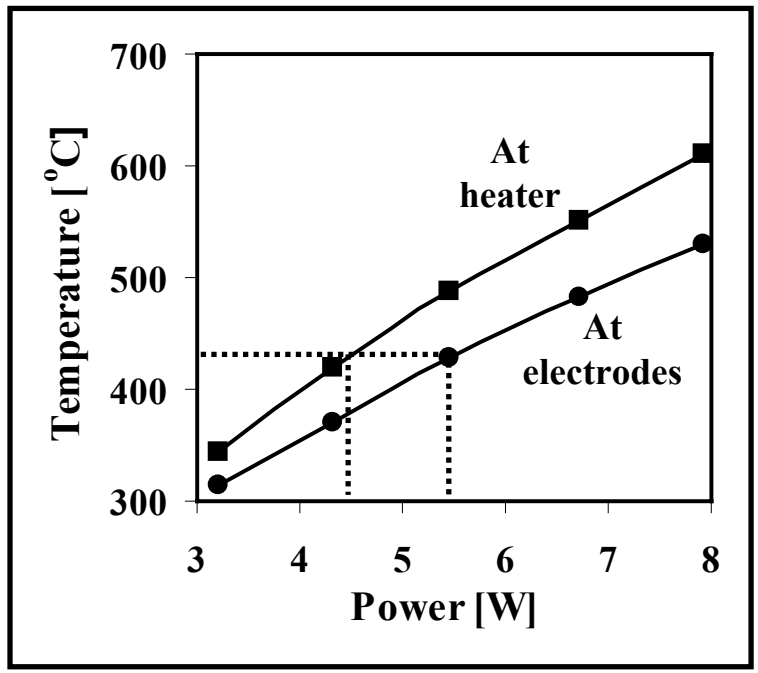
Heated substrates for the integrated sensors were supplied by Rick Soltis of the Ford Research Center

The integrated sensor consumes 5.5 W at the operating temperature of 440 °C…final design will reduce 10-20%

In the current design, the electrodes don't align with the heater:

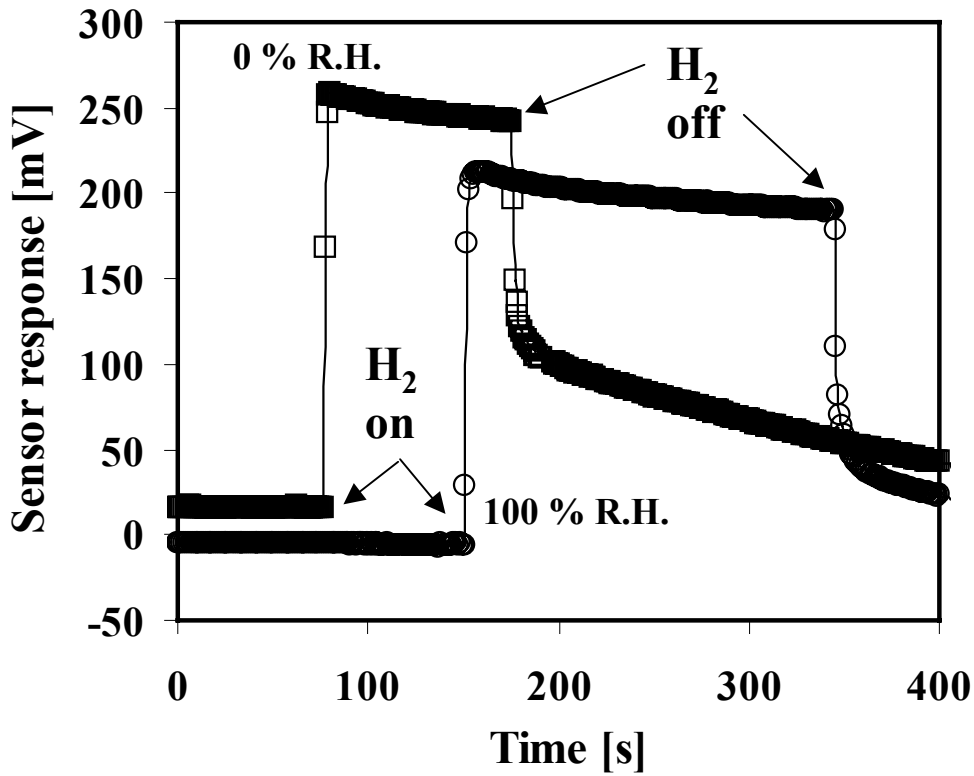


The misalignment requires higher power to heat electrodes:



The final design, currently being built, aligns the heater and electrodes

The integrated sensor responds in ≤ 2 seconds with a slight overshoot

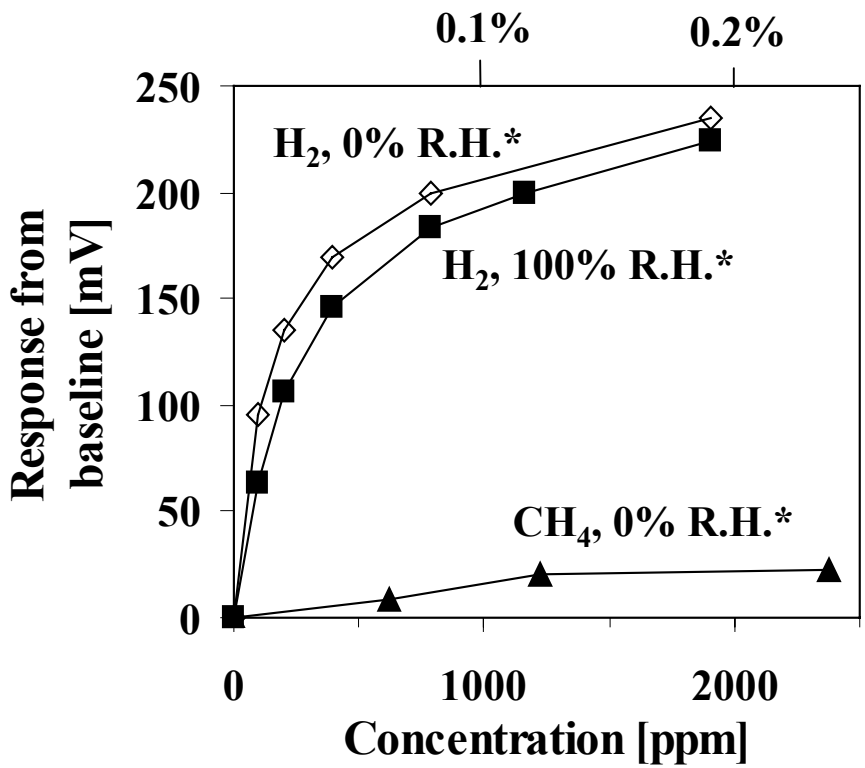


Test conditions:

- Operating temperature 440 °C
- Flowing air: 2 l/min
- 2000 ppm H_2 (0.2%)
- R.H. = Relative humidity
- 1 second between datum points

Electrode composition has been modified (from last year) to reduce selectivity versus humidity at the reduced operating temperature

The selectivity versus methane is high…The low operating temperature causes ~10% sensitivity to H_2O

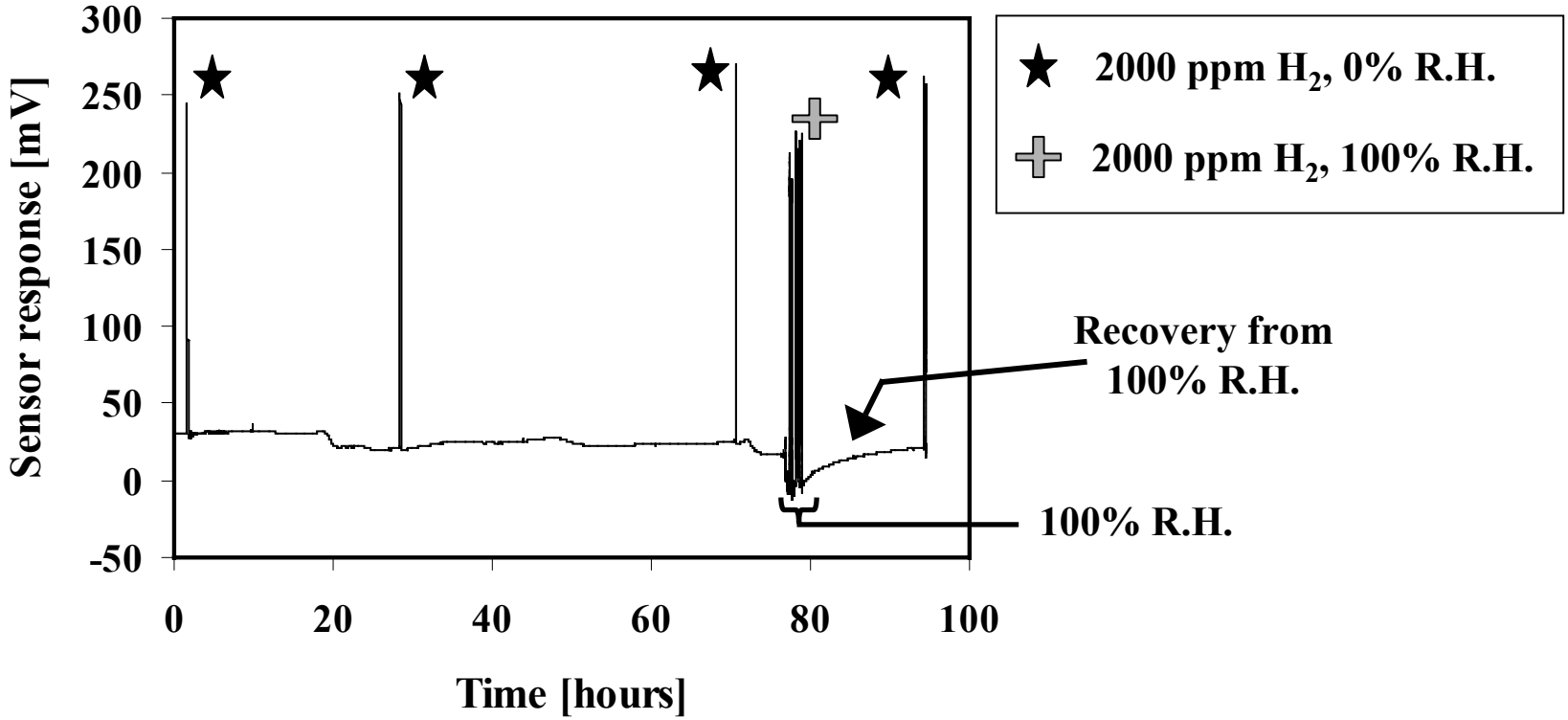


R.H. / 0.2% H_2	0% [mV]	100% [mV]
Baseline	20	-5
Absolute response	250	220
Response from baseline	230	215

*R.H = Relative humidity

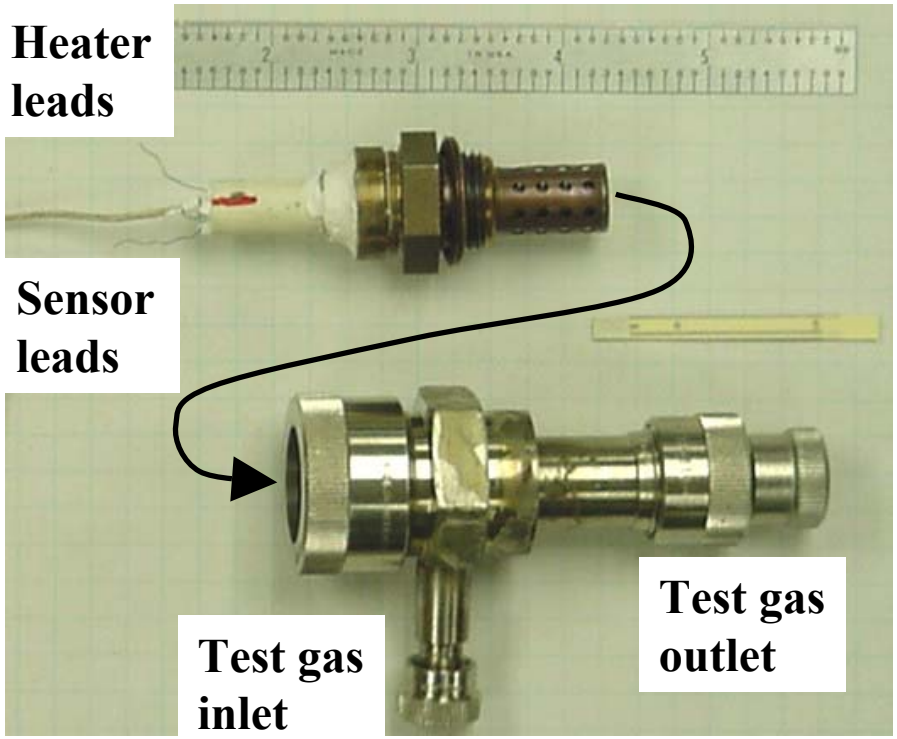
The sensor response saturates at ~300 mV when the H_2 concentration reaches ~2%

Long term testing indicates good baseline stability (no drift) and slow response to H_2O

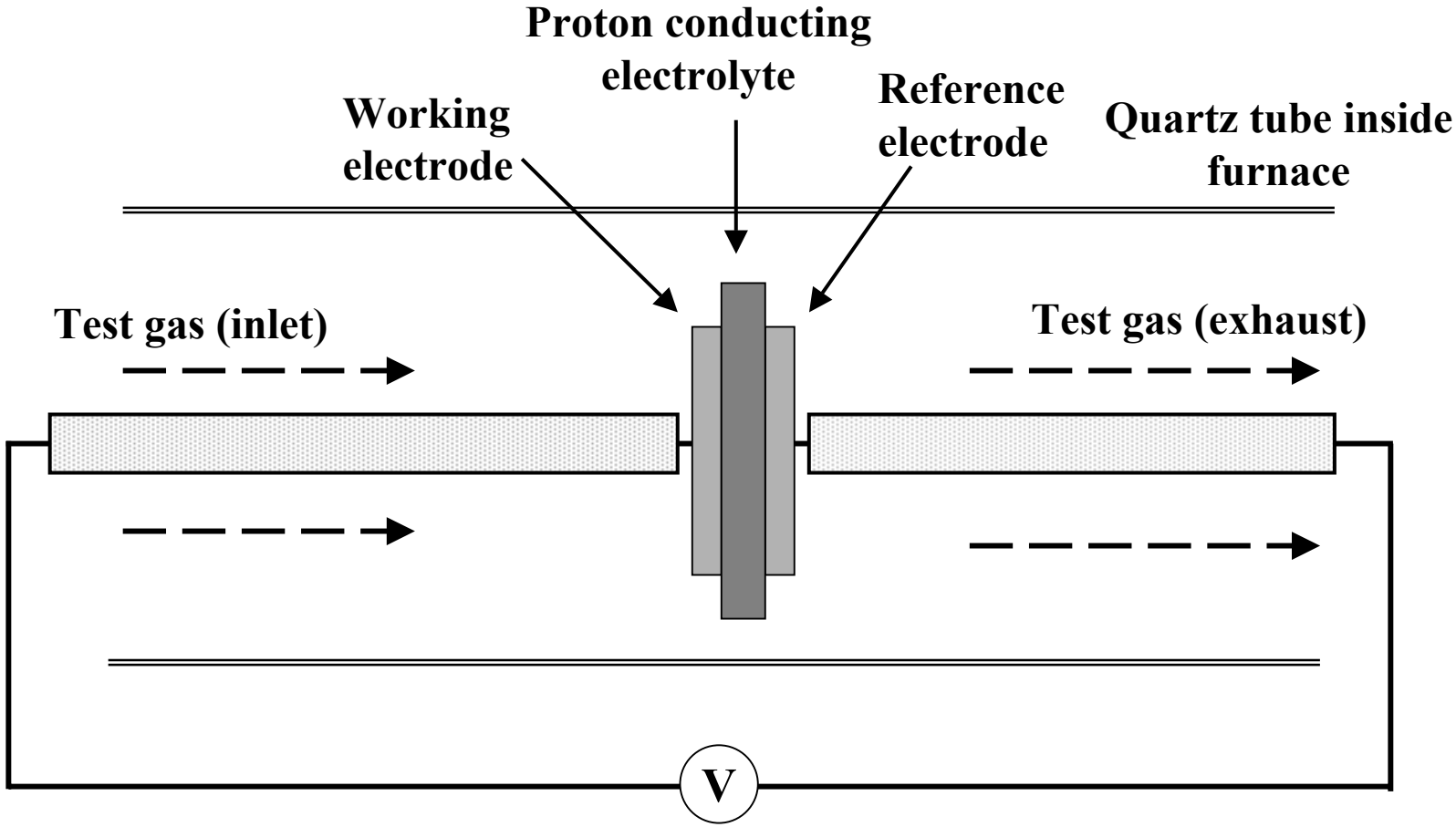


The difference in baseline between 0 and 100% R.H. is equivalent to ~25 ppm H_2 and can be corrected for in the sensor-control software

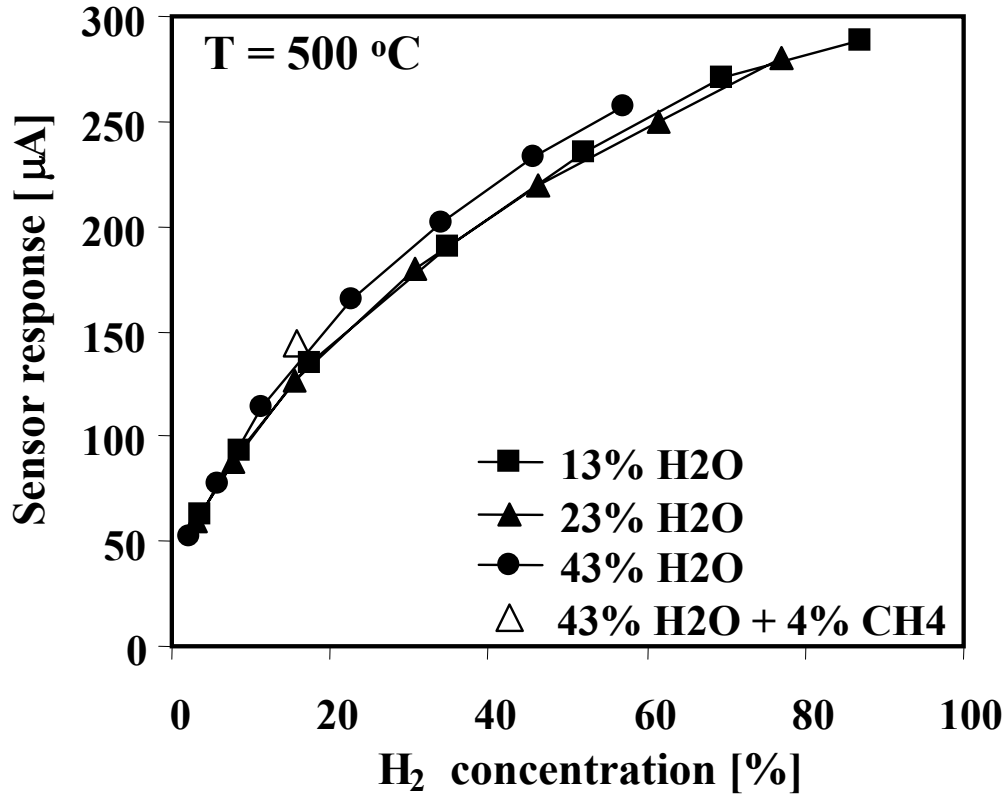
The integrated sensor can be easily packaged in a mountable, protective fixture



Fuel sensors are tested in a furnace by applying a voltage and measuring the current

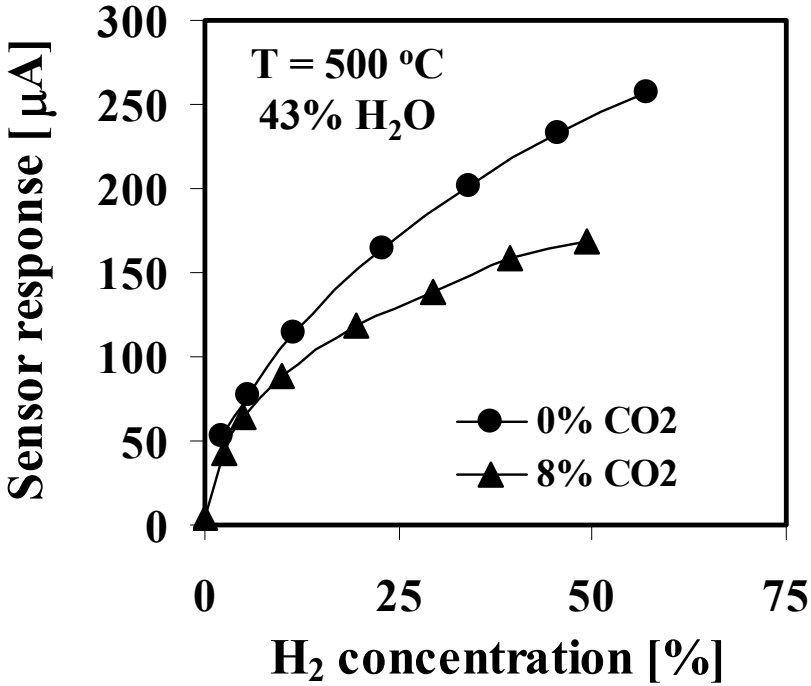


A first prototype of the proposed *Fuel Sensor* shows negligible CH_4 and H_2O cross-sensitivity



The data are promising, but the response is currently too slow (10's of seconds)

Presence of CO_2 causes a reversible signal reduction that may indicate an effect of O_2 partial pressure



- The signal is recovered on removal of the CO_2
- The effect is more severe at higher temperature
- O^{2-} and H^+ conductivities are closely related to oxygen deficiencies
- Oxygen pumps in the opposite direction as the hydrogen
- The mechanism can be clarified by isolating the reference electrode

Long term stability has not been established…

The approach to the Fuel Sensor development is to optimize the electrolyte stability/properties

- **Catalytic experiments to elucidate sensing mechanisms**
  - **Isolated reference electrode**
- **Sensor stability:**
  - **The stability of the electrolyte needs further, and longer term, testing**
  - **Verify phase stability using TGA and XRD**
  - **Stability can be modified by changing stoichiometry, at the expense of conductivity (and vice versa)**
- **Response time (substantial improvement needed):**
  - **Slow response is partially related to experimental setup (gas handling)**
  - **Electrolyte conductivity can be improved with modified stoichiometry**
  - **Operating temperature may limit reaction kinetics (i.e. response time)**
  - **Alternate electrode materials may provide enhanced kinetics**

Future milestones include completing the safety sensor and ramping up the fuel sensor development

- ***Safety Sensor:***
  - **Build final design (once heated substrates are delivered)**
  - **Locate external collaborator interested in testing / commercialization (Ford has agreed to test sensor)**
  - **Ford has expressed interest (supplied heated substrates gratis, currently testing prototype sensor)**

- ***Fuel Sensor (future milestones):***
  - **Evaluate various materials, processing, and designs (7/03)**
  - **Fabricate first prototype (9/03)**
  - **Seek industrial collaboration**
  - **Develop integrated fuel sensor**

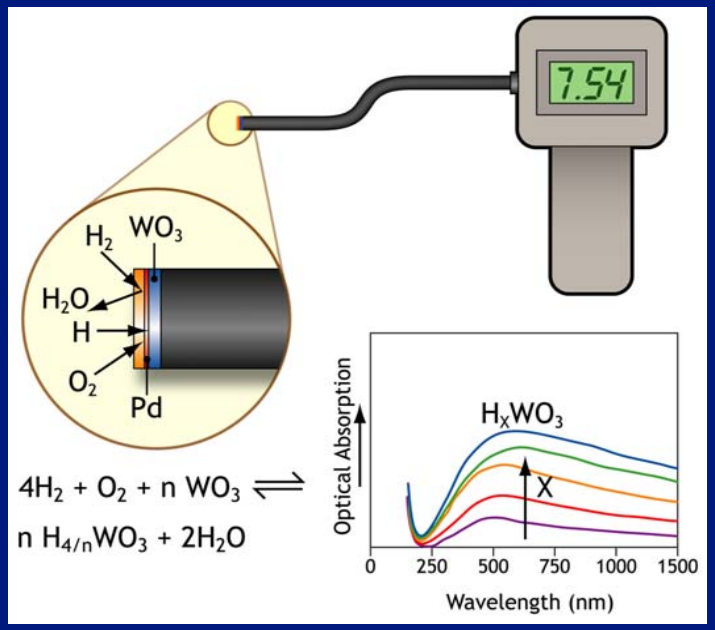
Initial results are promising, but there's a long way to go…

National Renewable Energy Laboratory

Hydrogen Safety Sensor Development

Interfacial Stability of Thin Film Sensors

R. Pitts, Ping Liu,
Dave Smith, Se-Hee Lee,
Ed Tracy



May 22, 2003

Program Relevance

- **Hydrogen Safety:** "**A catastrophic failure in a Program-funded project could cause irreparable damage to the entire transition strategy**. The Safety Plan delineates the steps that the Program is taking (including the use of safety sensors) to ensure that its projects are performed in a safe manner. … **Safety devices, including sensors**, fail-safes, and interlocks, are an integral part of any hydrogen process and must be included in all system designs."

- **Hydrogen Delivery (Pipelines):** "Develop lower cost material, seals, components, **sensors**, and controls."

- **Fuel Cells:** "Program objectives will be accomplished through R&D on materials and components as well as on high-volume manufacturing processes for fuel cells, fuel processors, and balance-of-plant components such as air compressors, and **sensors** and controls."

NREL

Safety Sensor Performance Goals

- Measurement range: 0.1–10% H_2 in air
- Operating temperature: -30–80 °C
- Response time: <1 s
- Accuracy: 5%
- Gas environment: ambient air, 10–98% RH range
- Lifetime: 5 y
- Interference resistant (e.g., hydrocarbons)

NREL

Approach

1. Use thin film materials that change color in the presence of hydrogen.
2. Optimize film structure to be selectively sensitive to hydrogen.
3. Probe optical state of films remotely with light beam.
4. Use design criteria to provide:
    - Stable, repeatable signal
    - Long service lifetime
    - Easy servicing (replacement)
    - Low cost optical elements

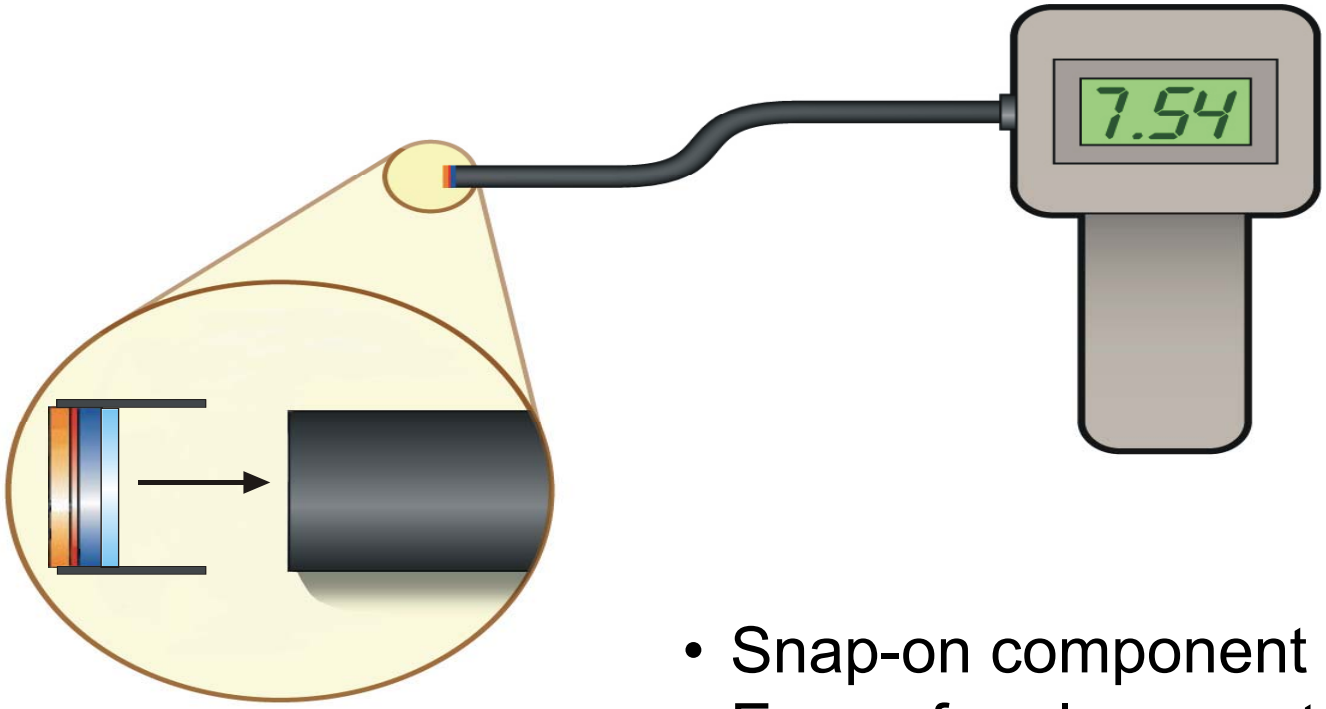
NREL

Why Thin Film/Fiber-Optic Sensor

- Inherently safe for detecting hydrogen leaks in air (no ignition energy source at the leak site).
- Immunity to electromagnetic interference.
- Can be fabricated in high volumes at low-cost (one control, many sensor heads).

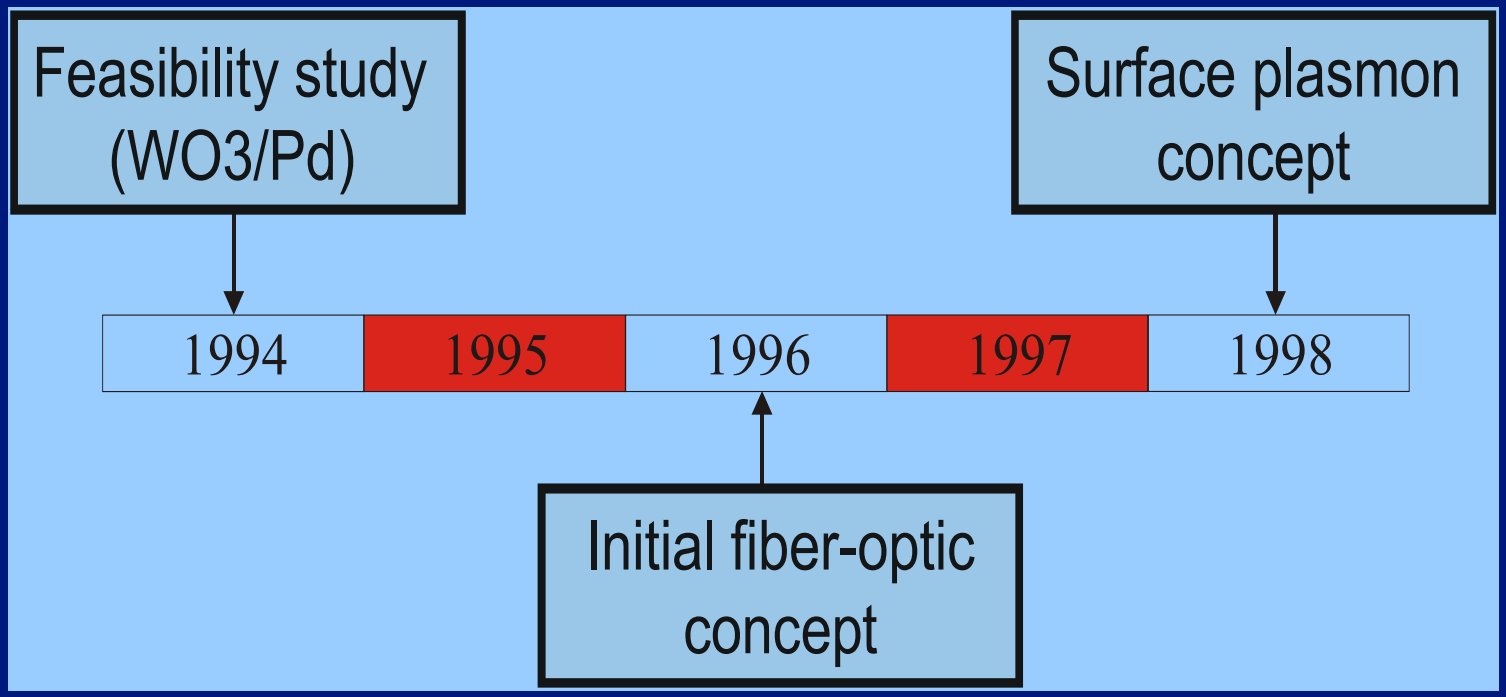
NREL

Quick-connect Sensor Head

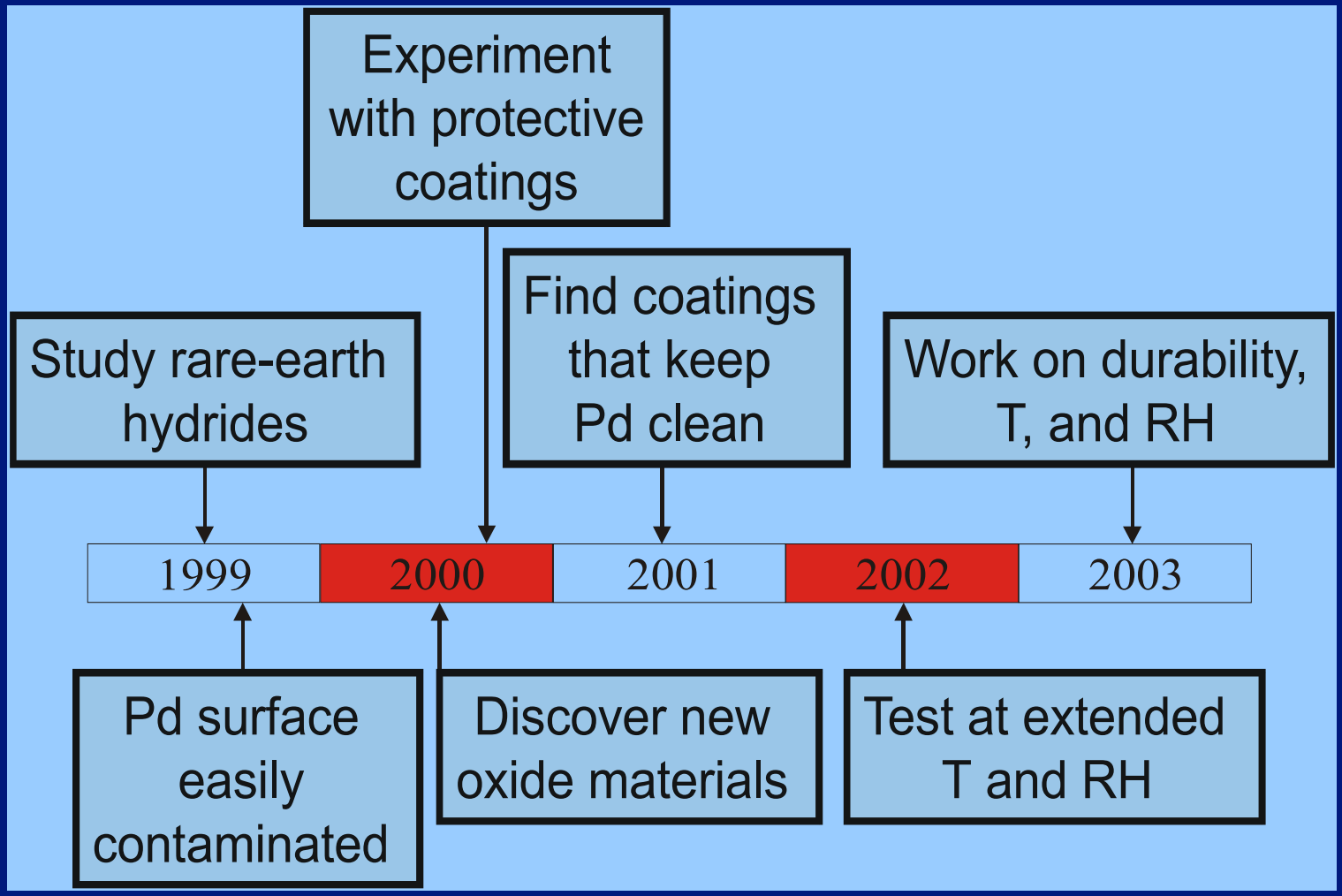


- Snap-on component
- Ease of replacement
- Low cost

Project Time-line



Time-line (continued)



Accomplishments

- **Milestone 1 (Feb. 2003):** Test thermal and relative humidity response in an interim target range of -10 to +60 ºC. This was done, reported, and extended to a range of -20 to +80 ºC by 4/03.

- **Milestone 2 (Aug. 2003):** Modify proprietary inorganic coating for the Pd catalyst to improve performance and increase sensor longevity (interim target lifetime 2 years). Test performance with accelerated as well as real time tests. This cannot be done on time, due to unanticipated technical (scientific) issues as well as funding issues.

NREL

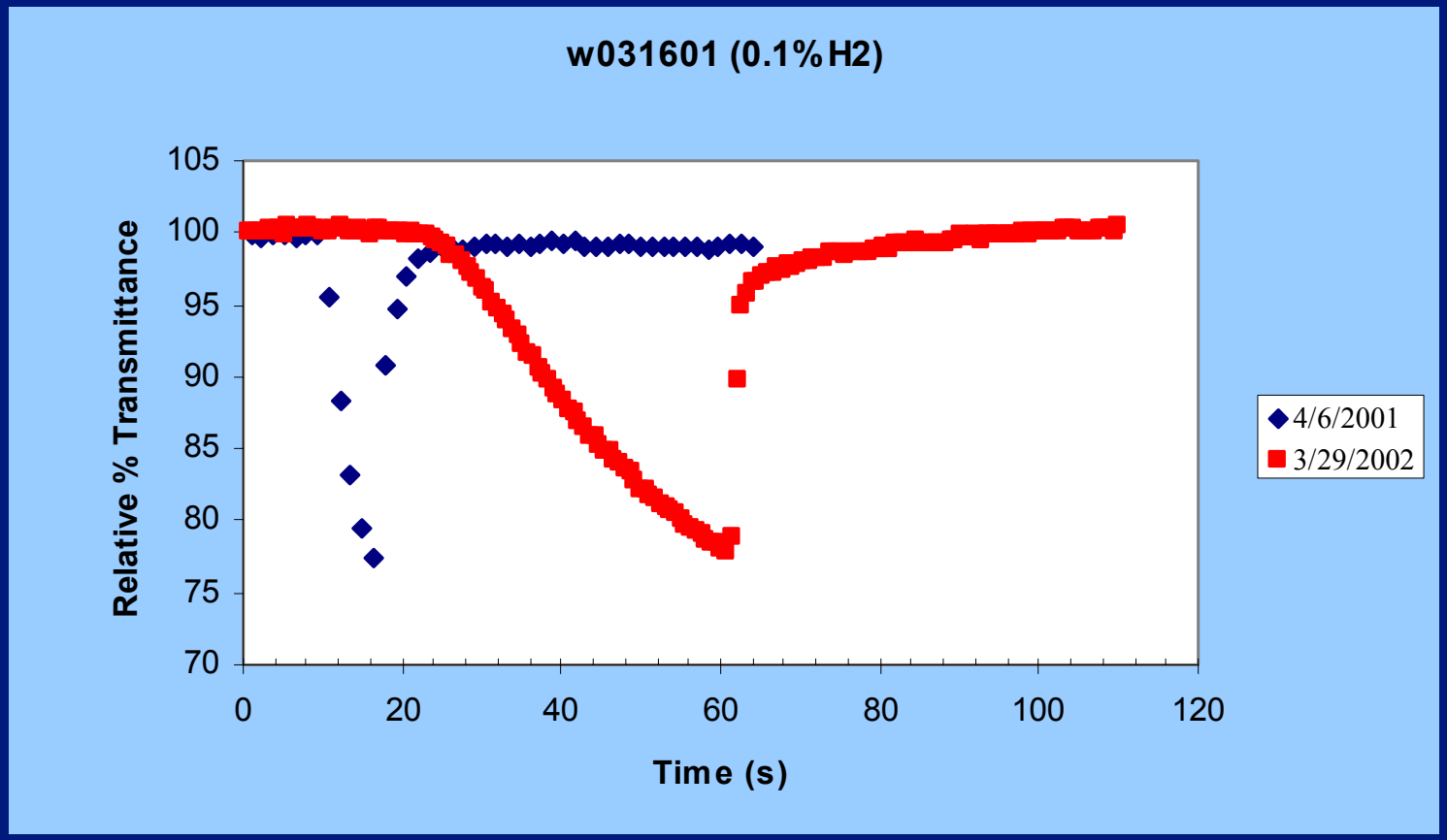
Accomplishments

- **Milestone 3 (May 2003):** Perform experiments with new polymeric, CVD coatings to determine the level of protection from liquid water. Target flat plate sensor lifetime of 2 weeks in aqueous media. Also determine if these coatings can be used to expand the sensor measurement range below 0 ºC. This milestone was delayed due to funding issues.

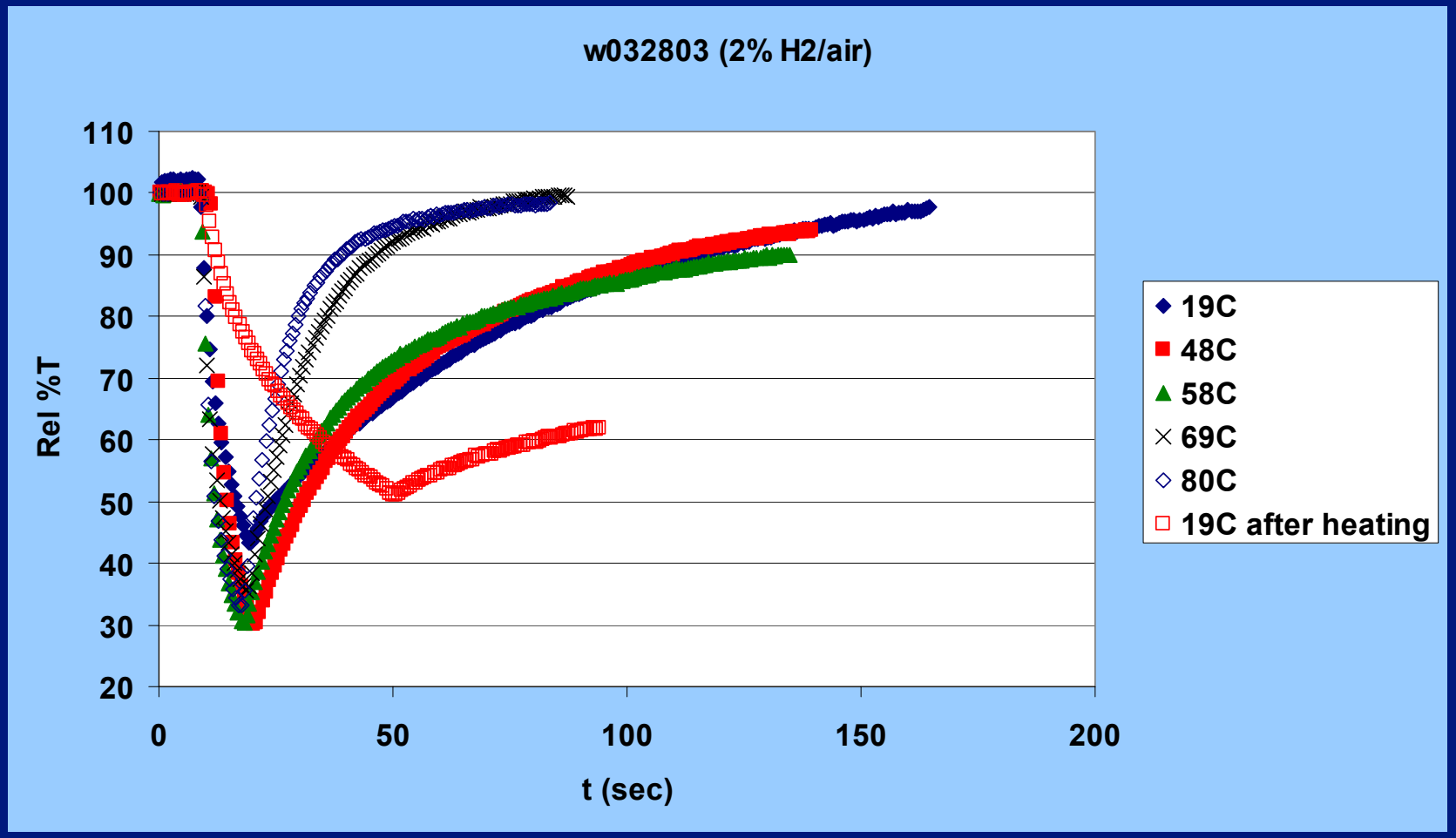
- **Milestone 4 (Aug. 2003):** Provide support for the bio-hydrogen production project by making large area sensor plates. Begin negotiations for technology transfer by end of year. The first element has been done, but the second element has been delayed by funding issues.

NREL

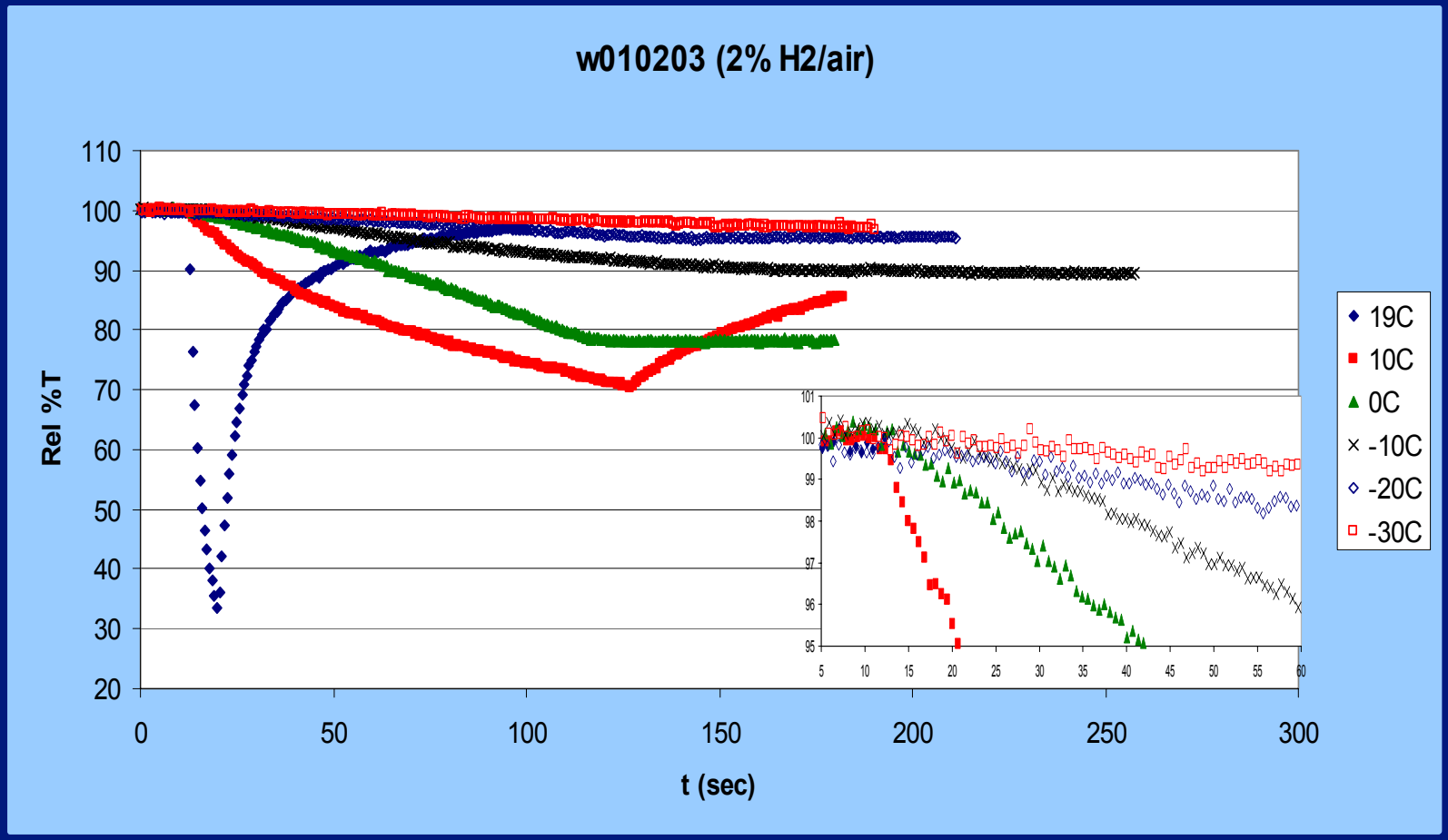
Response after 1 Year



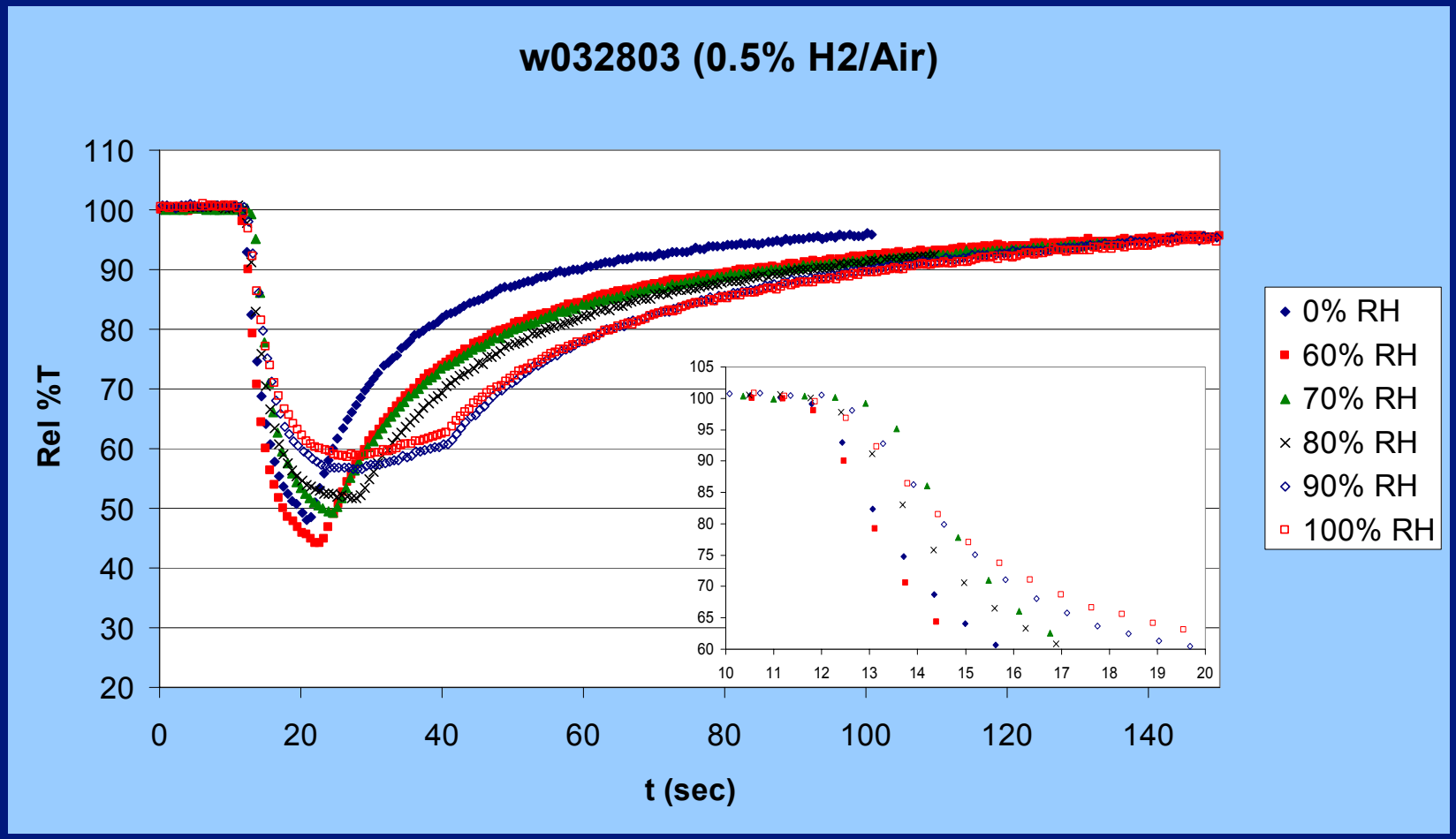
Response at Elevated Temperature



Response at Low Temperatures



Response at Various Relative Humidities



Safety Sensor Status

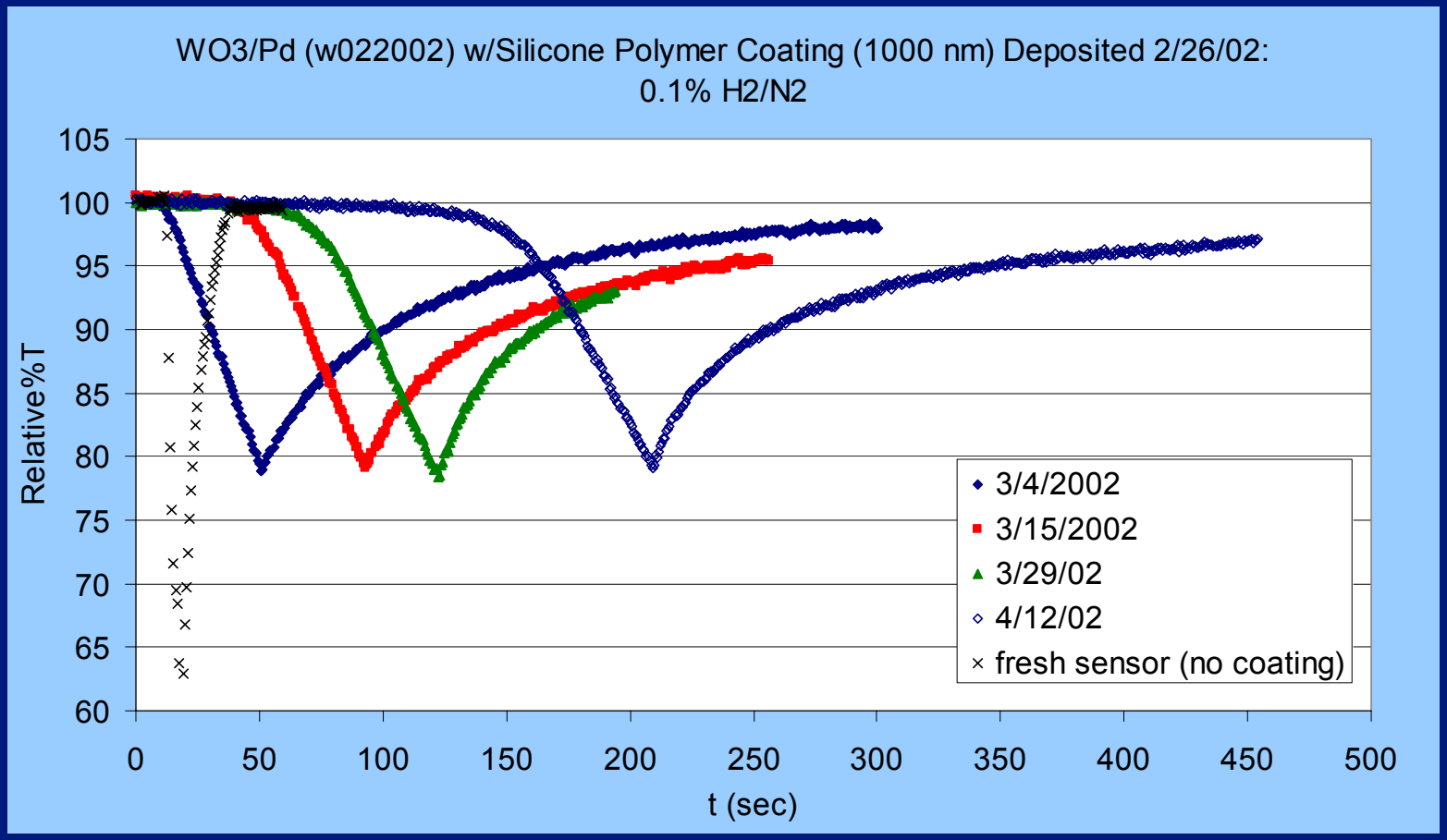
- Measurement range: 0.02 – 10% H_2 in air
- Operating temperature: -20 – +80 °C
- Response time: <1 s
- Accuracy: needs to be determined
- Gas environment: ambient air, 0 – 100% RH range
- Lifetime: 1 y
- Interference resistant (e.g., all other gases)

Significant Interactions

- 3 year CRADA with DCH Technologies for sensor development terminated at the end of FY01.
- Interaction with GVD Corporation on protective polymer films for bio-sensors.
- Responded to requests to provide measurement services for a small business.
- Interaction with Element 1 on potential collaborative work in related area.
- Interaction with Davidson Instruments on fiber-optic based sensors.

NREL

CVD Polymer Coating (GVD)



Response to Reviewers Comments

- Review workshop report for sensor design targets. (Done, targets modified beginning Qtr. 3, 2002)
- Resolve adverse effects of humidity and temperature. (Progress demonstrated, more work needed)
- Projected cost of sensors and control package still questioned. (Design study planned FY03, but delayed by funding issues)

Plans for FY 2004

- Continue fundamental study of best protective coating.
- Investigate ability of polymeric coatings to improve low temperature and high humidity response.
- Expand collaboration with private sector to design complete sensor package and perform cost analysis.
- Fabricate prototype.

NREL

Conclusions

- Fiber-optic H_2 sensors based upon chromogenic materials are sensitive, durable, and potentially low-cost.
- Performance is close to DOE goals for safety sensors. Durability is the primary issue.
- Fouling of the hydrogen dissociation catalyst can be controlled. However, fundamental work is needed to fully understand the material science aspects of the protective coating.
- Hotwire polymeric films with controlled morphology and surface properties hold promise for superior protection in wet environments.
- Technology transfer is on the horizon.

NREL

Development of Sensors for Automotive PEM-based Fuel Cells

DOE Agreement DE-FC04-02AL67616

United Technologies

Brian Knight – UTRC

Nancy Garland - DOE

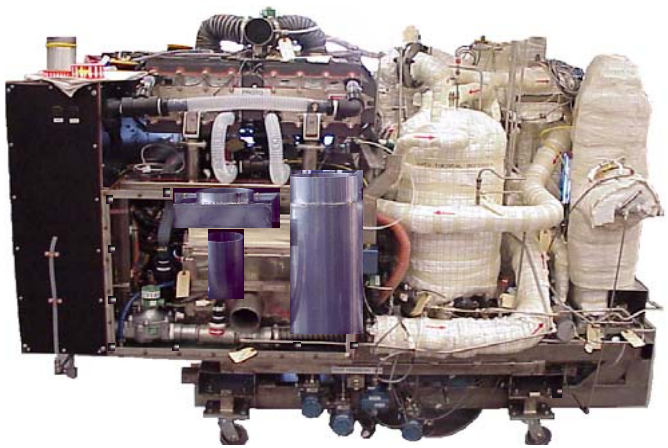
UTC Fuel Cells

A United Technologies Company

Research Center

DOE Hydrogen and Fuel Cells 2003 Annual Merit Review

May 22, 2003

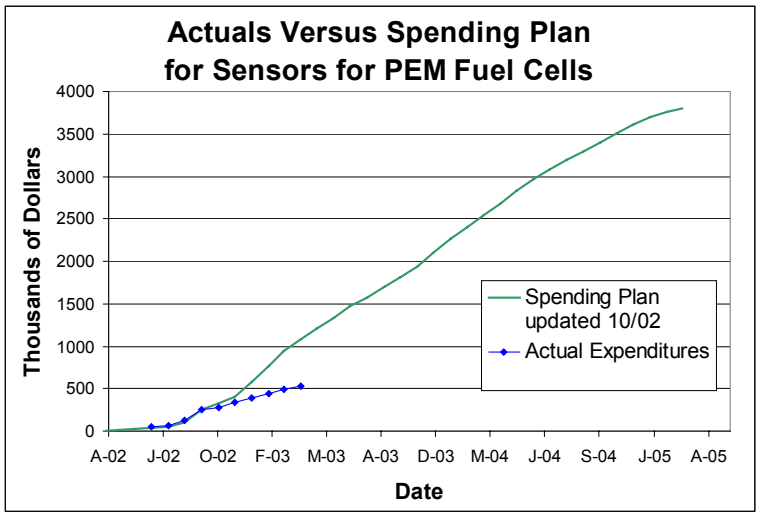


UTC FC Series 200 - 50 kW PEM

Development of Sensors for Automotive PEM-based Fuel Cells – Program Summary

- Project duration: 36 months (Apr 2002 – March 2005)

- Total cost: $3.7MM;
- DOE cost: $3.0MM (80%)
- UTC Cost Share: $0.7MM (20%)
- Total expended to date: $0.51MM



- Project Team
  - UTC Fuel Cells
  - UTRC
  - ATMI
  - Illinois Institute of Technology (IIT)
  - NexTech Materials

- Project Director: Tom Clark UTC FC

Sensors for Automotive PEM-based Fuel Cells Project

Team organization

UTC Fuel Cells
A United Technologies Company

United Technologies
Research Center

DOE program manager and technical advisor:

Name	Affiliation	Phone	E-mail
Nancy Garland	DOE	202-586-5673	nancy.garland@ee.doe.gov
Robert Sutton	ANL	630-252-4321	sutton@cmt.anl.gov

Contractor and subcontractor PIs:

Name	Affiliation	Phone	E-mail
Tom Clark	UTCFC	860-727-2287	tom.clark@utcfuelcells.com
Brian Knight	UTRC	860-610-7293	knightba@utrc.utc.com
Frank DiMeo	ATMI	203-794-1100 x4279	fdimeo@atmi.com
Joe Stetter	IIT	312-567-3443	stetter@iit.edu
Scott Swartz	NexTech	614-842-6606 x103	swartz@nextechmaterials.com

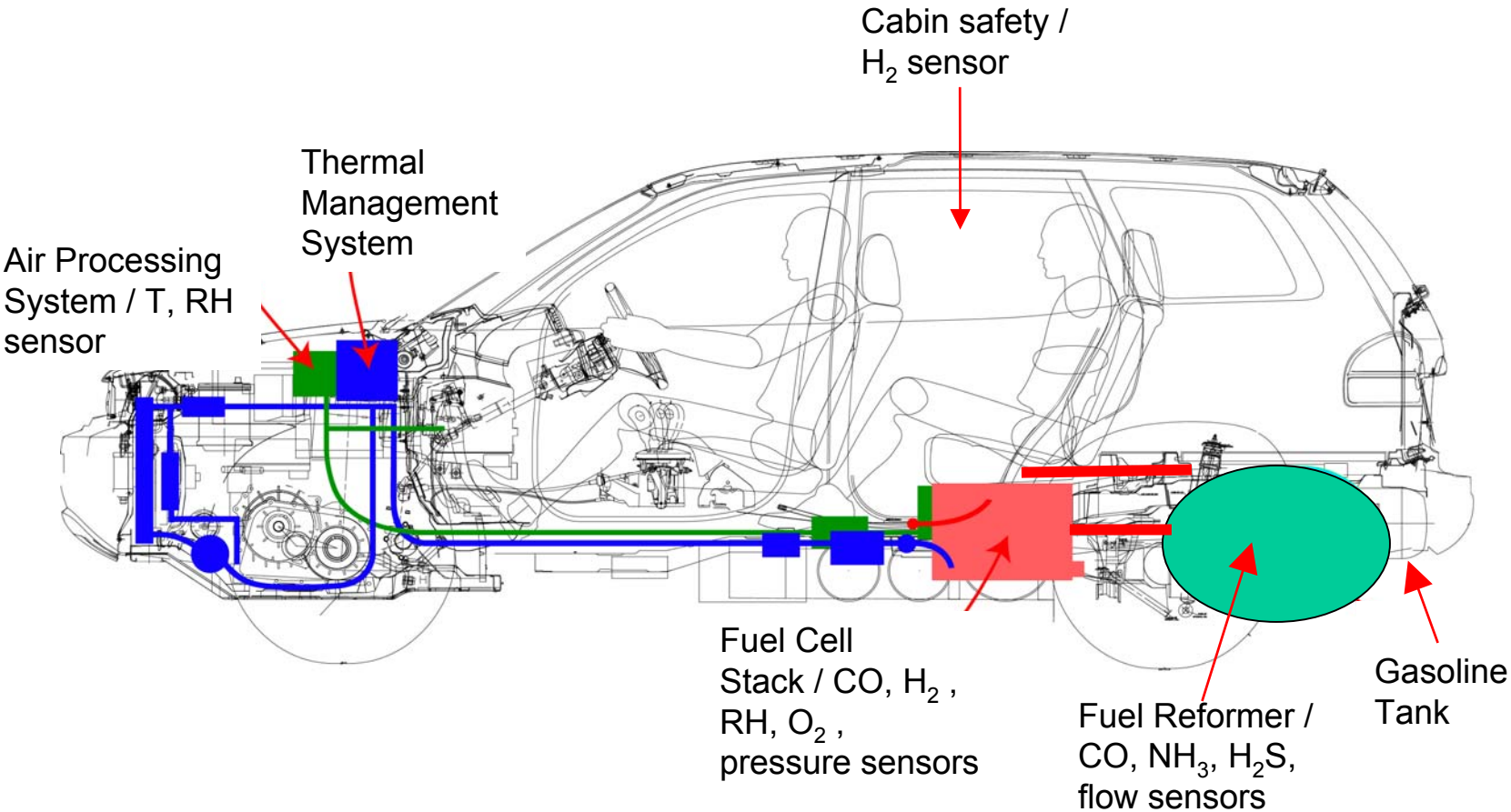
ATMI

ILLINOIS INSTITUTE OF TECHNOLOGY
Transforming Lives.Inventing the Future.www.iit.edu

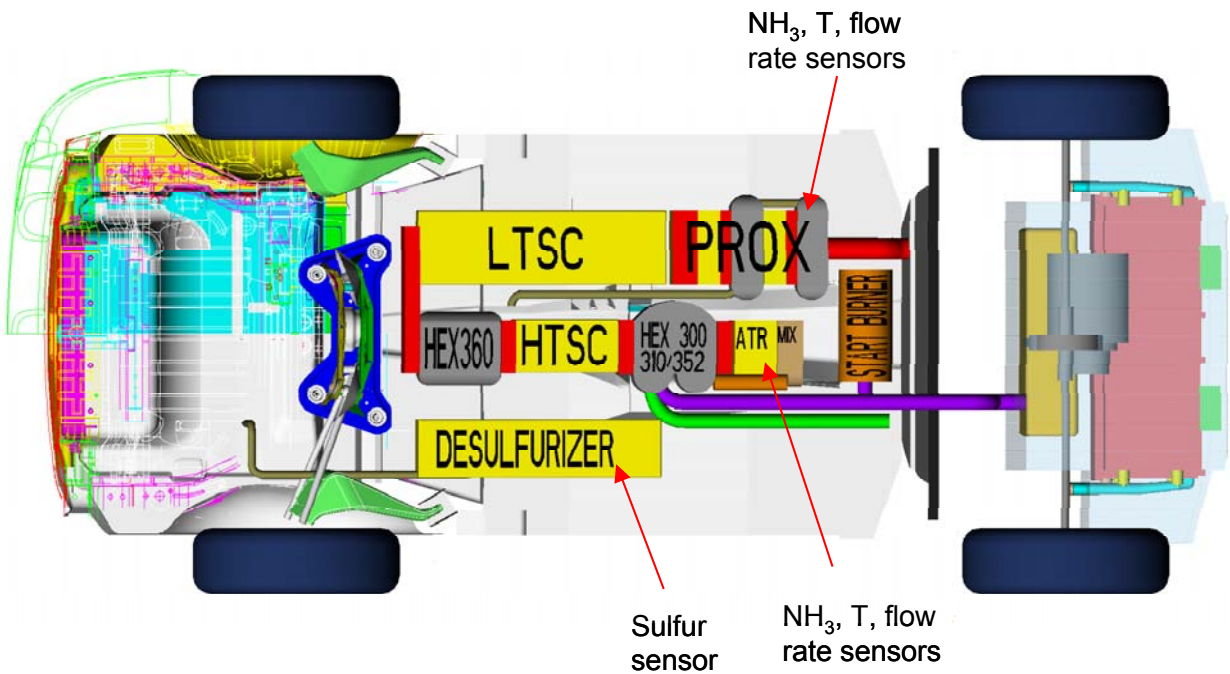
NEXTECH MATERIALS

Sensors for Automotive PEM Fuel Cells - Motivation

Sensor Performance and Cost Improvements Needed



Gasoline Fuel Reformer – Sensor Needs



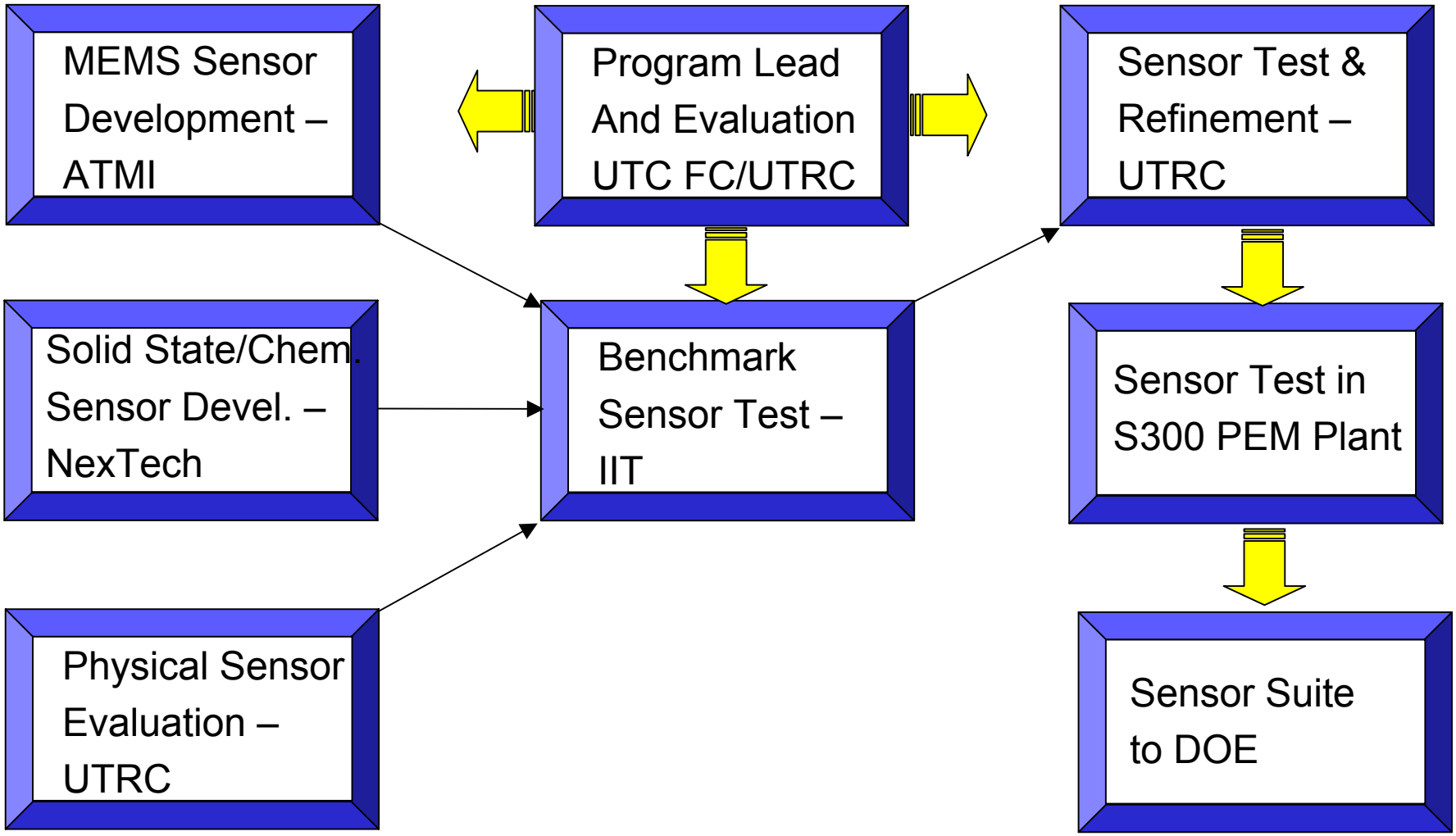
- Chemical sensors
  - –Process streams: before, in, and after reformer, before and in fuel cell stack: CO, H_2, O_2, H_2S, NH_3.
  - –Safety [H_2].
  - –Response times compatible with function being monitored.

Sensor Program Deliverables - Task 1 Milestone 22

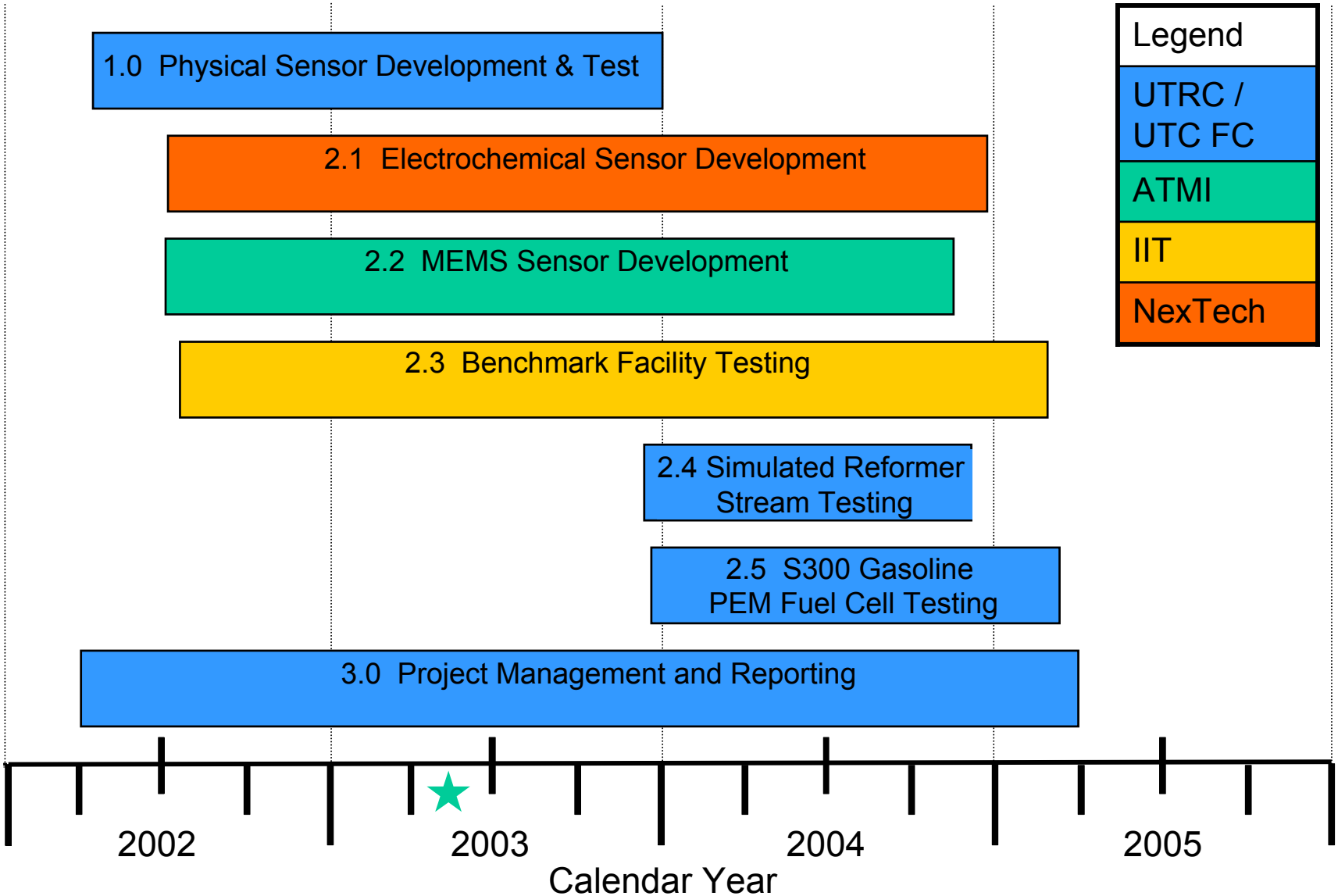
- Automotive PEM Fuel Cell Sensors Suite
  - Develop suite of sensors for CO, H_2, O_2, H_2S, NH_3, flow, temperature, pressure, and relative humidity
  - Meet performance requirements
  - Develop new measurement principles to meet sensitivity requirements
  - Improve reliability in harsh fuel cell system environments
  - Path to low cost (<$10 / sensor) at 500k qty
  - Develop test rig for sensor evaluation
- Program Reporting
  - Quarterly progress reviews
  - Annual and Final technical reports

Sensor Program Team Responsibilities

Team Member	T	ΔP	RH	flow	O_2	CO	H_2	SO_2	H_2S	NH_3	Technological Expertise / Responsibility
UTC FC	X	X	X	X	X	X	X	X	X	X	Testing on S300 Breadboard
UTRC	X	X	X	X	X	X	X	X	X	X	Testing in reformate simulator
ATMI							X	X	X	X	Develop Using MEMS Silicon Microhotplate
IIT	X		X		X	X	X	X	X	X	Testing in Benchmark Facility
NexTech						X		X	X	X	Develop Using Solid State Electrochemical


MEMS Sensor Development – ATMI
Program Lead And Evaluation UTC FC/UTRC
Sensor Test & Refinement – UTRC
Solid State/Chem. Sensor Devel. – NexTech
Benchmark Sensor Test – IIT
Sensor Test in S300 PEM Plant
Physical Sensor Evaluation – UTRC
Sensor Suite to DOE

Sensors for Fuel Cells Program Plan



Milestones and Deliverables

	Target Date
•Physical Sensors – UTRC	
—Develop physical and chemical sensor test facility	04/15/03
—Physical sensors survey and down-select	06/30/03
—Physical sensor test in simulated reformate stream	11/14/03
—Physical sensor performance review	11/24/03
•MEMS Sensor Development – ATMI	
—Deliver α prototype H2 sensor to IIT	04/14/03
—Deliver β prototype H2 sensor to UTRC	12/10/03
—Sensor performance review #1	02/04/04
—Deliver α prototype Sulfur sensor to IIT	08/25/03
—Deliver β prototype Sulfur sensor to UTRC	04/21/04
—Sensor performance review #2	06/17/04
—Deliver α prototype NH3 sensor to IIT	12/19/03
—Deliver β prototype NH3 sensor to UTRC	08/18/04
—Prototype delivery to UTC FC	10/21/04

Milestones and Deliverables

•Electrochemical Sensor Development – NexTech	Target Date
—Deliver α prototype CO, NH3, S-compound sensors to IIT	07/07/03*
—Sensor response optimization	09/30/03
—Sensor performance review #1	10/03/03
—Deliver β prototype CO, NH3, S-compound sensors to IIT	04/30/04
—Sensor performance review #2	06/25/04
—Deliver final prototypes to UTC FC	12/15/04

* Dependent upon budget release from DOE

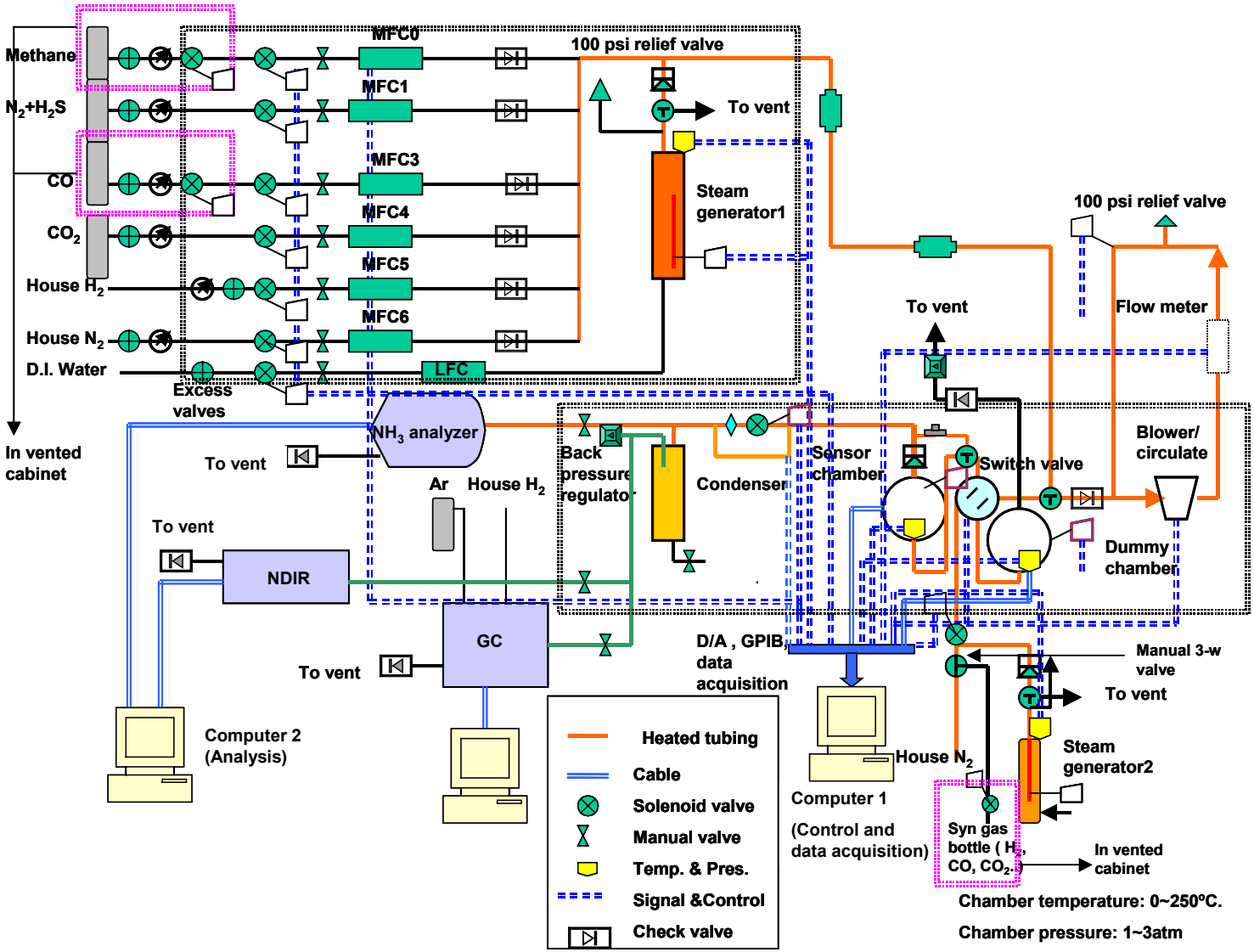
Milestones and Deliverables

	Target Date
•Benchmark Facility Testing – IIT	
—Overall sensor performance review	01/02/04
—Performance analysis and interface design	02/11/05
•S300 Gasoline PEM fuel cell testing – UTC FC	
—Physical sensor testing	06/15/04
—Chemical sensor testing	02/28/05
—Deliver sensor suite to DOE for go/no go decision	03/15/05

Technical Progress

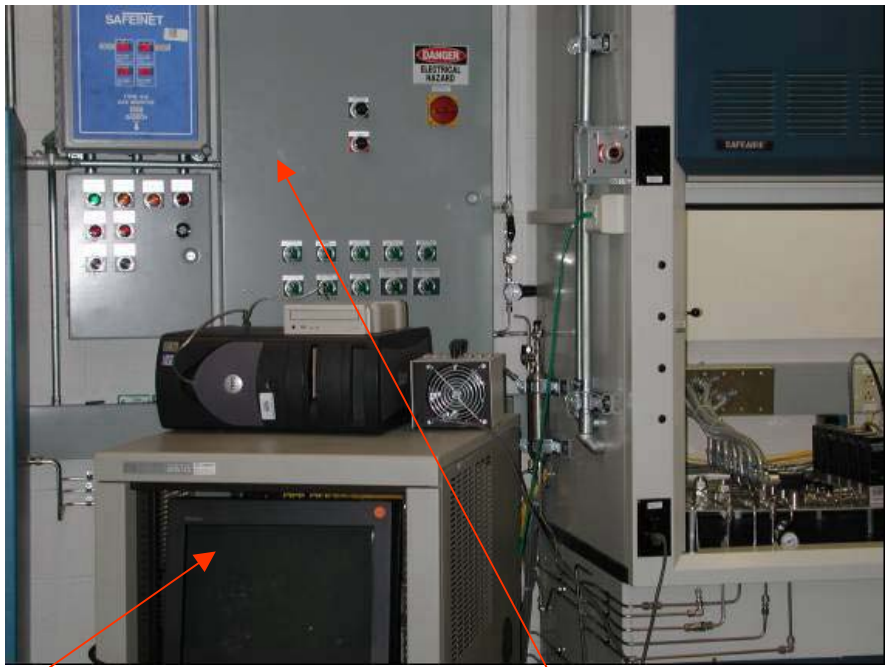
- ATMI
  - Alpha prototype H2 sensor delivered to IIT
- IIT
  - Modifying facility for new sensors; starting H2 sensor tests
- NexTech
  - Modifying CO sensor for integration with IIT/UTRC test facilities
- UTRC
  - Sensor Test Rig and Software Development complete
  - Preliminary Physical Sensor survey completed
    - Most promising technologies and corresponding vendors are identified; presently interacting with vendors and obtaining samples.

PEM Fuel Cell Gas Stream Simulator and Sensor Testing Rig



Sensor Test Facility at UTRC

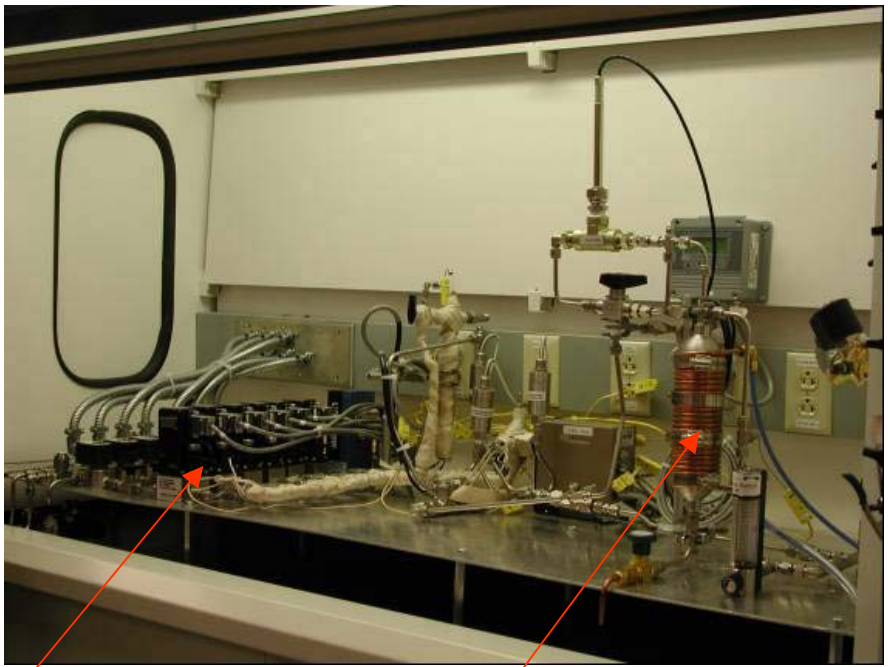
Overall System and Controls



Data Acquisition
And Control Computer

Facility Interface and
Safety System Control

Gas Flow Control and Test Chamber



Mass Flow Controllers

Steam Condenser

Physical Sensor Survey

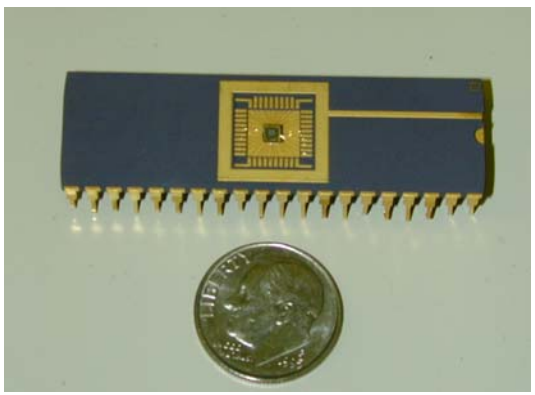
- Humidity Sensors
  - —Polymer Capacitive and MEMS Strain Gauge investigated
- Flow Rate Sensors
  - —Ultrasonic vortex shedding
  - —Turbine meter
  - —Thermal Dissipation
  - —Differential pressure flow sensing
- Differential Pressure Sensors
  - —Strain gauge
- Temperature Sensors
  - —Thermocouples, thermistors and RTD's

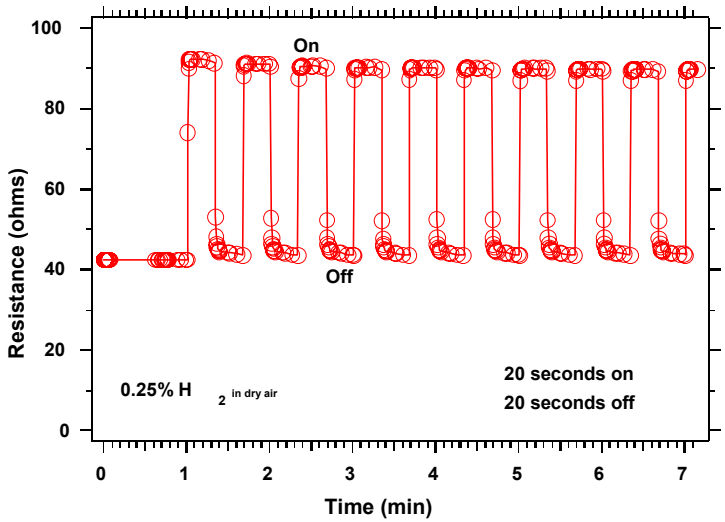
Selection of Physical Sensors for PEM Fuel Cell Power Plant

Technical and Cost Gap Findings

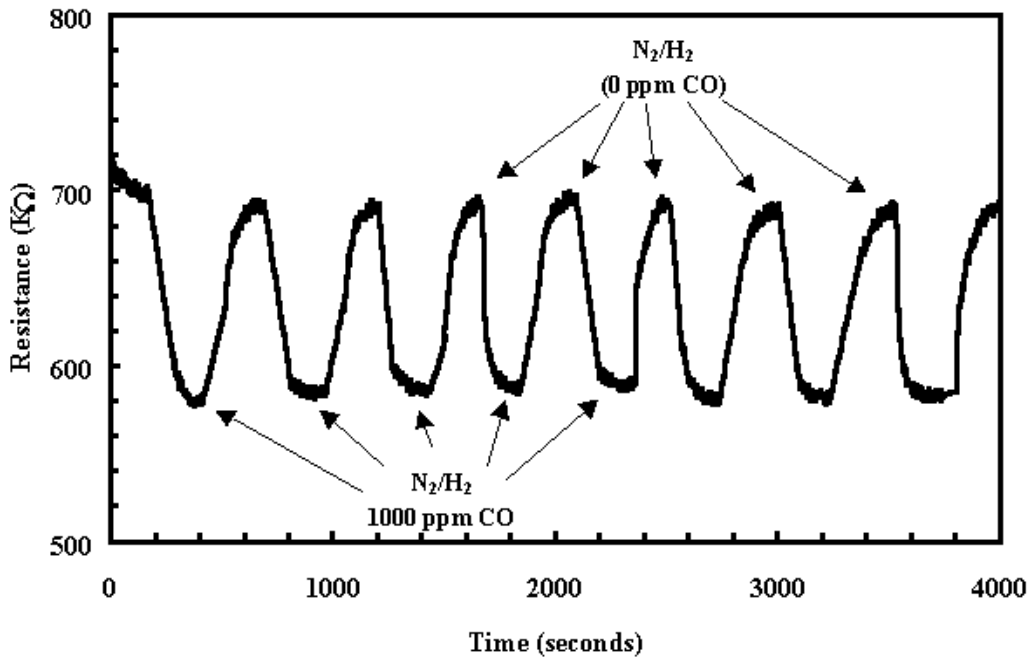
Sensor	Meet DOE/FC tech. specs	Further effort	Technical / Cost gap
Humidity	Most	Validate new technologies (MEMS sensors) to improve the condensation recovery time.	Medium
Flow rate	Most	Collaborate with vendors to improve stability. Identify new technologies.	High
Differential pressure	Most	Collaborate with vendor for miniaturization and significant cost reduction. Needs major development and modifications.	Medium
Temperature	Most	Identify inexpensive thermistor for high temp. Improve response time.	Low

- ATMI
  - H_2, SO_2, H_2S, NH_3 Sensor Development
  - Patented micro hotplate for H_2 detection
  - New sensing technologies being explored for fast response, sensitivity, and cost reduction





- NexTech Materials
  - –CO, SO_2, H_2S, and NH_3 Sensor Development
  - –Demonstrated sensitivity for ppm level CO in 75% H_2
  - –New sensing materials and technologies being explored for PEM systems to meet sensitivity, robustness, and cost requirements



Effect of carbon monoxide (1000 ppm) on resistance of NexTech sensor in a baseline gas composition of 50% hydrogen and 50% nitrogen.

Program Status Summary

- Physical and chemical sensor facility at UTRC built and physical sensor testing begun
- ATMI, IIT, and NexTech fully engaged in program as budget allows
  - Monthly telecons between UTRC and other subcontractors to focus closely on coordination issues started in March 2003
  - UTRC to visit all subcontractor sites within the next two months to increase direct communication and knowledge transfer
- Physical sensor evaluation underway
- H_2 sensor testing underway at IIT and UTRC

Micro-Machined Thin Film H_2 Gas Sensors

DOE Hydrogen and Fuel Cells
2003 Annual Merit Review

ATMI

Ing-Shin Chen, Phil Chen, F. DiMeo, Jeff Neuner,
Andreas Rohrl, Michele Stawasz, Jim Welch

Outline

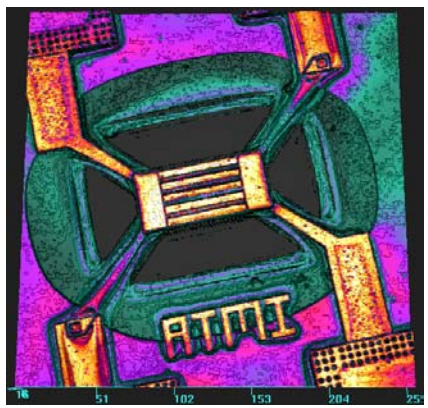
- Introduction
- Approach
- Project Timeline
  - Overall and FY2003
- Accomplishments/Progress
  - Focus on Understanding and Yield
- Communication/Collaborations
- Future Work

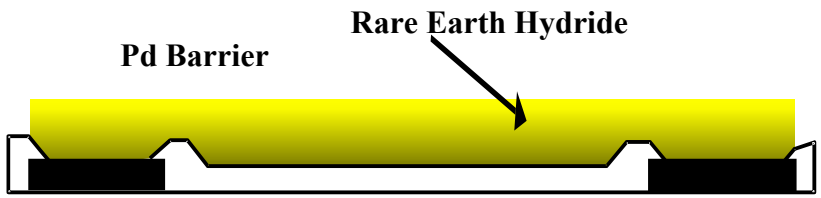
Introduction

- Project Relevance
  - **2002 National Hydrogen Energy Roadmap**
    - Delivery – Efforts should focus on the development of better components for existing delivery systems, including **hydrogen *sensors***…
    - Storage – Emerging hydrogen applications requires … "smart" tanks with **integrated or embedded *sensors***, …
    - Conversion – Other key research needs include … ***more* durable and lower-cost *sensors***…
    - Applications – Development needs include **low-cost, fast-response, and low-power consumption *sensors***…

Goals and Approach

- Project Goals
  - Demonstrate the capabilities of micromachined H_2 sensors
  - Develop an understanding of their performance
  - Critically evaluate the utility and viability of this technology for life safety and processing monitoring
- Approach
  - MEMS based platform coupled with multilayer hydride films
  - Thermally controlled chemi-resistive transduction

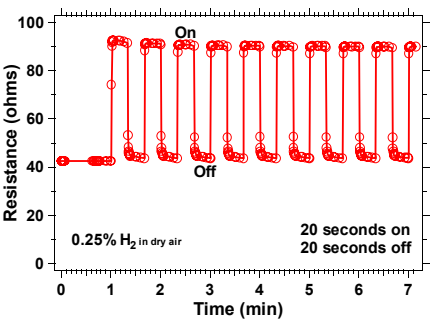


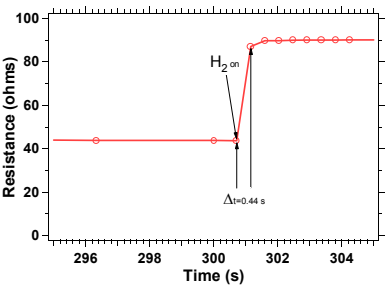


Overall Project Progression

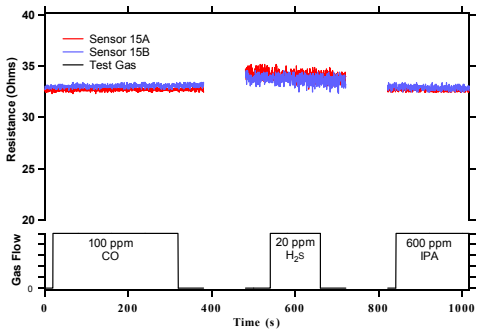
FY2000 FY2001/02 FY2003 FY2004

Proof of Concept





Feasibility Showstoppers

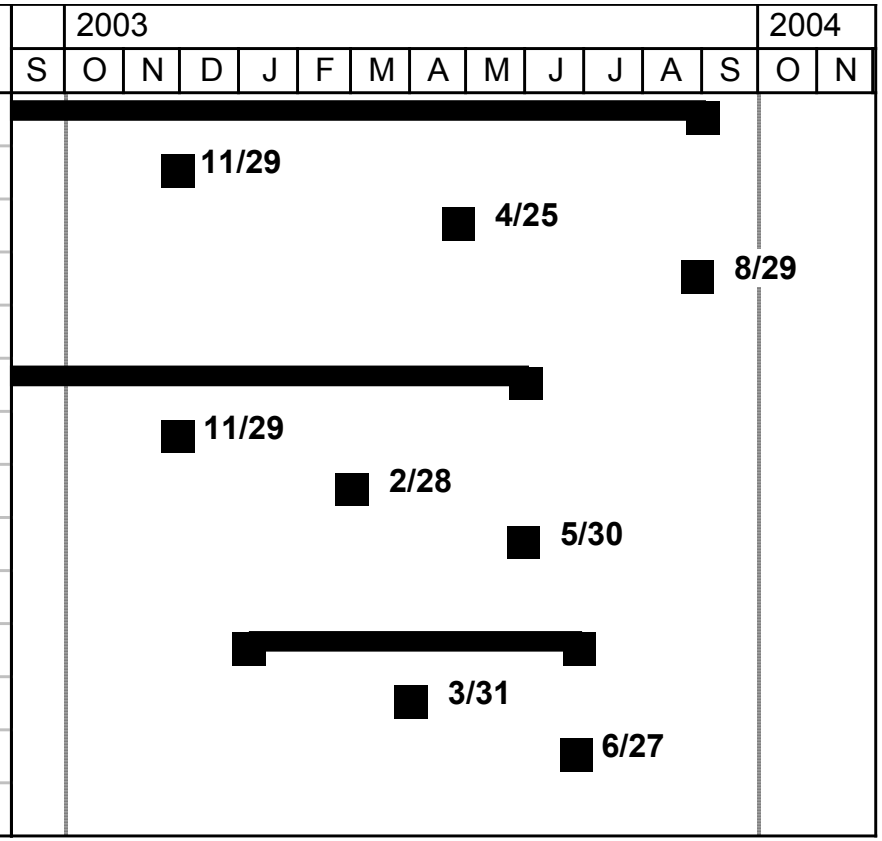


Field Testing Technology Extension

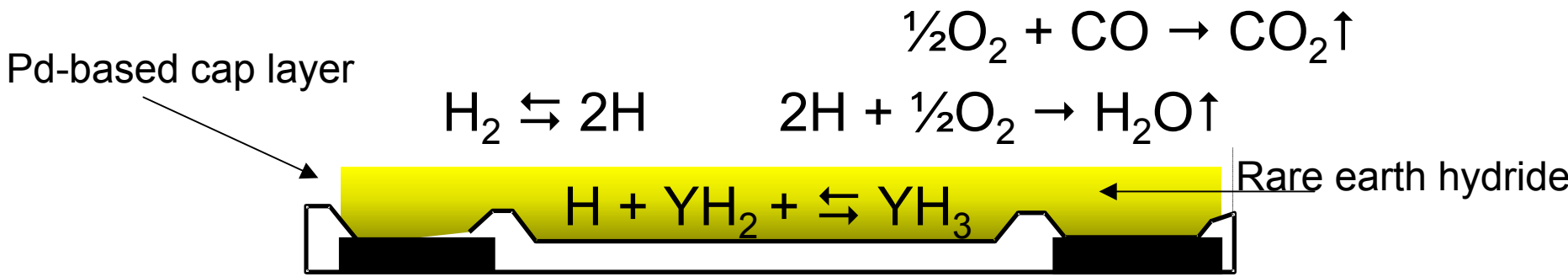
Reproducibility/Scale up
Fundamental Understanding
Systems Development
New Device Innovation

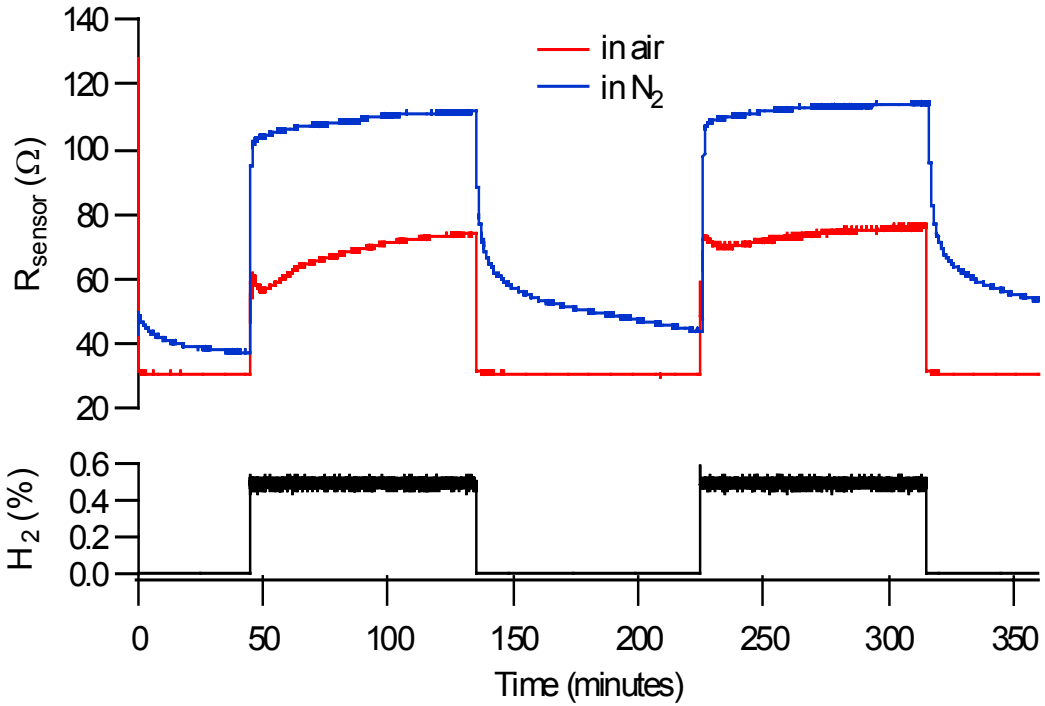
FY 2003 Timeline and Milestones

ID	Task Name
1	**Fabrication and Process Control**
2	Establish Process of Record
3	Evluate of Novel Process Step(s)
4	Optimize Fabrication Process
5	
6	**Sensor Characterization and Analysis**
7	Implement Quality Control Protocol
8	Characterize Sensor Device & Materials
9	Design Application-Specific Sensors
10	
11	**Systems Development**
12	Finalize Package Designs
13	Finalize Signal Conditioning Circuitry
14	



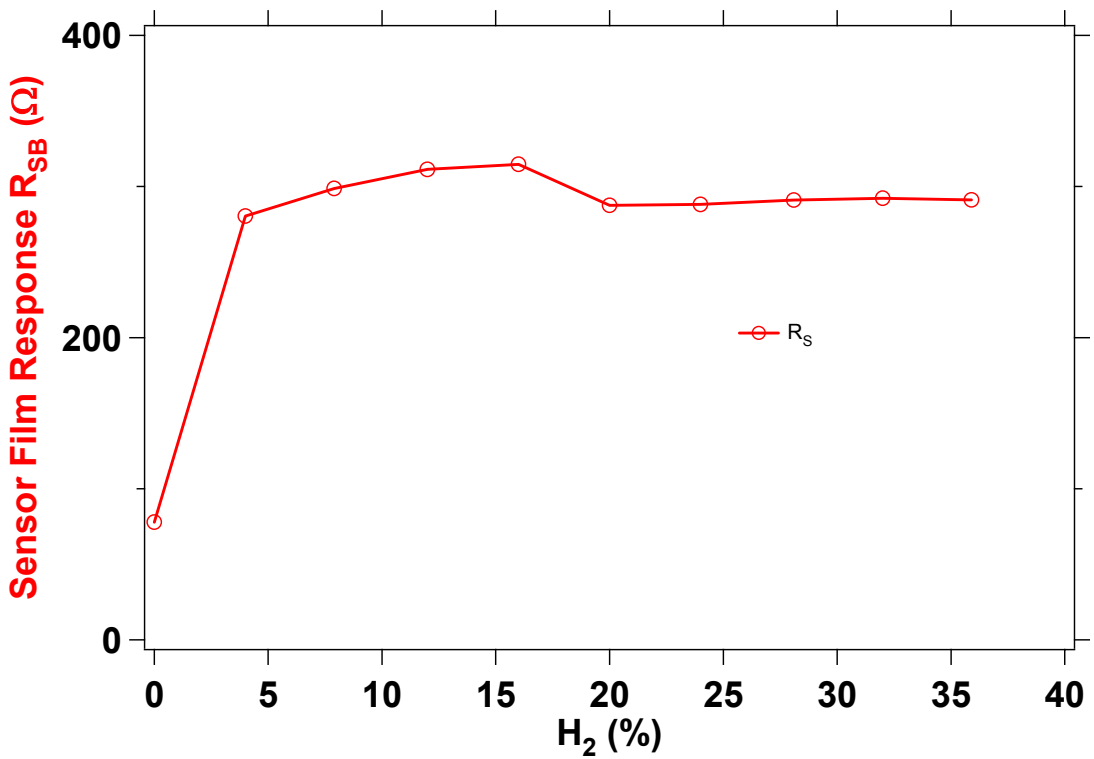
Device Model: Chemical, Electrical, Mechanical

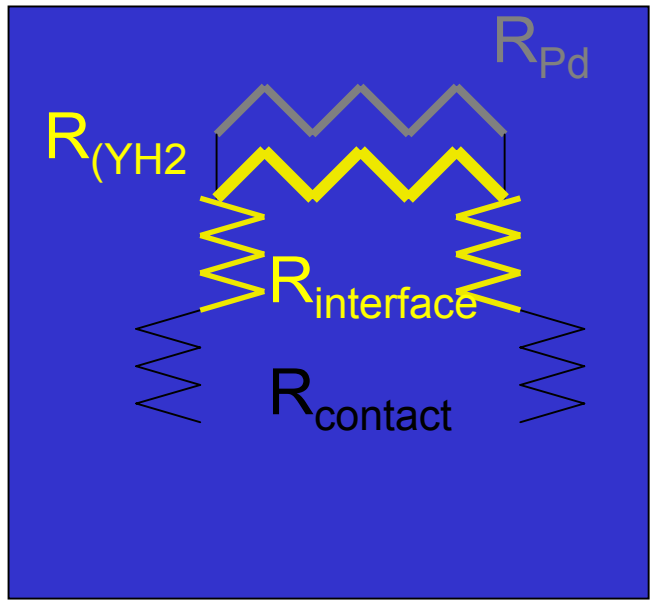




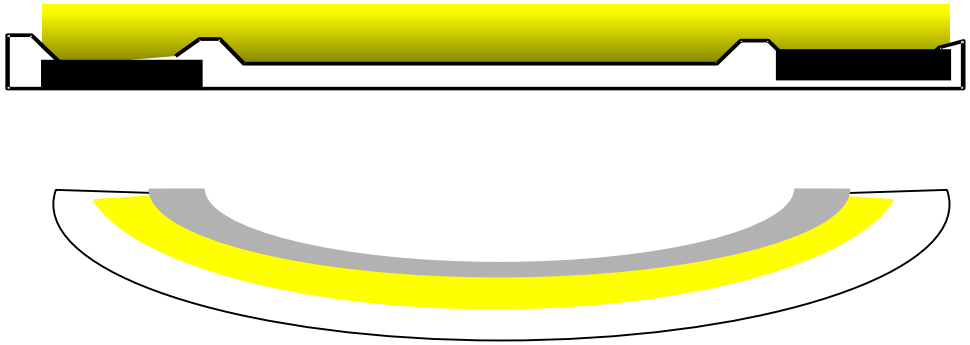
Device Model: Chemical, Electrical, Mechanical

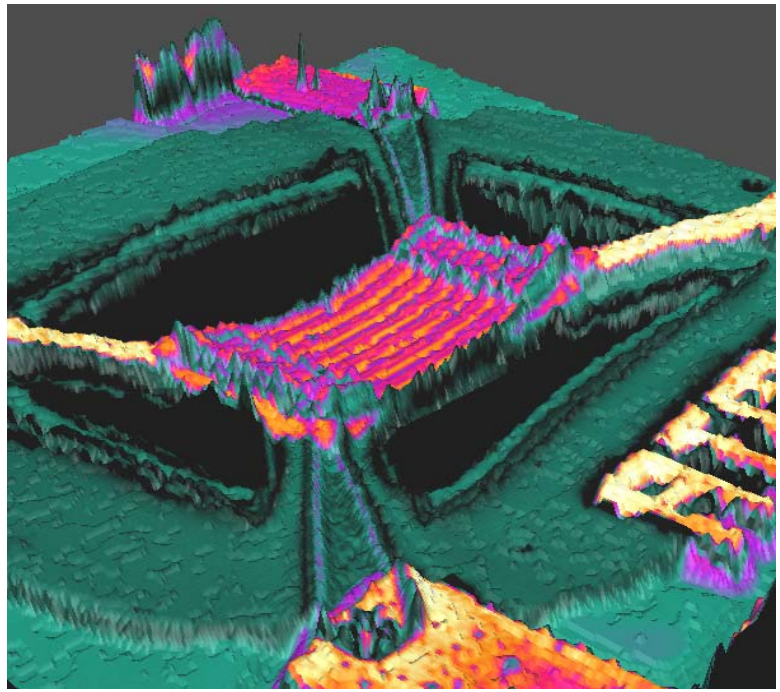
$$R_{sensor} = 2\,R_{contact} + 2\,R_{interface} + R_{Pd} // R_{(YH2 + \leftrightarrows YH3)}$$





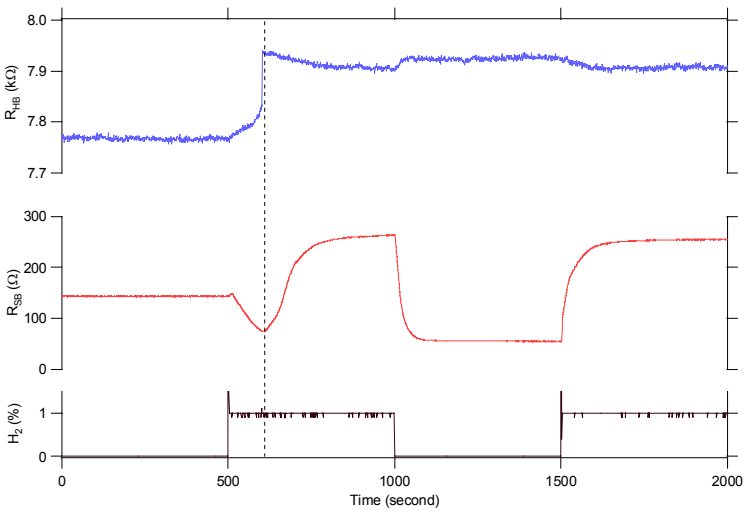
Device Model:
Chemical, Electrical, Mechanical

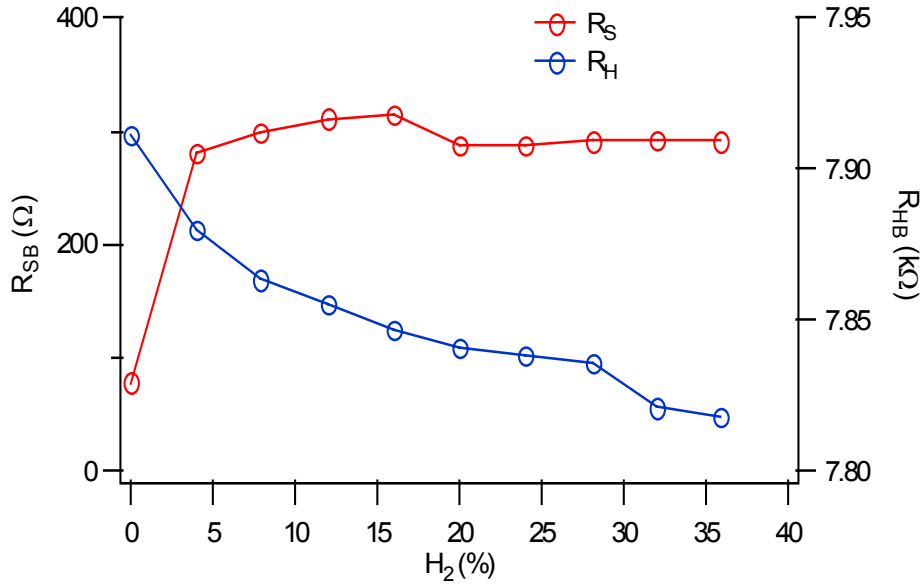




- Volume of YHx changes by 15% from x = 2 to x = 3,
- Confocal Microscopy capability enabled measurement of bending
- Poly Silicon resistance is modulated via piezo-resistive effect
  - "Strain Gauge H_2 sensor" Pat. Pending

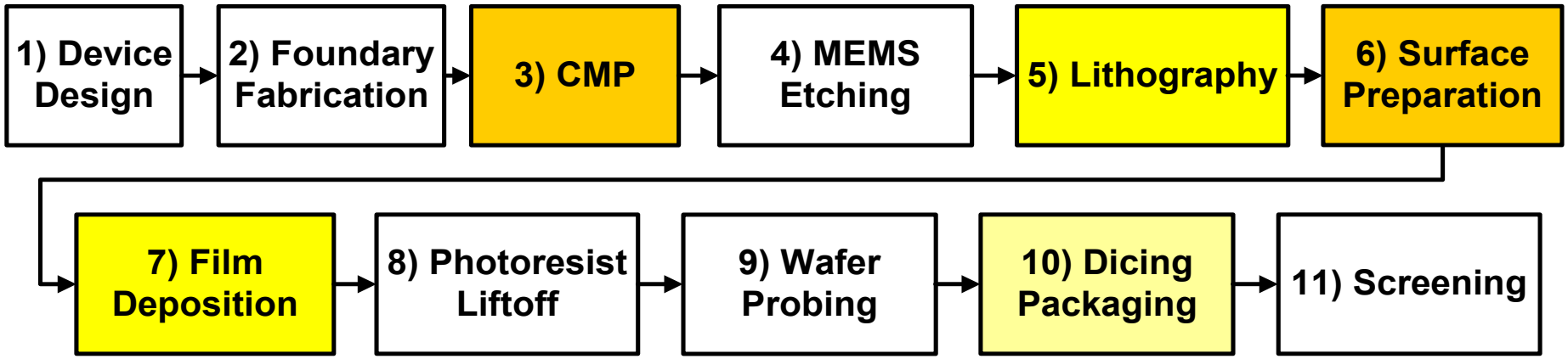
New Mechanical Transduction Data





- Potential for significant cost reduction
  - 2 wire sensor vs 4 wire sensor
  - Fewer layers
- Dual Transduction Cap

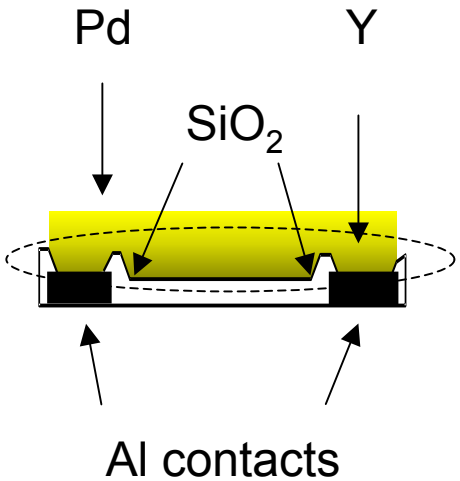
Fabrication/Process Control: Process of Record

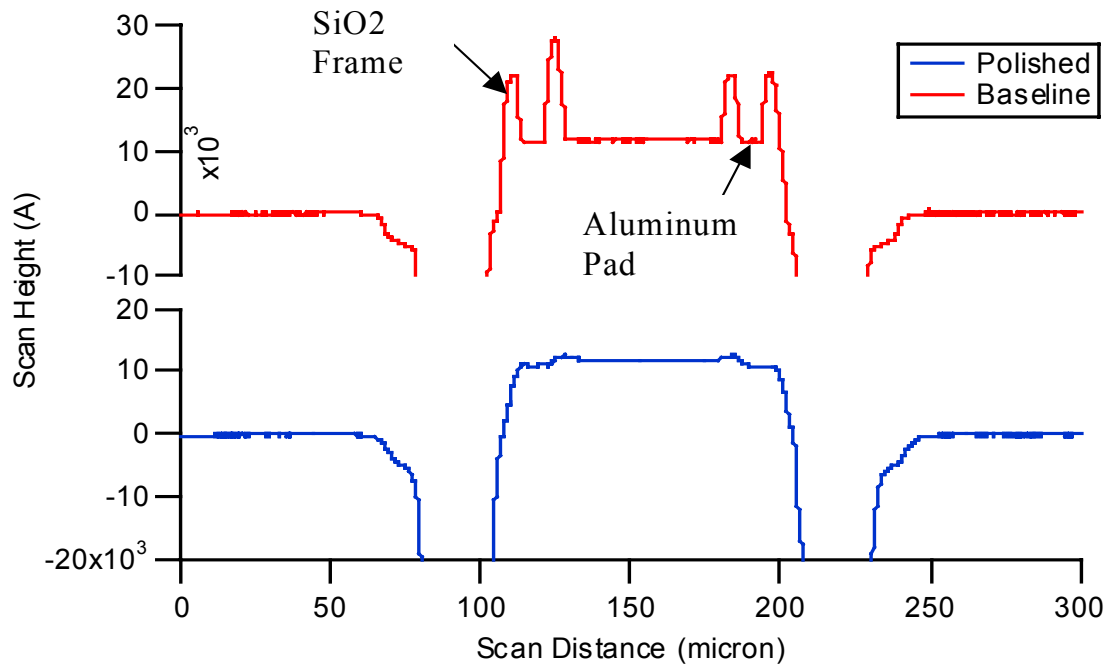


11 Total Process Steps with 110 Variables

- POR forms foundation for continuous process improvement
  - Currently on V7.1
- Designed experiments and detailed process analysis focused on critical steps

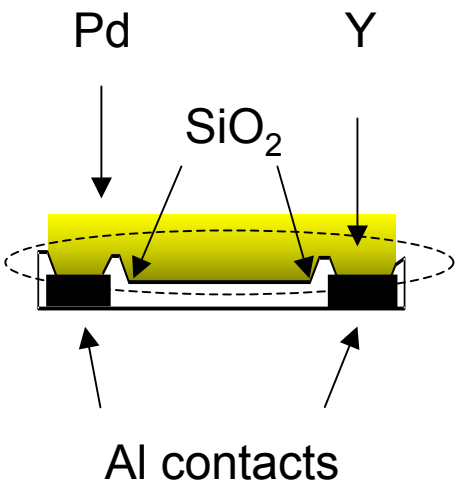
Fabrication/Process Control: Chemical Mechanical Polishing

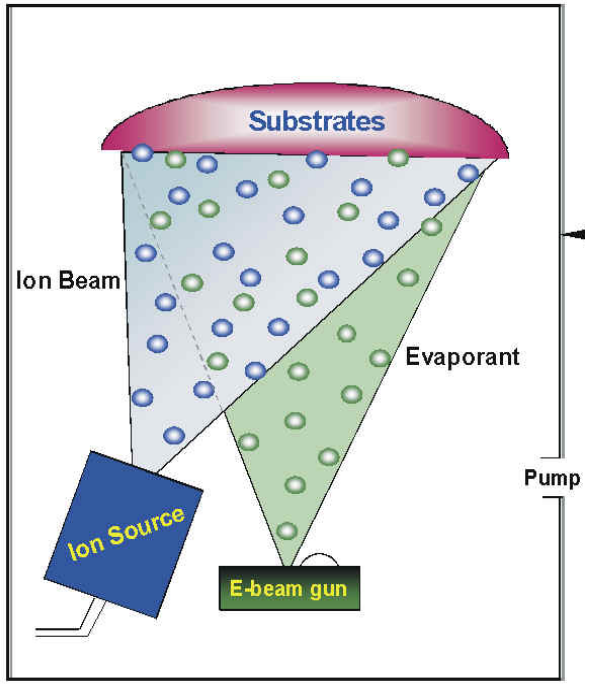




- SiO_2 frame height can be 5 to10X functional film thickness
- Surface preparation reduces frame height and improves uniformity and yield

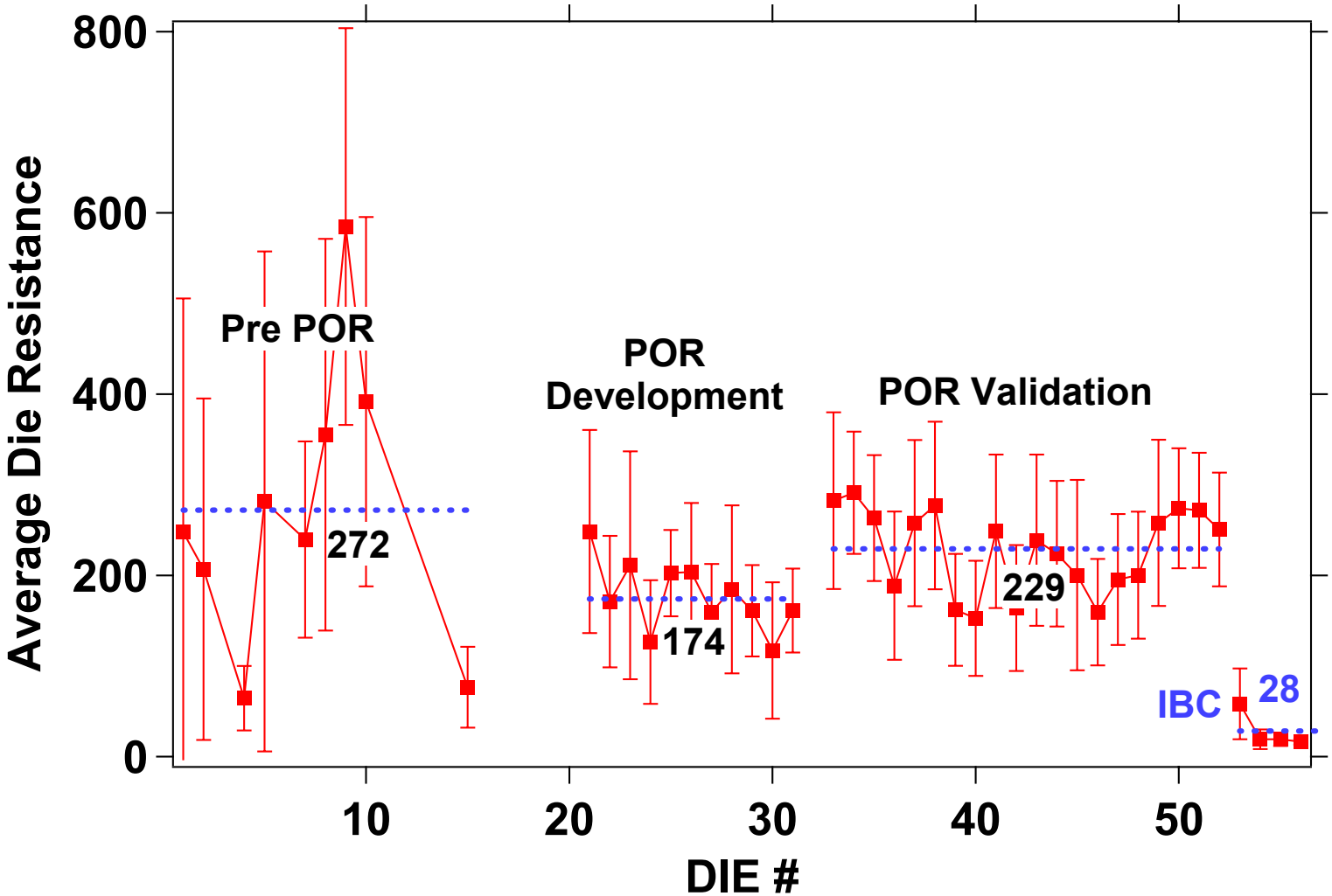
Fabrication/Process Control: Ion Beam Cleaning



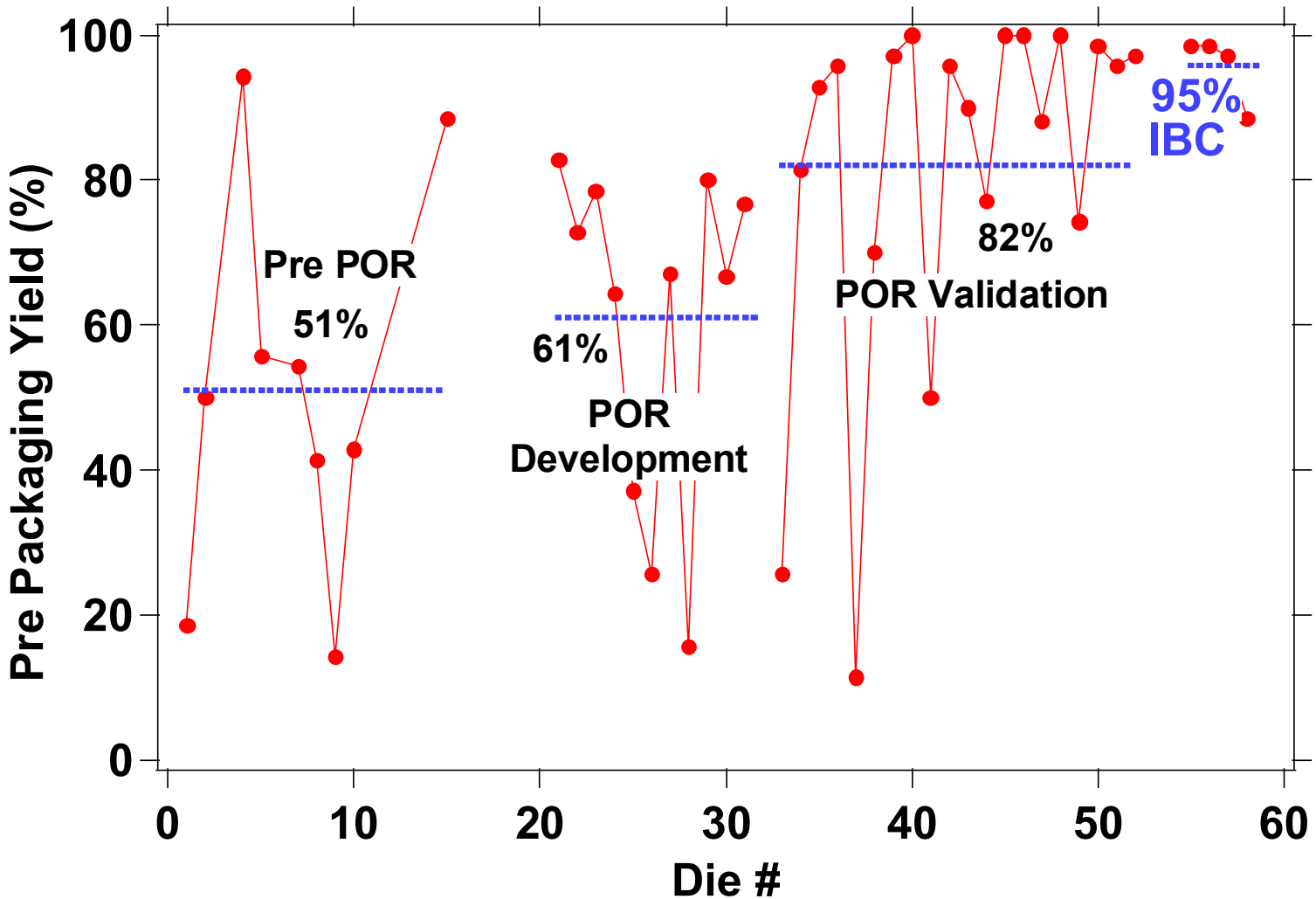


- *In situ* contact clean prevents Al contact surface re-oxidization and reduces contact resistance

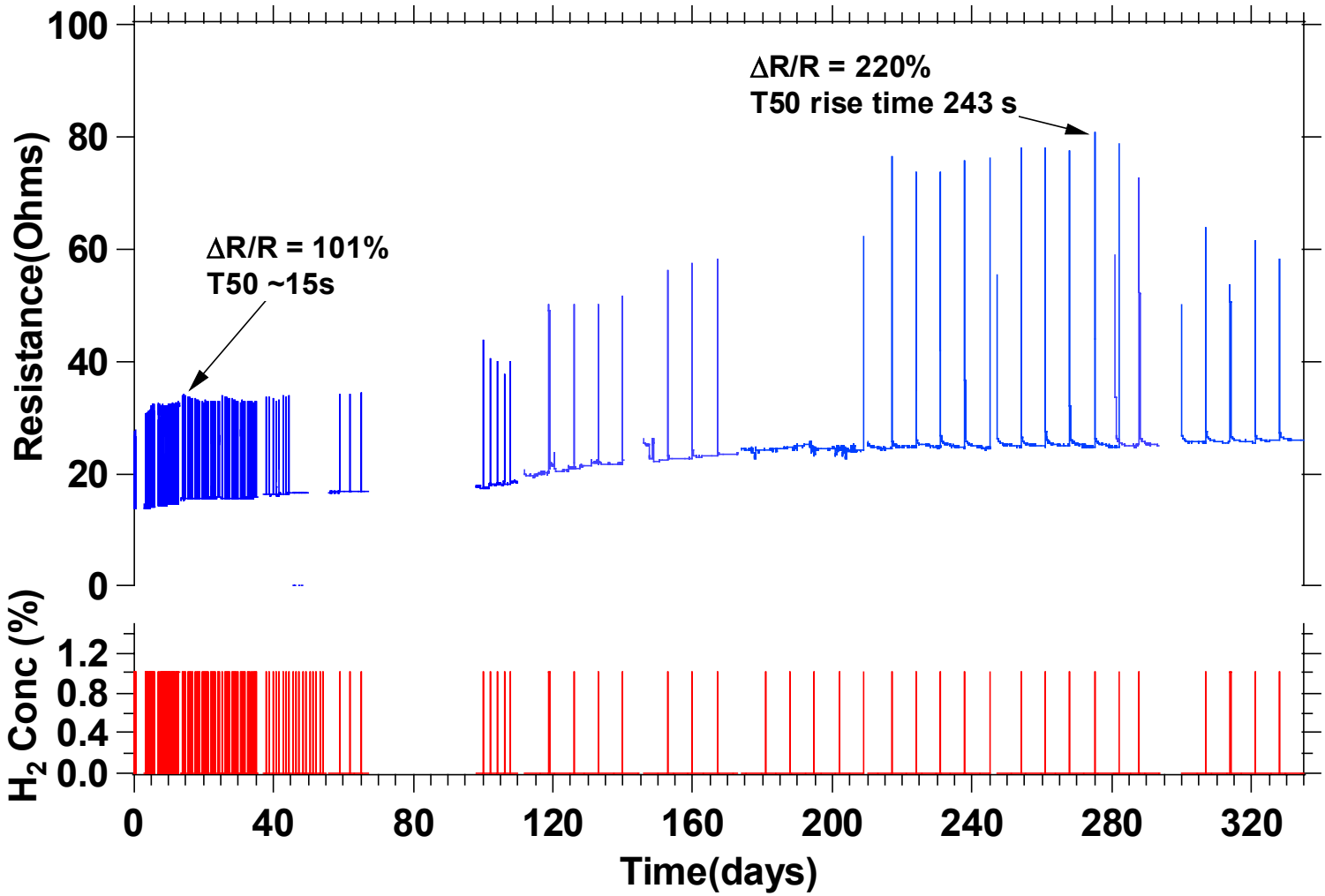
Fabrication/Process Control: Results for Die Resistances



Fabrication/Process Control: Results for Die Resistances



Systems Development: Long Term Data



Systems Development– Packaging and Signal Conditioning

- Signal Conditioning Board
  - Dual channels,PIC processor-based, on-board calibration, RS 232 and Analog out
- Self Contained Data Logging

Communication/Collaborations

- Publications and Presentations
  - "MEMS Based H_2 Gas Sensors", submitted *Journal of Electrochemical Society*
  - "Microelectronic H_2 sensing for Emerging Sensing", CMOC 2003
- Issued Patents
  - G. Bhandari and T.H. Baum, "Hydrogen sensor utilizing rare earth metal thin film detection element," U.S. Patent 6,006,582 (1999).
  - F. DiMeo and G. Bhandari, "Micro-machined thin film hydrogen gas sensor, and method of making and using the same," U.S. Patent 6,265,222 (2001).
- Allowed
  - F. DiMeo and T. Baum "Micro-Machined Thin Film Sensor Arrays For The Detection Of H2, NH3, And Sulfur Containing Gases, And Method Of Making And Using The Same"
- Pending
  - F. DiMeo, P. Chen, " Rare Earth Metal Sensor"
  - I.-S. Chen and F. DiMeo, "Micro-machined piezo-resistive gas sensor, and method of making the same,"
- Collaborations
  - ATMI Life Safety Systems, ATMI GaN Products, UTC Fuel Cells

Future Work: Complete Program Milestones

- Fabrication and process control
  - Continuous improvement and refinement
- Sensor characterization
  - Re-examine optimal operation conditions based on improved fabrication techniques
  - Explore new piezo-resistive device structures
- Systems
  - Complete datalogging prototype
  - Deploy prototypes internally at ATMI

Summary/Accomplishments

- Demonstrated CMOS based MEMS based H_2 Sensors with Sub second response time
- Demonstrated hydrogen selectivity
  - no response to CO, H_2S, IPA
- Engineered sensors to operate with low power (<6mW) consumption, enabling mobile applications
- Developed an understanding of sensor behavior
  - Basic electrical device model developed
  - Demonstrated novel piezo-resistive H_2 sensor

This technology looks promising for meeting the sensing challenges presented by emerging H_2 applications!

Sensor Development for PEM Fuel Cell Systems
DOE Cooperative Agreement DE-FC04-02AL67615
Project No. DOE #131

Fiscal Year 2003
Annual Progress Review

Robert Lowther, DOE Contract Manager,
Nancy Garland, DOE Principle Program Manager
Robert Sutton, ANL Technical Advisor

Dick Alderman, Primary Investigator
Bruce Figi, Program Manager

22 May, 2003

Program Objectives

Honeywell

Task 1 – Sensor Requirements

This task will define the requirements of each of the physical sensors. The preliminary sensor requirements will be evaluated against the requirements created from the customer interviews. A broad market survey will validate the requirements and provide the inputs to the design task.

Task 2 – Sensor Development

This task will be an initial development of the Physical Sensors to demonstrate their ability to meet the necessary requirements in a laboratory environment. Several subtasks are identified to meet this objective.

Task 3 – Prototype Sensor Development

The proposed Physical Sensors developed in Task 2 shall be manufactured into operating prototypes suitable for third-party fuel cell system testing and evaluation. This includes all necessary design, fabrication, and rework necessary to meet the requirements set forth in Task 1.

Task 4 – Field Testing

It is Honeywell's position that the proposed sensors will gain technical and/or cost advantage by combining their functionality into an overall system architecture and testing them in their intended fuel cell system environment. The purpose of this task is to test and demonstrate the sensors on operating fuel cells and reformers at third-party facilities.

Program Approach

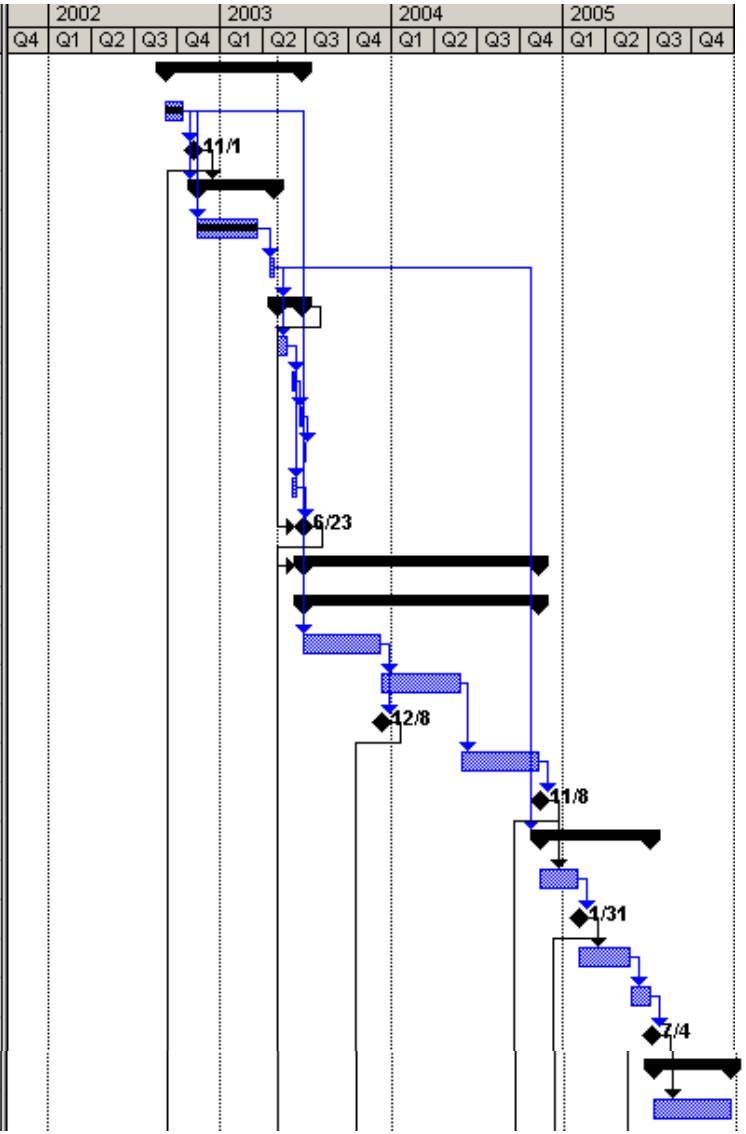
Honeywell

The technical approach for this program is to look at the fuel cell system and establish the requirements for each physical sensor, then develop packaging strategies for the sensors to minimize sensor cost. Prototype sensors will be designed, fabricated and tested in third party fuel cell systems and fuel processor companies.

Program Timeline

Honeywell

WBS	Task Name
1	**Sensor Requirements**
1.1	Preliminary Requirements Definition
MS-1.1	Preliminary Requirements Review
1.2	**Update Requirements**
1.2.1	Third Party Interviews
1.2.2	Evaluation of Third Party Requirements
1.3	**Finalize Requirements**
1.3.1	Determine sensor requirements from transcripts
1.3.2	Finalize Field Survey
1.3.3	Distribute Field Survey
1.3.4	Analyze Field Survey
1.4	Select Third Party Test Facilities
MS-1.2	Final Sensor Requirements Review
2	**Sensor Development**
2.1	**Physical Sensors**
2.1.1	Technology Concepts
2.1.2	Packaging Concepts
MS-2.1	Physical Sensors Test Plan Review
2.1.3	Preliminary Testing
MS-2.2	Physical Sensor Design
3	**Prototype Build & Test**
3.1	Fabrication
MS-3.1	Physical Sensors Demonstration
3.2	Testing
3.3	Rework
MS-3.2	Prototype Demonstration - Sensors Available for Test
4	**Field Testing**
4.1	Third Party Testing



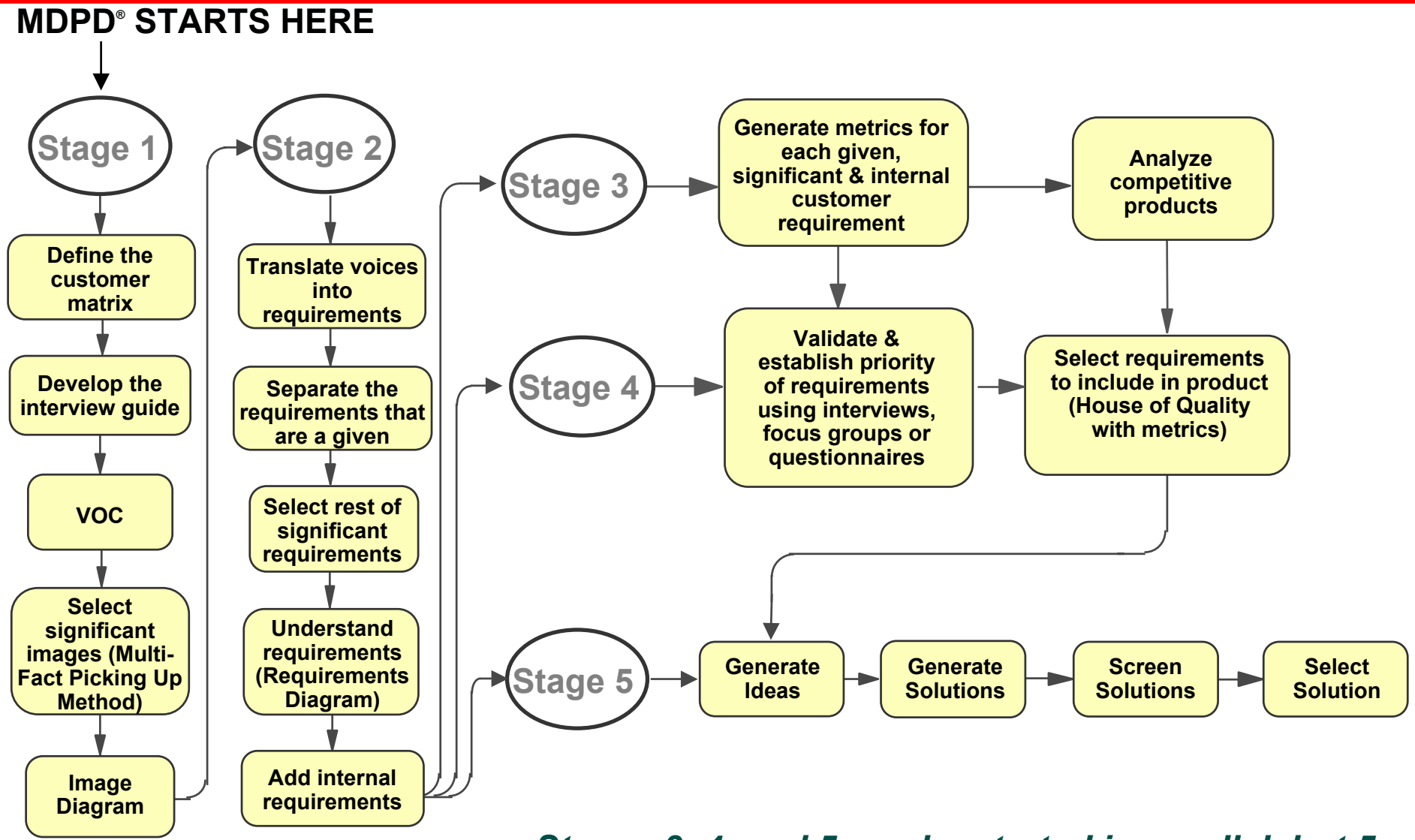
MDPD® Approach

Honeywell

- **Market Driven Product Definition (**MDPD®**).**
- **Why Follow a Process for Customer Visitation?**
  - Reduce risk of product not meeting customers' needs
  - Reduce dependency on individual knowledge basis and opinions
  - Discover customers' latent needs - "wows" and "delighters"
  - Establish measurable criteria
    - Ensure that product meets customer requirements
    - Use in competitive benchmarking

MDPD® Process Map

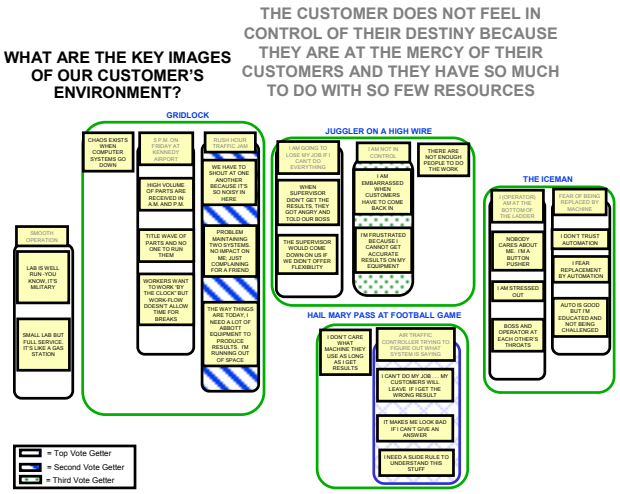
Honeywell



Stages 3, 4, and 5 can be started in parallel, but 5 should not be completed until 3 and 4 are done

Honeywell

Gather Customer Information



- The cross-functional team visits customer at customer's site
- Purpose is to listen to customer, not to sell or defend existing products
- Visit typically 12-20 customer sites
- Create a common image of the environment

Stage 1 – Interview List

Honeywell

COMPANY	INTERVIEWED	LOCATION
GM	11/13/2002	Honeoye Falls
UTC	11/20/2002	Hartford
Plug Power	11/21/2002	Albany
Avista	11/27/2002 (phone)	Spokane
Nuvera	12/11/2002	Cambridge
Ballard	01/09/2003	Burnaby
H2Fuel	01/28/2003	Chicago
Ballard	02/27/2003	Nabern
DaimlerChrysler	02/28/2003	Ulm
Ford	03/18/2003	Dearborn

Stage 1 – Customer Images

Honeywell

Identify IMAGES from the interview transcripts
Visual representation of the customers environment.

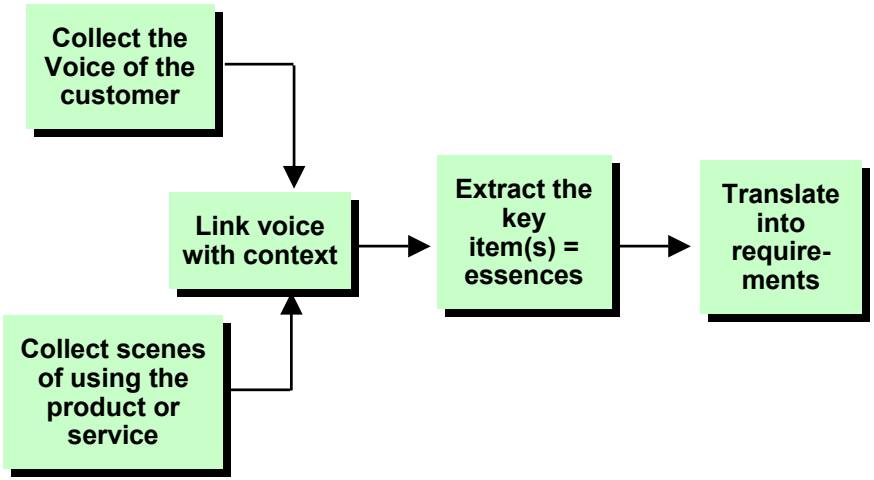
Examples:

•At start up you get big slugs of water flowing and yes that's a problem.

•We don't want big electronics hanging off these things.

•You have to be able to drive the car into a pond of water.

Develop Customer Requirements



- Link customer voices to the image to help define "delighters"
- Select key customer requirements
- Prioritize requirements

Stage 2 – Customer Voices

Honeywell

Identify VOICES from the interview transcripts
A statement of customer's need for the product.

Examples:

- Flow of humid streams has been a tough measurement.
- The head can't be any bigger than my thumb and have all the electronics.
- The connector has to be waterproof, IP67.

Stage 2 – Translation

Honeywell

Form a requirement from the voice and linked image if any.
Examples:

- Flow of humid streams has been a tough measurement.

The sensor has to perform in condensing environments.

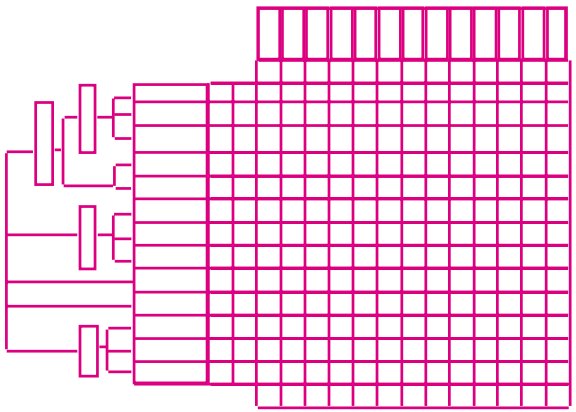
- The head can’t be any bigger than my thumb and have all the electronics.

The sensor interface electronics must have minimal impact on size.

- The connector has to be waterproof, IP67.

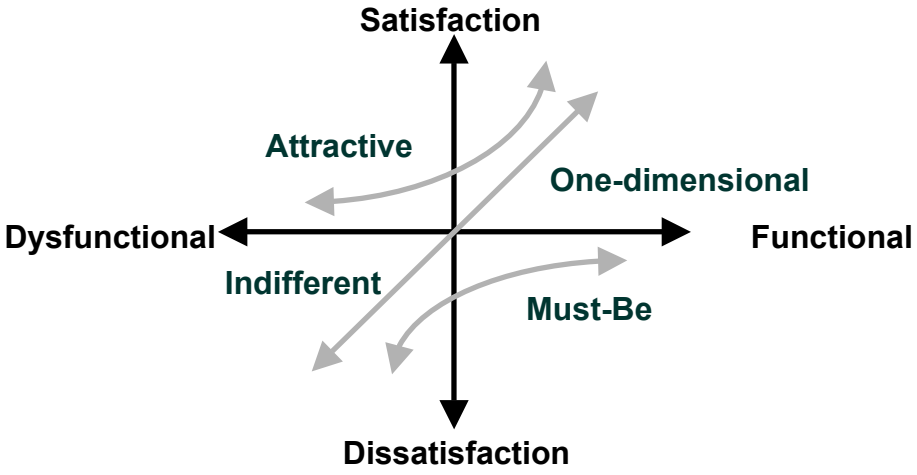
The sensor must be sealed like an automotive sensor today.

Develop Metrics for Requirements



- Create metrics for each important requirement
- Cross-check metrics with requirements to ensure coverage and to eliminate duplicates
- Create detailed instructions for performing the measure, enabling team to ensure that requirement is met

Validate, Prioritize, and Select Requirements



- Prioritize requirements by performing a survey of broader population.
- Use Kano method to distinguish “attractive” from “must-be” requirements.
- Include all “must-be” and several “attractive” qualities, and at least as much as the competition on “one-dimensional” requirements.

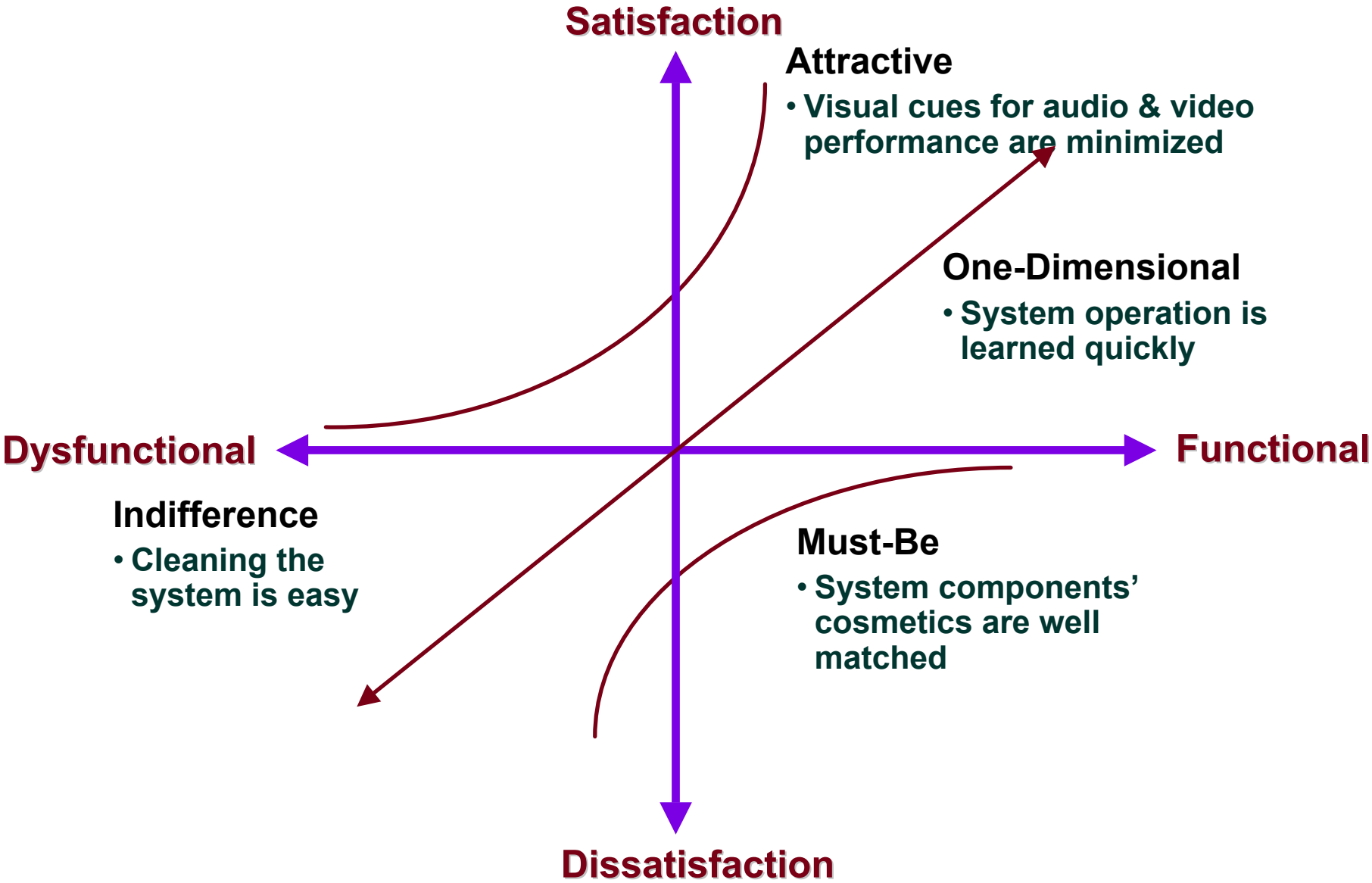
Create a Kano question set for a requirement created during translation

Use this 1-5 rating system, with the exact wording...

1a. If the cellular phone continued working after being dropped on cement, how would you feel?	1. I would be delighted. 2. I would be satisfied with it. 3. I would be neutral. 4. I could tolerate it. 5. I would dislike it very much.
1b. If the cellular phone broke after being dropped on cement, how would you feel?	1. I would be delighted. 2. I would be satisfied with it. 3. I would be neutral. 4. I could tolerate it. 5. I would dislike it very much.

Example Results

Honeywell



Field Survey

Honeywell

Deploy survey to the interview list plus many additional users.

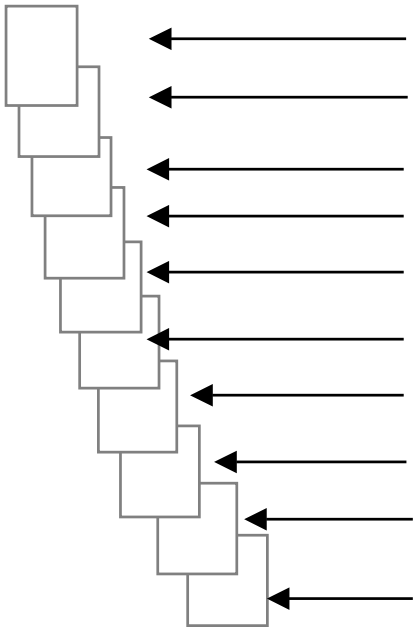
Analysis of survey responses should:

- Validate requirements list
- Establish relative importance for key requirements
- Identify features that must be in the product
- Identify features that have little importance
- Identify features that are attractive
- Form the basic specification metrics needed

Stage 5 - Generating Solutions

Honeywell

Generate Product Definition



- Brainstorm alternative solutions
- Select solutions that best meet requirements and better competitive offerings
- Remain within budget and market window constraints
- Document the features of the solution

Next Steps

Honeywell

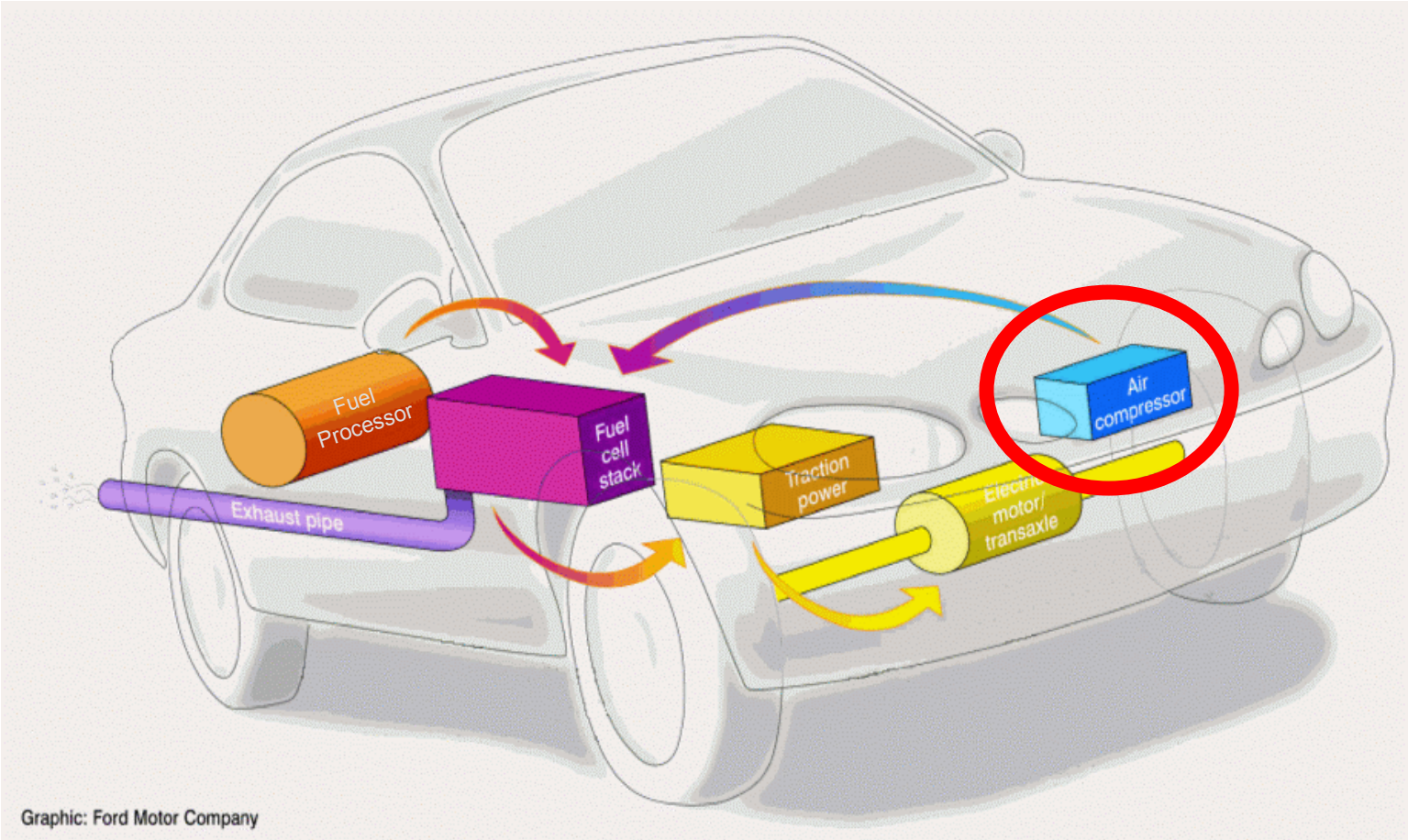
- Design and execute a field survey to validate the requirements and gather sensor metrics.
- Finalize sensor requirements and review with DOE.
- Brainstorm the requirements for the top 2-3 solutions for each sensor.
- Prioritize solutions.
- Create Engineering Development Specification (EDS) for top priority concept for each physical sensor.
- DOE review and approval of EDS.
- Begin sensor development.

Technical Hurdles

Honeywell

- General
  - Meeting cost targets.
- Relative Humidity Sensing
  - Stability over application life.
  - Ability to provide feedback in two phase flow.
- Flow Sensing
  - Providing a stable, accurate output in non-condensing and condensing environments.

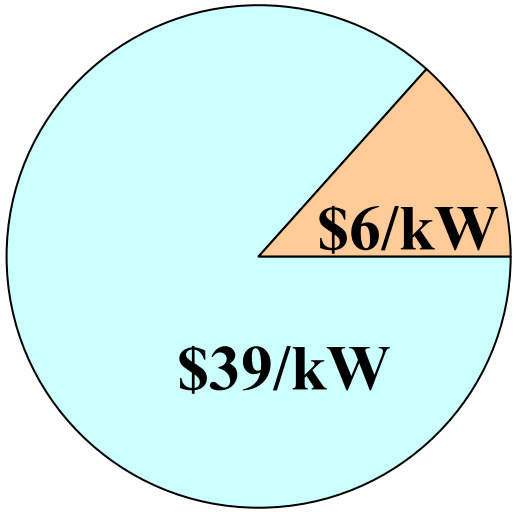
Air Management Subsystems



John Garbak

Barriers

Air Management Subsystem



Air Management
(50-kW System)

Fuel Cell Power System
$45/kW

NEEDS

- Minimize parasitic power consumption
- Reduce weight
- Improve efficiency
- Integrate with fuel cell and fuel processor
- Reduce cost

Status and Proposed Targets

Compressor/Expander for Transportation Fuel Cell System

Characteristics	Units	2003 status	2005	2010
50-kW Unit				
Efficiency at Full Flow	%	<70 (C), <80 (E)	80	80
Volume	L	10-12	8-11	8-11
Turndown Ratio		5	10-15	10-15
Cost	$	600	400	300
80-kW Unit				
Efficiency at Full Flow	%	-	-	80
Volume	L	-	-	15
Turndown Ratio		-	-	15
Cost	$	-	-	400

Projects
Air Management

• Turbocompressor for PEM Fuel Cells	Honeywell
• Hybrid Compressor/Expander Module	TIAX
• Motor Blower Technology for Fuel Cell Automotive Power Systems	UTC
• High-Efficiency, Integrated Compressor/Expander Based on Torroidal Intersecting Vane	Mechanology, LLC

Discussion Points

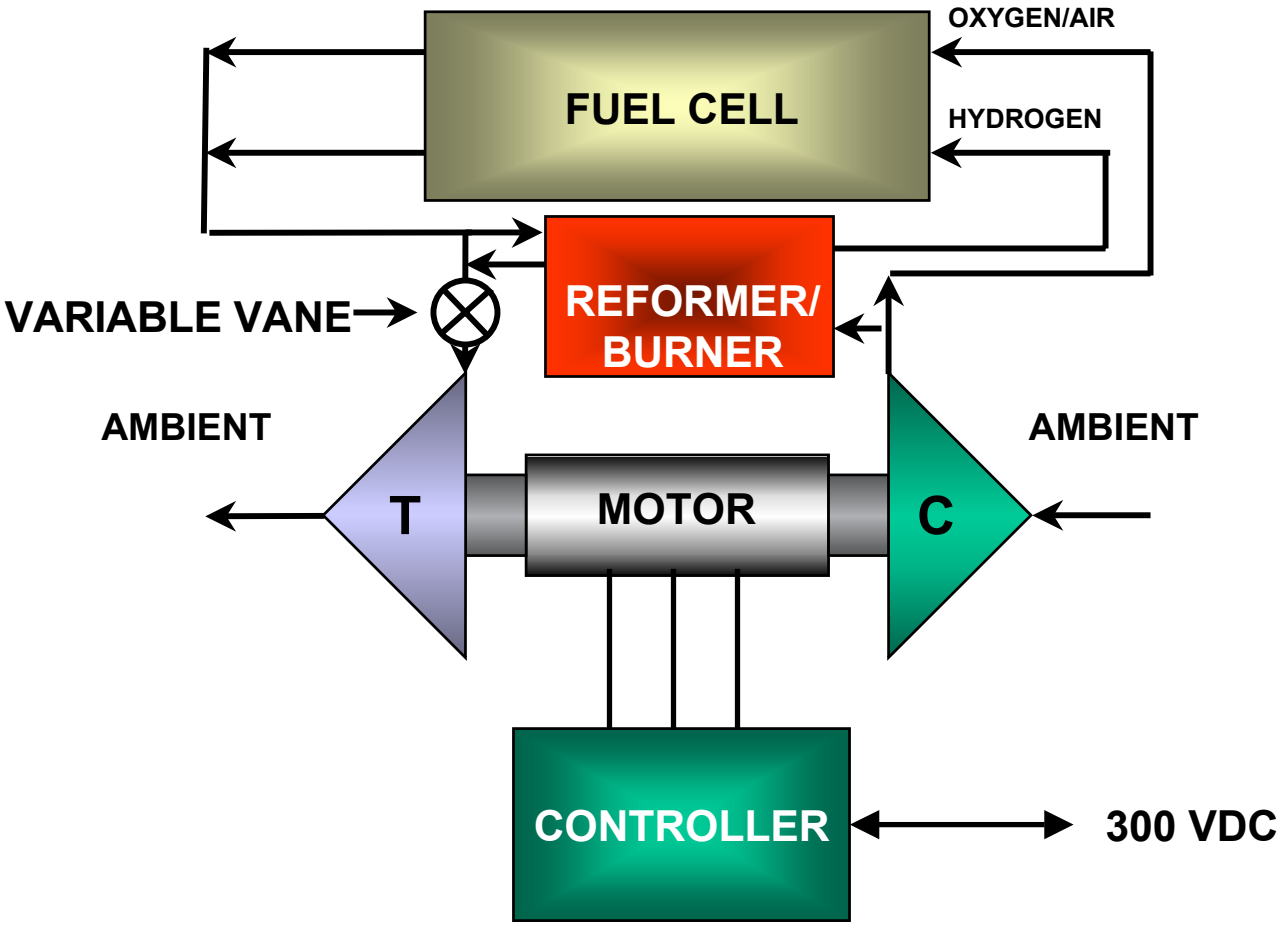
- Develop compressor/expander units for direct hydrogen systems.
- Need exists for compressor/ expander motor unit for fuel cells larger than 50kW.
- Will larger compressor/expander units be scalable from current work?
- How large a compressor/ expander unit will ultimately be needed?

FUEL CELL TURBOCOMPRESSOR

MAY 22, 2003

CLAREMONT RESORT & SPA
BERKELEY, CA

OPERATING PRINCIPLES & GENERAL DESCRIPTION



FUEL CELL SYSTEMS AND AIR MANAGEMENT RELATIONSHIPS

- FUEL CELL SYSTEM AIR MANAGEMENT PROVIDES:
  - AIR AT THE APPROPRIATE PRESSURE AND FLOW FOR THE FUEL CELL STACK AND IF PRESENT THE FUEL PROCESSOR
  - ENERGY RECOVERY FROM FUEL CELL EXHAUST TO REDUCE PARASITIC POWER REQUIRED FOR THE AIR MANAGEMENT
- FUEL CELL SYSTEM AIR MANAGEMENT CONSIDERATIONS:
  - FLOW RATE: AFFECTS THE FUEL CELL STACK EFFICIENCY AND THE PARASITIC POWER REQUIRED FOR THE AIR MANAGEMENT
  - PRESSURE: AFFECTS THE FUEL CELL STACK EFFICIENCY AND THE PARASITIC POWER REQUIRED FOR THE AIR MANAGEMENT
  - TEMPERATURE: THE AIR SUPPLY TEMPERATURE USUALLY TO BE WITHIN A SPECIFIC RANGE OF THE FUEL CELL STACK TEMPERATURE
  - HUMIDIFICATION: SOME FUEL CELL STACKS (E.G. PEM) REQUIRE HUMIDIFICATION TO MAINTAIN THE ELECTROCHEMICAL REACTION
  - WEIGHT AND VOLUME: DEPENDENT ON PRESSURE AS WELL AS COMPRESSOR TECHNOLOGY

DOE/FreedomCAR/Hydrogen technical barriers

4.4.4.2 Technical Barriers

- Although many issues are discussed below, it should be noted that cost and efficiency present two of the more significant technical barriers to the achievement of clean, reliable, cost-effective systems.

Transportation Systems Technical Barriers

- A. **Compressors/Expanders**. Automotive-type compressors/expanders that minimize parasitic power consumption and meet packaging and cost requirements are not available. To validate functionality in laboratory testing, current systems often use off-the-shelf compressors that are not specifically designed for fuel cell applications resulting in systems that are heavy, costly, and inefficient. Automotive-type compressors/expanders that meet the FreedomCAR program technical guidelines need to be engineered and integrated with the fuel cell and fuel processor so that the overall system meets packaging, cost, and performance requirements.

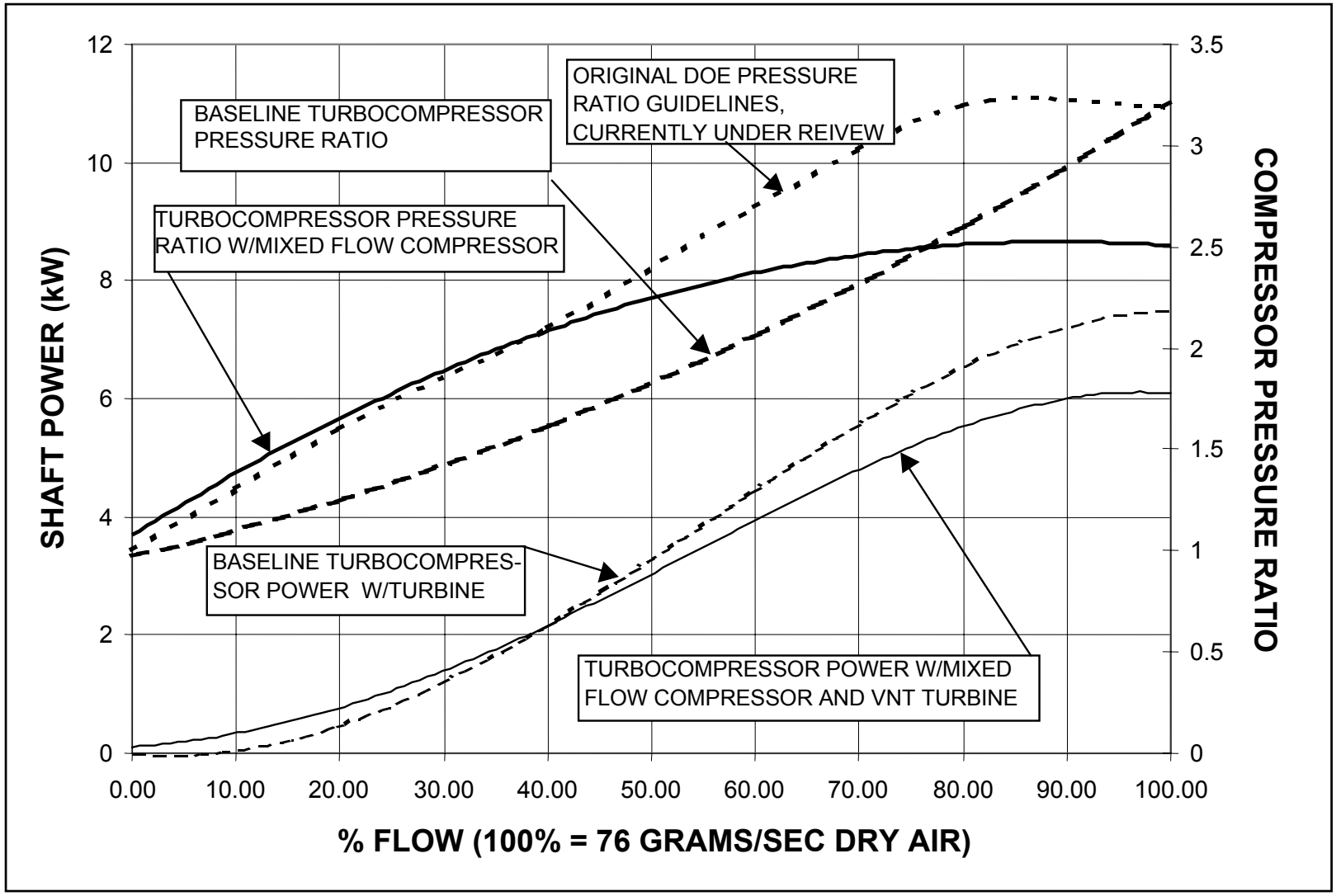
FUEL CELL TURBOCOMPRESSOR OBJECTIVES

- DEVELOP AN OPTIMUM (I.E. LOW COST, EFFICIENT, COMPACT AND LOW WEIGHT) TURBOCOMPRESSOR CONFIGURATION BY WORKING WITH FUEL CELL SYSTEM MANUFACTURERS AND CONTINUING THE WORK CURRENTLY BEING PERFORMED.
- REDUCE TURBOCOMPRESSOR/MOTOR CONTROLLER COSTS WHILE INCREASING DESIGN FLEXIBILITY.
- DEVELOP AND INTEGRATE THE TURBOCOMPRESSOR/MOTOR CONTROLLER INTO A FUEL CELL SYSTEM.

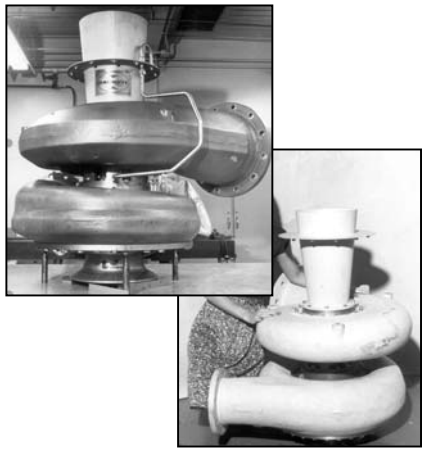
FUEL CELL TURBOCOMPRESSOR CONCEPT

- CONTAMINATION FREE AIR FLOW TO FUEL CELL
  - COMPLIANT FOIL AIR BEARINGS (NO LUBRICANTS)
- LIGHTWEIGHT - <18lb (8.2 Kg)
- COMPACT - 12 in x 8 in dia (9.9 liters)
- EFFICIENT
  - 70% COMPRESSOR
  - 80% EXPANDER/TURBINE
- HIGH TEMPERATURE CAPABLE EXPANDER/TURBINE
- VARIABLE GEOMETRY TURBINE (CAN BE USED AS BACKPRESSURE VALVE)
- ZERO MAINTENANCE
- RELIABLE
  - ONE MOVING PART
- LOW PRODUCTION COST POTENTIAL INCLUDING MOTOR AND CONTROLLER

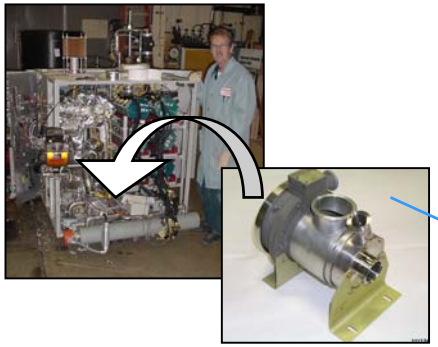
FUEL CELL TURBOCOMPRESSOR CONCEPT



FUEL CELL TURBOCOMPRESSOR HISTORY



2 Bootstrap Turbocompressors
(Full and Partial Flow Sizes)
TEPCO 5MW
Phosphoric Acid
Fuel Cell Power Plant
1981



Demonstration of Motor Driven
Turbocompressor
w/Increased Temperature
Capability Turbine in
DoE/Honeywell 50kW PEM
Fuel Cell System
2001

Demonstration of Motor
Driven Turbocompressor
DoE 50kW PEM Fuel Cell System
for Light Duty Vehicle
1997

Demonstration of
Motor Driven Turbocompressor
w/Mixed Flow Compressor and
Variable Nozzle Turbine
DoE 50kW PEM Fuel Cell System
for Light Duty Vehicle
2001

Motor Driven
Turbocompressor
DoE 50kW PEM Fuel Cell
System
for Light Duty Vehicle
2003

Honeywell

FUEL CELL TURBOCOMPRESSOR HISTORY

- CUSTOMER: DEPARTMENT OF ENERGY
- PHASE 1:
  - USING DOE GUIDELINES: ANALYZED, DESIGNED, FABRICATED AND DEMONSTRATED A TURBINE ASSISTED MOTOR DRIVEN COMPRESSOR (I.E. TURBOCOMPRESSOR) FOR A DoE 50kW PEM (PROTON EXCHANGE MEMBRANE) FUEL CELL SYSTEM
- PHASE 2:
  - USING DOE GUIDELINES, MODIFIED THE PHASE 1 UNIT AND INVESTIGATED IMPROVING THE COMPRESSOR OPERATING RANGE WITH INLET GEOMETRY
  - AGAIN, MODIFIED THE PHASE 1 UNIT BUT WITH AN INCREASED TEMPERATURE CAPABLE TURBINE (~300 DEG C) THAT WAS DEMONSTRATED IN A HONEYWELL 50kW PEM FUEL CELL SYSTEM

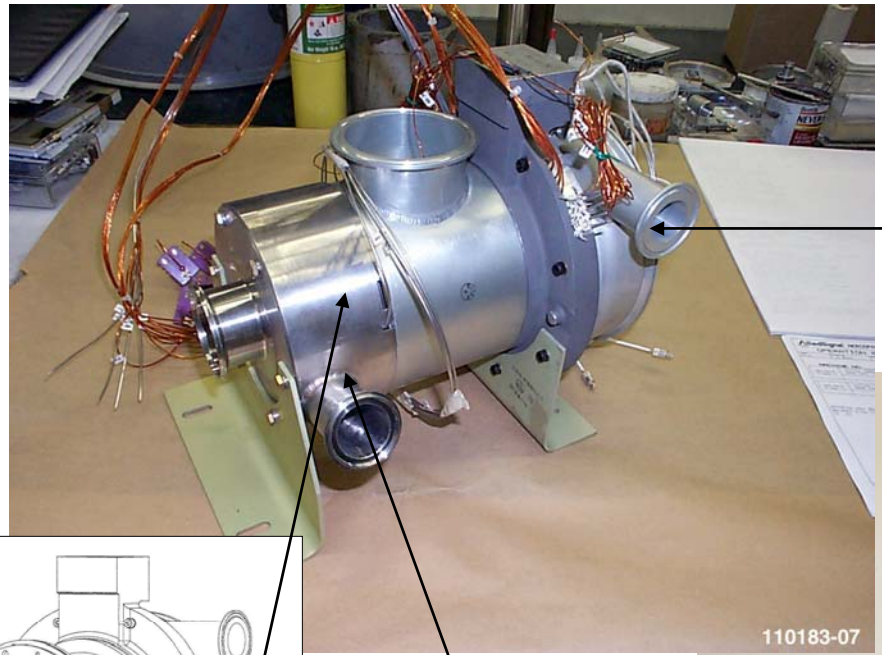
FUEL CELL TURBOCOMPRESSOR HISTORY

- PHASE 3:
  - USING MODIFIED DOE GUIDELINES: ANALYZED, DESIGNED, AND FABRICATED A MIXED FLOW COMPRESSOR AND TURBINE WITH VARIABLE INLET GEOMETRY
    - SACRIFICED HIGH PRESSURE RATIO TO IMPROVE THE LOW FLOW PRESSURE RATIO AND EFFICIENCY CHARACTERISTICS
  - ANALYZED, DESIGNED, AND FABRICATED A VEHICLE READY MOTOR CONTROLLER
  - FABRICATION AND PRELIMINARY TESTING COMPLETED
- PHASE 4:
  - PERFORM A TRADE STUDY TO DEFINE A COST AND PERFORMANCE ENHANCED TURBOCOMPRESSOR CONFIGURATION
  - DESIGN AND FABRICATE THE ENHANCED TURBOCOMPRESSOR
  - DESIGN AND FABRICATE THE ENHANCED MOTOR AND MOTOR CONTROLLER
  - TEST THE ENHANCED TURBOCOMPRESSOR/MOTOR CONTROLLER

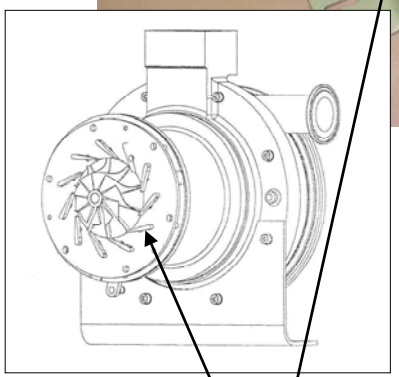
PHASE 3: TURBOCOMPRESSOR WITH VARIABLE GEOMETRY FOR PEM FUEL CELLS

- PROGRAM CLOSED OUT MID 2002
- TECHNICAL OBJECTIVE #1: TRADE STUDY
  - FINDINGS OF HIGH SPEED COMPRESSOR/EXPANDER SELECTED PRESENTED TO DOE
- TECHNICAL OBJECTIVE #2: TURBOCOMPRESSOR UPGRADE
  - ANALYSIS, DESIGN AND FABRICATION COMPLETED
    - MIXED FLOW COMPRESSOR
    - VARIABLE GEOMETRY TURBINE
      - USE OF ENGINE BOOSTING SYSTEMS DESIGN
- TECHNICAL OBJECTIVE #3: MOTOR CONTROLLER UPGRADE
  - UNIT 70% REDUCTION IN VOLUME FROM PHASE 2
  - INCORPORATES AUTOMOTIVE REQUIREMENTS
  - RUGGED DESIGN
  - LOW-COST ARCHITECTURE
  - TESTING COMPLETED PRIOR TO INTEGRATION WITH TURBOCOMPRESSOR

PHASE 3: TURBOCOMPRESSOR WITH VARIABLE GEOMETRY FOR PEM FUEL CELLS



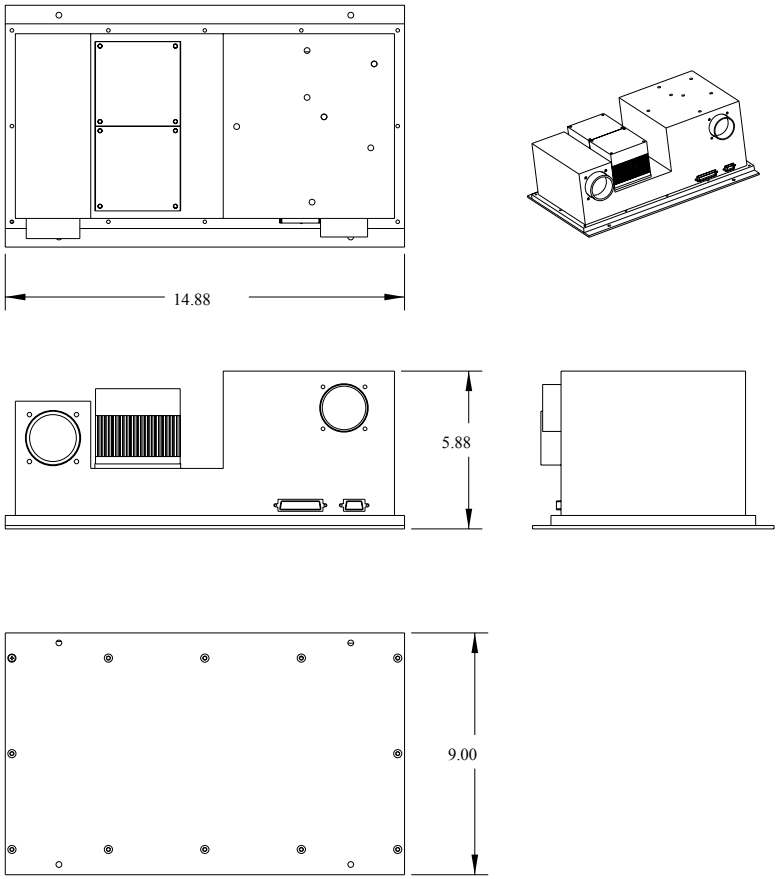
MIXED FLOW COMPRESSOR

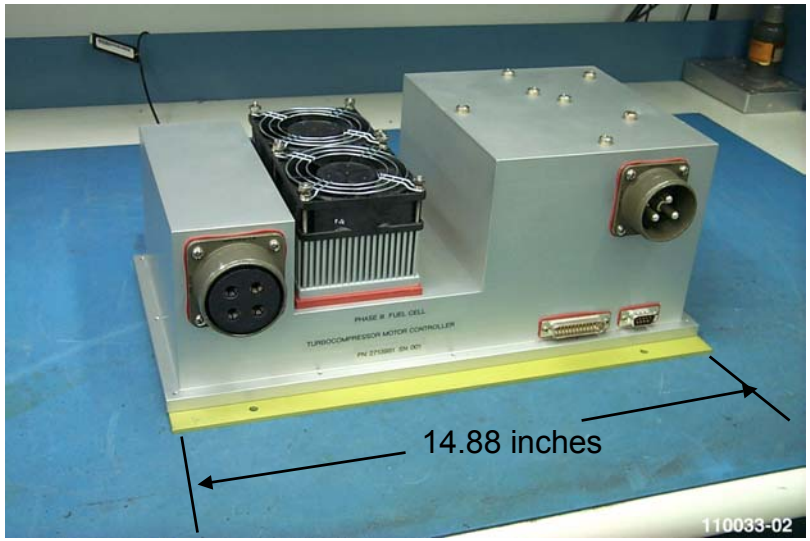


TURBINE

VARIABLE NOZZLE

PHASE 3: TURBOCOMPRESSOR WITH VARIABLE GEOMETRY FOR PEM FUEL CELLS





PHASE 3: TURBOCOMPRESSOR WITH VARIABLE GEOMETRY FOR PEM FUEL CELLS

- TECHNICAL OBJECTIVE #4: TURBOCOMPRESSOR TESTING WITH MOTOR CONTROLLER UPGRADE
  - COMPRESSOR MAPPING COMPLETED
    - EXPANDED SURGE MARGIN AND FLOW RANGE DEMONSTRATED
    - GOOD EFFICIENCY DEMONSTRATED
    - WHEEL TO BE MODIFIED TO FULLY MEET PERFORMANCE OBJECTIVES
    - MODIFICATIONS TO BE INCORPORATED INTO PHASE 4 DESIGN
  - UNIT OPERATED WITH MOTOR UP TO FULL SPEED AND POWER
  - STILL TO BE COMPLETED IN PHASE 4 PROGRAM
    - TURBINE MAPPING
    - POWER CONSUMPTION

PHASE 4 PROJECT DESCRIPTION

- TECHNICAL OBJECTIVE 1: PERFORM A TURBOCOMPRESSOR SYSTEMS PEM FUEL CELL TRADE STUDY TO DETERMINE THE ENHANCED TURBOCOMPRESSOR APPROACH
  - UTILIZE EXPERIENCE FROM PHASES 1-3
  - COMPRESSOR CONFIGURATION
  - TURBINE CONFIGURATION
  - TRADE PERFORMANCE IMPROVEMENTS VERSUS COMPLEXITY, COST, WEIGHT, AND VOLUME
- TECHNICAL OBJECTIVE 2: USING THE RESULTS FROM TECHNICAL OBJECTIVE 1, AN ENHANCED TURBOCOMPRESSOR WILL BE FABRICATED. THE DESIGN MAY BE MODIFIED TO MATCH THE FLOW REQUIREMENTS OF A SELECTED FUEL CELL SYSTEM DEVELOPER.
  - DESIGN FLEXIBLE FOR USE BY VARIOUS SYSTEM DEVELOPERS
  - LOW COST AND IMPROVED PERFORMANCE BEARINGS
  - IMPROVED SHAFT SEALS

PHASE 4 PROJECT DESCRIPTION

- TECHNICAL OBJECTIVE 3: DESIGN A COST AND PERFORMANCE ENHANCED COMPACT MOTOR AND MOTOR CONTROLLER
  - TRADE BETWEEN MOTOR TYPES
    - TWO POLE TOOTHED VS TOOTHLESS CONFIGURATION
  - 55% REDUCTION IN MOTOR CONTROLLER VOLUME FROM PHASE 3
  - 30% REDUCTION IN MOTOR CONTROLLER WEIGHT FROM PHASE 3
  - LOW COST DESIGN
- TECHNICAL OBJECTIVE 4: TURBOCOMPRESSOR/MOTOR CONTROLLER DEVELOPMENT
  - TEST MODIFIED TURBOCOMPRESSOR WITH NEW CONTROLLER

PHASE 4 PROJECT STATUS

- CONTRACT SIGNED MID DECEMBER 2002
- 27 MONTH PROGRAM SCHEDULED TO BE COMPLETED APRIL 2005
  - TECHNICAL OBJECTIVE #1: TRADE STUDY, JULY 2003
  - TECHNICAL OBJECTIVE #2: ENHANCED TURBOCOMPRESSOR, NOVEMBER 2004
  - TECHNICAL OBJECTIVE #3: ENHANCED MOTOR AND MOTOR CONTROLLER, SEPTEMBER 2004
  - TECHNICAL OBJECTIVE #4: INTEGRATED ENHANCED TURBOCOMPRESSOR, MARCH 2005

PHASE 4 PROJECT STATUS

- TECHNICAL OBJECTIVE #1: TRADE STUDY
  - INTERVIEWS WITH VARIOUS DEVELOPERS UNDERWAY
    - TO BE COMPLETED APRIL 2003
  - DEVELOPERS SHOWING INCREASED INTEREST IN TESTING TECHNOLOGY
    - LOW COST POTENTIAL
    - NO CONTAMINATION
    - SIZE AND WEIGHT ADVANTAGE
- TECHNICAL OBJECTIVE #2: ENHANCED TURBOCOMPRESSOR,
  - TEAM MEMBER REQUIREMENT DEFINITION UNDERWAY
    - USING RESPONSES FROM TECHNICAL OBJECTIVE #1
  - LAYOUT AND ANALYSES INITIATED
    - AERODYNAMIC
    - THERMAL
    - ROTORDYNAMIC
    - MATERIALS
    - BEARING

PHASE 4 PROJECT STATUS

- TECHNICAL OBJECTIVE #3: ENHANCED MOTOR AND MOTOR CONTROLLER
  - TEAM MEMBER REQUIREMENT DEFINITION UNDERWAY
    - USING RESPONSES FROM TECHNICAL OBJECTIVE #1
  - MOTOR DESIGN INITIATED
- TECHNICAL OBJECTIVE #4: INTEGRATED ENHANCED TURBOCOMPRESSOR
  - EFFORT TO START NOVEMBER 2004

QUESTIONS/COMMENTS?

MARK K. GEE

PROGRAM MANAGER - FUEL CELL TURBOCOMPRESSORS

Turbomachinery - Torrance, CA

Phone: 310-512-3606

E-mail: mark.gee@honeywell.com

Development of a Toroidal Intersecting Vane Machine Air Management System for Automotive Fuel Cell Systems

Sterling Bailey Ph.D., P.E.
Mechanology, LLC
sterling@mechanology.com

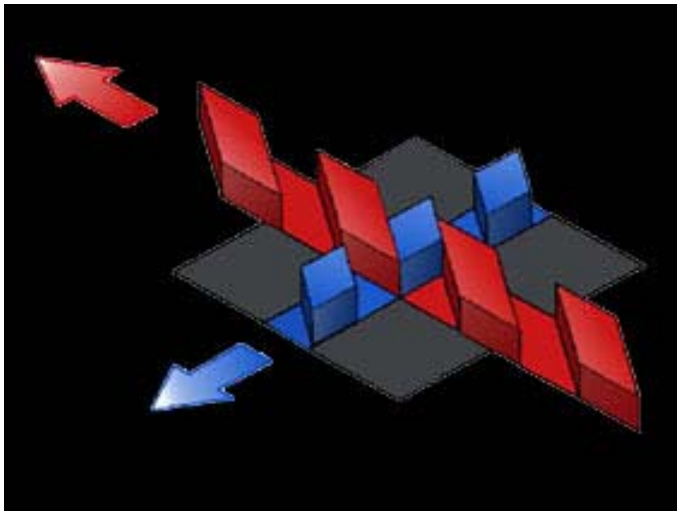
The focus of this program is to develop the innovative TIVM concept into working compressor/expander/motor hardware that satisfies the FreedomCAR Guidelines – and is easily adaptable to individual car system requirements – and to measure the TIVM air management system performance

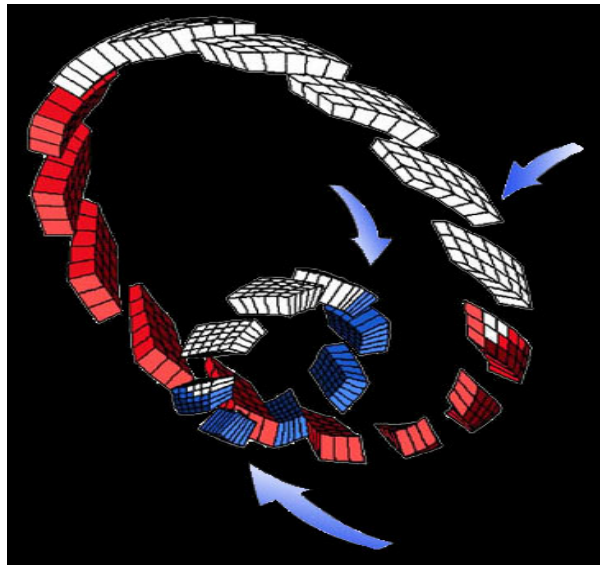
Relevance and Objective of The TIVM Compressor/Expander/Motor Development Project

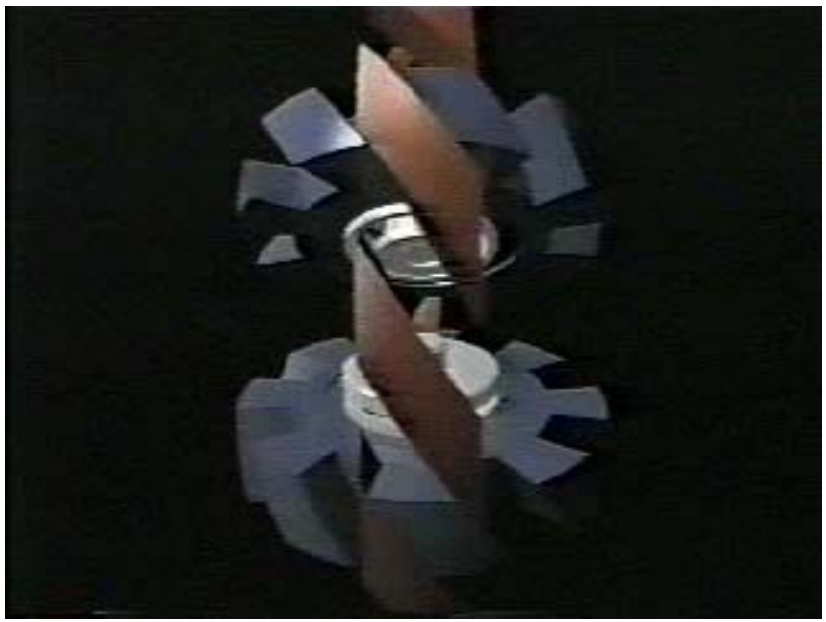
The Objective of Mechanology's TIVM CEM Development and Demonstration project is to overcome the following Transportation Systems Technical Barrier identified in the Draft Fuel Cell R&D Plan:

"**Compressors/Expanders**. Automotive-type compressors/expanders that minimize parasitic power consumption and meet packaging and cost requirements are not available. To validate functionality in laboratory testing, current systems often use off-the-shelf compressors that are not specifically designed for fuel cell applications resulting in systems that are heavy, costly, and inefficient. Automotive-type compressors/expanders that meet the FreedomCAR program technical guidelines need to be engineered and integrated with the fuel cell and fuel processor so that the overall system meets packaging, cost, and performance requirements. "

The Toroidal Intersecting Vane Machine Concept







Toroidal Intersecting Vane Machine Characteristics

Positive Displacement

- Compressor/Expander
- Compressor/Compressor
- Blower

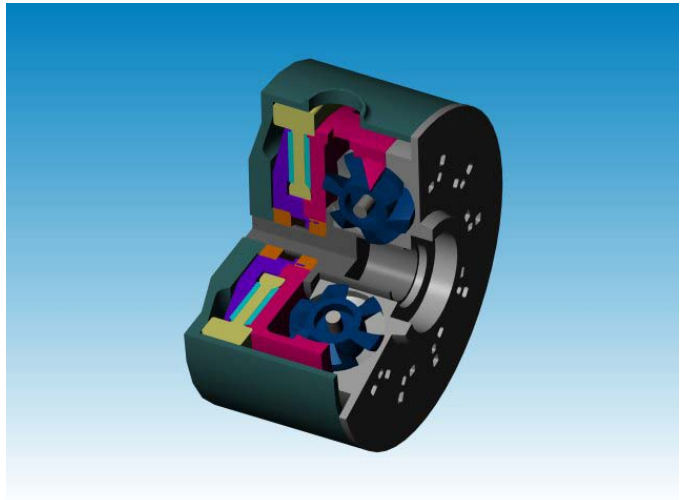
High Flow

High or Low Pressure

Small Volume

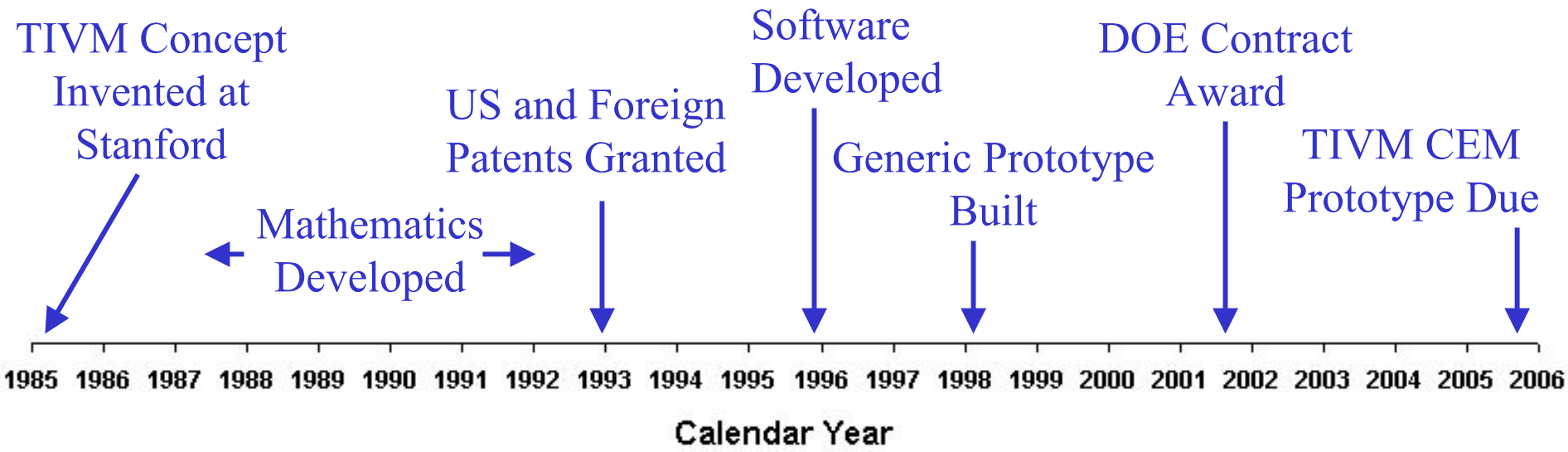
Low Production Cost

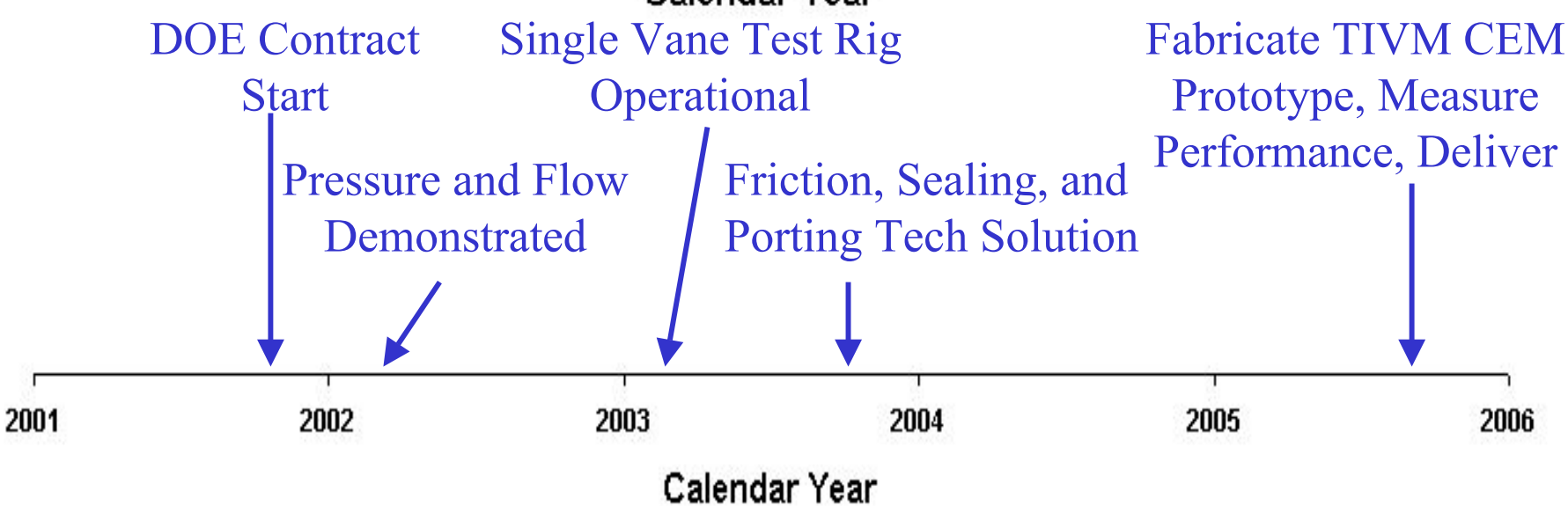
Many Spin-off Products



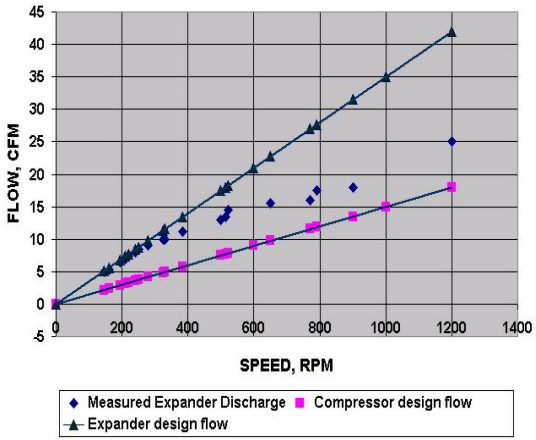
TIVM Attributes Provide Efficient Operation as an Integral Compressor/Expander for Automotive Fuel Cell Applications With Very Good Performance at High Turndown Ratios

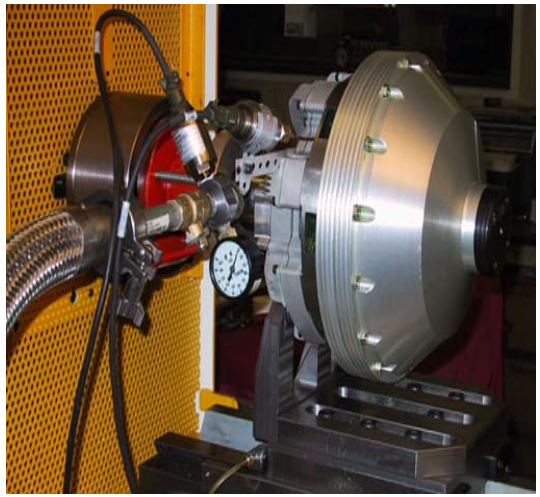
TIVM Development Timeline

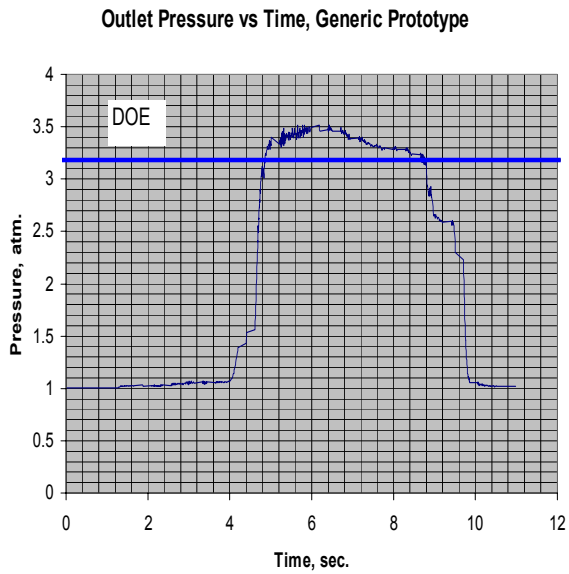


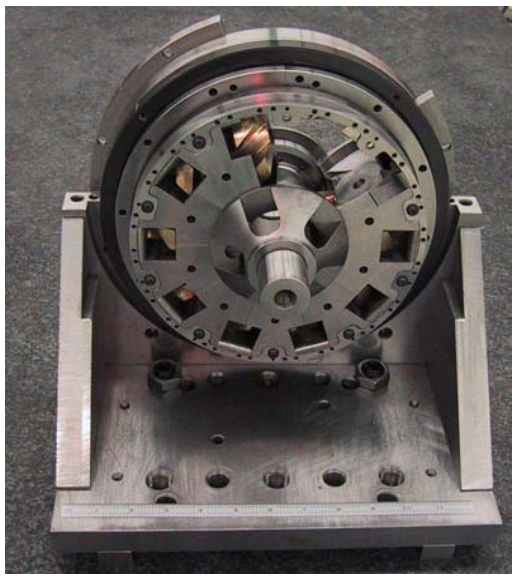


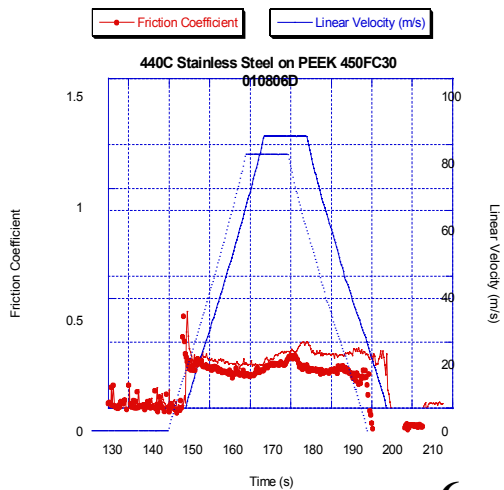
The Basic Viability of the TIVM Has Been Proven Through Hardware and Tests











Requirements Compliance Matrix for TIVM Compressor/Expander

Requirement	Value	Comment	TIVM Status
Flow	76 g/s (135 cfm) For 50 kWe	Flow consistent with design flow demonstrated with temporary seals - as expected for positive displacement device	Capability Demonstrated
Pressure	3.2 atm	3.5 atm pressure demonstrated with temporary seals - as expected for positive displacement device	Capability Demonstrated
Power	5.0 kW	Key remaining performance issue – requires low friction effective seals	6 kW - Remains to be Demonstrated
Size	8-11 liters	Acceptable to car makers and OEMs (Compressor, expander, and motor)	8 L – Acceptable (2005)
Weight	8-11 kg	Acceptable to car makers and OEMs	16 kg – Acceptable (2005)
Noise	<70 db	Use of polymer parts and compliant seals will mitigate	To Be Demonstrated
Cost	$400	Cost estimates based on vendor quotes Give several $100's in high volume	Expected to be acceptable

Three Key Performance Issues Needed to Satisfy the Power Requirement

- Seals to limit air leakage without adding excessive friction
- Confirmation of coefficient of friction for meshing vane interface – including high humidity environment
- Porting to assure low pressure drop, and power loss, across the compressor and expander inlet and discharge paths

These are not unusual engineering tasks that require inventions or new materials. Solid, disciplined engineering development will provide the required solutions

Requirements for Vane Seals

(For 6 kW Shaft Power at 100% Power and Flow)

Limit air leakage from compressor and expander to < 5%

- leakage rate < 0.38 g/s for full power and flow

- leakage rate < 0.076 g/s for 20% power and flow

Friction < 1.5 lb drag per rotor

Accommodate dimensional changes from wear, thermal expansion, fabrication tolerances, tolerance stack up. Requires compliance of ~15 x 10^-3 inches

Manufacturable in large volume

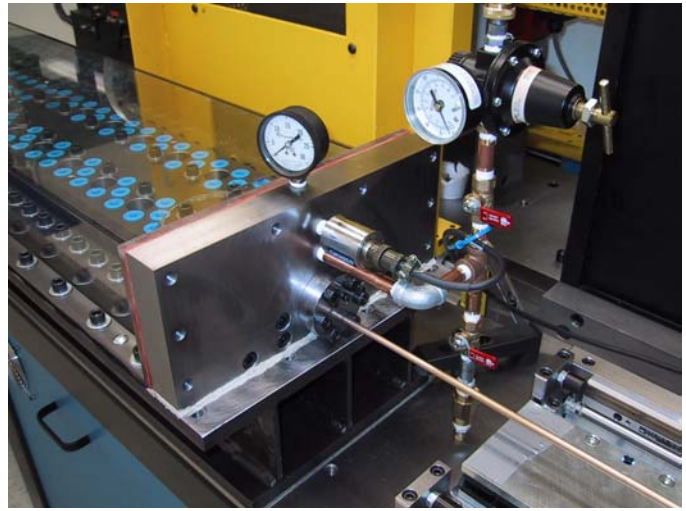
Cost effective

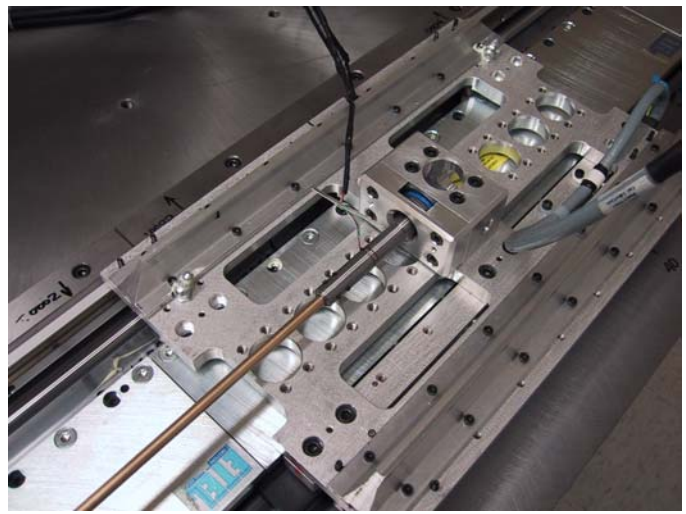
Single Vane Test Machine Features

- Designed for Development of Vane Seals
- Preserves Dimensional Scale of 50 kW TIVM / CE
- Leverages Existing Test Stand Hardware and Instrumentation
- Fast Turn Around Time for Test Specimens
- Static Sealing
- Dynamic Sealing (to 15 m/s vane velocity)
- Gas Pressure and Temperature (4 kHz)
- Seal Friction via Load Cell
- Linear Servo Motor

  Position feedback (5 micron)

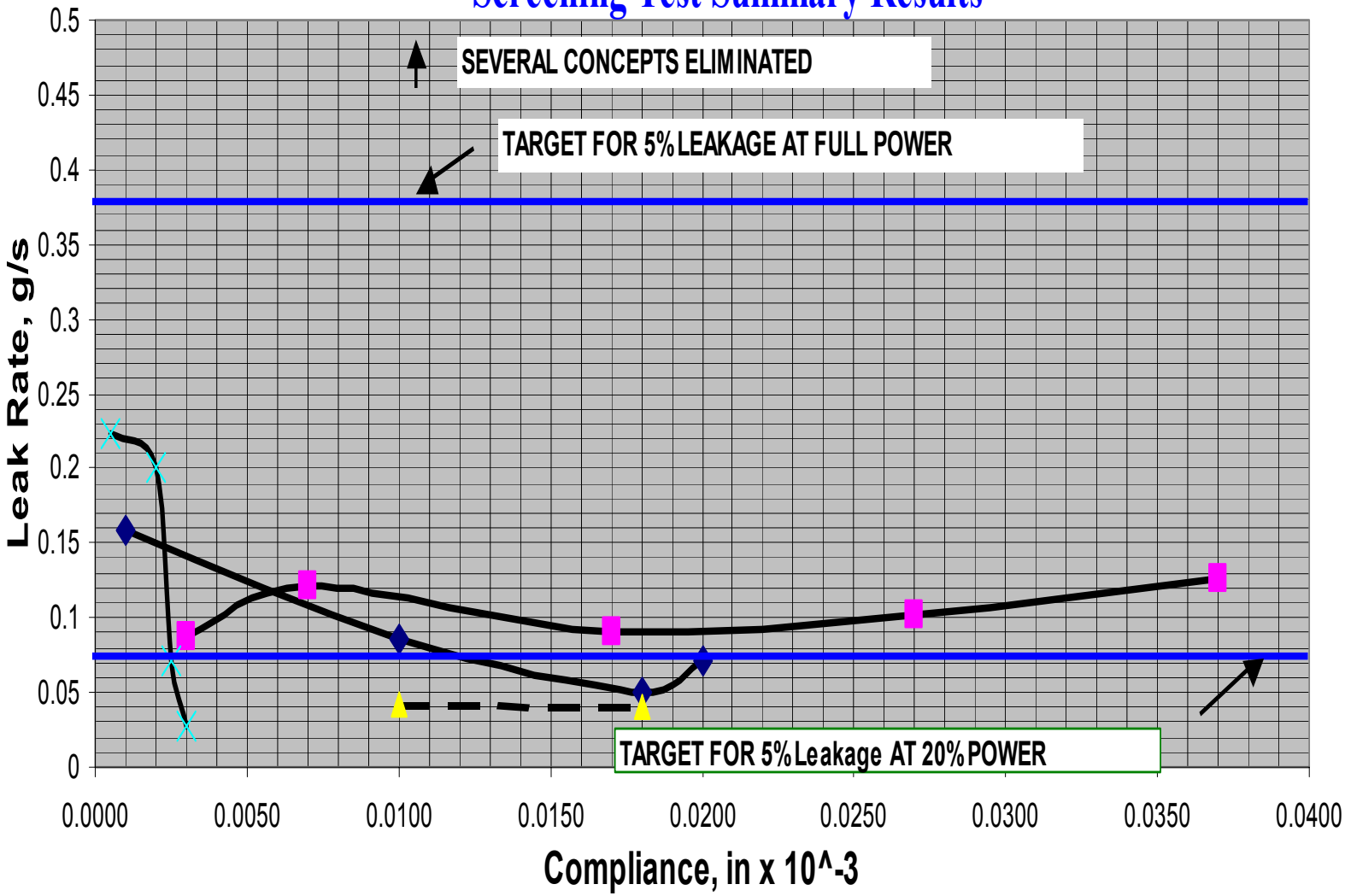
  Velocity control (0 to 15 m/s)





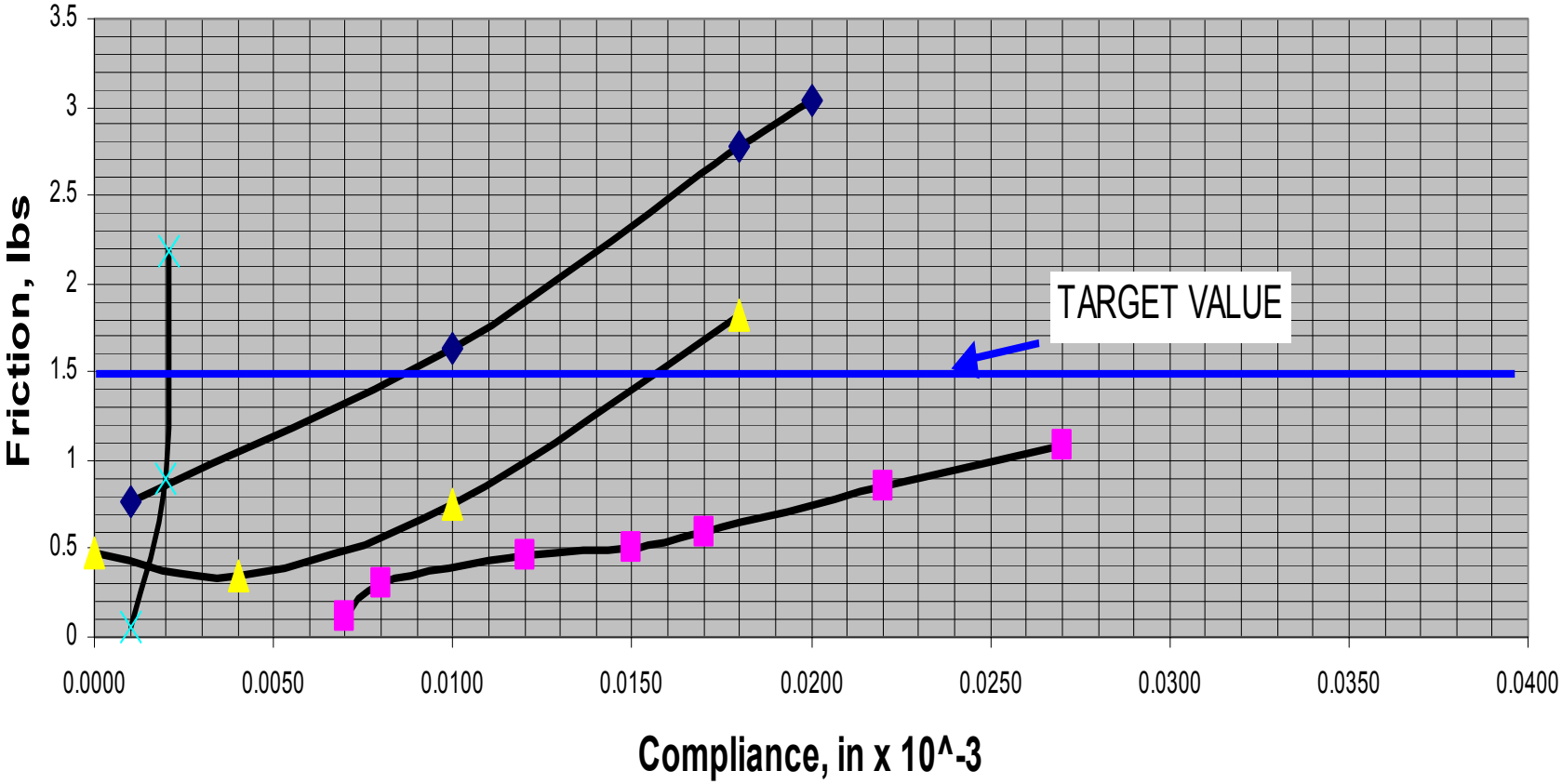
Leakage Rate vs Compliance For Several Seal Options

Screening Test Summary Results



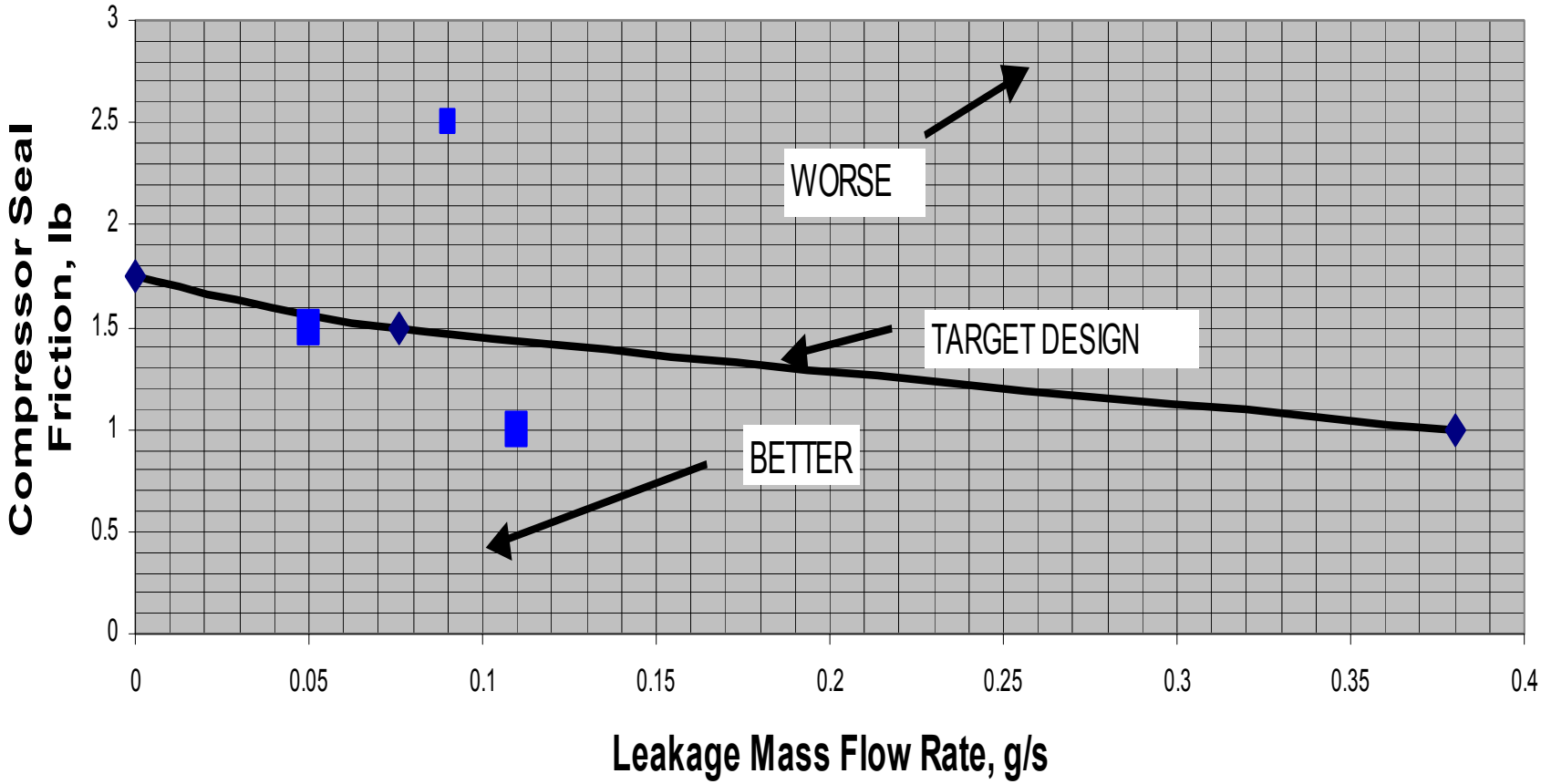
Two Seal Concepts Meet Full Power Requirements

Friction vs Compliance for Candidate Seals



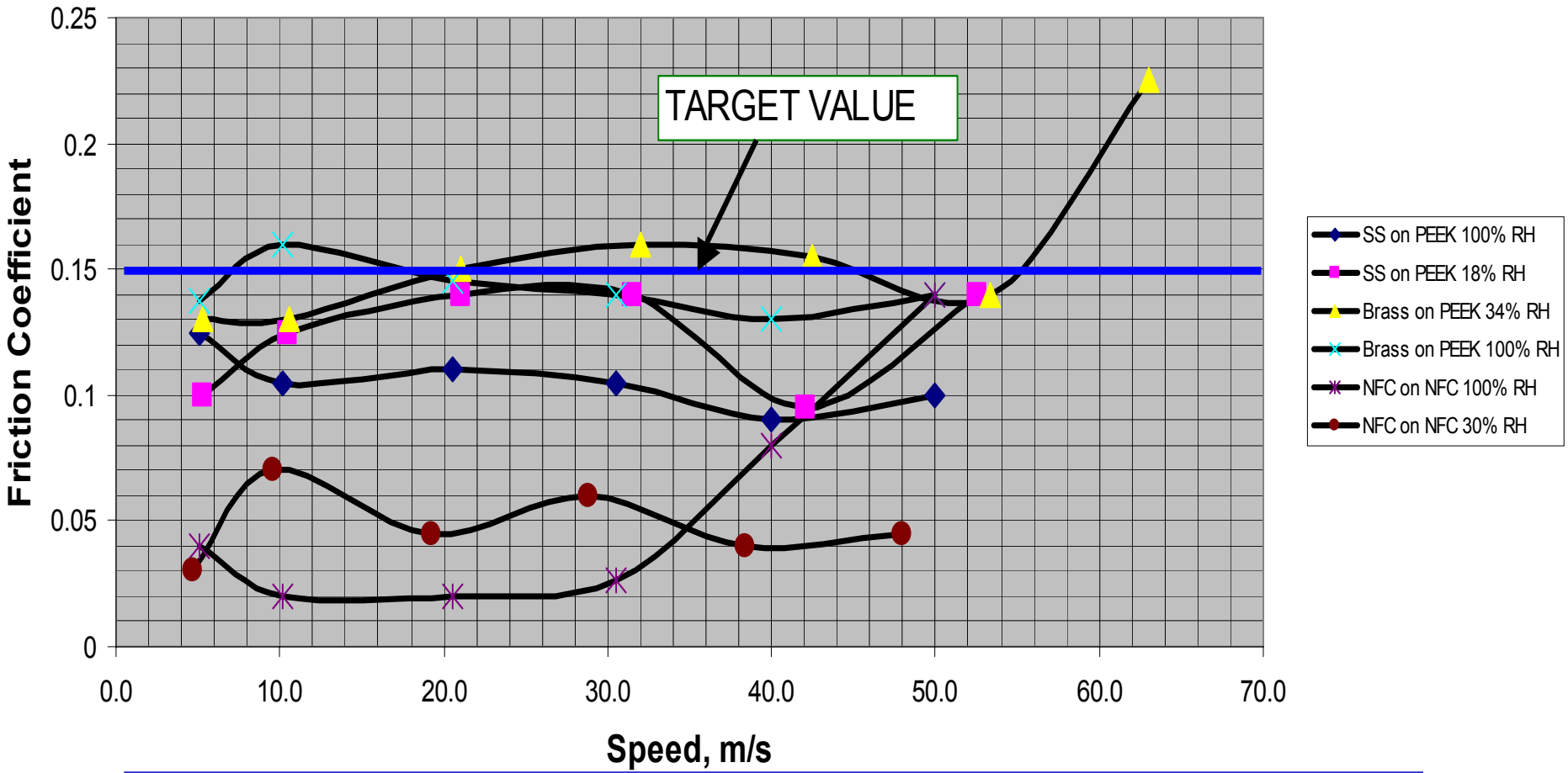
Two Seal Design Concepts Meet Friction Requirement

Leakage vs Friction Tradeoff for 6 kW Shaft Power



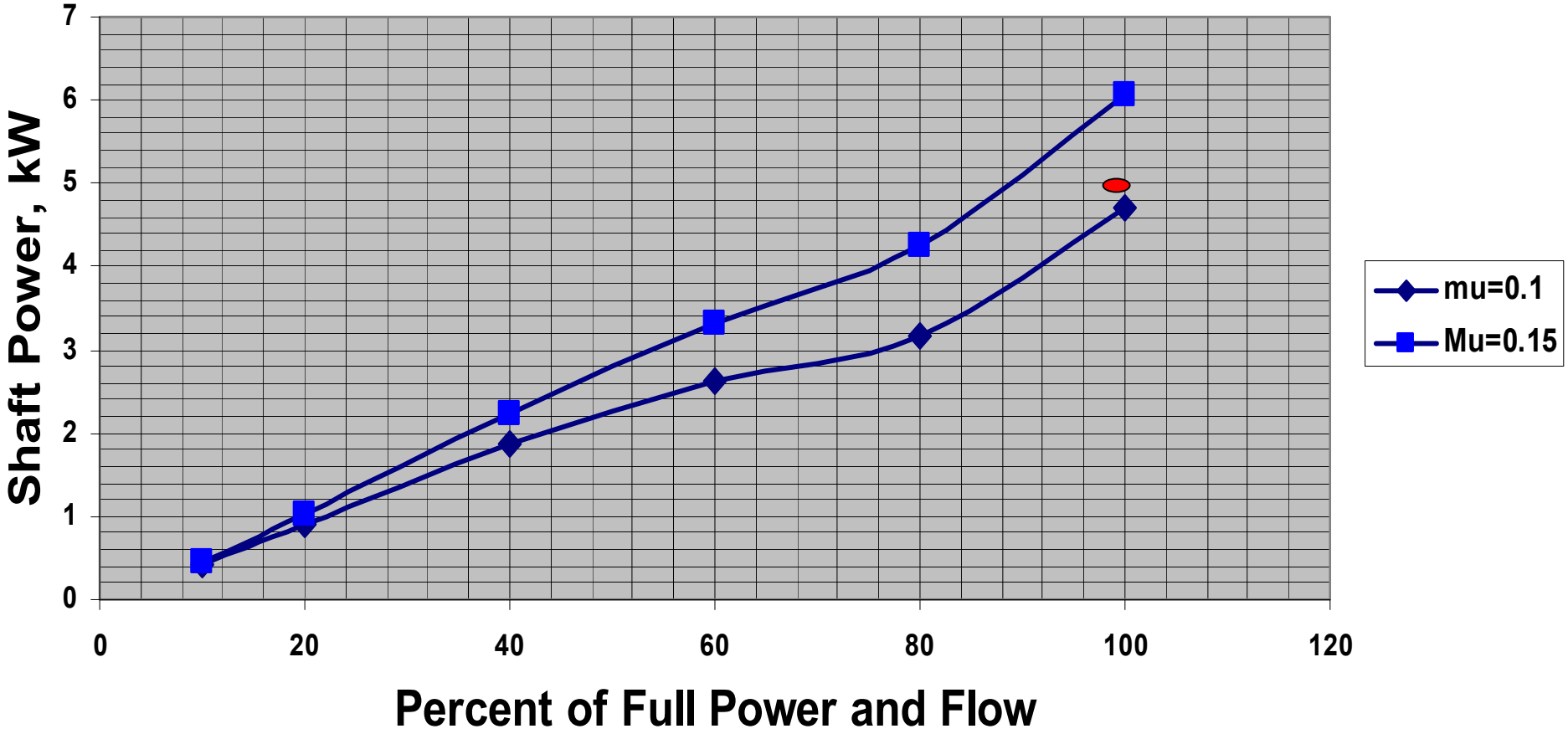
Two Seal Concepts Meet Leakage and Friction Requirements for 6 kW – Further Optimization Possible

Friction Coefficient vs Speed, Most Recent ANL Data



Vane to vane coefficient of friction of <0.15 is achievable

Shaft Power vs % Power and Flow, DOE Guidelines, Seal "B" Characteristics and 3.2 atm Pressure



Parasitic power load of <6 kW appears to be achievable

Future Plans

Complete seal measurements for combined leakage and friction – confirm satisfactory performance of at least one design – August 2003

Perform porting feature measurements to confirm satisfactory performance – August 2003

Complete investigation of additional innovation with potential to reduce shaft power by > 1kW.

Build fully operational prototype with selected seals and ports – measure integral performance

With accelerated funding, August 2004
At planned funding rate, September 2005

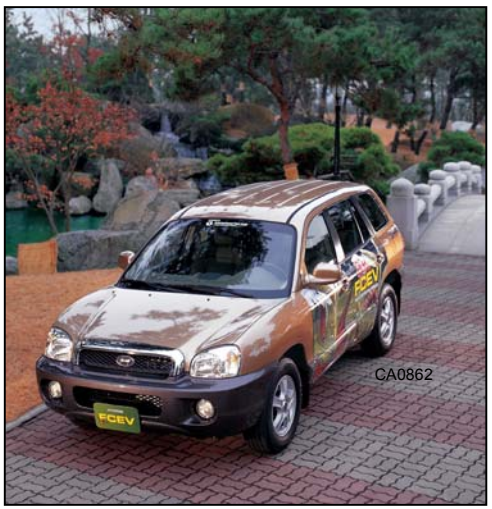
Integrate high efficiency motor – measure performance, deliver to Argonne National Laboratory for testing

With accelerated funding, September 2004

At planned funding rate, September 2005

UTC Fuel Cells

A United Technologies Company



PEM Fuel Cell Air Blowers
DOE Merit Review

May 22, 2003

Tom Clark & Michael Arner

Tom.Clark@utcfuelcells.com

Michael.Arner@utcfuelcells.com

195 Governor's Highway
South Windsor, Connecticut 06074 USA
(860) 727-2200
www.utcfuelcells.com

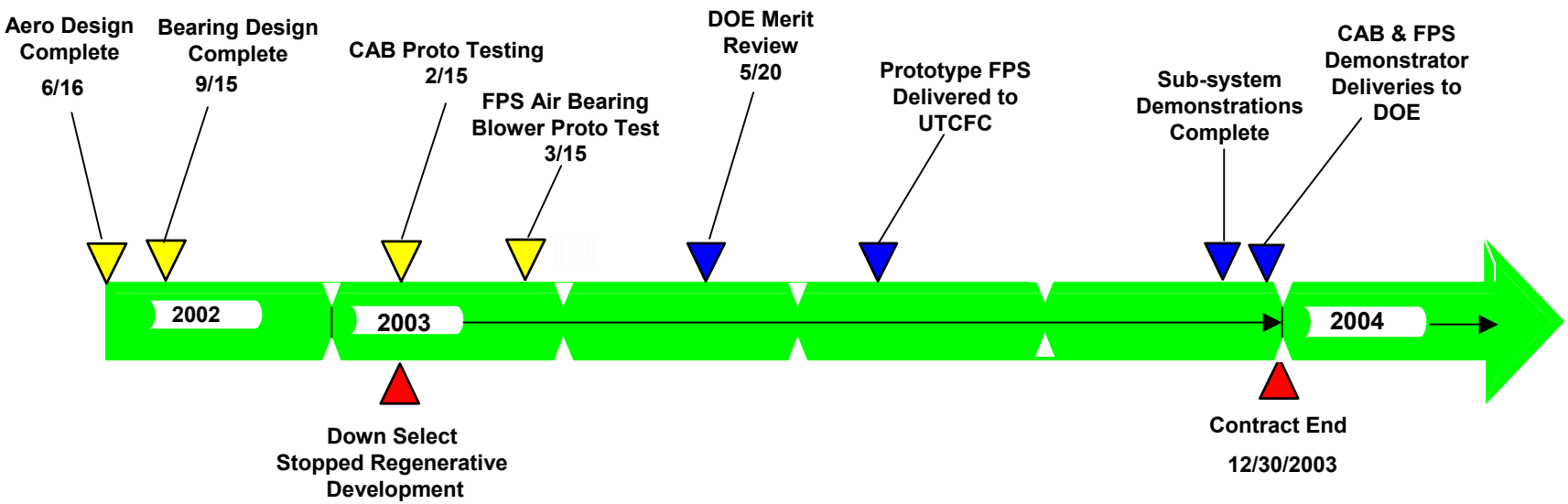
TMC-32502

UTC FUEL CELLS

Motor - Blower Technologies

Program Objectives / Schedule

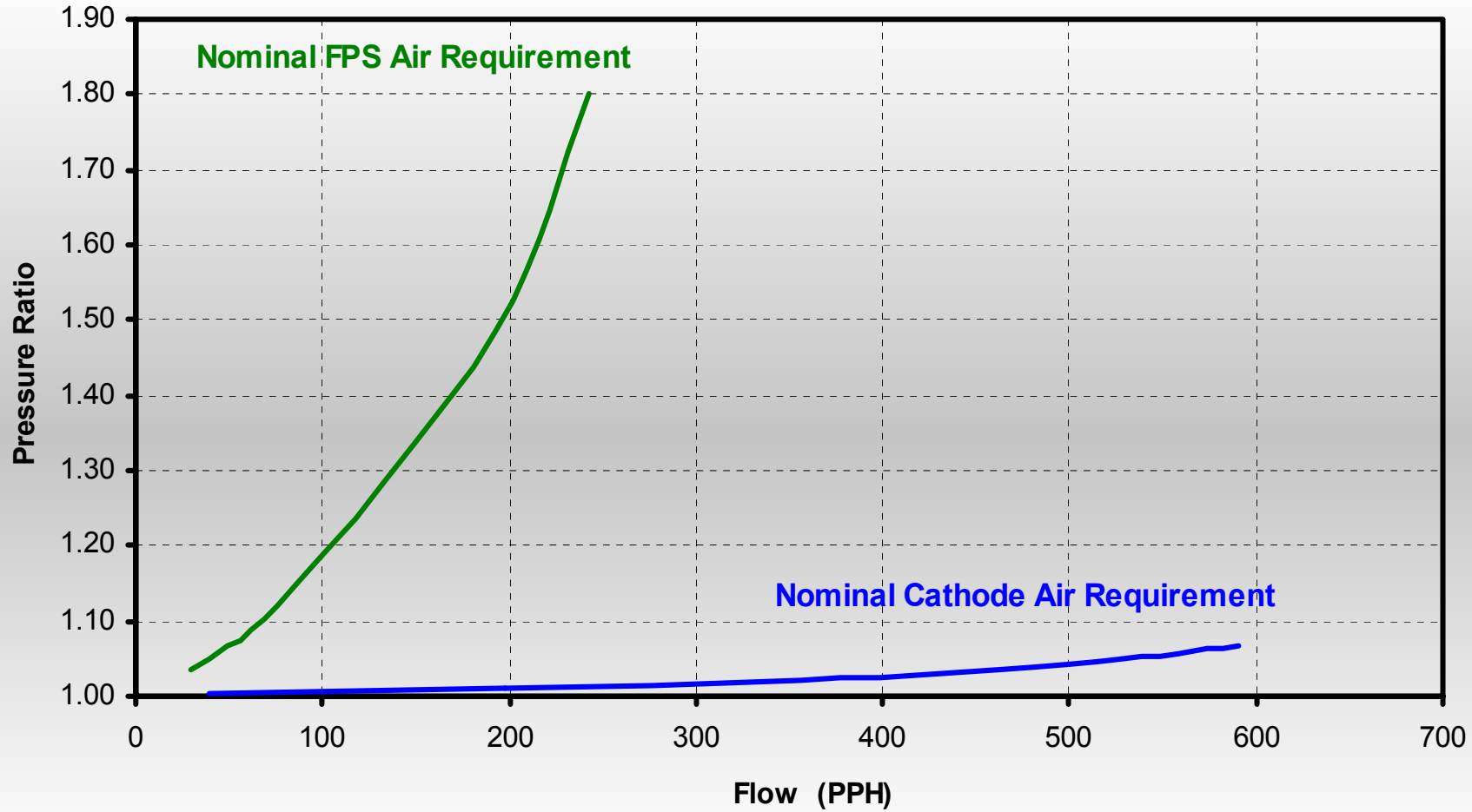
1. Develop a blower technology base for ambient fuel cells
2. Reduce weight and cost
3. Increase Performance
4. Improve Reliability
5. Develop a supplier base



UTC FUEL CELLS

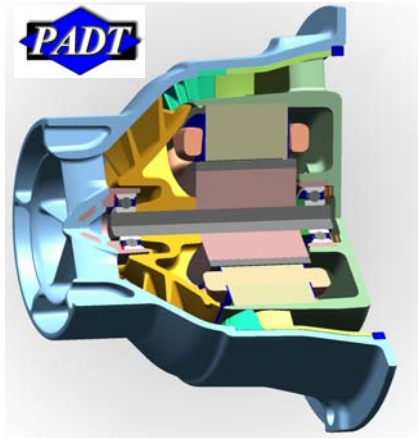
Motor - Blower Technologies

Ambient Pressure Fuel Cell Blower Performance Requirements
75 kW Power Plant



UTC FUEL CELLS

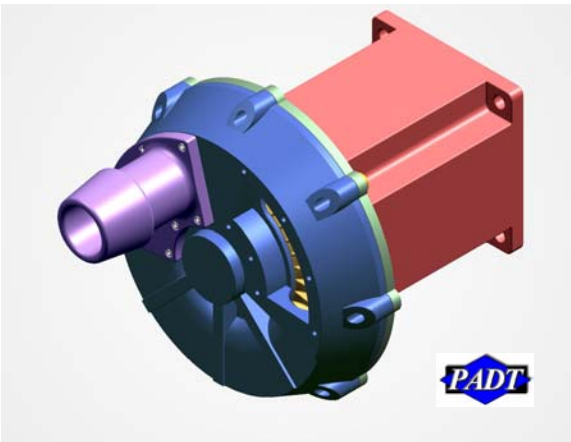
Motor - Blower Technologies



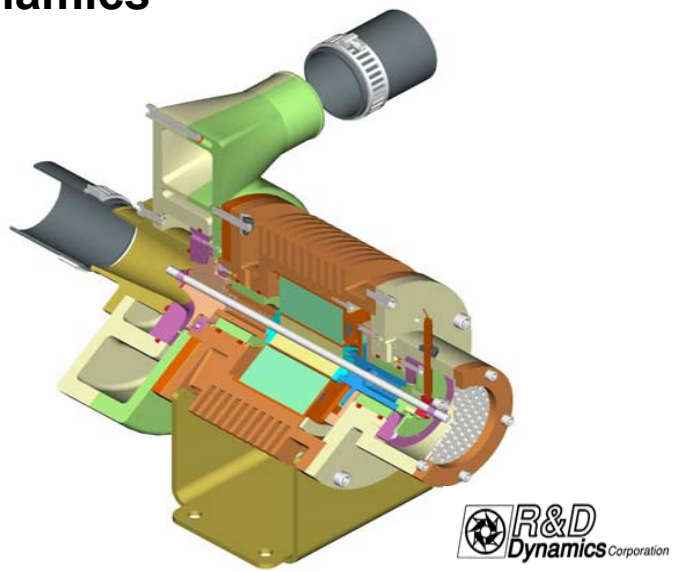
CAB Vane Axial

Three Blowers Being Developed by Two Subcontractors

1. **Vane Axial Cathode Air Blower, PADT**
2. **Regenerative FPS Air Blower, PADT**
3. **Centrifugal FPS Air Blower, R&D Dynamics**



FPS Regenerative



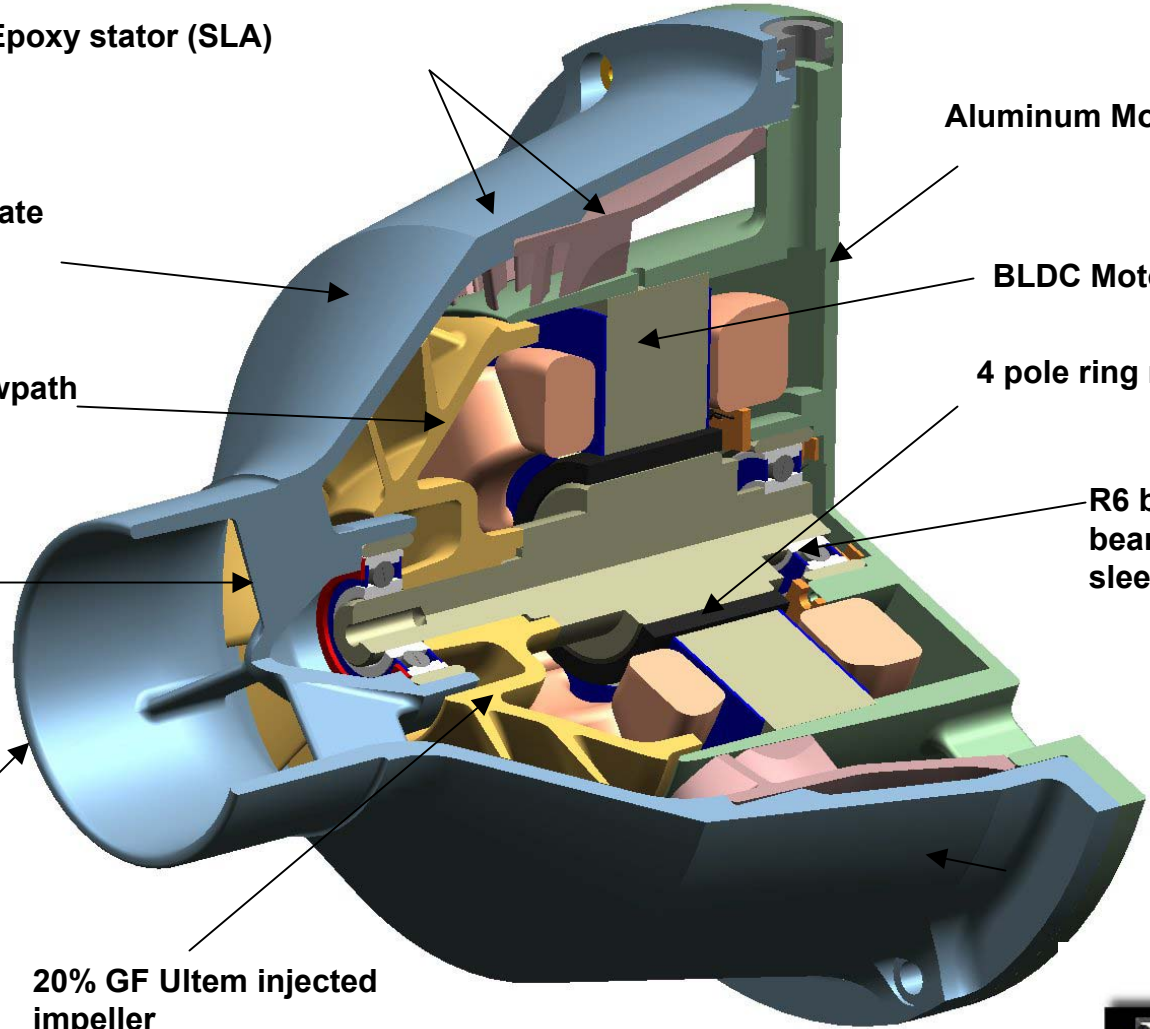
FPS Centrifugal

Cathode Air Blower Goals

- Performance: 1 psi @ 170 cfm
- Design for low cost < $75 at 100K units / year
- Demonstrate overall efficiency > 60%
- Design for 5000 hour service life
- Design blower that is easily scalable in flow
- Deliver hardware for Q4 2003 DOE P/P demonstration

UTC FUEL CELLS

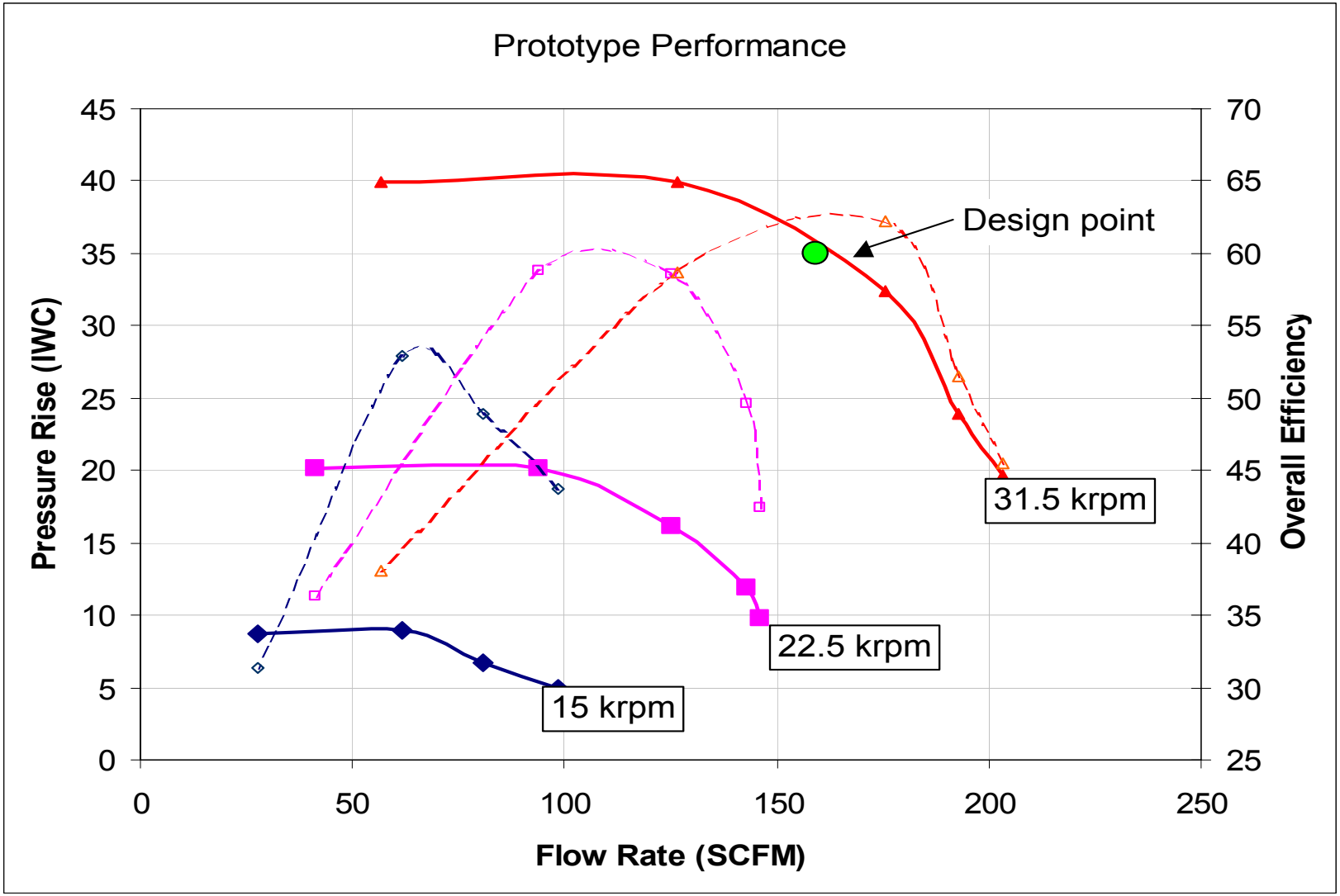
Motor - Blower Technologies



PADT

UTC FUEL CELLS

Motor - Blower Technologies



Prototype Exceeds Efficiency Target

Cathode Air Blower Status

- Design Features
  - Achieved compact integrated design
  - Selected mixed flow axial machine
  - Motor cooled by process fluid
  - Designed for manufacturability
  - Utilization of injection molded parts

- Technical Accomplishments
  - Prototype blower meets flow and pressure specifications
  - Custom motor and controller meets performance expectations
    - Resolved motor rotor heating by increasing switching frequency to 80 kHz
  - High volume configuration optimization underway
    - Volume quoted cost projection: $83.95
  - Remaining work emphasizes cost reduction and increasing robustness

UTC FUEL CELLS

Motor - Blower Technologies

Remaining CAB Technology Tasks

- Finalize blower design for high volume mfg.
  - Continued manufacturing cost analysis
  - Plastic over-mold motor housing test
  - Evaluate effects of thermally potted motor winding
  - Bearing liner overmold test
- Finalize blower detailed design for low-cost / initial volume mfg, make and test prototypes
- Complete blower durability / reliability testing
  - Bearing life, shock & vibration, creep, high temperature testing
- Develop and implement sensor-less motor controls into controller and redesign for low cost.

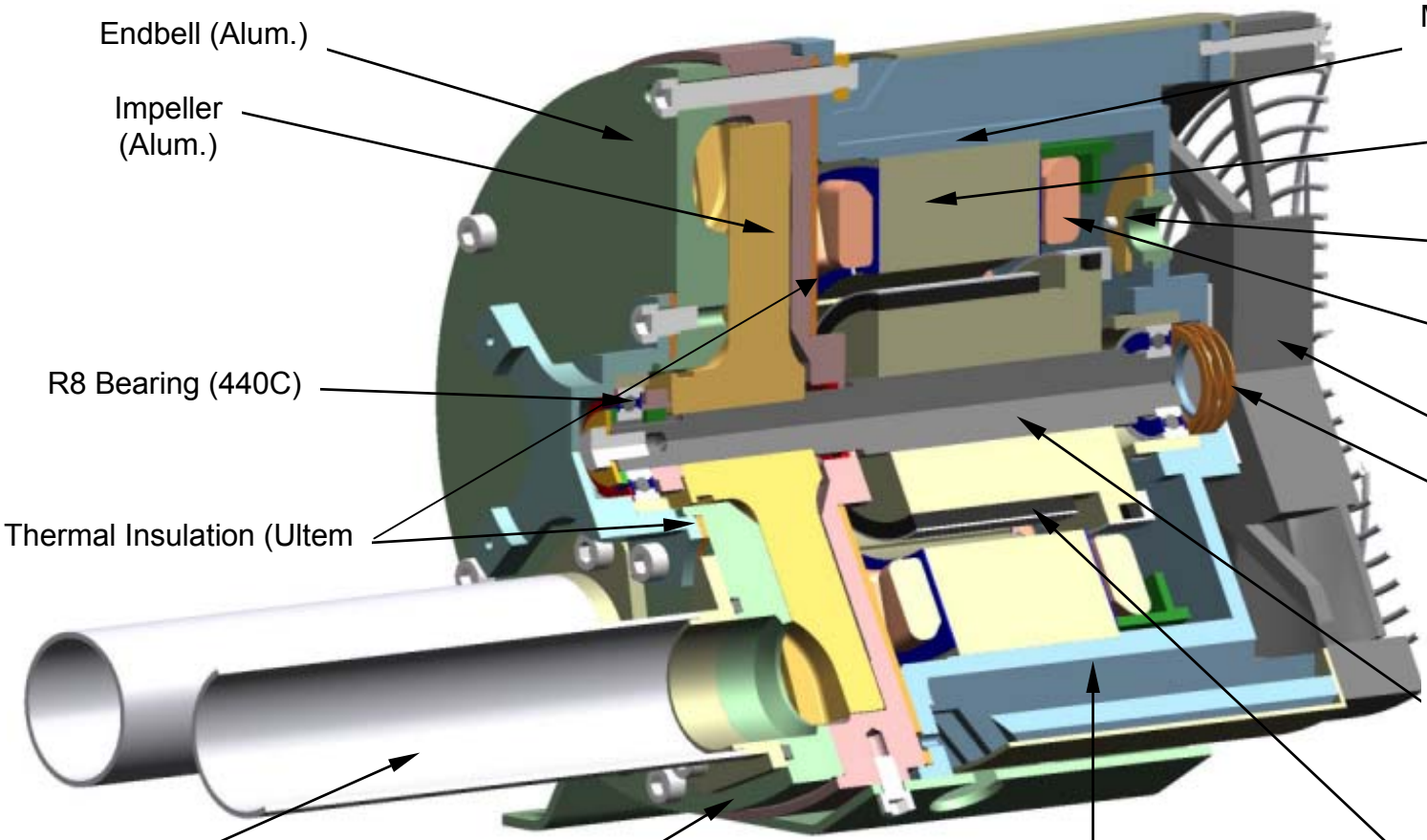
FPS Blower Goals

- Performance: 12 psi @ 70 cfm
- Design for low cost < $75 at 100K units / year
- Demonstrate overall efficiency > 50%
- Weight: 10 lbs (includes controller)
- Design for 5000 hour service life
- Develop novel regenerative blower technology that provides higher efficiency
- Deliver hardware for Q4 2003 DOE P/P demonstration

UTC FUEL CELLS

Regenerative FPS Blower

Motor - Blower Technologies



PADT

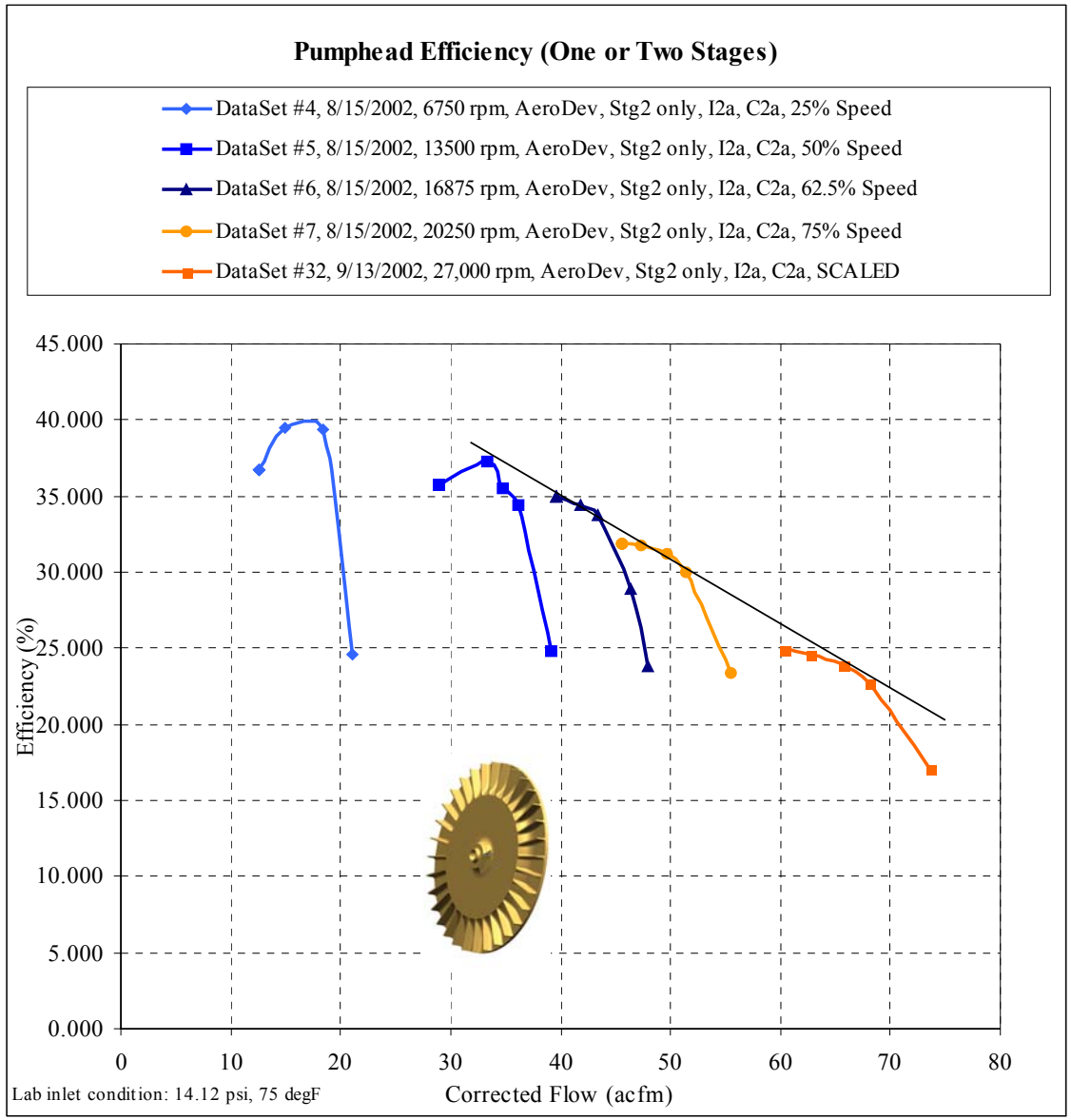
PADT FPS Regenerative Blower Project Status

- Extensive CFD work and testing has indicated **low efficiencies**
- Low aerodynamic efficiency compounds motor heating problem
- 2 stage approach was evaluated but was large, expensive and resulted in thermal growth issues
- Remaining work will entail aerodynamic testing of promising geometries

UTC FUEL CELLS
Motor - Blower Technologies

Aero Efficiencies are Low

- Regen. was chosen because it builds good pressure at low flow with lower RPM
- However, regens are inherently low in efficiency
- Carry over is main efficiency culprit which especially at high pressure ratios
- Motor rotor heating may also contribute to trend
- Test matrix underway with SLS hardware to establish peak efficiency



Regenerative Blower
Technical Lessons Learned

- Regenerative air blowers are most efficient at low pressure ratios, < 1.3
- Significant performance losses are incurred due to carry-over of preworked air from outlet to inlet.
- Exit to inlet port leakage impacts efficiency and elevates inlet air temperature
- Two stage regenerative approaches should be avoided.
  - Relative growth between stage 1 and stage 2 lead to large clearances and poor performance.
  - Transferring air from one stage to the next was very inefficient
  - Sealing between the stages was very difficult.
- Low pump head efficiencies lead to high motor heat rejection
- RPM reduction with a regenerative approach is ~ factor of 4 over centrifugal approach. However efficiency is approx. ½ of a centrifugal machine.

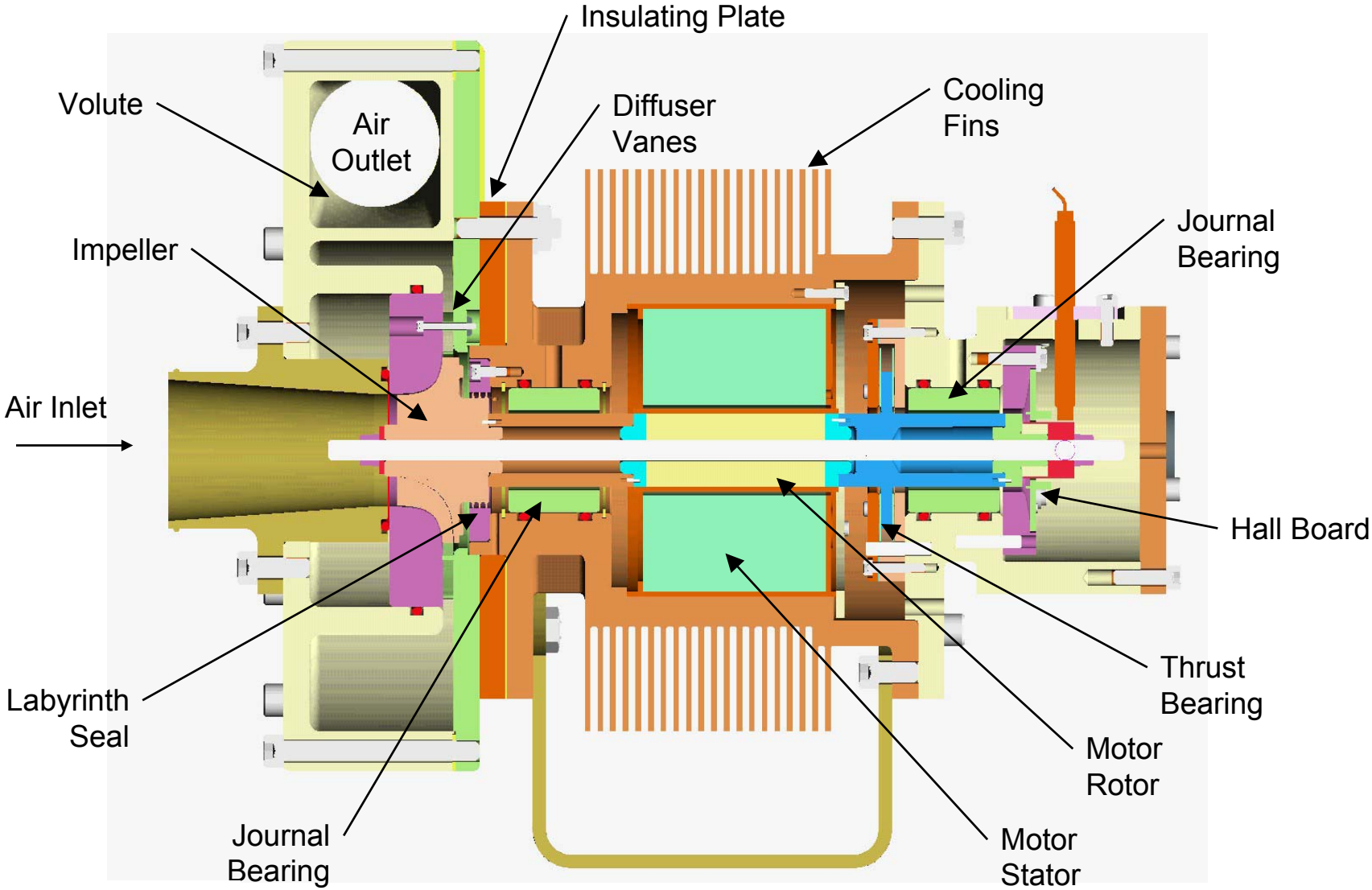
Regenerative Blower Down-select

- The regenerative approach is too inefficient for this particular specification
- CFD results did lead to modest improvements (3-5%) on paper. 6 sets of SLS hardware have been produced to explore the expected trends
- Test final set of SLS hardware and issue summary report
- Results of this work could be used in other fuel cell applications that are well suited to regenerative compressors. Hydrogen Recycle and Moderate pressure Cathode air deliveries are potential applications

UTC FUEL CELLS

Centrifugal FPS Air Blower

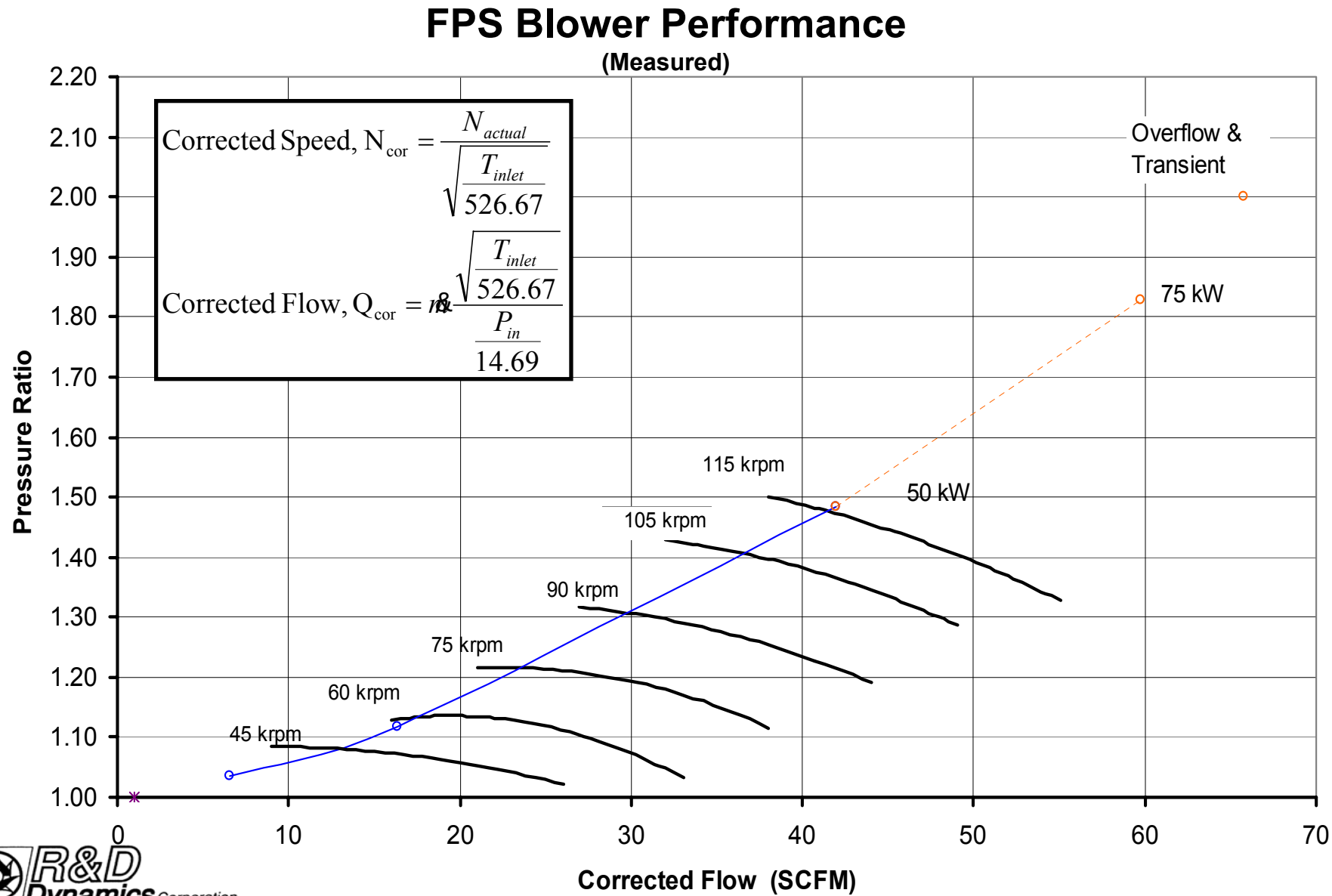
Motor - Blower Technologies



R&D Dynamics Corporation

UTC FUEL CELLS

Motor - Blower Technologies



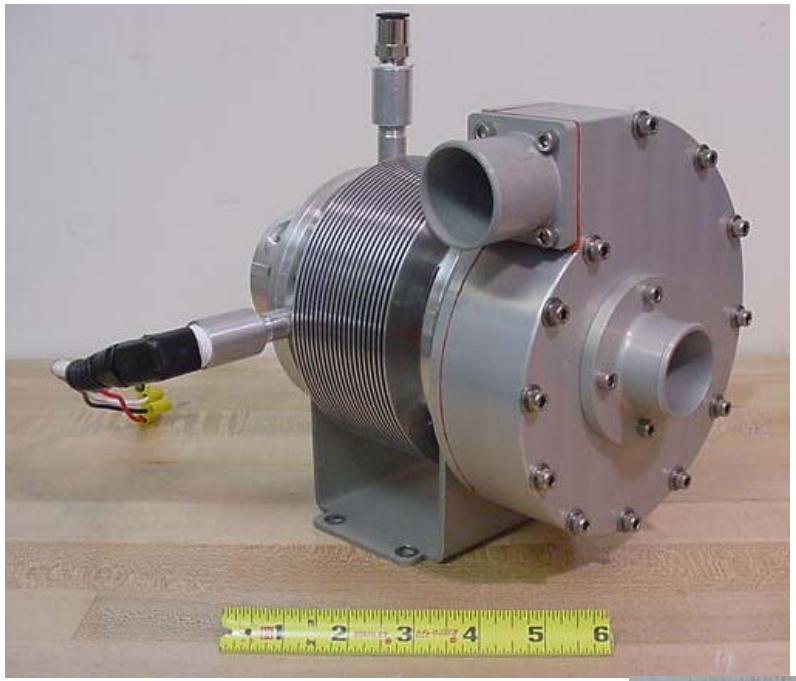
R&D Dynamics Corporation

FPS Centrifugal Air Blower Status

- Design Features
  - High speed centrifugal design, 140K rpm
  - Utilizes foil air bearing technology
  - Motor and controller air cooled
  - Total Weight 30 lbs
- Project Accomplishments
  - Foil air bearings and rotating group tested to 153 Krpm
  - Aerodynamic performance and controller verified to 108,000 rpm, performance meets predictions
  - Blower / controller cost projection, in volume: $163
- Technical Issue
  - Heat buildup demagnetizes motor rotor

UTC FUEL CELLS

Motor - Blower Technologies



FPS Blower

Rotating Assembly

R&D Dynamics Corporation

R&D Dynamics FPS Blower, Remaining Tasks

- Demonstrate blower with new motor and controller
  - New motor designed to minimize rotor heating and eddy current losses via laminated rotor magnet and proprietary rotor magnet sleeve
- Incorporate improved rotor cooling scheme
- Performance test to full speed
- Complete blower durability / reliability testing
  - Bearing life, shock & vibration, creep, high temperature testing
- Refine and finalize manufacturing cost estimates
- Evaluate and mitigate acoustic noise

Powered by
Innovation since 1886

CONCEPTS NREC

Scroll Corporation

DOE Compressor/Expander Module Development Program Merit Review Meeting

May 22, 2003

TIAX LLC
Acorn Park
Cambridge, Massachusetts
02140-2390

Ref: (75114/D0037)
DE-FC04-01AL67603

This presentation contains no proprietary information and is for FreedomCAR Merit Review use only.

Our objective for this meeting is to review the state of the technology and the plan to achieve the goals set forth for the Compressor/Expander Technology development program.

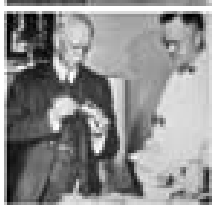
- We will review (briefly) the history of this line of Compressor/Expander Module development
- We will review the status of the current design versus the existing guidelines, especially with respect to packaging, cost and performance
- We will show designs that represent significant advances in reducing cost and package size and weight, while minimizing parasitic power consumption
- Review the current program status and the design challenges facing the turbo- and scroll- design teams

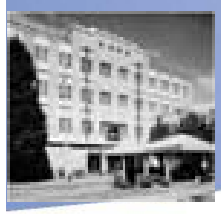
By way of introduction, TIAX LLC emerged intact from Arthur D. Little, Inc., advancing its 116-year heritage of helping clients realize the exponential power of technology & innovation.

TIAX Powered by Innovation since 1886

Arthur D Little

technology & innovation



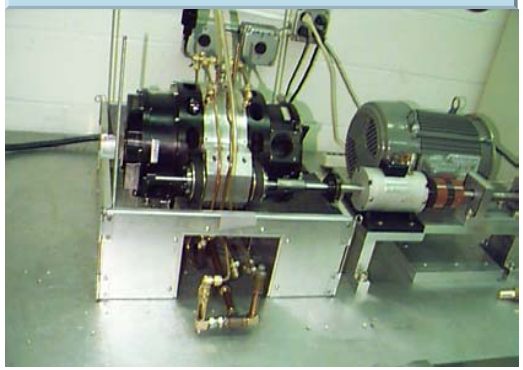


- Heritage
- T&I People
- T&I IP & Know-How
- T&I Facilities & Equipment
- T&I Resources & Relationships

- Independent company formed in May of 2002
- 300 staff of scientists, engineers, and industry experts
- Headquartered in Cambridge, MA
- West Coast offices in Cupertino, CA
- 50 laboratories
- ISO 9001:2000 Registered

The objective of this development program is to produce one working prototype system of a hybrid Compressor/Expander Module for an automotive fuel cell.

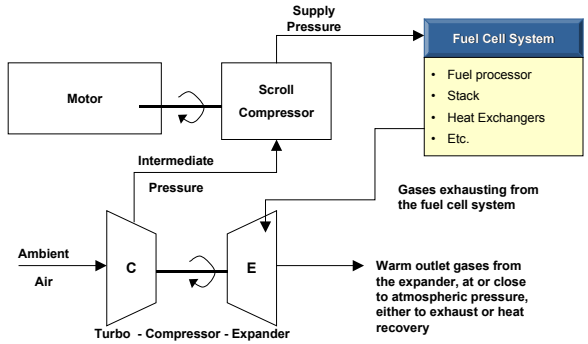
First Generation

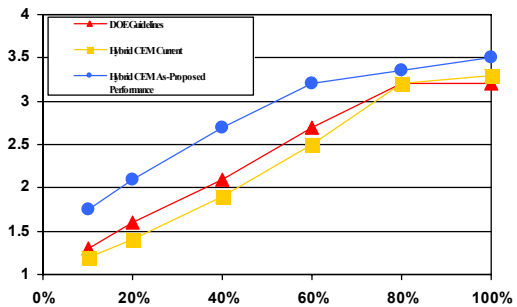


Second Generation

- A second generation scroll CEM met most of the DOE performance guidelines, but was substantially over target for weight and volume
- Turbomachines struggle off of their design point, but are much closer to the required weight and volume
- A hybrid system (essentially a turbocharged scroll compressor) was a logical compromise

As-Proposed Hybrid System Configuration





The hybrid approach offers significant improvements relative to the all-scroll second generation CEM previously developed and tested, while maintaining scroll-enabled pressure/flow and turndown performance.

	Parameter	DOE Guidelines	2nd Gen. Scroll Performance	Hybrid TurboScroll Targets
Compressor	Flow Rate: Dry Air (g/sec) Water Vapor (g/s)	64-76 0 to 4	61 See Note 1	64-76 0 to 4
	Stoichiometry	2.0	2.0	2.0
	Inlet Pressure (atm) Outlet Pressure (atm)	1.0 3.2	1.0 3.2	1.0 3.2
	Inlet Temperature: Design Point (°F) Extreme Range (°F)	 68 to 77 -40 to 140	 60 to 80 See Note 2	 68 to 77 -40 to 140
	Maximum Shaft Power (kW) Turndown Ratio Stages	12.6 10:1 1 or 2	13.0 10:1 1	SC:~6 TC: ~6 10:1 2
	Contamination	oil-free <100 ppm	<50 ppm[3]	Grease-lubed
	Efficiency: 100% flow 3.2 PR 80% flow 3.2 PR 60% flow 2.7 PR 40% flow 2.1 PR 20% flow 1.6 PR 10% flow 1.3 PR	 75% 80% 75% 70% 65% 50%	 --- 71% 69% 64% 49% 52%	 SC:70% TC:70% SC:70% TC:75% SC:70% TC:70% SC:65% TC:65% SC:50%: TC: ----- SC:50%: TC: -----

[1]Testing was done with dry air [2]Extreme condition testing not performed [3]Worst case estimate

Comparison with DOE Guidelines (cont'd)

	Parameter	DOE Guidelines	2nd Gen. Scroll Performance	Hybrid TurboScroll Targets
Expander	Flow Rate: Dry Air (g/sec) Water Vapor (g/sec)	56-70 9-16	77 See Note 1	Input
	Stoichiometry	2.0	2.0	2.0
	Inlet Pressure (atm) Outlet Pressure (atm)	2.8 1.0	2.7 to 3.2 1.0	Input Input
	Inlet Temperature: Design Point (°F) Extreme Range (°F)	 244 to 302 149 to 302	 84 to 289 See Note 2	 Input
	Maximum Shaft Power (kW) Turndown Ratio Stages	8.3 10:1 1	7.6 10:1 1	~6 10:1 1
	Efficiency: 100% flow 3.2 PR 80% flow 3.2 PR 60% flow 2.7 PR 40% flow 2.1 PR 20% flow 1.6 PR 10% flow 1.3 PR	 90% 90% 86% 82% 80% 75%	 --- 81% 80% 77% 63% 74%	 86% 86% 86% 78% 60% -

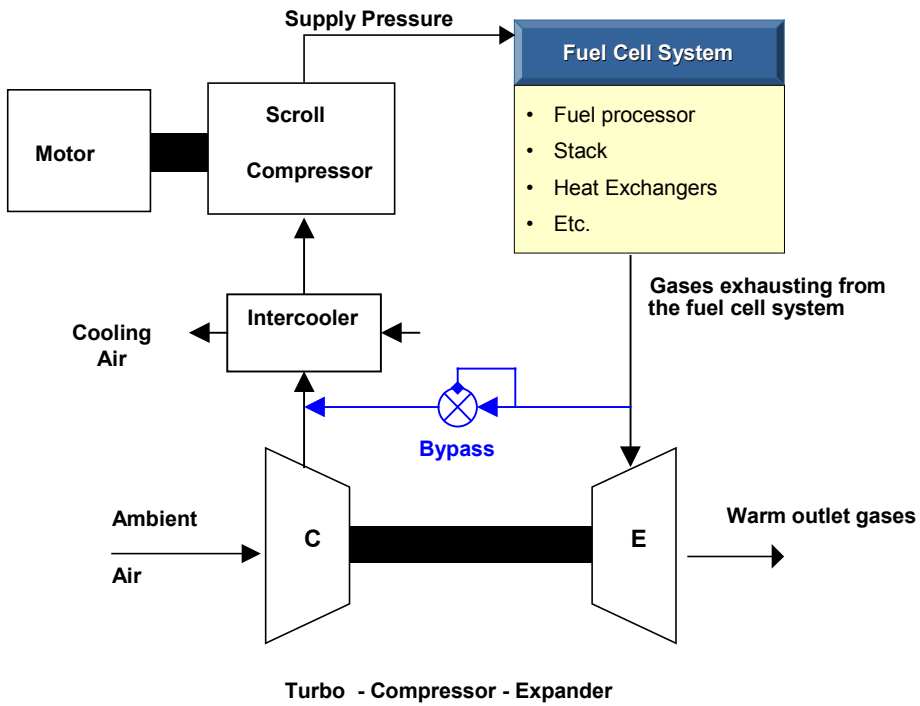
[1]Testing was done with dry air
[2]Extreme condition testing not performed
[3]Worst case estimate

Comparison with DOE Guidelines (cont'd)

	Parameter	DOE Guidelines	2nd Gen. Scroll Performance	Hybrid TurboScroll Targets
System	Maximum Overall Shaft Power (kW)	4.3	5.4	5.1
	Volume* (liters)	4	27	9
	Weight* (kg)	3	36.3	~12
	Production Costs* @ 100,000 Units/Yr	$200	$355	$300-$340[8]
	Start-up Response	<5s to 90% Max RPM	0.82 sec[6]	Stack capacity limited
	Transient Response	<4s for 20% to 90% max flow	0.72 sec[6]	Stack capacity limited
	Noise [7]	<80db	84dBA @40% 95dBA @80%	Speculative

*Without heat exchangers or motors/controllers
[6]Calculated value
[7]Noise measured at one meter without mufflers
[8]Using proprietary and Boothroyd-Dewhurst ground-up costing

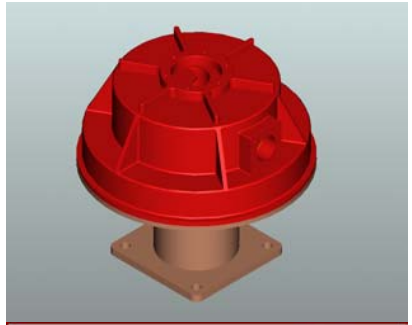
The latest System Block Diagram includes an intercooler between the turbo-compressor and the scroll, to reduce scroll operating temperatures and reject part of the heat of compression, and an optional bypass valve to redirect flow around the turbine and tailor the pressure/flow profile.



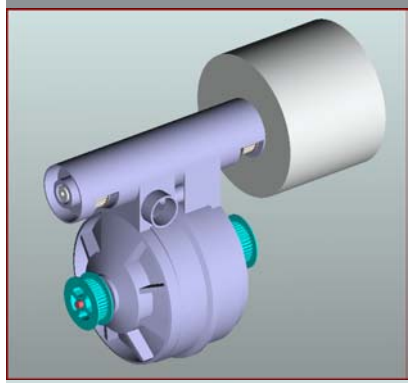
Hybrid TurboScroll Compressor/Expander Module

Three alternative configurations for the scroll compressor were studied in detail, resulting in complete layouts for all three designs.

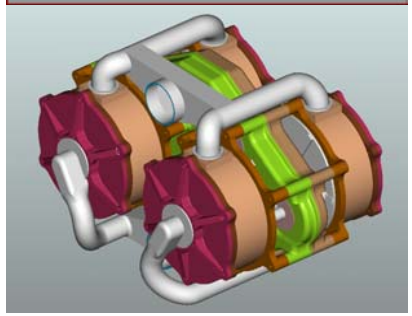
- **Single, back-to-back, co-rotating, and quad were in the preliminary concept list**
- **Relatively quick down-select to 3 alternatives**
- **Trade-offs are weakly linked to turbo-compressor configuration**
- **A relatively conservative approach is preferred, emphasizing compressor/expander system design over advancement of scroll design technology**



- **Single-Sided Orbiting Scroll Design (Conventional)**
  - Lowest Part Count
  - Acceptable Size and Weight
  - Acceptable Technical Risk



- **Co-Rotating Design (Unconventional Drive)**
  - Smallest Size and Weight
  - Acceptable Part Count
  - Best Potential for Low Speed Efficiency



- **Quad Orbiting Design (Unconventional Drive)**
  - Best Thermal and Lubricant Isolation
  - Potential Noise Advantage
  - Demonstrated and Proven Design Configuration

A set of selection criteria, defined and used to create a decision matrix, permitted efficient evaluation of the preliminary designs for the three configurations.

Design Configuration	Single Orbiting Scroll	Quad Orbiting Scroll	Co-Rotating Scroll
Maximum Speed	5,000 rpm or Less	6250-7000 rpm	6250 rpm or Higher
Size (5.0 L Goal)	7.2 L	11.0 L @ 6,250 rpm 8.3 L estimated @ 7,500 rpm	6.5 L
Weight (17 lb. goal)	18.8 lb	19.6 lb @ 6,250 rpm 16 lb estimated @ 7,500 rpm	17.3 lb
Cost Estimate (Drawing Count)	12 Fabrication drawings 4 Purchased drawings	30 Fabrication drawings 4 Purchased drawings	13 Fabrication drawing 8 Purchased drawings
Efficiency	- Main Crank Pin Bearing	- Flank length is 3-4 X's	- Windage loss - Shaft seals + Low Speed Efficiency
Noise	+ Lower Speed - Ball Thrust Bearing	+ Pulse Phasing of 4 scroll - Higher Speed	+ No ball thrust bearings - Two Rotating Rotors
Technical Risk	Medium	Low/Medium Proven Drive Mechanism	High

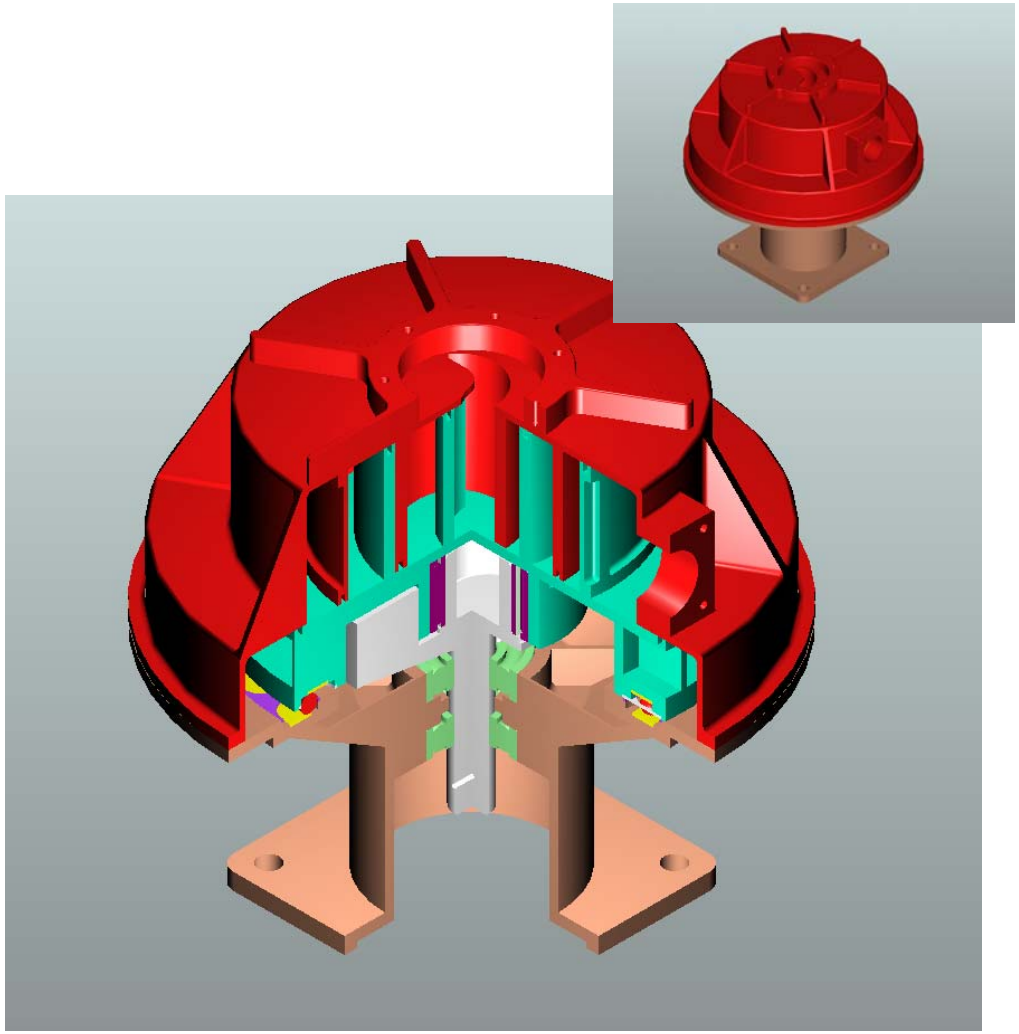
The Single-Sided orbiting scroll configuration was selected based on a decision matrix.

- Size and weight were not the lowest, but not far from being the best
- It had a significantly lower technical risk compared to the smallest/lightest design
- The lowest technical risk design was larger/heavier, with higher part count
- Performance was acceptable and comparable with the other concepts
- Noise was indistinguishable, with the Quad design having potential advantages

Technical Risk	Single Orbiting Scroll	Quad Orbiting Scroll	Co-Rotating Scroll
Lubricant Isolation	Isolating Grease in Thrust Bearing	Minimum Risk	Shaft Seal Failure
Thermal Management	Cooling Crank Pin Bearing	Cooling Fans Maybe Required	Needle Bearings at Gas Temp.
Lubricant Life & Service	Re-Greasing Crank Pin Bearing	Fully Isolated	Re-Greasing Needle Bearings
Volumetric Efficiency	Axial Deflection of Orbiting & Fixed scroll	•Long Flank Seal Length •Tolerance Stack up	•Deflections at High Speed •Tip Seal Performance •Shaft Seal Leakage
Mechanical Power Loss	•Main Crank Pin Bearing •Grease Seal Friction	•Multiple bearings •Grease Lube •Grease Seal Friction	•Windage loss • Shaft seal Friction
Obtaining 5000 hr life & Maximum Speed	•Main Crank Pin Bearing •Tipping of Scroll •Contact Stress on Balls	•Minimum Risk •Higher Risk @7250 rpm	•Life of Timing Teeth •Shaft Seals/Belts •Deflection of Shaft
Costly Purchased Parts Expensive Fabricated Parts	Main Crank Bearing	Conventional components	•Belts •Balancing •Quill Shaft Fabrication

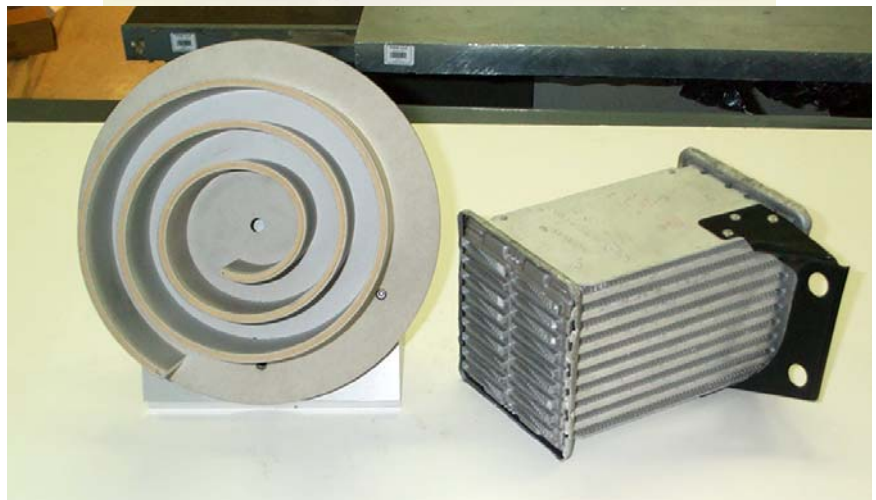
The potential technical risks for the Single Scroll Configuration have been identified, and will be resolved as detail design continues.

- Maintenance of flank clearances over operating regime
- Tipping of scroll during transient conditions
- Lubrication of bearings
- Life of lubricant
- Lubricant isolation
- Cooling crank pin bearing
- Bearing cost
- Stiffness of scroll support structures
- Contact stress on Oldham/thrust balls and retainer

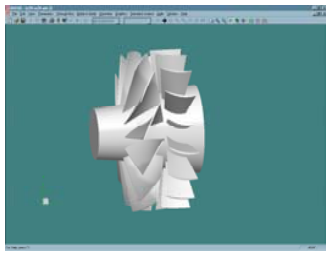


An off-the-shelf intercooler will be used, intact or modified, to provide rejection of the heat of compression of the turbo-compressor.

- The heat exchanger has excess heat rejection capability for our purposes
- Estimated turbo-compressor discharge conditions are as high as 215°F at a 2:1 pressure ratio
- Estimated reduction in inter-stage temperature to 120°F with intercooler
- ~4 kW of heat of compression will have to be rejected to the ambient through the inter-cooler
- This heat rejection contributes to the fuel cell system heat rejection



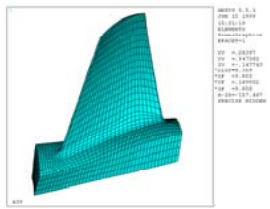
Concepts NREC, the turbo-machinery subcontractor for this program, has combined about 70 years in business, developing advanced turbo-machinery to meet demanding commercial and military requirements.



Fluid Dynamic Design

CONCEPTS NREC

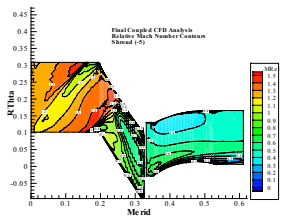
Manufacturing



Thermo-Mechanical Analysis

Wilder, VT Facility

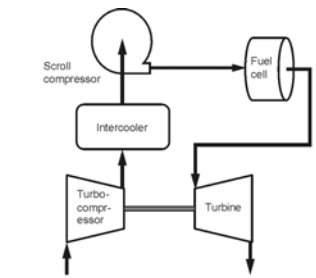
Testing



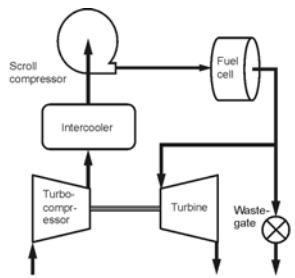
Computational Fluid Dynamics

Woburn, MA Facility

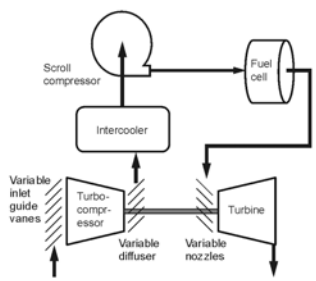
After establishing basic system requirements, a substantial variety of turbo-compressor combinations were studied.



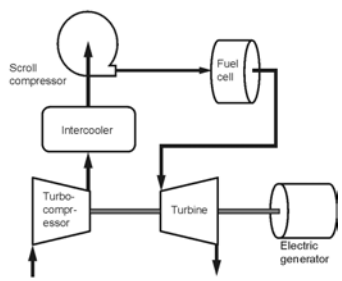
(a) Baseline fixed geometry turbine



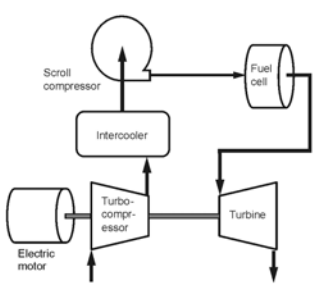
(b) Turbine with wastegate



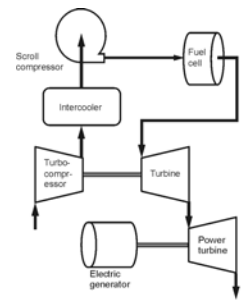
(c) Variable geometry turbo-compressor



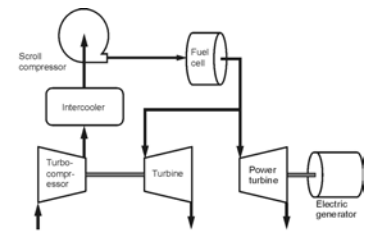
(d) Turbine with turbine-driven generator



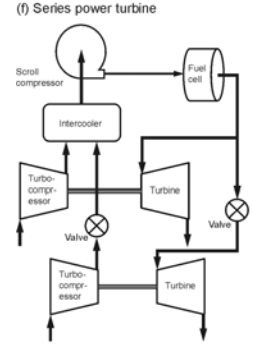
(e) Turbo-compressor with motor drive to compressor



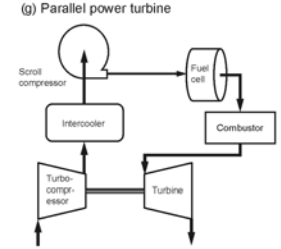
(f) Series power turbine



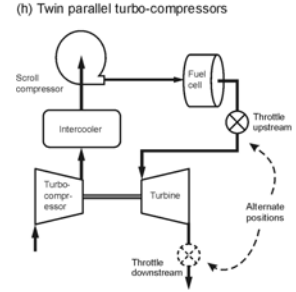
(g) Parallel power turbine



(h) Twin parallel turbo-compressors

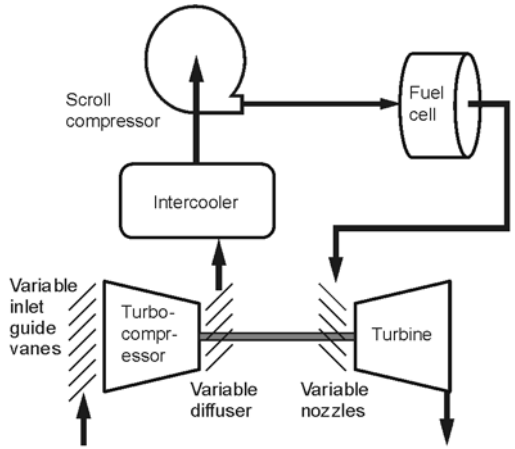


(i) Turbo-compressor with exhaust gas combustor

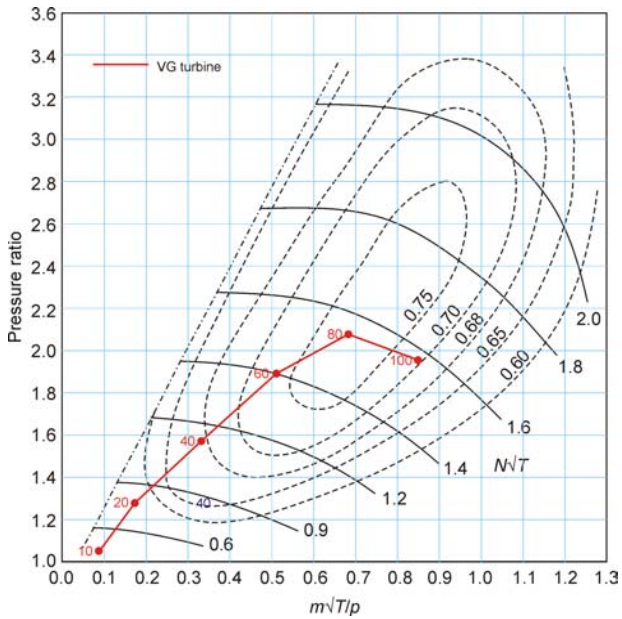


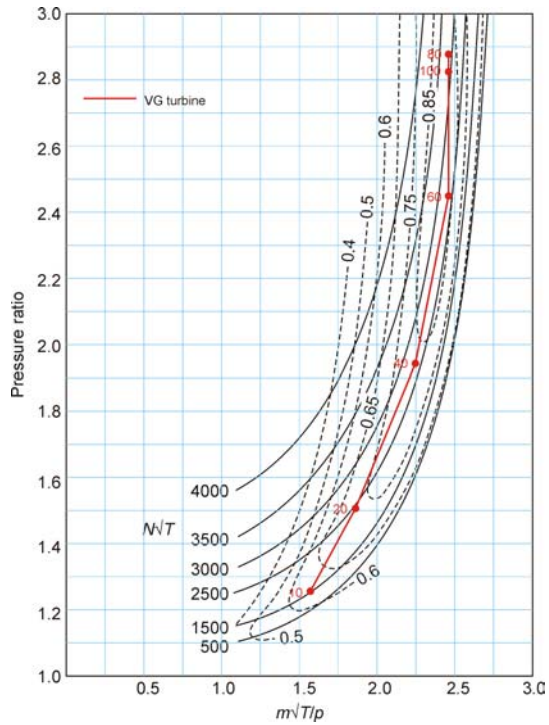
(j) Throttle valve upstream or downstream of turbine

Under the constraints governed by the DOE Guidelines, what would it take to get the most efficient air supply?



(c) Variable geometry turbo-compressor

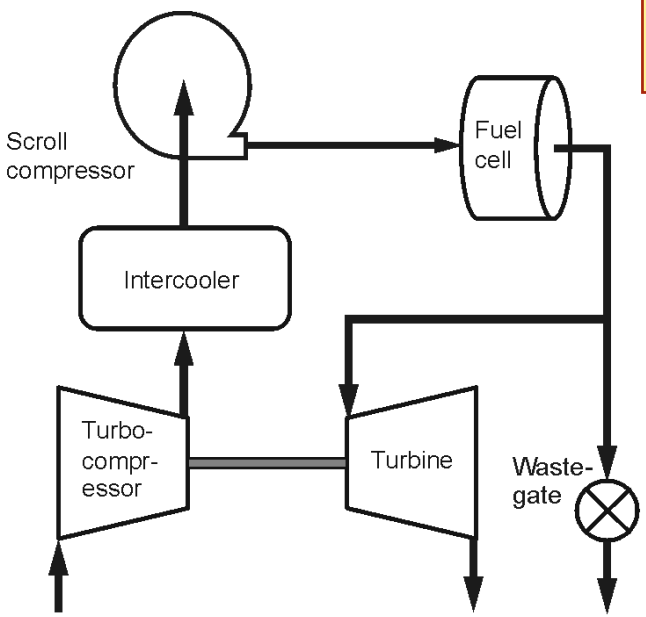




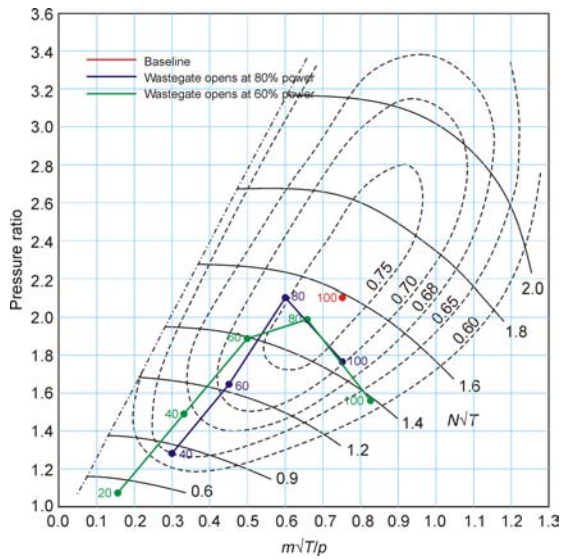
Variable geometries for compressor and turbine provide optimum flow adaptation to match operating regime with high efficiency regions, but…...

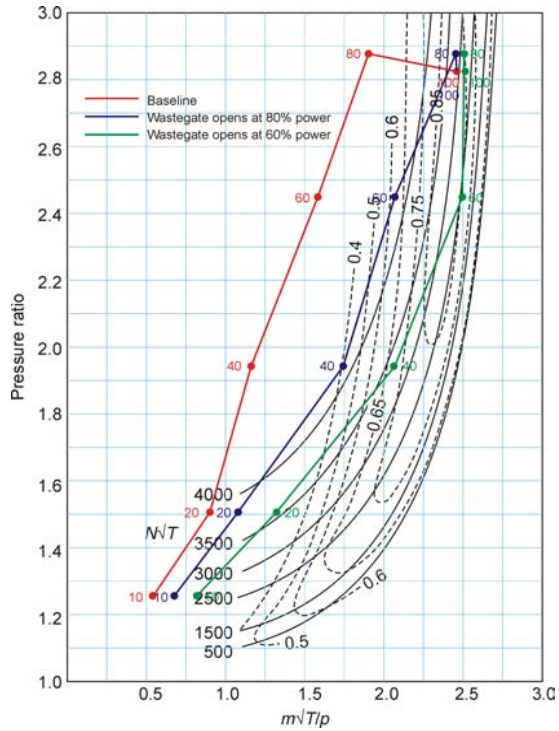
variable geometry components present mechanism size problems due to the small application.

How would a simple fixed geometry configuration compare in terms of power, cost and complexity?



Incorporating a wastegate allows us to meet DOE Guideline at high flows, but...

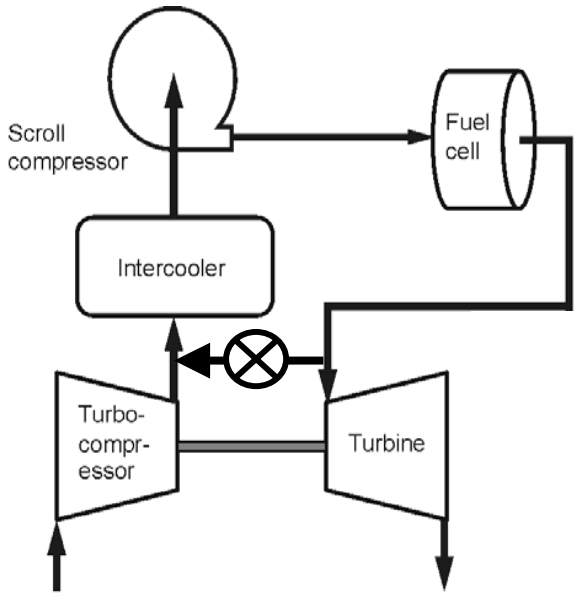


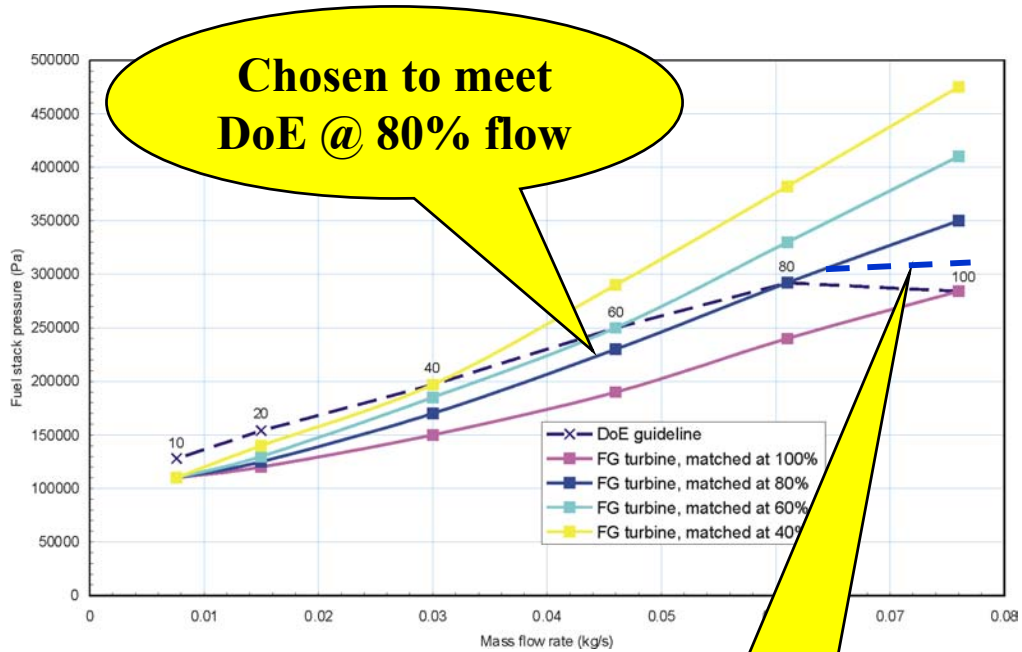


system efficiencies are compromised for certain operating regimes.

Recovering the bypassed enthalpy by recirculating part of the discharge gas may offer important advantages.

- **DoE guideline is met with some deviation at low flows**





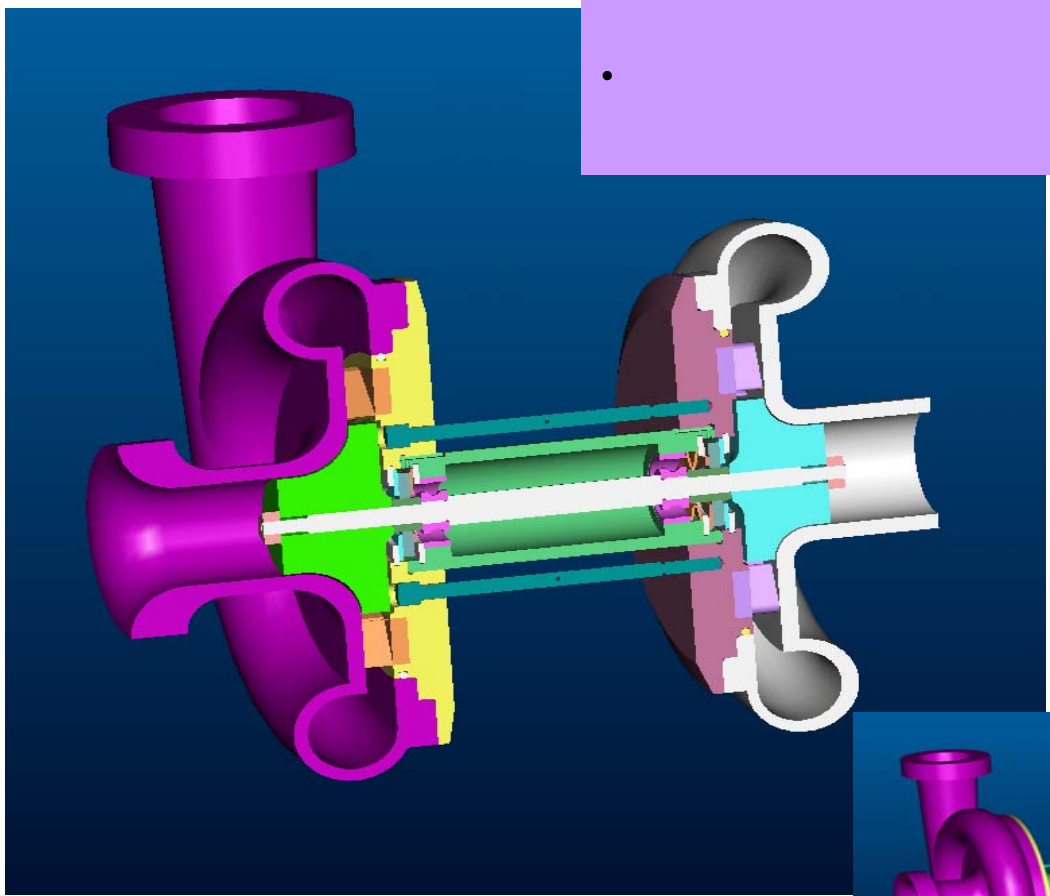
Chosen to meet DoE @ 80% flow

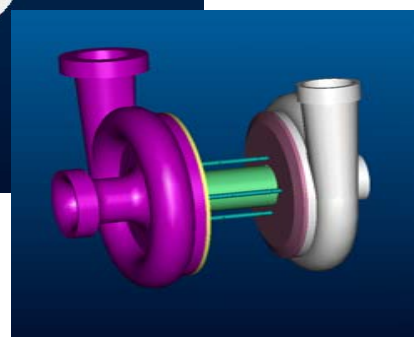
Operation with recirculation valve

Wastegate enthalpy partially recaptured by recirculation to intermediate pressure

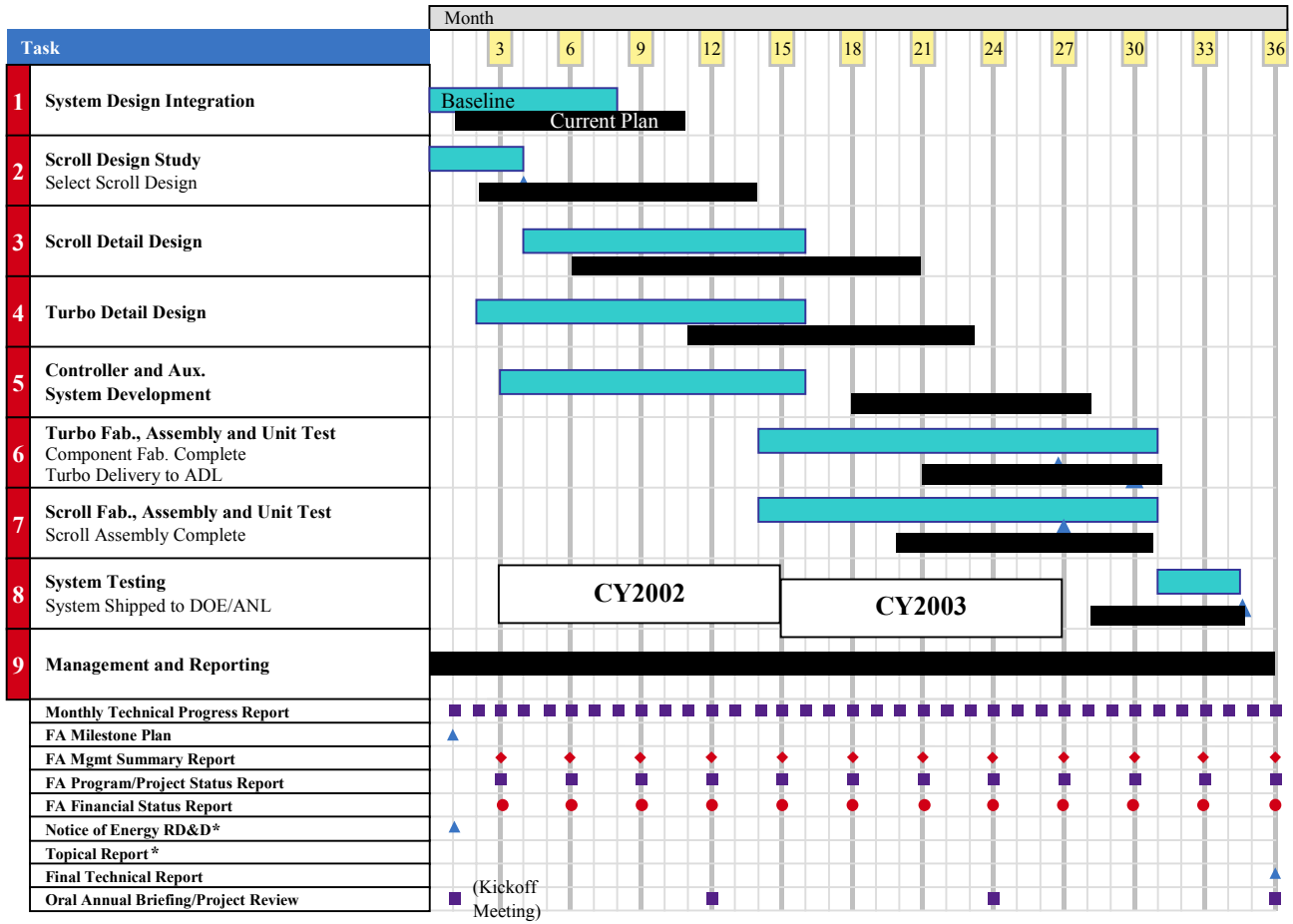
A simplified design, adapted from turbocharger technology, strikes a balance between cost, complexity, performance and risk.

- Aluminum wheels / housings: 1.7” Ø turbine, 2.0” Ø compressor
- Operating speed range up to 140,000 rpm
- Grease lubricated bearings: max. speed 150,000 rpm. No contamination of gas path
- Steel shaft
- ‘Stiff’ shaft design (first critical speed ~ 160,000 rpm
- Simple seals (labyrinths)





The overall program covers a span of thirty-six months, generally divided into design, fabrication and test phases.



Some key technical issues & risks, identified early in the program, have been addressed; some remain as issues for our near-term activities.

- **Several key issues…**
  - Lubricant selection and management
  - Inter-Cooler Integration
  - Size & Weight
  - Manufacturing Cost
  - Noise behavior
  - Stability & control
- **… will drive our near-term activity plan**
  - Development of final designs and drawings for turbo-compressor and scroll compressor
  - Development of final layouts for “production configuration” and “test configuration” systems
  - Development of control and auxiliary systems
  - Development of test programs for scroll compressor, turbo-compressor and system
  - Continuing assessment of key system technical risks & issues

Study of Fuel Cell Water Transport With Neutron Imaging

David Jacobson (NIST)

Paul Huffman (NIST)

Muhammad Arif (PI, NIST)

NIST CENTENNIAL 1901-2001

Relevance/Objective

4.4.3.2.4 Component Technical Barriers

(DOE R&D draft)

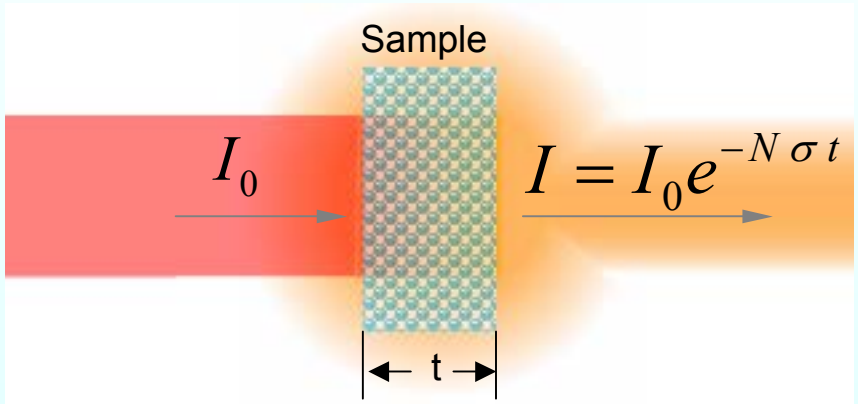
- **Thermal and Water Management**: …..Water management techniques to address humidification requirements and maintain water balance are required.

- **Component Durability:** MEA structural integrity and morphology.

Approach

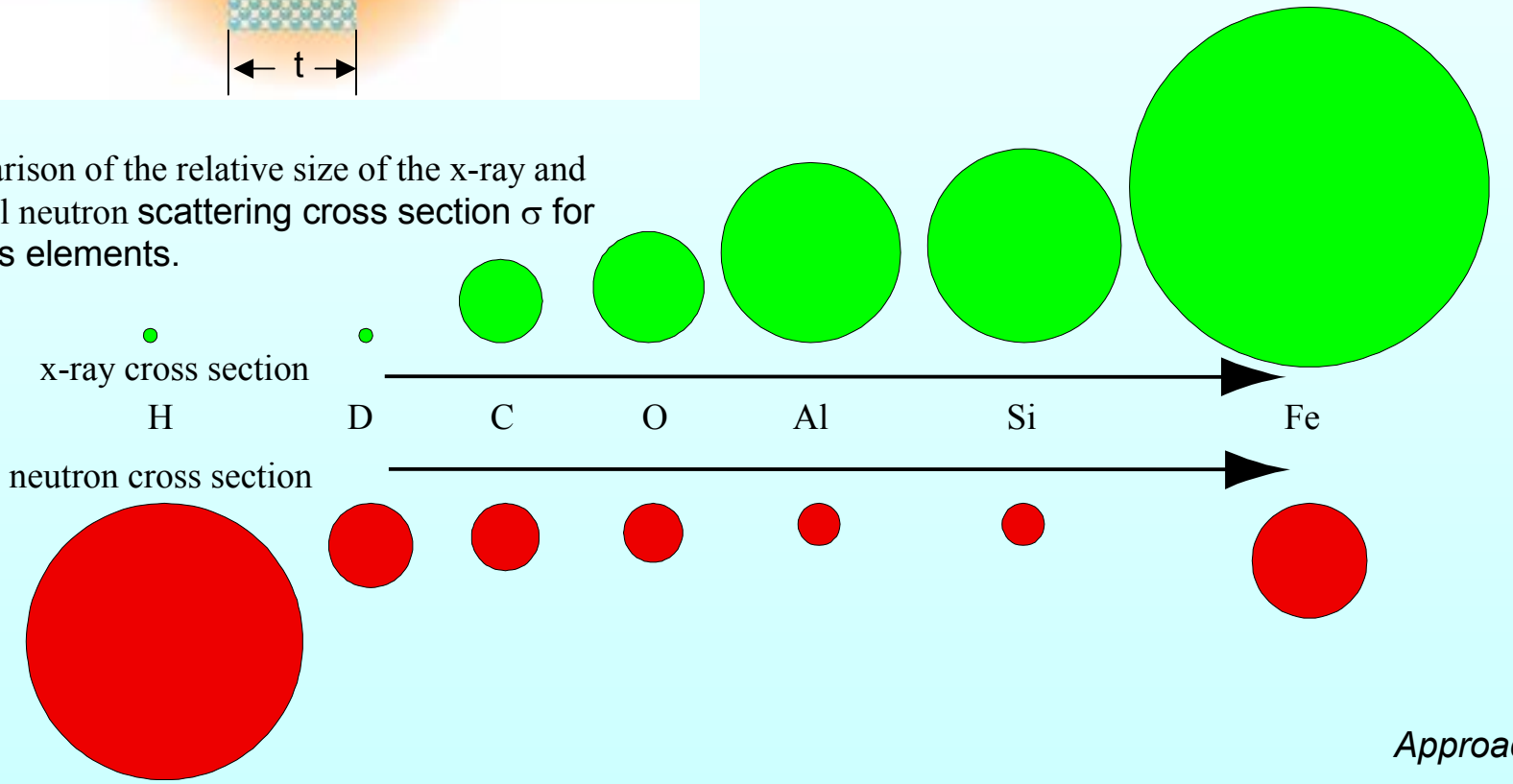
- Develop neutron imaging method to non-destructively visualize and quantify water transport in fully assembled operating fuel cells.
- Develop a nuclear reactor based state of the art ***neutron imaging user facility*** to study and characterize water transport for improving PEM fuel cell design, efficiency and reliability.
- Share research data with rest of the fuel cell community.
- Make scientific and technical development scalable to meet future needs.

Neutrons are perfect probes

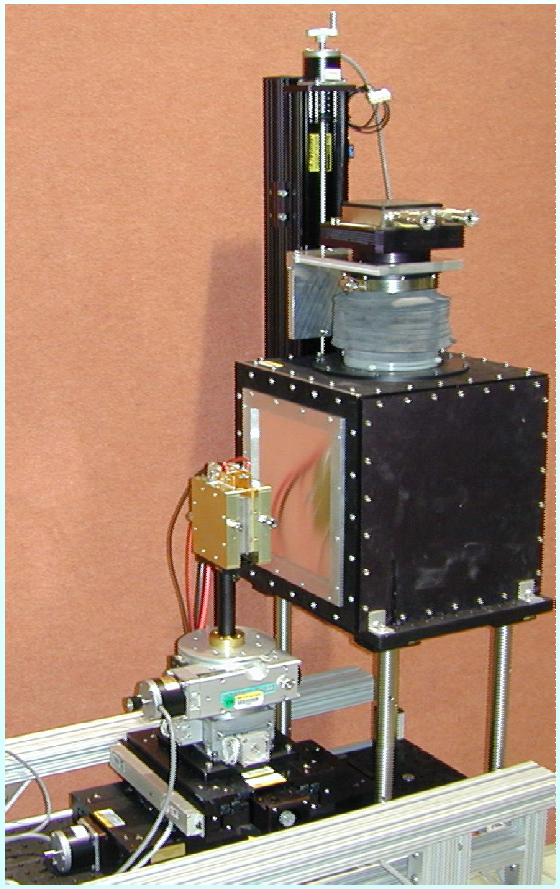


- N – numerical density of sample atoms per cm^3
- I_0 - incident neutrons per second per cm^2
- σ - neutron cross section in ~ 10^{-24} cm^2
- t - sample thickness

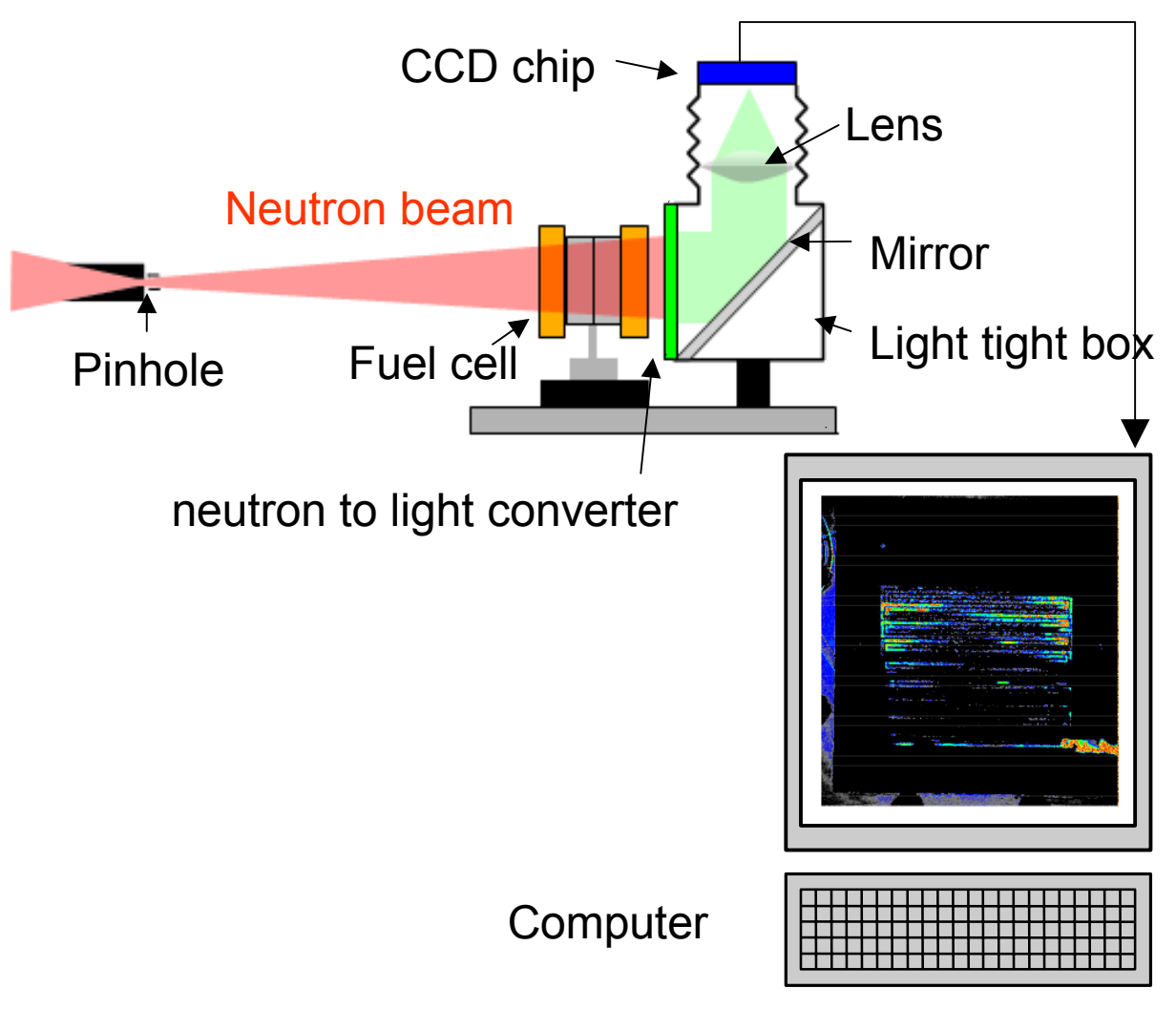
Comparison of the relative size of the x-ray and thermal neutron scattering cross section σ for various elements.



Neutron Imaging Setup



Picture of the detector and sample holder assembly



Project Timeline

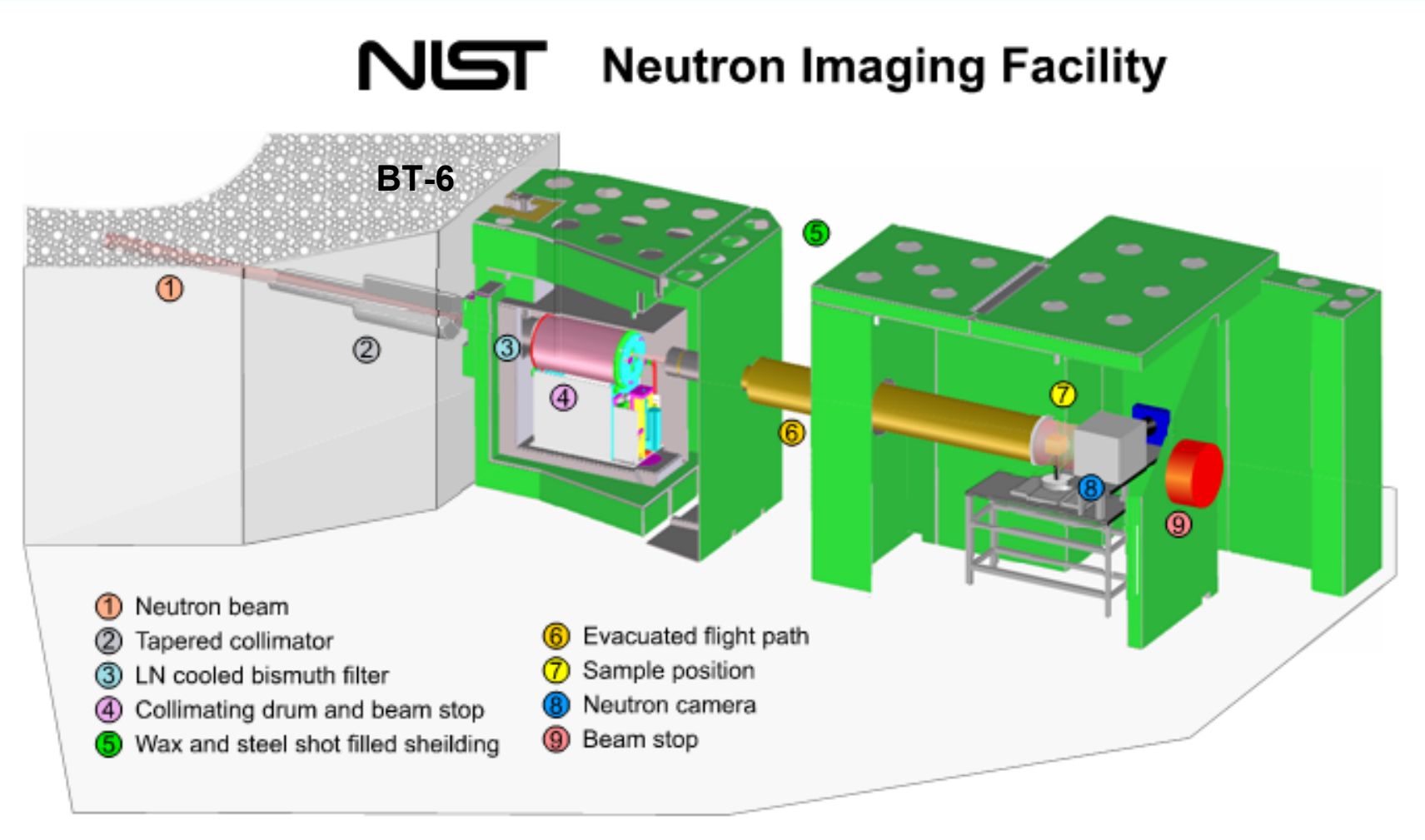
June 2000	Decision of DOE funding.
Sept.-Oct. 2000	**First demonstration of neutron imaging for real time visualization of water movement.**
Aug -Dec 2001	**Procure beam-line for facility development.**
	Design neutron optics for beam-line and decide on design.
	Initial test of *small* multi-stack fuel cells.
Jan. - Sept 2002	Construct Neutron Imaging Facility at BT-6 beam line at NIST reactor.
December 2002	**Industrial partners start using the facility on case by case temporary approval.**
March- April 2003	NIST reactor Safety Evaluation Committee approves routine operation of facility.
Present	**Scheduling and allocating beam time for internal and external users. Preparing results for publication.**

Accomplishment /Progress

Milestones
(2002-2003)

- Make the fuel cell imaging instrument fully operational by testing CCD detector system, constructing computer controlled fuel cell handling mechanism and optimizing data acquisition and analysis software. ***Completed***
- Study spatial and temporal distribution of hydrogen and water inside operating PEM fuel cells via neutron imaging and quantify hydrogen and water distribution. ***Completed and ongoing.***
- Share results with other fuel cell researchers in academic institutions and industry. Publish and present results in journals and conferences. ***Completed and in preparation (special care is needed to protect proprietary information)***

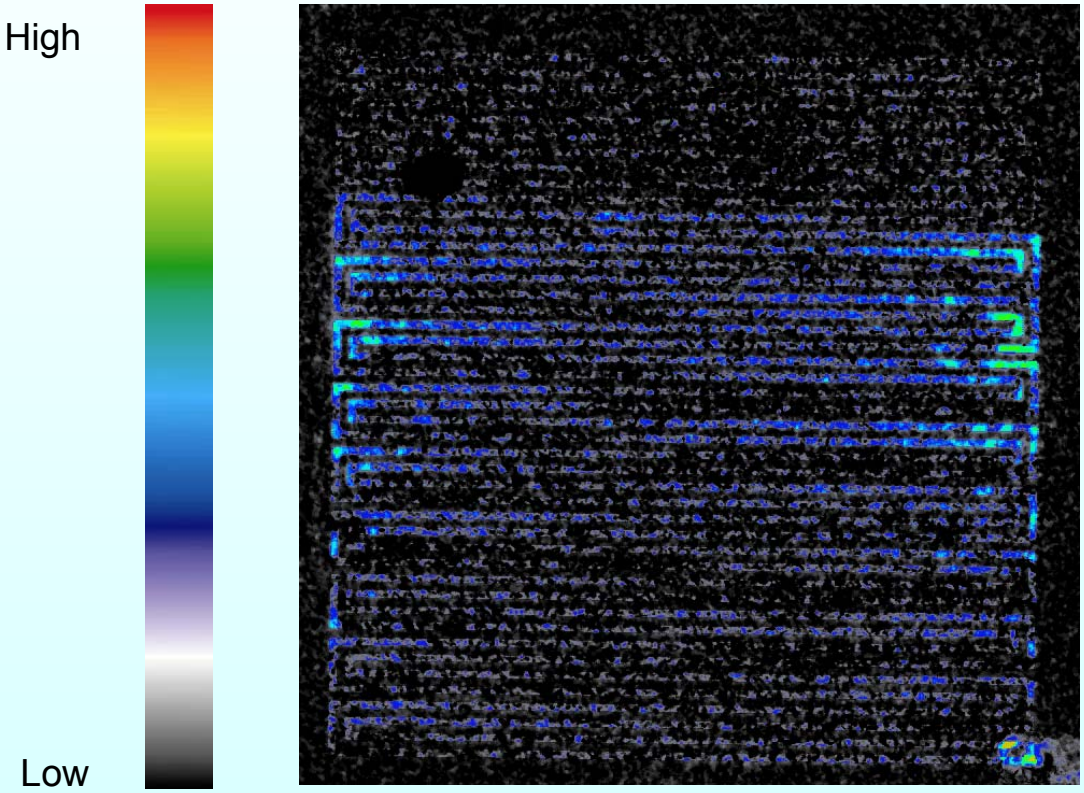
Dedicated Fuel Cell Test Station



- Intense neutron beam
- Single or multi-stack cell
- Variable beam diameter
- Variable resolution

Accomplishment

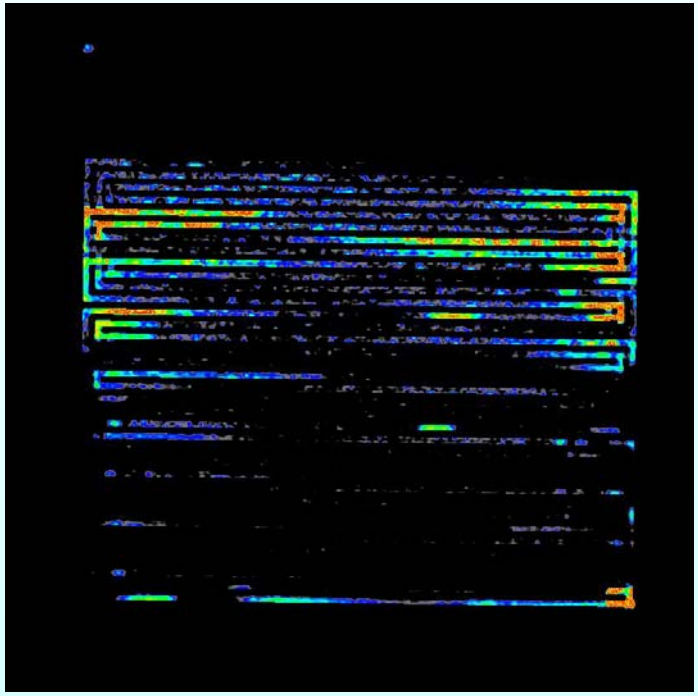
Water movement in fuel cells



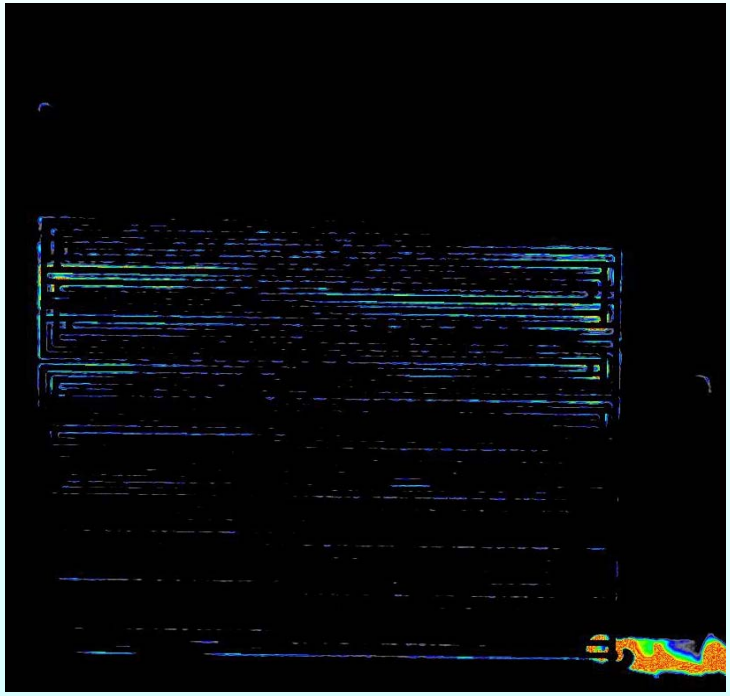
Water sensitivity:
Better than 1 micro-gram in weight
30-50 micro-meter in thickness

Accomplishment

Water inside fuel cell



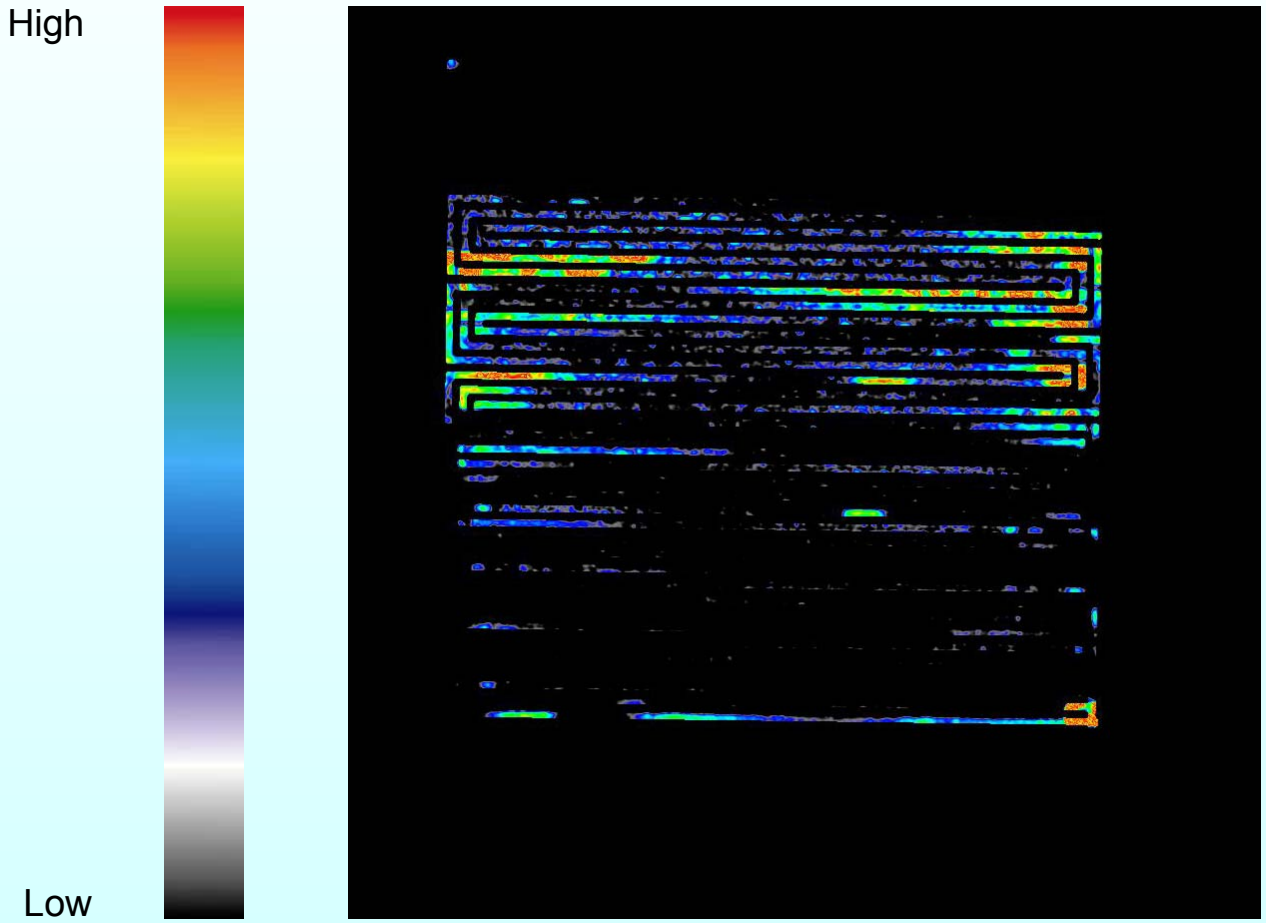
MEA + Cathode + Anode



MEA

Accomplishment

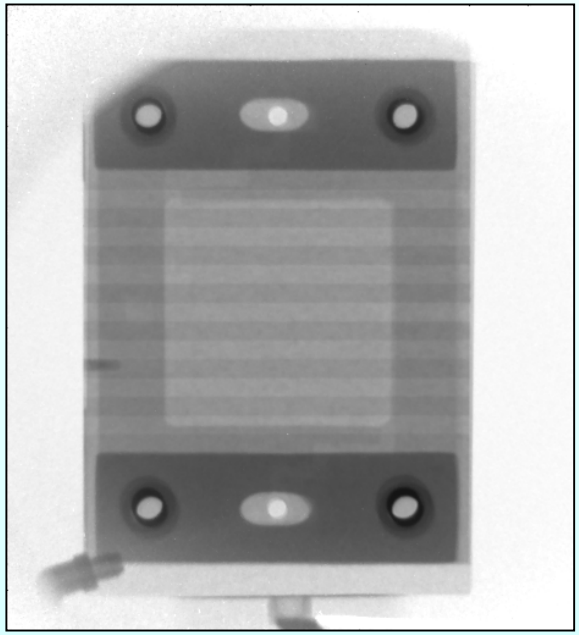
Cathode Image



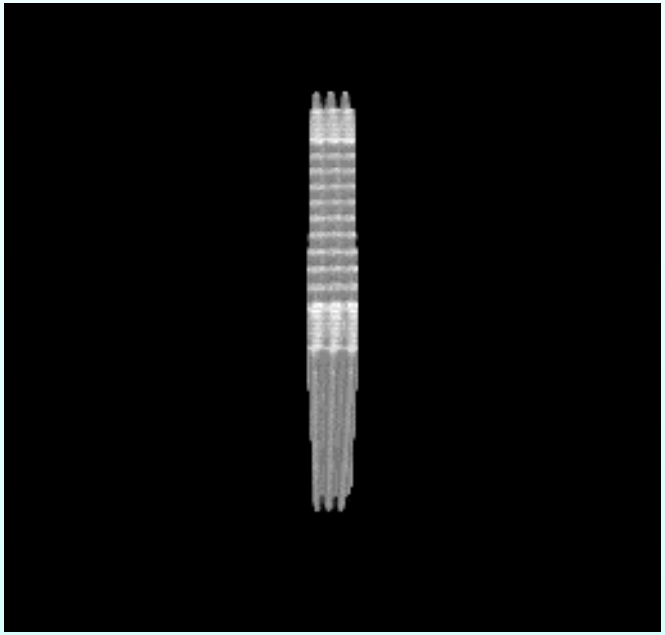
Anode Image ?

Accomplishment

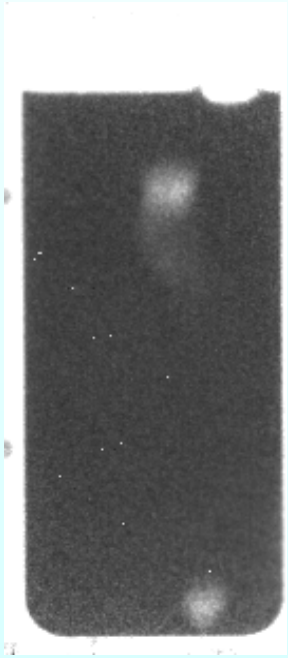
Extend measurements to 3-D



Single cell interior



Multi-Cell outer layer

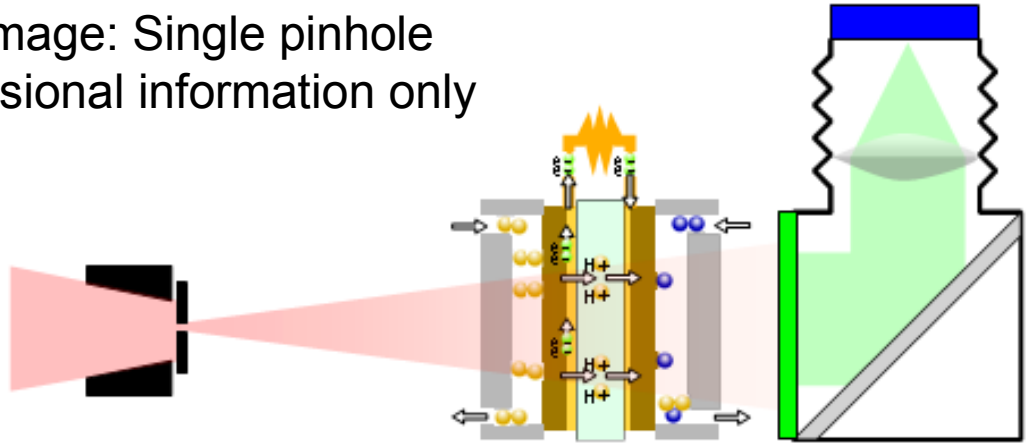


Time resolution:
40 millisecond

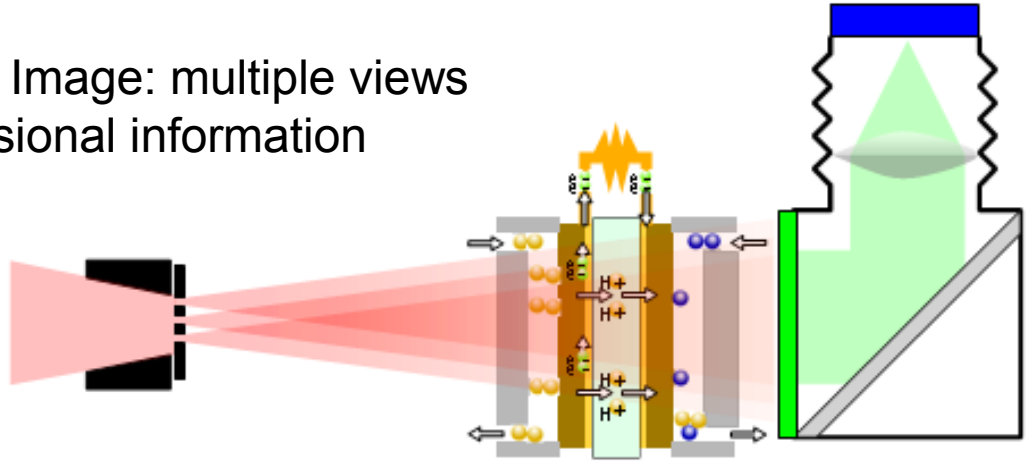
Accomplishment

Real time 3-D Imaging ?

Monoscopic Image: Single pinhole gives 2 dimensional information only



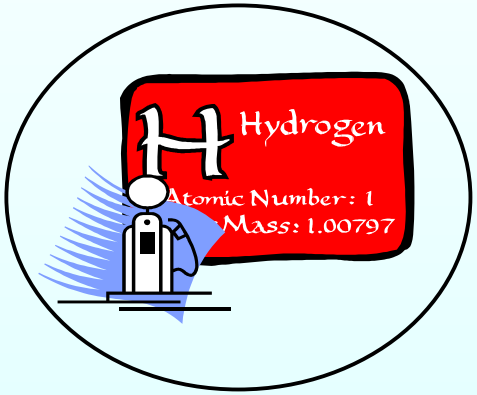
Stereoscopic Image: multiple views give 3 dimensional information



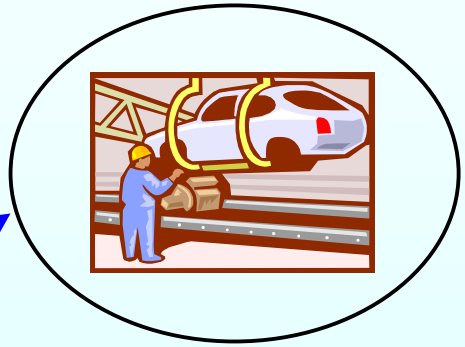
Real time 3 dimensional imaging of membrane would be possible!

Interactions/ technology Transfer

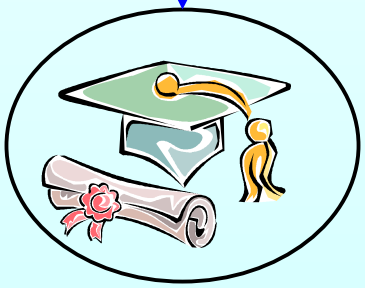
Linking Our Efforts



Fuel cell and component manufacturers *

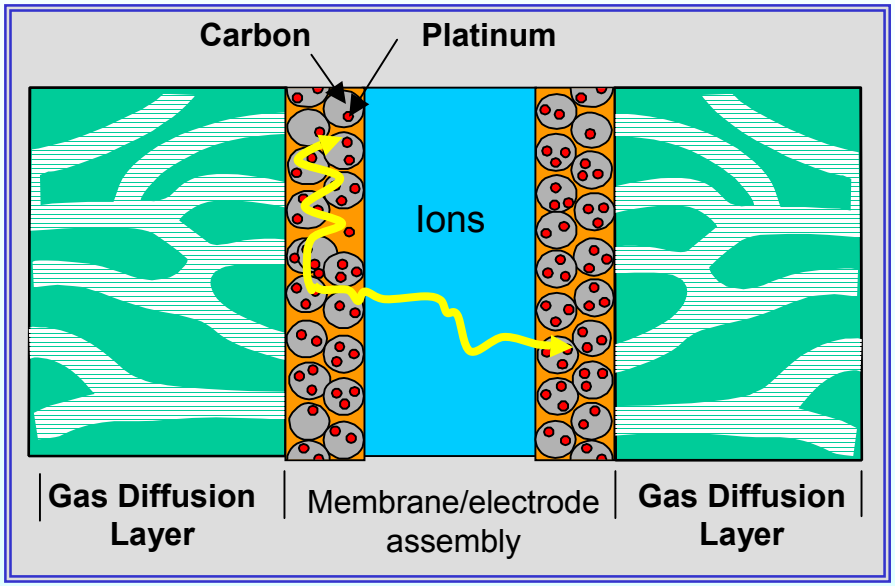


Automotive companies *



- MIT
- Univ. of Miami

Plans and Future Milestones



	Length	Time	
Materials	*0.1 – 10 nm*	*10^{-12} – 10^{-8} s*	Neutron Scattering
Morphology	*0.1 – 10 μm*	*➢1000 s*	Neutron imaging
Water transport	*5 - 100 μm*	*0.1 – 100 s*	Neutron Imaging

Future Milestones

2003-2006

- Extend current measurements of single cells to real world multi-stack cells
- Extend measurements to MEA specific water transport, morphology and structural durability
- Extend measurements to hydrogen storage materials
- Improve spatial and temporal resolutions to near or better than 10 micro-meters and a few tens of milliseconds respectively
- Explore possibilities of near real time 3-D imaging capability using a secondary beam line
- Transfer technologies to industry as they evolve

Bipolar Plate-Supported Solid Oxide Fuel Cell "TuffCell"

J. D. Carter, T. Cruse, J. Ralph,
R. Kumar, and D. Myers

Argonne National Laboratory
Argonne, IL

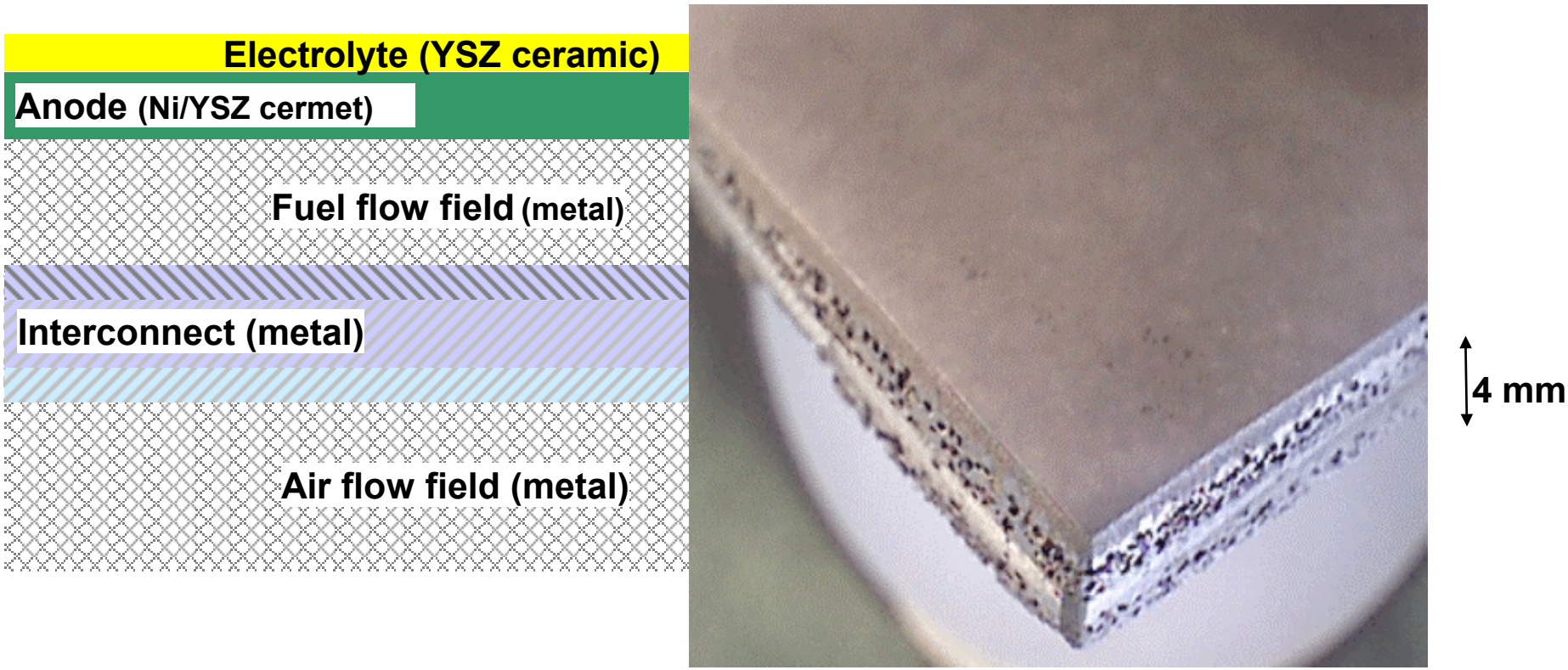
2003 Annual Review
DOE Fuel Cells Program
May 19-22, 2003

Relevance/Objective

- Relevance: DOE's Technical Target is to develop a 3-5 kW_e Auxiliary Power Unit (APU) at 150 W/kg and 170 W/L
  - This work addresses technical barriers D, L, M, O, P, and Q

- Objective: Develop an improved SOFC for APUs
  - SOFC advantages
    - High power density and efficiency
    - Fuel versatility/simplified fuel processing
    - Well-suited to duty cycle of APU
  - SOFC issues
    - Startup time, temperature cycling, and durability
      - Status: 2-3 hours, 10 cycles, 100 hours lifetime
      - Goal: 15-30 min, 500 cycles, 5,000 hours
    - Vibration and shock resistance
    - Cost
      - Status: >$2,000/kWe, goal: $400

Metallic Bipolar-Plate-Supported SOFC Design (TuffCell)

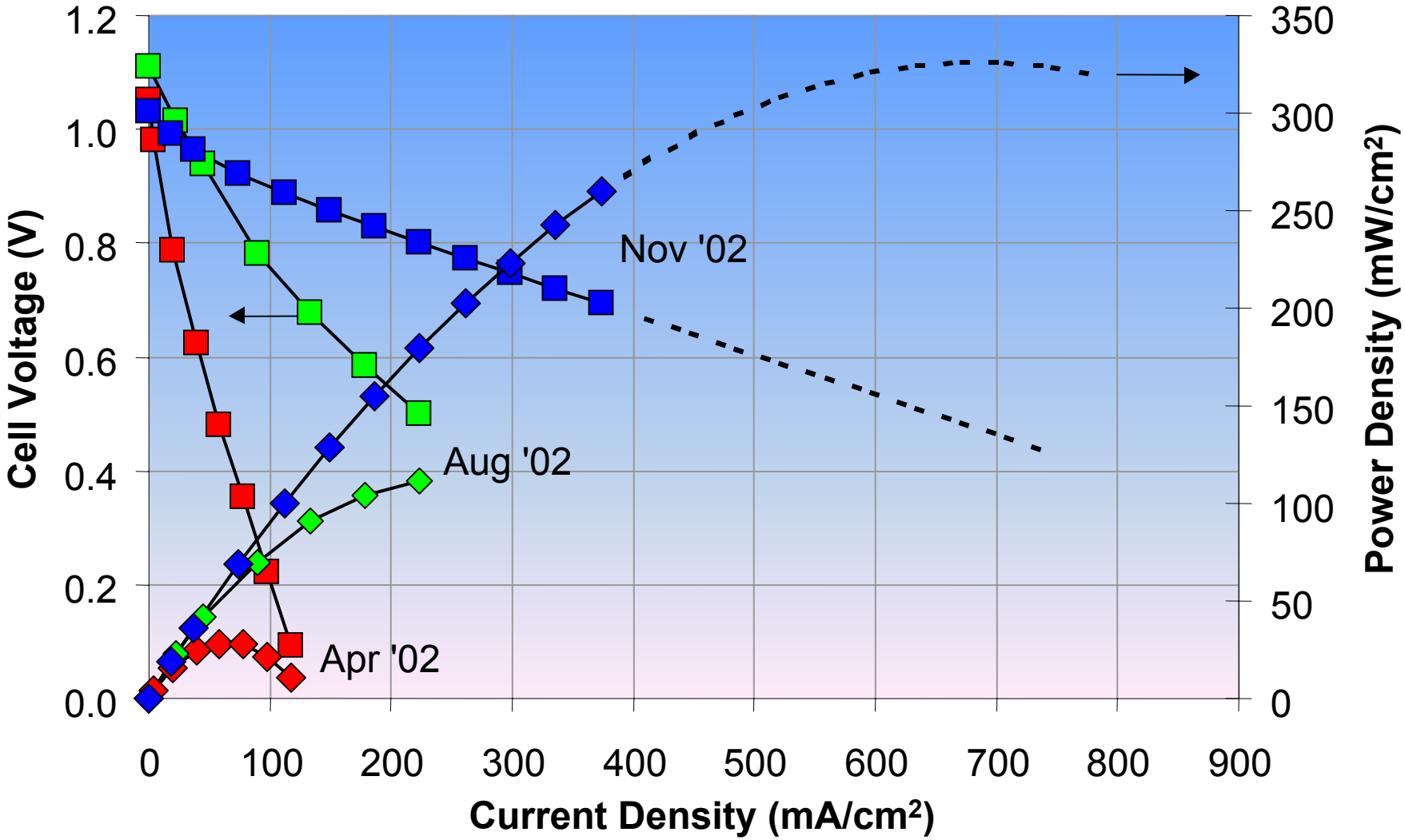


Essential stack elements integrated into a multilayer composite

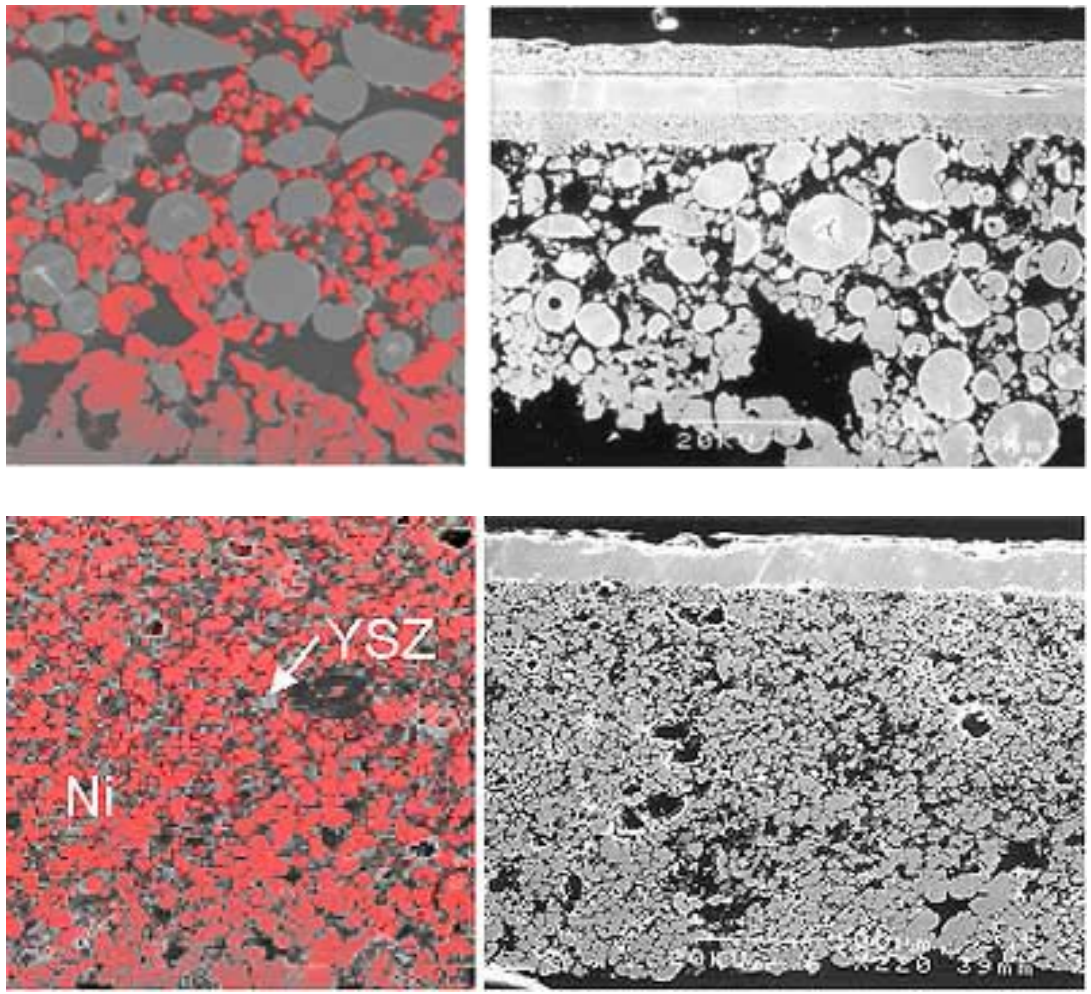
Metallic Bipolar-Plate-Supported Design Addresses SOFC Shortcomings for APUs

- Oxide and metal slurries are tape-cast into films, then films are laminated
- Metallic bipolar plate, anode, and electrolyte are sintered together in a single high-temperature process
- Cathode is slurry-coated onto electrolyte and sintered *in situ*
- Advantages:
  - Brittle ceramic components are bonded to tough metallic layers
  - Single high-temperature process lowers cost
  - Single electrical contact plane reduces interfacial impedance
  - Simplified gas sealing
  - Allows compositionally graded bipolar plates

Power Density of TuffCell Improved by an Order of Magnitude



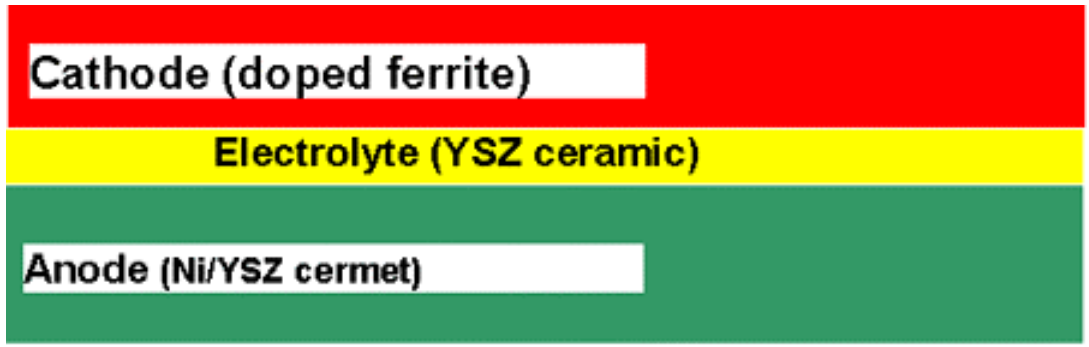
TuffCell Anode Microstructure Improved



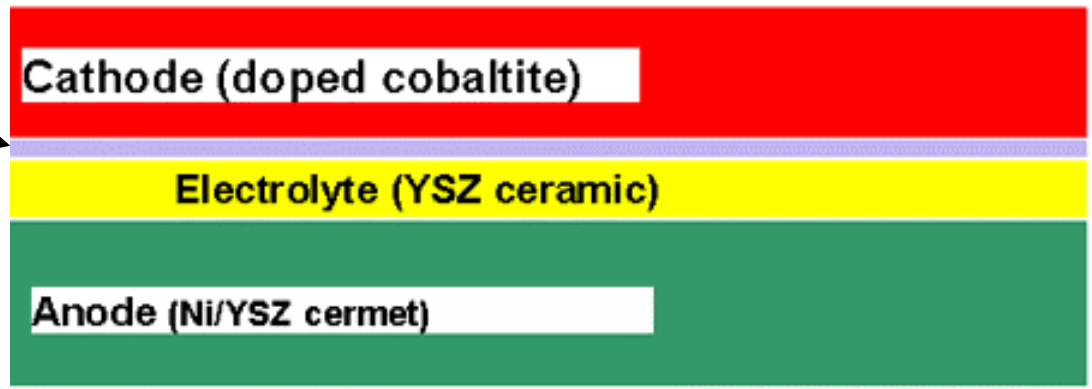
Apr '02

Aug '02

TuffCell Cathode Improved



Aug '02



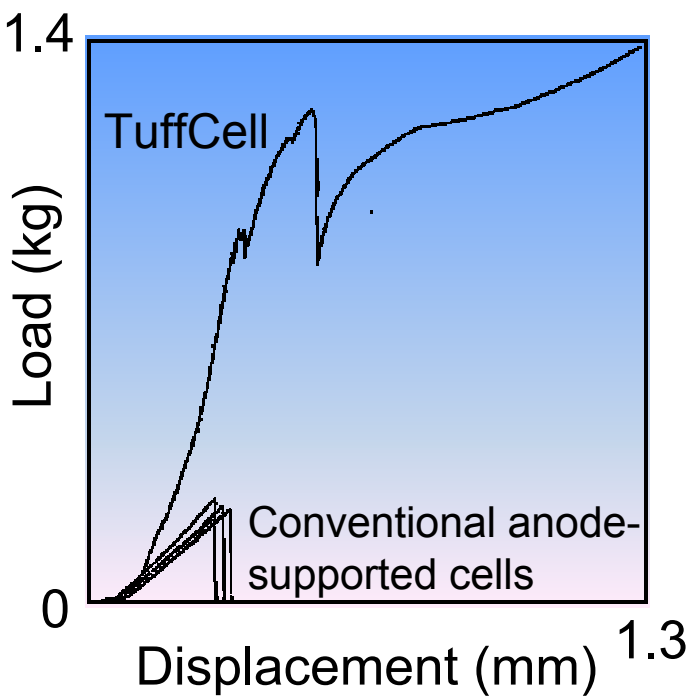
Barrier Layer (CGO ceramic)

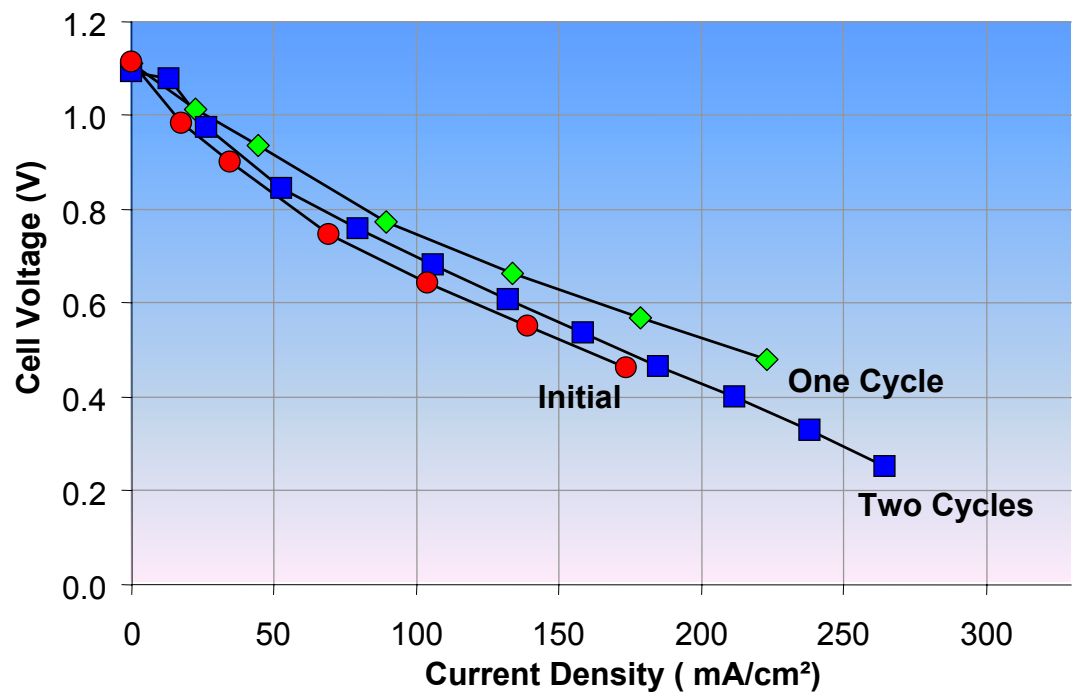
Nov '02

TuffCell's Superior Mechanical Properties, Cyclability Demonstrated

Physical tests:

- Impact test
- 4-point bend test
- Temperature cycling from RT to 800°C at ~10°C/min





Project Timeline

10/01
Began

12/01
Achieved sintered laminate

2/02
TuffCell has 4x strength of anode-supported cell

4/02
OCV of 1.14 V
25 mW/cm²

8/02
Power max. of 104 mW/cm²

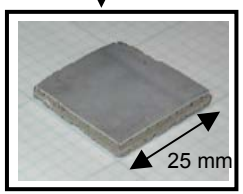
11/02
Power max. of >260 mW/cm²

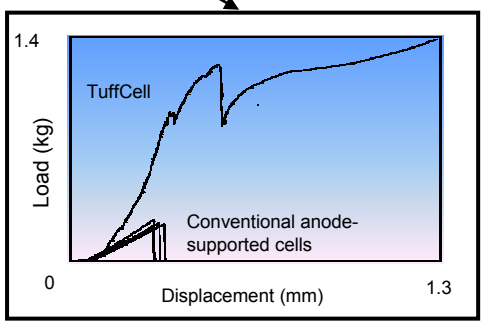
9/03
Design and fabricate a TuffCell short stack (2 cells) to achieve open circuit potential >90% of theoretical

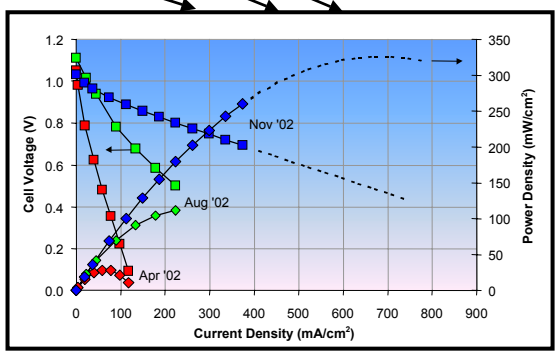
FY '02 | **FY '03**

$

DOE's APU Goals - 2010:
150 W/kg, 170 W/L, $400/kW$_e$, 500 cycles, 5000 h durability, 15-30 min startup







Reviewers' Comments--2002 Annual Review

- Incorporate more materials science in project; need CTE data
  - Published CTE data for conventional materials used for early cell fabrication. A dilatometer was purchased in FY '03 for determining cell component expansion and sintering behavior
- Evaluate start/stop data; demonstrate durability
  - Temperature cycling from RT to 800°C did not cause degradation in cell performance
- Improve current density
  - Current density at 0.7 V improved from 30 to 380 mA/cm²
- Scale up fabrication
  - Currently fabricating two-cell stack

Milestones

- Obtain TuffCell power density of 0.3 W/cm^2 with H_2/air

  Target: 02/03
  Achieved: >0.26 W/cm^2 11/02

- Design and fabricate a TuffCell short stack (2 cells) to achieve open-circuit potential >90% of theoretical (hydrogen/air)

  Target: 09/03
  Currently fabricating stack and manifold

Future Plans

- Test two-cell stack on simulated reformate/air
- Test startup time, cyclability, and durability
- Investigate improved materials for metallic support, anode, and cathode
- Improve fabrication procedure
- Collaborate with universities, industry, and other national laboratories

Benefits of This Project

- A TuffCell based auxiliary power system is:
  - Fuel-flexible
  - Compact
  - Rugged and durable
  - Faster-starting than current SOFCs
  - Cost-effective
    - Lower manufacturing cost
    - Lower materials cost
  - Highly efficient

Low Friction Coatings and Materials for Fuel Cell Compressors & Blowers

O. O. Ajayi, G. R. Fenske, and A. Erdemir
Argonne National Laboratory
Argonne, IL 60439

DOE 2003 Review
Fuel Cell for Transportation Program

Transportation Materials

Background

Technology Issue: Fuel cell stacks requires a compact lightweight highly efficient compressor/expander. No off-the-shelf compressor technology can meet the stringent requirements for this application. Several contractor have and are working on developing compressor/expander systems. Efficiency, reliability and durability of such system are dependent on effective lubrication of critical components such as bearings and seals. Such components cannot be oil lubricated - oil will contaminate fuel cell stacks.

Objectives: Develop and evaluate low-friction and wear-resistant coatings and/or materials for critical components of air compressor/expanders being developed for fuel cells.

Approach:

1. **Working with various contactors**
   - Identify tribologically challenging critical compressor components
   - Apply and evaluate Argonne's near-frictionless carbon coatings to the components when appropriate
   - Develop and evaluate polymer composite materials with boric acid solid lubricant.
   - Identify and evaluate other candidate materials for various specific compressor components

2. **Develop a material selection methodology applicable to all the DOE compressor contractor's tribological conditions and requirements**

Past Accomplishments:

- Worked with various contractors to address their tribological technical barriers:

Meruit: Turbo-Compressor Air Bearing

- **Developed and evaluated NFC coating for the radial and thrust air bearings - Without the NFC coating bearing cannot run. Coating reduced friction, wear and prevented scuffing or seizure.**

- **Conducted both lab and air bearing rig testing - Meruit has incorporated use of NFC coating into their air bearing design**

- **Variex - Variable Displacement Compressor**
  - **Achieved 50% reduction in friction compared to their prototype using Hitco C/C composite and anodized aluminum material combination.**
  - **Fabricated and evaluated friction and wear performance of Nylon-12 and boron oxide composite. Significant friction and wear reduction was observed, especially under high humidity**

Past Accomplishments:

Mechanology: Toroidal Intersecting Vane Machine (TIVM)

- Designed and constructed high speed test rig to evaluate friction and wear performance of materials under the very high sliding speed typical of TIVM machine vane
- Evaluated several candidate materials for TIVM vanes

Mesoscopic Devices (in progress)

- Friction wear testing of candidate polymeric materials for blowers
- Developing NFC coating for blower vane component

AD Little: Hybrid compressor/Expander Module
UTC Fuel Cells: Motor Blower/compressor Technology
Honeywell: Turbo-compressor/Expander

Mechanology TIVM: - Tribological Issues

This compressor concept offer a great potential for meeting the size, weight, and efficiency targets.

•Initial design and prototype fabrication of TIVM completed by Mechanology

•Analysis showed that friction will significantly impact the efficiency of compressor.

•ANL working with Mecahnology to develop and evaluate low friction and wear resistant surfaces for critical components.

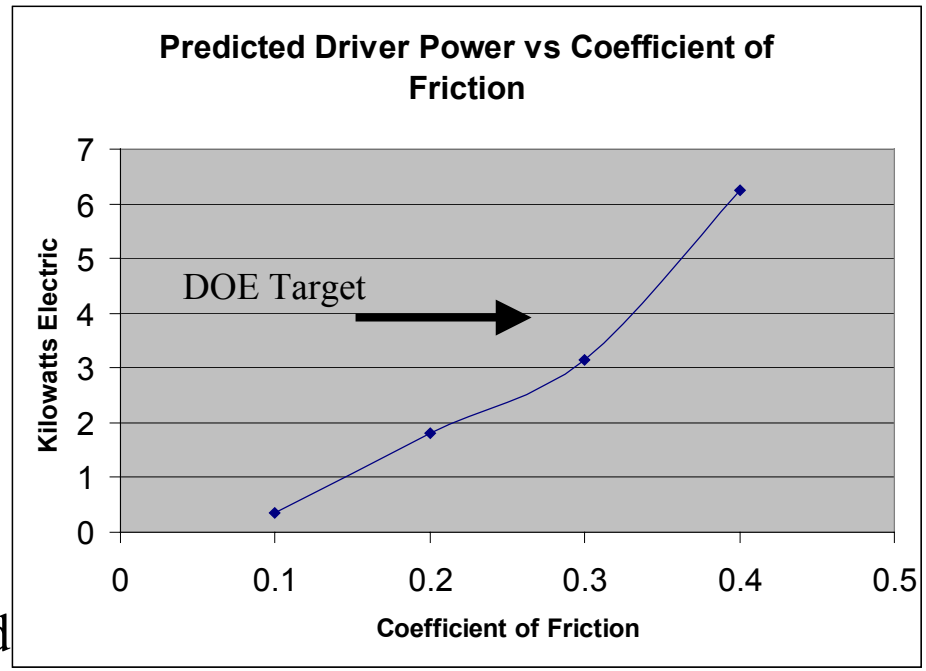
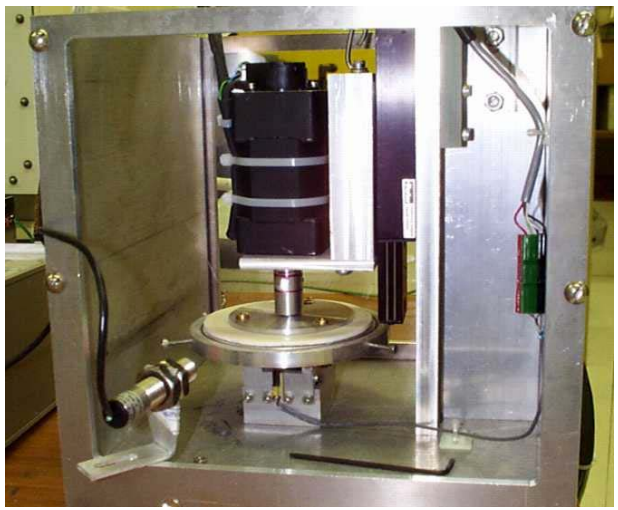


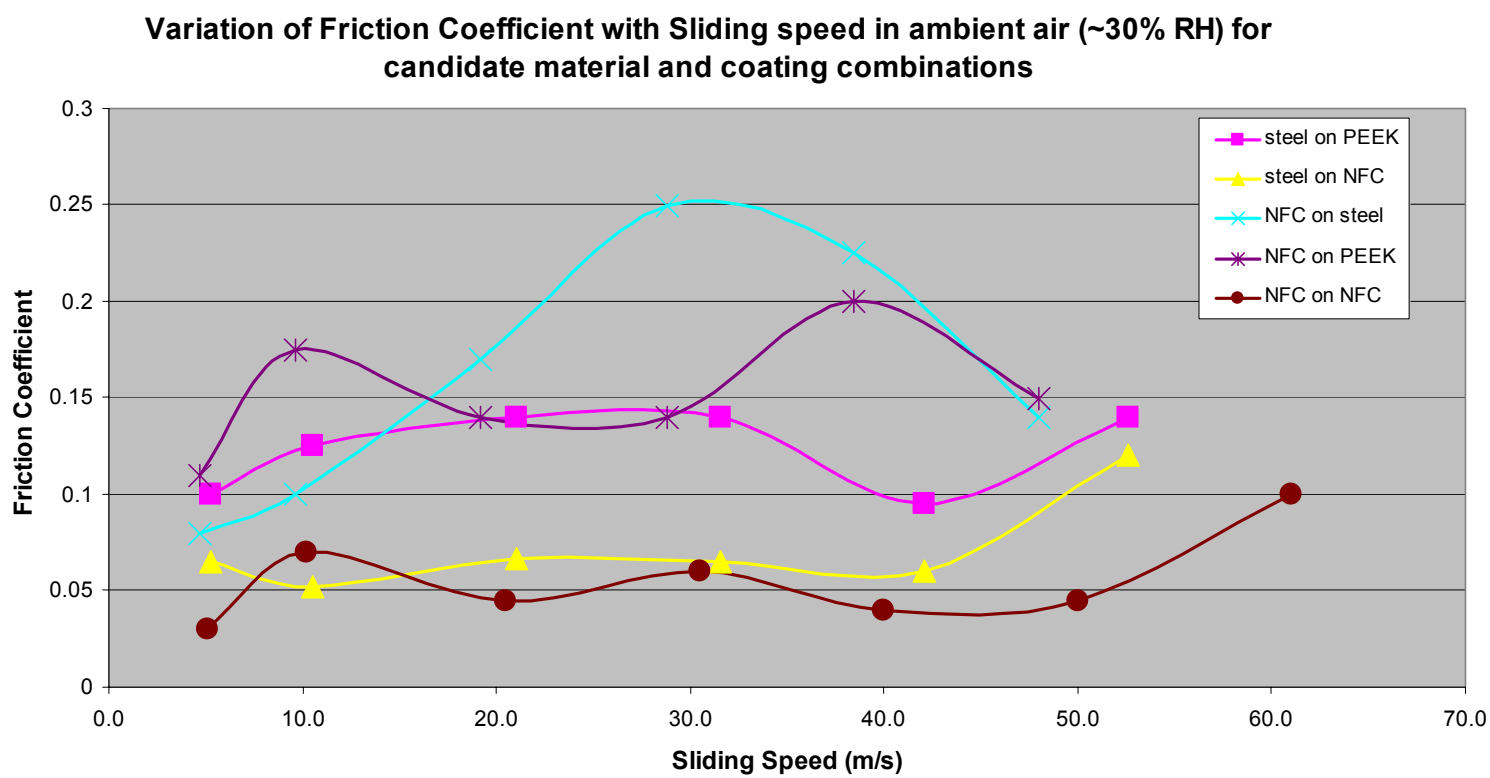
Figure from Mechanology phase I final report

Friction Test for (TIVM) Vane Materials

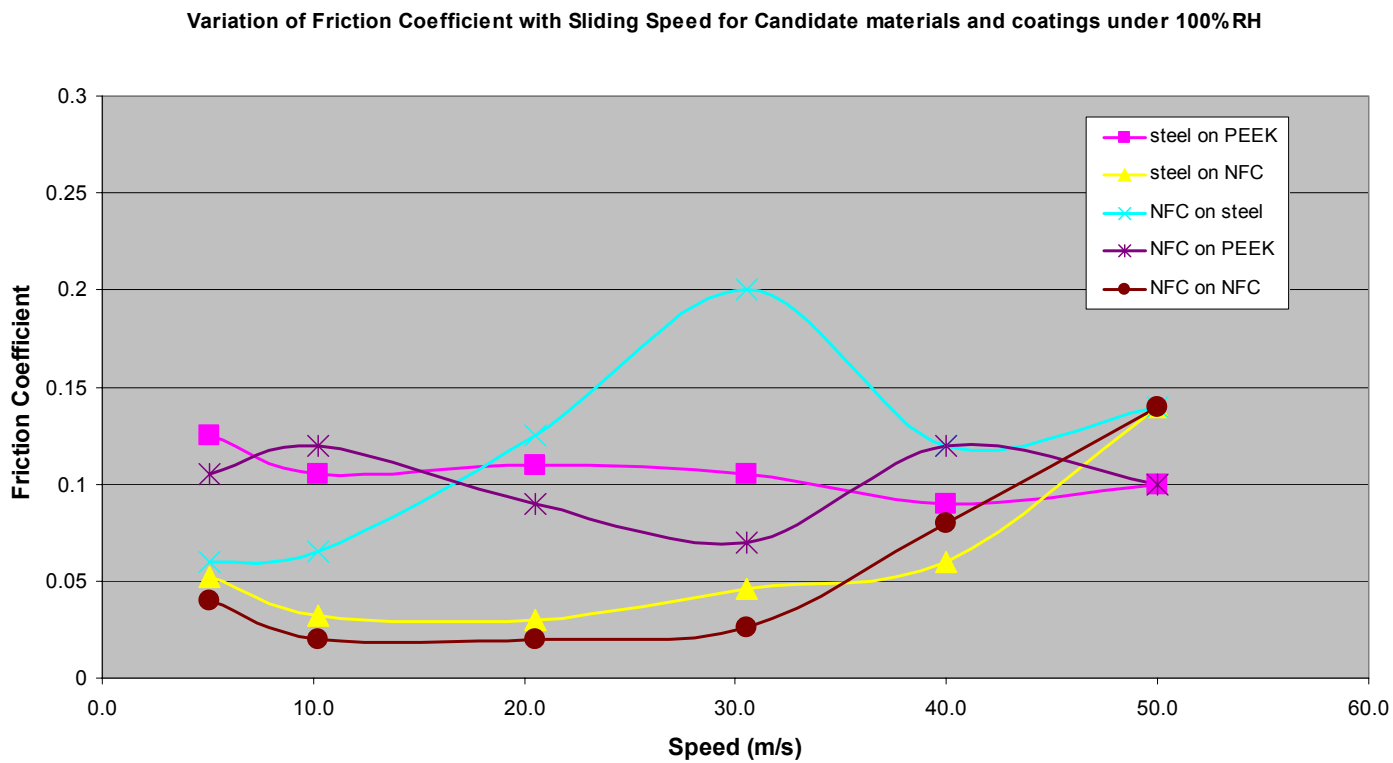


- Design sliding velocity for the TIVM vanes ranges from 60 - 75 m/s
  - Need to identify materials capable of such sliding speeds.
  - Other constraints include relatively low cost, light weight, easy to fabricate,
- Friction and wear test protocol was developed to evaluate the effect of sliding speed on friction coefficient
  - Uses three balls-on-disc contact configuration
  - Run tests at selected step speed for 3 minutes at each step, then calculate average friction for each speed step.
- Several materials screened: 440 C S.S., Bronze, Teflon, Delrin, PEEK, Torlon, Vespel, Armaloy coated bronze, NFC coated steel

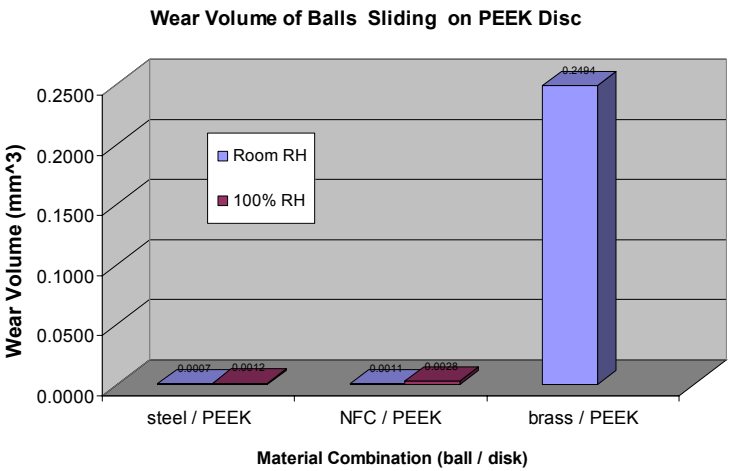
Frictional Performance – Room Air

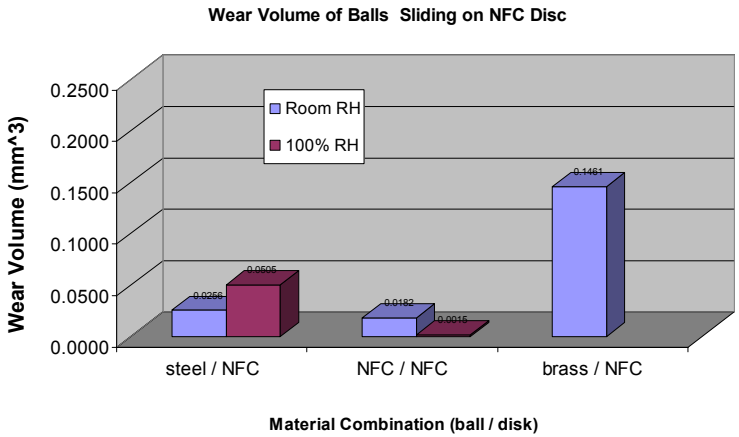


Frictional Performance – Humid Air



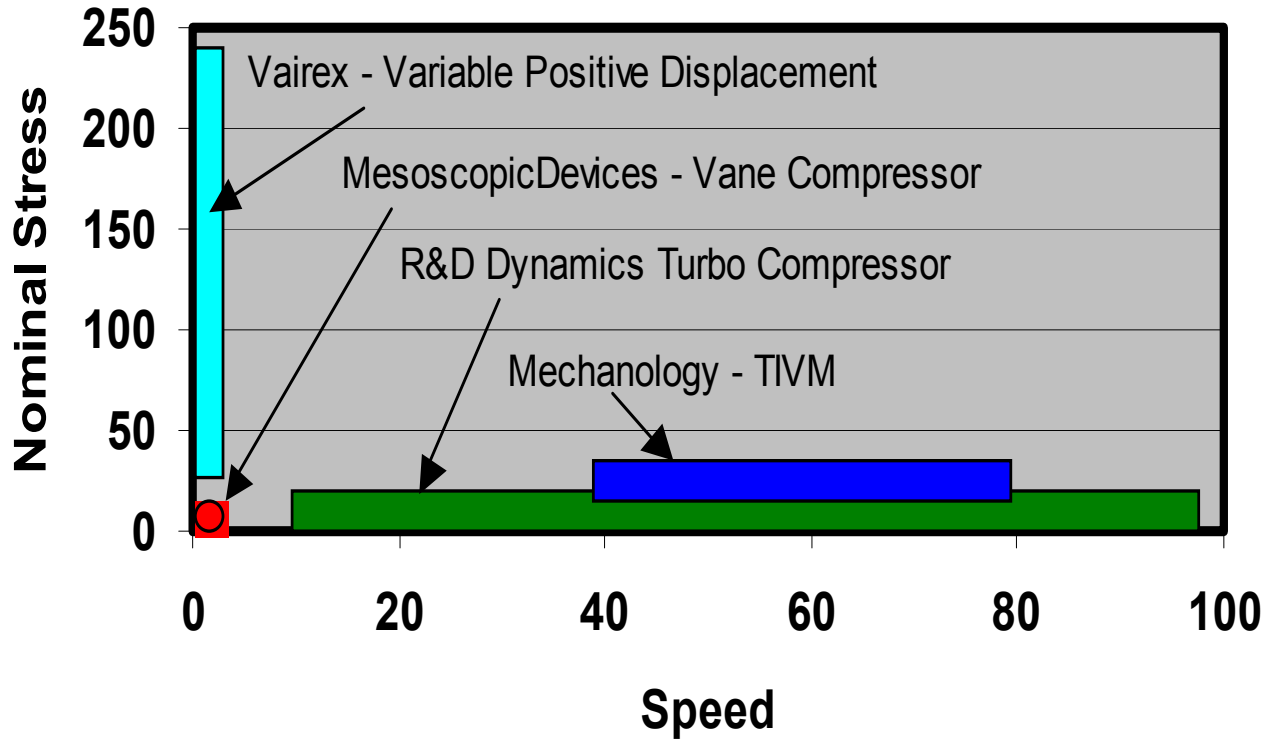
Wear Performance





Different Compressor/Blower Concepts Have Widely Different Operating Parameters, and Materials

- Nominal contact stresses range for a few psi to several hundred psi
- Sliding speeds range from < 0.5 m/s to greater than 80 m/s
- Materials of construction include: polymers, metals, ceramics, carbons, and composites



Contact Temperature and Tribological Performance

At high sliding speeds typical of compressors and blowers designs, contact temperatures frictional heating governs the tribological performance.

Bulk Temperature Calculation

Rate of bulk frictional heating q_b

$$q_b = \frac{\mu F v}{A_n}$$

Bulk temperature T_b

$$T_b - T_o = q \Big/ \left[\frac{k_1}{l_{1b}} + \frac{k_2}{l_{2b}} \right]$$

μ = friction Coefficient
F = Normal Force
v = Sliding velocity
A_n = Nominal contact area
A_r = Real contact area
T_o = Ambient temperature
k_1 = Thermal conductivity – body 1
k_2 = Thermal conductivity – body 2
l_b = nominal contact length
l_f = asperity contact length

Flash Temperature Calculation

Rate of asperity frictional heating q_f

$$q_f = \frac{\mu F v}{A_r}$$

Flash or asperity temperature T_f

$$T_f - T_o = q_f \Big/ \left[\frac{k_1}{l_{1f}} + \frac{k_2}{l_{2f}} \right]$$

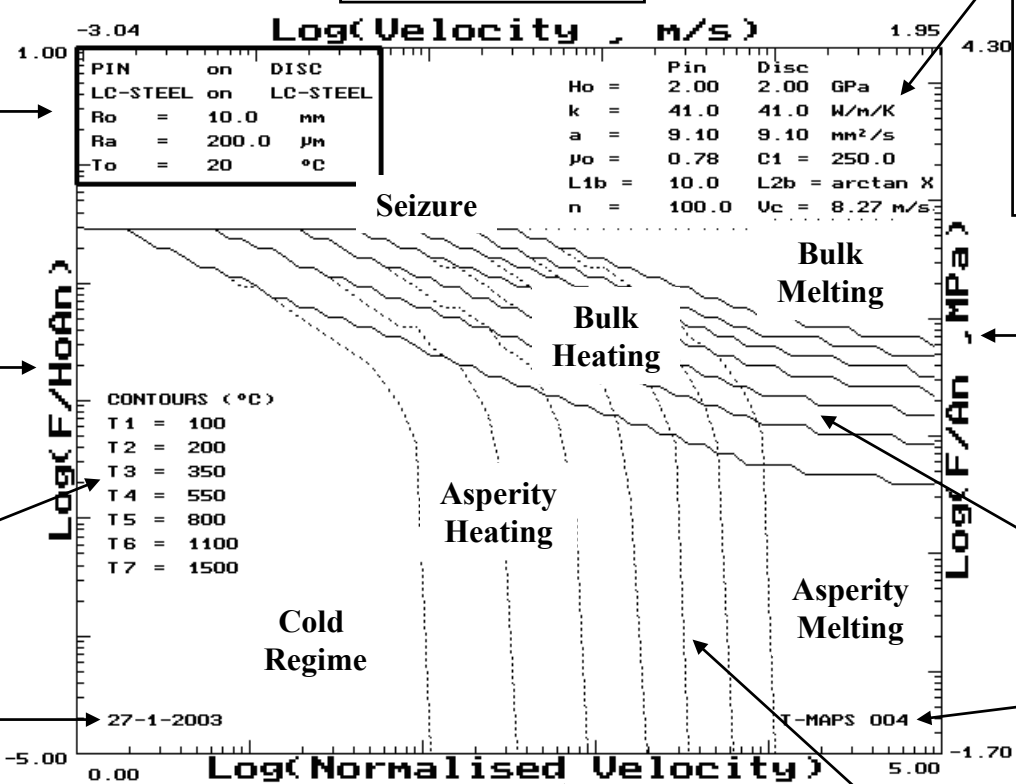
Concept of T-Maps – Methodology to Calculate Bulk and Asperity Heating Based on Frictional Heating

Transportation Materials

Main Heading:
Configuration,
Materials,
Contact Radius,
Asperity Radius,
Ambient Temperature

Axis of Sliding Velocity (m/s)

Material Data:
Hardness,
T-Conductivity,
T-Diffusivity,
Friction Constants,
Heat-Diffusion Lengths,
Asperity Lifetime and
Asperity-Melting Velocity



Axis of Normalized Bearing Pressure

Axis of Bearing Pressure (MPa)

Temperature Contour C

Contours of Bulk Temperature

Date of Computation

Version of the Program

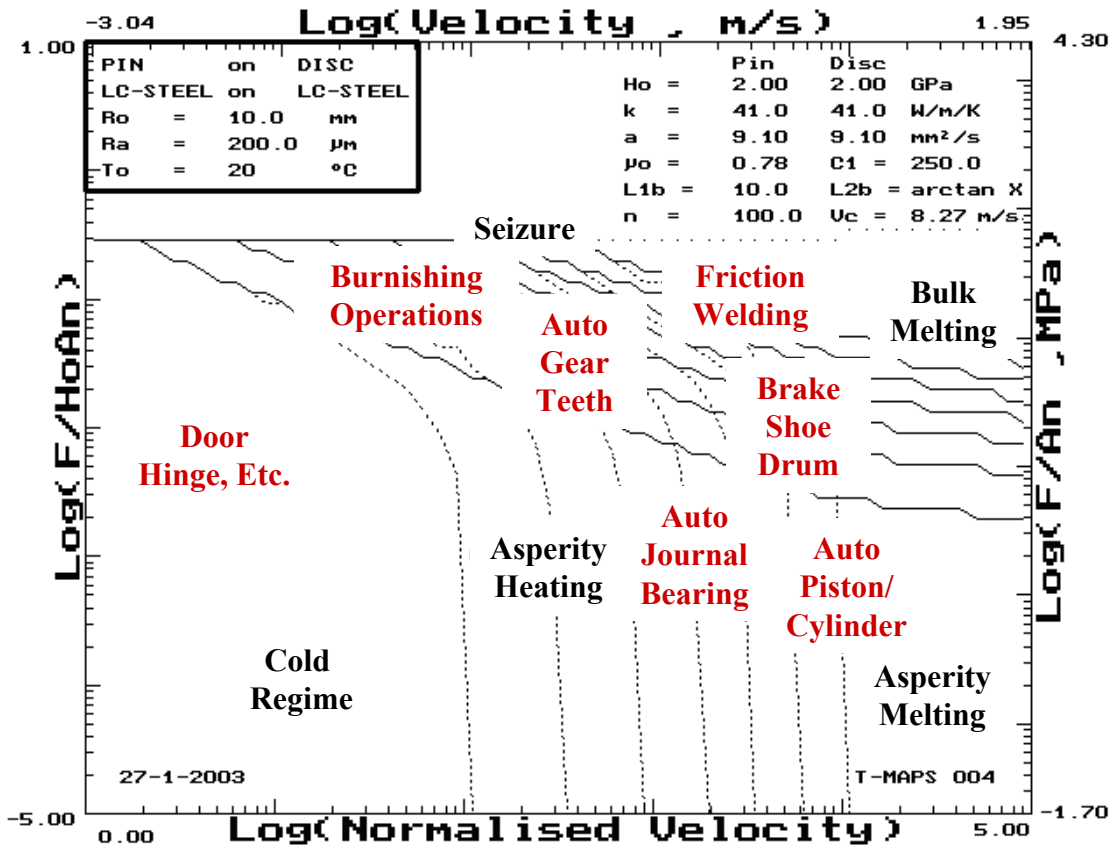
Axis of Normalized Sliding Velocity

Contours of Asperity Temperature

Concept of T-Maps – Methodology to Calculate Bulk and Asperity Heating Based on Frictional Heating

Based on operating contact conditions and material properties, map the various possible modes of failure.

- T-Map as an illustration of effect of sliding conditions on friction heating and failure mechanisms.



Transportation Materials

Future Activities

- Continue Collaborations with DOE supported Compressor/Blower Partners to Address Tribological & Material Issues
  - Mechanology
  - Meruit (respond to DOE solicitations as subcontractor where appropriate)
- Initiate Collaborations with:
  - UTC (R&D Dynamics) – Compressor
  - AD Little
  - Others
- Work with firms developing blowers for portable fuel cell applications (50 W to 5 kW)
- Host Compressor/Blower Workshop to Identify Critical Material Issues/Barriers
- Develop Material Selection Methodology Model
  - Wear/Friction Maps

Transportation Materials

Transportation Materials

Carbon Composite Bipolar Plate for PEM Fuel Cells

T. M. Besmann, J. J. Henry, J. W. Klett,
E. Lara-Curzio, and I. P. Kosacki
Metals and Ceramics Division
Oak Ridge National Laboratory

T. L. Starr
Chemical Engineering Dept.
University of Louisville

Hydrogen and Fuel Cells Merit Review Meeting
Berkeley, California May 19-22, 2003

Objective

To develop a slurry-molded, carbon fiber material with a carbon chemical vapor infiltrated (CVI) sealed surface as a bipolar plate that would meet cost and property goals.

Property	*Specification*
Bulk Conductivity	> 100 S/cm
H_2 permeability	$<2 \times 10^{-6}$ cm^3/cm^2-sec
Corrosion rate	<16 $\mu A/cm^2$
Cost	<$10/kW

Approach

- Bipolar plate utilize carbon/carbon concept
- Preform is slurry-molded carbon fibers
  - similar to paper or felt production
  - fibers ~100 μm plus filler particles
  - features stamped/embossed into preform
- CVI with carbon
  - seals and makes hermetic high-density surfaces
  - provides continuous, high-conductivity material

Advantages of Approach

- Preforms prepared from slurry-molded carbon fibers
  - net shape process/press-in features
  - process can be continuous (i.e., papermaking)
  - low-cost materials
- Appropriate surfaces sealed via deposition of carbon
  - high-conductivity (graphitic) carbon coating all surfaces
  - infiltration makes component fully integral
  - potential for continuous or semi-batch processing
- Negligible impurities/poisons with minimal corrosion
- Strength and toughness of carbon/carbon
- Very light weight (about half that of other approaches)
- Potential for integral diffuser/catalyst support, therefore, lower ohmic losses

Timeline of Project Accomplishments

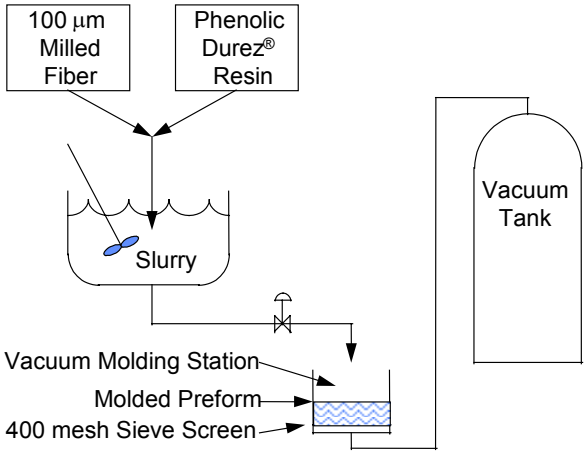
- **March 1998** — Project Initiated
- **July 1998** — 3-cm disks with machined flowfield; High conductivity meas.; Promising cell perf.
- **June 1999** — 100-cm^2 plates with machined flowfield; Good cell performance; High conductivity meas.; Light weight demonstrated; High strength/toughness; Initial samples to industry
- **June 2000** — Pressed preforms; Freeze/thaw testing; Low corrosion meas.; Multiple samples to industry
- **April 2001** — License signed with Porvair Fuel Cell Technologies
- **June 2001** — Two-sided 100-cm^2 plates with pressed flowfield evaluated; Thermal conductivity meas.; Resistivity/polarization meas.
- **June 2002** — Developed carbon composite with graphite particulate filler; Measured mechanical properties of plate material; Significantly improved wetting of bipolar plate surface; Determined surface roughness of finished plate
- **Sept. 2002** — Developed a series of bipolar plate materials/specimens that meet specific fuel cell manufacturer's design needs
- **Sept. 2003** — With licensee, developed manufacturing capability for specific bipolar plate designs through sample preparation, process modeling, and consultation

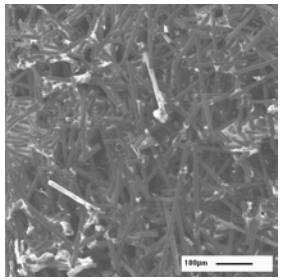
Current Accomplishments

- With licensee, have reduced thickness of plates from 2.5 mm to 1.5 mm
- Determined influence of CVI temperature on depth of infiltration
- Further characterized and measured mechanical properties of carbon composite plate material
- Determined electronic properties, including effect of surface roughness on resistance
- Developed initial model of chemical vapor infiltration process that is scalable to production – model demonstrated value through guidance on flow control improving uniformity

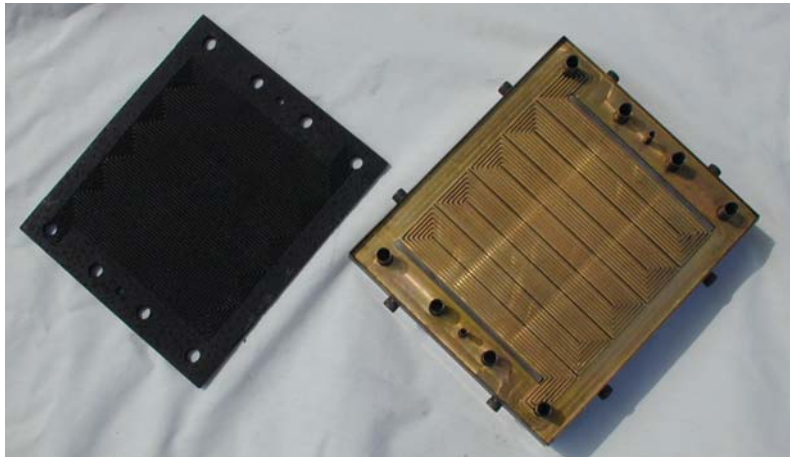
Carbon Composite Plate Fabrication

Slurry Molding of Preforms

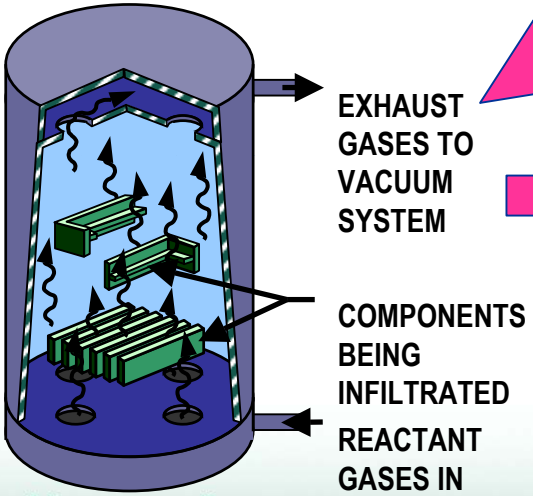


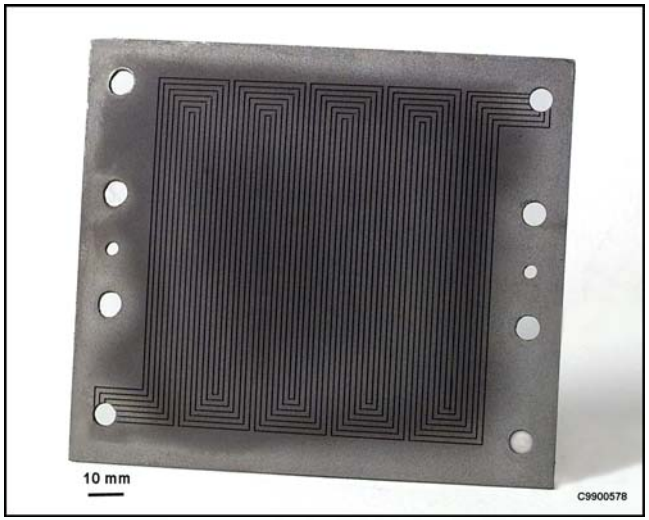


Press or Stamp Features



CVI Carbon





Porvair Preform Material Used in Study of Infiltration Depth as a Function of Reactor Conditions and Position

CVI Conditions:

Temperature

High Rate - 1500°C

Low Rate - 1350°C

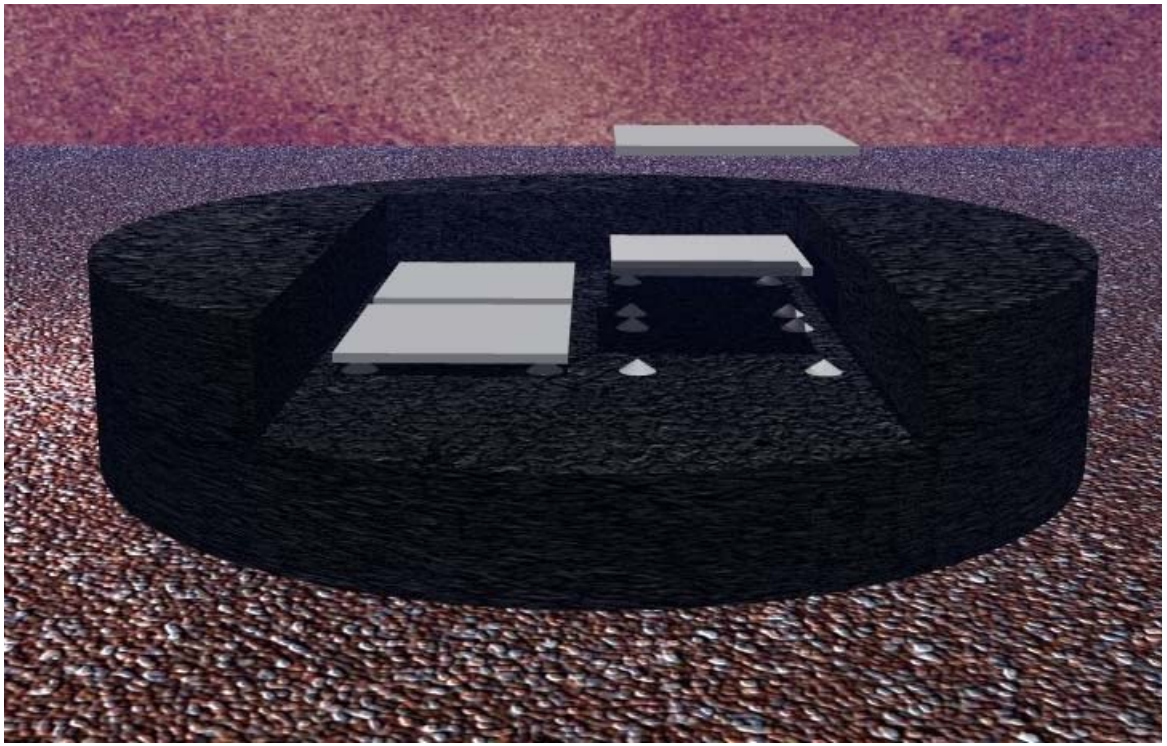
Flow

1 sccm methane

2.5 sccm argon

Pressure

4 kPa



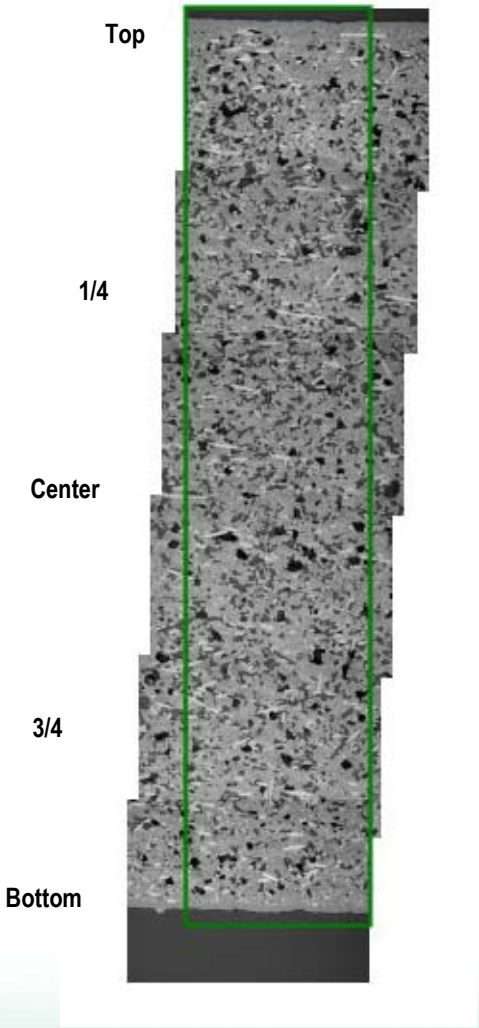
CVI Reactor Chamber Showing Position of Samples

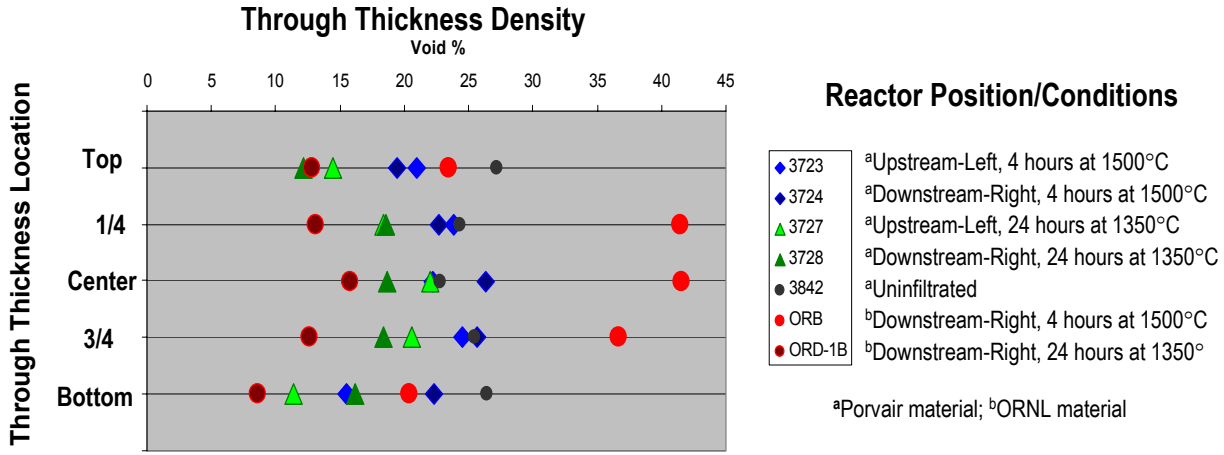
Effect of CVI Conditions/Material on Density Profile

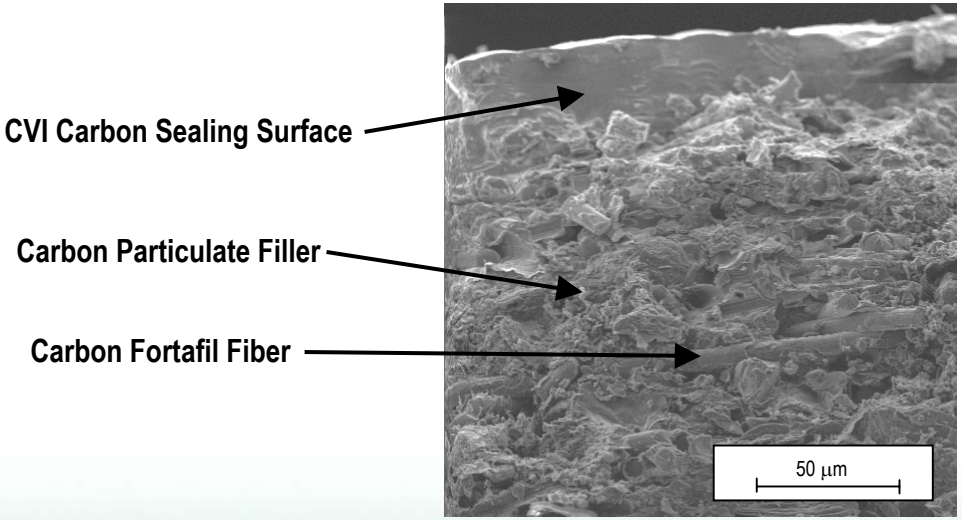
Image analysis reveals density gradients through plate thickness more pronounced for:

- *ORNL material, which has no filler particles and thus higher green state porosity*
- *More rapid infiltration (higher infiltration temperature) in ORNL material*

Mosaic of Optical Images of Plate Cross-Section (Porvair Material)



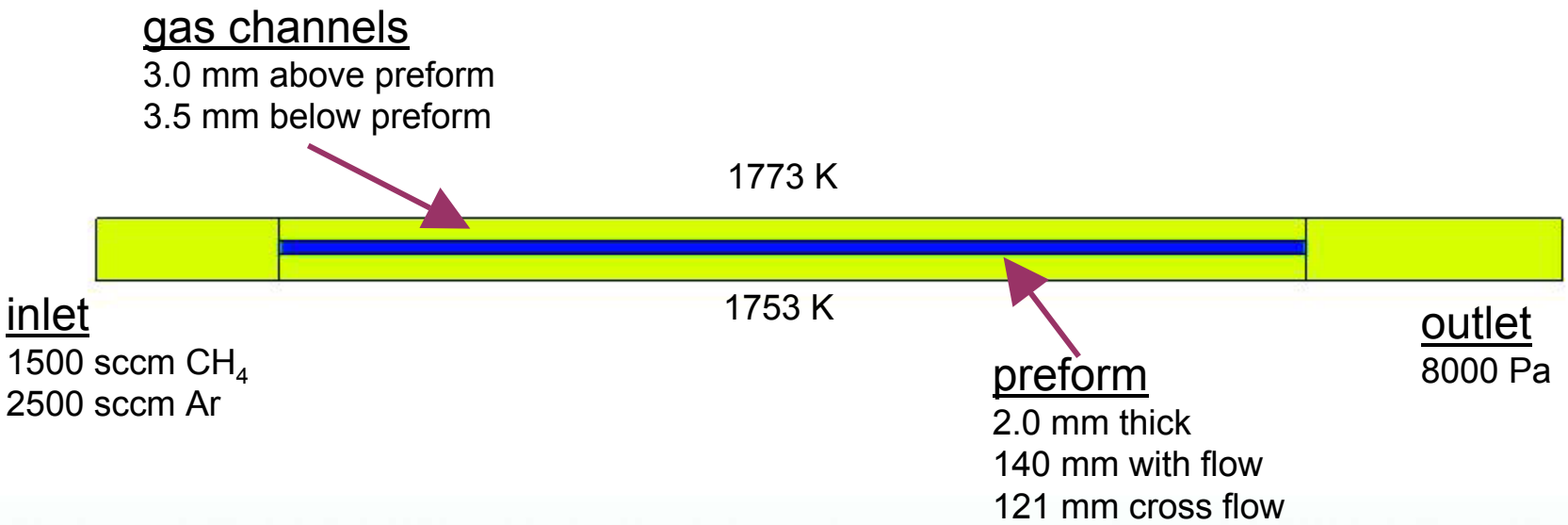




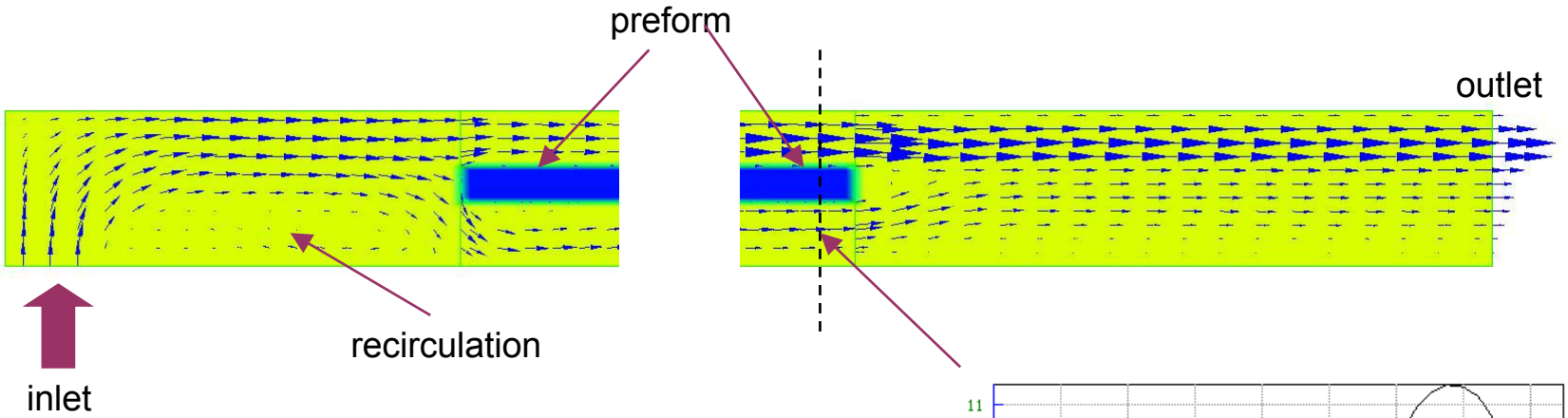
SEM Image of a Fracture Surface of an Infiltrated Bipolar Plate Produced From Porvair Preform Material Indicating That Carbon Deposition Is Limited Largely to the Exposed Surfaces

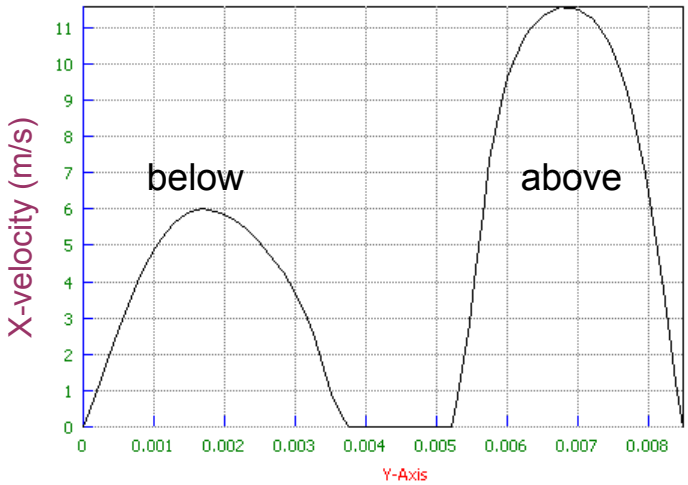
2-D Computer Model for CVI Reactor

- Commercial fluid dynamics code (CFD-ACE from CFD Research, Huntsville, AL) Cross-section reactor/preform geometry
- Kinetics and transport parameters from literature and from experiments at ORNL
- Finite-volume method with 136,000 element structured grid
- Boundary conditions match experiment
- Steady-state solution for gas flow



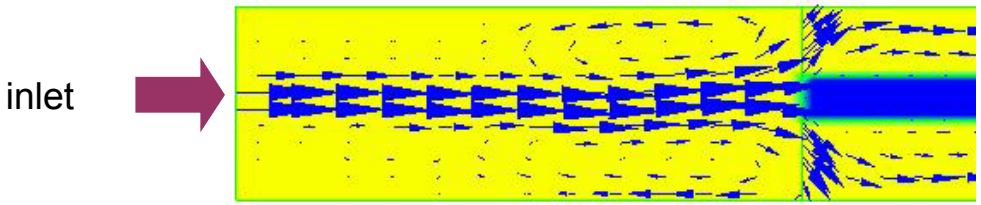
Original Inlet Design Yielded Non-Uniform Flow



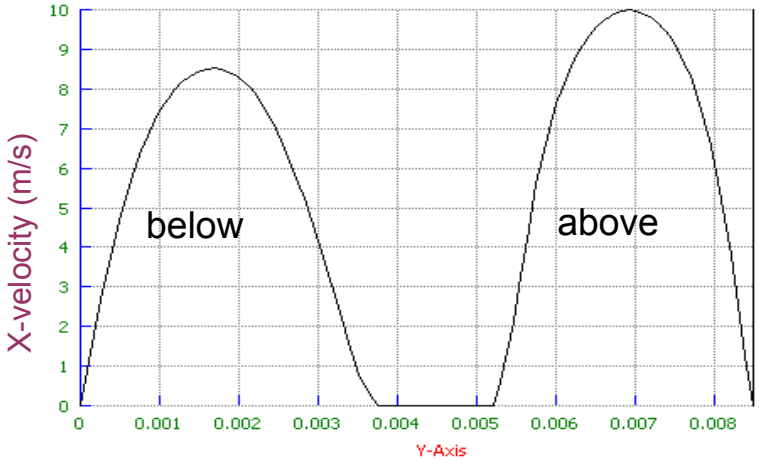


- **Single recirculation cell near inlet**
- **Parabolic, laminar flow above/below preform**
- **Higher velocity above preform**

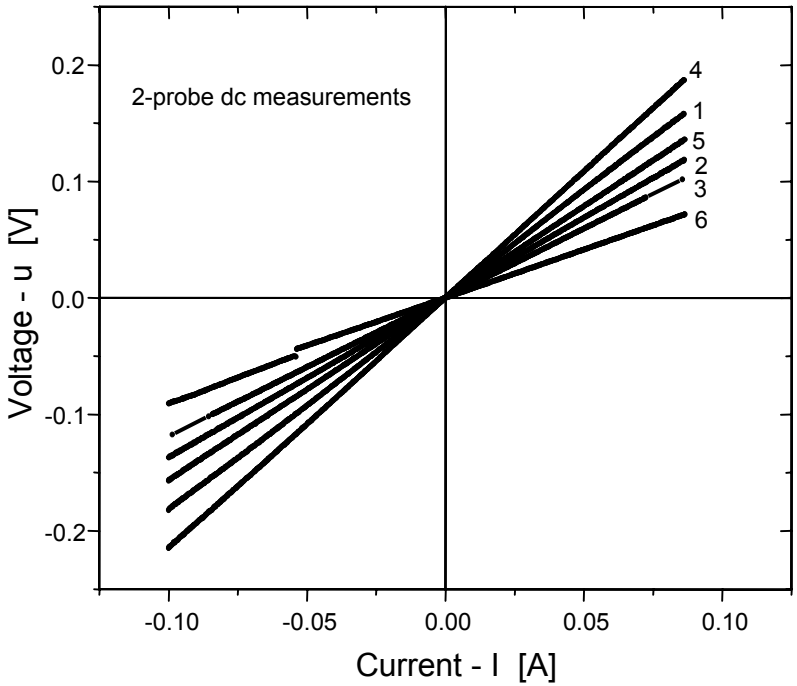
Installation of a Nozzle Yielded Uniform Flow



- **Nozzle turns and centers inlet flow**
- **Top/bottom recirculation cells**
- **Uniform velocity above/below preform**



Electronic Properties Are Weakly Related to Surface Roughness

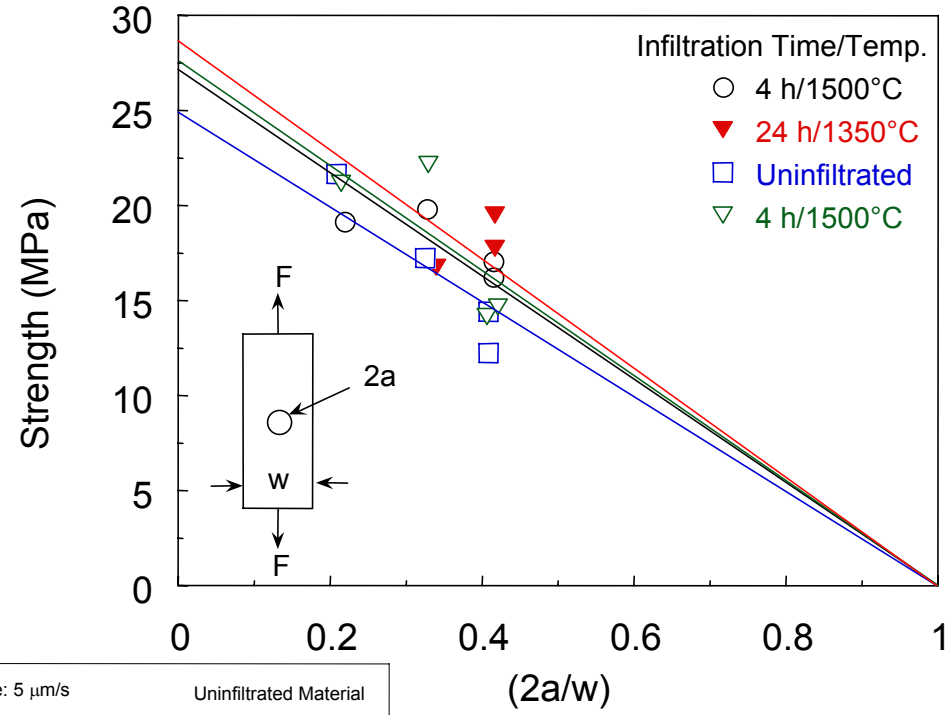


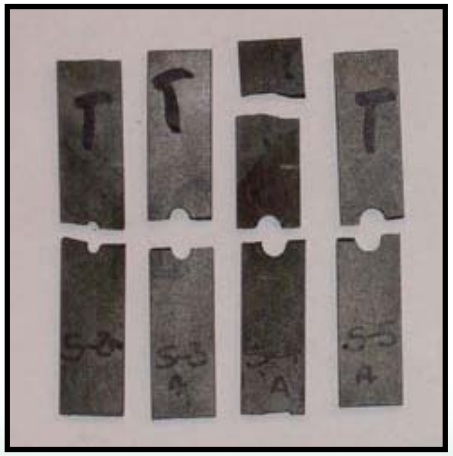
Porvair Material	Infiltration Treatment	Surface Roughness Rz µm	Resistance 2 Probe DC Ω	Conductivity 4 Probe V/I σ S/cm
No. 1 - V162C-L2 A	4hours at 1500°C	8.83	1.86	365
No. 2 - V1631-R1-C	24hours at 1350°C	12.9	1.37	417
No. 3 - V1631-R1-P	Uninfiltrated	13.5	0.86	369
No. 4 - V162C-L2 D-1	4hours at 1500°C	10.2	2.16	386
No. 5 - V163AR1A-1	24hours at 1350°C	14.3	1.57	383
No. 6 - V163A-R1-B	24hours at 1350°C	2.9	0.84	408

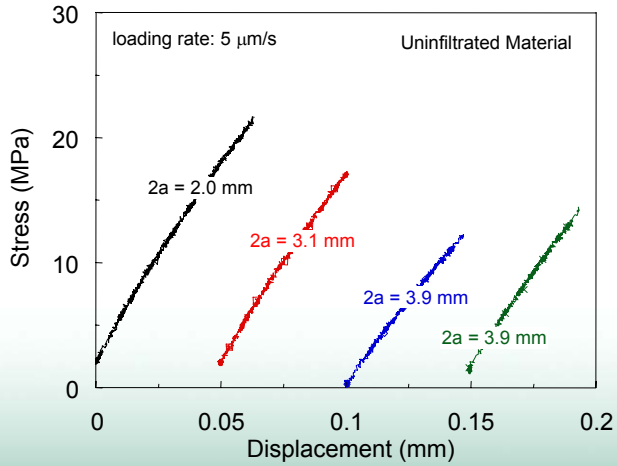
- *2-probe measurements are sums of all contact resistances*
- *Surface roughness does not correlate closely with contact resistance*
- *Sample no. 4 was not infiltrated and thus has fewer "interfaces" to offer resistance*
- *Sample no. 6 was polished and indicates a significantly lower contact resistance than that of unpolished samples (all others)*
- *Bulk conductivity as measured by a 4-probe technique varies little with sample preparation*

Porvair Material Has Reasonable Strength and Apparent Notch Insensitivity

- *The resistance of materials to crack propagation can be evaluated by the notch sensitivity test*
- *Test specimens with holes of various sizes are subjected to monotonic tensile loading*
- *Ultimate strength (un-notched) is at a minimum the zero intercept of the strength vs. 2a/w*



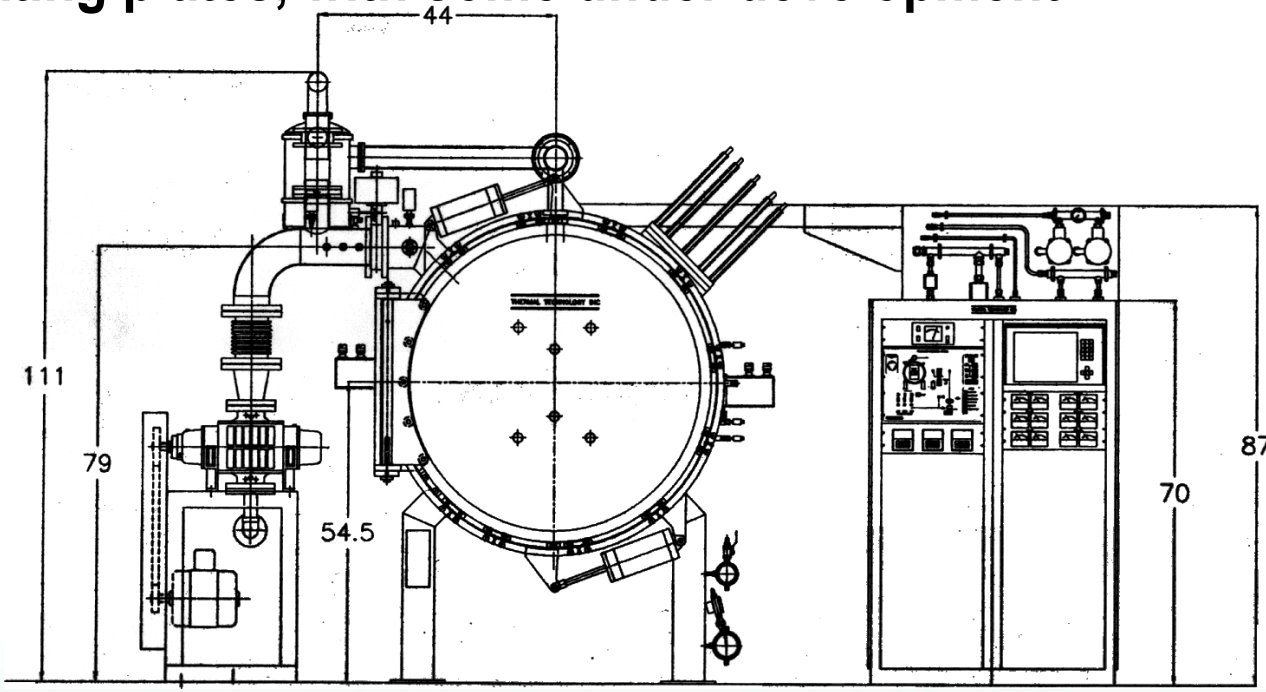




Industrial Interactions

- Supporting licensee Porvair Fuel Cell Technology in scaling up technology
- Porvair has been awarded a $6.1 M DOE program for scaling and applying the carbon composite bipolar plate technology
- Other companies evaluating plates, with some under development

Porvair Scale-Up CVI Furnace



Continuing Development and Technology Transfer of Carbon Composite Bipolar Plates

- Milestone FY 03 - Develop a carbon composite bipolar plate component with reduced thickness and optimized mechanical properties. (Sept. 2003)
- Develop CVI process model that is scalable to pilot and production facilities
- Determine electronic properties as a function of surface roughness
- Milestone FY 04 - Support continued scale-up of the licensee's operation through modeling of fabrication processes. (Sept. 2004)

Some Advisory Panel Comments From Last Year and Responses

- "Demonstrate durability of materials manufactured by industrial partner in larger hardware"
  - Mechanical property measurements were made to better characterize the material which showed notch insensitivity (good toughness)
  - Partner has produced significant numbers of plates that have performed in customer hardware
- "Providing different hydrophobicity could be interesting area to explore"
  - Licensee does not give this a high priority
- "Test method extensively"
  - Developing mechanical and electrical property test results

Cost Effective Surface Modification For Metallic Bipolar Plates

M.P. Brady, K.L. More, P.F. Tortorelli, L.R. Walker
Oak Ridge National Laboratory

K. Weisbrod, M. Wilson, F. Garzon
***Los Alamos National Laboratory**

H. Wang
***National Renewable Energy Laboratory**

I. Paulauskas and R.A. Buchanan
***University of Tennessee, Knoxville**

2003 Hydrogen and Fuel Cells Merit Review Meeting
May 19-22, 2003, Berkeley, California

***Collaborating Institutions**

Contact: bradymp@ornl.gov

Why Metallic Bipolar Plates?

- Better mechanical properties: Permits thinner plates for higher power densities- metals have potential for 0.1-1 mm thick, while composites typically 2-5mm
- Amenable to low cost/high volume manufacturing techniques (e.g. stamping or corrugation)
- Gas impermeable
- Higher electrical and thermal conductivities

Relates to DOE R&D Plan Component Technical Barriers Task 14 "Alternative bipolar plate materials/coatings that are low-cost, lightweight, corrosion-resistant, and impermeable"

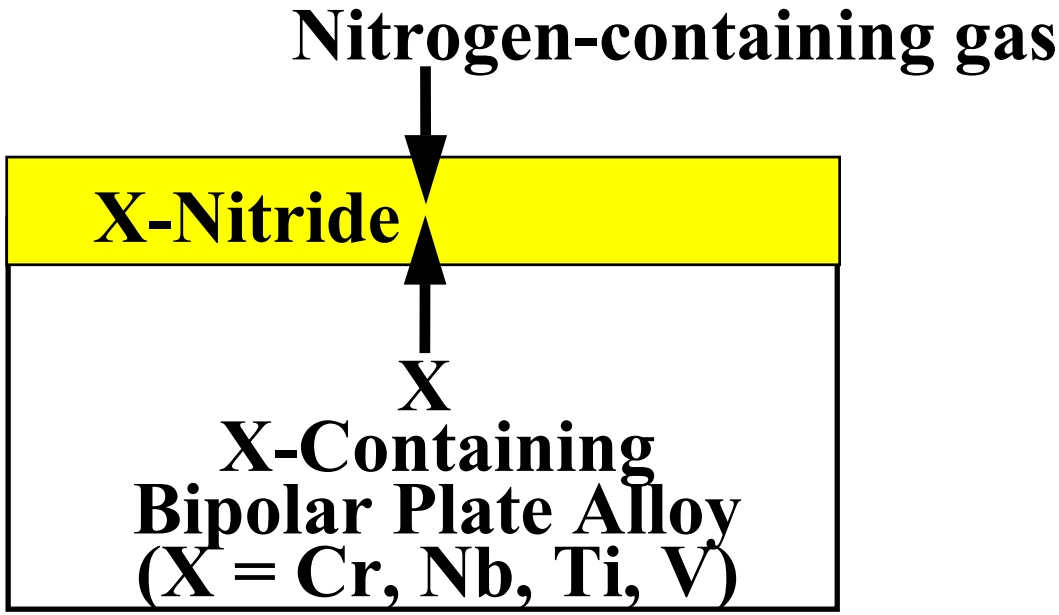
Most Metals Have Inadequate Corrosion Behavior in PEM Fuel Cell Environments

- **Contamination of Polymer Membrane by Metal Ions**

- **High Contact Resistance from Surface Oxide Formation**

- **Transition Metal Nitrides are Promising Coatings**
  - **Corrosion Resistant**
  - **Electrically Conductive**
  - **Need inexpensive, defect-free coating method**

Approach: Thermally Grown Nitride for Corrosion Protection



- Surface Conversion: High temperature favors complete surface metal reaction (amenable to complex geometries)
- Issues relate to achieving nitride continuity, adherence, and desired composition
- Stamp to final form then nitride: Industrially established and cheap

Objective

Develop an alloy which will form an electrical-conductive and corrosion-resistant nitride surface layer during thermal (gas) nitriding

- **Existing commercial alloys designed to form oxide scales, nitridation typically degrades corrosion resistance (primarily currently used for surface hardening)**

- **Must control gas-metal reactions by environmental and compositional manipulation to achieve desired surface**

Timeline and History of Project

- **2000: Showed thermally grown nitride on Nb-Ti base alloy can exhibit corrosion resistance in PEMFC Environment**

- **2001: Demonstrated external, continuous TiN base nitride formation on developmental Ni-Ti and Fe-Ti base alloys**

- **2002: Corrosion resistance demonstrated for nitrided Ni/Fe-Ti but problems at edges/corners, lack of robustness**
  - **New family of <u>Cr-nitride/Ni-Cr alloys</u> identified**
  - **Promise shown for edge/corner coverage**

Comments From 2002 Review (paraphrased)

- Good Approach and Promising Results

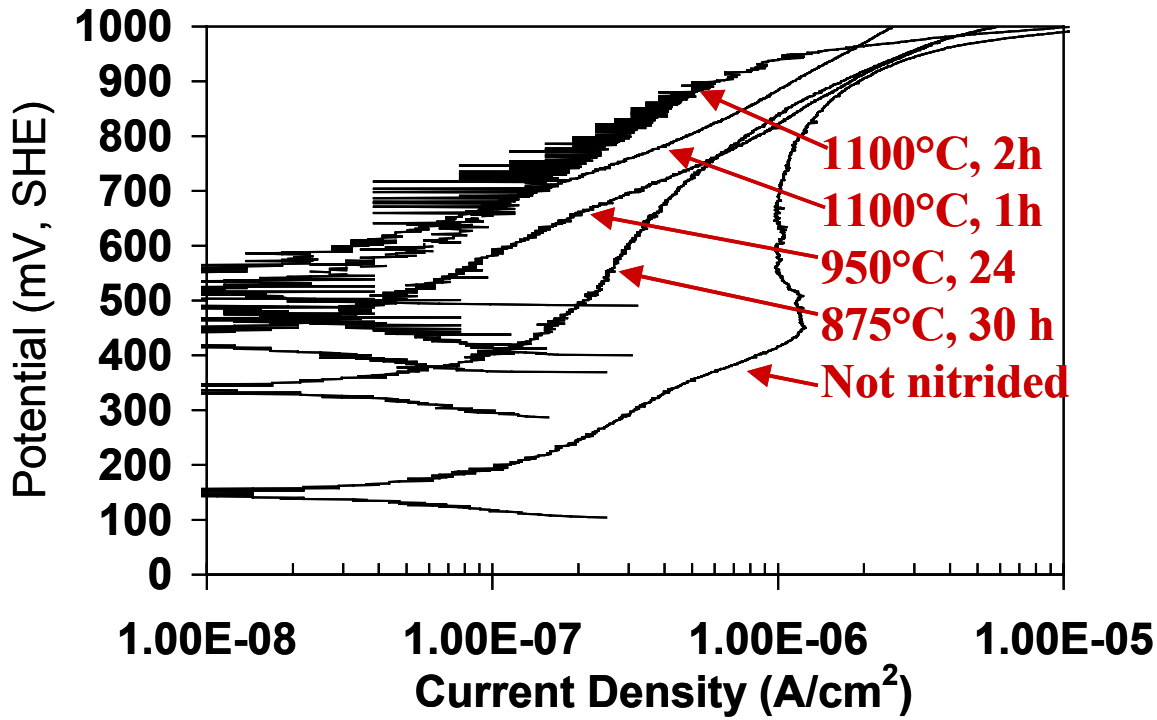
- Need to Demonstrate
  - Ability to protect flow field features
  - Long-term corrosion resistance
  - Successful in-cell test

↓

These Issues Formed the Basis of Our 2003 Milestone and Have Been Achieved

Nitrided Ni-50Cr Used as Model to Study Nitridation/Microstructure/Composition and Corrosion Resistance Relationships

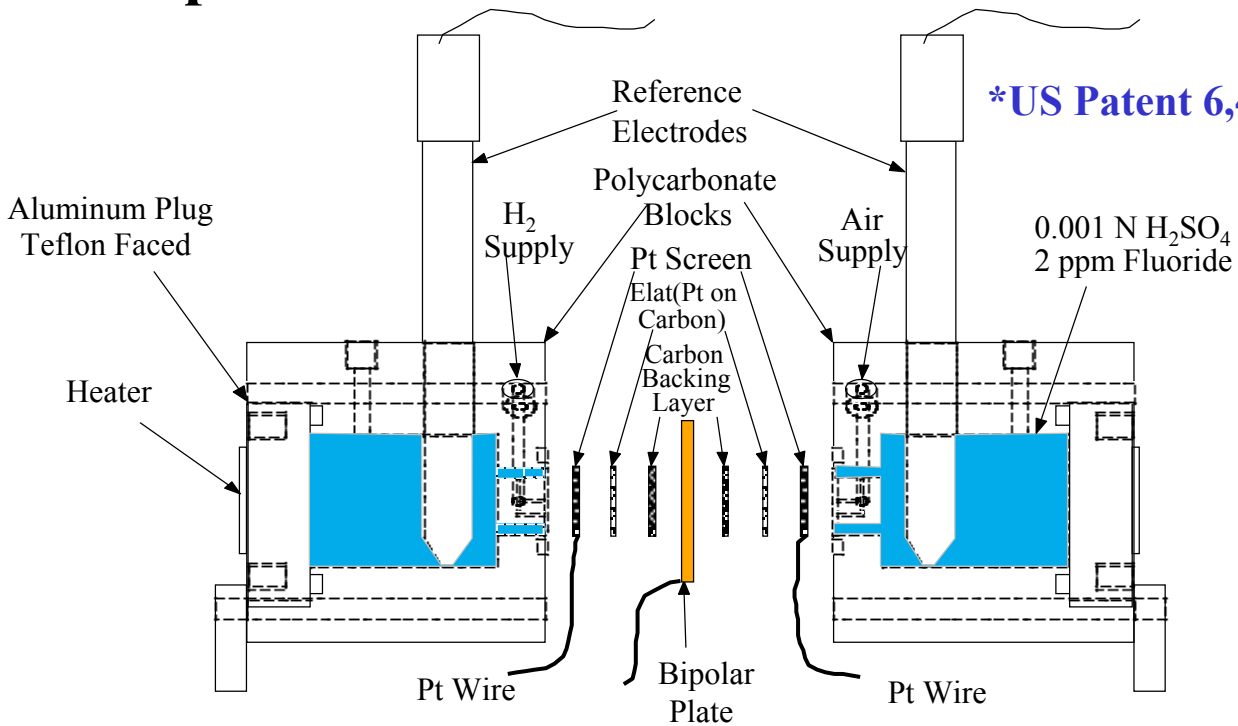
Anodic Polarization curves for Ni-50Cr Nitrided in Pure N_2
Aerated pH3 Sulfuric Acid (0.1 mV/s)



- **Corrosion resistance correlated with continuous CrN/Cr_2N surface**
- **Low temperature nitridation in NH_3 or plasma assisted environments possible- Pure N_2 used in demonstration stage for simplicity**

1100°C/1 h Nitrided Ni-50Cr Performed Well Over 4000 h in *LANL Corrosion Test Cell

Environment 80°C, pH3 H_2SO_4, 2 ppm F^-, open circuit potentials set by contact w/Pt in H_2/Air purged conditions (anode face experienced ~ -0.31V vs SHE and cathode face ~ +0.87V)



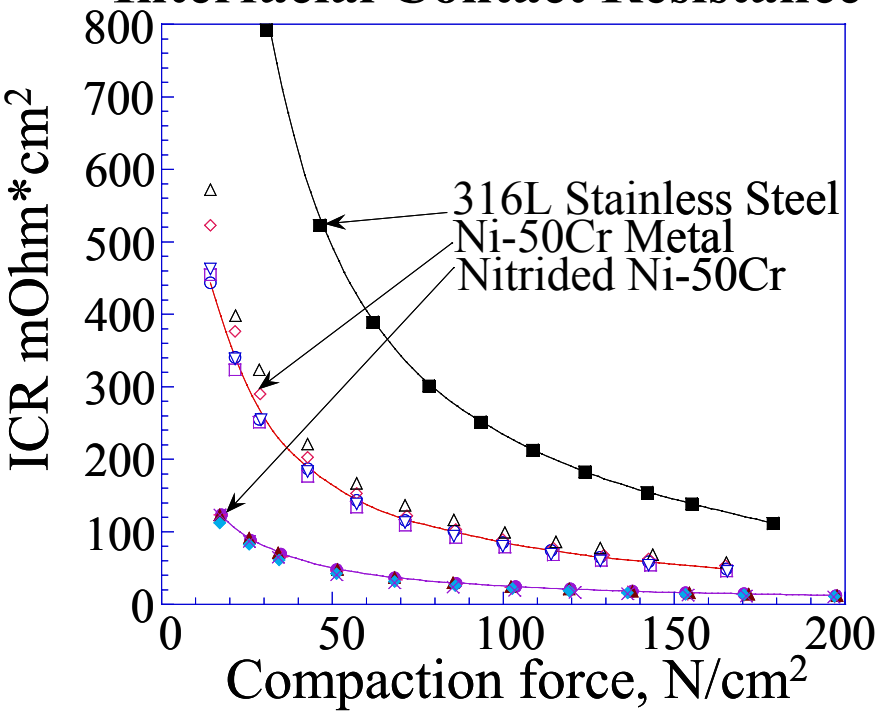
*US Patent 6,454,922 (Weisbrod)

- Resistance increase of <u>only</u> 2mV/1000 h anode and 2.7 mV/1000 h cathode (1A/cm^2)
- Little dissolution over 4000 h exposure: only 3.8ppm Ni at anode and 0.08 ppm Ni at cathode (Cr not detected)

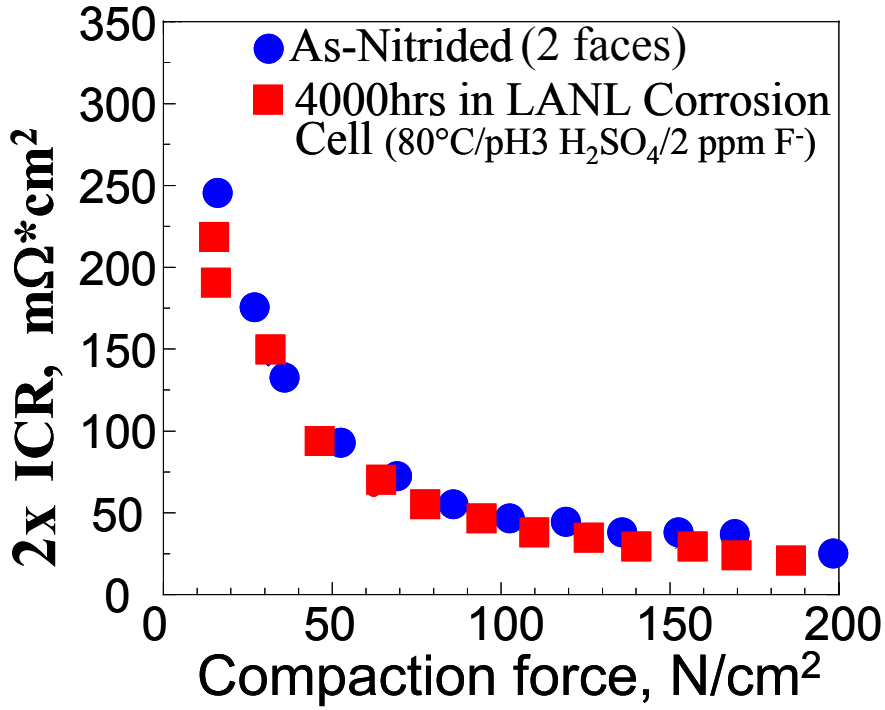
Nitrided Ni-50Cr Exhibits and Maintains Low Contact Resistance

(Measured at NREL)

Nitridation Significantly Lowers Interfacial Contact Resistance



***Low Resistance of Nitrided Ni-50Cr Maintained After <u>4000 hr Exposure</u>**

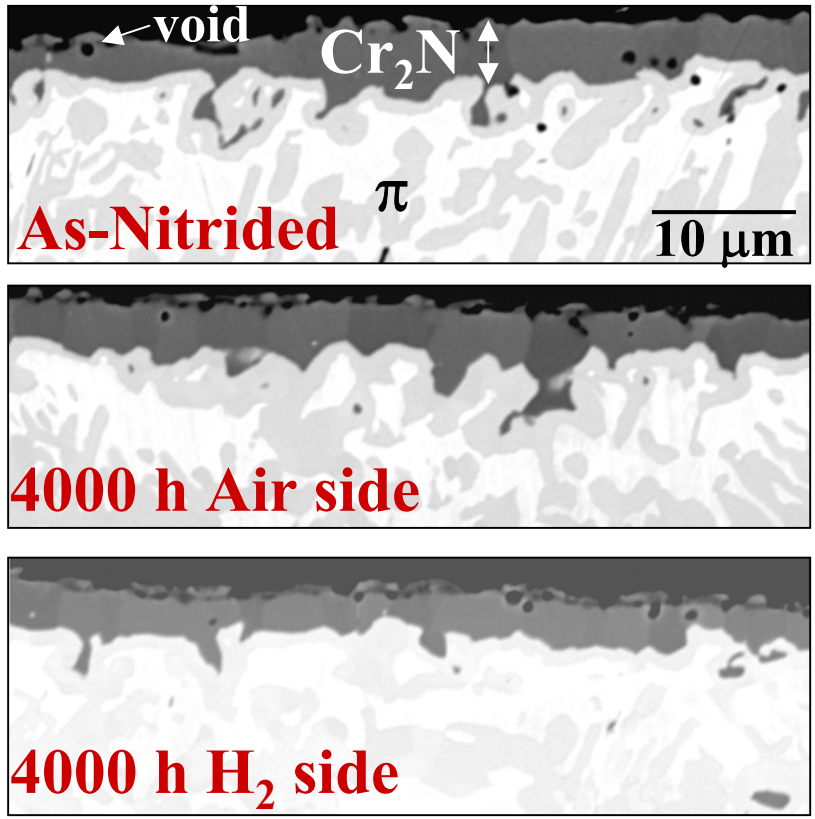


***Measurements for LANL 4000 h coupon include <u>BOTH</u> faces of coupon because 1-face was in anode environment, other in cathode**

-Control as-nitrided data from chart on left therefore doubled

CrN/Cr_2N Nitride Layer Held Up Well in 4000 h LANL Corrosion Cell Exposure

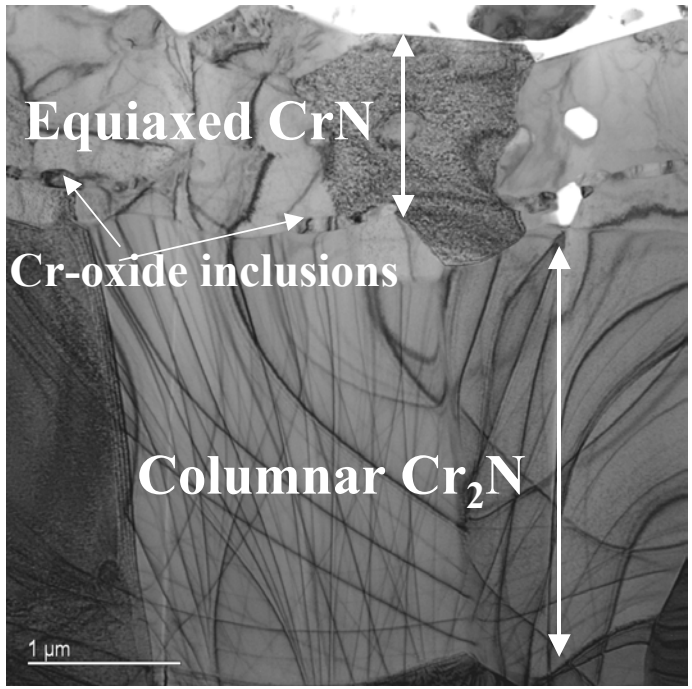
SEM Cross-Sections of 1100°C, 1h Nitrided Ni-50Cr



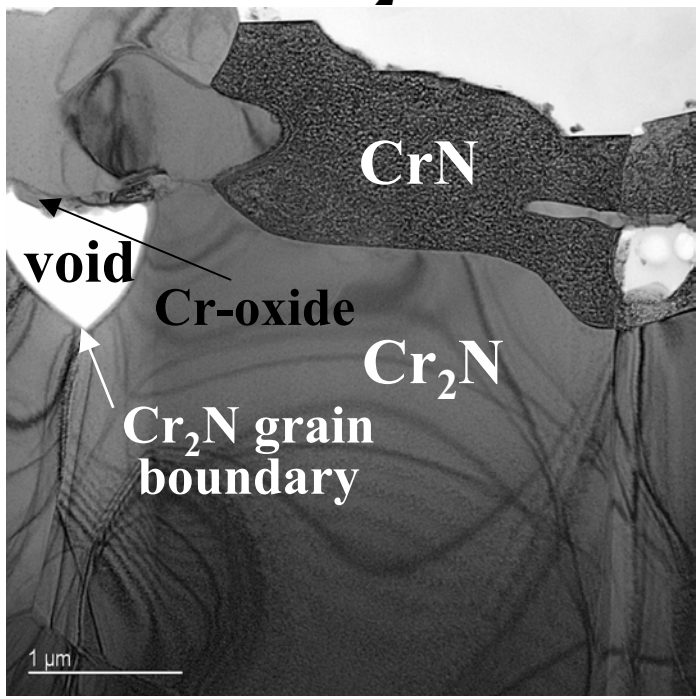
- **Semi-continuous CrN (~ 1 μm) overlying continuous Cr_2N layer**
  - deep internal nitridation zone of NiCrN π phase in Cr-depleted Ni(Cr)
- **No evidence of significant corrosive attack (may be increase in near surface voids at CrN/Cr_2N interface in H_2 exposed face)**

Cross-Section TEM for Insight into 4000 h Exposed Nitride from LANL Corrosion Cell

4000 h Air Side



4000 h H_2 Side

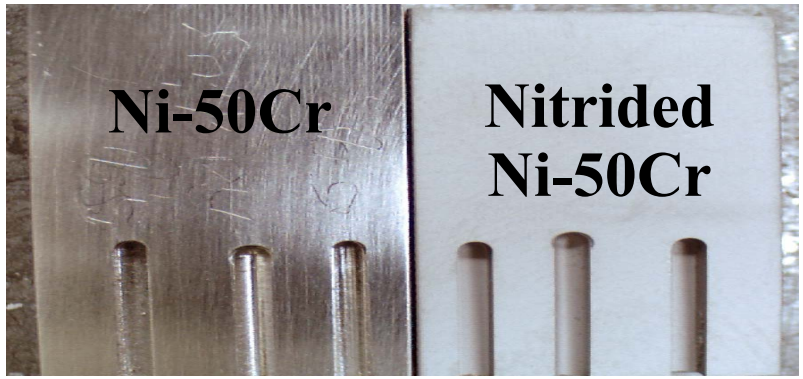


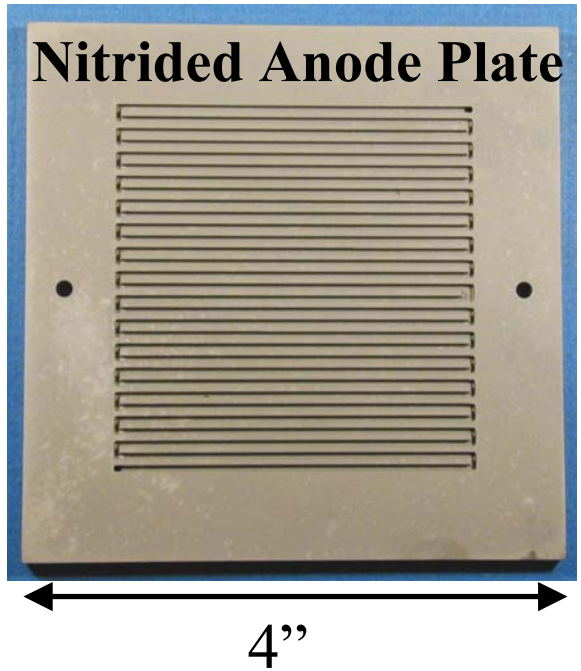
1 µm

- No evidence of significant surface oxidation or attack
- Voids primarily at Cr_2N grain boundaries near interface w/CrN may have formed during nitridation, not corrosive attack
- Findings used to guide optimization of nitride composition/structure

50cm^2 Active Area Anode and Cathode Plates Successfully Nitrided for Single-Cell Test

Nitride coverage of flow field grooves





- **Tests run at 0.7V, 80°C, 3 atm. (30 psi) using neat hydrogen at 0.3 sLPM and compressed air at 1.8 sLPM (Tested at LANL)**
  - -1st run: 500 h using Nafion 112 with 0.2/0.2 mg/cm^2 Pt anode/ cathode (MEA damaged by inadvertent loss of H_2 supply during test)
  - -2nd run: 500 h using Nafion 1135 with 0.23/0.37 mg/cm^2 Pt
  - -Nitrided Ni-50Cr plates exposed for 1000 h cumulative total

Membranes Clean After Two, 500 h In-Cell Exposures w/Nitrided Ni-50Cr Plates

- **X-ray fluorescence of anode/cathode MEAs show Ni/Cr levels of only 0.01- 0.3 μg/cm^2 - among cleanest membranes tested at LANL!**
  - Cr-rich liquid found in one alignment pin port of the cathode plate on cell disassembly- may have resulted from poor nitridation due to casting flaw (suspect local Cr-depleted inclusion)

- **No increase in cell resistance over the 2nd 500 h test (resistance data from 1st 500 h test unreliable due to MEA damage from H_2 interruption)**
  - Baseline interfacial resistance contribution of 5 mΩ-cm^2 cathode and 1 mΩ-cm^2 anode

VERY PROMISING INITIAL RESULTS!

What About Cost?

- **Initial input garnered from commercial alloy producers suggests Ni-(40-50)Cr in range of $10-15/lb possible (concern for impurity effects/rate of work hardening above ~42Cr)**

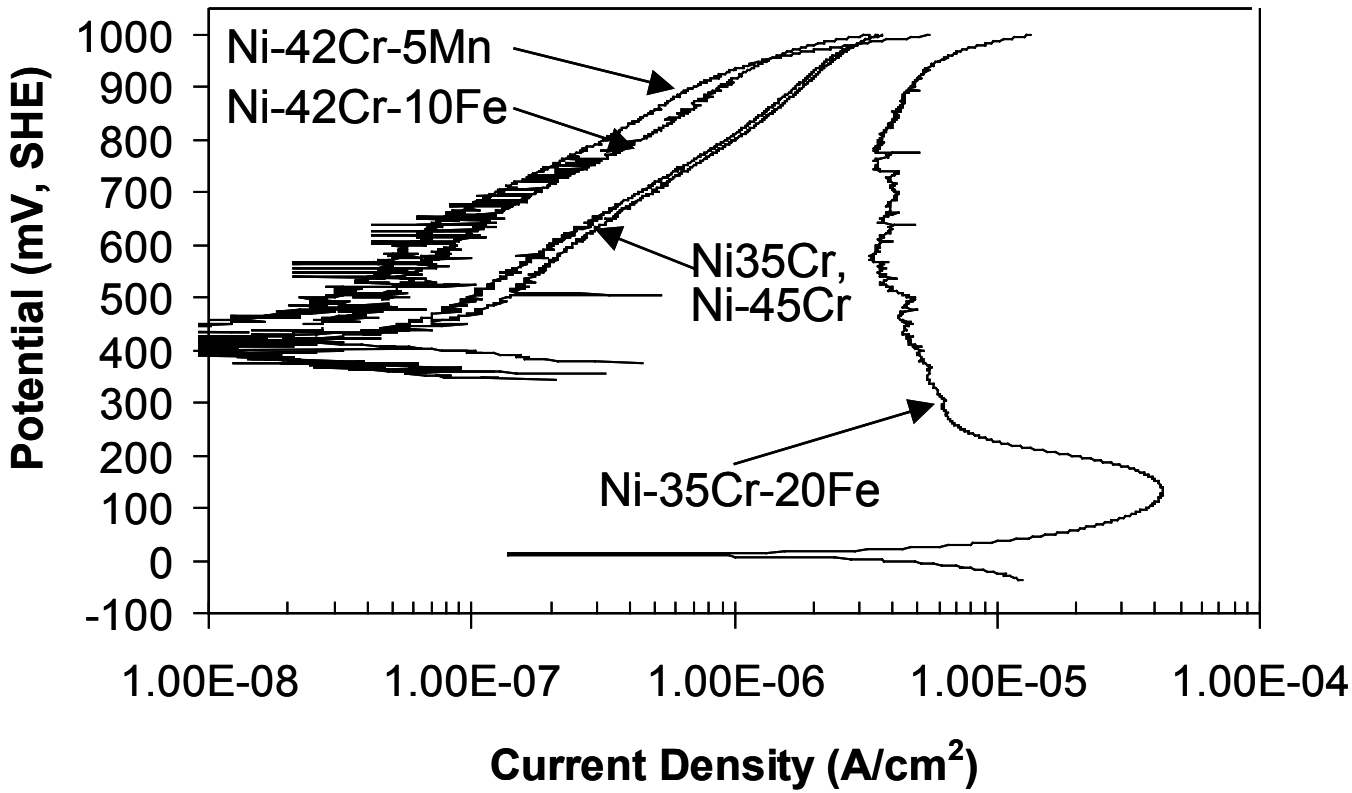
  Assuming $12.50/lb, 500 cm^2 plate (no stamping/nitriding)

  - 0.1mm thick ~ $1.10 / plate
  - 0.25mm thick ~ $2.75/ plate

- **Decrease Cr level/switch to Ni(Fe)- or Fe- base alloy to lower cost**
  - -Alloying additions to reduce level of Cr needed to form external nitride
  - -Modified nitridation conditions to promote external nitride formation

Preliminary Efforts Suggest Alloying Can Lower Cr Level Needed for Protective Nitride

Anodic Polarization curves for Alloys Nitrided at 1100°C, 2h in Pure N_2, Aerated pH3 Sulfuric Acid (0.1 mV/s)



- **Key issues are formation of external Cr-nitride and elimination of less corrosion-resistant mixed Ni/Fe-Cr nitride phases**

Future Plans

- **Further in-cell testing of nitrided Ni-50Cr**
  - **-Determine optimal Cr-nitride surface structure/composition**
  - **-Longer-term/more aggressive conditions and stack tests (tests also planned with DANA Corp and G.M.)**
  - **-Coupons/Plates Available for Testing- Please ASK!**

- **Demonstrate corrosion-resistant Cr-nitride formation on Ni(Fe)-or Fe-base alloy that can meet < $2/plate cost goals**
  - **-Key issue for next year**

- **Initiate transfer of technology to alloy producer(s)/fuel cell manufacturer(s) to examine scale-up issues**

Collaborations Significant Part of Effort

- **Corrosion Evaluation**
  - -Los Alamos National Lab (K. Weisbrod)
  - -U. Tennessee (R.A. Buchanan, I. Paulauskas)
  - -National Renewable Energy Lab (H. Wang)
  - -General Motors (R. Blunk, M. Abdelhamid)
- **In-Cell Testing**
  - -Los Alamos National Lab (M. Wilson, F. Garzon)
  - -General Motors (anode plate test planned for summer 03)
  - -DANA Corp (E. Steigerwalt): State Energy Demonstration Project for sealing/stack testing (also w/ Tennessee Tech and U. Minnesota)
- **Alloy Scale-Up Issues**
  - -Input/guidance received from several commercial alloy producers

Conclusions

- **Thermal nitridation is capable of protecting metal plates with complex surface geometries such as flow-field features**

- **Thermally grown CrN/Cr_2N shows excellent promise for PEMFC anode and cathode environments**
  - **-Low contact resistance maintained**
  - **-Low metal ion membrane contamination**

Carbon Foam for Fuel Cell Humidification

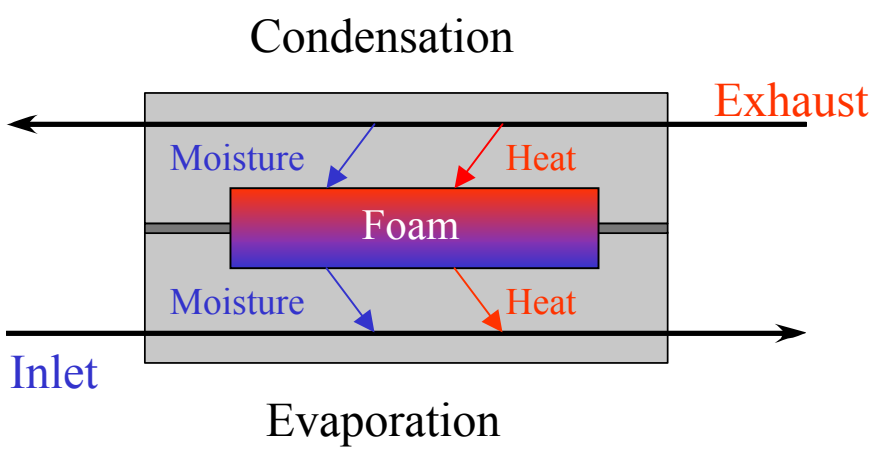
R. D. Ott, P. Kadolkar, J. W. Klett
Oak Ridge National Laboratory
Oak Ridge, TN

2003 Hydrogen and Fuel Cells Merit Review Meeting

Graphite Foam for PEM Fuel Cell Humidification

➢ Research Objective

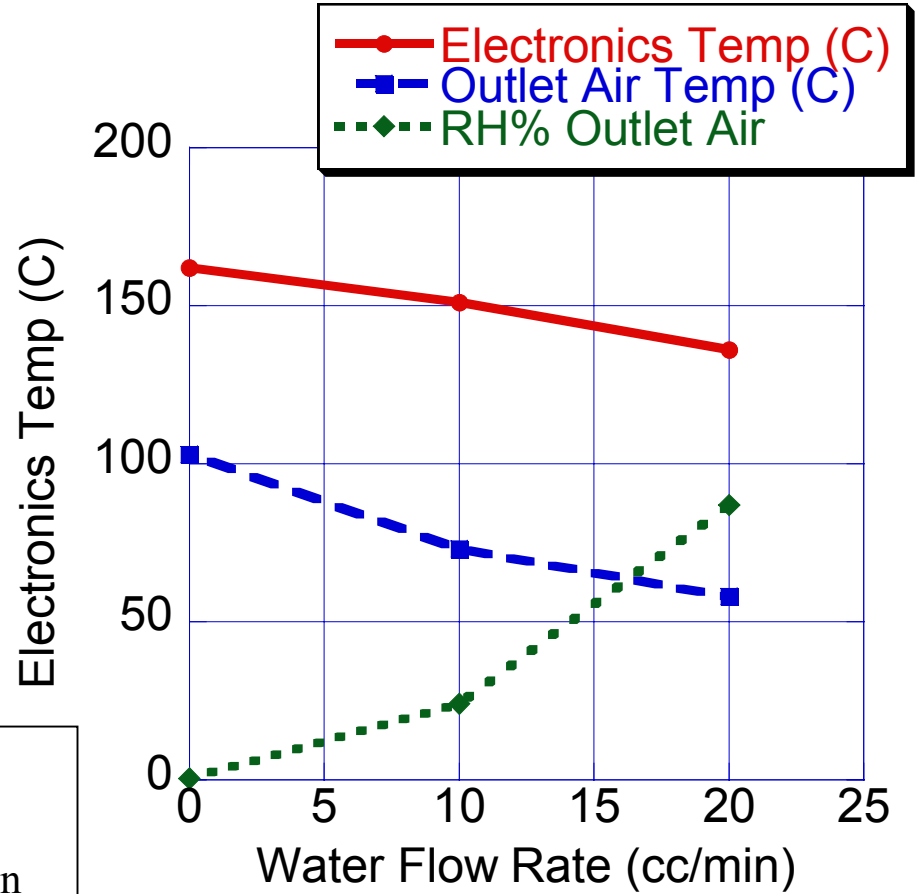
- Develop efficient designs for humidification systems for PEM fuel cells utilizing high thermal conductivity graphite foam
- Collaboration with Porvair Fuel Cell Technology
  - ➔ Expertise in heat exchange and recovery units
- Substitute graphite foam into a recovery unit illustrated below

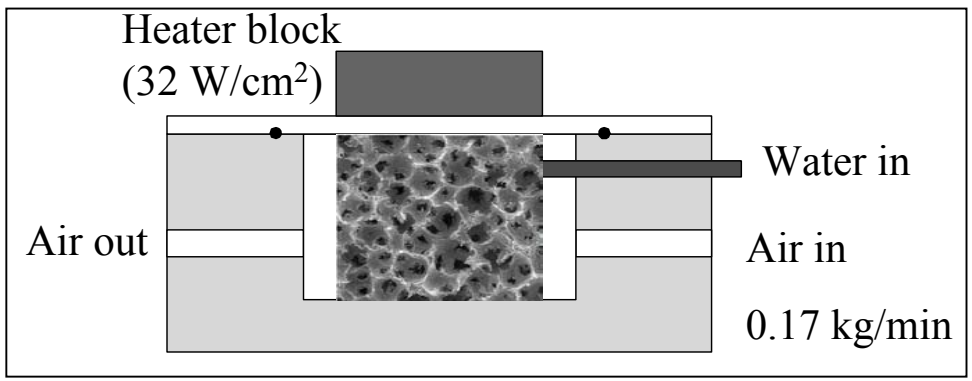


Schematic of heat/moisture recovery unit

Graphite Foam as a Humidifier

- Tests conducted to quantify the foam's ability to saturate air with water
  - With increased water flow rate into the foam
    - ➔ Decreased simulated electronics temperature (heater block)
    - ➔ Decreased outlet temperature
    - ➔ Increased RH of outlet air



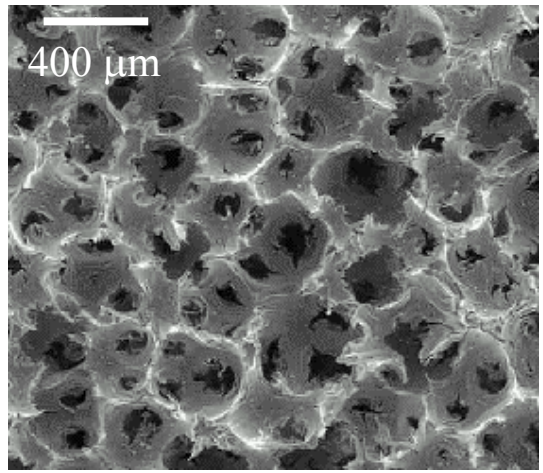


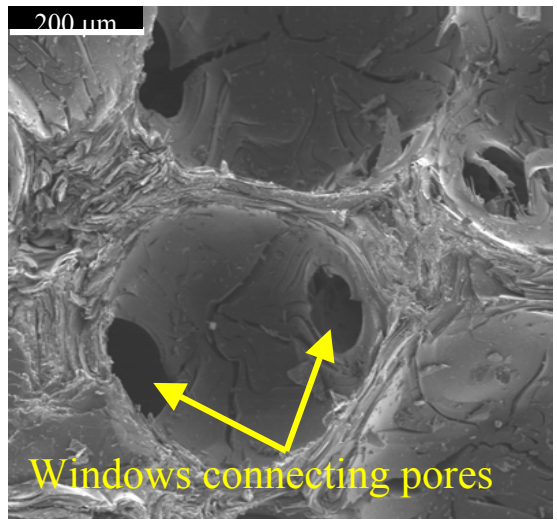
Current Status of Research

- Previous results show that the graphite foam has the ability to wick water by capillary action
- Goals for the graphite foam recovery unit
  - Maximize the recovery of the water from the outlet side of a fuel cell by condensation
  - Wick the water in order to evaporate it on the inlet side
  - Transfer adequate heat from exhaust side to inlet side
    - ➔ Ideal inlet conditions – saturated air at 80°C
- Current recovery units utilizing metal and ceramic foams
  - Not able to remove adequate heat from exhaust side to increase the temperature of inlet side – not able to deliver saturated air at 80°C
- Apply existing mathematical model to optimize humidification system with the graphite foam to obtain conditions that give:
  - Lowest pressure drop in system
  - Highest humidification of inlet air
  - Adequate heat flow to inlet air from exhaust

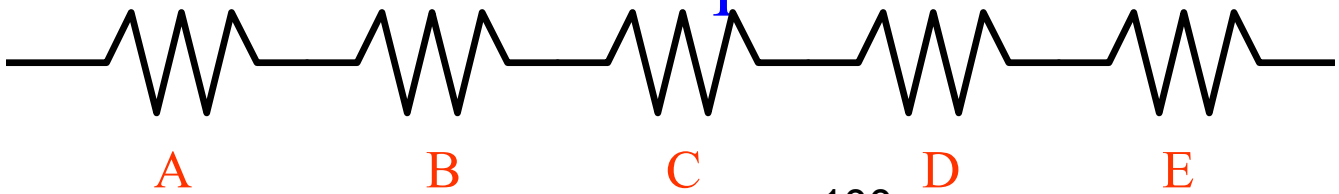
Near Term Research Tasks

- Evaluate the pore structure of the graphite foam
  - Optimize the pore structure to allow adequate capillary action to occur by condensation of water from the exhaust side in order to humidify the inlet air by evaporation
  - Determine what processing parameters control the size of the windows that connect the pores
    - The size of the windows will have a significant role in the capillary action of the graphite foam

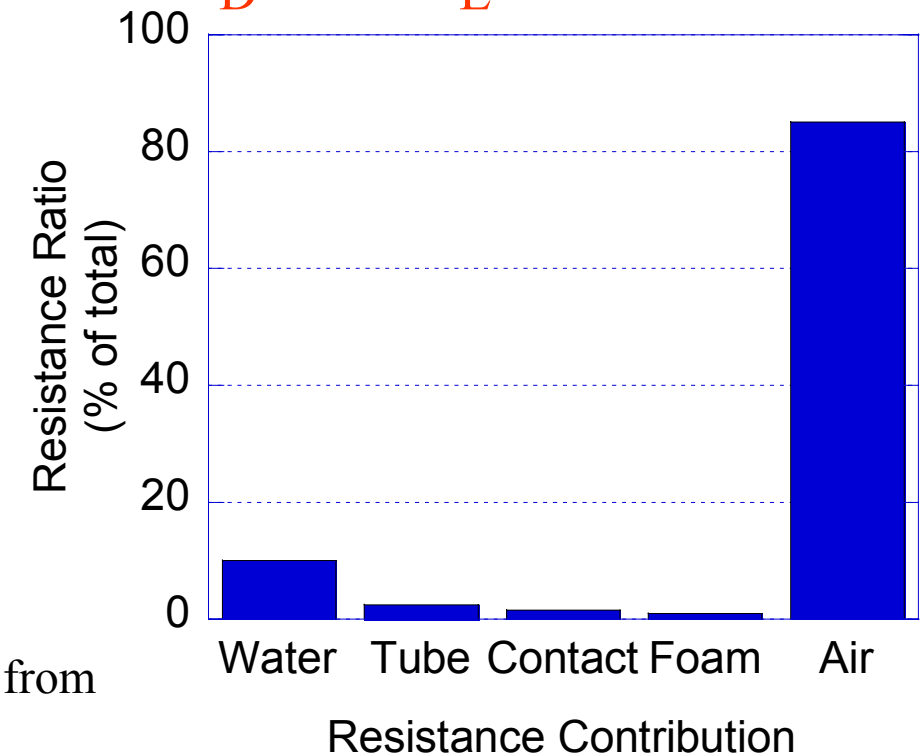




Resistance Model for Graphite Foam Radiator

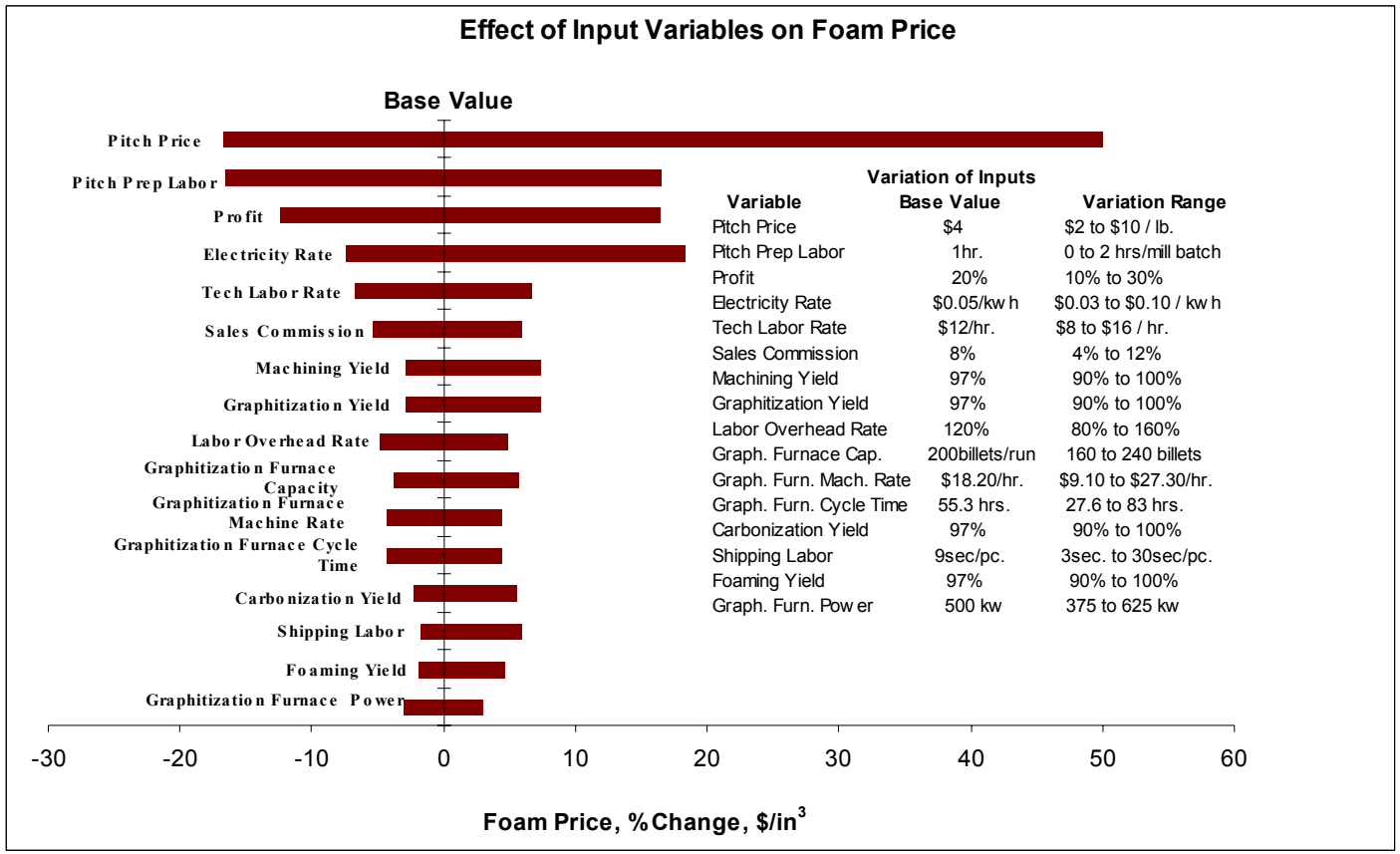


A	Convective resistance of water
B	Conductive resistance due to tube
C	Conductive resistance due to tube/foam contact
D	Conductive resistance due to foam
E	Convective resistance of air



- Highest resistance is on the air side
  - Function of how the heat is removed from the surface of the foam by air
- Shows that high thermal conductivity is not as crucial for radiator applications, possibly able to reduce cost by reducing furnace time, or a different type of pitch
- The foam's pores structure plays a significant role on being able to reduce the convective resistance of the air

Cost Model for Graphite Foam Production



Variation of Inputs

Variable	Base Value	Variation Range
Pitch Price	$4	$2 to $10 / lb.
Pitch Prep Labor	1hr.	0 to 2 hrs/mill batch
Profit	20%	10% to 30%
Electricity Rate	$0.05/kw h	$0.03 to $0.10 / kw h
Tech Labor Rate	$12/hr.	$8 to $16 / hr.
Sales Commission	8%	4% to 12%
Machining Yield	97%	90% to 100%
Graphitization Yield	97%	90% to 100%
Labor Overhead Rate	120%	80% to 160%
Graph. Furnace Cap.	200billets/run	160 to 240 billets
Graph. Furn. Mach. Rate	$18.20/hr.	$9.10 to $27.30/hr.
Graph. Furn. Cycle Time	55.3 hrs.	27.6 to 83 hrs.
Carbonization Yield	97%	90% to 100%
Shipping Labor	9sec/pc.	3sec. to 30sec/pc.
Foaming Yield	97%	90% to 100%
Graph. Furn. Pow er	500 kw	375 to 625 kw

- Cost model shows the ability to significantly reduce the manufacturing cost of the graphite foam by taking advantage of several factors such as:
  - Low cost pitch if appropriate for the given graphite foam application
  - Less furnace time if full graphitization is not needed for given application
- This shows that for a given application it may be possible to tailor the cost such that graphite foam has a similar cost as currently employed materials for that application

Research Tasks/Future Work

- Collaborate with Porvair Fuel Cell Technology in the following areas:
  - Modify current bench top test rig in order to correlate the pore/window size with the graphite foams ability to wick water by capillary action
  - Evaluate what effect altering the pore/window size has on the thermal properties of the graphite foam
  - Build a full scale recovery unit utilizing the graphite foam
- Need to recover as much water from the exhaust in order to minimize carrying water onboard vehicle
- Need to capture as much heat as possible from exhaust to adequately heat the inlet air to 80°C

Millstones

- 2003
  - Identify a pore size of graphite foam that will effectively wick water (by capillary action) and transfer heat through the foam for use in a humidification system that will deliver saturated air at 80°C
    - ➔ Currently on track
- 2004
  - Collaborate with a component manufacturer to build and test a full scale humidification system that utilizes graphite foam to condense moisture from the exhaust and reduce or minimize water additions.
    - ➔ Contacts have been made and discussions have been started on how best to attack this issue
- 2005
  - Work alongside a fuel cell manufacturer to field test a graphite foam recovery unit on a PEM fuel cell

Advanced Underground Vehicle Power and Control Fuelcell Mine Locomotive

U.S. Department of Energy

Office of Energy Efficiency and Renewable Energy

Golden Field Office

Hydrogen, Fuel Cells and Infrastructure Technologies Program

Cooperative Agreement: DE-FC36-GO9910458

15 September 1999 through 31 October 2002

Vehicle Projects LLC

Arnold R. Miller, PhD
President

David L. Barnes
General Manager

621 17th Street, Suite 2131
Denver, CO 80293

FOUR-TON MINE LOCOMOTIVE

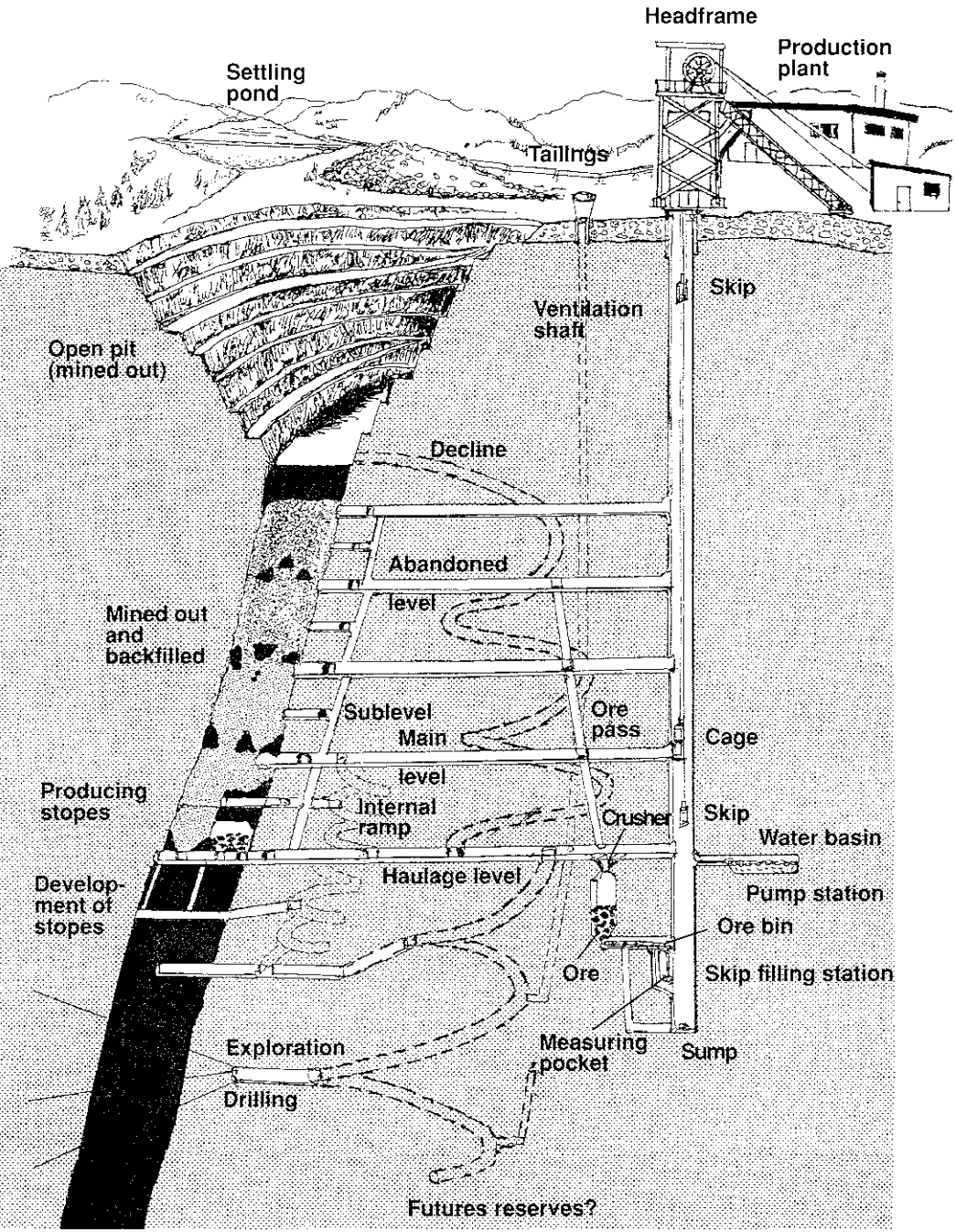
Reno, Nevada – November 2002

LOCOMOTIVE PROJECT PARTNERS

***CANMET* – Underground testing**
***Fuelcell Propulsion Institute* – Industry oversight and education**
***Hatch Associates Ltd* – Safety analyses**
***Kappes, Cassiday & Associates* – Surface test site**
***Mine Safety and Health Administration* – Risk evaluation of vehicle**
***Nuvera Fuel Cells* – Fuelcell stacks**
***Placer Dome Technical Services Ltd* – Underground production test site**
***RA Warren Equipment Ltd* – Base vehicle**
***Sandia National Laboratories/CA* – Powerplant development**
***Stuart Energy Systems Inc* – Vehicle refueling**
***University of Nevada at Reno* – Surface testing in Nevada**
***Vehicle Projects LLC* – Prime contractor and project management**

MINE-LOCOMOTIVE PROJECT OBJECTIVES

- **Develop a zero-emissions, fuelcell-powered metal-mining locomotive.**
- **Evaluate its safety and performance, primarily in surface tests.**
- **Evaluate its productivity in an underground mine (Placer Dome) in Canada.**



A PROBLEM AND OPPORTUNITY
Underground Traction Power

- **No existing technology is clean, safe, and productive**
  - **— Tethered**
  - **— Diesel**
  - **— Battery**
- **Solution by fuelcells will provide cost offsets**
  - **— Lower recurring costs**
  - **— Higher availability**
  - **— Lower ventilation costs**

LOCOMOTIVE PROJECT APPROACH

- Establish cross-functional project team including end-users
- Use commercially available battery-powered 4-ton locomotive
- Remove traction battery module and use existing electric drive
- Design fuelcell powerplant and metal-hydride storage to fit into existing battery compartment
- Design metal-hydride storage module for easy removal from locomotive for refueling on surface
- Design fuelcell powerplant module for easy removal from locomotive for transport to/from underground
- Allow for onboard refueling as an option
- Automate powerplant controls to allow for hands-free operation of locomotive
- Perform extensive safety and risk analysis to allow underground operation

VEHICLE PROJECTS LLC

LOCOMOTIVE SPECIFICATIONS

- 17.5 kW continuous gross power (no traction battery)
- 3 kg of hydrogen stored as metal hydride, 1.4 weight %
- 8 hours of operation without refueling
- Refueling in approximately 1 hour

Comparison of Battery and Fuelcell 4-Ton Locomotives

Parameter	Battery	Fuelcell
Power, rated continuous	7.1 kW (gross)	17.5 kW (gross)
Current, rated continuous	76 A	135 A
Voltage at continuous rating	94 V (estimated)	129.6 V
Energy capacity, electrical	43 kWh	53 kWh
Operating time	6 h (available)	8 h
Recharge time	8 h (min)	1 h (max)
Vehicle weight	3,600 kg	2,500 kg (without ballast)

Note: The fuelcell locomotive used a commercial battery locomotive chassis and electric drive. Battery-vehicle parameters are those of the commercial product.

Fuelcell energy capacity (available energy to the traction motor) is calculated as follows:

2 g (1 mole) hydrogen = 286.6 KJ
1 KJ = 0.000278 kWh
3 kg = 3,000 g x 143.3 KJ/g x 0.000278 kWh/KJ = 119.5 kWh
fuelcell stack efficiency = 50%
parasitic loss = 1 kW = 6% loss
energy capacity = 119.5 kWh x 44% = 53 kWh

PEM FUELCELL SPECIFICATIONS

NUVERA FUEL CELLS EUROPE Per Stack	
Rated continuous power	8.75 kW continuous
Voltage at rated power	64.8 V
Current at rated power	135 A
Open circuit voltage	92 V
Number of cells	92
Reluctant gas	99.995% pure hydrogen
Hydrogen pressure	1.7 bar absolute
Oxidant gas	Air
Air pressure	1.5 bar absolute
Air stoichiometric ratio	1.98
Humidifier	Stack integral
Maximum operating temperature	80° C
Weight	30 kg
Dimensions	25 x 18 x 55 cm
Volume	25 L

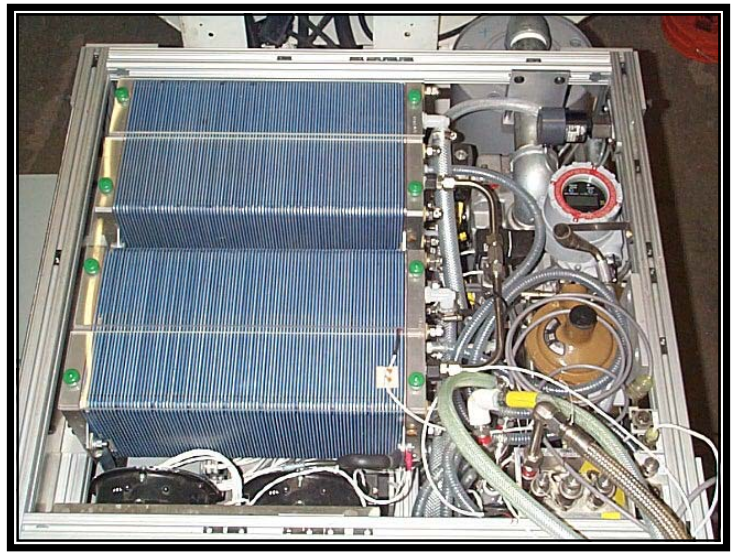
MAJOR BENEFITS

- **Health benefits of an electric vehicle coupled with the productivity of a diesel**
- **Reduced vehicle recurring costs**
- **Lower mine ventilation costs**

FUELCELL POWERPLANT MODULES

HYDRIDE ENERGY STORAGE

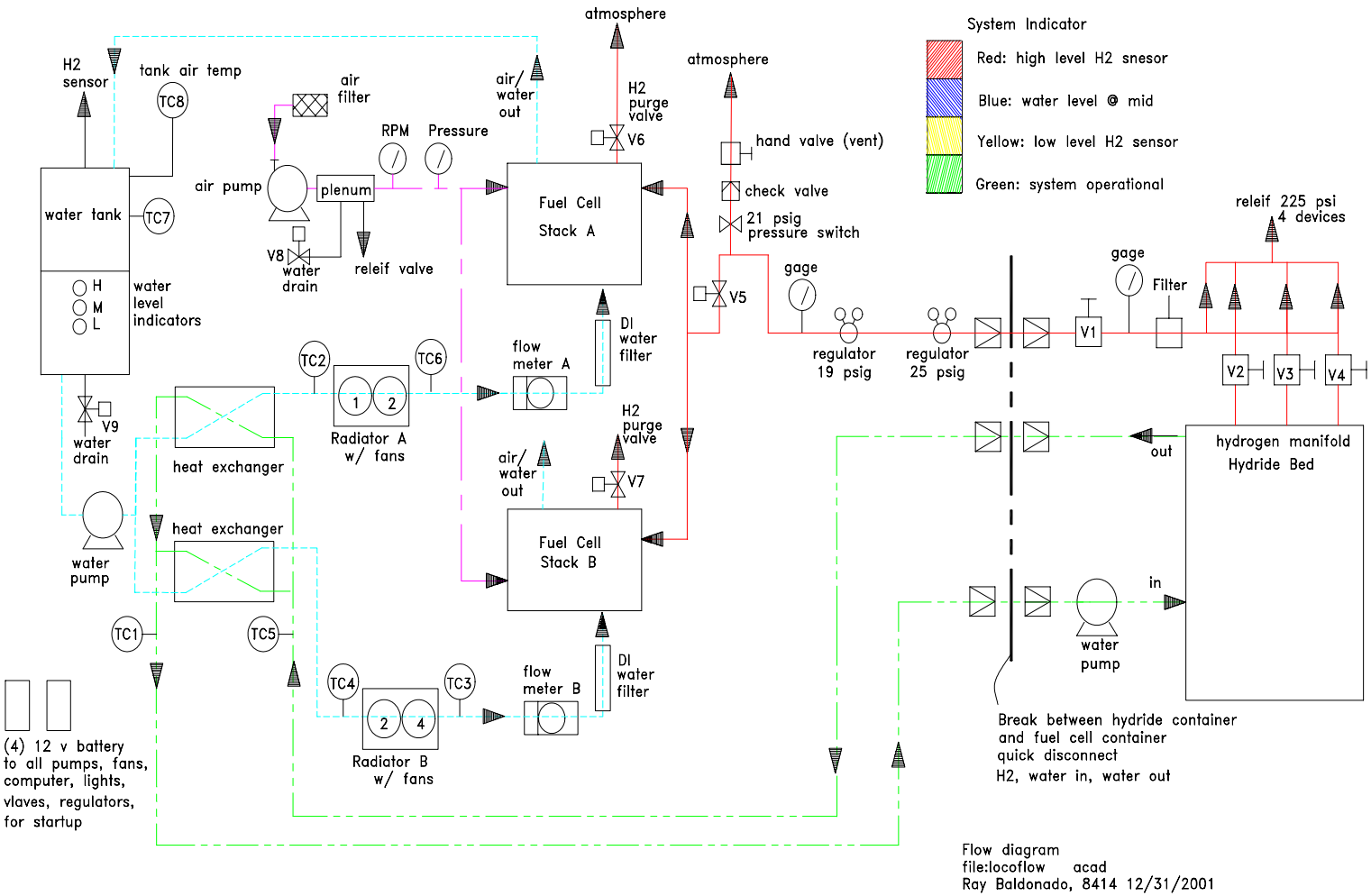
Vertical cylinders safely store enough reversible metal-hydride material to run the locomotive for 8 hours



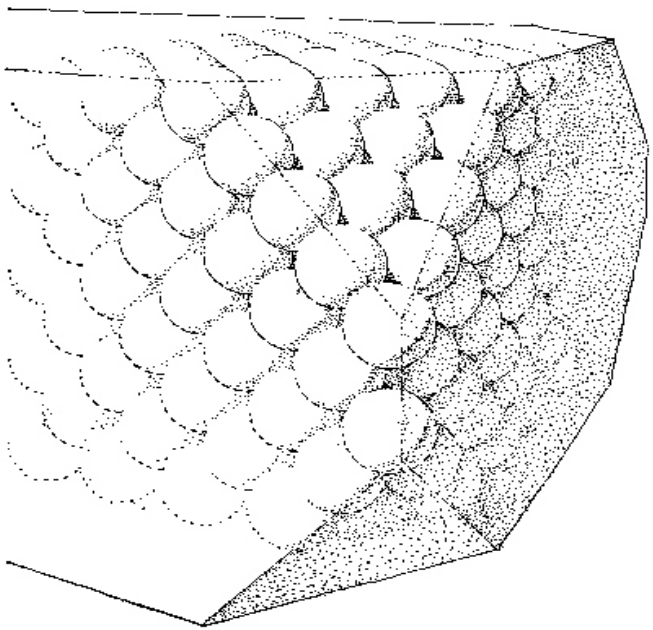
FUELCELL POWER SYSTEM

PEM fuelcell stacks (blue) provide 17.5 kW of continuous gross electrical power, over twice that of the battery vehicle

SCHEMATIC DIAGRAM



Metal-Hydride Storage of Hydrogen



Crystal Lattice

Metals, crystalline solids, consist of a regular array or *lattice* of spherical atoms. Spheres cannot pack perfectly, and the lattice of atoms also forms a superimposed lattice of holes or *interstices* (see illustration). The interstices interconnect to form a 3-D network of channels.

In a metal hydride, hydrogen chemically bonds to the metal atoms while occupying the interstices. Ferrous metals form hydrides that are readily reversible and constitute a safe, solid storage medium for hydrogen. By removing low-temperature heat from the crystal, hydrogen atoms enter the interstices throughout the crystal and *charge* the metal. Conversely, by providing low-temperature heat to a charged crystal, the process is reversed and the metal is *discharged*. The gas pressure is approximately constant during the process and can be very low, even below atmospheric.

Unlike liquid or gaseous fuels, metal hydrides are of low flammability. This is because hydrogen is trapped in the metal matrix and the rate at which hydrogen atoms can file through the channels, recombine into hydrogen molecules, and be released is limited by the rate of heat transfer into the crystal. Rupture of a hydride system is self-limiting: As hydrogen escapes, the bed automatically cools and lowers the rate of escape. The metal matrix, moreover, forces the hydrogen atoms close together, as close as in liquid hydrogen, and is responsible for the high volumetric energy density.

OPERATION

- Mine safety and productivity have been established
- Equal acceleration to battery version
- More than twice the power
- Ability to pull longer trains
- Shorter recharge time
- Longer operational time

PROJECT TIMELINE

Fiscal Year: Oct. – Sept.	FY 2000				FY2001				FY 2002			
Quarter:	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
Powerplant Fabrication			October 1999 – January 2002									
Fuelcell Fabrication		Initial Stacks: July 2000 – Dec. 2000						New Stacks: Mar. 2002 – June 2002				
Vehicle Integration						January 2001 – January 2002						
Risk Assessment				Initial: Jan. 2001 – July 2001					Final: Jan. 2002 – July 2002			
Engineering Refinements									March 2002 – July 2002			
Acceptance Tests									February 2002 – Sept. 2002			
Regulatory Approval									April 2002 – September 2002			
Underground Field Tests									Sept. 2002 – Oct. 2002			

Underground Field Tests
Placer Dome Gold Mine, Balmertown, Ontario

- Two week test period
- Locomotive put on production level 27 – 4,000 feet down
- 760 tons of ore and rock moved
- 30 hours actual operating time
- 67,000 litres (~6 kg) of hydrogen consumed
- No failures or downtime encountered
- Metal-hydride bed transported to surface for refueling
- Capable of longer operational shift than battery version

COST ANALYSIS

- 17.5 kW powerplant
- 3 kg hydrogen, 213 kg metal hydride
- Powerplant components cost – US $45,000
- Hydrogen storage cost – US $35,000
- Fuelcell stacks cost – US $90,000 (US $5,300 per kW)
- Total powerplant cost per kW (with labor) – US $13,000

- To get the cost of PEM fuelcells below US $1,000 per kW, a cost reduction of 30% per year for 5 years would result in US $900 per kW
- With other cost reductions of 10% per year, total powerplant cost could approach US $5,400 per kW in 5 years

COMMERCIALIZATION

Presently in discussions with a mine company to develop a 10-ton, 35 kW locomotive

Second mine company also interested in 10-ton locomotive

20-ton locomotives would be the next step up

VEHICLE PROJECTS LLC

Sulfur removal from reformate

Xiaoping Wang, Theodore Krause,
and Romesh Kumar

Chemical Engineering Division
Argonne National Laboratory

Hydrogen, Fuel Cells, and
Infrastructure Technologies
2003 Merit Review
Berkeley, CA
May 19-22, 2003

Introduction

- Hydrogen can be produced by reforming fuels such as gasoline, natural gas, and diesel.

- These fuels contain sulfur compounds that can poison catalysts in the fuel processor and fuel cells.
  - natural gas — 20 ppm S by volume
  - gasoline/diesel (future) — 30 ppm S by weight

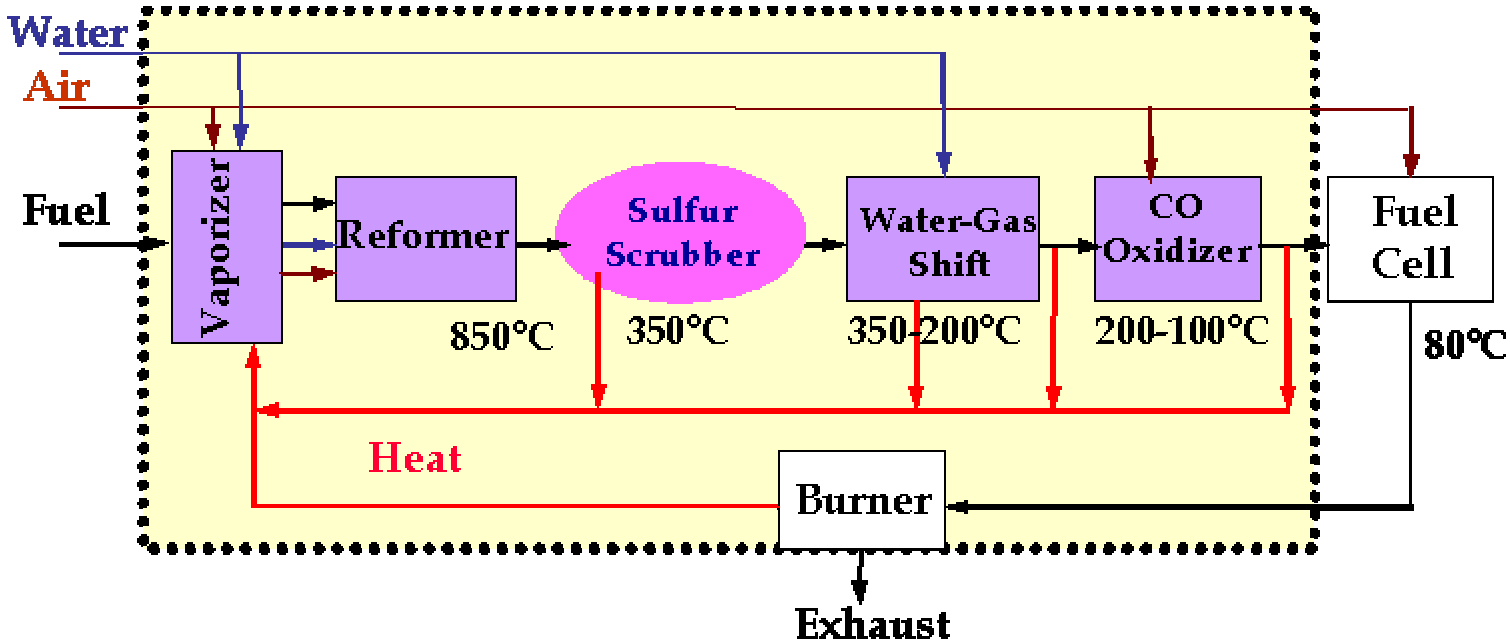
- Corresponding H_2S content of reformate (by volume)
  - natural gas — 10-14 ppm
  - gasoline/diesel — 3-5 ppm

Objective: develop a sulfur removal process for use in on-board fuel processor

- H_2S concentration in reformate (dry basis)
  - < 50 ppb (2005)
  - < 10 ppb (2010)
- Reactor size and cost
  - <0.06 L/kWe (<0.06 kg/kWe)
  - $\geq$ 50,000 h^{-1} gas hourly space velocity
  - $\leq$ \$1/kWe

This work addresses technical barriers J and L.

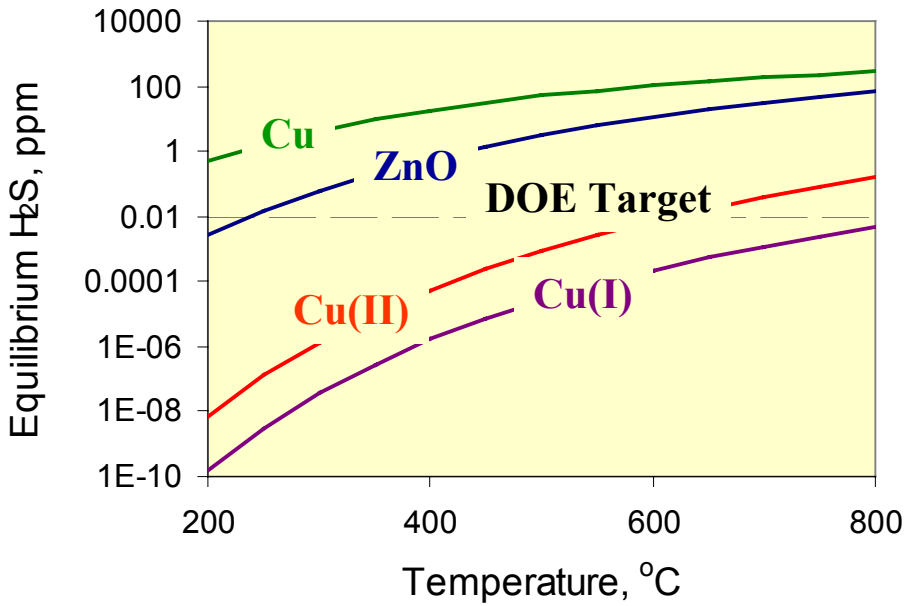
Our strategy is to remove H_2S from reformate within the fuel processor



- Requires that the reforming catalyst be sulfur-tolerant.
- The catalyst that is least tolerant defines the concentration to which H_2S must be reduced.

Copper oxide is our choice for H_2S removal

- Benefits
  - among the lowest H_2S equilibrium concentration of metal oxides
  - lower vapor pressure than ZnO allows for higher operating temperatures
  - low cost
- Challenges
  - Cu oxides reduce to metallic Cu under fuel processing conditions
  - metallic Cu has less favorable H_2S equilibrium than ZnO



Approach

- Synthesize mixed metal oxides to stabilize Cu in the oxide form
  - non-Cu transition metal oxide is resistant to reduction to metallic form under fuel processing conditions
  - mixed metal oxide is dispersed on a high surface area support, such as γ-Al_2O_3
- Determine the extent of desulfurization of a H_2S-containing simulated reformate as a function of operating parameters including
  - mixed metal oxide composition
  - temperature
  - gas-hourly space velocity
  - reformate composition

Reviewers' comments from FY02 Annual Review

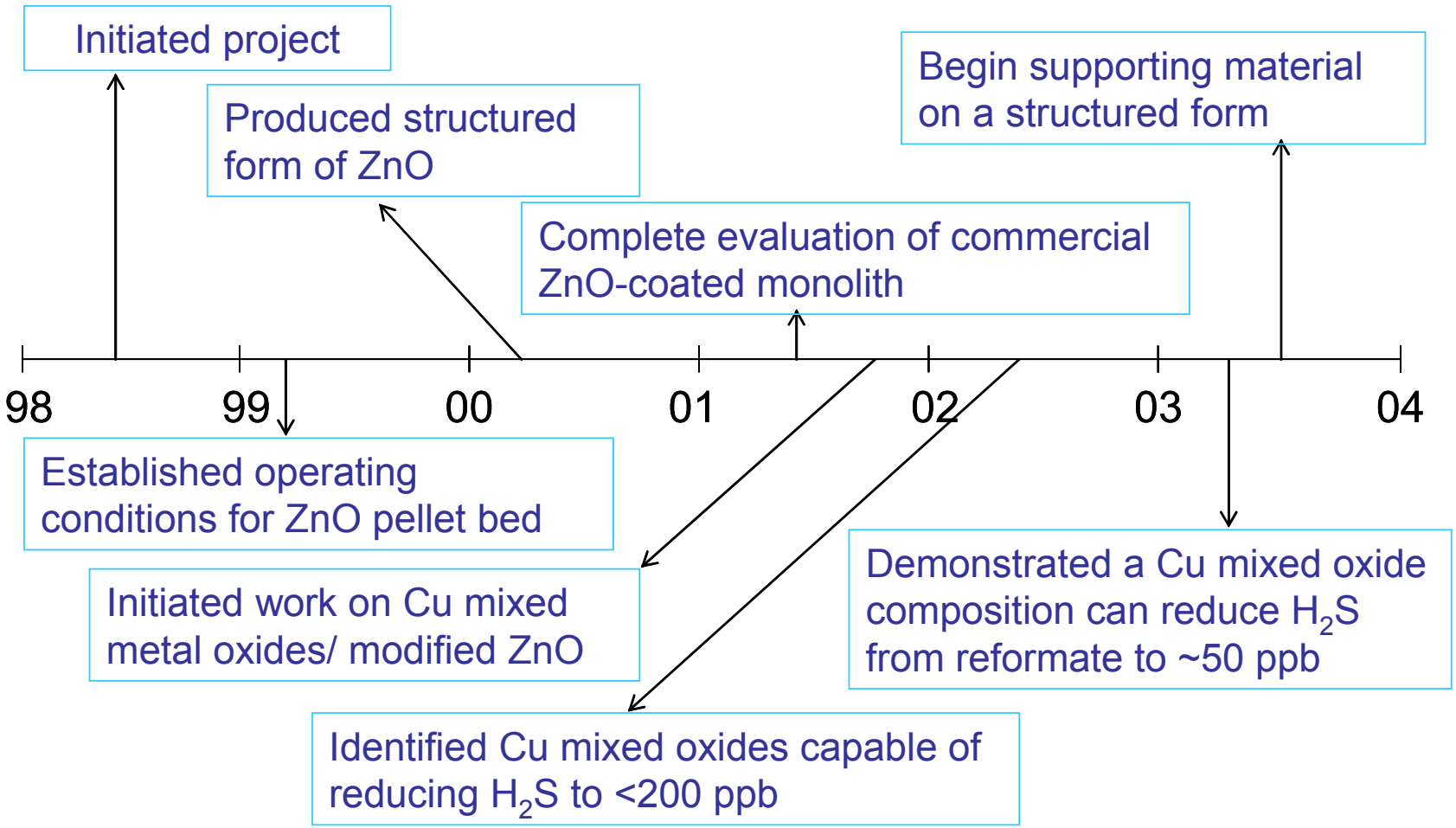
- Scope of work is too limited; expand to include liquid-phase desulfurization

  We believe that on-board liquid-phase desulfurization processes will not meet the DOE targets for size and weight for sulfur removal unit. Residual sulfur may be present in fuels that have been desulfurized off-board and will have to be removed on-board.

- Need for more surface characterization to better understand competitive adsorption

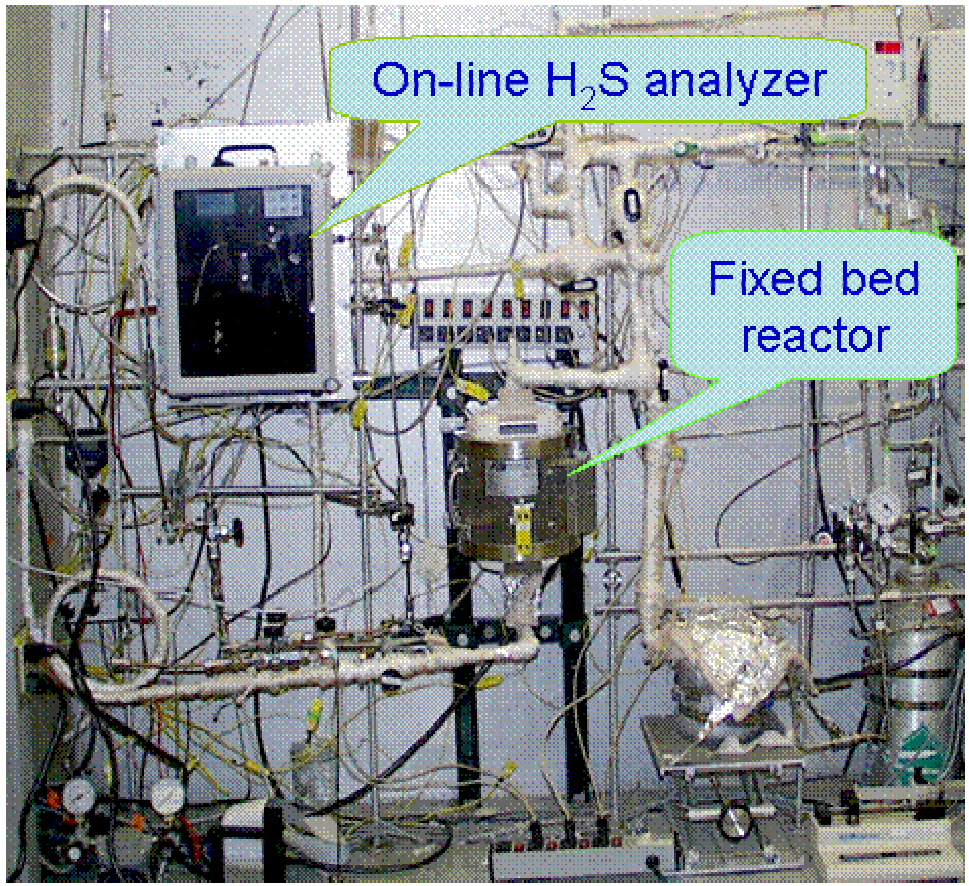
  Our main focus has been to identify a Cu-containing mixed oxide that can reduce the H_2S concentration in reformate to <100 ppb under fuel processing conditions. We plan to do characterization studies (SEM/TEM and EXAFS/XANES) to further improve the performance of this material.

Project timeline

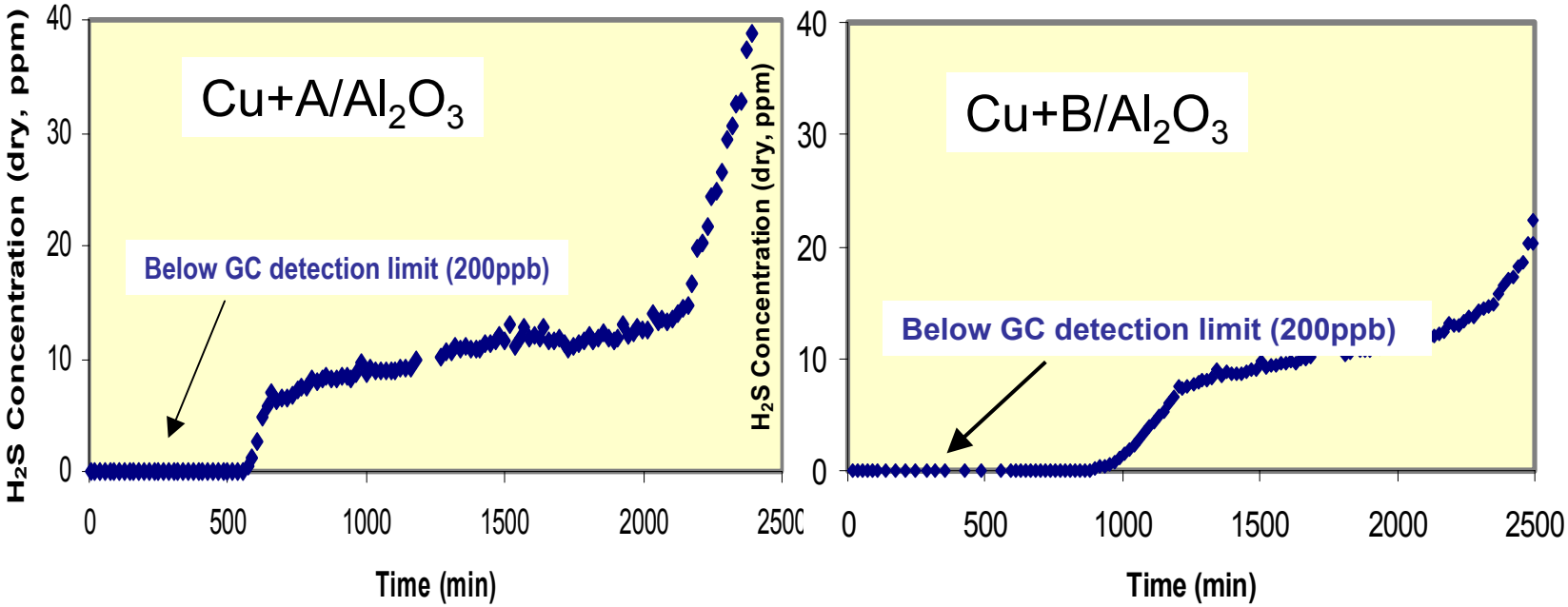


Microreactor system for evaluating the H_2S removal performance of candidate sorbents

- Fixed bed microreactor
- All fittings, tubing, and valves treated with Sulfinert® to minimize H_2S uptake by system hardware
- Flame photometric detector (FPD) for H_2S and COS (detection limit is 200 ppb)
- On-line H_2S analyzer for H_2S (detection limit is 20 ppb)



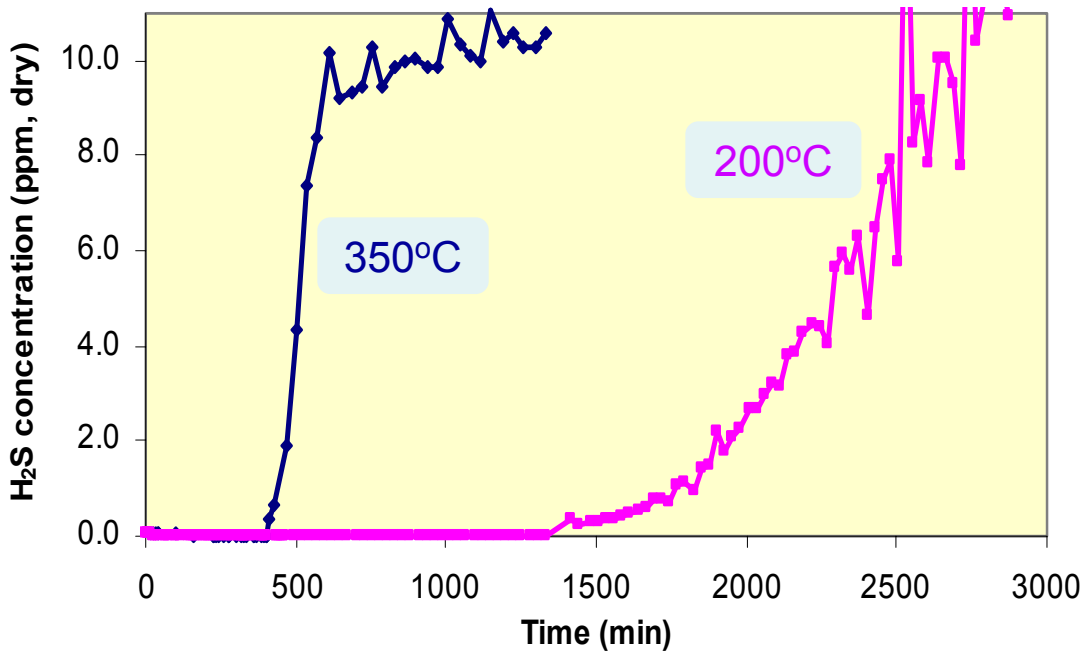
Cu+A and Cu+B were able to reduce the H_2S concentration to less than 200 ppb



Test conditions: T = 350°C, GHSV = 2000 h^{-1}, sorbent volume is 2 ml.

Inlet gas composition: 40 ppm H_2S, 19% H_2, 20% H_2O, 4% CO, 4.1% CO_2, 0.4% CH_4, balance N_2

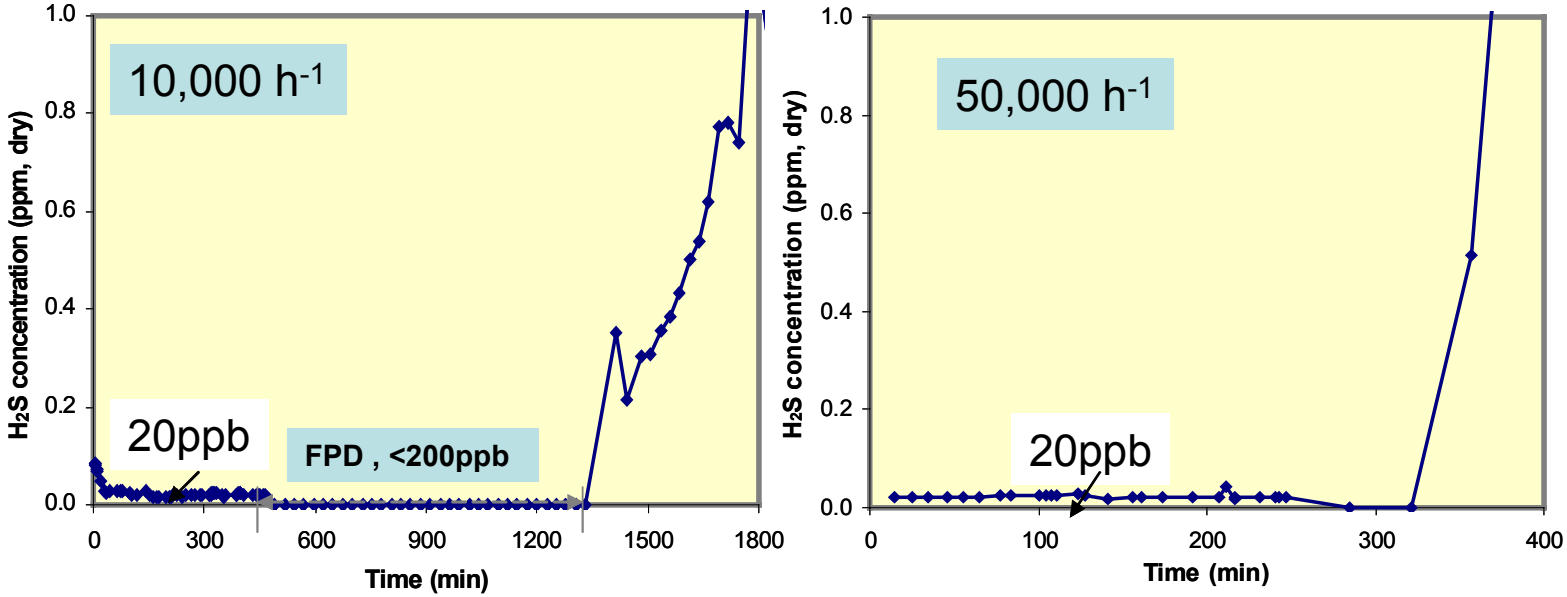
Longer breakthrough time observed at lower temperature for Cu+C/Al_2O_3



Test conditions: GHSV = 10,000 h^{-1}, sorbent volume is 1 ml, diluted to 2 ml with Al_2O_3.

Inlet gas composition: 10 ppm H_2S, 29% H_2, 20% H_2O, 6% CO, 6.1% CO_2, 0.2% CH_4, balance N_2

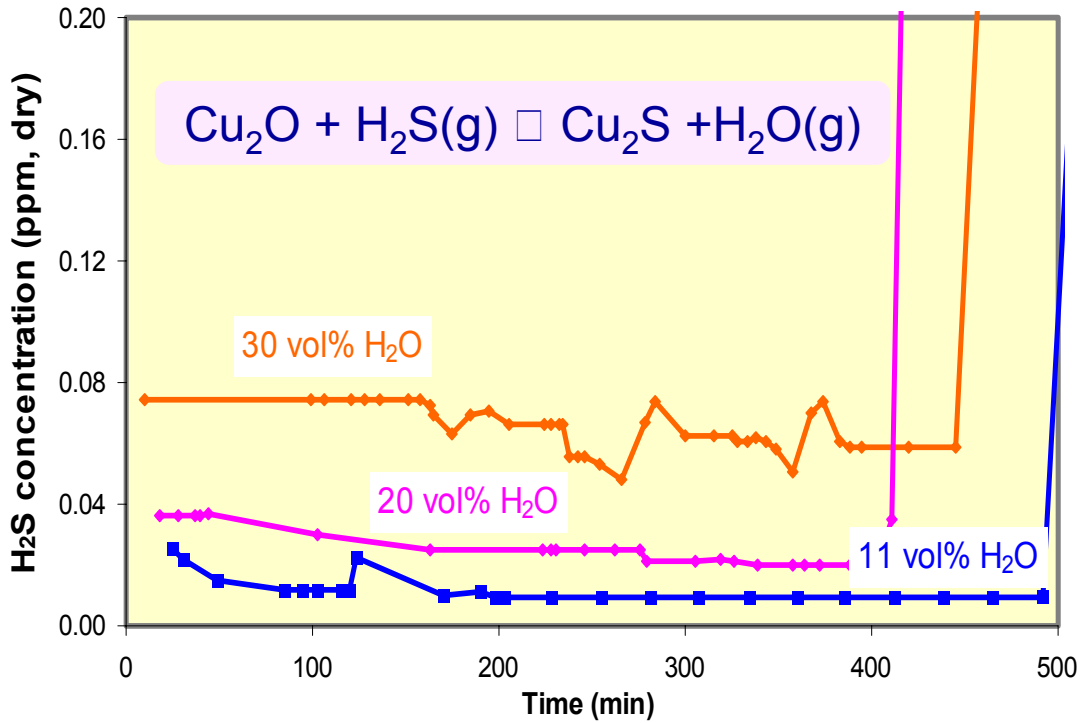
Shorter breakthrough time with increasing flowrate for Cu+C/Al_2O_3



Test conditions: T = 200°C, sorbent volume varied, diluted to 2 mL with Al_2O_3.

Inlet gas composition: 10 ppm H_2S, 29% H_2, 20% H_2O, 6% CO, 6.1% CO_2, 0.2% CH_4, balance N_2

Higher water content yields higher H_2S concentrations for $Cu+C/Al_2O_3$



Test conditions: T = 350°C, GHSV = 10,000 h^{-1}, sorbent volume is 1 ml, diluted to 2 ml with Al_2O_3

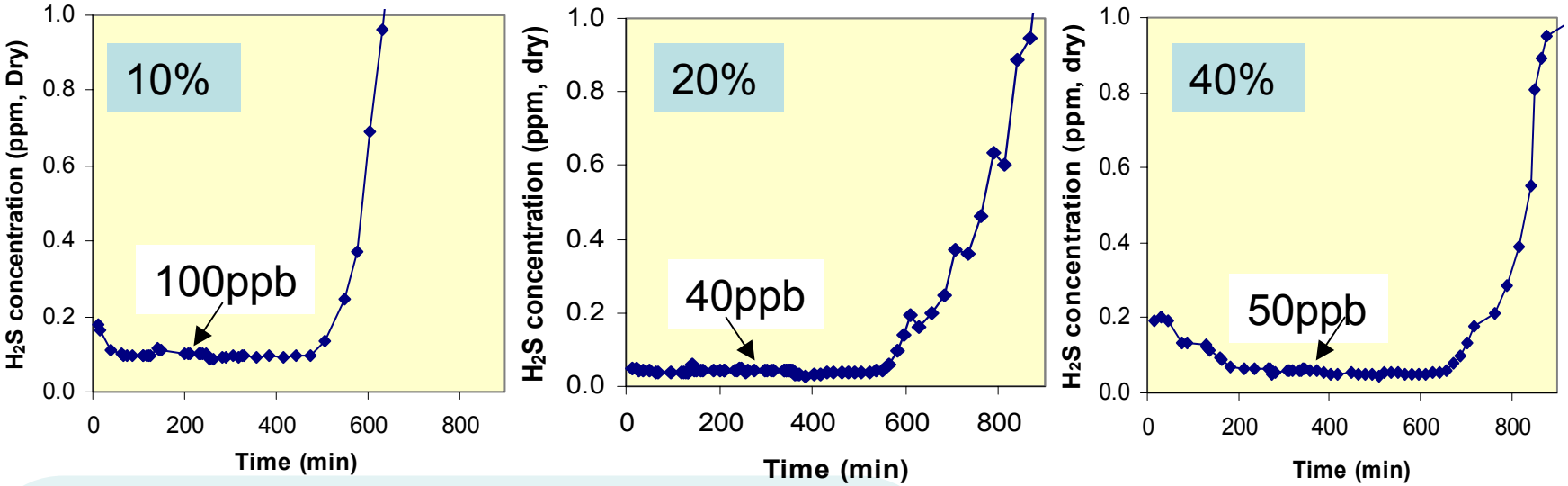
Inlet gas composition: 10 ppm H_2S, 29% H_2, varied H_2O, 6% CO, 6.1% CO_2, 0.2% CH_4, balance N_2

Copper utilization ranged from 32.8 to 57.9% for Cu oxides tested

Sorbent formulation	Surface area (m^2/g)	Sulfur uptake (%, based on Cu content)[a]
$Cu+A/Al_2O_3$	197.9	37.3
$Cu+B/Al_2O_3$	199.5	57.9
$Cu+C/Al_2O_3$	211.3	53.9
$Cu+D/Al_2O_3$	201.5	44.0
$Cu+E/Al_2O_3$	202.3	32.8
Cu/Al_2O_3	258.8	36.3

[a] Calculated based on H_2S uptake until breakthrough occurs (1 ppm H_2S).
Test conditions: T = 350°C, GHSV = 2000 h^{-1}, sorbent volume is 2 ml.
Inlet gas composition: 40 ppm H_2S, 19% H_2, 20% H_2O, 4% CO, 4.1% CO_2, 0.4% CH_4, balance N_2

Varied loading of Cu+C on Al_2O_3 affected both H_2S removal efficiency and capacity

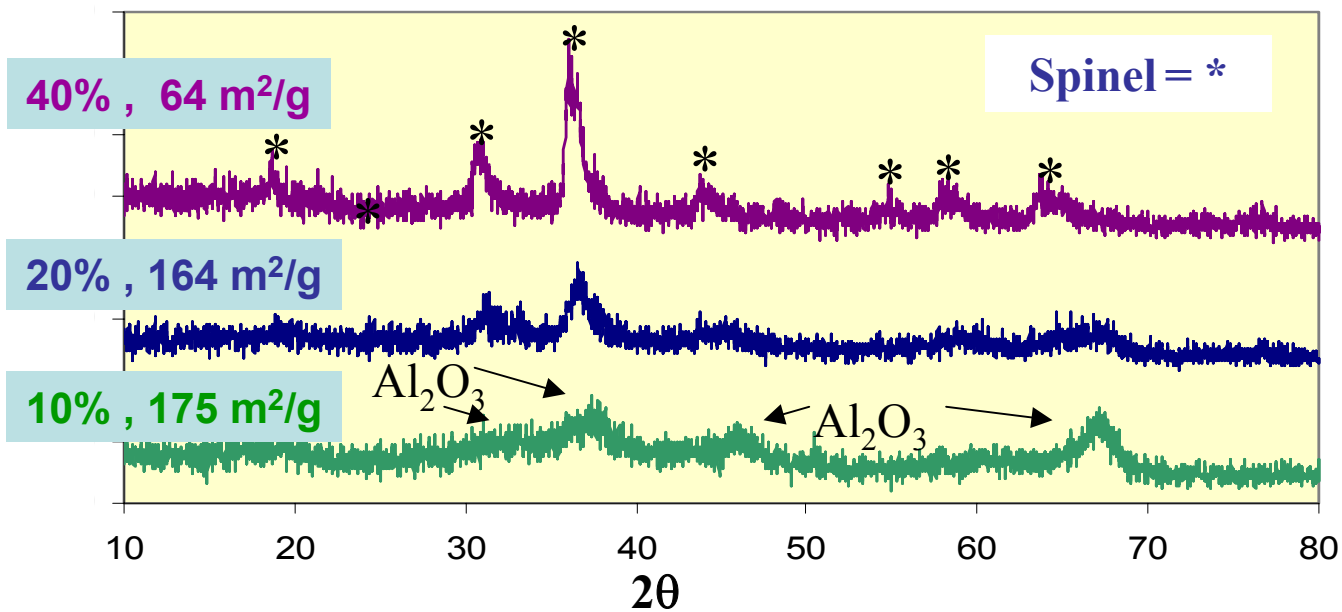


- Breakthrough time increased as the Cu loading was increased.
- The breakthrough time increased by ~200 minutes when the loading was increased from 10 to 20%.
- Only a slight increase in breakthrough time was observed when the loading was increased from 20 to 40%.
- An optimal loading (20%) gives best efficiency

Test conditions: T = 350°C, GHSV = 15,600 h^{-1}, sorbent volume is 1 ml, diluted to 2 ml with Al_2O_3

Inlet gas composition: 11 ppm H_2S, 31% H_2, 20% H_2O, 7% CO, 8% CO_2, 0.1% CH_4, balance N_2

XRD shows loss of surface at high Cu+C loading on Al_2O_3



- Surface area decreases as the loading is increased. The surface area decreased by ~60% when the loading was increased from 20 to 40%.
- Spinel formation at higher loadings may make the material less active which leads to a higher H_2S concentration.

Summary

- A Cu-based mixed oxide has been identified that can reduce the concentration of H_2S in a synthetic reformate from 10 ppm to <50 ppb at 200-350^oC.

- Initial rate studies show that <20 ppb H_2S can be achieved at a GHSV of 50,000 h^{-1} at 200^oC.

- Based on sulfur uptake and Cu loading, more than 50% of the Cu was utilized.

Technical Challenges/Issues

- Processing rates (GHSV) are still low.
  - 10,000-50,000 h^{-1} for powders
  - DOE target is 50,000 h^{-1} for supported material
- Long-term stability of Cu-based adsorbents under fuel processing conditions has not been determined.
  - Cu sintering at high temperatures may be problemetic
  - effect of air exposure needs to be explored
  - stability of the Cu-sulfur complexes during startup needs to be addressed

FY 2003 milestone

Milestone	Date
Demonstrate a sulfur "getter“ capable of reducing the H_2S concentration in a synthetic reformate to <50 ppb. (DOE FY2005 target for on-board reforming).	06/03

Showed that a Cu oxide-based composition reduced H_2S concentration from 10 ppm in reformate to <50 ppb.

Future work

- Optimize the composition and materials processing to achieve DOE targets for extent of sulfur removal, GHSV, and durability.
- Determine the stability of Cu-containing mixed oxides/sulfides during startup and air exposure at reaction temperatures.
- Determine the optimal structured form (monolith or foam).
- Long-term testing operating on reformate produced from a sulfur-containing fuel.
- Conduct characterization studies to improve the performance and address stability issues.
- Establish industrial collaboration. Several companies have requested samples for testing.

Assessment of Fuel Cells as Auxiliary Power Systems for Transportation Vehicles

DE-FC04-01ALL67604

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley, CA

May 19-22

TIAX LLC
Acorn Park
Cambridge, Massachusetts
02140-2390

Reference: D0036.00

As auxiliary power units (APUs), fuel cells may find opportunity for automotive-volume markets by offering some key potential advantages.

- Fuel Cell Technology could be ideal for APU on trucks and other vehicles due to the following advantages:
  - minimal emissions
  - quiet operation
  - minimal vibration
  - high efficiency
  - compact design
- Several designs / demonstration units have been built:
  - BMW/International Fuel Cells 5-kW hydrogen-PEM demo for 7-series passenger car
  - DaimlerChrysler/Ballard 1.4-kW hydrogen-PEM demo for Freightliner Class 8 heavy-duty truck cab
  - BMW/Delphi/Global Thermoelectric 1 to 5-kW gasoline SOFC technology development program

APU applications can provide entry markets for fuel cell technology at cost levels significantly higher than that of propulsion applications.

The overall objective is to determine the viability of PEM & solid oxide fuel cells in the application of APUs for on-road vehicles.

- The USDOE Vehicle Technologies Program of the Office of Energy Efficiency and Renewable Energy objectives are:
  - Assess viability as defined in terms of achieving performance & cost targets:
    - Fuel flexibility
    - Start-up time
    - Power level
    - Duty cycle
    - Overall vehicle efficiency
    - Weight and volume
    - First and O&M cost
    - Reliability, Maintainability
  - Determine R&D needs and possible USDOE roles based on projected benefits to the Nation:
    - Barrels of oil displaced
    - Criteria pollutants avoided
    - Safety & Noise
  - Compare performance of fuel cell APUs with alternative approaches (both performance & cost)
  - Estimate benefits to the Nation and also for acceleration of fuel cell market introduction
  - Determine development & commercialization timeline and R&D gaps

DOE is particularly interested in how fuel cell APUs can help facilitate the introduction of fuel cells for propulsion or hybrid electrics.

We are developing detailed conceptual designs for 3 fuel cell/APU systems for on-road transportation applications.

1. **Kick-off**
2. **Identify & Select APU Systems**
3. **Develop Design Concepts**
4. **R&D Gap Analysis**
5. **Analysis Update**

- Summarize PEM and SOFC performance parameters

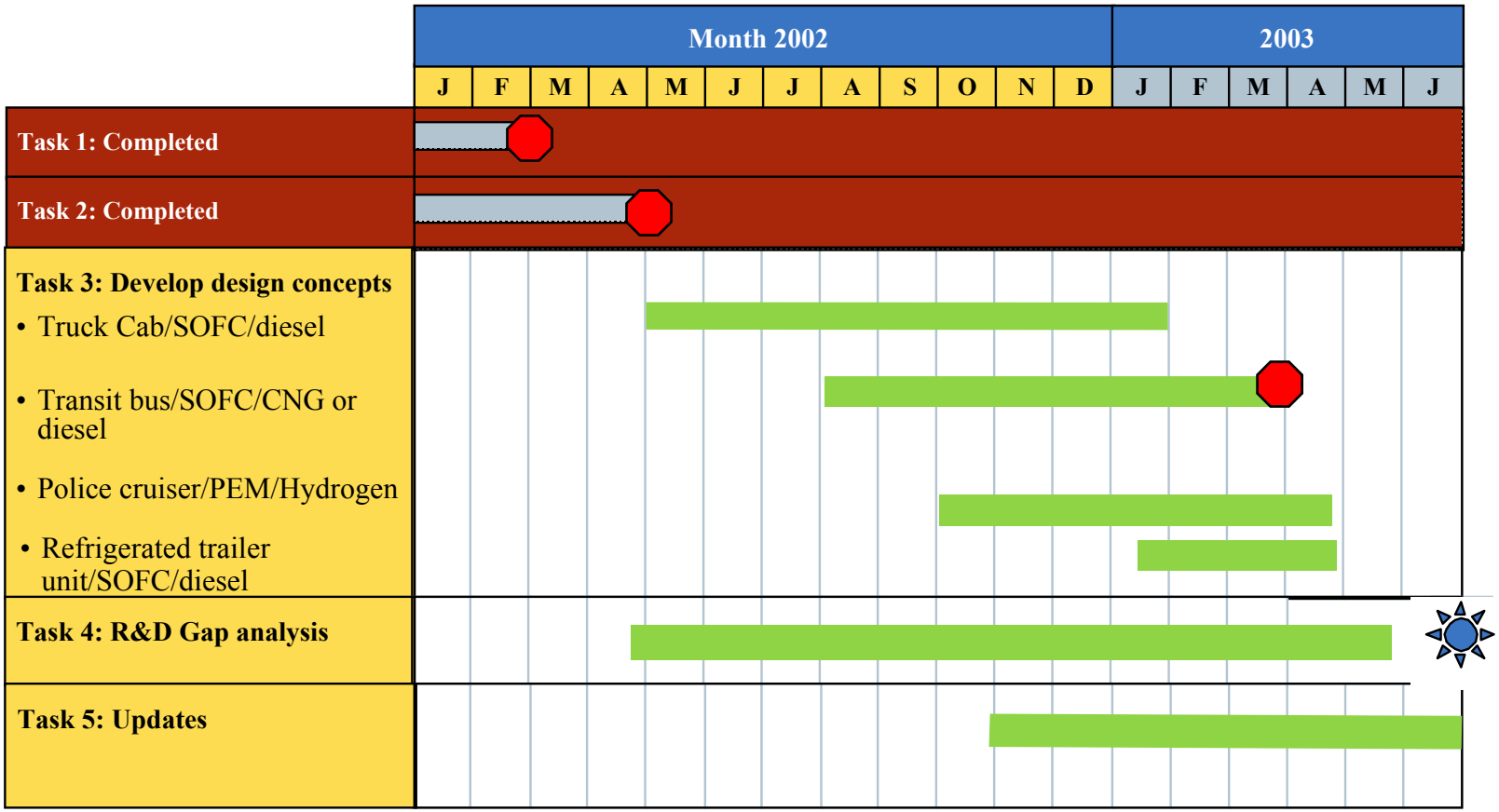
- Determine most promising future APU applications
- Refine likely duty cycles, power requirements, volume/weight targets

- Conceptual designs of 3 fuel cell /APU applications
- Conceptual design of interfaces with vehicle
- Compare conceptual system with competing technology

- Determine gaps among fuel cell cost & technical performance and market needs
- Layout required development efforts

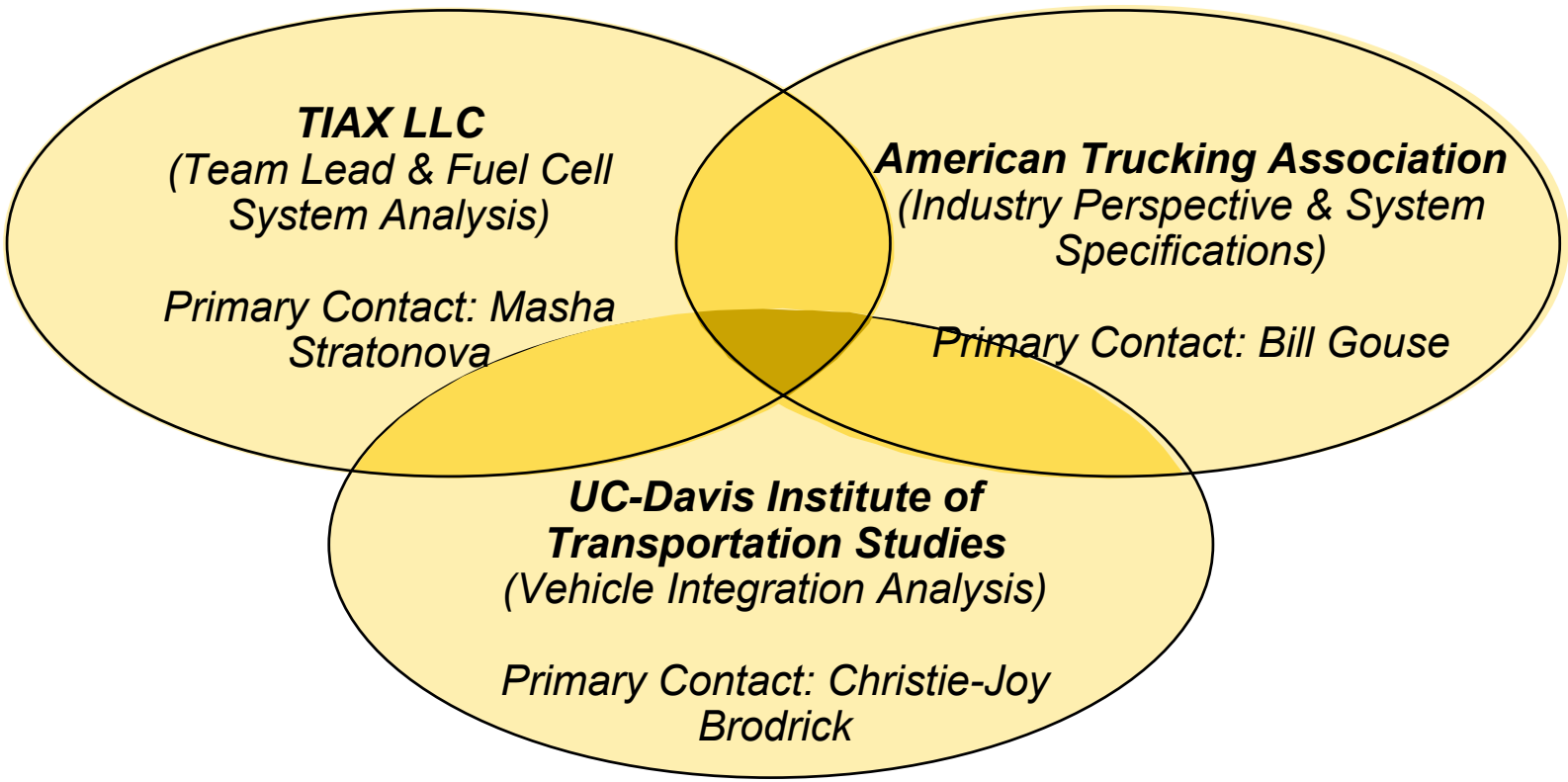
- Update with latest publicly available data

Our current effort is to finalize conceptual designs of APUs and complete R&D gap analysis.



Final Report Time Period Milestone

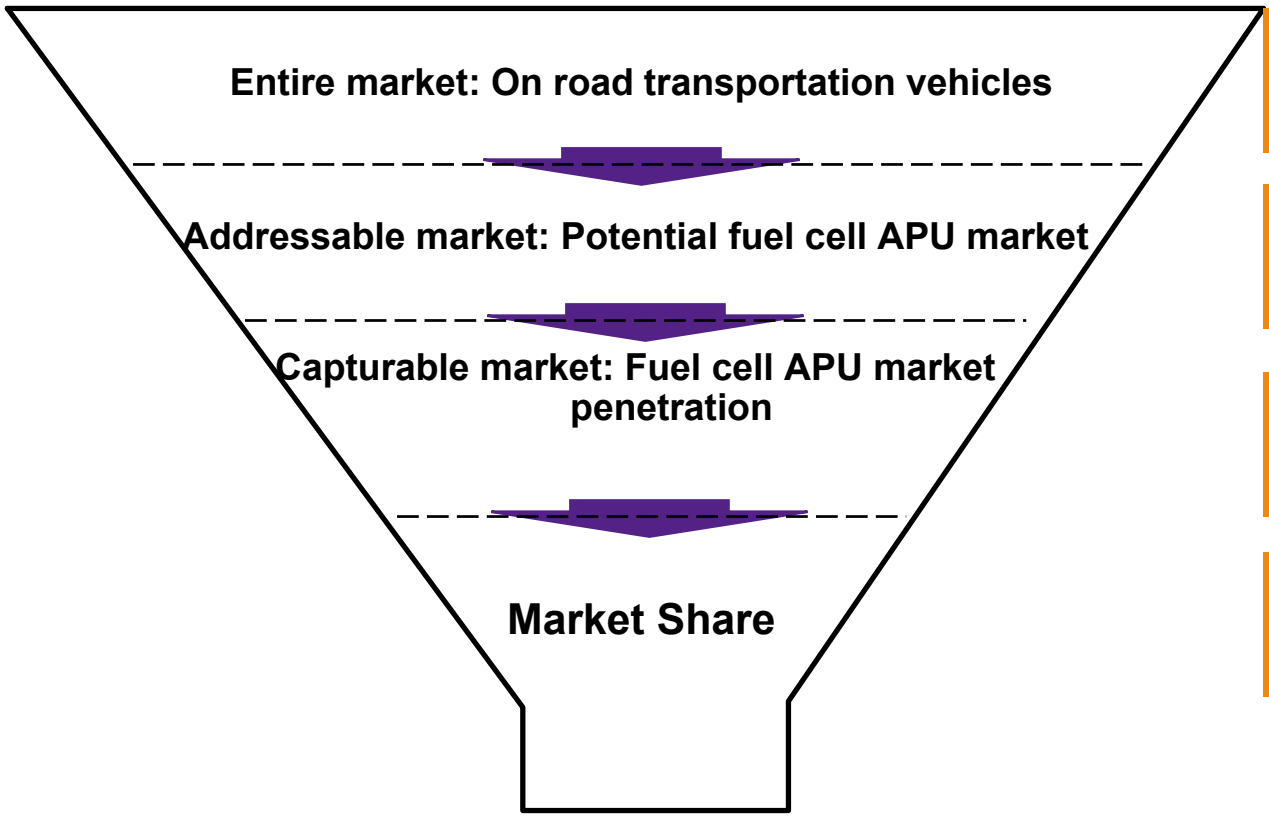
The DOE APU Fuel Cell Study Team consists of TIAX LLC and the University of California-Davis with input from the American Trucking Association.



We analyze PEM and planar, anode-supported SOFC for APUs based on an evaluation of the most important system characteristics.

- Solid Oxide Fuel Cell technology is most promising for most APU applications
  - High power density
  - High efficiency
  - Most compatible with diesel fuel operation (used as primary engine fuels in target heavy duty vehicle markets)
- Fossil Energy SECA program and industry is developing core planar solid oxide technologies applicable to both transportation and stationary applications.
- PEM technology was selected for applications in vehicles for which hydrogen was assumed to be the primary fuel.
  - PEM APUs operating on fuels other than hydrogen were not considered.

We use a market screening methodology to identify the likely addressable market for on-road transportation applications



Vehicle Markets Analysis

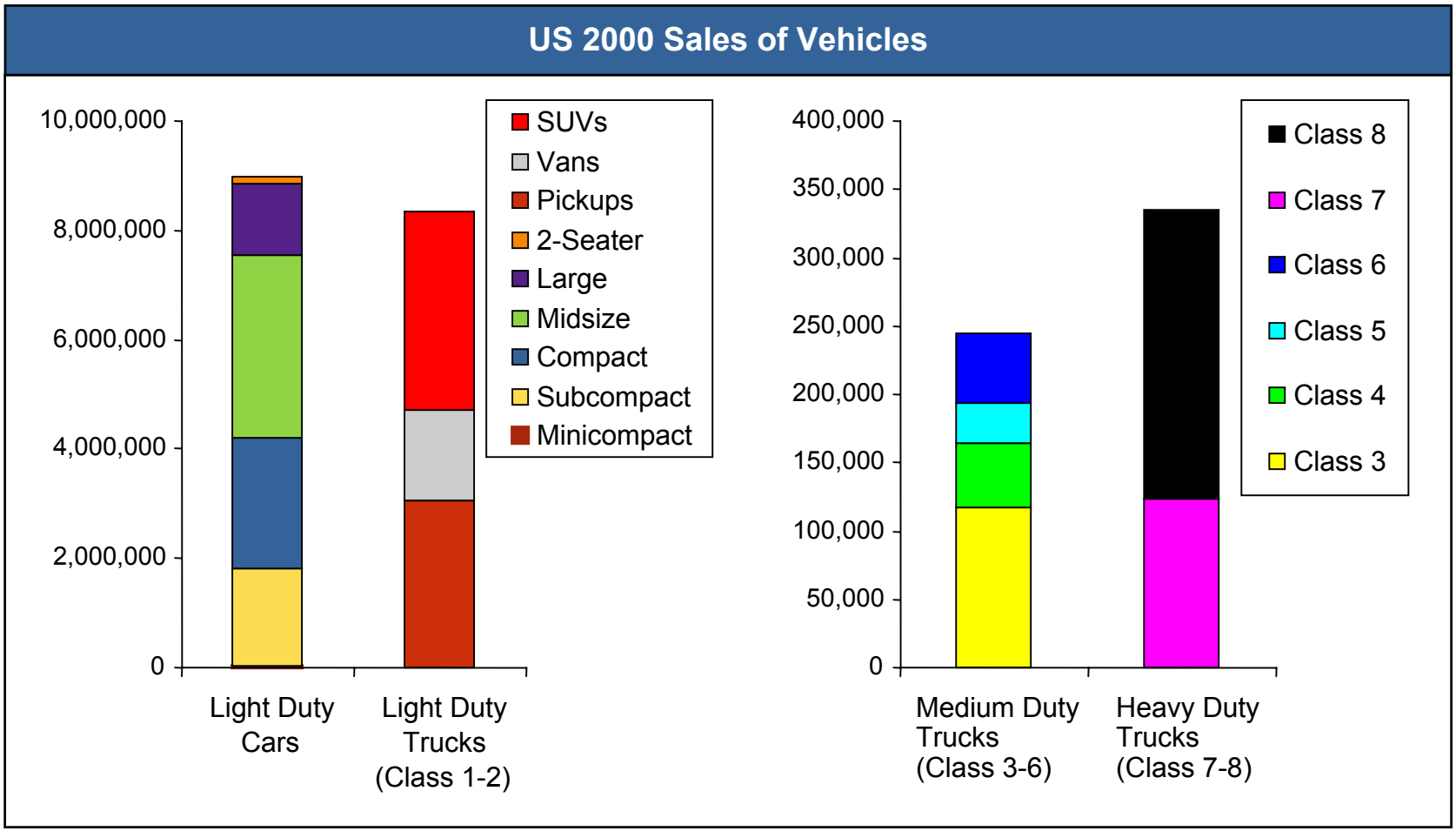
Compare cost and performance of FC APU with benefits to end applications

Market acceptance analysis as part of benefits projections

Outside scope of project

# total market capacity	x	% market addressable	x	Market penetration (% captured)	x	% market share	=	# installed capacity

For the entire market assessment and the initial screening, we considered market size for new vehicles and price of vehicle.



We also considered RVs, utility trucks and miscellaneous segments.

Vehicles meeting market and cost criteria are considered as a potential fuel cell APU market.

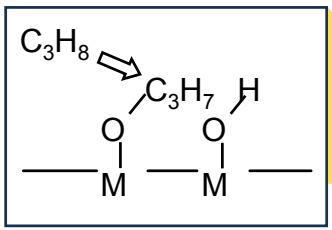
	APU Power & Packaging Constraints		
Market Segment	**Required power (kW)**	**Maximum allowable weight (kg)**	**Maximum allowable volume (L)**
Long-haul heavy-duty truck	3-6	*125*	*250*
Refrigeration trailer units	10-30	*125*	*250*
Specialized utility/PTO trucks	4-75	*400*	*250*
Transit, intercity buses	10-20	*100*	*200*
Recreational vehicles	2-7	*250*	*250*
Deluxe contractor truck	5-20	*250*	*250*
High-end passenger vehicles	1-3	*<50*	*<50*
Law enforcement vehicles	1-3	*<50*	*<50*

NOTE: Some values are based on estimates from personal communication with one or more sources, but are not conclusive. Weight and volume estimates are calculated from current space available for these systems and from PNGV research

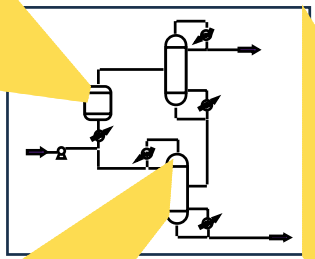
Based on the economic marketability, technical feasibility, and potential benefits, four applications were chosen for detailed analysis.

Heavy-duty truck sleeper cab	• Diesel fueled SOFC APU • APU provides for hotel loads and telematics while the truck is parked • Reduction in fuel consumption, emissions, noise; improved safety
Transit bus/motor coach	• CNG or Diesel fueled SOFC APU • APU provides for air conditioning and other electrical loads for passenger amenities • Potential fuel savings, emission reductions and noise reduction
Hydrogen fueled police car	• Compressed hydrogen fueled PEM APU • Electrical accessory loads • Reduction in fuel consumption, emissions, noise; improved safety
Refrigeration trailer unit	• Diesel fueled SOFC APU • APU provides cooling load • Potential fuel savings, emission reductions and noise reduction

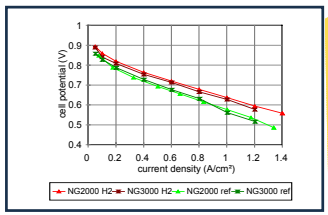
We are applying our multi-subsystem modeling methodology to design the conceptual fuel cell APU systems.



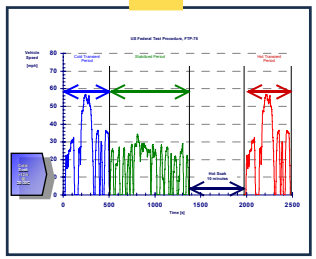
Reformer model



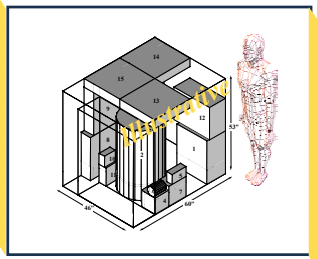
Thermodynamic System Model



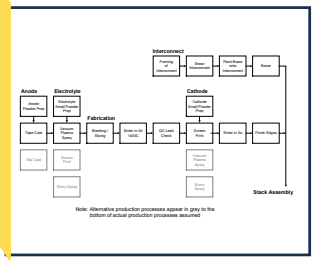
Fuel Cell Model



Vehicle Load Profile



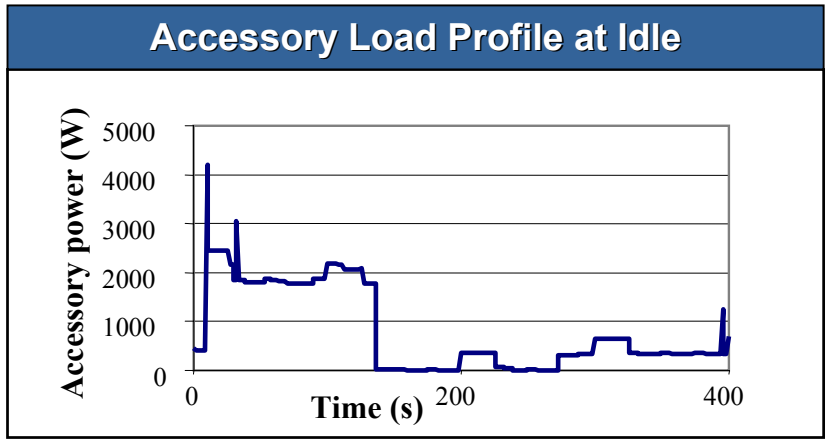
Conceptual Design and Configuration



Manufacturing Cost Model

$/kW

During stationary cycle, potential benefits for 4-kW SOFC APU to power sleeper cabs include significant fuel and emissions saving.



	Fuel (gal/yr)			NO_x (ton/yr)	PM (ton/yr)
Idling Mode	Light	"Typical"	Heavy	"Typical"	
Main Engine Idling	936	1,548	2,160	0.147	0.002
4-kW SOFC APU	180	288	468	~ 0	~ 0
Saving at Idle	756	1,260	1,692		
	80.8%	81.4%	78.3%	>99%	>99%

Note: Light – 600 rpm, 1 kW average accessory load; "Typical" – 860 rpm, 2 kW; Heavy – 1150 rpm, 3.5 kW
Values shown are for average idling duration (6 hrs/day)
Approx. 15-20% of market idles <2 hrs/day, 60-70% from 2-10 hrs/day, and 15-20% >10 hrs/day

Preliminary analysis of the APU system for long-haul trucks indicates a payback period of under 2 years resulting from annual fuel cost savings.

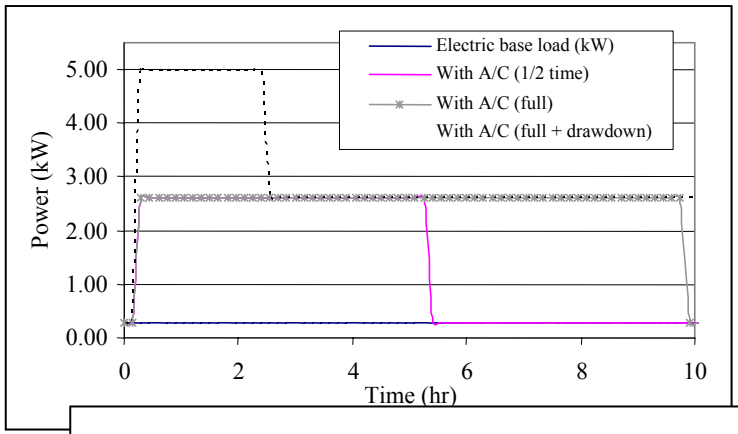
Economic Assumptions	
4-kW SOFC APU, installed package (Long-term cost assumption)	$580/kW
Diesel fuel cost	$1.7/gal

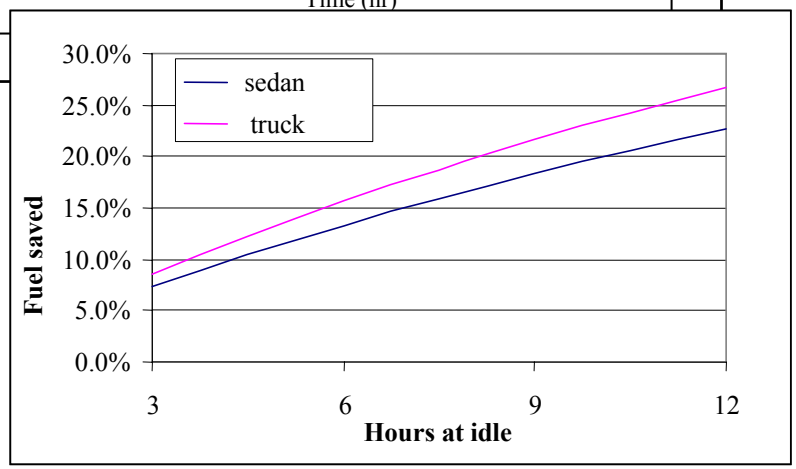
Application	Hours of Idling (hrs/yr/vehicle)	Annual Fuel Savings (gal)	Annual Fuel Cost Savings ($/yr)	Unit Cost ($)	Payback Period
Long Haul Trucks	1800-3000	900-2200	1530-3740	2,320	**0.6-1.5**

The low payback periods is likely to ensure a significant market penetration for the long haul truck applications.

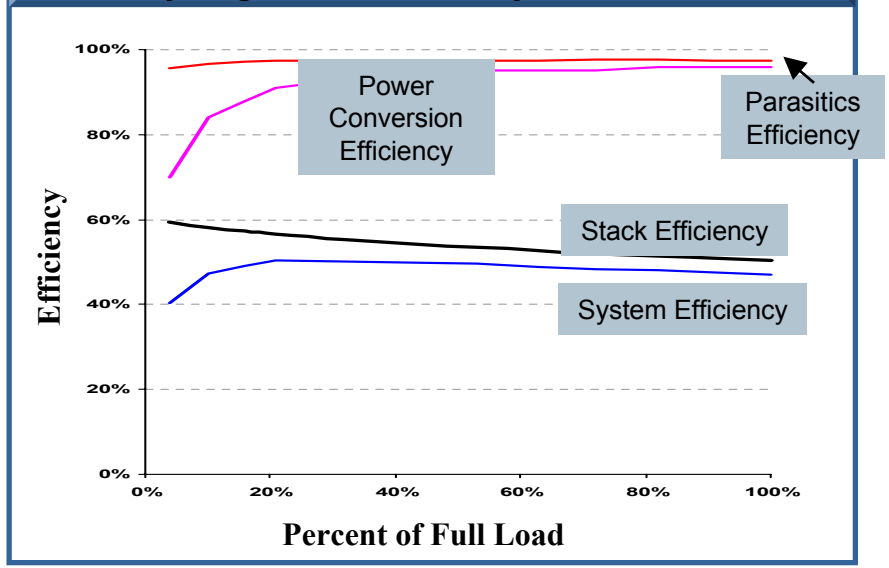
Hydrogen-fueled PEM APU for police cars was considered with an assumption that hydrogen infrastructure is available.

Simplified Electric Load Profiles at Idle





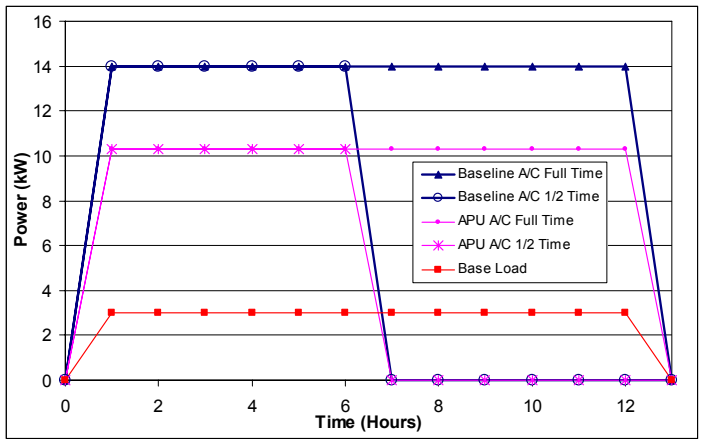
5 kW Hydrogen Fueled PEM System Performance



Note: Fuel saving estimate is based on gasoline equivalent.

Use of an APU in a transit bus does not lead to fuel saving benefits and only insignificantly reduces NO_x and particulate matter emissions.

Simplified Electric Load Profiles



	Engine Only	SOFC	Engine w/SOFC	Engine+SOFC	Reduction
Fuel	gal/h	gal/hr	gal/hr	gal/hr	%
Base load	3.5	0.23	3.4	3.6	**-2.1**
AC full time	4.2	0.91	3.4	4.3	**-1.2**
NO_x Emissions	g/mile	g/mile	g/mile	g/mile	%
Base load	24.6	0	23.2	23.2	5.8
AC full time	31.5	0	23.2	23.2	27
PM Emissions	g/mile	g/mile	g/mile	g/mile	%
Base load	0.3	0	0.3	0.3	1.1
AC full time	0.3	0	0.3	0.3	1.9

Fuel cells APUs offer benefits in high-volume markets and a possible near term channel for development of the technology.

- Fuel cell auxiliary power units can, in principle, be adapted to a range of non-propulsions applications for a number of applications including trucks, refrigerated trailers, law enforcement vehicles
- Several technology challenges must be overcome by both PEMFC and SOFC for widespread applicability as APUs
- Achieving a low manufacturing cost will be critical for broad SOFC and PEMFC commercialization

Fuel Cell Reformer Emissions

Work in Progress

2003 Hydrogen and Fuel Cells Merit Review Meeting

Berkeley CA

May 19-22, 2003

TIAX, LLC
1601 S. De Anza Blvd
Cupertino, California
95014

TIAX Ref: D0014

The purpose of this study is to determine the emissions from fuel cell vehicles with on-board reformers

- Fuel cell vehicles must meet the most stringent emission standards in order to provide value to the greatest number of stakeholders
- Quantifying emissions from reformer systems needs to take into account very low detection limits in order to verify emission benefits
- Data from fuel processor systems is used to evaluate potential emissions from vehicles with on-board fuel processors

DOE Technical Targets: Integrated FC Fuel Processor System
Operating on Tier 2 Gasoline (30 ppm S)

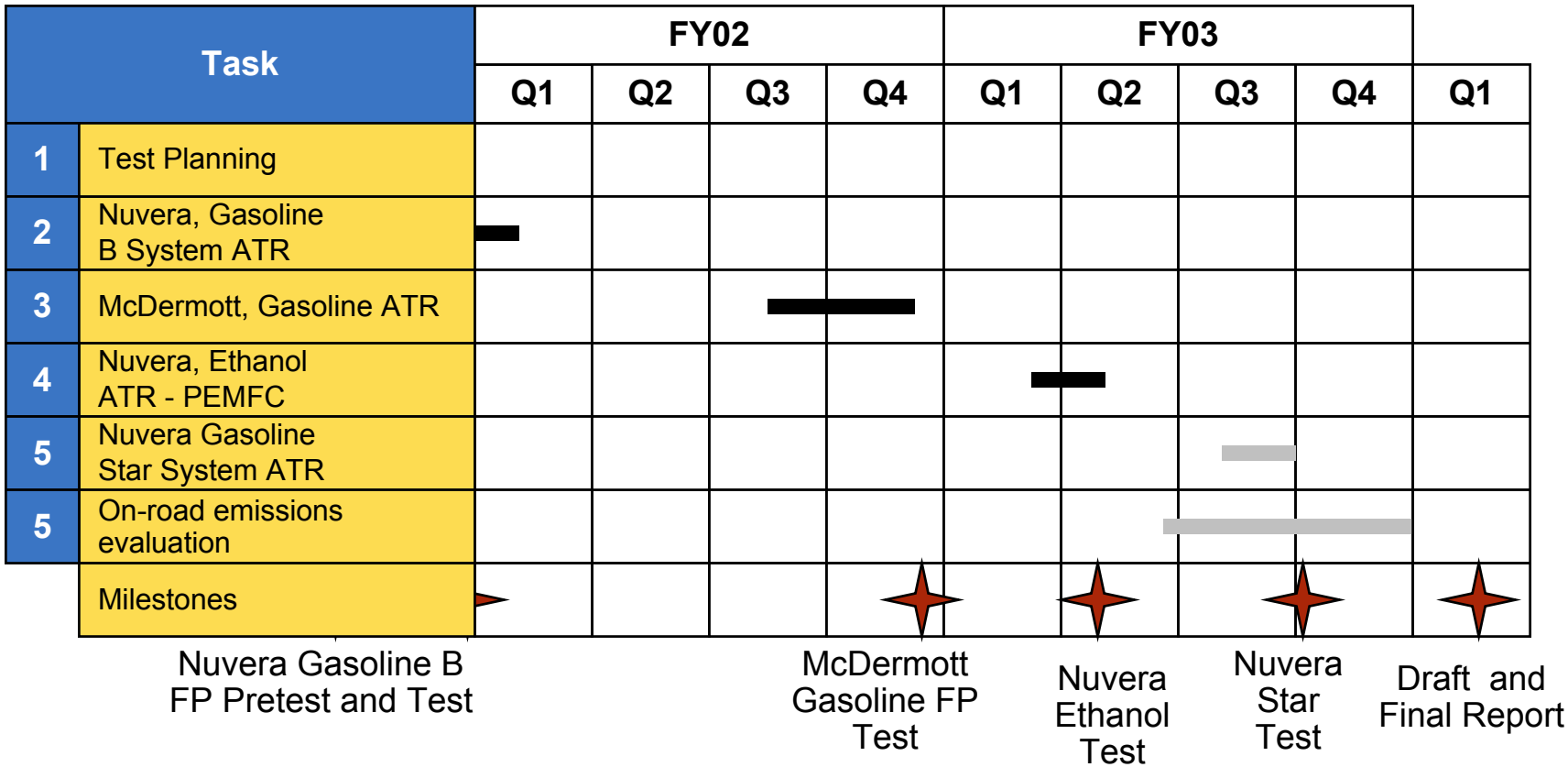
Characteristics	Units	Calendar year		
		2003	2005	2010
Energy efficiencya @ 25% of rated power	%	34	40	45
Energy efficiency @ rated power	%	31	33	35
Transient response (time from 10 to 90% power)	sec	15	5	1
Emissions [a]	g/mi	< Tier 2 Bin 5, 0.07 NOx and 0.01 PM		

a Emissions levels will comply with emissions regulations projected to be in place when the technology is available for market introduction.

DOE R&D Plan

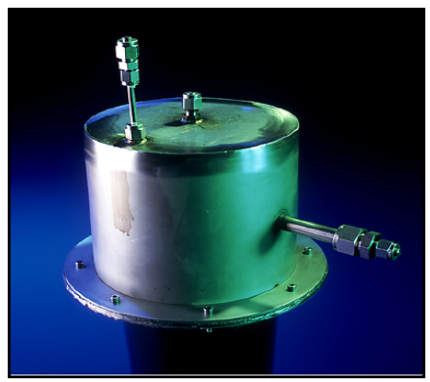
Fuel Processor Technical Barrier K: Emissions and Environmental Issues. Data on the effects of fuel/fuel blend properties on the potential formation of toxic emissions are limited. Fuel processor and stack emissions (including evaporative emissions) are not adequately characterized. Standardized emission test procedures are lacking. Start-up emissions are not well characterized.

Prior to finalizing our analysis, we intend to obtain input from a range of potential stakeholders in both conventional and hydrogen fuel chains.

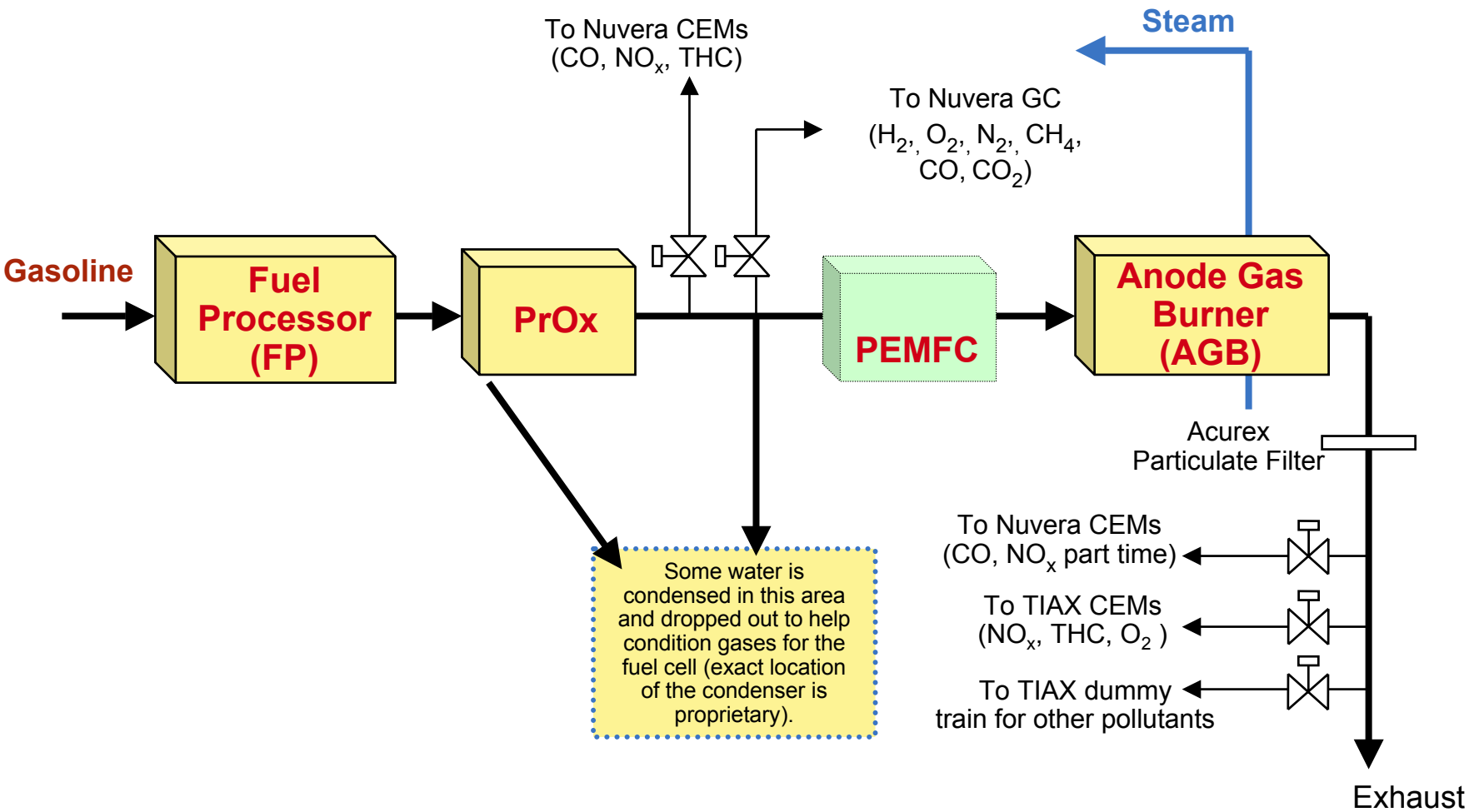


Four fuel processor systems will be tested.

System	Date Tested	AGB Feed	Power Rating
Nuvera, Gasoline B System ATR	October 2000	Gasoline Start-up PrOx Reformate (100% output)	50 kWe
McDermott, Gasoline ATR	September 2002	Gasoline	50 kWe Tested @ 10kWe PrOx
Nuvera, Ethanol ATR - PEMFC	January 2003	Ethanol Start-up PEMFC Anode Gas	10 kWe
Nuvera Gasoline Star System ATR	June 2003	Gasoline Start-up PrOx Reformate	50 kWe



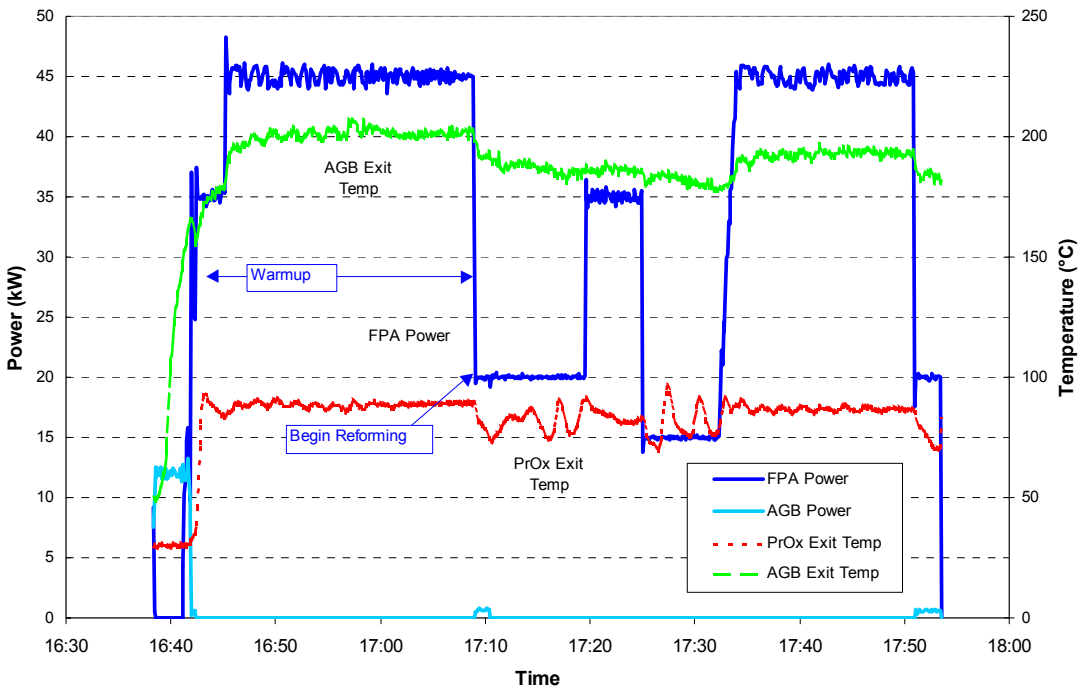
The Nuvera system was tested after the PrOx and after the AGB, without a fuel cell.



One test was completed in October 2000

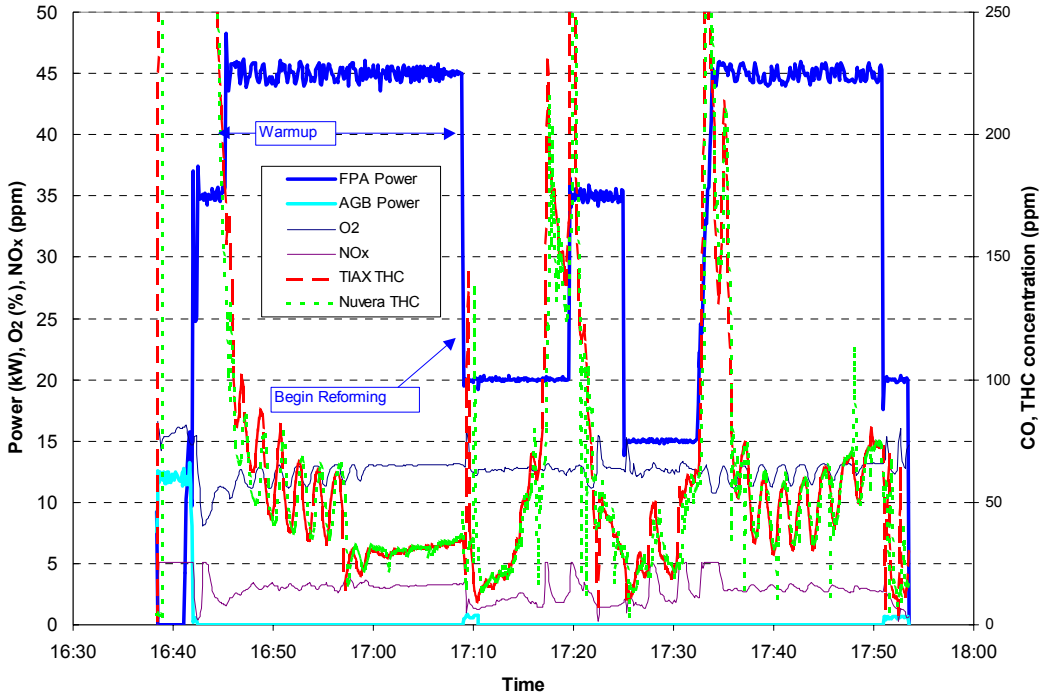
Test Cycle

- Initial AGB warmup to 150°C
- FPA heatup
  - PrOx exit to 90°C
  - AGB exit to 200°C
- FPA load
  - 20 kW initial
  - Rapid increase to 35 kW
  - Rapid decrease to 15 kW
  - Gradual increase to 45 kW
  - Gradual decrease to 20 kW



AGB Emissions

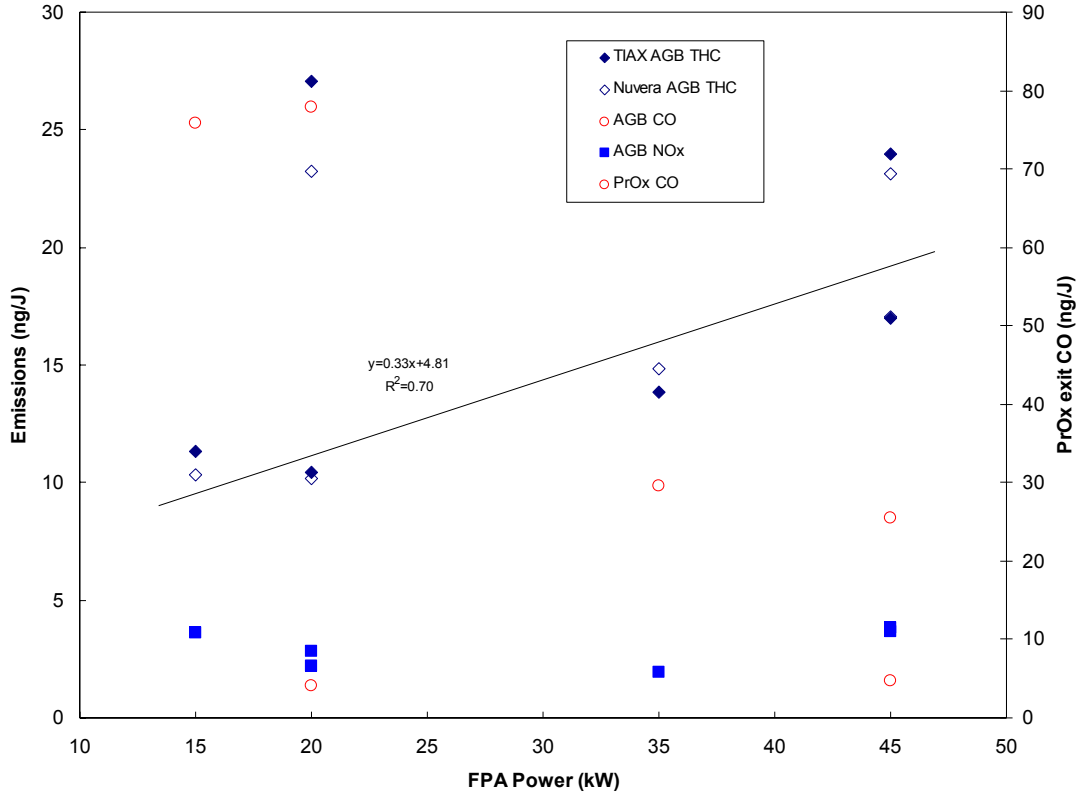
- AGB exit THC: TIAX and Nuvera instruments agree
- AGB exit NO_x
  - Pegs low level monitor (5 ppm) during AGB warmup
  - Nominally 3 ppm throughout remainder with a few spikes
- AGB exit O_2
  - Above 15% during AGB warmup
  - Nominally 12.7% throughout remainder
  - Cyclic during early FPA warmup, rated load operation
  - THC & NO_x cycles follow: dilution



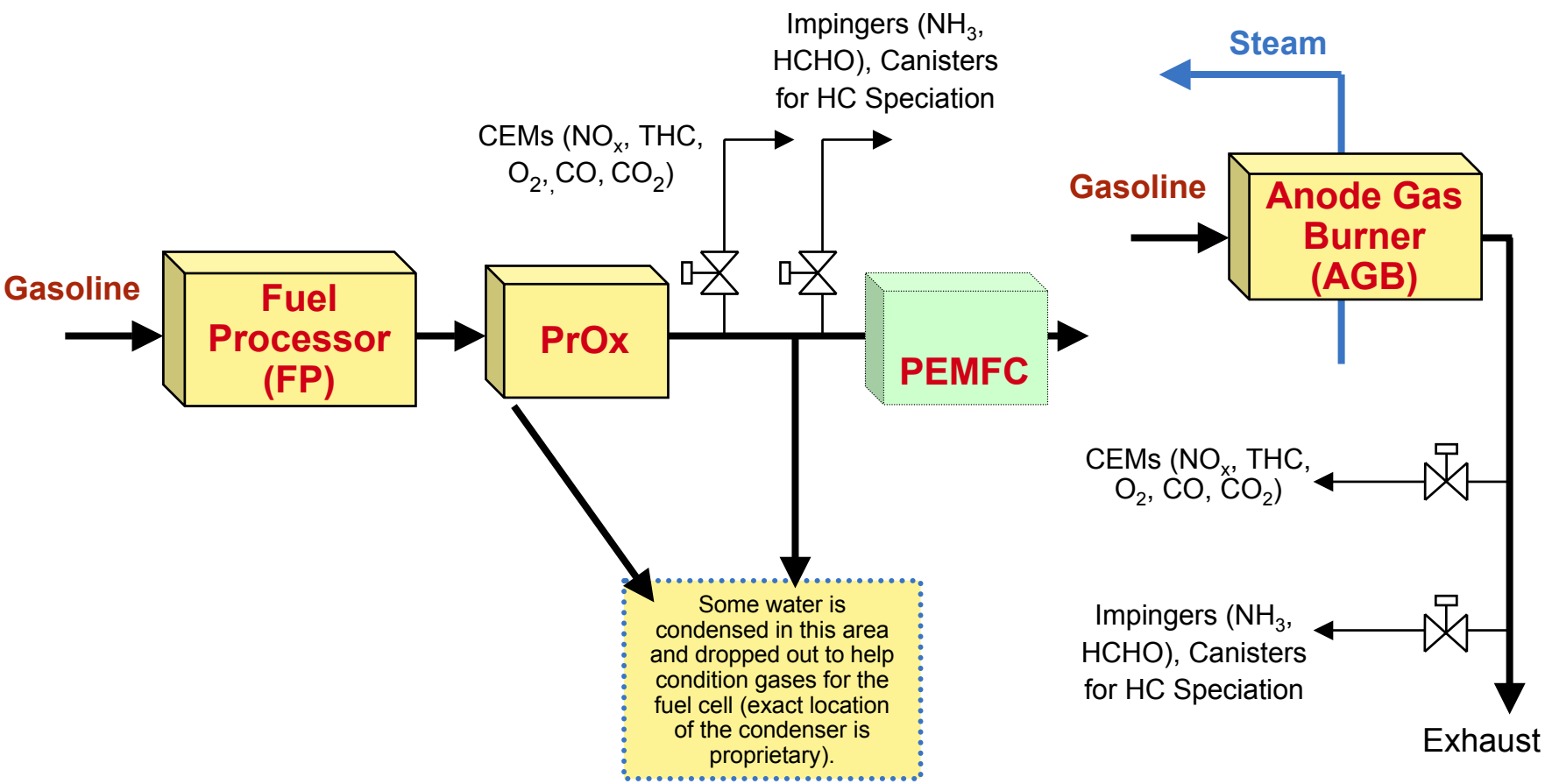
Nuvera Test Results Steady Operation Emission Rates

Emission rates (ng/J)

- AGB NO_x emissions low & invariant with load, 3.0 ng/J
- AGB CO emissions low & invariant with load, 1.5 ng/J
- AGB THC emissions appear to increase with FPA load
  - Ignoring high initial 20 kW result, acceptable linear correlation



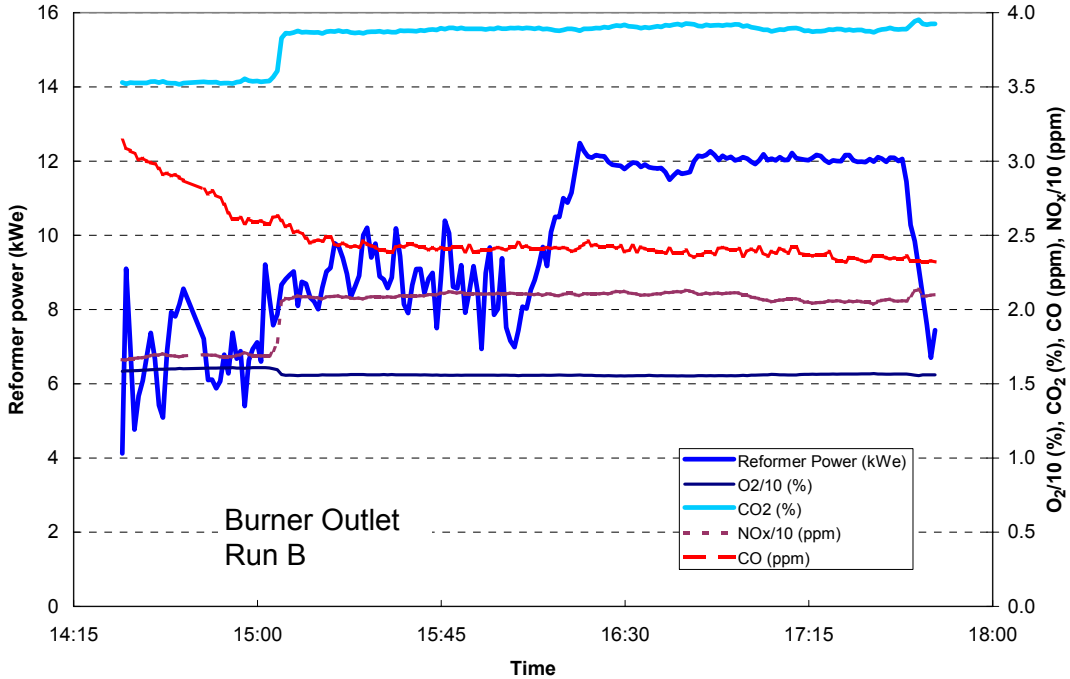
The MTI fuel process was tested at the PrOx exit. The AGB burned gasoline which provides data that reflects startup conditions.



MTI Test Results AGB Outlet Run B

AGB Emissions

- After 15:00
  - O_2 steady at 15.5%
  - CO_2 steady at 3.9%
  - NO_x steady at 20 ppm
  - CO steady at 2.4 ppm
  - THC less than the monitor detection limit of 0.2 ppm



On-road emissions will be modeled based on driving cycle energy requirements and start up energy.

- NOx and CO should meet the lowest emission standards
- A key target should be the CA PZEV NMOG standard for NMOG of 0.01 g/mi and NOx standard of 0.02 g/mi
  - Depends on start up energy and start up emissions
  - Some emission control during reforming may also be required
- A quick emissions example
  - During reforming
  - 5 ng/J x 1,800,000 J/mi = 0.009 g/mi
  - During startup
  - 500 ng/J x 1,700,000J/25 mi = 0.03 g/mi
  - Total = 0.039 g/mi
- **Calculations are illustrative only**

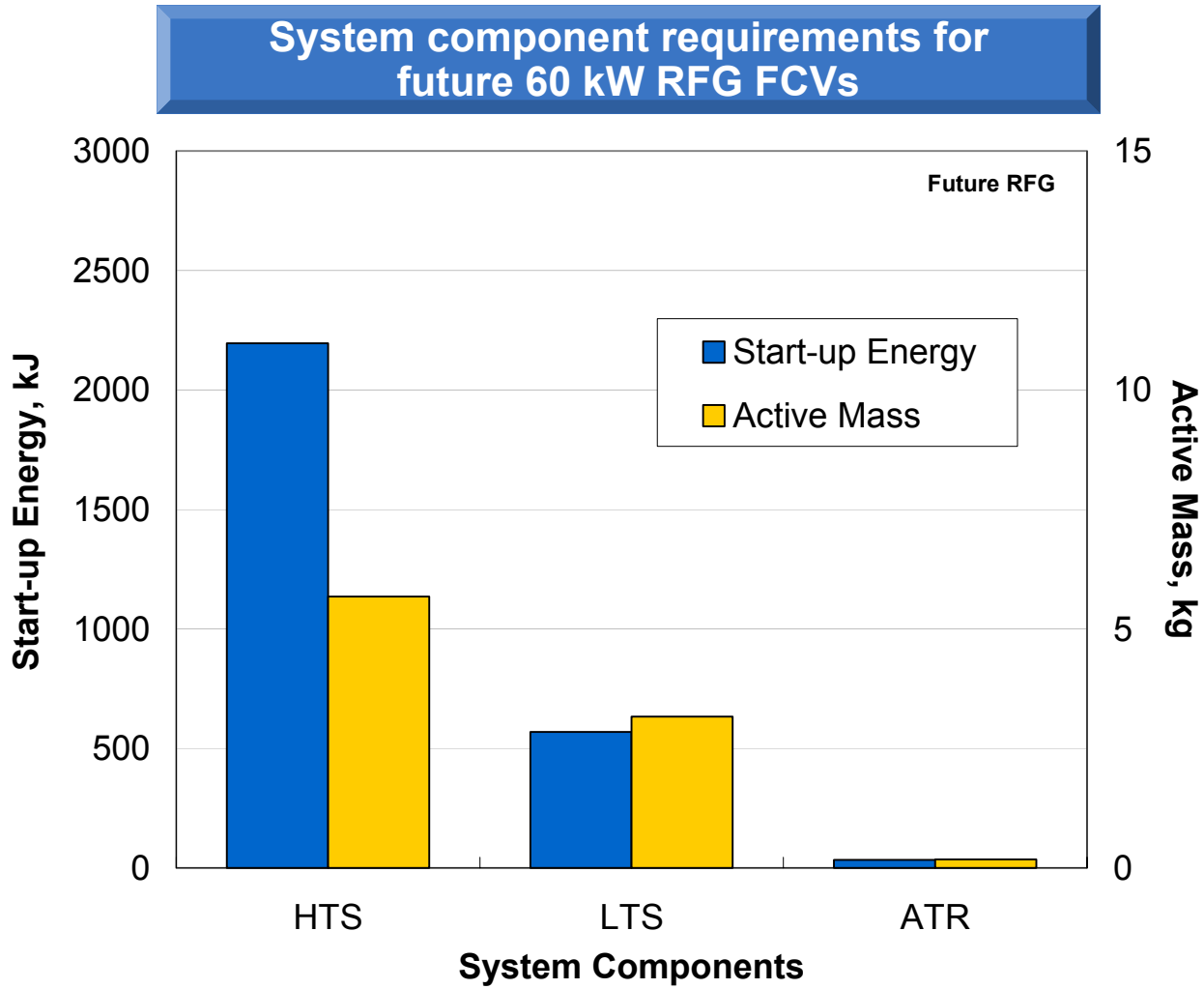
Start-up energy demand represents a significant portion of the energy for FCVs with on-board reformers.

- TIAX modeled energy inputs based on catalyst volume, heat capacity, system mass, and operating temperature
  - Start-up energy requirements are dictated by the energy input to the catalyst beds
  - Fuel cell generates power with hydrogen feed, even at low temperatures, so no start-up energy input is required
- Start-up energy inputs may need to occur twice a day for typical driving and represents up to 10 percent of the drive-cycle energy
  - Significant mass reductions in the fuel processor catalyst beds are projected

Energy requirements for future RFG ATR and Methanol SR FCVs

Fuel Processor, power unit size		Active Mass, kg	Start-up Energy, kJ	City Drive-cycle, kJ	Hywy Drive-cycle, kJ
RFG ATR	60 kW	9.0	2,800	17,700	21,900
	38 kW	5.7	1,770	15,600	20,600

The start-up energy requirement for system components decreases with active mass.



Starting the entire ATR represents a large fraction of the energy on a typical drive-cycle. Partial start-up of hybrids will reduce energy use.

- Partitioning the catalyst beds into 4 independent systems can improve turndown and cold start
  - Partial start-up on 25% of the HTS reduces start-up energy (with a partitioned reformer)
  - Applicable to hybrid configurations where batteries can power the vehicle
- Waste heat from the ATR system and anode gas can be used to warm up the remainder of the HTS

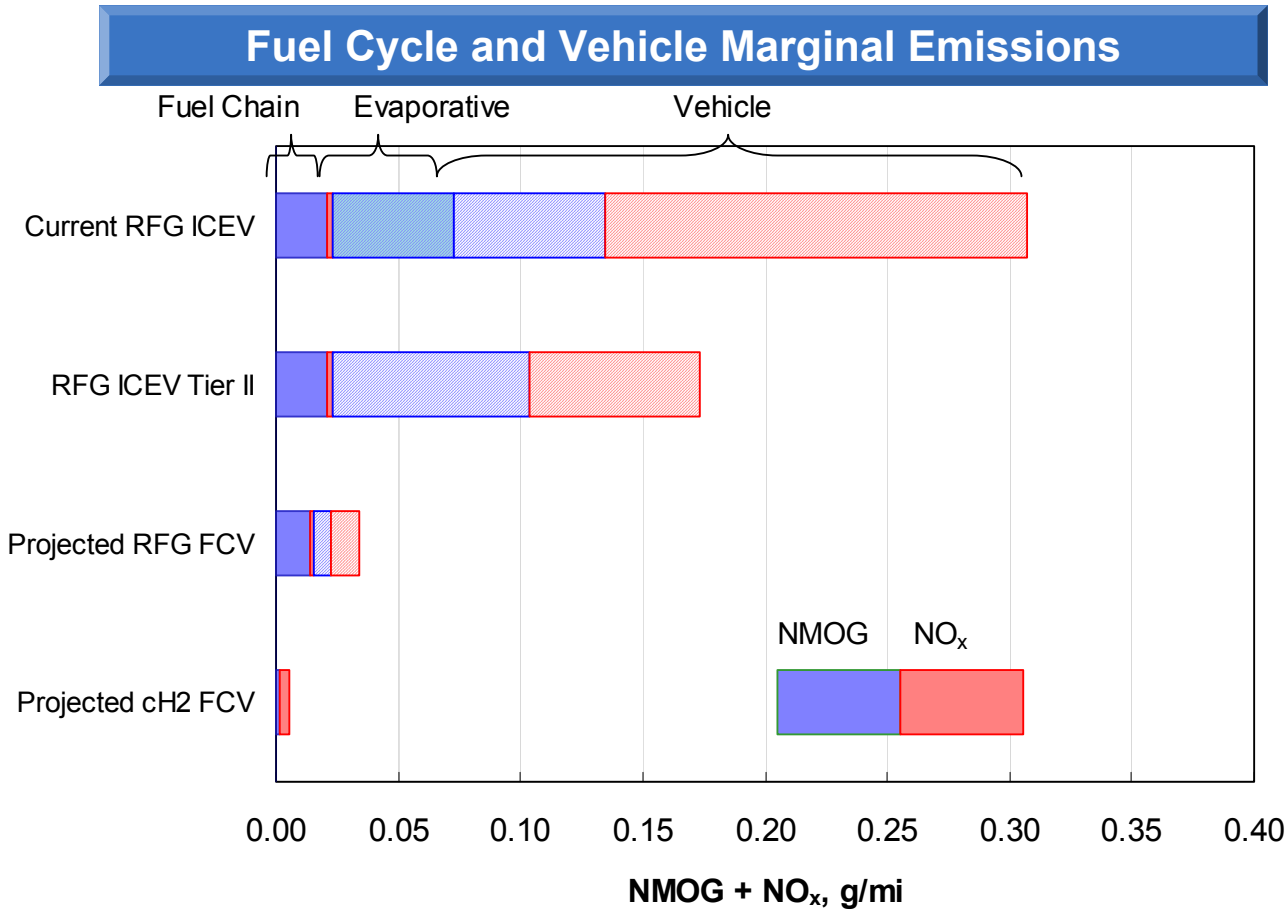
Energy requirements for future RFG ATR FCVs					CAFÉ Fuel Economy mpg
Fuel Processor, start-up fraction		Start-up Energy, kJ	City Drive-cycle, kJ	Hywy Drive-cycle, kJ	
RFG ATR, 60 kW	100%	2,800	17,700	21,900	45.6
RFG ATR, 38 kW Large Battery Hybrid	100%	1,770	15,600	20,600	52.2
	25%	440	15,600	20,600	56.1
		Partitioned start-up saves fuel			

ICEV emissions are projected to meet aggressive new standards. FCVs can also meet these standards if start-up emissions are controlled.

Vehicle	NMOG, g/mi		NO_x, g/mi	PM, g/mi
	Tailpipe	Evaporative	Tailpipe	Tailpipe
PNGV Goal/ CA LEV Standard[1]	0.08	2 g/test	0.07	0.01
PZEV Standard	0.01	0.0	0.02	0.01
CA MY 2002 On-road[2]	0.062	0.049	0.173	❾0.01
PZEV On-road	0.0065	0.0164[3]	0.024	❾0.01
RFG ATR FCV[4]	0.0065	0.0164[3]	0.012	❾0.01
cH2 NG SR FCV	0	0	0	0

[1] Emission standards represent maximum emission levels over the vehicle life. Tailpipe emissions are tested over the FUDS cycle. For PZEVs, the emission standards apply for 150,000 miles.
[2] On-road projections take into account reduced levels needed to meet in-use compliance, deterioration, as well as a mix of hot and cold start events and driving conditions.
[3] Inventory values are based on detection limits for certification testing. Actual levels may be lower.
[4] ATR FCV emissions are projections based on the assumption that cold-start emissions can be controlled to similar levels as ICEVs. Operating NMOG and NO_X emissions from reformer tests are near PZEV levels.

FCVs could provide the lowest overall criteria pollutant emissions, especially direct hydrogen.



"Current RFG ICEV" results are based on the inventory for California 2002 model year vehicle inventory values and fueling station requirements.

Proposed Future Work

If development goals are met, next generation fuel processor/fuel cell systems should be tested. Emissions from APUs and stationary hydrogen systems should also be characterized.

Future Work	Challenges
Measure emissions from stationary hydrogen generation systems	• Find developers interested in quantifying both start up and continuous emissions and assessing operational profiles
Measure emissions from promising APU technologies	• Few small scale APUs which reflect future commercial products are available
Characterize N_2O and other pollutant emissions	• Low detection levels and background emissions
Measure emissions from next generation fuel cell/fuel processor systems	• Limited availability of developed systems

Inputs from regulatory agencies and other stakeholders have been solicited as input to the project.

Outreach Efforts

- Participated in International Energy Agency Annex XV
- Made presentations on environmental impacts to CA Air Resources Board
- Submitted Paper to Dec ‘03 Fuel Cell Seminar

2003 NETL Onsite Merit Review

Development of Predictive Models for Diesel-Based Fuel Processors

National Energy Technology Laboratory

May 19, 2003

David A. Berry, Dushyant Shekhawat, and

Todd H. Gardner

Diesel Fuel Processing

R&D Goal and Objectives

- ***GOAL: Develop fundamental understanding and technology*** in diesel fuel reforming for the production of hydrogen and support the development of auxiliary power units (APUs) in commercial diesel truck transport as being sponsored by EERE's Hydrogen, Fuel Cells, and Infrastructure Technologies (HFC&IT) Program.

- ***OBJECTIVE: Develop a predictive model / methodology*** for diesel fuel reforming and provide ***necessary tools and information*** to fuel cell/fuel reforming developers and system integrators for ***technology development, performance optimization, and system control.***

Diesel Fuel Processing
Technical Issues / Challenges

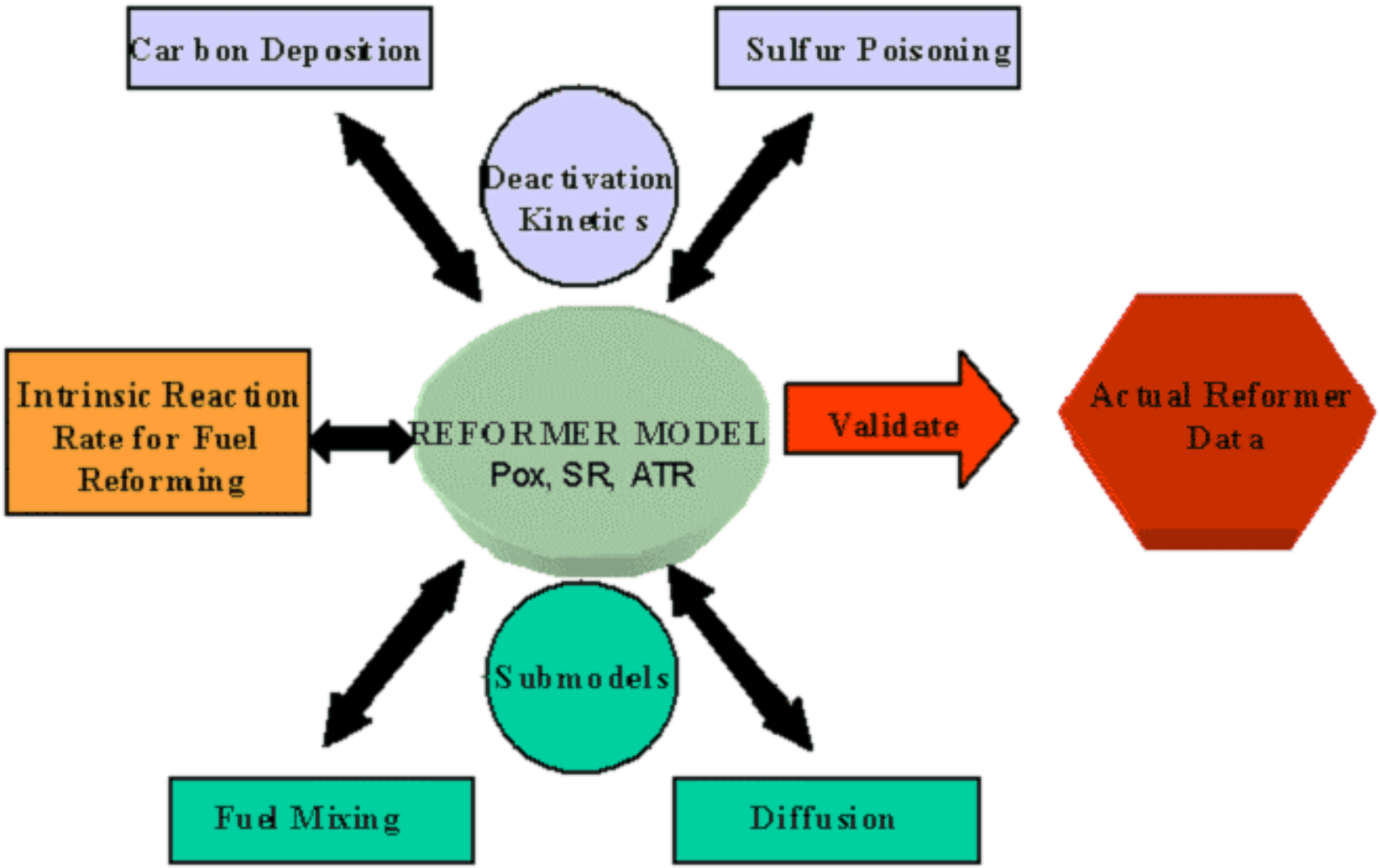
- **Diesel fuel is complex and difficult to reform :**
  - Diesel fuel is a complex, multi-component (>100 compounds) sulfur-containing fuel that exhibits varying reaction pathways and kinetic rates for differing fuels and catalyst types.
  - Deactivation of fuel reforming catalysts and fuel cell components via carbon deposition and sulfur poisoning are the principle technology barriers.
  - Improper reactant mixing in the reformer can lead to hot spots and carbon deposition.
- **System integration can be a significant challenge:**
  - Reformer integration with fuel cell system requires desulfurization, water management, and thermal considerations.
  - Certain FC applications may require high power density design with “fast” response and high efficiency for both steady-state and transient operations.
  - Hydrocarbon slip must be avoided to provide fuel cell with a clean synthesis gas.

Diesel Fuel Processing

Applicability to Fuel Cell APU Commercialization

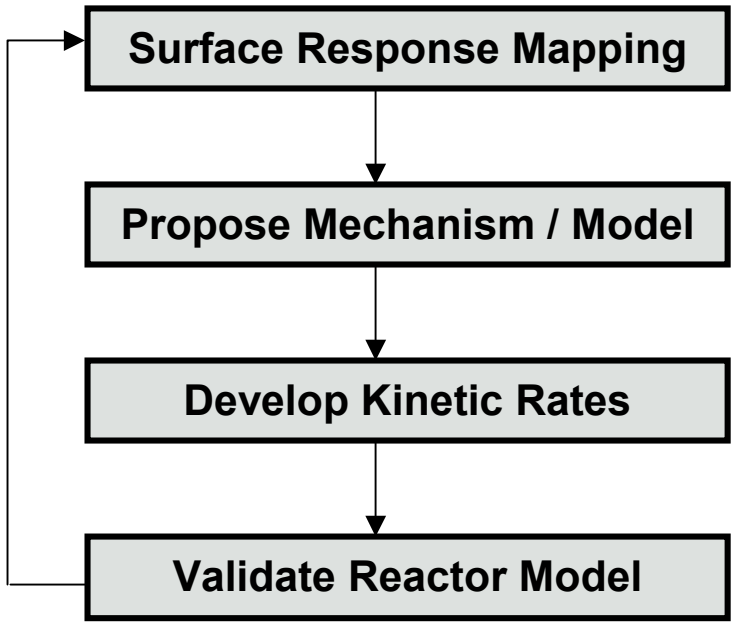
- Diesel-based fuel cell APUs are considered a significant high volume market for SOFC's.
- Fundamental understanding of diesel reforming and general methodology for kinetic rate determination would be very beneficial to catalyst developers. May extend to hydrocarbon fuels in general.
- A validated CFD model would be useful to fuel reforming developers and system integrators to predict steady-state and transient performance, develop control strategies, maximize efficiency, and minimize cost.

Reformer Model Needs



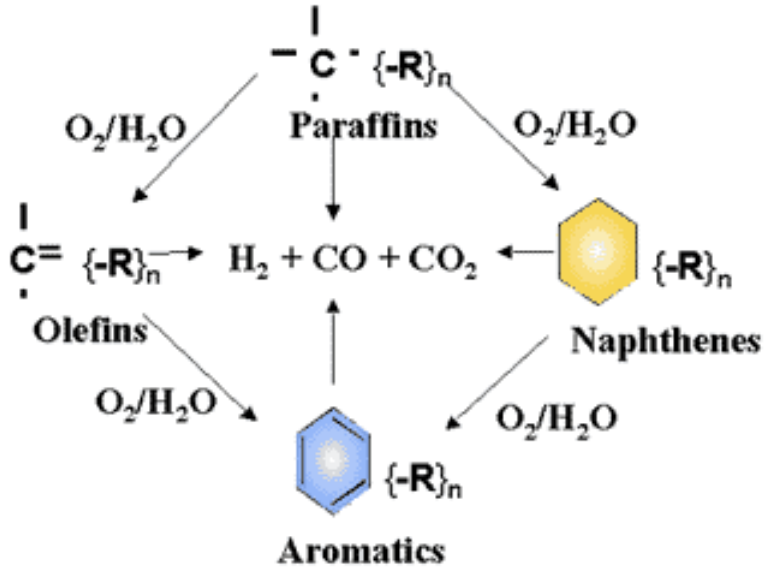
Diesel Fuel Processing
General Modeling Approach

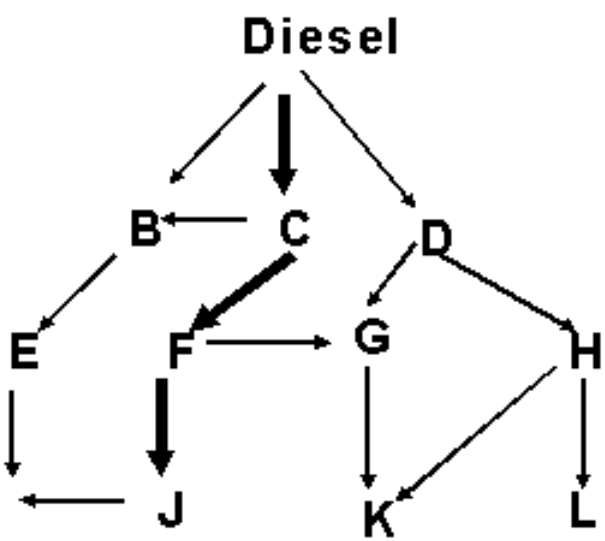
- **Response surface methodology**
  - Process parameter optimization study for the diesel ATR
  - Elucidation of complex chemical networks for the diesel ATR
- **Propose mechanism / model**
- **Develop kinetic rates**
  - Carry out kinetic measurements
    - Representative model compounds: single component & surrogate fuel mixtures
    - Real diesel
- **Validate model**
  - Experimental data



ATR Kinetic Modeling

- Dominant reaction pathways to be elucidated
- Assessment of kinetic parameters





Diesel Fuel Processing
Response Surface Mapping

- **Response Surface Methodology (RSM)**
  - A statistical tool used to map characteristic responses (e.g. selectivity, yield, conversion, carbon buildup, etc.) to input variables (O_2/C, H_2O/C, temp. and hydrocarbon type) over a defined region
    - Results in a deeper understanding of the reaction system and the interaction of parameters that affect the development of predictive models
    - Provides data that can validate kinetic models and proposed reaction pathways
  - Determination of operating conditions to achieve a desired specifications
    - Maximum CO and H_2 selectivity
    - Minimize carbon deposition
    - Minimize hydrocarbon slip

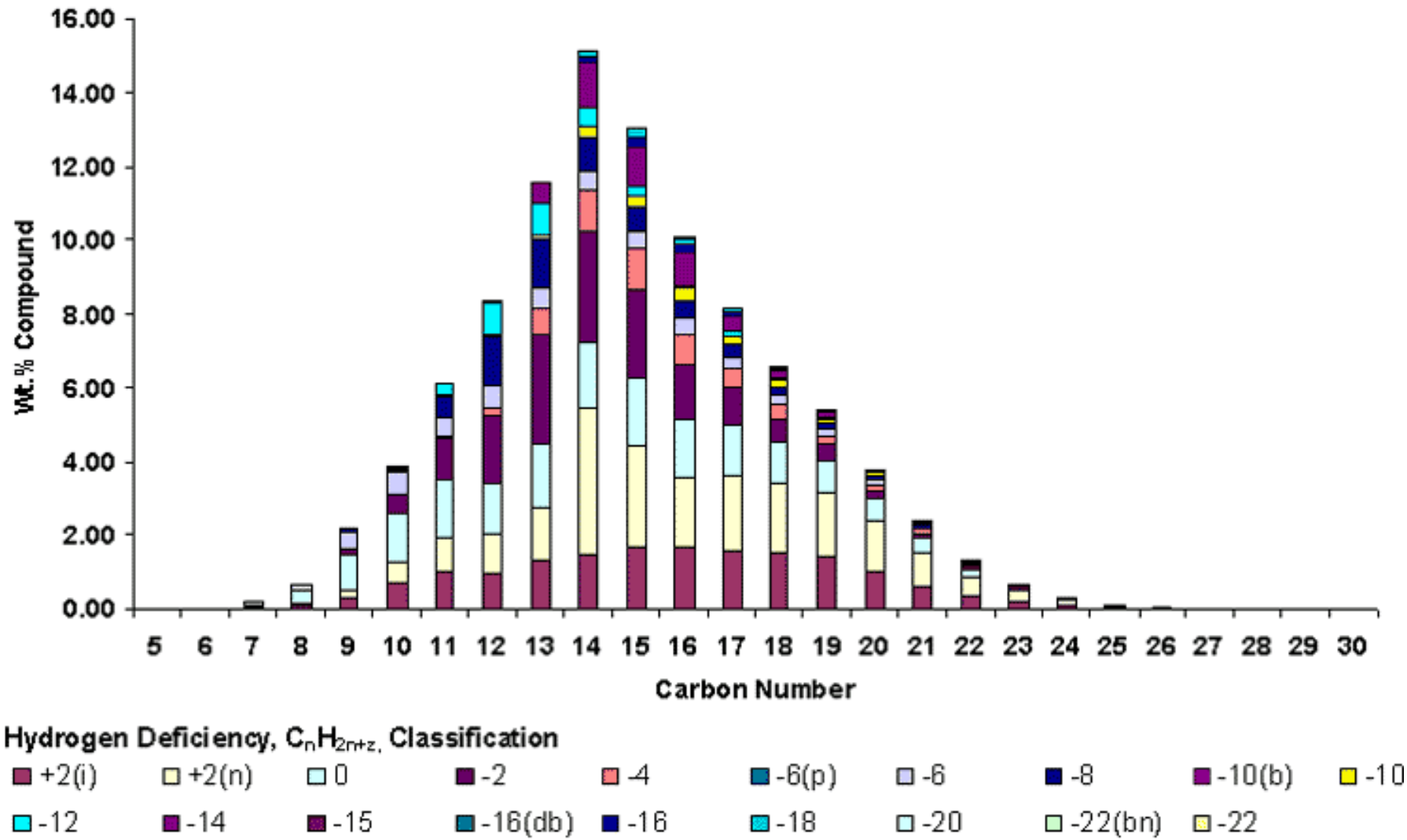
Diesel Fuel Processing

Diesel Fuel Composition – what to test?

- **Diesel Fuel Analysis**
  - Diesel fuel is a complex, multi-component mixture of paraffinic, aromatic and naphthenic hydrocarbons in the range of (C_7-C_{26})
    - An exponential increase in the number of hydrocarbon isomers with increasing carbon number makes compound identification difficult
      - Hydrocarbon compound classification may be made based on hydrogen deficiency, C_nH_{2n+z}
    - GC-FID/MSD – Dual detector system: simultaneous flame ionization detection and mass spectrometry (soft chemical ionization to avoid molecular fragmentation of heavy hydrocarbons)
    - Representative model compounds selected from each major homologous class present in diesel fuel include:
      - Parrafin: n-Tetradecane
      - Aromatic: 1-Methylnapthalene
      - Naphthene: Decalin

Diesel Fuel Processing

Diesel Fuel Composition – Con't.

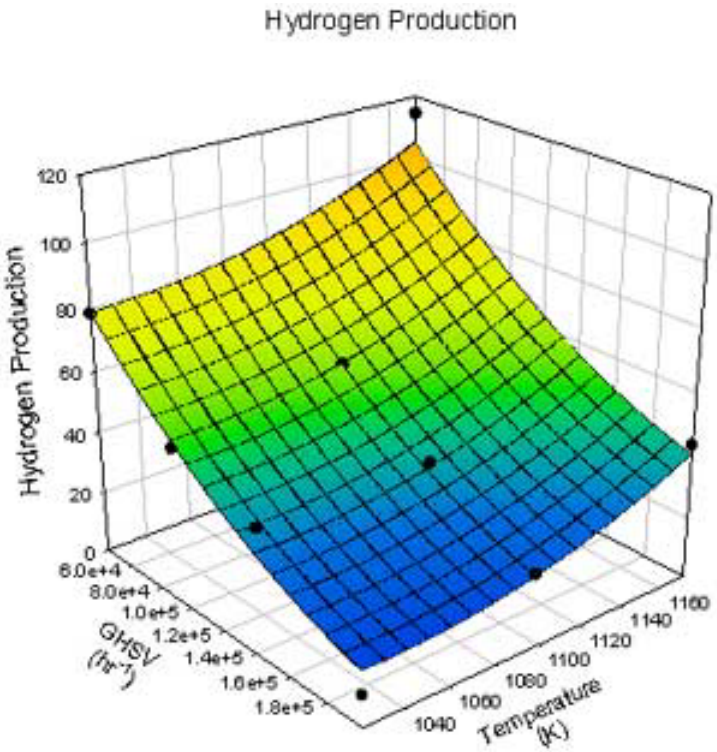


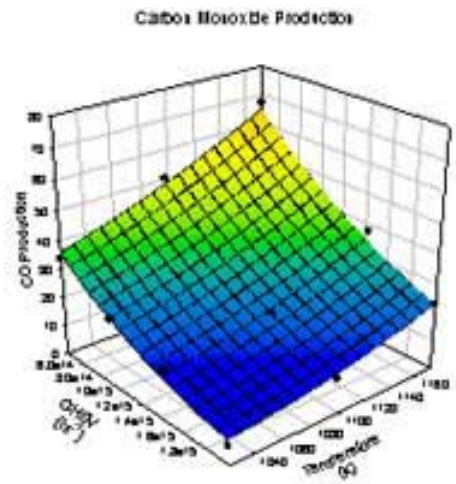
Diesel Fuel Processing

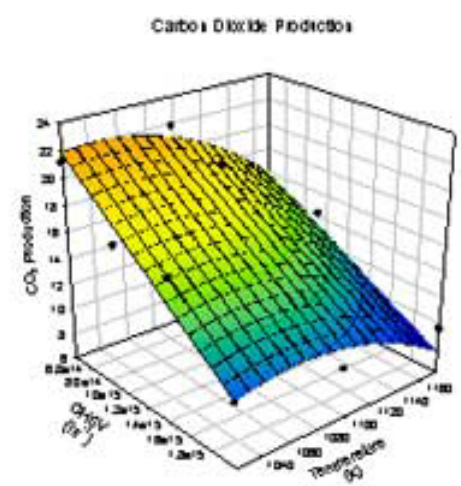
Experimental Conditions

	Paraffin	Aromatic	Naphthene
Model Compound	n-Tetradecane	1-methyl naphthalene	Decalin
O_2/C	0 - 0.5	0 - 0.5	0 - 0.5
H_2O/C	0 - 1.5	0 - 1.5	0 - 1.5
T (°C)	750 – 900	750 – 850	750 - 850
GHSV (h^{-1})	50,000 - 200,000	22,000 - 66,000	50,000 - 150,000

ATR of n-Tetradecane (O_2/C=0.3, S/C=1.5)

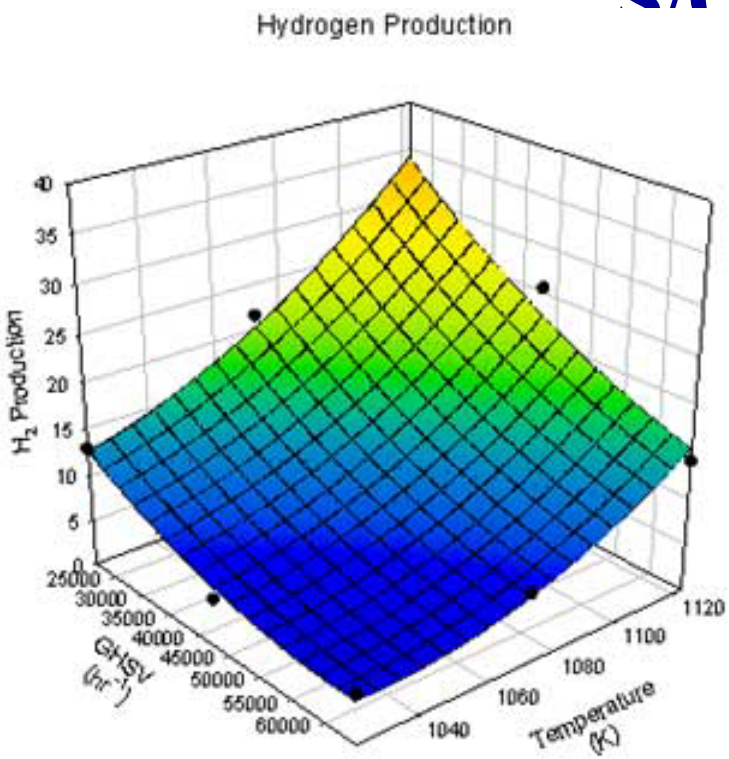


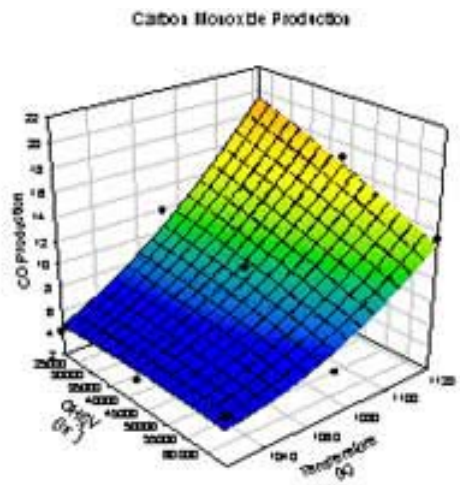


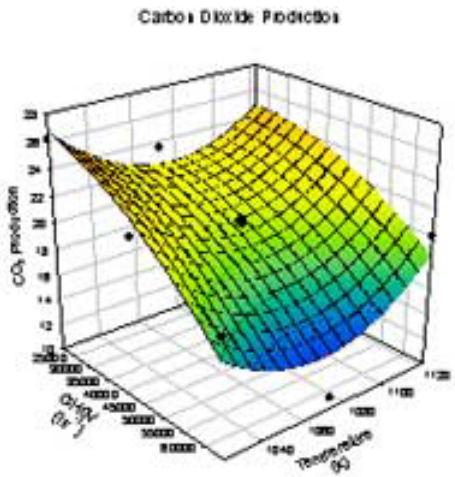


-Reverse WGS reaction dominates at higher T
- Olefins and aromatics produced at higher SV and lower T
- Naphthenes not observed

ATR of 1-Methylnaphthalene (O_2/C=0.3, S/C=1.5)

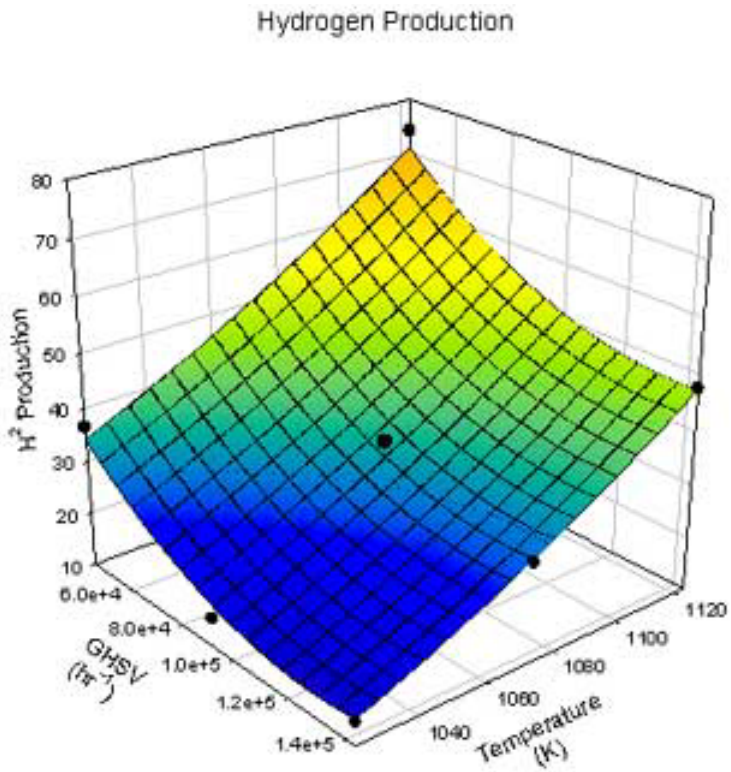


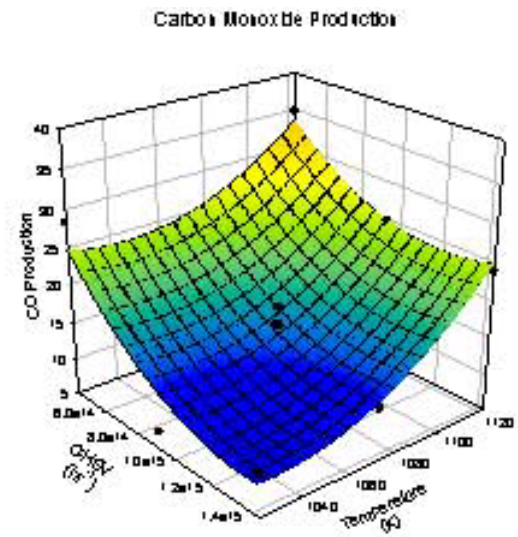


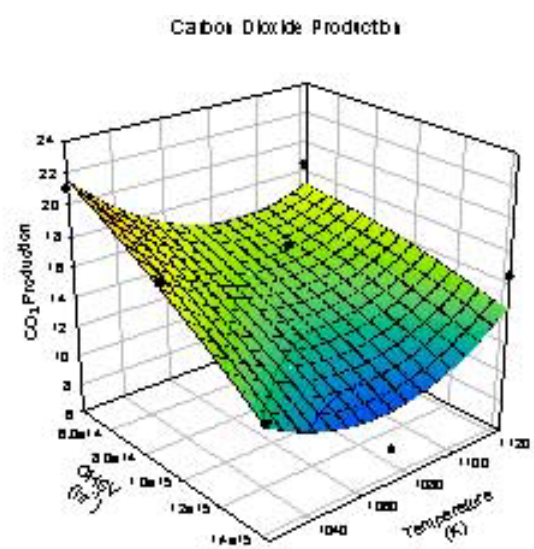


-Reforming rate increases significantly with increasing SV and T
-Slow reforming rate relative to paraffines and naphthenes
-Fast carbon deposition rate
-Naphthenes not observed
-Small concentrations of lower olefins observed
-Methane is the main paraffin formed

ATR of Decalin (O_2/C=0.3, S/C=1.5)

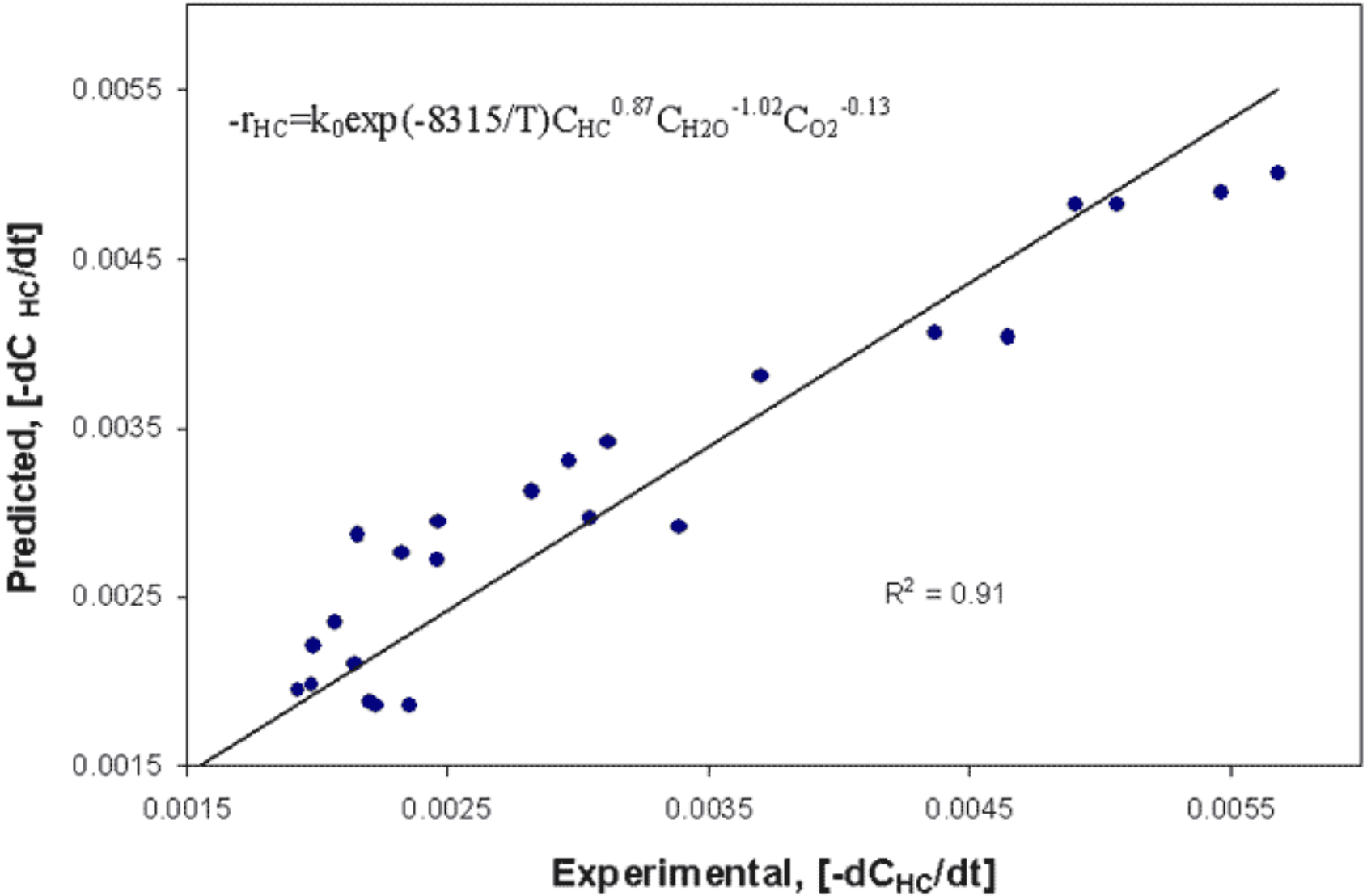






-Aromatics, paraffines, olefins observed in product
-Higher aromatic content in product

Experimental Vs Predicted Values for Diesel ATR on Pt/Al_2O_3



Diesel Fuel Processing

Conclusions / Accomplishments

- Tested three model compounds from the major representative functional groups in diesel fuel
- Developed surface response maps for steam reforming, partial oxidation and ATR over Pt catalysts for single component fuels
- Liquid product distribution varied with the type of reforming performed
- Higher olefins as well as aromatics content in product from ATR/SR/POX of paraffines at lower SV and higher T
- Significant coking observed from reforming (ATR/POX/ SR) of aromatics and naphthenes at higher T (~900 C)
  - Results in high pressure drops
- Quadratic fit of data from RSM was excellent (>90%)
- Reforming rate at the same conditions
  - Aromatics << Naphthenes < Paraffines
- H_2/CO/CO_2 production
  - Moles of (H_2/CO/CO_2) produced*100/moles of carbon fed
- Developed lumped parameter “power-law” ATR model

Diesel Fuel Processing

Future Plans/Collaboration/Tech Transfer

- **Continue Surface Response Mapping :**
  - Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists
  - Conduct combinatorial fuel compound studies
- **Develop Kinetic Submodels**
  - From response mapping, develop intrinsic reaction models for particular catalyst types
  - Continue collaboration/funding with Las Alamos National Laboratory LANL) to provide carbon deactivation kinetics
  - Continue collaboration with Argonne National Laboratory (ANL) to obtain experimental reactor performance data to validate reaction models and provide for fuel reactant mixing modeling capability suitable for CFD modeling codes.
- **Technology Transfer**
  - Continue dissemination of project results through EERE program reviews and FE SECA program reviews to principle developers such as Delphi Automotive, GE/Honeywell, Siemens-Westinghouse, and Cummings/McDermott.

2003 NETL Onsite Merit Review

Development of Predictive Models for Diesel-Based Fuel Processors

National Energy Technology Laboratory

May 19, 2003

David A. Berry, Dushyant Shekhawat, and

Todd H. Gardner

Diesel Fuel Processing

R&D Goal and Objectives

- ***GOAL: Develop fundamental understanding and technology*** in diesel fuel reforming for the production of hydrogen and support the development of auxiliary power units (APUs) in commercial diesel truck transport as being sponsored by EERE's Hydrogen, Fuel Cells, and Infrastructure Technologies (HFC&IT) Program.

- ***OBJECTIVE: Develop a predictive model / methodology*** for diesel fuel reforming and provide ***necessary tools and information*** to fuel cell/fuel reforming developers and system integrators for ***technology development, performance optimization, and system control.***

Diesel Fuel Processing
Technical Issues / Challenges

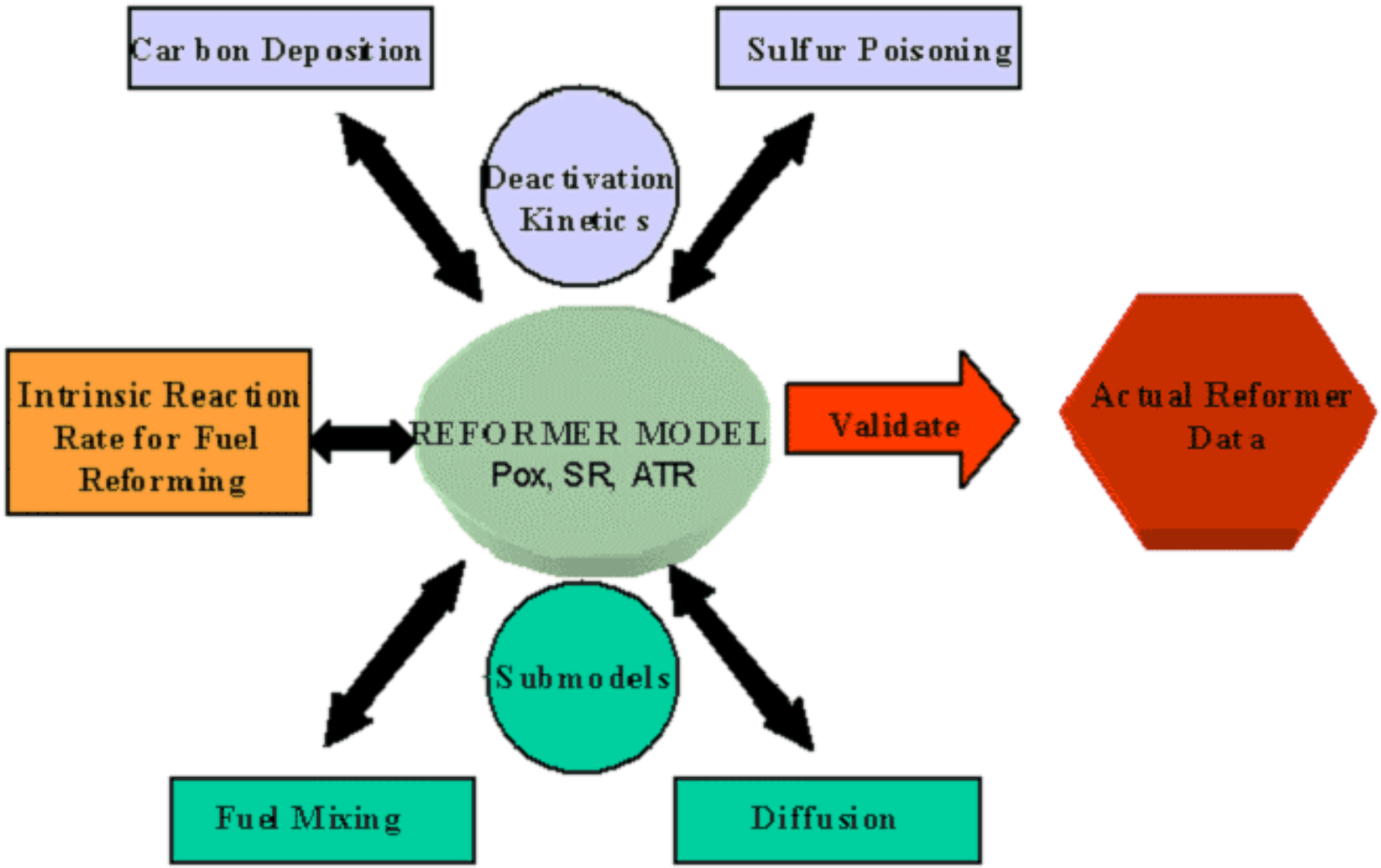
- **Diesel fuel is complex and difficult to reform :**
  - Diesel fuel is a complex, multi-component (>100 compounds) sulfur-containing fuel that exhibits varying reaction pathways and kinetic rates for differing fuels and catalyst types.
  - Deactivation of fuel reforming catalysts and fuel cell components via carbon deposition and sulfur poisoning are the principle technology barriers.
  - Improper reactant mixing in the reformer can lead to hot spots and carbon deposition.
- **System integration can be a significant challenge:**
  - Reformer integration with fuel cell system requires desulfurization, water management, and thermal considerations.
  - Certain FC applications may require high power density design with “fast” response and high efficiency for both steady-state and transient operations.
  - Hydrocarbon slip must be avoided to provide fuel cell with a clean synthesis gas.

Diesel Fuel Processing

Applicability to Fuel Cell APU Commercialization

- Diesel-based fuel cell APUs are considered a significant high volume market for SOFC's.
- Fundamental understanding of diesel reforming and general methodology for kinetic rate determination would be very beneficial to catalyst developers. May extend to hydrocarbon fuels in general.
- A validated CFD model would be useful to fuel reforming developers and system integrators to predict steady-state and transient performance, develop control strategies, maximize efficiency, and minimize cost.

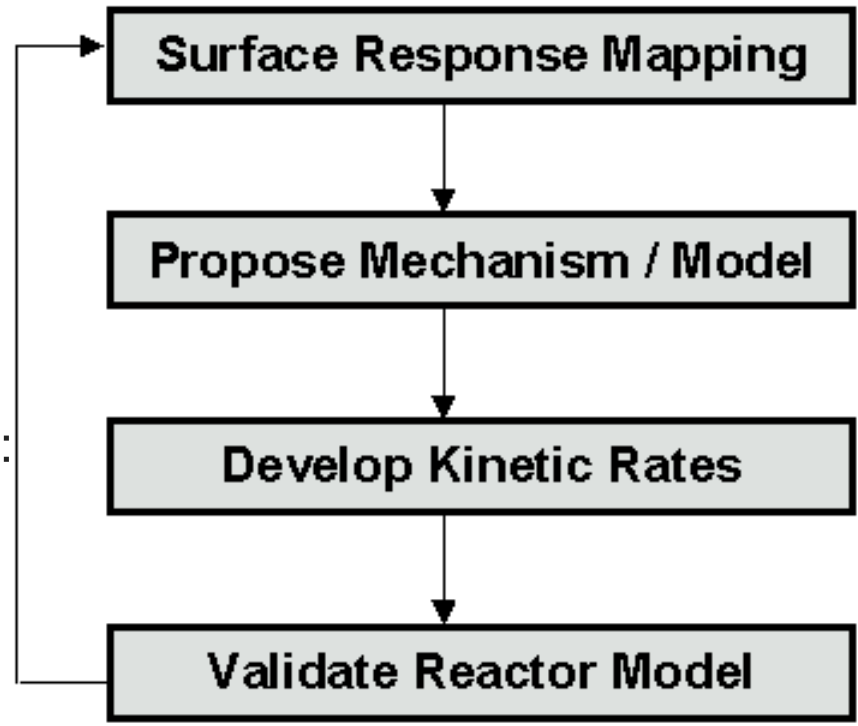
Reformer Model Needs



Diesel Fuel Processing

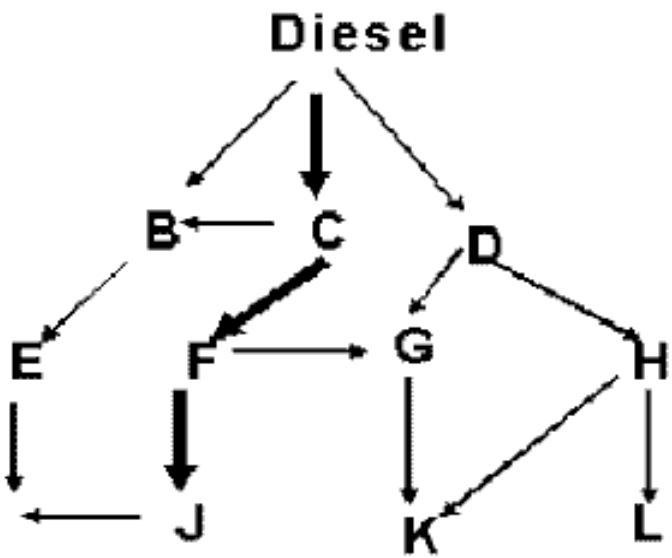
General Modeling Approach

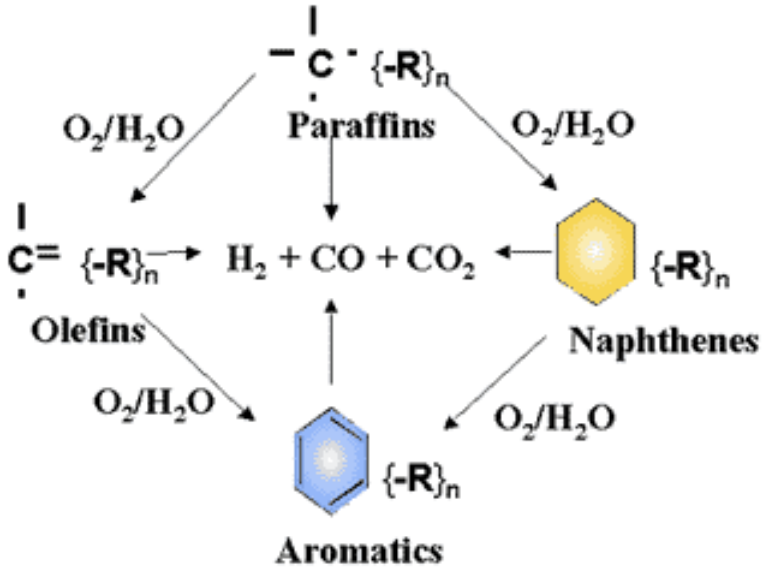
- **Response surface methodology**
  - Process parameter optimization study for the diesel ATR
  - Elucidation of complex chemical networks for the diesel ATR
- **Propose mechanism / model**
- **Develop kinetic rates**
  - Carry out kinetic measurements
    - Representative model compounds: single component & surrogate fuel mixtures
    - Real diesel
- **Validate model**
  - Experimental data



ATR Kinetic Modeling

- Dominant reaction pathways to be elucidated
- Assessment of kinetic parameters





Diesel Fuel Processing
Response Surface Mapping

- **Response Surface Methodology (RSM)**
  - A statistical tool used to map characteristic responses (e.g. selectivity, yield, conversion, carbon buildup, etc.) to input variables (O_2/C, H_2O/C, temp. and hydrocarbon type) over a defined region
    - Results in a deeper understanding of the reaction system and the interaction of parameters that affect the development of predictive models
    - Provides data that can validate kinetic models and proposed reaction pathways
  - Determination of operating conditions to achieve a desired specifications
    - Maximum CO and H_2 selectivity
    - Minimize carbon deposition
    - Minimize hydrocarbon slip

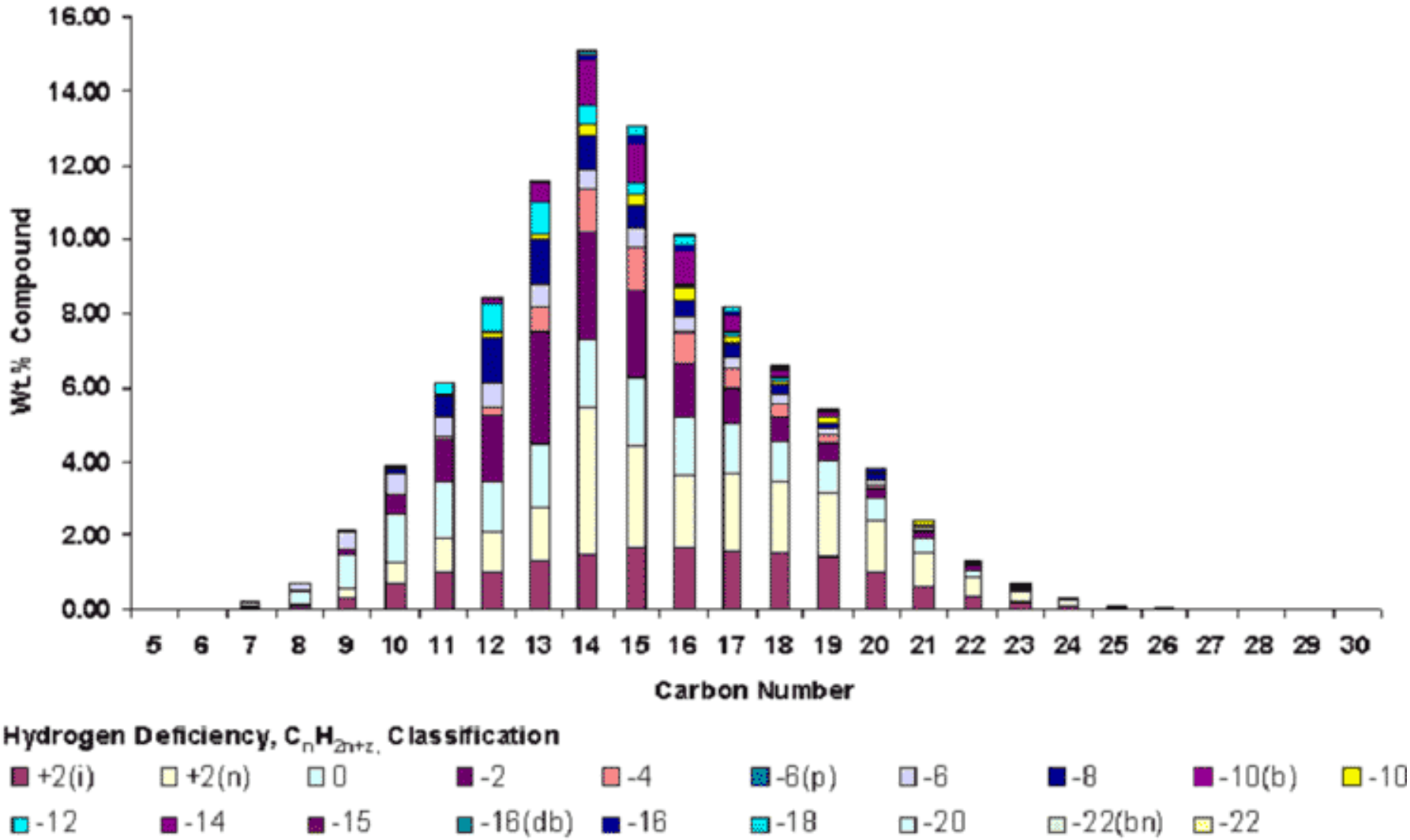
Diesel Fuel Processing

Diesel Fuel Composition – what to test?

- **Diesel Fuel Analysis**
  - Diesel fuel is a complex, multi-component mixture of paraffinic, aromatic and naphthenic hydrocarbons in the range of (C_7-C_{26})
    - An exponential increase in the number of hydrocarbon isomers with increasing carbon number makes compound identification difficult
      - Hydrocarbon compound classification may be made based on hydrogen deficiency, C_nH_{2n+z}
    - GC-FID/MSD – Dual detector system: simultaneous flame ionization detection and mass spectrometry (soft chemical ionization to avoid molecular fragmentation of heavy hydrocarbons)
    - Representative model compounds selected from each major homologous class present in diesel fuel include:
      - Parrafin: n-Tetradecane
      - Aromatic: 1-Methylnapthalene
      - Naphthene: Decalin

Diesel Fuel Processing

Diesel Fuel Composition – Con't.

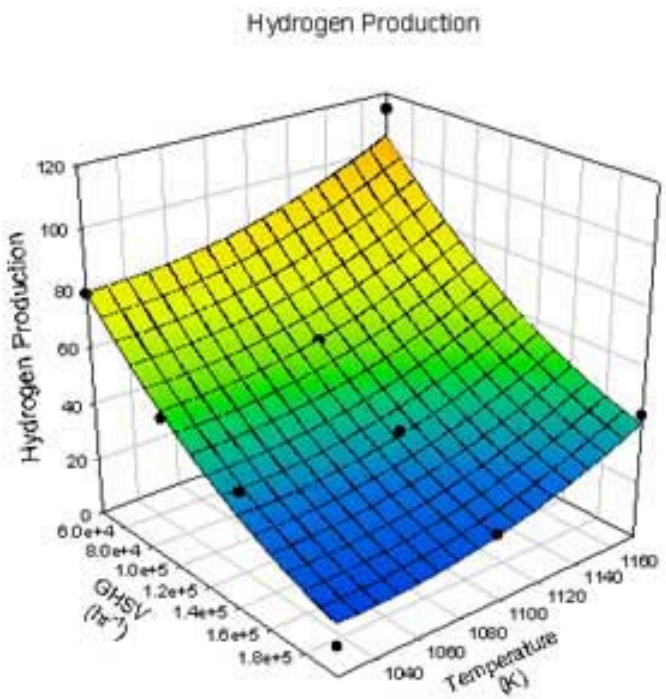


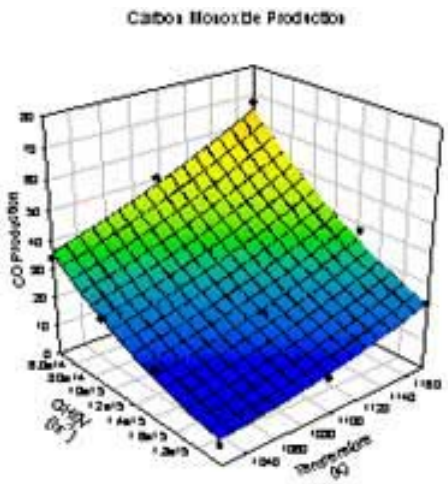
Diesel Fuel Processing

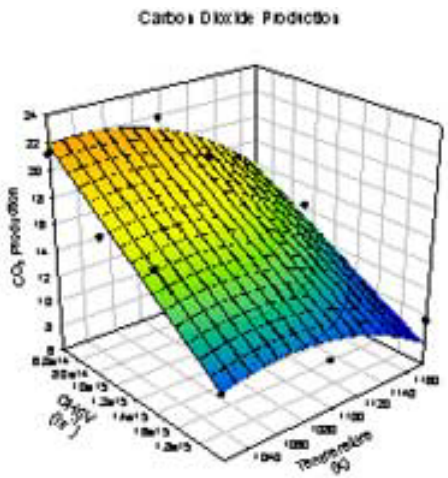
Experimental Conditions

	Paraffin	Aromatic	Naphthene
Model Compound	n-Tetradecane	1-methyl naphthalene	Decalin
O_2/C	0 - 0.5	0 - 0.5	0 - 0.5
H_2O/C	0 - 1.5	0 - 1.5	0 - 1.5
T (°C)	750 – 900	750 – 850	750 - 850
GHSV (h^{-1})	50,000 - 200,000	22,000 - 66,000	50,000 - 150,000

ATR of n-Tetradecane (O_2/C=0.3, S/C=1.5)

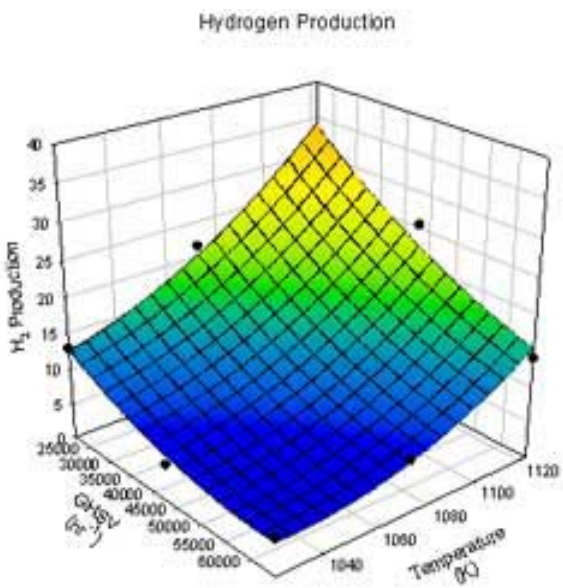


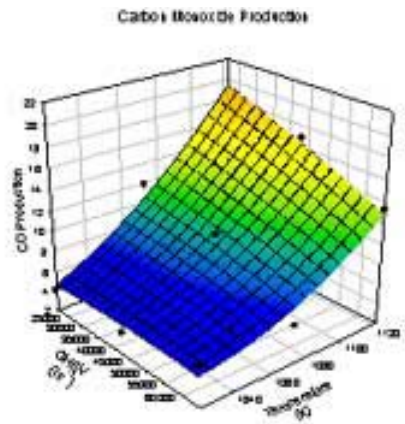


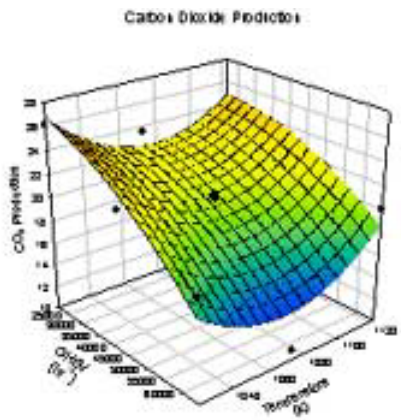


-Reverse WGS reaction dominates at higher T
- Olefins and aromatics produced at higher SV and lower T
- Naphthenes not observed

ATR of 1-Methylnaphthalene (O_2/C=0.3, S/C=1.5)

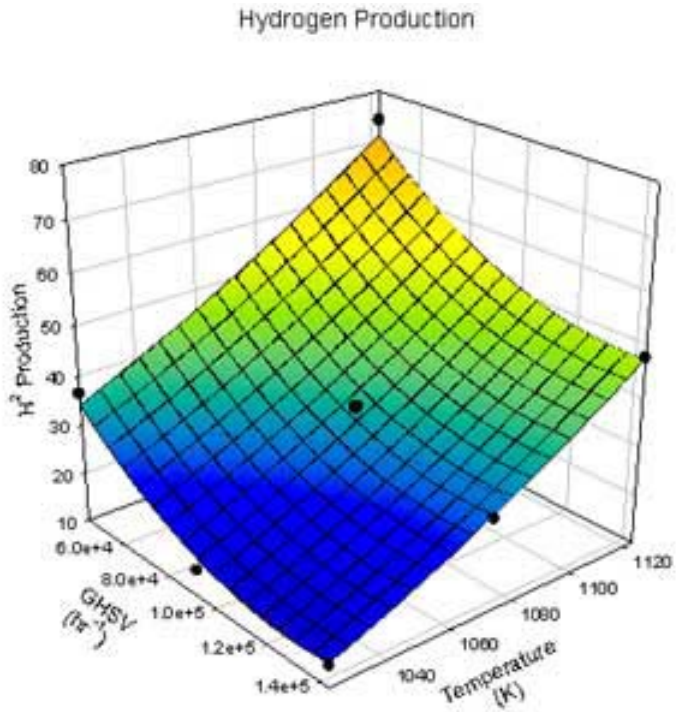


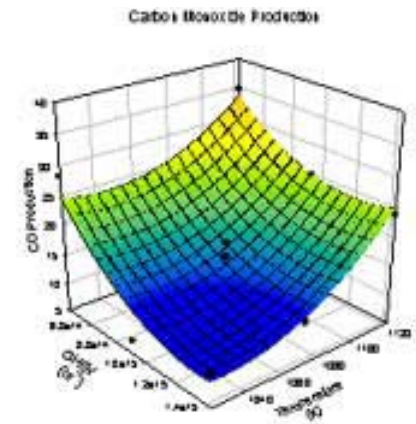


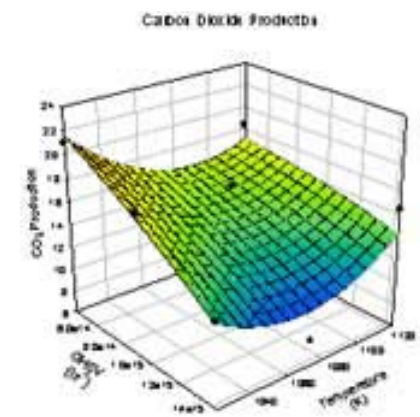


-Reforming rate increases significantly with increasing SV and T
-Slow reforming rate relative to paraffines and naphthenes
-Fast carbon deposition rate
-Naphthenes not observed
-Small concentrations of lower olefins observed
-Methane is the main paraffin formed

ATR of Decalin (O_2/C=0.3, S/C=1.5)

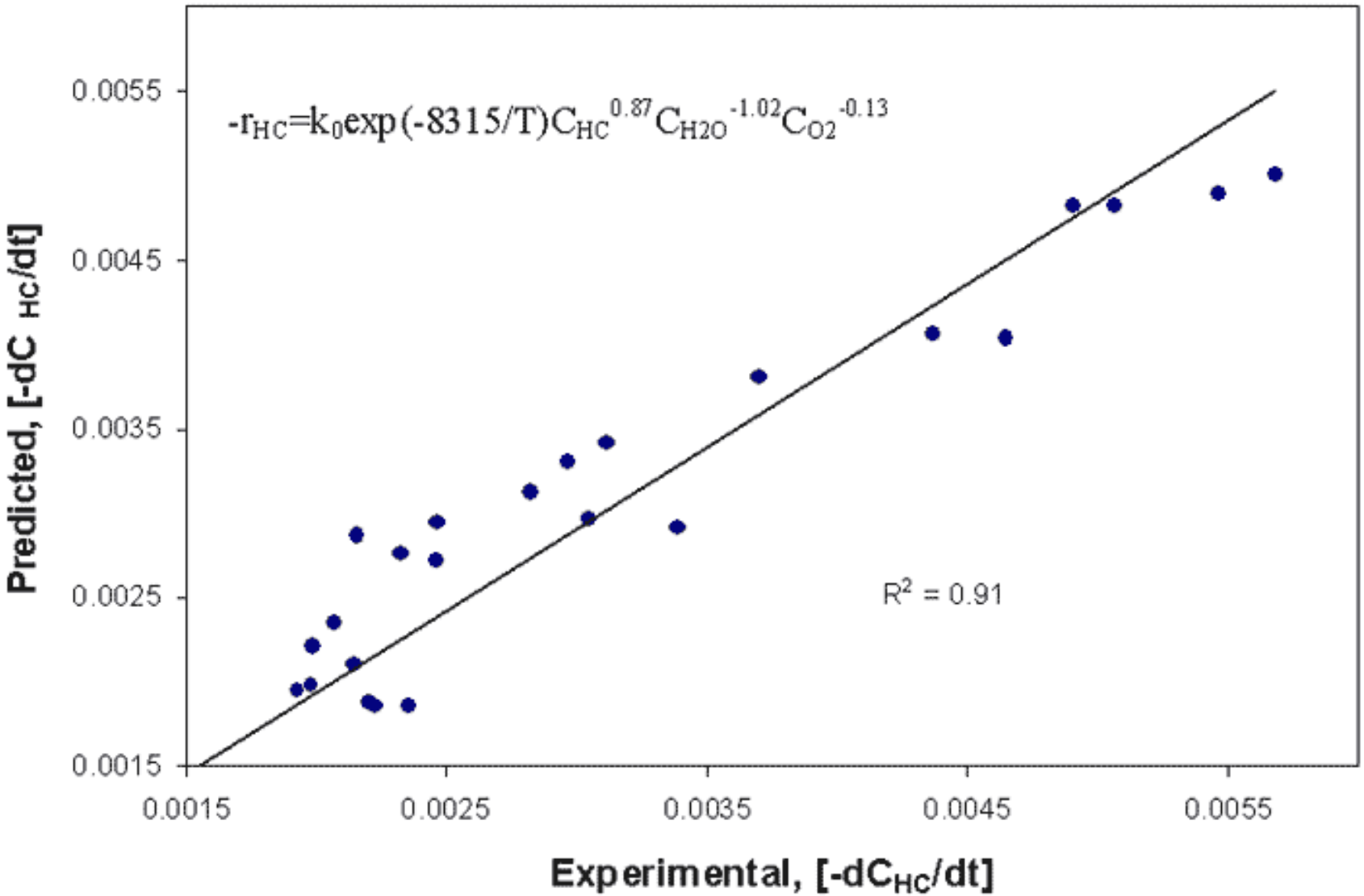






-Aromatics, paraffines, olefins observed in product
-Higher aromatic content in product

Experimental Vs Predicted Values for Diesel ATR on Pt/Al_2O_3



Diesel Fuel Processing

Conclusions / Accomplishments

- Tested three model compounds from the major representative functional groups in diesel fuel
- Developed surface response maps for steam reforming, partial oxidation and ATR over Pt catalysts for single component fuels
- Liquid product distribution varied with the type of reforming performed
- Higher olefins as well as aromatics content in product from ATR/SR/POX of paraffines at lower SV and higher T
- Significant coking observed from reforming (ATR/POX/ SR) of aromatics and naphthenes at higher T (~900 C)
  - Results in high pressure drops
- Quadratic fit of data from RSM was excellent (>90%)
- Reforming rate at the same conditions
  - Aromatics << Naphthenes < Paraffines
- H_2/CO/CO_2 production
  - Moles of (H_2/CO/CO_2) produced*100/moles of carbon fed
- Developed lumped parameter “power-law” ATR model

Diesel Fuel Processing

Future Plans/Collaboration/Tech Transfer

- **Continue Surface Response Mapping :**
  - Evaluate other fuel compounds within a classification to examine if similar reforming behavior exists
  - Conduct combinatorial fuel compound studies
- **Develop Kinetic Submodels**
  - From response mapping, develop intrinsic reaction models for particular catalyst types
  - Continue collaboration/funding with Las Alamos National Laboratory LANL) to provide carbon deactivation kinetics
  - Continue collaboration with Argonne National Laboratory (ANL) to obtain experimental reactor performance data to validate reaction models and provide for fuel reactant mixing modeling capability suitable for CFD modeling codes.
- **Technology Transfer**
  - Continue dissemination of project results through EERE program reviews and FE SECA program reviews to principle developers such as Delphi Automotive, GE/Honeywell, Siemens-Westinghouse, and Cummings/McDermott.

Gallium Nitride Integrated Gas/Temperature Sensors for Fuel Cell System

Monitoring for Carbon Monoxide and Hydrogen

Steve Pyke and Larry Sadwick
Fluence, PO Box 1257, Sisters, OR 97759
Innosys, 3622 W 1820 S, Salt Lake City, UT 84104

Relevance/Objective

- DOE workshop concensus on need for CO detection in hydrogen fuel at 1-100ppm(1)
- Adapt catalytic gate FET sensors for detecting 1-100ppm CO in hydrogen fuel
- Use GaN FET for increased sensitivity and faster response at higher temperature
- Improve precision and accuracy
- Field test for reliability and lifetime

- 1) Sensor Needs and Requirements for Proton-Exchange Membrane Fuel Cell Systems and Direct-Injection Engines, U. S. Department of Energy, Energy Efficiency and Renewable Energy/Office of Advanced Automotive Technologies,

  http://www.ott.doe.gov/pdfs/sensor_needs.pdf

Approach

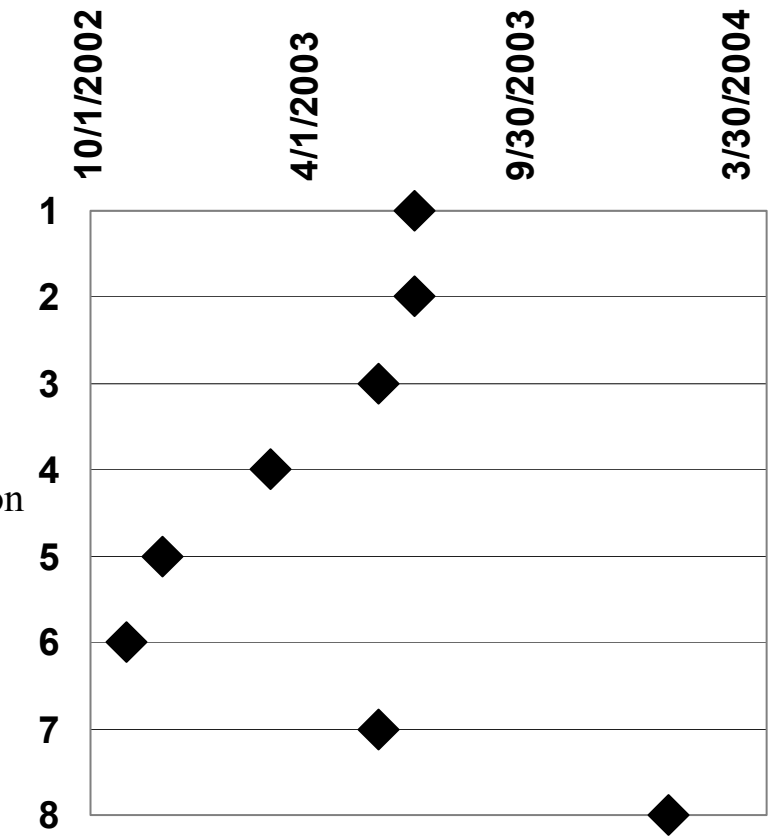
GaN based devices and circuits are an attractive option for high temperature electronic applications including gas monitoring. The effect of gas on GaN devices with metal gates has been studied and documented(1). Catalytic metals such as platinum, rhodium and palladium are good candidates for the gate metal in GaN field-effect-transistor (FET) sensors, because they form good Schottky barriers on n-GaN (necessary for FETs). The same metals are also candidates for CO detection in hydrogen, because each has shown catalytic activity in the preferential oxidation (PROX) process for oxidizing trace amounts of CO by reaction with oxygen in excess hydrogen.

1) Y. Kokubun, T. Seto and S. Nakagomi, Jpn. J. Appl. Phys., 40, L663-L665 (2001). J. Schalwig, G. Muller, M. Eickhoff, O. Ambacher and M. Stutzman, Sensors and Actuators B-Chemical, 87, 425-430 (2002), B.P. Luther, S.D. Wolter and S.E. Mohney, Sensors and Actuators B, 56,164 (1999), S.C. Pyke and L. Sadwick, DOE Report, http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/32405b16.pdf, 2002, S.C. Pyke and L. Sadwick, DOE Report, http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/30535ay.pdf, 2001, and S.C. Pyke, J-H. Chern, J. Hwu and L. Sadwick, DOE Report, http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/28890ii.pdf , 2000.

Project Timeline

Major milestones

1- Main effect testing CO (1-100ppm) and hydrogen (30-70%) **80% Complete**
2- Determine confounding effects due to multiple components **80% Complete**
3- 2nd generation fabrication for increased yield (>50%) **Sensors expected by 6/1**
4- Low cost electronics for improved precision **Noise reduced 10X**
5- Ceramic package **Achieved**
6- Outsource fabrication **Achieved**
7- Method for resolving components using array sensors **Achieved**
8- Field test four prototypes **TBD**



Significant Interactions or Collaborations

- **Invited paper for special session: "High Band Gap Material FET Chemical Sensors", IEEE Sensors 2003, Toronto, October 21-24**
- **Three year collaboration with Larry Sadwick at the University of Utah and Innosys for GaN device design and fabrication**
- **Collaboration with Prof Ed Yu at UCSD bio-sensor proposal, GaN modeling and analysis using AFM and SCM**
- **Planned sensor joint testing with Prof Anita Lloyd-Spetz, S-SENCE and Applied Physics, Linköping University, Sweden**
- **Advanced package development subcontract pending funding: Advanced Sensors, Delphi Energy & Chassis, Flint, MI**
- **Business development discussions in process: Underground Systems Inc. and Quantum Group**

Plans, Future Milestones

- 2nd generation sensors with Pt, Rh, PdAg and Ir
  - Main effect and interference testing
- Field test sites with the following:
  - Hydrogen production process from fossil fuel
  - Process control and analysis in place for validation
  - Wet and dry hydrogen sources
- Market driven product design
  - Redesign sensor for improved precision and accuracy
  - Heater for temperature control
  - Assess cost and reliability of digital vs analog electronics
- Commercial development
  - Hydrogen safety for industrial processes to battery rooms
  - Exhaust gas analysis for NOX and combustion control

Why Use a Gallium Nitride (GaN) FET Sensor?

- GaN is a semiconductor with a 3.4eV band gap attractive for electronics operating at higher temperature than possible with Silicon at 1.11eV
- A FET (field-effect-transistor) sensor is a device made using wafer-based, high-volume, standard industry processes for low unit cost and improved consistency

  -Greater consistency in device to device quality and performance is expected with the narrow dimensional tolerances standard in foundry businesses worldwide

Fiber Optic Temperature Sensor for PEM Fuel Cells

S.W. Allison, T.J. McIntyre, L.C. Maxey, M.R. Cates and W.W Manges

Peter Rainville* and Phillipe Bado**
* Nufern, Inc., **Translume, Inc.

Program Goals: Temperature Sensing

Program Target

- Operating Range: -40 to 150 C
- Response time: <0.5 sec with 1.5% accuracy (-40 to 100 C)
  <1 sec with 2 % accuracy (100 to 150 C)
- Gas environment
- Insensitive to flow velocity

Demonstrated by ORNL

- Operating Range: -250 to 1700 C
- Response time: <0.001 sec with 1.0% accuracy (-0 to 750 C)
- Gas environment: inside operating jet engine, induction furnace, and many laboratory atmospheres including PEM/MEA
- Insensitive to flow velocity: needs to be tested

Project Objectives

- Develop a low cost, robust temperature sensor for monitoring fuel cell condition and performance;
- Develop a fiber optic probe that could provide intra-cell thermal information;
  - thermal mapping;
  - location of hot spots;
- Develop a low-cost architecture for integrating the FO temperature sensor into the fuel cell control electronics -> plug-and-play modular design; and
- Establish a partnership with an approved equipment vendor to facilitate technology commercialization and implementation.

Why a Waveguide Temperature Sensor?

- Reliability - fiber optic sensors are immune to oxidizing or reducing atmospheres, they are electrical insulators and don't drift over time
- Speed - temperature measurements can be made in milli- to micro-seconds
- Simplicity - a fluorescent material, optical waveguide, LED, detector and some simple signal processing are all that is required
- Cost - the production cost is potentially very low, <$5.00
- Flexibility - our concepts will provide single point or multiple measurements of temperature and may enable measurement of other parameters (e.g. thermal gradients, stack compression uniformity and humidity)

Approach: Fluorescence Temperature Sensing

- Atoms in a matrix have electrons thermally excited
- Excited electrons de-excite
  - Radiative and Non-radiative processes compete
  - Non-radiative process increases with temperature
- Time characteristic of the net radiative de-excitation indicates temperature

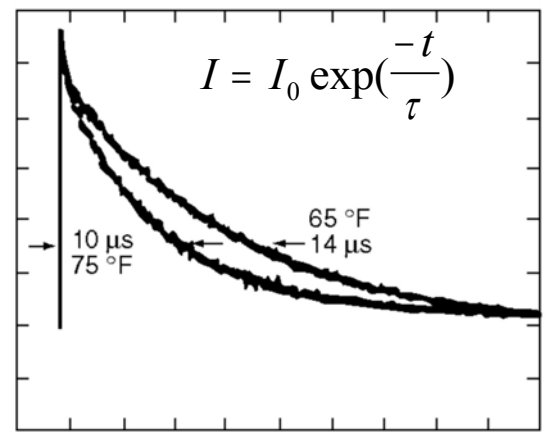
We will exploit this radiative (fluorescence) behavior to measure temperature.

Approach: Fluorescence Temperature Sensing

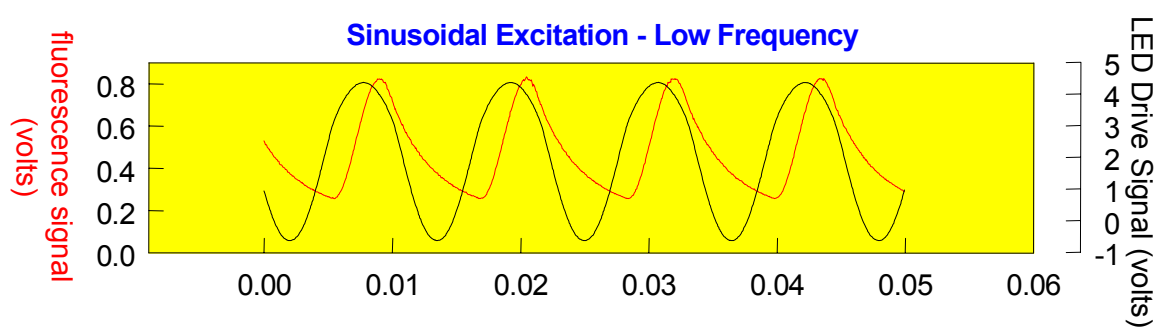
Temperature sensitive phosphor illuminated by excitation light from LED or laser diode

Phosphor glows. If excited by a short pulse, the glow duration indicates temperature. If excited by an oscillating signal, temperature is indicated by phase shift.

$$\tan(\phi) = 2\,\pi\,f\,\tau \qquad \text{where } \tau = f(T)$$



Time Dependence of a Fluorescence Signal at Two Temperatures



Approach: Fluorescence Temperature Sensing

Choosing the best phosphor for the measurement of interest is critical.

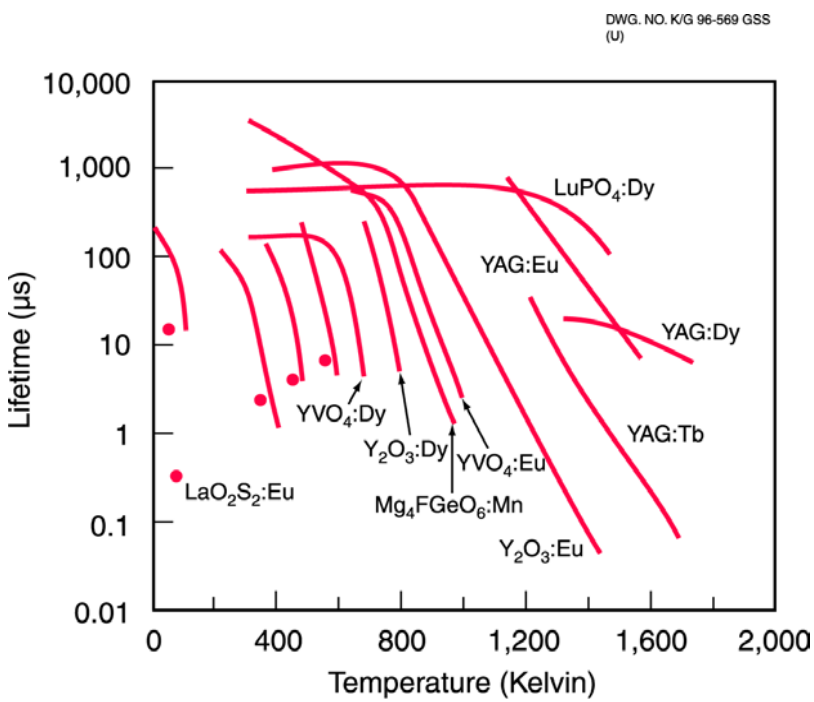
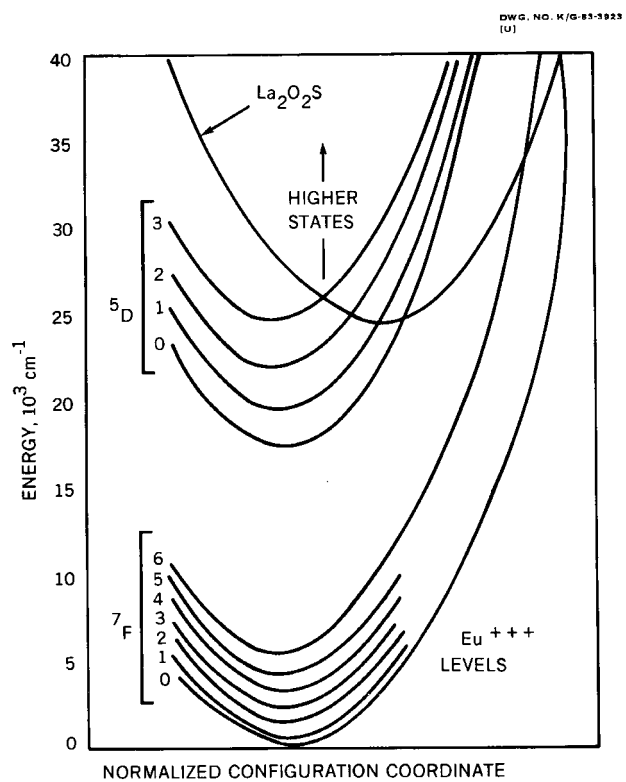
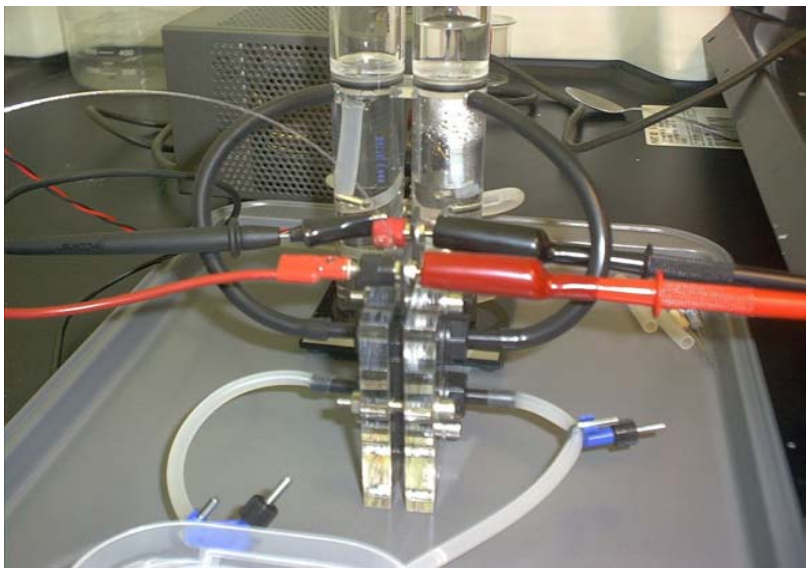


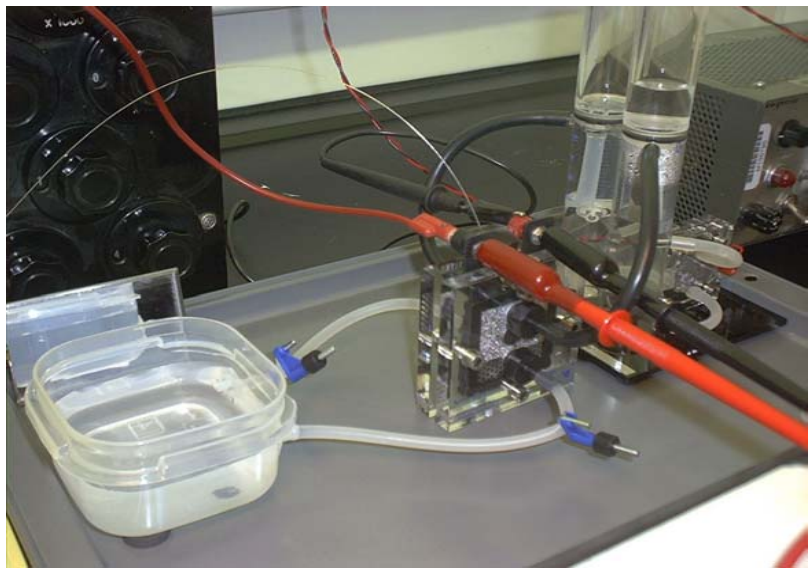
Figure 12. Lifetime versus temperature of selected phosphors.



Approach: Our Current Laboratory Setup

Fuel cell demo kit with 400 micron fiber inserted.

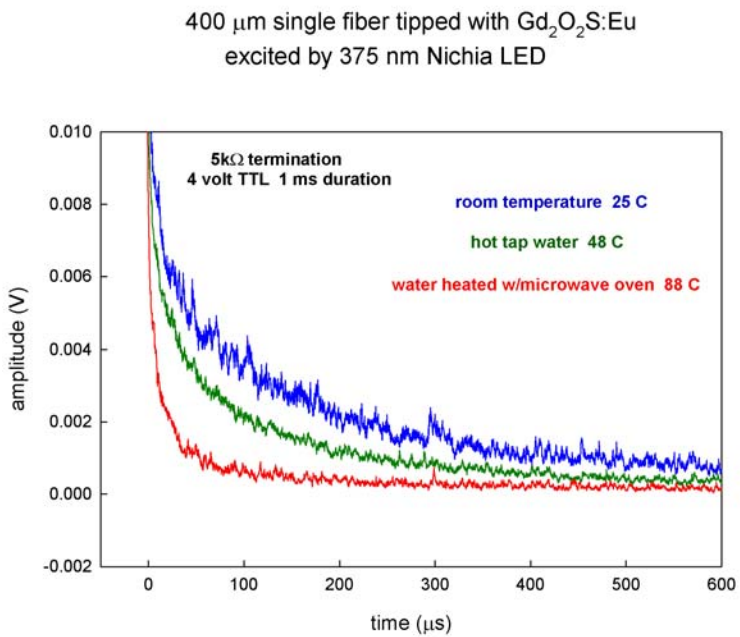


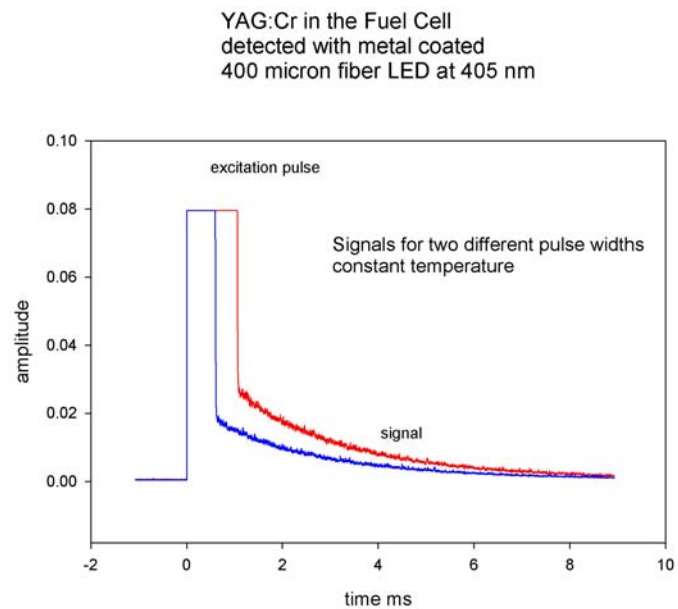


Demonstrated a temperature measurement without causing degradation to fuel cell performance.

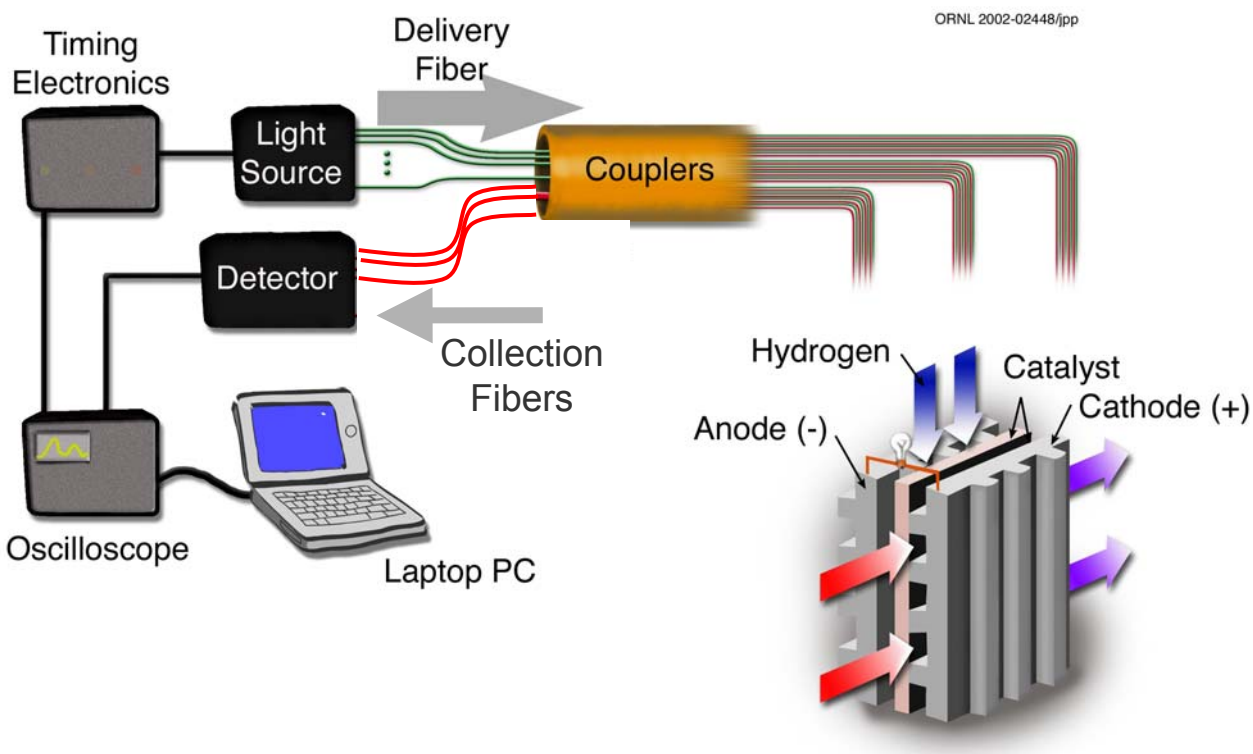
Approach: Some Preliminary Probe Data

Signals from Phosphor-tipped Fibers



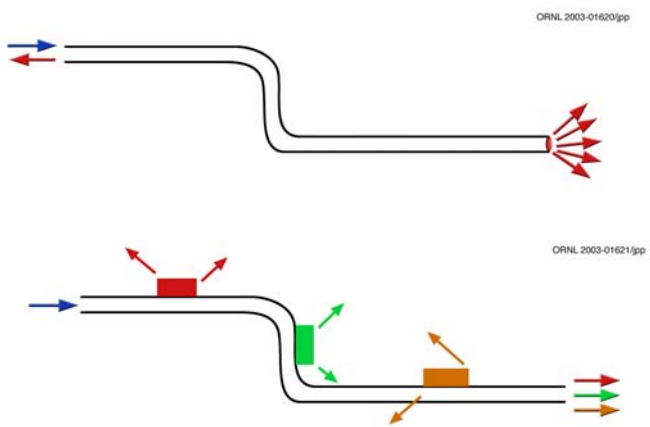


Approach: Our Future Setup to Explore Probe Designs

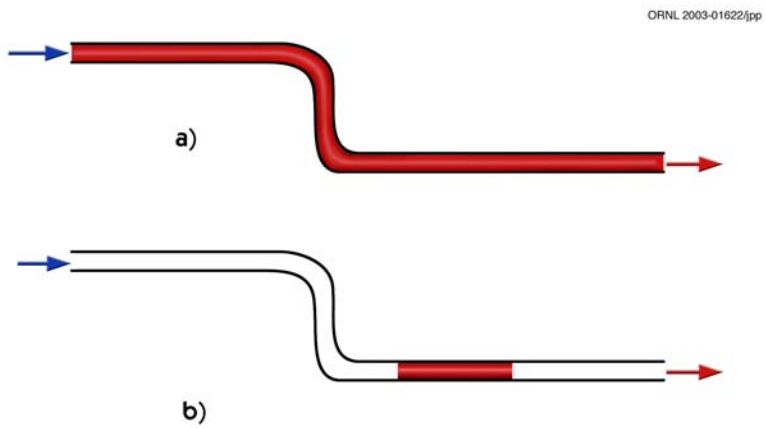


Approach: Various Probe Options Will Be Explored

Ways to exploit the concept of fluorescence in conjunction with optical fibers for measuring temperature



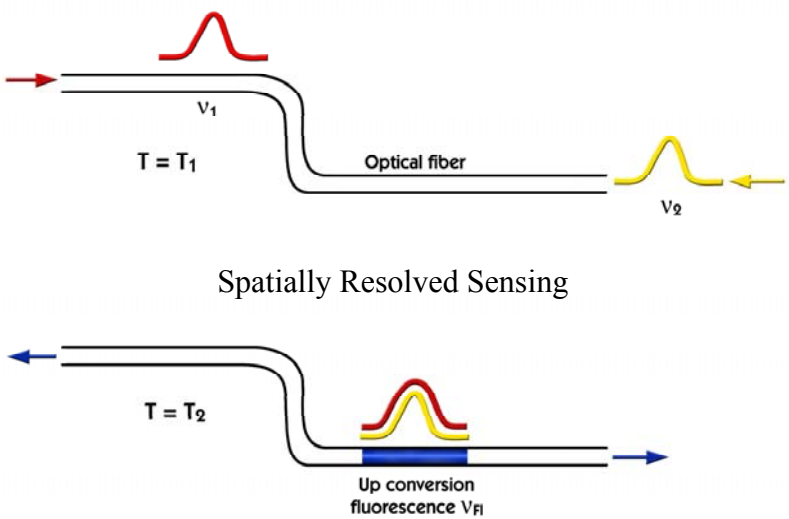
Phosphors coated onto fiber end and side provide highly localized temperature sensing



Rare earth doped fiber provides increased signal and offers novel sensing method

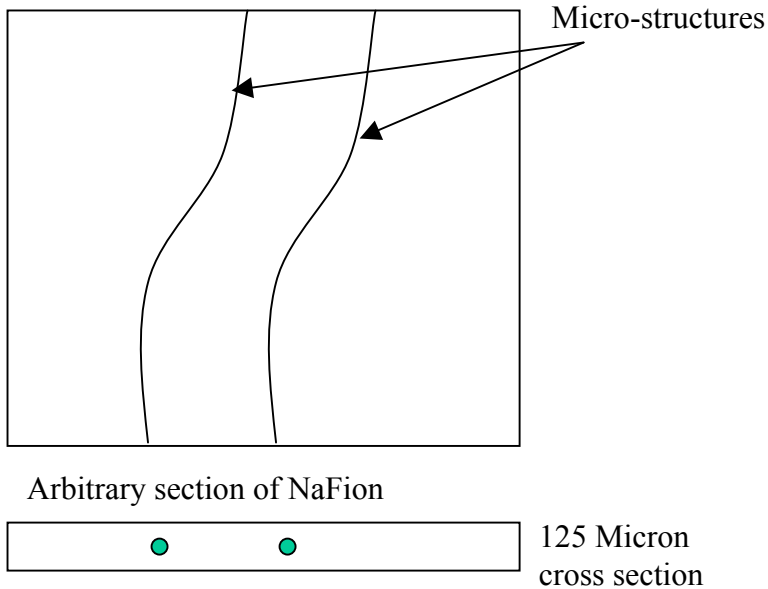
Some Advanced Concepts are Emerging

Two Photon Excitation



Embedded Micro-structures in PEM

(Initial test sample)



Accomplishments

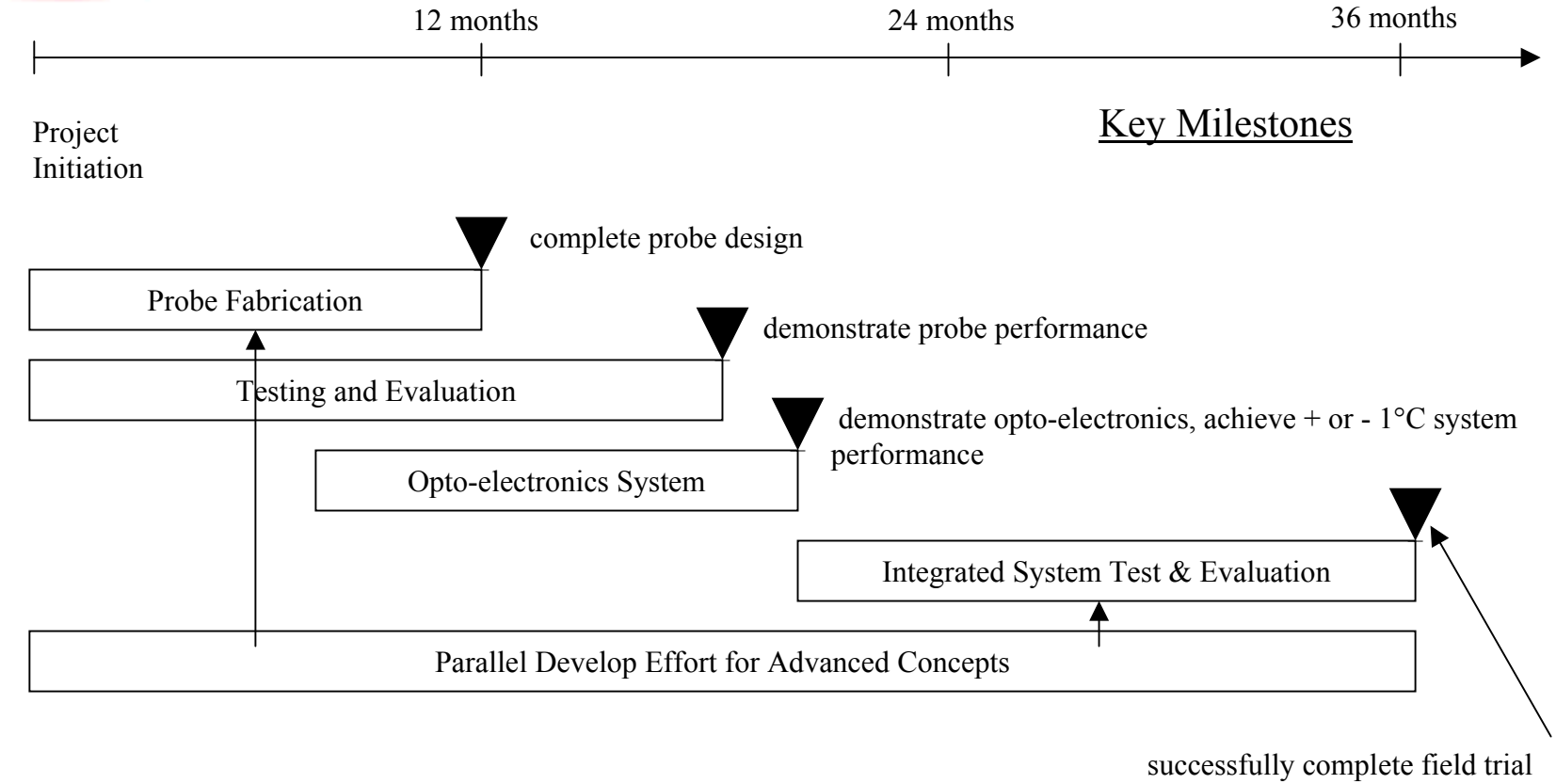
Project Began in January, 2003

- Identified and tested several effective phosphors and crystals.
- Fibers as small as 50 micron core/110 micron clad have been used in probe trade-off studies.
- Operated demonstrator fuel cell with phosphor deposited on PEM and fiber probe inserted.
  - Verified no degradation to FC operation
  - Attempting to measure very small internal temperature changes caused by operation of cell (200mW power output)
- Identified some novel probe/measurement options that may lead to very precise and low cost sensor options.

Collaboration Efforts

We are Already Working with:

- FreedomCAR Tech Team and Big-3 delegates to gain insight into system-level functional requirements;
- Fuel cell developers to understand implementation strategies and specific operational measurement needs;
- PNNL to fabricate custom fibers for studies;
- NuFern and Translume to develop sensor concepts and advanced concepts that may lead to novel, low cost and versatile probe designs;



Project Milestone

Future Plans

- Continue expanding our collaboration activities to ensure maximum benefit is provided to FC developers and end users - need more input from designers and end users.
- Need access to prototype MEAs or detailed guidance to fully explore the design space - HELP!
- Our plans include a parallel development effort on probe designs
  - Simple terminal sensing to prove concept
  - Advanced designs to push the utility envelope
- We think we can measure other parameters with the same or similar sensor implementation - we need your input.

UT-BATTELLE

Selective Catalytic Oxidation of Hydrogen Sulfide

Timothy Armstrong, Xianxian Wu, Andrew Kercher, Nidia Gallego, Steve Overbury, and William Shelton, Oak Ridge National Laboratory

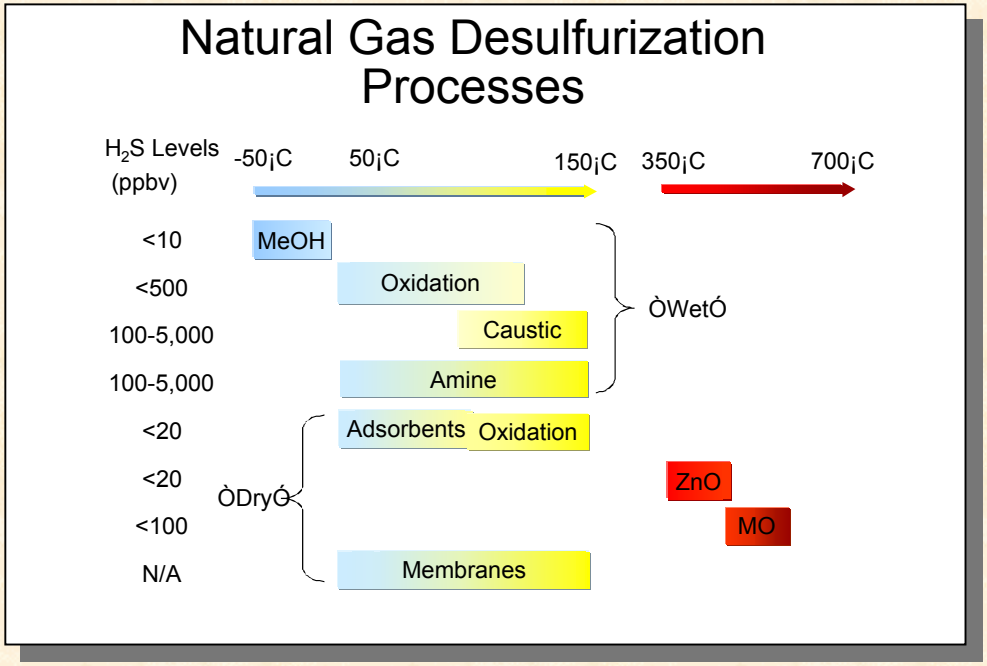
David Berry, Dushyant Shekhawat, and Todd Gardner, National Energy Technology Laboratory

Direct Sulfur Removal

Challenge: All fossil fuels have persistent S contamination. Production of H_2 in the next several decades will be derived from fossil fuels (NG, coal, petroleum). Desulfurized H_2 is a necessity to facilitate reforming to generation of pure H_2 for storage and use in fuel cells use.

- Objective: Develop a warm temperature method direct sulfur removal technology (*gaseous sulfur to solid sulfur*) with parts per billion separation efficiency.
- Goals:
  - Lower initial capital investment
  - Synergysm with available systems
  - Removal of sulfur to 'ppbv' levels
    - $H_2S + 1/2O_2 \rightarrow 1/nS_n + H_2O$

Conventional H_2S removal methods



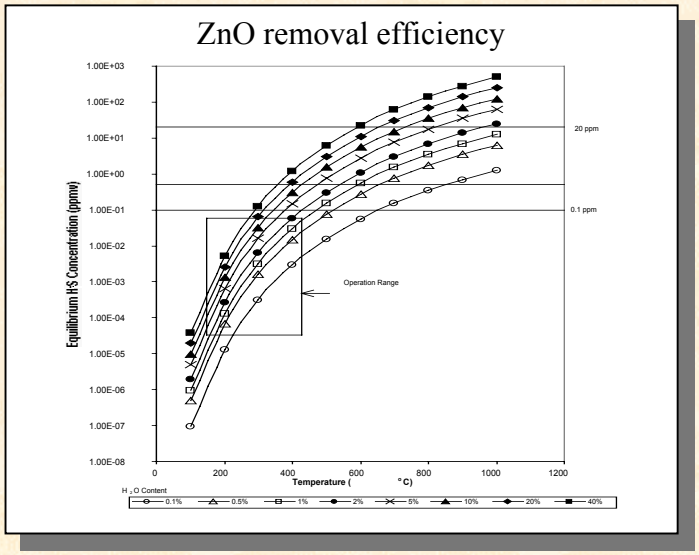
- Currently available catalysts do not meet required performance goals for any H_2 generating or utilization systems.
  - Adsorption processes remove organic sulfides and require high pressure H_2 to regenerate
  - High temperature MO catalysts have short lifetimes and show rapid decrease in activity
  - High-temperature processes generate SO_2
- Need to develop activated carbon catalysts that facilitate oxidation of H_2S:
  - High microporosity and preferential adsorption of H_2S over CO required.

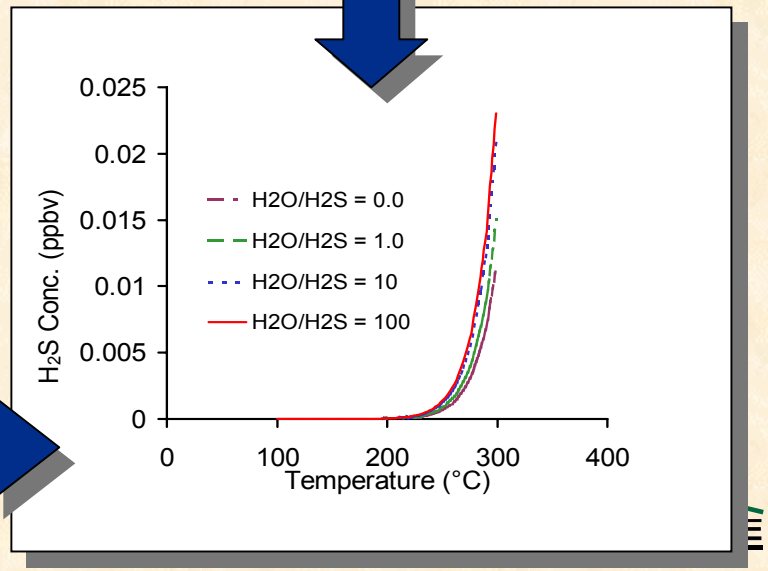
DOE technical targets assume a sulfur level of 6 ppm, *however this target requires development of sulfur tolerant catalysts and membranes.*

Advantages of SCOHS

- **Removal Efficiency:** SCOHS has part per trillion (ppt) thermodynamic sulfur removal efficiencies.
- **Water Sensitivity:** Unlike most metal oxide based systems, SCOHS is relatively insensitive to water content, which can be found in high concentrations in some reformate streams.
- **Operational Mode:** Can operate in continuous or discontinuous modes

- **Benefits:**
  - Water shift reaction catalyst
  - Separation/catalytic membranes
  - Fuel cells using natural gas, transportation fuels
  - Steam reforming catalyst



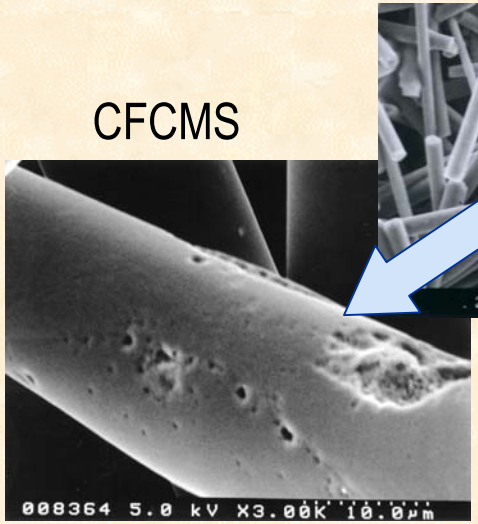


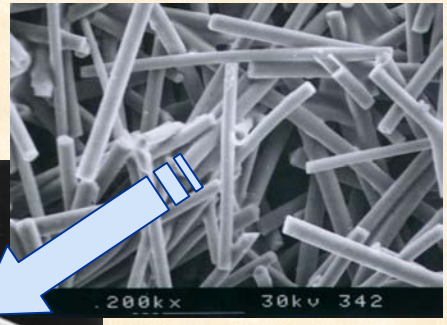
Exceptionally Low Sulfur Levels Can be Achieved with the SCOHS Process

- Carbon-based catalysts offer very exciting potential to reach low (ppt) sulfur levels

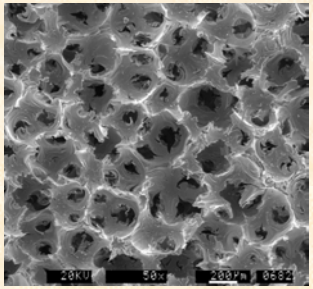
- There are several issues to address:
  - What is the mechanism for preferential adsorption of CO over H_2S?
  - Design materials selective to H_2S.
  - Can high sulfur conversion/removal efficiencies be obtained for H_2S?
  - Can carbon catalysts be synthesized with high activity?
  - What material purity/impurity are required?
  - What factors affect aging and reliability?

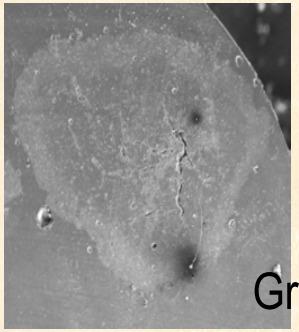
CFCMS





Foam





Granule

Fundamental Understanding Will Be Gained Through Kinetic Studis and In-situ Analysis

Kinetic Studies

- **Kinetics of sulfur adsorption and desorption will be monitored by temperature programmed desorption and reduction experiments and analyzed using IR spectroscopy**
- **Competitive adsorption will be monitored quantitatively using DRIFTS**

Characterization

- **In-situ EXAFS will be developed and used to investigate adsorbed sulfur species at reaction conditions (temperature and environment)**
- **NEXAFS will be investigated as a means to provide information on the electronic structure of the catalyst for correlation to its catalytic activity**
- **EDS and EELS will provide high resolution species identification of impurities and S distribution**
- **Ex-situ reactor available for understanding chemical, structural, and crystallographic changes**

Expected Results of Kinetic and In-situ Studies

Will independently quantify effects of:

[1] catalytic activity of various activated microporous carbons

[2] impurities on catalytic activity and structure

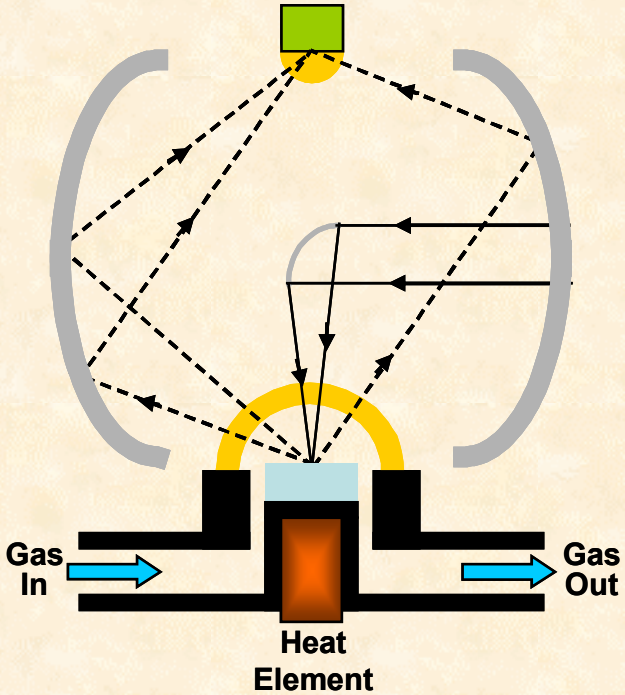
[3] Sulfur removal, conversion efficiency competitive adsorption of H_2S vs. CO

[4] competitive adsorption of H_2S vs. C on conversion efficiency

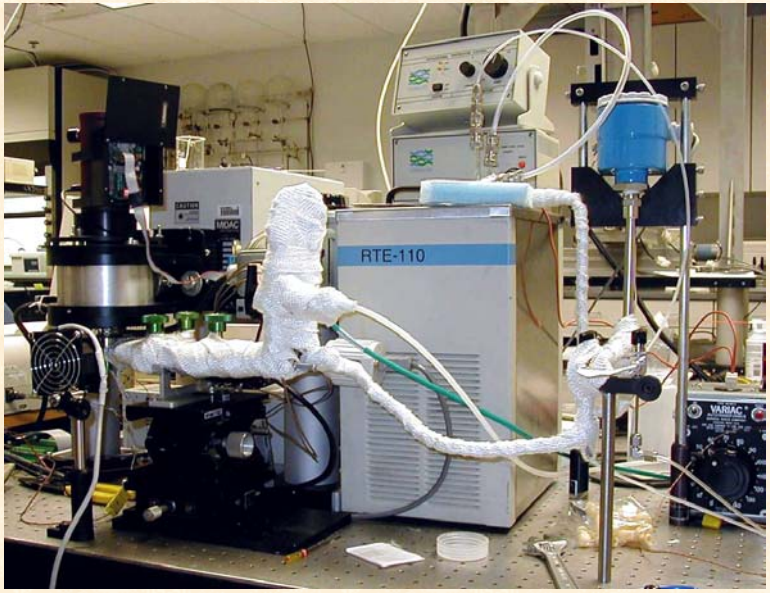
Provide fundamental scientific basis to develop breakthrough carbon catalyst technology with high sulfur and low CO selectivity for gas cleanup

DRIFTS

***D**iffuse **R**eflectance mid-**I**nfrared **F**ourier **T**ransform **S**pectroscopy*



DRIFTS can provide quantitative in-situ analysis of catalytic reactions by analyzing spectroscopic changes due to the functional group content



DRIFTS instrument made available through ORNL-NTRC collaboration:

- MIDAC FTIR spectrometer
- Harrick DRIFT accessory
- Spectral range 4000-500 cm-1
- 1 cm^{-1} resolution

Graphics courtesy of ORNL-NTRC

Prototype Structures for Activated Carbon Materials

- Generate prototype carbon structures consistent with experiment
  - STM studies
- Perform adsorption studies on a number of local configurations
  - activated carbon is amorphous: Adsorption occurs locally
  - Provide information on the variety and strength of bonding, heats of formation of key molecules (I.e. CO-S, etc.) on specific local environments
- This information would be used in conjunction with experiment to try to process out local atomic arrangements that favor CO-S formation
- First Principles Total Energy calculations
  - Input: atomic species
  - Local density approximation to density functional theory
    - Treating the quantum many body of effects of electron exchange and correlation

H_2S Catalytic Partial Oxidation Process Chemistry

- H_2S partial oxidation reaction
  - Discovered 1883 by Carl F. Claus
    - $H_2S + {}^1/_2O_2 \longrightarrow {}^1/_8S_8 + H_2O$
    - ${}^1/_8S_8^{(s,l)} \longleftrightarrow {}^1/_nS_n^{(g)}$

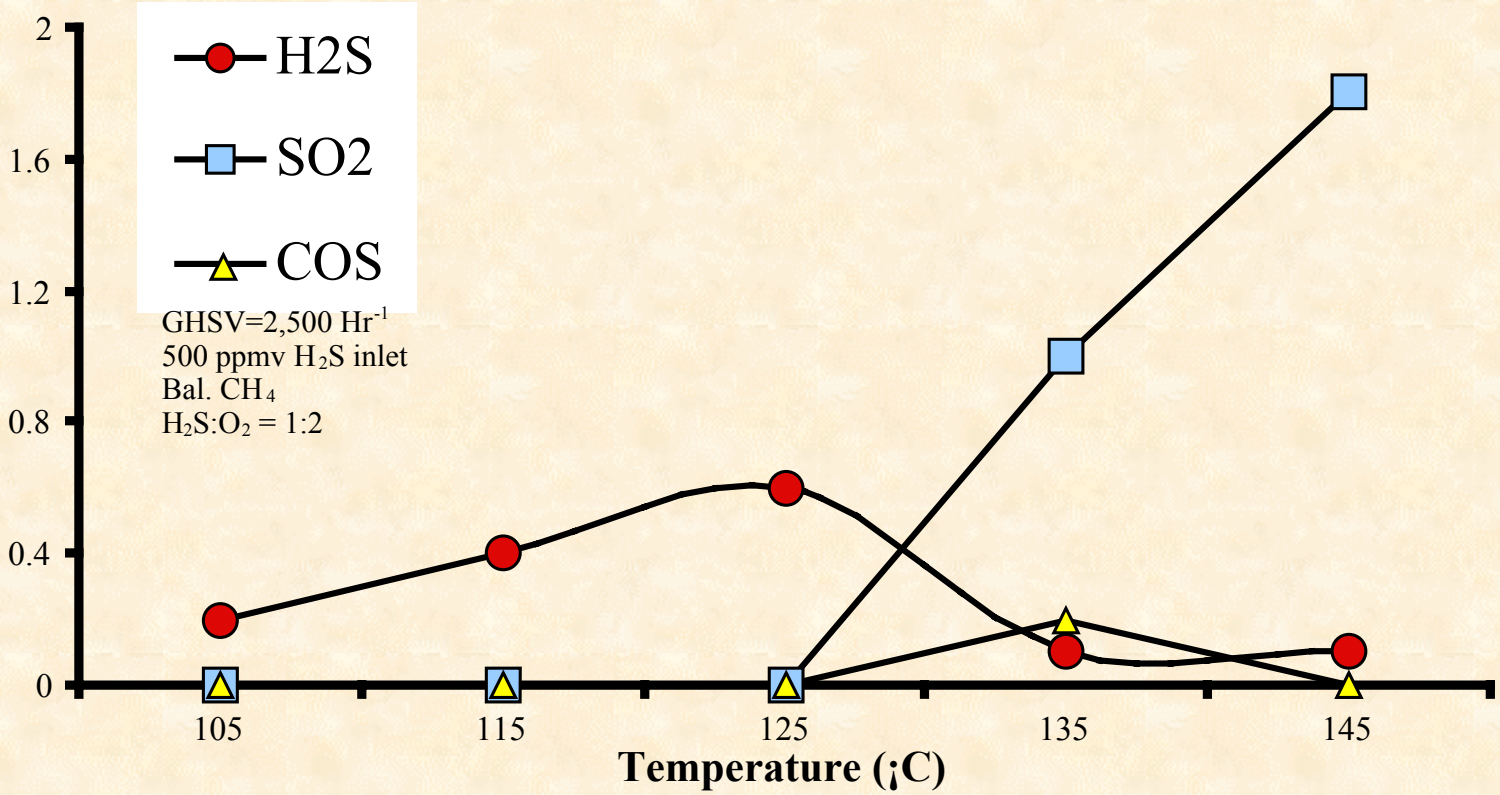
ΔH_r^{400K} (KJ/mol)	ΔG_r^{400K} (KJ/mol)
-208.3	-182.6

$P_v^{400K} = 6.92$ Pa

$P_v^{500K} = 764$ Pa

- Possible side reactions
  - ${}^1/_nS_n + O_2 \longrightarrow SO_2$ — -300.2 / -300.9
  - $H_2S + {}^3/_2O_2 \longrightarrow SO_2 + H_2O$ — -518.6 / -487.5
  - ${}^1/_nS_n + CO \longrightarrow COS$ — -31.0 / -28.4
  - $2CO \longrightarrow C^{(s)} + CO_2$ — -173.3 / -101.9
  - $CO + {}^1/_2O_2 \longrightarrow CO_2$ — -283.5 / -248.3

H_2S Partial Catalytic Oxidation Performance in Natural Gas



Testing and analysis carried out by NETL

Program Milestones

- **Fabricate and test several different types of catalysts from activated granular carbons to more sophisticated activated nanowebs and monolithic fibrous structures. (9/03)**

- **Establish a working simulation model capable of describing the catalytic reaction that can be used to guide catalyst synthesis. (9/03)**

Anticipated Developments

- **Development a reliable (ppb level) desulfurization catalyst with minimal or no CO adsorption**
- **Develop a continuous desulfurization process**
- **Develop an understanding of role of surface impurities and defects on adsorption of H_2S and CO in activated carbon**

Relevance to DoE R&D Plan

The presence of sulfur and other impurities is a fundamental barrier to the practical implementation of fuel cell concepts. In particular, fuel cell durability is strongly affected by impurity content.

- Sulfur affects the durability of *fuel cell components*, *fuel processors and distributed energy systems.*

Fuel-Flexible Fuel Processors Technical Barriers:

H_2 Purification/ CO Clean-up	"Liquid fuels contain impurities such as sulfur compounds. These compounds and their derivatives as well as CO must be removed to prevent loss of performance in the fuel cell."

Significant Collaborations

- Collaboration with NETL on reactor design and test methods
- Discussions with SGL Carbon on carbon materials development
- Interest in technology from:
  - ChevronTexaco
  - ConocoPhillips

Solid Oxide Fuel Cell Auxiliary Power Units for Long-Haul Trucks

Modeling and Control

Mohammad Khaleel, Brian Koeppel, Stewart Moorehead

Pacific Northwest National Laboratory

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Project Objectives

- Develop dynamic model of APU system including SOFC, diesel POX reformer, power conversion electronics and electrical hotel loads.
- Design a system controller to minimize diesel fuel consumption while satisfying electrical load requirements.
- Investigate different system configurations and their impact on overall efficiency.
- Determine the dynamic response of an APU systems to the vibration environment characteristic of a Class VIII truck.
- Develop a structural finite element model to determine dynamic stresses for a planar SOFC stack in the APU.
- Define vibrational limits for SOFC materials based on dynamic stresses and appropriate failure criteria.

Project Description

Long-haul trucks require electrical power to operate lights, heating/air conditioning and televisions while parked for the operator to rest. These loads are often referred to as hotel loads, since the truck cab serves as a hotel room for the driver. Auxiliary Power Units (APU) based on diesel generators are used to provide this power, rather than idling the engine, because they use less fuel and reduce wear and maintenance of the truck engine. While still in the research phase, Solid Oxide Fuel Cell (SOFC) based APUs hold the promise of greater energy efficiency, lower operating costs, lower emissions, and quiet operation. The SOFC APU Modeling and Control program at the Pacific Northwest National Laboratory (PNNL) has two primary goals: 1) develop control systems to utilize the APU efficiently for typical truck hotel loads and 2) develop a dynamic structural model to assess APU durability for the vibrational environment characteristic of large trucks.

Relevance

- Demonstrates component and system durability (FreedomCAR objective).
- Tool to minimize SOFC weight (FreedomCAR goal of 50% weight reduction for vehicle structure and subsystems).
- Improved modeling and control will increase efficiency and reduce costs (FreedomCAR goal of 45% efficiency in reformer based fuel cells).
- SOFC based truck APU will reduce long haul truck fuel usage and dependence on foreign oil (FreedomCAR objective).
- Tool for improving start-up time and reducing sulfur content in APU reformates (HFC&IT goals).

Accomplishments to Date

- Creation of APU System model in MATLAB.
- Electro-chemical and thermal model of SOFC during heat-up and operation phases.
- Dynamic model of truck HVAC system, including inrush current at startup and heat source of driver.
- Controller to regulate cathode air temperature during heat-up phase to prevent thermal shock and stress of SOFC stack.
- Creation of lumped parameter model in ANSYS to determine influence of APU components on stack dynamic response.
- Creation of detailed finite element model of SOFC stack to determine resonant frequencies and dynamic stresses due to harmonic excitation.

Project Timeline

Task	%	Start	Finish
Numerical Modeling			
System Controls Modeling	3	1-Oct-02	30-Sep-05
System Configuration and Connectivity Options	100	15-Dec-02	30-Jan-03
Develop Dynamic SOFC Model	90	1-Jan-03	31-May-03
Develop Dynamic Balance of Plant Model	60	1-Feb-03	15-Jun-03
Complete System Dynamic Models		15-Jun-03	15-Jun-03
Examine Dynamic Performance	5	1-May-03	15-Aug-03
Evaluate Dyanmic Performance During Start-up		15-Aug-03	15-Aug-03
Determine Control Variables	100	1-Jan-03	30-Jan-03
Determine Dependences of Variables	50	1-Feb-03	30-Jun-03
Design and Test Controller	10	15-Apr-03	15-Sep-03
Initial System Controller Complete		15-Sep-03	15-Sep-03
Incorporate Sulfur into Model		1-Oct-03	1-Feb-04
Collect Empirical Data from SOFC and POX		1-Jan-04	1-Jun-04
Develop System ID Models for Internal Variables		1-Feb-04	1-Jul-04
Improved System Model		1-Jul-04	1-Jul-04
Refine Controller to Increase Efficiency		1-May-04	1-Aug-04
Connectivity Options to Increase Efficiency		1-May-04	1-Aug-04
Increased System Efficiency		1-Aug-04	1-Aug-04
Design and source controller and APU hardware		1-Aug-04	15-Sep-04
Preliminary Design for APU Hardware		15-Sep-04	15-Sep-04
Implement Controller on Real APU		1-Oct-04	30-Sep-05
Functioning APU with Control		30-Sep-05	30-Sep-05
Structural Modeling	3	1-Oct-02	30-Sep-05
Material Property Definition	80	1-Dec-02	30-Jan-03
Dynamic Excitation Definition	80	1-Jan-03	30-Jan-03
Lumped Parameter Model	70	1-Jan-03	30-Apr-03
Finite Element Stack Model	60	1-Feb-03	30-May-03
Vibration Models & Methods Complete		30-May-03	30-May-03
Failure Modeling	5	1-May-03	1-Aug-03
Parametric Analysis	0	1-Jul-03	1-Sep-03
FY03 Analysis Completed		1-Sep-03	1-Sep-03
Modeling Support for Seal Testing		1-Oct-03	1-May-04
Modeling Support for PEN Testing		1-Oct-03	1-May-04
Lifetime Durability Modeling		1-Nov-04	1-Jul-05
Data Gathering			
Truck Experimental Data Collection		1-Oct-03	30-Sep-04
Identify Industry Collaborator		1-Jan-04	1-Jan-04
Determine APU mount locations		1-Mar-04	1-Apr-04
Define Test Conditions and Procedure		1-Mar-04	1-May-04
Gather Vibration Data		1-May-04	30-Jul-04
Log Data of Real Truck APU Usage		1-Jan-04	1-Apr-04
Component Dynamic Testing			
Seal and PEN Durability Testing		1-Oct-03	30-Sep-04
Define Geometry, Test Matrix and Procedure		1-Oct-03	30-Dec-03
Room Temperature Dynamic Testing		1-Jan-04	1-May-04
Elevated Temperature Dynamic Testing		1-Mar-04	1-Aug-04
Forensic Examination of Failure		1-Feb-04	30-Jul-04
Mock-Up Durability Testing		1-Oct-04	30-Sep-05
Define Representative Cell Geometry		1-Oct-04	30-Dec-04
Determine Method to Leak Check Geometry		1-Nov-04	1-Feb-05
Generate Test Matrix, Procedure, and Specimen		1-Nov-04	1-Mar-05
Room Temperature Dynamic Testing		1-Feb-05	1-Jul-05
Elevated Temperature Dynamic Testing		1-Apr-05	1-Aug-05
Forensic Examination of Failure		1-Mar-05	1-Sep-05
Testing Completed for Mockup		1-Sep-05	1-Sep-05

Collaborations

Georgia Tech : Failure modeling.

U. of Illinois at Chicago : Electrical system modeling.

Delphi : APU modeling and controls.

PACCAR : Real world data and relevancy.

Lumped Parameter Model

Simplified model to analyze vibration amplitude of planar SOFC stack due to base excitation of an APU system.

Approach

- Represent components as single degree-of-freedom (SDOF) oscillators with generalized mass and stiffness parameters using the assumed-modes method and Hamilton's Principle.
- Perform sine sweep over the frequency range of interest with appropriate base excitation and obtain stack loading history.

Results

- APU model implemented in ANSYS. Model outputs displacement, velocity, or acceleration response histories for each APU component.
- Solutions to assess Influence of APU components on stack response can be performed quickly.
- Frequency response curve for the SOFC stack is generated for use in detailed 3-D model.

Resonant frequencies predicted for the stack.

DOF	Component	Frequency (Hz)
U Z	Separator	188
U Z	PEN	389
U Z	Stack	8907
U X	Stack	3788
U Y	Stack	3788
ROT X	Stack	9472
ROT Y	Stack	9519
ROT Z	Stack	4339

Next Steps

- Include realistic inertial properties for APU components.

Hamilton's Principle

$$\int_{t_1}^{t_2} \delta(T-V)dt + \int_{t_1}^{t_2} \delta W_{NC} dt = 0$$

Potential and Kinetic Energy Expressions for Plate Bending

$$V = \frac{1}{2}\int_0^b\int_0^a D\left[\left(\frac{\partial^2 w}{\partial x^2}+\frac{\partial^2 w}{\partial y^2}\right)^2 - 2(1-\nu)\left(\frac{\partial^2 w}{\partial x^2}\frac{\partial^2 w}{\partial y^2}-\left(\frac{\partial^2 w}{\partial x \partial y}\right)^2\right)\right]dxdy$$

$$T = \frac{1}{2}\int_0^b\int_0^a \rho h(\dot{w})^2 dxdy \qquad \text{where } D = \frac{Eh^3}{12(1-\nu^2)}$$

Equation of Motion for SDOF Representation of Plate

$$m^*\ddot{Z}(t) + c^*\dot{Z}(t) + k^*Z(t) = 0$$

Generalized Parameter Expressions (undamped)

$$m^* = \int_A \rho h \Psi^2(x,y)dA$$

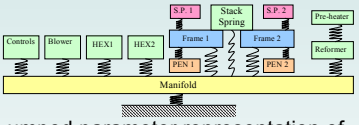
$$k^* = \int_A D\left[\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}\right)^2 - 2(1-\nu)\left(\frac{\partial^2\Psi}{\partial x^2}\frac{\partial^2\Psi}{\partial y^2}-\left(\frac{\partial^2\Psi}{\partial x\partial y}\right)^2\right)\right]dA$$

Assumed Mode Shape for Simply Supported Plate

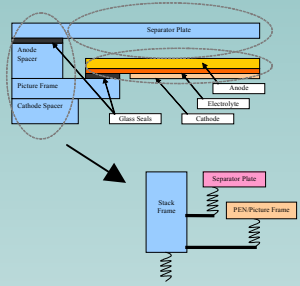
$$\Psi(x,y) = \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi y}{b}\right)$$

Generalized Parameters

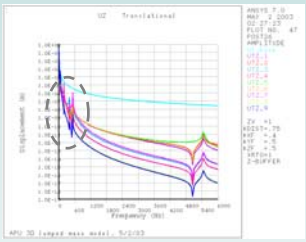
$$m^* = \rho h\frac{ab}{4} \qquad k^* = \left(\frac{Eh^3}{12(1-\upsilon^2)}\right)\left(\frac{\pi^4}{4ab}\right)\left(\frac{b^2}{a}+\frac{a^2}{b}\right)^2$$



Lumped parameter representation of APU model components



The cell is modeled as three masses representing the stiff outer frame, the separator plate, and the PEN/picture frame.



Resonant stack frequencies observed near 200-400 Hz.

3-D Finite Element Model

Detailed model to analyze dynamic stresses in the stack materials.

Approach

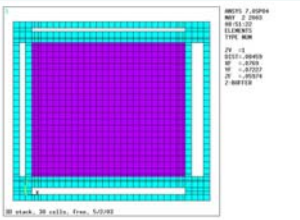
- Obtain spectrum response solution for full 3-D model of 30 cell SOFC stack based on response curve from lumped parameter model.
- Determine dynamic stresses in the stack materials, particularly for the PEN structure and glass seal interfaces.

Results

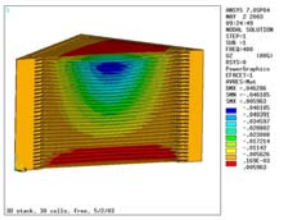
- Generic stack model generated in ANSYS. Model currently performs a modal solution to identify critical frequencies and a harmonic solution to obtain stresses at a given frequency.
- Dynamic stresses obtained for the PEN materials and glass seals. The model also includes contribution of thermal stresses due to temperature distribution and CTE mismatches.

Next Steps

- Extend solution method to perform spectrum response.
- Perform parametric analysis to identify sensitivity of stresses to various stack parameters.

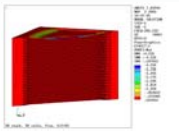
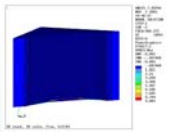
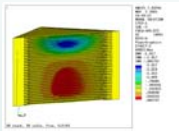
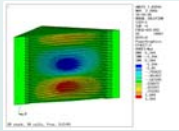


Footprint for generic stack (0.155 x 0.145 m)



Displaced geometry for 4 g translation loading at 400 Hz

Modal results for 30 cell stack

Frequency (Hz)	Mode Shape
285 (Separator Plate)	
366 (PEN)	
409	
410	

Component Failure Modeling

Incorporate failure models into the detailed FEA model to determine vibrational limits for the stack.

Approach

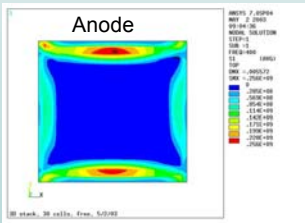
- Leverage existing DOE-funded failure modeling for SOFC materials.
- Incorporate fracture and thermal shock criteria into the FEA model.
- Identify vibrational limits for the APU based on component stresses and failure criteria.

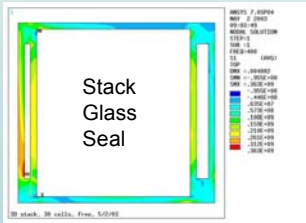
Results

- High localized stresses observed in the PEN and seals indicate that failure modeling is required for moderate acceleration loads.

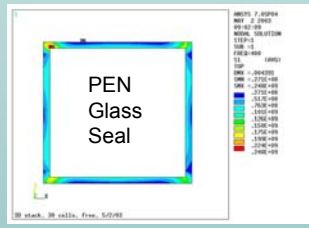
Next Steps

- Collaborate with Georgia Tech student to incorporate their SOFC failure models.





Principal stresses in the glass seals and PEN materials due to 4 g translational loading exhibit localized stresses in excess of estimated fracture strengths. (YSZ ≈ 100-300 MPa, Ni/YSZ ≈ 100 MPa, glass ≈ 50-100 MPa)



Solid Oxide Fuel Cell (SOFC) Modeling

Represent electro-chemical and thermal behavior of an SOFC.

Approach

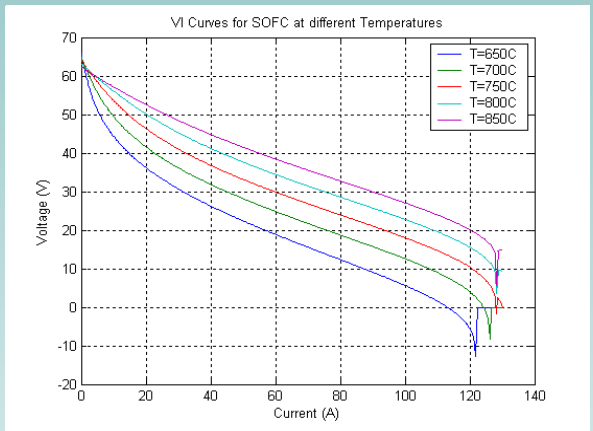
- Leveraging off existing DOE funded electro-chemical models of SOFCs, converting to MATLAB for use in controller development.
- Extending static models to include dynamics, focusing on thermal portion of the SOFC stack.

Results

- SOFC model implemented in MATLAB. Model outputs anode and cathode exhaust compositions and temperatures, fuel utilization, cell voltage and waste heat.
- Model predicts changes in stack temperature during heat-up and operation phases. Stack temperature affects electro-chemistry.
- Model captures important dynamics, showing effects of changing temperatures and behavior during heat-up phase.

Next Steps

- Improve thermal model during operation phase, incorporating results from CFD modeling efforts.



VI Curves for SOFC generated from MATLAB model show the dependence of fuel cell performance on stack temperature.

Auxiliary Power Unit (APU) System Model

The APU System model comprises the SOFC, reformer and support components that make up the APU, as well as the controller, power conditioning electronics and electrical hotel loads powered by the fuel cell.

Approach

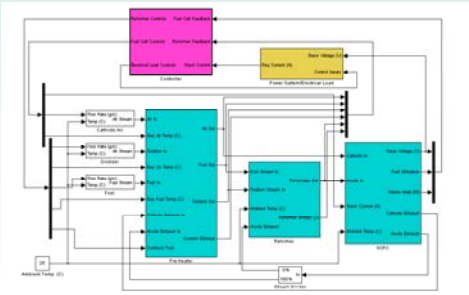
- Create modular models to allow investigation of different connectivity options and allow for continual improvements.
- Use diesel POX reforming for applicability to trucks.
- Model power system to convert SOFC voltage to fixed bus voltage. Focus electrical load models on a few major loads such as HVAC.

Results

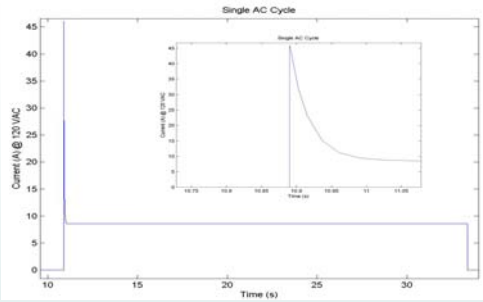
- Complete system model created in MATLAB.
- Model of HVAC based on commercial unit. Inrush current when AC turned on is included. Model uses physical dimensions of an actual truck and includes a 100W occupant heat source.

Next Steps

- Complete implementation of diesel based POX reformer.
- Incorporate latest power electronic modeling work.



MATLAB model of APU System including controller and electrical system/load.



Single Air Conditioner cycle (insert showing detail of inrush current).

Controls

The APU system is a challenging multi-input, multi-output (MIMO) control problem. The controller needs to make sure that the APU is operating at a point that can satisfy the electrical load requirements at all times, while minimizing fuel use. Long heat-up times for the SOFC mean that the controller must anticipate load requirements.

Approach

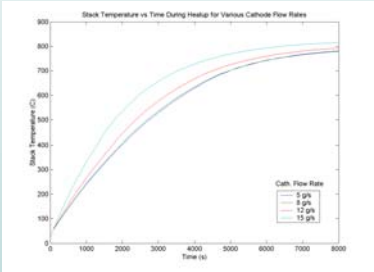
- Design separate controllers for heat-up and operating phases.
- Controller predicts load requirements based on prior usage.
- Build system identifiers to infer internal, distributed parameters of the SOFC stack. Knowledge of these variables can improve system performance and increase stack lifetime.

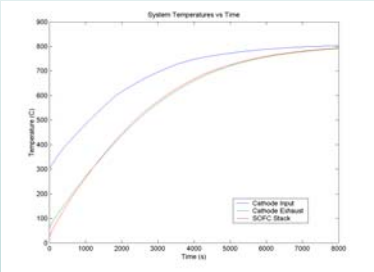
Results

- Completed controller for heat-up phase. Controls cathode air temperature based on stack temperature to prevent thermal shock and fatigue in SOFC stack.

Next Steps

- Implement operating phase controller.





Control Variables

Diesel flow rate
POX air flow rate and temperature
Reformate temperature
Cathode air flow rate and temperature
Anode re-circulation percentage
Stack current

System Outputs

Stack Voltage
Fuel Utilization
Anode and cathode exhaust
Stack Temperature

Reforming of Diesel Fuel for Transportation Applications

J. P. Kopasz, S. Lottes, D-J. Liu, R. Ahluwalia, V. Novick and S. Ahmed
Argonne National Laboratory

Applications of diesel fuel reforming

- Produce fuel (H_2-rich gas) for PEM and/or solid oxide fuel cells (SOFCs)
- Reduce NO_x emissions through reformate injection in internal combustion engine (ICE) and/or reformate feed to selective catalytic reduction unit

Challenges in Diesel Reforming

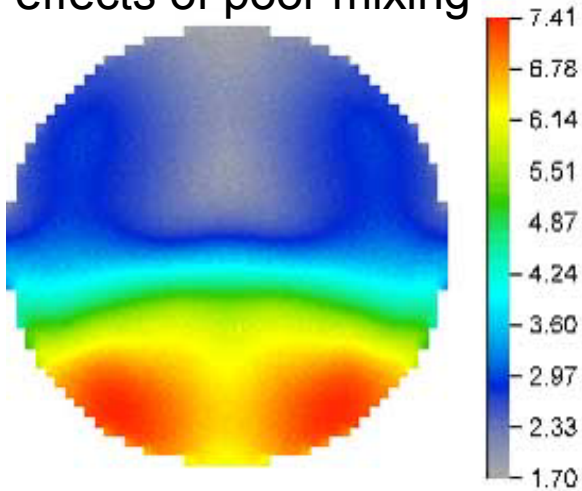
- Extending catalyst lifetime- high temperatures needed for diesel reforming degrade catalysts
- Preventing coking while maintaining high reforming efficiencies

To address these issues we are investigating

- Reactor engineering- to provide better reactant mixing, eliminate hot-spots and provide better temperature distribution
- CFD modeling of reactors
- Reforming chemistry- to determine how diesel fuel formulations, H_2O:C, and O_2:C ratios affect reforming efficiency, coking, and catalyst lifetime
- Work addresses technical barriers J, M and N

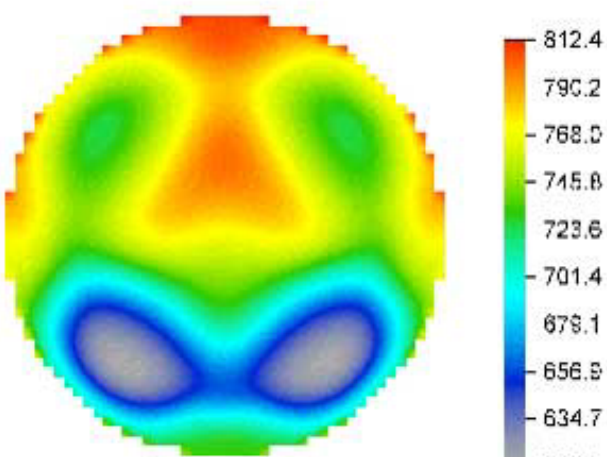
Modeling/Reactor engineering

CFD simulations show effects of poor mixing

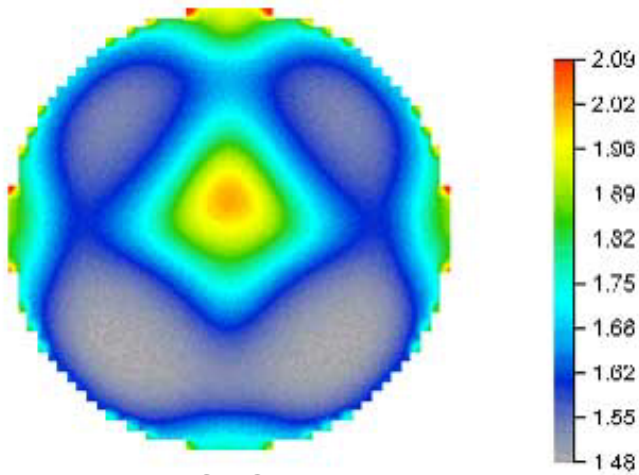


Fuel:Air Equivalence ratio

- Modeling and experiments indicate mixing of reactants is critical in avoiding hotspots and cold spots
- Proper mixing helps avoid coke formation by maintaining proper H_2O:C and O_2:C ratios



Catalyst Temperature



H_2O:C ratio

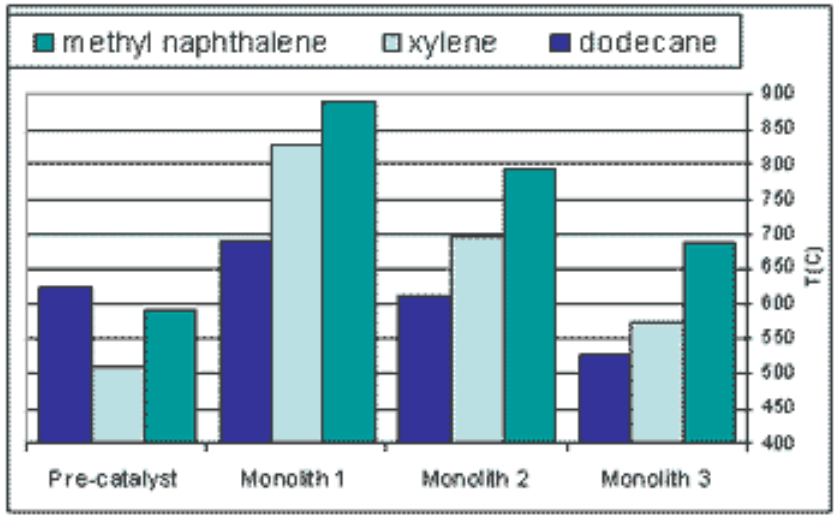
Developed injector nozzle to provide intimate mixing at reactor-relevant conditions

Developed 3- fluid injector nozzle which produces small droplets (<10μm), with low air-side pressure drop which intimately mixes fuel, steam and water prior to catalyst bed

3-fluid nozzle delivers a fine mist of fuel

Reforming Chemistry

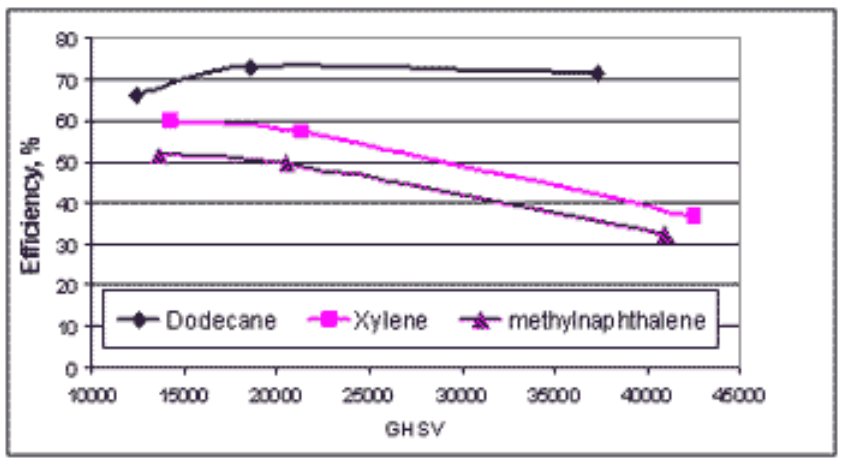
Effect of fuel on catalyst temperature



Determined effects of Fuel composition on catalyst temperature and reforming efficiency using pure component tests

Temperatures >850ºC lead to rapid catalyst deactivation

Effect of fuel on efficiency



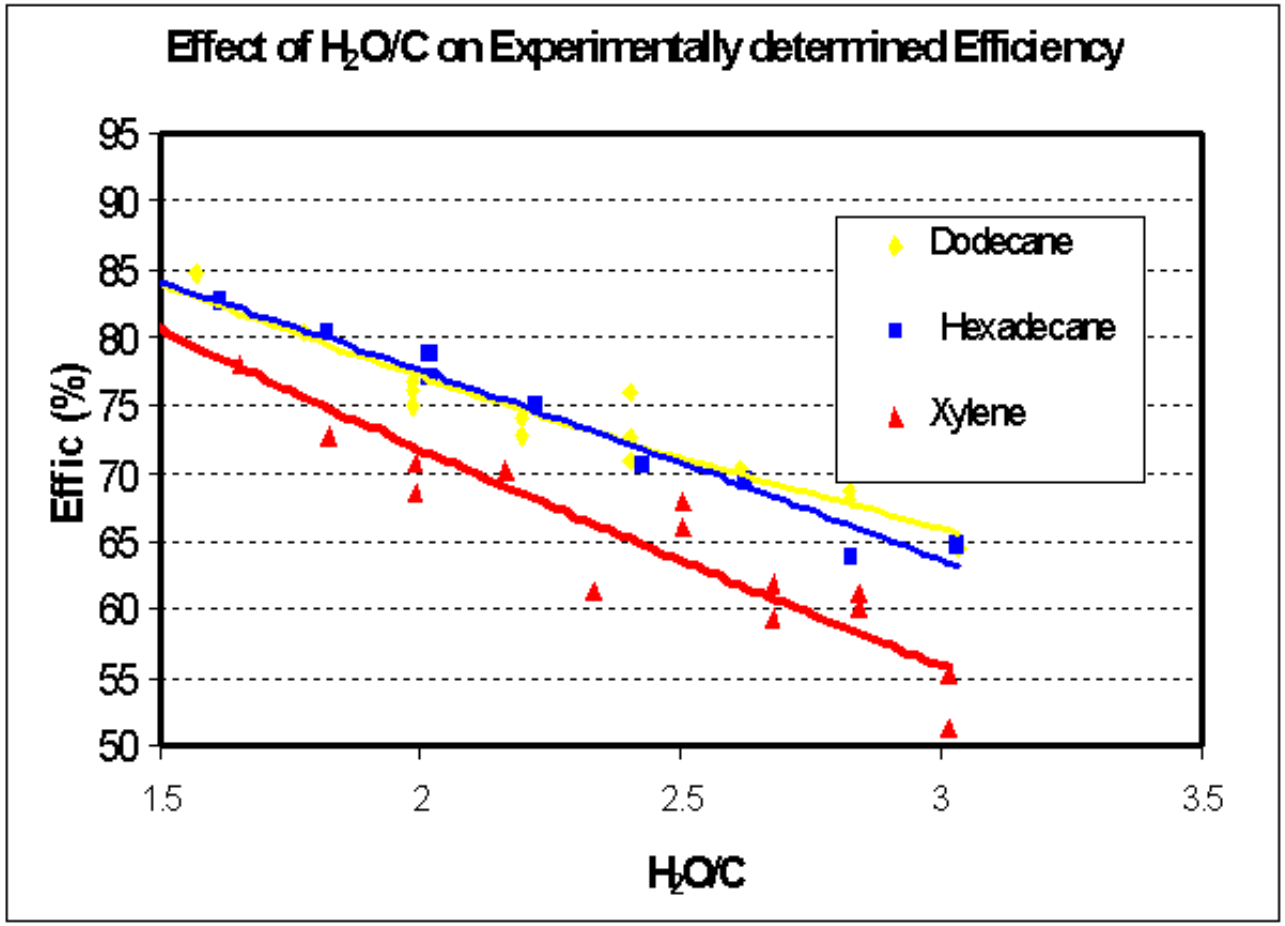
Fuel reforming efficiency to H_2 + CO, ηref

$$\eta ref = \{ct,_{H2}\Delta Hc,_{H2} + ct,_{CO}\Delta Hc,_{CO}\}/ct,_{fuel}\Delta Hc,_{fuel}$$

Ct,i = Molar flow rate of i

$\Delta Hc,i$ = Heat of combustion of i

Effect of Increasing H_2O:C Ratio



- To avoid coking, many reformers are run at high H_2O:C ratios
- Increasing H_2O:C has a negative impact on conversion efficiency

Conclusions/Accomplishments

- Proper delivery and mixing of reactants are needed to obtain high efficiencies and avoid hot spots and areas of low H_2O:C and O_2:C ratios
- Demonstrated operation of liquid fuel injector
- Determined substantial differences in reforming of different diesel fuel constituents
  - Aromatics result in higher maximum reforming temperatures and lower energy conversion efficiencies
  - *Di-aromatics are more difficult to reform than mono-aromatics.*
  - *Increasing H_2O:C ratio reduces coking but decreases overall efficiency*

Future Plans

- Determine how fuel composition affects catalyst durability
- Investigate reforming under POX conditions and in low H_2O:C regimes
- Collaborate with NETL (modeling efforts)

Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer

Greg A. Whyatt

Introduction

The objective of the FASTER (Feasibility of Acceptable Start Time Experimental Reactor) project is to build and test an experimental fuel processor with an acceptably short cold start-up time. The system will utilize an autothermal reformer (ATR) with water-gas shift (WGS) and preferential oxidation (PROX) reactors. Between the outlet of the ATR and the entrance to the WGS reactor is an assembly being provided by PNNL which is the subject of this poster. The assembly is designed to fit within the FASTER geometry and contains two primary components.

The first component is a recuperator in which heat is extracted from the ATR reformate to preheat the air and steam feed to the ATR. This cools the reformate to a temperature suitable for the WGS catalyst. The heat recovered from the hot reformate allows the system to operate in an energy efficient manner.

The second component is a microchannel mixer which is positioned at the reformate outlet from the recuperator. During startup, it is planned to mix air with the reformate and allow oxidation of reformate to occur on the WGS catalyst. The heat generated will allow the catalyst to be brought to temperature rapidly. Variations in oxygen concentration entering the WGS catalyst during startup could lead to local conditions in the WGS catalyst that either (a) result in inadequate heating to achieve the desired activity in the allotted start-up time, or (b) result in overheating and possible damage to the WGS catalyst.

Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer, (continued)

Recuperator

The micro-channel recuperator was designed to meet the performance specifications shown in Figure 1. For design purposes the operating pressure was assumed to be 16.7 psia.

In addition to the requirements placed on thermal performance, it was required that the temperature leaving the recuperator be very uniform to avoid uneven temperatures at the inlet to the WGS reactor. In addition, there was a desire to minimize the thermal mass of the recuperator to enable rapid start of the system. Finally, the entire assembly must fit within a 6-inch diameter cylinder while allowing for numerous tubes to carry process streams and instrumentation within an insulated region occupying the outer perimeter of the 6-inch cylinder.

While not specified, the turndown performance of the recuperator is important to the overall system in order to maintain efficiency while operating at less than full load conditions. The turndown performance is shown in Figure 2.

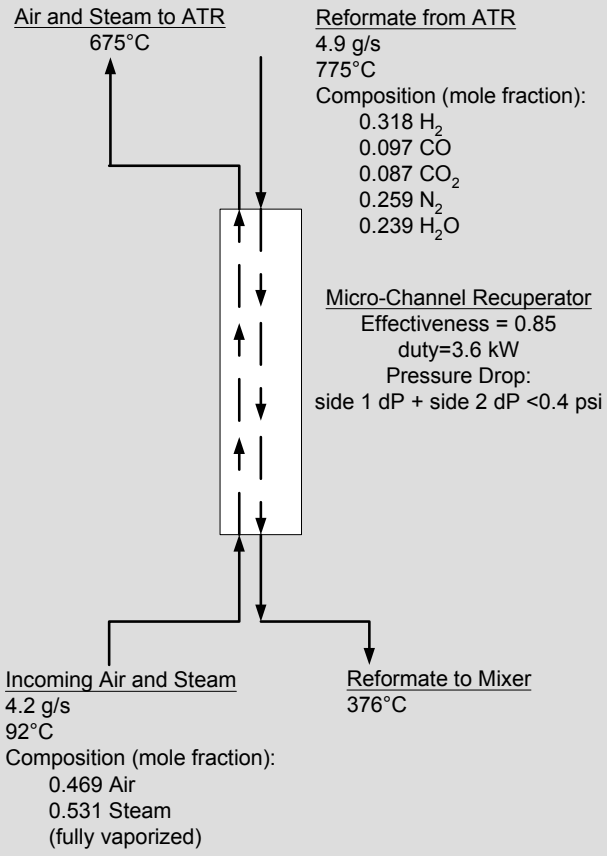


Figure 1. Performance Requirements for Recuperator.

Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer, (continued)

The recuperator is constructed using Inconel 600 to provide high temperature compatibility. The fabrication process will consist of photo-chemically etching patterns into thin Inconel sheets. The sheets are stacked and then diffusion bonded. During diffusion bonding the etched sheets are sealed to one another and the etched patterns form flow channels. Flow within in the heat exchange channels is laminar.

For rapid startup it is desired to minimize the thermal mass of the recuperator. The mass of the recuperator itself is estimated to be ~800 g. After adding tubing and ducting the weight is increased to 1100 g.

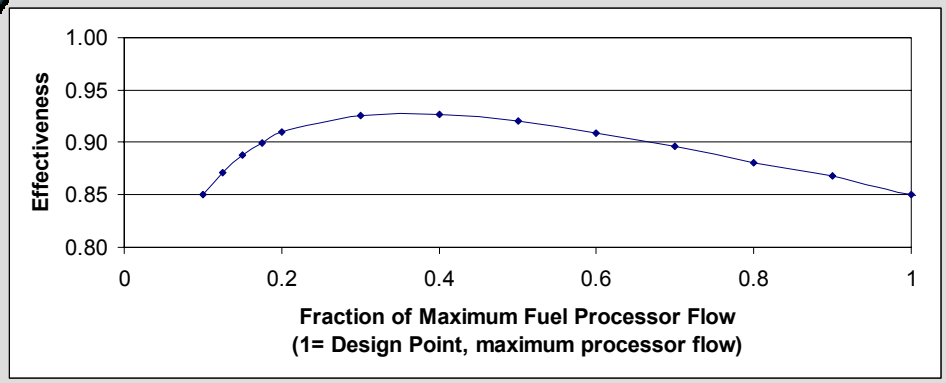
Mixer

The mixer utilizes laminar flow channels to uniformly distribute a flow of air into the reformate stream during startup. It is constructed in 316L stainless steel by bonding a stack of photo-chemically etched plates. The mixer is estimated to weigh 176 grams.

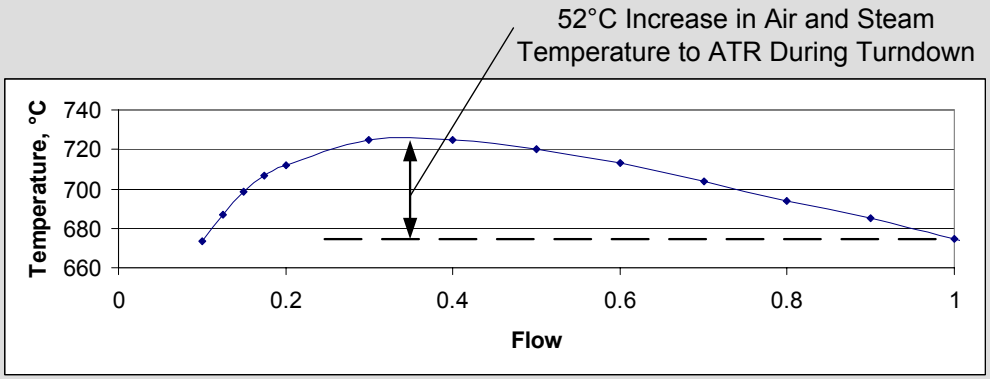
Complete Assembly

The assembly as it will look when delivered to ANL for incorporation into the FASTER reforming system is shown in Figure 3.

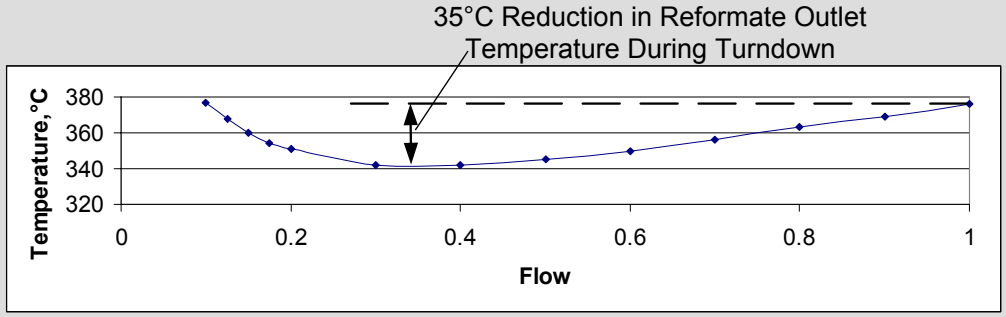
Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer, (continued)



This plot illustrates the variation in effectiveness as the total flow through the two sides of the exchanger are reduced proportionally from full capacity (1.0)



This plot illustrates the impact of turndown on the cooled reformate outlet temperature. Limiting variation is important to prevent adverse impacts on the WGS reactor.



This plot illustrates the impact of turndown on the superheated air and steam temperature The temperature does not decrease below the design point over the 10% to 100% capacity range.

Figure 2. Recuperator Turndown Performance.

Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer, (continued)

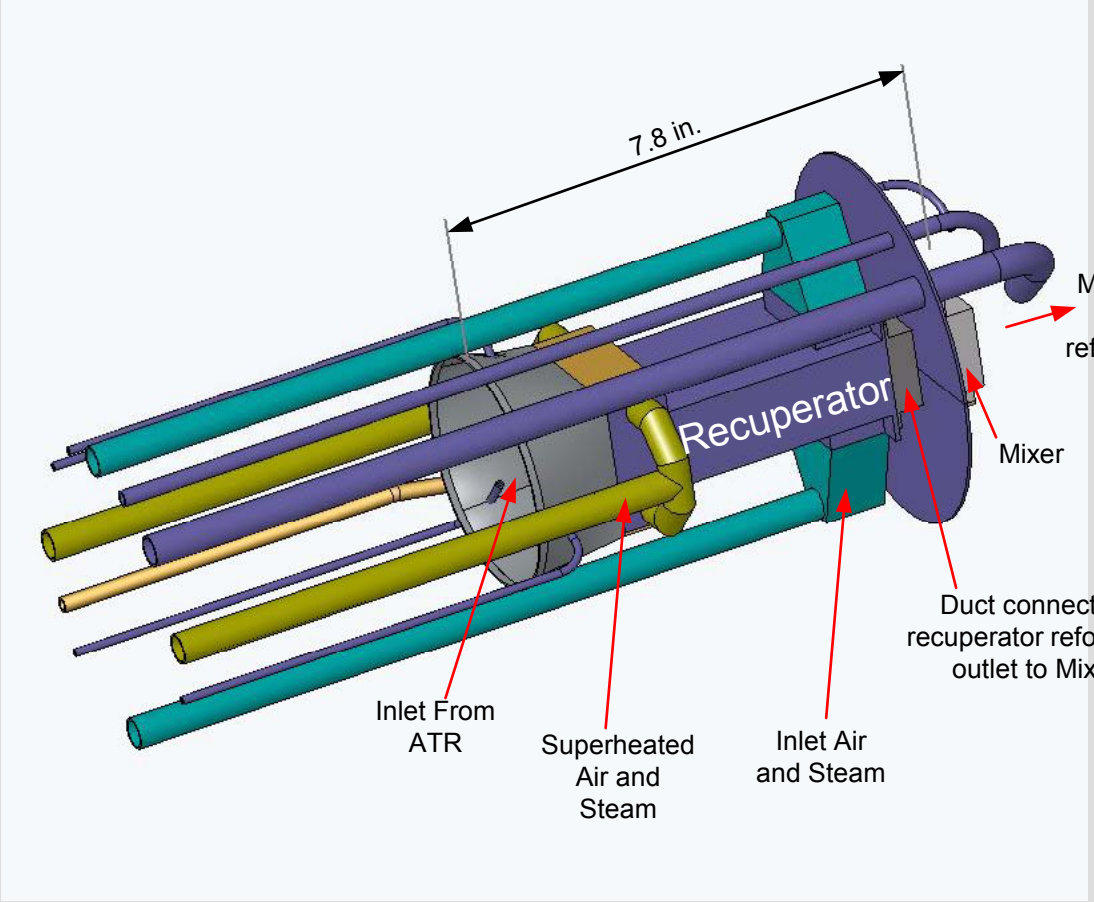
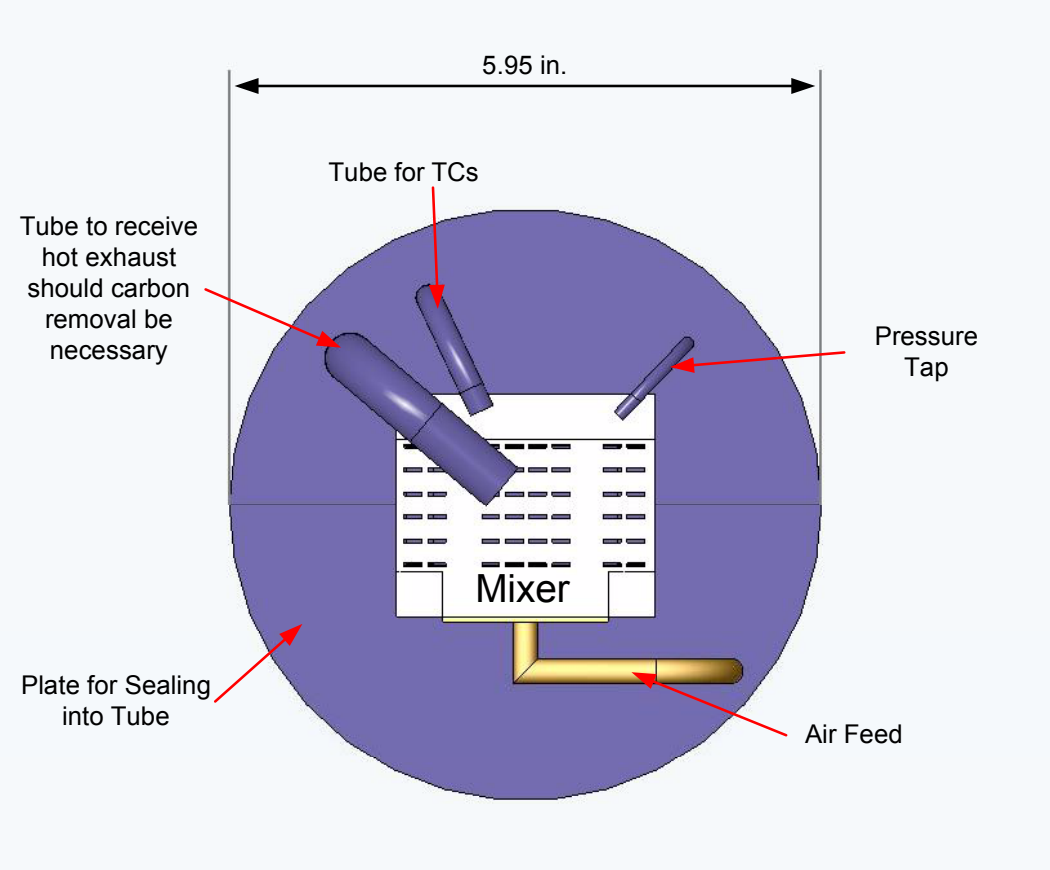


Figure 3. Recuperator/Mixer Assembly.

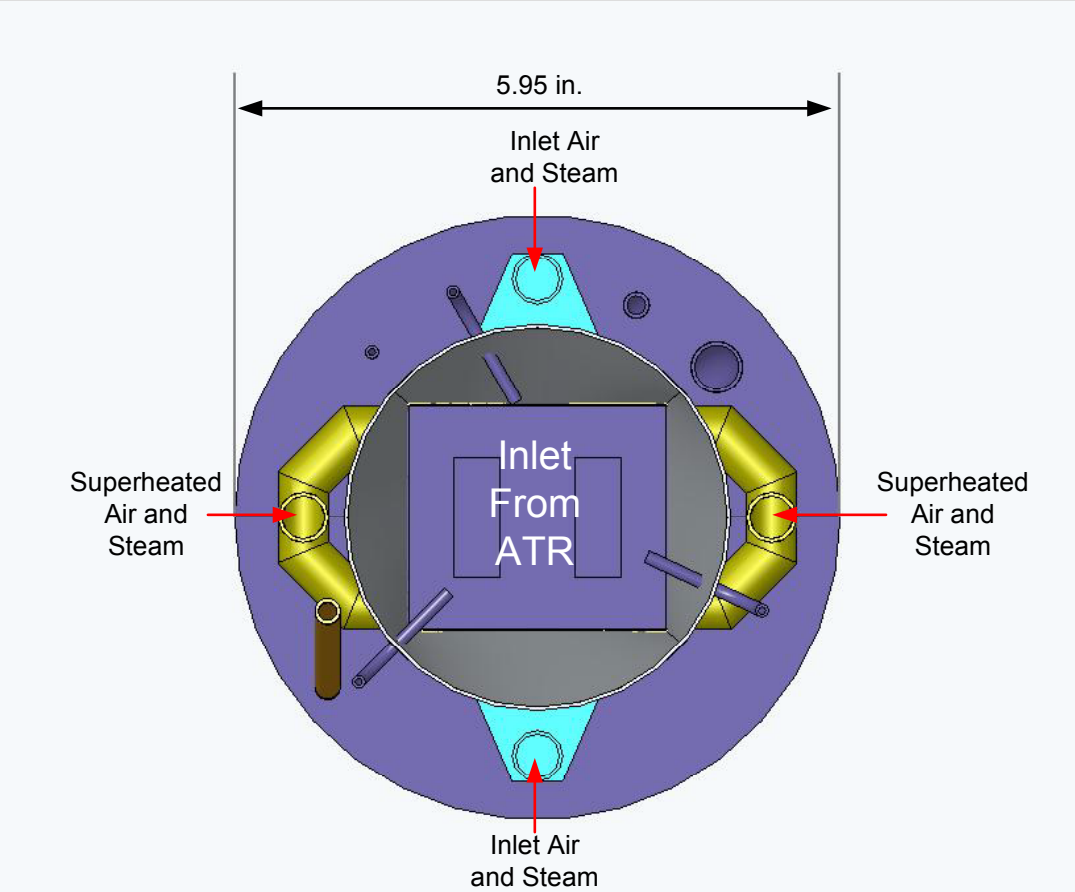
Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer, (continued)



View of assembly from the reformate discharge end. Slots in the mixer are for illustration only and are finer than shown.

Figure 3. Recuperator/Mixer Assembly, continued.

Micro-Channel Recuperator and Mixer for FASTER (Feasibility of Acceptable Start Time Experimental Reactor) Autothermal Reformer, (continued)



View of assembly from the reformate inlet end.

Figure 3. Recuperator/Mixer Assembly, continued.

Fast Start Reformer Components:
PrOx – CO Removal for Fast Start Fuel Processing

Michael A. Inbody, Rodney L. Borup, and José I. Tafoya
Fuel Cell Team / MST-11
Los Alamos National Laboratory
Los Alamos, NM 87545

Catalysts

Los Alamos NATIONAL LABORATORY

Fuel Cell Program

Technical Objectives

- Investigate and develop PrOx reactor component design for integration into a fuel processor system for demonstrating the feasibility of a fast start.
- Technical Targets (2010):
  - Cold startup time to maximum power - < 30 secs.
  - CO content in product stream - <10 ppm steady-state, <100 ppm transient

Approach

- Identify PrOx catalysts for use in a PrOx reactor component
  - Measure kinetic parameters for expected operating conditions.
- Collaborate on component design for the PrOx reactor.
- Investigate PrOx options enabling rapid start of a fuel processor.
- Measure PrOx component response to simulated startup conditions and events.

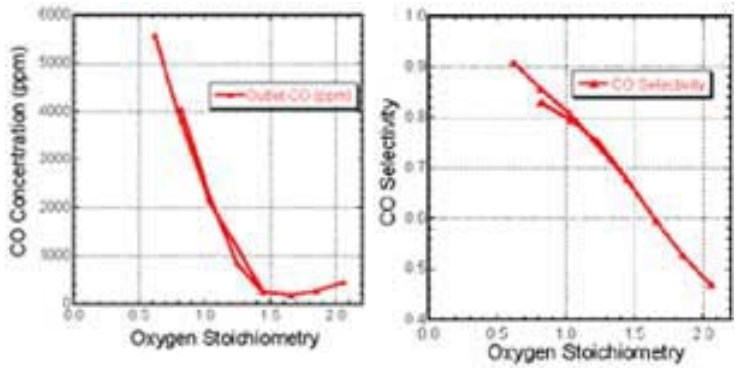
PrOx Startup Considerations

- Goal: Maintain fuel processor outlet CO concentration within fuel cell stack tolerances through the startup transient and transition to normal operation.
  - Reduce thermal mass ($m \cdot c_p$) of catalysts and components in contact with the flow
  - Low catalyst light-off temperature for CO oxidation
  - CO selectivity over a wide temperature range
  - Staged reactors for higher turndown or higher inlet CO (> 1%)
  - Oxidation of high concentrations of CO (for cases where WGS is not fully operational)

Accomplishments/Progress

- Obtained catalysts from various manufacturers on monolith, ceramic foam, and metal foam substrates.
- Identified a catalyst with low light-off temperature and good selectivity.
- Measured catalyst performance under range of expected operating conditions.
  - Data provided to ANL for fuel processor model and evaluation of kinetic parameters.
- Verified catalyst performance under similar linear face velocity as the PrOx component design
- Obtaining substrate for unique design geometry of PrOx component.

Catalyst CO Performance Measurements



- Measure outlet CO concentration and CO selectivity as a function of air stoichiometry
- Experiment – Single-Stage PrOx
  - PrOx catalyst monolith: 600 cpsi, 3 inch diameter by 5 inch long
  - 25 kW LHV Hydrogen flow
  - Inlet CO: 11700 ppm

PrOx Design and Operation Strategy

- 2-stage design may work for normal inlet CO concentrations (≈1%)
  - First stage: operate to bring outlet CO to 2000 to 1000 ppm.
  - Second stage: operate to bring outlet CO to < 10 ppm
    - Adiabatic temperature rise is small, so reverse water-gas shift reaction can be avoided, thus it can tolerate excess air.
- 3-stage design permits greater flexibility in handling higher CO concentrations (> 1%)
  - Handle higher CO concentrations with less parasitic hydrogen loss.
  - Handle higher inlet CO concentrations at startup.
  - First and second stage: operate to bring outlet CO to 2000 to 1000 ppm.
  - Third stage: operate to bring outlet CO to < 10 ppm.

Fast Start Reformer Components:
PrOx – CO Removal for Fast Start Fuel Processing

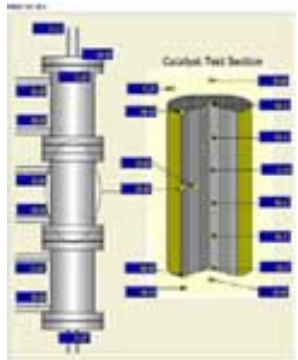
Michael A. Inbody, Rodney L. Borup, and José I. Tafoya
Fuel Cell Team / MST-11
Los Alamos National Laboratory
Los Alamos, NM 87545

Los Alamos NATIONAL LABORATORY

Fuel Cell Program

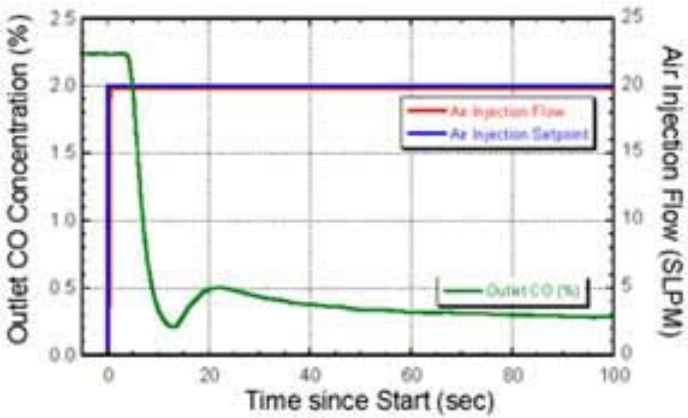
Accomplishments/Progress

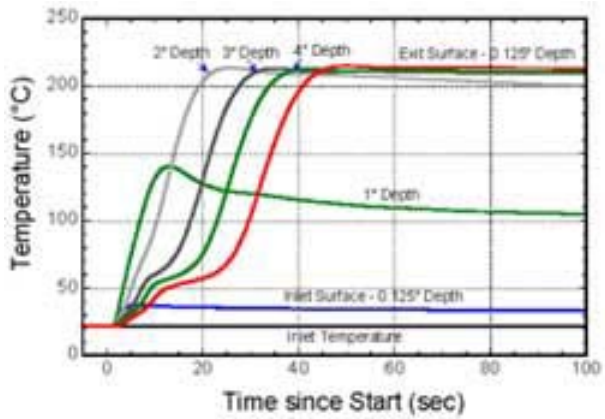
Single-Stage Startup Experiments



- Investigate startup response of a PrOx catalyst monolith from room temperature.
- Experiment – Single-Stage PrOx
  - PrOx catalyst monolith: 600 cpsi, 3 inch diameter by 5 inch long
  - Flows: 46.0% H_2, 32.9% N_2, 19.0% CO_2.
    - Dry gas temperature at inlet ≈ 20 ºC
    - GHSV ≈ 31,000 hr^{-1}
  - Primary gas flow established, then air injected at time = 0.0 s.

CO and T vs time for 2.2% CO inlet





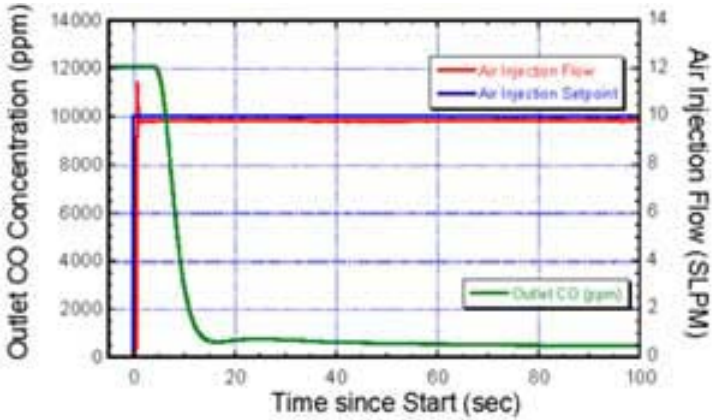
Fast Start Reformer Components:
PrOx – CO Removal for Fast Start Fuel Processing

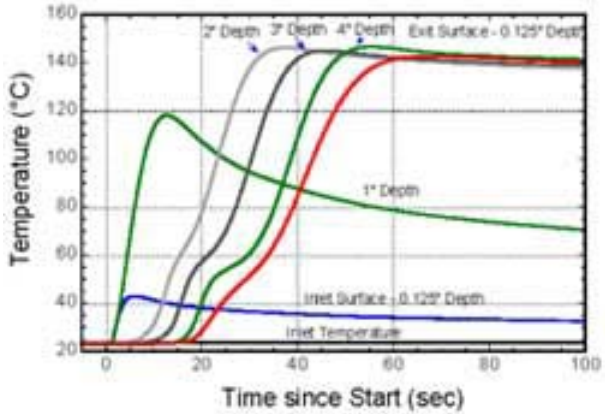
Michael A. Inbody, Rodney L. Borup, and José I. Tafoya
Fuel Cell Team / MST-11
Los Alamos National Laboratory
Los Alamos, NM 87545

Los Alamos NATIONAL LABORATORY

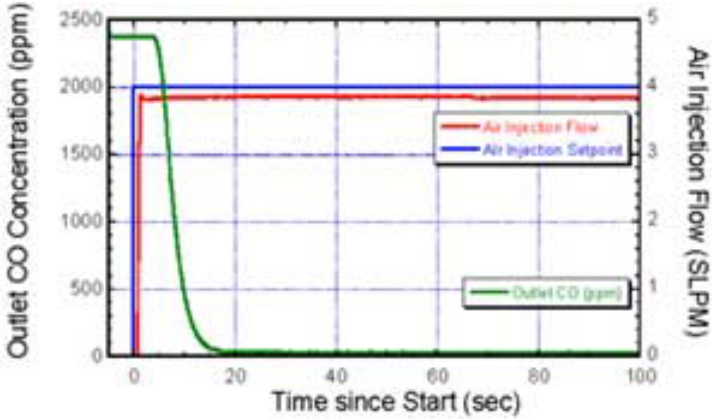
Fuel Cell Program

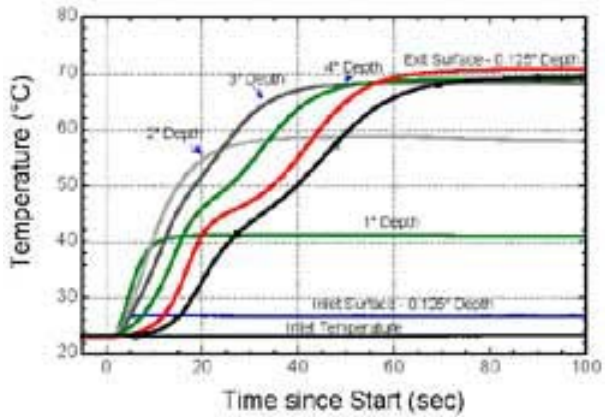
CO and T vs time for 1.2% CO inlet





CO and T vs time for 2350 ppm CO inlet





Summary – Single-stage Startup Experiments

- Outlet CO decreases rapidly to steady-state values in less than 30 s
- Low light-off temperature makes this possible.
- Temperature response takes longer to reach steady-state.
- Fast startup less than 30 s appears feasible.

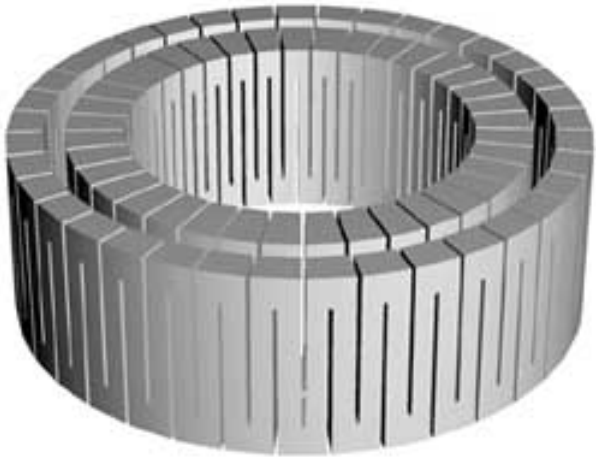
Plans/Future Work

- Fabrication of PrOx reactor component – July 2003
- Multi-stage PrOx experiments
  - Verify design performance
  - Demonstrate feasibility of staged performance and control
  - Investigate limits of high CO startup option
- Fuel Processor Integration
  - Collaborate on operation and controls

Annular Graphite Foam Heat Exchangers Were Developed for FASTER

April McMillan, Glenn Romanoski, James Klett
Tim Armstrong, Dave Stinton

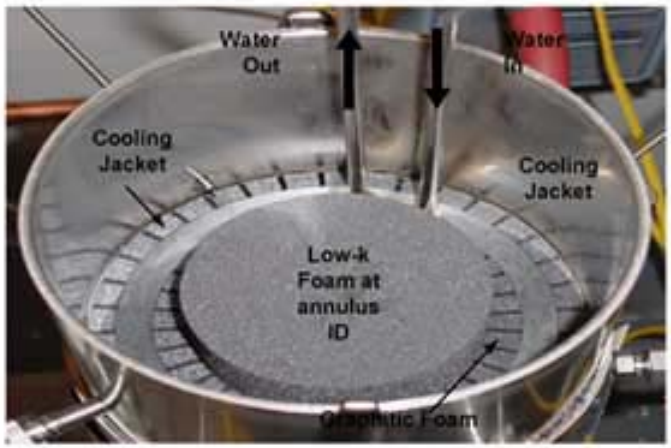
Objective:
To design and fabricate lightweight heat exchangers capable of handling a heat duty of 1KW. These heat exchangers must meet the operational and physical constraints of the FASTER system design for effective catalysis downstream.

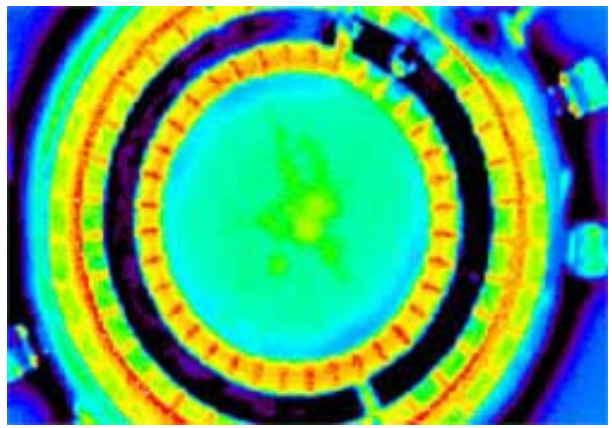


Performance Requirements

- Hot Gas : Flow = 300 slpm
- DT > 100°C (symmetric)
- DP < 0.1 psi
- Coolant : Water, 2-phase

Tests indicate that the heat duty is relatively constant for a given inlet gas temperature. Further, tests reveal that heat transfer through the graphite foam may be insensitive to water flow.





Early Results

- Hot Gas : Flow = 307 slpm
- DT ~200°C (symmetric)
- DP < 0.04 psi
- Coolant : Water, 2-phase