Florida Solar Energy Center

Creating Energy Independence Since 1975

Florida Hydrogen Initiative (FHI)

DOE Contract # DE-FC36-04GO14225

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Project ID#: TV012

Overview

Timeline

- Project Start Date: 10/1/04
- Project End Date: 6/30/12
- Percent Complete: 50%

Barriers

- Barriers addressed
  - Research and Development
  - Creating Partnership
  - Facilitating Technology Transfer

Budget

- Total project funding
  - DOE share: $3,946,155
  - Cost Share: $1,512,604
  - Total Project: $5,458,759
- Funding for FY09-FY11: None

Partners

- Florida Solar Energy Center
- EnerFuel, Inc.
- SRT Group, Inc., University of Florida
- Florida State University, Bing Energy, Inc.
- Florida Institute of Technology
- University of South Florida
- EnerFuels, Inc., University of Florida, UCT Coatings

Project Objectives/Relevance

- Develop hydrogen and fuel cell infrastructure
- Create partnerships
- Sponsor R & D
- Facilitate technology transfers
- Develop industry support
- Develop unique education programs

Approach

- Project solicited competitive proposals to conduct work
- Initially selected four projects
- Three projects are completed
- New project administration at Florida Solar Energy Center (FSEC) in June 2009
- Solicited new projects in October 2009
- Selected three R & D projects following DOE review and approval
- Three projects began April 2010

Approach (continued)

- **Request for Proposals ≈ $1.5 million**
- **Request for Proposals issued March 2010**
- **Five member peer review committee met and selected winning RFPs**
- **Five new projects reviewed and received DOE approval**
- **Sub-contracts written for five new projects**
- **New projects began December 1, 2010**

Key Results – Very Successful Year!

- Project has solicited proposals to conduct work
- Project composed of 12 projects – 3 projects completed
- Presently have 9 active projects
- 1 old project with new demo site
- 3 new projects started on April 1, 2010
- 5 new projects started on December 1, 2010
- All project $ are now committed
- New program kick-off meeting – January 5, 2011

Project Breakdown by Technology

Fuel Cells:
- **Methanol Fuel Cell Evaluation at FAU – EnerFuel, Inc./Florida Atlantic University**
- **Low Cost/High Efficiency of PEMFC System – Florida State University/Bing Energy, Inc.**
- **Advanced HiFoil™ Bipolar Plates – EnerFuel, Inc./University of Florida and UCF Coatings**
- **Mechanical and Chemical Durability of MEAs – FSEC**

Hydrogen:
- **Hydrogen Leak Detection – FSEC**
- **Production of Hydrogen from Biowaste – SRT Group, Inc./University of Florida**
- **Advanced Hydrogen Storage System – University of South Florida**

Hydrogen and Fuel Cells:
- **Low Cost Electrocatalysts – FSEC**
- **Hydrogen and Fuel Cell Technology Academic Program – Florida Institute of Technology**

Collaborations – Went from 5 to 11

Past Collaborations:

Chevron Technology Ventures/FSEC, Rollins College, Orlando Science Center, EnerFuel, Inc.

New Collaborations:

- **EnerFuel, Inc.**
- **Florida Solar Energy Center**
- **SRT Group, Inc. Miami and University of Florida**
- **Florida State University and Bing Energy, Inc.**
- **Florida Institute of Technology**
- **University of South Florida**
- **EnerFuel, Inc., University of Florida and UCT Coatings**

Proposed Future Work

- Finish fuel cell demonstration at FAU – EnerFuel, Inc.
- Develop needed documentation for sub-contracts
- Continue project monitoring of nine projects
- Conduct R & D and reporting for nine projects

Summary

Relevance: Conduct R, D & D, create partnerships, facilitate technology transfer

Approach: Solicit proposals to meet objectives, conduct R & D

Technical Accomplishments and Progress: Three projects completed. Nine active projects

Technology Transfer/Collaboration: Continue 11 active partnerships

Proposed Future Research: Continue conducting nine active projects, conduct project reviews

Hydrogen Technology (HyTech) Rest Area

Michel Fuchs
EnerFuel, Inc.
3/10/2011

Project ID #

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Project Overview

Timeline

- Start – Oct 2006
- Finish – July 2011
- 94% complete

Budget

- Total project funding
  - DOE - $607K
  - Contractor - $632K
- Funding received for FY07
  - $191.0K
- Funding received for FY08
  - $160.9K
- Funding received for FY09
  - $35.7K
- Funding received for FY10
  - $41.7K
- Funding for FY2011
  - $177.6K

Barriers

- **Barriers**
  - **C**. Performance
  - **E**. System Thermal and Water Management
  - **G**. Startup and shut-down time and Energy/Transient Operation
- **Targets**

	2003	2005	2011
Electrical Energy Eff.	30%	32	40
Transient response time	<3ms	<3ms	<3ms

Subcontractors

- **Florida Atlantic University (FAU)** – Demo site design and construction
- **Technology Research & Development Authority** – Assist in demo site preparations & public relations

Objectives

Overall	❖ Design, construct and demonstrate a $10kW_{net}$ PEMFC stationary power plant operating on methanol ❖ Achieve an electrical energy efficiency >32% ❖ Demonstrate transient response time <3ms
2010	❖Change demonstration scope and location from rest area demo to electrical vehicle charge station due to budget constraints ❖Construct charging station
2011	❖Commission charging station ❖Evaluate fuel cell power plant and charging station performance ❖Present results of project

Milestone

Month/Year	Milestone or Go/No-Go Decision
Jan-09	Milestone: Identified commercial bio-methanol supplier able to provide entire 5000 gallons necessary for project
Apr-09	Milestone: Obtain all permits required for construction, including Florida Turnpike Enterprise, Fire Marshall and County permits.
Jun-09	Milestone: Complete construction of fuel cell demonstration site.
Sept-09	Milestone: Complete fuel cell power plant, operating on renewable methanol and providing power to service station, demonstration phase.
May-2010	Milestone: Complete all permits required for construction of site at Florida Atlantic University.
Feb-2011	Milestone: Complete construction of electric vehicle charge station demo site
Jun-2011	Milestone: Complete demonstration and evaluation of fuel cell and charge station performance

Plan & Approach

- **Task 1: Citrus derived methanol**
  - Identify source
  - Clean-up methanol to fuel cell grade
  - Test methanol for compatibility w/ reformer
  - Work out transportation, storage logistics and associated NEPA compliance
  - Identify/establish safety protocols for use

100% Complete

- **Task 2: Demo site preps**
  - Obtain permitting & NEPA compliance for methanol storage
  - Identify electrical interface requirements
  - Establish location for fuel cell power plant and methanol storage

100% Complete

- **Task 3: Fuel cell power plant design**
  - DMFC vs. standard PEMFC trade study
  - Identify fuel cell stack source
  - Identify reformer source
  - Design system through modeling

100% Complete

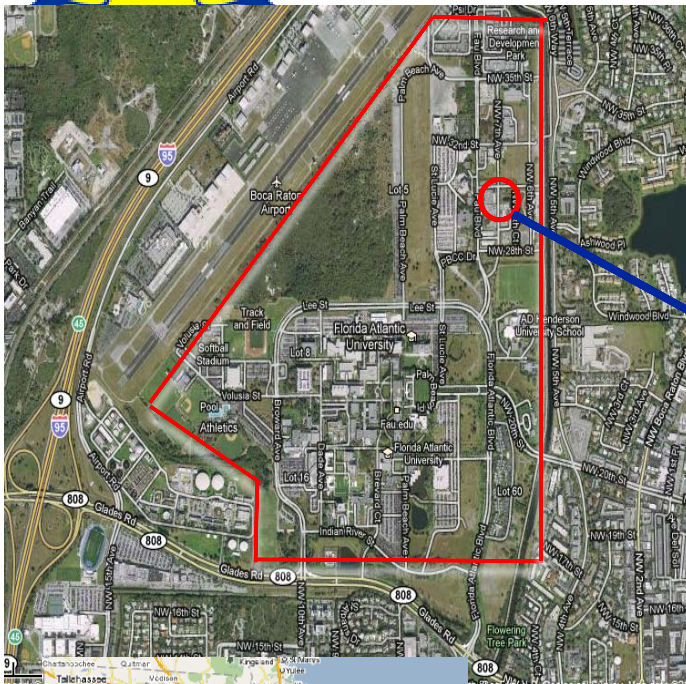
- **Task 4: Power plant construction and testing**
  - Construct power plant
  - Test and debug power plant
  - Benchmark performance

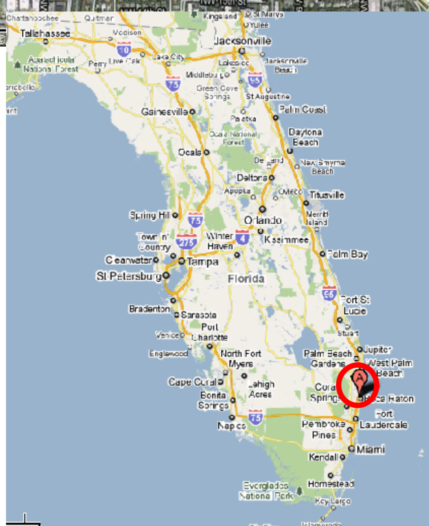
95% Complete

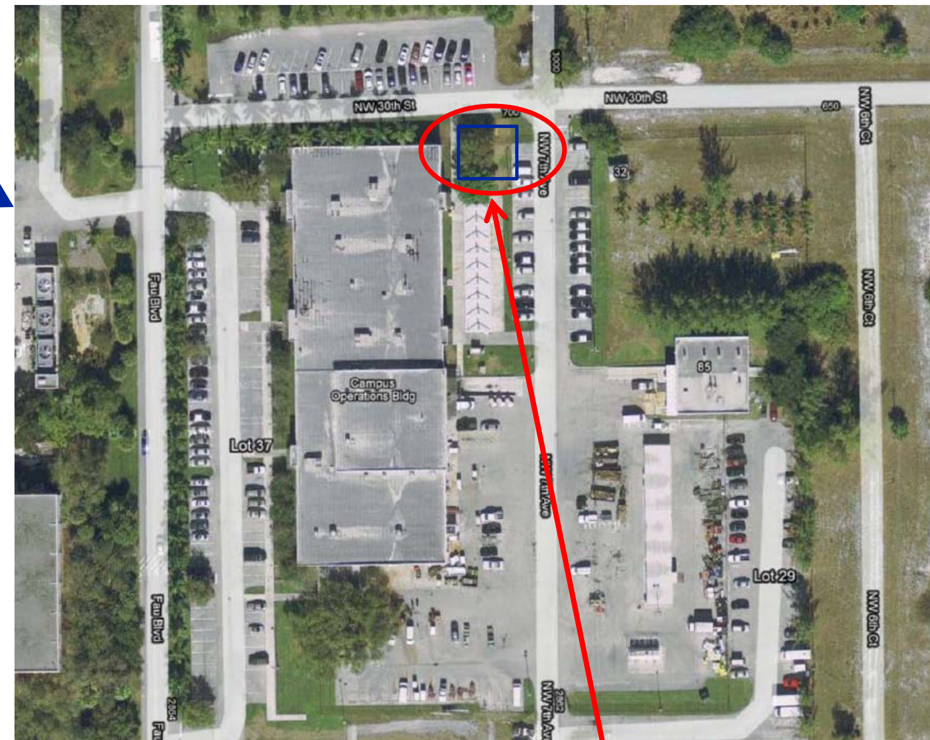
- **Task 5: Power Plant installation and demonstration**
  - Install power plant at demo site
  - Operate system for 3 months

70% Complete

Demonstration Site







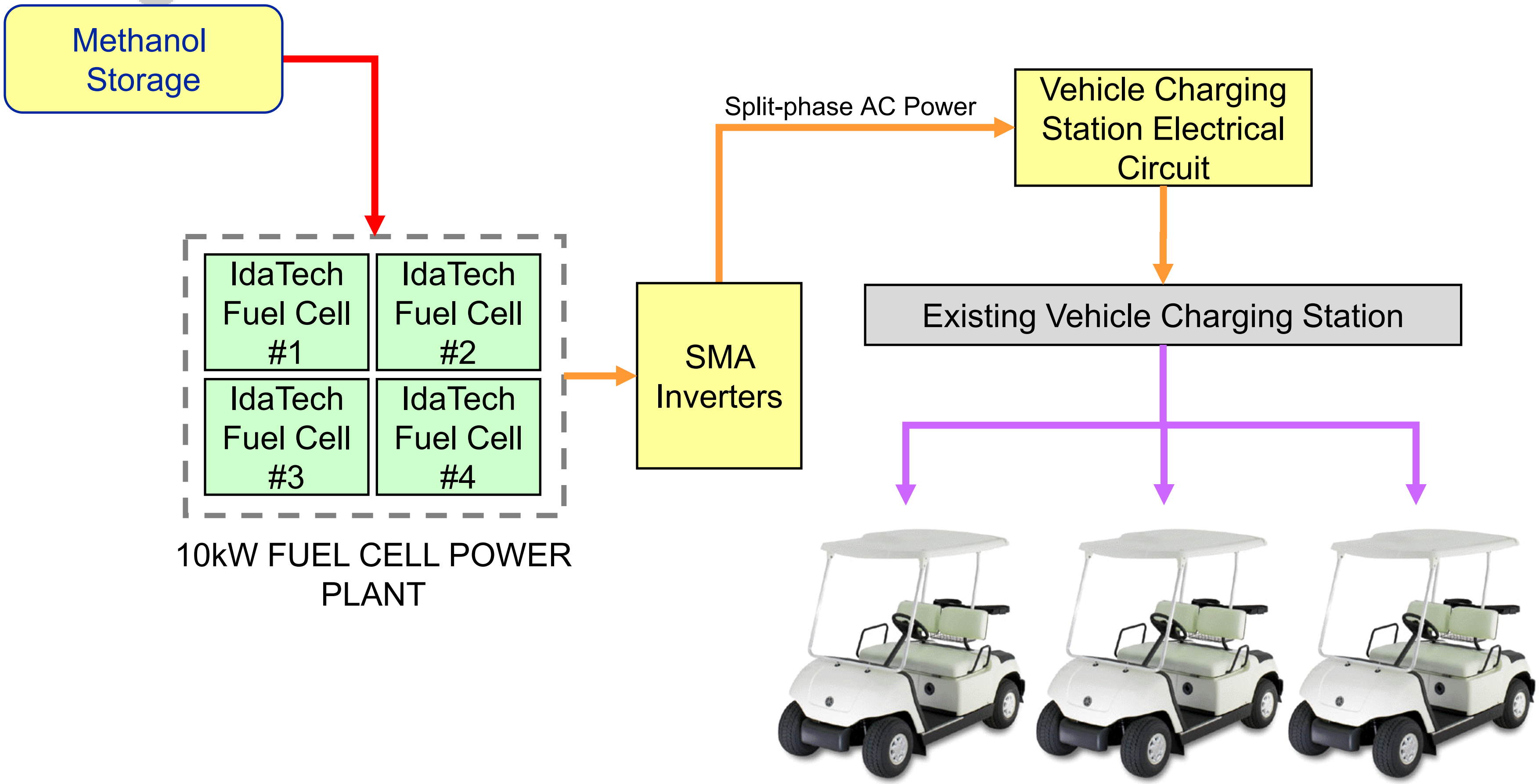
FAU
FLORIDA ATLANTIC UNIVERSITY

Vehicle charging station location

Accomplishments

- Changed demonstration from powering a portion of a rest area to powering an electric vehicle charging station
- Successfully incorporated the existing inverter & fuel cell systems into the design of the charging station
- Successfully tested complete system at EnerFuel prior to delivery to FAU.
- Installed FC's, batteries and inverters at FAU

EV Charging Station Design



Remaining Work

- **Qtr 1, 2011**
  - Complete charging station wiring
  - Test and fine tune system
  - Commission station

- **Qtr 2, 2011**
  - Operate charge station for period of 3 months
  - Collect operational data
  - Complete final report

HyTech Rest Area Project Summary

- **Relevance**
  - Demonstrate a “grid” independent “clean” power solution for electric vehicle charging using a methanol fueled fuel cell system
- **Approach**
  - Utilize a PEM based fuel cell power plant, with onboard reforming, to convert methanol to usable electrical power
  - Demonstrate project in high visibility university environment
- **Technology collaboration**
  - Participation with the Technological Research and Development Authority (TRDA) of Florida to promote project objectives
  - Participation with Florida Atlantic University to host demonstration as well as design, construct and evaluate electric vehicle charge station
- **Proposed future projects**
  - Develop and participate in additional alternative power generation and renewable fuel projects that lead to the development of viable commercial “clean” power solutions

Chemochromic Hydrogen Leak Detectors for Safety Monitoring

A Florida Hydrogen Initiative Project

Drs. Nahid Mohajeri and Nazim Muradov
University of Central Florida-FSEC

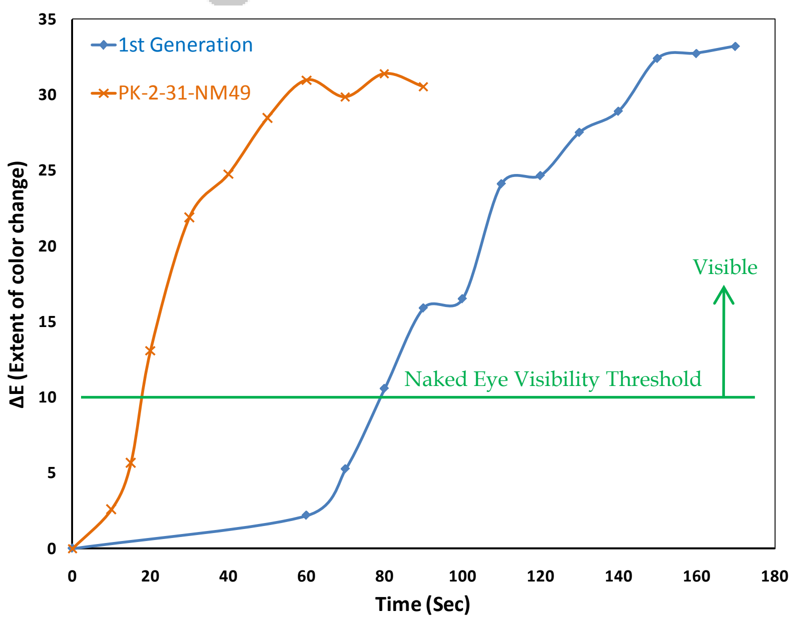
Relevance and Approach

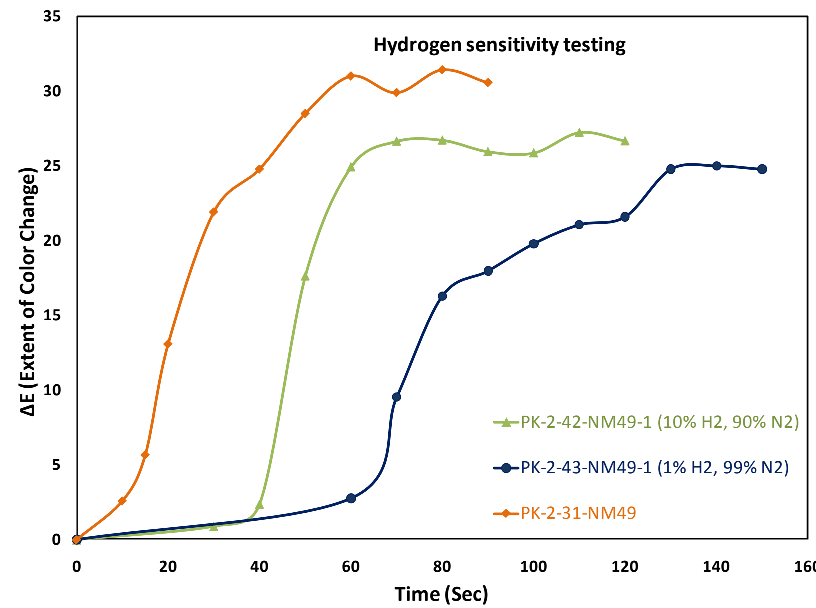
- **Relevance**: Safety is a major concern for many industries that produce, store, or utilize hydrogen. Developing chemochromic hydrogen detector will lead to lower cost, better reliability, user-friendliness, and superior field worthiness.
- **Approach**: developing two classes of chemochromic hydrogen sensors:
  - Irreversible
  - Reversible

Irreversible Chemochromic Sensor

- Goal:
  - To Improve field worthiness of FSEC's 1st generation chemochromic H_2 sensor by:
    - Increasing hydrogen sensing kinetics
    - Determining the sensitivity and selectivity toward hydrogen detection in the presence of other reducing gases
    - Optimizing the encapsulation methods
    - Studying the effect of environmental parameters such as UV, temperature, and water exposure.
    - Improving the worthiness and shelf life of the chemochromic H_2 sensors

Technical Accomplishments & Progress – Irreversible Sensor





- The kinetics for PK-2-31-NM49 chemochromic sensor is 80% faster than FSEC's 1st Generation
- The extent of color change (ΔE), in saturation, for PK-2-31-NM49 is almost the same as FSEC's 1st Generation

- PK-2-31-NM49 Chemochromic Sensor shows a great sensitivity and response to 10% and 1% H_2 gas mixture (1% curve exposure kinetics are as good as FSEC's 1st Generation sensor)
- No reaction with CH_4, CO, and H_2S was noticed after one hour at room temperature.

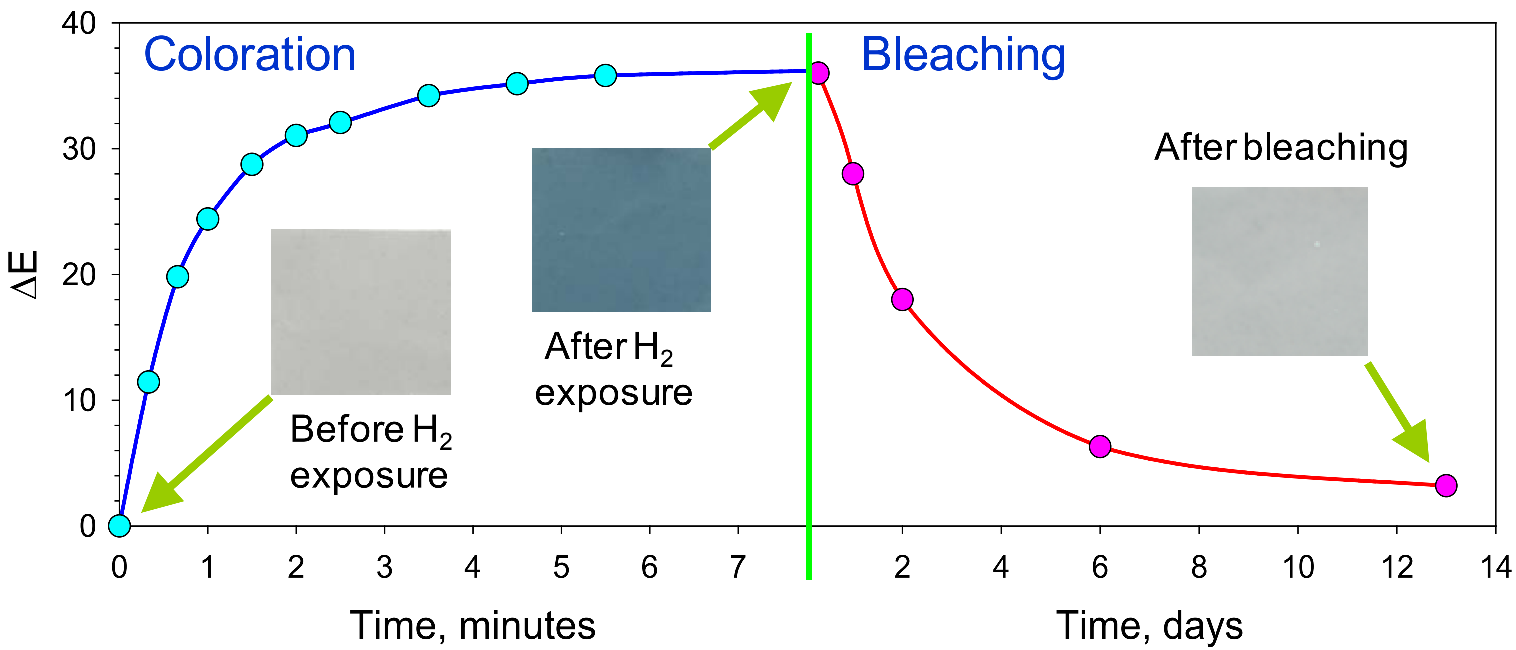
Summary and Future Work – Irreversible Sensor

- Several new chemochromic pigments have been synthesized and tested.
- Total of three new formulation show faster kinetics when compared to FSEC 1st Generation sensor.
- The discoloration kinetics for PK-2-31-NM49 chemochromic sensor is 80% faster than FSEC 1st Generation sensor.
- FSEC 1st Generation sensor has shown great selectivity and sensitivity toward H_2 gas.
- Encapsulation optimization and studying the effects of environmental factors are underway.

Reversible Chemochromic Sensor

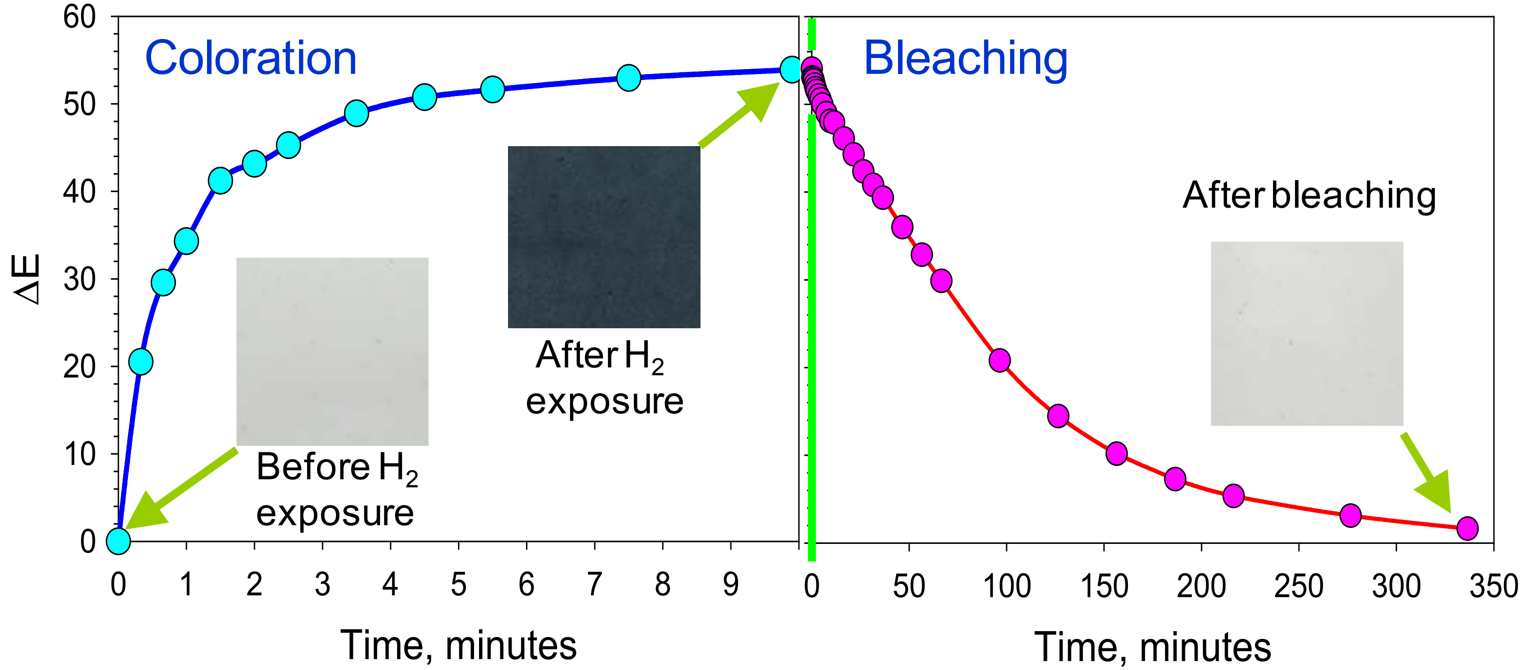
- Approach
  - Reversible H_2 sensors are based on transition metal compounds with tunable redox properties, e.g., Mo^{+6} / Mo^{+5}, W^{+6} / W^{+5}, V^{+5} / V^{+4}.
  - By chemically altering the reversible pigment formulations, the research shows the ability to fine tune the kinetics of bleaching from minutes to days.

Reversible Chemochromic Sensor



Mo-based slow-bleaching pigment formulation

Reversible Chemochromic Sensor



W-based fast-bleaching pigment formulation

Summary & Future Work- Reversible Sensor

- **Accomplishments**
  - synthesized and tested about 20 novel Mo-, W-, V- based chemochromic formulations
  - determined the effect of co-catalyst/activator on the rate of coloration in presence of H_2
  - evaluated the performance (sensitivity) of the sensors at different H_2 concentrations in air (from 1 to 100 vol.%)
  - determined the extent of interference with other reducing gases (CO, NH_3, CH_4, H_2S). Found no interference.
- **Future work: Determine environmental effect (UV, rain, dust) on the performance of the sensors. Conduct long-term field testing of the H_2 sensors.**

High Efficiency, Low Cost Electrocatalysts for Hydrogen Production and Fuel Cell Applications

Cunping Huang and Marianne P. Rodgers
Florida Soar Energy Center

Relevance

- Pt and its alloys are the most effective PEM fuel cell catalysts
- Factors limiting fuel cell commercialization include:
  - Costs
  - Efficiency of oxygen reduction reaction (ORR)
- Approaches to overcome these limitations involve reducing Pt loading while maintaining high performance
  - If Pt activity increases, loading can be reduced

Methods of Increasing Pt Activity

- Methods of increasing Pt activity include:
  - Optimization of the size and shape of the Pt partilces
    - Increase the surface area available
  - Alloying Pt with other metals
    - Attributed to structural changes
  - Depositing catalyst particles only where the electrocatalytic reaction takes place
    - Improves catalyst utilization
- For Pt in a PEM fuel cell catalyst layer to be active, it must be deposited at the "three phase reaction zone"
  - Catalyst, electrons, & electrolyte interface
  - Allows effective gas & water diffusion and proton & electron transport to and from catalyst

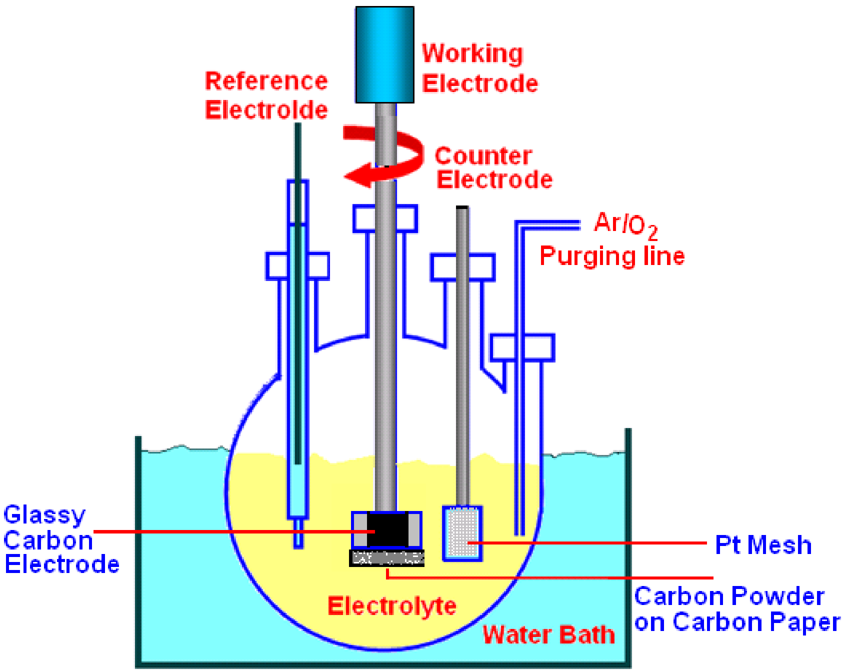
Approaches to Localize Catalyst to the Three Phase Reaction Zone

- Sputtering deposition
  - Comparable performance with lower loadings
  - Not appropriate for fabrication of large structures
- Pulse electrodeposition
  - Controlled particle size, stronger adhesion, uniform electrodeposition
  - Control of factors such as t_{off}, t_{on}, peak current density, catalyst precursor, co-catalyst, stabilizing agent

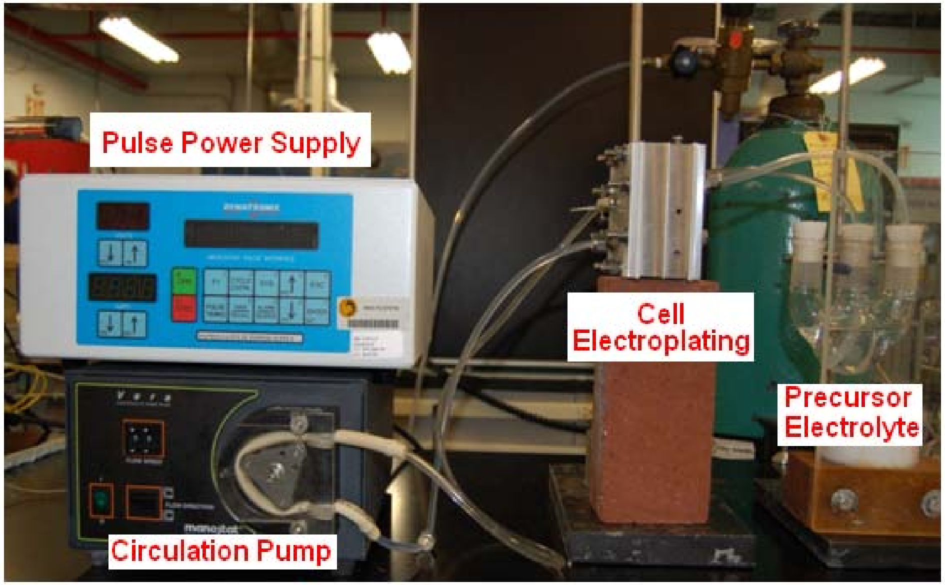
Approach

- Catalysts electrodeposited on carbon paper loaded with a carbon microporous layer and Nafion®, resulting in a 3-phase reaction zone
- Pulse electrodeposition carried out using a rotating disk electrode (RDE)
  - RDE brings analyte molecules from bulk solution towards the surface of electrode, resulting in mass transport faster than diffusion only
  - t_{off}, t_{on}, current density, electrode rotation rate, etc. will be varied and optimized
  - Catalyst activity will be measured using RDE

Pulse Electrodeposition/ORR Setups00



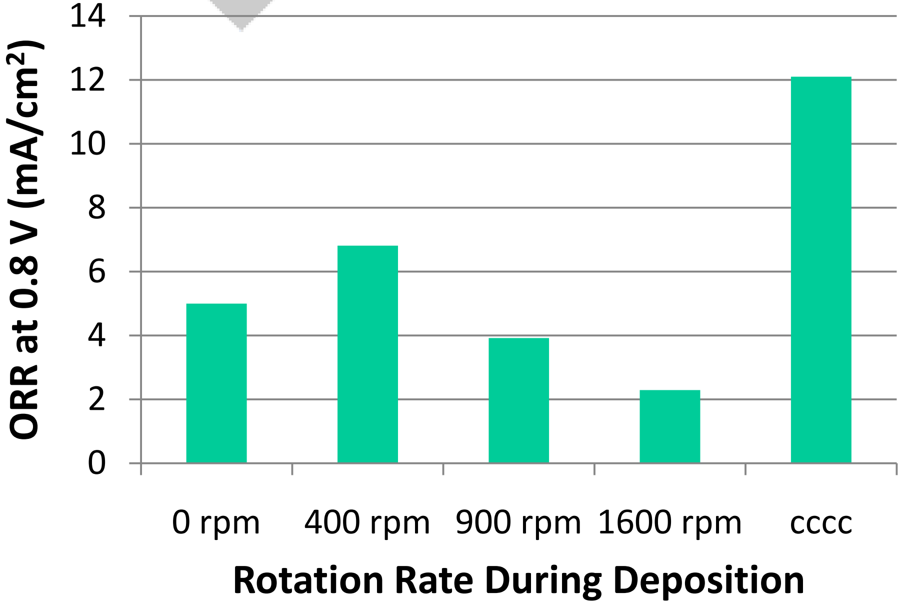
Rotation Disck Electrodeposition & Oxygen Reduction Reaction Setup

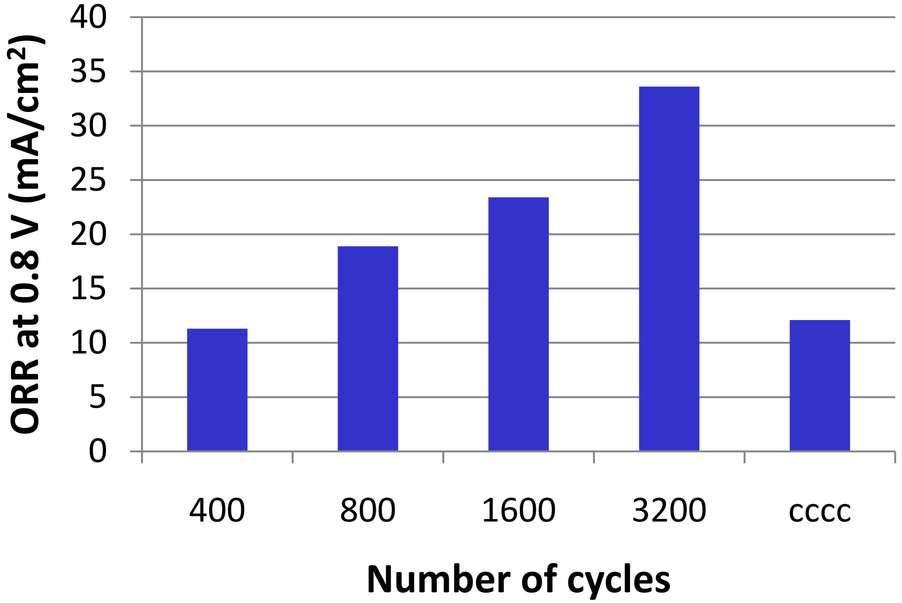


Large Scale Electrodeposition Setup

Technical Accomplishments and Progress

Oxygen Reduction Reaction (ORR) Activities





- The optimum rotation rate during deposition was 400 rpm
  - Deposited 400 cycles onto activated carbon/Nafion coated gas diffusion layers
- Increasing the number of deposition cycles to 3200 improved ORR activity to well above commercial materials
  - Deposited at 400 rpm onto Cabot Regal GP-3713/Nafion coated gas diffusion layers

ORR activity of samples at 298 K, 0.8 V, and 400 rpm. CCCC is commercial catalyst coated carbon cloth.

Project Summary and Future Work

- Pt catalysts prepared by the pulse electroplating technique show higher activities than that of commercial catalyst with reduced Pt loading.
- The same catalysts can also be used for H_2 production via water electrolysis with higher efficiency.
- Future work:

  Synthesizing alloy based electrocatalysts

  Catalysts Characterization

Understanding Mechanical and Chemical Durability of Fuel Cell Membrane Electrode Assemblies

A Florida Hydrogen Initiative Project

Darlene Slattery, Leonard Bonville, Nahid Mohajeri, Marianne Rodgers, Paul Brooker and Benny Pearman
University of Central Florida-FSEC

Relevance and Approach

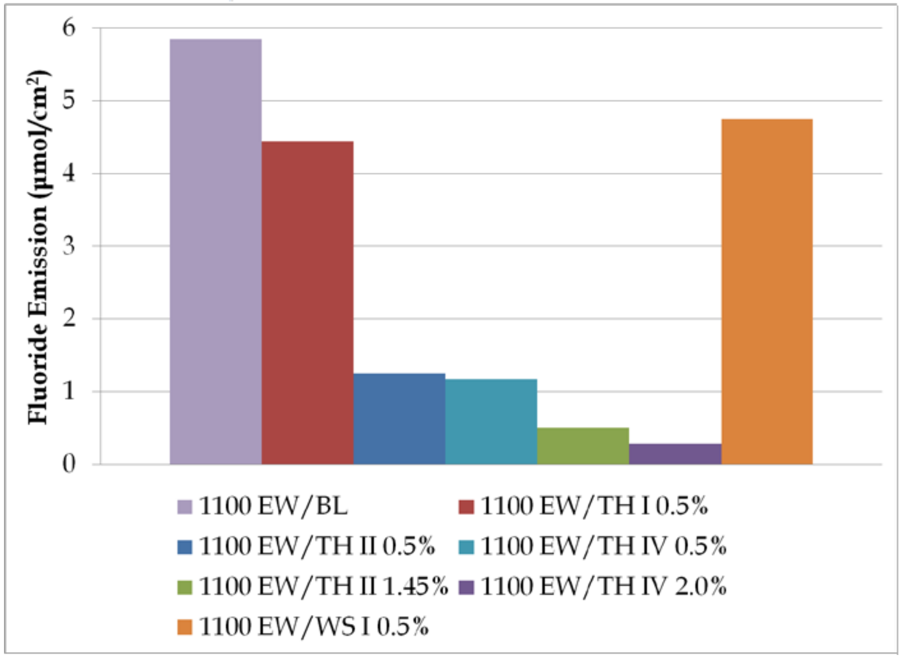
- **Relevance**: Durability is a major target for fuel cells. Understanding degradation mechanisms will lead to greater durability.
- **Approach**: Four tasks
  - Chemical mitigation of membrane degradation
  - Evaluation of platinum band formation
  - Development of Pt band formation mitigation strategy
  - Combination of chemical mitigation and Pt band reduction

Approach- Task 1

- Goal:
  - To investigate the effect of radical scavengers on membrane durability
  - It is hypothesized that the addition of various radical scavengers, such as ceria, would eliminate or substantially reduce the amount of generated radicals
    - Radicals within MEA will compromise integrity, leading to embrittlement and H_2-crossover
  - Fabricate membranes containing ionic and nanoparticular compounds such as: $Ce^{3+/4+}$, Zn^{2+}, MnO_2,CeO_2, ZnO_2, etc.
  - Vary shape, size and concentration of additives
  - Measure membrane properties
    - Proton conductivity
    - Durability in gaseous and liquid Fenton's tests
    - Accelerated fuel cell durability tests
    - Fuel cell performance
  - Optimize chemical mitigator types and levels

Technical Accomplishments & Progress – Task 1

Liquid Fenton Test



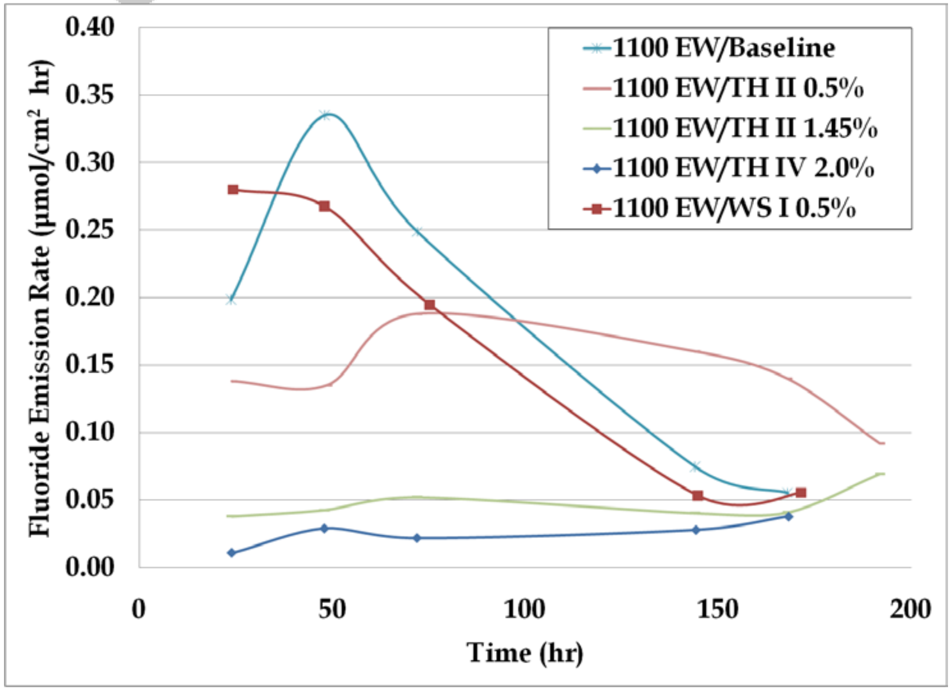
- Addition of ceria to the membranes greatly reduces their fluoride emission
- Synthetic method changes its efficacy
- Radical scavenging ability of ceria depends on its concentration

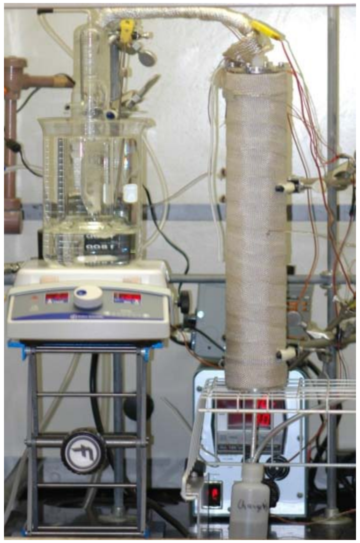
TH – Ceria synthesized via thermal hydrolysis

WS – Ceria synthesized via wet synthesis

Technical Accomplishments & Progress – Task 1

Gaseous Fenton Test





- Gaseous Fenton test confirms the results taken from liquid Fenton test
- Fluoride emission rate for membranes with 0.5% TH ceria is three times higher than membranes with 1.45% TH ceria

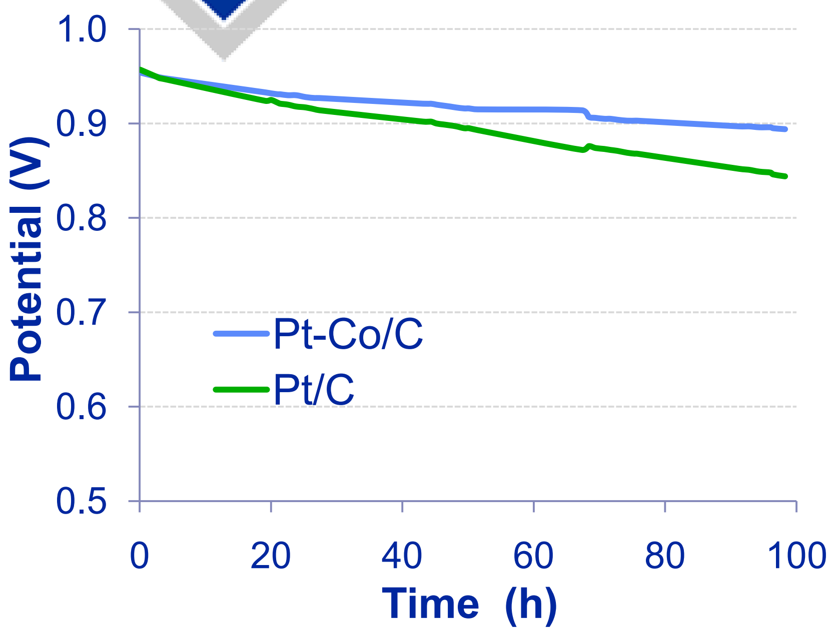
Summary and Future Work – Task 1

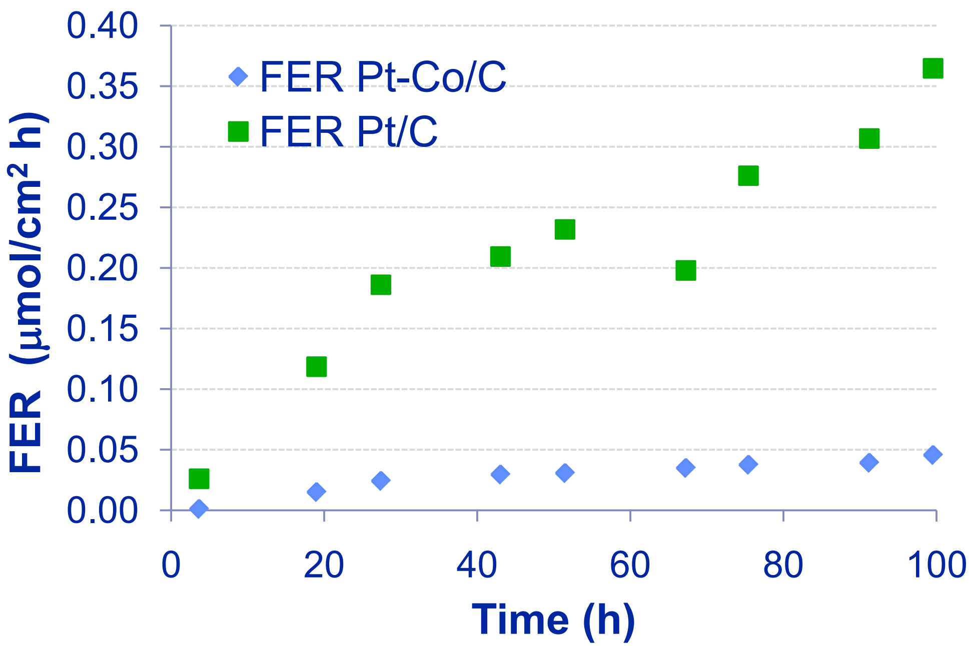
- It was found that in two Fenton tests, liquid and gaseous, the fluoride emission of 1100 EW PFSA membranes is reduced by the addition of cerium oxide to the membrane
- The formulation of the ceria changes its efficacy
- The durability improvement is furthermore dependent on the ceria concentration
- Analysis of cerium oxide is under way to determine the source of improvement
- Accelerated durability tests will be performed and compared to the Fenton tests

Approach- Task 2

- Goal:
  - To investigate the effect of catalyst type on membrane durability
  - It is hypothesized that, because the Pt-Co/C catalyst is more stable in fuel cells than Pt/C, it will lead to lower membrane degradation
    - Less Pt deposited inside the membrane
- Compare the durability of cells containing Pt/C and Pt-Co/C in their electrodes
  - All other aspects of the fuel cells are kept the same
- Open circuit voltage (OCV), 100 h, H_2/air, 90 ^oC, 30% RH
  - Electrochemical pre- and post-testing
    - Cyclic voltammetry, linear sweep voltammetry, polarization
  - During test monitor:
    - Voltage
    - Fluoride emission rate (FER)

Technical Accomplishments & Progress- Task 2





- Tested at OCV at 90 °C/30% RH, H_2/air
- Decay rates:
  - 1.1 mV/h for Pt/C
  - 0.60 mV/h for Pt-Co/C
- Examining the fuel cell condensate water for F^- is an in-situ, nondestructive technique for measuring the degradation rate
- The FER using Pt/C is higher than when Pt-Co/C is used

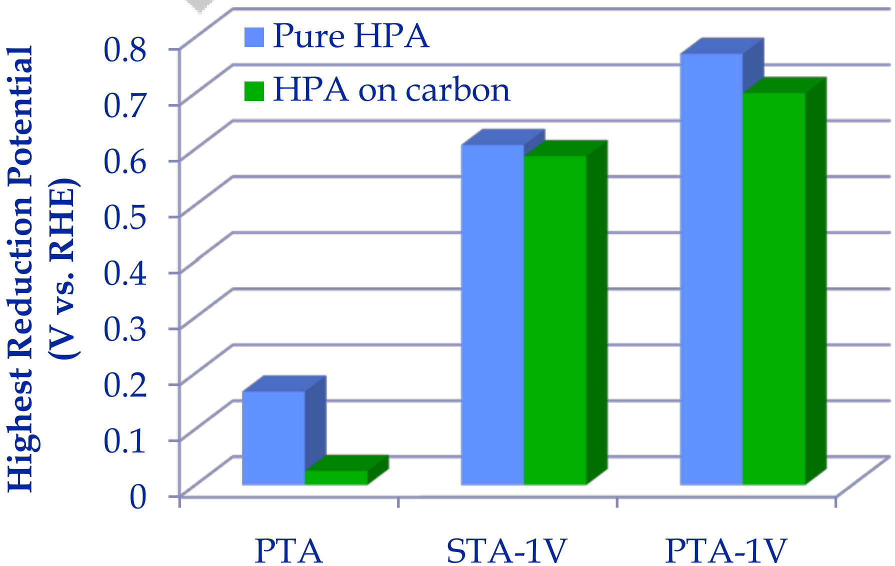
Summary and Future Work – Task 2

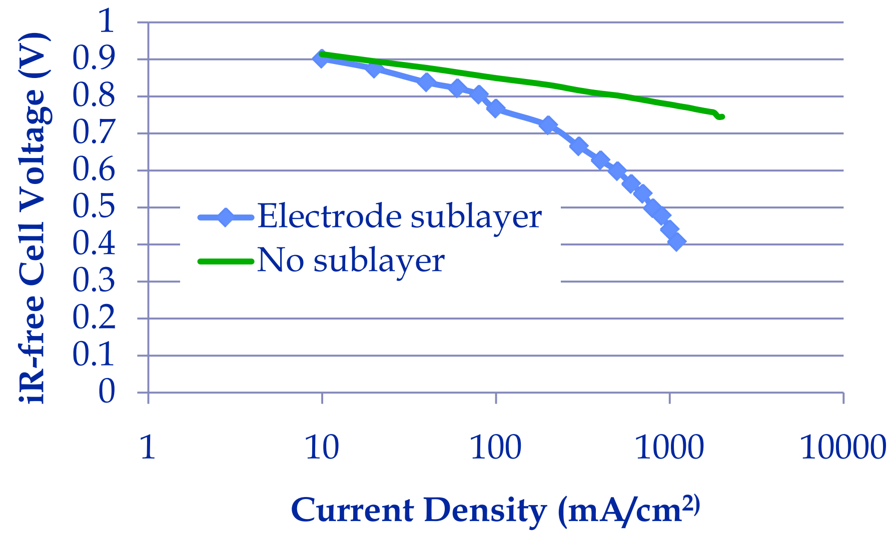
- Using Pt-Co/C rather than Pt/C results in improved cell durability
  - Lower FER and losses in performance and OCV
- It is hypothesized that the improved durability of the cell containing Pt-Co/C over Pt/C is due to the increased stability of the Pt-Co/C
- Further studies including scanning electron microscopy, and transmission electron microscopy are necessary to determine the amount and location of Pt in the membrane

Approach- Task 3

- Goal:
  - To investigate the effect of heteropolyacids (HPAs) within the electrode on membrane durability
  - It is hypothesized that the HPAs could prevent platinum ions from entering the membrane
    - Less Pt deposited in the membrane = less degradation
- Compare the durability of cells containing different HPAs in electrodes
  - HPAs are modified to exhibit different reduction potentials
  - All other aspects of the fuel cells are kept the same
- Test at open circuit voltage for 100 h, H_2/air, 90 ^oC, 30% RH
  - Electrochemical pre- and post-testing
    - Cyclic voltammetry, linear sweep voltammetry, polarization
  - During test, monitor voltage and fluoride emission rate (FER)

Technical Accomplishments & Progress – Task 3





- Synthesized HPAs with high reduction potentials
- Adsorption of HPA onto carbon results in a decrease in reduction potential
  - Micro-environment of HPA is more constricted within carbon
- Fuel cells were created with an electrode sublayer containing HPAs
  - The addition of a sublayer has led to increased performance losses
  - These losses may be diffusion and/or resistance related

Summary and Future Work – Task 3

- Several cells are currently being tested to determine the effect of HPA on platinum migration into the membrane
  - Higher reduction potentials should make the HPA more likely to reduce platinum ions
  - Tested membranes will be examined using SEM and TEM for presence of platinum
- Performance losses will be identified and sublayer will be optimized electrode to reduce these losses
  - HPAs may assist in reaction kinetics, which can only be seen in optimized electrodes

Florida Hydrogen Initiative
SRT Group Inc. (SRT)

Production of Low-Cost Hydrogen from Biowaste (HyBrTec™)

POC: Robin Z. Parker

(305) 321-3677

rzpsrt@thesrtgroup.com

Relevance :

- Conventional Biowaste-to-Fuel processing:
  - Anaerobic Digester
    - requires biological microorganisms (‘bugs’)…temperature dependent, large-volume, low-yields, H_2S contamination
  - Fermentation/Distillation
    - slow-processing ‘bugs’ (yeast) & requires heat for distillation
    - questionable economics, even with $0.45/gal tax credit
  - Gasification
    - not developed for small scale, requires oxygen plant
    - complex gas clean-up >700^o C
  - Pyrolysis
    - feedstock pretreatment & large footprint for upgrade of oil
    - temperature sensitive 200-300^o C – waste stream disposal

The HyBrTec™ Advantage:

- Exploits two thermochemical advantages that reduce the cost and energy of converting waste-to-fuel:
  - elevated temperature and pressure provides high product yield minimizing the size of equipment
    - improves the relationship between fuel production and consumption
  - the chemical bonds requiring energy to release hydrogen are weak, requiring less energy that what hydrogen will produce when burned with oxygen (air)

Approach:

- Bromination[1]
  - Produces hydrogen bromide (HBr) from wet-cellulosic waste
  - Co-produces carbon dioxide (CO_2) & thermal energy (exothermic)

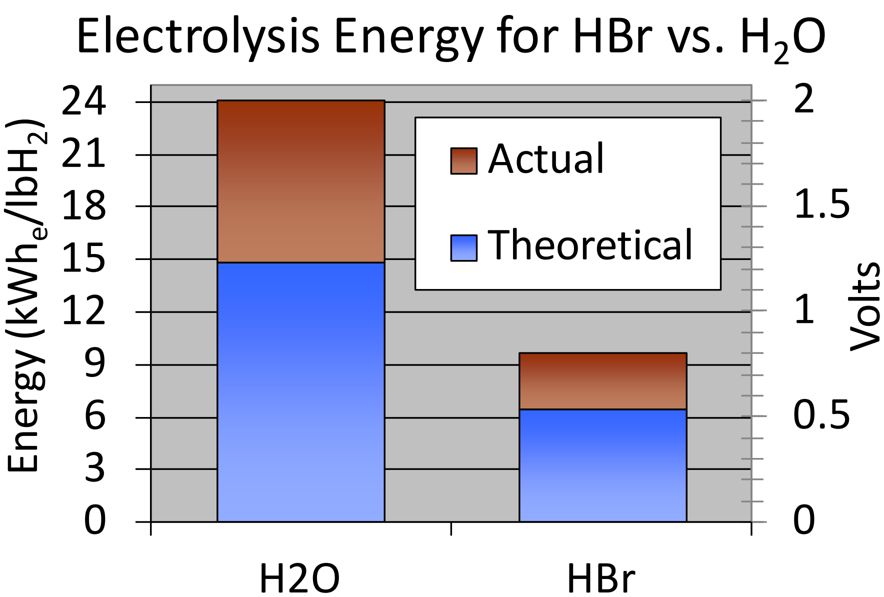
[1]Bromination is analogous to combustion (burning) wood (cellulose) with oxygen from air, only bromine is the oxidizer, consequently HBr is formed instead or H_2O.

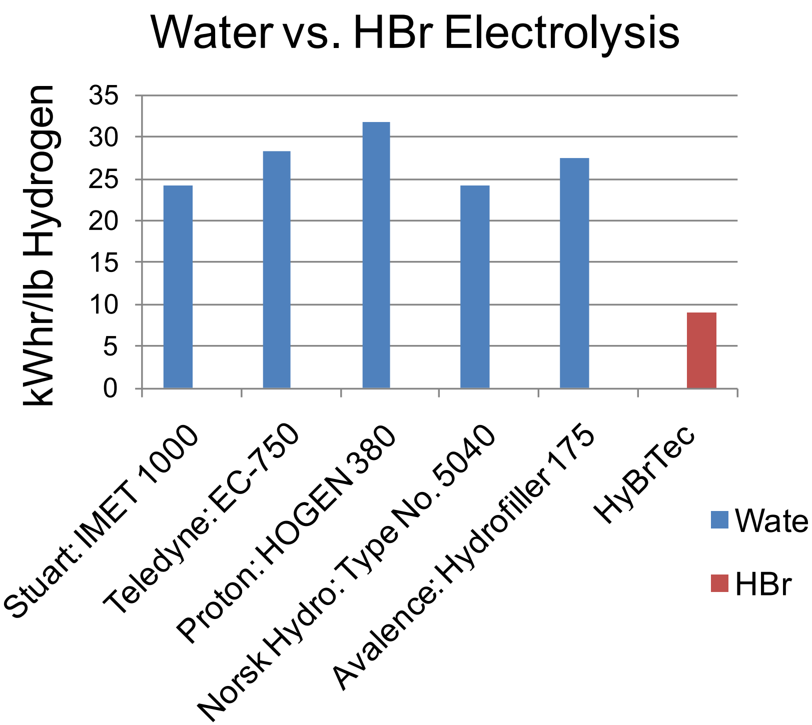
- Electrolysis
  - Dissociates hydrogen bromide ($E^o = 0.555V$) producing recyclable bromine and hydrogen (endothermic)

- Combustion
  - React hydrogen with the more energetic oxygen ($E^o = 1.229V$), affording a *theoretical process efficiency* >100%[2]

[2]Waste-to-fuel efficiency of 70%; >160% if omitting the energy content of waste.

Electrolytic Hydrogen Production (25°C):

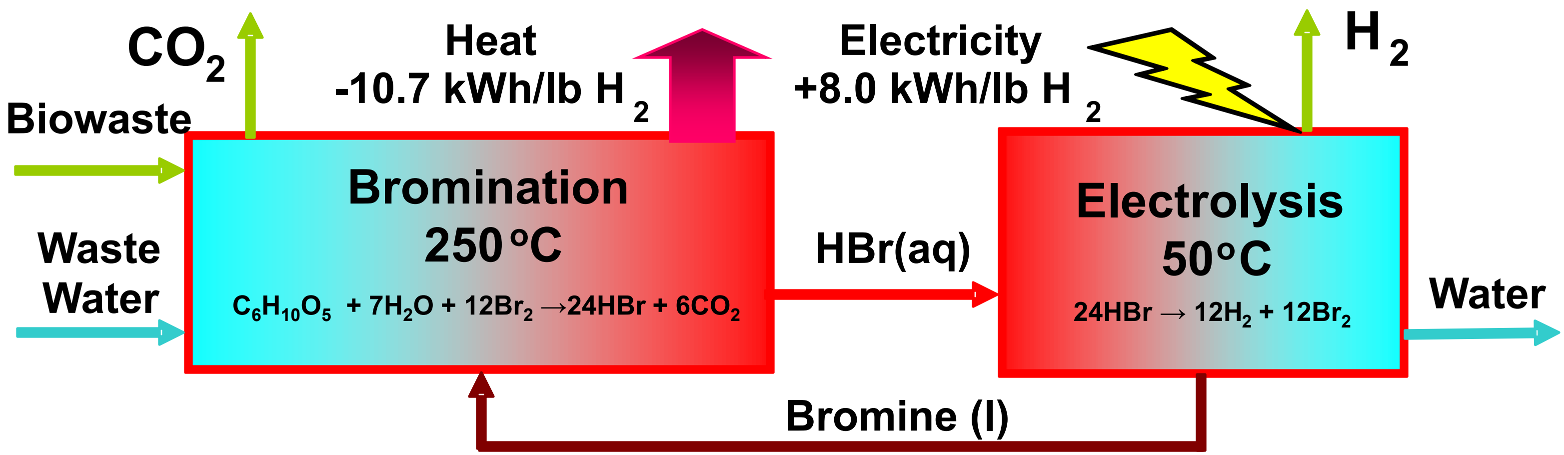




- H_2O electrolysis requires a pure feedstock
- HBr electrolysis improves with conductive contaminates

Summary of Electrolytic Hydrogen Production (Water Electrolysis), September 2004, NREL /MP-560-36734

HyBrTec™ Biowaste-to-Hydrogen:

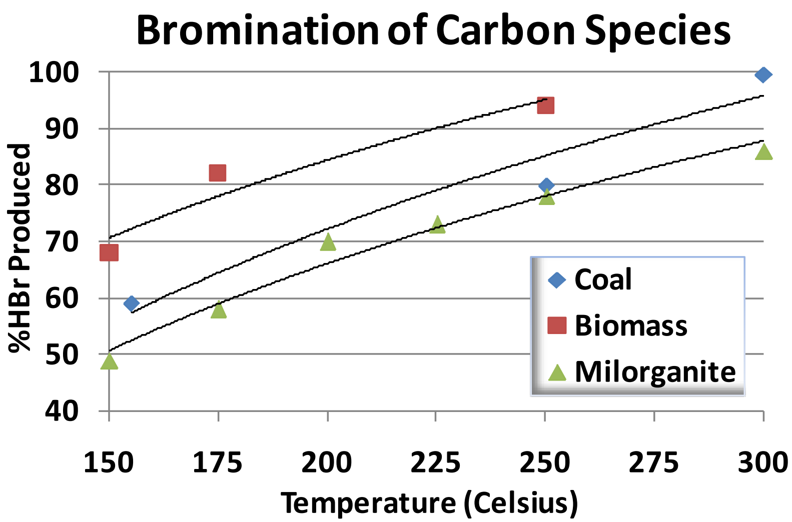


- **Bromination:** $C_6H_{10}O_5 + 7H_2O + \cancel{12Br_2} \rightarrow \cancel{24HBr} + 6CO_2$
- **Electrolysis:** $\cancel{24HBr} \rightarrow 12H_2 + \cancel{12Br_2}$
- **Overall:** $C_6H_{10}O_5 + 7H_2O \rightarrow 12H_2 + 6CO_2$
- **Net enthalpy change: -2.7 kWh/lb H_2**

What Happens to Contaminants?

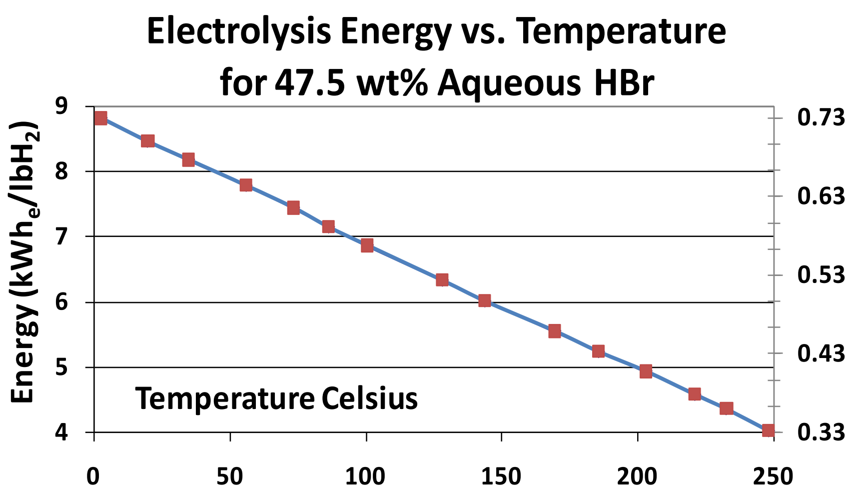
- Pathogens and organisms are killed by bromination
- Sulfur and nitrates are converted into sulfates and nitrogen in exothermic reactions that produce additional HBr
- Metals and other impurities that react with Br_2 to form metal bromides that are treated with dilute sulfuric acid to form metal sulfates and additional HBr
- Sulfates and unreacted carbon are removed with the ash, which is sterile and safe for use as fertilizer

Temperature Effect on Yield & Energy:



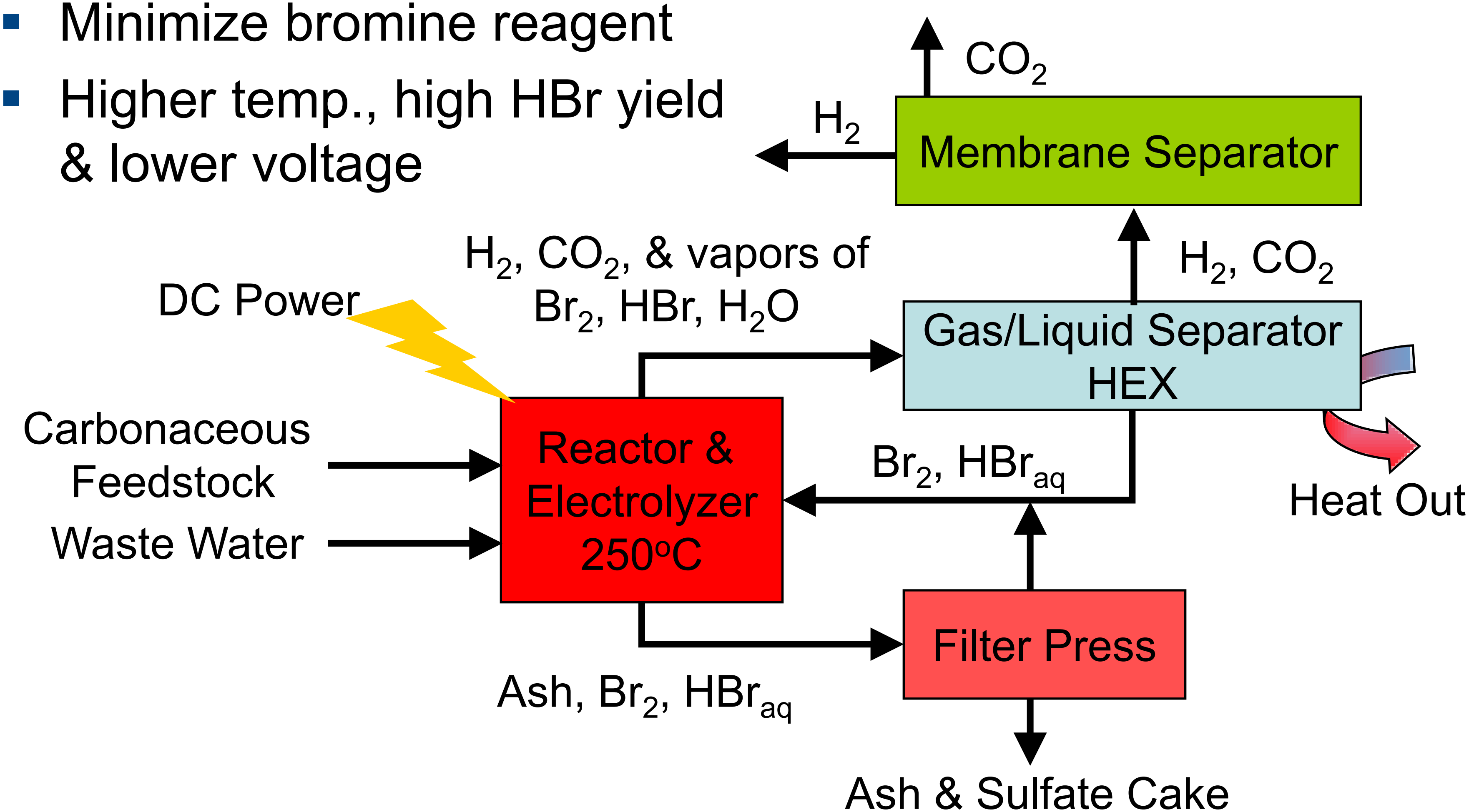
- Increase yield
- 95% biomass conversion to HBr @ 250°C

- Decrease energy
- HBr electrolysis requires 4kWh/lb H_2 @ 250°C



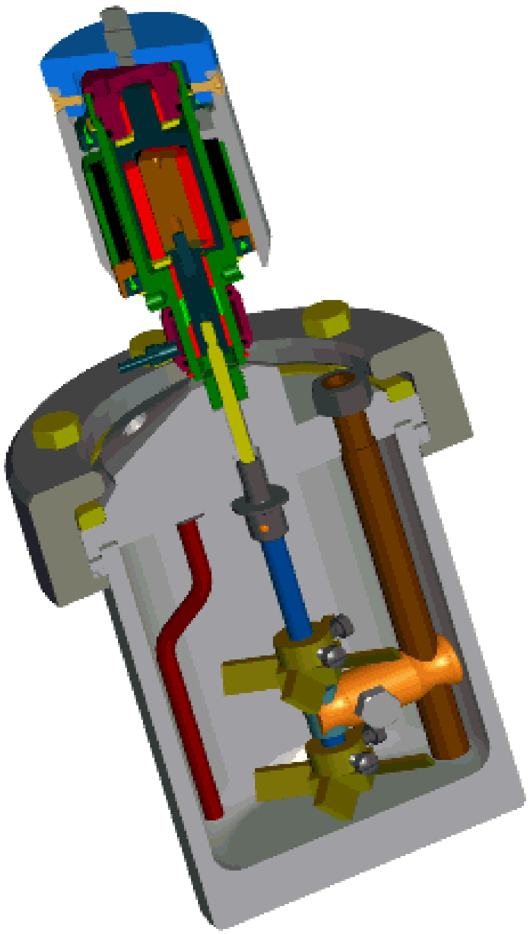
Integrate the Two Processes:

- Minimize bromine reagent
- Higher temp., high HBr yield & lower voltage



DOE/FHI 2011 Program:

- Integrate reactor/electrolysis vessel
  - $250K Program
  - Verify conversion efficiency of >85%
  - Confirm a hydrogen cost of <$1.00/lb
  - Assess regulatory and safety issues
  - Assess entry-markets, end-users issues
  - Assess energy and capital needs
  - Determine scale, cost & performance goals for follow-on prototype



SRT

Accomplishments and Progress:

- Designed & sourced reactor/electrolysis vessel
  - <300^{o} C, <5,000 psi
  - Designed novel MEA (cathode) and anode
  - Determined feedstock and byproduct analysis
- Preliminary bromination experiments are favorable
  - Establish experimental test matrix
    - quantity of cellulose vs. H_2O vs. Br_2 reagents
    - temperature vs. pressure vs. time
- Assembled prototype development team
- Expenditures (1/5/11-2/28/11): <$25K
- Anticipate completing program in 6 months

Future Work:

- High temperature HBr electrolysis
  - Slurry electrodes
  - Voltage vs. concentration vs. temperature
- Integrate bromination/electrolysis
  - Determine optimum temperature and pressure
- Analysis of byproducts
- Preliminary economic analysis

Collaborators (other than DOE & FHI):

- **US Army RDECOM, Aberdeen Proving Ground, MD**
  - DOD requirements for a 1-ton/day system
- **Electrolytic Technologies Corp.**
  - product line of halogen electrolysis system…
- **De Dietrich, Mountainside, NJ**
  - product line of reactors, Nutsche filters, Br_2 recovery systems…
- **Lawrence Livermore National Laboratory**
  - bromination-electrolysis reactor/HEX pressure vessel
- **Sandia National Laboratory, Livermore, CA**
  - controls, instrumentation, safety & UL certification

Florida Hydrogen Initiative (FHI)

Project: Development of a Low-Cost and High-Efficiency 500 W Portable PEMFC System

Jim P. Zheng, Richard Liang, and Wei Zhu, Florida State University, Tallahassee, FL 32310
Harry Chen, Bing Energy Inc. Tallahassee, FL 32310

Research Objectives:

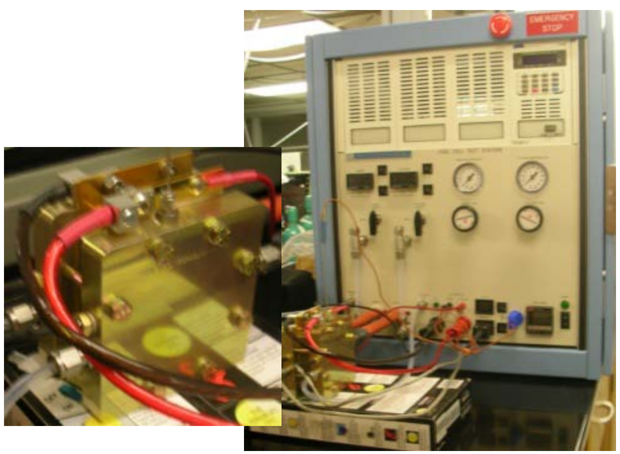
- Demonstrate new catalyst structures comprised of high conducting buckypaper and Pt catalyst nanoparticle coated at or near the surface of buckypaper
- Demonstrate efficiency and durability improvement and cost reduction of using CNT buckypaper based electrodes

Technical Approach

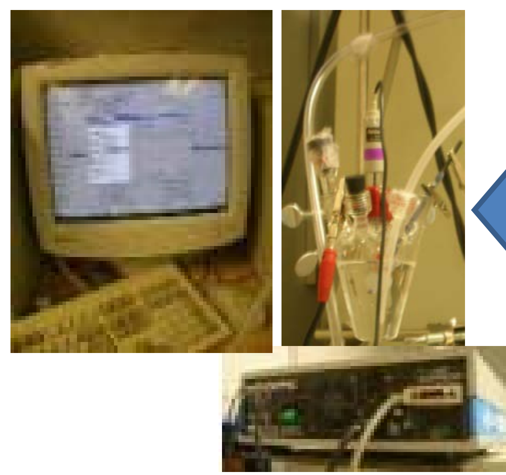
Carbon nanotube

Nanotube suspension

Buckypaper



Characterization of a PEM fuel cell using buckypaper catalytic electrode

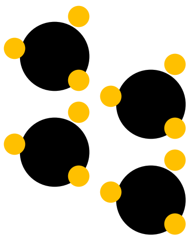


Catalyst characterization by cyclic voltammetry

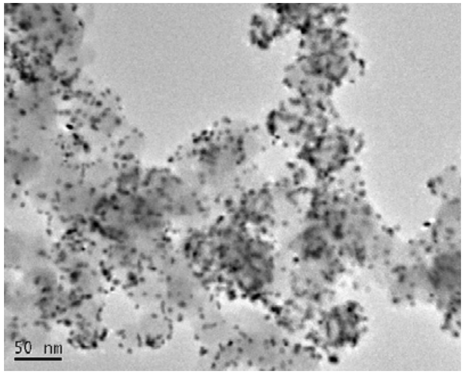
Electrodeposition of Pt

Innovative Fuel Cells Assembly

Conventional method

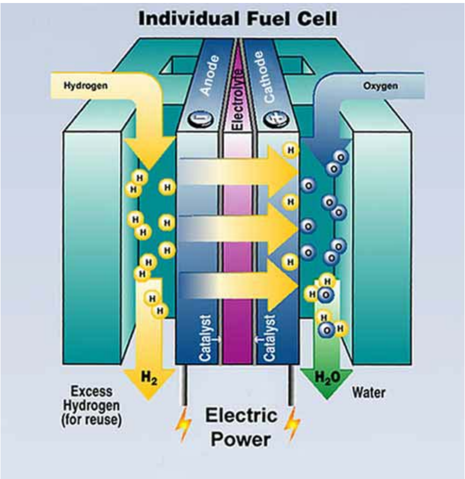


Pt/carbon coating



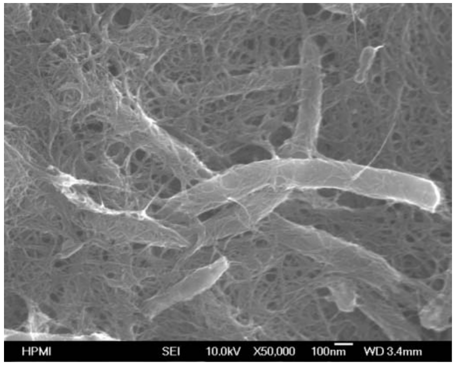
Catalytic electrode film

Disadvantages:
- Low Pt usage: due to Pt blocking by support materials and micropores
- Poor durability: carbon surface corroded under the severe condition

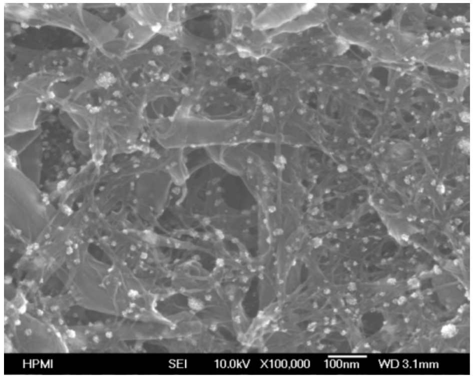


MEA & fuel cell assembly

Our method



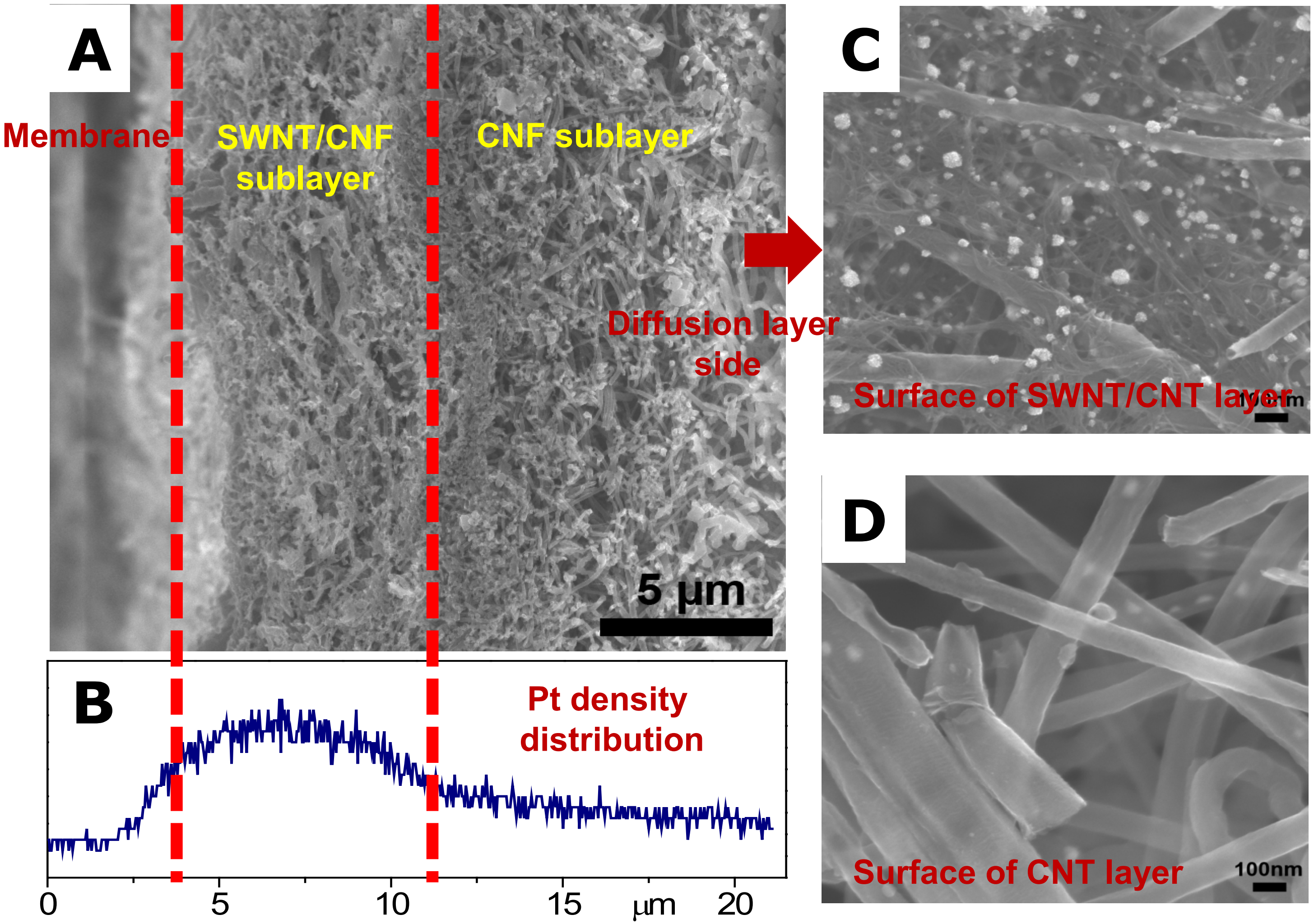
Buckypaper
(Mixture of CNT/CNF)



Pt/buckypaper coating

Advantages:
- High Pt usage: no Pt blocking
- Good durability: stable CNT surface

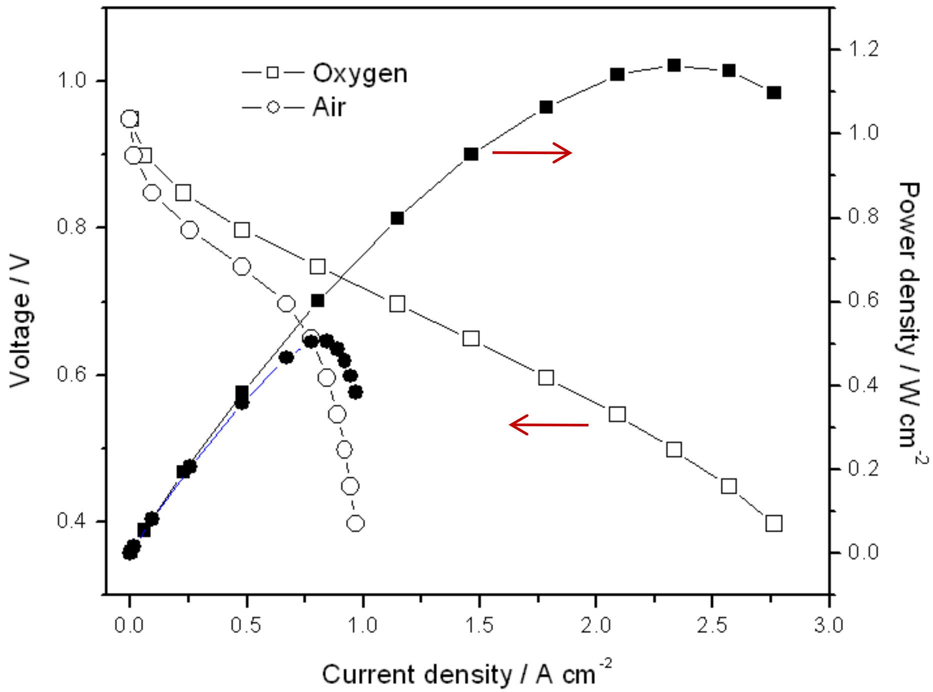
Images of Two-Layered Pt/Buckypaper

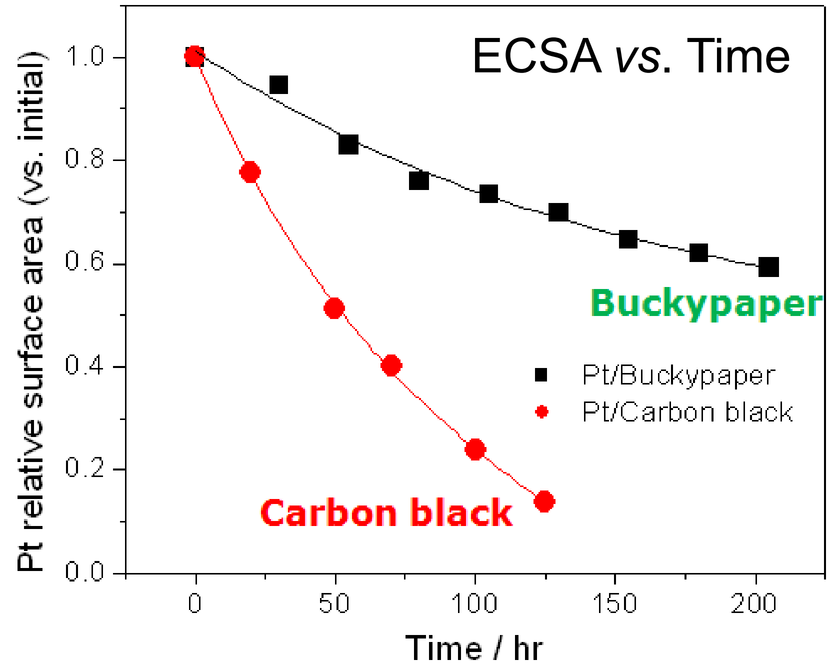


Unique Properties of buckypaper based catalytic electrodes

- The porosity in non-uniform in electrode
- The Pt is not uniformly distributed CNT surface
- High surface area
- Minimum micropore
- Highly electrical conductivity
- Good durability in electrochemical oxidation

Cell Performance





H_2-O_2 (Air) Fuel cells at 80 °C

•Cathode Pt loading 0.11 mg_{Pt}/cm^2, Anode Pt loading 0.05 mg/cm^2

•Rated power density: **956 mW/cm^2 (510 W/cm^2)** at 0.65 V

•Pt utilization: **0.167 g_{Pt}/kW (0.314 g_{Pt}/kW)**

Accelerated Durability Test

- Three-electrode cell setup
- 0.5 M H_2SO_4 electrolyte
- Fixed potential (0.95 V *vs* SCE) applied to working electrode for 200 hours
- ECSA characterized by CV every 5 hours

2015 DOE Targets and Current Results Achieved in FSU/BEI for Electrocatalyst and MEAs

Characteristic	Units	DOE Targets for Cell Stack	2009 FSU Status for H_2-O_2 (Air) FC
Platinum group metal total content (both electrodes)	g/kW (rated)	0.125	0.167 (0.314)
Platinum group metal (pgm) total loading	mg PGM /cm^2 electrode area	0.125	0.16
Electrochemical area loss	% after 100 hours @1.2V	<40	55
Electrocatalyst support loss	mV after 100 hours @1.2V	<30	60
Mass activity loss	% after 100 hours @1.2V	<60	57
Mass activity	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.44	0.3
Specific activity	μA / cm^2 @ 900 $mV_{iR\text{-}free}$	720	600
Performance @ rated power (MEA)	mW / cm^2	1,000	956 (510)

Current Research
Fuel Cell Module Development

Florida Institute of Technology
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Hydrogen and Fuel Cell Technology Academic Program

Relevance:

For hydrogen energy to become viable, an interdisciplinary approach to education should be developed and implemented.

The program will allow students to:

- Follow hydrogen technology from introduction to long-term applications
- Obtain a basic understanding of the fundamentals of the field
- Redirect their current technology focus as a means for new career options
- Measure students' gains in knowledge of hydrogen as a fuel source
- Interact with outside industries
- Satisfy the need for hydrogen technology graduates

Hydrogen and Fuel Cell Technology Academic Program

Approach:

- Develop Masters Degree area of specialization
- Develop modules for existing undergraduate courses
- Support senior design and capstone projects
- Prepare hydrogen-themed general chemistry lab experiments

Hydrogen and Fuel Cell Technology Academic Program

Technical Accomplishments & Progress

- Initial Hydrogen Knowledge and Opinion surveys administered to MAE and Chemistry students.
  - Results show a general need for hydrogen and fuel cell technology education.
  - Results show most students currently obtain their knowledge of energy from modern media such as television and the Internet rather than classroom instruction or print media.
  - Results show that students do not have a uniform projection of the future of hydrogen and fuel cell technology.
- Graduate courses and modules under development.
- Present pending curriculum at international conference, “Sustainability 2011: Is It Worth It?”

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Hydrogen-Themed General Chemistry Lab Experiments

Kurt Winkelmann, Department of Chemistry

Relevance

Improve students' views about chemistry and their knowledge about hydrogen as an alternative energy source

Approach

Add experiments to General Chemistry II lab course

Experiments are related to hydrogen fuel research

PI will adapt/improve published experiments

Experiments will use an inquiry pedagogy

Measure effect of experiments on students' views and knowledge about hydrogen (Hydrogen Knowledge and Opinion Survey, HKOS)

Measure changes in students' perspectives about chemistry (in-house survey)

Hydrogen Experiments

Produce H_2 by semiconductor photocatalysis

Absorb and store H_2 in metals

Produce H_2 by enzyme-catalyzed reactions

Detect an intermediate of H_2 combustion

Construct a solar powered H_2 electrolysis cell

Construct an H_2 fuel cell

Accomplishments and Progress

Beginning development of new experiments

Determining baseline HKOS responses

Future Work

Introduce new experiments in spring 2012

Continue collecting HKOS student responses

Florida Institute of Technology
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Hydrogen and Fuel Cell Technology Academic Program

Anticipated Results

- A strong curriculum on hydrogen and fuel cell technology that will assist undergraduate students in furthering their understanding of hydrogen and fuel cell technology and offer graduate students a career path into renewable energy.
- Students prepared for entry into research and other positions related to hydrogen technology within government, industry and academia.
- The strengthening of Florida as a cornerstone of the southeastern fuel cell and hydrogen hub.

Design and Development of an Advanced Hydrogen Storage System using Novel Materials

E.K. Stefanakos, D. Yogi Goswami, A. Kumar
CERC, University of South Florida

Project Goal

Design and develop novel conducting polymeric nanomaterials for on-board hydrogen storage with a system gravimetric capacity of 5.5 wt.% or greater and completely reversible hydrogen storage characteristics at moderate temperature (<100 ^{o}C).

DOE's new 2015 Technical targets for storage system

Gravimetric 0.055 kg H_2/kg Volumetric 0.040 kg H_2/L

CERC
Clean Energy Research Center

USF UNIVERSITY OF SOUTH FLORIDA

Specific objectives

Task 1: Fabrication of polymer nanostructures for reversible hydrogen storage

Task 2: Modification of polymer nanostructures for e.g. by CNT, Graphene and transition metal catalyst doping

Task 3: Engineering system design, development and testing

Task 4 Education and Outreach

Proposed Approach

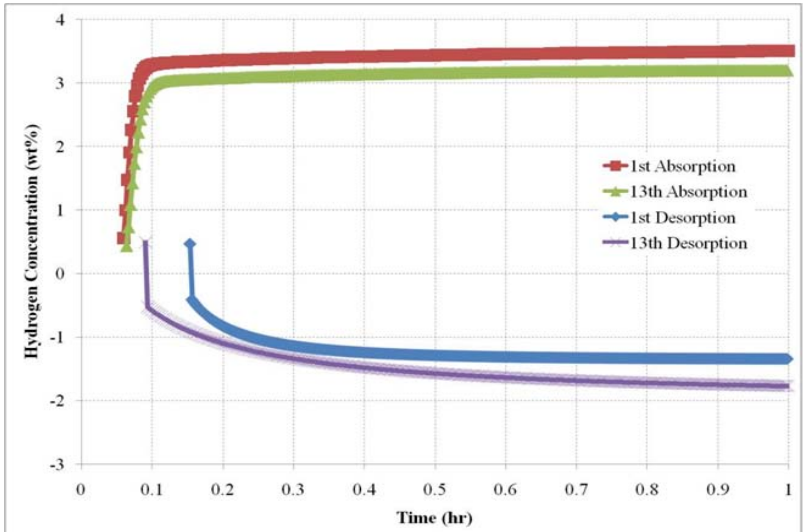
- Synthesis of polyaniline (PANI) - a solid state hydrogen storage material.
- Modification of synthesis parameters for optimized storage capabilities.

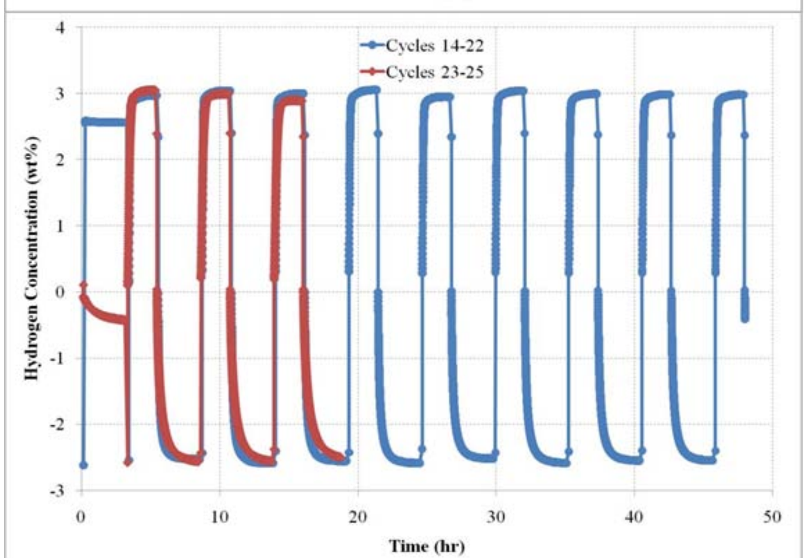
Major Challenges

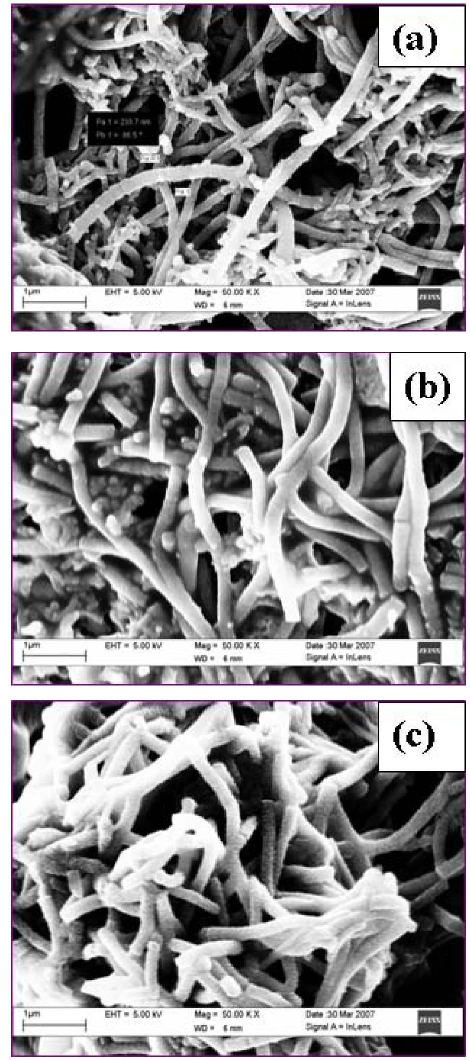
Develop polymer nanostructures that can store hydrogen at room temperature, and be reversible for many cycles

Preliminary Work at CERC

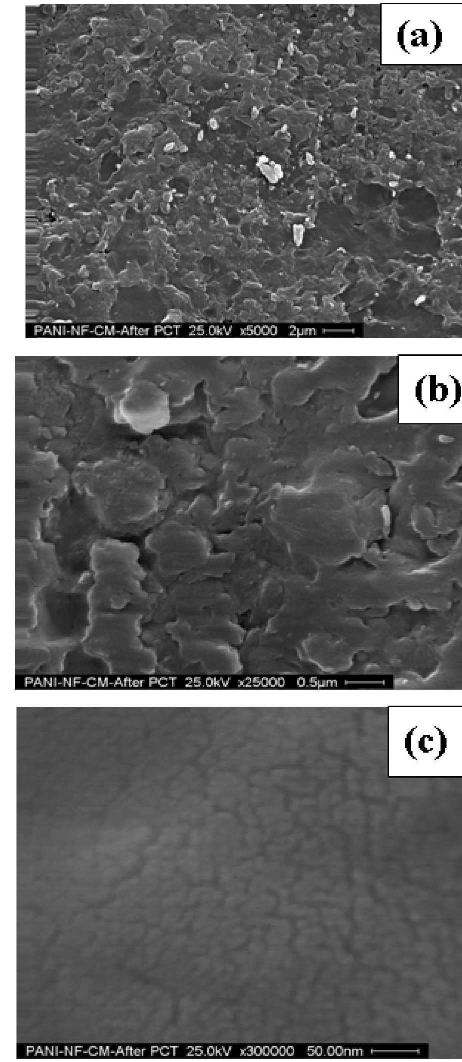
Hydrogen Sorption Kinetics - PANI Nanofibers







Before H_2



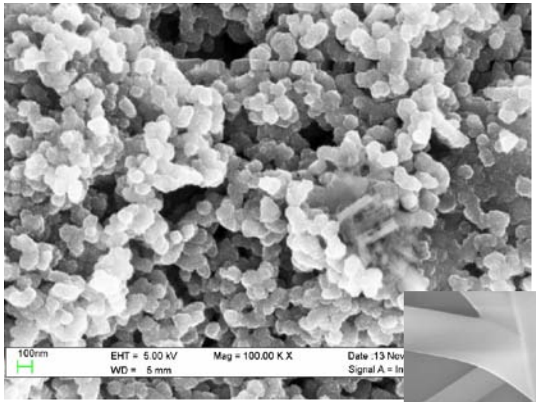
After H_2

M.U. Niemann, S.S. Srinivasan et. al., J. Nanoscience and Nanotechnology, 9, 2009, 1-5.

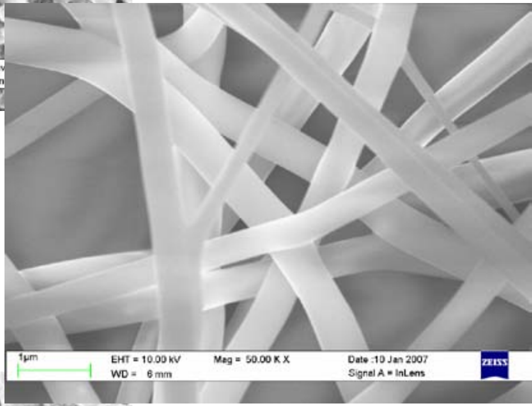
Preliminary Work at CERC

PANI Nanostructures for H_2 Storage

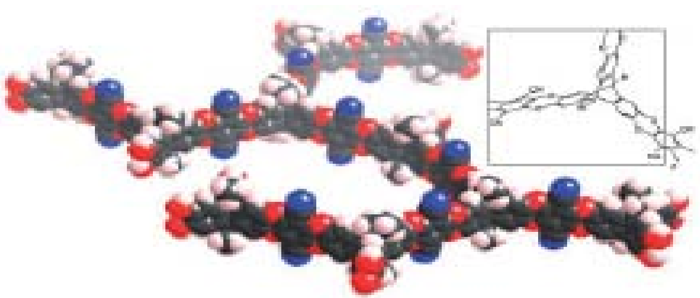
- PANI Nanospheres(NS) – Chemical Method



- PANI Nanofibers (NF)– Chemical (CM) Method

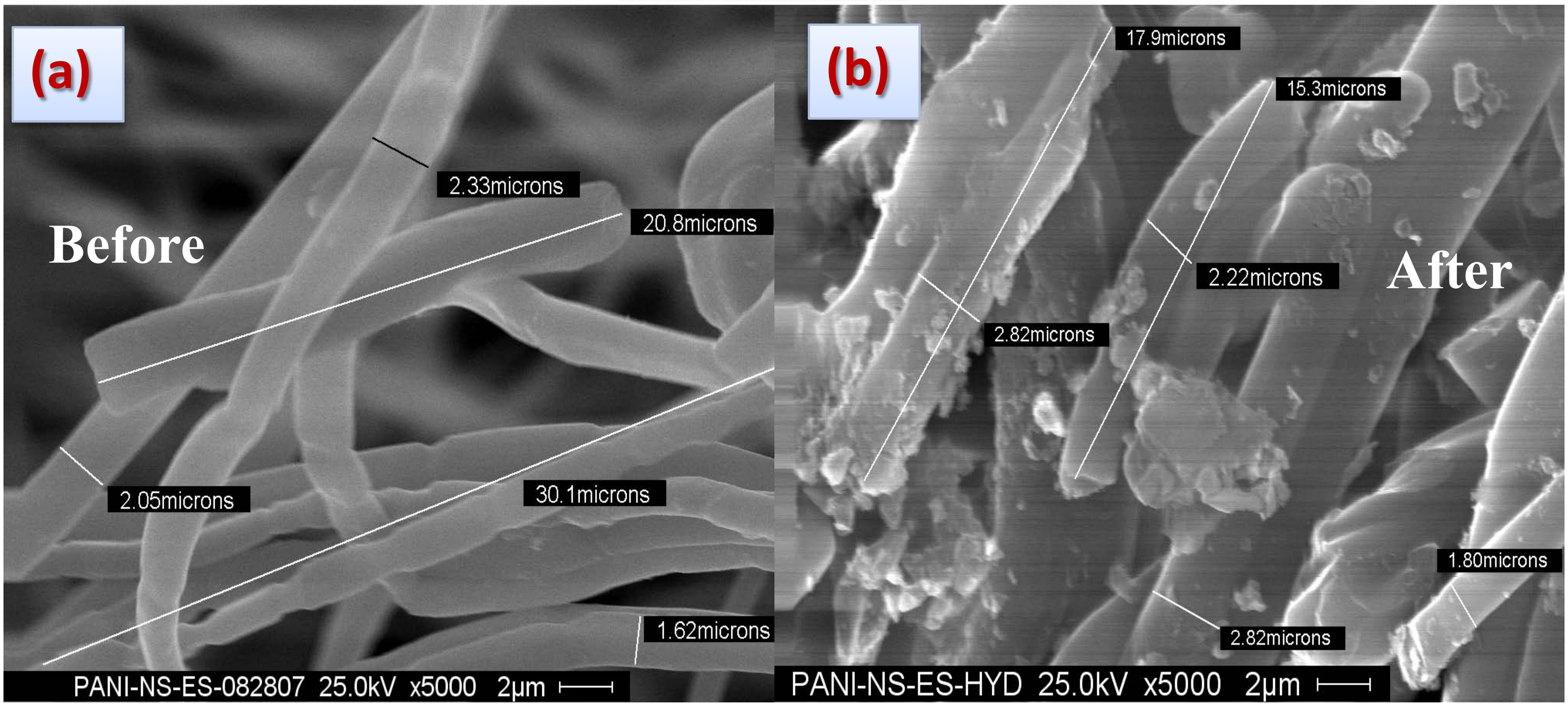


- PANI Nanofibers – Electrospun (ES) Method



Morphological Effects of H_2 Cycling on PANI NF-ES

SEM image



Preliminary Work at CERC

PANI Nanostructures Summary

Material	Capacity	Reversibility	Temperature	Comments
PANI Bulk	0.4 wt%	Small	125°C	
PANI NS-CM	6 wt%	Decreases to 0.5 wt%	30°C	Slow kinetics (hours)
PANI NF-CM	3 wt%	Reversible	30°C	Fast Kinetics (<10min)
PANI NF-ES	10wt%	Reversible with PCT, capacity decreases with kinetics measurement	100°C (kinetic) 125°C (PCT)	Kinetics combination of physisorption (rapid) and chemisorption (slow)

- PANI nanostructures combine physisorption and chemisorption
- Reversible storage of >3wt% possible at room temperature
- Reversible storage of <10wt% possible at 100°C

Project Timeline

TASK NAME	Q1	Q2	Q3	Q4	Q5	Q6
Task 1: Fabrication of polymer nanostructures for reversible hydrogen storage						
Task 2: Modification of polymer nanostructures for e.g. by CNT, Graphene and transition metal catalyst doping						
Task 3: Engineering system design, development and testing						
Task 4 Education and Outreach						

Critical Milestones and Deliverables

- Synthesis and characterization of conducting polyaniline which would be storing hydrogen with a system gravimetric capacity of 5.5 wt.% or greater and completely reversible hydrogen storage characteristics at moderate temperature (<100 ^oC).

- Demonstrate the hydrogen storage system

- Implementation of course, curriculum development and education outreach

Task 14: Advanced HiFoil™ Bipolar Plates

James Braun

Manager, Advanced Materials and Technology

EnerFuel, Inc.

1501 Northpoint Pkwy, Suite 101

West Palm Beach, FL 33407

(561) 868-6720 ext. 227 jbraun@enerfuel.com

DOE Contract #DE-FC36-04GO14225 FHI Project ID #

Sales@enerfuel.com

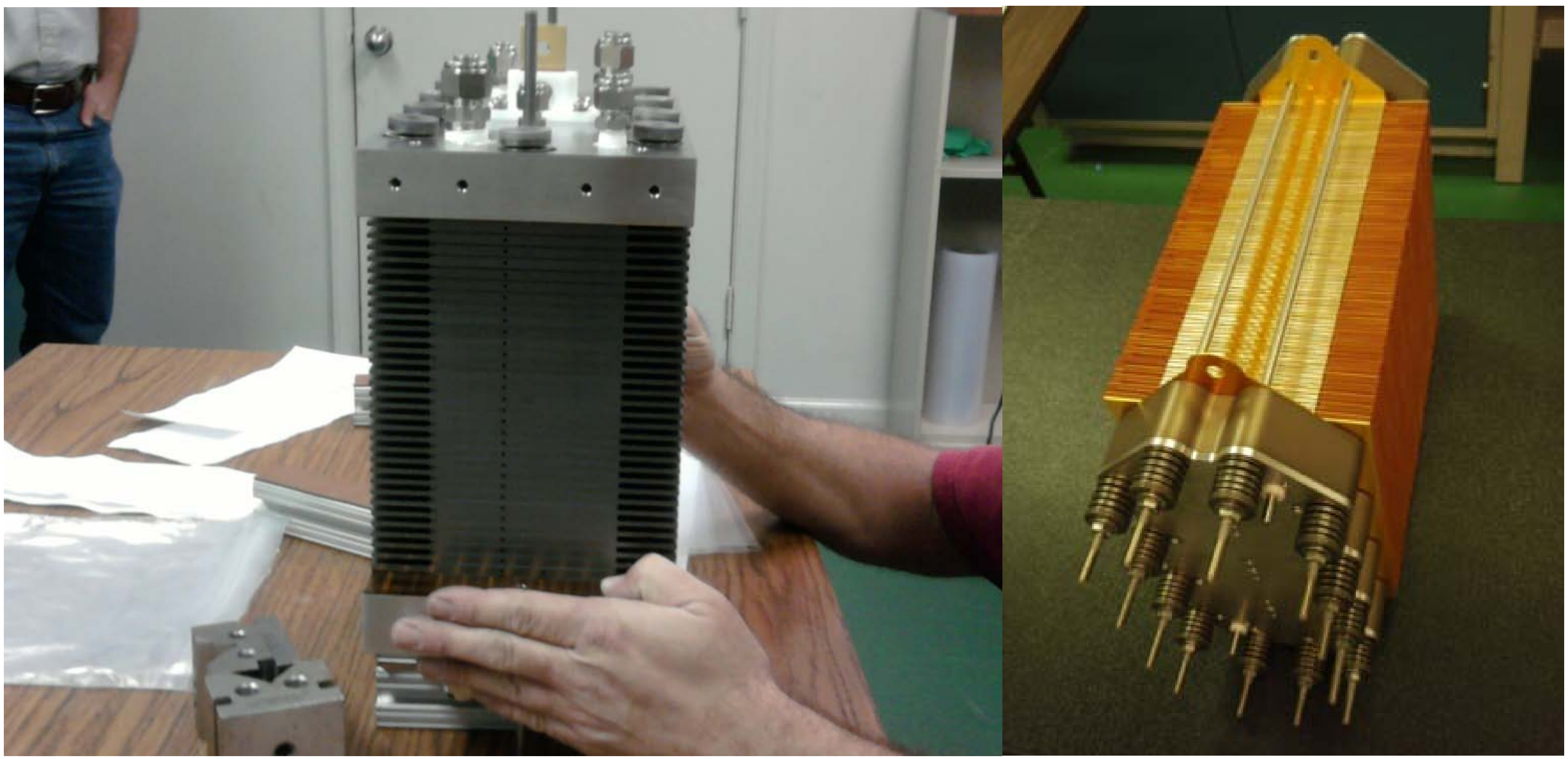
Project Goal - Relevance

Address **cost** and **durability** barriers for **H**igh **T**emperature **P**roton **E**xchange **M**embrane (**HT-PEM**) fuel cells by providing a low cost, easy to form, corrosion-resistant ***laminate*** bipolar plate having high thermal conductivity and improved mechanical strength/crack resistance

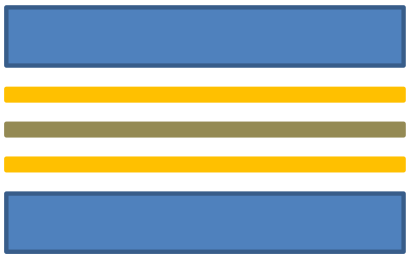
 Sales@enerfuel.com

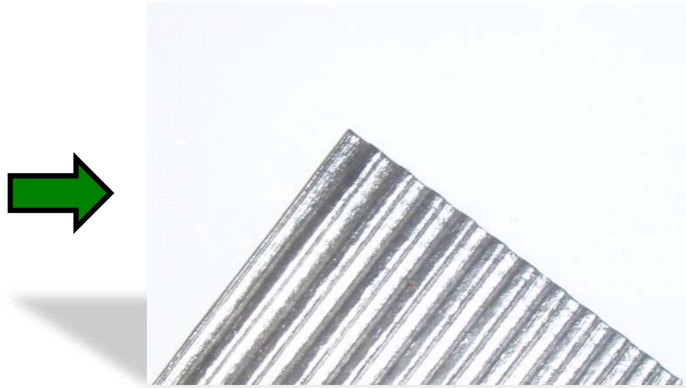
Existing Plate Technology

Existing bipolar plate technology includes machined expanded graphite composite plates (at left) and gold coated stainless steel plates (at right).



Patent-Pending Laminate Technology

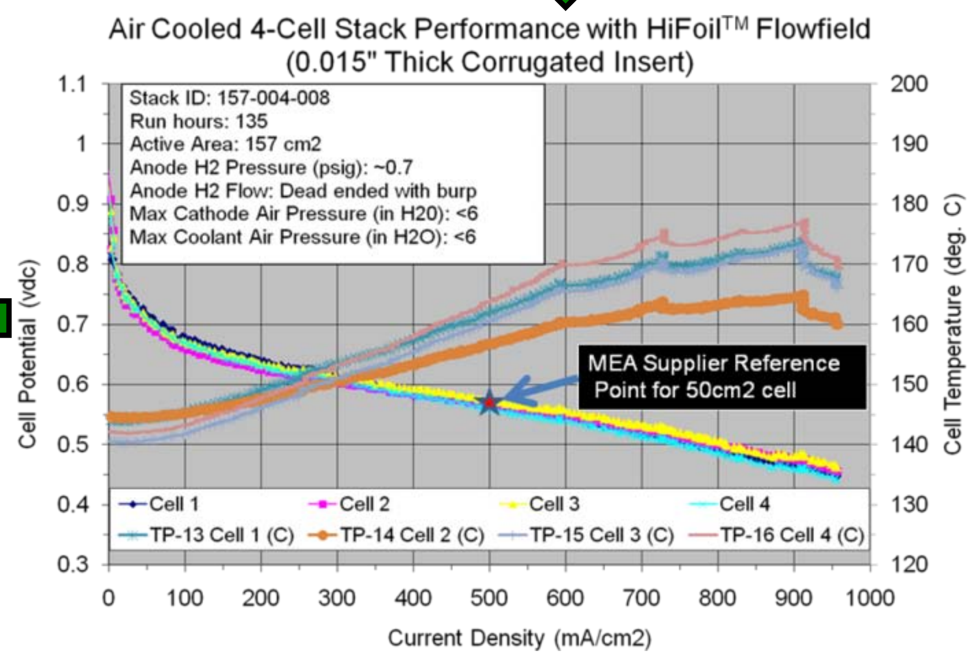




<u>HiFoil™ Laminate Technology</u>

Corrugated Inserts:

- Excellent performance
- Corrosion resistant
- HTPEMFC stack tested for 1,000 hours with no failure
- Ex-situ: thermal cycled from RT to 200°C over 10,000 times with no failure



Sales@enerfuel.com

Project Objectives and Approach

Project Objectives/Task Matrix Objective	Task 1. Laminate Fabrication	Task 2. Flow Field Formation	Task 3. Bipolar Plate Sealing	Task 4. HT-PEMFC Stack Testing	Task 5. Performance Validation	Task 6. Reports
1. Double-sided Plate - Achieve two-sided flow field formation in HiFoil™ laminates using a lab-scale embossing process	X	X				X
2. Integral Seal - Achieve a robust seal against porosity around fluid ports and plate edges using a dispensed sealant or coating			X			X
3. Stack Validation - Obtain performance data in an air-cooled, reformate capable HTPEM fuel cell stack				X		X
4. Meet DOE Targets - Meet or exceed DOE bipolar plate technical targets					X	X

Risk Mitigation Approach

Objective 1. Double-sided Plate

Flowfield Reproduction – material sticking in die. Mitigate with more stable expanded graphite layer, change layer thickness, reduce channel depth, increase draft angle and evaluate release agents.

Objective 2. Integral Seal

Sealing – gas leaks from edges of graphite layers. Mitigate by increasing graphite layer density near edges and increase encapsulation layer thickness and uniformity.

Objective 3. Stack Validation

Cell Compression – MEA over/under compressed. Mitigate by using tight tolerance frame hardstop.

Objective 4. Meet DOE Targets

Corrosion – metal ions contaminate MEA. Mitigate by upgrading metal alloy, Ni-B coating, increase conductive adhesive thickness and polymer content.

Electrical Resistance – through-plane resistance does not meet target. Mitigate by increasing metal/coating surface area and adhesive graphite content.

Cost – does not meet target. Mitigate using lower cost metal and reducing thicknesses.

Weight – does not meet target. Mitigate by reducing layer density and thickness.

Expected Results

Demonstration and characterization of **advanced fuel cell materials** that combine the strength of metal with the corrosion resistance of graphite, for use as a bipolar plate in High Temperature Proton Exchange Membrane (HTPEM) Fuel Cells operating at ~200°C . *Expected to lead to long life, high power density stacks and better thermal management/cell heat transfer.

• HiFoil™ samples fabricated	March-September 2011
• Flow fields formed	June-October 2011
• HTPEM single cell test	August 2011
• HTPEM sub-scale stack testing	November 2011 - May 2012

Collaborating Partners:

Dr. Yancy Riddle UCT COATINGS

Dr. Juan Nino UF UNIVERSITY of FLORIDA

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EnerFuel

Future Commercial Applications

Transportation


Car


Materials Handling


Buses


Scooters


Trains


Planes


Boats


APU – Trucks


APU – Military


APU – Police

Fuel Cell Cost ↓

Durability ↑

Stationary


Home Power


Office Building


Telecom Power


Facility Power

Remote Locations


Yachts


Cruise Ships


Space Shuttle


Submarine

Additional Uses

- Backup Power
- Base load power plants
- Off-grid power supply
- Notebook computers
- Smartphones