



2007 DOE Hydrogen Program Review

Hydrogen Production and Fuel Cell Research

University of South Florida
Presenter: Yogi Goswami

May 18, 2007

Project ID #
PDP41

PDP41 Project Tasks

H₂ Production and Fuel Cells (PDP41)

- Thermochemical H₂ Production
- Biomass H₂ Production
- Photocatalytic/Photoelectrochemical H₂ Production
- PEM Fuel Cell Research

H₂ Storage (Please see STP18)

D. Yogi Goswami¹, Elias K. Stefanakos¹
Man Su Lee², Stacey Dolan², H. Skip Ingley²

¹University of South Florida

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Thermochemical Hydrogen Production

Overview

Timeline

- Start - October 2005
- Finish - December 2007
- 70% complete

Barriers

- DOE 3.1.4.2.5 U - High Temperature Thermochemical Technology
- DOE 3.1.4.2.5 V – High-Temperature Robust Materials
- DOE 3.1.4.2.5 X - Coupling Concentrated Solar Energy and Thermochemical Cycles

Partners

- University of South Florida
- University of Florida

Objectives

- Investigate UT-3 thermochemical cycle and conduct kinetic studies
- Improve stability and performance of solid reactants for gas-solid reactions
- Lower hydrogen production cost by increasing hydrogen yield with an improved pellet formulation
- Reduce operating cost by lowering the reactor operating temperature

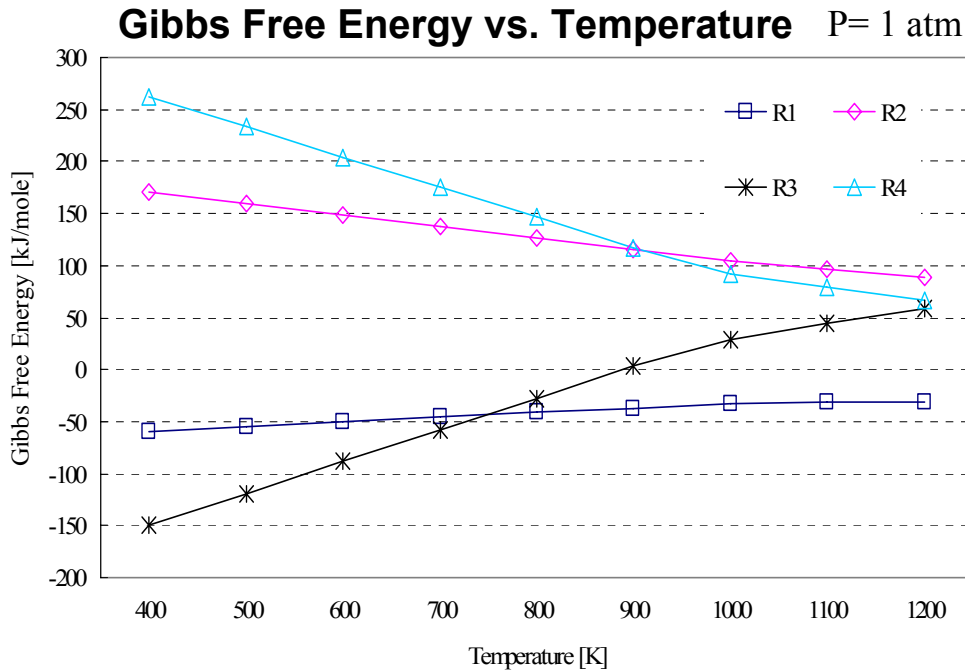
Approach

- Thermodynamic simulations for theoretical optimal operation conditions.
- Experiments on the feasibility of UT-3 thermochemical cycle for hydrogen production
 - Evaluation of characteristics of calcium oxide (CaO) solid reactants with pellet-type and film-type structures to improve their formulation
 - Chemical kinetic studies to evaluate and improve the cyclic life, reaction rates and conversion of the solid reactants using lab-scale apparatus

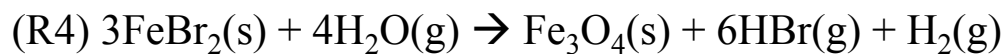
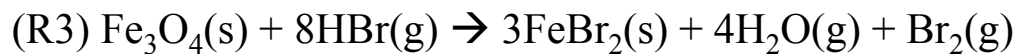
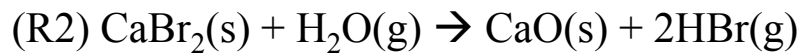
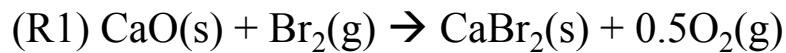
Accomplishments

- Thermodynamic simulations were conducted to find optimal operation conditions.
- The experimental set-up for kinetic studies was installed.
- CaO *pellets* were developed and tested. The large volume changes between CaO and CaBr₂ collapsed pores which degraded performance.
- CaO *films* were developed to overcome the problems with pellets.
- Kinetic studies on CaO pellets and films are underway.

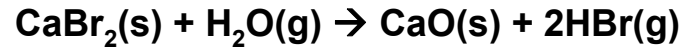
Results: General Characteristics of Reactions



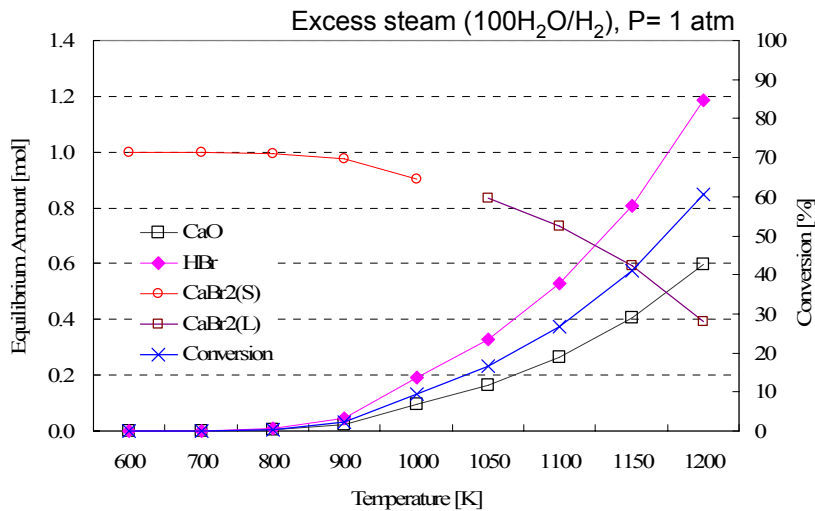
- Hydrolysis reactions(R2 & R4) of CaBr_2 and FeBr_2 are not spontaneous.
- High temperature is preferable for R2 and R4 because these reactions are endothermic, but it is limited due to the melting point of the bromide.
- Conversion of CaO to CaBr_2 increases volume by 76% which leads to a significant decrease of porosity.
- This reduction leads to low reactivity and degradation of the solid reactant.



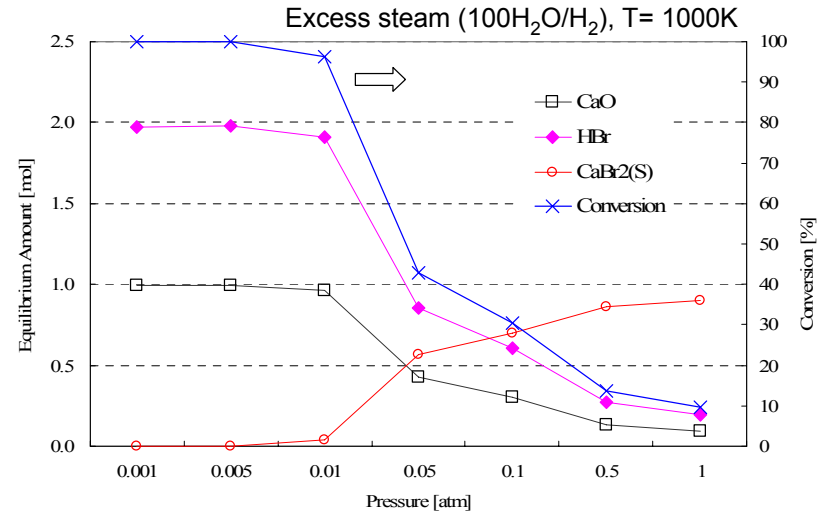
Hydrolysis of CaBr₂



* Effect of temperature

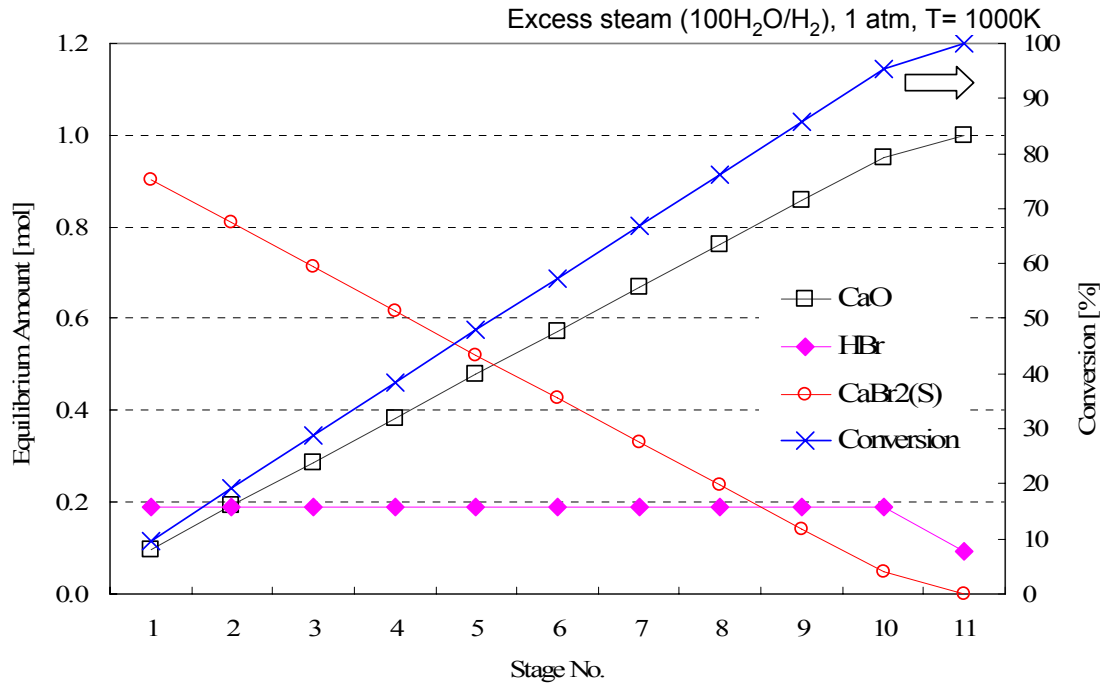
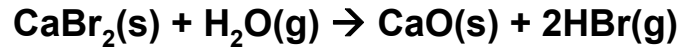


* Effect of pressure



- Hydrolysis of CaBr₂ is the slowest reaction in UT-3 cycle.
- The conversion was significantly increased with the elevation of temperature, but there is a limitation since calcium bromide melts at about 1000K.
- High conversion can be achieved at low pressure theoretically, but the low pressure condition may be impractical as well as inefficient for mass production of hydrogen.

Effect of Removal of HBr from Equilibrium States



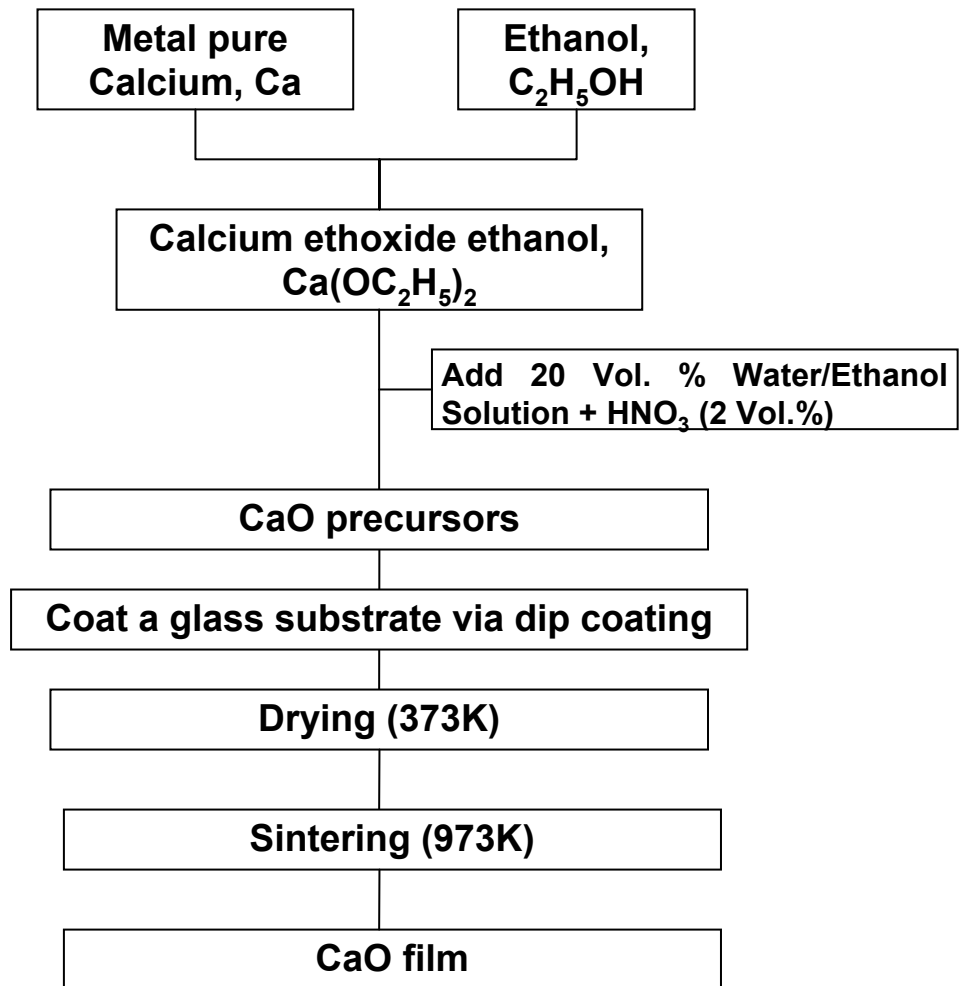
- The conversion efficiency can be higher even at atmospheric pressure if the gaseous products are removed immediately from the reactor.
- Simulation and experimental results confirm that conversion can be completed by removing the product gas, HBr, from the reactor.

Introduction of Calcium Oxide Film

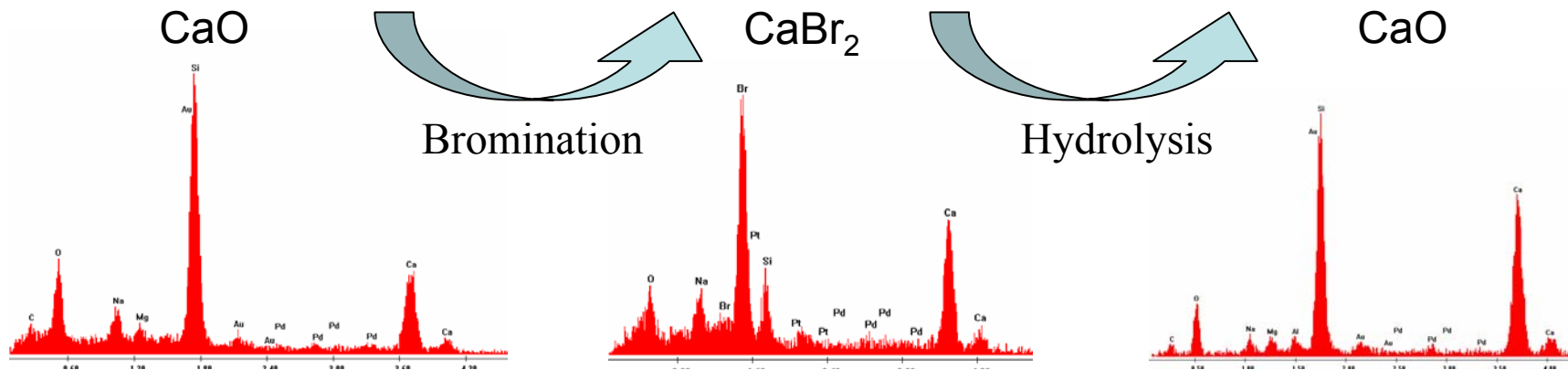
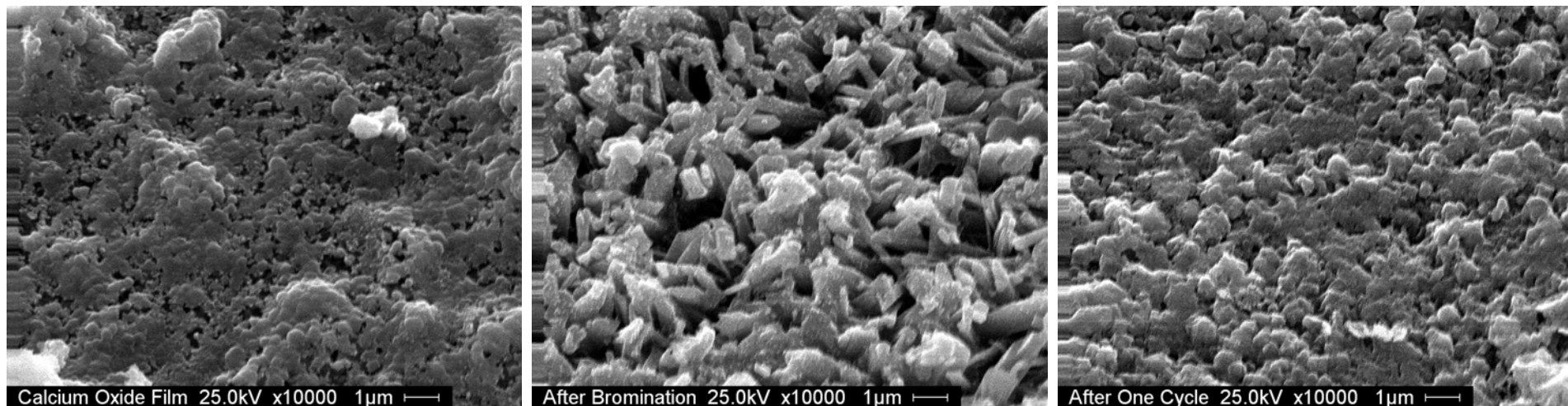
- The pellet-type reactants have higher mass transfer resistance due to volume changes.
- Concerns about attrition and degradation of reactant pellets
- A simpler and cheaper preparation step of the reactant is preferable.
- Film-type reactant increases the surface area of the calcium oxide reactant.
- Films are expected to have higher reactivity and longer lifetime in cyclic operation.

Preparation Steps of Calcium Oxide Film

- The preparation process for calcium oxide films is simple and low cost compared with the pelletization procedure.



SEM & EDS Analysis of Films



- Fabricated film consists of interconnected agglomerates of CaO particles shown in the first image.
- EDS spectra verify that bromination and hydrolysis reactions have occurred.

Future Work

FY 2007

➤ **Quarter 3:**

- Cyclic reactivity and durability of the CaO film will be evaluated.
- The cyclic structural changes of pellets will be examined by SEM to understand the mechanism of degradation and how to prevent it.
- Various pore forming agents will be evaluated to speed up the hydrolysis process.
- The effects of additives on the structure and strength of the pellets will be investigated by SEM (qualitative) and DMA (quantitative).

➤ **Quarter 4:**

- The CaO film coating will be applied to high porosity substrates for higher surface area.
- The practical process efficiency will be determined using the experimental results and theoretical thermodynamic analysis.

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H₂ Production from Biomass

Overview

Timeline

- October 2004
- Project End date December 2007
- Percent complete: 80%

Barriers

- 3.1.4.2. W (capital cost and efficiency of biomass gasification; improve H₂ yields)
- 3.1.4.2.4 V (feedstock cost and availability)

Partners

- University of South Florida
- University of Florida
- University of Central Florida

Objectives

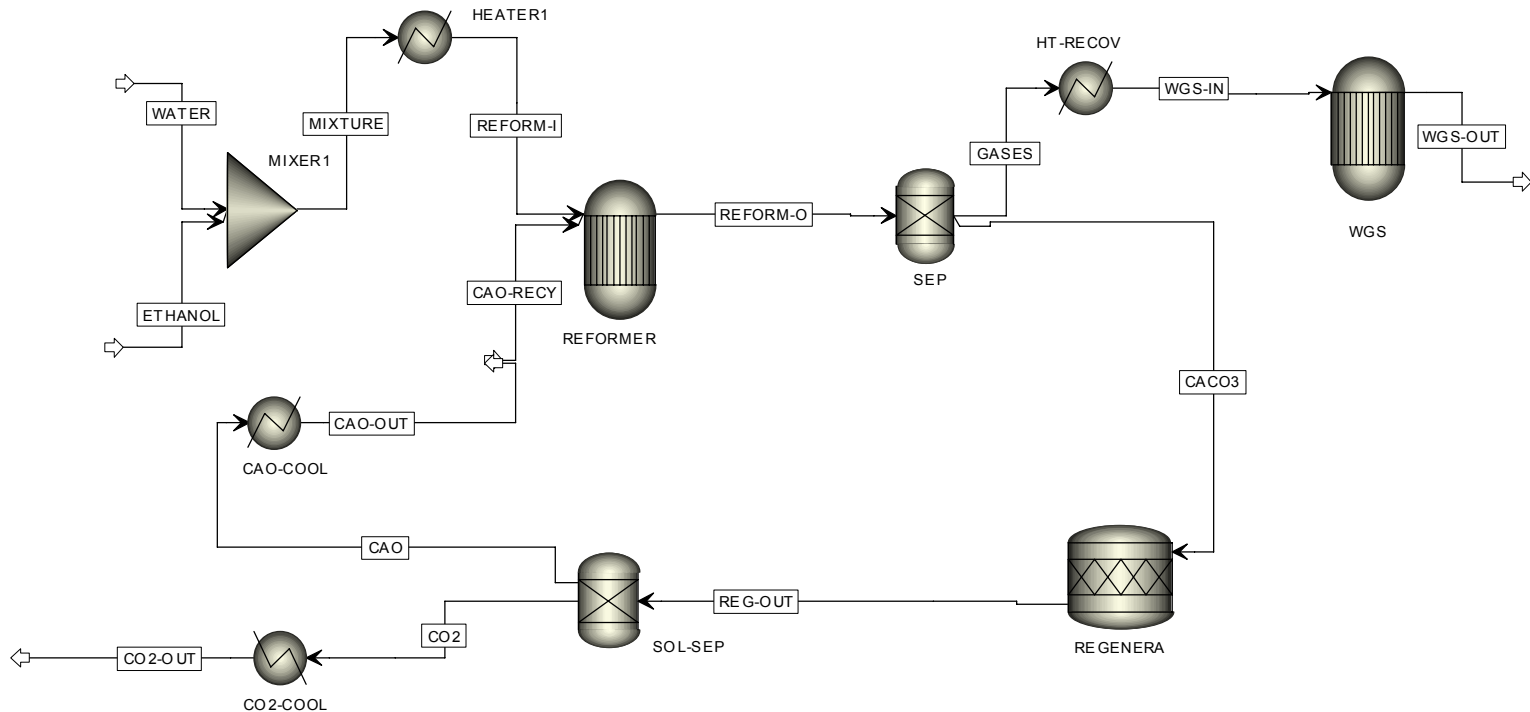
- Improve H₂ yield and process efficiency by
 - Better heat integration
 - Innovative approaches such as sorbents/catalysts
- Reduce capital cost by combining process steps and operations (gasification, reforming and shift)
- Conduct theoretical studies of sorbent enhanced biomass gasification
- Experimentally determine effect of sorbent addition on H₂ (& CO, CO₂) yields
- Conduct energy analysis of biomass gasification

Approach

- Thermodynamic studies (complete)
 - Determine process conditions for maximum thermodynamic H₂ yield
 - Develop ASPEN models for conventional & sorbent based biomass gasification
- Experimental studies (70% complete)
 - Fabricate test set-up
 - Conduct tests with and without sorbent to find H₂, CO & CO₂ yields
 - Regenerate sorbent
- Energy analysis (complete)
 - Study energy consumption of conventional & sorbent enhanced gasification
 - Identify energy efficient methods for regenerating spent sorbent

Results

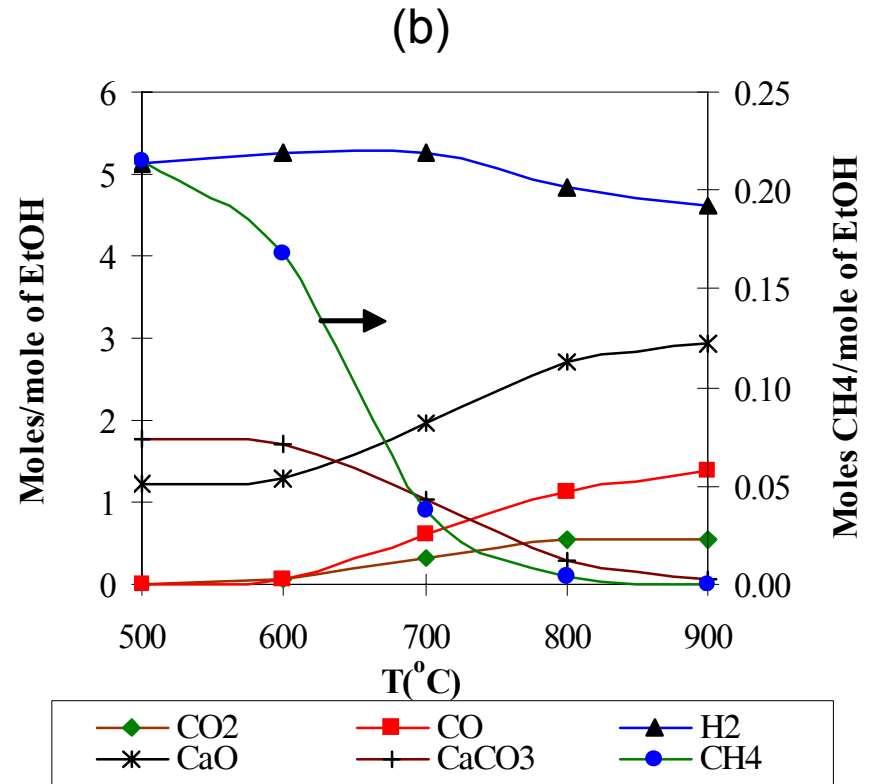
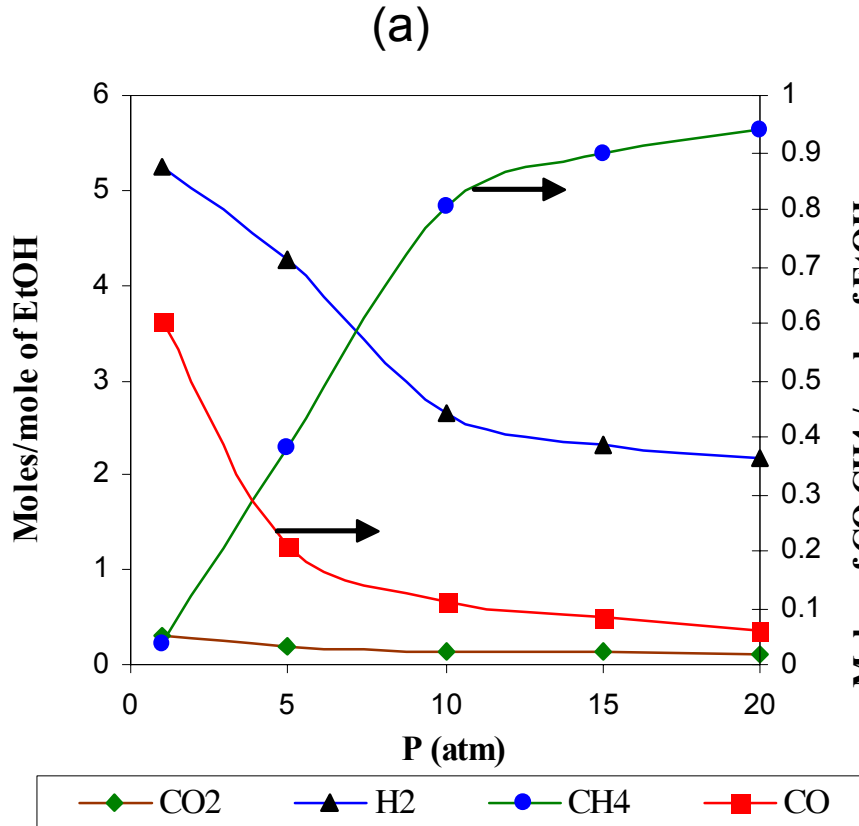
Ethanol Gasification with CO₂ Absorption



Flow sheet of ASPEN model for ethanol gasification with CaO sorbent

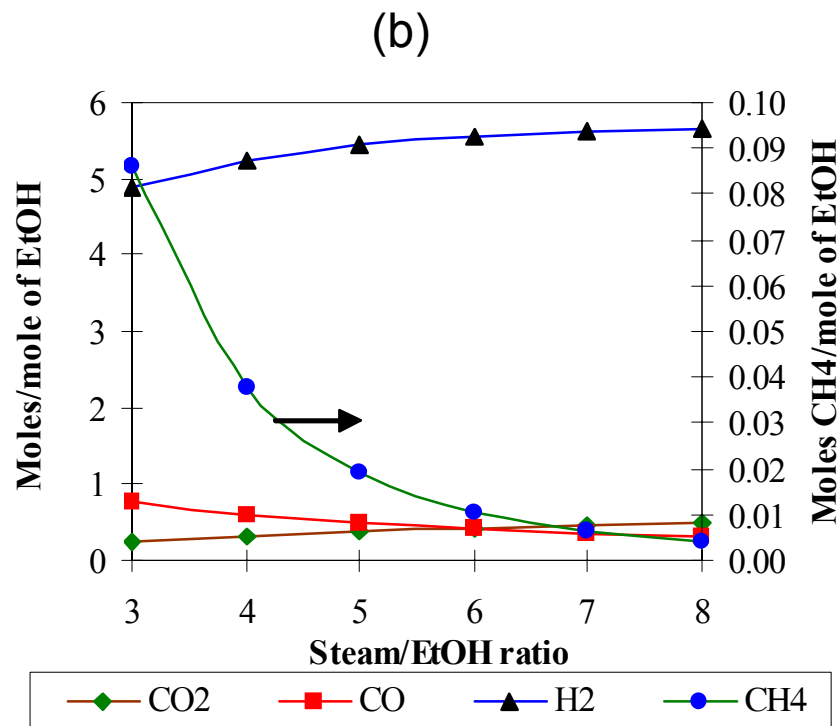
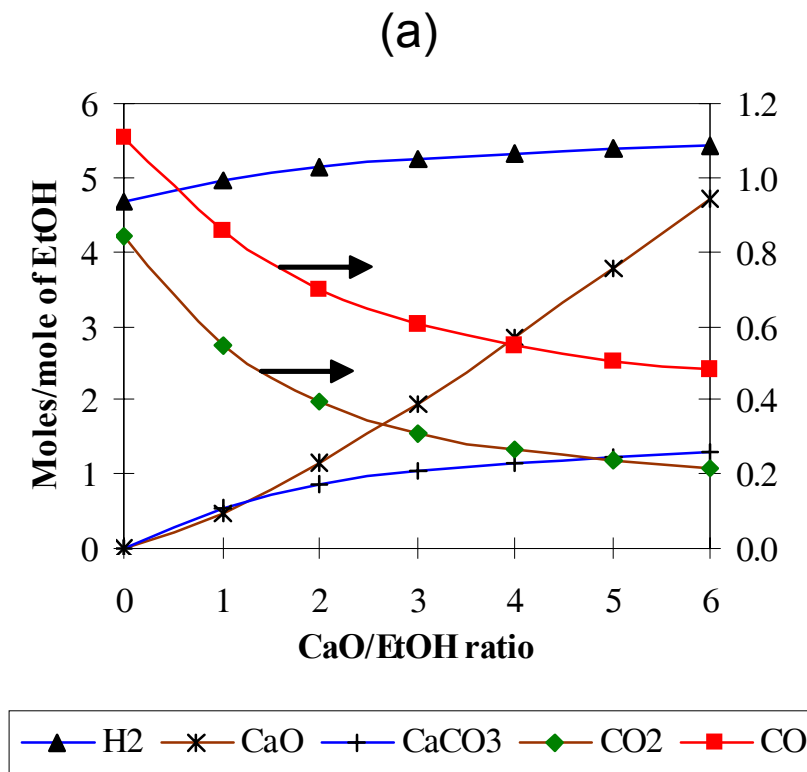
- Ethanol used as model biomass compound
- CaO used as model sorbent material

Simulation Results



Effect of pressure (a) and temperature (b) on the product yield for sorbent enhanced biomass reformation

Simulation Results



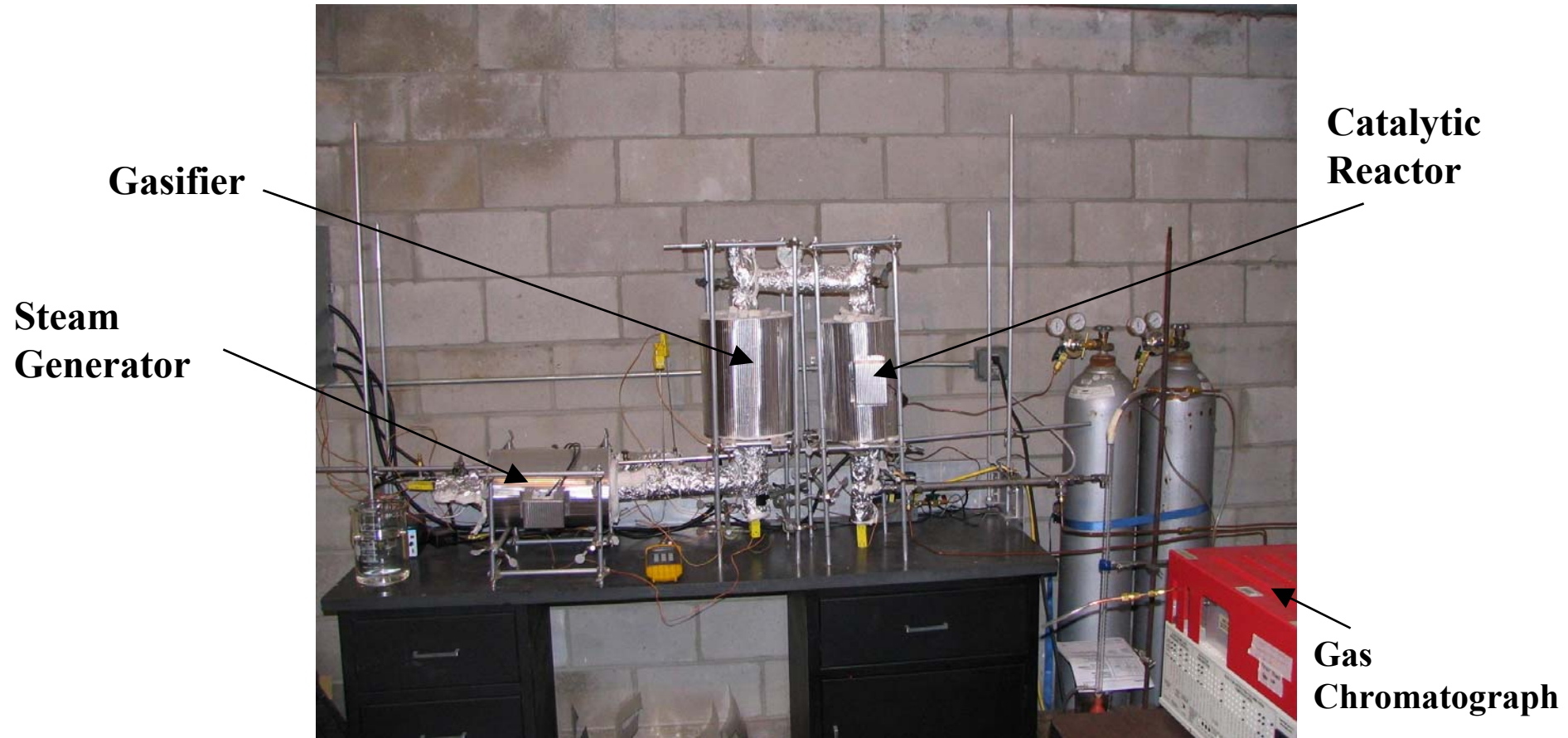
Effect of CaO/ethanol ratio (a) and steam/ethanol ratio (b) on the product yield for sorbent enhanced reformation

Energy Analysis

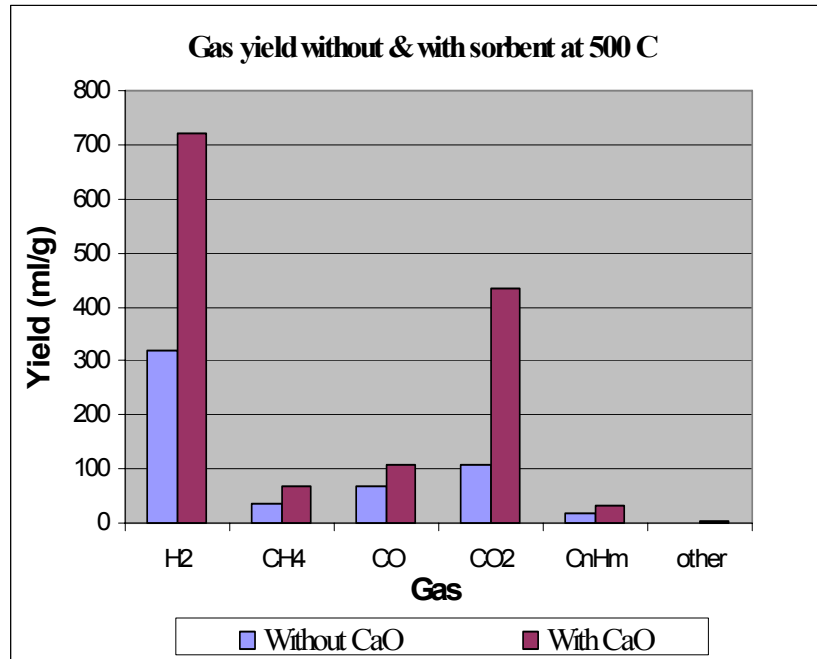
Comparative analysis of sorbent enhanced biomass reformation with conventional reformation

	NO SORBENT	WITH SORBENT
	Output (kmol/hr)	Output (kmol/hr)
H ₂	4.79	5.69
CO	0.097	0.089
CO ₂	1.53	0.762
CH ₄	0.001	0.053
H ₂ O	1.84	1.195
	Heat Duty (KW)	Heat Duty (KW)
Heater 1	+108.6	+108.6
Reformer	+65.9	+38
Heat Recovery	-33.9	-27.9
WGS	-15.8	-6.7
Regenerator	NA	+61.2
CO ₂ cool	NA	-12.4
CaO cool	NA	-34.9
LHV of Product Gas (KJ/hr)	1176.3 x 10 ³	1435.9 x 10 ³
LHV of biomass (KJ/hr)	1242 x 10 ³	1242 x 10 ³
Total heat supplied (KJ/hr)	628.1 x 10 ³	748.2 x 10 ³
Efficiency	62.9 %	72.1 %

Experimental Setup



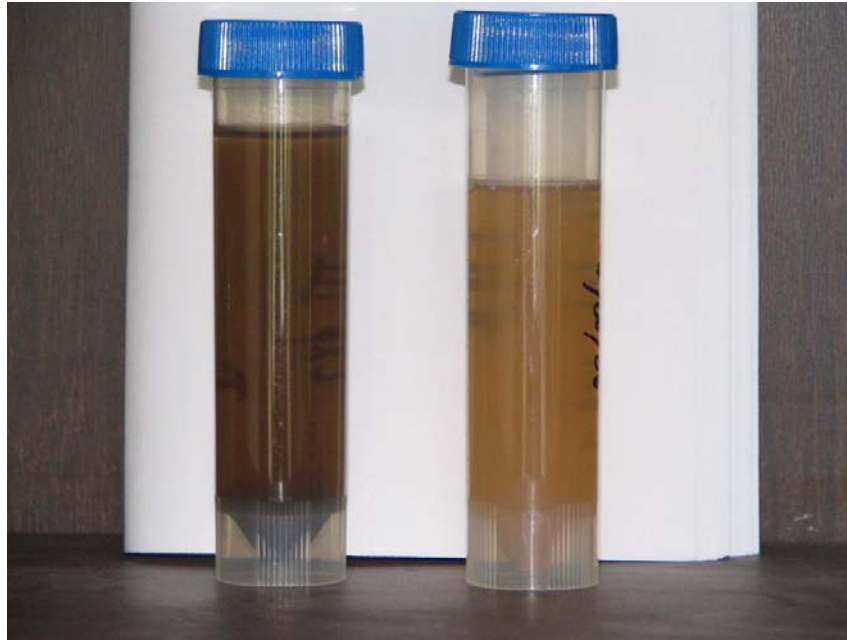
Steam gasified pine mulch at 500 °C with and without CaO sorbent



	No CaO	CaO
Total gas (ml/g)	549.9	1360
H ₂ (ml/g)	320.3	719.4
CH ₄ (ml/g)	34.1	66.6
CO (ml/g)	66.4	106.1
CO ₂ (ml/g)	108.8	432.5

- Shows 125% increase in hydrogen yield on using sorbent
- Total gas yield more than doubled in presence of sorbent
- Increase in CO and CO₂ indicates need for improving sorbent

Steam condensate containing tars without sorbent (left) and with sorbent (right)



- Product gas has less tars and particulates while using sorbent
- Gasification temperature reduced by about 200°C for comparable H₂ yields.
- Carbon conversion efficiency increased from 23% to 63%
- Similar but less dramatic increases were observed at higher reactor temperatures.

Future Work

FY 2007

➤ Quarter 3:

- Synthesize nanoparticulate sorbents with high absorption capacity and cyclic life

➤ Quarter 4:

- Test absorption capacity and cyclic life of improved sorbents

Summary

- Sorbent enhanced biomass gasification has proven to have great promise in hydrogen production from biomass due to:
 - Shows 125% increase in hydrogen yield on using sorbent
 - Gasification temperature reduced by about 200°C for comparable H₂ yields.
 - Total gas yield more than doubled in presence of sorbent
 - Product gas has less tars and particulates while using sorbent
 - Carbon conversion efficiency increased from 23% to 63%
 - Reduced heat duty of gasifier
- Sorbent enhanced gasification could lead to significant savings in equipment costs.
- Improvements in sorbent/catalytic materials are possible with additional research
- Regeneration of sorbent needs additional research

Photo-catalytic/Photoelectrochemical H₂ Production

Investigators: N. Kislov, S. Srinivasan, Nikhil Kothurkar, Lee Stefanakos, D. Yogi Goswami, D. Morel, C. Ferekides

Grad. Students: Mark Schmidt, Paula C. Algarin Amaris, S. Bates

Overview

Timeline

- Project start date: 1-1-05
- Project end date: 9-30-07
- Percent complete: 70%

Barriers

- 3.1.4.2
 - P: Materials Efficiency
 - Q: Materials Quality
 - R: System Efficiency

Objectives

Photocatalytic

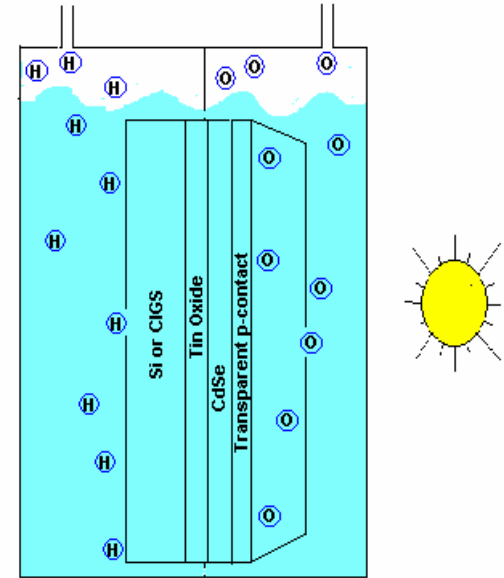
- Improve Photocatalytic Efficiency
- Extend Light Absorption of TiO_2 into the Visible Spectrum by Nitrogen Doping
- Determine the Relationship between the Materials Characteristics and Photocatalytic Activity

Photovoltaic

- Demonstrate working TO/Si devices with $V_{oc} > 500$ mV
- Develop doped ZnSe p-contacts
- Demonstrate operable CdSe/Si tandem devices

Photoelectrochemical

- Fabricate device with TiO_2 as a catalyst
- Design and fabricate photoelectrochemical testing unit



PEC cell for producing H from water.

Accomplishments

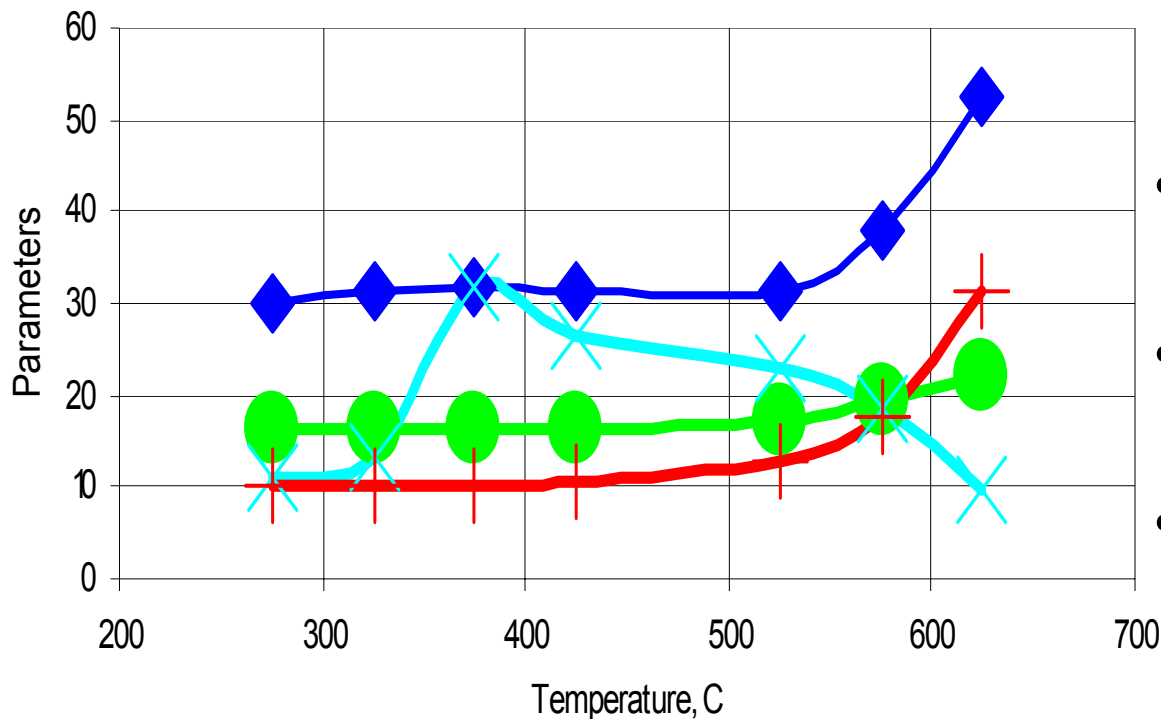
- Developed Novel and Versatile Thermochemical Doping Process
- Improved Photocatalytic Efficiency
 - 3X using simulated solar spectra
 - 2X using visible portion of spectra (UV filter)
- Band gap red shift by $\sim 0.4\text{eV}$
- Identified the causes of losses in J_{sc} in photovoltaic cell through analysis of QE spectra
- Observed that ZnSeTe ternary compound improves doping prospects
- Demonstrated working TO/Si devices with $V_{oc} > 500\text{ mV}$

Novel Nitrogen Doping Process



- Developed Novel Thermochemical System
- Enables Control of Microstructure, Composition and Optical Properties Over a Wide Range

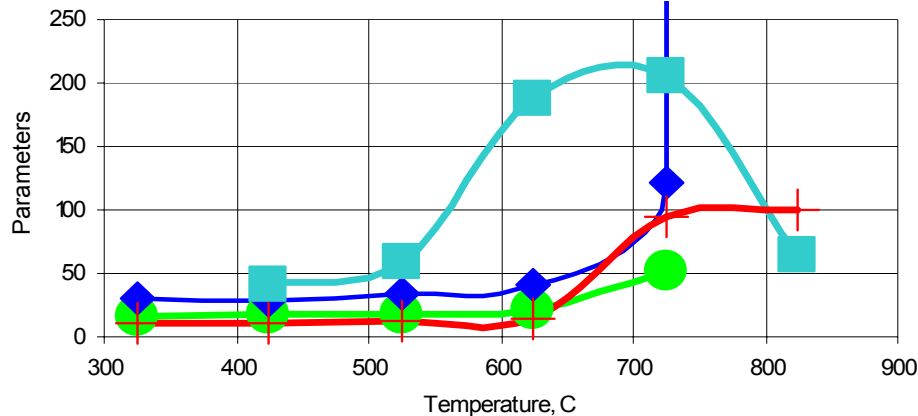
Effects of Thermal Treatment



- Thermal Treatment in N₂ Atmosphere
- Simulated Solar Radiation
- Optimal Treatment Temperature - 375°C

● Anatase nm
 ◆ Rutile nm
 ✕ (Relative Photonic Efficiency) x 10
 + [Mass fract rutile]*100

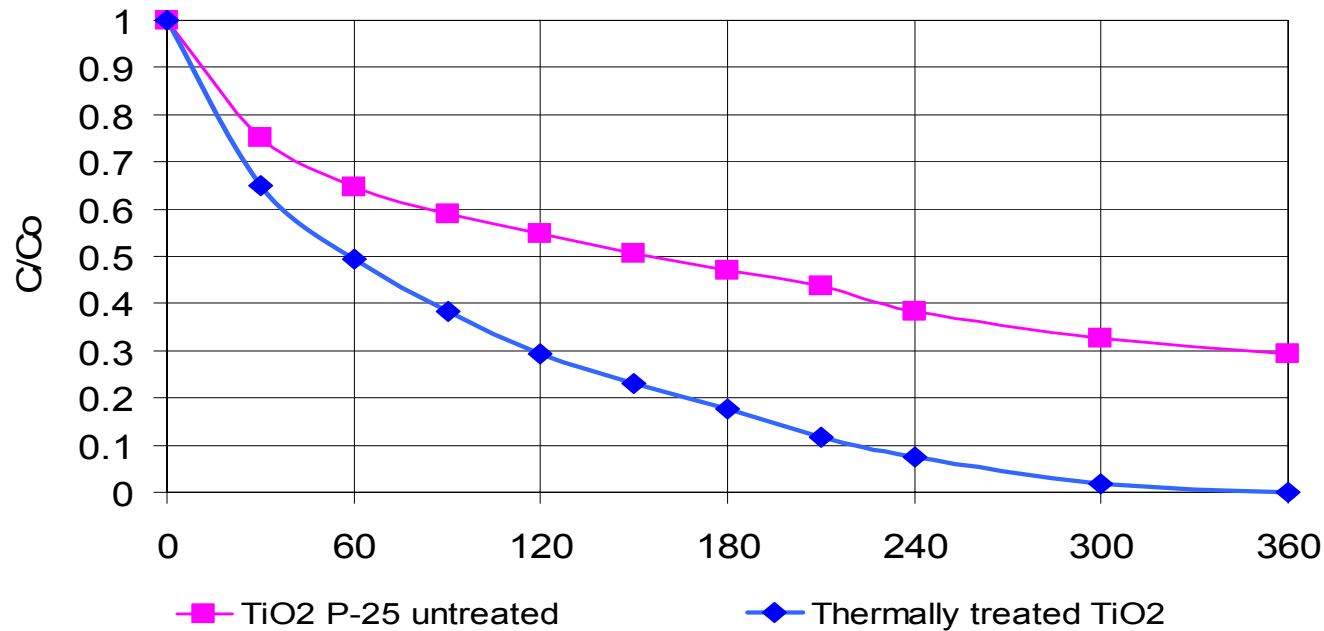
Effects of Thermochemical Doping



—●— Anatase nm —◆— Rutile nm —■— (Relative Photonic Efficiency) x 100 —+— [Mass fract rutile]*100

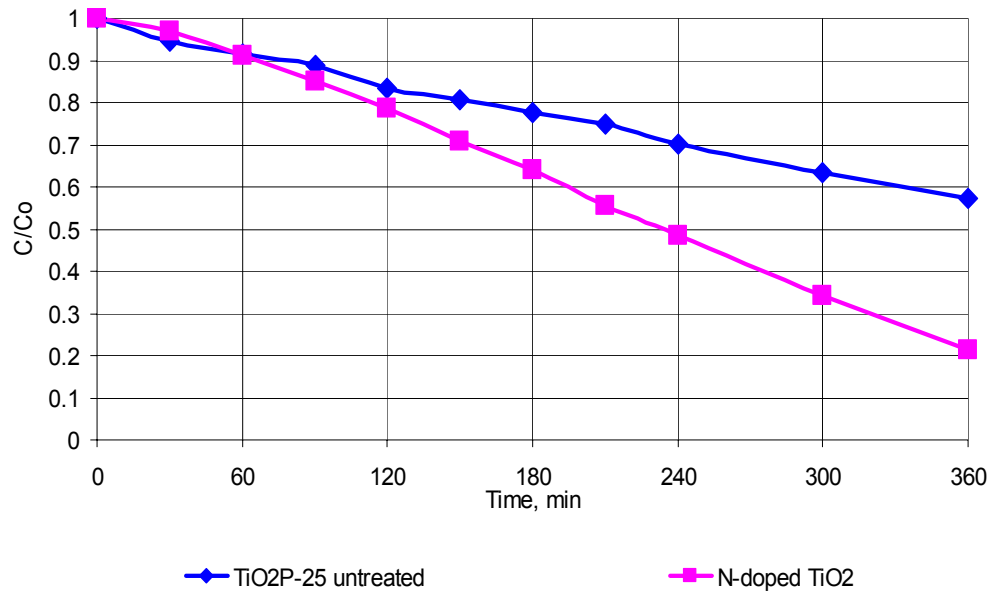
- Thermochemical Doping Treatment in NH_3 Atmosphere
- Simulated visible (UV Filtered) Solar Spectra
- Optimal Treatment Temperature - 675°C

Thermal Treatment Enhances TiO_2 Photocatalytic Performance by 3X



- Simulated Solar Spectrum used

N-Doping Enhances TiO_2 Photocatalytic Performance by 2X



- Simulated visible (UV Filtered) Solar Spectrum
- Increased Performance Due to Red Shift in Optical Absorption of 0.4eV

Photovoltaic Results

Observation	Cause	Effect on Voc
Red dropoff	Defects in the CdSe	Small
Uniform downshift	Defects in ZnSe/CdSe interface	Strong
Blue dropoff	Defects in the ZnSe	Negligible

- The key challenge is to achieve 15% efficiency with CdSe
- Identified the causes of losses in J_{sc} through analysis of QE spectra. These observations stem from extensive AMPS© simulations.

Conductivity of Co-Evaporated $ZnSe_xTe_{1-x}$ Films Doped with Nitrogen

Composition (%)		Conductivity
Zn	Te	Ω -cm
49.59	9.28	2.00E-08
48.92	4.06	1.18E-09
49.75	2.19	1.65E-10
49.31	6.39	7.65E-10
51.63	9.02	4.71E-10
51.81	10.88	5.88E-10
51.87	6.03	7.06E-10

- To achieve high Voc's in ZnSe/CdSe devices it is necessary to attain significant p-type doping in the ZnSe layer
- We and others have found that going to the ZnSeTe ternary compound improves doping prospects (see table).

Future Work

Photocatalytic

- Improve Photocatalytic Efficiency
- Extend Light Absorption of TiO_2 into the Visible Spectrum by Nitrogen Doping
- Determine the Relationship between the Materials Characteristics and Photocatalytic Activity

Photovoltaic

- Achieve improved doping in ZnSeTe contacts
- Test PV device performance in an electrochemical cell

Photoelectrochemical

- Fabricate device with TiO_2 as a catalyst
- Design and fabricate photoelectrochemical testing unit
 - Select electrolyte

H₂ Conversion: PEM Fuel Cells

Benjamin Grayson, Ala'a Kababji, Aaron Black, Amanda Gannon, Elias Stefanakos, John T. Wolan, Nikhil Kothurkar, Yogi Goswami, Elias Stefanakos

University of South Florida

Overview

Timeline

- October 2006
- December 2007
- Percent complete: 50%

Partners

- University of South Florida
 - Dr. Vinay Gupta, Department of Chemical Engineering, USF
- University of Florida
- University of Central Florida

Barriers

- 3.4.4.2
 - Durability
 - Cost
 - Electrode Performance
 - Thermal, Air and Water Management
 - Cold startup time to maximum power, survivability
 - Hydrogen Purification/CO Cleanup

Objectives

- Experimental setup for wide temperature range testing
- Add-on sub freezing module
- Test MEA at sub-freezing temperatures
- Develop mediation techniques to increase functionality at subzero temperatures
- Develop and model a novel bimetallic fuel cell catalyst to prevent anodic CO poisoning and reduced metal loading
- Develop a high-temperature, direct alcohol fuel cell membrane with reduced cross-over and increased water retention

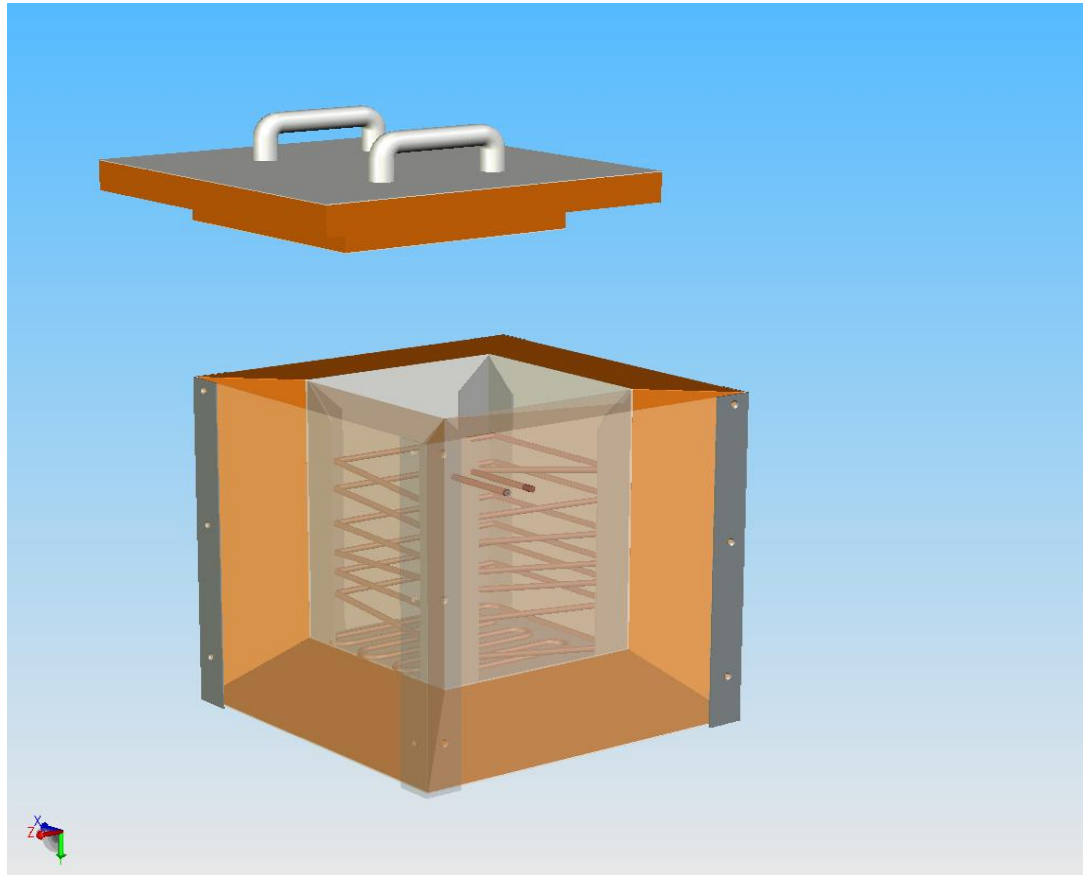
Approach

- Design a nano-bimetallic heterogeneous catalyst for the selective oxidation of CO; use surface and effluent gas characterization to determine possible reaction mechanisms, compositional and crystalline structure changes
- Fabricate β -zeolite nanocomposite membranes for high temperature operation ($\sim 120^\circ\text{C}$) with minimal fuel crossover; impedance characterization to determine efficiency and proton conductivity changes
- Test MEAs under different temperature regimes
- Quantify performance degradation caused by internal ice formation during low temperature startup and operation
- Develop shut down / startup procedures to minimize internal ice formation
- Test active heating schemes to minimize low temperature startup time and maximize cell efficiency

Accomplishments

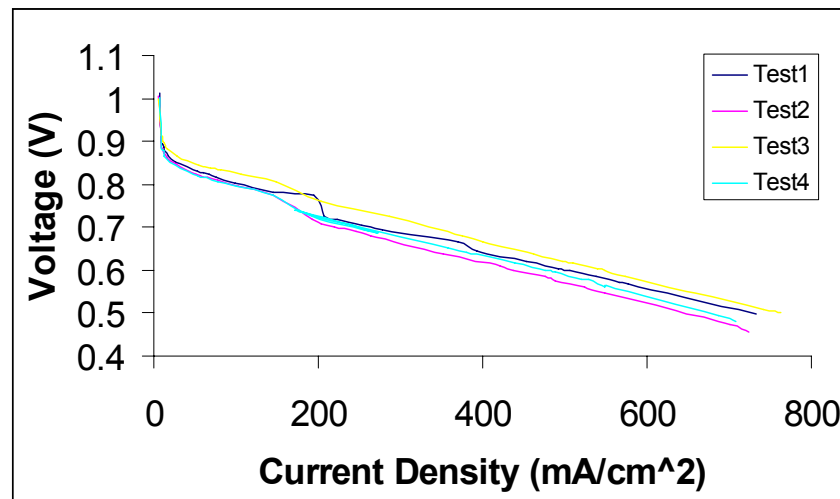
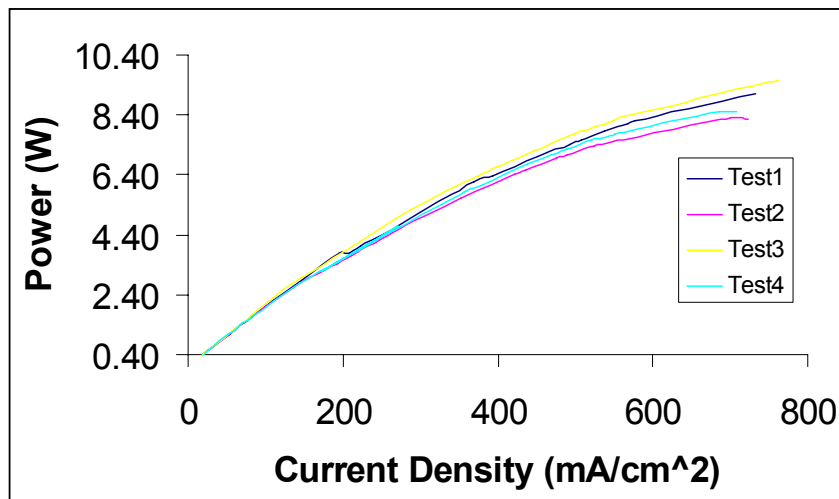
- Developed a kinetic mechanism via micro-reactor analysis of the nano-metal/TiO₂ catalyzed preferential oxidation of carbon monoxide. 100% oxidation at RT!
- β -zeolite/NafionTM membranes alcohol permeation experiments have shown decreased fuel crossover when compared to NafionTM films without the nanocomposite additives.
- Constructed fuel cell test bed
 - Reconstructed and improved test stand for greater data accuracy.
 - Major modifications include new fuel intake line heaters and insulation (to improve accuracy of inlet temperature and relative humidity)

The proposed chamber design below illustrates the housing and copper heat exchanger

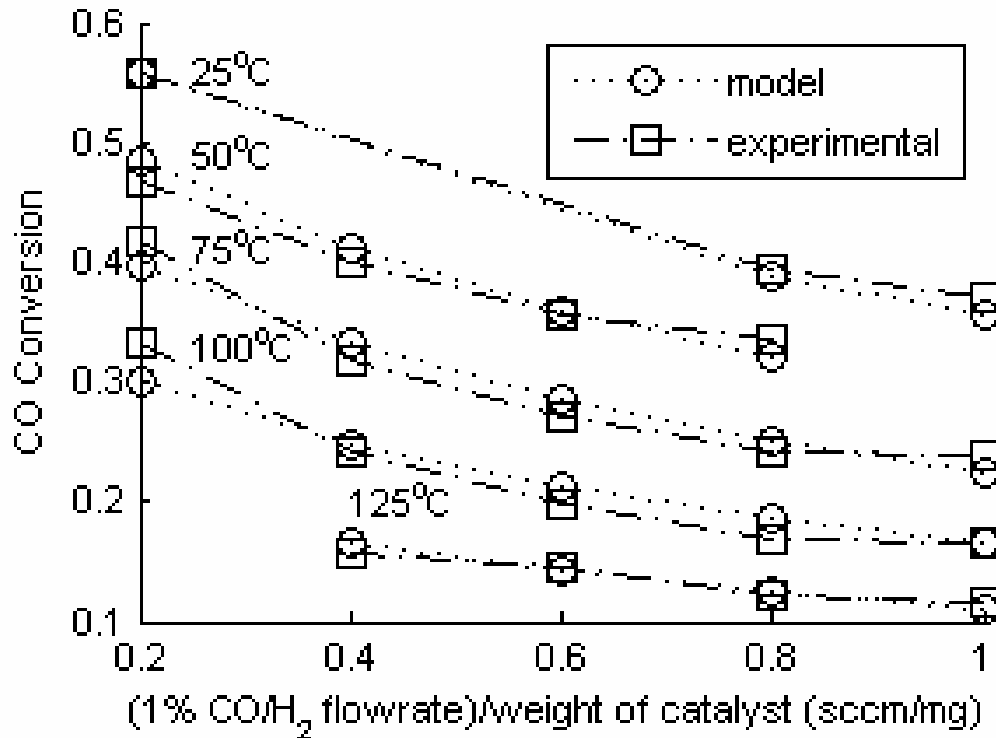


H₂ Conversion: PEM Fuel Cells

Repeatability Testing, Nafion® MEA



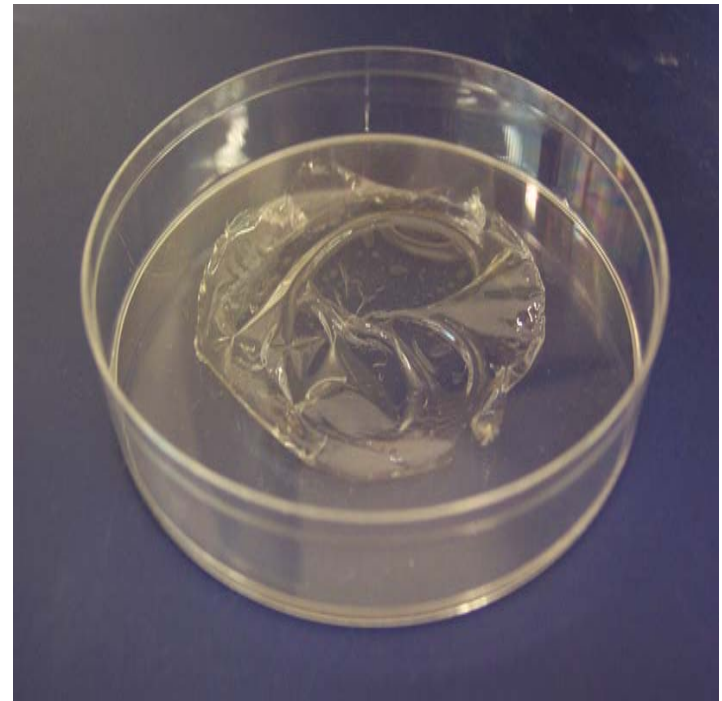
Catalyst Modeling



- Empirical model is able to predict selective CO selective oxidation
- Beneficial for determining operating parameters and maximizing fuel cell anode potential.

β -zeolite Composite Fuel Cell Membrane

- Reduced fuel crossover (20%)
- Increased proton conductivity while maintaining moisture content at elevated temperatures
- Development of manufacturing process complete



Future Work

- Nano-metallic/TiO₂ Catalyst modeling
 - Completion of non-elementary reaction model on both the experimental and reference nano-Au/TiO₂ carbon monoxide oxidation catalyst systems. Compare with experimental results.
- β-zeolite Membranes
 - Four point AC impedance to determine nanocomposite membrane proton conductivity
 - Enhance filtration for improved particle size control
- Bimetallic zeolite catalysts
 - Lower reaction temperature, pressure and increase the residence time
 - Study kinetics of the reaction, model the membrane reactor and include recycle
- Operational
 - Complete freezing module on test bed
 - Evaluation irreversible performance (voltage, current, power) loss by comparison with baseline test
 - Define a startup/shutdown humidification procedure to minimize internal ice formation and cell degradation
 - Test multiple cell heating schemes to help provide efficient low temperature operation

Development of High Performance, Low Cost PEM Electrolytes

Clovis A. Linkous

Florida Solar Energy Center

University of Central Florida

Overview

Timeline

- Start: 10-01-04
- End: 9-30-07
- 90% completed

Barriers

- 3.4.4.2 E – Durability of distributed power generation systems
- 3.4.4.2 O – Cost of fuel cell stack component materials
- 3.4.4.2 R – Thermal and water management in higher temperature membrane electrolytes

Partners

- University of South Florida
- University of Florida

Objectives

- Lower the cost of fuel cell-generated electricity by decreasing the cost per unit power for PEM electrolytes
- Improve long-term chemical stability of PEM electrolytes operating at ≤ 120 °C
- Maintain or improve high proton conductivity of PEM electrolytes
- Minimize water content necessary to support high proton conductivity

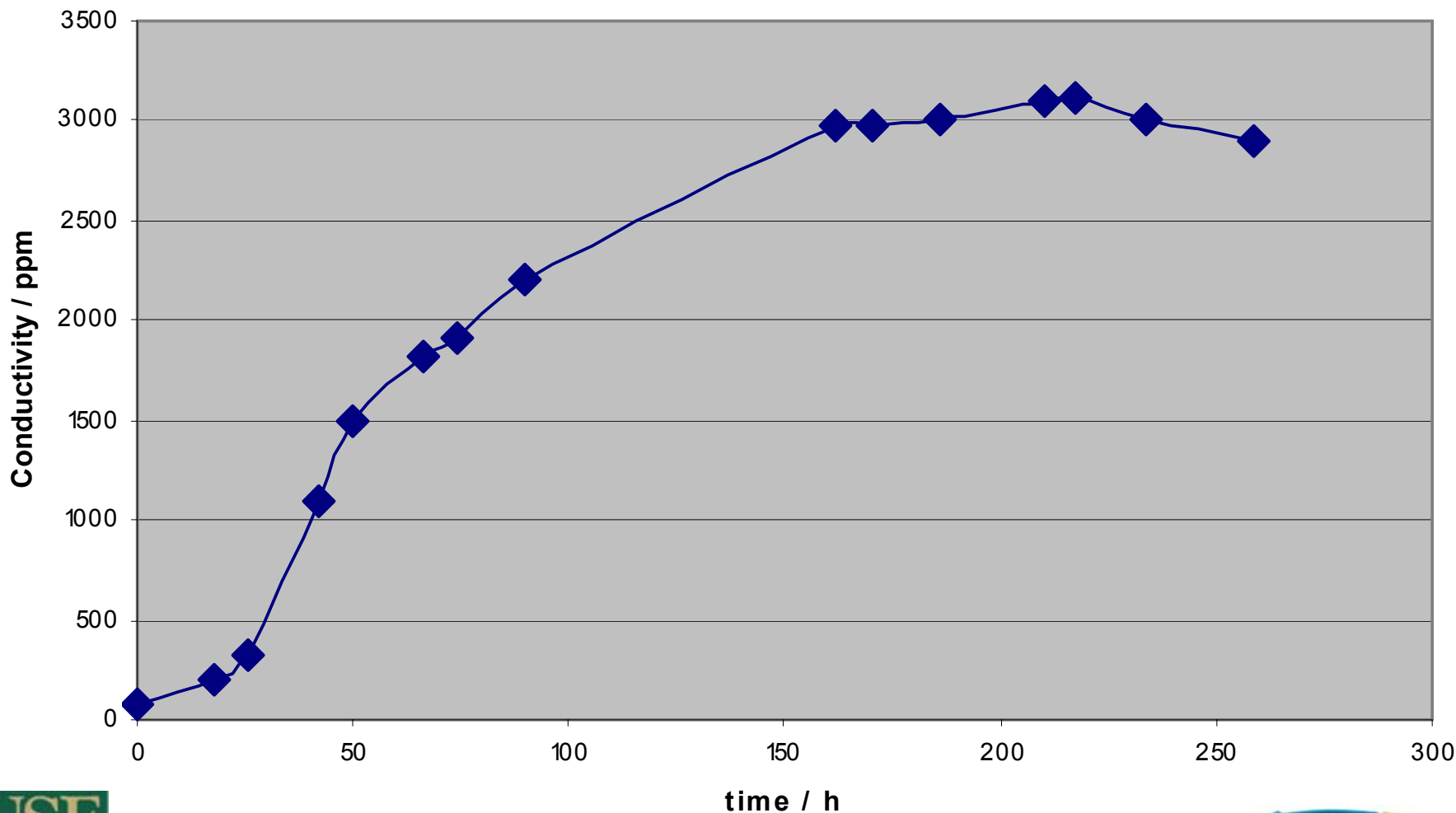
Approach

- Heavily sulfonate polymers to promote proton conductivity, but cross-link to prevent solubility and mechanical stability problems
- Develop accelerated test apparatus to evaluate prototype PEM's

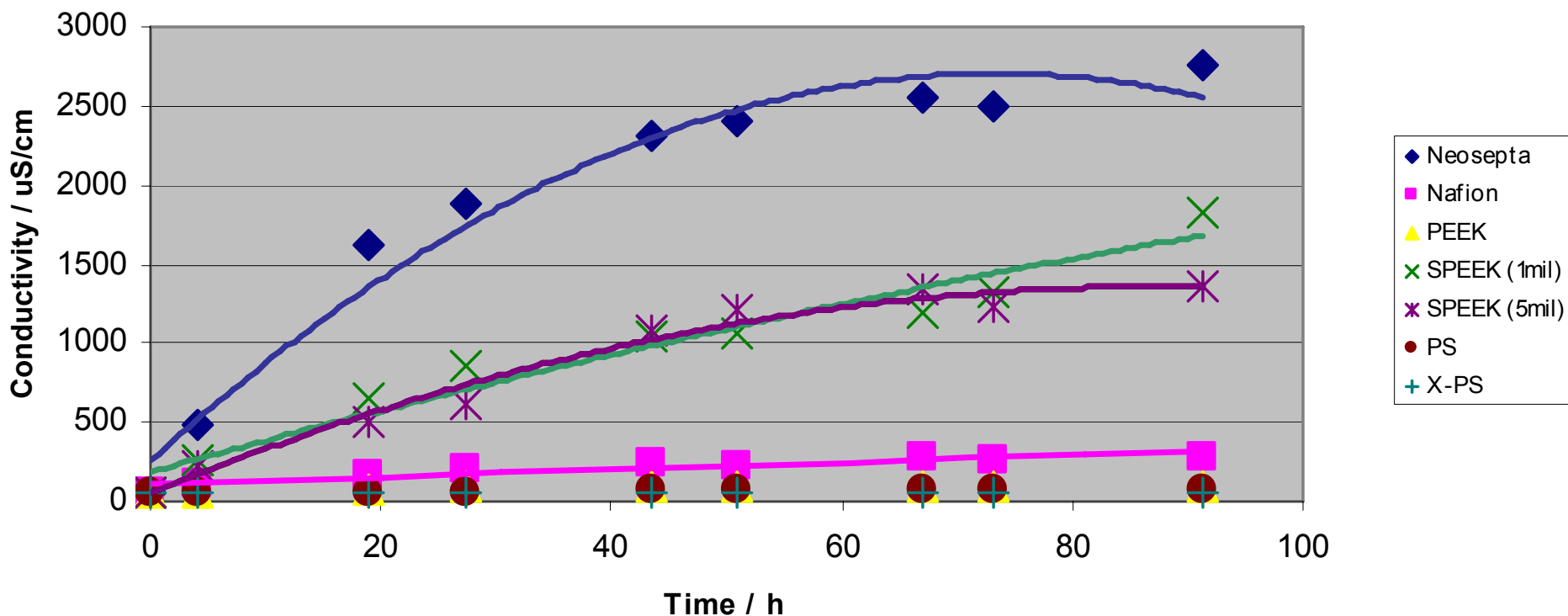
Accomplishments

- Evaluated accelerated testing methods (mechanical, permeation, and conductivity) for predicting stability of PEM electrolytes under oxidizing conditions
- The conductivity approach proved to be the most rapid and generally applicable
- Synthesized cross-linked, water insoluble SPEEK with low equivalent weight (~540 g/equiv)

Conductivity of 3.5% H_2O_2 solution vs time i.p.o. Neosepta[®] membrane at 50 °C



Conductivity of 3.5% H_2O_2 solution vs time i.p.o. various polymer membranes at 80 °C



Summary

- Polyaryletherketones offer a compromise between cost and oxidative stability for PEM membranes (intermediate between sulfonates of cheap but unstable polystyrenes and rugged but expensive polyperfluoroalkylethers)
- Cross-linking chemistry controls water uptake and renders low EW membranes insoluble
- Stability of PEM membranes toward peroxide species was effectively monitored by measuring the conductivity of the soaking solution.
- The sulfonic acid moiety itself may constitute an attack site for hydroxyl radicals.

Future Work

- Remainder of FY07
 - optimize conditions for catalyzed PEM cross-linking chemistry
 - Derive conductivity dependence vs temperature and relative humidity for cross-linked PEM membranes
 - Determine water uptake and swelling as a function of cross-linking content
 - Perform conductivity-based peroxide stability test on new PEM membranes
 - Prepare final report and publications