



2006 DOE Hydrogen Program Review

Production, Fuel Cell, and Delivery Research

University of South Florida

Presenters: Yogi Goswami and Elias Stefanakos

May 18, 2006

Project ID # PDP37

Participants and Projects

Participants

University of South Florida

- **CO-PI's: Yogi Goswami, Elias Stefanakos**
- V. Bhethanabotla (ChE), M. Calves (COT), C. Ferekides (EE), Y. Goswami (ChE), N. Kislov (CERC), B. Krakow (CERC), Ashok Kumar (ME), L. Langebrake (COT), D. Morel (EE), G. Moore (CERC), S. Onishi (COT), M. Ross (Civil E), M. Smith (CERC), S. Srinivasan (CERC), E. Stefanakos (EE), P. Wiley (EE), J. Wolan (ChE), 8 graduate students, 2 undergraduate.

University of Florida

- L. McElwee-White (Chemistry), B. Lear (ME), M. Su Lee (ME), S. Ingley (ME), Nikhil Kothurkar (ME), 6 graduate students

University of Central Florida

- Clovis Linkous (FSEC)

Projects

Hydrogen Production (STP37)

- Photoelectrochemical/Photocatalytic (USF)
- Thermochemical Cycle (UF)
- Biomass Gassification (UF)
- Solid State Ionic Conductors (USF)

Hydrogen Storage (STP43)

- Advanced material-based technologies for on-board vehicular storage (USF and UF)
- Nano-structured Materials (USF)
- Nano-structured Films (USF)

Fuel Cells (STP37)

- PEM Fuel Cell Research (UCF)
- PEM Fuel Cell Research (UF)
- PEM Fuel Cell Research (USF)

Delivery (STP37)

- Geologic Storage (USF)
- Thermal Hydrogen Compressor (USF)

Overview

Timeline

- Oct 2004 to Sept 2008
- 40% Complete

Budget

- Total project funding
 - DOE \$4.8M (\$1.2M/year)
 - Contractor \$1.25M
 - FY05 \$2.9M

Barriers

Task 1: Hydrogen Production

- 1.1: Photoelectrochemical/Photocatalytic
 - 3.1.4.2.6 AP, AQ (Materials efficiency, Materials durability)
- 1.2: Thermochemical Cycle
 - 3.1.4.2.7 AU (High temperature thermochemical technology development)
- 1.3: Biomass Gassification
 - 3.1.4.2.4 W, 3.1.4.2.4 V (Feedstock cost and availability, Capital cost and efficiency of biomass gasification/pyrolysis technology)
- 1.4: Solid State Ionic Conductors
 - 3.1.4.2.2 H, I, K (Fuel processor capital costs, System efficiency, Grid electricity emissions, Electricity costs)

Barriers (continued)

Task 2: Hydrogen Storage

- 2.1: Advanced material-based technologies for on-board vehicular storage
 - 3.3.4.2 A-D, J, P, Q (System weight and volume, System cost, Efficiency, Durability/Operability, Thermal management, Lack of understanding of H₂ physisorption and chemisorption, Reproducibility of performance)
- 2.2: Nano-structured Materials
 - 3.3.4.2 A-C, J, P, Q (System weight and volume, Efficiency, Durability/Operability, Thermal management, Lack of understanding of H₂ physisorption and chemisorption, Reproducibility of performance)
- 2.3: Nano-structured Films
 - 3.3.4.2.1 B, D (System cost, Durability/Operability)

Task 3: Fuel Cells

- 3.1.1: PEM Fuel Cell Research (UCF)
 - 3.4.4.2 A-D (Durability, Cost, Electrode performance; Thermal, Air, and water management)
- 3.2.2: PEM Fuel Cell Research (UF)
 - 3.4.4.2 A-D, J (Durability, Cost, Electrode performance ; Thermal, Air, and water management; Start-up time/Transient operation)
- 3.3.2: PEM Fuel Cell Research (USF)
 - 3.4.4.2 B, C, D, I (Cost, Electrode performance ; Thermal, Air, and water management; H₂ purity/CO Clean-up)

Task 4: Delivery

- 4.1: Geologic Storage
 - 3.2.4.2 G (Feasibility of geologic storage)
- 4.2: Thermal Hydrogen Compressor
 - 3.2.4.2 B (Reliability and costs of H₂ compression)

Task 1.1 (production): Photoelectrochemical

D. L. Morel, C. S. Ferekides, S. Vakkalanka, S. Bates

Objectives

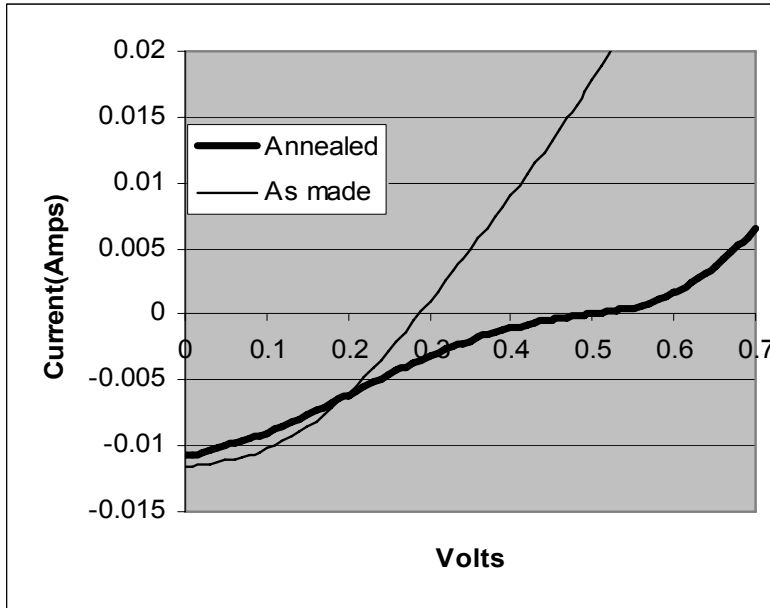
| | | |
|---------|--|-----|
| Overall | To produce H in the \$ 0.70 – 2.00/kg range | |
| | Photocatalyst efficiency(sunlight to hydrogen) | 14% |
| | Photocatalyst cost(\$/m ²) | 70 |
| | Membrane cost(\$/m ²) | 50 |
| 2004 | Develop design parameters for CdSe/Si tandem devices | |
| | Begin fabrication of Si devices | |
| | Initiate deposition of CdSe on Si | |
| 2005 | Demonstrate working TO/Si devices with Voc > 500 mV | |
| | Develop doped ZnSe p-contacts | |
| | Demonstrate operable CdSe/Si tandem devices | |

Approach

- Construct tandem solar cells with Si(CIGS) and CdSe
 - Multi-crystalline Si will be phase I, since it is proven technology, but may be too costly to meet the ultimate cost needed
 - CIGS is expected to offer a lower cost alternative for phase II
 - DOE Barrier: Materials Durability
- Band gaps are ideal at 1.1 and 1.7 eV
- Si and CIGS efficiencies are a given
- The key challenge is to achieve 15% efficiency with CdSe
 - DOE Barrier: Materials efficiency

Results

SnO₂/Si Device Performance



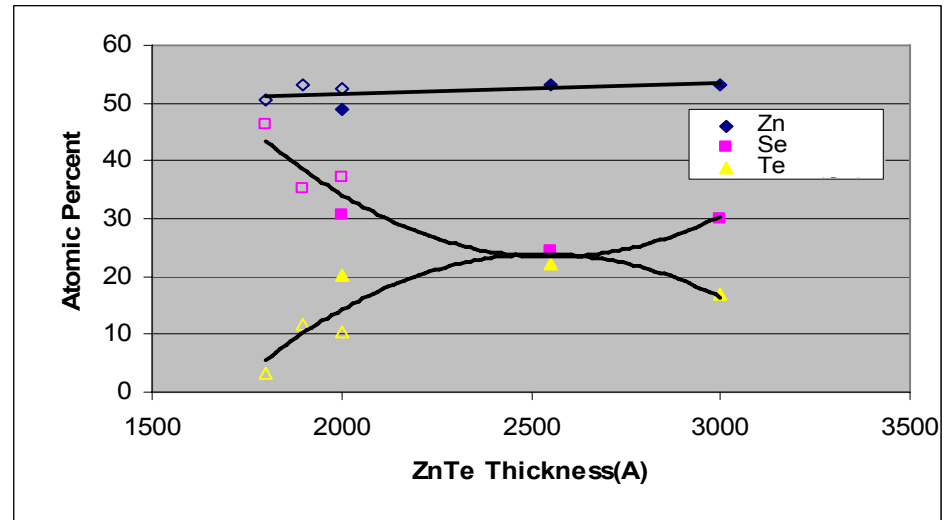
Device Fabrication

- Si is 0.1 Ω -cm 100 n-type
- SnO₂ is deposited by MOCVD

Results

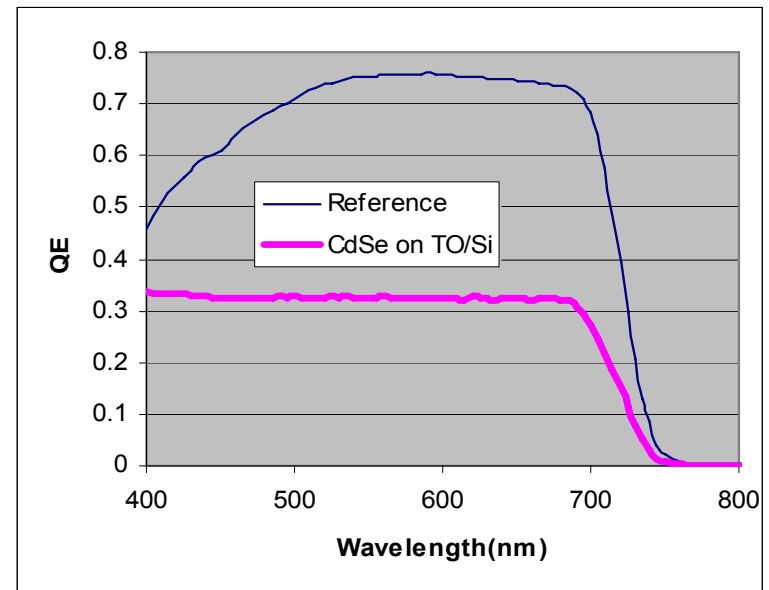
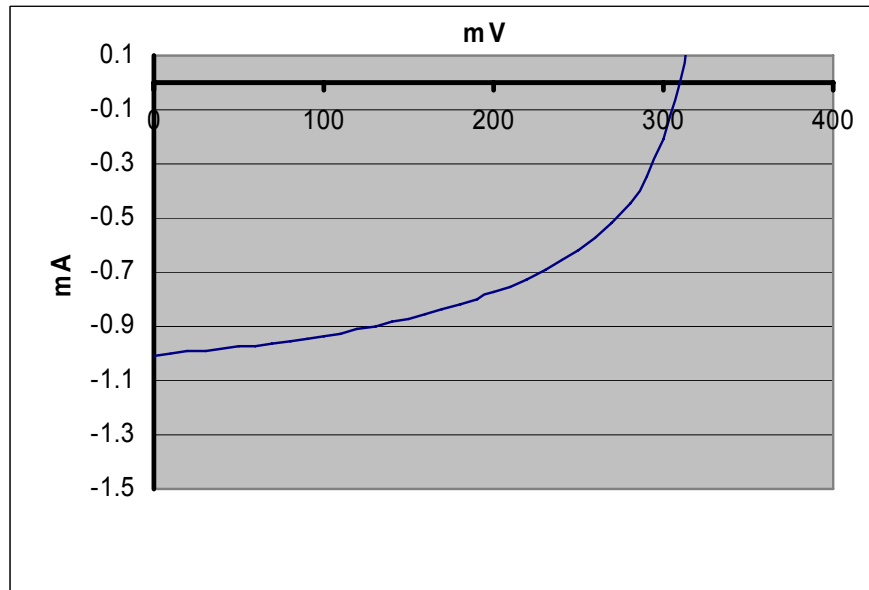
- The objective of 500 mV has been met
- Annealing (400C for 30 min.) significantly improves Voc but distorts the curve shape

P – Contact development



- ZnSe_xTe_{1-x} from MBE growth has exhibited good p-contact properties
- Using cost compatible deposition technologies creates difficulties for controlling stoichiometry requirements for effective doping
- We have discovered regimes in deposition space that result in Zn/Group IV \cong 1. Initial conductivities are of order 10⁹ Ω -cm.

Tandem Devices



- Operable Tandem devices have been fabricated
- Typical IV performance has been achieved for top CdSe devices
- CdSe QE is currently limited by the SnO_2 properties on Si

Future Work and Summary

Future Work

- Primary effort will be on further development of the p-contact. This is critical to generation of sufficiently high Voc's to dissociate water. While $\text{ZnSe}_x\text{Te}_{1-x}$ shows great promise when grown under ideal conditions, those properties may not be attainable with cost-effective growth technologies. If not, we have other options to pursue for the p-contact.
- Further work is needed on improving Si device performance, and particularly with respect to the SnO_2 contact. A key issue is developing this contact so that it optimizes Si performance while also serving as an effective growth surface and n-contact for the CdSe device.

Summary

- Primary near-term technical objectives have been met
 - Voc > 500 mV in Si devices
 - Operable tandem devices
- Key technical issue for current effort
 - Improved doping in CdSe p-contacts
 - Higher Voc's in CdSe devices

Task 1.1 (production): Photocatalytic

Nikolai Kislov, M. Schmidt, S. Srinivasan, E. Stefanakos, M. Smith

Objectives

- Develop doped or alloyed TiO_2 thin films with improved performance to demonstrate splitting of H_2O between 1.23 and 1.48 V

Approaches

- Extending light absorption into visible region by coupling of TiO_2 with a small bandgap semiconductor (ZnFe_2O_4 , Fe_2O_3 , or WO_3)
- TiO_2 bandgap reduction by carbon doping
- Preparation of photocatalytic films and nanoparticles using inexpensive spray pyrolysis deposition

Experimental techniques

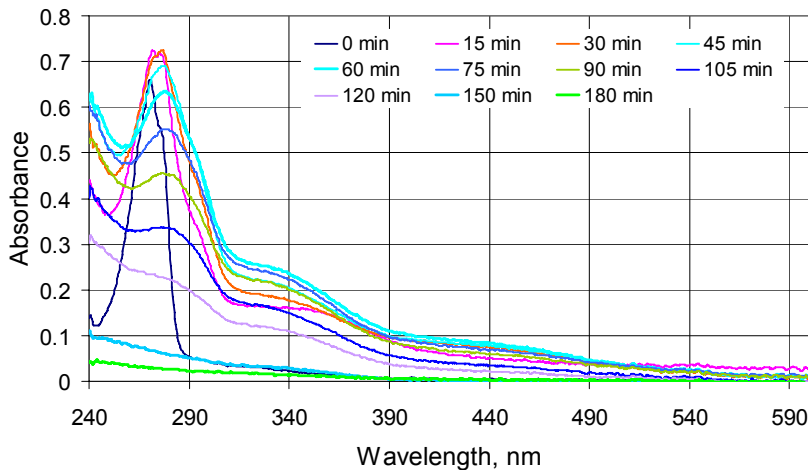
- Improvement of the accuracy of the photocatalytic phenol degradation analysis by using multicomponent approach
- Design of the reactor for visible light photolysis
- Preparing nanosized powders by High Energy Ball Milling
- Optical characterization of nanopowders (Kubelka-Munk theory)
- ZnFe_2O_4 characterization using optical, XRD, SEM, and AFM analysis

Task 1.1 (production): Photocatalytic

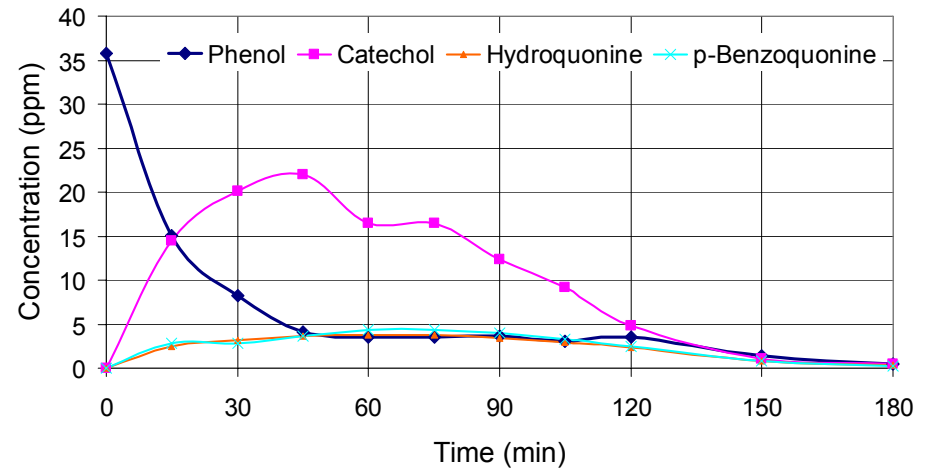
Accomplishments - $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ Nanocomposites

- Organic (phenol) degradation is used to estimate photocatalyst's redox reactions efficiency.
- A multicomponent approach in optical spectra analysis has been proposed for the result interpretation
- Expected Intermediate Products of Phenol Degradation (Catechol, Hydroquinone, p-Benzoquinone, o-Benzoquinone, Muconic acid, Dibenzofuran, Resorcinol, Oxalic acid)

Phenol Degradation by TiO_2 (Aldrich) Photocatalyst



Kinetics of Phenol Degradation by TiO_2 (Aldrich) Photocatalysis

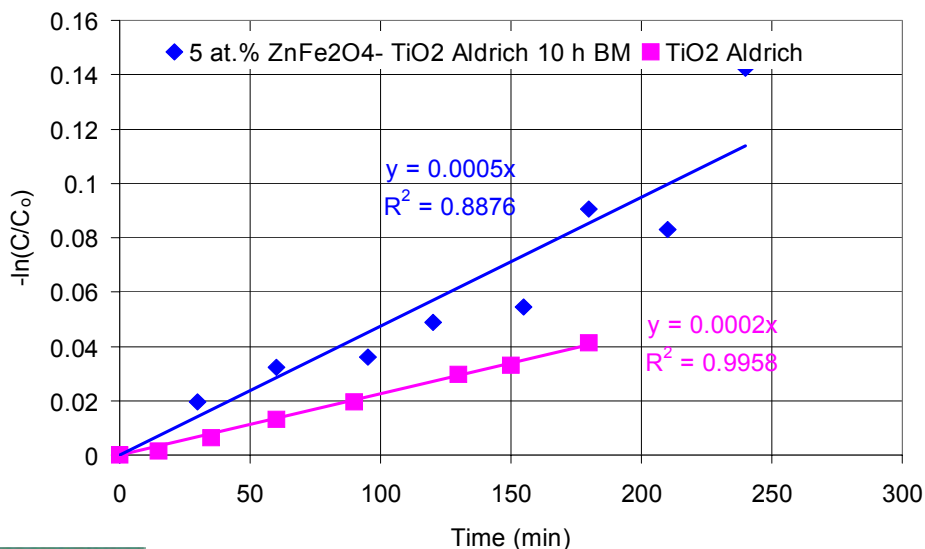


$$C(\lambda) = \sum a_k \cdot \phi_k(\lambda)$$

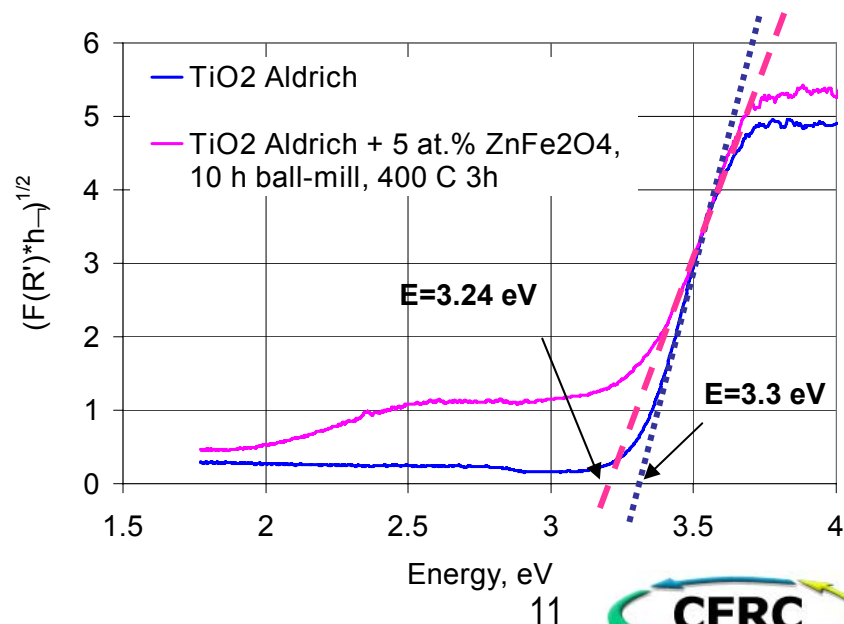
Sesha S. Srinivasan, Nikolai Kislov, Jeremy Wade, Matthew T. Smith, Elias K. Stefanakos, Yogi Goswami, "Mechanochemical synthesis, structural characterization and visible light photocatalysis of $\text{TiO}_2/\text{ZnFe}_2\text{O}_4$ nanocomposites," *Accepted by MRS Proceedings, 2006*

Task 1.1 (production): Photocatalytic Accomplishments - TiO₂-ZnFe₂O₄ Nanocomposites

- TiO₂-ZnFe₂O₄ nanocomposites were optimized based on control parameters such ball to powder weight ratio, milling duration, milling speed, and calcination temperature.
- Particularly, the nanocomposite having 5 at.% ZnFe₂O₄ and ball-milled for 10 hours is more than twice efficient in comparison with pure TiO₂ photocatalyst.



Red shift in optical absorption because of doping by ZnFe₂O₄

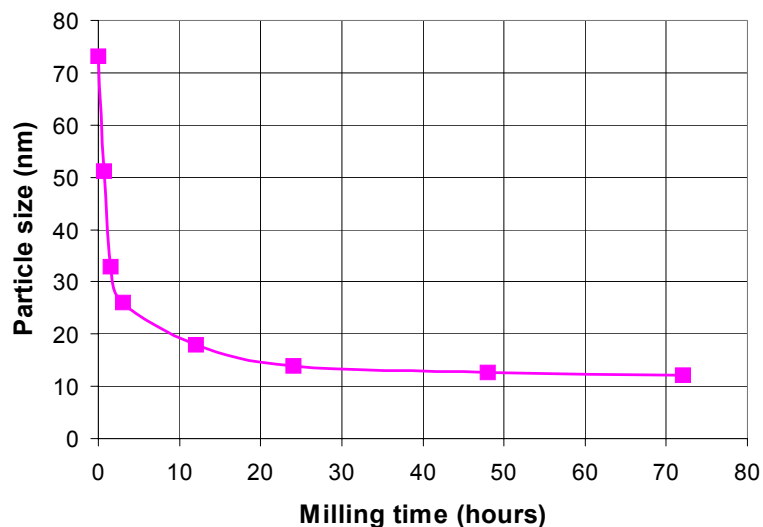


Task 1.1 (production): Photocatalytic

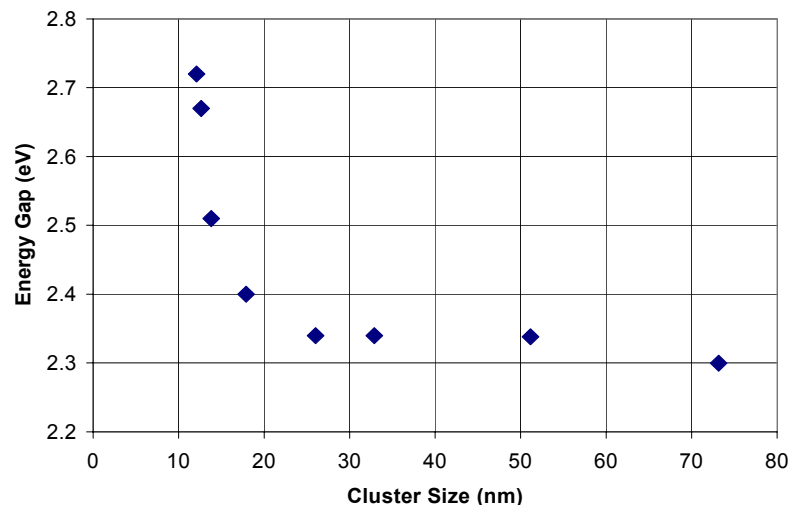
Accomplishments - TiO₂-ZnFe₂O₄ Nanocomposites

A detailed investigation of quantum-sized effects in ball-milled ZnFe₂O₄ has been performed in order to understand the photophysical properties of ZnFe₂O₄/TiO₂ nanoclusters

The dependence of the particle size of ZnFe₂O₄ on the milling time



The dependence of the optical bandgap of ZnFe₂O₄ on the cluster size

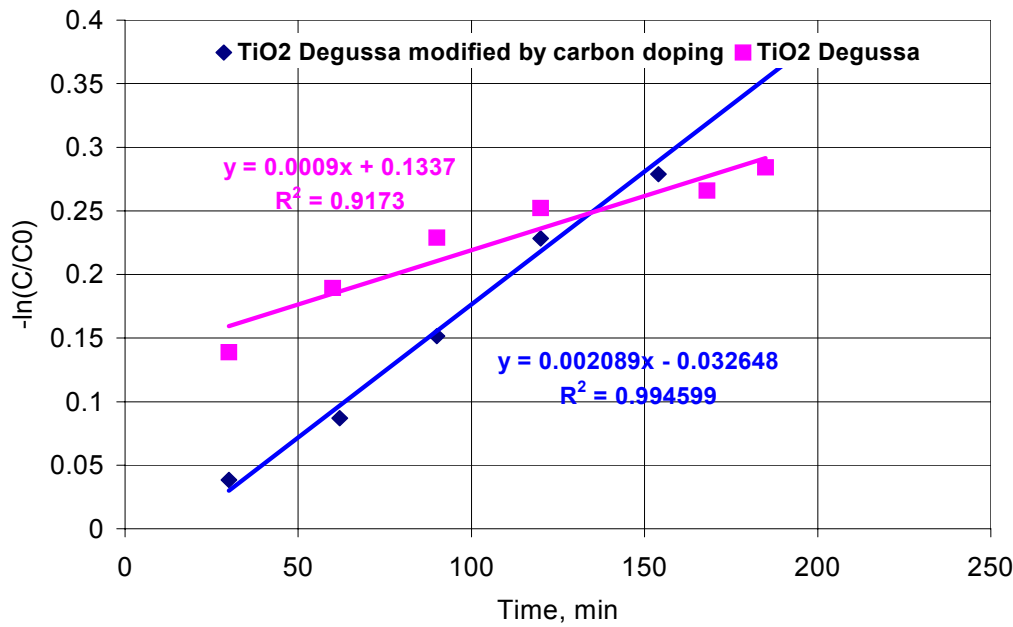


XRD Analysis was used for particle size estimation

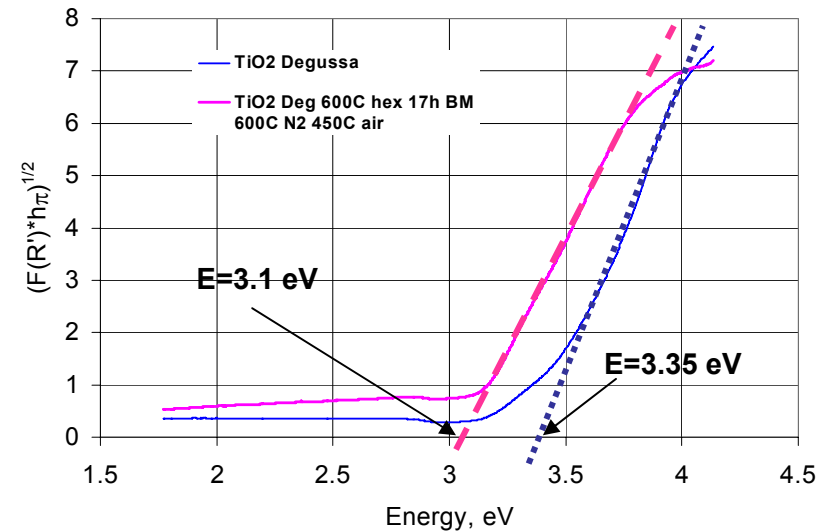
Task 1.1 (production): Photocatalytic

Accomplishments - Carbon doping of TiO₂

- Developed TiO₂ carbon doped photocatalyst having improved photocatalytic properties
- Particularly, the carbon doped TiO₂ photocatalyst is two times more efficient than pure TiO₂ photocatalyst



Red shift in optical absorption because of doping by carbon



Task 1.1 (production): Photocatalytic

Project Summary

Relevance:

Provided fundamental and experimental basis for development of efficient electrode materials for use in hydrogen production photochemical cell.

Approach:

- Extending light absorption into visible region by coupling of TiO_2 with a small bandgap semiconductor (ZnFe_2O_4 , Fe_2O_3 , or WO_3)
- TiO_2 bandgap reduction by carbon doping
- Preparation of photocatalytic films and nanoparticles using inexpensive spray pyrolysis deposition

Technical Accomplishments and Progress:

Demonstrated TiO_2 photocatalysts having improved photocatalytic activity in organic degradation experiments

Proposed Future Research:

- Complete experimental transformation from organic degradant to H_2 production using visible light photocatalysis.
- Design/construct apparatus and begin photocatalytic experiments
- Develop doped TiO_2 films having improved photocatalytic activity for water splitting experiments

Task 1.1 (production): Photoelectrochemical/Photocatalytic

Publications

- Sesa S. Srinivasan, Nikolai Kislov, Jeremy Wade, Matthew T. Smith, Elias K. Stefanakos, Yogi Goswami, “Mechanochemical synthesis, structural characterization and visible light photocatalysis of TiO₂/ZnFe₂O₄ nanocomposites,” Accepted by MRS Proceedings, 2006
- P. Mahawala, S. Vakkalanka, S. Jeedigunta, C. S. Ferekides and D. L. Morel, “Transparent Contact Development for CdSe Top Cells in High Efficiency Tandem Structures”, Proceedings of the 31st IEEE PVSC, Orlando, 2005.
- “Transparent high-performance CDSE thin-film solar cells”, Thin Solid Films, Volumes 480-481, 1 June 2005, Pages 466-470
P. Mahawala, S. Jeedigunta, S. Vakkalanka, C.S. Ferekides and D.L. Morel

Task 1.2 (production): Thermochemical

M. Su Lee, S. Dolan, H. Ingley – University of Florida

Y. Goswami, E. Stefanakos – Univ. of South Florida

Objectives

- Investigate UT-3 Thermochemical cycle and conduct kinetic studies
- Lower H₂ production cost by increasing H₂ yield with an improved pellet formulation
- Reduce operating cost by lowering the reactor operating temperature

Approach

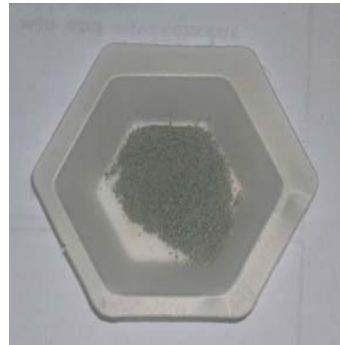
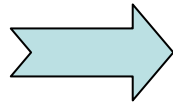
- Evaluation of characteristics of *Ca*-pellets and *Fe*-Pellets to improve their formulation
- Chemical kinetic studies to evaluate and improve the pellet cyclic life, reaction rates and conversion using lab-scale apparatus
- Feasibility experiments

Task 1.2 (production): Thermochemical Procedure to Make a Ca-pellet

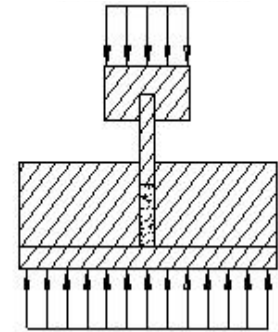
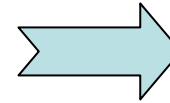


Chemistry of
Metal
Alkoxide

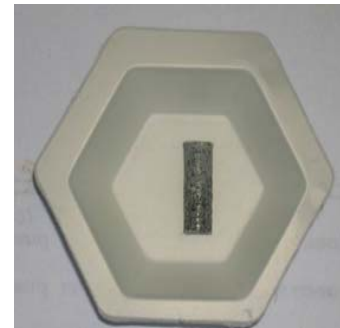
Drying and Mixing
with Additives



Sieved Powder

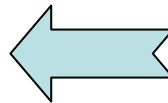


Die pressing



A Presintered
Pellet

Sintering



Remove
Additives



A Porous Ca-Pellet
supported by
 CaTiO_3

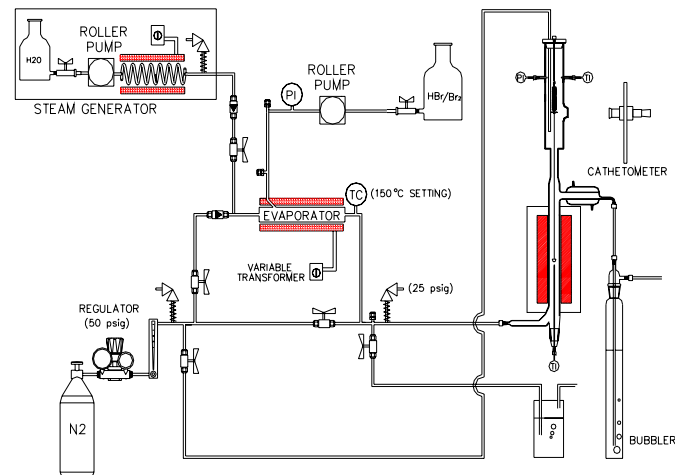
Accomplishments - Experimental Set-up and Thermogravimetric Balance



Experimental Set-up

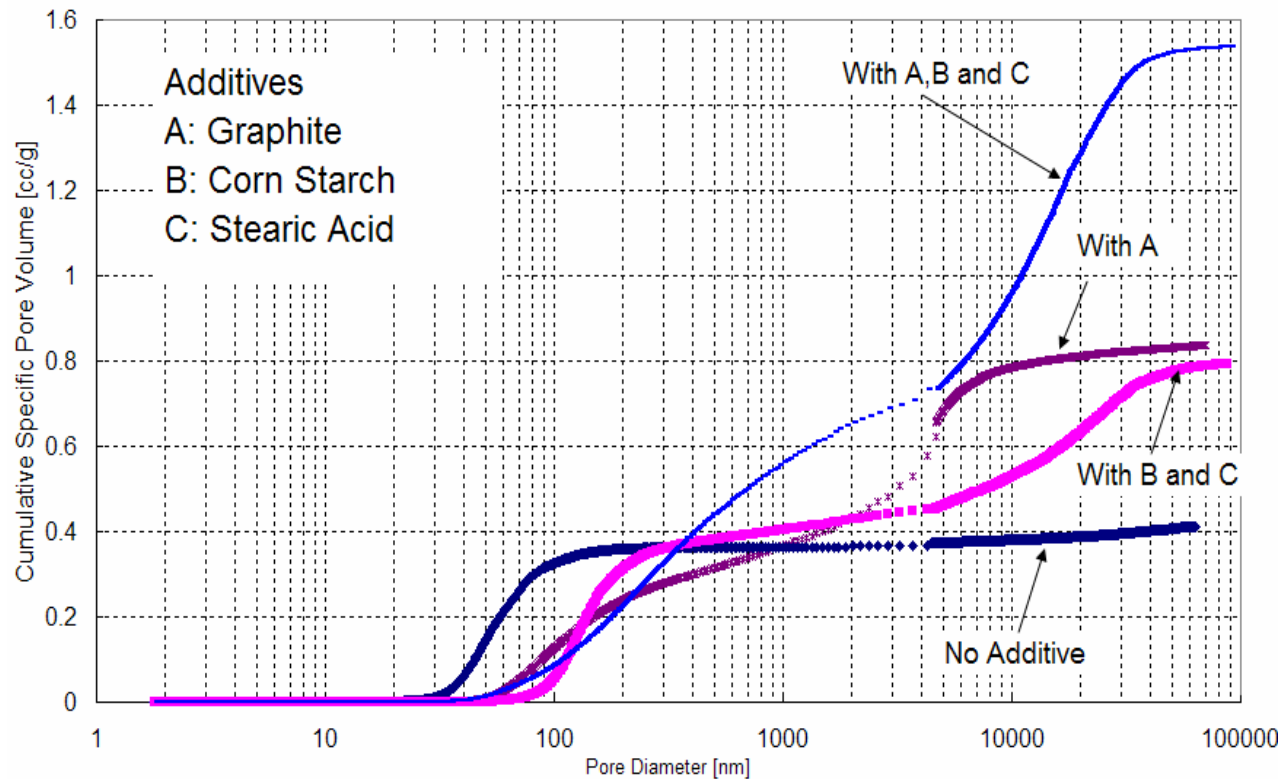


Thermogravimetric Balance



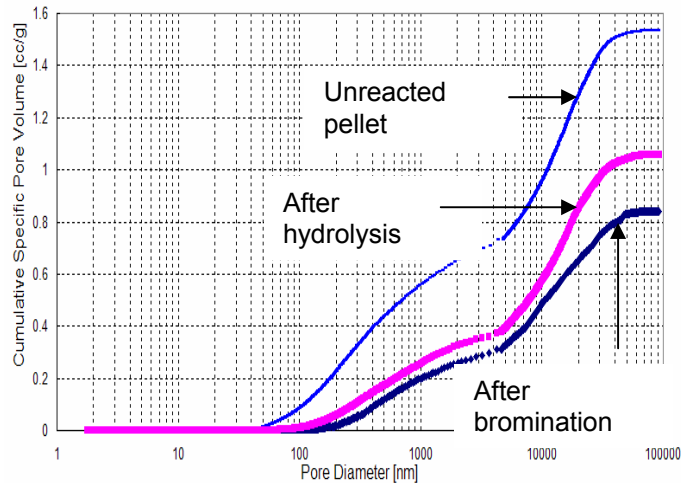
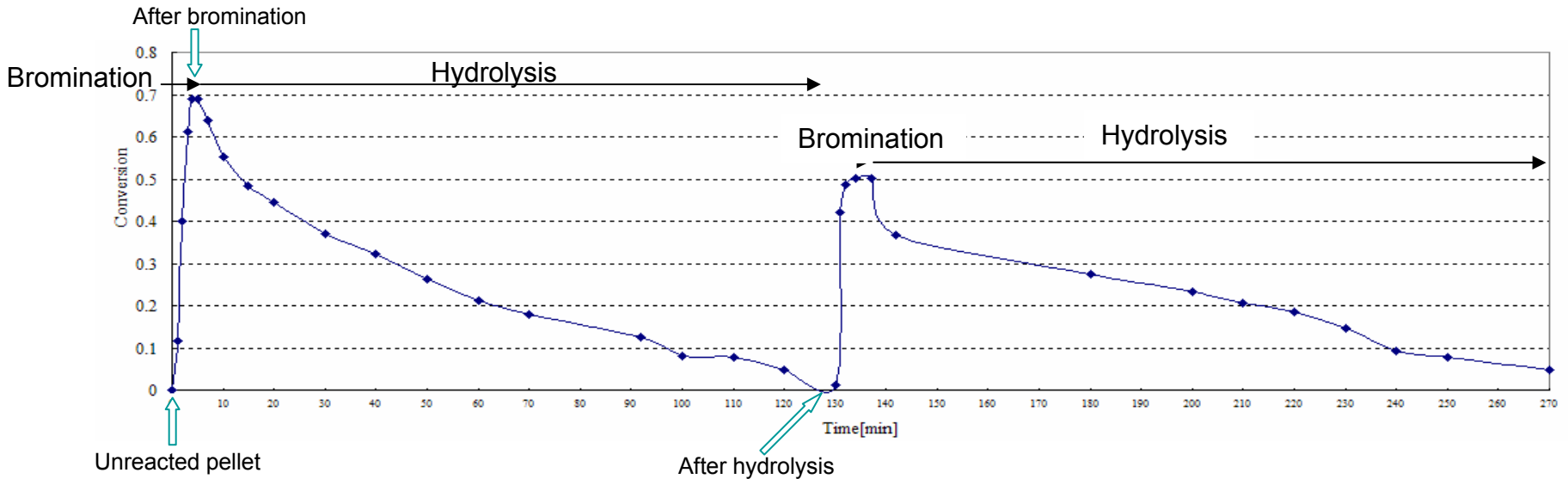
Task 1.2 (production): Thermochemical

Accomplishments - Pore Size Distributions of Ca-pellets by Additives



- Macropores contribute to diffusion characteristic inside the pellet.
- The addition of corn starch and stearic acid increases macropores greater than $5\mu\text{m}$ with a slight decline in strength while the addition of graphite decrease the strength steeply.

Accomplishments - Conversion Profiles of Reactions



- Initial trend of conversion profiles was in relatively good agreement with the results reported by M. Sakurai et al, 1995[1]
- Degradation and low hydrolysis rate were observed during the cyclic operations.
- Half of pore volume was reduced by increasing the volume of solid reactant in the process of bromination.
- Most of pores greater than 5 μ m were regenerated after hydrolysis while pores less than 5 μ m weren't. This showed that the reduction lead to degradation.

1) M. Sakurai, A. Tsutsumi and K. Yoshida, 1995, "Improvement of Ca-Pellet Reactivity in UT-3 Thermochemical Hydrogen Production Cycle." *Int. J. Hydrogen Energy*, Vol. 20, pp.297-301.

Summary

- **Objective** : Investigate various aspects of the UT-3 cycle in order to improve the process performance.
- **Approach** : Understand the reaction kinetics, solid reactant behavior and process thermodynamics
- **Technical Accomplishments and Progress**
 - Completed installation of laboratory scale facility
 - The bromination and hydrolysis of Ca-pellet has been conducted using laboratory experimental set-up.
 - Degradation and low hydrolysis rate was observed.
 - The pore size distribution data showed that the reduction of pore volume is a cause of degradation and low hydrolysis rate
- **Proposed future research**
 - Understand the mechanism of degradation and speed up the hydrolysis process
 - Develop a pelletization process for Fe-pellets
 - Study kinetics of Fe-pellets
 - Thermodynamic analysis of the cycle

Task 1.2 (production): Thermochemical

Publications

- Man Su Lee, Yogi Goswami, Ben Hettinger, and Sanjay Vijayaraghavan, “Development of Calcium Oxide Pellets for UT-3 Thermochemical Cycle”, Abstract accepted for 2006 ASME International Mechanical Engineering Congress and Exposition.

Task 1.3 (production): Biomass Gasification

M. Mahishi, M. Nath, N. Rajvanshi, W. Lear – Univ. of Florida

Y. Goswami, E. Stefanakos – Univ. of South Florida

Objectives

| | |
|---------|---|
| Overall | <ul style="list-style-type: none">• Improve H₂ yield and process efficiency (heat integration and alternate gas clean-up approaches)• Reduce capital cost by combining process (gasification, reforming and shift) steps and operations• Improve gasification efficiency by developing a model-based controller for a biomass gasifier |
| 2005 | <ul style="list-style-type: none">• Conduct theoretical studies of sorbent enhanced biomass gasification• Develop experimental set-up• Modeling of gasifier<ul style="list-style-type: none">– develop dynamic math model of a biomass gasifier– study the time dependence of reformat properties on biomass composition & steam to biomass ratio |
| 2006 | <ul style="list-style-type: none">• Experimentally determine effect of sorbent addition on H₂ (& CO, CO₂) yields• Conduct energy analysis of biomass gasification• Simulate in MATLAB/SIMULINK & design a model-based controller to<ul style="list-style-type: none">– take corrective action on system abnormalities– ensure uniform H₂ output |

Approach (Thermodynamics)

- Task 1: Thermodynamic studies (complete)
 - Determine process conditions for maximum thermodynamic H₂ yield
 - Develop ASPEN models for conventional & sorbent based biomass gasification
- Task 2: Experimental studies (50% complete)
 - Fabricate test set-up
 - Conduct tests with and without sorbent to find H₂, CO & CO₂ yields
- Task 3: Energy analysis (10% complete)
 - Study energy consumption of conventional & sorbent enhanced gasification
 - Identify energy efficient methods for regenerating spent sorbent

Task 1.3 (production): Biomass Gasification

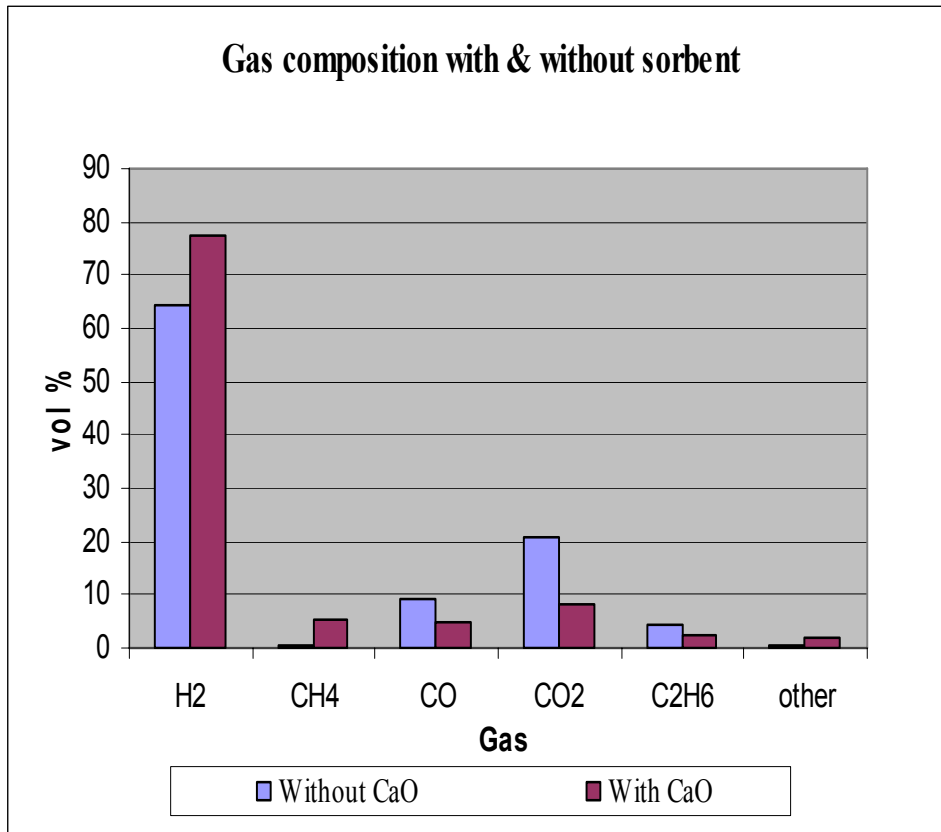
Approach (Optimization)

- Task 1: Modeling
 - Develop a physics-based thermodynamic model for discrete reformer elements.
 - Transform the PDE into a set of ODEs in time.
 - Linearize the model for development of a suitable controller.
- Task 2: Simulation
 - Solve ODEs in Matlab for
 - transient temperature distribution in reformer
 - reformat concentration as a function of time
- Task 3: Model Validation
 - Match the simulated results with experimental results
 - Validate the model
- Task 4: Controller Design
 - Design controller to reject the following disturbances into the system:
 - biomass inconsistencies
 - biomass flow rate
 - catalyst degradation
 - tar formation
 - Design an ideal model-based control scheme.
 - Implement the controller and evaluate the change in performance of the gasifier in terms on H₂ yield.

Task 1.3 (production): Biomass Gasification

Accomplishments (Thermodynamics)

Experimental result: Product gas composition of pine mulch steam gasified at 600°C with and without CaO sorbent



- H₂ yield increased by 20%; CO and CO₂ in product gas reduced by 44% and 60.6% respectively from base (no sorbent) case
- higher gas yield (about 30%) observed in presence of sorbent
- product gas has less tars and particulates while using sorbent
- higher H₂ yield obtained at lower temperature offers potential to reduce gasification temperature (by about 100-150°C)

Task 1.3 (production): Biomass Gasification

Future Work

FY 2006 (Thermodynamics)

- Quarter 3:
 - Conduct further experiments to determine gas yield (mainly H₂, CO, CO₂ yields) at different temperatures with and without sorbent
- Quarter 4:
 - Conduct an energy analysis of biomass steam gasification considering heat losses and equipment inefficiencies

FY 2006 (Optimization)

- Model validation by comparing with experimental results
- Design a few controllers to maintain optimal operating conditions of the reformer.
- Compare the results and propose the ideal controller

FY 2007 (Thermodynamics)

- Identify methods of regenerating spent sorbent using waste heat from other applications

Task 1.3 (production): Biomass Gasification

Publications

- “Hydrogen production from ethanol: A thermodynamic analysis of a novel sorbent enhanced gasification process”, Mahishi M.R., Sadrameli, S. M., Vijayaraghavan S., Goswami D. Y., American Society of Mechanical Engineers, Advanced Energy Systems Division (publication) AES vol 45, pp 455-463, 2005
- “A Novel Approach to Enhance the Hydrogen Yield of Biomass Gasification Using CO₂ Sorbent”, Mahishi M.R., Sadrameli, S. M., Vijayaraghavan S., Goswami D. Y. *under review with ASME Journal of Engineering for Gas Turbines and Power*

Task 1.4 (production): Solid State Ionic Conductor Development

B. Krakow, P. Wiley, L. Ecklund-Mitchell, D. Payne, E. Weaver, E. Stefanakos

Objective

- Economic electrolytic hydrogen production through better electrolytes and electrochemical cells

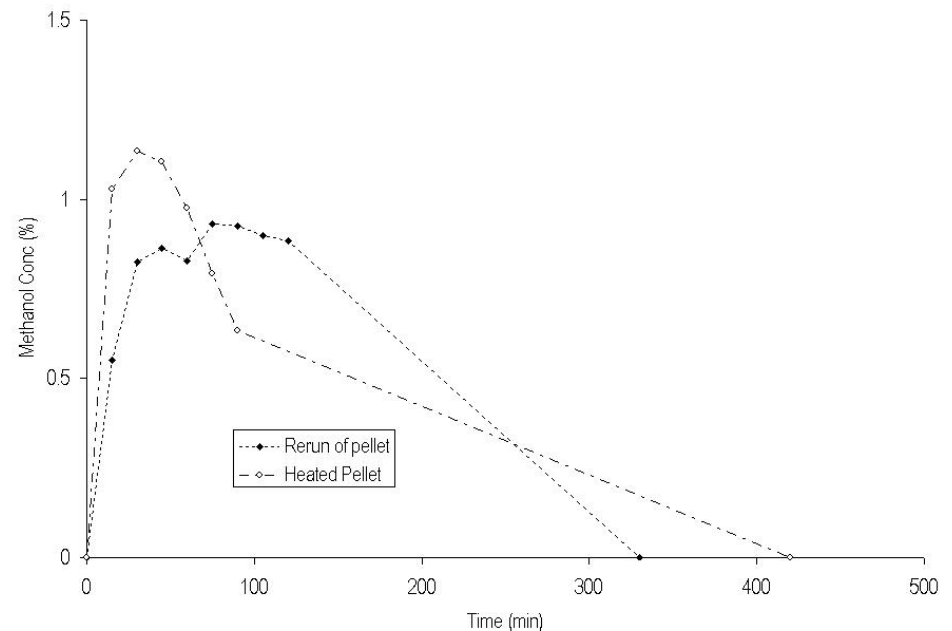
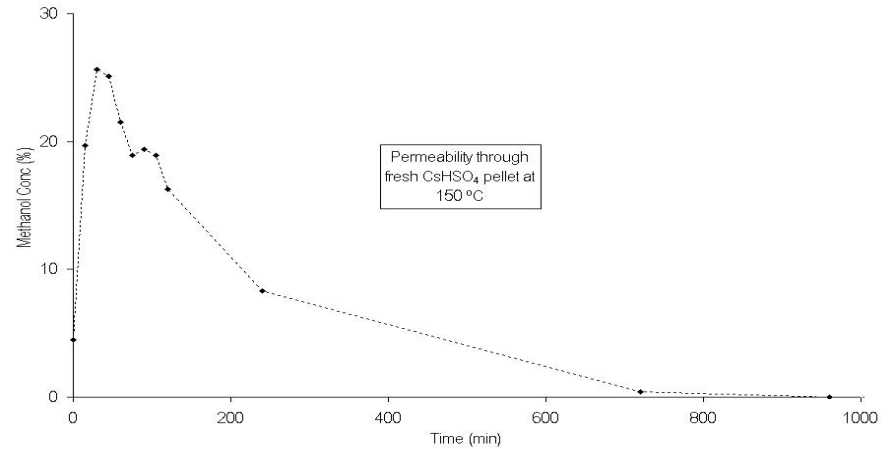
Approach

- Scavenging the anode with a reducing agent. This agent may be landfill gas (or other biogas), synthesis gas or industrial waste products.
- An optimum choice of temperature can provide a good balance of efficiency and low cost. The temperature should be above 150 °C (to lower the electricity demand) and below 300 °C (where a quantum jump occurs in cost and difficulty of system construction and operation).
- An electrolyzer with a scavenged anode is effectively a gas shift reactor in which electrolysis replaces shift, separation and purification with one step. This mitigates the need for economies of scale and addresses the most difficult barriers for both gas shift and electrolytic hydrogen production.
- To implement the stated solutions we are developing electrochemical cells with electrolytes that have the following characteristics:
 - True solid state proton conductors
 - Operate between 100 and 300 °C
 - No liquid water required and no water loss at elevated operating temperature
 - Reduced catalyst requirements
 - Impermeable to fuels, scavengers, reaction intermediates, molecular products and catalysts

Task 1.4 (production): Solid State Ionic Conductor Development

Permeability Results

- CsHSO_4 pellets impermeable to methanol were manufactured
- Permeability was only exhibited in the first hour of experiment, then stopped
- Impermeability due to methanol appears to be a combination of heating effect, and interaction to methanol itself
- Pellets rendered impermeable to methanol continued to be so several days later
- Initial permeability dropped by an order of magnitude for reused pellets

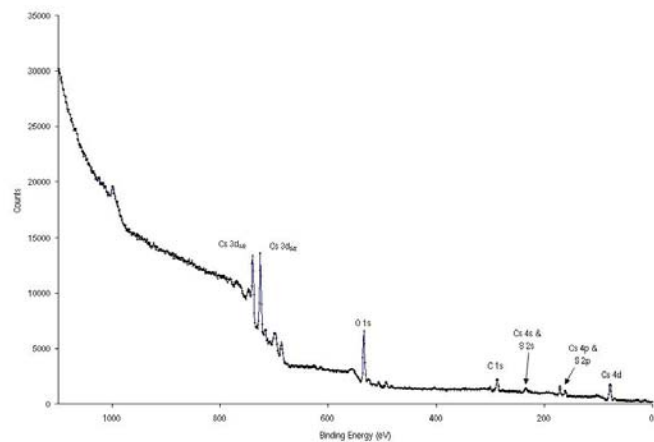
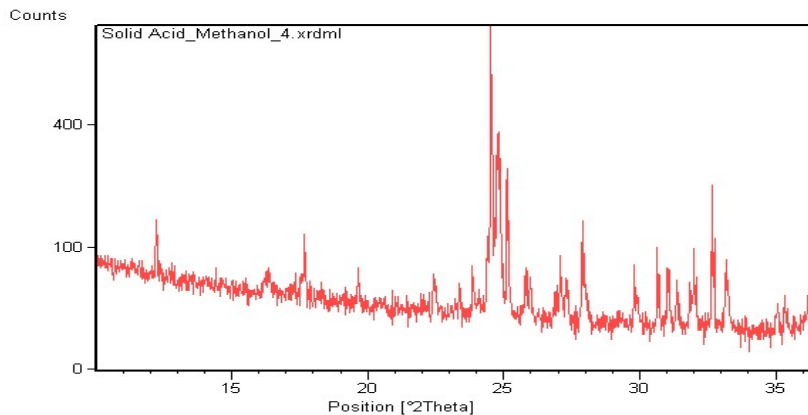
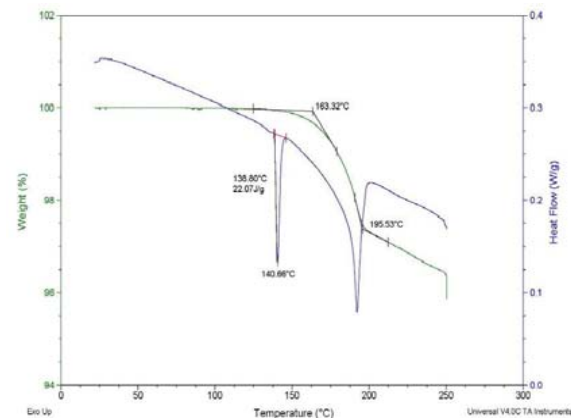


Task 1.4 (production): Solid State Ionic Conductor Development

Synthesis and Material Characterization

High purity CsHSO_4 was synthesized by reacting Cs_2SO_4 with sulfuric acid, then crystallizing out of solution with an organic (methanol). Quality of CsHSO_4 was confirmed with the following characterization methods:

- Combined TGA and DSC-distinct transition at 141 °C to high temperature phase at 22.1 J/g, chemical decomposition in air at 163 °C to melting at 196 °C
- XPS with Mg source-distinct crystalline peaks, Cs to S ratio of 1:1 on surface, some oxide formation on surface
- XRD-Crystalline peaks, strong match to known CsHSO_4 in $2\Theta = 10\text{-}75^\circ$ range



Future Work and Summary

Future Work

- Performance and stability
- Studies of electrolytes and cells will continue. New electrolyte materials will be sought and investigated for use with specific scavengers.
- We will apply metallurgical and semiconductor processing techniques to inorganic solid electrolyte materials to try to prepare strong and sturdy thin electrolytes.
- A monitoring and control system will be acquired and installed.
- Electrode attachment techniques to minimize contact resistance will be pursued.
- Catalysts and surface treatments will be applied to attempt to increase power densities.
- We will continue to test permeability of solid electrolytes to feedstocks and scavengers.

Summary

- Impermeability of pellets after high temperature treatment with methanol while maintaining other crucial characteristics (conductivity, strength) supports viability of CsHSO₄ as material in combined hydrogen production/separation processes.
- CsHSO₄ produced in current synthesis is high-purity, with sharp crystalline structure, and reproducible thermal properties.
- Groundwork has been laid to begin rigorous testing of performance of electrodes and catalysts to specific fuel gases

Task 3.1.1 (Fuel Cells): PEM Fuel Cell Research

C. Linkous – Univ. of Central 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

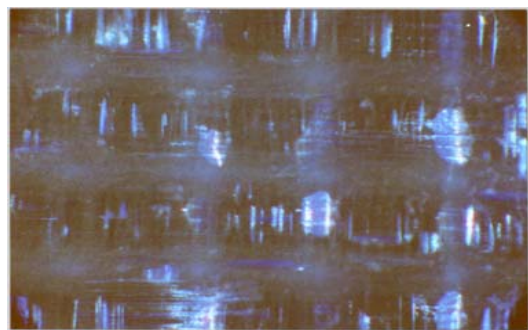
Approach

- Heavily sulfonate polymers to promote proton conductivity, but cross-link to prevent solubility and mechanical stability problems
- Use only as much fluorine in the polymer as is necessary to promote conductivity and chemical stability
 - place fluorines near the sulfonic acid groups to increase acidity
 - surface fluorinate to provide protection where hydroxyl radicals are generated
- Develop accelerated test apparatus to evaluate prototype PEM's

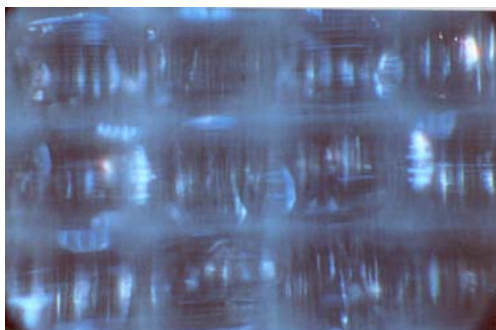
Accomplishments

- Demonstrated protection of amine substituents on benzyltrifluoride monomer by making the acetamide, a necessary step in the synthesis of fluorosulfonic PEEK polymer
- Developed mechanical, permeation, and conductivity methods for accelerated testing of PEM electrolytes under oxidizing conditions
- Synthesized highly conductive SPEEK (260 EW) to incorporate into cross-linked PEM electrolytes

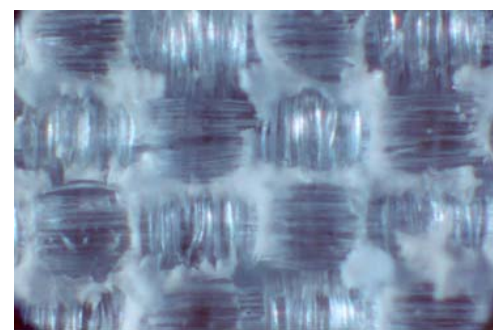
Accomplishments



Day 1



Day 3



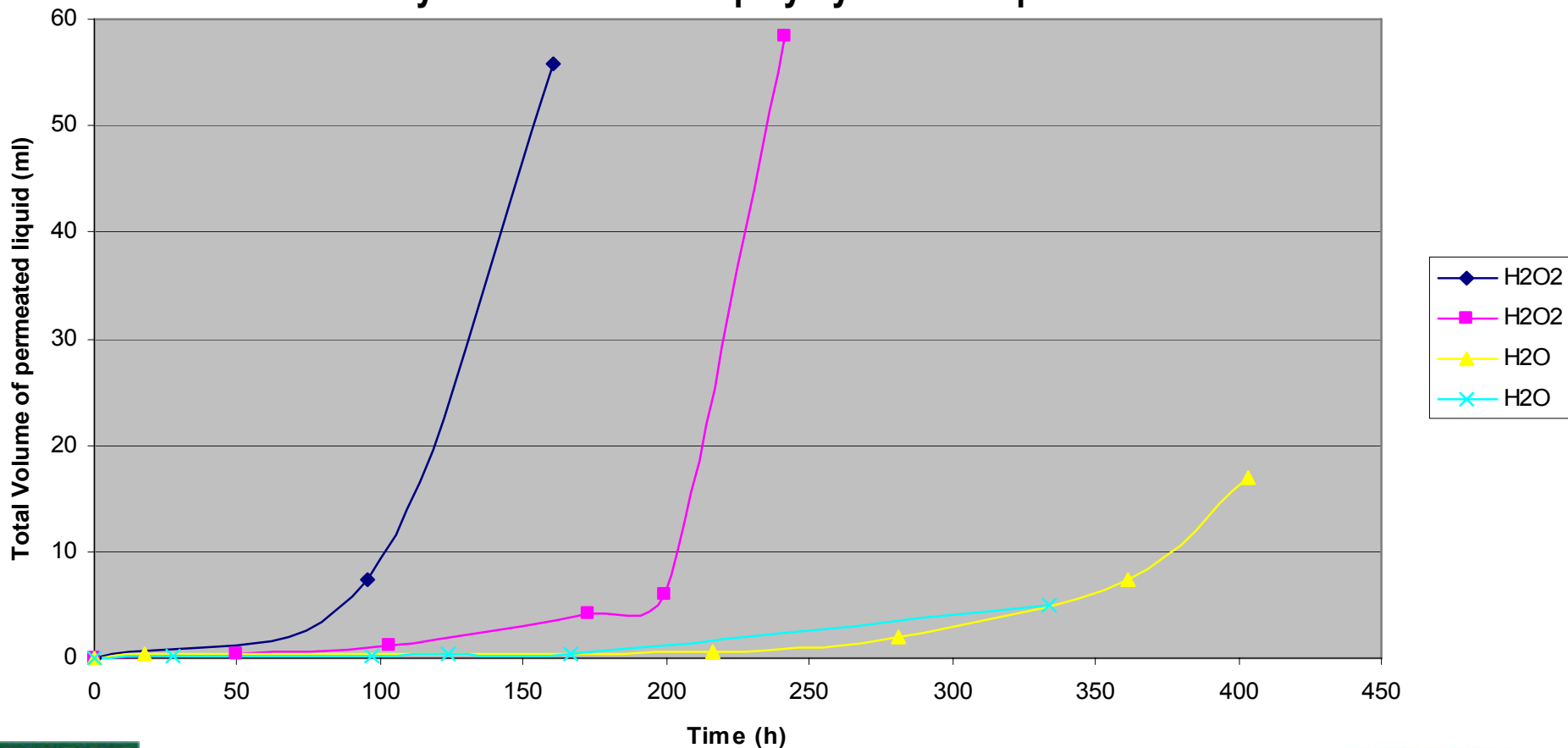
Day 11

Accelerated testing for peroxide stability on a fuel cell electrolyte

Neosepta[®] solid polymer electrolyte exposed to 3.5% H₂O₂ solution at 50 °C. (100x magnification)

Accomplishments

Permeability tests on 0.025mm polystyrene at 10 psi and 80 °C



Future Work

- Remainder of FY06
 - prepare fluorosulfonic acid versions of S-PEEK and other engineering polymers
 - determine limits of cross-linking, degree of sulfonation, and proton conductivity
 - finalize accelerated PEM test method
 - measure durability of surface-fluorinated PEM's
- FY07
 - combine cross-linking and partial fluorination strategies into new PEM membranes
 - test prototype PEM's in fuel cell configuration

Task 3.1.2 (Fuel Cells): PEM Fuel Cell Research (UF)

N. Kothurkar, Y. Goswami, E. Stefanakos

Objectives

| | |
|---------|---|
| Overall | <ul style="list-style-type: none">• Develop cheaper PEM material alternatives to Nafion®<ul style="list-style-type: none">•High Temperature, Low humidity operation•Low fuel crossover• Experimental setup for wide temperature range testing |
| 2005 | <ul style="list-style-type: none">•Set up experimental test bed•Synthesize polymer (ABPBI) for low humidity, high temperature operation |
| 2006 | <ul style="list-style-type: none">• Fabricate MEA•Test Performance of ABPBI at high temperature•Test Performance of ABPBI at sub-freezing temperature |

Approach

➤ Setup fuel cell test stand

- Construct test stand with temperature, humidity, etc. control
- Modify for low temperature operation for freeze testing

➤ PEM Material Development

- Synthesize ABPBI—poly(2, 5-benzimidazole)
- Fabricate membrane electrode assemblies (MEA)
- Test MEAs under different temperature regimes

Task 3.1.2 (Fuel Cells): PEM Fuel Cell Research (UF)

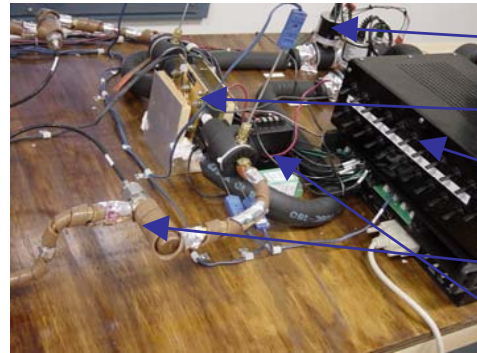
Accomplishments (Test set-up)



Mass Flow Cont.

Humidifier

Control Panel



Back pressure valves

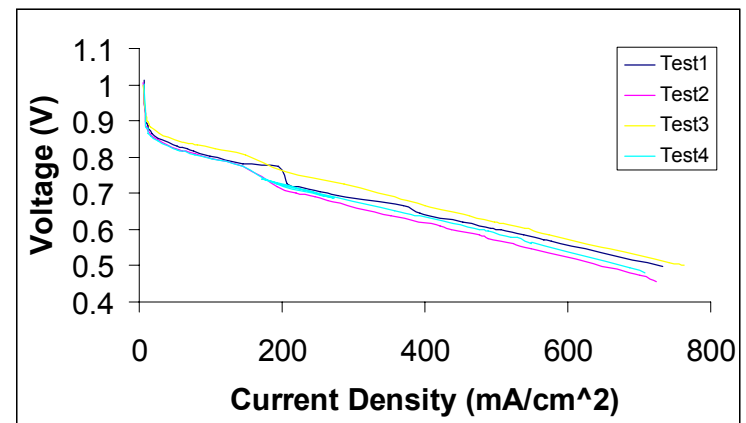
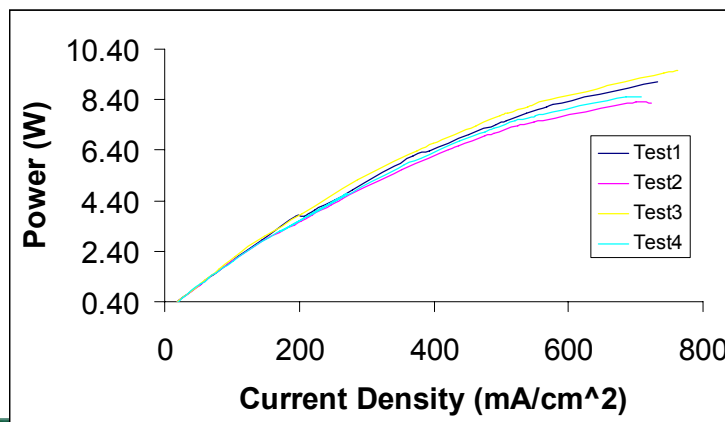
Single cell

Resistance Load

RH Probe

Current transducer

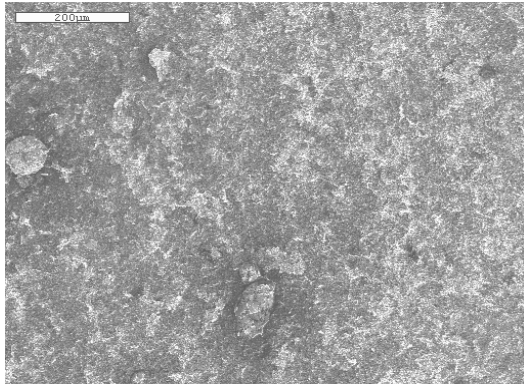
Test Bed



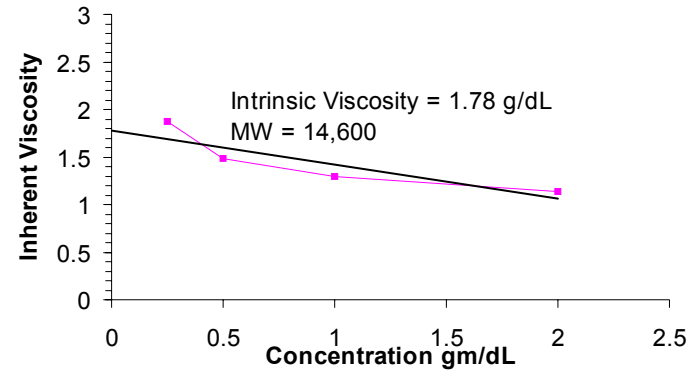
Repeatability Testing, Nafion® MEA

40

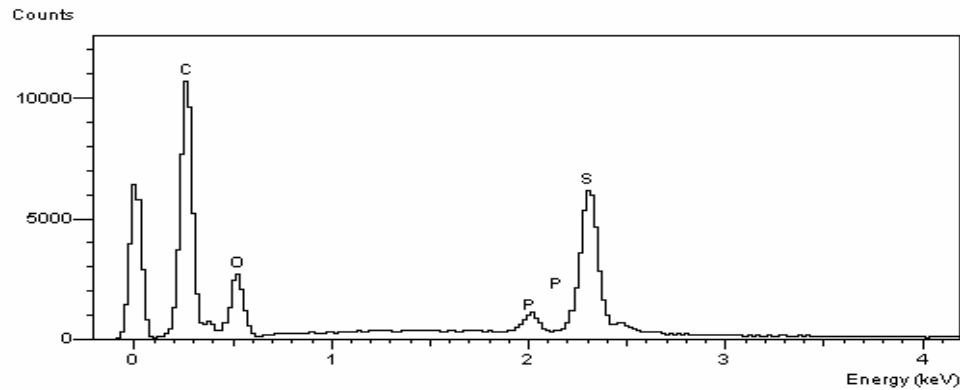
Accomplishments – Synthesis and Characterization of Poly(2,5-benzimidazole)



SEM BSE



Intrinsic Viscosity- MW



EDX-Elemental Analysis

Future Work

FY 2006

➤ Quarter 3:

- Increase molecular weight of ABPBI
- Develop catalyst formulation
- Fabricate MEA

➤ Quarter 4:

- Evaluate performance of ABPBI at high temperatures (120-180°C)
- Evaluate performance of ABPBI at sub-freezing temperatures.

FY 2007

- Evaluate and reduce phosphoric acid leaching

Task 3.1.3 (Fuel Cells): PEM Fuel Cell Research (USF)

J. Wolan, B. Grayson, E. Stefanakos, V. Gupta

Objectives

- Develop alternative anodic catalyst systems; increasing activity, reducing Pt loading and preventing CO poisoning through novel uses of alloying gold nano-particle/TiO₂ systems.
 - Additional improvements in anode tolerance to carbon monoxide are required to facilitate simplification of the system and to reduce cost and weight [1]
- Increase the operating temperature of polymer-based proton exchange fuel cells through the incorporation of nano-composite membrane additives; increasing catalyst activity and improving fuel cell efficiencies.
 - The proposed membrane material must meet the conductivity requirements over a range of operating conditions from -20°C to 120°C [2]
 - 0.10 S/cm proton conductivity at Operating Temp
 - 0.07 S/cm proton conductivity at Room Temp

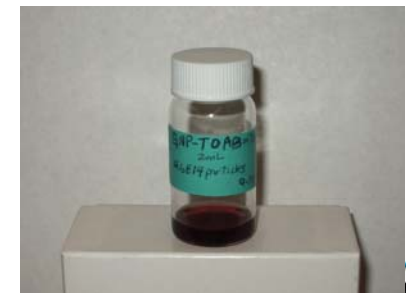
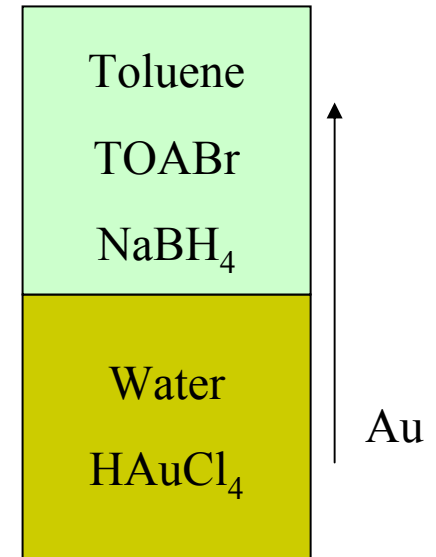
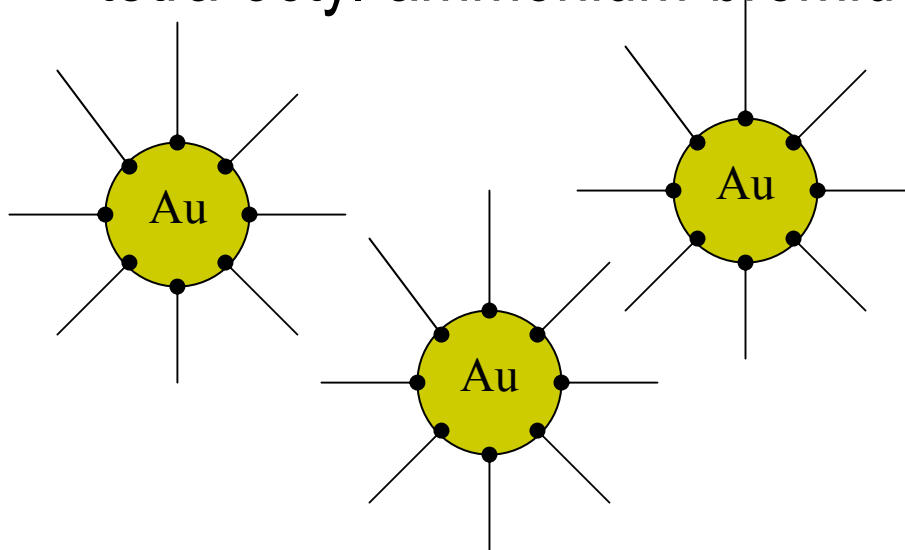
1. DOE, Multi-Year Research, Development and Demonstration Plan, pg 3-76
2. Draft Funding Opportunity Announcement Research and Development of Polymer Electrolyte Membrane (PEM) Fuel Cells for the Hydrogen Economy, 4/25/05

Approach

- Custom anodic catalysts consisting of platinum, ruthenium, and gold nanoparticles have been developed.
- Stabilized gold nanoparticles supported on TiO₂ selectively oxidize CO below 100°C
- β-zeolite nanoparticles have been incorporated with functionalized cast Nafion™ films; increasing operating temperatures while maintaining sufficient water retention.

Gold Nanoparticles Preparation*

- Two Phase Transfer Method
 - Results in gold particles <10 nm
 - TOABr = Stabilizing Agent
tetra-octyl-ammonium-bromide



Catalyst Results

- FTIR analysis comparing Pt/Ru/TiO₂ with Pt/Ru/Au/TiO₂ catalysts as shown in Fig. 1 shows improved CO oxidation of 3% at operation temps of 80-120°C.
- SEM images imply gold nanoparticles sizes less than 100 nm (Figure 2).
- XRD spectrum → TiO₂ to be anatase; a partial phase change to rutile occurs when exposed to temps. approaching 500-550°C which proves to be beneficial (Figure 3)
- XPS analysis is underway to determine the most active oxidation state of the gold catalyst species.

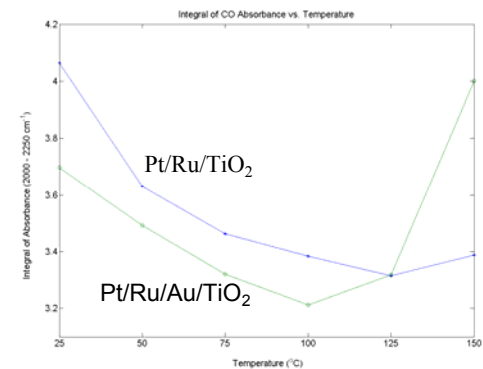


Figure #1

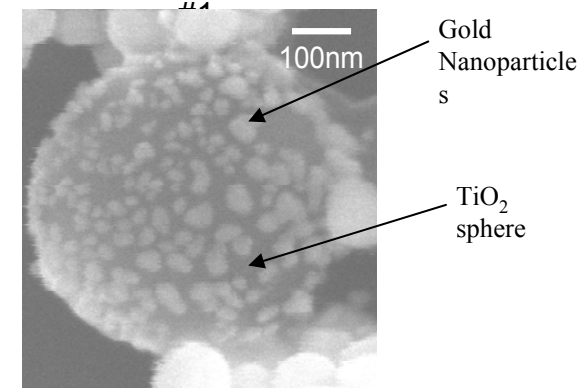


Figure #2

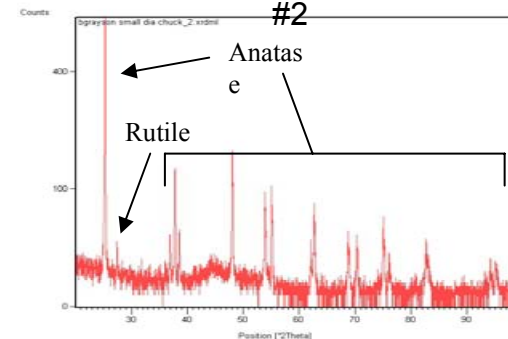
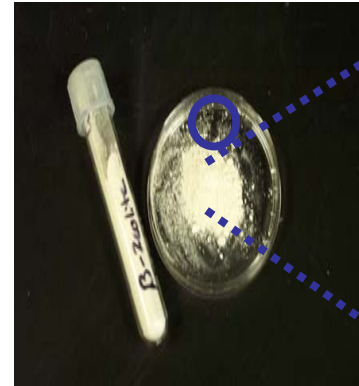


Figure #3

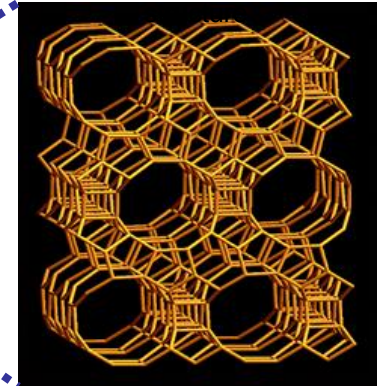
β -zeolite membrane creation for high temperature PEM

- β -zeolites were fully incorporated into cast Nafion™ films. Chosen due to their pore size, structure, acid stability, water retention, and increased proton conduction.
- Increased proton conductivity is achieved by functionalizing the films with phosphotungstic acid.
- XPS analysis of the zeolite crystals revealed no change in composition during particle reduction process

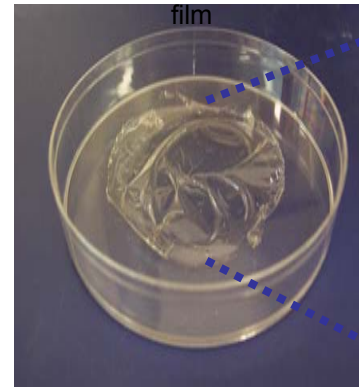
Ball milled β -zeolite



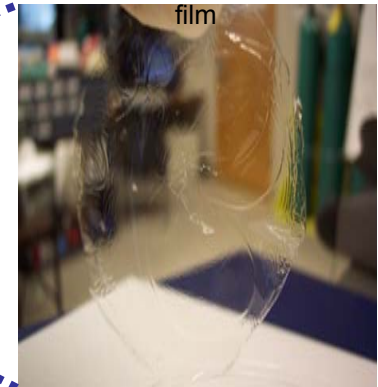
β -zeolite crystalline



Fully cast nanocomposite film



Fully cast nanocomposite film



Future Work and Summary

Future Work

- Optimize gold catalyst preparation techniques and increasing selectivity towards the production of CO₂ over H₂O formation
- Determine humidity effects on catalyst operation
- Further characterization of β -zeolites using XRD, TGA, and proton conductivity measurements
- Fully develop nanocomposite membranes capable of incorporation into a 25cm² membrane electrode assembly (MEA)
- Incorporate new MEA into a hydrogen fuel cell, operate at elevated temperatures and evaluate efficiency and performance.

Summary

- Pt/Ru/Au/TiO₂ nano-catalyst shows approx. 3% improvement over conventional catalyst in selective oxidation of CO in operation temperature ranges of 80-120°C.
- β -zeolite nanocomposite acid functionalized membranes have been successfully developed for incorporation into a high temperature proton exchange fuel cell MEA.

Task 4.1 (delivery) Geologic H₂ Storage

Kim Clayback, Mark Ross, G. Moore, E. Stefanakos

Objectives

- Identify and rank potential sites
- Define criteria and storage requirements for reservoirs
- Select an appropriate numerical model for reservoir performance
- Simulate full scale reservoir economics and operations

Accomplishments: Established criteria for reservoir

| | Formation Type | | |
|----------|----------------------------|---------------------------------|---------------------------------|
| | Caverns | Aquifers | Depleted Reservoirs |
| Depth | 455 - 915 m | 300 - 760 m | 150 - 1820 m |
| Pressure | 6.9 - 13.7 e3 kPa | 6.9 - 13.7 e3 kPa | 3.4 - 17.2 e3 kPa |
| Capacity | 0.6-3.0 e6 Nm ³ | 3.0 e6 - 6.0 e8 Nm ³ | 3.0 e6 - 6.0 e8 Nm ³ |
| Porosity | n/a | .25-.40 | .15-.30 |

Prioritized and identified a suitable geologic feature to simulate a hydrogen gas storage model in a solution mined cavern.

Accomplishments: Established Formation Benefits and Drawbacks

Benefits

- Depleted Reservoirs
 - Geologic characteristics generally well known
 - Transportation infrastructure in place
- Aquifers
 - Geographically well dispersed
 - Large volumetric storage possibilities
- Salt Caverns
 - Easiest, quickest recovery of gas
 - Lowest cushion gas requirement

Drawbacks

- Depleted Reservoirs
 - Possible chemical reactions with petroleum products
 - Not located near population (end user) centers
- Aquifers
 - Expensive exploration of geologic properties
 - Greatest cushion gas requirement
 - Additional cost of dehydration of gas during recovery process
 - Additional installation expense for wells at the perimeter for recovery
- Salt Caverns
 - Generally the smallest formation for storage use
 - Limited geographic distribution

Future Work

- Simulation of a brine compensated cavern model.
- Simulation of porous media reservoir with a numerical model.
- Engineering cost analysis of operational system.

Task 4.2 (delivery): Advanced Thermal H₂ Compressor

B. Krakow, S. Srinivasan, P. Wiley, D. Escobar, E. Stefanakos,

Objectives

- The objective of this project is reliable compression of hydrogen to the DOE target pressure of 5,000 - 10,000 psi with no lubricant contamination.
- System Design
 - Alloy Preparation
 - Power Supply Characteristics
 - Alloy Heat Capacity Measurement
 - Alloy Mass Calculation
- Address barrier 3.2.4.2 B (Reliability and costs of H₂ compression)

Approach

- An advanced hydride thermal compressor will be developed that is lighter, smaller, cheaper and faster than any built previously. The advanced approach will take advantage of the benefits of high temperatures and very rapid cycling achieved by employing electric discharge heating. It will have no moving parts other than valves (hence low maintenance, long life, reliable, no lubrication or hydrogen contamination by lubricants).

Efficiency benefits

- Carnot efficiency is enhanced by higher temperature differentials.
- No heat is dissipated by thermal cycling of the coolant. The heat capacities of the water and cooling tubes are no longer an issue because their temperatures are no longer cycling.

Size Reduction

- Cycling frequency up to 20 times greater.
- About 5 times fewer stages.
- Size and alloy requirements reduced by up to (5x20=) 2 orders of magnitude. Large economic implications.

Task 4.2 (delivery): Advanced Thermal H₂ Compressor Accomplishments

In the 6 months since this task began we have:

- Prepared and characterized (XRD and DSC) sample of ZrMn₂ alloy by ball milling and sintering the metal powders.
- Acquired ZrMn₂ DSC data with a view to determining its heat capacity (design parameter)
 - Calculated the required alloy mass
 - Calculated the required hydrogen mass
- Reactivated a high voltage power supply that was once used for lightning research and has properties needed for producing the electric discharge needed for this project..

Acknowledgements and Interactions

- **Hydrogen Workshop(s) at USF**
 - Dr. Jim Wang, SNL; Dr. Bill Tumas, LANL; Dr. Lin Simpson, NREL; Dr. Craig Jensen, Univ. Hawaii; Dr. Jim Fenton, FSEC; Dr. John Petrovic, DOE (agreed to visit in June'06)
- **US Department of Energy (DE-FG36-04G014224)**
 - IFE, Norway; AIST, Japan
 - University of Hawaii
 - HY-Energy Inc; SWRI
 - NREL; NNRC, USF
 - University of Florida
 - University of Central Florida (FSEC)
 - Sigma-Aldrich Fine Chemicals