# *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. Goswammi (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 emmissions, 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 $H_2$ 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 $H_2$ 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; $H_2$ 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 $H_2$ compression)

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# *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

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# Results

## *SnO2/Si Device Performance*



## *P – Contact development*
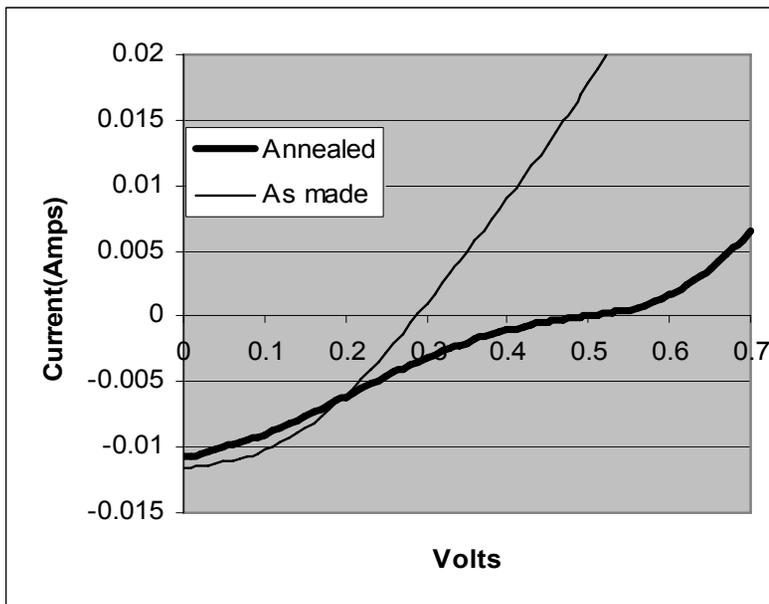


**Device Fabrication**
- Si is 0.1 $\Omega$-cm 100 n-type
- $SnO_2$ is deposited by MOCVD

**Results**
- The objective of 500 mV has been met
- Annealing(400C for 30 min.) significantly improves Voc but distorts the curve shape
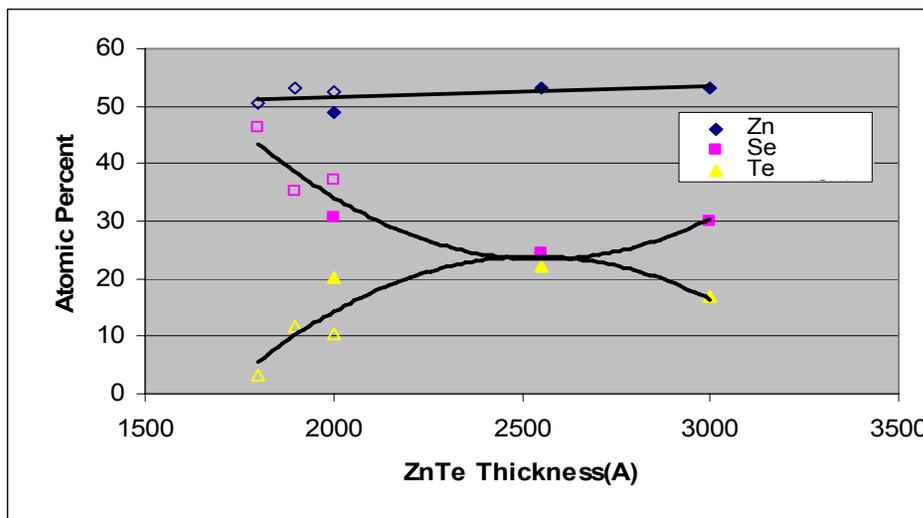
- $ZnSe_xTe_{1-x}$ from MBE growth has exhibited good p-contact properties
- Using cost compatible deposition technologies creates difficulties for controlling stoichiometry requirements for effective doping
- We have discovered regimes in deposition space that result in Zn/Group IV $\cong$ 1. Initial conductivities are of order $10^9$ $\Omega$-cm.

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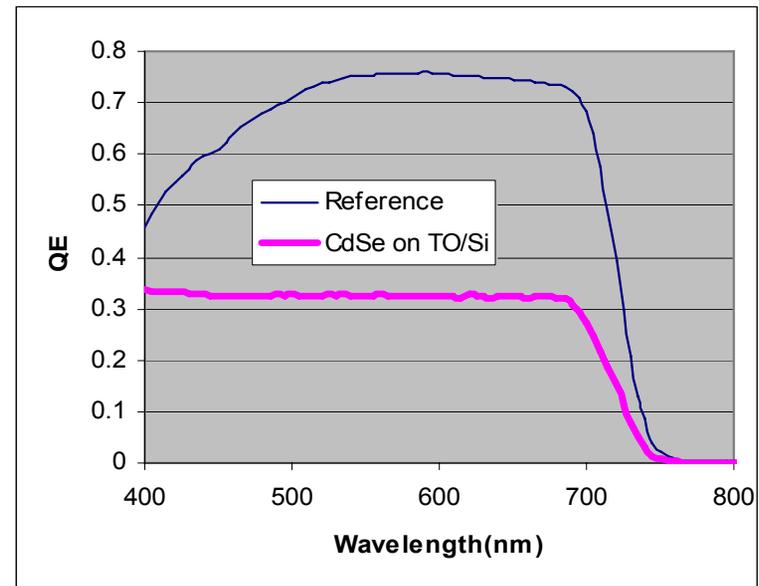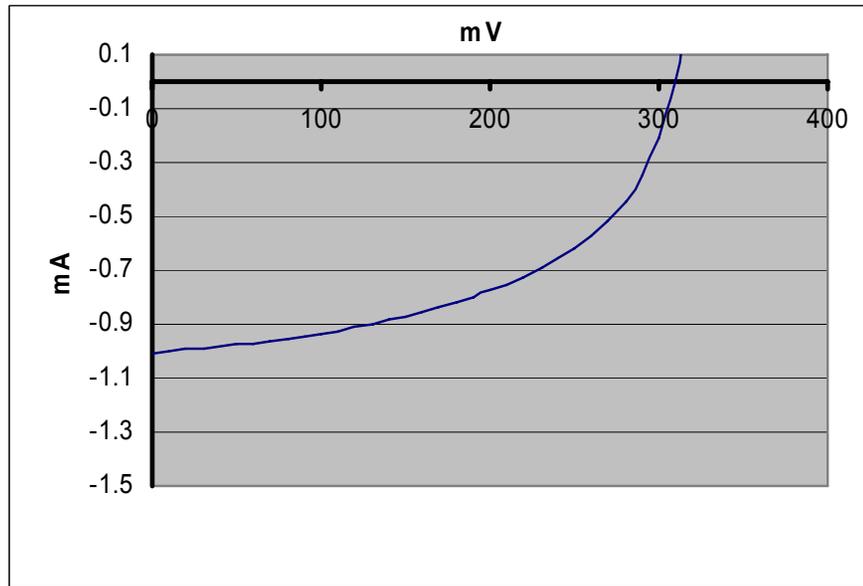
# *Tandem Devices*



- 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 $ZnSe_xTe_{1-x}$ 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

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# 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 ragion 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
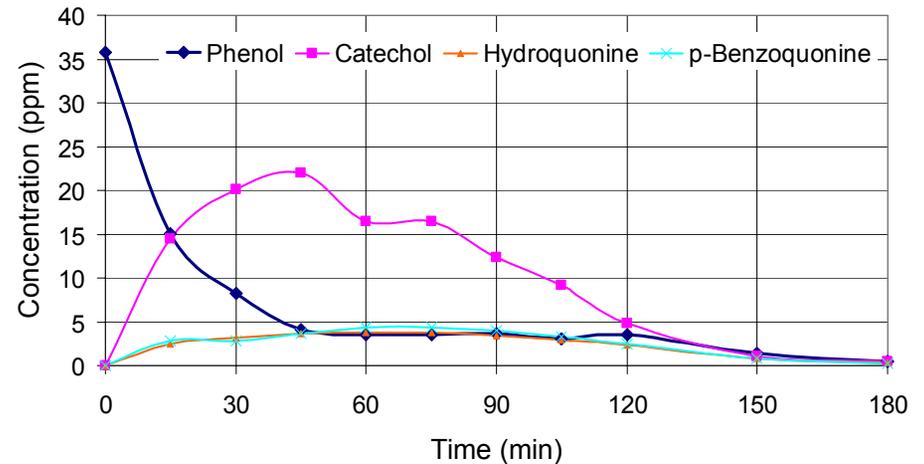# Accomplishments -TiO$_2$-ZnFe$_2$O$_4$ Nanocomposites

- 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, Hydroquonine, p-Benzoquonine, o-Benzoquonine, Muconic acid, Dibenzofuran, Resorcicol, Oxalic acid)

**Phenol Degradation by TiO2 (Aldrich) Photocatalyst**
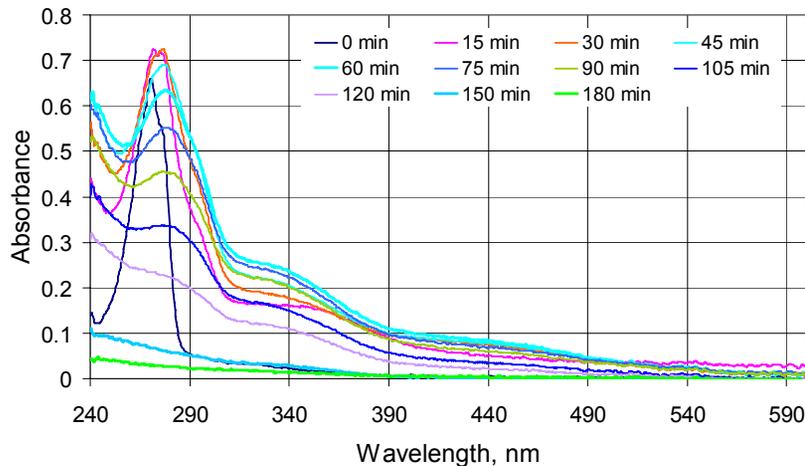
**Kinetics of Phenol Degradation by TiO2 (Aldrich) Photocatalysis**



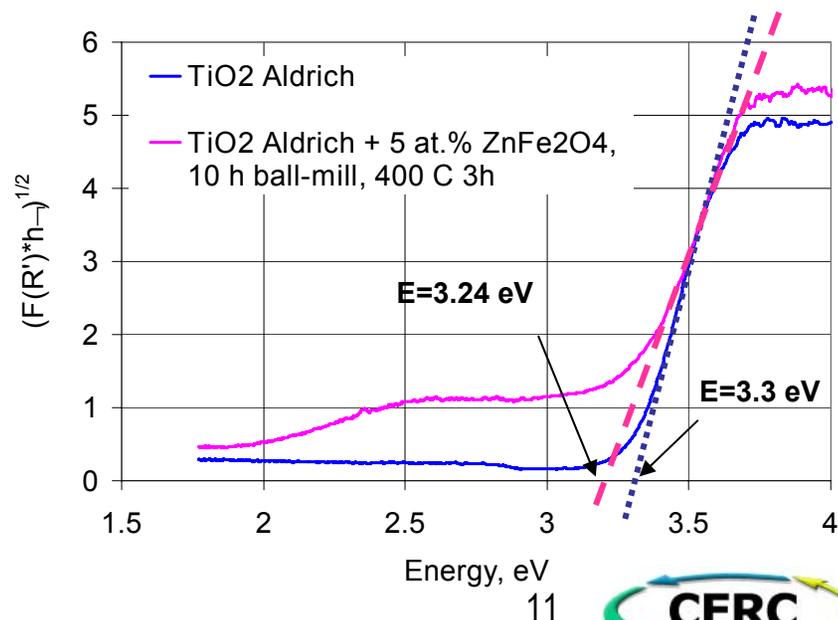$$C(\lambda) = \Sigma a_k \cdot \phi_k(\lambda)$$

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

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# *Accomplishments - TiO_2-ZnFe_2O_4 Nanocomposites*

- **$TiO_2$-$ZnFe_2O_4$ 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.% $ZnFe_2O_4$ and ball-milled for 10 hours is more than twice efficient in comparison with pure $TiO_2$ photocatalyst.**
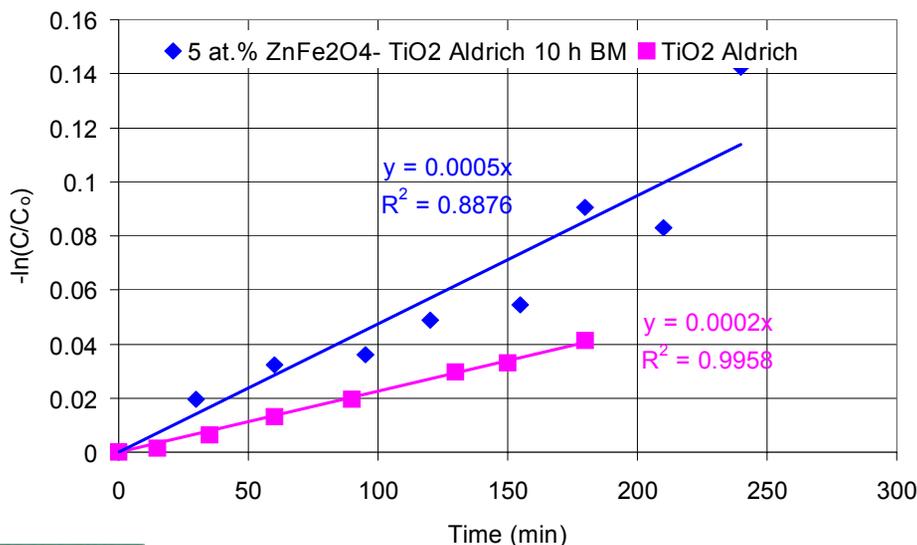
**Red shift in optical absorption because of doping by $ZnFe_2O_4$**



Left chart: x-axis "Time (min)", y-axis "$-\ln(C/C_o)$". Legend: ◆ 5 at.% ZnFe2O4- TiO2 Aldrich 10 h BM, ■ TiO2 Aldrich. Blue line: $y = 0.0005x$, $R^2 = 0.8876$. Magenta line: $y = 0.0002x$, $R^2 = 0.9958$.

Right chart: x-axis "Energy, eV", y-axis "$(F(R')*h\nu)^{1/2}$". Legend: TiO2 Aldrich; TiO2 Aldrich + 5 at.% ZnFe2O4, 10 h ball-mill, 400 C 3h. E=3.24 eV; E=3.3 eV.

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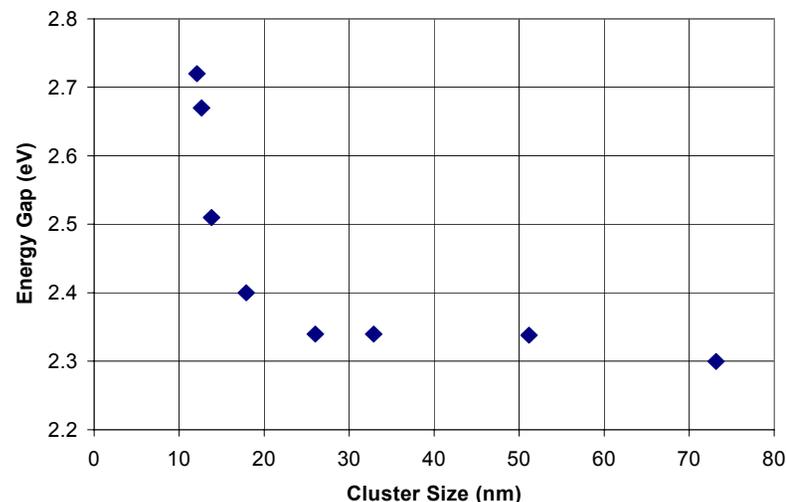# Task 1.1 (production): Photocatalytic
# Accomplishments - $TiO_2$-$ZnFe_2O_4$ Nanocomposites

**A detailed investigation of quantum-sized effects in ball-milled $ZnFe_2O_4$ has been performed in order to understand the photophysical properties of $ZnFe_2O_4/TiO_2$ nanoclusters**

**The dependence of the particle size of $ZnFe_2O_4$ on the milling time**
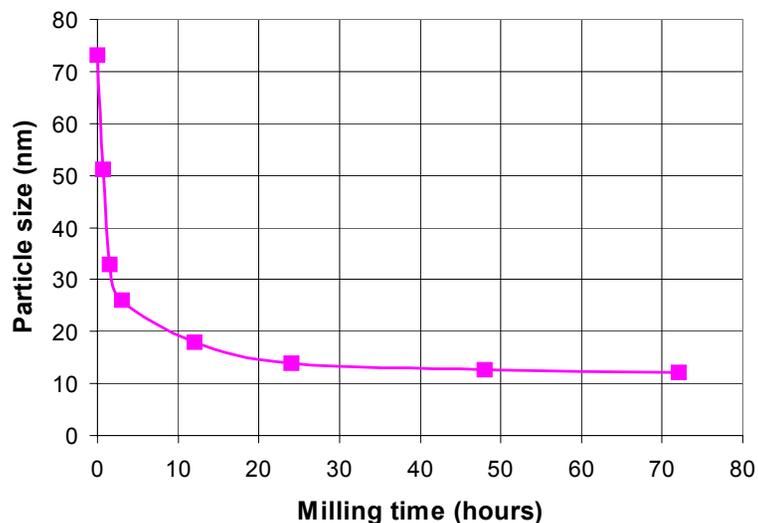
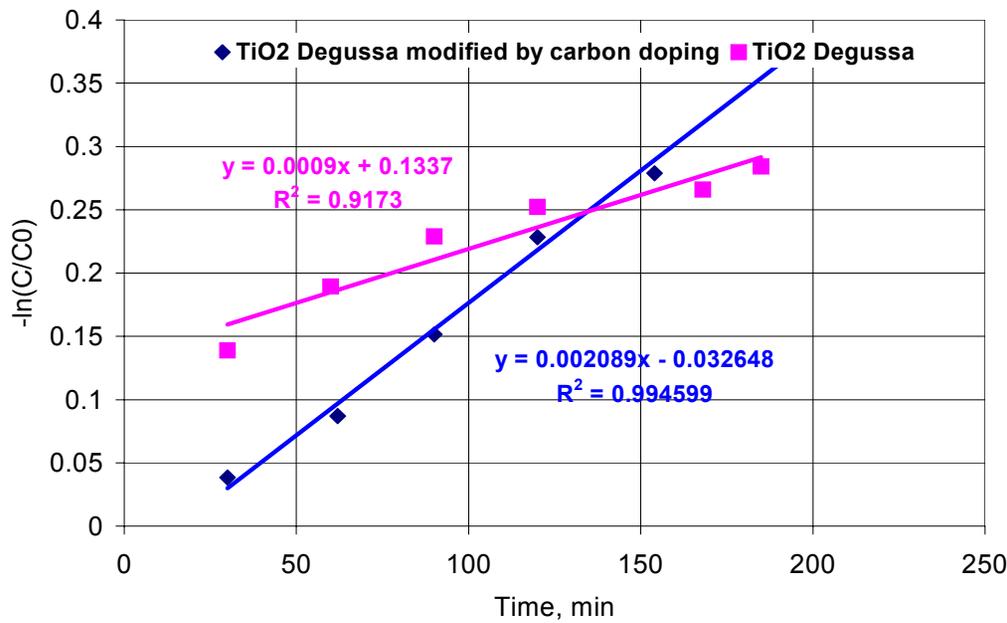**The dependence of the optical bandgap of $ZnFe_2O_4$ on the cluster size**
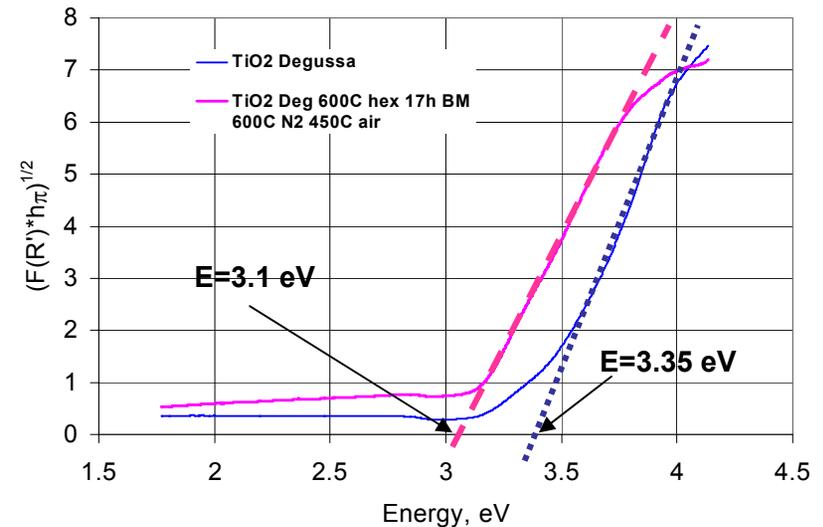


**XRD Analysis was used for particle size estimation**

# *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**

# *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

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## Task 1.1 (production): Photoelectrochemical/Photocatalytic
# Publications

- Sesha 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. Mahawela, 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 $H_2$ production cost by increasing $H_2$ 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

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# *Procedure to Make a Ca-pellet*

Drying and Mixing
with Additives

Chemistry of
Metal
Alkoxide
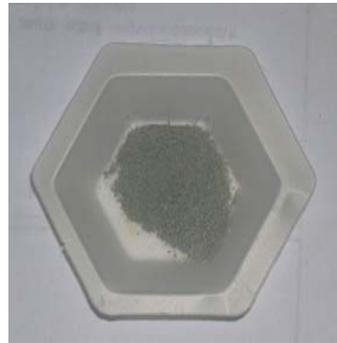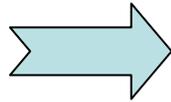
Sieved Powder

Die pressing
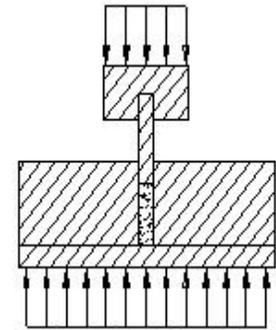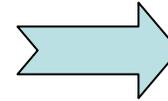
Sintering

Remove
Additives

A Porous Ca-Pellet
supported by
CaTiO3

A Presintered
Pellet

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# *Accomplishments - Experimental Set-up and Thermogravimetric Balance*



Thermogravimetric Balance



Experimental Set-up
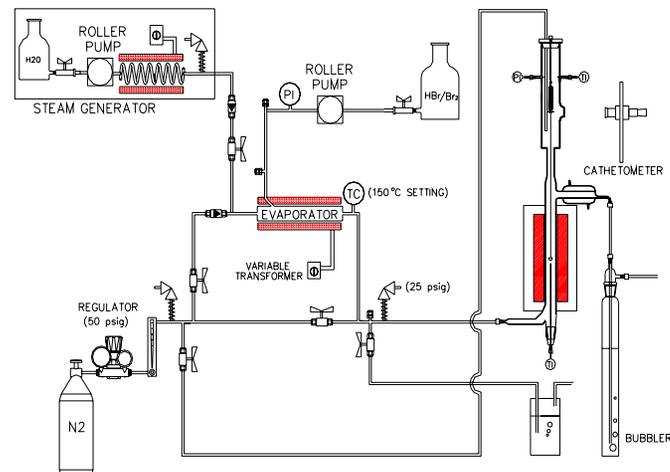
# *Accomplishments - Pore Size Distributions of Ca-pellets by Additives*
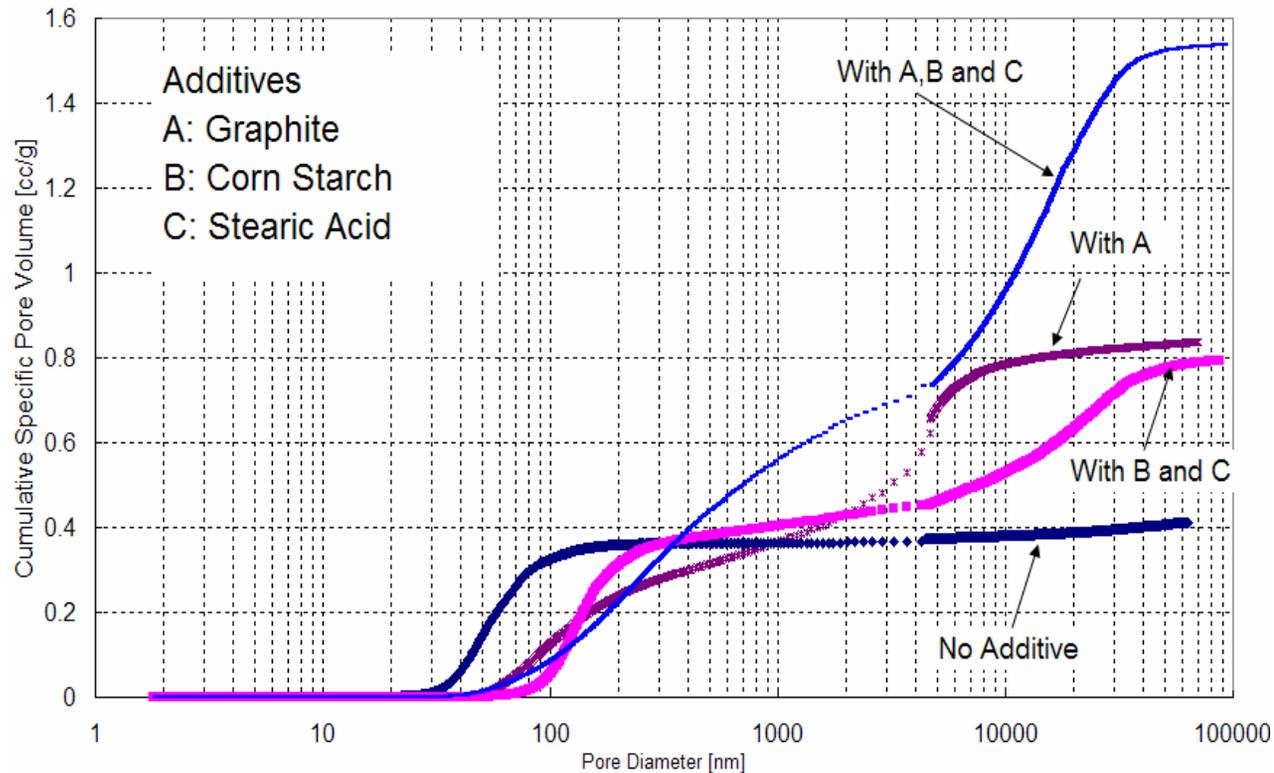


- Macropores contribute to diffusion characteristic inside the pellet.
- The addition of corn starch and stearic acid increases macropores greater than $5\mu m$ with a slight decline in strength while the addition of graphite decrease the strength steeply.

# Accomplishments - Conversion Profiles of Reactions
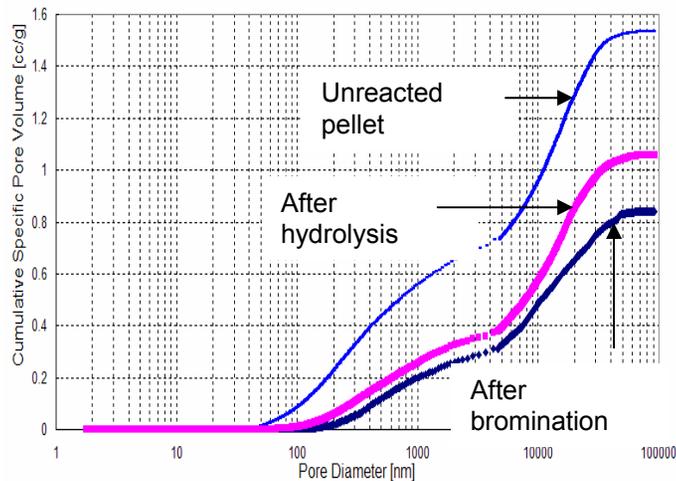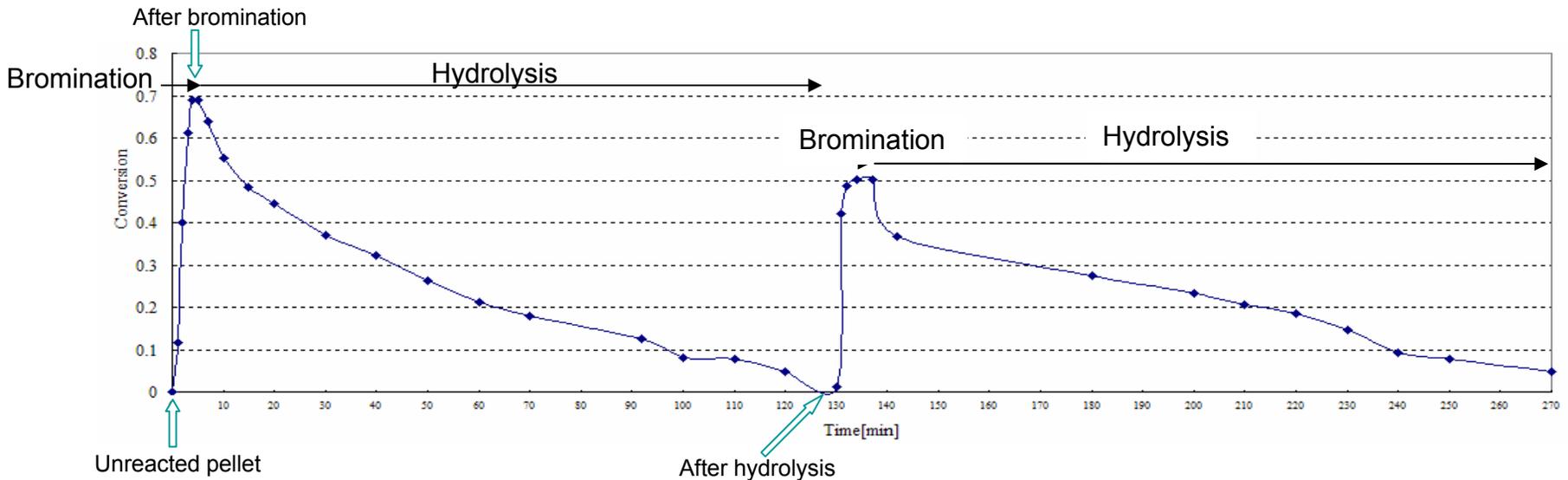


- Initial trend of conversion profiles was in relatively good agreement with the results reported by M. Sakurai et al, 1995[1]

- 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 5μm were regenerated after hydrolysis while pores less than 5μm 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.

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# *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

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## 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 | • Improve $H_2$ yield and process efficiency (heat integration and alternate gas clean-up approaches)<br>• Reduce capital cost by combining process (gasification, reforming and shift) steps and operations<br>•Improve gasification efficiency by developing a model-based controller for a biomass gasifier |
| 2005 | •Conduct theoretical studies of sorbent enhanced biomass gasification<br><br>•Develop experimental set-up<br><br>•Modeling of gasifier<br>    – develop dynamic math model of a biomass gasifier<br>    – study the time dependence of reformate properties on<br>      biomass composition & steam to biomass ratio |
| 2006 | • Experimentally determine effect of sorbent addition on $H_2$ (& CO, $CO_2$) yields<br>•Conduct energy analysis of biomass gasification<br>•Simulate in MATLAB/SIMULINK & design a model-based controller to<br>    – take corrective action on system abnormalities<br>    – ensure uniform H2 output |

# *Approach (Thermodynamics)*

- Task 1: Thermodynamic studies (complete)

  – Determine process conditions for maximum thermodynamic $H_2$ 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 $H_2$, CO & $CO_2$ yields

- Task 3: Energy analysis (10% complete)

  – Study energy consumption of conventional & sorbent enhanced  gasification

  – Identify energy efficient methods for regenerating spent sorbent

# *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
  - reformate 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 $H_2$ yield.

# *Accomplishments (Thermodynamics)*

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

**Gas composition with & without sorbent**
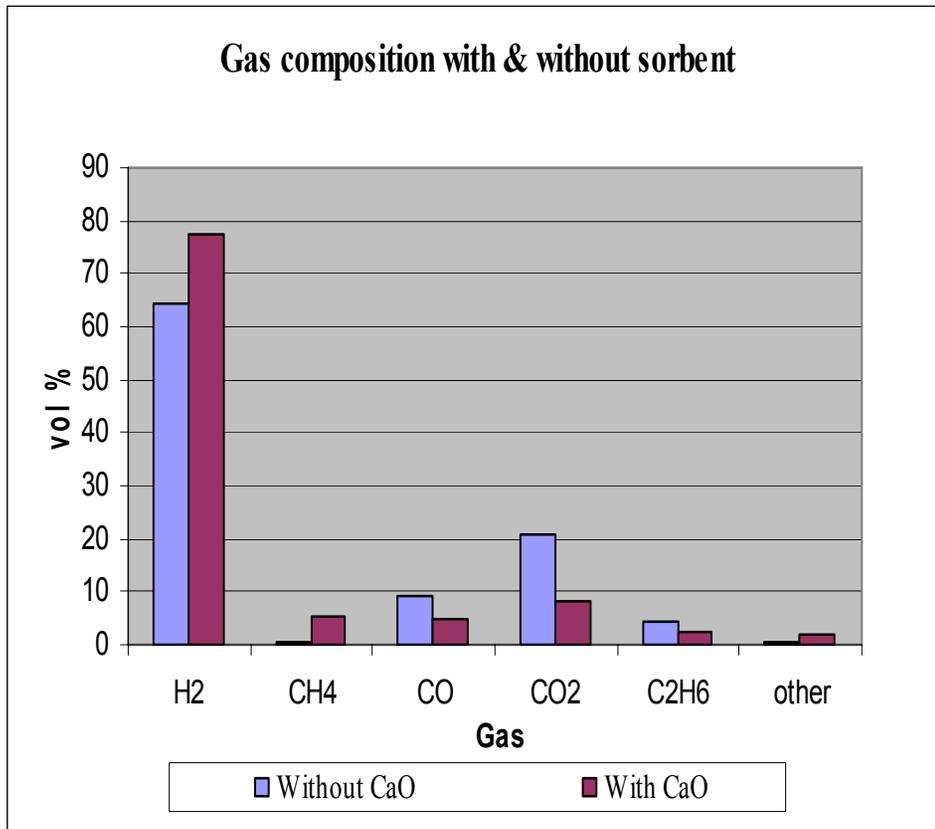


- $H_2$ yield increased by 20%; CO and $CO_2$ in product gas reduced by 44% and 60.6% respectively from base (no sorbent) case
- higher gas yield (about 30%) observed in presence of sorbent
- product gas has less tars and particulates while using sorbent
- higher $H_2$ yield obtained at lower temperature offers potential to reduce gasification temperature (by about 100-150°C)

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# *Future Work*

## FY 2006 (Thermodynamics)

➢ Quarter 3:

- Conduct further experiments to determine gas yield (mainly $H_2$, CO, $CO_2$ 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

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## 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 $CO_2$ 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

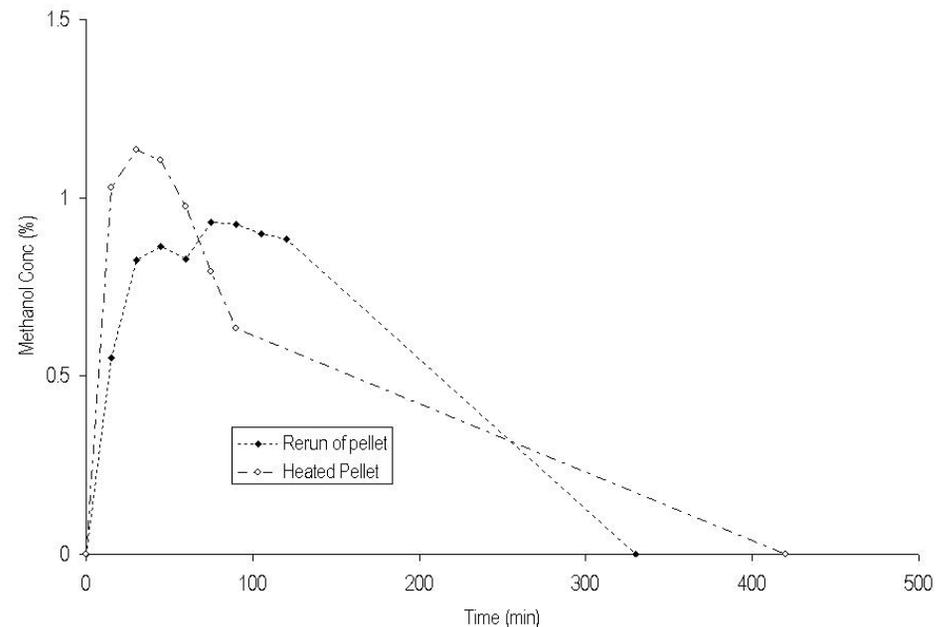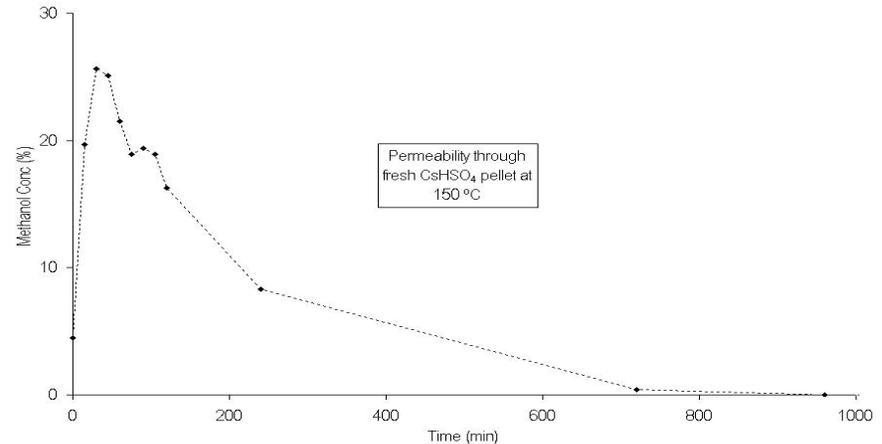• Economic electrolytic hydrogen production through better electrolytes and electrochemical cells

## 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 ºC (to lower the electricity demand) and below 300 ºC (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 ºC
  – 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

# *Permeability Results*

- CsHSO$_4$ pellets impermeable to methanol were manufactured

- Permeability was only exhibited in the first hour of experiment, the 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



Permeability through fresh CsHSO$_4$ pellet at 150 °C



Legend: Rerun of pellet, Heated Pellet

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# *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 ºC to high temperature phase at 22.1 J/g, chemical decomposition in air at 163 ºC to melting at 196 ºC
•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 $2\Theta$ = 10-75º range







31
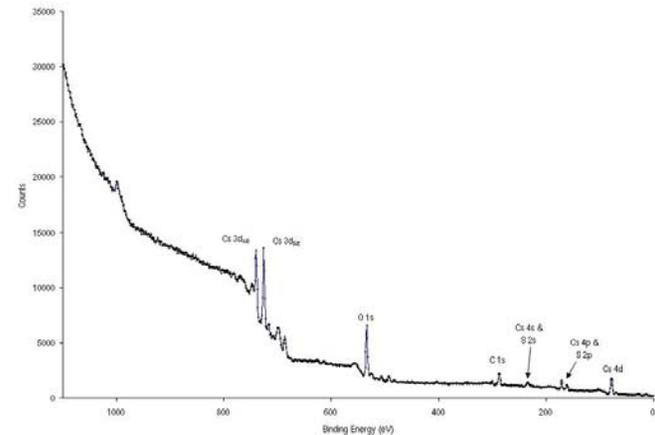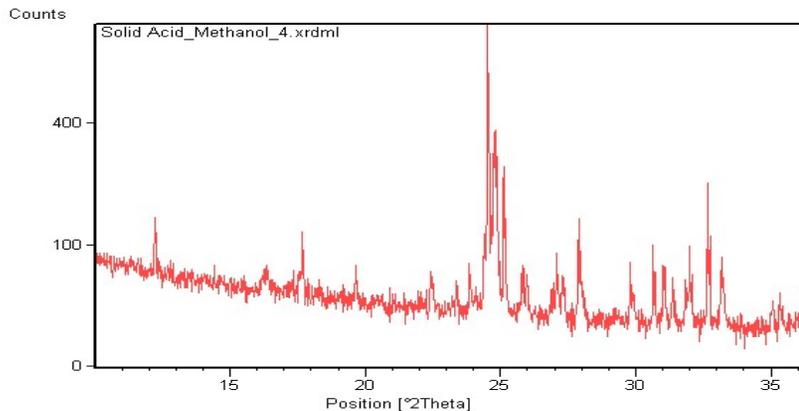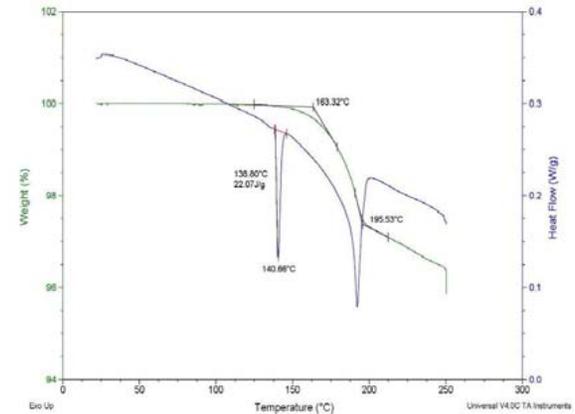
# *Future Work and Summary*

**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.
- $CsHSO_4$ 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 $\leq 120$ $^o$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
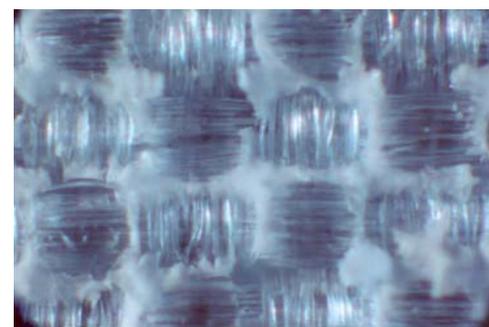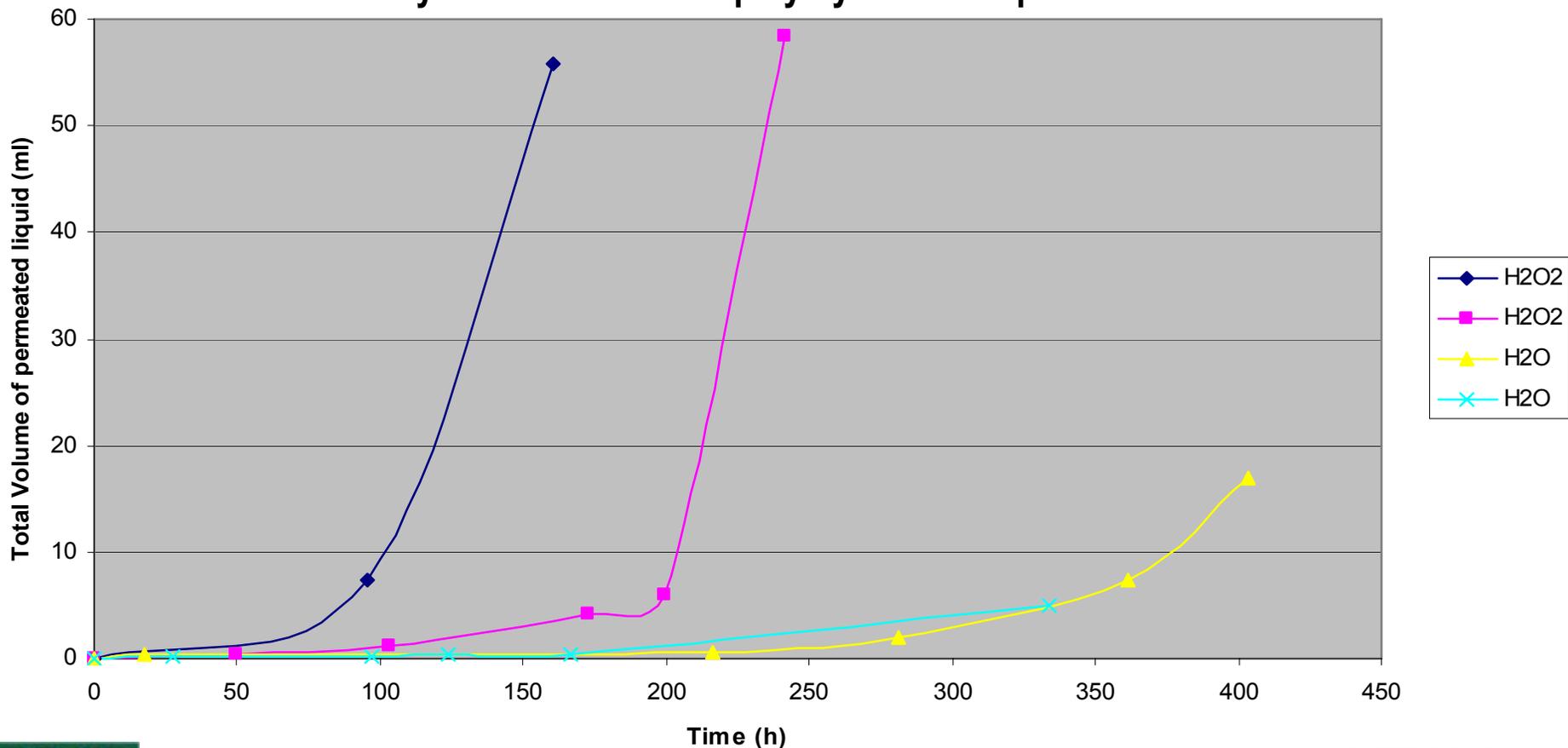
# *Accomplishments*
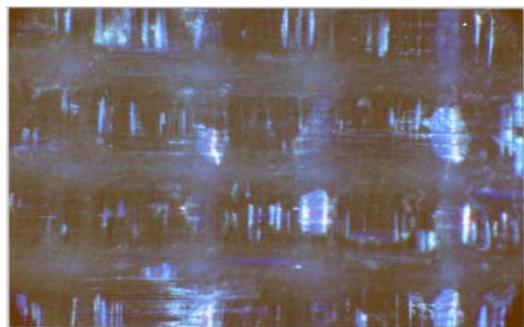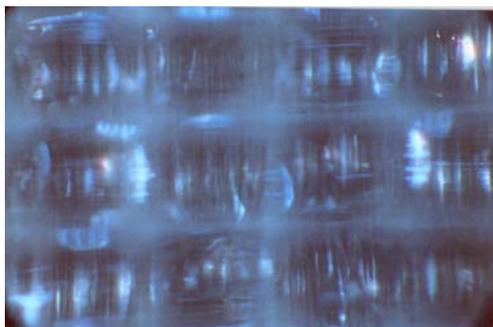


| Day 1 | Day 3 | Day 11 |

## Accelerated testing for peroxide stability on a fuel cell electrolyte

Neosepta® solid polymer electrolyte exposed to 3.5% $H_2O_2$ 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

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# Task 3.1.2 (Fuel Cells): PEM Fuel Cell Research (UF)
## N. Kothurkar, Y. Goswami, E. Stefanakos

# Objectives

| Overall | • Develop cheaper PEM material alternatives to Nafion® <br><br> •High Temperature, Low humidity operation <br><br> •Low fuel crossover <br><br> • Experimental setup for wide temperature range testing |
|---|---|
| 2005 | •Set up experimental test bed <br> •Synthesize polymer (ABPBI) for low humidity, high temperature operation |
| 2006 | • Fabricate MEA <br> •Test Performance of ABPBI at high temperature <br> •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

# *Accomplishments (Test set-up)*



Mass Flow Cont.

Humidifier

**Control Panel**
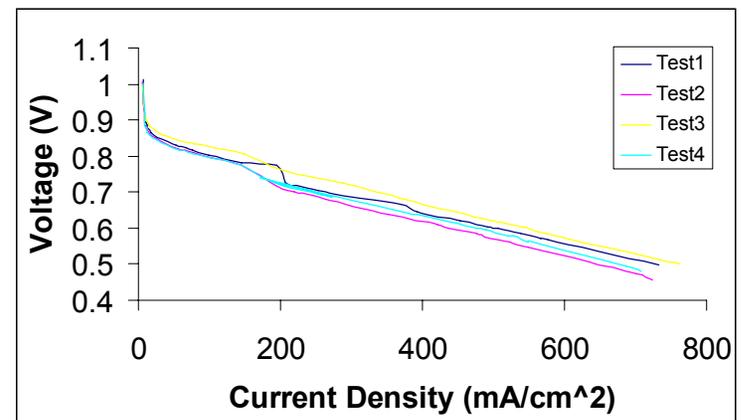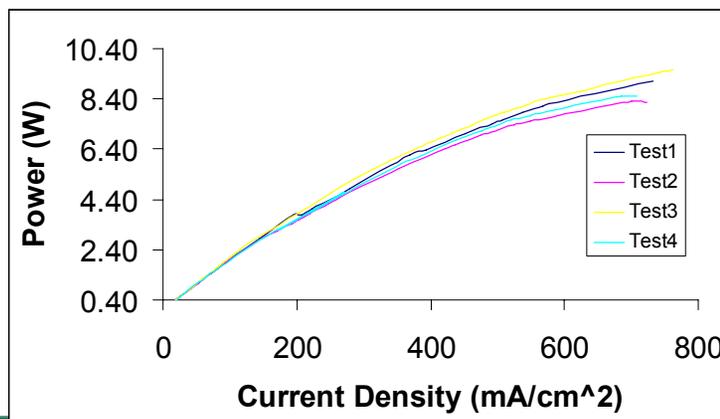


Back pressure valves

Single cell

Resistance Load
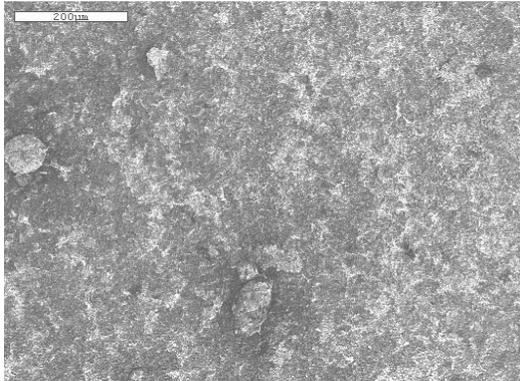
RH Probe

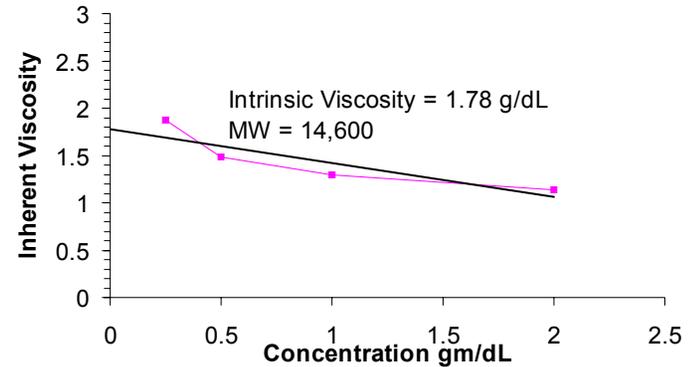Current transducer

**Test Bed**





**Repeatability Testing, Nafion® MEA** 40

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



**SEM BSE**



Intrinsic Viscosity = 1.78 g/dL
MW = 14,600

**Intrinsic Viscosity- MW**
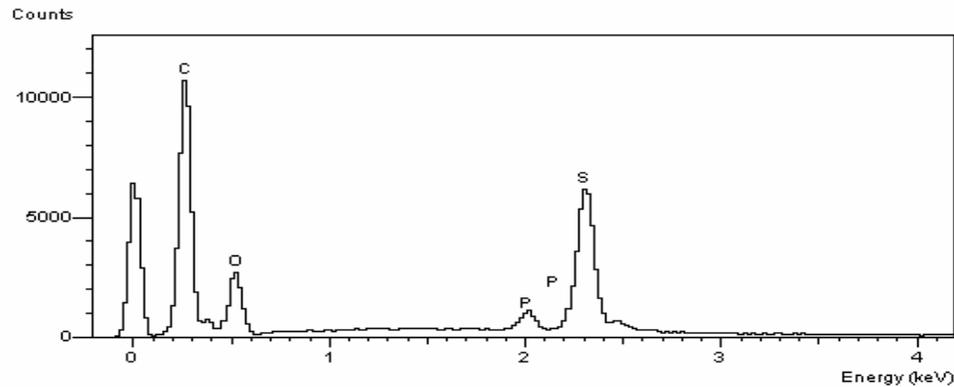


**EDX-Elemental Analysis**

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# *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/$TiO_2$ 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

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# *Approach*

- Custom anodic catalysts consisting of platinum, ruthenium, and gold nanoparticles have been developed.

- Stabilized gold nanoparticles supported on $TiO_2$ selectively oxidize CO below $100^oC$

- $\beta$-zeolite nanoparticles have been incorporated with functionalized cast Nafion$^{TM}$ films; increasing operating temperatures while maintaining sufficient water retention.

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# *Gold Nanoparticles Preparation\**

- ## Two Phase Transfer Method
  - Results in gold particles <10 nm
  - TOABr = Stabilizing Agent

    tetra-octyl-ammonium-bromide

Toluene

TOABr

NaBH$_4$

Water

HAuCl$_4$

Au

Au

Au

Au
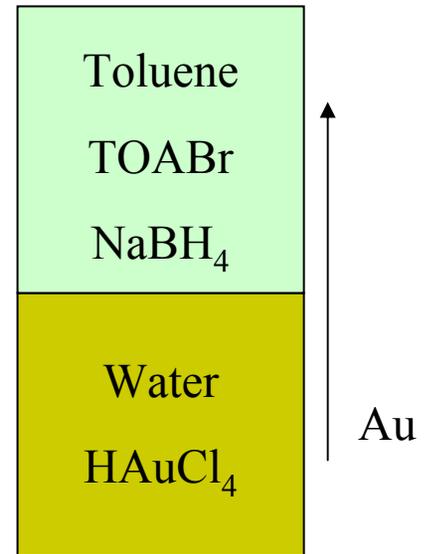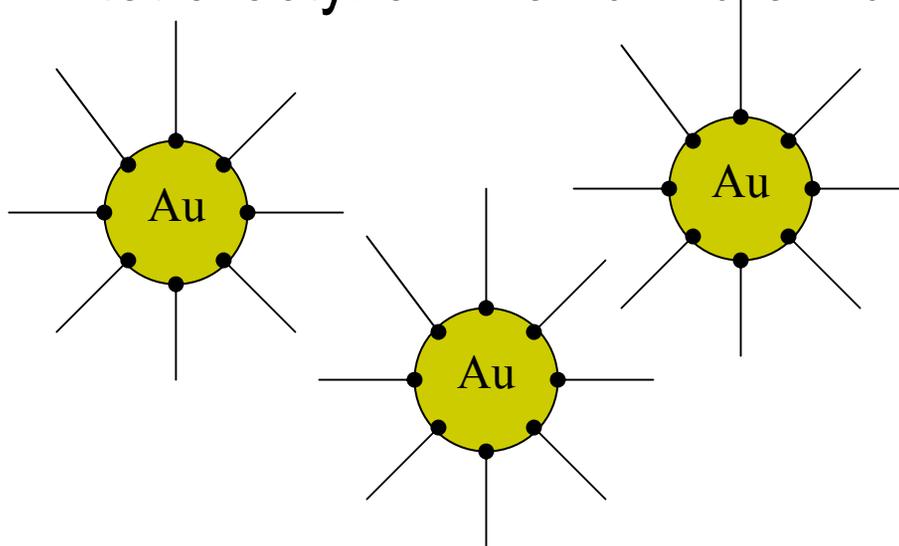
# *Catalyst Results*

- FTIR analysis comparing Pt/Ru/TiO$_2$ with Pt/Ru/Au/TiO$_2$ catalysts as shown in Fig. 1 shows improved CO oxidation of 3% at operation temps of 80-120$^o$C.

- SEM images imply gold nanoparticles sizes less than 100 nm (Figure 2).

- XRD spectrum →TiO$_2$ to be anatase; a partial phase change to rutile occurs when exposed to temps. approaching 500-550$^o$C which proves to be beneficial (Figure 3)

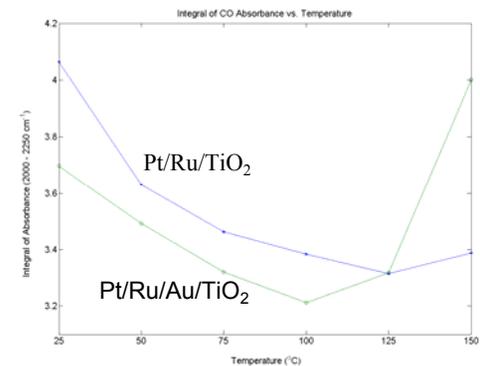- XPS analysis is underway to determine the most active oxidation state of the gold catalyst species.
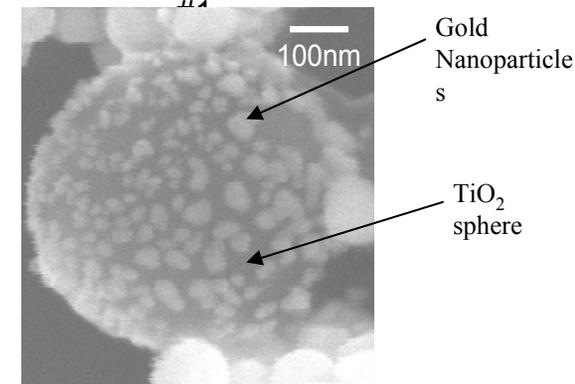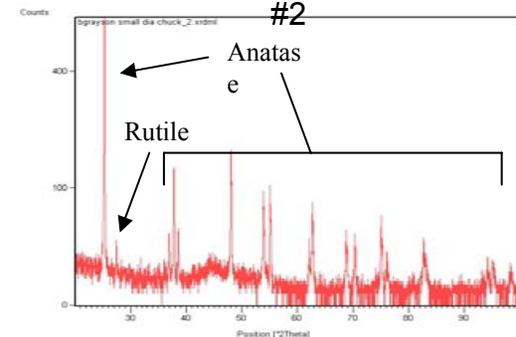


Figure #1



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
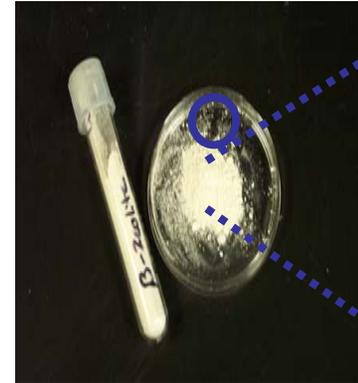
Ball milled β-zeolite     β-zeolite crystalline
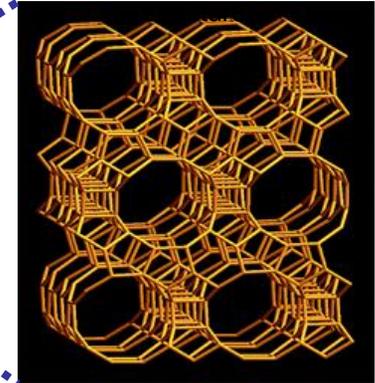
Fully cast nanocomposite film     Fully cast nanocomposite film

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# *Future Work and Summary*

## Future Work

- Optimize gold catalyst preparation techniques and increasing selectivity towards the production of $CO_2$ over $H_2O$ formation
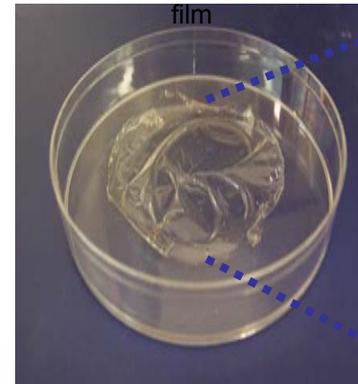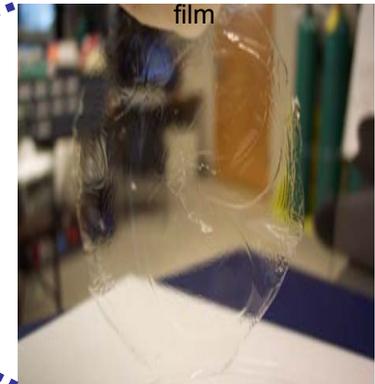- Determine humidity effects on catalyst operation
- Further characterization of $\beta$-zeolites using XRD, TGA, and proton conductivity measurements
- Fully develop nanocomposite membranes capable of incorporation into a $25cm^2$ membrane electrode assembly (MEA)
- Incorporate new MEA into a hydrogen 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.

- $\beta$-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 $H_2$ 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 Nm³ | 3.0 e6 - 6.0 e8 Nm³ | 3.0 e6 - 6.0 e8 Nm³ |
|  |  |  |  |
| **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

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# *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 H$_2$ 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 H$_2$ 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 H$_2$ Compressor
## Accomplishments

In the 6 months since this task began we have:

- Prepared and characterized (XRD and DSC) sample of ZrMn$_2$ alloy by ball milling and sintering the metal powders.

- Acquired ZrMn$_2$ 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-FG36-04GO14224)**
- 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