

VI.G.2 Fuel Cell and Hydrogen Research at the University of South Florida*

Elias K. Stefanakos (Primary Contact) and Yogi Goswami

University of South Florida

4202 E Fowler Ave, ENB118

Tampa, FL 33620

Phone: (813) 974-4413; Fax: (813) 974-5250; E-mail: stefanak@eng.usf.edu

DOE Technology Development Manager: Grace Ordaz

Phone: (202) 586-8350; Fax: (202) 586-9811; E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Reg Tyler

Phone: (303) 275-4929; Fax: (303) 275-4753; E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: Thomas Benjamin

Phone: (630) 252-1632; Fax: (630) 252-4176; E-mail: Benjamin@cmt.anl.gov

Contract Number: DE-FG36-04GO14224

Subcontractors:

University of Florida, Gainesville, FL,

University of Central Florida, Cocoa, FL

Start Date: October 2004

Projected End Date: June 2007

**Congressionally directed project*

Introduction

The University of South Florida, the University of Florida, and the University of Central Florida are conducting five projects related to hydrogen production, three projects related to hydrogen storage, and three projects related to polymer electrolyte membrane and electrode material improvements. Brief descriptions of progress of each of these projects is presented in the following pages.

1.1 Thermochemical Hydrogen Production

*D. Y. Goswami, M.S. Lee, B. Hettinger,
S. Vijayaraghavan
University of Florida
Phone: (352) 392-0812, Fax: (352) 392-1071
E-mail: goswami@ufl.edu*

Objectives

- Lower hydrogen production cost by increasing hydrogen yield with an improved pellet formulation
- Reduce operating cost by lowering the reactor operating temperatures.

Technical Barriers – Hydrogen Production

- AU. High Temperature Thermochemical Technology

Technical Targets

- Cost at Plant Gate: \$/gge H₂
- Energy Efficiency: 40%

Approach

- Increase H₂ yield through new pellet formulation
- Reduce the reactor operating temperature

Accomplishments

- Precursor for CaO reactant pellets synthesized using sol-gel techniques
- Pellet molding apparatus and procedure developed
- Pellet heat treatment designed
- Initial pellet characterization completed
- Achieved a much higher pore volume than the University of Tokyo pellet

- Flexible and robust (800°C, HBr, Br₂, steam) feed and reactor system set-up for 4 reactions
- Thermogravimetric balance designed and being built

Results

UT-3 thermochemical process has four solid reactants: CaO, CaBr, Fe₃O₄ and FeBr₂. CaO pellets are being formulated, synthesized, characterized and tailored in the current phase of the project. CaO is dispersed on CaTiO₃ substrate and the precursor is then molded into a pellet. Sol-gel chemistry is used to co-precipitate the CaTiO₃ and CaO to form an integral chemical formulation.

Summary

- The CaO pellet formulation process has been completed. Current results indicate better porosity than that reported in the literature. Additional strength testing is required before a firm conclusion can be drawn regarding these pellets.
- The reactor system has been built paying special attention to safety and material compatibility. Testing needs to be undertaken before any conclusions are drawn.

Future Directions

- Conduct CaO pellet kinetic study and thermogravimetric analysis
- Increase O₂ yield by modifying pellet formulation
- Formulate new Fe₃O₄ pellet
- Conduct Fe₃O₄/FeBr₂ pellet kinetic study and thermogravimetric analysis
- Increase H₂ yield by modifying pellet formulation
- Process simulation

1.2 Biomass Gasification Hydrogen Production

*D. Y. Goswami, H. Weaver, M. Mahishi,
S. Vijayaraghavan, M. Sadrameli*
University of Florida
Phone: (352) 392-0812, Fax: (352) 392-1071
E-mail: goswami@ufl.edu

Objectives

- To find new techniques (or improve existing ones) that can increase hydrogen yield and/or improve the energy efficiency of conventional biomass gasification
- To find suitable methods of removing/reforming tars from product gas
- To improve the economics of the process (mainly by reducing capital cost)

Technical Barriers – Hydrogen Production

- V. Feedstock Cost and Availability
- W. Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

Technical Targets

- Energy Efficiency: 50%
- Total Hydrogen Cost: \$1.75/gge H₂
- Capital Cost Contribution: \$0.55/gge H₂

Approach

- Process simulation and laboratory scale tests of biomass gasification
- Synthesis and characterization of nano-particle oxide supported catalysts
- Testing of catalysts in model biomass reactors

Accomplishments

- An 18-20% increase in hydrogen yield is predicted. A 100 – 150°C drop in gasification temperature is anticipated.
- Nano-particle supported catalyst synthesized and characterized
- Catalyst characterization reactor designed and being built

Results

Recently it has been shown in steam methane reforming that adding small amounts of CO₂ sorbents (such as CaO) to the steam reforming catalyst helps shift the equilibrium in favor of hydrogen. This is due to the continuous removal of CO₂ from the product gas stream, thereby preventing the reverse water-gas shift reaction. Apart from higher hydrogen yields, the sorbent addition also offers other advantages like combining reforming, shift and separation reactions into a single step potentially reducing the capital cost of the plant. The other advantages include easy CO₂ removal and avoiding separate water-gas shift catalysts. The sorbent is later regenerated in a different reactor. Since biomass steam gasification is similar in many ways to steam methane reforming the above idea can be applied to biomass steam gasification.

Summary

- Process simulation/thermodynamic studies predicted an 18-20% increase in hydrogen yield and 100 – 150°C drop in gasification temperature
- Nano-particle supported catalysts were synthesized and characterized
- Catalyst characterization reactors have been designed and are currently being built

Future Directions

- Conduct energy analysis of sorbent enhanced gasification
- Validate the sorbent enhancement concept
- Catalytic activity measurements using model reactor
- Study sorbent regeneration, in particular reduction of regeneration temperature and alternate sorbents
- Investigate different methods of catalyst preparation to obtain a uniform coating of Ni on the Al₂O₃ support
- Test various additives to improve catalyst activity and stability

1.3 Photoelectrochemical Hydrogen Production

D. L. Morel, C. S. Ferekides, S. Bates
University of South Florida
Phone: (813) 974-2508; Fax: (813) 974-5250
E-mail: morel@eng.usf.edu

Objectives

- Develop a photovoltaic (PV) device that can serve as the top cell in a tandem structure.
- Achieve voltage sufficient to generate H from water with tandem PV cells.

Technical Barriers – Hydrogen Production

- S. Cost
- AP. Materials Efficiency

Technical Targets

- Develop advanced renewable photoelectrochemical hydrogen generation technologies.
- By 2015, verify the feasibility of these technologies to be competitive.

Approach

- Develop SnO₂/Si devices that generate 600 mV.
- Develop high doping efficiency in large band gap materials such as ZnSe and ZnTe to serve as p-contacts to CdSe.
- Demonstrate open circuit voltage of 1 volt with ZnSe or ZnTe/CdSe/SnO₂ devices.
- Fabricate ZnSe or ZnTe/CdSe/SnO₂/Si devices.
- Demonstrate open circuit voltage of 1.5 volts in ZnSe or ZnTe/CdSe/SnO₂/Si tandem devices.
- Develop effective catalytic contacts to interface with the electrolyte in a photocatalytic cell.
- Demonstrate hydrogen generation in a photocatalytic cell with ZnSe or ZnTe/CdSe/SnO₂/Si tandem devices.
- Demonstrate sunlight to hydrogen efficiency of 14% for the photocatalytic cell.

Accomplishments

- A SnO₂/n-Si device process has been developed.
- Up to 500 + mV open circuit voltage has been demonstrated with SnO₂/n-Si.
- Operable CdSe devices have been deposited on SnO₂/Si substrates.
- The first operable tandem devices have been fabricated.

Summary

Achieved 500 mV open circuit voltage in a Si/TO device using SnO that is commensurate with CdSe requirements. Since CdSe devices are sensitive to SnO properties this is an important result in that it demonstrates overlap of the SnO properties required by the two absorbers.

Demonstrated representative CdSe devices deposited on SnO/Si substrates. It is not a given that using the same SnO process for Si that is used for glass will produce an identical SnO growth surface for CdSe. This result demonstrates that the SnO growth surface is at least similar and that with further work it might become identical.

Fabricated the first operable CdSe/Si tandem devices. Although the performance here is modest, the results demonstrate that the 470°C CdSe deposition temperature does not kill the underlying Si device. However, there are losses, but with further work we expect to eliminate them.

Future Directions

- Develop thermal budget compatibilities for the tandem structure.
- Develop advanced doping capabilities for ZnSe.
- Demonstrate a tandem open circuit voltage of 1 volt.

1.4 Photocatalytic Hydrogen Production

C.S. Ferekides, D.L. Morel, E.K. Stefanakos, S.S. Srinivasan, J. Wade, H. Dahbie
 University of South Florida
 Phone: (813) 974-1818; Fax: (813) 974-5250
 E-mail: ferekide@eng.usf.edu

Objectives

Powders and thin films of TiO₂ (and nanocomposites) are being prepared by:

- Using chemical preparation procedures involving sol-gel and co-precipitation/hydrolysis process
- Reverse micelles process
- Radio frequency (RF) sputtering

Technical Barriers – Hydrogen Production

- S. Cost
- AP. Materials Efficiency

Technical Targets

- Improve efficiency of water splitting from 70% to 90% while addressing cost

Approach

- TiO₂-ZnFe₂O₄ Nanocomposites
- TiO₂-CdS Nanocomposites
- TiO₂ by RF Sputtering

Accomplishments

TiO₂-ZnFe₂O₄ nanocomposite:

- For the first time, a photocatalytic reactor was created to analyze the photocatalysts exposed to Ultraviolet (UV), UV-Visible, and visible light irradiation.
- Organic degradation was used to simulate H₂ production by photocatalyst's redox reactions.
- Experiments successfully concluded the photo-activity of TiO₂-ZnFe₂O₄ catalysts at irradiation wavelengths longer than 400 nm.
- Optimized the factors influencing the ZnFe₂O₄ structure such as effects of Ph, calcinations temperature, precursor concentration.

- Optimized the alloying concentrations of TiO₂-(X)ZnFe₂O₄ to achieve the anatase structure.

TiO₂-CdS nanocomposite:

- TiO₂-anatase coupled CdS nanocomposite structure was prepared by reverse micelle process at room temperature.
- The experimental parameters such as water to surfactant ratio, water to alkoxide ratio, precursor concentrations, calcination temperature have been optimized to obtain TiO₂-CdS nanocomposite.
- The structure and microstructure characteristics and UV-Visible spectral response were determined by X-ray diffraction, scanning electron microscope (SEM) and UV spectrometer.
- The photocatalytic activity of the TiO₂-CdS nanocomposite was performed by degradation of phenol concentration under visible light irradiation.

RF sputtered TiO₂ thin films

- Process conditions modified to improve film morphology.
- Porous films have been prepared with RF sputtering, a process suitable for large area cost-effective coatings.
- As-deposited at room temperature films were found to be amorphous.
- Annealing in air at high temperatures yields polycrystalline TiO₂.
- Annealed films contain peaks corresponding to both the Anatase (desirable) and Rutile phases.
- Deposition at temperatures as low as 250°C yield polycrystalline films; Anatase phase seems to dominate, although both phases are present.

Summary and Conclusions

- Films with high Anatase content have been prepared at deposition temperatures of 250-300°C.
- RF-sputtering can be an effective process for porous TiO₂ films.
- The addition of N₂ during the sputtering process has not been found to enhance the optical transmission of TiO₂ beyond the UV range of the solar spectrum (i.e., at wavelengths above 450 nm).

1.5 Solid State Ionic Conductor Development

E.K. Stefanakos, B. Krakow, L. Ecklund-Mitchell, D. Payne, S. Srinivasan, M. Smith
 University of South Florida
 Phone: (813) 974-4784; Fax: (813) 974-5250
 Email: krakow@eng.usf.edu

Objectives

Economic hydrogen production by steam electrolysis via:

- Better electrolytes and electrochemical cells
- Scavenged electrodes

Technical Barriers – Hydrogen Production

- G. Capital Costs
- I. Grid Electricity Emissions
- K. Electricity Costs

Technical Targets

This project combines the use of steam electrolysis with biofuel scavenging to seek improvements over the following DOE 2015 targets for hydrogen production by electrolysis or biofuels alone:

- Cost: \$2.75-2.50/gge H₂
- Efficiency: 76-70%

Approach

- An electrolyzer with a scavenged anode is effectively a gas shift reactor in which electrolysis replaces shift, separation and purification with one step.
- The electricity required for water electrolysis can theoretically be cut by an order of magnitude (with proportional reductions of emissions and costs) by scavenging the anode with a reducing agent. This agent may be landfill gas (or other biofuel), synthesis gas or industrial waste products.
- An optimum choice of temperature can provide a good balance of efficiency and low cost. Such a temperature would 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).

Accomplishments

- Electrolyte Preparation: CsHSO₄ has been chosen to be the first solid state proton conductor to be studied. This compound has been prepared by reacting sulfuric acid with Cs₂SO₄ or Cs₂CO₃ and selectively precipitating CsHSO₄ by temperature control. One-half inch and two-inch diameter pellets of this material were made for study by pressing the powder at 490 MPa.
- Electrolytic Cell Fabrication: An electrolytic cell has been fabricated that is capable of operating in the 150-300°C range with the two-inch diameter electrolyte pellets.
- Controls: Flow and temperature control equipment has been assembled for the experiments.
- Testing: Differential scanning calorimetry of the powder showed that the cesium hydrogen sulphate we have made has a sharp phase change at 144.98°C. Conductivity measurements of the cesium hydrogen sulfate pellet indicated that the phase change is a transition to the superionic state. The conductivity increased by almost four orders of magnitude, within a few degrees.

Future Directions

- Performance and stability studies of electrolytes and cells will continue.
- New electrolyte materials will be sought and investigated for use with specific scavengers. Electrolyte, feedstock and scavenger will have to be matched for compatibility.
- We will apply metallurgical and semiconductor processing techniques to inorganic solid electrolyte materials to try to prepare strong and sturdy thin electrolytes.
- 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 test permeability of electrolytes to feed stock fuels and scavengers.

2.1 Transition Metal Complex Hydrides

Sesha S. Srinivasan¹, Mathew T. Smith¹,
Lisa McElwee-White², Yogi Goswami²,
Lee Stefanakos¹

¹University of South Florida, ²University of Florida
Phone: (813) 974-4413; Fax: (813) 974-5250
E-mail: stefanak@eng.usf.edu

Objectives

- Formulation and development of nanoscale transition metal hydrides with improved properties
- Synergistic approach in enhancement of sorption kinetics and H-capacity
- Developing new complex hydride materials

Technical Barriers – Hydrogen Storage

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- G. System Life-Cycle Assessments
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

DOE 2010 technical targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Approach

- Producing nano-structured transition metal hydride (n-Mg₂FeH₆) by (a) mechano-chemical process (reactive H₂ gas milling) and (b) chemical synthesis.
- Structural and microstructural characterizations of the as-synthesized and hydrogenated n-Mg₂FeH₆.
- Elemental analysis for the chemical stoichiometry.
- Thermal analysis of the n-Mg₂FeH₆.

- Hydrogenation and dehydrogenation kinetics and cycle life evaluations.
- Catalytic doping and lattice modification of host lattice.

Accomplishments

- Synthesis of nanostructured Mg₂FeH₆ by inexpensive mechano-chemical processing procedure under reactive gas (H₂) environment by optimizing the experimental conditions.
- Detailed characterization of the as-synthesized nano mixture of (2Mg+Fe) by powder X-ray diffraction, electron microscopy and thermal analysis.
- Low pressure of hydrogen absorption (20 bars) and desorption (0.5 bar) of the n-Mg₂FeH₆ and cycle life measurements.
- Hydrogen storage capacity of 5.5 wt.% at 300°C attained for the n-Mg₂FeH₆ using our synthesis approach.
- Structure-property correlations of the n-Mg₂FeH₆ before and after hydrogen cycling
- Improved dehydrogenation kinetics of n-Mg₂FeH₆ by catalytic doping with 2 mol% TiF₃.
- Reduction of operating temperature by 100°C for the n-Mg₂FeH₆ by suitable modification of the host lattice by Li⁺ addition during mechanical milling.

Future Directions

- Evaluate the sorption properties of catalyzed and Li substituted Mg₂FeH₆ at low temperatures.
- Continue the cycling experiments up to 1,000 cycles to meet the DOE 2010 targets.
- Continue exploring new complex chemical hydrides for hydrogen storage that meet the 2010 DOE technical targets.
- Address the associated problems in designing new complex systems for effective hydrogen storage capacity.
- Develop new complex hydrides to achieve reversible capacity above 6 wt% at T <100°C.
- Identify, synthesize, and evaluate new complex hydrides, such as Zn(BH₄)₂ and related complexes as potential systems for fuel cell applications.
- Develop new hydrogen storage materials and deliverables for the evaluation of reversible hydrogen characteristics.

2.2 Nanostructured Materials

Ashok Kumar, Elias Stefanakos

University of South Florida

Phone: (813) 974-2353; Fax: (813) 974-3610

E-mail: akumar@eng.usf.edu

Objectives

- Synthesize conducting polymer Polyaniline (PANI) as matrix material for nanocomposite material.
- Dope nanocomposite material with carbon nanotubes and fullerenes to increase hydrogen uptake.
- Optimize nanocomposite material components for hydrogen sorption.
- Optimize hydrogen sorption conditions
- Demonstrate hydrogen sorption capacities to meet DOE targets

Technical Barriers - Hydrogen Storage

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- C. Efficiency
- D. Durability
- E. Refueling Time
- G. System Life-Cycle Assessments
- M. Hydrogen Capacity and Reversibility
- Q. Thermal Management

Technical Targets

DOE 2010 targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L
- Operating temperature: -30°C to 50°C
- System fill time: 3 min

Approach

- Synthesize PANI nanocomposite and perform full material characterization
- Perform hydrogen sorption measurements on PANI and optimize temperature and pressure during sorption.
- Dope PANI with carbon nanotubes (CNTs) and metal oxides and perform full material characterization,
- Perform hydrogen sorption measurements on nanocomposite material and optimize temperature and pressure for maximum hydrogen sorption.
- Pass a current through the nanocomposite material during hydrogen sorption and optimize hydrogen sorption capabilities and allow for controlled uptake and release.

Accomplishments

- Discovered that carbon doped nanocomposite material can adsorb ca. 3 wt% hydrogen.
- Discovered that alignment of CNTs in nanocomposite increases hydrogen sorption capabilities by ca. 0.2 wt%.
- Found visual effect of hydrogen uptake in nanocomposite material in form of bubble when viewed on SEM.
- Determined that material meets operating temperature range at least above 0°C.

Future Directions

- Optimize environmental conditions during synthesis of nanocomposite material.
- Evaluate effect of temperature and pressure on hydrogen sorption capabilities.
- Synthesize nanocomposite material with different CNT and metal oxide compositions.
- Conduct experiments to evaluate effect of passing a current during the nanocomposite material on hydrogen sorption capabilities.

2.3 Nanostructured Film

*J. Bumgarner, S. Onishi, M. Calves,
L. Langebrake*

University of South Florida

Phone: (727) 553-3980; Fax: (727) 549-6654

E-mail: jbumgarner@marine.usf.edu

Objectives

- Design, build and operate a physical vapor deposition system to produce metal hydride nanocrystalline foils to be assembled in situ under vacuum for hydrogen storage.
- Metal hydride nanofoil coils are expected to achieve 2 kWhr/kg, the 2010 target.
- Meet storage cost of less than \$1.50/kW hr net or \$133/kg H₂ and all safety and toxicity standards.
- Capability of at least 1,000 cycles total lifetime at close to ambient operating temperatures.

Technical Barriers – Hydrogen Storage

- A. Cost
- B. Weight and Volume
- D. Durability

Technical Targets

DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Energy density: 1.5 kWh/L
- Refueling rate: 1.5 kg H₂/min
- Delivery temperature: 85°C
- Cycle life: 1,000 cycles

Approach

- Develop a hydrogen storage system using metal hydrides that exceeds the current available technology in storage performance, cost, space-factor, and safety and reliability for stationary and mobile applications.
- Design, construct and operate a physical vapor deposition system to produce freestanding nanocrystalline alloys for the cyclic storage of

hydrogen using baseline metal alloys for process development and characterization. Innovate deposition recipes with original metal alloy systems and multilayer foils for optimizing hydrogen storage at minimum cost without mechanical degradation.

- Reduce cost by scaling to larger systems, intrinsic high utilization percentage of source material, and depreciate equipment costs over large production runs. Reduce weight through the use of a light weight canister and tightly packed material with minimal voids, and through a separation technique for releasing the nanofilm from the deposition substrate, (rendering the bulk of the system weight in the storage medium).
- Improved efficiency and absorption kinetics given from very high surface area per gram of metal and small grain size in the nanocrystalline film resulting from the novel deposition process.

Accomplishments

- Completion of the design and drawing documentation for the physical vapor deposition system and the nanofoil handling system.
- The deposition and separation processes using existing equipment showed that thin foil of Pt metal can be deposited in a similar system
- The deposition of innovative films with the capability of sealing those films in situ in a canister, eliminating any influence of ambient atmosphere to the performance of the material. The completion of the tool emerged with the capability of placing it under load lock and vacuum.

Future Directions

- Initial operation of the deposition system and the demonstration of a sputtered metal film.
- Demonstration of the system characteristics using standard metal hydride materials such as Al or Mg. Free standing nanofoils will be produced and characterized.

3.1 PEM Material Improvements

J. Wolan, Elias Stefanakos

University of South Florida

Phone: (813) 974-6250; Fax: (813) 974-3651

E-mail: wolan@eng.usf.edu

Objectives

- Develop membranes and membrane electrode assemblies (MEAs) with reduced fuel crossover
- Design and test advanced cathode catalysts with low Pt loading
- Build and evaluate improved-performance hydrogen and ethanol single cells

Technical Barriers – Fuel Cells

- B. Cost
- C. Electrode Performance
- D. Thermal, Air, and Water Management
- F. Fuel Cell Power System Integration

Technical Targets

This project is conducting fundamental studies of fuel permeation and power output in polymer electrolyte membrane fuel cells (PEMFCs) using Nafion[®] and custom Nafion[®]-composite membranes. Knowledge gained from these experiments will aid in meeting the following DOE 2010 technical targets for membranes in transportation applications:

- Membrane Conductivity at
 - Operating Temperature: 0.10 S/cm
 - Room Temperature: 0.07 S/cm
- Operating Temperature: 120°C
- Oxygen cross-over: 2 mA/cm²
- Hydrogen cross-over: 2 mA/cm²
- Cost: \$40/m²

Approach

- Begin Nafion[®] permeation experiments.
- Design and build a hydrogen fuel cell test setup.

- Design composite-Nafion[®] membranes.
- Examine conductivity of custom membranes.
- Design alternative cathode catalyst using Co, Fe, Mo to reduce Pt loading.
- Evaluate cathode catalysts using Fourier Transform Infrared (FTIR).
- Build custom MEA from designed catalysts and custom membrane.
- Optimize current, voltage, and power output of custom MEA.

Accomplishments

- Successful casting of a custom Nafion[®] film.
- Developed creation procedure for Nafion[®] - zeolite/composite membranes.
- Developed design for test setup for pure hydrogen PEMFCs.
- Developed and built proton conductivity probe.
- MEA power output
 - Maximum power output ~ 18 mW
 - Maximum current ~ 400 mA
 - Maximum voltage ~ 300 mV

Future Directions

- Complete pure hydrogen test bed.
- Conductivity measurements at elevated temperatures and humidity are required.
 - Conductivity probe at room temperature has been developed and created.
- Build hydrogen fuel cell test bed.
- FTIR analysis of cathode catalysts.
- Permeation of ethanol experiments are continuing and will be used to compare fuel flux through Nafion[®] and the custom Nafion[®]-composite membranes.
- Continue creation of custom composite membranes consisting of (1) organic metal frameworks, (2) Gold nano-spheres.
- Increase power, current, and voltage output of custom MEA.

3.2 Modified Engineered Polymers

Clovis A. Linkous

University of Central Florida

Phone: (321) 638-1447; Fax: (321) 638-1010

E-mail: calink@fsec.ucf.edu

Objectives:

This project addresses the following objectives with regard to fuel cell research:

- Lower cost of fuel cell-generated electricity
- Decrease cost per unit power for proton exchange electrolyte membranes
- Improve long-term chemical stability of fuel cell PEM electrolytes operating at 120°C
- Maintain or improve high protonic conductivity of PEM electrolytes
- Minimize H₂O content to support high conductivity under stated conditions

Technical Targets and Background

DOE fuel cell power system targets of \$45/kW by 2010 and \$30/kW by 2015. We are attempting two strategies for lowering membrane cost: high density sulfonation and strategic fluorination. The former approach will involve attaching a high density of sulfonic acid groups along with cross-linking chemistry, to achieve high conductivity without creating solubility or mechanical failure issues. This will serve to decrease the area required to support a kilowatt of power without significant cost increase. The latter approach will lower costs by fluorinating the polymer only where it is necessary to maintain performance and prevent depolymerization.

Technical Barriers – Fuel Cells

- A. Durability
- B. Cost

Accomplishments

High Density Sulfonation:

We have been performing cross-linking chemistry on polystyrene sulfonic acid, a generic ion exchange material, to demonstrate and understand cross-linking effects. Styrene has been polymerized along with divinyl benzene to make a cross-linked

structure. The resulting resin was sulfonated by dissolving it in concentrated (~96%) sulfuric acid and stirring for several hours. The polymer was precipitated by extraction with ethanol.

While the resulting sulfonated polymer membranes were rendered insoluble in organic solvents, they were nevertheless soluble in water. Thus the negative solubility effect of increasing effective molecular weight due to cross-linking was overcome by the attachment of hydrophilic sulfonic acid groups.

Employment of a sufficient concentration of cross-linking agents will eventually render the membrane water insoluble, even at high sulfonation levels. Other cross-linking agents, such as carbon tetrachloride, dichloromethane, dichloroethane, and 1,4-dichlorobenzene have been acquired and are being subjected to Friedel-Crafts-type alkylation reactions with the polymer material.

Strategic Fluorination:

Efforts continue on the synthesis of the fluorosulfonic acid of polyetheretherketone (F-SPEEK). Early attempts gave low yield and many side products.

The other strategic fluorination approach is to perform a surface fluorination where oxidative attack is most prevalent. The first step is to identify a conductive polymer membrane that is highly susceptible to oxidative attack by peroxides. The thickness of the membrane can only be on the order of 50 m for utilization of transmission infrared spectroscopy.

Future Directions

Work will continue toward the fluorosulfonation and cross-linking of polyetheretherketone. Confirm whether the quaternary ammonium strategy can protect the amine groups while brominating the trifluoromethyl group. As for the cross-linking experiments, a variety of spacing units are being employed to determine the optimum between conductivity and cross-linker chain length. Once suitable conditions are determined for peroxide testing, Nafion[®]-clad membranes will be prepared, tested, and compared to their unclad substrates.

3.3 PEM Materials Improvement

*D. Yogi Goswami, Sanjay Vijayraghavan,
Nikhil Kothurkar, Patricia Alexander*

University of Florida

Phone: (352) 392-0812; Fax: (352) 392-1071

E-mail: goswami@ufl.edu

Objectives

- Synthesize and fabricate new low cost, high temperature, low humidity membranes: poly(2,5-benzimidazole) (ABPBI)
- Fabricate custom single cell test stand for broad temperature range testing
- Test under freezing conditions

Technical Barriers – Fuel Cells

- A. Durability
- B. Cost
- D. Thermal, Air and Water Management
- J. Startup Time/Transient Operation

Approach

- Identify cheaper alternatives to Nafion[®], which work under high temperature and low humidity conditions.
- Identify a low cost and simple technique to synthesize the materials.
- Fabrication of custom test stand to test alternative materials under broad range of temperature and humidity conditions.
- Synthesis of ABPBI and fabrication of MEAs.
- High temperature operation of ABPBI MEAs

- Low temperature (including freezing) testing during startup and operation.

Accomplishments

- Identified ABPBI-phosphoric acid as a low cost, high temperature, low humidity alternative to Nafion[®].
- Identified suitable low cost, high temperature, low humidity membrane material as ABPBI.
- Set up single cell test stand for MEA testing.

Future Directions

- Synthesize ABPBI and fabricate MEAs
- Test MEAs at high temperature.
- Test MEAs at low temperature (including freezing) during startup and operation.
- Improve catalyst bonding, reducing catalyst content and increasing catalyst efficiency by making a nanoparticulate sol.
- Control membrane microstructure to reduce phosphoric acid leaching.

Special Recognitions & Awards/Patents Issued

1. Non-Provisional Patent application # 10/711,552. "Hydrogen Storage Nano-foil and Method of Manufacture" filed September 24, 2004.
2. Continuation-In-Part to Non-Provisional Patent application # 10/711,552. "Hydrogen Storage Nano-foil and Method of Manufacture" to be filed Q3-2005.
3. Patent application to be submitted Q3-2005. "Reactive Sputtering of Nanostructured Multi-component Hydrides"

FY 2005 Publications/Presentations

1. "A thermodynamic analysis of hydrogen production by gasification of biomass", Madhukar Mahishi, Sanjay Vijayaraghavan, Deepak Deshpande, D. Yogi Goswami, accepted for publication at ISES 2005 Solar World Congress, August 6-12, 2005, Orlando, FL
2. "Hydrogen Production from Biomass: An energy analysis of Thermochemical Biomass Gasification", Madhukar Mahishi, Mojtaba S. Sadrameli, D. Yogi Goswami, Abstract accepted for 2005 ASME International Mechanical Engineering Congress and Exposition.
3. "p-Type Transparent Conducting Contacts for Thin-film Compound Semiconductor Solar Cells", P. Mahawela, S. Vakkalanka, C. S. Ferekides and D. L. Morel, Proceedings of the MRS, March, 2005, San Francisco.
4. Wade, J., Srinivasan, S., & Stefanakos, E., (2005). "An Investigation of $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ Nanocomposites for Visible Light Photocatalysis," Presentation at the 2005 MRS Spring Meeting, San Francisco, CA.
5. Wade, J. "An Investigation of $\text{TiO}_2\text{-ZnFe}_2\text{O}_4$ Nanocomposites for Visible Light Photocatalysis," Master's Thesis, University of South Florida, Tampa, FL (2005).
6. Srinivasan, S., Wade, J., & Stefanakos, E., (2005). "Visible light photocatalysis via nano-composite CdS/ TiO_2 materials," Mater. Res. Soc. Symp. Proc. Vol. 876E (2005)
7. "Measurement of Solid Ionic Electrolyte Conductivity." Horace Gordon, Jr., Don Payne, Burton Krakow, Elias K Stefanakos, Lars Ecklund-Mitchell. An Abstract accepted for a presentation at the 1st Symposium on Manufacturing of MEAs for Hydrogen Applications, Dayton, Ohio, August 9th-11th, 2005.
8. "H₂ Production by Electrochemical Dissociation of H₂S in IGGC plant". B. Krakow, E. Weaver, L. Ecklund-Mitchell, E. Stefanakos, G. Moore, M. Smith. An Abstract accepted for a presentation at the Twenty Second Annual International Coal Conference, Pittsburgh, PA, September 12 to 15, 2005.
9. "Byproduct Hydrogen Production." E.P. Weaver, M. Chettiar, B. Krakow, E.K. Stefanakos, G. Moore, M. Smith. An Abstract accepted for a presentation at the 2005 Fuel Cell Seminar, Palm Springs, California, USA., November 14-18, 2005.
10. Synthesis and characterization of nanoscale transition metal complex for hydrogen storage Sessa S. Srinivasan, Deepak Deshpande, Matthew T. Smith, Elias K. Stefanakos, Yogi Goswami, Michael Jurczyk, Arun Kumar, Ashok Kumar MRS Spring Meeting, San Francisco, CA, March 30, 2005
11. Thermal and volumetric studies of light weight hydrogen storage systems Sessa S. Srinivasan, Matthew T. Smith, Lisa McElwee-White, Elias (Lee) Stefanakos, Yogi Goswami, Craig M. Jensen MRS Fall Meeting, Boston, MA, November 29, 2005 [Abstract submitted]
12. Poster Presentation at MRS Fall 2004: Arun Kumar, Michael U. Jurczyk, Ashok Kumar, Sessa Srinivasan, Elias Stefanakos: Polymeric Carbon Nanocomposites for Hydrogen Storage
13. Oral Presentation at MRS Spring 2005: Michael U. Jurczyk, Arun Kumar, Ashok Kumar, Lee Stefanakos: Effect of Physical State of Carbon Nanocomposite on Hydrogen Adsorption and Desorption
14. Poster Presentation at MRS Spring 2005: Arun Kumar, Michael U. Jurczyk, Ashok Kumar, Lee Stefanakos: Nanocomposite with Carbon Nanotubes Aligned in High Magnetic field for Hydrogen Storage Applications