2005 DOE Hydrogen Program Review

Fuel Cell and Hydrogen Research

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Project ID # STP2

This presentation does not contain any proprietary or confidential information
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Projects

Hydrogen Storage (ST10)

- Transition Metal Hydrides (USF and
  UF)
- Nano-structured Materials (USF)
- Hydrogen Storage Components
  (USF)

Hydrogen Production (STP2)

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

Fuel Cells (STP2)

- Modified Engin. Polymers (FSEC)
- PEM Fuel Cell Research (UF)
- PEM Fuel Cell Research (USF)
Overview

Timeline
• Oct 2004 to May 2008
• 16% Complete

Budget
• Total project funding
  – DOE $4.8M
  – Contractor $1.25M
• Funding
  – FY04 $1.9M
  – FY05 $2.9M

Barriers
• Fuel Cells
  – DOE 3.4.4.2 (O-Q)
    • Durability, Heat Utilization, Electrode Performance, Cost, Reduced catalysts loadings
• H2 Production
  – DOE 3.1.4.2.5 V
    • Thermochemical technology, solar capital cost
  – DOE 3.1.4.2.2 G
    • Feedstock cost and availability, efficiency of gasification, CO emissions
  – DOE 3.1.4.2.4 T
    • Cost, efficiency, catalyst
  – DOE 3.1.4.2.4 Q
    • Cost, efficiency, catalyst
  – DOE 3.1.4.2.4 R
    • Cost, efficiency
Fuel Cell - Approaches

1. Strategic Polymer Fluorination
2. PBI-H$_3$PO$_4$ MEA Development
3. MEA Advancement

Targets:

- Fuel cell cost < $55/KW
- Power density ~0.5 W/cm$^2$
(Approach I) Strategic Fluorination

- 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
- Heavily sulfonate polymers to promote proton conductivity, but cross-link to prevent solubility and mechanical stability problems
- Develop accelerated test apparatus to evaluate prototype PEM’s
Technical Progress
(Approach I) Strategic Fluorination

• Successfully brominated benzyltrifluoride, the first step in making a fluorosulfonic PEEK polymer
• Developed catalytic peroxide decomposition method for accelerated testing of PEM electrolytes
• Prepared surface fluorinated (“Nafion-clad”) PEM’s based on polystyrene sulfonic acid
Initial Steps in Synthetic Scheme for PEEK Fluorosulfonic Acid (Approach I) Strategic Fluorination

Bromination of the trifluoromethyl monomer

Formation of the sulfonic acid
Approach 2
PBI-H₃PO₄ MEA Development

• Employ PEM material: PBI-H₃PO₄
  – Low cost, low humidity, high temperature, durability

• Identify specific challenges related to synthesis, MEA fabrication and performance

• Synthesize and characterize membranes

• Improve synthesis/fabrication to enhance performance and reduce cost
Technical Progress
(Approach 2) PBI-\( \text{H}_3\text{PO}_4 \) MEA Development

• Identification of low temperature PBI synthesis technique
  – Reduces cost of PBI material
  – Simplifies membrane manufacturing

• Development of test bed for evaluation of performance under varying operating conditions
Low-Temperature PBI Synthesis (Approach 2) PBI-H$_3$PO$_4$ MEA Development

3,4-diaminobenzoic acid + P$_2$O$_5$+Methane sulfonic acid, 150°C, ½ hr

150°C, ½ hr

Solution Casting

Extraction, Drying

H$_3$PO$_4$ impregnation

Catalyst application

MEA fabrication

(Approach 3) MEA Advancement

• Catalyst Development
  – Develop novel bimetallic metal/oxide catalysts to lower platinum loading

• Membrane Development
  – Decrease fuel crossover
    • Analyze pretreatments to maximize proton transport while minimizing molecular transport
    • Develop porous support
  – Develop nanocomposite membranes
Technical Progress
(Approach 3) MEA Advancement

- Fabrication and chemical analysis of cobalt-tin-ruthenium catalysts in custom MEAs initiated
- Nafion® pretreatments involving H₂O₂, HCl, and H₂SO₄ have been developed to determine effects on proton and molecular transport
- Analyzed Porous SiC(PSC) membrane support to reduce fuel crossover
  - Nafion® impregnated PSC membranes showed up to a six fold decrease in ethanol cross-over as compared to Nafion® 117 films.
Experimental Setup for Catalyst and Membrane Development

(Approach 3) MEA Advancement

PermeGear Crown Glass Side-Bi-Side permeation cell¹

25 cm² PEM single cell fuel cell, serpentine flow pattern²

¹ http://www.permegear.com
Future Work – Fuel Cells

• **Strategic fluorination**
  – Prepare fluorosulfonic acid versions of 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
  – Combine cross-linking and partial fluorination strategies into new PEM membranes
  – Test prototype PEM’s in fuel cell configuration

• **PBI MEA Development**
  – Characterization of high temperature performance

• **Freezing effects: (Nafion & alternatives)**
  – Performance characterization operating sub-freezing and post freeze/thaw cycling
  – Determination of effect on materials
  – Need fundamental understanding to reach DOE cold-start goals

• **Catalyst development**
  – Reduced precious metal loadings, bimetallics, low-cost systems for both H- and DEFC’s

• **Membrane development**
  – Effect of membrane pre-treatment on proton conductivity
  – Internally humidified nanocomposite membranes → zeolites, clathrates and nanocrystalline α-SiC
Publications and Presentations
Fuel Cells

H₂ Production Approaches

1. Solar Photocatalytic
   • Target: Improve efficiency of water splitting from 70% to 90% while addressing cost

2. Solar Photoelectrochemical
   • Target: Improve hydrogen production cell cost to ~$70/m²

3. Thermochemical Cycle
   • Target: Lower operating temperatures (to ~700°C) of cycle to improve economics

4. Biomass Gasification
   • Target: Maximize hydrogen yield and efficiency of process while reducing CO emissions to below 10% by volume.

5. Solid State Ionic Conductors
   • Target: Reduce current weight and increase operating temperatures of electrolyte system to 150°C
Accomplishments

(Approach 1) Solar Photocatalytic TiO$_2$-ZnFe$_2$O$_4$ Nanocomposites

- A new coprecipitation/hydrolysis technique was developed to create TiO$_2$-(X)ZnFe$_2$O$_4$ alloys
- XRD analysis was used to characterize dual-phase nanocomposites for various alloy concentrations and calcination temps
- UV-Vis spectroscopy was performed to analyze visible light absorption shifts
- Visible light absorption directly related to alloying concentration of low bandgap ZnFe$_2$O$_4$
- (Photoactive) Absorption shifts greater than 60nm can be achieved by proper alloying
Accomplishments

(Approach 1) Solar Photocatalytic TiO$_2$-ZnFe$_2$O$_4$ Nanocomposites

- Pure TiO$_2$, pure ZnFe$_2$O$_4$, and modified TiO$_2$-ZnFe$_2$O$_4$ alloys were created
- TiO$_2$-ZnFe$_2$O$_4$ nanocomposites have been optimized based on control parameters such as H$_2$O/alkoxide ratio, calcination temperature, SO$_4^{2-}$ impregnation, pH used for preparation, and precursor selection*.

For the first time, a photocatalytic reactor was created to analyze the photocatalysts exposed to UV, UV-Vis, and visible light irradiation.

- Organic degradation was used to simulate H$_2$ production by photocatalyst’s redox reactions
- Experiments successfully concluded the photoactivity of TiO$_2$-ZnFe$_2$O$_4$ catalysts at irradiation wavelengths longer than 400nm (shown right)

Visible Light (>400 nm) Photoactivity Experiment

Accomplishments

(Approach 1) Solar Photocatalytic TiO$_2$--CdS Nanocomposites

TiO$_2$-CdS nanocomposites were developed utilizing quantum sized CdS for visible light synthesization reactions*.

- EDS, SEM, and XRD measurements were used to structurally characterize and modify TiO$_2$-CdS for optimum photoactivity.
- UV-Vis spectroscopy revealed absorption at wavelengths of 490nm with photoactivity studied by degradation of organics.

Visible Light (>400 nm) Phenol Degradation

XRD Analysis of TiO$_2$, CdS, and TiO$_2$-CdS

Accomplishments

(Approach 1) Solar Photocatalytic TiO$_2$ by RF Sputtering

**SEM images of sputtered TiO$_2$ films:**
- Film morphology depends on deposition conditions
- Porous films with larger surface areas are preferred for photocatalytic applications

**XRD analysis of Sputtered TiO$_2$ Films:**
- As-deposited at room temperature films are amorphous (2$^{nd}$ from bottom)
- Annealing in air at high temperatures yields polycrystalline TiO$_2$ (3$^{rd}$ and 4$^{th}$ from bottom)
- 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 (top)
Future Work

(Approach 1) Solar Photocatalytic

I. TiO$_2$-ZnFe$_2$O$_4$ nanocomposites
   - Through September 30$^{th}$ (2005)
     • Use chemical procedures to inhibit the anatase-to-rutile transformation of TiO$_2$ for ZnFe$_2$O$_4$ alloying concentrations greater than 10mol%  
     • Enhance the photoactivity of the nanocomposites by 25% for organic degradation experiments.
   - FY 2006 (10/05-09/06)
     • Complete experimental transformation from organic degradant to H$_2$ production using visible light photocatalysis.

II. TiO$_2$ thin films by RF sputtering
   - Through September 30$^{th}$ (2005)
     • Begin doping (alloying) to modify absorption properties  
     • Demonstrate absorption for wavelengths above 400 nm  
     • Design/construct apparatus and begin photocatalytic experiments
   - FY 2006 (10/05-09/06)
     • Demonstrate photocatalytic activity for films with absorption above 400 nm  
     • Optimize process for maximum photocatalytic activity
Objectives

(Approach 2) Solar Photoelectrochemical

The overall objective of this project is to develop a tandem photovoltaic solar-electrolytic cell that will generate hydrogen from water in a cost-effective manner.

Objectives for the first year are:
- Fabricate representative Si/transparent conductor devices.
- Deposit representative CdSe devices on Si/transparent conductor devices.
- Demonstrate tandem compatibility.
(Approach 2) Solar Photoelectrochemical

- Thin-film solar cells have demonstrated potential for low cost and high efficiency.
- Tandem thin-film solar cells can produce voltages in excess of 1.5 volts that are needed to electrolyze water.
- With proper development of catalytic contacts and membranes the cells can be placed inside an electrolyzer cell.
- CdSe($E_g - 1.7$) and CuInGaSe($E_g - 1.0$) as a tandem have projected efficiency of 25 – 30%.
- CuInGaSe efficiency of 18% has been demonstrated.
- A CdSe top cell with $V_{OC}$ of order 1 volt is needed. This will first be developed on Si with SnO$_2$ as the common contact.
Accomplishments

(Approach 2) Solar Photoelectrochemical

Single Junction CdSe Devices: ZnSe:Cu/CdSe/SnO₂
- Jsc of 17.4 mA/cm²
- Voc of 575 mV (850 mV reported by others in other configurations)
- Transmission of 80% of sub band gap light to the underlying cell
Accomplishments

(Approach 2) Solar Photoelectrochemical

• A SnO$_2$/n-Si device process has been developed.
• $V_{OC}$’s up to 500 + mV have been demonstrated with SnO$_2$/n-Si.
• Operable CdSe devices have been deposited on SnO$_2$/Si substrates.
• The first operable tandem devices have been fabricated.

First Tandem Devices - $V_{OC}$
• 220 mV for CdSe
• 420 mV for the tandem
Future Work

(Approach 2) Solar Photoelectrochemical

**Remainder of FY 05**
- Demonstrate Voc’s of 500 mV for CdSe on TO/Si
- Demonstrate operable tandem devices

**FY 06**
- Develop thermal budget compatibilities for the tandem structure
- Develop advanced doping capabilities for ZnSe
- Demonstrate a tandem Voc of 1 volt.
(Approach 3) Thermochemical Cycle

- Test feasibility of UT-3 thermochemical cycle for hydrogen production
- Increase hydrogen yield through new pellet formulation
- Reduce the reactor operating temperature
Technical Accomplishments
(Approach 3) Thermochemical Cycle

New CaO reactant pellets:
- Precursor for pellet 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 Univ of Tokyo pellet. (Fig.1)

Fig.1 Pore Volume Distribution of New and UT-3 pellets.
Technical Accomplishments

(Approach 3) Thermochemical Cycle

XRD data confirms the presence of CaO reactant and CaTiO$_3$ substrate in the New pellet. (Fig.2)

27% of CaO reactant detected by chemical analysis in New pellet. (Fig.3)

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Ca/Ti</th>
<th>Max Heating Temp</th>
<th>Wt %CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized Powder 1</td>
<td>1</td>
<td>430°C</td>
<td>9.01%</td>
</tr>
<tr>
<td>Synthesized Powder 1</td>
<td>1</td>
<td>430°C</td>
<td>8.65%</td>
</tr>
<tr>
<td>Synthesized Powder 2</td>
<td>2</td>
<td>1000°C</td>
<td>27.71%</td>
</tr>
<tr>
<td>Synthesized Powder 2</td>
<td>2</td>
<td>1000°C</td>
<td>26.55%</td>
</tr>
<tr>
<td>Pure CaO</td>
<td>N/A</td>
<td>none</td>
<td>98.30%</td>
</tr>
<tr>
<td>Pure CaO</td>
<td>N/A</td>
<td>none</td>
<td>97.95%</td>
</tr>
<tr>
<td>Pure CaTiO3</td>
<td>1</td>
<td>none</td>
<td>3.29%</td>
</tr>
</tbody>
</table>
Technical Accomplishments

(Approach 3) Thermochemical Cycle

Feed and reactor system with thermogravimetric balance

(800°C, HBr, Br₂, steam)

Feed system set-up

Schematic diagram
Future Work
(Approach 3) Thermochemical Cycle

2005
• Operate bromination reactor to find O\textsubscript{2} yield
  \[ \text{CaO} + \text{Br}_2 \rightarrow \text{CaBr}_2 + \frac{1}{2} \text{O}_2 \]
• Conduct CaO pellet kinetic study and thermo-gravimetric analysis
• Use kinetic data to improve pellet formulation to increase O\textsubscript{2} yield

2006
• Formulating new Fe\textsubscript{3}O\textsubscript{4} pellet
• Operate bromination and hydrolysis reactors to find H\textsubscript{2} yield
  \[ \text{Fe}_3\text{O}_4 + 8\text{HBr} \rightarrow 3\text{FeBr}_2 + 4\text{H}_2\text{O} + \text{Br}_2 \]
  \[ 3\text{FeBr}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HBr} + \text{H}_2 \]
• Conduct Fe\textsubscript{3}O\textsubscript{4}/FeBr\textsubscript{2} pellet kinetic study and thermo-gravimetric analysis
• Use kinetic data to improve pellet formulation to increase H\textsubscript{2} yield
• Recommendation for future work
Objectives

(Approach 4) Biomass Gasification

- **Thermodynamic Analysis:**
  - Improve energy efficiency, increase $\text{H}_2$ yield of conventional steam biomass gasification (target increase of $\text{H}_2$ yield 18-20% - molar basis) and combine reforming, shift and separation processes using novel sorption enhancement technique
  - Relevance to DOE: Capital cost reduction by process integration

- **Catalysis:**
  - Develop new tar cracking catalysts with higher selectivity towards hydrogen that can operate at low temperature (500-600°C or below)
  - Relevance to DOE: Improved catalyst for tar cracking
Accomplishments

(Approach 4) Biomass Gasification

• Thermodynamic Analysis:
  – Basic thermodynamic studies completed
  – Preliminary modeling of sorbent enhanced gasification process using ASPEN™ simulator completed
  – Experimental set-up completed

• Catalysis:
  – Design of reactor system completed
  – Catalyst preparation and characterization in progress
Schematic of Sorbent Enhanced Gasification

(Approach 4) Biomass Gasification

- High $H_2$, low $CO$, Product gas
- $CO_2$
- Biomass
- Steam
- Spent Sorbent
- Regenerated Sorbent
- Gasifier
- Regenerator
- Supplemental Biomass
- Air
Simulation of Sorbent Enhanced Gasification

(Approach 4) Biomass Gasification

![Graph showing product yields of ethanol reforming with and without CaO sorbent.](image)

No CaO sorbent

With CaO sorbent

Fig.: Product yields of ethanol reforming (ethanol used as model biomass compound)

- **H₂ yield increases by 18% - 20%**
- **Gasification temperature decreases by 100°C.**
- **CO reduces to ppm level in the operating temperature range**
Experimental Set-up

(Approach 4) Biomass Gasification
TEM of Ni/Al$_2$O$_3$ Catalyst

(Approach 4) Biomass Gasification

- Nanoparticle alumina amorphous
- Ni inhomogeneously distributed on the surface after 450ºC calcination
- Structure visible after calcination at 800ºC
Future Work
(Approach 4) Biomass Gasification

Thermodynamics Analysis:
• FY 2005
  – Conduct energy analysis of sorbent enhanced gasification
  – Validate the sorbent enhancement concept
• FY 2006
  – Study sorbent regeneration, in particular reduction of regeneration temp and alternate sorbents

Catalysis:
• FY 2005
  – Build reactor assembly for testing of catalyst
  – Catalytic activity measurements using model reactor
• FY 2006
  – 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
The objective of this project is economic electrolytic hydrogen production. This will be sought through better electrolytes and electrochemical cells with which several barriers to this objective can be overcome as follows:

**Solutions to Barriers from DOE Technical Plan**

**Barriers 3.1.4.2.4 Q & S:** The electricity required for water electrolysis can theoretically be cut by an order of magnitude by scavenging the anode with a reducing agent. This agent may be landfill gas (or other biogas), synthesis gas or industrial waste products.

**Barrier 3.1.4.2.4 U:** The electricity required for water electrolysis can be further cut by replacing it with energy in the form of cheaper low quality heat to raise the temperature and evaporate the feedstock. An optimum choice of temperature can provide a good balance of efficiency and low cost. A sound temperature range 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).

**Barrier 3.1.4.2.1 A:** 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.

**Barriers 3.1.4.2.2 F & 3.1.4.2.4 T:** Landfills and modified incinerators could supply scavenger gas for practical electrolytic hydrogen production. The insolation incident on the large landfill sites could supply the DC power needed for electrolysis.
Plan of Attack
(Approach 5) Solid State Ionic Conductors

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 250°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

Electrolytic cells are being built for operation with the thin film solid state ionic conductors. The cells operate dry at temperatures between 125 and 300°C and pressures below the vapor pressure of water at these temperatures. Under these conditions, liquid water cannot exist so it cannot interfere with the use of potentially water soluble reactants, products, catalysts, scavengers, electrolytes or structural materials. Also, there will be no undesirable flooding of components by liquid water.

Performance and stability of electrolytes and cells are being studied with and without anode scavengers used to reduce the voltage requirement. Impermeability to anode scavengers will be tested.
Electrolyte Preparation

*(Approach 5) Solid State Ionic Conductors*

- 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 disks of this material were made for study by pressing the powder at 490 MPa.
- The conductivity of a disk increases by almost 4 orders of magnitude within a few degrees as can be seen in the adjacent figure.
Electrolytic Cell
(Approach 5) Solid State Ionic Conductors

- Steam or another gaseous source of hydrogen is fed into the top of the positive (lower) compartment where it reacts with the positive electrode to produce hydrogen ions. These pass through the solid electrolyte to the negative chamber where the negative electrode converts them to hydrogen gas that is withdrawn at the top of the negative compartment. Oxygen, or other remnant of the feed stock is withdrawn from the bottom of the positive compartment.
Future work
(Approach 5) Solid State Ionic Conductors

- 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.
- A monitoring and control system for flow of materials through the cell 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 Test permeability of electrolytes to feed stocks and scavengers and study performance and stability of the solid electrolytes.
Publications & Presentations

H₂ Production

• “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


Hydrogen Safety

- Failure of a prototype membrane leading to mixing of $H_2$ and oxidant gases, enabling onset of combustion inside device that could spread into laboratory
  - thorough testing of prototype membranes as single components under accelerated conditions before life-testing in fuel cell
  - check valves in gas lines
  - perform initial life tests on single, 25 cm$^2$ cells
- Handling reactive chemicals, catalysts, solvents and high pressure gases
- High pressure hydrogen gas regulations
- Methodologies for disposing/deactivating chemicals
- Safety and Risk Management training
- Regular monitoring of lab safety by the EHS&RM officials
- Complying with MSDS date sheet
- $H_2$/He leak testing with in-built automated alarm system and external leak check procedures
- Trained personnel for the safe operation of high pressure systems, reactive gases and explosive materials
- Standard operating procedures (protocols) establishment and regular maintenance/repair of the equipment
Interactions and Collaborations

- Jim Fletcher, University of North Florida
- Plug Power, Albany NY
- Rick Cooper, Polyfuel
- University of Hawaii, Dept of Chemistry
- Brevard Community College
- Nanomaterials and Nanomanufacturing Center, University of South Florida
- NREL