

## II.K.5 Developing Improved Materials to Support the Hydrogen Economy\*

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Projected End Date: Continuing 2007

\*Congressionally directed project

- Durability/Operability
- Control and Safety
- Device Configuration Designs
- System Design and Evaluation
- Grid Electricity Emissions
- System Efficiency
- Electricity Costs
- Variation in Standard Practice of Safety Assessments for Components and Energy Systems
- System Weight and Volume
- High-pressure Conformability
- Materials of Construction
- System Life-Cycle Assessments
- Lack of Understanding of Hydrogen Physisorption and Chemisorption
- Reproducibility of Performance
- Charging/Discharging Rates
- Hydrogen capacity within the storage medium (Doped and Undoped Alanates)
- Facility of hydrogen Desorption and Adsorption in Optimized Systems
- Renewable Integration
- Electricity Costs
- High-Purity Water Availability
- Fuel Cell Manufacturing and Process Costs
- Fuel Cell/Stack Durability
- Fuel Cell Electrode Performance
- Feedstock Issues
- Carbon Dioxide Emissions
- Impurities
- High Cost and Low Energy Efficiency of Hydrogen Liquefaction
- Fuel Processor Manufacturing
- Thermal, Air and Water Management

### Objectives

- Manage ongoing projects.
- Collect and review monthly project reports for go/no-go results.
- Initiate Phase II projects as appropriate.
- Prepare quarterly program reports from individual project reports; evaluate projects for potential Phase II awards.

### Technical Barriers and Technical Targets

EMTEC will solicit and fund hydrogen infrastructure related projects that have a near-term potential for commercialization. The subject technology must be related to the U.S. Department of Energy (DOE) hydrogen economy goals as outlined in the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYPP). Preference will be given to cross cutting materials development projects that lead to the establishment of manufacturing capability and job creation.

Specific barriers from the MYPP for the projects include:

- Capital Costs
- Operation and Maintenance (O&M)
- On-Board Hydrogen Storage
- System Cost

### Approach

EMTEC has used the U.S. Department of Energy hydrogen economy goals as outlined in the MYPP to find and fund projects with near-term commercialization potential. A request for proposal (RFP) process aligned with this plan requires performance-based objectives with go/no-go technology-based milestones. EMTEC manages this project for the DOE using the protocols that include a RFP solicitation process, white papers and proposals with peer technology and commercialization review (including DOE), EMTEC project negotiation and definition and DOE cost share approval. Our RFP

approach specifies proposals/projects for hydrogen production, hydrogen storage or hydrogen infrastructure processing which may include sensor, separator, compression, maintenance, or delivery technologies. EMTEC is especially alert for projects in the appropriate subject area that have cross cutting materials technology with near-term manufacturing opportunities. To date, EMTEC has selected projects which have been continuing development projects preparatory to commercialization. EMTEC's overriding objective is technology commercialization.

### Accomplishments

- EMTEC hosted the 2<sup>nd</sup> *Membrane Electrode Assemblies (MEAs) Manufacturing Symposium*, August 22-24, 2006 at the DoubleTree in downtown Dayton, OH. This symposium drew 151 participants from multiple countries. EMTEC continued the planning and organizing efforts for the 3<sup>rd</sup> *MEA Manufacturing Symposium*, to be held August 21-23, 2007, at the Dayton Marriott.
- EMTEC hosted another highly successful half-day Fuel Cell Manufacturing Short Course on March 6, 2007 at the Engineers Club of Dayton, OH. This course was presented by fuel cell expert, Dr. Jack Brouwer of the National Fuel Cell Research Center, University of California, Irvine.
- EMTEC attended and presented at the DOE Hydrogen Program review May 11, 2007.
- EMTEC continued the negotiations for competitively selected Round 1, 2, and 3 Phase II proposals, culminating in a total of four Phase II projects to date. Individual progress reports for the active projects funded through this period are included in this report.
- EMTEC hosted a new event entitled 1<sup>st</sup> *Ohio Summit on Supply Chain Opportunities in Alternative Energy* June 19-20, 2007 in Dayton OH. This highly successful event included sessions on alternative energy from hydrocarbon sources, wind, solar, biomass, and fuel cells/hydrogen. This event drew 168 participants and 27 exhibitors.

### Future Directions

- Manage ongoing projects.
- Initiate Phase II projects as appropriate.
- Collect and review monthly project reports for go/no-go results for Phase I/II projects.

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### Nanocatalyst Development Employing Electrically Mediated Processing for Hydrogen Generation

Faraday Technology, Inc.  
Project Number: EFC-H1-1-2A  
Project in Negotiation for Phase II

#### Objectives

The overall objective of the project is to develop a low-cost, mass fabrication technology for catalyzation of MEAs for proton exchange membrane (PEM) electrolyzers and regenerative fuel cells, a technology that directly supports the development of the hydrogen economy. This project meets the mission of EMTEC which is to improve the methods by which the quality of processed materials is determined, improve the current materials processing operations relative to quality, cost or responsiveness and develop alternative materials processing methods and/or operations. This project will meet the challenge of reducing electrolyzer cost by developing lower cost materials with improved manufacturing capability. **The overall objective for Phase II is to complete the development of a manufacturing process for fabricating MEAs for electrolyzers and regenerative fuel cell systems with an optimized bi-functional oxygen electrode.**

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### Novel Stackable Structural Reactor (SSR™) for Low-Cost Hydrogen Production

Catacel Corporation  
Project Number: EFC-H1-09-2A  
Round 1 – Phase II

#### Objectives

The Phase II Project Plan for SSR™ will finalize the development of the product, and prepare for commercialization. The project will result in pilot manufacturing capacity and field performance data that validates the lab estimates.

#### Accomplishments

- Two catalyst formulations have shown good conversion and stability when tested up to 150 hours in simulated field conditions.
- Materials have been exposed to simulated conditions for 1,000 hours without damage. After being exposed to severe oxidation for 1,000 hours, full size parts can easily be removed from customer tubes without damage to the tube.
- Details and methods of construction have been demonstrated that will allow SSR™ to be cost-competitive with current catalyst systems.
- Most of the assembly and coating methods have been demonstrated at bench-scale.

- Final negotiations are underway with a customer to put in a small plant to showcase the technology. This plant will be brought on-line 2Q 2007.

The project met all the above goals, with the exception of the final demonstration. The conservative customer base has continually demanded more proof-of-concept before risking a trial operation in their plants. Consequently, the project involved more “proving” than expected, and project funds were exhausted before the demonstration could take place. This also had the effect of shifting some of the budgeted resources into more appropriate categories.

Other funds have been secured to run a single tube, full-size part test at actual field flow conditions at Linde BOC starting in June 2007. Positive results from this test are expected to lead to a small field installation by the end of 2007.

In spite of the project delays, the SSR™ product has shown every indication that it will be very successful. Catacel Corporation and our various partners are committed to a commercial launch.

### Patents

- US Patent application 11/191683 filed 7/27/05, “Reactor Having Improved Heat Transfer”.
- US Trademark application 78/710819 filed 9/12/05 for “SSR”.

- Provisional patent application 60/874901 filed 12/14/06, “Stackable Structural Reactor Improvements”.

### Commercialization of Electromagnetic (EM) Solid State Welding for High Pressure Hydrogen Storage

IAP Research, Inc.  
Project Number: EFC-H1-11-1A  
Project Completed

### Low Cost MEMS Hydrogen Sensor for Transportation Safety

Makel Engineering, Inc. (MEI)  
Project Number: EFC-H1-15-2A  
Awarded Phase II

### Objectives

The objective of this project is the development of a low-cost, high performance hydrogen safety sensor for hydrogen-powered vehicles. The proposed system meets a need for a low cost sensor for on-vehicle safety, pipeline/fueling station monitoring for hydrogen distribution, and has the potential for use in closed-loop fuel cell control loops. In order to meet this emerging market need, MEI is adapting our hydrogen sensing technology and integrating recently developed hydrogen-sensitive nanomaterials into a highly manufacturable system platform. MEI will work with our partners to produce a second generation prototype system that will be tested on hydrogen-powered vehicles.

## Hydrogen Sensor

*Fast, Sensitive, Reliable, and Inexpensive to Produce*

2006 R&D 100 Award Winner

### FEATURES AND BENEFITS

Argonne's hydrogen sensor outperforms competing technologies.

#### Speed

- Requires no warm-up and responds in less than 75 milliseconds in a 2% hydrogen atmosphere. Competing sensors typically take one second to tens of seconds.

#### Sensitivity

- Detects hydrogen concentrations as low as 0.0025% (25 parts per million) without elaborate signal amplification.
- Minor leaks can be found before concentration levels require full system shutdown.

#### Selectivity

- Detects H<sub>2</sub> reproducibly, even in the presence of oxygen, water vapor, and other gases.

#### Low Power Use

- Unlike other sensors, requires no heaters or other supplementary power as some existing sensors do.

#### Simple, Inexpensive Fabrication

- Construction is based on scalable processes routinely used to make electronic components, resulting in minimizing the ultimate cost. Only \$50 worth of palladium is needed for approximately 16,000 sensors.

### Background

Hydrogen is a promising potential fuel for cars, buses, and other vehicles and can be converted into electricity in fuel cells. It also is already used in medicine and space exploration as well as in the production of industrial chemicals and food products.

Safety is an important issue when using hydrogen. An explosive mixture can form if hydrogen leaks into the air from a tank or valve, posing a hazard to drivers, equipment operators, or others nearby.

Commercially available sensors can detect the presence of hydrogen and then close valves, shut down equipment, or trigger alarms. However, current technologies typically have limitations related to cost, speed of operation, susceptibility to interference from other gases, and temperature range.

### Building a Better Sensor

Researchers at Argonne National Laboratory have created a tiny sensor – the world's fastest – that reliably overcomes the limitations associated with current hydrogen sensor designs.

The key to its unique performance is what Argonne researchers call its nanostructured, self-assembled thin-film construction. First, a one-molecule-thick layer of siloxane is applied to a glass substrate. The “sticky foot” of the siloxane molecule binds it strongly to the glass while the rest of the long-chain molecule remains slippery. Onto this slippery layer researchers evaporate an extremely thin blanket of tiny (2 to 10 nanometer) palladium beads.

Palladium particles are chosen because, when exposed to hydrogen, they adsorb the gas and swell slightly to form palladium hydride. In fact, some available “thick film” sensors rely on the different conductivity of palladium and palladium hydride to indicate hydrogen concentration.

In contrast, the Argonne design employs an ultra-thin layer of palladium beads that allows both faster hydrogen adsorption and greater sensitivity due to the mobility of the palladium hydride beads. As the enlarged beads move into contact with each other, they create pathways for electrical current. When hydrogen concentration drops, the particles shrink quickly and revert to palladium. Electrical conductivity also drops.



### Accomplishments

Phase I of this project was highly successful and culminated in an R&D100 award. A team consisting of Argonne National laboratory, MAKEL Engineering Inc and EMTEC completed sufficient industrial development and commercialization of Argonne sensor technology to qualify for the coveted R&D100 award for a nanostructured hydrogen sensor. This Argonne press release describes the technology. Phase II of this project will continue industrial application development by MEI.

### Development of Improved Materials for Integrated Photovoltaic-Electrolysis Hydrogen Generation Systems

Midwest Optoelectronics, LLC  
Project Number: EFC-H1-16-2A  
Project Completed

### Regenerative Solid Oxide Fuel Cell (RSOFC)

University of Dayton Research Institute  
Project Number: EFC-H2-20-2A  
Project Completed

### High Temperature Electrochemical Cells for Hydrogen Production and Regenerative Fuel Cells

NexTech Materials Ltd.  
Project Number: EFC-H2-15-1C  
Project Completed

### Novel Ceramic Hydrogen Sensors for Fuel Cell Applications

NexTech Materials  
Project Number: EFC-H2-21  
Awarded Phase II

#### Objectives

- Develop ceramic-based sensor formulation that is sensitive to low concentrations of hydrogen in air (1,000 ppm – 1%) for use as a safety sensor.
- Demonstrate that sensor does not give false alarms in the presence of interference gases (CO, CH<sub>4</sub>, volatile organic compounds, etc.).
- Demonstrate response time of less than 30 seconds in the presence of 1% hydrogen.
- Test proposed novel platform for improved hydrogen sensor.
- Fabricate a prototype based on the best performing sensor system and platform.

#### Accomplishments

- More tests were conducted to verify the timer circuit design used to control the power to the NiCr heater in the electronics package. The final components were verified and a 150 hour test was conducted. This final design will be on the printed circuit boards used for beta-prototypes.
- Additional testing was done to validate and verify the effect of relative humidity on the performance of the sensor. A test matrix was established to test the impact of the design specifications on performance of the sensor in both wet and dry environments.
- The assembly of the expanded hydrogen sensor test stand is nearly complete and the first round of sensors is scheduled to be loaded in early June 2007. This stand will be used first to evaluate various

sensor fabrication changes to optimize performance and manufacturing cost; then, it will be used to collect calibration data on beta-prototype sensors.

- The latest design for the hydrogen sensor printed circuit board includes the final design for the 555 timer circuit as well as the detection circuit which will sound a piezo-buzzer and turn on a light emitting diode when a pre-set level of H<sub>2</sub> has been reached. The next design iteration will include an onboard relay which will integrate NexTech's sensor into a control system which would automatically shut down the system once the pre-set level of H<sub>2</sub> has been detected. This relay has been ordered and will be tested in a bread-boarded circuit before the PCB design is redrawn.
- A new method for temperature compensation of the sensor signal was developed. The new method is a proportional correction which more accurately compensates temperature fluctuations during both baseline and response conditions. The previous method was a linear offset compensation which worked well to correct the baseline signal, but adversely affected the signal during a response if the temperature was greatly deviated from the average.
- A meeting with Precision Joining Technologies, Inc. (Dayton, OH) was set up for June 6, 2007 to discuss NexTech's needs for joining the sensor elements to the TO8 headers. Several attempts were made by NexTech to attach the sensors using soldering techniques, but the quality of the connection was not satisfactory for long-term stability. Precision Joining has a vast experience in joining similar types of metals using their portfolio of welding processes.
- An alpha-prototype sensor fabricated using a yttria-stabilized zirconia tubular support was tested with a reduced power consumption of only 398 mW. This is the first generation of NexTech hydrogen sensors which have operated at less than 400 mW. The reduction in power consumption is due to improved physical contact of the heater to the inside wall of the tube providing very efficient heat transfer from the resistive coil to the dense substrate.

### High Strength, Low Cost Microballoons for Hydrogen Storage

Powdermet Inc.  
Project Number: EFC-H2-15  
Awarded Phase II

#### Objectives

The goal of this project is to prove the concept and validate a system that delivers 4 wt% hydrogen stored in microballoons, including all balance of plant components and attachment specifications to a current fuel cell stack. This goal has two components: (1) storing at least 6 wt% hydrogen in coated microballoons

and (2) mechanical analysis, balance of plant components and construction of a 4 wt% “black box” prototype hydrogen delivery system.

Specific objectives in support of these goals are:

1. Scale-up carbon microballoon scaffold production.
2. Scale-up SiC coating of carbon microballoons.
3. Demonstrate 2.5-3 GPa coating strength SiC on 1 mm carbon microballoons.
4. Fill microballoons with H<sub>2</sub> at 8-15,000 psi.
5. Design hydrogen testing apparatus for crushing microballoons in a detector chamber.
6. Verify 6-9 wt% H<sub>2</sub> in 1 mm SiC microballoons.
7. Cost analysis and trade study on hydrogen filled microballoons vs. other competing technologies.
8. Determine the balance of plant components for a 4 wt% H<sub>2</sub> system.
9. Build a working prototype hydrogen delivery system “black box”.

### Accomplishments

A major change in project status was reported at the review meeting on March 30. A realistic fuel cell mission for this project involves a 50 W fuel cell that consumes ~2 g H<sub>2</sub>/hr. The corresponding microballoon consumption is ~65 cm<sup>3</sup>/hr or <1 L for a 12-hour mission. Although original objectives included preparation and filling of 40 L of microballoons per day, a net throughput of ~2 L per day of H<sub>2</sub>-filled microballoons suffices to operate two missions per day by conclusion of this project. Moreover, a volume of 65 cm<sup>3</sup> that contains 40 cm<sup>3</sup> H<sub>2</sub> at 9,000 psi suffices to operate the prototype hydrogen delivery system for one hour, thus permitting validation of the system’s operation. These microballoons are assumed to contain 10 wt% H<sub>2</sub>. For comparison, it has been assumed that balloons containing 6 wt% H<sub>2</sub> would permit completion of a system that contains 4 wt% H<sub>2</sub>.

Dimensional requirements for microballoons have been specified provisionally by a scaling analysis. Our target is to deliver microballoons (2+/-0.5) mm diameter to the hydrogen delivery device. Hydrogen content of balloons with variable radius  $r$  varies as  $r^3$  if all balloons are at constant pressure. The delivery device must accept variation in balloon diameter and amount of hydrogen. These variations can be compensated by adjusting the feed rate, which varies as  $1/r^3$ . But released pressure also cocks the feed device in a pneumatic model, where length of a constant-force spring would increase with balloon radius. Details are in the review presentation. Thomas Willis showed that balloon capture mechanisms and hydrogen feed regulators probably can accommodate a radius variation of +/- 25%, although this is a much larger variation than had been supposed. A target diameter of ~2 mm

appears acceptable, but permissible diameter variation needs to be considered further.

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### Electrochemical Coal Gasification with Novel Electrodes

Ohio University  
Project Number: EFC-H2-08  
Project Completed

### Fabrication of Metal-Carbon Nanostructure Composites

The University of Toledo  
Project Number: EFC-H2-22  
Project Completed

### Novel Materials for Reversible Hydrogen Storage

Hy-Energy LLC.  
Project: EFC-H2-11  
Project Completed

### Development of Complex Metal Hydrides for Hydrogen Storage Applications

GFS Chemicals, Inc.  
Project Number: EFC-H2-11-1A  
Project Completed

### Novel Intermediate-Temperature Reversible SOFC for a Renewable Energy System that can Co-Produce Power and Hydrogen

UC-Irvine, National Fuel Cell Research Center  
Project Number: EFC-H2-16

### Objectives

- Evaluate novel reversible solid oxide fuel cell (SOFC) materials sets produced with wet-chemical-route synthesis through preliminary manufacturing (dry pressed button cells) and performance tests;
- Select the best performing materials sets for manufacturability, performance and stability features;
- Manufacture planar anode-supported reversible SOFC button cells using the selected materials set by tape-casting, screen-printing, and co-firing processes;
- Accomplish electrochemical and stability tests of planar anode-supported reversible SOFC button cells; and
- Investigate market and commercialization potential of reversible SOFC technology.

### Accomplishments

In this reporting period significant progress has been made. The major successful accomplishments are:

1. Completed the composite cathode of SSC with LSGMC compositional matrix tests and determined the optimal composite cathode composition;
2. Pretreated the yttrium-doped strontium titanate (SYT) sample in a reducing atmosphere and conducted the four-terminal DC conductivity measurements;
3. Successfully fabricated flat/non-warping composite anode substrates of SYT with LSGMC and LDC by using an in-house tape-caster;
4. Submitted two papers for reporting of results on: (a) the electro-catalytic properties of the SSC-LSGMC composite cathodes, and (b) the emission of criteria pollutants from the glycine-nitrate combustion processes.

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### Reel to Reel Processing for Continuous Thermal Pressing of the Catalyst Film onto a Membrane for the High Volume, Low Cost Commercialization of Hydrogen Generating Membrane Electrolyte

Precision Energy and Technology  
Project Number: EFC-H2-23  
Project Completed

### Electrochemical Conversion of Biomass to Hydrogen

Technology Management, Inc.  
Project Number: EFC-H3-14  
Project Completed

### Improved Hydrogen Liquefaction Process

Praxair, Inc.  
Project Number: EFC-H2-2

#### Objectives

- Reduce the cost for hydrogen liquefaction.
- Reduce the electrical power consumption for hydrogen liquefaction.
- Increase the liquid hydrogen production rate for existing plants.
- Reduce hydrogen distribution costs.

This project will attempt to improve the electrical efficiency of hydrogen liquefaction. Our goal is to reduce the power consumption by about 20%. If this can be accomplished, assuming that the current efficiency is 25%, the final efficiency would be over 30%, which will exceed the 2010 target. Improving efficiency will reduce cost as long as the added capital cost is low enough. Therefore, maintaining low capital cost is another important goal of the project. Any improvement made in this project will apply to both small-scale (existing) and large-scale (future) plants.

#### Accomplishments

- Experimental system designed and assembled.
- Preliminary candidate materials identified.

Tests conducted at low pressure showed encouraging results. Because of this, we upgraded the system to test at pressures up to 400 psig. Tests on the same materials at higher pressure showed that they did not perform as well as they did at low pressure. Initial attempts to modify the materials to optimize high-pressure performance were not successful. Remaining materials development work will focus on modifying the materials so that performance at high pressure can be optimized.

Process development work indicates that the hydrogen liquefaction process will need to be redesigned to take full advantage of the improved ortho-para conversion process. Because some of these process changes could be significant, the next phase of this project will emphasize process development to design an optimized process. The cost of retrofitting existing processes appears to be prohibitive because of required downtime for installation. Further materials development work will focus on developing a material that meets or exceeds the best-performing materials studied to date while also optimizing the materials for the current process conditions. If this can be accomplished, a successful retrofit is more likely.

There is a potential economic benefit based on the results of Task 1. Using the best results to date, it could be possible to reduce hydrogen liquefaction power consumption by more than 1 kWh/kg.

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### Methanol Reformed Hydrogen For Portable PEM Fuel Cell Systems

Protonex Technology Corporation  
Project Number: EFC-H3-19  
Project Completed

### Development of High Pressure Electrolyzers for Backup Power Systems

Proton Energy Systems, Inc.  
Project Number: EFC-H3-3  
Project Completed

### Manufacturing UltraCell's Reformed Methanol Micro Fuel Cells

UltraCell Corporation  
Project Number: EFC-H3-34-1B  
Newly Awarded

### Low-Cost Manufacturing of Multi-Fuel Reactors for an Innovative High-Efficiency Planar Reformer

Delphi Automotive Systems, Inc.  
Project Number: EFC-H3-13-1B  
Project in Renegotiation

### Scalable Steam Methane Reformer System for Distributed Hydrogen Production

Catacel Corporation  
Project Number: EFC-H3-07-1A

#### Objectives

The overall objective of this Phase I project is to demonstrate the technical and commercial feasibility of a scalable steam methane reformer system for the distributed production of hydrogen.

#### Accomplishments

- NexTech has been working on a new low-temperature shift catalyst, and is expected to deliver it to Catacel for testing in early May.
- Considerable effort has been expended to solve the leaky heat exchanger problem. Roughly 30% of the units constructed currently have no leaks.

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### An Innovative and Cost Effective Micro-Process for Roll-To-Roll Solution Casting of Multi-Layer Proton Exchange Membranes with Superior Performance, Transport and Mechanical Properties in High Temperature/Low RH Operating Environments

Chemsultants International, Inc.  
Project Number: EFC-H3-5-1A

#### Objectives

Prove the feasibility of a new manufacturing process for roll-to-roll production of multi-layer PEM's based on interspersed, discrete layers of hydrophilic zirconium particles and recast Nafion<sup>®</sup> polymer developed by Case Western Reserve University that will be solution cast in a layered structure via a novel, advanced process to manufacture thin caliper (12-20  $\mu\text{m}$ ) membranes.

#### Accomplishments

Some initial incompatibility between Nafion<sup>®</sup> and the zirconium phosphate sulfophenylphosphonate (ZrSPP) particles was previously observed. Attempts were made to correct this phenomenon by converting the acid form to the tetraalkylammonium salt prior to addition to the Nafion<sup>®</sup>. However, other rheology issues were found to be unsolvable with the TEA. As a result the tetraethyl ammonium ZrSPP was converted to the acid form for further evaluation.

### Recast Single and Multilayer Membranes

Water uptake and fuel cell performance of selected recast membranes were tested during the reporting period. It was found that composite films containing ZrSPP showed increased water uptake as compared to those cast from neat Nafion<sup>®</sup> solutions. Also, fuel cell tests with a 5-layer composite membrane revealed reduced sensitivity to dehydration due presumably to improved water back-diffusion in the multilayer structure. Further details are given below.

#### Membrane Water Uptake

Good water sorption is one of the most important properties of PEM membranes. Selected membranes were equilibrated with liquid water at 25°C, weighed, dried at 100°C, and then reweighed.

The water uptake was calculated from the dry and wet membrane weights ( $m_{\text{dry}}$  and  $m_{\text{wet}}$ , respectively) as:

$$W = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}}$$

It can be seen that changing the annealing temperature in the range of 130-160°C does not alter significantly water uptake. It is evident, however, that the addition of ZrSPP particles to Nafion<sup>®</sup> induces a significant increase in membrane water content, for both a homogeneous zirconium dispersion and for a 5-layer film.

#### Fuel Cell Tests

Anode and cathode Pt/C powder electrodes were hot-pressed onto the opposing surfaces of a 5-layer Nafion<sup>®</sup>-zirconium membrane to create a fuel cell MEA (with an electrode area of 5.0  $\text{cm}^2$ ). The catalyst loading was 0.4  $\text{mg Pt/cm}^2$  for both the anode and the cathode. The 5  $\text{cm}^2$  cell was run at 80°C with a hydrogen flow rate of 100 sccm and an air flow rate of 500 sccm. After a break-in (conditioning) period, the cell was run with full (100%) humidification of the reactant streams. When the power output stabilized, voltage-current data were collected. The voltage from the 5-layer membrane was lower than that from the Nafion<sup>®</sup> 212 membrane at the same current density. This is due to the greater thickness (and greater electrical resistance) of the 5-layer membrane (90  $\mu\text{m}$ ), as compared to Nafion<sup>®</sup> 212 (70  $\mu\text{m}$  in thickness).

The water vapor content of the hydrogen feed stream was reduced to 50% relative humidity (RH) and the fuel cell performance curves for the 5-layer and Nafion<sup>®</sup> 212 membranes were recorded (after sufficient time for equilibration of the MEA at the new humidity condition). The power output for the commercial Nafion<sup>®</sup> decreased significantly, while the fuel cell performance of the 5-layer membrane remained

unchanged with the decrease in anode humidity. This experiment suggests that the multi-layered membrane structure is helping to promote water back-diffusion from the cathode to the anode during fuel cell operation. Thus, the 5-layer Nafion<sup>®</sup>/zirconium membrane is less sensitive to the anode humidification level. Also, the fuel cell open circuit voltage with the multilayer membrane was significantly higher than that with commercial Nafion<sup>®</sup> 212. This suggests that reactant gas crossover is reduced in the multi-layer composite membrane. More testing is needed to confirm the observed behavior and additional fuel cell experiments are planned for the near future.

### Lab Cast Membranes

Multi-layered Nafion<sup>®</sup> membranes incorporating the ZrSPP particles were produced in the laboratory and tested for mechanical strength and layer uniformity. The targeted total thickness was 2.0 mil (.002 inches). The membranes were cast from DuPont DE-2021 aqueous Nafion<sup>®</sup> solution, 20% solids, with certain percentages of ZrSPP (acid form) on solids. Each individual layer was dried for 15 minutes at 70°C prior to casting the next layer. After the final layer was dried, the entire membrane was annealed at 140°C for 1 hour.

### Optical Microscopy

The prepared films were embedded in microcrystalline wax and cross-sectioned to allow examination of the layered structure with a microscope. Optical microscopy was performed using an Olympus BX41 microscope with an Insight 14-bit Mosaic C-mount digital camera in conjunction with Spot<sup>™</sup> Image Capture Software. Three and five-layered Nafion<sup>®</sup>/ZrSPP composite membranes were prepared in the above manner and viewed under the microscope. Optical micrographs showed the layered structures and an even distribution of layers within the membranes. In addition, the measurements obtained for each layer with the microscope software program correlate exactly with the micrometer readings taken after each casting pass.

### Dispersibility of ZrSPP

The ZrSPP (acid form) material was finely ground with a mortar and pestle and wet with several drops of deionized water. The particles were very hygroscopic and attracted the water easily. After being placed in a sonicating bath for 15 minutes, the solution turned to a clear gel. The gel was left overnight and sonicated once more prior to addition of the Nafion<sup>®</sup> solution. This process seemed to enhance the dispersability of the nanoparticles in the Nafion<sup>®</sup> solution. Previous attempts at adding the nanoparticles to the Nafion<sup>®</sup> solution resulted in large aggregates and non-dispersed material settling out of solution. Membranes made with the new method were much improved and defects were minimal.

### Mechanical Testing

Tensile testing of one and two layered Nafion<sup>®</sup> films with various ZrSPP loadings was performed. Testing was done on both wet and dry membranes. Results show that tensile strength is reduced when membranes are in the wet state. In addition, tensile strength and elongation are reduced upon increased loading of ZrSPP nanoparticles for the 1-layer films. However, addition of layers seems to strengthen the membranes slightly by maintaining the tensile strength even after increasing the ZrSPP loading. Results indicate that addition of ZrSPP in a layered structure does not necessarily impede tensile strength. This will be a positive factor if the conductivity and/or water management of the 3- or 5-layer systems proves better than that of standard Nafion<sup>®</sup> 212.

### Lab Casting of Multilayered (Seven Layers of Alternating Neat and Filled Nafion<sup>®</sup>) Membrane

In preparation for casting of seven or more alternating layers of Nafion<sup>®</sup> (DE-2021) and Nafion<sup>®</sup>/ZrSPP composite material, an application thickness study was performed. The film applicator gap was incrementally increased and dried thickness of the film measured using a laboratory micrometer. Due to the leveling effects of the 20% solids Nafion<sup>®</sup> solution, a maximum value of approximately 0.70 mils can be obtained from one coating pass. This is a usual phenomenon for solutions with lower viscosity and solids content. The thickness data shows that very thin layers can be obtained with the DE-2021 Nafion<sup>®</sup> solution, allowing for subsequent building up of layers numbering seven or ten fold.

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## Nanofiber Paper for Efficient Hydrogen Generation

Inorganic Specialists, Inc.  
Project Number: EFC-H3-6-1B

### Objectives

- Demonstrate nanofiber paper for hydrogen production, and compare it to existing products.
- Develop continuous nanofiber papermaking for the hydrogen generation application.
- Compare different methods of catalyst deposition for its impact on hydrogen generation efficiency.

### Notre Dame's Activity

In general, the Notre Dame work plan is to hold one electrode (the anode) constant, making it larger than the cathode specimens so that the anode is not the limiting factor in electrolysis experiments. Then a series of catalyzed nanofiber paper and commercial electrodes will be tested against this standard for the production of hydrogen, and the relative performance will be evaluated.

But before implementing this plan, we need to verify that the nanofiber mat will not degrade under the test conditions where gas is being generated. Gas generation (especially at high rates) generates tremendous microscopic pounding on an electrode surface, and so corrosion (abrasion) of the electrode is a major issue. This factor has to be understood before we move on to the more refined issue of comparing different catalyzed samples.

An initial test to determine the onset potential for H<sub>2</sub> evolution and the carbon stability in a wet electrochemical cell was carried out. The medium consisted of 0.5 M H<sub>2</sub>SO<sub>4</sub> at an overpotential of 1.7 V vs. saturated calomel electrode. A conductive inert backing of e-beam deposited gold (Au) on stainless steel (SS) was prepared, but the 150 nm thickness of Au was not able to withstand rapid gas generation at high overpotentials. This result showed us it would be wise to do our nanofiber mat testing in a type of cell where the mat can be mechanically supported.

A suitable cell fixture was purchased from H-Tec. This cell should allow for the nanofibers to have the maximum available support due to the use of a perforated metal sheet that physically holds the nanofibers close to the membrane and eliminates possible break-up of the mat during the rapid bubble formation expected. Two 80 cm<sup>3</sup> gas storage tanks were also purchased from H-Tec.

#### **Inorganic Specialists Development Work**

We have been thrown off from our schedule by about a month by a fortuitous development. Applied Sciences has introduced a new nanofiber, PR-25, which is smaller in diameter than the PR-24 product we had previously been using. It is also at least 50 times more conductive. Since most nanofiber paper applications benefit from high conductivity, we have made the decision to switch to using PR-25. This has required some adjustment; PR-25 processes differently from the PR-24 that we are used to, and so the trip to Southeast Nonwovens was postponed until April as we did the work to adjust how we disperse the fiber, and make sure the new fiber releases well from the papermaking support. That development work is now essentially complete.

The advent of this high-conductivity fiber opens up new options; it allows us to design the electrolysis electrode according to Notre Dame's preference, which is to have a nanofiber gas diffusion layer (GDL) combined with a nanofiber catalyst support. We could not do this previously because the GDLs we had made out of PR-24 were not conductive enough. But now we are making and will test a bi-layer electrode consisting of a thick, hydrophobic PR-25 GDL which will have a thin top layer of catalyzed hydrophilic nanofibers.

For the initial testing, a 11"x11" 15-mil thick nanofiber GDL sheet was prepared and treated with a teflon binder to make it water-repellent. This sheet has one extremely smooth (almost glossy) face on it. Samples were cut from this sheet, and a thin layer (0.1 mil) of either catalyzed or uncatalyzed hydrophilic PR-24 nanofibers were deposited onto the smooth GDL face. This creates a bi-layer nanofiber electrolysis electrode, with a thick hydrophobic GDL and a thin hydrophilic surface layer. The uncatalyzed version was prepared so that a catalyst dispersion could be spray-applied. The catalyzed PR-24 nanofibers that were applied to one of these GDLs were prepared by the microwave procedure alluded to earlier.

The PR-25 nanofiber sheet we are testing has been made robust, with a 10% binder content applied in such a way as to retain conductivity. We have placed it in an ultrasonic bath to simulate the high agitation of gas evolution, and it held together nicely. Thus, we are hopeful for its performance in an actual electrolysis cell.

#### **Work by Inorganic Specialists for Related Programs**

Nanofiber paper samples for hydrogen electrolysis from ammonia were prepared and sent to Professor Botte at Ohio University in Athens. Professor Botte will electroplate her catalyst onto these materials, and test them in her EMTEC-funded work. We are furnishing her three types of nanofiber paper. We expect her results will provide both of us with valuable information on how to tailor nanofiber paper for electrolysis.

We have recently sold sheets of hydrophobic-treated nanofiber paper to an automotive manufacturer for evaluation as gas diffusers in fuel cells. This is another potential fuel cell-related product for nanofiber paper.

Graftech in Parma, OH has expressed interest in the papermaking approach as a way to make a high thermal conductivity material from nanofibers. This would be a special high density nanofiber paper developed in a state-funded project in association with Applied Sciences and the National Composite Center. It now seems likely that Graftech will authorize some funds to support the development of continuous papermaking. We plan on using their funds to buy items that will support papermaking in general (such as equipment for feedstock preparation) that are not provided in the EMTEC project. This leverages resources so that both projects benefit.

#### **Publications/Presentations**

1. A presentation at CARBON 2007 in Seattle in July has been scheduled. Also, some of our nanofiber fuel cell work will be presented in a talk by Notre Dame at the Electrochemical Society meeting in Chicago in May.

## Mill Scale-Steam Reforming: A Novel and Inexpensive Route of H<sub>2</sub> Generation for Fuel Cells

University of Toledo  
Project Number: EFC-H3-35-1B

### Accomplishments

Protocol has been established and confirmed for the preparation of zerovalent iron (ZVI) particles using cetyl trimethyl ammonium bromide (CTAB) as a surfactant, butanol as a cosurfactant and octane (oil) as the non-aqueous heterogeneous phase. The molar ratio ( $\omega$ ) of water to surfactant was maintained at 400, i.e.,  $\omega = [\text{H}_2\text{O}]/[\text{CTAB}] \sim 400$ . A freshly prepared aqueous solution of sodium borohydride was added to the Fe mill-scale solution where upon fine black particles, strongly magnetic in nature, were formed instantaneously.

### Process Parameter Optimization for Mill-Scale Conversion Scaling-Up into Nano Iron by Solvothermal Process

Although experiments carried out with commercial FeCl<sub>3,6</sub>H<sub>2</sub>O (Alfa aesar, ACS min 97%) via an ethanol dissolution route produced nano ZVI (NZVI) by the hydrazine monohydrate solvothermal process, experiments with mill-scale solution in mineral acid under identical process conditions for large-scale synthesis failed to result in NZVI. This could possibly be due to the presence of an appreciable amount of acid present in the system. Hence, a different approach eliminating the acid effect was adopted for the large-scale conversion of mill-scale to nanoscale iron. The iron in the mill-scale solution was first precipitated as Fe(OH)<sub>3</sub> with NaOH, centrifuged and dried under vacuum at 60°C and used in the subsequent solvothermal experiments. First, FeCl<sub>3,6</sub>H<sub>2</sub>O was used as the iron source to establish and optimize the process parameters. In a typical experiment, Fe(OH)<sub>3</sub> was precipitated from 10 g of FeCl<sub>3,6</sub>H<sub>2</sub>O with NaOH. The dried Fe(OH)<sub>3</sub> was put in 50 ml ethanol (solvent) and mixed with 12 g of NaOH pellets and the mixture was stirred for 1 hour. Hydrazine monohydrate (100 ml) was added and the reduction was carried out at 100°C for 10 hours and then naturally cooled to room temperature. The vessel was flushed with nitrogen to expel air and pressurized to about 780 psi. The product was washed several times with water and ethanol to remove the impurities. The process has been optimized for 4 g ZVI production from mill-scale waste.

### Metal-Steam Reforming (MSR)

A new gas chromatography unit from Shimadzu was installed. Accessories for the MSR reaction experiment such as a high performance liquid chromatography (HPLC) pump to flow H<sub>2</sub>O, pre-heater to convert water

to steam and condenser to condense excess/unreacted H<sub>2</sub>O were installed and connections were made. Calibration was carried out with a hydrogen-helium mixture in the range 1-30% H<sub>2</sub>. The experimental conditions were as follows: pre-heater temperature: 400°C; reactor temperature: 600°C; helium flow rate: 204 sccm; percent weight increase of the sample: 32-34%, equivalent to the theoretically predicted value.

Two observations are worth reporting. At a pre-heater temperature of 300°C and a reactor temperature of 50°C, condensation of the water was observed on the outside walls of the reactor. This could be due to the presence of water in the line (used for verifying the proper functioning of the HPLC pump). This also implies that water was allowed to react with nano iron even before the data was collected. This led to lower hydrogen generation from MSR in one case. In the next run, it was made sure that there was no water in the line to begin with, by ramping the pre-heater to above 100°C first, which was then connected to the reactor. Under these conditions the increase in sample weight after MSR was equivalent to 32.1% close to the theoretical value. However, it was observed that the stainless steel filter holding the sample also increased due to oxidation by steam under the employed conditions (from 10.04 g to 10.324 g), there by liberating additional hydrogen. Analysis of the gas chromatograph data also confirmed this as the amount of hydrogen generated was more than theoretically possible if the MSR of nano Fe alone was taken into consideration. To avoid this, we plan to employ a ceramic boat as container for nano Fe.

### Design and Construction of a Solar Reactor

In order to eliminate the currently used heat source for initiating and sustaining the MSR reaction, we envision utilizing a solar concentrator and designing a small prototype hydrogen generation set-up based on the solar-powered MSR technique. A design for the solar concentrator to facilitate MSR was arrived at during the meeting with Replex Inc. at Mount Vernon, OH. A 46.5-in diameter shallow polycarbonate reflector with a focal length of 36-in is being fabricated and mounted by Replex. This will be delivered to the University of Toledo for temperature profile determination and parameter optimization for the MSR reactions.

### Preparation of Nanoscale Tubular Membrane for Hydrogen Purification/Separation

MetaMateria Partners LLC  
Project Number: EFC-H3-33-1C

### Objectives

The objective of this project is the development and demonstration of a low-cost, high-flux, nano-enabled tubular membrane technology for the purification/separation of hydrogen obtained by steam methane

reforming. The proposed membrane will incorporate lower cost porous ceramic supports and inorganic separation membrane technologies which were developed independently by MetaMateria Partners (MMP) and Professor Henk Verweij of The Ohio State University (OSU), respectively. The layered inorganic composite will enable the selective diffusion of hydrogen gas at commercial rates. After successful demonstration of the technology in Phase I using a simulated reformer gas stream, Phase II will focus on manufacturing scale-up and commercialization of the technology.

### Accomplishments

A decision was made not to proceed with an injection die designed for producing four alumina tubes per injection. After completing the design, it was determined that sufficient similarities existed in the design and dimensions to an injection die MMP already possessed for production of cathode support tubes that was used in a project funded through the Army Tank-Automotive and Armaments Command. A decision was made to utilize this die rather than incur the expense of having a new die custom manufactured. The die has two cavities, each of which is about 30" in length. After the development problems are resolved with the support tubes using a smaller 8" die, the 30" dual cavity die can also be used to produce tubes in quantity to support the further needs of the project. The development work on the support tubes was focused on elimination of 30 to 50 micron diameter surface pores in the support tubes. The elimination of these large pores is vital to being able to lay down defect-free coatings. The AKP-30 intermediate layer does not fully fill these large surface pores. In order to understand and eliminate the source of these pores, several approaches were investigated. While pores in ceramic bodies can result from a number of different phenomena, including micelles, aggregates, poor mixing and gas-evolving reactions, the most common is probably trapped air that is retained in the slurry due to its high viscosity. The viscosity of the injection slurry can be adjusted by either changing the solids loading, the pH or through the addition of organic surfactants. Changing the solids loading of the slurry may have the undesired effect of causing drying cracks to develop and can also affect the drying and sintering shrinkage of the body. The MMP process utilizes organic additives that act as surfactants to lower the slurry viscosity and improve solids loading; however, these surfactants had not yet been optimized for use with the tabular alumina used in this project.

Zeta potential measurements are used to measure the interaction of the individual particles in a suspension as a function of either pH or surfactant concentration. The zeta potential as a function of pH for the as-received alumina powder was obtained. This curve was measured using a Colloidal Dynamics Zeta Probe. The zeta potential becomes more negative as the pH increases.

The shape of the curve changes with the addition of a surfactant. The curve was measured using the standard concentration of surfactant A to determine which pH would provide the best potential for measuring the impact of the concentration of the surfactant. Based on the curve, a pH value of 9.5 was selected.

A 3 wt% solution of surfactant A was prepared. The zeta potential was measured as a function of the amount of surfactant added. Based on the curve, the optimal amount of surfactant is between 2 and 3 mL of titrant as this is the point where the potential is unaffected by further additions. This level is higher than was being previously used in the tubes. Increasing the amount of surfactant has significantly reduced the presence of pores. It is anticipated that the pores will be effectively eliminated in the coming month.

### Intermediate Support Layer

Little work was done on the application of the intermediate support layer because of the focus on improving the surface quality of the support tubes.

### Diffusion Membrane

The first coatings were applied by OSU using colloidal mixtures prepared by MMP. This was done using a dip coating process where the surface of AKP-30 disks is brought into contact with the colloid. Photographs of the surface after drying and firing were taken without any flash to better capture the dark color of the coating which is attributed to the palladium particles. A scanning electron microscopy (SEM) image of the cross-section of the disk as well as a SEM image of the coated surface were also taken. Based on energy dispersive X-ray spectroscopy of the surface, the bright, large particles sitting on the surface are palladium particles while the zirconia is more uniformly distributed across the surface. These results suggest that the palladium has agglomerated and segregated from the zirconia particles. Lower particle concentrations and the use of surfactants will be investigated to improve the dispersion and the quality of the applied coatings.

### Conclusions

EMTEC is energetically pursuing the near term commercialization of the hydrogen infrastructure technology that in many cases has been developed with previous DOE support. The EMTEC programmatic collaborative approach is well suited to accelerate technology to market. EMTEC has selected high quality projects in the appropriate subject area that have cross cutting materials technology with near term manufacturing opportunities. EMTEC has selected only those projects with viable commercial application for Phase II awards.

**Publications/Presentations**

1. EMTEC exhibited and presented posters at the Fuel Cell Seminar, 2006.
2. EMTEC hosted a program review for active Hydrogen Program Awardees in February, 2007.