II.J.1 Developing Improved Materials to Support the Hydrogen Economy*

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Projected End Date: Continuing 2008

*Congressionally directed project

Objectives

- Manage ongoing technology commercialization projects.
- Collect and review monthly project reports for go/no-go results.
- Prepare quarterly reports from individual project reports; negotiate statements of work for selected projects and evaluate projects for capstone-year Phase IIIs.

Technical Barriers and Technical Targets

The Edison Materials Technology Center (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 hydrogen economy goals as outlined in the "Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan." Preference will be given to cross-cutting materials development projects that lead to the establishment of manufacturing capability and job creation.

Specific barriers for the projects include: Capital Costs, Operation and Maintenance (O&M), On-Board Hydrogen Storage, System Cost, 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.

Approach

EMTEC has used the U.S. Department of Energy hydrogen economy goals as outlined in the "Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan" 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 *3rd MEA Manufacturing Symposium,* held August 21-23, 2007, at the Dayton Marriott.
- EMTEC hosted another highly successful half-day Sustainable Energy Short Course on April 30, 2008 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 a poster at the DOE Hydrogen Program Merit Review, June 19–13, 2008.
- EMTEC continued the negotiations for competitively selected Round 2, and 3 Phase Phase I and 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 and attended individual project reviews for each of the active projects throughout the year since last report.

Future Directions

- Manage ongoing projects.
- Initiate selected capstone projects as approved/ appropriate.
- Collect and review monthly project reports for project performance.

Individual Projects (active; closed projects already reported on are not listed)

Faraday Technology, Inc. (Round 1 - Phase II)

Nanocatalyst Development Employing Electrically Mediated Processing for *Hydrogen Generation*

Project Objectives

The overall objective of the project is to develop a low-cost, mass fabrication technology for catalyzation of membrane electrode assemblies (MEAs) for proton exchange membrane electrolyzers and regenerative fuel cells.

Accomplishments

The MEA tests were carried out in a single cell with serpentine flow channels. Pure H_2 and pure O_2 gases humidified at 75°C were supplied with a flow rate of 150 cm^3 min^{-1} to the anode and cathode compartments, respectively. Polarization experiments were conducted with a fully automated test station at 75°C and at ambient pressure.

The limiting current density increased with the increase in platinum (Pt) loading and saturated at ~62 μg/cm^2 of Pt in the disk (Figure1a). The amount of H_2O_2 produced during oxygen reduction vs. electrode potential in 0.5 M H_2SO_4 electrolyte is shown in Figure 1b. The amount of peroxide formed decreased with increase in Pt loading and is less than 3% on the Pt/polymer-impregnated carbon composite (PCC) electrocatalyst over the entire potential range. Therefore, the Pt/PCC composite electrocatalyst is highly selective (>98%) towards oxygen reduction via a four electron process.

The single cell performance of the Pt/PCC composite catalyst using H_2 and O_2 as fuel and oxidant, respectively is shown in Figure 2 along with the polarization performance of commercial ETEK Pt/C. The polarization curve is comparable to that of a conventional Pt/C catalyst. The cell exhibited current densities of 0.67 Acm^{-2} and 1.2 Acm^{-2} at 0.7 and 0.6 V, respectively.

To date, there are no patents applied for or resulting from this award. However, there is intellectual property associated with the plating cell being developed.

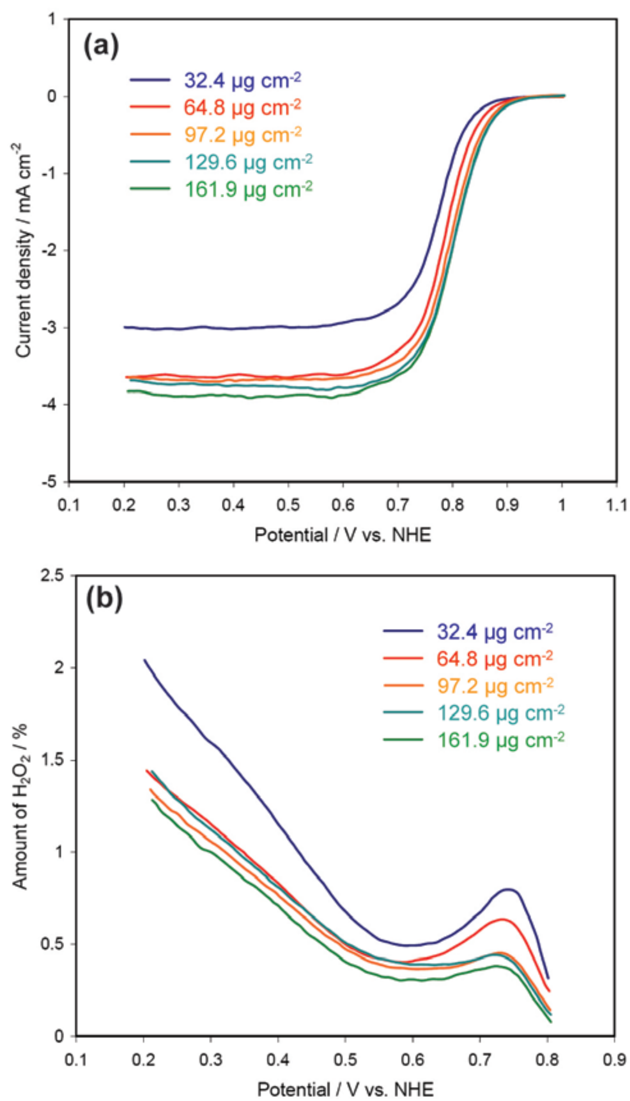

FIGURE 1. Effect of Pt loading on (1a) Oxygen Reduction Reaction Characteristics and (1b) Percent Hydrogen Peroxide Formation of Pt/PCC Catalyst

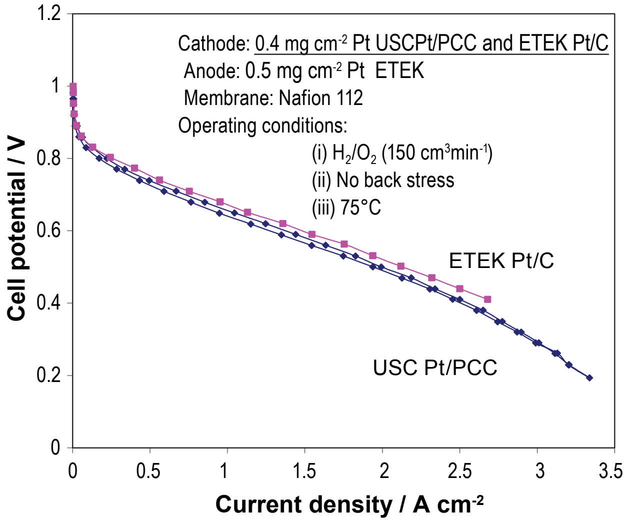

FIGURE 2. Polarization Curve of Commercial Pt/C (ETEK) and University of South Carolina Pt/PCC Catalyst in a 5 cm^2 Fuel Cell

Makel Engineering, Inc. (Round I - Phase II)

Low Cost MEMS *Hydrogen Sensor* for Transportation Safety

Project 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, Makel Engineering, Inc. (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.

Accomplishments

Research and development activities for Phase II are ongoing. Some delays have been encountered as our subcontractors have had to install/repair equipment or had delays in sensor processing due to equipment availability.

During the next reporting period, the following activities will be performed.

- Continue development of second generation/ nanomaterial sensor design, manufacturing plan and fabrication.
- Continue laboratory and field testing of prototype sensors.
- Continue design work for system prototype.

NexTech Materials (Awarded Phase II)

Novel Ceramic *Hydrogen Sensors* for Fuel Cell Applications

Project 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 to give false alarms in the presence of interference gases (CO, CH_4, 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

Electrode Studies: NexTech has been pursuing a production intent design for the deposition of conductive electrodes onto tubular sensor substrates.

Two different alternative electrode designs have been attempted to replace the current configuration. Four different types of samples were tested; the samples were made using a 2 x 2 matrix of different electrode materials. Each of the samples tested were able to sense hydrogen and demonstrated good performance except that each of the sensors had a very high operating temperature to reduce the baseline resistance of the sensor material down to an acceptable level. Each of the sensors operated between 1,200 to 1,500 mW which is nominally twice the heater power required for the current electrode design. The geometry of the sensor electrodes is believed to be responsible for the increased operating temperatures of the sensor.

Sensors were also fabricated using a second substrate material in an attempt to reproduce a design used earlier in the project. Sensors with the new electrode configurations were made in the past without requiring higher heater powers to operate. Samples were tested with both electrode configurations on the new substrates. The required heater input was approximately 800 mW which was much closer to expected values. The conductivity of the tube helps to drop the baseline resistance of the sensor, but does not greatly affect the response of the sensor to hydrogen.

Production Intent Processing: NexTech Materials continued efforts to move toward production intent processes for the fabrication of sensor elements. NexTech is currently looking into purchasing two pieces of equipment which will improve the current manufacturing process of sensor elements. Many of the steps of the fabrication process are currently done by hand which are labor intensive and results in high levels of part to part variation.

NexTech is pursuing two paths to improve the deposition of electrodes onto the support. The current variation in electrode deposition due to hand painting is believed to be a major contributor part-to-part variation among sensor sample since the electrode geometry will greatly impact the measured resistance of the active sensor layer.

Sensor Electronics: A modular approach - split the electronics into at least two units which can be developed independently. The first module to be designed will be the sensor control and signal conditioning module. This board will contain all the components and logic to control the sensor including heater control and temperature feedback for ambient temperature compensation. This board will also condition the sensor signal to convert it from a high impedance resistance to a 0-5 V (or similar) output.

This design approach will allow for greater flexibility in the final design of the sensor device. The control and conditioning module will accomplish necessary functions for any user inputs and outputs. This module will eventually be plugged into a variety of boards which will contain application specific functions, communications and user interfaces. Furthermore, this approach will allow NexTech to begin the electronics design before the final device is decided. A requirements sheet is currently being drafted and a meeting will be scheduled to begin the design of the first module.

Market Study: Fuel Cell Materials completed a market study in which various end users and original equipment manufacturer integrators were contacted to determine their requirements and applications for hydrogen sensors. This data will be used to down-select a sensor device design which matches the strengths of NexTech's sensor technology to the demands of the current hydrogen sensor market.

Powdermet Inc. (Awarded Phase II)

High Strength, Low Cost Microballoons for *Hydrogen Storage*

Project 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: (a) storing at least 6 wt% hydrogen in coated microballoons and (b) mechanical analysis, balance of plant components and construction of a 4 wt% "black box" prototype hydrogen delivery system.

Accomplishments

1. Scale-Up PAN Balloon Production Conditions: Powdermet finalized the parameters to successfully scale up the PAN balloons production
2. Coating Carbon Balloons

   The coated carbon balloons hold some hydrogen, but far away from what we need, and the leaking problem is serious.
3. Coating Alumina Balloons

   SiC coating: For SiC-coated alumina balloons, this is the best category we have so far, 50 psi hydrogen in the balloons. We are assuming each balloons have the same hydrogen pressure.

Proposed Future Work

- Task 1: SiO_2 coated Al_2O_3 microballoons using either TEOS or silane as the precursor
- Task 2: SiO_2 coated carbon microballoons using either TEOS or silane as the precursor
- Task 3: carbon balloons with Kion (dip and paralyze five to ten times)
- Task 4: carbon balloons with starfire (dip and paralyze five to ten times)

Precision Energy and Technology (PET) (Round 2 – Phase II)

Supporting Continuous Reel to Reel, *High Volume, Low Cost MEA Production* with a *Continuous Manufacturing of a GDE Anode and Cathode* Reel Manufacturing Process to Integrate *into the MEA Bonder System*

Project Objectives:

- Develop a system to continuously manufacture an electrode on a reel system of at least 50 meter length (see Figure 3).
- Develop an electrode fabrication method using suitable carbon-carbon-teflon-catalyst (particle-nanofiber-pitch-catalyst-teflon) techniques for improved quality and costs.

Praxair, Inc. (Round 2 – Phase I)

Improved Hydrogen Liquefaction Process

Project 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.

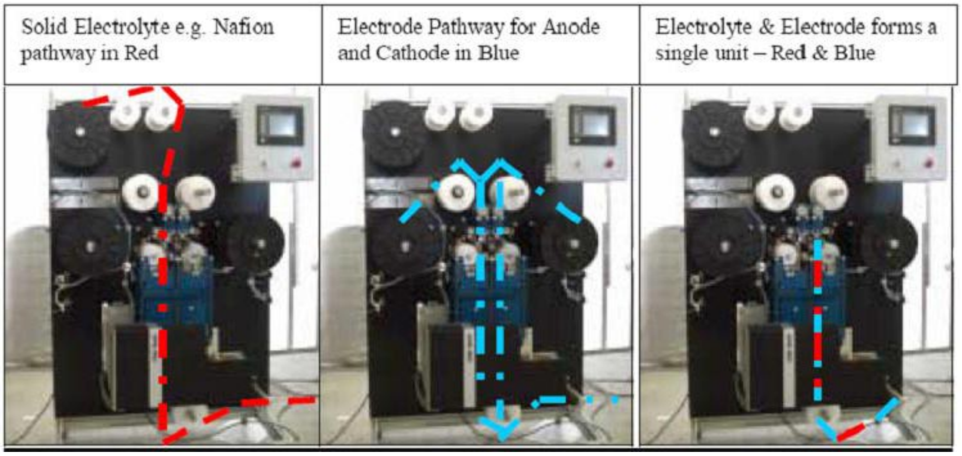

FIGURE 3. PET MEA Bonder Photo

Accomplishments

For all materials, the test sequence outlined in our previous reports has been followed throughout, and multiple tests at preferred conditions have been recorded to verify reproducibility. These repetition experiments have increased our confidence in the results of these demanding tests, but at the cost of putting us about three weeks behind schedule. Testing was completed in December.

Final data analysis and data reduction for all the candidate materials tested throughout the project is also complete. An analysis method has been developed, and associated performance criteria have been derived, to rank the materials and compare our results to project targets. The data reduction phase was completed in January. Results of the tests will be presented in the final report.

Delphi Automotive Systems, Inc. (Project in Renegotiation/Rescope – None to Report)

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

Catacel Corp. (Project Completed)

Scalable Steam Methane Reformer System for *Distributed Hydrogen Production*

Project Objectives

- Show feasibility of using the low-cost Catacel heat exchanger as a platform for service-station hydrogen production.

Accomplishments

- Testing will continue on the new shift catalyst.
- Several batches of heat exchangers had leak issues. This was traced to an employee training issue. We are now able to repeatedly make leak-free batches of heat exchangers.
- Heat exchangers fully characterized on hot gas rig.
- Durability work on heat exchangers will proceed.
- Condenser/vaporizer experiments will proceed.

Chemsultants, International, Inc. (Project Completed)

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.

Project Objectives

Prove the feasibility of a new manufacturing process for roll-to-roll production of multilayer proton exchange membranes based on interspersed, discrete layers of hydrophilic zirconium particles and recast Nafion® polymer that will be solution cast in a layered structure via a novel, advanced process to manufacture thin caliper (12-20 um) membranes.

Accomplishments/Findings

- As expected the control (Nafion® 212) and the multilayer are comparable at 100% relative humidity (RH). The control and multilayer are comparable at 100% RH at the anode and 50% RH at the cathode. However, at 50% RH the control is considerably better. The effect of the zirconium nano-particle at 10% loading is not effective.
- Since the above fuel cell tests of the multilayered Nafion® membranes showed minimal success it was decided to overload the middle layer of a

multilayer membrane using 30% of the ZrSPP nanoparticle. Previous work at Chemsultants and others concentrated on low levels (5-10%) of filler and appear to indicate that these were maximum concentrations for improved conductivities. However, most of the studies concentrated on high humidity and maximum temperatures of 80°C. Recent in-plane conductivity tests of a highly loaded middle layer of a three layer membrane show significantly higher values than neat Nafion® at temperatures of 100°C and humidity levels of 50% and below.

- The three layer membrane provides for the encapsulation of the highly filled, hydrophilic, less durable middle layer and increases the adhesion to the electrodes.
- The mechanical strength of Nafion® decreases with increasing concentrations of ZrSPP nanoparticles. Minimal strength losses occur below 10% ZrSPP concentrations. However to improve the mechanical strength of the highly, filled layer it is necessary to cast thin layers of neat Nafion® on either side of the filled layer.

Inorganic Specialists, Inc.

Nanofiber Paper for Efficient *Hydrogen Generation*

Project 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.

Accomplishments

Notre Dame 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.

Inorganic Specialists Development Work: 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've made the decision to switch to using PR-25. This has required some adjustment – PR-25 processes differently from the PR-24 that we're used to. 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 combined with a nanofiber catalyst support. We couldn't do this previously because the gas diffusion layers (GDLs) we had made out of PR-24 weren't 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.

MetaMateria Partners LLC (Project Completed)

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

Project 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 and Professor Henk Verweij of The Ohio State University, 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

Measurement of the Permeability and Selectivity of the Multilayer Membrane: Two primary difficulties arose during the completion of this task. The first challenge was the identification of high temperature seals to allow testing of the membrane above 250°C. The second difficulty was the well-known destructive α-β phase transition for palladium in the presence of hydrogen below about 300°C.

The combination of these two problems, and the short term of this 12 month project, prevented extensive testing of the membranes. However, the limited results that were obtained show very high hydrogen permeability and suggest high selectivity of hydrogen versus other gases.

EMTEC 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.

EMTEC Publications/Presentations:

1. EMTEC exhibited and presented posters at the Fuel Cell Seminar, 2007.

2. EMTEC conducted status and final reviews as required for projects from July 2007 – June 2008.