

II.J.2 Developing Improved Materials to Support the Hydrogen Economy*

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*Congressionally directed project

commercialization. The subject technology must be related to the U.S. Department of Energy hydrogen economy goals as outlined in the multi-year plan titled, "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.

Approach

EMTEC has used the U.S. Department of Energy hydrogen economy goals as outlined in the multi-year plan titled, "Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan" to find and fund projects with near-term commercialization potential. Our 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 through our request for proposal process which develop novel technologies preparatory to commercialization. EMTEC's overriding objective is technology commercialization.

Accomplishments

- From project start, EMTEC has funded and provided oversight to over 30 projects in various phases of development.
- EMTEC hosted and attended individual project reviews for the active projects and final site visits for the projects completed throughout the year. EMTEC is continuing site visits for remaining capstone projects.
- EMTEC attended the National Hydrogen Association Conference, March 30 – April 3, 2009.
- EMTEC hosted a half-day short course on April 30, 2009 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, May 18 - 22, 2009.

Objectives

- Foster the investigation and advancement of cross-cutting, breakthrough materials technologies to yield an award-winning program with active DOE Hydrogen Office participation (technology commercialization).
- Manage ongoing hydrogen infrastructure projects; collect and review monthly project reports for Go/No-Go results (near-term commercialization of technologies, products and processes in support of the hydrogen economy).
- Prepare quarterly project reports from individual project reports; negotiate statements of work for selected projects.

Technical Barriers

The projects under this award (this period) address a wide range of barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

Technical Targets

The Edison Materials Technology Center (EMTEC) will solicit and fund hydrogen infrastructure related projects that have a near-term potential for

Conclusions and Future Directions

EMTEC has leveraged DOE initiative and funds on a 1 to 1 match basis on this highly successful project; resulting in strong technology advancement as well as job creation and economic development. Having been successful in years past, EMTEC is evaluating various projects for R&D100 Award submissions.

Future Directions

- Manage and close-out ongoing projects.
- Finalize technical governance site visits with all remaining projects.
- Seek new opportunities to continue technology development and commercialization activities as appropriate for the most promising technologies.



Faraday Technology, Inc.

Project: EFC-H4-1A, Tunable Diode Laser Absorption Spectroscopy (TDLAS) Sensor for In-Line Continuous Monitoring of PEM Fuel Cells & Electrolyzers

Project Objectives

- Design and build of single-cell bipolar plates with simple channels and transparent ports parallel to each channel allowing introduction of the diagnostic laser.
- Redesign/adaptation of the TDLAS for sensing down the length of a channel.
- Demonstration of the TDLAS for moisture or oxygen sensing down the length of a channel in a bipolar plate.
- Conceptual design of a TDLAS capable of continuous, sequenced in-line sensing of a fuel cell or electrolyzer stack.
- Estimation of the capital and operating cost of the TDLAS for in-line fuel cell or electrolyzer stack monitoring.

Accomplishments

- Demonstrate ability of the TDLAS to rapidly respond to moisture changes within the bipolar plate channel, and to monitor the moisture content within the range of 0 to 30,000 ppm.
- Conceptual design of a TDLAS application for continuous in-line sensing of multiple ports in a bipolar plate and stack, including monitoring of the interior channels of a bipolar plate.

Introduction: There exists a need for close monitoring of the environmental conditions inside the electrolyzer of fuel cell bipolar plates.

Approach: Develop a standoff TDLAS application, where the measurement path is defined by the combination of a transceiver that illuminates and receives light scattered from a diffuse surface or transmitted through a channel. A transceiver unit transmits the laser beam that, like a flashlight, illuminates a distant diffuse surface. The transceiver collects laser light backscattered from the illuminated surface, and concentrates the received laser power onto the photodetector. The photodetector converts the received laser power into an electrical signal transmitted to a signal processor. The standoff TDLAS signal processor analyzes the photodetector's electrical signal to deduce the amount of target gas contained in the laser path (Figure 1).

Results: Figure 2 shows a plot of moisture concentration within the channel as a function of time. During the experiment, moist air, room air and dry air were alternately purged through the channel, and the results monitored using the TDLAS. Figure 2 shows the ability of the TDLAS to rapidly respond to moisture changes within the bipolar plate channel, and to monitor the moisture content within the range of 0 to 30,000 ppm.

Conclusions and Future Directions: Faraday, with input from Physical Sciences, Inc., designed and built a bipolar plate with sensor ports incorporated into the side of the plate, such that the TDLAS sensor was able to measure the moisture content of the channel. Physical Sciences, Inc. redesigned the TDLAS sensor for insertion into the ports incorporated into the bipolar plate. Design considerations included the placement and angle of insertion of the sensor. Faraday and Physical Sciences, Inc. successfully demonstrated the ability to sense moisture in the channel of a bipolar plate using the TDLAS, with moisture contents from 0 to 30,000 ppm. Faraday completed a conceptual design of a TDLAS application for continuous in-line sensing of multiple

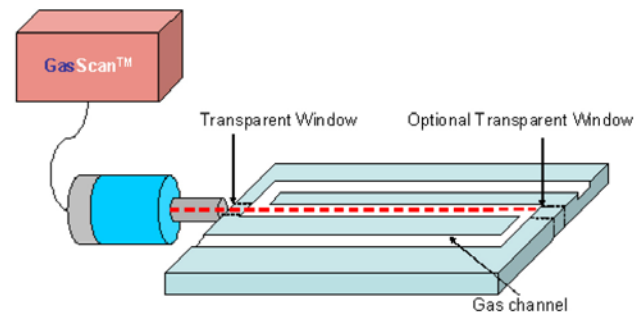


FIGURE 1. Anticipated configuration of the GasScan™ TDLAS sensor for in-line diagnostic monitoring of fuel cell and electrolyzer bipolar plates.

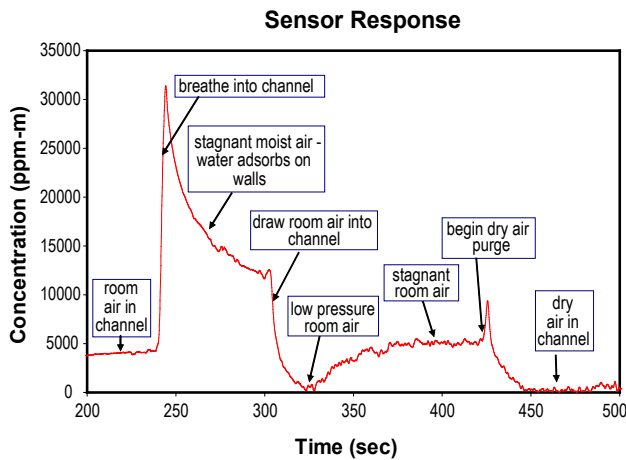


FIGURE 2. Sensor response in the current configuration to changes in moisture within the bipolar plate.

ports in a bipolar plate and stack, including monitoring of the interior channels of a bipolar plate.

At this early stage of development, an estimate has been made of approximately \$10,000 for the TDLAS control unit and \$500-1,000 for each measurement port. With future development, these cost estimates may decrease.

Future Directions: Continue exploring refinements of in-situ sensor technologies.

Makel Engineering, Inc.

Project: EFC-H4-15A, Low Cost MEMS Hydrogen Sensor for Transportation Safety

Project Objectives: A low-cost, high performance hydrogen safety sensor for hydrogen-powered vehicles is in development. 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. A second generation prototype system that will be tested on hydrogen-powered vehicles will be produced.

- Refine nanocluster sensor manufacturing processes for reliable production.
- Develop ultra-low power prototype personal hydrogen sensor system.
- Demonstrate prototype commercial system.

Accomplishments:

Initial prototype layouts have been generated for the ultra-low power circuitry that will allow the system to run for ~1 year without the need to change the battery. The device will incorporate a low-cost microcontroller, which can enter a “sleep” mode up to 99% of the time to conserve power (Figure 1).

Introduction: The use of hydrogen fuel in transportation applications requires the development of compact, reliable, low-cost instrumentation for safe operation and process control. Users and maintainers of these systems require a safety monitoring system, as hydrogen leaks present an explosion risk, especially in early devices as hydrogen containment technology is still being proven.

Approach: Adaptation of MEI’s thin film hydrogen leak detection sensor system originally designed for NASA, for use in automotive applications.

Results: Lower cost, automotive-grade electronics and packaging were designed and are being produced for use in Ford’s demonstration tests. Preliminary investigation of palladium nanocluster sensor elements produced by Argonne National Laboratory was performed by MEI.

Future Directions

- Continue development of “wearable” prototype design.
- Continue laboratory and field testing of low cost prototype sensors.
- Develop plan for additional market entry.

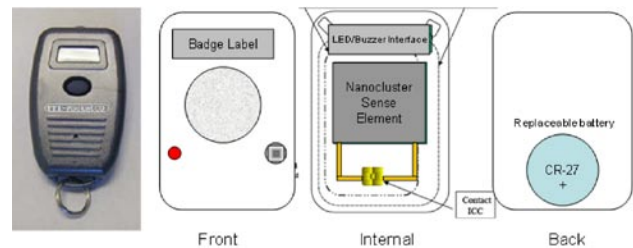


FIGURE 1. Commercially-Available, Keychain-Sized CO Detector (Left) and Concept Drawing of Personal Hydrogen Sensor Badge (Right)

Powdermet Inc.

Project: EFC-H4-12, High Strength, Low Cost Microballoons for Hydrogen Storage

Project Objectives

- Working prototype evaporative coating chamber for powders.

- 1 um Al coating on glass microballoons.
- Varying Al coating on glass microballoons from 100 nm to 2 um.
- Demonstrate 5,000 psi hydrogen storage in commerciality available glass microballoons.
- Record leak rate of 5,000 psi hydrogen-filled commerciality available glass microballoons.
- Coat up to 1 um Al coating onto 5,000 psi hydrogen filled glass microballoons.
- Record leak rate of coated vs. uncoated hydrogen filled commercial microballoons.
- Vary coating thickness from 100 nm to 2 um and measure leak rates vs. storage density.
- Produce 5-10 L of microballoon fuel filled at 5,000-8,000 psi.
- Use Microballoons in Phase II prototype hydrogen delivery system to power a fuel cell.

Accomplishments: Demonstrated that high strength coating using chemical vapor deposition (CVD) in a fluidized bed, very thin, high strength coatings (1-20 um) can be applied to the ultra lightweight (0.05 g/cc) carbon microballoon “scaffolds” in a very cost-effective manner, leaving no residual gas inside the spheres that potentially reduce capacity. In Phase I coatings on microballoons with a thickness of 1-15 μm were deposited.

Introduction/Approach: Powdermet is investigating alternative methods to “lock in” hydrogen to already commercially available high strength glass and silica microballoons for demonstrated use in a prototype delivery device (Figure 1).

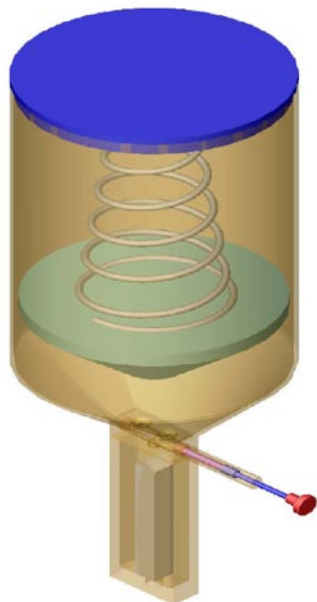


FIGURE 1. Prototype Microballoon Delivery Device

Powdermet’s evaporative powder coatings should take advantage of existing glass microballoon’s already high strength ability to store hydrogen and augment its ability to prevent the hydrogen from leaking over time. Existing glass and silicon microballoons have been shown to hold 10% hydrogen by weight, however, hydrogen leaking is a major problem.

Results: Although the first part of Phase II failed to produce large quantities of balloons that held substantial quantities of hydrogen, breakthroughs in microballoon development essential to other Powdermet products were achieved and a prototype delivery device was fabricated. Table 1 shows the potential for these microballoons to be a very effective weight-based storing solution for hydrogen although their volumetric potential is limited certain applications such as aircraft and personal portable power require weight savings over volumetric savings.

TABLE 1. Theoretical Analysis Meeting DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	DOE 2010 Target	Theoretical Limit Powdermet CVD Coated Carbon Microballoon @ 20,000 psi	Theoretical with Designed 1.5 Safety Factor (practical limit) @ 14,000 psi
Specific Energy	kWh/kg	2	5.49	3.67
Energy Density	kWh/L	1.5	1.32 (Assumes monosized spheres.)	0.84 (Assumes monosized spheres.)

Conclusions and Future Directions: Powdermet can take the state-of-the-art hydrogen-filled glass balloon technology and improve on this by eliminating the hydrogen leaking potential by using nanometer controlled evaporative coatings on the glass microballoons. This technology will enable Powdermet to reach its goal of microballoon hydrogen storage of 10% by weight and augment many other internal Powdermet projects allowing aluminum and other metal deposition on materials at “cold” substrate temperatures without the need for chemical vapor deposition.

Future Directions

- Assembly and operation of evaporative Al system for coating powders.
- Hydrogen storage in glass microballoons and leak rate measurements. Coating hydrogen filled microballoons and leak rate measurements.
- Scale up of process and prototype demonstration.

Precision Energy and Technology (PET)

Project: EFC-H4-23, 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

- Refine a system to continuously manufacture an electrode on a reel system of at least 50 meter length.
- Develop an electrode fabrication method using suitable carbon-carbon-teflon-catalyst (particle-nanofiber-pitch-catalyst-teflon) techniques for improved quality and cost.
- Develop improvements in catalysts blends for better costs and quality of reactions.
- Investigate the use of 3-dimensional catalyst techniques to improve reactions for hydrogen generation.
- Making membrane electrode assemblies (MEAs) more cost-effective and providing the marketplace multiple MEA products at the lowest production cost.

Accomplishments

- Developed reel-to-reel MEA process equipment (Figure 1).
- Developed plan and implement a design of experiments for the best performance versus cost trade-off for a matrix of catalysts types.
- Developed plan and implement a design of experiments for various layering techniques of the catalysts, carbon, and Nafion[®].

Introduction: With the Department of Energy's target of \$30 per kilowatt for proton exchange membrane (PEM) fuel cells, considerable work is needed in the high

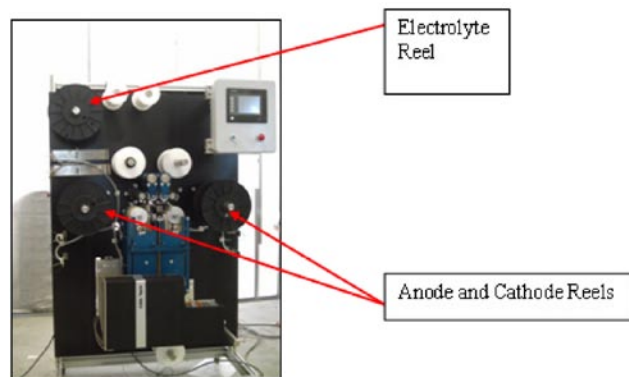


FIGURE 1. PET's MEA Bonder System

speed processing of the MEA bonding process. Up to this point, the majority of global MEA production has been by batch processing. In batch processing, all of the sub-component layers, (electrolyte membrane, cathode layer and anode layer) are pre-cut to size then formed into a single layer by a thermal pressing process.

Approach: MEAs are assembled in the bonder system (Figure 1) by continuously feeding a solid PEM style electrolytic film (e.g. DuPont Nafion[®] 112) from the top left reel and feeding the film down the center of the system. The anode and cathode reels, located on the left and right sides, unwind intermittently and are cut into individual panels that are held in position by pneumatic belts. The timing interval for electrode feed is controlled by the operator's electrode length setting. While platinum continues to be the major player in catalyst reactions, other materials are creeping into the blend. Nickel, cobalt, ruthenium, rhodium, etc. are being considered as part of the opportunities for lowering costs and improving reactions.

Results: Currently, the unit appears capable of producing 1,500 to 2,000 – 50 cm² units per day. At that rate, the MEA Bonder could produce half a million MEAs per year. This unit does have some limitations, though. The original specification required that the electrodes have a minimum of 50 mm to a maximum 150 mm width and a limit of 50 mm to 300 mm length. This does allow for a significant variety in sizes. Initial inquiries were for 6 cm² and 12 cm² area. PET is currently modifying the machine to produce the smaller size MEAs.

A review of the layering techniques in a performance versus costs analysis will provide direction in the manufacturing methods needed to optimize the costs versus performance curve. Evaluations of sputtered and laser ablation of platinum have been observed to produce a significant layer of platinum at .007 mg per cm². While the surface coverage was nearly continuous, the catalyst reaction was not. Additional work with layering the catalyst is showing promise. Some experiments with thin layering of catalyst, carbon, Nafion[®], show improvements worth examining.

Conclusions and Future Directions: Much work is still needed to enable high volume manufacturing of MEA that will meet cost and performance targets now and in the future.

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Special Recognitions & Awards/Patents Issued

1. Provisional Patent Filed: MEA Bonder electrolyte-electrode position control/timing the MEA.

Technology Management, Inc. (TMI)

Project: EFC-H4-14A, On-Farm Soybean-Powered TMI SOFC System Demonstration

Project Objectives

- Demonstrate a fuel cell system producing 1 kilowatt of electricity operating directly on soybean oil.
- Provide additional engineering data necessary for downstream product development.
- Improve the long-term performance of cell and stack components necessary for the demonstration and downstream products.

Accomplishments

- Site selected for demonstration – installation completed April 2009.
- Ten-cell stack operation on natural gas continuously for 1,400 hours.

Introduction: Under this award, TMI utilized this award to augment work for the demonstration of a fuel cell system producing 1 kilowatt of electricity operating directly on soybean oil being conducted on behalf of the Ohio Soybean Council (OSC). The overall demonstration project continued the commercialization efforts of TMI by advancing prototype system testing at an end-user site in order to provide additional engineering data necessary for downstream product development. TMI will use the Phase III funding to improve the long-term performance of cell and stack components necessary for the demonstration and downstream products.

Approach: Building on knowledge from previous short-term demonstrations (at the 2006 OSC board meeting and the 2007 Farm Science Review), this project tested a TMI solid oxide fuel cell (SOFC) system operating on actual end-user loads providing useful alternating current power for a period of approximately 30 days.

For a successful demonstration, improved stack longevity was demonstrated. Under this project, several advanced electrode materials developed by TMI were evaluate for long-term performance in tests of >1,000 hours. These materials were selected for mechanical stability with chemical stability considerations but were verified to ensure satisfactory long-term performance. A preliminary characterization of the advanced electrode degradation under several operating conditions was conducted. A variation was

used as a comparison to the base case. A large stack final evaluation was be conducted and compared to small stack testing. Testing primarily focused on single cells and small stacks but two full-kilowatt scale tests were conducted to benchmark performance as well. In addition, TMI evaluated fabrication methodologies relating to component quality and the impact on long-term degradation.

Results: Figure 1 shows the operation data of the fuel cell system on natural gas >1,300 hours. In the 1,000-2,000 hour continuous operation range, bulk electrode stability was shown to be a challenge.

Conclusions and Future Directions: Despite these challenges, the demonstration provided valuable operational and engineering information while producing usable electricity for the farm at levels similar to those demonstrated in the laboratory. At approximately 1 kW, the system was able to demonstrate 32.4% electrochemical efficiency on soybean oil at the farm.

The demonstration was successfully completed. The test system was decommissioned on June 16, 2009. A post-operative diagnostic was completed and several additional areas for improvement were identified. Overall, the fuel cells themselves were very effective for the demonstration. The catalyst used for this test was less mechanically stable than would be necessary in a full commercial system and will become an area of development. Work will also continue to improve cell and stack quality and performance to increase efficiency. This work will continue under TMI's business plan toward commercialization.

FY 2009 Publications/Presentations

TMI hosted two meeting sessions at the demonstration site sponsored by the OSC. The sessions were attended by representatives from the OSC, members of the Energy Subcommittee of the Ohio State Legislature, representatives from Senator

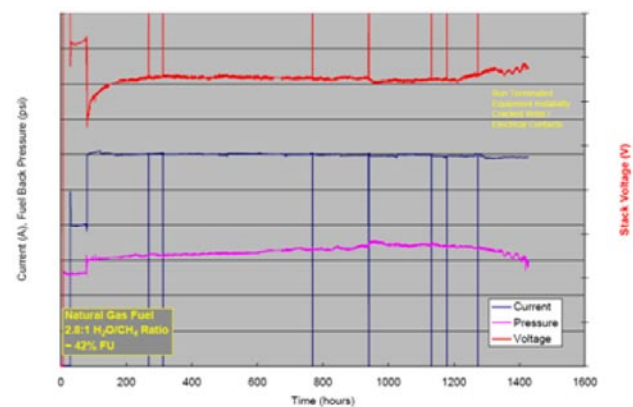


FIGURE 1. Stable Operation on Natural Gas for >1,300 Hours

Voinovich's office, representatives of Lockheed-Martin MS2 Division, representatives from the Ohio Agricultural Research and Development Center of The Ohio State University, local business interests, members of the media and the president of the Thomas Edison Birthplace Association, a direct descendent of Thomas Edison.

Catacel Corporation

Project: EFC-H4-9, Novel Stackable Structural Reactor (SSR[®]) for Low-cost Hydrogen Production

Project Objectives

- Prove technology in large-scale hydrogen generation plants.
- Complete product development and support manufacturing scale up and facilitate market insertion.

Accomplishments

- Documented key operating parameters of reference plant
- Manufactured and installed SSR[®] in reference plant – Similar to the recent Borcelik activity, Catacel will manufacture catalyst for the reference plant. This new catalyst will have a modified design based on the output of Task 1 to prevent the red rings. Working with the plant operator, Catacel will remove and store ceramic catalyst from the reference plant, and install SSR[®] using known methods.
- Document improvements in performance.

Introduction/Approach: The Catacel SSR[®] is intended to be a drop-in replacement for conventional ceramic catalyst media in the stationary steam reforming process that has been used for many years to produce hydrogen from natural gas. Current technology requires that the ceramic catalyst bed be replaced every three to five years due to mechanical degradation of the media. The Catacel SSR[®] will eliminate the periodic replacement that is required for ceramic packed beds. SSR[®] is expected to provide a significant capacity increase (~30%) or a significant energy savings (~20%) in most reformers that use this technology. In an existing plant, simple replacement of catalyst with SSR[®] is expected to show a 1-year payback on investment with energy savings.

Results: One potential SSR[®] problem has been observed at Borcelik. Visual inspection of the catalyst tubes through a peep-hole in the furnace while operating shows red bands that seem to be near the end of each individual SSR[®]. Hydro-Chem has expressed some

concern that these bands are hot spots that could lead to eventual tube failure. They have not, as yet, been concerned enough to require action. At this point, nobody knows exactly how hot the bands are, or if in fact they are a problem. Catacel strongly suspects these bands represent areas of reduced heat transfer, which could negatively impact the overall performance of SSR[®] in some way. In any path forward, Catacel must develop an understanding of the cause and affect of these bands and implement any necessary corrective action.

Very positive upside potential to the SSR[®] is being demonstrated by the Borcelik installation. To date the plant has been running for nearly a month. Installation went very smoothly, demonstrating that there is little or no risk to installing SSR[®] in other plants. And there is clear reward to other plants if the expected performance benefits can be realized.

Conclusions and Future Directions: The SSR[®] is proving itself as a viable cost-effective replacement for ceramic catalyst inserts for hydrogen generation. A Borcelik on-site action plan will be devised based on that activity. This plan will likely involve certain measurements to be made during operation, and methods for SSR[®] removal and inspection that will allow verification of the root cause(s). The plan will also provide for quick replacement or repairs to the Borcelik unit based on findings. Appropriate changes will be made to the baseline SSR[®] design which will eliminate the red ring issue.

Faraday Technology, Inc.

Project: EFC-H1-1-2A, Nanocatalyst Development Employing Electrically Mediated Processing for Hydrogen Generation

Project Objectives

Develop a low-cost, mass fabrication technology for catalyzation of membrane electrode assemblies (MEAs) for proton exchange membrane electrolyzers and regenerative fuel cells.

Accomplishments

- A catalyst-coated membrane approach was used to form thin-film MEAs to decrease the Pt-Ir catalyst loading (from 4 to 1.5 mg cm⁻²).
- Demonstrated composition of 85 wt% Pt and 15 wt% Ir shows higher round-trip efficiency (e_{RT}) at investigated current densities.
- Alpha-scale apparatus was tested and configured to produce a uniform distribution of catalyst across a gas diffusion layer.

Introduction/Approach: Utilize sophisticated, high frequency asymmetrical waveforms to electrodeposit optimized loadings of highly dispersed catalyst particles onto support structures, only in regions with access to all the reaction components (high utilization), for incorporation into an MEA.

Results: In electrolyzer mode (Figure 1), the performance of unsupported PtIr catalyzed MEA is higher than that of unsupported Pt catalyzed MEA due to higher reactivity of Pt-Ir catalyst for the oxygen evolution reaction (OER).

Table 1 shows the conversion efficiency values of unitized regenerative fuel cells (URFCs) at different current densities estimated as described in Ioroi et al. The results indicated that the composition of 85 wt% Pt and 15 wt% Ir shows higher round-trip efficiency (ϵ_{RT}) at investigated current densities.

Bifunctional electrocatalysts for oxygen electrode of an URFC were prepared with unsupported Pt and Ir black catalysts. The electrochemically active surface area and oxygen reduction reactivity of 85Pt:15Ir (composition of Pt:Ir is 85:15) was comparable to those of Pt black catalyst (composition of Pt:Ir is 100:0). The

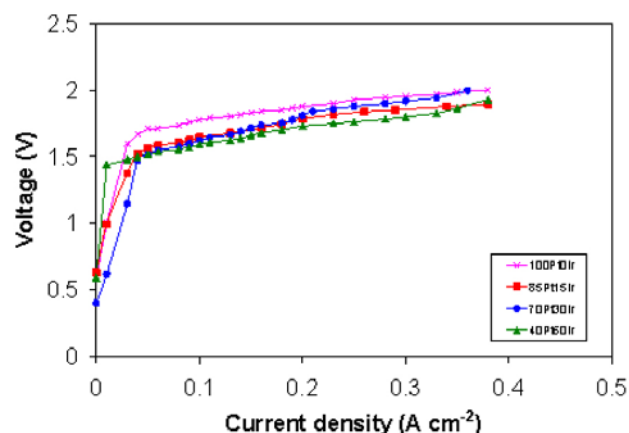


FIGURE 1. Current-Voltage Curves of Different Pt-Ir Catalysts in Water Electrolyzer Mode at 20°C

TABLE 1. Energy Conversion Efficiency of an URFC with various compositions of Pt-Ir Catalysts

Current density (mA cm ⁻²)	Composition of Pt and Ir	V _{FC} (V)	V _{WE} (V)	ϵ_{RT} (%)
50	100 : 0	0.832	1.71	49
	85 : 15	0.802	1.562	51
	70 : 30	0.652	1.516	43
	40 : 60	0.518	1.520	34
100	100 : 0	0.775	1.776	44
	85 : 15	0.740	1.645	45
	70 : 30	0.545	1.622	34
	40 : 60	0.313	1.592	20

onset potential for OER of the Pt-Ir black catalyst is about 240 mV more negative than that of the Pt black catalyst, which implies that unsupported Pt-Ir black catalyst is more effective than Pt black catalyst for oxygen evolution reaction. Based on the electrochemical characteristics of unsupported Pt-Ir catalyst, it is found that an URFC using 85Pt:15Ir catalyst shows highest round-trip efficiency at different current densities.

Conclusions and Future Directions: The processes and techniques developed in this work lead to implementation of an industrial process to produce in situ alloy deposits for a multitude of applications. For instance, these electrically mediated techniques can be reapplied for the production of solar cells, disinfection electrodes, corrosion production, thin film magnets, etc. Furthermore, the beta-scale reel-to-reel system will reduce the production cost and time, for any of these processes.

Inorganic Specialists, Inc.

Project: EFC-H3-6-1B, 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: Nanofiber paper is a platform technology. There are many applications for it beyond fuel cells. During the course of this project, some of these applications were pursued for other programs. The link that relates those other projects to this one is the manufacturing angle. Developing the ability to manufacture is a key milestone that will benefit all of these other embodiments of the paper.

The killer application for nanofiber paper – silicon-coated nanofiber paper as an anode in a lithium ion battery.

- A specially made nanofiber paper was silicon coated by Ultramet. Transmission electron microscopy analysis showed that the coating was about 23 nm thick, and that the sample was about 30% Si by weight. Silicon-coated nanofiber paper shows >1,000 mAh/g of energy storage, with stable cycling and low first-cycle irreversible loss. This is breakthrough, transformational technology of huge importance. A patent application has been filed.

High Density Nanofiber Paper for Thermal

Conduction: As part of a state-funded project, Graftech is interested in the papermaking approach as a way to make a high thermal conductivity material from nanofibers. Some samples have been provided to them for their analysis. Some of these had densities as high as 0.84 g/cc (normally the paper is closer to 0.2 g/cc). Other similar samples have been sold to Eaton Industries for the same purpose.

- **Other Electrolysis Testing:** Nanofiber paper samples for hydrogen electrolysis from ammonia were prepared and sent to Prof. Botte at Ohio University in Athens. Prof. 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.
- **Gas Diffusion Layer Material:** During this project we were approached by a major auto manufacturer, and subsequently sold them sheets of hydrophobic-treated nanofiber paper made to their specs for evaluation as gas diffusers in fuel cells. This is another potential fuel-cell-related product for nanofiber paper.
- **Larger Size Handsheets:** An apparatus was constructed to prepare extra large sheets (18"x18") of nanofiber paper for an Air Force Proproject.
- **Aerospace Composites:** During the project, individual sheets of nanofiber paper that were 12"x 12" in dimension and 10-20 mils thick were prepared for both Lockheed Martin and Boeing.
- **Nanofiber Paper with Nickel Nanostrands:** A paper variety with a heavy content of nickel nanostrands was prepared for an Air Force Proproject, and tested for its Lightning Strike protection.
- **Modifications of Commercial Fuel Cell Products:** A project is currently underway with BASF to modify their commercial fuel cell anodes and cathodes with nanofibers to improve their catalyst utilization and performance.

Introduction/Approach: Our studies have shown that nanofiber paper produces excellent catalyst utilization in fuel cells. Thus it makes sense to examine electrolyzers, which are essentially fuel cells operated in reverse, to see if the high surface area and catalytic enhancement of the nanofiber paper produces high efficiency, high output hydrogen generation (Figure 1). Furthermore, the practical application of this technology hinges on being able to make nanofiber paper commercially, and so the project includes the development of the first demonstration unit for continuous nanofiber papermaking.

Results: Test samples were prepared by modifying commercial MEA backings with combinations of hydrophobic and hydrophilic carbon nanofibers. Five

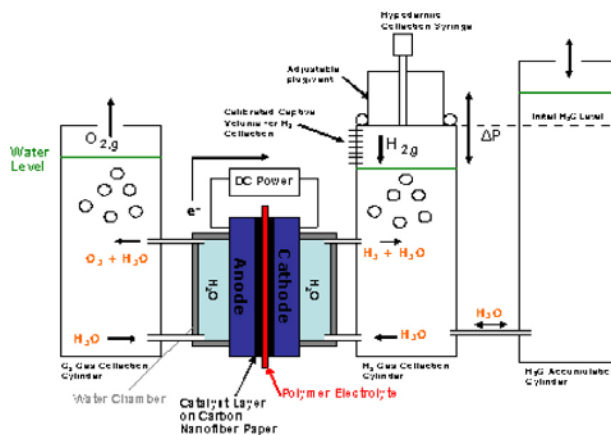


FIGURE 1. Water Electrolyser System to be used to Evaluate Nanofiber Papers as Catalyst Substrates

different combinations were examined. The first was made with pure hydrophobic nanofibers (labeled ‘0’). Then there were MEA samples made from hydrophilic/hydrophobic mixes of 25%, 50% and 75% (labeled ‘25’, ‘50’ and ‘75’, respectively). The purely hydrophilic nanofiber MEA was referred to as ‘100’.

The performance of the nanofiber MEAs shown in Table 1 did not match that of the standard. The first test at the low current of 35 mA resulted in similar efficiencies ~50% from all of the samples. However at higher currents the majority of the MEAs exhibited poorer efficiencies. The exception was the 25% hydrophilic sample, which maintained reasonable efficiency at all current levels, but still did not outperform the Toray standard. Note for the ‘0’ and ‘50’ samples at 75 mA the efficiency was so poor that the potential was beyond the measurable limit of the galvanostat. In these instances no reliable efficiency can be calculated, which is why these results are missing from Table 1. We can estimate that on those two occasions the efficiency would have been less than 10%

Further evidence of the degradation of the samples was observable with the potential sweep experiments. Examples of the potential sweeps of two samples ‘100’ and ‘25’ are presented in Figure 2. Initial scans were similar to the Toray standard peaking at ~-2 V and

TABLE 1. Performance of Nanofiber MEAs

	35 mA	55 mA	75 mA
Toray	57%	54%	59%
0	25%	11%	x
25	58%	50%	41%
50	49%	9%	x
75	48%	40%	32%
100	43%	36%	18%

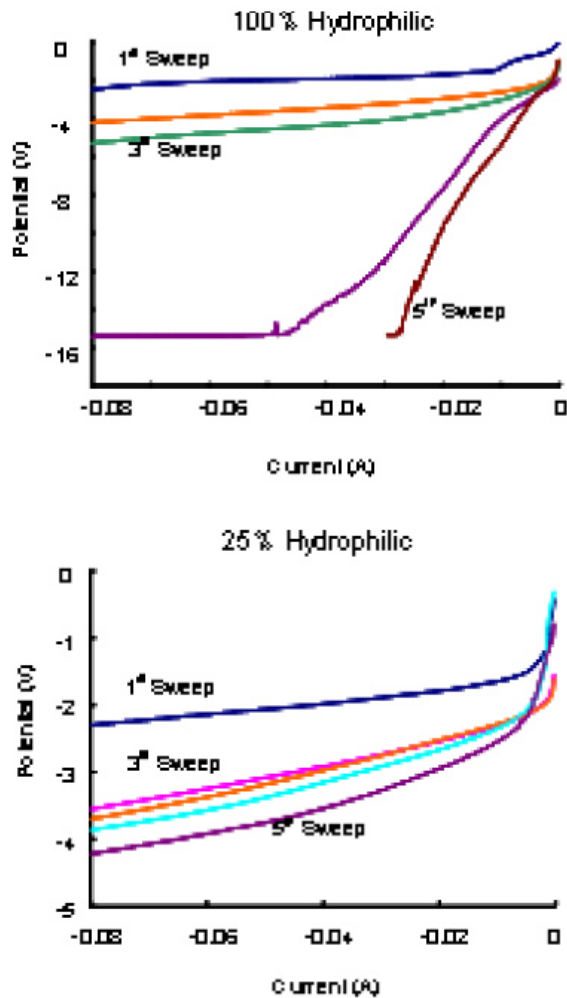


FIGURE 2. Potential Response of '100' and '25' when the Current was Swept to -80 mA

-80 mA. However subsequent runs failed to reproduce the initial performance. For the 100% hydrophilic sample each sweep was substantially worse than the previous one, until the last two sweeps hit the galvanostat's measuring limits. The best nanofiber sample ('25') also failed to reproduce its first sweep but did at least become consistent with sweeps that would

plateau to ~4 V at -80 mA. Even though this stability was the best seen of all of the nanofiber samples it was still worse than the Toray standard.

Conclusions and Future Directions: Our conclusion is that nanofiber samples prepared in this way (thin coatings on commercial supports, with sprayed-on catalyst) do not perform better than standard commercial electrolysis materials. The best sample which was made up of 25% hydrophilic and 75% hydrophobic nanofibers was not significantly different from the Toray standard at low current densities.

This behavior is in contrast to enormous performance improvements seen in a fuel cell configuration for both methanol oxidation and oxygen reduction. This implies that the advantages gained from nanofibers in the hydrogen and methanol oxidation reactions are of no consequence in the hydrolysis reaction. This was by no means an exhaustive study and it may still be possible for a nanofiber MEA to outperform a Toray MEA. Other parameters that may affect an MEA's performance should be considered (e.g. fabrication variables like pressing at higher temperatures). To create an electrolysis MEA with radically better properties will probably require a different fabrication process. Catalyzed nanofiber paper has been shown to enhance the performance of fuel cells through improved catalyst utilization. This project sought to translate those benefits to the reverse process of a fuel cell, electrolysis and hydrogen generation. It was ultimately found that the turbulent conditions and/or stressful voltages that accompany electrolysis were not compatible with the morphology of our catalysts on our nanofibers. Although we cannot rule out that the approach itself has merit, the procedures and materials we examined did not give the results that were sought.

Nonetheless, the design and creation of the first carbon nanofiber papermaking unit was a major achievement from this project. Nanofiber paper is a platform technology for a host of energy-related and composite applications, and the ability to manufacture it represents a true milestone in transitioning it from the lab to the commercial sphere.