

VII.6 Florida Hydrogen Initiative*

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Contract Number: DE-FC36-04GO14225

Subcontractors:

- EnerFuels, Inc., West Palm Beach, FL
- Florida Atlantic University, Boca Raton, FL
- Florida Solar Energy Center, Cocoa, FL
- SRT Group, Inc., Miami, FL
- Electrolytic Technologies Corporation, Miami, FL
- Florida State University, Tallahassee, FL
- Bing Energy, Inc., Tallahassee, FL
- Florida Institute of Technology, Melbourne, FL
- University of South Florida, Tampa, FL

Project Start Date: October 1, 2004
Project End Date: December 31, 2012

*Congressionally directed project

Fiscal Year (FY) 2012 Objectives

Develop Florida's hydrogen and fuel cell infrastructure and to assist the U.S. Department of Energy in its hydrogen and fuel cell programs and goals by:

- Developing hydrogen and fuel cell infrastructure
- Creating partnerships
- Sponsoring fuel cell and hydrogen research and development
- Facilitating technology transfer
- Developing industry support
- Developing unique hydrogen/fuel cell university level education programs

Technical Barriers

This project addresses technical barriers from the Technology Validation section of the Fuel Cell Technologies

Program Multi-Year Research, Development and Demonstration Plan as follows:

- (A) Lack of Fuel Cell Vehicle Performance Data and Durability Plan
- (C) Hydrogen Storage
- (D) Lack of Hydrogen Refueling Infrastructure Performance and Availability Data
- (G) Hydrogen from Renewable Resources
- (H) Hydrogen and Electricity Co-Production

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the DOE Technology Validation milestones 6, 11, and 24 from the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan.

- Validate onboard cryo-compressed storage system on a technology development vehicle achieving 1.5 kWh/kg and 1.0 kWh/L. (2Q, 2007)
- Decision to proceed with Phase 2 of the learning demonstration. (2Q, 2010)
- Validate a hydrogen cost of \$3.00/gasoline gallon equivalent (based on volume production). (4Q, 2009)

FY 2012 Accomplishments

- Project solicited proposals to conduct work.
- Project composed of 12 projects with three projects completed.
- Four projects scheduled for completion on June 30, 2012.
- Five projects scheduled for completion on December 31, 2012.



Introduction and Approach

The Florida Hydrogen Initiative (FHI) is a hydrogen and fuel cell project funded for the purpose of developing a hydrogen and fuel cell infrastructure. The FHI project has operated by funding individual projects which conduct the research, development and demonstration activities. Each of the individual projects have been approved by DOE and each project is then issued a subcontract with tasks, deliverables and a budget. At the present time, there are nine active projects with four in fuel cells, three in hydrogen and two in hydrogen and fuel cells.

Individual Project Descriptions

The nine active projects are briefly described as project tasks in the remaining sections.

Task 2. Methanol Fuel Cell Vehicle Charging Station
(Old Title – Hydrogen Technology Rest Area), Michel Fuchs, EnerFuel, Inc., (561) 868-6720 x239

This project is the oldest active project beginning in 2006. The project objectives are to design, construct, and demonstrate a 10 kW net polymer electrolyte membrane (PEM) fuel cell stationary power plant operating on methanol, to achieve an electrical energy efficiency of 32% and to demonstrate transient response time <3 ms. The project activities have completed the installation of the fuel cell at an electric vehicle charging station located at Florida Atlantic University in Boca Raton, FL. The system is undergoing testing and operation data is being collected. EnerFuel intends to finish the project by June 30, 2012. During a project visit, M. Fuchs stated that there would be dollars left over from the project and that EnerFuel would like to apply these remaining dollars to the bipolar plate project. Action on the change is awaiting further information from EnerFuel.

Task 7. Chemochromic Hydrogen Leak Detectors for Safety Monitoring – Dr. N. Mohajeri and Dr. N. Muradov, FSEC, (321) 638-1525

The objective of this project is to develop and demonstrate a cost-effective, high specific chemochromic (visual) hydrogen leak detector for safety monitoring at any facility engaged in handling and use of hydrogen. The work will lead to a new generation of versatile chemochromic hydrogen detectors that employ “smart” materials that cost less, possess fast discoloration kinetics, are user-friendly, are reliable and have superior field worthiness. Project scheduled for completion on June 30, 2012. The yearly results are summarized as follows:

Irreversible Sensor

- TiO_2 is the original material and the one that Japanese have patented. New material has been formulated with TiO_2 and Pt. (Dr. N. Mohajeri formulation.) Results show five times quicker response time than original material.
- Barium sulfate (BaSO_4) is a new pigment developed by N. Mohajeri. This material replaces the material in Japanese patent and is undergoing environmental testing by FSEC. Two provisional patents on material have been submitted.
- Outlook for project is very promising assuming that a manufacturing company is found for production and marketing (3M has expressed interest).

Reversible Sensor

- Synthesized and tested more than 20 novel molybdenum-, tungsten- and vanadium-based chemochromic formulations. Determined the effect of co-catalyst/activator on the rate of coloration in presence of H_2 .
- Evaluated the performance (sensitivity) of the sensors at different H_2 concentrations in air (from 1 to 100 vol.%).
- Determined the extent of interference with other reducing gases (CO , NH_3 , CH_4 , H_2S). Found no interference.
- Main work on tungsten- and molybdenum-based materials. FSEC has already received patent on reversible hydrogen sensing materials developed by Dr. N. Muradov.
- Outdoor and ultraviolet exposure for three months has shown slow degradation. Materials, particularly, Mo-based pigments, are ultraviolet sensitive. Materials work indoor.

Task 8. Development of High Efficiency Low Cost Electrocatalysts for Hydrogen Production and PEM Fuel Cell Applications – Dr. M. Rodgers, FSEC, (321) 638-1709

The objectives of this project are to develop highly active metal alloys with low Pt loading and metal-metal oxide-based electrocatalysts having nanosized grains. The new catalysts will be evaluated for their activity toward oxygen reduction applications for PEM fuel cells. The relevance of this project is that Pt and its alloys are the most effective PEM fuel cell catalysts, but their use is impeded by costs and the efficiency of the oxygen reduction reaction.

The main results is the development of a process of applying Pt to gas diffusion layer (GDL) using Pt nano particle (2 nm) seeds. The nano-particles are applied by sonication in a colloid solution and the Pt is applied by electrodeposition using rotating disk electrodes (400 rpm) in Pt solution. The results show the same performance as a commercial catalyst, but at one fifth the amount of Pt. These results assume that Pt is evenly distributed.

Future activities are to complete testing and to scale up size from 1 cm^2 to 5 cm^2 . Work has shown the need to develop a new process for the scale-up application. Present plans are to have a stationary GDL with fluid flow around the GDL. The work will also examine the use of other electrode materials.

Task 9. Understanding Mechanical and Chemical Durability of Fuel Cell Membrane Electrode Assemblies – Dr. D. Slattery, FSEC, (321) 638-1449

The objective of this project is to increase the knowledge base of the degradation mechanisms for membranes used

in PEM fuel cells. The approaches to mitigate membrane degradation can be classified into three areas: membrane composition changes; radical quenching; and platinum band formation mitigation. To meet the project objectives, four tasks are being conducted: (1) chemical mitigation of membrane degradation, (2) evaluation of platinum band formation, (3) development of Pt band formation mitigation strategy, (4) combination of chemical mitigation and Pt band reduction.

The results show that the addition of ceria (cerium oxide) has given durability improvements by reducing fluoride emission by an order of magnitude during an accelerated durability test (fluoride emission is measure of membrane degradation). Ceria has also shown two-fold decrease in open circuit voltage decay (taken from accelerated durability test). Ceria is radical scavenging additive to Nafion[®] membrane and has shown 5-fold reductions in fluoride emissions during liquid Fenton tests (commonly used to determine stability ex situ to fuel cell).

Other results show that PtCo/C is better than Pt/C (Cobalt and Pt are deposited on carbon support material) and that the incorporation of a heteropolyacid sublayer reduces fluoride emission by 2-3 factor. However, the sublayer is detrimental to cell performance and the process needs to include heteropolyacid as part of Pt layer to avoid performance degradation.

Project work is continuing by Benny Pearman, a UCF Ph.D. student, who is conducting research (oxidation state, Fenton testing) on ceria materials. He is currently focused on chemical behavior during fuel cell operation. He has also submitted proposal to the Oak Ridge National Laboratory (proposal accepted) to use their scientific instruments to assist in ceria and Pt band evaluation. The final report is in preparation.

Task 10. Production of Low-Cost Hydrogen from Biowaste (HyBrTec™) – Mr. R. Parker, SRT Group, Inc., (305) 321-3677

This project solves some of the problems associated with conventional biowaste-to-fuel processing using anaerobic digester by exploiting two thermochemical advantages that reduce both the cost and energy of converting waste-to-fuel. First, at moderate temperatures and pressures the chemical reactions are fast, the product yields are high, and significant thermal energy is released. This minimizes the size of equipment and use of the co-produced heat. Second, the intermediate hydrogen carrier chemical bond is weak, requiring less energy to free hydrogen than the hydrogen will produce as a fuel when burned with oxygen from air.

The project approach is a process which produces hydrogen bromide from wet-cellulosic waste and co-produces carbon dioxide. Next, electrolysis dissociates hydrogen bromide ($E^{\circ} = 0.555$ V) producing recyclable bromine and

hydrogen (endothermic). The hydrogen can then be used for combustion or in a fuel cell for power.

A bench-scale unit has completed testing and the results are being compiled. The unit is a reactor surrounded by a heating coil. Two ¼" diameter rods are immersed in the reactor and serve as cathode and anode of the electrolyzer. Results show that more cathode surface area is needed for electrolyzer and that the process can operate at 180°C. The initial analysis believed that the temperature would be higher at 225°C. Future plans are to separate reactor and electrolyzer and to get a glass lined reactor from De Dietrich (NJ) and an electrolyzer stack from Electrolytic Technologies Corporation of N. Miami Beach, FL.

Task 11. Development of a Low-Cost and High-Efficiency 500 W Portable PEMFC System – Drs. J. Zheng, R. Liang, and W. Zhu, Florida State University, Mr. H. Chen, Bing Energy, Inc., (850) 410-6464

The project research objectives are to develop a new catalyst structures comprised of high conducting buckpaper and Pt catalyst nanoparticles coated at or near the surface of buckpaper and to demonstrate fuel cell efficiency, durability improvements and cost reductions by using buckpaper based electrodes.

Project results are that Dr. Zheng has been working with Bing Energy, Inc. on the optimized single cells with buckpaper supported catalyst. Bing Energy has focused on the stack design, modeling, fixture, and tooling to accomplish the manufacture of membrane electrode assemblies (MEAs), components, and stack. The project has tested the performance and durability of the single cell per DOE's testing protocols to optimize the design. A table showing 2017 DOE Targets and current results achieved at Florida State University for electrocatalyst and MEAs has been presented. These results show the meeting of selected DOE performance goals and expectation of meeting all DOE goals.

Task 12. Interdisciplinary Hydrogen and Fuel Cell Technology Academic Program – Florida Institute of Technology, John Politano, Carolyn R. Lockyer, Mary Helen McCay, (321) 674-8960

This project has the objective to develop a hydrogen and fuel cell technology (HFCT) academic program at the Florida Institute of Technology (FIT) in Melbourne, FL. The FIT HFCT program will allow students to follow hydrogen technology from introduction to long-term applications, to obtain a basic understanding of the fundamentals of the field, to redirect their current technology focus as a means for new career options, to measure students' gains in knowledge of hydrogen as a fuel source, to interact with outside industries and to satisfy the need for hydrogen technology graduates.

The project results are the development of hydrogen- and fuel cell-related modules that have been implemented

into courses in the General Chemistry laboratory, MAE and Sustainability Engineering. A new hydrogen technology course will be implemented in both CHE and MAE as part of the new MSME and MSChE specializations in hydrogen technology. Projects were identified for consideration as junior/senior design projects. Surveys have been administered in courses in both the College of Engineering and College of Science to determine how the new hydrogen curriculum impacts student' knowledge and opinions of hydrogen and fuel technology.

New courses developed were: MAE 5330, Principles of Fuel Cells, CHE 5240, Electrochemical Engineering, and CHE 5250, Hydrogen Technology. The program specializations and new courses have been approved by the Florida Tech College of Engineering Council and the Florida Tech Graduate Council.

Task 13. Design and Development of an Advanced Hydrogen Storage System using Novel Materials – Drs. E. Stefanakos, D. Goswami, and A. Kumar, University of South Florida. (813) 974-4413

The project goal is to design and develop novel conducting polymeric nanomaterials for onboard hydrogen storage with a system gravimetric capacity of 5.5 wt% or greater and completed reversible hydrogen storage characteristics at moderate temperature (<100°C). The proposed approach was to conduct synthesis of polyaniline (PANI), a solid state hydrogen storage material and to modify the synthesis parameters for optimized storage capabilities. The major challenge is to develop polymer nanostructures that can store hydrogen at room temperature, and be reversible for many cycles.

Results show that the PANI storage figures originally reported by other researchers could not be duplicated at USF. As reported the results in the first two references were obtained from polymer samples provided to USF by a center in Italy. Later on USF tried to reproduce the results with samples obtained from the same individual or produced by us following similar manufacturing methods, but we were unable to duplicate the results. After going back and forth between the University of South Florida and Tuskegee University, we have come to the conclusion that our pressure-concentration-temperature instrument may not have been working correctly at the time we obtained the initial results indicated in the first two publications. Presently the gravimetric densities we are able to measure are less than 1%. The present approach is to modify the polymers in an effort to increase the gravimetric density.

Task 14. Advanced HiFoil™ Bipolar Plates – Mr. J. Braun, EnerFuel, Inc., (561) 868-6720

The project relevance is to address cost and durability barriers for high-temperature proton exchange membrane

fuel cells by providing a low cost, easy to form, corrosion-resistant laminate bipolar plate having high thermal conductivity and improved mechanical strength/crack resistance. The expected results will lead to longer life, high power density fuel cell stacks and better thermal management/cell heat transfer.

The project results showed that embossing could not be accomplished because the graphite was too rigid and brittle. The new concept is to replace interior metal sheet with sheet of graphite and to make the sheet continuous except for holes for ports. Outer sheets are made of graphite composite materials with the flow channels done by a molding process. The flow channels are presently machined. EnerFuel has operated a 4-cell stack (130 W) and a 36-cell stack (1.2 kW) that demonstrated the bipolar plates resistance to the electrochemical and acid MEA environment within the fuel cell. In a 36-cell test, the results showed that the heat transfer characteristics of the bipolar plate produced low cell-to-cell temperature and voltage variations. Based on these positive results, the company plans to demonstrate scalability by building a 132-cell stack (4.6 kW) that could be used for stationary fuel cell applications, such as telecommunication backup and micro-CHP, and transportation applications such as truck auxiliary power units and electric vehicle range extenders.

Conclusions and Future Directions

The FHI project is on schedule to be completed by December 31, 2012. Of the nine active projects, four are scheduled for completion by June 30, 2012. The future work will continue the project monitoring, review of the final reports and continuation of five projects. There are no open issues.

Patents Submitted/Issued

1. P. Brooker, N. Mohajeri "Chromochromic membranes for membrane defect detection", UCF 10390P (submitted).
2. N. Mohajeri "Doped palladium containing oxidation catalysts", UCF-10380P (submitted).
3. J.P. Zheng, Z.Y. Liang, B. Wang, C. Zhang, and W. Zhu, "Catalytic electrode with gradient porosity and catalyst density for fuel cells", US Patent Pub. No. US2011/0008705.

FY 2012 Publications/Presentations

1. R. Brooker, L. Bonville and D. Slattery. "Decreasing Membrane Degradation through Heteropolyacid Sub-layers." *Journal of the Electrochemical Society*, under review.
2. R. Brooker, D. Slattery, L. Bonville, and J. Fenton. "Mechanism of Platinum-band Formation Mitigation with Heteropolyacid Electrodes." Abstract # 1208, 220th ECS Meeting, October 9-14, 2011, Boston MA.

3. R. Brooker, D. Slattery, L. Bonville and J. Fenton. "Platinum Band Formation Mitigation through Heteropolyacid Sublayers." Abstract # LRD42-1, Fuel Cell Seminar, October 31-November 3, 2011, Orlando FL.
4. N. Muradov, A. T-Raissi, G. Bokerman, E. Hinkamp, Passive Chemochromic Hydrogen Leak Detectors for Safety Monitoring. Proceedings of XIX World Hydrogen Energy Conf., Toronto, Canada.
5. M. Rodgers, N. Mohajeri, L. Bonville, D. Slattery, "Accelerated testing of polymer electrolyte membranes in fuel cells containing Pt/C and PtCo/C catalysts", *Journal of the Electrochemical Society*, 159, B564, 2012.
6. M. Rodgers, L. Bonville, D. Slattery, Evaluation of the Durability of Polymer Electrolyte Membranes in Fuel Cells Containing Pt/C and Pt-Co/C Catalysts under Accelerated Testing, *Electrochemical Society Transactions*, 41(1) 1461, 2011.
7. W. Zhu, C. Zeng, J. Zheng, R. Liang, C. Zhang, and B. Wang, "Preparation of Buckypaper Supported Pt Catalyst for PEMFC Using Supercritical Fluid Method", *Electrochem. and Solid-State Lett.* **14**, B81 (2011).
8. W. Zhu, R. Liang, and J. Zheng, "A 3-D Catalytic Electrode Structure for Ultra-low Platinum Loading and High Performance PEMFCs", submitted to *Electrochem. Soc. Trans.*, presented at the 221st Electrochemical Society Meeting, Seattle, WA, May 6-10, 2012.
9. Invited Talk: J.P. Zheng, "A 3-D Catalytic Electrode Structure for High Performance and Low Cost PEMFCs", the 243rd American Chemical Society National Meeting, San Diego, California, March 27, 2012.
10. Invited Talk: J.P. Zheng, "A 3-D Catalytic Electrode Structure for Ultra-low Platinum Loading and High Performance PEMFCs", the 2012 Villa Conference on Energy and Environmental Research, Orlando, Florida, April 17, 2012.