

VII.8 Florida Hydrogen Initiative (FHI)*

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Subcontractors:

- EnerFuels, Inc., West Palm Beach, FL
- Florida Solar Energy Center, Cocoa, FL
- SRT Group, Inc., Miami, FL
- University of Florida, Gainesville, 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: June 30, 2012

*Congressionally directed project

Fiscal Year (FY) 2011 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 for applied technology demonstration projects.
- Sponsoring research and development in the production, storage and use of hydrogen and in the use and application of fuel cells.
- Facilitating technology transfers between the public and private sectors to create, build and strengthen high-growth potential, high technology companies.
- Developing industry support or potential for widespread applications.
- 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 Data
- (B) Hydrogen Storage
- (C) Lack of Hydrogen Refueling Infrastructure and Availability Data
- (H) Hydrogen from Renewable Resources
- (I) 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 on-board 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/gge (based on volume production). (4Q, 2009)

Accomplishments

- Project has solicited proposals to conduct work.
- Project composed of 12 projects with three projects completed.
- Presently have nine active projects – one old project with new demo site, three new projects started on April 1, 2010, and five new projects started on December 1, 2010.



Introduction and Approach

The FHI is a hydrogen and fuel cell program funded for the purpose of developing a hydrogen and fuel cell infrastructure. The FHI program has operated by funding individual projects which conduct the research, development and demonstration activities. Each of the individual projects are approved by DOE before work can begin. Following the change in operation and management of FHI, the project

management began the process of allocating the remaining funds (~\$2.5 million) to new projects and finishing and/or completing old projects. 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

With the above background, the nine active projects are briefly described in the following sections.

Task 2. Hydrogen Technology Rest Area – Michael Fuchs, EnerFuel, Inc.

The project objectives are to design, construct, and demonstrate a 10 kW_{net} polymer electrolyte membrane fuel cell (PEMFC) stationary power plant operating on methanol, to achieve an electrical energy efficiency of 32% and to demonstrate transient response time <3 ms. The yearly accomplishments successfully incorporated the existing inverter and fuel cell systems into the design of the charging station, completed system testing at EnerFuel prior to delivery to Florida Atlantic University. Final activities are to operate the charging station for a period of three months, determine overall electrical efficiency, document system transient response to load changes, and determine overall performance and effectiveness of charging station.

Task 7. Chemochromic Hydrogen Leak Detectors for Safety Monitoring – Dr. N. Mohajeri and Dr. N. Muradov, FSEC

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 two classes of chemochromic hydrogen sensors, an irreversible one and a reversible one. The yearly activities have evaluated the performance (sensitivity) of the sensors at different hydrogen concentrations in air (from 1 to 100 vol%) and found no interference with other reducing gases (CO, NH₃, CH₄, H₂S).

For the irreversible sensors, the results are several new chemochromic pigments that have been synthesized and tested. Three new formulations show faster kinetics with the response time for PK-2-31NM49 chemochromic sensor being 80% faster than first generation irreversible pigment. For the reversible sensors, the results are 20 novel Mo-, W-, V-based chemochromic formulations that have been synthesized and tested and the effect of the co-catalyst/activator on the rate of coloration in presence of hydrogen has been determined.

Task 8. Development of High Efficiency Low Cost Electrocatalysts for Hydrogen Production and PEM Fuel Cell Applications – Dr. C. Huang and Dr. M Rodgers, FSEC

The objectives of this project are to develop nanosized and high efficiency electrocatalysts based on alloys and

metal-metal oxides composites. The new catalysts will be evaluated for their activity toward H₂ evolution via water electrolysis as well as oxygen reduction reaction for PEMFC applications. The relevance of this project is that Pt metal catalysts are the most effective PEMFC catalysts, but their use is impeded by costs, efficiency, and life span for oxygen reduction reaction. Approaches to overcome these limitations involve reducing Pt loading while maintaining high performance of catalysts. The methods of increasing Pt activity include optimization of the size and shape of the Pt particles, alloying Pt with other metals, and depositing catalyst particles only where the electrocatalytic reaction takes place.

In PEMFC applications, for Pt in a catalyst layer to be active, it must be deposited at the “three phase reaction zone.” This can be done by sputtering deposition or pulse electrodeposition. The approach of catalyst preparation is to electrodeposit catalyst particles on three phase zones by coating a carbon microporous and Nafion® layer on carbon paper. A rotating disk electrode (RDE) technique is used to carry out pulse electrodeposition. The results indicate that Pt catalyst prepared by the pulse electroplating technique show higher activities than that of a commercial catalyst. The prepared catalysts can also be used for H₂ production via water electrolysis with higher efficiency. The future work is to synthesize alloy-based electrocatalysts and to perform catalyst characterization.

Task 9. Understanding Mechanical and Chemical Durability of Fuel Cell Membrane Electrode Assemblies – Dr. D. Slattery, FSEC

The objective of this project is to increase the knowledge base of the degradation mechanisms for membranes used in PEMFCs. The yearly results are that fluoride emission of 1100 equivalent weight perfluorinated sulfonic acid membranes can be reduced by the addition of cerium oxide to the membrane, the formulation of the ceria changes its efficacy, the improvements in durability are dependent on the ceria concentration, and improved cell durability can be achieved by using Pt-Co/C rather than Pt/C results and the addition of phosphotungstic acid to the electrode sublayer reduced membrane degradation.

The planned future work is to continue analysis of cerium oxide to determine the source of improvements, to conduct accelerated durability tests and compare the results to the Fenton tests, to determine the amount and location of Pt in the membrane by electron microscopy tests, to determine by cell testing the effect of heteropoly acid on platinum migration to identify performance losses and then optimize the sublayer electrode to reduce these losses.

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

The objective of this project is to conduct research and development on biowaste reactor (called HyBrTec™) that

does not have the problems associated with conventional biowaste-to-fuel processing using an anaerobic digester. This new reactor will reduce the cost and improve energy efficiency. The project approach is to produce hydrogen bromide (HBr) from wet-cellulosic waste (co-produces carbon dioxide and thermal energy) and then use electrolysis to dissociate hydrogen bromide ($E^\circ = 0.555$ V) producing recyclable bromine and hydrogen (endothermic), and follow with combustion in order to react hydrogen with the more energetic oxygen ($E^\circ = 0.1229$ V), affording a theoretical process efficiency of 100%.

The project is in its initial stages of development and the accomplishments to date are that the reactor/electrolysis vessel is designed, the preliminary bromination experiments at $<200^\circ\text{C}$ are favorable, and assembly of a bench-top 500 ml prototype reactor/electrolysis vessel has begun. The future work is to conduct the high temperature HBr electrolysis, integrate bromination/electrolysis to determine optimum temperature and pressure, perform analysis of by-products and conduct preliminary economic analysis.

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.

The project research objectives are to demonstrate new catalyst structures comprised of high conducting buckpaper and Pt catalyst nanoparticle coated at or near the surface of buckpaper and to demonstrate efficiency, durability improvement, and cost reduction using carbon nanotube buckpaper-based electrodes.

The technical approach is to use carbon nanotubes that are suspended on buckpaper, to use electrodeposition of Pt, and to characterize the catalysts by cyclic voltammetry of a PEMFC using the buckpaper. The results have developed an innovative fuel cells assembly, taken images of two-layered Pt/buckpaper and determined cell performance. Current results have been achieved by Florida State University/Bing Energy, Inc. for electrocatalyst and membrane electrode assemblies. These results show the meeting of some DOE goals with the future expectation of meeting all DOE goals.

Task 12. Hydrogen and Fuel Cell Technology Academic Program - Mary Helen McCay, PhD, PE, Kurt Winkelmann, PhD, Florida Institute of Technology, Melbourne Florida

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 resulting program will allow students to follow hydrogen technology from introduction to long-term applications, obtain a basic understanding, redirect their current technology focus as a means for new career options, measure students' gains in knowledge of hydrogen as an energy source and satisfy the need for hydrogen technology graduates. The approaches to accomplish the program goals are to establish a Masters Degree area of specialization,

develop modules for existing undergraduate courses, support senior design and capstone projects and prepare hydrogen-themed general chemistry lab experiments.

The FIT HFCT program began on December 1, 2011 and is in its initial stages of development. The technical accomplishments and progress are the hydrogen knowledge and opinion surveys have been administered to mechanical and aerospace engineering and chemistry students, graduate courses and modules are under development, and hydrogen-themed general chemistry lab experiments are designed to improve students' views about chemistry and their knowledge about hydrogen as an alternative energy source. The anticipated results are a strong curriculum on hydrogen and fuel cell technology that will assist undergraduate students in furthering their understanding of hydrogen and fuel cell technology, to offer graduate students a career path into renewable energy and prepare students for entry into research and other positions related to hydrogen technology.

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

The project objectives are to design and develop novel conducting polymeric nanomaterials for on-board hydrogen storage with a system gravimetric capacity of 5.5 wt% or greater and with complete reversible hydrogen storage characteristics at moderate temperature ($<100^\circ\text{C}$).

The proposed approach is to perform the 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. The preliminary work has used PANI nanostructures for H_2 storage and studies the morphological effects of H_2 cycling on PANI nanofibers that are electrospun. This work shows the PANI nanostructures combine physisorption and chemisorption, reversible storage of >3 wt% is possible at room temperature, and reversible storage of <10 wt%, is possible at 100°C .

Task 14. Advanced HiFoil™ Bipolar Plates – Mr. J. Braun, EnerFuel, Inc.

The project objectives are to address cost and durability barriers for high temperature proton exchange membrane fuel cells (HTPEMFC) by providing a low cost, easy to form, corrosion-resistant laminate bipolar plate having high thermal conductivity and improved mechanical strength/crack resistance. The existing commercial bipolar plate technology includes machined expanded graphite composite plates and gold-coated stainless steel plates – all costly. The new EnerFuel patent-pending laminate technology has shown excellent performance and corrosion resistance. A HTPEMFC stack was tested for 1,000 hours with no failure, and thermal cycled from room temperature to 200°C over 10,000 times with no failure.

The expected results are demonstration and characterization of advanced fuel cell materials that combine the strength of metal with the corrosion resistance of graphite, for use as a bipolar plate in HTPEMFCs operating at 200°C.

Conclusions and Future Directions

FHI has completed three projects and continues work on nine projects. All project budget funds are committed and the projects are scheduled for completion in 2012.

Publications/Presentations

1. Rodgers, M., Bonville, L., & Slattery, D. (2011, March). "Evaluation of the durability of polymer electrolyte membrane fuel cells containing Pt/C and Pt-Co/C Catalysts under accelerated testing." Paper presented at the Annual Joint Symposium & Exhibition of the Florida Chapter of the AVS Science and Technology Society, Orlando, FL.