V.M.1 Improving Fuel Cell Durability and Reliability

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Contract Number: DE-EE00003226

Project Start Date: August 1, 2010
Project End Date: October 31, 2013

Overall Objectives

Overall objective of the research project is to develop an in-depth understanding of the degradation processes in advanced electrochemical energy conversion systems. It is also the objective of the research project to transfer the technology to participating industries for implementation in manufacturing of cost-effective and reliable integrated systems. The project aims to:

- Advance fuel cell-based power generation systems architecture, including renewable hybridized energy conversion and storage.
- Develop novel cell and stack structural and functional materials and validate their performance under the nominal and transient operational conditions for the evaluation of long-term bulk, interfacial, and surface stability.
- Gain a fundamental understanding of chemical, mechanical, electrochemical, and electrical processes related to:
  - The utilization of fuels ranging from bio-derived fuels to liquid petroleum to hydrogen.
  - The role of fuel impurities on degradation and processes for removal from feedstock.
  - Surface and interface phenomena related to surface adsorption, interfacial compound formation, and electron/ion generation and transport, electrodics, and electrochemistry.

Novel membranes, heterogeneous catalyst materials, and structures will be developed and validated through experimentation. Collaborative research projects with industry will be developed to improve the performance stability and long-term reliability of advanced fuel cells and other power generations systems.

Fiscal Year (FY) 2013 Objectives

- Quantify the role of fuel impurities on degradation processes in advanced electrochemical energy conversion systems.
- Optimize novel cell and stack structural and functional materials from a durability, cost, and performance perspective.
- Demonstrate and improve performance stability and reliability through advanced materials and fabrication processes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

The projects associated with this project address technical aspects of stationary fuel cells and stationary fuel processors. DOE 2011 targets are as follows:

Stationary Proton Exchange Membrane Fuel Cell Stack Systems (5-250 kW) Operating on Reformate:

- Cost: $530/kWe
- Durability: 40,000 hours

Stationary Fuel Processors (equivalent to 5-250 kW) to Generate Hydrogen-Containing Fuel Gas

- Cost: $220/kWe
- Durability: 40,000 hours
- H_2S content in product stream: <4 ppbv (dry)

FY 2013 Accomplishments

- The Center for Clean Energy Engineering has successfully developed, in total, 18 industrially sponsored research, development, and engineering projects in the field of clean and sustainable energy.
- These collaborative projects have leveraged DOE funds with industrial financial support to accelerate the development of advanced materials, cell and stack components, catalysts and fuel cleanup, and balance-of-plant sub-systems.
- The industrial projects support the mission of DOE through the development of reliable and cost-effective advanced clean and efficient fuel cell power generation systems.

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INTRODUCTION

The scope of this energy systems and technology research and development initiative will focus on the development and validation of the mechanistic understanding and subsequent creation of novel cost-effective materials to mitigate degradation processes. Through a unique collaborative project with industry we will solve technology gaps through joint industry/university projects. These relationships will accelerate the development and deployment of clean and efficient multi-fuel power generation systems.

The scope of the research projects will include identification and prioritization of the technology gaps and research needs along with the development of enabling technologies that meet the overall stack and balance-of-plant improvements from a durability, cost, and performance perspective. Specifically the performance stability and reliability of the power generation systems will be improved through the implementation of advanced materials and fabrication processes. Technical areas of interest, to be addressed by the industry/university collaborations, will include a) performance stability and reliability of fuel cell systems; b) fuels, fuel processing, and catalysis; c) advanced functional and structural materials, processes and systems; d) hydrogen storage and power management; and e) renewable energy and resources.

APPROACH

The approach used for this project was to develop collaborative industry/university research projects aimed specifically at accelerating the development and deployment of clean and efficient multi-fuel power generation systems. Through a competitive process, faculty developed relationships with industry that provided additional amounts of cash and in-kind support, thus leveraging funding available through this project. By requiring a financial commitment from industry this methodology ensured that technology problems of commercialization relevance would be addressed. Industry collaborative projects have been developed with UTC Power, FuelCell Energy, UTC Research Center, NanoCell Systems, APSI, Oasys Water, Nissan, Corning, Proton OnSite, BC Hydro, Sci-Tech, and WR Grace & Company. The project topics have addressed issues ranging from performance stability and reliability of fuel cell systems to fuels, fuel processing, and catalysis and finally including advanced functional and structural materials, processes, and systems.

RESULTS

Role of Multi-Scale Water Transport in Dynamic Performance of Polymer Electrolyte Fuel Cells (Project PI: Ugur Pasaogullari, Industry Partner: Nissan). The collaboration between Nissan and UConn focused on understanding the transport phenomena at very high current density operation of polymer electrolyte fuel cells (PEFCs). The work in the last year resulted in detailed understanding of the micro-structure of the gas diffusion layers (GDLs) in PEFCs. GDLs were responsible for ~50% of the oxygen transport losses in PEFCs and high current density operation which required very effective oxygen transport to active reaction sites. Numerical models that describe the multi-phase transport phenomena at very high current density conditions were developed, and the results have been compared with neutron radiography results obtained at the National Institute of Standards and Technology Center for Neutron Radiography.

High-Performance Phosphoric Acid Fuel Cell Electrodes for Soluble Polymers and Alternate Fabrication Methods (Project PI: Ned Cipollini, Industrial Partner: UTC Power). A new method of fabricating phosphoric acid fuel cell (PAFC) cathodes was developed which promises many advantages over the present state-of-the-art method: 1) less expensive, 2) more controllable in thickness and Pt loading, 3) fewer defects, and 4) produces free-standing electrodes. Mixtures of poly tetrafluoroethylene (PTFE) or PTFE/perfluoro alkoxy, catalyst, and hydrocarbon lubricant/vehicle were rolled, much like bread dough, into a layer of desired thickness, dried, and sintered at 349°C or 330°C, respectively. Sub-scale fuel cell tests show that even without composition optimization, the performances of these experimental electrodes exceed that of conventional electrodes. We expect the process to be scalable and also applicable to the anode and matrix (without sintering) layers and to lead to lower cost/kW PAFCs.

Mechanistic Understanding of Matrix Stability in MCFCs (Project PI: Prabhakar Singh, Industry Partner: FuelCell Energy). Technical discussions progressed during the reporting period to identify electrical performance degradation mechanisms related to the electrolyte matrix stability under cell operation conditions. Role of the oxidant and fuel gas chemistry, fuel utilization, temperature, current density, and melt chemistry were examined using solid–gas–melt thermochemistry, microstructural, and chemical analysis of post tested samples. An experimental test matrix was designed in consultation with the industry partner and both short-term and long-term experiments were conducted using matrix constituents to examine the coarsening of the matrix. As received samples were examined at the matrix-anode and matrix-cathode interfaces. Samples were subsequently washed in glacial acetic acid-acetic anhydride mixture to dissolve and remove the electrolyte. Obtained samples were further analyzed for the morphology. Role of anode and cathode atmospheres, humidity level, and electrolyte basicity were experimentally evaluated. Nickel dissolution in the matrix was also analyzed.

Waste to Energy: Biogas Cleanup (Desulfurization) for Energy Generation (Project PI: Steven Suib, Industry Partner: FuelCell Energy). Over the past 12 months we have made significant progress in the area of sulfur getters for fuel cell systems. We have made adsorbents that work at various relative humidities and have excellent capacity. These unique cost-effective adsorbents are now being scaled.

Fuel Reforming Catalysts for Efficient Energy Usage (Project PI: Steven Suib, Industry Partner: APSI). Our work with APSI in the past 12 months has involved generation of novel catalysts for fuel reforming. We have also studied the mechanism of reaction of these catalysts. A final area of research has involved evaluation of such systems in combustion catalysis.

Structure-Activity Correlations in Soot Oxidation (Project PI: Steven Suib, Industrial Partner: Corning). In the last 12 months our work with Corning has involved the study of various carbonaceous materials that can ruin filer systems. Our work has fully characterized these different soot materials. We have also developed catalysts to destroy this soot.

Optimization of Fluid Catalytic Cracking (FCC) Selectivity Through Detailed Modeling of Catalyst Evaluation Experiments and the Contributions of Catalyst Components (Project PI: George Bollas, Industry Partner: W.R. Grace & Co.). Models of state-of-the-art catalyst evaluation procedures for the FCC process have been developed, incorporating key characteristics of different catalyst testing reactors. Model predictions (in good agreement with experimental data) have provided metrics for comparison and analysis of data from different reactors and for the study of the performance of catalyst decay functions on the same basis, and are providing theoretical insights to decoupling the effect of matrix type and zeolite diffusional properties on catalysts, as well as to the analysis of several different reaction kinetic networks. Predictive models have been developed capable of simulating FCC operation with catalyst blends, with using only pure catalyst experiments. Non-linearities of the blend catalyst performance were predicted successfully and understood. The effect of catalyst support (matrix) was decoupled from that of the active catalyst (USY zeolite) and the effect of each catalyst component was represented by sets of different lumped kinetics. It was shown that pre-cracking is a significant contribution from the matrix (yielding mostly light-cycle oil and naphtha) whereas the zeolite is responsible mainly for the selectivity to lighter products. Optimal catalyst formulations can be proposed through a user-friendly interface, developed for the analysis of FCC lab-scale data.

Nanostructured Catalyst Support Systems for Next Generation Electolyzers (Project PI: William Mustain, Industry Partner: Proton OnSite). During this project, the UConn/Proton team developed a new Pt/WC electro-catalyst that has very high activity and stability at a fraction of the Pt catalyst loading in the Proton commercial unit. The new catalyst reduces the total Pt loading by 80%, while retaining 96% of its activity during short-term operation. Both of these metrics are significantly better than existing commercial catalysts.

Reliability Evaluation and Enhancement of Synchronized Phasor Network (Project PI: Peng Zhang, Industrial Partner: BC Hydro). During 2012-2013, the project sponsored by DOE has resulted in a published U.S. patent and several innovations that improve the reliability of synchronized phasor networks and power grid. Approximate analytic variance for estimation method of phasor, frequency and rate of change of frequency were derived, which provided insight for reducing errors in phasor tracking algorithms. A generalized capacity outage tables approach was further studied to evaluate the reliability of active distribution systems considering different operation modes under single or multiple contingencies. The results have been published in the Institute of Electrical and Electronics Engineers journal and presented at the Institute of Electrical and Electronics Engineers PES General Meeting 2013 in Vancouver. Most recently, significant efforts were devoted to quantifying and enhancing the reliability of BC Hydro's synchronized phasor (synchrophasor) network which is planned to be connected as part of the Western Electric Coordinating Council wide area measurement system. Extensive sensitivity studies have been performed to identify the vulnerabilities in BC Hydro's synchrophasor network so as to provide the most cost-effective strategy to reinforce the network.

Plasmonic Nanostructures for Solar Energy Harvesting (Project PI: Brian Willis, Industry Partner: SciTech). A new nanofabrication procedure and reactor design has been completed to overcome a problem with shorting due to particulates. The new antenna design includes successively larger parallel arrays with minimal overlap area to enable multiple measurements per experiment. In situ analysis experiments were initiated to provide greater fundamental understanding of the atomic layer deposition growth process to optimize antenna growth conditions.

Waste Heat Recover and Utilization Using the Osmotic Heat Engine (Project PI: Jeff McCutcheon, Industry Partner: Oasys Water). During the last year, we have successfully integrated our custom built pressure retarded osmosis testing unit into our lab for testing various membranes for their osmotic power potential. We have evaluated our chemically modified retarded osmosis membrane platforms as well as our newly developed nylon-supported thin-film composite membranes and achieved power densities of up to 2.5 watts/m^2. Our nano-fiber platforms have shown much better performance. Our recent nano-fiber-supported thin-film composite membranes have exhibited power densities of up to 7.5 watts/m^2, far exceeding industry target of 5 watts/m^2.

Gasification Technology and Clean-Up for Integration with Solid Oxide Fuel Cell (Project PI: Radenka Maric). During this past year, we have modified the pilot gasifier unit to decrease the feed rate to match the feedstock supply. In addition, we developed a method for pelletizing various feedstock such as; biosolids (wastewater residuals), food waste and animal waste. These larger pellets as well as modifications to air distribution resulted in better operational control and production of a combustible gas with values of between 130 and 160 Btus per pound. This project was described in a webcast presented by Dr. Maric as part of the Energy and Water Conference sponsored by the Water Environment Federation in March 2013.

CONCLUSIONS AND FUTURE DIRECTIONS

Of the 11 projects listed above four of them will continue into FY 2014. At this time the list of projects is stable and we do not anticipate additional projects. We do, however, continue to expect the following achievements to continue from the above list of activities:

- Advanced functional and structural materials R&D will continue to address long-term surface, interface and bulk instabilities at the engineered systems level. Research will continue in areas related to solid- and liquid-gas interactions as they relate to surface corrosion, electrochemical poisoning, agglomeration and coarsening of porous aggregates, and catalytic degradation.
- UConn and its partners will continue to develop advanced fuel cleanup and processing technologies to enable multi-fuel capabilities of advanced fuel cell systems. Cost-effective technologies for the removal of contaminants from gas phase will be developed and validated.
- Developed technologies will be transferred to industries to accelerate the development and deployment of advanced fuel cell systems.
- Research findings will be presented and published in technical meetings and peer reviewed journals. Intellectual property will be disclosed through invention disclosures and review by the university's center for science and technology commercialization.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

Three invention disclosures have been filed with the University of Connecticut's Office of Economic Development and transferred to the client, UTC Power (now ClearEdge Power):

1. "Electrodes from Polymers Soluble at Elevated Temperatures." Case number 13-041.

2. "Phosphoric Acid Fuel-Cell (PAFC) Electrodes from Soluble or Meltable Polymers by Fibrillation of PTFE." Case number 13-042.

3. "Phosphoric Acid Fuel-Cell (PAFC) Electrodes by Fibrillation of PTFE." It has been assigned case number 13-043.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Lakshitha Pahalagedera, Hom N. Sharma, Chung-Hao Kuo, Saminda Dharmarathna, Ameya V. Joshi, Steven L. Suib, and Ashish B. Mhadeshwar, "Structure and Oxidation Activity Correlations for Carbon Blacks and Diesel Soot", in preparation for submission to Chemistry of Materials, 2012.

2. Y. Liu, and W.E. Mustain, "Evaluation of Tungsten Carbide as the Electrocatalyst Support for Platium Hydrogen Evolution/ Oxidation Catalysts", *Int. J. Hydrogen Energy*, 37 (2012) 8929

3. Fu, R.S., Khajeh-Hosseini-Dalasm, N., and Pasaogullari, U., "Numerical Validation of Water Transport in Polymer Electrolyte Membranes," ECS Transactions, 50 (2012).

4. McCutcheon, J.R., "Next Generation Membranes for Forward and Pressure Retarded Osmosis", 3rd Annual Water Industry Exhibition & Conference, May 2–4, 2012.

5. Arena, J., Manickam SS, Reimund, K.K., McCoskey, B.D., Freeman, B.D., McCutcheon, J.R., "Surface Modification of Thin Film Composite Membranes with Polydopamine for Engineered Osmosis", Oral Presentation at the North American Membrane Society Annual Meeting, New Orleans, LA, June 9–13, 2012.

6. A. Abdollahi, P. Zhang, and N. Zhou, "Generalized Subspace Least Mean Square Method for High-Resolution Accurate Power System Oscillation Mode Estimation," IEEE Trans. Power Systems, under review. Submission date: July, 2012.

7. H. Xue and P. Zhang, "Subspace-Least Mean Square Method for accurate harmonic and interharmonic measurement in power systems," *IEEE Trans. Power Delivery*, vol. 27, no. 3, Jul. 2012.

8. "Next Generation Membranes for Forward and Pressure Retarded Osmosis", International Union of Pure and Applied Chemistry. Blacksburg, VA, July 24–27, 2012.

9. Y. Wang, W. Li, P. Zhang and B. Wang, "Reliability analysis of Phasor Measurement Unit considering data uncertainty," IEEE Trans. Power Delivery, vol. 27, no. 3, pp. 1503-1510, Aug. 2012.

10. Huang, L., Bui, N.N., McCutcheon, J.R. "Nylon 6,6 Microfiltration Membranes as Supports for Thin Film Composite Membranes for Engineered Osmosis". American Institute of Chemical Engineers Annual Meeting, November 2012.

11. Bui, N.N., McCutcheon, J.R., "Hydrophilic Nanofibers as Supports for Thin Film Composite Membranes for Engineered Osmosis." American Institute of Chemical Engineers Annual Meeting, November 2012.

12. Bie, P.Zhang, G. Li, B. Hua, M. Meehan, and X. Wang, "Reliability evaluation of active distribution system including microgrids, " IEEE Trans. Power Systems, vol. 27, no. 4, pp. 2342-2350, Nov. 2012.

13. Y. Wang, P. Zhang, W. Li and W. Xiao, "Online overvoltage prevention control of photovoltaic generators in microgrids," IEEE Trans. Smart Grid, vol. 3, no. 4, pp. 2071-2078, Dec. 2012

14. McCutcheon, J.R., "Engineered Osmosis for Sustainable Water and Power", University of Kansas Department of Chemical and Petroleum Engineering Seminar Series, December 4, 2012.

15. McCutcheon, J.R.,"New Membrane Platforms for Pressure Retarded Osmosis", Statkraft, Oslo, Norway, December 12, 2012.

16. Y. Liu, T.G. Kelley, J.G. Chen and W.E. Mustain, "Metal Carbides as Alternative Electrocatalyst Supports", ACS Catalysis, 3 (2013) 1184

17. Lakshitha Pahalagedera, Hom N. Sharma, Chung-Hao Kuo, Saminda Dharmarathna, Ameya V. Joshi, Steven L. Suib, and Ashish B. Mhadeshwar, "Comparative Analysis of the Structure and Chemical Nature of Carbon", in preparation for submission to Analytical Chemistry, 2013.

18. A. Abdollahi, P. Zhang, and H. Xue, "Enhanced Subspace-Least Mean Square for fast and accurate power system measurement," IEEE Trans. Power Delivery, vol. 28, no. 1, pp. 383-393, Jan. 2013.

19. McCutcheon, J.R., "New Membrane Platforms for Engineered Osmosis", ACS Polymer Membrane Mediated Water Filtration Meeting, Pacific Grove, CA, February 28, 2013.

20. DOE visited Center for Clean Energy Engineering at University of Connecticut on March 28, 2013 to review projects associated with Fuel Cell Technology.

21. "Evaluation of Tungsten Carbide and Tungsten Oxide as Pt Supports for Oxygen Reduction Reaction", The Electrochemical Society, Toronto, May 2013. Presenting Author: Ying Liu.