V.K.4 Improving Reliability and Durability of Efficient and Clean Energy Systems*

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*Congressionally directed project

Fiscal Year (FY) 2012 Objectives

- Develop an understanding of the degradation processes in advanced electrochemical energy conversion systems.
  – 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 fundamental understanding of chemical, mechanical, electrochemical and electrical processes related to:
    - 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 subsequently validated.
- Develop collaborative research projects with industry to improve the performance stability and long-term reliability of advanced fuel cells and other power generations systems.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program 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 polymer electrolyte membrane (PEM) 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 2012 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, eight of these projects were added in FY 2012.
- 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 DOE mission 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, nzymSys, 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

1. Role of Multi-Scale Water Transport in Dynamic Performance of Polymer Electrolyte Fuel Cells (Project PI: Prof. Ugur Pasaogullari, industry partner – Nissan): The collaboration between Nissan and UConn focuses on understanding the transport phenomena at very high current density operation of PEM fuel cells (PEMFCs). Our work in the last year resulted in detailed understanding of the micro-structure of the gas diffusion layers (GDL) in PEMFCs. GDLs are responsible from ~50% of the oxygen transport losses in PEMFCs, and high current density operation requires very effective oxygen transport to active reaction sites. We have also developed numerical models that describe the multi-phase transport phenomena at very high current density conditions, and the results are being compared with neutron radiography results obtained at the National Institute of Standards and Technology Center for Neutron Radiography.
2 Modeling Resin Flow in Phosphoric Acid Fuel Cell (PAFC) GDLs (Project PI: Prof. Rajeswari Kasi, industry partner – UTC Power): UTC Power was interested in attaining stable graphitized GDLs that are used in PAFCs. This project successfully evaluated ways to improve GDL stability by 1) modeling the resin flow during GDL impregnation and lamination, 2) investigating the properties of GDLs at each experimental step, and 3) improving substrate manufacturing efficiency based on the model developed and properties of the GDLs.
3. High Performance Phosphoric Acid Fuel Cell Electrodes for Soluble Polymers and Alternate: Fabrication Methods (Project PI: Prof. Ned Cipollini, industrial partner – UTC Power): As none of the common perfluoropolymers form stable solutions at room temperature we have been able to produce viable electrodes by heating mixtures of perfluoroalkoxy (PFA) solid, cathode catalyst and solvent to 25ºC above the melting point of PFA, where it is soluble, and allowing the PFA to coat the catalyst as the PFA comes out of solution while cooling to room temperature. Catalyst layers were formed by doctor-blade techniques on carbon paper. Subscale fuel cell testing shows the performance of these electrodes is poorer than present state-of-the-art PAFC cathodes. The poorer performance has been attributed to low Pt loading and non-uniformity on the macro-scale of the uniform PFA coating on the catalyst. These both can be addressed by modifying processing conditions of the cathodes.

4. Mechanistic Understanding of Matrix Stability in Molten Carbonate Fuel Cells (MCFCs) (Project PI: Prof. Prabhakar Singh, industry partner – FuelCell Energy): The electrolyte matrix of the MCFC, commonly fabricated from lithium aluminate, have shown coarsening during long-term exposure. Experiments conducted in our laboratory have reproduced the in-cell observations on coarsening of the matrix. Role of additives and electrolyte chemistry has been examined. Faceted crystals grow during the exposure to the molten salt. Particle size distribution, phase identification have been performed.
5. Waste to Energy: Biogas Cleanup (Desulfurization) for Energy Generation (Project PI: Prof. Steven Suib, industry partner - FuelCell Energy): The hypothesis of this project is that development of novel adsorbents, catalysts, and mixed adsorbents will lead to more efficient cleanup of anaerobic digester gas (ADG). Mixed adsorbents are likely to be needed to efficiently getter all sulfur species in ADG. This project has focused on the optimization of adsorbents that can getter sulfur-containing species. Our results show that some of the adsorbents are 40 times better in terms of breakthrough times and adsorbed amounts than commercial activated carbon adsorbents. We are studying the mechanism of adsorption over these materials. Characterization studies are being done in order to optimize the performance of these materials.
6. Fuel Reforming Catalysts for Efficient Energy Usage (Project PI: Prof. Steven Suib, industry partner – APSI): The hypothesis of this project is that the development of next generation high surface area fuel reforming catalysts and determination of mechanisms of reaction will lead to enhanced efficiency, activity, and stability of these materials. Over the past year the focus has been on 1) the preparation of thin film reforming catalysts made with a novel process, and 2) the study of the mechanism of the fuel reforming process with an emphasis on mass spectrometry detection.
7. Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup (Project PI: Prof. Ashish Mhadshwar, industrial partner – nzymSys): The overall goal of this project is to test and demonstrate a novel enzymatic way to reduce the sulfur content in biogas, with a primary focus on hydrogen sulfide (H_2S) removal. The application of the novel enzymatic technology (nzymSys, Inc.) for (simulated) biogas desulfurization was investigated in a lab-scale semi-batch reactor. We observed that even dilute enzyme solutions (4-5 wt%) are effective in removing up to 100% of the feed H_2S, during 8-hour tests. The enzyme is also selective to H_2S, and does not show any adverse effect on the other dominant components in biogas, such as methane and carbon dioxide. Experiments with enzyme replenishment indicated that the biogas desulfurization process could be potentially operated continuously for consistent removal of H_2S. Long-term studies performed at higher enzyme concentration (20 wt%) demonstrated formation of sulfur precipitate, which could be recovered as a valuable product.
8. Structure-Activity Correlations in Soot Oxidation (Project PI: Prof. Ashish Mhadshwar, industrial partner – Corning): The overall research objective of this project is to develop structure-activity correlations for non-catalytic oxidation of soot to understand the dependence of oxidation kinetics on nature of soot. This work focuses on a comprehensive investigation of structure-activity relationships for 13 commercially available carbon blacks and two diesel engine soot samples (Corning). Various structural parameters, such as the average particle size, specific surface area, degree of organization, and average crystallite stacking height, are correlated with the thermogravimetric oxidation activity data. Our analysis for a large number of samples with multiple techniques has indicated unique and previously unknown correlations between soot structure and reactivity.
9. High Reliability, Low Cost Thermally Integrated Water-Gas Shift System Design Development Support (Project PI: Prof. Ashish Mhadshwar, industrial partner – FuelCell Energy): The overall goal of this project is to support FuelCell Energy, Inc. (FCE) in the design, development and scale up of a thermally integrated water-gas shift system to efficiently process reformate gas, such as from FCE's DFC® power plant anode exhaust. This task involves evaluation and analysis of the proprietary catalyst samples provided by FCE. Catalyst performance has been evaluated for CO oxidation, CO methanation, and water-gas shift reaction.
10. Stannate-Based Semiconductor Nanocomposites for Solar Energy Utilization (Project PI: Prof. Puxian Gao, industry partner - UTC Research Center): Zinc hydroxystannate nanocubes have been achieved in the forms of both free-standing particle in solution, and continuous thin film on substrates via hydrothermal synthetic strategy. Gradient stannate nanostructures have been successfully fabricated using non-equilibrium fast thermal annealing processes. Amongst various stannate-based nanostructures through thermal annealing, the amorphous zinc stannate nanocubes were found to be highly active in organic dye degradation under both ultraviolet and visible lights.
11. Optimization of Fluid Catalytic Cracking (FCC) Selectivity Through detailed Modeling of Catalyst Evaluation Experiments and the Contributions of Catalyst Components (Project PI: Prof. 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.

12. Evaluation of the Performance of Rapidly Quenched Yttria-Stabilized Zirconia (YSZ) Electrolytes in a Solid Oxide Fuel Cell and its Comparison with Conventional Solid Oxide Fuel Cell Architecture (Project: PI: Prof. Radenka Maric, industrial partner – NanoCell Systems): The electrical conductivity and microstructure of $La_{0.65}Sr_{0.3}MnO_3$ (LSM)–8 mol% YSZ cathode composite were investigated from room temperature to 1,000°C in air conditions. The results of half-cell the charge transfer resistance and ohmic resistance for LSM/YSZ samples using plasma-sprayed powder show that resistance of YSZ electrolyte remained very low with reducing temperature from 750-550ºC while the resistance of cathode significantly increased. The activation energy of YSZ for the conduction above 550°C is 93 and 103 kJ mol^{-1} below 550°C, respectively. The higher activation energy at low temperatures for conduction is due to the association of the point defects ($Y'_{Zr}V_{O^{\bullet\bullet}}$). The reason for the lower activation energy for conduction at temperatures higher than 550°C is due to the migration of $V_{O^{\bullet\bullet}}$. The electrode and electrolyte microstructures have not yet been fully optimized; thus, substantial performance improvement is envisioned.
13. Nanostructured Catalyst Support Systems for Next Generation Electolyzers (Project PI: Prof. William Mustain, industry partner – Proton OnSite): During this project, the UConn/Proton team has made significant progress in the identification of a new anode hydrogen evolution reaction catalyst with commercial potential. The team has identified a Pt/WC electrocatalyst that allows for only 20% of the Pt loading that is in the Proton commercial catalyst with 96% activity retention during ageing. This far exceeded the performance of other supported Pt commercial catalysts. In addition, the team has demonstrated high activity oxygen evolution catalysts using a new flame based synthesis approach that reduces the number of processing steps for membrane electrode assembly fabrication.
14. Reliability Evaluation and Enhancement of Synchronized Phasor Network (Project PI: Prof. Peng Zhang, industrial partner – BC Hydro): Over the past 12 months this project has resulted in an invention disclosure and several innovations that enable reliable integration of renewable resources into power systems. A new Monte Carlo-based method was proposed for reliability evaluation of active distribution systems with multiple microgrids. A combined statistical and fuzzy Markov method was devised for reliability evaluation of phasor measurement unit. An accurate high-resolution and robust method called S-LMS (subspace-least mean square) was invented for reliable estimation of power system phasor, harmonics, and interharmonics. An enhanced version of S-LMS was developed to speed up S-LMS more than 150 times by taking advantage of sparsity of power system signal. A precise method was derived to increase the accuracy of power system measurement by eliminating decaying dc components which expose during fault occurrence.
15. Plasmonic Nanostructures for Solar Energy Harvesting (Project PI: Prof Brian Willis, Industry Partner – SciTech): Tunnel diodes have successfully been nano-fabricated and converged to nano-dimensions using our atomic layer deposition processes. Particulate contamination has been found to limit our progress due to the susceptibility of the devices to short circuiting via particulates landing on the devices. A new series of experiments is in the planning stages to overcome these difficulties.

Conclusions and Future Directions

Of the 15 projects listed above 11 of them will continue into FY 2013. At this time the list of projects is stable and we do not anticipate additional ones. We do,however continue to expect the following achievements to continue from the above list of activities:

1. Advanced functional and structural materials research and development will continue to address long-term surface, interface and bulk instabilities at engineered systems level. Research will continue in areas related to solid–liquid–gas interactions as they relate to surface corrosion, electrochemical poisoning, agglomeration and coarsening of porous aggregates, and catalytic degradation.
2. 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.
3. Developed technologies will be transferred to industries to accelerate the development and deployment of advanced fuel cell systems.
4. 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

1. P.X. Gao, and C.H. Liu, Method of making gradient composite nanostructures through thermal engineering, UConn Invention Disclosure, in preparation, Fall 2011.

2. P.X. Gao, and C.H. Liu, Methods for making continuous stannate nanofilms, UConn invention disclosure, in preparation, 2012.

3. Peng Zhang, Robust high resolution spectrum estimation method for accurate phasor, harmonic and interharmonic measurement in power systems, Invention Disclosure, UConn #11-033.

FY 2012 Publications/Presentations

1. M. Dragan, R. Maric, P. Strutt, "Morphological and sintering properties of rapidly-quenched nanostructured YSZ powders synthesized by plasma solution spray", submitted to *Journal of Material Science* in April 2012.

2. Monica Navarro, Dariusz Orlicki, George M. Bollas, "Detailed modeling of FCC selectivity in catalyst evaluation experiments," Spring *ACS National Meeting*, March 2012, San Diego CA USA.

3. C.H. Liu, G. Wrobel, P.X. Gao, "Thermal Decomposition of Hydroxystannate Cubes into Stannate-based Semiconductor Nanocomposites for Energy Harvesting and Utilization," *MRS Fall meeting 2011*, Boston, Nov., 2011. (oral)

4. K.T. Liao, P. Shimpi, P.X. Gao, "Scale-up Synthesis of nanostructured copper hydroxystannates and Cu-Sn dendrite alloys on selected substrates," *MRS Fall meeting 2011*, Boston, Nov., 2011. (poster)

5. G. Wrobel, C.H. Liu, M. Piech, S. Dardona, P.X. Gao, "Synthesis and Fire Retardant Property of Zinc Hydroxystannate coated microfibers," *Sci. Adv. Mater., 2012*, in press.

6. C.H. Liu, H.Y. Chen, G. Wrobel, Y.B. Guo, S. Dardona, M. Piech, J.M. Bai, M.H. Shao, Z.H. Zhang, H.Y. Gao, P.X. Gao, "Controlled synthesis and structure tunability of photocatalytically active mesoporous zinc-based stannate nanostructures," to be submitted, 2012.

7. Lakshitha Pahalagedera, Hom N. Sharma, Chung-Hao Kuo, Saminda Dharmarathna, Ameya V. Joshi, Steven L. Suib, and Ashish B. Mhadeshwar, "How Does the Oxidation Activity of Carbon Blacks and Diesel Soot Correlate with the Structure*?"* in preparation for submission to *Carbon, 2012*.

8. Hom N. Sharma, Lakshitha Pahalagedara, Ameya Joshi, Steven L. Suib, and Ashish B. Mhadeshwar, "Non-catalytic Oxidation Kinetics of Carbon Black and Diesel Engine Soot Samples by Thermogravimetric Analysis," submitted to *Energy & Fuels, 2012*.

9. Lakshitha Pahalagedera, Chung-Hao Kuo, Saminda Dharmarathna, Hom N. Sharma, Ameya V. Joshi, Steven L. Suib, and Ashish B. Mhadeshwar, "Comparative Analysis of the Structure and Chemical Nature of Carbon Blacks and Diesel Soot," accepted, *AIChE Annual Meeting, 2012*.

10. Lakshitha Pahalagedera, Hom N. Sharma, Chung-Hao Kuo, Saminda Dharmarathna, Ameya V. Joshi, Steven L. Suib, and Ashish B. Mhadeshwar, "Influence of Particle Size and Microstructure on the Oxidation Behavior of Carbon Blacks and Diesel Soot," accepted, *AIChE Annual Meeting, 2012*.

11. Hom N. Sharma, Lakshitha Pahalagedara, Ameya Joshi, Steven L. Suib, and Ashish B. Mhadeshwar, "Non-catalytic Oxidation of Carbon Black and Diesel Engine Soot Samples - Kinetics and Structure-activity Relationships," accepted*, AIChE Annual Meeting, 2012*.

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

13. Z. Bie, P. Zhang, G. Li, B. Hua, M. Meehan, and X. Wang, "Reliability evaluation of active distribution system including microgrids," *IEEE Trans. Power Systems*, Accepted for publication.

14. Y. Wang, W. Li, P. Zhang and B. Wang, "Reliability analysis of Phasor Measurement Unit considering data uncertainty," *IEEE Trans. Power Delivery*, Accepted for publication.

15. 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.

16. A. Abdollahi, P. Zhang and H. Xue, "Enhanced Subspace Least Mean Square for fast and accurate power system measurement," Submitted to *IEEE Trans. Power Delivery*, 2012.

17. A. Abdollahi and P. Zhang, "Precise removal of decaying DC in DFT algorithm for power system measurement", *Proceeding of IEEE Power & Energy Society General Meeting*, San Diego, Jul. 2012.

18. Brian Willis, "Nanoscale Devices for Rectification of High Frequency Radiation from the Infrared through the Visible: A New Approach," *Journal of Nanotechnology*, vol. 2012, Article ID 512379, 19 pages, 2012.