

## V.L.9 Improving Reliability and Durability of Efficient and Clean Energy Systems\*

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\*Congressionally directed project

- Novel membranes, heterogeneous catalyst materials and structures will be developed and subsequently validated.

- Develop collaborative research projects with industries 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 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 reformat:
  - 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<sub>2</sub>S content in product stream: <4 ppbv (dry)

### FY 2011 Accomplishments

- The Center for Clean Energy Engineering has successfully developed 10 (year one) new 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 DOE through the development of reliable and cost-effective advanced clean and efficient fuel cell power generation systems.



### Fiscal Year (FY) 2011 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.
    - Electrodeics and electrochemistry.

## Introduction

The overall scope of the energy systems and technology research and development initiative, at the UCONN Center for Clean Energy Engineering, 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 program 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 generations 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.

During the first year industry collaborations have been executed with UTC Power, FuelCell Energy, UTC Research Center, nzymSys, NanoCell Systems, APSI, Oasys Water and W.R. 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

### **Modeling Resin Flow in Phosphoric Acid Fuel Cells (PAFCs) Gas Diffusion Layers (GDLs) – Project PI: Prof. Rajeswari Kasi, Industry Partner – UTC Power**

UTC Power (UTCP) is interested in attaining stable graphitized GDLs that are used in PAFCs. GDLs coated

with catalyst (also called electrodes) are used to facilitate electrochemical reactions in PAFCs manufactured by UTCP. Resin flow into carbon fiber substrates blocks the open pore structure of the fibers impacting mass flow of various components to the catalyst layer. Furthermore, attaining stable GDLs is important to (1) increase the lifetime of GDLs, (2) efficiency of the power plant and (3) in lowering the cost of stationary and backup power. Thus in keeping with energy efficiency and renewable energy effort of DOE, the stability of GDLs is important for fuel cells to provide a clean, reliable, low-maintenance option for critical energy needs. So, UTCP is interested in generally understanding the morphology of these GDLs and overall resin distribution.

To address this issue, we have used optical imaging tools to qualitatively investigate the morphology of the carbon scaffold at every step of production of the GDLs. This allows us to establish where the carbonized resin is present in the final substrate. UTCP has supplied us with proprietary materials made via proprietary processing conditions. Using imaging as a tool, we have been able to identify two samples that show relatively uniform carbonized resin distribution as compared to other test variants. Our imaging studies (both surface and cross-sectional) have supplemented UTCP to understand the resin distribution and its impact on GDL morphology. In closing, this collaboration between UCONN and UTCP has resulted in improved understanding of morphology and material properties for GDLs in PAFCs, in keeping with the efforts of DOE. Furthermore, the knowledge gained from this study will be useful to implement in other examples of supported catalysts where optimal distribution of catalytic sites is essential for best catalytic performance.

### **Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup – Project PI: Prof. Ashish Mhadshwar, Industrial Partner – nzymSys**

A system designed for the enzymatic desulfurization of biogas has been tested at the lab scale. We have investigated the effect of several operational parameters such as enzyme concentration, biogas flow rate and enzyme boost on process performance. To date, our results show H<sub>2</sub>S removal rates up to 100% without adverse effect on the methane and carbon dioxide concentration of the biogas. Long-term studies performed at high enzyme concentration (20 wt%) demonstrated formation of elemental sulfur, which could be recovered as a valuable product. As expected, the enzyme performance upon H<sub>2</sub>S removal decreases when biogas retention time in the liquid enzyme is reduced. The H<sub>2</sub>S breakthrough occurs at earlier times for higher biogas flow rates with a very steep change in concentration. Furthermore, fast enzyme saturation results upon increasing the gas flow rate. This could be overcome with enzyme replenishment, which indicates that this process could be potentially operated continuously for consistent removal of H<sub>2</sub>S. This simple, reliable, non-conventional technology has various advantages to become one of the most efficient and economical desulfurization technologies and it could

be considered for larger scale applications. Future work will concentrate on evaluate the effect of reactor scale up and effect on mixing (stirring and packing material) on enzymatic desulfurization of biogas.

### Waste to Energy: Biogas Cleanup (Desulfurization) for Energy Generation – Project PI: Prof. Steven Suib, Industry Partner – FuelCell Energy

This project involves the generation of getters (or adsorbents) and catalysts to react with sulfur species in feeds that would be used for fuel cells. The sulfur contaminants include hydrogen sulfide as well as various carbon sulfide materials. The major accomplishment of this work is that new adsorbents and catalyst materials have been made and are being tested for degradation of sulfur contaminants. Various materials have been prepared that are different from commercial desulfurization materials.

Testing of these systems with desulfurization studies clearly show that differences are observed for the various adsorbent materials. Breakthrough curves of various sulfur-containing species have been measured in this case of 0% relative humidity. In addition, studies have been done at various levels of relative humidity. Our results suggest that we have made materials that are more active than commercially available getters and adsorbents. Characterization studies are being done in order to optimize the performance of these materials.

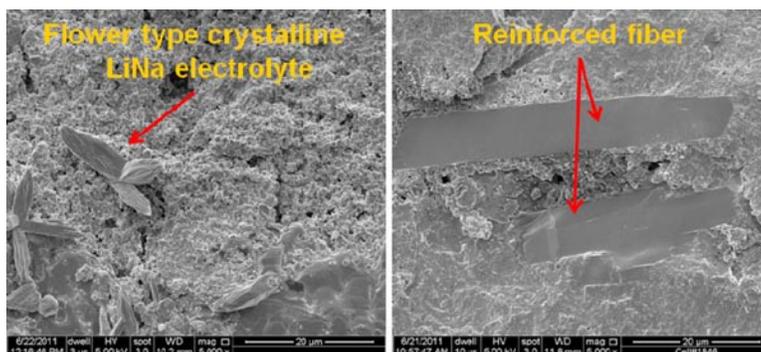
### Mechanistic Understanding of Matrix Stability in Molten Carbonate Fuel Cells – Project PI: Prof. Prabhakar Singh, Industry Partner – FuelCell Energy

Short-term and long-term electrically tested electrolyte matrix samples, obtained from our industrial partner FuelCell Energy, have been examined for morphological and structural changes to understand the coarsening and particle growth behavior. As received samples were examined at the matrix – anode and matrix – cathode interfaces. Samples were subsequently

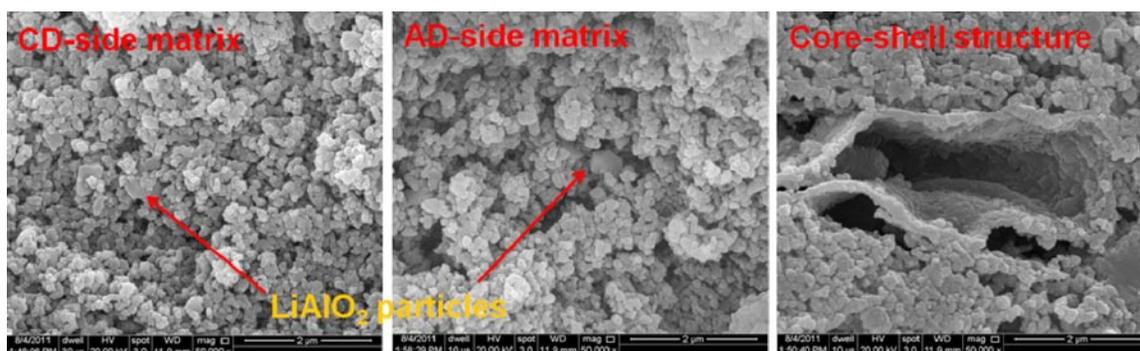
washed in glacial acetic acid-acetic anhydride mixture to dissolve and remove the electrolyte. Obtained samples were further analyzed for the morphology of  $\text{LiAlO}_2$  matrix material. It was observed that the matrix materials show different growth pattern in the anodic and the cathodic environments.

Two matrix samples tested for 240 and 6,984 hours were evaluated using X-ray diffraction, scanning electron microscopy (SEM), and Brunauer-Emmett-Teller techniques. As expected, the matrix samples containing electrolyte showed fully dense matrix structure (with localized porosity on the cathode side). The electrolyte was found susceptible to moisture as evidenced by localized overgrowth of hydrated crystals (Figure 1). Figure 2 shows the fractured cross-section of the matrix on the anode (AD-Side) and cathode (CD-side) tested for 240 h. The matrix morphology shows the presence of reinforcing fibers and core-shell structure. Very little change in the particle growth pattern is noted due to shorter exposure.

Figure 3 shows the cross-section of the electrolyte matrix electrically tested for 6,984 h. The matrix showed the features related to enforcement and core shell structure as observed earlier. Unlike the short-term tested sample, however, the long-term exposed sample showed growth in the particle size.



**FIGURE 1.** Field emission scanning electron microscope (FESEM) images of fracture cross-section of tested matrix. Flower type localized growth of Li-Na electrolyte and reinforced fibers in the matrix (right side).



**FIGURE 2.** FESEM images of fracture cross-section of matrix tested for 240 h. Core shell structure shows the agglomeration of  $\text{LiAlO}_2$  particles. Anode side matrix shows large crystallites.

It was also observed that the growth of particles in the anode side of the matrix was more pronounced than the particles present near the cathode electrode.

**Evaluation of the Performance of Rapidly Quenched Yttria-Stabilized Zirconia (YSZ) Electrolytes in a Solid Oxide Fuel Cell (SOFC) and Its Comparison with Conventional SOFC Architecture – Project PI: Prof. Radenka Maric, Industrial Partner – NanoCell Systems**

The microstructure and properties of rapidly quenched YSZ was investigated for 8 mol% YSZ (8-YSZ) powder manufactured by plasma sprayed using the solution precursor plasma spray technique, to produce metastable nanostructured powders using a pyrolytic melting or vaporization of an aerosol-solution precursor in a direct current-arc plasma. The preparation was done at the Center for Clean Energy Engineering at University of Connecticut in Storrs, Connecticut.

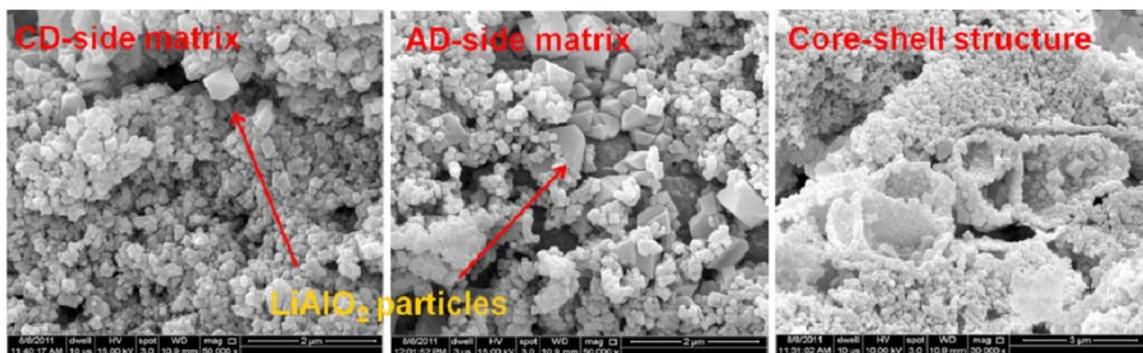
The material, plasma sprayed powder prepared in one processing step, was characterized for the microstructure of powder, thermal analysis and crystalline material structure at various temperatures and atmospheres. It showed stability of structure and composition in all the ranges of temperature and atmosphere the investigations were conducted. Conductivity tests for the plasma sprayed samples displayed slightly better conductivity than the most used YSZ powder, commercial available on market.

**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.**

An integrated model for Short Contact MicroActivity Testing (SCT-MAT) catalyst testing reactors (fixed bed) has been successfully developed. It couples a hydrodynamic model of a fixed bed reactor and a kinetic network that follows a lumping scheme. Moreover, it allows the comparison of predicted yields of the multicomponent

mixture from the reactor with experimental data provided by the industrial partner and acquired through a user interface developed in Microsoft Excel. The algorithm that simulates the fixed bed reactor solves a mathematical model derived from the continuity equation for multicomponent mixtures, using a more general approach than previous studies in the field, taking into account operational peculiarities of the SCT-MAT catalyst testing unit, as employed by the industrial partner. The kinetic network used involves parameters from lumping schemes. These parameters are obtained from an optimization algorithm developed to estimate reaction rates and constants, using the experimental data provided by the industrial partner. Thus, comparison between predicted and experimental yields of the different products of the catalyst testing reactors is available. More sophisticated hydrodynamic models have been developed for the Advanced Catalyst Evaluation (bubbling bed) and the Davison Circulating MicroActivity Riser catalyst testing reactors. Kinetic network models that provide a better insight of the reactions that take place in catalytic cracking reactors are being analyzed. In the near future, the effect of matrix type, zeolite content and diffusion characteristics, such as the crystal size, on the kinetic constants of the lumped kinetic network will be explored. In addition, a user-friendly interface has been developed in Microsoft Excel using visual basic serving two goals: (a) to facilitate the everyday use of the developed process models, and (b) to link the models with the extensive database provided by the industrial partner and ease usage of model during development.

These studies on reactor efficiency, lumped reaction kinetics and contributions of catalytic components will enhance productivity in catalyst research and development, will result in optimizing catalyst selectivity, and eventually lead to improving the overall refinery efficiency. Understanding the origins of coke deposits will help reducing the pollution from the FCC regenerator, while at the same time increasing FCC capacity by relaxing its carbon burning constraints. In that notion, this research project will aim to make FCC a cleaner process. Moreover,



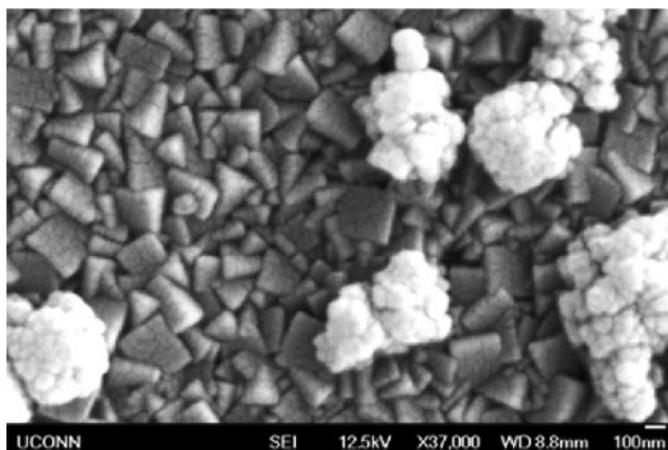
**FIGURE 3.** FESEM images of fracture cross-section of matrix tested for 6,984 h.  $\text{LiAlO}_2$  particle coarsening is evident in cathode and anode side matrix. Core-shell structure shows the overgrowth of  $\text{LiAlO}_2$  particles.

the fundamental knowledge acquired while decoupling reaction kinetics and catalyst deactivation and separation of the effects of zeolite and matrix on catalyst activity and selectivity, can be used to decouple gas and catalyst residence times to optimize biomass gasification and pyrolysis while decreasing secondary reactions.

#### Stannate-Based Semiconductor Nanocomposites for Solar Energy Utilization – Project PI: Prof. Puxian Gao, Industry Partner – UTC Research Center

First, continuous zinc hydroxystannate (ZHS) cube films have been achieved on both polycrystalline metallic substrates and transparent conductive substrates using hydrothermal synthesis method. As an example, via a fluidic chamber assisted hydrothermal method, continuous ZHS nanocube film have been fabricated on quartz or glass substrates, as shown in Figure 4. The temperature, pressure, and base concentration have been successfully used to control the cube coverage, crystallinity, size and film density.

Second, the structure evolution of ZHS cubes under various ambient annealing conditions has been extensively studied using a combination of structure, morphology and thermal analyses. Various in situ and ex situ microscopy and spectroscopy techniques have been utilized. The temperature windows of various phase transitions have been identified during the thermal decomposition of ZHS. Both temperature and ramping rate are found to be important parameters to control during the thermal processing of ZHS cube films, in order to achieve desired gradient functional composite cube films. The electronic and optical properties evolution in the ZHS cubes have been investigated. Using ZHS micro- or nano-cubes as template and precursor, gradient core-shell stannate-based composite cubes have been achieved after thermal processing. The optical and electronic properties of the gradient structures and corresponding photovoltaic cell performance are under investigation.



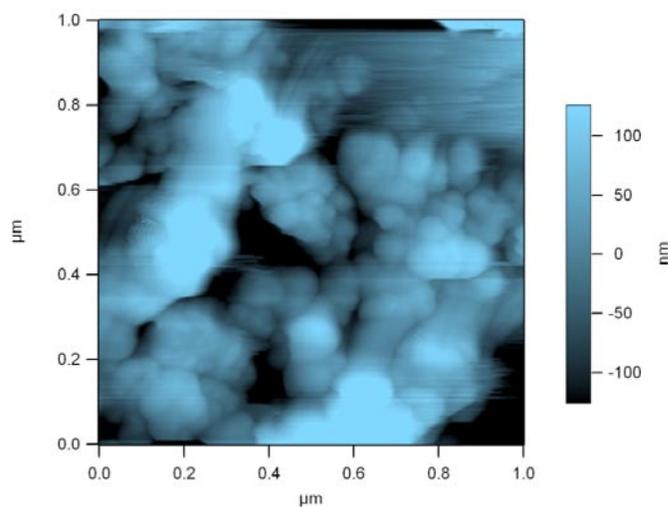
**FIGURE 4.** An SEM image for ZHS nano-cube films on quartz substrate synthesized by fluidic chamber assisted hydrothermal method.

#### Fuel Cell Electrode Microstructure: Nanoscale Stability and Efficiency – Project PI: Prof. Bryan Huey, Industrial Partner – UTC Power

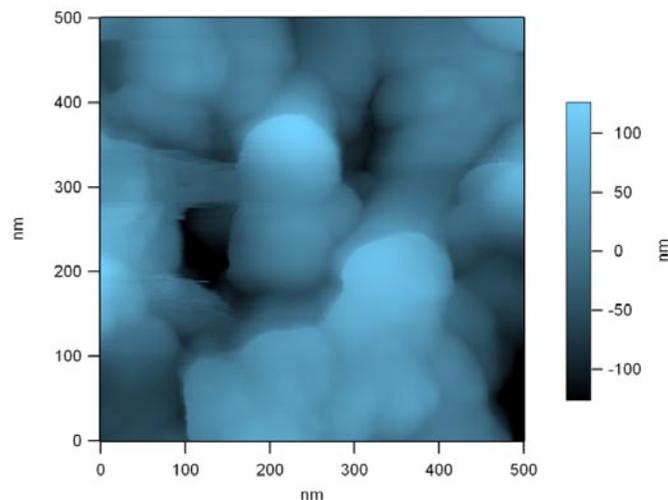
Main results focus on two key aspects of fuel cell electrode microstructures.

First, atomic force microscopy (AFM) reveals profound differences in the catalytic nanoparticles in their raw state (Figure 5) and as a floc (upon Teflon<sup>®</sup> coating, Figure 6). The particle size is larger, Teflon<sup>®</sup> is occasionally drawn into fibers by the manufacturing process, and the <50 nm particles common in the raw material increases to >100 nm following Teflon<sup>®</sup> coating.

Second, upon phosphoric acid (PA) loading of the electrode, the Teflon<sup>®</sup> is occasionally found to separate from the underlying catalyst particles. This is clearly observed



**FIGURE 5.** Pure Catalyst (10-100 nm particles)



**FIGURE 6.** Teflon<sup>®</sup> Floc (>100 nm particles)

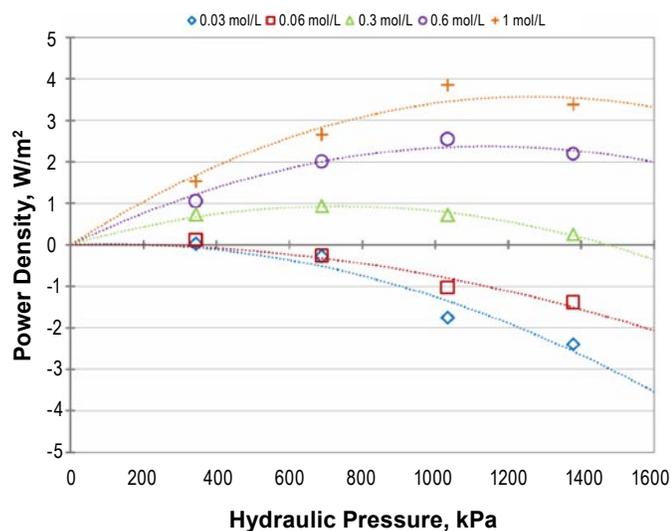
by AFM, both in topographic images where the Teflon<sup>®</sup> appears to have delaminated from the catalyst, as well as in simultaneous AFM phase contrast which reveals the local mechanical compliance. Notably, Teflon<sup>®</sup>/catalyst separation was only observed following PA loading, but never before PA exposure. It is unclear whether the PA loading procedure, or the simple act of Teflon<sup>®</sup> swelling upon PA exposure, causes such rupture.

### Waste Heat Recovery using the Ammonia-Carbon Dioxide Osmotic Heat Engine – Project PI: Prof. Jeff McCutcheon, Industrial Partner – Oasys Water

Salinity gradient power technologies are quickly coming to the forefront of alternative approaches for producing electricity. One such technology being developed by Oasys Water is the Osmotic Heat Engine, a modified version of an engine cycle that uses a liquid phase intermediate to transfer energy to a turbine. Our work has been primarily focused on developing new membranes for this process. Our approach has two tasks.

First, we have developed a unique benchtop system for testing membranes under pertinent conditions in the osmotic heat engine. These systems are generally unavailable, and our system has shown that it can measure the power generating capacity of membranes (in watts/m<sup>2</sup>). The system has yielded positive results using a commercial membrane designed for *forward osmosis*, a sister technology to osmotic power. Figure 7 shows power densities approaching 4 watts/m<sup>2</sup> using 1M NaCl salt solutions. This is near the industry target (4 watts/m<sup>2</sup>) and this is the first time this commercial membrane has been successfully tested under this condition.

The second task has been to develop new membrane technology for pressure retarded osmosis (PRO) specifically.



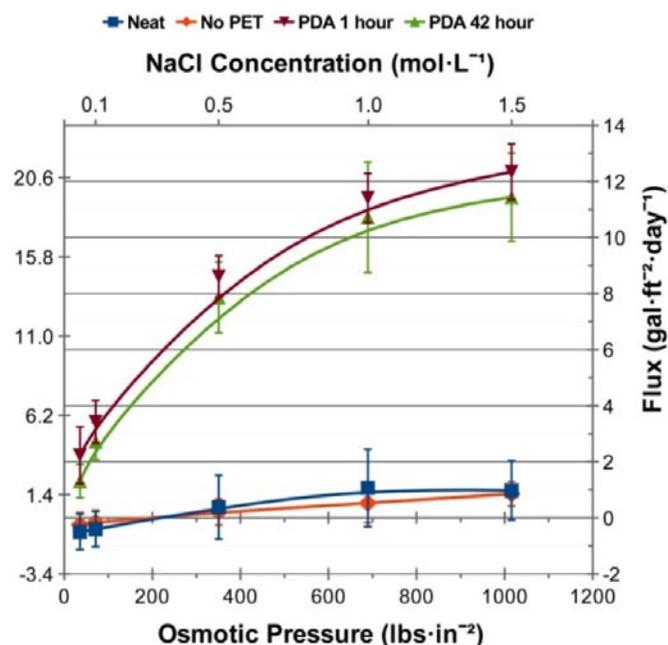
**FIGURE 7.** Power densities of commercial forward osmosis membrane using different salt concentrations over a range of hydraulic pressures.

We have found a way to modify current generation reverse osmosis (RO) membranes (which can operate under PRO conditions, but in the past have been very poor performers). We have modified RO membranes with polydopamine, a hydrophilic bio-inspired polymer to enhance osmotic flux. Our modifications have resulted in 8-12X increase in osmotic fluxes (Figure 8). Our next tasks will be to optimize this modification technique and test power density with the PRO system.

### Fuel Reforming Catalysts for Efficient Energy Usage – Project PI: Prof. Steven Suib, Industry Partner – APSI

The major accomplishment of this project is that a new method has been discovered that allows formation of a fuel reforming catalyst with much less catalyst. This decreases cost and increases efficiency of the reforming of fuel. This method has been submitted as a patent application. The ability of this next generation catalyst to activate the reforming of hydrocarbons is under investigation and looks promising. This method involves the use of thin metal foils of various compositions that are immersed in solutions of precursors of other metals to produce metal alloy catalysts.

Characterization of these materials has involved surface composition, bulk composition, structure, electronic, and morphological properties. Various methods like atomic absorption, inductively coupled plasma, energy dispersive X-ray analysis, SEM, scanning Auger microscopy, X-ray powder diffraction, surface area, and pore size distribution methods are being used. Catalytic testing of the catalyst is being done with various fuels. Characterization of reactants,



**FIGURE 8.** Osmotic fluxes of native and modified off the shelf reverse osmosis membrane from Dow Water and Process Solutions.

products and intermediates is done using gas chromatography, liquid chromatography, mass spectrometry, and temperature programmed desorption studies.

## Conclusions and Future Directions

The 10 first-year projects are still ongoing and will continue through the balance of this calendar year. As appropriate, this list may be expanded to include a small number of additional relevant projects that address the technology gaps and barriers described. Future directions may include:

- 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.
- 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.

## Patents Issued

1. Invention Disclosure filed for efforts associated with program on the Evaluation of Enzyme-Based Sulfur Removal Technology For Gas Clean up with nzymSys as the industrial partner.
2. P.X. Gao, and C.H. Liu, Method of making gradient composite nanostructures through thermal engineering, UConn Invention Disclosure, in preparation, Fall 2011.

## FY 2011 Publications/Presentations

1. P.X. Gao, P. Shimpi, W.J. Cai, H.Y. Gao, D.L. Jian, G. Wrobel, Hierarchical Composite Nanowires for Energy, Environmental and Sensing Applications, *Proceedings of SPIE* Vol. 7940, pp. 79401A1-11, 2011 (invited).
2. P.X. Gao, Hierarchical Composite Nanowires for Energy, Environmental and Sensing Applications, *SPIE Photonics West Conferences*, San Francisco, Jan. 25, 2011 (Invited).

3. P.X. Gao, P. Shimpi, H.Y. Gao, W.J. Cai, and G. Wrobel, Multifunctional Composite Nanostructures for Energy and Environmental Applications, *The 4th International Symposium for Advancement of Chemical Science: Challenges in Renewable Energy*, Boston, July 5-8, 2011.
4. G. Wrobel, M. Piech, S. Dardona, and P.X. Gao, *MS&T 2011 fall meeting*, Oct 16-21, 2011, Columbus, OH. (Accepted, oral presentation).
5. C.H. Liu, G. Wrobel, S. Dardona, M. Piech, and P.X. Gao, *MRS 2011 Fall meeting*, Boston, Nov. 28-Dec. 2, 2011, submitted.
6. K.T. Liao, P. Shimpi, and P.X. Gao, *MRS 2011 Fall meeting*, Boston, Nov. 28-Dec. 2, 2011, submitted.
7. G. Bollas, D Orlicki, and H Ma, FCC selectivity studied in lab-scale units and pilot plants, *ACS Annual Meeting*, August 2010, Boston, MA.
8. G. Bollas, D Orlicki, and H Ma, Some uses and misuses of FCC catalyst testing experimental data *AICHE Annual Meeting*, November 2010, Salt Lake City, UT USA.
9. R. Maric, M. Dragan, and J. Roller, 2011 HiTemp Conference, Sept. 20-22, 2011, Boston.
10. R. Maric, M. Dragan, and J. Roller, 2011 MRS Conference, Nov. 28 – Dec. 2, 2011, Boston.
11. Kailash Patil and Prabhakar Singh, "LiAlO<sub>2</sub> solubility measurement in (Li-K) carbonate melt," *Materials Science & Technology 2011 Conference & Exhibition*, October 16-20, 2011 Columbus, Ohio.

## Proposals Developed Leveraging Results of this Program

1. Small Business Innovation Research proposal submitted to Department of Defense on "Biogas purification for fuel cells".
2. P.X. Gao (PI), M. Piech (coPI), and S. Dardona (coPI), Thermally engineered graded composite nanostructures for solar energy harvesting, National Science Foundation GOALI proposal, in preparation, Fall 2011.