Improving Fuel Cell Durability and Reliability

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University of Connecticut
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Project ID #FC079

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CENTER FOR CleanEnergy ENGINEERING
UNIVERSITY OF CONNECTICUT

Overview

Timeline Data:
- ✓ Start date: August 1, 2010
- ✓ End date: July 31, 2013
- ✓ Percent complete: 60%

Barriers Addressed:
- ✓Durability
- ✓Cost
- ✓Performance

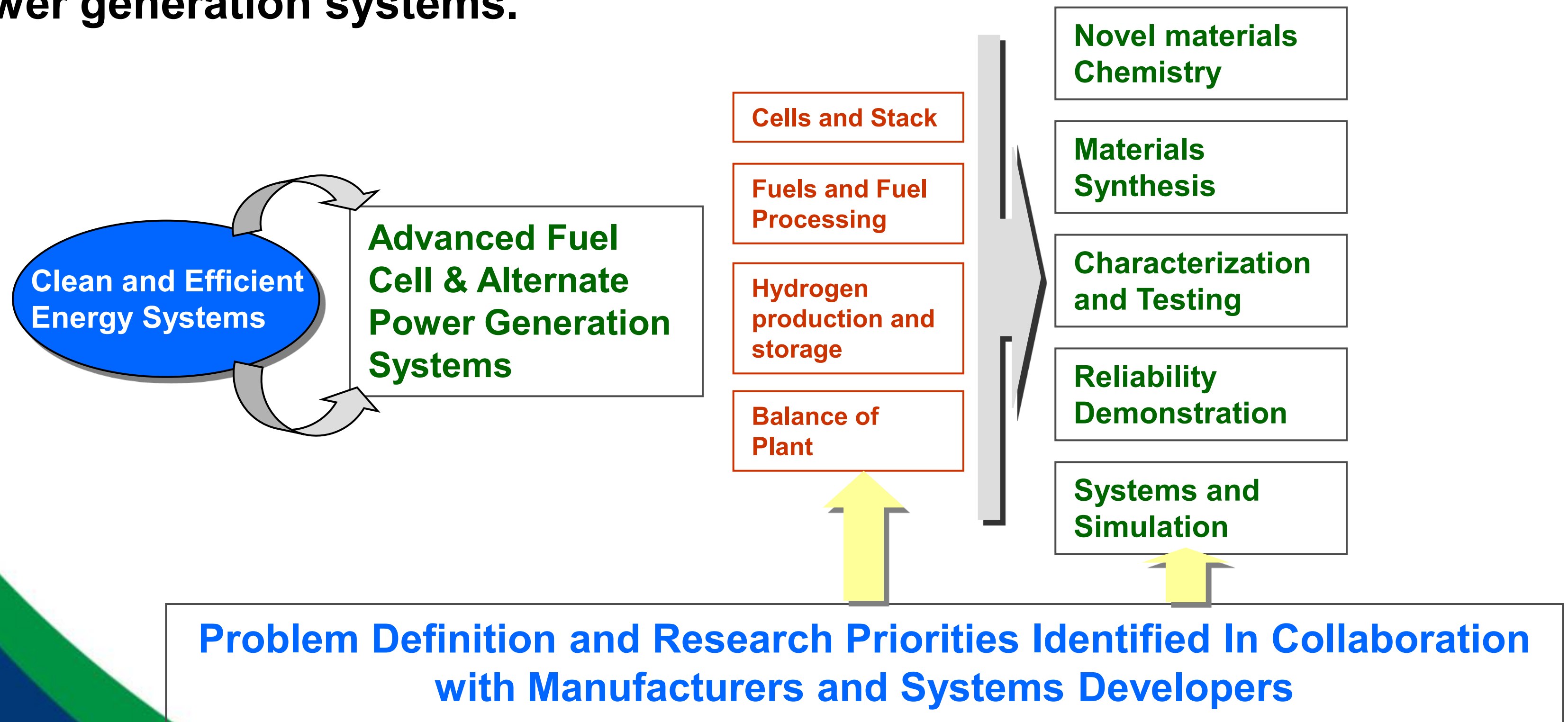
Budget:
- ✓ Total project funding
  - ➢ DOE share: $2,500,000
  - ➢ Contractor share: $ 625,000
- ✓ Funding for FY11: $ 443K
- ✓ Planned Funding for FY12: $ 1,200K

Partners:
- ✓ Interactions/ collaborations
- ✓ Project lead

Relevance

Objectives:

- Develop an understanding of the degradation processes in advanced electrochemical energy conversion systems.
- Develop collaborative research programs with industries to improve the performance stability and long term reliability of advanced fuel cells and other power generation systems.



Relevance (continued)

Technology Objectives:

- ✓ Advance fuel cell based power generation systems architecture, including renewable hybridized energy conversion and storage (Barriers: B-Cost, C-Performance)
- ✓ 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 (Barriers: A-Durability, B-Cost, C-Performance)
- ✓ 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 their 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.

Address Barriers ➡ A-Durability, B-Cost, C-Performance

Approach

The overall scope of the energy systems and technology research and development initiative, at 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.

- **The performance stability and reliability of the power generation systems will be improved through the implementation of advanced materials and fabrication processes.**

- **Specific technical areas of interest, to be addressed by the industry/university collaborations will include:**
  - Performance stability and reliability of fuel cell systems.
  - Fuels, fuel processing and catalysis
  - Advanced functional and structural materials, processes and systems
  - Hydrogen storage and power management
  - Renewable energy and resources

Collaborations

- Develop Collaborative Programs with Industry that Identify and Solve Technology Gaps through Joint Industry / University Research Programs. These relationships will accelerate the development and deployment of clean and efficient multi-fuel power generation systems.

- The scope of research programs 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.

Current Industrial partners Involved in collaborative energy systems research and development program at UConn include:

- ✓ FuelCell Energy
- ✓ UTC Research Center
- ✓ UTC Power
- ✓ Nissan Automotive
- ✓ nzymSys
- ✓ NanoCell Systems
- ✓ APSI
- ✓ Proton OnSite
- ✓ W.R. Grace
- ✓ Oasis water
- ✓ SciTech
- ✓ Precision Combustion

Ongoing Work

- Advanced functional and structural materials R&D 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.

Summary

- University of Connecticut Center for Clean energy Engineering (C2E2) is leveraging USDOE funds with industrial funds to accelerate the development of advanced clean and efficient energy systems. UConn has partnered with 10 industries (in total) to address the systems issues from advanced cell and stack to fuels cleanup and processing to thermal management and balance of plant materials.
- C2E2 and its industrial partners have successfully identified technology gaps and research needs for accelerating the development and deployment of advanced fuel cell systems.
- Research efforts will examine long term electrical performance degradation related to cell component materials stability (bulk and interfacial), electrodics, fuel impurities and nominal/transient operation. Mechanisms are being developed and validated.
- Technologies related to materials, processing, gas cleanup systems, balance of plant will be transferred to industries for implementation in manufacturing.

To Date this program has generated:

- 4 Patents
- 7 Journal Articles have or are being Published
- >15 Conference Presentations

Technical Approach & Accomplishments

Technical and programmatic tasks for years two and three:

- **Task 1: Performance stability and reliability of fuel cell systems**
  - **1.1 Role of Multi-Scale Water Transport in Dynamic Performance of PEMFCs**
    Industry Partner: Nissan Automotive, PI: Prof. Ugur Pasaogullari
  - **1.2 Modeling of Resin Flow in the Manufacture of PAFC GDLs**
    Industry Partner: UTC Power, PI: Prof. Rajeswari Kasi, Co-PI: Prof. Prabhakar Singh
  - **1.3 Develop Mechanistic Understanding of long term MCFC Matrix Stability**
    Industry Partner: FuelCell Energy, PI: Prof. Prabhakar Singh
  - **1.4 High Performance PAFC Electrodes for Soluble Polymers and Alternate Fabrication Methods**
    Industry Partner: UTC Power, PI: Prof. Ned Cipollini
- **Task 2: Fuels, fuel processing and catalysis**
  - **2.1 Biomass Cleanup (Desulfurization) for Energy Conversion**
    Industry Partner: FuelCell Energy, PI: Prof. Steve Suib
  - **2.2 Fuel Reforming Catalysts for Efficient Energy Usage**
    Industry Partner: Advanced Power Systems Inc., PI: Prof. Steve Suib
  - **2.3 Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup**
    Industry Partner: nzymSys, PI: Prof. Ashish Mhadeshwar
  - **2.4 High Reliability, Low Cost Thermally Integrated Water Gas Shift System Design Development Support**
    Industry Partner: FuelCell Energy, PI: Prof. Ashish Mhadeshwar
- **Task 3: Advanced functional and structural materials, processes and systems**
  - **3.1 Evaluation of the performance of rapidly quenched YSZ electrolyte in a SOFC and its comparison with conventional SOFC architecture**
    Industry Partner: NanoCell Systems Inc., PI: Prof. Radenka Maric
- **Task 4: Hydrogen Storage and Power Management**
  - **4.1 Nanostructured Catalyst-Support Systems for Next Generation Electrolyzers**
    Industry Partner: Proton OnSite, PI: Prof. William Mustain

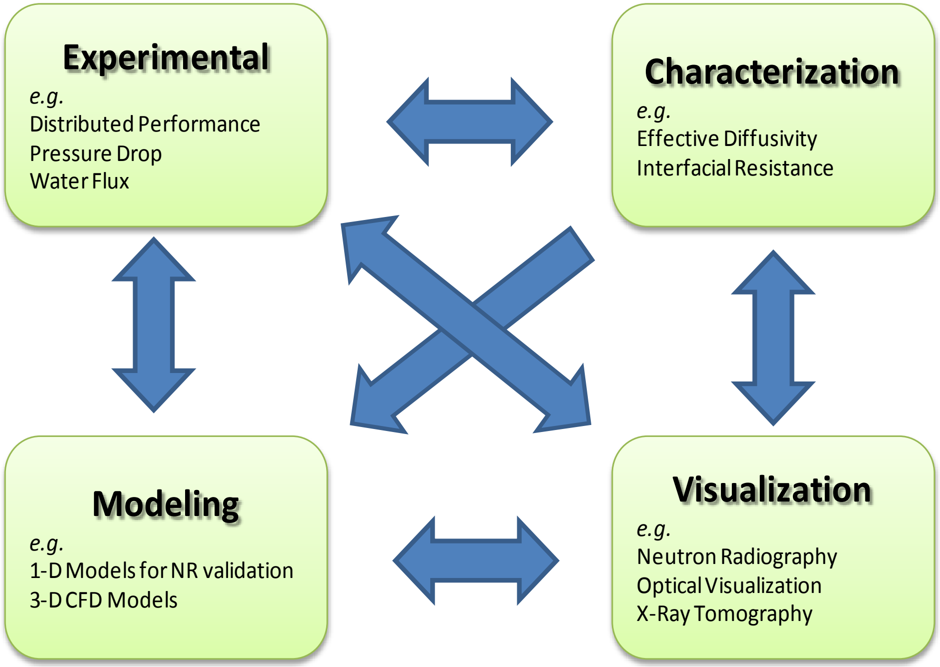
Task 1.1: Role of Multi-Scale Water Transport in Dynamic Performance of Polymer Electrolyte Fuel Cells

- Project Objectives:
  - Develop a computational model supported with experiments to enable very high power density operation that enables significant cost reduction (Target: \$30/kW by 2017)
  - Understand the effect of multi-phase water transport on dynamic response (Target: <30 s start-up to 90% power by 2015)

Prof. Ugur Pasaogullari (PI)
Industry Partner: Nissan Automotive

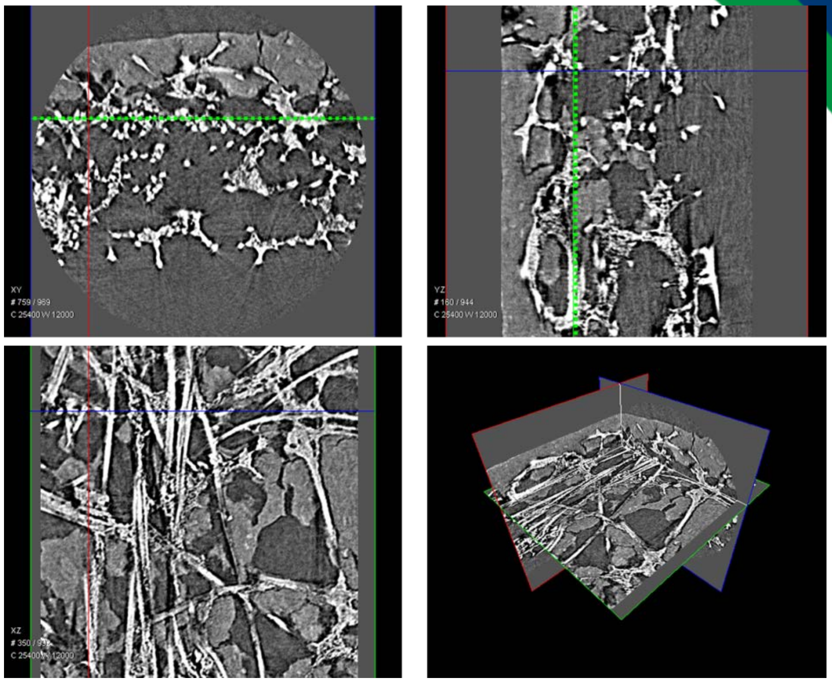
Project Approach

- Coupled experiments and computational models
  - Cell performance characterization:
    - Role of DM wettability on I-V
    - Effective diffusivity -limiting current
  - x-ray visualization
    - Micro-porous structure and liquid morphology in MPL and CL
    - Effective directional tortuosity
  - Neutron radiography
    - In-situ measurement of water
  - Material property characterization
  - 1-D, SS models for NR validation
    - Liquid water thickness comparison, systematic error analysis-finite resolution correction
  - multi-dimensional models for in-plane & through-plane phenomena description
    - Predict dynamic cell performance



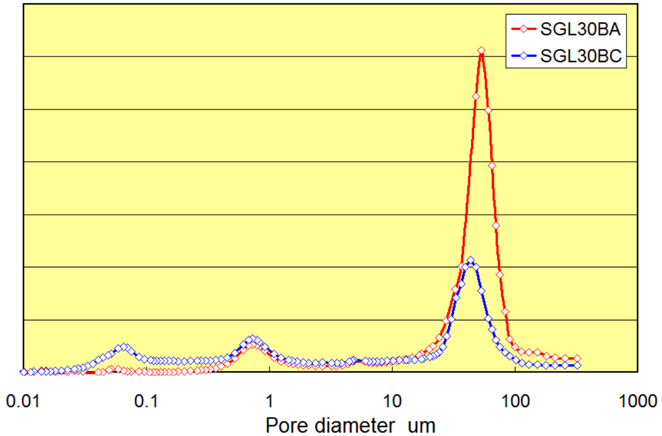
Accomplishments

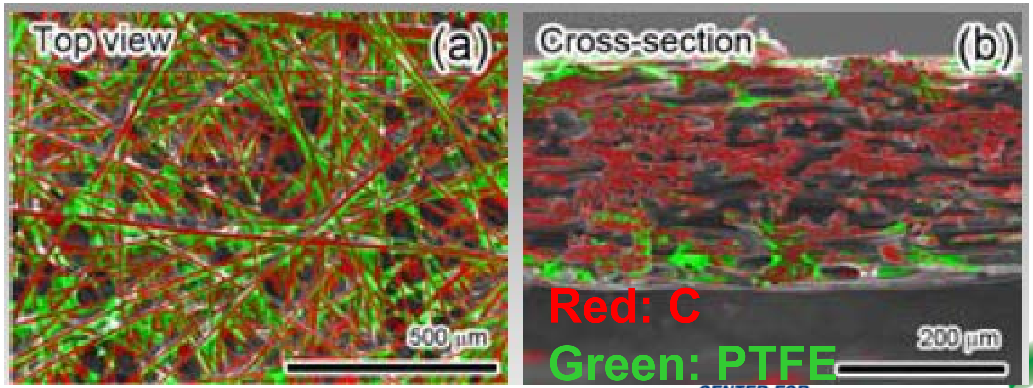
μXCT of untreated and treated GDLs



Sigracet® 10BC (treated with MPL)

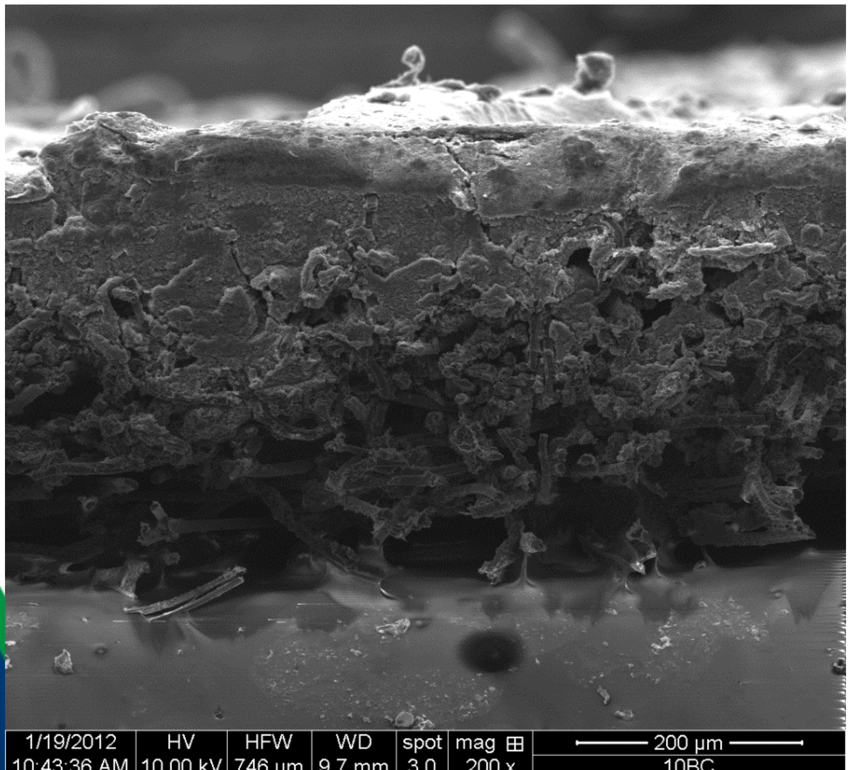
- Non-uniform MPL thickness and penetration into substrate
- MPL significantly alters the pore size distribution:
  - New smaller pores (ca. <0.1 μm)
  - Larger pores (10-100 μm) disappeared
    - MPL ink penetration?

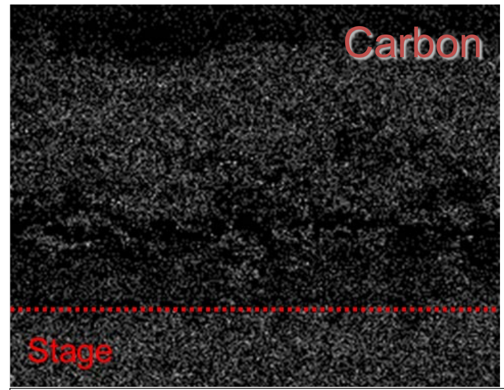


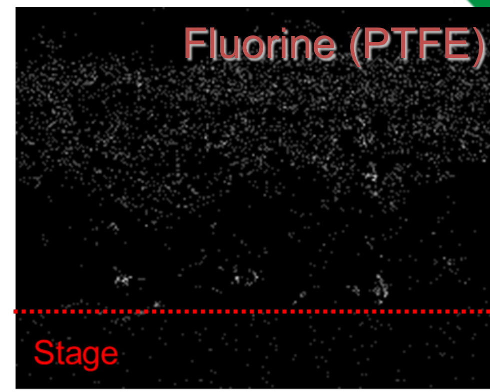


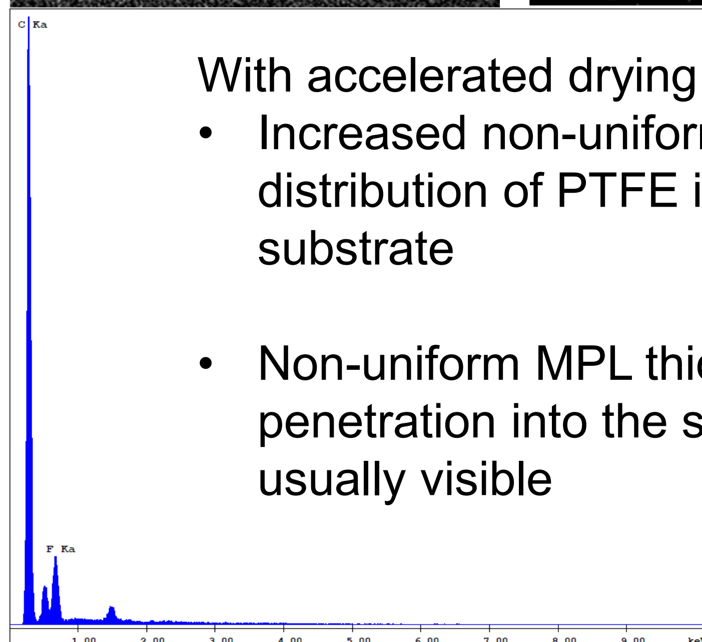
Accomplishments (2)

Effect of GDL Fabrication on PTFE distribution









With accelerated drying

- Increased non-uniformity in the distribution of PTFE in the substrate
- Non-uniform MPL thickness and penetration into the substrate is usually visible

Future Work

- Synchrotron x-ray imaging: *Anticipated* beam-time (APS) in Summer 2012
  - In collaboration with APS for preliminary testing
  - Designed and fabricated a sample holder that can control compression and liquid saturation level in MPL and CL
    - Prototype experiments are underway with in-house μXCT
- Neutron Radiography: <u>Confirmed</u> beam-time (NIST-NCNR) in Summer 2012
  - Effect of coupled wettability of DM surface and channel walls
- Computational Model Development
  - Dynamics of liquid water transport in gas channels

Task 1.2: Modeling of Resin Flow in the Manufacture of PAFC GDLs

Problem: Resin flow into carbon fiber based substrates blocks open pore structure of these fibers impacting properties like mass transport of liquids and gases to catalyst layers as well as thermal and electrical conductivity of the gas diffusion layer (GDLs).

To address this problem: establish and relate processing/manufacturing conditions that result in optimal properties of GDL with optimal carbonized resin distribution in the final GDL. This will increase efficiency and life of the power plant, and lower the cost.

Approach: Can imaging be used as a tool to understand and investigate carbonized resin distribution in the GDLs?

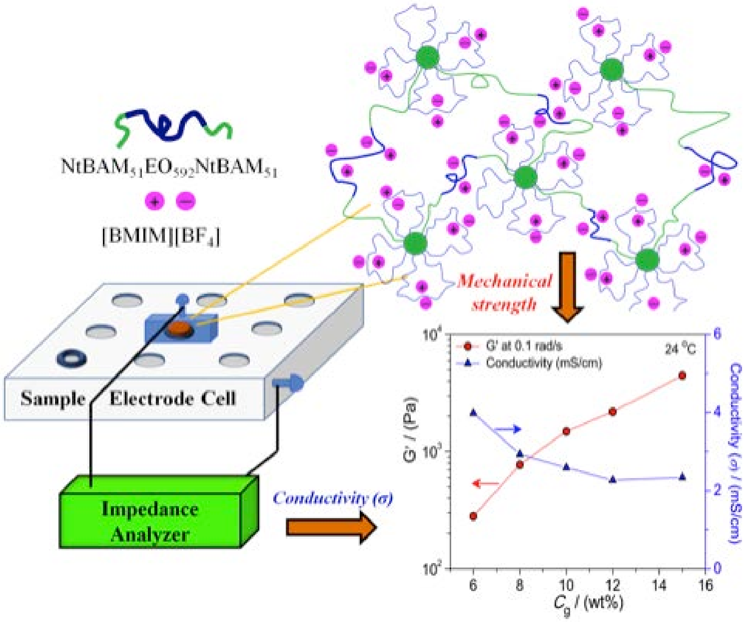
- Use optical methods and SEM to surface, cross section of the fibers at each step of the manufacturing process: raw carbon fibers or felt, impregnated felt, final substrate or GDL.
- Investigate resin distribution in each step: morphology
- Correlate processing/manufacturing parameters with carbonized resin distribution in the final GDL that will have optimal features and optimal costs for fuel cell applications.

Prof. Rajeswari Kasi (PI)
Industry Partner: UTC Power

Accomplishments

- Conducted comprehensive surface and cross-sectional imaging analysis of carbon fiber, impregnated felt, and final GDL substrates prepared under different processing parameters. A few thousand SEM images have been obtained and analyzed.
- By thorough morphological analysis, we were able to identify the GDL substrates (out of 14 samples) that show optimal carbonized resin distribution. This GDL also showed optimal subscale fuel cell and other parameter testing!
- Our general understanding and approach used in this project can be extended to other catalytic systems that are bonded /embedded/confined within porous medium. The pore size and its distribution will impact the catalytic property as will the mechanical, thermal and conducting features. This will be leveraged for grant applications to other federal funding sources.

Future Work: Develop polymer-ionic liquid gels that will serve as materials for solid-state electrochemical devices and porous scaffolds for catalysis (akin to GDLs). We have designed a polymer substrate that can gel ionic liquids with optimal mechanical, thermal and conducting features.



Task 1.3 MCFC Matrix Stability

Program Objective: Overall objective of the proposed effort is to (a) develop an integrated physico-electro-chemo processes based mechanistic understanding for the electrolyte matrix degradation in molten carbonate fuel cell (MCFC) power systems, and (b) identify and validate mitigation approaches that provides a stable electrical performance for >80,000 hours

Relevance to EERE Mission: The Office of Energy Efficiency and Renewable Energy (EERE) invests in clean energy technologies that strengthen the economy, protect the environment, and reduce dependence on foreign oil. The proposed research and development program supports the overall mission through the development of advanced matrix materials for MCFC power generation systems that meets the life and reliability requirements.

Prof. Prabhakar Singh (PI)
Industry Partner: FuelCell Energy

Approach

Problem definition: The conventional electrolyte matrix, consisting of $LiAlO_2$ ceramic particles and molten Li-Na-K carbonate electrolyte melt, shows structural and morphological changes resulting in

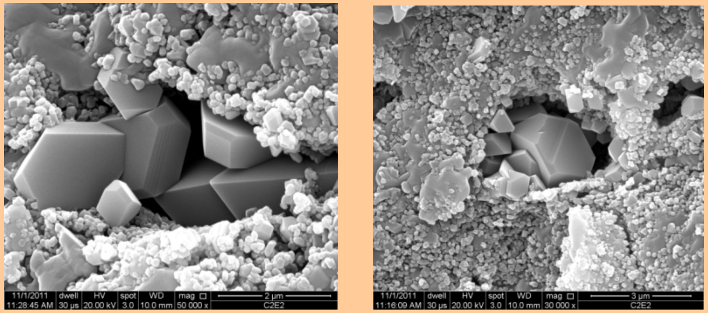
(1) coarsening and phase transformation of $LiAlO_2$ particles,
(2) particle and pore size distribution and
(3) reduction and redistribution of the electrolyte melt in the bulk matrix structure.

Above changes result in increased cell resistance, intermixing and gas cross over leading to degradation and lowering of the electrical performance of the cell and stack.

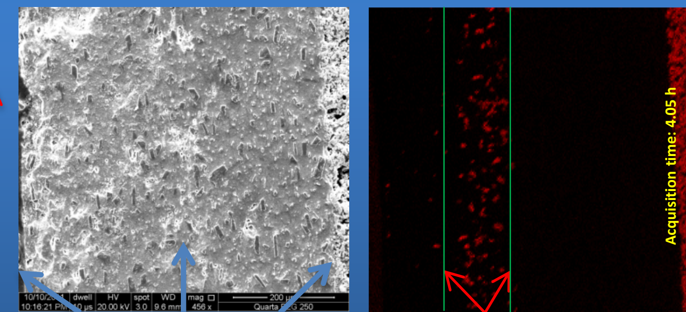
Technical Approach: The technical approach consists of understanding the processes influencing the matrix structural changes. Specifically, this technical approach consists of:

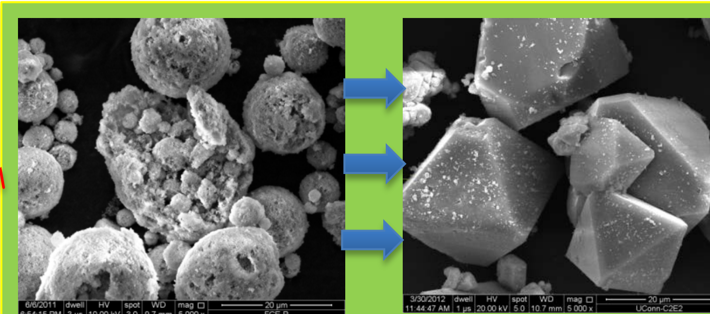
(a) measurement of solubility and identification of the role of acidic/basic conditions under the influence of partial pressure of oxygen and carbon dioxide at the operating temperature of 650°C,
(b) develop an understanding of the electrolyte matrix coarsening mechanism for the state of the art $LiAlO_2$ matrix material,
(c) quantify the coarsening and structural changes occurring in the state of the art matrix structure (tape cast matrix containing a mixture of molten carbonate electrolyte and $LiAlO_2$ ceramic), and
(d) identify, test and validate advanced matrix materials with reduced coarsening leading to enhance the overall life of the system (> 60,000 – 80,000 hrs.).

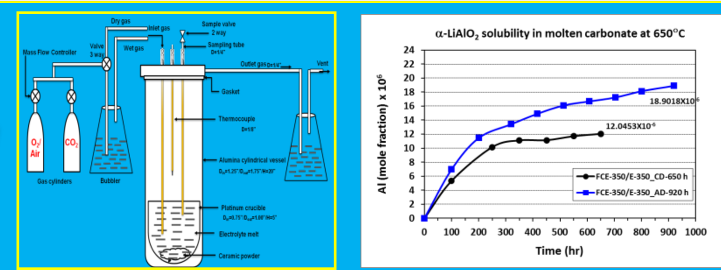
Accomplishments



Matrix Crystallization and Grain Growth







- Coarsening of matrix support has been experimentally validated. Well defined crystalline structure forms due to the dissolution and preferential precipitation (Solid – liquid interaction).
- Nickel precipitation in the electrolyte matrix has been observed due to the dissolution of the cathode and its subsequent precipitation (as metallic Ni) in the electrolyte matrix. The precipitation front is dictated by the oxygen potential $\{(PO_2)_{matrix} < (PO_2)_{Ni/NiO}\}$
- Bench top test set up has been assembled for the evaluation of matrix solubility in the anodic and cathodic environment. Solubility measurement s are being performed on modified matrix materials and electrolyte formulations.

Proposed Future Work

- ✓ Develop materials solubility data base through laboratory bench top experiments under anodic and cathodic exposure conditions.
- ✓ Develop and validate dissolution and growth mechanisms under acidic and basic fluxing conditions.
- ✓ Identify role of additives to the matrix bulk and electrolyte chemistry. Conduct experiments to quantify the role of additives on the material solubility, growth rate.
- ✓ Develop mechanism and optimize operating parameters to mitigate the matrix coarsening.

Task 1.4 High Performance Phosphoric Acid Fuel-Cell Electrodes from Soluble Polymers

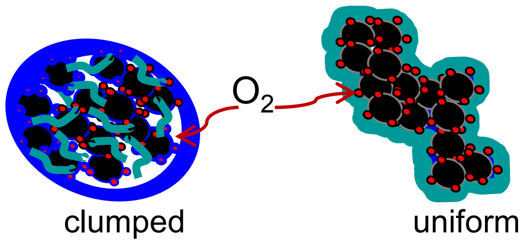
- Project Objective: Improve producibility, increase reliability, and enhance performance of present PAFC electrodes. Success in this program will enable reducing the cost of electrode fabrication; lower materials cost or improve efficiency by enhancing cell performance and decreasing performance decay.

- Project Goal: NG-fueled PAFCs meet or surpass most 2012 DOE requirements for distributed power including efficiency and lifetime, but factory costs are 5-10X Target. This project addresses factory costs at a fundamental level.

Dr. Ned Cipollini (PI)
Industry Partner: UTC Power

Approach:

- Identify optimum agglomerate structure, e.g.:
  - Black-carbon
  - Red Pt-alloy catalyst
  - Dark blue phosphoric acid
  - Green-blue PTFE
  - Distribution of PTFE key in controlling phosphoric acid film thicknesses



- Develop a reproducible, inexpensive method to make the desired structure
- Develop a Soluble Polymer Approach with:
  - A uniform PTFE distribution can improve mass transport significantly ~90 mV @ 200 mA/cm^2 4% O_2 over a clumped distribution
  - Viscosity of PTFE at melt point is ~10^6 cp, too high for appreciable uniformity if electrodes are made from PTFE dispersion + catalyst.
  - Use a soluble form of TEFLON® to produce uniform TEFLON layers
    - Soluble TEFLON is too expensive for commercialization and the approach will involve taking a known, inexpensive perfluorinated material and dissolving it in a solvent at high pressure and temperature.

Soluble Polymer Provides the following potential Benefits:

- Simplified manufacture of electrodes – becomes more PEMFC-like.
- Improved power density, ~ 25% under PAFC operating conditions
- Can help meet DOE goals of factory costs, and/or improved efficiency

Task 2.1: Waste to Energy: Biogas Cleanup (Desulfurization) for Energy Generation

Project Objective:

1. Synthesis of Novel Adsorbents and Catalysts for Trace Sulfur Species from Anaerobic Digested Gas.
2. Characterization of Adsorbents, Catalysts, Breakthrough Curves.
3. Study Effects of Co-adsorbed Species, Temperature, Pressure.
4. Studies of Mixed Adsorbents and Catalysts.
5. Licensing and Technology Transfer to FCE from UCONN of Next Generation Adsorbents for Cleanup of Anaerobic Digester Gas (ADG).

Relevance to DOE EERE: The U.S. Department of Energy funds research, development, and demonstration to help develop sustainable, cost-competitive biofuels, bioproducts, and biopower.

From DOE EERE website:

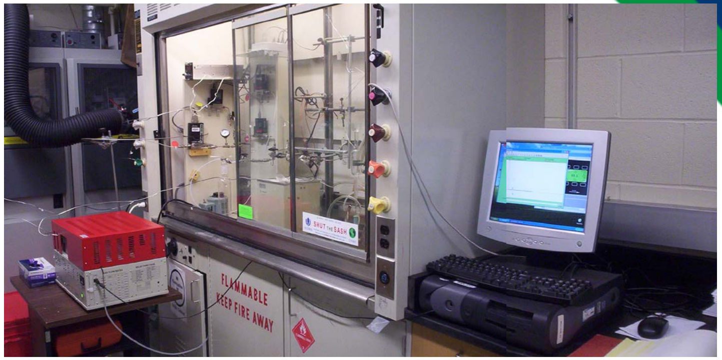
These R&D efforts focus on technologies and processes that can reduce the cost and increase the efficiency of producing biofuels, products, and power. Efficiencies can be achieved through methods for increasing the yields derived from conversion of various feedstocks, among other improvements.

Prof. Steven Suib (PI)
Industrial Partner: FuelCell Energy

Project Approach

Unique Aspects of our Approach:

1.Biogas Impurities - Goal to Find Adsorbents To Getter both S and N Poisons.
2. Manganese Oxide Adsorbents – Unique Materials with Excellent Adsorption Capacity.
3. Packed-bed Reactor – Novel Reactor Designs.
4. Experimental Setup – Breakthrough Curves.
5. Breakthrough and Sulfur Capacity (at 5 ppm). Very Low levels.



Durability and Performance:

1. Screening - 0% RH, Best DMS Removal, Sulfur Capacity of ~2 g-sulfur /100 g Sorbent.
2. At 20 and 40% RH, Fe-OMS2 Decreases Sulfur Capacity to 0.7.
3. Coating Sorbents with PDMS Decreases Sulfur Capacity, even at High Moisture Content.
4. XRD of the Adsorbents after Sulfur Removal Shows No New Crystal Phases – Stable System.
5. Direct Thermal Desorption of Adsorbents - Possible Oxidation of Sulfur to Sulfones.

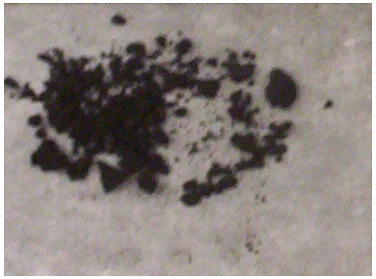
Milestones and Status:

1. Adsorbent Preparation, Optimization of Activity – Done.
2. Scale-Up of Adsorbent – In Progress.
3. Testing at FCE – Done.

Prof. Steven Suib (PI)
Industrial Partner: FuelCell Energy

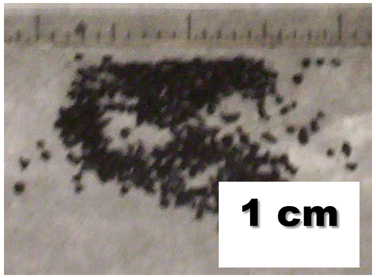
Accomplishments

Co-KOMS2

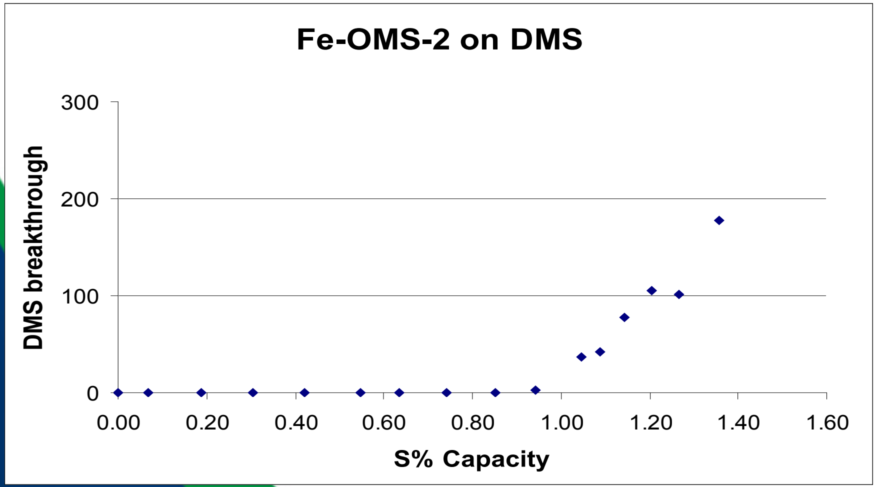


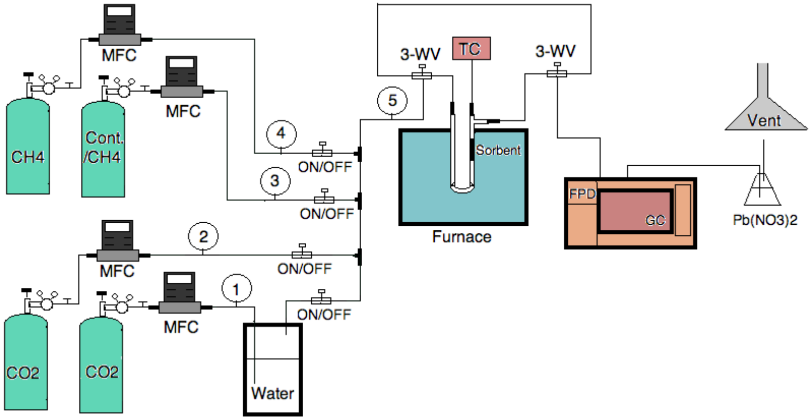
Sieves 14-20 mesh
(1.4 mm - 850 µm)

Co-KOMS2 granules



Synthesis of Adsorbents.

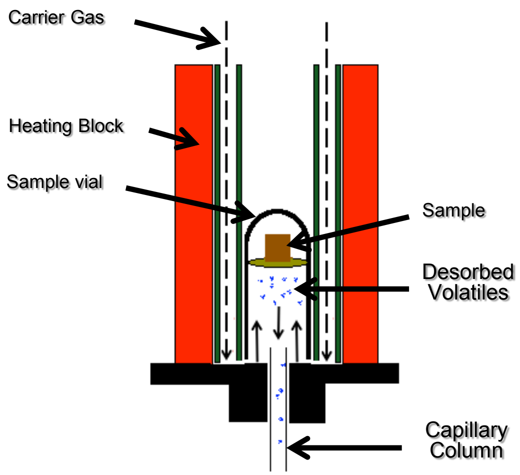




Design and Use of Adsorbent Test Apparatus

Excellent Breakthrough Curves Showing Enhanced Capacity and Stability.

Accomplishments



Direct Dynamic Thermal Desorption.

Compound	Formula	Molecular Weight (g/mol)
Nitrogen	N_2	28
Nitric Oxide	NO	30.01
Methyl Alcohol	CH_4	32.04
Water	H_2O	18
Dimethyl Disulfide	$C_2H_6S_2$	94.19
Dimethyl Sulfoxide	C_2H_6OS	78.13
Dimethyl Sulfone	$C_2H_6O_2S$	94.13

Comprehensive Competitive Adsorption.

#	Material	Cont.	Mass (g)	BT (h)	SC (*)	RH (%)	CO_2	Cont./CH_4	CH_4	Total (SCCM)
1	**Fe-OMS2**	DMS	0.1	**8.97**	**1.9**	**0**	14	14	7	35
2		DMS	0.1	**3.24**	**0.7**	**20**	14	14	7	35
3		DMS	0.1	**1.67**	**0.4**	**40**	14	14	7	35
4	**Fe-OMS2_PDMS**	DMS	0.1	**5.14**	**1.1**	**0**	14	14	7	35
5		DMS	0.1	**0.46**	**0.1**	**20**	14	14	7	35
6		DMS	0.1	**0.41**	**0.1**	**40**	14	14	7	35
7	**AMO**	DMS	0.1	**9.30**	**2**	**0**	14	14	7	35
8		DMS	0.1	**9.56**	**2.1**	**20**	14	14	7	35
9		DMS	0.1	tbd	tbd	**40**	14	14	7	35
10	**AMO_PDMS**	DMS	0.1	**4.02**	**0.9**	**0**	14	14	7	35
11		DMS	0.1	tbd	tbd	**20**	14	14	7	35
12		DMS	0.1	tbd	tbd	**40**	14	14	7	35

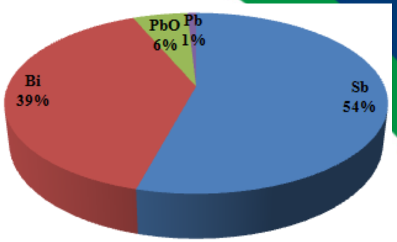
Optimization of Adsorbents

Future Work

1. Do Screening Studies of DMS at 0.5% O_2.
2. Look @ CS_2 and COS. Do Screening Studies With and Without Humidity set at 0.5% O_2.
3. Look at Spent Catalysts Using DART MS, TPD, IR Methods.
4. Try to Obtain Mechanistic Information Using O and S labeling and Other Kinetic Studies.
5. Looks at the Effects of Humidity, Siloxanes like D4, D5 at 1 ppm, and VOC's.
6. Study Competitive Adsorption of COS, CS_2, DMS With and Without Humidity.
7. Are these Processes Adsorptive, Catalytic or Both?
8. Scale- Up studies Underway, kG Batches of Adsorbent.
9. Adsorptive tests at FCE. **KEY MILESTONE.**
10. Ongoing Adsorptive Tests at Real Sites. **KEY MILESTONE.**
11. Extensions to Other Fuel Cleanup, like Natural Gas, Oil, Marine Fuel, Others.

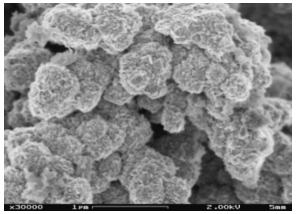
FuelCell Energy
Ultra-Clean, Efficient, Reliable Power

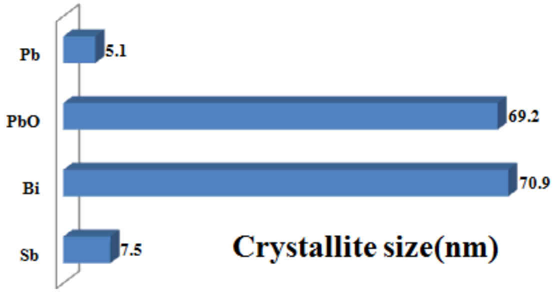
Task 2.2: Fuel Reforming Catalysts for Efficient Energy



Project Objective:

1. **Preparation of Next Generation Fuel Reforming Catalysts.**
2. **Characterization and Modeling of Catalysts and Reactions.**
3. **Catalytic Testing of Fuel Reforming Catalysts with Biodiesel and Lignin Feeds.**
4. **Measure the Effects of Fitch Fuel Catalysts on Emissions and Burner Efficiency.**
5. **Licensing and Technology Transfer to APSI, Inc. from UCONN of Next Generation Fuel Reforming Catalysts.**





Relevance to DOE EERE: The U.S. Department of Energy funds research, development, and demonstration to help develop sustainable, cost-competitive fuel reforming. **From DOE EERE website:**
Reforming renewable liquids to hydrogen is very similar to reforming natural gas. Renewable liquid fuels, however, are composed of larger molecules with more carbon atoms, so they are more difficult to reform than natural gas. Research is needed to identify better catalysts to improve yields and selectivity.

Project Approach

Unique Aspects of our Approach:

1. Synthesis – Use of Thin Films to Decrease Material Costs.
2. Use of Sol gel, Dip Coating Methods.
3. Mechanistic Studies Including Modeling Studies.
4. Characterization Using Surface, Mass Spec, Diffraction Methods.
5. Next Generation Alloy Catalysts.
6. Catalytic Testing Using Fuel Reforming and Biomass Reactors.

Durability and Performance:

1. Generation of A Mechanism of Reaction of the Fitch Fuel Catalyst.
2. Synthesis of Next Generation Fitch Fuel Catalysts.
3. Characterization of Next Generation Catalysts.
4. Catalytic Testing in Biomass Conversion Studies.

Milestones and Status:

STATEMENT OF WORK WITH TASKS/MILESTONES & DELIVERABLES

A. Synthesis of Thin Film and Nano-Size Catalysts.

B. Synthesis of Nanoalloy Catalysts.

C. Next Generation Nano-size Alloy Catalysts.

D. Deposition of FFC Nanoalloy on Supports.

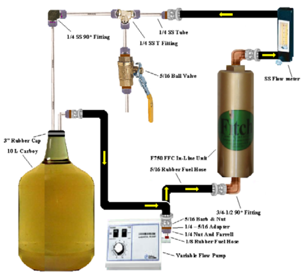
E. Nuclear Magnetic Resonance (NMR) Studies.

F. Fourier Transform Infrared (FTIR) Spectroscopy to Monitor Acid Sites.

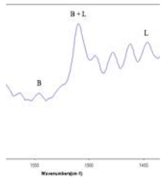
G. Acid Titrations.

H. Catalytic Reforming Studies.

I. ASTM Fuel Reforming Tests.

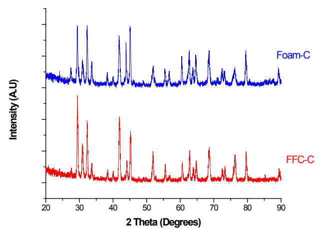


Reactor Studies.



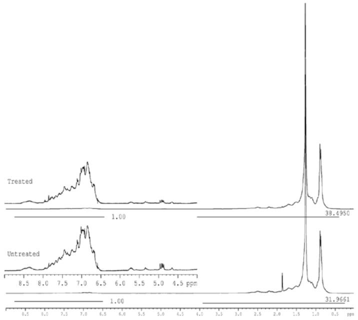
FTIR.

Accomplishments



XRD Data for Preliminary Data for Nano-size Alloy Catalysts on Metal Foam Support and Nano-size Alloy Catalyst.

NMR Data
Top: FCC
Bottom, No Catalyst



Samples	'R' value	Mean 'R' value
Blank Untreated ULSD (Distillate NO Catalyst)	32.54 32.05 32.44	32.34
Blank Treated ULSD (Distillate w/ Catalyst)	33.38 33.13 32.80	33.10
Untreated ULSD Residue (NO Catalyst)	31.97 31.44 32.34	31.92
Treated ULSD Residue w Catalyst)	38.50 37.61 38.30	**38.14**

R value is a measure of the ratio of the number of aliphatic protons to the number of olefinic plus aromatic, benzenoid, and polynuclear aromatic protons

PMR-NMR analyses of distillate and residue (ASTM D 86) of ULSD blank (Part A) and ULSD treated with Fuel Catalyst

Accomplishments

$SnCl_2$ | $SbCl_2$ | $BiCl_3$ | $PbCl_2$

↓ Solvent, Dry Ice, 5 min

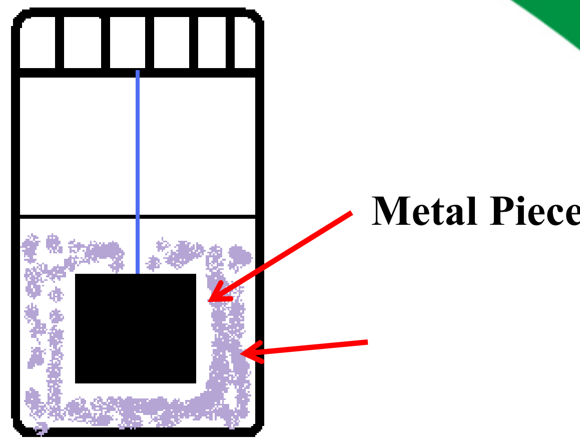
Mixture

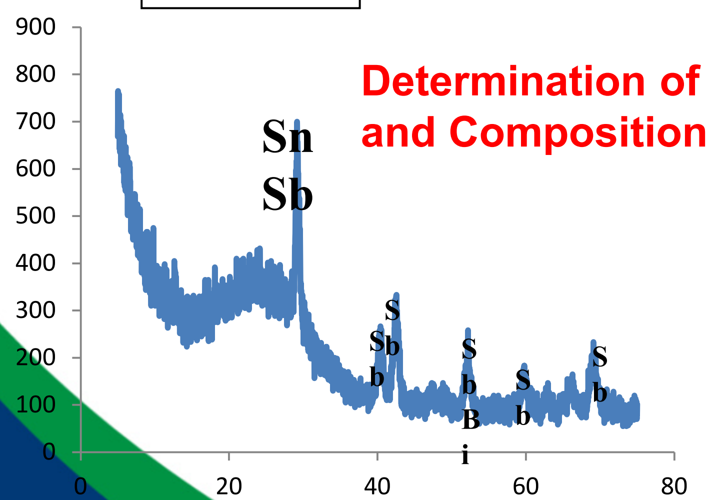
↓ Metal piece, Ice, 24 h

Slurry+Coating

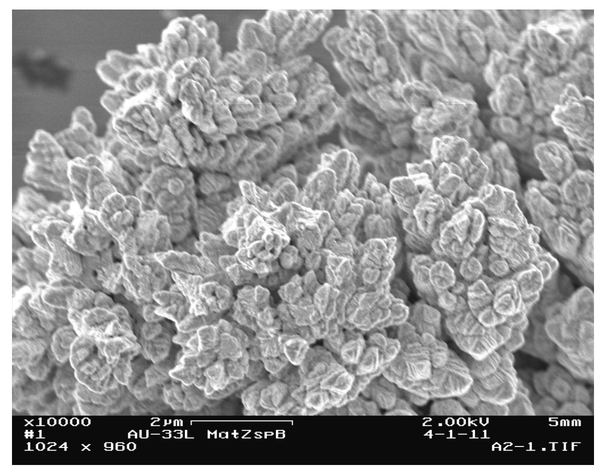
↓ Wash, Vacuum Dried @ 50°C

Product





Determination of Structure and Composition.



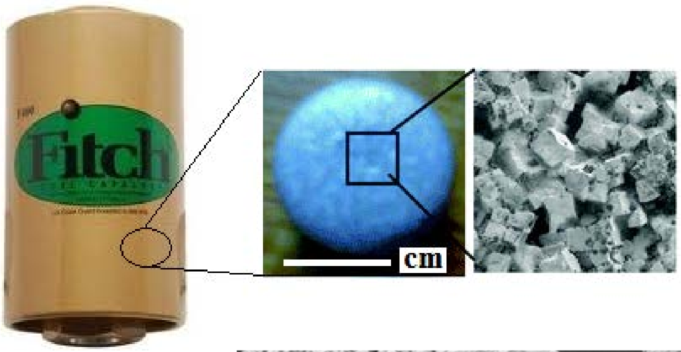
High Surface Area Active Catalyst

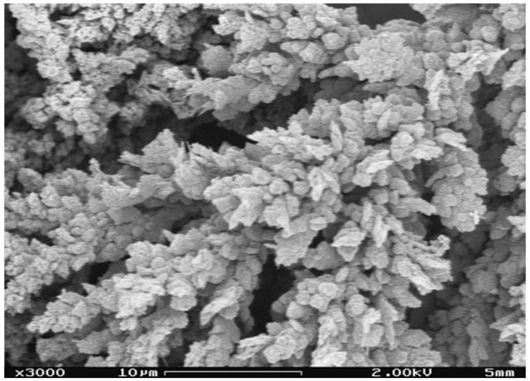
Novel Thin Film Catalysts having Excellent Reforming Activity

Prof. Steven Suib (PI)
Industrial Partner: APSI

Future Work:

1. **Synthesis of Thin Film Fitch Fuel Catalysts – this Research is Underway.**
2. **Catalysts Testing in Fuel Reforming.**
3. **Catalyst Testing in Biomass Conversion.**
4. **Full Characterization of Catalysts.**
5. **Mechanistic Studies.**
6. **Scale-Up Of Catalysts.**
7. **Patent Application. Milestone – Done.**
8. **Licensing to APSI. Milestone – Underway.**
9. **More Efficient Combustion and Small Scale Heating.**
10. **Upgrading of Fuels, Boilers, Heaters.**





Fitch

APSI

Novel High Activity Catalyst

Task 2.3: Evaluation of Enzyme-Based Sulfur Removal Technology for Gas Cleanup

Objectives:

Generate fundamental understanding of enzyme-based desulfurization of biogas and landfill gas. Evaluate the effect of operating conditions on removal efficiency of sulfur containing species. Understand the effect of other components on separation performance. Develop desulfurization kinetics for scale-up.

Relevance to EERE:

The Office of Energy Efficiency and Renewable Energy (EERE) invests in clean energy technologies that strengthen the economy, protect the environment, and reduce dependence on foreign oil. EERE also invests in developing energy efficient and environmentally friendly vehicle technologies. Once purified, biogas could be used as a renewable substitute for natural gas and to fuel natural gas vehicles.

Prof. Ashish Mhadeshwar (PI)
Industrial Partner: nzymSys

Project Approach

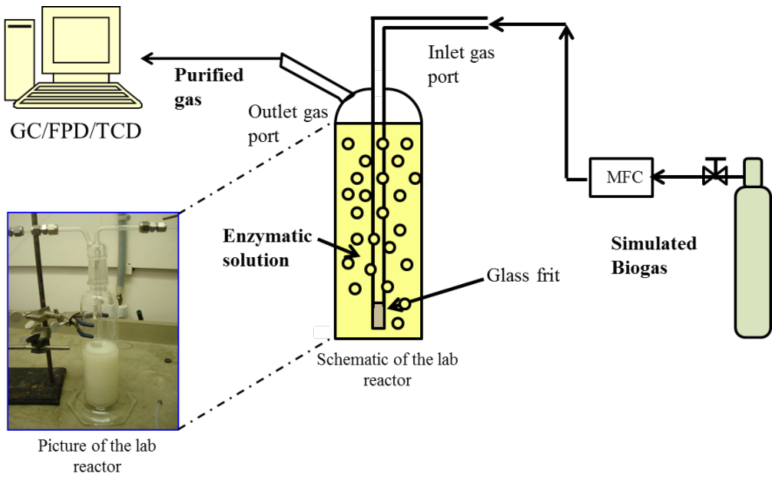
- Proof-of-concept experiments to demonstrate feasibility.
- Gas-liquid scrubber reactor design, setup, and operation.
- Equipment upgrade to resolve sulfur analysis issues.
- Testing of enzyme-containing liquid with simulated biogas (CH4, CO_2, and H_2S).
- Evaluation of reaction kinetics and effect of operating parameters (S-concentration in the gas, enzyme concentration, biogas flow rate, packing).
- Proof-of-concept experiments for long-term H_2S removal using enzyme replenishment.
- Process scale-up.

Completed   In progress

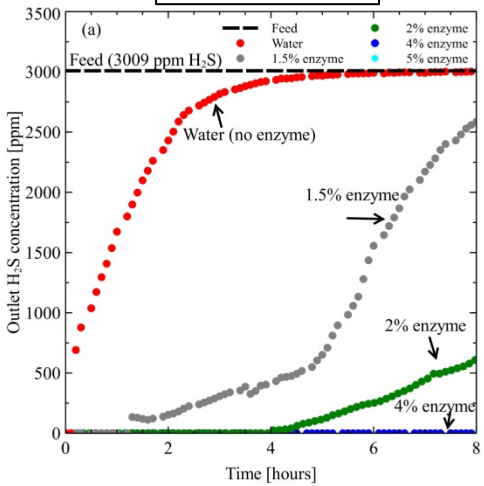
Prof. Ashish Mhadeshwar (PI)
Industrial Partner: nzymSys

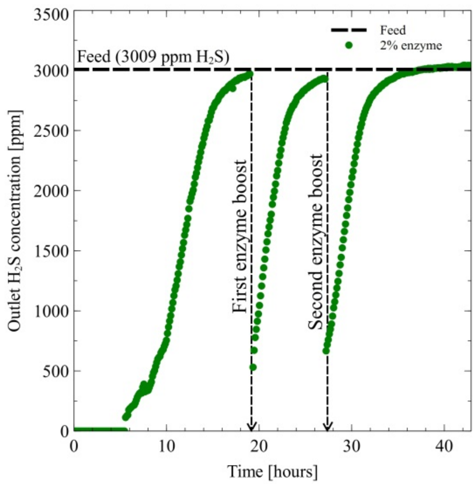
Accomplishments

Setup

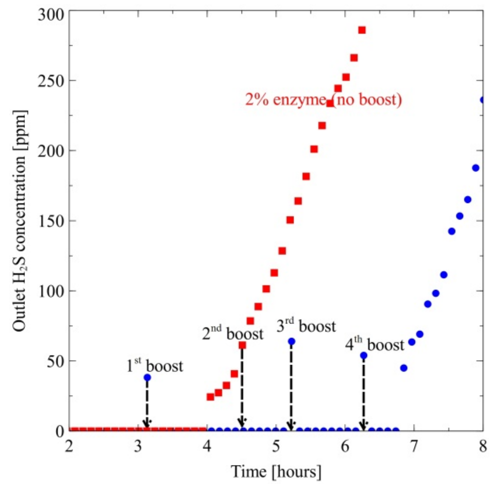


Performance

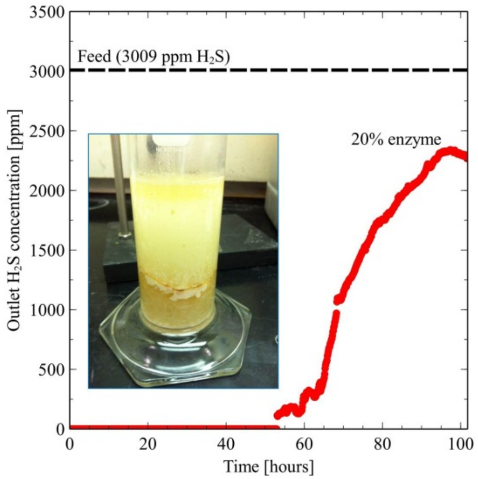




Late replenishment



Early replenishment



Long-term Sulfur recovery

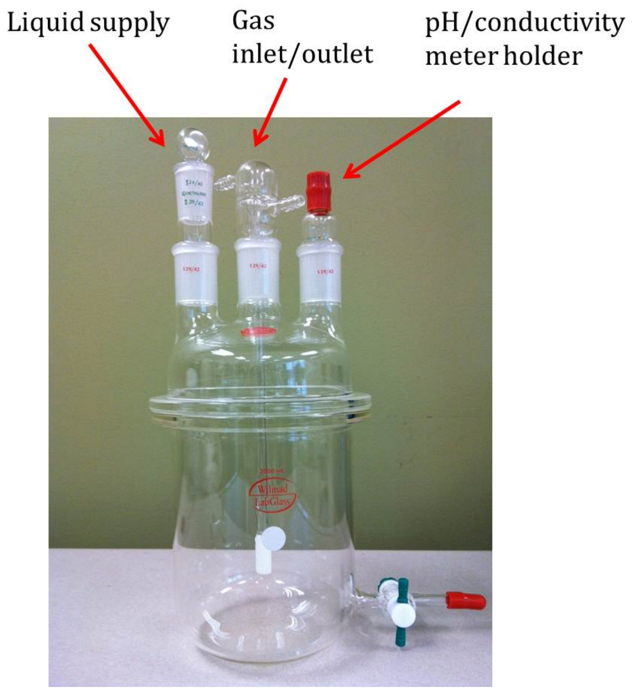
Accomplishments

- Enzyme activity is demonstrated with proof-of-concept experiments.
- Reactor setup with GC is operational. Appropriate safety measures are taken into account.
- Enzyme performance is demonstrated with simulated biogas (3000 ppm H_2S, 59.7% CH_4 and 40% CO_2) feed.
- Effect of operating conditions on performance is investigated.
- Effect of early enzyme replenishment is promising for continuous operation.
- Feasibility of sulfur recovery as a valuable product is demonstrated.
- 1 manuscript and 1 patent application in preparation. Three related proposals submitted to DoD Navy, NSF SBIR, and DuPont.

Proposed Future Work

Design, building, and demonstration of a large-scale reactor with enzyme replenishment and purge.

Evaluate the effect of reactor scale-up on sulfur removal from biogas.



Task 2.4: High Reliability, Low-cost Thermally Integrated Water Gas Shift (TI-WGS) System Design Development Support

Objectives:

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 (TI-WGS) system to efficiently process reformate gas, such as from FCE's DFC® power plant anode exhaust.

Relevance to EERE:

Development of a thermally integrated Water-Gas Shift system (TI-WGS) is key to the overall fuel cell operation and hydrogen co-production.

Project Approach:

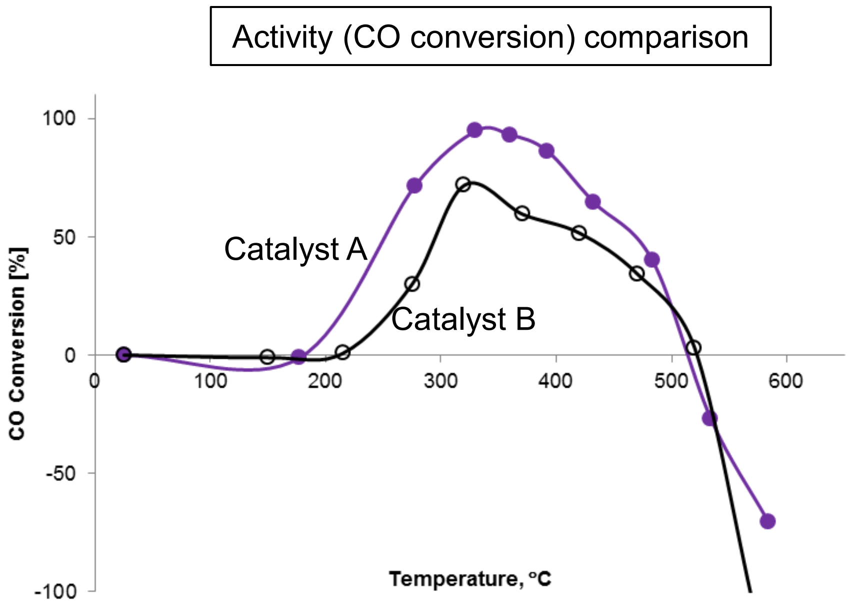
- Lab-scale TI-WGS data evaluation and design support (completed)
- Lab-scale catalyst evaluation and analysis in Uconn (completed)

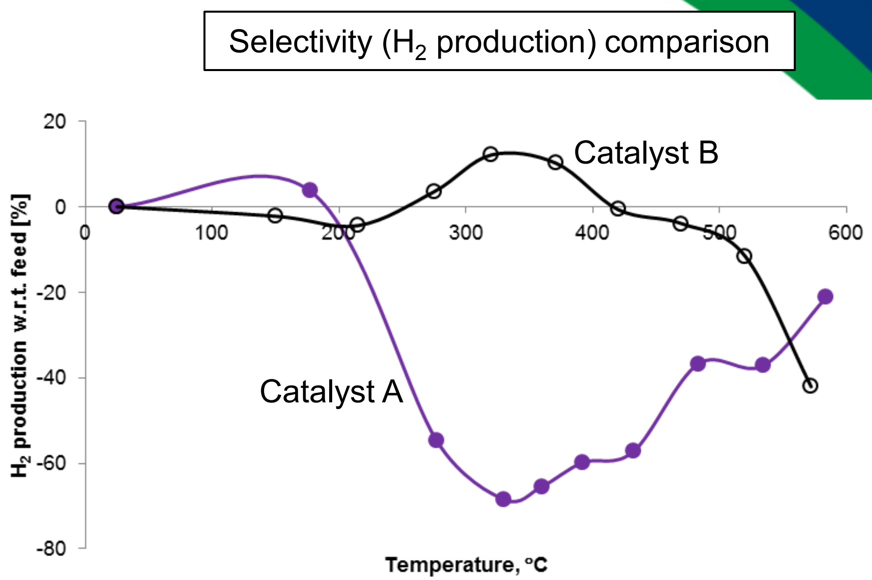
  BenchCAT reactor.

  - FCE has provided two types of catalysts (A and B)* to UConn, which are tested for CO oxidation, CO methanation, and WGS. Activity and selectivity differences between A and B are expected to provide insights regarding further scale-up for the FCE reactor system.
- Bench-scale FCE reactor catalyst evaluation and analysis (in progress)

Prof. Ashish Mhadeshwar (PI)
Industrial Partner: FuelCell Energy

Accomplishments





- Catalyst B shows promising WGS performance (lower activity but higher selectivity) compared to catalyst A. This information is valuable for further scale-up of the FCE reactor system.

- An FCE-UConn collaborative proposal submitted to the DOE SBIR Phase II program has been awarded. Findings from the current FCE-CDP project will be key for the Phase II program, which is expected to begin in March 2012.

Proposed Future Work: Bench-scale FCE Reactor catalyst evaluation and analysis.

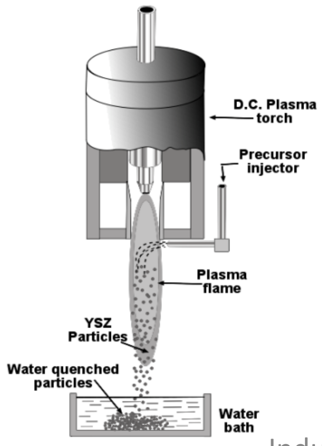
Task 3.1 Nanolayered Micro SOFCs: Their Materials and Fabrication

Project Objective – develop a manufacturing methodology for low cost micro direct methanol SOFCs to enter the battery replacement market. This involves:

- flexible fabrication development for manufacturing diverse products
- material property optimization
- cost minimization using low cost precursors and energy efficient processing

Project Approach - "far-from-equilibrium" processing to form nanolayered and microlayered structures. Distinctive advantages of Reactive Flame Spray and Reactive Thermal Plasma Spray methodologies include:

- integrated material synthesis and positive-electrolyte-negative (PEN) fabrication with a minimal number of process steps.
- energy conservation by avoiding costly high temperature furnace treatment.
- exploitation of electrocatalytic and ionic conduction characteristics of non-conventional metastable materials.
- rapid processing of large areas to manufacture (i) large SOFCs and (ii) arrays small multicellular micro SOFCs.
- facility for in-situ laser monitoring & feed-back control.



Prof. Radenka Maric (PI)
Industry Partner: NanoCell Systems

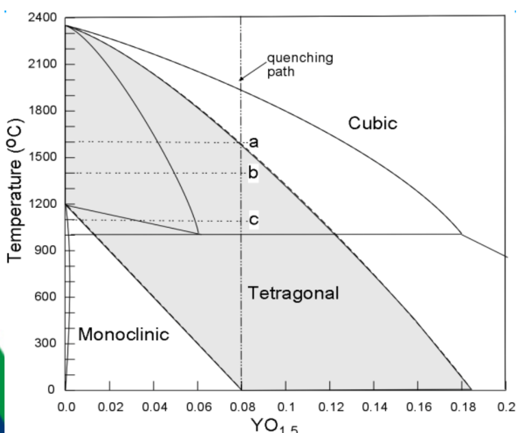
Accomplishments

Ionic conduction and fracture toughness enhancement of 8 YSZ

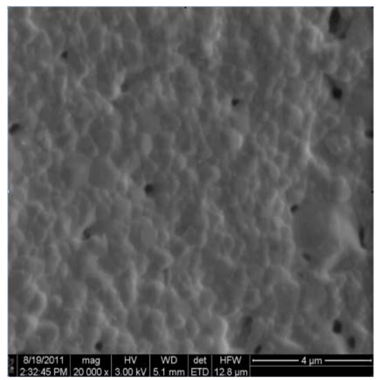
Recent findings include:

- 3-4 fold increase in 8YSZ ionic conductivity by metastable processing
- the importance of controlled quenching to produce the tetragonal phase
- retention of a nanograin size up to 1400^{o}C
- high fracture toughness
- the potential of exploiting metastable phase diagrams to obtain novel properties

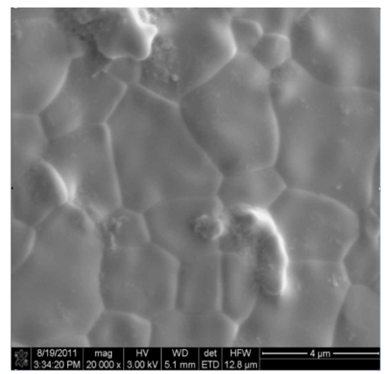
Morphology at 1400^{o}C



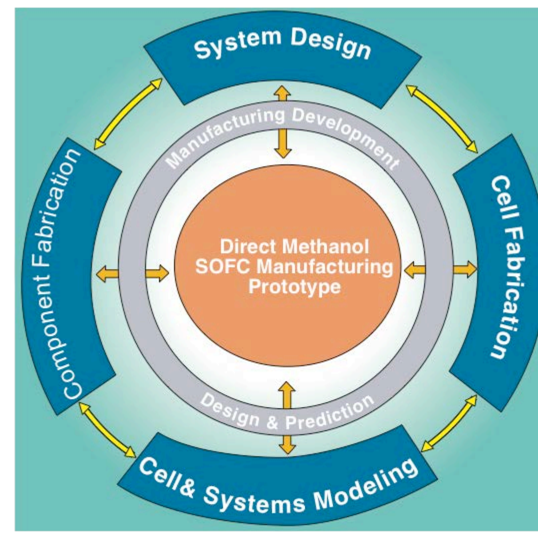
Metastable phase diagram



From metastable powder



From Tosoh powder



Prof. Radenka Maric (PI)
Industry Partner: NanoCell Systems

Task 4.1: Nanostructured Catalyst-Support Systems for Next Generation Electrolyzers

Project Objective and Relevance to EERE

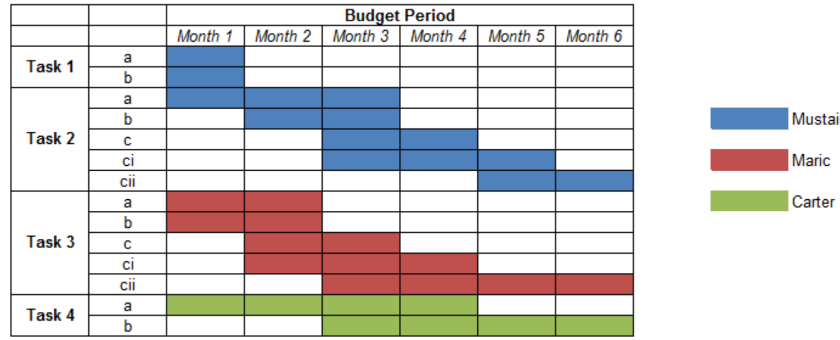
- The objective of this project is to demonstrate the use of non-carbon electrocatalyst support materials at the cathode of PEM-based that:
  - Enhance the intrinsic electrocatalytic activity of nanosized Pt clusters
  - Enhance PGM catalyst dispersion and stability at the cathode
- This project directly addresses one of the core goals of the EERE electrolyzer program by "reducing the capital cost of the electrolyzer and improving energy efficiency"*

*http://www1.eere.energy.gov/hydrogenandfuelcells/production/electro_processes.html

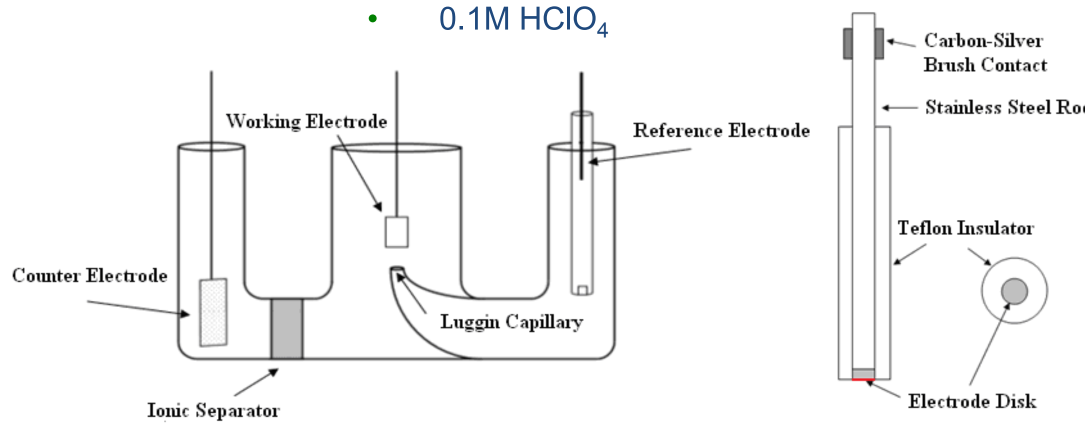
Prof. William Mustain (PI)
Industry Partner: Proton OnSite

Approach and Timeline

- Task 1: Baseline Pt activity of "Proton Catalyst" – One Catalyst
  - TF-RDE
  - 5 cm² PEMEC
- Task 2: Synthesize Nanostructured WC and TiAlN
  - SEM/TEM; XPS; XRD;
  - CV; TF RDE
  - Platinization
    - SEM/TEM/STM; BET; XRD; XPS
    - CV; TF-RDE; 5cm² PEMEC
- Task 3: Synthesize Spherical RSDT Ti_4O_7
  - XPS; TEM; XRD; BET
  - CV
  - Platinization
    - TEM; XPS
    - CV; TF-RDE; 5 cm² PEMEC
- Task 4: Pt Structural Changes during electrochemical operation
  - Pre and Post-mortem SEM/TEM
    - 2 TiAlN samples
    - 2 Ti_4O_7 samples

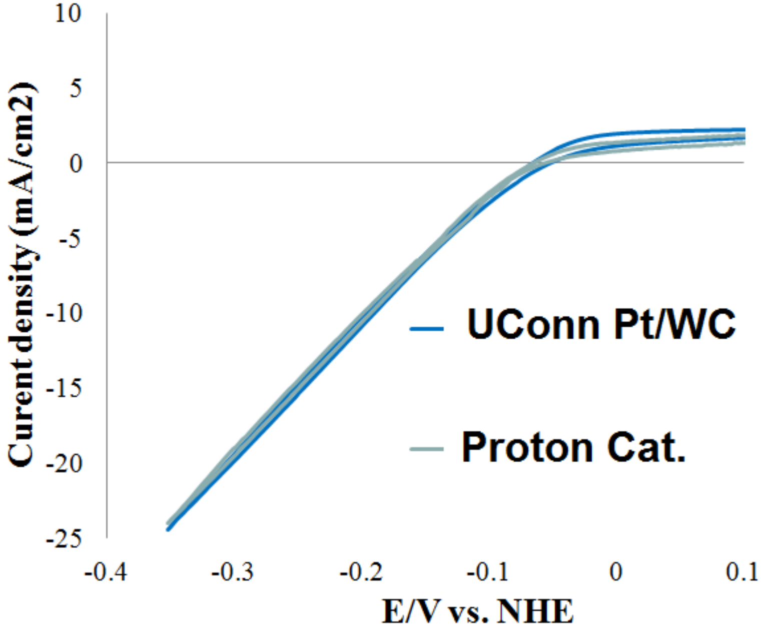


- Electrochemical Measurements
- Thin film RDE (Fig. Below)
  - Dispersed 20μL of 0.3 mg/mL dispersion onto a 5mm GCE
  - Added 20μL of DE-520 Nafion disperion
  - Pt Conditioning, HER
    - 0.1M $HClO_4$

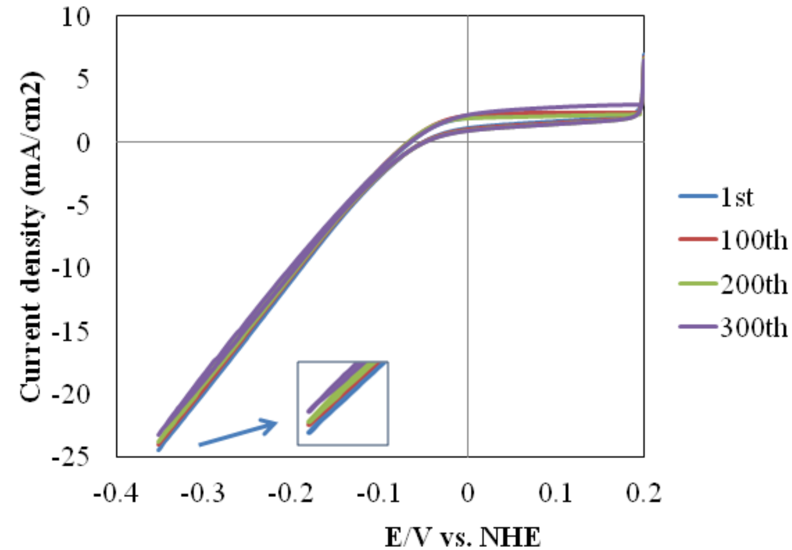


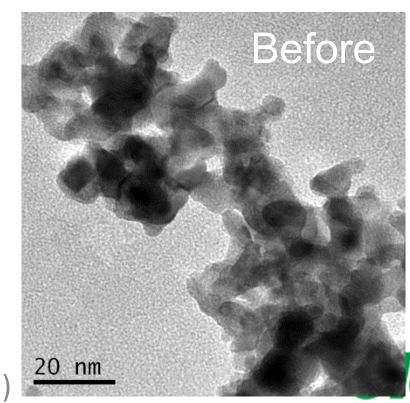
Major Accomplishments – HER on Pt/WC Electrocatalysts*

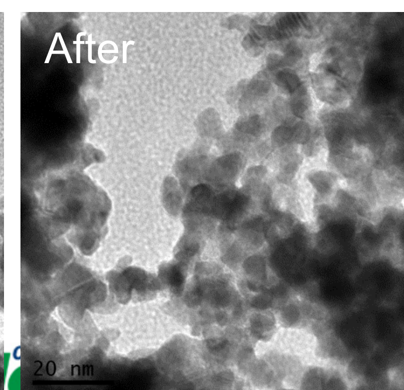
10X PGM reduction over Proton Conventional Catalyst



96% Activity Retention over 300 accelerated degradation cycles



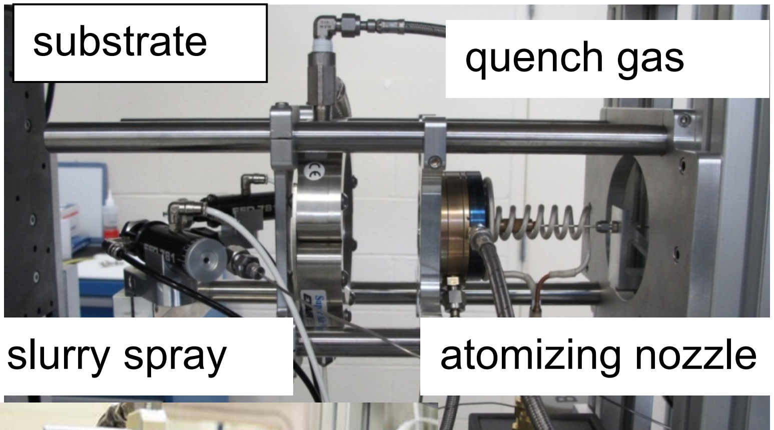


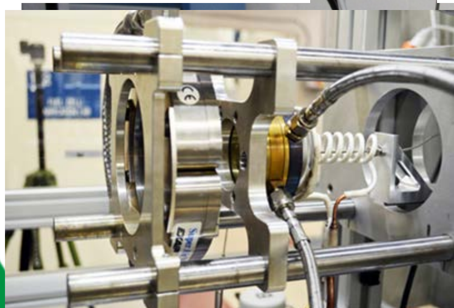


*Y. Liu and W.E. Mustain, "Evaluation of tungsten carbide as the electrocatalyst support for platinum hydrogen evolution/oxidation catalysts", Int. J. Hydrogen Energy, Accepted, In Press.

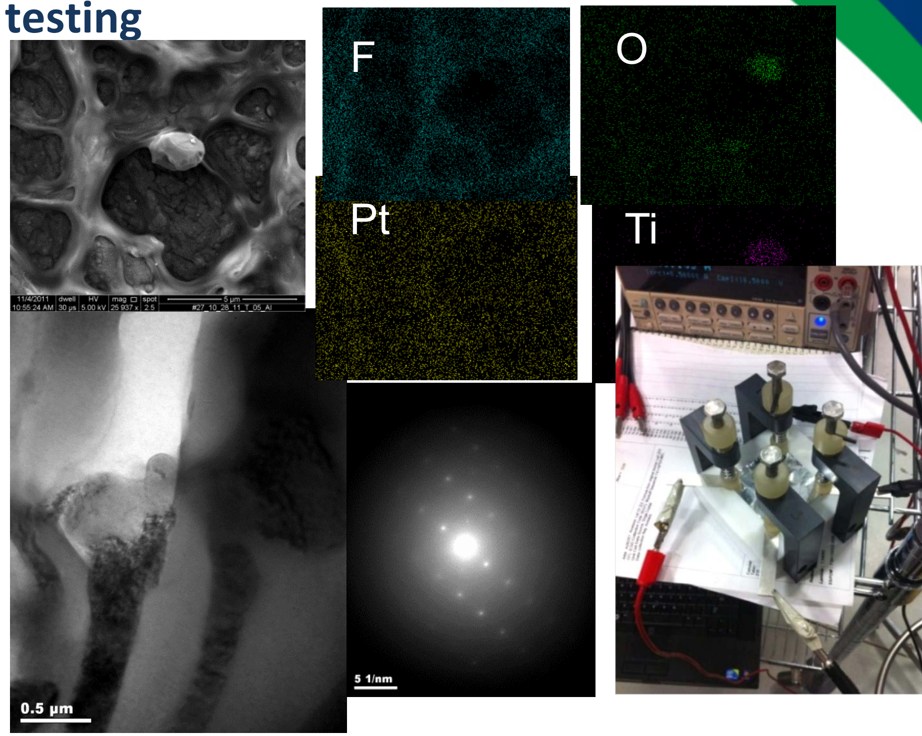
Major Accomplishments – RSDT & Ti_4O_7 supports

Finished assembly of flame-based RSDT synthesis reactor





Electrode fabrication by RSDT and initial testing



Future Work:

- 25 cm^2 Electrolyzer testing using Proton catalyst
- Synthesize & Characterize TiAlN with constructed CVD reactor
- Determine electrical conductivity of electrode layers with increasing amounts of ionomer (4 point probe method in-plane)
- Electrochemical characterization of Pt/Ti_4O_7 and Pt/TiAlN for OER and HER reactions

Selected Program Outcomes

Patents:

A patent application regarding synthesis of ultrathin films of next generation FCC materials has been submitted. This patent application is being evaluated by APSI and UConn for further processing.

D. Bloom, J. Fantry, A. Moreno, A. Mhadeshwar, P. Singh. Biogas desulfurization using enzyme-based technology, patent document in preparation.

P. Zhang and H. Xue, Robust High Resolution Spectrum Estimation Method for Accurate Phasor, Harmonic and Interharmonic Measurement in Power Systems, Provisional US Patent Application UConn #11-033.

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

Journal Publications:

Arena, J.T., McCloskey B., Freeman, B. McCutcheon, J.R., "Surface modification of thin film composite membrane support layers with polydopamine: Enabling use of reverse osmosis membranes in pressure retarded osmosis", *Journal of Membrane Science*, 375, 2011, 55-62.

A. Moreno, D. Bloom, P. Singh, J. Fantry, S. Gorton and A. Mhadeshwar, "Enzyme-based sulfur removal for biogas cleanup", Journal of Hazardous Materials, submitted (2011).

H. Xue and P. Zhang, "Subspace-Least Mean Square Method for accurate harmonic and interharmonic measurement in power systems," *IEEE Trans. Power Delivery*, under second round review. Submission date: June 2011.

Y. Wang, W. Li, P. Zhang and B. Wang, "Reliability analysis of Phasor Measurement Unit considering data uncertainty," *IEEE Trans. Power Systems*, under review. Submission date: August 2011.

P. Zhang and H. Xue, "Shifting window average method for accurate harmonic measurement in power systems," to be submitted to *IEEE Trans. Power Delivery,* in preparation.

A. Abdollahi and P. Zhang, "Analysis of Noise Effect in DFT Algorithm-Part I: Phasor and Frequency Measurement," to be submitted to *IEEE Trans. Instrumentation and Measurement,* in preparation.

Bui, N. Lind, M.L., Hoek, E.M.V., McCutcheon, J.R., "Electrospun supported thin film composite membranes for engineered osmosis", Journal of Membrane Science 385-386, 2011, 10-19.

> 15 Conference Proceedings