Improving Fuel Cell Durability and Reliability

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University of Connecticut
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Project ID #FC079

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Overview

Timeline Data:

- ✓ Start date: August 1, 2010
- ✓ End date: July 31, 2013
- ✓ Percent complete: 72%

Barriers Addressed:

- ✓Durability
- ✓Cost
- ✓Performance

Budget: (Based on DOE FY)

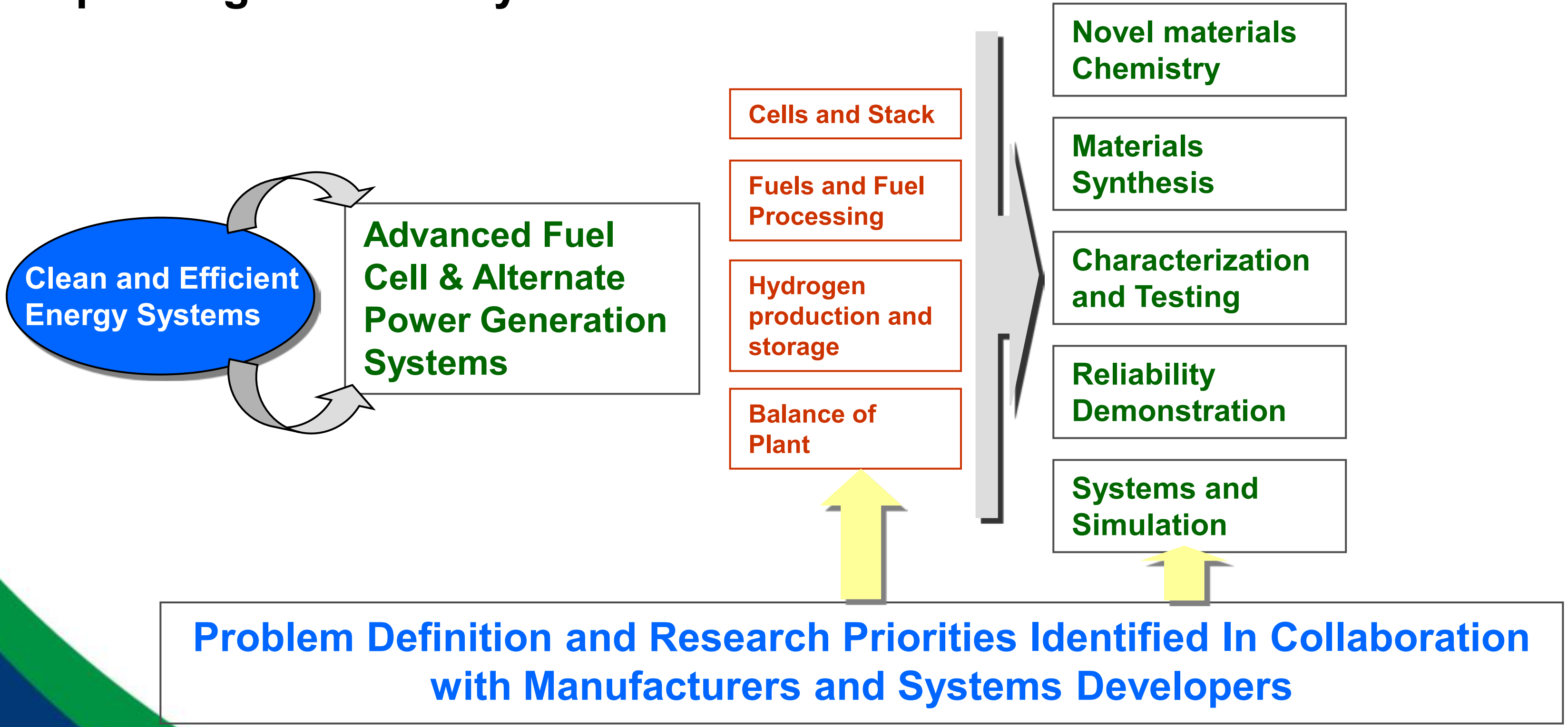
- ✓ Total project funding
  - ➢ DOE share: $2,500,000
  - ➢ Contractor share: $ 625,000
- ✓ Funding received in FY10: $ 0
- ✓ Funding for FY11: $ 443K (DOE share)
- ✓ Funding for FY12: $ 1,498K (DOE share)
- ✓ Funding for FY13: $ 559K (DOE share)

Partners:

- ✓ Interactions/ collaborations
- ✓ Project lead

Relevance

- 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.



Clean and Efficient Energy Systems

Advanced Fuel Cell & Alternate Power Generation Systems

Cells and Stack

Fuels and Fuel Processing

Hydrogen production and storage

Balance of Plant

Novel materials Chemistry

Materials Synthesis

Characterization and Testing

Reliability Demonstration

Systems and Simulation

Problem Definition and Research Priorities Identified In Collaboration with Manufacturers and Systems Developers

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**

Technical Approach

Technical and programmatic tasks:

- **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)

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

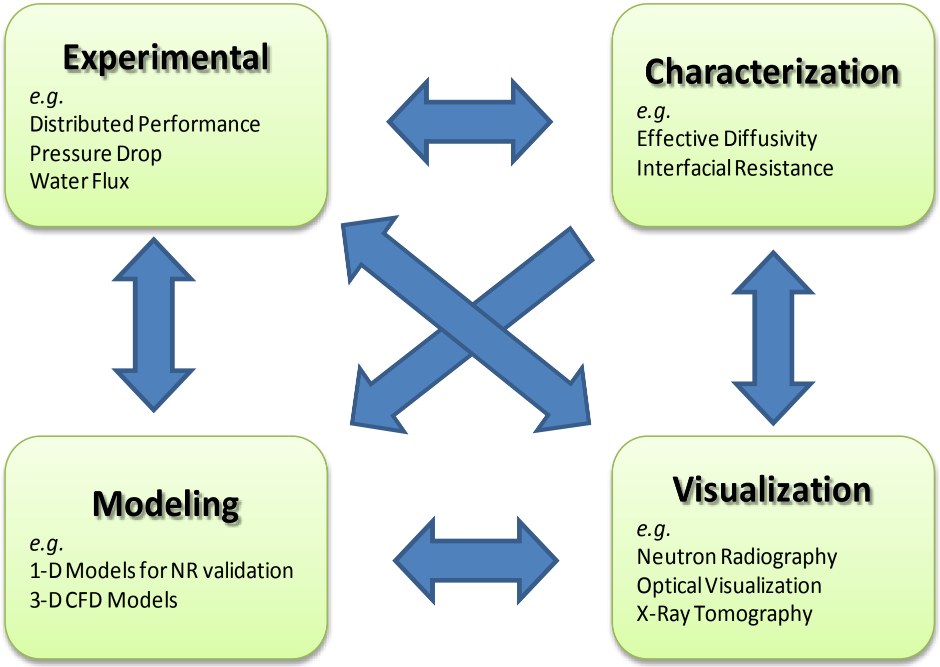
– Material property characterization

–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



Experimental
e.g.
Distributed Performance
Pressure Drop
Water Flux

Characterization
e.g.
Effective Diffusivity
Interfacial Resistance

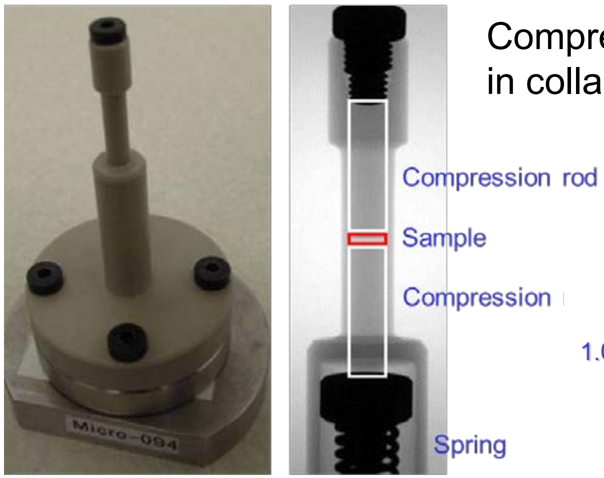
Modeling
e.g.
1-D Models for NR validation
3-D CFD Models

Visualization
e.g.
Neutron Radiography
Optical Visualization
X-Ray Tomography

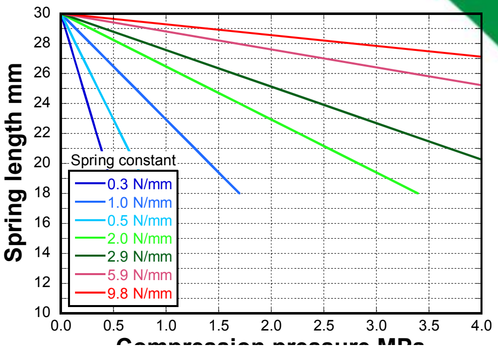
Accomplishments

Effect of compression on GDL microstructure

Sample holder

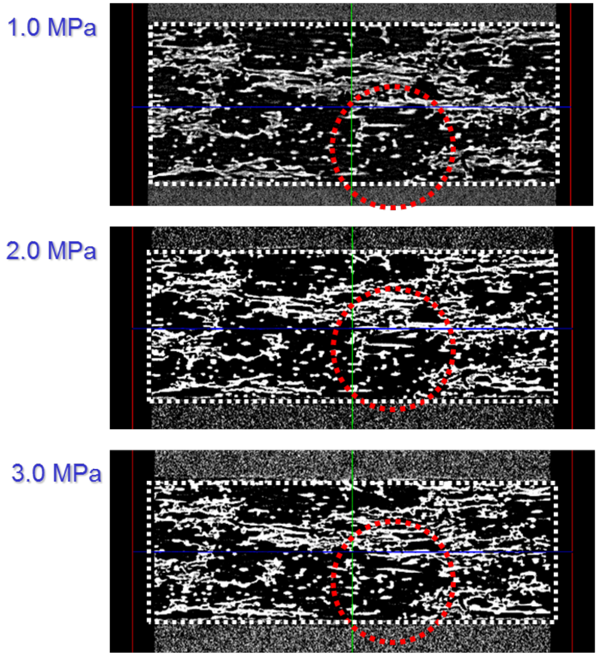


Compression fixture was designed/constructed in collaboration with TokyoTech (Dr. Sasabe)

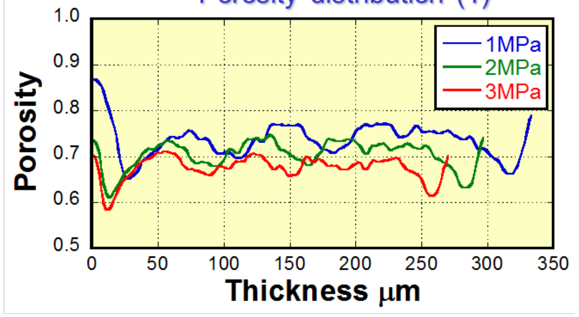


Uniform Compression

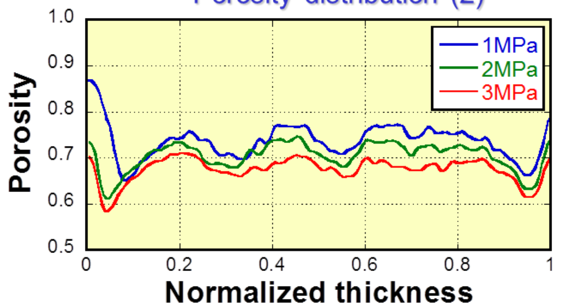
Slice images

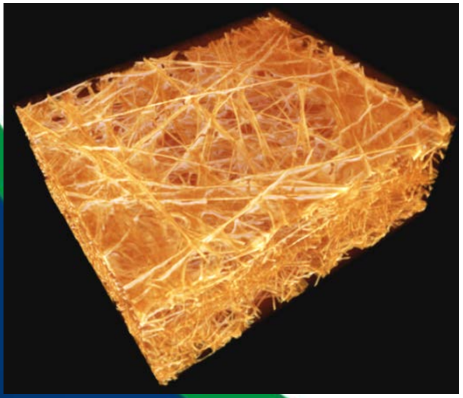


Porosity distribution (1)



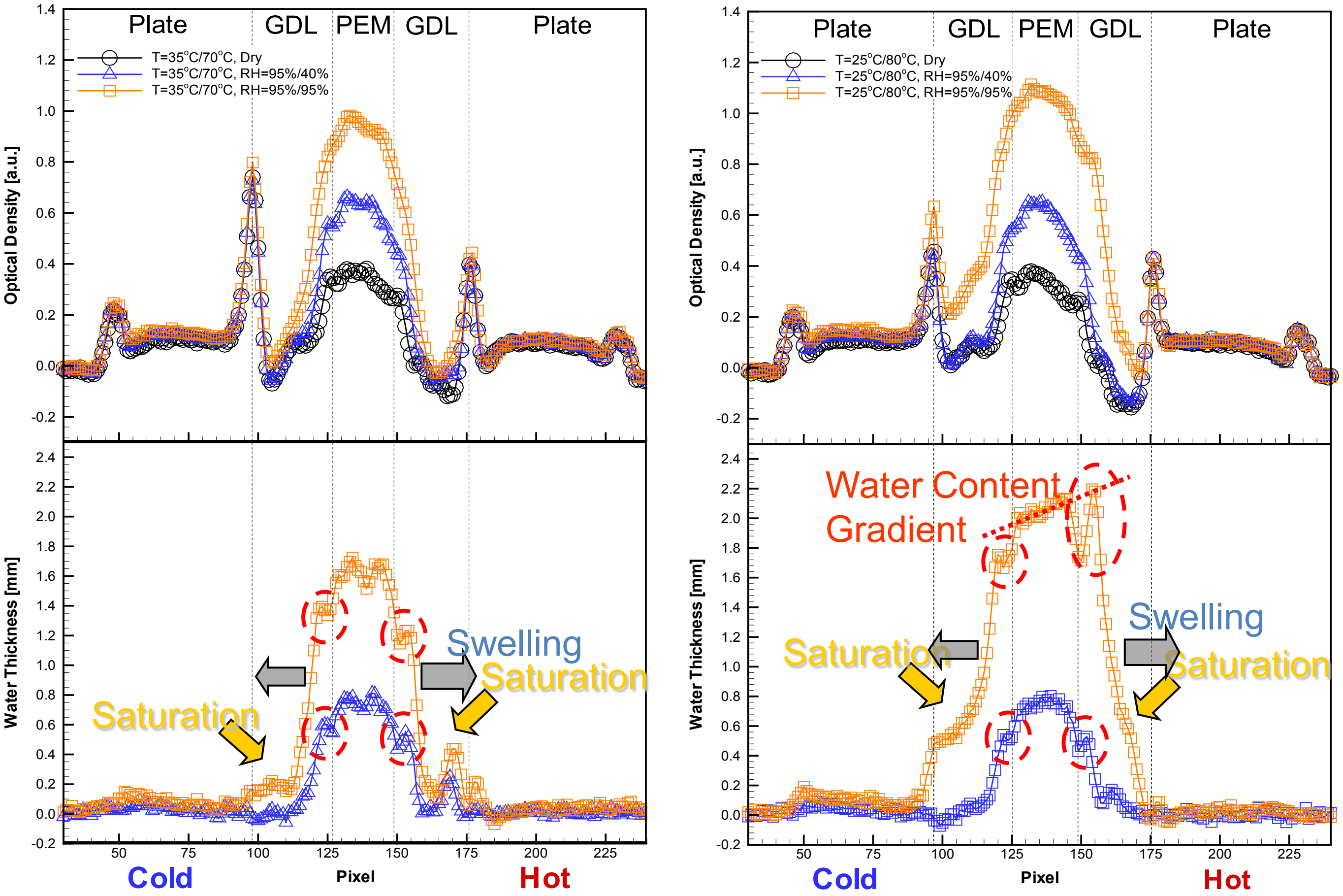
Porosity distribution (2)





Accomplishments

Neutron Radiography: Role of PEM Swelling



~40% increase in thickness (~100 μm or ~10 pixels) is reported for Nafion® immersed in liquid water.[a]

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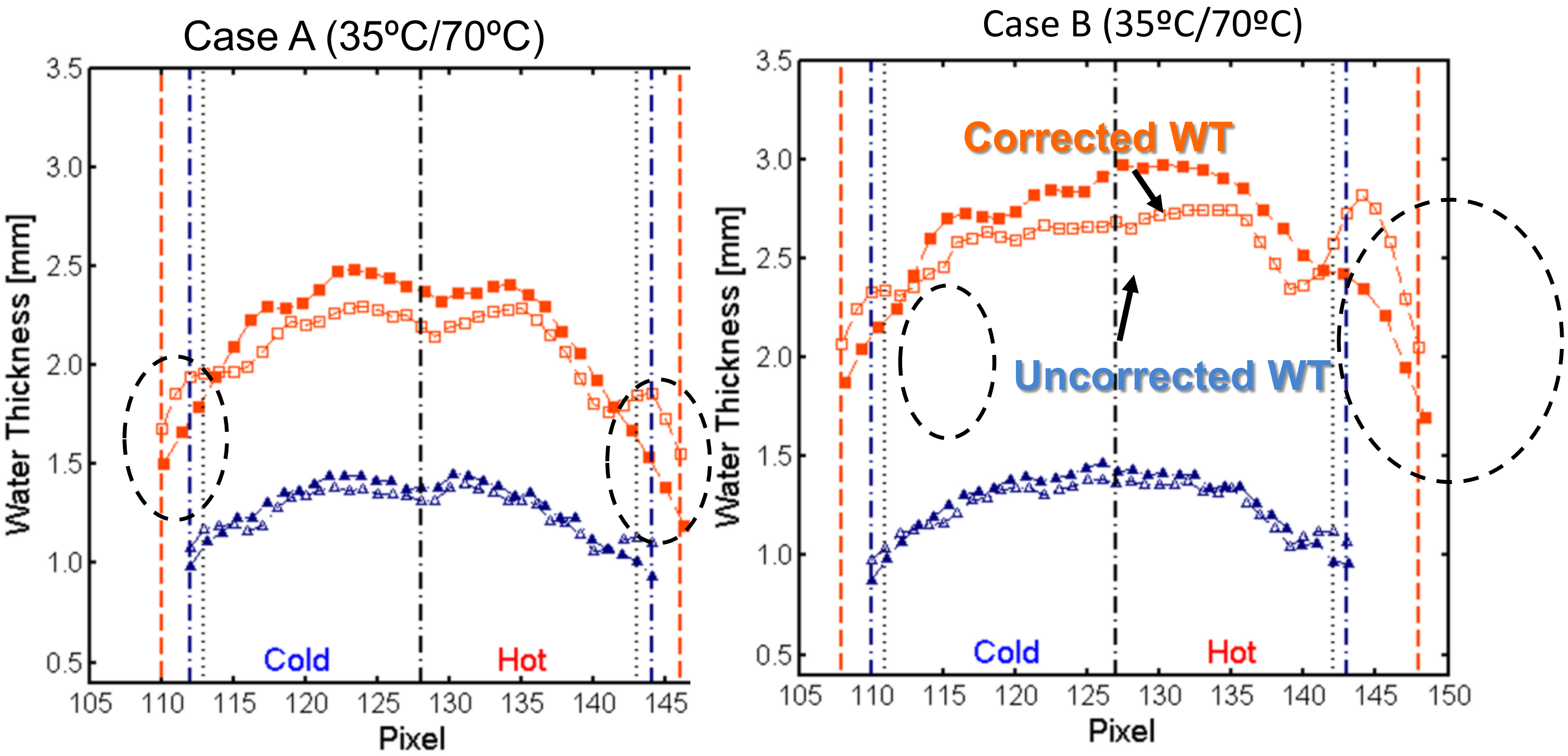
[a] J. T. Hinatsu et al., *J. Electrochem. Soc.*, **141** (6) 1493-1498 (1994).

Accomplishments

Corrected PEM Water Thickness


Case A (35ºC/70ºC)

Case B (35ºC/70ºC)

Corrective procedure eliminates the artifacts (peaks) at the interfaces

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

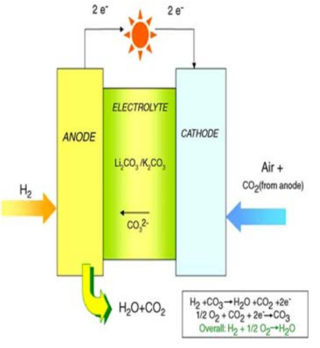


Fig. 1. A scheme of a molten carbonate fuel cell working.

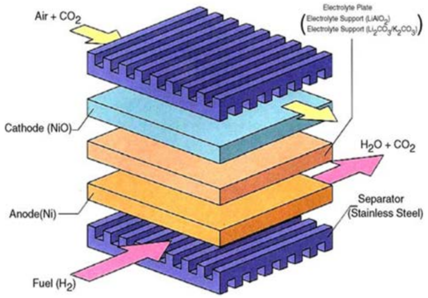


Fig. 2. A typical single cell cross-section.

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.

Accomplishments

- $LiAlO_2$ solubility measurement in "cathode and anode" atmosphere have been completed.
  - Powder morphology of FCE-P showed large $LiAlO_2$ particles after equilibration in molten carbonate for 920h.
- Obtained tested matrix samples from FCE for structural analysis
- Developed characterization plan for tested MCFC matrix obtained from FCE.
  - $LiAlO_2$ coarsening is predominant near anode side of the matrix compared to the cathode side.
  - Core-shell structure morphology is observed in all matrix samples.
  - Large alumina particles show a reaction surface layer formation due to interactions with the electrolyte.
  - EDS analysis show nickel precipitation in the matrix. The nickel precipitation front stays closer to the anode side of the matrix.
  - X-Ray Tomography identified nickel precipitation.

Experimental Plan: Analysis of matrix samples

Matrix samples

Before extraction of electrolytes

- **XRD analysis:** Phase analysis
- **FESEM analysis:** Surface and Cross-section
- **EDAX analysis:** Mapping of elemental
- **Tomography (X-radia):** 3D analysis

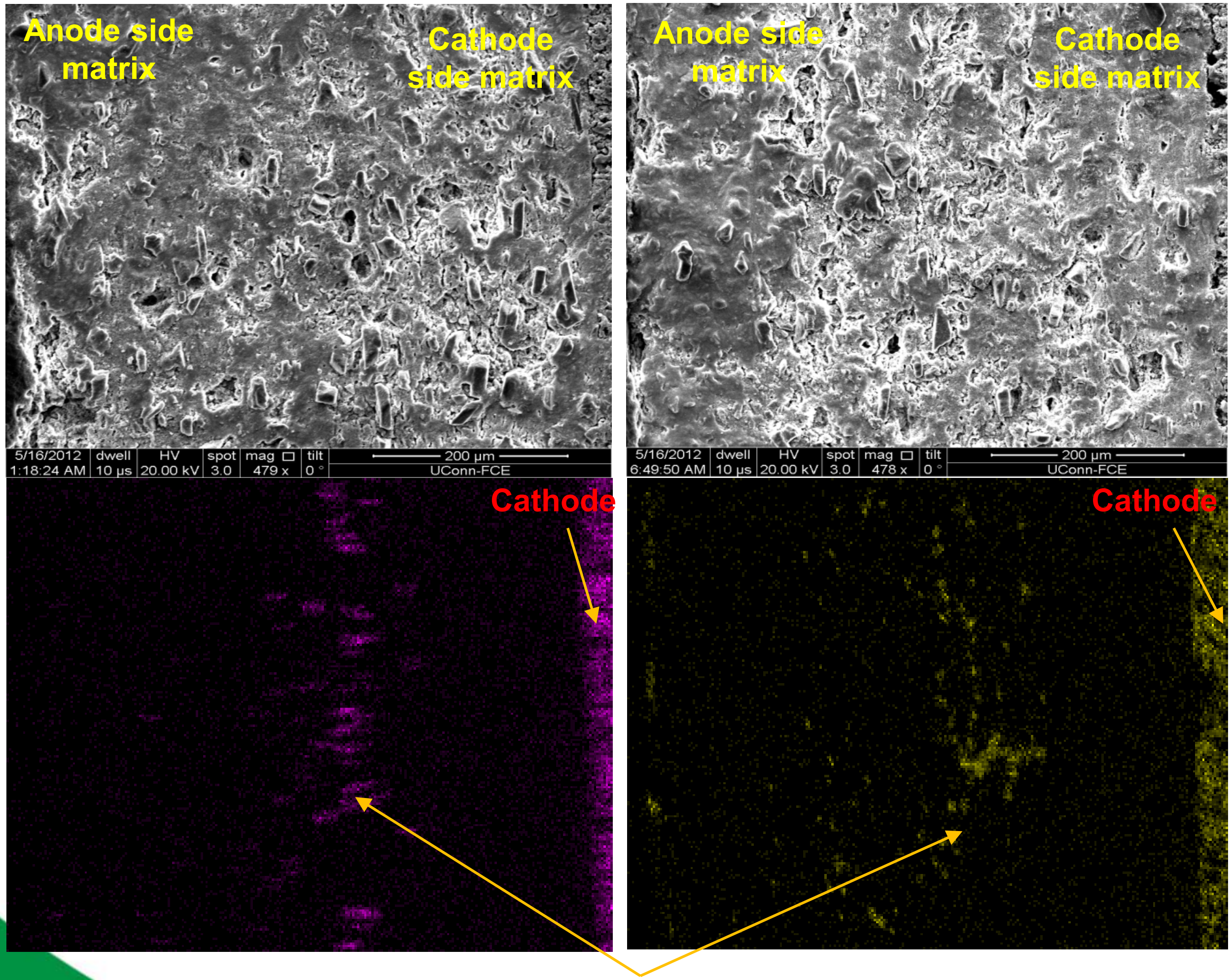
After extraction of electrolytes

- BET analysis
- Pore size distribution and porosity
- Particle size analysis

Matrix particle morphology, particle size, size distribution will be obtained.

EDS Analysis

Ni-mapping



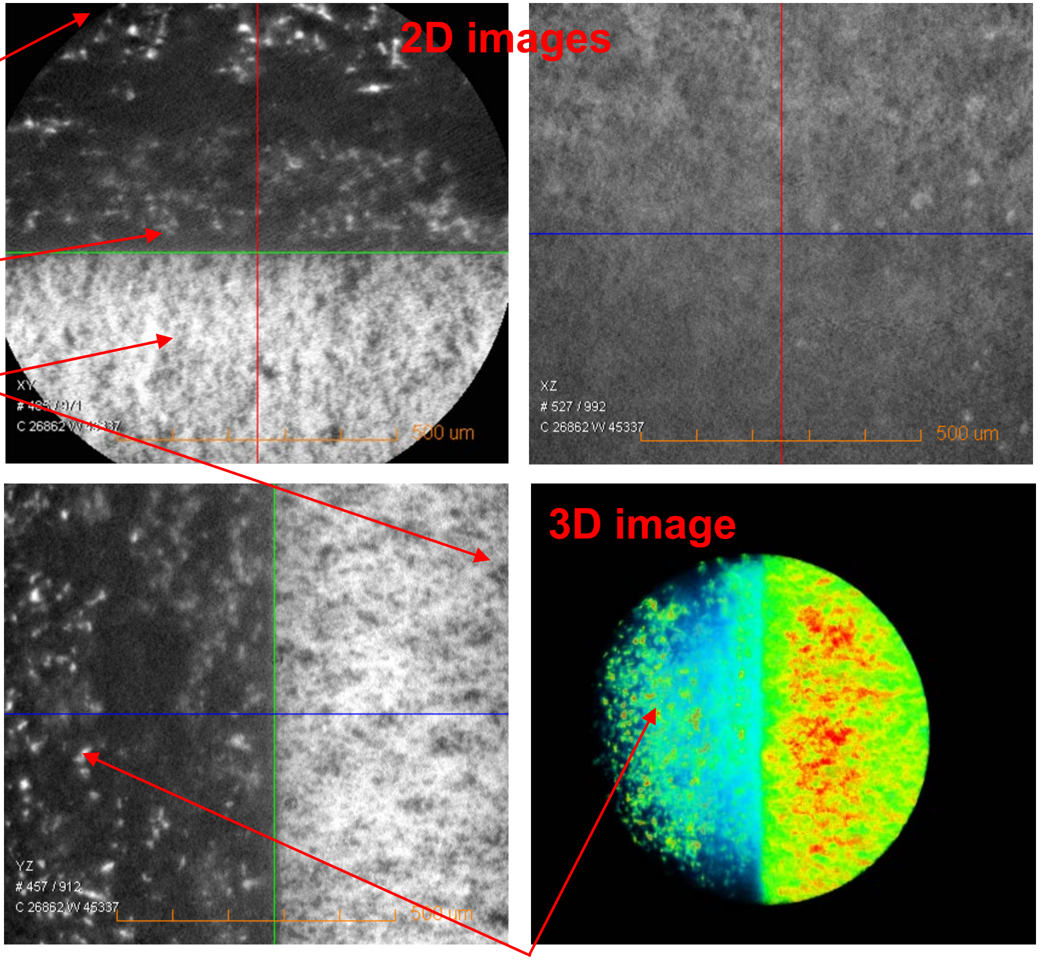
Ni-precipitation band

3D-Tomography

Anode side matrix

Cathode side matrix

Cathode



Ni-precipitates in anode side matrix

Cell # 7-2137 (5160 h)

Summary and Conclusions

- $LiAlO_2$ solubility measurements have been conducted in both cathode and anode environment.
  - The total α-$LiAlO_2$ (FCE-P powder) solubility is 12.045 $x10^{-6}$ mole fraction under cathode atmosphere for 650 h and 18.902 $x10^{-6}$ mole fraction under anode atmosphere for 920 h in molten carbonate.
  - XRD analysis of FCE-P showed γ-$LiAlO_2$, $LaAlO_3$ and α-$LiAlO_2$ as the major phases after exposure to molten carbonate for 920 h
  - Dissolved species of La and Al in molten carbonate take place leading to the formation of $LaAlO_2$ product.
  - BET results show a reduction in surface area after $LiAlO_2$ exposure to molten salt in both cathode and anode gas condition
  - Increase in particle size exhibited good correlation with changes in surface area
- The matrix coarsening near anode and cathode has been studied.
  - Enhanced coarsening is observed near the anode compared to cathode
  - Large $LiAlO_2$ particle shows the core-shell structure
- Ni-distribution, particle coarsening and matrix morphology have been examined.
  - Matrix showed Ni-precipitation near anode and wide Ni-precipitation band is observed in the matrix
  - The Ni^{2+} dissolves at the cathode and slowly diffuses towards the anode side matrix
- X-Ray Tomography was performed on tested sample.
  - Matrix showed the presence of nickel near anode side matrix and middle of the matrix
  - Matrix appeared to contain two distinct layers – porous and dense.

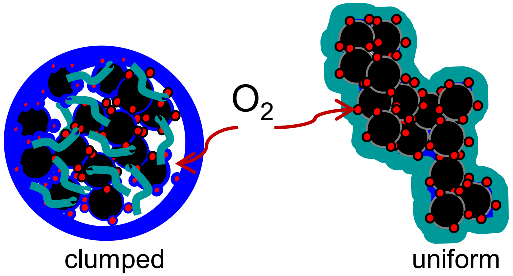
Task 1.4

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.

Approach



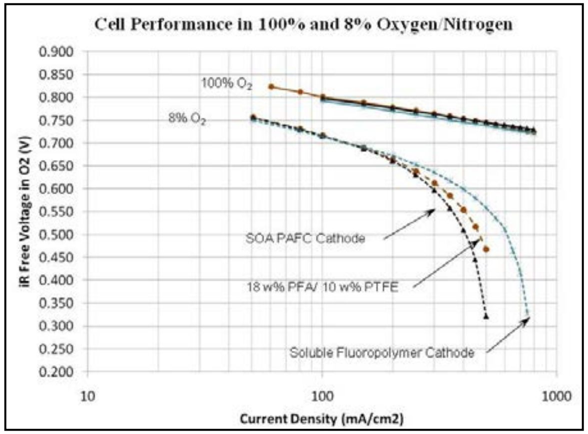
- Identify optimum agglomerate structure, e.g.:
  - Black-carbon
  - Red Pt-alloy catalyst
  - Dark blue phosphoric acid
  - Green-blue Fluoropolymer (e.g., PTFE)
  - Distribution of Fluoropolymer key in controlling phosphoric acid film thicknesses
  - Viscosity of PTFE at melt point is ~10^6 cp, too high for appreciable uniformity if electrodes are made from PTFE dispersion + catalyst (PAFC-commercial process).
- Previously developed an Approach using Soluble Fluoropolymers to produce the uniform Fluoropolymer layers:
  - A uniform Fluoropolymer distribution improving mass transport significantly ~90 mV @ 200 mA/cm^2 4% O_2 over a clumped distribution
  - Previously used Soluble Fluoropolymer was too expensive for commercialization
- Approach for CDP is to dissolve commercial perfluorinated materials 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

Accomplishments

- Dissolution of commercial fluoropolymers unsuccessful
  - Of PTFE, FEP and PFA, only PFA soluble in any solvent at elevated temperature.
  - PFA soluble only at elevated temperature, not at room temperature.
  - Uniform fluoropolymer layers on catalyst produced by heating PFA, catalyst and solvent together.
  - PEM-like fabrication nearly impossible because of low solubility of PFA at room temperature.
  - Cathode performance poorer than State of the Art (SOA) PAFC cathodes.
- Alternate fabrication method developed using Fibrillation of PTFE
  - Viable electrodes made by rolling Catalyst_PTFE mixtures between shims, dry and sinter.
  - Distinguished from previous work by using inert solvent and fibrillating only ~10% of the PTFE.
  - BENEFITS: Process simpler than PEM-like fabrication, Process is easily controlled, Performance equal or greater than SOA and Produces free-standing electrodes.
- Uniform fluoropolymer layer obtained by Sintering PFA-PTFE-Catalyst mixtures
  - Mixture of Catalyst-PTFE-PFA use PTFE to enable fibrillation fabrication
  - PFA melting point 33°C below PTFE, melt viscosity 10^5 times lower than PTFE enable flow for uniform coating.



Performance better than SO PAFC Cathode - see inset graph.

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.

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.

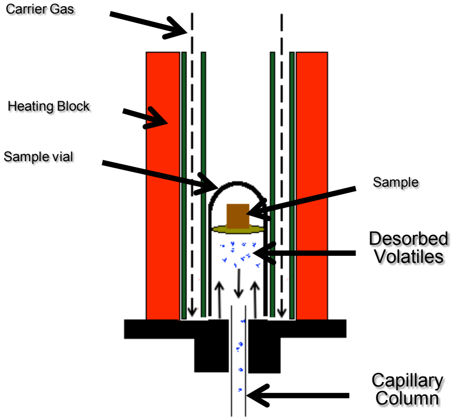
Durability and Performance:

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.

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

Task 2.2:

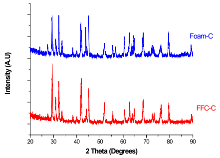
Fuel Reforming Catalysts for Efficient Energy Usage

Program Objectives

The goals of this project are as follows:

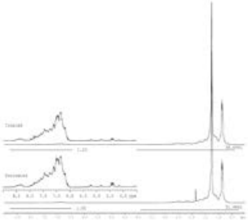
1. Preparation of Next Generation Fuel Reforming Catalysts.
2. Characterization and Modeling of Catalysts and Reactions.
3. Catalytic Testing of Fuel Reforming Catalysts with Biodiesel and Lignin Feeds.
4. Measure the Effects of Fitch® Fuel Catalysts on Emissions and Burner Efficiency.
5. Licensing and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

from UCONN of Next Generation Fuel Reforming Catalysts.



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

APSI, Lakewood, CT
Dr. Michael H. Best, President and CEO

Technical Approach

1. Synthesis – Use of Thin Films to Decrease Material Costs.

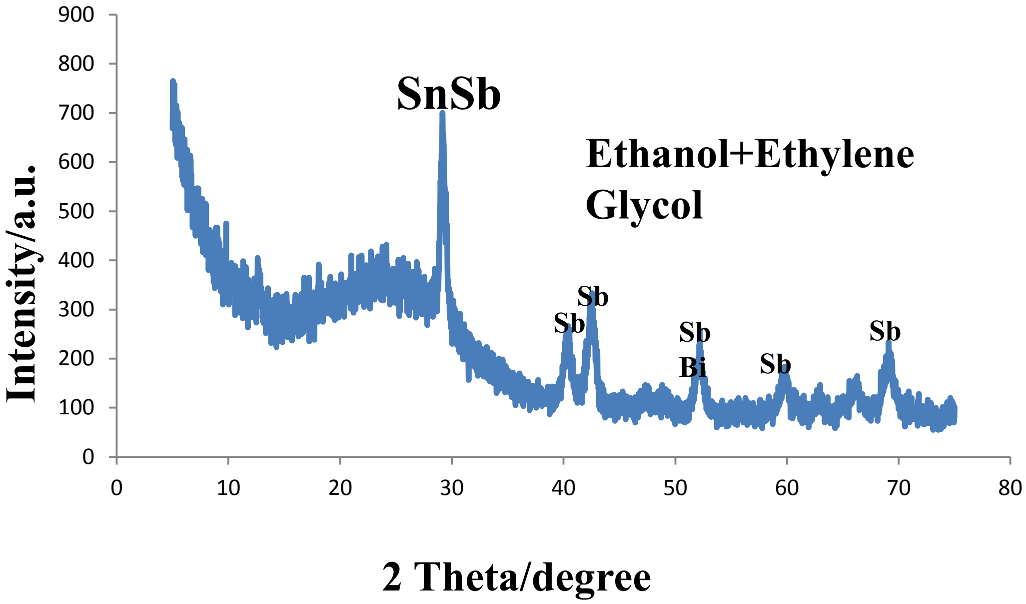
2. Use of Sol gel, Dip Coating Methods.

3. Mechanistic Studies Including Modeling Studies.

4. Characterization Using Surface, Mass Spec, Diffraction Methods.

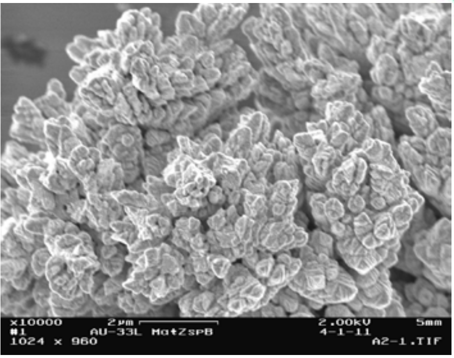
5. Next Generation Alloy Catalysts.

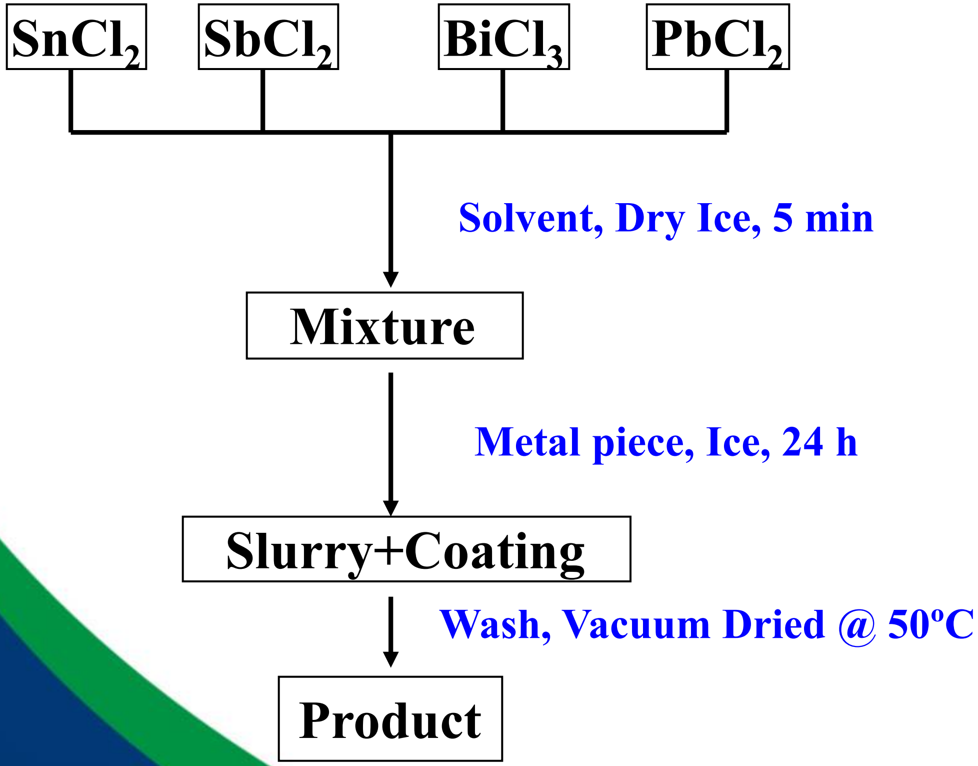
6. Catalytic Testing Using Fuel Reforming and Biomass Reactors.



Accomplishments & Highlights

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.





$SnCl_2$ **$SbCl_2$** **$BiCl_3$** **$PbCl_2$**

Solvent, Dry Ice, 5 min

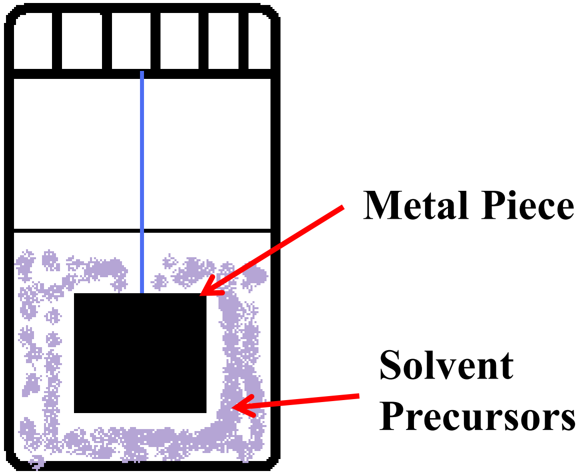
Mixture

Metal piece, Ice, 24 h

Slurry+Coating

Wash, Vacuum Dried @ 50ºC

Product



Metal Piece

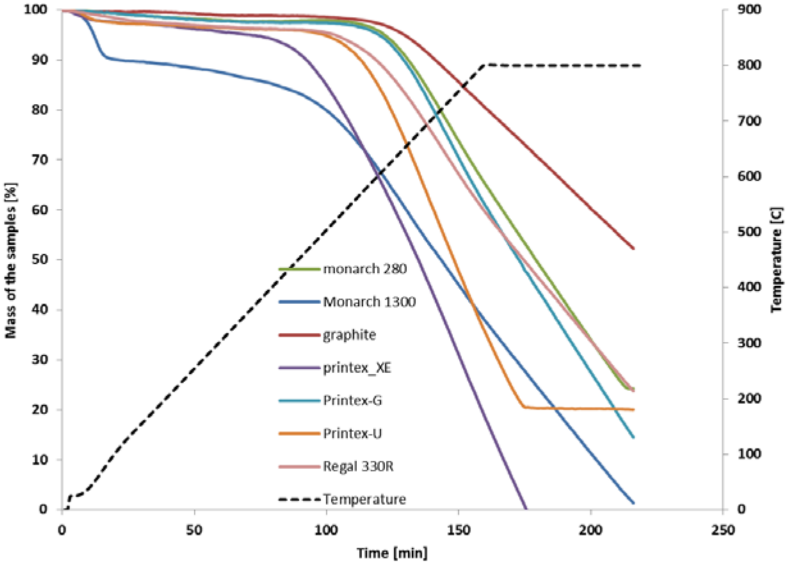
Solvent Precursors

Task 2.3:

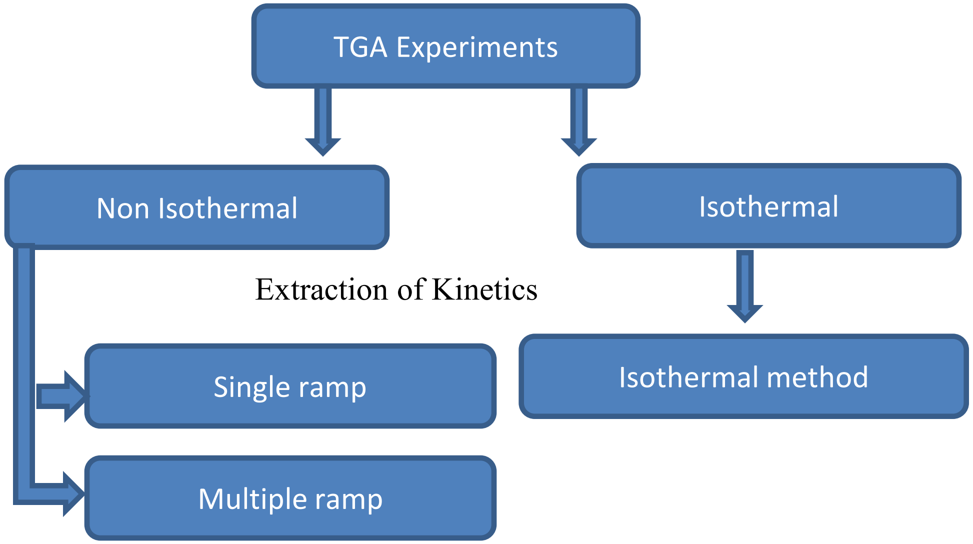
Soot Characterization and Kinetics

Program Objectives

- To Study Structure-Activity Correlation In Soot Oxidation.
- To Characterize Soot materials provided by Corning with Spectroscopic, Thermal, and Catalytic Tests.
- To Study and Model Carbonaceous Compounds
- as Models of Soot.
- To Study Ways to Decrease Soot Formation.



Technical Approach – TGA Experimental Protocol



TGA Experiments

Non Isothermal

Isothermal

Extraction of Kinetics

Single ramp

Multiple ramp

Isothermal method

Parameter	Range
Temperature	25 °C-800 °C
Ramp Rate	5-20 C/min
Flow rate: 10% O_2/Ar	20-80 ml/min
Crucible type	Pt and Al_2O_3
Purge gas	Nitrogen
Oxidant	10% O_2 and Air

Samples →

- **Diesel soot**
- **Graphite**
- **Mogul-E**
- **Monarch 1300**
- **Monarch 1400**
- **Monarch 280**
- **N 120**
- **N 339**
- **N 762**
- **Printex-G**
- **Printex-U**
- **Printex-XE2B**
- **Regal 330 R**
- **Regal 400 R**
- **VulcanXC72R**

Non isothermal test

25°C → 5-20 °C/min → 800°C → 15 min → 800°C → cooling → 20°C

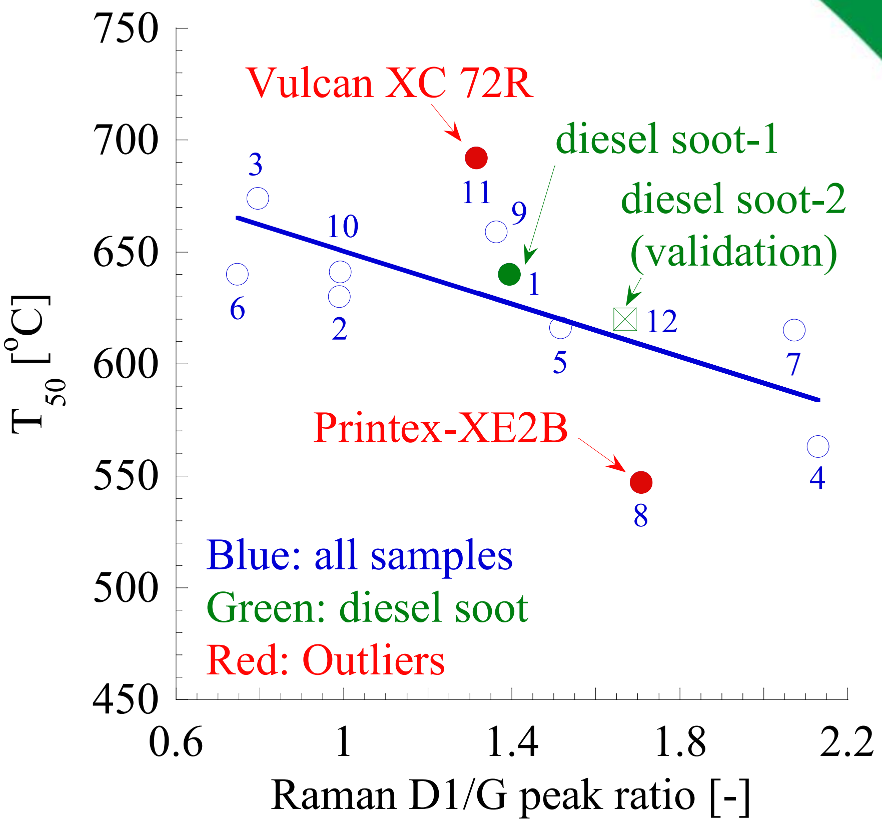
Isothermal test

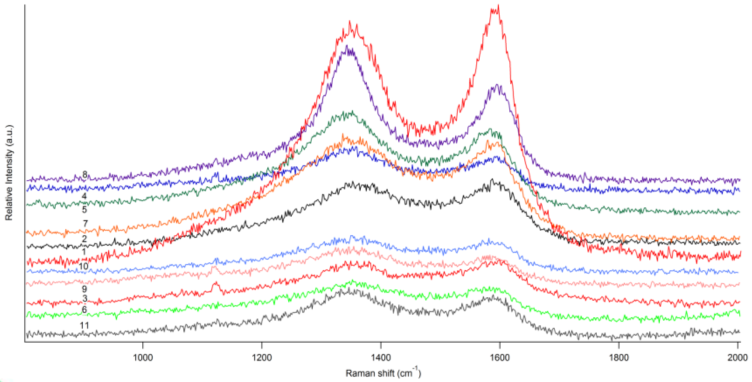
25°C → 20 °C/min → $T_{isothermal}$ → 2 hrs → $T_{isothermal}$ → cooling → 20°C

Printex is a registered trademark of Orion Engineered Carbons.
Mogul E, Monarch, Regal, and Vulcan are registered trademarks of Cabot Corporation.

Accomplishments

- X-ray Diffraction (XRD) studies
- Nitrogen Sorption studies
- Auger Spectroscopy
- Scanning Electron Microscopy (SEM)
- Fourier Transformation Infrared Spectroscopy (FT-IR)
- Transmission Electron Microscopy (TEM)
- Inductively Coupled Plasma (ICP)
- Direct Analysis in Real Time Mass Spectrometry (DART-MS)
- Raman Spectroscopy





Raman spectra (λ= 514 nm): two overlapping bands, one around 1600 cm^{-1} (G band) and the other around 1350 cm^{-1} (D band).

Summary

Summary

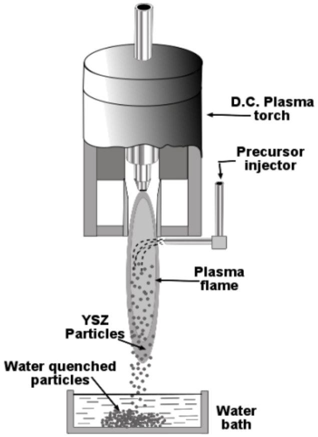
- Characterization of six different carbon black materials with XRD, SEM, Nitrogen sorption studies, FT-IR, Auger elemental analysis
- 7 different commercial samples studied using TGA
- Kinetic parameters calculated for various samples
- One successful benchCAT^{TM} run for Printex®-U

Task 3.1

Nano-layered Micro SOFCs: 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

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

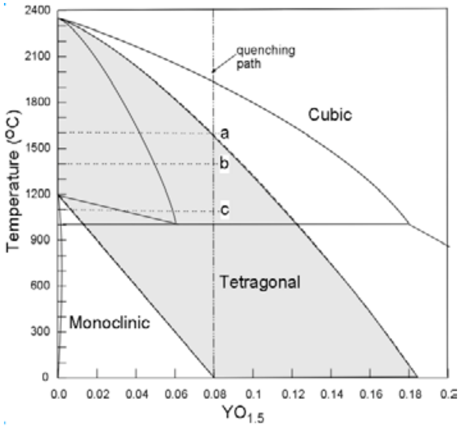
- Rapid processing of large areas to manufacture (i) large SOFCs and (ii) arrays small multicellular micro SOFCs.

- Facility for in-situ laser monitoring & feed-back control.

Accomplishments

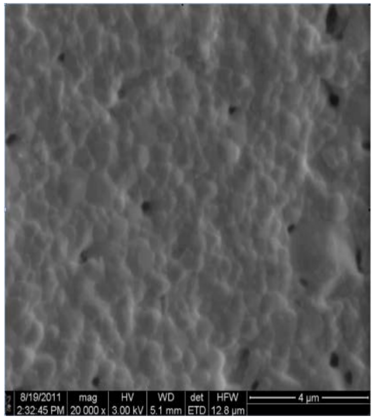
Recent findings include:

- 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°C
- high fracture toughness
- the potential of exploiting metastable phase diagrams to obtain novel properties

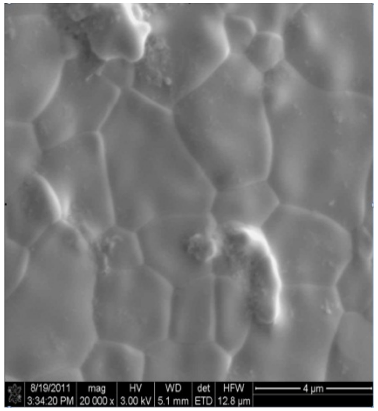


Metastable phase diagram

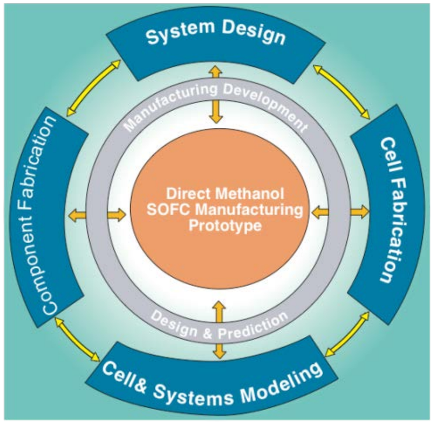
Morphology at 1400°C



From metastable powder



From Tosoh powder



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:
  - 9 Patents have or are being filed
  - 16 Journal Articles have or are being Published
  - >17 Conference Presentations