2010 DOE Hydrogen Program

Center for Fundamental and Applied Research in Nanostructured and Lightweight Materials

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Michigan Technological University

June 8, 2010

Project ID#: FC068

OVERVIEW

Timeline

- Project start date: July 1, 2008
- Project end date: June 30, 2010
- Percent complete: 100%

Budget

- Total project funding
  - DOE - $1.23 Million
  - Contractor - $352K
- Funding received in FY08: $139K
- Funding for FY09: $1.1 Million

Partners

- Dana Holding Corporation
- Clemson University
- Johns Hopkins University
- Michigan Technological University (Project Lead)

Barriers

A. Durability
B. Cost
C. Performance
D. Water Transport within the Stack
E. Thermal System and Water Management

Targets

- Fuel Cell Bipolar Plates:
  - Electrical Conductivity > 100 S/cm
  - Thermal Conductivity > 20 W/m·K
- Thermal cyclability in presence of condensed water
- Improved GDL performance, durability, and resistance to flooding
- Develop testing and characterization protocols and techniques
- Ability to tailor the properties of carbon foam supports to meet PEM fuel cell electrode requirements
- Ability to construct pseudomorphic overlayer catalysts, on carbon supports, that are designed to mimic conventional PEM anode catalysts

OBJECTIVES

This project involves fundamental and applied research in the development and testing of lightweight and nanostructured materials to be used in fuel cell applications.

Our research covers these areas:

Area I. Heat and Water Management

- Develop and test lightweight and nanostructured materials for fuel cell bipolar plates.
- Improve GDL performance and durability.
- Develop testing and characterization protocols and techniques for GDLs relative to water management.

Area II. Development of New Electrode Materials

- Develop graphitic carbon foams that will serve as current collectors, and catalyst supports.
- Develop durable carbon-supported catalysts that have reduced weight and cost compared to conventional PEM anode catalysts.

Area I. Heat and Water Management
RELEVANCE/APPROACH

RELEVANCE

- By 2010 to develop a 60% peak efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of $45/KW, by 2015 , a cost of $30/kW.
  - Develop improved bipolar plate material
  - Improve GDL performance and durability
  - Develop testing and characterization protocols and techniques
  - Alleviate flooding and/or dryout of membrane through advanced understanding of GDL water transport

APPROACH

- Develop carbon filled thermoplastic bipolar plates that meet conductivity targets (electrical conductivity> 100 S/cm, thermal conductivity > 20 W/m·K)
- Develop environmental chamber for measuring GDL wettability at fuel cell operating temperatures in air and hydrogen; thermal, humidity and gaseous control
- Measure contact angles from 0 to 80^{o}C in air and in hydrogen
- Develop characterization method for GDL compression and damage resulting from compression
- Image GDL under compression
- Assess damage resulting from compression

Area I. Heat and Water Management
MILESTONES

Milestones	Month/Year	Percent Complete
Compounded carbon nanotube/carbon black/synthetic graphite/ polypropylene conductive resins and molded test specimens for bipolar plate materials. Determined electrical conductivity, through plane thermal conductivity using guarded heat flow meter method and transient plane source test method, and rheological properties of each resin. Developed electrical conductivity models and through plane thermal conductivity models.	Nov-2008	100%
Completed in plane and through plane thermal conductivity testing and modeling on carbon nanotube/carbon black/ synthetic graphite/ polypropylene conductive resins using nanoflash test method.	Jun-2010	100%
Contact angle measurement apparatus and technique: There remains some development work on the humidity control for measuring the contact angle at elevated temperatures. A second-level thermostat is being constructed to maintain better humidity control and provide a sealed chamber for use with hydrogen.	Nov-2008	100%
Contact angle measurements on GDL samples: Contact angle measurements continue on the current GDL sample set.	Jan-2010	100%
Compression Fixture: The fixture is complete. A second set of springs will be ordered to improve the testing range for the stiffer GDL materials.	Nov-2010	100%
Compression-force measurements on GDL samples: Compression testing and imaging continue on the current GDL sample set.	Jan-2010	100%

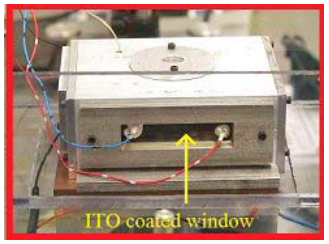
Area I. Heat and Water Management

TECHNICAL ACCOMPLISHMENTS

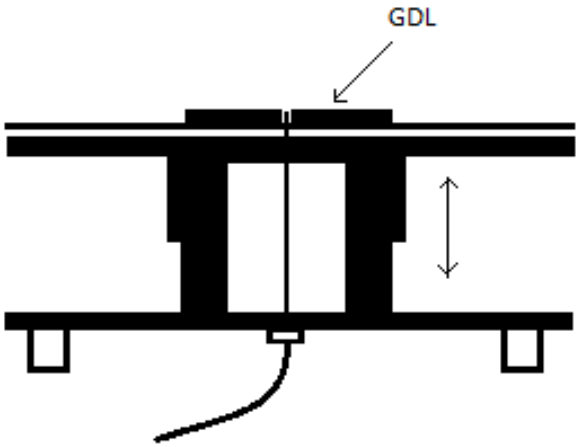
Movement of Water in Fuel Cell Electrodes

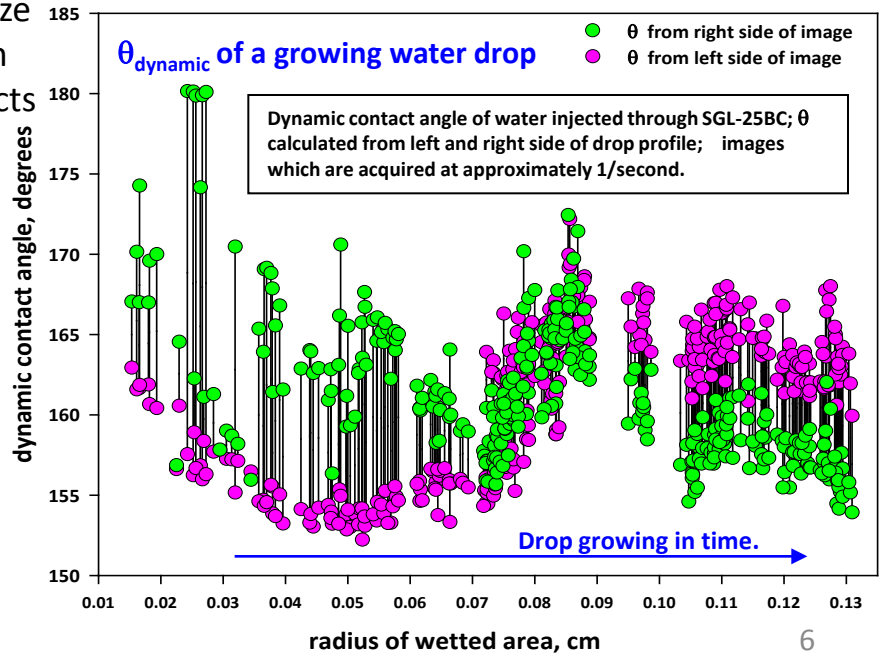
Technical Accomplishments

- 2nd-Level Thermostat fabricated for environmental chamber
  - Improved Temperature control
  - Improved Humidity control
  - Potential H_2 atmosphere
- Addressed dependence of contact angles on drop size
- Improved algorithm for contact angle determination
- Developed new drop deposition method which injects water through GDL



2nd-Level Thermostat



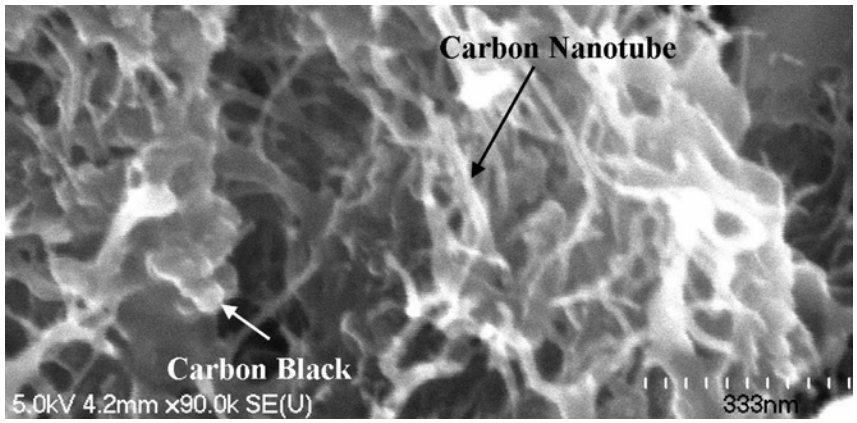


Area I. Heat and Water Management

TECHNICAL ACCOMPLISHMENTS

Conductive Bipolar Plates for Fuel Cells

- Most Conductive Material: 2.5 wt% Akzo Nobel Ketjenblack EC-600 JD carbon black/ 65 wt% Asbury Carbons Thermocarb TC-300 synthetic graphite particles/ 6 wt% Hyperion carbon nanotubes/ 26.5 wt% Dow homopolymer polypropylene H7012-35RN
  - Electrical Conductivity: obtained 91 S/cm (DOE target is 100 S/cm) via compression molding and 38 S/cm via injection molding
  - In Plane Thermal Conductivity: obtained 24 W/m·K (DOE target is > 20 W/m·K) via compression molding and 18 W/m·K via injection molding

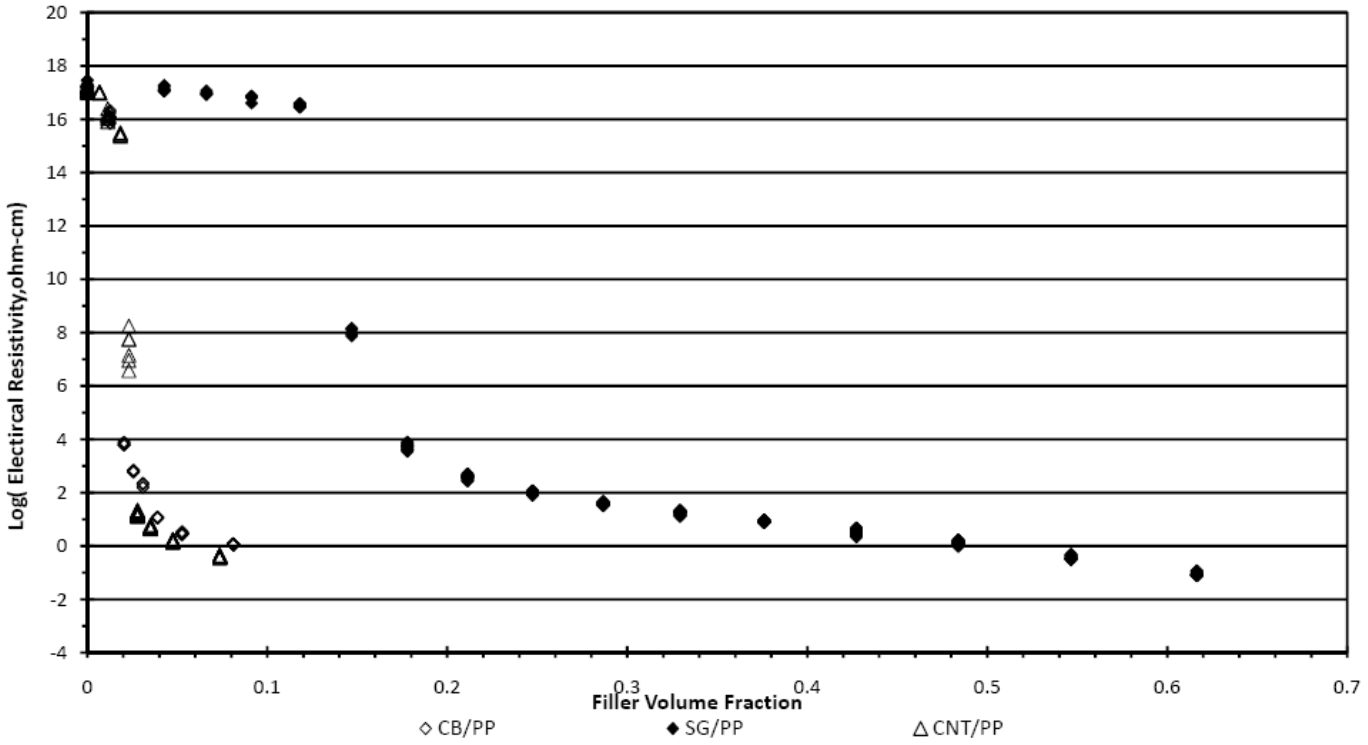


Area I. Heat and Water Management

TECHNICAL ACCOMPLISHMENTS

Conductive Bipolar Plates for Fuel Cells: Electrical Conductivity

- Percolation Threshold : Injection Molded Samples
  - Carbon Black : 1.4 vol%
  - Carbon Nanotubes: 2.1 vol%
  - Synthetic Graphite: 13 vol%



Area I. Heat and Water Management

TECHNICAL ACCOMPLISHMENTS

Conductive Bipolar Plates for Fuel Cells

- Through Plane Thermal Conductivity :

  Guarded Heat Flow Meter Method and Transient Plane Source Test Method: Injection molded samples

  - 15 wt% (8.1 vol%) Carbon Black (CB) / PP: 0.34 W/m·K
  - 15 wt% (7.4 vol%) Carbon Nanotubes (CNT) / PP: 0.47 W/m·K
  - 80 wt% (61.6 vol%) Synthetic Graphite (SG) / PP: 6 W/m·K

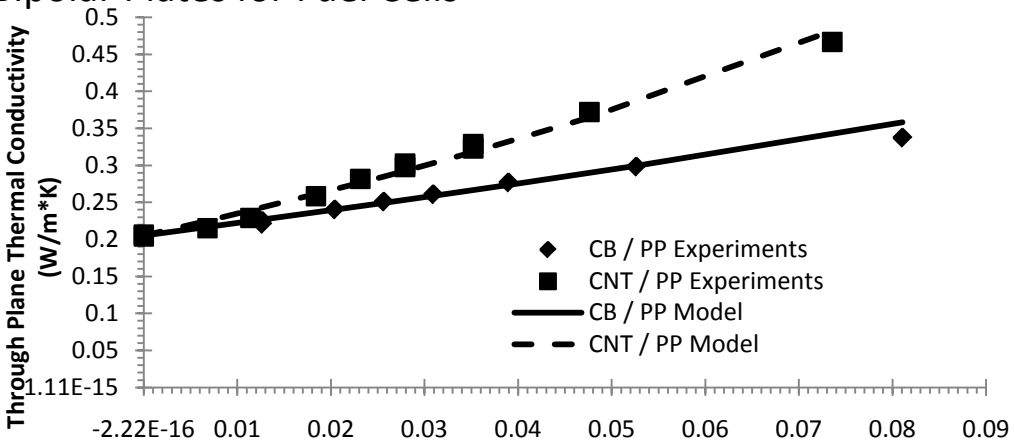
  Nielsen Through Plane Thermal Conductivity Model

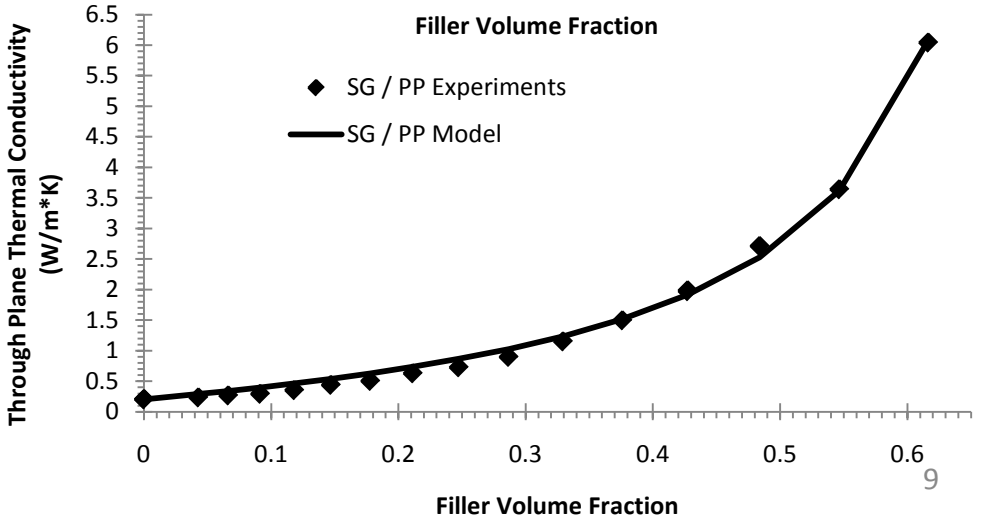
$$k_{through} = k_{polymer}\frac{(1+AB\phi)}{(1-B\psi\phi)} \qquad \psi \cong 1+(1-\phi_m)\phi/\phi_m^2$$

$$B = \left(\frac{k_{filler}}{k_{polymer}} - 1\right) \Big/ \left(\frac{k_{filler}}{k_{polymer}} + A\right)$$

  - CB / PP: k_{filler} = 2.1 W/m-K, A = 75.6, ϕ_m = 0.64
  - CNT /PP: k_{filler} = 20 W/m-K , A = 18.2, ϕ_m = 0.64
  - SG / PP: k_{filler} = 600 W/m-K, A = 8.35, ϕ_m = 0.741

$$\psi \cong 1+(1-\phi_m)\phi/\phi_m^2$$



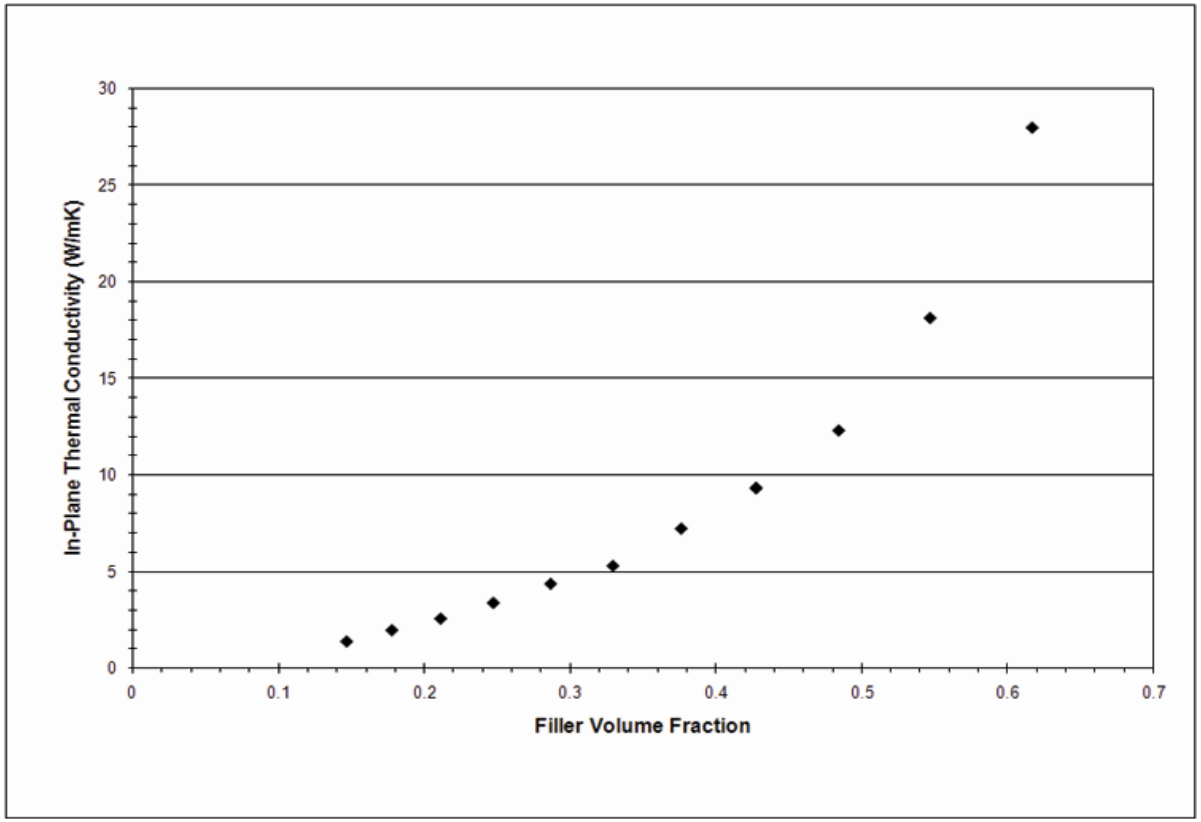


Area I. Heat and Water Management

TECHNICAL ACCOMPLISHMENTS

Conductive Bipolar Plates for Fuel Cells

- In Plane Thermal Conductivity: Transient Plane Source Test Method
  - 80 wt% (61.6 vol%) Synthetic Graphite/PP: 28 W/m·K



Area II. Development of New Electrode Materials

RELEVANCE

- Graphitic carbon can serve as a current collector and mechanical support for electrochemically-active mass and catalytic materials. A mesoporous carbon foam, in particular, offers an inexpensive, lightweight alternative to current electrode materials, and it can be machined to desired shapes. It is also tolerant of the corrosive environment within fuel cells. Both the electrical conductivity (degree of graphitization) and the porosity of the carbon foam are important for current collector and catalyst applications.
- Replacement catalysts for platinum are needed to reduce fuel cell cost. Synthesis of pseudomorphic overlayer bimetallic catalysts may reduce or eliminate platinum use in PEM fuel cells.

Area II. Development of New Electrode Materials

APPROACH

- Synthesize carbon foams of varying pore sizes at Clemson University using polyacrolnitrile (PAN) precursors. Thermally-induced phase separation (TIPS) of the polymer from the solvent phase is used to form the precursor material. The resulting foam is then pyrolized to produce a graphitic carbon foam. To date, green foam samples have been synthesized that range from 3% to 8% by weight PAN. Critical-point drying is done either at in-house facilities on the central Clemson Campus or at the Clemson Conservation Center.
- Measure the pore size distribution, surface area, and surface composition (via spectroscopic analyses) of candidate carbon foam electrode supports, both before and after electrochemical service.
- Use surface passivation and controlled deposition reaction to synthesize a pseudomorphic overlayer bimetallic catalyst on a carbon support. The bimetallic combination is being chosen to mimic the heat of adsorption and catalytic activity of a Platinum active site on a PEM fuel cell catalyst.

Area II. Development of New Electrode Materials

MILESTONES

Milestones	Progress Notes	Planned Completion Date	% Complete
Making a graphitized carbon foam from a PAN precursor	Completed	06/08/2010	100%
Synthesis and characterization of Pt/Ni Overlayer Catalysts	Completed	06/08/2010	100%
Extend catalyst synthesis procedure to a carbon support	In progress	06/30/2010	75%

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Synthesizing Graphitic Carbon Foams

- Porous, machinable current collectors and mechanical supports
- Pyrolysis of PAN-based foams in an oxygen-free environment at 1200°C
- Fuel cell electrodes with a large macropore/mesopore space to hold electrochemically-active material
- Carbon supports for fuel cell pseudomorphic overlayer catalyst(s) that promote dissociation of diatomic hydrogen into constituent protons and electrons

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Bimetallic Catalysts

Bimetallic catalysts are commonly used in many reactions

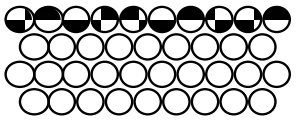
- Most are simple alloys of different metals

Non-equilibrated atomic arrangements would allow finer control of catalytic properties

- Supported by first principles computational and single crystal work

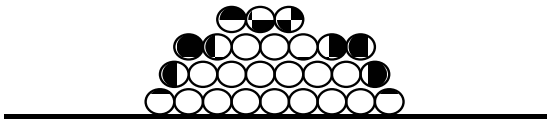
Industrial Examples:
Pt/Re Catalytic Reforming
Co/Mo Hydrotreating
Co/Ni Fischer-Tropsch
Zn/Cr Tetrahydrofuran

Single Crystal Pseudomorphic Overlayer



◐ Metal A
○ Metal B

Supported Particle Pseudomorphic Overlayer

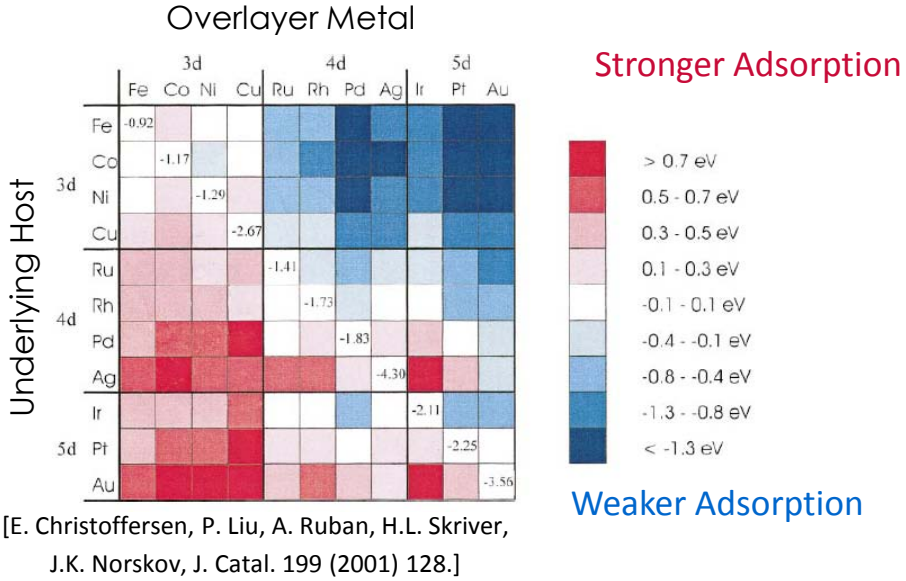


Oxide Support

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Catalyst Design



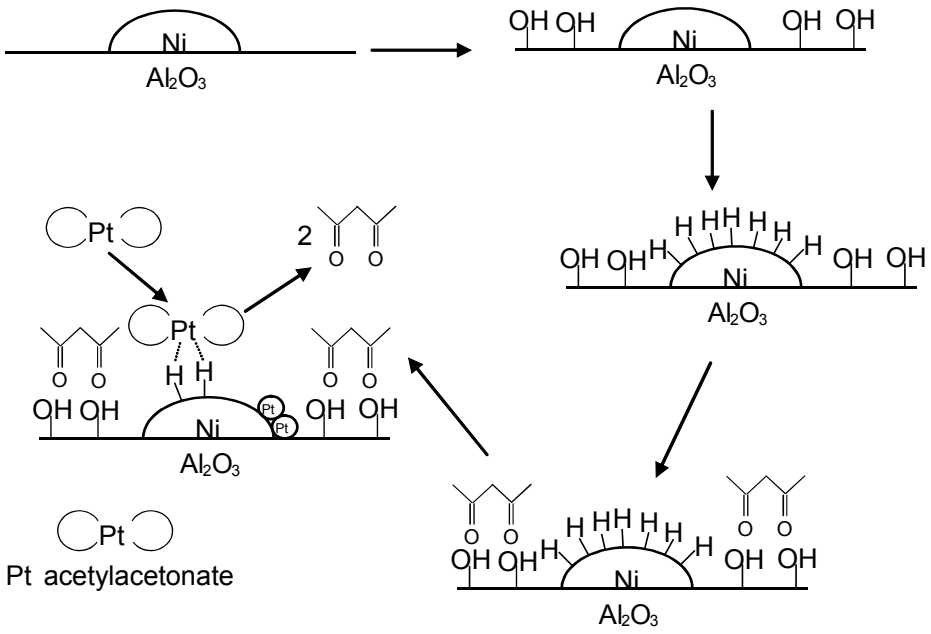
[E. Christoffersen, P. Liu, A. Ruban, H.L. Skriver, J.K. Norskov, J. Catal. 199 (2001) 128.]

- Structure results in unique properties:
  - Bonding strength can increase or decrease depending on the metal combination. Literature studies have determined precise values.
  - Bond strength can be correlated with center of the d-band calculated computationally.
- Nomenclature: Base@Overlayer; e.g. Re@Pd is Pd overlayer on Re base.
- First principle computational techniques have been used to predict d-band shifts and adsorption properties

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Reload Synthesis Procedure



- Synthesis procedure focuses overlayer deposition:
  - Hydroxylation and acetylacetone inhibit deposition on support.
  - Surface reaction with hydrogen also direct deposition while only allowing one layer of coverage.

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Catalyst Metal Loadings

- Synthesis Effects:
  - Maximum theoretical Pd loading of 0.13 wt%

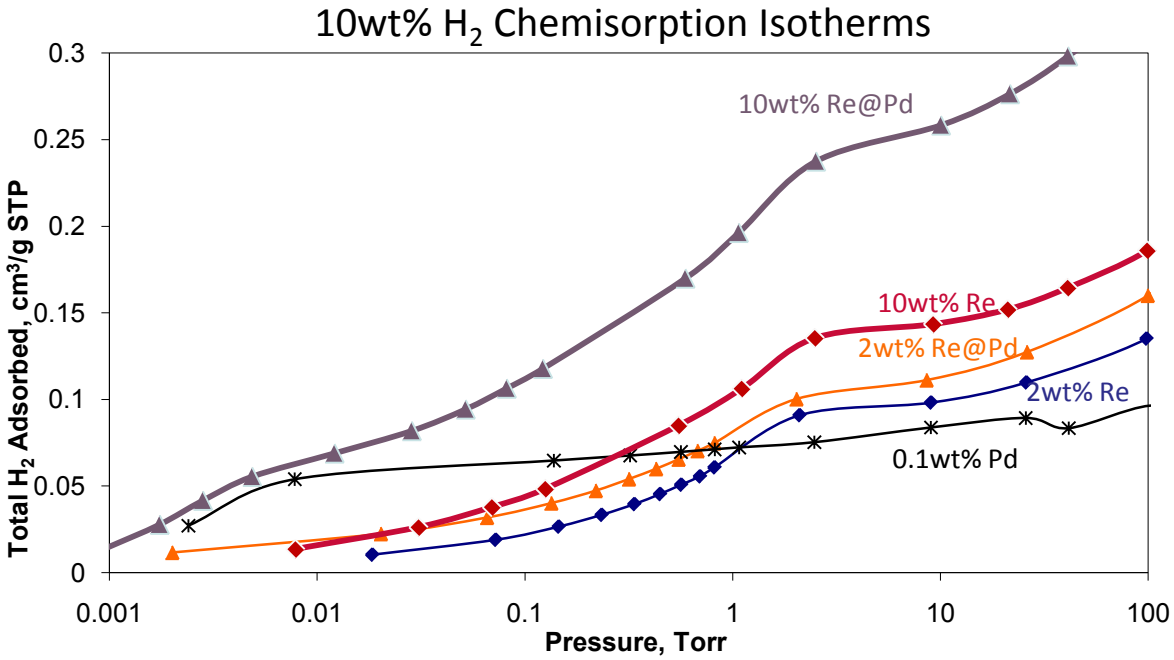
Catalyst	Pd (wt%)
Re	-
Re@Pd RT	0.008
Re@Pd HT	0.083
Re@Pd TD	0.073
Re@Pd NI	0.249
Pd	0.086

- Particle Size Effects:

Catalyst	Dispersion	Particle Size (nm)
2wt% Re	36.7%	2.72
10wt% Re	15.9%	6.29

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

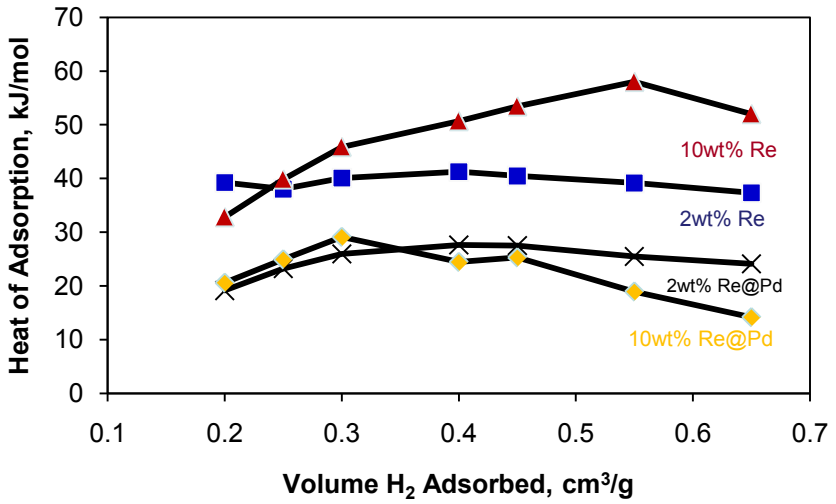


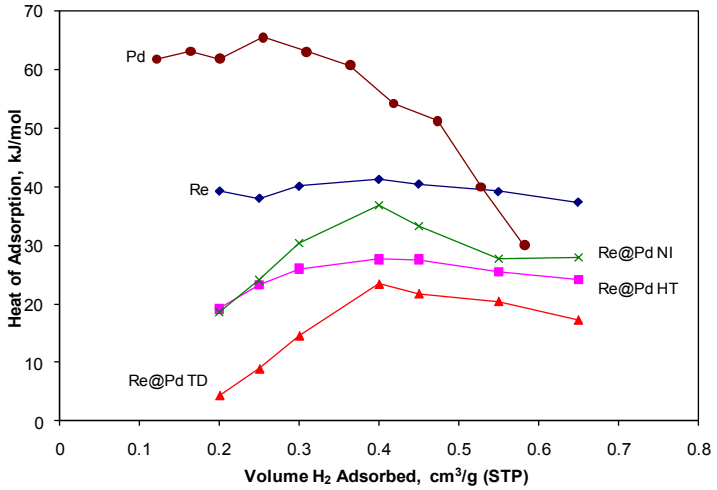
- 10wt% Re - similar adsorption to 2wt% Re
- 10wt% Re@Pd - more low pressure adsorption and surface sites
- Possible indication of some isolated Pd particles

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

H_2 Heat of Adsorption





- Re heat of adsorption:
  - Increases with particle size
  - Moves toward bulk values as particle size increases
- Pd overlayer on small and large particles results in similar heat of adsorption

NI = no inhibitors (hydroxylation or acetylacetone)
HT = High temperature deposition
TD = deposition procedure repeated three times

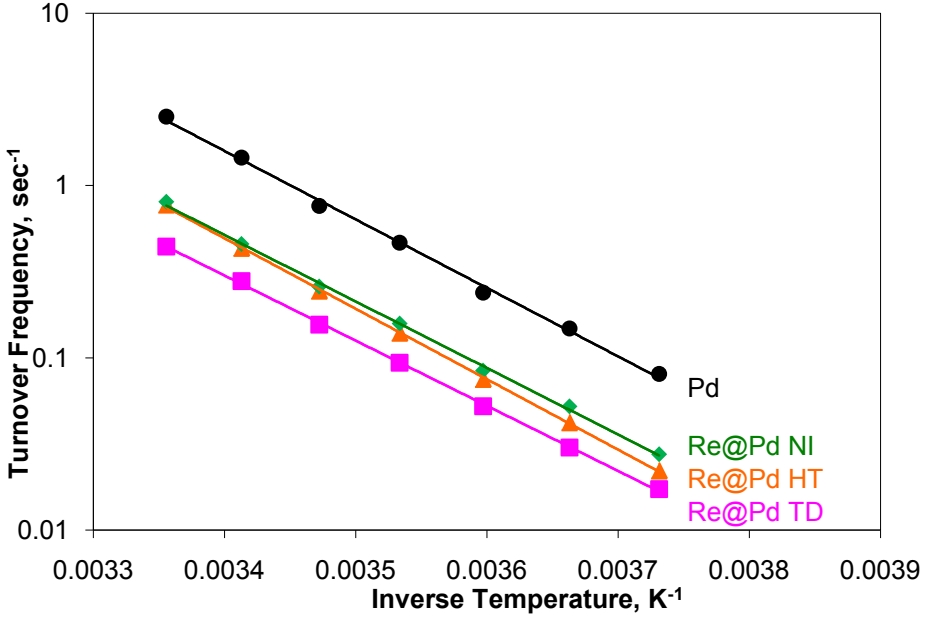
- Literature comparisons:
  - Pd: 67 kJ/mol for highly dispersed Pd/Al_2O_3 [1], 78 kJ/mol for single crystal Pd(111) at 100% coverage (computational) [3]
  - Re: 128 kJ/mol for Re wire (initial heat) [4], 139 kJ/mol (first principles computation at 33% coverage) [5]
  - Pd_{ML}/Re: +2 kJ/mol at 100% coverage (computational) [3]

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Overlayer Catalyst Activity

Ethylene Hydrogenation



Reactivity Summary

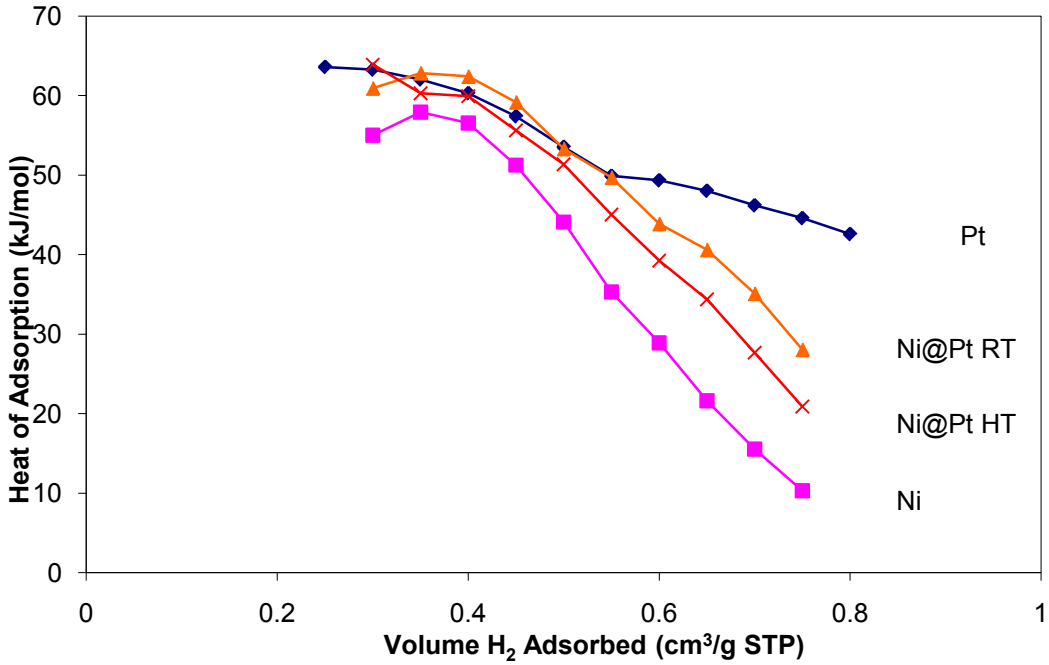
Catalyst	Apparent Activation Energy, kJ/mol	Reaction Order (10°C)	
		H_2	C_2H_4
2 wt% Re/Al_2O_3	103	1.0	0.0
0.1 wt% Pd/Al_2O_3	76.1	1.0	-0.11
2wt% Re@Pd HT	78.3	1.1	-0.12
2wt% Re@Pd TD	72.4	1.0	-0.12
2wt% Re@Pd NI	73.9	1.0	-0.12
10wt% Re@Pd	81.5	1.1	-0.13

- Pd activity comparable, but higher than Re@Pd catalysts
- Apparent activation (~75 kJ/mol) energies approximately constant for these catalysts

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

H_2 Heat of Adsorption

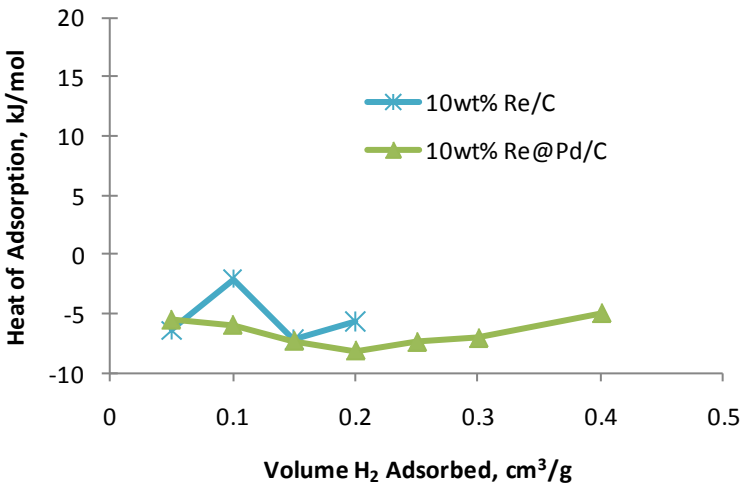


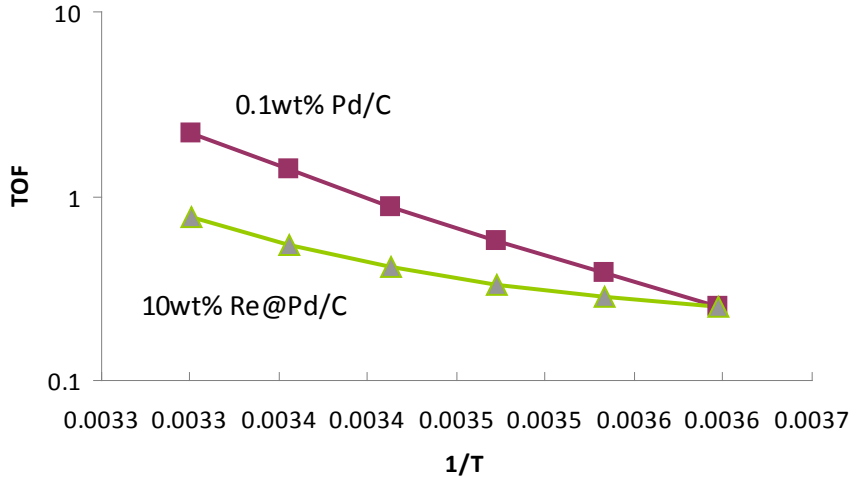
- H_2 ΔH_{ads} on Pt: 57 kJ/mol at high coverage [8]
- H_2 ΔH_{ads} on Ni: 50 kJ/mol at start of reversible adsorption [9]
- H_2 ΔH_{ads} on Pt_{ML}/Ni expected to be lower than Pt & Ni based on single crystal and computational studies [10]

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Carbon Support





Vulcan XC-72 carbon black

- H_2 ΔH_{ads} results not as clear as for alumina support
- Reactivity results consistent with alumina. Overlayer on C support shows largest apparent activation energy and reaction order change.
- Concerned about synthesis procedure depositing very small base Re particles.

Catalyst	Apparent Activation Energy, kJ/mol	Reaction Order	
		H_2	C_2H_4
0.1wt%Pd/Al2O3	76.1	1.0	-0.11
2wt% Re@Pd/Al2O3	78.3	1.1	-0.12
10wt% Re@Pd/C	36.7	0.8	-0.08
0.1wt%Pd/C (100%)	61	1.0	-0.07

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Current and Pending Work

- Direct methanol FC electrodes
  - Less expensive replacements for precious metal catalysts
  - More carbon monoxide tolerant electrodes
- Aqueous Phase Reforming (APR):
  - Potential process to produce H_2 from renewable feedstocks.
    - $C_nH_{2y}O_n$ ⇨ yH2 + nCO
    - $CO + H_2O$ ⇨ $CO_2 + H_2$
- Benefit: Both CO and H_2 have been shown to inhibit APR. Lower heats of adsorption decreases H_2 and CO surface coverage
  ⇨ more sites accessible for reactions.
- Computational predictions:
- Decrease in d-band center
- Result: Decrease in H_2 binding energy
  Decrease in CO binding energy

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Conclusions

- Supported Re@Pd overlayers found to have hydrogen heats of adsorption lower than that of pure components
  - Isotherms also support altered hydrogen adsorption on Pd in Re@Pd catalysts
- Ethylene hydrogenation results support decreased binding of hydrogen
  - Also suggest initial hydrogenation barrier strongest influence for apparent activation energy
- All results consistent with first principles and single crystal studies of Pd_{ML}/Re
- Activity can be correlated with computationally predicted shifts in the center of the d-band through heat of adsorption
- Strong indication that we can make catalysts that demonstrate the properties of pseudomorphic overlayer bimetallics.

Area II. Development of New Electrode Materials

TECHNICAL ACCOMPLISHMENTS

Exploring Alternatives to a Platinum-based Fuel Cell Anode Catalyst

- Extending recently developed synthesis method for bimetallic overlayer catalysts
- Selecting bimetallic combinations with desired fuel cell catalytic properties
- Refining synthesis procedure to construct an overlayer catalyst on a working graphitic carbon electrode

TECHNOLOGY TRANSFER/COLLABORATIONS

- Dr. Eve S. Steigerwalt, Technical Development Manager, Performance Plastics Center, Dana Holding Corporation, Paris, TN
- Dr. O. Thompson Mefford, School of Materials Science and Engineering, Clemson University
- RIT, GM: Visualization of Fuel Cell Water Transport and Performance Characterization Under Freezing Conditions, DOE DE-FG36-07GO17018
- MTU: Hydrogen Education Curriculum Path at Michigan Technological University, DOE DE-FG36-08GO18108
- MTU, State of Michigan: Fuel Cell Water Control System Prototype – Alternative Energy, Michigan Universities Commercialization Initiative (MUCI)
- MTU amended claims 066040-9791-01 filed on 01-19-2010 in response to USPTO 11-18-2009 office action A3694005. United States Patent Application No. 2006 0024583, "Nickel hydroxide impregnated carbon foam electrodes for rechargeable nickel batteries," filed 15 July, 2005, A. Singh, B. C. Cornilsen, M. E. Mullins, and T. N. Rogers (U.S. Provisional Application No. 60/588,108 filed July 15, 2004)
- Dr. Andres Hurtado, M.D., Kennedy Krieger Institute, Johns Hopkins University - In this project we have been developing new classes of materials that take advantage of the flexible properties of plastics combined with some of the chemical advantages of ceramic (inorganic) materials. The original object was to create better fuel cell membranes; however, an unexpected twist in our studies is that the new materials we developed were found to be excellent for supporting tissue growth.
- Technology and Commercialization Consultant: Mr. Ralph J. Brodd, President of Broddarp of Nevada, Inc.

FUTURE WORK

Area I. Heat and Water Management

- For carbon nanotube/carbon black/synthetic graphite /polypropylene materials for fuel cell bipolar plates
  - Determine through-plane and in-plane thermal conductivity using nanoflash method and develop models (currently writing papers)
  - Determine tensile and flexural properties and develop models (currently writing papers)

Area II. Development of New Electrode Materials

- Optimize carbon foam synthesis procedure to improve porosity and mechanical strength
- Refine synthesis techniques to construct a pseudomorphic overlayer catalyst on the surface area of a carbon foam support.

PROJECT SUMMARY

I. Heat and Water Management

Relevance:

- Develop improved bipolar plate materials
- Improve GDL performance and durability

Approach:

- Use combination of carbon fillers in thermoplastic to achieve desired fuel cell bipolar plate conductivity
- Measure contact angles in hydrogen and air to determine GDL wettability at fuel cell operating conditions

Technical Accomplishments:

- **Fuel Cell Bipolar Plates**: For 2.5 wt% Akzo Nobel Ketjenblack EC-600 JD carbon black/ 65 wt% Asbury Carbons Thermocarb TC-300 synthetic graphite particles/ 6 wt% Hyperion carbon nanotubes/ 26.5 wt% Dow homopolymer polypropylene H7012-35RN (DOE target of 100 S/cm and > 20 W/m·K)
  - Electrical Conductivity: Achieved 91 S/cm
  - Thermal Conductivity Achieved 24 W/m·K
- **Water Management:**
  - Fabricated environmental chamber; measured contact angles and characterized error; data indicates decrease in contact angle as temperature increases

Technology Transfer/Collaborations: Active partnerships with Dana, RIT and GM (DOE DE-FR36-07GO17018), Hydrogen Education Curriculum Path at Michigan Technological University (DOE DE-FG36-08GO18108), and State of Michigan: Fuel Cell water Control System Prototype-Alternative Energy, Michigan Universities Commercialization Initiative (MUCI)

Future Work:

- For carbon nanotube/carbon black/synthetic graphite /polypropylene materials for fuel cell bipolar plates
- Determine through plane and in plane thermal conductivity using nanoflash method and develop models
- Determine tensile and flexural properties and develop models
- Complete contact angle measurements for current GDL set for drop size and temperature dependencies
- Fabricate sealed, second level thermostat for measuring contact angles in humid, hydrogen environment for range of temperatures
- Complete compression imaging for current DGL set

PROJECT SUMMARY

II. Development of New Electrode Materials

Relevance: Porous graphitic carbon foams can serve as lightweight current collectors, active mass holders, and mechanical supports for electrodes and catalysts. Pseudomorphic overlayer bimetallic catalysts deposited on a carbon surface may reduce or replace Platinum use in PEM fuel cells.

Approach:

- Synthesize carbon foams having varying levels of porosity by pyrolizing PAN-based precursors
- Fabricate and test carbon-supported electrodes and catalysts
- Construct overlayer catalysts tailored to have desired catalytic activity

Technical Accomplishment and Progress:

- Investigated electrode applications for porous, graphitic carbon foams
- Developed procedures for selecting and synthesizing bimetallic overlayer catalysts, on an alumina support, having desired catalytic properties

Technology Transfer/Collaborations:

- MTU amended claims 066040-9791-01 filed on 01-19-2010 in response to USPTO 11-18-2009 office action A3694005. United States Patent Application No. 2006 0024583, "Nickel hydroxide impregnated carbon foam electrodes for rechargeable nickel batteries," filed 15 July, 2005, A. Singh, B. C. Cornilsen, M. E. Mullins, and T. N. Rogers (U.S. Provisional Application No. 60/588,108 filed July 15, 2004)
- Collaborating on carbon foam synthesis procedures with Dr. O. Thompson Mefford, Clemson University, School of Materials Science and Engineering
- Technology and Commercialization Consultant: Mr. Ralph J. Brodd, President of Broddarp of Nevada, Inc.

Proposed Future Research:

- Synthesize carbon foams with increased porosity and surface area and improved mechanical strength
- Refine catalyst synthesis procedure to construct pseudomorphic overlayer catalysts on a graphitic carbon support

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