

V.O.1 Center for Fundamental and Applied Research in Nanostructured and Lightweight Materials*

Michael E. Mullins (Primary Contact),
Julia A. King, Tony N. Rogers, J. Allen,
R. Gilbert, J.H. Holles, B. Cornilsen, and
J.M. Keith

Rm 203 CSE Bldg
Chemical Engineering Department
Michigan Technological University (MTU)
1400 Townsend Drive
Houghton, MI 49931
Phone: (906) 487-1445
E-mail: memullin@mtu.edu

DOE Technology Development Manager:
Dimitrios Papageorgopoulos
Phone: (202) 586-546
E-mail: Dimitrios.Papageorgopoulos@ee.doe.gov

DOE Project Officer: Greg Kleen
Phone: (303) 275-4875
E-mail: Greg.Kleen@go.doe.gov

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*Congressionally directed project

Area II: Development of New Electrode Materials

- Porous, machinable current collectors and mechanical supports.
- Pyrolysis of peroxyacetyl nitrate (PAN)-based foams in an oxygen-free environment at 1,200°C.
- Positive (cathodic) battery electrodes with a large macropore/mesopore space to hold electrochemically-active material.
- Supercapacitor battery anodes with a large accessible micropore surface area (i.e., >1,000 m²/g) for electric double layer charge storage.
- Carbon supports for fuel cell pseudomorphic overlayer anode catalyst(s) that promote dissociation of diatomic hydrogen into constituent protons and electrons.

Area III: Enabling Technologies for Membrane Synthesis

- Developed apparatus for continuous electrospinning of a single material fiber utilizing polymer solutions of a variety of types.
- Adapted the process to spin continuous fibers that are highly aligned utilizing a rotating electrode system.
- Developed a coaxial needle system to electrospin/electrospray core-shell fiber and particle of hybrid materials.
- Developed a novel pulsed direct current (DC) electro spray apparatus to allow better control over the particle size distribution and particle shell thickness.

Accomplishments

Area I: Heat and Water Management

- 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.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

Task	Target	Progress
1 - Development of Lightweight, Thermally-Conductive Bipolar Plates for Improved Thermal Management in Fuel Cells	Fuel Cell Bipolar Plates: - Electrical Conductivity >100 S/cm - Thermal Conductivity >20 W/m.K Develop testing and characterization protocols and techniques	100% Complete
2 – Exploration of Pseudomorphic Nanoscale Overlayer Bimetallic Catalysts for Fuel Cells	Ability to construct pseudomorphic overlayer catalysts on carbon supports, that are designed to mimic conventional PEM anode catalysts	100% Complete
3 – Development of Hybrid Inorganic/Organic Polymer Nanocomposites	Develop enabling technologies for rapid production techniques	100% Complete
4 – Development of Oriented Polymeric Materials for Membrane Applications	Demonstrate the production of nanostructured polymeric membranes utilizing electrodynamic synthesis methods	100% Complete
5 – Preparation of Graphitic Carbon Foam Current Collectors	Ability to tailor the properties of carbon foam supports to meet PEM fuel cell electrode requirements	100% Complete
6 – Development of Lightweight Carbon Electrodes Using Graphitic Carbon Foams for Battery and Fuel Cell Applications	Design a complete battery cell in symmetric and asymmetric designs	100% Complete
7 – Movement of Water in Fuel Cell Electrodes	Improved GDL performance, durability, and resistance to flooding	100% Complete

GDL = gas diffusion layer; PEM = proton exchange membrane



Introduction

In 2003, a National Academy of Sciences (NAS) report identified that several of the major stumbling blocks to the advent of practical fuel cells for application to transportation were associated with the lack of appropriate materials for the fuel cell construction. Specifically, they rely too heavily on precious metals, including platinum, to be affordable. The polymer electrolyte membrane, a key part of a fuel cell, needed to function better at high temperatures and better dissipate the main byproduct: water. Finally, virtually everything in the fuel cell needed to be lighter. The core projects for this DOE-sponsored Center at Michigan Tech have focused on several of the materials problems identified by the NAS. These include: new electrode materials, enhanced PEM materials, lighter and more effective

bipolar plates, and improvement of the carbon used as a current carrier. Our research into these areas has been approached via seven different tasks.

Approach

This project will involve fundamental and applied research in the development and testing of lightweight and nanostructured materials to be used in fuel cell applications and for chemical synthesis. The advent of new classes of materials engineered at the nanometer level can produce materials that are lightweight and have unique physical and chemical properties. The grant will be used to obtain and improve the equipment infrastructure to support this research, and will also serve to fund seven research projects. These include:

1. Development of lightweight, thermally-conductive bipolar plates for improved thermal management in fuel cells;
2. Exploration of pseudomorphic nanoscale overlayer bimetallic catalysts for fuel cells;
3. Development of hybrid inorganic/organic polymer nanocomposites with improved ionic and electronic properties;
4. Development of oriented polymeric materials for membrane applications;
5. Preparation of a graphitic carbon foam current collectors;
6. The development of lightweight carbon electrodes using graphitic carbon foams for battery and fuel cell applications; and
7. Movement of water in fuel cell electrodes.

Results

Task 1 - Development of Lightweight, Thermally-Conductive Bipolar Plates for Improved Thermal Management in Fuel Cells (King, Keith)

Fundamental and applied research needs to be done to improve the potential for fuel cells to be used in stationary and transportation applications. The goal of this project is to develop lightweight composite materials to be used for bipolar plates within a fuel cell. Bipolar plates require high thermal and electrical conductivity. Dr. King's research group extruded and molded into test specimens polypropylene (Dow H7012-35RN, a semi-crystalline thermoplastic homopolymer) based composites containing different carbon fillers (Akzo Nobel's Ketjenblack EC-600 JD carbon black, Asbury Carbon's Thermocarb TC-300 synthetic graphite particles, and Hyperion Catalysis International's FIBRIL carbon nanotubes). Composites containing varying amounts of a single filler (maximum of 15 wt% carbon black, 15 wt% carbon nanotubes, and 80 wt% synthetic

graphite particles) along with combinations of different fillers were fabricated and tested. Results indicate that the compression molded composite containing 2.5 wt% carbon black, 65 wt% synthetic graphite, and 6 wt% carbon nanotubes in polypropylene have an electrical conductivity of 91 S/cm and a thermal conductivity values of 6.6 W/m² K (through-plane) and 24 W/m² K (in-plane). These values are near the DOE conductivity targets of 100 S/cm and >20 W/m² K. Figure 1 shows a photomicrograph of this material.

Task 2 - Exploration of Pseudomorphic Nanoscale Overlayer Bimetallic Catalysts for Fuel Cells (Holles)

The reload synthesis technique has been used to prepare a series of bimetallic overlayer catalysts. Supported Re@Pd overlayers were found to have hydrogen heats of adsorption lower than that of pure components. Adsorption isotherms also support altered hydrogen adsorption on Pd in Re@Pd catalysts. Ethylene hydrogenation reactivity results support decreased binding of hydrogen. These reactivity results 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. Ethylene hydrogenation activity can be correlated with computationally predicted shifts in the center of the d-band through heat of adsorption (Figure 2). These results are a strong indication that we can make catalysts that demonstrate the properties of pseudomorphic overlayer bimetallics.

Task 3 - Development of Hybrid Inorganic/Organic Polymer Nanocomposites (Mullins)

We studied the effects of pulse width, pulse amplitude, and pulse frequency on the particle's shape, size, and size distribution systematically. We varied the pulse amplitude from 5 to 15 kV, pulse width from 15% to 95% and pulse frequency from 10 ms to 100 s; other parameters were kept constant. Particles were

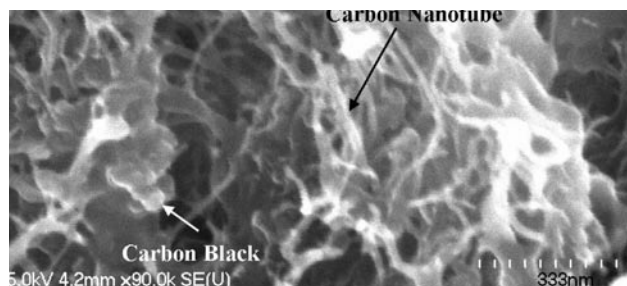


FIGURE 1. Most Conductive Material: 2.5 wt% Akzo Nobel Ketjenblack EC-600 JD carbon black/65 wt% Asbury Carbons Thermocarb TC-300 synthetic graphite particles/6 wt% Hyperion carbon nanotubes/26.5 wt% Dow homopolymer polypropylene H7012-35RN.

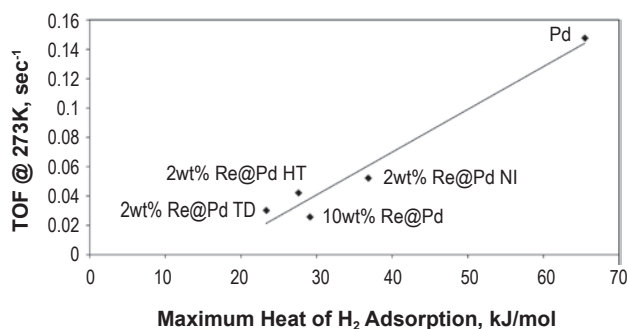


FIGURE 2. Relationship between measured H₂ ΔH_{ads} and turnover frequency (TOF) for ethylene hydrogenation. Heat of adsorption can be also be predicted based on computationally predicted shifts in the d-band. Thus activity can be correlated with d-band predictions.

successfully fabricated using the pulsed-DC voltage. Results from this study were presented at the 2009 Materials Research Society Fall Meeting and were published in the 2009 Materials Research Society Fall Meeting Proceedings Volume 1239 Symposium VV. Part of the results was included in the January Quarter Report. We have continued our experiments with the coaxial electrospinning needle to produce hybrid composite particles. We have been working with polymeric shell materials including poly-L-lactic acid (PLLA) with cores containing aqueous metallic solutions, aqueous polymeric solutions, and normal hydrocarbons with metal acetyl acetonates. Our preliminary results from fluorescent microscopy and field-emission scanning electron microscopy showed that the fluorescein dye was successfully encapsulated in the PLLA. We are continuing to look for the best core-shell pair which would allow us to obtain the complete engulfing. Also, we believe that with the best choice of the processing parameters, we should be able to produce core-shell particles with controllable size in just a single-step process.

Task 4 - Development of Oriented Polymeric Materials for Membrane Applications (Gilbert)

Highly aligned PLLA electrospun fibers were fabricated using an electrospinning technique. Before electrospinning, a layer of PLLA film was cast onto coverslips to secure fiber position and alignment following electrospinning. The working conditions for electrospinning were the following: working voltage: 14 kV; working distance: 11 cm; flow rate: 2 ml/hr; using a 22 gauge sharp-tip needle. The fiber samples were coated with 5 nm gold, and the images were taken using a field emission scanning electron microscope.

Task 5 - Preparation of Graphitic Carbon Foam Current Collectors (MTU: T. Rogers; Clemson University: O. Mefford) / Task 6 - Development of Lightweight Carbon Electrodes Using Graphitic Carbon Foams for Battery and Fuel Cell Applications (MTU: T. Rogers, B. Cornilsen, M. Chye, W. Yeo)

Under Task 5, investigators at Clemson University have synthesized PAN-based carbon foams that can function as mechanical supports for electrochemically-active material (e.g., nickel oxyhydroxide active mass) or catalytically-active metals. Because carbon foams are graphitic, they are excellent lightweight, porous current collectors for battery or fuel cell electrodes. Electrochemical deposition of nickel oxyhydroxide active mass has been used in Task 6 to demonstrate the use of carbon foams as scaffold materials in rechargeable positive (working) battery electrodes.

To test commercial foams (purchased from Poco Graphite and Koppers) and novel foams produced at Clemson University, we have examined the electrochemical performance of nickel electrodes by performing charge/discharge cycles in flooded and sealed cells. Significant progress has been made in optimizing active mass deposition in the working electrode of a nickel hydroxide battery cell as measured by efficiency of pore filling, accessibility to ion transport, and electrical contact with the carbon support. We have developed a flooded-cell protocol for depositing, forming, and cycling nickel-carbon foam working electrodes under positive-limiting conditions.

Using these electrodes, long-term cycling tests are being performed in asymmetric sealed cells (Figure 3),

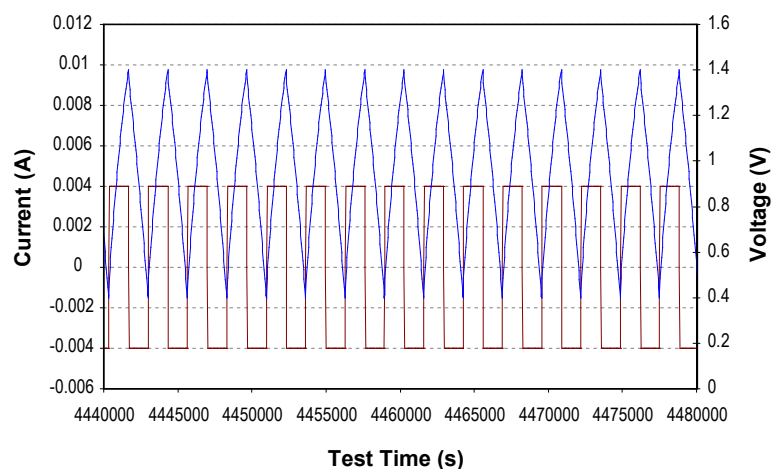


FIGURE 3. Charge-discharge curves from an asymmetric cell (SW #63 as positive and carbon-filled Teflon[®] negative electrode) at 1.44 mA/cm² current density. The positive electrode was deposited in 1.8 M Ni(NO₃)₂ and 0.26 M Co(NO₃)₂ solution for 48 minutes. The current profile is in pink and the voltage profile is in blue. The cell shown achieved approximate 1,600 cycles.

sometimes called an ultracapacitor configuration. In these cells, the nickel electrode serves as the positive, and up to three layers of a microporous carbon as the negative. The positive electrode stores and releases charge via a Faradaic (redox) mechanism, while the negative electrode uses an electrolytic mechanism, i.e., charge is stored in the electric double layer. Our negative electrode material is fabricated at Michigan Tech using Ketchen Black (manufactured by Akzo Nobel Corporation) and a Teflon[®] binder, and it has a measured capacitance of about 60 F/g. In sealed asymmetric cells that are negative electrode limited, we have achieved long-term performance in excess of 13,000 cycles before losing 20% of the initial cell's discharge capacity.

In a related electrocatalytic application, we have conducted successful hydrogen dissociation experiments on an alumina support as a prelude to future deposition of a bimetallic overlayer fuel cell anode catalyst on a carbon foam support. Such a catalyst may be able to reduce or replace the current use of platinum for the catalytically-active sites.

Task 7 - Movement of Water in Fuel Cell Electrodes (Allen)

Technical accomplishments for the last year include a 2nd-level thermostat fabricated for environmental chamber; improved temperature control (including improved humidity control, potential hydrogen atmosphere). We addressed dependence of contact angles on drop size and improved algorithm for contact angle determination. A new drop deposition method was developed which injects water through GDL. The experimental phase of the work is complete and the funds expended. During the next month we will continue to compile the final reports and complete the data analysis.

Conclusions and Future Directions

The Center for Nanostructured and Lightweight Materials is funded until the end of June 2010. Data collection and analysis is complete; the final technical report will be finished by September 28, 2010.

FY 2010 Publications/Presentations

1. J.A. King, M.E. Mullins, T.N. Rogers, J. Allen, R. Gilbert, J.H. Holles, B. Cornilsen, and J.M. Keith, "Center for Fundamental and Applied Research in Nanostructured and Lightweight Materials", DOE Hydrogen Program Annual Annual Merit Review and Peer Evaluation Meeting, June 8, 2010, Arlington, VA.
2. M.P. Latusek, R.M. Heimerl, B.P. Spigarelli, and J.H. Holles, "Correlation of H₂ Heat Adsorption and Ethylene Hydrogenation Activity for Supported Re@Pd Overlay Catalysts", *Journal of Catalysis*, in press.
3. M.P. Latusek, R.M. Heimerl, B.P. Spigarelli, and J.H. Holles, "Synthesis and Characterization of Supported Bimetallic Overlayer Catalysts", *Applied Catalysis A: General*, in press.
4. J.A. King, M.D. Via, J.M. Keith, and F.A. Morrison, "Effects of Carbon Fillers on Rheology of Polypropylene Based Resins," *Journal of Composite Materials*, Vol. 43, No. 25, pp. 3073-3089, December 2009.
5. J.A. King, B.A. Johnson, M.D. Via, and C.J. Ciarkowski, "Effects of Carbon Fillers in Thermally Conductive Polypropylene Based Resins", *Polymer Composites*, Vol. 31, No. 3, pp. 497-506, March 2010.
6. D. Lopez Gaxiola, J.M. Keith, J.A. King, and B.A. Johnson, "Nielsen Thermal Conductivity Model for Single Filler Carbon/Polypropylene Composites," *Journal of Applied Polymer Science*, Vol. 114, No. 5, pp. 3261-3267, December 2009.
7. J.A. King, D. Lopez Gaxiola, B.A. Johnson, and J.M. Keith, "Thermal Conductivity of Carbon Filled Polypropylene Based Resins", *Journal of Composite Materials*, Vol. 44, No. 7, pp. 839-855, April 2010.
8. D. Lopez Gaxiola, M. Jubinski, J.M. Keith, J.A. King, and I. Miskioglu, "Effects of Carbon Fillers on Tensile and Flexural Properties of Polypropylene Based Resins", *Journal of Applied Polymer Science*, in press.
9. T.N.G. Adams, T.R. Olson, J.A. King, and J.M. Keith, "In-Plane Thermal Conductivity Modeling of Carbon Filled Liquid Crystal Polymer Based Resins", *Polymer Composites*, under review.