V.K.3 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; Fax: (906) 487-3213
E-mail: memullin@mtu.edu

DOE Technology Development Manager: Dimitrios Papageorgopoulos
Phone: (202) 586-5463; Fax: (202) 586-2373
E-mail: Dimitrios.Papageorgopoulos@ee.doe.gov

DOE Project Officer: Gregory Kleen
Phone: (303) 275-4875; Fax: (303) 275-4788
E-mail: Greg.Kleen@go.doe.gov

Contract Number: DE-FG36-08GO88104

Subcontractor:
Clemson University, Clemson, SC

Project Start Date: July 1, 2008
Project End Date: January 31, 2010

*Congressionally directed project

Objectives

Area 1: Heat and Water Management

- Develop and test lightweight and nanostructured materials for fuel cell bipolar plates.
- Improve gas diffusion layer (GDL) performance and durability and develop testing and characterization protocols for GDLs relative to water management.

Area 2: Development of New Electrode Materials

- Develop graphitic carbon foams that will serve as current collectors and catalytic supports.
- Develop durable carbon-supported catalysts that have reduced weight and cost compared to proton exchange membrane (PEM) anode catalysts.

Area 3: Enabling Technologies for Membrane Synthesis

- Develop hybrid polymer membrane materials which are engineered at the micro and nanoscale.
- Demonstrate novel electrodynamic deposition methods (electrospinning and electrospraying) for a set of paradigm polymeric compounds in membrane form.
- Identify candidate materials for membrane synthesis using these methods.

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 (Planned completion date: 1/31/2010)

- **Task 1:** Fabrication, testing, and modeling of carbon filled polypropylene composites for fuel cell bipolar plates (70% complete).
- **Task 2:** Synthesis and characterization of Pt/Ni overlayer catalysts (45% complete).
- **Task 3:** Test hybrid materials fabricated (30% complete); development of electrospraying apparatus (80% complete).
- **Task 4:** Electrospinning of hybrid electrospinning composites (40% complete).
- **Task 5:** Microscopy and spectroscopic analyses of a commercial Poco Graphite foam sample and an MTU nickel-carbon electrode (40% complete); making a graphitized carbon foam from a peroxyacetyl nitrate precursor (50% complete); active mass deposition, forming, and cycling (70% complete).
- **Task 6:** Designing a swagelok battery cell (90% complete); ethylenediamine tetraacetic acid titrations of deposited active mass (40% complete); anode preparation (50% complete).
- **Task 7:** Contact angle measurement apparatus and technique (90% complete); contact angle measurements on GDL samples (25% complete; compression fixture (95% complete); compression-force measurements on GDL samples (25% complete).

Accomplishments

Area I: Heat and Water Management

- Developed a material containing 2.5 wt% AkzoNobel KetjenblackEC-600 JD carbon black/65 wt% Asbury Carbons ThermocarbTC-300 synthetic graphite particles/6 wt% Hyperion carbon nanotubes/26.5 wt% Dow homopolymerpolypropylene 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.
  - Studied movement of water in fuel cell electrodes:
  - Environmental chamber fabricated.
  - Second level thermostat design completed and fabrication started.
  - Analysis code completed.
  - Contact angle measurement error characterized.

Area II: Development of New Electrode Materials

- Synthesized graphitic carbon foams at Clemson University.
- Studied the structure and morphology of carbon foam electrode supports.
- Performed battery tests with synthesized electrodes.
- Synthesized pseudomorphic nanoscale overlayer bimetallic catalysis as an alternative to platinum-based fuel cell anode catalyst.

Area III: Enabling Technologies for Membrane Synthesis

- Developed novel polymer electrospraying/ electrospinning apparatus.
- Created three distinct variable diameter scaffolds by manipulating electrospinning parameters.
- Developed fluorescent, electrospun fibers by doping fluorescent dye into polymer solution without altering fiber alignment
- Developed dual nozzle electrospray apparatus for polymer hybrid materials.

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 PEM, 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:

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

Composites containing varying amounts of a single filler along with combinations of different fillers were fabricated and tested. Results to date 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/m·K (through-plane) and 24 W/m·K (in-plane). These values are near the DOE conductivity targets of 100 S/cm and >20 W/m·K.

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

Ethylene and carbon monoxide adsorption studies to determine heats of adsorption for the Pd/Re samples and the Pt/Ni samples are ongoing. In addition, X-ray absorption spectroscopy studies were performed at the National Synchrotron Light Source at Brookhaven National Laboratory on the Pd/Re samples. Extended X-ray absorption fine structure (EXAFS) analysis will be performed on this data to determine interatomic distances and coordination numbers for the Pd. This will provide important evidence of the local geometric environment around the Pd. An extensive amount of effort was devoted to interpreting and analyzing the data obtained to date for all Pd/Re and Pt/Ni samples. The key result obtained from this analysis is shown in Figure 1.

This figure demonstrates the relationship between the ethylene hydrogenation turnover frequency and the measure hydrogen heat of adsorption. It is also know from first principles computational studies that the heat of hydrogen adsorption can be correlated with the center of d-band. Thus we can now correlate for the first time, the activity of a high surface area supported metal catalyst with a computationally predicted parameter. Based on Figure 1, ethylene hydrogenation activity could be further increased by synthesizing a Pd monolayer on gold (Pd_{ML}/Au) catalyst. Unfortunately, other studies indicate that in a PdAu system, Au will preferentially segregate on the surface.

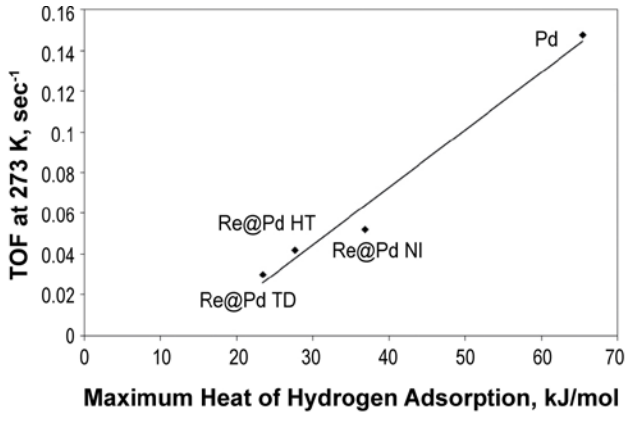

FIGURE 1. This figure demonstrates the relationship between the ethylene hydrogenation turnover frequency and the measure hydrogen heat of adsorption.

Activities during the upcoming period will include continuing ethylene and carbon monoxide adsorption studies. In addition, samples will be synthesized with higher weight loadings to help make EXAFS characterization easier. EXAFS analysis of the current samples is ongoing.

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

We made the particles using the newly purchased poly-L-lactic acid (PLLA, Grade 6202D) from NatureWorks, LLC. We purchased 6202D instead of 6200D, which was used in the first phase of the project, because the 6200D is no longer available. According to the manufacturer, 6202D is the best substitute for 6200D. In the lab, we used 1,2-dichloroethane as the organic solvent. The droplets formed were collected in a 200 mL distilled water-poly (vinyl) alcohol bath with magnetic stirring. The results for scanning electron microscopy (SEM) studied showed that the particles' size and distribution were huge and pores were formed on the particle's surface. The pores were mostly observed on the larger particles. The latter observation has never been found with the direct current voltage, which was used in the first phase of the project. This is a possibility due to the pulsed voltage applied. To solve this problem, we need to find a way to reduce the particles size. Currently, we are studying the effect of the pulse amplitude, polymer concentration, flow rate, and working distance on the pores. So far, it seems that reducing the flow rates might be the best option. At this point, effort will be taken to solve the problems before we study the effects of pulse width, pulse amplitude, and pulse frequency on the particle's shape, size, and size distribution systematically.

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

One limitation of electrospinning aligned polymer fibers is the ability to control fiber diameter. In the current literature, most electrospun fibers, whether randomly oriented or uniaxially aligned, have great diameter variability. Our laboratory is developing methods of controlling fiber diameter toward making better anisotropic fiber/film materials.

With fixed primary working conditions, the polymer solvent was altered to obtain aligned PLLA fibers with three different fiber diameters. Thick polymer fibers were fabricated by electrospinning an 8 wt% polymer solution formed by dissolving PLLA in a mixture solvent (50/50 wt% of chloroform and dichloromethane). Electrospinning this polymer solution generated fibers with an average diameter of about 1.6 μm (Figure 2A). When using 1,1,1,3,3,3 hexafluoro-2-propanol (HFP) as the solvent, average fiber diameter was reduced to 800 nm (Figure 2B). By doping polymer solution with

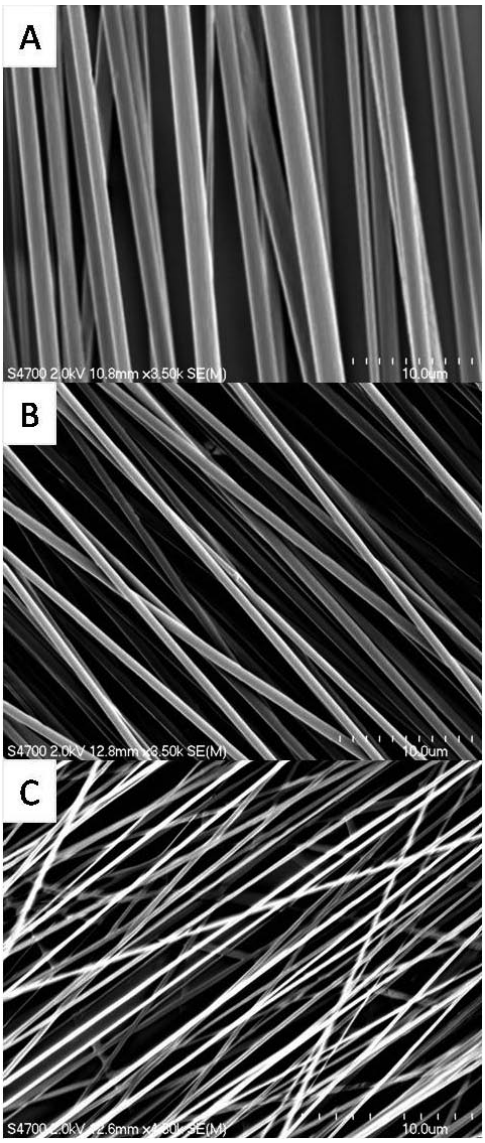

FIGURE 2. Generation of PLLA fibers with varying diameter. (A) thick fibers; (B) intermediate fibers; (C) thin fibers. Images obtained at 3,500x. Scale bar = 10 μm.

negatively charged species (BSA) at a concentration of 1 wt% with respect to mass of PLLA, the average fiber diameter was reduced to 300 nm (Figure 2C).

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 Area II, we have synthesized peroxyacetyl nitrate (PAN)-based carbon foams that can function as a mechanical support for electrochemically-active material (e.g., nickel hydroxide active mass) or catalytically-active metals. Because the carbon foam is

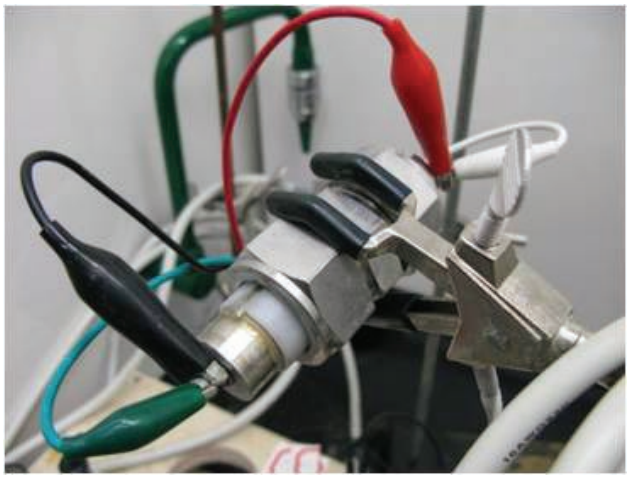

FIGURE 3. Swagelok Cell Connected to a Potentiostat for Cycling

graphitic, it is an excellent lightweight, porous current collector for a battery or fuel cell electrode. Our goals for carbon foams are to: (1) increase the macropore/mesopore space to hold more active electrode mass, and (2) increase the accessible micropore surface area so that a supercapacitor anode can be created. To test commercial foams and novel foams produced at Clemson University, we are examining the electrochemical performance of electrodes loaded with nickel hydroxide active mass by performing charge/discharge cycles in flooded and sealed cells (Figure 3). 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. In a related application, we have conducted successful preliminary electrocatalysis experiments (hydrogen dissociation) 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)

Compression-Force Imaging and Measurements on GDL Samples

Use of the compression sample holder[1] during SEM imaging of fuel cell GDLs has shown that damage due to compression, as could be found in fuel cell stacks, is easily visible at very low magnifications. Figure 4a is an SEM image of a Mitshubishi MRC 105 with 9 wt% polytetrafluoroethylene after compression. Damage along the boundary of the compression ring and channel edges

[1] The unique compression sample holder was described in the last quarterly report.

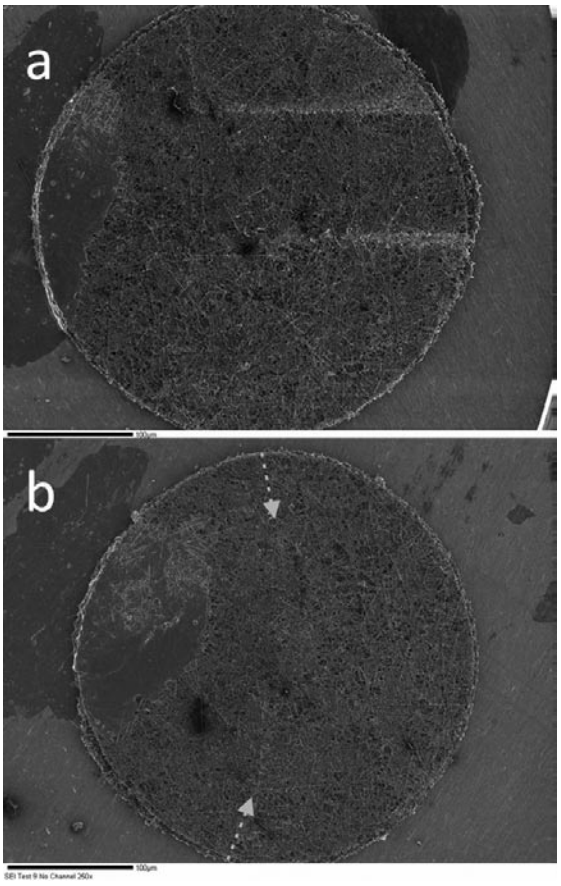

FIGURE 4. (a) GDL after compression with channel. Channel imprint is visible indicating loss of conductivity along channel edges. Loss of conductivity due to internal damage which decreases the electrical conductance of the GDL. (b) GDL after compression without channel. Imprint of compression ring is visible indicating loss of conductivity along channel edges. Loss of conductivity due to internal damage which decreases the electrical conductance of the GDL.

can be seen. The channel edges are perpendicular to the edge of the compression ring. The material on the left edge is carbon paint which is used to secure the sample and ensure good conductivity for imaging. Damaged regions can easily be seen by the bright regions which indicate charge accumulation due to reduced electrical conductivity. Conductivity is decreased because of fiber separation or breakage. Figure 4b shows a second sample (Mitshubishi MRC 105) compressed without the channel in the compression ring. The internal damage to the GDL resulting from compression is not easily seen from optical inspection, but the reduced electrical conductivity clearly is visible from SEM imaging.

The sample holder developed for SEM imaging of GDL samples under compression can also be used to measure the stress-strain characteristics of GDLs. Two types of tests were performed: single thickness GDL samples and 20-sample GDL stacks. The single GDL sample compression tests (1, 2, 7, and 8) show similar behavior. The 20-sample GDL stacks (tests 3-6) illustrate a greater stiffness than the single-thickness GDL sample.[2] The data is preliminary and further testing will be conducted.

Contact Angle Measurements on GDLs

The existing setup for contact angle measurements has been modified so as to facilitate the measurements at elevated temperatures while maintaining a high level of humidity. A second-level thermostat, has been assembled. This thermostat will be placed on the heated copper plate of the existing first-level thermostat. During the next quarter, the dependence of contact angle on temperature for various GDL samples will be studied.

Conclusions and Future Directions

The Center for Nanostructured and Lightweight Materials is funded until the end of December 2009. Additional key laboratory experiments are being conducted during the remainder of the year for all of the tasks above. Data collection and analysis should be completed by December 31, 2009.

- **Task 1:** Determine tensile and flexural properties of the carbon filled thermoplastic materials for fuel cell bipolar plates.
- **Task 2:** Activities during the upcoming period will include continuing hydrogen and carbon monoxide adsorption studies on the high weight loading Re sample. Once deposited, the overlayer materials will also be characterized using chemisorption.
- **Task 3:** The dual capillary electrospray apparatus will be used to produce core shell particles consisting of an interior liquid media and a polymer shell.
- **Task 4:** The electrospinning studies to control the diameter of polymer fibers will be concluded during the upcoming period.
- **Task 5:** During the summer, foam samples will be pyrolized and graphitized and sent to Dr. Rogers' laboratory at Michigan Tech for comparison to commercial foam materials in electrochemical service.
- **Task 6:** Future work will include varying the cut-off voltage, the nickel concentration in the deposition solution, and the pre-oxidation conditions and noting how these factors affect cycle life.
- **Task 7:** During the next quarter, additional stress-strain data will be collected for the GDL samples. A key issue to address is the role of surface friction

[2] The exception is test run 3 which is the initial compression of the 20-sample GDL stack. This test run exhibits a unique behavior associated with forcing the GDL samples into contact with one another.

between the GDL sample and the compression ring on the stress measurement. Contact angle measurements of water on GDL samples will be made for a range of temperatures up to 80°C.

FY 2009 Publications/Presentations

1. 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, under review.

2. 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, in press.

3. 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, in press.

4. J.A. King, B.A. Johnson, M.D. Via, and C.J. Ciarkowski, "Electrical Conductivity of Carbon Filled Polypropylene Based Resins", Journal of Applied Polymer Science, Vol. 112, No. 1, pp. 425-433, April 2009.

5. J.M. Keith, J.A. King, and B.A. Johnson," Electrical Conductivity Modeling of Carbon Filled Polypropylene Based Resins for Fuel Cell Bipolar Plates", Journal of New Materials for Electrochemical Systems, in press.

6. 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, in press.

7. B.A. Johnson, "Thermally and Electrically Conductive Polypropylene Based Resins for Fuel Cell Bipolar Plates", M.S. Thesis, Michigan Technological University, May 2009.

8. R.A. Hauser, J.A. King, J.M. Keith, I.M. Wescoat, and R.M. Pagel, "Factorial Design of Thermally Conductive Composite Materials for Fuel Cell Bipolar Plate Applications", American Institute of Chemical Engineers Annual Meeting, November 16-21, 2008, Philadelphia, PA.

9. W. Li, D. Meng, J.A. King, and J.M. Keith, "Fuel Cell Materials Research at Michigan Technological University, ABET&CONNECT 2008, October 10, 2008, Detroit, MI.

10. 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, May 18, 2009, Arlington, VA.

11. M.P. Latusek, R.M. Heimerl, B.P. Spigarelli, and J.H. Holles, "Correlation of H_2 Heat Adsoption and Ethylene Hydrogenation Activity for Supported Re@Pd Overlay Catalysts", Journal of Catalysis, in press.

12. 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.

13. H.B. Wang, M.E. Mullins, J.M. Cregg, A. Hurado, M.T. Trombley, and R.J. Gilbert, "Creation of Highly Aligned Electrospun Poly-L-Lactic Acid Fibers for Nerve Regeneration Applications", Journal of Neural Engineering, in press.