VII.B.5 Development of Polybenzimidazole-Based, High-Temperature Membrane and Electrode Assemblies for Stationary Applications

William Ernst (Primary Contact), Rhonda Staudt, Katrina Fritz Intwala
Plug Power Inc.
968 Albany Shaker Road
Latham, NY 12110
Phone:(518) 782-7700 x. 1126; Fax: (518) 782-7884; E-mail: william_ernst@plugpower.com

DOE Technology Development Manager: Kathi Epping
Phone: (202) 586-7425; Fax: (202) 586-9811; E-mail: Kathi.Epping@ee.doe.gov

DOE Project Officer: Reg Tyler
Phone: (303) 275-4929; Fax: (303) 275-4753; E-mail: Reginald.Tyler@go.doe.gov

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Subcontractors:
Rensselaer Polytechnic Institute, Troy, New York
Albany NanoTech, University at Albany, SUNY, Albany, New York
PEMEAS GmbH, Frankfurt, Germany
University of South Carolina, Columbia, South Carolina
Entegris, Chaska, Minnesota

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Projected End Date: July 31, 2006

Objectives

- Select the appropriate polymer chemistry for polybenzimidazole (PBI) membrane materials optimized to fuel cell requirements.
- Demonstrate the long-term performance of the PBI membrane, including mechanical, electrochemical, and operating properties, in cells and stacks.
- Provide a cost analysis of a low-cost membrane manufacturing process with projected costs consistent with meeting the specified high-volume targets.

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. Costs

Technical Targets

Characteristics	Units	Plug Power Status	2005 Target	2010 Target
Membrane conductivity @ operating temperature	Ohm-cm^2	0.1 @ 160 ºC	0.1	0.1
Oxygen Crossover	mA/cm^2	Need to confirm with final membrane	5	2
Hydrogen Crossover	mA/cm^2		5	2
Cost	$/kW	PEMEAS GmbH to provide cost estimate in 2006	50	5
Operating Temperature	ºC	Routinely run at 180°C	160	170
Durability	Hours	14,000 hours demonstrated by PEMEAS in 50 cm^2 testing	>15,000	>40,000

Approach

- Membrane – Screen candidate materials and membrane fabrication processes.
  - Screen polymer structures and conduct preliminary evaluation.
  - Perform detailed characterization of selected polymers.
  - Define low-cost membrane fabrication techniques for top candidates.
  - Demonstrate scaled-up fabrication process.
- Membrane electrode assembly (MEA) – Characterize MEAs fabricated from candidate polymer materials.
  - Screen candidate polymers in 10-50 cm^2 MEAs.
  - Perform detailed electrochemical evaluation of selected membranes in 50 cm^2 MEAs.
  - Evaluate optimum membrane in full-size MEAs in short stack.
  - Characterize long-term performance of MEA fabricated with optimum membrane material.
- Stack – Develop and demonstrate supporting hardware and cost model for PBI membranes.
  - Evaluate acid-absorbing materials and design and demonstrate an acid management scheme with at least two years of capacity.
  - Design and demonstrate a PBI-specific bipolar plate flow field.
  - Develop a model of phosphoric acid electrodes and develop a nanostructured electrode that maximizes catalyst utilization.
  - Build a cost projection model for PBI-based membranes and project cost based on anticipated market demand.

Accomplishments

- Rensselaer Polytechnic Institute (RPI) prepared four PBI membranes with reinforcing fillers and scaled up sufficient quantities for fuel cell and mechanical property testing. Techniques were developed to uniformly distribute fillers.
- Screening tests of the filled membranes were conducted by RPI, showing similar conductivities and current-voltage (I-V) curves when compared to unfilled membranes.
- Test fixtures were constructed to test MEA mechanical properties under realistic fuel cell operating conditions.

- An acid absorbent material was studied for use in preventing acid in the cathode and anode exhaust from contaminating the rest of the fuel cell system.
- A flow field model was created of a full-size plate, and several flow paths were studied to determine the optimum flow pattern.
- Initiated activities with Entegris to study flow field plate sealing technologies.
- Albany Nanotech developed a method for measuring catalyst layer porosity and pore connectivity using a focused ion beam (FIB) and imaging.

Future Directions

- Complete filled membrane characterization.
- Select primary membrane for scale-up at RPI.
- Build small-scale prototypes and demonstrate stack sealing concept with Entegris.
- Investigate failure modes associated with starts/stops and load cycling.
- Test full-size flow field and quantify efficiency improvement.
- Albany Nanotech will build nano-scale electrodes for Plug Power test and quantify Pt loading reduction and performance improvement.
- Build and test a full-size stack module with improved membrane, flow field and sealing concept.
- PEMEAS will develop a cost projection model for PBI-based membranes and project cost based on anticipated market demand.
- Demonstrate 1,000 hours life with low degradation rate and project 40,000 hours life.

Introduction

The goal of this project is to optimize a high-temperature polybenzimidizole (PBI) membrane to meet the performance, durability, and cost targets required for stationary fuel cell applications. Originally, the project objective included automotive applications, but with agreement from the DOE, the automotive effort has been discontinued. Working with Rensselear Polytechnic Institute's (RPI's) Polymer Science Laboratory, the project will focus on optimizing the PBI membrane material for operation at temperatures greater than 160°C with a lifetime of 40,000 hours. Supporting hardware such as flow field plates and a novel sealing concept are being developed to yield the low-cost stack assembly and corresponding manufacturing process.

The work since the last reporting period has focused on increasing the mechanical stability of the high-temperature membrane. Additional work was conducted on acid loss, flow field design and cathode electrode development. New subcontractors—Entegris, University of South Carolina and RPI's Fuel Cell Center—have been engaged since the last reporting period to assist in several key development areas.

Approach

The project has activities that are being conducted concurrently in three main areas: the membrane, the membrane electrode assembly (MEA) and the stack. The membrane activities focus on the formulation and characterization of the polymers, with specific effort on increasing the mechanical stability of the membrane. The MEA activities focus on full characterization of the performance under fuel cell operating conditions. The stack activities include supporting hardware, including flow field design, reactant and coolant sealing and electrode development.

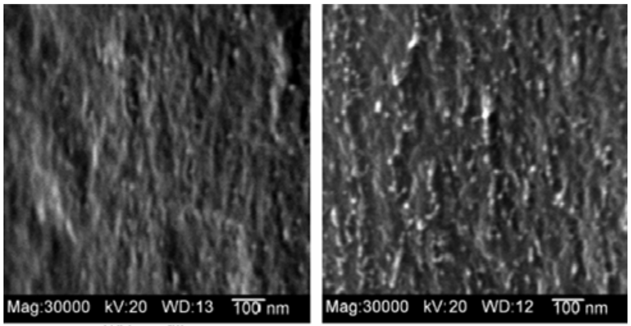
The individual activities are performed on a small scale, then put into actual fuel cell testing in 50 cm^2 size prior to scaling up to full-size. The concurrent activities are scheduled to converge in a full-size module demonstration, 16-20 full-size cells, in 2006.

Results

As previously reported [1], RPI has developed and evaluated five types of membrane compositions. The conductivity, mechanical strength, inherent viscosity and phosphoric acid and PBI content were measured. RPI created high-molecular-weight polymers, and the best membrane, type 2, was selected for further development. The mechanical properties of the membrane are such that it exhibits a high rate of creep under constant load. RPI has spent the last year enhancing the mechanical stability of the membrane with reinforcing filler. Figure 1 shows a type 2 composition with and without fillers. Several fillers are under evaluation with various loading levels. The initial screening of the membranes with filler shows that conductivity and MEA performance are not dramatically different, as shown in Figure 2. The testing of the mechanical stability of the filled membranes under real operating conditions is underway. Four mechanical test fixtures with temperature and humidity control have been constructed in order to perform the testing.

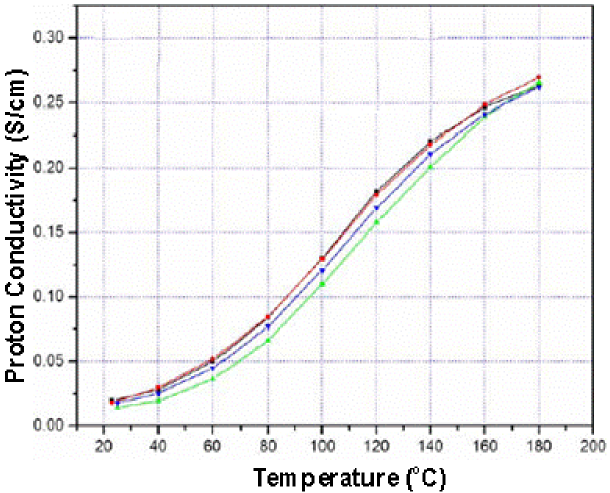
In this reporting period, further testing has been conducted to quantify the phosphoric acid loss rates of the type 2 MEA. The acid loss rates remain unchanged when the test cells are started and shut down using a specific protocol. Given the measured loss rates, a full-sized 5-kW stack is calculated to only lose 4% of the available acid per year when running continuously, making a 40,000-hour stack (5-year stack) possible, given no other failure modes. However, the acid leaving the stack in the reactant streams must be captured to prevent contamination of other system components downstream from the stack. The solution being studied is to pass the reactant streams through a pelletized bed. Figure 3 compares two pellet sizes and their ability to remove the phosphoric acid from the reactant steam. The next step is to properly size the pellets and the bed for use in a system. Additionally, the University of South Carolina has been asked to construct an acid movement model so that the effects of operating conditions can be better understood.

Flow field distribution studies were executed on full-sized plates. Models were created to study the effects of reactant flow in single-pass vs. multi-pass, co-flow vs. counter-flow, and high-power vs. low-power operation. The two configurations with the best uniformity are being built and tested to confirm the model results. Figure 4 shows a sample output

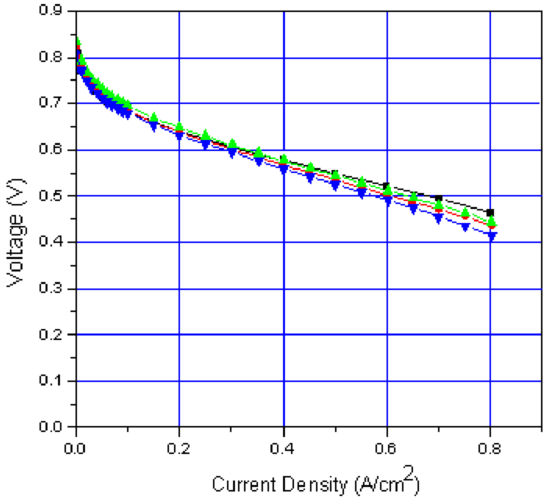


Without filler With filler

Figure 1. Type 2 Composition With and Without Fillers



Membrane Conductivity



MEA Performance

Figure 2. Conductivity and MEA Performance of Filled Membranes

of the model. The team is also working with the National Renewable Energy Lab (NREL) to optimize the configuration of the coolant flow path.

Progress has been made on developing techniques for evaluating cathode electrode structures with Albany Nanotech. Using a focused ion beam (FIB), a trench is formed in the catalyst layer, allowing the structure below the surface to be viewed, as shown in Figure 5 a and b. A black and white image, shown in Figure 5 c, is created and processed to reveal an apparent pore size as well as the connectedness of the pores. Several electrode samples using Pt on carbon catalysts were created using different processing methods. The process parameters yielded varying pore size and pore connectedness. The next step for Albany Nanotech is to develop Pt sputter deposition methods to

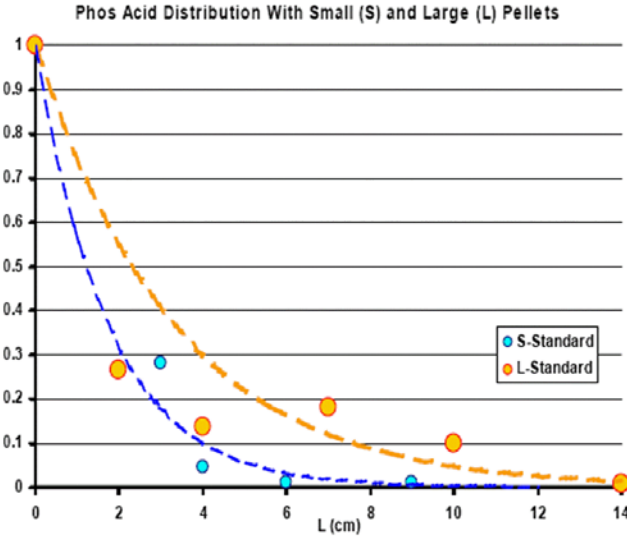


Figure 3. Phosphoric Acid Distribution with Large and Small Pellets

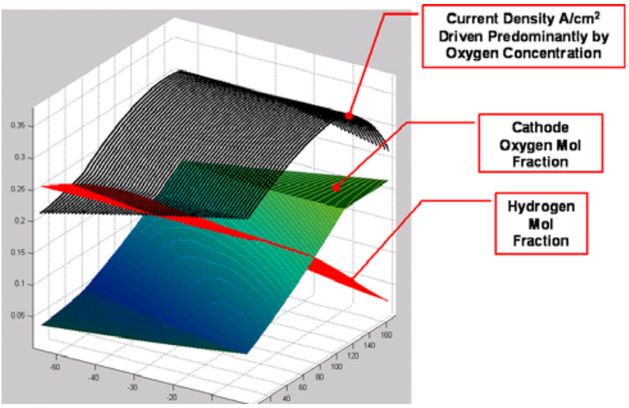


Figure 4. Flow Field Distribution Model

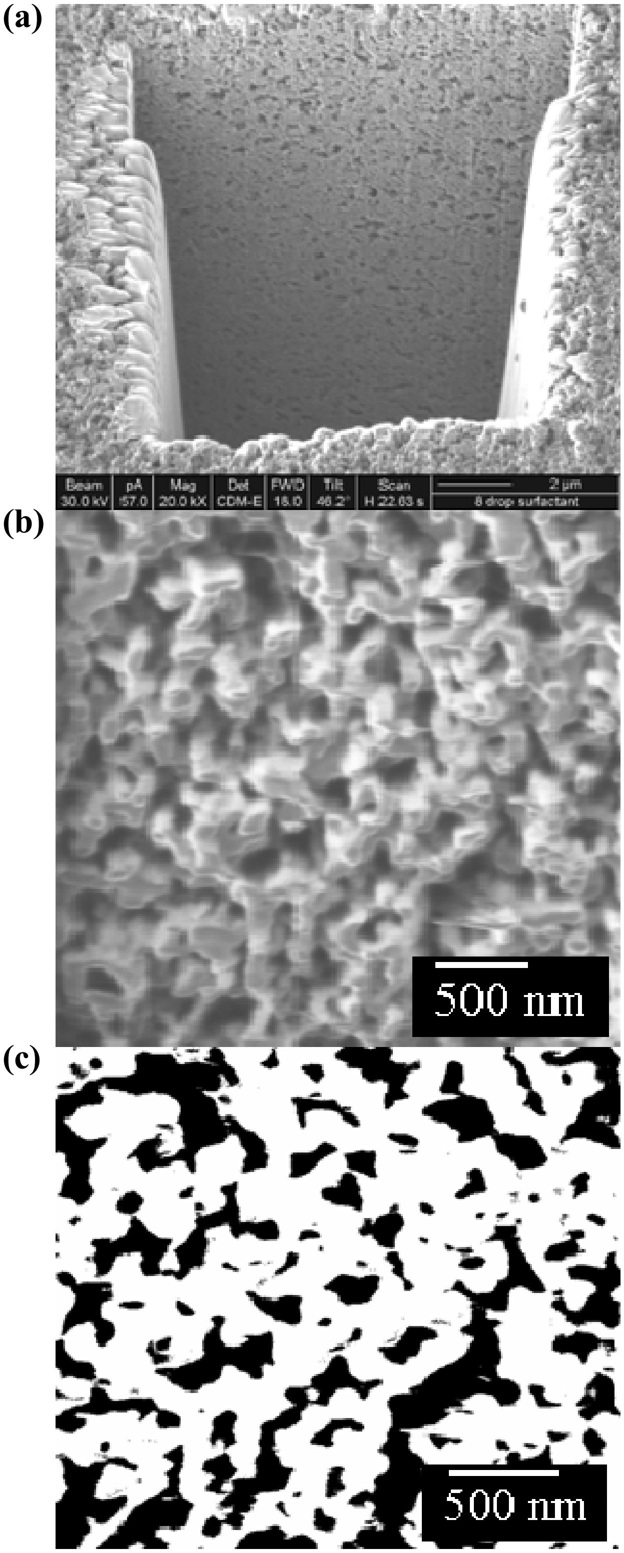


Figure 5. FIB Evaluation of Cathode Electrode Structures. (a) FIB Trench, (b) Original Image, (c) Black and white image model.

construct electrodes. Concurrently, an activity with the new Fuel Cell Center at RPI has been initiated to examine alterative cathode electrode structures.

Conclusions

- Fillers used to reinforce the PBI membrane do not adversely affect the conductivity or the performance at the level of loading.
- The phosphoric acid loss during operation is very small. A solution that passes the reactant stream from the stack to a pelletized bed has proven feasible.
- An optimized flow field that gives a more uniform flow can yield improved efficiency of the overall system.
- Developing a more active cathode electrode is required to meet performance goals.

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