IV.B.4 Development of Polybenzimidazole-based, High-Temperature Membrane and Electrode Assemblies for Stationary and Automotive Applications

Rhonda Staudt (Primary Contact), Brian Benicewicz, Jeffrey Boyer, William Ernst
Plug Power Inc.
968 Albany Shaker Road
Latham, NY 12110
Phone: (518) 782-7700, x1215; Fax: (518) 782-7961; E-mail: staudt_rhonda@plugpower.com

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

Subcontractors:
Rensselaer Polytechnic Institute, Troy, New York
Albany NanoTech, SUNY at Albany, Albany, New York
PEMEAS GmbH, Frankfurt, Germany

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:

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

- Focus 1: 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.
- Focus 2: Characterize membrane electrode assemblies (MEAs) fabricated from candidate polymer materials.
  - Screen candidate polymers in 10- to 50-cm^2 MEAs.
  - Perform detailed electrochemical evaluation of selected membranes in 50-cm^2 MEAs.
  - Evaluate optimum membrane in 440-cm^2 MEAs in short stack.
  - Characterize long-term performance of MEA fabricated with optimum membrane material.
- Focus 3: 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 2 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

- Identified the first five PBI compositions with unique chemical structure and fabricated membranes of each; high molecular weights were obtained.
- Characterized the first five PBI membranes; all of them exhibited higher phosphoric acid content than previously reported for PBI materials.
- Established the creep behavior for selected membranes.
- Demonstrated significantly improved MEA performance compared with previously reported data; the effect of pressure is approximately 50% of theoretical for phosphoric acid electrodes and approximately 2.5 times theoretical for Nafion®-based electrodes.
- Determined that steady-state phosphoric acid loss from PBI-membranes is less than theoretical and that acid loss during startup and shutdown cycles may be avoided by isolating the cell from the test station. Acid loss rates are compatible with cell lives in excess of 40,000 hours.
- Established an optimized flow field design for PBI membranes using 50-cm^2 test cells.

Future Directions

- Prepare additional polymers and membranes for testing.
- Test and evaluate lead candidate materials in 50-cm^2 single cells.
- Complete downselection of polymers to one to three candidate materials.
- Develop a concept to manage acid loss.
- Convert the lab-scale PBI-specific flow field design to prototypical size.
- Demonstrate and understand the MEA degradation rate.
- Demonstrate a PBI-based MEA that meets or exceeds program goals.
- Develop and exercise a model to project MEA cost at high volumes.

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 and automotive fuel cell applications. The ultimate result will be a PBI membrane material and a corresponding manufacturing process that will yield the low-cost membrane targeted by DOE, one that operates at greater than 120°C at pressures up to 3 atm with a projected design lifetime in excess of 40,000 hours. The corresponding MEA cost targets are <$10/kW for 500,000 automotive fuel cell stacks per year and <$1,500/kW for 1,000 stationary fuel cell stacks per year.

The work discussed herein is directed at meeting these objectives by taking advantage of preliminary development work conducted over the past four years by the team of Plug Power, Rensselaer Polytechnic Institute, Albany NanoTech/State University of New York (SUNY) at Albany, and PEMEAS GmbH (formerly Celanese Ventures GmbH). This team has demonstrated the potential for PBI membranes to meet or exceed DOE's technical goals. In this

project, the team will conduct extensive testing and verification of candidate PBI materials under automotive and stationary operating conditions, followed by selection of the best chemistry and manufacturing process that yield the low-cost membrane. Hardware to support PBI fuel cells will be designed and demonstrated.

Approach

The proposed work covers a three-year period and is divided into three principal parallel and integrated technology focuses. The first focus addresses screening of candidate polymers and membrane fabrication processes. Film properties will be measured and their relationship with polymer structure will be determined; the parameters that control film fabrication and manufacturing scale-up will be defined.

In the second focus, MEAs will be screened for numerous performance characteristics, followed by in-depth parametric studies for both short- and long-term application. Scaled-up MEAs with active areas of at least 250 cm^2 will be assembled into and evaluated in short stacks.

The third focus will result in the development and demonstration of hardware optimized for PBI-based MEAs. Specifically, membrane/electrode interfaces, flow fields, and acid management strategies will be investigated. Cathode performance improvements will be sought by optimizing standard electrode architectures and by investigating unique solutions such as nanotechnologies. The coupling of hardware and MEA performance will be a significant aspect of this work. A key deliverable will be a model to quantify the manufacturing cost of the selected PBI.

Results

Five different PBI polymer structures were prepared and fabricated into membranes. The results of the initial evaluation of these polymers and membranes are shown in Table 1. The inherent viscosity (IV) of the polymers suspended in solution generally exceeds the typical 0.8 to 1.0 deci-liters per gram (dL/g) found for plant-grade PBI. In the membranes, the acid content was significantly

Table 1. Results of Initial Evaluation of Five PBI Polymers

Compo-sition	IV (dL/g)	Polymer Content (wt%)	Acid Content (wt%)	Water Content(wt%)	n(H_3PO_4) /n(PBI)	Conduc-tivity (S/cm) at 160°C
1	2.9	6	65	30	38	0.18
2	4.1	4	72	24	49	0.18
3	0.8	15	60	25	46	0.2*
4	1.7	6	80	14	42	0.2*
5	1.2	21	63	16	10	0.1
* Measured at 140°C; Membrane melted at 160°C						

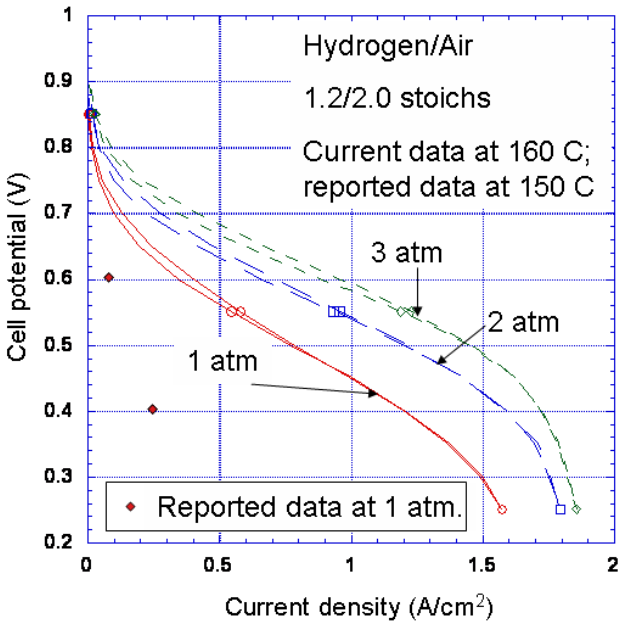


Figure 1. Representative Polarization Curves Illustrating the Effect of Operating Pressure on Performance of a 50-cm^2 Cell Fabricated With Polymer Composition 2 (Table 1) and Commercially Available Electrodes

greater, by about a factor of two, than previously reported data, possibly improving overall electrochemical performance of the cell.

An MEA was fabricated using PBI composition 2 of Table 1 and commercially available electrodes. The cell performed significantly better than in previously reported literature data at 1 atm (Figure 1). The effect of pressure is 75 mV for each decade

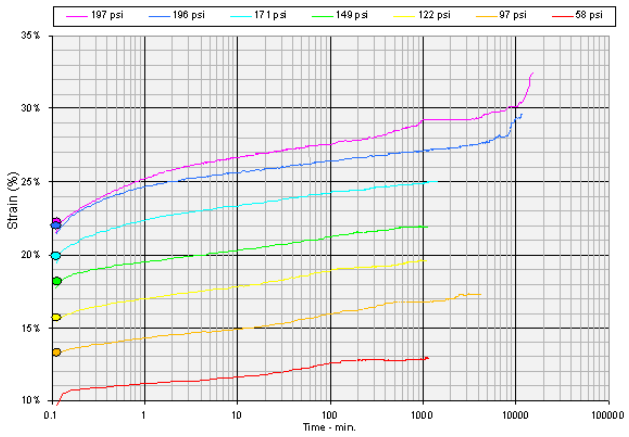


Figure 2. Representative Strain Versus Time Behavior for a PBI Membrane for Several Initial Compression Loads

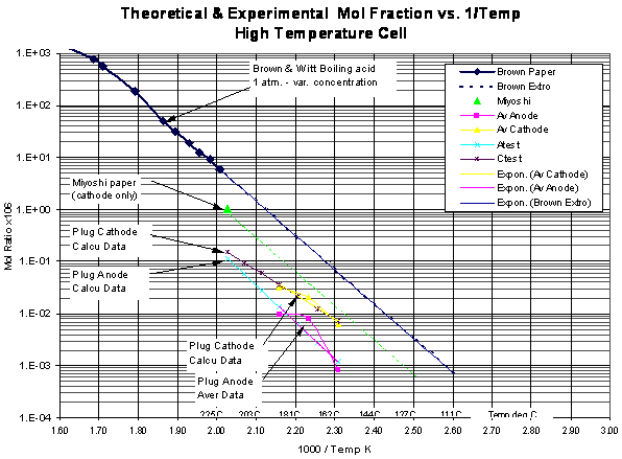


Figure 3. Rate of Phosphoric Acid Loss from a PBI Cell as a Function of Operating Temperature

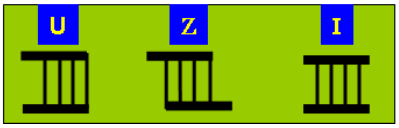
of increase in pressure, which is about half of the theoretical increase of 146 mV per decade for phosphoric acid fuel cells (Reference 1). This pressure effect is 2.5 times the theoretical effect of 29.9 mV per decade for Nafion®-type fuel cells.

Detailed mechanical characterization of the first five candidate membranes was started. Figure 2 illustrates representative creep behavior of these membranes and shows that these membranes undergo a high initial rate of creep. This behavior has significant ramifications for, and is being incorporated into, PBI-based stack designs. The creep behavior also has implications for cell life because either high contact resistance or puncturing of the membrane could result over time.

Acid transport mechanisms within and from a PBI cell were identified and quantified, and a numerical model was prepared. Current estimates of acid loss from an operating cell at steady state are significantly less than those reported in the literature for typical phosphoric acid cells (Figure 3). Phosphoric acid losses are exacerbated by the presence of liquid water in the cell. Liquid water may be present due to condensation within the cell or within the system during shutdown. Such startup and shutdown losses were eliminated in test cells by isolating the cells from the test system during test station startup and shutdown; the implications for system design and operation are being evaluated.

Table 2. Geometries Used in Numerical Analysis and Experiments to Determine Optimum PBI-Specific Flow Field Design

Experiment number	Channel/land ratio	Relative channel width	Relative flow area	Manifold configuration
1	1.0	1.0	1.0	U
2	1.0	2.0	2.0	Z
3	1.0	3.0	3.0	I
4	2.0	1.0	2.0	I
5	2.0	2.0	3.0	U
6	2.0	3.0	1.0	Z
7	3.0	1.0	3.0	Z
8	3.0	2.0	1.0	I
9	3.0	3.0	2.0	U



A numerical analysis and a corresponding set of designed experiments were performed to identify the geometric characteristics required to optimize a PBI-specific flow field for minimum reactant differential pressure along the cell. The geometric conditions are summarized in Table 2, and a representative set of numerical results is shown in Figure 4. These experiments showed that flow uniformity decreases as flow area increases, flow distribution is independent of channel width and channel-to-land ratio, and the cell manifold size and configuration strongly impact flow uniformity and pressure distribution.

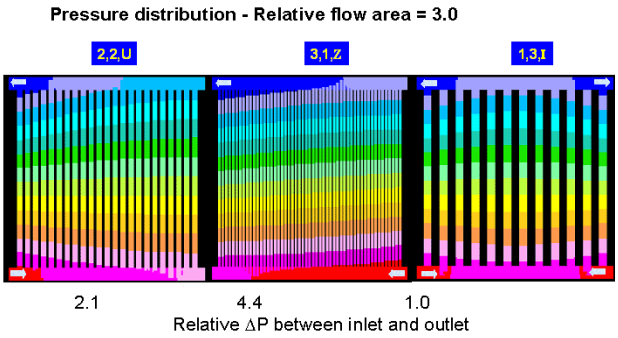


Figure 4. Representative Results of Numerical Modeling of Flow Fields (Descriptions of the geometries are provided in Table 2)

Conclusions

- Screening results have identified PBI-based membranes that may have improved performance capabilities relative to existing PBI materials.
- The effect of pressure on the performance of PBI-based materials is significant. The strong influence of pressure on these cells suggests that high power densities may be achievable with little pressure.
- Membrane mechanical behavior warrants attention in stack design, particularly compression and seal design.
- Startup and shutdown effects on phosphoric acid loss from PBI-based cells may be controllable by appropriate system design and operation.
- The geometric factors that influence pressure drop within PBI-based cells have been identified, but must be demonstrated on a larger active area.

References

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FY 2004 Publications/Presentations

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2. "NextGenCell – The Next Generation of Stationary Fuel Cells," Expression of Interest submitted to the European Commission, Plug Power Inc., Vaillant GmbH, and Celanese Ventures GmbH, March 2004.

3. B. Benicewicz, "PBI Membranes and MEAs for Stationary and Automotive Applications," presentation to Los Alamos National Laboratory, Los Alamos, New Mexico, March 2004.