

V.B.5 Development of Polybenzimidazole-based High Temperature Membrane and Electrode Assemblies for Stationary Applications

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Contract Number: DE-FC36_03GO13101

Subcontractors:

Rensselaer Polytechnic Institute, Troy, NY
 Entegris, Chaska, MN
 Albany Nano Tech, SUNY, Albany, NY
 University of South Carolina, Columbia, SC
 PEMEAS Frankfurt, Germany

Start Date: August 1, 2003
 Projected End Date: July 31, 2007

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 (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

Technical Targets

Characteristic	Units	Calendar Year			
		2004 Status	2005 Status	2006 Outlook	2010 Target
Membrane conductivity, operating temperature	Ohm-cm ²	0.10	0.10	0.10	0.10
Oxygen crossover	mA/cm ²	5	5	5	2
Hydrogen crossover	mA/cm ²	5	5	5	2
Cost	\$/kW		50	50	5
Operating temperature	°C	160	160	160	170
Durability	Hours	5,000	<i>> 15,000</i>	<i>> 15,000</i>	<i>40,000</i>
Survivability	°C	-20	<i>-30</i>	<i>-30</i>	<i>-40</i>

Red - Not assessed (bold)

Yellow - Limited data, projected to meet target (italics)

Blue - Meets target

Accomplishments

- Characterized MEA stress relaxation behavior over time, at room temperature and at operating temperature.
- Prepared membranes with fillers and evaluated stress relaxation behavior.
- Demonstrated 6.3 $\mu\text{V/hr}$ degradation rate with a 50 cm² test cell at 120°C, operating at steady-state, on an unfilled PBI membrane for 13,000 hours, H₂/air, with no humidification.
- Performed load cycle testing of filled membranes and showed encouraging results with a decrease in degradation rate of nearly half.
- Demonstrated successful acid trapping capability on a short stack test for 2,000 hours.
- Built initial model to understand the acid concentration changes in the MEA as a function of time, temperature and current density.
- Evaluated sealing adhesives for chemical compatibility with acid and coolant and performed lap shear tests with adhesive on bipolar plate material.

Introduction

The goal of this project is to optimize a high-temperature PBI membrane to meet the performance, durability, and cost targets required for stationary fuel cell applications. A membrane that operates at high temperatures is important to the fuel cell industry because it is insensitive to carbon monoxide, a poison to low temperature fuel cells, and does not require complex water management strategies. Alone, these two benefits could greatly simplify the fuel cell system. It is important to note that the simplified design of the high temperature fuel cell system can realize a cost benefit as the number of components is reduced by nearly 30%. There is also an inherent reliability benefit as components such as humidifiers and pumps for water management are unnecessary. Furthermore, combined heat and power (CHP) systems may be the best solution for a commercial, grid-connected, stationary product that must offer a cost benefit to the end user. For a low temperature system, the quality of the heat supplied is insufficient to meet consumer needs and comfort requirements, so peak heaters or supplemental boilers are required. The higher operating temperature of PBI technology allows the fuel cell to meet the heat and comfort demand without the additional equipment.

Working with Rensselaer Polytechnic Institute (RPI) 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. The work, since the last reporting period, has focused on evaluating the mechanical stability of membranes with fillers. 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. Additional work was conducted on acid loss, flow field design and cathode electrode development. Additional subcontractors (Entegris, University of South Carolina and RPI's Fuel Cell Center) initiated activities with regard to stack sealing, acid modeling, and electrode development.

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 cm² size prior to scaling up to full size. The concurrent activities were scheduled to converge in a full size module demonstration, 16-20 full-size cells in 2006 but due to budget constraints, the project will now extend until 2007.

Results

In the area of membrane development, it was demonstrated that the filled membranes had similar stress relaxation behavior as unfilled membranes at room temperature as shown in Figure 1. In particular composition 9 displayed a very high rate of stress relaxation in the initial minutes of the test. Even so, the team perceived an inherent benefit and decided to pursue testing of the filled membranes as an MEA in an aggressive load cycle test.

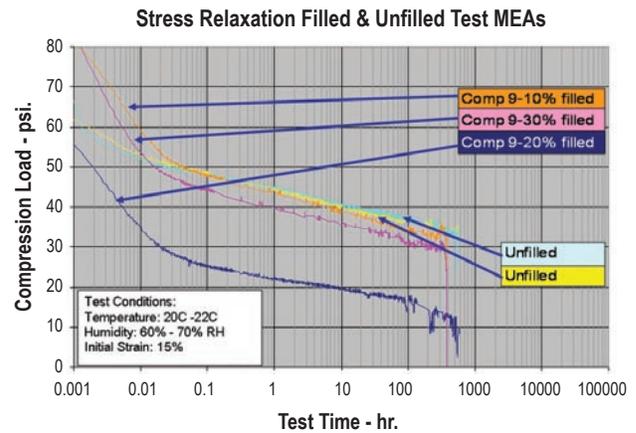


FIGURE 1. Stress Relaxation of Filled and Unfilled Membranes

The load cycling test results of the filled membrane compared to the unfilled membrane are shown in Figure 2. The load cycle for this test is 2 minutes at open circuit voltage (OCV), 30 minutes at 0.2 A/cm², and 30 minutes at 0.6 A/cm². For the equivalent test period, the degradation rate of the filled membrane was much lower as summarized in the table below. Degradation rates such as these would yield projected stack life of 6,000 hours with an unfilled membrane versus 14,000 hours with the filled membranes.

Load	Unfilled	Filled
OCV	33 $\mu\text{V/hr}$	20 $\mu\text{V/hr}$
0.2 A/cm ²	27 $\mu\text{V/hr}$	12 $\mu\text{V/hr}$
0.6 A/cm ²	40 $\mu\text{V/hr}$	19 $\mu\text{V/hr}$

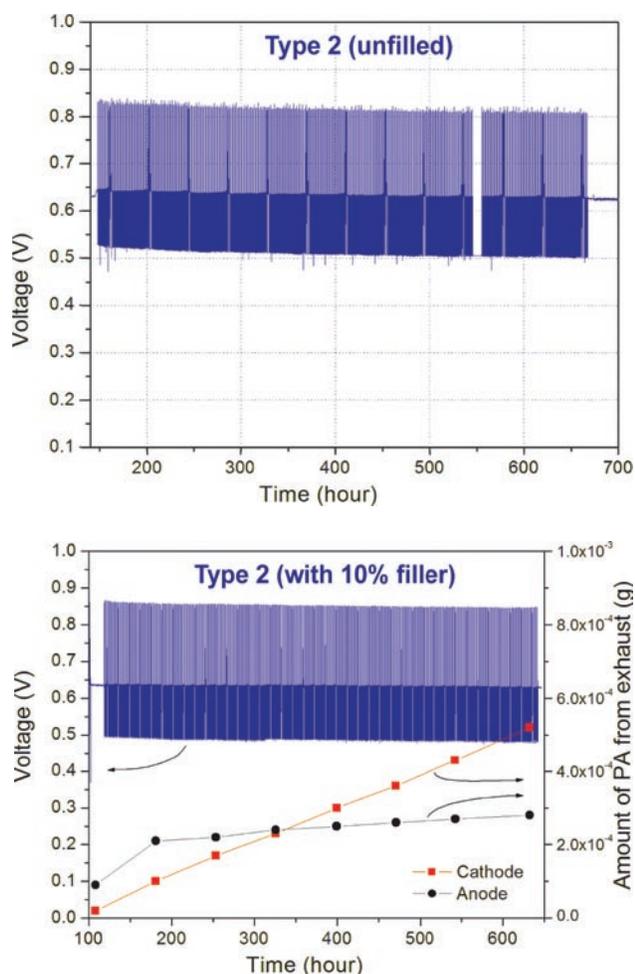


FIGURE 2. Load Cycling Test of Filled and Unfilled Membranes

These results are encouraging but are not conclusive given the sample size of one. Further testing of filled membranes will be performed to ensure reproducibility and understand the fundamental mechanism driving the behavior.

Activities with Entegris continued to progress but at a slower pace commensurate with the budget allocation for FY 2006. Entegris is pursuing a bond and seal design concept for the stack. Entegris has evaluated eleven adhesive materials, both conductive and non-conductive, and tested samples for temperature and acid compatibility. Lap shear testing was performed on samples with only two adhesives surviving the compatibility test. Currently bond line strength is being optimized using the specially designed fixture shown in Figure 3. The optimization of the bond line takes into account the stress relaxation behavior previously discussed. A finite element model has been constructed

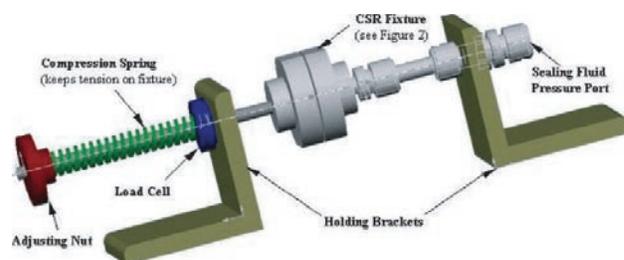


FIGURE 3. Bond Line Strength Test Fixture

for a full size plate to understand the strength characteristics required for the bond at assembly time and at operating temperature.

Given the budget constraints placed on the project in FY 2006, the team determined to discontinue cathode electrode development activities at RPI's Fuel Cell Center and Albany Nano Tech (ANT). The nano structured electrodes developed by ANT had yielded some promising results. However, the time frame to intercept the project did not appear feasible, and knowing that PEMEAS, the MEA supplier, was continuing to improve the cathode durability, the team determined that the ANT and RPI activities would be discontinued.

Conclusions and Future Directions

Remainder of 2006

- Continue operational characterization of filled and unfilled membranes.
- Continue testing to validate improved degrade rate of filled membranes.
- Build full size prototypes and demonstrate stack sealing concept with Entegris.
- Complete long term acid trap testing.

2007

- Re-start work at USC on acid model.
- Scale-up membrane and procure MEAs from PEMEAS utilizing their latest electrode.
- Test a full size module with improved membrane, flow field and sealing concept.
- PEMEAS and Entegris will deliver price estimate for MEA and stack.
- Demonstrate 1,000 hours life with low degradation rate and project 40,000 hours life.

Special Recognitions & Awards/Patents Issued

1. Patent application 11/312938: Fuel cell stack
2. Patent application 11/020636: Fuel cell stack & method for making same

FY 2006 Publications/Presentations

Publications

1. High Temperature Polybenzimidazoles for Fuel Cell Membranes via a Sol-gel Process. Xiao, L.; Zhang, H.; Scanlon, E.; Ramanathan, L.S.; Choe, E.W.; Rogers, D.; Apple, T.; Benicewicz, B.C. *Chem. Mater.*, 2005, accepted, in revision.
2. Advanced MEA Testing Systems for PEMFC. Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, 7/19/05. D. Giuliano, L. Xiao, B.C. Benicewicz.

Presentations

1. Synthesis and Evaluation of Poly (2,5-benzoxazole) as a Proton Exchange Membrane Fuel Cell Candidate. ACS Meeting, Chemical Education Division, San Diego, CA, 3/15/05. M. Kienzler, E.W. Choe, E. Scanlon, B.C. Benicewicz.
2. Advanced MEA Testing Systems for PEMFC. Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, 7/19/05. D. Giuliano, L. Xiao, B.C. Benicewicz.
3. Study of Steady-State and Dynamic Long Term Stability of PBI-Based Membranes. Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, 7/19/05. S. Yu, B.C. Benicewicz.
4. Study of Steady-State and Dynamic Long Term Stability of PBI-Based Membranes. Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, 7/19/05. S. Yu, B.C. Benicewicz.
5. High Temperature Technology Development, 2005 Fuel Cell Seminar, Palm Springs, CA, 11/17/05, R. Staudt.