

V.G.2 Lead Research and Development Activity for DOE's High Temperature, Low Relative Humidity Membrane Program

James Fenton (Primary Contact),
Darlene Slattery
University of Central Florida
Florida Solar Energy Center (FSEC)
1679 Clearlake Road
Cocoa, FL 32922
Phone: (321) 638-1002; Fax: (321) 638-1010
E-mail: JFenton@fsec.ucf.edu

DOE Technology Development Manager:
Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811
E-mail: Nancy.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

Technical Advisor: John Kopasz
Phone: (630) 252-7531; Fax: (630) 972-4405
E-mail: kopasz@anl.gov

Contract Number: DE-FG36-06GO16028

Subcontractors:
• BekkTech LLC, Loveland, CO
• Scribner Associates, Inc., Southern Pines, NC

Project Start Date: April 1, 2006
Project End Date: March 31, 2009

Objectives

- Demonstrate conductivity of 0.07 S/cm, at 80% relative humidity (RH), 25°C using new polymeric electrolyte phosphotungstic acid membranes.
- Demonstrate conductivity of >0.1 S/cm at 120°C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack.
- Standardize methodologies for in-plane and through-plane conductivity measurements.
- Provide High Temperature Membrane Working Group (HTMWG) members with standardized tests and methodologies.
- Organize HTMWG bi-annual meetings: <http://www1.eere.energy.gov/hydrogenandfuelcells/htmwg.html>

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
- (C) Performance
- (D) Thermal, Air and Water Management

Technical Targets

FSEC is developing and evaluating new polymeric electrolyte phosphotungstic acid composite membranes to increase conductivity. FSEC is also developing standardized experimental methodologies to:

- 1) measure conductivity (in-plane and through-plane),
- 2) characterize mechanical, mass transport, and surface properties of the membranes, and
- 3) predict durability of the membranes and their membrane electrode assemblies.

The membranes will meet the following DOE targets:

- A non-Nafion® membrane with a demonstrated conductivity of 0.07 S/cm at 80% RH at room temperature by the third quarter of year two.
- A membrane with a demonstrated conductivity of >0.1 S/cm at 120°C and 1.5 kPa water vapor partial pressure (50% RH measured at room temperature). This is a Go/No-Go decision point for the third quarter of year three.

Accomplishments

- Demonstrated conductivity of >0.07 S/cm at 80% RH at 30°C for the FSEC-3 membrane (exceeded third quarter of year two milestone).
- Developed protocol for standardized testing of conductivity.
- Protocol verified in-house and distributed to HTMWG members.
- Compared conductivity measurements for in- and through-plane.
- Established preliminary performance and endurance of the FSEC-3 membrane.



Introduction

Proton exchange membrane fuel cells (PEMFCs) have increasingly received worldwide attention due to their potential use in the hydrogen economy. Generally two regimes of PEMFC operation exist: the typical operating temperatures between 60–80°C and elevated temperatures higher than 100°C. The ability of current automotive radiators to reject heat is insufficient at continuous full power waste heat loads for 60–80°C fuel cell stack temperatures. Running the stack at 120°C under full load would allow the use of radiators similar to those available in automobiles today. This has driven the need for development of high-temperature membranes and membrane electrode assemblies that could operate at temperatures of up to 120°C, low RH and near-atmospheric pressure.

The objective of the current project is to develop a fuel cell membrane material that meets the goals outlined by the DOE in the multi-year plan. Additional goals are: operation at elevated temperatures (up to 120°C) with a demonstrated conductivity of >0.1 S/cm at 120°C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack (50% RH measured at room temperature). The material needs to operate over a range of operating conditions from -20 to 120°C because conductivity at the lower temperature is necessary to achieve both quick start-up from cold temperatures and efficiency targets. Inlet water pressures of 25 kPa today are acceptable, but 1.5 kPa at the end of this five-year project is required. The membrane electrode assemblies (MEAs) fabricated from the membranes must meet durability targets in the aggressive environment of a fuel cell, i.e., the material must have good chemical stability and be resistant to oxidation by radicals produced in the cell during operation.

Approach

FSEC is a development leader as well as a membrane developer. As development leader, FSEC develops and provides protocols, conducts standardized tests on samples from the group members, and provides fuel cell training with yearly hands-on “Short Courses” on conductivity and fuel cell performance testing, see http://www.fsec.ucf.edu/en/education/cont_ed/fuelcell/index.php. As a membrane developer, FSEC is developing membranes based on poly[perfluorosulfonic acids] (PFSA) and on sulfonated poly(ether ether ketone)s and sulfonated poly(ether ketone ketone) (SPEEK/SPEKK). New composite membranes containing small particle stabilized phosphotungstic acid are being fabricated using non-Nafion®-based PFSA of equivalent weight lower than 1100, SPEEKs with various sulfonation degrees, or SPEKK as the proton-conducting component in a blend with either poly(ether sulfone) (PES) or SPEKK with different sulfonation

levels. The FSEC team, along with subcontractors Bekktech LLC and Scribner Associates, working with the fuel cell community are developing standardized experimental methodologies to: 1) measure conductivity as a function of RH and mechanical properties of membranes, 2) characterize mechanical, mass transport, and surface properties of the membranes, and 3) predict durability of the membranes and their membrane electrode assemblies, which will be fabricated by the FSEC team for both the in-house research program and for membranes provided by the HTMWG. FSEC will develop and provide the DOE’s HTMWG with standardized tests and methodologies along with short course education offerings on these test methodologies and MEA fabrication techniques so that at the end of three years, all research program members will be able to understand and reproduce these processes in their own facility. An easily-implemented protocol and rapid test apparatus for evaluating the through-thickness conductivity (or resistance) of membranes over a broad range of conditions is also being developed.

Results

The first major milestone of the project, achieving a membrane conductivity >0.07 S/cm at 80% RH at 30°C, occurred and was met this year. The FSEC-3 membrane was tested at BekkTech and found to have a conductivity of 0.079 S/cm. This result may be seen in Figure 1. For comparison, the plot also shows Nafion® run under the same conditions. This membrane has not yet been optimized and it is anticipated that conductivity will improve with optimization.

In support of the HTMWG, testing of membranes from the group members was performed. Group members who sent membranes were Virginia Tech, Arkema, Giner, Penn State, University of Tennessee, Colorado School of Mines, Case Western (Pintauro), and Arizona State. Two of these membranes, in addition to the FSEC-3 membrane, exceeded the milestone. A summary of the test results can be seen in Figure 2.

The method used for determination of conductivity was an in-plane method. In-plane conductivity is the generally adopted method because of ease, but it measures the flow of protons along the plane of the surface of a membrane rather than through it. One of the FSEC tasks is to develop a through-plane method which is how protons move in a working fuel cell. Subcontractor Scribner Associates developed this new method and a series of Nafion® membranes were characterized by this method and compared to the in-plane data for identical samples. The thinner, dispersion-cast membranes, NRE-211 and NRE-212, had slightly higher in-plane conductivity results at higher temperatures. The thicker, extruded membranes, NE-1135 and N-117, exhibited slightly higher through-plane

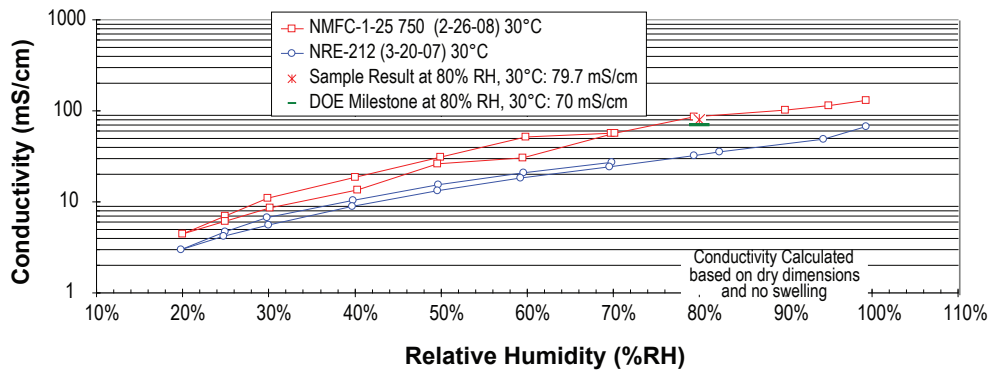


FIGURE 1. Conductivity of FSEC-3 Compared to Nafion®

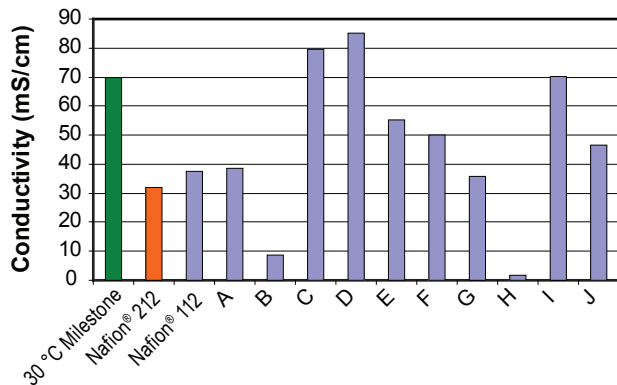


FIGURE 2. In-Plane Conductivity of HMTWG Membranes

conductivity results at higher temperatures. In general, there was a strong similarity in the results for the two methods.

In addition to having good conductivity, fuel cell membranes must also have good performance in a cell. The performance of FSEC-3 was evaluated at 80°C and ~100% RH under H₂/Air and H₂/O₂. The voltage, compensated for resistance losses, and the resistance of this MEA under H₂/O₂ is plotted in Figure 3. When the current density is 400 mA cm⁻², the voltage is 0.76 V. The area-specific resistance is low and constant at around 50 mOhm cm², equivalent to a conductivity of 170 mS/cm.

Durability of a fuel cell membrane is another important characteristic. As such, 100-hour tests under H₂/air at 30% RH, 90 and 100°C, and open circuit voltage (OCV) are being run. Improved resistance to degradation for FSEC-1 and FSEC-3 membranes over Nafion®-like membranes is displayed through decreased percent change over the 100 hours in hydrogen crossover, electrochemical active area, performance, resistance, OCV, mechanical strength, and thickness, as well as lower fluoride emission rate (FER), see Figure 4.

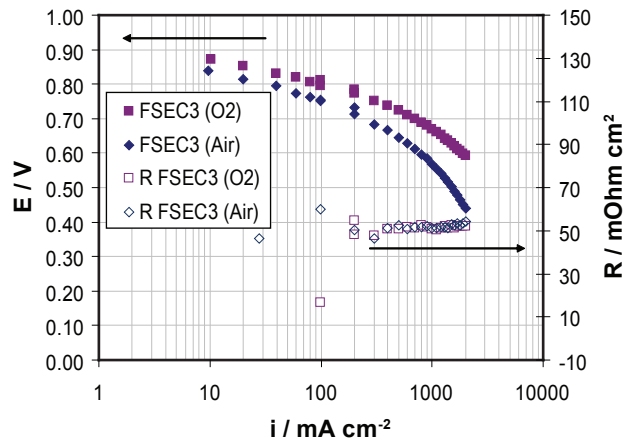


FIGURE 3. Performance of FSEC-3 at 80°C and ~100% RH under H₂/O₂

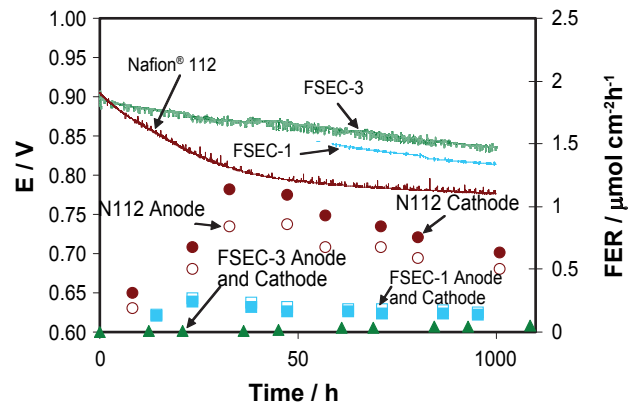


FIGURE 4. OCV Curve for 90°C, 30% RH Durability Test (left axis); FER during Degradation at 90°C/30% (right axis)

Conclusions and Future Directions

The unoptimized FSEC-3 membrane met the third quarter of year two milestone and was found to have good performance and durability. Of the nine working group samples that were tested, two were found to meet the milestone. Plans for the current contract year include:

- Optimization of the FSEC-3 membrane.
- Continued conductivity testing of HTMWG member membranes.
- Development and verification of a procedure for performing proton exchange membrane single cell test.
- Manufacture of MEAs from HTMWG membranes.

Special Recognitions & Awards/Patents Issued

1. Rhoden, S.L., Third Place Award for Graduate Student Posters at the 2008 Annual Joint Symposium of the Florida Chapter of the AVS Science and Technology Society and Florida Society for Microscopy.

FY 2008 Publications/Presentations

1. Agarwal, R.; Mohajeri, N.; Slattery, D. K.; Baik, J.; Fenton, James M., "Effect of relative humidity on the stabilized Nafion[®]/phosphotungstic acid composite membranes during fabrication process." Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2007), 52(2), 321-322.
2. Bekkedahl, Tim. "In-Plane Conductivity Testing Conditions for Samples Submitted to the Program." High Temperature Membrane Working Group Meeting, October 2007.

3. Linkous, C.A.; S.L. Rhoden, and K. Scammon, "X-Ray Photoelectron Investigation of Phosphotungstic Acid as a Proton-Conducting Medium in Solid Polymer Electrolytes," Hydrogen 2008-Materials Innovations in an Emerging Hydrogen Economy," American Ceramic Society, Cocoa Beach, Florida, February 24-27, 2008.

4. Rhoden, S.L.; C.A. Linkous, and K. Scammon, "X-Ray Photoelectron Investigation of Phosphotungstic Acid as a Proton-Conducting Medium in Solid Polymer Electrolytes," 2008 Annual Joint Symposium of the Florida Chapter of the AVS Science and Technology Society and Florida Society for Microscopy, Orlando, Florida, March 10-11, 2008.

5. Rhoden, S.L. and C.A. Linkous, "Increasing Conductivity of SPEEK and SPEKK Membranes Using Phosphotungstic Acid," 213th Electrochemical Society Meeting, Phoenix, Arizona, May 18-22, 2008.

6. "Procedure for Performing In-Plane Membrane Conductivity Testing," Distributed at the AMR, Washington, D.C., 2008.