V.D.4 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
E-mail: JFenton@fsec.ucf.edu

DOE Technology Development Manager: Jason Marcinkoski
Phone: (202) 586-7466
E-mail: Jason.Marcinkoski@ee.doe.gov

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

Technical Advisor: John Kopasz
Phone: (630) 252-7531
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, 2011

Objectives

- Fabricate membrane electrode assemblies (MEAs) from Team membranes.
- Test Team MEAs for fuel cell performance.
- Standardize methodologies for in-plane and through-plane membrane 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 (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Electrode Performance

Technical Targets

FSEC plays a supporting role to the six teams who are tasked with developing an improved high-temperature, low relative humidity (RH) membrane for proton exchange membrane (PEM) fuel cells. FSEC has developed standardized experimental methodologies to: (1) measure conductivity (in-plane and through-plane); (2) characterize mechanical, mass transport and surface properties of the membranes as working MEAs; and (3) predict durability of the membranes and their MEAs.

This project manufactures, tests and evaluates MEAs for performance and stability. Test results will be evaluated against DOEs 2010 membrane targets:

Oxygen Cross-Over	2 mA/cm^2
Hydrogen Cross-Over	2 mA/cm^2
Membrane Conductivity at 120°C	0.10 Siemens/cm

Accomplishments

- Verified ability to prepare an MEA using the DOE-recommended Pt/Co on carbon catalyst from Tanaka.
- Developed procedure for making and spraying ink based upon the use of 3M ionomer, as recommended by DOE.
- Prepared and tested MEAs fabricated from membranes provided by Giner, Fuel Cell Energy and Case Western.
- Established pinhole test method.
- Obtained and tested mechanical test apparatus.

✧ ✧ ✧ ✧ ✧

Introduction

Generally, two regimes of PEM fuel cell operation exist: the typical operating temperatures between 60–80°C, and elevated temperatures higher than 100°C. The ability for 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 MEAs that could operate at temperatures of up to 120°C, low RH and near atmospheric pressure.

The objective of this phase of the program is to fabricate and test MEAs from fuel cell membrane materials that meet the goals outlined by the DOE in the multi-year plan. Specific 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).

Approach

The High Temperature, Low Relative Humidity Membrane program encompasses six teams, each of which is skilled in producing novel membranes expected to meet the goals of the program. Some of these teams are not necessarily skilled in the ability to produce an MEA, or to test the MEAs in a fuel cell. FSEC's objective is to provide the expertise to test the membranes under fuel cell conditions. FSEC is working closely with the membrane manufacturers to develop appropriate methods for manufacture of the MEA and to test the MEAs according to a procedure that has been developed at FSEC. This approach involves a detailed logic flow chart that itemizes each step of the manufacture, fuel cell testing and post test analysis of the MEA. Each membrane manufacturer approves the steps of the logic flow chart in advance of the process. Furthermore, FSEC iterates with the teams to optimize the results.

Results

During this year, a total of 19 membranes were received from four of the teams. These varied from an extremely brittle membrane that required recasting to some high quality materials. Each was tested for material characteristics to determine suitability for fabrication into MEAs, see material characterization box of logic flow chart, Figure 1. Eight of the membranes were fabricated into MEAs and tested, and the procedures developed for the testing. For each MEA tested, a detailed report was prepared and sent to the supplier, along with photos of each step, data collected

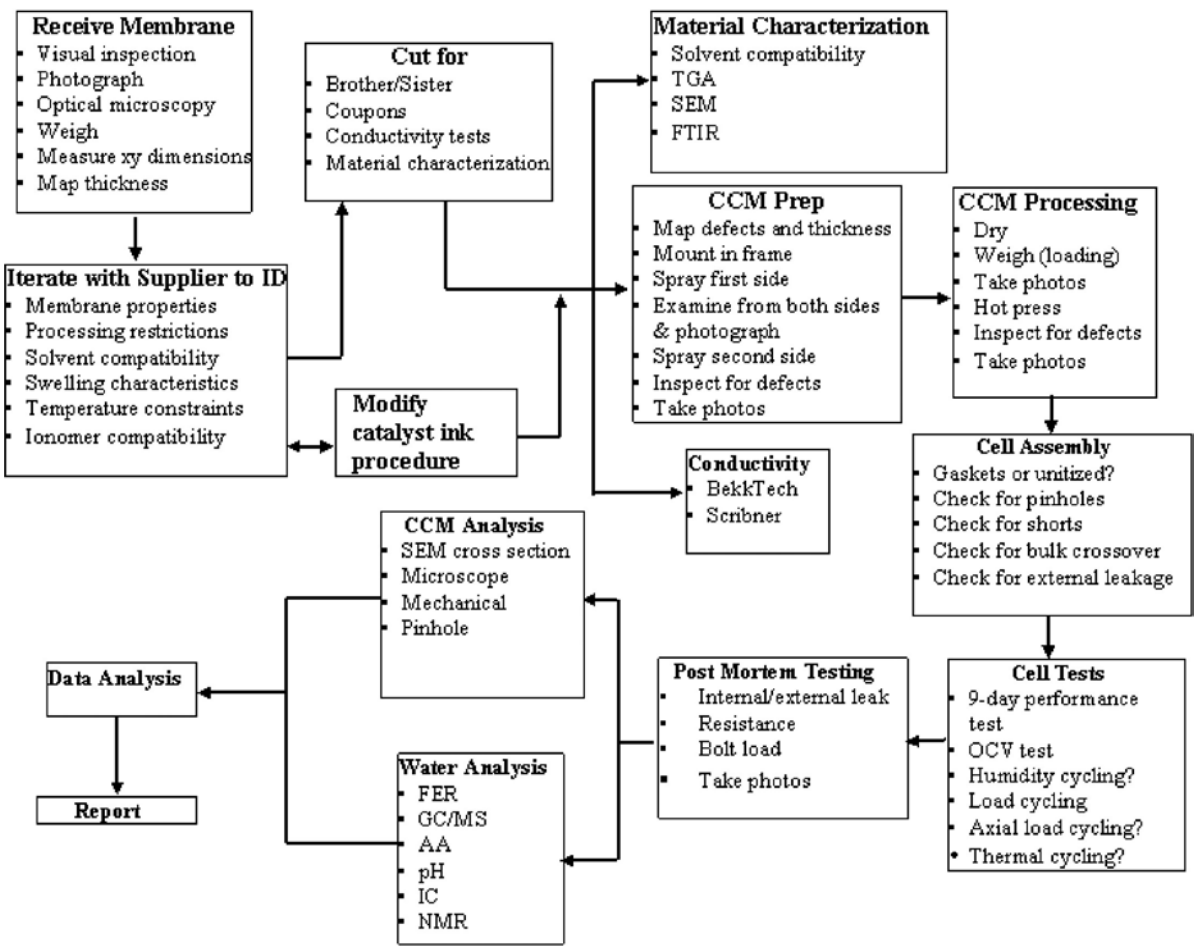

FIGURE 1. Logic Flow Chart

and, when possible, a coupon that was prepared identically to the MEA.

All membranes received to date were preliminary or baseline materials. The goal of using these materials for the development of MEAs was to resolve any issues resulting from the use of these novel materials. This will allow easier handling of the final membranes, which are not yet available. Three of the six teams have indicated that they are prepared to send next generation or final membranes for testing.

A previous method [1] for determining pinhole locations in MEAs from tested fuel cells was found not to be reproducible and was potentially damaging to the MEAs. This method was based upon the location of bubbles that appeared in a liquid injected to the cathode flow field of a transparent plate with controlled gas pressure applied to the anode. An alternative method has been developed based upon applying 4% hydrogen to the anode side of a fuel cell, with controlled flow and with the cathode side of the MEA exposed to the atmosphere. This results in the development of "hot-spots" at pinhole locations due to the direct reaction of hydrogen with oxygen. An infrared camera was used to determine the locations of these hot-spots. This method has been found to be reproducible and since the MEA is not exposed to substances it would not be exposed to during fuel cell testing, damage to the MEA is minimized. An example of an image of the pinholes taken using an infrared camera is shown in Figure 2. In this image hot spots are noted with approximate temperatures based on the emissivity of carbon.

An in-house built stress-strain setup was acquired and a procedure was formalized for stress-strain testing of team member membranes. Reproducibility and repeatability will be established as a part of completing the protocol. Team member membrane samples will be tested once the protocol is finalized, to ensure all samples were tested to the same procedure.

FIGURE 2. Infrared image of the hot spots on an MEA from a tested fuel cell. Hot spots are noted with approximate temperatures based on the emissivity of carbon.

Conclusions and Future Directions

- Reached agreement with all six Teams on logic flow chart for MEA development.
- Developed and tested MEAs from eight Team member membranes.
- Established collaboration with 3M to obtain advanced ionomer for use in MEAs.
- Fabrication and testing of additional MEAs will be done as membranes are received.
- Formalize the procedure for pinhole testing, and characterize the observed pinholes with scanning electron microscopy.

FY 2010 Publications/Presentations

1. Rodgers, Marianne P.; Agarwal, Rohit; Pearman, Benjamin P.; Li, Bo; Slattery, Darlene K.; Bonville, Leonard J.; Kunz, H. Russell; Fenton, James M. **Accelerated durability testing of perfluorosulfonic acid MEAs for PEMFCs using different relative humidities.** ECS Transactions (2009), 25(1, Proton Exchange Membrane Fuel Cells 9), 1861-1871.

2. Fenton, James M.; Rodgers, Marianne P.; Slattery, Darlene K.; Huang, Xinyu; Mittal, Vishal O.; Bonville, Leonard J.; Kunz, H. Russell. **Membrane degradation mechanisms and accelerated durability testing of proton exchange membrane fuel cells.** ECS Transactions (2009), 25(1, Proton Exchange Membrane Fuel Cells 9), 233-247.

3. Rodgers, Marianne P.; Pearman, Benjamin P.; Mohajeri, Nahid; Slattery, Darlene K.; Bonville, Leonard J.; Kunz, H. Russell; Fenton, James M. **Investigation of the Presence of a Saturating Media during Hot Pressing of Proton Exchange Membranes to Improve Performance**, submitted to ECS Transactions (2010), Fuel Cell Membranes, Electrode Binders, and MEA Performance.

4. Brooker, Paul; Rodgers, Marianne; Bonville, Leonard; Kunz, Russell; Slattery, Darlene; Fenton, James. **Effect of Spray Parameters on Electrode Surface and Performance**, submitted to ECS Transactions (2010), 217th ECS Annual Meeting, Vancouver, Canada.

References

1. X. Huang, W. Yoon, M.P. Rodgers, J.M. Fenton, "Interactions between chemical and mechanical degradation of PEMFC membrane and MEAs," Fuel Cells Durability & Performance: Real World Solutions to the Most Significant Challenges Facing Fuel Cells Commercialization, 4th International Conference, Las Vegas, NV, December 11–12, 2008.