V.C.1 Lead Research and Development Activity for DOE's High Temperature, Low Relative Humidity Membrane Program

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Fiscal Year (FY) 2012 Objectives

- Fabricate membrane electrode assemblies (MEAs) from team membranes.
- Test team MEAs for fuel cell performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability: Membrane and MEA durability

(C) Performance: High MEA performance at low relative humidity (RH) and high temperature

Technical Targets

FSEC plays a supporting role to the six teams who are tasked with developing an improved high temperature, low relative humidity membrane for polymer electrolyte membrane fuel cells (PEMFCs). 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 membrane electrode assemblies; and (3) predict durability of the membranes and their MEAs.

This project manufactures, tests and evaluates MEAs for performance and stability. Test results were evaluated against DOE's 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

FY 2012 Accomplishments

- FuelCell Energy (FCE) electrode composition (with FCE ionomer) optimized through FSEC/FCE collaboration.
- Prepared and tested Case Western Reserve (CWR) University 25 cm^2 MEA using FSEC's membrane catalyzing, cell assembly, and cell test procedures.

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Introduction

Generally, two regimes of PEMFC 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 120ºC 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 120ºC, low RH and near atmospheric pressure.

The objective of this phase of the project 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) wih unhumidified inlet streams, with a demonstrated conductivity of >0.1 S/cm at 120°C. Calculations indicate that with unhumidified inlets, the water produced in the MEA at rated power will result in water partial pressures of about 40 kPa.

Approach

The High Temperature, Low Relative Humidity Membrane project for the last three years, encompassed six teams, each of which is skilled in producing novel membranes expected to meet the goals of the Fuel Cell Technologies sub-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 worked 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 involved a detailed logic flow chart that itemized each step of the manufacture, fuel cell testing and post-test analysis of the MEA. Each membrane manufacturer approved the steps of the logic flow chart in advance of the process. Furthermore, FSEC iterated with the teams to optimize the results.

Results

The preparation of MEAs requires a certain amount of optimization in order to determine the full performance capability of a particular membrane. In the majority of the MEAs fabricated under this project, a 3M ionomer was used in the catalyst layer. However, FuelCell Energy chose to have its own ionomer used in order to achieve a better interface between the membrane and the catalyst layer. As a result, it was necessary to run a number of experiments with varying amounts of ionomer to determine the level for highest performance. As can be seen from the data in Table 1, the optimization of one parameter often leads to a decrease in another. In the case of the FuelCell Energy membranes, a decrease in fluoride emission rate (an increase in durability) led to an increase in resistance.

The FuelCell Energy B5 MEA exceeded the 2017 DOE target for performance and was found to be very durable. Additional work would need to be done to balance these improvements with the higher than desired area specific proton resistance.

Most of the membranes that were developed under this project were fluorocarbons and, therefore, the preparation of the MEAs was accomplished using a procedure based upon use of Nafion® membranes. However, the membranes developed by CWR were hydrocarbons and required alternative procedures. Early in the project, the CWR membranes were found to be highly conductive at low RH and high temperature but there were issues involved with the membranes cracking and crumbling during attempts at MEA manufacture. It had not been possible to obtain a large enough piece of membrane with the integrity to prepare a standard 25 cm^2 MEA. This year, we were able to recast and crosslink a piece of CWR membrane that was large enough to manufacture a standard size MEA (Figure 1). Because of concerns about the membrane withstanding the spraying process typically used to apply the electrode to the membrane, it was decided that a gas diffusion electrode (GDE) would be prepared and hot pressed onto the membrane. The procedure was successful and the resulting MEA was tested under the agreed to protocol conditions, i.e. 35% RH for all temperatures at the request of CWR. For comparison purposes, an NRE211 membrane was also prepared with a GDE and tested under the same conditions. As can be seen in Figure 2, the CWR membrane,

TABLE 1. Optimization of Ionomer Content in FuelCell Energy Membranes

Characteristic	Units	Target 2017	B5 Opt.	B9 Opt.	NRE211 CCM[1]
Area specific proton resistance at:					
120°C and 40-80 kPa H_2O partial pressure	Ohm cm^2	≤0.02	0.064[2]	0.110[2]	0.144[2]
80°C and 25-45 kPa H_2O partial pressure	Ohm cm^2	≤0.02	0.016[3]	0.045[3]	0.020[3]
Contact Resistance (Interrupt – ASR[4])					
120°C and 70 kPa water partial pressure	Ohm cm^2		0.042	0.039	0.036
80°C and 38 kPa water partial pressure	Ohm cm^2		0.030	0.009	0.037
Maximum hydrogen cross-over	mA/cm^2	2	1.6	<0.4	1.08
Minimum electrical resistance	Ohm cm^2	1,000	417	855	526
Performance @ 0.8V	mA/cm^2	300	209	137	158
Performance @ rated power	mW/cm^2	1,000	1,239	577	936
Total fluoride emission during stability test	mmol	-	89	62	

[1] Catalyst-coated membrane
[2] Measured at 120°C and 70 kPa water partial pressure
[3] Measured at 80°C and 38 kPa water partial pressure
[4] Area-specific resistance

FIGURE 1. CWR membrane after recasting and crosslinking

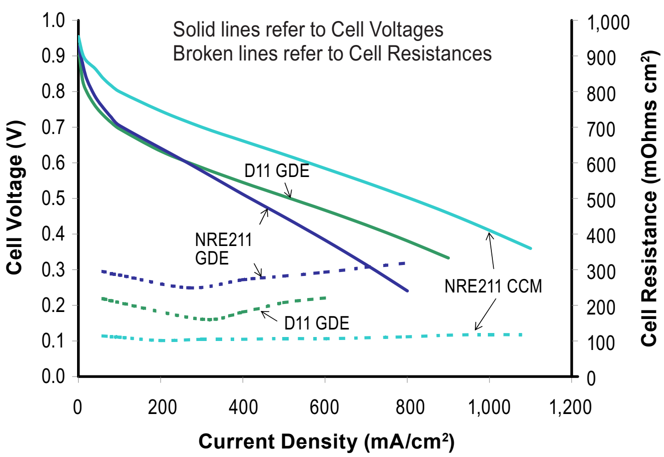

FIGURE 2. Comparison of performance of CWR and Nafion® MEAs GDE versus Nafion® CCM

D11, performed better than the NRE211 with a GDE. For comparison, the NRE211 with a standard CCM is also shown. Based upon subsequent preliminary data, a D11 prepared with a CCM outperforms the NRE211 CCM.

Conclusions and Future Directions

Project is complete and no additional work is anticipated. However, open issues include:

Examination of membrane /electrode interface:

- Study interfacial resistance:
  - Examine CWR MEAs by scanning electron microscope to determine degree of contact between membrane and GDE.
  - Decrease interfacial resistance of CWR MEAs by alternative electrode application methods.
  - Focus on interfacial resistance for MEAs made with FCE ionomers. Understand interfacial resistance for MEAs made with 3M ionomer and with Team member's ionomer.
- Determine differences in swelling rates between team member membranes and Nafion®.

Investigate mechanical properties as a function of degradation.

FY 2012 Publications/Presentations

- M.P. Rodgers, L.J. Bonville, H.R. Kunz, D.K. Slattery, J.M. Fenton, "Defining the correlation between membrane/MEA degradation rate from accelerated testing and lifetime", accepted in *Chemical Reviews*, 2012.
- M.P. Rodgers, P.B. Brooker, N. Mohajeri, L.J. Bonville, H.R. Kunz, D.K. Slattery, J.M. Fenton, "Verification of the correlation between membrane/MEA degradation rate from accelerated and lifetime testing", accepted in *Journal of the Electrochemical Society*, 2012.
- M.P. Rodgers, L.J. Bonville, H.R. Kunz, D.K. Slattery, J.M. Fenton, Defining the correlation between membrane/MEA degradation rate from accelerated testing and lifetime, Fuel Cell Seminar, Orlando, Florida, USA. November 2011 Presentation #LRD42-3.