V.C.9 Lead Research and Development Activity for DOE's High Temperature, Low Relative Humidity Membrane Program

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Subcontractors:

- BekkTech LLC, Loveland, CO
- Scribner Associates, Inc., Southern Pines, NC

Project Start Date: April 1, 2006
Project End Date: September 30, 2011

Fiscal Year (FY) 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.

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) Performance

Technical Targets

FSEC plays a supporting role to the five teams who are tasked with developing an improved high temperature, low relative humidity membrane for proton exchange 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 membrane electrode assemblies.

This project manufactures, tests and evaluates MEAs for performance and stability. Test results were evaluated against DOEs 2015 membrane targets as shown in Table 1 (A, B and D identify the teams and the numbers are those assigned by FSEC to identify a specific sample).

TABLE 1. Team Membranes Compared to Targets*

Characteristic	Units	Target	D7	B4	A4	NRE211
		2015				
Area specific proton resistance at:						
120°C, water partial pressures from 40 to 80 kPa	Ohm cm^2	≤0.02	0.05	0.08	0.14	0.18
80°C and water partial pressures from 25-45 kPa	Ohm cm^2	≤0.02	0.02	0.02	0.01	0.05
Maximum hydrogen cross-over [a]	mA/cm^2	2	1.9	2.7	0.70	0.76
Minimum electrical resistance [b]	Ohm cm^2	1,000	31	270	813	2100
Performance @ 0.8 V (¼ Power)	mA/cm^2 mW/cm^2	300 250	34 27	255 204	81 65	151 120
Performance @ rated power	mW/cm^2	1,000	108	817	260	480

*Values are at 80°C unless otherwise noted
[a] Measured in humidified H_2/N_2 at 25°C
[b] Measured in humidified H_2/N_2 using linear sweep voltammetry curve from 0.4 to 0.6 V at 80°C

FY 2011 Accomplishments

- Performed conductivity testing on baseline membranes from Giner, Inc. and FuelCell Energy (FCE), and prepared and tested MEAs from these membranes.
- Assisted Case Western Reserve with membrane casting and cross-linking.
- Prepared and tested MEAs from Case Western Reserve University membranes.

- Developed and verified a new method for determining location of crossover in MEAs.
- Established procedures for preparing transmission electron microscopy (TEM) samples and examined samples via TEM.
- Performed stress-strain experiments on several team member samples.
- Completed a study to determine the effect of cell pressure on performance.
- Performed durability test for sample from Giner.
- Collaborated with FCE to optimize ionomer loading in catalyst ink.
- Completed milestone “Define correlation between membrane/MEA degradation rate from accelerated testing and lifetime.”

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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. At higher temperatures, heat is more easily rejected from the cell stack, anode catalyst poisoning by CO is less important, water transport is simplified, the kinetics of fuel oxidation will be improved, and gas transport and the efficiency of the cell will be enhanced. However, operation of PEMFCs at high temperature and ambient pressure results in decreased relative humidity, which significantly increases membrane resistance, thus decreasing cell performance. This has driven the need for development of high-temperature membranes and membrane electrode assemblies that could operate at temperatures of up to 120ºC, low relative humidity (RH) and near atmospheric pressure.

The objective of this phase of the project has been 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 area specific resistance of <0.02 Ohm cm^2 at 120ºC and 40 kPa inlet water vapor partial pressure to the fuel cell stack (85% RH measured at 80°C).

Approach

The High Temperature, Low Relative Humidity Membrane program includes five 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 fabricate MEAs, and assemble cells to test the membranes under fuel cell conditions. FSEC has worked closely with the membrane manufacturers to develop appropriate methods for manufacture of the MEA and to test the MEAs according to a process data base 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

The program began five years ago with 11 teams initially funded to develop high conductivity membranes. After the Go/No-Go decision point, six teams were selected to continue and an additional one was discontinued this year. Over the course of the program, conductivity, stability and performance improved. Many membranes have shown promise. The collaboration between FSEC and the teams guided catalyst-coated membrane (CCM) development, and the program is proving to be an excellent model for future DOE membrane and MEA development projects.

Significant progress toward achieving DOE targets was made over the last five years as shown in Tables 2, 3, and 4 for three of the teams.

TABLE 2. Case Western Membranes Compared to DOE Targets*

Characteristic	Units	Target 2015	D6	D7	D9	NRE211
Membrane thickness	µm		200	63	122	25
Area specific proton resistance at:						
120°C and 70 kPa water partial pressure	Ohm cm^2	≤0.02	N/D	0.05	0.097	0.15
80°C and 38 kPa water partial pressure	Ohm cm^2	≤0.02	0.055	0.02	0.018	0.02
Maximum hydrogen cross-over [a]	mA/cm^2	2	10.8	1.9	136	0.76
Minimum electrical resistance [b]	Ohm cm^2	1,000	8.4	31	14	2100
Performance @ 0.8 V (¼ power)	mA/cm^2 mW/cm^2	300 250	N/D N/D	34 27	N/D N/D	151 120
Performance @ rated power	mW/cm^2	1,000	N/D	108	N/D	480

*Values are at 80ºC unless otherwise noted

[a]Measured in humidified H_2/N_2 at 25°C

[b]Measured in humidified H_2/N_2 using linear sweep voltammetry curve from 0.4 to 0.6 V at 80°C

N/D - not determined

In addition to the results for the samples from the teams shown in the tables, samples were received from Colorado School of Mines (CSM) and from Vanderbilt University. Difficulties were encountered with the CSM membranes because stickiness resulting from the Florida humidity made them hard to handle. No successful MEAs were fabricated. Two Vanderbilt membranes were received and MEAs constructed and tested. Data was not analyzed in time for this report.

TABLE 3. Fuel Cell Energy Membranes Compared to DOE Targets*

Characteristic	Units	Target	B2	B3	B4	B5	B7[c]	NRE 211
		2015						
Membrane thickness	μm		29	26	31	36	53	25
Area specific proton resistance at:								
120°C and 70 kPa water partial pressure	Ohm cm^2	≤0.02	0.08	0.08	0.08	0.08	0.23	0.15
80°C and 38 kPa water partial pressure	Ohm cm^2	≤0.02	0.02	0.02	0.02	0.02	0.05	0.02
Maximum Hydrogen cross-over [a]	mA/cm^2	2	1	0.95	2.7	1.8	0.48	0.76
Minimum electrical resistance [b]	Ohm cm^2	1000	1200	800	270	1336	500	2100
Performance @ 0.8 V (¼ Power)	mA/cm^2 mW/cm^2	300 250	104 84	177 142	255 204	209 167	150 120	113 91
Performance @ rated power	mW/cm^2	1000	334	567	817	668	482	363

*Values are at 80°C unless otherwise noted

[a] Measured in humidified H_2/N_2 at 25°C

[b] Measured in humidified H_2/N_2 using linear sweep voltammetry curve from 0.4 to 0.6 V at 80°C

[c] Membrane thickness double that of others in series

TABLE 4. Giner Membranes Compared to DOE Targets*

Characteristic	Units	Target	A1	A2	A3	A4	NRE211
		2015					
Membrane thickness	μm		22	40	28	27	25
Area specific proton resistance at:							
120°C and 70 kPa water partial pressure	Ohm cm^2	≤0.02	0.26	0.24	0.32	0.14	0.15
80°C and 38 kPa water partial pressure	Ohm cm^2	≤0.02	0.05	0.03	0.04	0.01	0.02
Maximum hydrogen cross-over [a]	mA/cm^2	2	0.75	1.6	0.61	0.70	0.76
Minimum electrical resistance [b]	Ohm cm^2	1,000	65	358	1073	813	2100
Performance @ 0.8 V (¼ Power)	mA/cm^2 mW/cm^2	300 250	94 75	222 177	112 89	81 65	151 120
Performance @ rated power	mW/cm^2	1,000	300	708	356	260	480

*Values are at 80°C unless otherwise noted

[a] Measured in humidified H_2/N_2 at 25°C

[b] Measured in humidified H_2/N_2 using linear sweep voltammetry curve from 0.4 to 0.6 V at 80°C

Conclusions and Future Directions

- Eleven teams were initially funded to develop high conductivity membranes.
- Six teams were selected to continue after Go/No-Go, five continuing this year.
- Conductivity, stability and performance improved over course of program.
- Many membranes have shown promise and should be pursued.
- Collaboration between FSEC and teams guided CCM development.
- This project is an excellent model for future DOE membrane development projects.
- Significant progress was made toward developing membrane suitable for fuel cell use.
- In the future, FSEC will continue to work closely with team members, preparing and testing MEAs in fuel cell hardware.
- Additional support will be provided to FCE for electrode optimization.
- FSEC will continue to work closely with Case Western Reserve University to reduce cross-over.
- FSEC is preparing procedures for testing cross-over and electrical resistance that follow DOE guidelines.

FY 2011 Publications/Presentations

1. Brooker, Paul; Bonville, Leonard; Kunz, Harold R.; Slattery, Darlene; Fenton, James. “Effect of Measurement Technique on PEMFC Performance” Presented at the 220th ECS Meeting, Montreal, QC, Canada, May 2011, abstract 199.

2. Rodgers, M.P.; Bonville, L.J.; Kunz, H.R.; Slattery, D.K.; Fenton, J.F., “Defining the Correlation Between Membrane/MEA Degradation Rate from Accelerated Testing and Lifetime”, Publication proposal submitted to Chemical Reviews, April, 2011.