V.C.3 High-Temperature Membrane with Humidification-Independent Cluster Structure

Ludwig Lipp (Primary Contact), Pinakin Patel, Ray Kopp
FuelCell Energy (FCE), Inc.
3 Great Pasture Road
Danbury, CT 06813
Phone: (203) 205-2492
Email: llipp@fce.com

DOE Managers
HQ: Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov
GO: Greg Kleen
Phone: (720) 356-1672
Email: Gregory.Kleen@go.doe.gov

Technical Advisor
Thomas Benjamin
Phone: (630) 252-1632
Email: benjamin@anl.gov

Contract Number: 36-06GO16033

Start Date: June 1, 2006
Projected End Date: August 31, 2012

Fiscal Year (FY) 2012 Objectives

- Develop humidity-independent, thermally stable, low equivalent weight composite membranes with controlled ion-cluster morphology, to provide high proton-conductivity at up to 120°C (overall goal: meet DOE 2015 targets).
- Improve mechanical properties to significantly increase the durability and reduce the gas cross-over.
- Reduce the membrane area specific resistance (ASR) to increase cell performance and lower the capital and operating costs.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Multi-Year Research, Development and Demonstration Plan [1] of the DOE Fuel Cell Technologies Program:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

This project is developing a multi-component composite (mC^2) membrane to meet the following DOE 2015 technical targets for membranes:

- Membrane Conductivity: At ≤120°C: 0.1 S/cm; at room temperature: 0.07 S/cm; at -20°C: 0.01 S/cm
- Membrane ASR: 0.02 Ωcm^2

FY 2012 Accomplishments

- Protonic Conductivity: Met DOE protonic conductivity target: achieved 0.113 S/cm (DOE Target >0.1 S/cm)

The membrane electrode assembly (MEA) was re-optimized for mC^2 in collaboration with the University of Central Florida (UCF), resulting in the following performance improvements:

- Electrical Conductivity: Met DOE electrical conductivity target: achieved 2,860 Ωcm^2 (DOE Target: >1,000 Ωcm^2)
- Cross-Over: Met DOE hydrogen cross-over target: achieved 0.3 mA/cm^2 (DOE Target <2 mA/cm^2)
- Cell Performance: Met DOE power density target: achieved 1,247 mW/cm^2 at rated power (DOE Target: >1,000 mW/cm^2)
- Additive Development: Developed process to stabilize protonic conductivity enhancer in mC^2

Introduction

This project is focused on the development of composite proton exchange membranes (PEMs) that can operate at low relative humidity (RH) and over a wide temperature range (-20 to 120°C). Their main application is in transportation fuel cells. In addition, FCE is considering use of these membranes for co-production of hydrogen from high-temperature fuel cells. The higher operating temperature imparts improved tolerance to impurities, such as carbon monoxide, thereby increasing the co-production efficiency and simplifying the system.

The goal is to develop a structure in which ion-conducting clusters remain intact at low RH. A major challenge is that current proton conducting polymers cannot sufficiently hold on to water under these conditions. Since the conduction mechanism relies on movement of hydrated species, the conducting path is compromised, resulting in

low performance. Membranes that can operate at lower RH at elevated temperatures up to 120°C will reduce the fuel cell system complexity and cost. This project is developing a composite membrane, in which both the ionic conductivity and mechanical properties are enhanced to meet DOE's 2015 and 2017 goals for transportation fuel cells.

Approach

The approach to address the DOE target parameters is summarized in Table 1. The emphasis in the past year has been to fabricate MEAs that can meet DOE's cell performance targets.

TABLE 1. Approach for the Composite Membrane

Target Parameter	DOE Target (2017)	Approach
Area specific proton resistance at: 120°C and 40-80 kPa water partial pressure	0.02 Ω cm^2	Multi-component composite structure, lower equivalent weight, additives with highly mobile protons
80°C and 25-45 kPa water partial pressure	0.02 Ω cm^2	Higher number of functional groups
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm^2	Higher molecular weight polymer for stronger membrane structure
Minimum electrical resistance	1000 Ω cm^2	Improved membrane thickness tolerance and additive dispersion
Cost	20 $/m^2	Simplify polymer processing
Performance @ 0.8 V (¼ rated power)	300 mA/cm^2	MEA with matching polymer in membrane and electrodes
Performance @ rated power	1,000 mW/cm^2	Optimized ionomer content in electrodes

Results

This year's efforts were focused on improving the MEA fabrication process with the mC^2 membrane. Cell performance analysis carried out by UCF in the previous year [2] suggested that electrode improvements would be necessary to realize the full potential of the mC^2 membrane. In particular, analysis results showed that the biggest losses while operating on H_2/air occur on the cathode electrode. Hence, the anode was kept the same and changes were made to the cathode. The changes were focused on the ionomer content. It was studied in a range from 15 to 32% by weight. Figure 1 shows cell performance results for each of four different ionomer contents in the cathode. Because of membrane fabrication-related differences in the average membrane thickness between MEA samples, the data are presented with an internal resistacne-free voltage. This allows elimination of the effect of membrane thickness on the cell resistance and therefore cell voltage. Moreover, the data were corrected for crossover hydrogen resulting from the variations in membrane thickness. This was done by deducting the limiting current density in the linear sweep voltammogram from the measured current densities in the polarization curves to isolate the effect of ionomer content in the cathode. Record performance was observed. The actual voltages measured were as follows:

- At 120°C and 35% RH: 510 mV at 1 A/cm^2
- At 95°C and 83% RH: 585 mV at 2 A/cm^2

Data at 120°C and 35% RH suggests that 29 wt% ionomer gives the highest performance in a current density range up to 1,000 mA/cm^2. From 1,000 to 2,000 mA/cm^2,

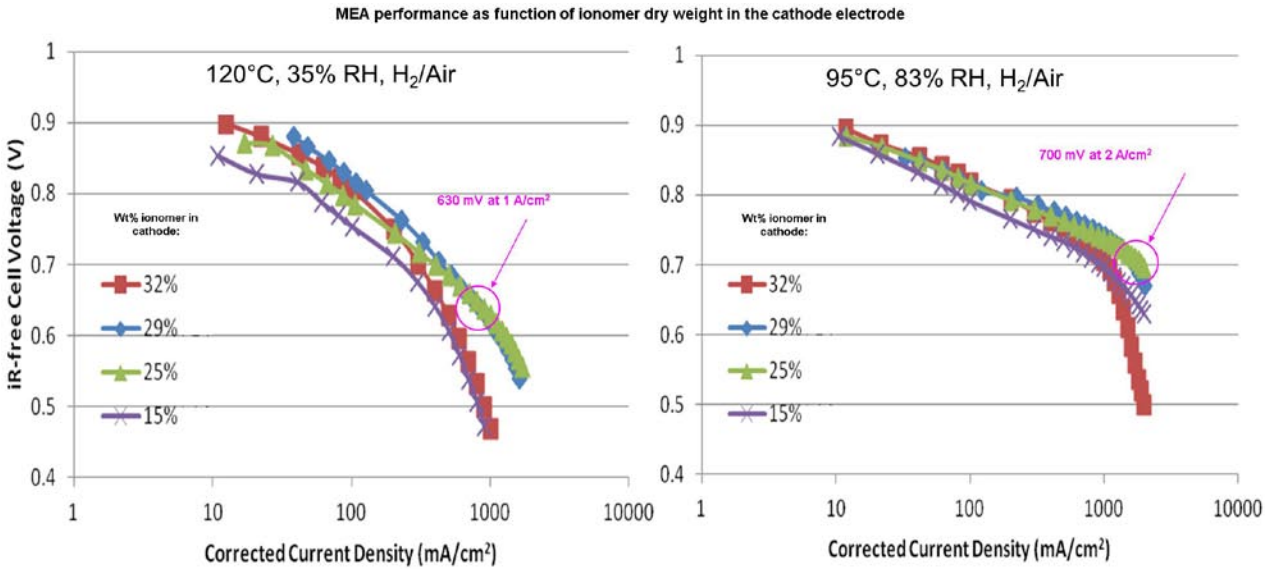

FIGURE 1. Re-optimization of MEA for mC^2 led to significantly improved performance

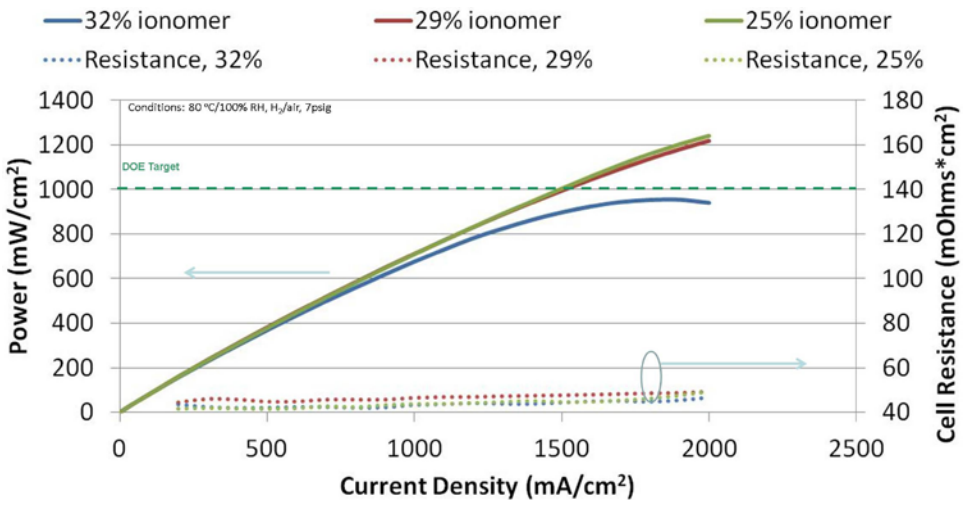

FIGURE 2. Electrode improvements led to higher power density

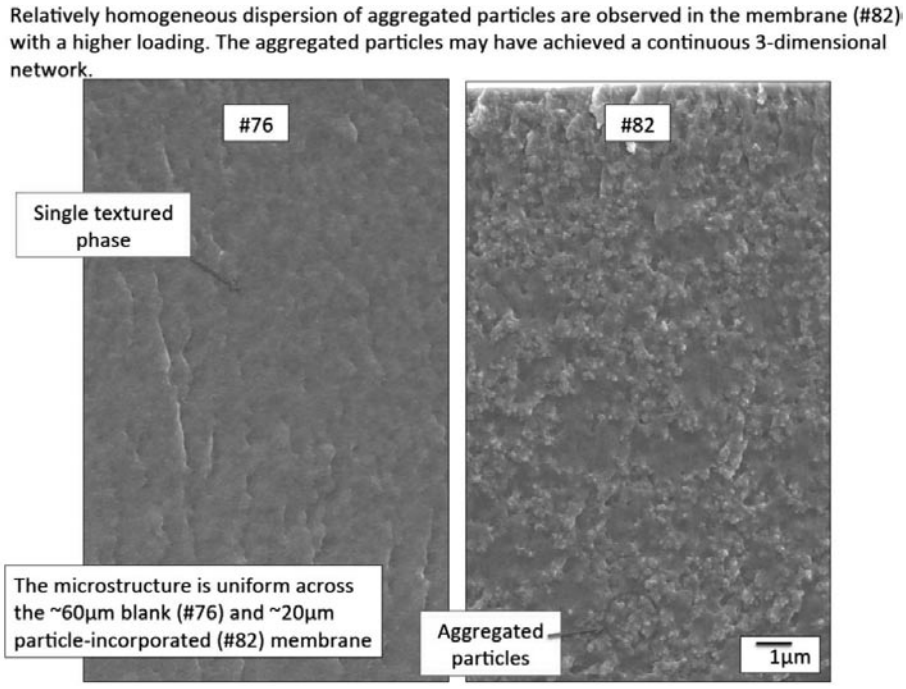

FIGURE 3. Achieved uniform distribution of additives in mC^2

25 wt% ionomer gives slightly higher performance than 29 wt%. Testing at 95°C gave similar results.

The three highest performing MEAs were then used to determine performance at rated power. As can be seen in Figure 2, the MEA with 25% ionomer in the cathode gave the highest power density, reaching 1,247 mW/cm^2 at 2,000 mA/cm^2. This result exceeds the DOE target by almost 25%.

The MEAs made by UCF using the improved mC^2 membrane survived UCF's 11-day test protocol (approved by DOE) without failures. This was enabled by improvements to the additive fabrication process. The superacid additive, which is designed to enhance the protonic conductivity of mC^2, was deposited onto the zeolite additive, which retains water in the membrane even at elevated temperature. This ensures immobilization of the superacid on the surface of the zeolite, were it is in direct contact with the ionomer, resulting in faster proton transfer and therefore enhanced membrane conductivity. Processing improvements led to uniform distribution of the additives throughout the mC^2, as can be seen in the scanning electron images in Figure 3. These

images were obtained by Dr. Kelly Perry and Dr. Karren More at the Oak Ridge National Laboratory. The left image shows the texture of the membrane without additives. The right image is that of an mC^2. It shows the additives in the form of nanometer-size aggregates, which may have achieved a continuous three-dimensional network. X-ray diffraction analysis showed that the nano-zeolite structure remained intact after superacid deposition.

The project's achievements to date are summarized in Table 2. A comparison of major DOE 2017 target parameters to the values measured by the project team and independently verified by UCF show that most performance targets have been met (indicated by a green check mark) and the remaining ones are approaching the target values.

Conclusions and Future Direction

An mC^2 membrane design for high temperature and low RH operation has been implemented to fabricate membranes and MEAs with enhanced performance at the DOE target conditions (Table 1). Accomplishments include:

- Re-optimized MEA for mC^2 with improved cathode electrodes incorporating advanced ionomer; incorporated in DOE high temperature membrane validation protocol implemented by UCF.
- Obtained record performance, especially at high current density, with the improved MEAs: 510 mV at 1 A/cm^2 at 120°C, 35% RH (Figure 1).
- Achieved high power density of 1,247 mW/cm^2 at rated power with the improved MEAs (Figure 2).
- Also met ASR, hydrogen cross-over and electrical resistance targets (Table 2).

TABLE 2. MEA Test Results Compared to DOE 2017 Targets

Characteristic	Units	DOE 2017 Target	FY11-12 Result
Area specific proton resistance[c] at:			
120°C and 40-80 kPa water partial pressure	Ohm cm^2	≤0.02	0.025
80°C and 25-45 kPa water partial pressure	Ohm cm^2	≤0.02	0.016 ✓
Maximum Hydrogen cross-over [a]	mA/cm^2	2	0.3 ✓
Minimum electrical resistance [b]	Ohm cm^2	1,000	2,860 ✓
Performance @ 0.8 V (¼ Power)	mA/cm^2	300	209
Performance @ rated power	mW/cm^2	1,000	1,247 ✓

* Values are at 80°C unless otherwise noted
[a] Measure in humidified H_2/N_2 at 25°C
[b] Measure in humidified H_2/N_2 using LSV curve from 0.4 to 0.6 V at 80°C
[c] Determined by subtracting contact resistances from cell current interrupt values

Future efforts should be directed towards more comprehensive characterization and improvement of mC^2 durability. These include mechanical and chemical stability to withstand continuous operation at elevated temperature and low relative humidity, as well as automotive cycling conditions. An intermediate temperature of 95°C has been suggested by car companies for the near-term.

FY 2012 Publications/Presentations

1. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2012 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 14–18, 2012.

References

1. DOE Multi-Year Research, Development and Demonstration Plan, Section 3.4 "Fuel Cells", http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf.

2. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", FY 2011 DOE Hydrogen and Fuel Cells Program Annual Progress Report, pages 688-691 (2011).