

## V.C.7 High-Temperature Membrane with Humidification-Independent Cluster Structure

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### 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  $\leq 120^\circ C$ : 0.1 S/cm; at room temperature: 0.07 S/cm; at  $-20^\circ C$ : 0.01 S/cm
- Membrane ASR: 0.02  $\Omega cm^2$

### FY 2011 Accomplishments

- Conductivity: Met DOE conductivity targets with polymer membrane and composite membrane: target of 0.1 S/cm (achieved  $>0.1$  S/cm).
- ASR: Met DOE membrane ASR target: 0.02  $\Omega cm^2$  (achieved 0.02  $\Omega cm^2$ ).
- Cross-over: Met DOE hydrogen cross-over target: 2 mA/cm<sup>2</sup> (achieved 0.48 mA/cm<sup>2</sup>).
- Polymer Development: Prepared chemically stabilized low EW co-polymer with increased molecular weight (for greater mechanical strength and durability).
- Additive Development: Synthesized zeolite with a mean particle size reduced by  $>60\%$  (30 nm compared to previously 80 nm) for improved dispersion and greater uniformity of ion-conducting clusters.
- Composite Membrane Fabrication: Integrated lower-cost protonic conductivity enhancer with 80% higher density of mobile protons.
- Membrane Electrode Assembly (MEA) Fabrication:
  - Improved process conditions for lower-EW polymer in collaboration with the University of Central Florida (UCF).
  - Fabricated more than half a dozen MEAs of up to 25 cm<sup>2</sup> active area for characterization testing (UCF).
- MEA Testing: MEA with 5% lower EW, chemically stabilized polymer in the electrodes comprehensively tested by UCF in 11-day cell test (DOE protocol).

### Fiscal Year (FY) 2011 Objectives

- Develop humidity-independent, thermally stable, low equivalent weight (EW) 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



### 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  $120^\circ C$ ). 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 goals for transportation fuel cells.

## Approach

The approach to address each of the DOE target parameters is summarized in Table 1. The emphasis in the past year has been to integrate a lower-cost protonic conductivity enhancer (di-valent superacid) into the composite membrane.

**TABLE 1.** Approach for the Composite Membrane

Target Parameter	DOE Target (2015)	Approach
Conductivity at: $\leq 120^{\circ}\text{C}$	0.1 S/cm	Multi-component composite structure, lower EW, additives with highly mobile protons
Conductivity at: Room Temp.	0.07 S/cm	Higher number of functional groups
Conductivity at: $-20^{\circ}\text{C}$	0.01 S/cm	Stabilized nano-additives
Inlet water vapor partial pressure	$< 1.5$ kPa	Immobilized cluster structure
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm <sup>2</sup>	Stronger membrane structure; functionalized additives
Area specific resistance	0.02 $\Omega\text{cm}^2$	Improved bonding capability for MEA
Cost	20 \$/m <sup>2</sup>	Simplified polymer processing
Durability with cycling	5,000 hours	Thermo-mechanically compliant bonds, higher glass transition temp.
Unassisted start from low temp.	$-40^{\circ}\text{C}$	Stabilized cluster structure design

## Results

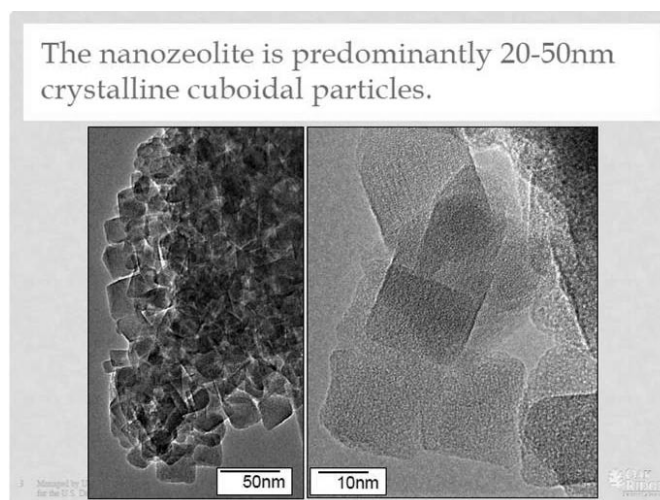
This year's efforts were focused on improving the performance and durability of the mC<sup>2</sup> membrane. The efforts were centered on improving the following mC<sup>2</sup> components:

- Co-polymer

- Water retention additive
- Protonic conductivity enhancer

The co-polymer provides the basic building block for the membrane. It is an advanced perfluoro sulfonic acid polymer (PFSA) with a short side chain. It has a higher density of functional groups (lower EW) compared to long side chain polymers, such as Nafion<sup>®</sup>. The lower EW leads to significantly higher proton conductivity. It comes without a reduction in mechanical strength, due to a higher crystallinity of the short side chain PFSA. Grades with higher molecular weight have been synthesized. This leads to greater polymer chain entanglement and therefore better mechanical properties. The higher molecular weight has the added benefit of improving the film forming properties of the polymer dispersion.

The membrane additives are designed to retain water at the low RH conditions and to enhance the composite membrane's proton conductivity by providing an alternate proton conduction path [2]. This path is designed to efficiently transport protons at high temperature as well as subfreezing conditions. Zeolite nanoparticles have been developed to retain water in the membrane. They have a high water uptake capacity without dimensional change, since the water is contained within the three-dimensional tunnel structure. Zeolite synthesis was improved, resulting in a reduction in mean particle size from about 80 nm to about 30 nm. The desired crystalline cuboidal structure of the particles was confirmed by transmission electron microscope (TEM) analysis, as shown in Figure 1. The analysis also confirmed a particle size of predominantly 20-50 nm. The TEM analysis was kindly provided by the Microscopy Group at Oak Ridge National Laboratory. Stability of the zeolite particles was analyzed by dynamic light scattering. Figure 2 shows a mean particle size of 33 nm, measured one year after zeolite synthesis.



**FIGURE 1.** Transmission Electron Microscopy of Zeolite Particles used as Water Retention Additive in mC<sup>2</sup>

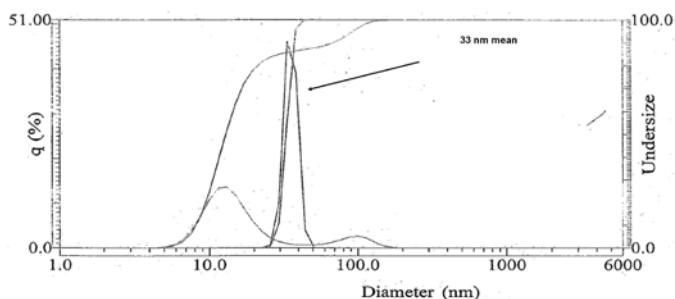


FIGURE 2. Demonstrated Long-Term (1 Year) Zeolite Particle Size Stability

To enhance the proton conductivity of the membrane, a novel superacid, developed in the previous year, was utilized in the mC<sup>2</sup> membrane. It has 80% greater density of highly mobile protons, to increase the transfer rate of protons through the membrane at all operating conditions.

**MEA Fabrication and Testing:** Membrane samples were supplied to UCF for characterization and MEA fabrication. UCF has been tasked by DOE to fabricate MEAs using membrane samples supplied by FCE, to independently validate their performance. A modified MEA fabrication process was developed, in order to ensure integrity of mC<sup>2</sup> membrane components. Using this process, several MEAs were fabricated by UCF, including B2, B3 and B7. Cell performance results of these MEAs at 120°C and low RH (35%) are shown in Figure 3. MEAs B2 and B3, made with short-side chain ionomer in the electrodes, had higher performance compared to a Nafion<sup>®</sup> reference MEA at practical current densities (300-1,000 mA/cm<sup>2</sup>). As expected, B2 and B3 had significantly lower cell resistance than the Nafion<sup>®</sup>-based MEA. B7 used a different ionomer in the electrodes. Compared to B2 and B3, it has 5% lower EW and is chemically stabilized. To better understand the performance of B7, a detailed performance analysis was carried out by UCF. It uses a method developed at the University of Connecticut [3] to calculate contributions of activation, membrane, electrode

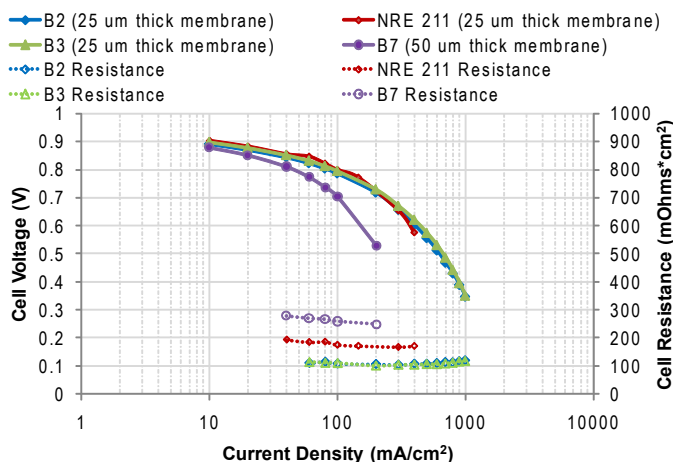


FIGURE 3. Cell Performance at 120°C: B2 and B3 have Lower Cell Resistance than NRE211

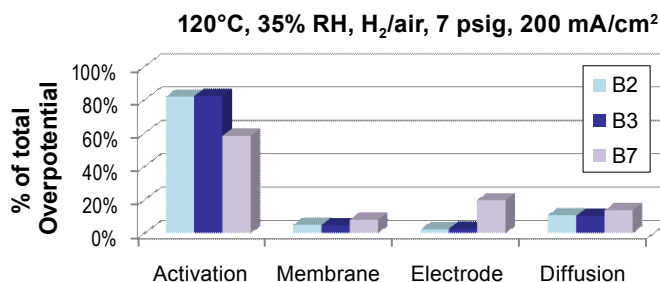


FIGURE 4. Fuel Cell Performance Analysis of Three Different MEAs

and diffusion to the cell’s overpotential. Data at 120°C and 35% RH, shown in Figure 4, indicates that B7 has increased electrode and diffusion resistance. This suggests a need to optimize the electrodes when using the lower EW, chemically stabilized ionomer. A study to look at the effect of ionomer content in the electrodes is underway at UCF.

TABLE 2. MEA Test Results Compared to DOE 2015 Targets

Characteristic	Units	Target 2015	B1	B2	B3	B7	NRE 211
Area specific proton resistance <sup>c</sup> at:							
120°C and 70 kPa water partial pressure	Ohm cm <sup>2</sup>	≤ 0.02	not determined	0.08	0.08	0.23	0.15
80°C and 38 kPa water partial pressure	Ohm cm <sup>2</sup>	≤ 0.02	not determined	0.02	0.02	0.05	0.02
Maximum Hydrogen cross-over <sup>a</sup>	mA / cm <sup>2</sup>	2	not determined	1	0.95	0.48	0.76
Minimum electrical resistance <sup>b</sup>	Ohm cm <sup>2</sup>	1,000	not determined	1,200	800	500	2100
Performance @ 0.8V (¼ Power)	mA / cm <sup>2</sup>	300	not determined	104	177	150	113
	mW / cm <sup>2</sup>	250	not determined	84	142	120	91
Performance @ rated power	mW / cm <sup>2</sup>	1,000	not determined	334	567	482	363

\* Values are at 80°C unless otherwise noted

<sup>a</sup> Measure in humidified H<sub>2</sub>/N<sub>2</sub> at 25°C

<sup>b</sup> Measure in humidified H<sub>2</sub>/N<sub>2</sub> using linear sweep voltammetry curve from 0.4 to 0.6 V at 80°C

<sup>c</sup> Determined by subtracting contact resistances from cell current interrupt values

All three MEAs tested by UCF (B2, B3, B7) passed comprehensive 11-day tests at UCF (per DOE-approved protocol). B7, which utilized chemically stabilized polymer, had the lowest hydrogen cross-over at the end of the test with 0.5 mA/cm<sup>2</sup>. This is well below the DOE 2015 target of 2 mA/cm<sup>2</sup>. UCF post-test analysis showed good integrity of the MEA; no pinholes were detected.

A comparison of the performance of the MEAs to the DOE 2015 targets is shown in Table 2. The parameters that already meet the DOE 2015 targets are highlighted in green. The remaining parameters show good progress towards the DOE targets (highlighted in yellow).

## Conclusions and Future Direction

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

- Synthesized water retaining additive (zeolite) with 60% lower particle size (Figure 1).
- Validated long-term particle size stability (Figure 2).
- Demonstrated significantly lower cell resistance of MEAs made with the advanced materials (Figure 3) meeting the DOE ASR target at 80°C (Table 2).
- Met the DOE hydrogen cross-over and electrical resistance targets (Table 2).
- Identified a need for electrode optimization using the improved ionomer (Figure 4).

In the remaining months of the current project we will continue the composite membrane development, with an emphasis on meeting the remaining DOE target parameters (highlighted in yellow in Table 2).

## FY 2011 Publications/Presentations

1. L. Lipp, “High Temperature Membrane With Humidification-Independent Cluster Structure”, 2011 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 9–13, 2011.

## 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](http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf).
2. L. Lipp, “High Temperature Membrane With Humidification-Independent Cluster Structure”, 2008 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, Arlington, VA, June 11, 2008.
3. M.V. Williams, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc., Vol. 152 (3) A635-A644 (2005).