

## V.D.8 High Temperature Membrane With Humidification-Independent Cluster Structure

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### 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 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 composite membrane ( $mC^2$ ) 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  $\Omega cm^2$

### Accomplishments

- Conductivity: Met DOE conductivity targets (both in-plane and through-plane).
- ASR: Met DOE membrane ASR target.
- Cross-Over: Almost met DOE hydrogen cross-over target.
- Polymer Development: Prepared three batches of improved low equivalent weight (EW) co-polymer, with increased molecular weight for higher mechanical strength.
- Additive Development:
  - Identified an improved protonic conductivity enhancer with 80% higher density of mobile protons.
  - Synthesized the improved protonic conductivity enhancer in 25 g batch size.
  - Fabricated and characterized nine additive batches (water retaining and proton conducting).
- Cost Reduction: Reduced the cost of the protonic conductivity enhancer by >80% by reducing cost of starting materials by 93%, reducing the number of processing steps from 12 to 7 and increasing the batch size by 25x.
- Composite Membrane Fabrication:
  - Developed new solvent system for better compatibility with the improved protonic conductivity enhancer.
  - Incorporated additives into  $mC^2$  at the nano-scale, without significant agglomeration.
  - Synthesized over 13 batches of  $mC^2$ .
- Membrane Characterization:
  - Measured in-plane conductivity of over 18 membrane samples.
  - Measured through-plane conductivity of two membrane samples.
- Membrane Electrode Assembly (MEA) Fabrication:

- Developed process compatible with mC<sup>2</sup> components in collaboration with the University of Central Florida (UCF).
- Fabricated >8 MEAs of up to 25 cm<sup>2</sup> active area (UCF).
- MEA Testing: Two MEAs comprehensively tested by UCF in 11-day cell tests (DOE protocol).



## 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 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 develop and integrate additives with a greater density of highly mobile protons.

## Results

This year's efforts were focused on improving the performance and lowering the cost of the multi-component composite membrane, named mC<sup>2</sup>. The efforts were centered on improving the following mC<sup>2</sup> components:

- Co-polymer
- Water retention additive
- Protonic conductivity enhancer

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

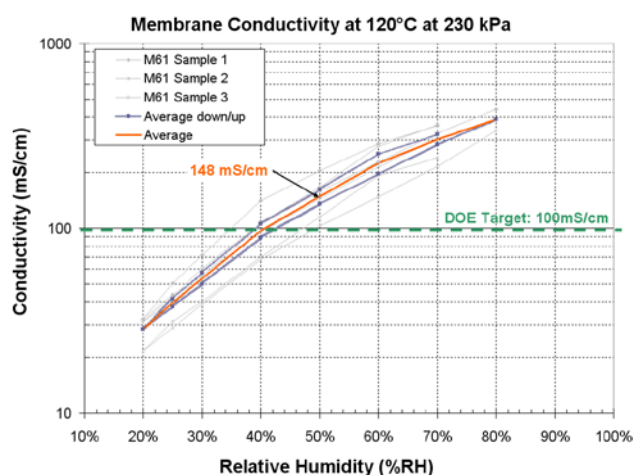
Target Parameter	DOE Target (2015)	Approach
Conductivity at: ≤120°C	0.1 S/cm	Multi-component composite structure, lower EW, additives with highly mobile protons
Room Temperature	0.07 S/cm	Higher number of functional groups
-20°C	0.01 S/cm	Stabilized nano-additives
Inlet water vapor partial pressure	<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 Ωcm <sup>2</sup>	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°C	Stabilized cluster structure design

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. During this year, the molecular weight was increased. 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. To enhance the proton conductivity of the membrane, a novel superacid was developed. It has highly mobile protons to increase the transfer rate of protons through the membrane. During the past year, its further development was focused on increasing proton density and lowering the cost.

**mC<sup>2</sup> Conductivity:** The composite membrane concept has been validated by demonstrating conductivity exceeding the DOE conductivity target at 120°C (Figure 1). This data was obtained with mono-valent protonic conductivity enhancer. An improved, di-valent conductivity enhancer was identified, which contains two highly mobile protons per molecule. Compared to the mono-valent conductivity enhancer, the molecule size is only about 10% larger. Therefore, the proton density is increased by 80%. The conductivity of a composite membrane incorporating the water retaining additive as well as the improved conductivity enhancer is expected to exceed that shown in Figure 1. The benefits of the improved conductivity enhancer are summarized in Table 2.

**mC<sup>2</sup> Fabrication:** Due to the altered chemistry of the improved conductivity enhancer, the mC<sup>2</sup> fabrication process used successfully for the mono-valent conductivity enhancer resulted in undesirable additive interaction and a poor quality membrane. This made



**FIGURE 1.** Composite Membrane with Mono-Valent Protonic Conductivity Enhancer Meets DOE Conductivity Target

**TABLE 2.** Improvements in Proton-Conducting Additive for mC<sup>2</sup>

Parameter	Baseline	Improved	Positive Impact
No. of mobile protons per molecule	one	two	Enhanced protonic conductivity
Thermal Stability	~200°C	300+°C	Greater robustness during synthesis of mC <sup>2</sup> and MEA
Processing Cost			
- Batch size	1 g	25 g	Improve process control for scale-up Lower processing cost Reduced raw material cost
- No. of steps	12	7	
- Precursor	expensive	lower cost	

changes to the solvent system and processing conditions necessary. The requirements of the solvent system include: (i) ability to fully disperse the co-polymer as well as the nano-additives, (ii) prevent agglomeration of the nano-additives, (iii) favorable film forming properties, (iv) evaporate from the membrane film in a reasonably short period of time (minutes to hours) without affecting additive dispersion and, (v) do not affect the mobility of the protons in the additives or the co-polymer. Since the processing steps have to be compatible with all membrane components, the changes in conductivity enhancer and solvent system have also required changes in the processing conditions.

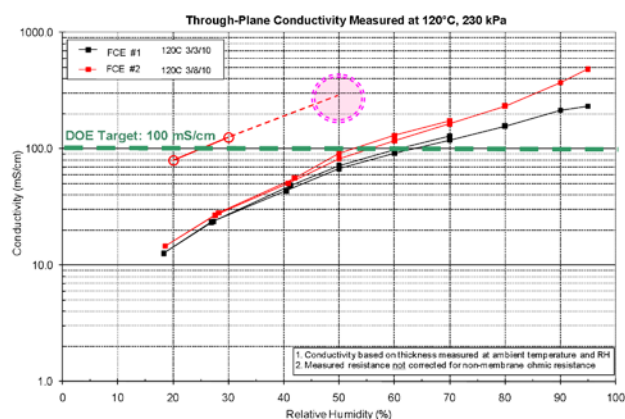
In order to facilitate mC<sup>2</sup> fabrication, the following improvements were made:

- Increased molecular weight of co-polymer to enhance chain entanglement and additive immobilization.
- Synthesized dispersion with 3x higher polymer content, to lower the solvent content and increase viscosity for improved film formation.
- Eliminated hot acid treatment step from mC<sup>2</sup> processing to avoid stability issues of the nano-additives.

While the membrane quality and conductivity have significantly improved after these changes, a stability problem has been identified. Further optimization of the solvent system and processing conditions are necessary to realize the full potential of the improved conductivity enhancer and obtain the expected conductivity results exceeding those shown in Figure 1. A systematic optimization study is underway. It includes microstructural analysis of the components and mC<sup>2</sup>, in order to detect interactions at the nano-scale level and guide the materials and processing changes.

**Membrane Characterization:** Membrane samples were supplied to UCF for characterization. Through-plane conductivity and resistance measurements for these membrane samples were obtained by UCF from its team member Scribner Associates, Inc. Figure 2 shows the through-plane conductivity at 120°C as a function of RH. The solid squares represent the conductivity before correction for non-membrane ohmic resistance. It approaches the DOE 2015 conductivity target of 100 mS/cm at 50% RH. The estimated corrected conductivity for sample #2 at 30% RH is 122 mS/cm, shown by the red empty circle. The extrapolated corrected conductivity up to 50% RH is shown by the dashed line. It significantly exceeds the DOE target. The correction is based on Scribner's previous data obtained with Nafion<sup>®</sup> membranes.

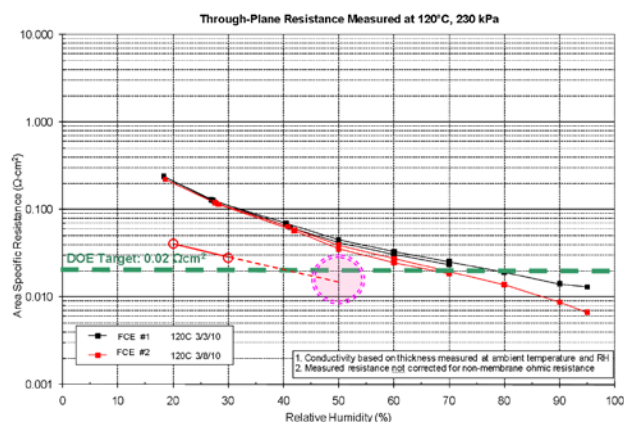
Through-plane membrane ASR measurements at 120°C are shown in Figure 3. The uncorrected resistance values are shown by the solid squares. The corrected ASR for sample #2 is shown by the



**FIGURE 2.** Membrane Through-Plane Conductivity Measured by Scribner Associates Meets the DOE Target

empty circles at 20 and 30% RH. When this data is extrapolated to 50% RH, it suggests that the membrane itself meets the DOE target. The ASR correction is based on Scribner's previous data obtained with Nafion® membranes. A study to determine the resistance contributions other than the membrane itself in the case of FCE's membrane is planned. It will allow estimating the (corrected) membrane conductivity and ASR with greater accuracy.

**MEA Fabrication and Testing:** UCF has been tasked by DOE to fabricate MEAs using membrane samples supplied by FCE, to independently validate their performance. The MEA fabrication process developed by UCF was adapted for the mC<sup>2</sup>, to avoid ion exchange with metal ions that could potentially have an adverse effect on additive stability. The modified process also significantly reduces the number of processing steps and processing time (lower cost). Using this process, MEAs were successfully fabricated by UCF, as shown in the inset in Figure 4. This MEA was fabricated using a 25  $\mu\text{m}$  thick baseline membrane and matching copolymer in the electrodes. The MEA was subjected to an 11-day cell test protocol developed by UCF in collaboration with DOE. The performance at 120°C, 35% RH and 7 psig on H<sub>2</sub>/air was over 600 mV, and about 750 mV at 95°C and 83% RH. The hydrogen cross-over was determined by linear sweep voltammetry, as shown in Figure 4. It meets the DOE 2015 target of 2 mA/cm<sup>2</sup> at 95°C and closely approaches it at 120°C. It can be seen that the hydrogen cross-over did not increase (day 6 vs. day 4) after testing at 120°C (day 5). The area specific cell resistance was 0.045  $\Omega\text{cm}^2$  at 95°C, 83% RH and 0.105  $\Omega\text{cm}^2$  at 120°C, 35% RH. It includes contributions from membrane, electrodes, gas diffusion layers and interfacial resistances between all cell components. The increase in cell resistance with increasing temperature and decreasing RH suggests that incorporating the additives developed in this program for the membrane into the electrodes has the potential



**FIGURE 3.** Membrane through-plane resistance measured by Scribner Associates approaches DOE target before correcting for non-membrane ohmic resistance, and meets it after correction.

to lower the overall cell resistance and increase the cell performance, especially at high temperature and low RH.

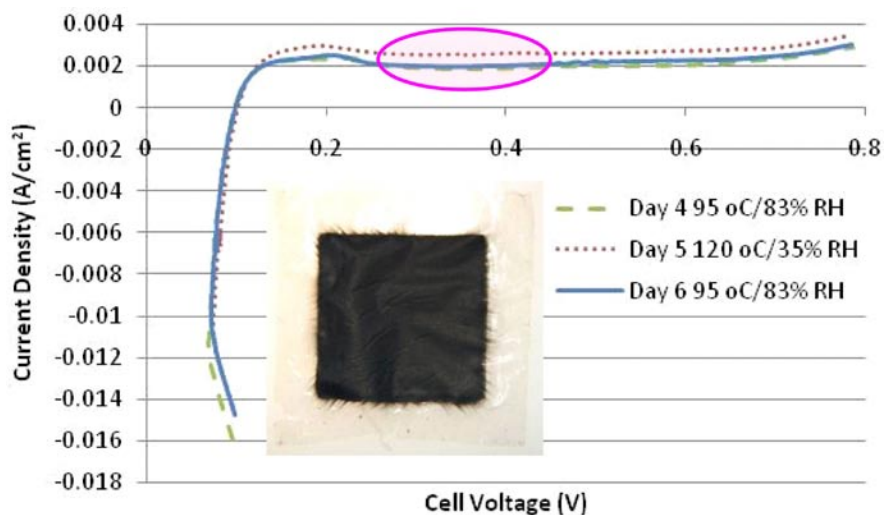
## Conclusions and Future Direction

A multi-component composite 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:

- Validated mC<sup>2</sup> concept by demonstrating conductivity in excess of the DOE targets via in-plane (Figure 1) and through-plane measurements (Figure 2).
- Identified and synthesized a protonic conductivity enhancer with 80% greater proton density and lower cost (Table 2).
- Measured membrane ASR that is estimated to meet the DOE 2015 target (Figure 3).
- Determined that the hydrogen cross-over of a 25  $\mu\text{m}$  membrane almost meets the DOE 2015 target (Figure 4).

In the final year of the current project we will continue the composite membrane development, with an emphasis on the following activities:

- Continue to develop advanced polymer dispersions with low equivalent weight (higher number of functional groups) and high molecular weight.
- Optimize and further simplify integration of the advanced additives.
- Continue to compare membrane conductivity and area specific resistance to the DOE 2015 targets (UCF).



**FIGURE 4.** Hydrogen cross-over of MEA fabricated and tested by UCF (inset) almost meets the DOE target.

- Perform fuel cell testing at 95°C and 120°C.
- Perform MEA characterization and durability testing per DOE protocol (UCF).

### FY 2010 Publications/Presentations

1. L. Lipp, "High Temperature Membrane With Humidification-Independent Cluster Structure", 2010 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 7-11, 2010.

### 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.