

# V.D.6 NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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Contract Number: DE-FG36-06GO16030

Subcontractor:

Eric Fossum, Wright State University, Dayton, OH

Start Date: March 1, 2006

Projected End Date: February 28, 2011

## Objectives

- Fabricate a new class of nanocapillary network (NCN) proton conducting membranes using different sulfonated polymers.
- Add sulfonated molecular silica to the polymers prior to fiber spinning.
- Characterize the membranes in terms of swelling, proton conductivity, thermal/mechanical stability, and gas permeability.
- Optimize the membrane structure (fiber diameter, mat density, polymer ion-exchange capacity, choice of impregnation polymer, etc.) to achieve the DOE's technical targets for membranes.

## 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
- (B) Cost
- (C) Performance

## Technical Targets

This project is focused on the fabrication and characterization of a new class of proton conducting membranes for high temperature hydrogen/air fuel cells. The technical targets of this project are listed in Table 1 for 2010.

**TABLE 1.** Progress towards Meeting Technical Targets for Membranes for Transportation Applications

Characteristic	Units	2010 DOE Targets	2010 Project Status
Inlet Water Vapor Pressure	kPa	< 1.5	< 1.5
Oxygen Cross-Over	mA/cm <sup>2</sup>	2	
Hydrogen Cross-Over	mA/cm <sup>2</sup>	2	2
Membrane Conductivity at Inlet Water Vapor Partial Pressure			
• Operating Temperature	S/cm	0.10	0.107 <sup>1</sup>
• 20°C	S/cm	0.07	
• -20°C	S/cm	0.01	
Operating Temperature (T)	°C	< 120	120
Area Specific Resistance	Ohm-cm <sup>2</sup>	0.03	0.10
Durability with Cycling			
• At operating T > 80°C	hours	~2,000	

<sup>1</sup> Proton conductivity at 120°C and 50% relative humidity (RH) – data from Bekktech LLC

## Accomplishments

- A new nanofiber membrane fabrication method was developed, where a separate impregnation step for the inert (uncharged) polymer was eliminated and where Norland Optical Adhesive 63 was replaced with a commercially-available polyphenylsulfone.
- Fabricated nanofiber composite membranes via a dual-fiber electrospinning, where perfluorosulfonic acid (PFSA) proton conducting nanofibers and uncharged polyphenylsulfone (PPSU) nanofibers are simultaneously electrospun.
- Developed two methods for processing the dual fiber mat into a fuel cell membrane: (i) “melting” PFSA ionomer around a PPSU nanofiber mat (where the nanofiber mat acts as a reinforcement)

and (ii) melting of the PPSU around a PFSA nanofiber mat. Membranes were prepared from method (i) using DuPont's Nafion<sup>®</sup> and 825 equivalent weight (EW) PFSA from 3M Corporation and from method (ii) using Nafion<sup>®</sup> PFSA.

- The new nanofiber membranes were characterized in terms of proton conductivity, water swelling, and mechanical properties. They were also tested in a H<sub>2</sub>/air fuel cell (initial fuel cell performance and durability testing).
- Work began on electrospinning mixtures of PFSA and sulfonated polyphenylene (as a replacement for sulfonated octaphenyl polyhedral oligomeric silsesquioxanes, sPOSS).
- Nafion<sup>®</sup> hollow bore nanofibers were electrospun in an attempt to improve membrane water retention at low humidity via capillary condensation in the hollow fiber bore.
- Work began on electrospinning Pt/C-loaded nanofibers for fuel cell electrodes.



## Introduction

Proton exchange membrane (PEM) hydrogen/air fuel cell operation with lightly humidified gases at 120°C would be highly advantageous with regards to heat rejection from a fuel cell stack, compatibility with automotive radiators, tolerance to CO impurities in the hydrogen gas stream, and fast electrode kinetics. For PEM fuel cell operation at T ≤ 80°C and high RH conditions, PFSA proton conductors (e.g., Nafion<sup>®</sup>) are the membrane material of choice due to their high conductivity and chemical/mechanical stability. Unfortunately, the conductivity of PFSA membranes drops dramatically at T > 100°C under low humidity conditions [1] due to an insufficient number of membrane-phase water molecules for protons to dissociate from sulfonic acid sites, a loss of percolation pathways for proton movement, and structural changes in the polymer which cause membrane pores to collapse.

In order to overcome the limitations of existing membrane materials, a new approach to fuel cell membrane design and fabrication has been developed, where a three-dimensional interconnected network of proton-conducting polymer nanofibers/nanocapillaries is embedded in an inert/impermeable polymer matrix. The nanocapillary network is composed of a high ion-exchange capacity sulfonic acid polymer to ensure high water affinity and a high concentration of protogenic sites. The inert (hydrophobic) polymer matrix controls water swelling of the nanofibers/nanocapillaries and provides overall mechanical strength to the membrane. First-generation membranes [2] were made using sulfonated poly(arylene ether sulfone) with sPOSS to

further boost conductivity. Norland Optical Adhesive 63 was employed as the inert embedding polymer. Second-generation membranes were fabricated with nanofibers containing 850 EW PFSA (from 3M Corporation) with/without sPOSS [3]. Films with sPOSS met the DOE's Year 3, 3<sup>rd</sup> quarter Go/No-Go conductivity target of 100 mS/cm at 120°C and 50% RH.

## Approach

Membranes were prepared by a newly developed dual nanofiber electrospinning technique using either 1,100 EW Nafion<sup>®</sup> or 825 EW PFSA from 3M Corporation as the proton conducting material and Radel<sup>®</sup> R-5500NT PPSU from Solvay Advanced Polymers LLC as the inert/uncharged polymer. PFSA materials were electrospun using a high molecular weight (MW) polymeric carrier, 300,000 MW poly(ethylene oxide) (PEO) for Nafion<sup>®</sup> or 400,000 MW PEO for 3M 825 PFSA (where the PEO concentration was 1-2 wt% of the total polymer content). PFSA/PEO and PPSU nanofibers were electrospun simultaneously using two separate spinnerets. Suitable post-treatment converted the dual-fiber mats into fully dense and defect-free membranes, while maintaining the nanofiber morphology of one polymer component. Membranes were made where: (i) PFSA nanofibers were surrounded by an inert (uncharged) PPSU matrix and (ii) inert (uncharged) PPSU nanofibers were surrounded by PFSA ionomer. After processing, membranes were boiled in acid and then water to remove the PEO carrier polymer. Both membrane structures were fabricated, but characterization work was only performed on the morphology where PFSA was surrounding a PPSU nanofiber mat. Membranes were evaluated in terms of: (i) in-plane proton conductivity (in room temperature water), (ii) in-plane volumetric and gravimetric swelling in boiling water, (iii) mechanical properties of dry films (from stress-strain curves), and (iv) H<sub>2</sub>/air fuel cell tests (after converting the membrane into a membrane-electrode-assemblies).

## Results

**Preparing Dual Fiber Electrospun Mats with PFSA and PPSU** – High quality dual fiber mats (Nafion<sup>®</sup>/PEO and PPSU nanofibers), of uniform thickness and fiber volume fraction were prepared, where approximately 70% of the fibers in the mat were composed of Nafion<sup>®</sup>/PEO. PFSA fibers were electrospun using a rotating drum collector, where the total polymer concentration in the electrospinning solution was 20 wt% (with a 99/1 PFSA/PEO wt ratio), the solution flow rate was 0.60 ml/hr, the electrospinning solvent was a 1-propanol/water mixture (2/1 vol ratio), the applied voltage was 4 kV, and the spinneret-to-collector distance was 5.5 cm. For PPSU electrospinning, a 25 wt% polymer solution was used with a N-methylpyrrolidone/

acetone solvent (4/1 vol ratio), with 7.5 kV potential, 8.5 cm spinneret-to-collector distance and a solution flow rate of 0.12 ml/hr. The mat was then compacted and annealed to produce a functional fuel cell membrane (a scanning electron microscope [SEM] image of the membrane is show in Figure 1).

**Membrane Evaluation** - Physical property data for a nanofiber composite membrane (PPSU nanofiber mat surrounded by Nafion® PFSA polymer) are contrasted with data for Nafion® 212 in Table 2 for a 60  $\mu\text{m}$  thick membrane containing 70 vol% PFSA nanofibers. Proton conductivity scaled linearly with PFSA content, but water swelling did not. Of particular note is the very low in-plane (areal) swelling (six-times lower than that of commercial Nafion®). As expected, the mechanical properties of the nanofiber composite membrane improved, as compared to Nafion® 212; the proportional limit stress of a dry nanofiber membrane at 80°C was 50% higher than that of Nafion®.

The low in-plane swelling of the nanofiber composite membrane improved membrane electrode



**FIGURE 1.** Freeze-fractured SEM cross-section of a Nafion®/PPSU nanofiber composite membrane (with Nafion® surrounding PPSU nanofibers; 70 vol% Nafion®).

**TABLE 2.** Conductivity, Swelling, and Mechanical Properties of a Nafion®-Based Nanofiber Composite Membrane and Nafion® 212

Membrane	Conductivity <sup>1</sup> [mS/cm]	In-Plane Swelling <sup>2</sup> (%)	Volumetric Swelling <sup>2</sup> (%)	Mass Swelling <sup>2</sup> (%)	Proportional Limit Stress <sup>3</sup> [MPa]
Nanofiber Composite <sup>4</sup>	66	6%	42%	31%	10.3
Nafion® 212	95	37%	75%	37%	6.8

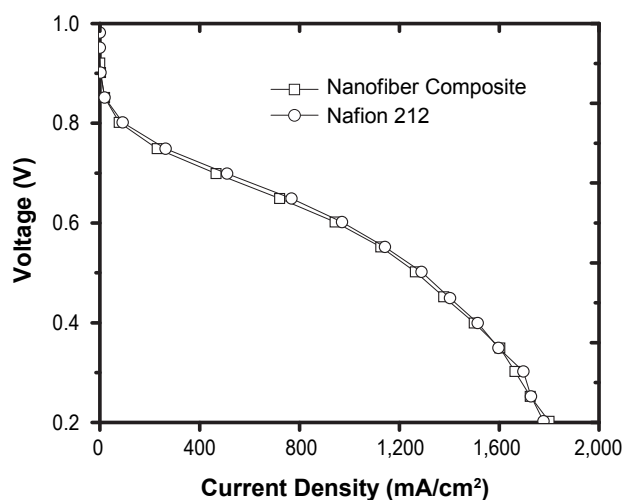
<sup>1</sup> In water at 23°C; <sup>2</sup> - In water at 100°C; <sup>3</sup> - Dry membrane at 80°C; <sup>4</sup> - 70 vol% Nafion® PFSA, 30 vol% polyphenylsulfone

assembly (MEA) in a fuel cell humidity cycling durability test. A 30  $\mu\text{m}$  thick nanofiber composite membrane was fabricated into a H<sub>2</sub>/air fuel cell MEA, using the decal method of electrode attachment (0.4 mg/cm<sup>2</sup> Pt loading for the anode and cathode with 30% Nafion® binder content). Voltage-current fuel cell performance curves (5 cm<sup>2</sup> MEA) at 80°C with fully humidified feed gases are shown in Figure 2. The performance of the nanofiber membrane MEA is very good and essentially identical to that of Nafion® 212. To evaluate durability, a 25 cm<sup>2</sup> MEA was subjected to an open circuit voltage (OCV) humidity cycling experiment (80°C with repeated cycling of 2 minutes 100% RH H<sub>2</sub> and air and then 2 minutes 0% RH H<sub>2</sub> and air). The OCV was monitored with time during humidity cycling and the hydrogen crossover was periodically measured in situ at 100% RH using a standard limiting current technique [4]. Durability results are shown in Figure 3. With a failure criteria defined as a drop in the OCV below 0.8 volts, it was found that Nafion® 212 failed after 546 hours whereas the nanofiber composite MEA failed after 842 hours (a 54% increase in lifetime vs. Nafion® 212). There was a dramatic increase in hydrogen crossover current density when the OCV dropped below 0.8 V, from 2 mA/cm<sup>2</sup> to 13 mA/cm<sup>2</sup>.

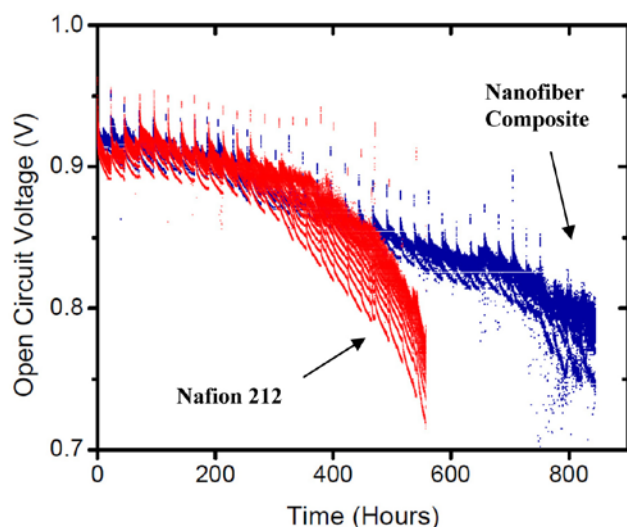
## Conclusions and Future Work

### Conclusions

- Norland Optical Adhesive was replaced by polyphenylsulfone as the inert/uncharged component in nanofiber composite membranes.



**FIGURE 2.** H<sub>2</sub>/air fuel cell performance of a nanofiber composite membrane MEA and a Nafion® 212 MEA. The nanofiber composite was 30  $\mu\text{m}$  thick (dry). Fuel cell conditions: 80°C, fully humidified gases, 100 mL/min H<sub>2</sub> flow rate, 500 mL/min air flow rate.



**FIGURE 3.** An OCV fuel cell durability test with RH cycling at 80°C for a 25 cm<sup>2</sup> MEA (voltage in wet-state is shown). Cycling conditions: 2 minutes 100% RH H<sub>2</sub>/air, 2 minutes 0% RH H<sub>2</sub>/air. Fuel cell operating conditions: 125 mL/min H<sub>2</sub>, 500 mL/min air. The nanofiber composite membrane was 30 μm thick (dry thickness).

- A new method for nanofiber composite membrane fabrication was developed (dual polymer fiber electrospinning followed by mat processing) with the elimination of a separate polymer impregnation step.
- Using the dual fiber approach, two types of nanofiber composite membranes were made: (1) a PPSU nanofiber mat embedded in PFSA polymer and (2) a PFSA nanofiber mat embedded in (surrounded by) a PPSU matrix.
- The proton conductivity of the processed dual fiber mats (where the PFSA polymer is either DuPont's Nafion® or an 825 EW polymer from 3M Corporation) scaled linearly with the membrane ionomer content.
- All dual fiber membranes exhibited very low in-plane (areal) swelling and reduced volumetric and gravimetric swelling.
- MEAs fabricated from a nanofiber composite membrane (Nafion® polymer with a reinforcing mat of PPSU nanofibers) performed well in a H<sub>2</sub>/air fuel cell at 80°C and 100% RH. The fuel cell polarization curve (power output) of a 30 μm thick composite membrane was identical to that of commercial Nafion® 212.
- The durability of MEAs made with a nanofiber composite membrane was significantly improved, as compared to Nafion® 212 (a 70% increase in MEA lifetime, as determined from OCV humidity cycling tests).

## Future Work

- Prepare and test nanofiber composite membranes with PFSA + sulfonated polyphenylene + polyphenylsulfone (using the dual fiber electrospinning approach).
- Examine different inert/uncharged polymers
- Prepare and test MEAs with nanofiber network composite membranes.
- Investigate and test electrospun nanofiber fuel cell electrodes (focus on the cathode).

## Patents

1. P.N. Pintauro, P. Mather, and R. Wycisk, "Fiber Network Membrane," U.S. utility patent (filed 2009).

## FY 2010 Publications/Presentations

1. K.M. Lee, J. Choi, R. Wycisk, P.N. Pintauro, and P.T. Mather, "Nafion Nanofiber Membranes," in Proton Exchange Membrane Fuel Cells 9, *Electrochemical Society Transactions*, **25(1)**, 1451-1458 (2009).
2. J. Choi, K.M. Lee, R. Wycisk, P.N. Pintauro, and P.T. Mather, "Sulfonated Polysulfone/POSS Nanofiber Composite Membranes for PEM Fuel Cells," *J. Electrochem. Soc.*, **157**, B914-B919 (2010).
3. J. Choi, K.M. Lee, R. Wycisk, P.N. Pintauro, and P.T. Mather, "Nanofiber Composite Membranes with Low Equivalent Weight Perfluorosulfonic Acid Polymers," *J. Mater. Chem.* 2010, DOI: 10.1039/C0JM00441C.
4. J.M. Lee, J. Choi, R. Wycisk, P.N. Pintauro, and P.T. Mather, "Perfluorosulfonic Acid Nanofiber Membranes" presented at the PEM Fuel Cell Symposium, Electrochemical Society Fall Meeting, Vienna, Austria, October 2009.
5. Peter N. Pintauro, "New Membrane Morphologies for Improved Fuel Cell Operation," invited seminar, Department of Chemical Engineering and Materials Science, Michigan State University, February 2010.
6. Peter N. Pintauro, "New Membrane Morphologies for Improved Fuel Cell Operation," invited seminar, Department of Chemical Engineering, University of Virginia, March 2010.
7. Peter N. Pintauro, "New Membrane Morphologies for Improved Fuel Cell Operation," invited seminar, Department of Chemical Engineering, Virginia Tech, April 2010.
8. Jason Ballengee, Peter N. Pintauro, Jonghyun Choi, Ryszard Wycisk and Kyung Min Lee, "The Use of Nanofiber Structures in Composite Fuel Cell Membranes," invited talk, Materials Research Society Meeting, San Francisco, April 2010.

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3. Choi, J., Lee, K.M., Wycisk, R., Pintauro, P. N., and Mather, P. T., *J. Mater. Chem.* (2010) DOI: 10.1039/C0JM00441C.
4. Tang, H., Peikang, S., Jiang, S. P., Wang, F., Pan, M., *J. Power Sources*, **170**(1), 85 (2007).