V.D.9 NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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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 proton conductivity target.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure 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 in terms of a Year 2 (3rd quarter) milestone and a Year 3 (3rd quarter) Go/No-Go target.

Accomplishments

- Developed a method for electrospinning nanofiber mats composed of perfluorosulfonic acid (PFSA) polymer, where the PFSA polymer was co-spun with a small amount of high molecular weight (MW) poly(ethylene oxide) (PEO) or poly(acrylic acid) (PAA).
- Fabricated mats from 1100 equivalent weight (EW) Nafion® and from low EW 3M Corp. PFSA polymers (733 EW and 825 EW).
- Fabricated PFSA nanofiber mats with an average fiber diameter in the range of 200 nm–6 μm.
- Developed procedures for converting electrospun PFSA mats into nanofiber network composite membranes (polymer annealing and interfiber welding, mat compaction, and embedding with inert polymer).
- Performed preliminary membrane characterization experiments (proton conductivity as a function of temperature and relative humidity [RH] and mechanical property tests).
- Prepared impregnated nanofiber membranes where the nanofibers were composed of 825 EW PFSA polymer (from 3M Corp.) with sulfonated octaphenyl polyhedral oligomeric silsesquioxanes (sPOSS) from Michigan Molecular Institute.
- Determined the proton conductivity of membranes containing 825 EW PFSA + sPOSS and sent samples out for independent conductivity testing.

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

Characteristic	Units	2007 DOE Milestone (Year 2, 3Q)	2010/2015 DOE Target (Year 3, 3Q)	2007 Status for NCN Membranes	2008 Status for NCN Membranes
Inlet water vapor pressure	kPa	50	<1.5	50	<1.5
Oxygen cross-over	mA/cm^2	5	2	0.01[1]	
Hydrogen cross-over	mA/cm^2	5	2		

Membrane Conductivity at inlet water vapor partial pressure
  Operating Temp
  20°C
  -20°C
	S/cm
	S/cm
	S/cm
		0.10
		0.07[1]
		0.01
			0.10
			0.07
			0.01
				0.072[2]	0.107[3]

Operating temperature	°C	<80	≤120	30	120
Area specific resistance	Ohm-cm^2	0.03	0.02	0.069	0.10

Durability with Cycling
  At operating T <80°C
  At operating T >80°C
	hours
	hours
		~2,000	5,000
			2,000 (5,000 for 2015)		

[1] at 25°C and 50% relative humidity (RH)
[2] Proton conductivity at 30°C and 80% RH – data from Bekktech LLC
[3] Proton conductivity at 120°C and 50% RH – data from Bekktech LLC

- The proton conductivity of a nanofiber membrane with 825 EW PFSA + sPOSS met the DOE 2008 Go/No-Go target of 0.10 S/cm at 120°C and 50% RH.

✧   ✧   ✧   ✧   ✧

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 faster electrode kinetics. For PEM fuel cell operation at T ≤80°C and high RH conditions, PFSA proton conductors (e.g., Nafion®) are the membrane material of choice due to their high conductivity and chemical/mechanical stability [1]. Unfortunately, the conductivity of PFSA membranes drops dramatically at T >100°C under low humidity conditions [2] 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 is being 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 were created using sulfonated poly(arylene ether sulfone) (sPEAS) for the nanofibers with sPOSS to further boost the conductivity and Norland Optical Adhesive 63 (NOA 63) as the inert embedding polymer [3]. The resulting membrane had a proton conductivity of 72 mS/cm at 30°C and 80% RH (measured by Bekktech), which met the 2007 DOE target. These membranes, however, did not meet the Year 3, 3rd quarter conductivity goal of 100 mS/cm at 120°C and 50% RH. Consequently, sPAES was replaced by a low EW PFSA polymer.

Approach

To achieve the Go/No-Go target conductivity, NCN membranes were prepared with electrospun nanofibers composed of PFSA, as a replacement for sPAES. 1100 EW Nafion® and low EW (733 and 825 EW) 3M Corp. PFSA polymers were examined. Nanofiber mats were also prepared from a mixture of 825 EW polymer with sPOSS (25 and 35 wt%). After electrospinning, the mats were processed into ion-exchange membranes by: (i) annealing the fibers at 140°C for 5 minutes (during annealing, intersecting fibers were welded to one another to create a 3-dimensional fiber network), (ii) compacting the mats (at 10,000 psi for five seconds) to increase the fiber volume fraction to 0.70-0.75, and (iii) imbibing an inert polymer, NOA 63, into the mats. The resulting membranes were evaluated by measuring in-plane proton conductivity as a function of temperature and RH.

Results

Preparing Electrospun Mats with PFSA Polymer – PFSA polymer with an EW of 825 was electrospun, yielding high quality nanofiber mats of uniform thickness and fiber volume fraction. Electrospinning was accomplished by adding a small amount of a high molecular weight, water soluble polymer to the spinning solution, either PEO or PAA. Fibers were electrospun with a very small amount of the dopant polymer, either 0.3 wt% PEO (10^6 MW) or 5 wt% PAA (450,000 MW), where the total polymer concentration in the electrospinning solution was 15 wt% and the electrospinning solvent was a 1-propanol/water mixture (2:1 weight ratio). For PFSA/PEO mats, the electrospinning conditions were 3 kV potential, 6 cm spinneret-to-collector distance, and 0.50 mL/h polymer solution flow rate. Scanning electron microscope (SEM) surface images of electrospun 825 EW PFSA mats are shown in Figure 1, for three different PEO dopant concentrations. An undesirable bead-on-fiber morphology was produced when the PEO concentration was decreased to 0.2 wt%. 825 EW PFSA was also cospun with PAA, with and without sPOSS. SEM images of the resulting nanofiber mats are shown in Figure 2, where the PFSA/sPOSS/PAA mat had a fiber composition of 60 wt% PFSA + 35 wt% sPOSS + 5 wt% PAA, an average fiber diameter of 247 nm, and a fiber volume fraction of 0.21.

Nanofiber Network Membrane Preparation - PFSA/PEO, PFSA/PAA, and PFSA/sPOSS/PAA nanofiber mats were first annealed at 140°C for 5 minutes. During annealing, intersecting fibers were welded to one another (see Figure 3). After annealing, there was a modest increase in the volume fraction of fibers in the mat (from about 0.20 to about 0.30). The annealed/welded mat was compacted further at 10,000 psi for 5 seconds to increase the fiber volume to 0.70-0.75. NOA 63 was then impregnated into the mat by immersion in liquid NOA with degassing under vacuum at 50°C for 30 minutes, removing the mat from the liquid and wiping excess NOA 63 from the mat surface, and exposing the mat to UV light (1 hour each side) in a nitrogen atmosphere. The final membranes had a dry thickness of approximately 100 μm.

Proton Conductivity of PFSA/sPOSS Nanofiber Network Membranes – In-plane proton conductivities of nanofiber network membranes were collected on a sample film 104 μm in thickness, where the nanofiber mat was composted of 60% 825 EW PFSA + 35 wt% sPOSS + 5 wt% PAA and the volume fraction of nanofibers was 0.74. Samples were tested in-house at 30°C and 80°C and duplicate membranes were sent to the University of Central Florida for independent conductivity measurements by Bekktech LLC (at 30°C, 80°C, and 120°C). The results are shown in Figure 4, where conductivity is plotted against RH for three

FIGURE 1. SEM surface images of nanofiber mats, made by cospinning 825 EW PFSA (from 3M Corp.) with 10^6 MW PEO (3,000x magnification). The PFSA/PEO weight ratio in the spinning solution is listed above each micrograph.

different temperatures. As can be seen, the proton conductivity of the nanofiber membrane was very high and met (slightly exceeded) the DOE Go/No-Go target of 100 mS/cm at 120°C and 50% RH.

Conclusions and Future Directions

Conclusions

- Electrospun nanofiber mats were fabricated from low EW, high ion exchange capacity PFSA polymer
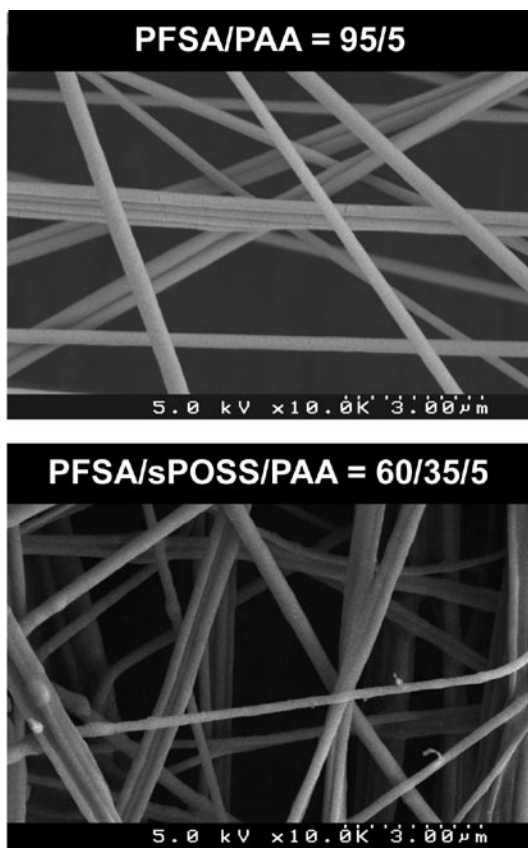
FIGURE 2. SEM surface images of nanofiber mats (10,000x magnification). Top: Nanofibers composed of 95 wt% PFSA (825 EW) + 5 wt% PAA. Bottom: Nanofibers composed of 60 wt% PFSA (825 EW) + 35 wt% sPOSS + 5 wt% PAA.
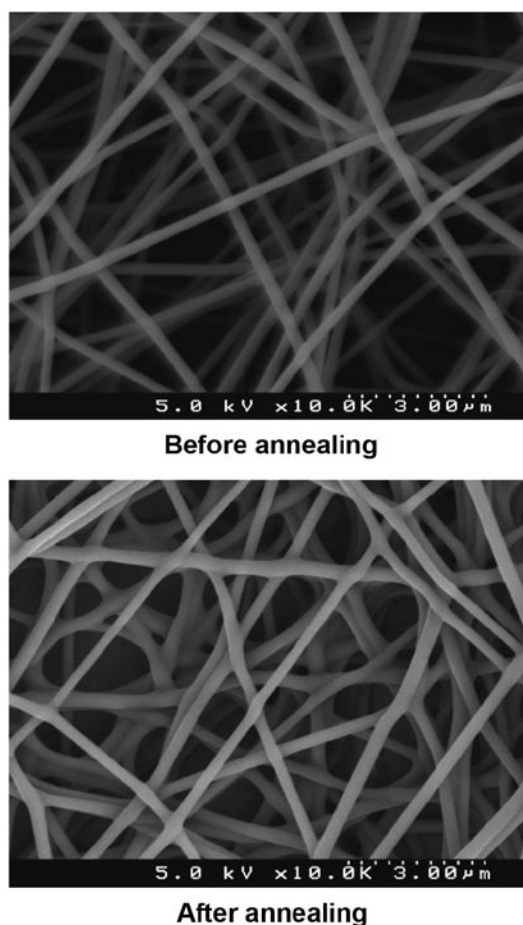

FIGURE 3. SEM images (10,000x magnification) of nanofiber mats before and after annealing (annealing conditions: 140°C for 5 min). Fiber composition: 95 wt% PFSA (825 EW) + 5 wt% PEO.

(825 EW PFSA, supplied by 3M Corporation). The fiber volume fraction of as-spun mats was approximately 0.20.

- Well-formed nanofiber mats (with no beads and droplets) were made by adding a high MW polymer dopant to the PFSA electrospinning solution, at a very low concentration. PEO and PAA were used successfully as dopants during electrospinning, at a minimum concentration of 0.3 wt% and 5 wt%, respectively (wt% is relative to the weight of PFSA).

- Welding of PFSA nanofibers occurred during polymer annealing, thus simplifying the mat processing steps.

- Mechanical compaction of PFSA mats (10,000 psi for 5 seconds) was used to increase the fiber volume fraction from 0.20-0.30 to 0.70-0.75.

- The inter-fiber voids were filled with NOA 63, followed by ultraviolet light curing.

- Electrospun fiber mats were produced from blends of 825 EW PFSA (from 3M Corp.) and sPOSS, purchased from Michigan Molecular Institute. The fiber volume fraction of an as-spun mat
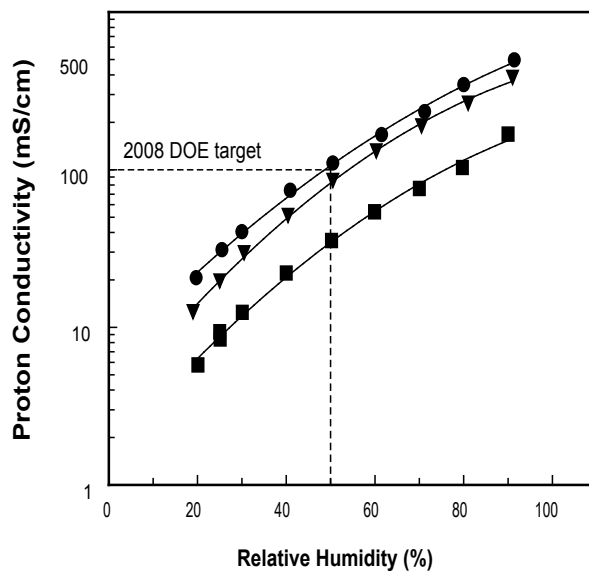

FIGURE 4. Proton conductivity vs. RH of nanocapillary composite membranes. Nanofiber mat was composed of 60 wt% PFSA (825 EW) + 35 wt% sPOSS + 5 wt% PAA. ● 120°C; ▼ 80°C; ■ 30°C.

was approximately 20%; and the average fiber diameter was in the 300-400 nm range. The final composition of the nanofibers was 60 wt% PFSA + 35 wt% sPOSS + 5 wt% PAA.

- The proton conductivity of the PFSA/sPOSS/ PAA mats was 107 mS/cm at 120°C and 50% RH, which exceeded the DOE 2008 Go/No-Go target of 100 mS/cm.

Future Work

- Investigate possible leaching of sPOSS from the nanofiber membranes - Identify sPOSS leaching by a loss in proton conductivity after soaking membranes in liquid water; prepare sulfonated POSS with a lower ion exchange capacity to eliminate leaching.

- Replace sPOSS with sulfonated poly(phenylene) to boost conductivity - Sulfonated poly(phenylene) will have improved chemical stability as compared to sPOSS, with no dissolution in water; add up to 60% high ion exchange capacity (e.g., 7.0 mmol/g) sulfonated poly(phenylene) to PFSA nanofibers to increase proton conductivity at low RH.

- Replace NOA 63 as the inert matrix polymer - Perform multiple embedding steps with a polymer/ solvent solution (with solvent evaporation between repeated embedding steps); examine polysulfone Radel R, polyvinylidene fluoride, and polyvinylidene fluoride/hexafluoropropylene copolymers (Kynar Flex) as the inert matrix material; add inorganic particles e.g., organically modified aluminosillicate (clay) or glass fibers to the embedding polymer for improved strength.

- Further characterize nanofiber membranes - Measure mechanical properties, gas permeability, and water vapor uptake as a function of temperature and RH.

- Prepare and test hydrogen/air fuel cell membrane electrode assemblies with nanocapillary network membranes.

- Examine different fiber morphologies with PFSA polymers (hollow bore nanocapillaries, core shell nanofibers, etc.).

Patents Issued

1. P.N. Pintauro, P. Mather, and R. Wycisk, "Fiber Network Membrane," U.S. Provisional Patent (2008).

FY 2009 Publications/Presentations

1. Jonghyun Choi, Kyung Min Lee, Ryszard Wycisk, Peter N. Pintauro, and Patrick T. Mather, "Composite Nanofiber Network Membranes for PEM Fuel Cells," in Proton Exchange Membrane Fuel Cells 8, *Electrochemical Society Transactions,* **16(2)** 1433 (2008).

2. Jonghyun Choi, Kyung Min Lee, Ryszard Wycisk, Peter N. Pintauro, and Patrick T. Mather, "Composite Nanofiber Network Membranes for PEM Fuel Cells," presentation given at the 2008 Fall Electrochemical Society Meeting, October 2008, Honolulu, HI.

3. Jonghyun Choi, Kyung Min Lee, Ryszard Wycisk, Peter N. Pintauro, and Patrick T. Mather, "Nanofiber Network Membranes for Fuel Cell Applications," presentation given at the Annual Meeting of the American Institute of Chemical Engineers, November 2008, Philadelphia, PA.

4. Peter N. Pintauro, "New Fuel Cell Membranes via Nanomorphology Manipulation" seminar given at Clarkson University, Department of Chemical and Biomolecular Engineering, Potsdam, NY, October 2008.

5. Peter N. Pintauro, "New Fuel Cell Membranes via Nanomorphology Manipulation" seminar given at the University of Kentucky, Department of Chemical Engineering, Lexington, KY, October 2008.

6. Peter N. Pintauro, "New Membrane Nano-morphologies for Improved Fuel Cell Operation" seminar given at Georgia Tech, Department of Chemical Engineering, Atlanta, GA, February 2009.

7. Peter N. Pintauro, "Composite Nanofiber Network Membranes For PEM Fuel Cells" presentation at Nissan Technical Center, North America, Farmington Hills, MI, March 2009.

8. Jonghyun Choi, Peter N. Pintauro, Kyung Min Lee, Ryszard Wycisk, and Patrick Mather, "Nanofiber Network Ion-Exchange Membranes for PEM Fuel Cells" presentation at the American Chemical Society Spring National Meeting, Salt Lake City, Utah, March 2009.

9. Peter n. Pintauro, "NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/ Air Fuel Cells" presentation at USCAR, Southfield, MI, March 2009.

10. Peter N. Pintauro, "New Membrane Nano-morphologies for Improved Fuel Cell Operation" seminar given at University of Louisville, Department of Chemical Engineering, April 2009.

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3. Choi, J., Lee, K.M., Wycisk, R., Pintauro, P.N., and Mather, P.T., "Composite Nanofiber Network Membranes for PEM Fuel Cells," in Proton Exchange Membrane Fuel Cells 8, *Electrochemical Society Transactions,* **16(2)** 1433 (2008).