V.G.13 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 milestones for Year 2 (3rd quarter) and Year 3 (3rd quarter).

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

Characteristic	Units	2007 DOE Milestone	2010/2015 DOE Target	Case 2007 Status for NCN Membranes
Inlet water vapor pressure	kPa	50	<1.5	50
Oxygen cross-over	mA/cm^2	5	2	<0.01

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[1]

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

[1] Proton conductivity at 30°C and 80% relative humidity (RH)
[2] Oxygen crossover at 25°C and 50% RH

Accomplishments

- Synthesized a series of sulfonated poly(arylene ether sulfone) polymers of different ion-exchange capacity (IEC).
- Developed electrospinning, mat densification, fiber welding, and fiber mat impregnation processes.
- Fabricated nanofiber membranes of different fiber volume fraction.

- Characterized the nanofiber membranes in terms of proton conductivity and swelling (in water), oxygen permeability, and mechanical strength.

- Prepared impregnated nanofiber membranes where the nanofibers were composed of sulfonated poly(arylene ether sulfone) with sulfonated octaphenyl Polyhedral Oligomeric SilSesquioxanes (sPOSS).

- Determined the proton conductivity of the sPOSS-containing nanofiber membranes and sent samples out for independent conductivity testing.

- The proton conductivity of the sPOSS-containing nanofiber membrane met the DOE 2007 target of 0.07 S/cm at 30°C and 80% relative humidity.

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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, perfluorosulfonic acid (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 [2,3] due to an insufficient number of membrane-phase water molecules for proton 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 PFSA 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 are embedded in an inert/impermeable polymer matrix. The NCN is composed of a high IEC 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 and provides overall mechanical strength to the membrane. Embedded nanofiber membranes have been fabricated and preliminary characterization tests have been performed. A series of membranes were created using sulfonated poly(arylene ether sulfone) for the nanofibers and Norland Optical Adhesive 63 (NOA 63) as the inert embedding polymer. To further improve proton conductivity at reduced humidity conditions, sulfonated poly(arylene ether sulfone) was blended

with sPOSS, electrospun into mats, and then processed into a membrane (densified, welded, and impregnated with NOA 63). The resulting membrane had a proton conductivity of 0.072 S/cm at 30°C and 80% RH (measured by Bekktech), which met the 2007 DOE target.

Approach

Nanofiber mats were prepared from sulfonated poly(arylene ether sulfone) (sPAES) with/without proton conducting inorganic particles (sPOSS). The ion-exchange capacity of the sPAES polymer was either 2.1 or 2.5 mmol/g. sPAES was made by copolymerizing sulfonated and nonsulfonated monomers. Nanofiber mats were densified by mechanical compression, and then the fibers were welded by exposure to organic solvent vapor. NOA 63, an ultraviolet (UV) curable thermoset), was used to embed electrospun mats after densification and welding. The proton conductivity of the sulfonated poly(arylene ether sulfone) mat was measured (in water at 25°C) at various stages of membrane fabrication (the initial mat, the densified mat, and the densified/welded mat).

Results

Preparing Electrospun Mats with Sulfonated Poly(arylene ether sulfone) – Mats of ionomeric nanofibers was electrospun from a solution of 25 wt% sulfonated poly(arylene ether sulfone) in dimethylacetamide. High molecular weight sPAES polymer with an IEC of 2.5 mmol/g and an intrinsic viscosity of 0.72 dL/g was prepared by polycondensation of three monomers. Large mats (16 cm x 6 cm) of electrospun fibers with a uniform mat thickness and fiber density were prepared using a rotating drum collector that oscillated laterally (horizontally). Mats were compacted/densified under mechanical pressure to increase the volume density of nanofibers, with no change in fiber diameter. To create interconnecting protonic pathways, intersecting fibers were welded by exposing the densified sPAES mat to dimethylformamide vapor at 25°C for 18 minutes.

Optical photographs and scanning electron microscope (SEM) images of the surface of a sPAES nanofiber mat, at three stages of membrane fabrication are shown in Figure 1. For the initial (as-spun) mat, the volume fraction of fibers was 0.11-0.18, the mat thickness was 114 μm and the number-average fiber diameter was 110 nm. The fiber density was calculated as the weight of the dry mat relative to that of a dry homogeneous sPAES film of the same size and thickness. The densified mat in Figure 1 was created by mechanical compaction at 13,000 psi for three minutes at 25°C, where the fiber volume fraction increased to 0.64, the mat thickness decreased to 32 μm, and the average fiber
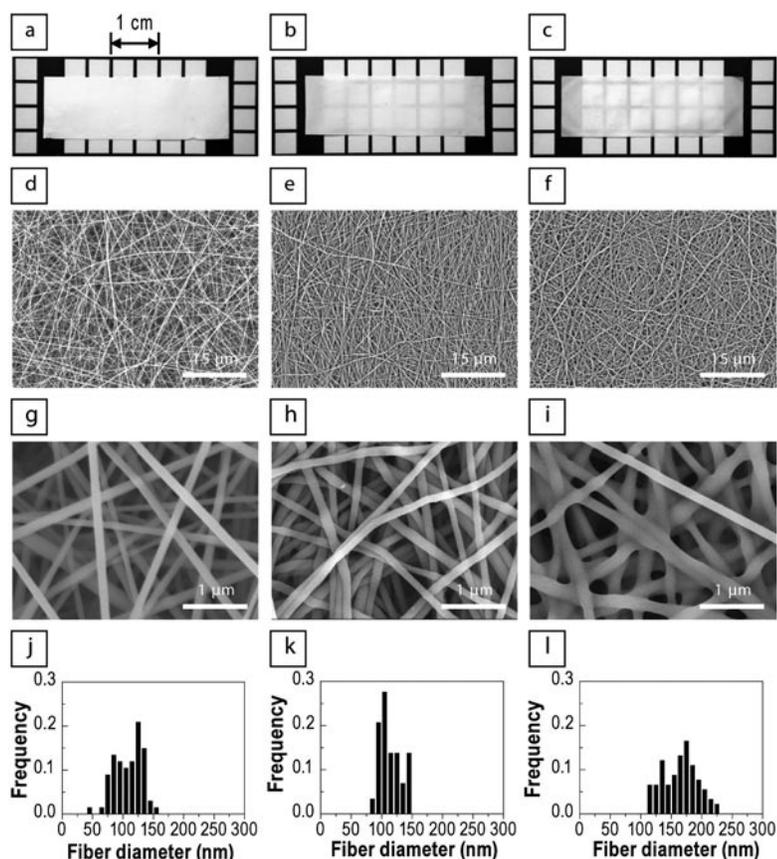
FIGURE 1. Electrospun fiber mat of sulfonated poly(arylene ether sulfone) at three stages of transforming the mat into an ion-exchange membrane: initial (as-spun) mat (**a,d,g,j**), mat after fiber densification (**b,e,h,k**), and mat after densification and fiber welding (**c,f,i,l**). **a-c** are optical photographs, **d-f** are SEMs of the mat surface at a magnification of 2,000x, **g-i** are scanning electron micrographs of the mat surface at a magnification of 30,000x, and **j-l** are histograms of the fiber diameter distribution, as determined from the 30,000x SEMs.

Characterization of Nanofiber Network Membranes Composed of Sulfonated Poly(arylene ether sulfone) and NOA 63 - A series of preliminary characterization experiments were performed on impregnated mats of different fiber volume fractions (11-80%) and the results were contrasted with similar measurements on neat films of sPAES (cast from dimethylacetamide) and UV-cured NOA 63. In-plane proton conductivity and equilibrium water uptake (swelling) at 25°C for nanofiber composite membranes of different fiber volume fraction (as measured before NOA 63 impregnation) are presented in Figure 2 (the data are also plotted against the effective membrane IEC, which is equal to the product of the fiber volume fraction and fiber polymer IEC). A fiber volume fraction of 1.0 denotes a homogeneous film of 2.5 mmol/g sPAES and a volume fraction of 0.0 corresponds to an uncharged NOA 63 film. Proton conductivity increased linearly with fiber volume fraction in the composite membranes and showed no percolation threshold, contrary to what is generally observed for immiscible conductor/insulator polymer blends. From though-plane conductivity experiments, it was concluded that the fiber network morphology and the proton conductivity were isotropic, i.e., at 55% and 70% fiber volume fractions, the in-plane and through-plane conductivities were identical (within experimental error) at 0.064 S/cm and 0.086 S/cm, respectively.

diameter was essentially unchanged at 114 nm. After compaction and fiber welding, the volume fraction of fibers and the average fiber diameter increased, to 0.73 and 165 nm, respectively, with essentially no change in mat thickness (35 μm).

After welding, the sPAES nanofiber mat was impregnated with NOA 63, a solvent-less photocurable urethane-based prepolymer, and exposed to UV light. Top-view optical photographs and freeze-fractured SEM cross-section images of the final nanofiber composite membrane clearly showed NOA 63 polymer filling completely the interfiber voids. The nanofiber network membrane had a more desirable morphology and better mechanical properties than a UV-cured polymer blend; for example, a membrane composed of 70 wt% sPAES and 30 wt% NOA 63 that was cast from dimethylacetamide solvent was brittle when dry and highly phase separated with isolated 5-10 μm domains of NOA 63, as revealed by SEM analysis.

In contrast to the conductivity data, a non-additive behavior with respect to composition was seen in the water-uptake results. At fiber volume fractions below 0.80, membrane swelling was less than expected, based on the amount of sulfonated polymer in the membrane. This deviation from the additivity rule was expected due to the ability of the NOA 63, which surrounds all sulfonated polymer nanofibers, to restrict fiber swelling. When the fiber volume fraction was greater than ≈0.80, water uptake was directly proportional to the volume fraction of sulfonated polymer, indicating either weak interconnectivity of the NOA 63 matrix or its insufficient strength to restrict swelling of the nanofibers.

The measured properties of the nanofiber network membranes compare very well those of a commercial Nafion® 117 sample, whose proton conductivity and water swelling at 25°C were 0.09 S/cm (both in-plane and through-plane) and 0.35 g H_2O/g, respectively. Additionally, the embedded nanofiber membranes
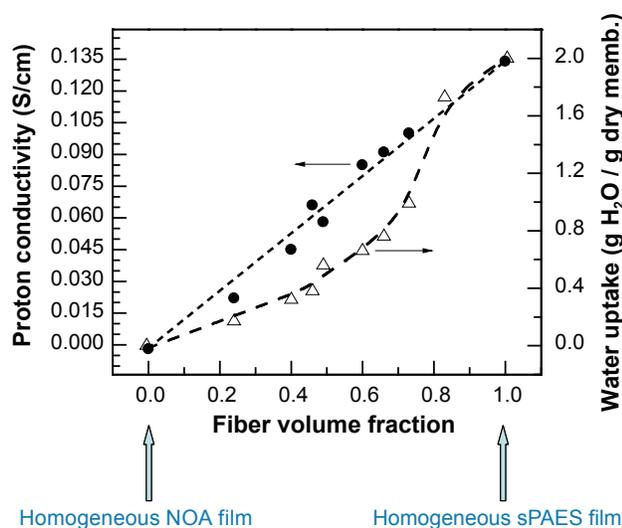
FIGURE 2. Proton Conductivity and Water Uptake at 25°C of Nanofiber Composite Membranes as a Function of Fiber Volume Fraction Prior to Embedding - The fibers were composed of 2.5 mmol/g sulfonated poly(arylene ether sulfone) and the inert matrix was UV-cured NOA 63.

exhibited good mechanical properties; the ultimate tensile strength for a nanofiber network membrane with a fiber volume fraction of 50% was 28 MPa, as compared to 15 MPa for Nafion® 117 (both membranes were equilibrated in air at 25°C and 35% RH).

Steady-state oxygen permeability experiments were performed to check for membrane defects and to assess the gas barrier property of the nanofiber composite membranes (an important and required attribute for fuel cell applications). The oxygen permeability in a membrane with a nanofiber volume fraction of 0.60 and a thickness of 45 μm was 0.18 Barrers. This permeability was unexpectedly low, given the nanofiber volume fraction, an O_2 permeability of 0.53 Barrers for a homogeneous 2.5 mmol/g sPAES film and a permeability of 0.038 Barrers for a dense NOA 63 film that was UV-cured. The oxygen barrier property of the nanofiber membrane was more than 50-times lower than that in Nafion® 117 (9.4 Barrers).

The results in Figures 1 and 2 show that defect-free nanofiber composite ion-exchange membranes can be fabricated with good proton conductivity (depending on the fiber volume fraction), low gas permeability, and good mechanical properties. The proton conductivities in Figure 2 (which were measured in water), however, did not meet the DOE target of 0.07 S/cm at 30°C and 80% RH. For this reason, nanofiber mats were prepared using an electrospinning solution of sPAES and sPOSS.

Nanofiber Network Membranes Containing Sulfonated Poly(arylene ether sulfone) and sPOSS - Nanofiber mats were prepared by electrospinning a solution of sulfonated poly(arylene ether sulfone) and either 35 wt% or 40 wt% sPOSS in 2-butoxyethanol.

The polymer IEC was 2.1 mmol/g. The chemical structure of the sPOSS species is shown in Figure 3. The mats contained fibers with an average diameter in the range of 300-500 nm. Mats were compacted mechanically to increase the fiber volume fraction and then intersecting fibers were welded by exposing the mat to 2-butoxyethanol vapor. Interfiber voids were filled with NOA 63 (which was crosslinked in situ by exposing the membrane to UV light). The final membranes had a thickness of 50-60 μm with a fiber volume fraction of 70-75%.

In-plane proton conductivity data were collected at Case Western Reserve University. Samples were sent to the University of Central Florida for independent conductivity measurement verification by Bekktech. Proton conductivity data collected at Case (30°C and a RH between 30% and 95%) are shown in Figure 4, for membranes with 35 wt% and 40 wt% sPOSS nanofibers. For comparison purposes, Nafion® 212 conductivity data are also shown in the figure. The proton conductivity of the nanofiber membranes was very high and exceeded that of Nafion® 212 for RHs >60%. At 95% RH, the proton conductivity was 0.23 S/cm (vs. 0.066 S/cm for Nafion® 212). At 80% RH, the conductivity was 0.094 S/cm, which exceeded the 2007 DOE target. At low humidities (<50%), the proton conductivity was low, e.g., 0.0095 S/cm vs. 0.0091 S/cm for Nafion® 212 at 40% RH. As shown in Figure 4, there was a modest improvement in proton conductivity with sPOSS loading. Bekktech-measured proton conductivities were slightly lower than those measured at Case (0.072 S/cm at 30°C and 80% RH), but still matched/exceeded the DOE target. The discrepancy in the conductivity numbers (Case vs. Bekktech) can not be explained at the present time.
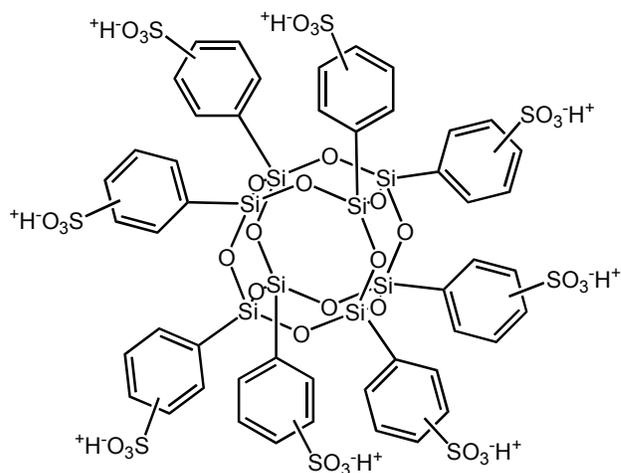

FIGURE 3. The Chemical Structure of the Sulfonated Octaphenyl Polyhedral Oligomeric Silsesquioxane (sPOSS)
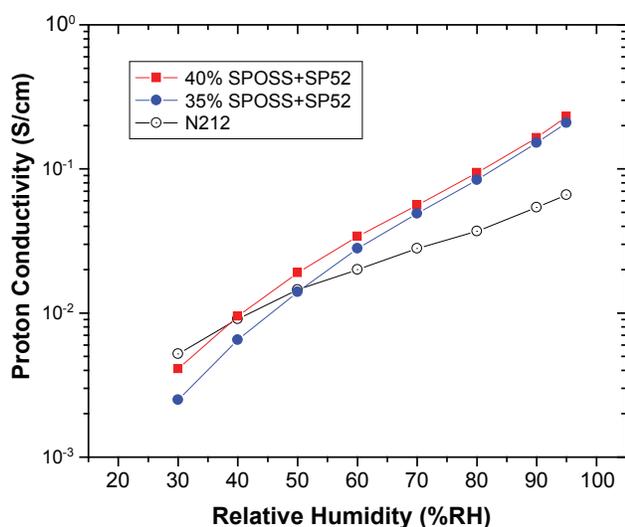
FIGURE 4. Proton Conductivity vs. RH of Nanofiber Membranes at 30°C - Sulfonated poly(arylene ether sulfone) at 2.1 mmol/g (denoted as SP52) with either 35 wt% or 40 wt% sPOSS. Nafion® 212 data are also shown (all data collected at Case Western Reserve University).

Conclusions and Future Directions

Conclusions

- Electrospun fiber mats were produced from high IEC sulfonated poly(arylene ether sulfone). The fiber volume fraction of as-spun mats was approximately 10-20%; fiber diameters were in the 100-150 nm range.
- Mechanical compaction was used to increase the fiber volume fraction to a maximum of ~80% (with no change in fiber diameter).
- Fiber welding was carried out by exposing a compacted densified mat to the organic solvent.
- The inter-fiber voids were filled with NOA 63, followed by UV light curing.
- Proton conductivity of the resulting nanofiber membranes scaled linearly with the volume fraction of proton conducting nanofibers. Swelling was less than expected, based on a similar scaling effect.
- The mechanical properties of the membranes were very good and the gas (oxygen) permeability in the membranes was very low (indicating no defects at the interface of the fibers and NOA 63).
- Electrospun fiber mats were produced from blends of high IEC sulfonated poly(arylene ether sulfone) and sulfonated polyhedral oligomeric silsesquioxanes (using 2-butoxyethanol as the solvent). The fiber volume fraction of as-spun mat was approximately 20%; fiber diameters were in the 300-500 nm range.
- Mechanical compaction was used to increase the fiber volume fraction to 70-75% (with no change in

fiber diameter). Fiber welding was carried out by exposing a densified mat to 2-butoxyethanol. The inter-fiber voids were filled with NOA 63 (followed by UV curing).
- The proton conductivity of the mats was >0.07 S/cm at 30°C and 80% RH (thus meeting the DOE 2007-08 milestone).
- The proton conductivity at low relative humidity was low.

Future Work

- Increase the proton conductivity of electrospun mats at low RH:
  - Use a higher IEC polymer to create the nanofibers.
  - Increase the sPOSS loading of the nanofibers.
  - Use POSS with phosphonic acid functionalities.
  - Investigate adding Poly(phenylene disulfonic acid) to the nanofibers (from M. Litt's project).
  - Add zirconium phosphate sulfophenyl phosphonate (high IEC) to the nanofibers for low RH/high temperature (>100°C) conductivity.
- Stabilize the nanofiber morphology:
  - Crosslinking of high IEC sPAES (creation of sulfone bridges or biphenyldisulfone bridges).
  - Covalent-bond stabilization of sPOSS.
- Replace NOA 63 for better chemical/thermal stability and better strength at high temperature:
  - Acid-resistant epoxy (either UV or thermal cure).
  - Melt embedding polyvinylidene fluoride.

Presentations

1. Peter N. Pintauro, Patrick Mather, Olivier Arnoult, Jonghyun Choi, Ryszard Wycisk, and Kyung Min Lee, "NanoFiber Network Membranes for PEM Fuel Cells," Electrochemical Society Meeting, Washington, D.C., October 2007.

2. Peter Pintauro, Patrick T. Mather, Ryszard Wycisk, Kyung Min Lee, and Jonghyun Choi, "NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells," FreedomCAR Tech Team Review, Southfield, MI, April 2008.

Publications

1. Peter N. Pintauro, Patrick Mather, Olivier Arnoult, Jonghyun Choi, Ryszard Wycisk, and Kyung Min Lee, "Composite Membranes for Hydrogen/Air PEM Fuel Cells," in Proton Exchange Membrane Fuel Cells 7, Electrochemical Society Transactions, vol. 11(1), pp. 79-87 (2007).

2. Jonghyun Choi, Kyung Min Lee, Ryszard Wycisk, Peter N. Pintauro, and Patrick T. Mather,"Nanofiber Network Ion-Exchange Membranes," Macromolecules, 41, 4569 (2008).

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3. Gasteiger, H.A., and Mathias, M.F., "Fundamental research and Development Challenges in Polymer Electrolyte Fuel Cell Technology," *Proceedings of the Proton-Conducting Membrane Fuel Cells III Symposium*, The Electrochemical Society (2002).