V.C.5 NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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Fiscal Year (FY) 2011 Objectives

- Fabricate a new class of nanofiber-based proton conducting membranes using different sulfonated polymers.
- 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.

TABLE 1. Progress towards Meeting Technical Targets for Membranes

Characteristic	Units	Target 2015	2011 Project Status
Maximum operating temperature	°C	120	
Area specific proton resistance at:			
Maximum operating temp and water partial pressures from 40 to 80 kPa	Ohm cm^2	≤0.02	0.05[a]
80°C and water partial pressures from 25-45 kPa	Ohm cm^2	≤0.02	0.06
30°C and water partial pressures up to 4 kPa	Ohm cm^2	≤0.03	
-20°C	Ohm cm^2	≤0.2	
Maximum oxygen cross-over [a]	mA/cm^2	2	
Maximum hydrogen cross-over [a]	mA/cm^2	2	2
Minimum electrical resistance	ohm cm^2	1,000	
Cost	$/m^2	≤20	27
Durability:			
Mechanical	Cycles w/<10 sccm crossover	≥20,000	12,600
Chemical	hours	>500	842

[a] Proton conductivity at 120°C and 50% relative humidity (RH) – data from Bekktech LLC

FY 2011 Accomplishments

- Fabricated nanofiber composite membranes via a dual fiber electrospinning, where perfluorosulfonic acid (PFSA) proton conducting fibers and uncharged polyphenylsulfone (PPSU) nanofibers are simultaneously electrospun.
- Further developed two methods for processing the dual fiber mat into a functional fuel cell membrane by: (i) allowing the PFSA ionomer fibers to soften and flow without affecting the PPSU mat in order to fill the voids

between PPSU fibers (the nanofiber PPSU becomes a membrane reinforcement mat) and (ii) allowing the PPSU nanofibers to soften and flow to fill all voids while maintaining the structure of the Nafion® mat. Membranes were prepared from method (i) using DuPont's Nafion® and 660 equivalent weight (EW) PFSA from 3M Company and from method (ii) using Nafion® PFSA.

- Nanofiber membranes were characterized in terms of proton conductivity, in-plane, volumetric, and gravimetric water swelling, and mechanical properties.

- Electrospun nanofiber Pt/C fuel cell cathodes were fabricated and tested.

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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 fast electrode kinetics. For PEM fuel cell operation at temperatures ≤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. Unfortunately, the conductivity of PFSA membranes drops dramatically at temperatures >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/without sulfonated octaphenyl polyhedral oligomeric silsesquioxanes (sPOSS) to further boost conductivity. Norland Optical Adhesive 63 (NOA63) 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]. These films met the DOE's Year 3, 3rd quarter Go/No-Go conductivity target of 100 mS/cm at 120°C and 50% RH. Third-generation

films were made using a new dual-fiber electrospinning approach where ionomer and inert polymer are electrospun simultaneously. Advantages of this method over traditional membrane fabrication techniques, e.g., polymer blends or the impregnation of an ionomer in an inert matrix, are: (i) there is no separate polymer impregnation step, (ii) the same dual-fiber mat can be processed into two different membrane morphologies: proton conducting ionomer nanofibers embedded in an uncharged/inert polymer matrix and inert/uncharged polymer nanofibers embedded in (and reinforcing) an ionomer matrix, (iii) there is wide choice of polymers for the ion conduction and inert (uncharged) polymers, (iv) there is intimate mixing of polymer components in the dry state with a polymer component domain size (the fiber diameter) as small as 100 nm, (v) separate polymer components are used for the mechanical and proton-conducting functions of the membrane, and (vi) the domain size and loading of the proton-conducting phase can be easily and independently controlled.

Approach

Membrane Fabrication – Membranes were prepared by a newly developed dual nanofiber electrospinning technique using either 1100 EW Nafion® or 660 EW PFSA from 3M Corporation as the proton conducting material and Radel® R-5500NT polyphenylsulfone (PPSU) from Solvay Advanced Polymers LLC as the inert/uncharged polymer. PFSA materials were electrospun using 0.33-2% poly(ethylene oxide) as a carrier polymer (which was later removed by boiling the final membranes in water). PFSA and PPSU nanofibers were electrospun simultaneously using two separate needle 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 a PPSU matrix (compacted the mat at room temperature and 3,500 psig for a few seconds, exposed the mat to chloroform vapor at 25°C for 16 minutes, and then annealed the membrane for 2 hours at 150°C in vacuum) and (ii) PPSU nanofibers were surrounded by PFSA ionomer (hot pressed the mat at ~15,000 psig and 127°C for 40 seconds and then annealed at 150°C for 2 hours in vacuum). Membranes were evaluated and contrasted in terms of in-plane proton conductivity, in-plane, volumetric, and gravimetric swelling in water, and mechanical properties.

Electrode Fabrication – An electrospinning ink was prepared by mixing Pt/C catalyst powder (40% Pt on carbon black, Alfa Aesar), Nafion® powder, and 450,000 MW poly(acrylic acid) (MW=450,000 g/mol, Aldrich) in an isopropanol/water solvent (2:1 wt ratio). The total polymer and powder content was 13.4 wt%, where the Pt/C:Nafion®:poly(acrylic acid) weight ratio was 75:15:10. The ink was electrospun at 1.5 ml/h with an applied voltage of 7 kV. Nanofibers were collected on a bare rotating drum or on carbon paper (SIGRACET®

GDL 25 BC, Ion Power, Inc) that was fixed to the drum. The drum oscillated horizontally to improve the uniformity of deposited nanofibers. Fuel cell membrane electrode assemblies (MEAs) were prepared with a Nafion® 212 membrane and a decal-processed anode at a loading of 0.40 mg$_{Pt}$/cm^2. Electrospun cathodes with a Pt-loading of 0.1 mg/cm^2, 0.2 mg/cm^2 and 0.4 mg/cm^2, respectively, were hot-pressed onto anode-coated Nafion® membranes. The resulting MEAs were evaluated in a series of electrochemical and fuel cell tests.

Results

Nanofiber Composite Membranes with 660 EW PFSA – Figure 1 shows proton conductivity as a function of RH for a nanofiber composite membrane (70 vol% 660 EW PFSA + 30 vol% PPSU with an effective ion-exchange capacity of 1.23 mmol/g), as compared to commercial Nafion® 212 and a solution cast film composed of neat 660 EW PFSA. The nanofiber composite film is more conductive than Nafion® 212 due to its higher ion-exchange capacity. The conductivity of the composite is slightly below a neat 660 EW film due to dilution of ionomer by the PPSU reinforcing nanofiber mat. The composite membrane, however, has greatly reduced in-plane volumetric swelling; 5% as compared to 24% for Nafion® 212 and the 84% for the neat 660 EW film (swelling was measured in 23°C water). Thus, the nanofiber composite has more than twice the conductivity of Nafion® 212 over a wide humidity range and 5-times lower in-plane swelling. Low in-plane membrane swelling has been identified as in important property that improves the durability of an MEA during fuel cell operation. Based on the 50% RH conductivity in Figure 1 (at 80°C), the nanofiber composite membrane
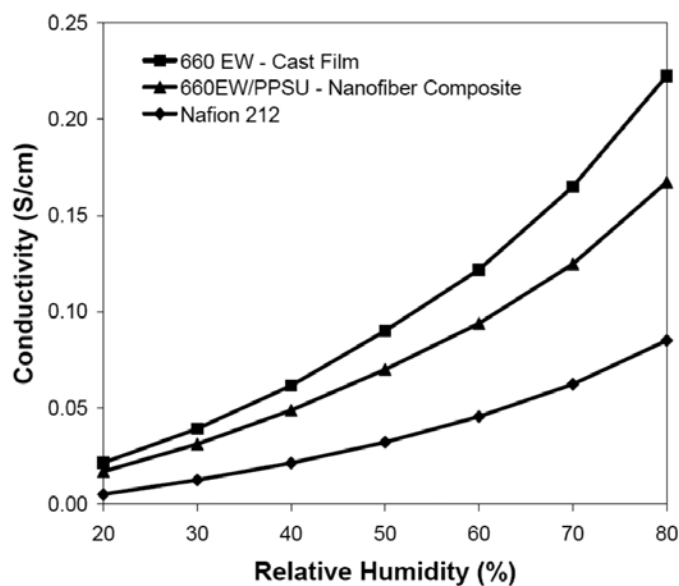
should have a proton conductivity of 0.090-0.095 S/cm at 120°C (slightly below the DOE target of 0.10 S/cm). The conductivity target can be achieved by decreasing slightly the PPSU content of the composite membrane or by using a slightly lower EW PFSA.

Nanofiber Composite Membranes with Nafion® – Proton conductivity (in 23°C liquid water) as a function of Nafion® volume fraction for the two nanofiber membrane structures (Nafion® with a PPSU nanofiber mat and Nafion® nanofibers surrounded by PPSU) is shown in Figure 2. There are no significant differences in conductivity between the two structures and proton conductivity scaled linearly with Nafion® volume fraction. The two morphologies exhibit the same volumetric and gravimetric water swelling but the in-plane swelling differs (see Figure 3), with the PPSU nanofiber reinforcing mat morphology exhibiting less swelling. The mechanical properties of the two composite membrane morphologies also differ, with the Nafion® nanofiber + PPSU matrix membrane exhibiting a larger Young's modulus (550 MPa) and proportional limit stress (30 MPa) than the inverse structure.

Nanofiber-Based Fuel Cell Cathode – Nanofiber cathode MEAs (where the average electrospun nanofiber diameter was 470 nm) performed very well in a hydrogen/air fuel cell operating at 80°C without back pressure. Exceptionally high fuel cell power densities were achieved at a low Pt loading, e.g. 524 mW/cm^2 at 0.6 V for 0.1 mg$_{Pt}$/cm^2, as shown in Figure 4. The catalyst mass activity, as measured at 0.9 V in an 80°C H$_2$/O$_2$ fuel cell with a pressure of 150 kPa$_{abs}$, was also exceptionally high at 0.23 A/mg$_{Pt}$. The accessible electrochemical surface area of the nanofiber cathode was very high (114 m^2/g$_{Pt}$) and it exhibited improved long-term stability vs. a decal cathode.

FIGURE 1. Proton conductivity of a nanofiber composite membrane (70 vol% 660 EW PFSA and 30 vol% polyphenylsulfone) at 80°C as a function of RH.
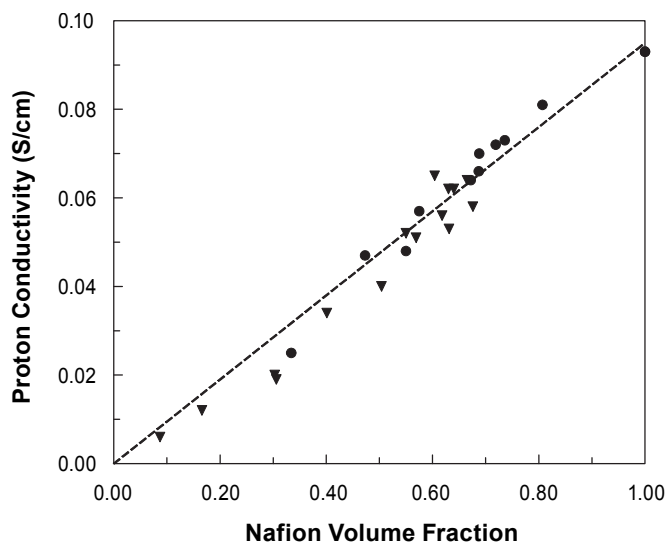

FIGURE 2. Proton conductivity of Nafion®/PPSU composite membranes as a function of Nafion® volume fraction. Conductivity measured in liquid water at room temperature. (▼) Nafion®-fibers/PPSU-matrix, (●) PPSU-fiber/Nafion®-matrix.
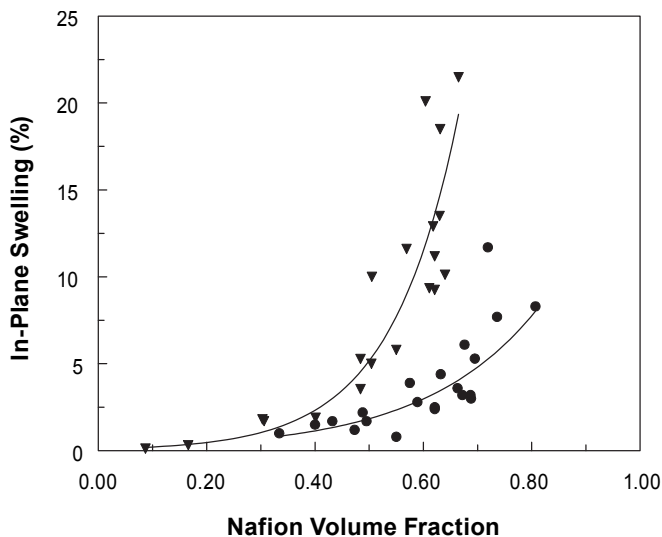
FIGURE 3. In-plane swelling of Nafion®/PPSU composite membranes as a function of Nafion® volume fraction. Swelling was measured in 100°C water. (▼) Nafion®-fibers/PPSU-matrix, (●) PPSU-fiber/Nafion®-matrix.

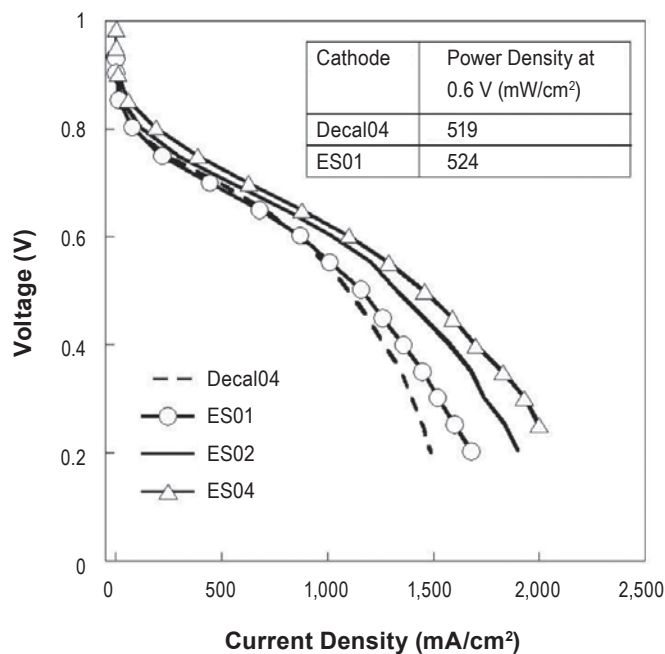| Cathode	Power Density at 0.6 V (mW/cm²)
Decal04	519
ES01	524

FIGURE 4. H₂/air fuel cell polarization curves at 80°C and ambient pressure with different cathodes, a Nafion® 212 membranes, and a 0.4 mg/cm² decal anode. Cathodes: Decal04 = 0.4 mg/cm² decal; ES01 = 0.1 mg/cm² nanofiber; ES02 = 0.2 mg/cm² nanofiber; ES04 = 0.4 mg/cm² nanofiber.

The outstanding performance was associated with a more uniform distribution of Pt/C particles and Nafion® binder in the nanofibers, thus allowing for better proton transport and oxygen diffusion to catalyst sites during fuel cell operation.

Conclusions and Future Work

Conclusions

- Two different membrane morphologies were generated from a dual nanofiber (Nafion® + PPSU) electrospun mat: Nafion® with a reinforcing nanofiber mat of PPSU and a nanofiber mat of Nafion® surrounded by PPSU polymer.

- The proton conductivity and volumetric/gravimetric water swelling are identical for the two membrane structures. The in-plane water swelling for membranes with a reinforcing PPSU mat is less than the inverse structure and the mechanical properties (Young's modulus and proportional limit stress) of membranes with a Nafion® nanofiber mat embedded in PPSU are better than films with the inverse structure.

- Dual fiber composite membranes were prepared and evaluated, where a PPSU nanofiber mat was surrounded by 660 EW PFSA (from 3M Corp.). The presence of the PPSU reinforcing mat lowered significantly volumetric and in-plane water swelling, for a membrane with 70 vol% PFSA. The membrane proton conductivity at 80°C and 50% RH was high (0.07 S/cm).

- Fiber composite membranes were estimated to cost $27/m² ($8/m² for sulfonated fluoropolymer and polyphenylsulfone and $19/m² for electrospinning and fiber mat processing).

- An electrospun nanofiber cathode was fabricated, where the fiber composition was 75 wt% Pt/C powder, 15 wt% Nafion®, and 10 wt% poly(acrylic acid). In a H₂/air fuel cell, a nanofiber cathode at 0.1 mg_Pt/cm² out-performed a 0.4 mg_Pt/cm² decal cathode.

Future Work

- Continue to prepare and test nanofiber composite membranes with low EW PFSA and polyphenylsulfone using the dual fiber electrospinning approach.

- Prepare and test MEAs with nanofiber network composite membranes containing low EW PFSA.

- Continue to investigate and improve on the performance/properties of electrospun nanofiber fuel cell electrodes.

- Prepare and test a nanofiber MEA (hot-press an electrospun nanofiber anode and cathode onto a nanofiber composite membrane).

Patents

1. P.N. Pintauro and W. Zhang, "Nanofiber Fuel Cell Electrode and Method of Forming Same" U.S. provision patent, filed October 2010.

FY 2011 Publications/Presentations

1. J.B. Ballengee and P.N. Pintauro, "Morphological Control of Electrospun Nafion Nanofiber Mats". *Journal of the Electrochemical Society,* **158**, B568-B572 (2011).

2. "Fabrication of Nanofiber Composite Fuel Cell Membranes via Dual Fiber Electrospinning," Jason Ballengee and Peter N. Pintauro, Extended Abstract #733, 218th Electrochemical Society Meeting, Las Vegas, NV, October 2010.

3. "NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells," Peter Pintauro and Patrick Mather, paper presented by Pintauro at USCAR, Southfield, MI, November 2010.

4. "Nanofiber-Based Membranes for PEM Fuel Cells," Invited Talk, XII International Symposium on Polymer Electrolytes, Padua, Italy, September 2010.

5. "New Membrane Morphologies for Improved Fuel Cell Operation," Chemical Engineering Department Seminar given by Peter Pintauro at University of Tennessee, October 2010.

6. "New Membrane Morphologies for Improved Fuel Cell Operation," Chemical Engineering Department Seminar given by Peter Pintauro at University of Connecticut, November 2010.

7. "New Membrane Morphologies for Improved Fuel Cell Operation," Department Seminar given by Peter Pintauro at Vanderbilt University, Department of Chemistry, November 2010.

References

1. Thampan, T., Malhotra, S., Tang, H., and Datta, R., *J. Electrochem. Soc.* **147**(9), 3242 (2000).

2. 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, *Electrochem. Soc. Trans.*, **16(2)** 1433 (2008).

3. Choi, J., Lee, K.M., Wycisk, R., Pintauro, P.N., and Mather, P.T., *J. Mater. Chem.* (2010) DOI: 10.1039/C0JM00441C.