V.M.21 NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

Peter N. Pintauro (Primary Contact) and
Patrick T. Mather

Case Western Reserve University
10900 Euclid Avenue
Cleveland, OH 44106
Phone: (216) 358-4150; Fax: (216) 368-3016
E-mail: pnp3@case.edu

DOE Technology Development Manager:
Amy Manheim

Phone: (202) 586-1507; Fax: (202) 586-9811
E-mail: Amy.Manheim@ee.doe.gov

DOE Project Officer: Jesse Adams

Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Technical Advisor: Walt Podolski

Phone: (630) 252-7558; Fax: (630) 972-4430
E-mail: podolski@cmt.anl.gov

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 molecular silica to the sulfonated 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.).

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

(D) Thermal, Air and Water Management

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 High Temperature, Low RH Fuel Cell Membranes

Characteristic	Units	3Q Year 2 Milestone	3Q Year 3 Milestone	Case 2007 Status
Proton Conductivity	S/cm	0.07 at 25°C and 80% RH	0.1 at 120°C and 25-50% RH	0.041*

*This conductivity was for a non-impregnated mat that was equilibrated in liquid water at room temperature.

Accomplishments

- Prepared sulfonated polymers (sulfonated poly(ether ether ketone) and sulfonated poly(arylene ether sulfone) of different ion-exchange capacity (IEC).
- Developed the electrospinning and mat densification processes (fabricated fiber mats with a different average fiber diameter; increased the density of fibers in a mat; developed a fiber welding strategy).
- Characterized the electrospun mats (measured proton conductivity of electrospun mats before inert polymer impregnation; performed thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) thermal analyses on electrospun mats).
- Performed initial impregnation experiments (used a solvent-less ultraviolet [UV] curable thermoset).

✧   ✧   ✧   ✧   ✧

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 under high relative humidity (RH) conditions at T $\leq$80°C, 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 the 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, an entirely new approach to fuel cell membrane design is being studied, where a three-dimensional interconnected network of proton-conducting polymer nanocapillaries are embedded in an inert/impermeable polymer matrix. The nanocapillary network will be 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 will control water swelling of the nanocapillaries (i.e., the diameter of the nanocapillaries will not change appreciably with temperature and relative humidity) and provide overall mechanical strength to the membrane. The resulting membrane morphology will resemble that of a phase separated block copolymer and is expected to better retain water and maintain proton conductivity under high temperature and low relative humidity conditions.

Approach

Nanofiber mats were prepared from sulfonated poly(ether ether ketone) (sPEEK) and sulfonated poly(arylene ether sulfone) (sPAES) of a given ion-exchange capacity (1.65 mmol/g for sPEEK). sPEEK was made by sulfonating poly(ether ether ketone) with concentrated sulfuric acid. sPAES was made by copolymerizing sulfonated and nonsulfonated monomers.

sPEEK mats were densified by heating in an oven or heating/compaction by a four-roller laminator and then the fibers were welded by exposure to ethanol vapor. NOA 63 (a UV curable thermoset) was used to embed sPEEK electrospun mats after densification and welding. The proton conductivity of the sPEEK 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

Electrospinning fibers of sPEEK - Electrospun nanofiber mats were prepared using a solution of 25 wt% sPEEK (1.65 mmol/g ion-exchange capacity) in

dimethylacetimide (DMAc). Fibers were collected on a 2.5-inch diameter rotating drum (1,800 rpm drum rotation speed), to produce large area fiber mats of uniform mat density. To ensure a homogeneous thickness of the mat, the entire drum moved laterally (horizontally) in a reciprocating manner during electrospinning. The final mat (obtained after 10 hours of electrospinning) was 8 cm wide and 16 cm long, with a thickness of 50 μm.

The resulting mats were inspected using scanning electron microscopy (SEM). Mat characterization indicated that the fibers had an average diameter of 150-200 nm, with a maximum diameter of 250-300 nm (see Figure 1a) and a fiber volume density of 12-15%, as compared to the density of a fully dense (solid) sPEEK film. The rotating/reciprocating drum method of electrospinning fibers was highly reproducible; mats of similar thickness and fiber density were routinely made in duplicate experiments. Increasing the sPEEK concentration in the spinning solution (to 30 wt%) resulted in mats with an average fiber diameter of about 2,450 nm (see Figure 1b). Such large fibers were not wanted and all further work was carried out using a 25 wt% sPEEK electrospinning solution.

Densifying Electrospun Mats – Both mechanical and thermal treatments were examined to densify sPEEK fiber mats (i.e., to increase the fiber density of the mats). In one method, an electrospun mat was suspended in a lab oven in a nitrogen atmosphere at 240°C for 3 minutes. In a second method, high temperature densification was combined with mechanical compaction using a four roller laminator, where the fiber mat was placed in a Teflon® frame and then sandwiched between two Teflon® sheets. The mat remained in the laminator for 1 minute, where the laminator temperature was 190°C. In a third method, mechanical compaction was carried out in the laminator with little or no heating (1 minute in the laminator at a temperature below 125°C).

Macroscopic shrinkage of the sPEEK mats was observed using the two heat treatment techniques (the length and width of a mat decreased by a factor of 3). The results of the mat densification experiments are summarized in Table 2. It can be seen that the initial mat has a relatively modest density, only about 15%. Mechanical compaction with the laminator increased the fiber density by a factor of about two. Significant mat shrinkage occurred when a sample was kept at an elevated temperature for 1-3 minutes (either in the oven or in the laminator), with a resulting mat density of 43-51%. Multiple data points in Table 2 for a given densification method are intended to show the general reproducibility in mat density.

An SEM study of fiber mats before/after mat densification revealed that the average fiber diameter increases during thermal treatment (see Figure 2). This
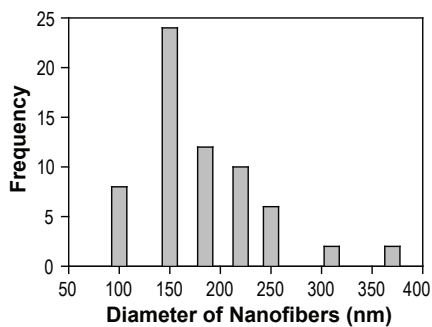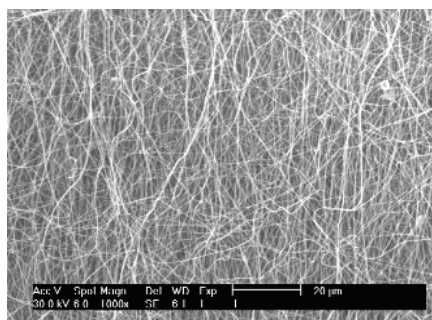
(a) 25 wt% sPEEK in DMAc
(12% mat density)
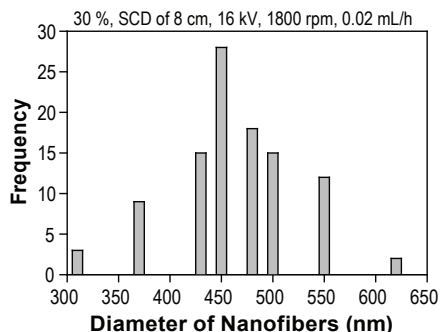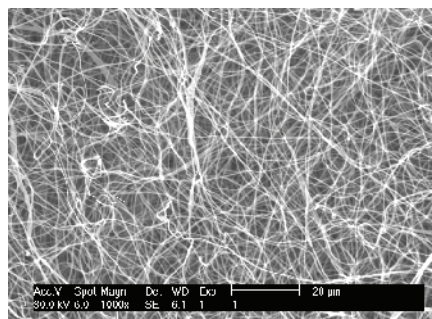
(b) 30 wt% sPEEK in DMAc
(13% mat density)

FIGURE 1. SEM Pictures and Fiber Diameter Histograms for Electrospun Mats using Sulfonated Poly(ether ether ketone) (sPEEK) in DMAc (1.65 mmol/g sPEEK ion-exchange capacity)

TABLE 2. Relative Densities of sPEEK Mats Processed using Various Compaction Methods

	Initial Mat	Mechanical Densification in Laminator	Thermal Densification in Oven (240°C)	Thermal/ Mechanical Densification in Laminator (200°C)	Solid Film
Relative mat density (%)	13	26	42	51	100
	15	26	51	43	
	15	24	38	46	

mat shrinkage and concomitant fiber expansion are associated with the thermal relaxation of stresses in electrospun fibers (such stresses are generated by polymer chain stretching and orientation during fiber spinning on the rotating drum apparatus).

Fiber Welding - To improve mat density and increase the interconnectivity between fibers, a vapor welding step was performed after mat densification in the oven or laminator. Ethanol was selected as the solvent to soften fibers in a densified mat, thereby inducing fiber welding. Mat samples were suspended over ethanol liquid in a sealed jar for a specified period of time and then were allowed to air dry. Scanning electron micrographs of initial and final mat samples showed that ethanol exposure times longer than 3 minutes led to overwelding, i.e., melting together of fibers (see Figure 3). Such films were nearly transparent, similar to a homogenous dense film of sPEEK. Semi-opaque films were found to be properly welded (up to 3 minutes of ethanol vapor exposure). Films that were pre-densified and then vapor welded had a mat density of 74% (as compared to a density of about 45% prior to welding). With a fiber density of 74%, both the mechanical and proton conducting properties of the sulfonated polymer mat are expected to be far superior to those of the initial electrospun material.

Proton Conductivity Measurements - The in-plane proton conductivity of densified and densified/welded mat samples (after equilibration in water at 25°C) are listed in Table 3. The proton conductivity (in water at 25°C) of the initial fiber mats after boiling in acid and washing in water was very low (0.008 S/cm) due to the low volume density of fibers and the absence of connectivity (welds) between fibers. (These mats were also difficult to physically handle and load in the conductivity cell, making this conductivity measurement less reliable than others.) The mat conductivity increased significantly after densification and densification/welding. For such mats, the conductivities compare well with predicted values, which were calculated using the measured mat density and the proton conductivity of a fully dense sPEEK film (i.e., 0.74 x 0.06 S/cm = 0.044 S/cm, which is close to the measured value of 0.041 S/cm). These results indicate

expansion in fiber diameter is significantly greater for mats heated in an oven to 240°C (free of friction) than the laminator densification method. The heat-induced

(a) Mat as spun from 25wt% sPEEK (IEC 1.65) in DMAc

(b) Same mat as (a) at 240°C for 3 min in N$_2$ atmosphere

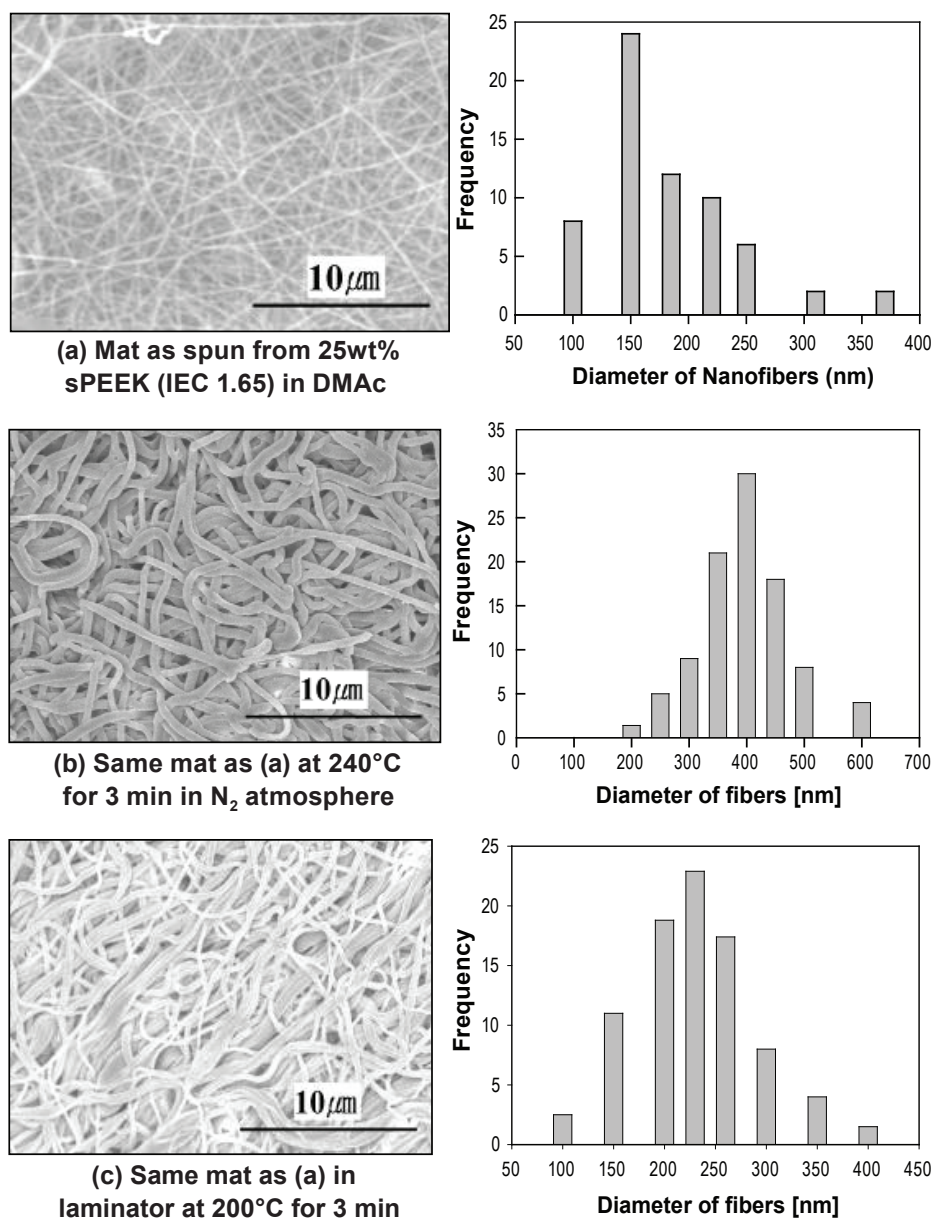**(c) Same mat as (a) in laminator at 200°C for 3 min**

FIGURE 2. SEM Pictures and Histograms of Fiber Diameters for (a) Initial Electrospun Mat, (b) Thermally Treated Mat (in Oven) and (c) Thermally/mechanically Treated Mat (in Laminator)
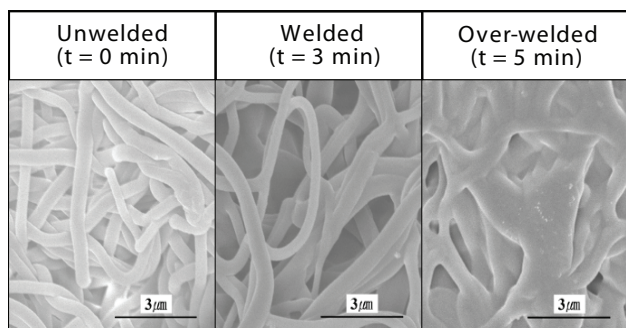

FIGURE 3. SEMs of Densified sPEEK Mats That Were Exposed to Ethanol Vapor for a Specified Period of Time, Showing Nanofiber Welding

TABLE 3. Proton Conductivities of Initial, Densified, and Densified/Welded Mats of Sulfonated Poly(ether ether ketone) with an Ion-exchange Capacity of 1.65 mmol/g

Material	Relative Density (%)	Proton Conductivity (S/cm) at 25°C In Liquid Water
Initial Mat	15	0.008
Densified Mat	45	0.016
Densified/Welded Mat	74	0.041
Homogeneous Solid Membrane (reference material)	100	0.060

that a higher IEC (and higher proton conductivity) polymer must be used for electrospinning.

Synthesis of Sulfonated Poly(arylene ether sulfone) – Water insoluble, high molecular weight (M_n=70,500; M_w=131,400), and high conductivity (0.12 S/cm in water at 25°C) sulfonated poly(arylene ether sulfone) was synthesized for next-generation of nanofiber mats. Thermogravimetric analysis indicated good thermal stability. Preliminary electrospinning experiments were performed and the resulting mats had an average fiber density in the 150-200 nm range.

Addition of Inert Polymer to Electrospun Mats – Norland optical adhesive (NOA 63), a UV curable thermoset was added drop-wise to a densified/welded mat of electrospun sPEEK fibers. The adhesive readily wetted the mat. SEMs after exposing the films to UV light indicated good adhesion/compatibility of the sulfonated polymer fibers and NOA 63.

Conclusions and Future Directions

Conclusions

- sPEEK can be electrospun into a mat with a uniform mat density and mat thickness, using a rotating drum collection apparatus.
- sPEEK fiber mats can be densified by heating in an oven or by compaction/heating in a four-roller laminator.
- sPEEK fibers in a densified electrospun mat can be welded by exposing the mat to ethanol vapor for ca. 3 minutes.

- The proton conductivity of a densified/welded mat of electrospun sPEEK fibers (with a mat fiber density of 74%) was 0.041 S/cm (in water at 25°C).

Future Work

- Refine methods for decreasing the fiber diameter and increasing the density of fibers in a mat.
- Use a higher IEC polymer to create the fibers (sPEEK and/or sulfonated polysulfone).
- Investigate electrospinning with high IEC polymers (in different counterion form).
- Continue investigating impregnation polymers (both UV and thermally curable polymers).
- Determine the proton conductivity and mechanical properties of mats before/after impregnation.

References

1. Gottesfeld, S., and Zawodzinski, T.A., "Polymer Electrolyte Fuel Cells," in Alkire, R., Gerischer, H., Kolb, D., Tobias, C., eds., Advances in Electrochemical Science and Engineering, Vol. 5, 197 (1998).

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

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).