NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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Project ID #FC14

Overview

Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 20%

Budget

- Total project funding
  - DOE $1,455,257
  - Contractor (CWRU) $481,465
- Funding received in FY06, $280,000
- Funding for FY07, $296,620

Barriers

- High proton conductivity membranes at high T and low RH.
- Membranes with good mechanical properties.
- Membranes with low gas permeability.

Interactions

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Dept. of Chemistry
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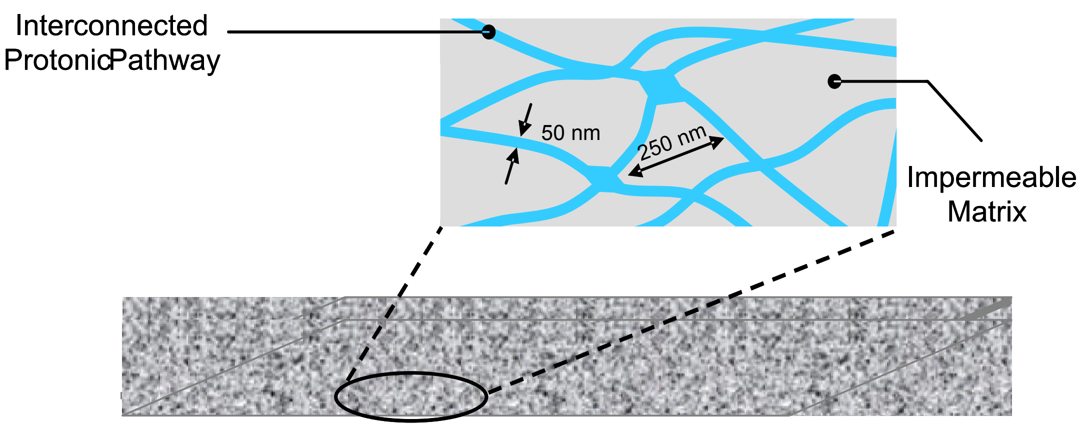
Objectives

- Fabricate and characterize a new class of NanoCapillary Network (NCN) proton conducting membranes for hydrogen/air fuel cells that operate under high temperature, low humidity conditions.
  - Electrospun nm-size fibers of high ion-exchange capacity polymer that are vapor welded and imbedded in an uncharged polymer matrix
  - Addition of molecular silica to further enhance water retention
  - Employ the concept of capillary condensation for membrane water retention.

Plan and Approach – Proposed Membrane Morphology

Structure for NanoCapillary Network (NCN) membranes:

The electrospun sulfonated polymer fibers with/without molecular silica are interconnected by vapor welding and the inter-fiber spaces are filled by a nonconducting, gas impermeable polymer



Plan and Approach

> **Task 1 Sulfonated Polymer Synthesis**

- Different polymer IECs
- With and without molecular-level silica
- Polymer crosslinking studies
- Polymer characterizations

> **Task 2 Electrospinning Process Development**

- Creation of a fiber mat
- Fiber Welding Studies

> **Task 3 Matrix Polymer Identification and Membrane Fabrication**

- Identify an inert (uncharged) polymer
- Develop method for adding polymer to the fiber mat

>**Task 4 Membrane Characterization**

- Bubble point test
- Equilibrium water swelling as a function of T and RH
- Preliminary through-plane and in-plane conductivity at different T and RH
- Thermomechanical analysis
- Mechanical properties
- Oxygen permeability
- SEM and TEM micrographs of membrane cross sections
- Thermal analysis (DSC and TGA) of the sulfonated and non-sulfonated polymers

> **Tasks 5 Membrane Composition/Structure Optimization**

Year 1 Tasks

Prepared Sulfonated Polymers

- Sulfonated poly (ether ether ketone)
- Sulfonated poly (arylene ether sulfone)
- Prepare polymers of different ion-exchange capacity (IEC)

Electrospinning Process Development

- Fabricated fiber mats with a different average fiber diameter
- Increase the density of fibers in a mat
- Develop fiber welding strategies

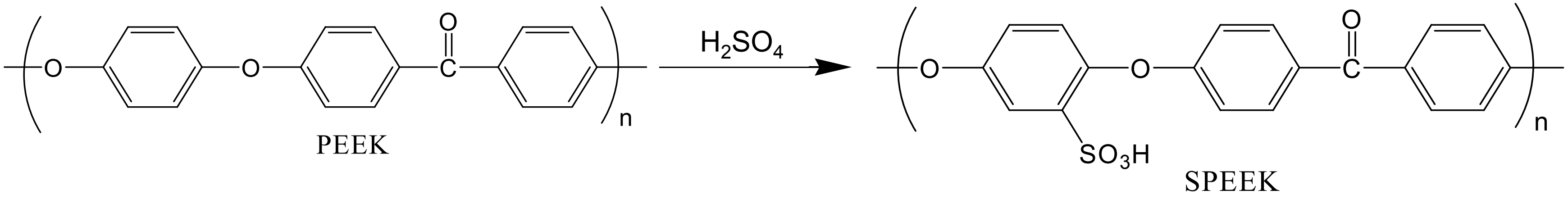
Mat Characterization Studies

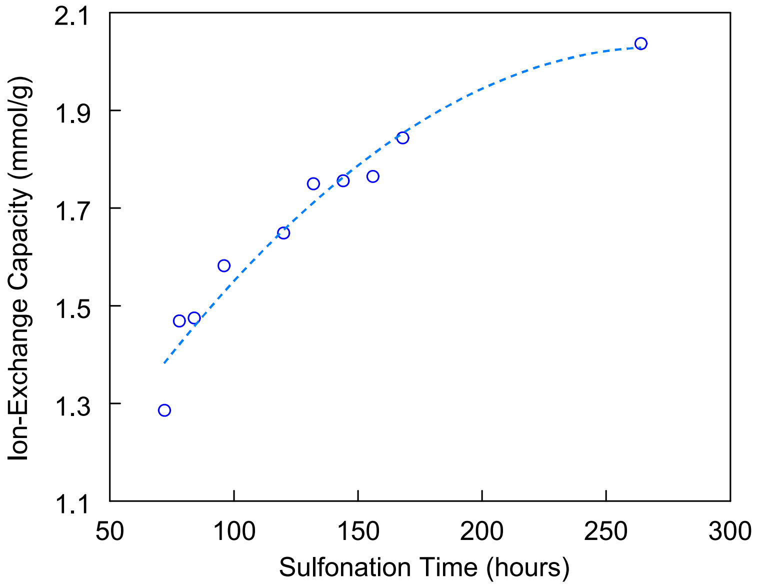
- Proton conductivity of the mat before inert polymer impregnation
- Thermal analysis of the mat (TGA and DMA)

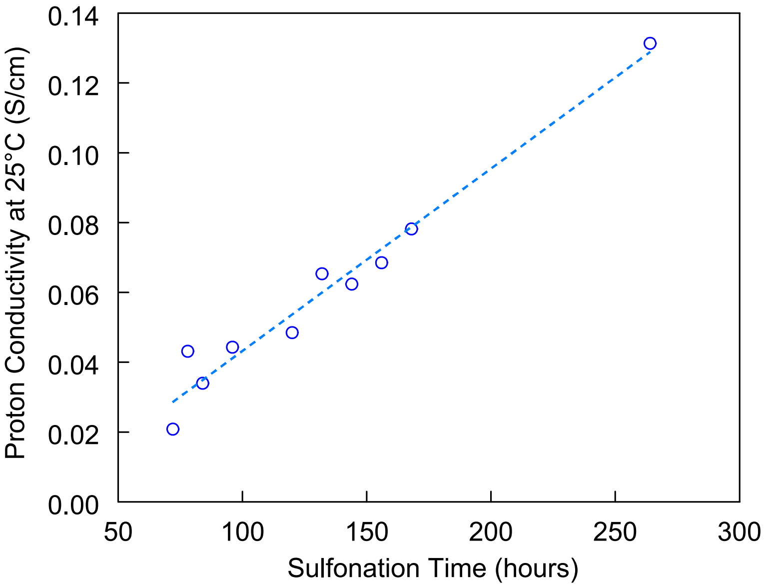
Initial Impregnation Experiments

- Use of a solvent-less UV curable thermoset

Sulfonation of Poly(ether ether ketone) (PEEK)



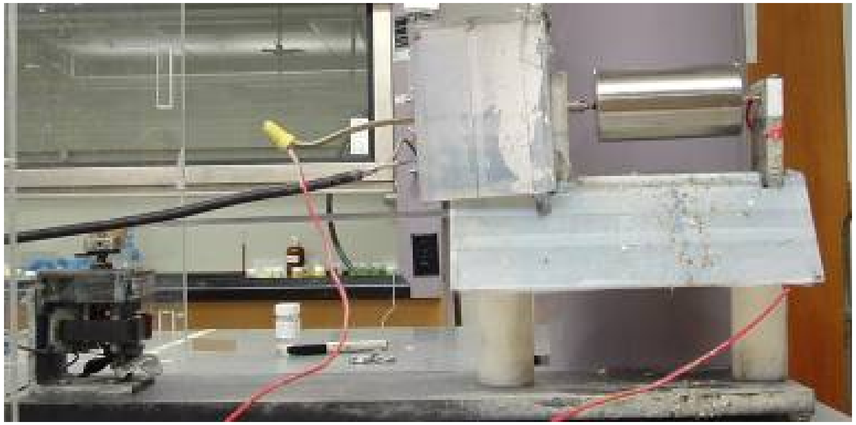




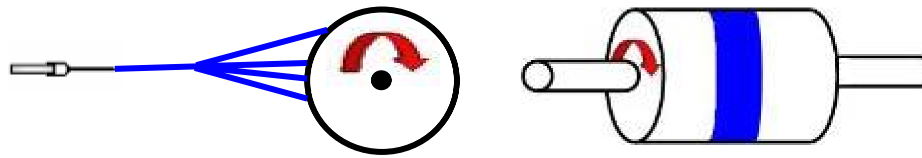
Poly(ether ether ketone) was sulfonated at room temperature to a range of different ion-exchange capacities (IECs) using concentrated sulfuric acid.

Electrospinning used 1.6 mmol/g IEC sPEEK (room temperature water-equilibrated membrane conductivity of 0.06 S/cm)

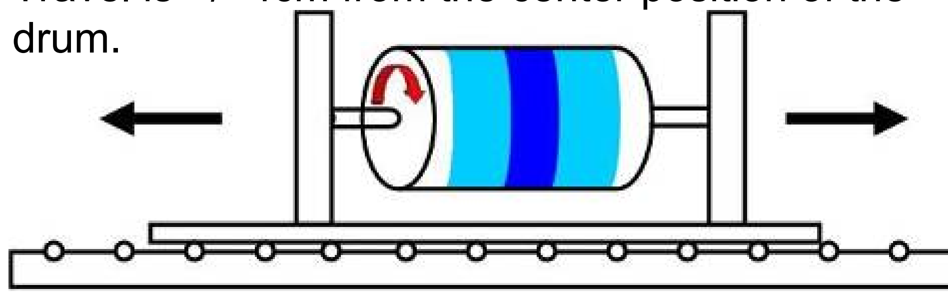
Electrospinning of sulfonated Poly(ether ether ketone) (sPEEK)



Drum rotation speed: from 0 to 1800 rpm



Lateral reciprocation:
Travel is +/- 4cm from the center position of the drum.

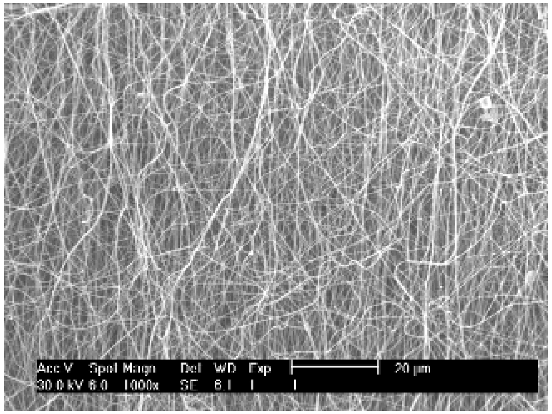


Electrospun Mat - 16 cm long, 8 cm wide and 50 μm thick after electrospinning for 10 hours; sPEEK (IEC 1.65) solution in DMAc.

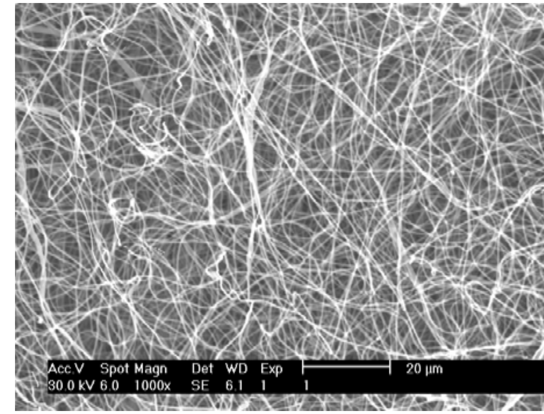
Result: Large area mats with uniform fiber density were produced

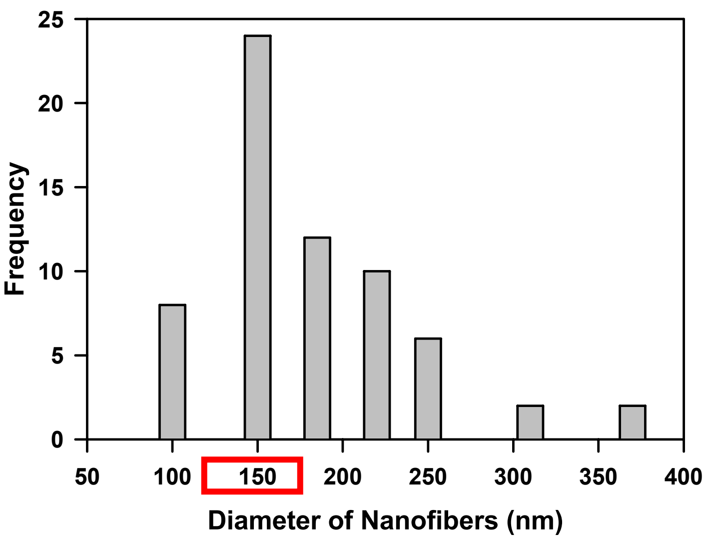
Electrospun Fiber Diameter

DOE Hydrogen Program

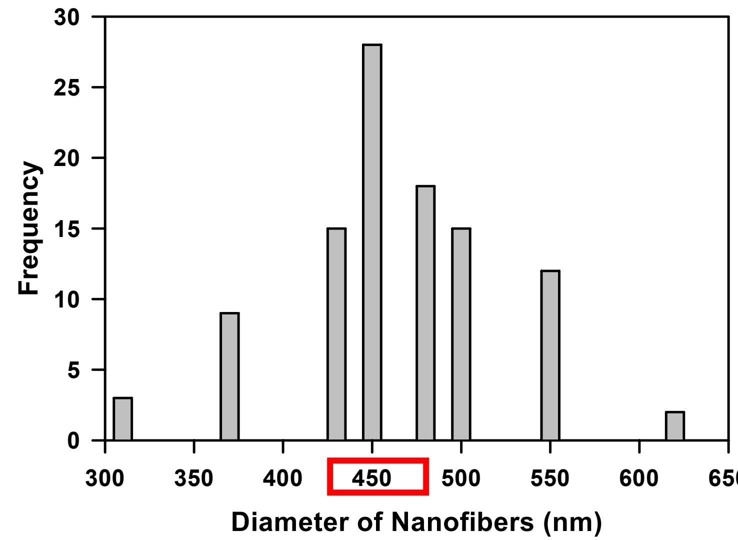


sPEEK (IEC 1.65) fibers electrospun on the rotating drum at 445 cm/s, 2kV/cm, 8cm spinneret-to-collector distance





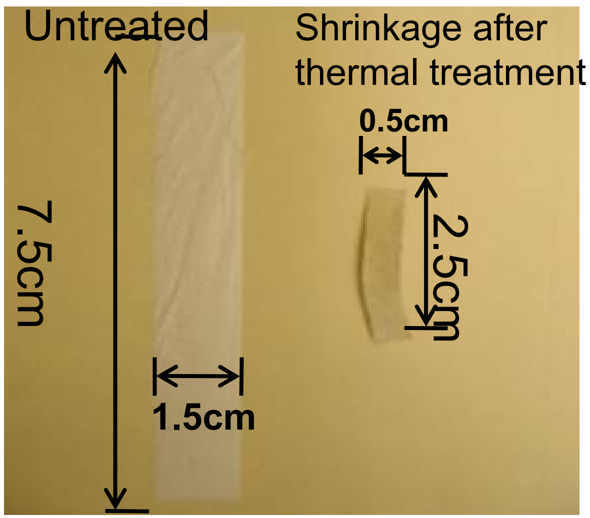
(a) 25 wt% sPEEK in DMAc and 12% mat density

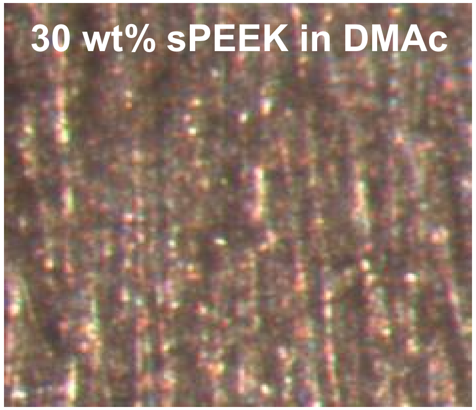


(b) 30 wt% sPEEK in DMAc and 13% mat density

Result: Fiber diameter can be control by solution concentration

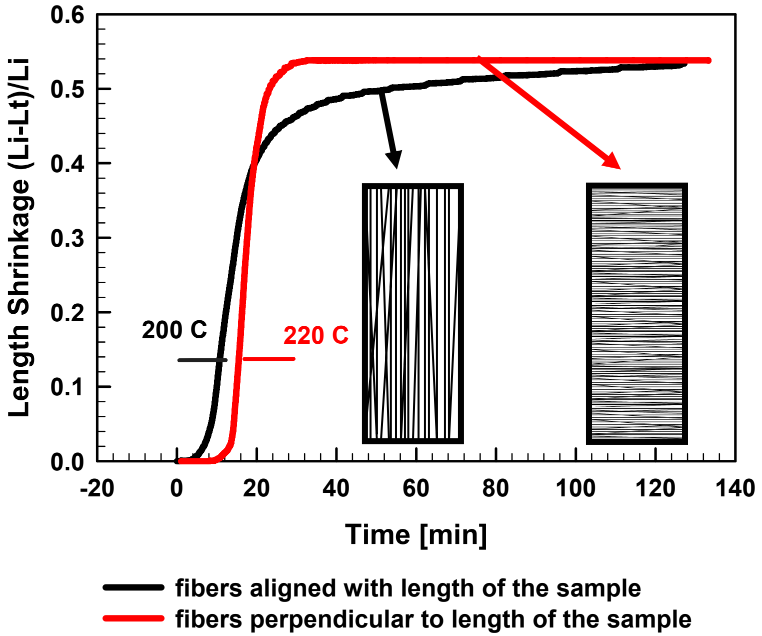
Enhancement of Fiber Density in a Mat
(heat treatment)





20 μm

Optical microscope images in reflection



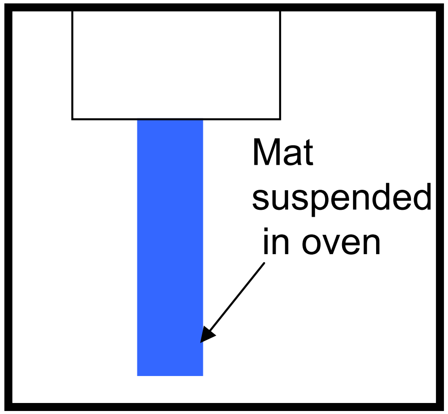
DMA study of the macroscopic orientation of electrospun fibers: Macroscopic orientation does not influence the shrinkage of the mat

Result: Thermal treatment near 200°C allows for significant mat shrinkage.

More on Enhancement of Fiber Density in a Mat

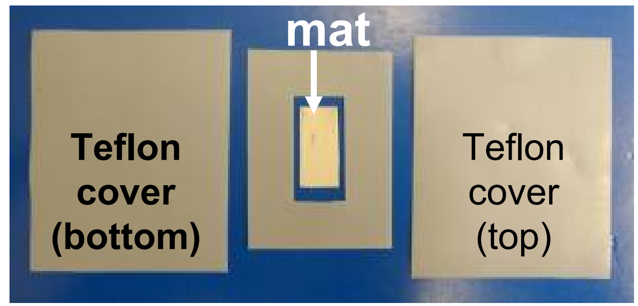
DOE Hydrogen Program

Use of oven



Mats were hung to avoid friction on the surface acting in opposite direction to shrinkage.

Use of laminator



A stack of the mat (in a Teflon frame) with two Teflon covers was passed through the laminator with controlled heating.

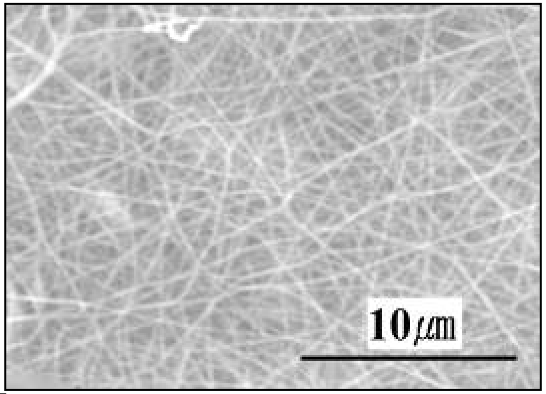
Sample	Initial Electrospun Mat (sPEEK IEC=1.65 mmol/g)	Densified Mat	
	Mat Density [%]	**Heat Treatment**	**Mat Density [%]**
A B C	13.6 12.6 12.8	In oven at 200°C	42.4 50.6 37.7
D E F	15.0 14.7 14.4	In laminator at 200°C	51.5 42.5 46.1

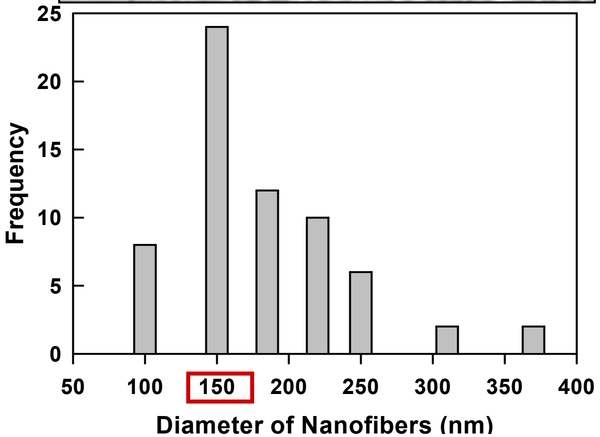
Result: Thermal treatment increases the mat density by a factor of 3

Heat Treatment in N_2 of sPEEK Mats

DOE Hydrogen Program

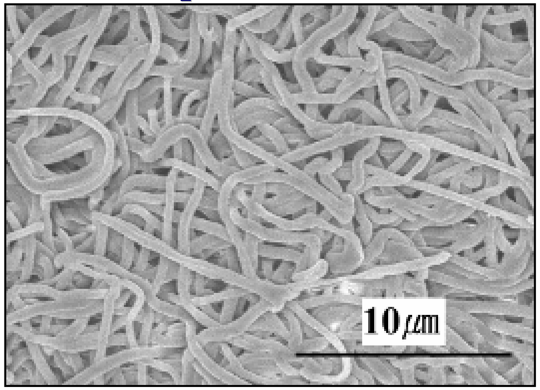
(a) Mat as spun from 25wt% sPEEK (IEC 1.65) in DMAc

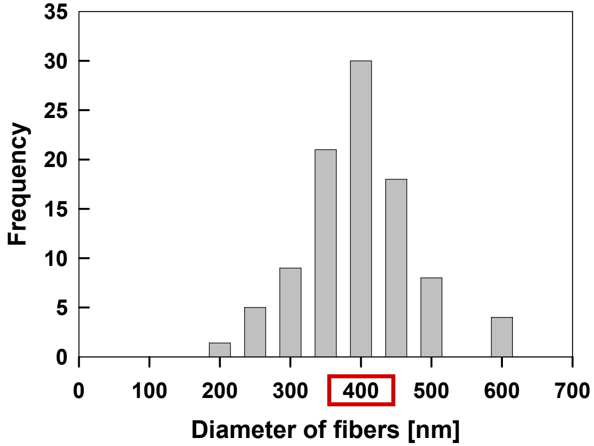




~14% mat density

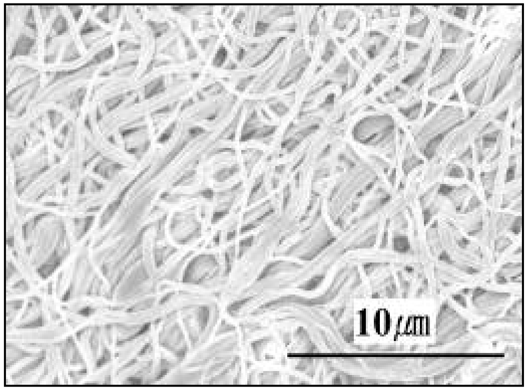
(b) Same mat at 200 °C for 3 min in N_2 atmosphere

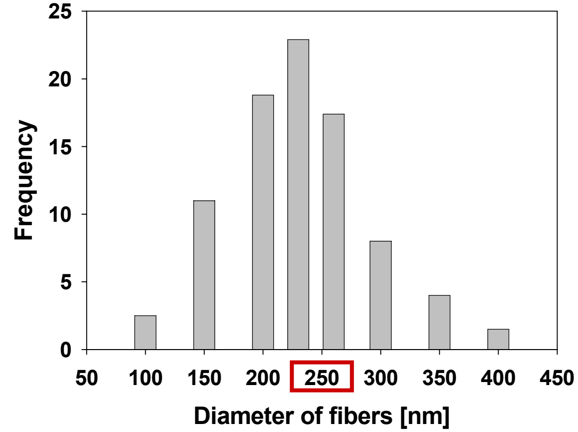




~42% mat density

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





~46% mat density

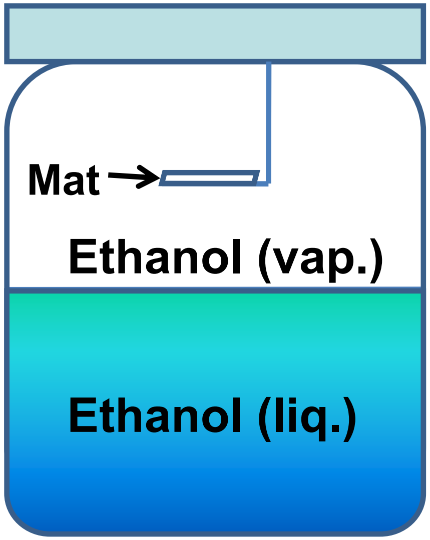
Results:

- **Thermal treatment increases fiber diameter (conservation of fiber volume results in an increase in fiber diameter when there is a shrinkage in mat length)**
- **For a similar mat density, the laminator method for mat compaction results in smaller fiber diameters, as compared to an oven treatment**

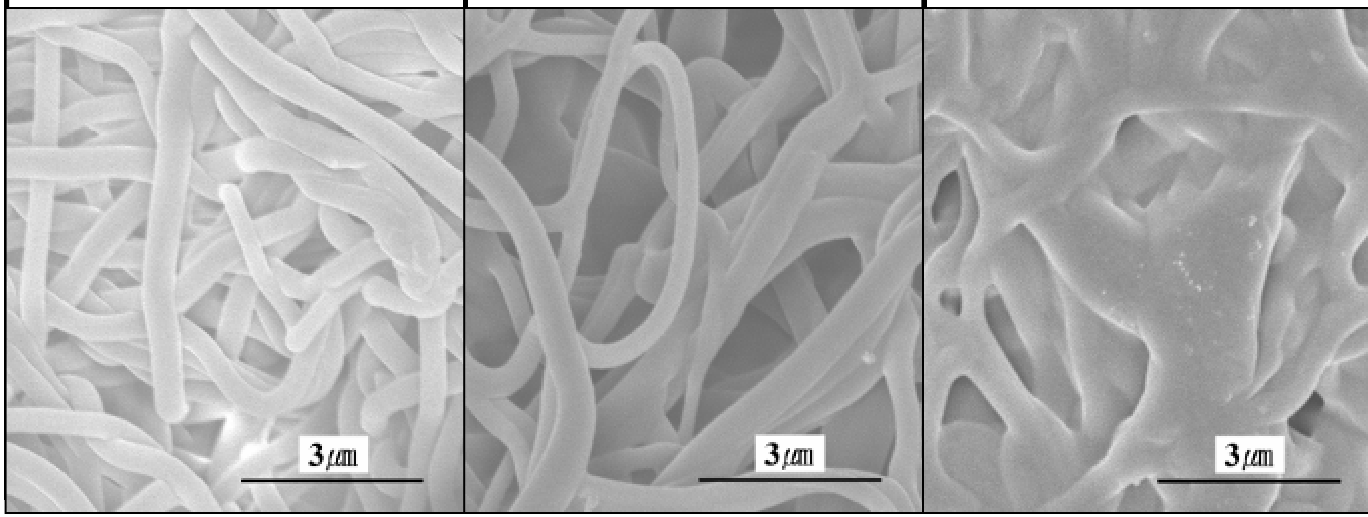
Vapor Welding of Fibers

DOE Hydrogen Program

- Densified fiber mats (~42% fiber content) were equilibrated with ethanol vapor at room temperature for a given period of time.
- The vapor-exposed mat was then dried under vacuum.



Unwelded (t = 0 min)	Welded (t = 3 min)	Over-welded (t = 5 min)

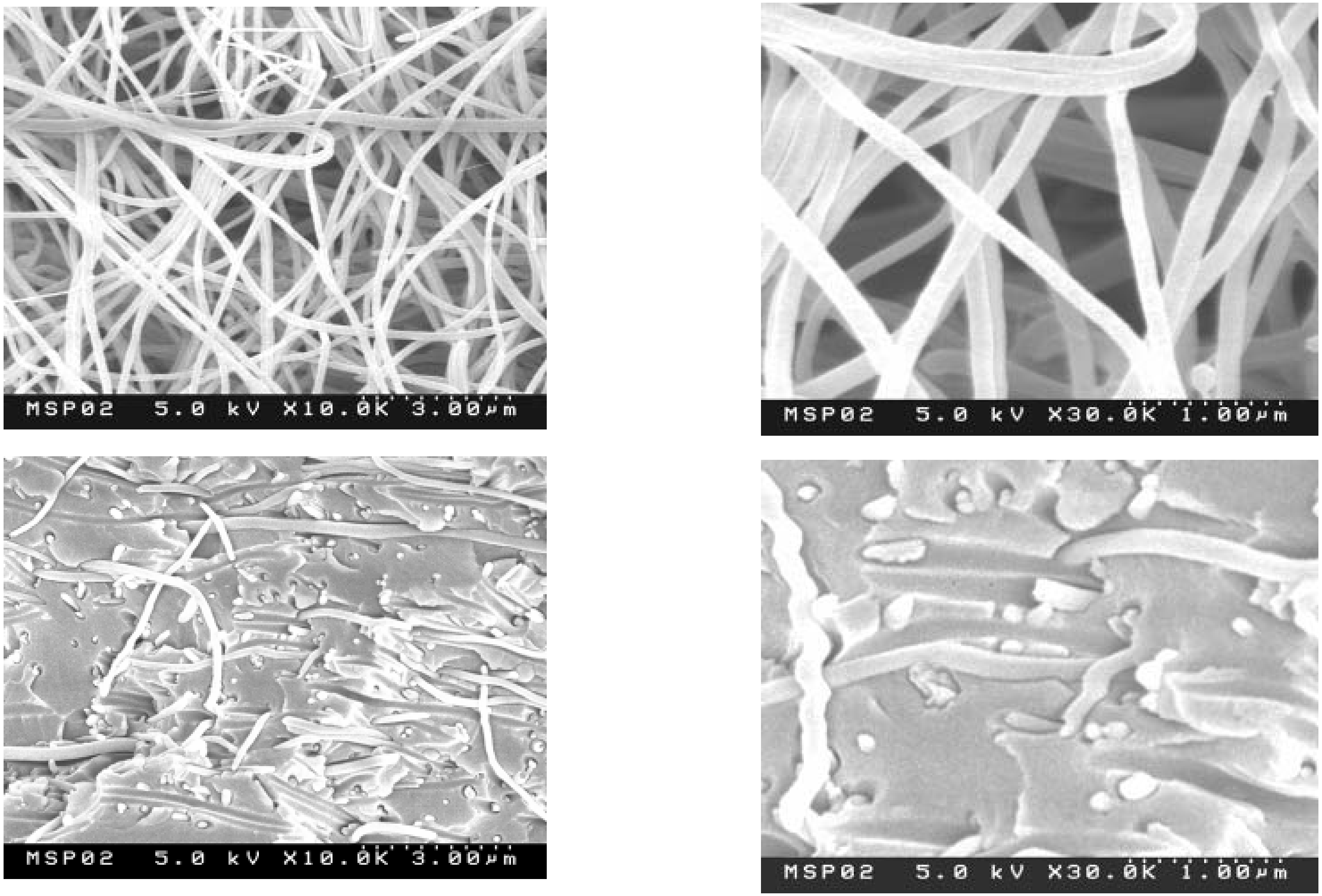


	Unwelded	Welded	Over-welded
Density of the mats	42%	74%	****
Conductivity (S/cm)	0.016	0.041	****

Results: (1) There is an increase in mat density with fiber welding and (2) The proton conductivity of a compacted/welded mat is consistent with the mat density and the conductivity of sPEEK.

Preliminary Results for Embedding Mats Using a UV-curable Thermoset

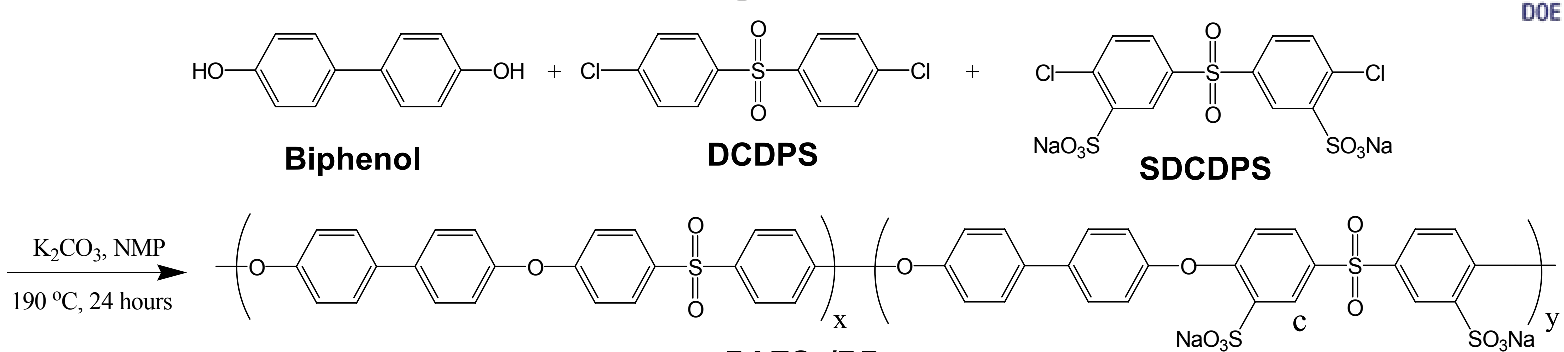
DOE Hydrogen Program



SEM micrographs of cross-section of the nascent, porous mat (top) and of the embedded, dense membrane (bottom) at two magnifications: 10K (left) and 30K (right).

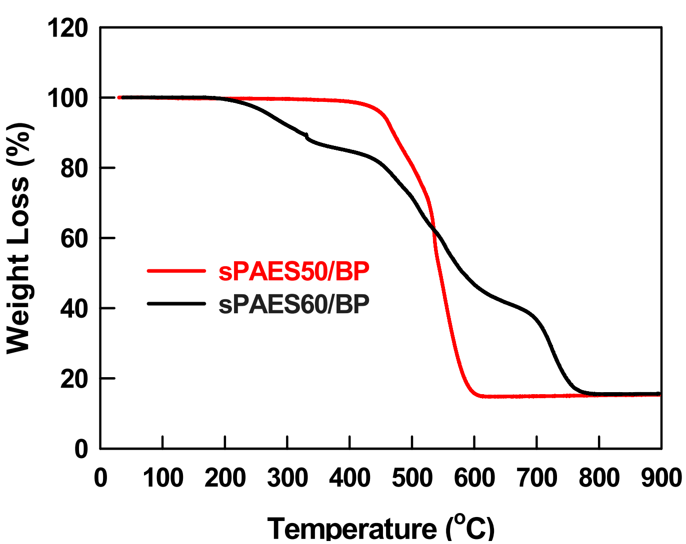
Results: NOA 63 (UV curable thermoset) is suitable to embed a sPEEK electrospun mat

Synthesis and Characterization of sPAES Polymers



sPAESy/BP

Sample code	Mn (g/mol)	Mw (g/mol)	Actual mol % of SDCDPS	Film Conductivity (S/cm)	Solubility in DI water
sPAES50/BP	67,400	109,300	42	0.07	Insoluble
sPAES60/BP	70,500	131,400	52	0.121	Insoluble



- *TGA results of sPAES/BP polymers measured in air*
- *Samples were pre-dried at 150 °C for 30 min under N_2 atmosphere*

Results: We have synthesize a high conductivity polymer, which will be electrospun into mats

Project Summary

Relevance: Membranes that conduct protons at high temperature and low relative humidity are needed for hydrogen/air PEM fuel cells.

Approach: Use an electrospun NanoCapillary Network (NCN) membrane micromorphology where an interconnected mat of proton conducting polymer nanofibers are imbedded in an inert polymer matrix.

Technical Accomplishments and Progress: Electrospun fiber mats have been fabricated from sulfonated poly(ether ether ketone). The mats have been compacted and the fibers welded. The proton conductivity of densified/welded mats has been measured.

Proposed Future Research: Increase the proton conductivity of fiber mats and impregnate the mats with inert polymer.

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Future Work 2007-08

DOE Hydrogen Program

Increase the proton conductivity of electrospun mats

- Refine methods for increasing the density of fibers in a mat by: (i) Changing the electro-spinning conditions (e.g., spinneret potential, flow rate, spinneret to collector distance) and (ii) Varying the mat compaction and welding methods.
- Use a higher IEC polymer to create the fibers (sPEEK and/or sulfonated polysulfone) with a homogeneous (fully dense) polymer conductivity of at least 0.12 S/cm.
- Investigate electrospinning with high IEC polymers in different counterion forms.

Impregnate compacted and welded fiber mats with an inert polymer

- Look at different impregnation polymers, different mat densities, and nanofiber mats of different IEC

Continue to investigate and characterize the properties of electrospun mats of an ion-exchange polymer

- Determine the mechanical properties of the mats as a function of ion-exchange capacity and mat density.
- Determine the effect of a water boiling pretreatment step on the proton conductivity of electrospun mats.