

# V.B.12 NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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## Objectives

- Fabricate a new class of nanocapillary network 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.

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) 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 target of this project is a fuel cell membrane with a proton conductivity equal to or greater than 0.1 S/cm at a temperature less than or equal to 120°C and 25-50% relative humidity.

## Approach

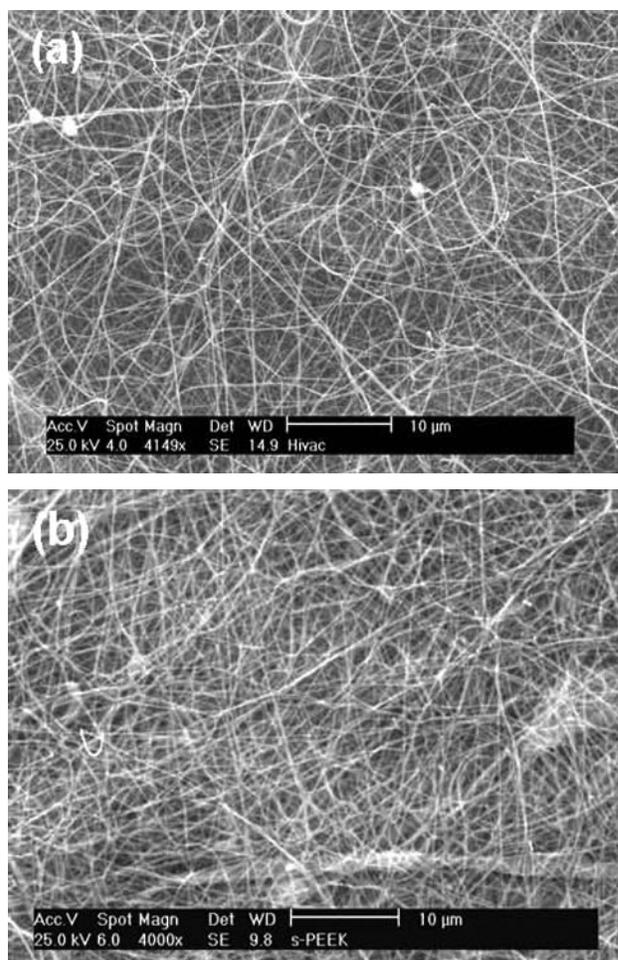
Membranes will be fabricated with a three-dimensional interconnected network of proton conducting polymer nanocapillaries that are embedded in an inert/impermeable polymer matrix. The nanocapillary network, occupying about 40-70% of the dry membrane volume, will be composed of a high ion-exchange capacity (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. To further enhance the water retaining capacity and proton conduction property of the nanocapillaries, the sulfonated polymer will be doped with molecular silica, specifically trisilanol POSS molecules, where POSS denotes polyhedral oligomeric silsesquioxane.

## Accomplishments

*Sulfonation of PEEK.* Poly(ether ether ketone) (PEEK) was sulfonated to a range of different ion-exchange capacities (IECs of 1.3-2.0 mmol/g) by varying the reaction time with concentrated sulfuric acid at 25°C. The proton conductivity of water equilibrated dense films increased from 0.02 S/cm (1.3 IEC) to 0.13 S/cm (2.0 IEC).

*Electrospinning.* Electrospun nanofiber mats were prepared from several concentrations of sulfonated (2.0 IEC) poly(ether ether ketone) (abbreviated as SPEEK), using dimethyl acetamide (DMAc) as the solvent, where the spinneret-to-collector distance (SCD) was either 8 cm or 4.5 cm (the spinneret potential and solution flow rate were held fixed at 17 kV and 0.1 mL/h, respectively). The spinning solution was varied in order to minimize fiber diameter while avoiding droplet

formation. Electrospinning of sPEEK/DMAc solutions with  $\leq 10$  wt-% sPEEK led to an undesirable bead-on-string fiber morphology. However, electrospun webs of nanofibers were successfully prepared using a 20 wt-% sPEEK/DMAc solution, as shown in Figure 1. The web density was increased by decreasing the SCD from 8 cm (Figure 1a) to 4.5 cm (Figure 1b). Also, the shorter SCD resulted in straighter fibers. Both figures show fiber diameters ranging from 70 nm to 400 nm, with an average diameter of 150 nm. The proton conductivity (in water at 25°C) of fiber mats (after boiling in acid and washing in water) was 0.02 S/cm. The low conductivity was attributed to excessive swelling of the mat (with significant fiber rearrangement).



**FIGURE 1.** Scanning electron microscopy images of electrospun sPEEK (20 wt% in DMAc), with webs having (a) lower and (b) higher densities through variation in spinneret-to-collector distance. Scale bar is 10 μm.