2006 DOE Hydrogen Program Review Presentation

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

Peter Pintauro[1] and Patrick T. Mather[2]
[1]Department of Chemical Engineering
[2]Department of Macromolecular Science and Engineering
Case Western Reserve University
Cleveland, Ohio 44106

5/19/2006

CASE
CASE WESTERN RESERVE UNIVERSITY

Project ID #FCP 4

Objectives

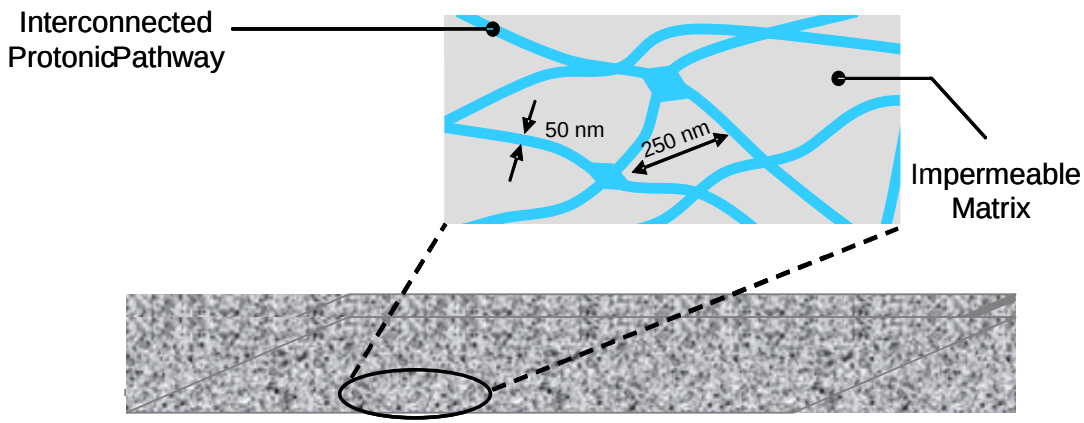
Fabricate and characterize a new class of NanoCapillary Network proton conducting membranes for hydrogen/air fuel cells that operate under high temperature, low humidity conditions.

- Electrospun nm-size fibers of high ion-exchange capacity polymer that are vapor welded and imbedded in an uncharged (impermeable and inert) polymer matrix
- Addition of molecular silica to further enhance water retention
- Crosslinking of high IEC fibers to prevent water dissolution
- Uncharged polymer matrix will control nanocapillary swelling and provide overall mechanical strength to the final composite membrane
- Employ the concept of capillary condensation for membrane water retention.

Proposed Membrane Morphology

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

Decouple the role of the proton-conducting channels from that of the polymer support matrix



Plan and Approach

Task 1 Sulfonated Polymer Synthesis - sulfonated poly(ether ether ketone), sulfonated poly(arylene ether sulfone), and sulfonated acrylate copolymer

- Different polymer IECs
- With and without molecular-level silica
- With and without crosslinking

Task 2 Electrospinning Process Development

- Creation of a fiber mat (fiber diameter 10-50 nm; 40-70% fiber mat volume fraction)
- Fiber welding studies

Task 3 Matrix Polymer Identification and Membrane Fabrication

- Identify an inert (uncharged) polymer – solvent-less room-temperature curing two-part commercial epoxy resin or a non-sulfonated UV-crosslinked acrylate copolymer
- Develop a method for adding polymer to the fiber mat

Task 4 Preliminary Membrane Characterization

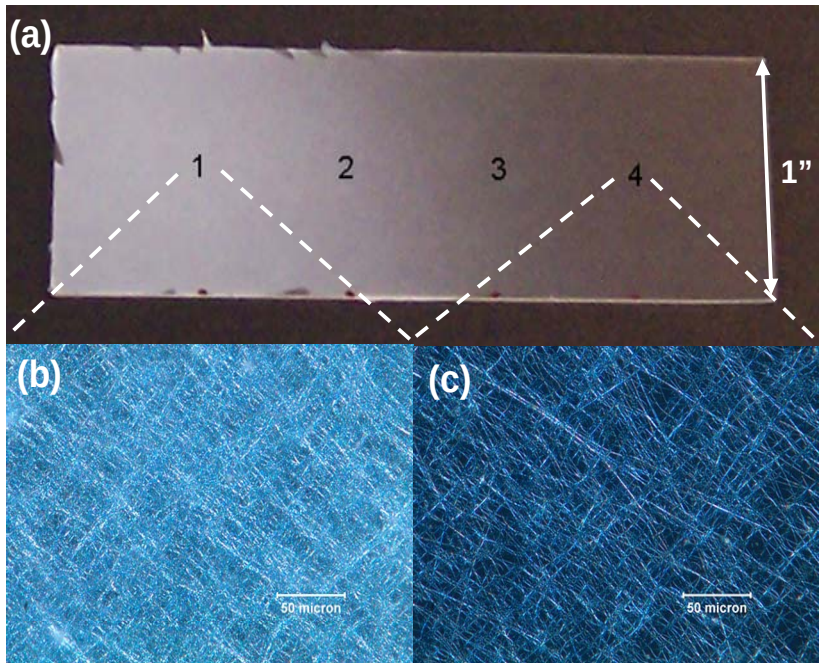
- 40-70 μm membrane thickness

Tasks 5 Membrane Composition/Structure Optimization

- Optimize on the choice of sulfonated and matrix (inert) polymers, fiber diameter, fiber mat density, membrane thickness, extent of fiber welding, amount of added molecular silica.

Preliminary Electrospinning Results

Sulfonated PEEK, electrospun onto ITO-coated glass

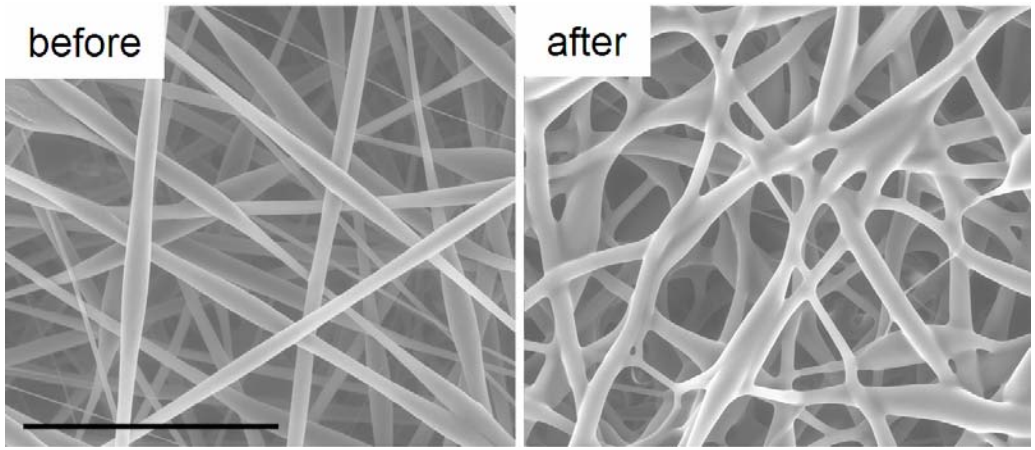


(a) A spatial gradient of fiber density from position “1” to “4”. Polarized optical microscope (POM) images

(b, c) reveal significant birefringence and thus molecular orientation. Only fibers oriented near +/- 45^{o} are visible in this configuration. Fiber diameter is < 1 μm.

CASE
CASE WESTERN RESERVE UNIVERSITY

Vapor Welding of Fibers



Solvent vapor welding of electrospun fibers. Polycyclooctene exposed to THF vapor. Scale bar is 100 μm

CASE
CASE WESTERN RESERVE UNIVERSITY

Critical Issues

- **That we can create a 3D interconnected network mat of very small diameter (10-50 nm) proton-conducting polymer nanocapillaries, where the network occupies about 40-70% of the dry membrane volume.**

- **That we can fill the inter-fiber void volume with an inert (uncharged) polymer with no pin hole defects in the resulting membrane.**

- **That capillary condensation (retention) of water within the nanocapillaries (due to their nm-scale diameter in combination with the high loading of sulfonic groups and restricted swelling) will promote proton conductivity under high temperature and low relative humidity conditions.**

- **That the incorporation of molecular-level silica into the sulfonated polymer nanocapillaries will further improve water retention and low RH proton conductivity.**