2006 DOE Hydrogen Program Review Presentation

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

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Project ID #FCP 4

Overview

Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 0%

Budget

- Total project funding
  - DOE $1,455,257
  - Contractor (CWRU) $481,465
- Funding received in FY05, $150,000
- Funding for FY06, $296,620

Barriers

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

Interactions

Eric Fossum, Dept. of Chemistry, Wright State University, Dayton, OH

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.

- Hydrogen/air PEM fuel cells are an important component of the DOE's Hydrogen Program.

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**

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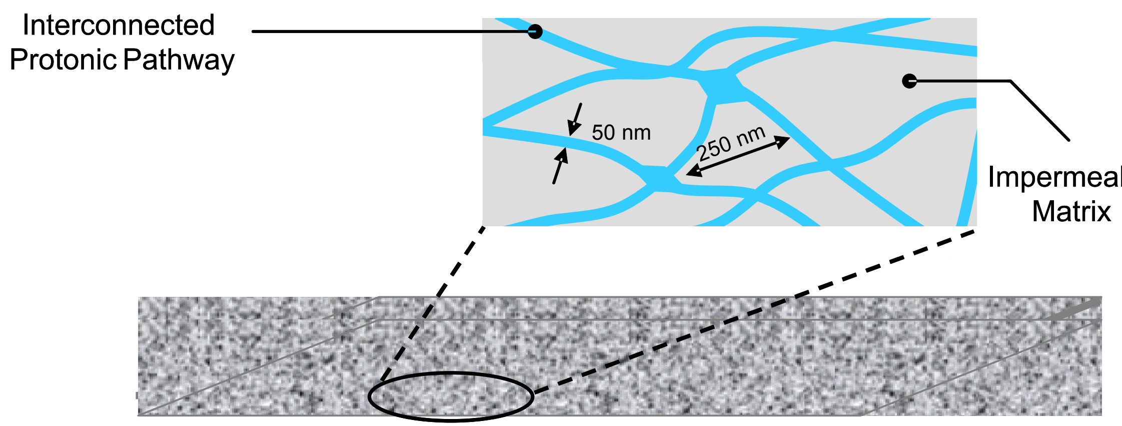
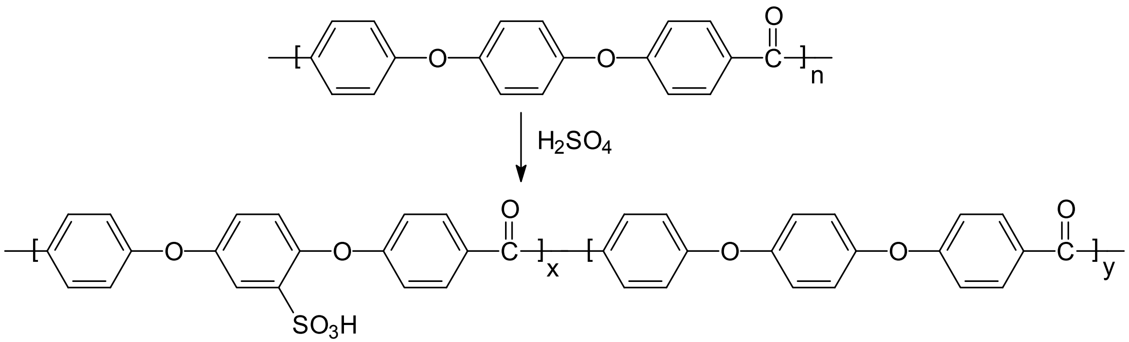
Plan and Approach – Proposed Membrane Morphology

Structure for NanoCapillary Network (NCN) membranes:

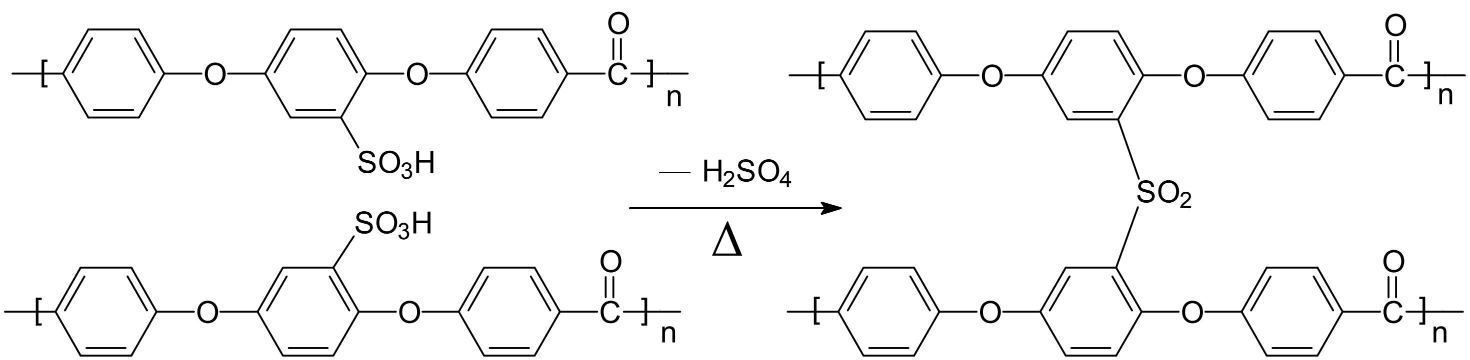
The electrospun sulfonated polymer fibers with/without molecular silica are interconnected by vapor welding and the inter-fiber spaces are filled by a nonconducting, gas impermeable polymer



Plan and Approach – Sulfonated Polymers



Sulfonation scheme for the preparation of sulfonated poly(ether ether ketone) - sPEEK



Crosslinking through thermal condensation of the sulfonic groups of sPEEK

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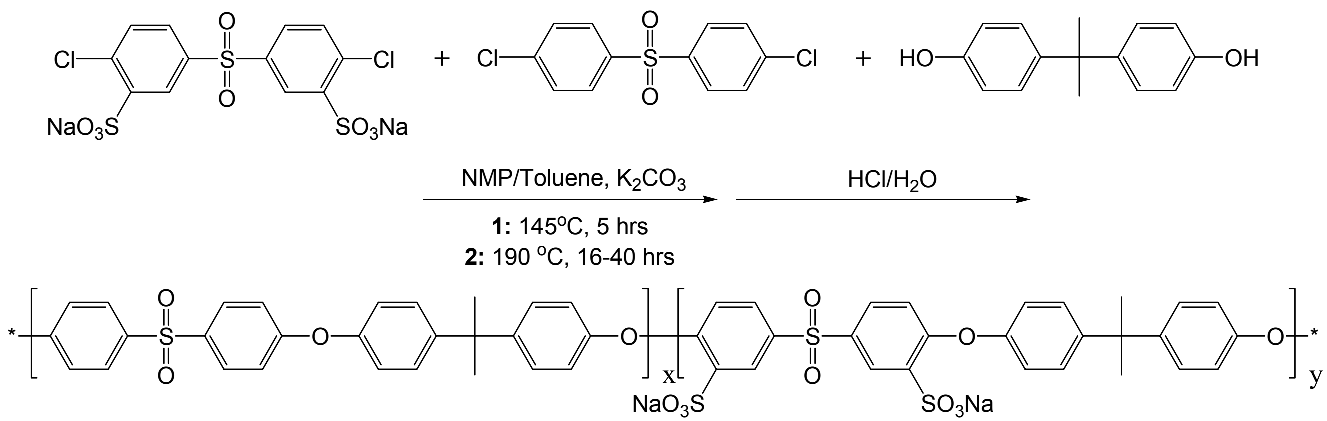
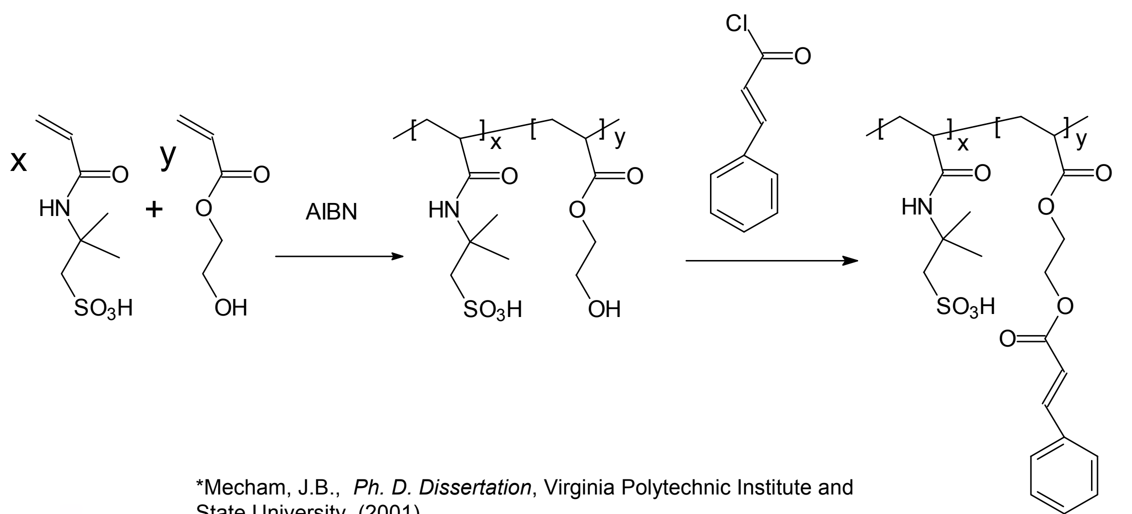
Plan and Approach – Sulfonated Polymers



Polymerization of a sulfonated monomer to sulfonated poly (arylene ether sulfone) – sPAES*



Synthetic steps leading to a photo-crosslinkable sulfonic acid acrylate copolymer - sACRYL

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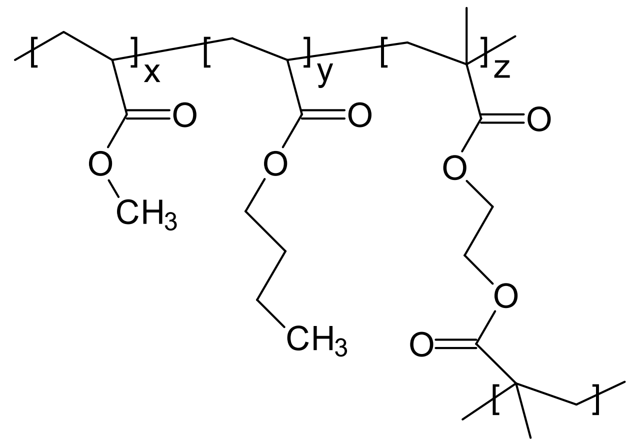
*Mecham, J.B., *Ph. D. Dissertation*, Virginia Polytechnic Institute and State University, (2001).

Plan and Approach – Inert Matrix Polymer

<u>Epoxy</u> – For sPEEK and aPAES, a room-temperature curing two-part commercial epoxy (e.g., Epoplast™ or Epon 862/Epi-cure W) will be used.

<u>Acrylate</u> - To serve as the matrix for sACRYL nanofibers, a methyl acrylate copolymer matrix will be formed *in-situ* by bulk photo-copolymerization of a mixture of methyl methacrylate, methyl acrylate)/butyl methacrylate, butyl acrylate)/ ethyleneglycol dimethacrylate, or trimethylolpropane trimethacrylate



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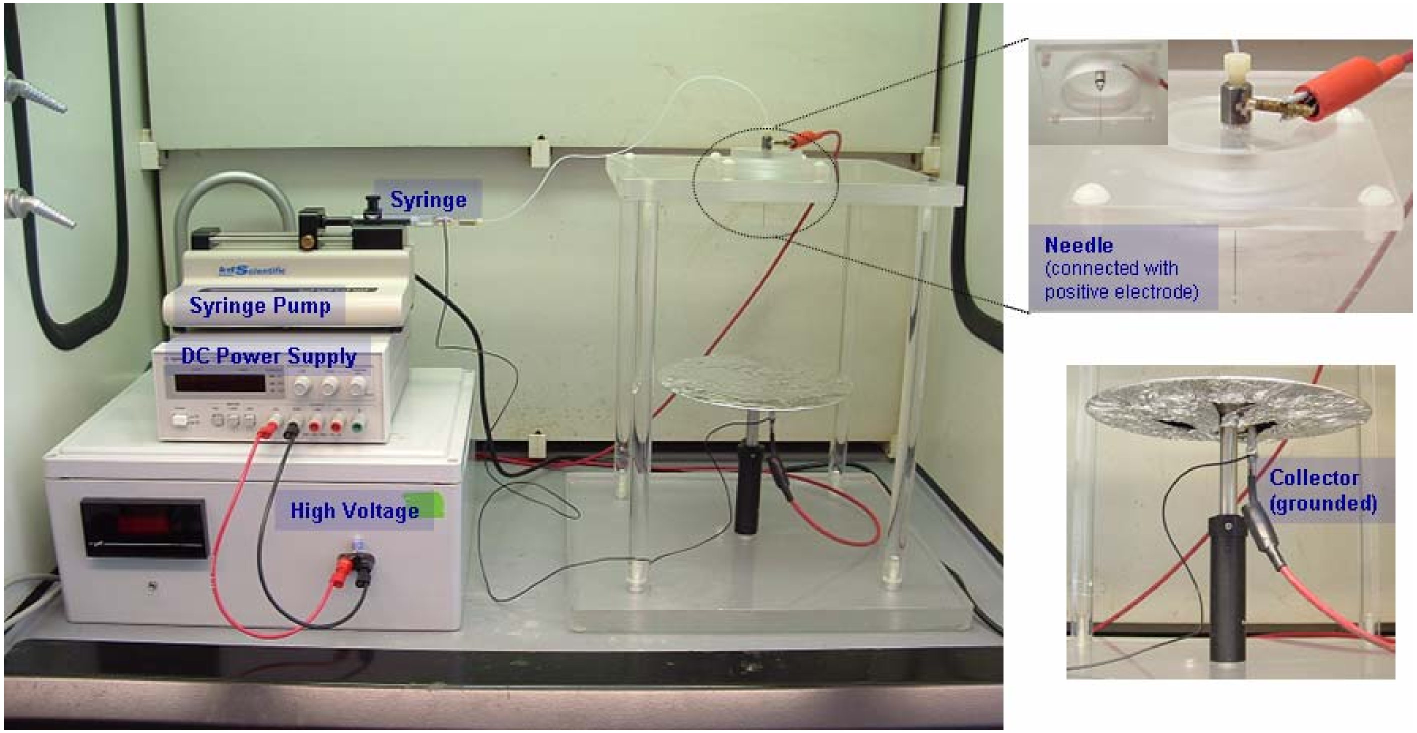
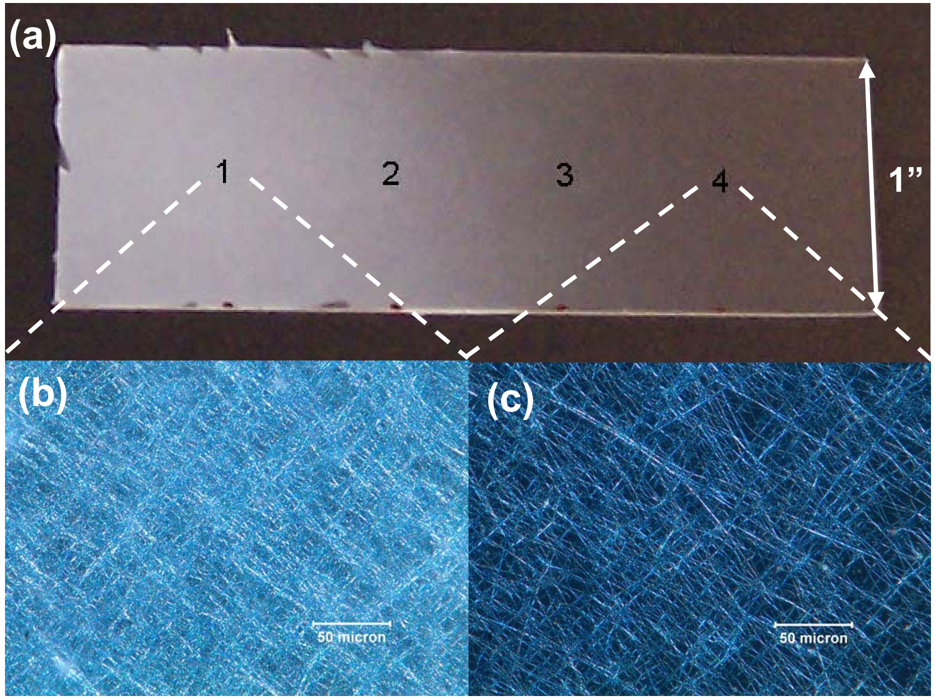
Accomplishments/Progress/ Results Slides



Set-up at CWRU for electrospinning of sulfonated polymer fiber capillary network. A syringe pump delivers polymer solution to the charged needle, expelling a fibrous stream to the grounded collector.

Accomplishments Slides (con't)



Preliminary data of sPEEK electrospun onto ITO-coated glass (a) showing 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. The POM scale bars are 50 mm.

Future Work

- **Fiscal Year 2005-06** - Prepare and characterize sulfonated polymers (without molecular silica), including sPEEK, sPAES, and sACRYL. Begin sulfonated polymer electrospinning experiments.

- **Fiscal Year 2006-07** – Synthesize and electrospin sulfonated polymers with molecular silica. Add an inert polymer to electrospun mats. Begin to characterize the resulting membranes.

Summary

- Approach: Fabricate and characterize NanoCapillary Network (NCN) proton conducting membranes for high T, low RH hydrogen/air fuel cells. The proposed membrane micromorphology is the 1st of its kind for fuel cell applications.

- Relevance: The proposed membranes will meet DOE performance targets – a proton conductivity $\geq$ 0.07 S/cm at 80% RH and room temperature (achieved by the 3rd quarter of year 2) and > 0.1 S/cm at 50% RH and 120^{o}C (achieved by the 3rd quarter of year 3)

- Technical Accomplishments and Progress: Electrospun fiber mats have been fabricated from sulfonated poly(ether ether ketone)

- Proposed Future Work: Create fiber mats from various sulfonated polymers (with and without molecular-level silica), add inert polymer to the inter-fiber voids and begin characterization of the resulting membranes.

Critical Assumptions and Issues

- **That we can create a 3D interconnected network mat of very small diameter (10-50 nm) proton-conducting polymer nanocapillaries, where the nanocapillary 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 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 membrane water retention, thereby increasing proton conductivity under low relative humidity conditions.**

- **That by the incorporation of molecular-level silica into the sulfonated polymer nanocapillaries, we will observe further improvements in water retention and low RH proton conductivity.**