

# 2006 DOE Hydrogen Program Review Presentation

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

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# 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

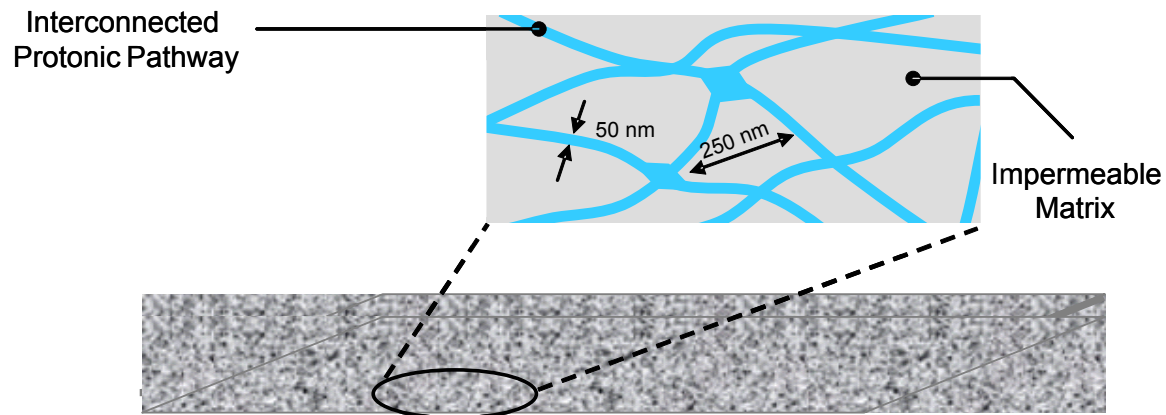
- Bubble point test
- Equilibrium water swelling as a function of T and RH
- Preliminary through-plane and in-plane conductivity at different T and RH
- Thermomechanical analysis
- Mechanical properties
- Oxygen permeability
- SEM and TEM micrographs of membrane cross sections
- Thermal analysis (DSC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

## > Tasks 5 Membrane Composition/Structure Optimization

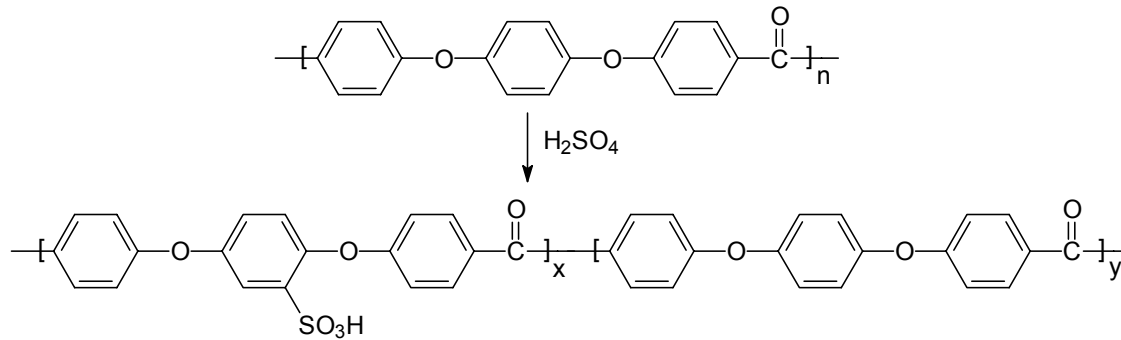
# Plan and Approach – Proposed Membrane Morphology

**Structure for NanoCapillary Network (NCN) membranes:**

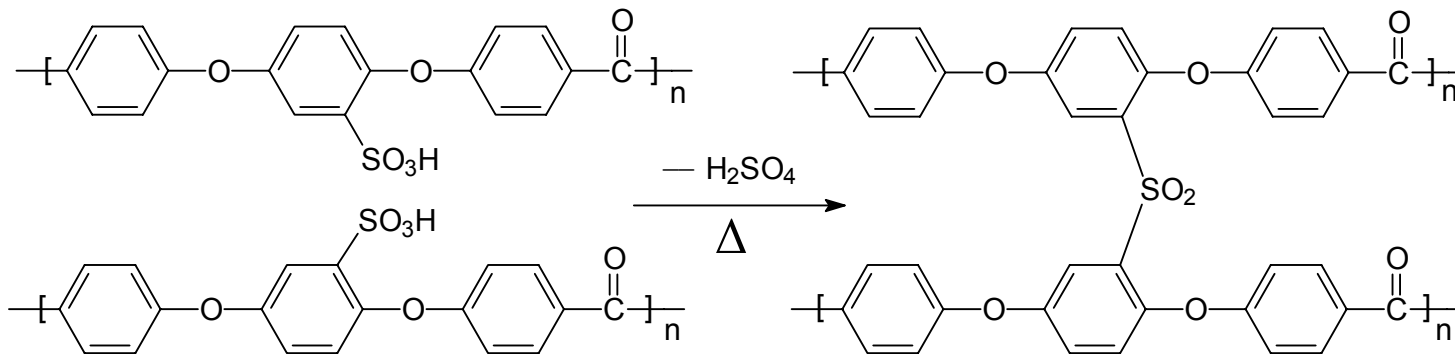
**The electrospun sulfonated polymer fibers with/without molecular silica are interconnected by vapor welding and the inter-fiber spaces are filled by a nonconducting, gas impermeable polymer**



# Plan and Approach – Sulfonated Polymers

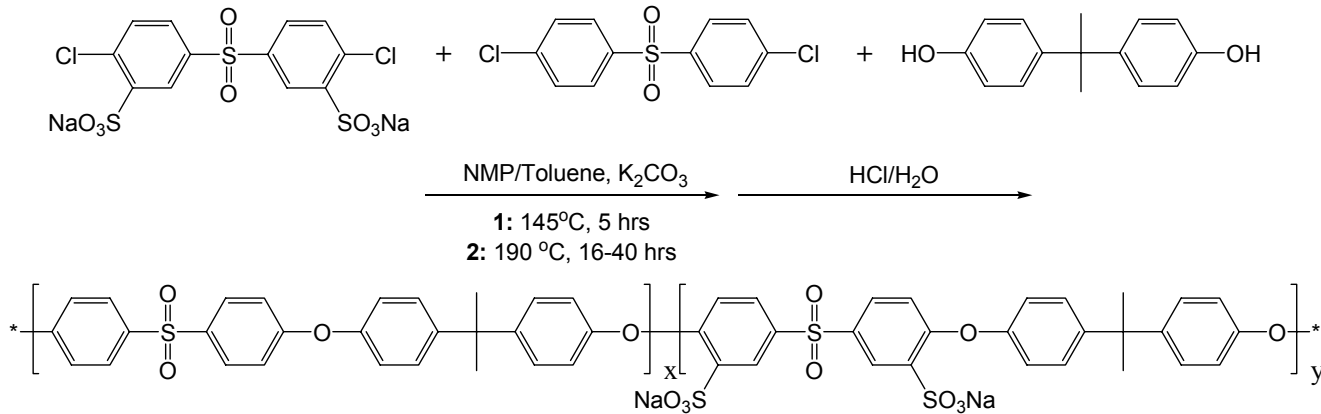


**Sulfonation scheme for the preparation of sulfonated poly(ether ether ketone) - sPEEK**

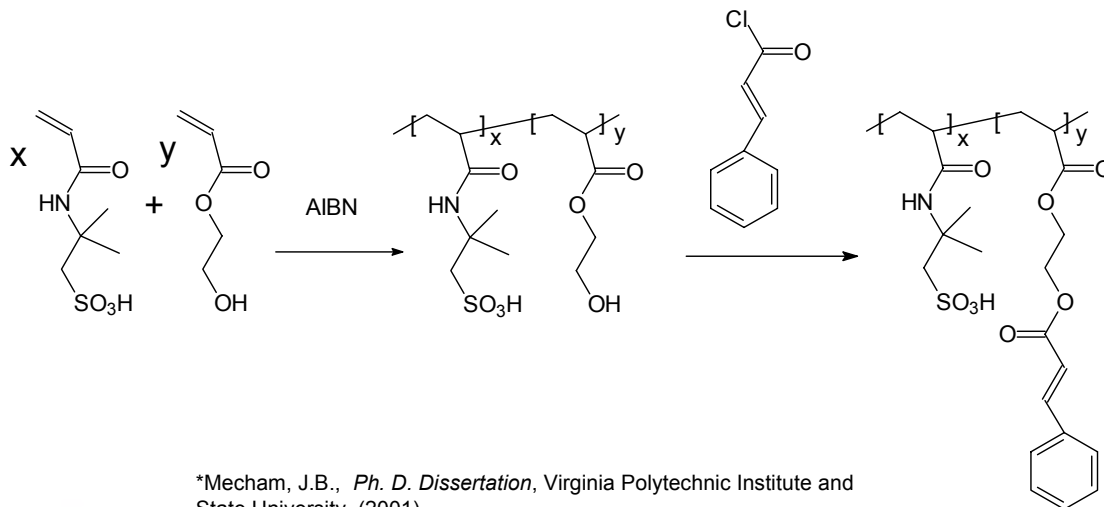


**Crosslinking through thermal condensation of the sulfonic groups of sPEEK**

# Plan and Approach – Sulfonated Polymers



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

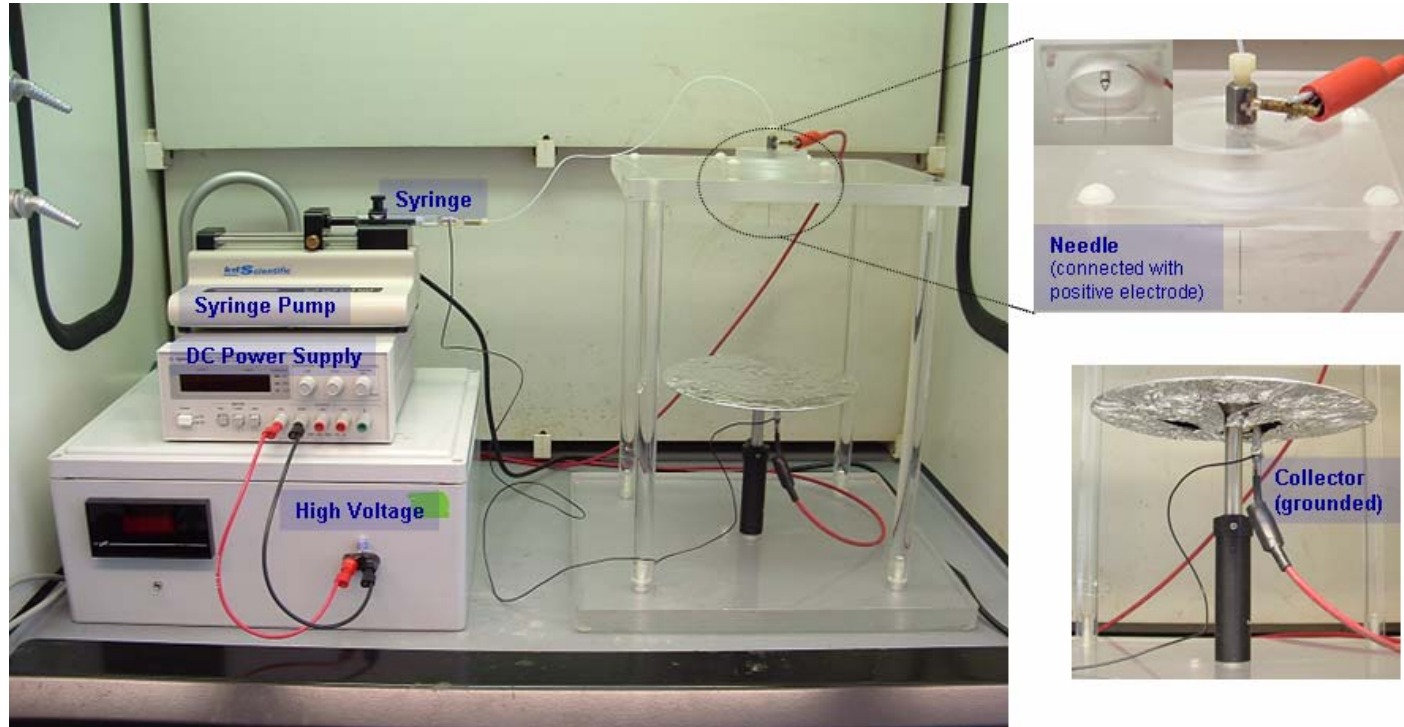


**Synthetic steps leading to a photo-crosslinkable sulfonic acid acrylate copolymer - sACRYL**



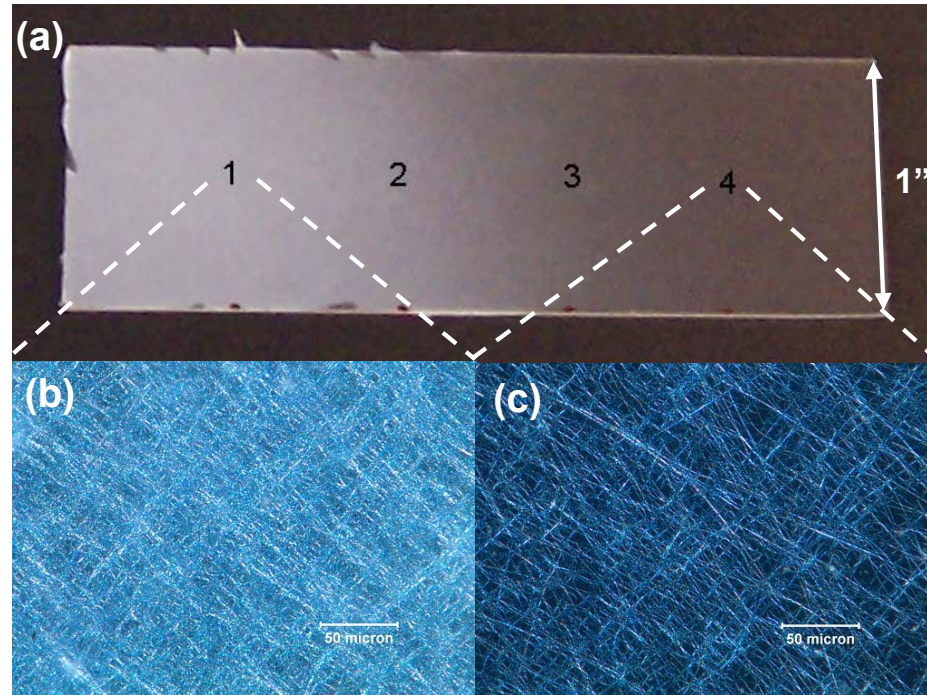


# Accomplishments/Progress/ Results Slides



**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  $\pm 45^\circ$  are visible in this configuration. The POM scale bars are 50  $\mu\text{m}$ .

# 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 1<sup>st</sup> 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 3<sup>rd</sup> quarter of year 2) and  $> 0.1$  S/cm at 50% RH and 120°C (achieved by the 3<sup>rd</sup> 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.