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DOE Hydrogen Program

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

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Project ID #FC20

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Overview

Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 40%

Budget

- Total project funding
  - DOE $1,455,257
  - Contractor (CWRU) $481,465
- Funding received in FY07, $300,000
- Funding for FY08, $350,000

Barriers

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

Interactions

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Project Objective

To 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.

2007-08 Project Goals

Fabricate membranes with the following properties:

1. **0.07 S/cm proton conductivity at 30°C and 80% relative humidity.**
2. **Good mechanical properties.**
3. **Low gas permeability.**

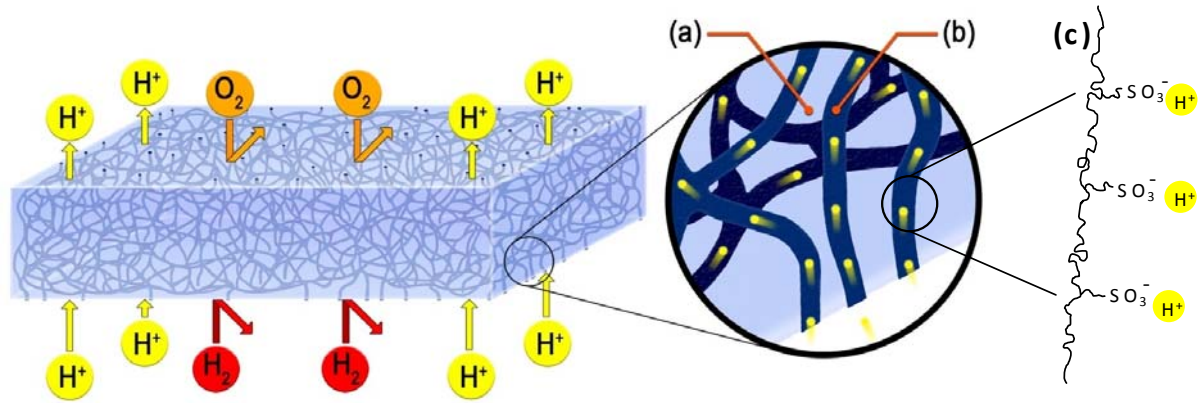
Identify a roadmap to achieve high conductivities at lower humidity and higher temperatures (Year 3 milestone of 0.1 S/cm at 50% RH and 120°C).

Milestones

Month/Year	Milestone or Go/No-Go Decision
Nov-07	Milestone: Fabricated a series of nanofiber network cation-exchange membranes with different volume fractions of interconnected fibers (from sulfonated poly(arylene ether sulfone)) in an inert matrix. Measure proton conductivity in water and water swelling (at 25°C), tensile strength, and gas (oxygen) permeability.
March-08	Milestone: Added varying amounts of sulfonated POSS (polyhedral oligomeric silsesquioxanes) to sulfonated poly(arylene ether sulfone) and electrospun nanofiber mats. Converted the mats into defect-free nanofiber network membranes. Measured proton conductivity at 30°C and 80% RH.
April-08	Go/No-Go Decision: Achieved a proton conductivity of 0.7 S/cm at 30°C and 80% RH, for a nanofiber network membrane containing proton conducting fibers (sPAES with sulfonated POSS) and Norland Optical Adhesive as the inert matrix.

Approach - Nanofiber Network Membranes

The Concept: Fabricate a phase separated membrane composed of ionomeric nanofibers embedded in a uncharged and inert polymer matrix. Artificially create the nanomorphology desired in a copolymer.



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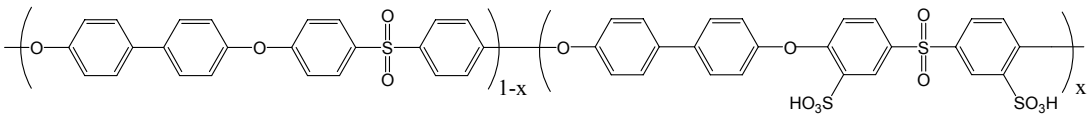


1- Decouple mechanical and proton-conducting functions of the membrane

2- Remove percolative problems of classical blended and composite systems

3- Control independently both the size and the loading of the proton-conducting phase

4- Use nano-fibers/capillaries and inorganic particles to exploit interfacial effects, capillary condensation and other nano-phenomena

Plan and Approach - Tasks

Red (done) – Green (ongoing) – Blue (upcoming)

> Task 1 Sulfonated Polymer Synthesis

- Different polymer IECs
- Polymer crosslinking studies
- Polymer characterizations

> Task 2 Electrospinning Process Development

- Creation of a fiber mat (with and without sulfonated POSS)
- Fiber Compaction and 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

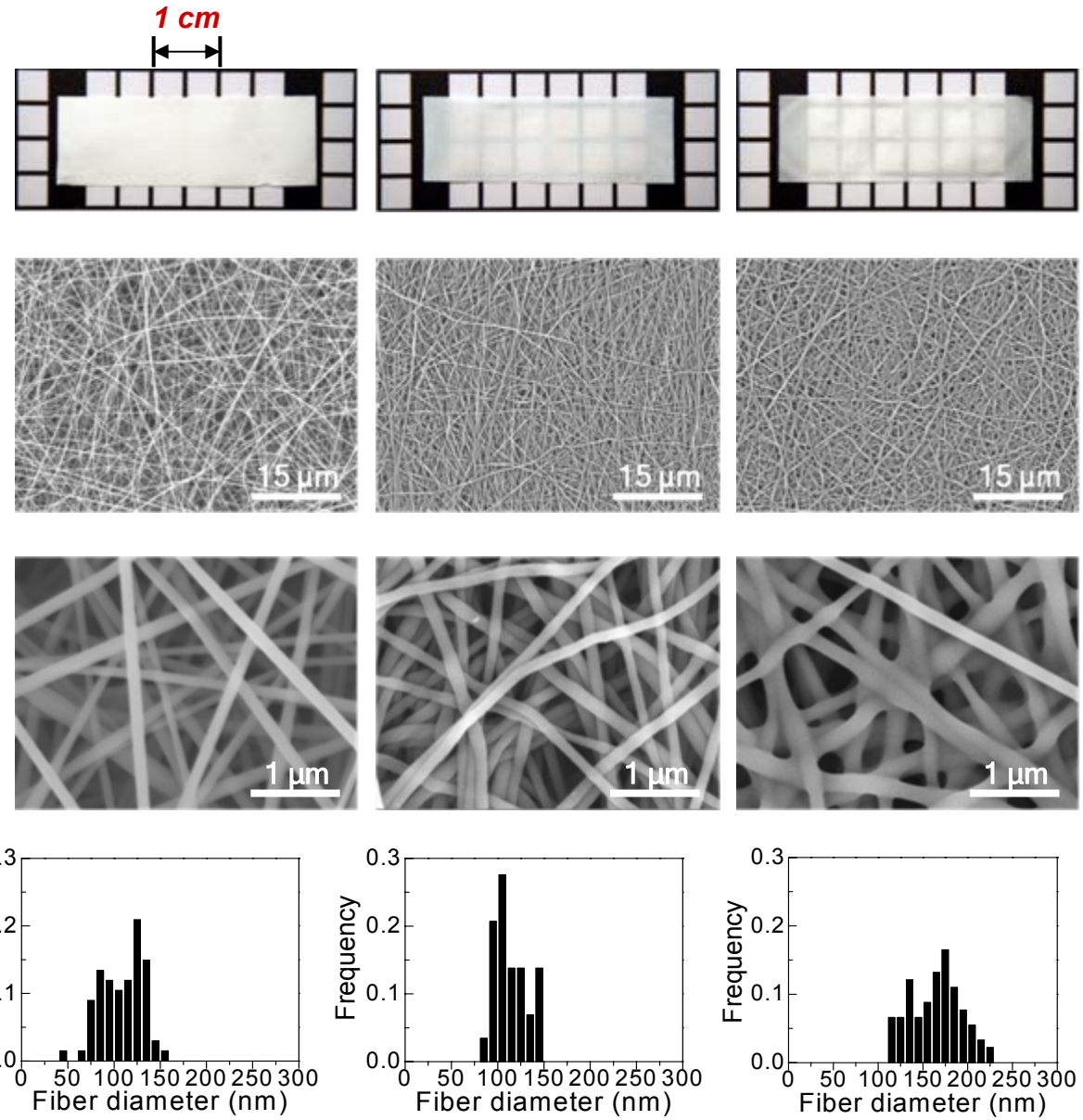
- Equilibrium water swelling as a function of T and RH
- Preliminary through-plane and in-plane conductivity at different T and RH
- Thermomechanical analysis
- Mechanical properties
- Oxygen permeability
- SEM and TEM micrographs of membrane cross sections
- Thermal analysis (DSC and TGA) of the sulfonated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

> Tasks 5 Membrane Composition/Structure Optimization

Membrane Fabrication Steps

1. Synthesize sulfonated poly(arylene ether sulfone) (sPAES) with a high Ion-exchange capacity (2.1-2.6 mmol/g) and high molecular weight .
2. Electrospun nanofiber mats (using DMAc and 2-butoxyethanol as the solvent). Use a rotating and oscillating drum as the fiber collector (to produce a large mat of uniform thickness and fiber volume fraction). Typical fiber density of the mats was 0.20.
3. Densify the fiber mats to increase fiber volume fraction. Use 3 minute compaction (with no heat). Pressure vs. fiber volume fraction relationship was determined. Fiber volume fraction can be controlled from 24-80%.
4. Weld intersecting fibers to make a 3-D fiber network. Expose densified mat to organic solvent in a sealed chamber (DMF or 2-butoxyethanol).
5. Fill the voids between fibers with NOA63 and UV cure.

Nanofiber Composite Membranes – Fabricated Structures



2.5 mmol/g IEC sPAES fibers

Electrospin

14 kV, 8 cm SCD, 1600 rpm, 0.04 ml/h. Fiber density = 0.20

Compact

fiber density = 0.30 at 700 psi; fiber density = 0.64 at 13,000 psi for 3 min

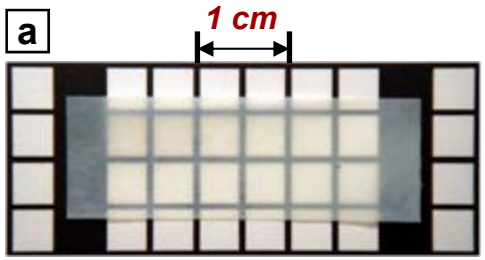
Create interfiber welds

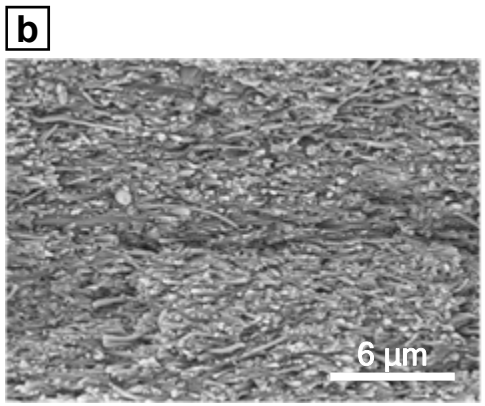
expose mat to DMF vapor 7- 18 minutes at 25°C

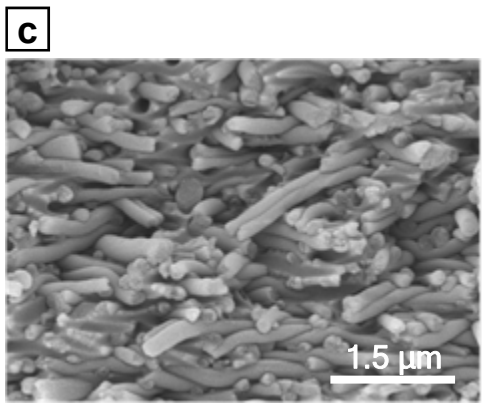
Impregnate the densified and welded mat with a solvent-less, inert, and uncharged polymer (Norland Optical Adhesive, NOA63, photopolymerizable thiol-ene based resin)

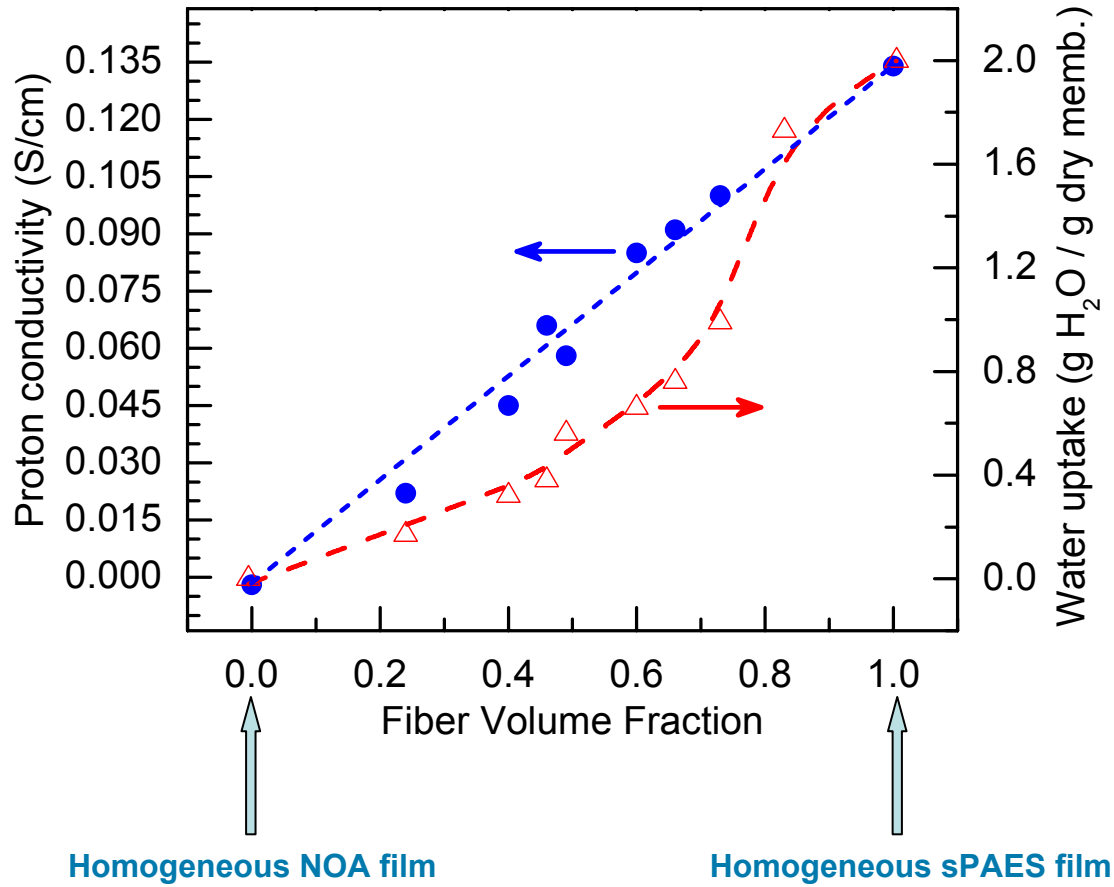
Nanofiber Composite Membranes – The Final Membrane

Embed the welded fibers in Norland Optical Adhesive (NOA63) – a solvent-less polyurethane photopolymer – and then UV cure.









Nanofiber Network Membranes

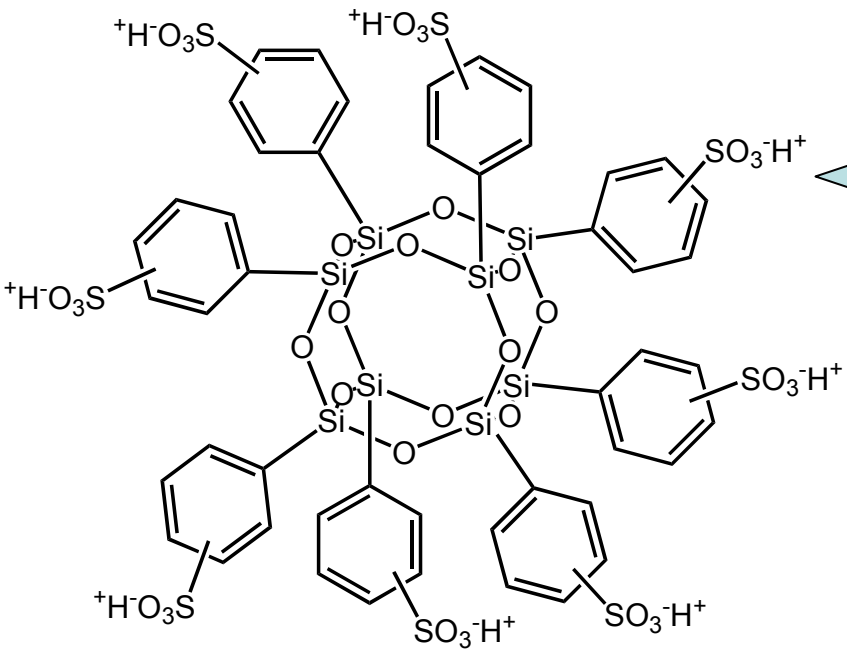
Gas Permeation and Mechanical Property Data

Tested sample	O_2 permeability (Barrer)	Young's Modulu's[a] (MPa)
Homogeneous solution cast film of sulfonated poly(arylene ether sulfone) - 2.5 mmol/g	0.53	409
UV cured NOA63 film	0.038	960
Nanofiber composite membrane of sulfonated poly(arylene ether sulfone) fibers impregnated with NOA63	0.18[b]	528[c]
Nafion ® 117	9.4	176

[a] determined from Instron tests at room temperature. All samples were dried in air for 48 hrs
[b] 60% fiber volume fraction
[c] 80% fiber volume fraction

High Conductivity Nanofiber Composite Membranes

Blends of sulfonated poly(arylene ether sulfone) and sulfonated POSS (polyhedral oligomeric silsesquioxanes) were electrospun



Sulfonated Octaphenyl Polyhedral Oligomeric Silsesquioxanes (SPOSS)

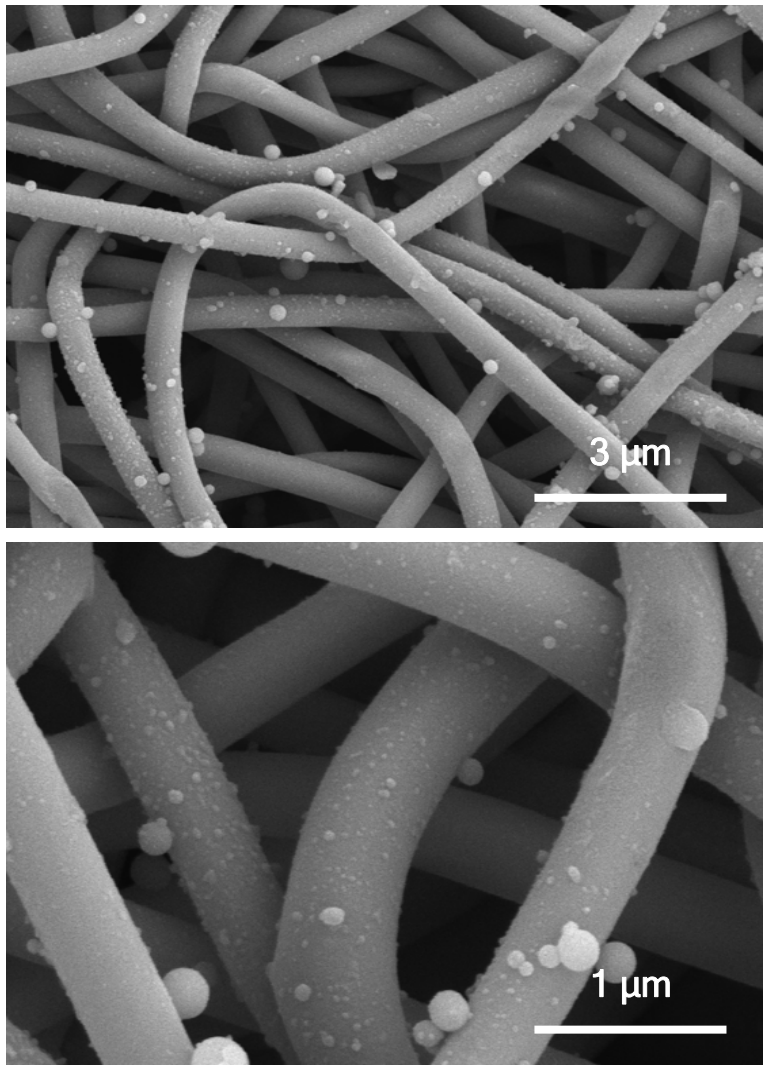
Cage Structure & Hydrophilic Acid Groups

Increase Water Retention and increase in the number of acid groups

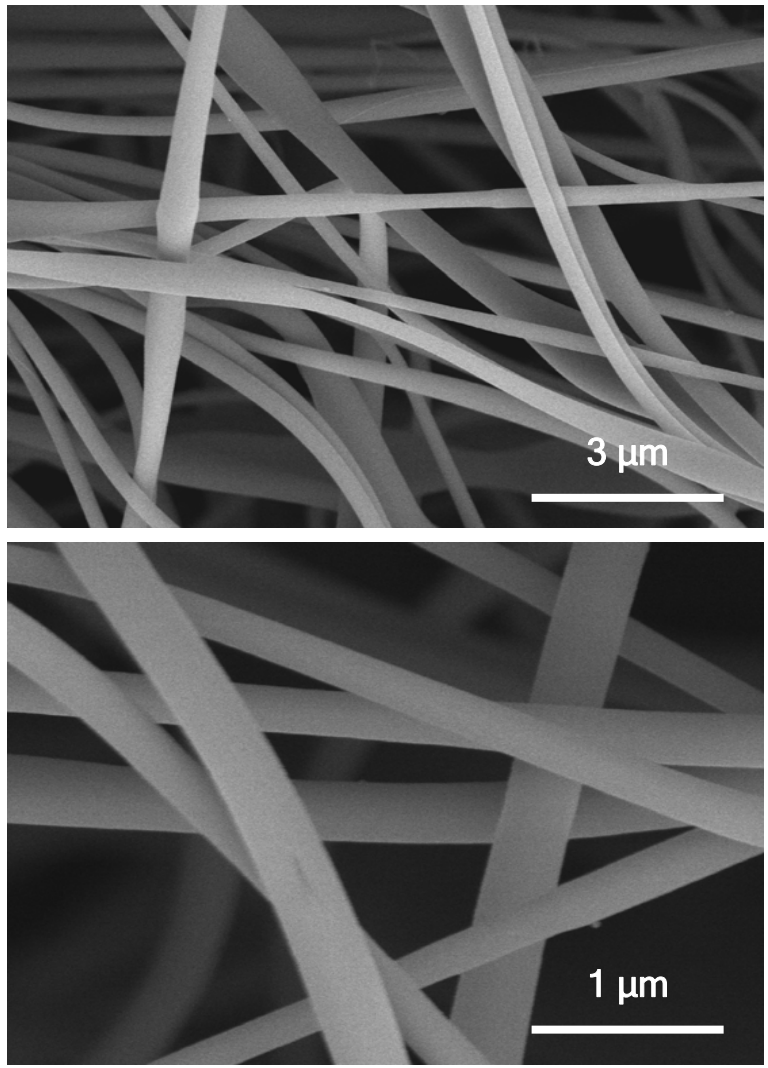
High conductivity at low humidity

SEMs of sPAES/sPOSS Electrospun Mats

40 wt% SPOSS+SPAES52



SPAES52



300-500 nm fiber diameter.

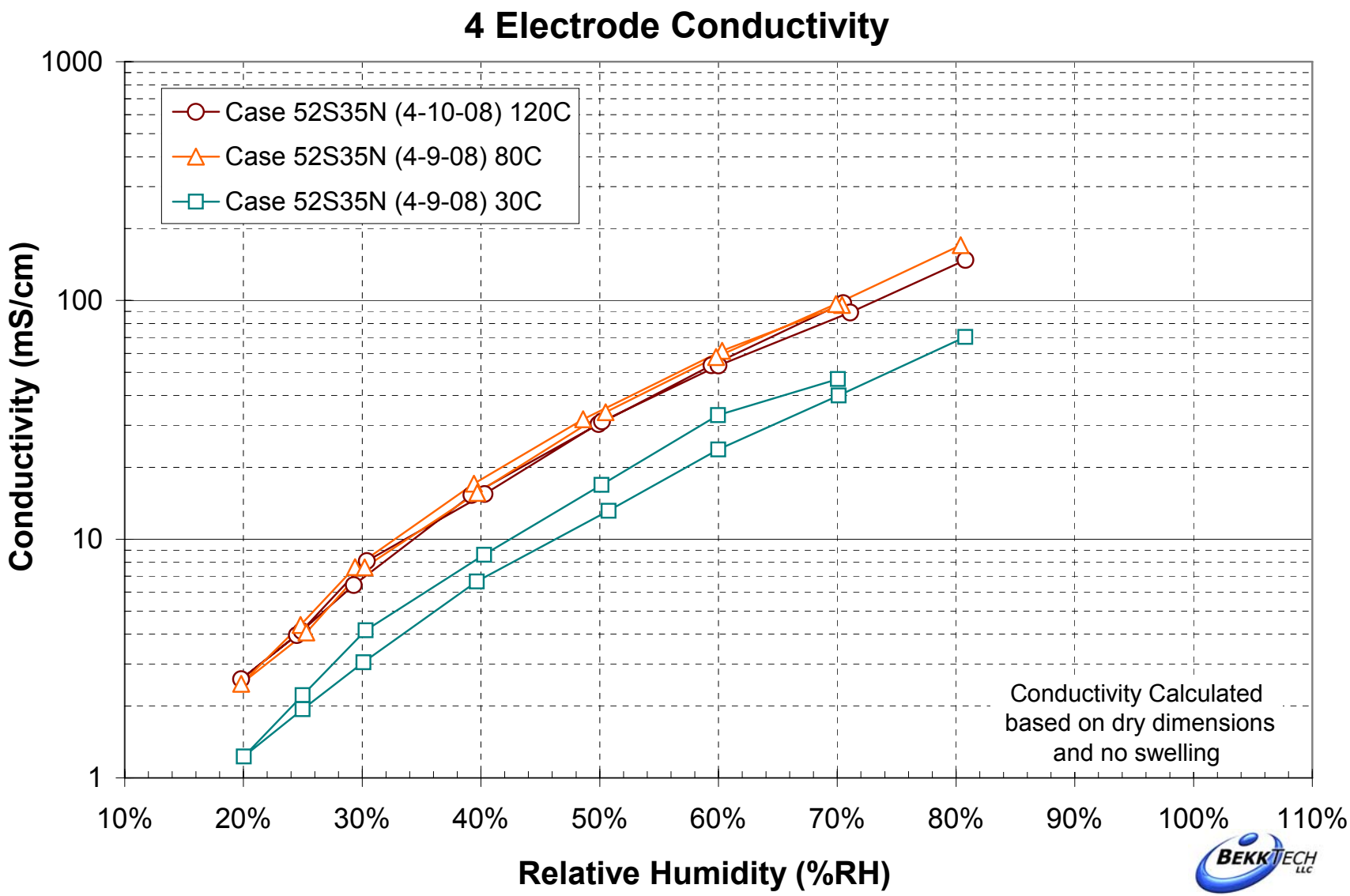
Proton Conductivity of sPAES/sPOSS Nanofiber Composite Membranes – **Our Results**

70-75% fiber volume fraction; 50-70 μm membrane thickness, 2.1 mmol/g IEC

In-plane conductivity measured in a Bekktech cell in a controlled humidity/temperature oven (30°C and 80% relative humidity)

Sample	σ (S/cm)
40% SPOSS + SPAES52 from 2-butoxyethanol	0.094
35% SPOSS + SPAES52 from 2-butoxyethanol	0.084
25% SPOSS + SPAES60 from 2-butoxyethanol	0.069
SPAES52 from 2-butoxyethanol (2.1 mmol/g IEC)	0.022
SPAES60 from 2-butoxyethanol (2.6 mmol/g IEC)	0.030
Nafion 212	0.038

Proton Conductivity of sPAES/sPOSS Nanofiber Composite Membranes – Bekktech Results



Summary of 2007-08 Work

DOE Hydrogen Program

Relevance: Seeking novel high performance membrane materials for high temperature and low relative humidity PEM fuel cell operation.

Approach: Nanofiber network membranes were fabricated from sulfonated poly(arylene ether sulfone) with/without sulfonated POSS. The inert matrix polymer for embedding the fibers was NOA63.

Technical Accomplishments and Progress: Demonstrated 0.07 S/cm proton conductivity at 30°C and 80% RH. Nanofiber network membranes exhibited good mechanical properties with low oxygen permeability.

Technology Transfer/Collaborations: Actively seeking an industrial collaborator. Presentations, publications, and a university invention disclosure.

Proposed Future Research: Increase membrane conductivity at low humidity and high temperature, without the loss of mechanical properties.

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Summary Table

Date	Membrane Material	Proton Conductivity
2006-07	Sulfonated poly(ether ether ketone) and NOA63 – 1.6 mmol/g IEC, fiber vol. fraction = 0.80	0.037 (in water at 25°C)
Nov. 2007	Sulfonated poly(arylene ether sulfone) and NOA63 – 2.5 mmol/g IEC, fiber vol. fraction = 0.77	0.11 (in water at 25°C)
March 2008	Sulfonated poly(arylene ether sulfone) with sPOSS and NOA63 – 2.1 mmol/g IEC, 40 wt% sPOSS, fiber vol. fraction = 0.70-0.75	0.07 (30°C and 80% RH) 0.17 (80°C and 80% RH) 0.062 (80°C and 60% RH)

DOE Year 2 milestone target (0.07 S/cm at 30°C and 80% RH) was met

Future Work 2008-09

DOE Hydrogen Program

- **Increase the proton conductivity of electrospun mats at low RH**
  - *Use a higher IEC polysulfone polymer to create the nanofibers*
  - *Increase the sPOSS loading in the nanofibers (> 40 wt%)*
  - *Use POSS with phosphonic acid functionalities*
  - *Investigate the addition of poly(phenylene disulfonic acid) to the nanofibers – from M.Litt's project*
  - *Add zirconium phosphate sulfophenyl phosphonate (high IEC) to the nanofibers for low RH/high T (> 100°C) conductivity*

- **Stabilize the nanofiber morphology**
  - *Crosslinking of high IEC sPAES (creation of sulfone or biphenyldisulfone bridges)*
  - *Covalent-bond stabilization of sPOSS*

- **Replace NOA63 for better chemical/thermal stability and better strength at high T**
  - *Acid-resistant epoxy (thermally cured EP42-2LV from Master Bond Inc.)*
  - *Polymer melt impregnation*

- **Upcoming Milestone: 0.1 S/cm at 120°C and 50% RH**