SCHOOL OF ENGINEERING
VANDERBILT UNIVERSITY

DOE Hydrogen Program

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 60%

Budget

- Total project funding
  - DOE $1,455,257
  - Contractor (CWRU and Vanderbilt) $481,465
- Funding received in FY08, $296,620
- Funding for FY09, $293,000

Barriers

- Barriers
  - Membrane performance (conductivity, mechanical properties, gas crossover)
  - Durability
  - Cost
- Targets
  - 0.10 S/cm proton conductivity at 120°C and 50% RH
  - 0.02 Ohm-cm^2 area specific resistance
  - 2 mA/cm^2 crossover for oxygen and hydrogen

Interactions

3M Corporation
Nissan Technical Center North America, Inc.

Objectives/Relevance

Project Objective

To 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.

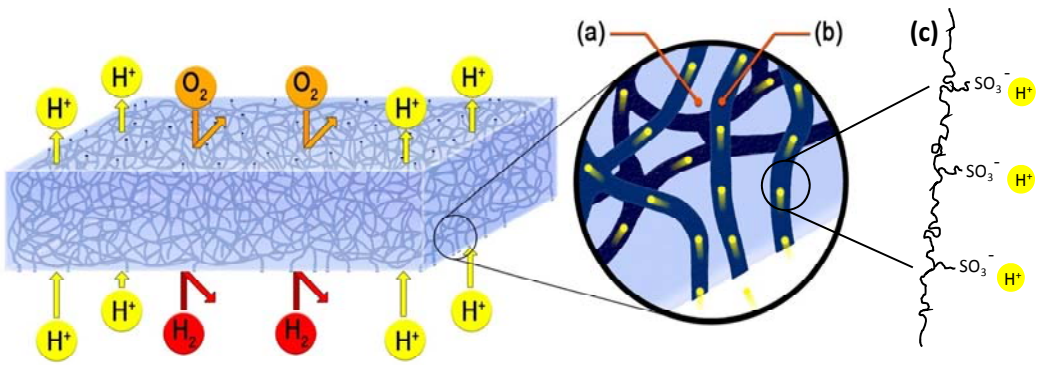
- High proton conductivity
- Low gas crossover
- Good mechanical properties

2008-09 Project Goal

Fabricate membranes with a proton conductivity of 0.10 S/cm at 120°C and 50% relative humidity (the Year 3 DOE go/no-go decision).

Relevance - NanoCapillary Network Membranes

The Concept: Use a "forced assembly" approach to fabricate a phase separated membrane composed of ionomeric nanofibers embedded in a uncharged/inert polymer matrix. Artificially create a nanomorphology similar to that for an ideal block copolymer.



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

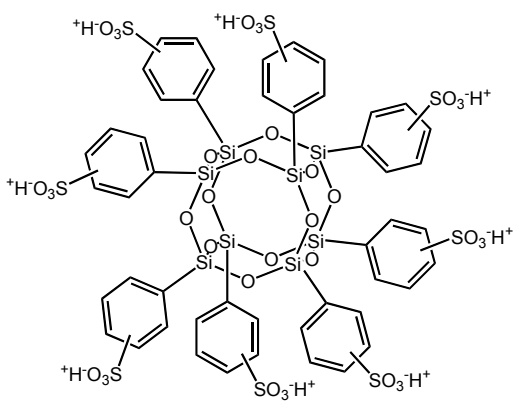
2 - Control independently both the size and the loading of the proton-conducting phase

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

Fiber composition:

- Sulfonated polysulfone
- Perfluorosulfonic acid

With/without SPOSS



SPOSS = sulfonated polyhedral oligomeric silsesquioxanes

Milestones

Month/Year	Milestone or Go/No-Go Decision
November 2007	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 2008	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 2008	Milestone: Achieved a proton conductivity of 0.07 S/cm at 30°C and 80% RH, for a nanofiber network membrane (nanofibers composed of sPAES + sulfonated POSS, with Norland Optical Adhesive 63 as the inert matrix).
December 2008	Go/No-Go Decision: Achieved a proton conductivity of 0.10 S/cm at 120°C and 50% RH for a nanofiber network membrane, where the fibers are composed of 825 EW PFSA polymer + SPOSS with Norland Optical Adhesive 63 as the inert matrix.

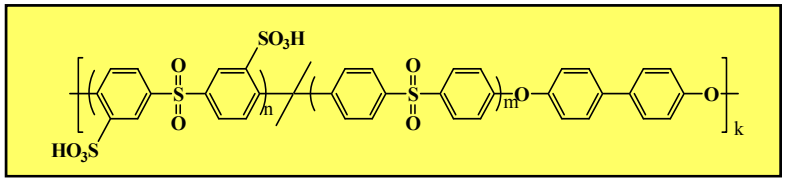
Summary of Accomplishments for Year 2

1. Preparation and characterization of nanocapillary network membranes, where the nanofibers were composed of sulfonated polysulfone (2.1 mmol/g IEC) + SPOSS.

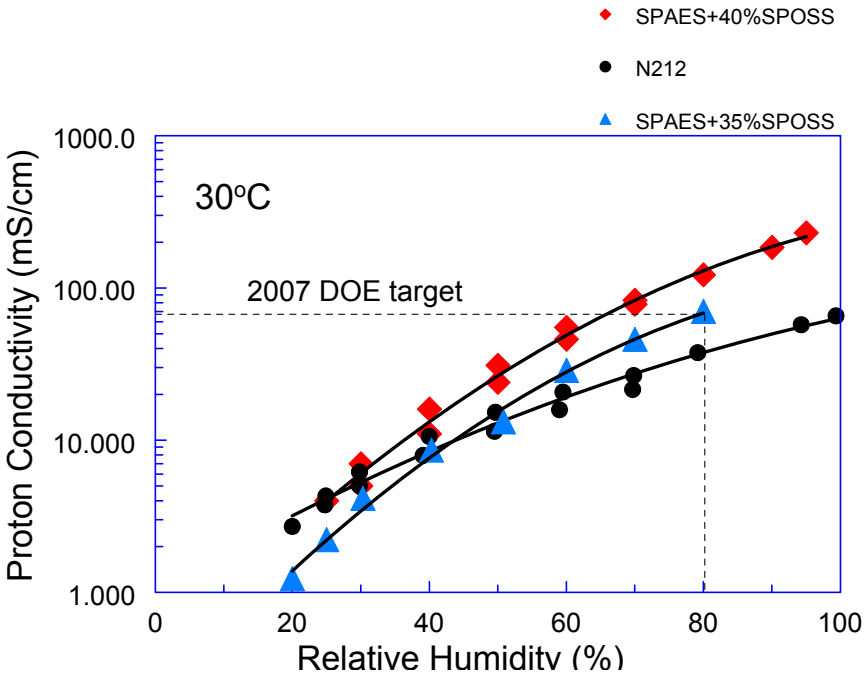
   - Fiber mat compaction, interfiber welding and mat impregnation with Norland Optical Adhesive 63 (a UV photo-curable urethane-based pre-polymer)

2. Membranes achieved the DOE Year 2 proton conductivity target of 0.07 S/cm at 30°C and 80% RH

3. Membranes exhibited low gas permeability and good mechanical properties



Tested sample	O_2 permeability (Barrer)	Young's Modulu's (MPa)
Homogeneous film of polysulfone (2.5 mmol/g)	0.53	409
UV cured NOA63 film	0.038	960
Nanofiber composite membrane	0.18	528
Nafion ® 117	9.4	176



Technical Approach for Year 3

1. Electrospin low EW perfluorosulfonic acid (PFSA) polymers - 733 EW and 825 EW from 3M Corporation.

2. Convert electrospun PFSA mats into nanofiber network composite membranes (polymer annealing and interfiber welding, mat compaction, and mat embedding)

3. Perform preliminary membrane characterization experiments (proton conductivity as a function of T and RH and mechanical properties)

4. Add sulfonated molecular silica (sulfonated POSS - polyhedral oligomeric silsesquioxanes) to further enhance proton conductivity.

Rationale for using PFSA:
- Better chemical stability
- Sulfonic acid groups are more acidic (high conductivity expected at lower IEC)
- Recommended by DOE project reviewers

The Problem:
PFSAs can not be electrospun unless an additional carrier polymer is used, e.g. poly(ethylene oxide) or poly(acrylic acid)

Electrospinning 3M PFSA (EW 825, 1.21. mmol/g IEC) with Poly(ethylene oxide)

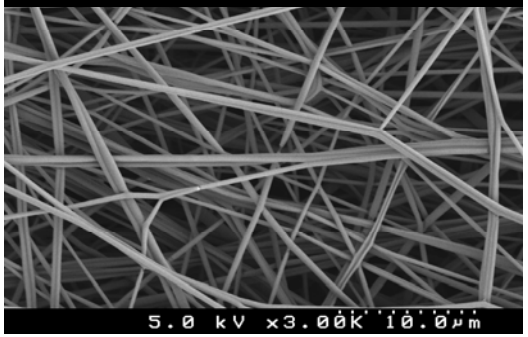
- Effect of PEO carrier content -

PFSA/PEO ratio (by wt)	Total polymer Concentration (wt%)	Electrospinning conditions	Spinnability
99/1	15	8 kV potential 6cm SCD 0.50 ml/h flow rate	Fibers 405 nm avg. dia. 0.20 fiber vol. fraction
95.5/0.5	15	3 kV potential 6cm SCD 0.50 ml/h flow rate	Fibers 370 nm avg. dia. 0.19 fiber vol. fraction
99.7/0.3	15	3 kV potential 6cm SCD 0.50 ml/h flow rate	Fibers 491 nm avg. dia. 0.22 fiber vol. fraction
99.8/0.2	15	3 kV potential 6cm SCD 0.50 ml/h flow rate	Beaded fibers 379 nm avg. dia. 0.17 fiber vol. fraction
99.9/0.1	15	3 kV potential 6cm SCD 0.50 ml/h flow rate	Droplets, no fibers

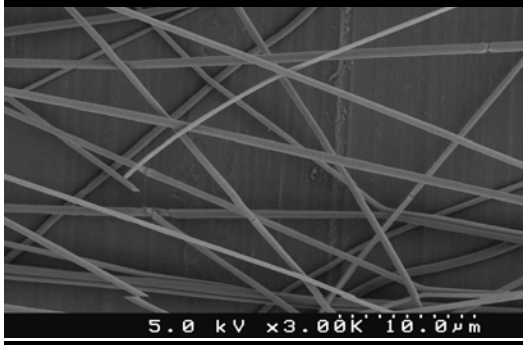
SCD = spinneret-to-collector distance

MW of PEO = 1,000,000 g/mol

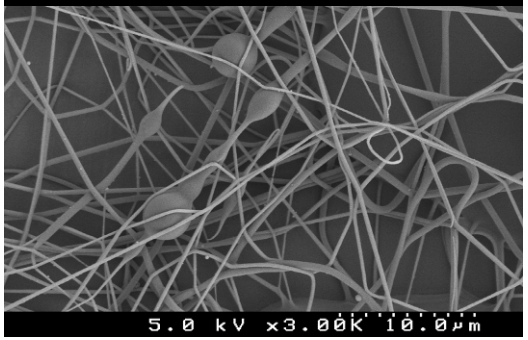
PFSA/PEO = 99.5/0.5



PFSA/PEO = 99.7/0.3



PFSA/PEO = 99.8/0.2



Electrospinning of 3M PFSA (EW 825) with Poly(acrylic acid)

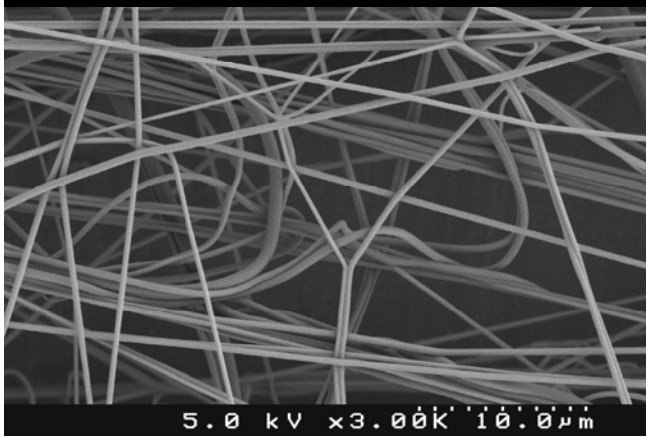
- Effect of PAA carrier content -

PFSA/PAA ratio (by wt)	Concentration (wt%)	Electrospinning conditions	Spinnability
90/10	15	4 kV potential 6cm SCD 0.50 ml/h flow rate	Fibers 402 nm avg. dia. 0.21 fiber vol. fraction
95/5	15	4 kV potential 6cm SCD 0.50 ml/h flow rate	Fibers 344 nm avg. dia. 0.23 fiber vol. fraction
98/2	15	3 kV potential 6cm SCD 0.50 ml/h flow rate	Droplets, no fibers
99/1	15	3 kV potential 6cm SCD 0.50 ml/h flow rate	Droplets, no fibers

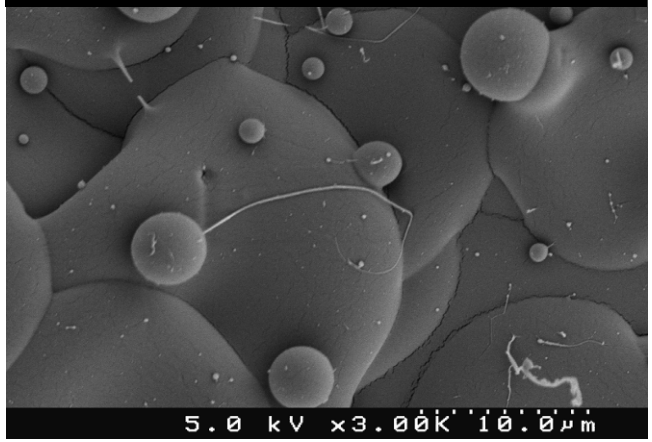
SCD = spinneret-to-collector distance

MW of PAA = 450,000 g/mol

PFSA/PAA = 95/5



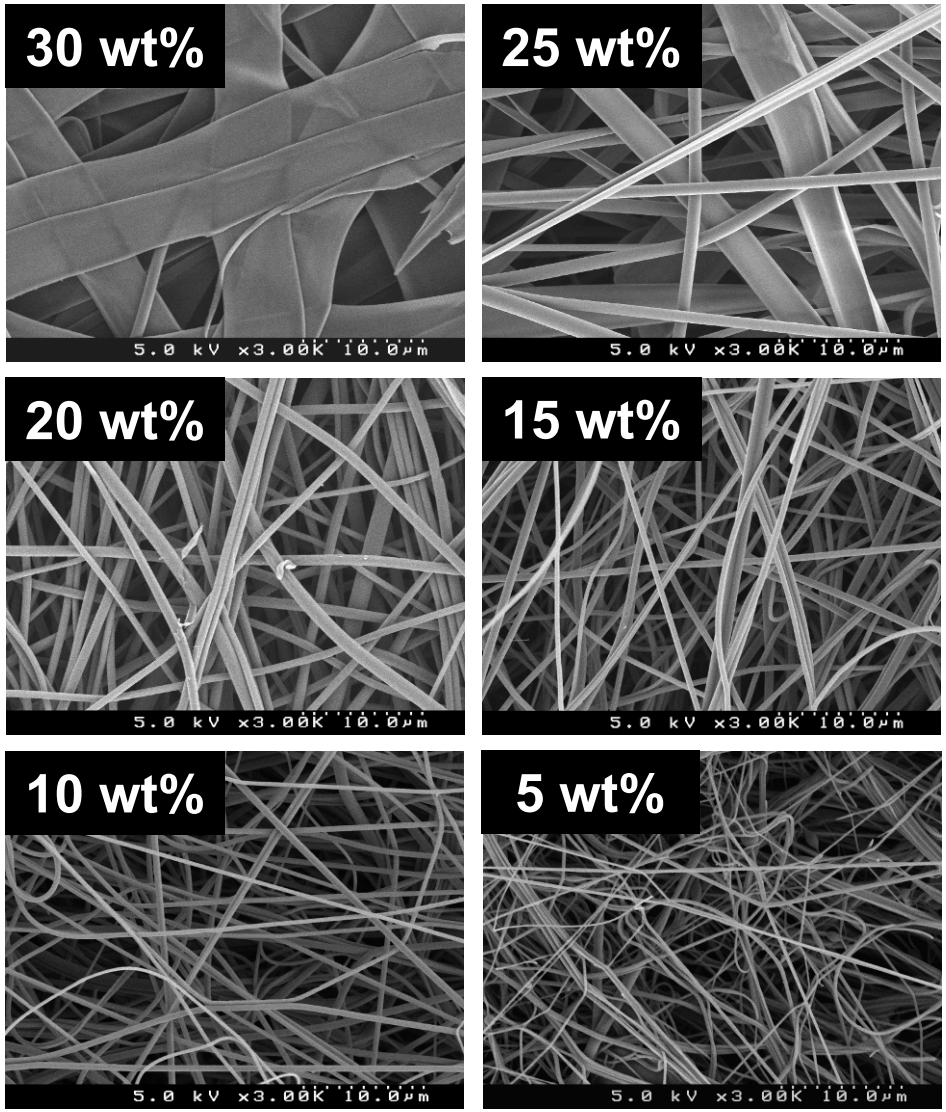
PFSA/PAA = 98/2

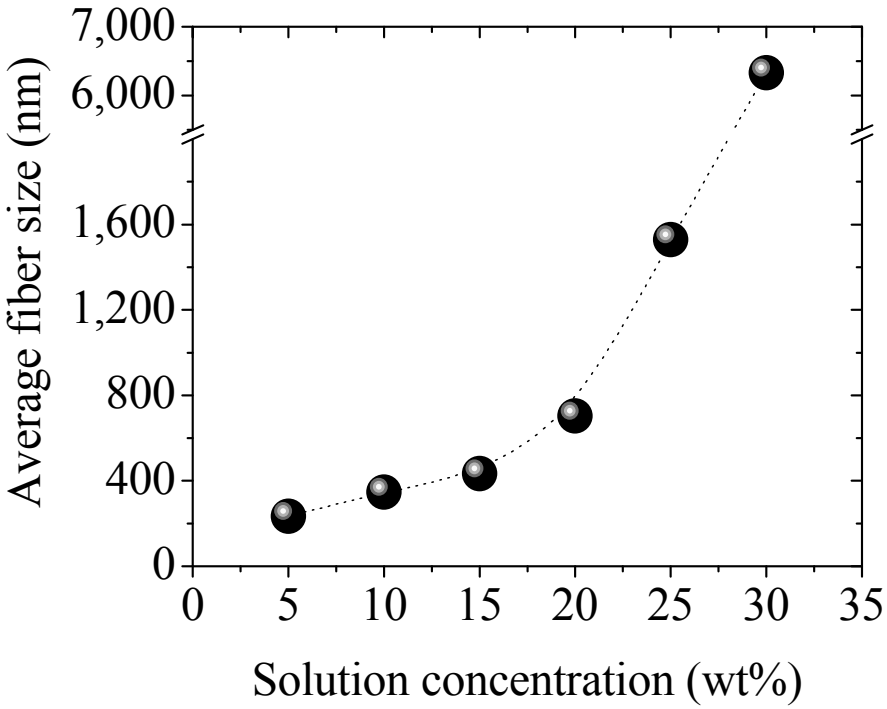


1) **Fibers formed at PFSA/PAA ratios of 90/10 to 95/5.**
2) **Droplets formed at PFSA/PAA ratios of 98/2 to 99/1.**
3) **More PAA is required in the spinning solution, as compared to PEO, to enable fiber formation.**

Effect of Spinning Solution Polymer Concentration

3M PFSA (733 EW, 1.36 mmol/g IEC) co-spun with 1 wt% PEO





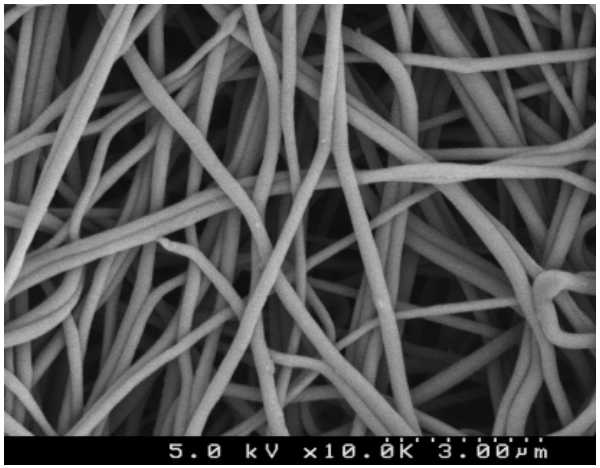
1) Average fiber size increased as the polymer concentration increased.
2) Fiber morphology transitioned from ribbons to cylindrical fibers as the polymer concentration decreased.

3M PFSA Nanofiber Composite Membranes

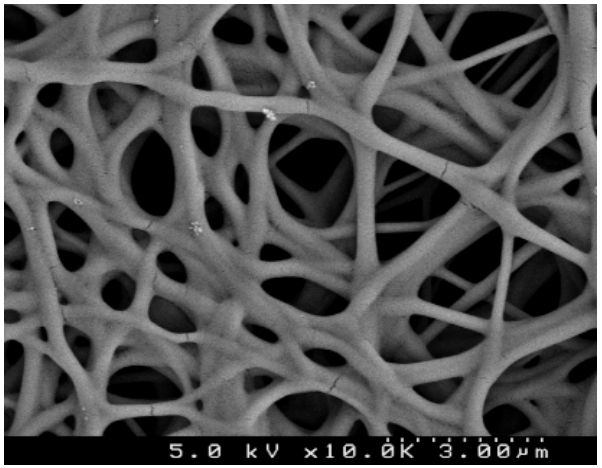
Processing steps for transforming a nanofiber mat into a fuel cell membrane

1	**Electrospinning nanofiber mat**
2	**Drying the mat** in vacuum for 16 hrs
3	**Annealing the mat** at 140°C for 5 min
4	**Densifying the mat** at 0 – 10,000 psi for 5 sec
5	**Embedding the mat with NOA** and UV curing for 2 hrs
6	**Removal of polymer carrier** by boiling in 1M sulfuric acid followed by boiling in water

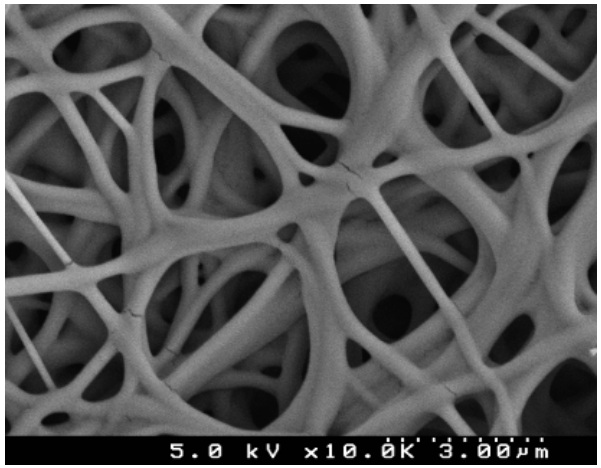
Examination of Annealing Time



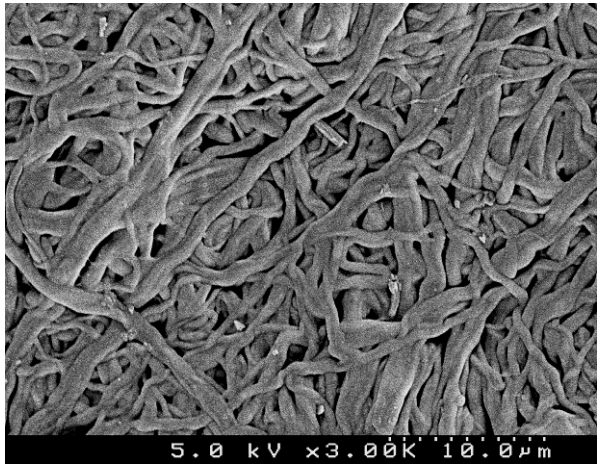
No annealing



At 140°C for 2 min



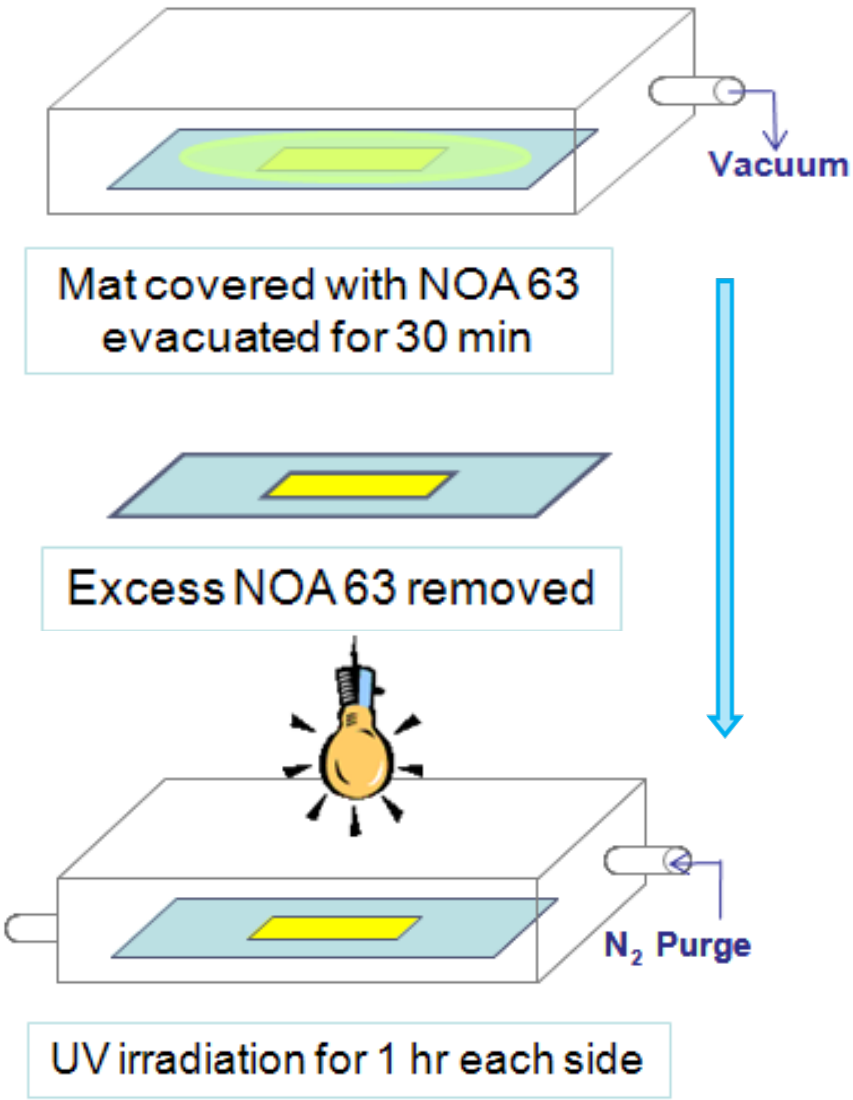
At 140°C for 5 min



Densified mat before annealing:
Fibers are fused

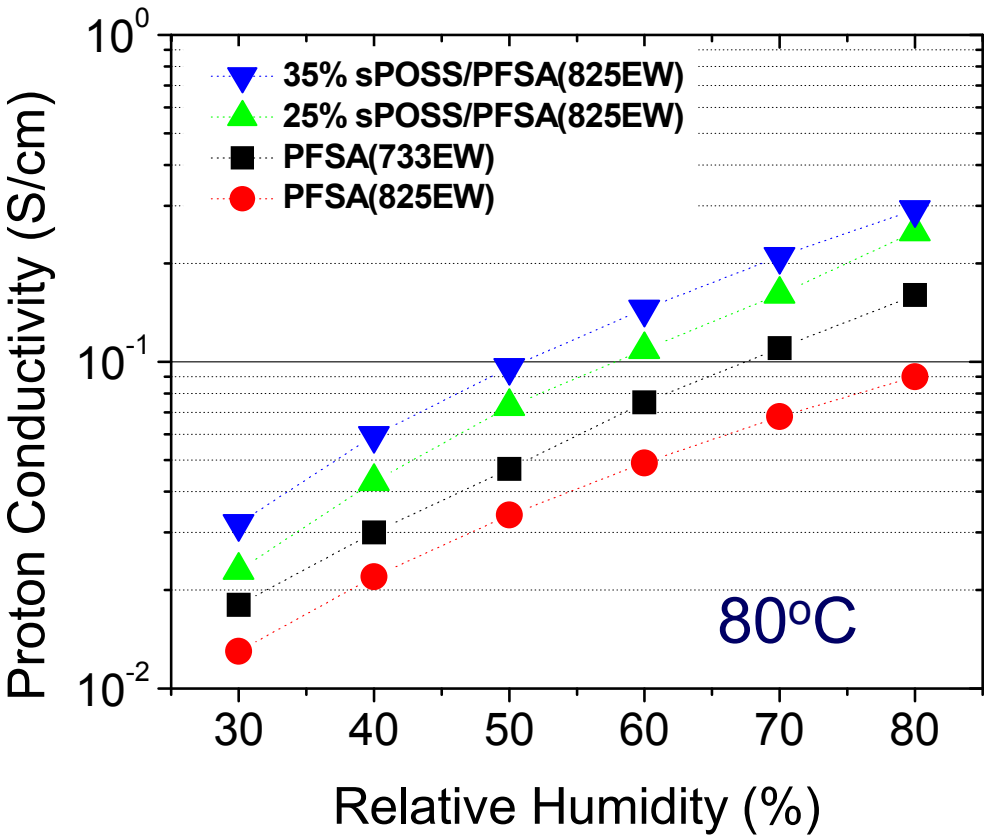
1) Annealing had to be performed prior to densification. Fibers were fused together (overwelded) if the mat was densified before annealing.
2) <u>Inter-fiber welding occurred during annealing</u> (due to the presence of a small amount of absorbed water in the fibers which plasticized the polymer).

Impregnation of Annealed/Welded/Densified Mats



1) Mat was immersed in liquid NOA 63 (Norland Optical Adhesive, a photo-polymerizable urethane-based resin), and vacuum was applied to remove all entrapped air (at 50°C)
2) Excess adhesive was removed from the mat surface
3) Both sides of the sample film were exposed to a UV light (365 nm) for 1 hr.

Proton Conductivity With and Without SPOSS



Large boost in conductivity with addition of SPOSS (for all values of RH)

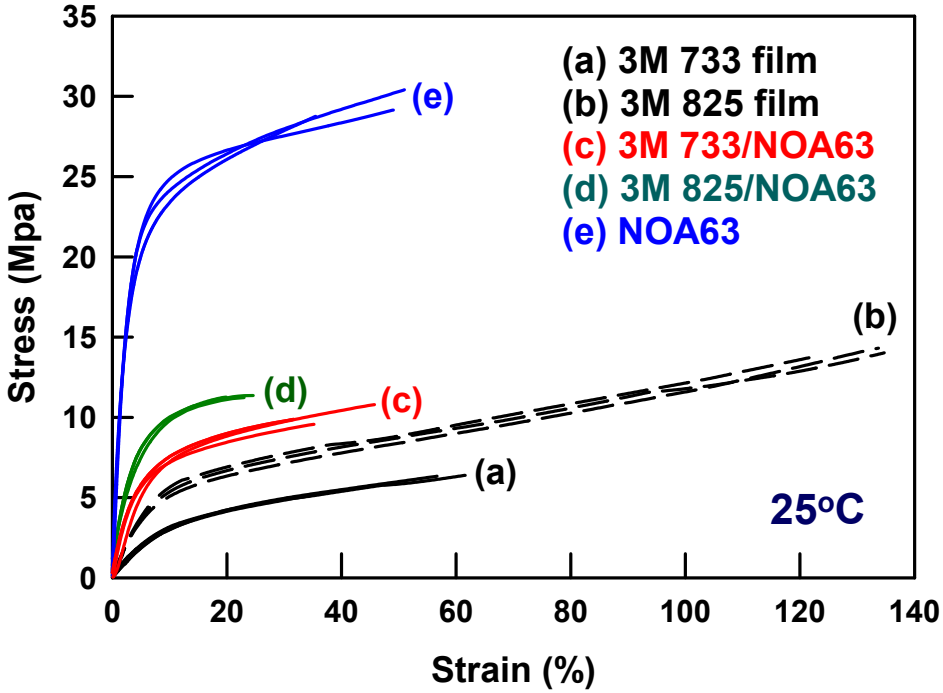
Samples

1) 35% SPOSS/3M PFSA (825 EW): fiber volume fraction=0.75, thickness=104 μm, NOA63
2) 25% SPOSS/3M PFSA (825 EW: fiber volume fraction=0.75, thickness=90 μm, NOA63
3) 3M PFSA (825 EW): fiber volume fraction=0.73, thickness=92 μm, NOA63
4) 3M PFSA (733 EW): fiber volume fraction=0.70, thickness=80 μm, NOA63

* Annealing condition for every sample = 140°C for 5 min

Membrane Mechanical Strength

(In wet state, no SPOSS)

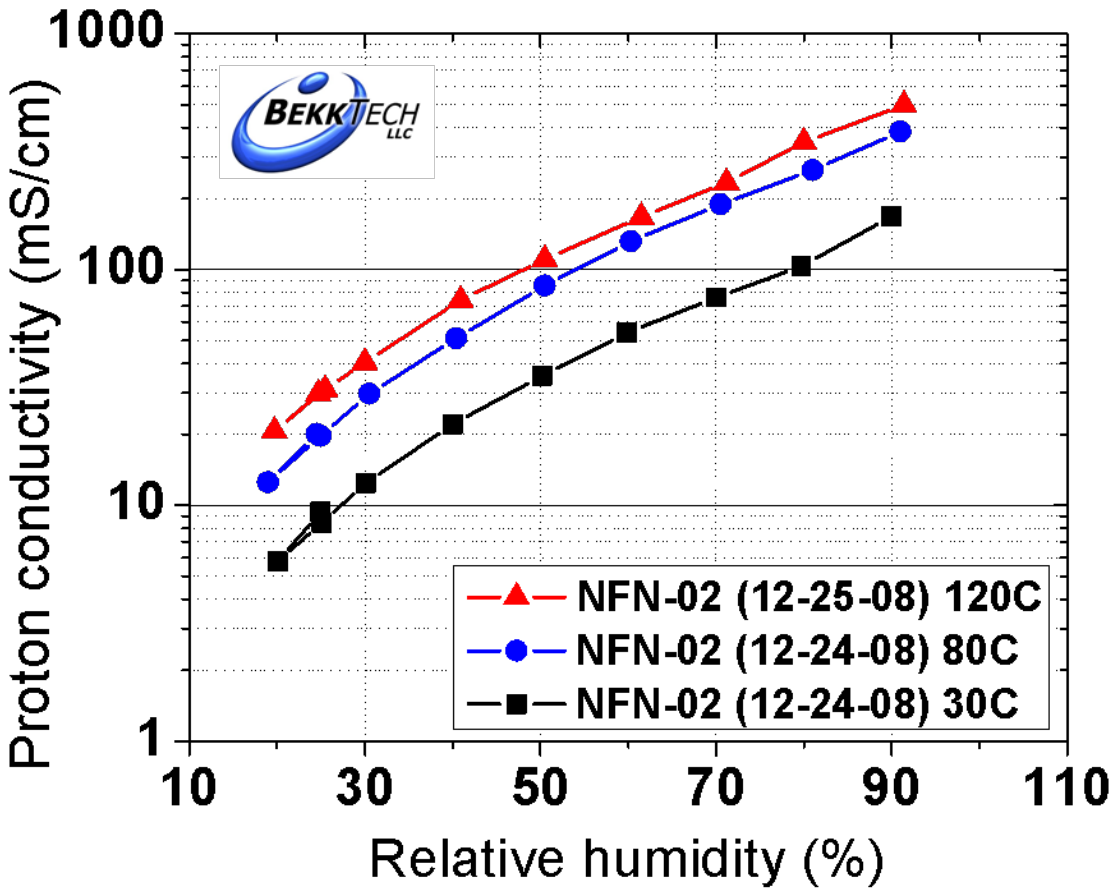


Mechanical properties of nanofiber composite membranes were significantly improved, as compared to homogeneous PFSA films.

Sample	Young's modulus (MPa)	Elongation at break (%)	Stress at break (MPa)
3M 733 film	45.4	62.0	6.4
3M 825 film	77.6	133.7	14.3
733/NOA63 (0.70 fiber vol. fraction)	161.6	45.7	10.8
825/NOA63 (0.74 fiber vol. fraction)	270.5	25.0	11.4
NOA63 film	835.0	51.0	30.4

Proton Conductivity at Different Temperatures and 20% < RH < 90%

Data collected by Bekktech LLC



Fiber composition

60 wt% 3M PFSA (825 EW)
35 wt% SPOSS
5 wt% poly(acrylic acid)

Fiber volume fraction = 0.74

Membrane thickness = 104 µm

The NCN membrane met the DOE conductivity target of 100 mS/cm at 120°C and 50% RH.

Collaborations

Partners

- **3M Corporation (Industry):** Provides samples of short side-chain low EW PFSA polymer (in solution) for electrospinning studies and membrane development; provides background information on casting membranes from solutions of low EW PFSA (e.g., polymer annealing conditions)
- **Nissan Technical Center North America, Inc. (industry):** Collaborations with Nissan Technical Center NA involve sharing of MEA testing protocols and testing of samples in the future.

Proposed Future Work

1. **Investigate possible leaching of SPOSS from the nanofiber membranes**
   - Prepare sulfonated POSS with a lower IEC
   - With lower IEC SPOSS, remove carrier polymer from PFSA/SPOSS nanofibers (an increase in proton conductivity is expected)
2. **Replace SPOSS with sulfonated poly(phenylene) to boost conductivity**
   - Sulfonated poly(phenylene) will have improved chemical stability as compared to SPOSS, with no dissolution in water
   - Add up to 60% high IEC (e.g., 7.0 mmol/g) sulfonated poly(phenylene) to increase low RH conductivity
3. **Study inert matrix polymer**
   - Further test the chemical stability of NOA 63
   - Perform multiple embedding steps with a polymer/solvent solution (with solvent evaporation between repeated embedding steps); polysulfone Radel R, PVDF, and PVD/HFP copolymers (Kynar Flex).
   - Add inorganic particles e.g., organically modified aluminosillicate (clay) or glass fibers to NOA for improved strength
4. **Further characterize nanocapillary network membranes (water uptake as a function of T and RH, mechanical properties, gas permeability)**
5. **Prepare and test MEAs with nanocapillary network membranes**
6. **Examine different fiber morphologies with PFSA polymers**
   - Create nano-porosity in the fibers
   - Create core-shell fibers

Summary of 2008-09 Work

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 low EW perfluorosulfonic acid polymer with/without sulfonated POSS. The inert matrix polymer for embedding the fibers was NOA 63.

Technical Accomplishments and Progress: Demonstrated a proton conductivity of 0.107 S/cm at 120°C and 50% RH. Nanofiber network membranes exhibited good mechanical properties.

Technology Transfer/Collaborations: Initiated collaborations with 3M Corporation and Nissan Technical Center North America. Presentations, publications, and a provisional patent.

Proposed Future Research: Increase membrane conductivity and durability. Look at replacing sulfonated POSS with high IEC, water insoluble sulfonated poly(phenylene). Test durability of NOA 63. Prepare and test MEAs with nanofiber network membranes. Perform preliminary cost analysis

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Summary Table

Date	Membrane Material	Proton Conductivity	Other Membrane Properties
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	0.109 (in water at 25°C)	Tensile strength: 528 MPa Oxygen permeability: 0.18 barrers
March 2008	Sulfonated poly(arylene ether sulfone) with SPOSS and NOA63 – 1.2 mmol/g IEC, 40 wt% SPOSS, fiber vol. fraction = 0.70-0.75	**0.07 (30°C and 80% RH) – DOE Milestone** 0.170 (80°C and 80% RH) 0.062 (80°C and 60% RH)	
December 2008	Perfluorosulfonic acid (825 EW) with 35 wt% SPOSS and 5 wt% PAA. Inert polymer: NOA 63; fiber vol. fraction = 0.74; membrane thickness=104 μm.	**0.107 S/cm (120°C and 50% RH) – DOE Go/No-Go**	