



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

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Project ID: FC038

# Overview

## Timeline

- Start date 4/15/2006
- End date 4/15/2011
- Percent complete 77%

## Budget

- Total project funding
  - DOE \$1,455,257
  - Contractor (CWRU and Vanderbilt) \$481,465
- Funding received in FY09, \$150,000
- Funding for FY10, \$300,000

## Barriers

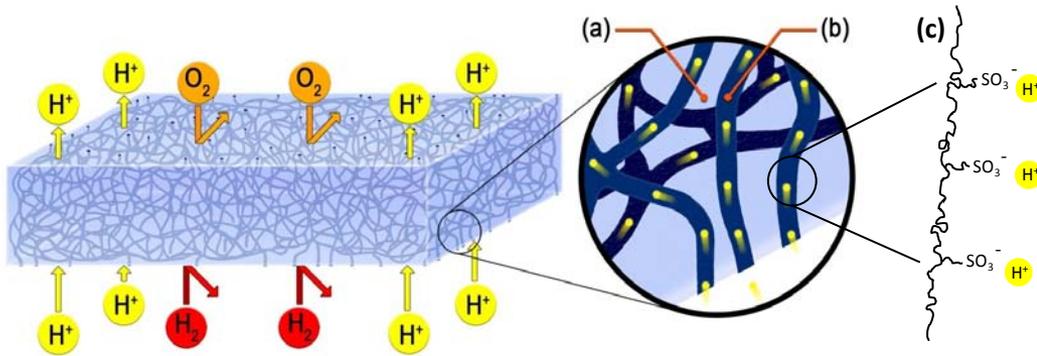
- Barriers
  - Membrane performance (conductivity, mechanical properties, gas crossover)
  - Durability
  - Cost
- Targets
  - 0.10 S/cm proton conductivity at 120°C and 50% RH
  - 0.02 Ohm-cm<sup>2</sup> area specific resistance
  - 2 mA/cm<sup>2</sup> crossover for oxygen and hydrogen

## Interactions

3M Corporation  
Nissan Technical Center  
North America, Inc.

# 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.



**Fiber composition:** Low EW perfluorosulfonic acid with sulfonated molecular silica

**Inert Matrix Polymer:** Norland Optical Adhesive (NOA) 63 (a UV-curable urethane-based pre-polymer)

- 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

# Objectives

## 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

## 2009-2010 Project Goals:

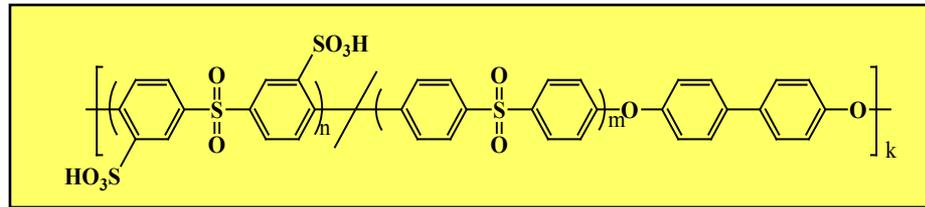
Prepare NanoCapillary Network proton exchange membranes where high ion-exchange capacity (IEC) sulfonated polyphenylene (from Morton Litt's group at Case Western Reserve University) replaces the sulfonated POSS and a commercially available polyphenylsulfone (uncharged) replaces NOA63.

# Milestones

<b>Month/Year</b>	<b>Milestone or Go/No-Go Decision</b>
March 2008	Milestone: Successfully electrospun sulfonated poly(arylene ether sulfone) (sPAES) and added varying amounts of sulfonated POSS (polyhedral oligomeric silsesquioxanes) to the ionomer nanofiber mats. Converted the mats into defect-free nanofiber network membranes.
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 0.107 mS/cm at 120°C and 50% RH for a nanofiber network membrane, where the fibers were composed of 825 EW PFSA polymer + SPOSS, with Norland Optical Adhesive 63 as the inert matrix.
March 2010	Milestone: Developed a new dual nanofiber electrospinning membrane fabrication scheme that eliminates the polymer impregnation step. NOA63 was replaced with polyphenylsulfone as the inert matrix polymer. Replaced sulfonated POSS with sulfonated polyphenylene.

# Summary of Accomplishments for Year 2

1. Nanocapillary network membranes with 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

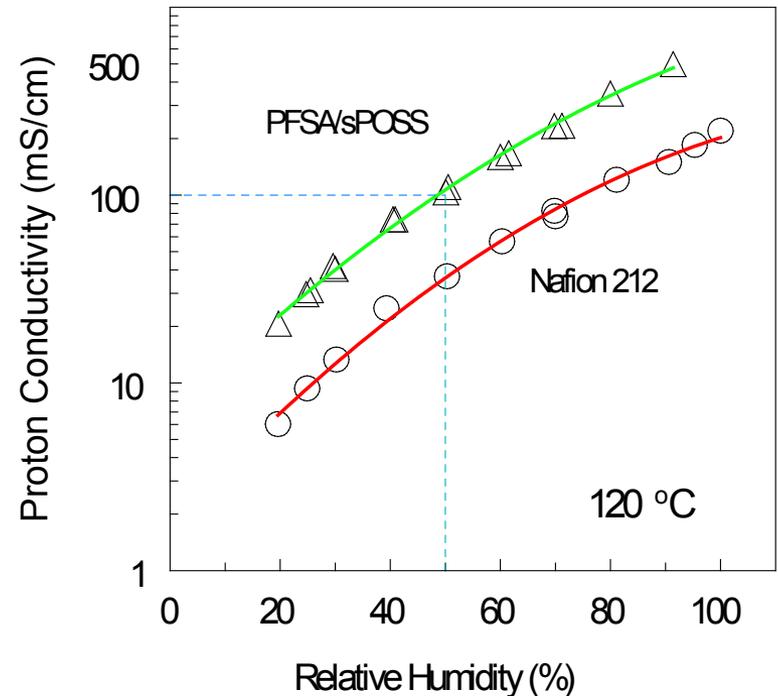
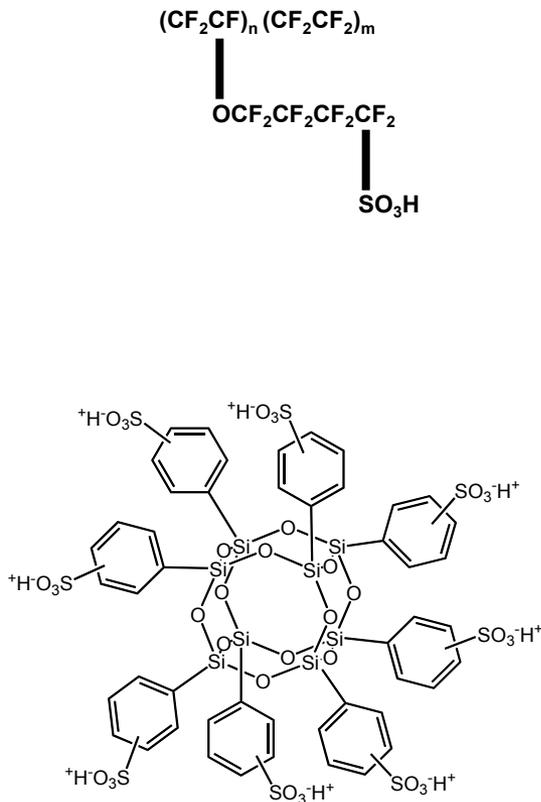


Tested sample	$\text{O}_2$ permeability (Barrer)	Young's Modulus (MPa)
Homogeneous film of sulfonated poly(arylene ether sulfone)	0.53	409
Nanofiber composite membrane	0.18 <sup>b</sup>	528 <sup>c</sup>
Nafion® 117	9.4	176

# Technical Accomplishments for Year 3

## High Conductivity Nanofiber Composite Membranes

- **825 EW PFSA polymer (from 3M Corp.)** was electrospun with sulfonated POSS + poly(acrylic acid)
- **Nanofiber mats** were welding and compacted
- **Void volume** was filled with Norland Optical Adhesive 63



**PFSA fibers with 35 wt% sPOSS met the 2009 DOE proton conductivity target of 100 mS/cm at 120°C and 50% RH**

## *Technical Accomplishments and Progress for Year 4*

- **Developed new nanofiber membrane fabrication methods; replaced Norland Optical Adhesive 63 with a commercially available polysulfone and eliminated a separate impregnation step.**
- **Characterized the new nanofiber membranes and tested them in a H<sub>2</sub>/air fuel cell (investigated initial performance and durability).**
- **Began electrospinning mixtures of PFSA and sulfonated polyphenylene (as a replacement for sulfonated POSS).**
- **Electrospun and Nafion<sup>®</sup> hollow bore nanofibers (seeking better water retention and high conductivity at low humidity).**
- **Began to electrospin Pt/C-loaded nanofibers for fuel cell electrodes.**

# Nanofiber Network Membrane Fabrication Techniques – Original Method

**Prepare an ionomer nanofiber mat,  
then embed the mat with an  
uncharged/inert polymer**

Nanofiber mat  
electrospinning



Mat compaction  
(to increase the  
volume density  
of fibers)



Creation of inter-  
fiber welds

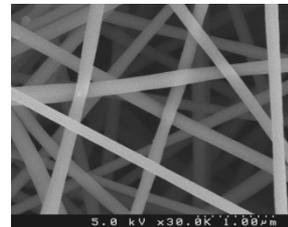


Impregnation  
with an inert  
polymer

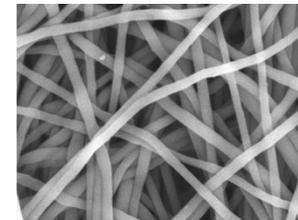
Method was used during Years 1-3 of the project to fabricate membranes with sulfonated polysulfone and with perfluorosulfonic acid nanofibers.

Inert/uncharged polymer was Norland Optical Adhesive 63 (a UV-curable urethane-base pre-polymer) that was impregnated into the mat.

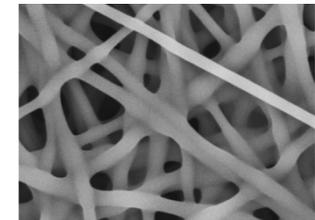
**2.5 mmol/g IEC sulfonated polysulfone nanofiber  
mat**



**As-spun mat**

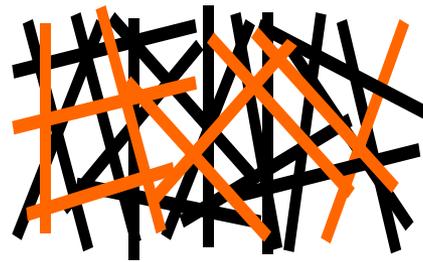


**Compacted  
mat**



**Compacted and  
welded mat**

# New Nanofiber Network Membrane Fabrication Technique – Methods #2 and #3 (Dual Fiber Electrospinning)



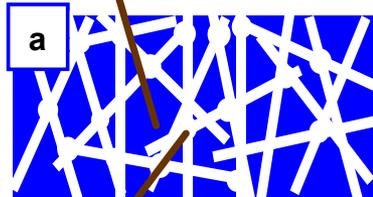
Simultaneously electrospin a dual nanofiber mat – one fiber is the ionomer and the second fiber is an uncharged/inert polymer (polyphenylsulfone or PVDF)

Mat Processing

## Method #3

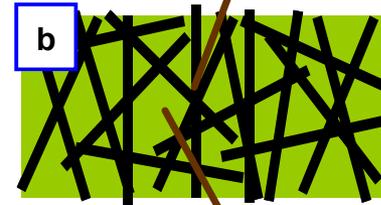
“Melt” inert polymer around ionomer nanofibers

Interfiber voids are filled with the inert polymer matrix that provides mechanical strength and controls swelling



Interconnected 3-D network of ionomer nanofibers

Interconnected 3-D network of inert polymer nanofibers that provides mechanical strength



Inter-fiber voids are filled with ionomer

## Method #2

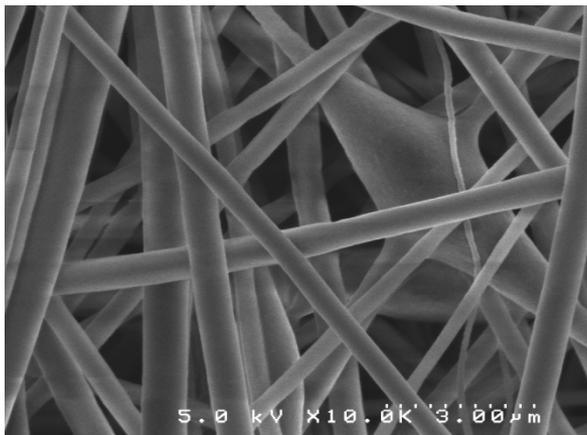
“Melt” ionomer around inert polymer nanofibers

# Dual Fiber Electrospinning: Nafion<sup>®</sup> PFSA (0.91 mmol/g IEC) and Polyphenylsulfone

	Nafion <sup>®</sup>	Polyphenylsulfone (PPSU)
<b>Polymer Comp.</b>	99:1 Nafion <sup>®</sup> :PEO (20 wt% total polymer)	20 wt%
<b>Solvent</b>	Isopropanol:Water in 2:1 vol. ratio	DMAc:Acetone in 8:2 vol. ratio
<b>Voltage</b>	4 kV	7.5 kV
<b>SCD</b>	6 cm	4 cm
<b>Flow Rate</b>	0.21 mL/hr	0.09 mL/hr

PEO= Poly(ethylene oxide)

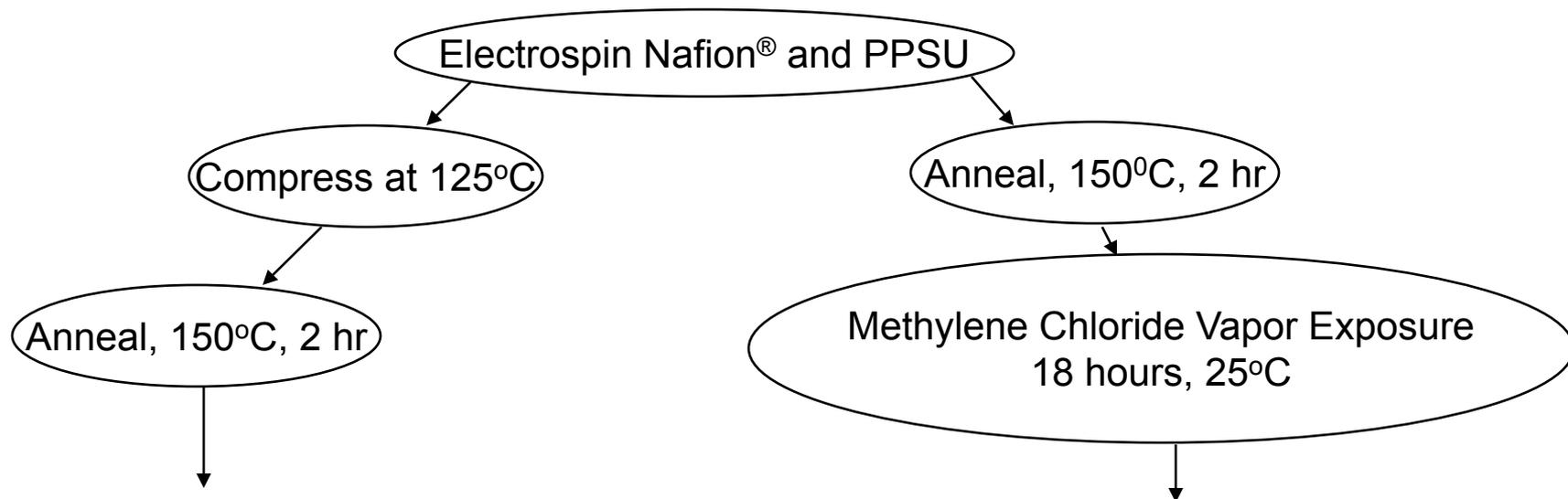
PPSU: Radel<sup>®</sup> R-5500NT polyphenylsulfone from Solvay Advanced Polymers LLC



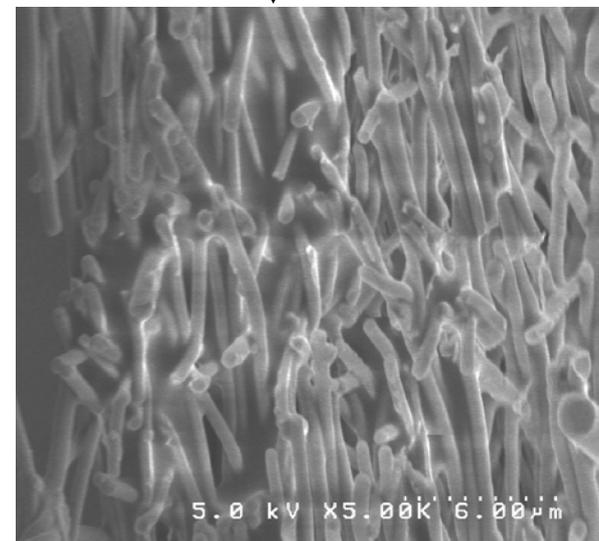
SEM image of a mat containing Nafion<sup>®</sup>/PEO and PPSU nanofibers (where the two polymer were electrospun simultaneously)

Dual fiber electrospinning of Nafion<sup>®</sup> and PVDF (Kynar<sup>®</sup> 760) was also performed successfully.

# Generating Alternative Nanofiber Composite Membrane Structures form a Dual Fiber Mat



Nafion<sup>®</sup> Matrix, PPSU Nanofibers  
~70% Nafion<sup>®</sup> by Volume



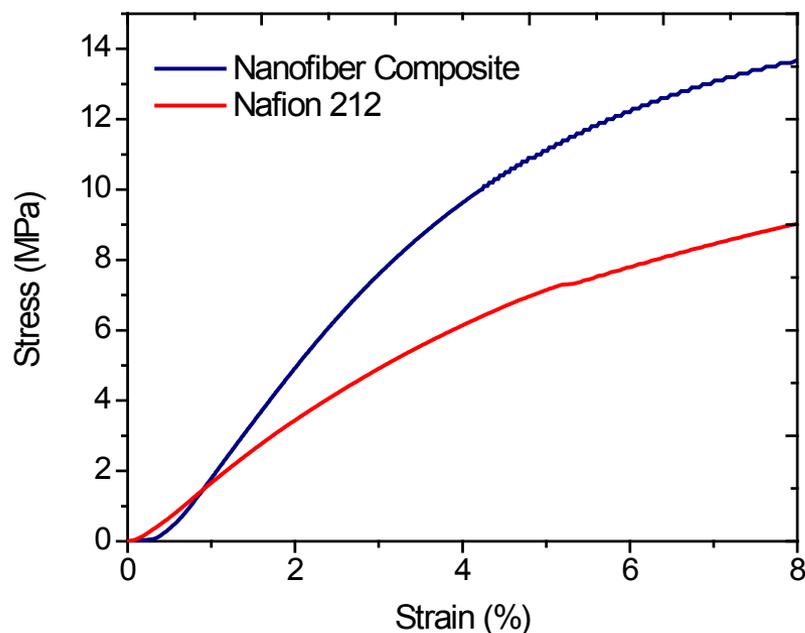
Nafion<sup>®</sup> Nanofibers, PPSU Matrix  
~60% Nafion<sup>®</sup> by volume

# Water Swelling and Mechanical Properties – Nafion<sup>®</sup> Surrounding PPSU Nanofibers

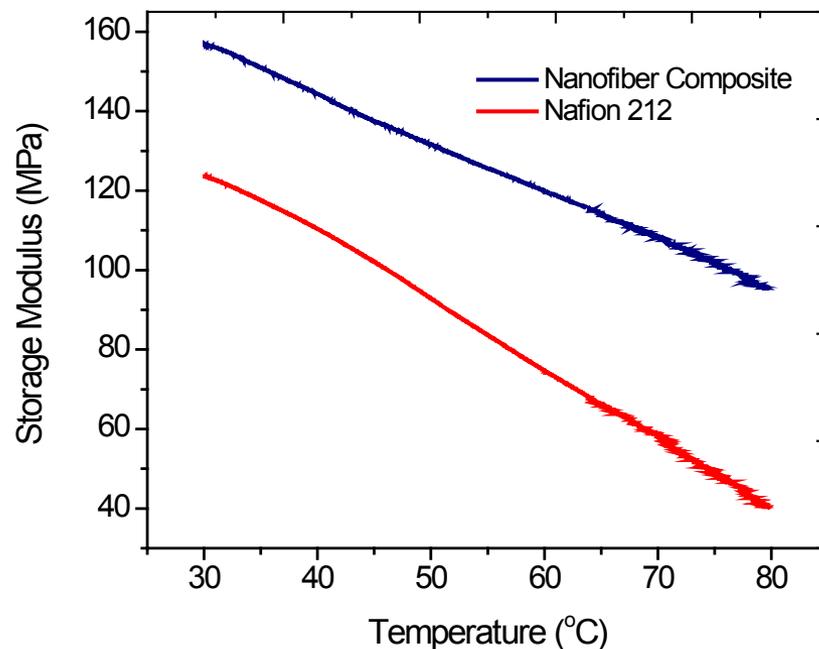
	In-Plane Swelling [%]	Volumetric Swelling [%]	Mass Swelling [%]
Nafion <sup>®</sup> 212	37	75	36
Nanofiber Composite	5	35	22

(Swelling data taken after equilibrating in 100°C liquid water)

*Dry Membrane (30°C, 30% R.H.)*

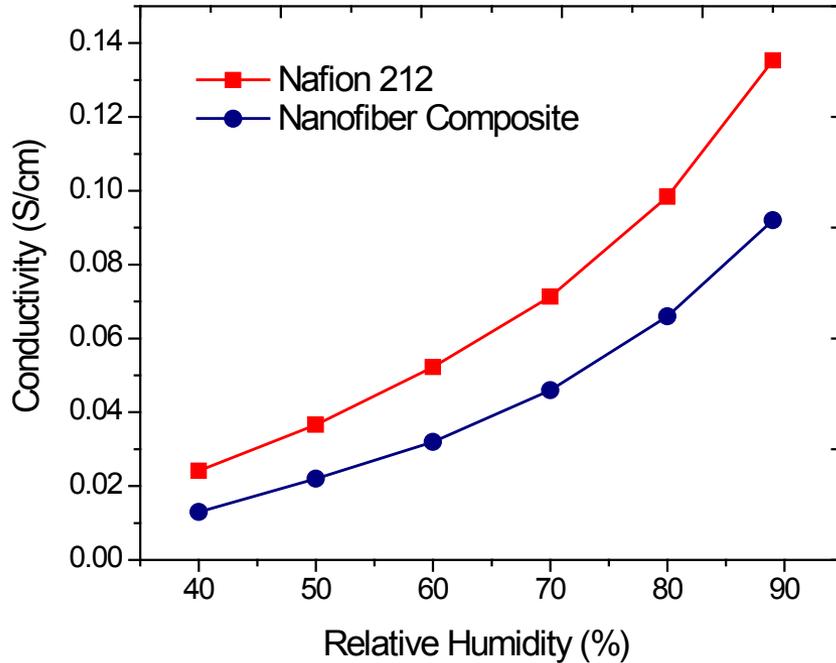


*Wet Membrane (Liquid H<sub>2</sub>O)*

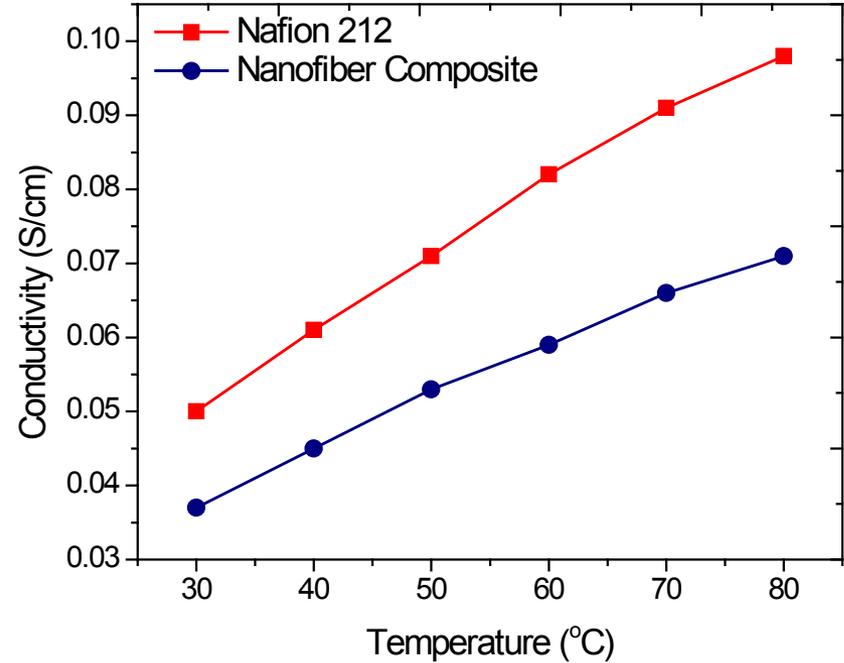


# Proton Conductivity – Nafion<sup>®</sup> Surrounding PPSU Nanofibers

## Proton Conductivity at 80°C

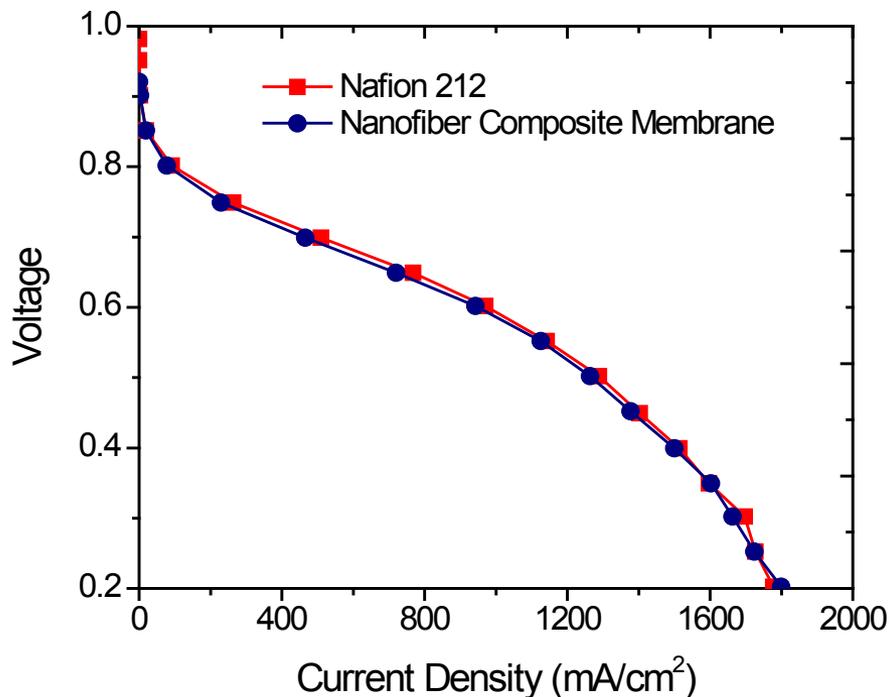


## Proton Conductivity at 80% RH



Conductivity is consistently ~70% of Nafion<sup>®</sup> (volume fraction of Nafion<sup>®</sup> in the membrane is also ~70%)

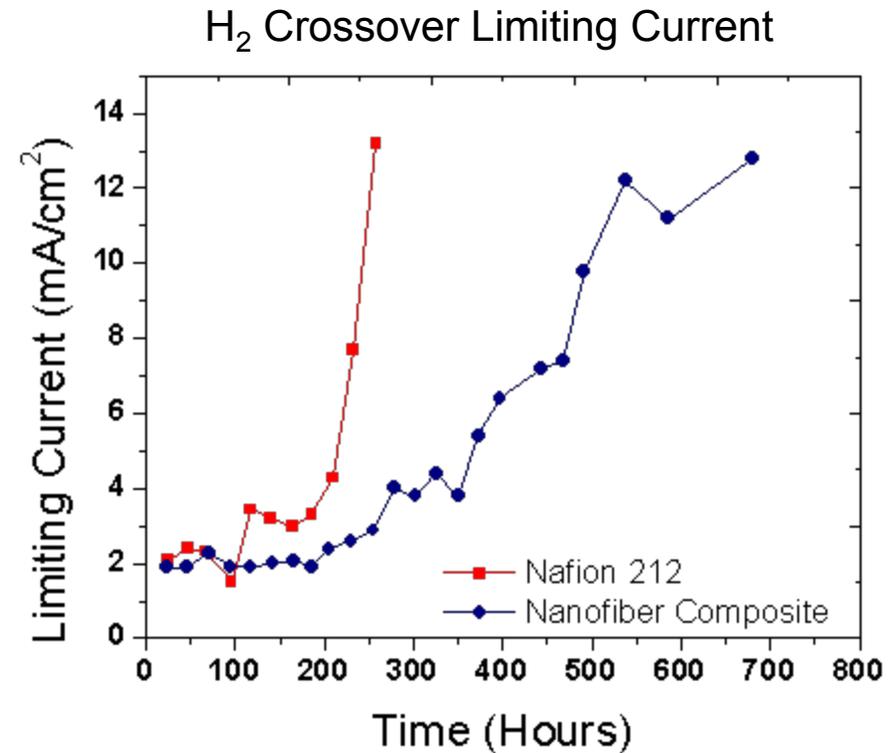
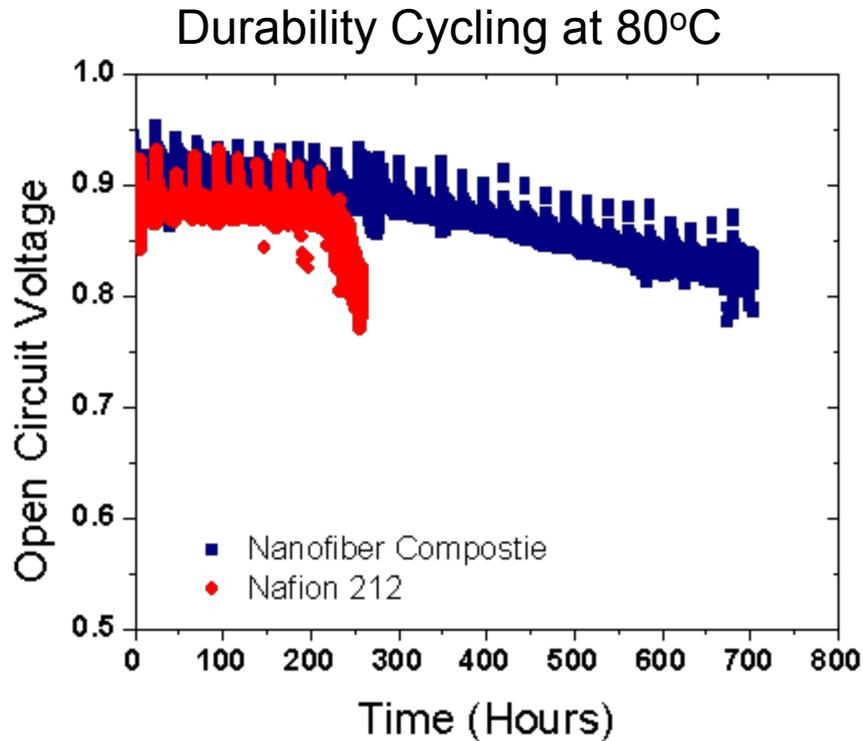
# *H<sub>2</sub>/Air Fuel Cell Performance - Nafion<sup>®</sup> Surrounding PPSU Nanofibers*



- 80°C, 100% RH
- 0.4 mg/cm<sup>2</sup> Pt loading (anode and cathode)
- 30% Nafion<sup>®</sup> binder content
- decal method for MEA preparation

— Nafion<sup>®</sup> 212 (51 μm)  
— Nanofiber composite (30 μm dry thickness)

# MEA Lifetime is Increased with the Composite Membrane



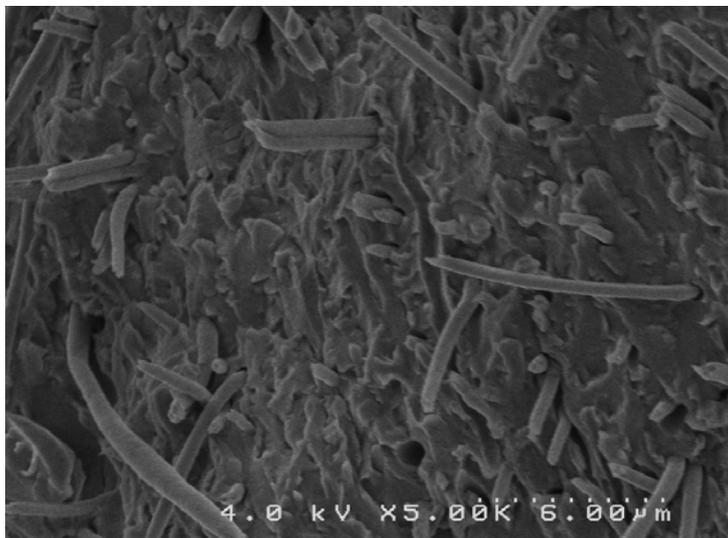
## Durability Cycling Test Conditions:

- Nanofiber Composite (30 micron thick membrane): 2 minutes at 0% R.H. Hydrogen & Air, 2 minutes at 100% R.H. Hydrogen & Air
- Nafion® 212 (51 micron thick membrane): 15 minutes at 0% R.H. Air, 15 minutes at 150% R.H. Air (always 150% R.H. Hydrogen)
- 0.4 mg/cm<sup>2</sup> Pt Loading
- 125 mL/min Hydrogen Flow Rate and 500 mL/min Air Flow Rate

## Limiting Current Test Conditions:

- Linear Sweep Voltammetry from 0-500 mV at 100% RH
- Hydrogen Flow Rate: 125mL/min
- Nitrogen Flow Rate: 500 mL/min

# Proton Conductivity and Swelling – 3M 825 EW PFSA Surrounding PPSU Nanofibers



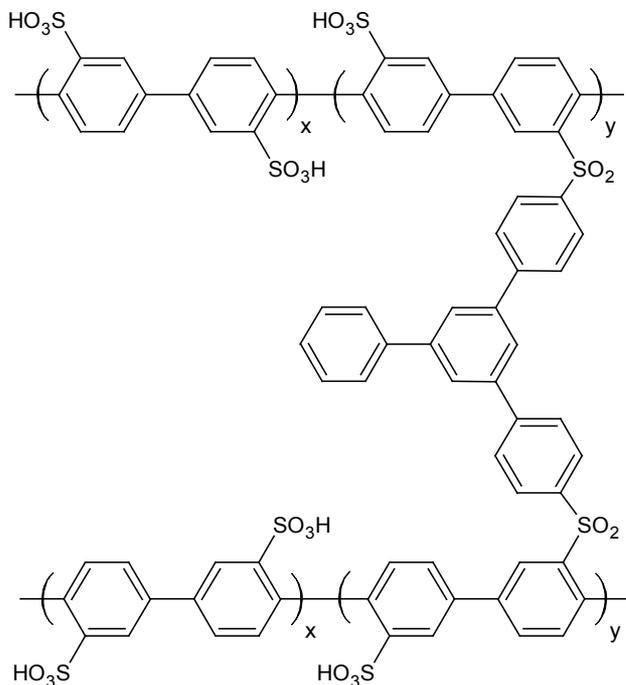
- Membrane was composed of ~80 wt% PFSA and 20 wt% PPSU
- PFSA was electrospun with 1 wt% PEO
- The nanofiber composite membrane has the same conductivity as Nafion<sup>®</sup> 212, but reduced in-plane swelling

## Preliminary Results

Material	Conductivity in Water at 23°C [S/cm]	In-Plane Water Swelling at 23°C [%]	Volumetric Water Swelling at 23°C [%]
Nanofiber Composite (3M 825 EW:PPSU)	<u>0.095</u>	<u>5</u>	<u>43</u>
Cast 3M 825	0.115	25	85
Nafion <sup>®</sup> 212	0.095	19	35

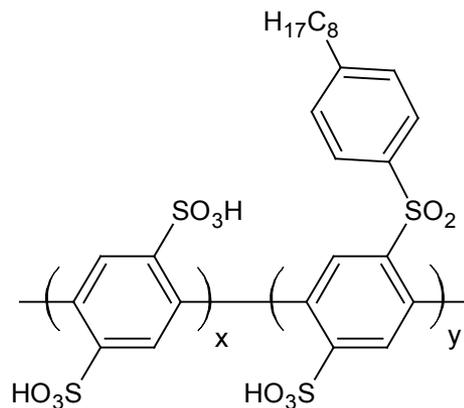
# Addition of Sulfonated Polyphenylenes to Nanofibers

The following polymers were synthesized by Morton Litt's group at Case Western Reserve University and sent to Vanderbilt:



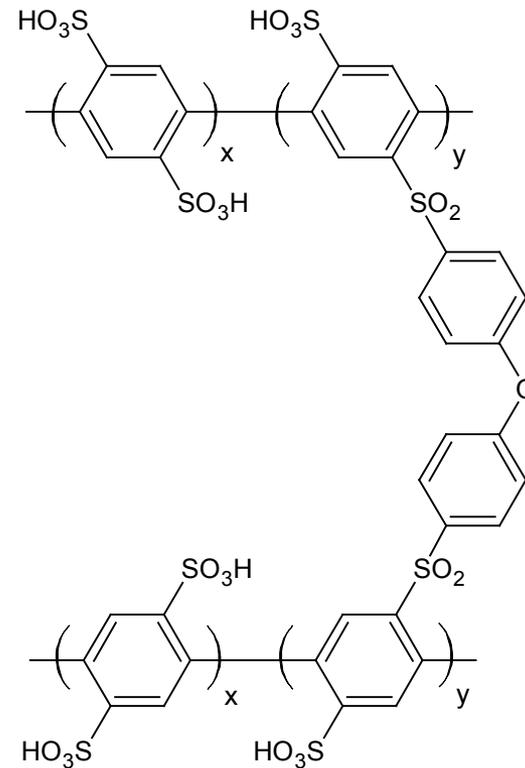
## TPB5

poly(4,4'-biphenyl-3,3'-disulfonic acid)-g-triphenylbenzene  
(5% target, 1% actual grafts/crosslinks)



## KOct

poly(1,4-phenylene-2,5-disulfonic acid)-g-octylbenzene  
(10% grafts)

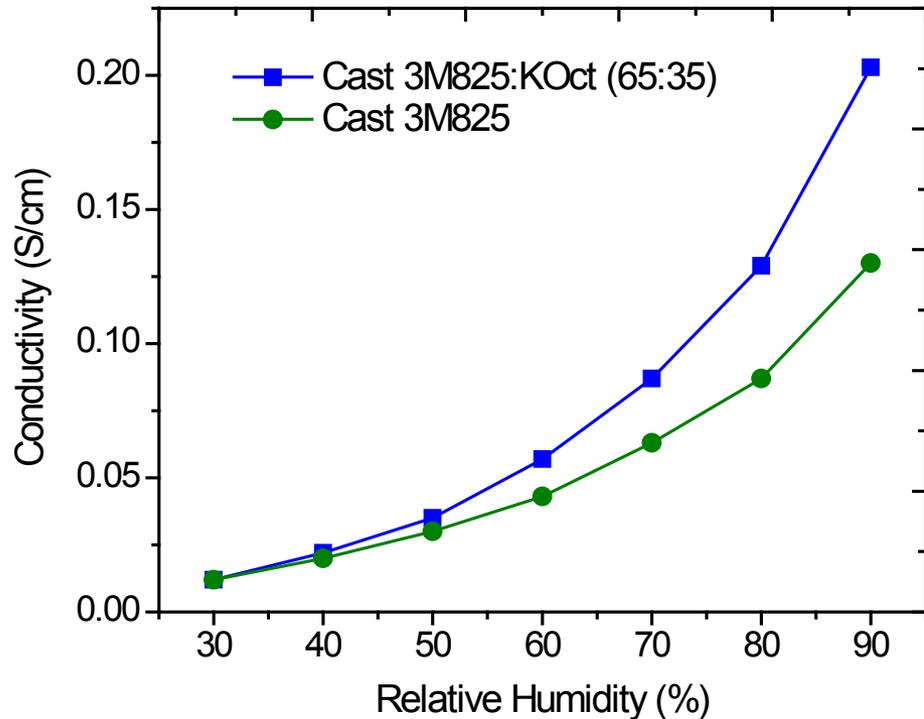


## DPE5

poly(1,4-phenylene-2,5-disulfonic acid)-g-diphenylether  
(5% target, 1% actual grafts/crosslinks)

# Results with Sulfonated Polyphenylene - Conductivity of Homogeneous Membranes

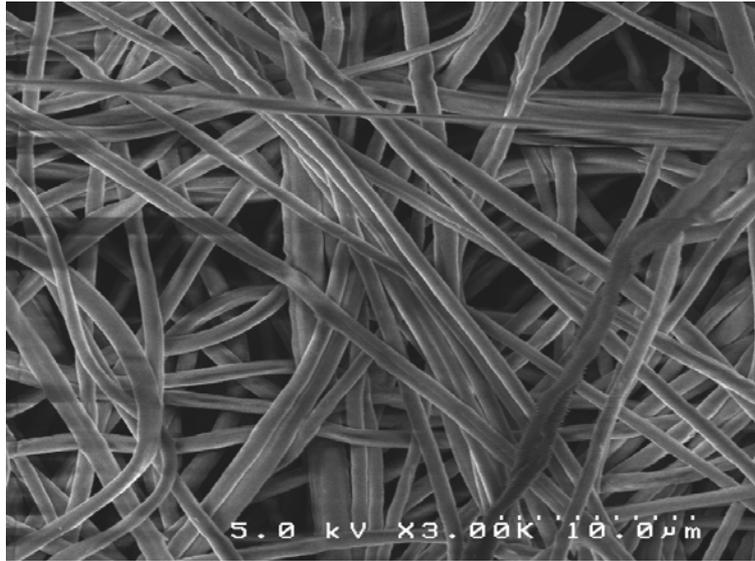
Conductivity at 40°C



Solution Cast 825 EW  
PFSA + KOct (35 wt%  
KOct)

- From an extrapolated Arrhenius plot of conductivity vs  $1/T$ : The conductivity of a homogeneous membrane at 120°C and 50%RH will be 0.125 S/cm.
- For a nanofiber mat with 0.70 volume fraction of proton conducting nanofibers, the expected proton conductivity will be 0.94 S/cm.

# Electrospinning PFSA (825 EW) with Sulfonated Polyphenylene (TPB5)

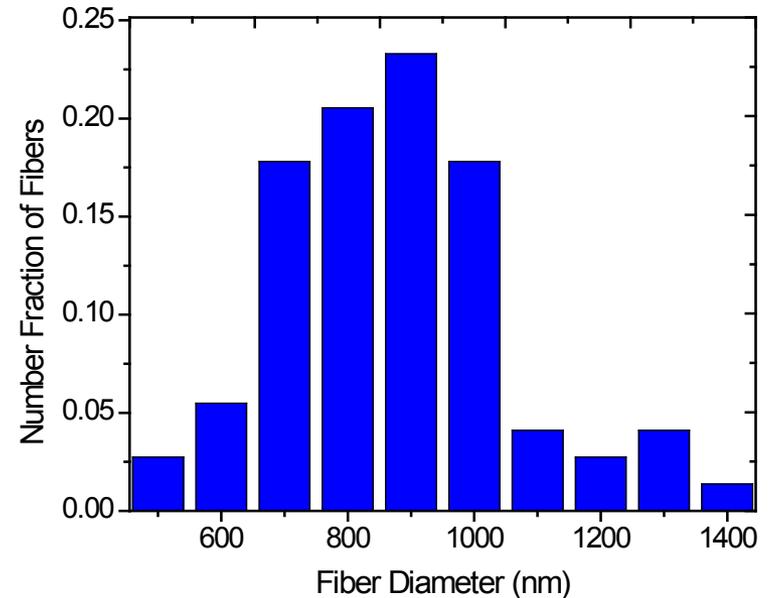


## Electrospinning Conditions

-17 wt% Polymer (3M (825 EW):TPB5:PEO, 74:25:1)\*; solvent was 1-propanol/water (2/1 vol/vol)

-7.5 kV, 6cm SCD, 0.6 mL/hr

\*Some TPB5 precipitated out of solution and was not incorporated into the nanofibers

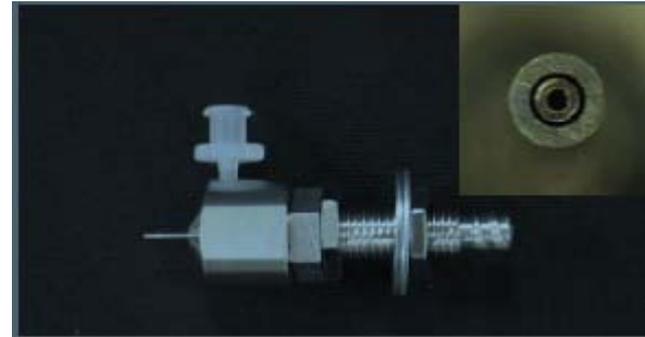


*Average Fiber Diameter = 825 nm*

**We have not yet made dual fiber mats with PFSA and sulfonated polyphenylene.**

# Electrospinning Nafion<sup>®</sup> Nanofibers with a Hollow Bore

Use a coaxial spinneret



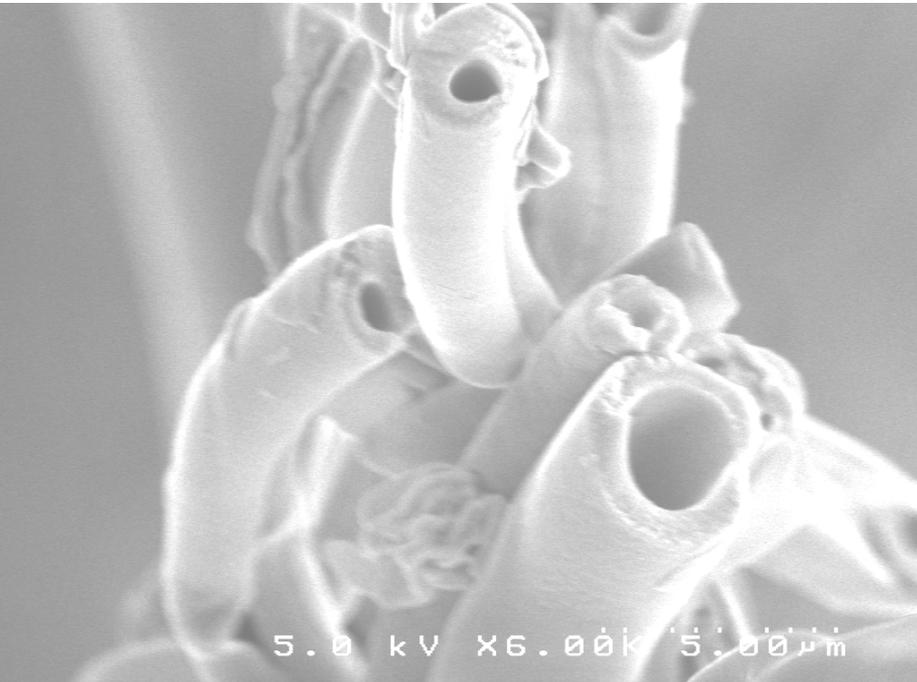
## Electrospinning Conditions:

	Sheath	Core
Composition	25 wt% 99:1 Nafion <sup>®</sup> :PEO (10 <sup>6</sup> MW)	Heavy Mineral Oil (Aldrich)
Solvent	Isopropanol: Water in 2:1 ratio	None
Voltage	7.5kV	
SCD	5 cm	
Flow Rate	0.6 mL/hr	0.05mL/hr

## Post electrospinning procedure:

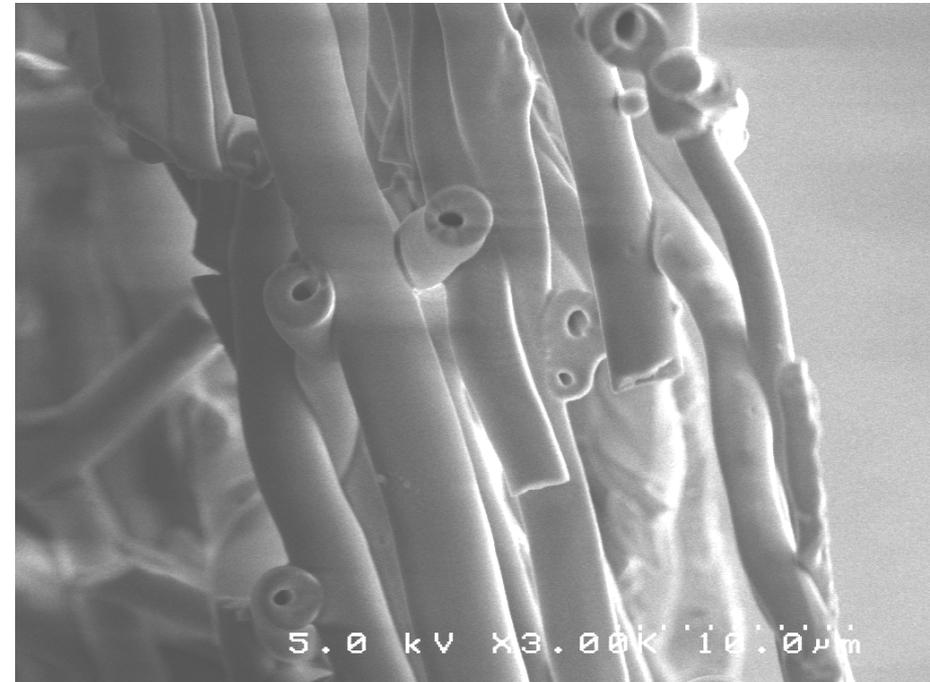
- 1) Anneal as-spun mat for 0.5 hours at 150°C.
- 2) Immerse the mat in octane overnight to extract mineral oil in the bore.

# *Electrospinning Nafion<sup>®</sup> Nanofibers with a Hollow Bore: SEMs of Fiber Mats*



SEM image of hollow fibers electrospun from: 25 wt% 85:15 Nafion<sup>®</sup>:PEO (300K MW)

Bore diameter: 1.4  $\mu\text{m}$   
Wall thickness: 1  $\mu\text{m}$   
Total fiber diameter: 3.4  $\mu\text{m}$



SEM image of hollow fibers electrospun from: 25 wt% 99:1 Nafion<sup>®</sup>:PEO (10<sup>6</sup>MW)

Bore diameter: 0.71  $\mu\text{m}$   
Wall thickness: 1  $\mu\text{m}$   
Total fiber diameter: 2.7  $\mu\text{m}$

From SEMs: >95% of the fibers contained a hollow bore

# *A Fuel Cell Cathode Composed of Electrospun Nanofibers*

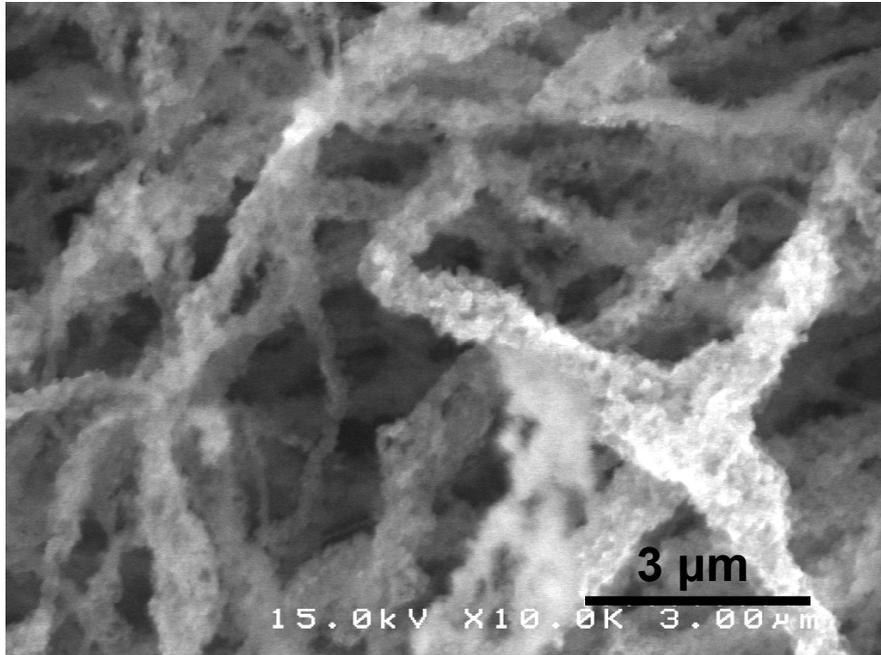
## **Electrode Electrospinning Conditions:**

<b>Composition</b>	<b>7.76 wt% catalyst/polymer in solvent, with 64:10:26 Pt(20%)/C:Nafion®:450K poly(acrylic acid)</b>
<b>Solvent</b>	Isopropanol/Water in 2:1 ratio
<b>Voltage</b>	3.5kV
<b>SCD</b>	6 cm
<b>Flow Rate</b>	0.3 mL/hr

## **Post electrospinning treatment and testing:**

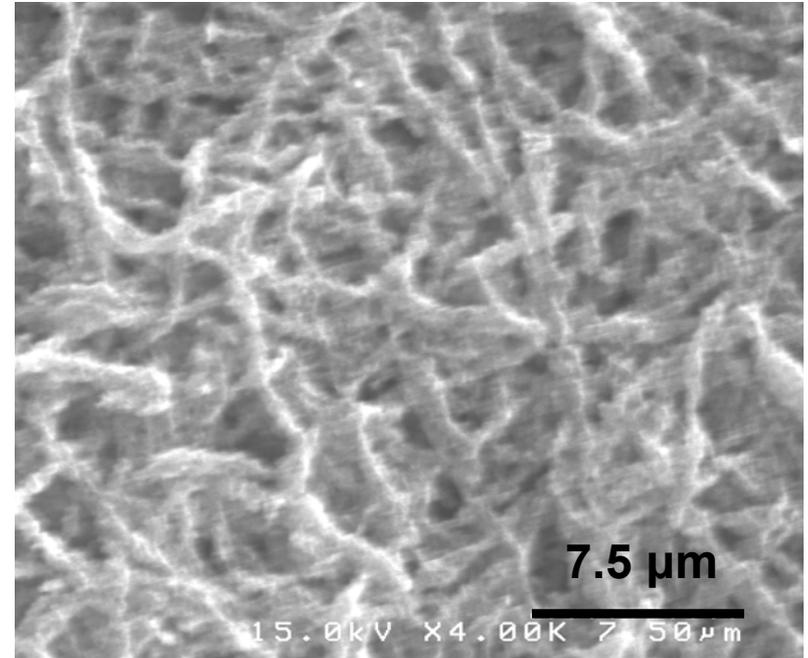
- (1) Anneal as-spun mat at 200°C in vacuum for 2 hr. (volume fraction of fibers is ~ 0.20)
- (2) Prepare MEA by hot pressing anode and cathode onto Nafion® 212 (use normal decal electrode/method to make anode)
- (3) Boil MEA in H<sub>2</sub>SO<sub>4</sub> and then boil in water, one hour each; no evidence of poly(acrylic acid) (PAA) removal.
- (4) Put MEA (5 cm<sup>2</sup>) into fuel cell test fixture; run break-in and V-i performance experiments

# SEMs of the Electrospun Nanofiber Fuel Cell Cathode



## SEM surface image of 64:10:26 (Pt/C: PFSA: PAA) Fibers

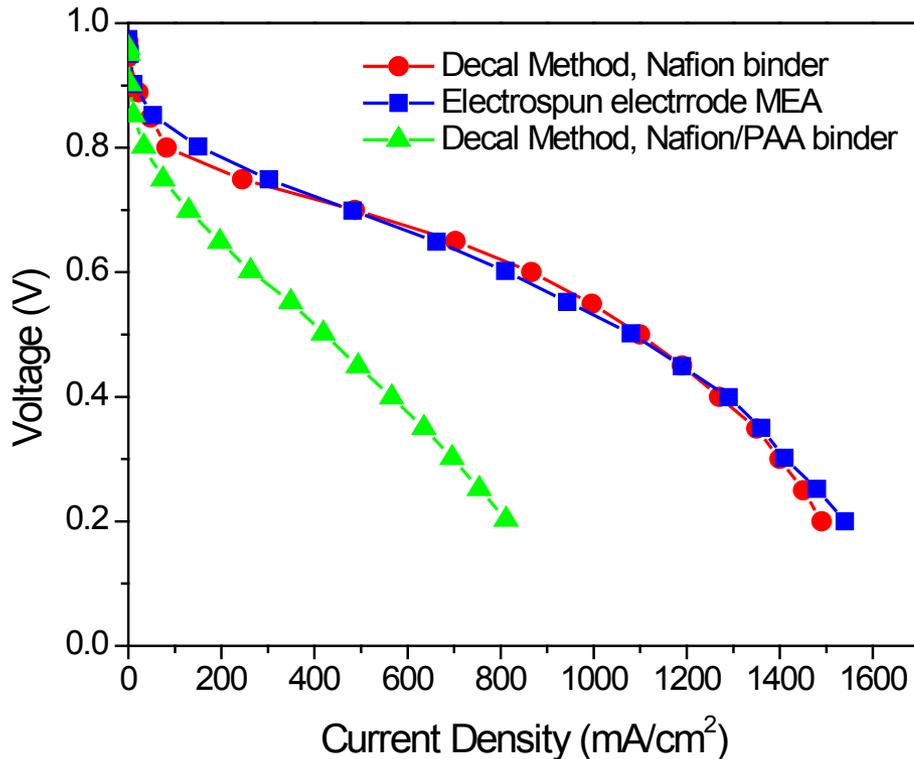
Fibers were annealed at 200°C  
Average fiber diameter = 420 nm



## SEM surface image of 64:10:26 (Pt/C: PFSA: PAA) fibers after 24 hrs of operation in cell (carbon paper removed)

Electrosprayed fuel cell electrodes with Nafion® binder [R. Benitez et al. *Journal of Power Source* 151 (2005)108-113] - The diameter of the catalyst cluster is ~19.1 µm.

# Fuel Cell Performance of an Electrospun Fiber Cathode



## Future Work:

- Remove or eliminate PAA
- Decrease fiber size
- Increase fiber porosity
- Optimize catalyst/ionomer weight ratio
- Continue fuel cell tests (short and long term)

Regular Decal method: 86 wt% Pt/C and 14 wt% Nafion<sup>®</sup>

Polarization curves at 80°C, 100% RH H<sub>2</sub>/air; Nafion<sup>®</sup> 212 membrane; 100 ml/min H<sub>2</sub>, 500 ml/min air, 0.40 mg/cm<sup>2</sup> anode and cathode Pt loading.

# 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.

# *Proposed Future Work*

- 1. Prepare and test nanofiber composite membranes with PFSA + sulfonated polyphenylene + polyphenylsulfone (use the dual fiber electrospinning approach).**
  - Determine the effect of sulfonated polyphenylene loading on membrane conductivity, swelling, and mechanical properties. Study 825 and lower EW PFSA ionomers.
  - Compare properties of composite membranes where ionomer nanofibers are surrounded by uncharged polymer and uncharged polymer nanofibers are surrounded by ionomer.
  - Investigate a sulfone bridge crosslinking scheme, with the addition of diphenylether or triphenylbenzene (for low EW PFSA with sulfonated polyphenylene).
- 2. Examine different inert/uncharged polymers**
  - Compare polysulfone, PVDF, and other uncharged polymers (e.g., polybenzimidazole) in nanofiber composite membranes; focus on water swelling and membrane mechanical properties. Identify the best uncharged polymer.
- 3. Further characterize electrospun hollow bore Nafion<sup>®</sup> fibers**
  - Convert the hollow bore fiber mats into membranes by compaction, welding and impregnation. Characterize the resulting films in terms of proton conductivity, water uptake/retention, and mechanical properties.
- 4. Prepare and test MEAs with nanofiber network composite membranes**
- 5. Continue to investigate and improve on the performance of electrospun nanofiber fuel cell electrodes (focus on the cathode).**
  - Decrease the electrode fiber diameter and/or create fiber porosity
  - Optimize the ink (and fiber) catalyst/polymer composition
  - Perform electrochemical characterization tests

# Summary of 2009-10 Work

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

**Approach:** Fabricate nanofiber network composite membranes from high IEC ionomers with highly charged particles (either sulfonated POSS or sulfonated polyphenylene).

**Technical Accomplishments and Progress:** Norland Optical Adhesive was replaced by polyphenylsulfone as the inert/uncharged component in nanofiber composite membranes. Sulfonated POSS was replaced by sulfonated polyphenylene. New methods for membrane preparation were developed (dual polymer fiber electrospinning followed by mat processing with the elimination of a polymer impregnation step).

**Technology Transfer/Collaborations:** Continued collaborations with 3M Corporation and Nissan Technical Center North America. Gave numerous presentations, wrote papers, and submitted a patent application.

**Proposed Future Research:** Prepare high conductivity fuel cell membranes using low EW PFSA with/without sulfonated polyphenylene. Investigate different uncharged polymer supports, including polyphenylsulfone, PVDF, and PBI. Investigate polymer crosslinking schemes. Test the new membranes in a H<sub>2</sub>/air fuel cell. Continue to develop methods for electrospinning nanofiber electrode structures.

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