SCHOOL OF ENGINEERING
VANDERBILT UNIVERSITY

DOE Hydrogen Program

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

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May 2012

Project ID: FC038

Overview

Timeline

- Start date 3/1/2006
- End date 2/29/2012 (received a one-year no-cost extension)
- Percent complete 100%

Budget

- Total project funding
  - DOE $1,455,095
  - Cost Share (CWRU and Vanderbilt) $406,479
- Funding spent in FY11 $130,000

Barriers

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

Interactions

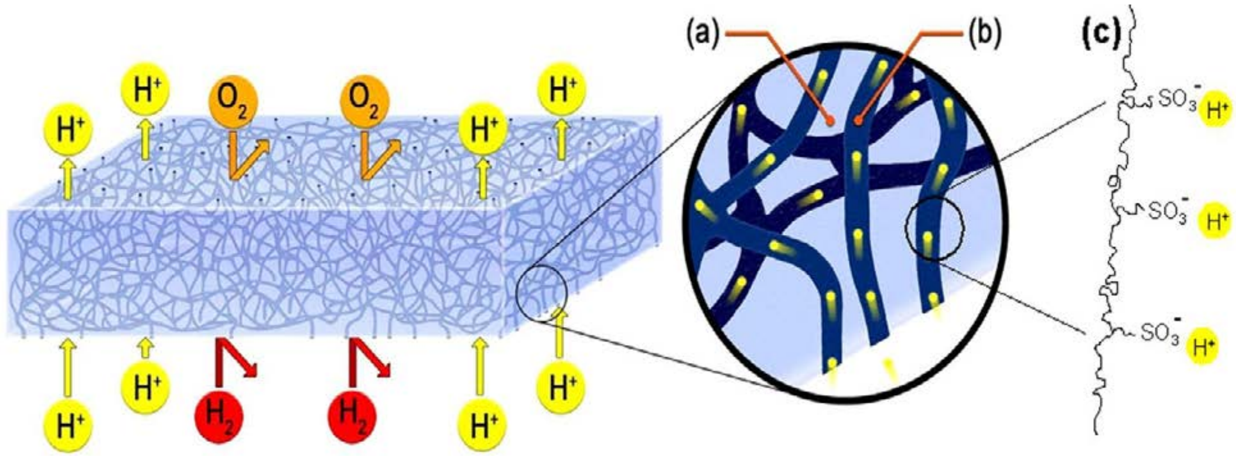
3M Corporation
Nissan Technical Center North America, Inc.
General Motors LLC

Objectives

Project Objective:

To fabricate and characterize nanofiber 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



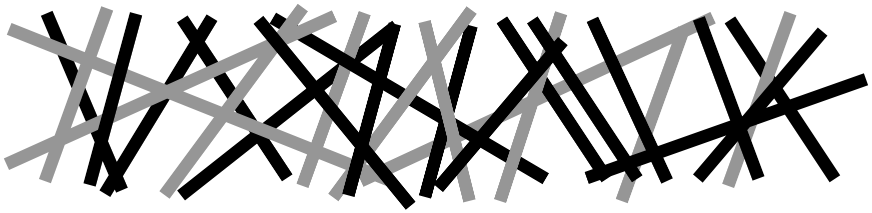
2011-2012 Project Goals:

1. Evaluate nanofiber composite membranes with 660 EW PFSA from 3M Company
   a. Use dual fiber electrospinning approach (with no polymer impregnation step)
   b. Test the membrane in a hydrogen/air fuel cell MEA
2. Develop fast processing conditions for converting a dual fiber electrospun mat into a fuel cell membrane.
3. Continue to investigate electrospun fuel cell electrodes

Milestones

Month/Year	Milestone or Go/No-Go Decision
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^{o}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 S/cm at 120^{o}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.
February 2011	Milestone: Prepared and assessed defect-free composite nanofiber membranes from low EW (660) PFSA and polyphenylsulfone (PPSU), using a dual fiber electrospinning approach. Prepared and tested high performance nanofiber fuel cell cathodes.
February 2012	Milestone: Achieved a proton conductivity of 0.093 S/cm at 120^{o}C and 50% RH for a nanofiber network membrane, where the fibers were composed of 660 EW PFSA polymer (from 3M co.) with polyphenylsulfone as the inert matrix. Tested this membrane in a H_2/air fuel cell at high and low RH conditions.

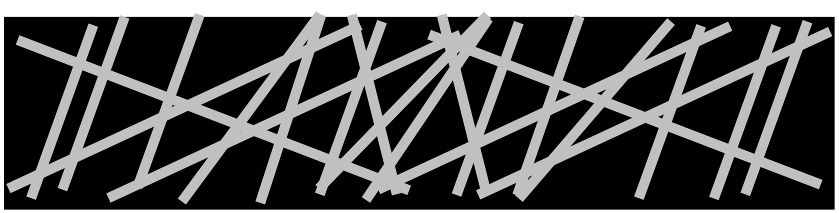
One Nanofiber Mat, Two Membrane Structures



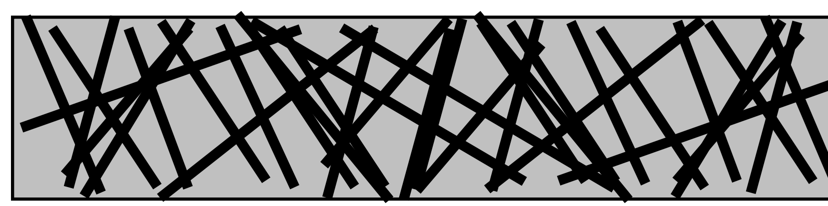
Electrospun mat of Nafion fibers and polyphenylsulfone fibers
(— Nafion; — polyphenylsulfone)

Pressure
+
Thermal Annealing

Pressure
+
Solvent Vapor Exposure



Membrane with Nafion reinforced by polyphenylsulfone fibers



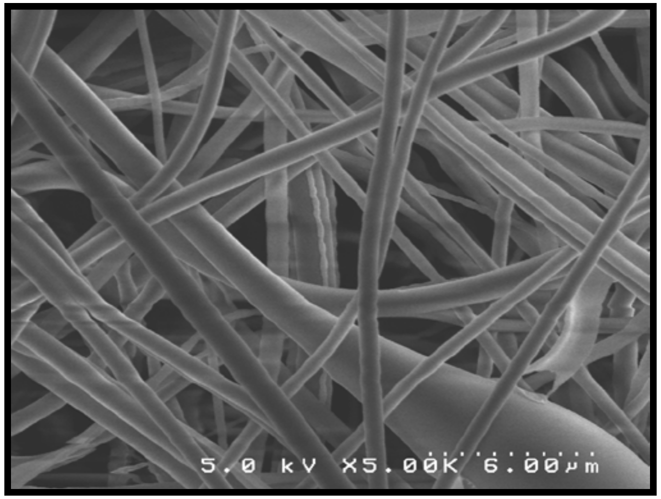
Membrane with Nafion fibers embedded in polyphenylsulfone

Nafion is a registered trademark of E.I. du Pont de Nemours and Company

Macromolecules, 2011.

Dual Fiber Mat → Composite Membrane

Electrospin Nafion® and polyphenylsulfone (PPSU)



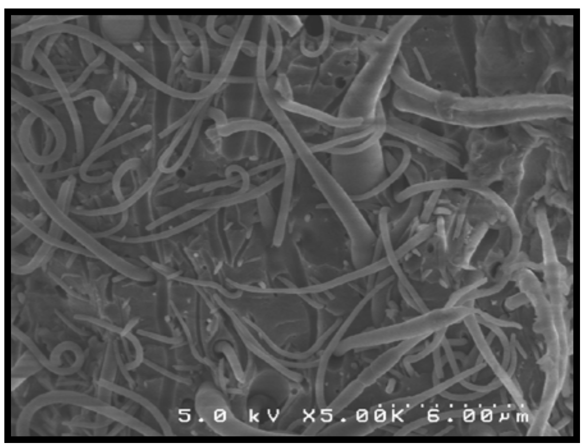
Surface of Mat

Nafion® melts/flows to fill inter-fiber void space

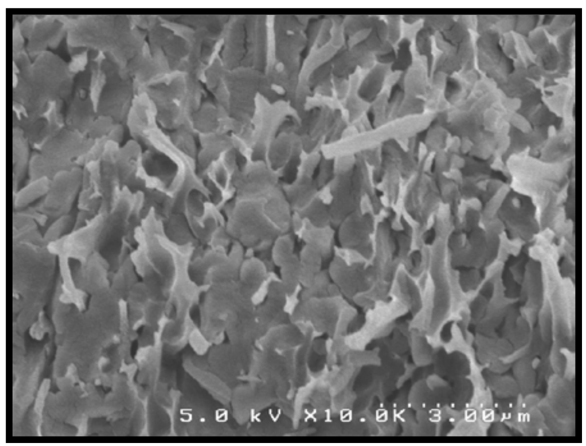
1) Hot Press at 15,000 psi and 127°C
2) Anneal – 2hr., 150°C
3) Boil in 1M Sulfuric Acid, 1hr
4) Boil in Water, 1hr

PPSU flows to fill inter-fiber void space

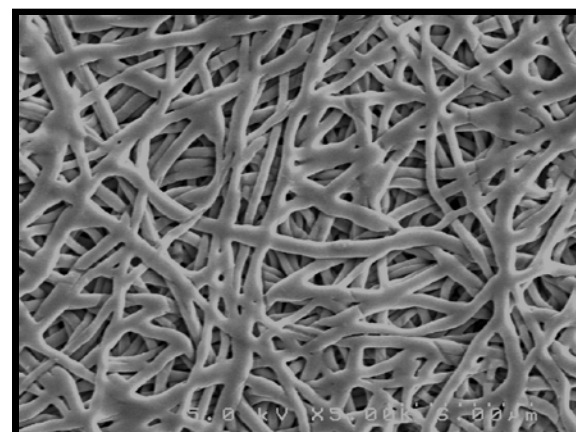
1) Cold Press at 3,500 psi and 23°C
2) Chloroform Vapor Exposure, 16 min., 23°C
3) Anneal – 2hr., 150°C
4) Boil in 1M Sulfuric Acid, 1 hr.
5) Boil in Water, 1.hr.



Cross-section



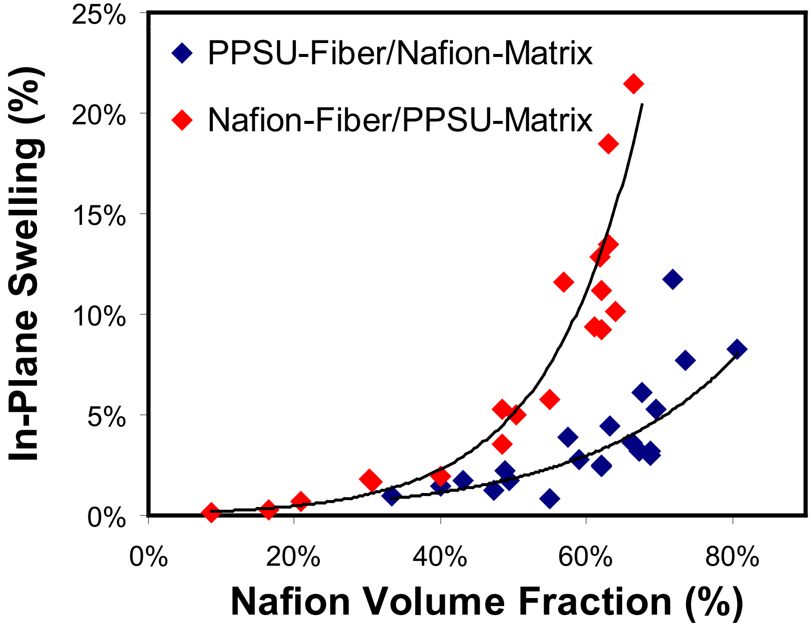
Cross-section



Surface after PPSU Removal

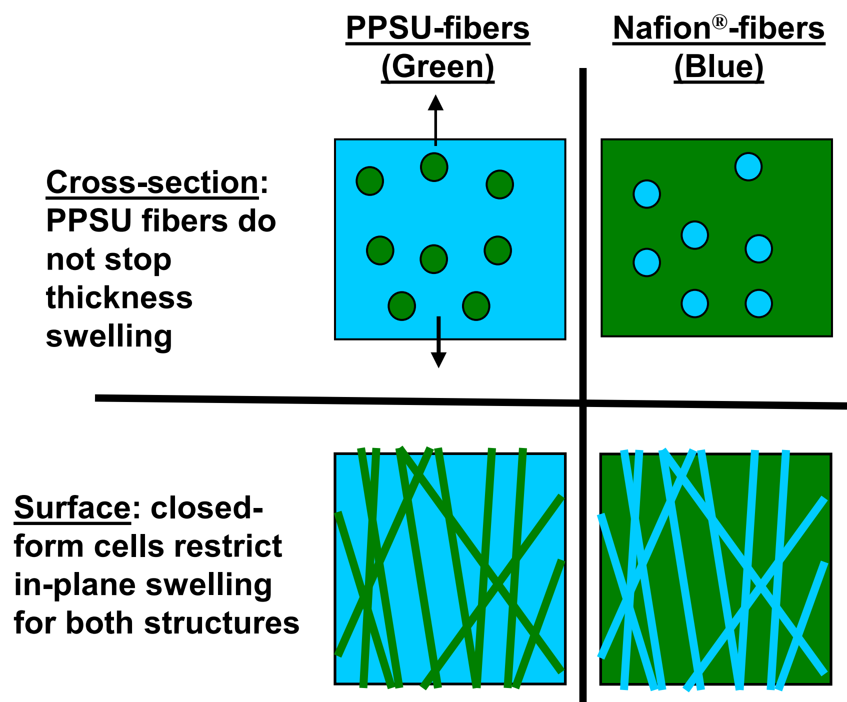
In-Plane Swelling in 100°C Water

- Swelling measured in water at 100°C
- Nafion® 212 in-plane swelling: 37%



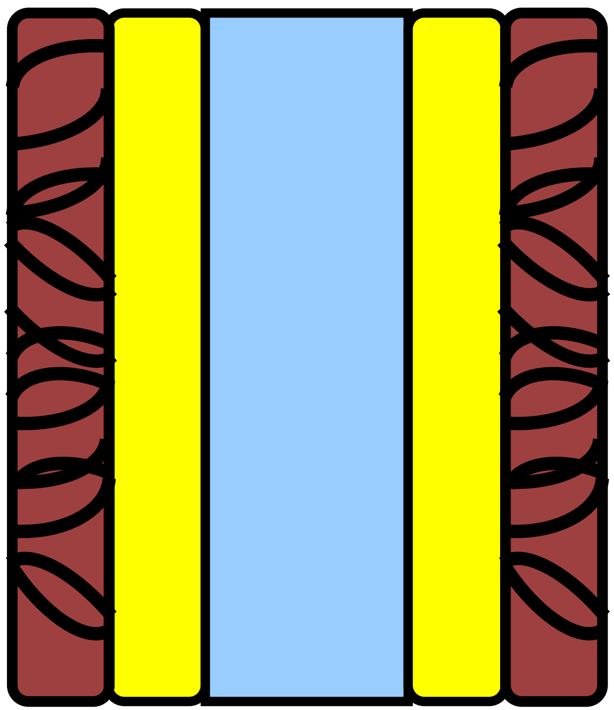
- Both membrane structures have the same volumetric swelling for a given Nafion® volume fraction
- In-plane swelling is significantly lower than Nafion® for both composite membranes

- PPSU-fiber/Nafion® -matrix has lower in-plane swelling
- PPSU-fibers/Nafion® -matrix can expand more easily in thickness direction (no 3-D connectivity of PPSU)
- Limited thickness swelling for Nafion® fiber/PPSU membrane (3-D PPSU connectivity)



Fuel Cell Testing: Nafion matrix with polyphenylsulfone fibers

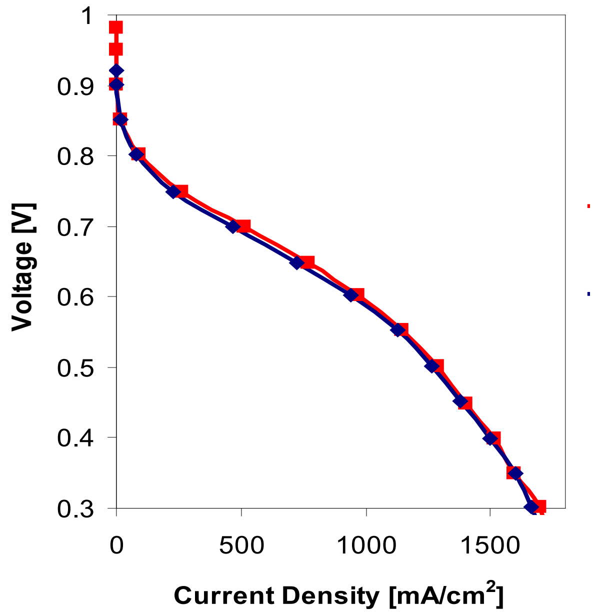
Material	**Conductivity [mS/cm] (23°C H_2O)**	**Membrane Resistance [mΩ-cm²] (80°C, 90%RH)**	**In-Plane Swelling (100°C H_2O)**	**Volumetric Swelling (100°C H_2O)**
Nanofiber Composite (70 vol% Nafion®, 30 vol% polyphenylsulfone0	66	45 (36 μ membrane)	**6%**	42%
Nafion® 212	95	45 (51μ membrane)	**37%**	75%



Fuel Cell Performance

Fuel cell conditions:

- 80°C, 100% RH, atmospheric pressure
- 0.4 mg/cm² Platinum Loading
- Nanofiber Composite is 31 microns thick

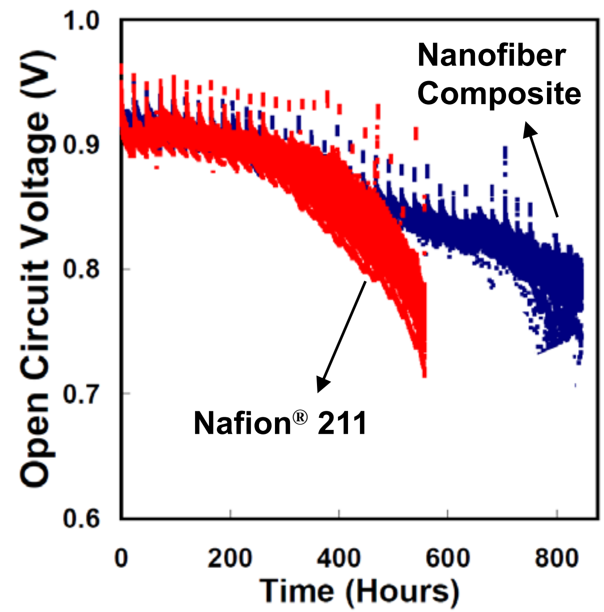


Nanofiber Composite = PPSU-fiber/Nafion-matrix

Equivalent Area Specific Resistance =
Equivalent Power Production
(~570 mW/cm² at 0.6V)

Fuel cell conditions:

- 2 minutes at 0% RH H_2/air, 2 minutes at 100% RH H_2/air
- Operating Temperature = 80°C
- 0.4 mg/cm² Platinum Loading



Hydrogen Crossover (Limiting Current)

Time (hours)	Nafion® 212 (mA/cm²)	NNM (mA/cm²)
$T_1 = 0$	1.5	1.9
$T_2 = 515$	13+	5.2
$T_3 = 845$	n/a	13+

54% Increase in Lifetime

(Failure when OCV falls below 0.8V)

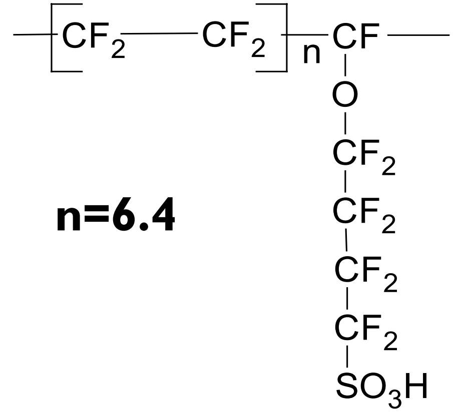
New Work

- Fabrication and characterization of nanofiber composite membranes with 660 EW PFSA (from 3M Co.)
- Rapid processing to convert dual fiber PFSA/polyphenylsulfone electrospun mats into fuel cell membranes
- Electrospun nanofiber fuel cell electrodes

Composite Membrane Fabrication with 660EW PFSA

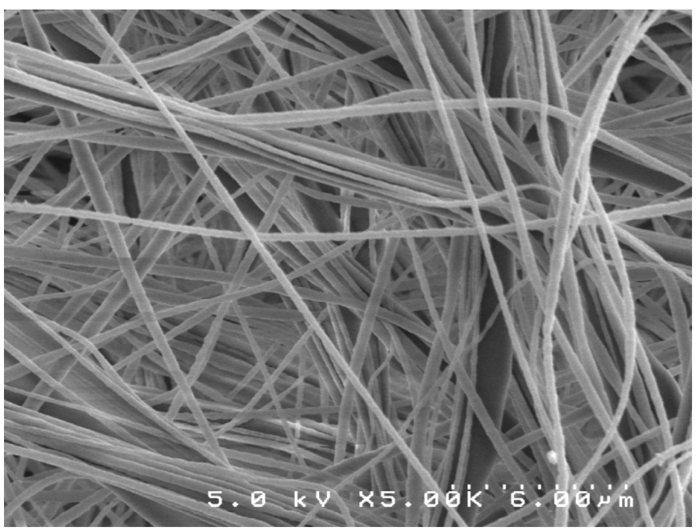
Membrane Processing (PPSU-fiber/660EW-matrix)

1) Dual-fiber Electrospinning 3M660/PEO and PPSU
2) Compress to 6000 psi at 127°C
3) Anneal 2 hours at 150°C in vacuum
4) Soak in 1M H_2SO_4 for 16 hours at 23°C
5) Soak in water for 6 hours at 23°C
   (replacing with fresh water periodically)

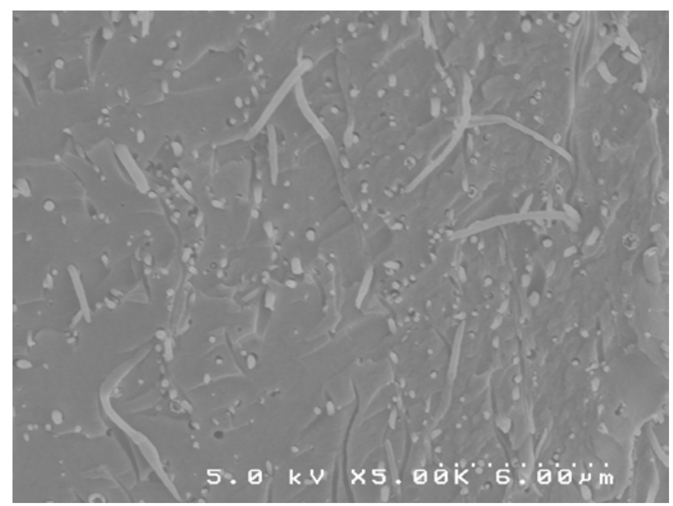


n=6.4

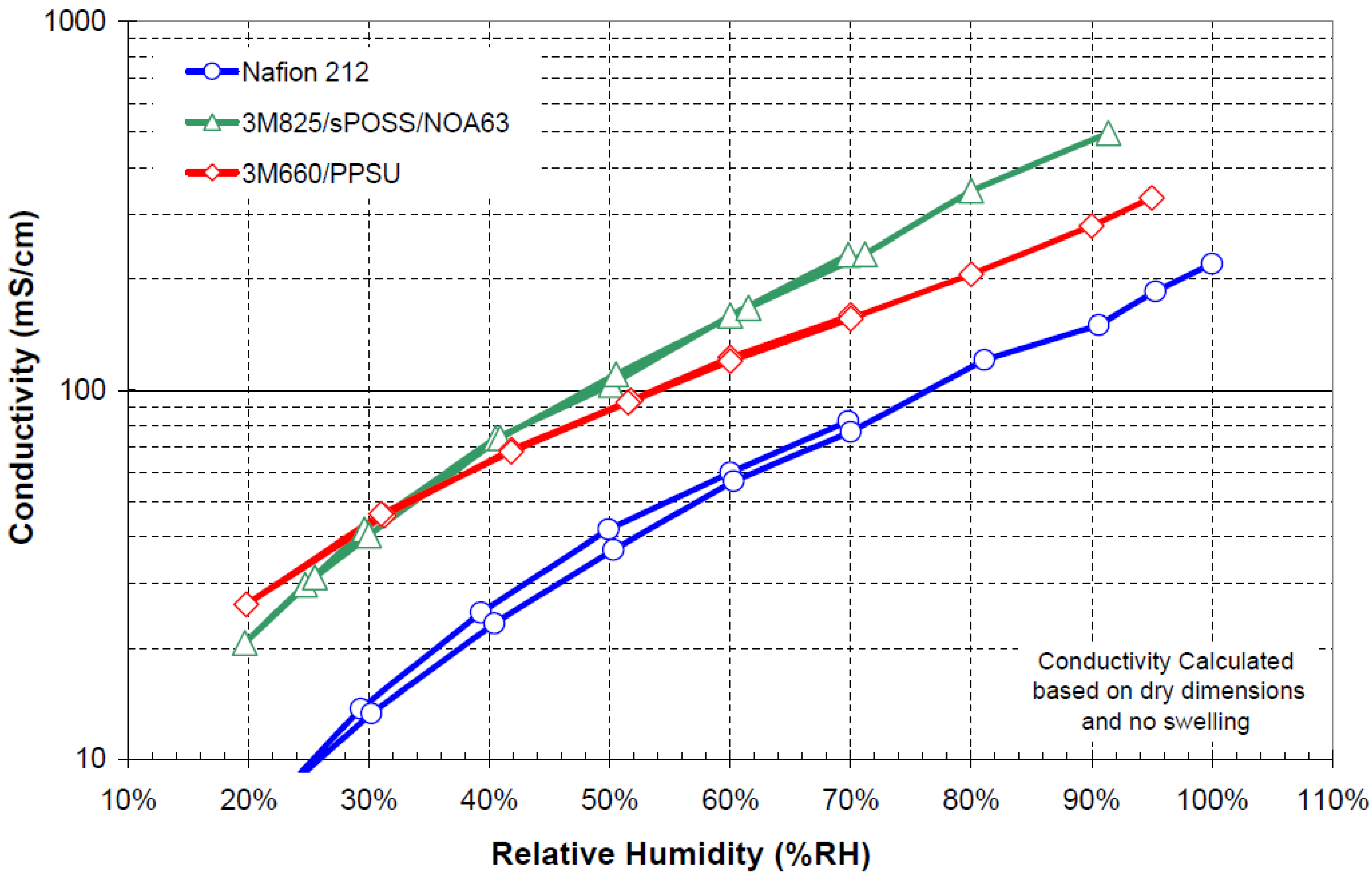
Surface of Dual-fiber Electrospun Mat



Cross-section of Dense Membrane (3M660 reinforced by PPSU fibers)



In-Plane Proton Conductivity at 120ºC



- **3M825/sPOSS/NOA63 : 74 vol% 3M825/sPOSS fibers* and 26 vol%NOA63 (108 µm thick)**
- **3M660/PPSU : 70 vol% 3M660 and 30 vol% PPSU fibers (54 µm thick)**
- **Nafion® 212 is a commercial film from DuPont (51 µm thick)**

***3M825:sPOSS ratio is 60:35 by weight**

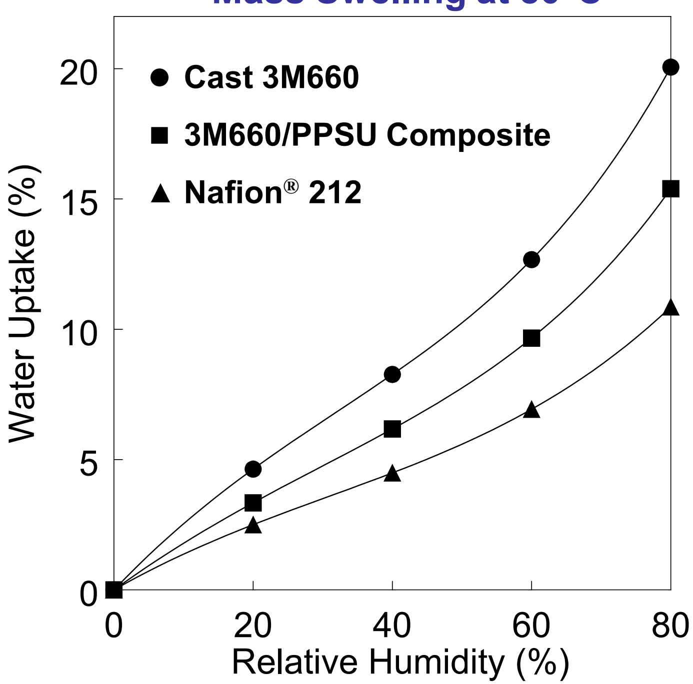
Water Uptake – 660EW Nanofiber Membranes

Swelling Data
(Swelling in 23°C liquid water)

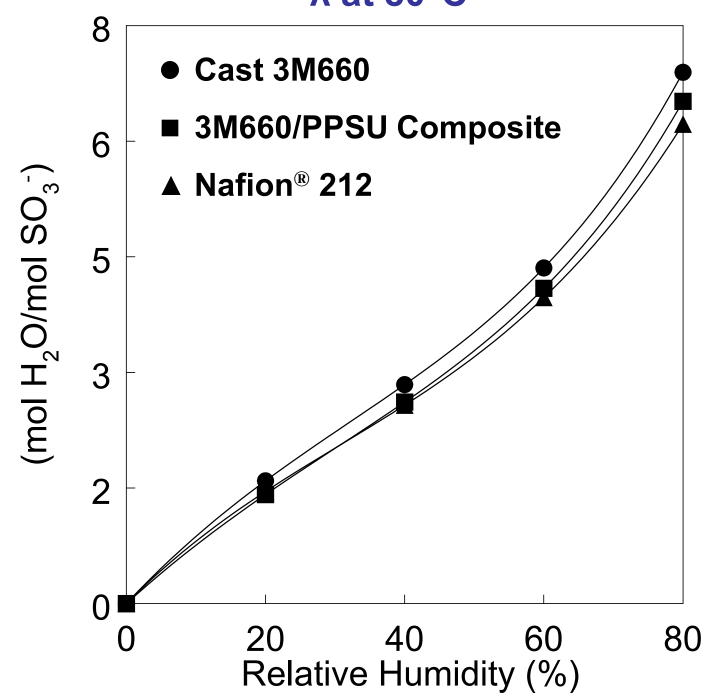
Membrane	Mass Swelling [%]	Volumetric Swelling [%]	In-Plane Swelling [%]
3M660EW/PPSU Composite	53	87	5
Cast 660 EW film	71	137	84
Nafion® 212	16	35	25

- Lower planar swelling than Nafion® 212, but over twice the conductivity
- 3M660 and the 3M660/PPSU composite have higher water uptake than Nafion® (due to higher IEC), but have the same λ.

Mass Swelling at 80°C

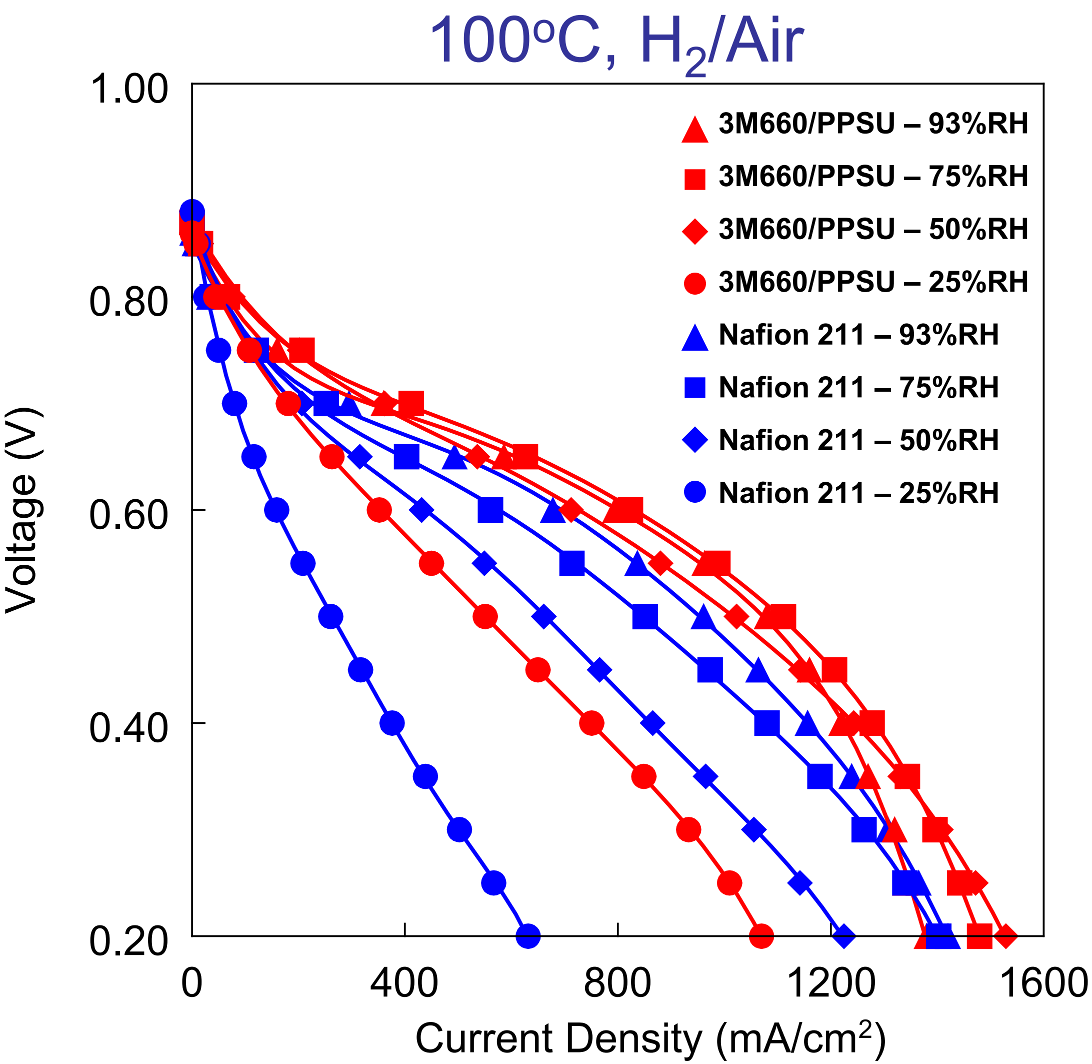


λ at 80°C



Fuel Cell Performance – 660EW Nanofiber Membranes

(nanofiber composite MEAs prepared at 3M Company)



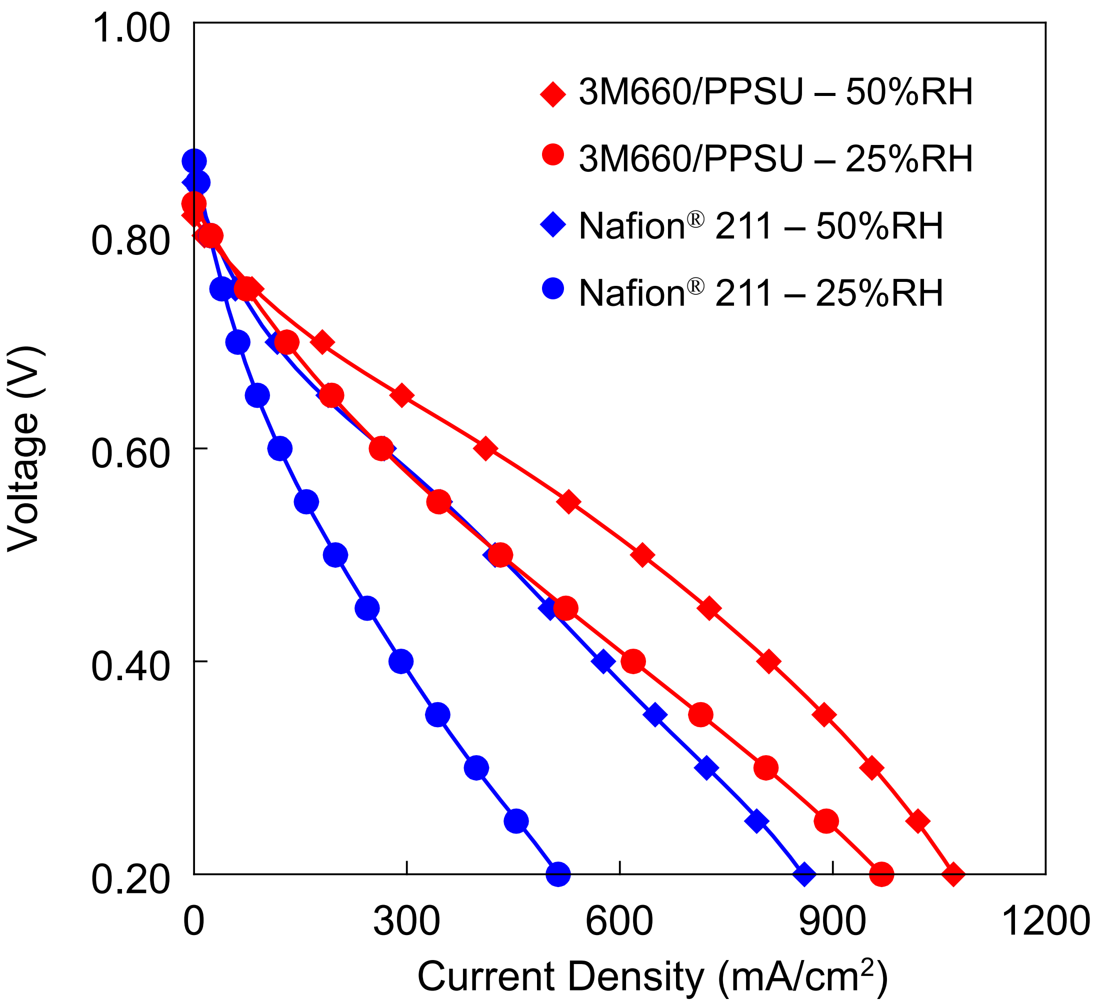
Initial fuel cell study:

- Composite membrane composition: 58 vol% 3M660 and 42 vol% PPSU
- Conductivity is 72 mS/cm at 80°C, 60%RH (vs. 46 mS/cm for Nafion)

Fuel cell conditions:

- 125 ml/min H_2 and 500 ml/min air, no back pressure
- N211: Nafion® 211 membranes with 0.4 mg_{Pt}/cm2 GDE w/ Nafion binder
- 3M660/PPSU: 3M660/PPSU composite (58 % 3M660 and 43 μm thick). 0.25 mg_{Pt}/cm^2 with 3M825 binder

Fuel Cell Polarization at 120^{o}C

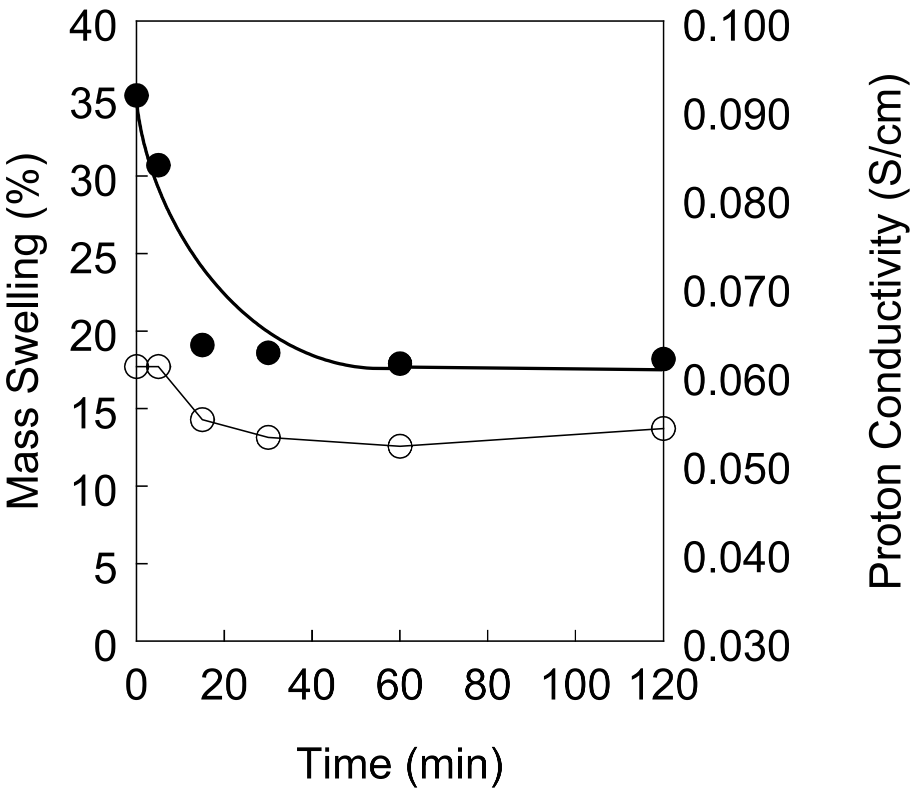


Fuel cell conditions:

- 125 mL/min H_2 and 500 ml/min air, no back pressure
- N211: Nafion® 211 membranes with 0.4 mg_{Pt}/cm^2 GDE w/ Nafion® binder
- 3M660/PPSU: 3M660/PPSU composite (58 % 3M660 and 43 µm thick). 0.25 mg_{Pt}/cm^2 with 3M825 binder

Rapid Processing of Dual fiber Mats - Effects of Annealing Time (150°C)

Mass Swelling and Proton Conductivity

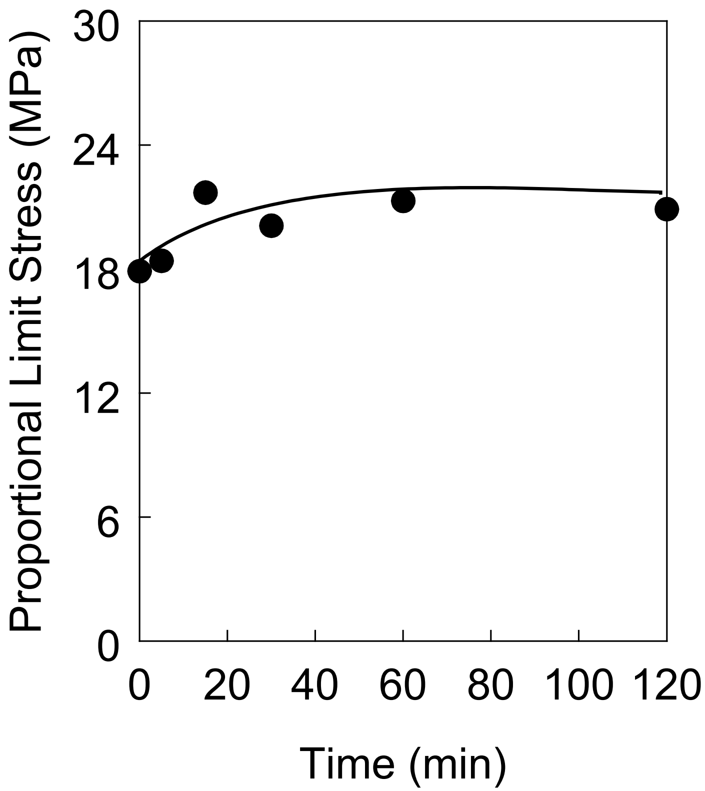


Closed symbols = Mass Swelling (100°C water)

Open Symbols = Proton Conductivity (25°C water)

PPSU-fiber structure

Proportional Limit Stress

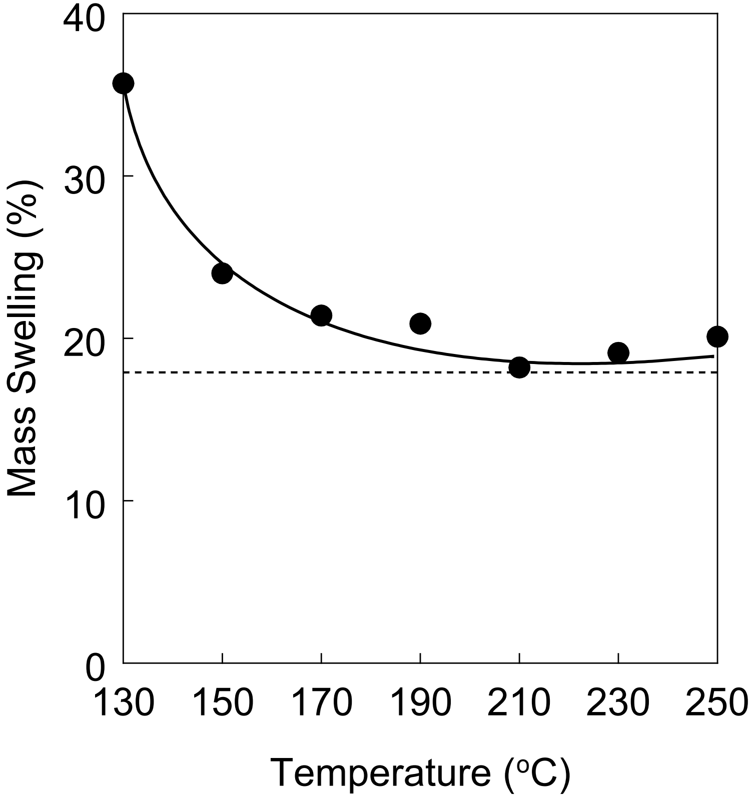


Data point are average of 3 tests, tested dry membranes at 30°C, 20%RH

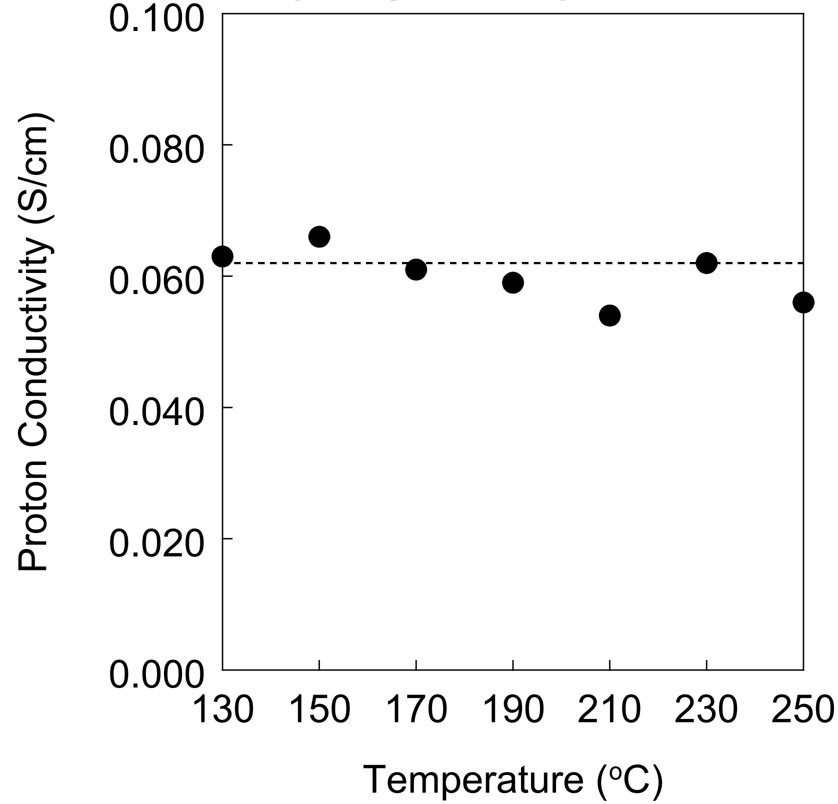
- **At 150°C, properties stabilize after 15 minutes of annealing**
- **Attributable to development of crystallinity of Nafion® component**

Effects of Annealing Temperature on Membrane Water Uptake and Conductivity

Mass Swelling as a function of annealing temperature (annealed 5 min.)



Proton Conductivity as a function of annealing temperature (annealed 5 min.)

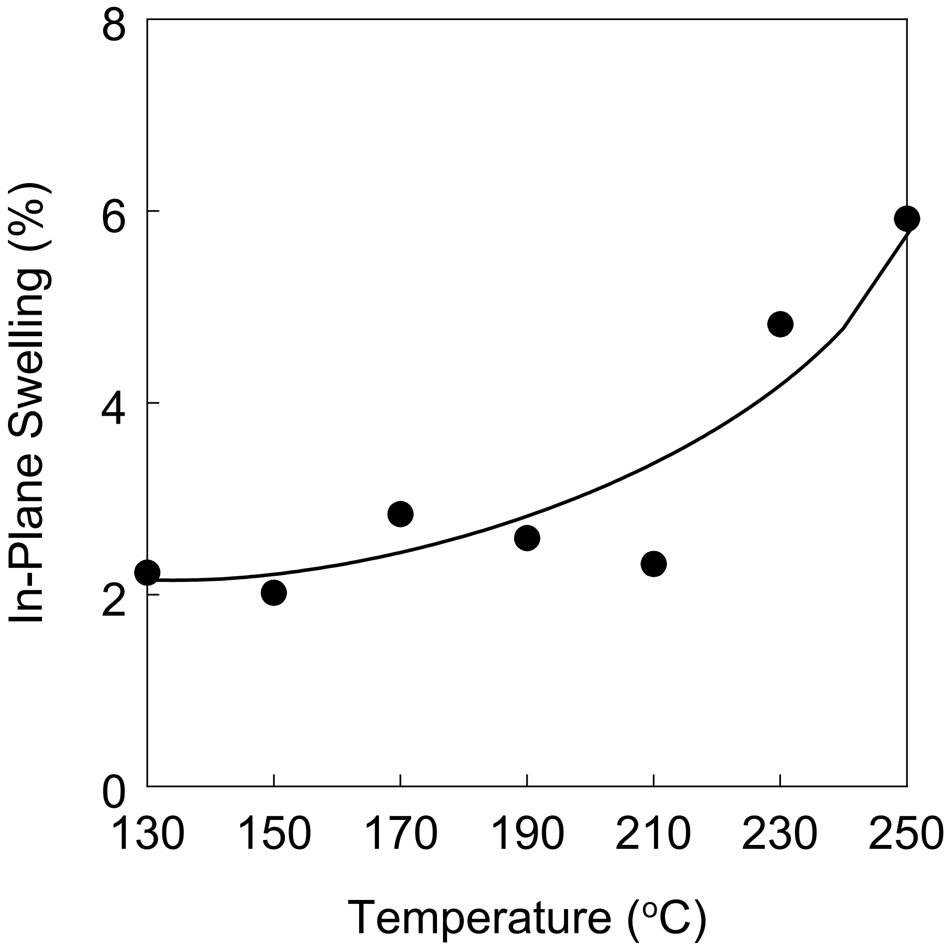


*Dashed line represents standard annealing (2 hours, 150°C)

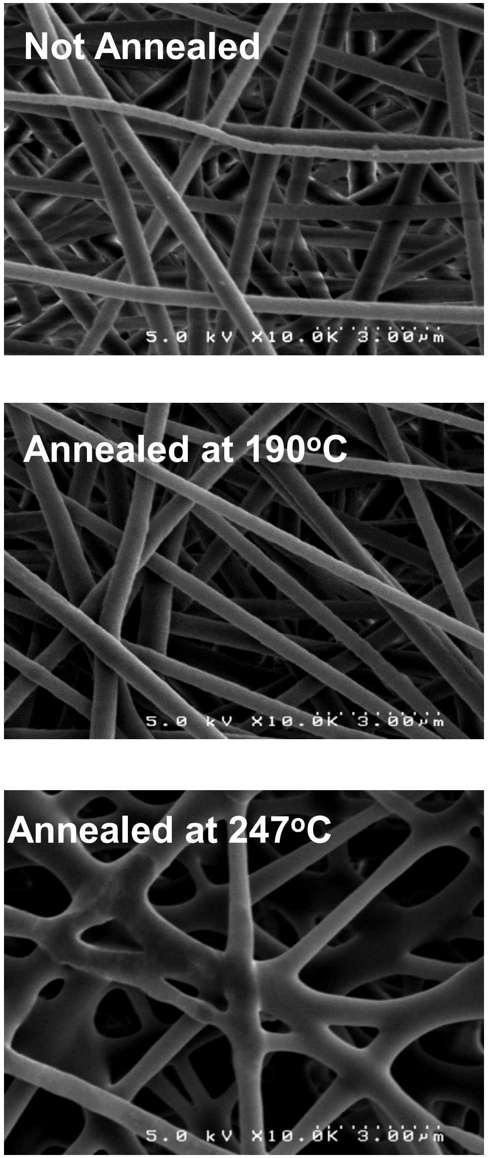
- **Increasing annealing temperature reduces mass swelling, but has little effect on proton conductivity, 5 minutes at 210°C is sufficient annealing.**
- **Shorter annealing at 210°C (2 min.) resulted in higher swelling.**

Effects of Annealing on In-Plane Swelling

In-Plane Swelling as a function of annealing temperature (annealed 5 min.)



PPSU Fiber Mats



*In-plane swelling for Nafion®-fiber/PPSU-matrix membrane of similar volume fraction is ~ 12%

Effects of Chloroform Vapor Exposure

(for membrane morphology where polyphenylsulfone surrounds PFSA fibers)

Chloroform Vapor Exposure at 25°C

Chloroform Vapor Exposure time (min)	Conductivity (mS/cm)	Mass Swelling (%)	Volumetric Swelling (%)	Proportiona l Limit Stress (MPa)
5	39	23	35	20.2
16	51	20	27	25.0

Chloroform Vapor Exposure at 50°C

Chloroform Vapor Exposure Time (min)	Conductivity (mS/cm)	Mass Swelling (%)	Volumetric Swelling (%)	Proportiona l Limit Stress (MPa)
1.5	45	59	48	19.6
3	53	23	28	23.3
5	52	25	27	21.7

*Conductivity in 25°C water, Swelling in 100°C water.

- **Chloroform vapor exposure time can be reduced to <u>3 minutes</u> at 50°C**

Summary: Rapid Processing of Nanofiber Membranes

Electrospinning is straight-forward to scale-up/speed-up: More syringes

Standard Processing of Nafion®-film reinforced by PPSU fibers	Rapid Processing of Nafion®-film reinforced by PPSU fibers	Standard Processing of Nafion® fibers encapsulated in PPSU	Rapid Processing of Nafion® fibers encapsulated in PPSU
1. Hot-press fiber mat ~40 seconds at 127°C 2. Anneal 2 hr., 150°C 3. Boil 1 hr in 1M $H_2SO_4$and 1 hr. in H_2O	1. Hot-press fiber mat ~40 seconds at 127°C 2. Anneal 5 min., 210°C 3. Boil 5 min. in 1M H_2SO_4 and 5 min. in H_2O	1. Compact mat ~10 seconds at 25°C 2. Expose to chloroform vapor for 16 min. at 25°C 3. Immediately dry 60 min. at 70°C. 4. Anneal 2 hr., 150°C 5. Boil 1 hr in 1M $H_2SO_4$and 1 hr. in H_2O	1. Compact mat ~10 seconds at 25°C 2. Expose to chloroform vapor for 3 min. at 50°C 3 Anneal 5 min., 210°C 4. Boil 5 min. in 1M H_2SO_4 and 5 min. in H_2O

Total processing time reduced from 4+ hours to 15-18 minutes, a 15-fold reduction

Membrane Properties: Rapid vs. Standard Processing

Membrane Structure and -Processing Method	Conductivity (mS/cm) 80°C, 80% RH	Mass Swelling (%) 100°C H_2O	Proportional Limit Stress (MPa) 30°C, 20% RH
Nafion®-fiber/Rapid	48	23%	21.9
Nafion®-fiber/Standard	49	22%	24.6
PPSU-fiber/Rapid	48	18%	23.5
PPSU-fiber/Standard	47	25%	21.5

Rapid = 3 min. in 50°C chloroform (if Nafion®-fiber structure), annealed 5 min. at 210°C, boiled 5 min. each in acid and water

Standard = 16 min. in 25°C chloroform (if Nafion®-fiber structure), annealed 120 min. at 150°C, boiled 60 min. each in acid and water

- **Rapid-processing of membranes results in comparable properties to those processed using standard procedures used previously.**

Collaborations

Partners

- **3M Corporation:** (1) Provided samples of short side-chain low EW PFSA polymer (in solution) for electrospinning studies and membrane development, (2) provided background information on casting membranes from solutions of low EW PFSA (e.g., polymer annealing conditions); and (3) prepared MEAs from 660 EW nanofiber composite membranes.
- **Nissan Technical Center North America, Inc.:** Collaborations with Nissan Technical Center NA involved: (1) sharing of MEA testing protocols and testing of nanofiber electrodes and (2) testing of electrospun cathode MEAs.
- **General Motors LLC:** Tested properties and durability of nanofiber composite fuel cell membranes (Nafion® with a reinforcing mat of polyphenylsulfone; membranes fabricated at Vanderbilt).
- **ORNL (Karren More):** SEM and TEM analyses of electrospun nanofiber electrodes

Summary

- 660 EW PFSA from 3M Company was successfully electrospun and a dual fiber mat (with electrospun nanofibers of polyphenylsulfone) was converted into a functional proton conducting membrane.
  - In-plane water swelling was very low (5% in RT water) and the conductivity was high (0.093 S/cm at 120^{o}C and 50% RH)
  - The membrane was fabricated into a fuel cell MEA (at 3M Co.) and H_2/air fuel cell tests at low RH were performed. The membrane performed significantly better than Nafion 212 for $25\% < RH < 93\%$ and $T = 100^{o}C$ and 120^{o}C.
- Methods were developed for the rapid processing of a dual fiber electrospun mat (Nafion® and polyphenylsulfone) into a defect-free fuel cell membrane. The total time for membrane processing was decreased from ~4 hours to ~15 minutes.
- Electrospun nanofiber electrode structures were fabricated and tested in a H_2/air fuel cell. A nanofiber cathode at 0.1 mg_{Pt}/cm^2 generated the same power as a decal cathode at 0.4 mg_{Pt}/cm^2. The nanofiber cathode also exhibited improved durability during voltage cycling and less mass transfer resistance (a current density of ~2 A/cm^2 was achieved at 0.4 V with humidified air and no backpressure).

Summary of 2011-12 Work

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

Approach: Fabricate nanofiber network composite membranes from high IEC (low EW) ionomers, using a dual fiber electrospinning approach (which circumvents the need for a polymer impregnation step).

Technical Accomplishments and Progress: Nanofiber composite membranes were fabricated from 660 EW PFSA and polyphenylsulfone. The membrane exhibited high in-plane proton conductivity at 120^{o}C and 50% RH (0.093 S/cm) and very low in-plane swelling (5%). The membrane worked well in a fuel cell at low RH feed gas conditions (2.5-times better than Nafion 212). Rapid processing conditions for converting a dual fiber mat (Nafion and polyphenylsulfone) into a defect-free fuel cell membrane were identified. Work has continued on the fabrication and testing of high performance nanofiber fuel cell cathodes .

Technology Transfer/Collaborations: Collaborations with 3M Company and Nissan Technical Center North America have continued. A US patent has been filed on the nanofiber fuel cell electrode technology. A multinational company who wishes to explore commercialization routes for the nanofiber electrode technology has signed an options agreement with Vanderbilt University. The PI gave numerous presentations and wrote papers on the DOE-supported research.

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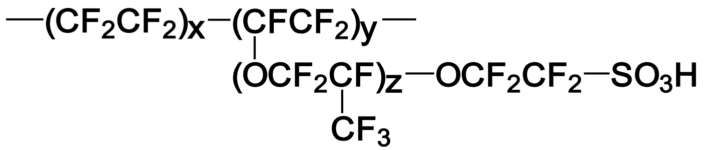
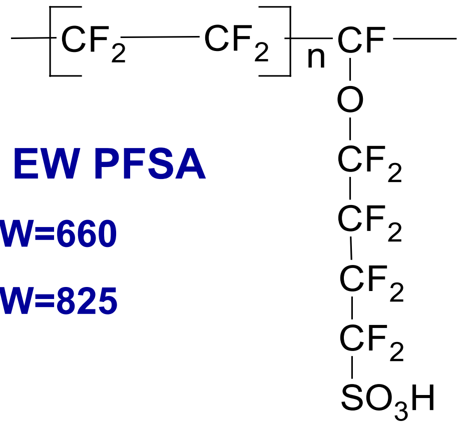
Project ID #FC038

Supplemental Slides

Polymer Components for the Nanofiber Membranes



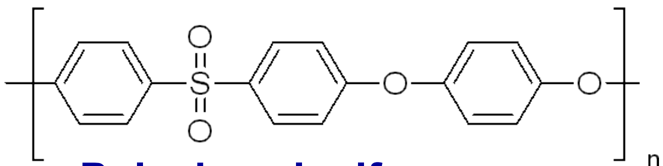
DuPont's Nafion®



3M's Low EW PFSA

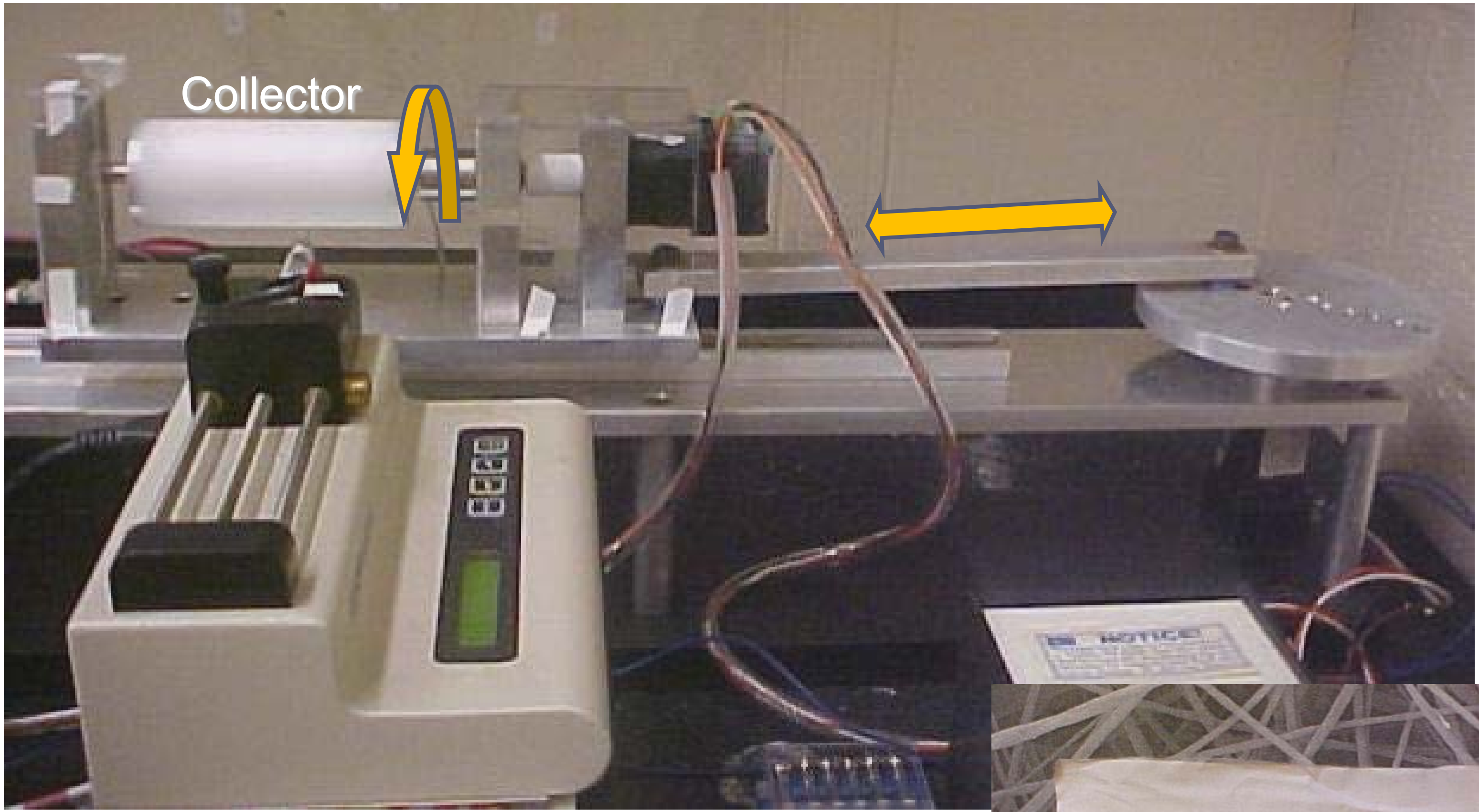
n=6.4 for EW=660

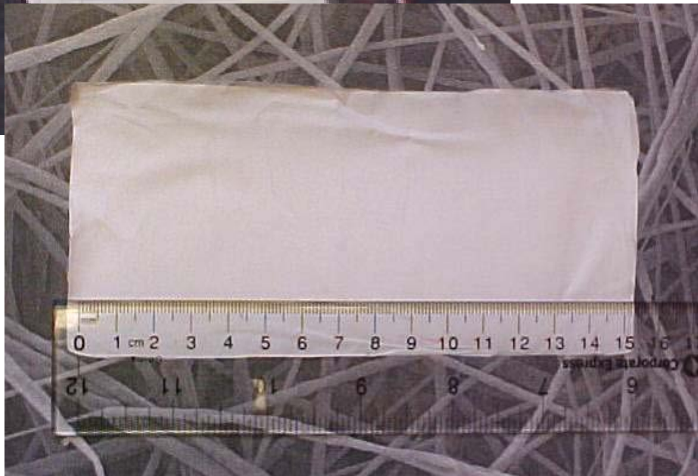
n=9.7 for EW=825



Polyphenylsulfone (PPSU)

Electrospinning – Rotating Drum Apparatus

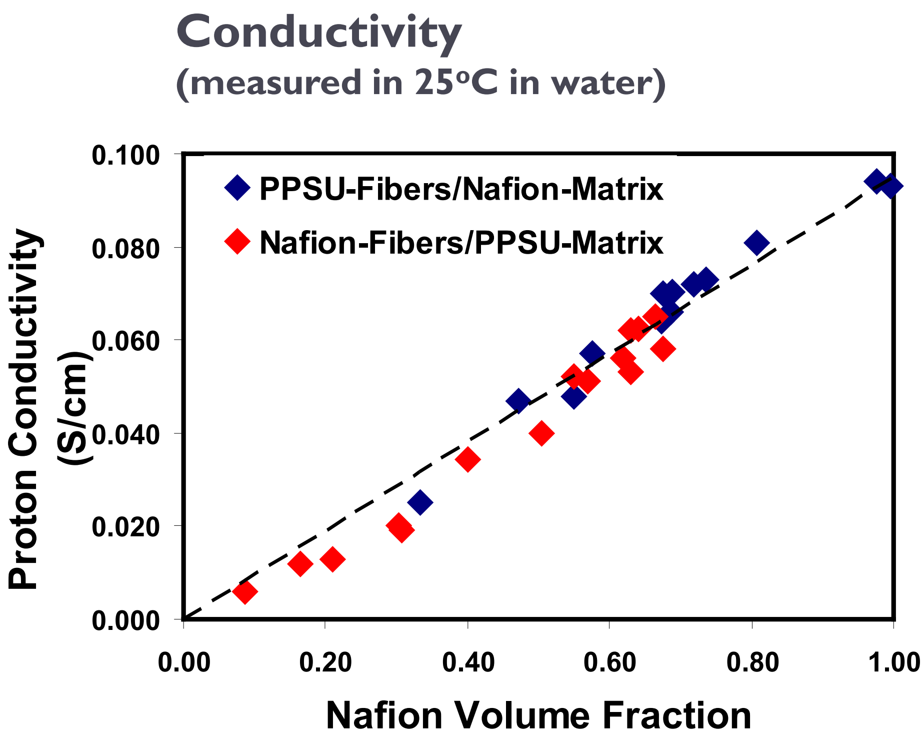


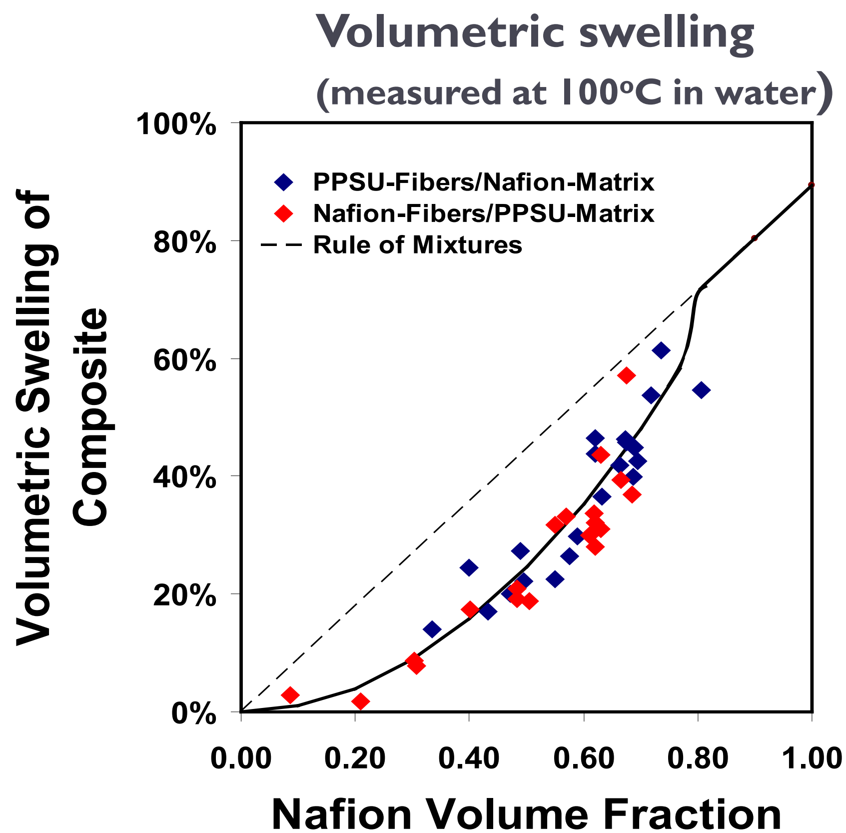


Uniform mats were made:

16 cm long, 10 cm wide and 10~120 μm thick

Conductivity and Volumetric Swelling: Nafion® with Polyphenylsulfone





- Conductivity can be predicted by a volume fraction Mixing Rule (dashed line, above)
- Electrospun membranes have an exceptionally low percolation threshold (≤ 9 vol% Nafion)

- Volumetric swelling is controlled by PPSU
- Volumetric swelling is lower than that predicted by a Mixing Rule.

Electrospinning Fuel Cell Catalyst into a Nanofiber Cathode

Prepare the Ink of Pt/C, Nafion and Polyacrylic Acid (PAA)

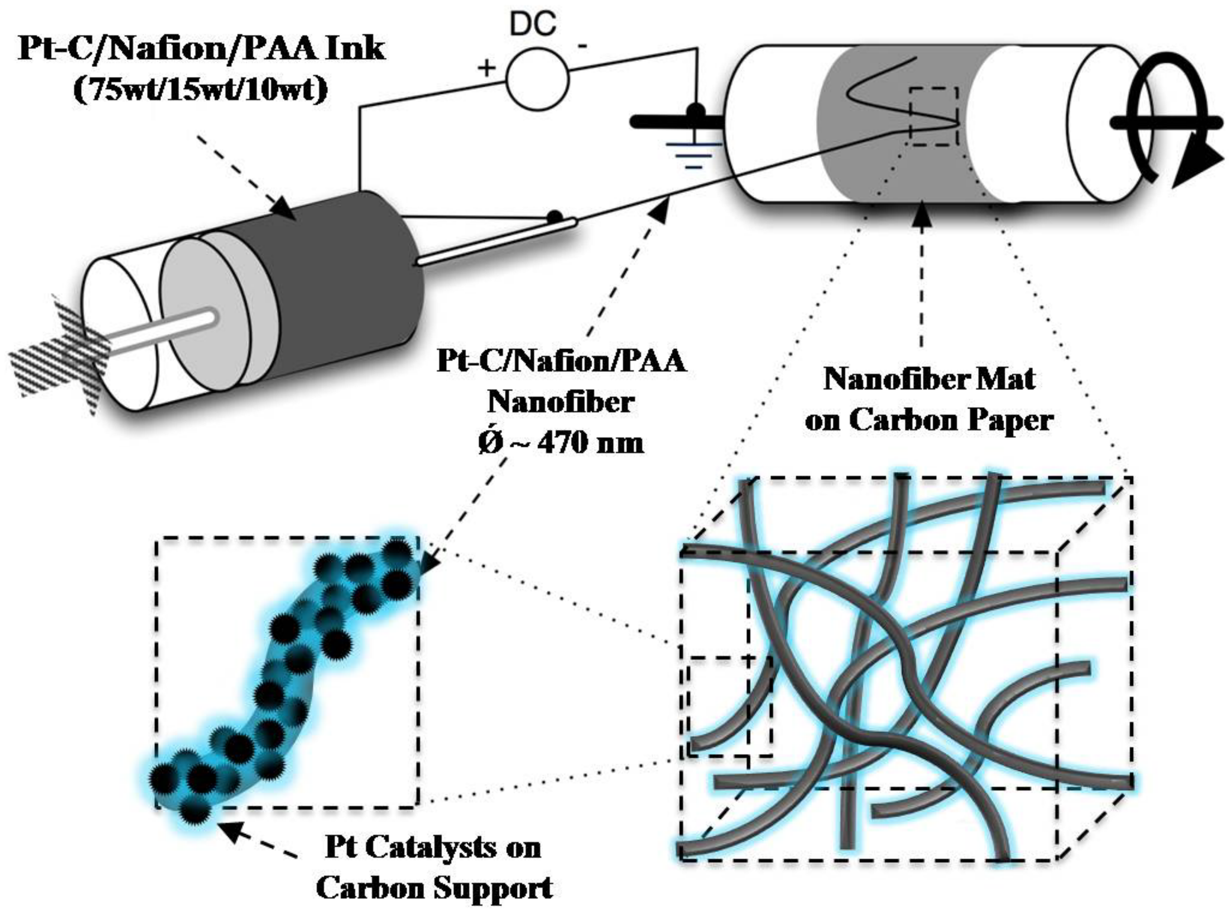
Electrospinning on Carbon Paper or Aluminum Foil

Anneal at 150°C

In Vacuum for 2h

Hot Press on PEM

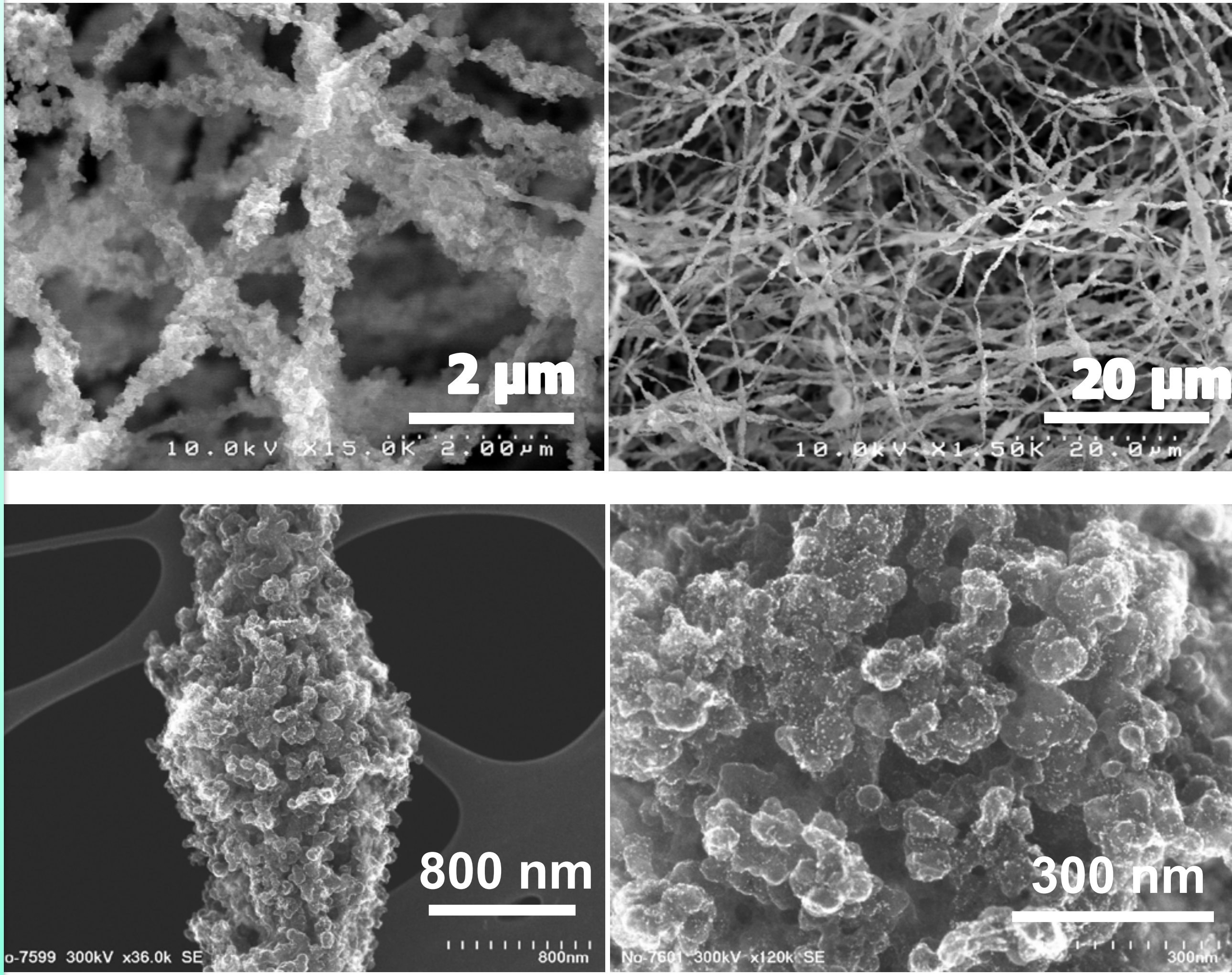
(Nafion 212)



Catalysts, proton conductive polymer, and electron-conductive pathways in one nanofiber

3-Dimensional Architecture of Nanofibers

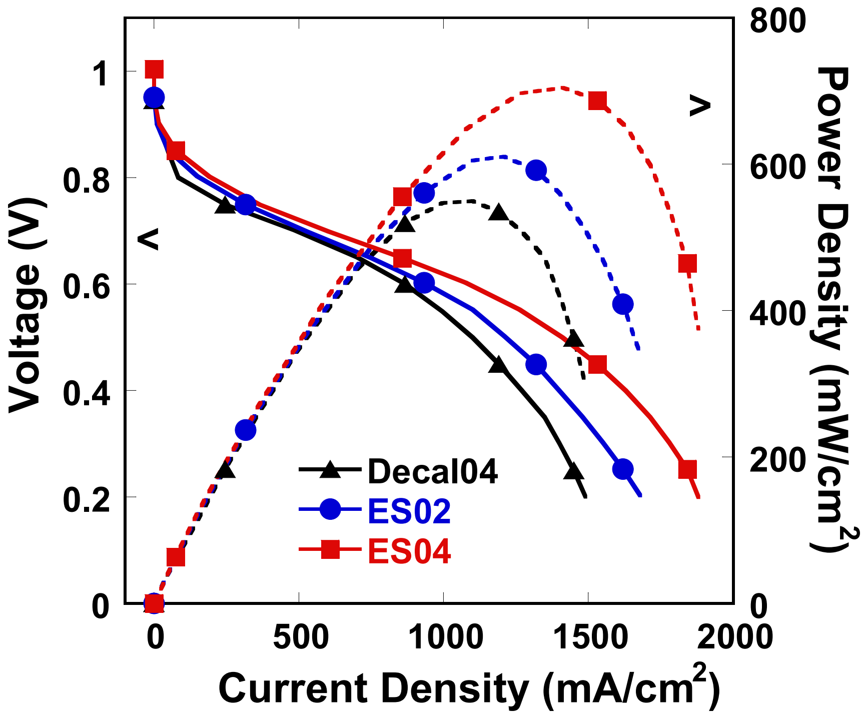
- Nanofibers with no beads an defects are roughened by Pt/C.
- Nanofiber architecture for improving accessibility of gas to Pt reaction sites
- High concentration of Pt/C catalysts (~70 wt%) insures high electron conductivity in the fibers.
- Sufficient Nafion® content (15 wt%) for proton conduction.
- SEMs courtesy of Dr. Karren More at Oak Ridge National Laboratory.

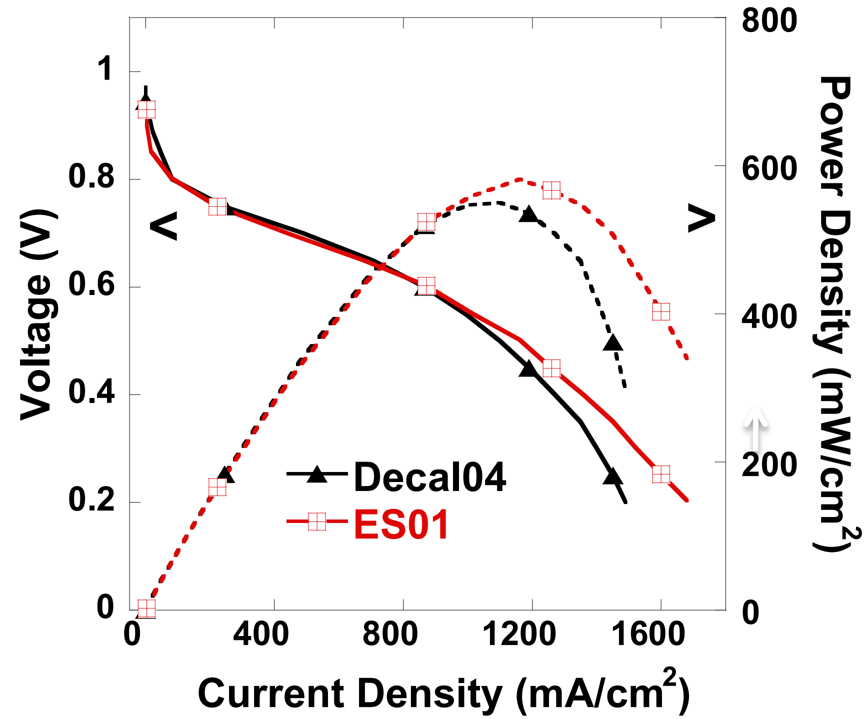


SEM images of nanofiber mat (top) and a single nanofiber (bottom)

4-fold Reduction in Pt-loading with No Loss in Performance

($5\ cm^2$ MEA; 80^oC; fully humidified H_2/air; no backpressure)

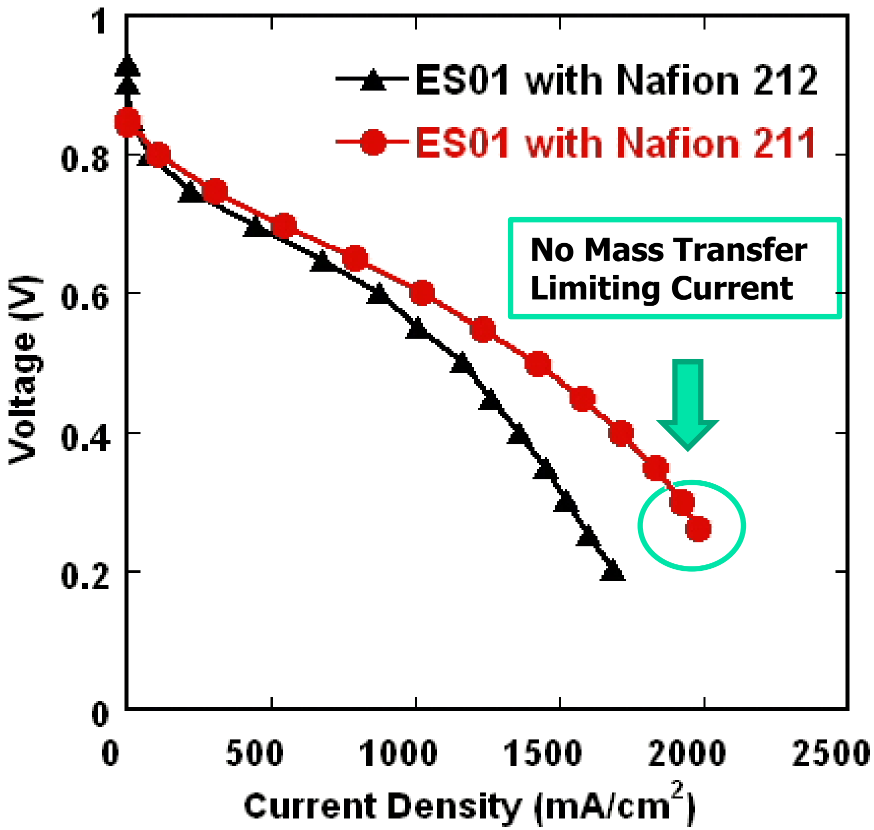


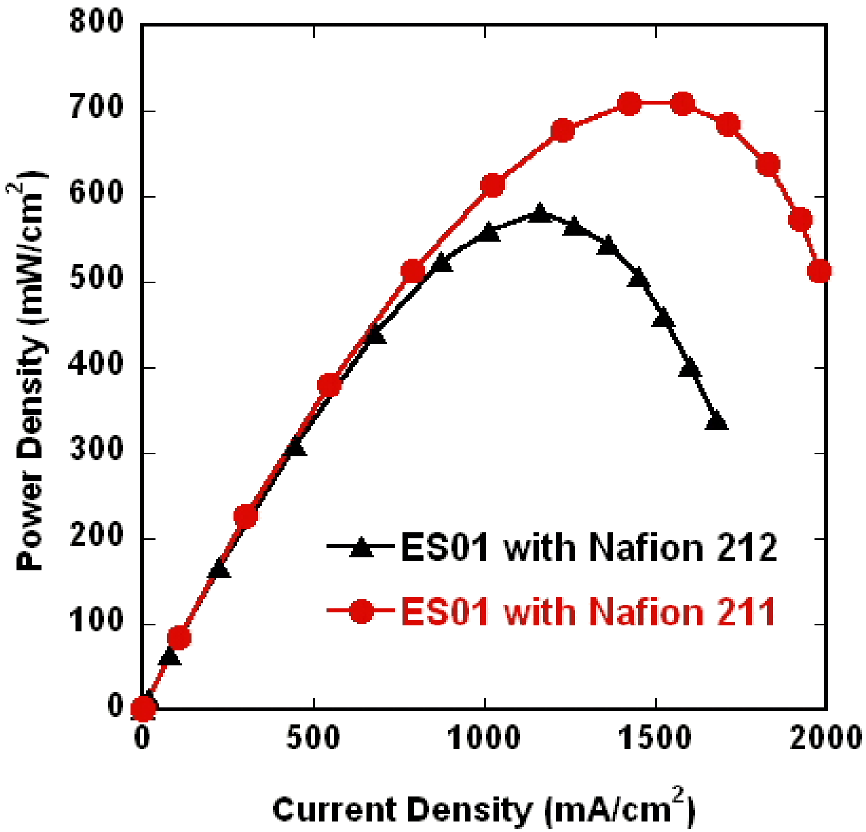


Cathode	Pt-loading (mg/cm^2)	Power Density @ 0.6V (mW/cm^2)	Mass Activity @0.9V (A/mg_{Pt})
Decal04	0.4	519	0.11
ES04	0.4	647	
ES02	0.2	561	
ES01	0.1	524	0.23

MEA with Nanofiber Cathode and Nafion® 211

(25 cm² MEA with Nafion® 211; 80°C; fully humidified H_2/air; No backpressure)





Membrane	Power Density at 0.6 V (mW/cm²)
Nafion 212	524
Nafion 211	613

- Non-optimized MEA
- No mass transfer limiting current out to 2 A/cm²
- No flooding even at high current densities
- Low IR drop (Nafion® 211 vs. Nafion® 212)