SCHOOL OF ENGINEERING
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Nanofiber Composite Proton Conducting Fuel Cell Membranes

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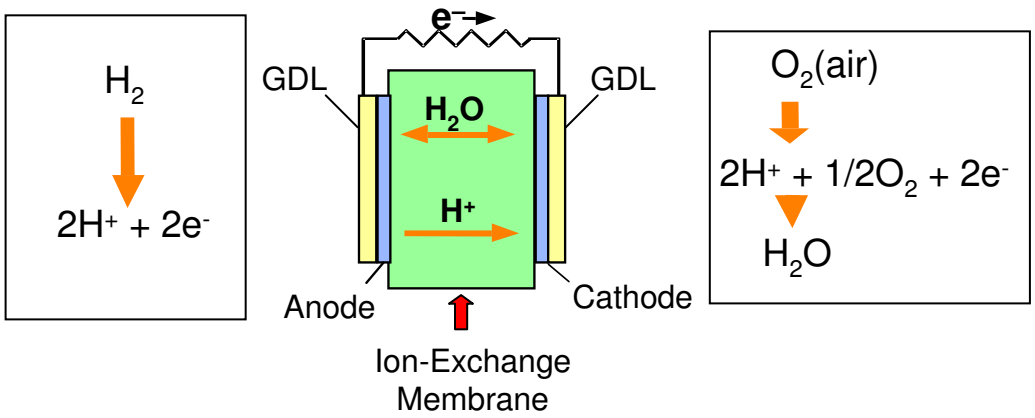
H_2-Air Proton-Exchange Membrane (PEM) Fuel Cell



$$2H_2 + O_2 \rightarrow 2H_2O$$

The Ideal Membrane:

- Low sheet resistance (high conductivity and very thin) at high and low T and humidity
- Low areal dimensional changes during membrane hydration and dehydration
- Mechanically robust with moderate volumetric swelling
- Low fuel and oxygen crossover

High conductivity requires a high membrane ion-exchange capacity

But: - Highly charged polymers swell excessively in water

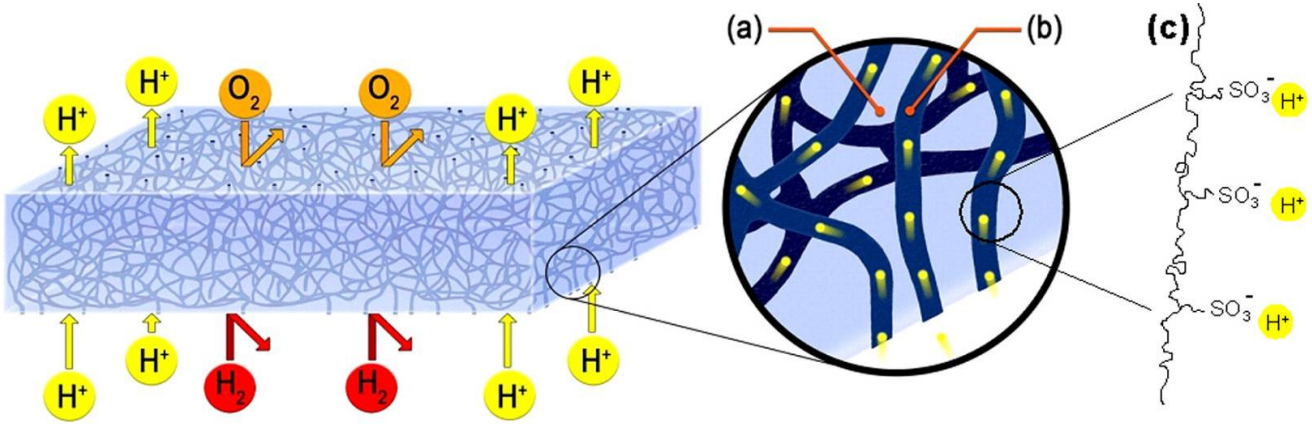
- High water swelling lowers the effective (volumetric) concentration of membrane fixed charge sites and decreases the membrane's mechanical properties

So: - A membrane composed of a single homopolymer will not work!

- Consider blends, block copolymers, and composites

Nanofiber Composite Membranes

1. Ionomer nanofibers surrounded by uncharged polymer.
2. Uncharged polymer nanofibers surrounded by (and reinforcing) an ionomer matrix.



(a) This "forced assembly" method allows for a wide choice of polymers for the ion conducting and uncharged phases (an alternative to blends and block copolymers)

(b) Intimate mixing of polymer components

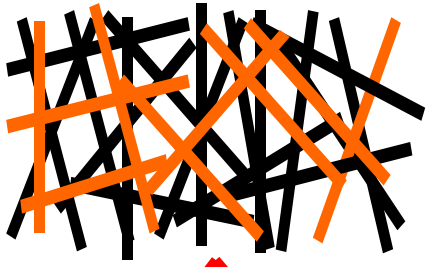
(c) Decouple mechanical and ion-conducting functions of the membrane.

(d) Control independently both the size and the loading of the ion-conducting phase.

(e) Membranes can be made without a polymer impregnation step.

Nanofiber Composite Membranes – Processing a Dual Fiber Mat

Simultaneously electrospin a dual fiber mat



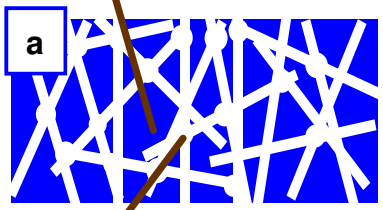
One fiber is a charged polymer (ionomer) like perfluorosulfonic acid (PFSA) and the second fiber is an uncharged/inert polymer (e.g., polyphenylsulfone)

Mat Processing

Method #1

"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

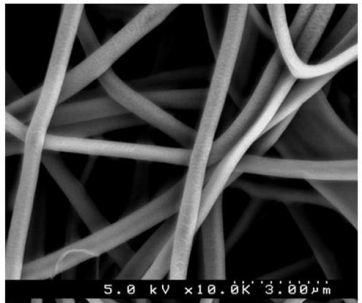
"Melt" ionomer around inert polymer nanofibers

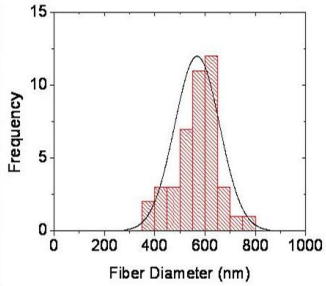
825 EW PFSA Nanofibers: Polymer Concentration Effect

1.21 mmol/g IEC PFSA from 3M Company

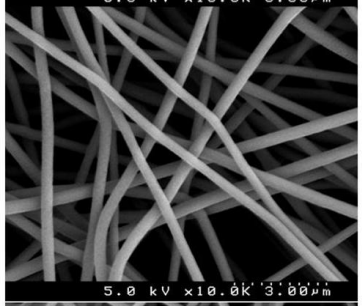
10 wt% solution

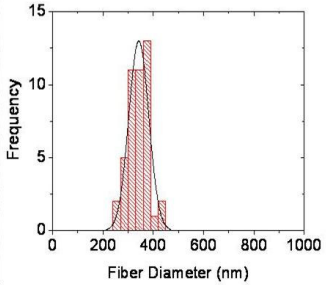
PFSA/PEO=75/25



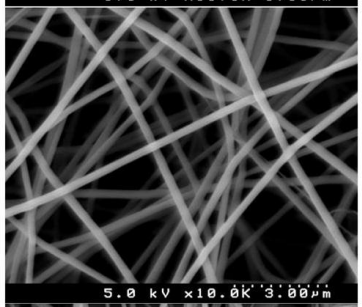


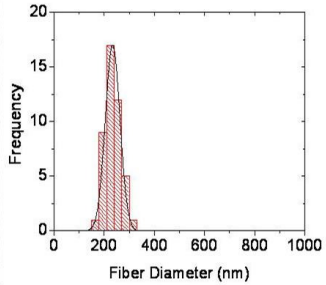
PFSA/PEO=90/10



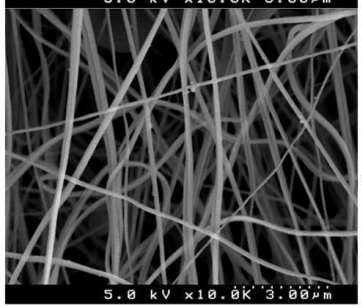


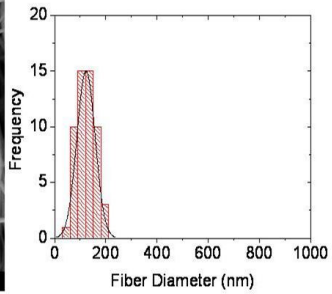
PFSA/PEO=95/5





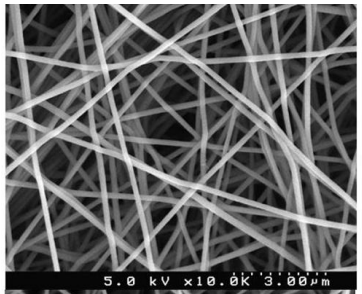
PFSA/PEO=99/1

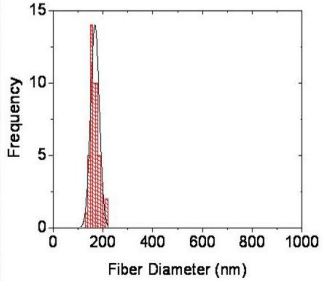




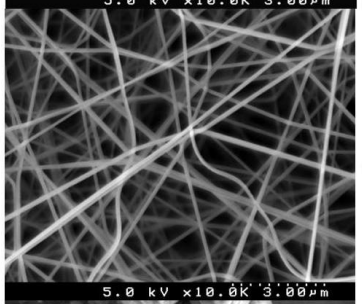
5 wt% solution

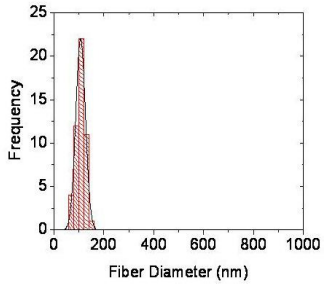
PFSA/PEO=90/10



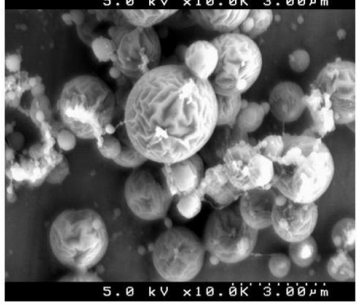


PFSA/PEO=95/5





PFSA/PEO=99/1



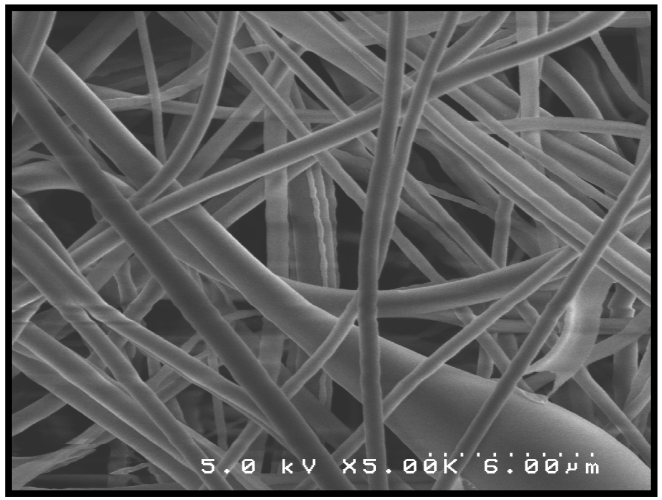
No Fiber Formed.

Converting a Dual Nanofiber Mat into a Composite Membrane: Nafion + Polyphenylsulfone

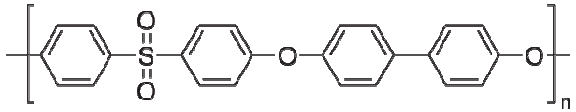
$$-(CF_2CF_2)_x-(CFCF_2)_y-$$
$$(OCF_2CF)_z-OCF_2CF_2-SO_3H$$
$$CF_3$$

Nafion softens/flows to fill inter-fiber voids

1) Hot Press (Compact) @ 6,000 psi and 127°C for 40 sec.
2) Anneal (5 min. at 210°C in vacuum)
3) Boil 5 min. in 1M H_2SO_4 and 5 min. in water



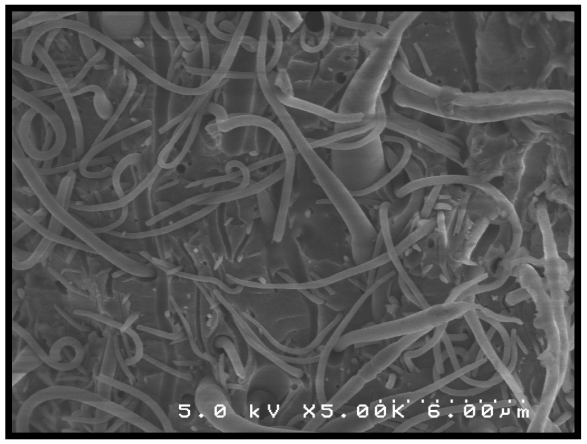
Dual Fiber Mat Surface



PPSU softens/flows to fill inter-fiber voids

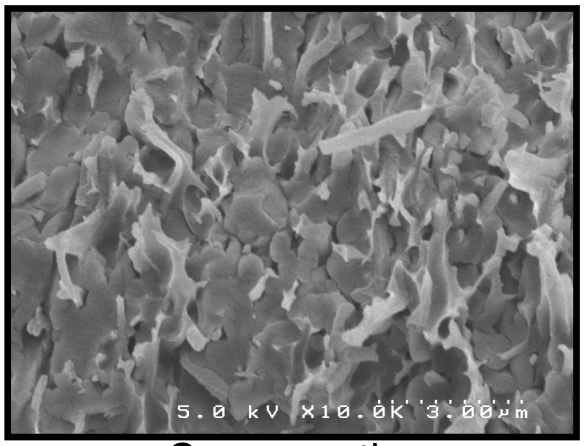
1) Cold Press (Compact) @ 1500 psi and 25°C for 10 sec.
2) Expose to chloroform vapor for 3 min. at 50°C
3) Anneal (5 min at 210°C in vacuum)
4) Boil 5 min. in 1M H_2SO_4 and 5 min. in water

Nafion with PPSU fibers

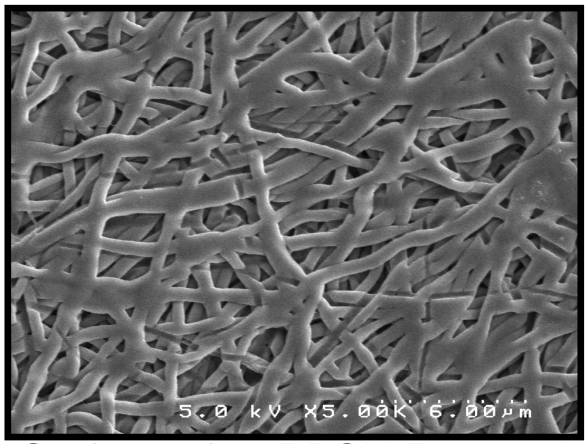


Cross-section

PPSU with Nafion fibers



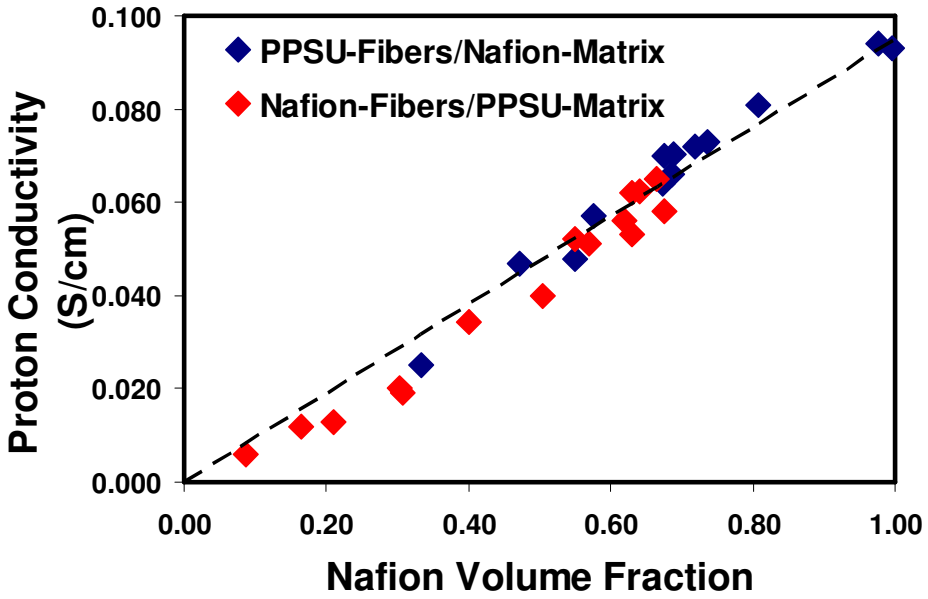
Cross-section



Surface after PPSU Removal

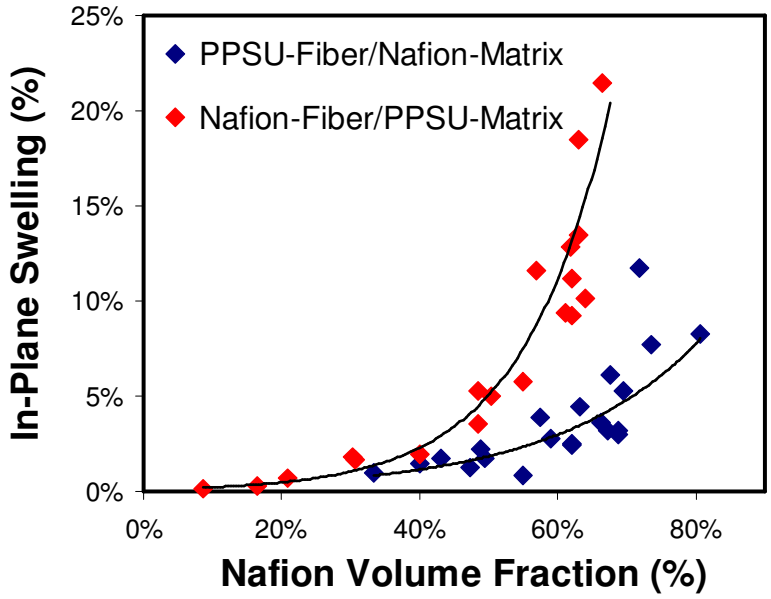
Conductivity and Volumetric Swelling: Nafion + Polyphenylsulfone

On-plane conductivity
(measured in 25°C in water)



- 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 of nanofiber composite membranes in water also obeys a simple Nafion volume fraction mixing rule.

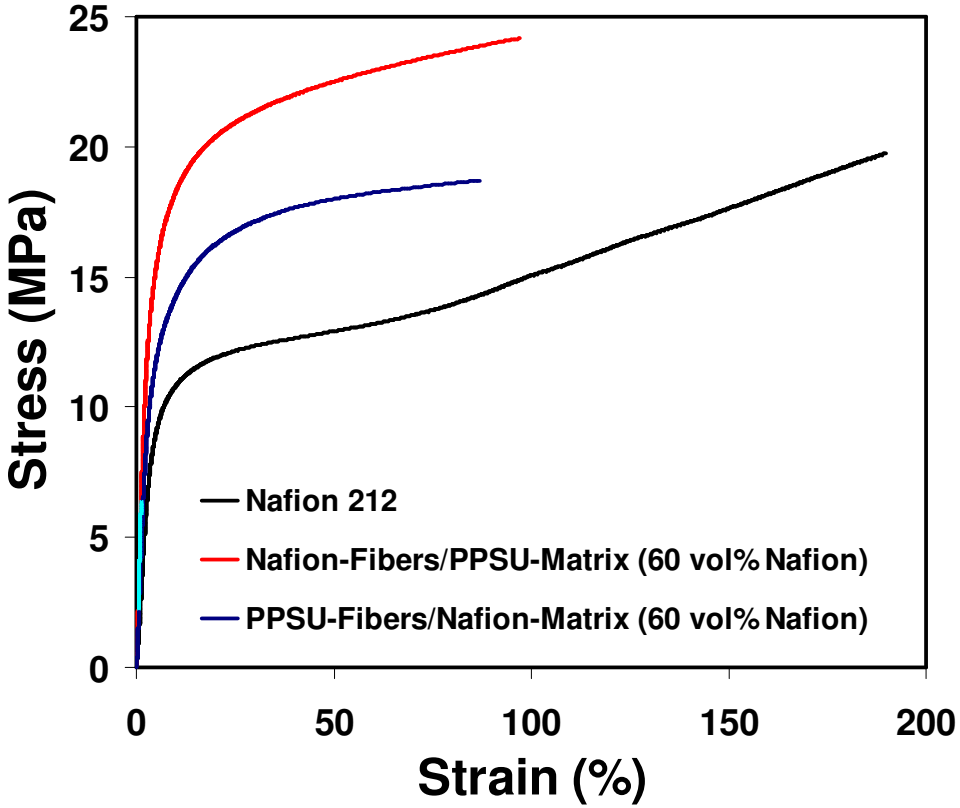
In-Plane volumetric swelling
(measured at 100°C in water)



- Both membrane structures have the same volumetric swelling for a given Nafion volume fraction (swelling is lower than predicted by a mixing rule).
- PPSU-fiber/Nafion-matrix has lower in-plane swelling.
- Higher thickness swelling for Nafion fiber membrane (3-D PPSU connectivity creates isotropic swelling)

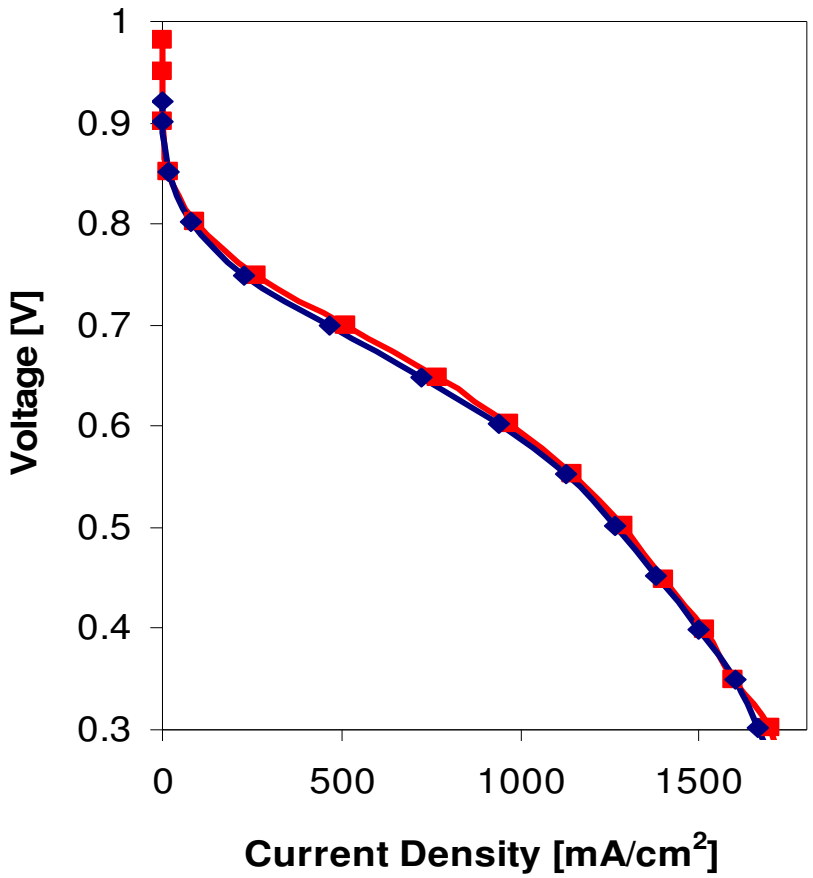
Mechanical Properties: Nafion + Polyphenylsulfone

Stress-strain curves at 30°C, ~20% RH



- **PPSU improves mechanical properties of composite membranes**
- **Nafion-fiber/PPSU-matrix has best mechanical properties (3-D PPSU connectivity)**

H_2-Air Fuel Cell Performance – Nafion with a PPSU Reinforcing Mat



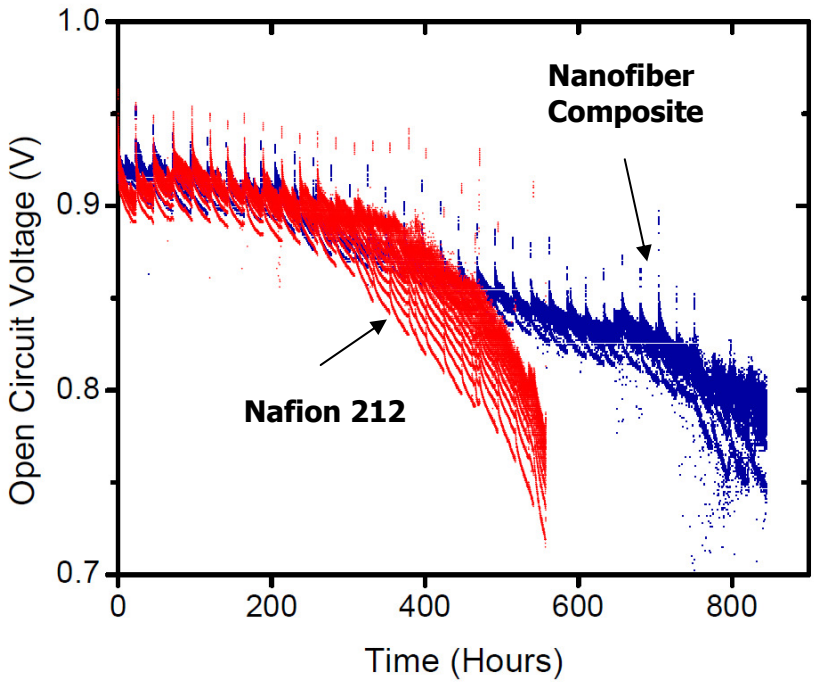
- 80°C, 100% RH
- Anode and Cathode: 0.4 mg/cm^2 Pt loading with 30% Nafion binder content

Nafion 212 (51 µm)

Nanofiber composite (30 µm dry thickness; Nafion with a PPSU nanofiber reinforcement mat; (~60 vol% Nafion)

Use thinner films in a membrane-electrode-assembly to compensate for the lower conductivity of a nanofiber composite membrane

H_2/Air Fuel Cell Durability Test (at Open Circuit Voltage)



- 25 cm^2 MEA
- 80°C, 100% RH
- Anode and Cathode: 0.4 mg/cm^2 Pt loading with 30% Nafion binder content

Nafion 212 (51 µm)

Nanofiber composite membrane – Nafion polymer with a PPSU reinforcement mat (dry membrane thickness - 30 µm)

- Cycling: 2 minutes 100% RH H_2/Air, 2 minutes 0% RH H_2/Air. 25 cm^2 cell, 125 mL/min H_2, 500 mL/min air flow rates,

- **Nafion 212 failed after 546 hours**
- **The Nanofiber Composite Membrane failed after 842 hour (a 54% increase in lifetime)**

Composite Membrane Fabrication with 660EW PFSA

	3M 660 EW	Polyphenylsulfone (PPSU)
Polymer Comp.	99.7:0.3, 660EW:PEO (30 wt% total polymer)	25 wt%
Solvent	n-propanol:water in 2:1 wt. ratio	DMAc:acetone in 8:2 wt. ratio
Voltage	7.0 kV	7.5 kV
SCD	5.5 cm	8.5 cm
Flow Rate	0.40 mL/hr	0.10 mL/hr

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

1)Dual-fiber Electrospinning 3M660/PEO and PPSU

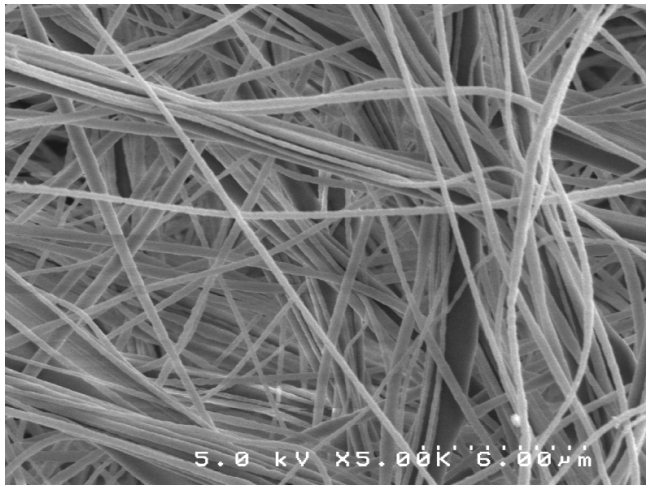
2)Compress to 6000 psi at 127°C

3)Anneal 2 hours at 150°C in vacuum

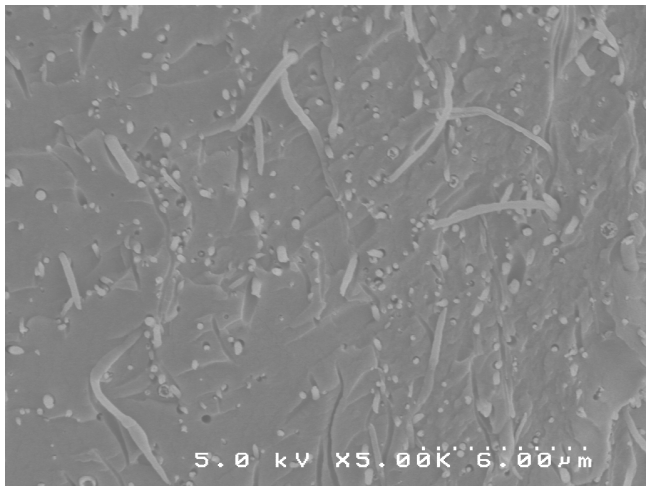
4)Soak in 1M H_2SO_4 for 16 hours at 23°C

5)Soak in water for 6 hours at 23°C (replacing with fresh water periodically)

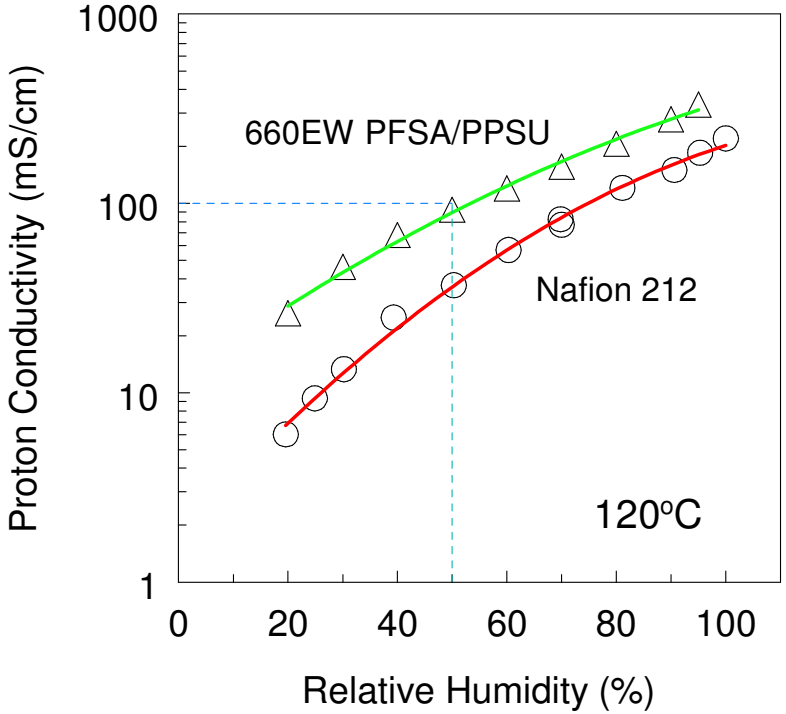
Surface of Dual-fiber Electrospun Mat



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



In-Plane Proton Conductivity and Swelling



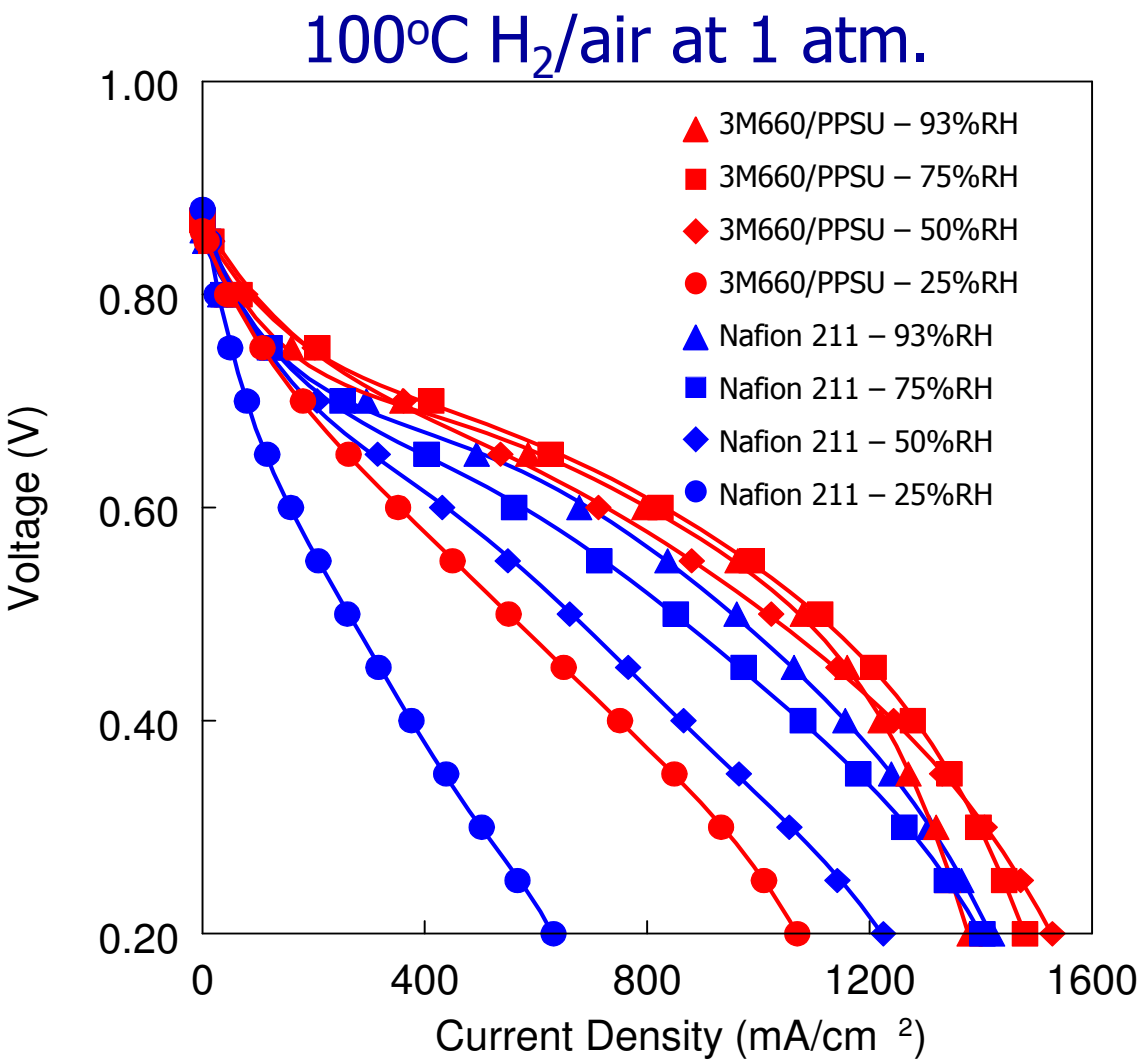
- 3M660/PPSU : 70 vol% 3M660 and 30 vol% PPSU fibers (54 μm thick)
- Nafion 212 is a commercial film from DuPont (51 μm thick)

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 in-plane 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 number of waters per sulfonic acid group.

Fuel Cell Performance – 660EW Nanofiber Membranes



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)
- Nanofiber composite MEAs prepared at 3M Company

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 (43 μm thick). 0.25 mg_{Pt}/cm^2 with 3M825 EW binder

Conclusions

- An entirely new membrane fabrication scheme has been developed.
- A dual fiber electrospinning method requires no polymer impregnation steps for membrane fabrication.
    - PFSA nanofibers surrounded by inert polymer (polyphenylsulfone)
    - Inert polymer (polyphenylsulfone) nanofibers surrounded by PFSA
- A nanofiber composite membrane (Nafion polymer with reinforcing polyphenylsulfone nanofibers; 30 μm in thickness) was processed into a hydrogen/air fuel cell MEA.
    - Power densities at 80°C and full humidification matched those of commercial Nafion 212
    - Nanofiber composite membrane exhibited superior durability during RH cycling (~50% improvement over Nafion 212)
- 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°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°C and 120°C.

Acknowledgements

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  - Jason Ballengee (current Ph.D. student)
  - Dr. Ryszard Wycisk (Research Associate Professor)
  - Dr. Jon Choi (former Ph.D. student)
- Thanks to Steve Hamrock and 3M Company for providing PFSA polymers and for preparing MEAs with 660 EW PFSA membranes.