U.S. DEPARTMENT OF ENERGY

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

Electrospinning Fuel Cell Membranes and Electrodes to Improve Activity and Durability

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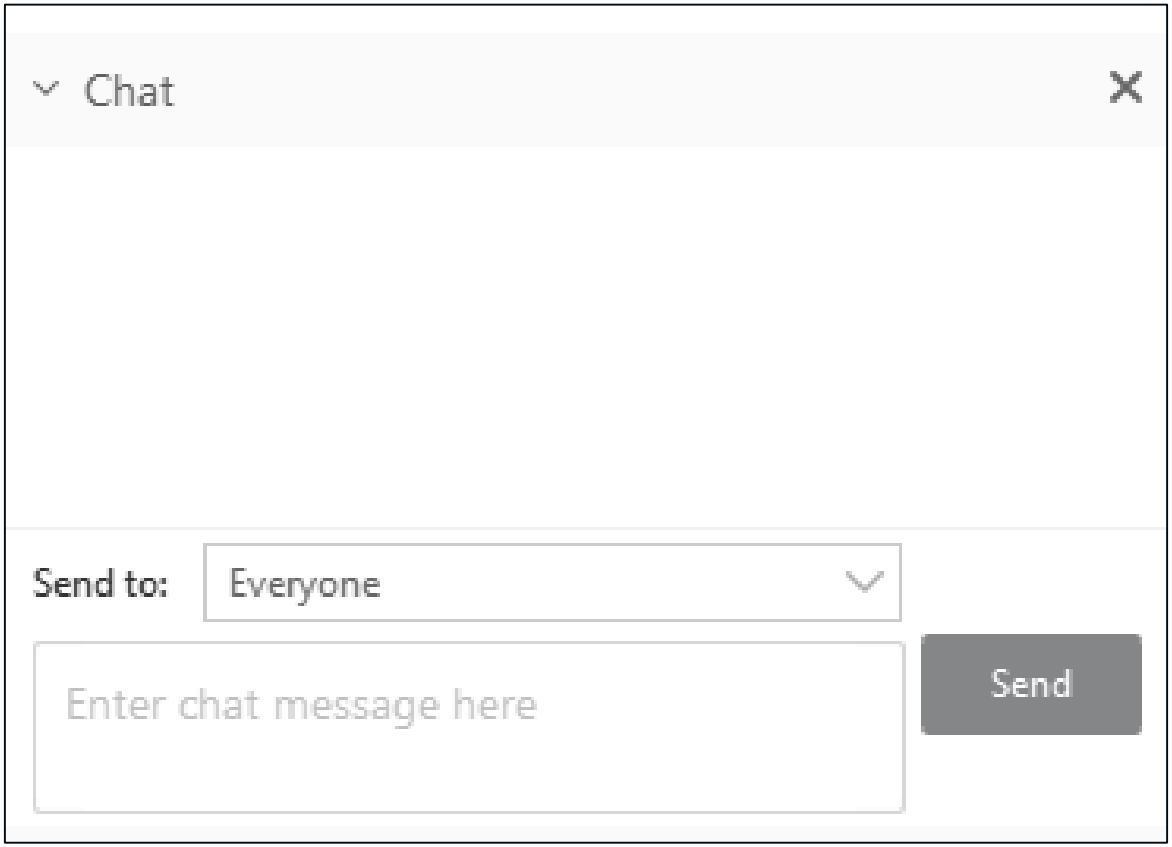
Fuel Cell Technologies Office Webinar

March 28, 2018

Question and Answer

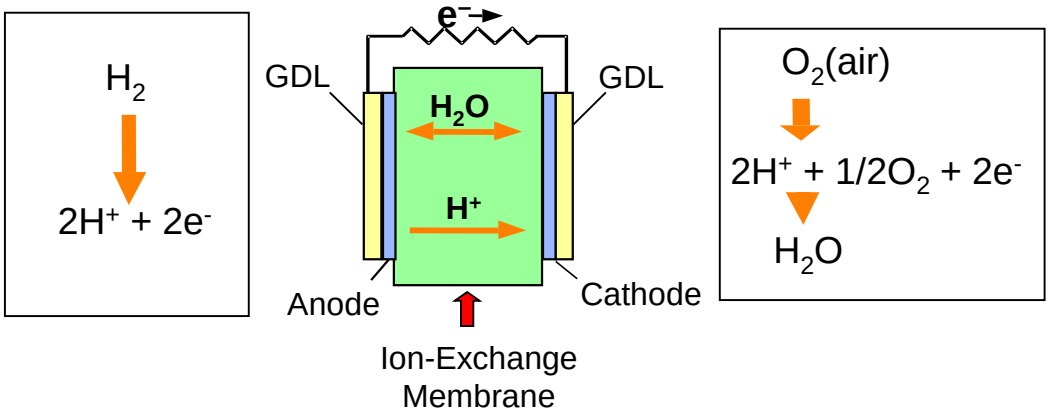
- Please type your questions to the chat box. **Send to: (HOST)**



Webinar Outline

- Nanofiber Composite Fuel Cell Membranes
  - The ideal membrane for a hydrogen/air PEM fuel cell
  - Introduction to polymer fiber electrospinning; Needle and needle-less electrospinning
  - Composite films made by dual nanofiber electrospinning
    - Fabrication method with Nafion® and polyphenylsulfone
    - Physical properties and fuel cell durability tests
    - Other nanofiber-based membranes for fuel cells
- Particle/polymer nanofiber mat electrodes for fuel cell membrane-electrode-assemblies
  - Why electrospin fiber mat electrodes?
  - Fabricating fiber electrodes
    - Preparation of ink and method of electrospinning
    - Physical structure of the fibers
  - Performance of fiber mat MEAs in a hydrogen/air fuel cell
    - Power output
    - Cathode durability
    - The use of different binders
- Future Challenges, Acknowledgements, and References

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



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

The Ideal Membrane:

- Low sheet resistance (thickness/conductivity), so membrane should be thin with a high conductivity.
- Low areal dimensional changes during membrane hydration and dehydration
- Mechanically strong with moderate volumetric swelling
- Low fuel and oxygen crossover

But:

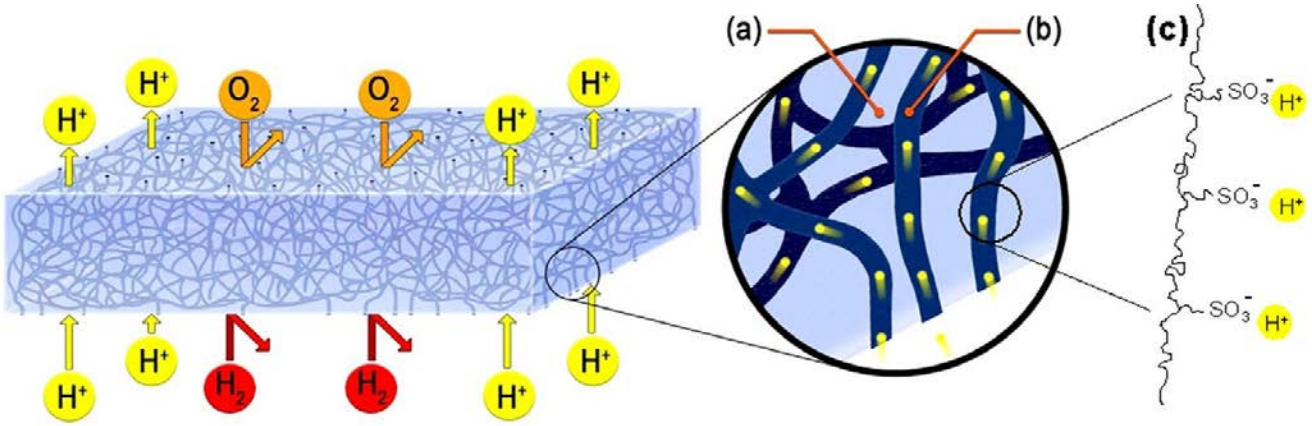
- High conductivity requires high membrane ion-exchange capacity
- Highly charged polymers swell greatly in water
- High water swelling will lower the effective (volumetric) concentration of membrane fixed charge sites and weaken the membrane mechanical properties.

Thus:

- A membrane composed of a single homopolymer may not work.
- Consider blends, block copolymers, and composites
- Consider polymer crosslinking or increasing the degree of polymer crystallinity

Nanofiber Composite Membranes

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



These two membrane structures are created by simultaneously electrospinning nanofibers of ionomer and uncharged polymer.

(a) This "forced assembly" method of creating a polymer mixture, which allows for a wide choice of polymers for the ion conduction and inert (uncharged) polymers.

(b) Intimate mixing of polymer components

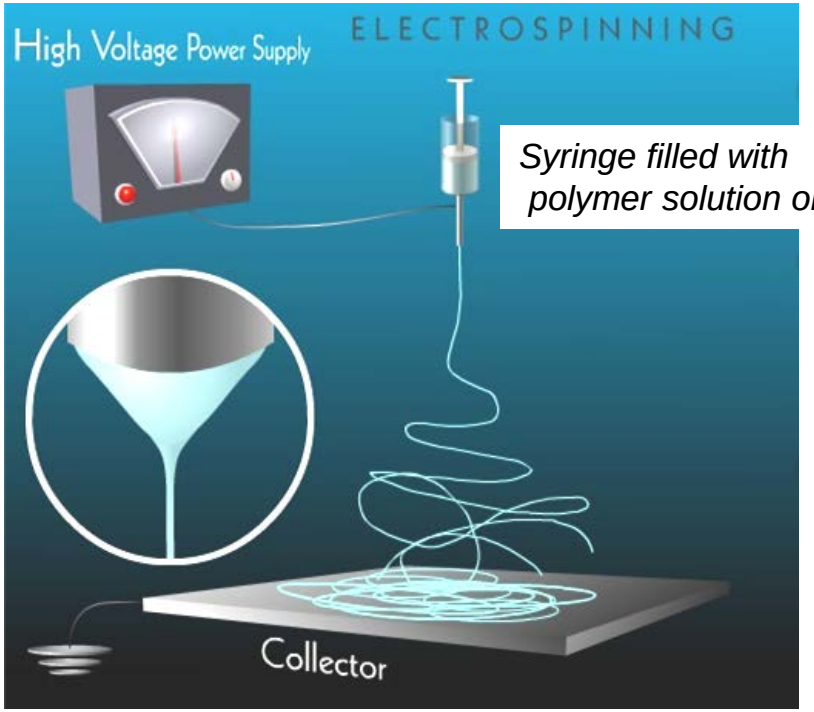
(c) Decouple mechanical and proton-conducting functions of the membrane.

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

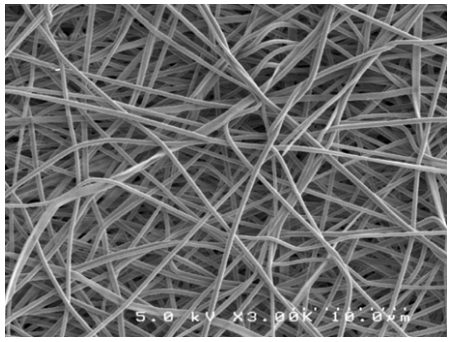
(e) Eliminate the need for a separate polymer impregnation step.

Nanofiber Electrospinning

Brief history: Cooley, Morton (1902) and Prof. Darrell Reneker, Univ. of Akron (1995)



www.nano.mtu.edu/Electrospinning_start.html

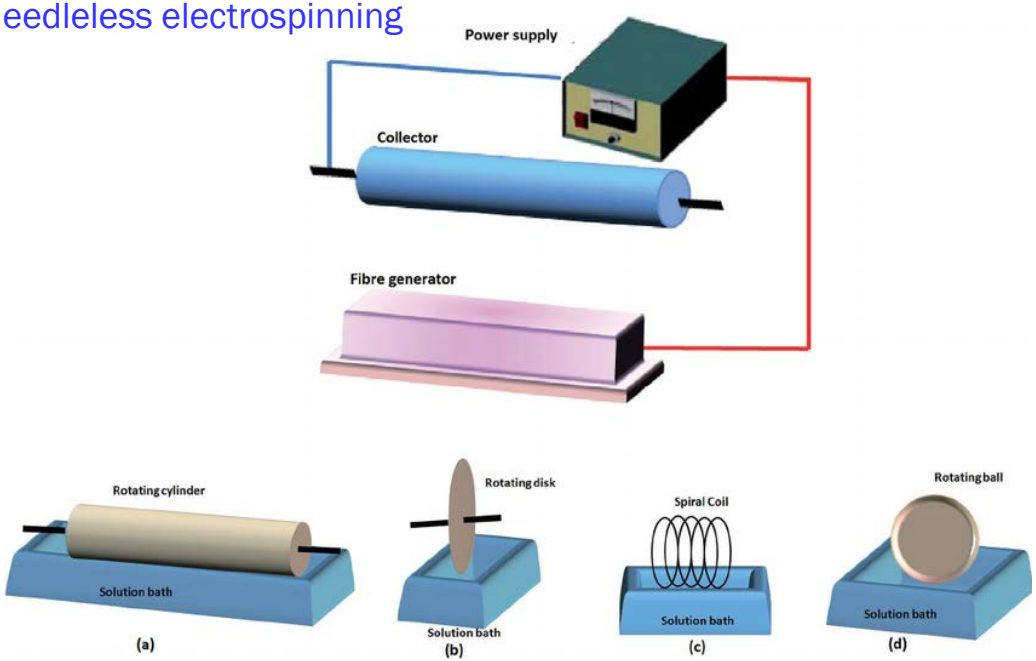


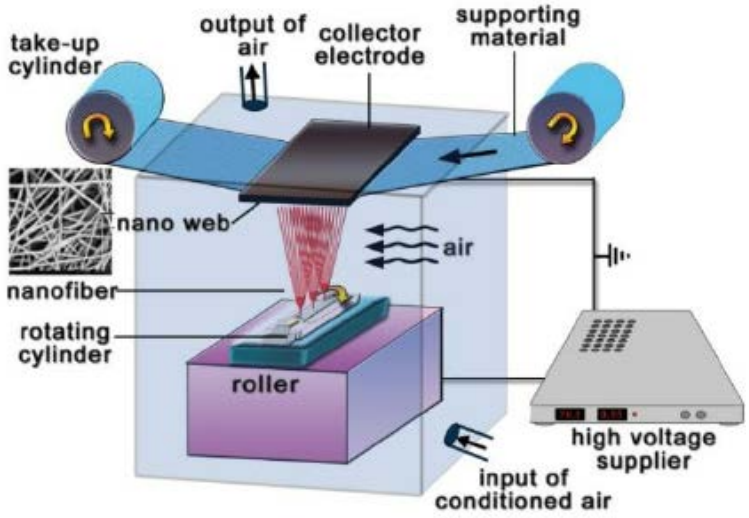
Process Variables:

1) Concentration of polymer in solution (there must be interchain polymer entanglements)
2) Applied voltage
3) Syringe-to-collector distance
4) Solution flow rate
5) Humidity
6) Solvent type: evaporation rate, conductivity.

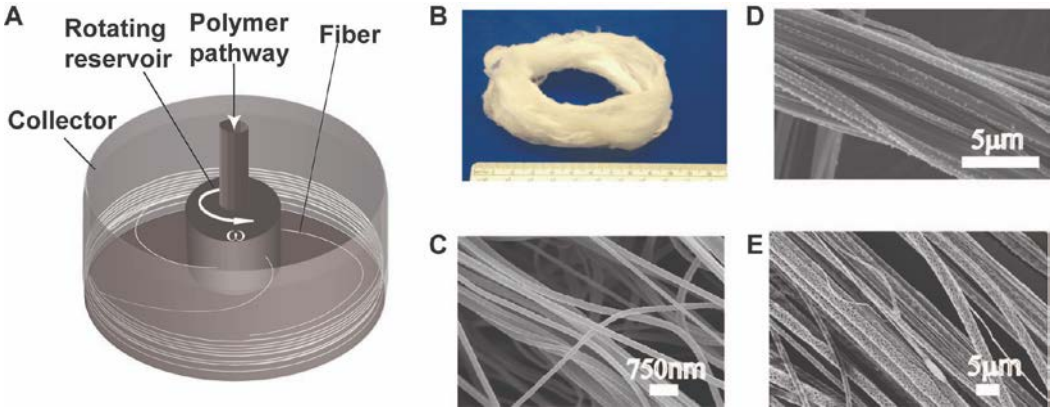
Needleless and Centrifugal Electrospinning

Needleless electrospinning

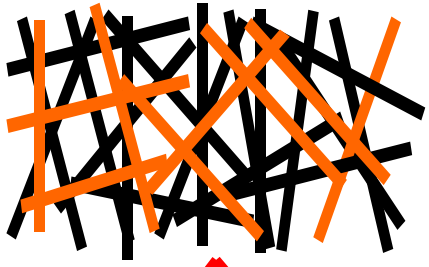




Centrifugal (rotary jet) electrospinning



Creating a Nanofiber Composite Membrane by Dual Fiber Electrospinning

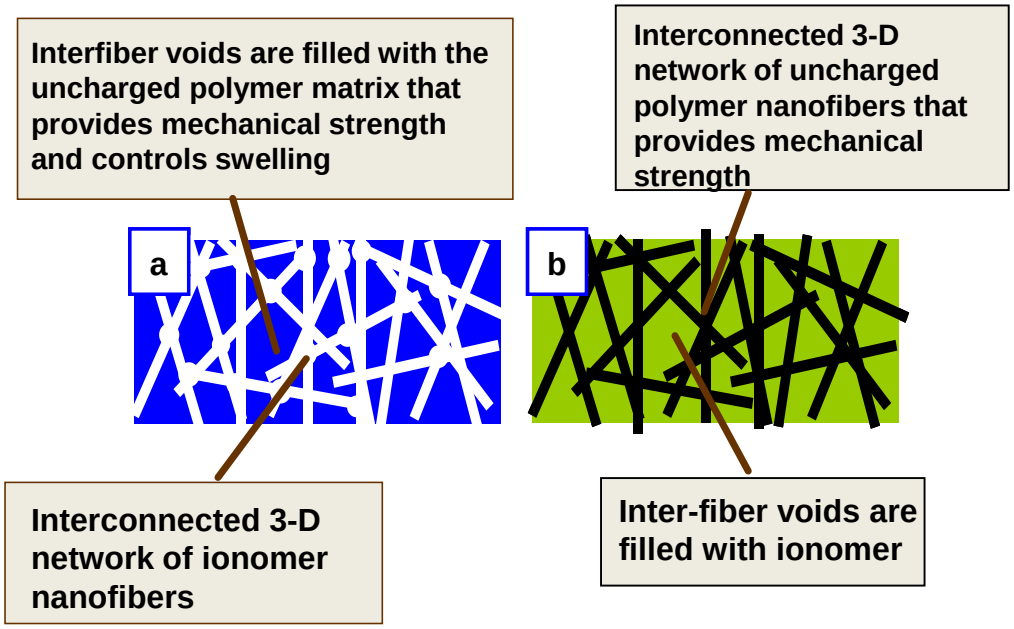


Simultaneously electrospin a dual fiber mat – one fiber is the ionomer (e.g., PFSA) and the second fiber is an uncharged/inert polymer (e.g., polyphenylsulfone)

Mat Processing

Method #1

"Melt" uncharged polymer around ionomer nanofibers



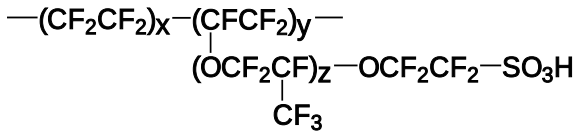
Method #2

"Melt" ionomer around uncharged polymer nanofibers

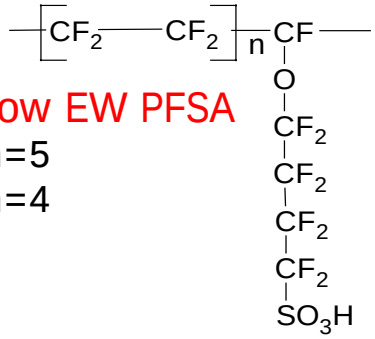
General Experimental Procedures

- Prepare an electrospinning solution (polymer and solvent)
- We must add a carrier polymer when spinning PFSA ionomers like Nafion®
- Identify the electrospinning conditions and solution composition that yields well-formed fibers (e.g., no beads)
- Process the fiber mat into a dense and defect-free membrane

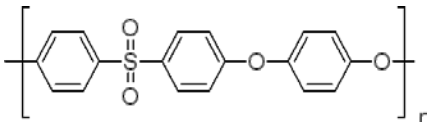
Possible polymers (ionomers for proton transport and uncharged polymers for reinforcement):



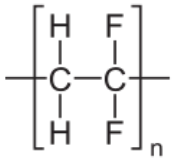
DuPont's Nafion®



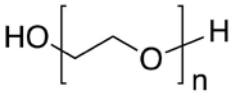
3M Co. low EW PFSA
825EW: n=5
733EW: n=4



Polyphenylsulfone (PPSU)

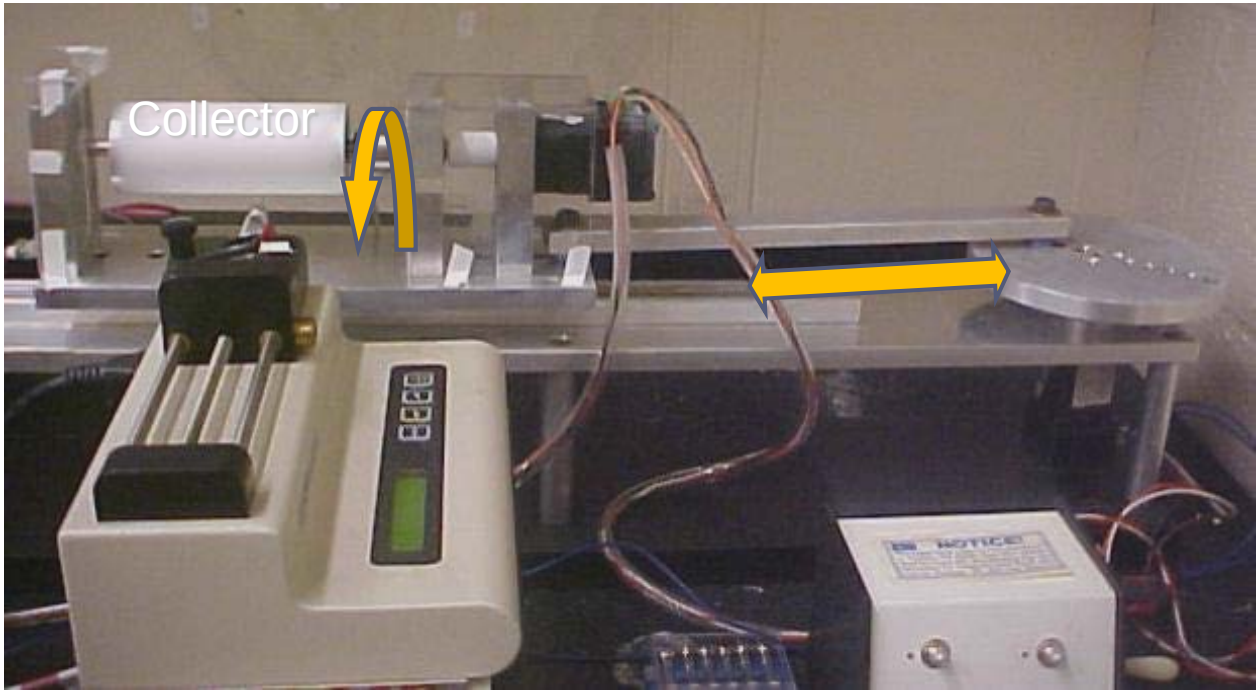


Poly(vinylidene fluoride) (PVDF)

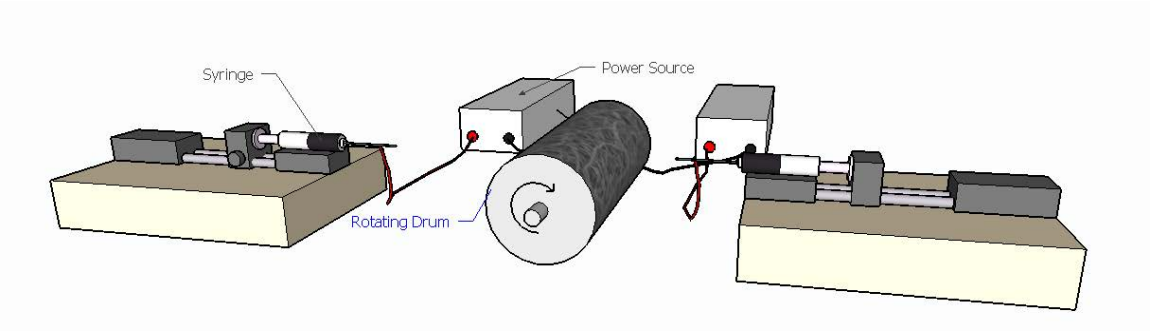


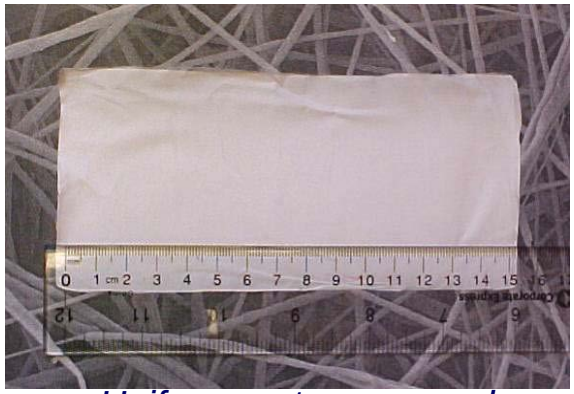
Poly(ethylene oxide) (PEO) – carrier polymer for PFSA

Electrospinning – Rotating Drum Apparatus



Dual fiber electrospinning:





Uniform mats were made:
16 cm long, 10 cm wide; 10~120 μm thick

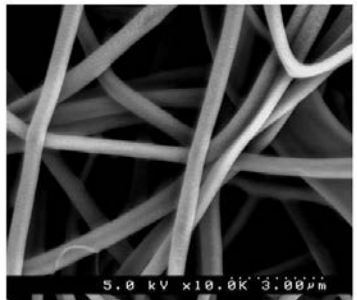
Examples of Electrospun PFSA Fibers with 825 EW PFSA and PEO as the Carrier Polymer

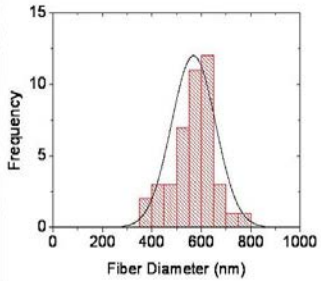
1.21 mmol/g IEC PFSA polymer from 3M Corp.

10 wt% solution

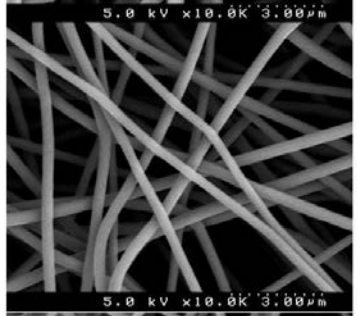
5 wt% solution

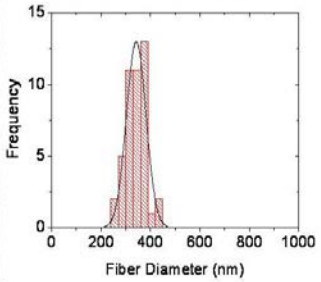
PFSA/PEO=75/25



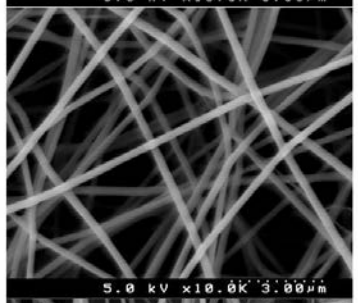


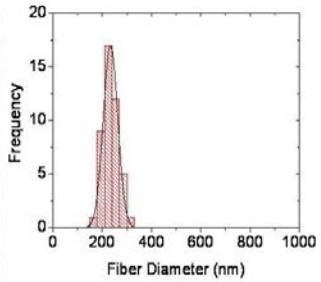
PFSA/PEO=90/10



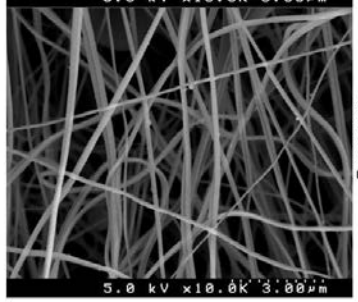


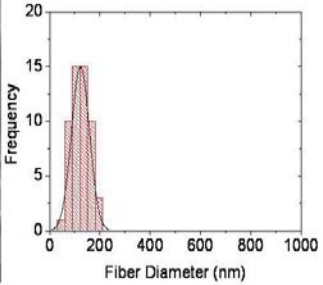
PFSA/PEO=95/5



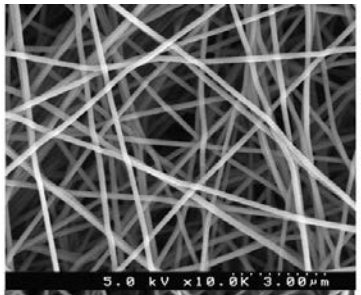


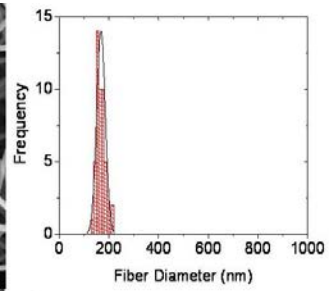
PFSA/PEO=99/1



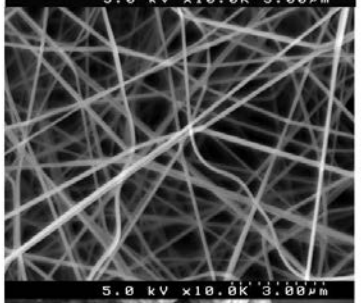


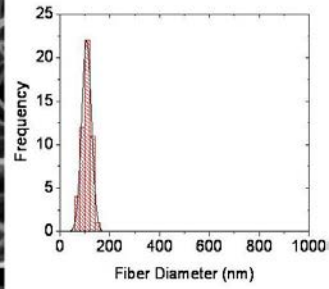
PFSA/PEO=90/10



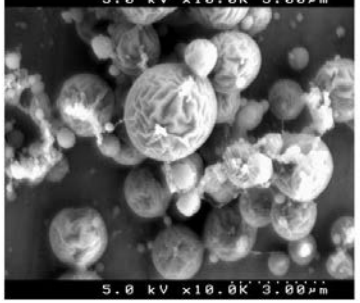


PFSA/PEO=95/5



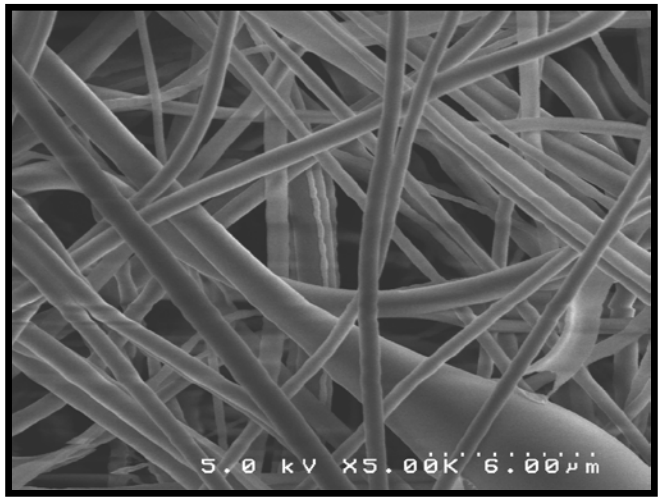


PFSA/PEO=99/1



No Fiber Formed.

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



Dual Fiber Mat Surface

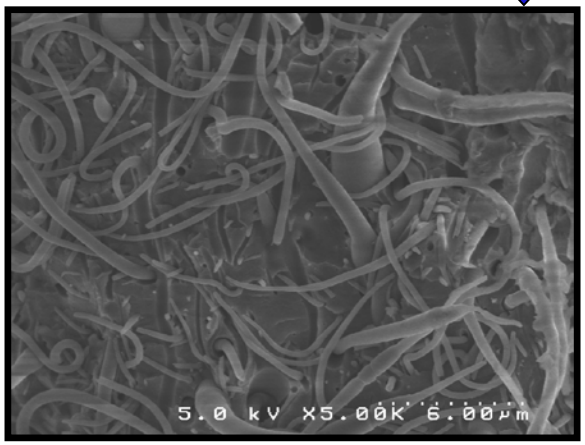
Nafion softens/flows to fill inter-fiber voids

1) Hot Press (Compact) @ 6,000 psi at 127°C, 4x 10 sec. presses
2) Anneal (150°C for 2 hrs in vacuum)
3) Boil in 1M Sulfuric Acid
4) Boil in Water

PPSU flows to fill inter-fiber voids

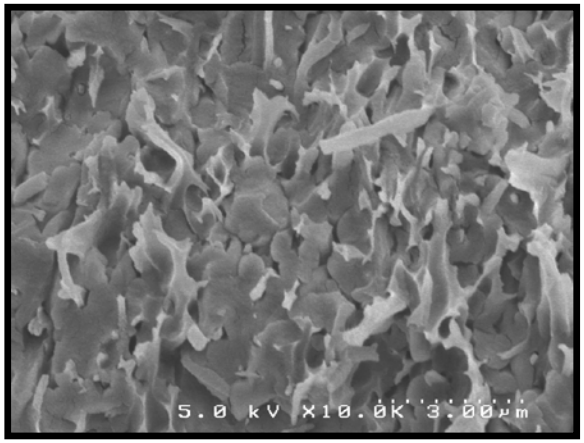
1) Cold Press (Compact) @ 1500 psi at RT, 4x 5 sec. presses
2) Chloroform Vapor Exposure (16 min. at RT)
3) Anneal (150°C for 2 hrs in vacuum)
4) Boil in 1M Sulfuric Acid
5) Boil in Water

Nafion with PPSU fibers

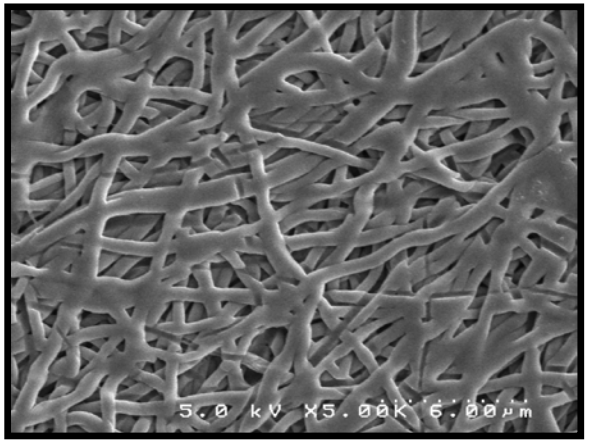


Cross-section

PPSU with Nafion fibers



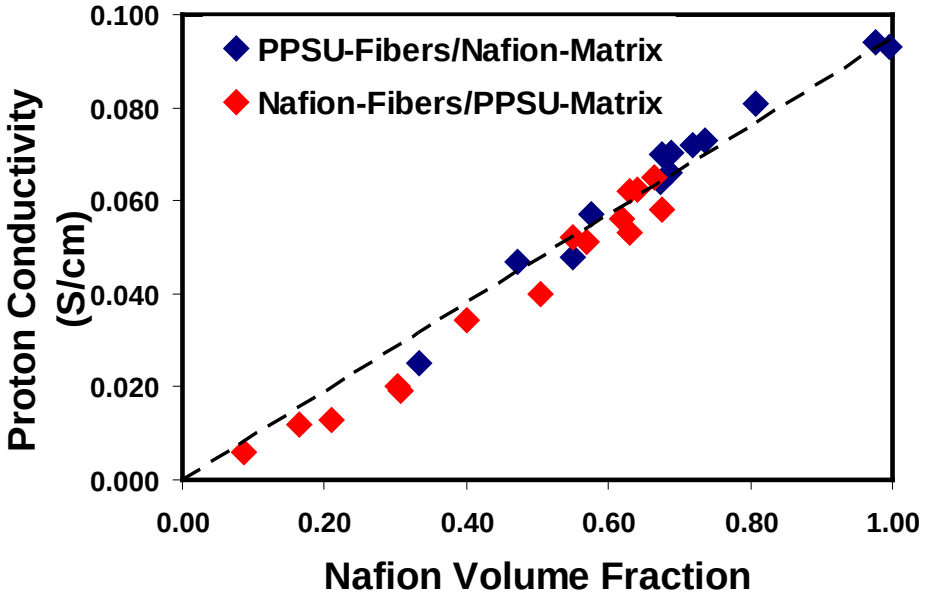
Cross-section



Surface after PPSU Removal

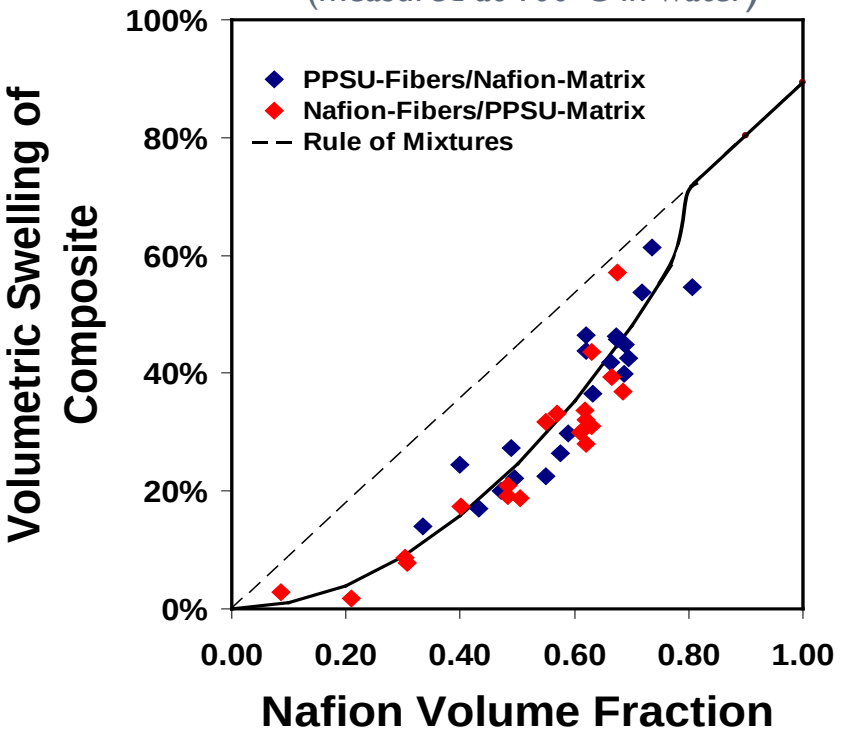
Conductivity and Volumetric Swelling: Nanofiber Composite Membranes Made with Nafion + Polyphenylsulfone

Conductivity
(measured in 25°C in water)



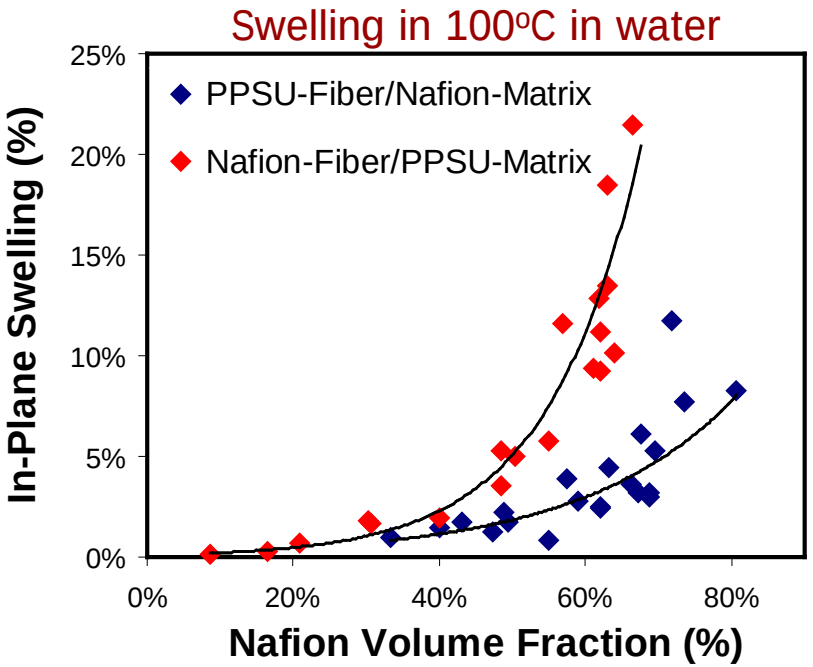
- Conductivity can be predicted by a volume fraction Mixing Rule (dashed line, above)
- Electrospun membranes have an exceptionally low percolation threshold (≤ 9 vol% Nafion)

Volumetric swelling
(measured at 100°C in water)



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

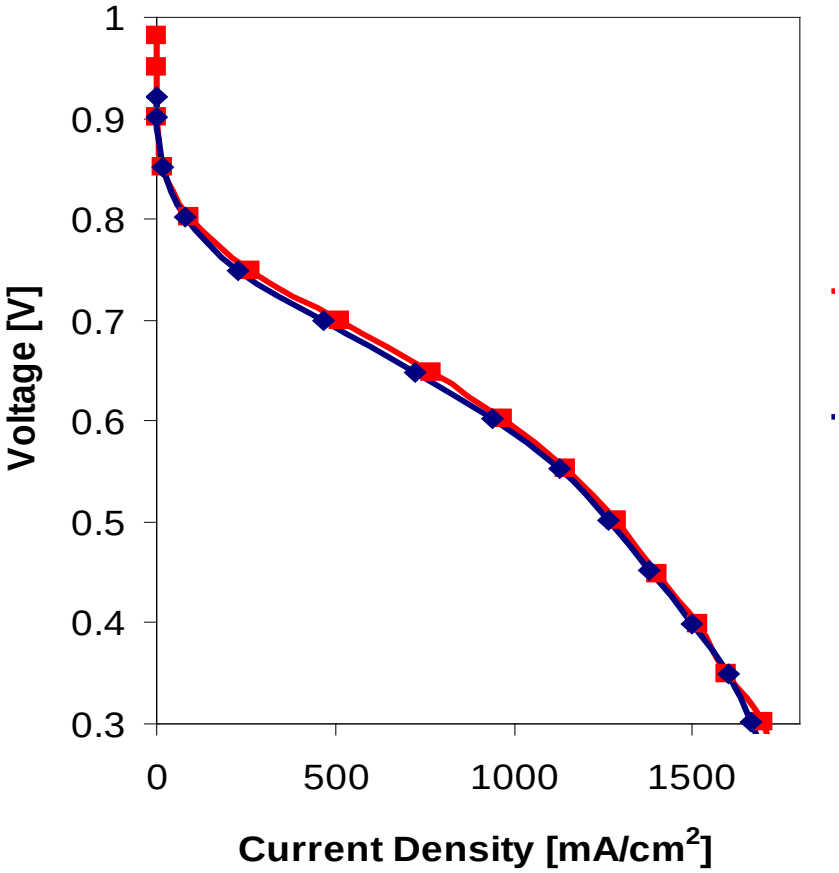
In-Plane Swelling of Nafion/PPSU Composite Membranes



- Both membrane structures have the same volumetric swelling and conductivity 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 the thickness direction (there is no 3-D connectivity of PPSU fibers)
- Limited thickness swelling for Nafion fiber/PPSU membrane (3-D PPSU connectivity creates isotropic swelling)

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



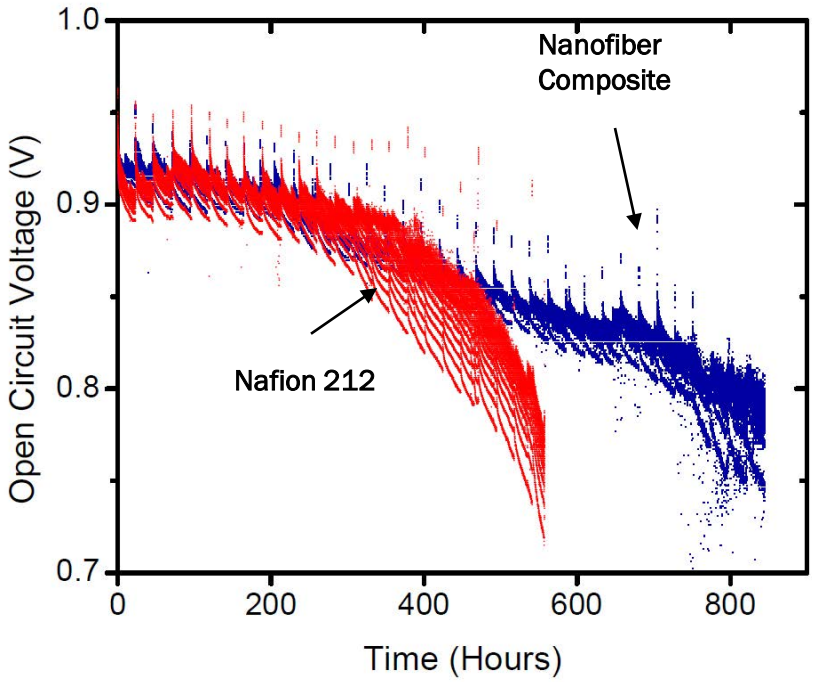
- 80°C, 100% RH
- Anode and Cathode: 0.4 mg/cm^2 Pt loading with 30% Nafion binder content

Nafion 212 (51 µm)

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

If membrane conductivity is low, use thinner films in a membrane-electrode-assembly to compensate for the lower conductivity of a nanofiber composite membrane. Match the sheet resistance (thickness/conductivity).

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



- 25 cm^2 MEA
- 80°C
- 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)

Electrospinning Fuel Cell Catalyst into a Nanofiber Mat Electrode

Electrode Issues:

- The need for high power at low Pt loading
- Durability (minimize carbon corrosion and Pt dissolution)
- System operation, e.g., getting air/oxygen in and water out at high current densities.

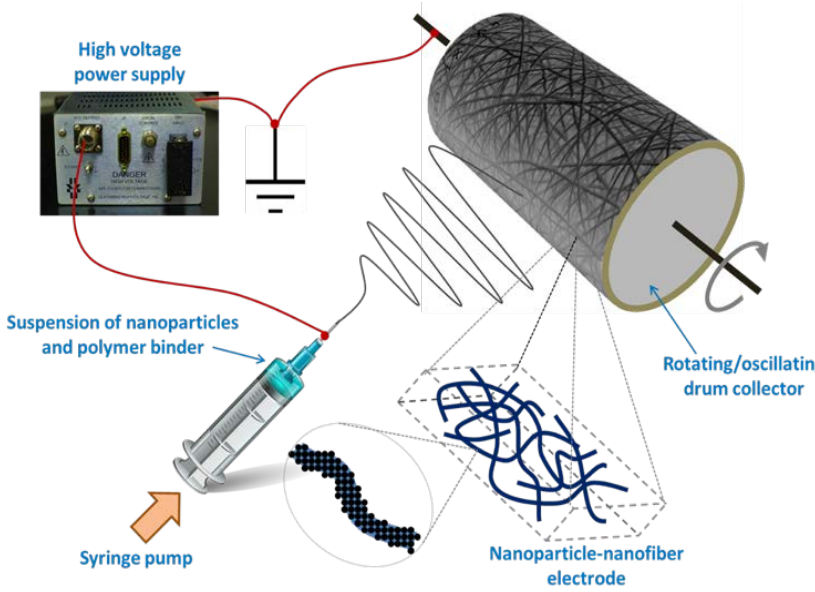
Ink:
Catalyst+PFSA/PAA + solvent

↓

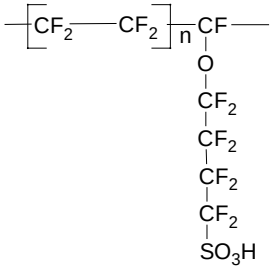
Electrospinning on Aluminum Foil or GDL or membrane

↓

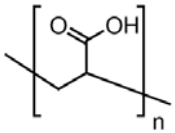
Hot Press to make MEA



PFSA = Perfluorosulfonic Acid Polymer (Nafion®)



PAA = Polyacrylic acid polymer (carrier)



- Nafion does not dissolve in alcohol/water solvents; if forms a micellar dispersion.
- A carrier polymer is required to spin Nafion fibers: poly(acrylic acid) (PAA), PVDF, or polyvinylpyrrolidone (PVP).
- Catalyst powder (Pt/C and PtCo/C) content in dry fibers is high (> 50 wt.%).

Experimental Electrospinning Conditions

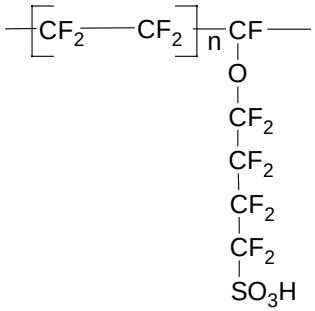
Preparing an Ink:

1. Mix 0.15 g catalyst with 0.55 g water
2. Mix the wet catalyst with 0.26 g commercial Nafion stock solution and 0.45 g isopropanol
3. Sonicate the catalyst/Nafion suspension for 90 minutes with intermittent mechanical stirring
4. Add 0.24 g of a 15 wt% poly(acrylic acid) solution in 2:1 wt ratio isopropanol:water
5. Stir the ink mechanically for approximately 48 hours.

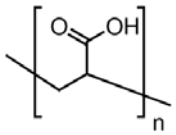
Typical electrospinning conditions:

	Voltage (kV)	Pump rate (mL/h)	collector distance (cm)	RH (%)	Carrier MW (kDa)	Nafion/carrier (weight ratio)
Catalyst/Nafion/PAA	10-12	1	8-10	40%	450	2

PFSA = Perfluorosulfonic Acid Polymer (Nafion®)

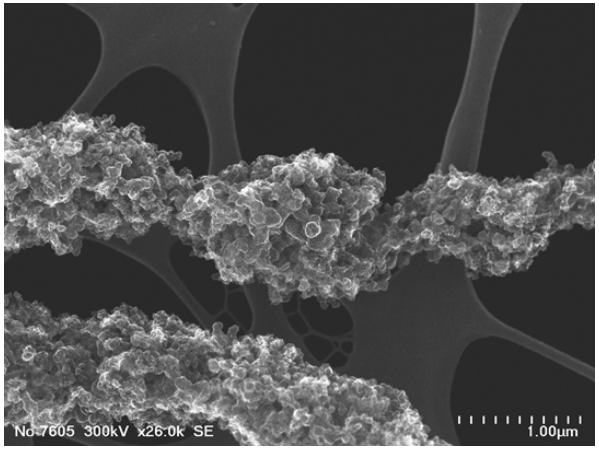


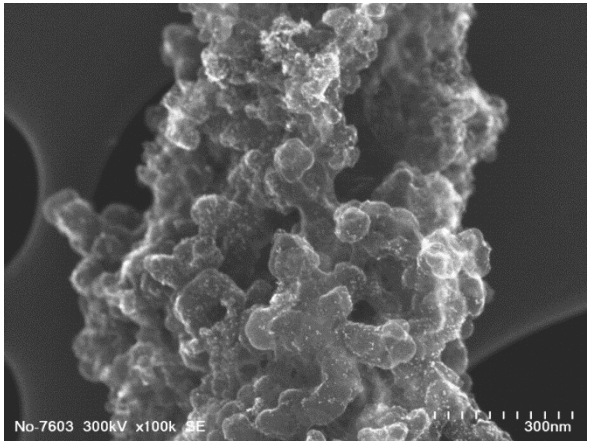
PAA = Polyacrylic acid polymer



Electrospun Nanofiber Electrode Mats

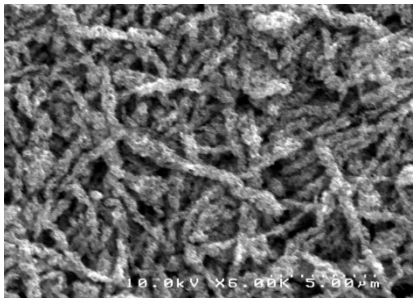
Nanofiber Composition
65-72 wt.% Pt/C
13-23 wt.% Nafion
12-15 wt.% poly(acrylic acid) PAA



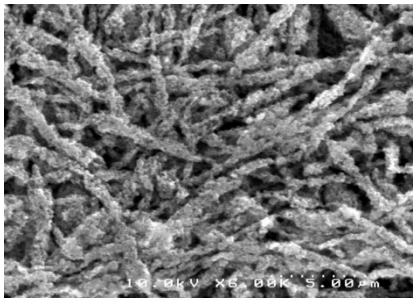


Fibers made with Johnson Matthey HiSpec 4000 Pt/C catalyst.
SEMs from Karren More at Oak Ridge National Lab

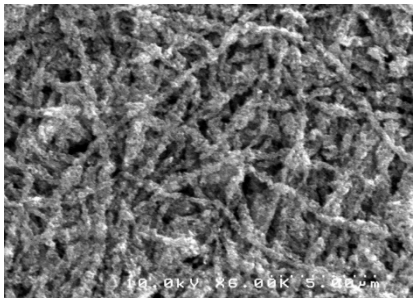
Fiber mat electrodes have inter- and intra-fiber porosity.



Hot-pressed @ 140°C and 10MPa



Hot-pressed @ 140°C and 16MPa



Hot-pressed @ 140°C and 80MPa

The fiber morphology is retained after hot pressing onto a membrane or GDL and during/after fuel cell operation.

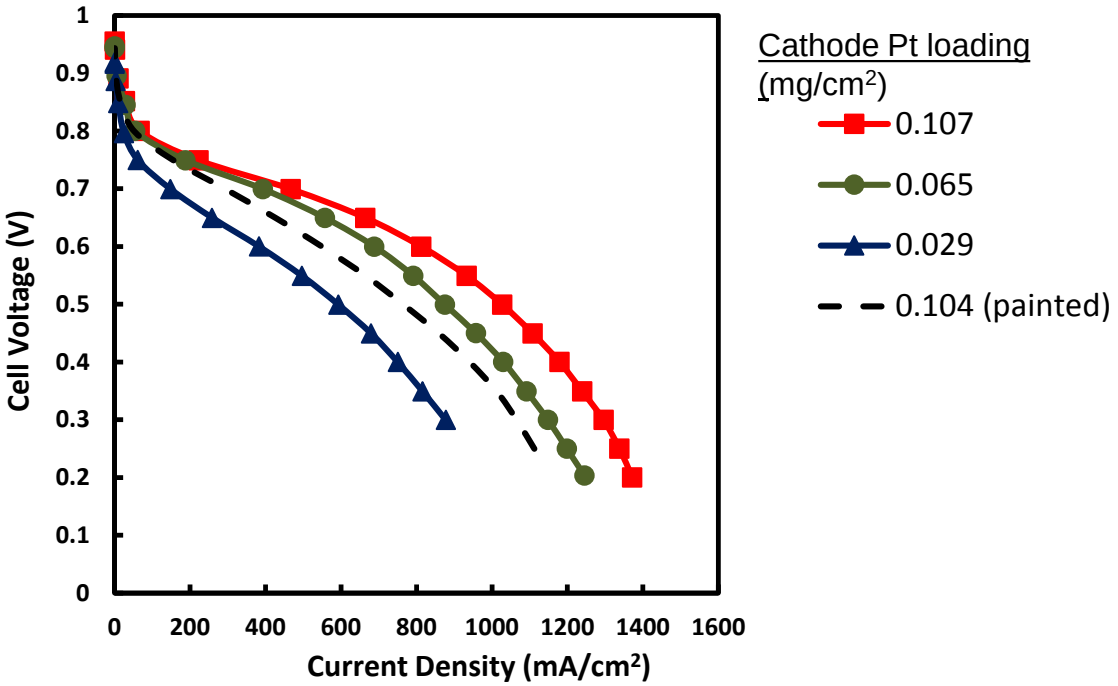
Preliminary Results - Comparison of Nanofiber and Painted Slurry Cathodes

MEAs:

- Johnson-Matthey Hi Spec 4000 Pt/C catalyst, Nafion 212, 5 cm^2 MEA
- Nanofiber electrodes 65 wt% Pt/C, 23% Nafion, 12% PAA
- Painted electrode 77 wt% Pt/C, 23% Nafion (no PAA)
- Anode Pt loading constant at 0.10 mg/cm^2

Operating conditions

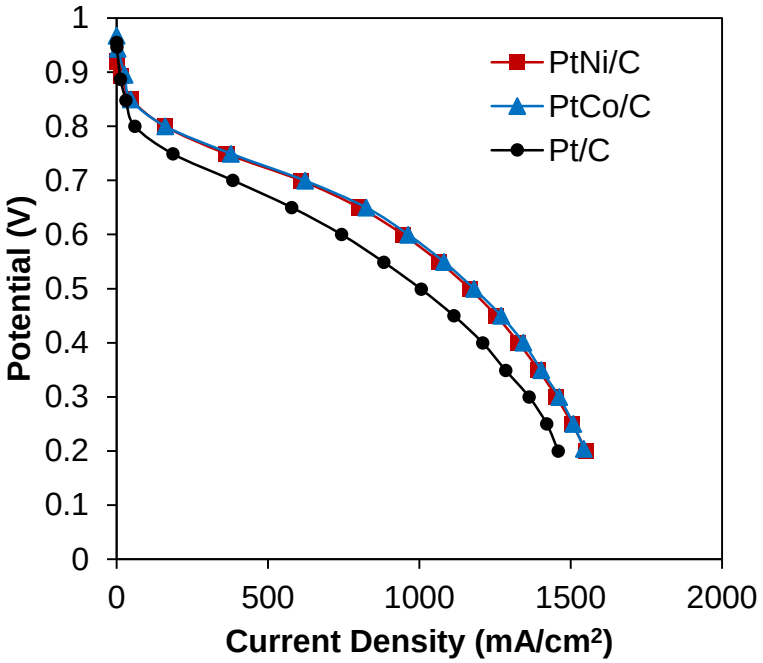
- 80°C, ambient pressure, 500 sccm air, 125 sccm H_2, 100% RH



Higher Power at the Same or Lower Pt Loading

- For the same Pt loading (0.10 mg/cm^2), there was a 33% increase in power at 0.65 V
- The power output of a nanofiber cathode at 0.065 mg_{Pt}/cm^2 was higher than a painted GDE at a Pt loading of 0.10 mg/cm^2
- Higher power is attributed to inter and intra-fiber porosity (higher electrode area and higher catalytic activity) and fast expulsion of product water

Pt/C, PtCo/C, and PtNi/C Nanofiber Cathode MEAs at 0.1 mg/cm² Pt Loading



PtCo/C (TEC36E52) Nanofiber cathode MEA

Cathode: 0.1 mg_{Pt}/cm^2 (PtCo/C)/Nafion/PAA – 55/30/15 (I/C = 1.6)
Membrane: Nafion 211
Anode: 0.1 mg_{Pt}/cm^2 Johnson Matthey (Pt/HiSpec 4000)/Nafion/PAA – 65/20/15

PtNi/C (TECNiE22) Nanofiber cathode MEA

Cathode: 0.1 mg_{Pt}/cm^2 (PtNi/C)/Nafion/PAA – 51/33/16 (I/C=1.2)
Membrane: Nafion 211
Anode: 0.1 mg_{Pt}/cm^2 Johnson Matthey (Pt/HiSpec 4000)/Nafion/PAA – 65/20/15

Pt/C (Johnson Matthey on HiSpec 4000) Nanofiber cathode MEA

Cathode: 0.1 mg_{Pt}/cm^2 (Pt/C)/Nafion/PAA – 65/20/15
Membrane: Nafion 211
Anode: 0.1 mg_{Pt}/cm^2 Johnson Matthey (Pt/HiSpec 4000)/Nafion/PAA – 65/20/15

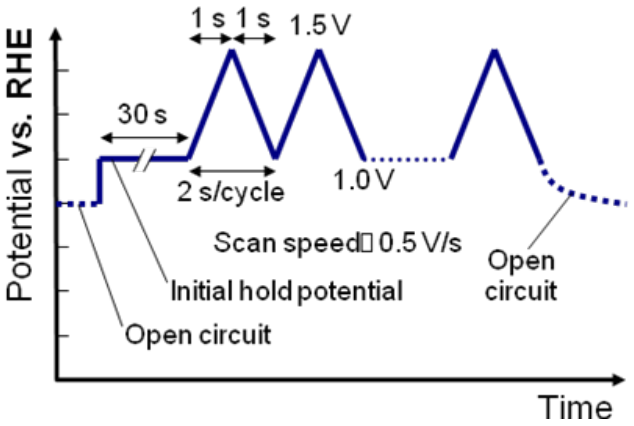
Fuel Cell Conditions:
H_2 (125 sccm) - Air (500 sccm)
Pressure 100 kPa absolute
Temperature: 80 °C
100% RH
GDLs: Sigracet 29BC

	Mass Activity at 0.9V (mA/cm²)	Power Density at 0.65V (mW/cm²)
Pt/C	180	376
PtCo/C	260	536
PtNi/C	241	520

Cathode Durability Testing – Voltage Cycling Experiments

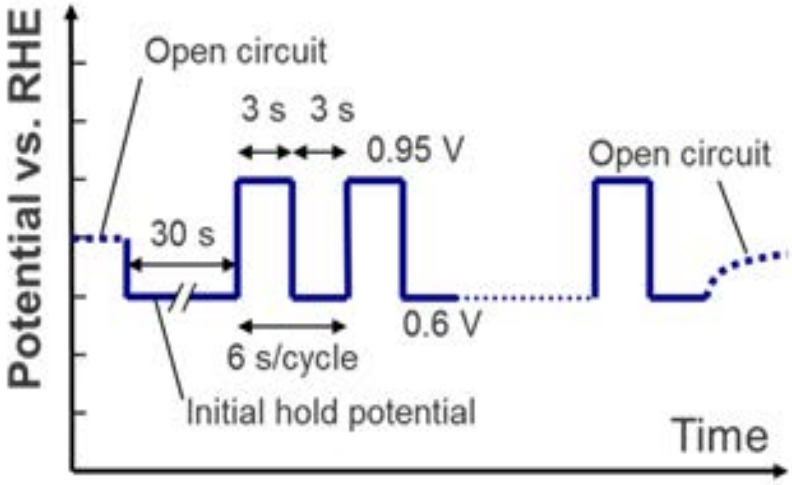
Automotive fuel cell must operate for 5,000 hours (150,000 mile lifetime at 30 mph).

Auto companies have devised voltage cycling (short-duration) accelerated stress tests (ASTs) to assess fuel cell durability.



Carbon corrosion test – cycling between 1.0 and 1.5 V

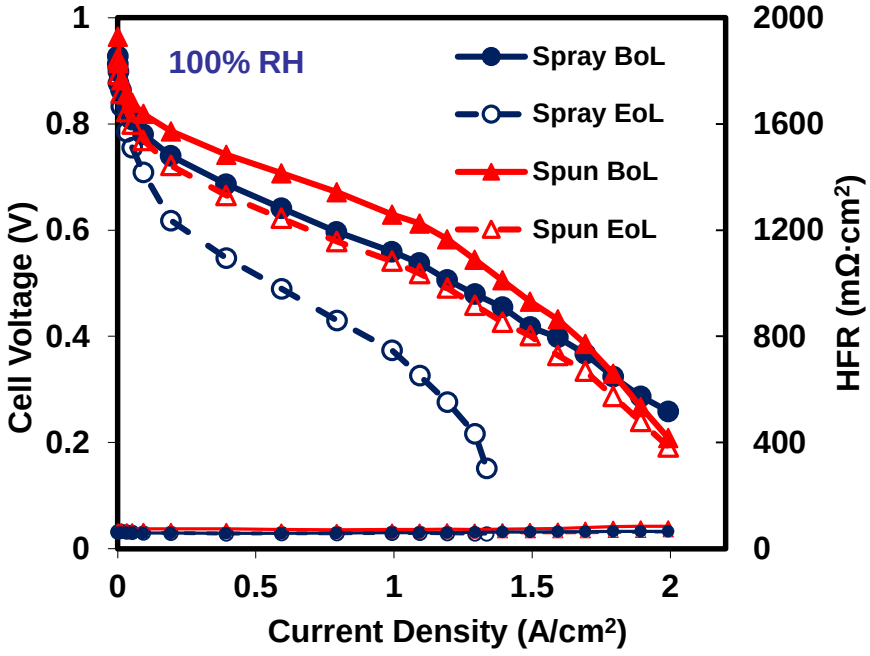
Simulates long-term fuel cell start-stop operation

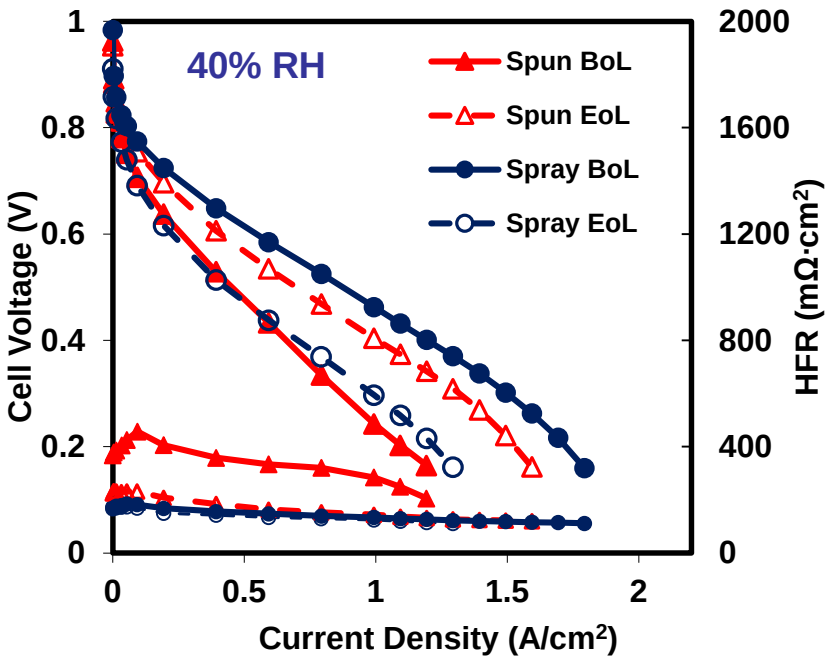


Pt dissolution test – cycling between 0.60 and 0.95 V

Simulates long-term fuel cell operation with acceleration/deceleration

Carbon Corrosion AST: Beginning-of-Life (BoL) and End-of-Life (EoL) Performance for Nanofiber and Sprayed Electrode MEAs





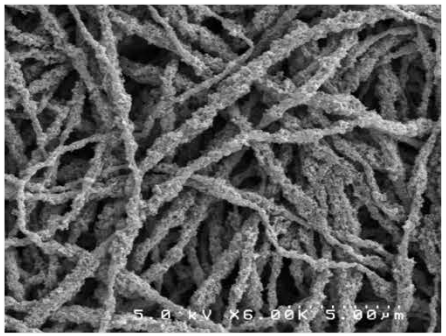
- 0.10 mg_{Pt}/cm^2 cathode and anode with JM HiSpec 4000 Pt/C catalyst, Nafion 211 membrane, 25 cm^2, 80°C, 2.0 atm (abs), 8000 sccm air and 4000 sccm H_2 (straight flow channels)
- The nanofiber electrodes had a composition of 72 wt.% Pt/C, 13 wt.% Nafion, and 15 wt.% PAA.
- Sprayed GDE electrodes from Nissan Technical Center North America had a neat Nafion binder.
- Start-stop cycling protocol: 1,000 cycles, triangular wave, 500 mV/s cycling between 1.0 and 1.5 V, (Carbon Corrosion Test)
- Conclusion: Nanofiber cathode at EoL did not flood

An Alternative Binder of PVDF or Nafion/PVDF for Pt/C Cathode Nanofibers

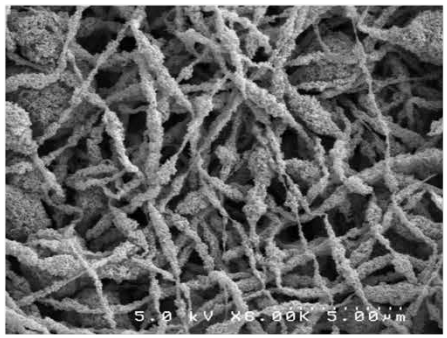
- PVDF is stable in a fuel cell environment, it is inexpensive, and it can be electrospun. We used Kynar® HSV 9000.
- PVDF is hydrophobic, which should reduce the amount of water near the carbon support and slow/stop carbon corrosion

  $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$

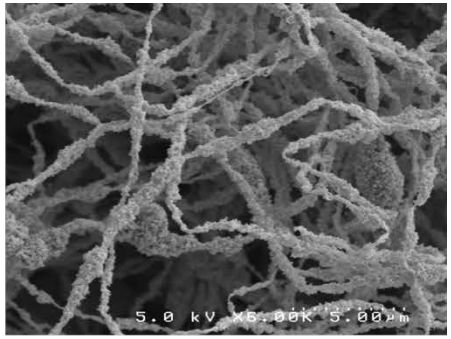
Neat PVDF



33:67 Nafion:PVDF



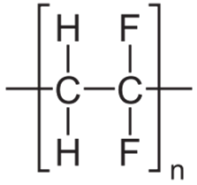
67:33 Nafion:PVDF

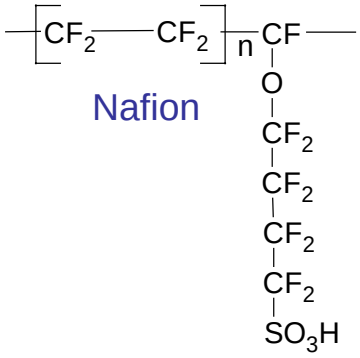


80:20 Nafion:PVDF

All mats are 70 wt.% catalyst and 30 wt.% total binder

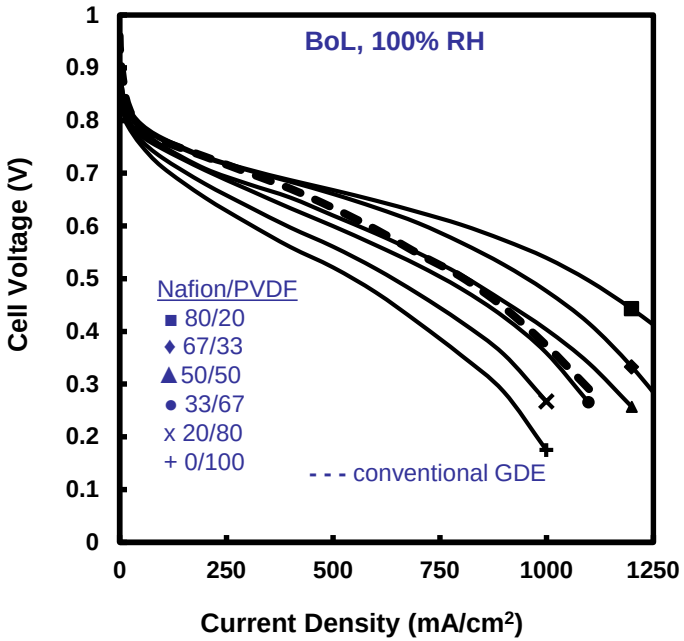
PVDF

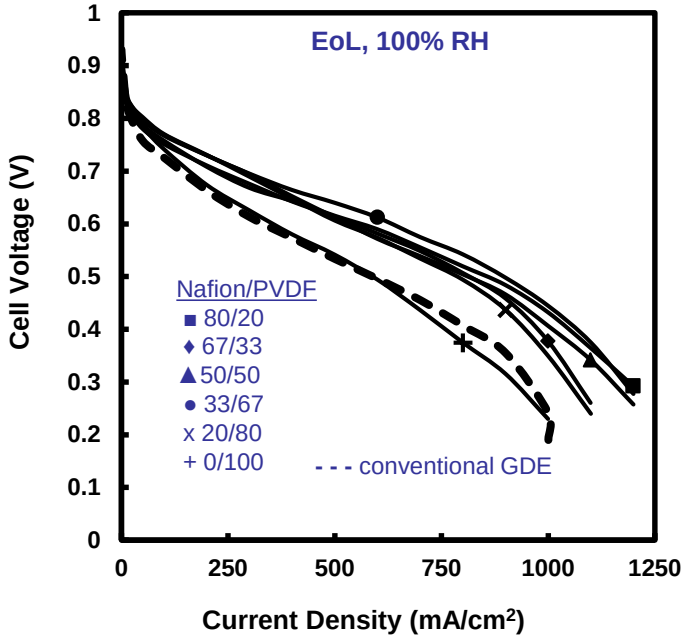




Nafion

BoL vs. EoL Pol Curves with Nafion/PVDF Binder (after 1,000 voltage cycles, 1.0 to 1.5 V)





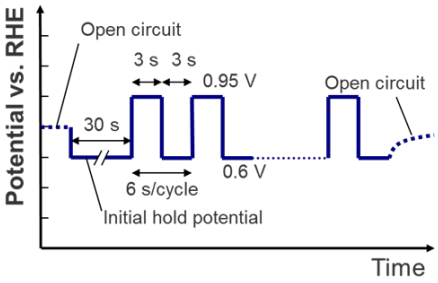
80°C
500 sccm air and 125 sccm H_2 (ambient pressure)
100% RH

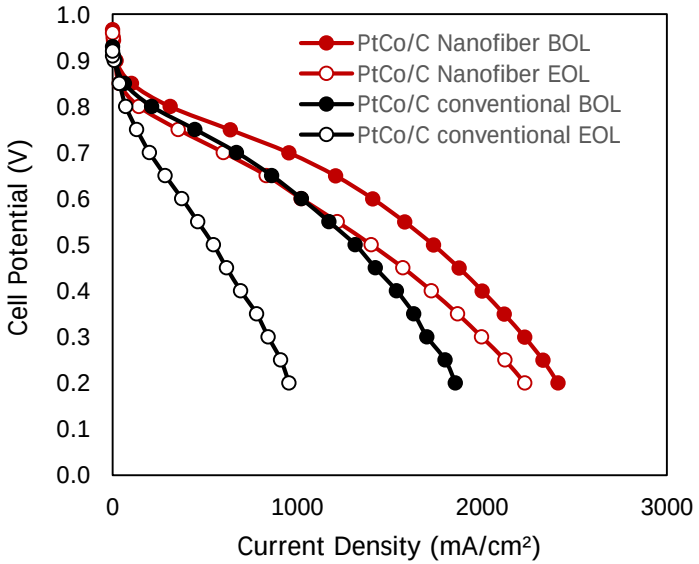
- 0.10 mg_{Pt}/cm^2 cathode and anode (all anodes have Nafion/PAA binder), Nafion 211 membrane, 5 cm^2 MEA,

- BoL power density is strongly dependent on binder composition; 80/20 Nafion/PVDF is best.
- EoL power densities are less dependent on binder composition. 33/67 Nafion/PVDF is best.
  - For high Nafion content binders EoL/BoL power is < 1
  - For low Nafion content binders, EoL/BoL power is > 1

PtCo/C Nanofiber Cathode MEAs: Initial Performance and Durability after a Metal Dissolution Accelerated Stress Test

Load cycling protocol





MEA (5 cm²) and Testing Conditions

Nanofiber Cathode:
PtCo/C/Nafion/PAA – 55/30/15
Loading: 0.1mg$_{Pt}$/cm^2

Slurry cathode: PtCo/C/Nafion – 55/45
Loading: 0.1mg$_{Pt}$/cm^2

Anode: 65/35 JM Pt(Hispec)/Nafion
Loading: 0.1mg$_{Pt}$/cm^2

Feed gas: H_2 (500 sccm); air (2000 sccm)
Membrane: Nafion 211
100% RH; 200 kPa$_{abs}$
Temperature: 80°C

	Nanofiber Cathode MEA		Conventional MEA	
	mW/cm^2 at 0.65 V	mW/cm^2 at Max Power	mW/cm^{2}at 0.65 V	mW/cm^{2}at Max Power
At BoL	783	868	559	655
At EoL (30,000 cycles)	541	707	185	277
EoL/BoL 100%	69%	81%	33%	42%

Nanofibers offer greater protection from load cycling degradation at 30,000 cycles.

Future Challenges

Membranes:

- Cost: Make membrane thinner (lower sheet resistance) with good mechanical properties and low gas crossover. Right now we are in the 15-20 μm range.
- Performance: Improve proton conductivity at low relative humidity. Create membranes that can hold onto water at high T and low RH.
- Durability: Minimize polymer degradation during fuel cell operation (the use of additives and/or new polymers).

Electrodes:

- Cost: Lower Pt loading, but maintain high power. Use roll-to-roll manufacturing processes for MEAs.
- Performance: Generate higher power by optimizing the cathode porosity and binder properties to improve O_2 access to catalyst sites, with fast removal of product water. Incorporate better oxygen reduction catalysts into MEAs. Decrease/control binder coating thickness on catalyst particles. Improve power output at low feed gas humidity conditions. Can an MEA work well at both high and low RH?
- Durability: Adjust electrode composition/structure to minimize power losses when there is metal dissolution, carbon corrosion, freeze/thaw cycling, etc.

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Thank you

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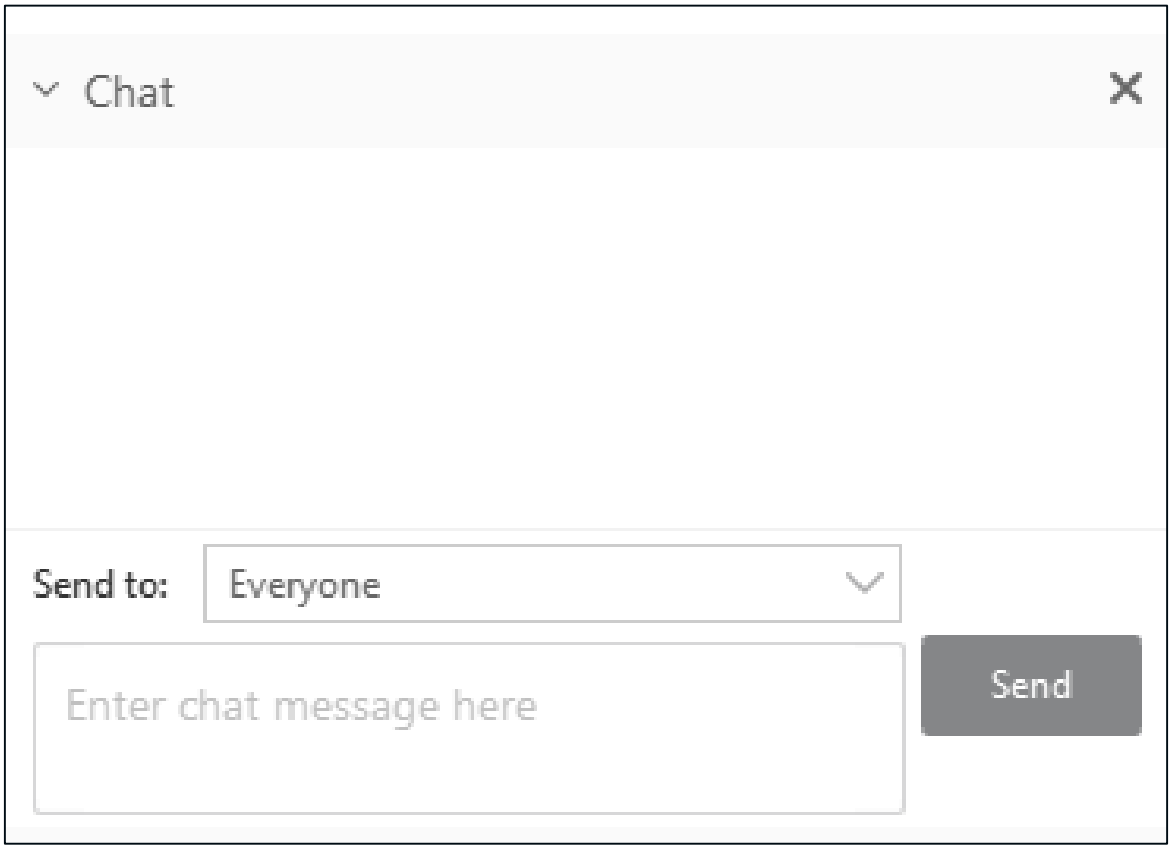
Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



Q&A

1. *Slide 4 - does the hydrophilic/hydrophobic domain size of the charged polymers electrospun differ significantly from that of traditional polymer membrane.*

   Yes, the domain size of both the ionomer and uncharged polymer is submicron (usually the diameter of the electrospun fibers, which is typically in the 100-500 nm range). After processing the fiber mat into a dense membrane, one of the fiber components is allowed to soften and flow, but the second component remains in fiber form, with a very small domain size.

2. *How much Electric Voltage is on the spinneret?*

   Typically the spinneret tip is polarized to about 8-12 kV relative to a grounded collector surface, but this is an experimental parameter that must be adjusted/optimized , to give well-formed fibers.

3. *How does the conductivity compare to conventional Nafion as the temperature increases? For example at 60 or 85^{o}C. (Will James).*

   Yes, we still see the properties of Nafion at elevated temperatures in our composite films. If Nafion losses water and conductivity at high T and low relative humidity, so will our reinforced composite films. We are not changing the properties of Nafion when we co-electrospin it with an uncharged polymer.

Q&A

4. *Since the swelling is dfferent for in-plane versus thru plane for thee two types of composites (Nafion matrix-PPSU fibers, vs PPSU matrix-Nafion fibers) have you looked to see if there are differences in thru-plane versus in-plane conductivity for the two different arrangements? (John Kopasz).*

   We do not see a difference between in-plane and through-plane conductivity. It appears that conductivity is a function of total water content and this property is the same for the two difference nanofiber composite membrane morphologies (Nafion matrix-PPSU fibers and PPSU matrix-Nafion fibers).

5. *Is the solvent for the catalyst ink aqueous or non-aqueous?*

   The solvent for inks containing Nafion + poly(acrylic acid) is a mixture of Isopropanol and water (see reference papers for details).

6. *Will these membranes work with PGM-free catalysts?*

   Yes, one can use nanofiber electrospinning to prepare electrodes with non-PGM catalyst. The electrode nanofiber morphology improves the performance of non-PGM cathode catalysts in fuel cell test, in terms of initial power and durability during long-term operation. We have a paper on this subject that will appear in print very soon. See: John Slack, Barr Halevi, Geoff McCool, Jingkun Li, Ryan Pavlicek, Ryszard Wycisk, Sanjeev Mukerjee, and Peter Pintauro, “Electrospun Fiber Mat Cathode with PGM-free Catalyst Powder and Nafion/PVDF Binder”, *ChemElectroChem* DOI: 10.1002/celc.201800283.

Q&A

7. *Slide 23…are the MEAs sprayed on the membrane like a CCM or are they electrospun on a substrate and then hot pressed to the membrane?*

   For the results presented on slide 23, we compare two different electrode configurations: a sprayed cathode MEA made a Nissan Technical Center North America and a nanofiber cathode MEA made at Vanderbilt University. The nanofiber cathode MEAs were made by pressing an electrospun mat onto a Nafion membrane (CCM method), whereas the sprayed electrocatalyst layer was fabricated by spraying an ink onto a gas diffusion layer (GDE method).

8. *What is the solvent for spinning PVDF based inks?*

   A mixed solvent was used for electrospinning inks with Nafion and PVDF. The solvent contained dimethylformamide (DMF), tetrahydrofuran (THF), and acetone (see reference paper for details).

9. *Your ionomer content in the fiber electrodes appears to be quite a bit lower than for traditional electrodes (which leads to low performance at low RH). Have you tried optimizing I/C for better low RH performance? What is the highest I/C ratio you've been able to achieve? (John Kopasz)*

   We typically use an I/C (ionomer/carbon) ratio of 0.70-1.1 in our electrospun cathode nanofibers, where it is assumed that all of the water soluble poly(acrylic acid) carrier is removed from the fibers during MEA break-in. We have not yet optimized the I/C ratio for optimum power density at low relative humidity (RH) operation.

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A. M Park and P. N. Pintauro, "Alkaline Fuel Cell Membranes from Electrospun Fiber Mats", *Electrochemical and Solid-State Letters*, **15**, B27-B30 (2012).

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Bipolar Membranes:

Chunhui Shen, Ryszard Wycisk, and Peter N. Pintauro, "High performance electrospun bipolar membrane with a 3D junction", *Energy & Environmental Science*,**10**,1435-1442 (2017).

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W. Zhang and P. N. Pintauro, "High Performance Nanofiber Fuel Cell Electrodes", *ChemSusChem*, **4**, 1753-1757 (2011).

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