Novel Electrospun Fuel Cell Proton Exchange Membrane

Zhihao Shang

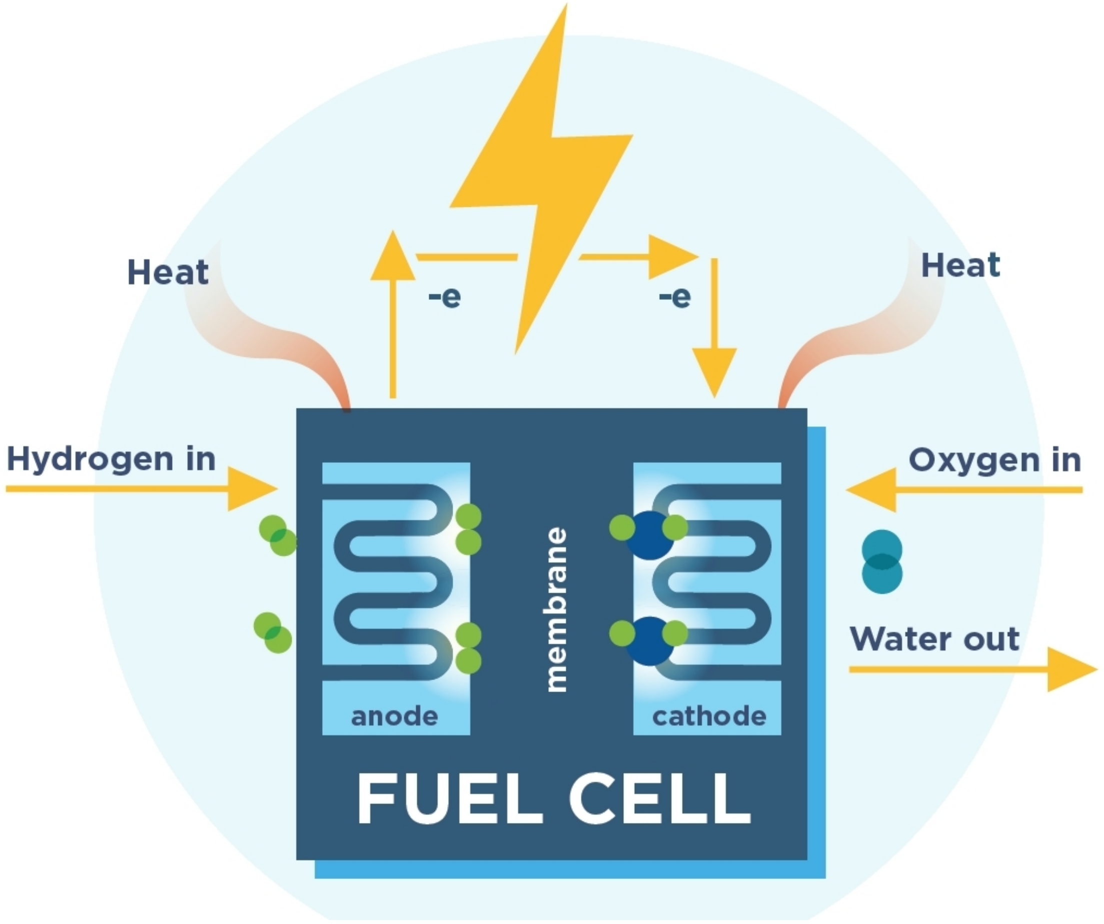
Advisor: Peter N. Pintauro

Ryszard Wycisk

Department of Chemical and Biomolecular Engineering
Vanderbilt University

Jan 26, 2021

What is Fuel Cell



Chemical Energy —redox→ Electric Energy

Fuel Cell Type

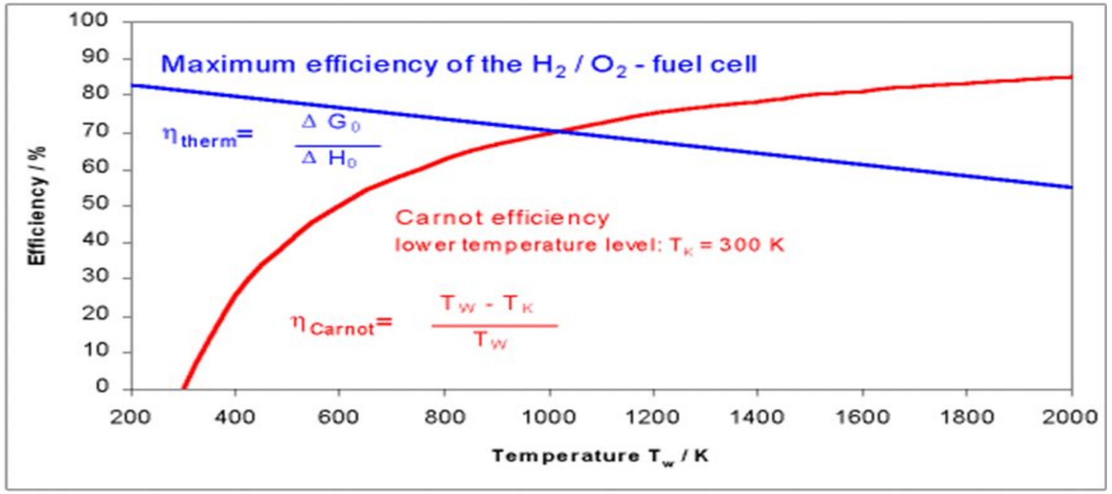
	Operating temp. (°C)	Fuel	Electrolyte
PEMFC	40-90	H_2 (/CO_2)	Polymer
AFC	40-200	H_2	KOH
DMFC	60-130	Methanol	Polymer
PAFC	200	H_2 (/CO_2)	Phosphoric Acid
MCFC	650	CH_4, H_2, CO	Molten Carbonate
SOFC	600-950	CH_4, H_2, CO	Solid Oxide

Noble metals: PEMFC, DMFC, PAFC; Noble metals/non-noble metals: AFC; Non-noble metals: MCFC, SOFC

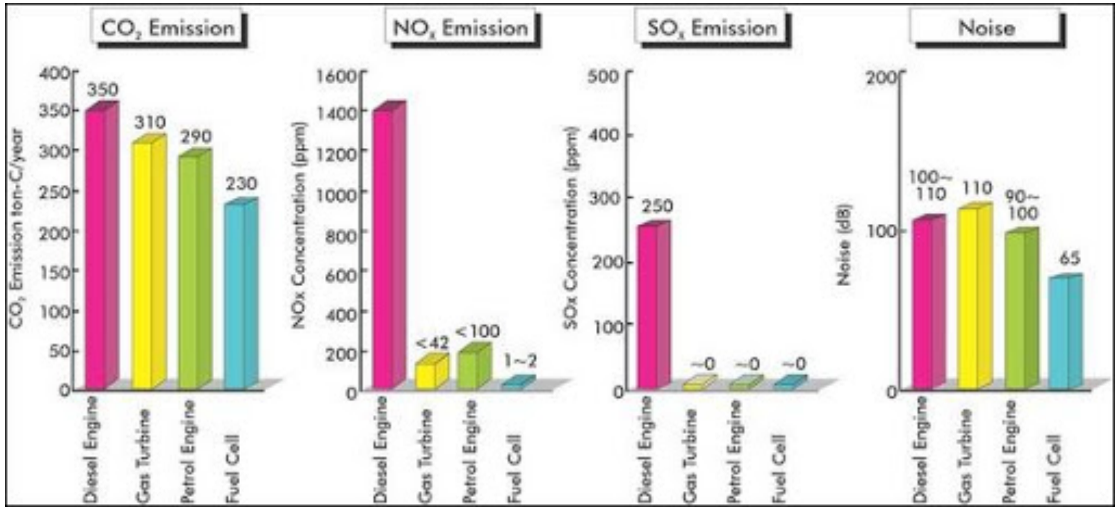
- http://www.fchea.org/h2-day-2019-events-activities/2019/8/1/fuel-cell-amp-hydrogen-energy-basics
- http://earthsci.org/mineral/energy/fuelcell/fuelcell.html

Advantages of Fuel Cell

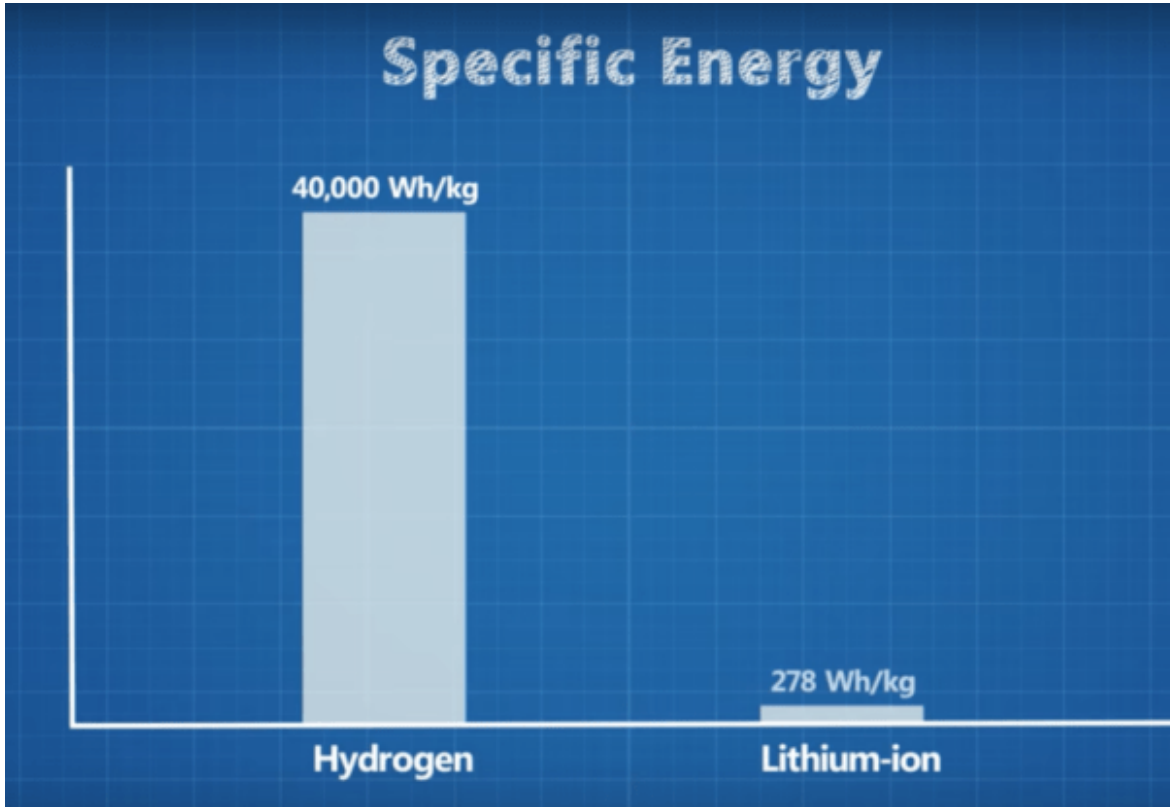
High conversion efficiency



Less pollution

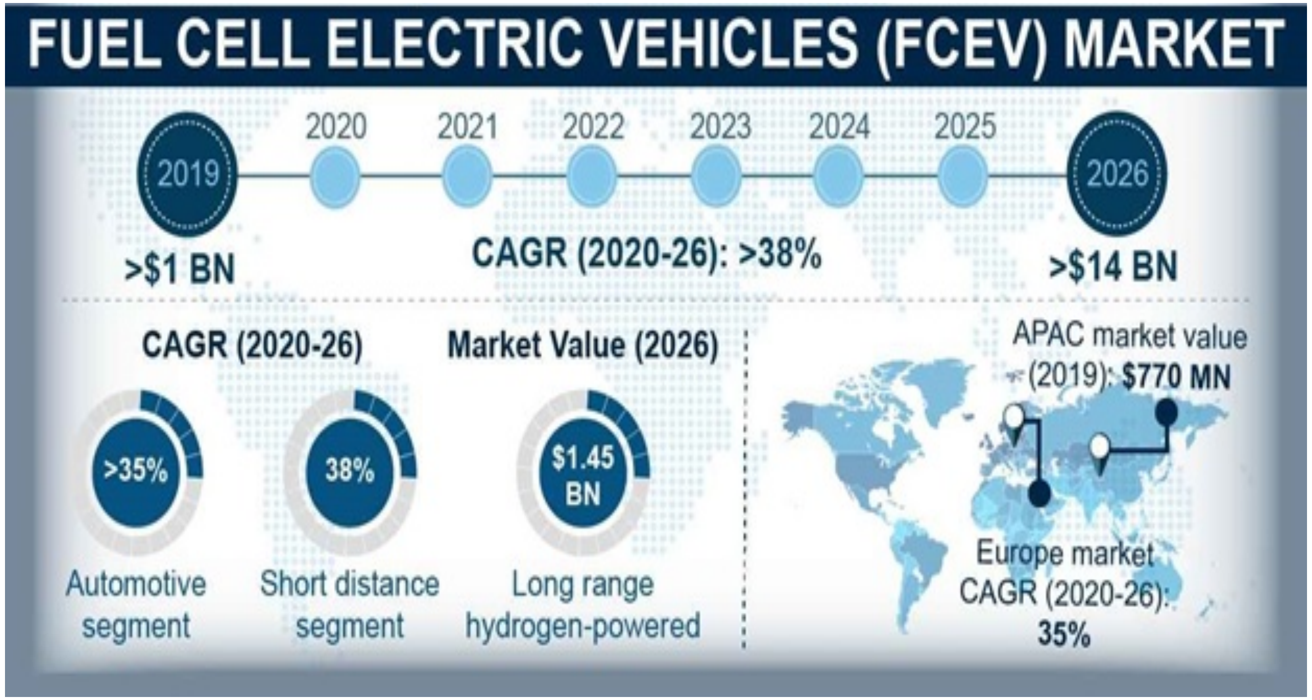


High specific energy



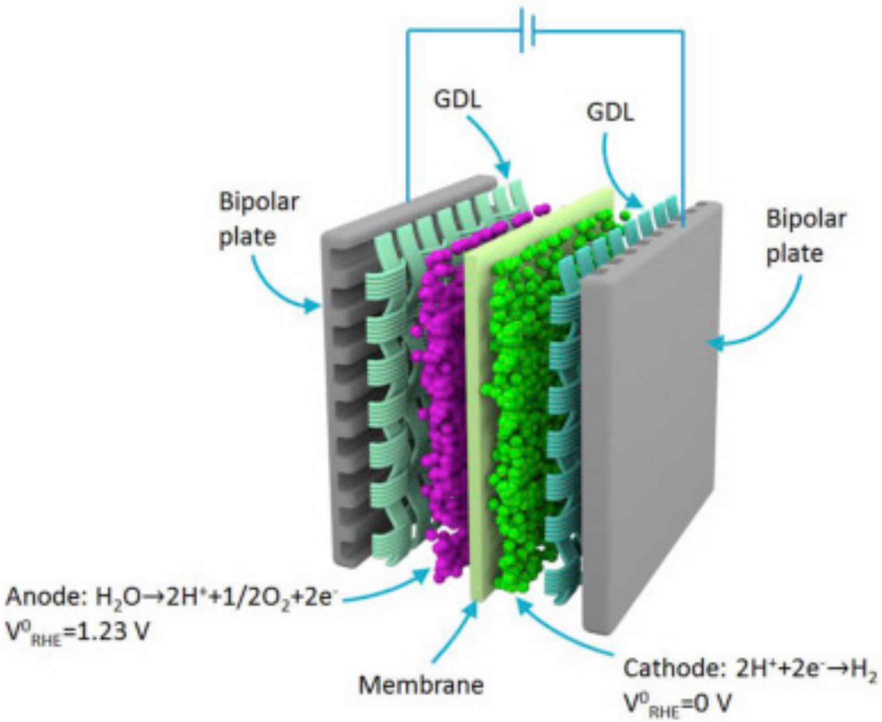
- https://slideplayer.com/slide/8527678/
- http://archive.siliconchip.com.au/cms/A_30527/article.html
- http://redgreenandblue.org/2018/08/13/hydrogen-fuel-cells

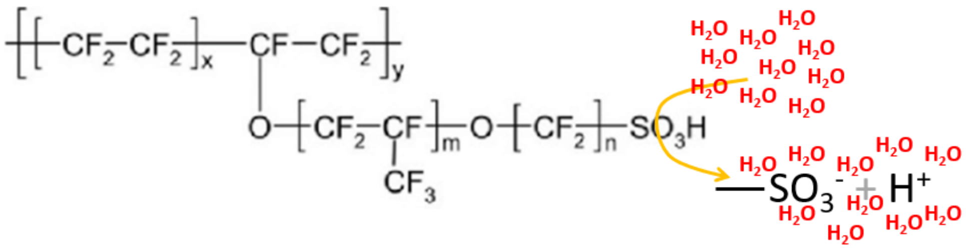
Fuel Cell Applications and Market



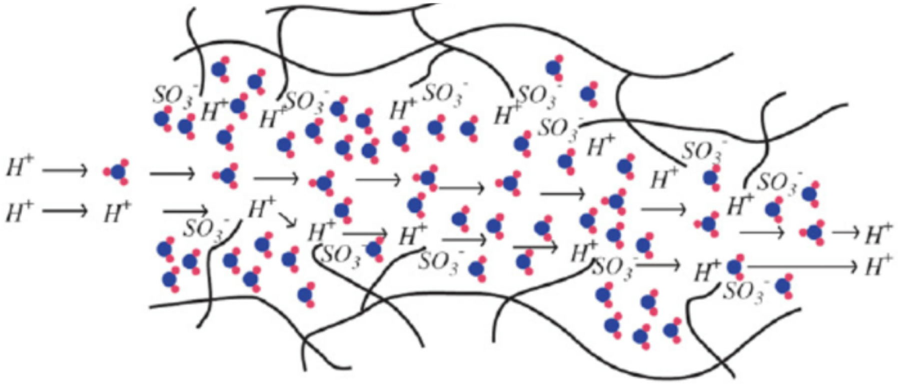
- https://www.slideshare.net/RajKumar1179/nano-fuel-cell
- https://www.gminsights.com/industry-analysis/fuel-cell-electric-vehicle-market

Proton Exchange Membrane





Chemical structure of Nafion®



Proton conducting mechanism of ionomer
Continuous channels between chains

Main requirements of PEM:

- ❖ High proton conductivity
- ❖ Dimension and mechanical stability
- ❖ Low fuel/oxidant permeability

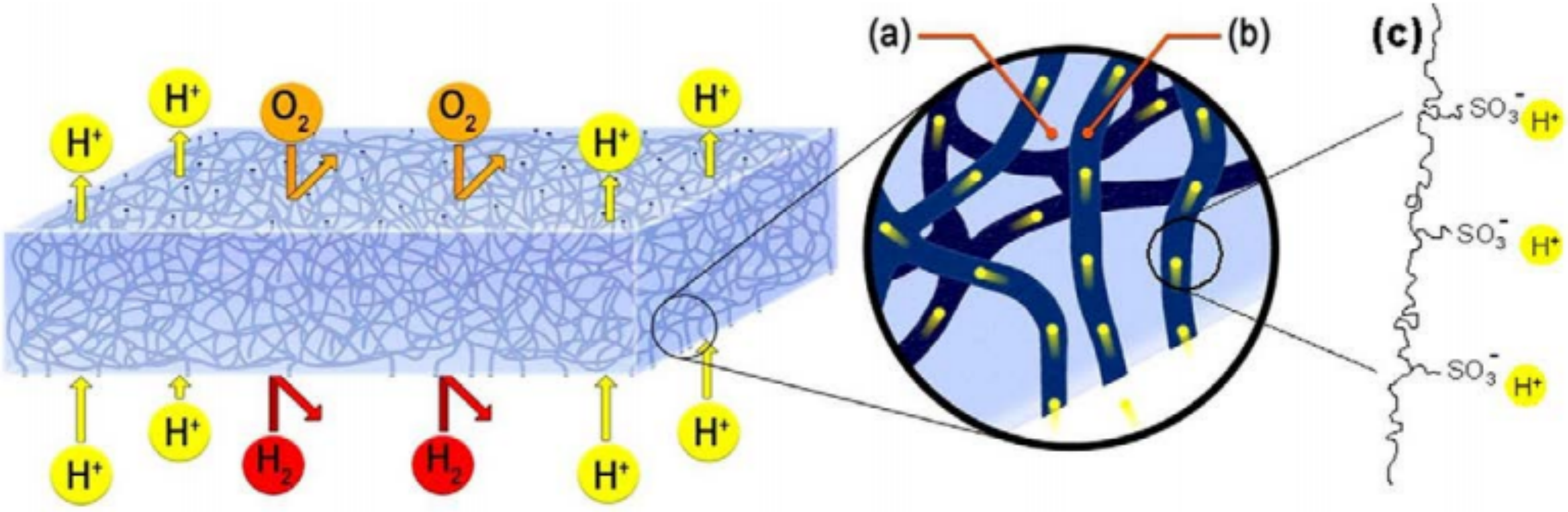
Advantages of Nafion®:

- ❖ High proton conductivity at 100%RH
- ❖ Good chemical stability

 • Feng, Qi, et al. *Journal of Power Sources* 366 (2017): 33-55.

Nanofiber Composite Membranes

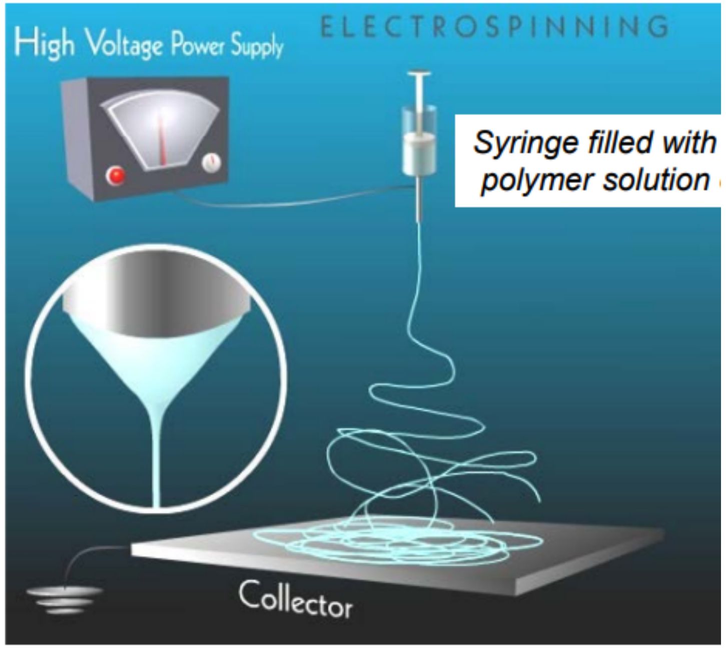
- Ionomer nanofibers surrounded by uncharged polymer
- Uncharged polymer nanofibers surrounded by (and reinforcing) ionomer matrix

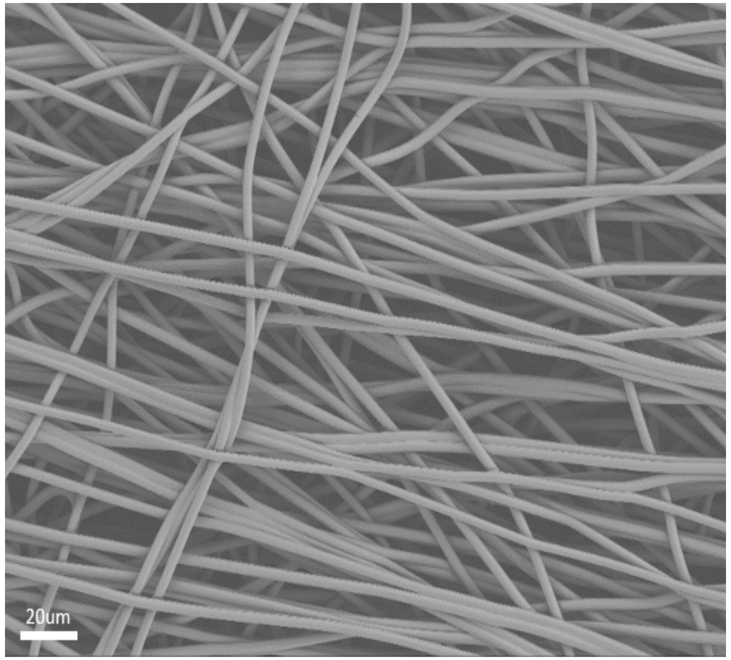


Structures are created by simultaneously electrospinning nanofibers of ionomer and uncharged polymer.

Nanofiber Electrospinning

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



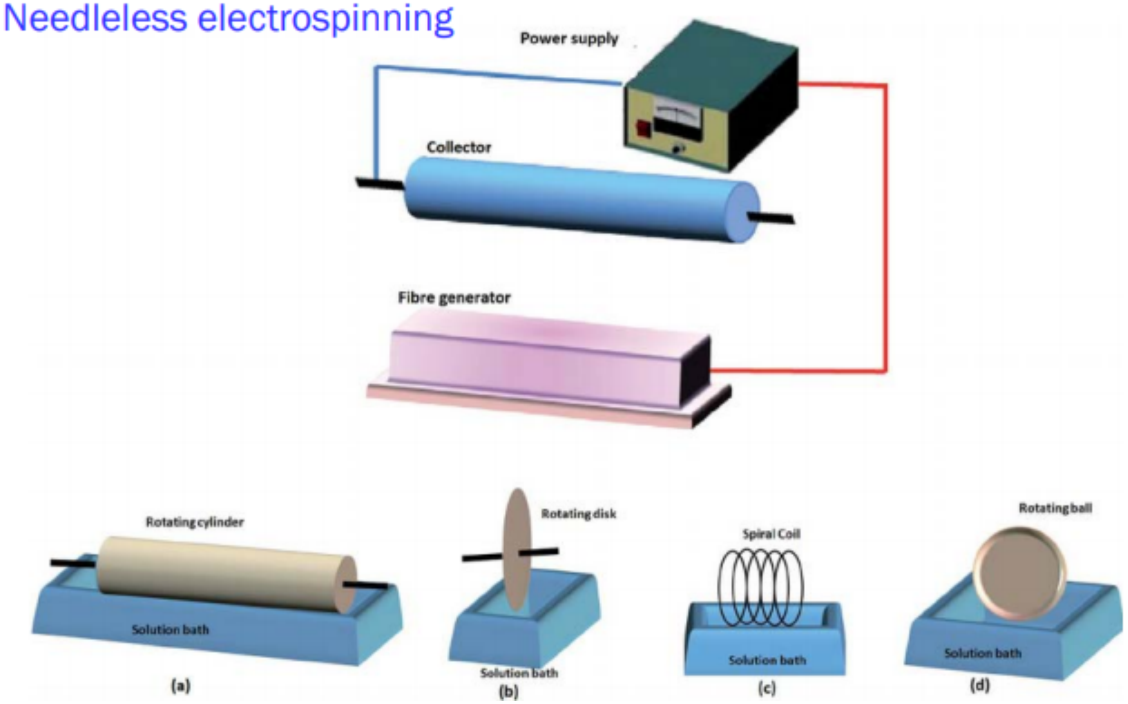


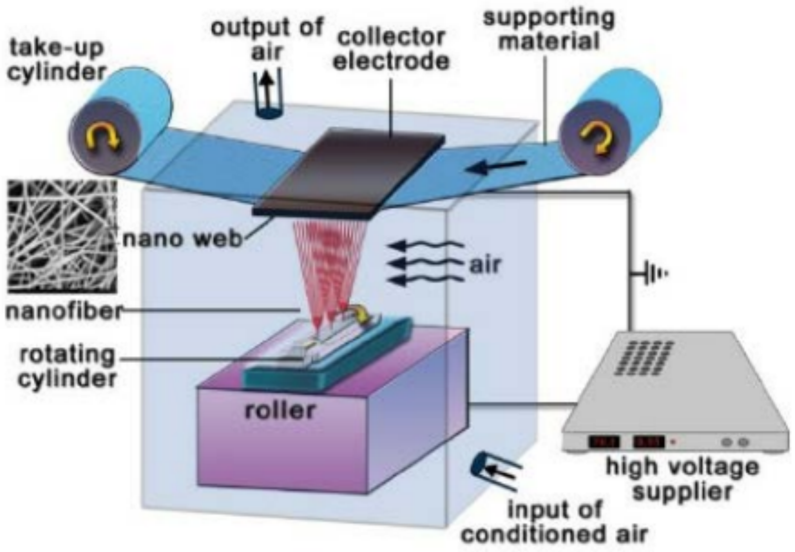
Process Variables:

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

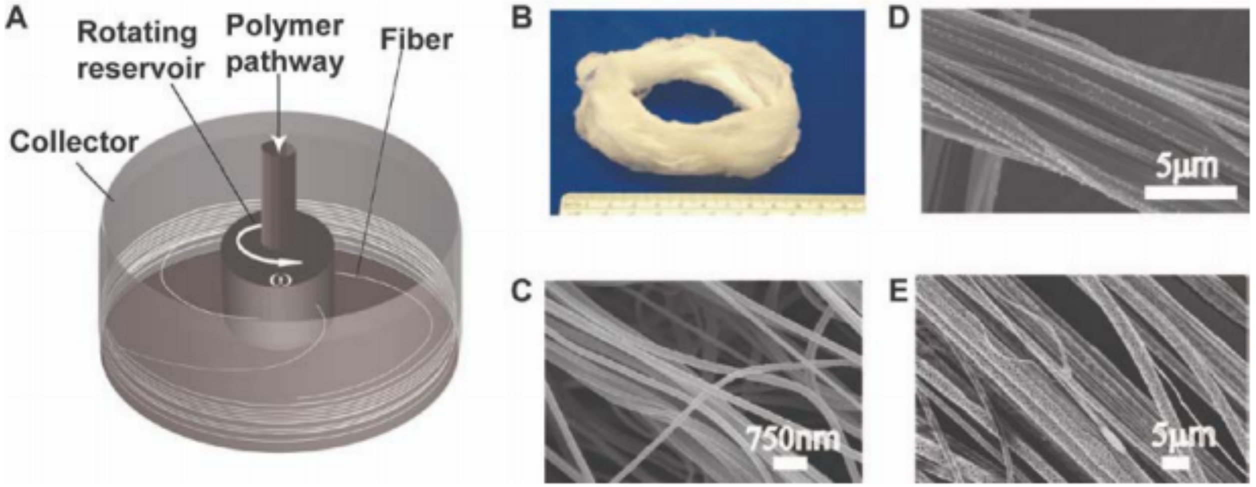
Needleless and Centrifugal Electrospinning

Needleless electrospinning

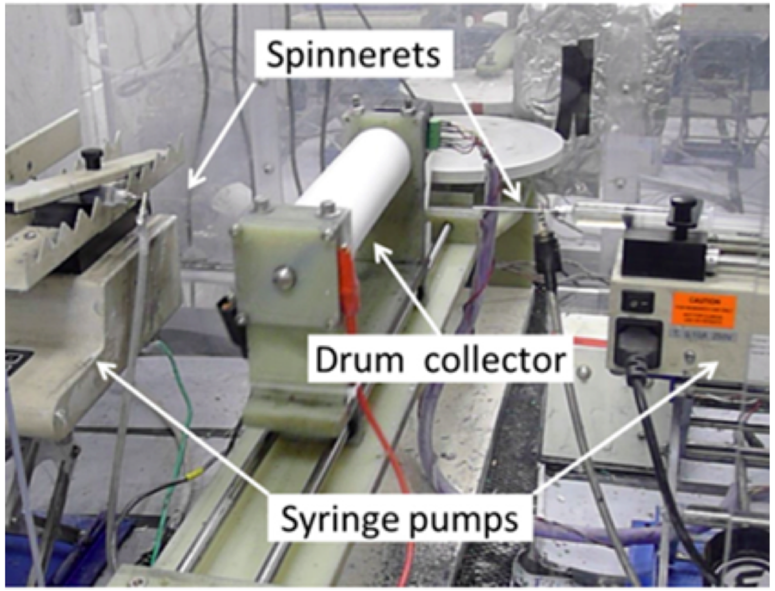


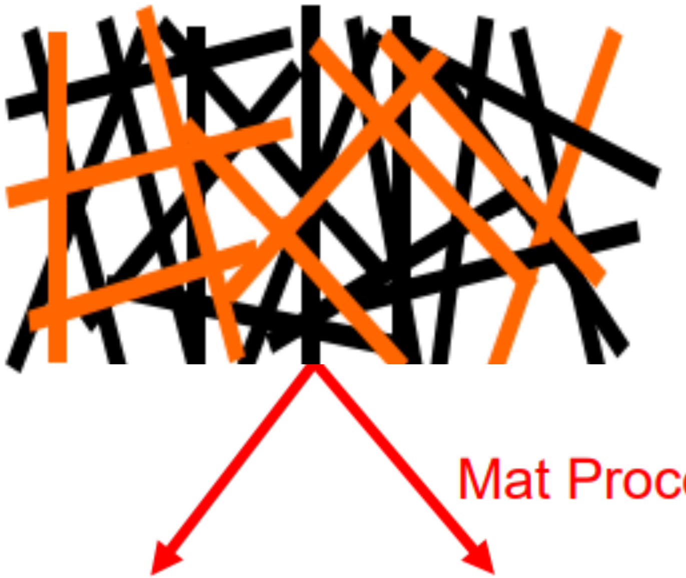


Centrifugal (rotary jet) electrospinning



Nanofiber Composite Membrane by Dual Fiber Electrospinning





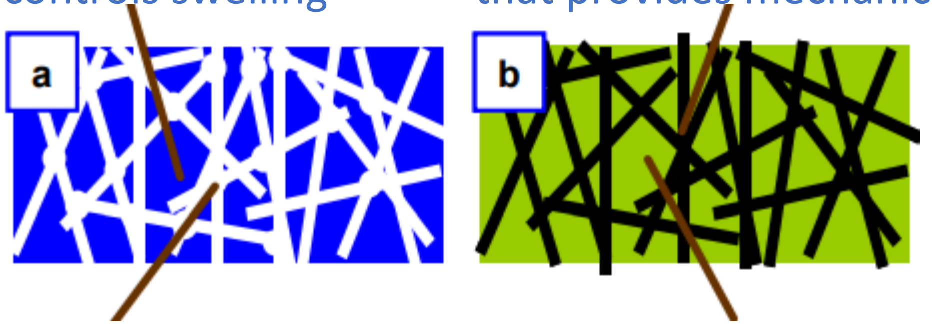
Simultaneously electrospinning dual fiber mat:
Ionomer (e.g., PFSA)
uncharged/inert polymer (e.g., polyphenylsulfone)

Mat Processing

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

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

Method 1
"Melt" uncharged polymer around ionomer nanofibers



Method 2
"Melt" ionomer around uncharged polymer nanofibers

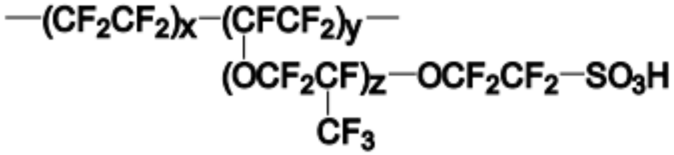
Interconnected 3-D network of ionomer nanofibers

Inter-fiber voids are filled with ionomer

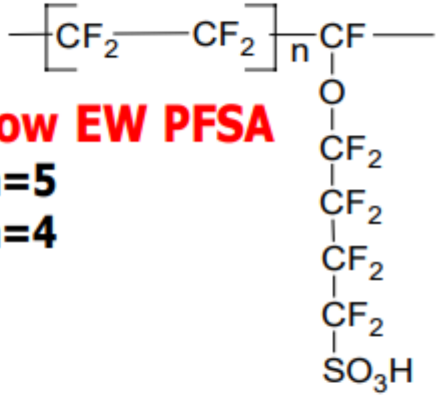
General Experimental Procedures

- Prepare electrospinning solution (polymer and solvent)
- Must add **carrier polymer** when spinning 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):



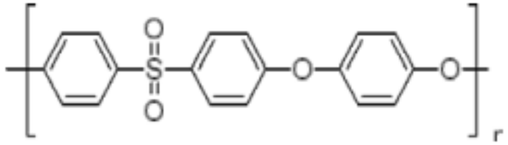
DuPont's Nafion®



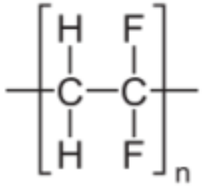
3M Co. low EW PFSA

825EW: n=5

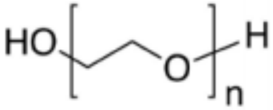
733EW: n=4



Polyphenylsulfone (PPSU)



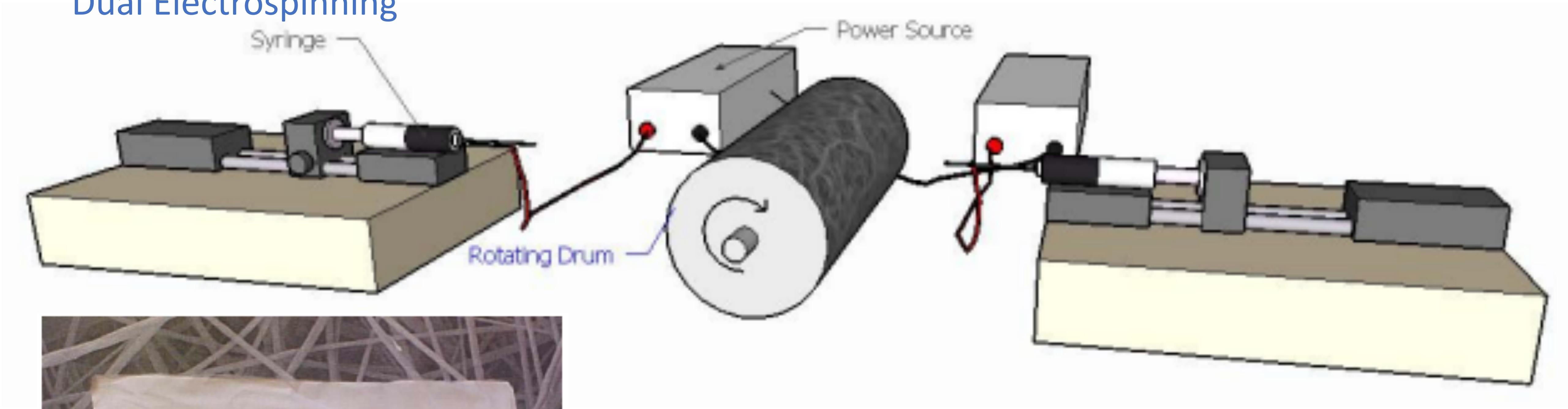
Poly(vinylidene fluoride) (PVDF)

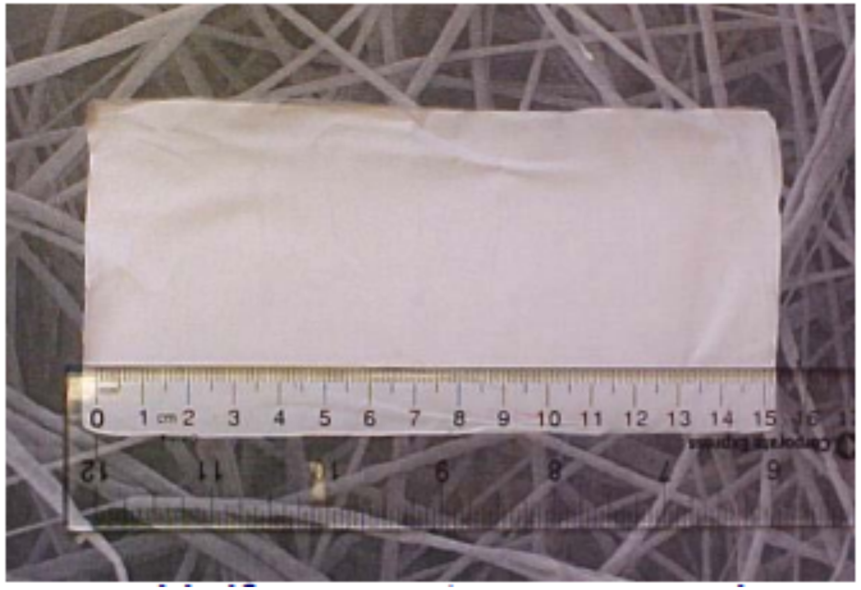


Poly(ethylene oxide) (PEO) – carrier polymer for PFSA

Electrospinning – Rotating Drum Apparatus

Dual Electrospinning



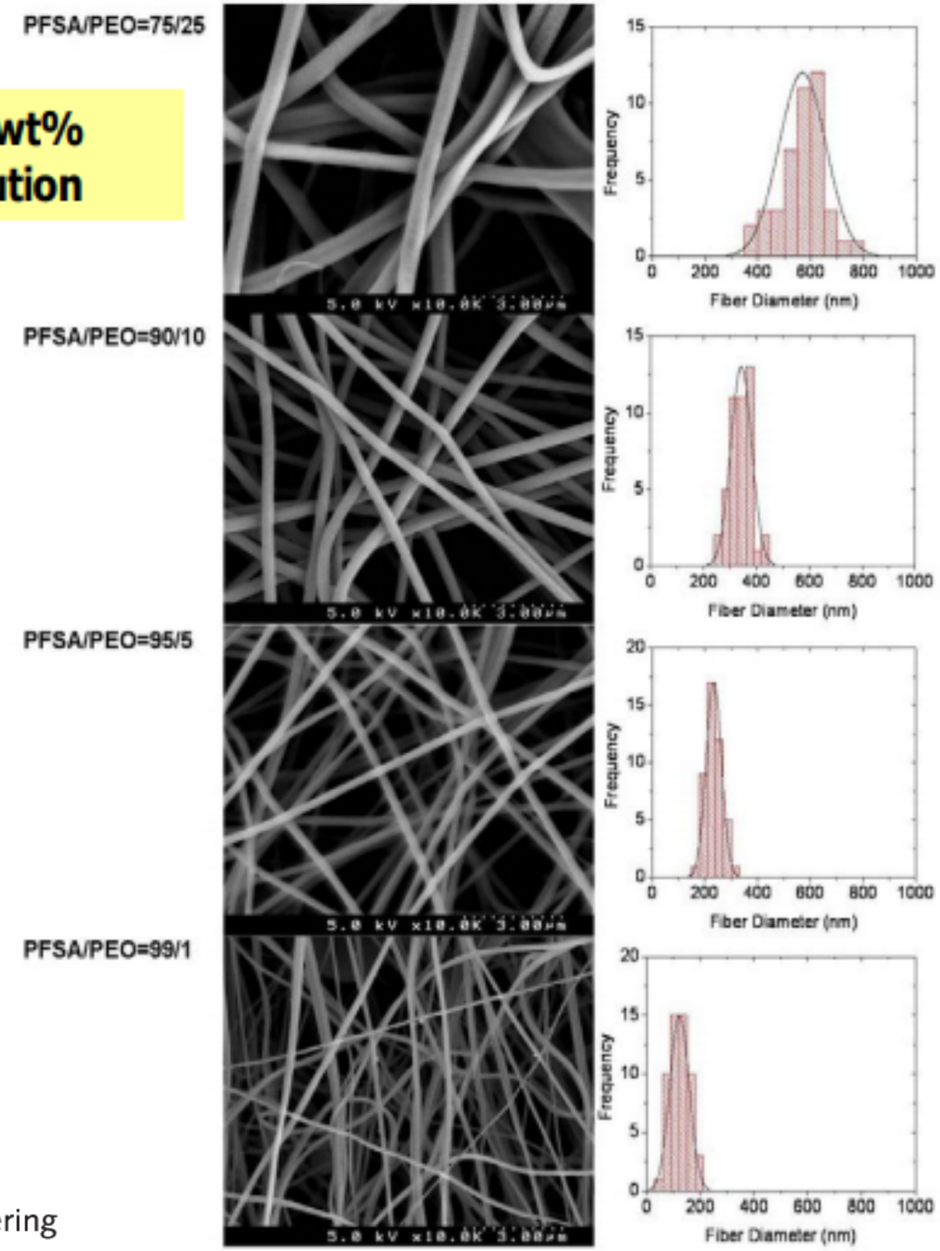


Uniform mats were made:
16 cm long, 10 cm wide; 10~120 µm thick

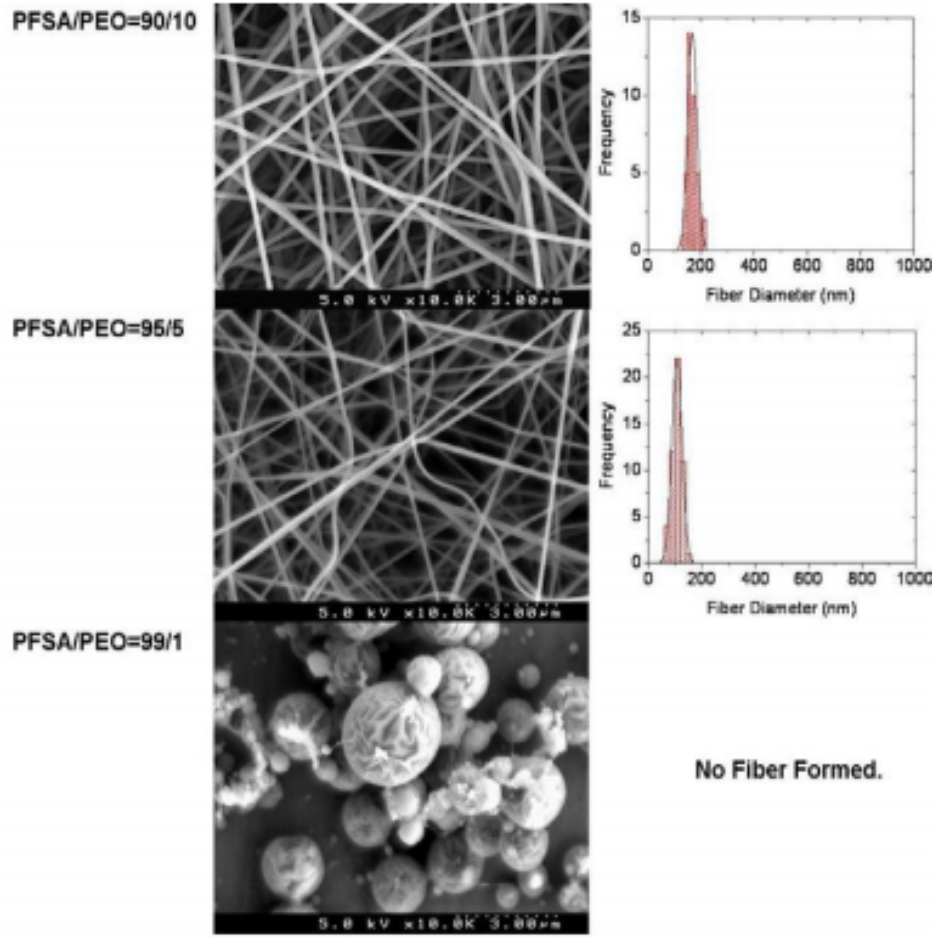
Electrospinning – Rotating Drum Apparatus

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

10 wt% solution



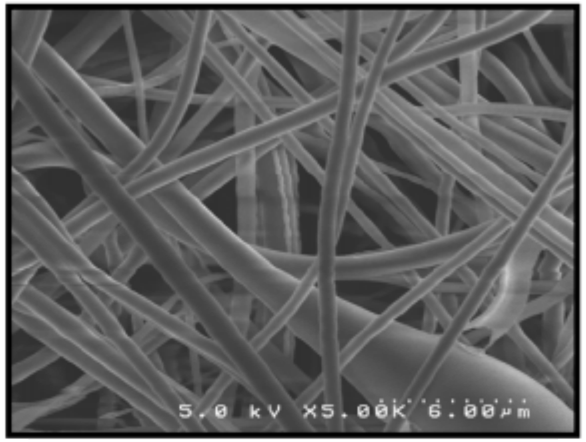
5 wt% solution



Converting Dual Nanofiber Mat into Composite Membrane: Nafion + Polyphenylsulfone

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

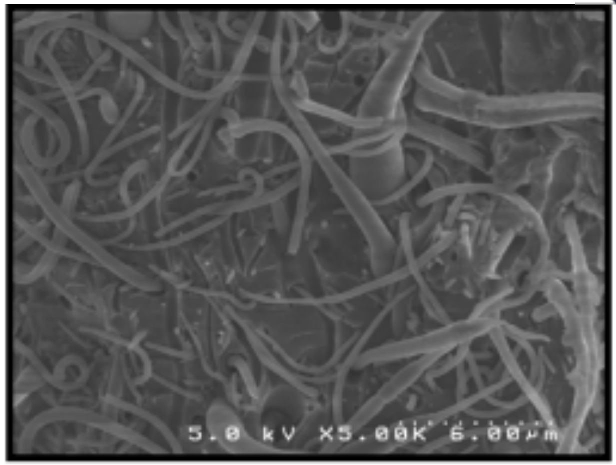


Dual fiber mat surface

PPSU flows to fill inter-fiber voids

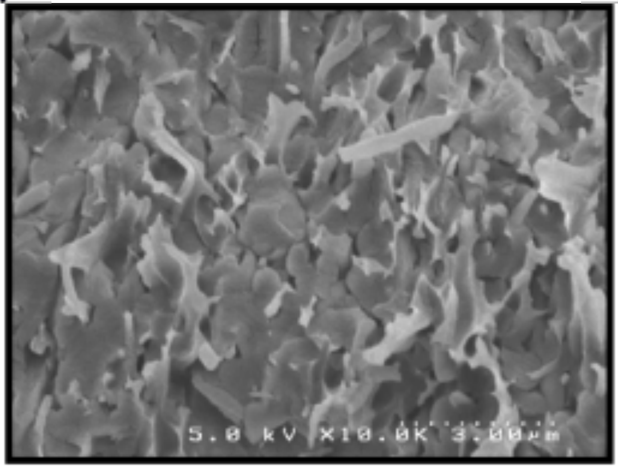
1) Cold Press (Compact) @ 1500 psi at RT, 4x 5 sec. presses
2) Chloroform Vapor Exposure (16 min. at RT)
3) Anneal (150°C for 2 hrs in vacuum)
4) Boil in 1M Sulfuric Acid
5) Boil in Water

Nafion With PPSU fibers

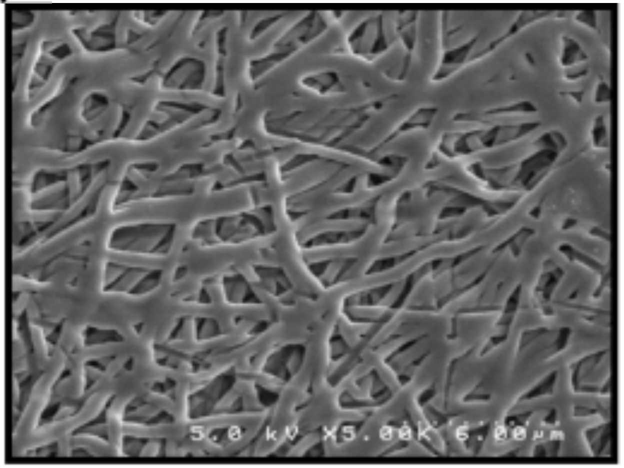


Cross section

PPSU with Nafion fibers



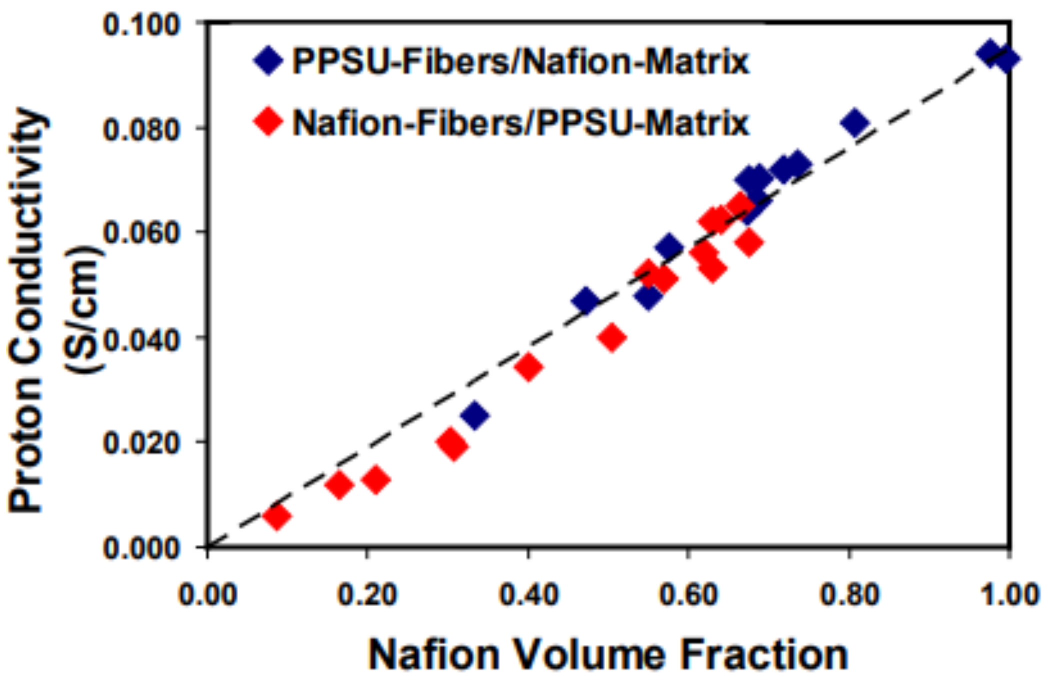
Cross section



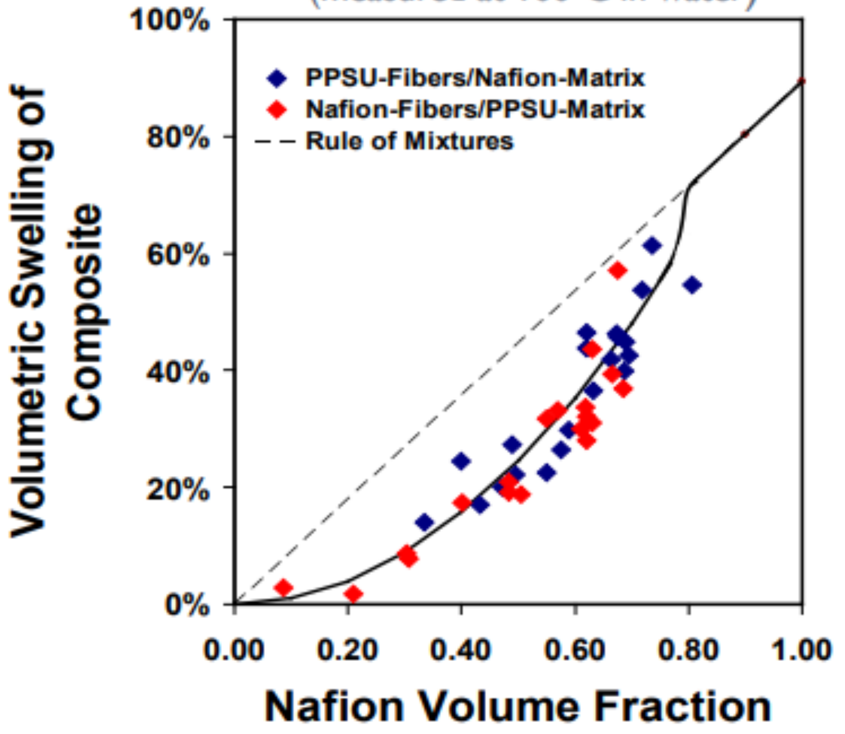
Surface after PPSU removal

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

Conductivity
(measured in 25°C in water)



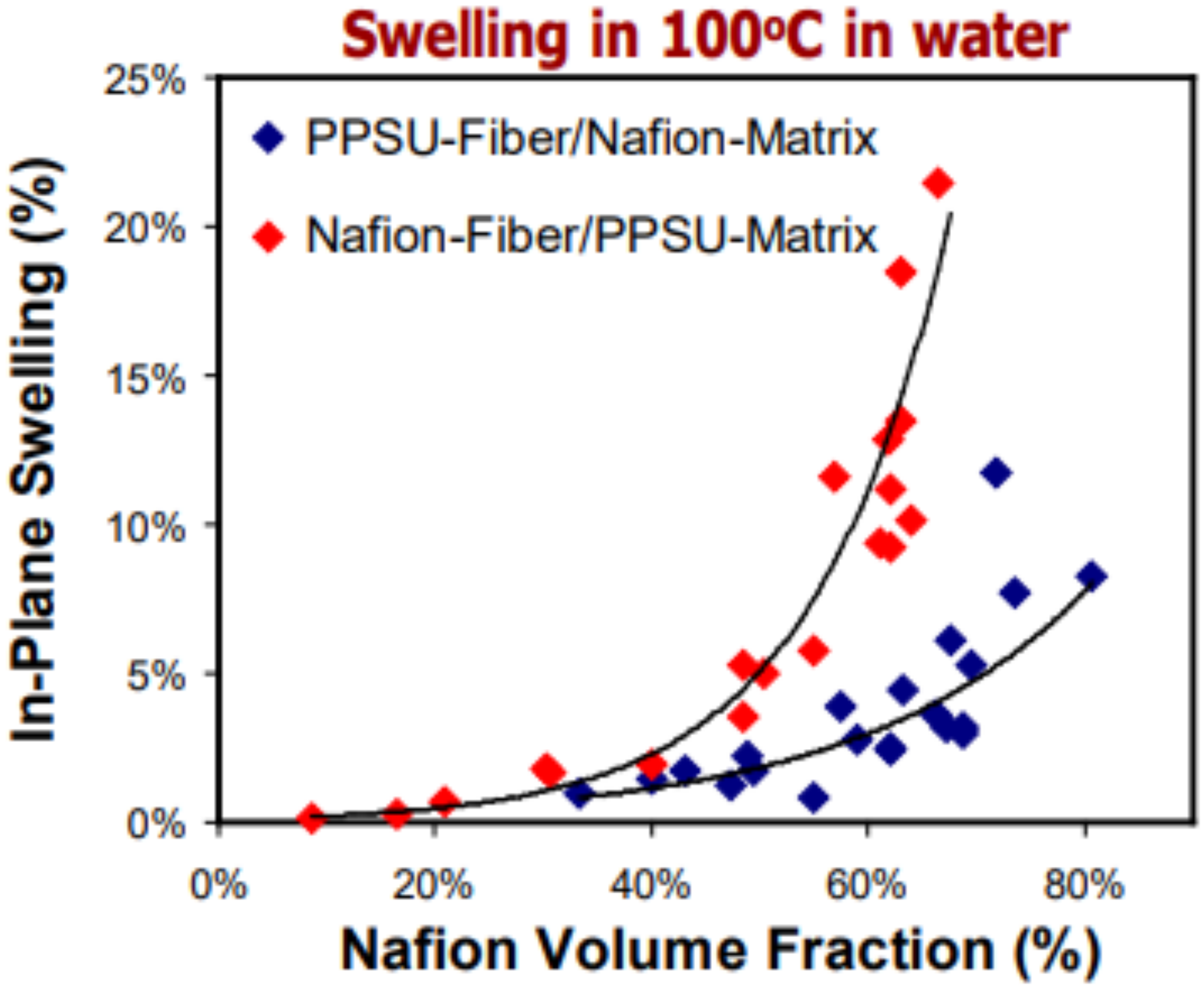
Volumetric swelling
(measured at 100°C in water)



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

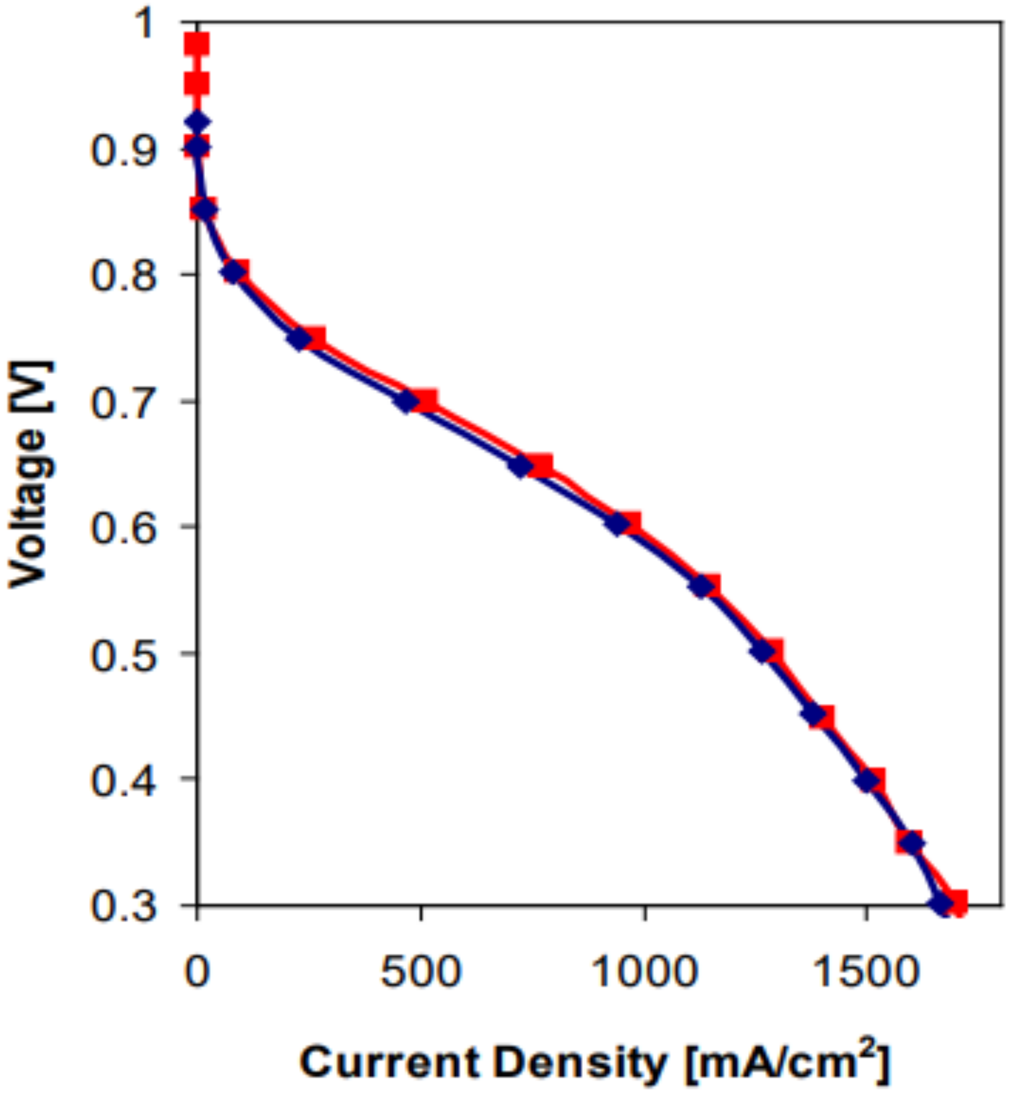
In-Plane Swelling of Nafion/PPSU Composite Membranes



- 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 PPSU Reinforcing Fiber Mat



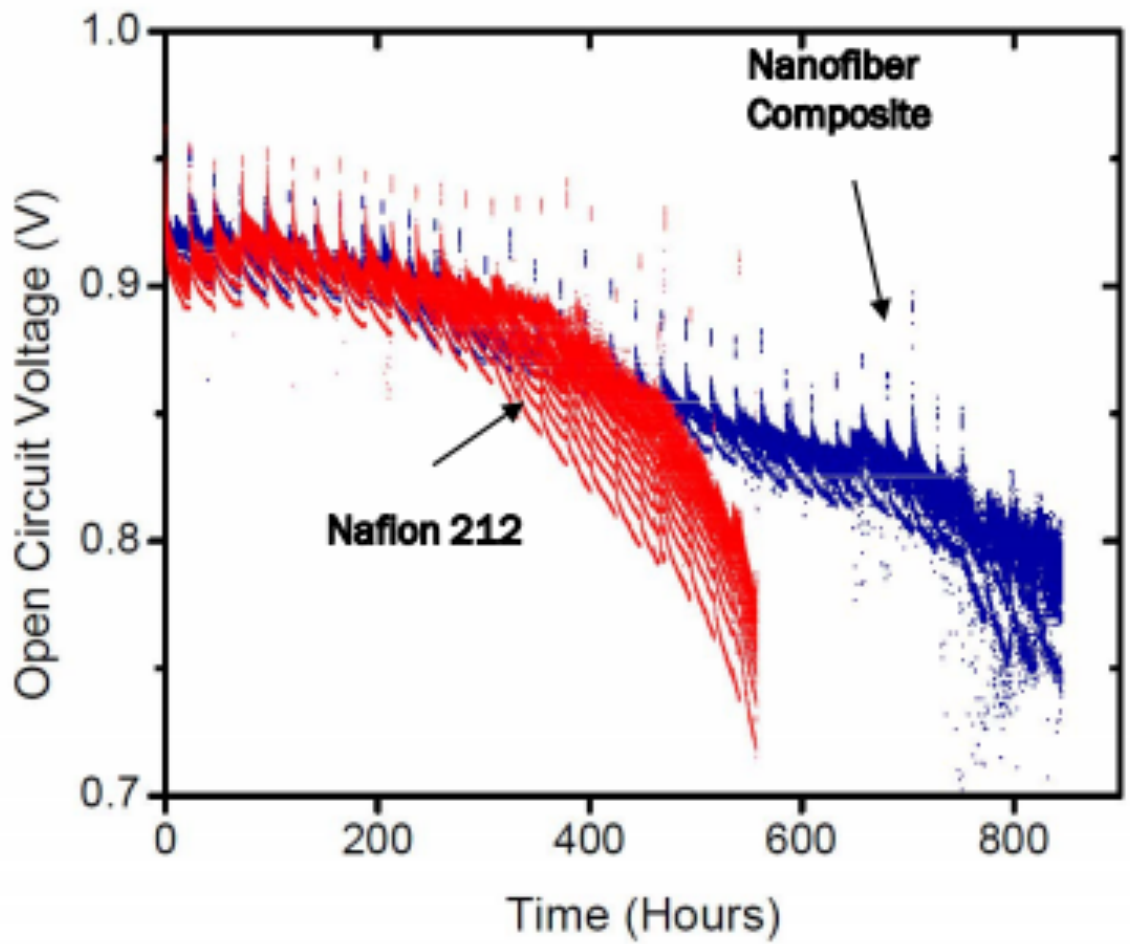
- 80°C, 100% RH
- Anode and Cathode: 0.4 mg/cm² Pt loading with 30% Nafion binder content

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 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^{o}C
- Anode and Cathode: 0.4 mg/cm^2 Pt loading with 30% Nafion binder content

Nafion 212 (51 µm)

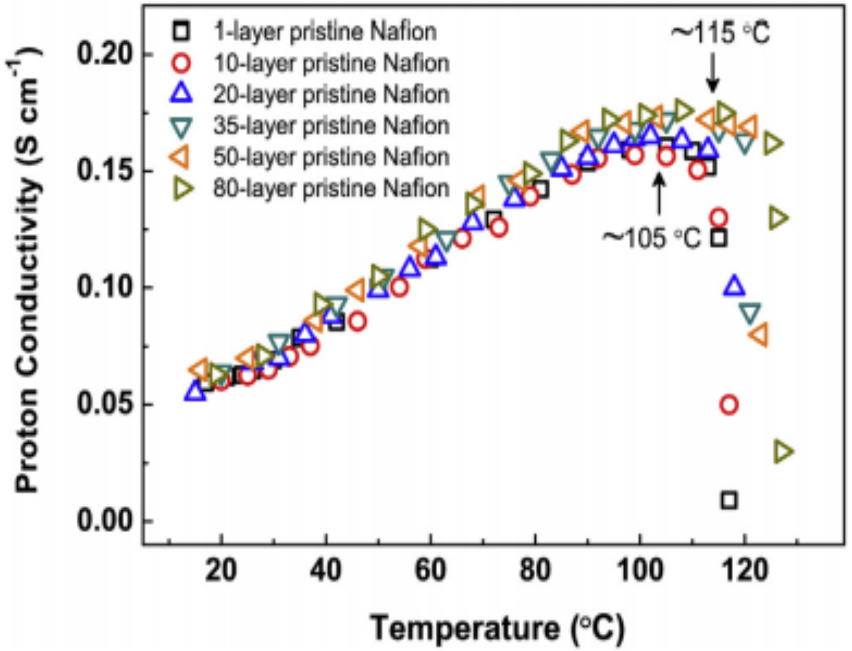
Nanofiber composite (30 µm dry thickness; Nafion with a PPSU nanofiber reinforcement mat; (~60 vol% Nafion)

Cycling: 2 minutes 100% RH H_2/Air, 2 minutes 0% RH H2/Air. 25 cm2 cell, 125 mL/min H2, 500 mL/min air flow rates

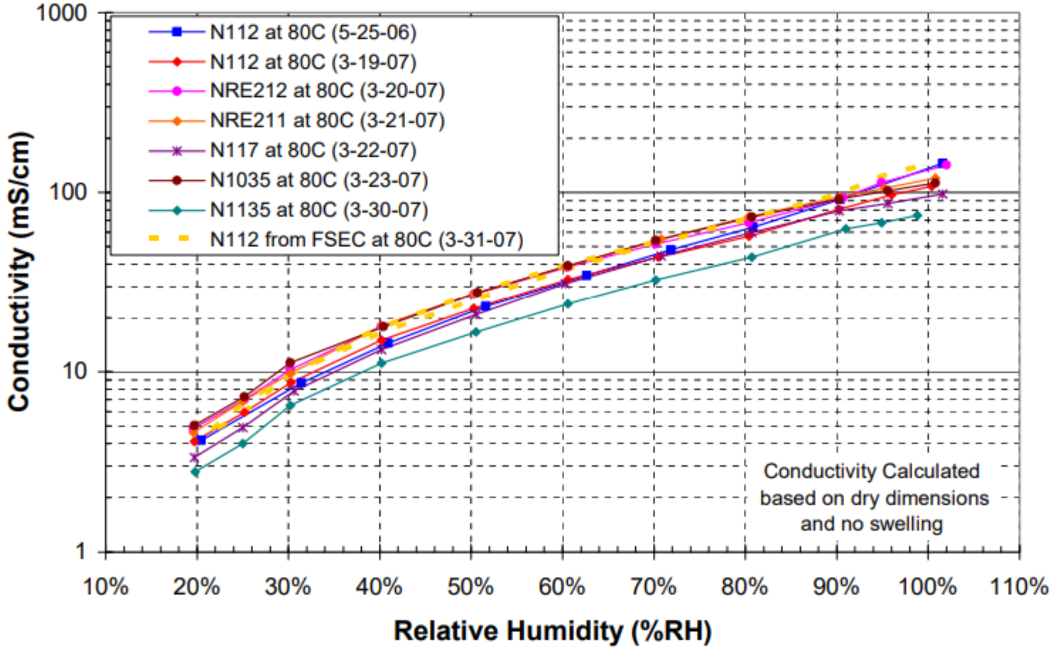
- Nafion 212 failed after 546 hours
- The Nanofiber Composite Membrane failed after 842 hour (a 54% increase in lifetime)

Nafion® Problems

Conductivity drop at high T



Conductivity drop at low RH



- Mechanical strength loss
- Environmental and health problems
- High price

Fuel cell operating condition
Present day: 80^{o}C, 100%RH

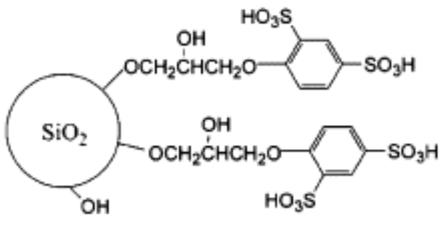
In the future: 120^{o}C, 40%RH

At high-volume production
Cost~$2000
(based on Toyota Mirai)

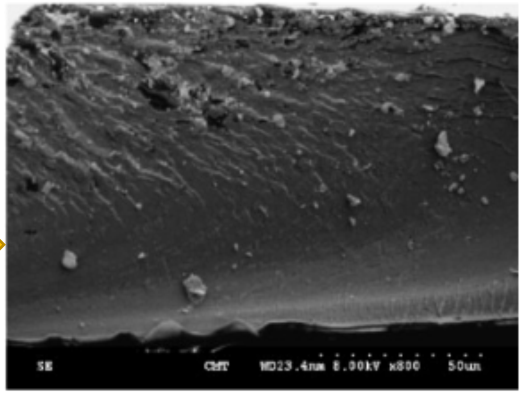
- Yin, Chongshan, et al. *Journal of Membrane Science* 591 (2019): 117356.
- Bekktech

Other People’s Work

Composite membranes: addition of hygroscopic inorganics



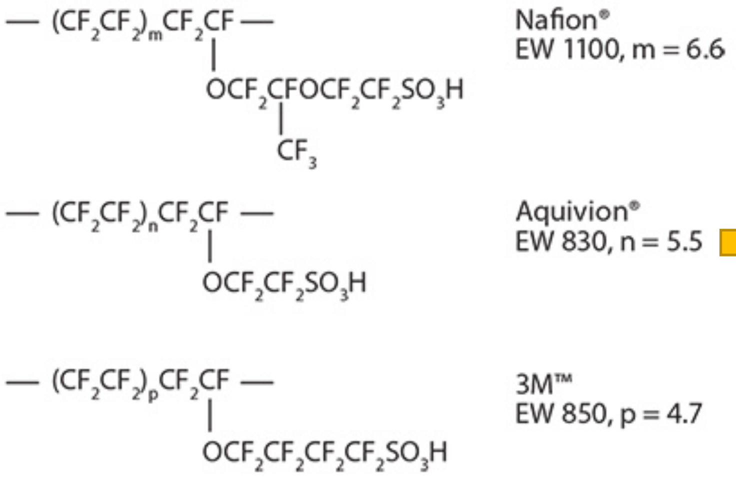
silica-SO_3H



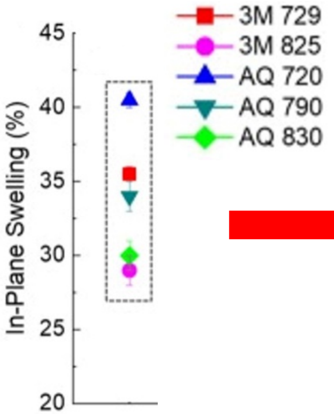
Cross-section SEM image

Problem: membrane brittle

High ion exchange capacity perfluoro-polymers



Ionomers with low EW



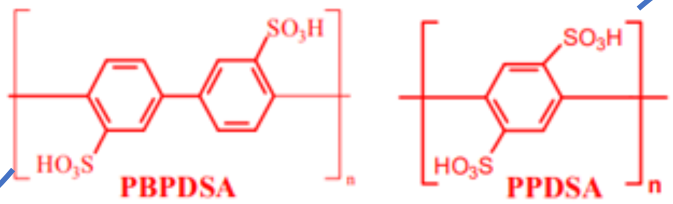
In-plane swelling

Problem: membrane swells too much in wet state

- Su, Yu-Huei, et al. *Journal of Membrane Science* 296.1-2 (2007): 21-28.
- Shin, Sung-Hee, et al. *ACS omega* 4.21 (2019): 19153-19163.

PolyPhenylene Sulfonic Acid(PPSA)

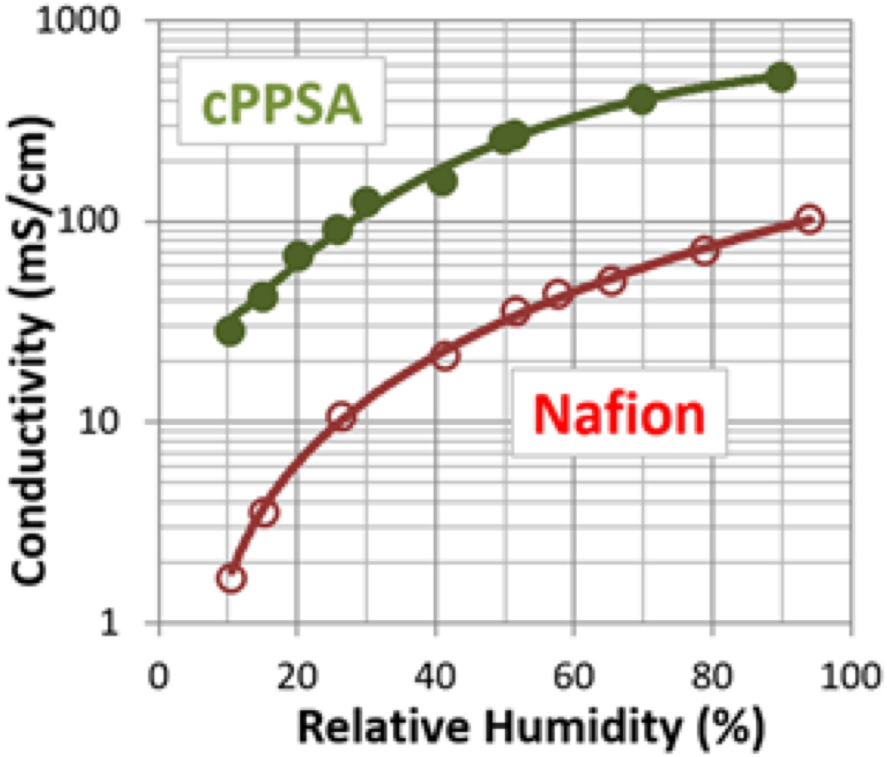
IEC:6.41mmol/g



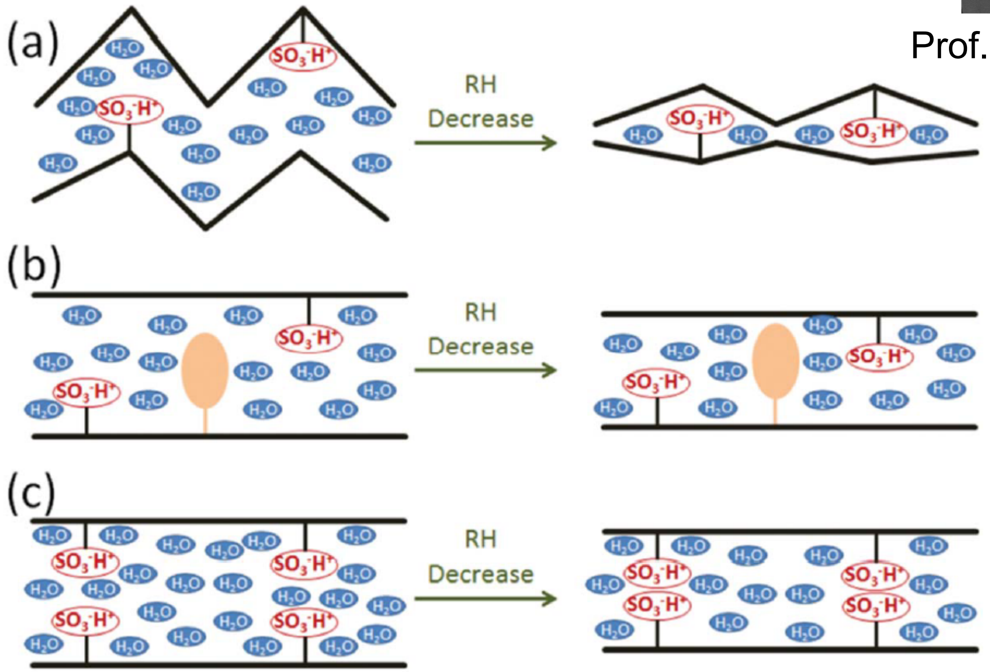
IEC: 8.47mmol/g

IEC of Nafion: 0.9mmol/g

Prof. Litt, CWRU



Conductivity of crosslinkable PPSA with Nafion



Stiff polymer that has nanopores can trap water by capillary condensation

Disadvantages: brittle in dry state and soft at higher hydration levels

- Litt, Morton, and Ryszard Wycisk. *Polymer Reviews* 55.2 (2015): 307-329.
- Litt, et al. *Macromolecules* 46.2 (2013): 422-433.

Acknowledgement

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Research Associate Professor of Chemical and Biomolecular Engineering

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U.S. DEPARTMENT OF ENERGY

Thank you!