Modified Perfluorosulfonic Acid (PFSA) Cation-Exchange Membranes

Peter N. Pintauro

Department of Chemical and Biomolecular Engineering
Vanderbilt University
Nashville, TN 37235

Objectives

- Improve membrane transport properties over standard Nafion®
- Extend practical range for the methanol feed concentration in a direct methanol fuel cell
- Improve dimensional stability and membrane mechanical properties (in the wet and dry states).
- Reduce cost of Nafion® based membranes
- Better understand the role of morphology

EXPECTED OUTCOMES – for Fuel Cells

(1) Decrease methanol crossover vs. standard Nafion

(2) Extended practical range for the methanol feed concentration in a DMFC to 5-10 M

(3) Improve High T, low RH membrane conductivity

(4) Reduced cost of Nafion based membranes ("Nafion dilution")

Nafion Modifications

1. Blends of Nafion and fluorinated polymers (Teflon-FEP, Teflon-PFA, and PVDF)
2. Nafion-PBI blends
3. Pre-stretched recast Nafion
4. Nanofiber network membranes with Nafion and low EW PFSA

Focus on fuel cell membrane properties (conductivity and water swelling)

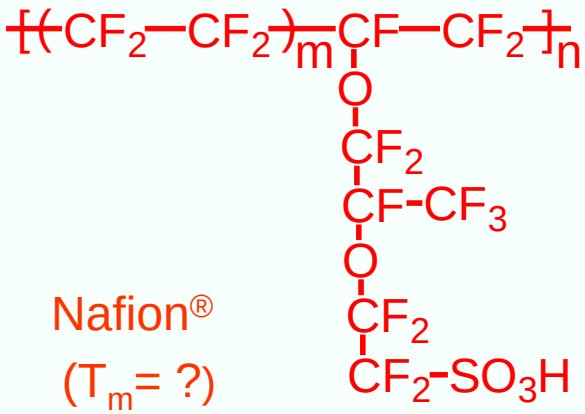
Performance in an actual fuel cell

1. Direct Methanol Fuel Cell (DMFC)
2. Hydrogen/air Fuel Cell

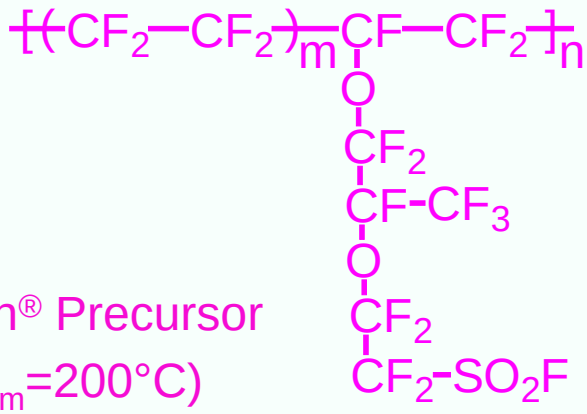
Why Modify Nafion?

- Creation of new phase with better intrinsic selectivity (high conductivity and low permeability) - miscibility or partial miscibility of polymer components is required.
- Reduction of swelling – Nafion with narrow pores is not the same as commercial Nafion (pore water dielectric constant profile can change leading to different methanol solubility)
- Improvement of dimensional stability and mechanical properties when wet and/or dry
- Increase tortuosity for methanol transport (by adding a methanol barrier component)
- Possible cost reduction (dilution of PFSA)

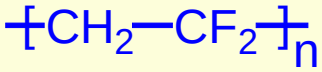
Nafion Blending – Polymer Components



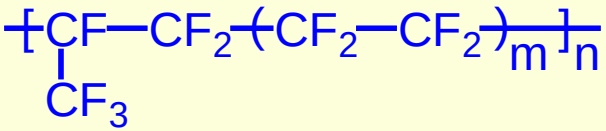
Nafion®
(T_m= ?)



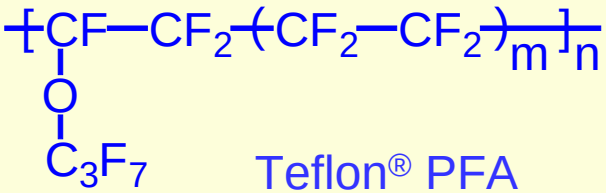
Nafion® Precursor
(T_m=200°C)



PVDF



Teflon® FEP



Teflon® PFA

Blended Membrane Fabrication

Nafion-FEP Composites

- Melt mix FEP and Nafion precursor (SO_2F form) at 300°C
- Hotpress films (25-100 µm) at 300°C and 5000 psi
- Hydrolysis of the sulfonyl fluoride groups in 15% NaOH aqueous solution at 70°C for 24-72 hours
- Sulfuric acid (1M) and water boiling for cleaning and swelling stabilization.

Nafion-PVDF Composites

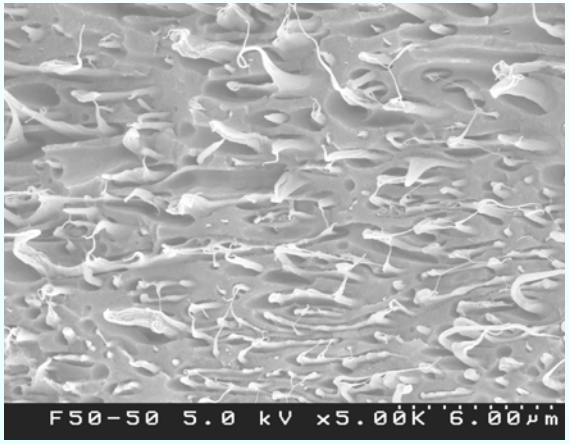
- Prepare dry Nafion by evaporating solvent from a commercial solution (Liquion 1100)
- Dissolve dry Nafion (SO_3H form), PVDF (and inorganic filler) in DMAc at room temperature.
- Spincoat a film on a silicon wafer and evaporating DMAc at 120°C. Final annealing step at 145°C for 1 hour
- Sulfuric acid (1M) and water boiling for cleaning and swelling stabilization.

Resultant membranes: 50-100 µm in thickness

BLEND MORPHOLOGY

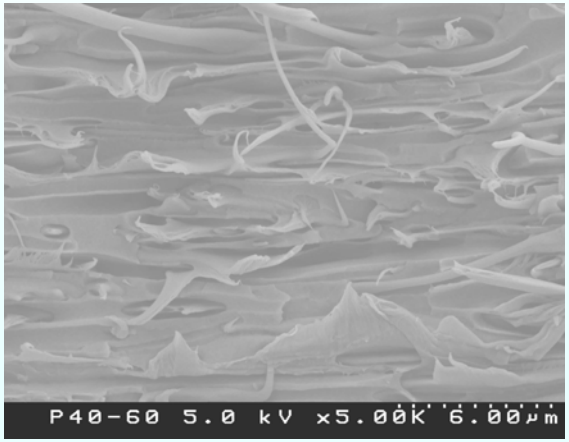
Scanning Electron Microscopy

Nafion-FEP 50-50

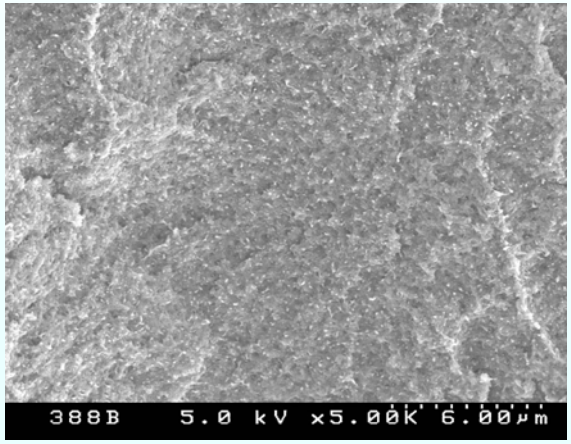


strong orientation and elongation of domains parallel to the membrane surface; large domain size (1-5 µm)

Nafion-PFA 40-60

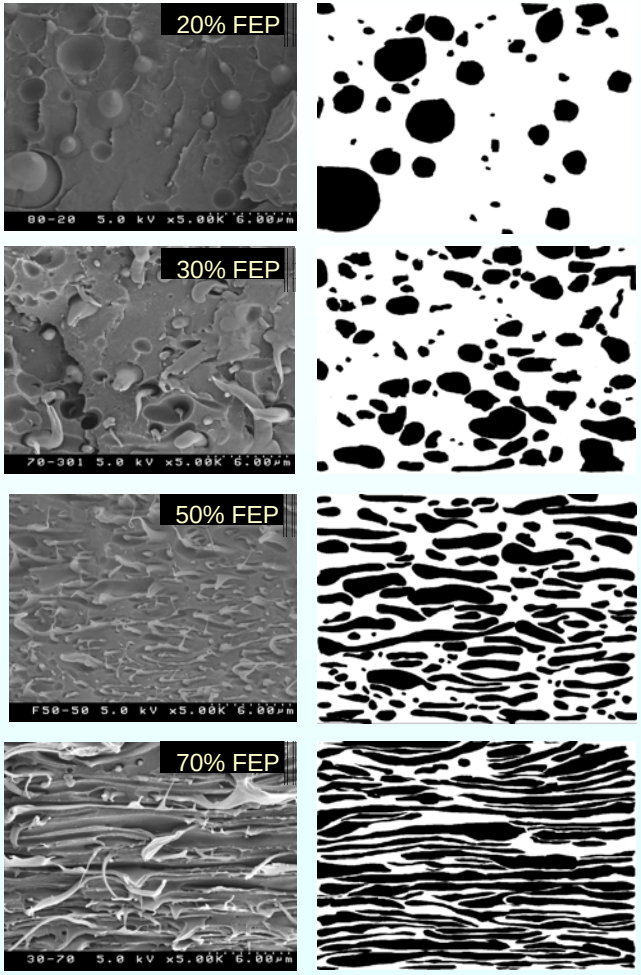


Nafion-PVDF 50-50



no orientation; much smaller domain size (< 1 µm)

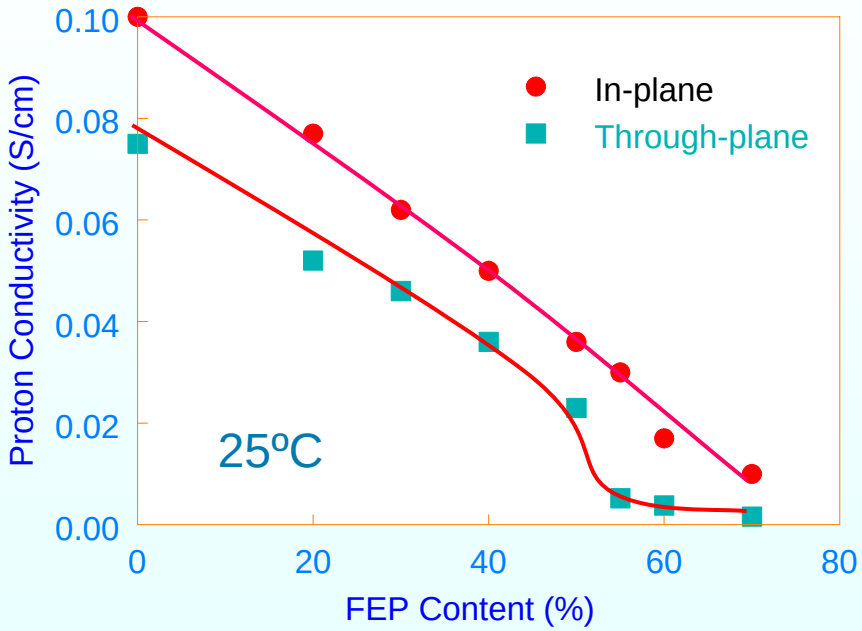
Composite Membrane Morphology

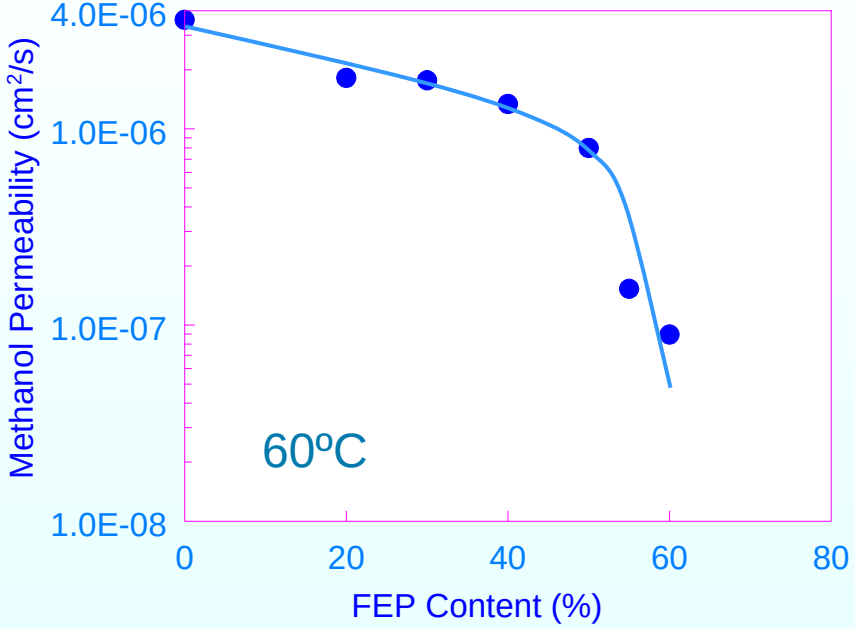


Membranes cross sections by SEM (left) and respective digitized images (right). Transition from spherical to elongated and flake-like domains can be observed.

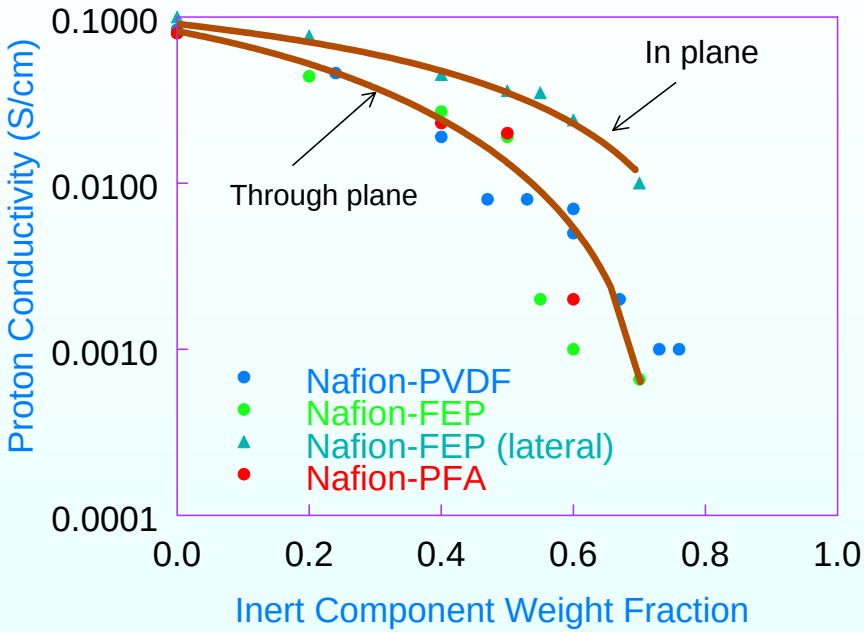
Nafion-FEP blends – Effect of FEP loading

PROPERTIES OF NAFION-FEP MEMBRANES

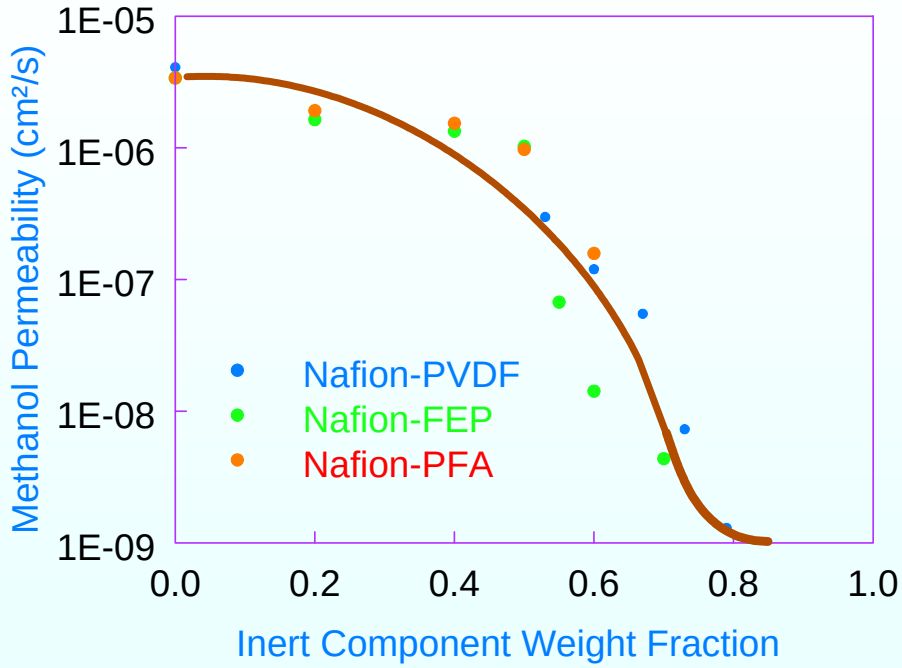




Properties of Nafion-Teflon and Nafion-PVDF Membranes



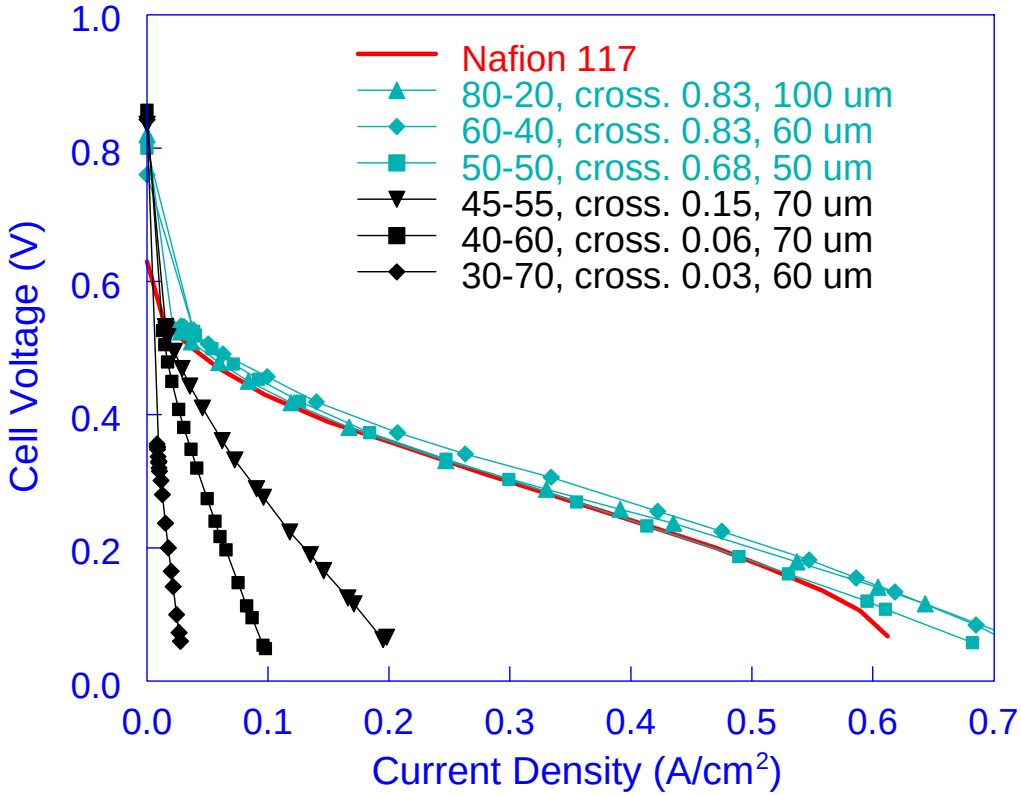
Conductivity at 25ºC in water



Permeability at 60ºC and 1.0M methanol

Fuel Cell Performance – Nafion/FEP Blends

1.0 M methanol, 60^0C, humidified air at 500 sccm and 1.0 atm.

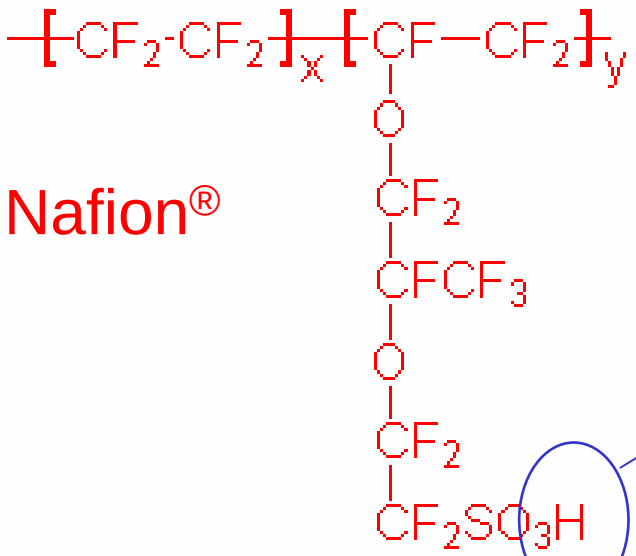


Membranes containing ≥ 50% Nafion show good electrochemical performance.

Crossover with a 50-50 membrane was 1.5x lower than that with Nafion 117.

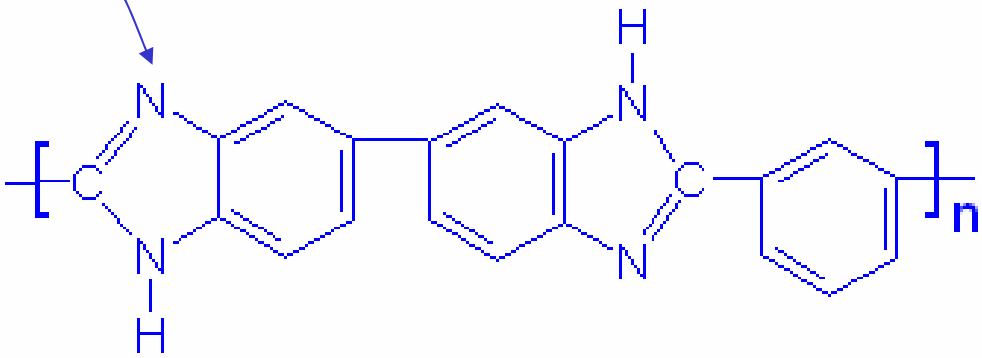
6-9 times less Nafion required (cost reduction) as compared to Nafion 117. Very convenient melt-processing used.

NAFION-PBI SYSTEM



Nafion®

ACID-BASE COMPLEX (IONIC AND HYDROGEN BONDING)

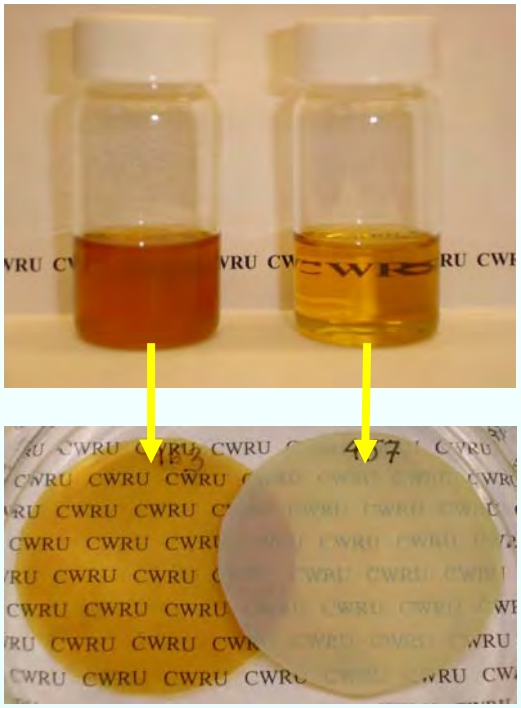


Polybenzimidazole

NAFION-PBI FABRICATION PROCEDURE

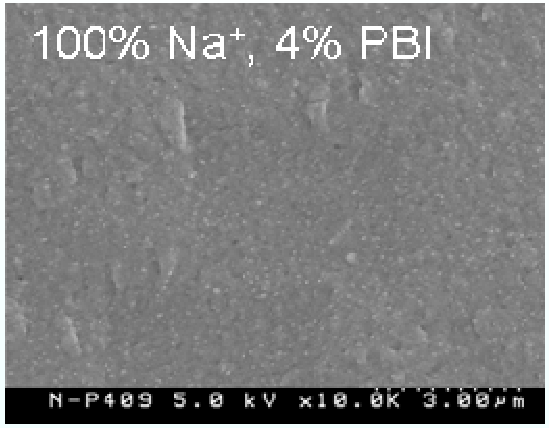
- Evaporation of solvent from commercial Nafion solution (Liquion 1100)
- Ion-exchange to adjust H^+/Na^+ ratio in the Nafion
- Dissolution of the exchanged Nafion and PBI in dimethylacetamide (DMAc)
- Casting membrane into glass dish, DMAc evaporation at 60°C overnight, and annealing at 150°C for 3 hours
- Treating the membranes with boiling 1M H_2SO_4 and then water to achieve full protonation and swelling stabilization.

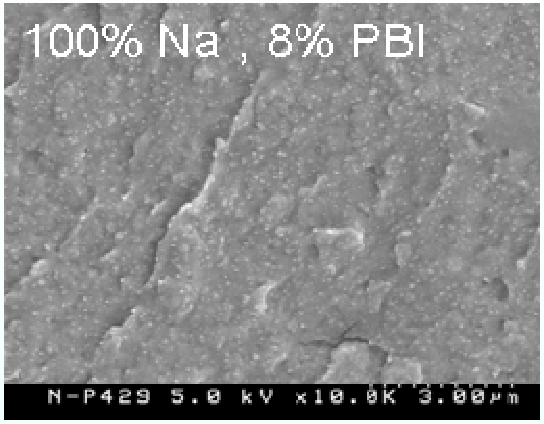
NAFION-PBI MEMBRANES

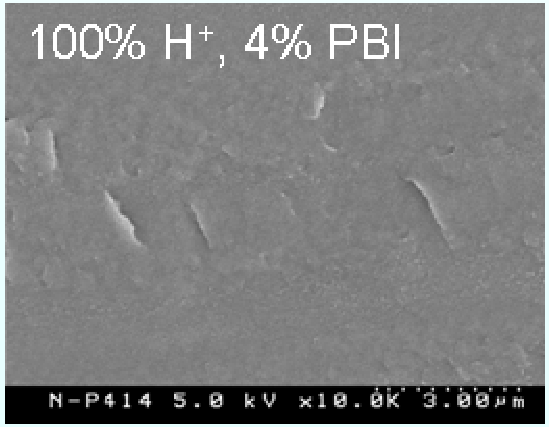


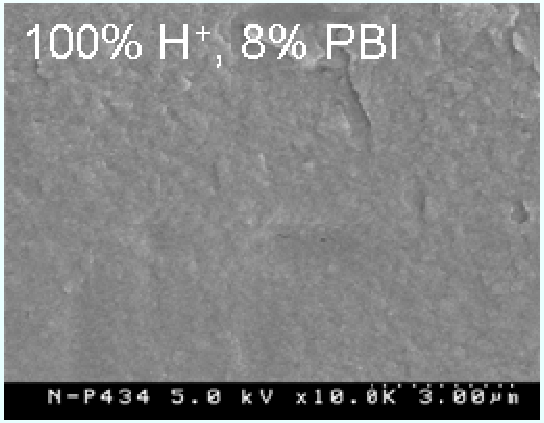
- Fully protonated Nafion/PBI
  - suspension in DMAc
  - clear, strong film (after solvent evaporation and annealing)
- Fully Na-exchanged Nafion/PBI
  - clear DMAc solution
  - translucent or opaque, elastic film (after solvent evaporation and annealing)

NAFION-PBI MEMBRANES





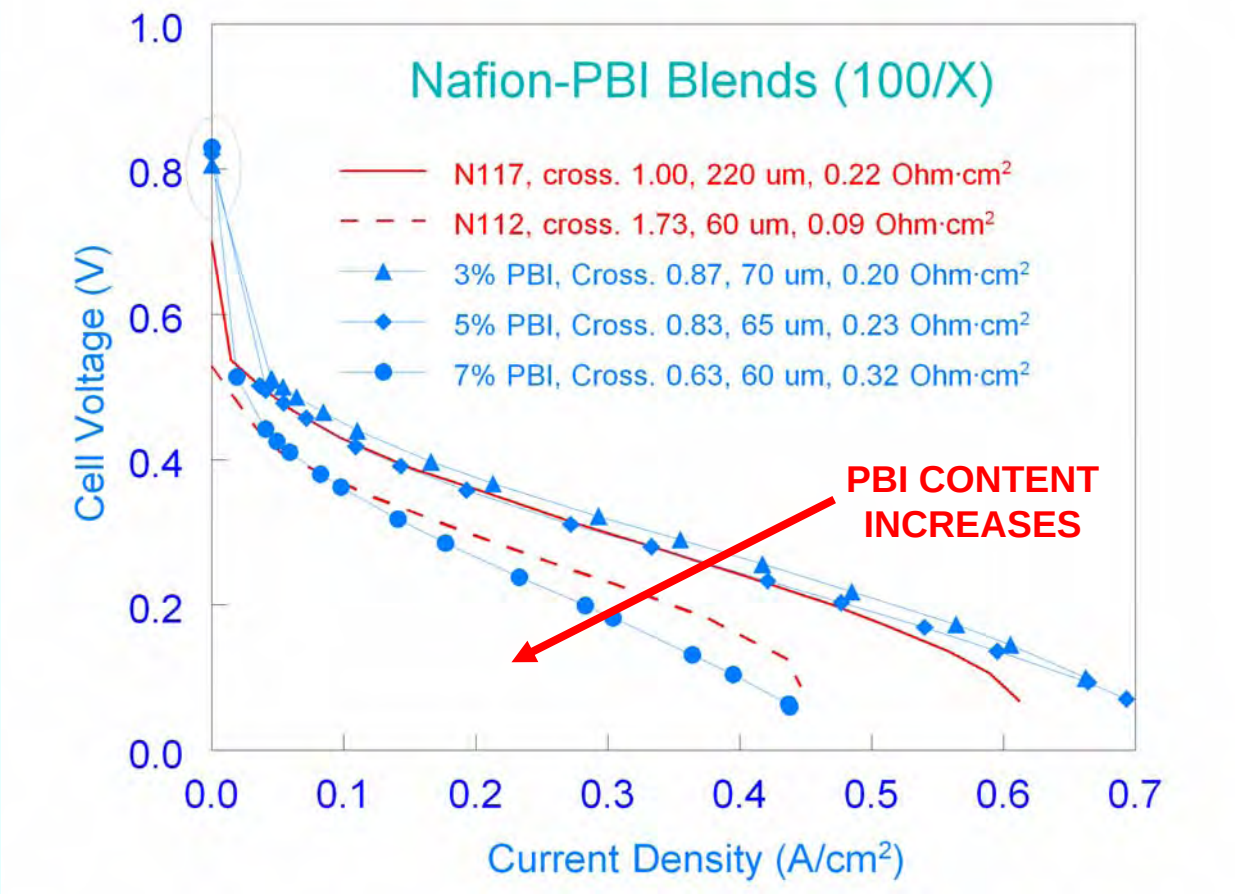




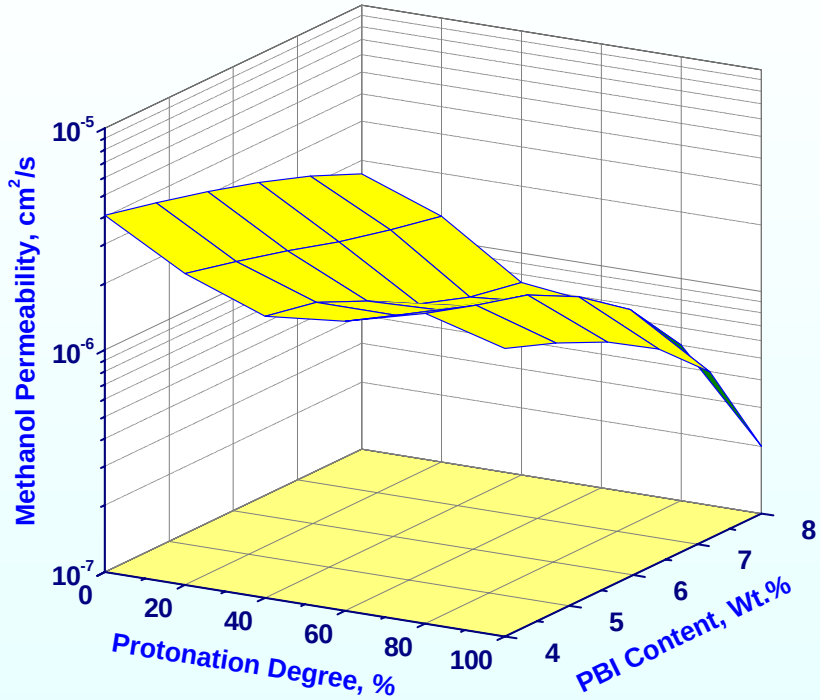
Spherical domains observed in membranes recast from blends of fully Na^+ exchanged Nafion and PBI. This was indicative of limited miscibility in that formulation.

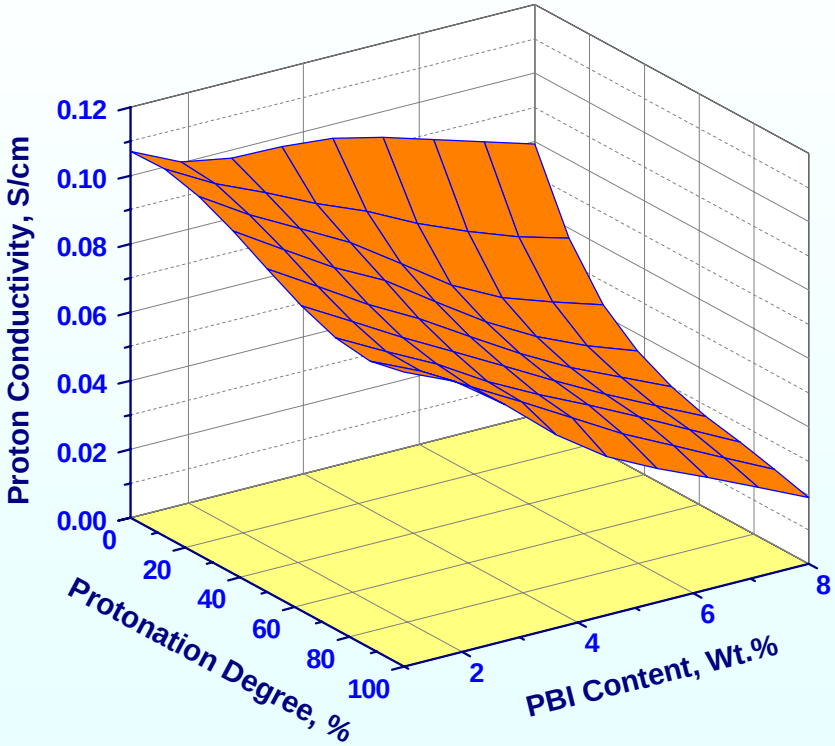
DMFC TESTS

EFFECT OF PBI CONTENT



NAFION-PBI Conductivity/MeOH Permeability





Methanol Permeability

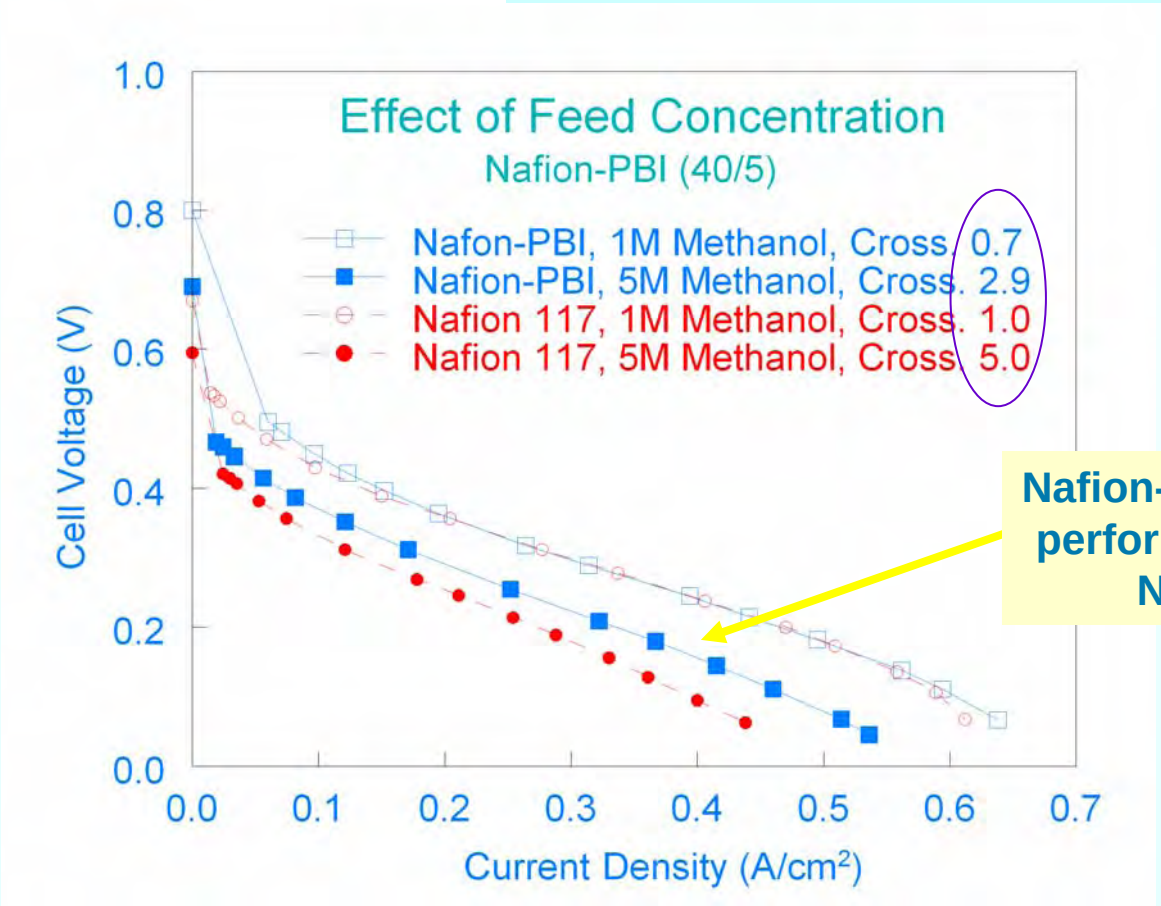
(1M Methanol vs. Water @60ºC)

Proton conductivity

(Water swollen samples @RT)

DMFC TESTS

EFFECT OF METHANOL CONCENTRATION



Nafion-PBI membrane performs better than Nafion 117

SUMMARY – Nafion-PBI Blends

1. Nafion-PBI membranes were prepared by solution casting. Prior to dissolution, the sulfonic groups of Nafion component were partially exchanged with sodium ions.
2. Best DMFC performance was obtained with membranes prepared from Nafion exchanged with 0-60% sodium and containing 3-6% PBI.
3. Nafion-PBI membranes showed improved resistance to higher methanol concentration.
4. Blended membranes required 2-4 times less Nafion to prepare MEA with DMFC performance equivalent or better than that with Nafion 117.

Pre-stretched Recast Nafion

Our Concept: **By stretching a Nafion membrane, it may be possible to preferentially orient ionic clusters and/or change the polymer crystalline to improve membrane properties.**

Preparation

1. **Prepare a Nafion solution: Mix Nafion powder with dimethylacetamide (10 wt% solution) and cast a film into a Teflon dish. Partially evaporate the solvent at 60°C.**
    a. **For thin final films (30-60 µm) - remove ~85% of the solvent.**
    b. **For thick final films (130-190 µm) - remove ~85% of the solvent and then re-equilibrate the film in a DMAc atmosphere.**

2. **Heat the film to 125°C and then uniaxially stretch the film to the desired draw ratio.**

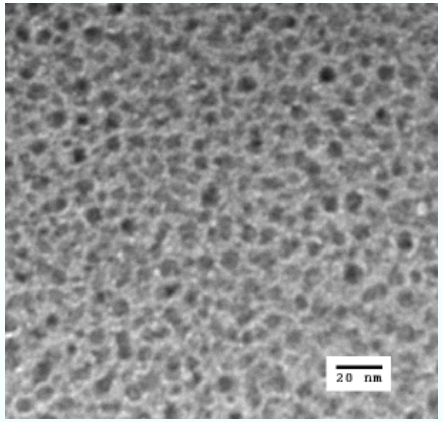
3. **Keep the film stretched at 125°C for 1 hour to fully evaporate solvent.**

4. **Anneal the stretched film, under tension, at 150°C for 2 hours.**

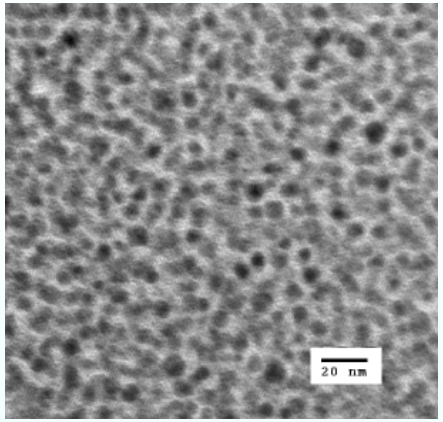
5. **Boil the membrane in 1.0 M H_sSO_4 for 1 hour and then boil in water. Store membranes in room temperature water. Wet membrane thickness was 30-150 µm.**

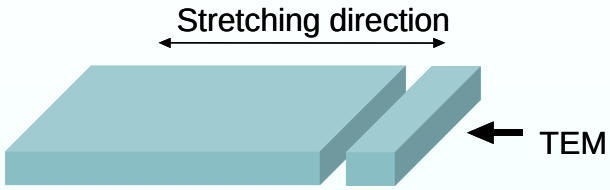
Transmission Electron Microscopy

Non-stretched

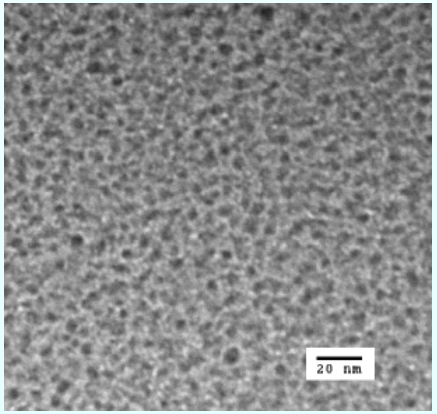


draw ratio 2

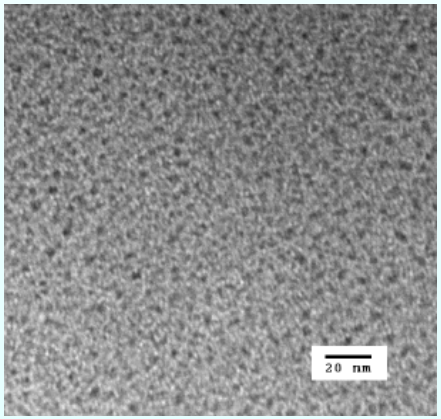




draw ratio 4



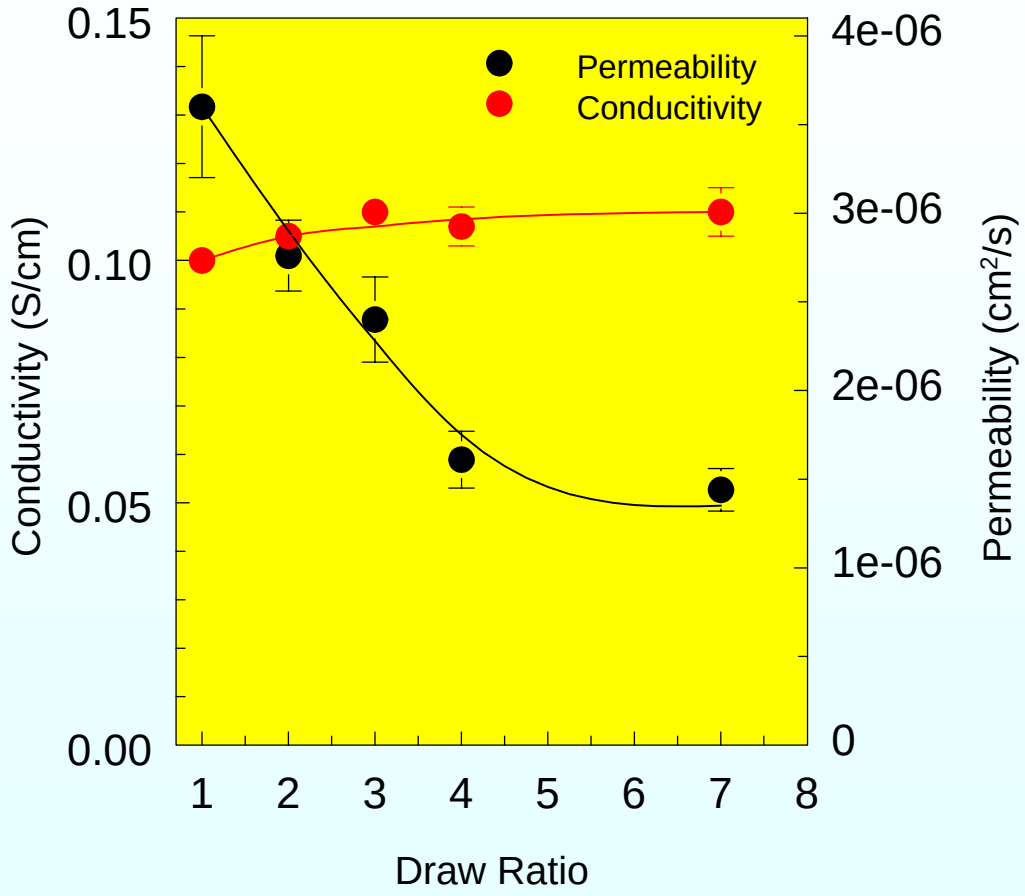
draw ratio 7



There is an increase in the number of ionic domains and a decrease in the size of the domains with stretching.

Dr. K. Shi, Inst. for Fuel Cell Innovation, National Research Council Canada, Vancouver, BC

Proton Conductivity and Methanol Permeability – Effect of Draw Ratio



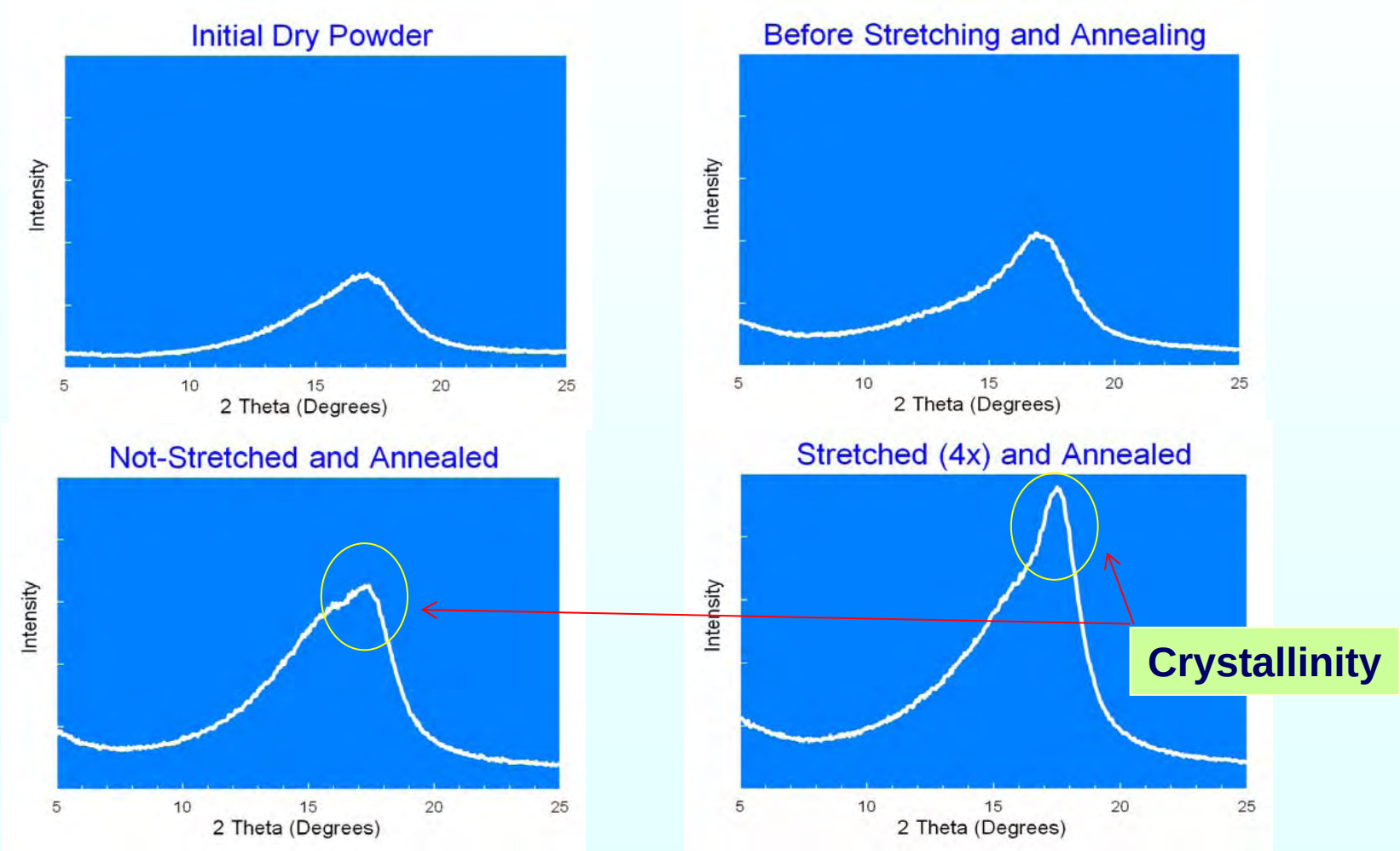
Through-plane conductivity of membranes immersed in water at 25°C.

Methanol permeability at 1.0 M MeOH at 60°C

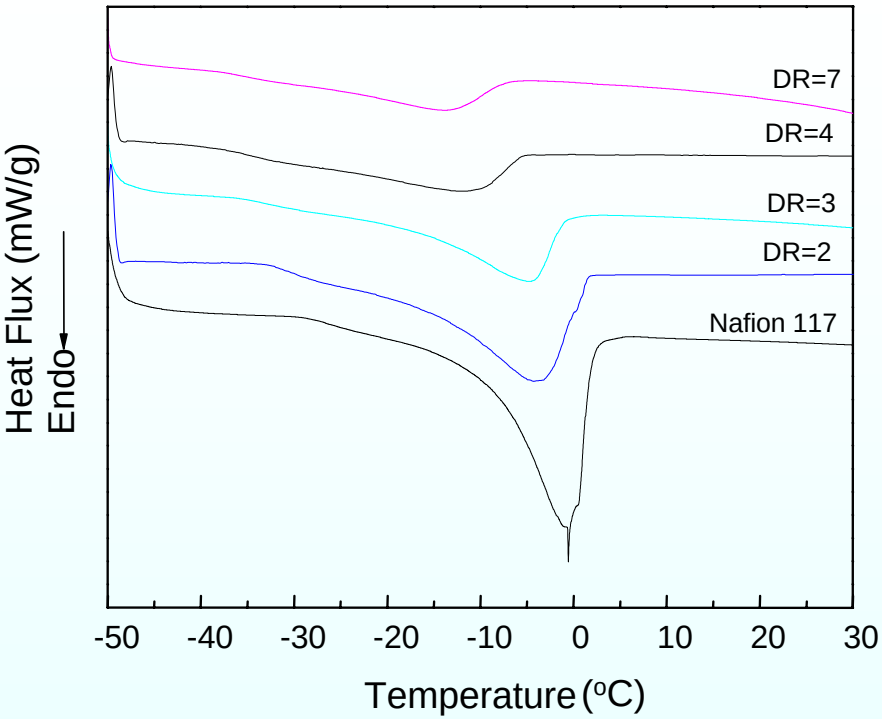
The only membrane where there is no change in proton conductivity when the methanol permeability is lowered.

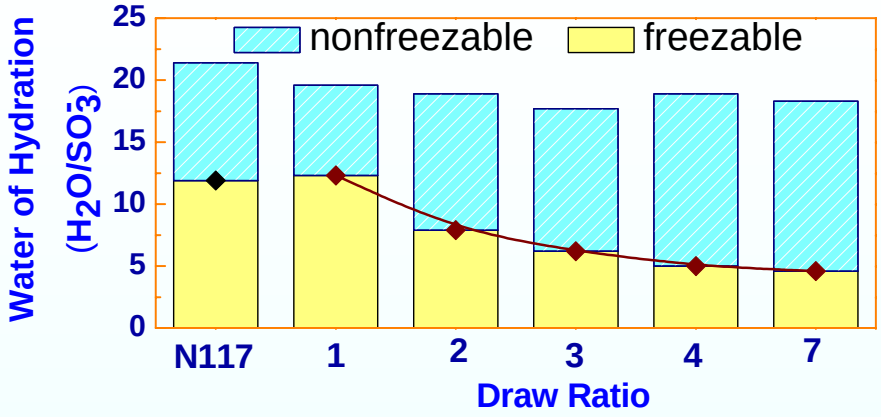
Wide-Angle X-Ray Scattering

All the measurements were performed in the reflection mode with the X-ray beam parallel to the stretching direction.

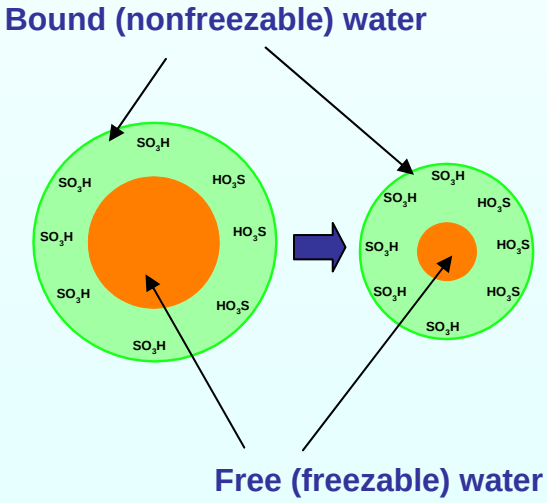


Low Temperature Differential Scanning Calorimetry





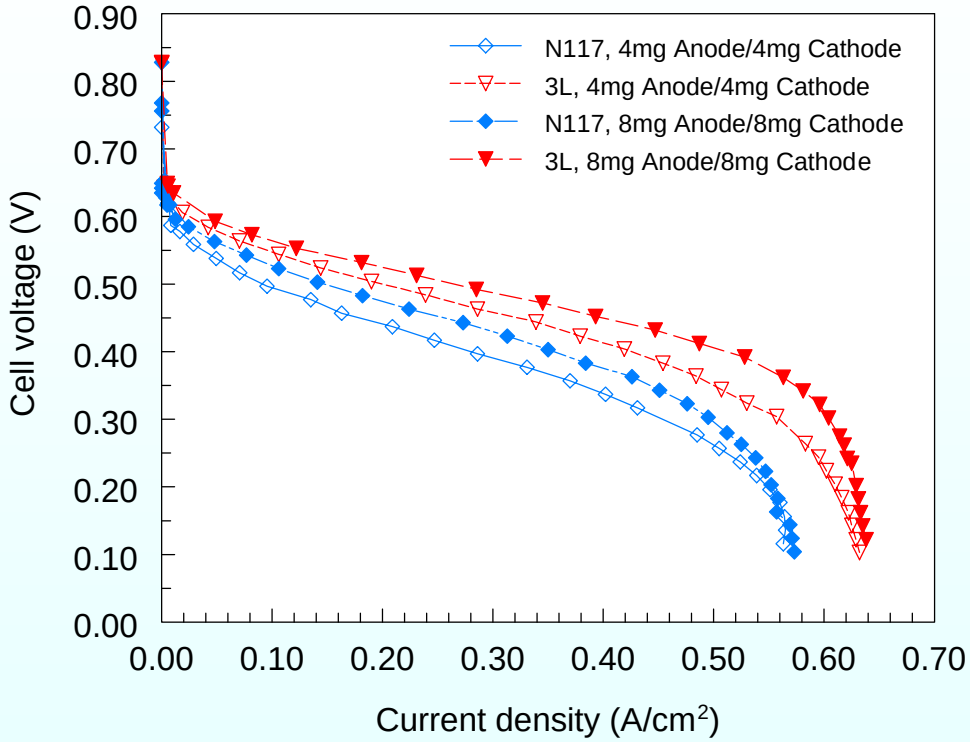
ΔH_f = 334 J/g (bulk free water), DSC heating rate: 5°C/min



With an increase in draw ratio, the amount of freezable water decreases – indicating a decrease in the size (diameter) of water-filled pores in stretched Nafion.

Fuel Cell Performance of Pre-Stretched Recast Nafion at 80°C

1M Methanol, 500 sccm air at 1 atm. (3 layers of stretched recast Nafion with a draw ratio of 4, total membrane thickness of 185 µm)



Improved fuel cell performance due to the combination of lower areal resistance and low methanol crossover.

Power Density (mW/cm^2) at 0.4V	N117	3-layer Stretched
4 mg/cm^2 anode and 4 mg/cm^2 cathode	112	168
8 mg/cm^2 anode and 8 mg/cm^2 cathode	137	206

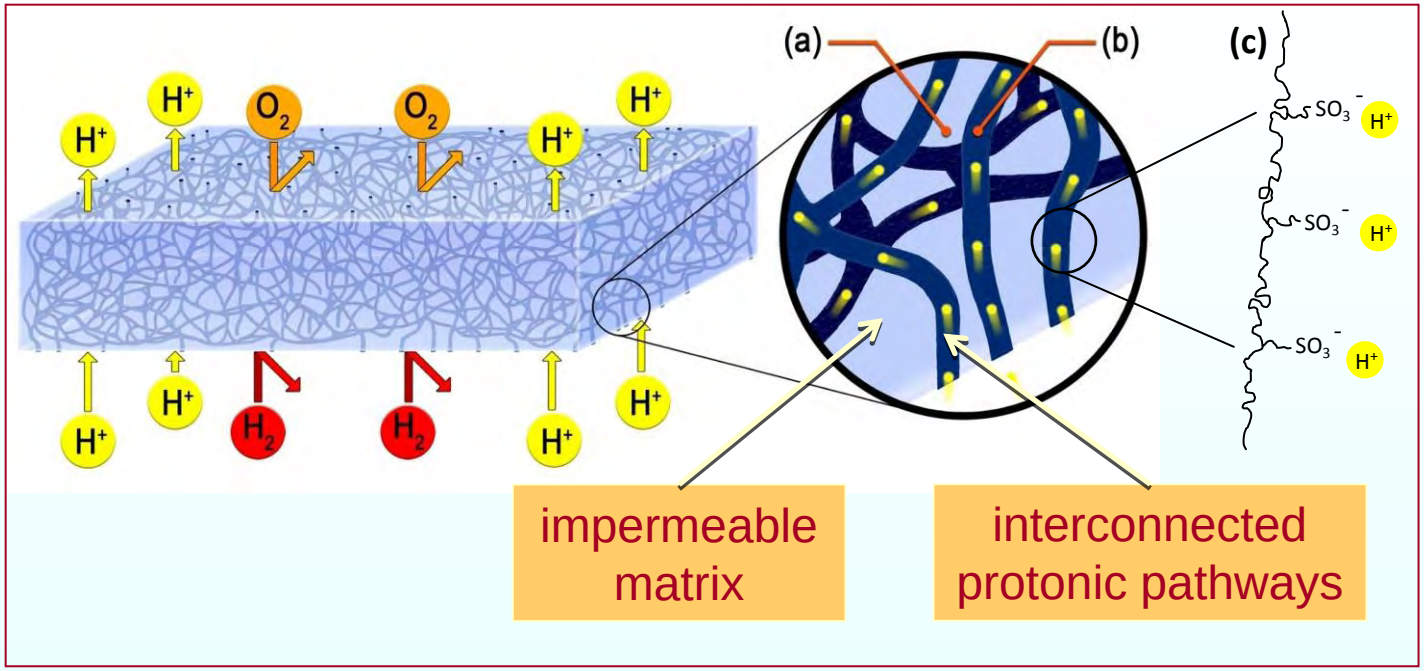
A Preliminary Picture of Pre-Stretched Nafion Nanomorphology

- **From WAXS, there is an increase in polymer crystalline with stretching –** but the increase in crystalline does not change the water swelling properties of the membrane.
- **There is less free (freezable) water in stretched Nafion –** pores have a smaller diameter; less rotational motion of water molecules indicating greater water binding/interactions and locally higher water viscosity (spin lattice relaxation time results); electro-osmotic drag of water with migrating protons is reduced.
- **The total water uptake in stretched recast Nafion and Nafion 117 is the same –** there must be a greater number of smaller diameter pores in stretched Nafion.
- **The water self diffusion coefficient and proton conductivity in stretched Nafion and Nafion 117 is the same –** maybe more pores and less pore tortuosity in stretched Nafion; proton conduction by Grotthus and vehicle mechanisms.
- **Why is stretched recast Nafion less permeable to methanol?** lower solubility of methanol in the stretched films or smaller mutual diffusion coefficient

Conclusions

- Pre-stretched Nafion possess a new (and permanent) nano-morphology with unique properties.
  - A greater number of smaller ionic/hydrophilic domains
  - Less freezable (and more non-freezable) water
  - Less methanol sorption, with no change in proton conductivity
  - A higher crystallinity (~25% vs. ~15%) and improved mechanical properties
  - A modest increase in the α-transition temperature
  - A low electro-osmotic drag coefficient (2.3 vs. 2.9 for commercial Nafion)
- In a methanol fuel cell: 50% high power densities with pre-stretched Nafion.
  - The area-specific resistance and methanol crossover of pre-stretched Nafion (draw ratio of 4) <u>are both</u> lower than in commercial Nafion

Nafion-Based Nanofiber Composite Membranes



The electrospun sulfonated polymer nanofibers are interconnected by fiber welding and the inter-fiber spaces are filled with a non-conducting, gas impermeable polymer.

ADVANTAGES OF THE PROPOSED STRUCTURE

1) Decoupling of mechanical and proton-conducting functions of the membrane

2) Removal of percolative problems of the classical blended/composite systems

3) Independent control of both: the size and the loading of the proton-conducting phase

4) High IEC polymers that are brittle and swell excessively in water can be utilized for the fibers

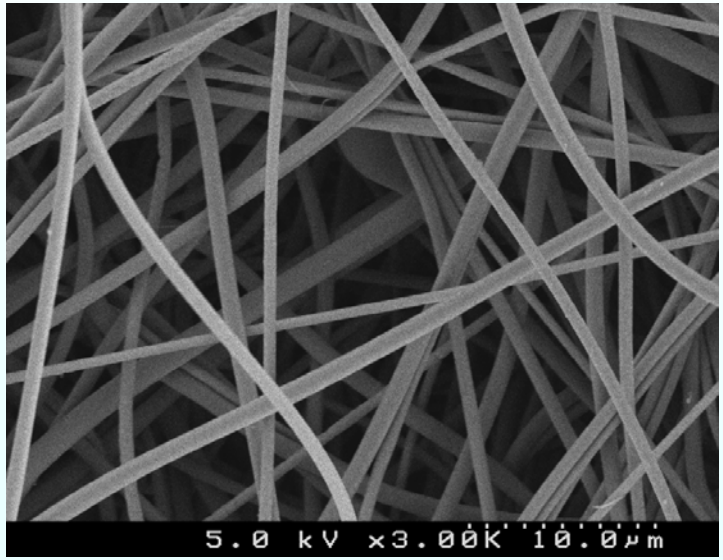
Electrospinning Nanofiber Mats From Nafion

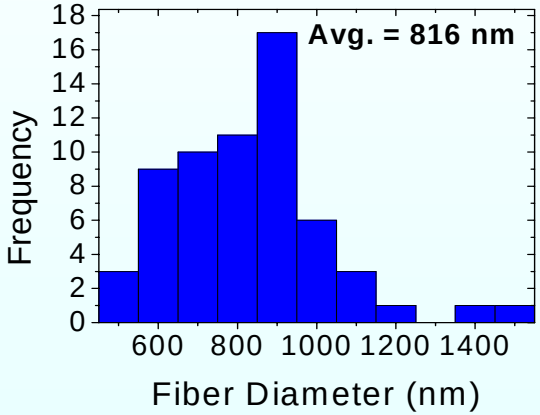
Electrospinning solution composition

23.8 wt% Nafion +0.24 wt% poly(ethylene oxide) (PEO)
+ 76 wt% isopropanol/water (2:1wt)

Electrospinning conditions

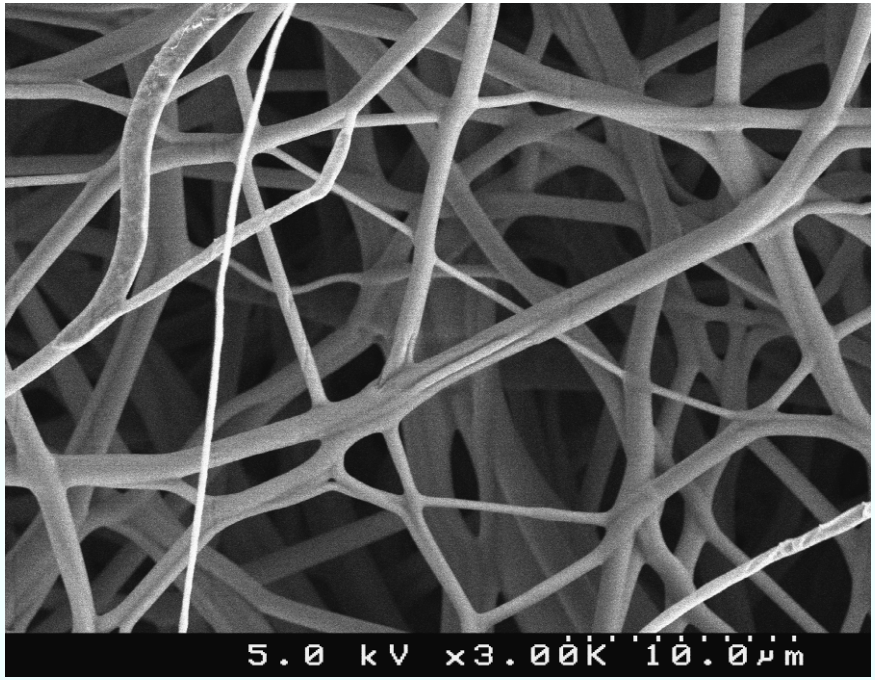
6 kV potential, 6cm SCD, 0.20 mL/h flow rate, 200 rpm drum rotation speed

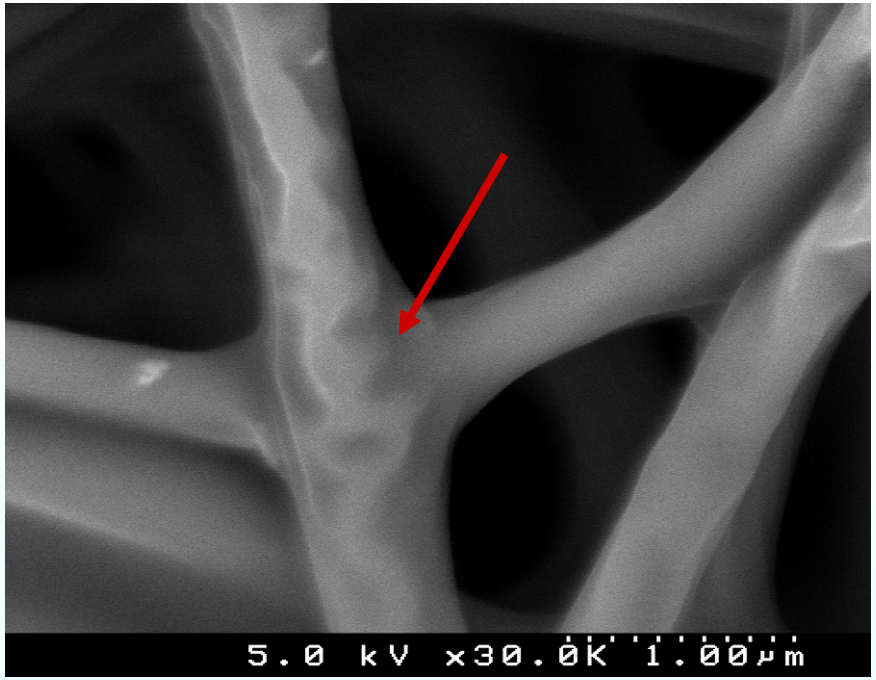




- Less PEO was added to the Nafion solution, but electrospinning was still possible, although the fiber diameter was larger than with sulfonated polysulfone.
- Fiber mats contained only 1 wt% PEO (450K MW) or 0.3 wt% PEO (1,000K MW) or 5 wt% PAA
- Fiber diameter ranged from approximately 160-800 nm.

Welding Of Nafion Nanofibers





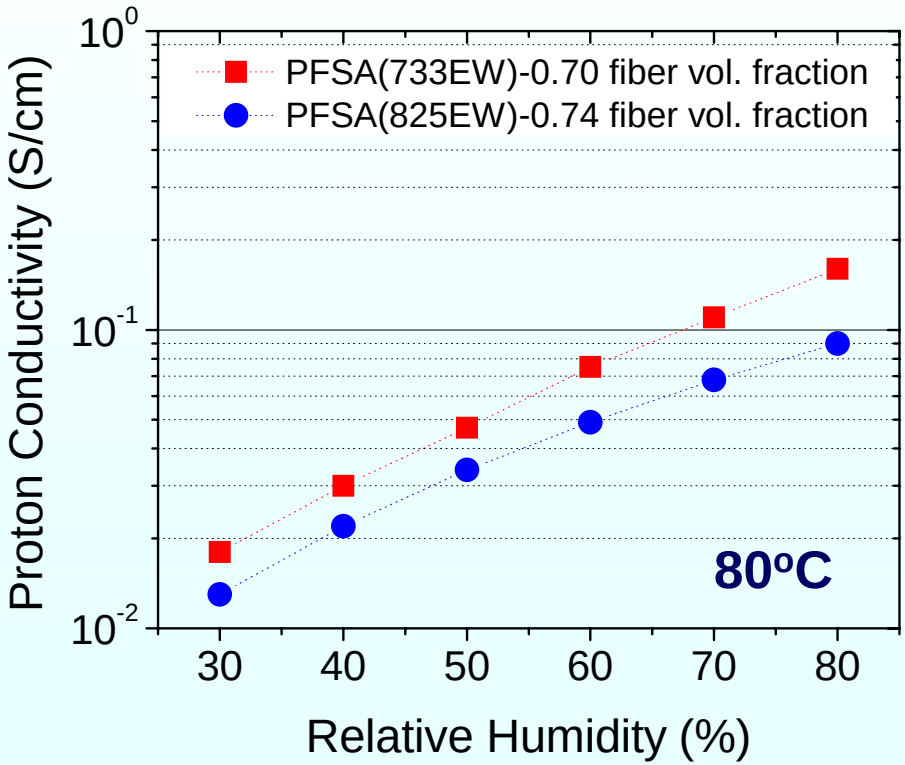
- Thermal annealing is an important step during solution casting of a homogeneous (dense) Nafion membrane. Nafion nanofibers were also annealed, at 150°C for 30 min.
- Inter-fiber welding occurred during annealing (due to the presence of small amounts of adsorbed water which plasticized the fibers; also the annealing temperature was above the T_g)

PFSA Nanofiber Composite Membrane Fabrication

1	**Electrospinning nanofiber mat**
2	**Drying the mat** in vacuum for 16 hrs
3	**Annealing the mat** at 140°C for 5 min
4	**Densifying the mat** at 0 – 10,000 psi for 5 sec
5	**Embedding the mat with NOA** and UV curing for 2 hrs
6	**Removal of polymer carrier** by boiling in 1M sulfuric acid followed by boiling in water

Nafion Nanofiber Composite Membrane – Proton Conductivity

Composite membrane: 0.72 fiber volume fraction; Norland Optical Adhesive 63 as the inert matrix; 68 µm dry thickness



Conductivity of the nanofiber membrane scales with the volume fraction of fibers.

Temperature response of conductivity is similar for nanofiber composite and commercial Nafion membranes.

Membranes with sPOSS met the DOE conductivity target of 0.1 S/cm at 120°C and 50% RH

Conclusions

- **Entirely new membrane fabrication scheme**
- **Membrane transport and mechanical properties have been decoupled**
- **Composite structure is a new platform for fuel cell membranes (for hydrogen/oxygen, DMFC, and alkaline fuel cells), battery separators (e.g., Li^+ ion conductors), and membranes for electrolytic processes**

- **The next steps:**
  - **Create nano-porosity in the fibers**
  - **Load the fibers with hydrophilic/charged nanoparticles or a hydrogel**
  - **Create core-shell fibers**
  - **Use low EW PFSAs (3M Corp.)**
  - **Fibers composed of a blend of low EW PFSA and sulfonated poly(phenylene)**

We have electrospun nanofibers composed of: 79 wt% 3M PFSA (825 EW) + 20 wt % poly(p-phenylene disulfonic acid) at 8.47 mmol/g + 1 wt% PEO (300K M).

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Personnel:

Ryszard Wycisk (Research Assistant Professor)
Jun Lin (Postdoctoral scholar)
Kyungmin Lee (Postdoctoral scholar)
Jon Choi (current PhD student)
Jeong Lee (former PhD student)
Pin-Han Wu (MS student)
Angelo Trivissano (undergraduate researcher)
Michael Kellner (high school student)

Dr. K. Shi, Institute for Fuel Cell Innovation, National Research Council Canada, Vancouver, BC (TEM work)