Dual-Nanofiber Composite Membranes for Formic Acid Fuel Cells

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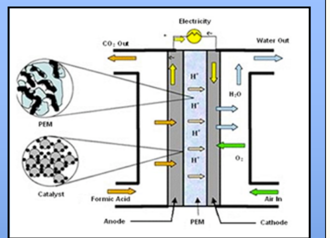
Introduction:



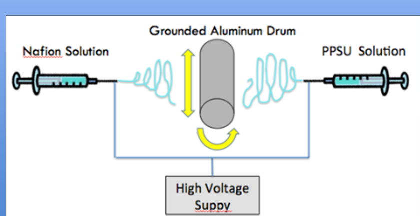
Direct formic acid fuel cells (DFAFCs) have great potential for portable power applications. DFAFCs have the advantages of high efficiency and reasonable power densities at low temperatures. While DFAFCs have been proven to be less susceptible to fuel crossover than direct methanol fuel cells, crossover still occurs and is a function of formic acid concentration and temperature. Unreacted fuel that permeates from the anode to the cathode has degradative effects on fuel cell performance. This research project is focused on making low formic acid crossover membranes. A dual-nanofiber electrospinning approach was employed where composite membranes composed of Nafion® and poly(phenylsulfone) were prepared. The resistance to water swelling of composite membranes should reduce the permeability of formic acid in DFAFCs, thus providing an alternative polymer electrolyte membrane for DFAFC applications.

Objective:

- Test the permeability of various nanofiber composite membranes in formic acid solution and compare with a commercial Nafion® film.
- Identify the membrane structure with superior resistance to crossover.

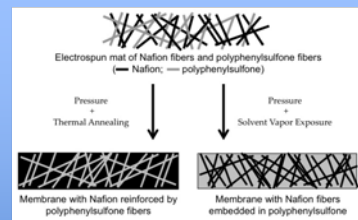
Methodology:

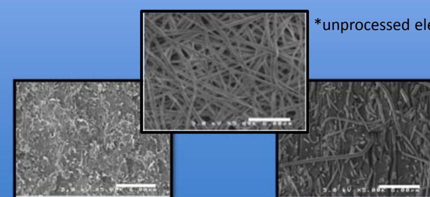
An **electrospinning** approach was used to create dual-nanofiber composite membranes comprised of Nafion and poly(phenylsulfone). Syringe pump flowrates and spinning times were adjusted to yield different volume fractions of the polymers and different membrane thicknesses.



Nafion Vol Fraction	PFSA Flowrate (mL/hr)	PPSU Flowrate (mL/hr)	Spin Time (hrs)	Thickness (µm)
0.4	0.2	0.05	15	30
0.5	0.2	0.04	22	35
0.6	0.2	0.03	18	40

Morphology:





*unprocessed electrospun mat

1) Nafion matrix/ PPSU fibers 2) Nafion fibers/ PPSU matrix

Membrane Characterization:

- Ionic Conductivity – In-plane ionic conductivity in 1 M formic acid was measured by AC impedance.

$$\sigma = \frac{L}{Rw\delta}$$

- σ = proton conductivity (S/cm)
- R = resistance (Ω)
- L = distance between electrodes (cm)
- w = width of sample (cm)
- δ = membrane thickness (cm)

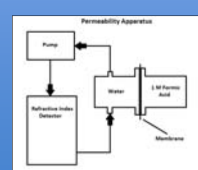
- Ion Exchange Capacity (IEC) – Acid exchange and base titration.

$$IEC = \frac{VN}{m_{dry}} \times 1000$$

$$Nafion\ volume\ fraction = \frac{IEC_{composite}}{IEC_{Nafion}} \times \frac{\rho_{composite}}{\rho_{Nafion}}$$

- IEC = ion exchange capacity (mmol/g)
- V = volume of NaOH titrating solution (L)
- N = normality of titrating solution (mol/L)
- m_{dry} = dry mass of membrane (g)

- Permeation – Permeability in 1 M formic acid was measured using a two-compartment diffusion cell with a refractive index detector.



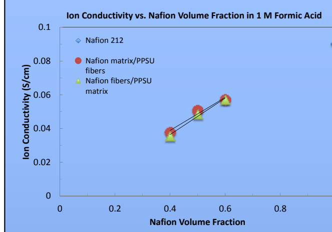
$$J = -Dk\frac{\partial C}{\partial x} = -Dk\frac{\Delta C}{\Delta x}$$

- J = Flux (mol/cm^2s)
- Dk = permeability (D=diffusivity; k=partition coefficient)
- ΔC = bulk solution concentration difference across the membrane
- Δx = membrane thickness

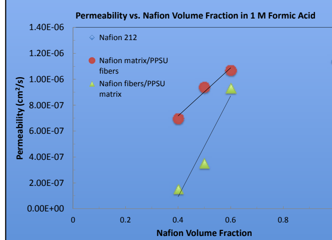
- Selectivity

$$Selectivity = \frac{Conductivity}{Permeability}$$

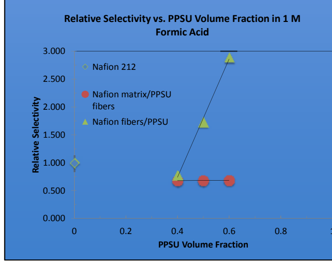
Results:



In-plane proton conductivity as a function of Nafion volume fraction, measured in 1M formic acid at room temperature.



Permeability of formic acid as a function of Nafion volume fraction, measured at room temperature with 1M formic acid.



Ratio of membrane selectivity to the selectivity of a Nafion membrane, as a function of poly(phenylsulfone) volume fraction in the composite membrane.

Conclusion:

The permeability and ionic conductivity of composite membranes decreases with decreasing Nafion content. Composite membranes with a low Nafion volume fraction show higher selectivity than commercial Nafion films. For more conclusive results, through-plane conductivity and in situ formic acid fuel cell performance and crossover tests need to be conducted.

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References:

Composite Fuel Cell Membranes from Dual-nanofiber Electrospun Mats. Jason B. Ballengee and Peter Pintauro. Macromolecules. 2011.

Crossover of Formic Acid Through Nafion Membranes. Young-Woo Rhee, Su Y. Ha and Richard I. Masel. 2002.