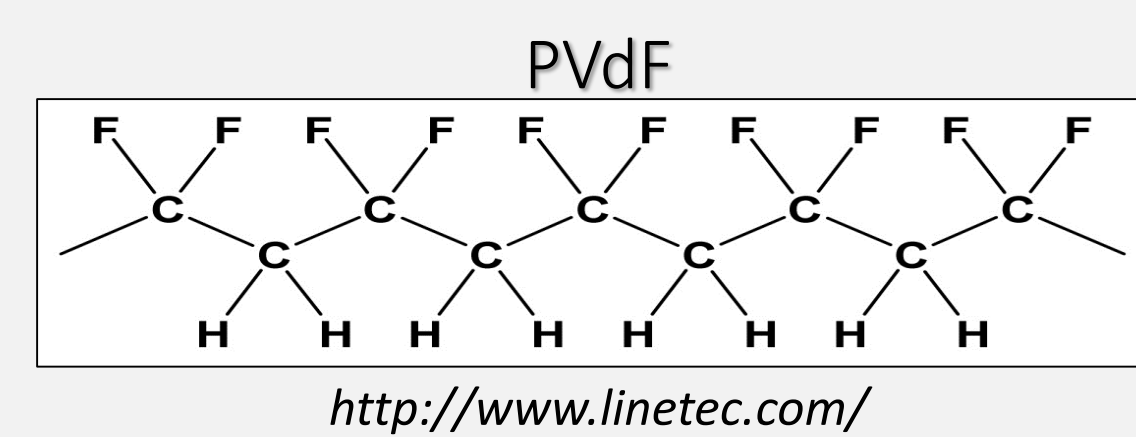
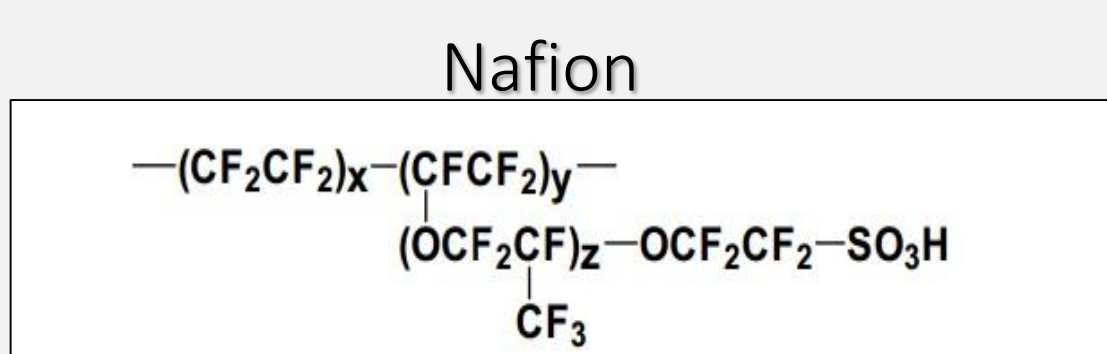
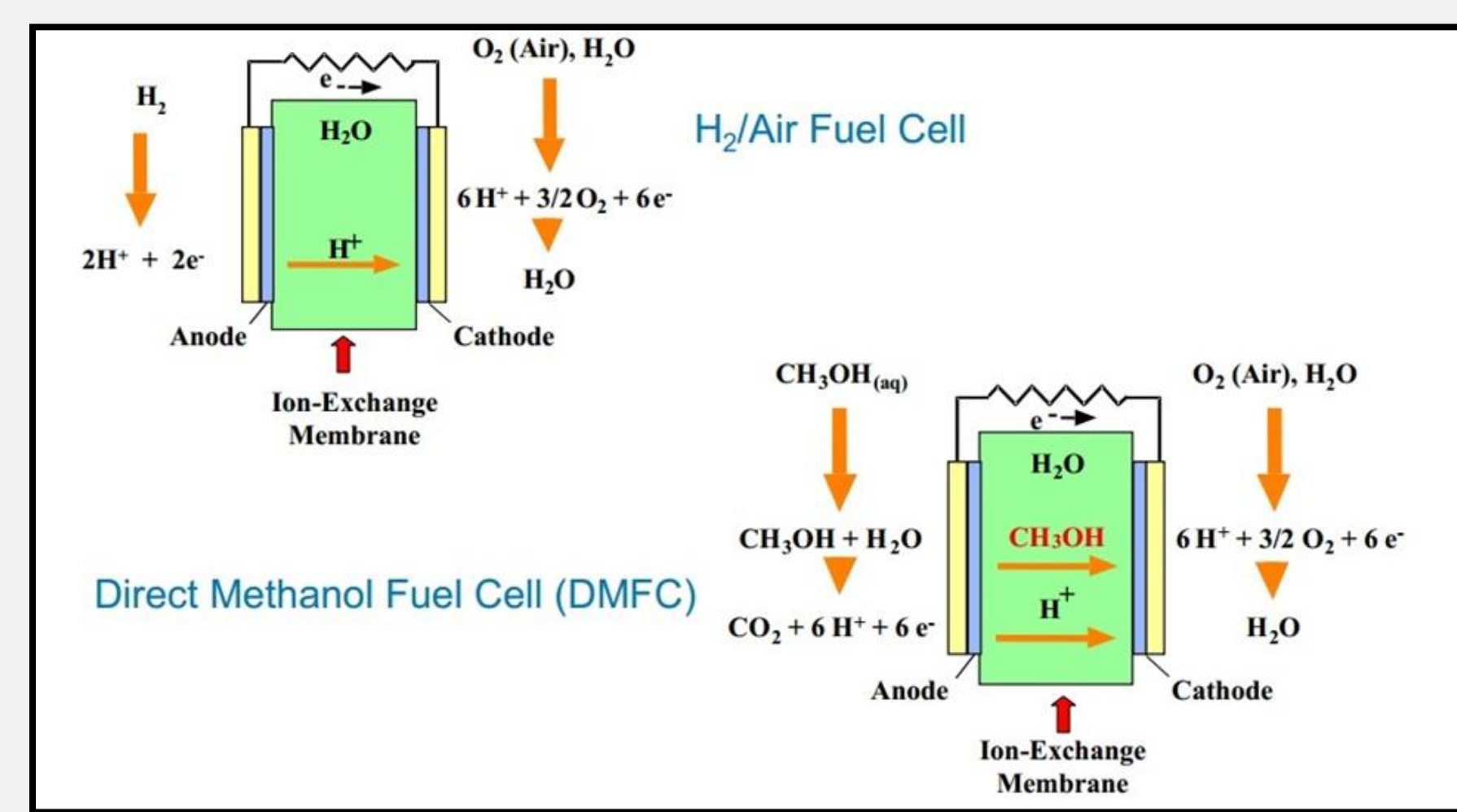


Optimizing the Fabrication of Solution-Cast Membranes for PEM Fuel Cells



Introduction

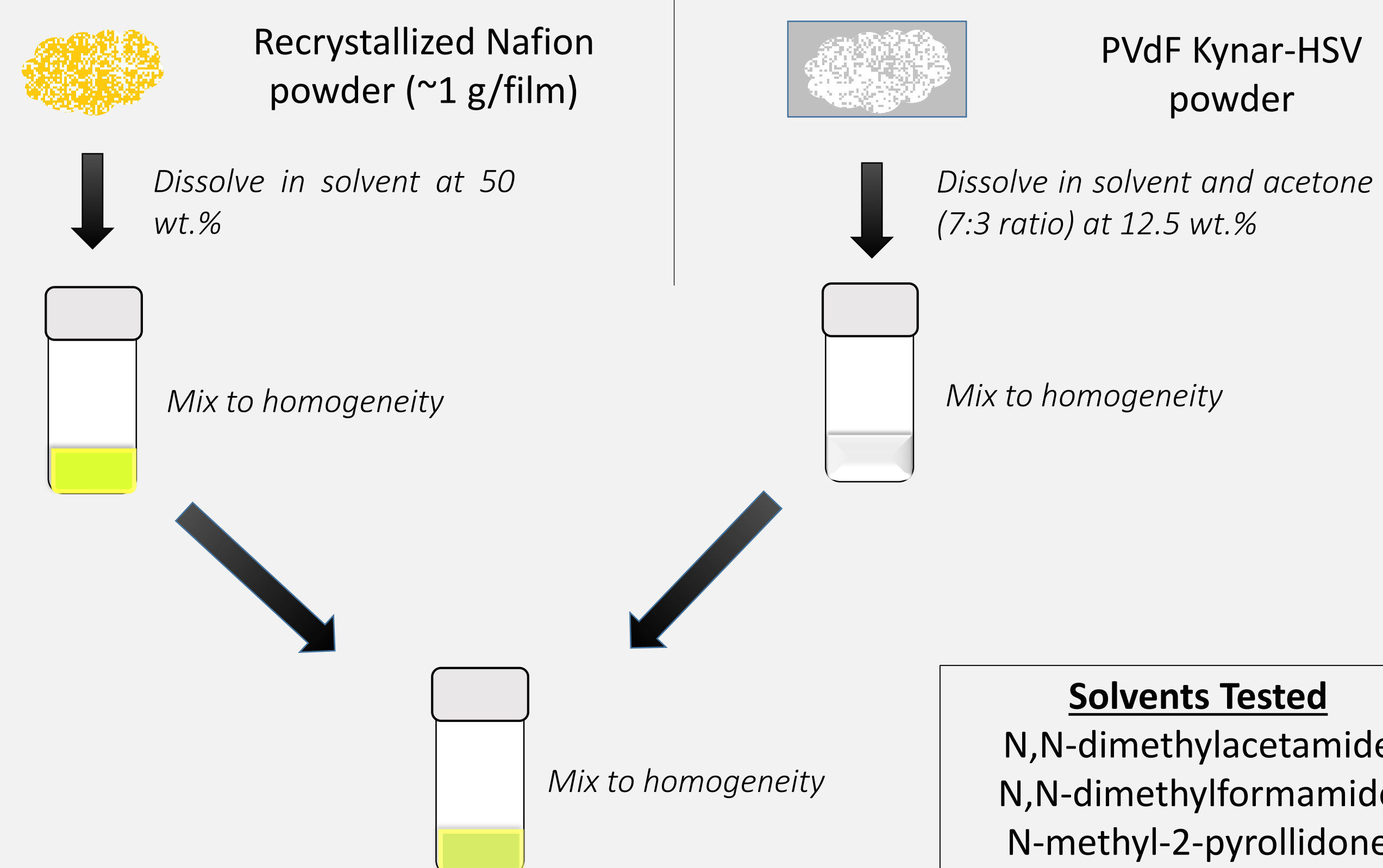
Fuel cells show promise to be highly efficient sources of clean energy in the near future. The proton-exchange membrane (PEM) in a fuel cell must exhibit high H⁺ conductivity and robust mechanical properties in order to be efficient. The most common membrane material is perfluorosulfonic acid polymer (PFSA), sold by DuPont under the name Nafion, which can be mixed with an inert reinforcing polymer such as polyvinylidene fluoride (PVdF) with the goal of maximizing conductivity and minimizing swelling between the wet/dry states. A variety of solvents and annealing conditions can be employed during fabrication. The present study concerns investigating the effect of these parameters on conductivity, water uptake, and swelling characteristics of the final membranes.



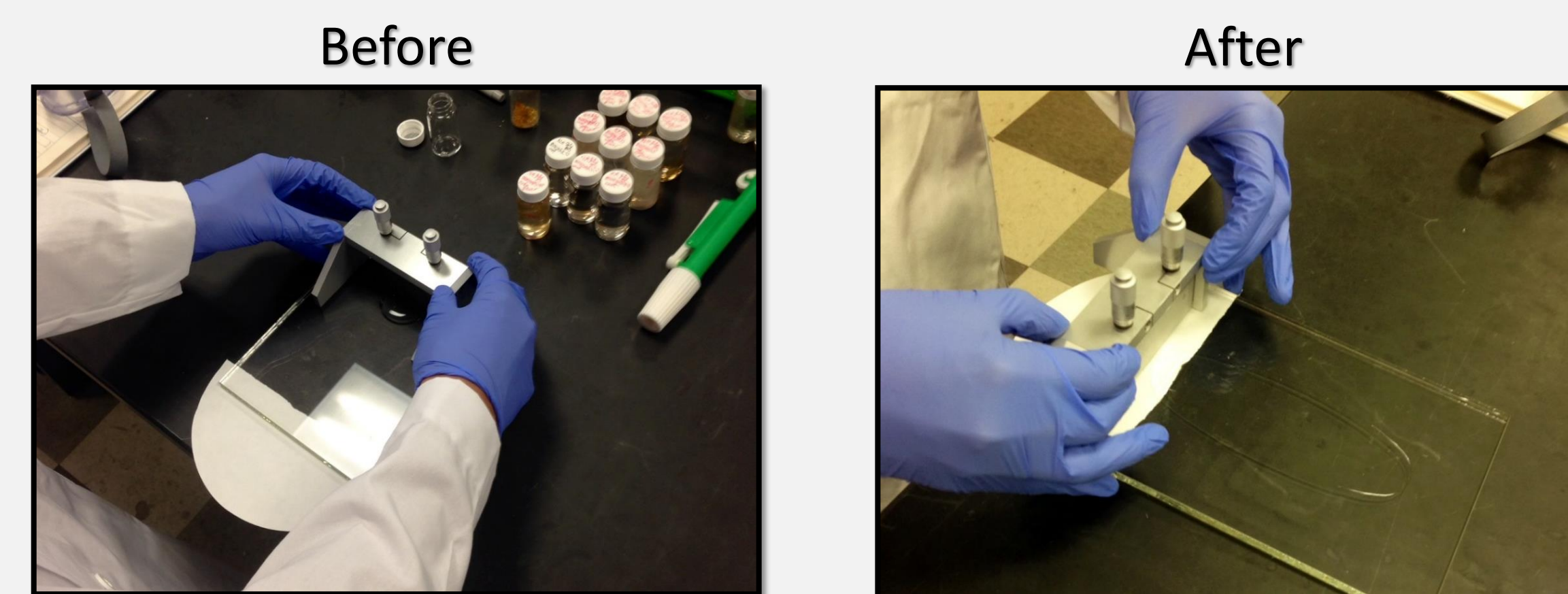
Objective

Employ variation of solvents, annealing temperatures, and annealing times in the fabrication of 80:20 (vol.) Nafion-to-PVdF solution-cast membranes for fuel cells. Investigate the effects of these conditions on the conductivity and swelling characteristics of the final membranes. Determine if and how the Nafion/PVdF ratio has an effect on the characteristics produced by the annealing condition leading to the highest conductivity for the 80:20 ratio.

Methods: Preparing Solutions



Methods: Casting and Processing



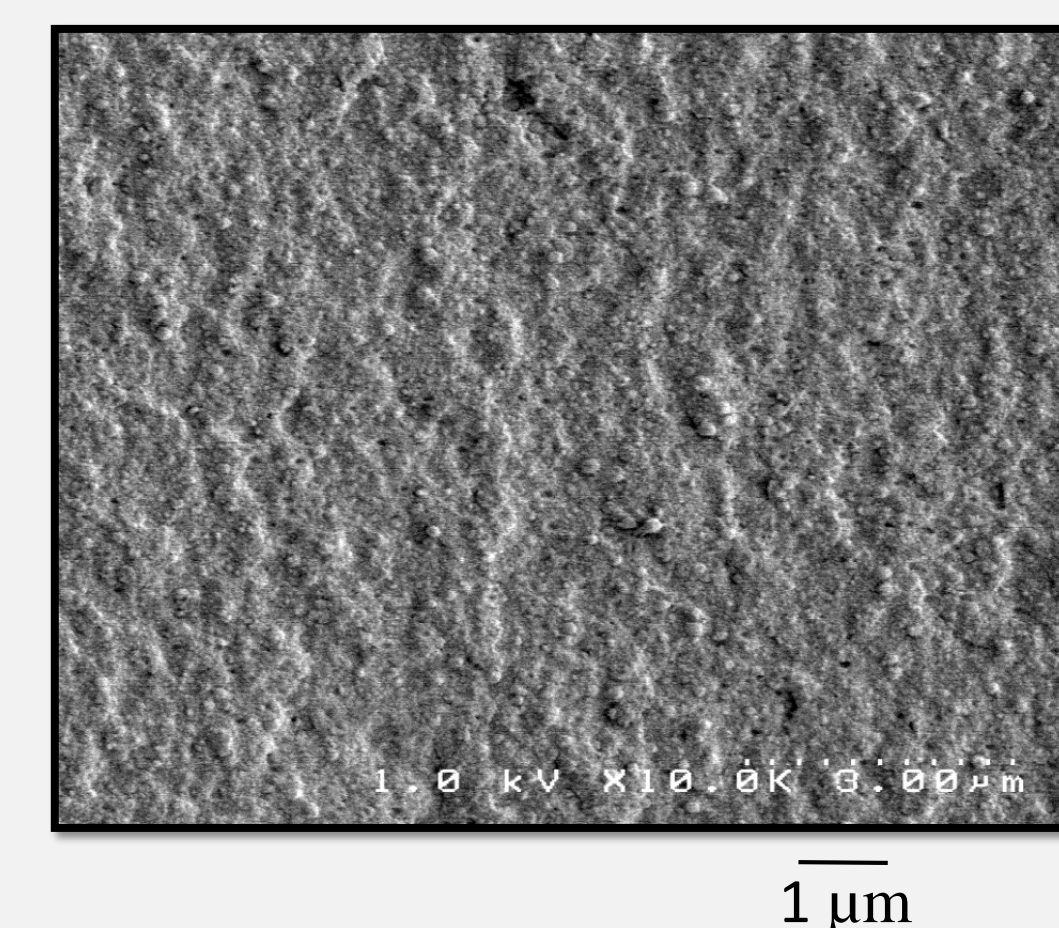
A knife thickness setting of 0.15 mm consistently yields membranes of 30-70 μm in thickness.

- Anneal under vacuum to fully develop polymer crystallinity
- Press 4 times at 360°F and 24,000 lb_f for 40 s; rotating 90° each time
- Boil in 200 mL of 1 M H₂SO₄ for 1 h in order to protonate sulfonic acid groups
- Boil in 200 mL of DI H₂O for 1 h to remove excess acid
- Soak in 200 mL of DI H₂O for at least 1 h to further remove excess acid
- Repeat twice

Imaging (SEM)

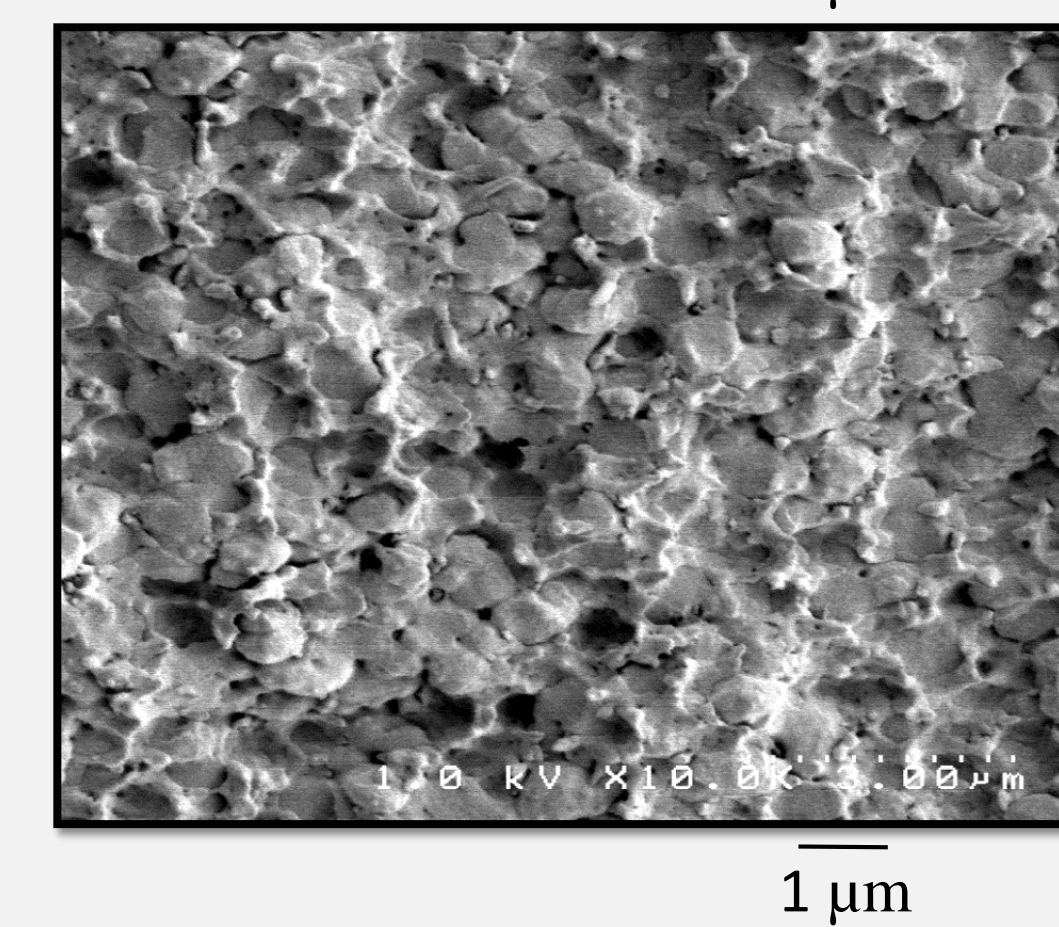
80:20 Nafion/PVdF, DMAc
 Annealed at 210°C for 1.5 h
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)

Membrane appears relatively homogeneous. Constituent polymers are blended well.



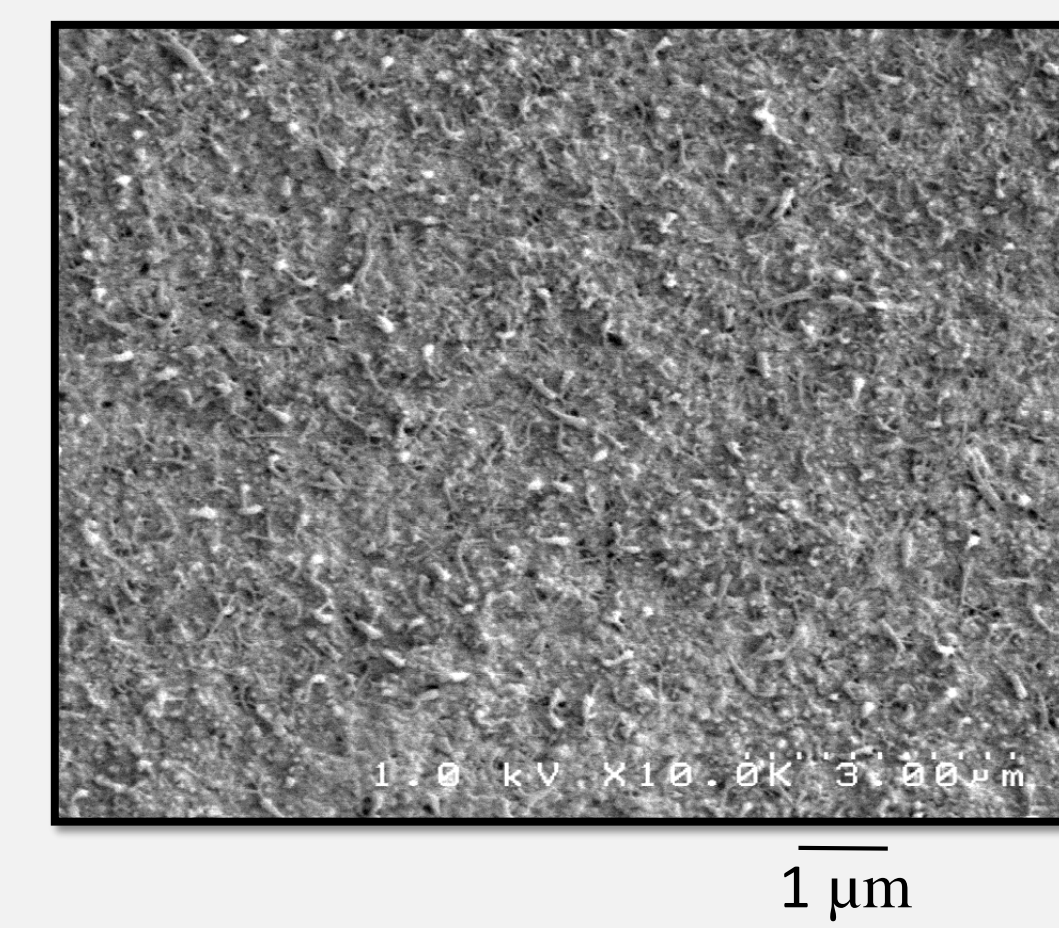
80:20 Nafion/PVdF, DMF
 Annealed at 150°C for 0.5 h
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)

Membrane exhibits large domains of phase separation on the order of 1 micron. Pores are visible as well.



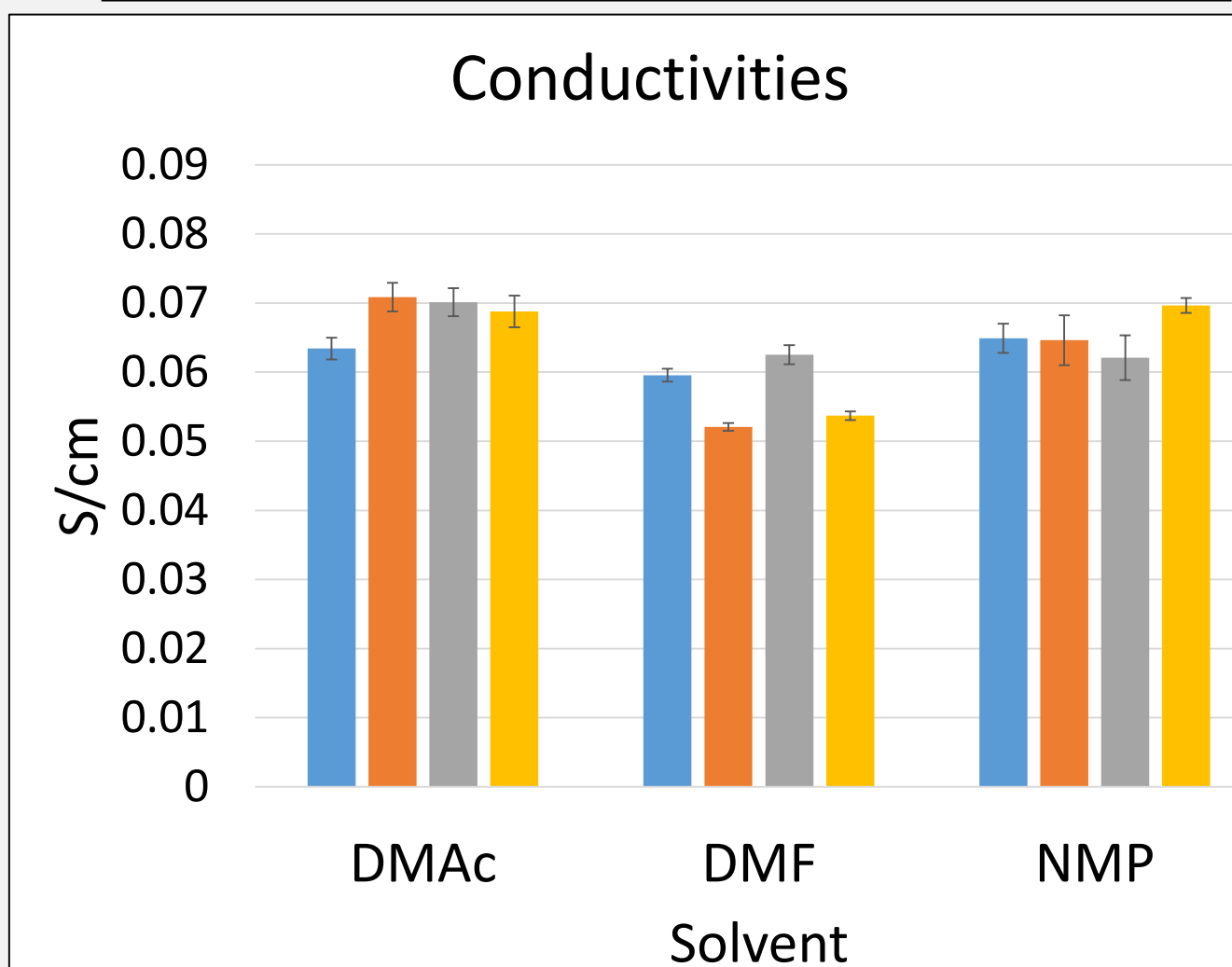
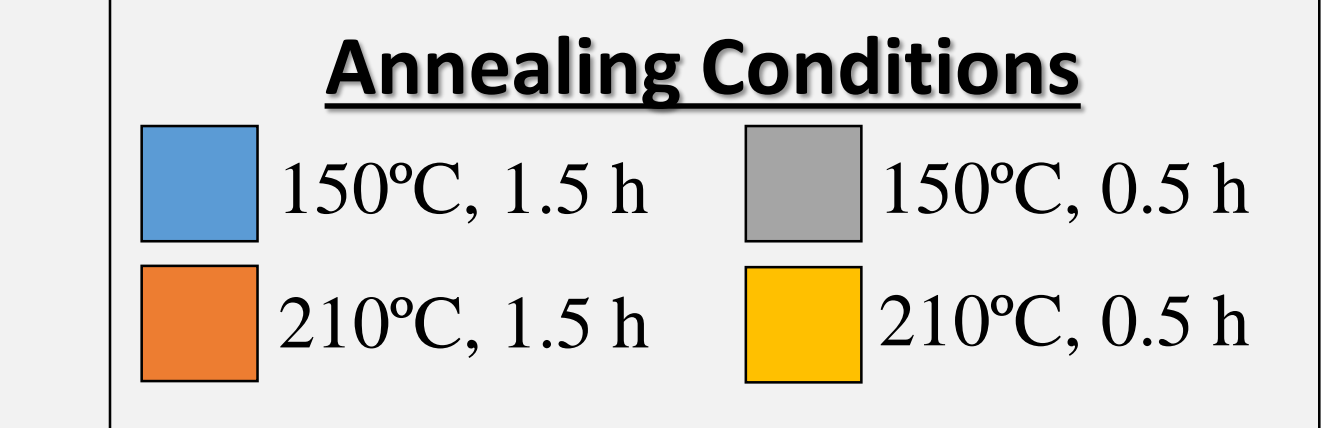
50:50 Nafion/PVdF, DMAc
 Annealed at 210°C for 1.5 h
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)
 (transparency comparison)

Membrane appears relatively homogeneous. Considering conductivity data, this phase separation is likely a function of solvent.

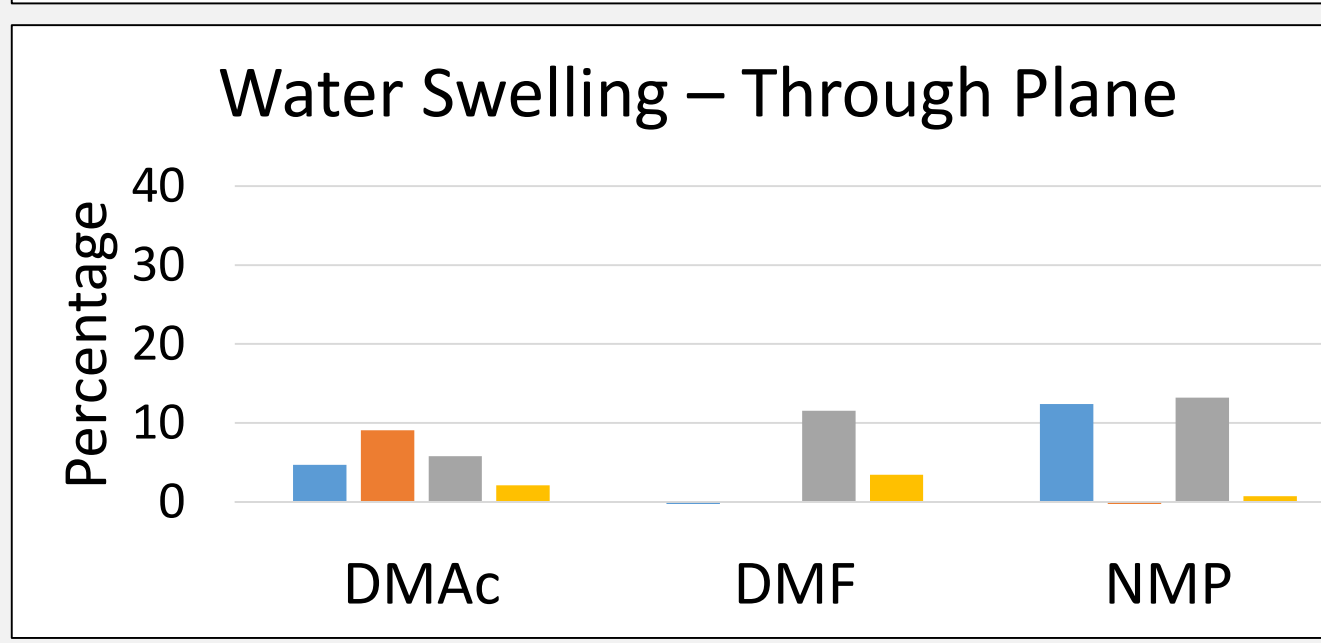
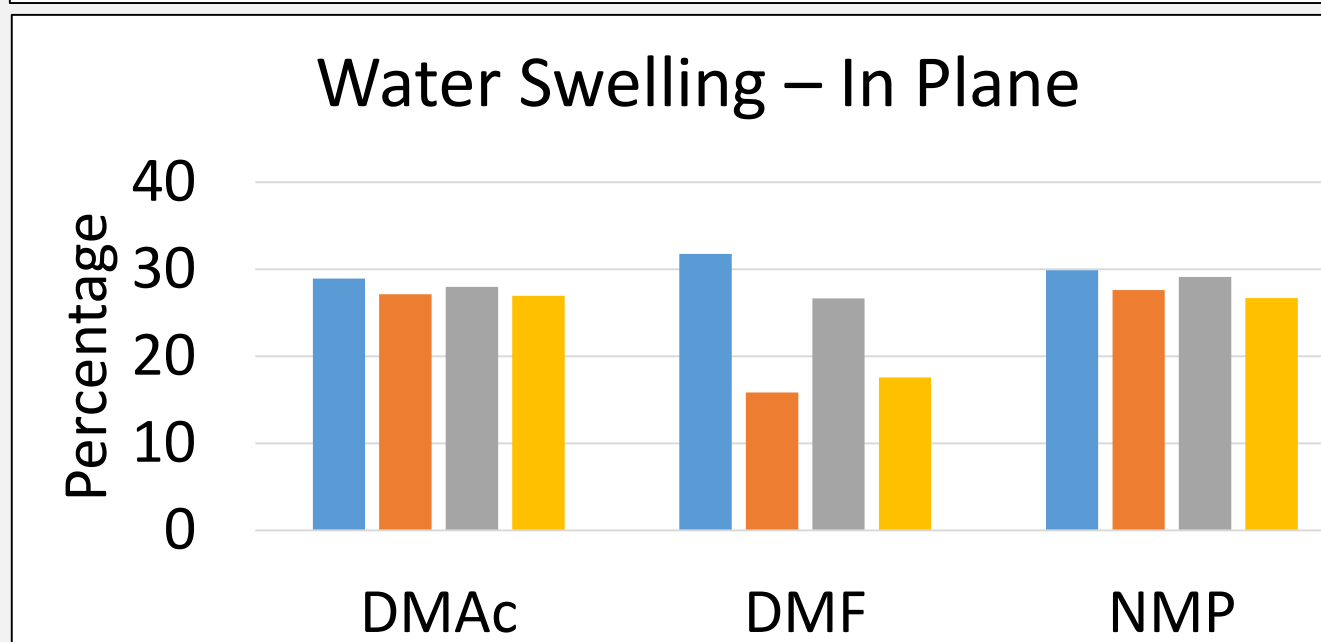
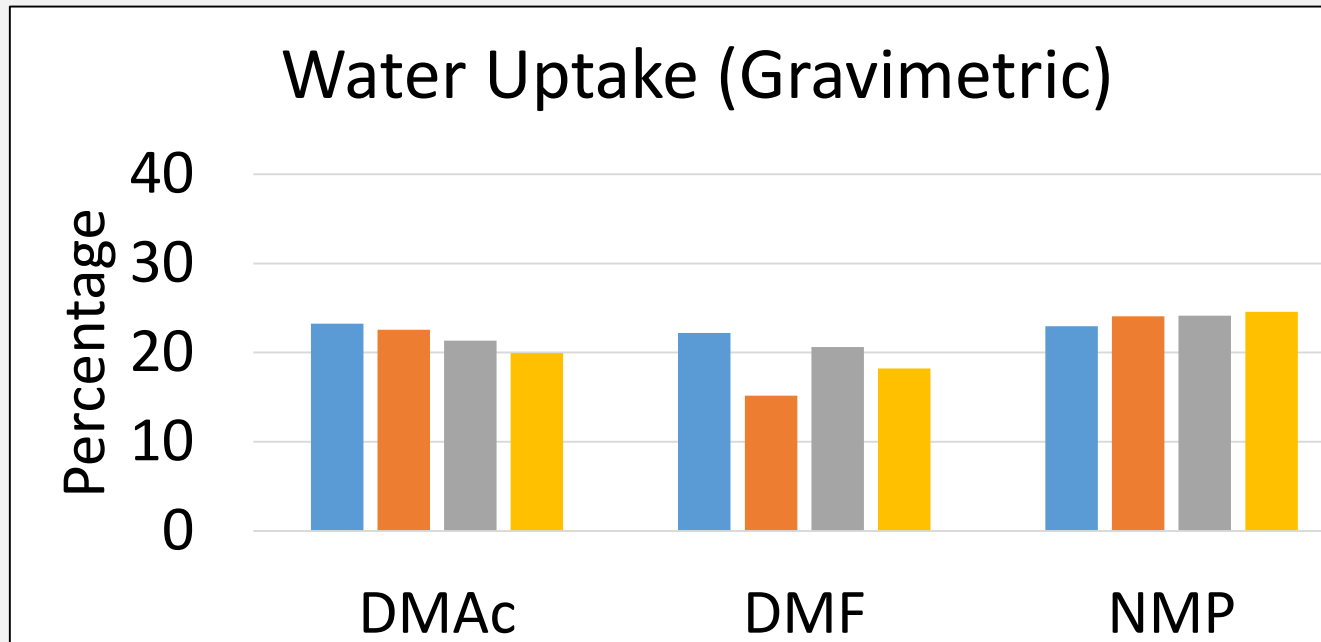


Membrane Performance

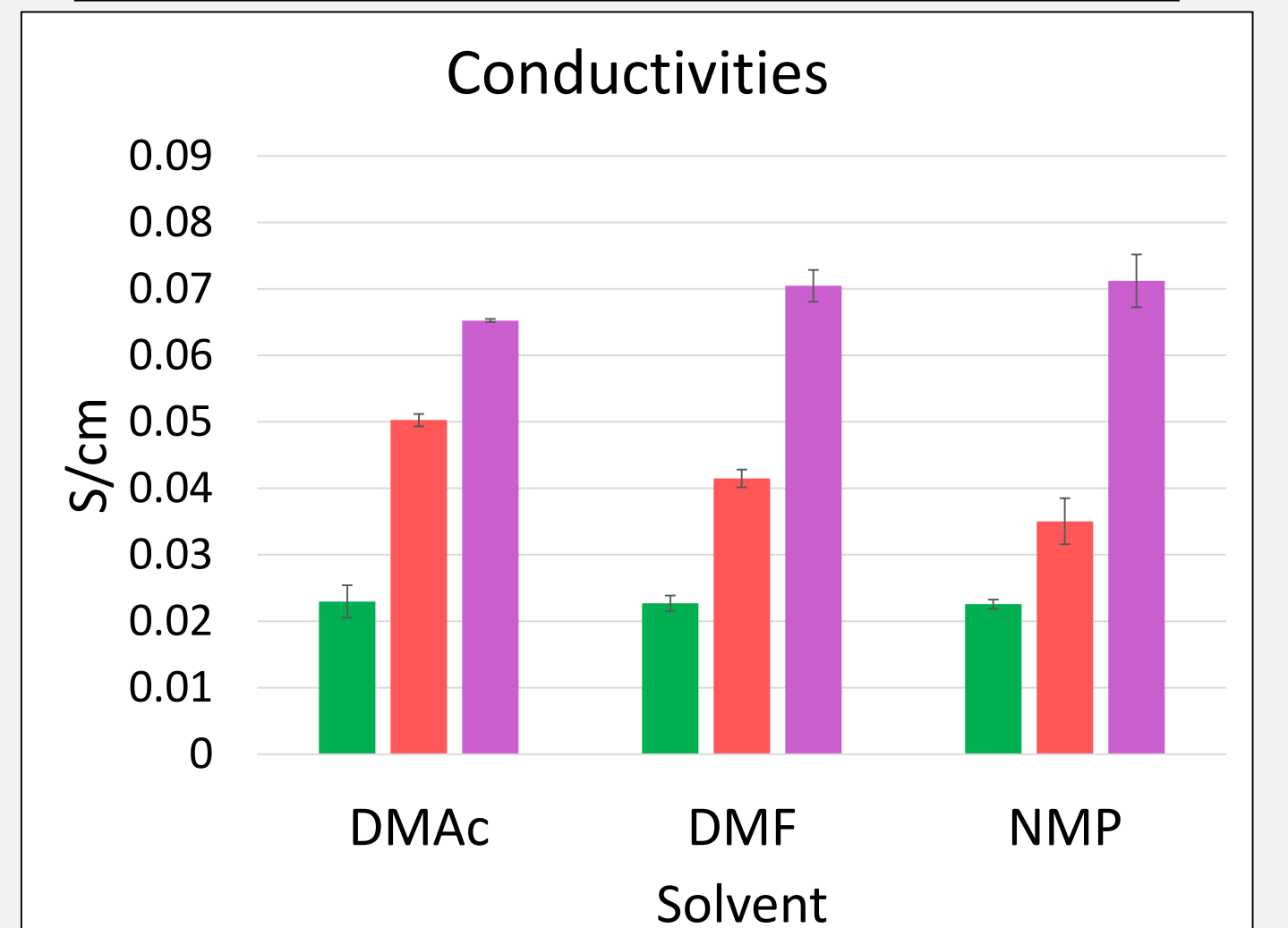
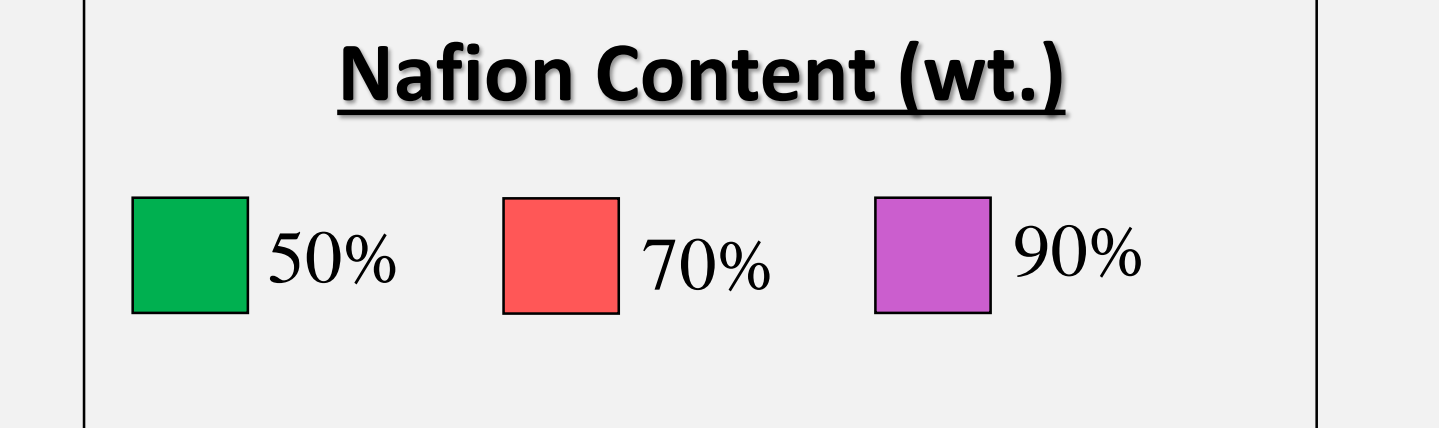
Part One: Variation of Solvent and Annealing Condition at 80% Nafion



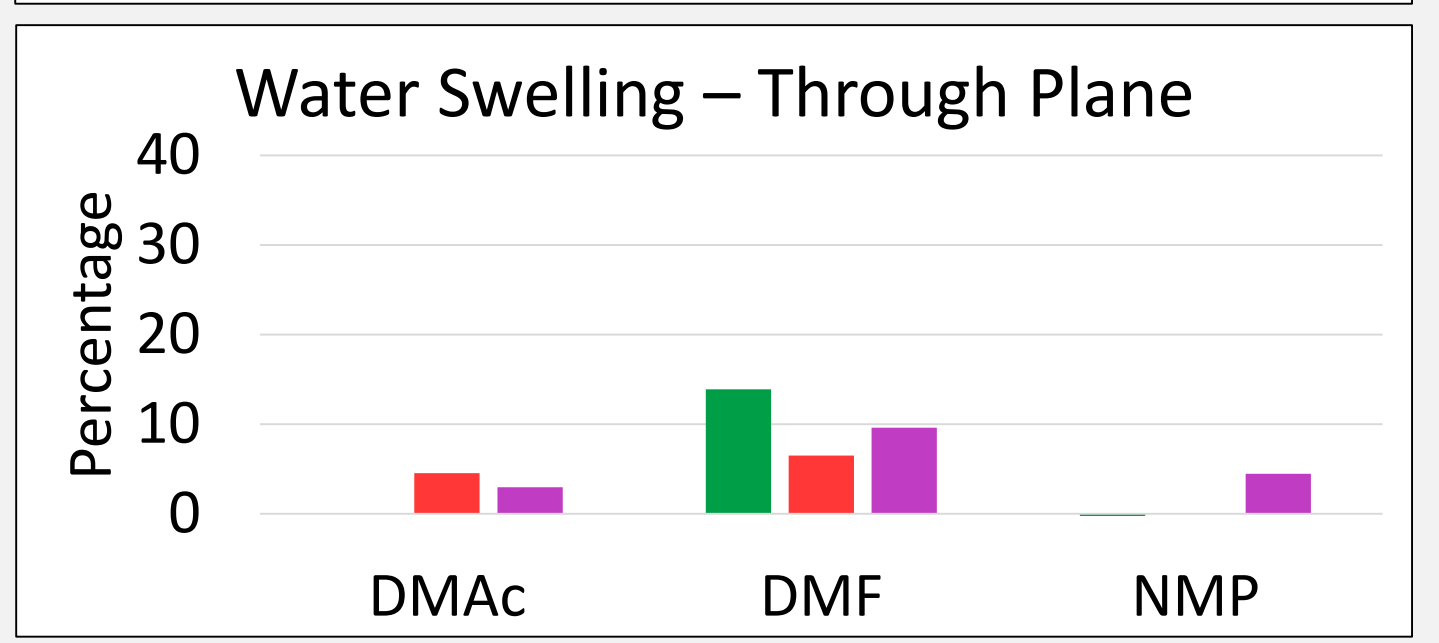
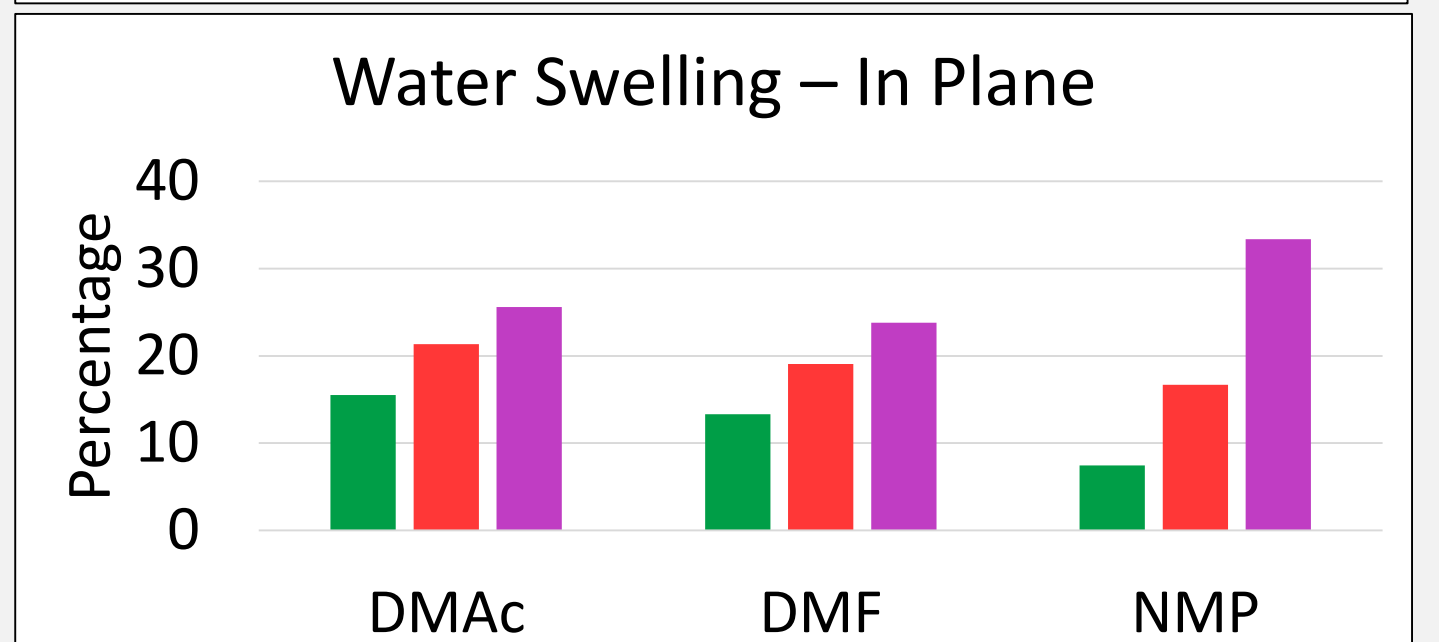
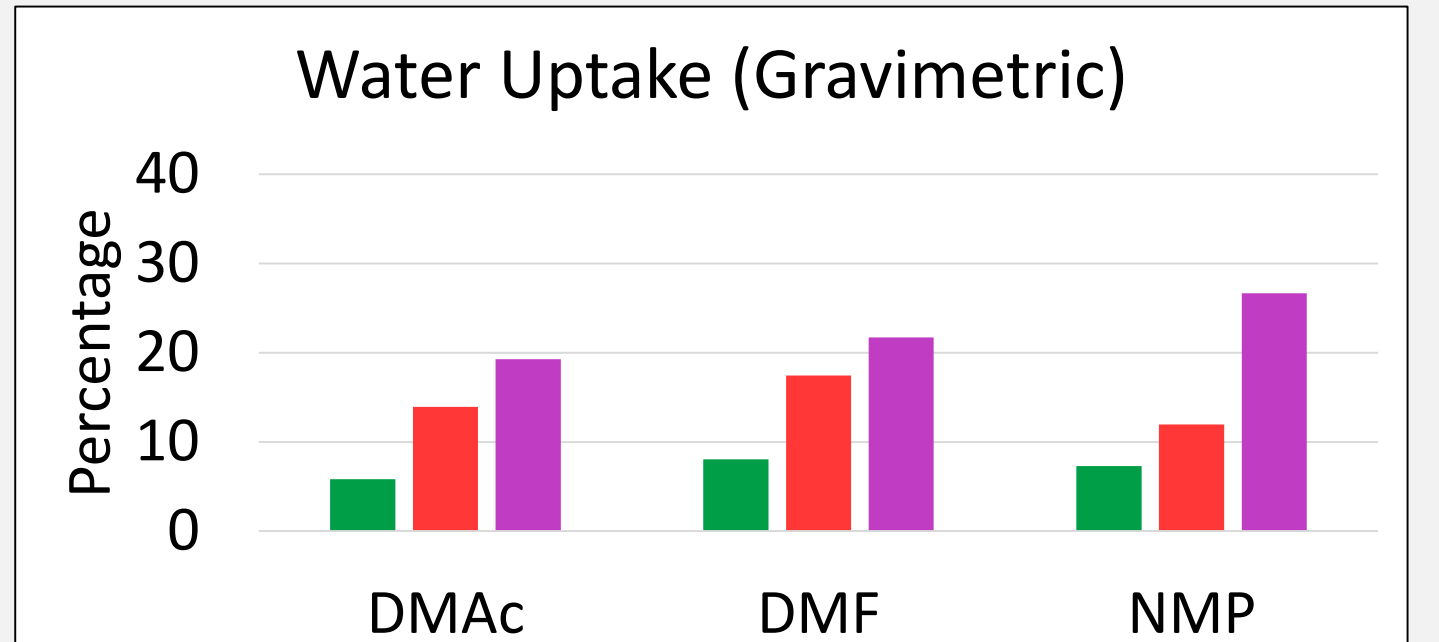
3 measurements per data point; error bars signify 1 std. dev.



Part Two: Variation of Nafion Content at Selected Annealing Condition



3 measurements per data point; error bars signify 1 std. dev.



Conclusions

In general, DMAc and NMP outperform DMF in terms of conductivity, with DMAc giving the best results. The annealing condition that yields the highest conductivity is a function of both solvent and proportion of Nafion, with membranes containing the highest and lowest proportions of Nafion showing sensitivity to higher annealing temperatures and subsequent losses in conductivity relative to their theoretical values. Phase separation consistently leads to a loss in conductivity as well. Water uptake and swelling properties are largely independent of solvent and annealing conditions. Future work will include testing additional combinations of solvents, annealing conditions, and Nafion proportions in order to draw further conclusions, as well as examining fuel crossover and tensile strength.

Acknowledgements

We gratefully acknowledge the financial support of the National Science Foundation (DMR-1263182), Department of Energy ARPA-E Grant No. DE-AR0000262, and Department of Energy EERE Grant No. DE-EE0006362.