Temperature-Dependent Chemical Properties of Nafion

Princeton PRISM REU Program

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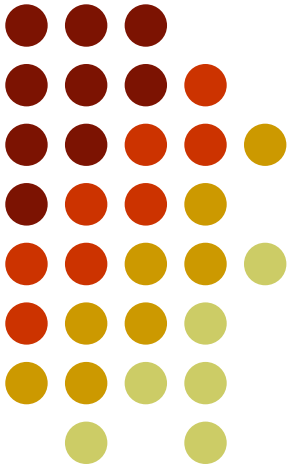
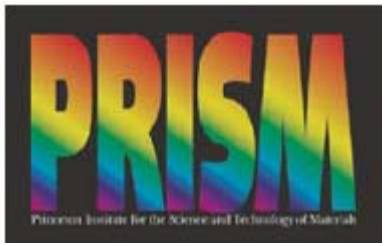
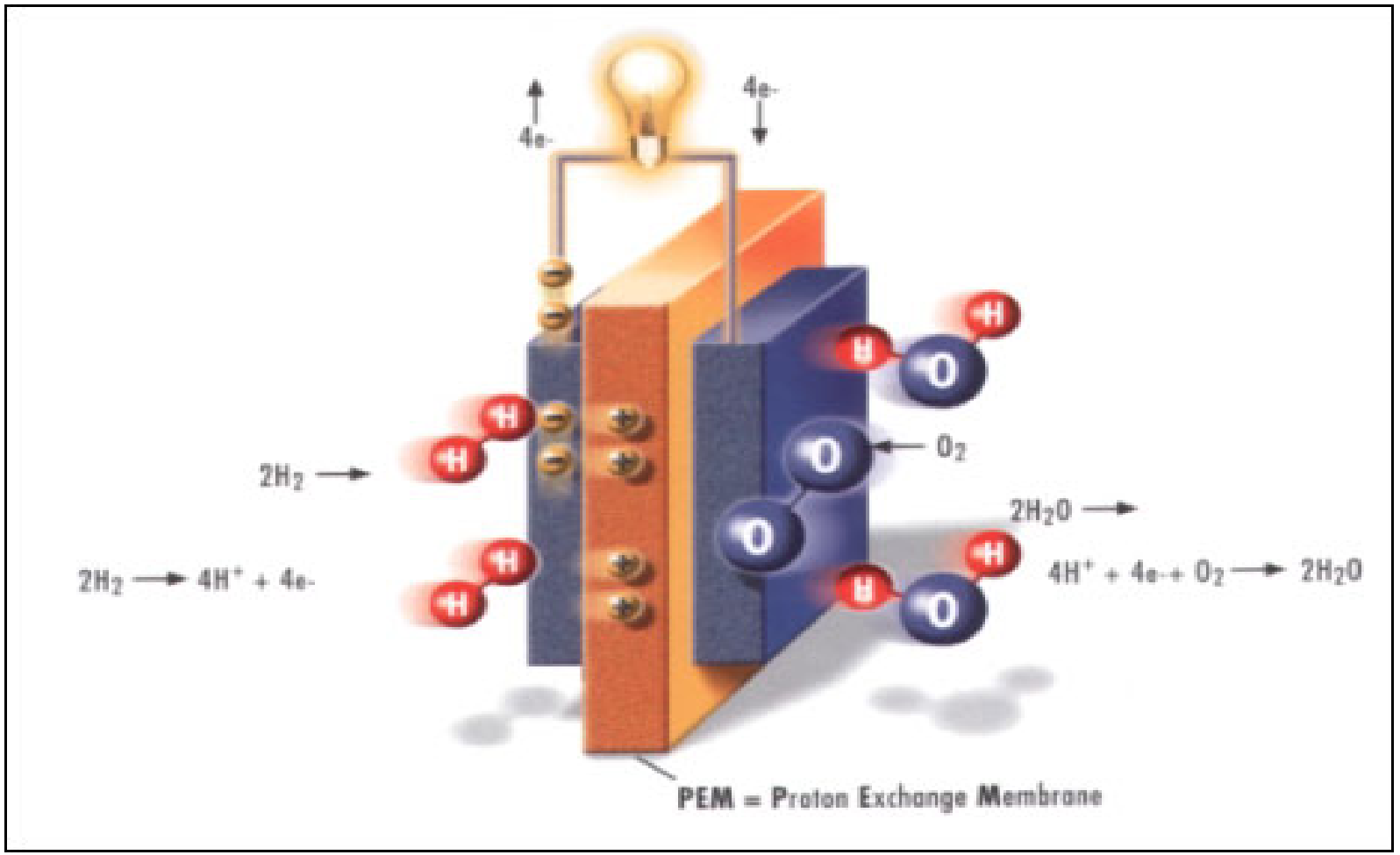




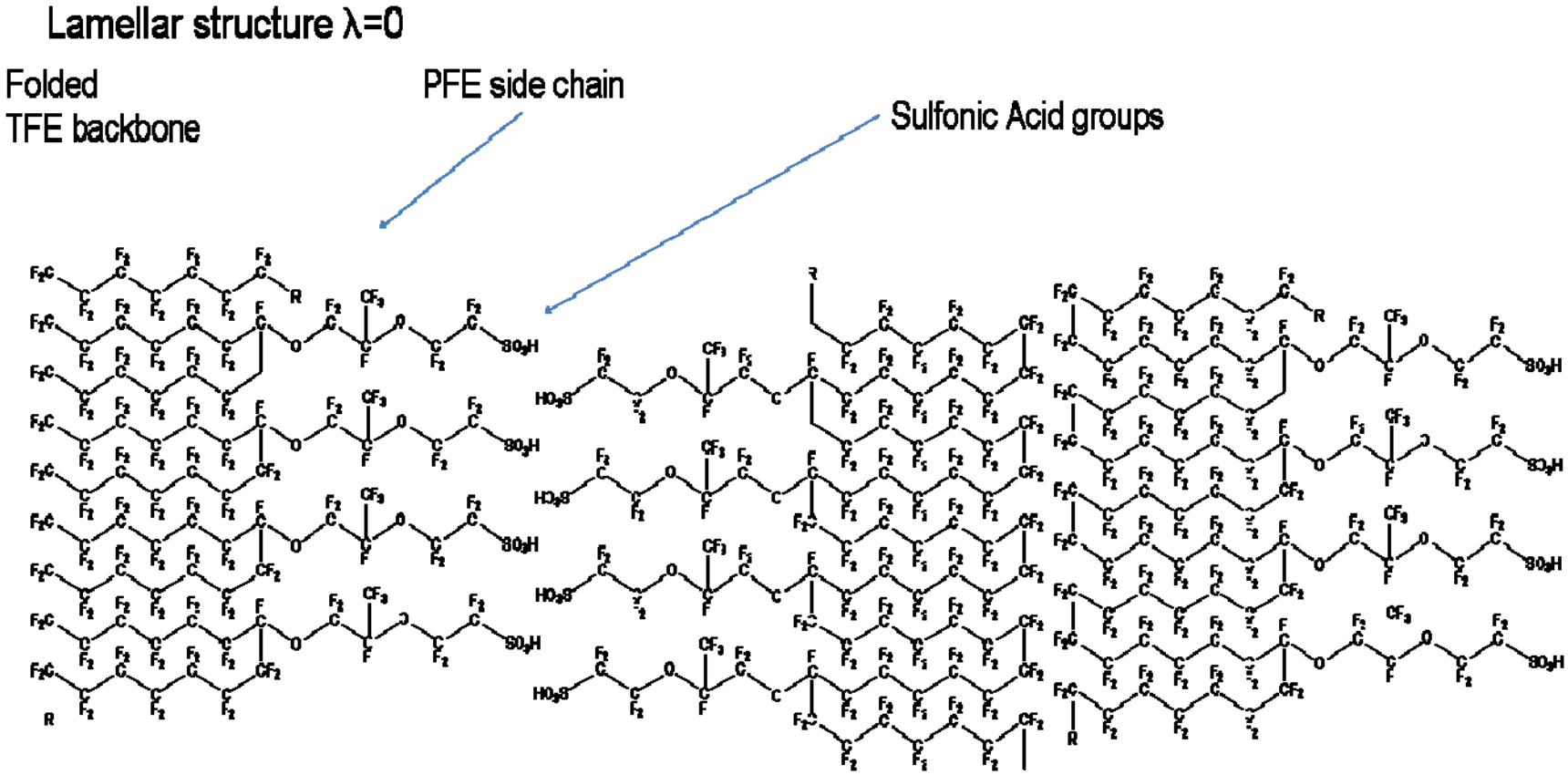
What is a fuel cell?



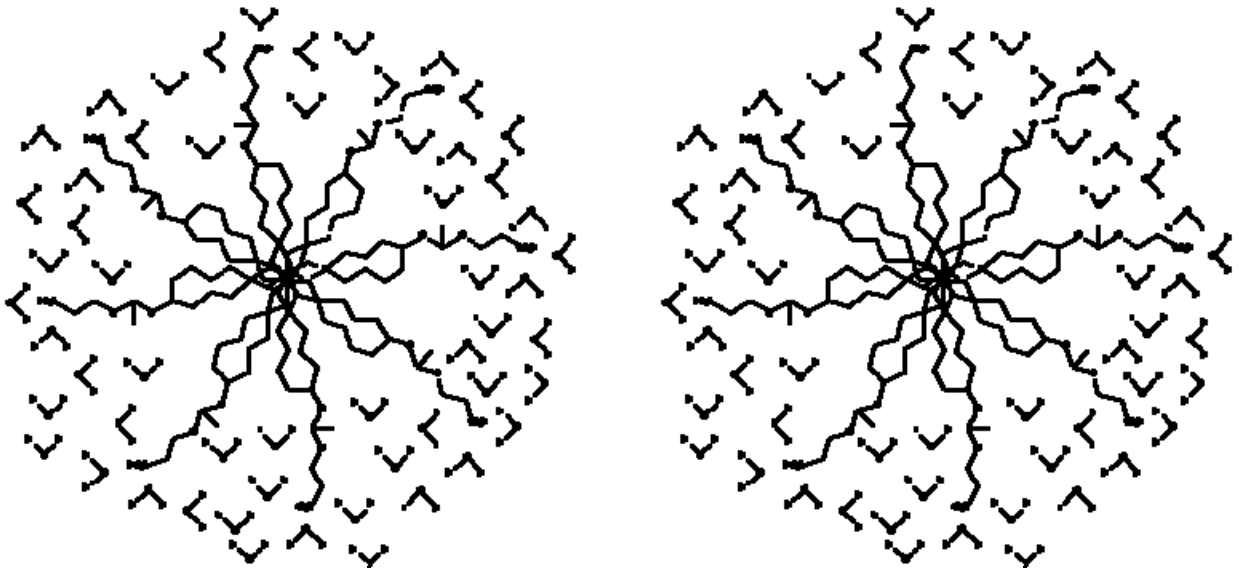
Polymer Electrolyte Membrane

- Two phase ionomer (ionic polymer)
- Conducts protons through hydrophilic phase, from anode to cathode in PEMFC
  - Must be hydrated to be conductive
    - Vehicular mechanism
    - Hopping mechanism
- Hydrophobic phase prevents electrons from cutting across and short-circuiting

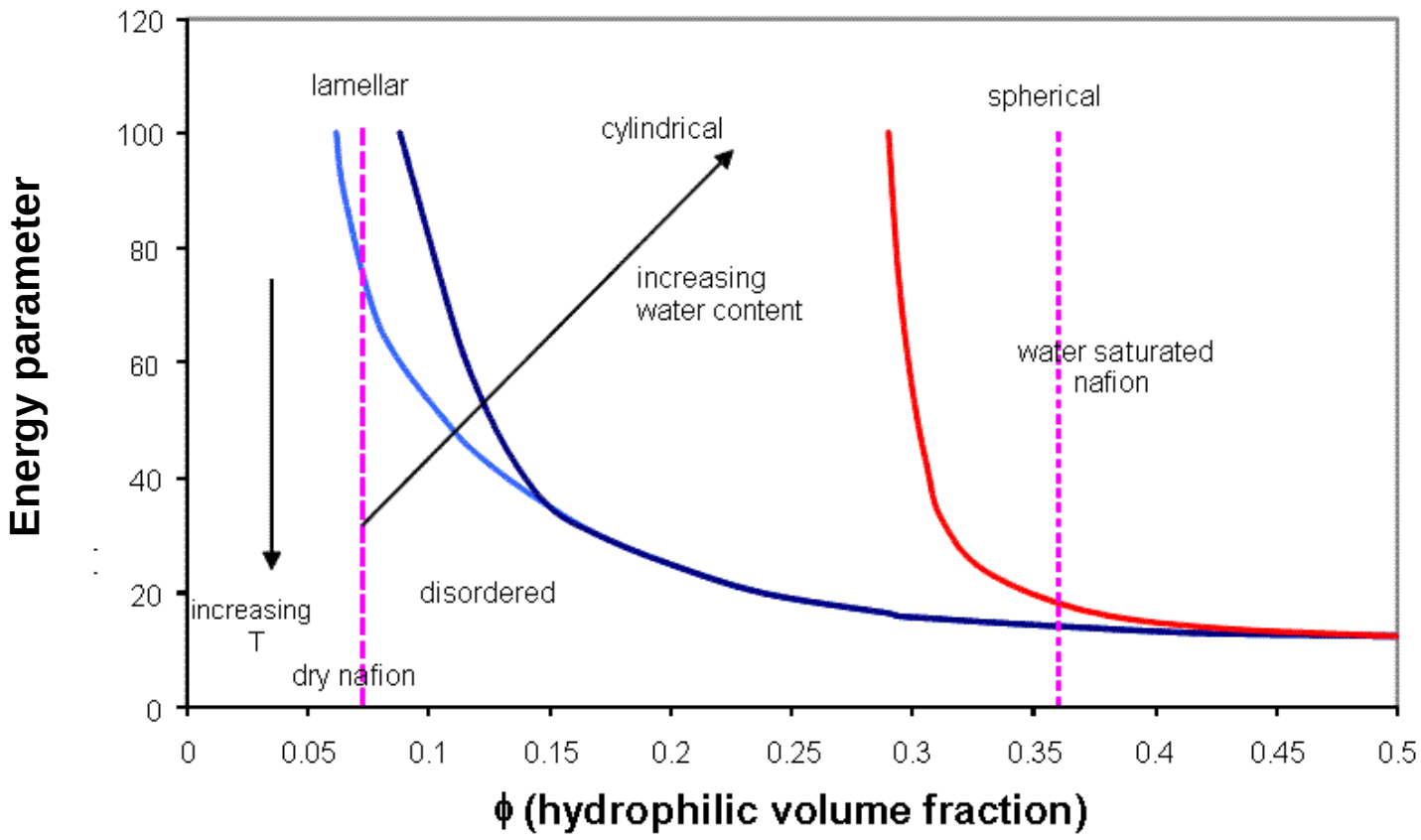
Nafion: Proposed dry structure



Nafion: Proposed hydrated structure



Phase diagram

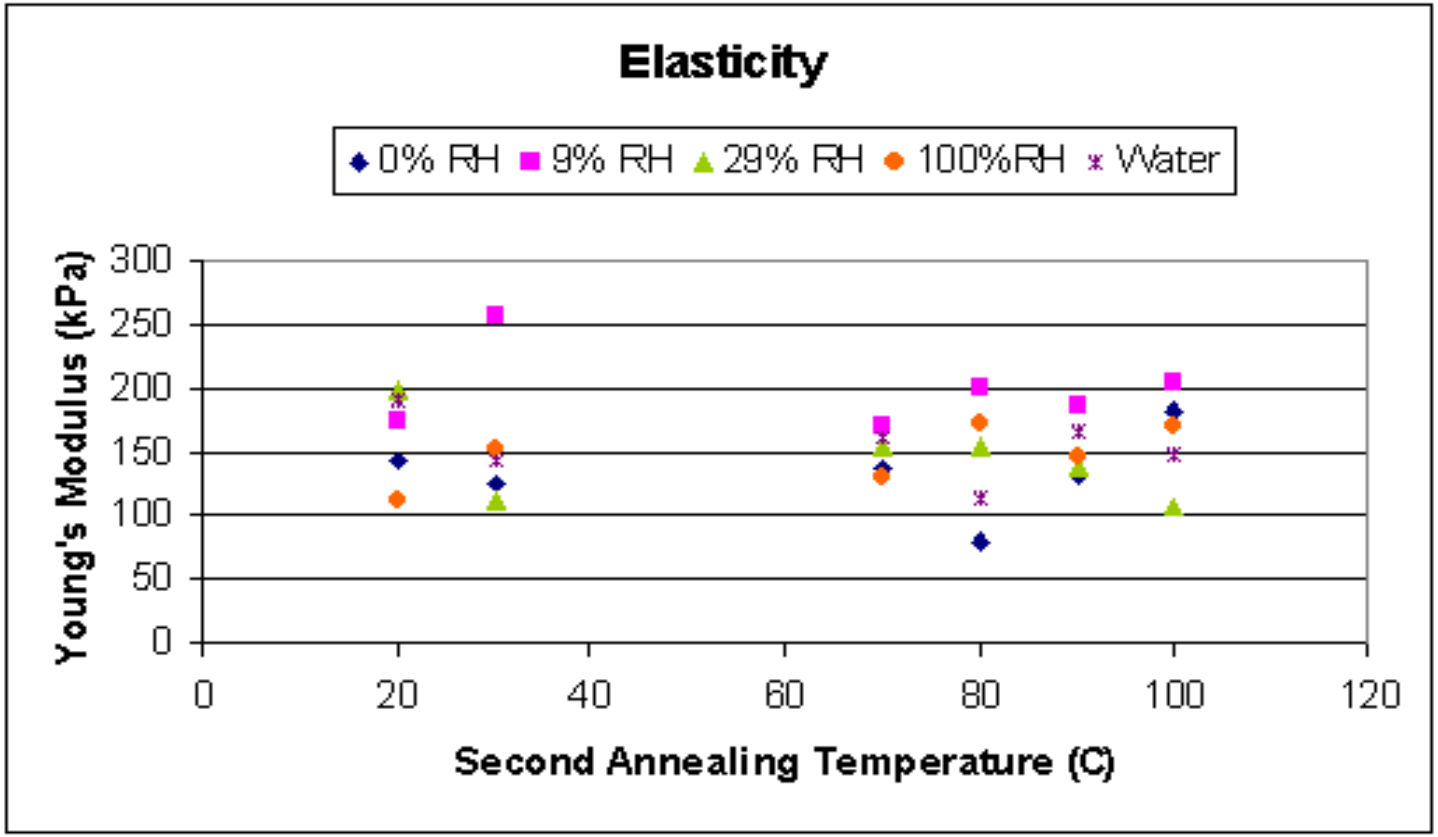


Initial goal

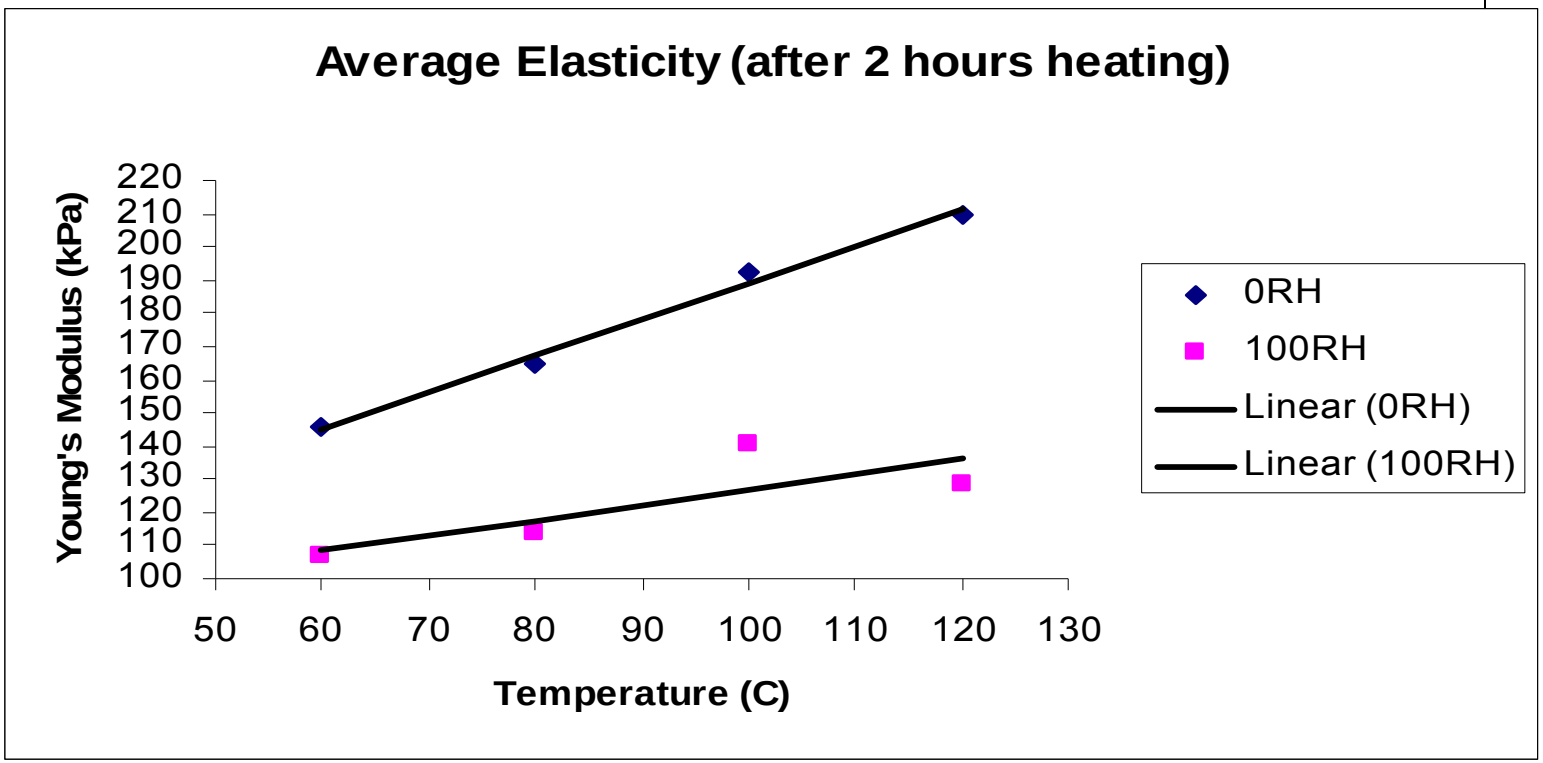
- Study mechanical properties of Nafion at different annealing temperatures (thermal history) and relative humidities
  - Temperatures
    - 150°C for 1 hour
    - 100°C, 90°C, 80°C, 70°C, 30°C, or room temp for ≥2 hours
  - Relative Humidities
    - 0%, 9%, 29%, 100%, or submerged in liquid water

Inconclusive data

- Samples subjected to tensile testing, and Young's (elastic) moduli calculated

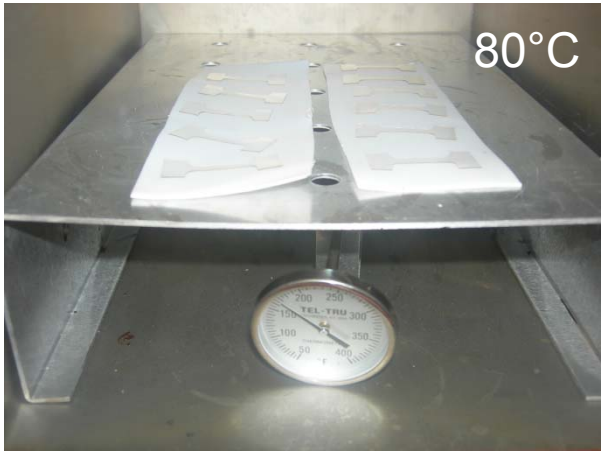


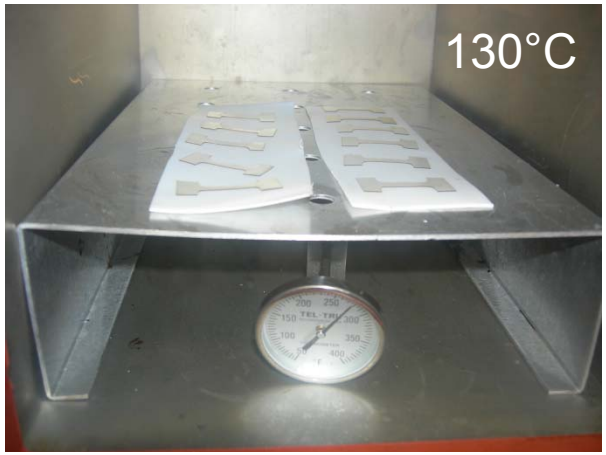
Fewer variables

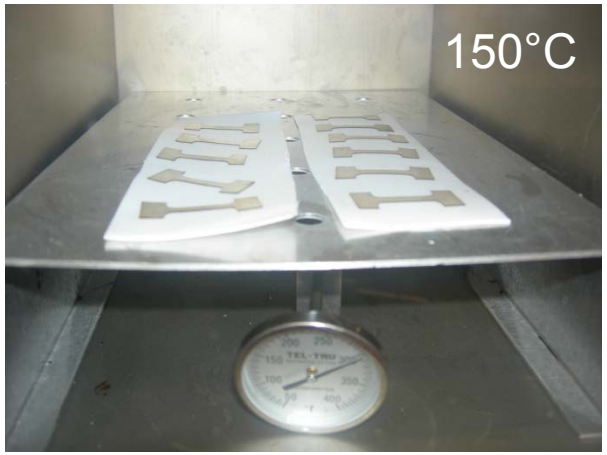


- Nafion stiffens with increase in temperature
- Dry Nafion categorically stiffer than hydrated Nafion

Color changes…

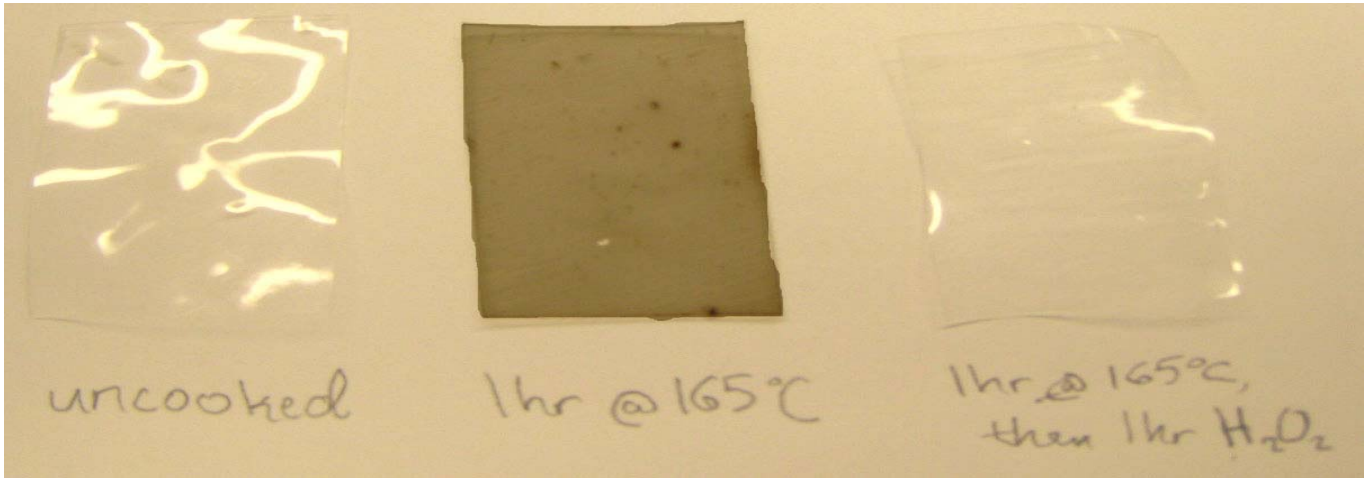






Project changes!

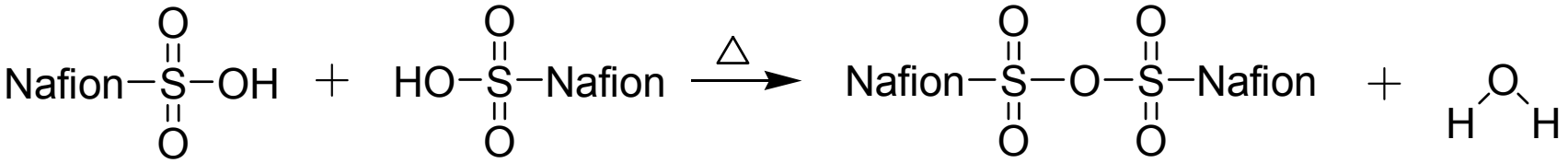
- At higher temperatures (>120°C), membranes turn brown:



- WHY?

New goal

- Analyze chemical composition of Nafion
- Proposed reaction:



- Formation of sulfonic anhydride
- Other cation forms (Na^+, TMA^+) did not darken

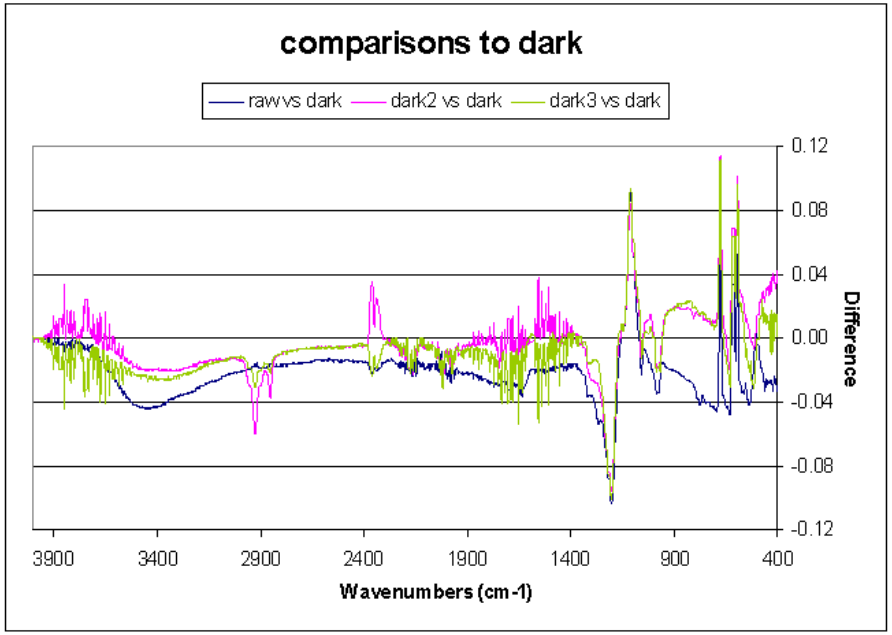
Methods and techniques

- Heat in clean oven
- Under N_2 atmosphere to exclude oxygen
- In Teflon box

- Membranes appear to darken as a function of temperature

Methods and techniques

- FTIR (Fourier Transform Infrared) Analysis



- Meaningful data hard to extrapolate

Methods and techniques

- Acid-base titration
  - If protons were lost in dehydration reaction, the equivalent weight would increase
    - Equivalent weight (EW) = grams of Nafion per mole of sulfonic acid groups
    - $EW = M_d/(V*[OH^-]) - 22$
- Average EW (nominally 1100):
  - Brown, 1068.44
  - H_2O_2 treated, 1071.9
  - Uncooked, 1074.18

Methods and techniques

- Conductivity tests
  - Intended to show inhibition of proton transfer if sulfonic anhydride bond formed
  - Smaller voltage drop should occur – increased resistance

- Result: All show very similar voltage drop
  - Darkened membranes have slightly larger change in voltage (ΔV_{brown}=0.167, $\Delta V_{uncooked}$=0.164)

Conclusions and summary

- Assumptions about structure may have been too general
- If anhydride does form, enhanced transport properties?
- May just be “organic impurities,” as DuPont claims
- Further exploration is needed

Acknowledgements

- Prof. Jay Benziger
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Questions?