Measuring Physical Properties of Polymer Electrolyte Membranes

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Overview

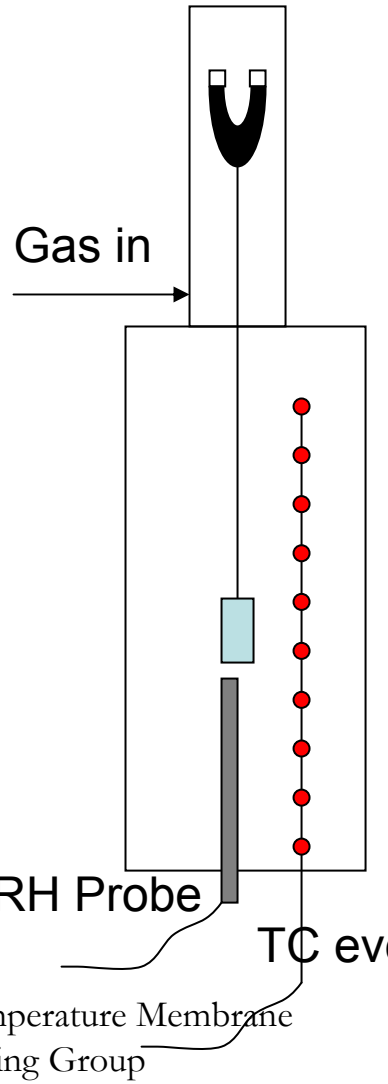
- Water Uptake
  - Liquid
  - As a function of RH and Temperature
- Conductivity (briefly)
  - In-plane
  - Submerged
- Gas Permeability
- Mechanical Properties
  - Time-Temperature-RH Superposition

Water Uptake

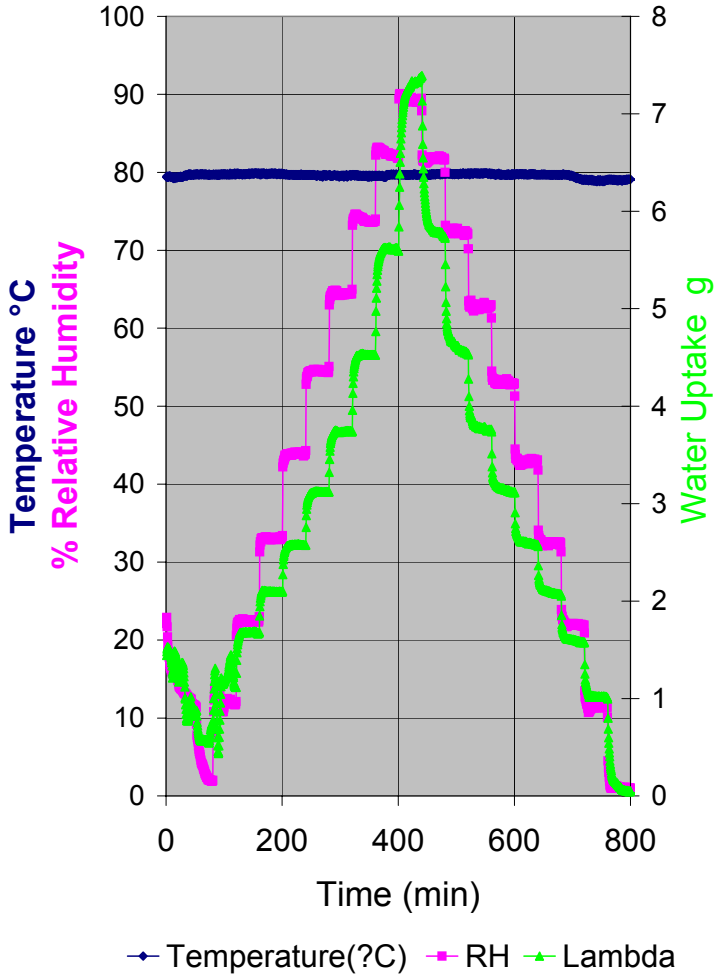
- Why Important?
  - All other properties are related back to water uptake.
  - Expansion due to water uptake must be accommodated by rest of the stack build.
  - PEM can not be water soluble.
    - GM Guideline: Less than 100% Volume expansion in liquid water at 100°C

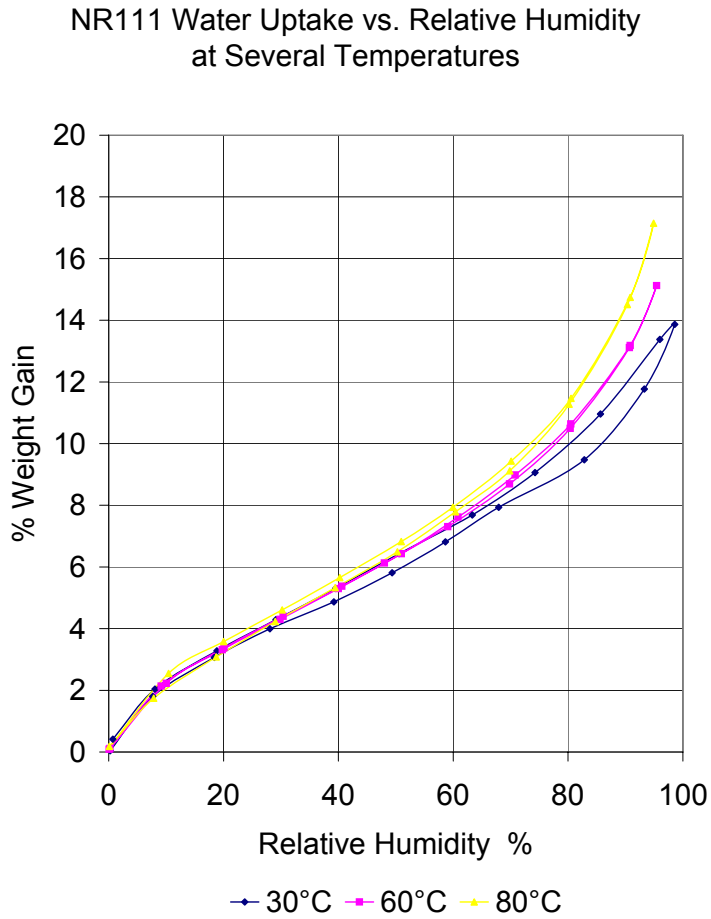
Water Uptake: As a Function of Temperature and Relative Humidity

- Magnetic Balance
  - Allows complete isolation of sample
  - MeOH, other isotherms possible
- RH controlled by mixing dry and wet streams together
  - Allows quick change of RH compared to saturator temperature.
  - If membrane is thick enough permeability and diffusivity can also be calculated
- Temperature Control Extremely Important
  - Water Jacket
  - 1°C difference = 5% RH difference
  - Thermocouple every inch along the column, +/- 0.1°C over 6" active region.
- RH measurement very important
  - Probe in close proximity to sample
  - **Probe calibrated by Pressure**



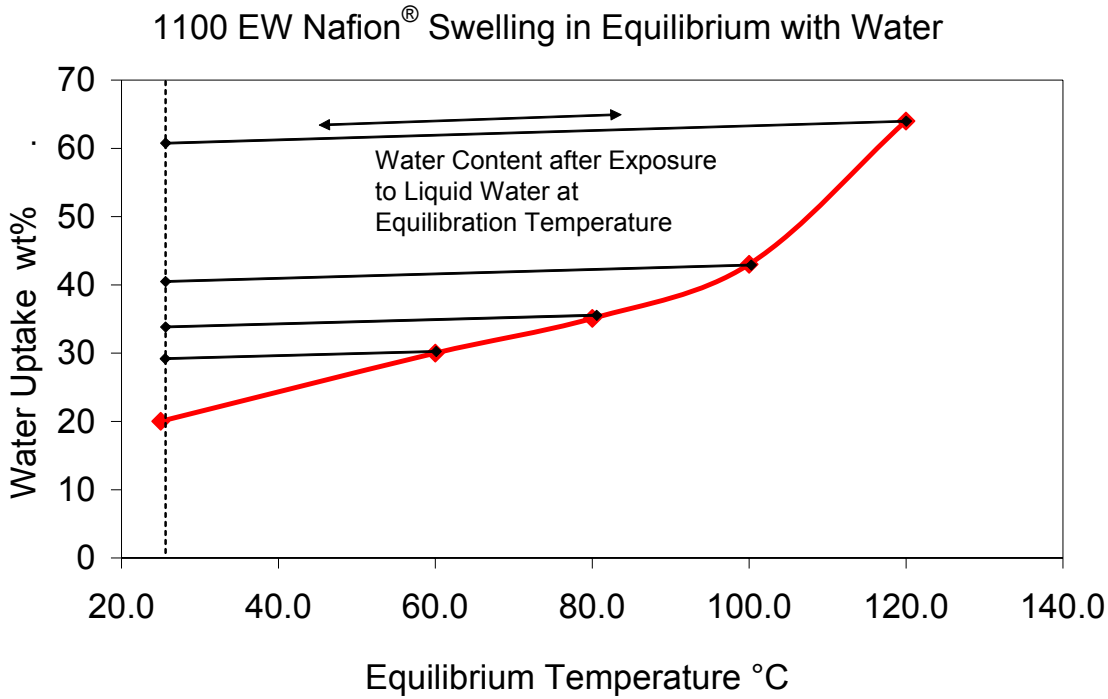
Water Uptake of Nafion Using the Magnetic Balance





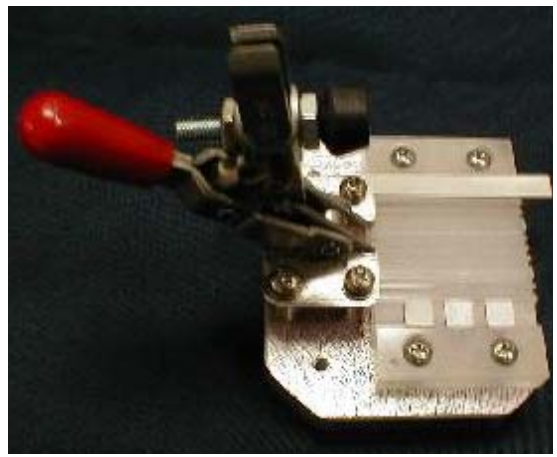
Water Uptake: Liquid Water

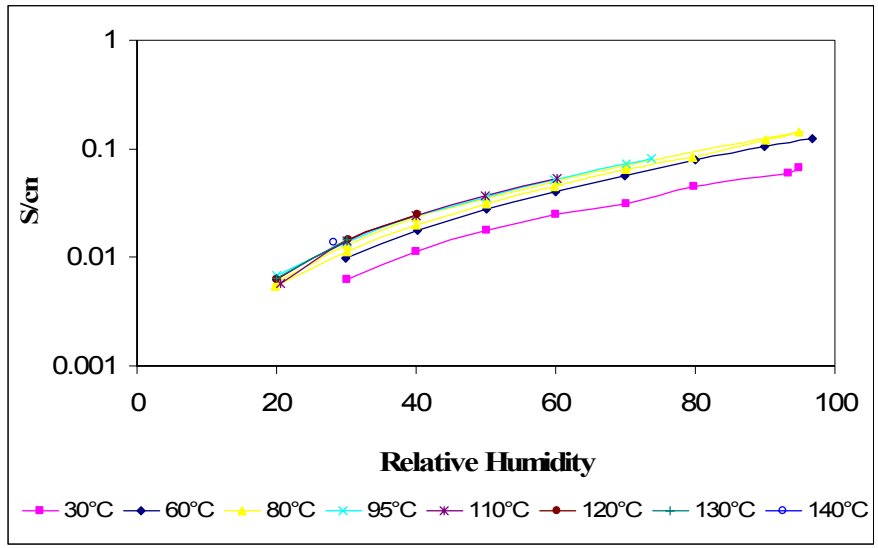
- Technique:
  - Submerged for 24 Hours
  - Removed and placed between 2 wetted clear films
  - X,Y,Z expansion measured
  - Surface moisture removed, placed in pre-weighed sealed container, container weighed for mass uptake



Conductivity: Briefly

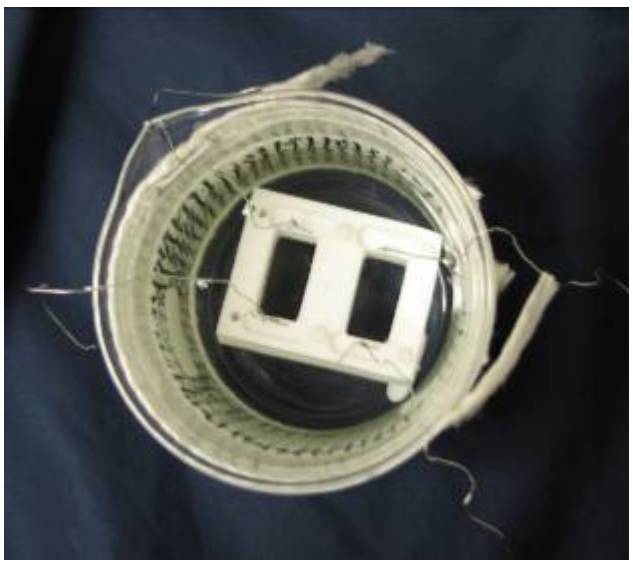
- In-plane Conductivity done as a function of temperature and RH, 3 Membranes at a time *with one always being Nafion 112.*
- RH sweep done at 30, 60, 80, 95, 110, 120, 140°C
  - Up and down at 80°C
- Submerged conductivity done with equivalent empty window to subtract solution conductivity

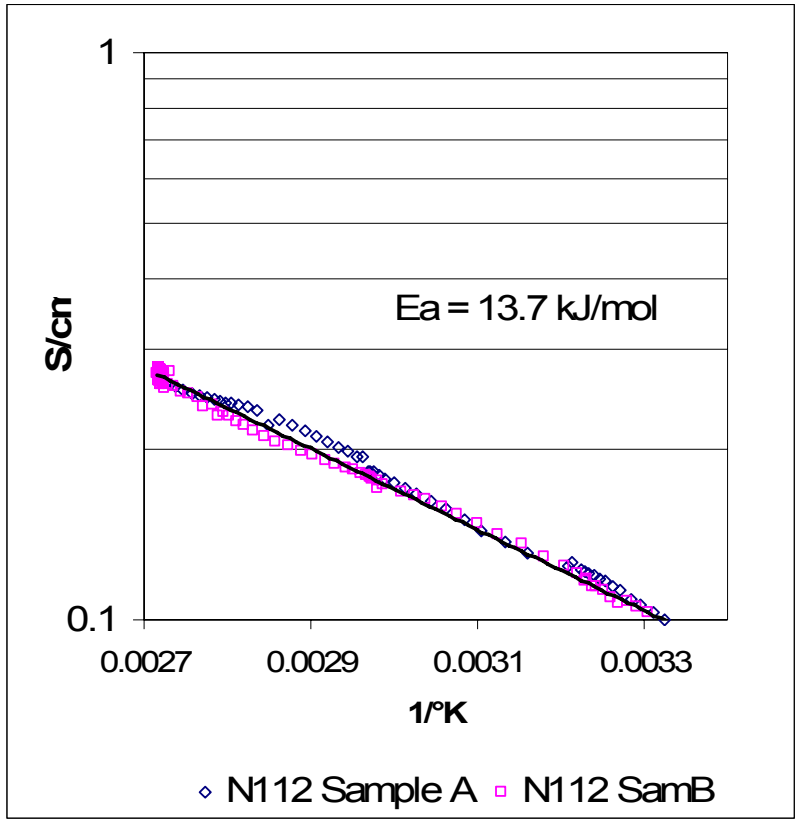




Conductivity: Submerged

- Submerged conductivity done with equivalent empty window to subtract solution conductivity
- Entire Apparatus is Pt and PTFE



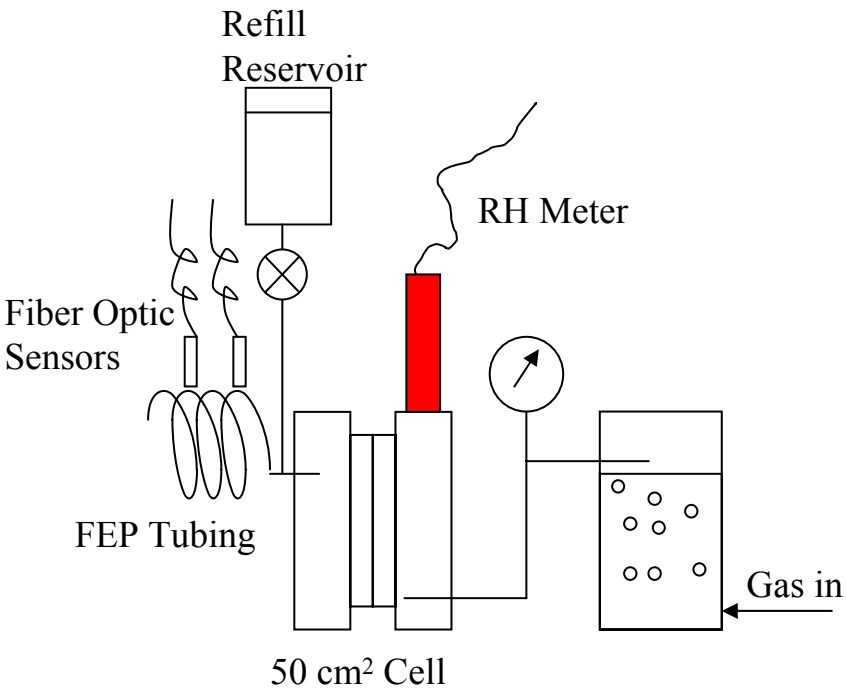


Gas Permeability

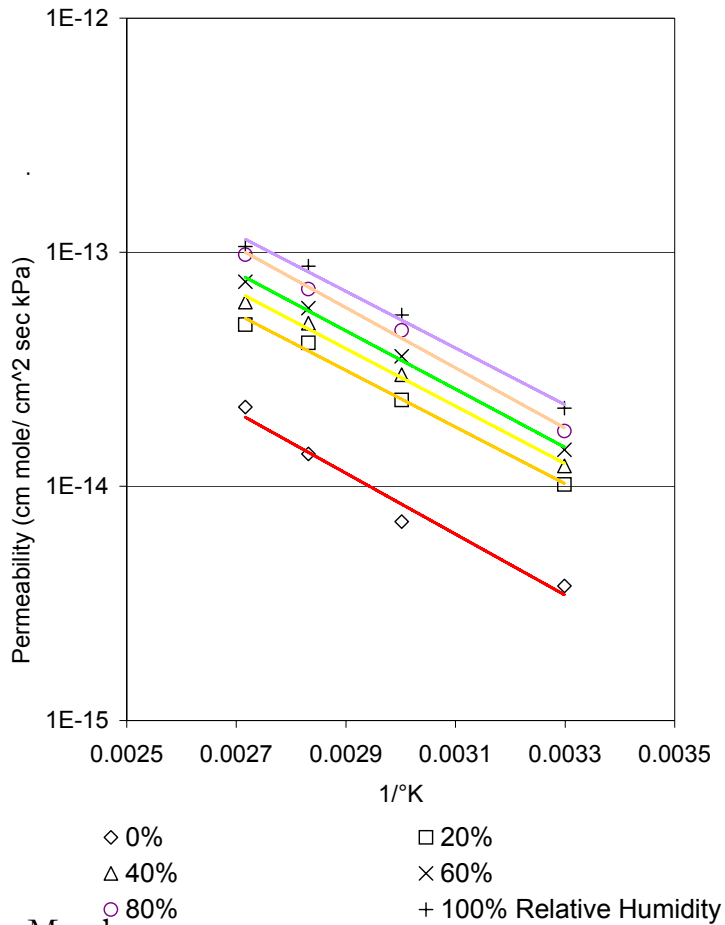
- Why Important?
  - Direct loss to efficiency
  - Gas Crossover Implicated in Degradation
  - N_2 Permeability determines H_2 Stoichiometry

Gas Permeability: Method and Results

Test cell is 50cm^2 cell most people have access to with inexpensive optical sensors added



N_2 Permeability of Nafion 1100



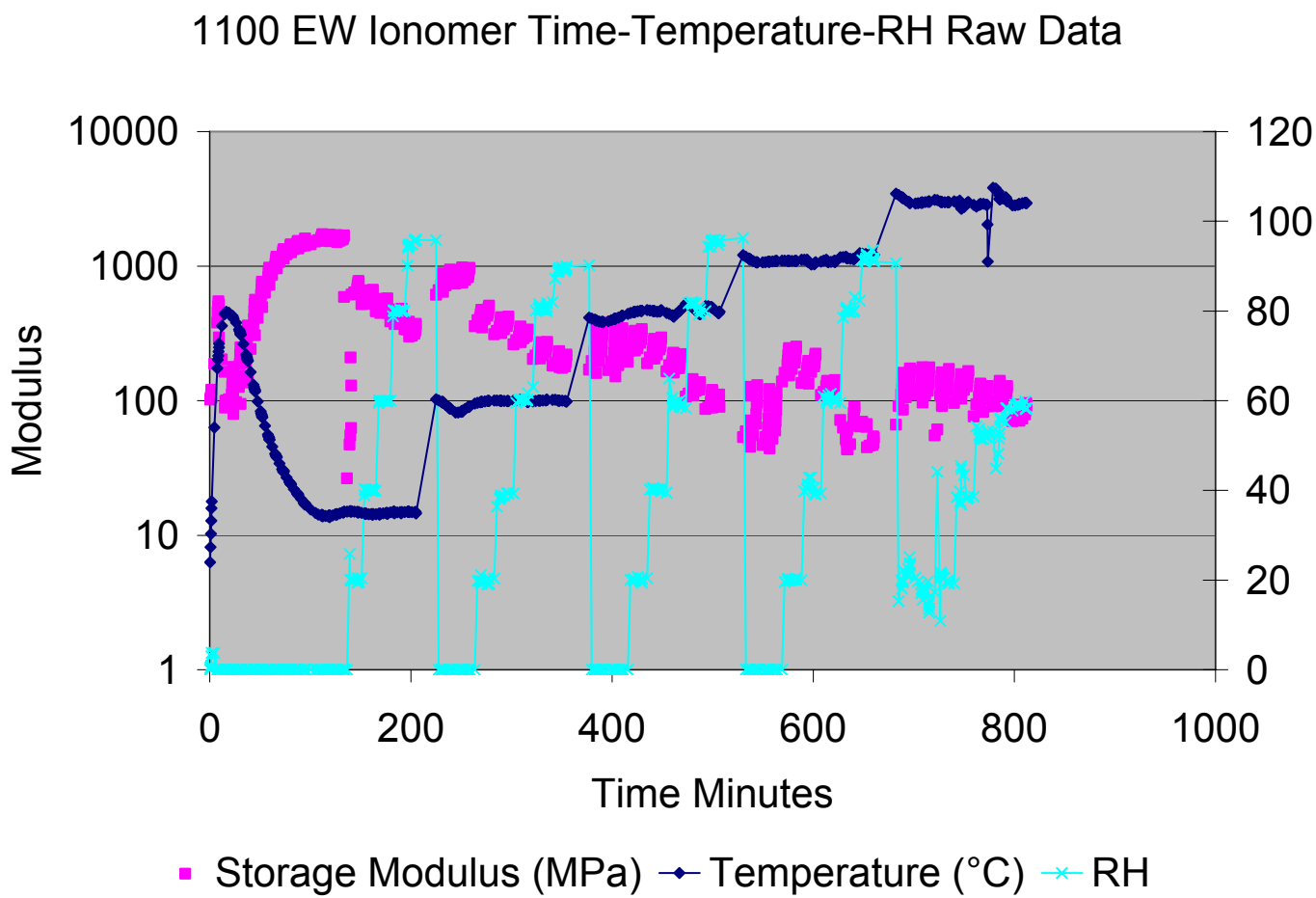
Mechanical Properties

- Why Important
  - Can limit how thin that you can go.
  - Relate back to water content.
    - If you know the equilibrium dimension at a given condition, then perturb that condition you can predict the stress developed, this relates back to mechanical failures.

Mechanical Properties: Time-Temperature-RH Superposition

- DMA Modified for RH control (Q800 TA Instruments)
- Three dimensional Matrix: Temp, RH and frequency
- Important that sample does not creep during testing
- Test also gives single axis swelling as a fxn of RH
- See work by Yeh-Hung Lai of GM and Dillard of Virginia Tech

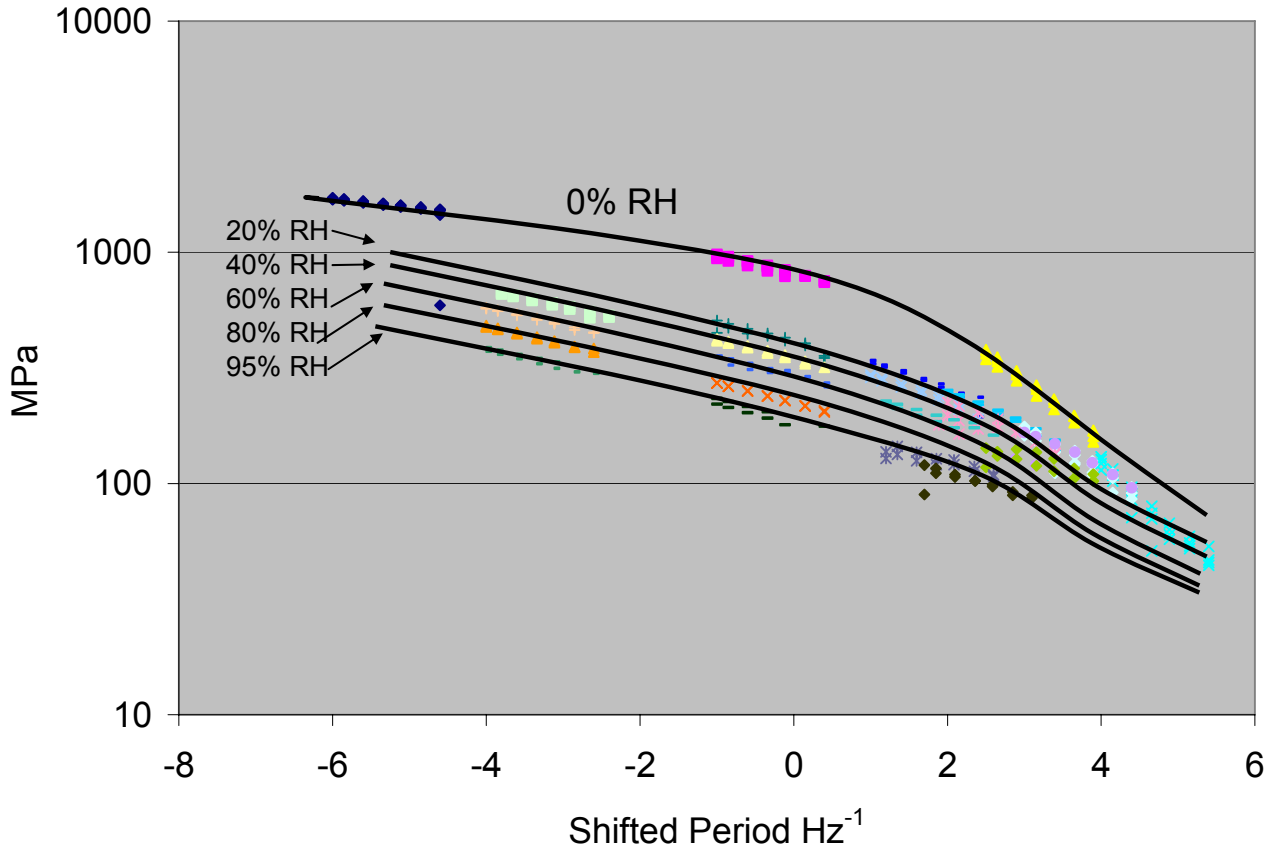
Time-Temperature RH Superposition: Raw Data



Mechanical Properties:

Time Temperature RH Superposition

Nafion 112 DMA scan. Frequency is shifted for Temperature, but not RH



Failure Modes

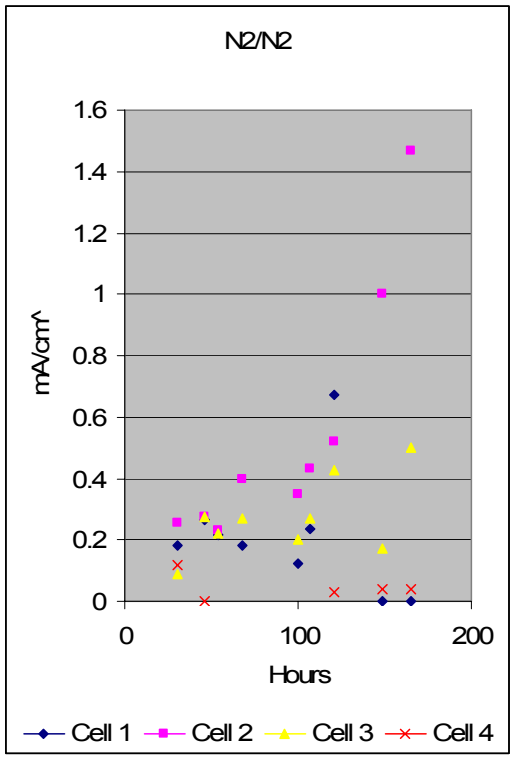
- Why Important?
  - Divorce Chemical and Mechanical Modes of Degradation
  - Accelerated Chemical Testing:
    - At Open Circuit Voltage
    - Increased Temperature
    - Decreased RH

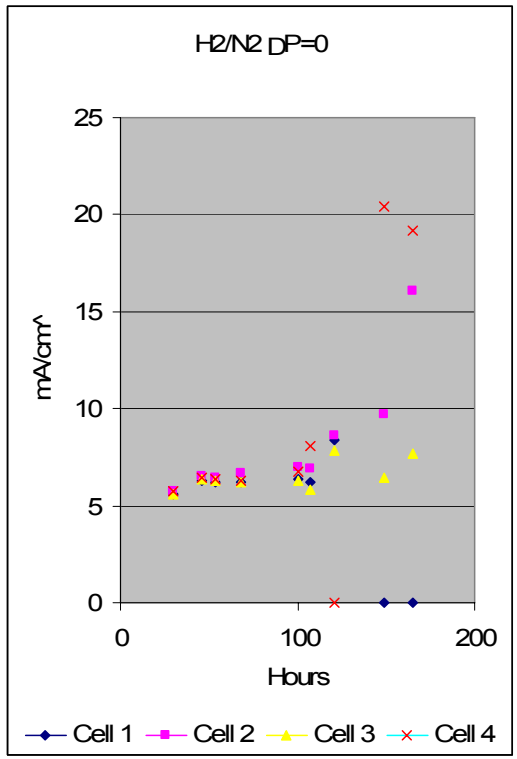
Failure Modes: Accelerated Chemical Testing

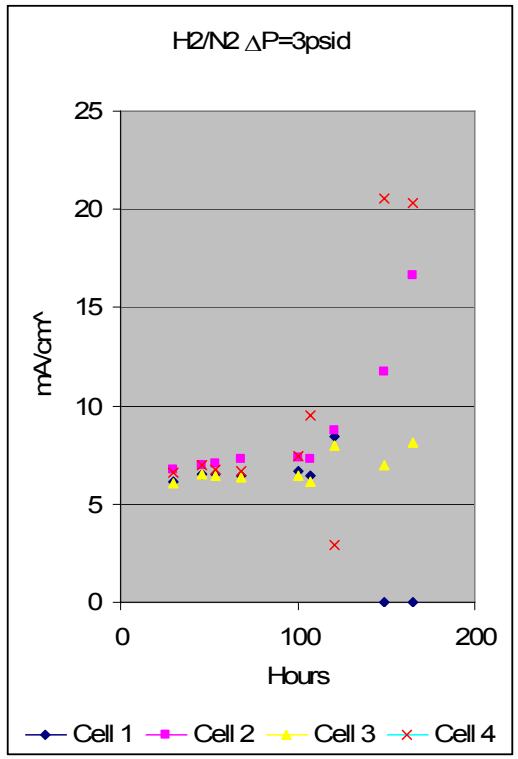
- Tests Conducted at 95°C, 50% RH with H_2/Air at 7 psig
- Water Collected for F^- analysis (perfluorinated only)
- H_2 cross-over
  - Electrochemical Measurement with N_2 at Cathode
    - Increase in current at equal pressure indicates membrane thinning
    - Increase in current with $H_2 > N_2$ pressure indicates pin-holing
  - Increase in N_2/N_2 current at give voltage indicates shorting

OCV Test:

Crossover Currents at 0.5 Volts (95°C 50% RH)







Summary

- Fairly quick screening methods developed to measure membrane critical parameters.
  - Water Uptake
  - Conductivity
  - Gas Permeability
  - Mechanical Properties
  - Secondary Characterizations
    - Water Hydraulic Permeability
    - Electroosmotic Drag Coefficient