Through-Plane & In-Plane Conductivity of Polymer Electrolyte Membranes

Scribner Associates, Inc.

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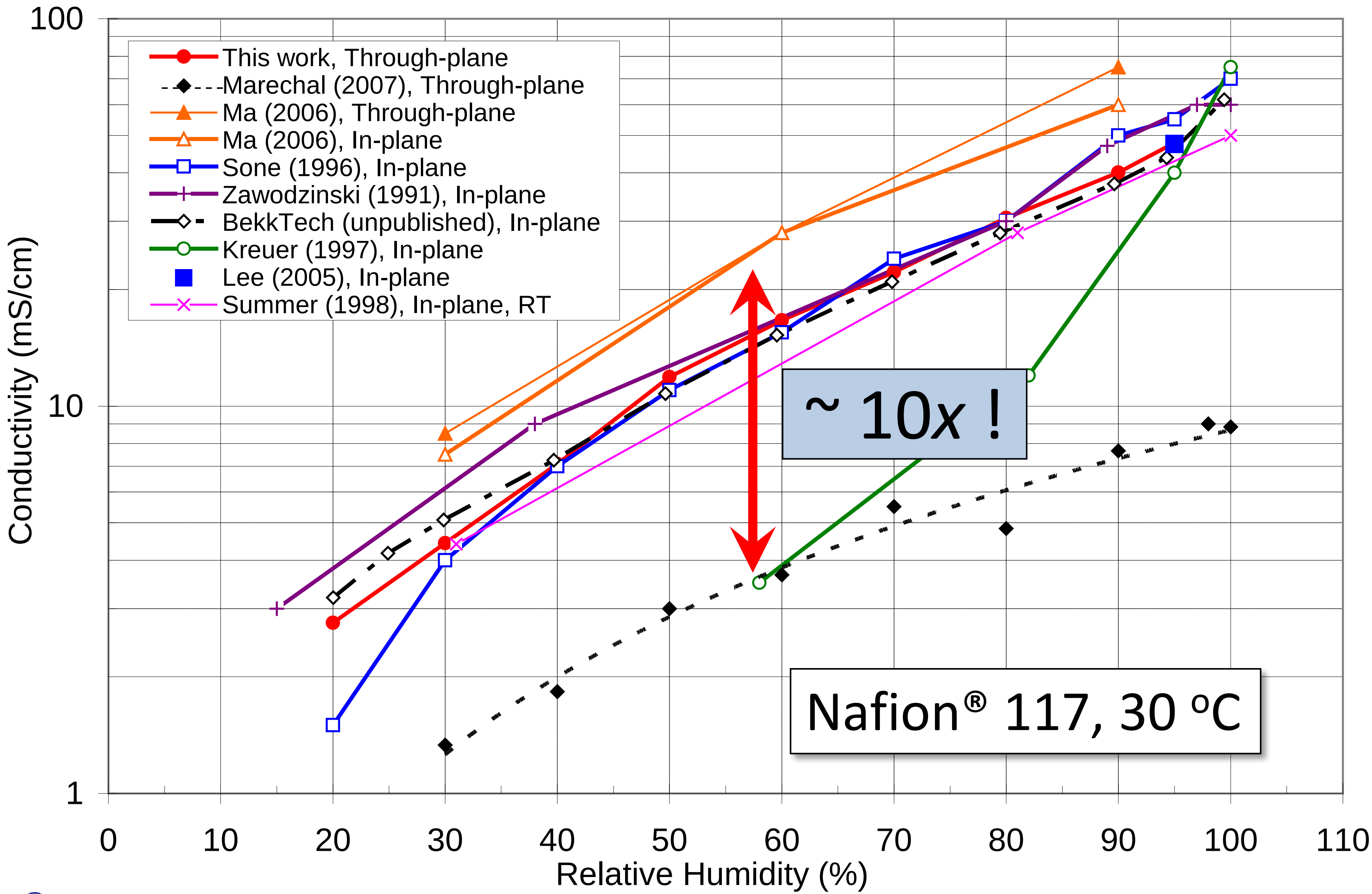
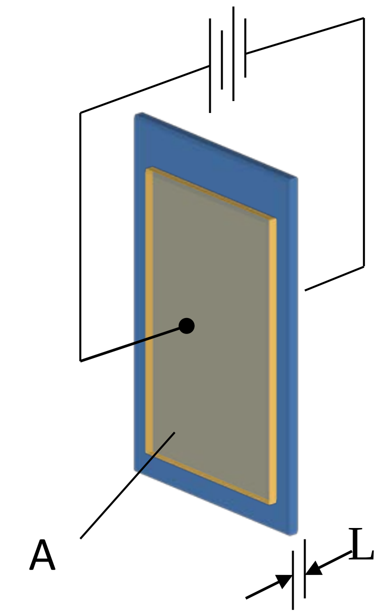
Large discrepancy in reported membrane conductivity data highlights need for accurate, robust measurement methods



***Objective*: Develop an accurate & reliable test apparatus & method for *through-plane membrane resistance* & *conductivity* measurements**

- Key desirable features
  - ✓ Uses bare (non-catalyzed) membrane relevant thicknesses – 10 to 200 μm
  - ✓ Operate over a wide range of conditions
    - 30 to > 120 °C
    - dry to > 95% RH
    - 1 to 3 atm_a
  - ✓ Rapid ~ 15 min per test condition
  - ✓ Robust - accurate, repeatable and reliable

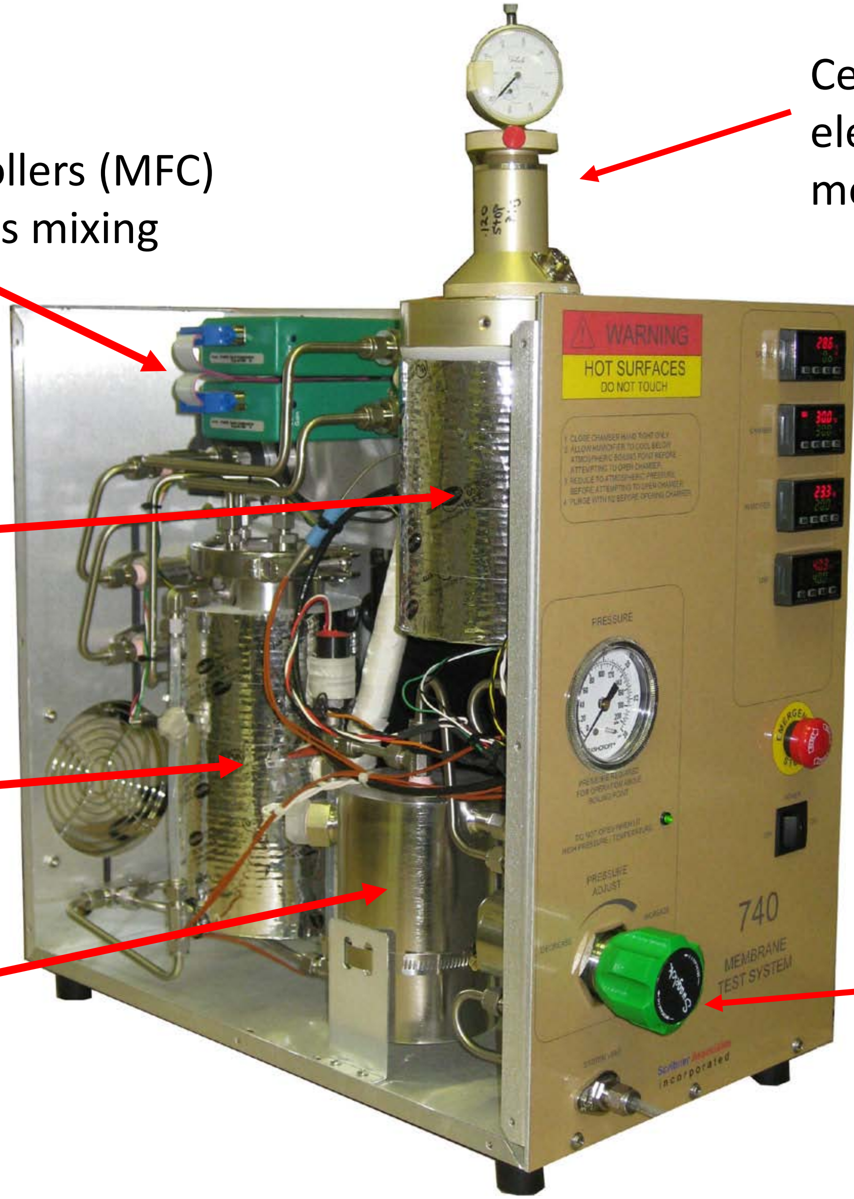


$$\sigma_{membrane} = \frac{L}{R_{membrane} \cdot A} \quad [S/cm]$$

Membrane Test System *MTS 740*

Mass flow controllers (MFC) for wet-dry gas mixing

Cell head w/ integrated electrodes, clamping mechanism, lead connector



Test chamber with *in-situ* dew point & sample temp

Temp controls – test chamber, humidifier, line

Auto-water humidifier

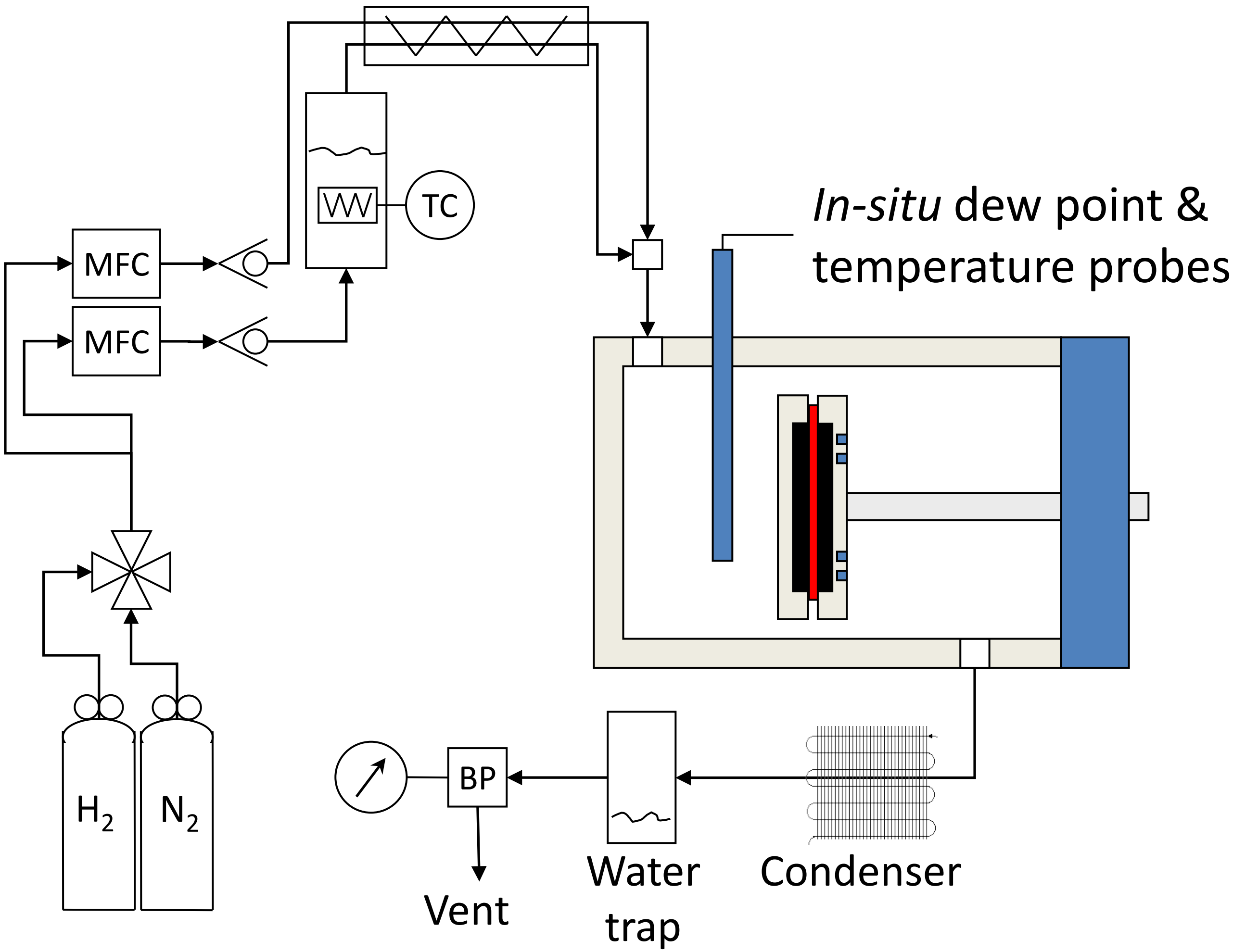
E-stop button

Backpressure regulator

Condensate collection tank

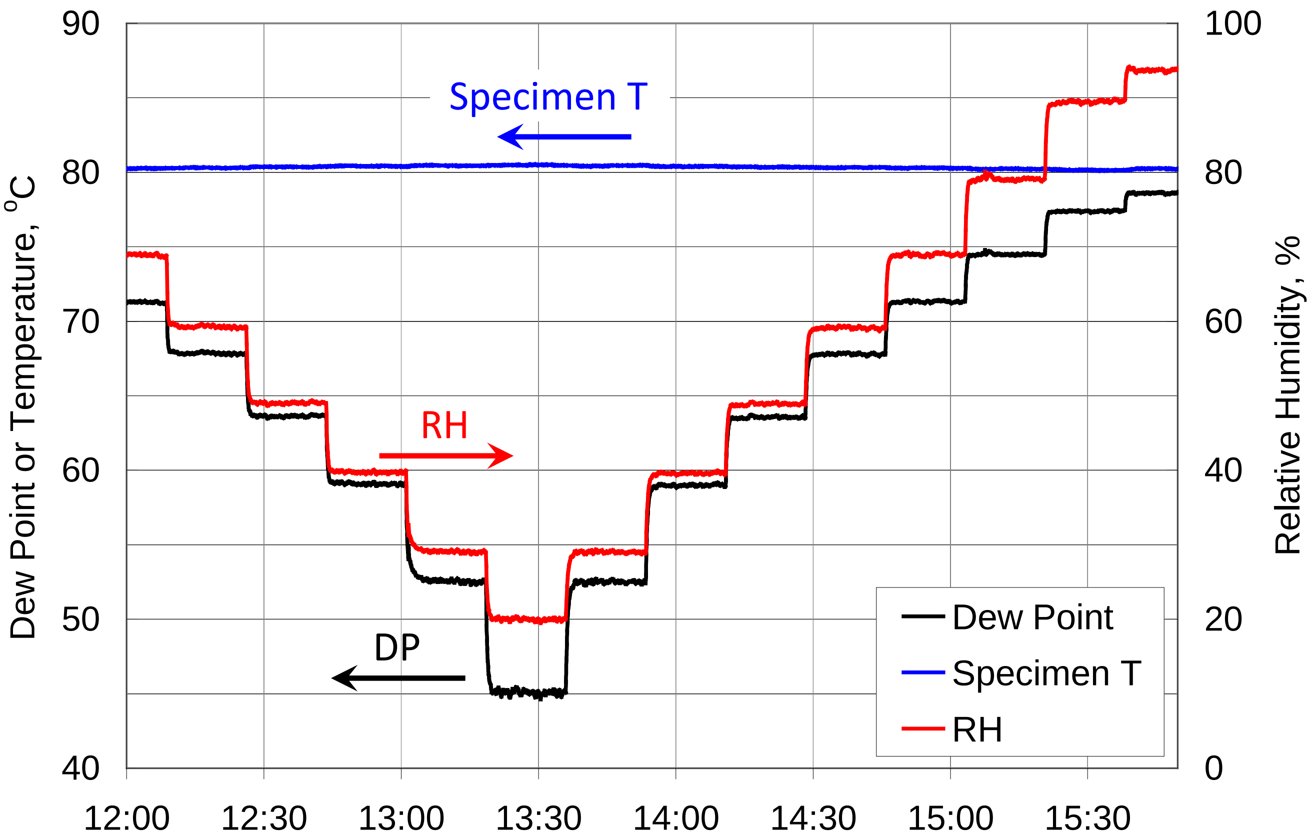
U.S. Patent No. 7,652,479

Wet-dry gas mixing for rapid RH cycling in both directions



Wet-dry gas mixing for controlled, rapid RH cycling

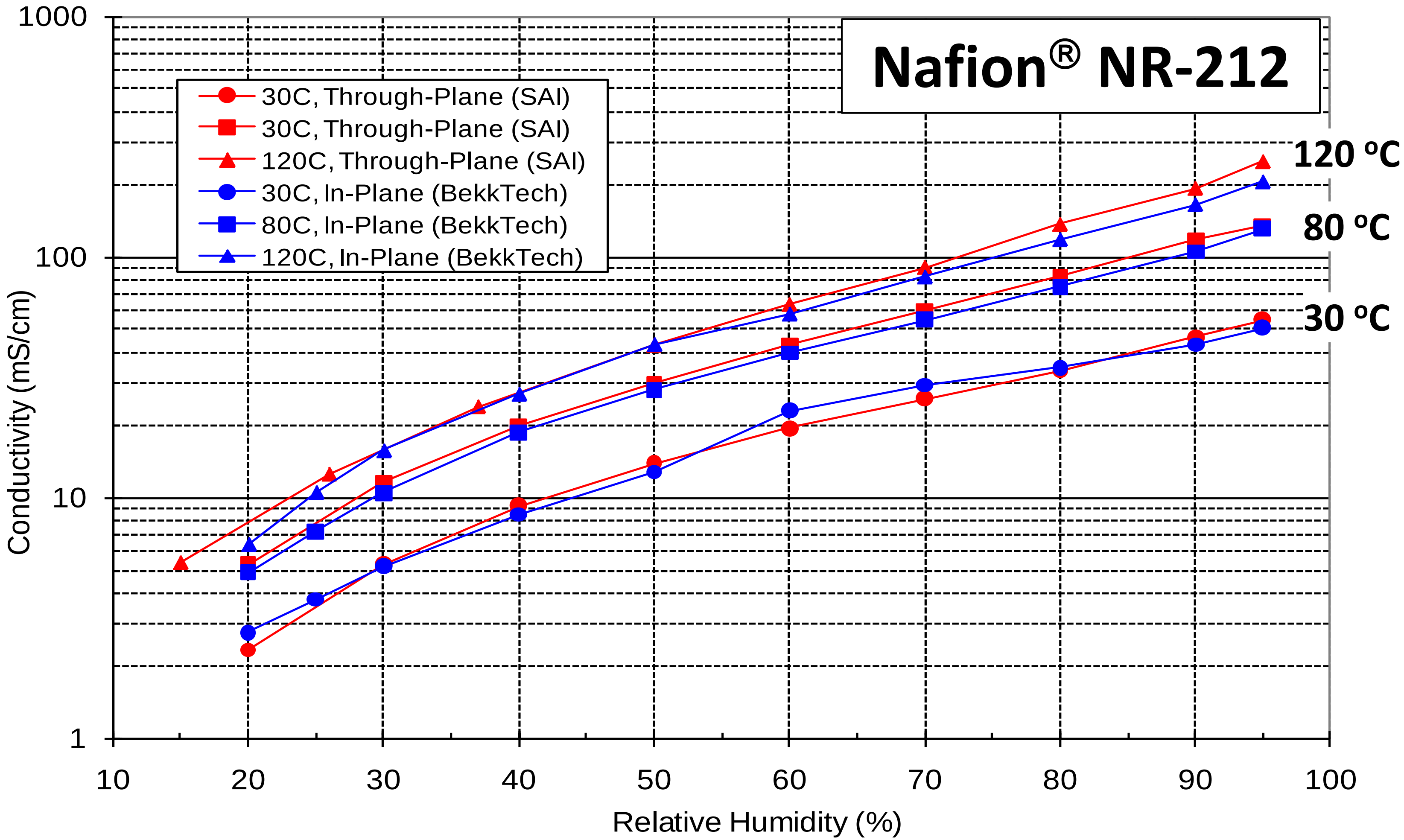
- Repeatable, reproducible and stable T, dew point & RH
  - ✓ ±2% from 20% to 95% RH
- Rapid RH cycling → time-efficient testing over wide RH range
- Dew point to 120 °C, sample to 150 °C



Nominal % RH	Difference from Nominal, % RH: 30 °C N = 15	80°C N = 11
20	0.5	-0.3
40	0.7	-0.5
60	-0.2	-0.8
80	-1.4	-0.4
90	-1.5	0.3
95	-2.2	-0.3

Comparing through-plane & in-plane conductivity of Nafion® NR-212

$\sigma_{in\text{-}plane} \cong \sigma_{through\text{-}plane}$ for dispersion cast Nafion®



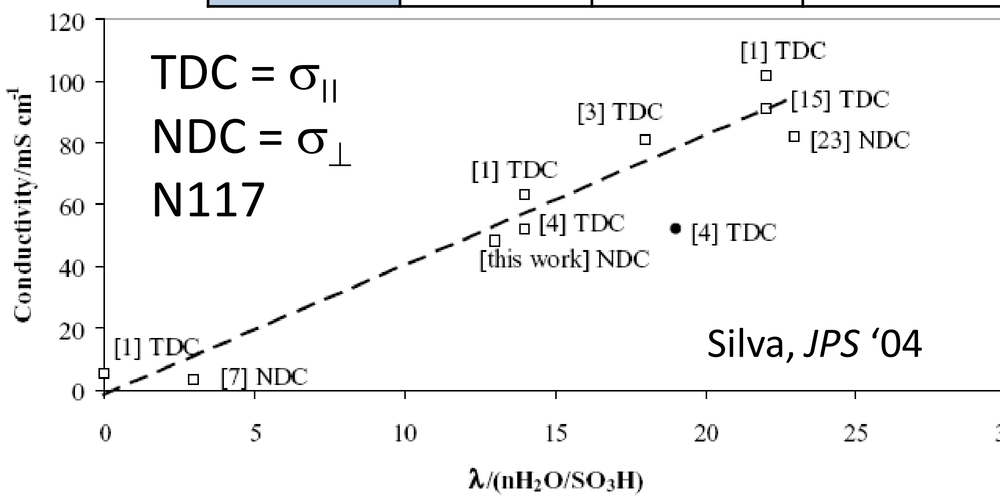
Is the conductivity of Nafion® isotropic? … No consensus in published literature

$\sigma_{||}$ = in-plane, $\sigma_{\perp}$ = through-plane

- Yes, it is isotropic, $\sigma_{||}:\sigma_{\perp} \cong 1$ [Nouel; Silva]
  - ✓ This work for NR-212
- No, it is anisotropic
  - ✓ $\sigma_{||}:\sigma_{\perp}$ = 3.6 [Gardner]
  - ✓ $\sigma_{||}:\sigma_{\perp}$ = 2.5 – 5 (with pressure) [Ma]
  - ✓ $\sigma_{||}:\sigma_{\perp}$ = 1.8 – 5 [Casciola]
- Discrepancy due
  - ✓ Different water content (λ)
  - ✓ Extruded (N11X) *vs.* dispersion cast (NR-21X)

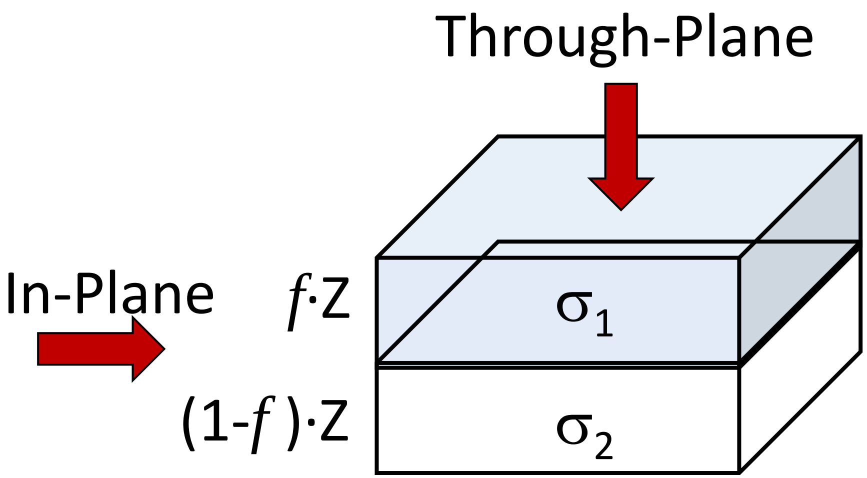
$\sigma_{||}:\sigma_{\perp} \cong 1$, NR-212, this work

% RH	30 °C	80 °C	120 °C
20	1.19	0.92	1.20
40	0.95	1.02	1.15
60	1.15	1.02	0.96
80	0.99	0.96	0.87
90	0.93	0.97	0.87
95	0.93	106	0.84



Gardner *et. al.*, *J. Electroanal Chem* **449** 209 (1998)
Ma *et. al.*, *JES* **153** A2274 (2006)
Casciola *et. al.*, *J. Power Sources* **162** 141 (2006)
Nouel, Fedkiw, *Electrochimica Acta* **43** 2381 (1998)
Silva, *et. al.*, *J. Power Sources* **134** 18 (2004)

Effective conductivity (σ_{eff}) of membrane with phases of unequal conductivity, *e.g.*, ionomer-impregnated non-conductive porous support



$$\sigma_{eff,\,in\text{-}plane} = f \cdot \sigma_1 + (1 - f) \cdot \sigma_2$$

$$\sigma_{eff,\,through\text{-}plane} = \frac{\sigma_1 \cdot \sigma_2}{(1 - f) \cdot \sigma_1 + f \cdot \sigma_2}$$

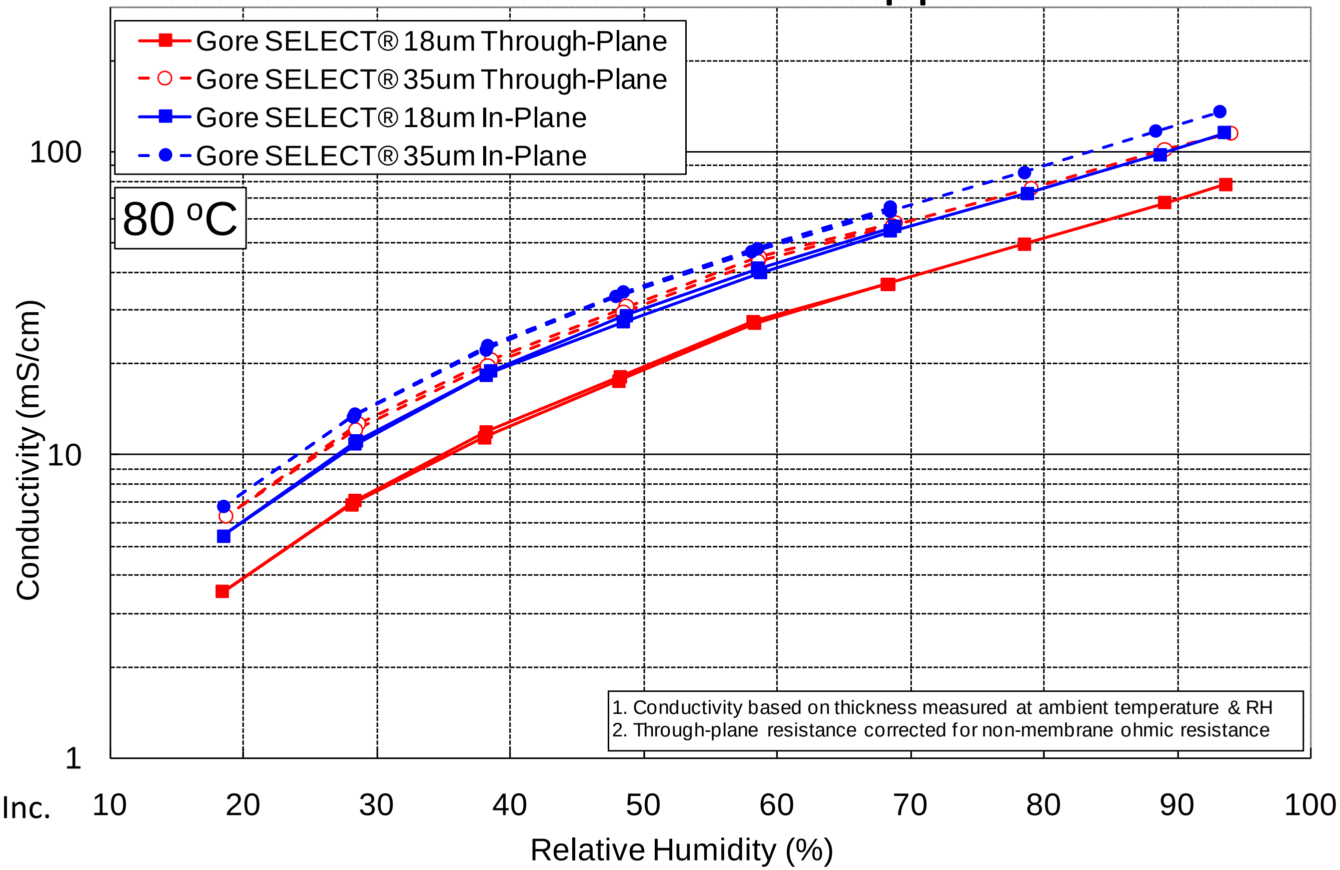
f = fractional thickness of phase 1

- $\sigma_{eff,\ in\text{-}plane} > \sigma_{eff,\ through\text{-}plane}$ for supported membrane
- $\sigma_{eff,\ in\text{-}plane} : \sigma_{eff,\ through\text{-}plane}$ is a maximum for $f = 0.5$
- $\sigma_{eff,\ in\text{-}plane} : \sigma_{eff,\ through\text{-}plane} \rightarrow 1$ as $f \rightarrow 0$ or 1
- $\sigma_{eff,\ in\text{-}plane} : \sigma_{eff,\ through\text{-}plane}$ increases as $\sigma_1 : \sigma_2 \rightarrow 0$ or $>> 1$

Comparing through-plane & in-plane conductivity (σ) of PFSA-based membranes with inert support *GORE-SELECT®*

- $\sigma_{eff,\ in\text{-}plane} > \sigma_{eff,\ through\text{-}plane}$ ✓
- $\sigma_{eff,\ in\text{-}plane} : \sigma_{eff,\ through\text{-}plane} \rightarrow 1$ as $f \rightarrow 0$ or 1 ✓
  - ✓ Ratio is greater for thin membrane with same support thickness

Thickness	$\dfrac{\sigma_{eff,in\text{-}plane}}{\sigma_{eff,through\text{-}plane}}$
18 μm	1.53 ± 0.16
35 μm	1.11 ± 0.10



Conclusions – Membrane Test System *MTS 740*

- ***Through-plane resistance & conductivity test system developed***
  - ✓ Bare membrane – rapid, lower cost assessment *vs*. MEA / fuel cell testing
  - ✓ Repeatable, accurate control of environmental conditions: cell to 150 ^{o}C, humidifier to 120 ^{o}C, dry to >95% RH
  - ✓ Robust method – repeatable and accurate
- ***Correction for non-membrane ohmic resistance contributions is important, especially for thin membranes with low resistance / high conductivity***
- ***Dispersion cast Nafion® NR-212 though-plane conductivity is the same as in-plane***
- ***Differentiate in-plane and through-plane conductivity for anisotropic material, e.g., GORE-SELECT® supported membrane***

GORE-SELECT, GORE and designs are trademarks of W. L. Gore & Associates, Inc.

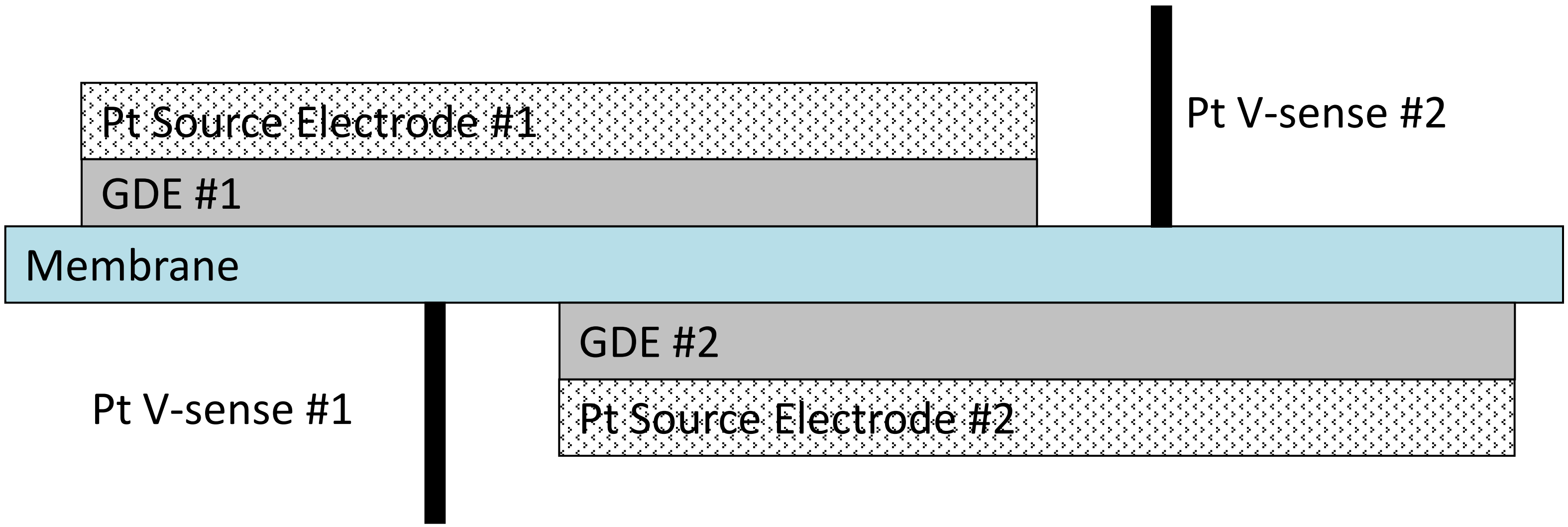
Supporting Information

- Electrode design
- Test procedure
- Analysis Procedure
- Determination of Cell Resistance

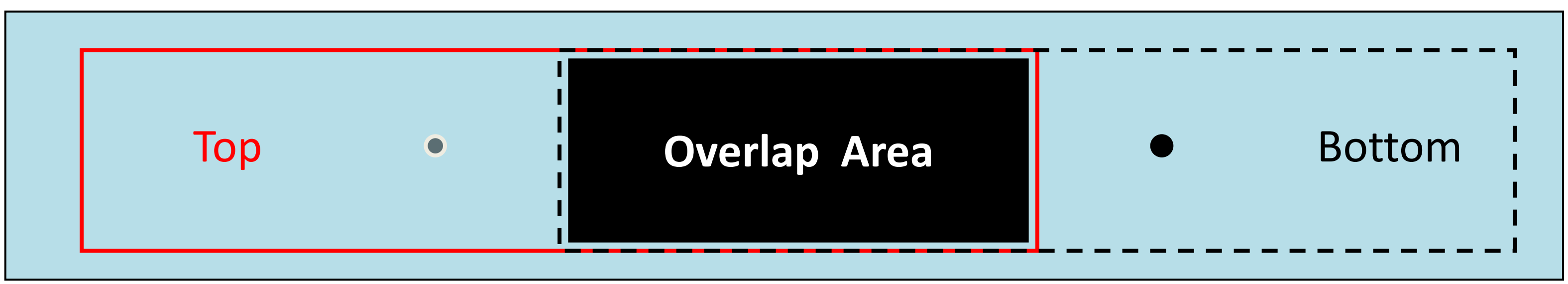
4-Electrode, “Offset” Electrode Design

Dimensions in mm

Side View

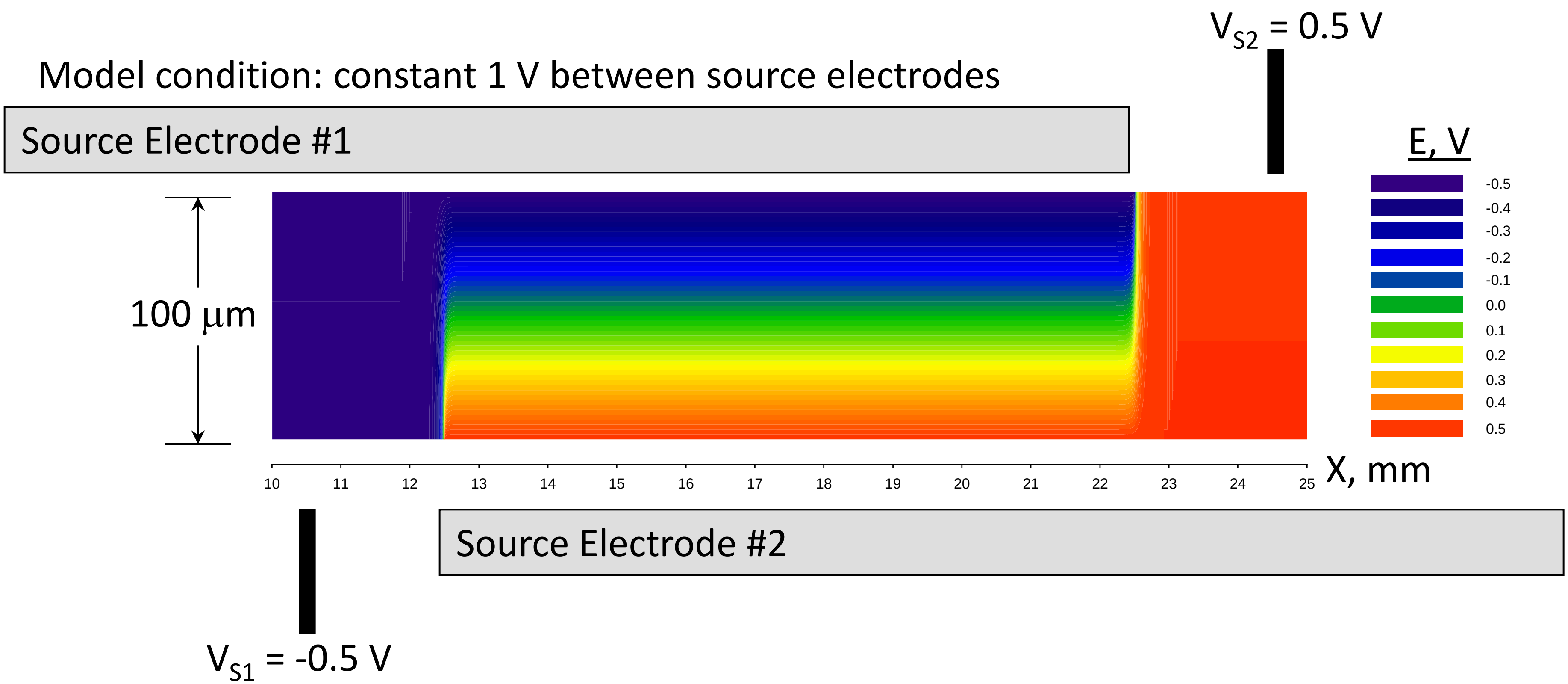


Top View



U.S. Patent No. 7,652,479

Offset electrode geometry for 4-probe conductivity measurement of thin film electrolytes



Y-axis is expanded 10x relative to X-axis

U.S. Patent No. 7,652,479

Procedure – Pre-test

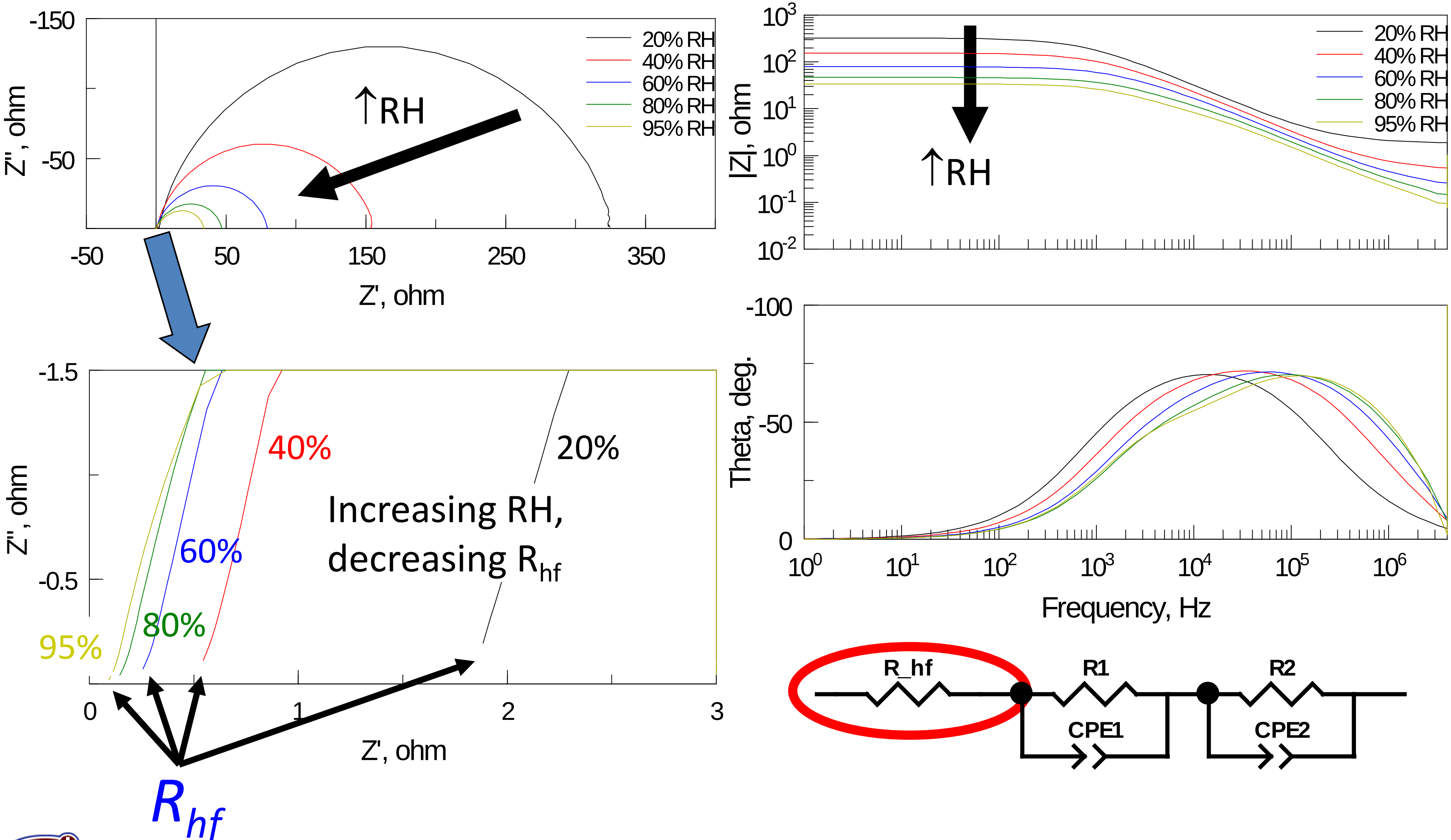
- As-received membrane, stored at ambient conditions
- 32 mm *x* 10 mm sample
- Measure "dry" membrane thickness
  - ✓ Mean of 5 locations, 3x measurements/location
  - ✓ Low load, high accuracy gage
- Cell Assembly
  - ✓ GDE (E-LAT) cut with jig
  - ✓ Glue GDE to Pt electrode with carbon paste
  - ✓ Load membrane between GDE-prepared plattens
  - ✓ Compress ~ 2,200 kPa (325 psi) using spring loaded cell head (dial gage)

Procedure

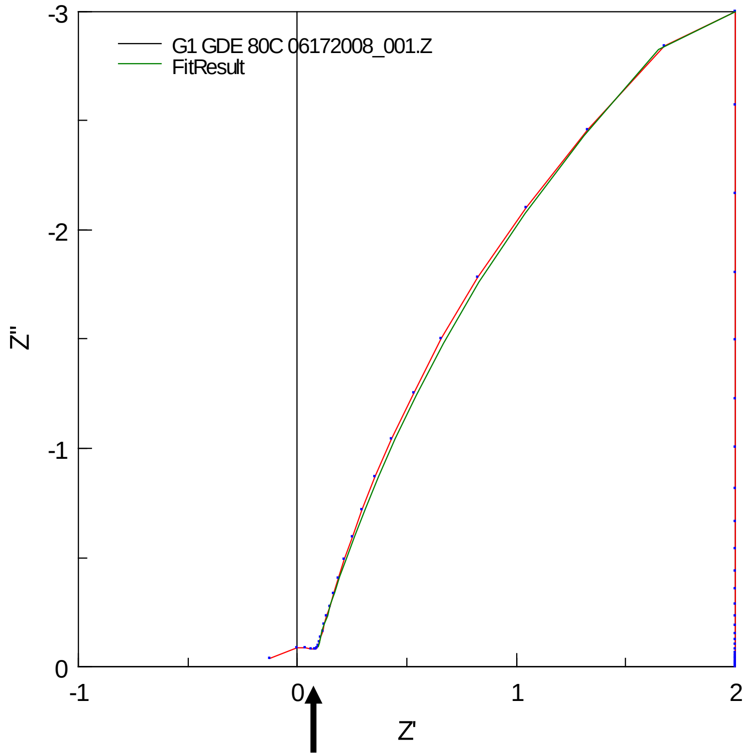
- Temperature series (°C): 80 → 30 → 120
- Per temperature
  - ✓ Wet-up 2 hr @ 70% RH
  - ✓ RH cycle: 70 → 20 → 90 → 95 %, 15 min step
  - ✓ Impedance sweep after 15 min
- ~ 1 day/temperature, ~6 hr
- Gas: H_2 or N_2
- Impedance Measurement
  - ✓ 4-electrode, 4 terminal
  - ✓ Solartron 1260 FRA (standalone) / ZPlot®
  - ✓ 10 MHz – 1 Hz, 10 mV_{AC}, 0 V_{DC}, 10 steps/dec (~ 2 min)

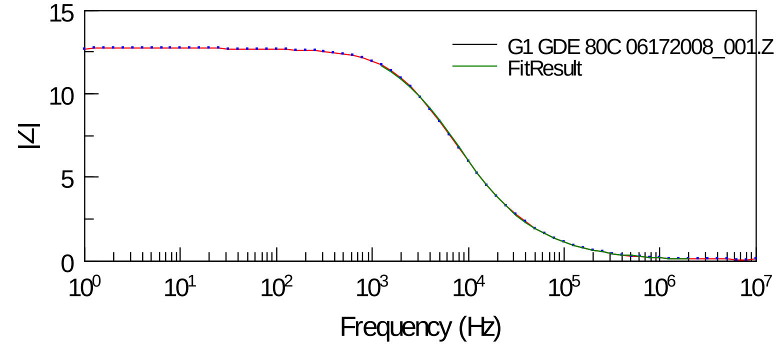
Temp, °C	Total Dry Gas Flow, sccm	Pressure, kPa_a
30	500	100
80	500	100
120	500	230

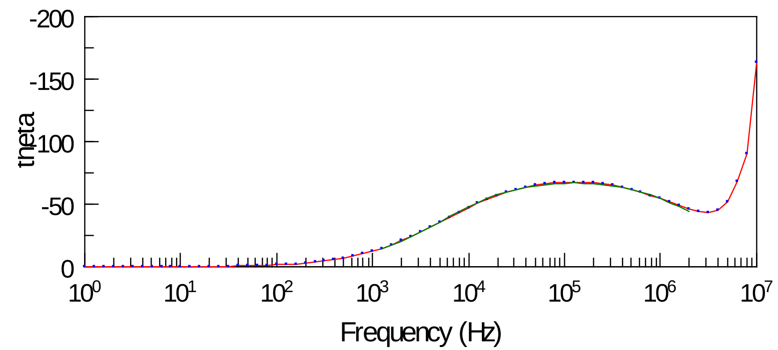
Post-test Procedure – EIS Analysis

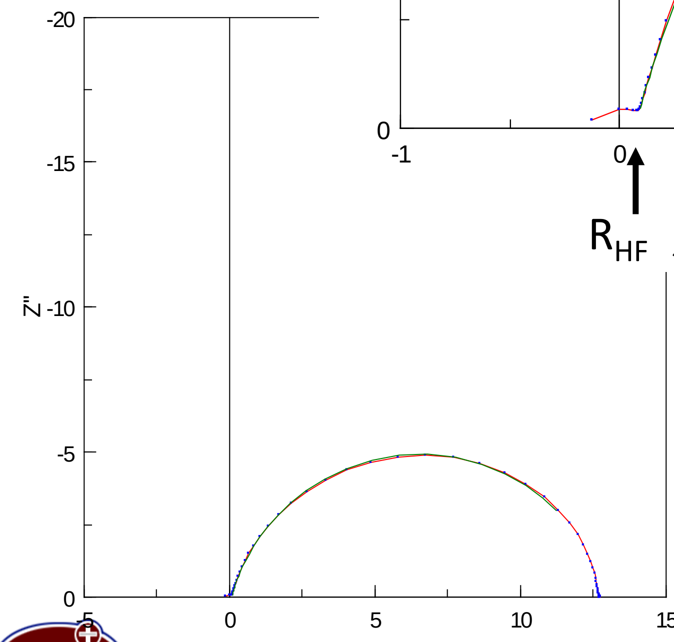


Post-test Procedure – EIS Analysis

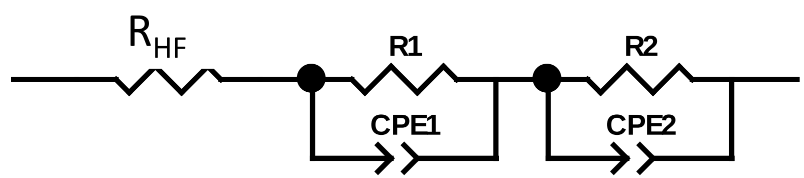








R_{HF}



Element	Freedom	Value	Error	Error %
R_b	Free(+)	0.068111	0.0011616	1.7055
R1	Free(+)	12.92	0.087668	0.67854
CPE1-T	Free(+)	1.3459E-05	3.089E-07	2.2951
CPE1-P	Free(+)	0.83049	0.0017289	0.20818

Through-plane Resistance & Conductivity

- Through-plane resistance includes ***non-membrane ohmic contributions, R_{cell}***

$$Cell\ Resistance,\ R_{cell} = R_{\Omega,\,electrode} + R_{\Omega,\,contact} + R_{\Omega,\,interface}$$

- Typically work in area specific resistance, *ASR*

$$ASR_{uncorrected} = R_{HF} \cdot A_{effective} \qquad [\Omega - cm^2]$$

- Accounting for the cell *ASR(T,RH)* gives the membrane resistance

$$ASR_{membrane}(T,RH) = ASR_{uncorrected}(T,RH) - ASR_{cell}(T,RH) \quad [\Omega - \mathrm{cm}^2]$$

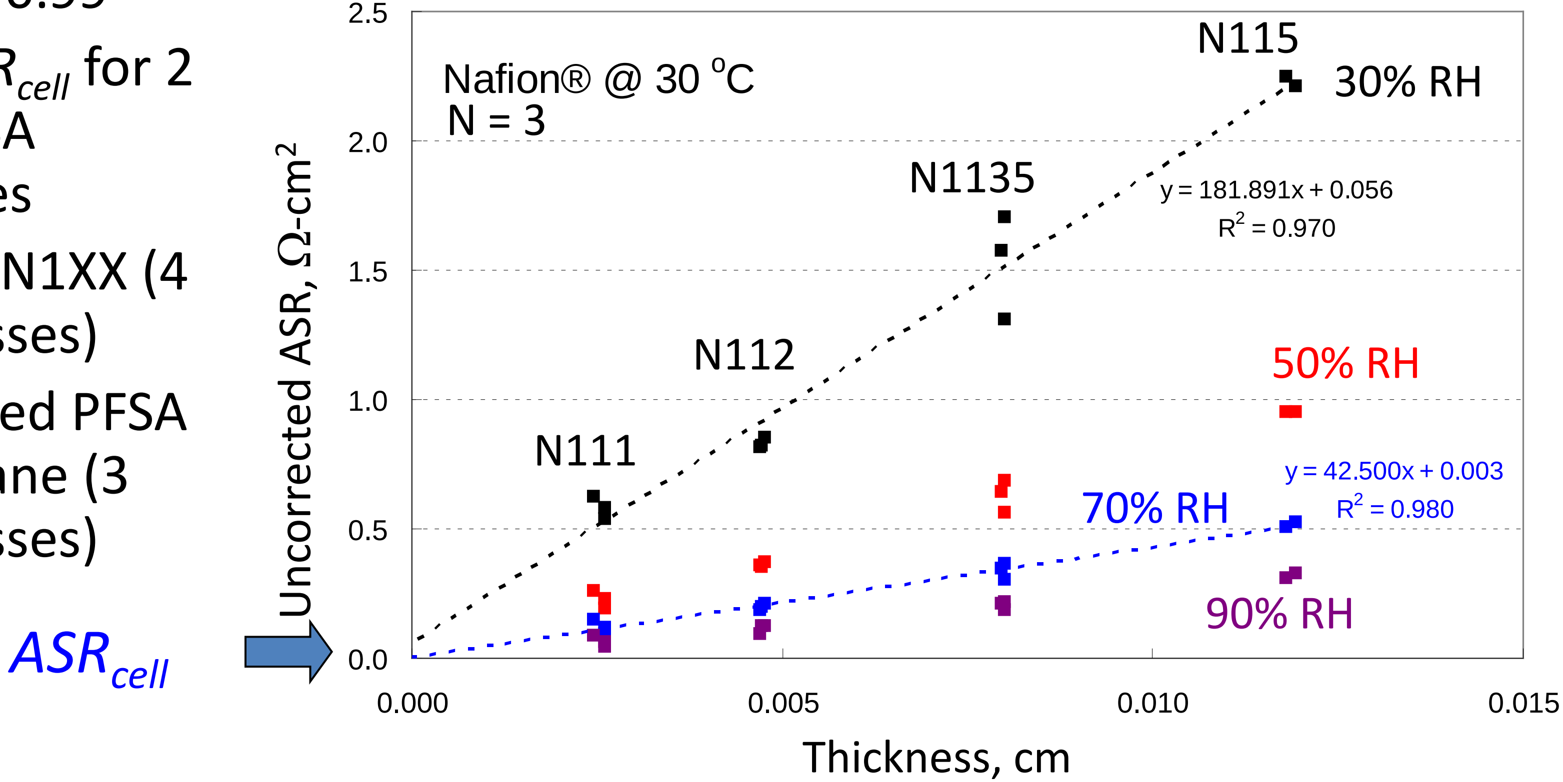
  - ✓ Note that all are a f (T, RH)

The challenge: need ASR_{cell} *(T,RH)*

Determine ASR_{cell} by extrapolating linear regression of ASR *vs*. thickness to L = 0. Do this for each T, RH

- R^2 = 0.95 - 0.99
- Similar ASR_{cell} for 2 sets of PFSA membranes
  - ✓ Nafion® N1XX (4 thicknesses)
  - ✓ Supported PFSA membrane (3 thicknesses)

L = membrane thickness

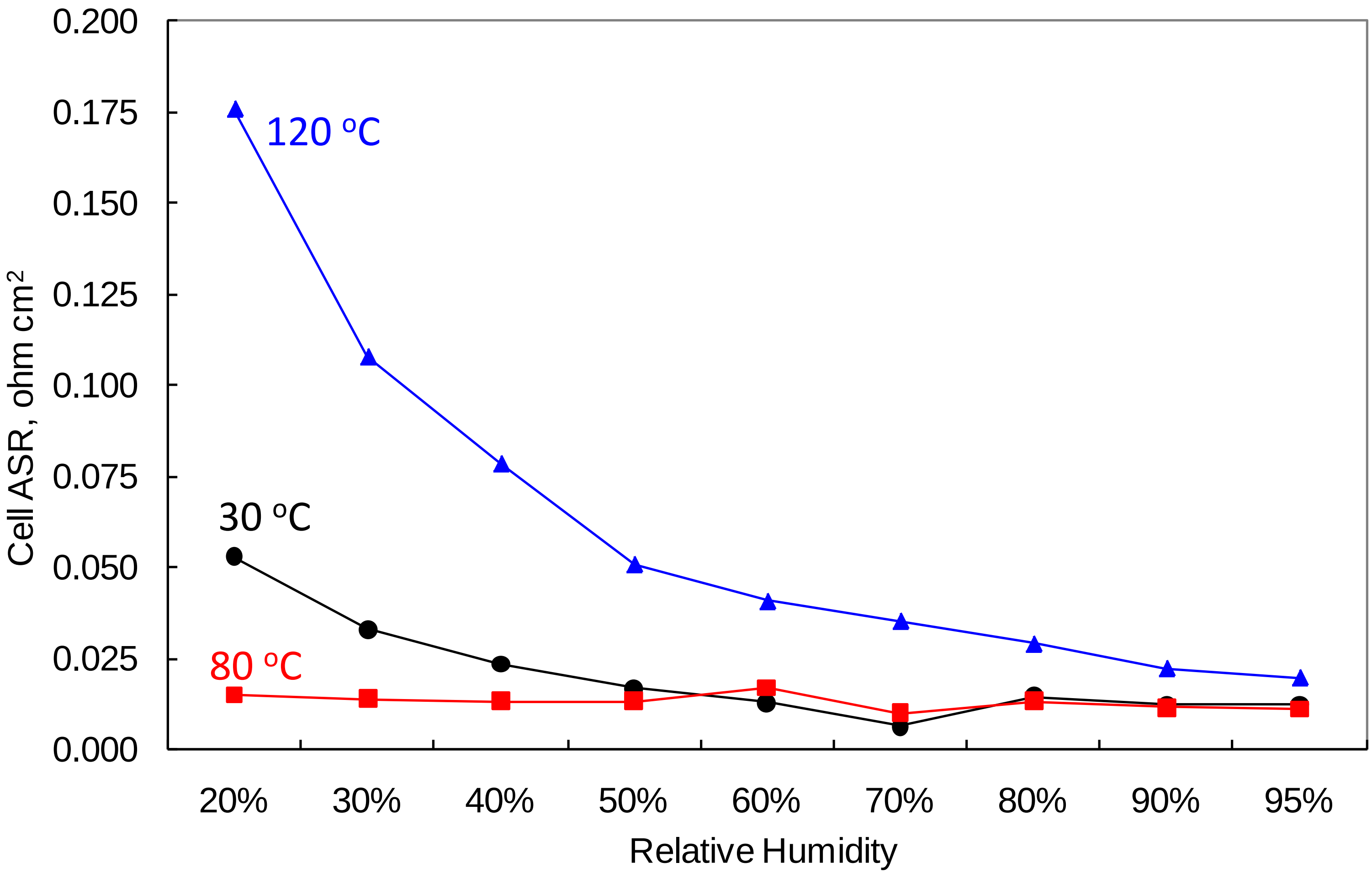


Key Assumptions:

1. Intrinsic through-plane conductivity is <u>not</u> a function of *L*
2. Cell resistance is constant from build-to-build

Cell resistance increases at low RH … dominated by interfacial resistance

- Increasing R_{cell} with decreasing RH also reported by W.L. Gore & Associates [1]



1. Johnson & Liu, "Ionic Conductivity of Perflourosulfonic Acid Membranes as a Function of Temperature, Humidity and Equivalent Weight“ ECS PV 2002-5, 132 (2002)

Ratio of cell to membrane resistance highlights importance of correcting for non-membrane ohmic contributions

- At low RH, ratio is small relative to the membrane resistance
  - ✓ $R_{cell} : R_{membrane}$ ~ 0.1 - 0.2
- At high RH, the cell resistance can be significant relative to the membrane resistance, especially for thin membranes