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

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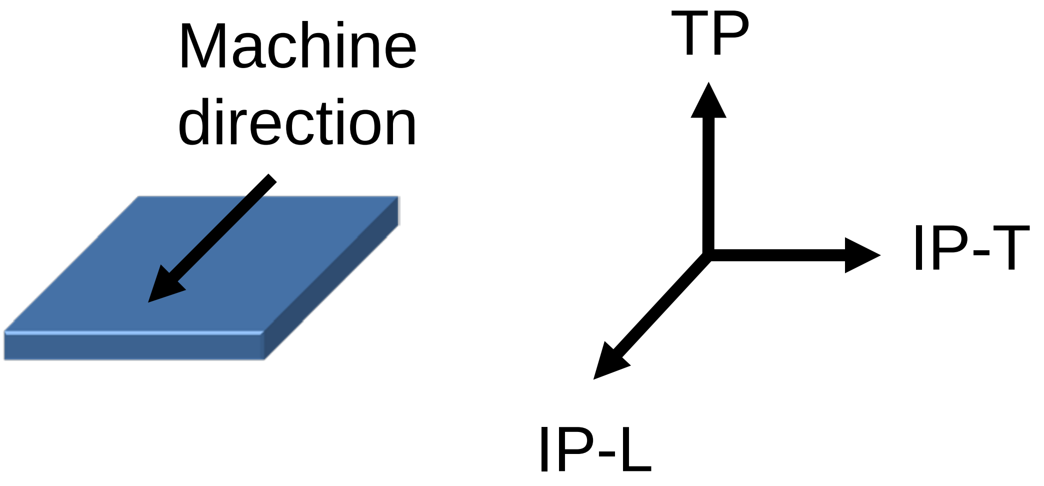
Orientation and Nomenclature

TP = through-plane or through-thickness

IP = in-plane

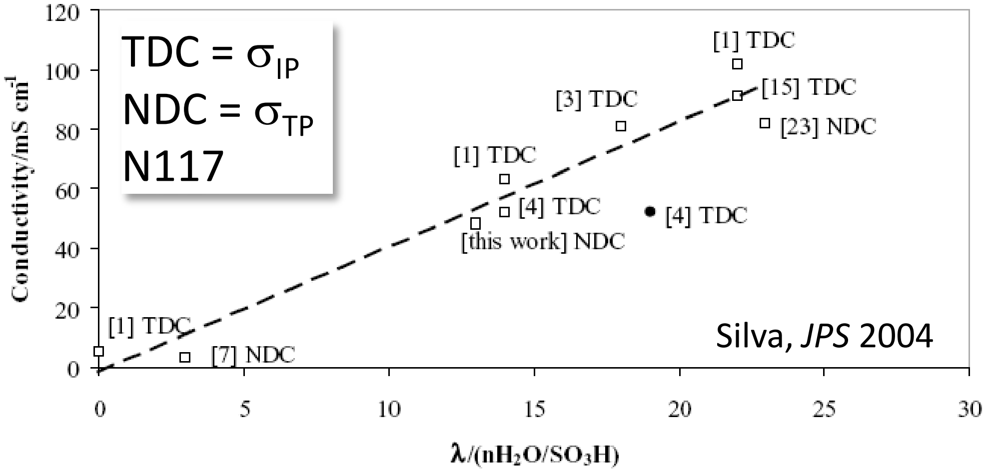
L = longitudinal = parallel to machine (extrusion) direction

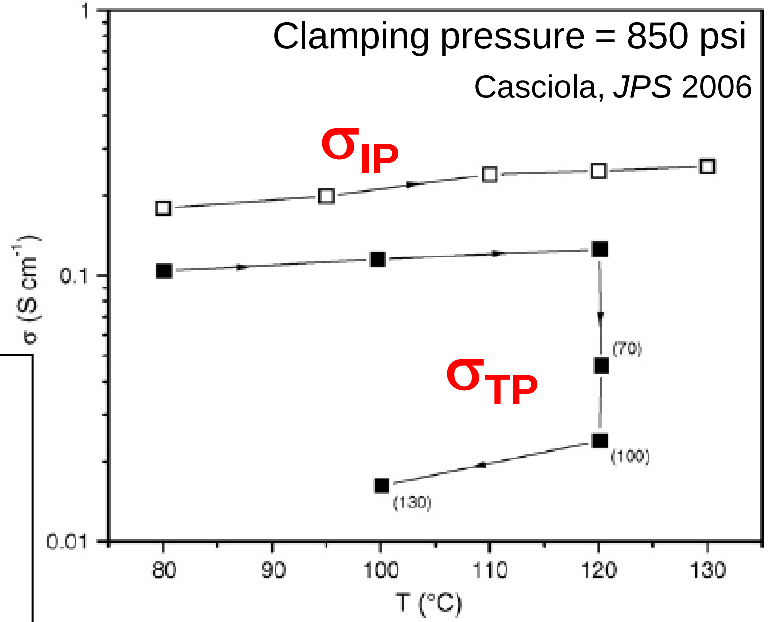
T = transverse = perpendicular to machine direction



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

- No, it is anisotropic
  - $\sigma_{IP}:\sigma_{TP}$= 3.6 [Gardner]
  - $\sigma_{IP}:\sigma_{TP}$ = 2.5 – 5 (w/ Pressure) [Ma]
  - $\sigma_{IP}:\sigma_{TP}$= 1.8 – 5 [Casciola]
  - ✓ This work (N112)
- Yes, it is isotropic, $\sigma_{IP}:\sigma_{TP} \cong 1$
  - Nouel, Silva
  - ✓ Cooper (NR-212)
- Discrepancy due
  - Different water content (λ)
  - Not accounting for non-membrane ohmic contributions in TP measurements
- Anisotropic within the plane for extruded material: $\sigma_{IP\text{-}Long} > \sigma_{IP\text{-}Trans}$

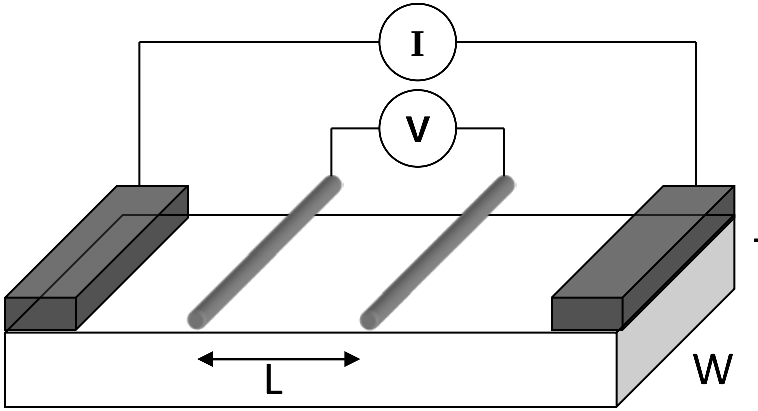




Casciola *et. al.*, *J. Power Sources* **162** 141 (2006)
Cooper, *JES* **157**, B1731 (2010)
Gardner *et. al.*, *J. Electroanal Chem* **449** 209 (1998)
Ma *et. al.*, *JES* **153** A2274 (2006)
Nouel, Fedkiw, *Electrochimica Acta* **43** 2381 (1998)
Silva, *et. al.*, *J. Power Sources* **134** 18 (2004)

Objective: Measure and compare in-plane and through-plane ion conductivity of polymer electrolyte membranes

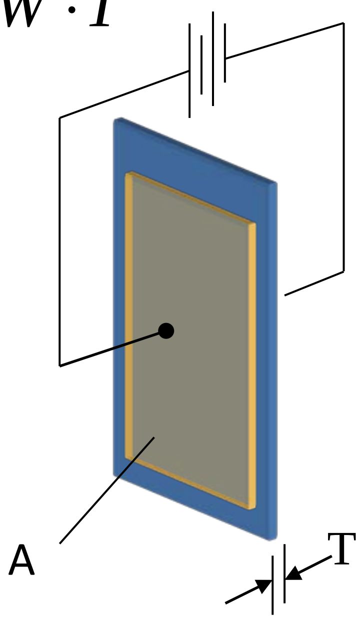
- In-plane
  - Pro: geometry allows true 4-electrode configuration → implementation & data interpretation are easy
  - Con: not orientation of interest



$$\sigma_{IP} = \frac{L}{R \cdot A} = \frac{L}{R \cdot W \cdot T}$$

- Through-plane
  - Pro: measured parameter is in orientation of interest
  - Con: measurement and data analysis more difficult
  - Instrument & methods recently developed [1]

$$\sigma_{TP} = \frac{T}{R \cdot A}$$



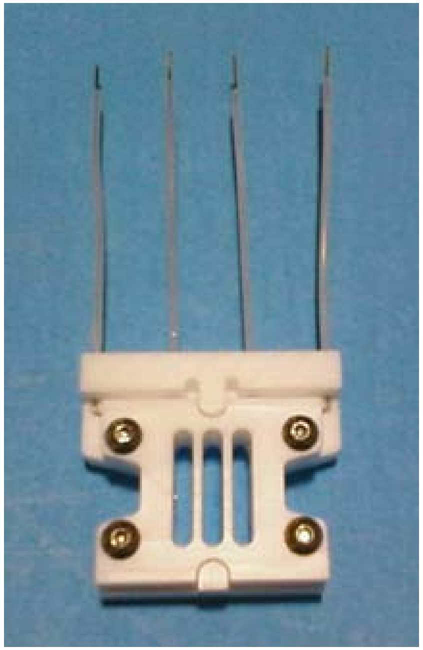
1. Cooper, *J. Electrochem. Soc.* **157**, B1731 (2010)

Experimental

- Materials
  - Nafion® 112 and NR-212 – non-supported PEM
  - GORE-SELECT® – supported PEM

- Through-plane – Membrane Test System *MTS 740* [1]
  - Integrated membrane clamp and electrodes
  - Environmental control & measurement – T, dew point, RH, gas flow, *etc.*

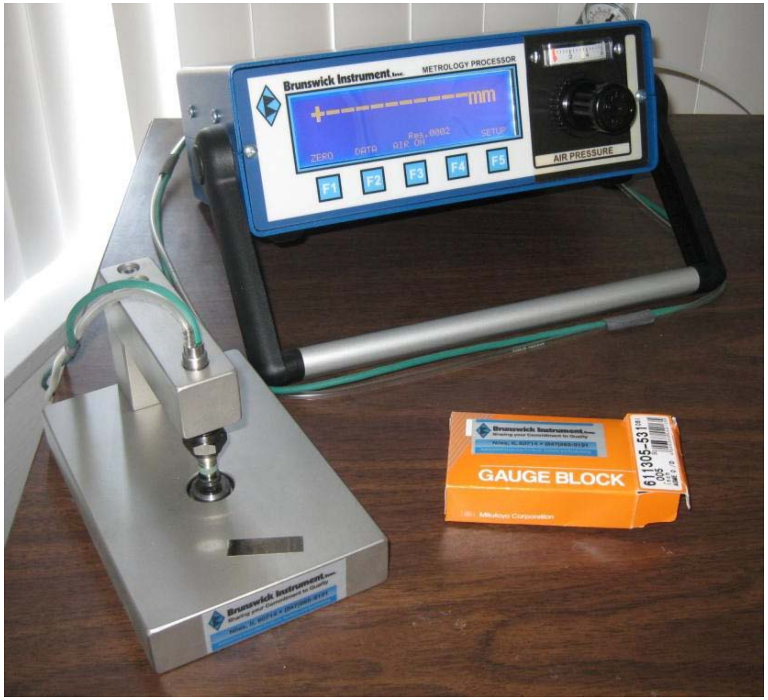
- In-plane – BekkTech BT-110 Conductivity Clamp
  - Located in MTS 740 chamber for environmental control



1. Cooper, *J. Electrochem. Soc.* **157**, B1731 (2010)

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
  - Brunswick Instruments
    - low load (50 g)
    - high accuracy gage (±0.2 μm for 50 μm sample)



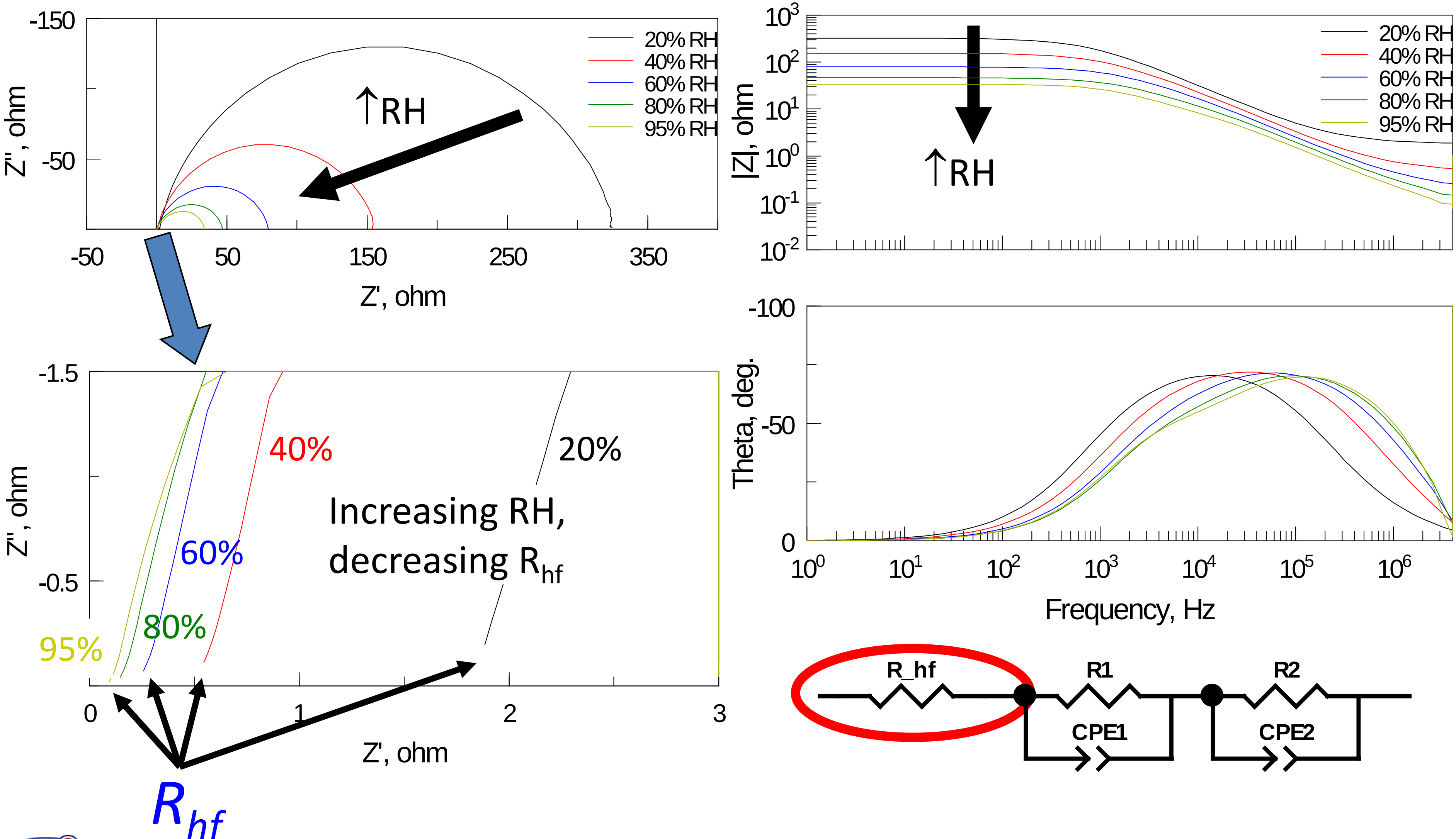
Brunswick Instruments Film Thickness Gage

Procedure

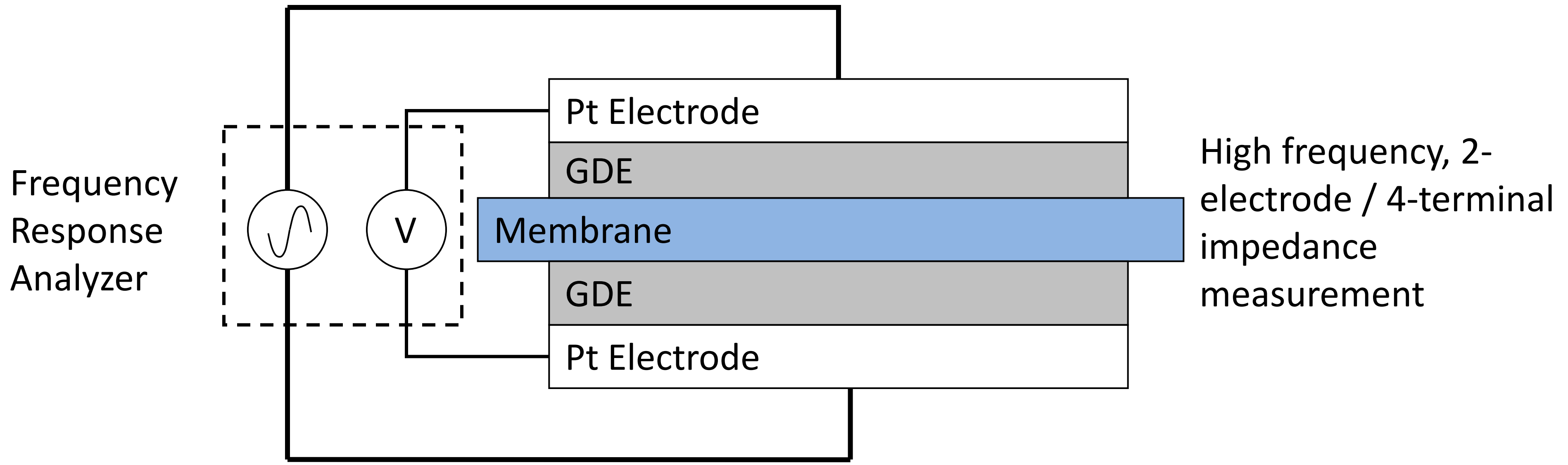
- Temperature series (°C): 80 → 30 → 120
- Per temperature
  - Wet-up 2 hr @ 70% RH
  - RH cycle: 70 → 20 → 95 %, 15 min or 95% → 20%, 30 min
  - Resistance measurement after 15 or 30 min
- Through-plane: 2-electrode / 4-terminal impedance measurement
  - 10 MHz – 1 Hz, 10 mV_{AC}, 0 V_{DC}
- In-plane: 4-electrode / 4-terminal DC measurement

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

Post-test Procedure – EIS Analysis of Through-Plane Data



Through-thickness Measurement Method and Ohmic Resistance Sources



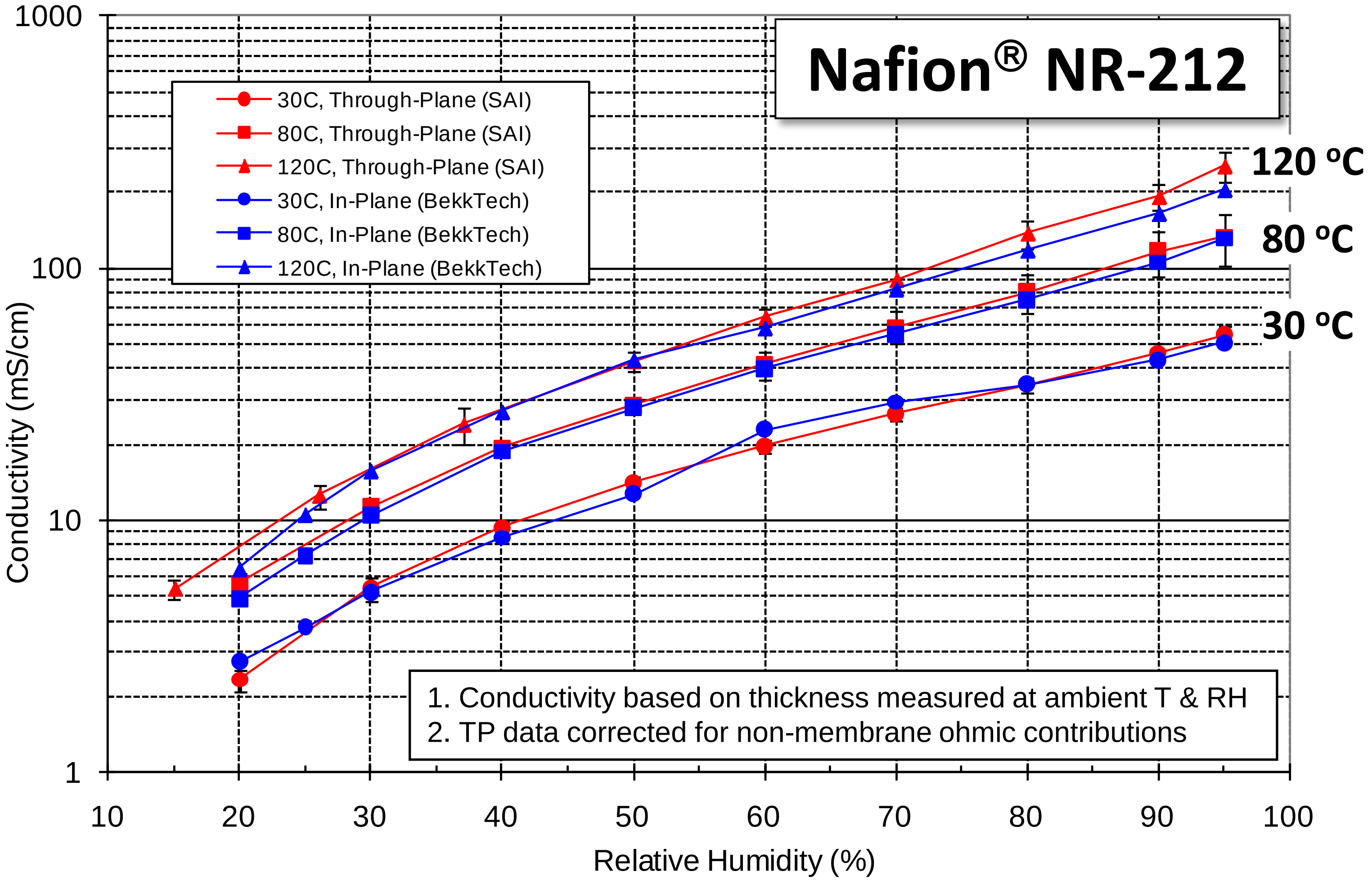
- Ohmic resistances that contribute to the high frequency resistance, R_{HF}:
  - Membrane – dominate
  - Pt electrode – very small
  - GDE – very small
  - Pt electrode / GDE contact – very small
  - GDE/membrane interface – *f* (RH,T); can be significant

  $R_{cell}(T,RH)$ (groups the four items from "Pt electrode – very small" to "GDE/membrane interface")
- Non-membrane ohmic resistances (R_{cell}) must be accounted [1]

1. Cooper, *J. Electrochem. Soc.* **157**, B1731 (2010)

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

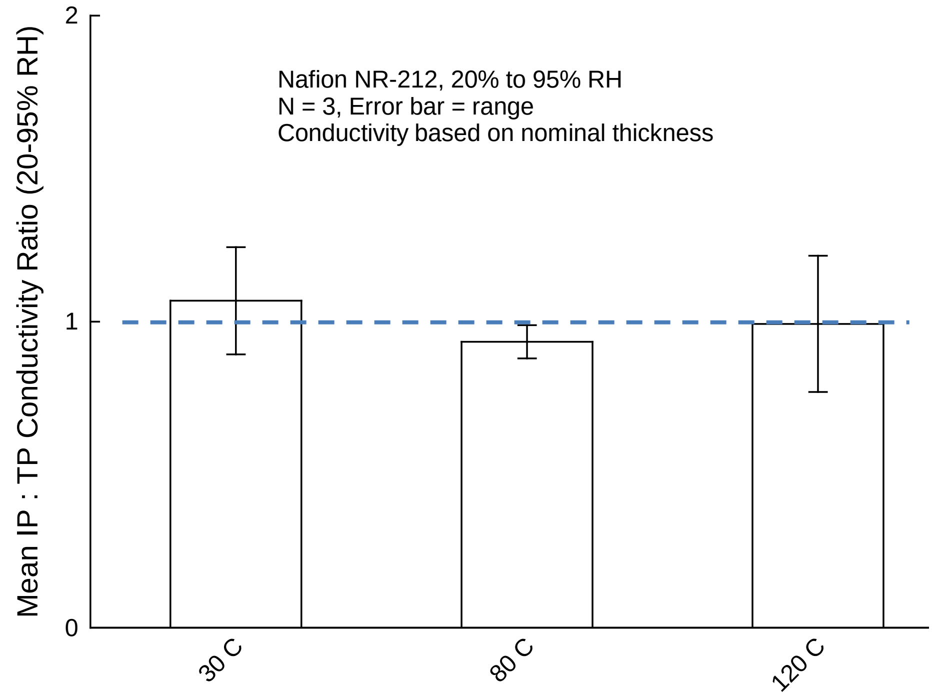
$\sigma_{\text{in-plane}} \cong \sigma_{\text{through-plane}}$



Is the conductivity of dispersion-cast Nafion® NR-212 isotropic? … YES

- **$\sigma_{IP} : \sigma_{TP} \cong 1$**
  - 3 temperatures
  - Low to high RH

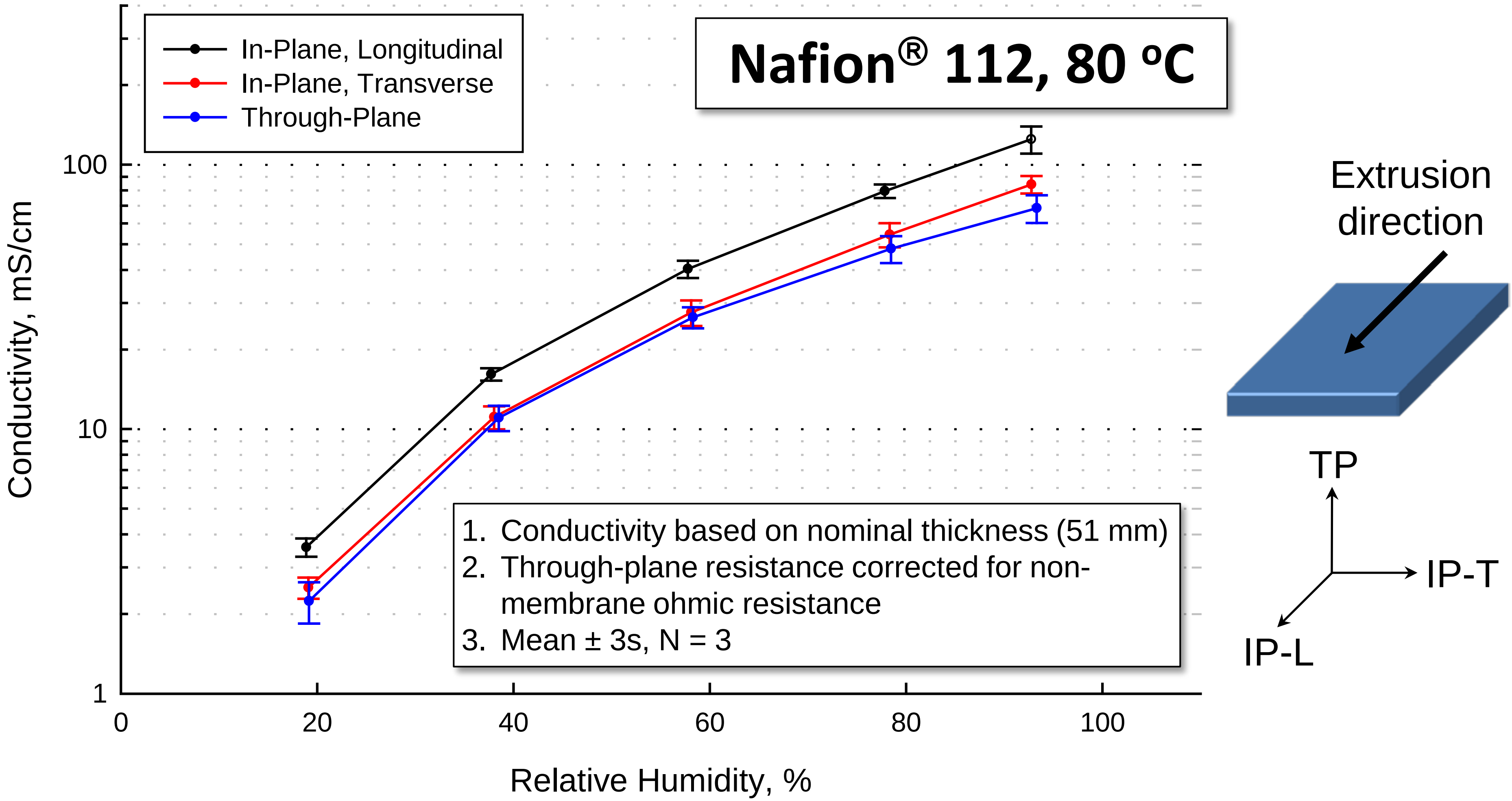
% RH	30 °C	80 °C	120 °C
20	1.30	0.87	1.20
40	1.03	0.94	1.11
60	1.10	0.95	0.92
80	1.03	0.93	0.86
90	1.00	0.90	0.86
95	1.05	0.98	0.81
$\bar{X}_{1s}$	$1.07_{0.08}$	$0.93_{0.03}$	$0.99_{0.14}$



σ_{IP} = in-plane, σ_{TP} = through-plane

Through-plane & in-plane conductivity of extruded Nafion® 112

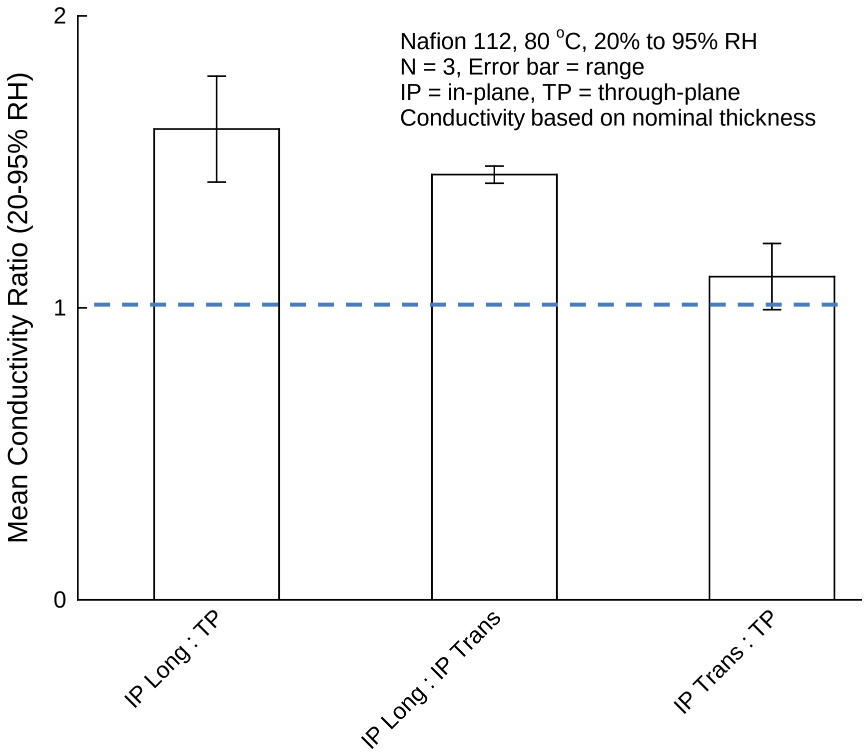
IP Longitudinal > IP Transverse > TP for extruded Nafion®



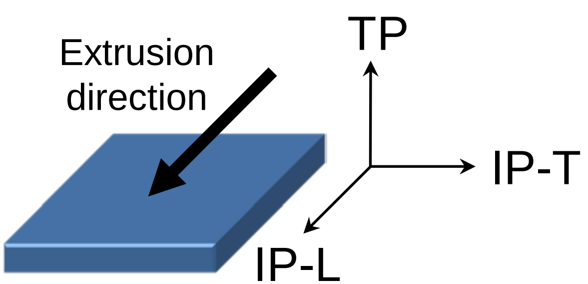
Is the conductivity of extruded Nafion® 112 isotropic? … NO

IP Longitudinal > IP Transverse > TP

Ratio of Conductivity			
% RH	IP-L : TP	IP-L : IP-T	IP-T : TP
20	1.60	1.42	1.12
40	1.46	1.45	1.00
60	1.52	1.46	1.04
80	1.65	1.46	1.13
95	1.82	1.48	1.23
$\bar{X}_{1s}$	$1.61_{0.14}$	$1.46_{0.02}$	$1.11_{0.09}$

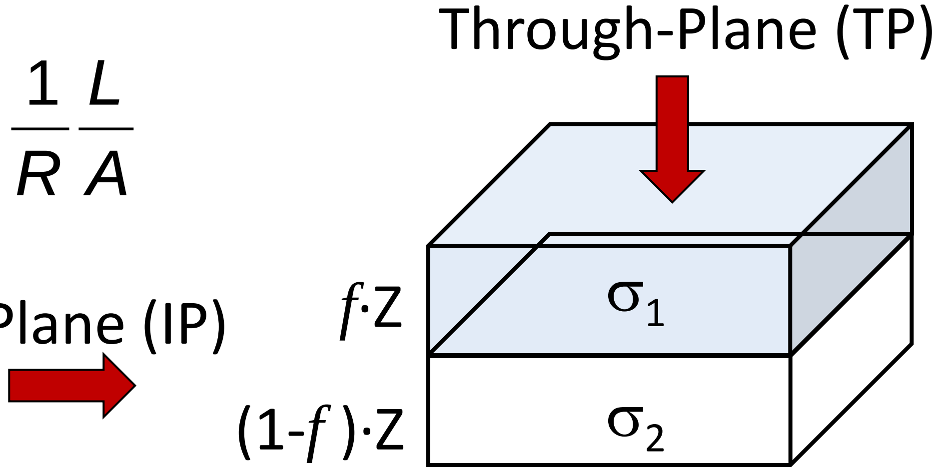


- Test for equality of means
  - $H_0 : \mu_1 = \mu_2$; $H_1 : \mu_1 \neq \mu_2$
  - $\alpha = 5\%$
- Statistically significant difference in means for all RHs
  - except IP-Trans *vs.* TP @ 40% RH



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

$$\sigma = \frac{1}{R}\frac{L}{A}$$



f = fractional thickness of layer 1

<u>In-Plane (IP)</u>

Resistances in parallel

$$\frac{1}{R_{total}} = \frac{1}{R_1} + \frac{1}{R_2}$$

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

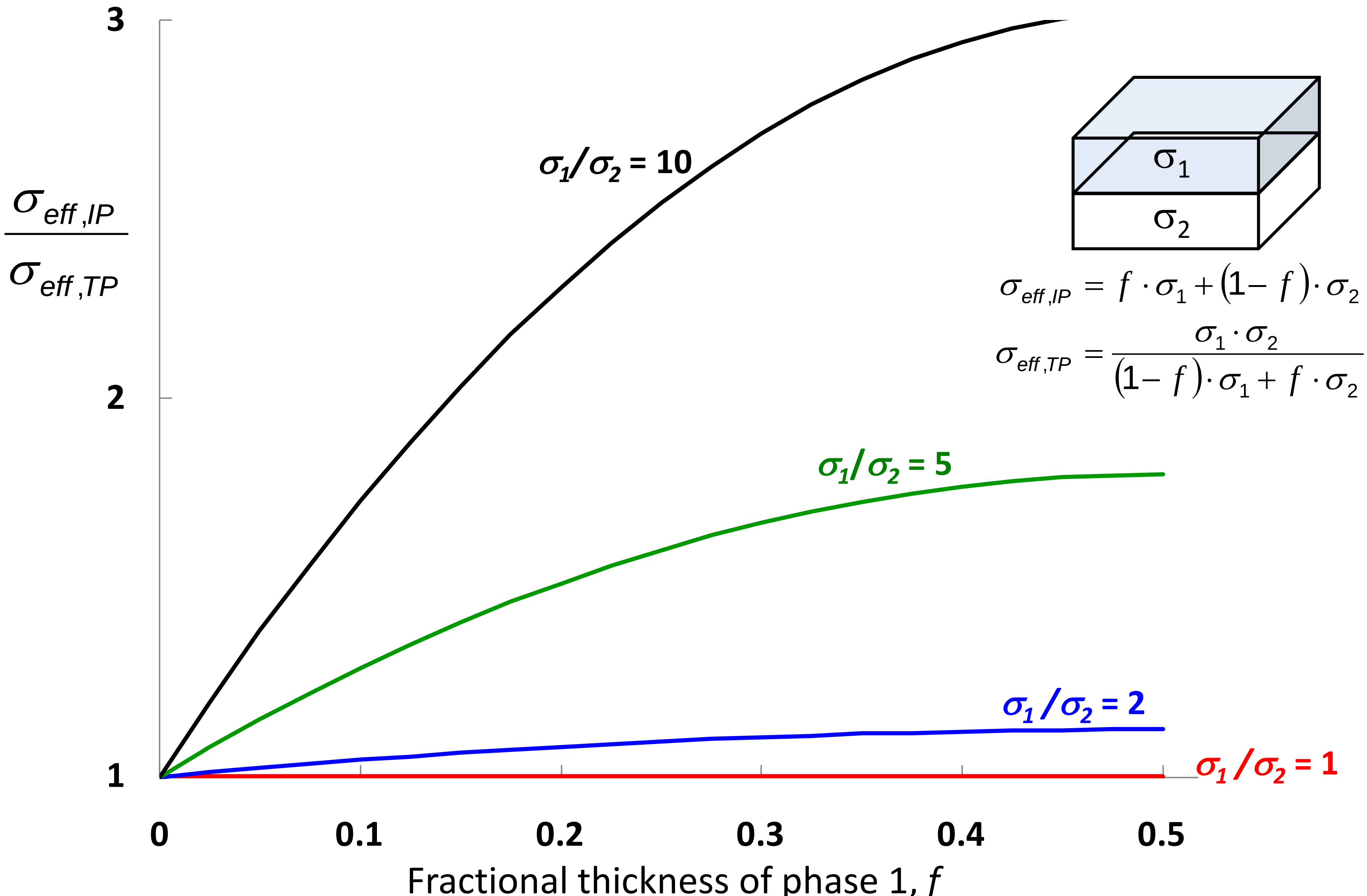
<u>Through-Plane (TP)</u>

Resistances in series

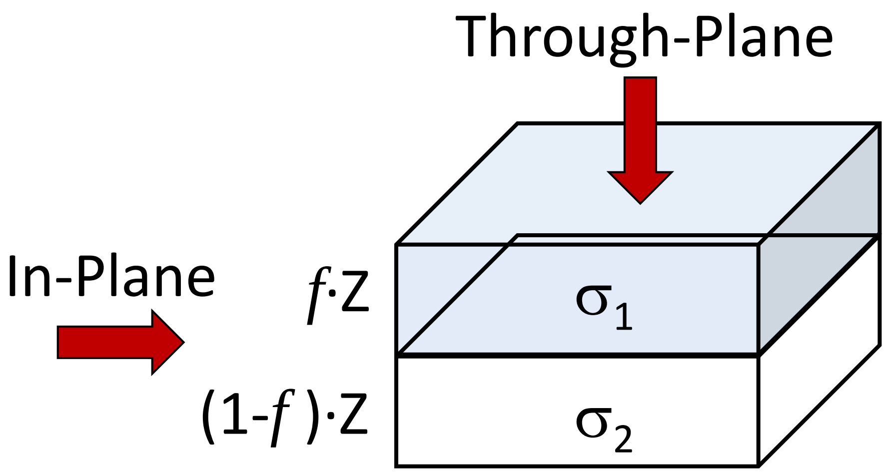
$$R_{total} = R_1 + R_2$$

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

Effective conductivity with phases of unequal conductivity



Effective conductivity with phases of unequal conductivity



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

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

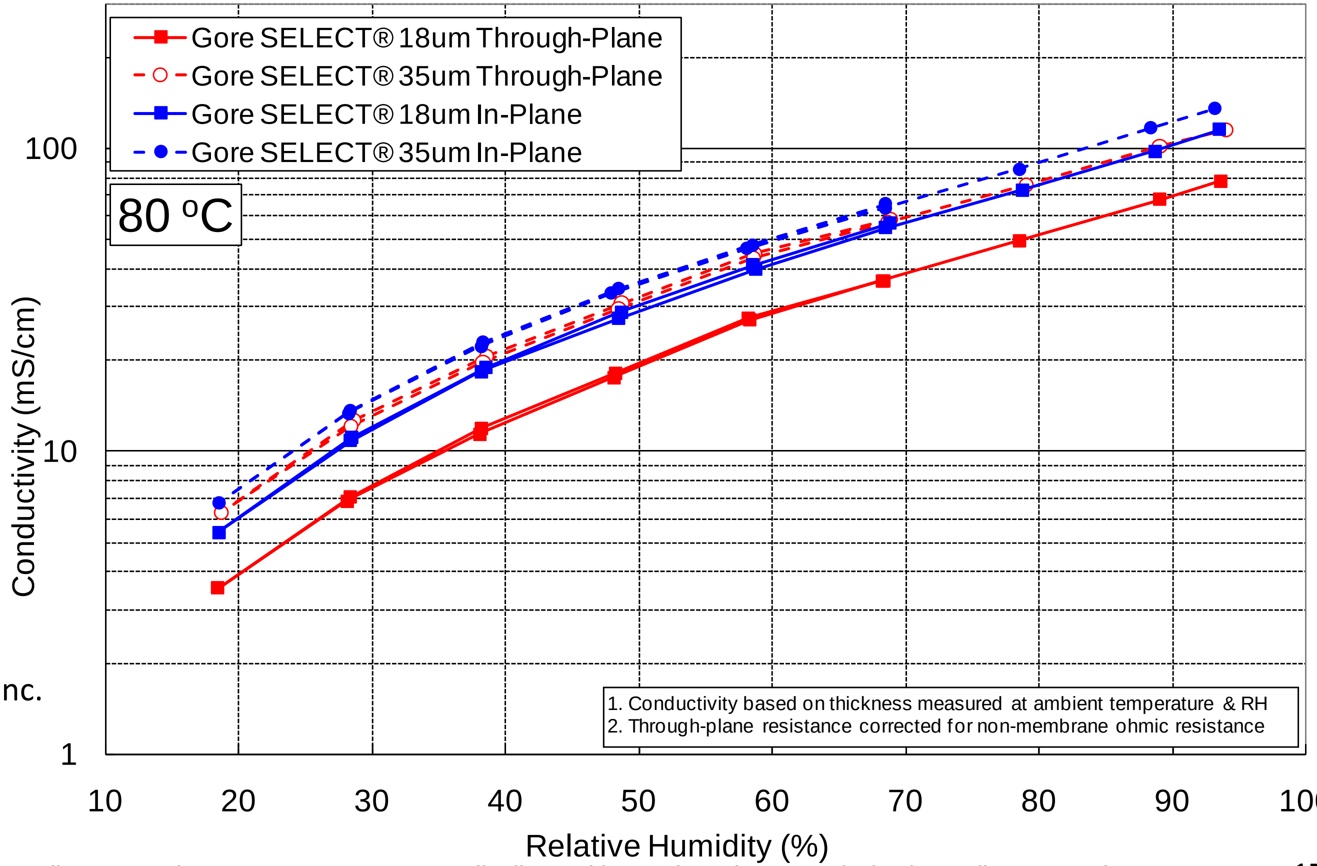
f = fractional thickness of phase 1

- $\sigma_{eff,\ in\text{-}plane} > \sigma_{eff,\ through\text{-}plane}$ 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 of PFSA-based membrane 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



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Conclusions

- Methods exist that can differentiate in-plane and through-plane ionic conductivity of PEMs
- Extruded Nafion® 112 exhibits anisotropic conductivity
  - $\sigma_{IP\text{-}Long} > \sigma_{IP\text{-}Trans} > \sigma_{TP}$
- Dispersion-cast Nafion® NR-212 exhibits isotropic conductivity
  - $\sigma_{IP} \cong \sigma_{TP}$
- Membranes with inert support, *e.g.*, GORE-SELECT®, exhibit anisotropic conductivity
  - Consistent with simple analytical treatment

Results highlight the need to consider potential for anisotropic behavior and measure appropriately

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