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
  - \( \sigma_{\text{IP}} : \sigma_{\text{TP}} = 3.6 \) [Gardner]
  - \( \sigma_{\text{IP}} : \sigma_{\text{TP}} = 2.5 - 5 \) (w/ Pressure) [Ma]
  - \( \sigma_{\text{IP}} : \sigma_{\text{TP}} = 1.8 - 5 \) [Casciola]
  - This work (N112)

- Yes, it is isotropic, \( \sigma_{\text{IP}} : \sigma_{\text{TP}} \approx 1 \)
  - Nouel, Silva
  - Cooper (NR-212)

- Discrepancy due
  - Different water content (\( \lambda \))
  - Not accounting for non-membrane ohmic contributions in TP measurements

- Anisotropic within the plane for extruded material: \( \sigma_{\text{IP-Long}} > \sigma_{\text{IP-Trans}} \)

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Casciola et. al., *J. Power Sources* **162** 141 (2006)
Ma et. al., *JES* **153** A2274 (2006)
Objective: Measure and compare in-plane and through-plane ion conductivity of polymer electrolyte membranes

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

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

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

\[
\sigma_{TP} = \frac{T}{R \cdot A}
\]

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

**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)
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

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Total Dry Gas Flow, sccm</th>
<th>Pressure, kPa_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>500</td>
<td>100</td>
</tr>
<tr>
<td>80</td>
<td>500</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>500</td>
<td>230</td>
</tr>
</tbody>
</table>
Post-test Procedure – EIS Analysis of Through-Plane Data

Increasing RH, decreasing $R_{hf}$

$R_{hf}$

$Z'$, ohm

$Z''$, ohm

$|Z|$, ohm

Frequency, Hz

Theta, deg.

$Z'$, ohm

$Z''$, ohm

$|Z|$, ohm

20% RH
40% RH
60% RH
80% RH
95% RH

$R_{hf}$
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

- Non-membrane ohmic resistances ($R_{cell}$) must be accounted [1]

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

\[ \sigma_{\text{in-plane}} \approx \sigma_{\text{through-plane}} \]

1. Conductivity based on thickness measured at ambient T & RH
2. TP data corrected for non-membrane ohmic contributions
Is the conductivity of dispersion-cast Nafion® NR-212 isotropic? … YES

\[ \sigma_{IP} : \sigma_{TP} \approx 1 \]
- 3 temperatures
- Low to high RH

<table>
<thead>
<tr>
<th>% RH</th>
<th>30 °C</th>
<th>80 °C</th>
<th>120 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.30</td>
<td>0.87</td>
<td>1.20</td>
</tr>
<tr>
<td>40</td>
<td>1.03</td>
<td>0.94</td>
<td>1.11</td>
</tr>
<tr>
<td>60</td>
<td>1.10</td>
<td>0.95</td>
<td>0.92</td>
</tr>
<tr>
<td>80</td>
<td>1.03</td>
<td>0.93</td>
<td>0.86</td>
</tr>
<tr>
<td>90</td>
<td>1.00</td>
<td>0.90</td>
<td>0.86</td>
</tr>
<tr>
<td>95</td>
<td>1.05</td>
<td>0.98</td>
<td>0.81</td>
</tr>
</tbody>
</table>

\[ \bar{x}_{1s} \] 107.08 0.930.03 0.990.14

\( \sigma_{IP} = \text{in-plane}, \ \sigma_{TP} = \text{through-plane} \)
Through-plane & in-plane conductivity of extruded Nafion® 112

IP Longitudinal > IP Transverse > TP for extruded Nafion®

1. Conductivity based on nominal thickness (51 mm)
2. Through-plane resistance corrected for non-membrane ohmic resistance
3. Mean ± 3s, N = 3

Nafion® 112, 80 °C
Is the conductivity of extruded Nafion® 112 isotropic? ... NO

### IP Longitudinal > IP Transverse > TP

<table>
<thead>
<tr>
<th>% RH</th>
<th>IP-L : TP</th>
<th>IP-L : IP-T</th>
<th>IP-T : TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.60</td>
<td>1.42</td>
<td>1.12</td>
</tr>
<tr>
<td>40</td>
<td>1.46</td>
<td>1.45</td>
<td>1.00</td>
</tr>
<tr>
<td>60</td>
<td>1.52</td>
<td>1.46</td>
<td>1.04</td>
</tr>
<tr>
<td>80</td>
<td>1.65</td>
<td>1.46</td>
<td>1.13</td>
</tr>
<tr>
<td>95</td>
<td>1.82</td>
<td>1.48</td>
<td>1.23</td>
</tr>
</tbody>
</table>

\[ X_{1s} \, 1.61_{0.14} \, 1.46_{0.02} \, 1.11_{0.09} \]

- 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

Nafion 112, 80 °C, 20% to 95% RH
N = 3, Error bar = range
IP = in-plane, TP = through-plane
Conductivity based on nominal thickness
Effective conductivity ($\sigma_{\text{eff}}$) of membrane with regions of unequal conductivity, e.g., ionomer-impregnated non-conductive porous support

\begin{align*}
\sigma &= \frac{1}{\frac{L}{R \cdot A}} \\
\text{In-Plane (IP)} &
\frac{1}{R_{\text{total}}} = \frac{1}{R_1} + \frac{1}{R_2} \\
\sigma_{\text{eff,IP}} &= f \cdot \sigma_1 + (1-f) \cdot \sigma_2 \\
\text{Through-Plane (TP)} &\cdot f = \text{fractional thickness of layer 1} \\
\sigma_{\text{eff,TP}} &= \frac{\sigma_1 \cdot \sigma_2}{(1-f) \cdot \sigma_1 + f \cdot \sigma_2}
\end{align*}
Effective conductivity with phases of unequal conductivity

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

Fractional thickness of phase 1, \( f \)

\( \sigma_1 / \sigma_2 = 1 \)
\( \sigma_1 / \sigma_2 = 2 \)
\( \sigma_1 / \sigma_2 = 5 \)
\( \sigma_1 / \sigma_2 = 10 \)
Effective conductivity with phases of unequal conductivity

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

\[
\sigma_{\text{eff,IP}} = f \cdot \sigma_1 + (1-f) \cdot \sigma_2
\]
\[
\sigma_{\text{eff,TP}} = \frac{\sigma_1 \cdot \sigma_2}{(1-f) \cdot \sigma_1 + f \cdot \sigma_2}
\]

\( f \) = fractional thickness of phase 1
Comparing through-plane & in-plane conductivity of PFSA-based membrane with inert support GORE-SELECT®

- $\sigma_{\text{eff, in-plane}} > \sigma_{\text{eff, through-plane}}$
- $\sigma_{\text{eff, in-plane}} : \sigma_{\text{eff, through-plane}} \rightarrow 1$ as $f \rightarrow 0$ or $1$

✓ Ratio is greater for thin membrane with same support thickness

<table>
<thead>
<tr>
<th>Thickness</th>
<th>$\frac{\sigma_{\text{eff, in-plane}}}{\sigma_{\text{eff, through-plane}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 µm</td>
<td>1.53 ± 0.16</td>
</tr>
<tr>
<td>35 µm</td>
<td>1.11 ± 0.10</td>
</tr>
</tbody>
</table>

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

1. Conductivity based on thickness measured at ambient temperature & RH
2. Through-plane resistance corrected for non-membrane ohmic resistance
Conclusions

- Methods exist that can differentiate in-plane and through-plane ionic conductivity of PEMs
- Extruded Nafion® 112 exhibits anisotropic conductivity
  - $\sigma_{\text{IP-Long}} > \sigma_{\text{IP-Trans}} > \sigma_{\text{TP}}$
- Dispersion-cast Nafion® NR-212 exhibits isotropic conductivity
  - $\sigma_{\text{IP}} \approx \sigma_{\text{TP}}$
- 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