Progress and Status on Through-Plane Resistance and Conductivity Measurement of Fuel Cell Membranes

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Acknowledgment
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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
  - Rapid ~ 15 min per test condition
  - Robust - accurate, repeatable and reliable

\[ \sigma_{\text{membrane}} = \frac{L}{R_{\text{membrane}} \cdot A} \quad [S/cm] \]
Membrane Test System **MTS 740**

- Mass flow controllers (MFC) for wet-dry gas mixing
- Test chamber with *in-situ* dew point & sample temp
- Auto-water humidifier
- Condensate collection tank
- Cell head w/ integrated electrodes, clamping mechanism, lead connector
- Temp controls – test chamber, humidifier, line
- E-stop button
- Backpressure regulator
- U.S. Patent No. 7,652,479
Wet-dry gas mixing for rapid RH cycling in both directions

In-situ dew point & temperature probes

MFC

MFC

H₂
N₂

Vent

Water trap

Condenser

BP

TC

WW

Vent

Condenser
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

<table>
<thead>
<tr>
<th>Nominal % RH</th>
<th>30 °C</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N = 15</td>
<td>N = 11</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>-0.3</td>
</tr>
<tr>
<td>40</td>
<td>0.7</td>
<td>-0.5</td>
</tr>
<tr>
<td>60</td>
<td>-0.2</td>
<td>-0.8</td>
</tr>
<tr>
<td>80</td>
<td>-1.4</td>
<td>-0.4</td>
</tr>
<tr>
<td>90</td>
<td>-1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>95</td>
<td>-2.2</td>
<td>-0.3</td>
</tr>
</tbody>
</table>
Comparing through-plane & in-plane conductivity of Nafion® NR-212

\[ \sigma_{\text{in-plane}} \approx \sigma_{\text{through-plane}} \] for dispersion cast Nafion®

- 30°C, Through-Plane (SAI)
- 30°C, Through-Plane (SAI)
- 120°C, Through-Plane (SAI)
- 30°C, In-Plane (BekkTech)
- 80°C, In-Plane (BekkTech)
- 120°C, In-Plane (BekkTech)

Conductivity (mS/cm) vs. Relative Humidity (%)
Is the conductivity of Nafion® isotropic? ... No consensus in published literature

\( \sigma_{\parallel} = \text{in-plane}, \; \sigma_{\perp} = \text{through-plane} \)

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

\[ \sigma_{\parallel} : \sigma_{\perp} \approx 1, \; \text{NR-212, this work} \]

<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>1.19</td>
<td>0.92</td>
<td>1.20</td>
</tr>
<tr>
<td>40</td>
<td>0.95</td>
<td>1.02</td>
<td>1.15</td>
</tr>
<tr>
<td>60</td>
<td>1.15</td>
<td>1.02</td>
<td>0.96</td>
</tr>
<tr>
<td>80</td>
<td>0.99</td>
<td>0.96</td>
<td>0.87</td>
</tr>
<tr>
<td>90</td>
<td>0.93</td>
<td>0.97</td>
<td>0.87</td>
</tr>
<tr>
<td>95</td>
<td>0.93</td>
<td>106</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Ma et. al., JES 153 A2274 (2006)
Casciola et. al., J. Power Sources 162 141 (2006)
Silva, et. al., J. Power Sources 134 18 (2004)
Effective conductivity ($\sigma_{\text{eff}}$) of membrane with phases of unequal conductivity, e.g., ionomer-impregnated non-conductive porous support

\[ \sigma_{\text{eff, in-plane}} = f \cdot \sigma_1 + (1 - f) \cdot \sigma_2 \]
\[ \sigma_{\text{eff, through-plane}} = \frac{\sigma_1 \cdot \sigma_2}{(1 - f) \cdot \sigma_1 + f \cdot \sigma_2} \]
\[ f = \text{fractional thickness of phase 1} \]

- $\sigma_{\text{eff, in-plane}} > \sigma_{\text{eff, through-plane}}$
- $\sigma_{\text{eff, in-plane}} : \sigma_{\text{eff, through-plane}}$
- $\sigma_{\text{eff, in-plane}} : \sigma_{\text{eff, through-plane}}$
- $\sigma_{\text{eff, in-plane}} : \sigma_{\text{eff, through-plane}}$

For supported membrane:
- Is a maximum for $f = 0.5$
- $\rightarrow 1$ as $f \rightarrow 0$ or $1$
- Increases as $\sigma_1 : \sigma_2 \rightarrow 0$ or $>> 1$
Comparing through-plane & in-plane conductivity ($\sigma$) of PFSA-based membranes 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>

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

GORE-SELECT, GORE and designs are trademarks of W. L. Gore & Associates, Inc.
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 °C, humidifier to 120 °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**

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Supporting Information

- Electrode design
- Test procedure
- Analysis Procedure
- Determination of Cell Resistance
4-Electrode, “Offset” Electrode Design

Dimensions in mm

Top View

- Pt Source Electrode #1
- GDE #1
- Membrane
- Pt V-sense #1
- GDE #2
- Pt Source Electrode #2

Overlap Area

U.S. Patent No. 7,652,479
Offset electrode geometry for 4-probe conductivity measurement of thin film electrolytes

Model condition: constant 1 V between source electrodes

Source Electrode #1

100 μm

Source Electrode #2

$V_{S1} = -0.5$ V

$V_{S2} = 0.5$ V

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: H₂ or N₂
- 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)

<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

Increasing RH, decreasing $R_{hf}$

$R_{hf}$
Post-test Procedure – EIS Analysis

- **$R_b$**
  - Value: 0.068111
  - Error: 0.0011616
  - Error %: 1.7055

- **$R_1$**
  - Value: 12.92
  - Error: 0.087668
  - Error %: 0.67854

- **CPE1-T**
  - Value: 1.3459E-05
  - Error: 3.089E-07
  - Error %: 2.2951

- **CPE1-P**
  - Value: 0.83049
  - Error: 0.0017289
  - Error %: 0.20818
Through-plane Resistance & Conductivity

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

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

Typically work in area specific resistance, $ASR$

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

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

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

✓ Note that all are a $f(T, RH)$

**The challenge: need $ASR_{\text{cell}}(T,RH)$**
Determine $\text{ASR}_{\text{cell}}$ by extrapolating linear regression of $\text{ASR}$ vs. thickness to $L = 0$. Do this for each $T$, $\text{RH}$.

- $R^2 = 0.95 - 0.99$
- Similar $\text{ASR}_{\text{cell}}$ for 2 sets of PFSA membranes
  - Nafion® N1XX (4 thicknesses)
  - Supported PFSA membrane (3 thicknesses)

$\text{ASR}_{\text{cell}}$

**Key Assumptions:***

1. Intrinsic through-plane conductivity is **not** a function of $L$
2. Cell resistance is constant from build-to-build
Cell resistance increases at low RH ... dominated by interfacial resistance

- Increasing $R_{\text{cell}}$ with decreasing RH also reported by W.L. Gore & Associates

1. Johnson & Liu, "Ionic Conductivity of Perflouro sulfonic 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
  \[ R_{\text{cell}} : R_{\text{membrane}} \approx 0.1 - 0.2 \]
- At high RH, the cell resistance can be significant relative to the membrane resistance, especially for thin membranes