ECS Transaction, **41** (1) 1371-1380 (2011)

# Characterizing Through-Plane and In-plane Ionic Conductivity of Polymer Electrolyte Membranes

Kevin R. Cooper

Scribner Associates Inc., 150 E. Connecticut Ave,
Southern Pines, North Carolina, USA 28387

Ionic transport resistance is a key performance property of polymer electrolyte membranes (PEMs) and can be determined for transport within the plane of material (in-plane, longitudinal or transverse directions) and through the thickness of the membrane (through-plane). The conductivity of extruded Nafion® 112, dispersion-cast Nafion® NR-212 and two Gore-Select® membranes that contain a non-conductive support were characterized as a function of orientation, temperature and relative humidity. The conductivity of extruded Nafion 112 was highest in the extrusion direction and lowest in the through-plane orientation. In contrast, the conductivity of dispersion-cast NR-212 was isotropic. The effective conductivity of Gore-Select material was higher in-plane *vs*. through-plane, consistent with the analytical treatment of a membrane composed of layers of unequal intrinsic ion transport resistivity. The results highlight the need to make measurements in the relevant orientation.

## Introduction

Ionic resistance and conductivity are key performance properties of polymer electrolyte membranes (PEMs) because the lower the conductivity the higher the resistive losses in the cell during operation. These properties can be determined for ion transport within the plane of material (in-plane direction, IP) or through the thickness of the membrane (through-plane orientation, TP) as illustrated in Figure 1. Although through-plane conductivity ($\sigma_{TP}$) is more relevant for fuel cells, measurement in the in-plane direction is more easily implemented and thus more often reported (1-8). In-plane measurements can be made at different orientations within the plane of the membrane (*i.e.*, longitudinal *vs*. transverse direction) although this orientation distinction is generally not considered or reported. Consideration of non-isotropic membrane conductivity is important because it may impact cell performance.

Thermo-mechanical processing of the polymer, leading to microstructural orientation, can influence mechanical and ionic conductivity of perfluorosulfonic acid (PFSA) PEMs (9, 10). Consequently, the longitudinal in-plane conductivity ($\sigma_{IP-L}$) may differ from the transverse in-plane conductivity ($\sigma_{IP-T}$) even for as-manufactured membranes. Jiang and co-workers (11) recently reported that extrusion-cast Nafion 112 exhibits anisotropic proton transport resistance: the in-plane proton conductivity was significantly higher when measured in the direction parallel to the extrusion (*i.e.*, longitudinal) direction as compared to the transverse orientation. They reported that the through-plane conductivity was greater than in the transverse direction but less than in the longitudinal direction.

Less clear is if anisotropic behavior is to be expected for dispersion-cast material such as Nafion NR-21X.

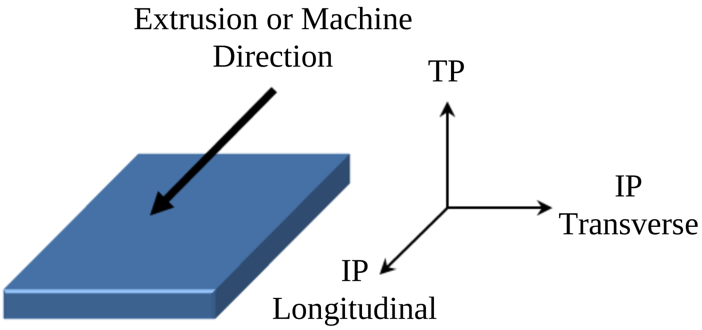

Figure 1. Nomenclature for extruded membrane. IP = in-plane, TP = through-plane.

In addition, anisotropic behavior may arise due to the presence of microscopic or macroscopic support structures and/or skin effects. For example, composite membranes that incorporate a non-conductive reinforcement, such as Gore-Select (12), are anticipated to exhibit anisotropic ion transport resistance. This expected anisotropy is an additional argument for determining the ionic resistance of intrinsically heterogeneous structures in the orientation that is relevant to the application.

Through-plane membrane resistance can be obtained from single cell testing (11, 13, 14) although approaches that use bare membrane have been reported (7, 15-22). When extracting the membrane through-plane resistance, non-membrane ohmic contributions such as the electronic resistance of the flow field and gas diffusion media and contact resistances, should be accounted for (11, 13, 14, 16, 22).

We recently reported on a new test system and measurement procedure that facilitates rapid, robust measurement of the through-thickness resistance of bare (non-catalyzed) membrane material over a broad range of temperature and humidity conditions (22, 23). Although developed specifically for through-plane measurements, the Membrane Test System (MTS) can also be used for in-plane ion transport resistance characterization.

We present the in-plane and through-plane resistance and conductivity of PFSA-based membranes as a function of orientation, temperature and relative humidity. Membranes investigated in this work were as-received extrusion-cast Nafion 112 and dispersion-cast Nafion NR-212, and two thicknesses of Gore-Select material. Conductivity was based on the nominal or actual membrane thickness measured at ambient conditions, and through-plane area specific resistance and conductivity were corrected for non-membrane ohmic contributions to the measured high-frequency resistance.

## Experimental

### Test Procedure

The Membrane Test System (MTS), procedure and data analysis were described in detail elsewhere (22). In general, the procedure consisted of measuring the dimensions of the specimen, assembling the test specimen into either the in-plane or through-plane test fixture, conditioning the membrane at the desired temperature and relative humidity (RH) followed by measuring the resistance of the sample throughout a prescribed RH cycle. In-plane measurements were made with an in-plane conductivity cell clamp (BT-110, BekkTech, LLC) located in the MTS chamber which provided thermal and humidity control.

Materials. Membranes characterized for their proton transport resistance were extruded Nafion 112 (51 μm) and 117 (178 μm), as well as dispersion cast Nafion NR-212 (51 μm); all had a nominal equivalent weight (EW) of 1100. Also evaluated were two thicknesses (18 and 35 μm) of Gore-Select material (unknown EW). After cutting and dimensioning, the Nafion 112 and 117 samples were boiled in ultra-high purity water for 1 hour and stored in air-tight container until tested. The Nafion NR-212 and Gore samples were stored at ambient conditions and tested in the as-received condition. Sample size was *ca*. 3 cm x 1 cm for both in-plane and through-plane measurements. Thickness was measured at five locations with a high-precision, calibrated film thickness gauge (Brunswick Instruments Inc. Film Thickness Measurement System-3) at ambient conditions (~ 22 °C, 50% RH). The mean thickness ($L$) was used to calculate the through-plane conductivity.

Test Conditions. Samples were tested over a range of temperature and humidity conditions: 30 to 120 °C, dry to 95% RH. Specimens were conditioned 2 hr at 70% or 80% RH followed by stepping through an RH cycle (either 70% to 20% to 95% at 10% intervals with a 15 min hold prior to the resistance measurement, or 95%, 80%, 60%, 40% and 20% RH with a 30 min hold prior to the resistance measurement). For Gore-Select and NR-212, this was performed at 30 °C and 80 °C at 101 $\text{kPa}_a$, and 120 °C at 230 $\text{kPa}_a$, where as for Nafion 112 tests were limited to 80 $^o$C. A total dry gas flow rate of 500 sccm facilitated attaining a steady-state RH within *ca*. 2 min after a step-change in the wet-dry gas ratio, *i.e.*, a change in RH.

Impedance Measurement and Data Analysis. After conditioning the membrane at a given RH, a voltage-controlled, swept frequency impedance spectroscopy measurement was performed using a Solartron Analytical 1260 Frequency Response Analyzer (10 $\text{mV}_{AC}$ at 0 $\text{V}_{DC}$, 2 MHz to 1 Hz, 10 steps/decade).

For through-plane measurements, impedance spectra were fit with an equivalent circuit model to determine the high frequency resistance $R_{\text{hfr}}$ in Ω, which was area-normalized by multiplying it by the active area for the through-plane measurement $A_{\text{TP}}$ = 0.5 cm$^2$,

$$ASR_{\text{hfr,TP}} = R_{\text{hfr}} \times A_{\text{TP}} \qquad [1]$$

where $ASR_{\mathrm{hfr,TP}}$ is the area-specific high-frequency resistance. The area-specific through-plane membrane resistance ($ASR_{\mathrm{membrane,TP}}$ in Ω-cm$^2$) was calculated by subtracting the area-specific non-membrane cell resistance ($ASR_{\mathrm{cell}}$) from the high frequency resistance,

$$ASR_{\mathrm{membrane,TP}} \;=\; ASR_{\mathrm{hfr,TP}} - ASR_{\mathrm{cell}} \qquad [2]$$

Through-plane membrane conductivity ($\sigma_{\mathrm{TP}}$ in S/cm) was calculated from equation [3] where $T$ is the dry thickness of the membrane,

$$\sigma_{\mathrm{TP}} \;=\; T \,/\, ASR_{\mathrm{membrane,TP}} \qquad [3]$$

In-plane conductivity was calculated from the membrane resistance $R_{\mathrm{membrane,IP}}$ obtained from the low-frequency region of the impedance spectra using equation [4],

$$\sigma_{\mathrm{IP}} \;=\; L_{\mathrm{IP}} \,/\, (A_{\mathrm{IP}} \times R_{\mathrm{membrane,IP}}) \qquad [4]$$

where $L_{\mathrm{IP}}$ is the distance between the voltage sense electrodes (0.425 cm) and $A_{\mathrm{IP}}$ is the dry sample width ($W$) multiplied by the dry membrane thickness, $A_{\mathrm{IP}} = W \text{ x } T$.

## Results and Discussion

The conductivity of Nafion 112, NR-212 and two Gore-Select ionomer membranes was determined as a function of orientation, temperature and relative humidity.

### Conductivity of Extruded Nafion 112

The conductivity of extrusion-cast Nafion 112 was observed to be orientation dependent: in-plane, longitudinal (parallel to machine direction) > in-plane, transverse (perpendicular to machine direction) > through-plane. This is demonstrated in Figure 2 where the mean and error bars representing one standard deviation of three replicates is shown.

Hypothesis testing on the equality of means ($H_0$: $\mu_1 = \mu_2$; $H_0$: $\mu_1 \neq \mu_2$, t-test, $\alpha = 0.05$) (24) for each orientation combination at each RH confirmed that the difference in means was statistically significant. Thus, there is strong statistical evidence that $\sigma_{\mathrm{IP\text{-}L}} > \sigma_{\mathrm{IP\text{-}T}} > \sigma_{\mathrm{TP}}$ at all humidities. (The exception was for the case of in-plane transverse *vs*. through-plane at 40% RH where the null hypothesis could not be rejected, indicating that there was a lack of statistical evidence to conclude that the means were unequal for that specific combination.)

The ratio of conductivity for the different orientation combinations at each RH are summarized in Table I. For Nafion 112, the mean conductivity ratio across all RHs ($\mu \pm 1s$) were: $\sigma_{\mathrm{IP\text{-}L}} : \sigma_{\mathrm{TP}} = 1.61 \pm 0.14$, $\sigma_{\mathrm{IP\text{-}L}} : \sigma_{\mathrm{IP\text{-}T}} = 1.46 \pm 0.02$ and $\sigma_{\mathrm{IP\text{-}T}} : \sigma_{\mathrm{TP}} = 1.11 \pm 0.09$. Ratios near unity are indicative of material with isotropic proton transport resistance. These results demonstrate that as-manufactured Nafion 112 exhibits anisotropic, orientation-dependent proton transport resistance.

These results are generally in agreement with those reported by Jiang *et. al.* (11) who also found that for Nafion 112, the in-plane proton transport conductivity in the longitudinal direction exceeded the conductivity in other orientations for a wide range of RH at 80 $^oC$. However, they reported that the through-plane proton conductivity was greater than the in-plane transverse conductivity whereas we observed evidence to the contrary (Figure 2). It is worth noting that the difference between the two studies is relatively small. Analysis of the data presented in Figure 7 in (11) reveals $\sigma_{IP-L} : \sigma_{TP}$ = 1.28-1.44, $\sigma_{IP-L} : \sigma_{IP-T}$ = 1.43-1.66, and $\sigma_{IP-T} : \sigma_{TP}$ = 0.80-0.91.

The source of this discrepancy is uncertain but may be due to (*i*) differences in the as-manufactured material properties of the different production lots used in the two studies, (*ii*) variation of the thermo-mechanical history of the membrane samples, and (*iii*) differences in the in-plane and/or through-plane procedure used in the two investigations. For example, to perform the through-plane measurements, Jiang and coworkers (11) fabricated, via the decal transfer process, membrane electrode assemblies using as-received Nafion 112. In contrast, this work used Nafion 112 samples that were boiled for 1 hour in ultra-high purity water prior to cell assembly and testing. These and other differences in the measurement procedures are likely the source of difference in the reported conductivities of Nafion 112.

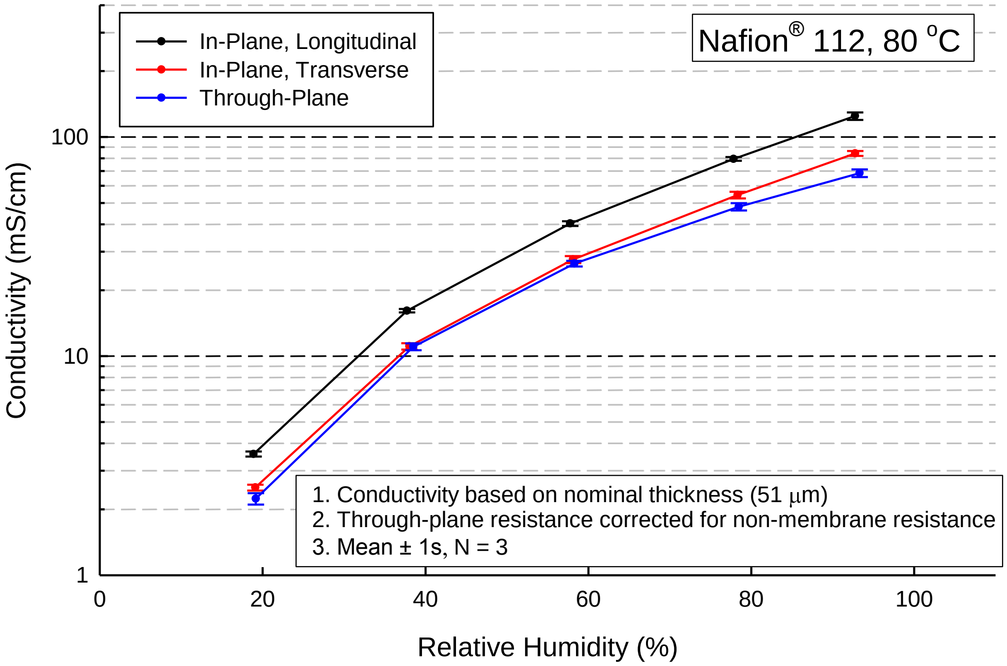

Figure 2. Conductivity of Nafion 112 at 80 $^oC$ is a function of orientation.

Table I. Ratio of conductivity for Nafion 112 at 80 $^oC$.

| 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 |
| μ ± 1s | 1.61 ± 0.14 | 1.46 ± 0.02 | 1.11 ± 0.09 |

## Conductivity of Dispersion Cast Nafion NR-212

In contrast to the extruded Nafion product, we previously reported that the conductivity of dispersion-cast Nafion NR-212 was essentially isotropic with respect to orientation (22). That is, the ratio of in-plane to through-plane conductivity from 20-95% RH was 1.07 ± 0.08 at 30 $^{o}$C, 0.93 ± 0.03 at 80 $^{o}$C and 0.99 ± 0.014 (at 120 $^{o}$C). These data are summarized in Table II. For the whole temperature and RH dataset, the mean conductivity ratio was 0.998 (minimum = 0.81 and maximum = 1.30), which contrasts significantly with the data for Nafion 112 (see Table I). In addition, hypothesis testing of the equivalency of in-plane and through-plane conductivity indicated that there was not a statistically significant difference between the two data sets.

Nafion NR-212 membrane is formed in a dispersion casting process which imposes significantly less mechanical stress on the membrane during manufacturing as compared to an extrusion process. Thus, it is conceivable that this product would exhibit similar if not the same proton transport resistance within the plane of the film as through the thickness.

Jiang and coworkers (11) investigated solution cast homogeneous membranes of different EW. Similar to the results reported here for Nafion NR-212, they found that the in-plane conductivity was nearly the same as the through-plane conductivity over the entire RH range. If one accepts that these cast membranes are isotropic with respect to proton transport resistance, then the fact that both studies observe this result indicates that the correction performed to account for the non-membrane ohmic resistance is methodologically valid and reasonably accurate.

Table II. Ratio of in-plane to through-plane conductivity for Nafion NR-212 at three temperatures.

| **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 |
| $\mu \pm 1s$ | 1.07 ± 0.08 | 0.93 ± 0.03 | 0.99 ± 0.14 |

## Conductivity of Gore-Select Membrane

Gore-Select membrane, manufactured by W.L. Gore & Associates, Inc. is a polymer electrolyte membrane containing a thin microporous expanded polytetrafluoroethylene (ePTFE) reinforcement (12). The reinforcement provides physical strength and permits the use of ionomers that do not have sufficient mechanical properties to be used as thin films. The support layer in a Gore-Select membrane consists of the non-conductive microporous ePTFE. The pores in the ePTFE matrix are filled with ionomer. It is important to note that the support layer thickness is less than the total membrane thickness such that there is a layer of pure ionomer on either side of the reinforcement.

This composite support layer is expected to have higher proton transport resistivity (lower conductivity) than the adjacent layers of pure ionomer.

The proton transport resistance was determined for two Gore-Select membranes as a function of orientation. Figure 5 shows that across a wide range of RH, the effective (*i.e.*, observed) in-plane conductivity was greater than the effective through-plane conductivity. The ratio of in-plane to through-plane conductivity was 1.53 ± 0.16 and 1.10 ± 0.10 for the 18 and 35 μm material, respectively.

These results are consistent with the analytical treatment which considers the layered membrane as resistances in parallel for the in-plane direction and resistances in series for the through-plane direction. In this analysis, shown in Figure 3, we consider one layer to be the total thickness of pure, non-supported ionomer (in practice, it is evenly distributed on either side of the support) and the second layer to be the ionomer-filled, non-conductive porous support. $\sigma_1$ and $\sigma_2$ are the conductivity of the two layers and $f$ is the fractional thickness of layer 1. This analysis assumes that the intrinsic conductivity of the two layers is not orientation dependent, *i.e.*, $\sigma_{i,\mathrm{IP}} = \sigma_{i,\mathrm{TP}}$. , where $i$ refers to either layer 1 or 2.

The layered-type membrane illustrated in Figure 3 is representative of Gore-Select membranes. For this type of structure, the effective in-plane conductivity exceeds the effective through-plane conductivity ($\sigma_{\mathrm{eff,IP}} > \sigma_{\mathrm{eff,TP}}$). As shown in Figure 5 and indicated above, the measured conductivity was higher in the in-plane direction as compared to the through-plane direction, consistent with the theoretical analysis.

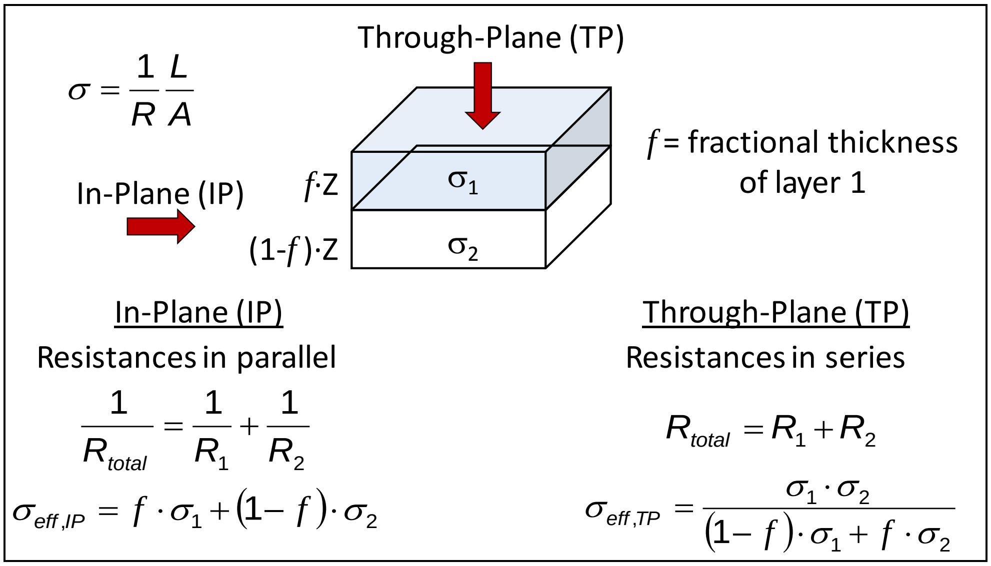

Figure 3. Analytical treatment of the effective conductivity of a layered membrane such as Gore-Select. Resistances are in parallel for the in-plane direction whereas resistances are in series in the through-plane orientation.

In addition, the ratio of in-plane to through-plane conductivity itself is a function of the relative thickness of the two phases. As the fractional thickness approaches 0 or 1, one of the two phases dominates and the effective membrane conductivity approaches the conductivity of that component. Therefore, the orientation dependence diminishes as $f \rightarrow 0$ or 1, *i.e.*, $\sigma_{\mathrm{eff,IP}} : \sigma_{\mathrm{eff,TP}} \rightarrow 1$ as $f \rightarrow 0$ or 1. Conversely, the ratio of effective conductivities is a maximum for the case where each phase is of equal thickness, $f \rightarrow ½$. These results are depicted in Figure 4.

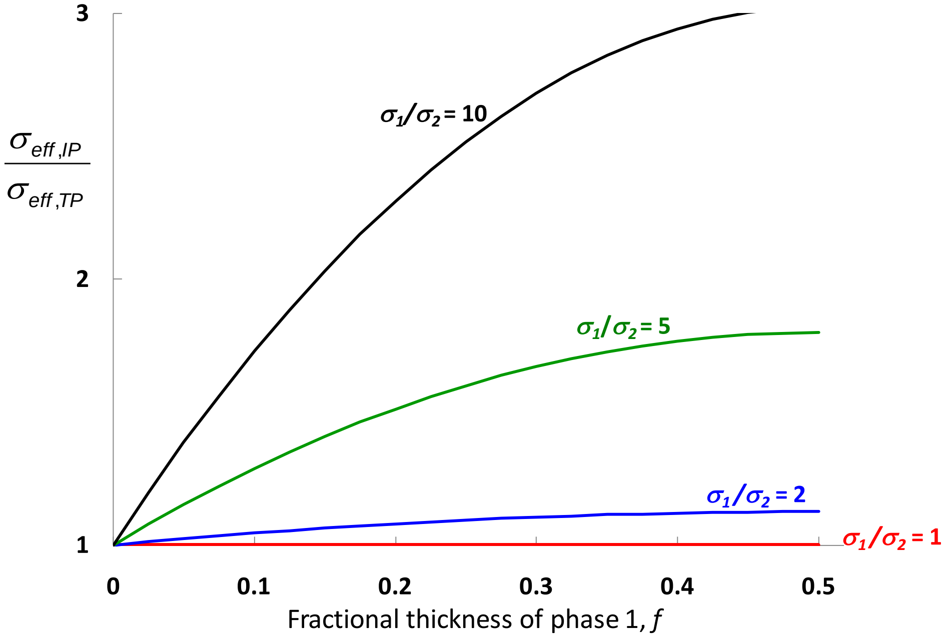

Figure 4. Ratio of the effective in-plane and through-plane conductivity ($\sigma_{\mathrm{eff,IP}}/\sigma_{\mathrm{eff,TP}}$) as a function of fractional thickness of one layer of the 2-layer material ($f$) and the ratio of the intrinsic conductivity of the two layers ($\sigma_1/\sigma_2$). See also Figure 3.

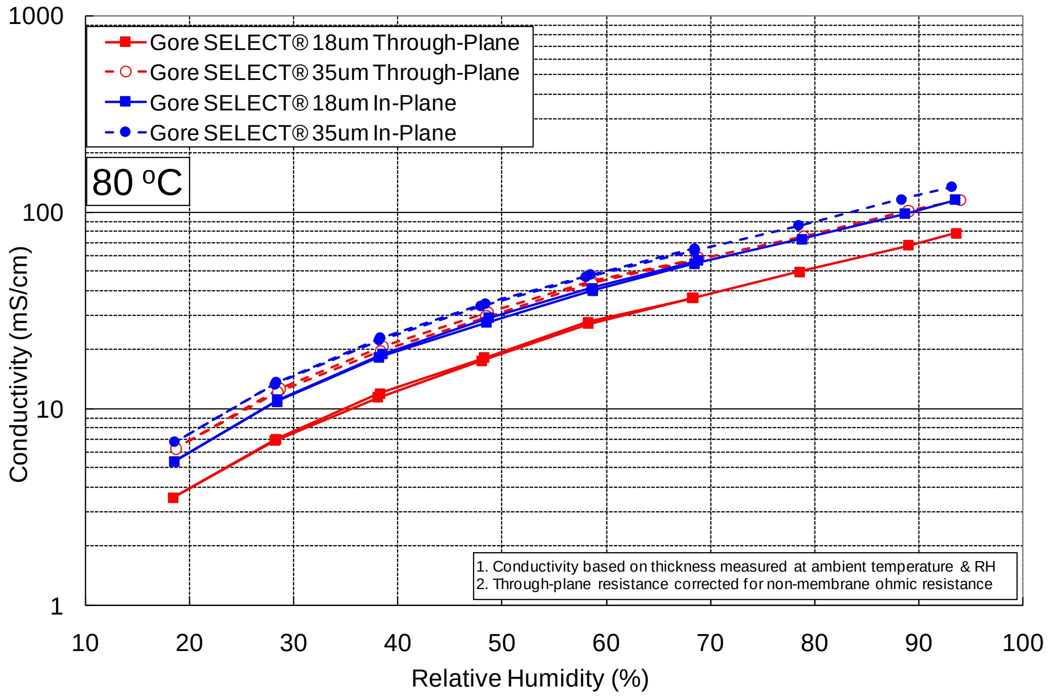

Figure 5. Effective in-plane and through-plane conductivity of 18 and 35 μm Gore-Select at 80 °C.

For the Gore-Select membrane, the through-plane conductivity was lower than the in-plane conductivity. This was observed over the full range of RH examined (20-95%). This anisotropic proton transport behavior arises because the Gore-Select membrane contains a non-conductive reinforcement with ionomer-filled pores in the middle of the membrane. Proton transport in the through-plane direction is inhibited by this layer. In the in-plane direction, proton transport is facilitated through the more-conductive pure ionomer regions that exist on either side of the middle reinforcement layer. The through-plane direction is the primary proton transport direction in a fuel cell application, and therefore the through-plane conductivity is more relevant than in-plane conductivity with respect to characterizing this membrane property.

## Conclusions

Extruded PFSA-based membranes such as Nafion 112 exhibit significant anisotropic proton transport resistance. For this material, in-plane conductivity parallel to the extrusion direction was 60% greater than in the through-plane direction. In contrast, dispersion-cast Nafion NR-212 displays equivalent ion transport resistance within and through the plane of the film.

Reinforced Gore-Select membrane exhibits anisotropic proton transport resistance. Enhanced conductivity in-plane *vs*. through-plane is consistent with the analytical treatment of a heterogeneous film with multiple layers of differing conductivity. The ratio of in-plane to through-plane conductivity was higher for the thinner composite membrane as compared to the thicker reinforced membrane, and occurs because for the latter the support layer is a small fraction of the overall membrane thickness and thus the material effectively behaves more homogeneous.

Consideration of non-isotropic membrane conductivity is important because it may impact cell performance. Because proton transport occurs primarily in the through-thickness direction in an operating fuel cell, measurement of the through-plane conductivity is more relevant than the in-plane conductivity for evaluating membrane performance and predicting fuel cell performance.

## Acknowledgements

A portion of this work was supported by the U.S. Department of Energy through the University of Central Florida. In-plane conductivity data for Nafion NR-212 courtesy of BekkTech LLC. Nafion is a registered trademark of E.I. du Pont de Nemours and Company. Gore and Gore-Select are registered trademarks of W.L. Gore & Associates, Inc.

## References

1. S. Slade, S.A. Campbell, T.R. Ralph and F.C. Walsh, *J. Electrochem. Soc.*, **149**, A1556 (2002).

2. T.A. Zawodzinski, M. Neeman, L.O. Sillerud and S. Gottesfeld, *J. Phys. Chem.*, **95**, 6040 (1991).
3. Y. Sone, P. Ekdunge and D. Simonsson, *J. Electrochem. Soc.*, **143**, 1254 (1996).
4. J.J. Fontanella, M.C. Wintersgill, R.S. Chen, Y. Wu and S.G. Greenbaum, *Electrochimica Acta*, **40**, 2321 (1995).
5. P.C. Rieke and N.E. Vanderborgh, *J. Membrane Sc.*, **32**, 313 (1987).
6. C.H. Lee, H.B. Park, Y.M. Lee and R.D. Lee, *Ind. Eng. Chem. Res.*, **44**, 7617 (2005).
7. S. Ma, Z. Siroma and H. Tanaka, *J. Electrochem. Soc.*, **153**, A2274 (2006).
8. B.D. Cahan and J. S. Wainright, *J. Electrochem. Soc.*, **140**, L185 (1993).
9. K.A. Mauritz and R. B. Moore, *Chem. Rev.*, **104**, 4535 (2004).
10. K.M. Cable, K.A. Mauritz and R.B. Moore, *Chem. Mater.*, **7**, 1601 (1995).
11. R. Jiang, C. K. Mittelsteadt and C.S. Gittleman, *J. Electrochem. Soc.*, **156**, B1440 (2009).
12. S. Cleghorn, J. Kolde and W. Liu, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, W. Vielstich, A. Lamm and H. A. Gasteiger, Eds., p. 566–575, John Wiley & Sons, Chichester (2003).
13. R. Makharia, M.F. Mathias and D.R. Baker, *J. Electrochem. Soc.*, **152**, A970 (2005).
14. B.S. Pivovar and Y.S. Kim, *J. Electrochem. Soc.*, **154**, B739 (2007).
15. G. Alberti, U. Constantino, M. Casciola, S. Ferroni, L. Massinelli and P. Staiti, *Solid State Ionics*, **145**, 249 (2001).
16. G. Alberti, M. Casciola, L. Massinelli and B. Bauer, *J. Membrane Sc.*, **185**, 73 (2001).
17. B.S. Pivovar, Y. Wang and E.L. Cussler, *J. Membrane Sc.*, **154**, 155 (1999).
18. M. Cappadonia, J.W. Erning and U. Stimming, *J. Electroanal. Chem.*, **376**, 189 (1994).
19. M. Rikukawa, D. Inagaki, K. Kaneko, Y. Takeoka, I. Ito, Y. Kanzaki and K. Sanui, *Journal of Molecular Structure*, **739**, 153 (2005).
20. A. Kishi and M. Umeda, *Electrochemistry (The Electrochemical Society of Japan)*, **75**, 130 (2007).
21. J.-S. Cho, Y. Hayashino, K. Miyatake, S. Takeoka and E. Tsuchida, *Polymers for Advanced Technologies*, **11**, 548 (2000).
22. K.R. Cooper, *J. Electrochem. Soc.*, **157**, B1731 (2010).
23. K.R. Cooper and L.L. Scribner, *Electrolyte Measurement Device and Measurement Procedure*, U.S. Patent No. 7,652,479 B2 (2010).
24. J.S. Milton and J.C. Arnold, *Introduction to Probability and Statistics: Principles and Applications of Engineering and the Computing Sciences,* New York: McGraw-Hill, Inc., p. 811 (1995).