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Measurement of Water Content in Polymer Electrolyte Membranes using High Resolution Neutron Imaging

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Sufficient water content within a polymer electrolyte membrane (PEM) is necessary for adequate ionic conductivity. Membrane hydration is therefore a fundamental requirement for fuel cell operation. The hydration state of the membrane affects the water transport within, as both the diffusion coefficient and electro-osmotic drag depend on the water content. Membrane's water uptake is conventionally measured *ex situ* by weighing free-swelling samples equilibrated at controlled water activity. In the present study, water profiles in Nafion® membranes were measured using the high-resolution neutron imaging. The state-of-the-art, 10 μm resolution neutron detector is capable of resolving water distributions across N1120, N1110 and N117 membranes. It provides a means to measure the water uptake and transport properties of fuel cell membranes in situ.

Introduction

Sufficient water content within a polymer electrolyte membrane (PEM) is necessary for adequate ionic conductivity. Membrane hydration is therefore a fundamental requirement for fuel cell operation. From this constraint stems the issue of water management in PEM fuel cells, one of the critical topics in optimizing the performance. The excess water produced at the cathode needs to be efficiently removed from the cell (to allow reactant access to the catalyst) while maintaining the sufficient level of membrane hydration. Furthermore, the hydration state of the membrane affects the water transport within, as both the diffusion coefficient and electro-osmotic drag depend on the water content. Membrane's water uptake is conventionally measured *ex situ* by weighing free-swelling samples equilibrated at controlled water activity (1-3).

Neutron imaging has been used extensively in water management studies due to its ability to measure water content in an operating fuel cell. The spatial resolution of this technique has been improved by a factor of 50 over the past four years, thus enabling to resolve water distribution across the cell thickness. In the present study, water profiles in Nafion® membranes were measured using the high-resolution (10 μm) cross-strip detector (XS I) with a pixel pitch of 5 μm, recently installed at the NIST Center for Neutron Research.

The main objective of this work is to gain fundamental understanding of water content measurement in Nafion® via neutron imaging. In addition, it is important to evaluate the difference between water uptake by the free-swelling membrane (1-3) and by the membrane constrained by the fuel cell assembly, examined in this work.

Experimental

Membrane Material and Fuel Cell Assembly

Nafion® membranes 1100 (equivalent weight) with different thickness were characterized in this study: N117, N1110, and N1120. Each membrane was conditioned by boiling in 3% H_2O_2 solution, rinsing in deionized (DI) water, boiling in 0.5 molar solution of H_2SO_4, rinsing in DI water, and boiling in DI water. Duration of each boiling step was 1 hour. Finally, the membranes were dried under vacuum at 70° C and cooled down to room temperature.

Imaging was performed in a non-operating setting, with the membrane exposed to nitrogen stream with controlled relative humidity. The cell hardware, specially designed to optimize neutron imaging, was similar to the setup used in our previous work (4), with several upgrades as follows. Thermal movements within the cell were mitigated by affixing the cell to a specially designed holder with minimal thermal expansion. Humidity and temperature were maintained by controlling the dew point temperature of the gas streams, temperatures of each plate of the test cell, and by additionally heating the inlet tubing to prevent injection of condensed water from the test stand installation. In addition, humidity was independently monitored by Vaisala HMT338 RH sensors placed at the outlet on each side of the test cell.

Three configurations with respect to the level of membrane constraint were considered in this study. Water uptake was measured in (i) unconstrained, (ii) constrained, and (iii) compressed membranes. (i) The unconstrained membrane case corresponds to the free-swelling membrane, similar to the *ex situ* water uptake evaluation via weight change. The unconstrained membrane was sandwiched between two flat plates, with a gap created by thick gaskets on each side of the membrane. The entire membrane active area was exposed thus allowing the membrane to expand into the gaps. (ii) The constrained membrane case corresponds to the operating fuel cell environment, where the membrane is sandwiched between the gas diffusion layers (GDLs) and cell hardware. To ensure uniform membrane compression and minimize swelling, conventional flow field was replaced by a metallic mesh, and the GDL placed between the membrane and the metallic mesh on each side. (iii) The compressed configuration was similar the constrained case, but with stronger constraint imposed on the membrane: by placing a double GDL on each side while keeping the same gaskets, or by keeping the single GDL while reducing the gasket thickness by more than 50 %.

Neutron Radiography

The imaging was performed at the NIST Center for Neutron Research, using newly installed high-resolution cross-strip detector (XS I) with a pixel pitch of 5 μm. Images were taken with the exposure time of 2 minutes.

Results and Discussion

Image processing was done by taking into account the beam hardening effect (characteristic of the detector) with optical density (OD) obtained as follows:

$$OD(t) = \ln\left(\frac{I_{wet} - I_{dark}}{I_{dry} - I_{dark}}\right) = \mu \cdot t + \beta \cdot t^2 \qquad [1]$$

where t is the water thickness (in mm), I_{wet} and I_{dry} are the wet and dry (or, reference) image, respectively, while the I_{dark} takes into account the background radiation. Dry image was obtained after drying the membrane in nitrogen stream at 80° C for 90 minutes. The constants μ and β were obtained by using the calibration cuvette with a known set of water thickness, and are measured to be $\mu = 0.37412\ \text{mm}^{-1}$, and $\beta = -0.00863284\ \text{mm}^{-2}$. The non-linear relationship between the optical density and water thickness brings additional challenge when calculating the water uptake by the membrane, since the membrane will contain some residual amount of water, $t_{residual}$, unless kept in vacuum at elevated temperature. Hence, the membrane water content in the reference "dry" image, $t_{residual}$, needs to be taken into account:

$$OD(t + t_{residual}) = \left(\mu + 2\beta \cdot t_{residual}\right) \cdot t + \beta \cdot t^2 \qquad [2]$$

To evaluate the amount of the residual water, several ex situ measurements were performed. First, thermo-gravimetric analysis (TGA) was performed by placing the membrane samples (equilibrated at room conditions) in a stream of dry nitrogen at 80° C, which corresponds to the drying procedure before each imaging run. The TGA results show the loss of water content of 1.7 after 90 minutes (where the water content is defined as $\lambda = n_{H2O}/n_{SO3^-}$). Further, samples that were pre-soaked in liquid water showed a similar water loss after drying in nitrogen for the same amount of time, indicating that the laboratory conditions should not significantly influence the water content in the reference image. Finally, the total water content in the membrane was measured by completely drying the sample in a vacuum TGA (70kPa) at 105° C. Initial measurements give the λ of 4, which is higher than obtained in previous work (1-3). Additional ex situ measurements are being performed to verify the above values. In the present report, residual water in the reference image was calculated based on the water content λ=2.3.

To calculate the water profiles across the membrane, 10 consecutive images were averaged (corresponding to the effective exposure time of 20 minutes), after exposing the membrane to a set humidity condition for at least an hour. In the current cell configuration, the central portion of the membrane (12 by 16 mm) is exposed to nitrogen flow. The outer region of the membrane is compressed between the gaskets and the plates (i.e. the membrane extended across the entire area of the end plates). Over time, water would diffuse in plane into the outer region of the membrane, and was accounted for in our data analysis.

The results are shown in Figure 1, where the water content λ is plotted as a function of relative humidity. The water content values obtained by neutron imaging agree reasonably well with the existing reports employing weight measurements [1-3]. Higher values measured at lower RH in the present study may be due to an underestimated water content in the previous work, as dry samples may absorb water from the ambient air while performing the weight measurement outside the RH-controlled cell. We are performing additional TGA measurements where the issue of exposing the sample to the ambient air is eliminated. Second, the limited time for drying the membrane introduces an uncertainty in our calculations, and should be prolonged in the future experiments.

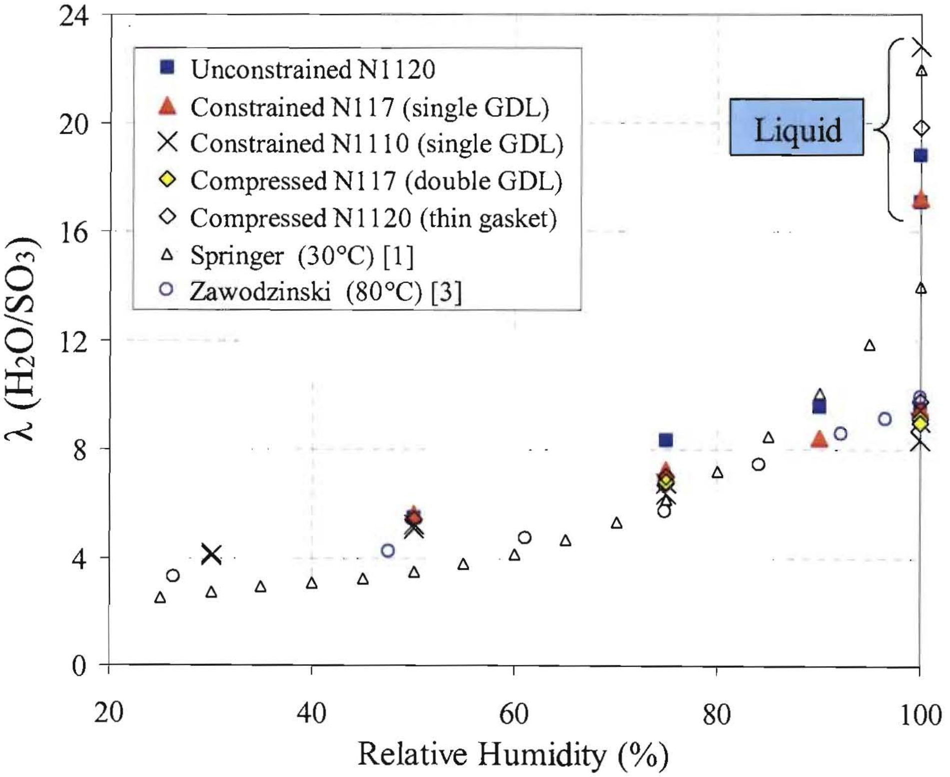

Figure 1. Water uptake by Nafion® membranes at 80° C measured by high-resolution neutron imaging ($\lambda_{reference}$=2.3).

When comparing the constrained and compressed cases, it is interesting that additional membrane compression did not cause significant reduction in water uptake. A possible explanation may be that the compression of the GDL mitigates the pressure exerted on the membrane itself. The unconstrained case shows slightly higher water uptake at elevated RH. However, it should be noted that the image processing requirement allows only limited membrane expansion (in the gaps of only 0.1 to 0.15 mm), which may be a limiting factor, especially in the liquid case. Membrane expansion in the in-plane direction was observed (rippling in the gap region), which may prevent the access of water to certain regions of the membrane, hence requiring significantly longer equilibration times at elevated RH.

Another lesson learned from these experiments is the choice of the gasket material. Namely, the PTFE-coated fiber glass gaskets used in many of the above experiments greatly distort the images due to the high neutron attenuation by fiber glass. This makes the edge detection (required for estimating the membrane swelling) extremely challenging. In addition, liquid water would wick over time into the fiber glass bundles, additionally distorting the neutron signal. PTFE was found to be advantageous as the gasket material for high-resolution neutron imaging in general.

Conclusions

The state-of-the-art, 10 μm resolution neutron detector is capable of resolving water distributions across Nafion® membranes. It provides a means to measure the water uptake and transport properties of fuel cell membranes. Present results should prove useful for interpreting the water profiles obtained by neutron imaging in operating PEM fuel cells and with thinner membranes.

Acknowledgments

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Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the products are necessarily the best available for this purpose

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