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EFFECT OF COMPRESSION ON CONDUCTIVITY AND MORPHOLOGY OF PFSA MEMBRANES

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Introduction

Polymer-Electrolyte-Fuel-Cells (PEFCs) are promising candidates for powering vehicles and portable devices using renewable-energy sources. The core of a PEFC is the solid electrolyte membrane that conducts protons from anode to cathode, where water is generated. The conductivity of the membrane, however, depends on the water content of the membrane, which is strongly related to the cell operating conditions. The membrane and other cell components are typically compressed to minimize various contact resistances.[1] Moreover, the swelling of a somewhat constrained membrane in the cell due to the humidity changes generates additional compressive stresses in the membrane.[2-3] These external stresses are balanced by the internal swelling pressure of the membrane and change the swelling equilibrium. For example, the swelling pressure during the hydration of a fully constrained PFSA membrane has been measured to go as high as 100 MPa (Fig. 1) [4]. It was shown using a fuel-cell setup that

compression could reduce the water content of the membrane[5] or alter the cell resistance.[1] Nevertheless, the effect of compression on the membrane's transport properties is yet to be understood, as well as its implications in the structure-functions relationships of the membrane. We previously studied, both experimentally and theoretically, how compression affects the water content of the membrane.[6] However, more information is required the gain a fundamental understanding of the compression effects.

In this talk, we present the results of our investigation on the in-situ conductivity of the membrane as a function of humidity and cell compression pressure. Moreover, to better understand the morphology of compressed membrane, small-angle X-ray-scattering (SAXS) experiments were performed. The conductivity data is then analyzed by investigating the size of the water domains of the compressed membrane determined from the SAXS measurements.

Experimental

Sorption and Conductivity. Nafion® NR212 and 117 membranes are used for the measurements. Membranes are pretreated following the standard procedure in the literature. Sorption isotherms of the membranes are obtained using a dynamic-vapor-sorption analyzer. Conductivity of the membrane as a function of pressure is measured in a fuel-cell testing system with compression control. The compression level in the cell is adjusted by means of pressurized gas. Environmental conditions are set by controlling the humidity and temperature of the inlet and outlet gases. Conductivity is determined as a function of humidity and pressure at 25 °C and 80 °C.

Small Angle X-ray Scattering (SAXS). Synchrotron SAXS measurements were carried out at the Advanced Light Source (ALS) Beamline 7.3.3 (Lawrence Berkeley National Laboratory), which was equipped with a CCD detector (2304 x 2304 pixels). The wavelength of the incident

X-ray beam was 10 A, and the sample-to-detector distance was 1.3 m. The scattering wave vector, q (= $4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle), was in the range of 0.1 – 0.03 A. From the SAXS spectra, domain spacing and domains size of the membranes are determined. The membranes were placed into a custom-made compression fixture with imaging windows for the beam. The compression load was controlled and monitored using a digital load cell. The membranes were equilibrated at different relative humidities using salt solutions prior to the measurements.

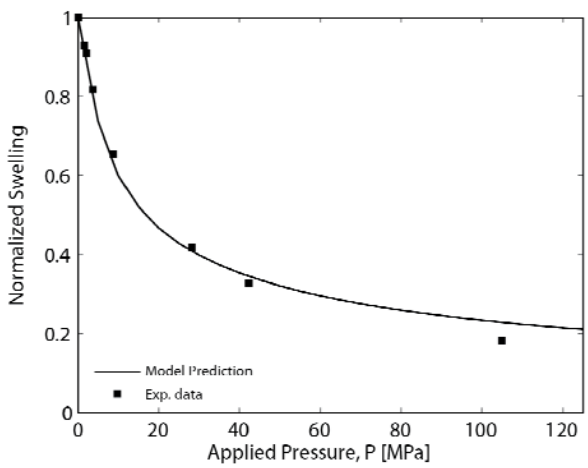

Figure 1. Model prediction and experimental data[4] for the reduction in swelling strain of an initially hydrated membrane as a function of applied hydrostatic pressure.

Results and Discussion

Conductivity depends on both the macroscopic water content and the domain spacing (i.e. distance between water domains) of the membrane. However, there is also a strong correlation between domain spacing and the water content. The impact of pressure or compressive load is to lower the water content and also change the shape and size of the morphological domains. These

changes have an impact on the relationship between conductivity and water content due to the changing tortuosity component between the membrane water domains.

Change in the membrane swelling as a function of applied pressure is determined from the equilibrium of chemical potentials, where the externally applied pressure is incorporated into the swelling pressure term.[2, 7] Model prediction and the experimental data are in good agreement showing that equilibrium water content decreases under externally applied pressure (Fig. 1).

SAXS spectra for wet membrane under compression are shown in Fig. 2. The ionomer peak, related to the size of water domains, moves leftward with increasing pressure. Domain spacing determined from the SAXS spectra indicates that the water domains become smaller in the thickness (i.e. compression) direction but elongate in the plane of the membrane (i.e. perpendicular to the compression direction). Also, the compression effect is found to be more pronounced at higher humidities.

Lastly, water content, domain spacing and conductivity data are analyzed together as a function of relative humidity and compression level to determine appropriate structure-function relationship. The preliminary findings of our investigations reveal that membrane conductivity can be related to the macroscopic swelling of the membrane and the microscopic size of the water-domains.

Conclusions

The conductivity-morphology relationship of the membrane is investigated as a function of humidity and compression loads. The nanostructure of the compressed membrane is investigated using SAXS. Conductivity of the compressed membrane can be correlated with the water content and the deformed nanostructure of the membrane under similar compression levels. The findings

of this work provide an alternative picture for the fundamentals of the membrane's transport mechanisms and have potential implications for optimized fuel-cell performance.

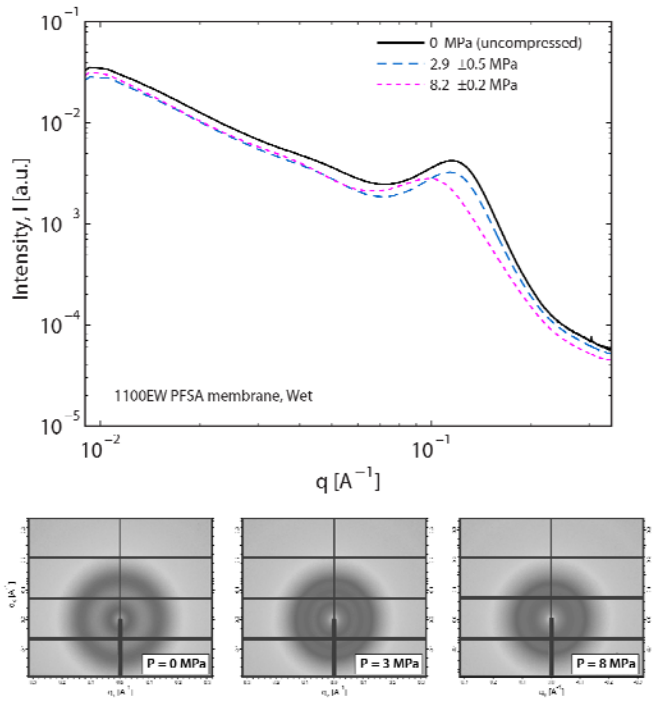

Figure 2. SAXS profiles of uncompressed and compressed PFSA membrane. Membrane was liquid-equilibrated prior to the tests. The corresponding SAXS spectra are shown below for each case.

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