Water Uptake in PFSA Membranes

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Perfluorosulfonic-acid (PFSA) membranes are the most widely studied ionomer for proton-exchange-membrane-fuel-cell applications, with Nafion® still considered to be the benchmark material.[1] Its exceptional proton conductivity along with good thermo-mechanical stability make it suitable for most electrochemical devices. The performance of a fuel-cell membrane is controlled by its transport properties and sorption behavior,[2] which are strongly correlated through the interactions between chemical structure and morphology. The morphology, sorption behavior, water content, λ, and transport properties (e.g. conductivity) of Nafion have been under investigation over the past few decades.[1,3,4]

Even though the findings in these studies have provided useful information on the water uptake and structure-function relationship of Nafion, the current understanding is confused due to the lack of a standard test procedure and complexity of the membrane morphology, which itself is still under debate. Thus, to gain a fundamental understanding on the sorption behavior and different water-content related processes, we use a systematic approach to investigate the water uptake and transport at multiple length and time scales by combining different experimental techniques including water uptake through dynamic vapor sorption and gravimetric techniques, small-angle x-ray scattering (SAXS) to determine the nanoscale morphology, and conductive atomic force microscopy.

In this talk, the water-uptake properties of PFSAs will be reviewed and discussed with a focus on the impact of membrane pretreatment and control of the transport due to the interfacial morphology of the membrane. Both Nafion and short-side chain PFSAs will be examined. The results of these studies can be summarized as shown in Fig. 1, which shows the domain spacing as determine by SAXS as a function of water content.[5] As can be seen, there is a general linear correlation in this seminal relationship, which shows both the uptake from vapor and liquid-equilibrated membranes including the impact of drying and subsequent relaxation under heating.

In addition to general water uptake, the talk will focus on the existence of Schroeder's paradox for these membranes. Schroeder's paradox is a well known, but not fully understood, phenomenon that exists in many polymers and gels. Essentially, the uptake of solvent in the polymer depends on the interaction with the boundary phase. For Nafion, this is often represented as an almost doubling of the water content in liquid versus saturated vapor. In this talk, we discuss the origin of this paradox through experimental examinations. The results show that the interface controls the water uptake (even in bulk membranes) and that the interfacial morphology depends on the interactions of the different polymer moieties with the external environment including its density and dielectric constant as shown in Fig. 2. In addition, it is thought that this paradox may not occur during operation. Using x-ray tomography at the Advanced Light Source, we will show that there is a continuous water profile and change from the liquid to the dry water-content values during gradient experiments as shown in Fig 3.
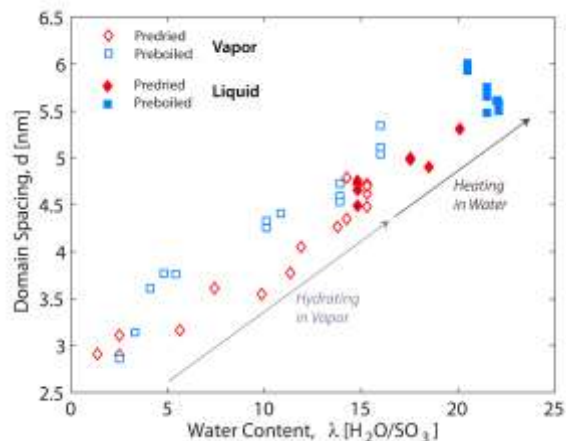
Acknowledgements

Figure 1. Water domain spacing as a function of water content for different solvents (vaor and water) and different thermal treatments.
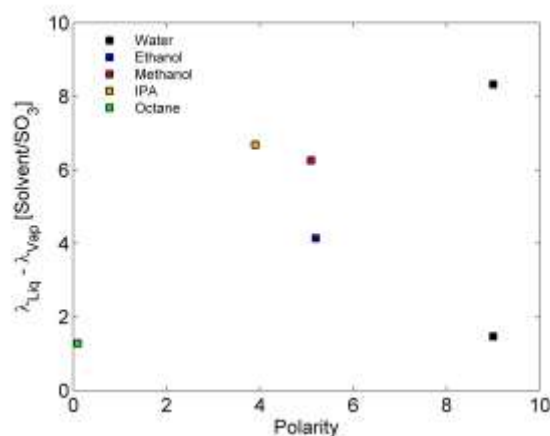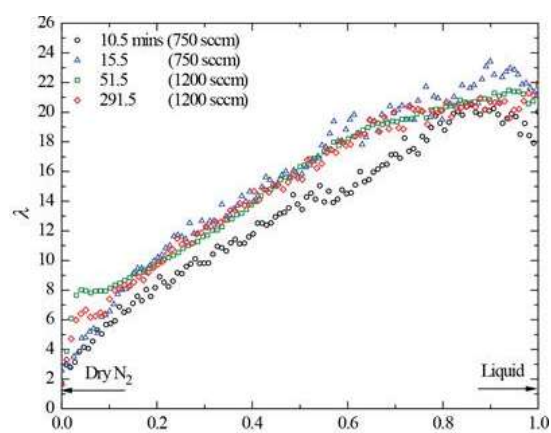

Figure 2. Schroeder's paradox for different solvents.

Figure 3. Measured, steady-state, local water content distribution under the dry/liquid boundary conditions as measured using x-ray tomography.

References

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