Perfluorosulfonic-acid (PFSA) ionomers are commonly used as the proton-exchange membrane (PEM) in most solid-state energy-conversion and storage devices due to their exceptional ionic conductivity and good permselectivity. Ionomers have multiple functionalities in PEM fuel cells; in addition to their role as the ion-conducting membrane, they form a nanometer-thick electrolyte film within the catalyst-layers (CLs) wherein the electrochemical reactions occur. Interactions of the membrane with the local environment and as a thin film within the CL result in highly complex material behavior that is highly dependent on the environmental conditions, ionomer thickness, and the material interactions, i.e., carbon, platinum, etc. Thus, characterization of the role of ionomer in fuel-cell catalyst layers requires an understanding the transport properties and water-uptake behavior throughout a wide thickness range including bulk membrane interfacial phenomena.

In this work, we investigate the morphology and swelling of PFSA ionomers and membranes with various chemical structures (e.g., side-chain length, ion-exchange capacity) in an effort to expand our understanding of CL ionomer films. In terms of bulk membranes, a key focus area is the understanding of the impact of the interface on getting water into the membrane such that the universal chemical \ mechanical energy balance for water uptake can be applied (see Figure 1). While the majority of the talk will focus on bulk membranes, the extension towards ionomer thin films that exist in the fuel-cell catalyst layer will also be made. Thin films serve as model systems for ionomer in the CL. These interfaces with the substrate will be discussed with results introduced using time-resolved, small- and wide-angle Grazing-incidence X-Ray Scattering (GISAXS/GIWAXS) and ellipsometry under different environmental conditions. Thus, one will compare the relationship shown in Figure 1 for that within the thin films. It will be shown how the film thickness and humidity affect the phase-separation and swelling behavior when the chemical structure of the ionomer is altered.

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