Effect of Confinement On Structure, Water Solubility, Water Transport and Mechanical Properties in Nafion Thin Films

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Fuel cells based on polymer electrolyte membranes (PEM) show promise as a means of energy conversion for a wide range of applications both in the transportation sector and for stationary power production due to their high charge density and low operating temperatures. Devices are assembled with multiple heterogeneous materials and failure, or performance losses, can largely occur at the interfaces between these materials. While the structure and transport of bulk PEMs for fuel cell applications have been studied extensively, there has been little effort focused on these materials at interfaces and under confinement as they exist within the membrane electrode assembly (MEA) of a working PEM fuel cell. Using a combination of neutron and x-ray reflectivity, grazing-incidence small-angle x-ray scattering (GISAXS), quartz crystal microbalance (QCM), as well as polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS) we have studied the polymer-substrate interfacial structure, thin film nano-scale structure, the swelling, and water transport behavior as a function of humidity, surface chemistry, and initial film thickness (< 220 nm). We have found the interfacial structure to be highly dependent upon the substrate surface chemistry. Moreover, when the polyelectrolyte is confined to thin films there is suppression in both swelling and water diffusivity. Specifically, we observe that the relative humidity-dependent, equilibrium swelling ratio and volumetric water fraction is constant for films above 100 nm. A clear transition in the swelling response, absorbed water content, and the diffusivity (as determined from the time-dependent PM-IRRAS signal) is observed for films thinner than 60 nm. More recently, we have used a technique developed at NIST to measure the mechanical properties of these systems. Preliminary results reveal that confinement also plays a significant role in the mechanical response of Nafion and may help in elucidating the molecular origins for the observed changes in water uptake and transport. It is speculated that these confinement affects should also have an impact on the proton conductivity and overall fuel cell performance. Our studies clearly show that the behavior of the materials under confinement can be quite different than in the bulk. Current fuel cell modeling efforts rely on bulk property values, when considering the catalyst layers and interfaces, to predict structure, transport and fuel cell performance. With this new information, researchers will be able to more accurately model the performance of the MEA within a working fuel cell which could lead to improvements in MEA design and more efficient operating conditions.