353e Sorption and Transport in Polymer Electrolyte Membranes

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The proton electrolyte membrane (PEM) plays a central role as the polymer electrolyte medium for the conduction of protons in a PEM fuel cell. Nafion®, the most common PEM developed so far, shows excellent proton conductivity, but only when soaked in water, which is the medium for proton transport. Our research efforts are focused on fundamental understanding to develop phenomenological sorption and proton transport models for PEMs, which can form the basis of improved membranes.

A thermodynamic model is developed to describe the sorption of water in Nafion® based on the Flory-Huggins activity model and an appropriate osmotic pressure correction term for the chemical potential of water within the swollen membrane. The model takes into account both of the physical and chemical equilibrium in water vapor-membrane system. The physical equilibrium, which is derived from the chemical potentials of water in the vapor and membrane phases, shows the activity of water inside of the membrane as a function of swelling pressure caused within the membrane as a result of stretching of the polymer chains upon water uptake. The chemical equilibrium is also accounted between the acid and absorbed water molecules in the membrane by dissociation and hydration of sulfonic acid group. The key variables for sorption are equivalent weight of ionomer, acid strength of the ionic groups, modulus of polymer elasticity, and interaction between water and polymer.

Continuing our modeling efforts, a comprehensive pore transport model is also developed to describe proton diffusion within Nafion® at various hydration levels by incorporating effects of water uptake and various proton transport mechanisms. In the model, the transport of protons in Nafion® is carried out via i) surface diffusion mechanism occurring close to the pore wall or under low water activity, i.e., in a layer of around 1 nm from the pore wall, and ii) bulk diffusion mechanism prevailing in the central region of the pore or under high water activity condition. In the bulk, proton diffusion is predominantly via the Grotthuss mechanism but the H3O+ ion also undergoes traditional mass diffusion, i.e., the so-called en masse diffusion. The diffusion coefficients are predicted within a general random walk framework obtained by the Einstein-Smoluchowski equation. The proton conductivity in Nafion® in contact with water vapor is, thus, accurately predicted as a function of relative humidity without any fitted parameters, and based on the our water sorption understanding. From the modeling results, it can be concluded that the proton conductivity of PEMs depends mainly on the water content and the distribution of water between surface and bulk of pore. The formation of high fraction of pore bulk water in PEMs is desirable for high conductivity because of the dominance of Grotthuss diffusion mechanism in conductivity, which occurs in bulk water rather than at the surface.