Water states and water/proton transport in nanopores of hydrated Nafion, a chosen electrolyte in polymer electrolyte membrane fuel cell, are explained using molecular dynamics (MD) aided bimodal pore-size/water-wetting model. The bimodal model is developed based on the effective Debye screening length for pore water confined by heterogeneously ionized surface, and using small-angle X-ray scattering (SAXS) measurements and existing pore-size distribution. The smaller pores (1 nm) critically confine water and promote capillary condensation (hydrophilic-like), while hindering transport. The larger pores (4 nm) delay the condensation (hydrophobic-like), while allowing bulk-like transport. In a pore network, the small pores selectively wet, while the large pores provide dominant adsorption and transport channels, a novel attribute of the bimodal model. Also, in contrast to the existing Nafion backbone-hydration model, a hydration-dependent, temperature-dependent sulfonic acid surface density is proposed.

The bimodal model succeeds in predicting the pore-water states and the transition in adsorption with capillary condensation in the large pores and negligible contribution from the small pores. These are in agreement with experiments. This transition also results in the proton conductivity jump by allowing dominant proton hopping through the larger pores in the network. The bimodal wetting describes the capillary water flow, where the small hydrophilic-like pores provide dominant flow channels, whereas water in the large pores remains immobile due to adsorption only. This water flow network results in lower liquid saturation distribution, in general agreement with the experimental results.

At elevated temperatures, it is suggested that the sulfonic acid surface site density reduces due to pore surface stretching (relaxing backbone), resulting in hydrophobicity, most pronounced in the large pores. This delays the capillary condensation and decreases adsorption, and masks the transition in proton conductivity. The pore-water state/content for optimal cell operation is also discussed.