A random pore network model is presented that illustrates water sorption of polymer electrolyte membranes (PEM), following the pressure-equilibrium mechanism proposed by Eikerling and Berg [1]. The network consists of cylindrical channels [2] which connect at nodes of vanishing volume. The main objective is to link the system dynamics and properties at the local pore level to macroscopic membrane features such as water uptake and conductivity by use of a Monte Carlo simulation.

This approach is novel in two ways. Firstly, percolation thresholds are determined and how they depend on the random distribution of surface charge densities of the nanopores which determine pore filling and swelling. Hysteresis can emerge as the membrane reaches its water sorption equilibrium from a dry or from a fully saturated state, respectively. Using efficient numerical algorithms to determine the water uptake of each pore, is an essential feature of the modeling effort.

Secondly, exact analytical expressions for hydronium and water flow inside nanopores with negatively charged walls [3] are employed to simulate charge and mass transport across the domain. This results in a linear solve for a semi-periodic domain. Operating conditions at cathode and anode enter through boundary conditions that describe protonic potential and liquid water pressure. In essence, non-equilibrium conditions are imposed onto an equilibrium membrane pore structure.

The numerical derivation of effective conductivities and water drag coefficients, and the main mechanism behind back diffusion are of primary interest and how they relate to operating conditions. The most serious challenge is to incorporate liquid pressure gradients across the membrane in a consistent manner, meaning through local swelling along individual pores.

This work aims to contribute to unraveling the main mechanism behind PEM water sorption and ion conduction. While many membrane properties (IEC, Young’s modulus, pore size and morphology) play a role in this regard, the statistical nature of the material, especially the spatial variation of these properties, and interfacial phenomena appear to be key elements.

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References