

MOLECULAR DYNAMICS AND KINETIC MONTE CARLO HYBRID APPROACH FOR EFFICIENT DYNAMICS AND PROTON CONDUCTION IN PHOSPHORIC ACID

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Proton conducting media are important materials to facilitate further the progress of efficient energy conversion systems, such as proton-exchange membrane (PEM) fuel cells. Nafion, a sulfonic acid based proton conductor, is one of the most promising and commonly used H⁺-conductors due to its high chemical stability and high proton conductivity. However, because of the hydration requirement, the operating temperature of the Nafion membranes is limited to the range from 0 to 100 °C. The operating temperature above this range is one of the ways to enhance the proton conductivity and cell performance. Therefore, H⁺-conductors with working temperature above 100 °C are urgently required to substitute water in the Nafion membranes. Phosphoric acid (boiling temperature is 213 °C) is one of the candidates that can serve that purpose, because it conducts protons even when it is anhydrous [1].

To systematically design the phosphoric acid based H⁺-conductors, one has, firstly, to accurately describe the proton conductivity in phosphoric acid. Molecular dynamics (MD) based on density functional theory (DFT) calculations is the most reliable method that can describe the proton dynamics based on the accurate DFT estimation of the energy barriers for the H⁺-hopping. However, this DFT-MD approach is very time consuming. The kinetic Monte Carlo (kMC) is one of the methods that can provide accelerated dynamics of the system, if the energy barriers for the H⁺-hopping are estimated beforehand, for example, using the DFT method. However, the drawback of the kMC approach is ability to treat only solid phases [2], not liquid. Another possible method, to have accelerated system dynamics, is the classical MD. But, with the conventional MD models it is difficult to accurately describe potential profiles for the H⁺-migration between molecules and ions. Therefore, to overcome the limitations of the MD and kMC methods, we combine classical MD and kMC methods to develop a hybrid MD-kMC model that can describe the proton conductivity in phosphoric acid. Parameters of the interatomic interaction were adopted from Yan *et al.* [3]. The energy barriers for the H⁺-hopping were initially estimated by DFT calculations and then were slightly adjusted to get better agreement with experimental values of the self-diffusion coefficients of ¹H (D_H) and ³¹P (D_P) at 100 °C [4].

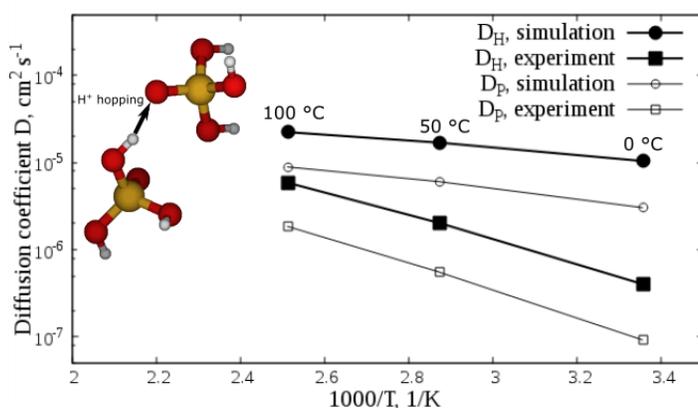


Figure 1 – D_H (filled) and D_P (open) derived from the simulation (circle) and experiment (square)

The accuracy of the developed model can be judged from Figure 1, where the self-diffusion coefficients D_H and D_P are estimated in the range of 0 - 100 °C. The absolute values of the self-diffusion coefficients are overestimated in comparison with experiment [4]. However, the value of D_H/D_P = 2.52 at 100 °C is close to the experimental value of 3.18, which proves significant contribution from the H⁺-hopping to the total diffusion of protons. In this paper we present details of the developed model, show how the model parameters affect the self-diffusion coefficients, and illustrate that this model can be easily extended for more sophisticated systems containing phosphoric acid.

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