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Molecular Dynamics Simulations of Transport Phenomena in Polymer Electrolyte Fuel Cell

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ABSTRACT Nanoscale transport phenomena in a membrane electrode assembly (MEA) of polymer electrolyte fuel cell (PEFC) is analyzed by large scale molecular dynamics (MD) simulations. Especially, the transport phenomena of proton in polymer electrolyte membrane (PEM) which has highly anisotropic water structures, oxygen permeability, oxygen scattering and proton diffusivity of ionomer in catalyst layer (CL), and scattering of oxygen molecule on ionomer were simulated, and nanoscale transport characteristics were analyzed in detail to achieve the design of new concept of MEA for next generation PEFC.

INTRODUCTION

These days new power sources instead of fossil fuel or nuclear power are getting important in our life. Fuel cell generates electricity from hydrogen and oxygen and its exhaust gas is only water. From the environmental point of view, it is expected to be a next-generation power supply system. Especially, polymer electrolyte fuel cell (PEFC) is getting under commercialization. To achieve the compact of the system and low cost of PEFC, development of high performance membrane electrode assembly (MEA) under high temperature, low humidity and low pressure is very important. Fundamental knowledge about transport phenomena in MEA is required to design high performance MEA at these conditions. Computer simulations, as well as many experimental schemes, are very effective to analyze the transport phenomena and many conventional computer simulations based on computational fluid dynamics with constitutive equations based on electrochemistry or experimental results has been performed [Wang, 2011]. However, flow fields in MEA, such as gas diffusion layer (GDL), micro porous layer (MPL), catalyst layer (CL) and polymer electrolyte membrane (PEM), are constructed by very small materials in the order of nanometer and have the same order of structure. In this region the flow field cannot be analyzed by conventional Computational Fluid Dynamics (CFD).

Molecular dynamics simulation is a powerful scheme to analyze these nanoscale transport phenomena and we have analyzed such nanoscale transport phenomena in PEFC by large scale molecular dynamics simulations. In this study, especially, the transport phenomena of proton in PEM which has highly anisotropic water structures, oxygen permeability, oxygen scattering and proton diffusivity of ionomer in CL were analyzed in detail. In the analysis of proton transfer in PEM and ionomer, we considered not only Vehicle mechanism but also Grotthus mechanism and the diffusivity of proton at various water contents was estimated.

PROTON TRANSFER IN PEM

In this study, reactive molecular dynamics simulations have been performed to study the effects of water cluster structure on proton transport properties by constructing the cluster models in the simulations. The anharmonic two-state empirical valence bond (aTS-EVB) model [Mabuchi, 2015] has been used to incorporate excess proton transport efficiently through the Grotthuss hopping mechanism. The proton transport properties have been estimated in terms of diffusion coefficient and proton distributions in the two hydrophilic cluster structures, i.e., the cylinder model and the lamellar model, that are the most typical proposed morphological models in PEMs. These systems are shown in Fig. 1. The cylindrical systems with radii from 0.5 nm to 1.7 nm and the lamellar systems with the thicknesses from 0.6 nm to 1.6 nm were constructed for the purpose of comparison. The water contents for all of the models were kept at $\lambda = 7$, where the parameter λ indicates the ratio of the number of water molecules to that of SO_3^-, which is equivalent to ~10 wt %, typical operating conditions in real PEM fuel cells. The diffusion coefficients in each dimension are calculated and correlated with the cluster size and the type of cluster models. The result is shown in Fig. 2. It is found that the proton diffusion shows the peaks in the 0.8 nm radius of the cylinder model and in the 0.9 nm thickness of the lamellar model, and decreases with increasing the cluster size. Nevertheless, the proton diffusions at any cluster size calculated in this study show the higher value than that in the random PEM model using the aTS-EVB method ($\sim 0.23 \times 10^{-5}$ cm^2/s), suggesting that the proton can be transferred effectively in the non-random cluster models. In the cylinder model with 0.8 nm radius, where the proton shows the higher diffusion, a comparatively large number of protons that are farther than the radius of the solvation shell are found in the center of cylinder, and thus the protons are freer to explore the free water region. Similarly, the more protons distribute in the surface of the lamellar model at larger thickness because the surface density of the sulfonate groups increases at larger thickness of the lamellar model. Our simulation results provide insight into quantitative information about the water cluster structure dependence of the proton transport properties at an atomic level.

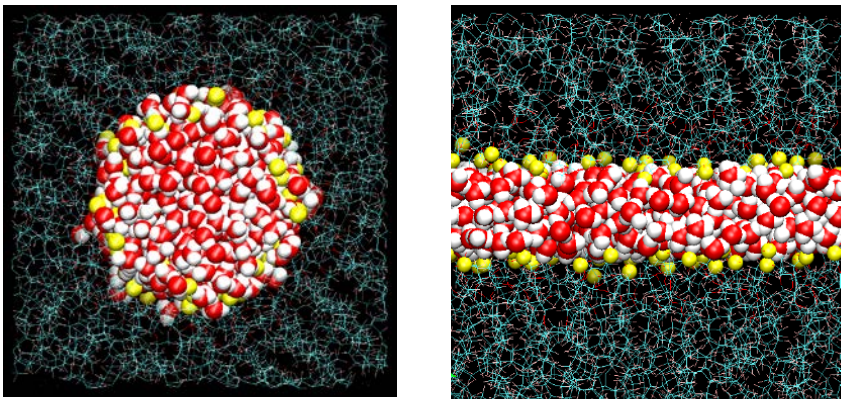

Figure 1 (Left) snapshot of the cylinder model. (Right) snapshot of the lamellar model.

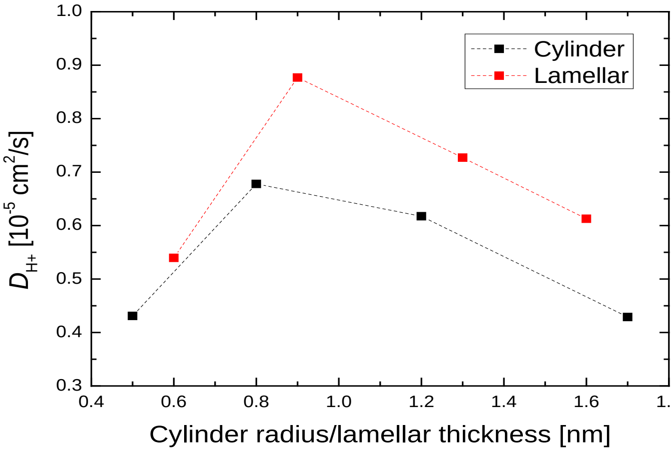

Figure 2 Proton diffusion coefficients for different water cluster models as a function of cylinder radii and lamellar thicknesses.

OXYGEN AND PROTON TRANSFER IN CL

In this research, transport phenomena of ionomer in CLs of the cathode side was simulated by MD simulation. Firstly the proton diffusivity in ionomer was investigated using MD simulations. The proton transport property was evaluated in terms of the 2 dimensional proton self-diffusion coefficient, and the morphology of Nafion ionomer thin films was evaluated in terms of the mass density distributions, the orientation of SO_3^- groups, and water cluster structures. The self-diffusion coefficient for the higher and lower hydrophobic wall is shown in Fig. 3. As shown in this figure, the self-diffusion coefficient for the higher hydrophobic wall is larger than that for the lower hydrophobic wall at any water content. Analysis of mass density distributions indicated different film morphology between the two walls, in terms of the distribution of sulfur atoms and solvent molecule. This suggests that the different self diffusion coefficient are caused by the orientation of SO_3^- groups and water cluster structures. Analysis of the orientation of SO_3^- groups indicated that, for the higher hydrophobic wall case, the SO_3^- groups in the upper side of the films become oriented in the direction to the wall with increasing water content, whereas the SO_3^- groups in the lower side of the films become oriented in the direction opposite from the wall with increasing water content. On the other hand, for the lower hydrophobic wall case, the orientational trend as observed in the higher hydrophobic case was not confirmed.

Next, we performed the oxygen permeation in the ionomer. Firstly, the density distributions were obtained to evaluate the structural properties of the ionomer. As a result, the region of the ionomer is divided into three region: ionomer/gas interface, bulk region, ionomer/Pt interface. Next, the number of permeated oxygen molecules through the ionomer was counted, and the oxygen permeability of the ionomer was estimated at different water content. The result is shown in Fig. 4. As shown in this figure, the oxygen permeability decreases with increasing water content. Gas permeability is estimated using the permeation coefficient which is obtained by the product of the diffusion coefficient and solubility coefficient of gas molecules, indicating that the diffusivity and solubility are governing factors of the permeability. Therefore, the oxygen diffusivity and solubility was evaluated to discuss the oxygen permeation mechanism in the ionomer. Consequently, the oxygen permeability decreases with increasing water content in each region, and the permeability in the ionomer/Pt interface is the smallest, which indicates that the oxygen dissolution in the ionomer/Pt interface is dominant in the oxygen permeation through the ionomer.

Finally, we analyzed the oxygen scattering phenomena on ionomer surface. Oxygen molecules were directed to the ionomer surface and the trajectory calculations were performed. The initial translational energy and incident angle were the same for all the incident molecules, but the initial position and orientation were given randomly in order to obtain the sufficient statistics. The energy transfer between oxygen molecules and the ionomer surface was evaluated by calculating between translational energy before and after the scattering. The energy distribution after scattering is shown in Fig. 5. As shown in this figure, the energy distribution obtained by MD simulation don't obey that obtained by diffuse reflection. Oxygen molecules with low incident energy tend to receive energy when they leave the

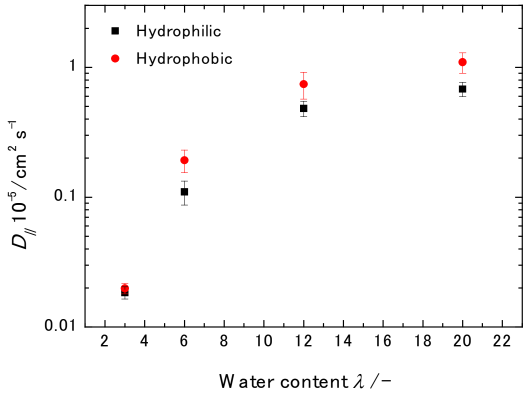

Figure 3 Diffusion coefficient of proton in ionomer.

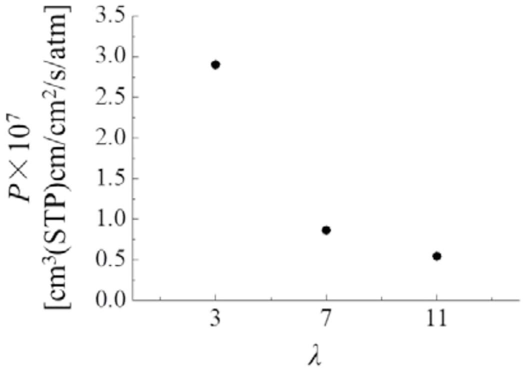

Figure 4 Oxygen permeability coefficient of ionomer at different water content.

surface after the collisions. Next, the scattering phenomena of oxygen molecules on ionomer surface was evaluated by examining the energy and angular probability distributions of scattered molecules. The energy distribution depends on the incident energy, and deviates from the distribution given by diffusive scattering model, that the incident molecules are assumed to accommodate completely with the surface. On the other hand, the scattering angle distribution is independent of the incident energy, and well-reproduced by the diffusive scattering model. These results suggest that oxygen molecules do not accommodate completely with the ionomer surface when they are reflected, however they are reflected following the diffusive scattering model because of the corrugation of the ionomer surface.

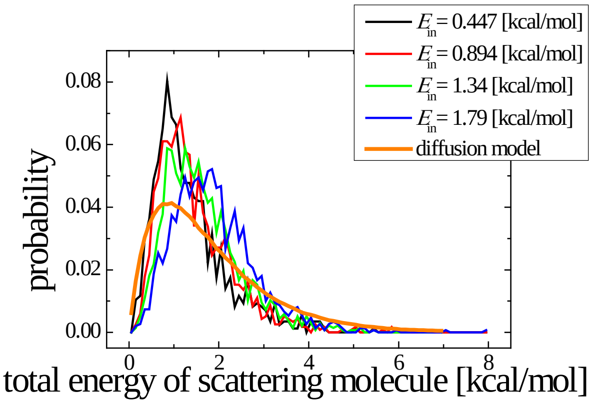

Figure 5 Energy distributions of scattereding oxygen molecules from ionomer surface forat θ_in= 60°.

CONCLUDING REMARKS

We performed large scale molecular dynamics simulations to analyze the nanoscale transport phenomena of materials in MEA of PEFC. Especially, he transport phenomena of proton in polymer electrolyte membrane (PEM) which has highly anisotropic water structures, oxygen permeability, oxygen scattering and proton diffusivity of ionomer in catalyst layer (CL) were simulated. From the results of this simulation we have obtained the knowledge about the nanoscale flow phenomena of proton, oxygen and water, which is difficult to analyze from the results by experiment. The knowledge helps us to design the new concept of MEA for higher efficiency and lower cost of PEFC in the future.

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