

Molecular Dynamics Study of Oxygen Permeation of Ionomer of Hydrocarbon

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INTRODUCTION

Polymer electrolyte fuel cell (PEFC) is focused worldwide as the energy conversion device for next generation. In particular, PEFC is the practical use in terms of high theoretical efficiency and applying various things such as automobile, portable devices, and stationary power generators. However, PEFC is not widespread in general because an actual power generation efficiency is lower than a theoretical power generation efficiency. PEFC is composed of membrane electrode assemblies (MEAs) that consist of a polymer electrolyte membrane (PEM), catalyst layers (CLs), microporous layers (MPLs), and gas diffusion layers (GDLs). In CLs, Pt catalyst is the particle which diameter is 3 ~ 4 nm and it is on a supported carbon. In addition, it is covered with an ionomer because of proton transfer to catalyst surface. The ionomer improves ability of proton transfer but it reduces oxygen permeability to Pt surface and therefore dissociative adsorption reaction becomes slow. It is necessary to research the oxygen permeation and proton transfer in such a situation to raise its efficiency. However, it is difficult to analyze by macroscopic experiment because these phenomena occur in the microscopic structure. For this reason, it is necessary to analyze the oxygen permeation and the proton transfer at the microscopic point of view.

In this research, we constructed the system of ionomer including hydrocarbon membrane, water molecule, oxonium ion and platinum surface by using molecular dynamics study, and researched about the effect of the water content of the ionomer on the structure of the ionomer and oxygen permeability.

METHOD

In this research, we simulated the system of CLs of the cathode side by molecular dynamics simulation. This system includes Pt wall, hydrocarbon membrane, water, oxonium ion and oxygen molecule.

Pt-Pt interactions were represented by spring mass model considering nearest neighbor atom. Hydrocarbon was represented by the flexible model which interaction was expressed by bond, angle, torsion, van der Waals, and coulomb potential. The F3C model [1] was adopted for water, and for oxonium ion, we selected similar model with four point charges. The Morse potential was used for intramolecular potential of oxygen molecule. The intermolecular potentials between hydrocarbon and water, hydrocarbon and oxonium ion were represented by Lennard Jones (LJ) potential and coulomb interaction. The interaction between Pt and water was represented by Spohr and Heinzinger potential [2] and that between Pt and oxonium ion was represented by the potential that the number of hydrogen atoms changes from two to three. The intermolecular potentials between oxygen and water, oxygen and oxonium ion were represented by LJ potential and Morse potential. The others were connected by LJ potential but the interaction between Pt-O₂ was not considered because we assumed all permeated oxygen

dissociated at Pt surface and this reaction speed was faster than oxygen dissolution or diffusion. We allowed oxygen molecules to pass through Pt surface and permeated oxygen were returned to gas space.

In this calculation, the platinum surface was placed at the bottom of simulation box and ionomer which was composed of hydrated hydrocarbon molecules were placed on the surface. The number of oxygen molecule was set at the number that is in the gas space corresponds to 1MPa. The number of oxygen in the gas space was constant to keep the pressure in the gas space constant and permeated molecules were returned to gas space. By this procedure, we made the constant oxygen mass flux in the ionomer.

RESULT AND DISCUSSION

Density distribution of hydrocarbon and liquid along z direction are shown in Fig. 1. From upper side, the density distribution of (1) hydrocarbon molecule and (2) water and oxonium ion distribution in case of water content $\lambda=3,7,11$, respectively. From Fig. 1(1), it is said that the hydrocarbon gathers toward the catalyst surface. This phenomenon occurs because Pt strongly attracts the other molecules. From Fig. 2(2), many water molecules distribute on high density hydrocarbon which are attracted by Pt. The density of water molecules on Pt surface is very low. From Fig. 2(1) and (2), hydrocarbon molecules absorb Pt surface stronger than water molecule. In the future, we will analyze oxygen permeation by using this system.

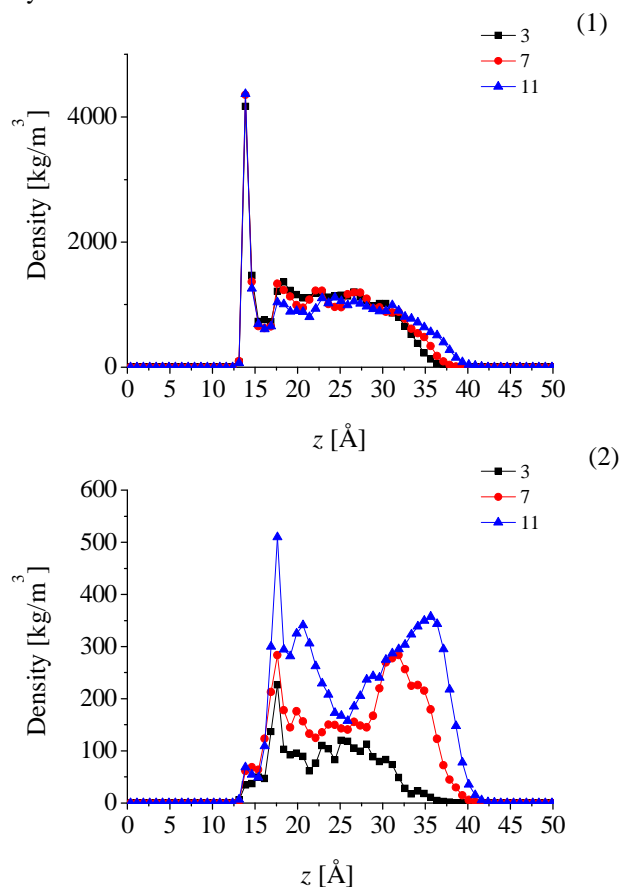


Fig. 1 Density distribution of (1)hydrocarbon molecule, (2)water and oxonium ion along z direction

REFERENCES

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