Electrical property of a sulfuric acid-water mixture from the first-principles molecular dynamics simulation

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Abstract

The electrical property of aqueous sulfuric acid has been studied by the first-principles molecular dynamics simulation. The calculated conductivity of aqueous sulfuric acid solution from our simulation is 0.33 S/cm, which agrees reasonably with an experimental value. This implies the applicability of the method used in this study for electrochemical systems.

Key words: first-principles molecular dynamics; aqueous sulfuric acid; proton transfer

1. Introduction

Nafion is commonly used as a membrane for hydrogen and methanol fuel cells. It is composed of sulfonic acid terminated perfluorovinyl ether side chain connected to a perfluorinated backbone. It is believed that the sulfonic group side chain is responsible for the proton transfer. To understand the proton transfer in Nafion at the atomistic level, a detailed computer simulation is necessary. Because classical force field simulations have an inherent difficulty on the description of bond-breaking and forming, the use of first-principles technique is desirable.[1] However, there are problems to be solved for the first-principles simulations of the proton transfer in Nafion. First, the first-principles simulation for Nafion membrane requires a lot of computational resources. In the present study, this problem has been partially resolved by using adaptive finite element basis, which proved to give a good parallel efficiency, and the use of massively parallel computers.

Second, to faithfully mimic the electrochemical system, the first-principles simulation should be able to treat the effects of an electric field. Thus, we have implemented a function to carry out first-principles molecular dynamics under a homogeneous electric field, following the method suggested by Umari *et. al*, [2] in our own DFT code *FEMTECK* (Finite Element Method based Total Energy Calculation Kit). However, the utility of the methods should be investigated for reliable model systems because, to the best of our knowledge, such a method have not been applied to the problem of proton transfer so far. Especially, we wish to know that such a simulation can reproduce electrical properties such as conductivity because conductivity is important in electrochemistry. The model system should have accumulated experimental data for comparison. In this respect, a sulfuric acid-water mixture can be regarded as a very good model system for the proton transfer simulations of Nafion. Thus, the purpose of this contribution is to check the utility of the present implementation of first-principles molecular dynamics method under an electric field. As addressed, our primary concern is to compare the electric conductivity of aqueous sulfuric acid evaluated from theory

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to an experimental one.

2. Computational Details

A simulation cell is composed of 12 H_2SO_4 and 36 H_2O in a cubic box of length 12.52Å imposing the periodic boundary condition. A homogeneous electric field of 1.03 V/nm in the x-direction was applied to the system. We used PBE functionals for electronic structure calculations. The separable norm-conserving pseudopotentials were employed, and only the Γ point was used to sample the Brillouin zone. As for the basis set, the adaptive finite-element method, was used in place of the ordinary plane waves. All production runs in the present paper were performed with an average cutoff energy of 40 Ry. All hydrogen atoms in the system were given the mass of deuterium to allow the use of a large time step of 1.21 fs in the production run. Statistics were collected during the production run of 13.76 ps at an average temperature of 311.1K. All the first-principles Born-Oppenheimer MD calculations were carried out with our own code *FEMTECK*.
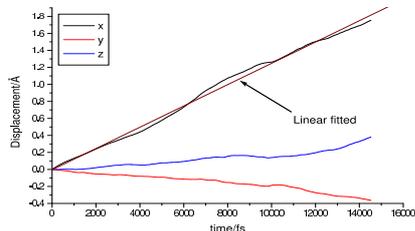
3. Results and Discussions

Fig. 1. Plot of displacement vs. time of protons.

Fig. 1 shows the displacement of protons as a function of time. As seen in the figure, the displacement of protons is very large in the x-direction, which is a consequence of the strong electric field applied to the x-direction. Since electric conductivity can be evaluated from the mobility of ions, we first calculate the mobility of protons from the results of first-principles simulation. By definition the mobility (u) of ions is expressed by;

$$u = s/E$$

where s is the velocity of ions and E is an electric field. The average velocity can be evaluated easily from the data shown in Fig. 1. Physically, the slope of the linear fitted line denotes the average velocity of protons. Division of the slope by the applied field yields the mobility of protons. In the present simulation, the mobility of protons is calculated to be $36.5 \times 10^{-5} \text{cm}^2/\text{sV}$.

From the mobility data, it is now possible to calculate the conductivity (κ) of the protons using the following relation;

$$\kappa = zucF$$

where z is the charge of an ion, u is the mobility of an ion, c is the concentration of an ion and F is the Faraday constant.

The conductivity of protons using the above relation is calculated to be 0.30 S/cm. Addition of the calculated conductivity of anion counterpart to the conductivity of protons yields the conductivity of aqueous sulfuric acid solution, 0.33 S/cm. An experimental value at our simulation conditions is 0.40 S/cm.[3] The calculated conductivity slightly underestimates the experimental value but would be acceptable. This implies that the method employed here is applicable to the simulation of the proton transfer in a polymer electrolyte membrane at the fuel cell operating conditions.

4. Summary

We have carried out the first-principles molecular dynamic simulations for aqueous sulfuric acid including the effect of an external electric field. The calculated conductivity agrees reasonably with the experimental value. The method employed in the present contribution, thus, is expected to be applicable to the electrochemical systems. Indeed, such a study is now ongoing in our laboratory and results will be reported elsewhere.

Acknowledgements

References

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