doi:10.1246/cl.2010.736

Theoretical Studies of the Mechanism of Proton Transfer at the Surface of Zirconium Phosphate

Takaya Ogawa,[1] Hiroshi Ushiyama,*[1] Koichi Yamashita,[1] Ju-Myeung Lee,[2] and Takeo Yamaguchi[2]
[1]*Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656*
[2]*Chemical Resources Laboratory, Tokyo Institute of Technology,*
R1-17, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503

(Received April 20, 2010; CL-100382; E-mail: ushiyama@chemsys.t.u-tokyo.ac.jp)

The mechanism of proton transfer on the surface of zirconium phosphate monohydrate, α-$Zr(HPO_4)_2 \cdot H_2O$ (ZrP), has been first investigated by quantum chemistry calculation. The reaction paths and the activation energies along the paths are examined, and the effects of ZrP surface and phosphate groups on the proton conductivity are discussed.

The development of proton conductivity of polymer electrolyte membrane fuel cells (PEFC) is desired significantly. In order to improve the proton conductivity at high temperature and low humidity, inorganic grains are blended with electrolyte in PEFC. The zirconium phosphate monohydrate, α-$Zr(HPO_4)_2 \cdot H_2O$ (ZrP), is one of the inorganic grains which are attracting great interest and has been examined experimentally in detail.[1] Recently, Anilkumar finely blended ZrP to sulfonated poly(ether sulfone) (SPES), and this composite shows higher proton conductivity than only SPES or ZrP at high temperature and low humidity.[2] Thus, the organic–inorganic interface is thought to cause this high proton conductivity. ZrP has phosphate groups at the surface with high density, and this structure is also thought to lead to high conductivity. However, the mechanism of the high surface conductivity of ZrP has never been clarified. In addition, acid groups, such as phosphate, are generally believed to contribute to high conductivity as a proton donor, but the role of the acid group for the organic–inorganic interface has never been clearly explained. The aim of this letter is to clarify the roles of organic–inorganic interface and acid groups on high proton conductivity by examining proton transfer on ZrP surface with ab initio quantum chemistry.

ZrP is a layered-structure material and a single layer is used as a surface model of ZrP. The effects of the other layer on the adsorption energy of water molecules have been also calculated. However, the effect of the other layer can be negligible. ZrP surface is modeled by a supercell that contains ZrP monolayer and a vacuum region of 40 Å. The size of a unit cell is 9.1 Å × 5.3 Å × 66.0 Å which includes two Zr atoms, sixteen O atoms, and four phosphate groups.

Density functional theory (DFT) calculations are performed with RPBE functional through this letter. Single Kleinman–Bylander projectors are used to represent each angular momentum channel,[3] and relativistic polarized calculations are used to estimate the effect of spin. A double-z split-valence basis set with polarization orbitals (DZP) is used.[4] Norm-conserving pseudopotentials are applied using the improved Troullier–Martins method with nonlinear core corrections.[5,6] The structure of ZrP surface model is optimized with periodic boundary condition with 2 × 2 × 1 k-grid sampling. All the calculations are performed with the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA)-2.0.1 package.[5]

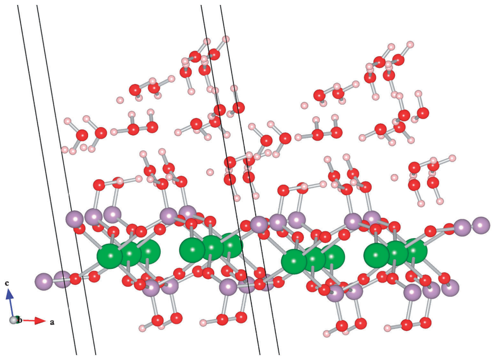

Figure 1. An example of modeling water-adsorbed ZrP surfaces system. Oxygen, hydrogen, phosphorous, and zirconium are shown in red, white, purple, and green, respectively.

We prepared five water-adsorbed ZrP surface systems. One of the examples of water-adsorbed ZrP surfaces is shown in Figure 1. Five water molecules are assigned to one phosphate group. The mechanism of proton transfer on ZrP is supposed to be the Grotthuss mechanism in which proton transfer takes place through the cleavage/formation of a hydrogen-bond network, and the transition states and minimum energy paths are obtained by the nudged elastic band (NEB) method.[7] The above method was applied to all hydrogen bonds in the prepared five water-adsorbed ZrP surface and three bulk water systems. Because some of paths include "concerted proton transfer" in which several proton transfers take place concertedly along one proton-transfer path, and then 76 proton-transfer paths including 298 proton-transfer events were obtained. Three water bulk systems with the weight density of $1\,[\mathrm{g\,cm^{-3}}]$ were also prepared to compare the mechanism of proton transfers on ZrP with that in bulk water.

We first examined the effect of strong interaction on the O–O distances between oxygen atoms that donate or accept protons. The O–O distances between water and water or POH on ZrP surfaces are classified into four groups, and the O–O distances in each group are examined as follows (Here we define "the bound water" as water which is bound by hydrogen bond from POH).

Group D1: Both oxygen atoms comprise the water molecules, which are not affected by POH in the ZrP system as shown $H_2O.1$ and $H_2O.2$ in Figure 2.

Group D2: One of the oxygen atoms comprises bound water and the other comprises the water, which is not affected by

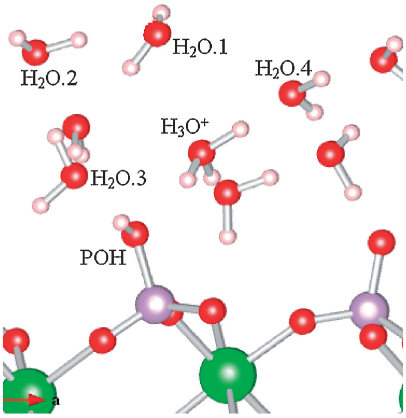

Figure 2. The atoms and molecules are labeled for classification of the hydrogen bonds.

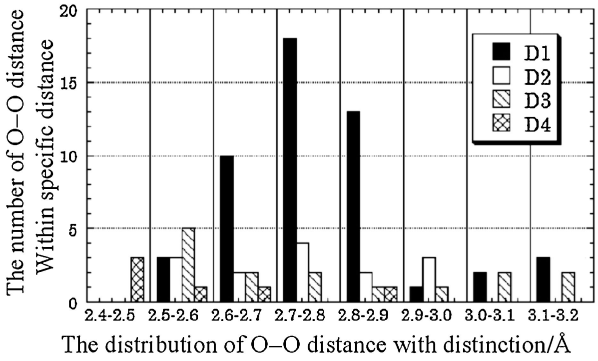

Figure 3. The distribution of the classified O–O distances.

hydrogen bond from POH in the ZrP system, for example, H_2O.2 and H_2O.3 in Figure 2.

Group D3: Both oxygen atoms comprise the POH or bound water in the ZrP system, H_2O.3 and POH in Figure 2.

Group D4: Either of two oxygen atoms composes H_3O^+ in the ZrP system such as H_3O^+ and H_2O.4 in Figure 2.

The histograms of the O–O distance distribution in each group are shown in Figure 3. The peak of distribution in group D1 is around 2.7–2.8 Å corresponding to radial distribution function of water bulk systems. This fact suggests water molecules in group D1 are not affected by the phosphate groups. The peaks of groups D2, D3, and D4, which are affected by the phosphate groups are shorter than 2.6 Å. It should be noted that the O–O distances in water located on the ZrP surface is shorter than that in bulk water. Water molecules in the groups D2 and D3 are located near surface and then make a strong hydrogen bond network between water molecules and the phosphate groups. It is also shown that the O–O distance of group D4 is much shorter than that of other groups, and this indicates that H_3O^+ makes O–O distances shorter. These results clearly show that the strong interaction between water and phosphate group causes the strong hydrogen-bond network.

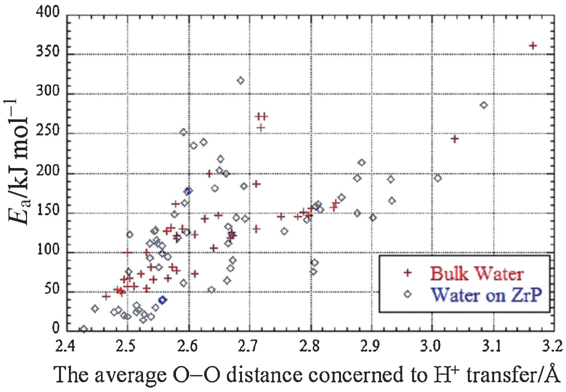

Figure 4. The activation energies are shown as functions of the O–O distance with proton transfer between them at the transition state.

The strong hydrogen-bond network can make the activation energy of proton transfer low. To see the effects of the strong hydrogen-bond network on the activation energies, the activation energies along the proton-transfer paths are shown as functions of the average O–O distance at the transition state in Figure 4. Figure 4 shows the activation energies are decreasing as the O–O distances become shorter. We consider that the strong interaction of ZrP and water molecules makes the hydrogen-bond network strong and then O–O distance becomes shorter than bulk water. As a result, the activation energy becomes lower than that of bulk water. These shorter distances can be considered to result from phosphate groups and high density of phosphate group on ZrP surface.

In summary, it has been first shown that phosphate groups contribute to high conductivity not only by proton donation but also making strong hydrogen-bond network on ZrP surfaces. These strong hydrogen-bond networks and sufficient size and number of phosphate groups on ZrP surfaces can make O–O distance shorter on the surface and is important to improve proton conductivity at the organic–inorganic interface of electrolyte. We believe that our findings in this letter can be a basic concept to understand the high proton conductivity at the organic–inorganic interface.

Reference

1 G. Alberti, M. Casciola, U. Costantino, R. Vivani, *Adv. Mater.* **1996**, *8*, 291.
2 G. M. Anilkumar, S. Nakazawa, T. Okubo, T. Yamaguchi, *Electrochem. Commun.* **2006**, *8*, 133.
3 L. Kleinman, D. M. Bylander, *Phys. Rev. Lett.* **1982**, *48*, 1425.
4 J. Junquera, Ó. Paz, D. Sánchez-Portal, E. Artacho, *Phys. Rev. B* **2001**, *64*, 235111.
5 N. Troullier, J. L. Martins, *Phys. Rev. B* **1991**, *43*, 1993.
6 N. Troullier, J. L. Martins, *Phys. Rev. B* **1991**, *43*, 8861.
7 N. González-García, J. Pu, A. González-Lafont, J. M. Lluch, D. G. Truhlar, *J. Chem. Theory Comput.* **2006**, *2*, 895.