Proton Polarizability on Pt Surface with Water Molecules

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ABSTRACT

We present theoretical studies of proton polarizability in the fuel cell system by the first-principles calculations based on the density functional theory for two model systems of a hydrogen on Pt surfaces with water molecules. We firstly discuss a hydrogen adatom at a hollow site on a Pt(100) surface with a water molecule by the supercell slab and Pt_{13} systems. The proton polarizability is investigated for a hydrogen adatom in a Pt(111)-(√3×√3)R30° surface with a water bilayer.

Keywords: DFT, Proton, Pt, Water

1 Introduction

Fuel cells with proton exchange membranes are actively studied to be used as electric cells in automobiles, mobile devices, and so on. Hydrogen molecules incoming into the hydrogen fuel cell as active material are dissociated to protons to oxidize on a carbon anode, due to catalytic effect of platinum clusters in the anode. The protons are transported to a cathode through the membrane. However, in microscopic view, it is not properly understood where protons are produced and what chemical processes are related with proton generation.

A proton in a bulk water exists into such a form as a hydronium ion; it is not at all isolated from electron cloud and weakly bonded with water molecules. The proton transfer is considered to occur via sequences of hydrogen-hopping from inside a hydronium ion to a neighbor water molecule [1]–[3].

Single water molecule is adsorbed at a top site on some metal surfaces, whose oxygen is oriented to the surface [4]–[6]. In vacuum, water molecules are formed into an ice-like structure on the surface at a low temperature. On the Pt(111) surface, water molecules can be formed into an ordered water-bilayer (WBL) [4], [5], [7]. Theoretical studies found that, in a interface between a liquid-water and the Ag and Cu surfaces, the molecules of the first water overlay are also adsorbed on top sites and a layered water-structure is constructed on the surfaces [8]–[10].

Molecular hydrogens are dissociated on Pt(100) [11], [12] and Pt(111) surfaces [13]–[16]. Therefore, the induced hydrogen molecules would be dissociated in the system of the Pt cluster with water molecules.

The first-principles study of hydrogen adsorbed between platinum and oxygen atoms in a Pt_{13} cluster with a water molecule have been done by Watari et. al. [17]. We study a proton on a Pt surface with water molecules with the first-principles calculations on the density functional theory (DFT) with the generalized gradient approximation and pseudopotentials by the scheme expressing wavefunctions with the linear combination of atomic orbitals.

2 Computational Details

2.1 Models

We use two models of a hydrogen adatom on Pt surfaces with water molecules. The first model is related to a Pt(100) surface. The clean Pt(100) surface can have the hexagonal topmost layer [18], but the hexagonal reconstruction is not considered in our model because it is disappeared upon the hydrogen adsorption [19]. Hydrogen atoms are disorderly adsorbed on the Pt(100) surface [19]. The model is constructed as comparable with the Pt_{13} cluster with fixed geometrical configuration of a water molecule. In the model, a water molecule is adsorbed on the hollow site on the Pt(100) surface, whose oxygen is oriented to metal surface. The bond axes of the water molecule are kept fixed on the (010) plane. In the other model, a hydrogen atom is placed between the Pt(111) surface and the WBL. The unit cell of the model system is (√3×√3)R30°, which is the same as the WBL-covered Pt(111) surface.

2.2 Methodology

We express wavefunctions with numerical atomic orbitals (NAO) to calculate electronic ground state of the model system within the DFT pseudopotential method. The NAO basis set used is composed of double-zeta numerical orbitals plus polarization functions. Each orbital is expanded in a basis set of plane waves with kinetic energy up to a cutoff value and expressed in the Fourier space. The maximum cutoff energy is 50 Ry. We generated pseudopotentials for hydrogen, oxygen, and only d-channel of platinum with using Rappe’s optimized scheme [20], and for other channels of platinum.
by using the Troullier and Martins method [21]. The exchange and correlation effects are expressed by employing the Perdew and Wang energy functional with the generalized gradient correction [22, 23]. The Pt(100) and Pt(111) surface is modeled by a periodic supercell with a slab separated by a vacuum region with a width of 14 and 16 Å, respectively. Therefore, the vacuum region for the systems with the water molecules and the hydrogen atom is greater than 10 Å, which is enough to prevent interactions between neighboring slabs. The lattice constant of the slab was fixed at calculated bulk lattice constant of 4.05 Å, which is in good agreement with the experimental value of 3.92 Å. A hydrogen atom and water molecules were placed on one side of the slab for surface unit cell, with the dipole interaction correction scheme for the repeated slab model calculation which makes it feasible to treat surface chemisorption problem [24]. In the Pt(001) system, Surface unit cells of c(2 × 2), c(4 × 4), and c(6 × 6) are used for water and hydrogen coverages of 1/3, 1/6, and 1/8 monolayer, respectively. A slab of the c(2 × 2) cell has five-layer thickness, while a slab of the c(6 × 6) cell has three-layer thickness. In the Pt(111) system, since the adsorbed hydrogen atom (Had) is one per (\sqrt{3}×\sqrt{3})R30° surface unit cell, the Had coverage is 1/3 monolayer. The Pt(111) slab is employed with three-layer thickness. The surface Brillouin zones are integrated with Monkhorst-Pack meshes of 4×4×1 for the Pt(100)-c(2 × 2), 2×2×1 for the Pt(100)-c(4 × 4) and c(6 × 6), and 6×6×1 for the Pt(111)-(\sqrt{3}×\sqrt{3})R30° [25]. The cold smearing method is used with the broadening width of 0.3 eV for the Fermi-level smearing [26]. The Pt slab is kept fixed at the bulk distance. We firstly optimized hydrogen and oxygen positions for the H2O/Pt(100)-c(2 × 2) system and the WBL-covered Pt(111) surface. The Had in the WBL-covered Pt(111) surface is also optimized together with relaxing hydrogen and oxygen atoms. In the H2O/H/Pt(100) systems, the water molecule is kept fixed at the geometry of the H2O/Pt(100)-c(2 × 2) system.

3 Results

3.1 H/Pt(001) with A Water Molecule

The calculated equilibrium height of the oxygen atom in the water molecule from the Pt(100) surface was 2.1 Å in the c(2 × 2) unit cell. In the total energy calculations of the H2O/H/Pt(100) system, the water molecule was at the equilibrium position of the water molecule on the Pt(100)-c(2 × 2) surface. Figure 1 shows those total energy curves versus the Had height from the surface. The Had isolated from the water molecule is adsorbed at height of 0.10 Å on the surface, while the bond length between the Had and the fixed oxygen atoms is 1.1 Å in the metastable hydronium-ion form.

Figure 1: Total energy curves for the Had between the fixed water molecule and the Pt(001) surface. The solid line shows bare total energy of the c(6 × 6) supercell calculation, while the dashed line shows modified total energy by subtracting lateral dipole-dipole interaction energy on the 2-dimensional super-lattice. The Had position is measured from the topmost layer of the Pt(001) surface to the vacuum. The energy zero is set to modified total energy of the stable state. The insertion shows modified total energies for the c(2 × 2), c(4 × 4), c(6 × 6) supercells.

Figure 2: Local density of state for the Had between the fixed water molecule and the Pt(001) surface. The energy zero is set to each Fermi level. The insertion is local density of state for the Had between the fixed water molecule and the Pt13 cluster. R(H) is the distance between the Had position and the cluster center. When R(H) is 3.6 a.u., the hydrogen atom is on the octahedral face, which is corresponding to the Pt(100) surface.
Figure 2 shows the LDOS for the s-component of the $H_{ad}$ at the stable, transition, metastable, and hydronium-ion states. The largest peak in each LDOS is due to intrinsic 1s state of hydrogen. In the stable state, the hydrogen 1s orbital is hybridized with the platinum 5d orbitals, and then hybridized states are constructed above the energy of the intrinsic 1s state. In the transition state, there are no significant hybridized states directly above the 1s state as appearing in the stable state, while a hydrogen LDOS peak at 22.5 eV is due to hybridizing with the oxygen 2s state. In the metastable state, the energy levels of the hydrogen 1s and oxygen 2s states are slightly lower than those in the transition state. In the hydronium-ion state, the hydrogen 1s orbital is more strongly hybridized with the oxygen 2s orbital than other states.

We calculated the atomic charge by the Mulliken population analysis. The charge of the metastable hydronium ion on the $c(6 \times 6)$ surface is +0.16 e. (Note that e is the elementary charge.) When the hydrogen-oxygen bond is 0.92 Å, the hydronium ion charge is +0.48 e, which fairly close to the value of the cluster model, +0.52 e. The change of the hydronium ion charge is found to be induced only by that of the $H_{ad}$. The hydrogen charge is -0.58 e as chemisorbed on the surface, and is neutral at the height from the surface layer of 1.1 Å. The total water charge, however, is kept around +0.3 e irrespective of the $H_{ad}$ position.

In the insertion of Figure 1, we also show energy curves for the $H_2O/H/Pt(100)$ systems with $c(2 \times 2)$ and $c(4 \times 4)$ supercells. The metastable state was disappeared in the two smaller supercells which is considered to be due to lateral Coulomb interaction on the surface super-lattice. This problem was not resolved by the crude correction of the lateral dipole-dipole interaction, as shown in Figure 1.

The electron density of the metastable state, as shown in Figure 3(b), shows large proton polarizability, while one of the stable states is slightly polarized in inverse, as shown in Figure 3(a). Proton polarizability in the hydronium-ion-like state is similar to one of the metastable state but electrons are transferred to the Pt surface, as shown in Figure 3(c).

### 3.2 H/Pt(111) with A Water-Bilayer

The equilibrium geometry of the WBL on the Pt(111) surface is indicated as a ball model in the Figure 4(d), which agrees with a theoretical study of Ref. [7]. Its electron density is shown in Figure 4(a). We calculated geometries and energies for hydrogen adsorbed at top-sites at center of WBL-hole and under the oxygen in the FLW molecule (UOFLW). The geometries are indicated in the (112) cross-section with electron densities as shown in Figures 4(b) and 4(c). While the WBL structure was not varied by the WBL-hole adsorption, as

Figure 3: Electron-density differences as $\rho_{SCF} - \rho_{atom}$ of (a) the stable, (b) the metastable, and (c) the hydronium-ion like states of the $c(6 \times 6)$ $H_2O/H/Pt(001)$ model system on the (100) plane with bond axes of the adsorbed water molecule are shown as contour graphics. $\rho_{SCF}$ is the self-consistent-field electron density, whereas $\rho_{atom}$ is the superimposition of the atomic electron-densities. Solid lines express positive values, and dotted lines do negative. Contour values are $\pm 0.001 \times 2^n e/\AA^3$, where $n$ is positive integer. Solid circles, squares, and triangles are located at the nucleus positions of Pt, O, and H, respectively.

Figure 4: Electron-density differences as $\rho_{SCF} - \rho_{atom}$ of the (a) Pt(111) with a water-bilayer (WBL), and hydrogen-adsorbed WBL-covered-Pt(111) surfaces at the top sites (b) at the center of the WBL-hole and (c) under the oxygen in the first-layer-water (FLW) molecule, on the (112) plane with bond axes of a second-layer-water (SLW) molecule and a $H_{ad}$-Pt bond axis, are shown as contour graphics. Details of those graphics are the same as in Figure 3. A ball-model of the WBL-covered Pt(111) surface is shown in the panel (d). The Pt, O, H atoms are indicated as the large, middle, and small spheres, respectively.
a result of the UOFLW adsorption the FLW molecule was lifted up, and the SFW molecule was rotated on the (112) plane with lifting the oxygen in its molecule. In other words, the added hydrogen-bond between the H_{ad} and the FLW oxygen induces reconstruction of the WBL hydrogen-bond-network. The adsorption energies are calculated by \( E[\frac{1}{2}H_2] + E[WBL/\text{Pt}(111)] - E[WBL/H/\text{Pt}(111)] \). The WBL-hole adsorption-energy is 114 meV, while the UOFLW one is 278 meV, which is close to the activation energy of the H_{2}O/H/\text{Pt}(100) system when the H_{ad} transferring from the stable to the metastable states, 276 meV.

By the Mulliken population analysis, we estimated the atomic charges of the Pt(111) systems. The H_{ad} is almost neutral; -0.04 and -0.08 e for the WBL-hole and the UOFLW adsorptions, respectively. This would be due to the close-packed atomic structure of the Pt(111) surface.

4 Summary And Discussion

The hydrogen LDOS’s of the supercell-slab model, as shown in Figure 2, agree well with ones of the cluster mode as shown in the insertion in Figure 2 [17]. The shift of the hydrogen 1s state can be interpreted in the term of the hydrogen charge. Because the hydrogen atom negatively ionizes in the stable state, the 1s energy level is upward shifted, whereas the energy level of the hydronium-ion-like state is downward shifted because it positively ionizes.

In the Pt_{13} cluster calculation, we can change total electron number of the H_{2}O/H/\text{Pt}_{13}. We found that the \([H_{2}O/H/\text{Pt}_{13}]^{+}\) system can discharge an electron from the Pt cluster almost without change of the hydronium-ion charge [17]. The hydronium-ion-like state of the supercell-slab model would be able to discharge an electron from the Pt surface in much the same way.

We consider that the metastable state is a precursor state before forming hydronium ion. If the H_{ad}'s are energetic (hot) atoms, which are produced in the dissociation process of incident hydrogen molecules, as described in Ref. [27], the hot hydrogen atoms would be able to migrate to the precursor state.

We studied the proton polarizability on the Pt surface with water molecules after dissociating hydrogen molecules. The proton polarizability in our present H_{2}O/\text{Pt}(100) system is increased by the H_{ad} migration to a precursor state. Therefore, in the WBL-covered Pt(111) system, the same phenomenon would occur.

Although the adiabatic energy surface of the H_{2}O/H/\text{Pt}(100) system with respect to the H_{ad} position showed that the hydronium ion should be formed by the possible hot-hydrogen-atoms.

REFERENCES