

OH adsorptions and water dissociation in water-bilayer on Pt(322) stepped surface: *Ab-initio* simulations

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Introduction

The oxygen reduction reaction (ORR) is the bottleneck of conventional fuel cells. The reaction seems simple enough. Adding four protons and electrons to oxygen on Pt electrode, water is obtained. Unfortunately, the reaction has a relatively high overpotential; that is, more energy is required to drive the reaction in practice than that predicted by thermodynamics. Moreover, even the mechanism of the reaction is not well understood. Therefore enhancement of the catalytic activity for the ORR is one of the most important subjects in the field of fuel cell. It has been reported that the reaction rate and the selectivity of an electrochemical reaction strongly depend on the surface structure of the electrode [1] [2]. Thus, the purpose of this study is to clarify the relationship between ORR and Pt step surface by means of first-principles molecular dynamics (FPMD).

Materials and Methods

Density-functional theory (DFT) calculations are performed to study the energetics of only a hydroxyl adsorption and one in H-up water bilayer (WB) on Pt(322) with stepped structure as a first step of the ORR mechanism in fuel cells before FPMD. In the case of one in WB, we investigate adsorption energies of OH molecules in sequentially subtracting an H atom up to 1/5 of water-coverage in WB on surface. We consider two different adsorption site, bridge-site and ontop-site, on each upper and lower step of Pt slab model and three different site, FCC-, HCP- and ontop-site, on surface terrace. Next, we perform the FPMD to investigate a behavior of water on Pt(111)- $3 \times 2\sqrt{3}$ flat surface and Pt(322)- $3 \times \sqrt{17}$ stepped surface w/ and w/o initial OH adsorptions, respectively.

The plane-wave pseudo-potential method as implemented in the STATE-senri package is used throughout the calculations. The PBE-GGA is employed for the exchange-correlation functional. A kinetic-energy cutoff of 25 Ry and charge density cutoff of 225 Ry are used for the smooth part of the electronic wave functions and the augmented electron density, respectively. Brillouin zone integration is done using a Monkhorst-Pack k -point grid (shifted at the Γ point) of $2 \times 2 \times 1$ throughout the calculations. All the atomic positions are relaxed until the maximum absolute value of the force vectors for all components is smaller than 1×10^{-3} Ha/a.u. $3 \times \sqrt{17}$ super-cell including 3 Pt layers with 48 atoms and 10 H₂O molecules with a vacuum region of ~ 12 Å is employed. Effective screening medium (ESM) method is adopted to simulate the metal/water interface. The ESM enables us to model the polarized surface without dipole correction.

Results and Discussion

As a result, in the case of only a hydroxyl adsorption on Pt stepped surface, the OH molecule prefers to adsorb at bridge-site on upper step of Pt stepped structure. This behavior is in good agreement with DFT study [3]. On the other hand, in the case of 1 OH introduction in WB on the Pt stepped surface, OH molecule prefers to adsorb at ontop-site on upper step site with keeping water bilayer network. Furthermore H₂O molecule on lower step tends to form H-down configuration. In the case of 2 OH introduction, we find that the second OH adsorption energy on the step structure is comparable to one on the terrace. Finally, in case of 3 OH introduction, the third OH molecule adsorption at the ontop-site on upper step of Pt(322) with a step structure is the most stable due to the hydrogen bonding network. Regarding the FPMD, we find that a H₂O dissociation and an adsorption of an OH molecule on stepped structure of Pt(322) w/o initial OH adsorptions as shown in Fig. 1. However, in case of the others, we cannot find the H₂O dissociation on not only Pt(111) flat surface w/ and w/o initial OH adsorptions but Pt(322) stepped surface w/ initial OH adsorptions. These results are consistent with the energetics approach of only a hydroxyl adsorption on Pt(322) stepped surface and with experimental data if we consider that our simulation shows on the way to the final water reaction.

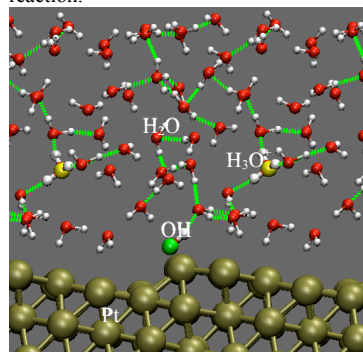


Figure 1. H₂O dissociation and an adsorption of an OH molecule on Pt(322) stepped surface w/o initial OH adsorptions. Dotted line denotes H-bonding network.

Significance

Pt(322) stepped surface is more reactive to water dissociation compared to Pt(111) flat surface. This tendency is consistent with the energetics approach of only a hydroxyl adsorption on Pt(322) stepped surface.

References

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