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DFT calculations on H, OH and O adsorbate formations on Pt(111) and Pt(332) electrodes

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ABSTRACT

Density functional theory combined with a modified Poisson–Boltzmann theory (DFT-MPB) is applied to H, OH and O adsorbate formations on electrified Pt(111) and Pt(332) surfaces in an acid aqueous solution. In this method, the chemical bonds between adsorbates and electrodes are quantitatively described by the DFT, and solvation and electric field effects by the electric double layer are described by combining explicit water adlayer models and modeled continuum electrolyte. The results indicated that H, OH and O are bound less strongly to (110)-step on Pt(332) than to terrace on Pt(111) in the electric double layer while the trend is opposite in vacuum. The trend in the electric double layer is consistent with our experimentally-obtained cyclic voltammograms, in which H and (hydr)oxides are formed less easily (at lower and higher potentials, respectively) on Pt(332) than on Pt(111). The small binding energies in the modeled electric double layer mainly stem from destabilizations of adsorbates by the presence of strongly adsorbed water molecules forming 1D H-bond networks on the step. Other effects also are found to contribute to the destabilizations: the strain on the Pt(332) terrace, the confinement by the Pt atoms near the step and the water orientation changes by the formations of adsorbates.

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1. Introduction

Low-coordinated surface Pt atoms strongly attract other atoms and molecules, in general. This tendency has been used to interpret mechanisms of various electrocatalytic reactions. The particle size effect on the oxygen reduction reaction (ORR) [1–3], for example, is considered to be closely related to the number of the low coordinated surface Pt atoms [4–7]. On a small particle, which has a large number of low coordinated surface Pt atoms, reduction rates of O and OH are slow because of their strong bonds with the surface.

The same discussion, however, cannot be simply applied to single crystal surfaces. As shown by past experimental studies [8,9], (n, n, n') $(n' = n - 1, n - 2, \ldots)$ surfaces with (110)-steps are more active for ORR than Pt(111) in $HClO_4$ solution. Furthermore, as shown in our voltammograms of Pt(111) and Pt(332) in Fig. 1 or in past experiments [10,11] by Feliu's group and Koper's group on Pt(553) and Pt(111), H and (hydr)oxides seem to be removed more easily (at lower and higher potentials, respectively) on the stepped surfaces than on Pt(111).

Feliu's group and Koper's group [10,11] considered that this easily desorbed H from Pt(553) is from (110)-steps of Pt(553) and reasoned that the binding energy of H atom on (110)-steps is smaller than that on (111)-terraces, from a result of a temperature programmed desorption measurement in a UHV condition [12]. They, further, considered that when H is desorbed from the step, OH or O is instantly formed there because the step strongly attracts OH or O, and that after this displacement, OH or O at the step repels other (hydr)oxides to prevent further oxidation at the adjacent terrace. This suggestion reasonably explains why the H desorption potential at the step is lower than that at the terrace and why the potential for further (hydr)oxide formation is higher than the (hydr)oxide formation initiation potential on Pt(111). In addition, this suggestion also explains other aspects of voltammograms and UHV experiments, such as pH- and cation-dependences of H-desorption potential at the step [11,13], the high reactivity of step sites for CO oxidation and its cation-dependence [14,15], and energy diagrams of H, OH and O adsorptions speculated from TPD analysis under UHV condition [12,16]. These experimental results can be evidences of the suggestion but only indirect ones.

Recently, atomistic simulations [17–23] using the density functional theory (DFT) [24,25] has become applicable to interfacial electrocatalytic reactions. The simulations have been intensively applied to Pt(111), and many valuable information on thermodynamics and kinetics of H, OH and O formations have been obtained [26–40]. The calculated reversible potentials [29–40] for H, OH and O formations agreed reasonably well with the experimental results [41–46], and detailed analysis showed that the solvation effects on stabilities of H and O are very small (less than 0.03 eV), while OH is

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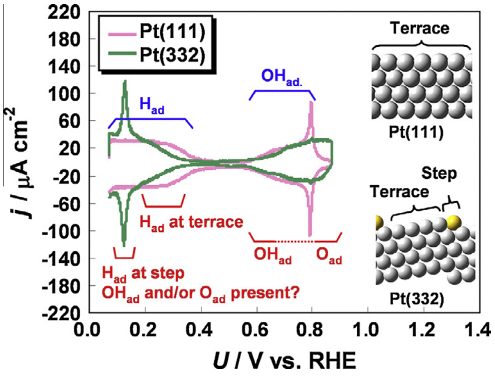

Fig. 1. Experimentally-obtained cyclic voltammograms of Pt(111) (peach) and Pt(332) (green) in 0.1 M $HClO_4$. Inset shows cross-sectional side views of Pt(332) and Pt(111) surfaces. Yellow spheres indicate step Pt atoms, and white spheres indicate other Pt atoms. Current densities on Pt(111) are attributed to H_{ad} and OH_{ad} formations as described by the blue letters above the cyclic voltammogram of Pt(111), and current densities on Pt(332) are attributed to H_{ad} and OH_{ad} (and/or O_{ad}) formations as described by the red letters below the cyclic voltammogram of Pt(332). Here, H_{ad}, OH_{ad} and O_{ad} mean adsorbed H, OH and O, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

substantially (more than 0.5 eV) stabilized by the solvation [32–38].

On stepped Pt surfaces, however, the simulations were not extensively done. Vehviläinen et al. [47] studied H adsorbed on Pt(111) and Pt(331) in vacuum and reported that the adsorption energy of H at the (110)-step is almost the same as that at the (111)-terrace. By using a similar computational method, Panchenko et al. [48] studied OH adsorbed on low-index platinum surfaces in vacuum and reported that the adsorption energy of OH on Pt(110) is 0.48 eV larger than that on Pt(111). These two DFT results may indicate that the OH formation potential at the (110)-step is 0.48 V negatively shifted from that on Pt(111) and overlaps the H-desorption potential. The estimated result, however, may contain large errors because adsorption energies on electrically neutral surfaces in vacuum can be significantly different from those on charged surfaces in electrolytes. It is also problematic to use the DFT results on Pt(110) for estimating the reversible potentials on other stepped surfaces because the energetics on Pt(110) are speculated to be significantly different from those on other stepped Pt surfaces by the experimentally-obtained voltammograms [9].

In this study, to clarify origins of the observed reactivity of (110)-steps, two DFT-based methods are applied to H, OH and O adsorbate formations on Pt(111) and Pt(332) in aqueous acid solution: a method using DFT calculations on electrically neutral surfaces in vacuum, in which the solvation and surface charging effects are totally omitted, and a method using DFT calculations on charged surfaces in the solution, in which the solvation effects on charged surfaces are approximated using a continuum electrolyte theory. Results by the two methods are compared, and the solvation and surface charging effects on the stepped Pt surface are discussed. Theoretical methodologies are described in Section 2. Results and discussion are presented in Sections 3. Conclusions are summarized in Section 4.

2. Computational method

The system considered in this study is Pt(111) and Pt(332) electrodes in $HClO_4$ solution. The state of the system is defined as 298.15 K for the temperature, 1 atm for the pressures of H_2 in gas phase, 0.035 atm for the pressure of H_2O in vapor phase in equilibrium with liquid water, and 1 mol L^{-1} for H^+ in the solution.

2.1. Free energy

Before describing the two DFT-based methods used to compute reaction free energies and reversible potentials of the H, OH and O adsorbate formations, general aspects and free energy equations are described on charged surfaces in the electrolyte, solutes in the electrolyte, and molecules in gas phase or vapor phase in this section.

2.1.1. Free energy of charged surface in electrolyte

2.1.1.1. Electrode potential and electric double layer. The electrode potential U scaled with a reversible hydrogen electrode (RHE) of an working electrode immersed in an electrolyte is defined as a difference between the electrochemical potential $\tilde{\mu}_e$ of electrons in the working electrode and that in the RHE, which is denoted as $\tilde{\mu}_e^{RHE}$, as shown below [18,19,23,30,49–51],

$$U = -\frac{\tilde{\mu}_e - \tilde{\mu}_e^{RHE}}{e}, \tag{1}$$

where e is the elementary charge. Here, the electrochemical potentials are in vacuum scale, and therefore, $\tilde{\mu}_e^{RHE}$ corresponds to the work function of the RHE.

When the electrode potential U is changed, the charge distribution across the electrolyte–electrode interface changes to adjust the electrochemical potential $\tilde{\mu}_e$ to the given U. This change includes contributions by electron transfers between the electrode and an external circuit and by ion transfers between the electrolyte near the surface and bulk electrolyte. When U is increased from the potential of zero charge (PZC), for example, a positive surface charge is induced by electron transfer from the surface to the external circuit, and a negative charge is accumulated in the electrolyte near the electrode by anion transfer from the bulk electrolyte to the surface and cation transfer from the surface to the bulk electrolyte. The generated interfacial polarization creates an electrostatic potential gap across the interface corresponding to the given U.

In addition to the adjustment of $\tilde{\mu}_e$, electric charges are distributed to minimize the interfacial free energy. When the surface is positively charged, for example, anion and cation are distributed near and far from the surface, respectively, for minimizing the electrostatic energy.

This polarized region is called the electric double layer and can be divided into two parts [50–54]: a compact layer, which is formed on the electrode surface, and a diffuse layer, which is formed outside of the compact layer. The structure of the compact layer depends strongly on the chemical natures of the electrolyte and electrode, and its thickness is believed to be 2–3 Å [55,56]. The structure of the diffuse layer is controlled by classical electrostatic interactions and is approximately proportional to $\exp(-\kappa \cdot z)$ in a low concentration condition [53,54], where κ is the inverse of the Debye length, and z is the distance from the electrode surface. By this exponential function, a screening length of the induced surface charge by the double layer is roughly estimated to be 30–300 Å for the electrolyte with an ionic concentration of 1–10^3 mol L^{-1}.

For building a consistent interfacial model, the free energy of the entire double layer needs to be described. Although equations describing the free energy can be obtained non-empirically by a first principles-based statistical theory [57] using a molecular dynamics or Monte Carlo approaches under a constrained electrode potential condition [58], its computational cost is too high to apply it to the long-ranged electric double layer. Approximations are, therefore, necessary.

2.1.1.2. Born–Oppenheimer and static solvation approximations. For reducing the computational cost, the electric double layer is divided into the interfacial region comprised of the electrode surface

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