First-principles Molecular Dynamics Simulations of Electrochemical Reactions at Water/Metal Interfaces

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We have simulated electrochemical reactions at water/metal interfaces by using first-principles molecular dynamics techniques. We have been working on hydrogen evolution reaction at water/Pt (111) interface and in this year, we have concentrated on the elucidation of the effect of interface hydrogen for the structure of water and chemical reactions at the interface. Particular attention is paid to the Pt-H stretching frequency (ν_{Pt-H}) of hydrogen on the atop site, which is often referred to as overpotentially deposited hydrogen and considered to be the reaction intermediate of the hydrogen evolution reaction. We investigate the origin of the large potential dependence of ν_{Pt-H} observed in the electrochemical experiments, by taking into account the effects of electric field, solvent, and hydrogen coverage to simulate water/metal electrode interfaces realistically. The electric field effect on ν_{Pt-H} without water solvent, the Stark tuning rate is less than 20 $cm^{-1}V^{-1}$. Although it is increased by factor of 2.5 by taking into account the solvent effect, the electric field effect alone cannot account for experimentally observed large potential dependent frequency shift. It is found that the coverage effect on ν_{Pt-H} is significant, indicating that the electric field, solvent and hydrogen coverage effects should be taken into account to fully explain the experimentally observed large frequency dependence on the electrode potential. The large hydrogen coverage effect on the vibration frequency shift is attributed to the shift of d-band center due to the hybridization between the hydrogen s state and the substrate d-band. We found that as increasing the hydrogen coverage, water/metal distance increases, indicating the repulsive interaction between water and adsorbed hydrogen on the electrode surfaces. Furthermore, we also simulated the effect of adsorbed hydrogen on the volmer process of hydrogen evolution reaction. It turned out that although the coverage of hydrogen is more than one monolayer (ML), the Volmer process takes place rather than the Heyrovsky process, indicating that the barrier for the Volmer process is smaller than that for the Heyrovsky process.

Keywords: DFT, Molecular Dynamics, Electrode, Water, Metal

1. Introduction

Catalytic reaction of hydrogen on the electrode surfaces is one of the simplest and the most fundamental issues and has been studied extensively for many years. Among them, hydrogen evolution reaction (HER) on Pt electrode is one of the most fundamental and important reactions in electrochemistry. The HER is also important due to its close relationship to the fuel cell technology. However, despite the apparent simplicity of the reaction, the mechanism is not fully understood. Elucidation of the mechanism of the hydrogen evolution at the atomistic level is thus needed. The HER is considered to proceed through the initial adsorption of protons from solution (Volmer step) and the associative desorption of hydrogen molecule via recombination of the adsorbed hydrogen (Tafel step) or via an electrochemical reaction of the adsorbed hydrogen and the proton in solution (Heyrovsky step). Understanding the adsorption state of hydrogen on the electrode surface serves as a basis for clarifying the microscopic mechanism of the HER. Hydrogen atoms adsorbed on Pt electrode surfaces are categorized to two types: one is the adsorbed species at potentials positive to the thermodynamic reversible potential of HER, the so-

called underpotentially deposited (UPD) hydrogen, and the other is called overpotentially deposited (OPD) hydrogen. The OPD hydrogen is considered to be the reaction intermediate of the HER.

In this work, we study the hydrogen adsorption on the Pt (111) surface by means of the *periodic* DFT which is superior in describing the metal surfaces. We take into account not only the electric field, but also the solvent and the hydrogen coverage effects to model the water/electrode interface realistically. The effect of the electrochemical environment on $\nu_{\text{Pt-H}}$ of hydrogen on the atop site is systematically examined and analyzed, and the origin of the large potential dependence of Pt-H vibrational frequency is investigated.

2. Method

All calculations in this work were carried out by using density functional theory as implemented in the STATE (Simulation Tool for Atom TEchnology) code which has been successfully applied to semiconductor as well as metal surfaces. The electron-ion interaction is described by pseudopotentials. Wave functions and the augmentation charge were expanded by a plane wave basis set with the cutoff energies of 25 Ry and 225 Ry, respectively. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) was used for the exchange-correlation energy functional. Pt surfaces were represented by three- or five-layer slabs, separated by a vacuum equivalent to six-layer slab (1.5958 nm).

3. Results and Discussions

Since hydrogen atoms always prefer the fcc-hollow site at $\Theta_{\text{H}} \leq 1$ ML, we assume that atop hydrogen appears after the fcc sites are fully occupied as discussed above. Here it should be noted that the hydrogen coverage on the Pt (111) electrode surface is estimated to be ~2/3 ML at the equilibrium potential. Thus the present result may not rigorously correspond to the actual situation in the experiments, but is sufficient to show the significance of the coverage effect on the vibrational property of adsorbed hydrogen. Coverage dependence of the hydrogen adsorption energy using the three-layer slab is shown in Fig. 1a. To illustrate how hydrogen atoms interact with neighboring H, adsorption energies at $\Theta_{\text{H}} \leq 1$ ML, where fcc-hollow sites are empty and at $\Theta_{\text{H}} > 1$ ML, where they are fully occupied are shown. At $\Theta_{\text{H}} \leq 1$ ML, the change of the adsorption energy is small, within ~7 kJ mol^{-1}. By increasing the slab thickness to five-layers, the
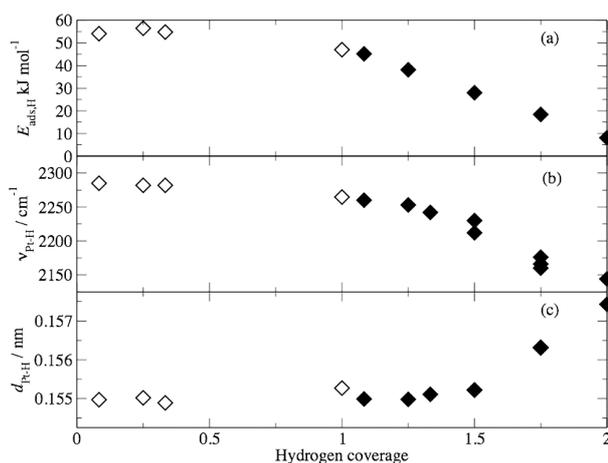
Fig. 1 Adsorption energy of hydrogen at the atop site in UHV, E_{ads}, (a), Pt-H stretching frequency $\nu_{\text{Pt-H}}$(b), and Pt-H bond length $d_{\text{Pt-H}}$(c) as a function of hydrogen coverage.

differences in the adsorption energies are affected no more than 1 kJ mol^{-1}. This indicates the lateral interaction between Pt-H$_{\text{atop}}$ is small and their effect on the Pt-H frequency is expected to be small. The dipole-dipole interaction is also small since the induced dipole moment is considerably small (0.12 Debye for hydrogen adsorbed on the atop site at 1 ML). On the other hand, by increasing the hydrogen coverage from 1 to 2 ML in the presence of hydrogen on the fcc-hollow site (H$_{\text{fcc}}$), the adsorption energy is decreased almost linearly, indicating the repulsive interaction between adsorbed hydrogen atoms.

Coverage dependence of the Pt-H stretching frequency and the bond length are show in Fig. 1b and 1c. It can be clearly seen that at $\Theta_{\text{H}} > 1$ ML the $\nu_{\text{Pt-H}}$ rapidly decreases as the hydrogen coverage increases and corresponding bond length is elongated. The change in the frequency is significant: from ~2260 cm^{-1} to ~2140 cm^{-1}. Our result clearly shows that the hydrogen coverage effect is quite large on the Pt-H stretching frequency, suggesting the large contribution from the effect of hydrogen coverage to the experimentally observed large potential shift of the Pt-H stretching frequency.

Refereces

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燃料電池の電極反応ナノシミュレーション

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　　燃料電池反応の微視的機構を解明するためには電極界面における水の性質を理解することが重要である。我々は第一原理分子動力学計算コードSTATE（Simulation Tool for Atom TEchnology）と有効遮蔽媒質（effective screening medium, ESM）法を用いて、電圧印加した白金電極／水界面の分子動力学シミュレーションを実行した。界面における水の構造を詳細に解析することにより、バルク状態とは異なる電位に依存した界面での水の構造を明らかにし、極めて大きな負電位を与えると界面の水は疎水性を示すことを予言した。界面の水の構造に加えて振動状態の解析を行うことにより実験との比較を行った。さらに、低電位においては電極表面に水素が吸着していると考えられることから、水素吸着白金／水界面についてもシミュレーションを実行し、界面における水の構造を解析した。実験的に観測されている、Pt-H伸縮振動について、振動モードの電位依存性は主として水素の吸着量に依存していることが明らかとなった。また、水素の吸着量が増えるに従い、水と金属電極との距離は増加し、吸着水素と界面での水は反発的な相互作用を強くしていることが明らかとなった。

キーワード：燃料電池, 第一原理分子動力学, 有効遮蔽媒質, 振動数, 白金電極／水界面