

Structural dependence of intermediate species for the hydrogen evolution reaction on single crystal electrodes of Pt

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ABSTRACT

Adsorbed hydrogen and water were measured during the hydrogen evolution reaction (HER) on the low and high index planes of Pt in 0.5 M H₂SO₄ using infrared reflection absorption spectroscopy. Hydrogen is adsorbed at the atop site (atop H) on Pt(110) during the HER, whereas adsorbed hydrogen at the asymmetric bridge site (bridge H) is found on Pt(100). The band intensity of the adsorbed hydrogen depends on temperature, indicating that the bands are due to the intermediate species for the HER. The band of the atop H appears on stepped surfaces with (110) step, whereas the asymmetric bridge H is observed on Pt(211) = 3(111)–(100) and Pt(311) = 2(111)–(100) that have (100) step. The absence of the atop H on Pt(100), Pt(211), and Pt(311) can be attributed to the relative stability of the bridge site.

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1. Introduction

Efficient hydrogen production from water is necessary for the development of new energy sources such as fuel cells. Water electrolysis is one of the important methods for the hydrogen evolution. Pt electrodes have extremely low overpotentials for the hydrogen oxidation reaction (HOR) and the hydrogen evolution reaction (HER); Pt is useful for the electrocatalysts of fuel cells and water electrolysis. The HOR/HER processes have been studied for decades [1–4]. The activity for the HER depends on the pH, electrode materials and the surface structure of the electrode. Adsorbed hydrogen (H_{ad}) is the key intermediate species for the HER on Pt electrode in acidic solution [5]. Two types of H_{ad} are suggested: the underpotential deposited hydrogen (H_{upd}) as a spectator species and the overpotential deposited hydrogen (H_{opd}) as an intermediate species [6].

Vibrational spectroscopy can identify the adsorption site of H_{ad}. Infrared reflection absorption spectroscopy (IRAS) found H_{ad} at the atop site of Pt in the H_{opd} and H_{upd} regions [7–9]. The band appears at 2090 cm^{−1} on polycrystalline Pt and Pt(111) [7]. According to the report of another group, the band was not found on defect-free Pt(111), and another band appeared at 2020 cm^{−1} on Pt(100) and Pt(111) in the H_{upd} region [8]. However, adsorbed CO is often produced by the reduction of dissolved carbonate species or CO₂, and the oxidation of carbon contamination, giving IR band around 2020 cm^{−1} [9]. Recently, surface enhanced infrared absorption spectroscopy (SEIRAS) suggests that the atop H_{opd} at 2080 cm^{−1} is a reactive intermediate during HER

on polycrystalline Pt electrode [5], whereas the structural dependence and band assignment of H_{opd} are controversial on Pt single crystals.

IR spectra indicate that water is adsorbed on the Pt surface during the HER [10]. Water preferentially binds at the atop sites of the Pt surface through the oxygen lone pair [11]. The adsorption energy of adsorbed water on Pt is comparable to that of adsorbed hydrogen [12]. The IR band of hydronium cation (H₃O⁺) appears on Pt and the band intensity depends on the electrode potential [5,10]. Interfacial water plays an essential role for proton transfer and proton hydration during the HER.

The relationship between the HER activity and the adsorption site of the intermediate H_{opd} is unclear. It is important to examine the structural dependence of the H_{opd} using well-defined surfaces. In this paper, we have studied the structural and the temperature dependence of the intermediate H_{opd} and adsorbed water on Pt electrodes using IRAS and the density functional theory (DFT) calculations. We identified the IR band of the intermediate H_{opd} on the low and high index planes of Pt. The adsorption site of the H_{opd} strongly depends on the surface structure of Pt during the HER.

2. Experimental

Platinum single crystals were prepared by the method of Clavilier et al. [13]. The samples were hydrogen-flame annealed, cooled in Ar + H₂ or Ar, and transferred to the IR cell after protecting the surface with a droplet of ultrapure water (Milli-Q Advantage). It is known that the reconstruction is induced on several Pt single-crystal surfaces [14–17]. For Pt(110) and Pt(211), the unreconstructed surfaces were prepared according to the procedure described elsewhere [16,17]. The solution was prepared with H₂SO₄ (Merck Suprapur) and ultrapure water. The reference electrode was the reversible hydrogen electrode

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(RHE). The infrared beam was incident at an angle of 60° . The IR cell was attached to a Fourier transform IR spectrometer (JASCO FT/IR-6100) with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The spectra were collected with p-polarized light at a resolution of 4 cm^{-1} . All IR spectra were obtained using subtractively normalized interfacial Fourier transform spectroscopy (SNIFTIRS). Reference potential is set at 0.8 V (RHE) to oxidize CO that is produced from contamination. Total 1024 scans were co-added in 8 cycles of 128 scans at both reference and sample potentials.

DFT calculations of the IR frequencies were carried out with the Gaussian 03 program using the LANL 2MB ECP basis for Pt and the 6-31G** basis for H at the BLYP level. The metal surfaces are modeled by three layered clusters consisting of 20 and 28 metal atoms. The Pt–H distance is optimized while the metal clusters are always kept fixed at the bulk structure. DFT calculations of the adsorption energies were carried out with the Vienna ab initio simulation program (VASP) [18]. The structure models were comprised of a 6 (low index planes) and 10 (Pt(211)) layer Pt slab with a 1×1 surface unit cell. The slabs were separated by approximately 1 nm of vacuum. The first Brillouin zone was sampled with a $10 \times 10 \times 1$ k-point mesh within the Monkhorst–Pack scheme [19]. Ionic cores were described by ultrasoft pseudopotentials and the Kohn–Sham one-electron valence states were expanded in a basis of plane wave with a cutoff energy of 400 eV. Electron exchange and correlation were described within the PW91 generalized gradient approximation (GGA) [20]. The calculated lattice constant of bulk Pt was 0.398 nm, which was within the error of 1.5% of the experimental value. The adsorption energy is defined as the energy difference per H atom between the adsorbed system and the sum of the Pt slab and H_2 molecule.

3. Results and discussion

We measured voltammograms of Pt electrodes in 0.5 M H_2SO_4 used in this study. The voltammograms were identical with those reported previously [13,21–23]. Fig. 1 shows the potential dependence of the IRAS spectra of the low index planes of Pt in 0.5 M H_2SO_4 at 298 K. A positive going band is observed between 1600 and 1630 cm^{-1} on all the surfaces. These bands are assigned to δ_{HOH} of adsorbed water. These bands show the red shift at positive potential. We reported that the frequency shift of δ_{HOH} on Pt group metals is due to the charge transfer from the water lone pair to the electrode [10]. Charge transfer from the oxygen lone pair to the metal causes a small expansion of the HOH angle, which means the decrease of the bending

frequency. The frequency of δ_{HOH} on Pt(110) is lower than those on Pt(111) and Pt(100), which indicates that water is strongly adsorbed on Pt(110). The adsorption energy of water at steps is higher than those at terraces [24]. The band intensities of δ_{HOH} on Pt(100) and Pt(110) increase at negative potentials. The increase of the band intensity on Pt(100) below 0.05 V is due to the coupling with the band of H_{ad} as discussed below. On Pt(110), the adsorption of (bi)sulfate anion above 0.2 V inhibits the adsorption of water [25,26]. Since (bi)sulfate anion is adsorbed on Pt(111) and Pt(100) above 0.4 V and 0.3 V, respectively, the coverage of water is unchanged between 0 and 0.2 V [26–28].

A broad band is found at 1750 cm^{-1} , which is assignable to the asymmetric bending mode of the hydronium cation (H_3O^+) [29]. The band intensity of H_3O^+ decreases below 0.05 V because of the decrease of H^+ concentration neighboring to the electrode surface by the hydrogen evolution. The band intensity of H_3O^+ also depends on the surface structure. This structural dependence may be due to the difference of the orientation of H_3O^+ and the HER mechanism. The negative going band at 1235 cm^{-1} is assigned to the symmetric SO_3 stretching mode of adsorbed (bi)sulfate anion at the reference potential.

Small positive going band appears at 2081 cm^{-1} on Pt(110) at 0 V where the HER occurs. This band is assigned to $\nu_{\text{Pt-H}}$ of the intermediate H_{opd} at the atop site (atop H) of Pt. The frequency of $\nu_{\text{Pt-H}}$ is identical to that on polycrystalline Pt reported previously [5,7]. On the other hand, a tail appears in the higher-frequency region of δ_{HOH} band below 0.05 V on Pt(100). The tail includes the $\nu_{\text{Pt-H}}$ band of the intermediate H_{ad} at asymmetric bridge site (bridge H) on Pt(100), as discussed below. However, no bands of H_{ad} is observed on Pt(111). DFT calculation predicts that the adsorbed hydrogen prefers the three-fold hollow site (hollow H) on the Pt(111). Previous high-resolution energy-loss spectroscopy (HREELS) studies show dipole active modes of the hollow H at 904 and 1224 cm^{-1} [30]. Under the conditions of our experiments, these bands could not be observed because of the overlap with the (bi)sulfate band (1235 cm^{-1}) and the transmission limit of the IR window. We tried to measure the band of hollow H in 0.1 M HF that has no IR active species around 1200 cm^{-1} . However, no band was found around 1200 cm^{-1} even in 0.1 M HF. The band intensity of hollow H may be too weak to be detected using IR spectroscopy, because the dipole component of the hollow H along the surface normal is small or dynamic dipole is effectively screened by surface atoms [31]. Since the band intensity of δ_{HOH} does not decrease during HER, the intermediate H_{opd} is coadsorbed with water on the Pt electrode.

Fig. 2 shows the temperature dependent IRAS spectra on the low index planes of Pt at 0 V. The intensity of 2080 cm^{-1} band on Pt(110)

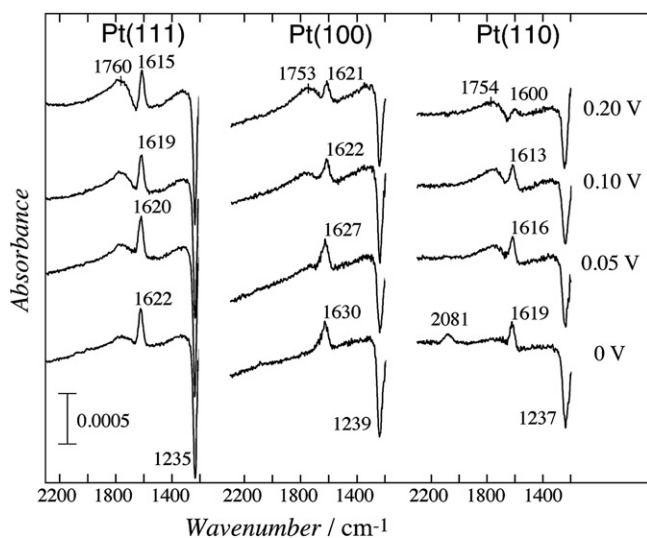


Fig. 1. Potential dependence of the IRAS spectra of Pt(111), Pt(100), and Pt(110) in 0.5 M H_2SO_4 . Reference potentials are 0.5 V (Pt(111)), 0.8 V vs. RHE (Pt(100), Pt(110)).

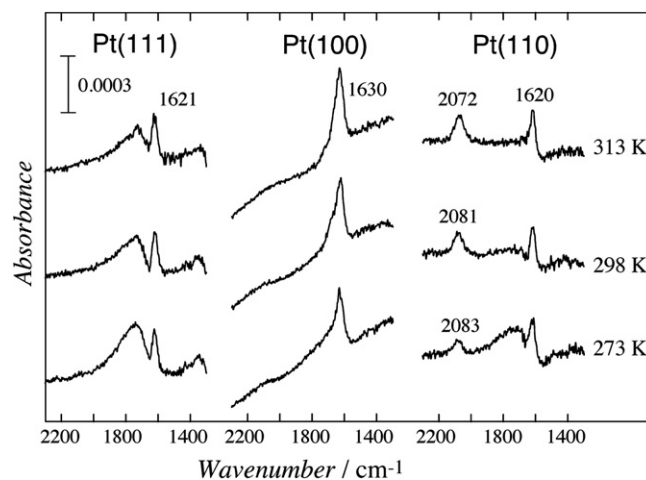


Fig. 2. Temperature dependent IR spectra of Pt(111), Pt(100), and Pt(110) in 0.5 M H_2SO_4 at 0 V (RHE). Reference potentials are 0.8 V (RHE).

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