Priority Communication

The effect of surface strain on the CO-poisoned surface of Pt electrode for hydrogen adsorption

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A B S T R A C T

The impact of mechanical strain is studied at CO-poisoned Pt(1 1 1) surface for hydrogen adsorption. Our experiment first investigates a coupling parameter of interest, ζ_H, which quantifies the variation of hydrogen adsorption potential in response to surface strain. The result exhibits a bigger ζ_H at CO-poisoned surface than the value measured at clean surface. Since adsorption potential is linked to adsorption energy, it indicates significantly the larger effect of tensile strain on decreasing hydrogen adsorption energy at CO-poisoned surface, comparing to the clean surface. DFT calculations at an atomic level support the experimental observation and explain this behavior can be attributed to the strain-induced reduction in CO-poisoning effect on hydrogen adsorption energy.

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1. Introduction

Carbon monoxide (CO) poisoning is notoriously common for a wide range of catalytic reactions involving precious metals such as Pt and Pd. For instance, in proton exchange membrane fuel cells, CO can adsorb preferentially on the Pt anode surfaces, blocking the active sites that are required for hydrogen electrosorption, which substantially restricts its reactivity. In the past decade, alloying of Pt with transition metals (PtM, M = Ru, Sn, Mo,...) [1–3] was mainly adopted as a general method to improve the resistance against CO poisoning, namely to decrease the CO coverage on the surface. Recently, core-shell and alloy systems in many new heterogeneous catalysts have been found exploiting strained active layers to modulate reactivity and/or selectivity [4–6].

Moreover, surface strain has been widely studied to control the adsorption of atoms as well as molecules, and to tune the reaction rate at metal surfaces [7–15]. The chemical response to strain of an adsorbate is strongly dependent on the surface orientation, even on the steps [16,17]. It is significant that density functional theory (DFT) [10] indicates that an increase in the in-plane lattice parameter (tensile strain) makes Pt(1 1 1) clean surfaces bind H atom more strongly, which is also supported by experiments [12–15,18,19]. The tensile strain could also enhance the CO binding at metal surface when one investigates the strain effect on the CO adsorption in electrolyte. However, the effect of surface strain on a saturated CO-poisoned surface has been not reported so far. Thus, it is not clear that the CO-poisoned surface under tensile strain becomes more active or less active for hydrogen adsorption. In this paper, we examine the variation of hydrogen adsorption energy with tensile strain at CO-poisoned surface of Pt electrode. The experimental results exhibit an interesting larger effect of tensile strain on decreasing hydrogen adsorption energy at CO-poisoned surface than that at clean surface. Finally, we show this can be explained at an atomic level by DFT calculations.

2. Methodology

2.1. Experimental procedures

Since the value of electrode potential, U_H, of hydrogen electrosorption process can measure the hydrogen adsorption energy, $\Delta E_{ad,H}$, as $\Delta E_{ad,H} = -zFU_H$ (where z and F denote valency of adsorbate and Faraday constant) [11–15], we examine the variation of hydrogen adsorption potential with surface strain in experiments. Recent work advertises Dynamic Electro-Chemo-Mechanical

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Analysis (DECMA) as a convenient experimental probe of electro-capillary coupling parameter ζ, which quantifies the variation of electrode potential, U, with surface tangential strain, e_{area}: namely, $\zeta = dU/de_{area}$ [11–14]. The procedures of this study are largely identical to those of earlier report of DECMA on polarizable electrodes [12,13]. In the interest of a self-contained description, we present a brief display of the procedures.

The working electrodes (WE) are 100 nm thin platinum films, sputtered onto 125 mm thick polyimide substrates (Upilex, UBE) with 1–2 nm titanium as an adhesion promoter and annealed at 300 °C in a vacuum of 10^{-6} mbar for 1 h. X-ray rocking curves of films prepared in this manner reveal a strong (1 1 1)-texture (see Fig. S1 in Supporting Information). Pt wire is used as the counter electrode. All potentials in this work are quoted *versus* the standard hydrogen electrode (SHE) and are positive by 197 mV compared to potentials measured *versus* Ag/AgCl in 3.5 M KCl. The electrolytes are prepared from H_2SO_4 (Suprapur, Merck) and ultra-pure water (18.1 MW cm, Sartorius). The glass electrochemical cell is placed into Piranha solution (5 Volume parts of concentrated H_2SO_2 + 1 part of 30% H_2O_2) for 24 h and then rinsed thoroughly with ultra-pure water.

DECMA uses a lock-in amplifier to detect the potential modulation when the electrode is subjected to cyclic strains. The experimental setup is schematically shown in Fig. S2 (see Supporting Information). A piezo actuator (PI-840 Physik Instrumente), fed by a function generator, imposes a sinusoidal cyclic elastic strain on the polyimide substrate of the WE. The grip displacement at any given time is read from the sensor in the piezo-actuator and is used as the reference signal in the lock-in amplifier (SR 7270, Signal Recovery). We use a strain frequency of 20 Hz with maximum amplitude of 0.02%. The amplitude of strain-induced cyclic potential variation is on the order of 0.2 mV in this study.

2.2. Computational details

All calculations are performed with DFT, which is implemented in DMol^3 code [20]. The generalized gradient approximation (GGA) is treated by the PW91 [21]. A double numerical plus polarization (DNP) is used as the basis set. The inner electrons of Pt atoms are treated by an effective core potential (ECP); other atoms in this study are treated with an all-electron basis set. The convergence tolerance of energy is 2×10^{-5} Ha, and the maximum force and displacement are 0.004 Ha/Å and 0.005 Å for the geometry optimization, respectively. The real-space global orbital cutoff radius is set to be 4.0 Å. The Brillouin zone is sampled by $3 \times 3 \times 1$ k-points. All structures are optimized without any symmetry constraints.

A $3 \times 2\sqrt{3}$ super-cell for a Pt(1 1 1) is constructed at low CO coverage (0.083 ML, 0.167ML and 0.25 ML) and high coverage of 0.667 ML. A $2 \times 2\sqrt{3}$ super-cell is used at the coverage of 0.5 ML. All configurations use a four-layer slab. The equilibrium lattice constant for bulk Pt is calculated to be 3.95 Å, in good agreement with the respective experimental values 3.92 Å. Vacuum space is set to 15 Å in the z direction to avoid interactions between periodic images. During the optimization, the atoms in the top three layers of the metal surface are allowed to relax, whereas the bottom layer is fixed. The hydrogen adsorption energy ($\Delta E_{ad,H}$) in calculation is defined as $\Delta E_{ad,H} = E_{total} - E_{surf} - 1/2\, E_{H_2}$, where E_{total}, E_{surf} and E_{H_2} denote the total energies of Pt surface with adsorbed species (*e.g.* CO, H), the corresponding Pt surface and the gas phase of H_2, respectively. Negative adsorption energy indicates that the adsorbed species can be stably attached to catalyst surface. In our study, adsorption energy of H atom is calculated based on the Fcc adsorption site [22]. The possible adsorption configurations of CO at different coverage are examined and the energy of each configuration is provided in Supporting Information.

3. Results and discussion

3.1. Experimental measurement on variation of hydrogen adsorption potential with surface strain

The hydrogen adsorption is studied on 111-textured thin films of platinum for CO-poisoned surface in 0.5 M H_2SO_4 solution. Fig. 1(a) shows cyclic voltammograms of Pt electrodes for CO-free surface and CO-poisoned surface. The data for CO-free surface are consistent with the clean surfaces of the polycrystalline, thin film metal electrode [12,13]. After bubbling CO gas in electrolyte for 20 min while holding the electrode potential at 50 mV to allow the adsorption of CO on electrode surface, part a) of Fig. 1 shows a sharp current peak at the electrode potential of 0.9 V, indicating the CO oxidation process occurring. It thus states the presence of CO on the surface. In order to avoid the removal of CO, the potential range of interest is limited at the negative side of the onset potential of CO oxidation in our study.

The DECMA data of aforementioned ζ, which measures the variation of electrode potential with the surface strain, are shown in Fig. 1(b) and (c) for CO-free surface and CO-poisoned surface. The
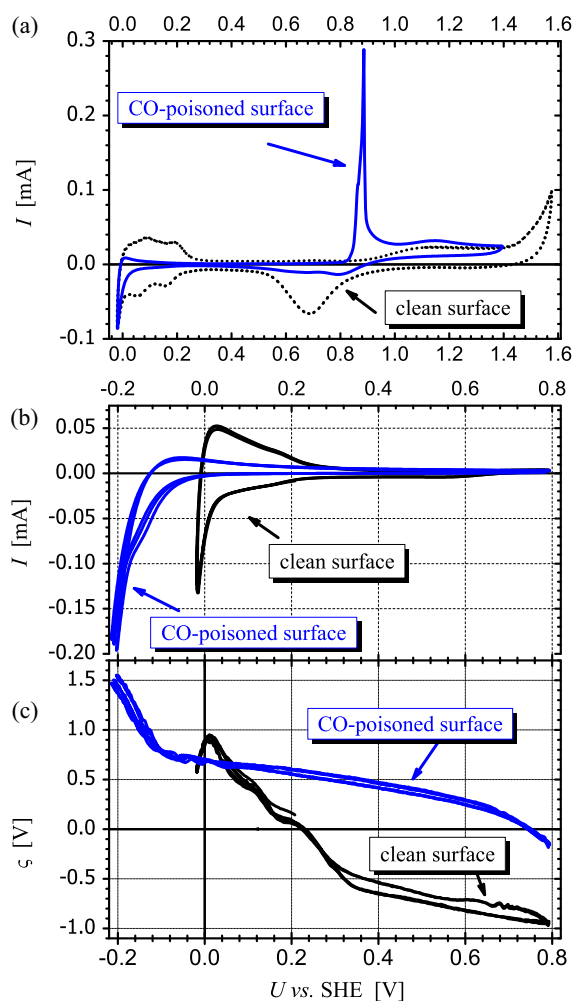
Fig. 1. (a) Cyclic voltammograms of current, I, *versus* electrode potential, E, within different potential windows at the CO-free (black dotted line) and CO-poisoned (blue solid line) surfaces of 111-textured Pt thin films electrode. The sharp current peak indicates the CO oxidation around the potential of 0.9 V. The results of dynamic electro-chemo-mechanical analysis of Pt electrode at the CO-free clean (black) and the CO-poisoned surface (blue): (b) the *in situ* cyclic voltammogram (CV); (c) the coupling parameter, ζ, at cyclic strain frequency of 20 Hz. All experiments are conducted in the electrolyte of 0.5 M H_2SO_4 and at the potential sweep rate of 10 mV/s.