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Electrocatalytic activity of surface oxides on platinum nanofacets and surfaces

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ABSTRACT

We investigated electrochemical behavior of surface oxides of platinum formed by annealing in air. We studied the catalytic activity for CO electrooxidation using electrochemical, X-ray, and DFT methods. We find that all oxidized platinum surfaces are highly active initially for CO electrooxidation reaction in so-called preignition region. While the high activity of the monolayer oxide formed on extended Pt surfaces decreases after the initial CO-oxidation cycle, bilayer oxide formed on nanoscaled facets sustain the high CO electrooxidation activity. DFT calculations show that OH binds, as strongly to bilayer surface oxides as to metallic surface while CO does not, suggesting the bifunctional property of the bilayer oxide surface.

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1. Introduction

Catalytic conversion of small molecules such as CO, H_2, methanol electrooxidation or O_2 reduction is not only of fundamental interest, but also a part of technological challenges in the development of efficient catalysts and deployment of energy conversion devices such as fuel cells. In particular, CO adsorption and oxidation on platinum surfaces has been one of the most studied benchmark model systems for gas phase catalysis, leading to fundamental understanding of catalytic processes [1]. Similarly CO adsorption and electrooxidation in electrolytes has been extensively studied for electrocatalysis as a model system for oxidation reaction [2] and for practical mitigation of CO poisoning in methanol oxidation [3].

Electrooxidation of CO has been extensively studied on platinum [4–11]. These studies were performed on extended single crystal surfaces with rigorous surface preparation protocols coupled with modern surface characterization tools. Tremendous progress has been made in elucidating the nature of electrooxidation due to many powerful surface characterization techniques which are available for extended single crystal surfaces. However, there is still a gap between the single crystal surfaces and nanoparticle catalysts, primarily because our understanding of processes on the extended single crystal surface does not simply scale to the nanosize catalysts.

In an attempt to close the gap, interest in tailor-faceted nanocrystals [12,13], nanofacets on high-index surfaces [14] and nanosize islands and defects on low-index surfaces [15] have steadily increased in recent years. In these cases, it was shown that that CO electrooxidation is enhanced by the presence of nanoscale defects such as kinks, steps [16] or adislands [15]. The importance of surface defects has been confirmed for realistic nanoparticle catalysts by electron microscopy and surface averaging voltammetry [16]. On the contrary, there have been few studies on the effect of surface oxides despite that it is well known that nanoparticles [17] or nanoclusters [18] can easily support significant surface oxide layers while it is difficult to grow self-supporting oxides on extended surfaces of platinum.

Preparation of Pt (1 0 0) and (1 1 1) extended surfaces and precise measurements of CO electrooxidation on them have been pioneered by UHV-transfer surface electrochemistry [19]. Since then, CO electrooxidation on Pt is one of the most extensively studied systems in electrocatalysis over the last few decades [20–23]. Even after numerous studies, the oxidation peaks have not been clearly understood. Especially in the flame-annealing method of sample preparation, some amount of surface oxides might have been unavoidable and contributed to confusion. Here, we used controlled air-annealing and H_2-annealing, precisely reproducible in terms of oxygen content and temperature.

Surface X-ray scattering (SXS) at synchrotron sources can be used to probe structural and chemical characteristics of catalytically active surfaces [24]. Recently our group developed methods of controlling the size and spatial orientation of nanosized platinum surfaces [25] and determined the surface oxide structures on nanofacets. [26,29] The nanofacets form during annealing

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a high-index surface in air and consist of alternating 111 and 100 nanofacets approximately 10 nm across and several hundred nanometers long [14]. Combining voltammetry measurements with SXS measurements and density functional theory (DFT) calculations, we can determine the relationship between the electrocatalytic activity and surface characteristics and unambiguously demonstrate that the oxide-covered nanoscaled platinum surfaces are highly active for CO electrooxidation.

2. Experimental

Platinum single crystals, grown in our laboratory, were cut, polished and bulk annealed according to an established procedure [7]. Pt (1 1 1) and Pt (1 0 0) platinum metal terminated surfaces were annealed with an induction heater in 3% H_2/Ar mixture at 1900 K for 5 min, referred to as 'H_2-annealed' hereinafter, then cooled down to room temperature. For the surfaces annealed in air, the Pt (1 1 1) and Pt (1 0 0) crystals were re-annealed at 1450 K for several minutes, referred to as 'air-annealed' hereinafter, and cooled down in synthetic air (21% O_2/79% N_2). Nanofaceted Pt surfaces were prepared using procedure published elsewhere [14]. Annealing in air is done at the same temperature and duration as described above for extended surfaces. A droplet of ultrapure deionized water was placed on the surface and the crystal was transferred to either an X-ray cell or electrochemical cell under the Ar or N_2 protective atmosphere. For CO-oxidation measurements, air-annealed single crystal electrodes were immediately immersed in CO saturated 0.1 M perchloric acid at open circuit potential. Potential was then set to −0.2 V. The electrodes were cycled 30 times from −0.2 V to either the onset or end of the main surface CO stripping peak depending on the purpose of the experiment. Ag/AgCl reference electrode was connected by the electrolyte bridge. All current voltage curves were performed with sweep rate of 50 mV/s. Surface qualities before and after CO cycles were determined by SXS. X-ray surface characterization was carried out using a rotating anode X-ray source and 4-circle diffractometer (extended surfaces) or at beamlines 12-BM and 11-ID-D of the advanced photon source (nanofaceted surface).

In DFT calculations, $(\sqrt{2} \times \sqrt{2})$ supercells of Pt (1 0 0) with 1 ML oxygen coverage were considered in a periodic slab model with thickness of 7 layers (28 Pt) for the determination of the binding energies of CO and OH adsorbed on PtO-like layers. Our previous calculations [26] indicate that the PtO-like structures have much lower energies than the O/Pt (0 0 1) (1 × 1) 1 ML configuration the strain lowers the overall surface energy of O 1 ML on the Pt (0 0 1) surface quite significantly. Therefore, the calculations of binding energies of molecules were performed on PtO-like structures with a uniaxial in-plane strain of the slab of 9%. For comparison to Pt surface without oxide layers, Pt (1 0 0) surface slab with a thickness of 8 layers was used for calculations of symmetric adsorption on both sides of the slab. The theoretical value of the Pt lattice parameter (a_{Pt}) optimized at the GGA level was 3.98 Å, and a vacuum region of $4 \times a_{Pt}$ was used throughout. Details of the methods for the DFT calculations of surface energy changes due to oxygen coverage are previously published [25,27]. The oxygen chemical potential at T and P_{O2} is simply related to the chemical potential at T and atmospheric pressure that are obtained from thermochemical tables [28].

3. Results and discussion

3.1. Electrochemical reduction of surface oxides and oxygen coverage determination in CO-free solution

The structures of the oxides formed on Pt (1 0 0), Pt (1 1 1), and nanofaceted Pt surfaces prepared in air (see Section 2) are previously determined [26,29]. The nanofacets have unique bilayer oxide structures while the extended surfaces support only partial monolayer oxides. The oxides of these surfaces are electrochemically reduced in 0.1 M perchloric acid and compared in Fig. 1. The scans were initiated at 0.6 V and cycled twice to −0.2 V. The arrows in Fig. 1 shows the current waves associated with the reduction of the air-formed oxides. The cathodic wave from the Pt (1 0 0) surface marked by the arrow in (a) corresponds to a coverage of 0.23(1) monolayer (ML) of O^{-2}. The SXS data of this surface do not support any significant restructuring of the platinum layers, and we conclude that this is oxygen adsorbed on the top Pt layer. The 0.23 ML surface coverage is consistent with the 1/4 ML oxide predicted by DFT calculation [26]. The cathodic wave from the Pt (1 1 1) surface in (b) shows two desorption features at ∼0.55 V and at ∼0.35 V. Only the latter is marked by an arrow because the former coincides with the "butterfly" region of anion adsorption on the clean Pt (1 1 1) surface. We assume that this feature is the top O^{-2} desorption coinciding with the position of anion desorption. The feature at ∼0.35 V arises from more strongly bound O^{-2} probably on hollow sites. Since our SXS work [26] on the extended (1 1 1) surface does not show any significant restructuring of the surface, we conclude that oxygen is adsorbed only on the topmost Pt layer. Stronger binding on hollow sites [30,31] in a non-electrochemical environment is known to occur on the Pt (1 1 1) surface. The charge below the peak at ∼0.35 V corresponds to an O^{-2} coverage of 0.14(1) ML and the total charge including the feature at 0.55 V is similar to that of the Pt (1 0 0) surface.

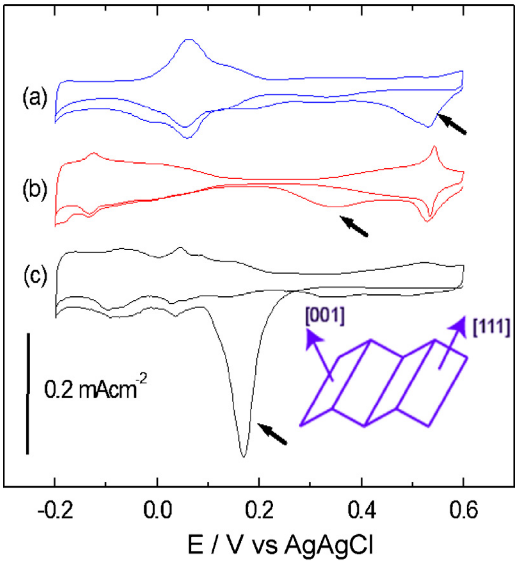

Fig. 1. Voltammograms of air-annealed Pt (1 0 0) (a), Pt (1 1 1) (b), and nanofacets (c) in 0.1 M perchloric acid. The inset shows schematically the 10 nm facets.

The largest oxygen stripping wave appears in nanofaceted surfaces shown in (c). The desorption peak is at ∼0.17 V, even more negative than on the extended Pt (1 1 1) surface. This indicates that the oxygen is adsorbed very strongly, which is expected for the reduction of the bilayer oxides [26,29]. Since the electrochemical measurements from the nanofacets are the combination of (1 1 1) and (1 0 0) facets, the charge amounts for each will remain unknown. Integrating the current below the peak yields a total charge of 340(10) $\mu C\,cm^{-2}$, which corresponds to 0.78(3) ML of O_2^-, close to what is expected from the Pt–O bilayer oxides assuming that the areas of (1 0 0) and (1 1 1) nanofacets are approximately equal. A full ML O^{-2} is expected for (1 0 0) facets where 1/2 of the top Pt atoms are place-exchanged, and a 2/3 O^{-2} layer is expected for (1 1 1) facets where 1/3 of the top Pt atoms are place-exchanged