First-principles studies of surface oxide formation on Pt electrode

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Introduction

Pt and its alloys are used as electrocatalysts in proton-exchange membrane fuel cells (PEMFC). However, existing fuel-cell technologies still have drawbacks, such as instability and dissolution of Pt on the electrodes, especially during the stop-and-go driving of an electric car [1]. Some experiments show that Pt oxide layer formed by anodic polarization induces corrosion under an inverse cathodic polarization condition; the extent of the corrosion is considered to be dependent on the formed Pt oxide [2, 3]. So to understand the mechanism of Pt surface oxide formation during polarizations is one of the key steps to increase the stability of Pt catalysts. There have been a lot of theoretical and experimental studies in this area [4]; recently Jerkiewicz et al. combined cyclic-voltammetry and other investigation techniques to study surface-oxide growth at platinum electrodes [5]. They proposed that when electrode potential $0.85 \leq U \leq 1.10$V vs. RHE, the first half monolayer of O* is formed through discharge of H_2O on the Pt surface; when $1.20 \leq U \leq 1.40$V, subsequent discharge of H_2O molecules leads to formation of the second half-monolayer of O* that is accompanied by the interfacial place exchange of O* and surface Pt atoms to form surface oxide PtO. Here we use first-principles studies to investigate this PtO formation process theoretically.

Calculation Methods

Total energy calculations by density functional theories (DFT) are performed by VASP with PBE-GGA pseudopotentials and projector-augmented wave (PAW) method. We build different Pt surface structures ((111), (100) and (211) surfaces) and study the energetics of oxygen in different chemical states, including surface adsorbates and interstitial states with various coverage. Reaction energies at zero-K temperature are transformed into free energy values of electrochemical reactions dependent on U by applying some simple thermodynamics model. We also use Nudge Elastic Band method to study the transformation mechanism from Pt + adsorbed O* on top of surface to surface oxide with oxygen as interstitials.

Results and Discussion

On clean Pt (111) electrode, O* begins to adsorbed on top of the surface when electrode potential U is more than ~0.7 V vs. RHE. Meanwhile, coverage of adsorbed O* increases linearly as U increases, as shown in Fig. 1. On the other hand, oxygen interstitial atoms below top (111) layer are very unstable; they can only exist when U is very high. Finally we find some stable structures, which have both adsorbed O* on top of surface and interstitial O* inside surface, can be stable at relative low U. These "quasi-3D" oxygen adsorption states and the corresponding oxygen coverage also change as U changes, as shown in Fig. 1. In addition, as oxygen coverage or electrode potential increases, these quasi-3D structures would become more stable than adsorbed O*, which agrees with previous experiments [5]. So these "quasi-3D" oxides may illustrate the correct atomic information of thin oxide layer on Pt (111) surface. We also calculate the activation energies of the quasi-3D structures formation and the results are also coverage dependent. At (3×3) Pt (111) surface unit cell with 1 ML O*, the activation energy for the formation of the first interstitial oxygen atom is only ~0.1 eV, which indicates relative high reaction rate at high U values, also agreeing with experiments [6]. Similar phenomena are observed on other surfaces facets ((100) and (211)) with different electrode potentials.

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Significance

The oxide formation mechanism on Pt surface is critical for the studies to increase the stability of Pt catalysts, which has already been a hot topic in PEM fuel cells studies [7]. In addition, oxide formation on different Pt facets occurs with different rates and reversibility. This mechanism can be used as a new method to produce nobel metal nanoparticles with stable high-index facets, which could be high efficient catalysts in many reactions [6].

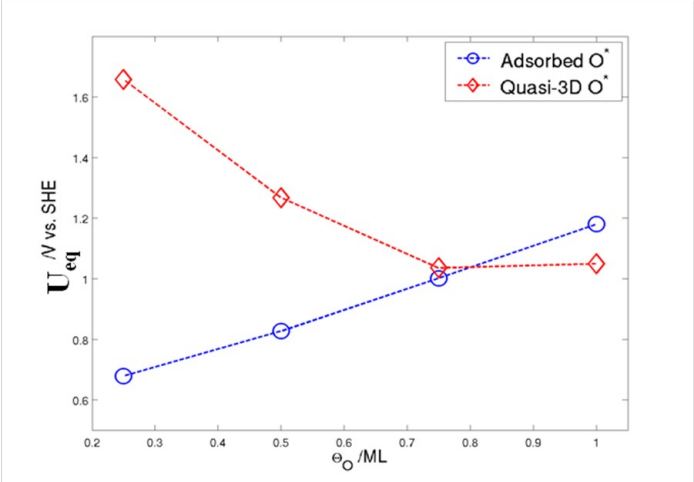

Figure 1. Changes of equilibrium electrode potential (U_{eq} vs. RHE) with different oxygen coverage for both surface adsorbed O* and "quasi-3D" oxide structures.

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