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Electrochimica Acta 53 (2008) 6081–6088
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Irreversible adsorption of Sn adatoms on basal planes of Pt single crystal and its impact on electrooxidation of ethanol

Qing-Wei Zheng, Chun-Jie Fan, Chun-Hua Zhen, Zhi-You Zhou, Shi-Gang Sun *,[1]

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Received 12 November 2007; received in revised form 18 January 2008; accepted 25 January 2008
Available online 5 February 2008

Abstract

The behaviours of irreversible adsorption (IRA) of Sn adatoms on Pt(1 0 0), Pt(1 1 1) and Pt(1 1 0) electrodes were characterized using cyclic voltammetry. It has revealed that Sn can adsorb irreversibly on Pt(1 0 0) and Pt(1 1 1), while not significantly on Pt(1 1 0) electrode. Quantitative analysis of the relationship between $1-\theta_H$ and θ_{Sn} suggests that Sn adatoms may adsorb preferably on hollow sites of Pt(1 1 1) (threefold) and Pt(1 0 0) (fourfold) planes, which is in accordance respectively with the values 0.31 and 0.21 of coverage of IRA Sn adatoms in saturation adsorption determined on these electrodes. The IRA Sn adatoms on different basal planes of Pt single crystal yield different impact on the electrocatalytic oxidation of ethanol. It has revealed that the IRA Sn adatoms on Pt(1 0 0) electrode have declined the activity for ethanol oxidation, while IRA Sn adatoms on Pt(1 1 1) have enhanced remarkably the electrocatalytic activity with Sn coverage θ_{Sn} between 0.09 and 0.18. The oxidation peak potential E_p and the current density j_p of ethanol oxidation on Pt(1 1 1)/Sn were varied with θ_{Sn}, and the highest j_p (1258 $\mu A\,cm^{-2}$) as well as the lowest E_p (0.20 V) were measured simultaneously at θ_{Sn} around 0.14. In comparison with the data obtained on a bare Pt(1 1 1), the E_p was shifted negatively by 65 mV and the j_p has been enhanced to about 1.7 times on the Pt(1 1 1)/Sn ($\theta_{Sn}=0.14$), which is ascribed to hydroxyl species adsorption at relatively low potentials on Pt(1 1 1)/Sn surfaces. The current study is of importance in revealing the fundamental aspects of modification of the basal planes of Pt single crystal using Sn adatoms, and the impact of this modification on electrocatalytic activity towards ethanol oxidation.

Keywords: Irreversible adsorption; Sn adatoms; Pt(1 1 1); Pt(1 0 0); Pt(1 1 0); Ethanol electrooxidation

1. Introduction

The study of the surface structure of Pt electrodes modified by metal adatoms and the role of adatoms in electrooxidation of small organic molecules is of both fundamental and technological importance in electrocatalysis and fuel cell applications [1]. It is well known that the modification of the electrode surface with adatoms such as Ru, Sn, Pb, As, Sb, Bi, etc. can enhance the catalytic properties of Pt electrode [2–6]. Different techniques to modify electrode surface using adatoms were developed [7], among them the under potential deposition (UPD) [1] and the irreversible adsorption (IRA) [4,6] are most convenient and were frequently employed. The presence of adatoms formed from UPD or IRA procedure [2,4,5] on electrode surface can modify the electronic and chemical properties of substrates, and as a consequence improve the catalytic properties of electrodes [8–12].

The electrochemical properties of Sn adlayers on Pt have been studied so far mostly on polycrystalline surfaces [13,14]. For a better understanding of the metallic adlayer structures, single crystal electrodes with well-defined atomic arrangement have been introduced. Stamenkovic et al. [15] have characterized bimetallic single crystals of Pt_3Sn(1 1 0) and Pt_3Sn(1 1 1) in ultra high vacuum by using Auger electron spectroscopy (AES), low energy ion scattering spectroscopy (LEISS) and low energy electron diffraction (LEED). Following characterization in the UHV, the Pt_3Sn(1 1 0) and Pt_3Sn(1 1 1) were transferred into an electrochemical cell to study their electrocatalytic properties for CO adsorption and oxidation by using in situ infrared spectroscopy. They demonstrated that continuous oxidative removal of adsorbed CO starts as low as $E<0.1$ V (vs. RHE), which is an

* Corresponding author. Tel.: +86 592 2180181; fax: +86 592 2183047.
E-mail address: sgsun@xmu.edu.cn (S.-G. Sun).
[1] ISE member.

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doi:10.1016/j.electacta.2008.01.078

important property for CO-tolerant catalysts. Electronic effects, surface structure and intermolecular repulsion between adsorbed species are ascribed for the high catalytic activity of $Pt_3Sn(h\,k\,l)$ alloys. To the best of our knowledge, the studies so far concerning modification of Pt single crystal electrodes using Sn adatoms were mainly focused on Pt (1 1 1) plane and employing UPD method [16–18]. Massong et al. [16] reported the electrochemical properties of UPD Sn on Pt(1 1 1) at potentials below 0.8 V and with low Sn coverage. A specific reversible redox current peak around 0.6 V (vs. RHE) was observed, ascribing to a surface redox processes of Sn adatoms on Pt(1 1 1) similar to those previously observed for As, Bi and other adatoms. The eps number (electrons transferred per surface site as obtained from the corresponding suppression of hydrogen adsorption) was determined at 1, which was interpreted to a one-electron process of hydroxyl species adsorption. Recently, the PtSn alloy nanomaterials were attractive and used as catalysts in electrooxidation of ethanol [17–19].

In the UPD experiments, the metal ions are always present in solutions, which will certainly influence the precise determination of adatom coverage and introduce complexity in studying electrochemical properties of the adatom modified electrodes [1]. In contrast with UPD, the irreversible adsorption presents advantages consisting in that the adsorption of adatoms can be done outside the electrochemical cell and does not require applying a reduction potential [6]. After the adsorption, the electrode is transferred into an electrochemical cell that contains a study solution without metal ions, so that the adatom coverage can be determined precisely, and the surface processes as well as the electrocatalytic properties of the adatom modified electrode may be finely investigated.

Besides the UPD process on Pt single crystal electrode, Sn also shows irreversible adsorption properties [1]. Haner et al. [5] studied the geometric and electronic effects of tin adatoms by depositing spontaneously tin on Pt single crystal surfaces, but they did not observe any enhancement of activity for methanol oxidation. Similar results of irreversibly adsorbed tin on Pt single crystal electrodes were also reported by Campbell et al. [20].

In order to investigate further the surface modification process of Sn adatoms on Pt single crystal electrodes, three basal planes of Pt single crystal, Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) were prepared and modified by IRA Sn adatoms in the present study. The oxidation of ethanol was employed as a probe reaction to test the electrocatalytic properties of the Pt($h\,k\,l$)/Sn electrodes. The study has put emphasis upon the surface processes of Pt single crystal basal planes towards Sn adatom modification, and the surface structure effects in electrocatalysis as well.

2. Experimental

Pt(1 0 0), Pt(1 1 0) and Pt(1 1 1) were prepared in our laboratory through the method described previously [21]. Before each measurement the Pt single crystal electrodes were treated using Clavilier's method [22], i.e. they were annealed in a hydrogen–oxygen flame, quenched with super pure water and transferred into electrochemical cell under the protection of a droplet of pure water. After a well-defined cyclic voltammogram that characterizes the surface structure of each electrode has been recorded in cell 1 that contains 0.5 M H_2SO_4 solutions, the Pt single crystal electrode was immersed in 1 M H_2SO_4 solution containing 10^{-3} M Sn^{2+} ions for 1 min, then rinsed with super pure water and transferred back to cell 1 or cell 2 (perchloric acid solutions) at 0.0 V (vs. SCE). Coverage of IRA Sn adatoms (Sn_{ad}) in saturation adsorption was thus formed and determined. Starting from the saturation coverage of Sn_{ad}, different sub-coverage of Sn_{ad} was obtained by partially stripping Sn_{ad} in cell 1 by applying a votammetry in controlling the upper limit of potential scan (E_u) and the number of potential cycling. The calibration of the designated coverage of Sn_{ad} was then carried out in cell 2, and the electrode was transferred finally into cell 3 that contains ethanol solution for further electrocatalytic study.

The solutions were prepared using Millipore water (18.0 MΩ cm) provided from a Milli-Q Lab apparatus (Nihon, Millipore Ltd.), super pure H_2SO_4 or $HClO_4$, ethanol and $SnSO_4$ of analytical grade. A saturated calomel electrode (SCE) was served as reference electrode. Potentials in this paper were reported versus the SCE scale. The solution was deaerated by bubbling pure N_2 gas before experiment, and kept a flux of N_2 over it during measurements to prevent possible interference of oxygen and impurities from the atmosphere. All experiments were carried out at room temperature around 20 °C.

3. Results and discussion

3.1. Electrochemical characterization of surface modification of Pt(1 1 1), Pt(1 1 0) and Pt(1 0 0) with IRA Sn adatoms

The adsorption and desorption of hydrogen is highly sensitive to the atomic arrangement of Pt single crystal electrodes, and has been conveniently employed to characterize the surface structure of the electrode. It is known that the surface structure of Pt single crystal electrodes remains stable unless a significant amount of oxygen is adsorbed on the surface, and a well-defined structure of Pt single crystal surface can be maintained in 0.5 M H_2SO_4 solution at electrode potentials below 0.75 V.

Fig. 1a shows cyclic voltammograms of Pt(1 1 1) (dot lines, $E_u = 0.75$ V) and the Sn_{ad} modified electrode Pt(1 1 1)/Sn (solid lines, varying E_u) recorded in 0.5 M H_2SO_4 solution. It can observe that the electrochemical adsorption of hydrogen yields a current plateau between −0.20 and 0.0 V, and the sulfate adsorption gives a 'butterfly' peak in the potential region from 0.07 to 0.30 V on bare Pt(1 1 1), signifying a well-defined order structure of Pt(1 1 1). On the Pt(1 1 1)/Sn of saturation adsorption IRA Sn_{ad}, the sulfate adsorption current is completely suppressed, and the hydrogen adsorption is inhibited to a large extent. Along with increasing progressively E_u, two oxidation current peaks appear respectively around 0.33 and 0.60 V in the positive going potential scan (PGPS), attributing respectively to adsorption of hydroxyl species [16,18] and Sn_{ad} oxidation. The desorption of hydroxyl species in the negative-going potential scan (NGPS) gives rise to a sharp current peak near 0.30 V with E_u at 0.45 V, while the reduction of oxidized Sn_{ad} adatoms occurs in sev-