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Sb 在 Au 电极上不可逆吸附的电化学过程

吴启辉^{1,*} 甄春花² 周志有² 孙世刚^{2,*}¹厦门大学物理系, 福建 厦门 361005; ²厦门大学化学系物理化学固体表面国家重点实验室, 福建 厦门 361005)

摘要: 用电化学循环伏安法和电化学石英晶体微天平(EQCM)技术研究了 Sb 在 Au 电极上不可逆吸附的电化学过程. 研究表明, 在-0.25 V 到 0.18 V(*vs* SCE)范围内, Sb 可在 Au 电极上稳定吸附, 并且在 0.15 V 附近出现特征氧化还原峰. 根据 EQCM 实验数据, 在电位 0.18 V 时, Sb 在 Au 电极上的氧化产物是 Sb₂O₃; 同时 Sb 的吸附阻止了电解液中阴离子和水在 Au 电极上的吸附. 当电极电位超过 0.20 V 时, Sb₂O₃ 会被进一步氧化成 Sb⁵⁺化合物, 同时逐渐从 Au 电极表面脱附.

关键词: 电化学石英晶体微天平; Sb 吸附; Au 电极

中图分类号: O646; O647

Electrochemical Behavior of Irreversibly Adsorbed Sb on Au Electrode

WU Qi-Hui^{1,*} ZHEN Chun-Hua² ZHOU Zhi-You² SUN Shi-Gang^{2,*}¹Department of Physics, Xiamen University, Xiamen 361005, Fujian Province, P. R. China; ²State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, Fujian Province, P. R. China)

Abstract: The electrochemical processes of irreversibly adsorbed antimony (Sb_{ad}) on Au electrode were investigated by cyclic voltammetry (CV) and electrochemical quartz crystal microbalance (EQCM). CV data showed that Sb_{ad} on Au electrode yielded oxidation and reduction features at about 0.15 V (*vs* saturated calomel electrode, SCE). EQCM data indicated that Sb_{ad} species were stable on Au electrode in the potential region from -0.25 to 0.18 V (*vs* SCE); the adsorption of Sb inhibited the adsorption of water and anion on Au electrode at low electrode potentials. Sb₂O₃ species was suggested to form on the Au electrode at 0.18 V. At a potential higher than 0.20 V the Sb₂O₃ species could be further oxidized to Sb(V) oxidation state and then desorbed from Au electrode.

Key Words: EQCM; Sb adsorption; Au electrode

Much attention has recently been paid to electrocatalysis caused by the deposition of foreign atoms (such as Sb^[1,2], Sn^[3], and Bi^[4]) on a Pt or Au electrode of which coverage is less than unity. Currently, two basic methods (underpotential deposition and immersion deposition) are used to form atomic monolayers of various metals on electrode surfaces. The modified metallic layer prepared with the immersion deposition has been emphasized^[5-7], because the surface coverage of the deposited species can be easily controlled by the immersion time and the bulk concentration of the adsorbing species. Recently, many literatures have reported the electrochemical behavior of Sb_{ad} on

Au electrodes based on CV and electrochemical scanning tunnel microscopy (STM) data^[2,8-11]. The existence of oxygenated species of the adatoms has been found with the voltammetry. But the detailed oxidation processes and the effect on the adsorption of water and anions have not yet been examined. In order to better understand the electrochemical properties of the modified electrodes, it is necessary to investigate the electrochemical behavior of foreign atoms on electrodes.

The electrochemical quartz crystal microbalance (EQCM) is a powerful method that can measure the change in interfacial mass due to the adsorption/desorption on/from an electrode^[12,13]; com-

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*Corresponding author. Email: qihui_wu@xmu.edu.cn, sgsun@xmu.edu.cn; Fax: +86592-2183047.

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binning with the electrochemical data, the adsorption/desorption species on/from the electrode surfaces could be clarified^[1]. Previous studies on various systems have showed the utility of this method for revealing the surface process of the electrodes^[14-17]. We have reported previously a new aspect of the surface electrochemical process of irreversibly adsorbing Sb on Pt electrode^[1], and confirmed that the redox reaction of Sb_{ad} at potentials below 0.50 V (*vs* SCE) involves a three-electron process. In this article, we present the results concerning the electrochemical behavior and surface processes of Sb adatoms on Au electrode.

1 Experimental

A QCA-917 quartz crystal analyzer (SEIKO EG&G) interfaced with an XHD-II potentiostat (Xiamen University, China) and a microcomputer were used both for electrochemical measurements and simultaneous measurements of resonant frequency of the quartz crystal. An AT-cut quartz crystal of $f_0=9$ MHz covered on both sides with Au film (Model QA-AM9-Au, SEIKO, EG&G) was used as working electrode. The surface area of Au electrode was approximately 0.2 cm². Before the irreversible deposition of Sb and any CV measurements, the Au electrodes were cleaned in 0.1 mol·L⁻¹ HClO₄ solution *via* electrochemical potential scans from -0.25 to 1.35 V (*vs* SCE) until obtained the standard CV curves. The EQCM signal was recorded as Δf ($=f-f_0$) *versus* electrode potential. The relationship between the surface mass change (Δm) and the resonant frequency change (Δf) for an EQCM electrode is given by Sauerbrey equation^[18],

$$\Delta f = -C_f \Delta m \quad (1)$$

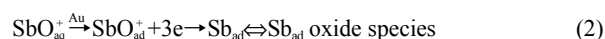
where C_f is the sensitivity factor of the quartz crystal employed in the measurement. The f_0 of quartz crystal for an EQCM electrode in solution was measured at 8.88 MHz, which yielded a $C_f=0.178 \times 10^9$ Hz·g⁻¹·cm²^[1,17]. A platinum foil and SCE were used as the counter and the reference electrodes, respectively. All potentials were quoted *versus* the SCE scale.

The solutions were prepared from ultrapure water (>18 MΩ·cm⁻¹) purified through a Milli-Q Lab system (Nihon Millipore Ltd.), super pure perchloric acid (HClO₄) and Sb₂O₃ (Aldrich, 99.99%). The solution containing Sb ions was obtained by saturating 0.1 mol·L⁻¹ HClO₄ solution with Sb₂O₃ and the concentration of Sb ions was measured to be approximately 1 mmol·L⁻¹.

The irreversible Sb adsorbed Au electrodes (Au/Sb_{ad}) were prepared by immersing a clean Au electrode, protected with oxygen free HClO₄ droplet during transfer, in 1 mmol·L⁻¹ Sb₂O₃+0.1 mol·L⁻¹ HClO₄ solution for 10 min without any potential control. Before the Au/Sb_{ad} electrodes were fixed on the EQCM cell for CV and EQCM measurements, they were rinsed with pure water for three times to remove the solution sticking on the electrode surface. The electrolytes (0.1 mol·L⁻¹ HClO₄) were purged with pure nitrogen gas for at least 10 min at open circle potential (about 0.05 V (*vs* SCE)) before electrochemical and EQCM measurements. All experiments were carried out at room temperature around 20 °C.

2 Results and discussion

Fig. 1 shows the stable scan of CVs (a) and frequency change (Δf) (b) of Au and Au/Sb_{ad} electrodes in 0.1 mol·L⁻¹ HClO₄ solution between -0.25 V and 0.18 V. In Fig. 1(a), no any (or very small) reduction and oxidation peaks are found on Au electrode. While, a broad oxidation and reduction couple in the potential range between 0.00 V and 0.20 V is observed on Au/Sb_{ad} electrode, which could be attributed to the oxidation and reduction of Sb species on Au electrode^[2,8-11]. The appearance of the redox features confirms the irreversible adsorption of oxygenated Sb(III) species during the contact of Au electrode with the Sb₂O₃-saturated solution. Solution chemistry suggests that the dominant form of Sb₂O₃ in acidic solution (pH=0-1) is oxygenated Sb(III) (SbO⁺)^[19]. The interaction between SbO⁺ and Au electrode is so strong that the adsorbed Sb species remain on the surfaces even after rinsing with water. The same oxidation and reduction charges have been measured from the CV curve in Fig. 1(a) after correction of the double-layer background on Pt/Sb_{ad} electrode. This suggests that Sb_{ad} species is stable on Au surface in this potential range. The surface electrochemical processes could then be described as follows:



In Fig. 1(b), the behaviors of Δf of Au and Au/Sb_{ad} electrodes are quite different. On Au electrode the frequency keeps decreasing in the positive going potential sweep (PGPS), although without any intensive current peaks found in the CV curve. According to Eq. (1), the decrease in Δf indicates the increase of elec-

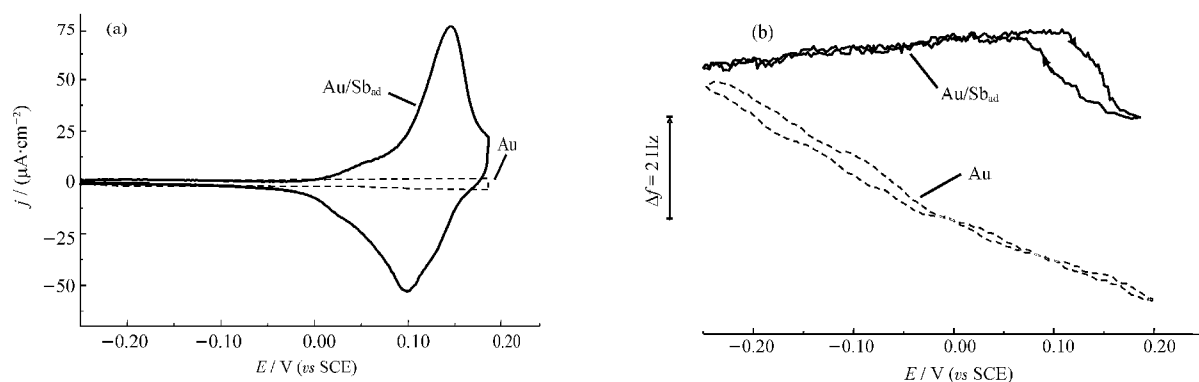


Fig. 1 The stable cyclic voltammogram (a) and frequency change (b) of Au and Au/Sb_{ad} electrodes in 0.1 mol·L⁻¹ HClO₄ solution between -0.25 V and 0.20 V at a sweep rate of 50 mV·s⁻¹

trode surface mass. The Au electrochemical process at double-layer region in acid solution has already been discussed. At the beginning, Bruckenstein and Shay^[20] ascribed the increase of surface mass to the adsorption of anions existing in the solution, but later on, Gordon *et al.*^[21] thought that anions would not adsorb on Au surface at this potential range, the increase of surface mass was then due to the adsorption of water. Gordon^[21], Conway^[22] *et al.* have found that the oxidation behaviors of Au electrode were quite different in different acid solutions, then indicated that there was strong interaction between Au electrode and the anions in the solutions. Based on previous studies, we could therefore propose that in the double-layer region, the main electrochemical process of Au electrode is partially discharging adsorption of the acidic anions (ClO_4^-) on Au surface with co-adsorption of water molecular *via* hydrogen bonding^[23]. In the negative going potential sweep (NGPS), the Δf increases again and returns to the beginning point due to the desorption of anions and water from the electrode surface. This result indicates that the Δf change on Au surface is reversible within this potential window. On Au/Sb_{ad} electrode, in the PGPS, the frequency increases slightly at potential lower than 0.11 V, and then there is a dramatic drop at potential higher than 0.11 V. In the NGPS, the frequency increases at the reduction potential region of Sb_{ad} and quickly matches reversibly together with that in PGPS. The increase of Δf in the potential range between -0.25 V and 0.11 V indicates the decrease of electrode mass, and also suggests that water and anions in the solution could not adsorb on Au/Sb_{ad} electrode in this potential region, which is similar to that of Pt/Sb_{ad} electrode^[1]. The reason for the decrease in electrode mass is still unknown to us, but it could probably be assumed due to the reduction of SbO^+ adsorbed on the Au surface at low electrode potentials, which pushes away of H_3O^+ from the Au/Sb_{ad} surface with increasing electrode potential. The decrease of Δf in the PGPS could be assigned to the oxidation of Sb_{ad}; more surface mass due to the adsorption of oxygen ions or OH^- species is expected. In the NGPS, the increase of Δf is due to the reduction of surface Sb_{ad} oxides. The electrode mass decreases due to the desorption of oxygen ions or OH^- species, which adsorb on the surface during the oxidation of Sb_{ad}. In Fig. 1(b), it is worthwhile to note that the frequency completely returns to the

beginning value on Au/Sb_{ad} electrode after a complete potential cycling, which confirms that the surface mass does not change. This suggests again that Sb_{ad} species is stable on Au electrode in this potential region even under oxidation and reduction reactions.

The change of Δf due to the Sb_{ad} oxidation has been measured as 1.75 Hz, which indicating an increase of $9.8 \text{ ng} \cdot \text{cm}^{-2}$ in electrode surface mass. Combined with the Faraday's laws, the Eq. (1) can be arranged as,

$$M/n = (F \Delta f) / (C_t \Delta Q) \quad (3)$$

where F and M represent the Faraday constant and the molar mass of the adsorbing species, respectively; n is the charge number of the adsorbing species; and ΔQ is the total oxidation charge for the oxidation reaction that has been calculated to be $114.0 \mu\text{C} \cdot \text{cm}^{-2}$ from the CV curve in Fig. 1(a). The value of M/n is peculiar to a substance adsorbing on the electrode, which is the power evidence to determine the species adsorbing on electrode surface. An M/n value of 8.3 is obtained from our experimental data according to Eq. (3). The value is very close to O^{2-} species, whose M/n is 8, while it is far away from OH^- species, whose M/n is equal to 17. It is therefore reasonable to suggest that O^{2-} species is adsorbed on the electrode surface during the oxidation of Sb_{ad}. The change of surface mass is $9.8 \text{ ng} \cdot \text{cm}^{-2}$, which means that the amount of $0.61 \text{ nmol} \cdot \text{cm}^{-2}$ of O^{2-} is adsorbed onto electrode surface. A three-electron transfer reaction was reported at this potential region for Sb_{ad} oxidation reaction^[2,8-11]. According to oxidation (or reduction) charge (ΔQ), the amount of Sb_{ad} can be easily evaluated at $0.39 \text{ nmol} \cdot \text{cm}^{-2}$. Thus, the molar ratio of Sb_{ad} and O^{2-} is close to 2/3, it can be thus confirmed that the surface Sb_{ad} oxide species is Sb_2O_3 .

Shown in Fig. 2 are the first scan of CVs (a) and the Δf (b) of Au and Au/Sb_{ad} electrodes in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{HClO}_4$ solution in the potential range from -0.25 to 1.35 V. In Fig. 2(a), the oxidation of Au electrode is roughly started at 0.65 V with the feature A0 and followed by two stronger oxidation peaks (A1 and A2) at higher potentials. In the NPGS, a sharp reduction peak is found at about 0.86 V. On Au/Sb_{ad} electrode, two oxidation peaks for Sb_{ad} are found; the first is at 0.15 V, which has been discussed in Fig. 1(a), the second one is broad with peak maximum at about 0.32 V. It indicates that at high potential region Sb_{ad}³⁺ will be further

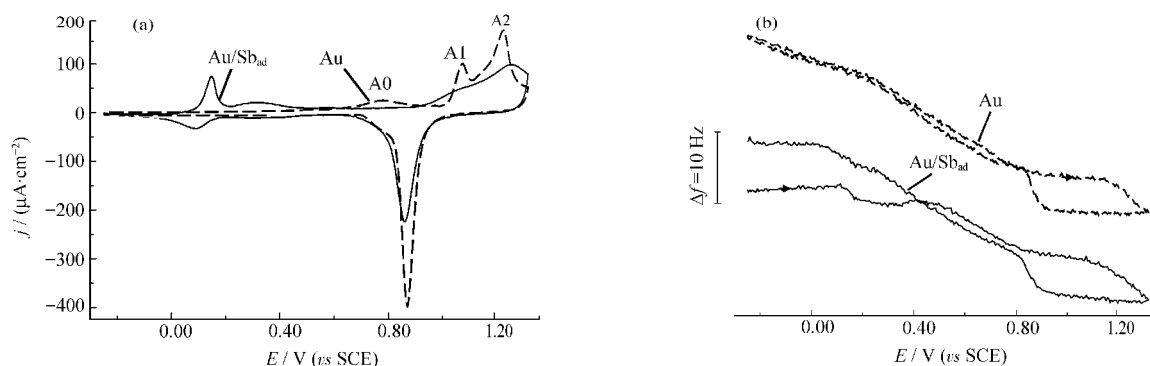


Fig. 2 The first cyclic voltammograms (a) and frequency changes (b) of Au and Au/Sb_{ad} electrodes in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{HClO}_4$ solution between -0.25 V and 1.35 V at a sweep rate of $50 \text{ mV} \cdot \text{s}^{-1}$

oxidized. The ratio of the oxidation charge for the two peaks has been calculated to be 3/2. Because the total amount of Sb_{ad} is the same for these two oxidation reactions, if the first reaction is three-electron transfer^[8-11], the second one should thus be two-electron reaction, which supports that at high electrode potentials Sb_{ad} can be further oxidized to +5 oxidation state. The A0 oxidation peak on Au electrode is completely prohibited on Au/ Sb_{ad} electrode. Moreover the current intensities of peaks A1 and A2 are decreased due to the adsorption of Sb. Simultaneously, in the NGPS, the intensity of reduction peak for Au electrode reduces. It is interesting to see that after electrode potential cycling to high potential, the intensities of the two Sb_{ad} reduction peaks are both smaller than their oxidation peaks, implying that the amount of Sb_{ad} on Au surface decreases. This indicates that after oxidized to +5 oxidation state, the Sb_{ad} species would not be stable on Au surface and partially desorbs.

In Fig 2(b), it is clear that the Δf decreases with the potential increase from -0.25 to 0.82 V due to adsorption of water and anions on Au electrode^[21,23]. It is confusing that in the beginning region of Au oxidation potential, the decrease rate of Δf becomes much slow, and then a big drop is found at about 1.15 V. These results indicate the complexity of Au oxidation process. Gordon^[21], Conway^[22] *et al.* have reported that in the acid solutions, at the beginning of Au oxidation, the adsorbed anion would be gradually removed from the Au surface, at the same time more oxygen or OH^- species would adsorb on electrode surface. Our EQCM results seem to support their hypothesis due to the very slow Δf decrease at the potential range from 0.82 to 1.15 V. In the NGPS, corresponding to the CV curves, no any frequency change is observed when potential scans from 1.35 to 0.75 V. A big jump is found due to the reduction of Au surface at 0.85 V and quickly return to the value in PGPS at 0.75 V. After a complete potential cycling, no any frequency change is observed. On Au/ Sb_{ad} electrode, the Δf slowly increases from -0.25 to 0.11 V, and then decreases due to the oxidation of Sb_{ad} until 0.39 V. It has been noted that the Δf decreases much slowly in the second Sb_{ad} oxidation potential range, and even increase is observed just after the second Sb_{ad} oxidation potential. These phenomena are probably due to the partial removal of Sb(V) oxides from Au surface during/after the oxidation of Sb_{ad} to +5 oxidation state. When potential is higher than 0.5 V, the frequency change on Au/ Sb_{ad} electrode is similar to that on Au electrode, this implies that water and anions in solution can adsorb onto Au/ Sb_{ad} electrode again after partial removal of Sb_{ad} . After a complete potential cycling, the Δf has been increased about 6.67 Hz, which means that the surface mass decreases about 37.33 $\text{ng} \cdot \text{cm}^{-2}$ due to desorption of Sb_{ad} at high electrode potentials.

3 Conclusions

The EQCM technique is a convenient method to study the surface processes and electrochemical behavior for Sb modified Au electrodes. In the present article, the quantitative results for

the Sb_{ad} on Au electrode have been obtained by combination of CV and EQCM data. It has been suggested that Sb_{ad} species is stable on Au electrode under oxidation-reduction reactions when potential is lower than 0.18 V (*vs* SCE). The surface Sb_{ad} oxide species in this potential region is suggested mainly as Sb_2O_3 . At potentials higher than 0.20 V the Sb(III) can be further oxidized to Sb(V) species and then progressively desorbs from Au electrode surface. Further, EQCM data imply that the adsorption of Sb will strongly affect the electrochemical process of Au by inhibiting the adsorption of water and anions in the solution. The results may be useful for the further study of the electrochemical catalysis of Sb modified Au electrodes.

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