

A New Method to Control the Coverage of Irreversibly Adsorbing Sb on Au Electrode

Ho Ryul Ryu and Choong Kyun Rhee

Department of Chemistry, Chungnam National University, Taejon 305-764, Korea

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We report on the development of a new method to control the coverage of a metal film prepared with immersion method. An Sb species in solution adsorbed irreversibly at an open circuit potential (~ -0.2 V) as an oxygenous Sb(III) on a clean Au electrode, and the adsorbates showed voltammetric features in the potential range from 0.1 V to -0.4 V. The full coverage of the Sb adsorbates was ~ 0.45 . On the contrary, the Sb species in solution did not adsorb at all on iodine-covered Au electrode surfaces, when the iodine coverages were more than 0.25. As the iodine coverage decreased below 0.25, however, the irreversible adsorption of Sb took place and the coverage of Sb increased accordingly. This electrochemical behavior has been interpreted as the penetration of the adsorbing Sb species in solution through open spaces among the iodine lattices of coverages less than 0.25. With the manipulation of the iodine coverage, the controllable range of Sb coverage was from 0 to 0.45, *i.e.* the full coverage of Sb. In addition, the reversible deposition of Sb on an iodine-saturated Au electrode with voltammetric scan has been observed, which is contrasted with the adsorptive behavior of Sb on the clean Au electrode.

Introduction

One of the key issues in the current electrochemistry is the deposition of ultrathin metal films on electrodes to modify the electronic and/or steric properties of the electrode surfaces. Such a modification is very important in various technical aspects, particularly in fuel cell technology. For example, the deposition of numerous metal atoms onto Pt electrode surfaces enhances the catalytic activity in the oxidation of small organic molecules.^{1,2}

There are two electrochemical methods to deposit metal ultrathin films on electrode surfaces: underpotential deposition (UPD) method³ and immersion method.^{4,5} In the UPD method, metal ions in solution are reversibly reduced to a metallic atomic layer on a metal electrode of different element. In the immersion method, after contacting a metal electrode with a solution of a metal species to be deposited, an atomic layer of the metal ionic species is formed *via* irreversible adsorption. Since the irreversibly adsorbed species generally retains its oxidation states as in solution, an electrochemical reduction of the adsorbates is needed to obtain metallic films.⁵

In a practical point of view, the immersion method has received more attention than the UPD method.⁷ The reason is that the metallic layers deposited with the former method are much more stable, due to their irreversible nature, than those with the latter method. Such an attention resulted in many recent studies on the metallic layers prepared with the immersion method, regarding electrocatalytic modifier.⁸⁻¹¹

In the modification of electrocatalyst surfaces, the manipulation of metal adsorbate coverages is instrumental, because the catalytic activities of modified electrodes show dependence on the modifier coverages.^{8-12,14-16,18} In the immersion method, two techniques have been conventionally utilized to control metal adatom coverage: one is to control the contacting time and solution concentration for irreversible adsorption, and the other is to control the ox-

idative stripping time and potential of irreversibly adsorbed layers.

In this paper, demonstrated is a new method to control the coverages of a metal film prepared with the immersion method. The model system is irreversibly adsorbing Sb on a polycrystalline Au electrode. The basic idea of our method is the steric hindrance of preadsorbed iodine on Au surfaces to the irreversible adsorption of Sb. In conjunction with the new method, the adsorptive behavior of Sb on clean and iodine-covered Au electrodes is compared.

Experimental

A thin layer electrochemical cell (TLE),² as shown in Figure 1, was exclusively used in this work. The purpose of

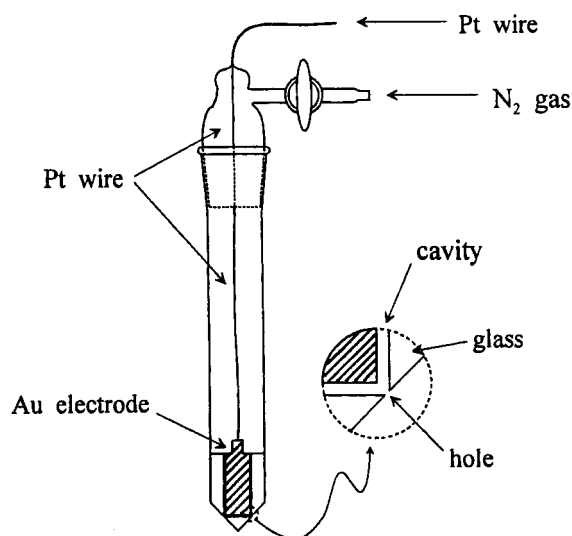


Figure 1. A schematic of the thin layer electrochemical (TLE) cell.

the TLE was fast change of the electrolytic solution confined in the cavity between the working electrode and the glass wall of the cell. By purging the cell with N_2 gas, the solution in the cavity was expelled out, while the electrode was kept in the inert atmosphere. When purging was stopped, the cavity became filled with the solution around the cell by capillary action. A series of operations to change the solution in the cavity is called "rinse", thereafter. The volume of the cavity was measured to be $6.92\ \mu\text{L}$ using the coulometry of $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple.²⁹

The working electrode used in this work was a polycrystalline Au cylinder (99.99%). A clean surface of the Au electrode was routinely prepared with hydrogen flame annealing, HNO_3 treatment and oxidation/reduction cycles. The surface area of the working electrode was measured to be $1.14 \pm 0.01\ \text{cm}^2$ with the iodine adsorption method.²⁹

Electrochemical measurements were carried out using a home-built potentiostat. The reference electrode used in this work was Ag/AgCl ($[\text{Cl}^-]=10^{-3}\ \text{M}$), but the potential scale reported in this paper is against Ag/AgCl ($[\text{Cl}^-]=1\ \text{M}$). All cyclic voltammograms were taken at a scan rate of $5\ \text{mV}/\text{sec}$. All the solutions were made with ultrapure water ($>18\ \text{M}\Omega/\text{cm}$, Barnsted), Sb_2O_3 (Aldrich), NaClO_4 (Aldrich), HClO_4 (Merck) and CH_3COONa (Merck).

Results and Discussion

Electrochemical Behavior of Sb on Clean Au Electrode. Figure 2(a) shows a typical cyclic voltammogram of a clean Au electrode in $1\ \text{M}\ \text{NaClO}_4/200\ \text{mM}$ acetate buffer ($\text{pH}=4$) solution (hereafter, clean solution). A contact between the clean Au electrode and $0.25\ \text{mM}\ \text{Sb}_2\text{O}_3/1\ \text{M}\ \text{NaClO}_4/200\ \text{mM}$ acetate buffer ($\text{pH}=4$) solution (hereafter, Sb solution) was made, for immersion, by filling up the cavity with the Sb solution at an open circuit potential ($\sim 0.20\ \text{V}$) for 2 minutes and the rinsing procedure with the Sb solution was repeated several times. Then, the cavity was rinsed

several times with the clean solution, and the cyclic voltammogram as presented with the solid line in Figure 2(b) was obtained. Although there was no Sb species in the cavity, the voltammetric features in the potential range from $0.10\ \text{V}$ to $-0.40\ \text{V}$ were discernible. When a clean Au electrode was rinsed with the clean solution, no peak was observed in the particular potential range. These observations indicate that an amount of an Sb species remains on the electrode surface even after the final rinse with the clean solution.

This electrochemical behavior of Sb on the Au electrode can be interpreted in terms of a strong interaction between an Sb species in solution and the Au electrode surface. When a clean Au electrode contacts with the Sb solution, the Sb species in solution adsorbs strongly and the adsorbates remain, even after rinsing, on the electrode surface. In the first cathodic scan from the open circuit potential, the adsorbed Sb species is reduced, and in the following anodic scan, the reduced Sb species is oxidized to the originally adsorbed state. In fact, the voltammetric features in the potential range from 0.1 to $-0.4\ \text{V}$ were persistent with cyclic voltammetric scans when the anodic end of the scan was less than $+0.2\ \text{V}$.

The unique way to remove the strongly adsorbed Sb is an oxidative resorption. When the anodic scan was expanded to a potential more than $+0.2\ \text{V}$, observed was an oxidation current concomitant with the Au surface oxidation current (not shown here). In the following cathodic scan, only reduction peaks related to the Au surface oxide and the strongly adsorbed Sb appeared. Furthermore, the reduction charge of the Sb adspecies diminished and its decreased amount depended on the oxidation time and potential. These observations reveal that the adsorbed Sb oxidatively desorbs into solution and that the soluble Sb species of higher oxidation state is not subject to any electrochemical reduction.

Based on the observations so far, the adsorptive behavior of the Sb species under study can be classified as an irreversible adsorption. The reason for the classification is that the most distinguishing characteristic of the irreversible adsorption is the uniqueness of oxidative resorption in removing the adspecies, as exemplified with S and I on Pt.^{25,26} To our knowledge, the irreversible adsorption of metal species on Au electrode surfaces are rarely studied, while the phenomena of various metal species are very well-known for Pt electrodes.⁷⁻²¹

The chemical nature of the irreversibly adsorbed Sb species is best estimated to be an oxygenous Sb(III). In this work, the voltammetric features of the adsorbed Sb species on the Au electrode showed the pH dependence of $\sim 60\ \text{mV}/\text{pH}$. Identical pH dependence of the irreversibly adsorbed Sb on Pt(111) and Pt(100) were observed.⁷ This observation was interpreted to indicate that the adspecies contains oxygen atom(s) and that an equal number of hydrogen ions and electrons are involved in the rate-determining step. Considering the oxidation and reduction of the adsorbed Sb, it is concluded that the oxidation state of the Sb adsorbate is III because the possible oxidation states of Sb are 0, III and V. Accordingly, the following reaction scheme is proposed for the irreversible adsorption of Sb on clean Au electrode.

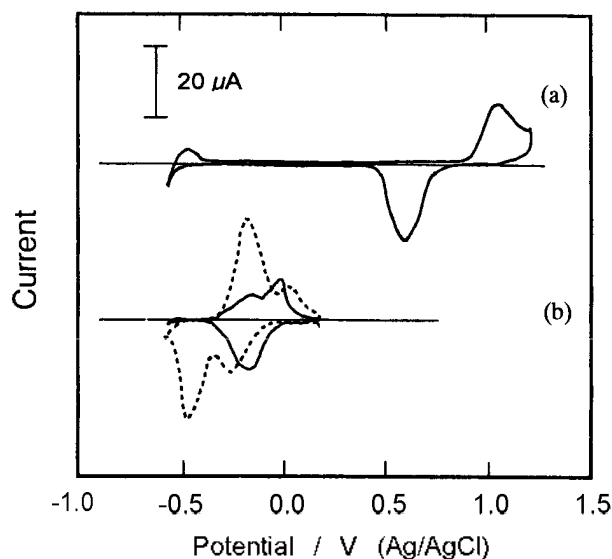
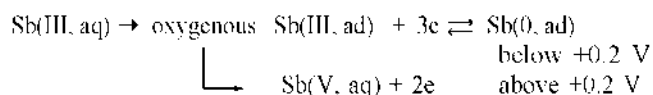


Figure 2. Cyclic voltammograms of (a) a clean Au electrode in the clean solution and (b) the Au electrode after contacting with the Sb solution (—): the Au electrode in the Sb solution(---).



The reduction charge of the irreversibly adsorbed Sb layer was $272 \mu\text{C}/\text{cm}^2$, which corresponds to the coverage of ~ 0.45 (defined as ratio of the number of Sb atoms to that of Au atoms on the electrode surface).

The dashed line shown in Figure 2(b) is a typical cyclic voltammogram of the Au electrode in the cavity filled with the Sb solution. Clearly, two reduction peaks at -0.27 V and -0.48 V were observed. When the cavity was rinsed with the clean solution at 0.2 V , only the redox process related to the irreversibly adsorbed Sb layer was observed. The disappearance of the peak at -0.48 V indicates that the bulk metallic Sb layer deposits from the solution on the first metallic Sb layer which is formed via the reduction of the irreversibly adsorbed layer. Under such conditions, the reduction peak of the irreversible Sb adsorbates shifted from -0.20 V to -0.27 V .

Electrochemical Behavior of Sb on iodine-Covered Au Electrode. Figure 3(a) is the cyclic voltammogram of an iodine-saturated Au electrode in $1 \text{ M NaClO}_4/200 \text{ mM acetate buffer (pH=4)$ solution, *i.e.* the clean solution. The adsorption of iodine was carried out by contacting a clean Au electrode with 1 mM NaI solution at an open circuit potential ($\sim 0.1 \text{ V}$) for 2 minutes. A brief description of the electrochemical behavior of iodine on Au is as follows²¹: The oxidative stripping of the adsorbed iodine to iodate (IO_3^-) started at 1.0 V with the surface oxidation of the Au electrode. The cathodic peak at 0.65 V corresponds to the reduction of the surface oxide and the two

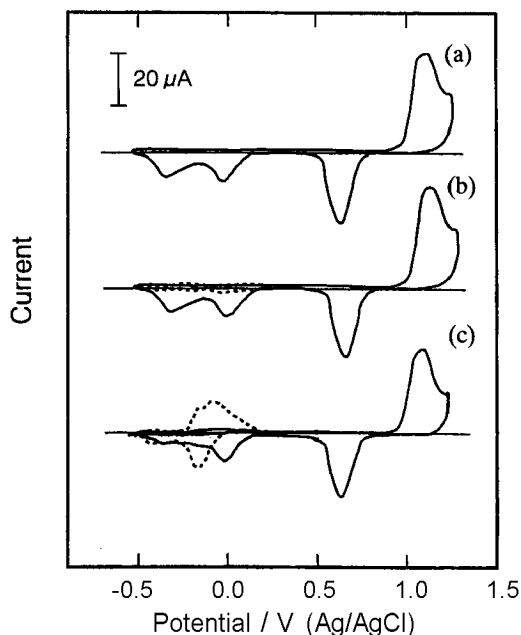


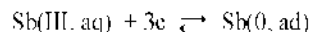
Figure 3. Cyclic voltammograms of an iodine-saturated Au electrode (a) in the clean solution, (b) in the clean solution, after contacting at open circuit potential with the Sb solution, with the potential range between -0.5 V and -0.4 V (---); with the potential range between -0.5 V and -1.3 V (-), and (c) in the Sb solution (-); in the clean solution after rinsing at $+0.2 \text{ V}$ (---).

peaks at 0.0 V and -0.3 V do to the reductive adsorption of iodate to iodine. The full coverage of iodine was measured to be ~ 0.45 .

The adsorptive ability of the Sb species in solution on the iodine-saturated Au electrode surface was examined. A contact between the Au electrode fully covered with iodine and the irreversibly adsorbing Sb species was made by filling up the cavity with the Sb solution without potential control. Then, the cavity was rinsed with the clean solution so that there was no Sb species in the cavity. The dashed line in Figure 3(b) was obtained in the potential range between -0.5 V and $+0.4 \text{ V}$. Clearly, there is no redox process in the studied potential range, which indicates that any Sb species does not exist on the iodine-saturated Au surface. When the voltammetric potential range was expanded, only the electrochemical processes related with the preadsorbed iodine were observed (the solid line in Figure 3(b)). These observations reveal that the Sb species in solution does not adsorb on the iodine-saturated Au electrode, but does on the clean one. The reason for this behavior is that the preadsorbed iodine layer keeps the Sb species in solution from contacting with the electrode surface.

In spite of the inability for the Sb species to adsorb on the iodine-covered Au electrode, a metallic layer of Sb can be deposited electrochemically on the surface. The dashed line in Figure 3(c) is the cyclic voltammogram of the iodine-covered Au electrode in the Sb solution, which is nearly identical with that of the irreversibly adsorbed Sb layer. A plausible picture of the situation is that the metallic Sb layer is deposited on the Au electrode surface but under the adsorbed iodine layer, or I/Sb/Au . Such a sandwiched structure of a metal monolayer was experimentally verified for the underpotential deposition of Ag and Pb on iodine-saturated Pt electrode surfaces.²⁶⁻²⁸ It is noteworthy, also, that the peak at -0.47 V became small although there was enough Sb species in the cavity for the bulk deposition. Actually, the reduction charge from 0.0 V to -0.5 V was $275 \mu\text{C}/\text{cm}^2$, which is close to the full coverage of the irreversibly adsorbed Sb on the clean Au electrode surface. This phenomenon implies that the iodine adatoms prevent the bulk deposition of Sb and that they alter the deposition potentials of Sb species.

More interesting is that the deposition behavior of Sb becomes chemically reversible in the presence of iodine. After rinsing the cavity with the clean solution at 0.2 V , only the current peaks related to the adsorbed iodine were observed as shown with the solid line in Figure 3(c). This observation indicates that the oxidation product of the metallic Sb on the Au surface and under the adsorbed iodine is soluble, which is contrasted with the irreversibly adsorbed, thus insoluble one on the clean Au surface. On the iodine-saturated Au electrode, the electrochemical behavior of the Sb species in solution can be presented as follows:



Controlling the Coverage of the Irreversibly Adsorbing Sb. A new idea to control the coverage of the irreversibly adsorbing Sb is illustrated in Figure 4. When an amount of the iodine on the iodine-saturated Au electrode is desorbed to a submonolayer coverage, the distances between the adsorbed iodine atoms will be increased unless

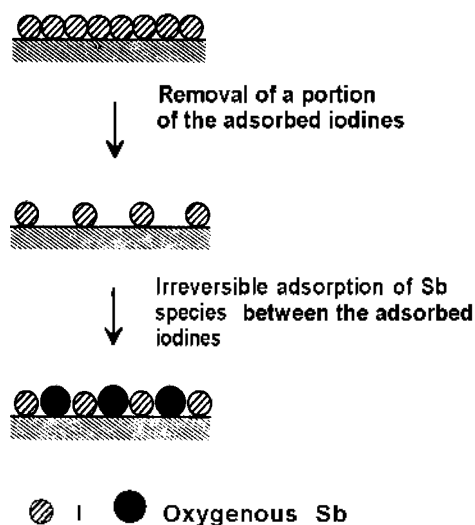


Figure 4. A schematic presentation of a new method control the coverage of irreversibly adsorbing Sb on Au electrode.

the islands of iodine are formed. Then, open spaces will be formed among the ad-structure of iodine so that only the Au atoms not covered with iodine are exposed to the surrounding solution through the open spaces. If the open site is spacious enough for the Sb species to contact the Au electrode, then the irreversible adsorption of Sb will take place. By controlling the distribution and/or size of the open sites with the coverage of iodine, the surface amount of the irreversibly adsorbed Sb can be manipulated.

The irreversible adsorption of Sb among the preadsorbed iodine of 0.15 coverage is demonstrated in Figure 5. To control the coverage of iodine, there are two possible methods to desorb the iodine from the iodine-saturated Au surface¹⁰: one is the oxidative resorption of the adsorbed iodine to iodate and the other is the reductive resorption of the adsorbed iodine to iodide. In this work, the coverage of iodine was manipulated with the oxidative resorption. Specifically, an iodine-saturated Au electrode was held at +1.0 V for 15 seconds for the oxidation of the adsorbed iodine and the cavity was flushed to halt the oxidation. Then, the coverage of the remaining iodine was confirmed with the dashed line in Figure 5. The cavity, in which there was the Au electrode with the adsorbed iodine of the pre-determined amount, was filled with the Sb solution for 2 minutes without potential control to allow the adsorption of Sb. After rinsing the cavity with the clean solution, the solid line in Figure 5 was obtained, which clearly shows the presence of the irreversibly adsorbed Sb. The coverage of the Sb adsorbed in this way was 0.16, which is below the full coverage of 0.45.

The coverage of the irreversibly adsorbed Sb depends on that of the preadsorbed iodine as shown in Figure 6. While the adsorption of Sb is negligible above 0.25 coverage of iodine, the amount of Sb is increasing below the particular coverage. This observation clearly demonstrates that the coverage of Sb is possible to manipulate from 0 to the full monolayer coverage with the adsorbed iodine. In addition, such a coverage dependence implies that there is a critical size of the space formed among the iodine surface structure

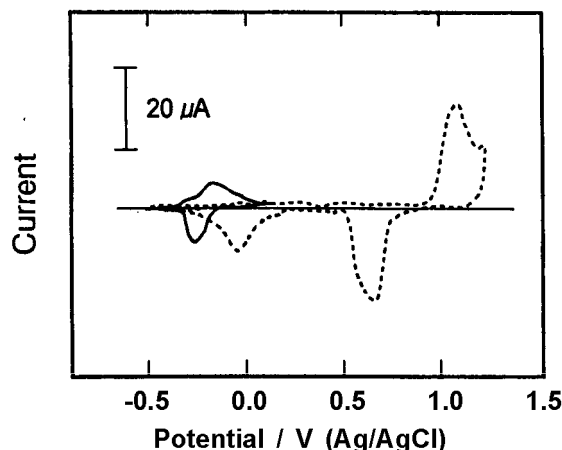


Figure 5. Cyclic voltammograms of the Au electrode with adsorbed iodine of 0.15 coverage before (---) and after contacting with the Sb solution (-).

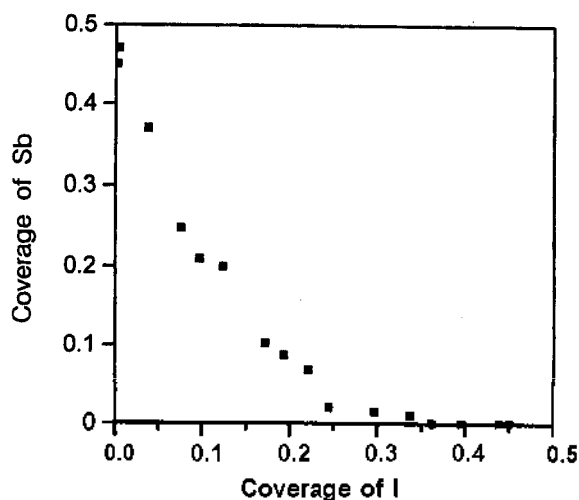


Figure 6. Plot of Sb coverage vs. the preadsorbed iodine coverage on Au electrode.

for the solution Sb species to penetrate through.

Currently, a molecular level investigation using in-situ scanning probe microscope technique is in progress to scrutinize 2-dimensional structures of irreversibly adsorbing Sb on clean and iodine-covered Au single crystal electrodes.

Conclusion

1. An Sb species in solution adsorbs irreversibly as an oxygenous Sb(III) on a clean Au electrode and the adsorbates show voltammetric features in the potential range from 0.10 V to -0.40 V. The full coverage of the Sb adsorbates is ~0.45 and the only way to desorb the Sb adatoms is oxidation to an Sb(V) solution species.

2. The Sb species in solution does not adsorb on an iodine-saturated Au electrode surface, while one monolayer of Sb reversibly deposits on the particular surface during voltammetric scans.

3. Demonstrated was a new method to manipulate the coverage of the irreversibly adsorbing Sb *via* submonolayers of iodine. The controllable range of the Sb coverage

is from 0 to the full coverage of 0.45.

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