Co-adsorption of Irreversibly Adsorbing Sb and Te on Pt(111)

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Presented is a voltammetric study of co-adsorption of irreversibly adsorbing Sb and Te on Pt(111). When a layer of Sb and Te was formed via simultaneous adsorption, the reduction peak of Te was observed at 0.30 V in the initial cathodic scan. In contrast, sequential adsorption of Sb followed by Te adsorption led to a Te reduction peak at 0.50 V in the initial scan. As the voltammetric scan was continued, in addition, the voltammogram of the simultaneously co-adsorbed layer changed, while that of the sequentially co-adsorbed layer did not. These observations are discussed in terms of formation of a homogeneously mixed layer and a layer consisting of heterogeneously separated domains of Sb and Te. Also, the difference in the adsorption strength of Sb and Te was observed.

Key Words : Pt(111), Sb, Te, Irreversible adsorption, Voltammetry

Introduction

The importance of electrochemically deposited metal layer has been emphasized because of many technical applications. One example is that Ru nano-islands, spontaneously deposited on Pt electrodes, enhance the catalytic activity towards methanol oxidation.[1] In addition, further catalytic enhancement of methanol oxidation has been achieved with mixed layers of Ru, Os and Ir on Pt electrodes.[2] Another example is electrochemical atomic layer epitaxy (ECALE) utilizing surface-limited underpotential deposition to produce compound semiconductors such as CdTe and CdSe.[3,4]

Understanding the formation of metallic layers is important in scientific point of view as well as in technical point of view. Our group has found that on Au(111) and Au(100), underpotential deposition and irreversible adsorption of Sb worked together to reach to a full coverage.[5,6] On Pt(111), a part of the irreversible adsorbed Sb became electrochemically inactive below 0.2 V and the underpotentially deposited Sb turned all the adsorbed Sb inactive below the particular potential.[7] On the other hand, irreversibly adsorbed Te on Pt(111) showed an electrochemical behavior similar to but slightly different from that of Sb.[8,9] Specifically, the irreversibly adsorbed Te became inactive with underpotential deposition of Te, although it did not become inactive by itself. Such a behavior of Te on Pt(111) was proved due to formation of compressed layers of mobile Te atoms.

In this work, we are presenting the voltammetric behavior of Sb and Te irreversibly co-adsorbed on Pt(111). The interaction of Sb and Te depends on the procedure of adsorption, *i.e.* simultaneous adsorption and sequential adsorption. The behavior of co-adsorbed layers of Sb and Te produced in the different ways will be discussed in terms of mobility of the adsorbed atoms and domain formation.

Experimental Section

The Pt(111) single crystal electrodes used in this work were made with the bead method.[10] A Pt wire (diameter = 0.5 mm, Aldrich, 99.99%) was melt in a hydrogen-oxygen flame to form a platinum single crystal bead, and the orientation of the bead was confirmed with a He-Ne laser. For voltammetric experiments, one of the (111) facets was cut and polished to be mirror-like down to an 1/10 micrometer diamond paste, and a meniscus position was maintained. Annealing in a hydrogen flame and quenching in a hydrogen-saturated water led to well-ordered and clean Pt(111) electrode surfaces.

The solutions used in this work were made from water (> 18 $M\Omega\cdot cm^{-1}$, Barnsted), H_2SO_4 (Merck, Suprapur), Sb_2O_3 (Aldrich, 99.99%) and TeO_2 (Aldrich, 99.9995%). The saturation of 0.05 M H_2SO_4 solution with Sb_2O_3 and TeO_2 led to the solutions of each metal ion and the concentrations were measured to be approximately 0.05 mM and 0.14 mM for Sb and Te, respectively.

Voltammetric studies were performed using a conventional three-electrode system, and the reference electrode was a Ag/AgCl electrode contacting a chloride solution of 1.0 M. The potential values reported in this work were as measured with the reference electrode. The voltammetric scan rate was 50 mV/sec.

Results and Discussion

Figure 1 shows the individual cyclic voltammograms of Sb and Te irreversibly adsorbed on Pt(111). The irreversible adsorption was carried out with dipping a Pt(111) electrode into the 0.05 M H_2SO_4 solutions saturated with Sb_2O_3 or TeO_2 without potential control. The adsorption times were 3 min and 15 min for Sb and Te, respectively. Upon taking out the Pt(111) electrode from the solution containing one of the metal ions, the electrode was thoroughly rinsed with water

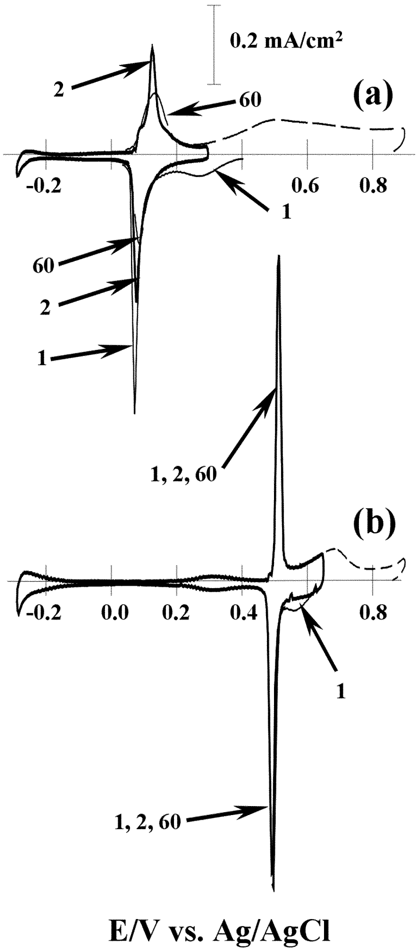

Figure 1. Individual cyclic voltammograms of (a) Sb and (b) Te irreversibly adsorbed on Pt(111) in 0.05 M H_2SO_4 solution. The figures indicate the numbers of the voltammetric cycles. The dashed lines are the stripping voltammograms.

for a few seconds to remove any remnant of the solution. Then, the Pt(111) electrode was transferred to a clean 0.05 M H_2SO_4 solution and a cathodic voltammetric scan was taken from the open circuit potentials (0.50 V for Sb and 0.64 V for Te, respectively). The peaks of Sb appeared at 0.30 V and 0.08 V in the initial cathodic scan (the thin line designated with '1' in Figure 1(a)) and at 0.12 V in the following anodic scan (the thick line designated with '2' in Figure 1(a)), and the charge of the initial cathodic peak was 238 ± 6 μC/cm^2 corresponding to 0.33 ML with the assumption that three electrons were involved. The cyclic voltammogram of the irreversibly adsorbed Sb changed gradually and converged finally to the one designated with '60' in Figure 1(a). Specifically, the coverage of Sb decreased to 0.26 ML in the second cycle and converged to 0.20 ML in the 60th cycle. Such a decrease in charge has been observed and ascribed to the formation of an electrochemically inactive adspecies below 0.20 V.[7] In addition, the irreversibly adsorbed Sb, regardless of its electrochemical activity below 0.20 V, was oxidatively stripped in the potential region above 0.31 V as shown with the dashed line in Figure 1(a). On the other hand, the irreversibly adsorbed Te showed a redox behavior at 0.50 V and the charge under the peak of 4-electron process (236 ± 20 μC/cm^2) corresponded to 0.25 ML (Figure 1(b)).[8] The redox behavior of Te, in contrast to that of Sb, did not change in the 0.05 M H_2SO_4 solution as detailed in ref. 8. The oxidative stripping of the irreversibly adsorbed Te started at 0.58 V as seen with the dashed line in Figure 1(b). An interesting feature common to the initial scans of Sb and Te is that there were cathodic pre-peaks (0.3 V for Sb and 0.55 V for Te) before reduction of the oxygenated metal ions started. These pre-peaks are probably due to capacitive currents resulting from the desorption of adsorbed bisulfate anions on the layers of adsorbed oxygenated metal ions.[7,8]

Figure 2 shows the cyclic voltammograms of a Pt(111) electrode covered with simultaneously adsorbed Sb and Te. The simultaneous adsorption of Sb and Te was carried out in a mixture of the Sb_2O_3-saturated 0.05 M H_2SO_4 solution (50%) and the TeO_2-saturated 0.05 M H_2SO_4 solution (50%) for 15 min without potential control. In the initial cathodic scan (the thin line in Figure 2(a)) from the open circuit potential (0.68 V), a broad and large reduction peak at 0.30 V and a relatively sharp peak at 0.08 V were observed. It is remarkable that in the initial scan in Figure 2(a), the Te reduction peak at 0.50 V, as observed in Figure 1(b), disappeared. In the following anodic scan, however, the oxidation peaks of Sb and Te appeared respectively at 0.08 V and 0.50 V, which were identical with the potential values observed in Figure 1. Due to the presence of the Te oxidation current, the oxygenated Te layer was certainly reduced in the previous cathodic scan, and the charge increase of the peak at 0.30 V upon co-adsorption was clearly related to the reduction of Te. The cathodic shift of the Te reduction peak, therefore, indicates obviously that the oxygenated Te was strongly influenced by the presence of the oxygenated Sb. From the coulometry of the reduction peak of Sb in the initial scan, it was found that the coverage of Sb was 0.19 ML (138 ± 11 μC/cm^2). In addition, no hydrogen charge in the initial scan indicates strongly that the surface was fully covered with Sb and Te.

As the cyclic voltammetric scan continued, the voltammogram changed significantly. Although the redox potentials of Sb and Te were identical to those observed their individual ones, the peaks related to the irreversibly adsorbed Sb became smaller with the simultaneous increase of the hydrogen charge as designated in Figure 2(b). Since the potential range of the voltammetric scan was between –0.29 V and 0.57 V, the observed decrease of the Sb redox charge would result simultaneously from the oxidative stripping of the adsorbed Sb and the formation of the electrochemically inactive Sb adspecies. In the long run, the redox couple of the adsorbed Sb shifted to the potential around 0.2 V. Concomitantly, the peaks of Te became gradually but noticeably sharper without potential shift and the charge under the redox peak increased ultimately to be 189 ± 18 μC/cm^2, or 0.19 ML. The change of the Te redox behavior implies that there was a significant modification in the Te layer during the continuous voltammetric cycles.

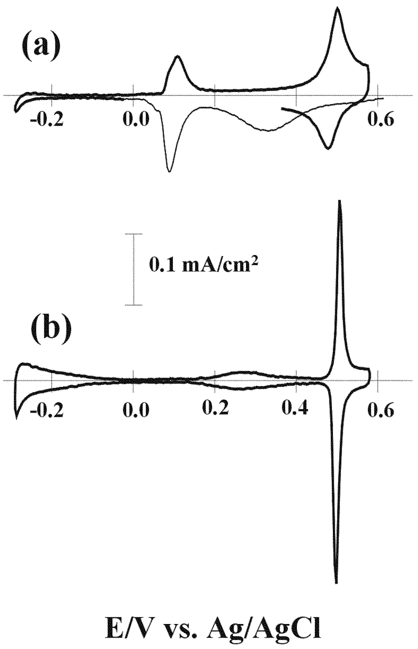

Figure 2. Cyclic voltammograms of Sb and Te simultaneously adsorbed on Pt(111) in 0.05 M H_2SO_4 solution: (a) the first scan and (b) the 100th cyclic scan.

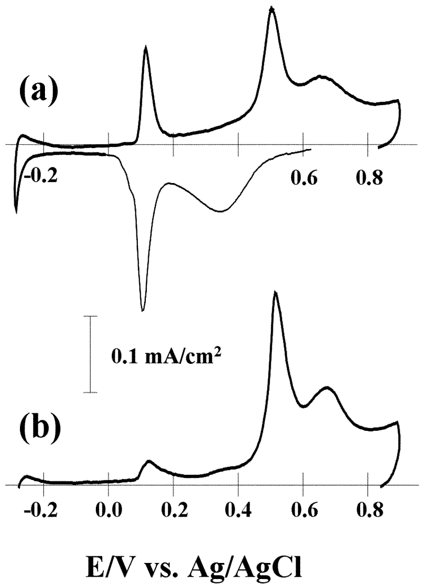

Figure 3. Stripping voltammograms of Sb and Te simultaneously adsorbed on Pt(111) in 0.05 M H_2SO_4 solution after (a) the first scan and (b) the 100th cyclic scan between –0.29 V and 0.30 V.

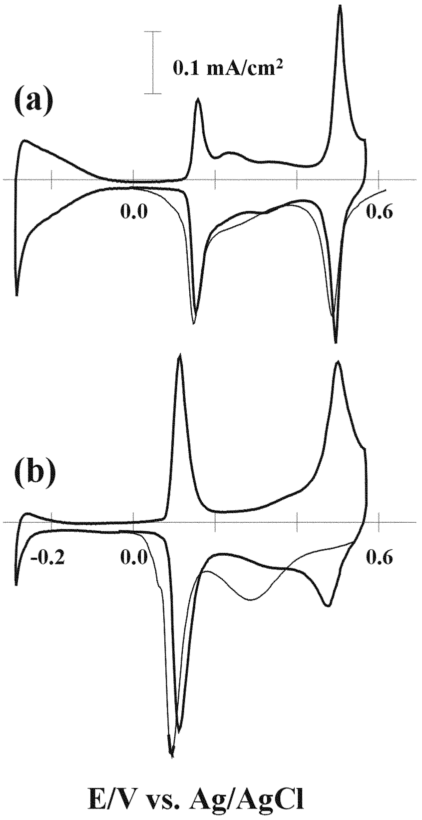

Figure 4. Cyclic voltammograms of Sb and Te sequentially adsorbed on Pt(111) in 0.05 M H_2SO_4 solution: (a) Sb adsorption was followed by Te adsorption and (b) Te adsorption was followed by Sb adsorption. The thin lines are the initial voltammograms and the thick lines are the following ones. See the text for the details of the adsorption procedure.

The voltammograms shown in Figure 3 are the stripping ones obtained after cyclic scanning of a simultaneously adsorbed layer of Sb and Te on Pt(111) between –0.29 V and 0.30 V. In this particular potential range, it is worthy to emphasize that there was no stripping of Sb at all, as signaled by no change in the hydrogen charge below 0.0 V. To observe the evolution of the Te peak during the cyclic scans, however, the adlayer of Sb and Te on Pt(111) was anodically stripped after scanning in a certain number of cycles. The shape of the initial reduction scan (the thin line in Figure 3(a)), obtained after contacting a clean Pt(111) electrode into the mixture of Sb and Te, was identical with that in Figure 2. In the following anodic stripping scan, the oxidation current of Sb became visible at 0.12 V and the oxidation peak of the adsorbed Te at 0.50 V appeared on a slowly rising current background resulting from a sequential stripping of the adsorbed Sb and Te. As the number of the voltammetric cycles increased (Figure 3(b)), it is quite clear that without stripping the adsorbed Sb, the oxidation peak of Te did not become sharp as much as one with Sb stripping (Figure 2). The charge concerning the Te oxidation, however, increased and converged to the coverage of 0.18 ML, close enough to the ultimate coverage value in Figure 2. Along with the charge increase of Te, the charge related to Sb decreased due to the formation of the electrochemically inactive species. Therefore, a partial stripping of Sb, as in Figure 2, enhanced the modification of the Te layer.

Figure 4 shows the cyclic voltammograms of Pt(111) covered with Sb and Te adsorbed in two sequences. Figure 4(a) was obtained after irreversible adsorption of Sb followed by that of Te. Specifically, a clean Pt(111) electrode was dipped into an Sb solution diluted by 3.5 times from the Sb_2O_3-saturated solution for 1 min to obtain a coverage of oxygenated Sb similar to those in Figure 2(a) and Figure 3(a), and then the adsorption of the oxygenated Te was carried out in the TeO_2-saturated solution for 10 min. It is quite remarkable that in the initial scan (the thin line in Figure 4(a)), the reduction peak of Te was observed at 0.50 V, identical with the potential obtained with the Pt(111) covered with Te only (Figure 1(b)). In addition to this, the charge related to the adsorbed Te did not change at all, while the redox process of Sb showed the identical behavior as in Figure 2(a). When the adsorption procedure was reversed, however, the obtained result (Figure 4(b)) was identical with those of Figures 2 and 3. Here again, the adsorption of Te was carried out by dipping a clean Pt(111) electrode into a Te solution diluted by 60 times from the TeO_2-saturated solution for 5 min to obtain a coverage of oxygenated Te similar to those in Figure 2(b) and Figure 3(b), and then the adsorption of the oxygenated Sb was carried out in the Sb_2O_3-saturated solution for 3 min.

The results presented so far indicate that an interaction between the irreversibly adsorbed oxygenated Sb and Te on Pt(111) depends on the procedure of adsorption, i.e. a simultaneous adsorption and a sequential adsorption. When a Pt(111) electrode was contacted with a solution of Te only, the irreversibly adsorbed oxygenated Te layer was reduced at 0.50 V (Figure 1(b)); when a Pt(111) electrode was dipped into a mixed solution of Sb and Te, the oxygenated Te layer was reduced at 0.30 V. This specific cathodic shift of the reduction potential of the oxygenated Te in the presence of the oxygenated Sb implies a thermodynamic stabilization of the oxygenated Te or a kinetic hindrance of the oxygenated Te reduction. A formation of a homogeneously mixed layer of the oxygenated Sb and Te would be a highly possible way for all the oxygenated Te to be strongly influenced by the oxygenated Sb. In the case of sequential adsorption as in Figure 4(a), on the other hand, the reduction peak of the oxygenated Te appeared at the same potential as in Figure 1(b). This result supports obviously that there was no interaction between the oxygenated Sb and Te. Thus, it is logical to state that there were separate domains of two oxygenated metal ions. Conclusively, a simultaneous adsorption of Sb and Te led to homogeneously mixed layers of the two oxygenated metal ions, while a sequential adsorption in the order of Sb and Te resulted to separated domains of the respective oxygenated metal ions.

The Te redox peak potential, after the first reduction of a mixed oxygenated layer of Sb and Te (*i.e.* simultaneously adsorbed layer), converged to that of Te on the Pt(111) electrodes covered with Te only, especially in the case of a slow stripping of Sb (Figure 2). When the mixed layer of Sb and Te was reduced, the two elements were obviously distributed homogeneously on the surface. As the Sb desorbed slowly, rooms were available to the mobile Te atoms,[8,9] so that the Te atoms segregate to form the domains of Te only to show the voltammetric peak of pure Te on Pt(111). When the desorption of Sb was not allowed as in Figure 3, the modification of the Te redox behavior was not discernible as much as in Figure 2, most likely due to a limited availability of spaces for surface diffusion. When the separated domains of Sb and Te (*i.e.* sequentially adsorbed layer) were formed as in Figure 4(a), the evolution of the Te redox peak was not observed at all even when the desorption of Sb took place. On the other hand, the redox potential of Sb in the absence of Te was 0.11 V in Figure 1(a); the ultimate potential of Sb in the presence of Te, regardless of adsorbing way, was 0.20 V as in Figure 2(b) and Figure 3(b). The anodic shift of electrochemically active Sb with co-adsorbed Te implies that the Sb domains would be strongly influenced by the presence of Te also, most likely due to mixed regions of Te and Sb.

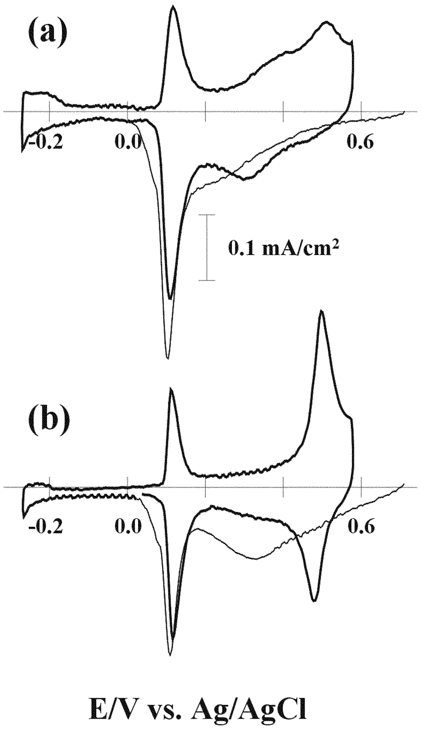

Figure 5. Cyclic voltammograms of Sb and Te sequentially adsorbed on Pt(111) in 0.05 M H_2SO_4 solution: (a) a full adsorption of Sb was followed by Te and (b) a full adsorption of Te was followed by Sb. The thin lines are the initial voltammograms and the thick lines are the following ones. See the text for the details of the adsorption procedure.

The adsorption abilities of Sb and Te are different. To examine the difference in the adsorption strength, a Pt(111) electrode fully saturated with a metal ion was exposed to the solution containing the other metal ion. To guarantee saturating adsorption of metal ions, the adsorption conditions employed in Figure 1, *i.e.* 3 min in the Sb_2O_3-saturated 0.05 M H_2SO_4 solution for Sb adsorption and 15 min in the TeO_2-saturated 0.05 M H_2SO_4 solution for Te adsorption, were practiced. When the Pt(111) electrode saturated with the oxygenated Sb was dipped into the TeO_2-saturated 0.05 M H_2SO_4 solution for 15 min, the specific electrode did not show any current related to Te as in Figure 5(a). When a Pt(111) electrode saturated with Te was exposed to the Sb_2O_3-saturated 0.05 M H_2SO_4 solution for 3 min, the redox peak of Te was recognizable as in Figure 5(b). These results reveal clearly that the adsorption strength of Te was lower than that of Sb. Furthermore, it is certain that the displacement of adsorbed Te with oxygenated Sb took place in a random way, since the reduction peak of Te in the initial cathodic scan was observed at 0.30 V.

The difference in the adsorption abilities of Sb and Te confirms the formation of the separated domains in a sequential adsorption as in Figure 4(a). When the irreversible adsorption of Sb was conducted onto the Pt(111) electrode covered with Te domains (Figure 4(b)), the displacement of the adsorbed Te could be predicted. Indeed, the reduction peak of Te in the initial scan was observed at 0.30 V and this observation directly specifies the presence of a mixed layer of Sb and Te, thus the displacement of the adsorbed Te with adsorbing Sb. In the reverse case (Figure 4(a)), the absence of the Te reduction peak at 0.30 V indicates no displacement, thus separated domains of Sb and Te.

Summary

The interaction between the irreversibly adsorbed oxygenated Sb and Te on Pt(111) depends on the procedure of adsorption. A simultaneous adsorption of Sb and Te led to homogeneously mixed layer of the two oxygenated metal ions, while a sequential adsorption in the order of Sb and Te resulted to separate domains of the respective oxygenated metal ions. Due to the different adsorption abilities of Sb and Te, mixed layers of Sb and Te were formed when adsorption of two metal ions was performed sequentially in the order of Te and Sb. The presented work is not able to provide any atomic level picture concerning co-adsorption process, so that further works may be followed.

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