



Comparison of platinum with IrO₂–Ta₂O₅ system for the stannous ion consumption in methane sulfonic acid baths with and without catechol

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Received 17 June 1999; accepted in revised form 22 September 1999

Abstract

The stannous ion consumption in methane sulfonic acid (MSA) baths with and without catechol was quantitatively evaluated using platinum and IrO₂–Ta₂O₅/Ti anodes. The stannous ion is consumed at the same rate with both anodes, accompanied by the generation of tin sludge on the anode surfaces in the bath without catechol, while these undesirable phenomena are significantly suppressed in the bath containing catechol. Spectroscopic measurements indicate that stannous ion and catechol form a complex at the mole ratio of 1:2, thus preventing the oxidation of stannous ions. This complexation effect is independent of the anode material at low current density, but depends on the anode material at high current density. The stannous ion consumption at high current density is sufficiently inhibited only with the IrO₂–Ta₂O₅/Ti anode due to the low oxygen evolution potential. Voltammetric measurements also suggest that the continuous oxidation of stannous ion in the catechol-containing bath is simultaneous with oxygen evolution.

Key words: catechol, IrO₂–Ta₂O₅/Ti electrodes, methane sulfonic acid, stannous ion consumption, tin plating

1. Introduction

The Ferrostan bath based on phenolsulfonic acid (PSA) is widely utilized as an electrolyte for commercial electroplating processes [1–4]. It has been recently reported that tin plating at current densities greater than 220 A dm⁻² can be achieved using conventional PSA baths [4]. However, commercial tin plating still needs the development of more suitable electrolytes instead of the PSA bath for a high current density (HCD) operation to further optimize the productivity of tin-plated steel strip. This approach also emanates from the chemical nature of PSA that has serious drawbacks in terms of toxicity and effluent disposal.

One of the key factors in developing the bath for HCD tin plating is the stability of the bath relating to the anodic consumption of stannous ions. Soluble tin anodes are popular in commercial electroplating lines (ETL), but the applicability for HCD electrolyses must be limited due to the slow dissolution rate of tin. On the other hand, a platinum-plated titanium electrode has also been adopted for commercial ETL [1], and such an anode, having a high resistance to anodic corrosion, is more preferable for HCD operations. Although in this case, the anodic reaction during electrolysis is mainly oxygen evolution, stannous ions should be simultaneously oxidized to stannic ions on the anode from a thermodynamic viewpoint ($E^0(\text{Sn}^{4+}/\text{Sn}^{2+}) = 0.15 \text{ V}$ at 25 °C vs. NHE). This causes problems such as difficulty in controlling the stannous ion concentration in the bath and increase in tin sludge on the anode. These undesir-

able results are particularly serious at high current density. Therefore, it is important to know the stannous ion consumption in a novel electrolyte for HCD tin plating.

During the search for an appropriate electrolyte for the HCD tinning process, we investigated the methane sulfonic acid (MSA)-based bath which is a promising candidate [5, 6]. Therefore, a quantitative evaluation of the stannous ion consumption in the MSA bath was carried out, giving special attention to the effects of anode material on the consumption rate. Following the usual technique to improve the properties of the deposited films in plating technology, but in order to inhibit the stannous ion consumption in this study, a MSA bath containing an additive reagent, catechol, was also examined.

2. Experimental

2.1. Quantitative analysis of Sn(II) consumption

An H-shaped cell consisting of anode and cathode compartments separated by an anion exchange membrane (Asahi Glass, Selemion AMV) was used for the quantitative analysis of the stannous ion consumption. Anolytes comprised 5 vol% MSA and 0.1 M SnSO₄ with and without 0.1 M catechol, which were carefully prepared using distilled water deaerated by N₂ gas bubbling so as to prevent the chemical oxidation of the stannous ions before use. The catholyte contained 5

vol% MSA and 0.133 M Na_2SO_4 so that the ionic strength was the same as that of the anolyte. All reagent-grade chemicals were used as received. The actual volume of these solutions was 0.2 dm^3 .

Two kinds of anode material were prepared: one was a platinum plate and the other was a titanium plate coated with thermally prepared iridium–tantalum oxides ($\text{IrO}_2\text{--Ta}_2\text{O}_5/\text{Ti}$) of which the nominal Ir:Ta ratio was 7:3 and the thickness was ca. $2 \mu\text{m}$. The latter was prepared by thermal decomposition at 500°C for 10 minutes of the coating solution which comprised $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ and TaCl_5 dissolved in *n*-butanol solution containing 6 vol% HCl. The preparation of the coating solution and the pretreatment of the titanium substrate were described elsewhere [7]. The geometrical surface area of both electrodes was 2 cm^2 . A platinum plate counter electrode (16 cm^2) and a KCl-saturated Ag/AgCl reference electrode were also used.

Constant current electrolyses were carried out and then the anolyte was filtered. The filtered solution was diluted with 20 vol% HCl. The residue on the filter paper was dried under vacuum and dissolved in 20 vol% HCl solution. Each solution was titrated with a standardized solution of potassium iodide and potassium iodate to determine the Sn(II) concentration. The total tin in both solutions was also determined using a Hitachi Model 170-0110 atomic absorption spectrometer. The concentration of Sn(IV) was calculated as the difference between the total tin and Sn(II). The maximum error for the determination of Sn(II) induced by 5 vol% MSA was less than 1.2% and the effect of 0.1 M catechol was negligible. These components also showed no influence on the total tin measurement. The above procedures were carefully carried out so as to prevent Sn(II) oxidation by air.

2.2. Spectroscopic measurements

UV-visible absorption spectra at 190–820 nm were measured to study the interaction between Sn(II) and catechol using 2-mm path length cuvettes having two quartz windows (Hellma, 220-QS). The spectroscopic measurement was conducted using a Hewlett-Packard Model HP8452A diode array spectrophotometer (2 nm resolution) interfaced to a computer.

2.3. Voltammetric measurements

A preliminary analysis of the anodic reaction in the MSA bath was performed by linear sweep voltammetry. A conventional three-electrode cell equipped with a platinum wire working electrode (1 mm diam.) was used. The exposed surface area of the working electrode was 0.31 cm^2 . The counter and reference electrodes were the same as in the previous section.

2.4. Other instrumentation

The constant current electrolysis and the linear sweep voltammetry were done using a Hokuto Denko Model

HA-305 potentiostat/galvanostat, HB-105 function generator, a Rikadenki RW-21T X–Y recorder, and a Soar Model HC-545A digital multimeter. In these experiments, the cell was placed in a thermostat with circulating water controlled at $20 \pm 0.5^\circ\text{C}$ and N_2 gas flowed over the electrolyte in the cell. A JEOL Model JPS-90SX X-ray spectroscope with an energy of 10 kV was also used to analyze the surface of the platinum plate anode after the electrolysis.

3. Results and discussion

3.1. Quantitative analysis of Sn(II) and Sn(IV)

Figure 1 shows the concentration changes in the stannous and stannic ions in the MSA bath without catechol during electrolysis at 2.5 A dm^{-2} . In this figure, the concentration of stannic ion corresponds to that dissolving in the bath, which is generated by the electrochemical oxidation of stannous ion. The stannous ion concentration decreased with time irrespective of the anode material, and was accompanied by no appearance of stannic ions in the bath. Otherwise, the stannous ion consumption resulted in the generation of tin sludge on both anodes. The quantitative analysis described in section 2.1 revealed that the sludge mostly consisted of stannic compounds. The XPS analysis of the anode surface after the electrolysis also suggested that the sludge involved stannic acid. When the MSA bath containing catechol was used, stannous ion consumption was not observed for both anodes as shown in Figure 2. After the continuous electrolysis for 50 h, both stannic ions in the bath and the tin sludge on the anode were not produced. These results clearly indicate that in the presence of catechol the electrochemical oxidation of stannous ion on both anodes is inhibited.

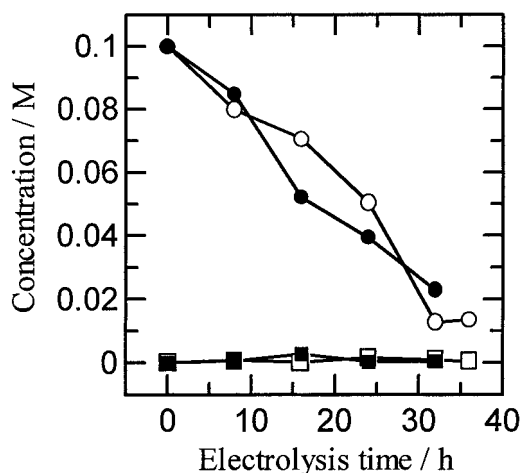


Fig. 1. Concentration changes of Sn(II) (○, ●) and Sn(IV) (□, ■) in the 5 vol% MSA bath containing 0.1 M SnSO_4 during the electrolysis with platinum plate (●, ■) and $\text{IrO}_2\text{--Ta}_2\text{O}_5/\text{Ti}$ (○, □) anodes at 2.5 A dm^{-2} .

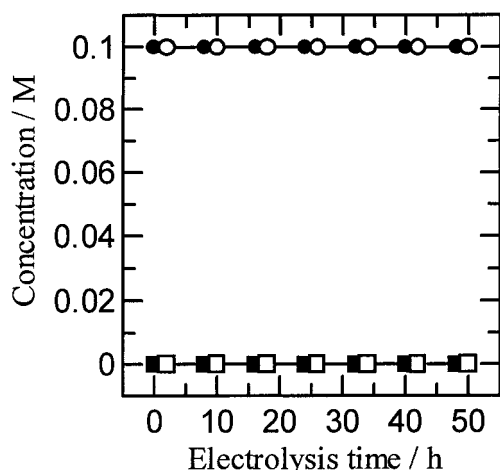


Fig. 2. Concentration changes of Sn(II) (○, ●) and Sn(IV) (□, ■) in the 5 vol% MSA bath containing 0.1 M SnSO₄ and 0.1 M catechol during the electrolysis with platinum plate (○, ■) and IrO₂-Ta₂O₅/Ti (○, □) anodes at 2.5 A dm⁻².

Stannous ion consumption at the higher current density was also examined using the bath with catechol. The results showed a significant difference in the stannous ion consumption by the anode material as shown in Figure 3. The concentration of stannous ion decreased when the platinum anode was used. Stannic ions were simultaneously detected in the bath, although in aqueous solutions, the stannic ion itself is unstable and easily deposits as stannic acid. This is caused from stabilizing stannic ions due to a well-known complexation with catechol giving [Sn(O₂C₆H₄)₃]²⁻ [8]. Stannous ion consumption also resulted in the formation of tin sludge on the platinum anode, which is the reason why the Sn(II) decrease disagrees with the Sn(IV) increase in Figure 3. On the other hand, the concentration of stannous ion was unchanged with the IrO₂-Ta₂O₅/Ti anode and thus no stannic ion and tin sludge arose. This shows that the advantage of catechol in

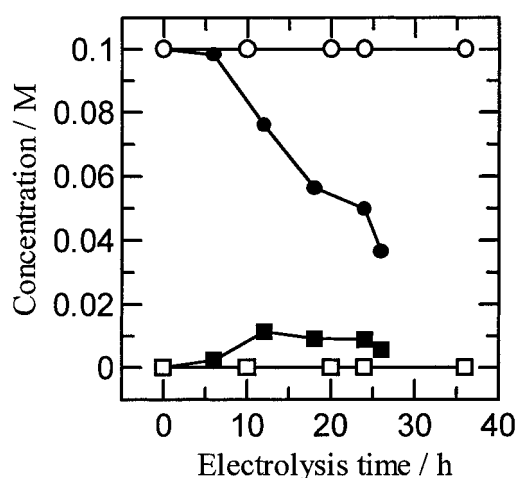


Fig. 3. Concentration changes of Sn(II) (○, ●) and Sn(IV) (□, ■) in the 5 vol% MSA bath containing 0.1 M SnSO₄ and 0.1 M catechol during the electrolysis with platinum plate (●, ■) and IrO₂-Ta₂O₅/Ti (○, □) anodes at 25 A dm⁻².

preventing stannous ion oxidation is maintained even at high current density.

During the electrolysis described above, the anode potential was measured and then compensated for IR drop using a current-interruption method. Table 1 summarizes the corrected potentials of the platinum plate and IrO₂-Ta₂O₅/Ti anodes for each electrolysis condition. The anode potential at 2.5 A dm⁻² in the bath without catechol was 0.1 V more anodic than that in the bath containing catechol, independent of the anode material. This is probably caused by the tin sludge covering the anode surface in the former case, thus increasing the oxygen overpotential. It has been reported that O₂ evolution during Cl₂ generation can be suppressed by adding SnO₂ to the RuO₂-based coating of dimensionally stable anodes, resulting in the enhancement of the selectivity in Cl₂ production [9, 10]. Therefore, the increase in the oxygen overpotential by tin sludge is reasonable, since tin sludge is mostly composed of stannic compounds.

Considering this result with the effect of catechol on the stannous ion consumption at the low current density, catechol appears to stabilize stannous ion in the MSA bath so as to prevent the oxidation of stannous ion. This effect is similar with both anodes at low current density, but not at high current density, while at both current densities, the oxygen evolution potential of the platinum anode is 0.4 to 0.5 V higher than that of the IrO₂-Ta₂O₅/Ti anode. Provided that the oxidation process of the 'stabilized' stannous ion depends on the anode potential, it can be considered that the stannous ion consumption is inhibited at the high current density because of the low oxygen overpotential of the IrO₂-Ta₂O₅/Ti anode.

3.2. Spectroscopic measurements

Based on the results in the previous section, the interaction between stannous ion and catechol was investigated using UV-visible absorption spectrometry. Absorption spectra were initially measured in aqueous solutions containing SnSO₄ or catechol, and the results are shown in Figures 4 and 5. The SnSO₄ solution shows a broad absorption peak at around 196 nm, and the catechol solution gives three absorption peaks at 196, 216, and 276–278 nm. Since these solutions were found to have absorption peaks in the same wavelength region, the absorption spectra of the solution containing both of them were measured using the catechol solution as a blank. As shown in Figure 6, the overall appearance of the spectra of this solution is different from those shown

Table 1. Anode potentials vs Ag/AgCl during the electrolysis

Bath	Without catechol		With catechol	
	<i>i</i> /Adm ⁻²	2.5	2.5	25
Platinum	2.1	2.0	2.6	
IrO ₂ -Ta ₂ O ₅ /Ti	1.6	1.5	2.2	

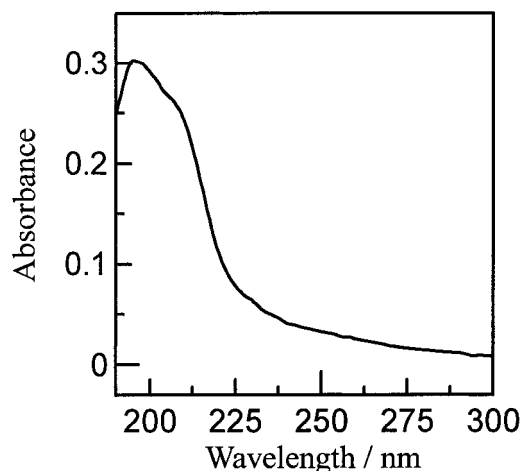


Fig. 4. Absorption spectrum of 2.0×10^{-5} M SnSO_4 solution. Blank: water.

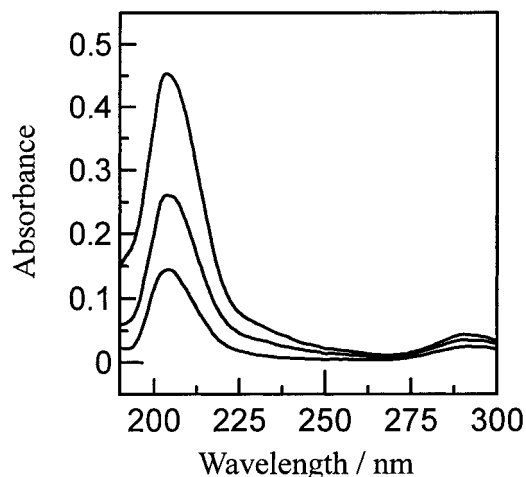


Fig. 6. Absorption spectra of 2×10^{-5} M catechol solutions containing 0.50×10^{-5} , 1.0×10^{-5} , and 2.0×10^{-5} M SnSO_4 (bottom to top). Blank: 2×10^{-5} M catechol.

in Figures 4 and 5, and a new absorption peak at 202–204 nm appears, suggesting the complexation of stannous ion with catechol. (The absorbance at 280–300 nm also changed with the SnSO_4 concentration, but this absorption peak is weak and broad.) In all cases, no absorption peak was observed in the wavelength range of 300–820 nm.

The possibility of such a complexation was examined from the dependence of the peak absorbance at 202 nm on the concentration ratio of stannous ion to catechol using the mole ratio and continuous variation methods, of which the results are shown in Figures 7 and 8, respectively. An inflection point is seen in Figure 7 and a maximum point is observed in Figure 8, when the concentration ratio of $[\text{Sn(II)}]:[\text{catechol}]$ is 1:2. These results indicate that stannous ion and catechol form a complex at this mole ratio. Therefore, it is concluded that this complexation makes the electrochemical oxidation of stannous ion more difficult compared to 'free' stannous ion.

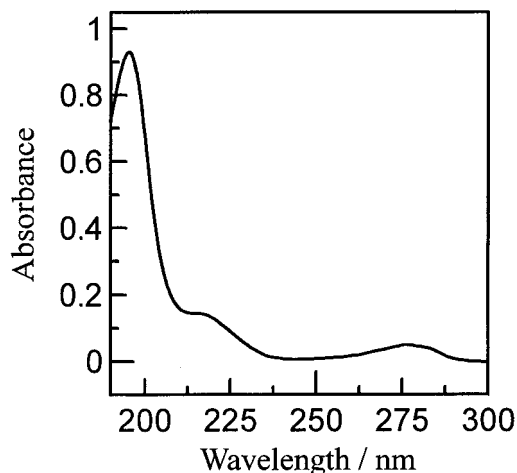


Fig. 5. Absorption spectrum of 2.0×10^{-5} M catechol solution. Blank: water.

3.3. Voltammetric measurements

The anodic reaction in the MSA solution containing catechol was preliminarily studied using a three-electrode cell equipped with a platinum wire working electrode. Figures 9 and 10 show linear sweep voltammograms obtained in 5 vol% MSA solutions with and without 0.05 M catechol. Comparison of these voltammograms clearly indicates that the anodic wave in Figure 10 corresponds to the oxidation of catechol, which produces *o*-quinone through a well-known phenol-quinone reaction [11].

The linear sweep voltammograms obtained in 5 vol% MSA solution containing 0.05 M catechol and 0.1 M SnSO_4 are displayed in Figure 11. The voltammogram of the first scan (solid line) shows an anodic wave, of which the onset potential is almost the same as that of the anodic wave in Figure 10. However, the former peak current density is much smaller than the latter one and

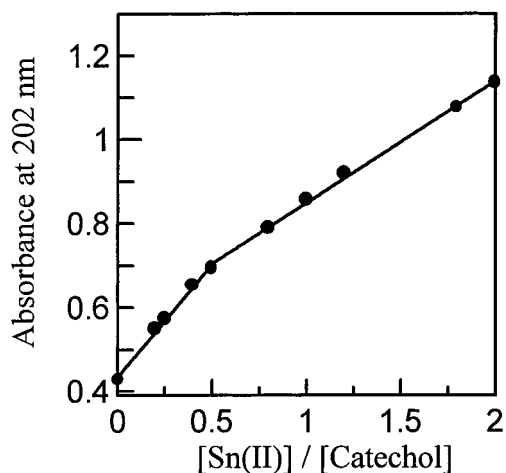


Fig. 7. Relation between the absorbance at 202 nm and the concentration ratio, $[\text{Sn(II)}]/[\text{catechol}]$, followed by the mole ratio method. The catechol concentration, $[\text{catechol}]$, is constant at 1.0×10^{-4} M. Blank: water.

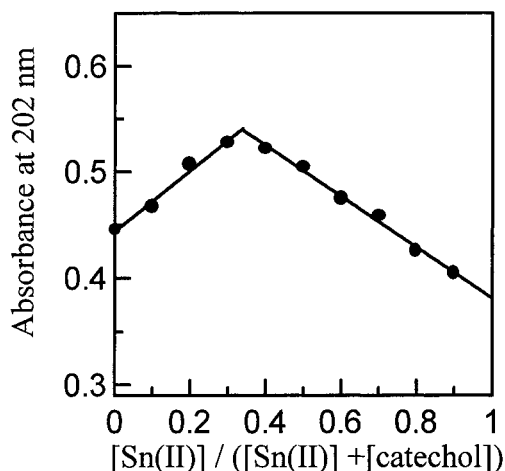


Fig. 8. Relation between the absorbance at 202 nm and the concentration ratio, $[\text{Sn(II)}]/([\text{Sn(II)}] + [\text{catechol}])$, followed by the continuous variation method. The total concentration of Sn(II) and catechol, $[\text{Sn(II)}] + [\text{catechol}]$, is constant at 1.0×10^{-4} M. Blank: water.

no net current after the anodic wave in Figure 11 is seen prior to oxygen evolution. These results indicate that the oxidation of catechol is suppressed by the coexistence of stannous ions in the solution. Therefore, the complexation of stannous ion with catechol inhibits their electrochemical oxidation.

On the other hand, the anodic wave seen in the first scan completely disappears on the subsequent scans. This implies that the oxidation of the Sn(II)-catechol complex becomes more difficult on the pre-scanned electrode, although oxygen evolution can still occur. However, this means that the Sn(II)-catechol complex is oxidized at higher potentials, not that the oxidation of the complex is entirely prevented, since stannous ion is consumed with the platinum electrode in the MSA bath containing catechol at high current density, as shown in Figure 3. In this case, the oxidation of the Sn(II)-catechol complex no longer occurs at potentials lower than at least that of oxygen evolution. The continuous oxidation of the complex will be

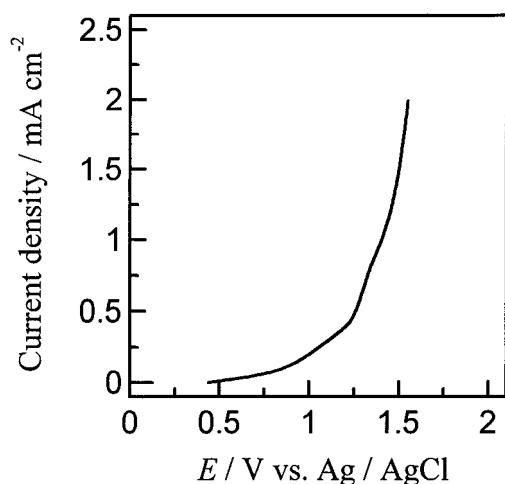


Fig. 9. Linear sweep voltammogram with a platinum wire electrode in 5 vol% MSA solution at 100 mV s^{-1} .

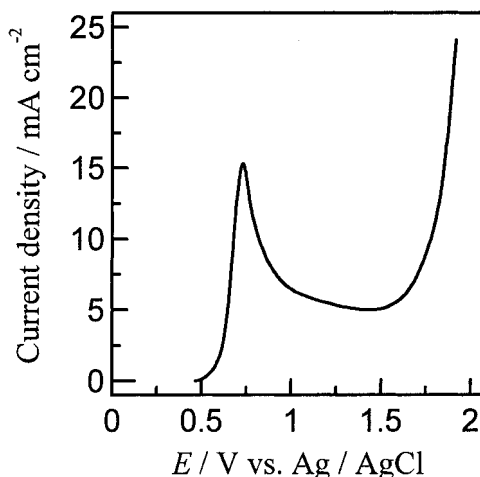


Fig. 10. Linear sweep voltammogram with a platinum wire electrode in 5 vol% MSA solution containing 0.05 M catechol at 40 mV s^{-1} .

simultaneous with oxygen evolution, only if the oxygen evolution potential is sufficiently high to cause the oxidation of the complex. Based on the above discussion, it appears that stannous ion consumption in the catechol-containing bath depends on the oxygen evolution potential, which, in turn, depends on the anode material. In order to fully explain this relation, the reason for the increase in the oxidation potential of the Sn(II)-catechol complex on the pre-scanned electrode requires clarification. One possible reason is the change in the electrode surface before and after the first scan. A surface characterization study of the electrode surface is now in progress.

4. Conclusions

Quantitative analysis of stannous ion consumption in a methane sulfonic acid bath for tin plating revealed that catechol added to the bath suppressed the electrochem-

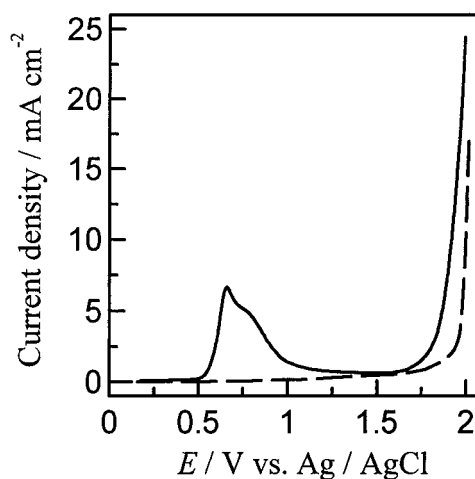


Fig. 11. Linear sweep voltammograms with a platinum wire electrode in 5 vol% MSA solution containing 0.1 M SnSO_4 and 0.05 M catechol at 40 mV s^{-1} . First scan (solid line), second scan (dash line).

ical oxidation of stannous ion and the precipitation of tin sludge consisting mostly of stannic compounds. This is attributable to the complexation of stannous ion and catechol at the mole ratio of 1:2. The complexation effect works sufficiently at low current density, but not at high current density. In the latter case, the anode material is critically important because the occurrence of Sn(II)-catechol complex oxidation depends on the oxygen evolution potential. While the addition of catechol is effective in suppressing stannous ion consumption in the MSA bath, an anode having a low oxygen overpotential, such as an IrO₂-Ta₂O₅/Ti anode, is favorable in order to inhibit the oxidation of stannous ions, especially during electrolysis at high current density.

Acknowledgements

The authors are grateful to the Center for Instrumental Analysis, Kyushu Institute of Technology, for the XPS measurements.

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