



Short communication

Polarization behaviour and lifetime of IrO₂–Ta₂O₅–SnO₂/Ti anodes in *p*-phenolsulfonic acid solutions for tin plating

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1. Introduction

Insoluble electrodes consisting of iridium and tantalum oxides thermally prepared on a titanium substrate have received much attention as oxygen evolution anodes in industrial electroplating processes. In commercial electroplating lines, the application of the IrO₂–Ta₂O₅/Ti anode has increased, replacing other insoluble anodes such as the platinum-coated titanium electrode, and a lifetime of more than 10 000 h has been demonstrated under severe operation conditions of 100 A dm⁻² and 333 K in practical use [1, 2]. The IrO₂-based coating provides excellent catalytic and corrosion-resistant properties, if the electrolyte is an inorganic acid solution such as a sulfuric acid-based bath for electroplating. However, iridium oxide, along with other platinum-group metals or their oxides, shows a high consumption rate if the electrolyte contains organic compounds [3, 4]. As a result, little has been done to develop the IrO₂–Ta₂O₅/Ti anode for commercial electroplating lines using organic acid-based baths, for example, the Ferrostan bath based on *p*-phenolsulfonic acid (PSA) for electroplating.

By contrast, we studied the electrochemical behavior of the IrO₂–Ta₂O₅/Ti anode in a PSA solution in order to determine the real applicability of this anode for electroplating lines [5]. The results indicated that PSA was oxidized at potentials less positive potential than that of oxygen evolution and the oxidation of PSA produced an organic film that originated from the PSA on the anode during oxygen evolution. The organic film on the anode adversely affected the electrocatalysis of the IrO₂–Ta₂O₅ catalytic layer and caused a drastic decrease in the lifetime of the anode. However, it was also found that the addition of SnO₂ on the outermost surface of the coating layer suppressed the accumulation of the organic film, thus suggesting the prolongation of the anode lifetime in the PSA solution. It is, therefore, possible that the IrO₂–Ta₂O₅ coating layer containing SnO₂ has enhanced durability for use in the PSA-based tin plating bath.

In this paper, the anodic polarization behaviour and lifetime for oxygen evolution of IrO₂–Ta₂O₅–SnO₂/Ti

anodes in a PSA solution are reported. The manifested advantage of the SnO₂ addition in the IrO₂–Ta₂O₅ system to improve the anode lifetime is shown.

2. Experimental details

The preparation procedure of IrO₂-based coatings consisted of dipping a pretreated titanium substrate in a coating solution, drying at 393 K for 10 min, and calcining at 573 K for 20 min and at 743 K for 20 min. These procedures were repeated ten times for making each of the coatings that originated from four kinds of coating solutions having the different compositions shown in Table 1. The coating solution of electrode A, that is, the IrO₂–Ta₂O₅/Ti electrode, was prepared by dissolving H₂IrCl₆·6H₂O and TaCl₅ into *n*-butanol containing 6 vol% HCl so that the total metal (Ir + Ta) content was 70 mg cm⁻³. The detailed procedure to prepare this coating solution is described elsewhere [6, 7]. The appropriate mixtures of this coating solution with another one containing SnCl₂·2H₂O in *n*-butanol (Sn content 70 mg cm⁻³) were used to prepare three kinds of IrO₂–Ta₂O₅–SnO₂ coatings for electrodes B, C and D as shown in Table 1. The oxide loading was about 2.6 mg cm⁻² for each electrode. All reagent grade chemicals were utilized as received, and the titanium substrate (10 mm × 50 mm × 1.5 mm) was pretreated by polishing with emery paper (grade 1000), ultrasonic wave cleaning in acetone, and etching in boiling 10 wt% oxalic acid. The exposed surface area of each electrode was limited to 10 mm × 10 mm on one side by masking as described elsewhere [6].

Polarization measurements and constant current electrolyses were carried out using 0.176 mol dm⁻³ Na₂SO₄ solutions with and without 0.454 mol dm⁻³ PSA, of which the pH was adjusted to 0.8 using sulfuric acid. The former is designated as the sulfuric acid bath and the latter as the PSA bath in the following sections. Platinum mesh or zirconium plate counter electrodes and a KCl-saturated Ag/AgCl reference electrode were used. The anodic polarization curves were made by

Table 1. Atomic ratio of Ir, Ta and Sn in coating solutions

Electrode	Atomic ratio
(A)	Ir : Ta = 8 : 2
(B)	(Ir + Ta)* : Sn = 9.5 : 0.5
(C)	(Ir + Ta)* : Sn = 9.0 : 1.0
(D)	(Ir + Ta)* : Sn = 8.5 : 1.5

*Ir : Ta = 8 : 2

repeating the measurement of the electrode potential after applying a constant current for 5s using a Hokuto Denko Model HA-303 potentiostat/galvanostat, model HB-105 function generator and a Yokogawa Denki model AR1100A analysing recorder. The measured potential was compensated for the IR drop by a current-interruption method. The constant current electrolysis was performed using the above instrumentation with a Yokogawa Denki model 7541 digital multimeter. The electrolysis period in which the cell voltage increased 5V more than the initial value was termed the anode lifetime [5, 6]. Temperature was controlled within ± 0.5 K using a thermostat with circulating water.

3. Results and discussion

The oxygen evolution behaviours were initially examined using the sulfuric acid bath. Figure 1 shows the Tafel plots of four kinds of IrO_2 -based electrodes in the sulfuric acid bath. In this experiment, at least three samples for each electrode were confirmed to give the same result except at high current densities such as 0.4 A cm^{-2} or more, and one of them is shown for each electrode in this figure. It is clearly seen that the polarization characteristics are almost identical, irrespective of the coating composition, which suggests that the addition of SnO_2 and its composition under the

present experimental conditions have less influence on the oxygen evolution in the sulfuric acid bath.

This is reasonably understood from the catalytic activity of SnO_2 for oxygen evolution. Although SnO_2 has been examined as an additive in the catalytic layer of the oxide-coated electrode in order to modify the electrocatalytic properties [8–11], the electrocatalytic activity of SnO_2 for oxygen evolution in acidic media is not very high, especially in comparison with IrO_2 . In addition, the real Sn ratio in the IrO_2 - Ta_2O_5 - SnO_2 coating is considered to be lower than the nominal one in the coating solution, since the surface characterization studies of binary and ternary oxides system containing SnO_2 prepared by thermal decomposition have indicated the low yield of SnO_2 due to SnCl_4 volatilization [9–11]. Therefore, the real difference in the IrO_2 ratio between the four kinds of coating layers is expected to be small, thus resulting in almost the same oxygen overpotential in the sulfuric acid bath.

However, it is presumed from the results shown in Figure 1 that the active electrode surface areas are almost the same irrespective of the SnO_2 ratio in the coating layer. This was supported by the voltammetric charge measurements in a certain potential range, which suggested that the three kinds of IrO_2 - Ta_2O_5 - SnO_2/Ti anodes have the same or a slightly smaller surface area compared to the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ anode.

In contrast, the oxygen evolution potential in the PSA bath was changed by the addition of SnO_2 in the coating layer as shown in Figure 2. The three kinds of IrO_2 - Ta_2O_5 - SnO_2/Ti anodes (B, C and D) show the oxygen evolution potentials lower than the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ anode (A), and the oxygen evolution on the IrO_2 - Ta_2O_5 - SnO_2/Ti anode occurs at lower potentials with the increasing ratio of SnO_2 . The oxygen overpotential of the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ anode increases in the PSA bath compared to that in the sulfuric acid bath, which is

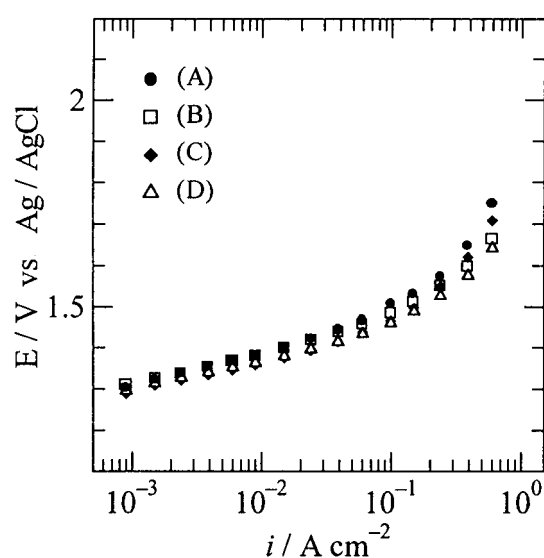


Fig. 1. Tafel plots of the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ (A) and IrO_2 - Ta_2O_5 - SnO_2/Ti (B, C, D) anodes in a sulfuric acid solution (pH 0.8) at 298 K.

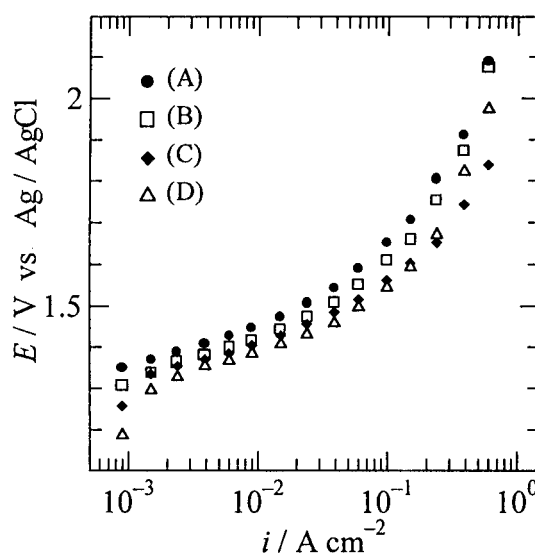


Fig. 2. Tafel plots of the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ (A) and IrO_2 - Ta_2O_5 - SnO_2/Ti (B, C, D) anodes in a sulfuric acid solution containing $0.454 \text{ mol dm}^{-3}$ PSA (pH 0.8) at 298 K.

caused by the simultaneous oxidation of PSA resulting in the formation of an organic film on the anode [5]. Therefore, the results shown in Figure 2 indicate that the increase in oxygen overpotential due to the organic film formation degrading the electrocatalytic activity of IrO_2 is restrained on the SnO_2 -mixed coating layer, depending on the SnO_2 ratio.

In each of Figures 1 and 2, the deviation from linearity at higher current densities is observed. One of the possible reasons is the change in the rate determining step (RDS) of the oxygen evolution reaction. For example, the Tafel slopes for the IrO_2 - Ta_2O_5 (70:30 mol%) coating for oxygen evolution were reported as 60 mV at low current densities and 120 mV at high current densities due to the difference in RDS [12]. It was also found that the Tafel plots of IrO_2 - Ta_2O_5 (65:35 mol%) coating could be classified into two regions depending on the current density [13, 14]. Another reason is that the transition from kinetic control to diffusion control would be included in the higher current density region. In the present study, the consideration for the effect of the mixed, that is, kinetic and diffusion, control would become important for oxygen evolution in the PSA bath, because the organic film originated from PSA is formed on the electrode.

The modification of the catalytic activity of the IrO_2 -based coating by the SnO_2 addition results in a durability improvement of the anode in the PSA bath. Figure 3 shows the variation in the cell voltage during constant current electrolyses. The cell voltage decreases during the initial stage of the electrolysis, which is a general feature of this type of experiment using the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ anode. This is attributable to the increase in cracking of the coating accompanied by the appearance of IrO_2 particles hidden in the inside of the coating layer. The cell voltage then maintains the same

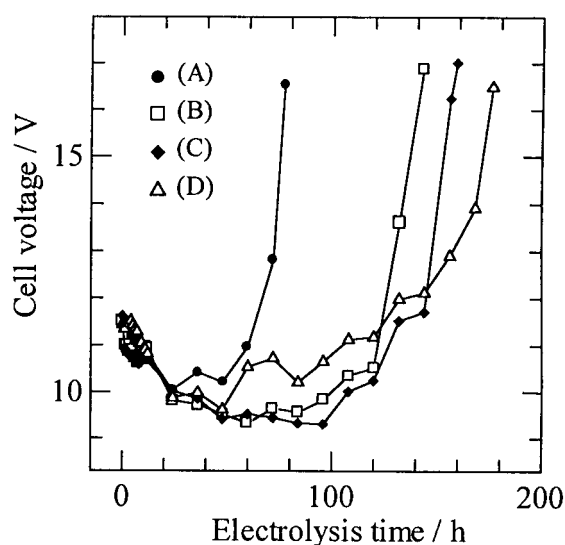


Fig. 3. Changes in the cell voltage during the constant current electrolysis at 2 A cm^{-2} in a sulfuric acid solution containing $0.454 \text{ mol dm}^{-3}$ PSA (pH 0.8) at 323 K using the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ (A) and IrO_2 - Ta_2O_5 - SnO_2/Ti (B, C, D) anodes.

level or gradually increases over a certain period, and steeply increases at the end. The final change in the cell voltage is caused by the corrosion of the titanium substrate, and the relation between the deterioration of the coating layer and the cell voltage described above is explained in detail elsewhere [7]. It should be noted that the judgement of the lifetime in this manner is also utilized in commercial application and the cathode potential hardly affects the cell voltage.

The lifetime of the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ anode in the PSA bath drastically decreases compared to that in the sulfuric acid bath [5]. However, the lifetime in the PSA bath is prolonged by the SnO_2 addition and is extended with the increasing ratio of SnO_2 in the catalytic layer. In the lifetime test experiments, a constant nominal current is applied to the electrodes, although the electrolysis time obtained strongly depends on the real current density applied, which in turn depends on the real surface area. However, it should be noted that the improvement in lifetime with the increasing ratio of SnO_2 is not probably caused by the difference in the real surface area due to the change in composition, since the composition change is minor in the present study. Moreover, the electrolysis times obtained, considering the nominal current density used, are of interest from the practical point of view.

As previously mentioned [5], the enhanced durability of the IrO_2 - Ta_2O_5 - SnO_2/Ti anode in the PSA bath is presumably attributed to the complete oxidizing of PSA promoted by SnO_2 . This is caused by the difference in the oxygen evolution mechanism on SnO_2 and IrO_2 ; OH radicals are generated during oxygen evolution in the former case, but not in the latter one [15]. In the case of the IrO_2 - Ta_2O_5 - SnO_2/Ti anode, the electrochemical combustion of PSA implies that the growth of the organic film is suppressed. This mechanism seems to be reasonable based on the present results, that is, the dependences of the oxygen overpotential and lifetime of the IrO_2 - Ta_2O_5 - SnO_2/Ti anode on the SnO_2 ratio. Although further studies are needed to fully understand the role of SnO_2 mixed in the coating layer, a significant improvement in the durability of the IrO_2 -based anode has been achieved and this is of practical importance. Moreover, the results obtained in this study also suggest that the prolongation of the lifetime by the SnO_2 addition is also possible for use in other electroplating baths containing organic compounds other than PSA, if the organic compounds induce the degradation of the catalytic activity by the formation of an undesirable organic film on the anode.

4. Conclusions

The oxygen overpotential of the IrO_2 - Ta_2O_5 - SnO_2/Ti anode in a solution containing PSA is less positive potential than that of the IrO_2 - $\text{Ta}_2\text{O}_5/\text{Ti}$ anode, although the oxygen overpotentials of both anodes are almost identical in the solution without PSA. The addition of SnO_2 in the catalytic layer of the IrO_2 -

Ta₂O₅/Ti anode is also beneficial for prolonging the lifetime of the anode in PSA solution. These advantages are not caused by the increase in the active surface area and the enhancement of the catalytic activity attributed to SnO₂ for oxygen evolution. The enhanced durability of the IrO₂-Ta₂O₅-SnO₂/Ti anode is attributable to the complete oxidizing of PSA promoted by SnO₂ on the anode, which results in the suppression of growth of the organic film originating from the PSA.

References

1. M. Matsunaga, M. Morimitsu, H. Meng, T. Kunihiro and R. Otagawa, in Proceedings of AESF/SFSJ Advanced Surface Technology Forum, AESF, Orlando, FL (1998), p. 185.
2. R. Otagawa, H. Shimizu, T. Inoue, M. Morimitsu and M. Matsunaga, in Proceedings of 9th Continuous Steel Strip Plating Symposium, AESF, Orlando, FL (1999), pp. 11–16.
3. C.G. Ferron and P. F. Duby, in F. Hine, B. V. Tilak, J. M. Fenton and J. D. Lisius, (Eds.), Proceedings of the Symposium on Performance of Electrodes for Industrial Electrochemical Processes, PV 89-10, The Electrochemical Society Proceedings Series, Pennington, NJ (1989), p. 259.
4. M. Takahashi, *Soda To Enso* (Electrochemical Society of Japan; in Japanese) **39** (1988) 531.
5. H. Meng, M. Morimitsu, M. Matsunaga and R. Otagawa, *Denki Kagaku* **66** (1998) 1148.
6. R. Otagawa, M. Morimitsu and M. Matsunaga, *Electrochim. Acta* **44** (1998) 1509.
7. R. Otagawa, K. Soda, S. Yamauchi, Y. Nagatoishi, M. Morimitsu and M. Matsunaga, *Denki Kagaku* **65** (1997) 987.
8. J. F. C. Boodts and S. Trasatti, *J. Electrochem. Soc.* **137** (1990) 3784.
9. C. Comninellis and G. P. Vercesi, *J. Appl. Electrochem.* **21** (1991) 136.
10. C. P. De Pauli and S. Trasatti, *J. Electroanal. Chem.* **396** (1995) 161.
11. T. A. F. Lassali, L. O. S. Bulhoes, L. M. C. Abeid and J. F. C. Boodts, *J. Electrochem. Soc.* **144** (1997) 3348.
12. G. N. Martelli, R. Ornelas and G. Faïta, *Electrochim. Acta* **39** (1994) 1551.
13. R. Mraz and J. Krysa, *J. Appl. Electrochem.* **24** (1994) 1262.
14. J. Krysa, L. Kule, R. Mraz and I. Rousar, *J. Appl. Electrochem.* **26** (1996) 999.
15. C. Comninellis, *Electrochim. Acta* **39** (1994) 1857.