

## Formation Mechanism of Non-conductive PbSO<sub>4</sub> on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti Anodes in Copper Foil Production

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This study elucidated electrochemical behaviors of an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode and pre-deposited PbO<sub>2</sub> layers of two types on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anodes in H<sub>2</sub>SO<sub>4</sub> solutions. The onset potential for the reduction of β-PbO<sub>2</sub> of a pre-deposited PbO<sub>2</sub> layer prepared from acidic solutions was more positive than the oxygen evolution potential on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode. Formation of a non-conductive PbSO<sub>4</sub> film on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anodes in copper foil production can be attributed to the formation of a local cell consisting of a PbO<sub>2</sub> cathode and an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode during an open-circuit condition.

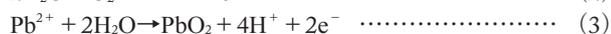
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### 1. Introduction

An IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> coated Ti anode prepared by thermal decomposition has excellent catalytic properties for oxygen evolution in acidic solutions<sup>1)–33)</sup> and its long lifetime has been proven for applications in electrogalvanizing and electroplating of steel<sup>8),12)–18)</sup>. The IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode has been also applied for copper foil production<sup>34)–37)</sup>. Copper foil production is a process to produce a thin film of copper, and uses a rolling drum type cathode and a U-shape IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode, in which the electrolyte is an acidic copper sulfate solution. Here, the cathodic reaction is copper deposition (1).



The current density in copper foil production is much lower than that of zinc or tin electroplating of steel so that a long lifetime could be achieved with a decrease in the oxygen evolution potential compared to commercially used Pb alloy electrodes. However, there are some cases where the oxygen evolution potential happens to increase without the consumption of the oxide coating, but with the deposition of PbO<sub>2</sub> on the coating. This is caused by unwanted side reactions of Pb(II) ions existing in the electrolyte. In copper foil production, the anodic reaction is mainly oxygen evolution (2), but the electrolyte also contains Pb(II) ions as an impurity, and Pb(II) ions are also oxidized to form PbO<sub>2</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode (3). The deposited PbO<sub>2</sub> deteriorates the catalytic activity of the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode.



Moreover, the deposited PbO<sub>2</sub> is known to be partially reduced to PbSO<sub>4</sub> (4) on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode, for which the reduction mechanism has been unknown.



Since PbSO<sub>4</sub> is non-conductive, a continuous copper foil production is disturbed by removing PbSO<sub>4</sub> on the anode in actual uses. From the situation described above, this study aimed to resolve the formation mechanism of PbSO<sub>4</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode in copper foil production.

### 2. Experimental

Three kinds of samples were prepared. An IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> coating (sample A) was prepared by thermal decomposition on a titanium substrate which had been degreased with acetone, etched in 10 % oxalic acid solutions at 90 °C for 60 min, washed with distilled water, and dried. A precursor solution was prepared by dissolving H<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O and TaCl<sub>5</sub> into 1-butanol containing 6 vol% HCl, in which Ir : Ta ratio was 80 : 20 mol% and then which was coated on the titanium substrate. Thermal decomposition was carried out at 470 °C for 20 min for one coating. The composition and the thermal decomposition temperature are similar to those of commercially available IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anodes. Total metal concentration of the precursor solution was 70 g dm<sup>-3</sup>, and the coating and heating processes were repeated five times. The detailed preparation procedure of the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode is described elsewhere<sup>38),39)</sup>. Two types of pre-deposited PbO<sub>2</sub> layers on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anodes were prepared. It is known that orthorhombic α-PbO<sub>2</sub> and tetragonal β-PbO<sub>2</sub> can be prepared by anodic electrolysis of a substrate in alkaline solutions and in acidic solutions, respectively<sup>40),41)</sup>. Sample B was prepared by the pre-deposition of PbO<sub>2</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode (sample A). The pre-deposition was carried out by anodic electrolysis of the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode in 30 wt% Pb(NO<sub>3</sub>)<sub>2</sub> (pH = 0.7) solutions at 40 mA cm<sup>-2</sup> for 5 min to have a β-PbO<sub>2</sub> layer. The other pre-deposited PbO<sub>2</sub> layer (sample C) was prepared by anodic electrolysis of the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode (sample A) in PbO sat. 4.0 mol dm<sup>-3</sup> NaOH solutions at 1 mA cm<sup>-2</sup> for 15 min to get an α-phase. X-ray diffraction with Cu Kα radiation (Bruker AXS Model D8 FOCUS) was performed to analyze the crystallographic structure of the

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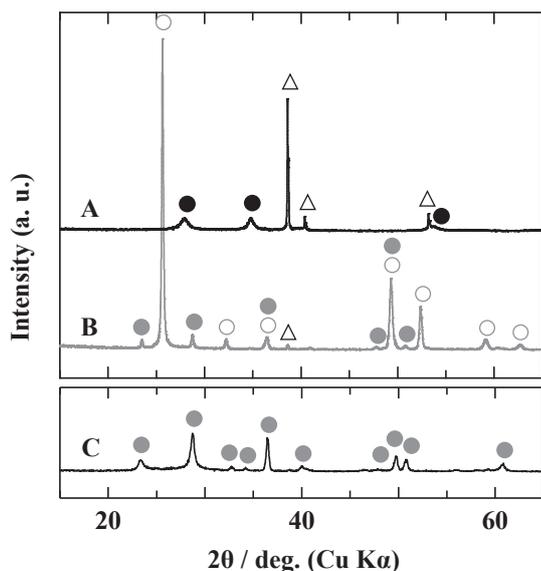
samples. The surface morphology of the samples was observed by SEM (ZEISS, Model SUPRA<sup>M</sup> 55VP), using a normal SE detector and an incident electron beam of 15 keV acceleration voltage. Cyclic voltammetry of the samples was conducted using a conventional three-electrode cell with a KCl sat. Ag/AgCl reference electrode and a platinum plate counter electrode. The electrolytes used in this study were 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solutions. A potenti/galvanostat (EG&G, Model 263A) controlled by an electrochemical analysis software (EG&G, Model 270) was used.

### 3. Results and Discussion

**Fig. 1** shows X-ray diffraction patterns of the samples. Three diffraction peaks at  $2\theta = 28.0^\circ, 34.7^\circ, 54.0^\circ$  are seen for sample A, which are assigned to the diffraction indexes 110, 101, and 211 of IrO<sub>2</sub>, respectively. There are also three diffraction peaks of Ti from the substrate in **Fig. 1A**. It is noted that Ta<sub>2</sub>O<sub>5</sub> prepared by thermal decomposition is amorphous as the thermal decomposition temperature is lower than at least 600 °C<sup>42)</sup>. Therefore, sample A consisted of crystalline IrO<sub>2</sub> and amorphous Ta<sub>2</sub>O<sub>5</sub>, which is in good agreement with our previous works<sup>25,26,38,39,43,44)</sup>. The diffraction peaks of  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> were confirmed on the diffraction pattern for sample B (**Fig. 1B**), which result proved that sample B comprised of  $\beta$ -PbO<sub>2</sub> with a small ratio of an  $\alpha$ -phase on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode.

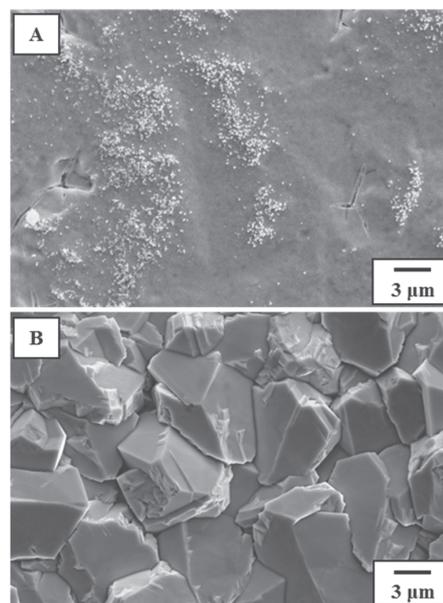
Surface morphologies of two samples (sample A and B) are depicted in **Fig. 2**. Sample A showed a well-known feature of IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> coatings<sup>3,4,10,20,33,38,39,44)</sup>; there are aggregated IrO<sub>2</sub> particles, flat areas, and cracks. Cracks are at least a few micrometers in length, and the morphology is heterogeneous and a so-called "mud-cracked" surface. In **Fig. 2B**, the deposits of PbO<sub>2</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode can be seen, which result has no contradiction to the XRD result in **Fig. 1B**.

Cyclic voltammograms recorded with sample A (IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode) and B (pre-deposited mixture of  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> on IrO<sub>2</sub>-

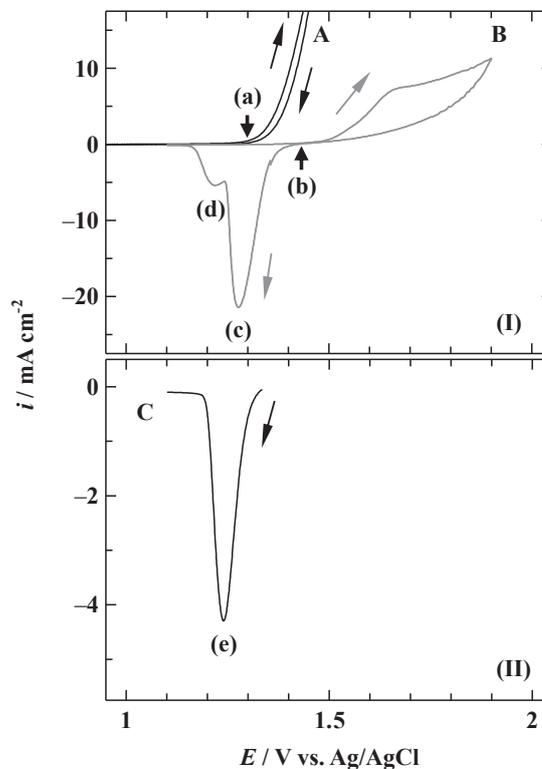


**Fig. 1** X-ray diffraction patterns of sample A (IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode), sample B (pre-deposited PbO<sub>2</sub> on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared from acidic solutions), and sample C (pre-deposited PbO<sub>2</sub> on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared from alkaline solutions). ●: IrO<sub>2</sub>, △: Ti, ●:  $\alpha$ -PbO<sub>2</sub>, ○:  $\beta$ -PbO<sub>2</sub>.

Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared from acidic solutions) in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solutions are shown in **Fig. 3(I)**. Sample A showed the increase in the current density starting at ca. 1.3 V (a), which corresponds to oxygen evolution. Sample B had a higher rest potential (b) than that of sample A, and two cathodic waves appeared



**Fig. 2** Surface morphologies of sample A (IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode) and sample B (pre-deposited mixture of  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared from acidic solutions).



**Fig. 3** (I) Cyclic voltammograms of sample A (IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode) and sample B (pre-deposited mixture of  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared from acidic solutions) and (II) Linear sweep voltammogram of sample C (pre-deposited  $\alpha$ -PbO<sub>2</sub> on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared from alkaline solutions) in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solutions at 25 °C. Scan rate: 5 mV s<sup>-1</sup>.

on the cathodic scan from the rest potential. The first cathodic wave (c) is the reduction of  $\beta$ -PbO<sub>2</sub>, and the second one (d) is that of  $\alpha$ -PbO<sub>2</sub>, which result in the generation of PbSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> solutions. We prepared an  $\alpha$ -PbO<sub>2</sub> pre-deposited sample (sample C) by anodic electrolysis of the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode from alkaline solutions, and confirmed that the deposited layer was a single phase  $\alpha$ -PbO<sub>2</sub> by X-ray diffraction as shown in Fig. 1C. A linear sweep voltammogram of the pre-deposited  $\alpha$ -PbO<sub>2</sub> layer on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode (sample C) in 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solutions is also shown in Fig. 3 (II). A cathodic wave (e) was observed and the peak potential of the wave (e) proved that the second cathodic wave (d) in Fig. 3 (I) corresponded to the reduction of  $\alpha$ -PbO<sub>2</sub>. The results in Fig. 3 suggest that if PbO<sub>2</sub> is deposited on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode in H<sub>2</sub>SO<sub>4</sub> solutions, which is similar to the copper electroplating bath, and partially covers the anode surface, a local cell consisting of a PbO<sub>2</sub> cathode and an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode can be made during an open circuit condition. Pb(II) ions in the electrolyte used in copper foil production is easily oxidized and produce PbO<sub>2</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode, and no reduction of PbO<sub>2</sub> occurs when the electrode is anodically charged, i.e., the electrolysis is continued. However, if the electrolysis is temporally stopped, the local cell is instantaneously closed, resulting in the reduction of PbO<sub>2</sub> to PbSO<sub>4</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode.

#### 4. Conclusion

An IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode and two types of pre-deposited PbO<sub>2</sub> layers on IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anodes were prepared. The IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode consisted of crystalline IrO<sub>2</sub> and amorphous Ta<sub>2</sub>O<sub>5</sub>, and the surface was heterogeneous and showed the "mud-cracked" morphology with aggregated IrO<sub>2</sub> particles, flat areas, and cracks. The pre-deposited PbO<sub>2</sub> layer on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared from acidic solutions was composed of a  $\beta$ -phase with a small ratio of an  $\alpha$ -phase. The onset potential for the reduction of  $\beta$ -PbO<sub>2</sub> of the pre-deposited PbO<sub>2</sub> layer prepared from acidic solutions was more positive than the oxygen evolution potential on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode in H<sub>2</sub>SO<sub>4</sub> solutions. The results suggest that if PbO<sub>2</sub> is deposited on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode in H<sub>2</sub>SO<sub>4</sub> solutions and partially covers the anode surface, a local cell comprised of a PbO<sub>2</sub> cathode and an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode can be made during an open circuit condition, and if the electrolysis is temporally stopped, the local cell is instantaneously closed, resulting in the reduction of PbO<sub>2</sub> to PbSO<sub>4</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode.

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