Distinction of Conductive PbO₂ and Non-conductive PbSO₄ in Deposited Mixtures on IrO₂-Ta₂O₅/Ti Anodes Using SEM with Low Accelerated Incident Electrons

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1. Introduction

IrO₂-Ta₂O₅/Ti anodes prepared by thermal decomposition have excellent catalytic properties for oxygen evolution in acidic solutions, and the long lifetime has been proven in industrial electrolysis such as electrowinning and electroplating[1]. We have recently reported a big problem in practical uses of IrO₂-Ta₂O₅/Ti anodes[2-3]; if Pb(II) ions exist in electrolytes, e.g., the solutions of Cu foil production or Cu electrowinning, Pb(II) ions are oxidized to form PbO₂ on the commercially available IrO₂-Ta₂O₅/Ti anode prepared at a high temperature such as 470 °C or higher during the electrolysis, and then PbO₂ is partially reduced to non-conductive PbSO₄ when the electrolysis is temporarily stopped. While the mixture of PbO₂ and PbSO₄ deposited on the anode can be analyzed by X-ray diffraction (XRD) to detect the existence, it is difficult to show their surface distribution by conventional elemental analysis methods such as energy dispersive X-ray analysis (EDX), because the energies of characteristic X-rays of Pb Kα and S Kα peaks are very close (Pb Kα = 2.350 keV, S Kα = 2.308 keV). On the other hand, we have also reported that the nano-structured IrO₂ particles dispersed in the amorphous Ta₂O₅ matrix are successfully distinguished on secondary electron microscope (SEM) images obtained at low acceleration voltage like 5 keV or lower[4-5]. In this paper, the results by the same technique applied to distinguish conductive PbO₂ and non-conductive PbSO₄ deposited on IrO₂-Ta₂O₅/Ti anodes are shown, and the benefit of using low accelerated incident electron beams and the in-lens secondary electron detector is reported.

2. Experimental

Titanium plates (10 x 50 x 1 mm) were used as the substrate of the anode samples and were pretreated by ultrasonic wave cleaning in acetone and etching in 10 wt% oxalic acid at 90°C for 60 min, washing with distilled water, and drying before creating IrO₂-Ta₂O₅ coatings. The IrO₂-Ta₂O₅ coating was prepared by thermal decomposition of the precursor solution painted on the substrate through drying at 120 °C for 10 min and heating at 470 °C for 20 min, in which the painting to heating process was repeated 5 times to obtain IrO₂-Ta₂O₅/Ti anode (Sample A). The precursor solution was prepared by dissolving H₂IrCl₆·nH₂O and TaCl₅ into n-butanol containing 6 vol% HCl so that the total metal (Ir + Ta) concentration was 70 mg cm⁻² and the iridium mole ratio was 50 mol%. The anodic electrolysis of the IrO₂-Ta₂O₅/Ti anode in 30 wt% Pb(NO₃)₂ (pH = 0.7) solutions at 40 mA cm⁻² for 5 min at 70°C was carried out using the platinum cathode to deposit PbO₂ and the resulted anode was assigned as Sample B. The electrolysis using 0.5 mol dm⁻³ H₂SO₄ with 100 ppm PbSO₄ solutions at 1 A cm⁻² for 5 h at 70 °C was also performed to prepare another sample (Sample C). X-ray diffraction with Cu Kα radiation (Bruker AXS Model D8 FOCUS) was used to analyze those samples, and the surface morphology was observed using high-resolution SEM (ZEISS, Model SUPRA® 55VP) with two different modes. The high-voltage mode used a normal SE detector and an incident electron beam of 15 keV acceleration voltage, and the low-voltage mode used an in-lens SE detector and 1 keV as previously described[6-7]. Such a low acceleration voltage is advantageous for suppressing the penetration of the electron beam into the oxide coating, i.e., the penetration depth at 1 keV is 5 nm, which is about 1/8 at 15 keV[8]; so that the SEM image at 1 keV is limited to the information of the outermost surface[9-10].

3. Results and Discussion

Sample A presented some diffraction peaks corresponding to crystalline IrO₂ and the titanium substrate, as shown in Fig. 1A, while no diffraction of Ta₂O₅ was seen because the heating temperature was lower than 600°C required for crystallization of Ta₂O₅. This is in good agreement with our previous studies[11-12], and the coating comprising crystalline IrO₂ and amorphous Ta₂O₅ was formed for Sample A. Fig. 1B was obtained with Sample B, in which the diffraction patterns of α- and β-PbO₂ are shown, indicating that the surface deposit of Sample B was the mixture of β-PbO₂ with a

![Fig. 1 X-ray diffraction patterns of the samples.](image-url)
small ratio of $\alpha$-phase, as similar to the literature\(^5\). Sample C gave the
diffraction peaks of PbSO\(_4\) as well as $\alpha$- and $\beta$-PbO\(_2\) as shown in Fig. 1C, which means that PbO\(_2\) deposited on the IrO\(_2\)-TaO\(_5\) coating in H\(_2\)SO\(_4\) is easily reduced just after the electrolysis ends, due to the local
cell reaction mechanism as explained in our recent paper\(^6\); PbO\(_2\) is the
local cathode and the IrO\(_2\)-TaO\(_5\) coating which is not covered with
PbO\(_2\) is the local anode during the open-circuit condition.

Fig. 2 summarizes the SEM images obtained at 15 keV. The SEM
image of Sample A (Fig. 2A) shows a well-known feature of IrO\(_2\)-
TaO\(_5\) coatings\(^{21-23,26-31}\), i.e., aggregated IrO\(_2\) particles, flat areas, and
-cracks; the heterogeneous morphology is generally called as a “mud-
-cracked” surface. In Fig. 2B and C (Sample B and Sample C), some
deposits are seen on the aggregated IrO\(_2\) particles of IrO\(_2\)-TaO\(_5\) coat-
ings, which would be PbO\(_2\) for sample B and the mixture of PbO\(_2\) and
PbSO\(_4\) for sample C, based on the XRD results. However, no one can
distinguish PbO\(_2\) with PbSO\(_4\) from such SEM images.

In Fig. 3, SEM images of sample C for the same area obtained
at 15 keV (left) and at 1 keV (right) are compared, in which the deposits
are seen with different brightness in the image at 1 keV. Considering the effects of the conductivity on the contrast of the
SEM image that the higher conductive part shows brighter image,
observed at the same area of the sample by changing the acceler-
a tion voltage of the electron beam. Therefore, SEM observation at
1 keV indicates that the depth of the electron beam more clearly
reflects the difference in conductivity which is given as the differ-
e nce in brightness. The SEM measurement technique shown in this
study is helpful for the similar situation that the target for analysis
is the mixture containing compounds that are difficult to distin-
guish by characteristic X-ray.

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