Insoluble Anodes for Copper Foil Production (I): Inhibition of Non-conductive $PbSO_4$ Film Formation

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An insoluble anode for oxygen evolution has been widely used in electrogalvanizing and electrotinning of steel. One of the most favorable anodes consists of an IrO_2-Ta_2O_5 catalytic layer coated on a titanium substrate. This type of anode has been also applied for copper foil production, although the replacement of a previously used Pb alloy anode with the IrO_2-based anode presents a problem particular to copper foil production, which is related to the impurity, Pb(II) ions, contained in the copper electroplating bath. Pb(II) ions are oxidized to PbO_2 on the IrO_2-Ta_2O_5/Ti electrode during oxygen evolution, and PbO_2 deposited on the anode hinders a high catalytic activity of IrO_2 during a long-term operation. Moreover, the deposited PbO_2 is known to be reduced to $PbSO_4$ on the electrode, for which the reason has been unknown. Since $PbSO_4$ is non-conductive, a continuous copper foil production is disturbed by removing $PbSO_4$ on the anode in actual uses. From the situation described above, this study aimed to resolve the reason for the formation of $PbSO_4$ on the IrO_2-Ta_2O_5/Ti electrode in copper foil production and then to develop the method to suppress the undesirable reaction.

Figure 1 depicts the cyclic voltammograms recorded with IrO_2-Ta_2O_5/Ti electrodes with and without pre-deposited PbO_2 at 5 mV/s in a 0.5 mol/dm^3 H_2SO_4 solution. The pre-deposition was carried out by the anodic electrolysis of the electrode in 30 wt% $Pb(NO_3)_2$ solution. The obtained PbO_2 consisted of beta-phase with a small ratio of alpha-phase. The freshly prepared electrode showed the increase in current density starting at *ca.* 1.3 V, which corresponds to oxygen evolution. The PbO_2 pre-deposited electrode had a higher rest potential than the fresh electrode, and two cathodic waves appeared on the first scan from the rest potential. The first cathodic wave is the reduction of beta-PbO_2, and the second one is that of alpha-PbO_2. Both of them results in the generation of $PbSO_4$ in the H_2SO_4 solution. Therefore, the result in Fig. 1 suggests that if PbO_2 is deposited on the IrO_2-Ta_2O_5/Ti electrode in H_2SO_4 solution, which is similar to the copper electroplating bath, and partially covers the electrode surface, a local cell consisting of PbO_2 cathode and IrO_2-Ta_2O_5 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_2 on the IrO_2-Ta_2O_5/Ti electrode, and no reduction of PbO_2 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_2 to $PbSO_4$ on the IrO_2-Ta_2O_5/Ti electrode.

Considering the above mentioned mechanism, the local cell formation should be inhibited to avoid the undesirable generation of $PbSO_4$ film. This needed the control of oxygen evolution potential and/or the onset potential of PbO_2 reduction so that no oxygen evolution can occur at more negative potential than the PbO_2 reduction, for which the former case was attempted in this study. We chose SnO_2 as a main component of the electrode material to satisfy the above requirement. The SnO_2-based electrodes were prepared by thermal decomposition of the coating solution containing different ratios of Sn(II) and Ir(IV) ions on a titanium substrate. The Ir mole ratios in the coating solutions ranged from 0 to 5 mol%. Figure 2 shows the cyclic voltammograms of three kinds of SnO_2-based electrode compared with that of an IrO_2-Ta_2O_5 electrode. The result indicates that oxygen evolution potential depends on the composition of the SnO_2-based electrodes, in which the electrodes containing Ir below 1 mol% show higher oxygen evolution potential than the onset potential of PbO_2 reduction (dash line). In fact, it was confirmed that no local cell could be made between the electrodes (Ir = 1 mol% and less) with and without pre-deposited PbO_2. Therefore, the undesirable reduction of PbO_2 to $PbSO_4$ on the insoluble oxide anode in copper foil production can be inhibited by controlling oxygen evolution potential, which should be more positive than the onset potential of PbO_2 reduction. This study demonstrated that the potential control can be accomplished by selecting an appropriate oxide component for the electrode material so as to satisfy the requirement for oxygen evolution potential.

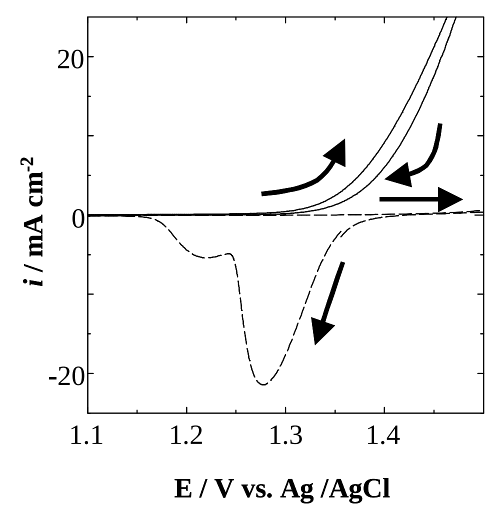

Fig. 1 Cyclic voltammograms of the IrO_2-Ta_2O_5/Ti electrodes with (dash line) and without (solid line) pre-deposited PbO_2 in H_2SO_4 solution.

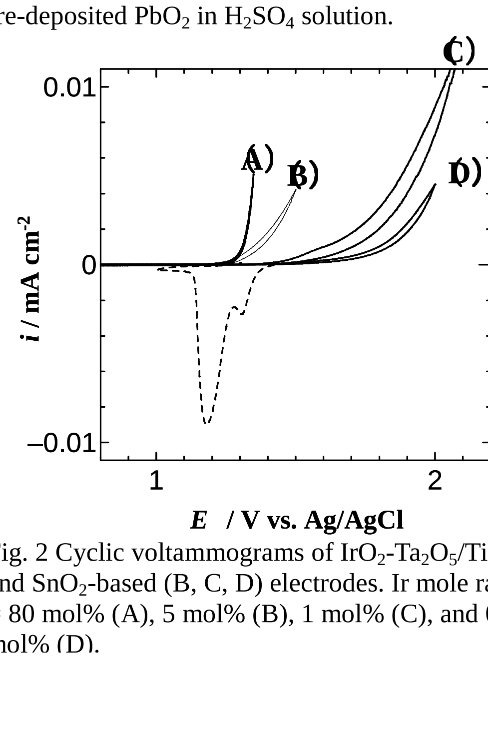

Fig. 2 Cyclic voltammograms of IrO_2-Ta_2O_5/Ti (A) and SnO_2-based (B, C, D) electrodes. Ir mole ratio = 80 mol% (A), 5 mol% (B), 1 mol% (C), and 0.5 mol% (D).