Accelerated Oxygen Evolution and Suppressed MnOOH Deposition on Amorphous IrO_2–Ta_2O_5 Coatings

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This paper reports novel catalytic properties of amorphous IrO_2–Ta_2O_5 coatings prepared by thermal decomposition for industrial electrolysis applications, especially zinc electrowinning. The coating formed on a titanium substrate can accelerate oxygen evolution in H_2SO_4 solutions and suppress the anodic deposition of MnOOH. The results are valuable to reduce the anode potential and prevent the deactivation of the anode surface by MnOOH deposition in zinc electrowinning.

Zinc electrowinning uses a sulfuric-acid-based solution containing Zn^{II} ions, and the electrolysis produces high purity zinc on the cathode. The solution also contains Mn^{II} ions as a minor component, as MnO_2 or $KMnO_4$ are added to the solution as the oxidizer to dissolve $ZnO{\cdot}Fe_2O_3$ generated in the Zn^{II} extraction process. Although the main reaction on the anode of zinc electrowinning is oxygen evolution, the deposition of MnOOH caused by Mn^{II} oxidation on the anode simultaneously occurs.[1] The deposition and accumulation of nonconductive MnOOH on the anode is detrimental, because the anode surface is deactivated for oxygen evolution. A titanium electrode coated with a mixture of IrO_2 and Ta_2O_5 is known to possess high catalytic activity and long lifetime for oxygen evolution in acidic media,[2,3] but even these electrodes are unable to avoid MnOOH deposition.[4] This situation motivated us to develop a novel electrode so as to suppress this unwanted anodic deposition and focused on IrO_2–Ta_2O_5/Ti electrodes prepared by thermal decomposition of a precursor solution at various temperatures. This report presents a variation in crystallographic structure of IrO_2 with temperature and demonstrates accelerated oxygen evolution and suppressed MnOOH deposition on an amorphous IrO_2–Ta_2O_5 coating.

A titanium plate (1 cm × 5 cm × 1 mm, 99.9% purity) was degreased in acetone and etched in 10% oxalic acid solution at 90 °C for 60 min. A precursor solution was prepared by dissolving $H_2IrCl_6{\cdot}6H_2O$ and $TaCl_5$ into 1-butanol with 6 vol % HCl, in which the Ir:Ta ratio was 80:20 mol % and the total metal concentration was 70 g L^{-1}. The titanium plate was dipped into the precursor solution, dried at 120 °C for 10 min, and heated at a temperature between 360 and 470 °C to coat the plate with a mixture of IrO_2 and Ta_2O_5. This process was repeated five times, and the average amount of the coating was ca. 0.9 mg cm^{-2}. The crystallographic structure of IrO_2–Ta_2O_5 coatings was characterized by X-ray diffraction (XRD) with Cu Kα radiation. Electrochemical measurements were conducted using a three-electrode cell equipped with a platinum counter electrode and a KCl saturated Ag/AgCl reference electrode. The working electrode was IrO_2–Ta_2O_5/Ti mounted in a PTFE holder to limit the exposed surface area to be 1 cm^2.[5] At least three electrodes for each thermal decomposition temperature were used in the experiments. Reagent grade concd H_2SO_4, $MnSO_4{\cdot}5H_2O$, and distilled water were used to prepare 2.0 mol L^{-1} H_2SO_4 solutions with and without 0.10 mol L^{-1} Mn^{II}. All measurements were conducted at 40 °C without stirring.

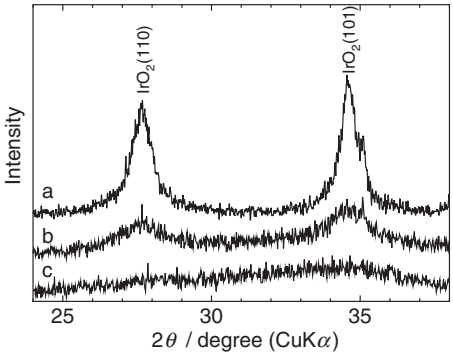

Figure 1. X-ray diffraction patterns of IrO_2–Ta_2O_5/Ti electrodes prepared at 470 (a), 380 (b), and 360 °C (c).

Commercially available IrO_2–Ta_2O_5/Ti electrodes are usually produced through thermal decomposition of a precursor solution at 450 °C or more, and the coating consists of a mixture of crystalline IrO_2 and amorphous Ta_2O_5.[3] The electrode prepared at 470 °C in this study demonstrated a similar feature in XRD data as shown in Figure 1a. However, decreasing temperature induced a phase transition from crystalline IrO_2 to amorphous as seen in Figures 1b and 1c, in which two diffraction peaks of IrO_2, (110) and (101), are depressed at 380 °C and are merged into a broad and weak peak at 360 °C. The results indicate that the amorphization of IrO_2 substantially occurs at 380 °C and further proceeds at 360 °C. It is noted that thermal decomposition of the precursor solution used in this study produces amorphous Ta_2O_5 and no remained chloride in the coatings irrespective of thermal decomposition temperature between 360 and 470 °C.

Cyclic voltammetry was performed in a sulfuric acid solution without $MnSO_4$ to evaluate double layer charge. The voltammogram was measured in the potential range from 0.50 to 1.0 V to calculate the double layer charge per unit geometrical surface area (1 cm^2), Q_{dl}. The average Q_{dl} values of the electrodes prepared at 470, 380, and 360 °C were 5.7, 45, and 46 mC cm^{-2} as the scan rate was 100 mV s^{-1}. The double layer charge reflects the active surface area of the electrode, and the obtained results for Q_{dl} suggests that a significant increase in the active surface area can be achieved by the amorphization of IrO_2 in the IrO_2–Ta_2O_5 coatings by only changing thermal de-

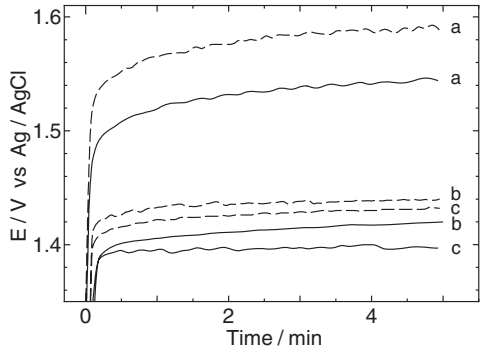

Figure 2. Potential variations of IrO_2–Ta_2O_5/Ti electrodes prepared at 470 (a), 380 (b), and 360 °C (c) during constant current electrolysis at 50 mA cm^{-2} in 2.0 mol L^{-1} H_2SO_4 with (dash line) and without (solid line) 0.10 mol L^{-1} $MnSO_4$ at 40 °C.

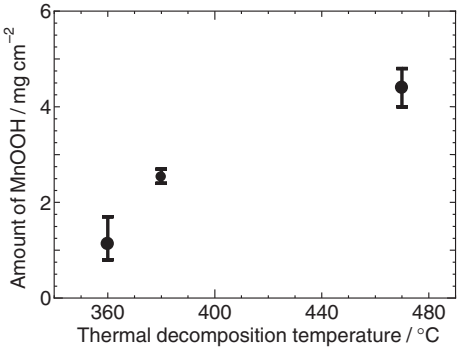

Figure 3. Amount of MnOOH deposited on IrO_2–Ta_2O_5/Ti electrodes during constant current electrolysis at 10 mA cm^{-2} for 20 min in 2.0 mol L^{-1} H_2SO_4 containing 0.10 mol L^{-1} $MnSO_4$ at 40 °C.

composition temperature. This is also supported by the fact that oxygen evolution current observed in the H_2SO_4 solution without Mn^{II} by cyclic voltammetry was much enhanced on the coating comprising amorphous IrO_2 compared to that comprising crystalline IrO_2. Oxygen evolution potential was further measured by constant current electrolysis, and the results are shown in Figure 2. The oxygen evolution potential at 50 mA cm^{-2}, a typical value of current density for zinc electrowinning, was reduced by ca. 0.15 V on the electrode prepared at 360 °C compared to that at 470 °C for the H_2SO_4 solution, and this difference was also observed for the solution containing Mn^{II}. The result indicates that the anode potential reduction and electric energy saving in zinc electrowinning can be possible by using the amorphous IrO_2–Ta_2O_5/Ti electrode. This is due to large active surface area of the amorphous coating, which makes the real current density small, resulting in low oxygen overpotential.

The anodic behaviors of Mn^{II} ions added into the H_2SO_4 solution were examined by cyclic voltammetry at a slow scan rate (1 mV s^{-1}) and constant current electrolysis. The cyclic voltammogram measured with the electrode prepared at 470 °C showed an oxidation wave on the anodic scan from the rest potential, which was followed by a rapid increase of current due to oxygen evolution. The reverse scan presented a reduction wave in the same potential region as the oxidation wave. Those waves are attributed to the oxidation of Mn^{II} and the reduction of MnOOH deposited on the electrode, which is in a good agreement with the results reported in the literature.[1] On the other hand, the voltammograms obtained with the electrodes calcined at 380 and 360 °C revealed that the current increased monotonously without the oxidation wave during the anodic sweep. This suggests that oxygen evolution is more promoted in the potential region where the oxidation of Mn^{II} occurs and agrees with the result shown in Figure 2. However, the reduction wave was still observed in the voltammogram. This seemed to imply that Mn^{II} oxidation to produce MnOOH deposits was not completely inhibited on those electrodes. However, cyclic voltammetry is a potentiodynamic method so that the reaction product is supposed to increase with increasing active surface area of an electrode even at the same potential. Commercial zinc electrowinning always uses a galvanostatic, i.e., constant current, electrolysis, thereby it is expected that the larger an active surface area is, the smaller the current density and reaction product. In this study, constant current electrolysis using the H_2SO_4 solution containing $MnSO_4$ was carried out, and the weight of the electrode before and after the electrolysis was measured to calculate the amount of MnOOH deposited on the electrode. Figure 3 depicts the results obtained by the electrolysis at 10 mA cm^{-2} for 20 min. It is clear from this figure that the amount of MnOOH is reduced with lowering thermal decomposition temperature. It can be concluded that the amorphous IrO_2–Ta_2O_5 coating can accelerate oxygen evolution and suppress MnOOH deposition which potentially occur in the same potential region in H_2SO_4 solutions.

Although the mechanism to suppress MnOOH deposition is now under investigation, it is worth to note a possibility of a mechanism hereafter: Oxygen evolution in acidic aqueous solution results from water decomposition and produces protons. Protons are also generated through the deposition of MnOOH, following two steps,

$$Mn^{II} \rightarrow Mn^{III} + e \quad (1)$$

$$Mn^{III} + 2H_2O \rightarrow MnOOH + 3H^+ \quad (2)$$

where the second step is a chemical reaction. If oxygen evolution is accelerated so as to increase protons at the electrode/solution interface, the reaction rate of eq 2 is expected to be greatly reduced so as to counteract the increase of protons by oxygen evolution, from Le Chatelier's principle of chemical equilibrium. This mechanism gives no contradiction to the fact that cobalt oxyhydroxide deposition on the anode of cobalt electrowinning is difficult in a strongly acidic solution at pH lower than 1.[6]

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