Oxygen Evolution Overpotential of Pb-based Insoluble Anode Containing Ru Oxide Powders Prepared by Liquid-phase Reaction and Heating

Hiroki TAKAHASHI1, Yuuji OZAWA1, Keisuke OHKUBO1, Masami TAGUCHI1 and Kazunari SUZUKI2

1Department of Materials Science, Graduate School of Engineering Science, Akita University, Akita 010-8502, Japan
2Metallurgical Laboratory, DOWA METALS & MINING CO., LTD., Akita 011-0911, Japan
E-mail : tkhsrk@gipc.akita-u.ac.jp

Ruthenium oxide powders were produced by the reaction of an RuCl₃ solution with H₂O₂, followed by heating of the resulting precursor at a temperature between 200°C and 600°C in air. Pb-based anodes containing these heated products of 1.0 mass% were prepared by the powder-rolling method, and the effect of the heated product as an electrode catalyst on lowering the anode potential was investigated in order to develop an energy-saving insoluble anode for Zn electrowinning. Based on XPS results, RuO₂ with a significant amount of RuO₂·nH₂O was produced by heating the precursor at 250°C or lower. The ratio of RuO₂ to RuO₂·nH₂O increased remarkably above 300°C and the potential of the Pb-based anode decreased in inverse proportion to the RuO₂ content of the heated product. The lowest anode potential of 1.72 V vs. NHE, which was about 360 mV lower than that of the anode with the unheated precursor, was observed for the Pb-based anode containing the product heated at 400°C. However, the anode potential of the Pb-based anode increased again when the heating temperature was 500°C or higher. The subsequent increase in the anode potential was probably caused by a decrease in the active sites of the oxygen evolution reaction, that is, the grain growth of the heated product decreased the effective reaction area of the RuO₂ catalyst.

Keywords : Ruthenium Oxide, Oxygen Evolution Overpotential, Liquid-phase Reaction, Insoluble Anode, Zinc Electrowinning

1 INTRODUCTION
Zn electrolysis is a material production method that consumes large amounts of electric power. The industrial power prices of Japan are quite high compared to those of the other advanced nations1). Additionally, since the Great Eastern Japan Earthquake of March 11th, 2011 power prices have tended to increase2). Under such a situation, a sharp reduction in the production cost of Zn is needed in order to maintain global competitiveness. For this requirement, the most important matter is to reduce the electric power required for Zn electrowinning.

The main Zn electrowinning electrochemical reactions are shown by equations (1) - (3)3).

Anode : H₂O → 2H⁺ +1/2O₂ + 2e⁻  
(1)
Cathode : Zn²⁺ + 2e⁻ → Zn  
(2)
Total : H₂O + Zn²⁺ → 2H⁺ + 1/2O₂ + Zn  
(3)

The composition of the bath voltage, \( V_T \) (V), for Zn electrowinning is represented by equation (4).

\[ V_T = E_{th} + E_{th} + \eta_c + |\eta_a| \]  
(4)

where \( E_{th} \) (V) is the theoretical decomposition voltage, \( E_{th} \) (V) is the ohmic loss, \( \eta_c \) (V) is the anode overpotential and \( \eta_a \) (V) is the cathode overpotential. Furthermore, the electric energy required for Zn electrowinning, \( W \) (Ws), is the product of the bath voltage \( V_T \) (V) by the amount of electric charge passed \( Q \) (C), and the \( Q \) required to produce Zn of 1 t is essentially determined by Faraday’s law. Therefore, it is important to reduce the bath voltage \( V_T \) in order to reduce the energy consumption. However, the theoretical decomposition voltage \( E_{th} \) which is one of the parameters of the bath voltage, is a constant value which is thermodynamically determined. Moreover, there is limited scope for reducing the ohmic loss \( E_{th} \) and the cathode overpotential \( \eta_c \) since technical improvements are already near their limit. Thus, it becomes very important to reduce the anode overpotential \( \eta_a \) in order to reduce the bath voltage. In addition, a significant part of the anode overpotential is the oxygen evolution overpotential. Therefore, it can be concluded that an effective way to reduce the electric power required for Zn electrowinning is to reduce the oxygen evolution overpotential on the Pb-based insoluble anode4).

Our research team has produced a Pb-based anode containing homogeneously distributed oxide powders as the electrode catalyst by adopting a new powder-rolling method5), which replaces the conventional cast-rolling method6). Pb-based anodes containing various oxide catalysts have been produced by this powder-rolling method and the anode potential investigated by galvanostatic electrolysis. A remarkable decrease in anode potential was observed in a Pb-based powder rolled anode containing RuO₂ powder as the electrode catalyst (See Figure 1). It was concluded that the alternative Pb-based anode incorporating RuO₂ powder was very effective in decreasing the oxygen evolution overpotential and reducing the electric power required for Zn electrowinning7).
However, a required precondition is that RuO₂ powder be cheaply manufactured in large quantities in order to put the invention to practical use. In the field of catalytic chemistry, a technique for obtaining nanoscale oxide particles by reacting a precious metal chloride solution and hydrogen peroxide to produce an insoluble precursor and then heating the precursor in the atmosphere has been widely used\(^1\)\(^,\)\(^2\)\(^,\)\(^3\)\(^,\)\(^4\). For example, Chang and Hu combined an H₂O₂ solution with an RuCl₃ solution to produce a precursor and then applied the heated precursor product to a capacitor material\(^4\)\(^,\)\(^5\). According to their research, Ru oxide can be prepared more easily than with a general sol-gel process and the yield of RuO₂ in the heated product is relatively high.

In this study, the process of cheaply manufacturing RuO₂ powder in large quantities was investigated in order to put the Pb-RuO₂ powder-rolled anode to practical use. The investigation consisted of producing the precursor by reacting an H₂O₂ solution with an RuCl₃ solution, and then heating individual precursor samples for 2 h at 200°C, 250°C, then in 100°C steps from 300-600°C. The chemical bonding state and specific surface area of the heated products were analyzed using XRD, XPS and BET methods. Subsequently, Pb-based anodes containing 1.0 mass% of the heated products were prepared by the powder-rolling method and the anode potential of the oxygen evolution reaction on the Pb-based anode was measured during galvanostatic electrolysis. Additionally, the cause of the oxygen evolution overpotential decrease in the Pb-based powder-rolled anode was discussed based on the analysis results, such as the chemical bonding state of the heated product.

### 2 EXPERIMENTAL

#### 2.1 Preparation of Ru oxide powder

The flow diagram for the preparation of the Ru oxide powder is shown in Figure 2. The Ru oxide powder was prepared by producing the precursor from the reaction of the RuCl₃ and H₂O₂ solutions, then heating it. First 0.50 g of the RuCl₃ reagent (Wako, 99.9 mass%) was dissolved in 50 ml of pure water. The pH of the solution was then adjusted to about 5 by adding a 5 mass% NaOH solution. This adjustment is needed to prevent a backward reaction during the next step: adding the H₂O₂ solution. Adding about 50 ml of the H₂O₂ solution (Wako, 30 mass%) into the RuCl₃ solution caused vigorous oxygen evolution, and brown powdery products precipitated in the solution. Based on the literature\(^13\)\(^,\)\(^14\), it was presumed that the following reactions occurred in this operation:

\[
\begin{align*}
2\text{RuCl}_3 + 5\text{H}_2\text{O}_2 &\rightarrow 2\text{RuO}_2 \cdot n\text{H}_2\text{O} + 2\text{O}_2 + 2(1-n)\text{H}_2\text{O} + 6\text{HCl} \quad (5) \\
\text{RuO}_2 \cdot n\text{H}_2\text{O} + \text{H}_2\text{O}_2 &\rightarrow \text{RuO}_3 + (n+1)\text{H}_2\text{O} \quad (6)
\end{align*}
\]

The centrifugal separation and washing of the precipitate was repeated 3 times. The precipitate was then dried at about 60°C for 24 h to become the "precursor". Furthermore, precursor samples were heated in the range 200-600°C for 2 h in air using an electric furnace. Henceforth, the final substance obtained by this operation will be called the "heated product" in this study.

#### 2.2 TGA, XRD, XPS and BET analysis

An analysis of the precursor by TGA ( Rigaku, TG8120) was first conducted in order to clarify the chemical reaction during the heating process. Al₂O₃ reagent ( Wako, 99.99 mass%) was used as the reference, and the mass loss ΔW (g) and the electromotive force E (μV) produced by the difference in temperature between the sample and reference were measured in air at a scan rate of 10°C min⁻¹ from room temperature to 800°C. The chemical nature of the product obtained by heating the precursor for 2 h at a range of temperatures was analyzed by X-ray diffraction ( Rigaku, SmartLab-2080A211) using Cu Kα. The accelerating voltage and the emission current were 45 kV and 200 mA, respectively. The XPS (KRATOSANALYTICAL, AXIS-ULTRA) analysis was also performed using aluminum as the X-ray source. The sample was irradiated with X-rays at an accelerating voltage of 15 kV and emission current of 9 mA, and the X-ray photoelectron spectrum of C1s, O1s and Ru3p levels were measured. The measured spectra were analyzed by wave separation based on a mixed Gaussian/ Lorentzian function after charge correction of the spectra using the binding energy of the C1s level\(^19\). The specific surface area of the heated product was determined by BET (Quantachrome, Autosorb-
3B) measurement. Before the measurement, the sample was placed in a glass cell and heated in a vacuum for 5 h with the objective of removing any water and impurities. N₂ gas was then adsorbed in order to measure the specific surface area.

2.3 Evaluation of oxygen overpotential of Pb-based anode

The Pb-based anode, in which the heated product of 1.0 mass% was homogeneously dispersed, was prepared by the powder-rolling method. First, the desired amount of Pb powder (Wako, purity 95.0 mass%) and the heated product of 4.5 g in total were carefully mixed. Next, the mixture was compressed for 120 s at a pressure of about 40 MPa into a tablet of 4 mm thickness and 10 mm diameter. The Pb-based anode with a commercial RuO₂ product (Sigma Aldrich, 99.9%) was also prepared as reference. After soldering a Cu wire to one side of the tablet for electrical connection, it was covered with an epoxy resin except for a reaction area of 78.5 mm² to form the Pb-based powder-rolled anode. The surface of the Pb-based powder-rolled anode was abraded to a grid size of 800 using water-resistant emery papers and then subjected to galvanostatic electrolysis at 60 mA cm⁻² for 5 h using a potentio-galvanostat (Hokuto Denko, HZ-3000). The electrolyte was a 1.53 mol L⁻¹ (150 g L⁻¹) H₂SO₄ solution held at 40°C. The counter electrode and reference was a Pt sheet and an Ag/AgCl electrode in a 3.33 mol L⁻¹ KCl solution, respectively. All the measured potentials were quoted with respect to the normal hydrogen electrode (V vs. NHE).

3 RESULTS AND DISCUSSION

3.1 Thermal analysis curve of precursor and chemical compounds in heated product

Figure 3 shows the TG and DTA curves of the precursor measured in air. The precursor was prepared by adding a H₂O₂ solution to a RuCl₃ solution. The abscissa is the temperature of the sample, T (°C), the left vertical-axis is the mass loss of the sample, ΔW (mg) in the TG curve, and the right one is electromotive force, E (μV) in the DTA curve generated by the difference in temperature between the sample and reference. In the TG curve, the mass of the precursor continuously decreased from room temperature to about 600°C, with the mass loss low at temperatures over 600°C. In the XPS analysis mentioned later, the mass loss of ΔW can be explained as being related to the dehydration of the precursor as RuO₂·nH₂O transforms to RuO₂. Related to this point, the n value of RuO₂·nH₂O was calculated to be 1.38 from the total mass loss during heating. In the DTA curve, a large peak was observed near 350°C. Based on a comparison of the shapes of the DTA curve and the TG one, the large peak might be closely related to crystallization of the RuO₂.

Figure 4 shows the XRD patterns of the products obtained by heating the precursor in air for 2 h at various temperatures. For the RuCl₃·nH₂O reagent, there are three weak, but obvious peaks due to the (100), (200) and (202) planes of β-RuCl₃. On the other hand, no diffraction peak corresponding to the Ru oxide was detected for the precursor and the 200°C heated product, and this fact revealed that these powders retained an amorphous structure. The weak diffraction peaks from the (110), (101) and (211) planes of RuO₂ were detected for the 250°C heated product, while there were many RuO₂ peaks for the products heated at 300°C and higher. Based on a comparison of the TG and DTA curves of the precursor in Figure 3, it can be confirmed that the transition of the hydrated Ru oxide to the anhydrous one occurred at 250°C or more and the crystallization of the anhydrous Ru oxide started near 300°C. Moreover, when the heat treatment temperature was raised from 500 to 600°C, the RuO₂ diffraction peaks sharpened significantly. From this, the crystallite size of the RuO₂, D (m), was calculated by the Scherrer equation using the diffraction peak of the (211) plane.
where $K$ is the form factor of 0.9, $\lambda$ is the X-ray wavelength of $1.5418 \times 10^{-10}$ m, $\beta$ is the full width of half maximum (rad) and $\theta$ is the diffraction angle (rad). Figure 5 shows the relationship between the precursor heating temperature and the RuO$_2$ crystallite size in the heated product. As a result, it became clear that the RuO$_2$ crystallite size increased significantly over 500 °C. To be precise, the crystallite size of the RuO$_2$ is about 15 nm in the heating range of 300-400°C, while it increased to 25 and 60 nm at 500 and 600 °C, respectively.

### 3.2 Chemical bonding state of heat-treated product

Figure 6 shows the X-ray photoelectron spectrum of the Ru3p level of the products obtained by heating the precursor in air for 2 h at various temperatures. The binding energies of 462.2, 463.8 and 466.9 eV, which are shown by the dashed lines in this figure, correspond to RuO$_2$,$^{17}$ RuO$_2$$\cdot$$n$H$_2$O$^{18}$ and RuO$_3$,$^{19}$ respectively. Therefore, it can be judged that most of the separated spectrum belongs to the RuO$_2$$\cdot$$n$H$_2$O for the precursor and the 200 °C heated product. In both samples, the intensity of the peak resulting from RuO$_2$ is quite weak. However, the peak resulting from RuO$_2$ increased in the 250 °C heated product. Moreover, it can be observed that the peak resulting from RuO$_2$ became larger and that from RuO$_2$$\cdot$$n$H$_2$O decreased in the heated products at temperatures of 300 °C and above.

Figure 7 shows the relationship between the heating temperature of the precursor and the chemical compound amounts in the heated products. The amounts of RuO$_2$, RuO$_2$$\cdot$$n$H$_2$O and RuO$_3$ in the precursor, which were calculated from each area of the separated waveform shown in Figure 6, were 12, 69 and 19 mol%, respectively. For the 200 °C heated product, the RuO$_2$ content increased and the RuO$_2$$\cdot$$n$H$_2$O and RuO$_3$ content decreased, but the change in the contents was slight for all the chemical compounds compared to the precursor. On the other hand, in the 250 and 300 °C heated products both the RuO$_2$$\cdot$$n$H$_2$O and RuO$_3$ content decreased, while that of RuO$_2$ significantly increased. To be exact, the RuO$_2$ content of 35 mol% at 250 °C increased to 55 mol% at 300 °C. Additionally, both the increase in RuO$_2$ content and the decrease in RuO$_2$$\cdot$$n$H$_2$O were suppressed and the RuO$_3$ content slightly decreased in the 400 to 600°C heated products. The increase in RuO$_2$ content was only 5% when the temperature was raised from 400 to 600°C. That is, the RuO$_2$ content of 62 mol% at 400°C was limited to 67 mol% even at 600°C. Therefore, by combining all results from XRD and XPS, it can be judged that the RuO$_2$$\cdot$$n$H$_2$O to RuO$_2$ reaction became active around 250°C and the greater part of the RuO$_2$ production was completed by heating at 400°C or higher.

### 3.3 Oxygen evolution overpotential of Pb-based anode dispersed heated product as electrode catalyst

The oxygen evolution overpotential of the Pb-based powder-rolled anode, having the heated product dispersed in the Pb substrate as the electrode catalyst, was evaluated by galvanic electrolysis. EPMA observations revealed that the heated products were homogeneously dispersed in the Pb substrate in the content range of 1 to 5 mass%. Figure 8 shows the backscattered electron image of a Pb-based anode containing 1.0 mass% RuO$_2$ prepared by the powder-rolling method. The RuO$_2$ powders, which appear as black dots, are evenly dispersed in the Pb substrate.

Figure 9 shows the change in the potential of the Pb-based
powder-rolled anodes containing the 1.0 mass% heated products. The electrolytic solution is 1.53 mol L\(^{-1}\) (150 g L\(^{-1}\)) \(\text{H}_2\text{SO}_4\) at 40 °C and the current density is constant at 60 mA cm\(^{-2}\). The obtained potential was converted to normal hydrogen electrode (E = 206 -0.7(t-25); 0 ~ 60°C)\(^{20}\). For the Pb-based powder-rolled anodes with the precursor and the 200°C heated product, although the anode potential continuously decreased during the electrolysis, the final potential after 5 h of electrolysis remained at a high value of around 2.07 V vs. NHE. The Pb-based powder-rolled anode with the 250°C heated product showed a unique change in the electrode potential. The anode potential was near 1.86 V vs. NHE at the start of the electrolysis, but it rapidly increased over 0.3 h, and the final value at 5 h was 2.08 V vs. NHE. The final value of the anode potential is not different from those of the Pb-based powder-rolled anodes with the precursor and the 200°C heated product. On the other hand, the potential was very low for the anodes with heated products in the temperature range 300-500°C. Especially, the lowest potential of 1.72 V vs. NHE was observed for the Pb-based powder-rolled anode with the 400 and 500°C heated products. These anode potentials were 360 mV lower than that of the Pb-based anode with the precursor or the 200°C heated product, and 50 mV lower than that of the anode containing a commercial RuO\(_2\) reagent as the electrode catalyst.

Previous studies have reported that the anode potential was almost 1.99 V vs. NHE for the current cast-rolled insoluble anode used in industry, the Pb-0.70 mass%Ag cast-rolled anode\(^{55}\). Therefore, the Pb-based anode with the 400 or 500°C heated product might attain a decrease in the oxygen evolution overpotential of 270 mV compared to the insoluble anode currently used in Zn electrowinning. If the bath voltage of the Zn electrowinning decreased by 270 mV, a calculation yields a reduction in electric power consumption of 248 kWh t\(^{-1}\). So the Zn electrowinning energy consumption might be reduced 8% using our alternative anode, as the standard energy consumption is estimated to be about 3100 kWh t\(^{-1}\). However, for the anode with the 600°C heated product, the potential rose again to 1.97 V vs. NHE, which is 250 mV higher than that of the anodes with the 400 or 500°C heated product. 

Figure 10 shows the relationship between the heating temperature of the precursor and the anode potential of Pb-based anode containing heated product of 1.0 mass% after 5 h electrolysis. (40°C, 150 g L\(^{-1}\) \(\text{H}_2\text{SO}_4\), 60 mA cm\(^{-2}\))

3.4 Effect of chemical compounds in heated product on the decrease of the anode potential

Figure 11 shows the relationship between the potential of the Pb-based anode with the 1.0 mass% heated product and the percentage of chemical compounds in the product heated at various temperatures. The abscissa, the left vertical-axis and the right one are the heating temperature, the anode potential after a 5 h electrolysis, and RuO\(_2\) or RuO\(_2\cdot n\text{H}_2\text{O}\) content in the heated product, respectively. When the potential decreased significantly between 250 and 300°C, RuO\(_2\) increased, with a reciprocal decrease in 1.0 mass% heated products after a 5 h electrolysis. Although the potentials of the anodes with 200 and 250°C heated products were similar to that of the anode containing the precursor, the anode potential dropped drastically at 300°C. The anode potential then decreased to its lowest level for 400 and 500°C, but the potential increased remarkably again at 600°C. Thus, it is recognized that the heated products obtained between 400 and 500°C can effectively reduce the oxygen evolution overpotential. Moreover, the Pb-based anode with the best-qualified catalyst can reduce the anode potential by 50 mV compared to the anode using a commercial RuO\(_2\) product.

Figure 11 Relationship between heating temperature of precursor and anode potential of Pb-based anode containing heated product of 1.0 mass% after 5 h electrolysis, with chemical compound amounts from Figure 7 overlaid. (40°C, 150 g L\(^{-1}\) \(\text{H}_2\text{SO}_4\), 60 mA cm\(^{-2}\))
RuO$_2$·$n$H$_2$O. Therefore, it can be concluded that the transformation from RuO$_2$·$n$H$_2$O to RuO$_2$ during the heat-treatment of the precursor is closely related to reducing the anode potential, that is, oxygen evolution overpotential of the Pb-based anode. Moreover, Figure 10 reveals that the potential of the anodes with the 400 and 500°C heated products was lower than that of the anode using a commercial RuO$_2$ product, and the result can be explained by the fact that the RuO$_2$ content of the former is higher than that of the latter (See Figure 7). When the heating temperature was raised to 600°C, the RuO$_2$ content became higher than that in the product at 400 or 500°C, but the anode potential rapidly increased at 600°C. The high oxygen evolution overpotential of the anode with 600°C heated product did not relate to the higher RuO$_2$ content. The cause is probably due to the crystallite size of the RuO$_2$ and the specific surface area of the heated product.

Figure 12 shows the relationship between the anode potential of the Pb-based anode and the crystallite size of the RuO$_2$ in the heated products. Figure 11 revealed that the decrease in the potential of the Pb-based anode was strongly affected by the RuO$_2$ content in the heated product. However, the potential of the anode with the 600°C heated product was not low, although the RuO$_2$ content was the highest of all of the heated products. Furthermore, it is obvious in this figure that the crystallite size of the RuO$_2$ rapidly increased at 500°C and above. That is, the crystallite size of 15-16 nm in the 300 and 400°C heating range increased to 27 and 60 nm at 500 and 600°C, respectively. Moreover, the crystal growth of the RuO$_2$ at high temperature suggests that the reaction area of the electrode catalyst would be reduced.

Figure 13 shows the relationship between the crystallite size of the RuO$_2$ and the specific surface area of the heated product, which was determined by BET measurement. As the heating temperature increased, the crystallite size of the RuO$_2$, $D$, increased and the specific surface area of the heated product, $S$, decreased. Although the RuO$_2$ content of the heated product increased at 300°C and above (See Figure 7 & 11), the specific surface area of the heated product also decreased remarkably accompanying the growth of the product grain at 400°C and above. As previously mentioned, the active site of the oxygen evolution reaction is recognized to be RuO$_3$, not RuO$_2$·$n$H$_2$O or RuO$_2$. Moreover, it can be presumed that the remarkable reduction in the active oxygen evolution relative to the growth of the heated product.

**Figure 12** Relationship between heating temperature of precursor and anode potential of Pb-based anode containing heated product of 1.0 mass% after 5 h electrolysis, with RuO$_2$ heated product crystallite size from Figure 5 overlaid. (40°C, 150 g L$^{-1}$ H$_2$SO$_4$, 60 mA cm$^{-2}$)

**Figure 13** Relationship between heating temperature of precursor and specific surface area of heated product. RuO$_2$ heated product crystallite size from Figure 5 is also plotted.

### 4 CONCLUSION

To develop an energy-saving insoluble anode for Zn electrowinning, RuO$_2$ powder was prepared by production of a precursor by a liquid phase reaction followed by heating of the precursor. Then galvanostatic electrolysis of Pb-based anodes containing the heated products in the Pb substrate was carried out. The obtained results can be summarized as follows:

1) By reacting the RuCl$_3$ solution with the H$_2$O$_2$ solution, a precursor mainly composed of RuO$_2$·$n$H$_2$O was obtained. Heating at 250°C or lower for 2 h produced RuO$_2$ with significant amounts of RuO$_2$·$n$H$_2$O and RuO$_3$. Moreover, with heated products of 300°C or higher the RuO$_2$ content significantly increased, while the RuO$_2$·$n$H$_2$O and RuO$_3$ contents reciprocally decreased.

2) With increase in the heating temperature, the potential of the Pb-based anode with the heated product changed remarkably. The Pb-based anode with the 400°C product showed the lowest anode potential, 1.72 V vs. NHE, which was 360 mV lower than that of the anode with the untreated precursor.

3) The potential of the Pb-based anode with the 300°C heated product decreased, with the RuO$_2$ content increasing and both RuO$_2$·$n$H$_2$O and RuO$_3$ content decreasing. Therefore, it can be said that the RuO$_2$ in the product caused the decrease in the oxygen evolution overpotential or anode potential of the Pb-based anode. On the other hand, an increase in the anode potential by heating at 600°C was related to the decrease in the active oxygen evolution sites due to the grain growth of the heated product.

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