Effects of Amorphization of RuO₂-Ta₂O₅ Catalytic Coating (Ru=30 mol%) on Oxygen Evolution in Sulfuric Acid Solution*

by Tian ZHANG^a and Masatsugu MORIMITSU^b

RuO₂-Ta₂O₅ catalytic coatings (Ru=30 mol%) for oxygen evolution were prepared by thermal decomposition at 260 °C, 300 °C, and 500 °C. The crystallographic, surface morphological, and electrochemical properties of the coatings were investigated by X-ray diffraction, SEM, cyclic voltammetry, and chronopotentiometry. The XRD and SEM results revealed that RuO₂ in the coating has less crystallinity with decreasing thermal decomposition temperature and the amorphization of RuO₂ occurs at 260 °C. The amorphous coating accelerated oxygen evolution in H₂SO₄ solutions with the increase in double layer charge and showed lower oxygen evolution potential than amorphous IrO₂-Ta₂O₅ coatings.

KEY WORDS: RuO₂-Ta₂O₅ Catalytic Coating, Oxygen Evolution, Amorphization, Thermal Decomposition Temperature

1. Introduction

Platinum group metal oxides have been widely used as the catalyst for oxygen and chlorine evolution in acidic aqueous solutions with their applications in hydrometallurgy¹⁻⁸⁾, electroplating^{9, 10)}, and chloro-alkali industry¹¹⁻¹⁴⁾. A typical example is iridium oxide (IrO₂), which has high electrocatalytic activity and corrosion resistance to oxygen evolution, and these features are enhanced with the addition of tantalum oxide (Ta₂O₅)^{15, 16)}. The IrO₂-Ta₂O₅ catalytic coating is usually prepared by thermal decomposition of a precursor solution containing iridium and tantalum salts. Our previous studies⁴⁻⁸⁾ have revealed that low thermal decomposition temperature, e.g., 360 °C, makes the catalytic coating amorphous, and such amorphous coatings show lower oxygen or chlorine evolution potentials than commercially available crystalline IrO₂-Ta₂O₅ coatings prepared at 450 °C or higher, suggesting that the electric energy consumption of the industrial electrochemical process is drastically reduced by using the amorphous IrO₂-Ta₂O₅ coating as oxygen or chlorine evolution anodes.

On the other hand, ruthenium oxide (RuO₂) is well known to exhibit higher catalytic activity than IrO₂ for oxygen evolution in acidic media and is the most active catalyst among platinum group metal oxides^{1, 17)}, and various kinds of mixed oxides comprising RuO₂ such as RuO₂-TiO₂^{12, 14)}, RuO₂-SnO₂^{13, 18)}, RuO₂-IrO₂^{19, 20)}, and RuO₂-Ta₂O₅^{21, 22)} have been investigated. Although crystalline and amorphous RuO₂ films prepared by electrodeposition or RF magnetron

sputtering followed by annealing have been reported to show a difference in catalytic activity for oxygen evolution, in which the amorphous RuO₂ film has higher catalytic activity than the crystalline one²³⁾, there has been little work on the effects of the crystallinity of RuO₂ in such mixed metal oxide coatings prepared by thermal decomposition on oxygen evolution, especially the effects of amorphization of RuO₂ in RuO₂-Ta₂O₅ coatings at low Ru ratio. This paper presents RuO₂-Ta₂O₅ coatings (Ru=30 mol%) prepared at different thermal decomposition temperatures and the effects of amorphization of RuO₂ on double layer charge and oxygen evolution potential in sulfuric acid solutions.

2. Experimental

2 · 1 Electrode preparation

RuO₂-Ta₂O₅ coatings were prepared by thermal decomposition on titanium plates (1 cm × 5 cm × 1 mm) which had been degreased in acetone and etched in oxalic acid solutions (10 wt%) at 90 °C for 1 hour. A precursor solution was prepared by dissolving RuCl₃·3H₂O and TaCl₅ into 1-butanol containing 6 vol% HCl. The total metal concentration was 50 g dm⁻³ with Ru:Ta mole ratio of 30:70. The titanium substrate was dipped into the precursor solution, dried at 120 °C for 10 min, and thermally decomposed at a temperature of 260 °C, 300 °C, or 500 °C for 20 min. This process was repeated 7 times. The crystallographic structure and surface morphology of the coatings were characterized by X-ray diffraction method (XRD) with CuKα radiation (Rigaku, Ultima IV) and SEM (ZEISS, Model ULTRA 55).

2 · 2 Electrochemical measurements

Electrochemical measurements were conducted with a conventional three-electrode cell with 2.0 mol dm⁻³ H₂SO₄ solutions. The working electrode was the prepared RuO₂-

*Received 18 April, 2015; accepted for publication 13 July, 2015

a. PhD candidate, Department of Science of Environment and Mathematical Modeling, Doshisha University, 1-3 Tatara-miyakodani, Kyotanabe, Kyoto 610-0394, Japan

b. Professor, Department of Environmental Systems Science, Doshisha University (Corresponding author, E-mail: mmorimit@mail.doshisha.ac.jp)

Fig.1 (A) XRD patterns of RuO₂-Ta₂O₅/Ti electrodes prepared at (a) 500 °C (red), (b) 300 °C (blue), and (c) 260 °C (black). (B) Normalized XRD patterns constructed from the results in Fig. 1(A).

Ta₂O₅/Ti electrode, of which the geometrical surface area was limited to 1 cm² by using a PTFE holder. A platinum plate counter electrode and a KCl-saturated Ag/AgCl reference electrode were also used. The double layer charge and polarization for oxygen evolution were investigated by cyclic voltammetry. Oxygen evolution potential was further measured by chronopotentiometry. The measurements were done with a potentio/galvanostat (EG&G, Model 263A) controlled by electrochemical analysis software (EG&G, Model 270), and the solutions were held at 40 °C without stirring. Each measurement used at least three electrodes prepared with the same condition to check the reproducibility.

3. Results and discussion

Fig. 1 shows XRD patterns of RuO₂-Ta₂O₅/Ti electrodes prepared at different thermal decomposition temperatures. All samples presented the intense peaks of the titanium substrate at $2\theta = 38.4^\circ$, 40.2° , 53.0° . Besides these peaks, the electrode calcined at 500 °C showed clear diffraction peaks attributed to 110, 101, and 211 of crystalline RuO₂, while the peak intensity decreased at 300 °C and no peak from RuO₂ appeared at 260 °C. A very small peak at 35.1° on the diffraction pattern of the electrode prepared at 260 °C is assigned to Ti and such a small peak from the substrate is thought to be also overlapped with RuO₂ 101 peak of the electrodes prepared at 500 °C and 300 °C. The diffraction intensity was normalized with the strongest peak at 53.0° for Ti in Fig. 1 (A), and the results are shown in Fig. 1 (B). The electrode obtained at 260 °C showed the halo peak ranging between 20° and 40° . The above results indicate that RuO₂ has less crystallinity with lowering thermal decomposition temperature and the amorphization of RuO₂ occurs at 260 °C. Ta₂O₅ is amorphous in these coatings because no clear diffraction peaks were observed. It is also noted that the halo peaks contain the attribution from amorphous Ta₂O₅, because crystalline Ta₂O₅ shows some diffraction peaks at $2\theta = 20^\circ$ to 40° .

The surface morphologies of the RuO₂-Ta₂O₅ coatings are presented in Fig. 2, in which the low magnification images (left side of Fig. 2) demonstrate that the coating prepared at 500 °C is mud-cracked surface consisting of RuO₂ aggregates, flat

areas, and cracks, although the aggregates decrease at 300 °C and disappear at 260 °C. This is also supported from the high magnification images (right side of Fig. 2), showing that the size and shape of RuO₂ changes with thermal decomposition temperature; large tetragonal or needle-like RuO₂ is seen at 500 °C or 300 °C, while nano RuO₂ particles of 50 nm or less are generated on the flat areas at 260 °C, although such nano particles are invisible on the low magnification image. From the SEM results, low temperature thermal decomposition produces the amorphous RuO₂-Ta₂O₅ coating which comprises nano RuO₂ particles dispersed in amorphous Ta₂O₅ matrix. Since Ta₂O₅ has no catalytic activity for oxygen evolution, the XRD and SEM results suggest that the amorphous coating obtained at 260 °C has higher active surface area for oxygen evolution than the other coatings prepared at 300 °C and 500 °C. It is noted that although the XRD pattern of the coating prepared at 260 °C shows a small Ti peak at around 35° and no clear peaks of RuO₂ within the experimental resolution, the SEM image in Fig. 2 shows the presence of nano RuO₂ particles, which suggest that these nanoparticles are crystalline and are not detected by XRD, because they are small in amount and/or masked by the halo peak.

Cyclic voltammetry was performed in H₂SO₄ solutions to evaluate double layer charge (C_{dl}), in which the voltammograms were obtained in the potential range prior to oxygen evolution, i.e., no Faradic reaction occurs, as shown in Fig. 3. The double layer charge of each coating was calculated by integration of the voltammogram. The double layer charge can be used to estimate the active surface area of the oxide coatings for oxygen evolution in acidic media²⁴⁾. The C_{dl} of the coatings obtained at 500 °C, 300 °C, and 260 °C were 5.30 mC cm⁻², 16.0 mC cm⁻², and 37.4 mC cm⁻²; the active surface area of the coating prepared at 260 °C was expected to be 7 times larger than that at 500 °C. This suggests that the active surface area of the coating is drastically increased by amorphization of RuO₂.

The anodic polarization behaviors of the RuO₂-Ta₂O₅ coatings were examined by cyclic voltammetry, and the results are presented in Fig. 4. The overpotential for oxygen evolution is apparently reduced for the coating prepared at lower decomposition temperature; the onset potential for oxygen

Fig.2 Surface morphologies of $\text{RuO}_2\text{-Ta}_2\text{O}_5$ coatings prepared at 500 °C (a), 300 °C (b), and 260 °C (c). Magnification: (left) 1,000 for all coatings, (right) 50,000 for the coatings prepared at 500 °C and 300 °C and 200,000 for the coating prepared at 260 °C.

Fig.3 Cyclic voltammograms of $\text{RuO}_2\text{-Ta}_2\text{O}_5/\text{Ti}$ electrodes prepared at 500 °C (dash), 300 °C (dot dash), and 260 °C (solid) in $2.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution at 40 °C. Scan rate 5 mV s^{-1} .

Fig.4 Cyclic voltammograms of $\text{RuO}_2\text{-Ta}_2\text{O}_5/\text{Ti}$ electrodes prepared at 500 °C (dash), 300 °C (dot dash), and 260 °C (solid) in $2.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution at 40 °C. Scan rate 5 mV s^{-1} .

evolution shifts to the negative direction and the current density at 1.4 V is drastically increased from 500 °C to 260 °C. This is consistent with the result of double layer charge, suggesting that oxygen evolution is more promoted with the increase in active

surface area.

The current density for each voltammogram in Fig. 4 was divided by C_{dl} for each coating, and the results are shown in Fig. 5. If the difference in catalytic activity for oxygen

Fig. 5 Modified cyclic voltammograms of Fig. 4 with the current density, i , divided by double layer charge, C_{dl} . Thermal decomposition temperature: 500 °C (dash), 300 °C (dot dash), 260 °C (solid).

evolution of the three types of RuO₂-Ta₂O₅ coatings is simply due to the active surface area under the condition that the double layer charge reflects the active surface area, the voltammograms shown in Fig. 5 would be overlapped. This is the case for the coatings prepared at 260 °C and 300 °C, although the coating prepared at 500 °C still shows lower current density than those two coatings. This implies that the improvement in catalytic activity with decreasing thermal decomposition temperature is not only caused by the increase in active surface area but also resulted from the change in intrinsic property of the mixed oxide, *i.e.*, the activity per reactive site for oxygen evolution which is alternatively expressed by exchange current density. The difference in catalytic activity between the coatings prepared at 300 °C and 500 °C in Fig. 5 seems to agree with a large change in diffraction intensity and surface morphology for RuO₂ shown in Figs. 1 and 2.

The high catalytic activity of the amorphous RuO₂-Ta₂O₅ coating was also revealed by chronopotentiometry, in which the current density was 50 mA cm⁻² based on the geometrical surface area of the electrode, and oxygen evolution potential was compared to the amorphous IrO₂-Ta₂O₅/Ti electrode reported previously⁴⁾, in which Ir:Ta mole ratio was 80:20 and thermal decomposition temperature was 360 °C. As shown in Fig. 6, the oxygen evolution potential measured with the RuO₂-Ta₂O₅ coating prepared at 260 °C was 0.11 V lower than that at 300 °C and 0.47 V lower than that at 500 °C. Moreover, the amorphous RuO₂-Ta₂O₅/Ti electrode showed 0.04 V lower oxygen evolution potential than the amorphous IrO₂-Ta₂O₅/Ti electrode. Since Ta₂O₅ is known to be inactive to oxygen evolution, the above results indicate that the amorphous RuO₂-Ta₂O₅ (Ru=30 mol%) coating has higher activity than the amorphous IrO₂-Ta₂O₅ (Ir=80 mol%) coating, even though the ratio of the active component for oxygen evolution is small.

4. Conclusions

The crystallographic structure of RuO₂ in RuO₂-Ta₂O₅ coatings changes from crystalline to amorphous when the thermal decomposition temperature is reduced from 500 °C

Fig. 6 Chronopotentiograms measured with RuO₂-Ta₂O₅/Ti anodes prepared at 500 °C (dash), 300 °C (dot dash), and 260 °C (solid), and amorphous IrO₂-Ta₂O₅/Ti anode (dot) at 50 mA cm⁻² in 2.0 mol dm⁻³ H₂SO₄ solution at 40 °C.

to 260 °C. This also induces the distinct change in surface morphology that nano RuO₂ particles are generated on the amorphous coating. The amorphization of RuO₂ significantly increases the active surface area for oxygen evolution, resulting in a drastic reduction in oxygen overpotential in H₂SO₄ solutions and a higher catalytic activity compared to amorphous IrO₂-Ta₂O₅ coatings.

Acknowledgements This work was financially supported by Grant-in-Aid for “Kyoto Environmental Nanotechnology Cluster” from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan and Grant-in-Aide for “Kyoto Area Super Cluster Program” from Japan Science and Technology Agency (JST).

References

- 1) S. Trasatti: *Electrochim. Acta*, **45** (2000), 2377-2385.
- 2) Z.S. Msindo, V. Sibanda and J.H. Potgieter: *J. Appl. Electrochem.*, **40** (2009), 691-699.
- 3) M. Spasojevic, L. Ribic-Zelenovic, P. Spasojevic: *Ceramics International*, **38** (2012), 5827-5833.
- 4) M. Morimitsu and N. Oshiumi: *Chemistry Letters*, **38** (2008), 822-823.
- 5) M. Morimitsu and K. Uno: *Proc. of Hydrometallurgy of Nickel and Cobalt 2009* (2009), pp. 571-580.
- 6) M. Morimitsu, N. Oshiumi and N. Wada: *Proc. of Copper 2010* (2010), Vol. 4, pp. 1511-1520.
- 7) M. Morimitsu, N. Oshiumi and T. Yamaguchi: *Proc. of Lead-Zinc 2010* (2010), pp. 813-818.
- 8) M. Morimitsu: *Proc. of Electrometallurgy 2012*, TMS (2012), pp. 975-984.
- 9) R. Otogawa, M. Morimitsu, M. Matsunaga: *Nippon Kagaku Kaishi*, **5** (2000) 299-350.
- 10) Y. Kamegaya, K. Sasaki, M. Oguri, T. Asaki, H. Kobayashi, T. Mitamura: *Electrochim. Acta*, **40** (1995), 889-895.
- 11) Z. Yi, C. Kangning, W. Wei, J. Wang, S. Lee: *Ceramics International*, **33** (2007), 1087-1091.
- 12) G.R.P. Malpass, D.W. Miwa, A.C.P. Miwa, S.A.S. Machado, A.J. Motheo: *J. Hazardous Materials*, **167** (2009), 224-229.
- 13) X. Wang, D. Tang, J. Zhou: *J. Alloys and Compounds*, **430** (2007), 60-66.
- 14) V. Trieu, B. Schley, H. Natter, J. Kintrup, A. Bulan, R. Hempelmann: *Electrochim. Acta*, **78** (2012), 188-194.
- 15) R. Tolba, M. Tian, J. Wen, Z. Jiang, A. Chen: *J. Electroanalytical Chem.*, **649** (2010), 9-15.
- 16) J.-Y. Lee, D.-K. Kang, K.-H. Lee, D.-Y. Chang: *Materials Science and Applications*, **2** (2011), 237-243.
- 17) N. Mamaca, E. Mayousse, S. Arrii-Clacens, T.W. Napporn, K. Servat, N. Guillet, K.B. Kokoh: *Appl. Catalysis B: Environmental*, **111-112** (2012), 376-380.
- 18) C.-C. Hu, K.-H. Chang, C.-C. Wang: *Electrochim. Acta*, **52** (2007), 4411-4418.
- 19) A. Barbu, V. Plichon: *Electrochim. Acta*, **42** (1997), 489-492.
- 20) L.E. Owe, M. Tsyppkin, K.S. Wallwork, R.G. Haverkamp, S. Sunde: *Electrochim. Acta*, **70** (2012), 158-164.
- 21) J. Ribeiro, A. R. De Andrade: *J. Electrochem. Soc.*, **151** (2004), D106-D112.
- 22) H. Chen, H. Lai, J. Jow: *Mat. Chem. Phys.*, **125** (2010), 652-655.
- 23) E. Tsuji, A. Imanishi, K. Fukui, Y. Nakato: *Electrochim. Acta*, **56** (2011), 2009-2016.
- 24) J. Aromaa, O. Forsen: *Electrochim. Acta*, **51** (2006), 6104-6110.

硫酸浴中での酸素発生に及ぼすRuO₂-Ta₂O₅ 触媒層 (Ru=30mol%) の非晶質化の影響*張 天¹ 盛 満 正 嗣²

酸素発生用 RuO₂-Ta₂O₅ 触媒層 (Ru=30 mol%) を熱分解法により 260℃, 300℃, 500℃で作製し, その結晶構造, 表面形態, 電気化学特性を X 線回折, SEM, サイクリックボルタメトリー, クロノポテンシオメトリーで研究した。X 線回折および SEM による結果から, 触媒層中の RuO₂ は温度が低くなると結晶性が低下し, 260℃では非晶質化が生じることが明らかになった。非晶質の触媒層では, 二重層の充電電量の増加とともに硫酸浴中での酸素発生が促進され, 非晶質の IrO₂-Ta₂O₅ 触媒層よりも低い酸素発生電位を示した。

*2015 年 4 月 18 日受付 2015 年 7 月 13 日受理

1. 同志社大学大学院理工学研究科 博士後期課程学生

2. 正会員 博士 (工学) 同志社大学理工学部環境システム学科教授

[著者連絡先] E-mail: mmorimit@mail.doshisha.ac.jp

キーワード: RuO₂-Ta₂O₅ 触媒層, 酸素発生, 非晶質化, 熱分解温度