

Effects of Crystallographic Structure of IrO₂-Ta₂O₅ Catalyst on Oxygen Evolution in Alkaline SolutionsS. Unoki¹, T. Zhang¹, and M. Morimitsu^{1,2,*}¹Dept. of Sci. of Environment and Mathematical Modeling,²Department of Environmental Systems Science,
Doshisha University

Kyo-tanabe, Kyoto, 610-0394, Japan

*E-mail: mmorimit@mail.doshisha.ac.jp

Oxygen evolution in alkaline aqueous solutions is of importance in some electrochemical fields such as water electrolysis for hydrogen production and the anodic reaction in electroplating. The anode material available to this reaction is limited, because most of all metals including noble metals and their oxides tend to dissolve into the alkaline solution during oxygen evolution, which is in contrast to oxygen evolution in acidic aqueous solutions. This is the reason why it is difficult to develop a novel anode material which enables to reduce overpotential for oxygen evolution in alkaline solutions. On the other hand, one of the authors of this paper has previously reported that IrO₂-Ta₂O₅ coatings prepared by thermal decomposition show a high durability for oxygen evolution in 4 mol/L NaOH solutions, when the titanium electrode covered with the coating is operated even at 1 A/cm², and the lifetime of the coating depends on the coating amount with the observed lifetime more than 1500 hours [1]. The author has also reported that the IrO₂-Ta₂O₅ coating has the catalytic activity for oxygen evolution in acidic aqueous solutions, which changes with the crystallographic structure and surface morphology of the coating, and the amorphization of the coating promotes oxygen evolution, resulting in lower overpotential compared to the crystalline coating [2-4]. From the above background, this work aimed to prepare different crystallographic structure of IrO₂-Ta₂O₅ coatings and to examine oxygen evolution behaviors in concentrated alkaline solutions. A continuous electrolysis was also performed to access the stability of the coatings.

IrO₂-Ta₂O₅ coatings were prepared by thermal decomposition of a precursor solution dissolving H₂IrCl₆ · 6H₂O and TaCl₅ on a titanium plate; the plate was dipped into the precursor solution, dried at 120 °C, and finally calcined at 360 °C or 470 °C for 20 minutes. This coating to calcination process was repeated to obtain IrO₂-Ta₂O₅ coated Ti electrodes. The crystallographic structure of the coating was characterized by XRD and the surface morphology was observed by SEM. All electrochemical measurements were carried out with 5.0 mol/L KOH solution and a three-electrode cell comprising a platinum plate counter electrode and an Hg/HgO reference electrode in 5 mol/L KOH solution. Constant current electrolysis was also done with a two-electrode cell equipped with a platinum plate cathode.

XRD measurements revealed that the IrO₂-Ta₂O₅ coating obtained at 470 °C showed diffraction peaks corresponding to crystalline IrO₂, while that prepared at 360 °C presented no peak for IrO₂. There was no diffraction peak for Ta₂O₅ for both coatings, so that the coating of 470 °C was a mixture of crystalline IrO₂ and amorphous Ta₂O₅ and that of 360 °C comprised amorphous IrO₂ and Ta₂O₅. The surface morphology of the coating also depended on

thermal decomposition temperature; decreasing temperature made the coating surface more smooth without aggregated IrO₂ particles as seen on the coating of 470 °C. These results were similar to those in our previous studies [2-4].

Cyclic voltammograms were measured to compare the polarization behaviors of the coatings, and the typical results are shown in Fig. 1. The voltammograms indicate that the double layer charging current of the amorphous coating (360 °C) is larger than that of the crystalline one (470 °C), and the calculated double layer charge increased by 6.7 times. This difference in double layer charge strongly affected the polarization for oxygen evolution; higher current was seen with the amorphous coating than with the crystalline coating at the same potential, suggesting that the amorphous coating has enhanced activity for oxygen evolution. The onset potential of oxygen evolution became lower by amorphization of the coating, resulting that the oxygen overpotential is 0.198 V for the amorphous coating or 0.244 V for the crystalline coating, which is 46 mV reduction in overpotential by amorphization.

Constant current electrolysis at 50 mA/cm² was performed with each anode and the cell voltage was monitored for 100 hours. The cell voltage with the amorphous coating was almost constant and 80 mV lower than that with the crystalline coating. After the electrolysis, each coating was observed by SEM and compared to the SEM image before the electrolysis. The results suggested that the coating was consumed by the electrolysis, and the amorphous coating seemed to be more consumed than the crystalline one.

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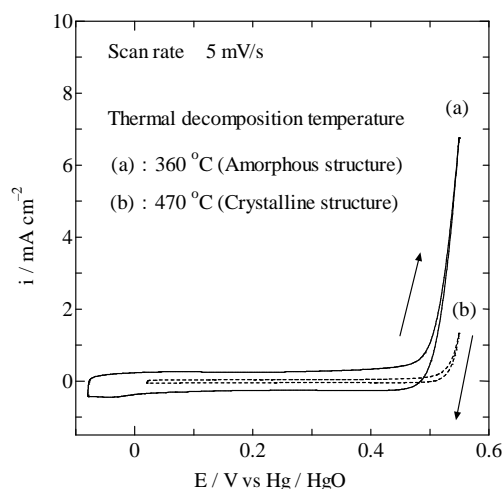


Fig. 1 Cyclic voltammograms of IrO₂-Ta₂O₅/Ti electrodes prepared at 360 °C (a) and 470 °C (b) in 5 mol/L KOH solution.

References

- 1) M. Morimitsu, C. Murakami, K. Kawaguchi, R. Otagawa, and M. Matsunaga, *J. New Mat. Electrochem. Systems.*, Vol. 7, pp. 323-327 (2004).
- 2) M. Morimitsu and N. Oshiumi, *Chemistry Letters*, Vol.38, No.8, pp. 822-823 (2009).
- 3) M. Morimitsu, N. Oshiumi, T. Yamaguchi, *Proc. Lead-Zinc 2010*, pp. 813-818, CIM (2010).
- 4) M. Morimitsu, *Proc. of Electrometallurgy 2012*, pp. 49-54, TMS (2012).