Effect of Adding Polyethylene Glycol to the Precursor Solution of Amorphous IrO$_2$-Ta$_2$O$_5$ Electrocatalsysts for Oxygen Evolution Reaction

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ABSTRACT

We report amorphous iridium oxide (IrO$_2$) and tantalum oxide (Ta$_2$O$_5$) electrocatalsysts supported on titanium fiber felt as effective anodes for oxygen evolution reaction (OER). The IrO$_2$-Ta$_2$O$_5$ electrode, prepared by thermal decomposition of the precursor added with polyethylene glycol (PEG), achieved a current density of 10 mA cm$^{-2}$ at a low overpotential of 0.24 V in a sulfuric acidic solution. The high OER activity is because PEG generated mesopores in the amorphous IrO$_2$-Ta$_2$O$_5$ layer after heating at 350°C. The increase in the double-layer capacitance, proportional to the electrochemically active surface area (ECSA), was responsible for the high current density at low overpotentials. Furthermore, the addition of the polymer to the precursor suppressed the dissolution of Ir from the anode during the OER stability test and improved the durability of the IrO$_2$-Ta$_2$O$_5$ electrocatalyst coated on the Ti felt.

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Keywords: Water electrolysis, Electrocatalytic water oxidation, Dimensionally stable anode, Mixed metal oxide

1. Introduction

Expanding the use of renewable energies such as solar and wind power raises supply-demand mismatches due to their intermittent and unpredictable nature. Therefore, it is required to convert excess electricity into chemical energy such as hydrogen (H$_2$) and secondary batteries to use it according to the demand.

It is crucial to develop an excellent OER electrcatalyst. It is directly linked to the production cost of H$_2$. The electrochemical water splitting requires high activation energy for sluggish OER, and the overpotential of OER is larger than that of HER. Therefore, it is crucial to develop an excellent OER electrcatalyst.

Iridium oxide (IrO$_2$), an optimum electrocatalyst for PEMWE, has high OER activity in an acidic atmosphere. It has been reported that the durability in OER is improved by mixing tantalum oxide (Ta$_2$O$_5$) with IrO$_2$. Especially, titanium (Ti) substrates coated with a mixed oxide layer of IrO$_2$ (70 mol%) and Ta$_2$O$_5$ (30 mol%) are the best OER electrocatalyst having high activity and long lifetime. Nano-sized IrO$_2$ catalysts have also been reported to have high OER activity due to the increase in the electrochemically active surface area (ECSA).

We have successfully improved the activity of the IrO$_2$-Ta$_2$O$_5$ by using sintered Ti fibers with a three-dimensional (3D) porous structure (Ti felt, Fig. S1 of the Supporting Information) instead of the conventional Ti substrate, which is a geometrically flat and dense plate. Large surface area of the substrate is beneficial in increasing the ECSA and the contact area between the electrocatalyst and the substrate layers. High-temperature calcination usually forms rutile-type IrO$_2$ crystallites, but the IrO$_2$ coated on Ti felt was amorphous even after calcination at 650°C. Amorphous IrO$_2$ has been reported to exhibit high OER activity compared to crystalline IrO$_2$.

However, low durability during OER was an issue for amorphous IrO$_2$ electrocatalysts.

In this study, we focused on polyethylene glycol (PEG), a typical high-viscosity polymer, to improve the OER activity and the durability of amorphous IrO$_2$-Ta$_2$O$_5$ layer coated on a Ti felt substrate, which was prepared by thermal decomposition of the precursor at 350°C. In the electrolytic industry, water-soluble binding agents such as PEG and polyvinyl alcohol have been used to prepare a dense IrO$_2$-Ta$_2$O$_5$ layer with few cracks. The addition of PEG to the precursor solution would result in that the IrO$_2$-Ta$_2$O$_5$...
layer is fixed more tightly to the Ti felt substrate. The polymer also may work as a template fabricating porous nanostructures to increase the ECSA. To determine the appropriate amount of PEG added, we investigated the OER activity and the stability of the IrO₂-Ta₂O₅ layers coated on Ti felt for acidic water electrolysis. We also studied morphology, crystallinity, and chemical state of the IrO₂-Ta₂O₅ electrocatalysts using scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray fluorescence (XRF) spectroscopy.

2. Experimental

2.1 Preparation of IrO₂-Ta₂O₅/Ti felt anodes

Tantalum chloride (TaCl₅, 99.99%) was obtained from Kojundo Chemical Laboratory Co., Ltd. Other reagents were obtained from Fujifilm Wako Pure Chemical Corporation. The molar ratio in the IrO₂-Ta₂O₅ layer was adjusted to Ir : Ta = 7 : 3. Hydrogen hexachloroiridate(IV) n-hydrate (H₂IrCl₆·nH₂O, Ir = 37.4%) was dissolved in 2-propanol (99.7%) to prepare a stock solution (0.2184 mol L⁻¹). The powder of TaCl₅ 0.0602 g was dissolved in 3.0 mL of 2-propanol and 0.8 mL of hydrochloric acid (HC1, 35.0%). This TaCl₅ solution (679 ìL, 0.030 mmol Ta) was mixed with the H₂IrCl₆ solution (321 ìL, 0.070 mmol Ir) and the mixture was then masked with polytetrafluoroethylene film (thickness 2, Nikko Techno, Ltd.) was cut into 1.0 cm × 2.5 cm and ultrasonically washed in acetone and deionized water for each 10 min. The cleaned felt was then washed with polytetrafluoroethylene film tape to open the area of 1.0 cm × 1.0 cm. A 10-μL drop of the precursor solution was cast on this Ti felt using a micropipette (Nichiryo Co., Ltd.), and dried in an oven at 80 °C for 5 min. After repeating this drop-coating casting three times, the precursor was thermally decomposed in the air at 350 °C for 1 h using an electric furnace. Thus prepared IrO₂-Ta₂O₅ layer coated on Ti felt is referred to as IrO₂-Ta₂O₅/Ti felt. The electrodes prepared by adding PEG are called IrO₂-Ta₂O₅(PEGx)/Ti felt, where x is the amount of PEG added (0, 10, 30, and 50 mg mL⁻¹).

2.2 Electrochemical measurements

The OER activity was evaluated in 0.1 mol L⁻¹ H₂SO₄ aqueous solution (pH = 1.0) at room temperature in an air atmosphere using the Zennium electrochemical workstation (Zahnber-Elektrik GmbH & Co. KG). We used an Ag/AgCl reference electrode (0.198 V vs. RHE, BAS, Inc.), a Pt wire counter electrode, and the IrO₂-Ta₂O₅/Ti felt samples with a geometric size of 1 cm². We performed cyclic voltammetry (CV) at a scanning rate of 10 mV s⁻¹ except for Tafel analysis at 1.0 mV s⁻¹. Chronopotentiometry for durability test was performed with a current density (j) of 50 mA cm⁻². The j is based on the geometric size of the electrodes. The electrolyte resistance (R) was measured by the electrochemical impedance method (amplitude ±10 mV, frequency 1000 Hz) at 0 V vs. Ag/AgCl. Hereafter, the potentials vs. Ag/AgCl (EAg/AgCl) are converted into the potential vs. RHE (ERHE) using the following equation.

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.198
\]  

(1)

2.3 Characterization method

SEM observation and energy dispersive X-ray spectroscopy (EDS) analysis were performed using a JSM-7800F microscope (JEOL Ltd.). The composition of IrO₂ and Ta₂O₅ was confirmed by XRF spectroscopy using NEX CG (Rigaku Corporation). XRD patterns were measured with CuKα radiation at 45 kV and 200 mA using a SmartLab diffractometer (Rigaku Corporation). The Brønsted–Emmett–Teller specific surface area (S BET) was determined from the N₂ adsorption isotherm at liquid nitrogen temperature (−196 °C) using Belsorp-mini (MicrotracBEL Corp.). Before the adsorption measurement, the electrode sample (geometric size 24 cm², ca. 0.4 g) was evacuated at 200 °C for 2 h. The components of the electrolyte solution after OER analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) by ICP-OES-9820 (Shimadzu Corporation) after filtration through a Nylon membrane filter (Advantec Toyo Kaisha, Ltd., 0.20 μm).

3. Results

3.1 Electrocatalytic activity of IrO₂-Ta₂O₅/Ti felt

Figure 1 shows the j–E curves of the IrO₂-Ta₂O₅/Ti electrodes in dilute sulfuric acid. The forward and reverse scans in the CV were averaged to facilitate the evaluation of j and overpotential for OER. The E was corrected for ohmic drop (IR loss) using the R (about 5 Ω) obtained by impedance measurement. IrO₂-Ta₂O₅(PEG50)/Ti felt, which was prepared from the precursor solution with 50 mg mL⁻¹ of PEG, promotes OER at potentials higher than 1.4 V vs. RHE, and achieves j = 35 mA cm⁻² at 1.66 V vs. RHE. The OER activity was higher than IrO₂-Ta₂O₅(PEG 0)/Ti felt prepared without PEG added. The E to achieve j = 10 mA cm⁻² was 1.47 V vs. RHE for IrO₂-Ta₂O₅(PEG50)/Ti felt, which was lower than 1.49 V vs. RHE for IrO₂-Ta₂O₅(PEG 0)/Ti felt. The PEG addition improved the OER activity of IrO₂-Ta₂O₅/Ti felt.

Figure 2 shows j at E RHE = 1.66 V for IrO₂-Ta₂O₅(PEGx)/Ti felt electrodes prepared by different PEG addition. The CV measurement was performed in five samples for each electrode. Increasing the amount of PEG increased j up to 30 mg mL⁻¹ and slightly decreased at 50 mg mL⁻¹. The errors were less than 3.0 mA cm⁻² for each sample prepared in different lots. Therefore, the j was significantly enhanced by the addition of PEG to the precursor for thermal decomposition at 350 °C.

Figure 3 shows the E-time curves of IrO₂-Ta₂O₅(PEGx)/Ti felt electrodes. We evaluated the durability of the OER electrocatalysts at j = 50 mA cm⁻² for 4 h. For IrO₂-Ta₂O₅(PEG 0)/Ti felt without PEG added, the E was gradually increased from 1.57 V to 1.63 V with time. On the other hand, the change of E with time for the electrodes prepared with PEG was smaller than PEG-free electrode. The increasing rate of E was 7.7 mV h⁻¹ for IrO₂-Ta₂O₅(PEG 0) and 4.4 mV h⁻¹ for IrO₂-Ta₂O₅(PEG10) during the time of 0.5–4 h (Fig. S2). These results indicate that the addition of PEG improved the stability of IrO₂-Ta₂O₅ electrocatalyst for OER.

3.2 Characterization of IrO₂-Ta₂O₅/Ti felt

Figure 4(a) shows the XRF spectrum of IrO₂-Ta₂O₅(PEG50)/Ti felt.
Peaks of Ir and Ta were observed in addition to Ti from the substrate. The peak area shows that the molar ratio of Ir to Ta was about 7 : 3, which is consistent with the percentage in preparation. Figure 4(b) shows the XRD pattern of IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt. The observed peaks were due to hexagonal $\alpha$-Ti originated from the substrate. We cannot find the diffraction peaks of rutile-type IrO$_2$ crystallite. The IrO$_2$-Ta$_2$O$_5$ layers were amorphous on the Ti felt.

Figure 5 shows the SEM images of IrO$_2$-Ta$_2$O$_5$(PEG 0)/Ti felt and IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt. In the PEG-free sample, the IrO$_2$-Ta$_2$O$_5$ layer generated by thermal decomposition exhibited a flat surface. On the other hand, small pores of several hundred nanometers were formed on the surface of the IrO$_2$-Ta$_2$O$_5$ layer prepared by adding 50 mg mL$^{-1}$ of PEG. The combustion temperature of PEG was around 250 °C as confirmed by thermogravimetry and differential thermal analysis (TG-DTA, Fig. S3). The pores observed by SEM are the voids left after the combustion of PEG at 350 °C for 1 h. The pore formation would increase the surface area of the electrocatalyst.

The nitrogen adsorption measurement revealed that the total pore volume of IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt is higher than IrO$_2$-Ta$_2$O$_5$(PEG 0)/Ti, as shown in Fig. 6. The Barrett–Joyner–Halenda (BJH) analysis shows that mesopores of about 5–10 nm formed in IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt (Fig. S4). The $S_{\text{BET}}$ of IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt was 3.04 m$^2$ g$^{-1}$, which was higher than IrO$_2$-Ta$_2$O$_5$(PEG 0)/Ti of 2.54 m$^2$ g$^{-1}$. It should be noted that the value includes the weight of Ti felt. The $S_{\text{BET}}$ of PEG 0/Ti felt was less than the quantification limit by the nitrogen adsorption method. Considering that the mass loading of the IrO$_2$-Ta$_2$O$_5$ layer, the $S_{\text{BET}}$ of the IrO$_2$-Ta$_2$O$_5$ layer was calculated to be 80 and 54 m$^2$ g$^{-1}$ for PEG50 and PEG-free samples.

3.3 Stability of IrO$_2$-Ta$_2$O$_5$/Ti felt

Table 1 shows the results of ICP-OES measurement of the electrolyte after 4-h OER (Fig. 3). Iridium species was dissolved from IrO$_2$-Ta$_2$O$_5$/Ti felt, and the dissolved amount was affected by adding PEG to the precursor. The dissolution ratio of Ir from the deposited mass was 5.0 % for IrO$_2$-Ta$_2$O$_5$(PEG 0)/Ti felt. The dissolution of Ir was suppressed when adding 10 mg mL$^{-1}$ of PEG. Furthermore, the increase in the amount of PEG added decreased the dissolution ratio. The dissolution ratio of Ir was only 0.3 % for IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt, which was prepared with the largest amount of PEG added. XRF measurement of the spent IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt also show that the mass ratio of Ir and Ta to Ti was not
changed after 4-h OER. No solid particle as suspension and precipitate was confirmed in the electrolyte, suggesting that the physical peel-off of the IrO$_2$-Ta$_2$O$_5$ layer is almost nothing.

The results of the E-time curve measurement and ICP-OES analysis confirmed that the addition of PEG much improved the durability of the IrO$_2$-Ta$_2$O$_5$ electrocatalyst during OER. The suppression of the Ir dissolution is 95% compared to the PEG-free sample. It should be noted that Ta, which is an electrocatalyst component, was not detected by ICP-OES analysis. However, SEM observation with EDS analysis confirmed that Ta was present as particles with a diameter of several μm in the electrolyte (Fig. S5). This is why Ta was not detected by ICP-OES analysis since the electrolyte solution was filtered with a membrane before the measurement. The Ta-rich solid particles did not contain Ir, suggesting that the leached Ir species is soluble in the electrolyte.

The SEM observation of IrO$_2$-Ta$_2$O$_5$(PEG 0)/Ti felt after the OER for 4 h show that parts of the electrocatalyst layer were peeled off from the substrate, and the surface structure became rough (Fig. S6). On the other hand, there was little change in surface shape before and after the reaction for IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt. The results support that the addition of PEG improved the durability of the IrO$_2$-Ta$_2$O$_5$ electrocatalysts.

4. Discussion

The electrocatalytic activity of IrO$_2$-Ta$_2$O$_5$/Ti felt was improved by the PEG addition in the range of 10 to 30 mg mL$^{-1}$ (Fig. 2). No crystalline component related to IrO$_2$ and Ta$_2$O$_5$ was detected by XRD, indicating that the electrocatalytic active layer was amorphous (Fig. 4). In addition, the stability of the electrocatalyst in OER was significantly enhanced by the addition of PEG owing to the suppression of the Ir dissolution. In summary, PEG was an excellent additive to improve the OER activity and the durability of amorphous IrO$_2$-Ta$_2$O$_5$ electrocatalyst.

The IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt achieved $j = 10$ mA cm$^{-2}$ at IR-corrected 1.47 V vs. RHE (Fig. 1). This high OER activity can be explained by high ECSA and the smaller Tafel slope. To confirm this, we estimated the electrochemical double-layer capacitance ($C_{dl}$) from the non-Faradaic region in CV (Fig. S7) and plotted it on the left axis of Fig. 7. The addition of PEG increased the $C_{dl}$ of the IrO$_2$-Ta$_2$O$_5$ electrocatalyst. The increase in $C_{dl}$, which is proportional to ECSA, is not fully consistent to the increased $S_{BET}$. The ECSA of IrO$_2$-Ta$_2$O$_5$/Ti felt showed more significant change than the $S_{BET}$. However, the large ECSA with more exposed sites would be somewhat related to the increase in $S_{BET}$ and the formation of mesopores (Figs. 5, 6, S4). Assuming a specific capacitance in 1 M H$_2$SO$_4$ is 0.035 mF cm$^{-2}$,$^{21}$ the ECSA of IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt was calculated to be 4800 cm$^2$.

![Figure 7. Effect of the PEG addition on the double-layer capacitance ($C_{dl}$) and $j_{1.43V}$ of IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt. The $C_{dl}$ was calculated at 0.86 V vs. RHE from CV data in 0.1 M H$_2$SO$_4$ (pH = 1). The $j_{1.43V}$ was estimated at 1.43 V vs. RHE (0.2 V of overpotential) from the Tafel plot.](image)

We also analyzed the Tafel plots with a scan rate of 1.0 mV s$^{-1}$ (Fig. S8). The Tafel slopes were in the range of 52–63 mV dec$^{-1}$ and the Tafel slope tended to decrease with the addition of PEG (Table S1 in the Supporting Information). We also estimated the $j_{1.43V}$, current density at 1.43 V vs. RHE (0.2 V of overpotential for OER), from the extrapolation of the Tafel plot and plotted the value on the right axis in Fig. 7. It was found that the $j_{1.43V}$ at the low overpotential increases with increasing the PEG added. This behavior is very similar to the rise of $C_{dl}$ relative to the PEG added. This similar tendency indicates that ECSA dominates the OER activity at low overpotential. We further normalized the current density by the ECSA (Fig. S7). The ECSA-normalized current density ($j_{ECSA}$) was different for each electrode, indicating that the ECSA is not only the factor deciding the OER activity in the whole range. In contrast, the ECSA-normalized onset potential was almost the same for each electrode. The ECSA of IrO$_2$-Ta$_2$O$_5$/Ti felt mainly determines the $j$ at small overpotential, but the $j$ at large overpotential is related to both ECSA and Tafel slope.

5. Conclusions

We investigated the performance of the IrO$_2$-Ta$_2$O$_5$ electrocatalysts by changing the amount of PEG added to the precursor solution for thermal decomposition at 350°C. We found that PEG was an excellent additive in preparing an amorphous IrO$_2$-Ta$_2$O$_5$/Ti felt anode with high electrocatalytic activity and increased OER stability. The overpotential to reach $j = 10$ mA cm$^{-2}$ was only 0.24 V for IrO$_2$-Ta$_2$O$_5$(PEG50)/Ti felt prepared with 50 mg mL$^{-1}$ of PEG. The PEG addition increased the $S_{BET}$ and the $C_{dl}$ (i.e., ECSA) by generating mesopores during the polymer’s combustion in calcination. The high ECSA explained the high OER activity at low overpotential. The IrO$_2$-Ta$_2$O$_5$ layer after heating at 350°C was amorphous even when adding PEG. The PEG addition also improved the durability of the amorphous IrO$_2$-Ta$_2$O$_5$ layer during OER and suppressed the dissolution of Ir from the anode to the electrolyte. In conclusion, we found that a large number of mesopores were formed in the amorphous IrO$_2$-Ta$_2$O$_5$ layer by using PEG as an additive to the precursor, which resulted in the increased ECSA, the lowering of the onset potential for OER, the suppression of Ir dissolution, and the extended lifetime of the anode.

Supporting Information

The supporting information is available on the website at DOI: [https://doi.org/10.5796/electrochemistry.21-00001](https://doi.org/10.5796/electrochemistry.21-00001).

| Table 1. Dissolution ratio of iridium from IrO$_2$-Ta$_2$O$_5$(PEGx)/Ti felt to the electrolyte after OER at 50 mA cm$^{-2}$ for 4 h. |
|---|---|---|
| Sample | Concentration of Ir [ppm]$^a$ | Dissolution of Ir from electrode [%]$^b$ |
| PEG 0 | 0.4040 | 5.01 |
| PEG10 | 0.0654 | 0.78 |
| PEG30 | 0.0354 | 0.42 |
| PEG50 | 0.0229 | 0.27 |

$^a$The Ir concentration in the 50-mL electrolyte solution was analyzed by ICP-OES.

$^b$The Ir dissolution was calculated considering the Ir mass in each IrO$_2$-Ta$_2$O$_5$(PEGx)/Ti felt. The Ir loading was about 0.4 mg cm$^{-2}$.
Acknowledgment

This work was supported by JST PRESTO [grant number JPMJPR18T1] and JSPS KAKENHI [grant number JP20H02525].

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