Water Electrolysis Using Thin Pt and RuO_x Catalysts Deposited by a Flame-Annealing Method on Pencil-Lead Graphite-Rod Electrodes

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ABSTRACT: An inexpensive, simple, and high-activity catalyst preparation method has been introduced in this work. Pt and RuO_x catalysts were fabricated by soaking inexpensive graphite electrodes (pencil-lead graphite rod: PGR) in catalyst precursor solutions and using a simple flame-annealing method, which results in lower amount of Pt and RuO_x catalyst layers. From X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure analysis, it has been found that platinum and ruthenium were deposited as zero-valence metal (Pt) and oxide (RuO_x), respectively. Catalytic activities of Pt/PGR and RuO_x/PGR for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were evaluated using neutral 1 M Na₂SO₄ aqueous electrolyte, respectively. Although HER and OER currents using PGR without catalysts were -16 mA cm^{-2} (at $-1.5 \text{ V vs Ag/AgCl}$) and $+20 \text{ mA cm}^{-2}$ (at $+2.0 \text{ V vs Ag/AgCl}$), they were improved to -110 and $+80 \text{ mA cm}^{-2}$ with catalysts (Pt and RuO_x), respectively. Such an inexpensive and rapid catalyst electrode preparation method on PGR using flame-annealing is a very significant method in the initial catalyst activity evaluation requiring a large amount of trial and error.

1. INTRODUCTION

Natural energies such as sunlight and wind power are indispensable in order to manage global energy and environmental issues and are the most important energy sources for mankind in the future. However, it is necessary to overcome the unstable generation due to weather variation, which is one of the weak points of natural energy. Therefore, a cost-effective huge energy storage system should be established as soon as possible. One of the candidates is a hydrogen energy system.^{1–3} The technology of producing high-purity hydrogen by water electrolysis using electric power obtained from natural energy is the most attractive method of converting natural energy into chemical energy because it does not emit any CO₂.^{4–6} In order to reach a practical energy conversion efficiency, it is necessary to lower the overpotential of the hydrogen evolution reaction (HER) at the cathodic side and the oxygen evolution reaction (OER) at the anodic side. Although noble metals such as platinum, iridium, and ruthenium can exhibit high catalytic activity,^{7–9} these elements are of low natural abundance and quite expensive. Hence, it is important to reduce the amount of noble-metal catalysts on electrodes.

In this work, we have prepared Pt and RuO_x catalysts deposited on a pencil-lead graphite rod (PGR) by coating the precursor solution and using flame-annealing, which is a very

easy method to fabricate electrocatalysts in a short time. In addition, because the required amount of catalyst is quite low in this method, it is possible to produce high-active electrocatalysts at a very low cost. This method is very convenient in the field of catalyst development which requires a large amount of trial and error. In this work, specially, the performance of water-electrolysis catalysts (Pt and RuO_x) deposited on a PGR by flame-annealing was analyzed and evaluated by energy-dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), electrochemical measurement with cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and stability test in water electrolysis using Hoffman electrolysis apparatus.

2. EXPERIMENTAL SECTION

2.1. Fabrication Method of Catalyst-Deposited PGR by Flame-Annealing. In this study, a PGR (the hardness:

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Figure 1. (a) Schematic illustration of the preparation process of catalyst-deposited PGR electrodes by flame-annealing; (b) photographs of the PGR surface with/without catalysts (Pt and RuO_x).

4B, uni exchangeable pencil graphite rod, $\varnothing 2.0 \text{ mm} \times 130 \text{ mm}$, Mitsubishi Pencil Co., Ltd., Japan), which is low cost and useful as a base material for the catalyst-deposited electrode, was used as a base material for the catalyst-deposited electrode in water electrolysis.¹⁰ Figure 1a shows the schematic illustration of the fabrication procedure of Pt and RuO_x catalysts deposited on a PGR by flame-annealing. The PGR electrodes with Pt and RuO_x catalysts were named Pt/PGR and RuO_x /PGR, respectively.

First, the corn-shaped tip at the top edge of the PGR was cut, and then, the cross-section was scraped by a file to be a flat-shaped edge. In order to remove the coating polymer on the surface and to activate the graphite, the whole of the PGR was annealed for 1 min in a flame using liquefied petroleum gas until the PGR emitted red light by heat.¹⁰ The PGR was air-cooled to room temperature.

Next, a catalyst precursor solution of Pt and RuO_x , which were selected as the high activity catalysts for HER and OER, respectively, was prepared.^{11–15} For the Pt precursor solution, 20 mg of hexachloroplatinic(IV) acid ($\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Kishida Chemical Co., Ltd.) was dissolved in 1 mL of ethanol (EtOH). For the RuO_x precursor solution, ruthenium(III) nitrosyl nitrate solution (Ru 1.5%, solvent content: water 95.0%) ($\text{Ru}(\text{NO})(\text{NO}_3)_3$, Strem Chemicals, Inc.) was used as purchased. Each precursor solution was transferred into an elongated test tube to a depth of 4 cm or more, which is to deposit the catalyst on the PGR over the range of 4 cm. The

PGR were immersed in each metal catalyst precursor solution for 10 s.

For Pt/PGR, immediately after taking out from the Pt-precursor solution, flame-annealing was applied for 20 s. At this time, the PGR was slid to rod axis direction and rotated 180° to the left and right directions by hand so that the catalysts could be evenly annealed. The Pt catalyst was deposited on the PGR surface by immersing and annealing, repeatedly. For the optimization of Pt catalyst deposition times on the PGR by flame-annealing, the number of dip times was varied by 1, 2, 3, 4, 5, 7, and 9 times, and the annealing duration was varied for 5, 10, 20, 30, 40, and 80 s.

For RuO_x /PGR, when the PGR with RuO_x precursor solution was subjected to the same annealing for 20 s as Pt, RuO_x could not be uniformly coated on the PGR surface, and a stable electrocatalyst could not be produced, due to the water solvent for the RuO_x precursor solution. Therefore, the method of preparing the RuO_x catalyst is different from a Pt catalyst. First, after immersing in the precursor solution, preannealing was performed for 2 s. This operation was repeated to cover the whole PGR with the RuO_x catalyst. For preannealing, the PGR with RuO_x precursor solution was slid quickly in the horizontal direction in order to prevent the strong annealing on the PGR. After that, RuO_x on the entire PGR was immediately projected in the flame by postannealing for 10 s (Figure 1a). Further optimization, the number of dip times was varied at 1, 2, 3, 4, 5, 7, and 9 times, and the post-

annealing time was varied at 5, 10, 20, 30, 40, and 80 s. The optimization results for the number of immersions and annealing times in the catalyst deposition will be shown in the [Result and Discussion](#) section.

2.2. Material Analysis Methods. The structure of the PGR electrode surface was observed by scanning electron microscopy (SEM, JSM-6510, JEOL). The chemical-bonding state of Pt/PGR and RuO_x/PGR and the relationship between catalyst and PGR were characterized by EDX (TM3030, HITACHI) spectroscopy, XPS, and total-electron-yield (TEY) and total-fluorescence-yield (TFY) NEXAFS spectroscopy with soft X-ray (BL-09A, in NewSUBARU SR facility,¹⁶ University of Hyogo, Japan). For XPS, Pt and RuO_x deposited on a quartz glass substrate by flame-annealing were measured as a reference. This is to confirm whether catalyst formation by flame-annealing affects the substrate. In addition, XPS and XAFS also measured RuO₂ powder (Kishida Chemical Co., Ltd.) as a reference.

2.3. Electrochemical Measurements. The electrochemical performance of Pt/PGR and RuO_x/PGR was characterized by CV, EIS, and Faraday efficiency measurement or stability test using Hoffman electrolysis apparatus (H-shaped test tubes). In this study, 1 M Na₂SO₄ aqueous electrolyte was used for all measurements.

CV and EIS were performed using a three-electrode system with a platinum foil (20 × 60 mm, 24 cm²) for the counter electrode and a silver/silver chloride (Ag/AgCl) electrode for the reference electrode. The reaction area of the working electrode was 2.54 cm². For CV, the applied potential was set at −1.5 to 0 V (vs Ag/AgCl) for the HER electrode (cathodic side) and 0 to 1.5 V (vs Ag/AgCl) of the OER electrode (anodic side), and the scan speed was 25 mV s^{−1}, and the results at the third cycle were shown. Further, platinum rods [ϕ 2.0 mm × 100 mm Nilaco Co., Ltd., Japan] of the same diameter as the PGR were measured as a reference.

EIS measurements were performed by applying various frequency voltage waves from 10 mHz to 1 kHz with an amplitude of 10 mV at the bias voltage of −1.5 V (in HER) and +1.5 V (in OER) against the Ag/AgCl reference electrode. In order to stabilize the electrode, a resting time of 3 min was set before measurements.

The Faraday efficiency measurement and stability test were performed on a two-electrode system using PGR electrodes for both HER and OER electrodes. For the Faraday efficiency measurement and stability test, Pt/PGR and RuO_x/PGR were used for HER and OER electrodes, respectively. Without the catalyst, the PGR electrode couple was used for the comparison. For CV, the distance between the electrodes was 5 mm. For Faraday efficiency measurement and stability test in the Hoffman electrolysis apparatus, the distance between electrodes were 60 mm.¹⁰ For the Faraday efficiency measurement, the applied potential was set at 10 V, which is due to the significant solution resistance by the electrode distance (60 mm) in the Hoffman electrolysis apparatus, and the Faraday efficiency and hydrogen and oxygen evolution rates were measured until the hydrogen amount reached up to an apparatus limit of 50 mL. The stability test was performed with a constant voltage at 10 V, and the current variation was measured.

3. RESULT AND DISCUSSION

The photographs of PGR, Pt/PGR, and RuO_x/PGR are shown in [Figure 1b](#). The surface of Pt/PGR and RuO_x/PGR are more

metallic glossy than that of PGR without the catalyst by flame-annealing. The surface structures of PGR, Pt/PGR, and RuO_x/PGR were confirmed by SEM images ([Figure 2](#)). From the

Figure 2. SEM images of PGR (a,b), Pt/PGR (c,d), and RuO_x/PGR (e,f).

SEM image, it was confirmed that the Pt or Ru catalyst was deposited so as to cover the entire surface of the PGR. Also, the structure of the deposited catalyst was not porous, and it appeared that the catalyst had been deposited along the shape of the PGR. [Table 1](#) shows the results of elemental analysis by

Table 1. EDX Analysis Data of PGR, Pt/PGR, and RuO_x/PGR Surfaces

element at. %	PGR	Pt/PGR	RuO _x /PGR
C	81.2	61.5	63.5
O	14.3	14.6	21.6
Na	0.2		
Al	1.6	3.7	2.1
Si	2.3	4.6	3.2
Cl			
K	0.08		
Ca	0.08		
Fe	0.2		
Ru			9.6
Pt		15.5	

EDX. For PGR, C was 81.2%, and O was 14.3%, the surface consisted mainly of carbon and oxygen. Pt/PGR and RuO_x/PGR were detected with Pt of 15.5% and Ru of 9.6%, respectively. The carbon content decreased by depositing catalysts on the PGR surface. Pt/PGR showed no change in oxygen content. However, in RuO_x/PGR, the oxygen amount was increased to +7.3% from that of PGR before deposition. Therefore, it is considered that Ru is combined with oxygen in the air during flame-annealing and is deposited on the PGR surface as an oxide. Pt was deposited on the surface as a zero-valent metal.

The chemical-bonding condition results by XPS of PGR, Pt/PGR, and RuO_x/PGR are shown in Figures 3 and 4. In order

Figure 3. XPS spectra of Pt/PGR: (a) Pt survey; (b) Pt 4f; (c) Pt 4d; (d) C 1s; and (e) O 1s.

to investigate the state of chemical bonding of Pt and RuO_x with the PGR, catalysts were deposited on a quartz substrate and compared with the XPS results on the PGR. Figure 3a shows the survey of PGR, Pt/quartz, and reference Pt/PGR from 0 to 1000 eV. Similarly, the XPS survey of PGR, RuO_2 (reference), $\text{RuO}_x/\text{quartz}$, and RuO_x/PGR is shown in Figure 3a. The without-catalyst PGR shows conspicuous peaks of C 1s and O 1s (Figure 3a). Hence, carbon and oxygen are the main components of the PGR as observed by EDX and XPS. In Pt/PGR, peaks of Pt 5p; 52 eV, 4f_{7/2}; 71 eV, 4f_{5/2}; 74 eV, 4d_{5/2}; 315, 4d_{3/2}; 332 eV, and 4p_{3/2}; 520 eV are shown in Figure 3a–c. These Pt peaks were considered to be zero-valent metal that is not bonded to other elements.^{17,18} In addition, the C 1s peak decreased (Figure 3d), which is due to the Pt covering on the PGR surface.^{19–21} Similarly, the O 1s peak of Pt/PGR also decreased (Figure 3e). Because no conspicuous shift of the oxygen peak was observed, it was considered that Pt was not bonded with oxygen (Figure 3e). In addition, Pt peaks of Pt/PGR and Pt/quartz were quite similar (Figure 3a–c). For C 1s and O 1s, Pt chemical bonding was not conspicuously changed between the PGR or quartz glass substrate (Figure

Figure 4. XPS spectra of RuO_x/PGR : (a) survey; (b) Ru 3d/C 1s; (c) Ru 3p; and (d) O 1s.

3d,e). This suggested that the state of the Pt catalyst was not particularly affected by the substrate.

In RuO_x/PGR , peaks of Ru 4p; 45 eV, 3d_{5/2}; 280–283 eV 3d_{3/2}; 284–286 eV, 3p_{3/2}; 462 eV, 3p_{1/2}; 484–497 eV 3s; 588 eV, and MVV; 980 eV are shown in Figure 4a–c. On comparison with RuO_2 reference, it was considered that RuO_2 was formed on the PGR and quartz by flame-annealing (Figure 4b).^{17,22} Ru 3p_{3/2} and 3p_{1/2} were observed between 460 and 500 eV (Figure 4c). The peak near 497 eV in RuO_x/PGR and $\text{RuO}_x/\text{quartz}$ was considered to be shifted to Ru 3p_{1/2} due to RuO_4 from several refs 23–25. From Figure 4d, the O 1s peak shifted when comparing PGR with others. From the above observations, RuO_2 was formed mainly by flame-annealing, and the presence of RuO_4 was also suggested.

The atomic-bonding conditions between Pt, Ru, carbon, and oxygen on the PGR were analyzed using TEY and TFY-NEXAFS by soft X-ray irradiation. The results of Pt/PGR and RuO_x/PGR are shown in Figures 5 and 6. Figures 5a,c and 6a,c show the results of the TEY method, and Figures 5b and 6b show the results by the TFY method. The TEY method is sensitive to the outermost surface; on the other hand, the TFY method is a bulk-sensitive measurement. In the PGR, π^* (= C) and σ^* (= C) peaks were observed at about 285.5 and 293 eV, respectively, indicating sp² of graphite.^{26–30} In TEY C K-edge of Pt/PGR and RuO_x/PGR , π^* and σ^* peaks of graphite

Figure 5. TEY and TFY-XAFS analysis of Pt/PGR: (a) TEY, C K-edge; (b) TFY, C K-edge; and (c) TEY, O K-edge.

Figure 6. TEY and TFY-XAFS analysis of RuO_x/PGR: (a) TEY, C K-edge; (b) TFY, C K-edge; and (c) TEY, O K-edge.

were hardly confirmed (Figures 5a and 6a). However, at TFY C K-edge, peaks of π^* and σ^* were noticeable, confirming that Pt and RuO_x covered the PGR surface (Figures 5b and 6b), uniformly. The O K-edge of Pt/PGR and RuO_x/PGR is shown in Figures 5c and 6c. In the PGR, peaks were observed at 532 and 538 eV, which are attributed to π^* ($=O$) and σ^* ($-O$), respectively.^{31–33} In addition, because oxygen peaks were not observed in the TEY spectrum of Pt/PGR, it was considered that Pt does not combine with oxygen and exists as Pt of 0 valence. In RuO_x/PGR and RuO₂, two peaks in π^* were observed, both of which had the same peak shape. This XAFS result supports the XPS result, indicating the presence of

RuO₂. From the results of EDX, XPS, and NEXAFS, it was considered that Pt covered uniformly the PGR as the metallic condition, and it had not bonded with carbon or oxygen. In RuO_x/PGR, on the other hand, ruthenium and oxygen were combined during flame-annealing, and it was thought that they were deposited on the PGR surface as RuO₂, mainly. Also, the relationship between the deposited catalysts and the carbon of the PGR was not suggested. From these considerations, it was found that flame-annealing can coat Pt and RuO_x on the PGR surface. In addition, it was found that Pt was deposited as 0 valence metal and that Ru became RuO₂ on the PGR surface.

In order to investigate the catalytic activity of each electrocatalyst on the PGR, first, the results of activity evaluation by CV are shown in Figure 7. In each electro-

Figure 7. HER polarization curves of Pt/PGR, Pt rod, and PGR (a) and OER polarization curves of RuO_x/PGR, Pt rod, and PGR (b) at a scan rate of 25 mV s^{−1} (vs Ag/AgCl) in Na₂SO₄ (1 M) aqueous electrolyte.

chemical measurement, Pt/PGR (20 s annealing duration, 5 times dipping–annealing cycles) was used for HER electrodes, and RuO_x/PGR (10 s annealing duration, 5 times dipping–annealing cycles) was used for OER electrodes. Pt/PGR showed current improvement at lower voltage than the PGR (Figure 7a). Also, Pt/PGR shows a CV curve similar to the Pt rod measured as a reference. From the above, it can be said that the Pt-deposited PGR with high HER activity using low amount of Pt catalyst can be easily produced by flame-annealing.

Figure 7b shows the OER catalytic activities of RuO_x/PGR. The current rising voltage using RuO_x/PGR electrode was lower than that of the PGR and Pt rod. Hysteresis was observed between forward and reverse potential sweeping directions, which was considered to be the effect of the capacitance of the electrocatalyst on the PGR with a large specific surface area.¹⁰ In addition, this capacitance effect did not change significantly before and after catalyst deposition. This suggested that the catalyst on the PGR surface did not have a porous structure, as observed by SEM (Figure 2). From the above results, it was revealed that OER activity was improved by coating with RuO_x on the PGR surface. From the

results of CV tests, it was found that electrocatalysts by flame-annealing depositions can perform with high electrochemical catalytic activity and be fabricated very easily in a short time with less catalyst usage.

Optimization of flame-annealing time and number of dipping times into catalyst precursor solutions were performed for water electrolyzing. The results are shown in Figures 7 and 8 for Pt/PGR and RuO_x/PGR, respectively. For Pt/PGR,

Figure 8. Variation of current density of Pt/PGR electrodes for the optimization of HER electrodes with different annealing time (with 5 dip times) (a) and different annealing cycles (with 20 s annealing time) (b) at -1.5 V vs Ag/AgCl reference electrode.

considering the average value and variation of current density results, it was decided that the optimal annealing duration and the annealing cycles should be 20 s and 5 times, respectively. For RuO_x/PGR, the optimal annealing duration and the annealing cycles should be 10 s and 5 times, respectively. Excessive flame-annealing reduced the catalytic activity of Pt/PGR and RuO_x/PGR. Furthermore, because the increase of the current density was not observed when the number of dips exceeded 5 times in both cases, the optimal number of dipping times should be 5 times (Figure 9).

The catalyst weight and film thickness of Pt and RuO_x deposited on the PGR were estimated from the following calculations. The amount of catalyst precursor solution used was calculated from the reduced weight of the precursor solution used for catalyst deposition on the PGR. The consumed amount of precursor solution by 5 times dipping–annealing cycles was 0.067 mg for Pt and 0.043 g for RuO_x, respectively. The concentrations of PtCl₆·6H₂O and Ru(NO)(NO₃)₃ used were 0.039 mol L⁻¹ and 0.05 mol L⁻¹, respectively (solvent: PtCl₆·6H₂O is ethanol; Ru(NO)(NO₃)₃ is deionized water). Because PtCl₆·6H₂O was changed to Pt and Ru(NO)(NO₃)₃ to RuO₂, the deposition amounts of Pt and RuO₂ were calculated from the molecular weights before and after the change. The molecular weight of each is PtCl₆·6H₂O; 517.9, Pt; 195.1, Ru(NO)(NO₃)₃; 317.1, and RuO₂; 133.1. Next, the amount of Pt and RuO₂ deposited per unit area (cm²) was calculated. The amount of catalyst deposited per unit surface area was calculated in two patterns, in consideration of the apparent surface area and the mesoscopic surface area. Apparent surface area: 2.54 cm² {the apparent

Figure 9. Variation of current density of RuO_x/PGR electrodes for the optimization of OER electrodes with different annealing time (with 5 dip times) (a) and different annealing cycles (with 10 s annealing time) (b) at $+1.5$ V vs Ag/AgCl reference electrode.

surface area of the PGR (cylinder) was calculated as follows; $S = \pi r^2 + 2\pi rh$ (S ; apparent surface area, π ; ratio of the circumference of a circle to its diameter, r = radius, h = height)} and mesoscopic surface area: from Brunauer–Emmett–Teller studies in our previous paper; the PGR has a specific surface area of 3.3 m² g⁻¹.¹⁰ Because the PGR is 0.25 g at a length of 4 cm, the specific surface area possessed by 4 cm PGR is 0.825 m² (8250 cm²). The catalyst deposition amount is divided by these surface areas to obtain Pt, RuO₂ deposition amount per unit area. An approximate film thickness was calculated from the density of Pt and RuO₂. Density of the formed substance: Pt 21.45 g cm⁻³ and RuO₂ 6.97 g cm⁻³. The above calculations are summarized below

$$\begin{aligned} & \text{Catalyst deposition amount per unit area [g cm}^{-2}\text{]} \\ &= \{ \text{deposited catalyst weight [g]} \\ & \quad \times (\text{molecular weight of deposited material} \\ & \quad / \text{catalyst molecular weight before deposition}) \} \\ & \quad / \text{surface area [cm}^2\text{]}^* \end{aligned}$$

Surface area [cm²]*; apparent surface area: 2.54 cm², and mesoscopic surface area: 8250 cm².

$$\begin{aligned} & \text{Catalyst deposit thickness [nm]} \\ &= (\text{catalyst deposition amount per unit area [g cm}^{-2}\text{]} \\ & \quad / \text{density of deposited material [g cm}^{-3}\text{]}) \times 10^7 \end{aligned}$$

Table 2 shows the catalyst deposition amount and film thickness calculated by the above calculations. The data in Table 2 show the case of 5 times dipping–annealing cycles. The weight of the Pt and RuO₂ deposited on the PGR is calculated as about 0.25 and 0.36 mg cm⁻² from the decrement of the catalyst precursor solution. The approximate catalyst deposition film thickness was calculated by two patterns in consideration of the apparent area and the mesoscopic structure. The actual film thickness was expected to be

Table 2. Amount of Catalyst Deposited and the Film Thickness of the Catalyst by 5 Times Dipping–Annealing Cycles of Pt/PGR and RuO_x/PGR^a

material	catalyst amount on PGR (mg cm ⁻²)	catalyst deposit thickness (nm)	
		projected surface area (2.54 cm ²)	mesoscopic surface area (8250 cm ²)
Pt	0.25	114.52	0.04
RuO ₂	0.36	513.60	0.16

^aThe catalyst film thickness was calculated as both the apparent surface area and the specific surface area considering the porous structure. Numerical values are approximate values derived from calculations (The amount of deposition measured three samples and the average was calculated.).

between these values. Hence, it can be considered that very thin nanoscale catalyst films were deposited on the porous PGR as the mesoscopic point of view.

Hydrogen and oxygen evolution rates were observed using a two-electrode cell with Pt/PGR and RuO_x/PGR as HER and as OER electrodes, respectively, and the Faraday efficiency was calculated. The PGR electrode couple were also used for reference. It was confirmed that the hydrogen and oxygen generation rates were both improved by the presence of the catalyst (Figure 10a). Figure 10b shows the Faraday efficiency

Figure 10. (a) Time course of generated gas volumes by overall water electrolyzing of HER (●) and OER (■) using PGR electrodes and of HER (○) and OER (□) using Pt/PGR and RuO_x/PGR electrodes, respectively; (b) Faraday efficiency during water electrolysis using PGR electrodes; and (c) Faraday efficiency during water electrolysis using Pt/PGR and RuO_x/PGR electrodes. The electrolyte was Na₂SO₄ (1 M) aqueous solution.

using PGR electrodes, and Figure 10c shows Faraday efficiency using Pt/PGR and RuO_x/PGR electrode couple. In both cases, the Faraday efficiency of H₂ generation was high as around 95%. In O₂ generation, however, the Faraday efficiency using the PGR electrode was 45.4% and using Pt/PGR–RuO_x/PGR electrode couple was near twice of the Faraday efficiency as 89.2%.

The current variation with time during hydrogen and oxygen evolution is shown in Figure 11a. Using the PGR electrode

Figure 11. Durability test of water electrolysis *I*–time data (a) and photographs of OER electrode (anode) using PGR (b) and RuO_x/PGR (c).

couple, the current value decreased rapidly in 50 min. This current decrease indicates that the oxygen evolution electrode has been destroyed by corrosion with the deterioration of the electrode function. The photographs of the PGR anode during water electrolysis are shown in Figure 11b. It was confirmed that the PGR electrode was broken from the top with the time duration and was collapsed in 50 min, completely. In the Pt/PGR–RuO_x/PGR electrode couple, on the other hand, a rapid decrease in the current value was confirmed at 330 min. Similar to the PGR without catalysts, the anode was destroyed with time duration and completely disappeared at 330 min (Figure 11c). The increase in the current value of Pt/PGR–RuO_x/PGR over 1–2 h was thought to be due to the temporary increase in the electrode surface area due to electrode breakage. Experiments with the two-electrode cell revealed that the water electrolysis durability was improved using catalysts (Pt and RuO_x) on the graphite electrode. In particular, the effect of the catalyst is remarkable on the OER, and it was found that the durability of the anode is improved by coating RuO_x. The corrosion destruction of this PGR anode will be investigated in detail in the next paper.

In order to understand the electrochemical phenomena, EIS was performed on PGR, Pt/PGR, and RuO_x/PGR. The Cole–Cole plots from EIS are shown in Figure 12. The equivalent circuit used for fitting is illustrated in Figure 12a. *R*_s, CPE-T, and *R*_p represent the series resistance of the cell, the electrochemical interface capacitance of the electrode surface, and the electrochemical interface resistance of the electrode surface, respectively. Hence, a lower *R*_p suggests higher electrochemical catalytic activity. A lower CPE-P suggests the significant depression of semicircle and the larger porosity of

Figure 12. EIS spectra and fitting result of electrocatalysts PGR in Na_2SO_4 (1 M) aqueous electrolyte: (a) an equivalent circuit for the EIS analysis. The fitting results are shown in each result as the solid lines; (b) PGR ($\square$) and Pt/PGR ($\circ$) at -1.5 V (vs Ag/AgCl); (c) PGR ($\square$) and RuO_x/PGR ($\circ$) at $+1.5$ V (vs Ag/AgCl); and (d) expanded figure of (c).

the electrode. The fitted results are shown in Table 3. In this work, we have focused on the R_p value. In the HER, Pt/PGR

Table 3. EIS Fitting Data of PGR, Pt/PGR, and RuO_x/PGR in Na_2SO_4 (1 M) Aqueous Electrolyte at the Bias Voltage of -1.5 V (in HER) and $+1.5$ V (in OER) against Ag/AgCl Reference Electrode

electrocatalyst	R_s [Ω]	CPE-T [F]	CPE-P	R_p [Ω]
HER Electrode				
PGR	1.96	0.12	0.55	1.53
Pt/PGR	2.20	0.40	0.42	0.67
OER Electrode				
PGR	1.58	0.11	0.58	7.50
RuO_x/PGR	1.50	0.25	0.51	0.44

shows 2.3-times lower resistance value of R_p than PGR, which can be seen that the water-electrolysis catalytic activity of Pt/PGR is higher than that of PGR itself (Figure 12b). In the OER, on the contrary, RuO_x/PGR showed 17-times lower resistance (R_p) than PGR, and it was confirmed that the performance of the OER can be affected by the catalyst deposition on carbon electrodes much significantly than that of the HER (Figure 12c,d).

Pt/PGR and RuO_x/PGR were compared to previously reported benchmarks and highly active base metal catalysts (Table 4). For the HER, the overpotential of Pt/PGR was -15.5 mV, close to the benchmark Pt/C of -10.9 mV.³⁴ In the

Table 4. Comparison of This Study with Other Studies^{a,b}

	catalyst	Electrolyte	η at 10 mA cm^{-2} [mV]	References
HER	Pt/PGR	1 M KOH	-15.5	this work
	Pt/C	1 M NaOH	-10.9	34
	NiMoCo	1 M NaOH	-70	35
OER	RuO_x/PGR	1 M KOH	311.6	this work
	Ru	1 M NaOH	290	35
	NiFe	1 M NaOH	340	35

^aOverpotential of Pt/PGR and RuO_x/PGR was obtained from linear sweep voltammetry measurement in 1 M KOH using a Pt foil as a counter electrode and reversible hydrogen electrode as a reference electrode. ^b η : overpotential with a current density of 10 mA cm^{-2} .

OER, the overpotential of RuO_x/PGR was 311.6 mV, which was close to 290 mV of the reference Ru catalyst.³⁵ In addition, Pt/PGR and RuO_x/PGR showed lower overpotentials as compared with the base metal-based catalyst.³⁵ When investigating the overpotential due to the activity of the catalyst using the PGR, it is necessary to pay attention to the capacitance effect of the PGR, as shown in Figure 7. Also, in this study, the electrode reaction area was large (2.54 cm^2); so, the overpotential was inevitably higher than the reference. However, from these results, it is considered that catalyst-deposited PGR can be used sufficiently for evaluating catalytic ability.

4. CONCLUSIONS

In this paper, the flame-annealing deposition methods for very thin Pt and RuO_x catalyst layers on very cheap PGR electrodes and the water-electrolysis performance were described. Using the very simple and short-time flame-annealing method, electrocatalysts with high HER and OER activities were fabricated using quite low amount of catalysts. By flame-annealing deposition, it was found that H_2PtCl_6 became a zero-valent metal Pt and that $\text{Ru}(\text{NO})(\text{NO}_3)_3$ reacts with oxygen in the air and was deposited on the PGR surface as RuO_x . Pt/PGR and RuO_x/PGR electrodes showed high catalytic activity for the HER and OER, respectively. Although the PGR anode itself is not stable for the long-term stability test for the OER in water electrolysis, the RuO_x/PGR electrode showed longer stability during the water electrolysis as the OER electrode. In conclusion, the method of producing the electrocatalyst by PGR and flame-annealing is extremely inexpensive and simple and can be produced in a short time. Therefore, it is very effective for the initial catalyst search and a very important technology in the development of a catalyst requiring a large amount of trial and error.

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Notes

The authors declare no competing financial interest.

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