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 Na$_2$SO$_4$ aqueous electrolyte, respectively. Although HER and OER currents using PGR without catalysts were $-16$ mA cm$^{-2}$ (at $-1.5$ V vs Ag/AgCl) and $+20$ mA cm$^{-2}$ (at $+2.0$ V vs Ag/AgCl), they were improved to $-110$ and $+80$ 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 CO$_2$.$^{4-6}$ 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:...
4B, uni exchangeable pencil graphite rod, φ 2.0 mm × 130 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 (PtCl$_6$·6H$_2$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%) (Ru(NO)(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 duration was varied for 5, 10, 20, 30, 40, and 80 s.

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$_x$).
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 RuO₄/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, University of Hyogo, Japan). For XPS, Pt and RuO₄ 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 RuO₄/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 [φ2.0 mm × 100 mm Nilaco Co., Ltd., Japan] of the same diameter as the PGR as a reference 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 RuO₄/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 RuO₄/PGR are shown in Figure 1b. The surface of Pt/PGR and RuO₄/PGR are more metallic glossy than that of PGR without the catalyst by flame-annealing. The surface structures of PGR, Pt/PGR, and RuO₄/PGR were confirmed by SEM images (Figure 2). From the 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 EDX. For PGR, C was 81.2%, and O was 14.3%, the surface consisted mainly of carbon and oxygen. Pt/PGR and RuO₄/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 RuO₄/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\textsubscript{x}/PGR are shown in Figures 3 and 4. In order to investigate the state of chemical bonding of Pt and RuO\textsubscript{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\textsubscript{2} (reference), RuO\textsubscript{x}/quartz, and RuO\textsubscript{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\textsubscript{7/2}; 71 eV, 4f\textsubscript{5/2}; 74 eV, 4d\textsubscript{5/2}; 315, 4d\textsubscript{3/2}; 332 eV, and 4p\textsubscript{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.\textsuperscript{17,18} In addition, the C 1s peak decreased (Figure 3d), which is due to the Pt covering on the PGR surface.\textsuperscript{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 3d,e). This suggested that the state of the Pt catalyst was not particularly affected by the substrate.

In RuO\textsubscript{x}/PGR, peaks of Ru 4p; 45 eV, 3d\textsubscript{5/2}; 280–283 eV 3d\textsubscript{3/2}; 284–286 eV, 3p\textsubscript{1/2}; 462 eV, 3p\textsubscript{3/2}; 484–497 eV 3s; 588 eV, and MVV; 980 eV are shown in Figure 4a–c. On comparison with RuO\textsubscript{2} reference, it was considered that RuO\textsubscript{2} was formed on the PGR and quartz by flame-annealing (Figure 4b).\textsuperscript{17,22} Ru 3p\textsubscript{3/2} and 3p\textsubscript{1/2} were observed between 460 and 500 eV (Figure 4c). The peak near 497 eV in RuO\textsubscript{x}/PGR and RuO\textsubscript{x}/quartz was considered to be shifted to Ru 3p\textsubscript{1/2} due to RuO\textsubscript{4} from several refs\textsuperscript{23–25}. From Figure 4d, the O 1s peak shifted when comparing PGR with others. From the above observations, RuO\textsubscript{2} was formed mainly by flame-annealing, and the presence of RuO\textsubscript{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\textsubscript{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 PGR, \( \pi^* \) (\( \equiv \) C) and \( \sigma^* \) (\( \equiv \) C) peaks were observed at about 285.5 and 293 eV, respectively, indicating sp\textsuperscript{2} of graphite.\textsuperscript{26–30} In TEY C K-edge of Pt/PGR and RuO\textsubscript{x}/PGR, \( \pi^* \) and \( \sigma^* \) peaks of graphite...
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 RuOₓ/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 RuOₓ 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 electrochemical measurement, Pt/PGR (20 s annealing duration, 5 times dipping—annealing cycles) was used for HER electrodes, and RuOₓ/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 RuOₓ/PGR. The current rising voltage using RuOₓ/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. 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 RuOₓ 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 RuO2/PGR, respectively. For Pt/PGR, 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 RuO2/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 RuO2/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 RuO2 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 before deposition. The consumed amount of precursor solution by 5 times dipping-annealing cycles was 0.067 mg for Pt and 0.053 g for RuO2, 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 surface area of the PGR (cylinder) was calculated as follows; \( S = \pi r^2 + 2\pi rh \) (S: apparent surface area, \( \pi \); 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. 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

Catalyst deposition amount per unit area [g cm⁻²]

\[
= \{ \text{deposited catalyst weight [g]} \} \\
\times (\text{molecular weight of deposited material} \nonumber \\
/\text{catalyst molecular weight before deposition}) \\
/\text{surface area [cm}^2\text{]} \nonumber \\
\]

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

Catalyst deposit thickness [nm]

\[
= \left( \text{catalyst deposition amount per unit area [g cm}^{-2}\right) \times 10^7 \\
/\text{density of deposited material [g cm}^{-3}\right) \nonumber \\
\]

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
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 using PGR electrodes, and Figure 10c shows Faraday efficiency using Pt/PGR and RuO$_x$/PGR electrode couple. The current variation with time during hydrogen and oxygen evolution is shown in Figure 11a. Using the PGR electrode 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. $R_p$, 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 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 H$_2$ generation was high as around 95%. In O$_2$ 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%.

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*

| material | catalyst amount on PGR (mg cm$^{-2}$) | 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                                 |

*The 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.).
In this paper, the flame-annealing deposition methods for very thin Pt and RuOx 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 H2PtCl6 became a zero-valent metal Pt and that Ru(NO)(NO3)3 reacts with oxygen in the air and was deposited on the PGR surface as RuOx. Pt/PGR and RuOx/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 RuOx/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.

4. CONCLUSIONS

In this study, the electrode reaction area was large (2.54 cm2); 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.

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

| Catalyst | Electrolyte | Overpotential $\eta$ at 10 mA cm$^{-2}$ | References |
|----------|-------------|----------------------------------------|-------------|
| HER      | Pt/PGR      | 1 M KOH, −15.5 mV                        | this work   |
|          | Pt/C        | 1 M NaOH, −10.9 mV                      | 34          |
| OER      | RuOx/PGR    | 1 M KOH, 311.6 mV                       | this work   |
|          | Ru          | 1 M NaOH, 290 mV                        | 35          |
|          | NiFe        | 1 M NaOH, 340 mV                        | 35          |

$^a$Overpotential of Pt/PGR and RuOx/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$$\eta$: overpotential with a current density of 10 mA cm$^{-2}$.
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Notes
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