



Short communication

One-compartment electrochemical H₂ generator from borohydride

Shin-ichi Yamazaki*, Kentaro Kuratani, Hiroshi Senoh, Zyun Siroma, Kazuaki Yasuda

Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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ABSTRACT

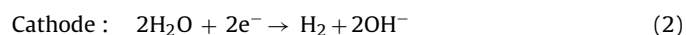
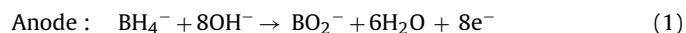
A one-compartment membrane-less electrochemical H₂ generator from borohydride was realized using a Rh porphyrin and RuO₂ as the anode and cathode, respectively. H₂ generation from this cell was successfully controlled electrochemically by varying the potential applied. The regulation of H₂ generation was based on the selectivity of the anode and cathode. We found that RuO₂ exhibits H₂O electro-reduction activity without electro-oxidation or chemical decomposition of borohydride, and used the catalyst as a selective cathode in the electrochemical H₂ generator. Anode and cathode potentials of the electrochemical H₂ generator were measured separately. The both potentials were discussed in terms of the catalytic activities of a Rh porphyrin and RuO₂.

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1. Introduction

Chemical hydrides such as borohydride (BH₄⁻) have attracted considerable interest due to their high energy density [1,2]. The rapid, safe, and controllable generation of H₂ from these hydrogen-storage materials is very important for their use in ubiquitous energy devices. For this purpose, a wide variety of studies on catalysts and systems for H₂ generation have been performed [3–5].

Recently, Senoh et al. presented a new electrochemical H₂ generator from BH₄⁻ [6]. In the cell, H₂ generation from BH₄⁻ is separated into the following anode (BH₄⁻ electro-oxidation) and cathode (H₂O electro-reduction) reactions:



A Pt or a Au catalyst was used for anode catalysts, and a Pt catalyst was used for cathode catalysts. In this electrochemical system, the rate of H₂ generation could be controlled by varying current applied. In their study [6], they successfully controlled H₂ generation to some extent.

However, two points should be addressed to improve this H₂ generator. One is a problem with electrocatalysts. Conventional electrocatalysts (Pt, Au, etc.) are not the most suitable materials. When a Pt catalyst is used, uncontrollable H₂ generation occurs

due to the chemical decomposition of BH₄⁻ (Eq. (3)):



Furthermore, a Pt anode catalyzes H₂O electro-reduction. This indicates that the reactions (Eq. (1)) and (Eq. (2)) occur on the same electrode. The overall reaction is also a decomposition of BH₄⁻ (Eq. (3)). When a Au catalyst is used as an anode catalyst, uncontrollable H₂ generation can be suppressed, however, the catalyst requires large overpotentials. The other is a problem of separation between anode and cathode compartments. A cathode Pt catalyst reacts with BH₄⁻. The reaction of BH₄⁻ with a cathode catalyst (crossover reaction) results in the decrease of cathode potential. The cathode must be strictly separated from the anode to prevent access of BH₄⁻. However, few electrolyte membranes are appropriate for separating the anode from the cathode.

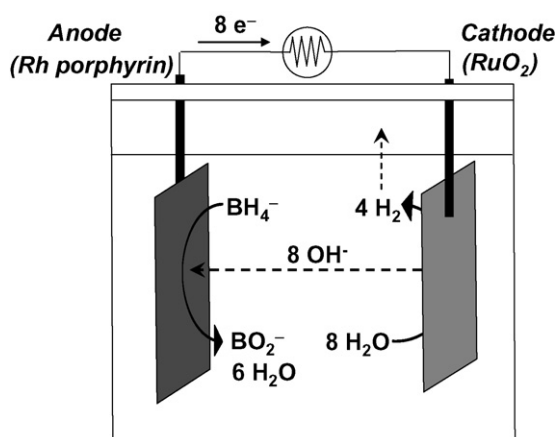
In order to counteract these two problems, we have sought *selective* anode and cathode catalysts with high activity. In our previous study [7], we developed a new anode catalyst for BH₄⁻ electro-oxidation using rhodium porphyrins. This catalyst can oxidize BH₄⁻ at low potentials without the chemical decomposition of BH₄⁻ or H₂O electro-reduction; this catalyst is selective for anode reaction. These properties counteract the problems with anode catalysts.

If we could find a selective cathode catalyst that can catalyze H₂O electro-reduction at low overpotentials without reacting with BH₄⁻, it would not be necessary to separate the anode and cathode. A one-compartment structure would drastically simplify the structure of the H₂ generator, and eliminate the problems regarding the crossover of BH₄⁻.

This situation encouraged us to search a selective cathode catalyst for H₂O reduction in an electrochemical H₂ generator. Pt-based

* Corresponding author. Fax: +81 72 751 9629.

E-mail address: s-yamazaki@aist.go.jp (S. Yamazaki).



Scheme 1. One-compartment electrochemical H₂ generator.

catalysts, which are usually used for H₂O reduction, are unsuitable because it reacts with BH₄⁻ dramatically. We paid special attention to ruthenium dioxide (RuO₂). It was reported that RuO₂ has electrochemical H₂O reduction activity in basic solution [8–12]. In contrast to Pt-based catalysts, RuO₂ exhibits little activity for H₂ oxidation [12]. RuO₂ might have high selectivity toward H₂O reduction. This idea raises the expectation that RuO₂ can catalyze H₂O reduction without reacting with BH₄⁻.

In the present study, we developed a one-compartment electrochemical H₂ generator. This cell requires the application of some voltage, but voltage needed for significant H₂ generation is low. The generation of H₂ from BH₄⁻ could be successfully controlled by potential applied. The concept and structure of this cell are shown in Scheme 1. This cell is based on the selectivity of anode (a Rh porphyrin catalyst) and cathode (a RuO₂ catalyst). We found that certain kinds of RuO₂ have virtually no catalytic activity toward chemical decomposition of 10 mM BH₄⁻, even though it exhibited strong electrochemical H₂O reduction activity. The electrochemical BH₄⁻ oxidation activity by the RuO₂ was much smaller than the H₂O electro-reduction activity. This catalyst as well as a Rh porphyrin catalyst enables us to construct an electrochemically controllable one-compartment H₂ generator.

2. Materials and methods

2.1. Materials

Commercially available anhydrous RuO₂ was purchased from Wako. Amorphous RuO₂ was prepared as described in the literature [13]. Sodium borohydride was purchased from Kishida Chemical. Rh(III) octaethylporphyrin chloride ([Rh^{III}(OEP)]Cl) was synthesized by the reflux of Rh₂Cl₂(CO)₄ and octaethylporphine [14,15]. Carbon-supported Rh(OEP) (Rh(OEP)/C) was prepared by depositing [Rh(OEP)]Cl on carbon black with an equilibrium adsorption method, as described in Refs. [7,15].

2.2. Modification of glassy carbon (GC) electrodes

Five milligrams of RuO₂ or Rh(OEP)/C were suspended in a mixed solvent (0.5 mL, ethanol:water = 1:1) containing 5 μL Nafion (5% solution, Aldrich). The aliquot (2 μL) of this suspension was mounted on a glassy carbon electrode (*A* = 0.0707 cm²) and dried at room temperature. The experimental details are shown in Refs. [7,15].

2.3. Measurement of voltammograms

All electrochemical measurements were performed using an ALS electrochemical analyzer. Voltammograms of RuO₂ and Rh(OEP)/C were measured in a three-electrode system. The modified glassy carbon electrodes were used as working electrodes. A Ag|AgCl|KCl(sat.) electrode and a platinum coil electrode were used as a reference and a counter electrodes, respectively. All potentials were referred to RHE. Voltammograms of an electrochemical H₂ generator were measured in a two-electrode system. The Rh(OEP)/C-modified electrode was used as a working electrode, and the RuO₂-modified electrode was used as a reference (counter) electrode. All voltammograms were recorded at a scan rate of 10 mV s⁻¹ in deaerated 0.1 M NaOH solution.

2.4. Measurement of H₂ generation from a one-compartment electrochemical cell

The experiment was performed using the electrochemical cell shown in Scheme 1. A RuO₂-modified GC electrode was used as a cathode, and a Rh(OEP)-modified GC electrode was used as an anode. An aliquot (100 μL) of catalyst suspension described above was mounted on both sides of a GC plate (1.5 cm × 1.5 cm) (total amount 200 μL), and dried at room temperature [7]. The electrodes were immersed in 0.1 M NaOH solution containing 10 mM NaBH₄. The cell was purged with argon gas and sealed with a silicone plug to prevent gas exchange. After the immersion at room temperature, the gas phase above the solution was examined to determine the H₂ concentration by gas chromatography. The gas phase was again purged with argon gas. After the electrolysis for at room temperature, the gas phase was analyzed again. The applied voltage denotes anode (Rh(OEP)/C) potential vs. cathode (RuO₂) potential. The charge transferred during electrolysis was recorded. H₂ generation from only RuO₂ was measured by the same method.

2.5. Measurement of anode and cathode potentials of the H₂ generator

Ag|AgCl|KCl(sat.) electrodes were immersed in the electrochemical H₂ generator, and the potential difference between Ag|AgCl|KCl(sat.) and anode was measured by a potentiometer under the operation of the H₂ generator. The potential difference between Ag|AgCl|KCl(sat.) and cathode was measured by the same method. The potential differences were referred to RHE.

3. Results and discussion

3.1. Electrochemical reactivities of RuO₂ toward H₂O reduction and BH₄⁻ oxidation

Fig. 1 shows cyclic voltammograms of an anhydrous RuO₂ (Wako). RuO₂ exhibited strong H₂O reduction activity below 0 V. Although this catalyst did not give as high an activity as Pt catalyst, the onset potential of RuO₂ for H₂ generation was close to 0 V (vs. RHE). Upon the addition of 1 mM BH₄⁻, the oxidation current increased slightly (Fig. 1A, line b). However, the current increase was much lower than the H₂O reduction current even under electrode-rotation conditions (Fig. 1A, line c). In particular, at low potentials (below 0.25 V vs. RHE), the BH₄⁻ oxidation current can be neglected. Even when BH₄⁻ concentration was increased to 10 mM, the BH₄⁻ oxidation current did not increase significantly (Fig. 1B, lines b and c), and remained much lower than H₂O reduction current.

In contrast, Pt cathode catalysts, which are most often used for electrochemical H₂ generation, have strong BH₄⁻ electro-oxidation activity [7]. The electro-oxidation of crossover BH₄⁻ by cathode Pt

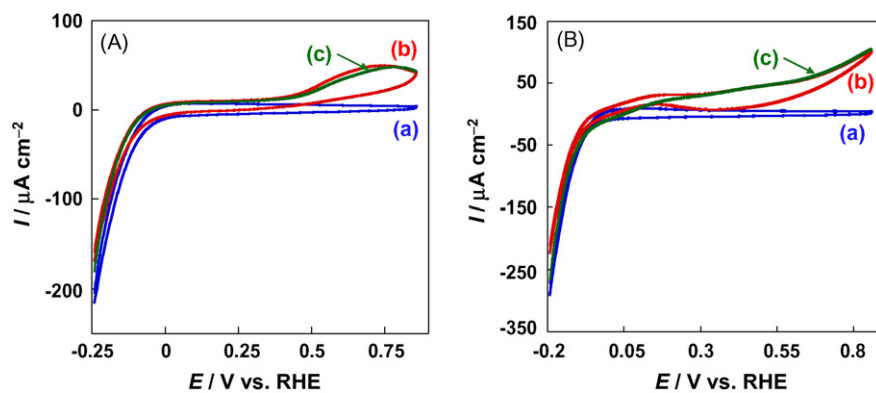


Fig. 1. (A) Voltammograms of commercially available RuO₂ in 0.1 M NaOH solution (a) in the absence of BH₄⁻, (b) in the presence of 1 mM BH₄⁻, and (c) in the presence of 1 mM BH₄⁻ with electrode rotation (3600 rpm). (B) Voltammograms of commercially available RuO₂ in 0.1 M NaOH solution (a) in the absence of BH₄⁻, (b) in the presence of 10 mM BH₄⁻, and (c) in the presence of 10 mM BH₄⁻ with electrode rotation (3600 rpm). The voltammograms were recorded at a scan rate of 10 mV s⁻¹ at 25 °C.

catalysts is a significant problem in the cell using BH₄⁻ as a fuel. A lack of BH₄⁻ electro-oxidation activity is an important property that is needed to construct a one-compartment H₂ generator mentioned above.

3.2. Chemical decomposition of BH₄⁻ by RuO₂

Since the chemical decomposition of BH₄⁻ by electrocatalysts results in the uncontrollable generation of H₂, the reactivity of RuO₂ toward BH₄⁻ under open circuit conditions was examined. Few H₂ bubbles were generated when the RuO₂ electrode was soaked in the BH₄⁻ solution (10 mM in 0.1 M NaOH), in contrast to Pt catalyst, which generated abundant bubbles immediately after the immersion into BH₄⁻ solution. The results of a gas chromatography analysis gave a quantitative basis for this observation. H₂ generation from a RuO₂-modified electrode through the chemical decomposition of BH₄⁻ was only 1.8 nmol min⁻¹, while that from a carbon-supported Pt catalyst was 5525 nmol min⁻¹ (taken from Ref. [7]). Thus, RuO₂ exhibited virtually no activity for the chemical decomposition of BH₄⁻. This property would also be desirable for cathode catalysts in a controllable H₂ generator.

3.3. Electrochemical reactivities of amorphous RuO₂ toward H₂O reduction and BH₄⁻ oxidation

The electrochemical activity of other RuO₂ that have an amorphous structure was also tested. Fig. 2 shows voltammograms for an amorphous RuO₂-modified electrode. Although amorphous

RuO₂ exhibited H₂O reduction activity, it exhibited stronger electro-oxidation activity toward 1 mM BH₄⁻ (Fig. 2A, line c). The increase in the BH₄⁻ concentration from 1 mM to 10 mM drastically increased the BH₄⁻ oxidation current at low potentials. The ratio of BH₄⁻ electro-oxidation/H₂O electro-reduction strongly depended on RuO₂ used, and was much higher in amorphous RuO₂. This relatively higher BH₄⁻ electro-oxidation activity might be unfavourable for its use as a cathode catalyst in the electrochemical H₂ generator. Thus, RuO₂ (Wako) was used in the following experiments.

3.4. The reactivity of Rh(OEP) toward 10 mM BH₄⁻

We previously found that carbon-supported Rh octaethylporphyrin (Rh(OEP)/C) could act as a catalyst for BH₄⁻ electro-oxidation without promoting H₂O reduction or BH₄⁻ chemical decomposition. [7]. However, the electrochemical reactivity toward high-concentration BH₄⁻ (>10 mM), which is used in H₂ generators, remains to be clarified. In this study, the electrochemical oxidation of 10 mM BH₄⁻ by Rh(OEP)/C was examined by voltammetry.

The results are shown in voltammograms of Fig. 3. On the addition of 10 mM BH₄⁻, the oxidation current increased drastically (Fig. 3, lines b and c). Under electrode rotation condition (3600 rpm), it exceeded 70 mA cm⁻² (Fig. 3, line c). The H₂O reduction current was virtually zero in the presence of 10 mM BH₄⁻. This property exhibits marked contrast to that with RuO₂ (Wako), which catalyzes only H₂O electro-reduction without catalyzing

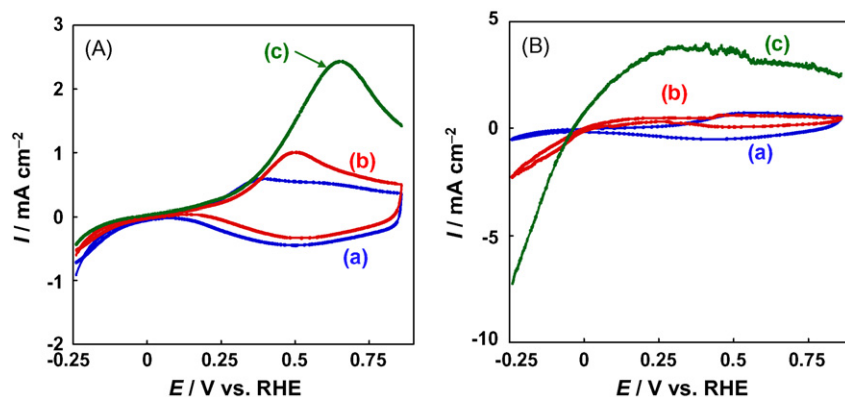


Fig. 2. (A) Voltammograms of amorphous RuO₂ in 0.1 M NaOH solution (a) in the absence of BH₄⁻, (b) in the presence of 1 mM BH₄⁻, and (c) in the presence of 1 mM BH₄⁻ with electrode rotation (3600 rpm). (B) Voltammograms of amorphous RuO₂ in 0.1 M NaOH solution (a) in the absence of BH₄⁻, (b) in the presence of 10 mM BH₄⁻, and (c) in the presence of 10 mM BH₄⁻ with electrode rotation (3600 rpm). The voltammograms were recorded at a scan rate of 10 mV s⁻¹ at 25 °C.

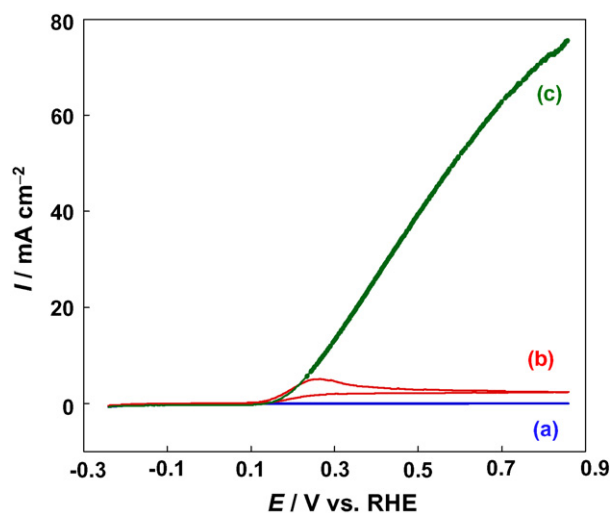


Fig. 3. Voltammograms of Rh(OEP)/C in 0.1 M NaOH solution (a) in the absence of BH_4^- , (b) in the presence of 10 mM BH_4^- , and (c) in the presence of 10 mM BH_4^- with electrode rotation (3600 rpm). The voltammograms were recorded at a scan rate of 10 mV s^{-1} at 25°C .

BH_4^- electro-oxidation. Thus, Rh(OEP)/C meets the requirements as a selective anode catalyst in the one-compartment electrochemical H_2 generator.

Electrode rotation drastically enhanced the oxidation current (Fig. 3), indicating that mass transfer of BH_4^- is involved in the determination of the reaction rate. However, the reaction is limited not only by the diffusion but also by the BH_4^- oxidation. The oxidation current did not give steady-state current (Fig. 3, line c), while the diffusion-controlled steady-state current was observed for the electro-oxidation of 1 mM BH_4^- [7]. This indicates that BH_4^- oxidation process also participates in the determination of the reaction rate at a high BH_4^- concentration (10 mM).

3.5. The regulation of H_2 generation from a one-compartment electrochemical cell using RuO_2 cathode and Rh porphyrin anode

The results above revealed that Rh(OEP)/C can catalyze the electro-oxidation of BH_4^- (Eq. (1)) without promoting the electro-reduction of H_2O (Eq. (2)), and that RuO_2 (Wako) can catalyze the electro-reduction of H_2O without promoting the electro-oxidation of BH_4^- . Both electrocatalysts are virtually inactive toward chemical decomposition of BH_4^- . When the Rh porphyrin catalyst is used as an anode catalyst and the RuO_2 catalyst is used as a cathode catalyst, a one-compartment electrochemical H_2 generator can be realized (Scheme 1). Because this cell is based on their selectivity, no membrane or separator is needed. The generation of H_2 from this cell with and without potential application was examined by gas chromatography.

Under open circuit conditions, the rate of H_2 generation from the cell was $3.7 \text{ nmol min}^{-1}$. Thus, the generation of H_2 from the chemical decomposition of BH_4^- was successfully suppressed. Since the rate of H_2 generation with RuO_2 was $1.8 \text{ nmol min}^{-1}$, as mentioned above, about half of H_2 generation under open circuit conditions should be due to Rh(OEP) catalyst.

The increase in the applied voltage (anode vs. cathode) enhanced the rate of H_2 generation drastically. Fig. 4 plot (a) indicates the relationship between H_2 generation rates and applied voltages. The rates of H_2 generation at 0.2 and 0.3 V were ca. 18 times and 54 times higher than that under open circuit conditions, respectively. Above 0.3 V, the ratio exceeds 50, indicating that H_2 generation was almost completely ascribed to the electrochemical reaction (Eqs. (1) and (2)). This ratio indicates that the electrochem-

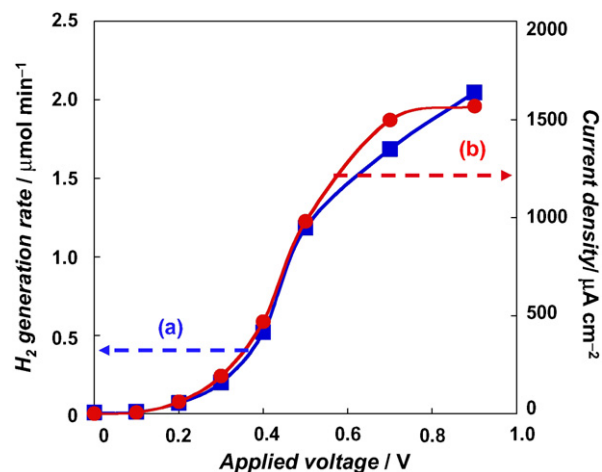


Fig. 4. H_2 generation rates from the one-compartment H_2 generating cell and the current density of the cell. An applied voltage is defined as the potential of anode vs. cathode. A solution of NaOH (0.1 M) containing BH_4^- (10 mM) was used as an electrolyte solution. The electrochemical H_2 generator was operated at 25°C .

ical regulation of H_2 generation was successfully achieved in the low potential regions.

The total amount of H_2 generated (11.9 μmol) did not reach half as high as the amount of electrons transferred (31.6 μmol , 3.05 C) at 0.3 V. The residue should be attributed to the charge storage at electrolyte/ RuO_2 interface and the redox reaction of Ru in RuO_2 . H_2 leakage from the cell might be partly responsible for the residue.

Steady-state current densities were measured and also shown in Fig. 4 (plot b). The magnitude of current increased with the increase in potential. The trend coincides with that of H_2 generation rates. The coincidence also indicates that almost all the H_2 generation was caused by the electrochemical reaction. A cyclic voltammogram of this electrochemical cell was also measured. The result (Fig. 5) was similar to that of the plot (b) in Fig. 4.

This H_2 generator has a drawback in that it requires potential application from an external power supply. This might not only complicate H_2 generation systems but also cause a loss of energy. However, the onset potential of the cyclic voltammograms of Fig. 5 was as low as 0.15 V, and significant H_2 generation started to occur

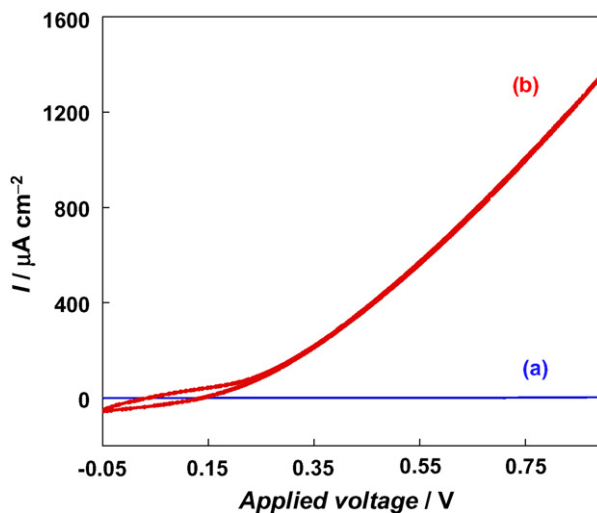


Fig. 5. A cyclic voltammogram of the electrochemical H_2 generator (a) in the absence of BH_4^- and (b) in the presence of 10 mM BH_4^- . The Rh(OEP)/C-modified electrode was used as a working electrode, and the RuO_2 -modified electrode was used as a reference (counter) electrode. A solution of NaOH (0.1 M) was used as an electrolyte solution. The voltammogram was recorded at a scan rate of 10 mV s^{-1} at 25°C .

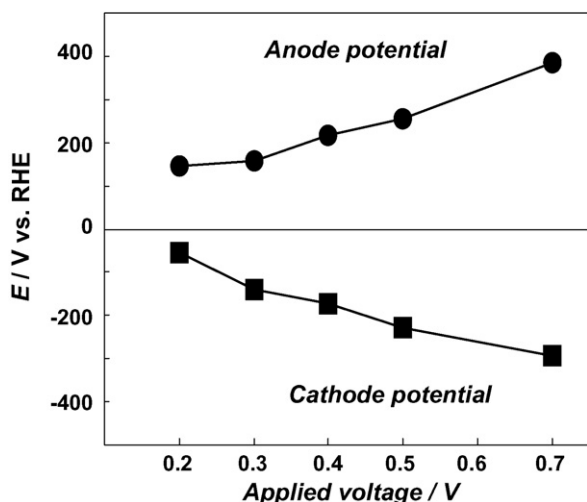


Fig. 6. Anode and cathode potentials of the electrochemical H_2 generator at several applied voltages. An applied voltage is defined as the potential of anode vs. cathode. The anode and cathode potentials were measured using $Ag|AgCl|KCl(\text{sat.})$ electrodes, and referred to RHE. A solution of $NaOH$ (0.1 M) containing BH_4^- (10 mM) was used as an electrolyte solution. The experiments were performed at 25 °C.

at 0.2 V; such potential regions are comparable to the anode potential in direct methanol fuel cells, and are much lower than the cathode (O_2 reduction) potential in fuel cells. Therefore, the potential loss might be acceptable.

3.6. Anode and cathode potentials of the electrochemical H_2 generator

To analyze the property of the electrochemical cell in detail, the potentials of anode ($Rh(OEP)/C$) and cathode (RuO_2) were measured at several applied voltages in which significant amount of H_2 was generated. The results were shown in Fig. 6.

Anode and cathode potentials were determined to be ca. 0.15–0.4 V and ca. –0.05 to –0.3 V, respectively as shown in Fig. 6. The redox potentials of anode (Eq. (1)) and cathode (Eq. (2)) reactions are –0.4 and 0 V, respectively. Hence, the overpotential (measured potential – redox potential) of anode was as high as ca. 0.55 V, while that of cathode remained as low as 0.05 V at an applied voltage of 0.2 V. The overpotential of anode was higher than that of cathode in the potential regions; the anode catalysts should be mainly improved to decrease the applied voltage.

3.7. The interpretation of anode and cathode potentials in terms of behaviours of the electrocatalysts

The potentials of anode and cathode were discussed in terms of the electrochemical behaviours of anode and cathode catalysts. Fig. 3 shows that the oxidation current of $Rh(OEP)/C$ remains virtually zero below 0.15 V, and drastically increased above 0.15 V. This behaviour coincides with the behaviour of anode potential. This overpotential up to 0.15 V would be attributed to the intrinsic activity of $Rh(OEP)$. Fig. 3 also indicates that mass transfer of BH_4^- affects

the current significantly at higher potentials. The slightly steep increase in anode potential from 0.5 to 0.7 V might be attributed to the limitation of diffusion.

Fig. 1 shows that RuO_2 gave monotoneous increase of the H_2O reduction current below 0 V. The onset potential almost reaches the redox potential (0 V) of the cathode reaction, while that of $Rh(OEP)/C$ is much higher than the redox potential (–0.4 V) of anode reaction. RuO_2 is an efficient catalyst for H_2O reduction, and high catalytic activity is responsible for the relatively small cathode overpotential in Fig. 6. However, the current density (Fig. 1) is much lower than that of $Rh(OEP)/C$ (Fig. 3). This would be attributed to the low surface area of RuO_2 . Since the amorphous structure decreases selectivity toward H_2O reduction (Fig. 2), the increase of surface area without destroying crystalline structure would be important to enhance the performance of the cell. Thus, the analysis revealed three points to be improved (i) the intrinsic activity of $Rh(OEP)$, (ii) the surface area of RuO_2 , and (iii) the mass transfer of BH_4^- .

4. Conclusions

We found that RuO_2 has strong H_2O -reducing activity without electro-oxidation or chemical decomposition of BH_4^- , in contrast to Pt catalysts. With this cathode catalyst and a Rh porphyrin anode catalyst, we developed a one-compartment electrochemical H_2 generator. H_2 generation from the cell could be successfully controlled by varying the electrode potential based on the selectivity of both the anode and cathode. The current density of the H_2 generator increased concomitant with the increase in the amount of H_2 generated. Anode and cathode potentials of the cell were also measured. The polarizations of both electrodes were explained by the catalytic properties of RuO_2 and a Rh porphyrin.

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