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Metallocomplex-based borohydride electro-oxidation catalysts

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ABSTRACT

We have found that certain kind of complexes on carbon black catalyze borohydride electro-oxidation. All of the Rh porphyrins tested in this study exhibited high activity regardless of the structure of the porphyrin ligands. While other metalloporphyrins also catalyzed borohydride electro-oxidation, the activities were much lower than those of Rh porphyrins. Even Rh tetrakis(4-methylphenyl)porphyrin, which exhibited the highest activity, scarcely catalyzed the chemical decomposition of borohydride under open-circuit conditions. These metalloporphyrin-based catalysts tested do not promote H_2 electro-oxidation. Other Rh complexes ($Rh_2Cl_2(CO)_4$ and Rh phthalocyanin) also catalyze borohydride electro-oxidation. $Rh_2Cl_2(CO)_4$ oxidizes borohydride at lower potentials than Rh porphyrins; it can catalyze borohydride even below 0 V vs. RHE. A one-compartment H_2-generator that also generates electric power was constructed using $Rh_2Cl_2(CO)_4$ as an anode catalyst.

1. Introduction

In the development of a proton exchange membrane fuel cell (PEMFC), H_2 storage is one of the main obstacles. Even though various materials and technologies for H_2 storage have been investigated, this still remains a difficult problem to be overcome. This problem is derived from the fact that H_2 is a gas, and hence direct liquid-fed fuel cells (DLFCs), in which a liquid fuel is used in place of H_2, have also been developed.

Direct methanol fuel cells (DMFCs) have attracted considerable attention for several decades as the most promising candidate of DLFCs. Methanol undergoes 6-electron oxidation; almost all of the methanol is converted to CO_2. Methanol has properties that are favorable for its use as a fuel in DLFCs. However, adsorbed CO, which is generated and accumulated during methanol electro-oxidation, decreases the activity of Pt catalysts. This problem of CO poisoning increases anode overpotential of DMFC. Due to the lower activity of Pt-based anode catalysts toward methanol oxidation, significant amounts of noble metals are needed in an anode catalyst. Furthermore, due to methanol crossover, the performance of the cathode catalyst is significantly decreased [1].

These problems of DMFC have prompted the development of DLFCs that use fuels other than methanol. A borohydride (BH_4^-) solution has been considered to be a promising fuel for use in DLFCs. The redox potential of BH_4^- is ca. −1.24 V (vs. a standard hydrogen electrode). The potential corresponds to ca. −0.4 V vs. a reversible hydrogen electrode (RHE). BH_4^- ideally undergoes 8-electron oxidation as shown in Eq. (1).

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (1)$$

Although the high energy density and relatively high safety of BH_4^- are attractive, direct borohydride fuel cells (DBFCs) have several problems. The product BO_2^- accumulates and the waste must be collected. The regeneration of BH_4^- from BO_2^- requires a lot of energy. In addition, there is a significant problem with anode catalysts [2–5].

So far, various electrode materials have been tested for use as the anode catalyst in DBFCs. Pt functions as an anode catalyst in DBFCs. It catalyzes BH_4^- electro-oxidation at low overpotentials and gives high oxidation current. It is also highly stable toward corrosion. However, Pt catalysts stimulate chemical decomposition of BH_4^-.

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \quad (2)$$

This reaction leads to the uncontrollable generation of H_2, and diminishes the number of electrons (n) in the electro-oxidation of BH_4^- [2–5]. Gyenge demonstrated the existence of a reaction pathway in which Pt catalyzes hydrolysis of BH_4^- and the generated hydrogen undergoes electro-oxidation by Pt [6].

On the other hand, Au catalysts for the electro-oxidation of BH_4^- have also been studied [2–9]. In contrast to Pt catalysts, Au hardly catalyzes the chemical decomposition of BH_4^-, and hence higher n values can be obtained [2–4,7–9]. However, the overpotentials for BH_4^- electro-oxidation with a Au catalyst are

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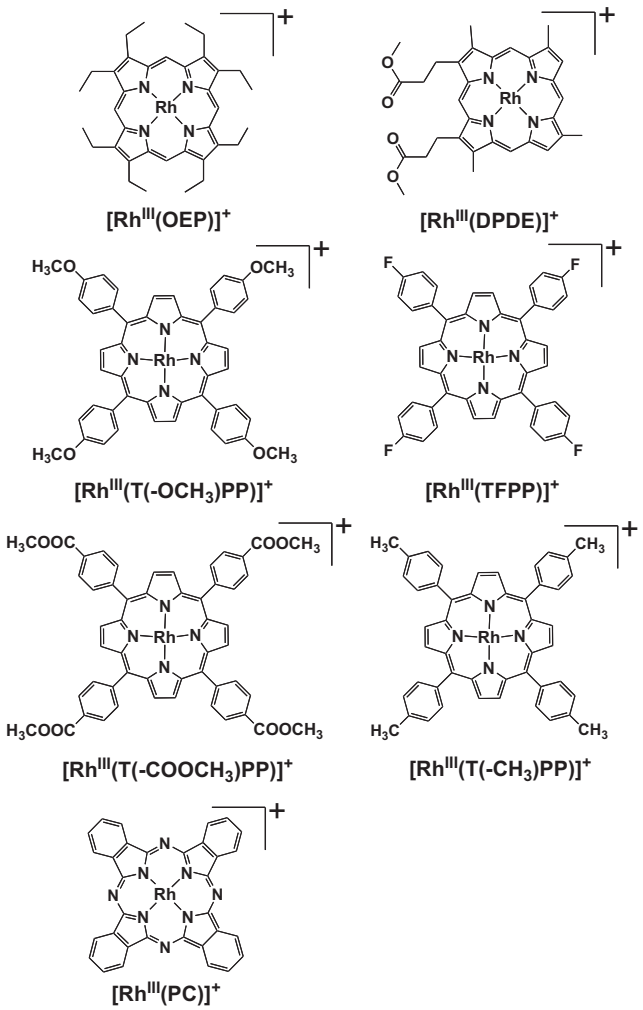
higher than those with a Pt catalyst. To decrease overpotential with the higher coulombic efficiency, Pt–Au alloys have been intensively studied [10–12]. Especially, a Pt–Au alloy prepared by galvanostatic replacement of Ni exhibited better coulombic efficiency with low overpotential [7]. Other Pt alloys [3,12] and hydrogen storage alloys [2,3,13,14] were also studied for this purpose.

These circumstances led us to study a new catalyst that catalyzes the electro-oxidation of BH_4^- without the chemical decomposition of BH_4^-. We paid special attention to complex-based electrocatalysts. It is well known that hydrogen atom coordinates on certain kinds of complexes of Rh or other noble metals [15–17]. Some of these complexes have a catalytic activity. On the other hand, we have found that Rh porphyrin acts as an efficient electrocatalyst for the electro-oxidation of some low-molecular-weight compounds such as CO [18–21], oxalic acid [22,23], and glucose [24]. Thus, we were encouraged to examine the activities of Rh porphyrin catalysts toward BH_4^- electro-oxidation.

In our previous paper [25], we found that several carbon-supported Rh octaethylporphyrin and Rh tetrakis(4-carboxyphenyl)porphyrin catalyzed the electro-oxidation of BH_4^- at low overpotentials. These catalysts scarcely bring about the chemical decomposition of BH_4^-. The n value exceeds 7 due to low hydrolysis activity and the loading of Rh is below 1%. Since the active sites in this catalyst are single molecules, the metal loading could be significantly lower than that with conventional catalysts.

The activity of a complex-based catalyst is expected to depend on the ligand structure and central metal. The catalytic activity might be enhanced by varying the ligands and metal, and thus it may be possible to reduce the cost by the use of less-expensive central metal. Hence, complex-based catalysts other than the previous two catalysts [25] should be examined with regard to their BH_4^- electro-oxidation activity. The investigation of other complex-based catalysts is also important for us to elucidate the relationship between the activity and structure.

In this study, we examined the activities of various complex-based catalysts toward BH_4^- electro-oxidation. The roles of the central metals and ligand structures in the activity were examined. Many metalloporphyrins exhibited BH_4^- electro-oxidation activity; Rh porphyrin catalysts gave the best activity among the porphyrins tested. Typical porphyrin-based electrocatalysts did not exhibit H_2 oxidation activity or chemical decomposition activity under open-circuit conditions, in contrast to a Pt catalyst and Rh black. Rh complexes other than porphyrins were shown to have BH_4^- electro-oxidation activity. Especially, $Rh_2Cl_2(CO)_4$ oxidized BH_4^- at low overpotentials. Using this catalyst as anode, a one-compartment electrochemical H_2-generator that generated electric power was constructed.



Scheme 1. Chemical structures of Rh porphyrins used in this work.

2. Experimental

2.1. Chemicals

Rh porphyrins were synthesized by refluxing the corresponding porphyrin ligands and $Rh_2Cl_2(CO)_4$ as described in the literature [19]. The abbreviations for the complexes are as follows; [Rh^{III}(T(–CH$_3$)PP)]$^+$ (T(–CH$_3$)PP = 5,10,15,20-tetrakis(4-methylphenyl)porphinate), [Rh^{III}(T(–OCH$_3$)PP)]$^+$ (T(–OCH$_3$)PP = 5,10,15,20-tetrakis(4-methoxyphenyl)porphinate), [Rh^{III}(TFPP)]$^+$ (TFPP = 5,10,15,20-tetrakis(4-fluorophenyl)porphinate), [Rh^{III}(T(–COOCH$_3$)PP)]$^+$ (T(–COOCH$_3$)PP = 5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphinate), [Rh^{III}(DPDE)]$^+$ (DPDE = deuteroporphinate dimethyl ester), [Rh^{III}(OEP)]$^+$ (OEP = 2,3,7,8,12,13,17,18-octaethylporphinate). Rh phthalocyanin ([Rh^{III}(PC)(Cl)]) was synthesized as described in the literature [22]. The chemical structures are shown in Scheme 1. The product was confirmed by elemental analysis and ESI-MS analysis.

Octaethylporphyrins ([Cu^{II}(OEP)], [Fe^{III}(OEP)(Cl)], [Pd^{II}(OEP)], [Ru^{II}(OEP)(CO)], and [Co^{II}(OEP)]) were purchased from Aldrich, while [Pt^{II}(OEP)] was purchased from a Frontier Science, and used as received. Sodium borohydride ($NaBH_4$, Kishida) was used as the BH_4^- source. All other reagents were commercially available. Water was purified using PURELAB Ultra (ORGANO).

2.2. Catalysts

Complexes except for Rh(PC)/C were adsorbed on carbon black (Vulcan XC72R) by the *evaporation-to-dryness* method, and the resulting powders were used as catalysts. Briefly, in the *evaporation-to-dryness method*, carbon black was added to CH_2Cl_2 or ethanol containing a porphyrin. The solvent was removed with a rotary evaporator, and the resulting powder was collected. Due to its low solubility, Rh(PC)/C was prepared by mechanical mixing [Rh^{III}(PC)(Cl)] and carbon black with a mortar [22]. The amount of complexes was fixed at 30 μmol g_{carbon}^{-1}, which corresponds to 0.31% (w/w) Rh loading in Rh complex catalysts. The Pt/C and Rh black were purchased from Johnson–Matthey, and used as received.

2.3. Electrochemical measurements

To evaluate the catalytic activities of catalysts using a rotating disk electrode, the catalysts (0.02 mg) were immobilized on a rotating glassy carbon (GC) electrode (0.07065 cm^2) as described in the literature [25]. A Nafion thin film was used for the immobilization. Since Nafion is a cation-exchange membrane, it might impede the transfer of OH^-, which is needed for oxidation of BH_4^- to BO_2^-. To check this point, we compared the BH_4^- electro-oxidation activities of Au electrode with and without a Nafion film. The BH_4^- oxidation on Au electrode is not impeded by Nafion film (data not shown), indicating that the Nafion membrane is too thin to impede the diffusion of BH_4^- to the electrocatalyst.

A modified electrode was used as a working electrode. A Ag|AgCl|KCl (sat.) electrode and a Pt electrode were used as a reference and counter electrodes, respectively. All potentials of the results are vs. RHE. To discuss electrochemical H_2 generation, the potential scan was started from potentials significantly lower than 0 V. On the other hand, with regard to Rh black and $Rh_2Cl_2(CO)_4$/C that have strong H_2O reduction activity, the potential scan was also started above 0 V to minimize H_2 oxidation. The measurements were performed in 0.1 M NaOH (pH 13.0) at 25 °C. The electrode rotation rate was set at 3600 rpm. At lower electrode rotation rates, the limitation by mass transfer is serious. At higher electrode rotation rates, the catalyst powders come off by vigorous rotation. Then, we adopted 3600 rpm. For the measurements of BH_4^- electro-oxidation activity, the concentration of BH_4^- was fixed at 1 mM.

2.4. Determination of H_2 generated from BH_4^-

The generation of H_2 from BH_4^- was measured by gas chromatography. Catalysts (2 mg) were immobilized on both sides of a GC plate (1.5 cm × 1.5 cm). The plate was immersed in a vessel. $NaBH_4$ (10 mM) in 0.1 M NaOH was added in the vessel and the solution was purged with argon gas. The gas phase was analyzed by gas chromatography after the reaction.

2.5. Analysis of a one-compartment H_2-generator from BH_4^-

The performance of a one-compartment H_2-generator was measured using a two-electrode system. A GC electrode modified with $Rh_2Cl_2(CO)_4$/C was used as the anode, and a GC electrode modified with Pt/C (Johnson-Matthey, 40%) was used as the cathode (see Section 2.3). The potential was recorded under constant current conditions.

3. Results and discussion

3.1. Electro-oxidation of BH_4^- by Rh porphyrin catalysts

In our previous study [25], we demonstrated that Rh(OEP)/C and Rh(TCPP)/C prepared by the *equilibrium adsorption method* could catalyze the electrochemical oxidation of BH_4^-. In this study, we examined other various carbon-supported Rh porphyrins (Scheme 1) with regard to their BH_4^- electro-oxidation activity. The amount of Rh porphyrins adsorbed on carbon black was fixed at 30 μmol g_{carbon}^{-1} using the *evaporation-to-dryness method* to facilitate a quantitative comparison between Rh porphyrins.

Typical voltammograms of a Rh porphyrin catalyst (Rh(T(–CH_3)PP)/C) for BH_4^- electro-oxidation are shown in Fig. 1A. In the absence of BH_4^-, faradaic current was hardly observed (line a). On the addition of BH_4^- (1 mM), the oxidation current departs at ca. 0.15 V (line b). The current decreased above ca. 0.2 V due to the limitation of bulk diffusion. With electrode rotation (3600 rpm), a drastic increase in the current was observed (line c).

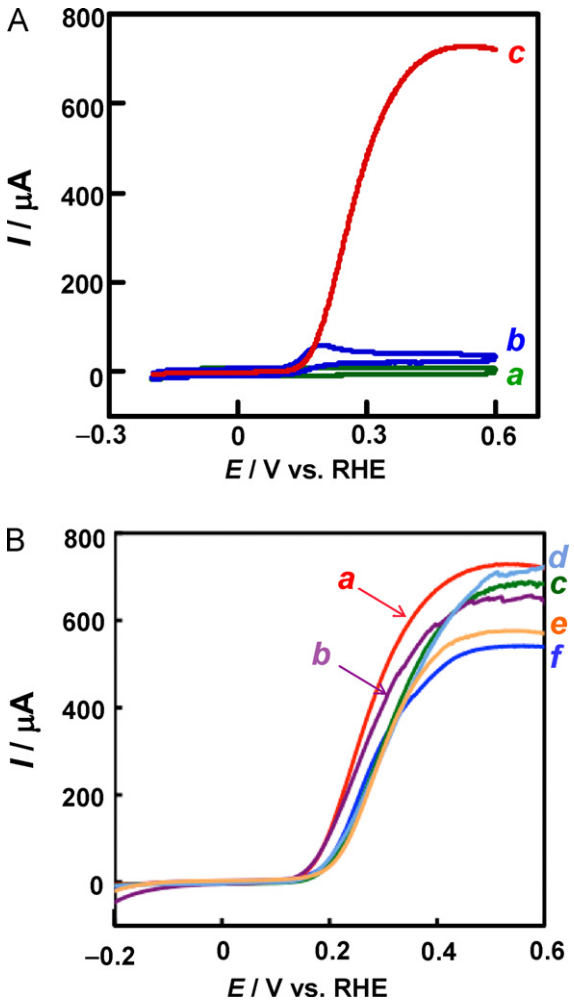


Fig. 1. BH_4^- electro-oxidation by Rh(porphyrin)/C. (A) Cyclic and linear sweep voltammograms of Rh(T(–CH_3)PP)/C (a) in the absence of $NaBH_4$, (b) in the presence of $NaBH_4$ (1 mM), and (c) in the presence of $NaBH_4$ (1 mM) with electrode rotation at 3600 rpm. (B) Linear sweep voltammograms of (a) Rh(T(–CH_3)PP)/C, (b) Rh(T(–OCH_3)PP)/C, (c) Rh(TFPP)/C, (d) Rh(T(–$COOCH_3$)PP)/C, (e) Rh(DPDE)/C, and (f) Rh(OEP)/C in the presence of $NaBH_4$ (1 mM) with electrode rotation at 3600 rpm. Measurements were performed in a 0.1 M NaOH solution at 25 °C (scan rate = 10 mV/s).

Fig. 1B shows a comparison of the activity of BH_4^- electro-oxidation by several carbon-supported Rh porphyrins. The voltammograms were recorded in the presence of 1 mM $NaBH_4$ under electrode rotation (3600 rpm). All carbon-supported Rh porphyrins that were tested in this study exhibited strong activity, as did the Rh(TCPP)/C and Rh(OEP)/C in our previous study [25]. The catalytic activities are higher than those of an Au electrode [25]. $E_{1/2}$ (the potential at which the current is half of the apparent limiting current) of Au electrode is ca. 0.49 V [25], which is much higher than that of Rh porphyrin-based catalysts (0.26–0.32 V).

It was reported that $[Rh^{III}(OEP)]Cl$ reacts with BH_4^- to generate $[Rh^{I}(OEP)]^-$ in alcoholic basic solution. The generated $[Rh^{I}(OEP)]^-$ was easily protonated with acid to form Rh(OEP)–H complex [26,27]. The conditions for the measurement of BH_4^- electro-oxidation in this work are similar to the condition in their works [26,27] (except for the content of methanol), hence, the Rh(porphyrin)–H (or its deprotonated form) would be generated during electro-oxidation of BH_4^-. Because this process is a two-electron reduction, BH_3OH^-, the product of two-electron oxidation of BH_4^-, would be generated. BH_3OH^- is thought to be oxidized at potentials more negative than BH_4^- [28], and hence BH_3OH^- would

undergo immediate two-electron oxidation by Rh(OEP). Thus, BH_4^- oxidation would proceed via successive two-electron oxidation.

The activity did not significantly depend on the structure of porphyrin ligand. In the oxidation of glucose, the presence of *meso*-phenyl groups substantially decreased the oxidation activity [24]. However, in the oxidation of BH_4^-, there is only a small difference in activity between Rh porphyrins with and without *meso*-phenyl groups. Thus, the bulkiness of *meso*-phenyl groups did not affect the BH_4^- electro-oxidation activity.

p-Substituted Rh tetraphenylporphyrins with electron-donating groups (–CH_3 (line a) and –OCH_3 (line b)) showed slightly higher activities than those with electron-withdrawing groups (–F (line c) and –$COOCH_3$ (line d)). This suggests that the electronic properties of the substituents might play a role in the catalytic activity. However, the difference in onset potentials was only ca. 20–30 mV.

To examine whether Rh porphyrin is reduced to Rh(0) particle under strong reducing conditions, XPS spectroscopy of Rh(T(–CH_3)PP)/C treated with $NaBH_4$ was measured. However, the amount of Rh porphyrins (30 μmol g^{-1}) was too low to be detected by XPS. To obtain the information on the state of Rh, the BH_4^- electro-oxidation activity of Rh black was evaluated for comparison. The results of the measurements with two potential ranges are shown in Fig. 2. Regardless of the presence of BH_4^-, cathodic current for H_2O reduction (H_2 generation) flowed below 0 V (Fig. 2A). The clear oxidation/reduction current, which would be caused by H adsorption/desorption on Rh black, was observed even without BH_4^-. BH_4^- electro-oxidation starts to flow at around 0 V (Fig. 2B). These behaviors are similar to those of Pt/C catalysts [25]. Rh black is a precious metal catalyst like Pt/C, and Rh(0) metal is responsible for the activity. The reactivity of Rh black is totally different from that of Rh porphyrin catalysts (Fig. 1A and B). Based on this comparison, in the catalysis with Rh porphyrins, the involvement of Rh(0) particles (possibly generated during the reaction) is negligible.

3.2. Electro-oxidation of BH_4^- by other metalloporphyrins

To examine the effect of the central metal, other octaethylporphyrins on carbon black were examined with regard to their BH_4^- electro-oxidation activity. The activity of carbon black alone was also examined. The results are shown in Fig. 3.

All of the porphyrins tested here had higher BH_4^- electro-oxidation activity than carbon black. Especially, Cu(OEP)/C (line a), Ru(OEP)/C (line b), Pd(OEP)/C (line c) and Co(OEP)/C (line d) exhibited significantly high activity.

Rh(OEP)/C exhibited much higher activity than other metalloporphyrins. Rh–H species, which have been reported in several other reactions, might be related to this high activity, as mentioned above. Although the activity is still low, the potent BH_4^- electro-oxidation activity of Cu(OEP)/C (line a) and Co(OEP)/C (line c) should be emphasized. Catalysts that use less-expensive metals for BH_4^- electro-oxidation were identified. These catalysts may be useful for reducing the cost of anode catalysts.

3.3. Electro-oxidation of BH_4^- by other Rh complexes

We examined the catalytic activities of Rh complexes other than porphyrin complexes. $Rh_2Cl_2(CO)_4$/C and Rh(PC)/C were examined with regard to their activities toward the BH_4^- electro-oxidation.

Voltammograms of $Rh_2Cl_2(CO)_4$/C for BH_4^- electro-oxidation with two potential ranges are shown in Fig. 4A and B. This complex-derived catalyst exhibited high activity toward BH_4^- electro-oxidation (Fig. 4A, line c). The behavior of this catalyst somewhat resembles those of Pt/C [25] and Rh black (Fig. 2, line c) in that the H_2O reduction current below 0 V and BH_4^- electro-oxidation at around 0 V were observed (the behaviors at higher

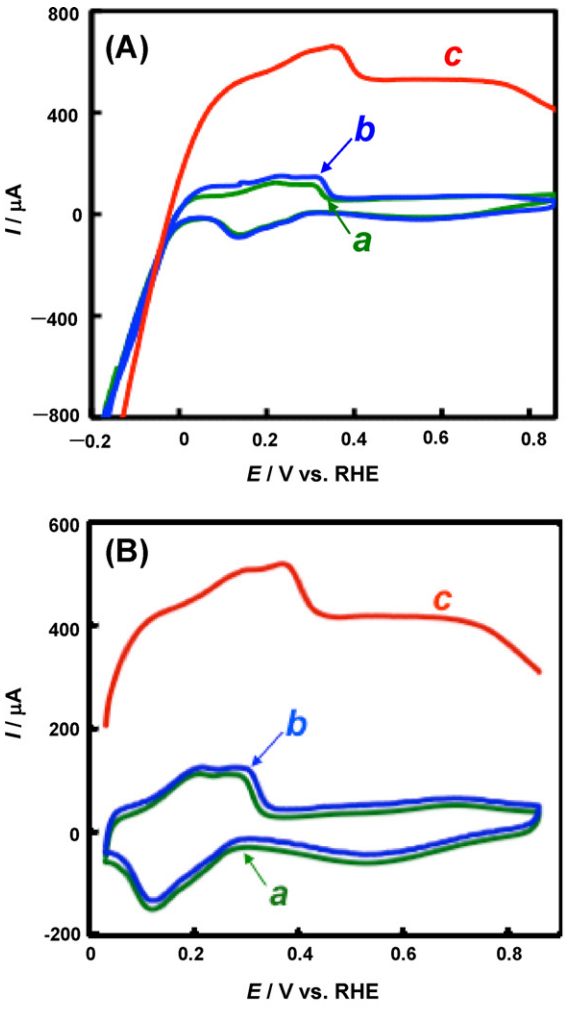


Fig. 2. BH_4^- electro-oxidation by Rh black. Cyclic and linear sweep voltammograms of Rh black (a) in the absence of $NaBH_4$, (b) in the presence of $NaBH_4$ (1 mM), and (c) in the presence of $NaBH_4$ (1 mM) with electrode rotation at 3600 rpm. Measurements were performed in a 0.1 M NaOH solution at 25 °C (scan rate = 10 mV/s). Potential ranges are (A) −0.24 V to 0.86 V and (B) 0.03–0.86 V.

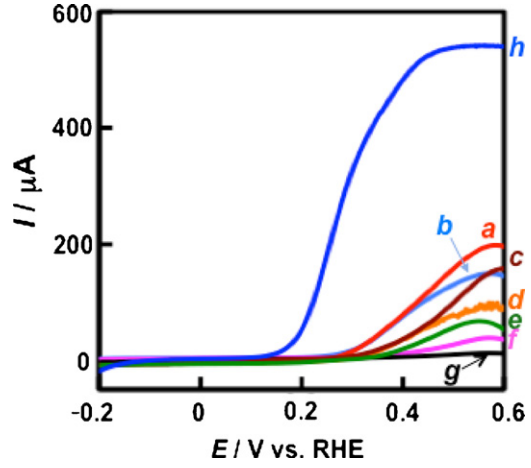


Fig. 3. BH_4^- electro-oxidation by other carbon-supported metalloporphyrins. Linear sweep voltammograms of (a) Cu(OEP)/C, (b) Ru(OEP)/C, (c) Pd(OEP)/C, (d) Co(OEP)/C, (e) Fe(OEP)/C, (f) Pt(OEP)/C, (g) carbon black, and (h) Rh(OEP)/C in the presence of $NaBH_4$ (1 mM) with electrode rotation at 3600 rpm. Measurements were performed in a 0.1 M NaOH solution at 25 °C (scan rate = 10 mV/s).

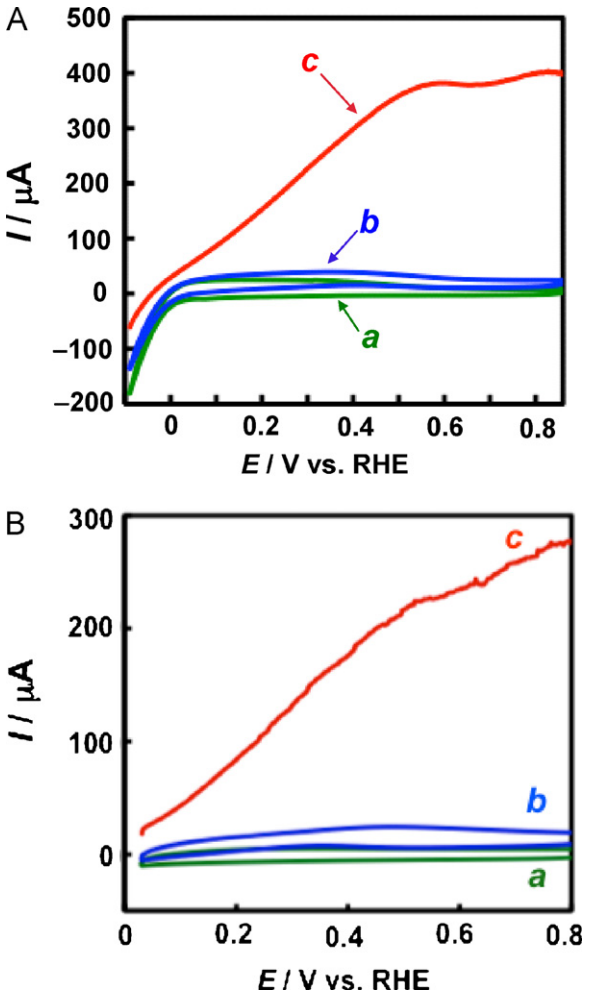


Fig. 4. BH_4^- electro-oxidation by $Rh_2Cl_2(CO)_4$. Cyclic and linear sweep voltammograms of carbon-supported Rh complexes (a) in the absence of $NaBH_4$, (b) in the presence of $NaBH_4$ (1 mM), and (c) in the presence of $NaBH_4$ (1 mM) with electrode rotation at 3600 rpm. Measurements were performed in a 0.1 M NaOH solution at 25 °C (scan rate = 10 mV/s). Potential ranges are (A) −0.09 V to 0.86 V and (B) 0.03–0.86 V.

potential regions are totally different) (Fig. 4B). The participation of Rh(0) particles generated by BH_4^- cannot be completely excluded.

We also examined the activity of Rh(PC)/C toward BH_4^- electro-oxidation. The results are shown in Fig. 5. The electrochemical behavior closely resembles that of Rh porphyrins. Rh(PC)/C also exhibited high activity. However, the overpotential for BH_4^- electro-oxidation was significantly higher than that of Rh porphyrins. Similar but different electronic structures would be responsible for the difference in the activity between Rh(PC)/C and Rh(porphyrin)/C.

3.4. H_2-generation from BH_4^- with catalysts under open-circuit conditions

While Pt/C exhibits high BH_4^- electro-oxidation activity, it stimulates uncontrollable H_2-generation under open-circuit conditions [25]. To discuss such chemical decomposition, H_2-generation from BH_4^- under open-circuit conditions has to be analyzed.

Table 1 shows H_2-generation from BH_4^- with the catalysts under open-circuit conditions. H_2-generation (chemical decomposition of BH_4^-) on Rh(T(−CH_3)PP)/C was successfully suppressed, even though high BH_4^- electro-oxidation activity was observed. In contrast, Rh black gave a significantly high H_2 generation rate that is

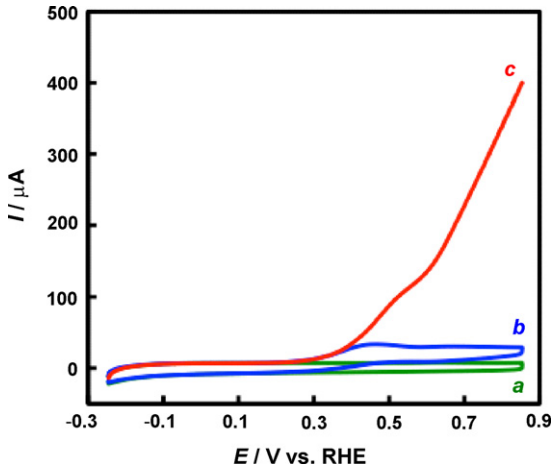


Fig. 5. BH_4^- electro-oxidation by Rh(PC)/C. Cyclic and linear sweep voltammograms of carbon-supported Rh complexes (a) in the absence of $NaBH_4$, (b) in the presence of $NaBH_4$ (1 mM), and (c) in the presence of $NaBH_4$ (1 mM) with electrode rotation at 3600 rpm. Measurements were performed in a 0.1 M NaOH solution at 25 °C (scan rate = 10 mV/s).

comparable to that of Pt/C [25]. The difference in the H_2-generation rate also supports the notion that Rh(T(−CH_3)PP) complex is not reduced to Rh(0) particles. The H_2-generation rate of $Rh_2Cl_2(CO)_4$/C is higher than that of Rh(T(−CH_3)PP)/C, but much lower than that of Rh black.

The H_2 generation rate seems to be related to the H_2O reduction activity. Table 1 also shows the currents at −0.05 V. Rh(T(−CH_3)PP)/C and Cu(OEP)/C hardly catalyzed H_2O electro-reduction up to −0.2 V (Figs. 1 and 3). In contrast, Rh black and Pt/C exhibited strong H_2O reduction activity below 0 V. This implies that BH_4^- decomposition proceeds via an electrochemical pathway, in which BH_4^- undergoes electro-oxidation and H_2O electro-reduction occurs simultaneously.

3.5. Electro-oxidation of H_2

To obtain further insight into the mechanism of BH_4^- electro-oxidation on complex-based catalysts, the activities of the complexes toward H_2 electro-oxidation were examined. The results are shown in Fig. 6.

Rh(T(−CH_3)PP)/C scarcely exhibited H_2 oxidation activity in an alkaline solution (Fig. 6, line a). In our previous paper [25], we demonstrated that Rh(OEP)/C and Rh(TCPP)/C scarcely exhibit H_2 oxidation activity, but have strong BH_4^- electro-oxidation activity. The present results suggest that this phenomenon is common among Rh porphyrins. Cu(OEP)/C, which exhibits strong BH_4^- electro-oxidation activity, also hardly catalyzed H_2 electro-oxidation (Fig. 6, line b).

Table 1
H_2 generation rate from BH_4^- on the catalysts under open circuit conditions.

Catalysts	H_2 generation rate[a] (nmol min^{-1})	Reduction current at −0.05 V[b] (μA)
Rh(T(−CH_3)PP)/C	1.4	10
Cu(OEP)/C	3.0	5.6
$Rh_2Cl_2(CO)_4$/C	380	88
Rh black	3481	205
Pt/C[c]	5525	184

[a] The H_2 generation was performed under open-circuit conditions. The detailed conditions are described in Section 2.
[b] The results were taken from the voltammograms without BH_4^-.
[c] The data for Pt/C were taken from Ref. [25].

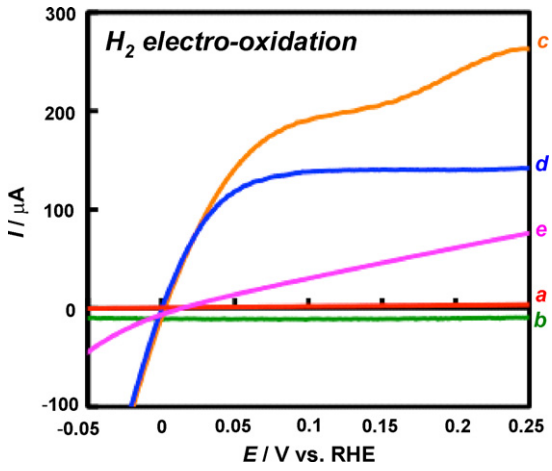


Fig. 6. H_2 electro-oxidation by catalysts. Linear sweep voltammograms of (a) Rh(T(–CH_3)PP)/C, (b) Cu(OEP)/C, (c) Rh black, (d) Pt/C, and (e) $Rh_2Cl_2(CO)_4$/C under a H_2 atmosphere with electrode rotation at 3600 rpm. Measurements were performed in a 0.1 M NaOH solution at 25 °C (scan rate = 10 mV/s).

In contrast to these porphyrin-based catalysts, Rh black (line c) and Pt/C (line d) gave high H_2 oxidation current. $Rh_2Cl_2(CO)_4$/C (line e) also exhibited some H_2 oxidation activity, albeit this was lower than those of Pt/C and Rh black. It is unclear whether the $Rh_2Cl_2(CO)_4$ complex or possible Rh(0) particles catalyze H_2 oxidation.

For the electro-oxidation of BH_4^- on Pt catalysts, the reaction pathway is under discussion. Two pathways are possible: a direct pathway and an indirect pathway [5,6]. In the former pathway, BH_4^- is oxidized on Pt directly to BO_2^-. In the latter pathway, BH_4^- undergoes hydrolysis to generate H_2, and H_2 is oxidized electrochemically on the Pt catalysts. Indirect pathway does not occur below 0 V since H_2 electro-oxidation only starts above 0 V.

Lack or weakness of H_2 oxidation activity suggests that an indirect pathway can be neglected or less significant with BH_4^- electro-oxidation by complex-based catalysts. It follows that BH_4^- electro-oxidation on complex-based catalysts is not limited by the H_2 oxidation potential (0 V); the oxidation below 0 V might occur. In fact, oxidation current below 0 V was clearly observed in the voltammograms of $Rh_2Cl_2(CO)_4$/C.

3.6. Electrochemical one-compartment H_2-generator of BH_4^-

Electrocatalysts for BH_4^- oxidation were used as anodes not only in DBFCs but also in electrochemical H_2-generator. In the H_2 generator, BH_4^- is oxidized at the anode, and H_2O is reduced at the cathode. The interesting properties of complex-based catalysts for BH_4^- electro-oxidation lead to a one-compartment electrochemical H_2 generator. A one-compartment DBFC was already realized [29,30].

Some catalysts exhibit high BH_4^- electro-oxidation without BH_4^- hydrolysis. This characteristic can be applied to a *controllable* one-compartment electrochemical H_2-generator. We demonstrated a one-compartment electrochemical H_2-generator using a selective BH_4^- electro-oxidation catalyst (Rh(OEP)/C) and H_2O reduction catalyst (RuO_2) [31]. The porphyrin-based catalysts that are found in this study, for example Rh(T(–CH_3)PP)/C, can be used as an anode for this electrochemical cell.

On the other hand, $Rh_2Cl_2(CO)_4$/C gave a clear oxidation current at around 0 V vs. RHE. H_2O is reduced by a Pt catalyst with almost zero overpotentials. Hence, electric power might be generated from the combination of BH_4^- electro-oxidation and H_2O electro-reduction with $Rh_2Cl_2(CO)_4$/C and Pt/C as an anode and cathode, respectively. Two-compartment H_2 generators with the generation of electric power were already realized [26,32]. However, the existence of membrane complicates the structure of the H_2 generator. Then, we tried to make a one-compartment H_2 generator with power generation using these catalysts. The H_2-generator is outlined in Fig. 7.

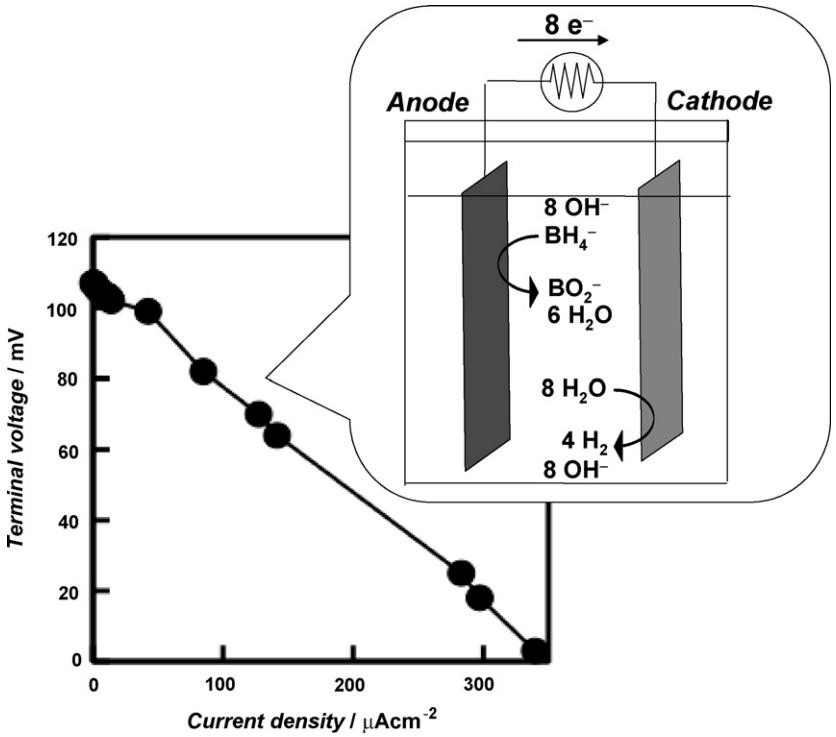


Fig. 7. Schematic representation of a one-compartment electrochemical H_2-generator that also generates electric power and performance of the cell with a $Rh_2Cl_2(CO)_4$/C anode and Pt/C cathode. The concentration of BH_4^- was fixed at 10 mM.

Because this cell has no membrane, BH_4^- reacts not only with the Rh-complex catalyst (anode) but also with the Pt catalyst (cathode). On the addition of BH_4^- to the cell, H_2 was dramatically generated on Pt catalysts, since Pt/C catalysts are very active toward BH_4^- hydrolysis as described above. This phenomenon is observed in a H_2 generation vessel containing Pt catalysts.

After the anode and cathode were connected, electric power was generated during H_2 generation, as shown in Fig. 7. Without BH_4^-, no electric power was generated. The onset potential for BH_4^- electro-oxidation on $Rh_2Cl_2(CO)_4$/C is a little lower than that on Pt/C catalysts. Hence, the current flowed from $Rh_2Cl_2(CO)_4$/C to Pt/C with the generation of electric power: $Rh_2Cl_2(CO)_4$/C oxidizes BH_4^- and Pt/C reduces H_2O spontaneously, as shown in Fig. 7.

The amount of BH_4^- consumed for power generation should be very low compared to that consumed for hydrolysis; most of H_2 generated should be attributed to chemical hydrolysis of BH_4^- on Pt catalysts. However, this result is interesting in that H_2-generation from BH_4^- in a one-compartment cell can produce slight electric power. This cell can collect slight power from H_2-generation on catalysts.

4. Conclusions

We have demonstrated that some complexes on a carbon support can catalyze the electro-oxidation of BH_4^-. Especially, Rh complexes showed high activity. A typical Rh porphyrin exhibited BH_4^- oxidation current without chemical decomposition. The activity of Rh porphyrins on a carbon support did not significantly vary with the porphyrin structure. $Rh_2Cl_2(CO)_4$/C gave BH_4^- electro-oxidation activity below 0 V. With the use of this catalyst, we have developed a one-compartment H_2-generator that also generates electric power.

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