Short communication

Electrochemical oxidation of hydrazine derivatives by carbon-supported metalloporphyrins

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ABSTRACT

Hydrazine hydrate has been studied as a fuel for use in anion exchange membrane fuel cells. To overcome its toxicity, derivatives of hydrazine have also been studied as possible fuels. However, conventional electrocatalysts show only weak activity in the electro-oxidation of hydrazine derivatives. In this study, we report that carbon-supported cobalt porphyrin catalysts can catalyze the electro-oxidation of certain hydrazine derivatives as well as hydrazine. The dependence of this activity on the concentration suggests that the carbohydrazide strongly interacts with the Co porphyrin. High activity of a Co porphyrin in the oxidation of certain kinds of hydrazine derivatives opens a big possibility to application including a vehicle that safer hydrazine derivatives can also be oxidized in fuel cells.

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1. Introduction

Hydrazine hydrate is a strong reducing agent that has high energy density and high reactivity with appropriate catalysts. Direct hydrazine fuel cells have been studied as potential future polymer electrolyte fuel cells that may deliver high power density [1–6].

An anion exchange membrane (AEM) is generally used as an electrolyte for hydrazine fuel cells. In an AEM-FC, the environment is not acidic. Hence, the problem of corrosion is overcome, and base metals can act as electrocatalysts. Actually, hydrazine fuel cells that use an AEM and non-noble metal catalysts have recently been reported to have good performance [6]. To date, a wide variety of anode catalysts that use a base metal for the oxidation of hydrazine have been developed. Co, Ni and Co–Ni alloy have been studied as novel anode catalysts [6–9].

On the other hand, not only hydrazine hydrate but also hydrazine derivatives (Chart 1) such as carbohydrazide (carbodihydrazide or 1,3-diaminourea) and methyl carbazate have been studied as fuels to overcome the toxicity of hydrazine. Unfortunately, on metal catalysts, the rate of the oxidation of these

derivatives is much lower than that of hydrazine [9]. If we wish to use hydrazine derivatives as fuels, we must first develop a catalyst that can oxidize them at a high rate.

Against this background, we focused on metallomacrocycle complexes. We have already studied Rh porphyrins adsorbed on a carbon black as anode catalysts [10–19]. These electrocatalysts can oxidize CO [10–13,20], BH_4^- [14–16], oxalic acid [17,18], and glucose [19] at low overpotentials. A membrane electrode assembly (MEA) that contains Rh porphyrins generates electricity ($44\,mW\,cm^{-2}$) when CO is supplied to the anode [10]. This result indicates that porphyrins adsorbed on carbon deliver high power in polymer electrolyte fuel cells, and suggests that such metalloporphyrin-based electrocatalysts may work in an AEM-FC using hydrazine (and its derivatives).

To date, the electro-oxidation of hydrazine by Co macrocycles [21,22,24,26–30] and Fe-macrocycles [23,25] has been studied. This reaction was investigated in terms of its analytical application and mechanistic viewpoints. However, little is known about the application of this reaction for catalysts. Furthermore, the oxidation of hydrazine derivatives by metallocomplexes has not yet been examined. Since metallomacrocycles have electronic properties that are completely different than those of bulk metal catalysts, these catalysts may have activity in the oxidation of hydrazine derivatives, which can hardly be oxidized by bulk metal catalysts. We try to adsorb metallomacrocycles on a carbon black to
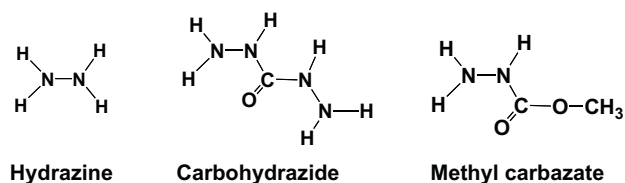
Chart 1. Structures of hydrazine derivatives.

use them as catalysts in fuel cells. Because fuel-cell applications require high current, metalloporphyrins should be adsorbed on a conductive support with a large surface area, such as a carbon black.

In this study, we report that Ru-, Rh-, Co-, and Fe-porphyrins adsorbed on carbon black acted as electrocatalysts that oxidize hydrazine and its derivatives. A Co-porphyrin catalyst gave a high current density for the electro-oxidation of carbohydrazide as well as hydrazine, in contrast to conventional electrocatalysts. The current per 1 g of metal is extremely high. The dependence of the activity on the ligand structure was examined. The current density of carbohydrazide oxidation with the best catalyst reached $40\,mA\,cm^{-2}$.

2. Experimental

2.1. Materials

Carbohydrazide and methyl carbazate were kindly donated by Otsuka Chemicals. [Co^{II}(OEP)] (OEP = 2,3,7,8,12,13,17,18-octaethylporphinate), [Fe^{III}(OEP)(Cl)], [Ru^{II}(OEP)(CO)], [Pd^{II}(OEP)], [Cu^{II}(OEP)], [Mn^{III}(OEP)(Cl)], [Pt^{II}(OEP)], [Co^{II}(TPP)] (TPP = 5, 10, 15, 20-tetraphenylporphinate), and [Co^{II}(T(—OCH_3)PP)] (T(—OCH_3)PP = 5, 10, 15, 20-tetrakis(4-methoxyphenyl)porphinate) were purchased from Aldrich. [Co^{III}(TPPS)(Cl)] (TPPS = 5, 10, 15, 20-tetrakis(4-sulfonatophenyl)porphinate) and [Co^{III}(TCPP)(Cl)] (TCPP = 5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphinate) were purchased from Frontier Scientific.

2.2. Synthesis

2,3,7,8,12,13,17,18-Octaethylporphyrinato rhodium (III) chloride ([Rh^{III}(OEP)(Cl)]) was synthesized as described in a literature [31] with modifications. $Rh_2Cl_2(CO)_4$ (82.2 mg) and 2,3,7,8,12,13,17,18-octaethylporphyine ($OEPH_2$) (206 mg) were dissolved in toluene (240 mL). The solution was refluxed for 15 h. After the reflux, the suspension was filtered, and the filtrate was collected. The solvent was removed under reduced pressure, and the residue was dissolved in ethanol. The suspension was filtered again. The product was crystallized in the ethanol solution (filtrate). Purple crystals were obtained. ESI-MS (in ethanol): m/z 635.4 ([Rh^{III}(OEP)]$^+$) Anal. Calcd for [Rh^{III}(OEP)(Cl)]·H_2O: C, 62.74; H, 6.73; N, 8.13. Found: C, 62.63; H, 6.66; N, 8.10. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.25 (s, 4H), 4.24–4.06 (m, 16H), 2.00 (t, 24H, $J = 8$ Hz). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 142.9, 140.5, 98.4, 20.1, 18.6.

2.3. The preparation of the catalysts

Carbon-supported metalloporphyrin was prepared by an evaporation-to-dryness (impregnation) method. Carbon black (Vulcan XC 72R) (30 mg) was added to 20 mL of appropriate solvent (see below) containing a porphyrin in a sample vial. The suspension was subjected to ultrasonication for a few minutes, and stirred for 30 min. The solvent was removed with a rotary evaporator and the resulting powder was collected. The amount of metalloporphyrins

deposited was fixed at $30\,\mu mol\,g_{carbon\,black}{}^{-1}$. The prepared catalysts were denoted as M-OEP/C such as Co-OEP/C and Fe-OEP/C. Since the oxidation number and small-molecule ligands (Cl and CO) of the central metal during the catalytic cycle are unclear, this information is not presented in the denotation of the catalysts. The solvents used in this preparation were ethanol for Rh-OEP/C, acetic acid for Co-TCPP, distilled water for Co-TPPS/C, and CH_2Cl_2 for the other catalysts.

2.4. Electrochemical measurements

A modified rotating disk glassy carbon electrode (electrode diameter = 3 mm, outer diameter = 6 mm) was used as a working electrode. A Ag|AgCl|KCl(sat.) was used as a reference electrode. All of the potentials in the results are vs. a reversible hydrogen electrode (RHE) at the temperature at which the measurements were performed. A platinum coil was used as a counter electrode. The measurement was performed in a 1 M NaOH solution. All voltammograms were measured at a scan rate of $10\,mV\,s^{-1}$.

2.5. Differences in potential between reference electrodes

The difference in potential between Ag|AgCl|KCl(sat.) and RHE was determined by the following experiment. Ag|AgCl|KCl(sat.) and platinum electrodes were immersed in 1 M NaOH. The solution was purged with hydrogen, and the difference in potential between a Ag|AgCl|KCl(sat.) electrode and a platinum electrode was measured using a potentiometer under a hydrogen atmosphere. Ag|AgCl|KCl(sat.) was shown to be 1006 mV more positive than RHE in 1 M NaOH.

2.6. Modification of a rotating disk electrode with carbon-supported metalloporphyrins

RDE was modified as follows. Five milligrams of the Vulcan XC 72R-supported metalloporphyrins were dispersed in 0.5 mL of a mixed solvent (water:ethanol = 1:1). A portion (2 μL) of this suspension was dropped onto a rotating glassy carbon (GC) disk electrode (BAS) and the solvent was allowed to evaporate at room temperature. The catalyst (0.02 mg) was then mounted on a glassy carbon working electrode (0.0707 cm^2). After the mount of the catalyst, a portion (2 μL) of diluted solution (1/180) of an ionomer solution (AS-4, 5 wt%, Tokuyama) was dropped on the electrode. The electrode was dried at room temperature.

3. Results and discussion

3.1. Electrocatalytic oxidation of hydrazine by metalloporphyrins on carbon black

Fig. 1 shows cyclic voltammograms of hydrazine (0.95 M) by several carbon-supported metalloporphyrins. Among the porphyrins tested, only Co-OEP/C, Fe-OEP/C, Rh-OEP/C, and Ru-OEP/C exhibited clear hydrazine-oxidation activity. Other carbon-supported porphyrins ([Pd^{II}(OEP)], [Cu^{II}(OEP)], [Mn^{III}(OEP)(Cl)], and [Pt^{II}(OEP)]) exhibited only slight activity (see the inset in Fig. 1). The activity was similar to that with a carbon black (Vulcan XC-72R) support (line i). Hence, these metalloporphyrins have virtually zero activity. Metalloporphyrins that have group 8 and 9 elements as a central metal showed high activity. So far, electro-oxidation by Co- and Fe-phthalocyanines and porphyrins has been reported [21–30]. These previous reports coincide with the present result with a carbon-supported metalloporphyrin catalytic system. While Rh-OEP/C exhibited the highest activity, Co-OEP/C and Fe-OEP/C are rather attractive for the development of low-cost anode catalysts.
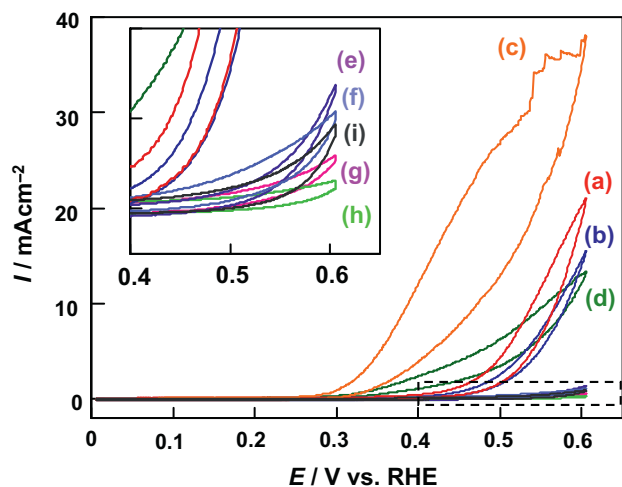
Fig. 1. Electro-oxidation of hydrazine by carbon-supported metalloporphyrins. Cyclic voltammograms of (a) Co-OEP/C, (b) Fe-OEP/C, (c) Rh-OEP/C, (d) Ru-OEP/C, (e) Pd-OEP/C, (f) Cu-OEP/C, (g) Mn-OEP/C, (h) Pt-OEP/C, and (i) carbon black (Vulcan XC 72R) in the presence of hydrazine (0.95 M). Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV s^{-1}) under an argon atmosphere. Inset: an expanded figure of the dotted square.

With Co-OEP/C, the current density reached 20.2 mA cm^{-2} at 0.6 V vs. RHE. Electrode rotation did not increase the oxidation current, indicating that the current is determined by a kinetic process of hydrazine electro-oxidation. Since a low amount of cobalt is used in metallocomplex-based electrocatalysts, the current per 1 g cobalt is high (4.0×10^4 A g$_{Co}^{-1}$ at 0.6 V). This high activity per unit metal is favorable in terms of cost and resources.
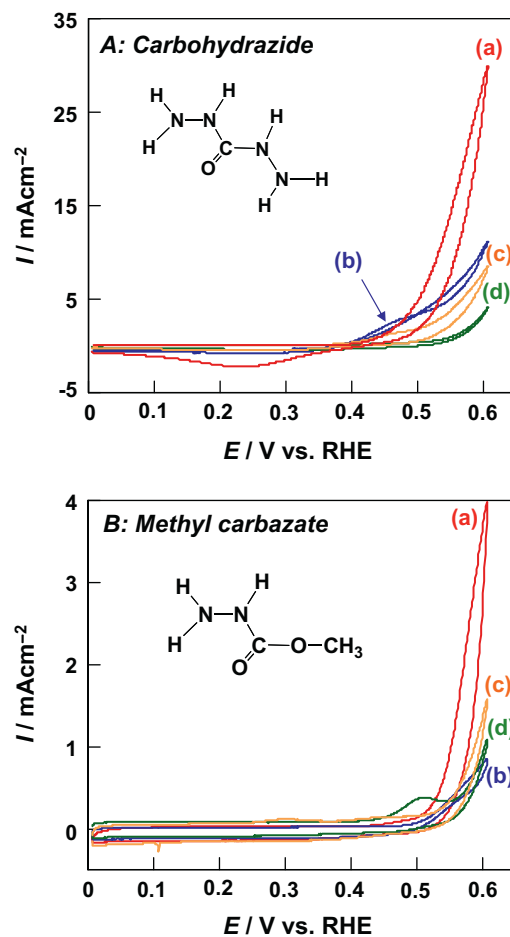
3.2. Electrocatalytic oxidation of hydrazine derivatives by metalloporphyrins on carbon black

We tested the activities of Co-OEP/C, Fe-OEP/C, Rh-OEP/C, and Ru-OEP/C in the electro-oxidation of hydrazine derivatives such as carbohydrazide and methyl carbazate. Fig. 2A shows the cyclic voltammograms of the catalysts mentioned above in the presence of carbohydrazide. All of the catalysts exhibited significant activity in the oxidation of carbohydrazide. However, the reactivity with carbohydrazide was totally different from that with hydrazine. While Co-OEP/C and Fe-OEP/C exhibit high activity in the oxidation of carbohydrazide, Rh-OEP/C and Ru-OEP/C exhibit much weaker activity with carbohydrazide than with hydrazine. The activity of Co-OEP/C was significantly greater than those of the other catalysts. We concentrated on Co-porphyrin catalysts for the electro-oxidation of carbohydrazide. Asazawa et al. reported that bulk metal catalysts have much lower activity with hydrazine derivatives than with hydrazine [9]. Interestingly, with Co-OEP/C, the oxidation current for carbohydrazide is comparable to (or higher than) that for hydrazine.

The cyclic voltammograms in Fig. 2B show the oxidation of methyl carbazate by the catalysts mentioned above. Although Co-OEP/C, Fe-OEP/C, Rh-OEP/C and Ru-OEP/C oxidized methyl carbazate, their activities were much lower than those toward carbohydrazide and hydrazine. In the oxidation of methylcarbazate, Co-OEP/C again exhibited the highest activity. Both of carbohydrazide and methyl carbazate are derivatives of carbazate (Chart 1): the former is an amide and the latter is an ester of carbazate. While the structures are similar, the reactivities of the two derivatives on M-OEP/C are surprisingly different.

3.3. The effect of porphyrin structure on the activities

In general, the electrocatalytic activities of metallocomplexes depend on the structure of ligand [21], and hence the activity in

Fig. 2. Electro-oxidation of hydrazine derivatives by carbon-supported metalloporphyrins. (A) Cyclic voltammograms of (a) Co-OEP/C, (b) Fe-OEP/C, (c) Rh-OEP/C, and (d) Ru-OEP/C in the presence of carbohydrazide (0.93 M). (B) Cyclic voltammograms of (a) Co-OEP/C, (b) Fe-OEP/C, (c) Rh-OEP/C, and (d) Ru-OEP/C in the presence of methyl carbazate (0.93 M). Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV s^{-1}) under an argon atmosphere.
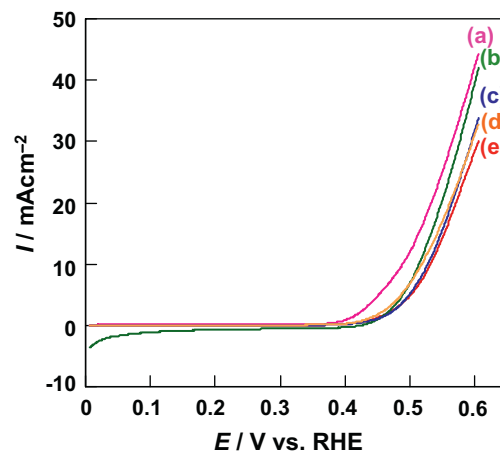
Fig. 3. The dependence of electro-oxidation activity on the ligand structure. Cyclic voltammograms of (a) Co-TCPP/C, (b) Co-TPPS/C, (c) Co-T($-$OCH$_3$)PP/C, (d) Co-TPP/C, and (e) Co-OEP/C in the presence of carbohydrazide (0.93 M). Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV s^{-1}) under an argon atmosphere.
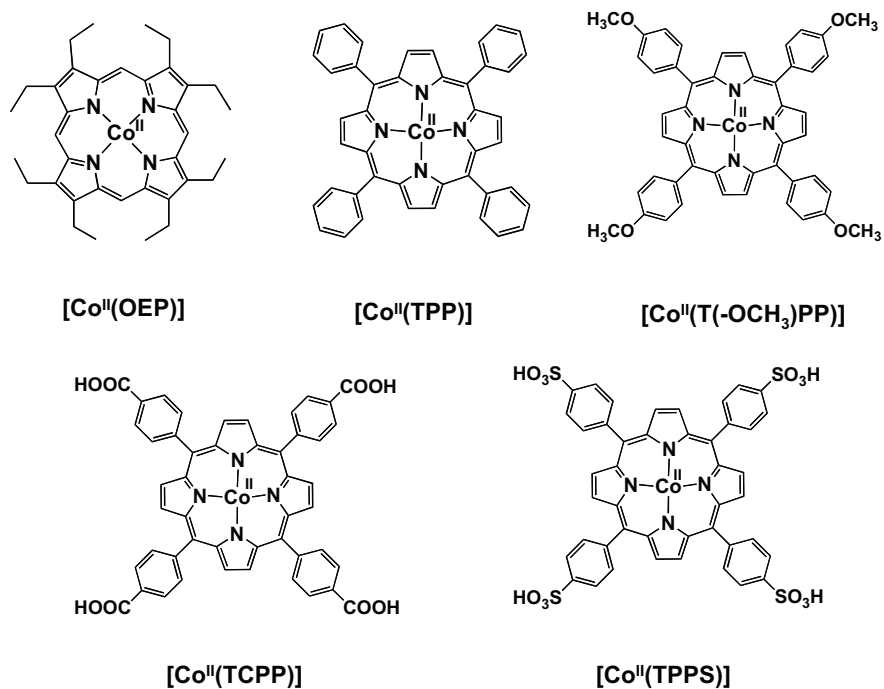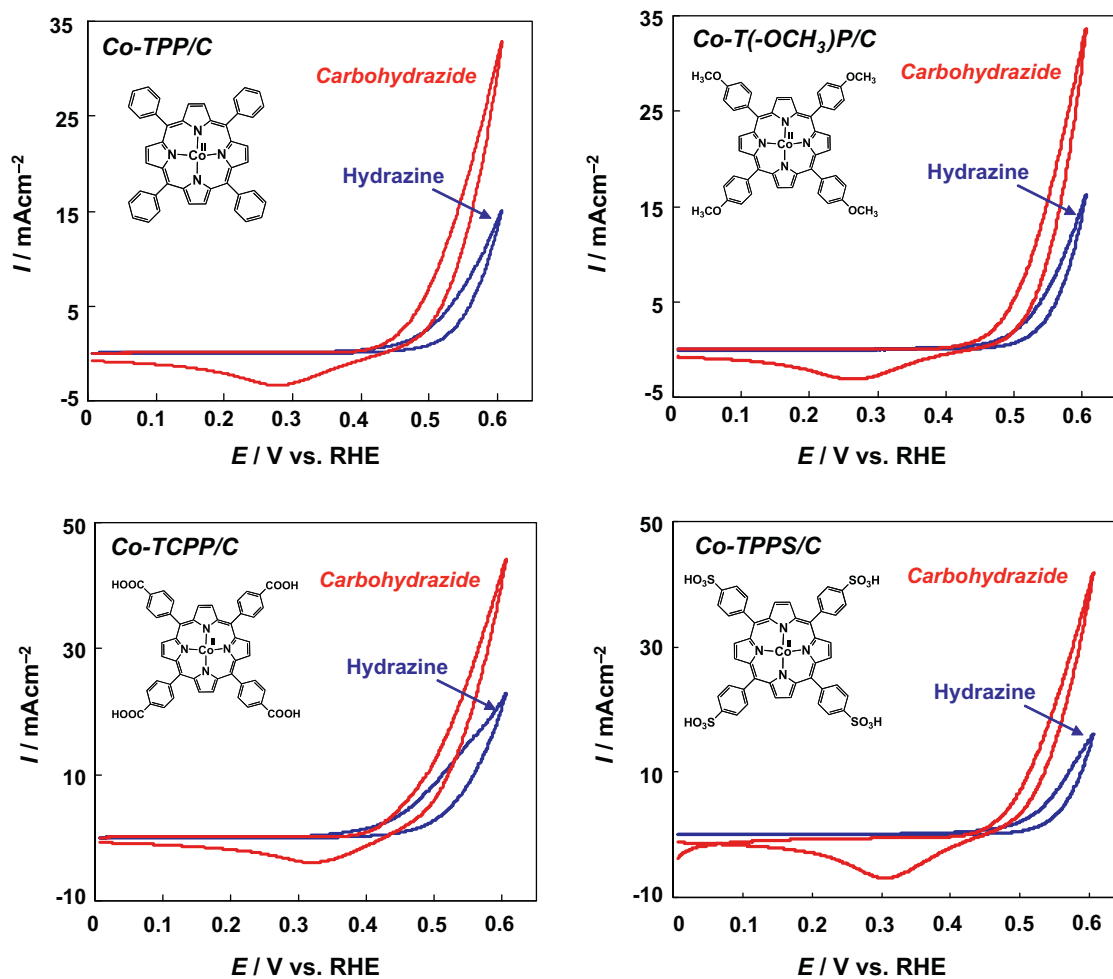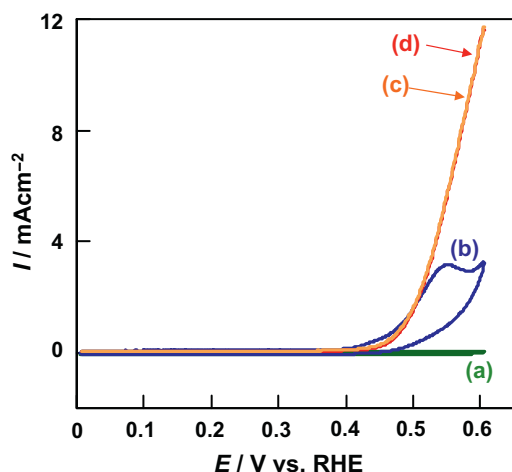
Chart 2. Structures of Co porphyrins.

Fig. 4. The activity of several carbon-supported Co porphyrins toward carbohydrazide and hydrazine. Cyclic voltammograms of several carbon-supported Co porphyrins in the presence of 0.93 M carbohydrazide or 0.95 M hydrazine. The measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV s^{-1}) under an argon atmosphere.

Fig. 5. Electro-oxidation of carbohydrazide (10 mM) by Co-OEP/C and carbon black. Cyclic and linear sweep voltammograms of Co-OEP/C (a) in the absence of carbohydrazide, (b) in the presence of carbohydrazide (10 mM), (c) in the presence of carbohydrazide (10 mM) with electrode rotation at 3600 rpm, and (d) in the presence of carbohydrazide (10 mM) with electrode rotation at 6400 rpm. Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV s^{-1}) under an argon atmosphere.

the oxidation of carbohydrazide might be enhanced by manipulation of the ligand. Therefore, we examined the activities of several carbon-supported Co porphyrins (Chart 2) in the oxidation of carbohydrazide. The linear sweep voltammograms in Fig. 3 show the electro-oxidation of carbohydrazide. Co-TPP/C, Co-T(−OCH$_3$)PP/C, Co-TCPP/C, and Co-TPPS/C exhibited higher activities than Co-OEP/C. The activity was successfully enhanced by ligand manipulation. Co tetraphenylporphyrin derivatives (Co-TPP/C, Co-T(−OCH$_3$)PP/C, Co-TCPP/C, and Co-TPPS/C) exhibited higher activity than Co-OEP/C. Especially, the Co tetraphenylporphyrin derivatives with carboxy groups and sulfo groups exhibited better activities. With both Co-TPPS/C and Co-TCPP/C, the current density at 0.6 V exceeds 40 mA cm^{-2}, which is significantly higher than the values with other bulk metal catalysts [9].

The activity of the catalysts toward hydrazine oxidation was also examined. The results are shown in Fig. 4. Co-TPP/C, Co-T(−OCH$_3$)PP/C, and Co-TPPS/C exhibited lower activity of hydrazine oxidation than Co-OEP/C. In the oxidation of hydrazine, the superiority of Co tetraphenylporphyrin derivatives was not observed. All of the catalysts oxidized carbohydrazide at a higher rate than hydrazine (Fig. 4). We should re-emphasize the higher activity of a Co porphyrin toward carbohydrazide than hydrazine.

3.4. The activity of a Co porphyrin toward a low concentration of carbohydrazide

To obtain further information regarding electro-oxidation of carbohydrazide, the activity of Co-OEP/C toward a low concentration of carbohydrazide (10 mM) was examined. The results are shown in the voltammograms in Fig. 5. Clear oxidation activity was observed. At low concentrations of carbohydrazide, mass transfer has a significant effect on the current. Thus, the electrode rotation increased the oxidation current (lines c and d). The voltammograms at 3600 rpm (line c) and 6400 rpm (line d) are almost the same. Hence, the current at 6400 rpm (line d) reflects the intrinsic activity without the effect of mass transfer. Co-OEP/C showed significant activity toward 10 mM carbohydrazide (at 0.6 V, ca. 12 mA cm^{-2}, 38% of the activity at 0.93 M) even though the concentration of carbohydrazide decreased by 1/93.

The high activity of Co-OEP/C at a low concentration of carbohydrazide suggests the formation of a complex between carbohydrazide and the Co porphyrin. This possible interaction might be related to the high activity of Co-OEP/C in the electro-oxidation of carbohydrazide. The high activity at lower concentrations should help to mitigate the local depletion of fuel when the fuel cell is operated under high current conditions.

4. Conclusions

We prepared hydrazine electro-oxidation catalysts using Co-, Fe-, Ru-, and Rh-porphyrins. We also demonstrated that carbon-supported Co porphyrins catalyzed the electro-oxidation of carbohydrazide at a high rate. The rate of the oxidation of carbohydrazide is comparable to (or higher than) that of hydrazine on Co porphyrins, while the oxidation of carbohydrazide is much weaker than that of hydrazine with bulk metal catalysts. The concentration-dependence of this reaction indicates that carbohydrazide and a Co porphyrin strongly interact.

The strong activity toward carbohydrazide suggests that hydrazine derivatives, which would be safer than hydrazine, can act as a fuel for fuel cells. Furthermore, the current per 1 g of metal is extremely high. The electrocatalysts described here for the oxidation of carbohydrazide and hydrazine are favorable in terms of resources and cost. Unfortunately, the overpotentials for the oxidation of hydrazine and carbohydrazide are still high. Further studies will be needed to improve these catalysts.

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