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Reversible Electrochemical Conversion between Rh(II) and Rh(III) States in Rh Porphyrin Adsorbed on Carbon Black

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We have clearly demonstrated reversible cyclic voltammograms for the redox reaction between the Rh(II) and Rh(III) states in rhodium octaethylporphyrin [Rh(OEP)] adsorbed on carbon black in an acidic aqueous solution. The emergence of the reversible wave can be ascribed to the suppression of the undesirable reactions between two molecules of [Rh^{II}(OEP)] because of its strong interaction with the carbon black. The generated [Rh^{II}(OEP)] exhibits a potent catalytic O_2 reduction activity.

Rh porphyrins catalyze various catalytic reactions such as dioxygen activation,[1] C−H bond activation,[1b,2] reductive coupling of ethene and acrylates,[3] and alkyl group abstraction.[4] In these catalytic reactions, divalent rhodium species, Rh(II) porphyrins, have been emphasized as the reactive intermediate.[1−5] Rh(II) has seven d electrons that provide a remarkable reactivity comparable to that of radicals. Hence, the generation and stabilization of Rh(II) porphyrins are major subjects in the fields of both coordination chemistry and catalyst development.[5]

In this context, the electrochemical reduction of Rh(III) porphyrins has been extensively studied in organic solvents. The majority of the Rh porphyrins exhibits irreversible cyclic voltammograms.[6,7] Electrochemical, spectroscopic, and synthetic analyses indicate that the irreversibility can be attributed to the instability of the mononuclear Rh(II) porphyrin in an organic solvent. Kadish and co-workers claimed that the dimerization of the Rh(II) porphyrins results in this irreversibility.[6] However, Savéant and co-workers clearly demonstrated that the irreversibility is caused not by the dimerization but by the disproportionation of the Rh(II) porphyrin (coupled with ligation/deligation reactions) and the sluggish electrode reaction of the Rh(I) porphyrin.[7]

A great deal of effort to stabilize Rh(II) porphyrins has been performed in order to obtain reversible cyclic voltammograms of Rh porphyrins.[6,7] Soft and strong ligands such as phosphines can stabilize the Rh(II) state, so that the rhodium porphyrin exhibits reversible cyclic voltammograms.[6b,7] Low-temperature cyclic voltammetry is also an effective technique.[6,7] DiMagno and co-workers successfully observed the clear generation of the Rh(II) porphyrin from the Rh(I) porphyrin using a strong electron-withdrawing porphyrin ligand (F_{28}TPP).[8] However, it is possible that these techniques of Rh(II) state stabilization might suppress the catalytic activity of the Rh(II) porphyrin as well as undesirable Rh(II) porphyrin decomposition.

So far, all of these experiments have been performed in organic solvents; few data are available for an electrode reaction by Rh porphyrins adsorbed on electrodes. By adsorption on the electrodes, the diffusion of the Rh(II) porphyrin would be suppressed, resulting in the suppression of the disproportionation of the Rh(II) porphyrins. It is then expected that the Rh(II) porphyrins can exist as a more stable species on the surface of the electrodes than in solution. Nevertheless, Rh(II) porphyrins stabilized by adsorption would probably preserve their catalytic activity, because this method of stabilization can use a conventional porphyrin ligand and does not require special axial ligand and/or low temperature. Rh(II) porphyrins adsorbed on an electrode can also be used as an electrode catalyst. Such an approach to

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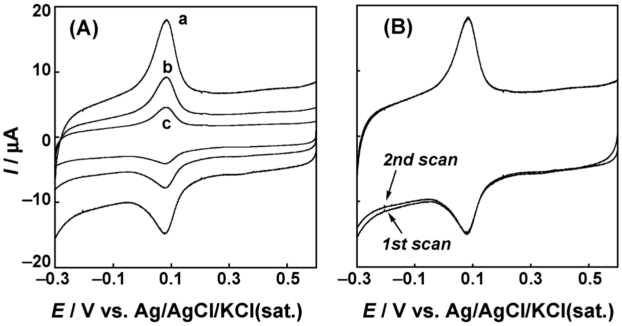

Figure 1. (A) Cyclic voltammograms of Vulcan XC 72R-supported [Rh(OEP)] at several scan rates: (a) 20, (b) 10, and (c) 5 mV s^{-1}. The measurements were performed in deaerated 0.1 M H_2SO_4 solution at 25 °C. (B) Cyclic voltammograms obtained by repeated scans of A (scan rate = 20 mV s^{-1}).

the stabilization of the Rh(II) state would be attractive from the viewpoints of electrochemistry and catalyst development.

We previously demonstrated that the cobalt(II) octaethylporphyrin (OEP) complex is adsorbed on carbon black (e.g., Vulcan XC 72R)[9] much more strongly than Co(II) porphyrins containing a meso-phenyl group.[9] Therefore, we used Vulcan XC 72R as a conductive support and OEP as a porphyrin ligand.

In this paper, we clearly show reversible cyclic voltammograms of Rh porphyrins synthesized without the use of a special axial ligand and detect Rh(II) porphyrins in an aqueous solution using rhodium octaethylporphyrin [Rh^{III}(OEP)Cl] adsorbed on Vulcan XC 72R for the first time. We also clearly demonstrate a potent oxygen reduction activity of the Rh(II) porphyrins in aqueous solution.

Detailed experimental procedures are described in the Supporting Information. [Rh^{III}(OEP)Cl] was synthesized according to the method of Ogoshi et al.[10] with a slight modification. [Rh^{III}(OEP)Cl] was adsorbed on Vulcan XC 72R by an equilibrium adsorption method. The prepared Vulcan XC 72R-supported [Rh^{III}(OEP)Cl] was fixed at the electrode surface with Nafion. Electrochemical measurements were performed in a 0.1 M H_2SO_4 solution. Because of the strong adsorption of [Rh^{III}(OEP)Cl] on the electrode and its hydrophobicity, no adsorbed molecules were dissolved in the aqueous solution.

Figure 1 A includes the cyclic voltammograms of Vulcan XC 72R-supported rhodium octaethylporphyrin [Rh(OEP)] at several scan rates in 0.1 M H_2SO_4 aqueous solution under anaerobic conditions. The clear Gaussian shape of the voltammograms suggests that the wave is derived from a molecule strongly adsorbed on the Vulcan XC 72R. The results of the repeated scans in Figure 1B indicate no degradation of Vulcan XC 72R-supported [Rh(OEP)] during the potential sweep. The absence of degradation was also confirmed by the results that the total charges of anodic and cathodic waves in Figure 1 were almost the same. The peak separation was virtually zero, and the dependence of the peak current on the scan rates was linear up to 200 mV s^{-1} (Figure 2).[11] These results also indicate the strong adsorption of [Rh(OEP)] on the Vulcan surface. From the reversible voltammograms in Figure 1A,B, no signal for the existence of the ECE mechanism was observed in contrast to past results;[6,7] chemical reactions such as the generation of the [Rh^{I}(OEP)] species by disproportionation and the possible dimerization of [Rh^{II}(OEP)] in aqueous solution did not occur. Under our conditions, the strong adsorption of [Rh(OEP)] on Vulcan XC 72R prevents these reactions, as expected.

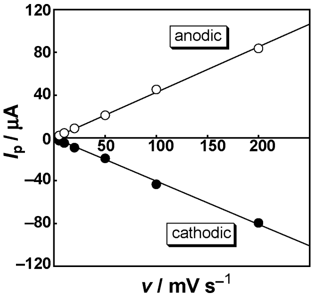

Figure 2. Plot of peak current vs scan rate. The conditions of the measurements are the same as for Figure 1.

The width of the peak at half-height [$\Delta E_{p/2}$, 95 mV (cathodic) and 82 mV (anodic) at scan rate = 20 mV s^{-1}] indicates that the number of electrons (n) involved in the electrode reaction is almost unity.[12] This indicates that the cathodic reaction can be ascribed to the reaction [Rh^{III}(OEP)]$^+$ + e$^-$ → [Rh^{II}(OEP)] and the anodic reaction to the reaction [Rh^{II}(OEP)] → [Rh^{III}(OEP)]$^+$ + e$^-$. The clear voltammograms enable us to determine the redox potential of the reaction [Rh^{III}(OEP)]$^+$ + e$^-$ $\rightleftarrows$ [Rh^{II}(OEP)] on the Vulcan surface in 0.1 M H_2SO_4 aqueous solution. The value is calculated to be 82 mV vs Ag/AgCl/KCl(sat.).

Savéant and co-workers emphasized that ligation is an important factor dominating the disproportionation of Rh(II) porphyrins in nonaqueous solution.[7] To examine the ligation effect, we measured cyclic voltammograms of [Rh(OEP)] in the presence of a high concentration of Cl$^-$ (0.22 M). A negative shift (34 mV shift) in the redox potential was observed, indicating that [Rh(OEP)] undergoes ligation of Cl$^-$. However, the reversible wave shape was not altered by the Cl$^-$ ligation. In the presence of a high concentration of OH$^-$ (pH 8.5), similar behaviors were observed. Thus, the ligation of Cl$^-$ and OH$^-$ does not affect the reversibility. In our system, the possibility that ligation causes disproportionation of [Rh^{II}(OEP)] can be discarded.

In the present system, the free diffusion of [Rh^{II}(OEP)] is suppressed by its strong adsorption on Vulcan XC 72R. Because of this effect, a [Rh^{II}(OEP)] molecule cannot approach the next [Rh^{II}(OEP)] molecule closely, so that electron transfer between the two molecules (disproportionation) fails to occur. The emergence of the reversible wave

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[11] The adsorption amount ($A\Gamma$) of [Rh(OEP)] on the electrode surface was calculated to be 4×10^{-10} mol from the slope of the line in Figure 2 based on the equation: $I_{p,c} = -9.4 \times 10^{8} A\Gamma v$ ($n = 1$, at 25 °C)

[12] The number of electrons involved in the electrode reaction was calculated by the equation $n = 90.6/\Delta E_{p/2}$ (at 25 °C).

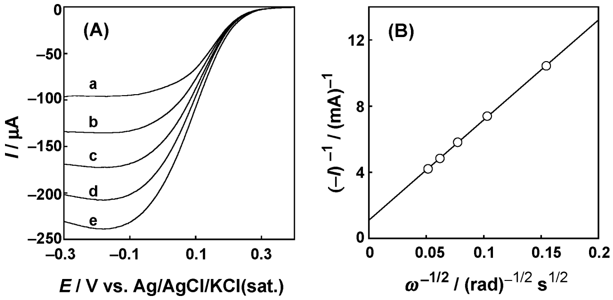

Figure 3. (A) Linear sweep voltammograms of electrocatalytic O_2 reduction exhibited by Vulcan XC 72R-supported [Rh(OEP)] at several electrode rotation rates: (a) 400, (b) 900, (c) 1600, (d) 2500, and (e) 3600 rpm. The experiments were performed in oxygen-saturated 0.1 M H_2SO_4 at 25 °C. Scan rate = 10 mV s^{-1}. (B) Koutechy−Levich plot at −0.15 V [vs Ag/AgCl/KCl(sat.)] of electrocatalytic O_2 reduction by Vulcan XC 72R-supported [Rh(OEP)].

should therefore be ascribed not to the suppression of ligation to [Rh^{II}(OEP)] but to the suppression of diffusion of [Rh^{II}-(OEP)].

As mentioned above, it has been demonstrated that Rh-(II) porphyrin species catalyze very versatile reactions including dioxygen activation[1−4] via a radical reaction mechanism. Hence, it is not surprising that the electrochemically generated [Rh^{II}(OEP)] on Vulcan XC 72R exhibited catalytic activity. We examined O_2 reduction by [Rh^{II}(OEP)] as an example of the possible reactions. Although many cathode catalysts using porphyrin have been intensively studied so far,[13] few studies have focused on Rh(II) porphyrins despite their high reactivity. Holze and co-workers observed electrocatalytic O_2 reduction by Rh porphyrin.[14] However, in that study, Rh porphyrin on the electrode partially dissolved into the test solution. To the best of our knowledge, clear electrocatalytic O_2 reduction by a strongly adsorbed Rh porphyrin on the electrode has not been yet demonstrated. Strong adsorption of a porphyrin on carbon black facilitates detailed electrochemical analysis (as below) and would be favorable for application to a cathode catalyst for fuel cells.

Figure 3A shows the linear sweep voltammograms exhibited by Vulcan XC 72R-supported [Rh(OEP)] in an O_2-saturated 0.1 M H_2SO_4 aqueous solution. The dramatic increase in the cathodic current indicates that the potent electrocatalytic O_2 reduction by [Rh^{II}(OEP)] occurred.[15] The Koutechy−Levich plot of this reaction is shown in Figure 3B. The number of electrons transferred to O_2 is calculated to be ca. 2.2 from the slope of this plot, indicating that the major product of O_2 reduction is H_2O_2. A possible reaction mechanism is as follows:

$$[\mathrm{Rh^{III}(OEP)}]^+ + e^- \rightarrow [\mathrm{Rh^{II}(OEP)}] \quad (1)$$

$$[\mathrm{Rh^{II}(OEP)}] + O_2 \rightarrow [\mathrm{Rh^{III}(OEP)}(O_2^{-\bullet})] \quad (2)$$

$$[\mathrm{Rh^{III}(OEP)}(O_2^{-\bullet})] + H^+ \rightarrow [\mathrm{Rh^{III}(OEP)}]^+ + HO_2^{\bullet} \quad (3)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (4)$$

The half-wave potential (89 mV, at 3600 rpm) is similar to the redox potential (82 mV) of the reaction [Rh^{III}(OEP)]$^+$ + e^- ⇄ [Rh^{II}(OEP)], indicating that the catalytic current can be reasonably ascribed to reactions 1−4.[16] In this catalytic reaction sequence, the clear participation of [Rh^{II}(OEP)] can be observed.

Compared to the previous Pt-alternative catalysts such as [Co(OEP)] and cofacial cobalt porphyrins,[13] the onset potential of the electrocatalytic O_2 reduction by [Rh(OEP)] is more negative. However, it is much more positive than the redox potential of $2H^+ + 2\ e^- \rightleftarrows H_2$. It is possible that the Vulcan XC 72R-supported [Rh(OEP)] might be applicable for a cathode catalyst in a polymer electrolyte fuel cell. Virtually identical reversible voltammograms were observed during the time course of the measurements (ca. 30 min). Therefore, possible acid-induced demetalation from [Rh(OEP)] would not occur under our conditions.

In summary, we have demonstrated for the first time clear cyclic voltammograms of the system Rh(III) porphyrin + e^- ⇄ Rh(II) porphyrin at room temperature without modification of the porphyrin of special axial ligands. The emergence of the clear wave can be ascribed to the suppression of possible undesirable reactions between [Rh^{II}-OEP] species, which are quite unstable in organic solution, on the surface of Vulcan XC 72R during the time course of the measurements. The generated [Rh^{II}(OEP)] shows good O_2 reduction activity. A reaction scheme was determined by considering the properties of linear sweep voltammograms.

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Supporting Information Available: Experimental details including the [Rh^{III}(OEP)Cl] synthesis, the adsorption of [Rh^{III}(OEP)-Cl] on Vulcan XC 72R, the preparation of a modified electrode, and the electrochemical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The slight decrease in the catalytic current at −0.2 to −0.3 V (observed at 1600−3600 rpm) can be ascribed to the effect of mass transfer in Nafion film. The decrease is not very significant; hence, the analysis (at −0.15 V) is not affected by the decrease.

(16) The possibility that the oxygen complex [Rh^{III}(OEP)($O_2^{-\bullet}$)] exists as a stable species in an acidic aqueous solution during the reaction is very low.