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Efficient Electrochemical Conversion of Carbon Monoxide by Rhodium Octaethylporphyrin Adsorbed on Carbon Black

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We have found efficient electrocatalytic removal of CO by rhodium octaethylporphyrin on carbon black at a wide potential range. Using carbon-supported rhodium octaethylporphyrin, we have separated the Rh(II) state participating reaction and the Rh(III) state participating reaction with CO. We have clearly demonstrated electrocatalytic CO oxidation by rhodium(III) porphyrin. The onset potential for CO oxidation is much lower than that for CO oxidation by conventional Pt/Ru catalysts and cobalt porphyrin.

For the development of a fuel cell, a critical problem is CO poisoning of the anode catalyst. CO adsorption on the platinum anode catalyst causes a drastic decrease in the cell performance.[1] From this viewpoint, CO-tolerant anode catalysts such as Pt/Ru alloy and Pt/metal oxide have been extensively investigated.[1,2] It has been proposed that electrocatalytic CO oxidation would play an important role in CO tolerance.[2b,d] On the other hand, the removal of CO from the anode gas by electrochemical CO oxidation has been performed using a Pt/Ru alloy catalyst.[3] From this context, electrochemical CO oxidation catalysts attract increasing amounts of interest. However, unfortunately, conventional catalysts require a large overpotential for CO oxidation;[1,2] the exploration of the electrochemical CO removal catalyst at lower potential is strongly requested for the solution of CO poisoning.

Metalloporphyrins might be one of the promising catalysts of electrochemical CO removal. van Veen et al. reported that rhodium tetraphenylporphyrin can perform electrocatalytic CO oxidation.[4] However, little is known about this interesting catalysis. It is attributed to the complexity of rhodium porphyrin catalysts.

Rhodium porphyrins can catalyze various useful catalytic reactions,[5−9] not only CO molecule activation[6,7] but also C−H bond activation,[8] etc. As the reactive species in these catalytic reactions, rhodium(II) and rhodium(III) porphyrins are emphasized.[5−9] For the development of rhodium porphyrin catalysis, it is important to understand and regulate the reactive species during the catalytic reactions. However, the reactive species in electrocatalytic CO oxidation have not been clearly identified and regulated,[4] despite the fact that this reaction has attracted much interest for the above-mentioned reasons.

Most of the difficulties could be attributed to the intermolecular reactions between rhodium(II) porphyrins.[5,10,11] Rhodium(II) porphyrin can undergo dimerization to produce

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the rhodium(II)−rhodium(II) porphyrin dimer in both organic and aqueous solutions.[10] Furthermore, Savéant and co-workers clearly demonstrated that the disproportionation of rhodium(II) porphyrin can occur in solution so as to produce rhodium(I) and rhodium(III) porphyrins during the electrochemical reduction of the rhodium(III) porphyrins.[11] These intermolecular reactions cause irreversible and complex cyclic voltammograms (CVs) of Rh macrocycles including porphyrins.[11−13] To understand the reactive species, one should suppress these intermolecular reactions of the rhodium(II) porphyrins and separate the rhodium(II) and rhodium(III) porphyrin participating reactions.

In our previous study, we intended to suppress the intermolecular reactions of a rhodium porphyrin by adsorbing it on carbon black.[14] We succeeded in obtaining clear reversible CVs of rhodium octaethylporphyrin ([Rh^{III}(OEP)]Cl) on carbon black. A clear Gaussian-shaped voltammogram, which is derived from the molecule strongly adsorbed on an electrode surface, suggests that the possible intermolecular reactions be successfully suppressed.[14] In such a heterogeneous system, the number of electrons transferred to electrodes (n) is calculated from the width of the peak at half-height. The peak width of the CV clearly indicates that the electrode reaction is a one-electron reaction; hence, the wave should be ascribed to the reaction between Rh(II) and Rh(III) states because we used carbon-supported [Rh^{III}(OEP)Cl].[14] The observed one-electron reaction discards the possibility of the participation of the Rh(I) states in adsorbed rhodium porphyrin, in contrast to rhodium porphyrin in solution.[11] Clear and simple voltammograms can allow us to distinguish between the [Rh^{II}(OEP)] and [Rh^{III}(OEP)]$^+$ participating reactions.

The separation and regulation of the Rh(II) and Rh(III) states in the rhodium porphyrin in our system can provide a clue for the elucidation of the electrocatalytic reaction between CO and rhodium porphyrin. Using carbon-supported [Rh^{III}(OEP)Cl], we have clearly separated the two reactions (CO with [Rh^{II}(OEP)] and CO with [Rh^{III}(OEP)]$^+$). We have also demonstrated CO oxidation by [Rh^{III}(OEP)]$^+$ and found the CO participating reduction by [Rh^{II}(OEP)].

The detailed experimental procedures are described in ref 14 and the Supporting Information. [Rh^{III}(OEP)Cl] was synthesized according to the method of Ogoshi et al. with a slight modification.[15] [Rh^{III}(OEP)Cl] was adsorbed on Vulcan XC 72R using an equilibrium adsorption method. The prepared Vulcan XC 72R supported [Rh^{III}(OEP)Cl] was fixed at the electrode surface with Nafion.

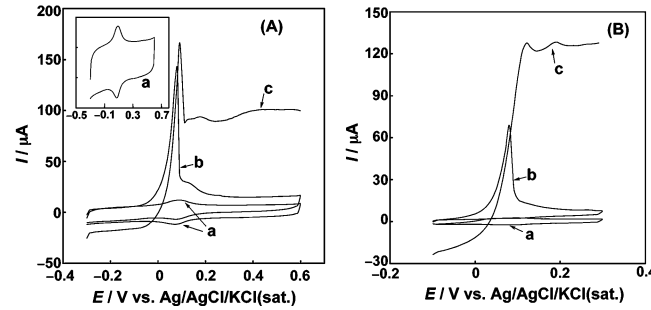

Figure 1. (A) CV and LSV of [Rh(OEP)] at scan rate = 50 mV s^{-1} (a) under an argon atmosphere without a rotating electrode, (b) under a CO atmosphere without a rotating electrode, and (c) under a CO atmosphere with a rotating electrode (3600 rpm). Inset: an expanded figure of curve a. (B) CV and LSV of [Rh(OEP)] at scan rate = 10 mV s^{-1} (a) under an argon atmosphere without a rotating electrode, (b) under a CO atmosphere without a rotating electrode, and (c) under a CO atmosphere with a rotating electrode (6400 rpm). The measurements were performed in a 0.1 M H_2SO_4 aqueous solution at 25 °C. To prevent contamination of the coordinating ion or ligands, ultrapure water was used in the experiments.

Figure 1A (inset curve a) is a CV of Vulcan XC 72R supported [Rh^{III}(OEP)Cl] in an argon-saturated atmosphere at a scan rate of 50 mV s^{-1} in an aqueous solution. The peak separation of this CV is also virtually zero, indicating that the CV is derived from the molecule strongly adsorbed on an electrode surface. From the peak width, the clear reversible voltammogram (curve a) in Figure 1A should be ascribed to the conversion between [Rh^{III}(OEP)]$^+$ and [Rh^{II}(OEP)]. In this experiment, the strong adsorption of [Rh(OEP)] on carbon black prevents undesirable reactions so as to stabilize [Rh^{II}(OEP)] on the surface, as demonstrated in our previous paper.[14]

The introduction of CO gas into the test solution produced a drastic change in the CV of [Rh(OEP)] (Figure 1A, curve b). The drastic increase in the anodic current clearly indicates electrocatalytic CO oxidation by [Rh^{III}(OEP)]$^+$. A sharp anodic peak in Figure 1A does not mean that the catalytic active species decompose above the peak potential. In fact, after the measurement of CVs in the presence of CO, the properties of the CV of [Rh(OEP)] under an argon atmosphere did not change (data not shown), indicating that [Rh^{III}(OEP)]$^+$ is preserved after the CO oxidation. Such a peak generation occurs when the rate of catalytic reactions exceeds that of mass transfer. This phenomenon is clearly analyzed from theoretical viewpoints by Savéant and co-workers.[16] The reaction is so fast that the mass transfer of CO is the rate-determining step. A linear sweep voltammogram (LSV) under rotating-electrode conditions provided a steady-state anodic current even above the peak potential (Figure 1A, curve c). The enhancement of the mass transfer by electrode rotation results in the emergence of the steady-state current. These features are much more prominent in the LSV at a slower scan rate (10 mV s^{-1}) and higher electrode rotation rate (6400 rpm), as shown in Figure 1B (curve c).

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The steady-state current above the redox potential of [$Rh^{III/II}$(OEP)] indicates that [Rh^{III}(OEP)]$^+$ would catalyze the CO oxidation. Our results clearly show that [Rh^{III}(OEP)]$^+$ catalyzes the CO oxidation. From the magnitude of the steady-state current and the amount of adsorbed species, the second-order rate constant of this reaction is calculated to be $(9.1 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$.

The proposed reaction mechanism can be written as follows:

$$[Rh^{III}(OEP)]^+ + CO \leftrightarrows [Rh^{III}(OEP)(CO)]^+ \tag{1}$$

$$[Rh^{III}(OEP)(CO)]^+ + H_2O \leftrightarrows [Rh^{III}(OEP)(COOH)] + H^+ \tag{2}$$

$$[Rh^{III}(OEP)(COOH)] \rightarrow CO_2 + [Rh^{III}(OEP)]^+ + H^+ + 2e^- \tag{3}$$

This reaction mechanism was proposed by Anson and coworkers concerning the electrocatalytic CO oxidation by [Co(OEP)].[17] The onset potential for the CO oxidation (ca. −0.1 V vs Ag/AgCl/KCl(sat.)) by [Rh^{III}(OEP)]$^+$ is much lower than those for the CO oxidation by [Co(OEP)] and noble metal catalysts such as Pt and Pt/Ru alloys. The property would be favorable for the electrochemical removal of CO.

For the electrocatalytic CO oxidation by cobalt and rhodium porphyrins, the onset potential is closely correlated with the redox potential of the central metal, because trivalent species participate in CO oxidation for both porphyrins. The redox potential of [Rh(OEP)] is much lower to that of [Co(OEP)], resulting in the low onset potential for the CO oxidation. Thus, the regulation of the Rh(II) and Rh(III) states in the rhodium porphyrin in our system provides mechanistic insight for the onset potential of electrocatalytic CO oxidation by rhodium porphyrin.

Interestingly, below the redox potential of [Rh(OEP)], the cathodic current also increased, and a steady-state current was observed at the higher electrode rotation rates (Figure 1, curve c). This cathodic current was not observed without CO under rotating-electrode conditions (data not shown). [Rh^{II}(OEP)] exists as the predominant species in this potential region. The cathodic current should be ascribed to the CO participating reduction by [Rh^{II}(OEP)]. This reaction was not observed without rotating the electrode. The efficient supply of CO, the removal of the product, or both might be required for driving this reaction.[18]

The product analysis of the test solution after potentiostat electrolysis at −0.2 V revealed a slight generation of formaldehyde (0.036 μmol). However, the amount of formaldehyde was much lower than the total amount of product (0.66 μmol) calculated from the number of electrons. Almost all products would be gaseous compounds. It is well-known that a CO molecule is activated upon coordination to [Rh^{II}(OEP)].[5] It is possible that the activated CO molecule participates in the cathodic reaction. The details of the cathodic reaction remain to be clarified.

In conclusion, we have succeeded in clearly separating the Rh(II) and Rh(III) states in [Rh(OEP)] on the surface of carbon black and distinguishing between the [Rh^{II}(OEP)] and [Rh^{III}(OEP)]$^+$ participating reactions with CO. We have clearly demonstrated the CO oxidation by [Rh^{III}(OEP)]$^+$. The high reactivity of [Rh(OEP)] toward CO at a wide potential range would be attractive in terms of the electrochemical removal of CO from a fuel cell anode catalyst.

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Supporting Information Available: Experimental details including the synthesis of [Rh(OEP)] and the adsorption of [Rh(OEP)] on carbon black (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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