Effects of *p*-substituents on electrochemical CO oxidation by Rh porphyrin-based catalysts[†]

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Electrochemical CO oxidation by several carbon-supported rhodium tetraphenylporphyrins with systematically varied *meso*-substituents was investigated. A quantitative analysis revealed that the *p*-substituents on the *meso*-phenyl groups significantly affected CO oxidation activity. The electrocatalytic reaction was characterized in detail based on the spectroscopic and X-ray structural results as well as electrochemical analyses. The difference in the activity among Rh pophyrins is discussed in terms of the properties of *p*-substituents along with a proposed reaction mechanism. Rhodium tetrakis(4-carboxyphenyl)porphyrin (Rh(TCPP)), which exhibited the highest activity among the porphyrins tested, oxidized CO at a high rate at much lower potentials (<0.1 V vs. a reversible hydrogen electrode, at 60 °C) than the present PtRu catalysts. This means that CO is electrochemically oxidized by this catalyst when a slight overpotential is applied during the operation of a proton exchange membrane fuel cell. This catalyst exhibited little H₂ oxidation activity, in contrast to Pt-based catalysts.

1. Introduction

Carbon monoxide (CO), which is strongly adsorbed on the Pt anode catalyst in a proton exchange membrane fuel cell (PEMFC), interferes with H_2 oxidation on the catalyst.^{1,2} Even in the presence of less than 100 ppm CO, H_2 oxidation activity dramatically decreases.³ Many CO conversion catalysts^{4,5} and CO-tolerant anode catalysts^{6–12} have been developed to solve this problem of CO poisoning. However, CO poisoning remains a serious problem in the realization of a stationary PEMFC.

CO can be removed from the surface of a Pt catalyst by electrochemical oxidation [eqn (1)].

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$
 (1)

However, the overpotential for CO electro-oxidation on a Pt-based catalyst is extremely high. Even PtRu catalysts, which are usually used as CO-tolerant anode catalysts, catalyze CO oxidation at much higher potentials (more than $ca. 0.3 \text{ V}^8$) than the potential regions for PEMFC (at least below 0.1 V). Electrochemical removal of CO by Pt-based

catalysts is difficult during fuel cell operation. The high overpotential for CO oxidation prevents CO removal, and results in CO poisoning of Pt catalysts.

If CO could be removed by electrochemical oxidation during fuel cell operation, it may be possible to counteract CO poisoning in PEMFC. We previously reported that carbon-supported Rh octaethylporphyrin (Rh(OEP)/C) can catalyze electrochemical CO oxidation at a high rate at low overpotentials.¹³ We also demonstrated a direct CO-PEMFC based on the high CO oxidation activity of Rh(OEP).¹⁴ This PEMFC uses CO, which is a strong poison for Pt catalyst, as a fuel and delivers high power (>95 mA cm⁻² at 0.47 V, 44 mW cm⁻²). The overpotential for CO oxidation with Rh(OEP)/C is much lower than that with PtRu catalyst. However, the onset potential for CO oxidation is still slightly higher than 0 V *vs.* a reversible hydrogen electrode (RHE). Thus, the onset potential needs to be decreased.

In some electrochemical reactions such as thiol oxidation and disulfide reduction, the substituents have significant effects on the electrocatalytic activity of metalloporphyrins or metallophthalocyanins.^{15,16} Also, in the case of Rh porphyrins, a change of substituents may improve the activity of CO oxidation.

To increase the activity by changing substituents, it is important to understand the relationship between the substituents and activity. Such an understanding can be obtained by clarifying the mechanism of the electrocatalytic reaction. In previous studies, the effects of the substituents on thiol oxidation and disulfide reduction could be clearly explained by the mechanisms of these reactions.^{15,16} This information should be useful for identifying good catalysts for the reaction. A mechanistic analysis of electrocatalytic CO oxidation by Rh porphyrins should also be helpful for the design of substituents for improving the catalysts.

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In this study, we paid special attention to the effects of substituents on the activity, and to the mechanism of the electrocatalytic CO oxidation. We concentrated on the effects of the *p*-substituents of the *meso*-phenyl group attached to the porphyrin ring, since the *p*-substituent effect can be discussed systematically by the Hammett approach. In this paper, several Rh tetraphenylporphyrins (Scheme 1) with a wide variety of *p*-substituents were examined with regard to their CO oxidation activity. The effects of p-substituents on the CO oxidation activity were examined quantitatively and systematically. The mechanism of CO oxidation was investigated by electrochemical, structural, and spectroscopic approaches. We found a drastic difference in CO oxidation activity among carbon-supported Rh tetraphenylporphyrins, even though their chemical structures are different only in the *p*-substituents. The effects of *p*-substituents are also discussed from mechanistic viewpoints. We found that a rhodium 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (Rh(TCPP))-derived catalyst exhibited the highest activity among the Rh porphyrin catalysts tested. This complex can electrochemically oxidize CO below 0.1 V (vs. RHE), which has not been previously realized using Pt-based anode catalysts.

2. Experimental

2.1 General

Tetracarbonyldi- μ -chlorodirhodium(I) (Rh₂Cl₂(CO)₄) was purchased from Wako Chemicals. All of the porphyrin ligands used in this study are commercially available. The water used in this study was purified using an Organo Puric-MX unless otherwise stated. UV-vis spectra were measured using a Shimadzu UV-1500 PC photodiode array spectrophotometer equipped with a quartz cell (light path = 1 cm). Electrochemical measurements were performed using an ALS electrochemical analyzer (Model 627B) equipped with a rotation controller (BAS RDE-2). ESI-MS spectroscopy was performed using an Esquire3000plus ion trap mass spectrometer (Bruker Daltonics). IR spectra were measured using a FT-IR spectrophotometer (IFS-66v/S, Bruker). Product analysis was performed by a gas chromatograph (Shimadzu, GC 2014) with a TCD detector.

2.2 Synthesis

Rh porphyrins were synthesized by refluxing $Rh_2Cl_2(CO)_4$ and the corresponding ligands in appropriate solvents, and purified by a conventional method. The product was analyzed by elemental analysis and ESI-MS. The experimental details



Scheme 1 Structures of Rh porphyrins tested in this work.

of the synthesis are described in the ESI.[†] The abbreviations for the complexes are as follows; $[Rh^{III}(TCPP)]^+$ (TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl)porphinate), $[Rh^{III}(T(-COOCH_3)PP)]^+$ (T(-COOCH_3)PP = 5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphinate), $[Rh^{III}(T(-OCH_3)PP)]^+$ (T(-OCH_3)PP = 5,10,15,20-tetrakis(4-methoxyphenyl)porphinate), $[Rh^{III}(TPP)]^+$ (TPP = 5,10,15,20-tetraphenylporphinate), $[Rh^{III}(T(-CH_3)PP)]^+$ (T(-CH_3)PP = 5,10,15,20-tetra(4-methylphenyl)porphinate), $[Rh^{III}(TFPP)]^+$ (TFPP = 5,10,15,20-tetrakis(4-fluorophenyl)porphinate), and $[Rh^{III}(TBPP)]^+$ (TBPP = 5,10,15,20-tetrakis(4-bromophenyl)porphinate).

2.3 Adsorption of Rh porphyrins on a carbon support by the evaporation-to-dryness (impregnation) method

Carbon-supported $[Rh^{III}(porphyrin)]^+$ (Rh(porphyrin)/C) was prepared by the evaporation-to-dryness (impregnation) method as follows. Carbon Black (Vulcan XC 72*R*) (30 mg) was added to 20 mL of appropriate solvent (see below) containing a porphyrin in a sample vial. The suspension was shaken vigorously, subjected to sonication 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 Rh porphyrins deposited was fixed at 30 µmol $g^{-1}_{carbon black}$. The solvents used in this preparation were ethanol for Rh(TCPP)/C and Rh(T(-CH₃)PP)/C, and CH₂Cl₂ for the other catalysts.

2.4 Adsorption of a Rh porphyrin on a carbon support (carbon black, Vulcan XC 72*R*) by the equilibrium adsorption method

Rh(TCPP)/C was also prepared by the equilibrium adsorption method as follows. Two conditions were tested for preparation. The two conditions differed by the ratio of amount of carbon to the volume of solvent.

Condition A: Carbon Black (Vulcan XC 72R) (30 mg) was added to 10 mL of ethanol containing porphyrin (0.46 mM) in a sample vial. The suspension was homogenized as described above. The suspension was stirred for 3 h and filtered through filter paper (ADVANTEC, No.5C). The pellet was then collected.

Condition B: Carbon Black (Vulcan XC 72R) (40 mg) was added to 5 mL of ethanol containing porphyrin (0.46 mM) in a sample vial. Other procedures were the same as in Condition A.

The equilibrium amount of porphyrin adsorbed per unit carbon mass was determined by measuring the filtrate concentration by UV-vis spectroscopy after the adsorption.

2.5 Electrochemical measurements

A modified rotating disk glassy carbon electrode (modified RDE, described below) was used as a working electrode. A Ag|AgCl|KCl(sat.) and a reversible hydrogen electrode (RHE) were used as reference electrodes in the experiments at 25 and 60 °C, respectively. In the experiments at 60 °C, RHE was placed at room temperature. All of the potentials in the results are *vs.* RHE at the temperature at which the measurements were performed (see ESI).† A platinum coil was used as a

counter electrode. The measurement was performed in a 0.1 M H_2SO_4 solution. All voltammograms were measured at a scan rate of 10 mV s⁻¹.

2.6 Modification of RDE with Vulcan XC 72*R*-supported Rh porphyrins

RDE was modified as described in the literature.¹⁷ Five milligrams of the Vulcan XC 72*R*-supported Rh porphyrins was dispersed in 0.5 mL of a mixed solvent (water–ethanol = 1:1) containing 5 μ L Nafion (Aldrich, 5%). A portion (2 μ L) 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 cm²).

2.7 Structure determination by X-ray crystallography

Crude [Rh^{III}(TCPP)(CO)(CI)] and [Rh^{III}(T(–OCH₃)PP)(C₂H₅OH)-(Cl)] complexes were recrystallized to obtain fairly good single crystals suitable for X-ray analysis from a mixed solvent (2-propanol and hexane) and ethanol, respectively. X-Ray diffraction data were collected by a Bruker SMART AXS CCD area-detector diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) at a temperature of 183 K. All crystallographic calculations were conducted using SHELXTL¹⁸ (Bruker AXS Inc.). Other details are given in the ESI.†

2.8 Product analysis

Electrolysis for analysis of the products of CO oxidation by Rh(TCPP)/C was performed as follows; a 0.1 M H₂SO₄ solution was placed in a cell. This cell was composed of two compartments separated by a glass filter. The Rh(TCPP)/ C-modified working electrode ($A = 4.5 \text{ cm}^2$) and the reference electrode were immersed in one compartment. The counter electrode was immersed in the other compartment. The compartment with the working and reference electrodes was purged with neat CO gas, and the compartment with the counter electrode was purged with argon gas. After the two compartments were purged, the cell was sealed with a silicone plug to prevent gas exchange during electrolysis. The potential of the working electrode was held at 0.31 V (vs. RHE) at 25 °C. The charge was recorded during electrolysis. After the electrolysis was finished, the gas phase above the solution was sampled and analyzed by gas chromatography.

3. Results

3.1 Characterization of Rh porphyrin complexes

Elemental analysis and ESI-MS spectroscopy clearly indicated the generation of trivalent Rh porphyrin complexes. UV-vis spectra of the Rh porphyrins are shown in Fig. S1.† All Rh porphyrins exhibited similar spectra regardless of the electronic properties of the *p*-substituents. The *p*-substituents have little effect on the electronic properties of the porphyrin ring in Rh porphyrins.

Single crystals of $[Rh^{III}(TCPP)(C_3H_7OH)(Cl)]$ and $[Rh^{III}(T(-OCH_3)PP)(C_2H_5OH)(Cl)]$ complexes were obtained



Fig. 1 ORTEP drawings of (A)[Rh^{III}(TCPP)(C₃H₇OH)(Cl)](H₂O)-(C₃H₇OH)₂ and (B) [Rh^{III}(T($-OCH_3$)PP)(C₂H₅OH)(Cl)] with 25% probability ellipsoids. Hydrogen atoms and uncoordinated solvents are omitted for clarity.

by recrystallization from a mixed solvent system (2-propanol: hexane = 2:9 and from ethanol, respectively. Their crystal structures were determined by single-crystal X-ray diffraction analysis, and are shown in Fig. 1. In the crystal structure of [Rh^{III}(TCPP)(C₃H₇OH)(Cl)], C₃H₇OH, which is used for crystallization, coordinates on the Rh atom. This indicates that the axial ligands of a Rh porphyrin are labile. In both structures, phenyl groups at the meso positions are situated at various angles (94, 61, 127, and 82° in [Rh^{III}(TCPP)(C₃H₇OH)(Cl)] and 66, 64, 71 and 73° in [Rh^{III}(T(-OCH₃)PP)(C₂H₅OH)(Cl)], see ESI[†]) vs. the porphyrin ring. The overlap between the orbitals of the porphyrin ring and meso-phenyl groups is reduced in this configuration. Hence the electronic effect of the *p*-substituents on meso-phenyl groups would be slight. In the structure of [Rh^{III}(TCPP)(C₃H₇OH)(Cl)], a molecule is connected to the neighboring molecules via hydrogen bonds between carboxy groups. Some solvent molecules participate in these hydrogen bonds. The O6 and O7 atoms form direct hydrogen bonds without participation of the solvent. In the structure of [Rh^{III}(T(-OCH₃)PP)(C₂H₅OH)(Cl)], the O4 atom participates in the formation of a hydrogen bond with the O1 atom in ethanol.

3.2 Electrochemical CO oxidation activity of carbon-supported Rh porphyrins prepared by the evaporation-to-dryness (impregnation) method

Since Rh porphyrins were used as an electrocatalyst, they were adsorbed on Carbon Black, which has good conductivity. Adsorption was performed by the evaporation-to-dryness method. In this method, the amount of Rh porphyrins on the carbon support can be controlled. The amounts were fixed at 30 μ mol g⁻¹. We measured the electrochemical CO oxidation activity by carbon-supported Rh porphyrins prepared by this method.

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Fig. 2 shows voltammograms of several carbon-supported Rh porphyrins under CO atmosphere with electrode rotation at 6400 rpm in 0.1 M H₂SO₄. Rh porphyrins exhibited clear CO oxidation activity. Carbon-supported inorganic salts of Rh such as Rh₂Cl₂(CO)₄ showed little CO oxidation activity compared to Rh porphyrins (data not shown), while some researchers have reported CO oxidation activity with a similar water-soluble Rh complex ([Rh(CO)₂Br₂]⁻).¹⁹ CO electro-oxidation by Rh black required large overpotentials (data not shown), as in the case of Pt catalyst. These data suggest that the porphyrin structure is very important for a high rate of CO oxidation in low potential regions.

A significant difference was observed in the activities of the Rh porphyrin catalysts. Some of the Rh porphyrins tested exhibited strong CO oxidation activity even in low potential regions (<0.25 V vs. RHE). Especially with Rh(TCPP)/C, Faradaic anodic current starts to flow at ca. 0.1 V vs. RHE. In contrast, Rh(TPP), Rh(TFPP), Rh(TBPP), and Rh(T(-CH₃)PP) exhibit significantly lower activity. The only difference in their structures is the difference between the *p*-substituents on the *meso*-phenyl group. This difference in the activity is somewhat surprising if we consider that the *meso*-phenyl groups in tetraphenylporphyrin ligands are not conjugated with a porphyrin ring (Fig. 1) and the substituents on the *meso*-phenyl group would have a less significant effect on the electronic property of the ring.

The dependence of the activity on the electrode rotation rate was also examined with all of the catalysts tested. The current below 0.25 V did not depend on the rotation rate. Therefore, the currents below 0.25 V should be free of the effect of diffusion in bulk solution and reflect the activity of Rh porphyrin catalysts. CO oxidation in these potential regions (<0.25 V vs. RHE) is important for fuel cell applications. We adopted the current at 0.25 V as an index of the catalytic activity since in the very low potential regions (<0.25 V) some catalysts hardly exhibit activity and quantitative comparison is difficult. The results are shown in Table 1. The CO oxidation activity at 0.25 V increases in the order: Rh(TCPP)/C > Rh(T(-COOCH_3)PP)/C > Rh(T(-OCH_3)PP)/C > Rh(T(-CH_3)PP)/C > Rh(TPP)/C, Rh(TFPP)/C, Rh(TBPP)/C (Table 1).

There appears to be no clear relationship between the activities of the catalysts and the Hammett constants of the *p*-substituents on the *meso*-phenyl groups (Table 1). For example, although –COOH, –COOCH₃, –Br, and –F are all electron-withdrawing groups, their activities are totally different. This indicates that the electronic properties of *p*-substituents are hardly correlated with the rate of CO electro-oxidation.



Fig. 2 Linear sweep voltammograms of (a) Rh(TCPP)/C, (b) Rh(T(-COOCH₃)PP)/C, (c) RhT(-OCH₃)PP/C, (d) Rh(T(-CH₃)PP)/C, (e) Rh(TPP)/C, (f) Rh(TBPP)/C, and (g) Rh(TFPP)/C prepared by the equilibrium adsorption method. The measurements were performed under a CO atmosphere with electrode rotation at 6400 rpm (scan rate = 10 mV s⁻¹) in 0.1 M H₂SO₄ at 25 °C.

The activity is also not related to steric hindrance by *p*-substituents. Thus, the drastic difference in activity in Fig. 2 cannot be explained by the difference in the properties of porphyrin alone. This strongly suggests that the configuration of porphyrin molecules on the surface of the carbon support might play a role in this difference in activity.

3.3 Electrochemical CO oxidation activity of carbonsupported Rh porphyrins prepared by the equilibrium adsorption method

The possible importance of the configuration of the molecules on the surface encouraged us to examine the effect of the preparation method on the activity of Rh porphyrin-based catalysts. Therefore, we tested the equilibrium adsorption method for preparing carbon-supported Rh porphyrins for comparison to the results with the evaporation-to-dryness method. Two different conditions (A and B, see section 2.4.) were used to prepare the catalyst using the equilibrium adsorption method.

In general, the evaporation-to-dryness method can be used to control the amount of complexes on Carbon Black. However, a disadvantage is that even molecules that interact less with carbon might also be adsorbed on the catalyst surface, so as to cause the undesirable aggregation and multilayer adsorption of the porphyrins. In contrast, in the equilibrium adsorption method, molecules that interact less with carbon would be washed away, and only molecules that strongly interact with

Table 1	Hammett constant of	<i>n</i> -substituent a	and CO	oxidation	activity	of Rh	porphy	rins
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Porphyrins	Hammett constant of <i>p</i> -substituent (σ_p)	CO oxidation current at 0.25 V/ μA
Rh(TCPP)	0.44	46
Rh(T(-COOCH ₃)PP)	0.44	20
Rh(TBPP)	0.22	2.4
Rh(TFPP)	0.06	0.4
Rh(TPP)	0	1.4
$Rh(T(-CH_3)PP)$	-0.14	3.4
$Rh(T(-OCH_3)PP)$	-0.28	6.7



Fig. 3 Linear sweep voltammograms of (A) Rh(TCPP)/C prepared by the equilibrium adsorption method (condition *A*), (B) Rh(TCPP)/C prepared by the equilibrium adsorption method (condition *B*), and (C) Rh(TCPP)/C prepared by the evaporation-to-dryness method (taken from Fig. 2). The measurements were performed under a CO atmosphere with electrode rotation at 6400 rpm (scan rate = 10 mV s⁻¹) in 0.1 M H₂SO₄ at 25 °C.

carbon would be adsorbed on the catalyst surface. Aggregation and multilayer adsorption can be minimized with this method. The amount of porphyrins (Table 1) adsorbed on Carbon Black was evaluated by measuring the difference between concentrations before and after adsorption.

The activities of Rh(TCPP)/C prepared with the equilibrium adsorption method are shown in Fig. 3 and Table 2 in comparison to the activity of the catalyst prepared by the evaporation-to-dryness method. The results in Fig. 3 clearly indicate that the activity is increased with the equilibrium adsorption method. The activity per Rh atom was also increased with the equilibrium adsorption method (Table 2). Especially with catalyst (B), even though the amount adsorbed is less than with the evaporation-to-dryness method, higher activity was observed. Such a drastic difference in activity between the two preparation methods supports the hypothesis that the configuration of porphyrin molecules on the surface of Carbon Black is important for their activity. The onset potential for CO oxidation with the catalyst (A) is much lower than those for PtRu catalysts and for Rh(OEP)/C reported previously.13 The catalysts prepared with this method (condition A) were used for further experiments.

In their pioneering work, van Baar *et al.* described the electrochemical CO oxidation activity of carbon-supported Rh tetraphenylporphyrins, as measured by a floating electrode technique.^{20,21} However, the activity per Rh atom is low, and their evaluation methods are unsuitable for quantitative electrochemical analysis. In this study, we measured CO oxidation activity using a quantitative rotating electrode

method. We were able to discuss the *meso*-substituent effect and the superiority of the equilibrium adsorption method using this quantitative evaluation method, and discovered a new CO oxidation catalyst that has high activity per Rh atom, while the study by van Baar *et al.* paid little attention to the effects of *meso*-substituents and the adsorption method.

3.4 Product analysis of the electrochemical CO oxidation activity of carbon-supported Rh porphyrins prepared by the equilibrium adsorption method

To investigate the reaction product and the overall number of electrons transferred, the dependence of current on the rotation rate was examined (Fig. S2). In potential regions above 0.3 V, the current slightly increased with the rotation rate; diffusion in the bulk affects the current. The Koutecky-Levich plot at 0.45 V is shown in Fig. S2. The number of electrons transferred in CO oxidation is calculated to be 2.16 from the slope of this plot (see ESI[‡]). This value is close to 2, and thus stoichiometry is consistent with reaction (1).

This stoichiometry was also confirmed by a product analysis. The generation of a significant amount of CO_2 from the electrochemical oxidation of CO was verified using gas chromatography. The amount of CO₂ generated (14 µmol) is nearly equivalent to half the amount of electrons transferred (38 µmol). This also supports the stoichiometry of eqn (1).

3.5 Electrochemical H₂ oxidation activity of Rh(TCPP)/C

To discuss the application of Rh porphyrin-based catalysts to fuel cell technology, we also examined their H₂ oxidation activity. Fig. 4 shows voltammograms of Rh(TCPP)/C prepared by the equilibrium adsorption method (condition A) in atmospheres of (a) argon and (b) H_2 . The change from argon to H_2 only slightly increased the anodic current. Electrode rotation did not increase the current (line c), indicating that the H_2 oxidation current is completely determined by the kinetic activity of the catalyst. This indicates that Rh(TCPP)/C has slight H₂ oxidation activity, but this activity is very low compared to its CO oxidation activity (Fig. 3). If we subtract the anodic current of line (a) from that of line (b), we obtain the intrinsic H₂ oxidation current. The current at 0.25 V is ca. 1/110 of that observed in CO oxidation. The saturated concentration of H_2 (0.78 mM) is comparable to that of CO (1 mM) based on their solubility. Considering the difference in solubility, the activity of Rh(TCPP)/C toward CO is 85 times as high that toward H₂. Our previous study also suggested that the Rh(OEP) catalyst was selective in a PEMFC.¹⁴ van Veen et al. stated that Rh porphyrin catalyst has high selectivity

Table 2 CO oxidation activity of the Rh(TCPP)/C catalysts prepared with several methods

Preparation methods		Adsorption amount (µmol per 1 g Vulcan XC 72 <i>R</i>)	CO oxidation current at 0.25 V/μA	CO oxidation current at 0.25 V per Rh porphyrin 1 μmol/mA μmol ⁻¹
Equilibrium adsorption method	Condition A	49	111	113
* *	Condition B	22	95	216
Evaporation-to-dryness method		30	46	77



Fig. 4 Voltammograms (scan rate = 10 mV s⁻¹) of Rh(TCPP)/C prepared by the equilibrium adsorption method (condition *A*) under (a) an argon atmosphere, (b) a H₂ atmosphere, and (c) a H₂ atmosphere with electrode rotation at 6400 rpm. Other details of the measurements are shown in the captions for Fig. 2 and 3.

using CO–H₂ and CO–N₂ mixtures.²² They also demonstrated H₂ oxidation by heat-treated noble-metal porphyrins.²² However, there has been no previous demonstration of the quantitative relation between H₂ and CO oxidation activities of Rh porphyrins. The present experiments directly and quantitatively demonstrate the selectivity of Rh(TCPP)/C toward CO. The high selectivity is a distinguishing property of porphyrin-based catalysts compared to bulk noble-metal catalysts.

3.6 Electrochemical CO oxidation activity of Rh(TCPP)/C at 60 $^{\circ}$ C.

The CO oxidation activity of Rh(TCPP)/C at a higher temperature (60 °C) was also examined because actual fuel cell catalysts are used at a somewhat higher temperature. The experiment at 60 °C is also important for the analysis of the dependence of activity on temperature. The results are shown in Fig. 5A. The increase in temperature reduced the overpotentials for CO oxidation. The current started to flow below 0.1 V, and the current at 0.15 V exceeded 70 μ A, while the current at 0.15 V at 25 °C was only 8 μ A (Fig. 3A).

The results of a Tafel analysis of Rh(TCPP)/C from 0.08 V to 0.12 V are shown in Fig. 5B. In these potential regions, the current does not depend on the rotation rate (Fig. 5A), indicating that the rate is a completely kinetic process. Hence, the current at 6400 rpm is adopted as a kinetic current. In this figure, the logarithms of the kinetic currents are plotted against the potentials. The slope of this plot (Tafel slope) is 62 mV/decade. Other Rh porphyrin-based catalysts (RhT(-COOCH₃)PP/C, RhT(-OCH₃)PP/C, and Rh(TPP)/C) gave similar Tafel slopes (69, 74, and 67 mV/decade, respectively) (Fig. S3). This indicates that the same rate-determining step is involved in the CO oxidation by the Rh porphyrins used.

3.7 Analysis of CO coordination on Rh porphyrin

To investigate the mechanism of CO electro-oxidation, the coordination of CO on Rh porphyrin was examined by UV-vis spectroscopy and IR spectroscopy. Fig. 6A shows UV-vis spectra of $[Rh^{III}(T(-OCH_3)PP)(Cl)]$ in CH₂Cl₂. The



Fig. 5 The CO oxidation activity at 60 °C of Rh(TCPP)/C prepared by the equilibrium adsorption method (condition *A*). (A) Voltammograms of Rh(TCPP)/C under (a) an argon atmosphere, (b) a CO atmosphere without electrode rotation, and a CO atmosphere with electrode rotation at (c) 400, (d) 900, (e) 1600, (f) 2500, (g) 3600, (h) 4900, and (i) 6400 rpm (scan rate = 10 mV s⁻¹). (B) A logarithmic plot of potential *vs.* current of CO oxidation by Rh(TCPP)/C.

introduction of CO gas to the CH_2Cl_2 solution of the Rh porphyrins caused a clear red shift and hyperchromic effects (line b). The solution after the introduction of CO was exposed to air, however, the spectra did not change (line c). These results indicate that CO can easily coordinate on Rh porphyrins, and the product complex is somewhat stable toward oxygen in CH_2Cl_2 . Similar absorption behaviors were observed for other Rh porphyrins. The spectra of other Rh porphyrins after CO coordination are shown in Fig. 6B. The *p*-substituents on the *meso*-phenyl groups have little effect on either the CO coordination process or the electronic properties of the CO complex generated.

The product of the CO coordination of a Rh porphyrin was collected by removal of the solvent. The powder was subjected to IR analysis. The IR spectra of [Rh^{III}(T(–OCH₃)PP)(Cl)] are shown in Fig. 7. After the reaction with CO, absorbance bands in wavenumber regions around 2100 cm⁻¹ emerged, while absorbance was not observed before CO coordination. This absorbance can be reasonably ascribed to CO coordinated on the Rh atom in the Rh porphyrins. The wavenumber regions are significantly higher than those of other metalloporphyrin-CO complexes (for example, for Fe porphyrins, <2010 cm⁻¹).^{23,24} These regions are also higher than that of CO adsorbed on a Pt metal catalyst (<2050 cm⁻¹),^{25,26} and close to that of free CO (2143 cm⁻¹). Similar IR spectra of CO on Rh(TPP) have been reported in the literature.^{23,27}



Fig. 6 UV spectra of $[Rh^{III}(T(-OCH_3)PP)(CI)]$ in CH_2Cl_2 (a) before, (b) after CO bubbling, and (c) after exposure to air following the CO bubbling. (B) UV spectra of CO complexes of Rh porphyrins: (a) $[Rh^{III}(T(-OCH_3)PP)(CI)]$, (b) $[Rh^{III}(T(-COOCH_3)PP)(CI)]$, (c) $[Rh^{III}(TPP)(CI)]$, and (d) $[Rh^{III}(TFPP)(CI)]$. The concentration of Rh porphyrins was fixed at 3 μ M. Neat CO was bubbled for 3 min. Exposure to air was performed for 10 min.



Fig. 7 FT-IR spectra of $[Rh^{III}(T(-OCH_3)PP)(Cl)]$ (a) after and (b) before CO addition. (c) FT-IR spectra of $T(-OCH_3)PPH_2$. Inset: an expanded figure from 1800 cm⁻¹ to 2200 cm⁻¹.

4. Discussion

4.1 Plausible reaction mechanism

The easy CO coordination on Rh atom observed in UV-vis spectra (Fig. 6) suggests the participation of Rh porphyrin–CO complex in the catalytic reaction. The higher wavenumber region in IR spectra (Fig. 7) indicates that the CO complex can



Scheme 2 A proposed reaction mechanism for the electrocatalytic CO oxidation by a Rh porphyrin.

undergo nucleophilic attack more easily than other CO complexes. These experimental results lead us to a plausible reaction mechanism (Scheme 2). In this scheme, CO first coordinates on the Rh atom in a Rh porphyrin. Next, the coordinated CO undergoes nucleophilic attack by a water molecule to generate a Rh porphyrin–COOH complex *via* a transient intermedate ([Rh porphyrin–COOH complex *via* a transfer from the Rh porphyrin–COOH complex to the Carbon Black surface occurs concomitant with proton release to generate CO_2 and free Rh porphyrin. Similar reaction mechanisms have been reported for electrocatalytic CO oxidation.^{20,21,28}

According to the mechanism in Scheme 2, the reaction rate can be shown as eqn (2) if we consider the equilibrium of CO binding (K_1) and H₂O addition to the CO complex (K_2), and assume that the electron transfer (k_3) is the rate-determining step. The kinetic current (I_k) can be shown as follows:

$$I_k = nF \operatorname{Au}\Gamma \ k_3 \frac{\left(\frac{K_2}{K_2+1}\right)[\operatorname{CO}]}{\left(\frac{K_1}{K_2+1}\right) + [\operatorname{CO}]}$$
(2)

The value k_3 can be expressed using the Butler-Volmer equation.

$$I_{k} = nF \operatorname{Au} \Gamma \frac{\left(\frac{K_{2}}{K_{2}+1}\right) [\operatorname{CO}]}{\left(\frac{K_{1}}{K_{2}+1}\right) + [\operatorname{CO}]} k_{0} \left[\exp \frac{nF(1-\alpha)}{RT} \left(E - E_{\mathrm{rds}}^{\circ}\right) \right]$$
(3)

where *n* indicates the number of electrons transferred. The parameter *u* is the ratio of complex used to the total amount (the ratio of effective molecules). *F*, *A*, Γ , α , and *E*_{rds} are Faraday constant, surface area, amount of complex on electrode, transfer coefficient, and the redox potential of the rate-determining process, respectively.

The value of *n* was determined to be 2 in section 3.4. Assuming that α is 0.5, the Tafel slope is theoretically 66 mV/decade at 60 °C by replacing *n* with 2. Actually, the obtained Tafel slope was within 62–74 mV/decade. Eqn (3) can be changed to eqn (4) by replacing *n* with 2.

$$I_{k} = 2F \operatorname{Au} \Gamma \frac{\left(\frac{K_{2}}{K_{2}+1}\right) [\operatorname{CO}]}{\left(\frac{K_{1}}{K_{2}+1}\right) + [\operatorname{CO}]} k_{0} \left[\exp \frac{2F(1-\alpha)}{RT} \left(E - E_{\mathrm{rds}}^{\circ}\right) \right]$$

$$(4)$$

A UV-vis analysis clearly indicates that CO easily coordinates on the Rh atom in Rh porphyrins (the first process in Scheme 2). The CO complexes of Rh porphyrins were characterized using IR. The higher wavenumber regions in the IR spectra indicate that electron-donation from Rh metal to CO is weak; the electron density on CO would be lower than those in CO-complexes of other metalloporphyrins such as Fe

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porphyrins. The significance of the reduced electron density on CO with regard to electrochemical CO oxidation by Co porphyrin was documented by Shi *et al.*²⁸ The electron deficiency in CO on Rh porphyrin assists the nucleophilic attack by water (the second process in Scheme 2).

The Tafel slope of 62–74 mV/decade suggests that the last process in Scheme 2 is an apparent 2-electron-transfer process (see ESI).† It follows that the Rh–COOH complex would undergo heterolytic cleavage, as shown by the arrows in Scheme 2. Similar values for the Tafel slope for some Rh porphyrins indicate that there is no difference in the properties of the rate-determining step.

UV-vis analysis of CO coordination on Rh porphyrins strongly suggested that there is little difference in K_1 among the porphyrins tested. The similar spectra of CO complexes of Rh porphyrins (Fig. 6) suggests similar reactivity of the CO complexes, and implies that there is little difference in K_2 and k_3 among the porphyrins. The drastic difference in the CO oxidation activity can be ascribed to the parameter u.

4.2 Explanation of the difference in the activity between Rh porphyrins

A significant difference in CO oxidation activities among Rh porphyrins was observed in Fig. 2. Zagal *et al.* extensively studied the metalloporphyrins and metallophthalocyanins with various substituents with regard to the activities of thiol electro-oxidation and disulfide electro-reduction.^{15,16} They found a close correlation between the electronic properties of the substituents and the activities.

The substituents cause a change in the redox potentials of the porphyrins/phthalocyanines, and eventually affect the electrocatalytic activity. The electronic effect of the substituents on the redox potential were clearly explained in terms of Hammett constants.^{29,30} Hence, in the reactions in previous works, the electrocatalytic activity is directly related to the Hammett constants of the substituents.

In this work, the activity of CO oxidation was not related to the Hammett constants of the *p*-substituents. This situation is in marked contrast to the results in the previous works mentioned above. In this work, the substituents are not directly on the porphyrin ring but rather on *meso*-phenyl groups. The X-ray crystal structure in Fig. 1 clearly shows that the porphyrin ring is scarcely conjugated with *meso*-phenyl groups. The electronic properties of *p*-substituents have little influence on the electronic state of the Rh atom in the Rh porphyrins tested in this work. This is consistent with the findings that the UV-vis spectra of the Rh porphyrins were almost the same (Fig. S1).† This could explain why the electronic properties of substituents hardly affected the activity of CO oxidation activity.

The X-ray structure also indicates that a p-substituent is too far from the Rh atom to have any steric effect. The activity is also not related to the bulkiness of the p-substituents; a bulky COOCH₃ group enhances activity, while a bulky Br does not.

Thus, the difference in activity cannot be explained by electronic and steric properties of a single molecule of porhyrin. Porphyrin–Carbon Black interactions and porphyrin– porphyrin interactions should be taken into consideration to explain this difference. These interactions affect the configuration of porphyrin molecules on the carbon surface and the u values in eqn (2)–(4).

Interestingly, the activity of Rh(TCPP)/C per Rh atom increased with the equilibrium adsorption method. This suggests that the configuration of Rh porphyrins on Carbon Black significantly affects the activity. A porphyrin molecule is adsorbed on Carbon Black due to various kinds of interactions such as π - π stacking interactions, electrostatic interactions, van der Waals interactions, and hydrogen bond formation. These interactions cause a favourable configuration (monolayer adsorption), and increase the *u* value in eqn (4). On the other hand, a porphyrin molecule can interact with neighboring porphyrin molecules *via* π - π stacking. The latter interaction results in an unfavourable configuration (aggregation or multilayer adsorption), and reduces the use of Rh porphyrins. This decreases the *u* value (eqn (4)).

Rh(TCPP), RhT(-COOCH₃)PP, and RhT(-OCH₃)PP exhibited higher activity. These Rh porphyrins have p-substituents that include O atoms. There are many O-derived functional groups (-OH, -O-, COOH, etc.) on the surface of Carbon Black.³¹⁻³⁴ These functional groups can interact with the substituents of Rh(TCPP), RhT(-COOCH₃)PP, and RhT(-OCH₃)PP via a hydrogen bond. This interaction with carbon promotes the favourable configuration of porphyrin molecules, and is associated with high activity. A carboxy group can make hydrogen bonds most easily with O-containing functional groups. This can explain the highest activity of Rh(TCPP)/C. The other porphyrins (Rh(TPP), Rh(T(-CH₃)PP, Rh(TFPP), and Rh(TBPP)) exhibited much lower activity than the three O-containing porphyrins. These porphyrins have no p-substituents that can interact with the functional groups on the surface of Carbon Black, and tend to aggregate via intermolecular π - π stacking. This possible aggregation of porphyrin molecules may be responsible for their lower activity.

4.3 Reason for the low activity toward electrochemical H_2 oxidation

Many other CO oxidation catalysts (e.g. Pt-based catalysts) have strong activity in H₂ electro-oxidation. However, Rh porphyrin catalysts exhibited little activity toward H2 oxidation. The H₂ oxidation activity of Pt catalysts has been well documented. In the proposed mechanism, the oxidative cleavage of H₂ on the Pt surface generates two Pt-H bonds. These Pt-H bonds are oxidized electrochemically. The key point of this catalytic cycle is that two adjacent Pt atoms are involved. Rh atoms in the Rh porphyrin catalyst are separated from each other, unlike in bulk metal catalysts, and this prevents the easy cleavage and coordination of H₂. This may cause the low H₂ oxidation activity. The UV-vis spectra of some Rh porphyrins in CH₂Cl₂ did not change after H_2 bubbling, in contrast to CO bubbling. This indicates that H₂ does not coordinate on the Rh atom, and supports the hypothesis discussed above.

Conclusions

We investigated CO oxidation by several carbon-supported Rh tetraphenylporphyrins with systematically varied *meso*substituents. We found that Rh(TCPP)/C exhibits the highest activity among the porphyrins tested. This catalyst can catalyze CO oxidation at low overpotentials (less than 0.1 V vs. RHE, at 60 °C). This result means that CO is electrochemically oxidized by this catalyst when a slight overpotential is applied under PEMFC operation. This situation is in marked contrast to that with Pt-based catalysts, which require a large overpotential for CO oxidation. The catalyst shows high selectivity toward CO compared to H₂. The lack of H₂ oxidation activity indicates that this catalyst should be combined with a Pt catalyst, which can strongly oxidize H₂. The optimal combination of these two catalysts should be examined further for use in fuel cell applications.

We also found that the *p*-substituents on the *meso*-phenyl groups dramatically influenced CO oxidation activity. The effects of the substituents on the meso-phenyl group were discussed in terms of a proposed reaction mechanism of CO activation. No clear relationship was observed between the activity and the electronic or steric properties of *p*-substituents. The CO coordination process and the CO complex of Rh porphyrin were not significantly different among the Rh porphyrins tested. These results strongly suggest that the differences in activity can be attributed not to the intrinsic properties of a single porphyrin molecule, but rather to porphyrincarbon interactions. The substituents that are associated with high CO oxidation activity contain an O atom, and this can promote the formation of hydrogen bonds with functional groups on the carbon surface. The increased interaction due to this bond formation may be responsible for the high activity.

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