Electroreduction of Oxygen at a Pt/C-Modified Electrode with a Cobaltporphyrin Complex

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Cobalt complexes that reversibly bind and release O_2 functioned as O_2 carriers, or O_2-enriching media, at the surface of a cathode to enhance the current for the reduction of O_2. The effect of the cobalt complex to accumulate O_2 was evidenced by the higher open-circuit potential, which reflected the equilibrated concentration of O_2 at the electrode surface. The combination of the cobalt complex and the conventional Pt/C catalyst resulted in a significant increase in the steady-state current for the four-electron reduction of O_2, particularly at small overpotentials where typical fuel cells operate, based on the facilitated transport of O_2 from the atmosphere to the catalyst at the electrode surface.

The development of new materials designed to improve the performance of polymer electrolyte fuel cells is a highly topical research field.[1–3] The basic elements of a typical fuel cell consist of an electrolyte phase in contact with an anode and a cathode. The fuel and oxidant gases flow past the backside of the anode and cathode, respectively, and react electrochemically in the region of the three-phase boundary established as the gas/electrolyte/electrode interface. The nature of this interface plays a critical role in the electrochemical performance of fuel cells. Thus, the cell current and voltage depend on both the interfacial electron transfer at the electrode and the transport of O_2 onto the electrode from the atmosphere.[4] The inherent slow kinetics of the electrochemical reactions of O_2 have prompted extensive studies to enhance the rate of electron transfer, which have spawned a number of electrocatalysts.[5–8] However, less attention has been given to achieve electrode materials with enhanced O_2 transport properties. Most of the previous studies have been devoted to maintain a large interfacial contact area using a porous structure (i.e., gas diffusion electrodes) to achieve practical current densities. Indeed, recent issues for the establishment of high-performance fuel cells concern cathode materials to avoid "suffocation" of the fuel cell. For this purpose, several specific properties would be required for the cathode material, such as reversible O_2 binding from the atmosphere, a rapid release of O_2 to allow facile reduction at the electrode, and durability under strongly acidic conditions.

Cobalt complexes that reversibly bind and release O_2 in response to the O_2 concentration are candidates for O_2-enriching materials.[9] Recently, we reported that polymer–cobalt complexes efficiently acted as O_2-enriching materials, and that the current for the reduction of O_2 at a glassy carbon electrode significantly increased compared with a control electrode without the cobalt complex.[10,11] The modified electrode composed of a liquid membrane of picket-fence cobaltporphyrin in benzonitrile adsorbed at the flat surface of the glassy carbon electrode, which was placed in an aqueous buffered ($pH = 10$) electrolyte solution to prevent an irreversible oxidation of the cobalt(II) complex. Under those conditions, however, one must apply such a large overpotential of ca. 1 V to reduce O_2 that the cell voltage becomes inevitably very low. Furthermore, the liquid membrane of the organic solvent is disadvantageous in handling use for practical applications. Here, we describe that a simple tetraphenylporphyrinatocobalt(II)–benzylimidazole ([Co(tpp)(bim)]) complex, less susceptible to proton-induced decomposition and the irreversible oxidation even in strongly acidic media such as an aqueous $HClO_4$ and a Nafion membrane, can be employed as an effective O_2-enricher. We also report that a desirable system for fuel cell applications can be realized when the O_2-enriching layer is combined with the conventional Pt/C catalyst, a platinum particle embedded in a carbon particle. The [Co(tpp)(bim)] complex helps O_2 reduction by complexing O_2 from the electrolyte solution and thereby increasing the local concentration of O_2 at or near the active catalytic surface. The main evidence for this is the higher open-circuit potential and the larger reduction current of O_2 at small overpotentials in the presence of the cobalt complex. In this report, we focus on the improved performance of the modified electrode; a detailed elucidation of the mechanism of O_2 enrichment awaits future investigations.

Experimental

Materials. 5,10,15,20-Tetraphenylporphyrinatocobalt(II) ([Co(tpp)]), benzylimidazole (bim), and Nafion 117 were purchased from Aldrich Co. A platinum-embedded carbon particle (Pt/C, $\phi = 40$ nm) was obtained from Tanaka Kikinzoku Kogyo Co. Perchloric acid (70%) was purchased from Kanto Chem. Co. All solvents were purified by distillation in the usual manner prior to use.

Preparation of the Modified Electrode. Solutions of [Co(tpp)] (1.3 mg, 0.0020 mmol) in THF (0.4 mL) and bim (1.2 mg, 0.0075 mmol) in THF (0.4 mL) were mixed (1/3.8 in mol/mol) to complex the imidazolyl residue of bim with the fifth coordination site of [Co(tpp)] (Chart 1). To the resulting solution was dispersed the Pt/C catalyst (5.65 mg). The prepared dispersion (5.0 µL) was carefully transferred to the surface of a glassy carbon

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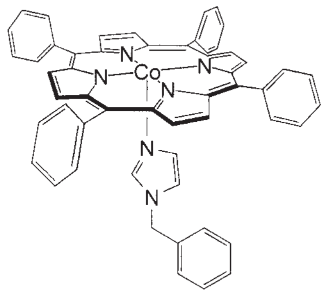


Chart 1. Tetraphenylporphyrinatocobalt(II)–benzylimidazole ([Co(tpp)(bim)]) complex.

disk electrode (0.28 cm^2), which was dried in air. Then, a solution of Nafion (0.08 mg, 5.0 µL) was transferred to the electrode surface to cover the composite layer of the catalyst and the cobalt complex. The thickness of the Nafion film was ca. 1.7 µm, which was calculated based on the amount of Nafion, the surface area of the electrode, and the density of Nafion (1.58 g cm^{-3}). After the solvent was completely removed by evaporation, the resulting modified electrode was immersed in an aqueous solution of $HClO_4$ (0.1 M) to record the open-circuit potential and the current for the reduction of O_2.

Measurements. Conventional electrochemical two-compartment cells and commercially available instrumentations were employed. The glassy carbon (GC) disk was used as the working electrode and polished before each experiment. The auxiliary electrode, a coiled platinum wire, was separated from the working solution by a fine-porosity frit. The reference electrode was a saturated calomel electrode (SCE), which was placed in the main cell compartment. The electrolyte solution was an aqueous solution of $HClO_4$ (0.1 M). The formal potential for the reduction of O_2 to H_2O was $E^f(O_2/H_2O) = 0.99$ V vs this SCE. A Nikko Keisoku DPGS-1 dual potentiogalvanostat and a Nikko Keisoku NFG-3 universal programmer were employed with a Graphtec WX 2400X-Y recorder to obtain voltammograms at room temperature.

Results and Discussion

Tetraphenylporphyrinatocobalt(II) ([Co(tpp)]) has been found to be a stable metal complex with O_2-transporting properties.[12,13] When [Co(tpp)] is complexed with bim as an axial ligand, the O_2-binding affinity of the [Co(tpp)(bim)] complex is presumed to be still low but significantly enhanced with p_{50} (partial pressure at which half of the cobalt binds O_2) of ca. 790 cmHg.[12] Remarkably, the binding and releasing of O_2 to and from the cobalt complex, determined by the laser flash photolysis, are very rapid with rate constants of 1.3×10^9 M^{-1} s^{-1} and 1.7×10^8 s^{-1}, respectively.[12] These results suggest that the O_2-binding and -releasing processes may not be the rate-determining step for the overall electroreduction of O_2.

The concentration of O_2 ($C_{O_2,x}$, where x is the distance from the electrode surface) is a function of an electrode potential equilibrated with the O_2/H_2O redox couple (i.e., $O_2 + 4e^- + 4H^+ = 2H_2O$). While a large overpotential is required to reduce O_2 at the bare surface of a glassy carbon electrode, the electrode potential of the O_2-reducing Pt/C surface is assumed to be equilibrated with the O_2/H_2O couple. In this case, the electrode potentials is approximated as

$$E = E^{0\prime} + (RT/4F)\ln C_{O_2,0} \tag{1}$$

where

$$E^{0\prime} = E^0 + (RT/F)\ln C_{H^+} - (RT/2F)\ln C_{H_2O} \tag{2}$$

Under strongly acidic aqueous conditions, $E^{0\prime}$ is assumed to be constant. The bulk concentration of O_2 ($C_{O_2,\infty}$) is reflected in the rest potential (E_r), or the open-circuit potential, and hence the shift in rest potentials (ΔE_r) accompanied by a change in the bulk O_2 concentrations from C_1 to C_2 is given by

$$\Delta E_r = (RT/4F)\ln(C_2/C_1) \tag{3}$$

Table 1 gives the rest potentials measured at a Pt/C-modified electrode immersed in an aqueous solution of $HClO_4$ saturated with argon, air, or O_2. It is known that O_2 can permeate through a Nafion membrane. Note that the potentials under argon might have been influenced by the presence of unremovable O_2 adsorbed at the electrode surface (vide infra). On the other hand, they evidently shifted positively with an increase in $C_{O_2,\infty}$. Without the cobalt complex, the potential shift of $\Delta E_r = 0.01$ V caused by the changes in electrolyte conditions from the air- to the O_2-saturated solutions is in almost agreement with the calculated value of $\Delta E_r^{calc} = 0.01$ V for $C_2/C_1 = 1/0.2$ (atm/atm) (Eq. 3), although the potentials are supposed to be lower than the equilibrated values because of the inherent slow kinetics of the electroreduction of O_2. However, the coincidence of ΔE_r with the calculated value suggests that the rest potentials are a good approximation of the equilibrium potentials due to a lack of substantial current during the measurement. Remarkably, E_r shifted more positively in the presence of the cobalt complex (Table 1), which could suggest an enhanced activity of the catalyst. We propose that the local concentration of O_2 equilibrated at the electrode ($C_{O_2,0}$) could be even higher than $C_{O_2,\infty}$ as a result of O_2 enrichment by the [Co(tpp)(bim)] complex. The enriched O_2 roughly amounts to $C_{O_2,0}/C_{O_2,\infty} \approx 100$ for a shift of $\Delta E_r = 0.03$ V in an O_2 saturated solution (Table 1). The remarkably high O_2 concentration in the enriched layer suggests that it should be very thin, which is reminiscent of the O_2 hopping mechanism from the cobalt complex

Table 1. Open-Circuit Potentials (E_r) at Modified Electrodes Immersed in an Aqueous Solution of $HClO_4$ (0.1 M) Saturated with Argon, Air, or O_2 at 20 °C

Electrode[a)]	E_r under argon (V vs SCE)	E_r under air (V vs SCE)	E_r under O_2 (V vs SCE)
GC	0.51	0.55	0.56
Pt/C on GC	0.55	0.68	0.69
Pt/C + Co on GC[b)]	0.58	0.69	0.72

a) All electrodes were coated with Nafion (see Experimental Section). b) GC electrode modified with Pt/C and the [Co(tpp)(bim)] complex.

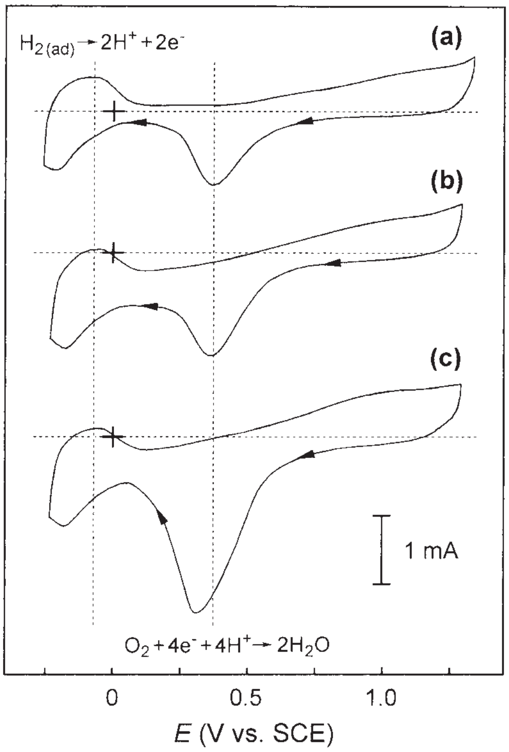


Fig. 1. (a) Cyclic voltammogram recorded for an aqueous solution of $HClO_4$ (0.1 M) using a glassy carbon disk electrode ($A = 0.28$ cm^2) modified with the Pt/C catalyst under argon. The active surface area of Pt/C determined from the amount of charge for the reoxidation of adsorbed H_2 was 5.85 cm^2. Scan rate = 25 mV s^{-1}. (b) Repeat of (a) under O_2. (c) Repeat of (a) using the electrode modified with the [Co(tpp)(bim)] complex and the Pt/C catalyst under O_2. The active surface area of Pt/C was 5.58 cm^2.

to the Pt/C catalyst, although a fuller mechanistic study was outside the scope of this study.

When a large overpotential is applied, the diffusion layer will be thicker than the enriched layer of O_2, and thus the contribution from the enriched O_2 to the overall reduction current will be overshadowed by the larger diffusion-limited mass transfer from the bulk solution. In this case, the lack of poisoning of the Pt/C surface by the cobalt complex can be assessed from the magnitude of the diffusion-limited current. For this purpose, the behavior of the modified electrode was examined by cyclic and rotating-disk voltammetry. Figure 1 shows cyclic voltammograms obtained in argon- and O_2-saturated $HClO_4$ solutions. The reduction peak near −0.2 V and the oxidation peak near −0.1 V corresponded to the reduction of protons in the Nafion membrane and the re-oxidation of hydrogen molecules adsorbed at the platinum surface, respectively. The charge consumed for the oxidation of the adsorbed hydrogen ($H_{2(ad)}$) was used to evaluate the electrochemically active surface area of the Pt particle on the electrode, assuming a value of 220 μC cm^{-2} for the oxidation of $H_{2(ad)}$ on the Pt surface.[14] Throughout voltammetric experiments, Pt/C-modified electrodes with almost the same active surface area (5.6–5.9 cm^2) were employed to allow a comparison of the electrode performance. The current for the reduction of O_2 near 0.3 V was overlapped with the peak for the reduction of the oxide layer near 0.38 V, and was gradually diminished in repeated scans as a result of a decrease in the active surface area. The presence of a reduction peak near 0.3 V in the first scan, even in the argon-saturated $HClO_4$ solution, indicates that the Pt/C catalyst is also reducing O_2 irreversibly adsorbed at the surface of the catalyst by virtue of exposure to the atmosphere during electrode preparation (Fig. 1(a)). However, the peak current increased in the O_2-saturated solution (Fig. 1(b)) and became even larger in the presence of the [Co(tpp)(bim)] complex (Fig. 1(c)). The potential for the cobalt-catalyzed reduction of O_2 is by ca. 0.4 V more negative than that for the Pt/C-catalyzed reduction, and hence the Pt/C surface reduces O_2 much faster than the cobalt complex, which means that the cobalt complex does not act as an O_2-reducing catalyst. We can only assume from the enhanced reduction current in the presence of the cobalt complex that it acts as an O_2-enriching medium.[10,11]

Current–potential curves obtained at a rotating disk electrode modified with the cobalt complex and the Pt/C catalyst at various rotation rates are shown in Fig. 2(a). The steady-state current at rotating electrodes corresponds to the flux of electroactive species transported from the bulk solution to the electrode surface, and thus does not contain any contribution from the adsorbed species. The limiting currents correspond to the amount of O_2 reduced at sufficient overpotentials, and are controlled by the diffusion-limited transport of O_2 from the bulk solution. Indeed, the limiting currents significantly increased with an increase in the rotation rate of the electrode. The limiting currents were plotted as the Koutecky–Levich plots in Fig. 2(b).[15] The number of electrons transferred during the O_2 reduction ($n = 3.5$) can be roughly evaluated from the slope of the plots by comparison with the diffusion-limited currents calculated for the two- and four-electron reduction of O_2 (dashed lines in Fig. 2(b)).[16] Note that the electrode area used is not the area of the catalyst surface, but the physical area of the electrode, because the Koutecky–Levich equation refers to the rate of O_2 transport from the bulk solution to the electrode surface. Parallel experiments using electrodes with different physical areas gave almost an identical number of electrons transferred for the O_2 reduction, suggesting that almost all of the electrode surface was successfully covered with the catalyst. The limiting currents were almost identical to, or slightly larger than, those obtained without the cobalt complex, indicating that at least the cobalt complex does not poison the Pt/C catalyst. The relatively small kinetic current in Fig. 2(b) also indicates that the cobalt complex does not impede the catalysis of O_2 reduction by the Pt/C surface. On the other hand, the very small dependence of the current on the electrode rotation rate at smaller overpotentials is considered to arise from the O_2 enrichment effect. This effect is more clearly shown in the steady-state polarization curves in Fig. 3 (vide infra).

The polarization curves for the kinetically limited steady-state currents at the rotating disk electrode for the reduction of O_2 at small overpotentials, normalized by the active surface area of the Pt/C catalyst, are shown in Fig. 3. When mass transport and electron transfer occur in series, the rates of both processes must be the same at steady state. Thus, for the case where electron transfer at the electrode surface is the rate-limiting process,

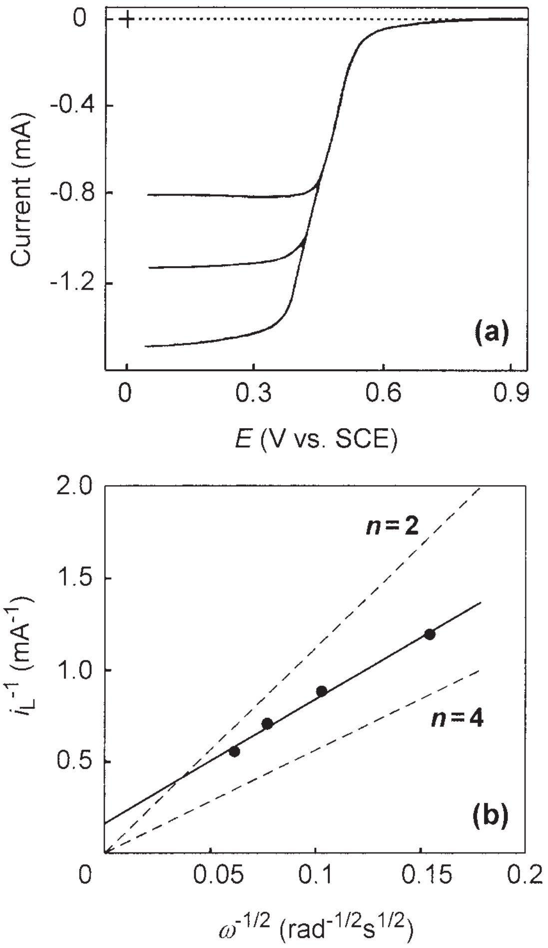


Fig. 2. (a) Current–potential curves for the reduction of O_2 obtained with the rotated glassy carbon electrode modified with the [Co(tpp)(bim)] complex and the Pt/C catalyst. The active surface area of Pt/C was 5.58 cm^2. The electrolyte solution was an O_2-saturated aqueous $HClO_4$ (0.1 M). Electrode rotation rate was 400, 900, and 1600 rpm. Scan rate = 5 mV s^{-1}. (b) Koutecky–Levich plots of the plateau currents in (a) versus (electrode rotation rates)$^{-1/2}$. Dashed lines represent the diffusion limited currents for the two- ($n = 2$) and four-electron ($n = 4$) reduction of O_2 calculated using $D = 2.9 \times 10^{-5}$ cm^2 s^{-1}, $C = 1.3 \times 10^{-6}$ mol cm^{-3}, v (kinetic viscosity) = 0.01 cm^2 s^{-1}, and A = 0.28 cm^2.

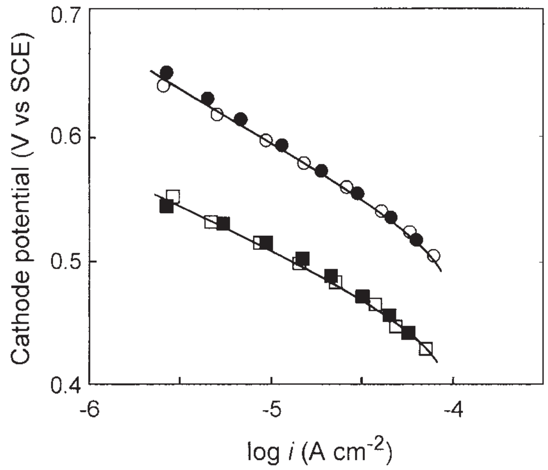
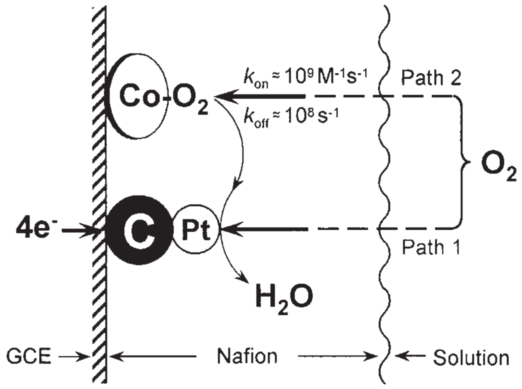


Fig. 3. Steady-state polarization curves for O_2 reduction on rotated modified electrodes recorded in an O_2-saturated aqueous solution of $HClO_4$ (0.1 M). The electrode was a glassy carbon disk modified both with the [Co(tpp)(bim)] complex and the Pt/C catalyst with the active surface area of 5.85 cm^2 (●), or the disk modified only with the Pt/C catalyst with the active surface area of 5.58 cm^2 (■). Open circles (○) and squares (□) represent plots of data obtained from repeated experiments using the same Pt/C-modified electrodes with and without the [Co(tpp)(bim)] complex, respectively. Electrode rotation rate = 900 rpm.



Scheme 1.

$$k_{ET}C_{O_2,0} = i/nFA \tag{4}$$

where k_{ET} is a heterogeneous rate constant as a function of the electrode potential. In this case, the effect of O_2 enrichment by the cobalt complex can be manifested in the magnitude of the current. The presence of the cobalt complex led to a significant increase in the current density at a given potential, as shown in Fig. 3. The larger steady-state current means that the transport of O_2 to the Pt/C surface can be facilitated both by the very rapid binding and releasing of O_2 at the cobalt center and by the high carrier concentration at the electrode surface. Thus, the cobalt complex provides another path for O_2 transport (path 2 in Scheme 1), in addition to diffusion from the bulk solution (path 1). The highly reproducible values of the current, even after prolonged electrolysis, indicated that the cobalt–Pt/C system is sufficiently stable under these electrolyte conditions. The similarity of the linear region and the slope of the plots to those obtained without the cobalt complex confirms that the cobalt complex does not take part in the catalysis at small overpotentials, but contributes only to increase $C_{O_2,0}$.

Conclusion

The [Co(tpp)(bim)] complex that reversibly binds and releases O_2 functions as an O_2-enriching medium for cathodes to enhance the current for the reduction of O_2. A combination of the conventional Pt/C catalyst and the O_2 enricher resulted in a significant positive shift in the open-circuit potential, which reflected the larger O_2 concentration equilibrated at the electrode. An increase in the current for the reduction of O_2 was established, particularly at small overpotentials where typical fuel cells operate, based on the O_2 enrichment effect of the cobalt complex without poisoning of the Pt/C catalyst.

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