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The Catalytic Electroreduction of Dioxygen on Iron Protoporphyrin IX Modified Glassy Carbon Electrodes

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The catalytic electroreduction of dioxygen at iron(III) protoporphyrin IX (hemin) modified glassy carbon electrodes was investigated in an aqueous solution within the pH range 1—13. The reduction potential of dioxygen on a hemin chemically modified electrode was more anodic than that on a hemin adsorbed electrode by a few tens of mV. The results of rotating disk and ring-disk voltammetric measurements indicated that the oxygen molecule is reduced via a one-step reduction accompanying four-electron and four-proton transfer at pH<11, and via two successive reductions accompanying two-electron transfer and, subsequently, two-electron and four-proton transfer at pH>12. The quantity of peroxide formation at hemin-adsorbed electrodes decreased with increasing pH, up to 10, and then increased with increasing pH beyond 12. The possible overall mechanisms for the catalytic reduction of dioxygen are described.

The catalytic electroreduction of dioxygen has been extensively studied in conjunction with a number of applied aspects of electrochemistry.[1)] Metal macrocyclic complexes, such as iron and cobalt porphyrins,[2—18)] iron and cobalt phthalocyanines[3,16—22)] and dicobalt cofacial porphyrins[23—25)] have interested many researchers. The majority of authors have reported that the overall oxygen reduction on electrodes modified with macrocyclic complexes had been proceeded via a so-called electrochemical regeneration mechanism,[8)] although there have been many discussions concerning the reduction routes of dioxygen.

We have been interested in preparing efficient, stable electrodes modified with iron porphyrin[14,17)] and phthalocyanine[22)] complexes. In this paper we report on an electrochemical study concerning the catalytic dioxygen reduction on glassy carbon electrodes modified by iron protoporphyrin IX (hemin). Hemin is expected to be a good model compound for developing new applications to catalytic electrochemical reactions, since hemin is less expensive than synthesized metalloporphyrins and has functional vinyl and caboxy groups at the porphyrin periphery.

Experimental

Materials and Modification of Glassy Carbon Electrodes. The water-soluble carbodiimide hydrochloride (WSCD · HCl, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride) used for the dehydration procedure[14)] was obtained from the Peptide Institute, Inc. (Osaka). The catalase used was Sigma type C-100. All the other chemicals of guaranteed reagent grade (Wako Pure Chemical Industries) were used without further purification.

The working electrodes used for cyclic or rotating disk voltammetry were prepared by inserting a glassy carbon rod (GC-30, Tokai Carbon, Ltd.) into a Teflon tube to give an exposed disk of ca. 0.23 cm^2 area. The rotating ring(Pt)-disk(GC-30) electrode (RRDE, Nikko Keisoku) was used to detect an intermediate or by-product formed in the reduction of oxygen. The value of the collection efficiency (N) of this RRDE was determined in a 1.0×10^{-3} mol dm^{-3} $K_3[Fe(CN)_6]$ aqueous KCl (0.1 mol dm^{-3}) solution, and was 0.39 (±0.005) at various rotation rates (150—2500 rpm).

The mechanical and chemical treatments for the preparation procedure of a chemically modified electrode and an adsorbed electrode are reported in a reference,[14)] except for the following procedures regarding modification. Dehydration condensation of hemin to an electrode surface covered with the hydroxyl group was carried out by immersing the GC electrode in a stirred dichloromethane solution containing 1.2×10^{-4} mol dm^{-3} hemin and 7.5×10^{-3} mol dm^{-3} WSCD · HCl for one hour at room temperature. This chemically modified electrode was then immersed in 0.1 mol dm^{-3} $NaHCO_3$ and stirred slowly for 10 min in order to remove any adsorbed dehydration agent and hemin from the surface. A hemin-adsorbed electrode was prepared by applying of drops of 25 μl of 8.0×10^{-5} mol dm^{-3} hemin in a 0.02 mol dm^{-3} NH_3 aqueous solution with a microsyringe, and drying in a desiccator for over 3 h. A newly adsorbed electrode was washed in a basic electrolytic solution of pH 8. The former chemically modified electrode is abbreviated as GC–O–Hemin, and the latter adsorbed electrode as GC · Hemin.

Electrochemical Measurements. Cyclic voltammetric measurements were performed using a Nikko Keisoku NPGFZ-2501-A potentiogalvanostat. For rotating disk voltammetry, a Nikko Keisoku DPGS-1 potentiogalvanostat, an NPS-2 potential sweeper, an RRDE-1 rotator, and an SC-5 speed controller were used.

The dioxygen reduction experiments were carried out in air-saturated solutions. All of the potentials are given with respect to a saturated calomel electrode (SCE).

The buffer solutions, which also served as supporting electrolytes, were prepared from acetate, phosphate, borate, and glycine. The pH adjustment was achieved by using H_2SO_4 and/or NaOH; the ionic strength was adjusted at 0.1 mol dm^{-3} with Na_2SO_4. The pH of solutions was measured with a Toa HM-20S pH meter. All of the measurements were performed at 25 °C.

Results and Discussion

Cyclic Voltammetry. Figure 1 shows some typical

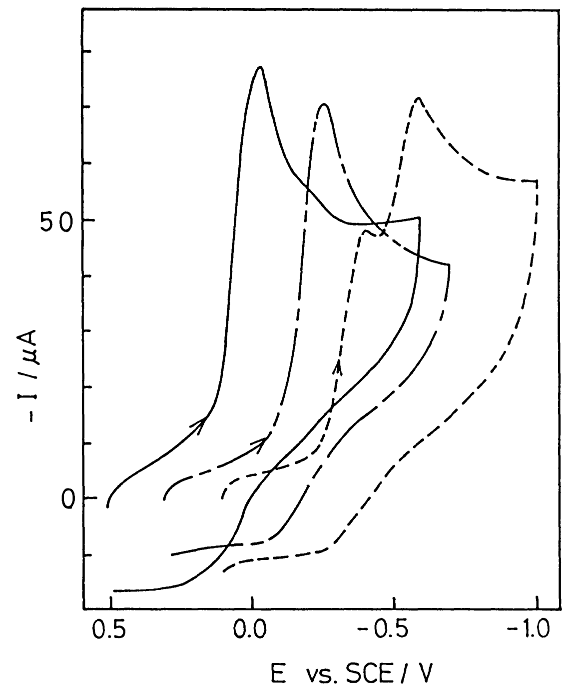

Fig. 1. Cyclic voltammograms for dioxygen reduction on a GC–O–Hemin chemically modified electrode in air-saturated solutions. —: pH 2.43,— — —: pH 8.06, ----: pH 12.57.

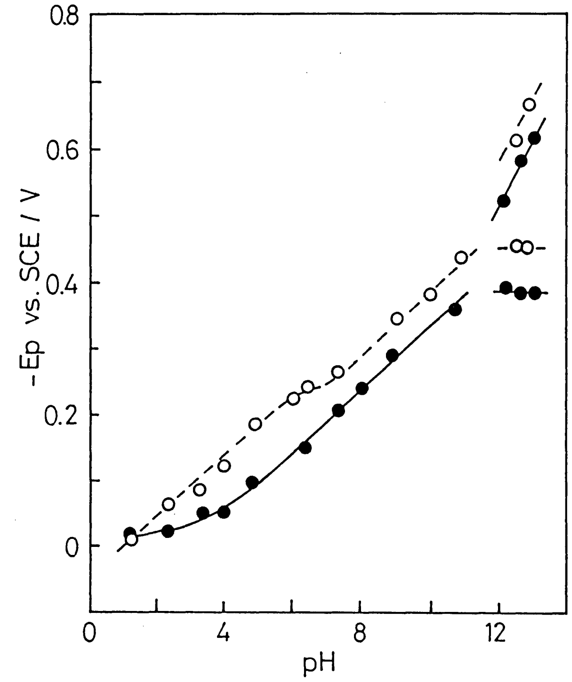

Fig. 2. pH dependence of the peak potential for dioxygen reduction. ●: on GC–O–Hemin, ○: on GC • Hemin.

cyclic voltammograms measured on GC–O–Hemin chemically modified electrodes in air-saturated aqueous solutions of various pH. Similar cyclic voltammograms were also obtained on GC • Hemin adsorbed electrodes in aqueous solutions. The shapes of the cyclic voltammograms observed on hemin-modified electrodes were almost the same as those on [tetrakis(4-carboxyphenyl)porphinato]iron(III), [Fe$^{\mathrm{III}}$(tcpp)]$^+$, modified electrodes,14) except for a small difference in the peak potential. A discrete, successive two-step reduction wave was observed in a high pH solution (pH>12), especially remarkable on a chemically modified electrode; however, only one current peak was observed in solutions of pH<11.

Two different dependences of the peak potential (open circle: GC • Hemin; solid circle: GC–O–Hemin) on the pH of the solutions are shown in Fig. 2. The peak potential shifts with a slope of ca. −55 mV/pH in the pH range 5—11 on GC–O–Hemin electrodes. Two successive reduction peaks at pH>12 shift with slopes of 0 mV/pH and ca. −110 mV/pH, respectively. Nernstian theory indicates that dioxygen reduction was achieved by the addition of one proton per one electron at pH 5—11; on the other hand it was achieved by an electron addition reaction only, followed by the reduction of a two-proton addition per one-electron addition at pH>12. The peak potential on the GC–O–Hemin electrode at pH<5 gradually shifted from a straight line over the range 5<pH<11 to the peak potential observed on the GG • Hemin electrode. This phenomenon implies that some ester bondings in the GC–O–Hemin electrodes were broken by the action of acid, and that the degree of bond-breaking depends on the pH of solutions.

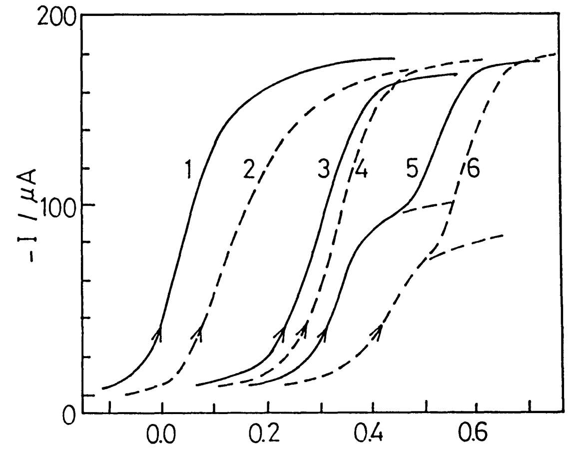

Fig. 3. Current-potential curves for dioxygen reduction on rotating modified electrodes. —: GC–O–Hemin; ----: GC • Hemin. 1,2: pH 4.02; 3,4: pH 8.98; 5,6: pH 12.80. Rotation rate: 500 rpm; potential sweep rate: 20 mV s^{-1}.

Figure 2 also shows that the pH dependence of the reduction potential of dioxygen on a GC • Hemin electrode is more cathodic than that on a GC–O–Hemin electrode by a few tens of mV, suggesting a higher energy barrier for electron transfer on the GC • Hemin

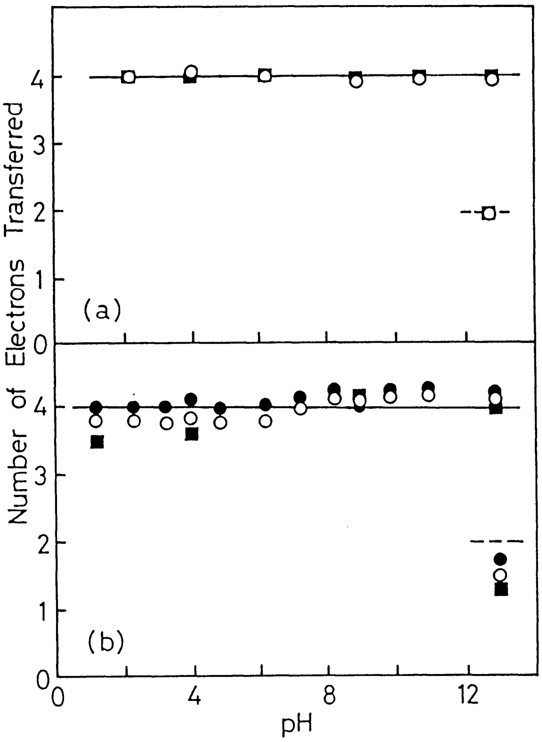

Fig. 4. Number of electrons transferred for dioxygen reduction on rotating modified disk electrodes as a function of the pH. (a) GC–O–Hemin electrode, (b) GC • Hemin electrode. —: one step or total number; ----: the first step of two steps. Rotation rates (rpm): ● 250, ○ 500, and □ 1000.

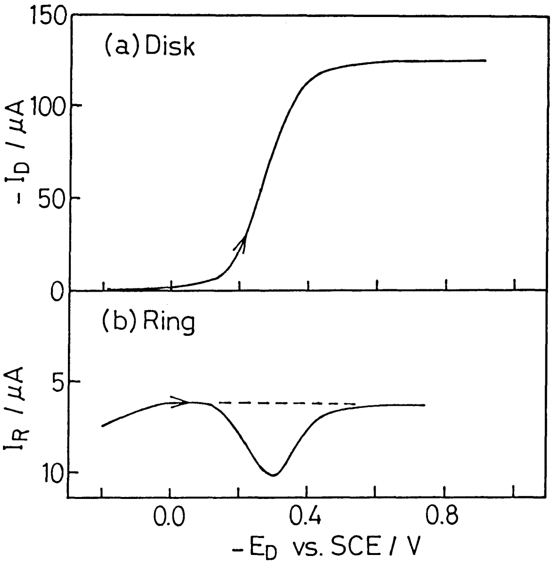

Fig. 5. Rotating ring(Pt)-disk(GC • Hemin) voltammogram of an air-saturated solution of pH 6.23. The ring potential was 0.59 V, the scan rate of disk potential (E_D) 20 mV s^{-1}, and the rotation rate 250 rpm.

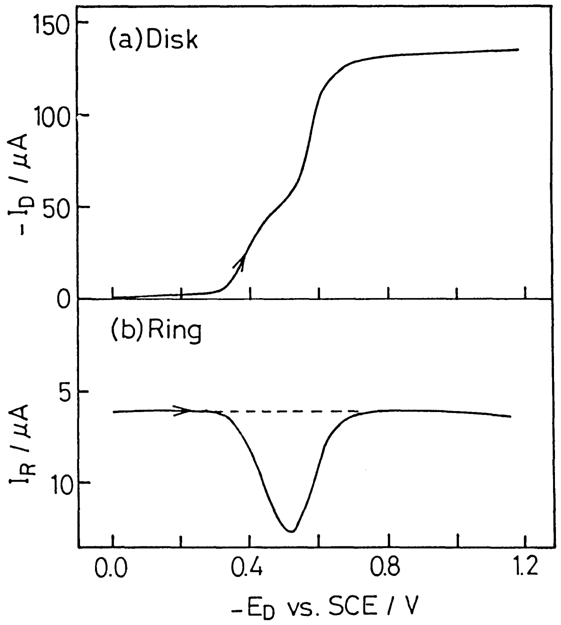

Fig. 6. Rotating ring(Pt)-disk(GC • Hemin) voltammogram of an air-saturated solution of pH 12.67. The ring potential was 0.11 V, the scan rate of disk potential (E_D) 20 mV s^{-1} and the rotation rate 250 rpm.

electrode. Furthermore, the pH dependence line on the GC • Hemin electrode has a transfer region within the range of pH 6—7. The appearance of a transfer region within this pH range must be ascribed to the dissociation of the carboxyl group of adsorbed hemin molecule.[17,22] These observations suggest that the electron predominantly passes through the linkage between the carboxy group of hemin and GC surface.

Rotating Disk Voltammetry. Rotating disk voltammetric measurements (RDE) were carried out in order to estimate the number of transferred electrons in dioxygen reduction on both chemically modified and adsorbed electrodes. Some typical voltammograms are shown in Fig. 3. In RDE experiments, the shapes of the hydrodynamic voltammograms observed on hemin-modified electrodes are also almost same as those on a [Fe^{III}(tcpp)]$^+$ modified electrode.[14] The number of transferred electrons was calculated using the Levich equation from the limiting current of these voltammograms. The values of the parameters used in the calculation were the same as those used in a previous study.[14] The relationships between the number of transferred electrons and the pH of solutions are shown in Fig. 4. The oxygen molecule was reduced on both modified electrods via a continuous transfer of four electrons at pH<11, and via two successive reactions, each of which comprised a two-electron transfer at pH>12. The reduction mechanism of dioxygen on GC • Hemin adsorbed electrodes is therefore essentially the same as that on GC–O–Hemin chemically modified electrodes, except that the potential on the former electrode was more cathodic than that on the latter one, as is shown in Figs. 2 and 3.

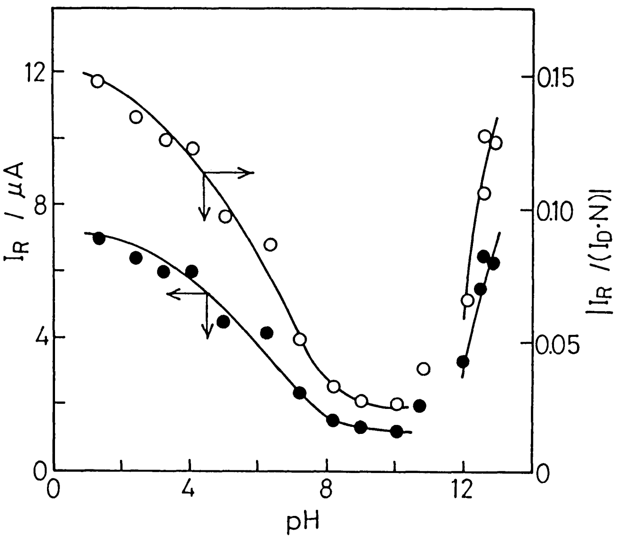

Fig. 7. pH dependence of the ring current (I_R, ●) and ratio of peroxide released from the disk electrode to dioxygen reduction (○).

Rotating Ring-Disk Voltammetry. Rotating ring-disk voltammetric measurements were carried out in order to detect intermediate species using a ring-disk electrode having a GC • Hemin adsorbed disk. Figures 5 and 6 show typical ring-disk voltammograms in both neutral and basic solutions. Hydrogen peroxide was reported as being either an intermediate or initial product of dioxygen reduction on both metalloporphyrin and metallophthalocyanine adsorbed electrodes.[1] The ring electrode was set at a potential corresponding to the diffusion-limiting value for peroxide oxidation. Although a relatively large residual current was observed at the Pt-ring electrode, the peak current is a measure of the rate of peroxide generation on the disk electrode. Maximum formation of the intermediate was observed at the increasing part of the disk current for both $\mathrm{pH}<11$ (Fig. 5) and $\mathrm{pH}>12$ (Fig. 6). It was no longer detectable at a greater cathodic potential, i.e. at the plateau of disk current waves.

Figure 7 (solid circle) shows the reoxidation current of formed peroxide as a function of the pH. The ratio of peroxide formation to dioxygen reduction was calculated using the collection efficiency (N) of the RRDE (Fig. 7, open circle). Figure 7 shows that the quantity of peroxide formed on the disk electrode decreased with increasing pH up to ca. pH 10, and then increased with increasing pH at $\mathrm{pH}>12$, indicating that the reduction mechanism of dioxygen markedly differed at around pH 11. That is, the reduction of dioxygen on the hemin-modified electrode occurs more effectively at $9<\mathrm{pH}<10$. Figure 8 shows the effect of the addition of catalase on the ring current. The ring peak current was no longer detectable by the addition of a small amount of catalase (7.4×10^{-7} mol dm^{-3}). This result indicates that the intermediate species of dioxygen reduction is undoubtedly peroxide.

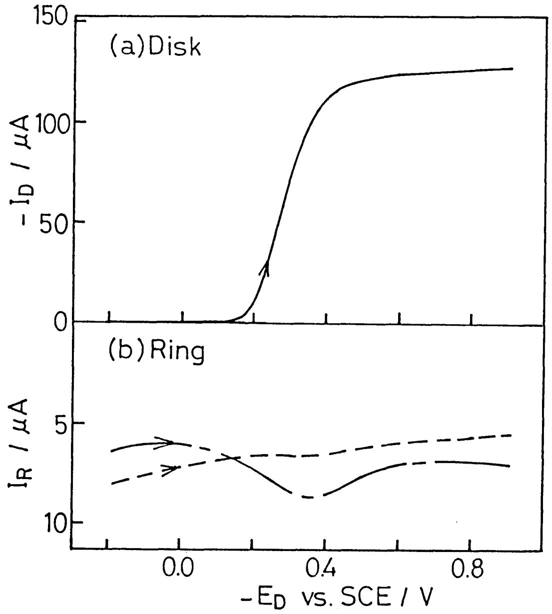

Fig. 8. Rotating ring(Pt)-disk(GC • Hemin) voltammograms in a catalase-added air-saturated solution of pH 7.20. The ring potential was 0.53 V, the scan rate of disk potential (E_D) 20 mV s^{-1}, and the rotation rate 250 rpm. [Catalase]/ 10^{-7} mol dm^{-3}: ———1.5, ----7.4 [O_2]: 2.4×10^{-4} mol dm^{-3}.

Conclusion

The reduction of dioxygen on iron(III) protoporphyrin IX modified electrodes can be summarized as proceeding via the so-called EC catalytic regeneration mechanism.[8] At $\mathrm{pH}<11$, the modified iron(III) protoporphyrin IX molecules were reduced to the iron(II) species (Eq. 1); then, the iron(II) species were regenerated to the iron(III) species according the reduction of dioxygen to water (Eq. 2):

$$\mathrm{Fe(III)\cdot P} + e^- \longrightarrow \mathrm{Fe(II)\cdot P} \qquad (1)$$

and

$$4\mathrm{Fe(II)\cdot P} + \mathrm{O_2} + 4\mathrm{H^+} \longrightarrow 4\mathrm{Fe(III)\cdot P} + 2\mathrm{H_2O}. \qquad (2)$$

Here, Fe(III) • P and Fe(II) • P represent iron(III) and iron(II) protoporphyrin IX, respectively.

On the other hand, at $\mathrm{pH}>12$, the iron(II) protoporphyrin IX (Eq. 1) reduces dioxygen to peroxide ion (Eqs. 3, 4, 5, and 6) at the reduction potential of the first peak. Most of the peroxide ions formed become strongly bound to the axial position of iron(III) protoporphyrin IX fixed on the glassy carbon:

$$\mathrm{Fe(II)\cdot P} + \mathrm{O_2} \longrightarrow \mathrm{Fe(III)\cdot P\text{-}O_2^-}, \qquad (3)$$

$$\mathrm{Fe(III)\cdot P\text{-}O_2^-} + e^- \longrightarrow \mathrm{Fe(II)\cdot P\text{-}O_2^-}, \qquad (4)$$

$$\mathrm{Fe(II)\cdot P\text{-}O_2^-} \longrightarrow \mathrm{Fe(III)\cdot P\text{-}O_2^{2-}}, \qquad (5)$$

$$\mathrm{Fe(III)\cdot P\text{-}O_2^{2-}} + e^- \longrightarrow \mathrm{Fe(II)\cdot P\text{-}O_2^{2-}}, \qquad (6)$$

and

$$2\mathrm{Fe(II)\cdot P\text{-}O_2^{2-}} + 2\mathrm{H_2O} \longrightarrow \mathrm{Fe(III)\cdot P} + 4\mathrm{OH^-}. \qquad (7)$$

Then, a further reduction of peroxide ions (Eq. 7) to hydroxide ions occurred at the second peak potential (transport of two electrons and four protons per one peroxide ion). A small amount of peroxide ions was released into the solution prior to the second reduction (depending on the solution pH) by rotating the electrode, and then re-oxidized at the ring electrode.

The reduction mechanism of dioxygen in an aqueous solution on an iron protoporphyrin IX modified electrode is approximately the same as that on a $[Fe^{III}(tcpp)]^+$ modified electrode,[14] but differs from that on a [tetrakis(4-carboxy)phthalocyanato]iron(III) modified electrode.[22]

The iron protoporphyrin IX chemically modified electrode can be applied to the electrochemical technology of redox enzymes, since iron protoporphyrin IX is the redox center of many charge-transfer proteins, such as cytochromes.

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