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CATALYTIC ELECTROREDUCTION OF MOLECULAR OXYGEN AT GLASSY CARBON ELECTRODES MODIFIED WITH IRON PORPHYRINS

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The reduction of molecular oxygen (O_2) at glassy carbon surfaces modified with iron porphyrins was studied by cyclic voltammetry and differential pulse polarography in 0.05 mol dm^{-3} aqueous H_2SO_4 solution. O_2 was reduced more effectively at the electrode modified with iron porphyrin lying in parallel to the electrode surface than at the one with iron porphyrin protruding vertically from the surface.

In view of the increasing need for catalysts in the electroreduction of O_2, the metal macrocyclic compounds, in particular the iron and cobalt phthalocyanines and porphyrins, have received a great deal of attention.$^{1)}$ Especially, these compounds chemically bound or adsorbed on glassy carbon (GC) electrodes have been in common use, and the information about their catalytic capability for O_2 reduction has been accumulated.$^{2,3)}$

Surface roughness, thickness (multilayer or monolayer) or density (coverage), and orientation of catalysts on the electrode, all these factors, independently or *cooperatively, may affect* the catalytic activity for the O_2 reduction. We used several kinds of iron porphyrins of a similar structure to modify GC electrode chemically, and compared their cyclic voltammetric waves for O_2 reduction.

Pretreatment of GC (0.785 cm^2, Tokai Carbon, GC-20) used as the working electrode consisted of polishing one side with fine emery paper and alumina until mirror-like finish. As candidates of metal macrocyclic complexes to be immobilized on GC surface, iron complexes of the following porphyrins were prepared and covalently bound to the electrode surface by means of the conventional method$^{2,4,5)}$: *meso*-tetra(*o*-aminophenyl)porphyrin (Fe^{III}T*o*APP)$^{6)}$, *meso*-α(*o*-aminophenyl)-β, γ, δ-triphenylporphyrin

($\mathrm{Fe^{III}}$*o*ATPP),[7] and *meso*-α(*p*-aminophenyl)-β, γ, δ-triphenylporphyrin ($\mathrm{Fe^{III}}$*p*ATPP). $\mathrm{Fe^{III}}$*p*ATPP was obtained by hydrolyzing the corresponding monoacetoaminophenyltriphenylporphyrin which was synthesized from *p*-acetoaminobenzaldehyde, benzaldehyde, and pyrrole by the Adler-Longo mixed condensation procedure.[8]

The cyclic voltammograms (*i*-*E* curves) were recorded at various scan rates (v) for $\mathrm{Fe^{III}}$*o*ATPP-modified GC in a 0.05 mol $\mathrm{dm^{-3}}$ H_2SO_4 solution saturated with N_2 or O_2 (air). The *i*-*E* curves were quite similar to those observed for $\mathrm{Fe^{III}}$T*o*APP[2] dissolved in 0.05 mol $\mathrm{dm^{-3}}$ H_2SO_4 and, therefore, the overall reaction was recognized to proceed *via ec catalytic* regeneration mechanism as expressed in eqns. (1) and (2).

$$\mathrm{Fe^{III}}o\mathrm{ATPP} + e \underset{}{\overset{E^{\circ\prime}}{\rightleftharpoons}} \mathrm{Fe^{II}}o\mathrm{ATPP} \tag{1}$$

$$\mathrm{Fe^{II}}o\mathrm{ATPP} + (1/2)O_2 + H^+ \longrightarrow \mathrm{Fe^{III}}o\mathrm{ATPP} + (1/2)H_2O_2 \tag{2}$$

where $\mathrm{Fe^{III}}$*o*ATPP is reduced at GC electrode and the electrogenerated $\mathrm{Fe^{II}}$*o*ATPP is reoxidized rapidly with O_2 to $\mathrm{Fe^{III}}$*o*ATPP. Typical *i*-*E* curves for the reduction of O_2 at $\mathrm{Fe^{III}}$*o* ATPP- and $\mathrm{Fe^{III}}$*p*ATPP-modified GC electrodes are shown in Fig.1 (A) and (B), respectively. Though the electrodes were pretreated and modified with iron porphyrins under the identical conditions, a certain difference was observed in the height of O_2 reduction peak (i_p) around -0.1 V especially at higher scan rates. The

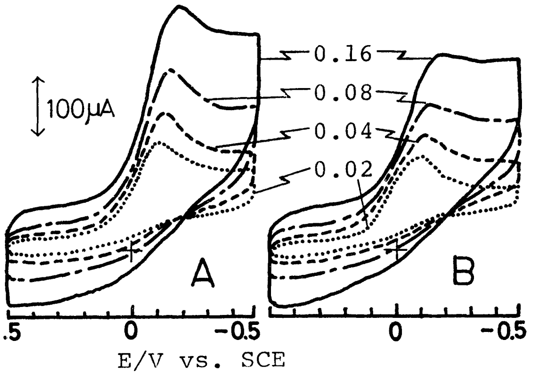

Fig.1 *i*-*E* diagrams at porphyrin modified GC electrodes in air-saturated 0.05 mol $\mathrm{dm^{-3}}$ H_2SO_4 solution; $\mathrm{Fe^{III}}$*o*ATPP-(A) and $\mathrm{Fe^{III}}$*p*ATPP-modified(B). Numbers indicate scan rates in V $\mathrm{s^{-1}}$. Measurement was carried out from low to high scan rates.

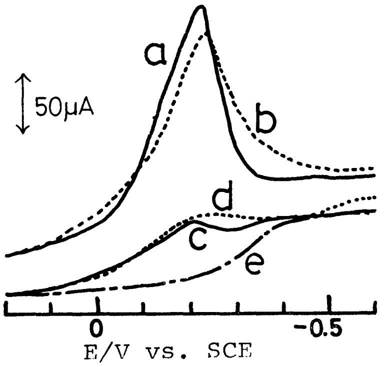

Fig.2 Differential pulse polarograms for $\mathrm{Fe^{III}}$-*o*ATPP-(———) and $\mathrm{Fe^{III}}$*p* ATPP-modified(-----) GC electrodes in air- (a and b) and N_2-saturated (c - d) 0.05 mol $\mathrm{dm^{-3}}$ H_2SO_4 solutions. Curve e is that for non-modified GC.

cyclic voltammetric behavior of Fe^{III}*o*ATPP resembled that of Fe^{III}T*o*APP-bound GC electrode,[2)] where Fe^{III}T*o*APP is bound to GC by two amide linkages.[9)] The slope of i_p *vs.* $v^{\frac{1}{2}}$ plot was that expected for a two-electron, diffusion controlled reduction of O_2 to H_2O_2. The peak height for Fe^{III}*o*ATPP-modified electrode was larger than that exhibited by Fe^{III}*p*ATPP-modified electrode at a fixed scan rate, whereas the differential pulse polarograms in N_2-saturated solution (Fig.2 curves c and d) were almost the same. And the cathodic peak potentials at Fe^{III}*o* ATPP-bound electrode (Fig.2, curves a and c) were more positive in both N_2- and air-saturated solutions than those at Fe^{III}*p*ATPP-bound electrode.

As mentioned earlier, several factors may influence on cyclic voltammetric curves. First, surface roughness relates to the background current; the rougher, the larger. However, the difference of contribution from the background current may be neglected when the waves in Fig.1 (A) and (B) are compared at fixed scan rates, since GC electrodes showed nearly identical cyclic voltammograms when porphyrins were not immobilized (see Fig.2 in ref.2). The second factor is the thickness or density of the porphyrin on the electrode. In this connection, the possibility of multilayer coating seems to be small, for both Fe^{III}*o*ATPP and Fe^{III}*p*ATPP are monofunctional (NH_2 group) porphyrins and the electrodes modified with these porphyrins were well rinsed after chemical immobilization. Besides, densities of Fe^{III}*o* ATPP and Fe^{III}*p* ATPP on electrode do not seem to be much different from each other as seen from curves c and d in Fig.2.

The third factor, which appears the most important, is the orientation of porphyrins at the GC surface. Now that porphyrins are large molecules with a flat structure, there will be a considerable difference in the distance between the electrode surface and the iron active centers depending on whether porphyrins attach vertically or in parallel to the GC surface. Electrons will be easily transferred if the distance is shorter. The Corey-Pauling-Koltun molecular models suggest that Fe^{III}*o*ATPP cannot attach vertically while Fe^{III}*p*ATPP cannot be bound in parallel to the GC surface (Fig.3 A and B, respectively). It is also conceivable that the easiness for O_2 molecule to approach the vicinity of the active centers by diffusion might be different; if the porphyrin molecules are bound vertically to the GC surface, particularly with a high density, then the access of O_2 molecules will be more difficult than in the case

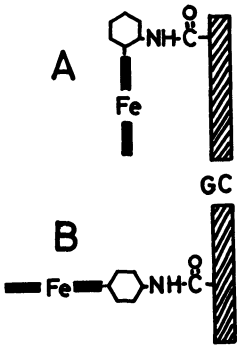

Fig.3 The ideal schematic orientations of (A); Fe^{III}*o*ATPP and (B); Fe^{III}*p* ATPP on the GC surface.

the porphyrins attach in parallel to the GC surface. If the porphyrins are bound to the GC surface of unevenness of several angstroms or several tens of angstroms, the effects of the orientation on the catalytic activity may not be so simple. But the difference in the peak current (Fig.1) seems to reflect, at least partly, these effects.

The present results, thus, suggest that the orientation of the porphyrin molecules is an important factor which governs the catalytic activity for the O_2 reduction and that the parallel, i.e., face (porphyrin) to face (GC electrode), orientation is more favorable. It will be possible to regulate catalytic efficiency by designing the spatial structure of catalyst at the electrode surface.

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