Electrocatalytic Reduction of Dioxygen to Water by a Carbon Electrode Coated with (*μ*-Oxo)bis[(*meso*-tetraphenylporphyrinato)iron(III)]: a Convenient Template for Cofacially Oriented Iron(II) Porphyrins

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(Received November 5, 1997; CL-970846)

Electroreduction of an oxo-bridged iron(III) porphyrin dimer adsorbed on an electrode surface produced solid state, cofacially fixed two iron(II) porphyrin molecules when immersed in aqueous acid, allowing an efficient catalysis of the four-electron reduction of O_2 to H_2O.

Herein we report that *μ*-oxo-bridged metalloporphyrin dimers could be versatile and convenient electrocatalysts for the four-electron reduction of O_2. The recent extensive studies on the electroreduction of O_2 envolved a wide variety of metal complexes that can be used as catalysts when immobilized at the electrode surface.[1] The catalyzed reaction can proceed by a two-electron pathway to produce H_2O_2 or by a net four-electron pathway to yield H_2O. The reductive cleavage of O=O bond by a four-electron, four-proton reaction provides not only a clean energy transformation process relevant to the biological respiratory systems[2,3] but also a redox system for the O_2-oxidative polymerization of organic molecules.[4-7] The recent topics also involve application of such catalysts to fuel cell technologies. To enhance the rate of the electroreduction of O_2, metalloporphyrins have frequently been employed as catalysts. The typical examples are provided by mononuclear cobalt porphyrins[8] and iron porphyrins[9,10] which reduce O_2 to H_2O_2 predominantly. Dicobalt cofacial porphyrins[11,12] are among the few electrocatalysts which are able to promote the direct reduction of O_2 to H_2O by a four-electron mechanism in acidic media where O_2 molecule is supposed to coordinate to form a μ-peroxo bridge between the two cobalt centers allowing subsequent scission of the O-O bond. However, the cofacial diporphyrin complexes are usually difficult to synthesize and only given in a low yield.

The electrocatalytic behavior of a *μ*-oxo iron(III) porphyrin dimer was investigated by cyclic voltammetry. The dotted curve in Figure 1(a) shows the typical steady-state current-potential responses obtained at a glassy carbon electrode in argon saturated aqueous acid when (*μ*-oxo)bis[(*meso*-tetraphenylporphyrinato)iron(III)] ([Fe(TPP)]$_2$O) is adsorbed on the electrode surface. When the electrode was transferred to an O_2 saturated solution, a large catalytic current appeared near -0.2 V as shown by the solid curve. The presence of a quasi-reversible voltammetric response near 0.3 V is a feature common to all carbon electrodes. The third peak near -0.5 V corresponded to the direct reduction of O_2 at an uncoated portion of the carbon electrode.

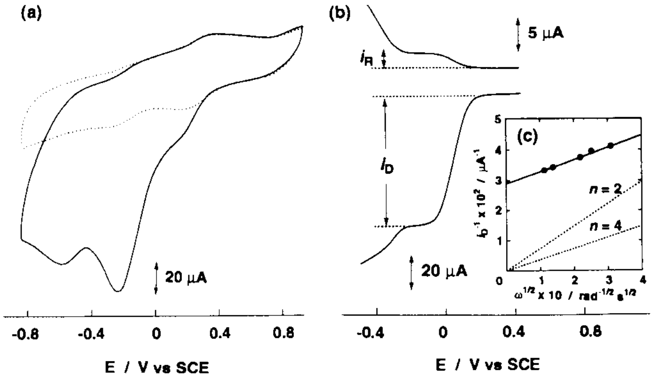


Figure 1. (a) Cyclic voltammetry of [Fe(TPP)]$_2$O adsorbed on a glassy carbon electrode; the dotted curve was recorded under Ar and the solid curve under O_2. The 6mmϕ disk electrode was coated using the 0.005 cm^3 toluene solution of 0.1 mmol dm^{-3} [Fe(TPP)]$_2$O. Supporting electrolyte: 0.5 mol dm^{-3} $HClO_4$ + 0.1 mol dm^{-3} NH_4PF_6. Scan rate: 50 mV s^{-1}. (b) Rotating ring-disk voltammogram in the same solution using a platinum ring-glassy carbon disk electrode recorded under O_2. The disk was coated with [Fe(TPP)]$_2$O. Ring potential was at 1.1 V. Electrode rotation rate: 500 rpm. (c) Koutecky-Levich plots for the reduction of O_2 at rotating disk electrode coated with [Fe(TPP)]$_2$O. The dashed lines are calculated for a four-electron and two-electron, convection-diffusion-limited reduction of O_2, respectively.

A quantitative kinetic data of the electroreduction of O_2 by [Fe(TPP)]$_2$O was obtained by means of rotating disk voltammetry (Figure 1(b)). The slope of the Koutecky-Levich plots (Figure 1(c))[13] corresponded to the value of n = 3.7 (n = number of electrons transferred), which means that the electrocatalytic reduction of O_2 resulted in the formation of H_2O by a four-electron transfer process. It is also supported by the collection experiments of H_2O_2 at a ring electrode. The voltammograms obtained with a rotating platinum ring-glassy carbon disk electrode under the same electrolyte conditions are shown in Figure 1(b), where the platinum ring was maintained at 1.1 V to oxidize the H_2O_2 generated by the reduction of O_2 at the disk. Comparison of the observed collection efficiency with the intrinsic value of the electrode (N_0 = 0.36) which was determined in independent experiments with $Fe(CN)_6^{3-/4-}$ couple revealed that [Fe(TPP)]$_2$O resulted in a catalysis to reduce most of the O_2 by four electrons. The ratio of the ring to disk currents in Figure 1(c) ($N = i_R/i_D$ = 0.026), normalized for the collection efficiency of the ring $((N_0\text{-}N)/(N_0+N))$, corresponds to the reduction of 87% of the O_2 molecules to H_2O. The value of N showed virtually no dependence on the electrode rotation rate, which indicate that a small amount of H_2O_2 is formed not as an intermediate but as a parallel side product in O_2 reduction. The selectivity for the four-electron pathway is in good agreement with the value expected on the basis of the slope of the Koutecky-Levich plots. When the voltammogram was recorded in the same electrolyte solution but in the presence of 1 mmol dm^{-3} H_2O_2

under argon, no catalytic current was observed. Thus the performance of the $[Fe(TPP)]_2O$-modified electrode offered a great contrast to that of the precedented mononuclear iron porphyrin-modified electrode[9] where both H_2O and H_2O_2 were yielded and Fe(TPP) was also a catalyst for the reduction of H_2O_2.[9,10] Indeed, control experiments using a carbon electrode coated with Fe(TPP)Cl resulted in more extensive formation of H_2O_2 (i_R/i_D = 0.12, at 500 rpm) under the same electrolyte conditions.

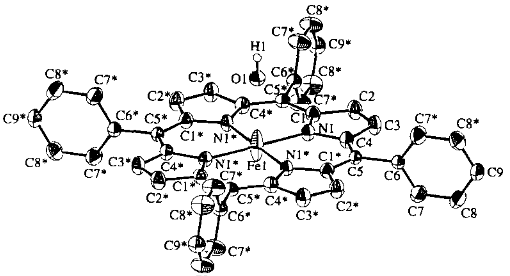
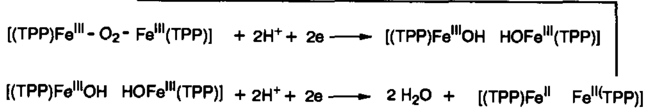


Figure 2. ORTEP view (30% probability ellipsoids) of Fe(OH)TPP. Hydrogen atoms on the porphyrin ring was omitted for clarity.

It has been reported that addition of O_2 to solutions of Fe(TPP) leads to the formation of $[Fe(TPP)]_2O$ through a peroxo-bridged iron(III) porphyrin dimer.[14] We have found that the reduction of the μ-oxo iron(III) dimer in the solution of argon-saturated acidic toluene by electrolysis and/or by reducing agent such as sodium hydrosulfite produces Fe(TPP) quantitatively. Addition of O_2 to the solution of 50 μmol dm^{-3} $Fe^{II}TPP$ in CH_2Cl_2 in the presence of 5 mmol dm^{-3} CF_3COOH and 50mmol dm^{-3} sodium hydrosulfite produced $Fe^{III}(OH)TPP$ which was identified by X-ray crystallography (Figure 2).[15] Addition of 5 mmol dm^{-3} CF_3COOH to the solution of 50 μmol dm^{-3} $[Fe(TPP)]_2O$ in CH_2Cl_2 produced both $Fe^{III}(OH)TPP$ and $Fe^{III}(TPP)$. These reactions were essentially quantitative. The catalytic reduction of O_2 proceeds at potentials in the vicinity of the reduction peak of $Fe^{III}(OH)TPP$ under acidic solution (E_{pc} = -0.21 V). Thus the catalytic cycle is proposed as scheme 1.



$$[Fe^{III}(TPP)]_2O + 2H^+ + 2e \longrightarrow [(TPP)Fe^{II}\ \ Fe^{II}(TPP)] + H_2O$$

$$[(TPP)Fe^{II}\ \ Fe^{II}(TPP)] + O_2 \longrightarrow [(TPP)Fe^{III}\text{-}O_2\text{-}Fe^{III}(TPP)]$$

$$[(TPP)Fe^{III}\text{-}O_2\text{-}Fe^{III}(TPP)] + 2H^+ + 2e \longrightarrow [(TPP)Fe^{III}OH\ \ HOFe^{III}(TPP)]$$

$$[(TPP)Fe^{III}OH\ \ HOFe^{III}(TPP)] + 2H^+ + 2e \longrightarrow 2\,H_2O + [(TPP)Fe^{II}\ \ Fe^{II}(TPP)]$$

Scheme 1.

The need for the four-electron reduction of O_2 as pointed out earlier is the capacity of forming an intercalated μ-peroxo complex such as the Co-O-O-Co complex using the difacial cobalt porphyrins and the dimeric iridium porphyrins. The use of μ-oxo iron(III) porphyrin proved valuable in this study. It may be surprising that, when comparisons are made between the catalytic behavior of $[Fe(TPP)]_2O$ and Fe(TPP), the μ-oxo bridge causes a significant increase in the selectivity of the four-electron pathway. It should be noted that the cofacially adsorbed iron(II) porphyrin molecules would be produced at the surface of the electrode by the electroreduction of the adsorbed μ-oxo dimer with the elimination of H_2O in aqueous acid. It may safely be stated that the resulting cofacially oriented porphyrin molecules would allow coordination of dioxygen to form a μ-peroxo bridge and subsequent scission of the O-O bond to produce $Fe^{III}(OH)TPP$. Thus the contrast to the electroreduction of O_2 using mononuclear Fe(TPP) originates from the capability of forming the μ-oxo bridge in the solid state upon reaction with O_2. The present result would also lead to an estimate that μ-oxo dimers are versatile templates leading to the face-to-face arrangement of a wide variety of metal complexes in the solid state, which could offer effective coordination sites of small molecules.

This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 09555297, 09650982 and 085344) and International Scientific Research Program (Joint Research No. 08044174) from the Ministry of Education, Science, Sports and Culture, Japan.

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15 Crystal and refinement data for Fe(OH)TPP: $C_{44}H_{29}N_4FeO$, formula weight = 685.59, tetragonal, space group *I4/m* (#87), a = 13.542 (1) Å, c = 9.823 (1) Å, V = 1801.3 (2) $Å^3$, Z = 2, D_{calc} = 1.264 g cm^{-3}, D_{meas}= 1.261 ± 0.090 g cm^{-3}, R (Rw) = 0.133 (0.095) for 988 diffraction data with $I > 3\sigma(I)$ and 90 variables.