Reduction of Oxygen at an Electrode Modified by Cobaltporphyrin Liquid Membrane

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The picket-fence cobaltporphyrin (CoP) having rapid and reversible oxygen-binding properties was employed to accumulate oxygen from a bulk solution to a diffusion layer at an electrode surface. Modification of a carbon electrode with a thin CoP liquid membrane resulted in a significant increase in the reduction current of oxygen, which proved to be a new type of modified electrode to reduce the diffusion resistance of oxygen from the bulk solution onto the electrode surface.

During the past 10 years, the authors have been studying metalloporphyrins as efficient oxygen carriers and applying them to oxygen absorbents, optical oxygen sensors, and oxygen permselective membranes.[1–3] A typical example is *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis(*o*-pivalamidophenyl) porphyrinatocobalt[4] (picket-fence porphyrin, CoP), which has four pivalamido groups on one side of the porphyrin plane to provide a cavity for the oxygen-binding and the other side is available for complexing with an imidazole ligand to improve the oxygen-binding affinity. The reversible oxygen-binding property of CoP is expected to allow the efficient accumulation of oxygen from a pH-buffered aqueous solution, which should contribute to an increase in the diffusion-limited current for the electroreduction of oxygen. We now propose a new idea of electrode modification to accumulate oxygen near the electrode surface, in contrast to the conventional modified electrode to enhance the rate of electron transfer,[5–7] that could practically be employed in air-assisted batteries and fuel cell applications.

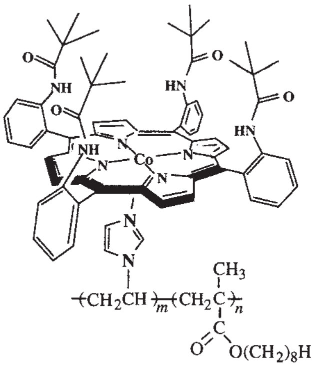

Chart 1. Picket-fence cobaltporphyrin combined with poly(vinylimdazole-*co*-octyl methacrylate).

CoP was synthesized as described in the literature.[4] The polymer ligand (L) used was poly(octyl methacrylate-*co*-vinylimidazole) (OIm). The advantages of the polymer ligand are nonvolatile, insoluble in the aqueous phase, and a long lifetime of the ligated-CoP as an oxygen carrier. OIm was prepared by the copolymerization of 1-vinylimidazole and octyl methacrylate: The 1-vinylimidazole content and the molecular weight of OIm were 45 mol% and 1.3×10^5, respectively. The solutions of OIm and CoP (the molar ratio of imidazole residue of OIm to CoP was 10 to 1) in benzonitrile (containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte) were mixed to complex the imidazole residue of the copolymer with the fifth coordination site of CoP (Chart 1).[8]

The complexed CoP in hydrocarbon solvents displayed a reversible change in the UV/vis absorption spectrum from the deoxy form ($\lambda_{\max} = 530$ nm) to the oxy or oxygen-binding one ($\lambda_{\max} = 548$ nm) with an isosbestic point at 538 nm, in response to the partial oxygen pressure of the atmosphere. The spectral change was attributed to the reversible oxygen-adduct formation of the CoP complex (eq 1).

$$\text{OIm-CoP} + \text{O}_2 \underset{k_{\text{off}}}{\overset{k_{\text{on}}}{\rightleftharpoons}} \text{OIm-CoP–O}_2 \quad K = k_{\text{on}}/k_{\text{off}} = 1/p_{50} \quad (1)$$

The reversible oxygen-binding was also confirmed in an electrolyte solution of benzonitrile employed for electrochemical measurements. The oxygen-binding behavior in benzonitrile was monitored at the absorbance ascribed to the oxy form at 548 nm. The oxygen-binding equilibrium curve obeyed a Langmuir isotherm (Figure 1, inset) to give the oxygen-binding affinity, p_{50} (partial pressure at which half of the CoP binds oxygen). The low value of p_{50} (11 cmHg) reflects the high oxygen-binding affinity of CoP even in the electrochemical solvent. The binding and dissociation rate constants of oxygen to and from the CoP in the solution ($k_{\text{on}} = 2.0 \times 10^7\ \text{M}^{-1}\cdot\text{s}^{-1}$, $k_{\text{off}} = 2.7 \times 10^4\ \text{s}^{-1}$), determined by the laser flash photolysis of the oxygen-adduct, are so large that the oxygen-binding and releasing processes may not be the rate-determining step for the overall electrolysis of oxygen.

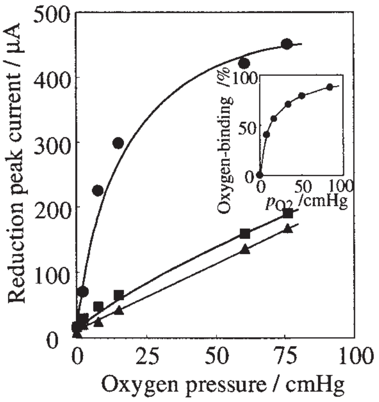

Figure 1. Change in reduction peak current of oxygen with the oxygen pressure and CoP concentration. The thin layer contained (●) 50 mM, (■) 5 mM, and (▲) 0 mM CoP in benzonitrile. Scan rate: 100 mV s^{-1}. Inset: Oxygen-binding equilibrium curve of the CoP complex in the solution (obtained from the UV/vis absorption spectrum).

The solution of OIm-CoP in benzonitrile (1.5 μL) was carefully transferred to the surface of the glassy carbon disk to produce a red-colored liquid membrane with a thickness of ca. 50 μm. The oxygen-binding property of CoP allowed the efficient accumulation of oxygen from the aqueous solution onto the thin layer of organic solution (immiscible with water) placed at the electrode surface.[9] The oxygen enriched CoP-OIm membrane is expected to increase the reduction current of oxygen.

Figure 2 shows the cyclic voltammograms obtained for the liquid membranes coated on the glassy carbon electrode in a 0.1 M sodium carbonate/sodium bicarbonate buffer (pH = 10) in air. The electroreduction of oxygen occurred at −0.65V vs SCE. The peak current (i_p) obtained with a 5 mM CoP liquid membrane was 65 μA that was significantly larger than that with a benzonitrile thin layer in the absence of CoP (42 μA) under the same conditions because of the accumulation of oxygen in the CoP liquid membrane.

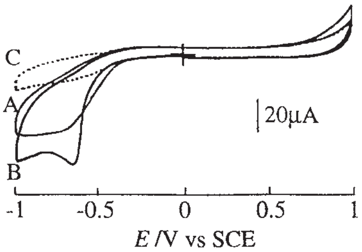

Figure 2. Cyclic voltammograms for the liquid membranes adsorbed on a glassy carbon electrode by transferring 1.5 μL benzonitrile (A), a 5 mM solution of CoP in benzonitrile (1.5 μL) (B) to the electrode surface, and a bare electrode (C) which was immersed in a 0.1 M $Na_2CO_3/NaHCO_3$ buffer (pH = 10) in air. The supporting electrolyte in the benzonitrile layer was 0.1 M tetrabutylammonium tetrafluoroborate. Scan rate: 100 mV s^{-1}.

Figure 1 shows the peak current based on the oxygen reduction obtained from the cyclic voltammetry recorded at various upstream oxygen pressures (p_{O2}) and the CoP concentration. The curve obtained with the CoP-OIm liquid membrane, similar to the UV/vis result, obeyed a Langmuir isotherm, whereas that of the pure benzonitrile layer obeyed a Henry isotherm. The reduction current of oxygen for the CoP-OIm membrane was much larger than that of the benzonitrile membrane and remarkably increased with the oxygen pressure and CoP concentration. This result indicates that the CoP carrier in the membrane reversibly binds oxygen and makes the current based on the oxygen reduction increase. (The reduction of molecular oxygen including that released from the CoP-oxygen adduct became manifest only in the membrane involving CoP with high concentration where the contribution of the oxygen-adduct is much higher than that of molecular oxygen physically dissolved in benzonitrile.) This conclusion was also supported by the fact that the current linearly increased with oxygen pressure for the benzonitrile thin layer without CoP that does not accumulate oxygen more than the physical solubility. It was also found that p_{50} evaluated by cyclic voltammetry was 9 cmHg, similar to the spectroscopically determined value.

Oxygen can be reduced in an alkaline aqueous solution either by two electrons ($O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$) or four electrons ($O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$) or both. The rotating platinum ring-glassy carbon disk voltammetry (RRDV) shown in Figure 3 was used to detect the partially-reduced product, HO_2^-, that is undesirable for practical applications in air batteries.[10] The ring potential of RRDV was set at a value ($E_R = 0.6$ V) to re-oxidize HO_2^- ($HO_2^- + OH^- \longrightarrow O_2 + H_2O + 2e^-$) transferred from the disk, which was determined from Fig. 3B. The collection efficiency of HO_2^- ($N = 0.013$) normalized by the intrinsic value of the electrode ($N_0 = 0.3$) suggests that over 90% of the oxygen is reduced by four electrons to OH^- regardless of the basicity of the solvent.

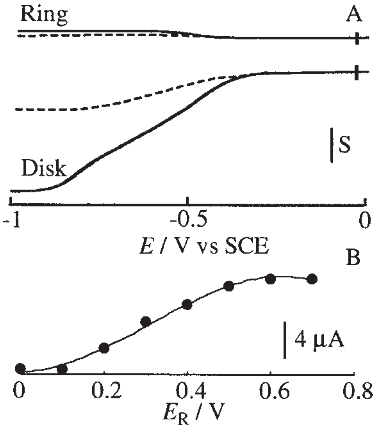

Figure 3. (A) Current-potential curves for the reduction of oxygen at a rotating platinum ring-glassy carbon disk electrode (disk area = 0.28 cm^2) for a 5 mM CoP liquid supported membrane (solid curve) and a blank membrane (dotted curve) with intrinsic collection efficiency of $N_0 = 0.3$ in air. The potential of the ring electrode was maintained at 0.6V to oxidize HO_2^-. Rotation rate: 1000 rpm. Scan rate: 5 mV s^{-1}. The current scale was S = 2 and 50 μA for the ring and disk currents, respectively. (B) Change of the ring current in pH = 10 buffer with the ring potential in air. Scan rate: 5 mV s^{-1}. Rotor speed: 250 rpm. The supporting material was a microporous flat membrane made from polypropylene and polyethylene (Celgard 2500: Hoechst Celanese Co.; pore dimensions, 0.05 × 0.19 μm; porosity, 0.43; thickness, 25 μm). The CoP solution was sunk into the supporting material which was placed at the electrode surface.

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