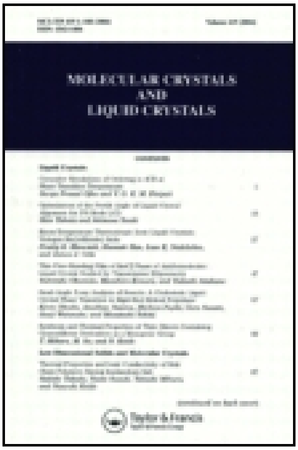

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4-Electron Reduction of Dioxygen On a Glassy Carbon Electrode Modified by Polyaniline-Co_2-Porphyrin Complex

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4-Electron Reduction of Dioxygen On a Glassy Carbon Electrode Modified by Polyaniline-Co_2-Porphyrin Complex

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The 4-electron reduction of oxygen to water in an acidic atmosphere (pH: 0.5) takes place on a glassy carbon electrode by electro-catalysis under the atmospheric conditions using the dinuclear Co-porphyrin-polyaniline complex. The π-conjugated polymer complex shows an excellent and stable catalytic activity in strong acidic conditions.

Keywords: 4-electron reduction of oxygen; dinuclear Co-porphyrin; π-conjugated polymer complex

INTRODUCTION

Research of the breath reaction, the 4-electron reduction of oxygen to water is important in order not only to determine the life mechanism but also to make novel catalysts.[1-3] In our bodies, the breath enzyme, cytochrome oxidase, dominates the 4-electron reduction of oxygen to water under atmospheric pressure. Many researchers have spent much effort on the structural analysis of the enzyme[4,5] and mimicking the catalytic reactions.[6-9]

Frequently, metalloporphyrins are employed as catalysts to promote the reaction. However, monomeric metalloporphyrins such as the cobalt and iron ones, allow only the 2-electron reduction of oxygen to hydrogen peroxide. Multi-nuclear porphyrins such as dimeric porphyrin,[10,11] tetranuclear ruthenated porphyrin[12,13] and polymeric metalloporphyrin[14] were employed in order to allow the efficient multi-electron transfer to oxygen for the preferential 4-electron reduction of oxygen. However, most of the catalysts show less stable activity under a strong acidic atmosphere.

It is well-known that poly aniline as a π-conjugated conductive polymer shows excellent redox activity in strong acidic atmosphere(pH < 3).[15] As a strategy to achieve the multi-electron transfer to oxygen, polyaniline should be employed as a conductive polymer electrolyte matrix for the multi-electron transfer mediator.

In the previously reported paper[16] a catalysis for the oxygen reduction was observed on a glassy carbon electrode modified monolayer of dinuclear Co porphyrin with less stability. Our results reveals that the four-electron reduction of oxygen could be achieved with high stability using polyaniline-Co2 porphyrin catalyst(Fig. 1).

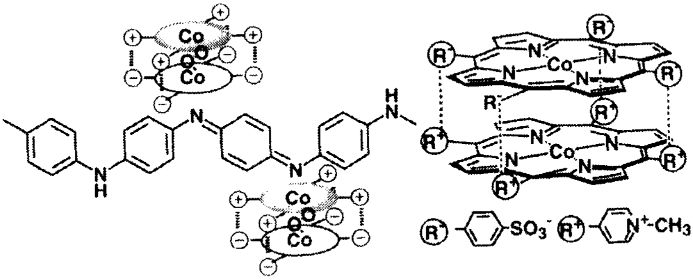

FIGURE 1 Polyaniline-Co2 porphyrin catalyst(PAn-Co2P)

EXPERIMENTAL

$Co^{II}TPPS$ and $Co^{II}TMPyP$ immediately aggregate to precipitate a powder after mixing due to the hydrophobisity of the dimeric porphyrin. The precipitate is soluble in DMSO below a 0.1 mM concentration. The formation of the dimeric porphyrin in DMSO is supported by the previously reported results. The catalytic behavior of the polyaniline-CoTMPP-CoTPPS complex(PAn-Co_2P)(Fig. 1) was studied using cyclic voltammetry on the modified glassy carbon electrode. Poly(aniline) as an emeraldine base(0.15 mM) and dinuclear Co-porphyrin(0.05 mM) were mixed in 10 mL of DMSO with a 3 : 1 molecular unit stoichiometry. The homogeneous polymer catalyst film(Co_2P: $4.42x10^{-7}$mol/cm^2) on the electrode was prepared by the cast method.

RESULTS AND DISCUSSION

In Fig 2(a), the dotted curve shows the typical cyclic voltammogram measured at a glassy carbon electrode in argon saturated aqueous acid when the PAn-Co_2P complex is modified on the electrode surface. When the electrode was transferred to an air saturated solution, a large catalytic current appeared at $Ec_{1/2}$ = ca. 0.1V vs SCE. This peak potential is positively shifted by 300 mV when compared to the peak potential for O_2 reduction on the 5,10,15,20-tetrakis(4-methoxyphenyl)-*21H,23H*-porphine cobalt(II)(CoTMPP) adsorbed electrode, where 2 electron reduction of oxygen takes place. These results support the fact that the catalytic reduction of O_2 proceeds.

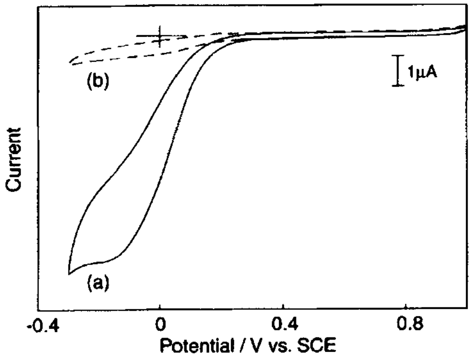

FIGURE 2 Cyclic voltammograms reduction of O_2 on the glassy carbon electrode modified PAn-CO2P in the acidic conditions under the air atmosphere(a) and undr N_2 atmosphere(b). in 0.1 M H_2SO_4 aqueous solution(pH:0.23).

Quantitative kinetic data for the electro-reduction of oxygen by the PAn-Co_2P was obtained using rotating disk voltammetry(RDV). A controlled experiment using the CoTMPP modified electrode shows a slope of 2 ± 0.2 for the electron transfer reaction in the Koutecky-Levich plots.[17] The stable catalytic activity of Co_2P was not measured on the electrode by the RDV due to the solubility. For PAn-Co_2P catalyst, the Koutecky-Levich plots of the plateau current became linear. The slope is matched to the n value (n = number of electrons transferred) of 3.6 ± 0.1, which means that the PAn-Co_2P acts as an excellent catalyst for the four-electron reduction of oxygen to water.

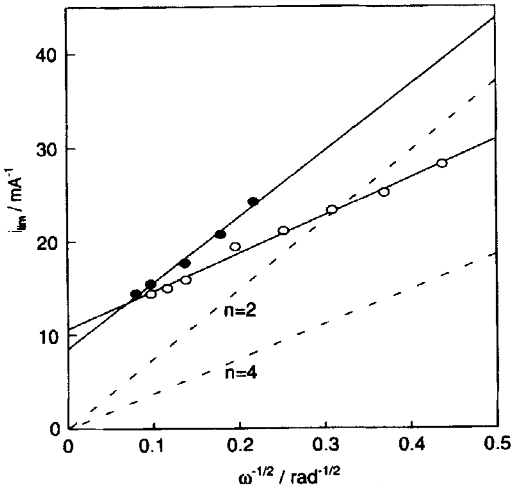

FIGURE 3 Kouteckey-Levich plots of the plateau current in rotating disk voltammetry for reduction of O_2 on the PAn-Co2P modified electrode(●) and CoTPP(○). Dotted lines are calculated plots for 2-electron and 4-electron reduction of oxygen.

The results of the four-electron reduction of oxygen during the catalysis by PAn-Co_2P are also confirmed by the electrochemical detection of hydrogen peroxide as a side-product at a ring-disk electrode. The voltammograms were obtained with a rotating Pt ring glassy carbon disk electrode under the same conditions, where the Pt ring-disk electrode had an applied potential at 1.0 V to detect the H_2O_2 generated by the reduction of oxygen as a side reaction at the disk electrode. The theoretical collection efficiency of the ring disk electrode was determined to be $N_0 = 0.38$ in an independent experiment with the $Fe(CN)_6^{3+/4+}$ couple. Comparison of the resulting collection efficiency with the theoretical one reveals the selectivity of the 4-electron transfer during the electro-reduction of oxygen. The rotating ring disk voltammetry(RRDV) at the Pan-Co_2P modified electrode results in the reduction of ca. 50 % of the oxygen molecules to water after the normalization of the collection efficiency$[(N_0-N)/(N_0+N)]$ using the ratio of the ring-disk to disk current.

It has been reported that the addition of O_2 to Co complex solutions such as Co(salen) leads to the formation of the μ-peroxo dimer.[18] The four-electron reduction of O_2 takes place through the formation of the μ-peroxo complex such as the Co-O-O-Co complex as an intermediate. We have already concluded that using the dinuclear vanadium catalyst 4-electron reduction of oxygen efficiently proceeds via a formation of μ-peroxo structure through the injection of sequential multiple electron transfer to the oxygen.[2,3] It may be safely stated that polyaniline acts as a multiple electron transfer mediator for the injection to μ-peroxo dinuclear Co-porphyrin complex. Detail mechanism and structure will be reported in near future.

CONCLUSION

Most of the previously reported electrode-catalysts for the 4-electron reduction of oxygen efficiently act only under monolayer adsorbed conditions due to the low conductivity. The conductive polymer complex provides a stable catalytic activity even at low pH. The potential of the easy to prepare the component promises to expand the wide application of this catalyst.

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