Four-Electron Reduction of Dioxygen Catalyzed by Self-Doped Polyaniline-Co-Porphyrin Complex

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The four-electron reduction of oxygen to water in a pseudo-neutral atmosphere(pH: 6.2) takes place on a glassy carbon electrode by electro-catalysis using the Co-porphyrin-polyaniline complex which shows a stable redox activity over a wide pH range due to the self-dopable carboxy substituents in the polymer chain.

Research of the breath reaction, the four-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 four-electron reduction of oxygen to water under atmospheric pressure at mild temperature in ca. pH 7 solution. 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 two-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 four-electron reduction of oxygen. And most of the catalysts show activity only under a strong acidic atmosphere yet.

We have already reported that poly(2,3-dicarboxyaniline) (**1**) as a novel self-doping conductive polymer shows excellent redox activity over a wide pH range (pH < 8) due to the self-dopable acidic group and acts as a polymer ligand for macromolecular metal-complexes.[15] The redox potential of **1** obeys a Nernst equation ($E(V) = 0.17 - 0.054[pH]$, $0 < pH < 7$). As a strategy to achieve the four-electron transfer to oxygen in neutral solution, **1** should be employed as a conductive polymer electrolyte matrix for the multi-e]ectron transfer mediator from electrode to oxygen. For pH > 4.5, only H_2O_2, i.e. a two-electron product is formed.

In the present study we have observed a catalytic efficiency up to 95% for the four-electrcn reduction of oxygen to water using a glassy carbon electrode modified by a polymer complex of Co porphyrin with **1**. Also, our results reveals that the four-electron reduction of oxygen could be firstly achieved under pseudo-neutral conditions (0.2M KPF_6 aqueous solution: pH = 6.2) by polyaniline-Co-porphyrin complex even though Co-porphyrin or **1** allows to undergo only two-electron reduction.

The catalytic behavior of the polyaniline-5,10,15,20-tetrakis(4-methoxyphenyl)-*21H,23H*-porphine cobalt(II) (**2**) complex was studied using cyclic voltammetry on the modified glassy carbon electrode. Poly(2,3-dicarboxyaniline) as an emeraldine base (2 mmol) and cobalt(tetra-4-methoxyphenyl) porphyrin (3 mmol) were mixed in 10 mL of DMSO with a 1.5 :1 molecular unit stoichiometry. The homogeneous polymer catalyst film (**2**: 0.7 mmol/cm^2) on the electrode was prepared by the spin cast method. In Figure l(a), the curve shows the typical rotating disk voltammogram measured at a glassy carbon electrode in nitrogen saturated aqueous acid when the polyaniline-Co-porphyrin complex is modified on the electrode surface in which the current is corresponding to the reduction of the polymer complex. When the electrode was transferred to an air saturated solution, a large catalytic current appeared at $Ec_{1/2}$ = ca. 0.1 V vs SCE. The potential coincides with the redox potential of **1** in the same acidic atmosphere. These results support the fact that the catalytic reduction of O_2 proceeds through the mediation of **1**. The direct reduction of O_2 to H_2O_2 by at uncoated portion of the carbon electrode is observed at a less anodic potential near -0.5 – -0.75 V.

Quantitative kinetic data for the electro-reduction of oxygen by the polyaniline-Co-porphyrin was obtained using rotating disk voltammetry (Figure lb). A controlled experiment using **2** modified electrode shows a slope of 2 ± 0.2 for the electron transfer reaction in the Koutecky-Levich plots.[11,12] For polyaniline-Co-porphyrin, the Koutecky-Levich plots of the plateau current became linear. The slope is matched to the n value (n = number of electrons transferred) of 3.9 ± 0.1, which means that the polyaniline-Co-porphyrin acts as an excellent catalyst for the four-electron reduction of oxygen to water. The results of the four-electron reduction of oxygen during the catalysis by the polymer complexes are also confirmed by the electrochemical detection of H_2O_2 as a side-product at a ring-disk electrode. The voltammograms were

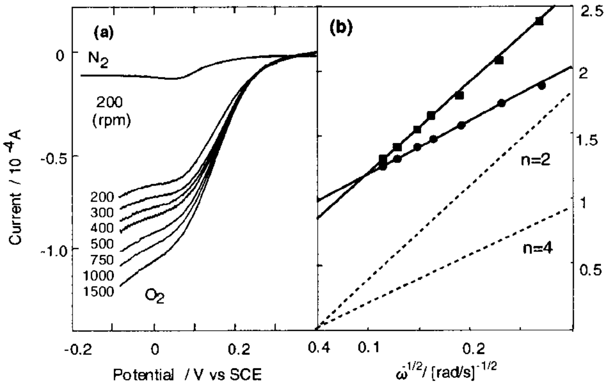

Figure 1 (a) Rotating disk voltammetry for reduction of O_2 on the glassy carbon electrode modified poly(2,3-dicarboxylaniline)- **2**(0.7 mmol/cm^2). Supporting electrolyte:0.5 M $HClO_4$ + 0.5 M $(NH_4)PF_6$ aqueous solution. Rotating rates(rpm) were listed in the figure. (b) Koutecky-Levich plots of the plateau current in rotating disk voltammetry for reduction of O_2 on the electrode modified by the polyaniline-**2** complex(●) and **2**(■). Dash lines are calculated plots for 2-electron and 4-electron reduction of oxygen.

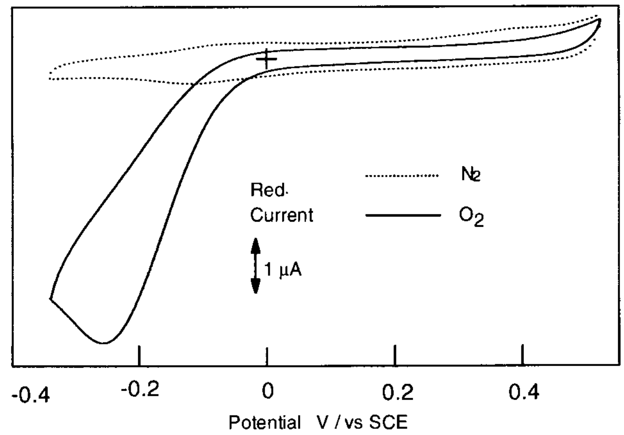

Figure 2 Cyclic voltammograms reduction of O_2 on the glassy carbon electrode modified poly(2,3-dicarboxylaniline)- **2**(0.7 mmol/cm^2) in the neutral conditions under the air atmosphere. Dotted line is the voltamogram in N_2 atmosphere. Supporting electrolyte: 0.2M KPF_6 aqueous solution: pH6.2.

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 1.1 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 $N_0 = 0.36$ 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 four-electron transfer during the electro-reduction of oxygen. Controlled experiments using **2** modified electrode shows 95% formation of H_2O_2 through the two-electron transfer reaction after the normalization of the collection efficiency$[(N_0\text{-}N)/(N_0+N)]$ using the ratio of the ring-disk to disk current. The rotating ring disk voltammetry (RRDV) at the polyaniline-Co-porphyrin modified electrode results in the reduction of more than 95% of the oxygen molecules to water. The selectivity of the four-electron pathway is good agreement with the n value determired by the Koutechky-Levich plots.

It has been reported that the addition of O_2 to Co complex solutions such as Co(salen) leads to the formation of the oxygen adducts.[16] The four-electron reduction of O_2 takes place through the multiple electrons injection to the oxygen adduct. Thus the oxygen reduction was influenced by the charge transfer rate in the polymer complex. The polymer complex with higher concentration of **2** ([**2**]/{ [**2**]+[**1**] } > 60%), which show low charge transfer rate[17] ($k < 1.2 \times 10^{-1}\ M^{-1}s^{-1}$) due to the low conductivity results in a low selectivity of the four-electron reduction. At the low concentration ratio, the selectivity of the four-electron reduction decreases because the direct two-electron reduction by **1** dominates the reaction. Consequently the polymer complex having a 1 : 1.5 molecular unit ratio of **2** and polymer shows the maximum selectivity of the four-electron pathway. It should be noted that **1** acts as an efficient electron transfer mediator for the oxygen adduct of **2** from the electrode.

Most of the previously reported electrode-catalysts for the four-electron reduction of oxygen act only under a strong acidic atmosphere. In the absence of acid (pH = 6.2 in 0.2 M KPF_6 aqueous solution), the catalytic current was also observed on the electrode modified by polyaniline-Co-porphyrin complex even in the pseudo-neutral atmosphere (Figure 2). Additionally the plateau currents in RDV obey the Koutecky-Levich equation, where the calculated n value is 3.8 ± 0.1 by RDV and the selectivity is ca. 90% by RRDV. The polymer matrix containing acidic domains of the carboxy group in the polymer complex provides a stable electron mediation through redox reaction of **1** even at elevated pH. The redox potential of **1** is located at -0.07 V vs SCE. The acidity is estimated to be pH = ca. 4.5 on the basis of the Nernst plot of **1**. This means the acidity is kept in the matrix domain.

The potential of the easy to prepare the component promises to expand the wide application of the catalyst.

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17 $i_k = 10^3 k_{ct} FCnT_{Co}$ k_{ct}: charge transfer rate [$M^{-1}s^{-1}$], i_k: intercept of Koutecky-Levich Plots, F: Faraday constant [C/mol], C: O_2 concentration [mM], n: number of electron transferred, T_{Co}: Co concentration [mol/cm^2].