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Electrocatalytic Reduction of Dioxygen at Schiff base Co(II) Complexes supported Glassy Carbon Electrode in various pH Solution

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Abstract : Electrocatalytic reduction of dioxygen has been investigated by cyclic voltammetry at glassy carbon electrode modified with new Co(II)-Schiff base complexes in aqueous solutions of various pH. The reduction potentials of dioxygen at chemically adsorbed electrodes show the dependence of pH between pH 4 and 14. The catalytic effect is large and the reaction occurs *via* two or four electron transfer in various pH solution.

Keywords : Electrocatalytic dioxygen reduction, Co(II)-Schiff base complexes, Modified electrodes, Catalytic effect, Various pH solution, Cyclic voltammetry.

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1. Introduction

The electrocatalytic reduction of dioxygen species in both aqueous and nonaqueous solutions has been receiving a great deal of attention due to its implications in practical applications such as fuel cells and batteries, as well as biological reactions[1-17]. Phthalocyanines or porphyrins of cobalt and iron are known as effective catalysts for oxygen reduction. Carbon based oxygen electrodes are modified by the adsorption of these macromolecular compounds, which mediate the electron transfer. Oxygen is reduced to hydrogen peroxide and/or water at these modified electrodes *via* a two- or four-electron transfer reaction. Collman and Anson et al.[9-11] have synthesized and characterized cobalt cofacial porphyrin derivatives as oxygen reduction catalysts in an effort to reduce the intermediate step during the oxygen reduction since the rate of the overall reaction is often limited by one or more steps of the reduction. As a result, some of these compounds were found to reduce dioxygen species directly to water *via* a four- electron transfer reaction.

We have been studying the oxygen reduction because the reaction is used as a cathode reaction in fuel cells and metal air batteries[15-16]. In our present report, we describe catalytic effect of Schiff base complexes such as Co(II)-bis(2-hydroxy-1-naphthylidene)ethylenediimine; [Co(II)(NED)] and Co(II)-bis(2-hydroxy-1-naphthylidene)-1,2-phenyl enediimine; [Co(II)(NOPD)] for the reduction of dioxygen. The catalytic effects are large and the reaction occurs *via* two or four-electron transfer to produce hydrogen peroxide or water.

2. Experimental

Pyridine(Fischer Scientific), potassium ferricyanide(Mallinckrodt Chemical), potassium hydroxide(Alfa ultra pure), ethanol(Merck), 1,2-phenylenediamine(Aldrich), ethylenediamine(Junsei), cobalt acetate(Aldrich) and 2-hydroxy-1-naphthaldehyde(Aldrich) were used as received. Potassium hydroxide solution for electrochemical experiments was prepared using doubly distilled deionized water. A quadridentate Schiff base ligands, bis(2-hydroxy-1-naphthylidene)ethylenediimine; (NED) and bis(2-hydroxy-1-naphthylidene)-1,2-phenylenediimine; (NOPD), were prepared by a following method. The solution of 0.1 mole 1,2-phenylenediamine or ethylenediaminein ethanol was slowly added to the same volume of 0.1 mole 2-hydroxy-1-naphthaldehyde in ethanol under the nitrogen atmosphere. When the mixed solution was slowly stirred, a yellow o-BSDTH_2 precipitate was obtained. The [Co(II)(NOPD)] and [Co(II)(NED)] complexes were prepared by slowly adding 0.1 mole NOPD and NED in ethanol to the same volume of 0.1 mole $Co(NO_3)_2 \cdot 6H_2O$ in ethanol while stirring under the nitrogen atmosphere. A dark brown precipitate was then recrystallized and dried at 60℃ under reduced pressure.

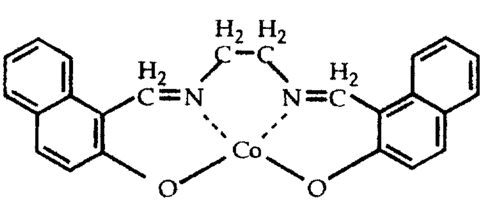
Elemental analysis (C,H,N) was performed with a Yanaco-CHN Coder MT-3 Analyzer and the cobalt content was determined with a Perkin-Elmer model 603 atomic absorption spectrophotometer, respectively. Infrared and UV-visible spectra were recorded with Shimadzu IR-430 infrared and Hitachi-557 UV-visible spectrophotometers. Thermogravmetric analysis was carried out with a Perkin-Elmer model 2 thermogravimetric analyzer. An EG & G Princeton Applied Research model 273 potentiostat/galvanostat was used for electrochemical measurements.

A single compartment cell, which housed a glassy carbon working, Hg/Hg_2SO_4(sat'd K_2SO_4) reference and platinum wire counter electrodes, was used for electrochemical measurements. The working electrode was polished to a mirror finish with 0.1 μm alumina powder, subsequently cleaned in an ultrasonic cleaning bath to remove solid particles, and finally rinsed with a copious amount of doubly distilled deionized water before use. To prepare a catalyst modified electrode, the electrode was then dried in an oven and coated with the catalyst molecule by dipping in a 1 mM [Co(II)(NOPD)] or [Co(II)(NED)] solution in pyridine. After the solvent has evaporated, the chemically modified electrode is immersed into a dioxygen-saturated aqueous solutions of various pH.

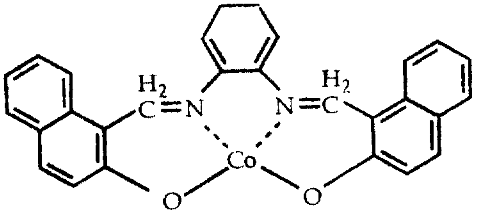
3. Results and Discussion

The results of elemental analysis of the Schiff base [Co(II)(NOPD)] and [Co(II)(NED)] complexes agree well with predicted compositions of the proposed complex on Scheme 1. Also, the content of cobalt is in excellent agreement with the proposed complex of one base molecule

Scheme 1



Co(II)-NED; Co(II)[N,N-bis(2-hydroxy-1-naphthyidene)-ethylenediimine]



Co(II)-NOPD; Co(II)[N,N-bis(2-hydroxy-1-naphthyidene)-o-phenylenediimine]

with one cobalt(II) ion. The complex is not soluble in water but soluble in relatively nonpolar solvents such as pyridine.

Electrocatalytic reduction of dioxygen has been investigated by cyclic voltammetry at bare glassy carbon electrode and glassy carbon electrode modified with new Co(II)-Schiff base complexes in aqueous solutions of various pH. *Fig. 1* shows cyclic voltammograms (CVs) traces for the dioxygen reduction at bare glassy carbon electrode with scan rate (20 mV/s) in a dioxygen-saturated aqueous solutions of various pH. The reduction potential (Ep) of dioxygen is about -1.3 V vs. Hg/Hg_2SO_4 at pH 0 and shifted to more negative at pH 4, but the Ep is shifted to more positive at pH >4.

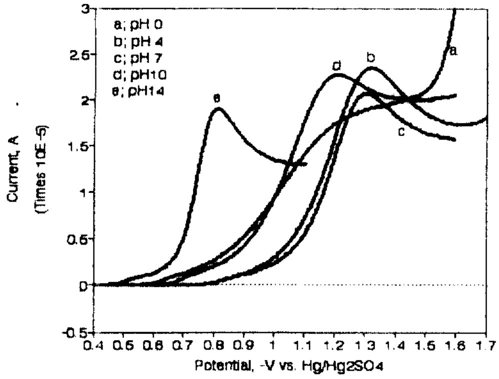


Fig. 1. Cyclic voltammograms of dioxygen reduction at bare glassy carbon electrode in a dioxygen saturated aqueous solutions of various pH ; a) pH 0, b) pH 4, c) pH 7, d) pH 10, and e) pH 13, respectively. Scan rate was 20 mV/sec.

The electrochemical reduction of dioxygen is totally irreversible at all pH solutions employed.

Cyclic voltammograms are obtained to determine the peak potentials where dioxygen is reduced at glassy carbon electrode adsorbed with cobalt(II)-Schiff base.

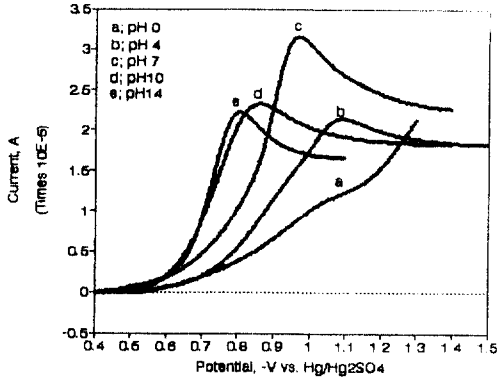


Fig. 2. Cyclic voltammograms of dioxygen reduction at glassy carbon electrode adsorped with Co(II)-NED in a dioxygen saturated aqueous solutions of various pH ; a) pH 0, b) pH 4, c) pH 7, d) pH 10, and e) pH 13, respectively. Scan rate was 20 mV/sec.

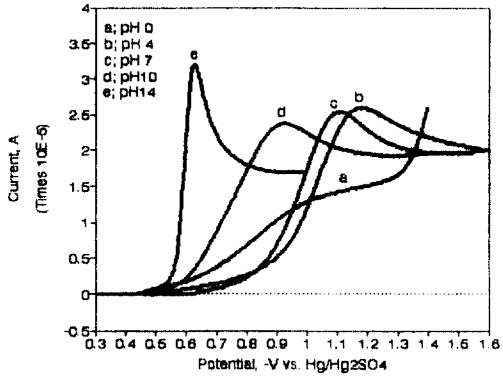


Fig. 3. Cyclic voltammograms of dioxygen reduction at glassy carbon electrode adsorped with Co(II)-NOPD in a dioxygen saturated aqueous solutions of various pH ; a) pH 0, b) pH 4, c) pH 7, d) pH 10, and e) pH 13, respectively. Scan rate was 20 mV/sec.

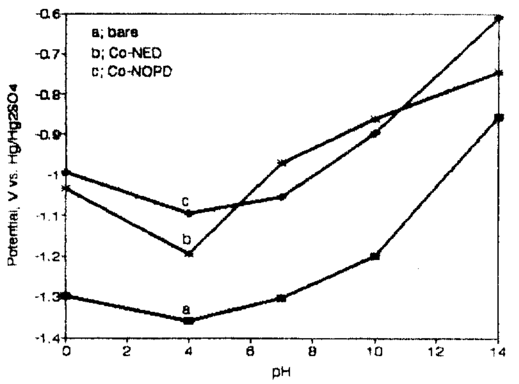


Fig. 4. Plots of Ep vs. pH obtained from CVs of Fig. 1~3 : a) at bare glassy carbon electrode, b) at glassy carbon electrode adsorbed with Co(II)-NED, and c) at glassy carbon electrode adsorbed with Co(II)-NOPD.

Fig. 2-3 illustrates CVs for the dioxygen reduction at glassy carbon electrode adsorbed with Co(II)-NED and Co(II)-NOPD in a dioxygen-saturated aqueous solutions of various pH. Unfortunately, an estimation of formal potentials of the Co(II)-Schiff base complexes by this means was not feasible because voltammetric responses from the electrodes adsorbed with the Cobalt(II) Schiff base in the absence of dioxygen were not measurable. *Fig. 4* shows the plots of Ep vs. pH obtained from CVs of *Fig. 1~3.* As shown in *Fig. 4,* Ep is shifted to positively 400mV and 350mV at electrodes adsorbed with Co(II)-NED and Co(II)-NOPD when compared with that at bare electrode in strong basic solution (pH 10), respectively.

The Ep of dioxygen reduction is shifted linearly to positive from pH 4 to pH 14 at all electrodes studied. Dioxygen can reduce at the chemically modified electrodes by a $2e^-$ process to yield H_2O_2 as an intermediate or via a 4e-reduction to provide H_2O. *Fig. 5* shows the plots of peak current vs. (scan rate)$^{1/2}$ from the cyclic voltammograms of dioxygen reduction as a function of scan rate. The currents of dioxygen reduction are increased with the increase of scan rates, the relationship between peak current and scan rate is as follows [18]

$$i_p = (2.99 \times 10^5) n (\alpha n_a)^{½} A C_o^* D_0^{½} v^{½} \qquad (1)$$

where, i_p is the reduction peak current of oxygen, n is the number of electrons transferred number, α the transfer coefficient, n_a the apparent number of electrons transferred. A the electrode area, Co^* the bulk concentration of oxygen, D_0 the diffusion coefficient of oxygen.

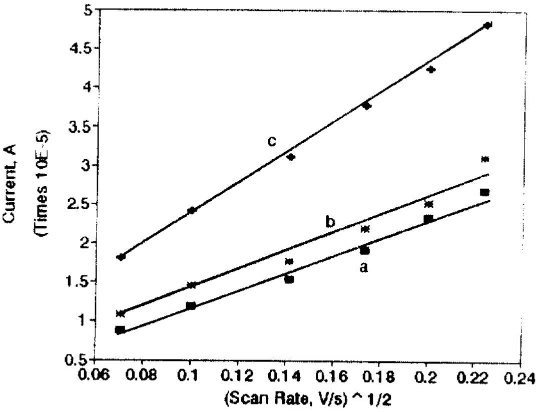


Fig. 5. Plots of peak current vs. (scan rate)^{½} : a) at bare glassy carbon electrode, b) at glassy carbon electrode adsorbed with Co(II)-NED, and c) at glassy carbon electrode adsorbed with Co(II)-NOPD.

Also the relation between the ip vs. Ep is[18]

$$i_p = 0.227 nFACo^* k^o \exp[-(\alpha n_a F/RT)(E_p - E^{o'})] \qquad (2)$$

Where, k^o is the exchange rate constant in cm/s, $E^{o'}$ the formal potential of oxygen.

Fig. 6 shows the plots of ln(ip) vs. (Ep-$E^{o'}$) at chemically adsorbed glassy carbon electrode. Kinetic parameters, i.e., αn_a and k^o values were calculated from slopes and intercepts of the i_p vs. (E_p-$E^{o'}$) plots, respectively. The D_0 values of oxygen reduction was used 2.5 × $10^{-5}cm^2/s$[19]. The Co^* value was taken to be 1mM for the calculation from the solubilty of oxygen in 1.0 M KOH solution. Table 1 summarizes the electrokinetic parameters for dioxygen reduction at chemically adsorbed glassy carbon electrode with Co(II)-NED and Co(II)-NOPD in a dioxygen saturated aqueous solutions of various pH.

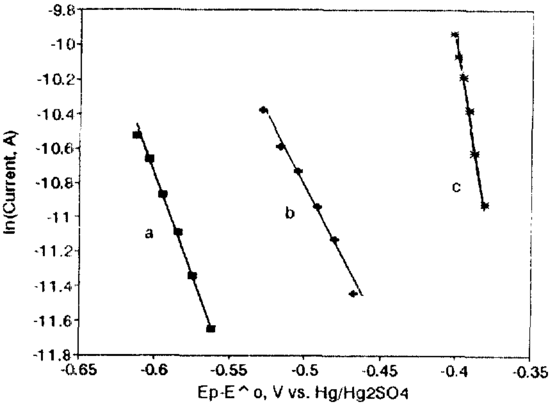


Fig. 6. Plots of ln(ip) vs. (Ep-$E^{0'}$); a) at bare glassy carbon electrode, b) at electrode adsorbed with Co(II)-NED, and c) at electrode with Co(II)-NOPD.

The exchange rate constant at glassy carbon electrode adsorbed with Co(II)-NED and Co(II)-NOPD is slightly large when compared with that at bare electrode.

The n value obtained from the slope equation (1) and (2) on the catalysts modified electrode is different from that determined at bare glassy carbon electrode. Dioxygen reduction catayzed by the Co(II)(NED) and Co(II)(NOPD) mainly occurs through the 4e^- reduction pathway resulting in the formation of H_2O at pH 4-10, but reduction process carries out 2e^- reduction pathway of doxygen to hydrogen peroxide on the bare glassy carbon electrode. The electrocatalytic reduction of dioxygen is irreversible and diffusion controlled.

Acknowledgment

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Table 1. Kinetic parameters for dioxygen reduction at glassy carbon electrodes adsorbed with Co(II)-Schiff bases in various pH solutions.

pH	Catalyst	Ep(V)	Ip(A)	αn_a	n	k^0(cm/s)
0	Bare	-1.298	1.74E-5	0.45	1.93	1.89E-8
	Co-NOPD	-0.993	1.87E-5	0.41	2.15	5.69E-7
	Co-NED	-1.033	1.30E-5	0.32	2.25	3.84E-7
4	Bare	-1.359	2.34E-5	0.48	2.01	2.20E-8
	Co-NOPD	-1.094	2.77E-5	0.36	3.38	4.33E-7
	Co-NED	-1.195	2.26E-5	0.41	3.45	2.12E-7
7	Bare	-1.303	2.27E-5	0.43	2.14	4.42E-8
	Co-NOPD	-1.053	2.54E-5	0.33	3.37	2.5E-7
	Co-NED	-0.970	3.04E-5	0.47	3.35	6.87E-7
10	Bare	-1.198	1.81E-5	0.34	2.15	2.44E-8
	Co-NOPD	-0.895	2.53E-5	0.46	3.39	1.2E-7
	Co-NED	-0.862	2.43E-5	0.35	3.48	2.01E-7
14	Bare	-0.858	1.89E-5	0.42	2.19	1.46E-8
	Co-NOPD	-0.611	3.21E-5	0.50	2.36	4.25E-7
	Co-NED	-0.744	2.22E-5	0.50	2.27	8.49E-8

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