Electrocatalytic Reduction of Dioxygen on a Glassy Carbon Electrode Modified with Adsorbed Cobaloxime Complex

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The preparation and electrochemical properties of a glassy carbon (GC) electrode modified with cobaloxime complex were investigated. The complex of the type $[\text{Co}^{\text{III}}(\text{DO})(\text{DOH})\text{pn}]\text{Cl}_2$ where $(\text{DO})(\text{DOH})\text{pn} = \text{N}^2, \text{N}^{2'}\text{-propanediylbis-2,3-butanedione-2-imine-3-oxime}$ was adsorbed irreversibly and strongly on the surface of preanodized glassy carbon electrode. Electrochemical behavior and stability of modified GC electrode were investigated by cyclic voltammetry. The electrocatalytic reduction of dioxygen has been studied using this modified glassy carbon electrode by cyclic voltammetry, chronoamperometry and rotating disk electrode voltammetry as diagnostic techniques. The modified electrode showed excellent electrocatalytic ability for the reduction of dioxygen to hydrogen peroxide in acetate buffer (pH 4.0) with overpotential 1.0 V lower than the plain glassy carbon electrode. The formal potential for this modified electrode is not shifted to more negative potentials by repeated reduction-oxidation cycles in oxygen-saturated supporting electrolyte solution. The apparent electron transfer rate constant (k_s), the transfer coefficient (α) and the catalytic rate constant of O_2 reduction at a GC modified electrode were determined by cyclic voltammetry and rotating disk electrode voltammetry and were found to be around 2.6 s^{-1} , 0.33 and $2.25 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Based on the results, a catalytic mechanism is proposed and discussed.

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Introduction

The multielectron reduction of dioxygen has gained considerable attention over the past two decades. Direct reduction of O_2 requires overpotential at most conventional electrodes. The involvement of dioxygen in energy conversion and storage has led to a quest for newer catalysts for its electroreduction under different experimental conditions. Numerous complexes of water soluble Fe^{2+} ,^{1,2} Co^{2+} ,³⁻⁵ and Mn^{2+} porphyrins⁶ have been used as homogeneous catalysts for electroreduction of dioxygen. This reaction can proceed *via* two electrons to yield hydrogen peroxide or *via* four electrons to give water as the final product in aqueous solutions. In the solution, some of the compounds applied as catalysts for oxygen reduction react only slowly with O_2 and more of them are insoluble in aqueous media. But upon adsorption on electrode surfaces they become active catalysts for the reduction of O_2 .⁴⁻⁷ Therefore, modification of the electrode surface by electron transfer material is a common approach for preparing electrodes with electrocatalytic activity for dioxygen reduction. In this connection a wide variety of compounds have been proposed as electrocatalysts for the reduction of O_2 . Cobalt porphyrins,^{8,9} some complexes of Cu^{2+} ,^{10,11} and Fe^{3+} ¹² with chelating ligands, macrocyclic Co^{2+} complexes^{7,13,14} and vanadium-salen complexes¹⁵ have been applied by Anson in electrocatalysis of dioxygen reduction. The Pt, GC and OPG modified with vitamin B¹²,¹⁶ iron porphyrins¹⁷ and metal phthalocyanines¹⁸ and Co^{2+} -Schiff base complexes¹⁹ have been applied for electrocatalysis of O_2 reduction. The electrodes modified with

naphthoquinone and anthraquinone derivatives have been applied for O_2 reduction.²⁰⁻²⁴ We reported recently the electrocatalytic reduction of O_2 at the glassy carbon electrodes modified with adsorbed anthraquinone derivatives.^{25,26} In the present work we have examined the catalytic behavior of cobaloxime complexes (Fig. 1), which adsorbed on a preanodized glassy carbon electrode. The chemical and electrochemical studies of cobaloximes have received considerable attention for several years.²⁴⁻²⁹ Although there are many studies on the electrochemical reduction of dioxygen using various modified electrodes, there are no reports about the electrochemical reduction of dioxygen with cobaloxime modified GC electrodes. The electrochemical properties, stability and electrocatalytic activity of modified electrodes toward the electrocatalytic reduction of dioxygen were studied, using various electrochemical procedures such as cyclic voltammetry, chronoamperometry and rotating disk electrode (RDE) voltammetry. The electron transfer rate constant, the transfer coefficient and the catalytic rate constant for O_2 reduction at the surface of this modified electrode were determined. A possible mechanism for the catalytic reduction of O_2 is proposed.

Experimental

The cobaloxime complex (Fig. 1) was synthesized and characterized by IR, NMR and elemental analysis.²⁹ HPLC grade acetonitrile (Fluka) was used. Doubly distilled deionized water was used throughout. TBA(PF_6) [$(n\text{-But})_4(\text{PF}_6)$] and other reagents employed were of analytical grade from Merck or Fluka chemical companies and used without any further purification. The high purity (99.999%) nitrogen was used for deaeration of the solution. A single compartment cell with a

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Fig. 1 Structure of the $[\text{Co}((\text{DO})(\text{DOH})\text{pn})\text{Cl}_2]$ complex.

three-electrode configuration was used. The working electrode was a GC disk (2.0 mm diameter) from Methrom, which is modified as mentioned below. A platinum wire was used as the counter electrode. All potentials are quoted vs. Ag/AgCl (satd), 3 M KCl reference electrode in aqueous solutions. In acetonitrile, the working electrode was a platinum disk (3.0 mm diameter) and the reference electrode was an Ag/AgCl (satd) electrode immersed in a salt bridge consisting of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, which was placed in the main cell compartment. All applied electrodes were from Methrom.

The procedure of GC electrode pretreatment, activation and modification were as follows. Prior to use, the working electrode was polished mechanically with 0.05 μm alumina powder to obtain a mirrorlike surface and then washed with distilled water and acetone. Electrochemical activation of the electrode was performed by continuous potential cycling from -0.5 to 1.8 V at a sweep rate of 100 mV/s in H_2SO_4 (0.5 M) solution until a stable voltammogram was obtained. The preanodized glassy carbon electrode was then placed in the deposition solution (1.0 mM cobaloxime complex in acetonitrile) at open circuits for varying time periods (2–6 h).³⁰ The electrode was then thoroughly rinsed with doubly distilled water. The electrochemical measurements were carried out at a thermostated temperature of $25.0 \pm 0.1^\circ\text{C}$. Electrochemical experiments were carried out with a Methrom multipurpose instrument Model 693VA processor, equipped with a 694VA stand and a thermal printer. A Methrom drive shaft for rotating disk electrode was used.

Results and Discussion

Electrochemical properties of cobaloxime complex in acetonitrile solution

The cyclic voltammogram of the cobaloxime complex at various scan rates on the surface of Pt disk electrode is shown in Fig. 2. The two nearly reversible voltammetric responses correspond to the $\text{Co(III)}/\text{Co(II)}$ and $\text{Co(II)}/\text{Co(I)}$ couples as reported earlier.²⁷ The formal potentials E^0 are taken as the mid-points of the anodic and cathodic peak potentials for two couples are located about -230.0 and -750.0 mV vs. Ag/AgCl (satd), 0.1 M $\text{TBA}(\text{PF}_6)$ in acetonitrile as the reference electrode. The plots of peak currents vs. (scan rate)^{1/2} for both cathodic and anodic peaks are linear at the sweep rates of 20 to 2000 mV/s. For both couples, the ratios of anodic to cathodic peak currents are unity and the separation between the cathodic and anodic peak potentials is about 65 mV at low scan rate (20 mV/s), as expected for reversible diffusion controlled processes. The values of cathodic and anodic peak potentials do not shift toward the negative and positive direction with increasing scan

Fig. 2 Cyclic voltammograms for 1.0 mM cobaloxime complex on Pt disk electrode (3.0 mm diameter) in acetonitrile solution containing 0.1 M $\text{TBA}(\text{PF}_6)$ at scan rates: a) 100, b) 200, c) 300, and d) 400 mV/s.

rate. As Marzilli reported,²⁷ the reactions are as follows for the first and second reversible couples:

Electrochemical behavior and stability of the GC modified electrode

Figure 3 shows the cyclic voltammograms of the modified GC electrode in acetate buffer solution (pH 4.0) at various potential scan rates. A pair of well-defined redox peaks corresponding to the $\text{Co(III)}/\text{Co(II)}$ at 150 mV vs. Ag/AgCl (satd), 3 M KCl, provides evidence for prolonged surface attachment. The ratio of anodic to cathodic peak currents obtained at various scan rates was almost unity. The anodic and cathodic peak currents are directly proportional to the scan rate in the range below 100 mV/s, as shown in Fig. 3B, as predicted for a diffusionless system. At higher sweep rates, the peak current vs. sweep rate plot deviates from linearity and the peak current becomes proportional to the square root of the sweep rates, indicating diffusional behavior in charge transport. The peak to peak potential separation (ΔE_p) is small and about 30.0 mV for sweep rates below 30.0 mV/s. At higher sweep rates, peak separation begins to increase, indicating the limitation due to charge transfer kinetics. Based on the Laviron theory³¹ the electron transfer rate constant (k_s) as well as the transfer coefficient (α) can be determined by measuring the variations of peak potentials with scan rate. The values of $\Delta E(E_p - E^0)$ were proportional to the logarithm of the scan rate for scan rates more than 500 mV s⁻¹ (Fig. 3C). The calculated values of k_s and α for cobaloxime deposited at the GC electrode surface at buffer solution (pH 4) were about 2.6 s⁻¹ and 0.33, respectively. The surface coverage Γ can be evaluated from the equation:

$$\Gamma = \frac{Q}{nFA} \quad (3)$$

where Q is the charge obtained by integrating the cathodic peak under the background correction (at a low scan rate of 10 mV/s), and the other symbols have their usual meanings. In the present case, the calculated value of Γ is 1.8×10^{-9} mol/cm² (the

Fig. 3 A) Cyclic voltammetric response of a modified GC electrode in buffer solution (pH 4.0) at scan rates: (a) 10; (b) 20; (c) 30; (d) 40; (e) 50; (f) 60; (g) 70; (h) 80; (i) 100 mV/s. (B) The plots of the cathodic and anodic peak currents vs. scan rate. (C) The variation of $\Delta E_p(E_p - E^0)$ vs. $\log v$ for GC-modified electrode.

immersion time of preanodized GC electrode in deposition solution is 3 h). The stability of the modified electrode and the reproducibility of its electrochemical behavior were investigated by cyclic voltammetry after storing it in acid or basic solutions for a long period of time and then recording the cyclic voltammograms. After immersion of the modified electrode in 0.5 M H_2SO_4 for 40 h and in basic solution (pH 8.0) for 24 h, only a slight decrease in the corresponding cyclic voltammograms (<5%) was observed. Although the adsorptive complex was continuously detached from the electrode surface after prolonged soaking in basic solution, the very last few monolayers of the adsorptive complex remained at the electrode surface even after brief polishing with alumina on a polishing cloth. Sometimes it required extensive polishing with sand paper in order to remove the residual adsorptive complex. This is most probably due to the fact that the complex used was not only simply adsorbed, but also trapped in inside pores or crevices of the GC electrode. In addition, there were no changes in the height or separation of the cyclic voltammograms after 500 cycles repetitive scanning in buffer solution (pH 4.0). The stability and reproducibility of the electrocatalytic effect of the modified electrode were examined by repetitive recording of the cyclic voltammograms in O_2 saturated solution at (pH 4.0). In contrast to electrodes modified with porphyrin compounds⁸ in this study, the cycling under O_2 (more than 1000 cycles at scan rate 20 mV/s) did not convert the adsorbed cobaloxime complex into a complex with a more negative formal potential for the Co(III)/Co(II) couple. This is one of the advantages for this modified electrode.

Catalytic reduction of O_2 at the surface of modified electrode

One of the objectives of this work was the development of a modified electrode capable of the electrocatalytic reduction of O_2 . In order to test the electrocatalytic activity of the GC-

Fig. 4 Cyclic voltammograms of a modified GC electrode in buffer solution (pH 4.0) at scan rate 10 mV/s in the absence of O_2 (a) and in saturated O_2 solution (b). Inset, similar conditions for an unmodified GC electrode.

modified electrode, the cyclic voltammogram was obtained in the absence and presence of O_2 in buffer solution (pH 4.0), the curves are presented in Fig. 4. The modified GC electrode in buffer (pH 4.0) without dioxygen in solution exhibits a well-behaved redox reaction (Fig. 4a), but in the O_2 saturated solution there is a dramatic enhancement of the cathodic peak current, and the anodic peak current disappeared (Fig. 4b). As shown in (Fig. 4), the cathodic peak potentials for reduction of O_2 on the surface of modified and unmodified electrodes are about 100 and -900 mV under identical conditions and the plain GC electrode exhibits a peak current lower than the modified electrode. As shown in the inset of Fig. 4, on the plain glassy carbon electrode the reduction of O_2 is observed but no anodic peak is found, which indicate an irreversible heterogeneous charge transfer in this system. So a decrease in overpotential of ca. 1.0 V and an enhancement of peak current at the surface of this modified electrode indicate an electrocatalytic process. Figure 5 shows the influence of O_2 concentration on the cyclic voltammograms of the modified GC electrode. As seen when increases the times that oxygen is bubbled through the solution, the cathodic peak current increase and the anodic peak decrease. Figure 6 shows the cyclic voltammograms of a modified GC electrode at various scan rates obtained in buffer solution (pH 4.0) saturated with O_2 . The peak current for the cathodic reduction of dioxygen is proportional to the square root of the scan rate (Fig. 6B). These results indicate that at sufficient overpotential the reaction is mass transport controlled. The catalytic reduction peak potential for O_2 shifts slightly to a more negative potential and the anodic peak begins to grow with increasing scan rate, suggesting a kinetic limitation existing in the reaction between the cobaloxime complex and O_2 . These results show that the overall electrochemical reduction of O_2 at the surface of this modified electrode might be controlled by the cross exchange process among dioxygen and the redox sites of

Fig. 5 Cyclic voltammograms of the modified GC electrode in 0.1 M acetate buffer solution (pH 4.0) at 10 mV/s in the absence (a) and presence (b – g) of increasing concentration of O₂. The oxygenation time is (a) 0.0; (b) 10; (c) 25; (d) 40; (e) 70; (f) 110; (g) 150 s.

the surface-attached cobaloxime complexes and the diffusion of O₂. A similar behavior has also been reported for some other modified electrodes.^{32,33}

Chronoamperometric studies

The catalytic reduction of O₂ at the surface of modified GC electrodes was studied by chronoamperometry. The double potential-step technique at an initial and final potential of –200.0 and 300.0 mV vs. Ag/AgCl (satd), 3 M KCl, was used for this purpose. Chronoamperometric measurements in the absence and presence of dioxygen are depicted in Fig. 7. As shown in Fig. 7A (chronoamperograms a & b), when the potential step is –200 mV in O₂ saturated solution, the current is about –45 and –10 μA respectively, at the surface of modified and unmodified GC electrodes. When the potential step converts to +300 mV, the currents observed for modified and unmodified GC electrodes are about +10 and 6 μA (Fig. 7A, chronoamperograms a' & b'). This is indicative of the irreversible nature of the catalytic reduction of dioxygen.²⁴ For the modified electrode in the absence of O₂ (Fig. 7B chronoamperograms a & a'), the currents for initial and final step potential is about 15 μA and this is indicative of the reversible nature of Co(III)/Co(II) couple. In the absence of O₂, the plot of net currents (point by point subtraction of the background current) against $t^{-1/2}$ shows a straight line, which extrapolates to close to the origin (Fig. 7C, curve 1). Since the oxidized and reduced forms of complex are to be insoluble in water, such a near correlation behavior may be explained by finite diffusion in thin film.^{24,33} But in the presence of O₂, the corresponding plot of net currents vs. $t^{-1/2}$ (Fig. 7C, curve 2) is linear in a short time period, while it deviates from linearity in a longer time period. The extrapolation of the linear part of the I vs. $t^{-1/2}$ plot will result in an intercept at about 7 μA. Since the direct reduction of O₂ at a plain GC electrode shows only a residual current, the transient current seems to be largely due to the catalytic reduction of O₂ by the cobaloxime complex used. According to the integrated Cottrell equation,^{34,35} Eq. (4), the number of electrons involved in O₂ reduction can also be estimated from the slope of the plot of Q vs. $t^{1/2}$ which resulted

Fig. 6A) Cyclic voltammograms of a modified GC electrode in (pH 4.0) O₂ saturated aqueous solution at various scan rates: (a) 10; (b) 20; (c) 30; (d) 40; (e) 50; (f) 60; (g) 70; (h) 80; (i) 100 mV/s. B) Plot of I_{pc} vs. $v^{1/2}$. C) Tafel plot derived from a current-potential curve at scan rate 10 mV/s. D) Plot of E_{pc} vs. $\log v$.

from chronoamperometric experiments carried out on cobaloxime complex/GC electrode (Fig. 7D).

$$Q = \frac{2nFACD^{1/2}t^{1/2}}{\pi^{1/2}} \quad (4)$$

When $A = 0.0314 \text{ cm}^2$, $C = 1.25 \text{ mM}$, $D = 1.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and slope $34.944 \text{ } \mu\text{C s}^{-1/2}$, it is calculated that $n = 2.10$. It is estimated that the total number of electrons involved in the reduction of O₂ is 2.0 and that the reduction product is H₂O₂.

Kinetics of the electrocatalytic reduction of O₂

In this work, RDE voltammetry was used for the estimation of the catalytic reaction rate constant (k) between the adsorbed cobaloxime complex and dioxygen. The RDE voltammograms were recorded for O₂ saturated solution in buffer solution (pH 4.0) and at various rotation rates using a modified glassy carbon rotating disk electrode with a coverage of $1.1 \times 10^{-9} \text{ mol cm}^{-2}$ (the immersion time of preanodized GC electrode in deposition solution is 2 h). A set of current potential curves is shown in Fig. 8A. The Levich plots were made for a potential kept at –300 mV, i.e. just on the plateau obtained when the voltage was scanned slowly during rotation. The limiting current I_L is defined as the difference between the currents on a modified electrode at –300 mV in deaerated and O₂ saturated solutions. Figure 8B represents the Levich plot for the electroreduction of O₂ at a modified GC electrode, and the clear lack of linearity suggests immediately that the reaction is limited by kinetics and not by mass transport. Similar results have also been reported

Fig. 7 Chronoamperometric response in buffer solution (pH 4.0) obtained by the double potential-step technique at an initial and final potential of -200 and 300 mV. A) a & a' for modified GC electrode in O_2 saturated solution. b & b' as a & a' for unmodified GC electrode. B) a & a' for modified GC electrode in the absence of O_2 , b & b' as a & a' for unmodified GC electrode. C) plots of net currents vs. $t^{1/2}$ for the modified GC electrode in the absence (1) and saturated O_2 solution (2). D) the plot of Q vs. $t^{1/2}$ for modified GC electrode in O_2 saturated solution (pH 4.0) at -200 mV.

in the literature.^{10-12,24} The Levich plot in Fig. 8B is very close to the calculated line for a two-electron process ($n = 2$). Under these conditions, the Koutecky-Levich equation formulated as follows can be used to determine the rate constant for the catalytic reaction rate between the reduced cobaloxime complex and O_2 :

$$\frac{1}{I_{\text{Lim}}} = \frac{1}{I_{\text{Lev}}} + \frac{1}{I_k} \quad (5)$$

and

$$I_{\text{Lev}} = 0.62nFAD^{2/3}\nu^{1/6}C_{O_2}\omega^{1/2} \quad (6)$$

$$I_k = nFA\Gamma C_{O_2} \quad (7)$$

Here C_{O_2} is the bulk concentration of the reactant (dioxygen) in solution, Γ is the total surface coverage, ν is the kinematic viscosity, ω is the angular frequency of rotation and k is reaction rate constant, which all other symbols have their conventional meanings.

As shown in Fig. 8C, the Koutecky-Levich plot is linear with a slope close to that of the calculated line for the reduction of O_2 via two electrons. From the above equation it is apparent that the value of k can be determined from the intercept of the plot I_{lim}^{-1} vs. $\omega^{-1/2}$. The value obtained for the rate constant from the intercept of Koutecky-Levich plot was found to be $2.24 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This value is comparable with those reported previously for the electrocatalytic reduction of dioxygen at the electrodes modified with other mediators.^{13,14,24-26} The diffusion coefficient of O_2 in buffered aqueous O_2 saturated solution (pH 4.0) was determined as $1.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ using the Levich equation at various rotation speeds of the rotating GC electrode.

Fig. 8A) Current-potential curves at a rotating modified GC electrode in buffer solution (pH 4.0) (a) in the absence of O_2 at rotation rate 200 and (b - i) at different rotation rates in O_2 saturated solution: (b) 200; (c) 400; (d) 600; (e) 800; (f) 1000; (g) 1400; (h) 1800; (i) 2400 rpm, for each voltammogram potential scan rate 6 mV/s. B) Levich plot of limiting currents at -300 mV and theoretical Levich plots for two and four electron reduction of O_2 respectively. (C) Koutecky-Levich plots of the data.

The value of kinematic viscosity of water (ν) and the concentration of O_2 in solution used in this calculation were $0.01 \text{ cm}^2 \text{ s}^{-1}$ and 1.25 mM , respectively.^{20,21} The value obtained for the diffusion coefficient of O_2 is comparable with the reported values.^{24-26,36} On the basis of previous reports,^{16,18} in order to get information on the rate-determining step, a Tafel plot was drawn, derived from data of the rising part of the current-voltage curve at scan rate 10 mV/s (cyclic voltammogram "a" in Fig. 6) in buffer solution (pH 4.0) saturated with dioxygen. A slope of $-190.7 \text{ mV decade}^{-1}$ is obtained to indicate the one-electron transfer to be rate limiting assuming a transfer coefficient of $\alpha = 0.31$ (Fig. 6C). The Tafel slope b , can be obtained by another method. As shown in Fig. 6D, the peak potential E_p is proportional to $\log \nu$. The slope of E_p vs. $\log \nu$ is $\partial E_p / \partial (\log \nu) = -102.67 \text{ mV}$. The Tafel slope may be estimated according to Eq. (8):³⁷

$$E_p = \frac{(b \log \nu)}{2} + \text{Constant} \quad (8)$$

On the basis of this equation, the slope of E_p versus $\log \nu$ plot is $b/2$, where b indicate the Tafel slope. So, $b = 2 \times \partial E_p / \partial (\log \nu) = -205.34 \text{ mV}$. This slope indicates a one-electron transfer to be rate-limiting assuming a transfer coefficient of $\alpha = 0.29$. These results are close to there obtained from polarization measurements, slope -190.7 mV and $\alpha = 0.31$. A catalytic mechanism that is compatible with the behavior observed is given in reactions (9) - (13).

Here L is the oxime ligand. The formal potentials E_2^f and E_3^f are unknown, but they must be at least as positive as 0.15 V to account for the presence of only one cathodic peak in Figs. 4, 5 and 6, where the reduction of $(\text{LCo})^{2+}$ and the catalyzed reduction of O_2 proceed simultaneously. Such behavior has also been reported for similar modified electrodes.^{7,13,14,16,18}

Conclusion

Cobaloxime complex deposited at the surface of GC electrode acts as a catalyst for the electroreduction of O_2 to H_2O_2 in aqueous buffer (pH 4.0) solution with an overpotential of about 1.0 V lower than that at a bare GC electrode. The cyclic voltammograms of the resulting modified electrode revealed the presence of a single one electron couple redox reaction with formal potential 0.15 V with respect to Ag/AgCl (satd), 3 M KCl. On the basis of the Tafel plots the charge transfer step of the rate-limiting reaction is suggested to be a one-electron transfer, with a transfer coefficient of *ca.* 0.3. It is concluded that the catalytic process is controlled by the rate of electron transfer between O_2 and adsorbed complex and diffusion of O_2 . In contrast to electrodes modified with porphyrin compounds the potential of this modified electrode by repeated reduction-oxidation cycle in the presence of O_2 (for time >20 h) is not shifted to more negative potentials. The study on the electrochemical properties and electrocatalytic activity of cobaloxime dimmer compounds for O_2 reduction continues in our laboratory.

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