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Electroreduction of oxygen enriched in a [poly(ethyleneiminato)]cobalt(II) layer

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An aqueous solution of a [poly(ethyleneiminato)]cobalt(II) complex that reversibly binds and releases O_2 functions as an O_2-enriching medium for an O_2 electrode to enhance the current for the uncatalyzed reduction of O_2. The effect of the electrochemically inactive cobalt complex is to supply reducible O_2 to the solution within the diffusion layer near the electrode by releasing the bound O_2 from the O_2 adduct, which contributes to a decrease in the diffusion layer thickness of O_2. Based on the rapid release of O_2 from the O_2 adduct, a diffusion-limited current is obtained for the reduction of O_2. The hypothetical concentration of the enriched O_2 supplied under pure diffusion control (*i.e.* unperturbed by the kinetics of the O_2 binding) is several times larger than that of the actual concentration of O_2 due to the higher solubility of the O_2 adduct than the physical solubility of O_2 in H_2O at room temperature under an atmosphere of air. An insoluble membrane of a cobalt(II) complex with a cross-linked poly(ethyleneimine) ligand that has the ability to swell serves as an O_2-enriching material to concentrate O_2 from aqueous electrolyte solutions. A new type of O_2-diffusion electrodes for metal/air batteries and fuel cells is proposed using the O_2-enriching material immobilized at the electrode surface.

Introduction

The design of O_2 electrodes with improved performance in metal/air batteries and fuel cells is one of the important goals in electrochemical oxygen technologies.[1] This design process should take into account both the interfacial electron transfer at the electrode and the transport of O_2 onto the electrode from the atmosphere. The inherent slow kinetics of electrochemical reactions involving O_2 have prompted extensive studies to enhance the rate of electron transfer, which have spawned a number of electrocatalysts such as metallic particles, metal oxides, alloys, and organic macrocycles.[1] On the other hand, less attention has been given to the development of electrode materials with enhanced O_2 transport properties. Even with the recent gas-diffusion electrodes with extended reaction zones at electrode/liquid/gas interface, the reduction of O_2 is so rapid that the discharging current is often limited by the transport of O_2 and that the battery is "suffocated".

One could suppose that an increase in the local concentration of O_2 near the electrode leads to a larger diffusion-limited current for the reduction of O_2. A metal complex that reversibly binds and releases O_2 in response to the concentration of O_2 is the best candidate for an O_2-enriching material,[2] because the O_2 adduct dissolves more readily than O_2 in electrolyte solutions and supplies O_2 to the electrode by releasing the bound O_2 within the diffusion layer near the electrode.[3] Fig. 1(a) shows the hypothetical contribution of the O_2 adduct with a concentration of $C^*_{O_2\ \mathrm{adduct}}$ to the decrease in the diffusion layer thickness of O_2 (δ_S) from that (δ_{O_2}) formed with a lower concentration of O_2 ($C^*_{O_2}$). In this case, the electroactive species, O_2, is generated by its release from the O_2 adduct, which precedes the electron transfer at the electrode. The O_2-binding equilibrium favors the nonreducible O_2 adduct over the reducible O_2, and thus the release of O_2 should precede the reduction of O_2. Nevertheless, the reduction of O_2 is not governed by the kinetics of the preceding reaction when the binding and the release of O_2 is so rapid that the equilibrium is always maintained in an experiment of sufficiently long duration t.[4] A dimensionless kinetic parameter $\lambda = (k_f + k_b)t$ has been defined for the chronoamperometric analysis of a general C_rE_r (reversible heterogeneous electron transfer preceded by reversible homogeneous chemical reaction) reaction ($X \rightleftharpoons O$ and $O + ne^- \rightleftharpoons R$ where $K = k_f/k_b = C_O/C_X$).[5] A sufficiently large time scale λ is required for an ideal O_2-enriching material to supply O_2 to the electrode under pure diffusion control.

In this paper, we report that a [poly(ethyleneiminato)]cobalt(II) complex dissolved in an aqueous electrolyte solution is an excellent O_2-enriching material. The cobalt(II) complex with amine ligands is one of the most familiar metal complexes with a reversible O_2-binding property in aqueous solutions,[6] and their O_2 adducts have been well characterized as binuclear complexes $[LCo^{III}–O_2–Co^{III}L]$.[7–9] Remarkably, the dissociation of O_2 from the polymeric complex is very rapid with a rate constant of $1.1 \times 10^5\ s^{-1}$, and yet the O_2-binding constant is moderate with P_{50} of *ca.* 5 mmHg depending on the concentration of the cobalt center.[10,11] According to the diagnosis of the kinetic behavior using the values of log K and log λ,[5] a diffusion-limited current response is expected for the reduction of enriched O_2. Furthermore, a cobalt(II) complex with a cross-linked poly(ethyleneimine) ligand[12–15] can provide an insoluble and swellable O_2-enriching membrane to modify the electrode surface which can operate even in pure electrolyte solutions when the diffusion layer thickness of O_2 is much smaller than the membrane thickness (ϕ) (Fig. 1 (b)). This type of modified electrode, unprecedented to the best of our knowledge, effects the enhancement of the O_2 reduction current when $t \ll \phi^2/4D_{O_2}$ ($\delta = 2(Dt)^{1/2} \ll \phi$).

Experimental

Materials

Poly(ethyleneimine) ($\bar{M}_n$ = *ca.* 6×10^4, 50 wt% solution in H_2O) was obtained from Aldrich. Cobalt(II) chloride, potassium dihydrogenphosphate, sodium hydrogenphosphate, acetic acid, and sodium acetate were obtained from Kanto Chem. Co. and used without purification. Poly(epichlorohydrin) ($\bar{M}_n$ = *ca.* 7×10^5) was obtained from Acros Chem. Co. and purified

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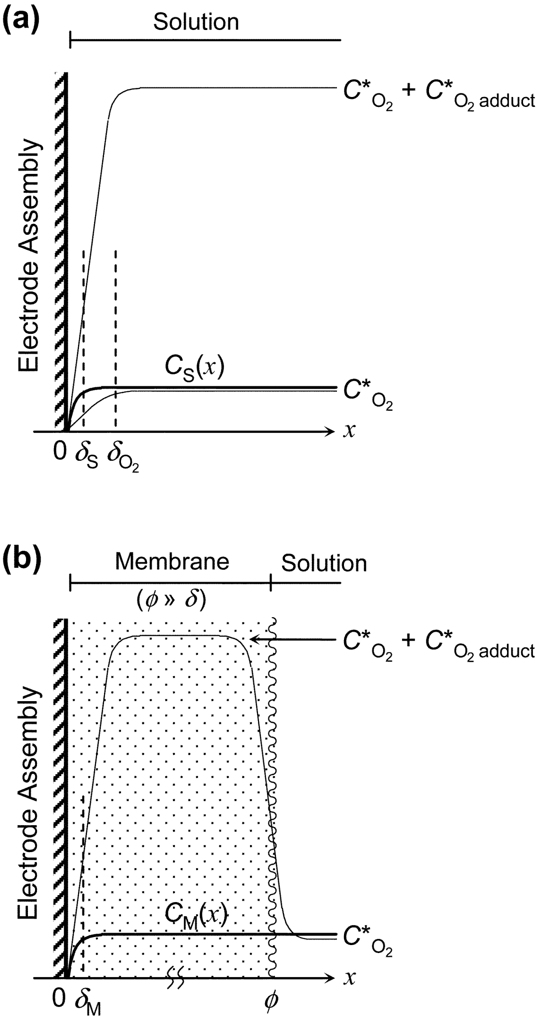

Fig. 1 Schematic concentration profile for the reduction of O_2 where the current is determined by the mass transfer of O_2 onto the electrode surface. The system is a stationary electrode immersed in an electrolyte solution containing both O_2 and a [LCo^{III}–O_2–$Co^{III}L$] complex (a), or in an electrolyte solution of only O_2 after modification of the electrode surface with the membrane of a polymeric [LCo^{III}–O_2–$Co^{III}L$] complex of thickness ϕ (b). The concentration of O_2 is shown as $C_S(x)$ and $C_M(x)$ with bold curves as a function of the distance (x) from the electrode surface in the solution (a) and in the membrane (b), respectively. The concentrations of O_2 and the [LCo^{III}–O_2–$Co^{III}L$] complex at $x = \infty$ are shown as $C^*_{O_2}$ and $C^*_{O_2\ adduct}$, respectively.

by precipitation from a solution of benzene and methanol. All solvents were purified by distillation before use.

A cobalt(II) complex with a cross-linked poly(ethyleneimine) ligand was prepared according to the method described in the literature[12] with slight modifications as follows. A solution of poly(epichlorohydrin) (0.03 g) and poly(ethyleneimine) (0.03 g) in DMF (6 mL) was heated to 60 °C slowly enough to prevent gelation. After stirring for 1 h, the hot solution (200 μL) was transferred onto the surface of a glassy carbon disk electrode (A = 0.28 cm^2). The solvent was allowed to evaporate at 100 °C for 2 h. The thickness of the resulting polymer film was approximately 70 μm based on the density of the polymer (*ca.* 1 g cm^{-3}). Cobalt(II) chloride was incorporated into the polymer film by immersing the coated electrode in the aqueous saturated solution of cobalt(II) chloride for 24 h.

Modification of a MnO_2/C paste electrode (*vide infra*) with the cobalt(II) complex was accomplished by adhesion to the MnO_2/C electrode of a free standing thin film of the polymeric cobalt(II) complex which was prepared as follows. A hot concentrated solution of poly(epichlorohydrin) (1 g) and poly(ethyleneimine) (1 g) in DMF (10 mL) was layered on a PTFE plate with an area of 9 cm^2 and the solvent was allowed to evaporate at 100 °C for 20 h. Washing the product with methanol followed by drying under vacuum for 20 h afforded a transparent film of the cross-linked poly(ethyleneimine) ligand with a thickness of *ca.* 3 mm. The film was dipped into the saturated solution of cobalt(II) chloride for a sufficiently long time (3–4 days) to give the desired film of the cobalt(II) complex. The amount of cobalt(II) chloride in the polymeric complex was estimated to be $CoCl_2$: ligand = 0.14 (w/w).[11]

Apparatus and procedures

All measurements were performed at room temperature. Electrochemical measurements were carried out in conventional three-compartment glass cells. The working electrode was either a MnO_2/C paste electrode or a glassy carbon disk electrode. The MnO_2/C electrode was a gift from Matsushita Electric Co.; the electrode assembly consisted of a carbon paste pellet containing MnO_2 particles as the catalyst, which was embedded in a nickel mesh electrode and adhered on one side to a PTFE plate to provide structural integrity and with the other side exposed to the electrolyte solution or adhered to the film of the polymeric cobalt(II) complex. The apparent size of the electrode assembly was 3 × 3 cm^2. The glassy carbon disk electrode was obtained from Nikko Keisoku Co. and polished before each experiment with 0.05 μm alumina paste. The auxiliary electrode, a coiled platinum wire, was separated from the working solution by a fine-porosity frit. The reference electrode was a commercial SCE which was placed in the mail cell compartment. A Nikko Keisoku DPGS-1 dual potentio-galvanostat and a Nikko Keisoku NFG-3 universal programmer were employed with a Graphtec WX2400 X-Y recorder to obtain the current decay curves in potential step experiments and the cyclic voltammograms. The electrolyte solution was a phosphate buffer (pH = 5.8), an acetate buffer (pH = 5.6), or a 15 wt% aqueous solution of ammonium chloride (pH = 4.8). The concentration of O_2 in the electrolyte solution ($C^*_{O_2}$) was controlled by saturating the solution with a composition-defined mixture of O_2 and N_2 gases at 25 °C and 1 atm.

Results and discussion

Previous studies have revealed the reversible O_2-binding property of cobalt(II) amine complexes and the structure of the O_2 adduct, μ-peroxo dicobalt(III) complexes, based on the spectral changes upon coordination of O_2 and the amount of O_2 uptake.[2,10,11] In this report, a diffusion-limited current for the electroreduction of O_2 was exclusively used as the probe to determine the O_2-binding property of the cobalt amine complexes, with a view to using them as O_2-enriching materials in O_2 electrodes. A sufficiently high rate of O_2 reduction at the electrode must be achieved if they are to be used for this purpose, which can be accomplished using a suitable electrocatalyst or by applying a large overpotential with respect to the thermodynamic potential (or both). The electrode material was a high surface area carbon paste kneaded with MnO_2 powder as the immobilized catalyst, which was molded into a pellet and reinforced with a nickel mesh and a PTFE plate to complete the electrode assembly (see Experimental section). The open circuit potential of the MnO_2/C electrode immersed in a pH 5.6 acetate buffer at 25 °C under 20% O_2 was +0.39 V *vs.* SCE. The current for the reduction of O_2 was recorded every 10 s by applying a potential pulse at E = −0.7 V (Fig. 2(a), open circles). Essentially identical i–t plots were obtained at smaller overpotentials for the reduction of O_2 (*i.e.*, at higher electrode potentials up to +0.1 V). At t > 10 s, the current decay followed the Cottrell equation for planar diffusion with negligible variation of $it^{1/2}$ (Fig. 2(b), open circles), which indicated that the planar diffusion of O_2 could be closely approximated even with the paste electrode at a sufficiently

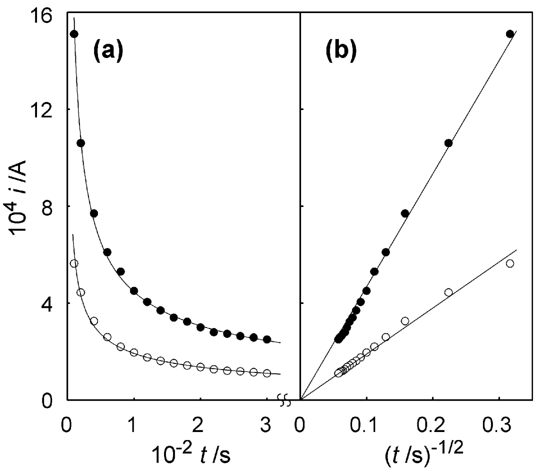

Fig. 2 Reduction current decays (a) and Cottrell plots (b) in a long time regime ($10 < t < 300$ s) after the application of a potential pulse at -0.7 V *vs.* Ag/AgCl. The currents were recorded with the MnO_2/C electrode immersed either in a solution of $CoCl_2$ (10 mmol L^{-1}) and poly(ethyleneimine) (20 mmol unit L^{-1}) dissolved in a pH 5.6 acetate buffer (●) or in a blank solution of the acetate buffer in the absence of $CoCl_2$ and poly(ethyleneimine) (○). Both solutions were saturated with 20% O_2 ($C^*_{O_2} = 0.2$ mmol L^{-1}).

large t when the diffusion layer thickness $2(D_{O_2}t^{1/2})$ became much larger than the geometric roughness of the electrode surface. Further support for this interpretation is provided by the coincidence of the calculated electrode area with the apparent geometric size of the MnO_2/C electrode; the value of $it^{1/2}$ is approximate for O_2 diffusivity $D_{O_2} = 2 \times 10^{-5}$ cm^2 s^{-1} and 20% O_2 solubility $C^*_{O_2} = 0.2$ mmol L^{-1} at 25 °C,[16] when n, the number of electrons electroreducing the O_2, equals 4 and the electrode area A is 3×3 cm^2. The upward deviation of the i–t plots from the Cottrell equation at the initial stage of the electrolysis ($t < 5$ s), probably due to the nonfaradaic charging process and the reduction of O_2 at the inner pore of the electrode, is outside the scope of the present study. It may be added that only the nonfaradaic current was observed under argon in a shorter time regime ($t < 1$ s).

The i–t plots were recorded in a solution prepared by dissolving poly(ethyleneimine) (20 mmol unit L^{-1}) and cobalt(II) chloride (10 mmol L^{-1}) in a pH 5.6 acetate buffer under 20% O_2 (Fig. 2(a), closed circles). The large formation constant of the cobalt(II) amine complex ensures that a reasonable amount of the polymeric complex is formed in the solution.[2] In the presence of the cobalt(II) complex, there are at least three features that warrant attention. In the first place, a larger current was obtained for the reduction of O_2, and yet the Cottrell equation for planar diffusion was rigorously obeyed (Fig. 2(a) and (b), closed circles). Secondly, the time-independent parameter $it^{1/2}$ increased with the addition of poly(ethyleneimine) and reached a maximum value near 50 mmol unit L^{-1} (Fig. 3, closed circles), which suggests that the O_2 adduct was a six-coordinate μ-dioxo dinuclear complex $[N_5Co^{III}–O_2–Co^{III}N_5]$ with a stoichiometric relationship of [ethyleneimine unit] : [Co] = 5. Thirdly, while the physical dissolution of O_2 in solutions without the cobalt(II) complex obeyed a Henry isotherm where $it^{1/2}$ was proportional to the concentration of O_2 (Fig. 4, open circles), the variation of $it^{1/2}$ in the presence of the cobalt(II) complex conformed to a Langmuir isotherm for dual-mode dissolution (Fig. 4, closed circles): onto the Henry isotherm was piggybacked a flux of enriched O_2 (the shaded area in Fig. 4) which steeply increased at low concentrations of O_2 and predominated over the physical flux, and finally became constant at higher concentrations of O_2. This flux curve of the enriched O_2 corresponds to the O_2-binding equilibrium curve of the cobalt(II) complex.[10] The O_2 affinity of P_{50} = *ca.* 2 mmHg (*i.e.*, 3×10^{-3} mmol L^{-1}) is comparable with the previous result (*ca.* 5 mmHg) determined spectrally.[10] These results demonstrate that the cobalt(II) complex acts as the O_2-enriching medium, not as an electrocatalyst for the reduction of O_2.

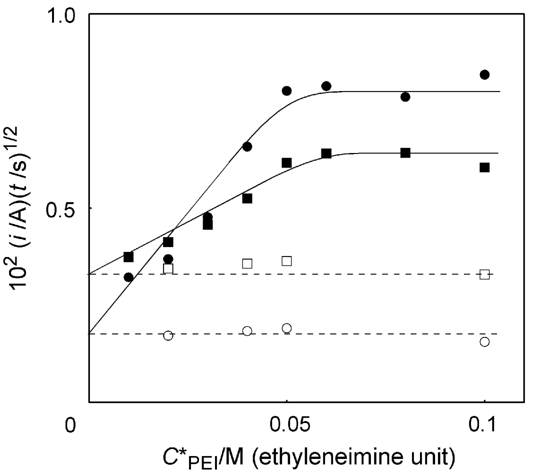

Fig. 3 Products of diffusion-controlled currents and $t^{1/2}$ for the reduction of O_2 obtained with solutions prepared by dissolving $CoCl_2$ (10 mmol L^{-1}) and various concentrations of poly(ethyleneimine) (C^*_{PEI}) in a pH 5.6 acetate buffer (●) or 15 wt% aqueous NH_4Cl (pH = 4.8) (■). Open circles show the reduction currents obtained with a blank solution of acetate buffer (○) or NH_4Cl (□) in the absence of $CoCl_2$ and poly(ethyleneimine). All solutions were saturated with 10% O_2 ($C^*_{O_2} = 0.1$ mmol L^{-1}). Other conditions are as in Fig. 2.

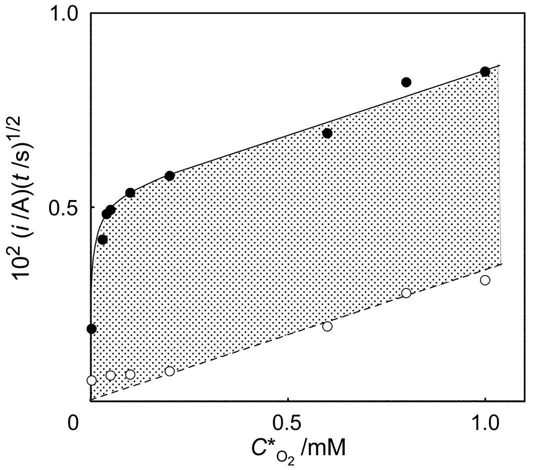

Fig. 4 Products of diffusion-controlled currents and $t^{1/2}$ for the reduction of O_2 obtained either with a solution of $CoCl_2$ (10 mmol L^{-1}) and poly(ethyleneimine) (50 mmol unit L^{-1}) in a pH 5.6 acetate buffer (●) or with a blank solution of the acetate buffer in the absence of $CoCl_2$ and poly(ethyleneimine) (○). The solutions were saturated with various concentrations of O_2 ($C^*_{O_2}$). Other conditions are as in Fig. 2.

A remarkable aspect of O_2 enrichment using the cobalt(II) complex is the lack of the kinetic perturbation during the release of O_2 from the μ-dioxo cobalt(III) complex, which is evidenced by the diffusion-limited current response consistently obtained for the reduction of enriched O_2. A sufficiently large parameter of $\lambda^{4,5}$ may be accomplished not only by the rapid release of O_2 from the cobalt(III) complex,[10] but also by the long time over which measurements were taken ($t > 10$ s) which is rather typical in the practical use of batteries. It follows that the cobalt(II) complex solution can be regarded as a better solvent for O_2 than H_2O. The hypothetical concentration of enriched O_2 ($C^*_{O_2} + C^*_{O_2\ \mathrm{adduct}}$ in Fig. 1(a)) deduced from the reduced diffusion layer thickness (δ_S) was several times larger than the concentration of physically dissolved O_2 and could be controlled by varying the concentration of the cobalt(II) complex as shown in Fig. 3. However, weakly acidic electrolyte solutions must be employed to balance the stability of the cobalt complex and the activity of the MnO_2 catalyst; the effect of the cobalt(II) complex became less prominent in more acidic solutions (Fig. 3, closed squares) and in basic solutions, due to the concomitant decomposition of the cobalt complex.

An important extendability of the cobalt(II) complex that surpasses liquid solvents in the dissolution of O_2 is the feasibility of forming an insoluble and swellable membrane using a cross-linked poly(ethyleneimine) ligand,[12] which serves as an O_2-enriching material to concentrate O_2 from aqueous electrolyte solutions. A high O_2 affinity and the rapid release of O_2 also holds for the complex when the ligand is cross-linked with poly(epichlorohydrin).[11] An O_2-diffusion electrode can thus be obtained using O_2-enriching material immobilized at an electrode surface. A thin membrane of the cobalt(II) complex attached to an electrode surface as well as a free-standing thick membrane were obtained simply by dipping the cross-linked ligand into an aqueous solution of $CoCl_2$ for a sufficiently long time[11] (see Experimental section). In a cyclic voltammogram recorded with a glassy carbon disk electrode, the uncatalyzed reduction of O_2 was observed at potentials lower than −0.3 V (Fig. 5(a)). A significant increase in the current magnitude was noticed when the electrode surface was modified with a thin membrane of the cobalt(II) complex (Fig. 5(c)). It may be noted that the peak potential for the reduction of O_2 slightly shifts to a more positive value, which indicates that the polymeric cobalt(II) complex, at least in the membrane attached to the electrode surface, could give rise to concomitant electrocatalytic reduction of O_2 even though it acts as a pure O_2 carrier in solution (*vide supra*). Semi-infinite diffusion of O_2 within the cobalt membrane is approximated when the thickness of the membrane (ϕ) is much larger than the diffusion layer thickness of O_2 (δ_M) (Fig. 1(b)). The free-standing thick membrane of the cobalt complex (ϕ = 3 mm) adhered to the MnO_2/C paste electrode allowed the reduction current of O_2 to be enhanced for several minutes (Fig. 6, closed circles). When the enriched O_2 in the membrane was used up after a prolonged period of electrolysis, the magnitude of the current plummeted because the flux of O_2 was then controlled by mass transfer from the outside of the membrane, but was reinstated after waiting for several minutes at rest (*i.e.* open circuit) in order to allow saturation of the membrane with O_2 from the bulk solution.

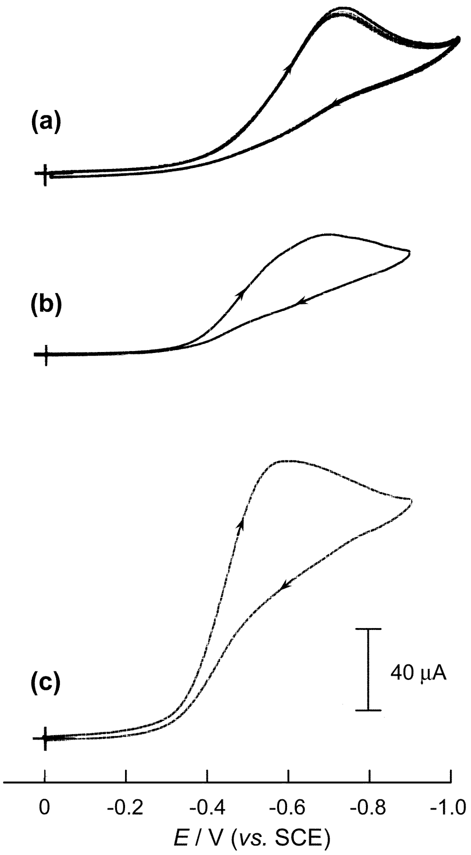

Fig. 5 Cyclic voltammograms for the reduction of O_2 recorded with (a) a glassy carbon disk electrode with a diameter of 6 mm, (b) the same electrode modified with a cross-linked poly(ethyleneimine) film, and (c) the same electrode modified with a cross-linked poly(ethyleneimine) film in which cobalt(II) chloride was incorporated. The thickness of the film was *ca.* 7 μm. The electrolyte solution was a pH 5.8 phosphate buffer saturated with 100% O_2. Scan rate = 25 mV s^{-1}.

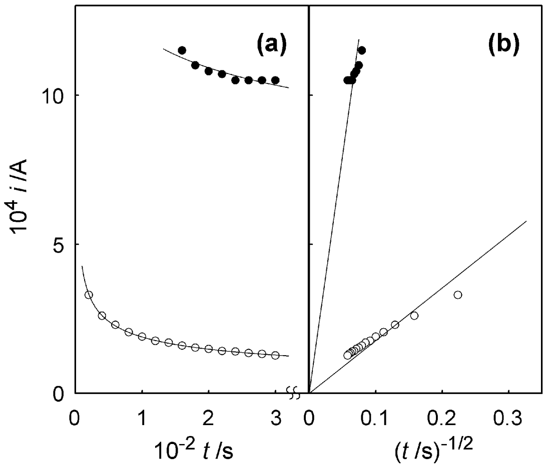

Fig. 6 Reduction current decays (a) and Cottrell plots (b) after the application of a potential pulse at −0.7 V *vs.* Ag/AgCl recorded with the MnO_2/C electrode modified with the free standing film of the cross-linked [poly(ethyleneiminato)]cobalt(II) chloride (●) or with the cross-linked poly(ethyleneimine) film in the absence of cobalt(II) (○). The electrolyte solution was a pH 5.6 acetate buffer saturated with air.

More detailed studies on the concentration profile of O_2 within the membrane during electrolysis, the identification of the catalytic activity of the membrane of the cobalt complex, and the discharging property of the O_2 battery using the O_2-enriching materials are the subject of our ongoing research which will be reported in the near future.

Conclusions

The [poly(ethyleneiminato)]cobalt(II) complex that reversibly binds and releases O_2 depending on the concentration of O_2 can be regarded as an O_2 enricher in aqueous solutions. The high solubility as well as the kinetic and thermodynamic aspects of the cobalt(II) complex, characterized by the rapid release of O_2 and the relatively high O_2 affinity, are the key to allow the accumulation and the diffusion-limited mass transport of O_2. These features are typically observed as the enhanced and yet diffusion-limited reduction current of enriched O_2 at the electrode which is in contact with a layer of the cobalt complex. The accumulation of O_2 to increase the local concentration of O_2 near the electrode is accomplished using an insoluble membrane of the cobalt(II) complex with a cross-linked poly(ethyleneimine) ligand. The modified electrode has no leachable components, making it suitable for use in O_2 batteries to effect the enhancement of the O_2 reduction current not continuously but at least transiently.

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References

1 K. Kinoshita, *Electrochemical Oxygen Technologies*, Wiley, New York, 1992.

2 H. Nishide, X. Chen and E. Tsuchida, in *Functional Monomers and Polymers*, ed. K. Takemoto, R. M. Ottenbrite, and M. Kamachi, Marcel Dekker, New York, 1997, ch. 6, pp. 173.

3 X.-S. Chen, H. Nishide, K. Oyaizu and E. Tsuchida, *J. Phys. Chem. B*, 1997, **29**, 5725.

4 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 2001.

5 J.-M. Savéant and E. Vianello, *Electrochim. Acta*, 1963, **8**, 905.

6 G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1.

7 J. Simplicio and R. G. Wilkins, *J. Am. Chem. Soc.*, 1969, **91**, 1325.

8 C. G. Barraclough, G. A. Lawrance and P. A. Lay, *Inorg. Chem.*, 1978, **17**, 3317.

9 F. R. Fronczek, W. P. Schaefer and R. E. Marsh, *Acta Crystallogr. Sect. B*, 1974, **30**, 117.

10 H. Nishide, H. Yoshioka, S.-G. Wang and E. Tsuchida, *Makromol. Chem.*, 1985, **186**, 1513.

11 E. Tsuchida, H. Nishide and H. Yoshioka, *Makromol. Chem., Rapid Commun.*, 1982, **3**, 693.

12 T. Saegusa, A. Yamada, S. Kobayashi and S. Yamashita, *J. Appl. Polym. Sci.*, 1979, **23**, 2343.

13 S. Kobayashi, H. Shirasaka, K.-D. Suh and H. Uyama, *Polym. J.*, 1990, **22**, 442.

14 T. Saegusa, H. Ikeda and H. Fujii, *Macromolecules*, 1972, **5**, 108.

15 W. Lautsch, W. Broser, W. Rothkegel, W. Biedermann, U. Doering and H. Zoschke, *J. Polym. Sci.*, 1952, **8**, 191.

16 R. E. Davis, G. L. Horvath and C. W. Tobias, *Electrochim. Acta*, 1967, **12**, 287.