

Abstract

One of the characteristic chemical functions of cobalt complexes is the specific and reversible binding ability with molecular oxygen from air. Therefore, cobalt complexes could be applied as oxygen carriers and provide enormous potential applications, in particular in the air separation membrane and oxygen electrode. This thesis aimed at investigating the effect of polymer matrices on the oxygen-binding affinity of cobalt complexes, and oxygen permeation through carrier-mediated membranes, studying the mechanism of the oxidation of cobalt complexes, and prolonging the lifetime of oxygen carriers. In addition, the cobalt complexes were firstly applied to accumulate oxygen from the atmosphere to an electrode, and were expected to enhance the diffusion-limited current for the oxygen reduction.

Besides the chemical reactivity of cobalt complexes, the chemical structure of the polymer matrix has to be carefully designed to obtain a solid membrane easily applicable to air separation. In order to clarify the effect of the polymer matrices on the facilitated oxygen transport, poly(1-trimethylsilyl-1-propyne) (SP), poly(octyl methacrylate-*co*-vinylimidazole) (OIm), poly(lauryl methacrylate-*co*-vinylimidazole) (LIm), and poly(vinylidene dichloride-*co*-vinylimidazole-*co*-methyl methacrylate) (CIm) were synthesized. The membranes having both the selective and reversible oxygen-binding properties were prepared by complexing picket-fence cobaltporphyrin (CoP) with four polymer matrices. The CoP membranes reversibly changed from the deoxy form to the oxygen-binding one with an isobestic point in response to the partial oxygen pressure of the atmosphere in UV-visible spectra to obtain the oxygen-binding equilibrium curves. The curves obeyed the Langmuir-type isotherm for the CoP membranes to give the oxygen-binding affinity (p_{50}). The oxygen-binding equilibrium constant (K) of CoP fixed in the membranes remained constant, indicating that the oxygen-binding properties were not directly affected by the matrix species. Oxygen permeability coefficient (P_{O_2}) for the CoP membranes steeply increased with a decrease in the upstream oxygen pressure (p_{O_2}), indicating the CoP carrier fixed in the membrane interacts with oxygen and facilitates oxygen transport. The facilitation factor (defined as the ratio of P_{O_2} at the low and high p_{O_2}) was in the order of SP>LIm>OIm>CIm. The oxygen permeation through the CoP membranes was properly analyzed by a dual-mode model to give the physical diffusion coefficient of oxygen through the membrane (D_D), and the apparent diffusion coefficient of oxygen for hopping between the fixed carriers (D_C). The D_C value was smaller than that of D_D , but the D_C/D_D ratio still remained in the range of 1/5—1/50, indicating that CoP fixed in the membrane reversibly binds oxygen and facilitates oxygen transport. Despite the low oxygen permeability of the CIm-CoP

membrane, it exhibited the highest facilitation and separation factor, which could provide the product with the high oxygen concentration.

However, the CoP complex slowly loses its oxygen-binding ability due to irreversible oxidation reactions, limiting the lifetime of the membrane. The stability of carrier-mediated membranes is very important issue that will ultimately determine whether this technology is used for large-scale gas separation.

Fluorine-containing polymers possess unique properties such as high thermal and chemical stability, oleophobicity and hydrophobicity. A membrane having both a long operational lifetime and low water vapor permeability was prepared by coating a perfluororesin on the CoP polymer membrane. The oxygen-binding affinity of the CoP was not influenced by the coat, and the facilitated oxygen transport occurred even in the perfluororesin-coated membrane, whereas the water vapor permeability was significantly suppressed in comparison with that of the uncoated membrane. Lifetime of the CoP as an oxygen-carrier in the membrane was prolonged, for example, the half-lifetime of the perfluororesin-coated OIm-CoP membrane in water was 21 days, which was significantly long in comparison with the uncoated membrane. The results showed that in the solid membrane a water molecule (proton) attacks the CoP-bound dioxygen to yield a hydrodioxy radical and Co P, which diminishes the oxygen-binding ability of CoP and that of the membrane.

According to the above results, the fluorine-containing polymer as well as the ligand of the CoP, poly(vinylimidazole-*co*-fluoropentyl methacrylate) (FIm), was carefully designed and synthesized. A membrane having both a long operational lifetime and high oxygen permeability was prepared by complexing CoP with FIm. The lifetime of the CoP as an oxygen-carrier was prolonged even in a humid atmosphere (half-lifetime >200 days) due to the hydrophobic property of the FIm polymer. Oxygen permeation was selectively facilitated with the CoP fixed in the FIm membrane, and a high oxygen permeability ($10^{-7} \text{ cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$) maintaining the permselectivity ($P_{\text{O}_2}/P_{\text{N}_2}$ was estimated to be 12 at $p_{\text{O}_2}=1.5 \text{ cmHg}$) was observed. This high oxygen permeability for the fluorinated polymer would be ascribed to the fluoroalkyl side chain that has the high solubility of gases.

In addition to air separation membrane, the cobalt complexes with the reversible oxygen-binding property was used to accumulate oxygen from the atmosphere, which should contribute to an increase in the diffusion-limited current for the reduction of oxygen at the cathode in air batteries and fuel cells.

The oxygen concentration in the air-saturated water is *ca* 0.4 mM at 25 °C, and the reduction current of oxygen was determined by the oxygen concentration near the cathode and the thickness of the diffusion layer. The solution of CoP complexed with an

imidazole polymer was coated on a glassy carbon surface. The reduction current of oxygen at the cathode modified with the liquid CoP membrane (containing the supporting electrolyte) was significantly larger than that of the control membrane without CoP and remarkably increased with the CoP concentration. For example, the reduction current of oxygen for a 50 mM CoP membrane was around 10 times larger than that of the control membrane. The reduction current obeyed a Langmuir type while that of the control membrane without CoP behaved a Henry type. The results of rotating platinum ring-glassy carbon disk voltammetry suggested that over 90% of the oxygen was reduced by four electrons to hydroxyl regardless of the basicity of the solvent.

Then, a water-soluble (polyethyleneiminato)cobalt(II) complex (PEI-Co) that reversibly binds and releases oxygen was also carefully chosen as an oxygen-enriching medium for an oxygen electrode to enhance the current for the reduction of oxygen. Based on the high oxygen-binding affinity and the rapid release of oxygen from the oxygen adduct, a large diffusion-limited current was obtained for the reduction of oxygen at an electrode in the PEI-Co buffer solution, and the Cottrell equation for planar diffusion was rigorously obeyed. The time-independent parameter, the product of current and the square root of time, increased with the ratio of the PEI concentration to the CoCl_2 one, and reached a maximum value at 5, which suggests that the oxygen-adduct was a six-coordinate μ -oxo dinuclear complex. For the practical application, an insoluble and swellable membrane of a cobalt(II) complex with a cross-linked polyethyleneimine ligand was carefully prepared, and served as an oxygen-enriching material to accumulate oxygen from aqueous electrolyte solutions. A significant increase in the current magnitude was obtained when the electrode surface was modified with the thin PEI-Co membrane.

At last, a simple tetraphenylporphyrinatocobalt(II) (CoTPP) that reversibly binds and releases oxygen, and is less susceptible to the proton-induced oxidation in comparison with picket-fence cobaltporphyrin, functions as an oxygen-enriching medium for oxygen electrode to enhance the reduction current. A combination of the catalyst (Pt/C) and the oxygen enricher (CoTPP) resulted in a significant positive shift in the open circuit (equilibrium) potential and an increase in the diffusion-limited current density for the electroreduction of oxygen, which could practically be employed in superior air batteries and fuel cells.

The effect of the cobalt complex is to supply reducible oxygen to the solution within the diffusion layer near the electrode by releasing the bound oxygen from the oxygen adduct, which contributes to decrease the diffusion layer thickness of oxygen. A new type of oxygen-diffusion electrode for metal/air batteries and fuel cells is proposed using the oxygen-enriching material immobilized at the electrode surface.