Enhanced Oxygen Permeation through a Porous Glass Membrane Containing Phthalocyanato– and Porphyrinato–Cobalt Complexes as an Oxygen Carrier

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The pore surface of a porous glass membrane was modified with phthalocyanato- and tetraphenylporphyrinato-1-(benzylimidazole)cobalt(II) complexes, which specifically and reversibly binds molecular oxygen from air. The lower oxygen-binding affinity enhanced surface oxygen diffusion which improved permeability (3.0×10^{-11} kmol m s^{-1} m^{-2} kPa^{-1}) and (oxygen/nitrogen) permselectivity (10).

Phthalocyaninatometals have been extensively used as dyes and pigments in the paint, printing textile, and paper industries due to their extremely intense blue-green color, and high dyeing power. Due to their thermal and photochemical stability, phthalocyanines have the potential to be used for a variety applications in, such as sensors, catalysts, and photoconductors.[1,2]

Another attractive feature of phthalocyanine is its ability to active oxygen.[3] For example, during the catalytic oxidation of an aldehyde,[4] oxygen coordinates to the porphyrin, or phthalocyanines, to produce first an oxygen radical, and then, this oxygen radical reacts with the aldehyde. Since the reaction rate is extremely high, auto-oxidation of Co ion in the porphyrin complex, or phthalocyanine complex from Co(II) to Co(III) is observed at room temperature in solution in the presence of water. Therefore, it was difficult to observe reversible oxygen binding without a hydrophobic cavity. We were able to observe the reversible oxygen binding involving simple and planar porphyrins, azaporphyrins or phthalocyanines with the help of a polymer matrix, which produced a hydrophobic structure.[5–7] We also prepared oxygen-facilitated transport membranes, which have high oxygen permeability and (oxygen/nitrogen) permselectivity.

One of the advantages of using a porous membrane for gas separation is that high permeation can be obtained. Through a porous membrane, which has a pore size less than the mean free path of the permeate molecule, gas molecules permeate by Knudsen diffusion mechanism, in which the permeate diffuses with repeated collisions against the pore wall. On the other hand, the permselectivity for mixed gases is inversely proportional to the square root of the molecular weights of the permeants; for example, (oxygen/nitrogen) permselectivity is 0.94. We previously reported the enhanced oxygen diffusion in a porous membrane, which has chemically modified with a cobalt porphyrin that has a high oxygen-binding affinity, like the cobalt picket fence porphyrin (a typical oxygen carrier in the solution state).[8,9] However, the permeability and permselectivity at 0.93 kPa were still low (3.3×10^{-12} kmol m s^{-1} m^{-2} kPa^{-1} and 1.5, respectively). Using a complex, which reversibly binds oxygen and rapidly releases it, is another possible candidate to achieve better oxygen diffusion through a porous membrane, which causes a higher oxygen permeability and permselectivity.

This paper describes the chemically specific surface diffusion of oxygen through a porous glass membrane with a modified pore surface using both tetra-*t*-butylphthalocyanatocobalt (CoPc) and tetraphenylporphyrinatocobalt (CoTPP), and 1-benzylimidazole (BIm) as a fixed oxygen carrier (Chart 1). BIm was selected as a ligand, due to its small molecular size because the polymer ligand will fill the pores of the porous glass membrane. The temperature dependency of this enhanced oxygen diffusion is also discussed.

Results and Discussion

A hollow vycor glass membrane was filled with a THF solution containing CoPc and BIm, and the pore surface of the glass membrane was physically modified with the CoPc-BIm complex under a nitrogen atmosphere to form a uniform blue-colored membrane. The homogeneous introduction of CoPc into the membrane was confirmed because of the homogeneous blue coloring of the broken pieces of the glass membrane.

The pore structure of the porous membranes modified with CoPc- or CoTPP-BIm was studied using BET nitrogen desorption measurements. The pore volume of the membrane was estimated by subtracting the specific volume of the membrane

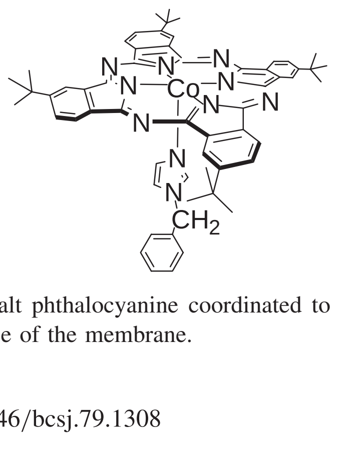

Chart 1. Cobalt phthalocyanine coordinated to BIm on the pore surface of the membrane.

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Table 1. Physical Parameters of the Porous Membranes before and after Coating with the CoPc- and CoTPP-BIm

	CoPc-BIm	CoTPP-BIm	Unmodified
Surface area /$m^2\ g^{-1}$	223	222	238
Mean pore diameter/nm	4.3	4.3	4.5
Pore volume /$cm^3\ g^{-1}$	0.24	0.23	0.27

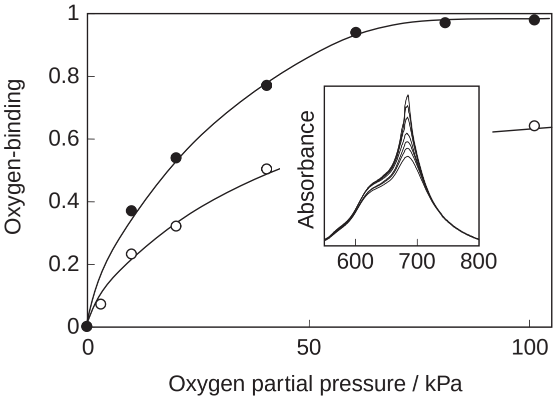

Fig. 1. Oxygen-binding equilibrium curves for the CoPc-BIm membrane. ●: −55 °C; ○: −45 °C. Inset: Visible absorption spectra change of CoPc-BIm membrane at −55 °C; Oxygen partial pressure: 0, 5, 10, 40, 60, 80, and 100 kPa.

itself from that measured by Hg and is shown in Table 1. The surface area, mean pore diameter, and pore volume of the membrane after the incorporation of CoPc- or CoTPP-BIm decreased. The data support the incorporation of CoPc- or CoTPP-BIm into the micropores of the porous glass membrane. The average pore size was still large, which allowed gas-phase diffusion of oxygen and nitrogen.

Reversible oxygen binding to the CoPc-BIm complex was monitored by visible spectroscopy. The spectral changes in the membrane at −55 °C in response to the oxygen partial pressure is shown in the inset of Fig. 1. The peak with an absorption maximum at 685 nm in visible absorption spectrum, is attributed to the penta-coordinated CoPc-BIm complex. The absorbance at 685 nm gradually increased in response to the partial pressure of oxygen with isosbestic points at 560 and 730 nm. The spectrum obtained after flowing oxygen into the CoPc-BIm membrane rapidly returned to that obtained before the oxygen exposure under nitrogen. These results indicate that the CoPc-BIm was complexed with oxygen without forming an intermediate, and the spectroscopic changes in response to the oxygen partial pressure was attributed to the reversible oxygen binding to the CoPc-BIm shown in the following equation.

$$\text{CoPc-BIm} + O_2 \rightleftharpoons O_2\text{–CoPc-BIm}. \tag{1}$$

Table 2. Oxygen-Binding Affinity and Thermodynamic Parameters for the CoPc- and CoTPP-BIm Complexes

CoP-BIm		p_{50}[a)] /kPa	ΔH /kJ mol^{-1}	ΔS /J $K^{-1}\ mol^{-1}$
CoPc	membrane	31	−33	−130
	soln	15	−59	−180
CoTPP	membrane	17	−38	−160
	soln	0.47	−42	−170

a) At −50 °C.

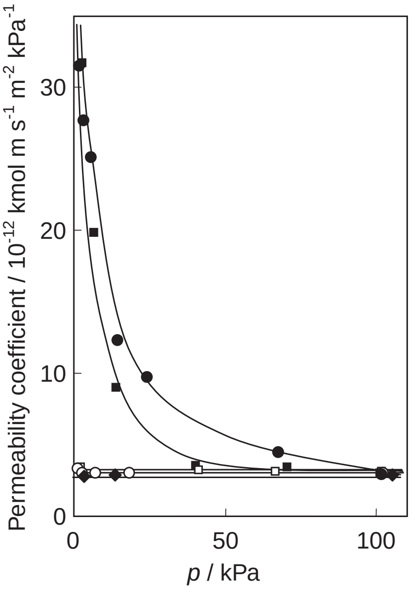

Fig. 2. Oxygen and nitrogen permeability coefficients for the CoPc- and CoTPP-BIm membranes at 25 °C; closed plots for oxygen and open plots for nitrogen, ●: CoPc, ■: CoTPP, ◆: the control membrane with inactive Co(III)Pc.

The oxygen-binding behavior from −45 to −60 °C was monitored using the absorbance ascribed to oxygen binding. The oxygen-binding equilibrium curves obeyed a Langmuir isotherm (Fig. 1), from which the oxygen-binding affinity p_{50} (oxygen partial pressure at which half of the CoPc binds with oxygen) can be determined, and the values of p_{50} are listed in Table 2. Compared to the CoTPP-BIm membrane, the oxygen-binding affinity of the phthalocyanine membrane at −50 °C is low (large in p_{50}).

The enthalpy and entropy changes (ΔH and ΔS) for the oxygen binding of the CoPc-BIm complex were estimated from the temperature dependency of p_{50} and are listed in Table 2. The data are similar to previously reported data;[6–8] the oxygen-binding formation is an exothermic reaction (a negative ΔH value). ΔH of the CoPc-BIm complex is slightly lower than that of the CoTPP-BIm complex. The ΔS value was relatively higher for the CoPc-BIm complex, but the ΔH of the CoTPP-BIm compared to that of CoPc was lower. Therefore, p_{50} for CoTPP-BIm complex results in a higher oxygen-binding affinity than that of CoPc-BIm at −50 °C.

The oxygen and nitrogen permeability coefficients (P_{O2} and P_{N2}) through the membrane containing CoPc-BIm at various upstream oxygen and nitrogen pressures are shown in Fig. 2. At 25 °C, the P_{N2} is larger than the P_{O2} in the higher upstream nitrogen pressure region and is independent of the nitrogen partial pressures because the fixed carrier in the membrane (CoPc) does not bind to nitrogen, but permeates through the

Table 3. Permeability Coefficients, (Oxygen/Nitrogen) Permselectivity, and Facilitation Factors (F) of the Porous Membrane Modified with the CoPc-BIm on Its Surface at Various Temperature

Temperature /°C	P_{O2} /10^{-12} kmol m s^{-1} m^{-2} kPa^{-1}		P_{N2} /10^{-12} kmol m s^{-1} m^{-2} kPa^{-1}	P_{O2}/P_{N2}		F
	2.7 kPa	100 kPa		2.7 kPa	100 kPa	
15	16	3.2	3.3	4.6	0.93	4.9
25	30	2.9	3.1	9.7	0.93	10
35	22	1.9	2.0	11	0.93	12

membrane by gas-phase diffusion. On the other hand, the P_{O2} is smaller with $P_{O2}/P_{N2} = 0.93$ at higher oxygen pressures and steeply increases with a decrease in the oxygen pressure, which gives a selectivity of 9.7 at a pressure of 2.7 kPa. The data indicate that the CoPc fixed on the pore surface of the membrane interacts specifically with oxygen and increases the diffusion of oxygen in the membrane.

Gas-phase diffusion through the membrane containing CoPc was confirmed by using a control membrane—the same membrane modified with inactive Co^{III}Pc—for oxygen binding. The oxygen permeation in the control membrane was found to be independent of the upstream pressure at 25 °C (Fig. 2), and $P_{O2}/P_{N2} = 0.93$, which theoretically corresponds to the Knudsen diffusion for the porous membrane. As well, it is clear that the CoPc-BIm fixed in the pore surface of the vycor glass membrane interacts specifically and reversibly with the oxygen-enhancing surface oxygen diffusion and oxygen permeation.

P_{O2} and P_{N2} of the vycor membranes modified with CoTPP-BIm are also shown in Fig. 2. As shown in Table 1, the physical parameters of the membrane are almost the same. P_{N2} of both membranes, therefore, is almost the same (3.1×10^{-12} for CoPc and 3.2×10^{-12} for CoTPP kmol m s^{-1} m^{-2} kPa^{-1}) (Table 3). The same trend for P_{O2} was observed, and it was smaller with $P_{O2}/P_{N2} = 0.93$ at higher oxygen pressures and steeply increased with a decrease in the oxygen pressure, which gives a selectivity of 8.9 at pressure of 2.7 kPa. These results indicate that physical diffusion obeyed Knudsen diffusion, and in addition to this physical diffusion, chemical diffusion related to surface diffusion occurred, Eq. 2.

$$P_{O2} = P_s + P_g = \frac{1}{\tau} D_s \frac{C_s K}{(1 + Kp)^2} + \frac{\varepsilon}{\tau} D_g \frac{1}{RT}, \qquad (2)$$

where D_s and D_g are diffusion constants for the surface and gas-phase diffusions, respectively, C_s is the concentration of active oxygen carrier in the membrane with oxygen-binding equilibrium constant $1/p_{50}$, p is upstream pressure, e is pore volume, t is tortuosity, R is gas constant, and T is temperature.

Interestingly, the pressure at which P_{O2} starts to increase is higher for the CoPc-BIm membrane (96 kPa) than that for the CoTPP-BIm membrane (67 kPa). In other words, the weaker binding of oxygen to the CoPc (higher p_{50}) facilitates chemical oxygen diffusion through the modified glass surface.

The temperature dependency of the diffusion of nitrogen and oxygen is shown in Fig. 3. Based on the data, there is an inverse proportionality between the permeation of nitrogen and temperature. In contrast to the temperature dependence of P_{N2}, P_{O2} has a maximum at ca. 25 °C. This indicates that the CoPc fixed on the pore surface specifically interacts with oxygen, and the surface diffusion of oxygen involves a chemical reaction with CoPc in addition to its gas-phase diffusion. The small maximum that was observed in the temperature dependency of P_{O2} and caused by enhanced oxygen diffusion was affected by the balance of both the equilibrium of oxygen-binding and -releasing reaction and reaction rate of these reactions. The activation energies also support the fact that surface diffusion involves a chemical reaction.

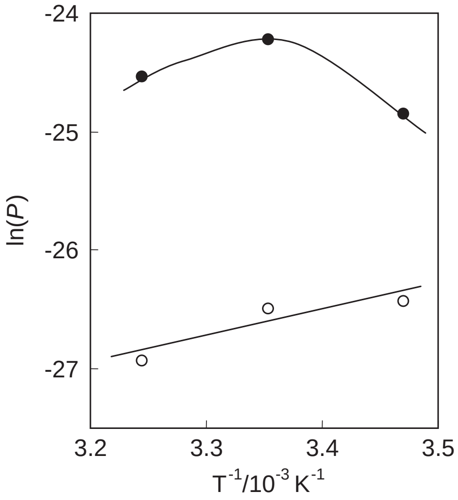

Fig. 3. Temperature dependency of the permeability coefficients for a vycor membrane modified with the CoPc-BIm complex at $\Delta p = 2.7$ kPa; ●: O_2, ○: N_2.

Conclusion

Reversible oxygen binding to the phthalocyanatocobalt and porphyrinatocobalt complexes using a small molecular ligand was observed at low temperature in a solid membrane state. The lower oxygen-binding affinity of the CoPc- and CoTPP-BIm fixed in the pore surface of the porous glass membrane enhanced surface oxygen diffusion, which, in turn, enhanced permeability and permselectivity.

Experimental

Materials. 2,9,16,23-Tetra-*t*-butylphthalocyanine (purchased from Aldrich Co., Ltd.) was metallated with cobalt(II) acetate to obtain 2,9,16,23-tetra-*t*-butylphthalocyaninatocobalt(II) (CoPc) using the reported method.[7] Tetraphenylporphyrinatocobalt(II) (CoTPP), and 1-benzylimidazole (BIm) were purchased from the Aldrich Co., Ltd. and used as received. A Porous Vycor glass membrane #7930 (Corning Inc.) with a mean pore diameter of 4 nm, a diameter of 25.4 mm, and a thickness of 1.1 mm was used as the supporting membrane. Before modifying its pores with the complex, the membrane is activated. For this, the glass membrane was kept in fuming nitric acid for 1 day and was washed with enough water until a pH of 7 was obtained. The solvent was completely removed in vacuo at 120 °C overnight.

Preparation of the Modified Glass Membrane. Solutions of CoPc (1.9 mg, 3.1 mmol) in THF (0.5 mL) and BIm (2.5 mg) in THF (0.5 mL) were mixed, and the activated vycor glass membrane was dipped into the resulting solution in an oxygen-free atmosphere. The membrane was dried in a vacuum overnight to get a uniformly modified membrane. The same procedure was employed to obtain the CoTPP-BIm glass membrane.

Determination of the Pore Structure of the Membrane. The pore structure of the vycor glass membrane before and after the incorporation of the complex was evaluated by BET nitrogen adsorption measurements (ASAP 2010). The pore volume of the membrane was estimated by subtracting the specific volume of the membrane itself from that measured by Hg.

Spectroscopic Measurements. Oxygen binding to the CoPc complexed with BIm in the membrane and in dichloromethane was measured using a UV spectrophotometer (JASCO V-550). The samples prepared under a nitrogen atmosphere were kept at low temperature, and their spectral changes were recorded for different oxygen partial pressures.

Permeation Measurements. Oxygen and nitrogen permeability coefficients for various upstream pressures were measured under a low vacuum in the permeation apparatus chamber at various temperatures with a stable thermostat (Rika Seiki K-315 N-03). The pressures in the upstream and downstream regions were detected using a Baratron absolute pressure gauge (MKS Instr.). The permeation coefficients were calculated from the slopes of the steady-state straight-line sections of the permeation curves. Permeation was measured at various temperatures by changing the temperature of the bath, in which the cell containing the membrane was kept.

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