# Chemically Specific Surface Diffusion of Oxygen through a Porous Membrane Modified with Cobalt Porphyrin on Its Pore Surface

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Chemically specific surface diffusion of oxygen was observed on a porous glass membrane modified on its pore surface with cobalt porphyrin (CoP) which binds oxygen specifically and reversibly from air. The membrane displayed both permselectivity for oxygen and high permeability. The enhanced and specific diffusion of oxygen was mathematically analyzed with a parallel model involving surface diffusion of oxygen via CoP fixed on the pore surface and gas phase or Knudsen diffusion.  $\alpha^{3}\beta$ -CoP was characterized by larger rate constants of oxygen binding ( $k_{on}$ ) and oxygen dissociation ( $k_{off}$ ), gave a larger surface diffusion constant of oxygen ( $D_{\rm S} \sim 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup>), and brought about higher oxygen permeability through the membrane.

## Introduction

Gas separation performed on the largest scale is that of nitrogen and oxygen from air. Nitrogen and oxygen gases are the second and the third largest commodity chemicals in the United States<sup>1</sup> and the third and the first in Japan,<sup>2</sup> respectively, in 1993. Gas separation by a membrane is increasing because of low equipment and running costs and because it is a simple and compact device for the separation.<sup>3</sup> However, only limited cases such as small size nitrogen production from air are presently economical using the membranes, compared to competing separation processes such as cryogenic distillation and pressure swing adsorption, due to restricted permeability and permselectivity of currently available polymer membranes. Although the effects of the chemical structure of polymers on their gas permeability are being studied, the permeability vs permselectivity relationship for oxygen/nitrogen separation still remains an inverse correlation.<sup>3,4</sup> To overcome the competitive processes, the requisites for the air separation membrane in the next generation are both high permeability and high permselectivity, e.g. a high permeability coefficient of oxygen  $(P_{O_2})$ of more than 10<sup>2</sup> Barrers<sup>5</sup> and high oxygen/nitrogen selectivity of more than 10.

One of the characteristic chemical functions of metalloporphyrins is the efficient oxygen carriage as hemoglobin in a living body.<sup>6</sup> Carrier-mediated transport or facilitated transport membranes<sup>7</sup> are expected to be a promising candidate to produce the high-performance membrane to break through the above inverse relation. We have succeeded in facilitated oxygen transport using cobalt porphyrins as a fixed carrier of oxygen in solid or solvent-free polymer membranes: They exhibited  $P_{O_2} \sim 1$  Barrer and  $P_{O_2}/P_{N_2} \sim 10.^8$ 

The polymer dense membranes, however, inherently have an upper limitation of  $P_{O_2}$  of  $10^2$  Barrers due to the permeation process, *i.e.* the dissolution and diffusion process, despite the oxygen permselectivity contributed to the facilitated transport. A porous membrane is characterized by huge permeability coefficients of permeant gaseous molecules (*e.g.*, for oxygen:  $P_{O_2} \ge 10^4$  Barrers). A gaseous molecule permeates through a porous membrane (its pore size is less than the mean free path of the permeant molecule) in the gas phase or by Knudsen diffusion, where the permeant diffuses with repeated collisions against the pore wall. On the other hand, the permselectivity

(ratio of permeability coefficients of two different permeants) for mixed gases is inversely proportional to the square root of the molecular weights of the permeants. For oxygen and nitrogen, which have almost the same molecular weight,  $P_{O_2}/P_{N_2} = 0.94$ . Surface diffusion of a gaseous permeate has been proposed and discussed for a porous membrane of which the pore surface has an affinity for the gaseous molecule. However, to date, surface diffusion was observed only for condensable gases such as carbon dioxide and hexane.<sup>9</sup>

We preliminarily reported<sup>10</sup> enhanced diffusion of a noncondensable gaseous molecule, oxygen, in a porous membrane chemically modified with cobalt porphyrin (CoP) which binds oxygen specifically and reversibly from air. This paper describes the chemically specific surface diffusion of oxygen observed on a porous glass membrane modified on its pore surface with both an imidazolyl residue and CoP as a fixed oxygen carrier (Chart 1). The enhanced diffusion of oxygen was mathematically analyzed according to Fick's law with a parallel model involving surface diffusion and gas phase diffusion in the membrane pore (Chart 2). We discuss the relation of the oxygen-binding reactivities of the fixed CoP determined spectroscopically and the analyzed surface diffusion constant of oxygen using two species of CoP (Chart 1) which are atropisomers of each other.

### **Results and Discussion**

Oxygen-Binding Reaction with the Cobalt Porphyrin Bonded on the Pore Surface. A hollowed Vycor glass membrane (mean pore size  $\phi = 4$  nm) was successively reacted with (3-chloropropyl)dimethoxymethylsilane (3 molar equivs of the silanol groups on the glass surface) and a large excess of imidazole to introduce the imidazolyl group through covalent bonds with silanol on the pore surface. The imidazolyl group chemically bound to the pore surface was analyzed using elemental analysis and ESCA, and ca. 0.5 molar equiv of the silanol group was converted to the imidazolyl group. [meso- $\alpha, \alpha, \alpha, \alpha$ -Tetrakis-(o-pivalamidophenyl)porphinato]cobalt(II)<sup>11</sup> ( $\alpha^4$ -CoP) and [meso- $\beta$ -(o-pivalamidophenyl)- $\alpha$ , $\alpha$ , $\alpha$ -tris(o-pivalamidophenyl)porphinato]cobalt(II) ( $\alpha^{3}\beta$ -CoP) as an oxygen carrier were fixed on the pore surface in the porous glass through ligation with the imidazolyl group (Chart 1); the hollow glass was filled with a dichloromethane solution containing CoP, and a vacuum applied from the exterior resulted in evaporation of dichloromethane and introduction of CoP. Homogeneous

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CHART 2: Oxygen Transport through the CoP-Modified Porous Membrane



introduction of CoP into the membrane was recognized by the homogeneous red coloring on the broken pieces of the membrane and by the homogeneous Co distribution in the membrane as determined by X-ray microanalysis. The five-coordinated structure of deoxy-CoP was confirmed by ESR spectroscopy:  $g_{II} = 2.04$ ;  $g_{\perp} = 2.32$ . The imidazolyl group is allowed to ligate to the cobalt(II) from the unhindered side of the CoP porphyrin, with the other side remaining as a pocket for oxygen binding.

The amount of oxygen taken up by the membrane was measured with a sorption apparatus to give sorption isotherms of oxygen and nitrogen (Figure 1). The oxygen sorption amount is much enhanced by the CoP modification. For example, the oxygen sorption amoung for the  $\alpha^4$ -CoP-modified membrane is augmented ca. 35 times in comparison with that for the unmodified control membrane and is ca. 40 times larger than that of nitrogen for the CoP-modified membrane even at 15 cmHg of atmospheric oxygen pressure (air). The sorption isotherm obeyed that of Langmuir in contrast to the linear Henry-type isotherms of oxygen for the unmodified membrane and of nitrogen for the CoP-modified membrane. The Langmuir isotherm gave the saturated amount of oxygen sorption  $(C_S)$ (listed in Table 2, mentioned later). C<sub>S</sub> was, for example, 3.0 cm<sup>3</sup> (STP) cm<sup>-3</sup> for the membrane containing 3%  $\alpha^4$ -CoP, which nearly corresponded to the introduced amount of CoP. The isotherm for  $\alpha^{3}\beta$ -CoP is located on the right side in comparison with that for  $\alpha^4$ -CoP, indicating weaker oxygenbinding affinity of  $\alpha^{3}\beta$ -CoP, mentioned below. The sorption amount of oxygen was enhanced at lower temperature, as shown



**Figure 1.** Sorption isotherms of oxygen  $(\alpha^{3}\beta$ -CoP ( $\bullet$ ) 25 °C; ( $\blacktriangle$ ) 35 °C, ( $\blacklozenge$ ) 45 °C;  $\alpha^{4}$ -CoP (O) 25 °C; unmodified control membrane ( $\bullet$ ) 25 °C) and nitrogen (( $\blacksquare$ ) 25 °C) for the CoP-modified membranes.

in Figure 1, in contrast to the fact that the oxygen sorption for the unmodified control membrane and the nitrogen sorption were almost independent of temperature. These results indicated that the CoP fixed in the membrane acts as a chemically specific and Langmuir-type oxygen-binding site.

The deeply red-colored membrane piece reversibly displayed the visible absorption spectrum ( $\lambda_{max} = 528$  nm) attributed to deoxy-CoP under nitrogen atmosphere and the spectrum ( $\lambda_{max} = 548$  nm) attributed to oxy-CoP (Co/O<sub>2</sub> = 1/1 adduct) immediately after exposure to oxygen. The deoxy-oxy spectral change was rapid and reversible in response to the partial pressure of the atmosphere, with isosbestic points at 483 and 538 nm. The Co/O<sub>2</sub> = 1/1 adduct formation was also recognized *in situ* in the membrane state by ESR spectroscopy. After introducing air to the membrane, the g-values of deoxy-CoP mentioned above shifted to  $g_{II} = 2.09$  and  $g_{\perp} = 2.02$  and the eight-line hyperfine splitting pattern was observed: This revealed formation of the oxygen adduct.

IR absorption of the membrane piece also supported the oxygen adduct formation of CoP. Strong IR absorption at 1150 cm<sup>-1</sup> for <sup>16</sup>O<sub>2</sub> and 1060 cm<sup>-1</sup> for <sup>18</sup>O<sub>2</sub> attributed to an end-on-type metal-bound dioxygen appeared with an increase in partial oxygen pressure ( $v_{O_2} = 1556$  cm<sup>-1</sup> for gaseous <sup>16</sup>O<sub>2</sub>). Because the concentration of the CoP moiety in the solid-state membrane is much higher (>40 mM) than that of a homogeneously solubilized CoP in solution (typical concentration, 1 mM), even a simple spectrophotometer is effective for observing the oxygen-binding reaction to and bonding characteristics of CoP.

The oxygen-binding affinity or equilibrium constant (K in eq 1) of the fixed CoP was determined from a spectral measurement in the visible region of the membrane at an oxygen partial pressure 0-76 cmHg (oxygen-nitrogen mixed gas). The binding equilibrium curves obeyed Langmuir isotherms to yield K and the oxygen-binding affinity  $p_{50}$  (oxygen partial pressure at which half of the CoP binds with oxygen or 1/K), given in Table 1. The K or  $p_{50}$  values of the CoPs are appropriate to uptake oxygen from air. A cavity structure around the oxygenbinding site in the porphyrin is important not only to form the reversible oxygen adduct but also to control the oxygen-binding reactivity. Enthalpy and entropy changes ( $\Delta H$  and  $\Delta S$ ) for the oxygen binding were determined from the temperature dependence of K and are also given in Table 1.  $\Delta H$  or enthalpy gain through the oxygen binding becomes smaller for  $\alpha^{3}\beta$ -CoP, of which the oxygen-binding affinity is reduced in comparison with  $\alpha^4$ -CoP. These equilibrium constants for the oxygen binding, K,  $\Delta H$ , and  $\Delta S$ , agreed with those of the CoPs ligated with

TABLE 1: Equilibrium Constant, Enthalpy and Entropy Change, and Binding and Dissociation Rate Constants for the Oxygen Binding of the CoP Fixed in the Porous Membrane Surface at 25 °C



Figure 3. Effect of upstream gas pressure on time lag in the oxygen ((◊) 15 °C, (◊) 25 °C, (△) 35 °C) and nitrogen ((□) 15 °C, (□) 25 °C, (**D**) 35 °C) permeation for the  $\alpha^4$ -CoP-modified membrane.

TABLE 2: Structural Parameters of the CoP-Modified **Porous Membranes** 

	a4-CoP		$\alpha^{3}\beta$ -CoP		unmodified
parameters	(1)	(2)	(1)	(2)	membrane
pore volume ( $\epsilon$ )/cm <sup>3</sup> cm <sup>-3</sup>	0.23	0.23	0.23	0.22	0.28
specific surface area $(S_v)/m^2 g^{-1}$	169	154	180	190	250
mean pore size (r)/nm	3.0	2.7	3.0	2.7	4.0
(pore size distribution $\pm 1 \text{ nm}/\%$ )	(62)	(61)	(69)	(73)	(51)
tortuosity ( $\tau$ )/cm cm <sup>-1</sup>	37	32	41	33	5.0
saturated amount of oxygen sorption $(C_s)/cm^3 cm^{-3}$	1.8	3.0	0.9	1.4	0

studied by BET nitrogen adsorption measurements.<sup>12</sup> The pore volume or the void ( $\epsilon$ ) of the membrane was estimated by subtracting the specific volume of the membrane itself from that measured by Hg. The specific surface area  $(S_v)$  was also determined by the BET nitrogen adsorption. Pore size (r) and distribution were determined from the pressure at equilibrium at each supplied pressure of nitrogen.<sup>13</sup> Tortuosity ( $\tau$ ) was estimated by assuming gas phase diffusion in tubes.<sup>14</sup> The introduction of CoP decreases  $\epsilon$ ,  $S_v$ , and r and increases  $\tau$  and  $C_{\rm S}$  (Table 2). These data support the incorporation of CoP on the inside of the micropores of the membrane. The average pore sizes were still 2.7-3.0 nm to allow gas phase diffusion of oxygen and nitrogen.

Oxygen Permeation through the Cobalt Porphyrin-Modified Membrane. The peremation time courses for the CoPmodified membranes reached steady-state straight lines, of which the slopes gave permeation coefficients (P). Before the steady state, there was an induced period. The time lag  $(\theta)$ was estimated from the crossing point of the steady-state straight line and the abscissa on the permeation curve. The  $\theta$  values for the oxygen and nitrogen permeation ( $\theta_{0}$ , and  $\theta_{N_2}$ ) are shown in Figure 3 vs upstream oxygen and nitrogen pressure  $(p_2(O_2))$ and  $p_2(N_2)$ ). Although  $\theta_{N_2}$  is short and independent of  $p_2(N_2)$ ,  $\theta_{\rm O_2}$  is longer than  $\theta_{\rm N_2}$  and increases with the decrease in  $p_2$ -(O<sub>2</sub>). In Figure 2, one also notices that  $\theta_{O_2}$  and  $p_2(O_2)$ dependence of  $\theta_{O_2}$  decrease with temperature. These results are explained as follows: The CoP fixed on the pore surface in the membrane interacts specifically with oxygen and retards the



Figure 2. Plots of apparent oxygen-binding rate constant vs atmospheric oxygen concentration in the recombination reaction of the photodissociated oxygen to the CoP fixed in the membrane at 25 °C ((•)  $\alpha^{3}\beta$ -CoP, (O)  $\alpha^{4}$ -CoP). Inset: Spectral change after laser flash irradiation.

imidazole in toluene.

$$CoP + O_2 \xrightarrow{k_{on}} CoP - O_2 \qquad K = k_{on}/k_{off} \qquad (1)$$

Photodissociation and recombination of bound oxygen from and to the CoPs fixed in the membrane were observed by laser flash photolysis. An example of the recombination time curve of oxygen is shown in Figure 2 (inset) for the  $\alpha^{3}\beta$ -CoP-modified membrane. The reaction was completed within a few microseconds, and it was very rapid despite a reaction in the solid. The oxygen-binding and -dissociation rate constants ( $k_{on}$  and  $k_{\text{off}}$  in eq 1) were estimated by pseudo-first-order kinetics in the spectral time courses in the oxygen recombination, as shown in Figure 2, and are given also in Table 1. The  $k_{on}$  and  $k_{off}$ values are comparable with those of the corresponding CoPimidazole in toluene solution. The oxygen-binding kinetics directly in response to the atmospheric oxygen pressure suggests that CoP is located on the inside surface on the micropores.

For the  $\alpha^{3}\beta$ -CoP, the  $k_{on}$  and especially the  $k_{off}$  values increase with significant reduction of bulkiness in the substituent group on the porphyrin plane or in the oxygen-binding and -dissociation pathway to and from the cobalt centered in the porphyrin. The oxygen-binding affinity  $K (= k_{on}/k_{off})$  is also yielded by the effect of the substituents on the porphyrin plane. The much enhanced  $k_{off}$  for  $\alpha^{3}\beta$ -CoP brought about the reduced oxygenbinding affinity, as given in Table 1. Anyway, CoP is kinetically active to bind oxygen even after fixation in the membrane and acts as an effective carrier for the passage of oxygen.

Structure of the Cobalt Porphyrin-Modified Membrane. The pore structure of the membrane modified with CoP was



Figure 4. Effect of upstream gas pressure on the permeability coefficients (( $\bullet$ ) oxygen, ( $\blacksquare$ ) nitrogen) and the oxygen/nitrogen permselectivity (inset) for the  $\alpha^{3}\beta$ -CoP-modified membrane and the inactive Co<sup>III</sup>P-modified control membrane (( $\bullet$ ) oxygen) at 25 °C.



**Figure 5.** Temperature dependency of the permeability coefficients ((a)  $(\bigcirc)$  oxygen,  $(\Box)$  nitrogen) and the surface diffusion constants ((b)  $(\textcircled{O}) \alpha^3 \beta$ -CoP,  $(\bigcirc) \alpha^4$ -CoP,  $(\Box)$  gas phase diffusion constant of nitrogen) for the CoP-modified membranes.

diffusion of oxygen through the membrane, and the reactivity (the rate constants  $k_{on}$  and  $k_{off}$ ) of the CoP increases with temperature.

Gas phase diffusion through the CoP-modified membrane was confirmed using a control membrane, *i.e.*, the same membrane modified with inactive Co(III)P for the oxygen binding. As shown in Figure 4, the permeability coefficients for the control membrane were independent of upstream pressure with  $P_{O_2} = 6.5 \times 10^3$  and  $P_{N_2} = 7.0 \times 10^3$  Barrers at 25 °C and  $P_{O_2}/P_{N_2} = 0.93$  (theoretical for the gas phase diffusion  $(M_w(O_2)/M_w(N_2))^{-1/2} = 0.93$ ): Gas phase or Knudsen diffusion is predominant for the membrane.

 $P_{O_2}$  and  $P_{N_2}$  for the  $\alpha^3\beta$ -CoP-modified membrane are also shown in Figure 4.  $P_{N_2}$  is larger than  $P_{O_2}$  at a higher region of

upstream nitrogen pressure  $p_2(N_2)$  and is independent of  $p_2(N_2)$ , because nitrogen permeates through the membrane according to gas phase diffusion and the fixed carrier CoP does not bind with nitrogen. On the other hand,  $P_{O_2}$  is small, with  $P_{O_2}/P_{N_2} = 0.94$  at the high  $p_2(O_2)$  region, but steeply increases with a decrease in  $p_2(O_2)$ :  $(P_{O_2}/P_{N_2})$  reaches 1.5 at  $p_2(O_2) = 0.7$  cmHg. These data indicate that the CoP fixed on the pore surface interacts specifically with oxygen and augments the diffusion of oxygen in the membrane, ascribed to chemically specific surface diffusion (Chart 2). In contrast to the temperature dependence of  $P_{N_2}$ ,  $P_{O_2}$  has a minimum at *ca.* 35 °C for both of the CoP membranes, as shown in Figure 5. This means that the surface diffusion of oxygen involves a chemical reaction with CoP in addition to its gas phase diffusion.

Analysis of the Surface Diffusion of Oxygen in the Porous Membrane. We analyzed this surface diffusion with a parallel model which involves surface diffusion of oxygen via the CoP fixed on the pore surface and gas phase or Knudsen diffusion. Total gas flux could be considered to be the sum of the surface diffusion and the gas phase diffusion, as given in eq 2,

$$P_{O_2} = P_{S} + P_{g} = \frac{1}{\tau} D_{S} \frac{C_{S} K}{\left(1 + K p_{2}\right)^{2}} + \frac{\epsilon}{\tau} D_{g} \frac{1}{RT}$$
(2)

where  $D_S$  and  $D_g$  are diffusion constants for the surface diffusion and the gas phase diffusion of oxygen, respectively.  $C_S$  is the saturated amount of oxygen sorption or the concentration of active CoP in the membrane with the oxygen-binding equilibrium constant K (given in eq 1).  $p_2$  is the upstream gas pressure of oxygen.

The permeability coefficient of the surface diffusion  $(P_S)$  was obtained by subtracting the permeability coefficient of the gas phase diffusion  $(P_g)$  measured for an ideal gas (here helium) from the total gas diffusion.

Substituting the K value given in Table 1, the  $C_S$ ,  $\epsilon$ , and  $\tau$  values in Table 2, and the  $p_2$  value in eq 2 yields the gas phase diffusion constant of oxygen,  $D_g(O_2)$  and that of nitrogen,  $D_g(N_2)$ , and the surface diffusion constant of oxygen,  $D_S(O_2)$ , listed in Table 3.  $D_g(O_2)$  and  $D_g(N_2)$  were estimated to be almost the same values for the four different membranes. The ratio of  $D_g(O_2)$  and  $D_g(N_2)$  is 0.94. These data support the validity of the analysis and the gas phase diffusion in the membranes.  $D_S(O_2)$  is smaller than  $D_g(O_2)$  and depends on the CoP species or the oxygen-binding property of CoP: The membrane modified with  $\alpha^3\beta$ -CoP with the larger rate constants of oxygen binding and dissociation leads to a large  $D_S(O_2)$  to yield larger surface diffusion or higher oxygen permeability ( $P_S$ ).

The temperature dependency of the diffusion constants is also shown in Figure 5. The activation energy of  $D_g(N_2)$  is 0, which is also consistent with that of the gas phase diffusion for nitrogen. On the other hand, the linear Arrhenius plots of  $D_{S^-}(O_2)$  give the activation energy of oxygen for the chemically specific surface diffusion  $(E_{D_S})$ . The activation energies also support that the surface diffusion involves a chemical reaction.

The  $D_S(O_2)$  value for the  $\alpha^3\beta$ -CoP-modified membrane is *ca*. 10 times greater than that for the  $\alpha^4$ -CoP membrane, which

TABLE 3: Permeability Coefficient of Oxygen for Surface Diffusion, Permselectivity (at  $p_2(O_2)=0.7$  cmHg), Gas Phase Diffusion Constants of Oxygen and Nitrogen, Surface Diffusion Constant of Oxygen, and Activation Energy of the Surface Diffusion of Oxygen for the CoP-Modified Membranes at 25 °C

••	-						
membrane	$\frac{C_{\rm S}}{(\rm cm^3 \ cm^{-3})}$	$\frac{10^{-3}Ps(O_2)}{(\text{Barrers})}$	$P_{\rm O_2}/P_{\rm N_2}$	$10^2 D_g(N_2)$ (cm <sup>2</sup> s <sup>-1</sup> )	$10^2 D_g(O_2)$ (cm <sup>2</sup> s <sup>-1</sup> )	$\frac{10^4 D_{\rm S}(O_2)}{({\rm cm}^2~{\rm s}^{-1})}$	$\frac{E_{D_{S}}}{(\text{kcal mol}^{-1})}$
$\alpha^4$ -CoP (1)	1.8	1.6	1.2	0.99	0.93	0.24	11
(2)	3.0	2.8	1.3	1.0	0.94	0.27	
$\alpha^{3}\beta$ -CoP(1)	0.9	3.1	1.4	1.0	0.94	3.8	9.0
(2)	1.4	3.6	1.5	1.0	0.94	2.4	

corresponds to the larger of the  $k_{on}$  and  $k_{off}$  values of  $\alpha^{3}\beta$ -CoP. The kinetically higher oxygen-binding and -dissociation reactivity of the  $\alpha^{3}\beta$ -CoP fixed on the pore surface leads to the larger  $D_{\rm S}({\rm O}_2)$ . Especially,  $k_{\rm off}$  is clearly reflected in the  $D_{\rm S}({\rm O}_2)$ . The  $E_{D_s}$  values for the  $\alpha^3\beta$ -CoP- and  $\alpha^4$ -CoP-modified membrane are comparable with the activation energies of the oxygendissociation step given in Table 1.

In eq 2,  $C_S$  also contributes to  $P_{O_2}$  in addition to  $D_S(O_2)$ . The membranes with higher  $C_S$  yield larger  $P_{O_2}$  and higher  $P_{O_2}$ /  $P_{N_2}$ . However,  $D_S(O_2)$  is independent of  $C_S$ , the carrier concentration, or the distance between the carriers fixed on the pore surface, probably because  $D_{S}(O_{2})$  is postulated as the diffusion constant of oxygen for an ideal hopping via the fixed CoP carrier, which does not conflict with eq 2. Anyway, the enormously large  $C_{\rm S}$  of  $\geq 1$  cm<sup>3</sup>/cm<sup>3</sup> is caused by the large surface area of the porous membrane and enhances  $P_{\rm S}$  by overcoming the small  $D_{\rm S}({\rm O}_2)$ .

The requisites for establishing a much higher  $P_{O_2}$  are a higher  $C_{\rm S}$ , a moderate K, and a higher  $D_{\rm S}$ . The third is connected with a larger  $k_{on}$  and  $k_{off}$  in the oxygen-binding reaction of the carrier CoP. If one could prepare a porous membrane bearing a wider surface area of 250 m<sup>2</sup>/g (ca. only twice that of the membrane used in this experiment) and modified with a stronger binding affinity and kinetic parameter (ca. also only twice that of the present  $\alpha^{3}\beta$ -CoP) of  $K = 0.1 \text{ cmHg}^{-1}$  and a larger surface diffusion constant of  $D_{\rm S} = 10^{-3} {\rm ~cm}^2 {\rm ~s}^{-1}$ , an outstanding permeability coefficient of  $P \sim 10^5$  Barrers and an oxygen/ nitrogen permselectivity of >10 are estimated with eq 2 for  $p_2$ = 1 cmHg. The CoP-modified porous membranes have potential as oxygen permselective membranes in the next generation.

#### **Experimental Section**

Materials. [meso- $\alpha, \alpha, \alpha, \alpha$ -Tetrakis(o-pivalamidophenyl)porphinato)cobalt](II) ( $\alpha^4$ -CoP) was synthesized as in previous literature.<sup>11</sup> meso- $\alpha, \alpha, \alpha$ -Tris(o-pivalamidophenyl)- $\beta$ -(o-pivalamidophenyl)porphyrin ( $\alpha^{3}\beta$ -CoP) was prepared by reacting meso- $\alpha, \alpha, \alpha$ -tris(o-aminophenyl)- $\beta$ -(o-aminophenyl)porphyrin with an excess of pivaloyl chloride. The product was purified by chromatography on a silica gel column using chloroform/ diethylether (10/1 v/v) as the eluent ( $R_f = 0.27$ ). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  ppm: -2.72 (2H, inner-H), 0.10, 0.16, 0.21 (36H, -(CH<sub>3</sub>)<sub>3</sub>), 7.2-7.9 (16H, phenyl-H), 8.6 (4H, amino-H), 8.8 (8H, pyrrole-H). UV/vis  $\lambda_{max}$ : 644, 588, 547, 514, 429 nm in toluene. Cobalt ion was inserted into the porphyrin plane by reaction with cobalt acetate, and the CoP was purified with a silica gel column using chloroform/diethylether (10/1 v/v for  $\alpha^{3}\beta$ -CoP). UV/vis  $\lambda_{max}$ : 525, 411 nm in toluene.

A hollowed Vycor glass membrane 7930 (Corning Inc.) was kept in fuming nitric acid for 1 day. After washing with water up to pH 7, the glass was heated stepwise to 120 °C for 3 h and then heated further in vacuo for 5 h. The activated glass was soaked in a toluene solution of (3-chloropropyl)dimethoxymethylsilane (4.1 mmol per gram of the porous glass) and a large excess of imidazole successively and was then refluxed for 24 h. After washing sufficiently with triethylamine and toluene, the imidazolyl group chemically bound to the pore surface was obtained, as shown in Chart 1. The hollow glass was filled with a dichloromethane solution containing the CoP (8.3 and 12  $\mu$ mol per gram of the porous glass for the membranes (1) and (2), respectively), and a vacuum applied from the exterior resulted in evaporation of dichloromethane and introduction of CoP. Homogeneous introduction of CoP into the membrane was recognized by the homogeneous red coloring on the broken pieces of the membrane and by the homogeneous Co distribution

in the membrane, as determined by X-ray microanalysis (Xray microanalyzer JEOL JXA-733).

Spectroscopic Measurements. Oxygen binding to the CoP fixed in the membranes was measured by a spectral change in visible absorption using a spectrophotometer (Shimadzu Model UV-2100). ESR spectroscopy on CoP was measured with a JEOL FE-2X ESR spectrometer operating at the X-band at 110 and 210 K, placing the membrane piece in a glass tube with a vessel for deaeration. The magnetic fields were corrected using the splitting of Mn(II) in MnO ( $\Delta H = 86.9$  G).

A pulsed laser flash was applied perpendicularly to the light path of the spectrophotometer (UNISOKU TSP-601), and the membrane was placed at an angle of 45° to both pathways. Changing the monitored wavelength from 400 to 440 nm allowed a differential spectrum before and after the flash irradiation, and 410 and 430 nm were selected as the monitoring wavelengths. These wavelengths agreed with the maxima of the oxy- and deoxy-CoP in the Soret band region, respectively. The rapid absorbance change for the recombination reaction of oxygen with the CoP was recorded with a contact-type photomultiplier.

Sorption of Oxygen and Nitrogen and Structural Parameters of the Porous Membrane. The sorption amount of oxygen or nitrogen was measured by a pressure decrease in the condition of a constant volume by a Baratron absolute pressure gauge (MKS Instr.). The apparatus consisted of a vacuum line mounted in a thermocontrolled air bath.

The pore volume of the porous membrane was measured with the same apparatus by subtracting the actual specific volume estimated from nonadsorbed helium from the apparent specific volume measured by Hg. The specific surface area of the porous membrane was estimated from the measurement of nitrogen adsorption under liquid nitrogen conditions (BET method).<sup>12</sup> The pore size distribution was calculated from the relationship between the amount of adsorbed nitrogen and the pore size.<sup>13</sup> Tortuosity was estimated by assuming gas phase diffusion in tubes.14

Permeation Measurement. Oxygen and nitrogen permeability coefficients for various upstream pressures were measured with a low-vacuum permeation apparatus in the chamber with a stable thermostat (Rika Seiki K-315N-03). The pressure on the upstream and the downstream sides was detected using a Baratron absolute pressure gauge (MKS Instr.). The permeation coefficients were calculated from the slopes of the steadystate straight-line sections of the permeation curves. Oxygen and nitrogen permeation was also measured for the mixed gases of oxygen and nitrogen in the upstream side with a gas chromatograph (Shimadzu GC-8A). The cell involving the membrane was kept in a bath maintained at a temperature of 10-60 °C.

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