Polycarbonate/(*N,N'*-dialicylidene ethylene diamine) Cobalt(II) Complex Membrane for Gas Separation

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SYNOPSIS

A polycarbonate/(*N,N'*-dialicylidene ethylene diamine) cobalt(II) (cosalen) complexed membrane was prepared by introducing oxygen carrier (cosalen) into polycarbonate for gas separation. With increasing amount of oxygen carrier in the membranes, the selectivity of O_2/N_2 increased and the permeabilities of both O_2 and N_2 decreased. The selectivity of O_2/N_2 decreased with increasing operating temperature. The pure gases sorption measurements indicated that the affinity between oxygen and the membranes was appreciable higher than that of nitrogen. According to the X-ray analysis of the complexed membranes, the decreased gas diffusivities were caused by the increase of the packing density. The selectivity of O_2/N_2 was 15 and oxygen permeability for the cobalt complexed membrane with 3 wt % oxygen carrier was 0.33 barrers at 5°C. Furthermore, a dual mode sorption mechanism was utilized to describe the behavior of gas sorption and permeation through the cobalt complexed membrane. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

An ideal gas separation membrane has good permeability and high selectivity. Much effort has been made in the past to prepare high oxygen selectivity membranes. Johnson and coworkers examined the use of facilitated transport for gas separation.[1] Many investigations on all kinds of modified facilitated membranes, which contain cobalt Schiff base–oxygen carriers, have been reported.[2-5] Oxygen sorption and desorption from these membranes are rapid and reversible and form a Langmuir type adsorption isotherm.[6] The principle of facilitated transport has been applied to liquid membranes and solid polymer membranes. However, the instability of the immobilized organic solvent limited the application of liquid membrane.[1] Solid polymer complex membranes containing immobilized oxygen carrier for facilitated transport was reported to have higher selectivity but lower permeability than liquid membranes. By a series of combinations of chemical modifications on both the oxygen carrier and polymer matrix, several researchers successfully improved the gas permeability of the complex membrane and the stability of the oxygen carrier.[7,8]

The first cobalt Schiff base–oxygen carrier was synthesized by Tsumaki in 1938.[1] Calvin and coworkers[9,10] observed the different sorption rates of the cobalt–oxygen carrier as being due to the different lattice faces exposing conditions such as temperature and partial pressure of oxygen. The kinetic oxygen uptake for different types of cobalt Schiff base–oxygen carrier was found to be first order with respect to oxygen pressure. From the studies of cobalt Schiff base–oxygen carrier reported by Calvin and coworkers,[11-13] and Crumbliss and Basolo,[14] the oxygen carrier showed rapid and reversible uptake of oxygen in a nonaqueous solution. In our previous report[15] the metal salt complexed polycarbonate (PC) effectively improved the gas permeability and selectivity of the PC membrane. In this study, we attempted to add cosalen to the PC membrane to study the gas separation performance of the complex membrane. We explored the effect of the amount of oxygen carrier and operating conditions on oxygen permeation and sorption behaviors. Dual mode sorption was utilized to describe the gas sorption and permeation of the prepared complexed membranes. The relationship between dual mode pa-

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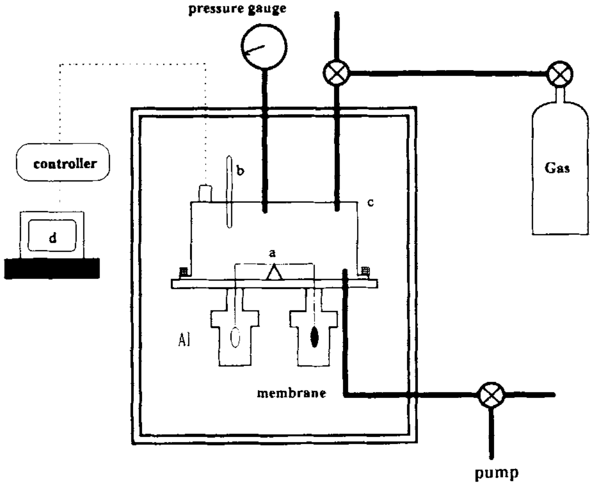

Figure 1 Apparatus of gas sorption: (a) electrobalance (Cahn model 202), (b) thermal couple, (c) stainless chamber, and (d) computer.

rameters and oxygen carrier content in the complexed membranes is discussed. The relationship between packing density and oxygen carrier content in the membranes was studied using X-ray diffraction.

EXPERIMENTAL

Materials

PC (Uplion S-2000) (M_w 28,000) was supplied by Mitsubishi Gas Chemical Co. Dichloromethane, ethylene diamine, salicylaldehyde, and cobalt acetate were supplied by Merck Co. All chemicals were reagent grade and were used without further purification.

Synthesis of Oxygen Carrier

The oxygen carrier (cosalen) was prepared by dissolving ethylene diamine, cobalt acetate, and salicylaldehyde in ethanol solution refluxed for 2 h. The cosalen crystals formed immediately and were allowed to grow for 2 h out of contact with air, then were cooled and washed with water. The oxygen carrier was filtrated and dried in a vacuum oven for 24 h at 150°C. These procedures followed the report of Bailes and Calvin.[16] The oxygen carrier adsorbed 4.92% by weight of oxygen.[13] Some of the oxygen carrier characterization data were described in previous reports.[13,16]

Membrane Preparation

The PC membrane was prepared from a casting solution of PC in dichloromethane. The PC/oxygen carrier complexed membranes were prepared from solutions of varying oxygen carrier content (0.6–3 wt %). The membranes were formed by casting the solution onto a glass plate to a predetermined thickness, using a Gardner knife at room temperature. The membranes were dried in vacuum for 24 h before the gas sorption and permeation measurement. When the oxygen carrier content was over 3 wt %, precipitation of the oxygen carrier occurred leading to poor membrane formation.

Gas Permeability Measurements

The apparatus for measuring the permeability of gas through the membrane was as in our previous report.[15] The gas permeability was measured by the following equation:

$$P = \frac{l}{(p_1 - p_2)} \frac{q/t}{A}$$

where P is the gas permeability [cm^3 (STP) cm/cm^2 s cmHg], q/t is the volume flow rate of the gas permeate [cm^3 (STP)/s], l is the thickness (cm), p_1 and p_2 are the pressures (cmHg) on the high pressure and low pressure side of the membrane, respectively, and A is the effective membrane area (cm^2). The gas selectivity is related to the gas permeability ratio by the following expression:

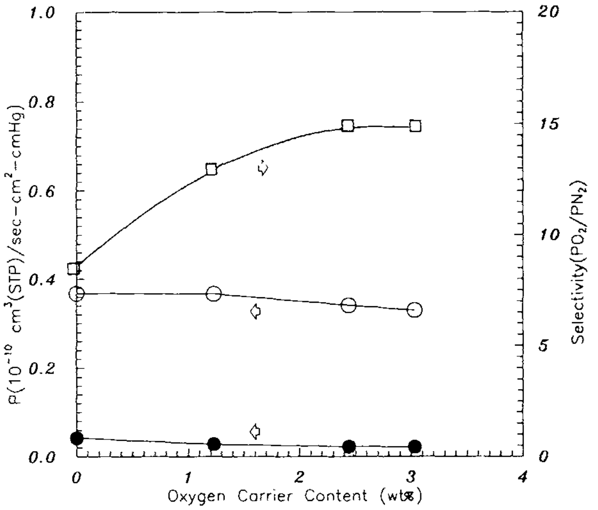

Figure 2 Effect of oxygen carrier content in PC complexed membrane on gas permeability and selectivity, P_{O_2}/P_{N_2}. Membranes measured at 5°C: (○) P_{O_2} and (●) P_{N_2}.

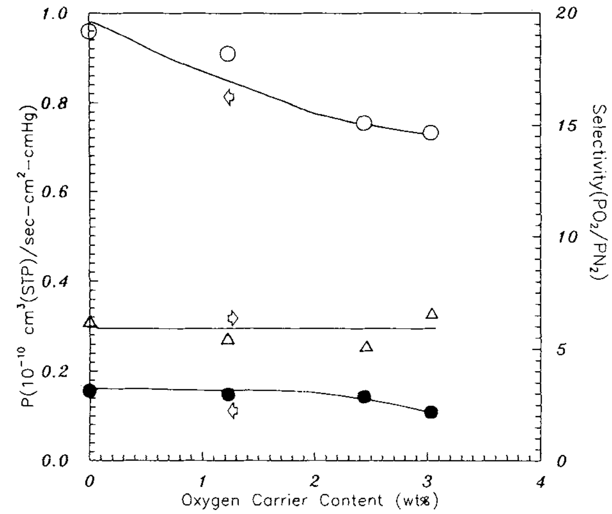

Figure 3 Effect of oxygen carrier content in PC complexed membrane on gas permeability and selectivity, P_{O_2}/P_{N_2}. Membranes measured at 35°C: (○) P_{O_2} and (●) P_{N_2}.

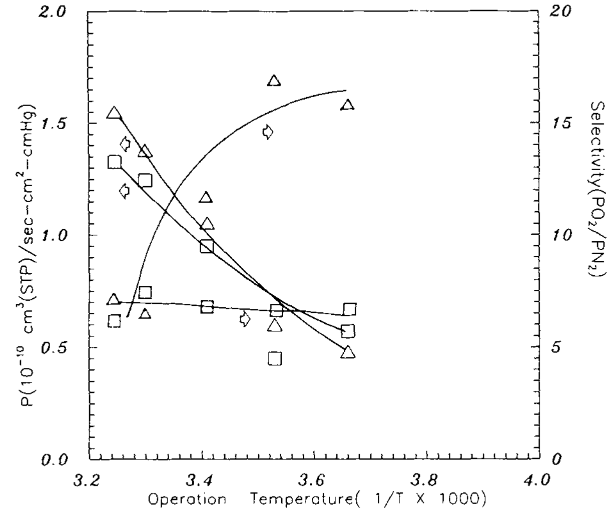

Figure 5 Effect of operation temperature on gas permeability for PC complexed membrane with 3 wt % oxygen carrier content (□) PC and (△) PC complexed membrane with 3 wt % oxygen carrier content.

$$\text{selectivity} = \frac{P_{O_2}}{P_{N_2}}$$

Gas Sorption Measurements

The experimental setup for gas sorption measurement is shown in Figure 1. A microbalance (Cahn Model D-202 Electrobalance) was enclosed in a stainless chamber. The chamber was enclosed in a constant temperature box. The system pressure was then vacuumed to about 4×10^{-3} torr before the gas sorption measurement. The system was kept at these conditions until sorption equilibrium was reached. The dual mode sorption parameters were determined by the following:

$$C = k_d p + \frac{C'_H b p}{1 + bp}$$

where k_d is Henry's low coefficient, C'_H and b are

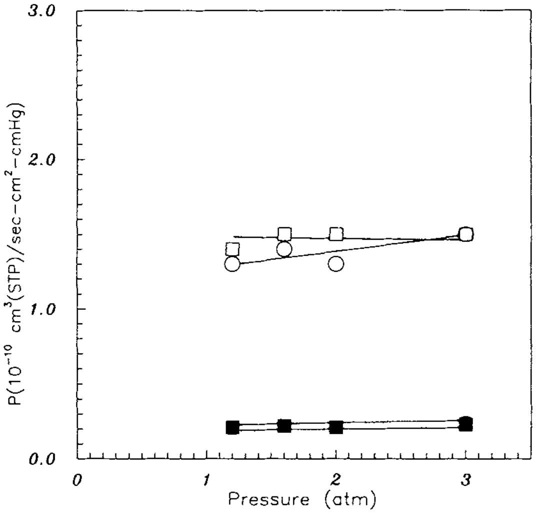

Figure 4 Effect of upstream pressure and on gas permeability for PC complexed membrane with 3 wt % oxygen carrier content, (□) P_{O_2} and (■) P_{N_2}; and PC, (○) P_{O_2} and (●) P_{N_2} membrane. Membrane measured at 35°C.

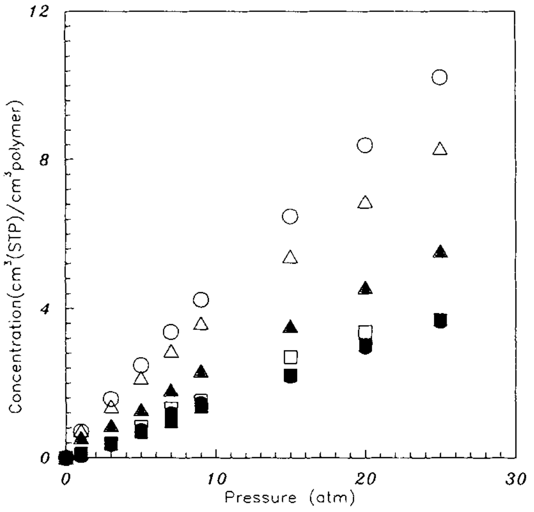

Figure 6 Effect of pressure on the sorption concentration for complex membranes at 5°C. PC: (□) O_2 and (■) N_2; with 1.2 wt % carrier: (△) O_2 and (▲) N_2; with 3.0 wt % carrier: (○) O_2 and (●) N_2.

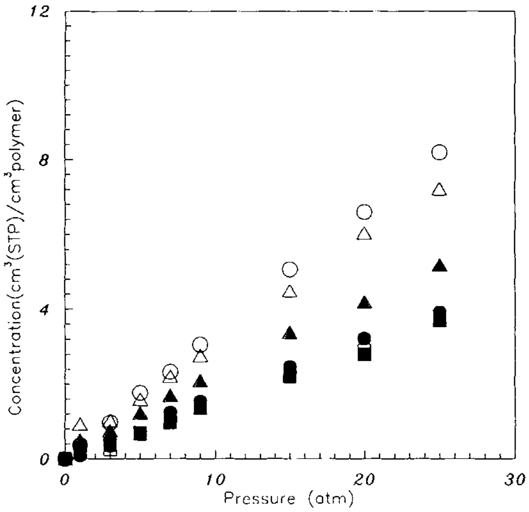

Figure 7 Effect of pressure on the sorption concentration for complex membranes at 35°C. PC: (□) O_2 and (■) N_2; and with 1.2 wt % carrier: (△) O_2 and (▲) N_2; with 3.0 wt % carrier: (○) O_2 and (●) N_2.

saturation capacity and the affinity constant for the Langmuir mode, respectively.

Property Measurements

WAXD scans were generated by a Shimadzu XD-5 diffractometer operating with copper radiation.

RESULTS AND DISCUSSION

Effect of Oxygen Carrier Content on Gas Permeability and Selectivity of P_{O_2}/P_{N_2}

The effect of oxygen carrier content on the pure gas permeability and selectivity of O_2/N_2 is shown in Figures 2 and 3 at 5 and 35°C, respectively. The oxygen permeabilities were 0.37 and 0.96 barrer and O_2/N_2 selectivity of PC membrane was 8.8 and 6.3 at 5 and 35°C, respectively. The O_2/N_2 selectivity was significantly improved up to 15.0 by the complexation of PC membrane with 3 wt % coselen at 5°C, but no significant improvement was observed at 35°C. When the oxygen carrier content in the casting solution was over 3%, precipitation of the oxygen carrier occurred leading to poor membrane formation. With the increase of oxygen carrier content in complexed membranes, the gas permeability decreased marginally and O_2/N_2 selectivity increased at 5°C. Comparing Figures 2 and 3, it was obvious that the selectivity of O_2/N_2 at 5°C is higher than that at 35°C. It was suggested that the affinity

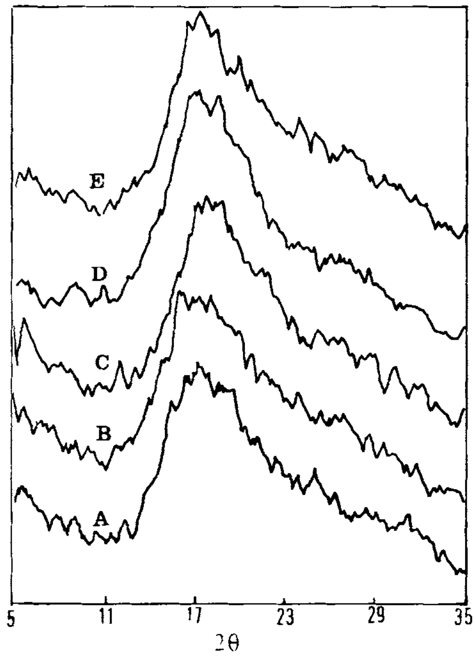

Figure 8 X-ray diffraction patterns of PC complexed membrane: (A) PC; (B) oxygen carrier content 0.6 wt %; (C) oxygen carrier content 1.2 wt %; (D) oxygen carrier content 1.8 wt %; (E) oxygen carrier content 3.0 wt %.

Table I Permeability, Solubility, and Diffusivity of O_2 at 5° and 35°C at 3 atm

	5°C			35°C		
Membrane	P_{O_2} (barrers)	S_{O_2} (cm³ (STP)/ cm³ atm)	D_{O_2} (10^{-8} cm²/s)	P_{O_2} (barrers)	S_{O_2} (cm³ (STP)/ cm³ atm)	D_{O_2} (10^{-8} cm²/s)
PC	0.37	0.13	2.20	0.96	0.23	3.21
Complexed membrane (1.2 wt %)	0.37	0.46	0.60	0.81	0.34	1.78
Complexed membrane (3.0 wt %)	0.33	0.52	0.48	0.73	0.32	1.72

Table II Dual Mode Sorption Parameters for PC Membranes at 5°C

Membrane	Gas	k_D $\left[\frac{\text{cm}^3\ (\text{STP})}{\text{cm}^3\ \text{atm}}\right]$	C_H $\left[\frac{\text{cm}^3\ (\text{STP})}{\text{cm}^3}\right]$	b (atm^{-1})
PC	O_2	0.11	1.15	0.06
	N_2	0.14	0.24	0.01
Complexed PC	O_2	0.29	1.17	0.10
(0.12 wt %)	N_2	0.19	0.66	0.11
Complexed PC	O_2	0.37	1.03	0.32
(3.0 wt %)	N_2	0.14	0.19	0.07

of complexed membranes with O_2 is higher than that with N_2 at low temperature. The difference of gas permeability between pure gas and mixed gas was very minor. Therefore, the following different operating conditions were all conducted with air as feed.

Effect of Operating Condition

The effect of operating upstream pressure on the gases permeability and O_2/N_2 selectivity was measured and is shown in Figure 4. These results indicated that the O_2 and N_2 permeabilities through the complexed membranes were not influenced by the upstream pressure in the range of 1–3 atm. According to the previous reports,[1,3,7] the sorption capacity of the oxygen carrier was strongly influenced by temperature. The effect of operating temperature on the gas separation performance is shown in Figure 5. This study shows that gas permeability gradually increased and the O_2/N_2 selectivity rapidly decreased with increasing operating temperature. We found that the dependence of the selectivity of O_2/N_2 of the complexed membrane on operating temperature was similar to the liquid membrane with oxygen carrier content.[1]

Sorption Isotherm

To understand the gas transport behavior in the complexed membrane, a pure gas sorption experiment was necessary to understand the affinity between gases and complexed membranes. The O_2 and N_2 sorption isotherms at 5°C to membrane with different oxygen carrier content are shown in Figure 6. The amount of adsorbed oxygen increased as the oxygen carrier content in the complexed membranes increased. On the other hand, the amount of adsorbed nitrogen was not influenced by the oxygen carrier content in the membranes. In other words, the difference of the amount of adsorption between oxygen and nitrogen increased with increasing oxygen carrier content. Therefore, the complexed membrane with 3 wt % oxygen carrier had a good O_2/N_2 separation factor of 15 at low temperature.

The sorption amount of O_2 and N_2 of membranes containing various oxygen carrier content are shown in Figures 6 and 7. The sorption amount of oxygen and nitrogen measured at 35°C was smaller than that at 5°C. This experimental data showed that the thermal effect on the sorption capability of complexed membranes plays an important role. The low temperature produced higher oxygen sorption in the complexed membranes than the high temperature

Table III Dual Mode Sorption Parameter for PC Membranes at 35°C

Membrane	Gas	k_d $\left[\frac{\text{cm}^3\ (\text{STP})}{\text{cm}^3\ \text{atm}}\right]$	C_H $\left[\frac{\text{cm}^3\ (\text{STP})}{\text{cm}^3}\right]$	b (atm^{-1})
PC	O_2	0.11	0.65	0.15
	N_2	0.14	0.03	0.62
Complexed PC	O_2	0.27	0.47	0.27
(1.2 wt %)	N_2	0.18	0.64	0.07
Complexed PC	O_2	0.31	0.38	0.11
(3 wt %)	N_2	0.15	0.25	0.07

did. The reason is that the affinity between oxygen and the complexed membranes at low temperature is higher than that at high temperature. But the same result was not found in the nitrogen sorption measurement.

Gas Diffusivities

Table I lists the permeability, solubility, and diffusivity of pure oxygen and nitrogen for the complexed membranes at different temperatures. The diffusivity was calculated by dividing permeability by solubility. The oxygen permeability and diffusivity decreased with increasing oxygen carrier content in the membranes. The solubility of oxygen in the complexed membranes showed a large difference between low temperature (5°C) and high temperature (35°C). The difference was not observed for the nitrogen under the same conditions. It was suspected that the affinity between oxygen and complexed membranes is higher at low temperature. The oxygen and nitrogen diffusivities increased as the operation temperature increased. The oxygen and nitrogen diffusivities decreased with increasing the oxygen carrier content in the membranes.

X-Ray Analysis

The gas transport behavior through the membrane is determined not only by the gas sorption in the membrane, but also by the gas diffusion behavior in the membrane. To further investigate the gases diffusion of the complexed membrane, it was very important to study the packing density of the membranes that were prepared under various conditions. The packing density of the membranes was analyzed by X-ray diffraction. The X-ray diffraction analysis of the complexed membranes showed that the mean peak intensity of the spectra increased with increasing the oxygen carrier content in the membranes (Fig. 8). The peak position of complexed membranes shifted to a lower position than that of the PC membrane. This indicated that the packing density of complexed membrane increased with increasing oxygen carrier content in the membranes.

Dual Mode Sorption Parameters

The dual mode sorption patterns are listed in Tables II and III. The Henry's law constant, k_d, can be interpreted in terms of pure component and the interaction with the other components. The experimental results showed that the k_d increased with decreasing sorption temperature and oxygen carrier content. Tables II and III also indicate that the k_d of oxygen increased with the amount of oxygen carrier in the complexed membranes. The k_d values of nitrogen were smaller than that of the oxygen, whether at 5 or 35°C. The results support the idea that the introduction of oxygen carrier into the membranes raises the affinity between the polymer matrix and oxygen. The Langmuir capacity constant, C'_H, was related to free volume of polymers by Munuganadam, Koros, and Paul.[16] Tables II and III show that the Langmuir capacity of oxygen decreased irregularly with increasing oxygen carrier content. These results indicate that the packing density of the complex membrane increased with increasing oxygen carrier content in the membrane. However, it is difficult to explain the relationship between the hole affinity constant, b, and the oxygen carrier content in the membranes. Further investigation is needed.

CONCLUSION

Decrease of gas permeability and increase of O_2/N_2 selectivity were obtained by increasing the oxygen carrier content in the membranes. Sorption measurements indicated that the sorption amount of O_2 increased with the increase of oxygen carrier content in the membranes. The affinity between O_2 and complexed membranes was higher than that of N_2, especially at low temperature.

From the X-ray diffraction analysis of the complexed membranes, it is suggested that the decrease of gas permeabilities were caused by the increasing of packing density. In the analysis of dual mode sorption parameters, Henry's law constant (k_d) for oxygen increased with the increase of oxygen carrier content. The hole capacity constant of Langmuir (C'_H) decreased with the increase of oxygen carrier content in the membranes. Comparing the permeability, solubility, and diffusivity of oxygen and nitrogen at various temperatures, it was concluded that the oxygen carrier in the membranes caused the decrease of the gas permeability and diffusivity and the increase of oxygen solubility, especially at low operating temperature. The O_2/N_2 selectivity of 15 was obtained for the complexed membrane at 5°C, which is higher than that of PC membrane possessing 8.8 O_2/N_2 selectivity.

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