

Preparation of Poly(acrylic acid)/Poly(vinyl alcohol) Membrane for the Facilitated Transport of CO₂

HIDETO MATSUYAMA,¹ MASAOKI TERAMOTO,¹ KENJI MATSUI,² YOSHIRO KITAMURA²

¹ Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

² Department of Environmental Chemistry and Materials, Okayama University, 2-1-1 Tsushima-naka, Okayama 700-8530, Japan

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ABSTRACT: Poly(acrylic acid) (PAA)/poly(vinyl alcohol) (PVA) membrane was prepared for the facilitated transport of CO₂. The carrier of CO₂ was monoprotonated ethylenediamine and was introduced in the membrane by ion exchange. The ion-exchange capacity of the membrane was 4.5 meq/g, which was much higher than that of the Nafion 117 membrane. The membrane was highly swollen by the aqueous solution. Much higher selectivity of CO₂ over N₂ and higher CO₂ permeability were obtained in the PAA/PVA membrane than in the Nafion membrane because of the higher ion-exchange capacity and solvent content. The highest selectivity was more than 1900 when the CO₂ partial pressure in the feed gas was 0.061 atm. Effects of ion-exchange capacity, membrane thickness, and annealing temperature in conditions of membrane preparation on membrane performance were investigated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 936–942, 2001

Key words: facilitated transport; carbon dioxide; poly(acrylic acid); poly(vinyl alcohol); gas separation

INTRODUCTION

Gas separation by facilitated transport membrane is an attractive way to achieve high selectivity as well as high permeation rate.¹ A carrier immobilized in the facilitated transport membrane can react with only a specific gas, which leads to high selectivity. Recently, the use of ion-exchange membranes as the support for the facilitated transport membrane has been reported for preventing membrane degradation.^{2–10} When an ionic carrier is immobilized in the ion-exchange membrane by the attractive electrostatic force,

washout and evaporation of carrier are prevented. In this type of facilitated transport membrane, properties of the ion-exchange membrane, such as the ion-exchange capacity and water content, greatly influence the membrane performance. The higher ion-exchange capacity brings about higher carrier concentration in the membrane, which in turn leads to higher selectivity and permeation rate. The hydrophilic water-swollen ion-exchange membrane is favorable toward obtaining high stability as a result of retention of the aqueous carrier solution. In addition, the highly water swollen membrane has another advantage, in that a high permeation rate is obtained because of the high mobility of the complex between carrier and gas. Thus, appropriate design of the ion-exchange membrane is essential to

Correspondence to: H. Matsuyama.

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attain higher performance of the facilitated transport membrane. However, there have been few studies focused on the development of ion-exchange membranes suitable for supports of the facilitated transport membranes.

Previously, we prepared a cation-exchange membrane by grafting acrylic acid onto a microporous polypropylene membrane by a plasma-grafted polymerization technique.^{11,12} The grafted membrane, containing ethylenediamine as a carrier, showed remarkably high selectivity of CO₂ over N₂. For example, when the CO₂ partial pressure in the feed gas was 0.047 atm, the selectivity reached 4700, a result that was attributable to the high ion-exchange capacity (13.1 meq/g dry grafted layer) and the high water content (80%) of the prepared ion-exchange membrane.

From the commercial point of view, the plasma-grafted polymerization method may not be suitable for prompt operation and mass production. In this work, we prepared an ion-exchange membrane composed of poly(acrylic acid) (PAA) and poly(vinyl alcohol) (PVA). Because PAA and PVA are highly hydrophilic, the aqueous carrier solution can be efficiently retained in the membrane. The monoprotonated ethylenediamine (EDAH⁺) was immobilized in the membrane by the electrostatic force between PAA and EDAH⁺, and the facilitated transport of CO₂ was investigated under various experimental conditions.

EXPERIMENTAL

Preparation of PAA/PVA Membrane

PAA ($M_v = 450,000$) and PVA (99+% hydrolyzed powder, $M_w = 89,000$ – $98,000$) were purchased from Aldrich Chemical Co. (Milwaukee, WI). The dope solution was prepared by adding a 15 wt % PAA solution to a 10 wt % PVA solution. The composition of the solution was varied by adjusting the weight ratio of the two solutions. The dope solution was cast onto a glass plate and placed in a drying oven at 60°C for 20 h. The normal cast solution thickness was 1000 μm . It was changed from 50 to 200 μm when membranes with various thicknesses were necessary. The PAA/PVA membrane was finally obtained by annealing the dried membrane at several temperatures (usually 140°C) for 1 h. The membrane with the glass plate was immersed in a water bath for 20 h to detach the membrane. The membrane was soaked in aqueous ethylenediamine (EDA) solutions of var-

ious concentrations, adjusted to pH 11 with HCl, for 24 h to introduce EDAH⁺ as the principal counterion. The commercial Nafion 117 membrane (Aldrich Chemical Co.) was also used in a control experiment. The membrane thickness of the Nafion membrane was 186 μm .

Characterization of PAA/PVA Membrane

To obtain the ion-exchange capacity of the membrane, the membrane was soaked in 1 mol/dm³ KCl solution for 24 h. The membrane was then soaked in water for 24 h to release the free K⁺, which is not a counterion to the ion site of the membrane. Finally, the membrane was soaked in 0.1 mol/dm³ HCl and the K⁺ concentration released into the HCl solution was measured by an atomic absorption spectrophotometer (Jarrell Ash AA-855). Similarly, to obtain the carrier amine concentration in the membrane, the membrane containing EDAH⁺ was soaked in 0.1 mol/dm³ NaOH solution and the concentration of EDA released was measured spectrophotometrically.¹³

The solvent content of the membrane was obtained from eq. (1) by the weight of the membrane swollen in 2 vol % EDA solution (W_s) and the dry membrane weight (W_d).

$$\text{Solvent content} = (W_s - W_d)/W_s \quad (1)$$

The swollen membrane thickness was measured by a micrometer (MDC-25M, Mitsutoyo, Japan).

Gas Permeation Experiment

The permeation cell consisted of two 3.7-mm-deep compartments for a feed and a sweep gas. The PAA/PVA membrane was sandwiched between the two compartments. The membrane area was 9.1 cm². The feed gas was a mixture of CO₂ and N₂. The N₂ flow rate was 200 cm³/min and the CO₂ flow rate was varied to change the CO₂ partial pressure in the feed gas. The sweep gas was helium and the flow rate was 75 cm³/min. Both gases were saturated with water upstream of the cell and were supplied to the cell at atmospheric pressure. The outlet sweep gas was analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC-8APT; Shimadzu, Kyoto, Japan). The permeation experiment was carried out in a constant-temperature environment maintained at several temperatures (usually 25°C).

RESULTS AND DISCUSSION

Table I shows the ion-exchange capacities of the PAA/PVA membranes prepared from the dope so-

Table I Ion-Exchange Capacity of the Membrane and Retention Factor of PAA in the Membrane

PAA : PVA Ratio in the Dope Solution	Theoretical Ion-Exchange Capacity (meq/g)	Actual Ion-Exchange Capacity (meq/g)	Retention Factor of PAA in the Membrane
1 : 9	1.4	1.3	0.93
2 : 8	2.8	2.7	0.96
3 : 7	4.2	3.4	0.81
4 : 6	5.6	4.5	0.80

Annealing temperature, 140°C.

lutions with several PAA : PVA ratios. When the PAA : PVA ratio in the dope solution was more than 4 : 6, the membrane was too soft to be used for the transport experiment. The retention factor of PAA in the membrane, which can be calculated from a theoretical ion-exchange capacity estimated from the PAA : PVA ratio and an actually obtained ion-exchange capacity, is also included in this table. In all cases, the retention factors were more than 0.8, which indicates that most of the PAA was efficiently retained in the membrane. When the PAA : PVA ratio in the dope solution was 4 : 6, the ion-exchange capacity was 4.5 meq/g, which is much higher than 0.91 meq/g of the Nafion 117 membrane.³

The effects of the ion-exchange capacity and the annealing temperature on the membrane thickness and the solvent content are shown in Figures 1 and 2, respectively. As the ion-exchange capacity increased (i.e., the content of PAA in-

creased), the solvent content increased monotonically. This is because PAA is more hydrophilic than PVA. When the ion-exchange capacity is 4.5 meq/g, the solvent content was about 0.78, which is much higher than the water content of 0.11 of the Nafion membrane.³ The increase of the annealing temperature brought about the decrease of both the membrane thickness and the solvent content. When the annealing temperature is high, the membrane structure becomes denser, which leads to the lower solvent content.

Figure 3 shows the relation between the EDA concentration C_M in the PAA/PVA membrane and the EDA concentration C_A in aqueous solution, in which the membrane was soaked. C_M is the dimensionless concentration defined as the EDA concentration in the membrane divided by the ion-site concentration. Thus, unity of C_M means that the EDA concentration in the membrane is just the same as the ion-site concentration. In the low C_A region, C_M increased drastically with the

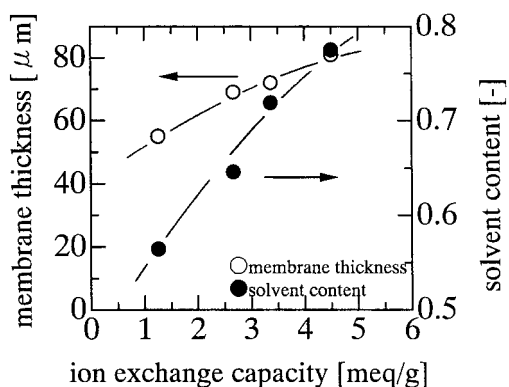


Figure 1 Effect of ion-exchange capacity on membrane thickness and solvent content. In the membrane preparation, the PAA : PVA ratio in the dope solution was changed. Cast membrane thickness: 1000 μm; annealing temperature: 140°C.

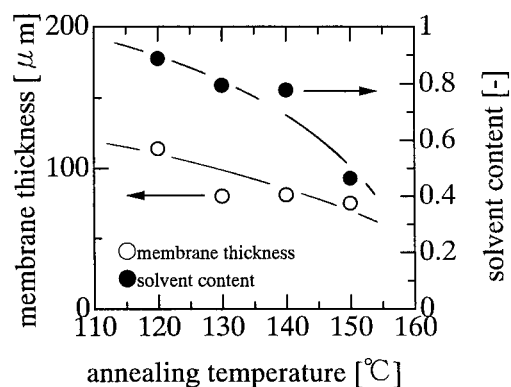


Figure 2 Effect of annealing temperature on membrane thickness and solvent content. Ion-exchange capacity of the membrane: 4.5 meq/g; cast membrane thickness: 1000 μm.

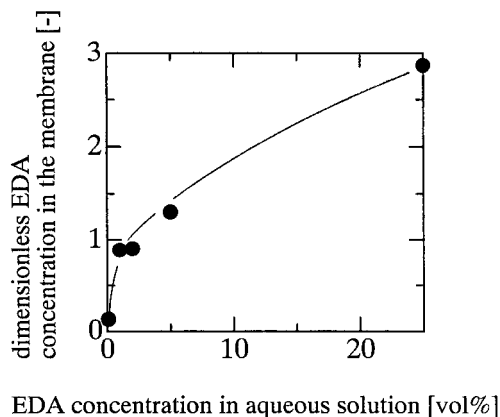


Figure 3 Relation between dimensionless EDA concentration in the PAA/PVA membrane and EDA concentration in aqueous solution.

increase of C_A resulting from the incorporation of EDA^+ by the ion exchange. Then the degree of increase of C_M leveled off. The increase of C_M in the high C_A region is brought about by the free EDA, which is not the counterion to the ion site. The EDA concentration in the aqueous solution was fixed at 2 vol % in all permeation experiments because C_M is close to unity in this condition.

The effect of CO₂ partial pressure in the feed gas on membrane performance is shown in Figure 4. The ordinates in this figure are permeability P , permeance R , and selectivity of CO₂ over N₂. The permeance is defined by eq. (2) and the relation between R and P is expressed by eq. (3).

$$R = N/\Delta P \quad (2)$$

$$R = P/L \quad (3)$$

where N is the gas flux, ΔP is the partial pressure difference between the upstream and downstream side of the membrane, and L is the membrane thickness. The selectivity is the ratio of R_{CO_2} to R_{N_2} . Data for the commercial Nafion membrane are also included in this figure. The permeability of CO₂ in the PAA/PVA membrane decreased with the increase of CO₂ partial pressure, whereas P_{N_2} was nearly constant because N₂ permeates through the membrane by the normal Fickian mechanism. The decrease in P_{CO_2} is attributed to the saturation of carrier and is characteristic of the facilitated transport membrane. The CO₂ permeability and selectivity in the PAA/PVA membrane were much higher than those in the Nafion membrane. This is because the PAA/

PVA membrane has higher ion-exchange capacity and higher solvent content. The selectivity in the membrane reached more than 1500 when the CO₂ partial pressure was 0.061 atm.

Figure 5 shows the effect of ion-exchange capacity of the membrane. As the ion-exchange capacity increased, P_{CO_2} increased because the facilitated transport was enhanced by the higher carrier concentration. Contrary to this, P_{N_2} slightly decreased with the increase of ion-exchange capacity. The N₂ solubility in the carrier solution incorporated in the membrane becomes lower in the higher carrier concentration condition as a result of the salting-out effect, which leads to the decrease in P_{N_2} . Because the tendency in P_{CO_2} is opposite to that in P_{N_2} , the selectivity increased dramatically with the increase of ion-exchange capacity.

Figure 6 shows the effect of the membrane thickness. The permeances of both CO₂ and N₂ increased with the decrease of the membrane

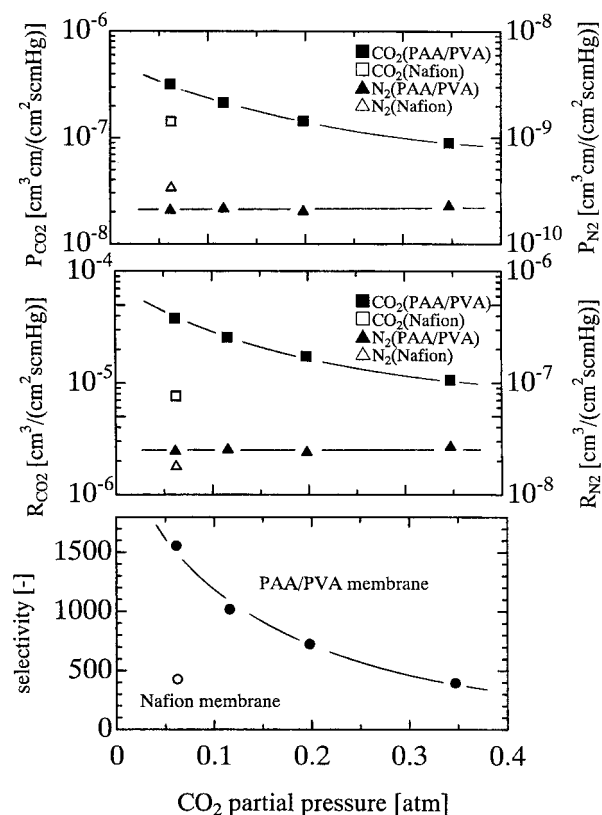


Figure 4 Effect of CO₂ partial pressure in feed gas on membrane performances. Membrane thickness: 84 μm ; ion-exchange capacity of the membrane: 4.5 meq/g; annealing temperature: 140°C; experimental temperature: 25°C.

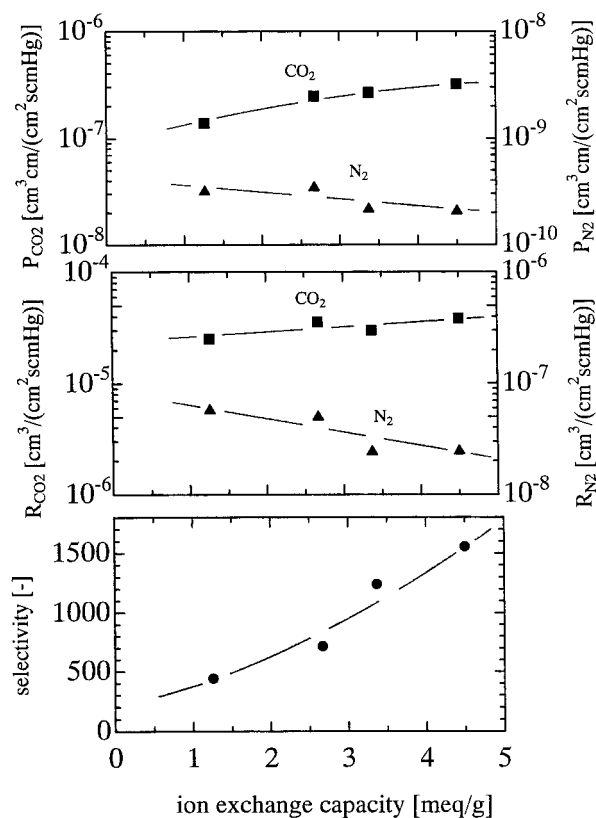


Figure 5 Effect of ion-exchange capacity of the membrane on membrane performances. CO₂ partial pressure in the feed phase: 0.061 atm; membrane thickness: 84 μ m; annealing temperature: 140°C; experimental temperature: 25°C.

thickness because the diffusion rate in the membrane is inversely proportional to the membrane thickness. On the other hand, as the membrane thickness decreased, a decrease in P_{CO_2} was observed, whereas P_{N_2} was nearly constant. The result of the constant P_{N_2} indicates that the membrane structure was hardly altered in the change of the membrane thickness. If the CO₂-facilitated transport rate is limited by the complex formation rate rather than by the complex diffusion, the permeance is scarcely influenced by the membrane thickness. Therefore, the permeability, which is the product of the permeance and the membrane thickness, decreases with the decrease of thickness. This tendency is the same as that reported previously in the supported liquid membrane¹⁴ and the solution-cast perfluorosulfonic acid ionomer membrane.¹⁵

The effect of the annealing temperature in the membrane preparation condition is shown in Figure 7. Annealing at high temperature brought

about decreases in CO₂ and N₂ permeabilities; however, the degree of decrease was less in the case of CO₂. Therefore, the selectivity increased with the temperature. The highest selectivity was more than 1900. As shown in Figure 2, the solvent content becomes lower with the increase of the annealing temperature. The less swollen membrane structure leads to lower diffusivity in the membrane, which causes a decrease in P_{N_2} . Furthermore, the lower solvent content brings about the higher carrier concentration in the membrane and contributes to enhancing the facilitated transport of CO₂. This is probably the reason that the degree of decrease was less in P_{CO_2} .

Figure 8 shows the effect of the experimental temperature. The CO₂ permeance at 45°C was about 1.5-fold higher than that at 25°C, although the selectivity slightly decreased with the temperature. In the practical removal of CO₂ from flue gases, a membrane must be operated at more than 50°C.¹⁶ It was confirmed that the PAA/PVA

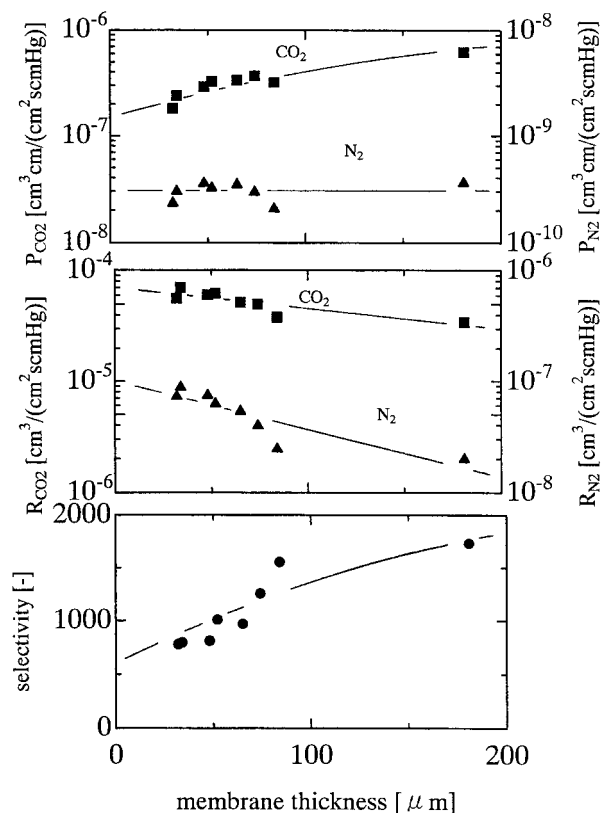


Figure 6 Effect of membrane thickness on membrane performances. CO₂ partial pressure in the feed phase: 0.061 atm; ion-exchange capacity of the membrane: 4.5 meq/g; annealing temperature: 140°C; experimental temperature: 25°C.

membrane was useful even at temperatures close to this practical condition.

CONCLUSIONS

PAA/PVA membranes were prepared for the facilitated transport of CO₂. The typical ion-exchange capacity was 4.5 meq/g and was much higher than 0.91 meq/g of the Nafion 117 membrane. The PAA/PVA membrane was very highly swollen by the aqueous EDA solution. The solvent content increased with the increase of the ion-exchange capacity of the membrane, whereas it decreased with the increase of the annealing temperature.

EDAH⁺ was introduced in the PAA/PVA membrane by the attractive electrostatic force, and the facilitated transport of CO₂ was investigated. The PAA/PVA membrane showed much higher selectivity and CO₂ permeability than did the Nafion

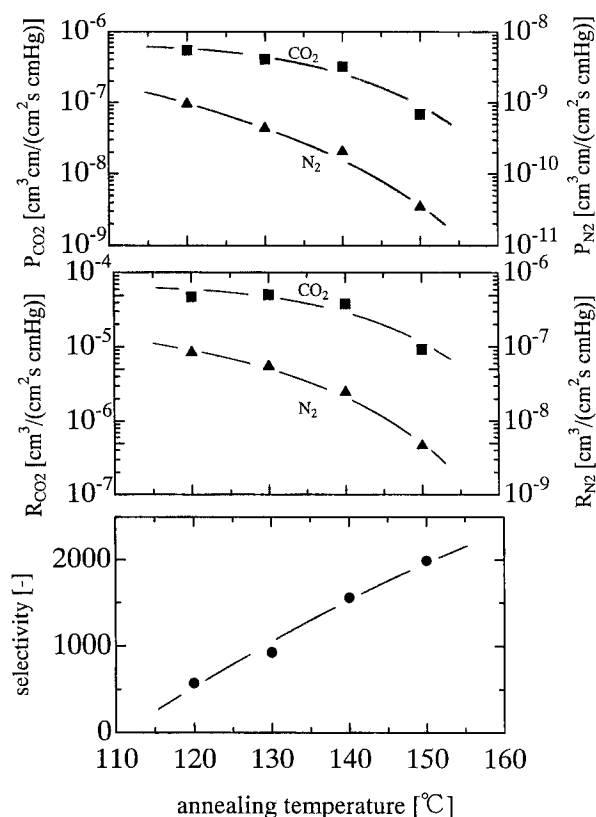


Figure 7 Effect of annealing temperature on membrane performances. CO₂ partial pressure in the feed phase: 0.061 atm; cast membrane thickness: 1000 μm ; ion-exchange capacity of the membrane: 4.5 meq/g; experimental temperature: 25°C.

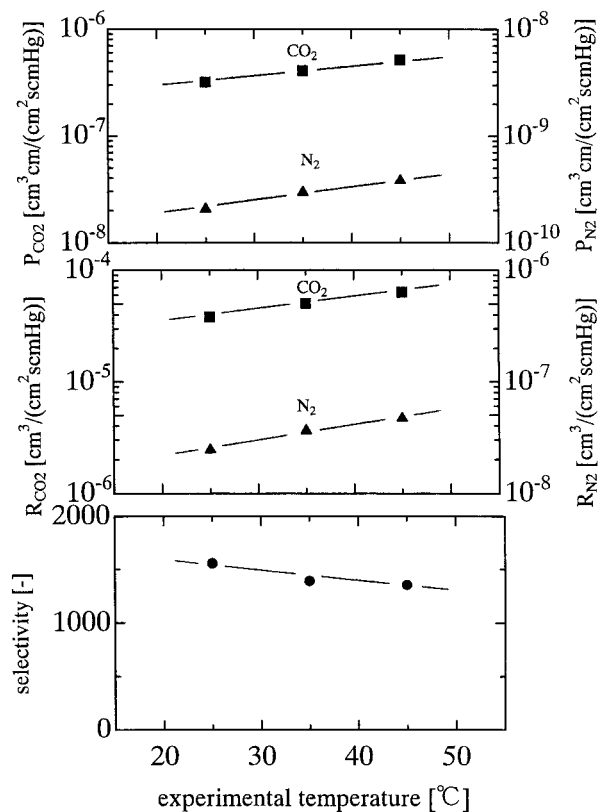


Figure 8 Effect of experimental temperature on membrane performances. CO₂ partial pressure in the feed phase: 0.061 atm; membrane thickness: 84 μm ; ion-exchange capacity of the membrane: 4.5 meq/g; annealing temperature: 140°C.

membrane because of the high ion-exchange capacity and solvent content. The highest selectivity was more than 1900 when the CO₂ partial pressure in the feed gas was 0.061 atm. As the ion-exchange capacity increased, the selectivity and the CO₂ permeance increased monotonically. A decrease of the membrane thickness brought about an increase of the CO₂ permeance and a decrease of the selectivity. On the other hand, the increase of the annealing temperature led to an increase of the selectivity and a decrease of the CO₂ permeance.

REFERENCES

- Way, J. D.; Noble, R. D. in *Facilitated Transport*; Ho, W. S.; Sirkar, K. K. Eds.; Membrane Handbook; Van Nostrand Reinhold: New York, 1992; p. 833.
- LeBanc, O. H.; Ward, W. J.; Matson, A. L.; Kimura, S. G. *J Membr Sci* 1980, 6, 339.

3. Way, J. D.; Noble, R. D.; Reed, D. L.; Ginley, G. M.; Jarr, L. A. *AIChE J* 1987, 33, 480.
4. Noble, R. D.; Pellegrino, J. J.; Grosogeat, E.; Sperry, D.; Way, J. D. *Sep Sci Technol* 1988, 23, 1595.
5. Pellegrino, J. J.; Nassimbene, R.; Noble, R. D. *Gas Sep Purif* 1988, 2, 126.
6. Langevin, D.; Pinoche, M.; Selebny, E.; Metayer, M.; Roux, R. *J Membr Sci* 1993, 82, 51.
7. Pellegrino, J.; Wang, D.; Rabago, R.; Noble, R.; Koval, C. *J Membr Sci* 1993, 84, 161.
8. Eriksen, O. I.; Aksnes, E.; Dahl, I. M. *J Membr Sci* 1993, 85, 89.
9. Eriksen, O. I.; Aksnes, E.; Dahl, I. M. *J Membr Sci* 1993, 85, 99.
10. Pellegrino, J.; Kang, Y. S. *J Membr Sci* 1995, 99, 163.
11. Matsuyama, H.; Teramoto, M.; Iwai, K. *J Membr Sci* 1994, 93, 237.
12. Matsuyama, H.; Teramoto, M.; Sakakura, H.; Iwai, K. *J Membr Sci* 1996, 117, 251.
13. Citron, I. M.; Mills, A. *Anal Chem* 1964, 36, 208.
14. Watari, T.; Huang, Q.; Teramoto, M. *Kagaku Kogaku Ronbunshu* 1998, 24, 155.
15. Matsuyama, H.; Matsui, K.; Kitamura, Y.; Maki, T.; Teramoto, M. *Sep Purif Technol* 1999, 17, 235.
16. Haraya, K.; Nakajima, M.; Itoh, N.; Kamisawa, C. *Kagaku Kogaku Ronbunshu* 1993, 19, 714.