Gas Permeabilities of NH_3-Plasma-Treated Polyethersulfone Membranes

T. Iwa,[1] H. Kumazawa,[1] S.-Y. Bae[2]

[1]*Department of Chemical Process Engineering, Toyama University, 3190 Gofuku/Toyama 930-8555, Japan*
[2]*Department of Chemical Engineering, Hanyang University, Ansan 425–791, Korea*

Received 30 September 2003; accepted 5 May 2004
DOI 10.1002/app.20961
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of NH_3-plasma treatment on glassy polyethersulfone (PES) membranes upon the diffusion process for CO_2, O_2, and N_2. was investigated from the permeability measurements. The permeation behavior for O_2 and CO_2 in untreated and NH_3-plasma-treated PES membranes was simulated well in terms of the dual-mode mobility model. For O_2 transport, NH_3-plasma treatment on PES membrane had a little influence on the diffusion process of Langmuir species and very little influence on the diffusion process of Henry's law species. For CO_2 transport, it promoted the transport of Henry's law mode but had very little influence on the transport process of Langmuir species. Both the mean permeability coefficient to CO_2 and the ideal separation factor for CO_2 relative to N_2 took maximum values at a treatment power of 40 W. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 758–762, 2004

Key words: diffusion; gas permeation; membranes; plasma treatment; poly(ether sulfones)

INTRODUCTION

The fixation and removal of CO_2 emitted from fossil fuel combustion facilities has been considered as a way to prevent CO_2 buildup in the atmospheric sphere. One possible removal process for this purpose is membrane-based separation. It has been expected that the surface modification of membrane by plasma treatment tends to induce an increase in the permselectivity of CO_2 relative to nitrogen (N_2) as well as the permeability to CO_2. The plasma treatment on the membrane has been believed to exert an influence mainly on the diffusion process of dissolved gas molecules, and macroscopically the permeability or diffusivity has been determined as a lumped parameter. Glassy polymer membranes have been recommended as the base polymer of CO_2 separation membrane because of their high chemical and thermal stability. NH_3-plasma treatment as a surface modification way of the glassy polymer membrane, among others, possibly tends to be able to introduce basic functional groups, which can interact with sorbed CO_2, to the membrane surface. In glassy polymer membranes, in which two kinds of populations, Henry's law and Langmuir populations, conceptually execute different diffusive movements, a question to be asked and solved has been how the plasma treatment affects the respective modes of diffusion.

In our preceding works,[1,2] the effects of NH_3-plasma treatment on two kinds of glassy polymer membranes on the diffusion process for penetrant gases, CO_2, O_2, and N_2 have been discussed: glassy poly(phenylene oxide) (PPO) membrane,[1] which has high chemical and thermal stability, and poly(methyl methacrylate) (PMMA) membrane,[2] which has been recognized to exhibit high permeability to CO_2. The sorption equilibria and permeation behavior for O_2 and CO_2 in untreated PPO membranes were simulated well in terms of the dual-mode sorption and mobility model. For O_2 transport, the NH_3-plasma treatment on PPO membrane had an influence on the diffusion process of Henry's law species, whereas, for CO_2 transport, it promoted the transport of Langmuir mode, presumably through an increased Langmuir capacity constant for CO_2. The mean permeability coefficients for CO_2 in PMMA membrane decreased with increasing upstream pressure up to $\sim$ 0.9 MPa, and the pressure dependence of mean permeability coefficient in this region could be interpreted by a dual-mode mobility model. Above 1.0 to 1.2 MPa of upstream pressure, the logarithmic permeability coefficients in treated as well as untreated membranes increased linearly with the upstream pressure, presumably due to the plasticization action of sorbed CO_2. The mean permeability coefficients for O_2 and N_2 substantially remain constant irrespective of the upstream pressure. For O_2 transport, the permeability increases a little with increasing treatment power, and for N_2 transport, it was not affected by the treatment power. For CO_2 transport, NH_3-plasma treatment pro-

Correspondence to: H. Kumazawa (kumazawa@eng.toyama-u.ac.jp).

Journal of Applied Polymer Science, Vol. 94, 758–762 (2004)

TABLE I
Dual-Mode Sorption Parameters for CO_2 and O_2 in PES Membranes at 30°C

Gas	k_D [m^3 (STP) m^{-3} MPa^{-1}]	b (MPa^{-1})	C'_H [m^3 (STP) m^{-3}]	Source
Cast membrane				
CO_2	7.90	4.94	19.0	Ref. 4
O_2	1.28	0.207	8.50	Ref. 4
Commercial membrane				
CO_2 (35°C)	7.91	5.13	17.2	Ref. 4
O_2 (35°C)	0.707	0.418	8.50	Ref. 4
CO_2	6.23	3.09	29.8	Ref. 5
CH_4	1.66	1.21	10.8	Ref. 5

moted the transport of Langmuir mode, presumably through an increased Langmuir capacity constant for CO_2, whereas it had only an influence on the mobility of Henry's law species. The NH_3-plasma treatment to PPO and PMMA membranes resulted in an increase in the separation factor of CO_2 relative to N_2 as well as the permeability to CO_2. It is desirable that this speculation for CO_2 transport through NH_3-plasma-treated glassy polymer membrane is confirmed also for the other glassy polymer membranes.

In the present work, thus, NH_3-plasma treatment has been applied on glassy polyethersulfone (PES) membrane, which exhibits high permeability to CO_2. The effects of NH_3-plasma treatment on the diffusion processes of Henry's law and Langmuir modes in PES membranes have been estimated from the permeability measurements. The degree of improvement of permselectivity for CO_2 relative to N_2 induced by NH_3-plasma treatment was discussed from the points of view of gas permeation and diffusion processes.

EXPERIMENTAL

Membrane preparation

Homogeneous dense PES membranes were prepared by casting a 10 wt % solution of PES resin (Victrex 4800P, Mitsui Chemicals Inc., Japan) in dichloromethane on a flat glass plate and then keeping it in a container of dry air for 2 h. The membranes were then degassed in a vacuum oven at 170°C for 4 days. Commercial dense PES membranes were also used, which were supplied from Sumitomo Bakelite Inc., Japan. The glass transition temperature was reported to be 225°C by the manufacturer.

Plasma treatment

The plasma treatment was performed in a flow-type cylindrical plasma reactor with an external electrode (Yamato, PR-510A), employed in our preceding works.[1,2] The internal diameter and length of the reactor are 21.5 and 27.5 cm, respectively. NH_3 balanced with N_2 up to 2,010 ppm was used as the treatment gas, and the flow rate was maintained at 10 cm^3 (STP)/min. The glow discharge was generated under a pressure of 0.5 Torr (mmHg) at a fixed frequency of 13.56 Hz. The electric power of discharge was varied up to 60 W. The duration ranged up to 1 min.

Measurements of steady-state permeation rates

The steady-state permeation rates for CO_2, O_2, and N_2 through cast and commercial PES membranes with and without NH_3-plasma treatment were measured by a variable-volume method employed by Stern et al.[3] The gas to be permeated was fed into the upstream side, while the downstream side was filled with the same gas at 0.101 MPa. The volumetric flow rate through the membrane to the downstream side was measured by observing the displacement of a small amount of 1-propanol in a capillary tube connected to the downstream pressure side. The mean permeability coefficient was calculated from this steady-state permeation rate. The permeation area of the cell was 19.6 cm^2. Sorption equilibrium data for CO_2 and O_2 with dense PES membrane samples were taken from our previous paper.[4]

RESULTS AND DISCUSSION

Sorption equilibria

Measured sorption isotherms for CO_2, O_2, and N_2 in cast and commercially available dense PES membranes at 30°C exhibited similar downward concave patterns characteristic of glassy polymers.[4] The sorption behavior can be described well by the dual-mode sorption model:

$$C = C_D + C_H = k_D p + C'_H bp/(1 + bp) \tag{1}$$

The values of the dual-mode sorption parameters in eq. (1) were estimated from data analysis by the Marquardt method[4] and are listed in Table I. In the same table, the dual-mode sorption parameters for CO_2 and

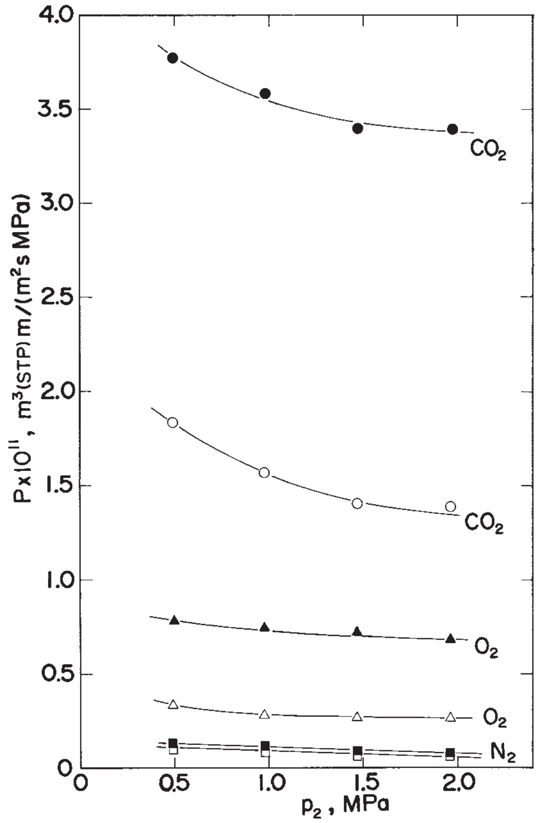

Figure 1 Dependencies on upstream pressure of mean permeability coefficients for CO_2, O_2, and N_2 in untreated cast and commercially available PES membranes at 30°C. Full symbols refer to cast membrane, whereas open symbols refer to commercial membrane.

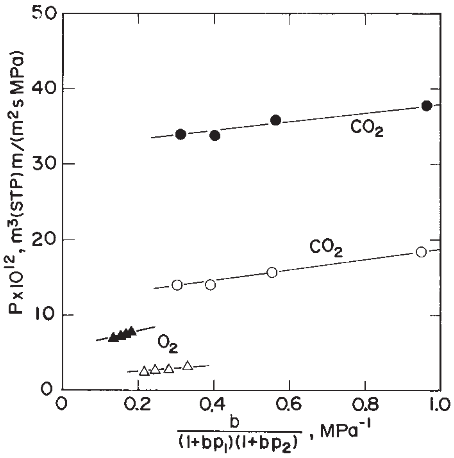

Figure 2 Test of dual-mode mobility model for CO_2 and O_2 in untreated PES membranes at 30°C. Full symbols refer to cast membrane, whereas open symbols refer to commercial membrane.

CH_4 in a commercial membrane (ICI 600P) at 35°C[5] are listed.

Permeabilities

The experimental results on mean permeability coefficients for CO_2, O_2, and N_2 in untreated cast PES membranes at 30°C are plotted against the upstream pressure in Figure 1. In the same figure, the mean permeability coefficients for the same gases in commercial PES membranes are also plotted. It is apparent that the mean permeability coefficients for CO_2 and O_2 in both cast and commercial membranes decrease with increasing upstream pressure, characteristic of glassy polymers, whereas those for N_2 substantially remain constant regardless of the upstream pressure. It was then examined whether the dual-mode mobility model was operative for the pressure dependencies of the mean permeability coefficients to CO_2 and O_2:

$$P = k_D D_D + C_H' b D_H / (1 + bp_1)(1 + bp_2) \qquad (2)$$

The mean permeability coefficient data for CO_2 and O_2 were plotted on the basis of eq. (2) in Figure 2. Such plots gave essentially straight lines, which imply that the dual mode mobility model driven by concentration is applicable to these systems. From the slope and intercept of each straight line, the values of diffusion coefficients of Henry's law and Langmuir species, D_D and D_H, were determined and are listed in Table II. In the same table, similar diffusion parameters for cast PES membranes taken from our previous paper[4] are also listed.

The mean permeability coefficients for CO_2 in PES membranes treated with HN_3 plasma at different powers of treatment under a constant duration of exposure of 1 min were also plotted on the basis of eq. (2) in Figure 3, where Langmuir affinity constant b is assumed not to be affected by the plasma treatment. It is shown that the plots for treated as well as untreated membranes exhibit the straight lines closely parallel to each other. Figure 4 shows the similar plots for O_2, where b is also assumed not to be affected by the plasma treatment. They are also found to give the straight lines with different slopes and nearly the same intercepts. From both figures, first, it can be judged that the dual-mode mobility model can be

TABLE II
Dual-Mode Transport Parameters for CO_2 and O_2 in PES Membranes at 30°C

Gas	$D_D \times 10^{13}$ ($m^2\ s^{-1}$)	$D_H \times 10^{13}$ ($m^2\ s^{-1}$)	Source
Cast membrane			
CO_2	40.6	3.11	This work
CO_2	14.3	2.92	Ref. 4
O_2	4.14	3.01	This work
Commercial membrane			
CO_2	14.9	4.07	This work
O_2	2.83	0.441	This work

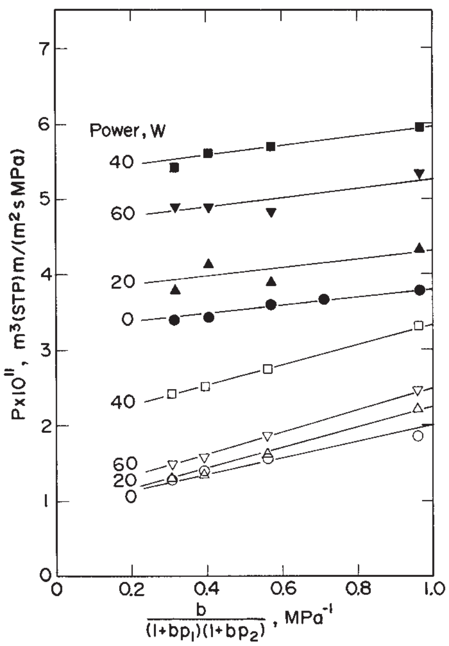

Figure 3 Test of dual-mode mobility model for CO_2 in PES membranes with treated NH_3-plasma at different powers of treatment. Full symbols refer to cast membrane, whereas open symbols refer to commercial membrane.

applicable to the permeation for CO_2 and O_2 in NH_3-plasma-treated PES membranes as well: eq. (2) for untreated membranes and

$$P = \bar{k}_D\bar{D}_D + \bar{C}_H'b\bar{D}_H/(1 + bp_1)(1 + bp_2) \qquad (3)$$

for NH_3-plasma-treated membranes.

Second, Figure 3 reveals that, for CO_2 transport, NH_3-plasma treatment has an influence on the diffusion process of Henry's law species, but very little

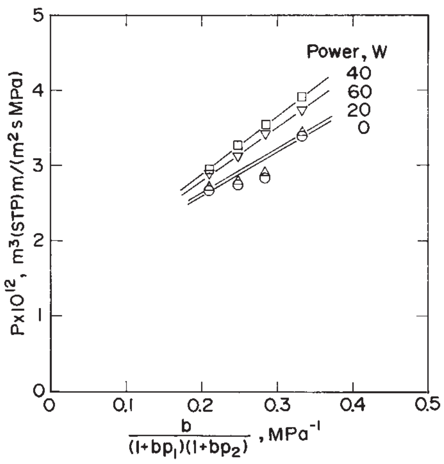

Figure 4 Test of dual-mode mobility model for O_2 in commercial PES membranes with treated NH_3-plasma at different powers of treatment.

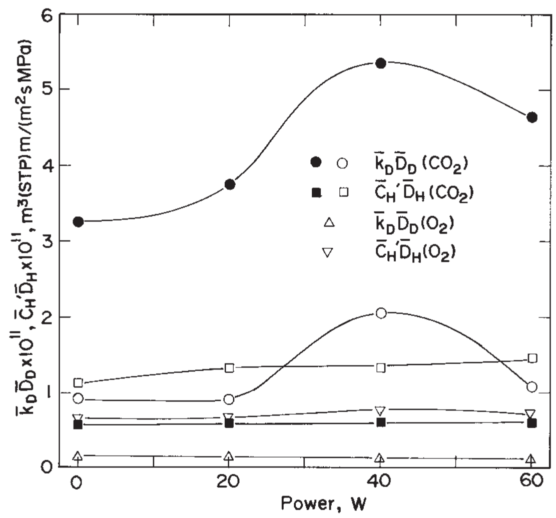

Figure 5 Variation of $\bar{k}_D\bar{D}_D$ and $\bar{C}_H'\bar{D}_H$ for CO_2 and O_2 transport in PES membranes with power of NH_3-plasma treatment. Full symbols refer to cast membrane, whereas open symbols refer to commercial membrane.

influence on the diffusion coefficient of Langmuir species. On the contrary, Figure 4 reveals that, for O_2 transport, NH_3-plasma treatment has a little influence on the diffusion process of Langmuir species and very little influence on the diffusion coefficient of Henry's law species.

To evaluate the effect of the power of plasma treatment on the diffusion processes of both Henry's law and Langmuir species, the values of $\bar{k}_D\bar{D}_D$ and $\bar{C}_H'\bar{D}_H$ calculated from the intercept and slope, respectively, of each straight line in Figures 3 and 4, were plotted against the power of plasma treatment in Figure 5. It was apparent that, for O_2 transport, the plasma treatment exerted only a little influence on $\bar{C}_H'\bar{D}_H$. For CO_2 transport in cast and commercial membranes, $\bar{k}_D\bar{D}_D$ took a maximum value at a treatment power of 40 W, whereas $\bar{C}_H'\bar{D}_H$ was almost independent of the power. If the diffusion coefficient of Henry's law species $\bar{D}_D$ for CO_2 is not affected by the plasma treatment like in case of O_2 transport, then the Henry's law constant for CO_2 is supposed to be increased by the plasma treatment. This may be because the Henry's law constant for CO_2 apparently tends to be increased by NH_3-plasma treatment through an interaction of dissolved CO_2 with the basic functional group (e.g., $-NH_2$) generated by the treatment, rather than the diffusivity of Henry's law. Figure 6 reveals the ESCA spectra of PES membranes with and without treated NH_3-plasma.[6] Actually, the N1s peak appears in a NH_3-plasma-treated PES membrane, presumably based on the NH_2 group.

In Figure 7, the dependencies on the NH_3-plasma treatment power of the mean permeability coefficient to CO_2 and the ideal separation factor for CO_2 relative to

N_2 defined as their permeability ratio at 0.981 MPa were shown. Both the mean permeability coefficient to CO_2 and the ideal separation factor took maximum values at a treatment power of 40 W.

CONCLUSION

The permeation behavior for CO_2 and O_2 through PES membranes with and without treated NH_3-plasma can be simulated well in terms of a dual-mode mobility model. For O_2 transport, NH_3-plasma treatment has a little influence on the diffusion process of Langmuir species and very little influence on the diffusion process of Henry's law species. For CO_2 transport, NH_3-plasma treatment has an influence on the diffusion process of Henry's law species but very little influence on the diffusion process of Langmuir species. This may be because the Henry's law constant for CO_2 apparently tends to be increased by NH_3-plasma treatment through an interaction of dissolved CO_2 with the basic functional group (e.g., $-NH_2$) generated by the treatment, rather than the diffusivity of Henry's law. Both the mean permeability coefficient to CO_2 and the ideal separation factor for CO_2 relative to N_2 took maximum values at a treatment power of 40 W.

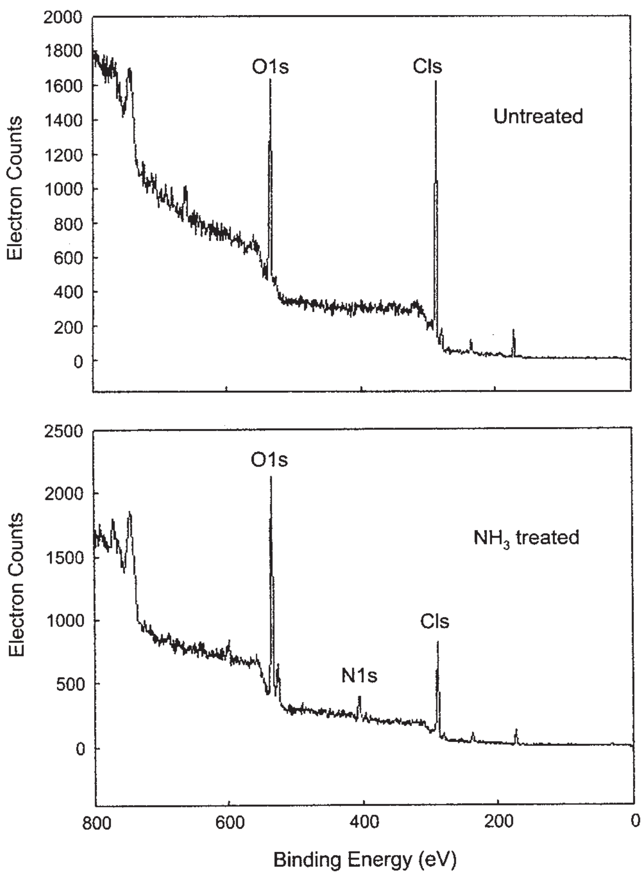

Figure 6 ESCA spectra of PES membranes with and without treated NH_3-plasma.

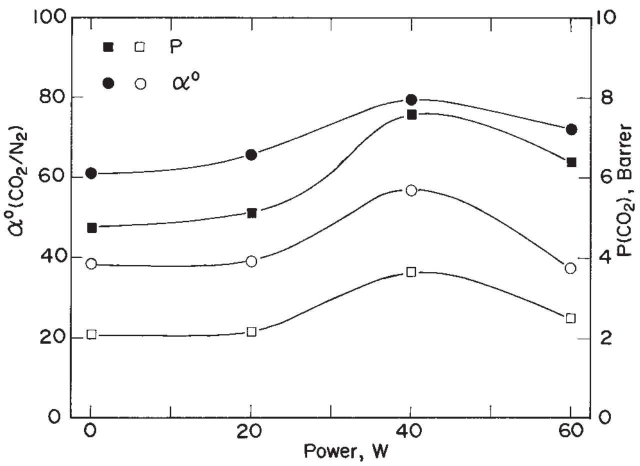

Figure 7 Variation of mean permeability coefficient to CO_2 and ideal separation factor for CO_2 relative to N_2 in PES membranes with power of NH_3-plasma treatment. Full symbols refer to cast membrane, whereas open symbols refer to commercial membrane.

NOMENCLATURE

Symbols

b = Langmuir affinity constant (MPa^{-1})
C = concentration of total sorbed species [m^3 (STP)/m^3]
C_D = concentration of Henry's law species [m^3 (STP)/m^3]
C_H = concentration of Langmuir species [m^3 (STP)/m^3]
C'_H = Langmuir capacity constant [m^3 (STP)/m^3]
D = diffusion coefficient of penetrant gas (m^2/s)
k_D = Henry's law constant [m^3 (STP) / (m^3 MPa)]
P = mean permeability coefficient [m^3 (STP) m/(m^2 s MPa)]
p = pressure of penetrant gas (MPa)
α^o = ideal separation factor for CO_2 relative to N_2

Subscript

D = Henry's law mode
H = Langmuir mode
1 = downstream surface
2 = upstream surface

An overbar symbolizes an average value in the NH_3-plasma-treated membrane.

References

1. Kumazawa, H.; Yoshida, M. J Appl Polym Sci 2000, 78, 1845.
2. Yamamoto, Y.; Maegawa, M.; Kumazawa, H. J Appl Polym Sci 2003, 87, 1068.
3. Stern, S. A.; Gareis, P. J.; Sinclair Mohr, P. H. J Appl Polym Sci 1963, 7, 2935.
4. Kumazawa, H.; Wang, J.-S.; Sada, E. J Polym Sci Part B: Polym Phys 1993, 31, 881.
5. Sanders, E. S. J Membr Sci 1988, 37, 63.
6. Park, H.-J.; Noh, S.-H.; Bae, S.-Y.; Moon, S.-K. Hwahak Konghak 2002, 40, 687.