Mechanism of Gas Transport of NH_3-Plasma-Treated Poly(phenylene oxide) Membrane

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ABSTRACT: The effect of NH_3-plasma treatment on glassy poly(phenylene oxide) (PPO) membranes on the diffusion process for carbon dioxide (CO_2), oxygen (O_2), and nitrogen (N_2) was investigated from the permeability measurements. 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, 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. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1845–1852, 2000

Key words: polyphenylene oxide; carbon dioxide; plasma treatment; permselectivity; dual-mode mobility model

INTRODUCTION

Ever-increasing fossil fuel usage causes atmospheric buildup of carbon dioxide (CO_2). CO_2, which is exhausted in massive amounts, is regarded as one of the most influential greenhouse gases. The fixation and removal of CO_2 from fossil fuel combustion facilities has been considered as a way to prevent CO_2 buildup. One possible process for this purpose is membrane 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). It has been believed that plasma treatment exerts influence mainly on the diffusion process of dissolved gas molecules, and macroscopically the permeability or diffusivity has been determined as a lumped parameter. In glassy polymer membranes, in which two kinds of population conceptually execute diffusive movement, a question to be asked and

solved is how the plasma treatment affects the respective modes of diffusion.

In the present work, NH_3-plasma treatment was used as a surface modification way of the glassy polymer membrane, because of an expected increase in the permselectivity for CO_2 relative to N_2. The poly(phenylene oxide) (PPO) membrane, which has highly chemical and thermal stability, was used as the glassy polymer membrane. It was one aim to elucidate the effect of NH_3-plasma treatment on PPO membranes on the diffusion process for CO_2, oxygen (O_2), and N_2. Actually, the effects of NH_3-plasma treatment on the diffusion processes of Henry's law and Langmuir modes have been estimated from the permeability measurements. Another aim was to discuss the degree of improvement of permselectivity for CO_2 relative to N_2 induced by NH_3-plasma treatment from the points of view of gas diffusion and dissolution processes.

EXPERIMENTAL

Membrane Preparation

Homogeneous dense PPO membranes were prepared by casting a mixed solution of PPO and

$CHCl_3$ on a flat glass plate. The concentration of PPO in $CHCl_3$ solutions was fixed at 23 wt %.

Plasma Treatment

The plasma treatment was performed in a flow-type cylindrical plasma reactor with an external electrode (Yamato, PR-510A, Tokyo, Japan). The internal diameter and length of the reactor are 21.5 and 27.5 cm, respectively. NH_3 diluted with N_2 up to 2010 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 at a fixed frequency of 13.56 Hz. The electric power of discharge was varied up to 100 W. The duration ranged up to 1 min.

Measurements of Sorption Equilibria and Steady-State Permeation Rates

Sorption equilibria for CO_2, O_2, and N_2 with dense PPO membrane samples were measured by means of a pressure decay method.[1] The sorption cell is similar to one designed by Koros et al.,[2] and the pressure in the sorption cell was continuously measured by a pressure transducer. The steady-state permeation rates for CO_2, O_2, and N_2 through dense PPO membranes with and without NH_3-plasma treatment were measured by a variable-volume method used by Stern et al.[3] The gas to be permeated was fed into the upstream side, whereas 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.

RESULTS AND DISCUSSION

The measured sorption isotherms for CO_2, O_2, and N_2 in PPO membrane at 30°C are shown in Figure 1. Each isotherm, especially for CO_2, exhibits a nonlinear pattern similar to those observed for glassy polymers. The isotherms could be described well in terms of the dual-mode sorption model:
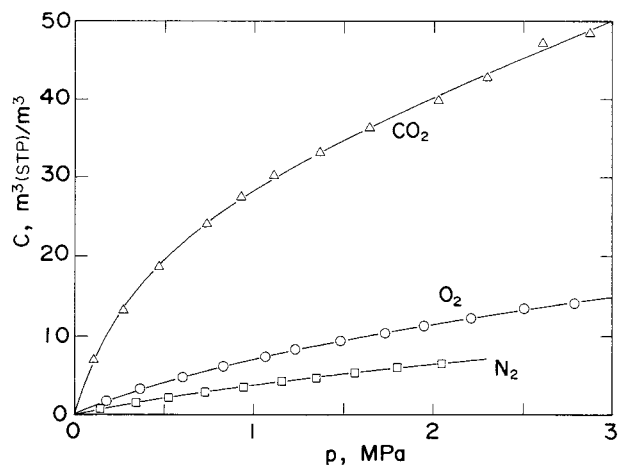
Figure 1 Sorption isotherms for CO_2, O_2, and N_2 in PPO membrane at 30°C.

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

The dual-mode sorption parameters of the dual-mode sorption model were determined by a nonlinear regression method, and are listed in Table I. The solid curves in Figure 1 represent the sorption isotherms calculated using eq. (1) and these estimates. In the same table, the dual-sorption parameters for the same systems previously measured[4–7] are listed.

The experimental results on mean permeability coefficients ($\bar{P}$) for CO_2, O_2, and N_2 in untreated dense PPO membranes at 30°C are plotted as a function of upstream pressure in Figure 2. The permeability coefficients for CO_2 and O_2 decrease with increasing upstream pressure, characteristic of glassy polymers, whereas those for N_2 essentially remain constant irrespective of upstream pressure. The thicknesses of the dense membrane used for CO_2 and O_2 permeation range from 46.9 to 50.4 μm and from 44.8 to 47.2 μm, respectively. The pressure dependencies of the mean permeability coefficients for both gases are shown to be essentially independent of the thickness of the membrane, so that all of the membranes prepared are believed to be dense and homogeneous. Then, it was examined whether the dual-mode mobility model was operative or not for the pressure dependencies of the mean permeability coefficients for CO_2 and O_2:

$$\bar{P} = k_D D_D + \frac{C'_H b D_H}{(1 + bp_1)(1 + bp_2)} \quad (2)$$

**Table I   Sorption Parameters for Gases in PPO Membrane**

Gas	Temperature (°C)	$k_D \times 10^6$ [m³(STP)/m³ Pa)]	$b \times 10^6$ (Pa^{-1})	C'_H [m³(STP)/m³)]	Source
CO_2	30	8.35	2.35	28.7	This work
O_2	30	2.47	0.715	11.0	This work
N_2	30	1.41	0.471	7.48	This work
CO_2	35	7.83	2.05	29.7	Ref. 4
CO_2	35	9.38	2.47	27.5	This work
N_2	35	1.18	0.395	7.1	This work
CO_2	35	9.09	1.92	32.7	Ref. 6
CH_4	35	3.16	1.05	22.2	Ref. 6
N_2	35	1.51	0.47	9.95	Ref. 6
CO_2	35	7.78	2.13	32.6	Ref. 7
CO_2	45	5.78	1.62	30.0	Ref. 7
CO_2	55	4.47	1.26	28.4	Ref. 7

The mean permeability coefficient data for CO_2 and O_2 in untreated PPO membranes were plotted on the basis of eq. (2), respectively, in Figures 3 and 4. These plots gave essentially straight lines, implying that the dual-mode mobility model is applicable to these systems. From the slope and intercept of each straight line, the 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 untreated PPO membranes previously determined[4,6] are also listed.

In Figure 4, the permeabilities for O_2 through NH_3-plasma-treated PPO membranes at different powers of treatment under a constant duration of exposure of 1 min are also plotted. The plots for treated as well as untreated membranes exhibit straight lines parallel to each other. For O_2 transport, the dual-mode mobility model is applicable also to NH_3-plasma-treated membranes. The dual-mode mobility model in itself should work well only for dense homogeneous membranes, but here it is operative to the treated membranes as well. The plasma-treated membrane can be approxi-
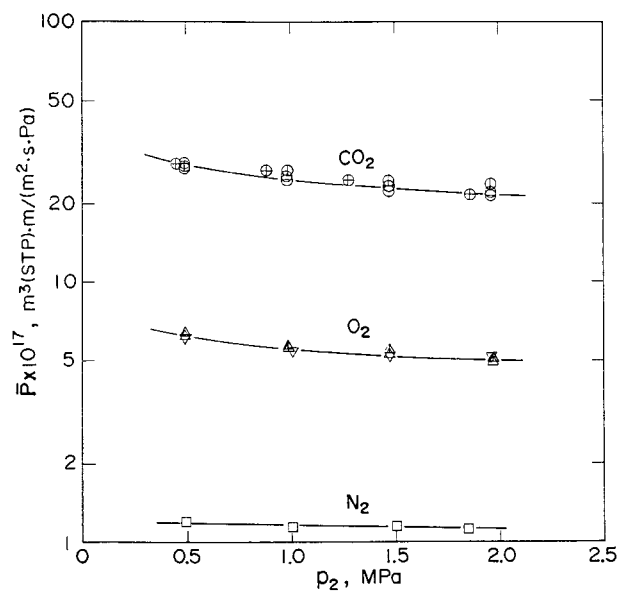
Figure 2   Relations of mean permeability coefficients for CO_2, O_2, and N_2 in PPO membrane to upstream pressure at 30°C.
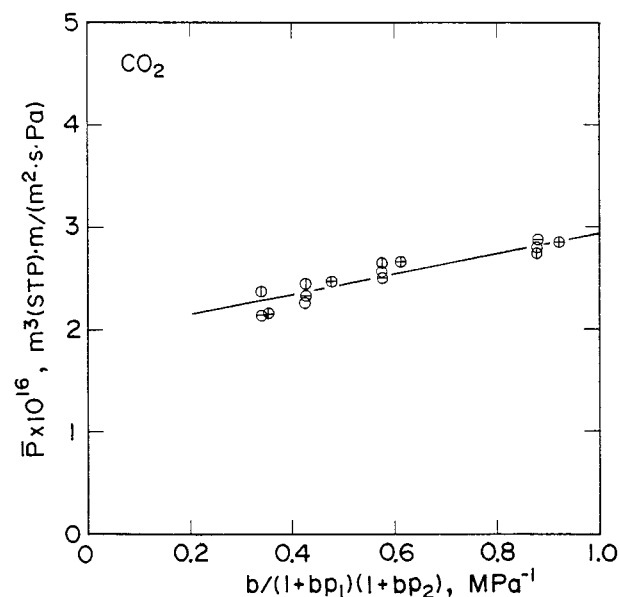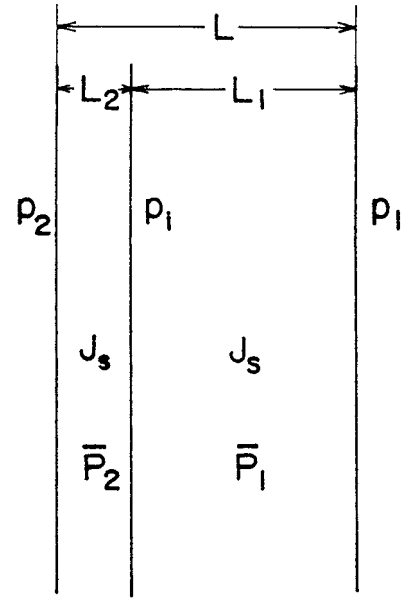

Figure 3   Test of dual-mode mobility model for CO_2–PPO membrane.
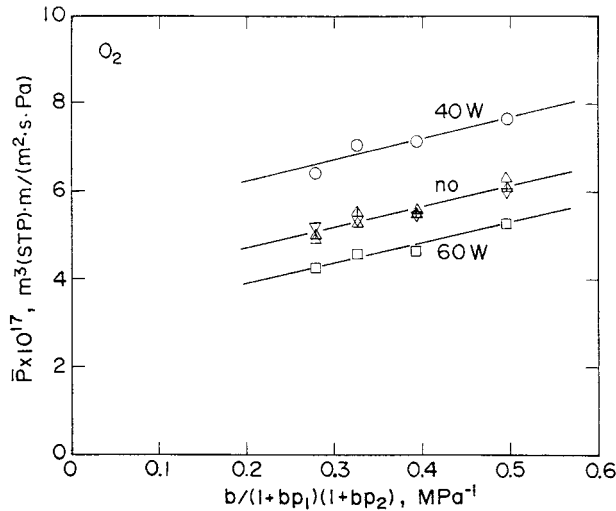
Figure 4 Test of dual-mode mobility model for O_2–PPO membrane.

Figure 5 Conceptual sketch of plasma-treated membrane.

mately replaced with a composite membrane composed of a thin surface layer treated by NH_3 plasma and a remaining base polymer layer. The process of gas permeation through such a composite membrane which is an extension of our previous concept[8] will be considered below.

The conceptual sketch of NH_3-plasma-treated membrane (composite membrane) is depicted in Figure 5. At steady state, the permeation flux through the thin surface layer of thickness L_2 is equal to that through the base-polymer layer of thickness $L_1 = (L - L_2)$. Let the pressure of a penetrant gas on the upstream and downstream sides of this composite membrane be designated by p_2 and p_1, respectively, and the pressure in between these two layers be replaced by p_i. Then, the permeation flux at steady state is written as:

$$J_s = \frac{\bar{P}_2(p_2 - p_i)}{L_2} = \frac{\bar{P}_1(p_i - p_1)}{L_1} \tag{3}$$

where $\bar{P}_2$ and $\bar{P}_1$ refer to the mean permeability coefficients through plasma-treated layer and untreated base-polymer layer, respectively, and can be written in terms of the dual-mode mobility model as:

$$\bar{P}_1 = k_D D_D + \frac{C'_H b D_H}{(1 + bp_1)(1 + bp_i)} \tag{4}$$

$$\bar{P}_2 = k_D^* D_D^* + \frac{(C'_H)^* b^* D_H^*}{(1 + b^* p_2)(1 + b^* p_1)} \tag{5}$$

Table II   Dual-Mode Diffusion Parameters for Gases in Untreated PPO Membrane and for O_2 in NH_3-Plasma-Treated PPO Membrane

Membrane	Gas	Temperature (°C)	$D_D \times 10^{11}$ (m²/s)	$D_H \times 10^{11}$ (m²/s)	Source
Untreated PPO	CO_2	30	2.37	0.338	This work
Untreated PPO	O_2	30	1.53	0.427	This work
NH_3-plasma (40 W) treated PPO	O_2	30	2.13	0.444	This work
NH_3-plasma (60 W) treated PPO	O_2	30	1.13	0.411	This work
Untreated PPO	CO_2	35	4.3	0.42	Ref. 4
Untreated PPO	CO_2	35	3.68	0.368	Ref. 6
Untreated PPO	CH_4	35	0.62	0.043	Ref. 6

In eq. (5), the asterisk (*) designates diffusion and sorption parameters in the NH_3-plasma-treated layer. The permeation flux can also be expressed in terms of a measurable mean permeability coefficient through the composite membrane ($\bar{P}$), *viz*:

$$J_s = \frac{\bar{P}(p_2 - p_1)}{L_1 + L_2} \qquad (6)$$

From eq. (3), the following equation holds:

$$J_s = \frac{\bar{P}_2(p_2 - p_i) + \bar{P}_1(p_i - p_1)}{L_1 + L_2} \qquad (7)$$

A combination of eqs. (6) and (7) yields:

$$\bar{P} = k_D^* D_D^* \frac{p_2 - p_i}{p_2 - p_1} + k_D D_D \frac{p_i - p_1}{p_2 - p_1}$$
$$+ \frac{(C_H')^* b^* D_H^*}{(1 + b^* p_2)(1 + b^* p_i)} \frac{p_2 - p_i}{p_2 - p_1}$$
$$+ \frac{C_H' b D_H}{(1 + b p_i)(1 + b p_1)} \frac{p_i - p_1}{p_2 - p_1} \qquad (8)$$

From the experimental evidence in Figure 4 that the mean permeability coefficients for O_2 through NH_3-plasma-treated PPO membrane vary linearly with the term $b/[(1 + b p_2)(1 + b p_1)]$, eq. (8) can be rewritten as:

$$\bar{P} = \bar{k}_D \bar{D}_D + \frac{\bar{C}_H' b \bar{D}_H}{(1 + b p_1)(1 + b p_2)} \qquad (9)$$

where Langmuir affinity constant b is assumed not to be affected by the plasma treatment, i.e., $b = b^*$. Besides, both the diffusion coefficient of Langmuir species and the Langmuir capacity constant are believed not to be influenced by the plasma treatment (i.e., $\bar{D}_H = D_H$, $\bar{C}_H' = C_H'$), because the slope of the straight line remains essentially constant regardless of the power of the treatment. Then eq. (9) is reduced to:

$$\bar{P} = \bar{k}_D \bar{D}_D + \frac{C_H' b D_H}{(1 + b p_1)(1 + b p_2)} \qquad (10)$$
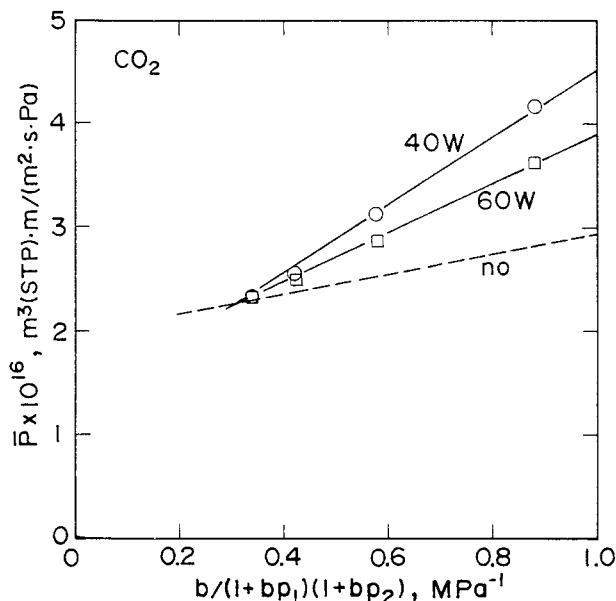
From the slope and intercept of each straight line depicted in Figure 4, the diffusion coefficients D_D and D_H were determined, and are listed in Table
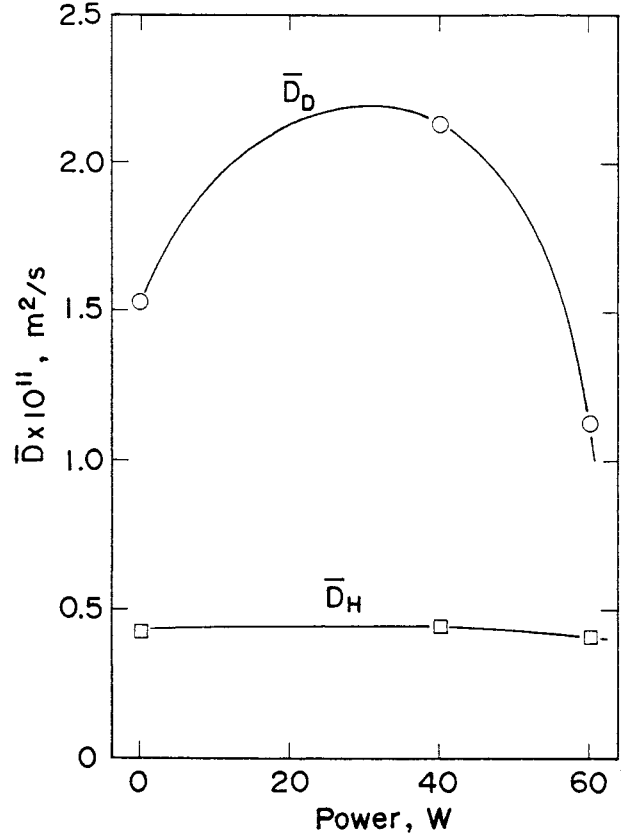
Figure 6 Diffusion coefficients of Henry's law and Langmuir species for O_2 in NH_3-plasma-treated PPO membranes at different powers of treatment.
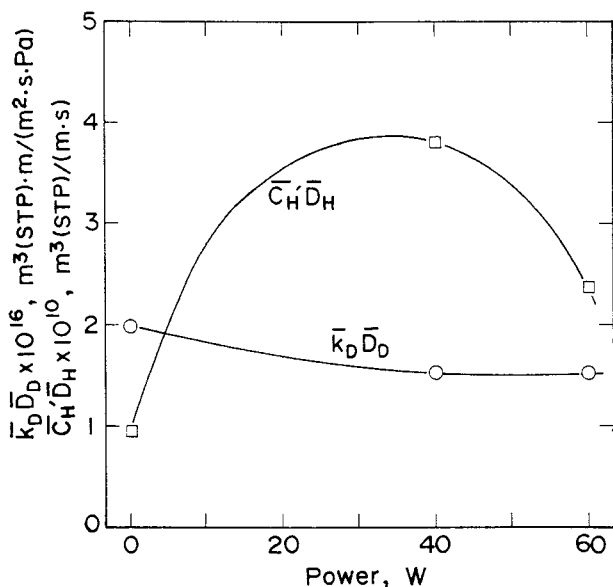
II. Also they were plotted against the power of plasma treatment in Figure 6. It was apparent that for O_2 transport, D_D took a maximum value at power 40 W, whereas D_H was almost independent of the power. It suggests that NH_3-plasma treatment should have an influence on the diffusion process of Henry's law species. A crosslinked thin layer due to N_2 diluted with NH_3, tends to be formed on the membrane surface (i.e., casing effect), as the power increases.

Similarly, the permeabilities for CO_2 in NH_3-plasma-treated PPO membrane are plotted on the basis of eq. (2) in Figure 7. For the sake of comparison, the same relationship for the untreated membrane depicted in Figure 3 is presented as a broken line. Only within the upstream pressures covered, a linear relationship prevails, and the slope of the straight line depends on the power of treatment. For CO_2 transport, NH_3-plasma treatment affects the product of C_H' and D_H in eq. (9). The values of $\bar{C}_H' \bar{D}_H$ and $\bar{k}_D \bar{D}_D$ evaluated from the
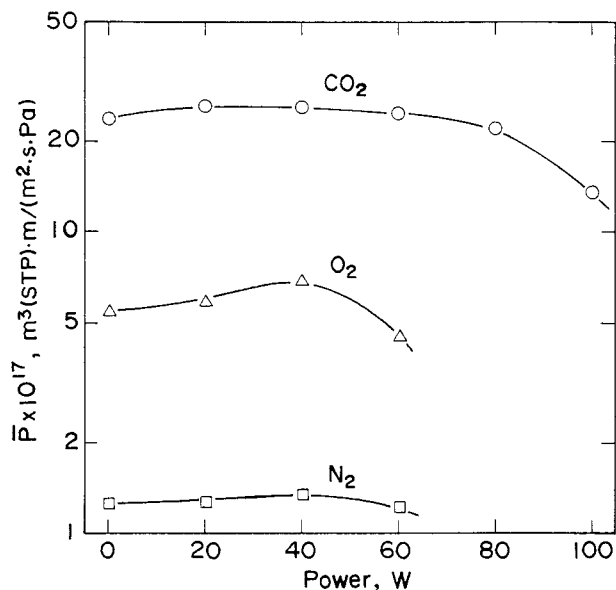
Figure 7 Test of dual-mode mobility model for CO_2–NH_3-plasma-treated PPO membrane at different powers of treatment.

Figure 9 Dependence of mean permeability coefficients for CO_2, O_2, and N_2 in NH_3-plasma-treated PPO membrane on power of treatment.

slope and intercept, respectively of each straight line are plotted against the power of treatment in Figure 8. If the diffusion coefficient of Langmuir species is not influenced by the plasma treatment as in the case of O_2 transport, i.e., $D_H^* = D_H = 3.38 \times 10^{-11}$ m²/s, then the Langmuir capacity

Figure 8 Variations of $k_D D_D$ and $C_H' D_H$ in CO_2 transport with power of treatment.

constant for CO_2 is supposed to be increased by the plasma treatment. Such an increase can be explained qualitatively by the interaction of sorbed CO_2 (A) with basic groups (B) generated by NH_3-plasma treatment, which is assumed to be described as a reversible reaction:

$$A + B = AB \qquad (11)$$

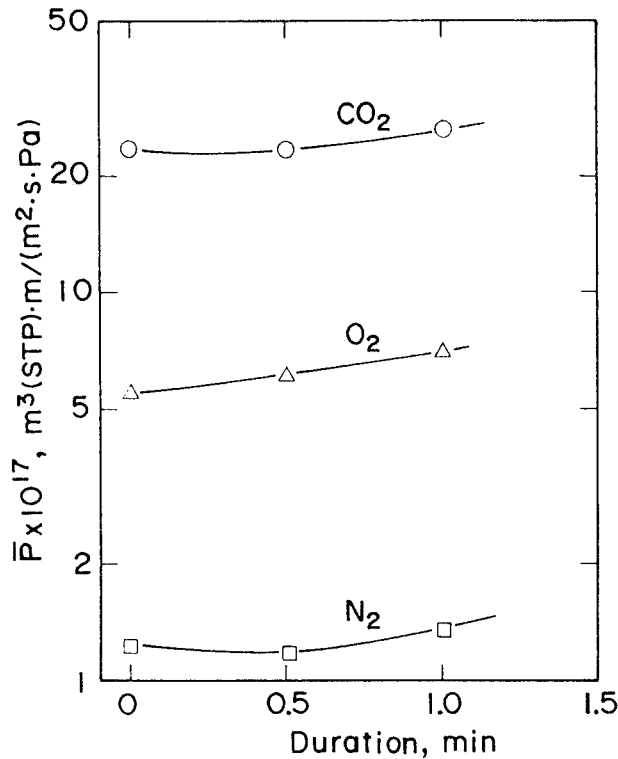with an equilibrium constant K. At an equilibrium:

$$K = \frac{[AB]_e}{[A]_e[B]_e} = \frac{[B]_0 - [B]_e}{[A]_e[B]_e} \qquad (12)$$

where the subscript e refers to the concentration at an equilibrium, and the subscript 0 refers to the initial value. The total concentration of sorbed CO_2 at the equilibrium, $[A]_{tot}$ is given as:

$$[A]_{tot} = [A]_e + [AB]_e \qquad (13)$$

Combining eqs. (12) and (13), one gets:

$$[AB]_e = \frac{K[B]_0[A]_e}{1 + K[A]_e} \qquad (14)$$

Figure 10 Dependence of mean permeability coefficients for CO_2, O_2, and N_2 in NH_3-plasma-treated PPO membrane on duration of treatment.

Equation (14) implies that the Langmuir capacity constant for CO_2 is apparently increased by the NH_3-plasma treatment.

The effects of power and duration of NH_3-plasma treatment on the permeabilities for N_2, O_2, and CO_2 are indicated in Figures 9 and 10, respectively, where all of permeability data were taken at an upstream pressure of 1.47 MPa. The variations of their permeabilities with these two factors are reflected by the effects of abrasion and casing (formation of crosslinked thin layer) induced by the plasma treatment.

CONCLUSION

The sorption equilibria and permeation behavior for O_2 and CO_2 in dense PPO membranes are simulated well in terms of the dual-mode sorption and mobility model. For O_2 transport, NH_3-plasma treatment on PPO membrane had an influence on the diffusion process of Henry's law species, whereas the diffusivity of Langmuir species was almost independent of the power of NH_3

plasma. For CO_2 permeation, NH_3-plasma treatment exerted on the transport of Langmuir mode, i.e., promoted the transport of Langmuir mode. This is presumably because the Langmuir capacity constant for CO_2 apparently tends to be increased by NH_3-plasma treatment through an interaction of sorbed CO_2 with basic groups generated by the treatment, rather than the diffusivity of Langmuir species does.

NOMENCLATURE

Symbols

b Langmuir affinity constant (Pa^{-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 in membrane (m^2/s)
J_s steady-state permeation flux [$m^3(STP)/(m^2 s)$]
k_D Henry's law constant [$m^3(STP)/(m^3 Pa)$]
L thickness of membrane (m)
L_1 thickness of base-polymer layer of membrane (m)
L_2 thickness of plasma-treated layer of membrane (m)
$\bar{P}$ mean permeability coefficient [$m^3(STP)m/(m^2 s Pa)$]
$\bar{P}_1$ mean permeability coefficient in base-polymer layer of membrane [$m^3(STP)m/(m^2 s Pa)$]
$\bar{P}_2$ mean permeability coefficient in plasma-treated layer of membrane [$m^3(STP)m/(m^2 s Pa)$]
p pressure of penetrant gas (Pa)
p_i pressure in between plasma-treated and base-polymer layers as depicted in Figure 5 (Pa)

Subscripts

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

Superscripts

*   sorption and diffusion parameters in the NH_3-plasma-treated layer

overbar   average value in the NH_3-plasma-treated membrane

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