

Gas Permeability and Permselectivity of Plasma-Treated Polyethylene Membranes

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ABSTRACT: The effects of NH₃-plasma and N₂-plasma treatments on rubbery polyethylene (PE) membranes on the permeation behavior for carbon dioxide (CO₂), O₂, and N₂ were investigated with permeability measurements. The NH₃-plasma and N₂-plasma treatments on PE membranes increased both the permeation coefficient for CO₂ and the ideal separation factor for CO₂ with respect to N₂. For O₂ transport, both the permeation coefficient for O₂ and the

ideal separation factor for O₂ with respect to N₂ were increased. NH₃-plasma and N₂-plasma treatments on polymer membranes possibly bring about an augmentation of permeability and permselectivity simultaneously. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 383–387, 2006

Key words: membranes; modification; polyethylene (PE)

INTRODUCTION

Ever-increasing fossil fuel consumption has been causing the atmospheric buildup of carbon dioxide (CO₂). CO₂, which is exhausted in massive amounts, has been recognized as one of the most influential greenhouse gases. The fixation and removal of CO₂ from fossil-fuel-combustion facilities has been considered a promising way to prevent CO₂ buildup in the atmosphere. One possible process for this purpose is membrane-based separation. It has been thought that the surface modification of a membrane by NH₃-plasma treatment, among others, would induce an increase in the permeability to CO₂ through an interaction of dissolved CO₂ with the basic functional group (e.g., —NH₂) from the treatment, whereas it would exert a negligible influence on the permeability to N₂. As a result, the plasma treatment would induce increases in both the permeability coefficient for CO₂ (P_{CO_2}) and the separation factor for CO₂ with respect to N₂.

In our previous works,^{1–3} the effects of NH₃-plasma treatment of two kinds of glassy polymer membranes on the diffusion process for penetrant gases (CO₂, O₂, and N₂) were discussed: a glassy poly(phenylene oxide) (PPO) membrane,¹ which had high chemical and thermal stability, and poly(methyl methacrylate) (PMMA)² and poly(ether sulfone) (PES) membranes,³ both of which exhibited

high permeability to CO₂. The sorption equilibria and permeation behavior for O₂ and CO₂ in untreated PPO membranes were simulated well in terms of the dual-mode sorption and mobility model. For O₂ transport, the NH₃-plasma treatment of the PPO membrane had an influence on the diffusion process of Henry's law species, whereas for CO₂ transport, it promoted the transport of the Langmuir mode, presumably through an increased Langmuir capacity constant for CO₂. The mean P_{CO_2} values for the PMMA membrane decreased with increasing upstream pressure up to about 0.9 MPa, and the pressure dependence of the mean permeability coefficient in this region could be interpreted by a dual-mode mobility model. Above 1.0–1.2 MPa of upstream pressure, the logarithmic permeability coefficients in treated and untreated membranes increased linearly with the upstream pressure, presumably because of the plasticization action of sorbed CO₂. The mean values of the permeability coefficients for O₂ (P_{O_2}) and N₂ (P_{N_2}) substantially remained constant, regardless of the upstream pressure. For O₂ transport, the permeability increased a little with increasing treatment power, and for N₂ transport, it was not affected by the treatment power. For CO₂ transport, NH₃-plasma treatment promoted the transport of the Langmuir mode, presumably through an increased Langmuir capacity constant for CO₂, whereas it had only an influence on the mobility of Henry's law species. The permeation behavior for O₂ and CO₂ in untreated and NH₃-plasma-treated PES membranes was also simulated well in terms of the dual-mode mobility model. For O₂ transport, NH₃-plasma treatment of a

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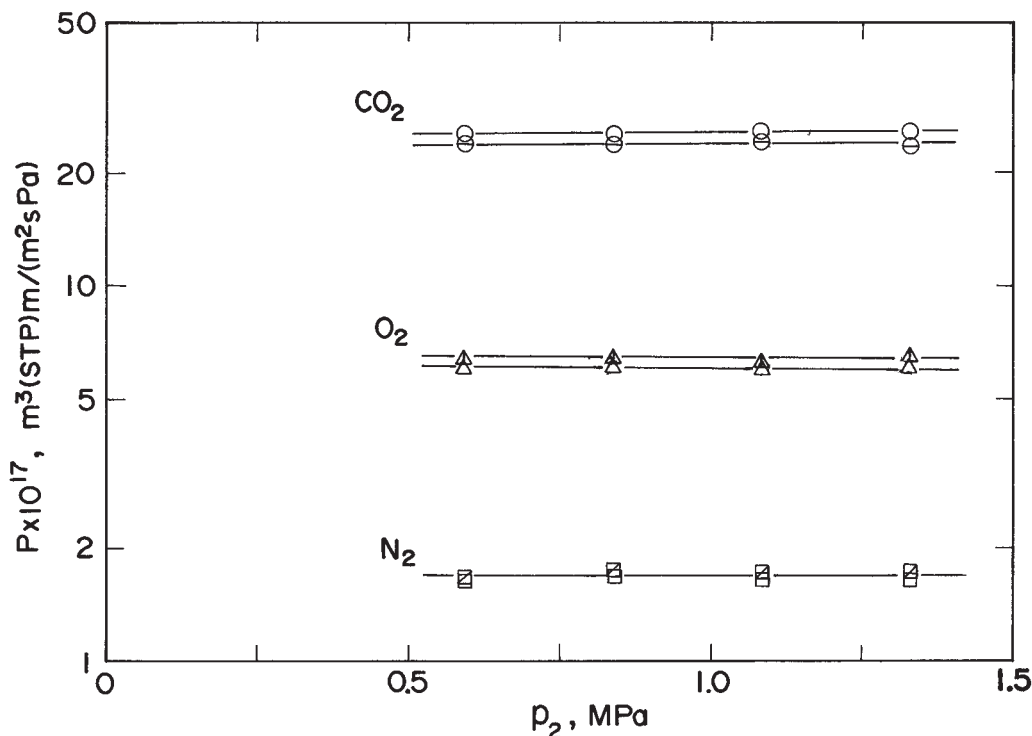


Figure 1 Pressure dependence of P_{CO_2} , P_{O_2} , and P_{N_2} in untreated PE membranes at 30°C.

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 CO₂ 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 P_{CO_2} value and the ideal separation factor for CO₂ with respect to N₂ [$\alpha^0(CO_2/N_2)$] took maximum values at a treatment power of 40 W.

The NH₃-plasma treatment to PPO, PMMA, and PES membranes resulted in an increase in $\alpha^0(CO_2/N_2)$ and the permeability to CO₂. It is desirable that this speculation for CO₂ transport through NH₃-plasma-treated glassy polymer membranes is confirmed also for rubbery polymer membranes as well as other glassy polymer ones.

In this work, NH₃-plasma and N₂-plasma treatments were applied to a typical rubbery polymer membrane, a polyethylene (PE) membrane under plasma discharge powers up to 100 W and a plasma exposure time of 1 min. The degrees of improvement of both the permeability for CO₂ and permselectivity for CO₂ with respect to N₂ induced by NH₃-plasma and N₂-plasma treatments were investigated from measurements of P_{CO_2} and P_{N_2} .

EXPERIMENTAL

A homogeneous, dense PES membrane was supplied by Dainippon Jushi Co., Ltd. (Tokyo, Japan). The

glass-transition temperature was reported to be -120°C by the manufacturer.

The plasma treatment was performed in a flow-type cylindrical plasma reactor with an external electrode (PR-510A, Yamato, Tokyo, Japan) employed in our preceding works.¹⁻³ The internal diameter and length of the reactor were 21.5 and 27.5 cm, respectively. N₂ and NH₃ balanced with N₂ up to 2010 ppm were used as the treatment gas, and the flow rate was maintained at 10 cm³ (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 100 W. The duration of the plasma discharge was fixed at 1 min.

The steady-state permeation rates for CO₂, O₂, and N₂ through PE membranes with and without treated NH₃ plasma and N₂ plasma were measured at a constant temperature of 30°C by a variable-volume method employed by Stern et al.⁴ The gas to be permeated was fed into the upstream side, whereas the downstream side was filled with the same gas at an atmospheric pressure. The volumetric flow rate through the membrane to the downstream side was measured by the observation of the displacement of a small amount of 1-propanol in a capillary tube connected to the downstream pressure side. The permeability coefficient was calculated from this steady-state permeation rate. The permeation area of the cell was 19.6 cm².

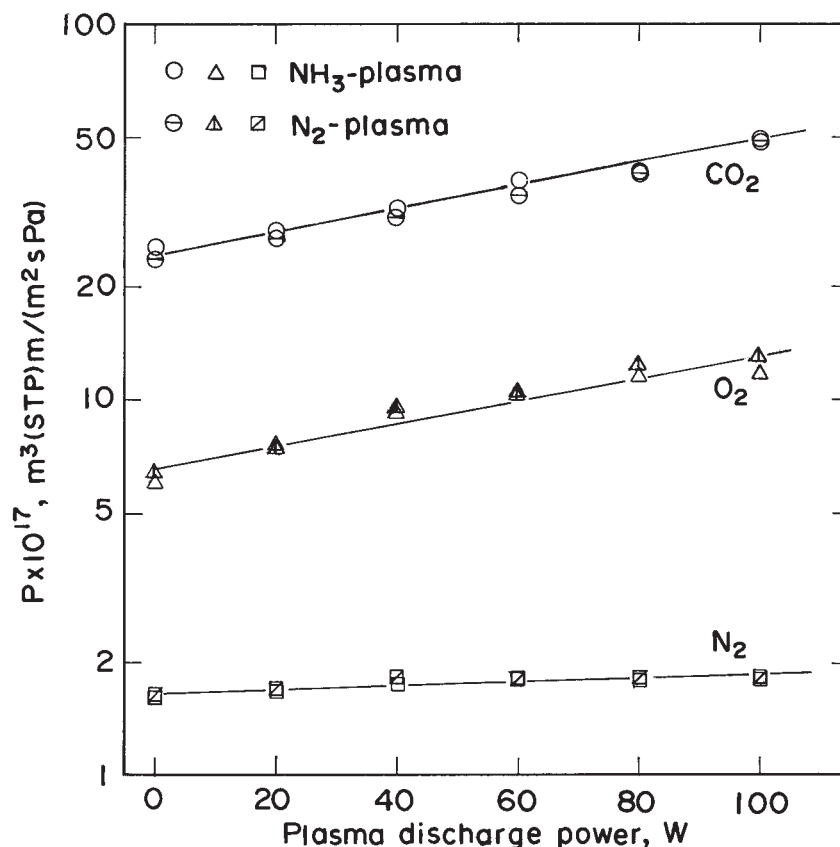


Figure 2 Relationship between the gas permeability coefficient and plasma discharge power at a plasma discharge duration of 1 min.

RESULTS AND DISCUSSION

The experimental results for P_{CO_2} , P_{O_2} , and P_{N_2} in the untreated PE membrane at 30°C are plotted against the upstream pressure in Figure 1. The permeability coefficients for these three gases were almost independent of the upstream pressure; this is characteristic of typical rubbery polymer membranes. The P_{CO_2} , P_{O_2} , and P_{N_2} values in both NH₃-plasma-treated and N₂-plasma-treated PE membranes were also almost independent of the upstream pressure up to 1.3 MPa.

Figure 2 indicates the relations of the P_{CO_2} , P_{O_2} , and P_{N_2} values in both NH₃-plasma-treated and N₂-plasma-treated PE membranes to the plasma discharge power up to 100 W. The effect of the NH₃-plasma treatment was very similar to that of N₂ plasma on the gas permeabilities. The permeability to N₂ was not affected by the plasma treatment, whereas that to CO₂ and O₂ increased with increasing plasma discharge power.

Next, $\alpha^0(\text{CO}_2/\text{N}_2)$ and the ideal separation factor for O₂ with respect to N₂ [$\alpha^0(\text{O}_2/\text{N}_2)$], which are defined by the permeability ratios $P_{\text{CO}_2}/P_{\text{N}_2}$ and $P_{\text{O}_2}/P_{\text{N}_2}$, respectively, were plotted against P_{CO_2} and P_{O_2} (Fig. 3). This figure clearly reveals that the ideal separation factor increased with an increasing permeability coef-

ficient with respect to both CO₂ and O₂. The NH₃-plasma treatment of the PE membrane tended to induce a considerable increase in both the gas permeability and permselectivity simultaneously. The N₂-plasma treatment induced a similar promotion effect.

Figure 4 shows the relationship between $\alpha^0(\text{CO}_2/\text{N}_2)$ and P_{CO_2} in various glassy polymer membranes and a rubbery polymer (PE) one with no plasma treatment. The data for glassy polymer membranes [polyimide (PI), poly(ether imide) (PEI), and cellulose triacetate (CTA) membranes] were taken from our previous articles.⁵⁻⁷ The permeability coefficients of the glassy polymer membranes were evaluated at an upstream pressure of 0.5 MPa. Similar relationships of NH₃-plasma-treated PPO, PMMA, and PES membranes were plotted and were taken from our previous articles.¹⁻³ With untreated membranes, a negative correlation like a straight line appeared: the ideal separation factor decreased with an increasing permeability coefficient. The arrows exhibit the direction of research and development (R&D) for CO₂ separation membranes. The NH₃-plasma treatment of the polymer membranes brought about increases in the CO₂ permeability and permselectivity with respect to N₂ simulta-

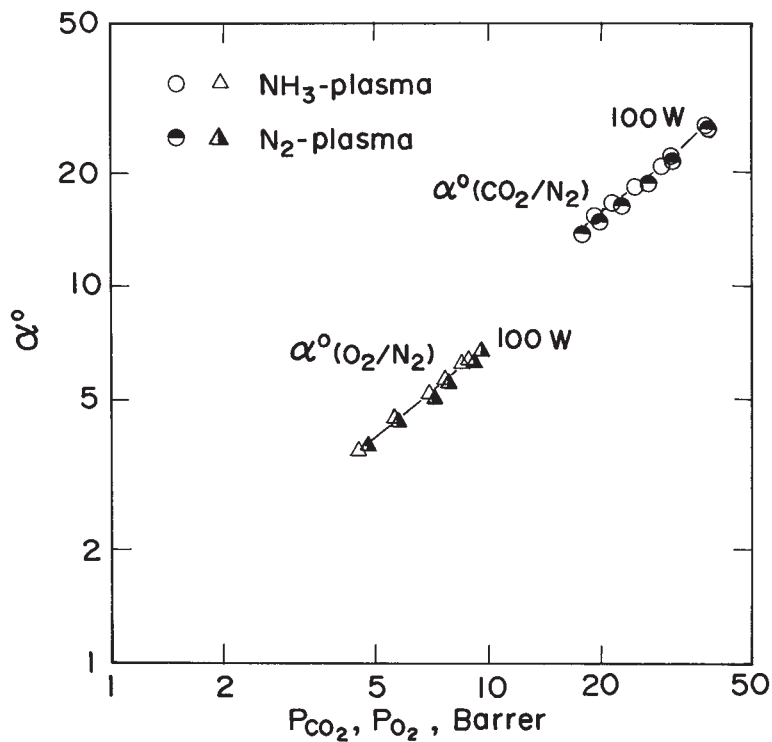


Figure 3 Relations of $\alpha^0(\text{CO}_2/\text{N}_2)$ and $\alpha^0(\text{O}_2/\text{N}_2)$ with P_{CO_2} and P_{O_2} in NH_3 -plasma-treated and N_2 -plasma-treated PE membranes at 30°C .

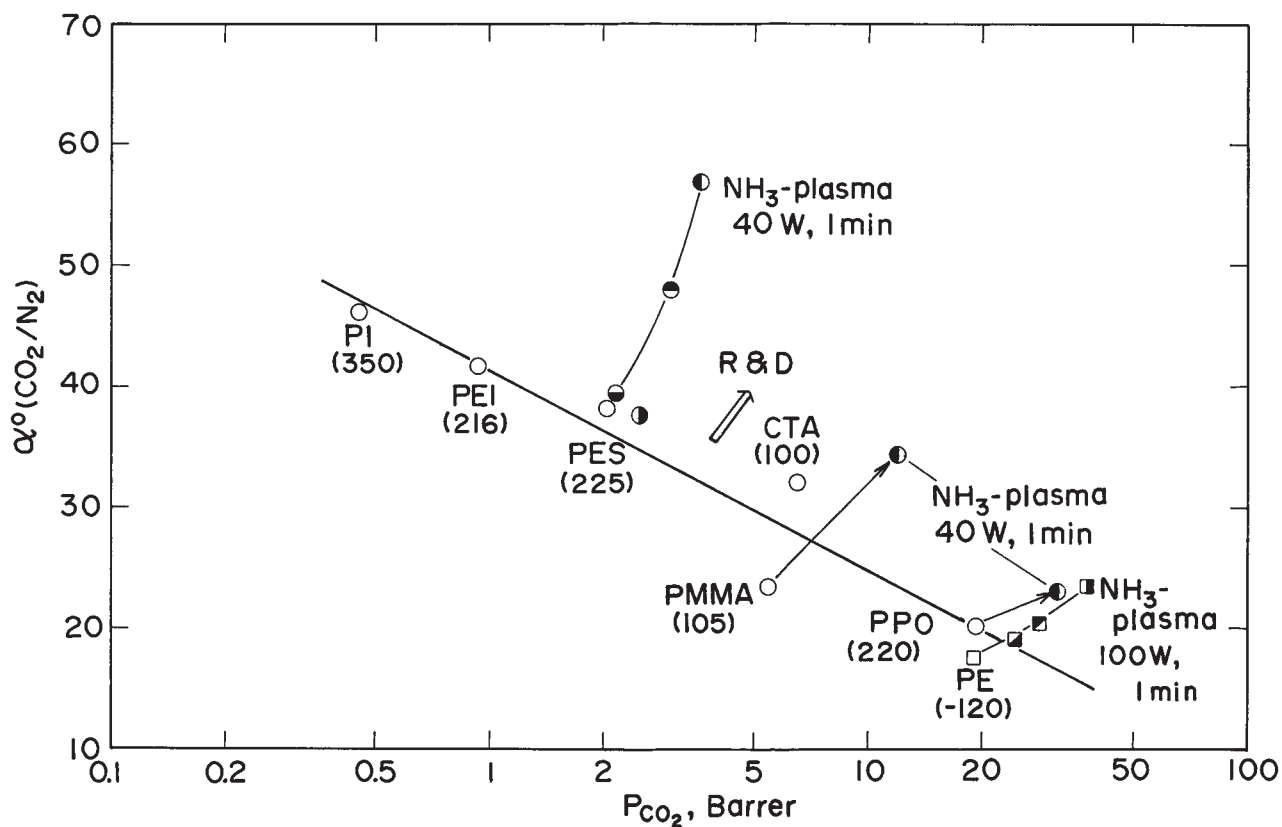


Figure 4 Relationship between $\alpha^0(\text{CO}_2/\text{N}_2)$ and P_{CO_2} in various polymer membranes at 30°C . The numerical values in parentheses represent the glass-transition temperature ($^\circ\text{C}$).

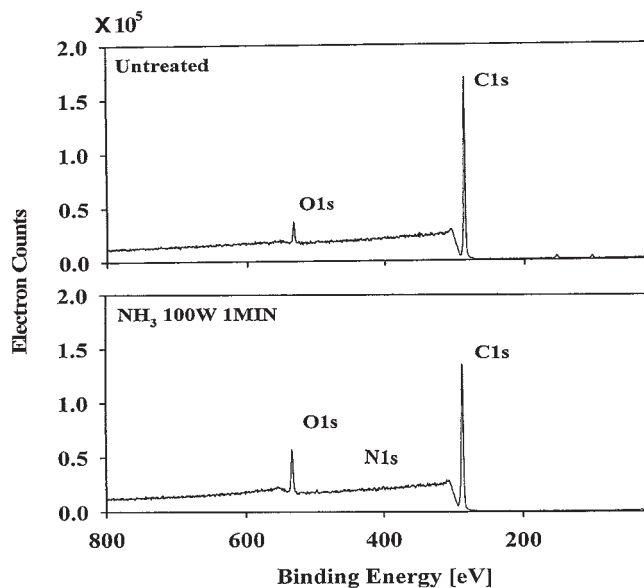


Figure 5 ESCA spectra of untreated and NH_3 -plasma-treated PE membranes.

neously. Such a trend coincided with the direction of R&D, as depicted in Figure 4.

Figure 5 reveals electron spectroscopy for chemical analysis (ESCA) spectra of PE membranes with and without treated NH_3 plasma. For the NH_3 -plasma-treated PE membrane, a slight but definite peak of N1s appears at a binding energy of 400–405 eV, presumably on the basis of the HN_2 group. The solubility of CO_2 in the NH_3 -plasma-treated PE membrane could be augmented through an interaction with the basic functional group, $-\text{NH}_2$. Thus, P_{CO_2} could be increased, whereas P_{N_2} remained unchanged. P_{O_2} could also be increased, as shown in Figure 5, although the interaction of sorbed O_2 with the NH_2 group is not understood yet.

CONCLUSIONS

NH_3 -plasma and N_2 -plasma treatments of PE membranes can increase both P_{CO_2} and $\alpha^0(\text{CO}_2/\text{N}_2)$. Such a favorable trend coincides with the direction of R&D for CO_2 separation membranes. NH_3 -plasma and N_2 -plasma treatments of polymer membranes possibly bring about an augmentation of the permeability and permselectivity simultaneously.

NOMENCLATURE

$\alpha^0(\text{CO}_2/\text{N}_2)$	ideal separation factor, defined by the permeability coefficient ratio, for CO_2 with respect to N_2
$\alpha^0(\text{O}_2/\text{N}_2)$	ideal separation factor, defined by the permeability coefficient ratio, for O_2 with respect to N_2
CO_2	carbon dioxide
CTA	cellulose triacetate
ESCA	electron spectroscopy for chemical analysis
p_2	pressure of the penetrant gas for the upstream surface of the membrane (Pa or MPa)
P_{CO_2}	permeability coefficient for CO_2 [$\text{m}^3(\text{STP}) \text{ m}/(\text{m}^2 \text{ s Pa})$ or Barrer; 1 Barrer = $1.33 \times 10^{-17} \text{ m}^3 (\text{STP}) \text{ m}/(\text{m}^2 \text{ s Pa})$]
P_{N_2}	permeability coefficient for N_2 [$\text{m}^3(\text{STP}) \text{ m}/(\text{m}^2 \text{ s Pa})$ or Barrer; 1 Barrer = $1.33 \times 10^{-17} \text{ m}^3 (\text{STP}) \text{ m}/(\text{m}^2 \text{ s Pa})$]
P_{O_2}	permeability coefficient for O_2 [$\text{m}^3(\text{STP}) \text{ m}/(\text{m}^2 \text{ s Pa})$ or Barrer; 1 Barrer = $1.33 \times 10^{-17} \text{ m}^3 (\text{STP}) \text{ m}/(\text{m}^2 \text{ s Pa})$]
PE	polyethylene
PEI	poly(ether imide)
PES	poly(ether sulfone)
PI	polyimide
PMMA	poly(methyl methacrylate)
PPO	poly(phenylene oxide)
R&D	research and development

References

- Kumazawa, H.; Yoshida, M. *J Appl Polym Sci* 2002, 78, 1845.
- Yamamoto, Y.; Maegawa, M.; Kumazawa, H. *J Appl Polym Sci* 2003, 87, 1068.
- Iwa, T.; Kumazawa, H. *J Appl Polym Sci* 2004, 94, 758.
- Stern, S. A.; Gareis, J. P.; Sinclair, T. F.; Mohr, P. H. *J Appl Polym Sci* 1963, 7, 2935.
- Sada, E.; Kumazawa, H.; Xu, P.; Kiyohara, T. *J Appl Polym Sci* 1989, 38, 687.
- Kumazawa, H.; Wang, J.-S.; Fukuda, T.; Sada, E. *J Membr Sci* 1994, 93, 53.
- Sada, E.; Kumazawa, H.; Xu, P.; Wang, S.-T. *J Appl Polym Sci* 1990, 28, 113.