

Transport of a Gas through Asymmetric Polysulfone Membranes with Deposited Plasma-Polymerized Thin Layer

E. SADA, H. KUMAZAWA, P. XU, and H. INOUE, *Department of Chemical Engineering, Kyoto University, Kyoto 606, Japan*

Synopsis

A plasma-polymerized thin layer was deposited on the top surface of the skin layer of the asymmetric polysulfone (PSF) membrane to plug ultrafine pores passing through it. Trifluoromethane was used as the monomer gas of plasma polymerization. The steady-state permeation rates for oxygen and nitrogen through the asymmetric PSF membranes with the plasma modification were measured to evaluate the permselectivity and permeability. If ultrafine pores passing through the asymmetric membrane can be plugged by the plasma-polymerized thin layer, the separation factor of oxygen relative to nitrogen can be increased with the permeation rate coefficient of oxygen still kept large. This condition was met when the vaporization time of the cast solution during the preparation of an asymmetric membrane ranged from 10 to 120 s and the plasma polymerization time ranged from 15 to 30 min.

INTRODUCTION

Nonporous synthetic membranes for gas separation normally have high permselectivity but have the drawback of low permeation fluxes. In order to overcome such a drawback, asymmetric or composite membranes consisting of a functional dense skin layer and a porous support matrix structure are used and besides, the skin layer is made as thin as possible. However, the thinner the skin layer is, the greater is the possibility of forming ultrafine pores passing through the membrane. The transport of gases through such ultrafine pores is mainly controlled by Knudsen diffusion, which plays a slight role in the separation of gases. In the present work, a plasma-polymerized thin layer is deposited on the top surface of the skin layer of the asymmetric membrane to plug ultrafine pores passing through it. The glassy polysulfone (PSF) was used as the material of the asymmetric membrane, because it has the excellent properties of chemical and thermal stability. Trifluoromethane was used as the monomer gas for the plasma-polymerization. In these asymmetric PSF membranes with deposited plasma-polymerized thin layer, the material (PSF) of the asymmetric membranes determines the separation properties of the membranes. The steady-state permeation rates for pure oxygen and nitrogen were measured to evaluate the permselectivity and permeability of the membranes prepared. Further, the permeabilities for carbon dioxide were measured to get information on the mechanism of permeation for a gas through the glassy polymer membrane with plasma modification.

EXPERIMENTAL

Membrane Preparation

Homogeneous dense and asymmetric polysulfone (PSF) membranes were prepared by casting a mixed solution of PSF (UCC, P-1700), *N,N*-dimethylacetamide and acetone on a flat glass plate. The case solution for asymmetric membranes was left on the glass plate for 10–300 s. Detailed description of these two types of PSF membranes can be found elsewhere.¹

Plasma Polymerization

The plasma polymerization was carried out in a flow-type cylindrical reactor with external electrode (Yamato, Pr-510A). The inner diameter and length of the reactor are 21.5 cm and 27.5 cm, respectively. Trifluoromethane was used as the monomer gas, and the flow rate was maintained at 27.5 cm³ (STP)/min. The glow discharge was generated under a pressure of 0.8 Torr at a fixed frequency of 13.56 MHz. The electric power of discharge was maintained at 300 W. The exposure (i.e., polymerization) time ranged from 10 to 30 min.

Measurements of Sorption Equilibria and Permeation Rates

Equilibrium sorption of oxygen and nitrogen by a homogeneous dense PSF film sample was measured by a pressure decay method. Commercially available films samples (Toray Co., Ltd., Trayslon-PS; glass transition temperature = 190°C, film thickness = 50 μm) were employed as the homogeneous film. The detailed description of the sorption cell and the procedure has been reported in our previous paper.² The steady-state permeation rates for oxygen, nitrogen, and carbon dioxide through asymmetric PSF membranes with and without deposited plasma-polymerized thin layer were measured by a variable-volume method. As a reference, the permeabilities for oxygen and nitrogen through homogeneous dense PSF membranes were also measured. Details of the permeation cell and the procedures have been described elsewhere.²

All of sorption and permeation runs were carried out at a fixed temperature of 40°C.

RESULTS AND DISCUSSION

Sorption Equilibria

The sorption equilibria for oxygen and nitrogen in homogeneous PSF film (Trayslon-PS) at 40°C are shown in Figure 1. The sorption isotherms for both gases exhibit negligible curvature and can be described well in terms of Henry's law, viz.,

$$C = k_D p \quad (1)$$

The Henry's law solubility coefficients calculated from the slopes are listed in Table I. The sorption equilibria for carbon dioxide in the same film at four levels of temperature between 30 and 45°C had been measured in our previous

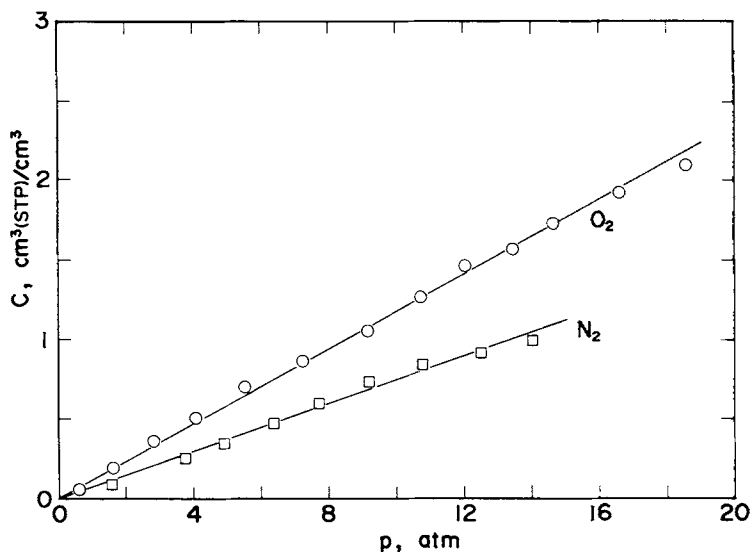


Fig. 1. Sorption equilibria for oxygen and nitrogen in homogeneous dense PSF (Trayslon-PS) at 40°C.

work.³ The isotherm at each temperature could be described well in terms of the dual-model sorption mode, viz.,

$$C = k_D p + \frac{C'_H b p}{1 + b p} \quad (2)$$

The values of the dual-mode sorption parameters at 40°C are also listed in Table I.

Permeabilities by Oxygen and Nitrogen in Homogeneous PSF Membranes

The experimental results on mean permeability coefficients for oxygen and nitrogen through two kinds of homogeneous PSF membranes are shown as a function of upstream pressure in Figure 2. The PSF membranes employed are commercially available: one called Trayslon-PS and a one prepared by casting method.¹ The permeabilities for both gases are shown to be independent of

TABLE I
Sorption Parameters for O₂, N₂, and CO₂ in PSF Film (Trayslon-PS) at 40°C

Gas	k_D	b	C'_H
	[cm ³ (STP)/(cm ³ atm)]	(atm ⁻¹)	[cm ³ (STP)/cm ³]
O ₂	0.118	—	—
N ₂	0.075	—	—
CO ₂	0.547	0.168	18.3

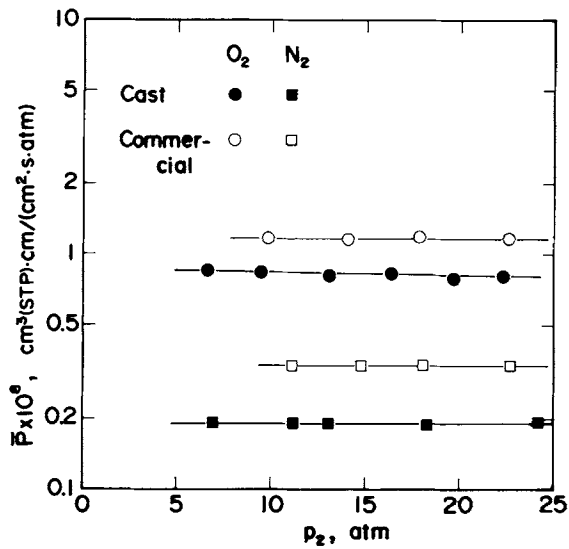


Fig. 2. Pressure dependence of permeabilities for oxygen and nitrogen in homogeneous dense PSF membranes.

upstream pressure. This experimental evidence along with Henry-type sorption isotherms suggests that the permeability should be expressed as

$$\bar{P} = k_D D_D \quad (3)$$

The ratio of the permeability for O₂ to that for N₂ is estimated to be 3.50 in a commercially available membrane and 4.40 in a cast one. Such a ratio, which is also called ideal separation factor, is regarded as an upper bound of separation factor in case of the asymmetric membrane.

Permeabilities for Oxygen, Nitrogen, and Carbon Dioxide in Asymmetric PSF Membranes With Deposited Plasma-Polymerized Thin Layer

In order to understand the composition of the plasma-polymerized thin layer, first, ESCA studies were performed on the top surface deposited under different polymerization conditions (Shimazu, ESCA-750). A typical example of the ESCA spectra is shown in Figure 3. The plasma-polymerized thin layer of this specimen was prepared by deposition for an exposure time of 20 min. The relative atomic concentrations calculated from peak areas depicted in Figure 3 were: $F_{1s}/C_{1s} = (\text{peak area of } F_{1s})/(\text{peak area of } C_{1s}) = 1.16$. This approximately gives the ratio of F to C in the plasma polymer.

The permeation rate coefficients of O₂, N₂ and CO₂ in an asymmetric PSF membrane with deposited plasma-polymerized thin layer (sample no. 10) are shown as a function of upstream pressure in Figure 4. Here, the permeation rate coefficient defined as $J_s/(p_2 - p_1)$ is related to the mean permeability coefficient \bar{P} as follows

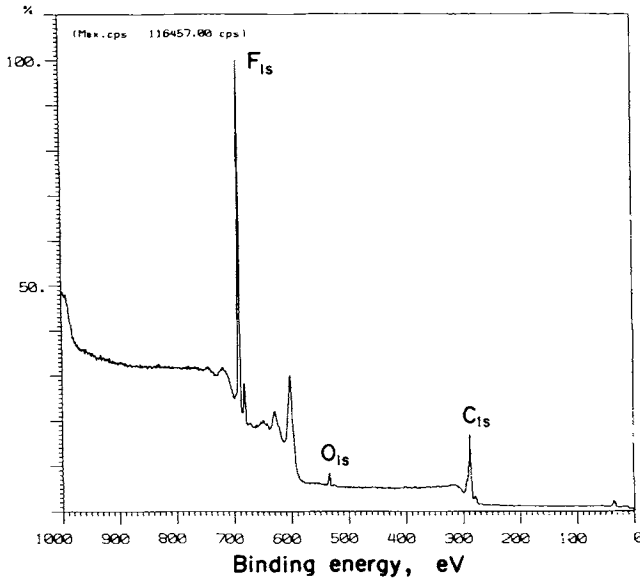


Fig. 3. ESCA spectrum of a plasma-polymerized thin layer.

$$J_s / (p_2 - p_1) = \bar{P} / \delta \tag{4}$$

The coefficients of O₂ and N₂ are found to increase slightly with increasing pressure, whereas the permeabilities for the same gases through homogeneous dense membranes are independent of pressure as shown in Figure 2. The ratio

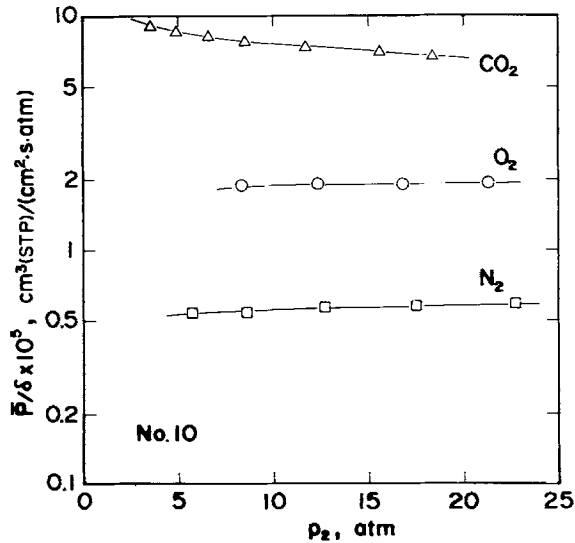


Fig. 4. Pressure dependence of permeation rate coefficients for oxygen, nitrogen, and carbon dioxide through an asymmetric PSF membrane with deposited plasma-polymerized thin layer. (no. 10).

of the coefficients of O_2 and N_2 is calculated to be 3.42, being less than the ideal separation factor for a homogeneous membrane (4.40). In the membrane of no. 10, thus, ultrafine pores passing through it (i.e., pinholes), seem to remain unfilled even after a plasma-polymerized thin layer has been deposited on the top of the base membrane. If the diffusion in the ultrafine pores is controlled mainly by Knudsen diffusion, the permeation rate coefficient increases with an increase in pressure. On the contrary, the permeation rate coefficient of CO_2 decreased with pressure. This is still a similar pattern to the permeation of the same gas through glassy polymer membranes, though the membrane used involves the ultrafine pores. Then, it was checked whether the dual-mode mobility model driven by gradients of chemical potential where the permeation rate coefficient can be described as

$$\frac{\bar{P}}{\delta} = \frac{k_D D_D}{\delta} + \frac{C'_H D_H}{\delta(p_2 - p_1)} \ln \frac{1 + bp_2}{1 + bp_1} \quad (5)$$

was applicable or not.

The permeation rate coefficient data for membranes of no. 10 as well as no. 35 were plotted on the basis of eq. (5) in Figure 5. The plots give essentially straight lines. From the slope and intercept of each line, the diffusion coefficients divided by the thickness of the functional skin layer, D_D/δ and D_H/δ can be determined. The values of the diffusivity ratio, D_H/D_D , are calculated as 0.35 and 0.11 for sample nos. 11 and 35, respectively. As the skin layer becomes thin, the diffusivity ratio decreases.

Figure 6 shows the dependence of the ideal separation factor on the permeation rate coefficient of O_2

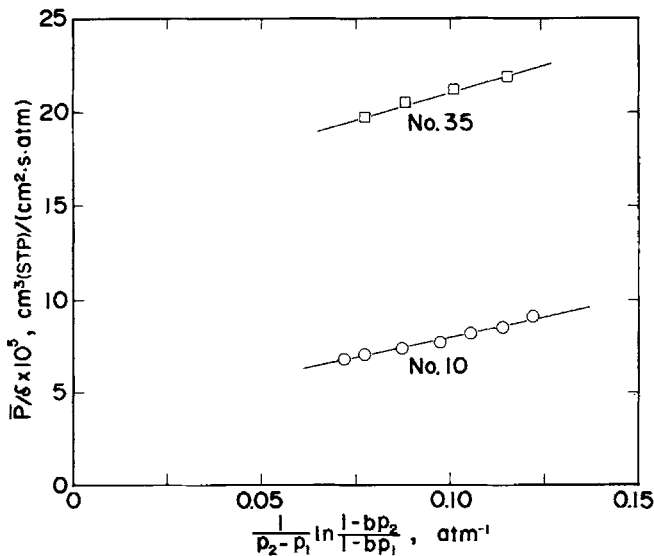


Fig. 5. Test of dual-mode mobility model driven by gradients of chemical potential for pressure dependence of permeation rate coefficients for carbon dioxide through asymmetric PSF membranes with deposited plasma-polymerized thin layer.

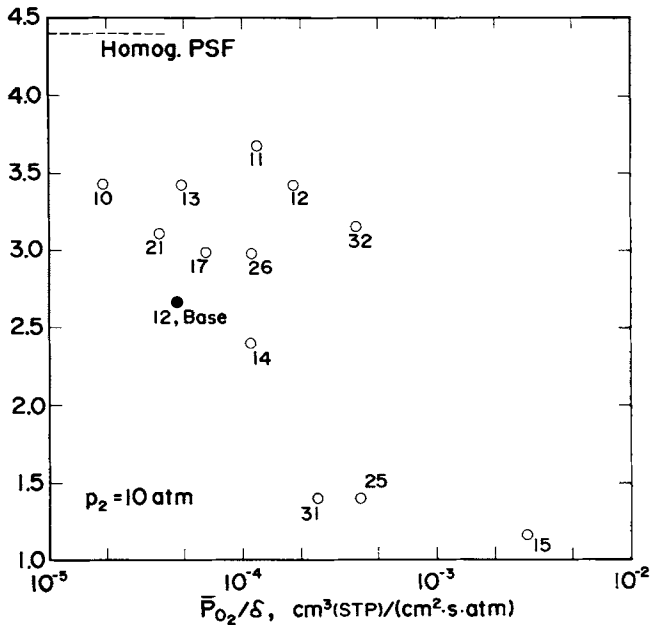


Fig. 6. Relation of ideal separation factor for oxygen relative to nitrogen to permeation rate coefficient for oxygen in asymmetric PSF membranes with deposited plasma-polymerized thin layer.

$$J_{O_2}/(p_2 - p_1) = \bar{P}_{O_2}/\delta \tag{6}$$

in a variety of asymmetric PSF membranes with deposited plasma-polymerized thin layer. Here, the separation factors plotted have been estimated at the upstream pressure of 10 atm, because the permeation rate coefficients of both O₂ and N₂ depend upon the upstream pressure. When the permeation rate coefficient of O₂ is smaller than 10⁻⁴ cm³ (STP)/(cm² s atm), the separation factor always ranges from 3.0 to 3.5. On the other hand, when the coefficient is larger than 10⁻⁴ cm³ (STP)/(cm² s atm), the separation factor does not seem to exhibit a reproducible value. In some membranes, it decreases up to less than 1.5. The pressure dependencies of the permeation rate coefficients of O₂ and N₂ through the former membranes are shown in Figure 7. The coefficients of both gases are found to be only slightly dependent on the applied pressure except for those of N₂ in no. 17. Figure 8 shows the similar plots for the latter membranes. In the membranes of nos. 25 and 31 exhibiting small separation factors, larger pressure dependencies of the permeation rate coefficients for both gases are observed, whereas in the membranes of nos. 12 and 32 possessing the separation factor of as large as 3.0–3.5, the permeation rate coefficients only slightly depend on the applied pressure. Thus, if ultrafine pores passing through the membrane can be filled up by plasma-polymerized thin layer, the separation factor can be increased with the permeation rate coefficient kept large. This condition could be met when the vaporization time of the cast solution during the preparation of a base asymmetric membrane ranged from 10 to 120 s and the plasma polymerization time ranged from 15 to 30 min.

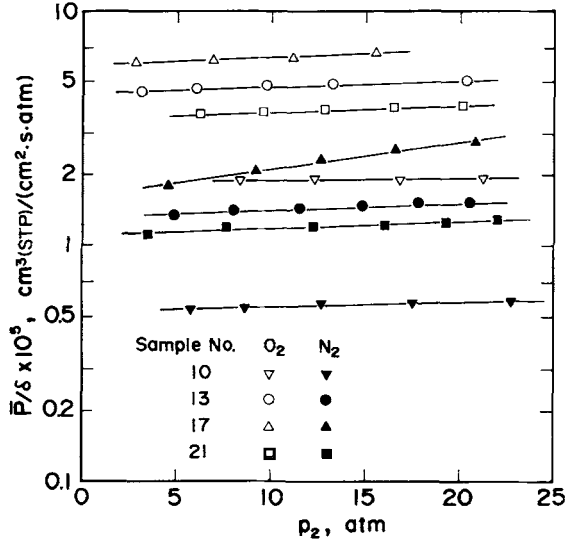


Fig. 7. Pressure dependence of permeation rate coefficients for oxygen and nitrogen through membrane samples, nos. 10, 13, 17, and 21.

However, Figure 6 also shows that in the membrane of no. 12 both the separation factor and the permeation rate coefficient are increased by deposition of plasma-polymerized thin layer. This experimental evidence suggests that the permeation properties of the base membranes with and without plasma modification are different from each other even when they are provided from the same batch of cast film. This is, the pinholes of the asymmetric PSF mem-

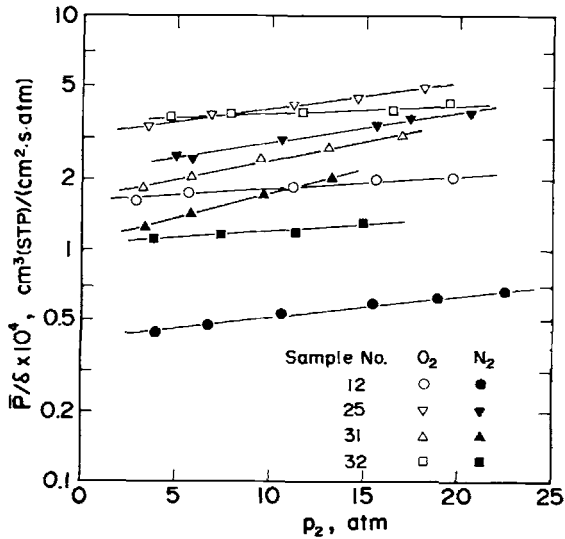


Fig. 8. Pressure dependence of permeation rate coefficients for oxygen and nitrogen through membrane samples, nos. 12, 25, 31, and 32.

brane are randomly formed in the casting process and are not apt to be uniformly distributed. Accordingly, even in the membranes provided from the same batch of cast film, the same permeation rates are not always achieved.

Figure 9 shows the pressure dependences of the permeation rate coefficients of O₂ and N₂ in the membrane of no. 36 with and without the plasma modification. It is apparent that the permeation rates of both gases are decreased and the separation factor is increased from 4.0 to 5.5 by the plasma modification. Besides, the separation factor of the membrane with deposited thin layer is higher than that for the homogeneous dense one (4.4). It seems to be of interest to evaluate the magnitude of the separation factor of the plasma polymerized thin layer by use of the experimental results depicted in this figure.

The permeation rate through the membrane with deposited plasma-polymerized thin layer can be described as

$$J_s = \frac{\Delta p}{\delta/\bar{P}} = \frac{\Delta p}{\delta_1/\bar{P}_1 + \delta_2/\bar{P}_2} \tag{7}$$

where δ_1 and δ_2 refer to the thicknesses of the plasma-polymerized thin layer and of the skin layer of the asymmetric membrane, respectively, and \bar{P}_1 and \bar{P}_2 to the inherent permeabilities of both the layers, respectively. δ denotes the total thickness of the functional layer ($= \delta_1 + \delta_2$). \bar{P} is the overall permeability of the membrane. From the above equation, the separation factor of the plasma-polymerized thin layer, $(\bar{P}_{O_2}/\bar{P}_{N_2})_2$, can be derived as 6.49. In this membrane, not only the material of the base asymmetric membrane but also that of the plasma polymer may contribute to the separation property.

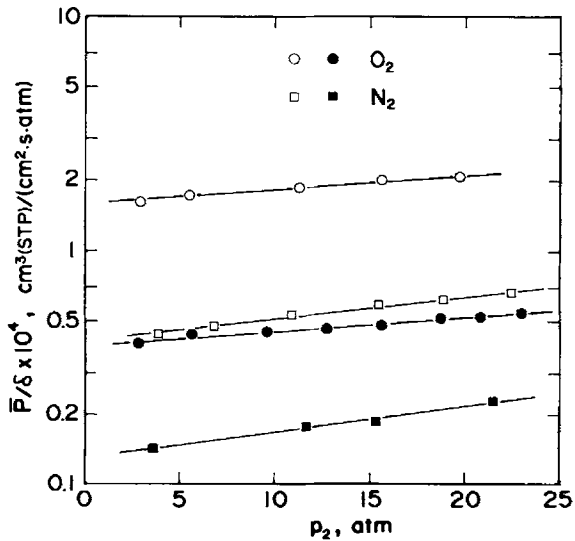


Fig. 9. Pressure dependence of permeation rate coefficients for oxygen and nitrogen through asymmetric PSF membranes, no. 36, with (open keys) and without (full keys) deposited plasma-polymerized thin layer.

CONCLUSION

If ultrafine pores passing through the asymmetric PSF membrane can be plugged by a plasma-polymerized thin layer, then the separation factor of oxygen relative to nitrogen can be increased with the permeation rate coefficient of oxygen still kept large. In such composite membranes, the material (PSF) of the base asymmetric membrane determines the separation properties.

APPENDIX: NOMENCLATURE

b	Langmuir affinity constant (atm^{-1})
C	total sorbed concentration [cm^3 (STP)/ cm^3]
C_D	concentration of Henry's law population [cm^3 (STP)/ cm^3]
C_H	Langmuir capacity constant [cm^3 (STP)/ cm^3]
D_D	diffusion coefficient of Henry's law population (cm^2/s)
D_H	diffusion coefficient of Langmuir population (cm^2/s)
J_s	steady-state permeation flux [cm^3 (STP)/($\text{cm}^2 \text{s}$)]
k_D	Henry's law solubility coefficient [cm^3 (STP)/($\text{cm}^3 \text{atm}$)]
\bar{P}	mean permeability coefficient [cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{s atm})$]
p	pressure of penetrant gas (atm)
\bar{P}_1	mean permeability coefficient in plasma-polymerized thin layer [cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{s atm})$]
\bar{P}_2	mean permeability coefficient in skin layer of asymmetric membrane [cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{s atm})$]
p_1	downstream pressure of penetrant (atm)
p_2	upstream pressure of penetrant
S	ideal separation factor of oxygen relative to nitrogen, $\bar{P}_{\text{O}_2}/\bar{P}_{\text{N}_2}$

Greek Symbols

Δp	$p_2 - p_1$, pressure difference across the membrane (atm)
δ	thickness of functional layer (cm)
δ_1	thickness of plasma-polymerized thin layer (cm)
δ_2	thickness of skin layer of asymmetric membrane (cm)

References

1. E. Sada, H. Kumazawa, and P. Xu, *J. Polym. Sci., Polym. Phys.*, **27**, 919 (1989).
2. E. Sada, H. Kumazawa, H. Yakushiji, Y. Bamba, K. Sakata, and S.-T. Wang, *Ind. Eng. Chem. Res.*, **26**, 433 (1987).
3. E. Sada, H. Kumazawa, P. Xu, and M. Nishigaki, *J. Membrane Sci.*, **37**, 165 (1988).

Received November 21, 1989

Accepted February 25, 1990