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THE PERMEATION RESISTANCE OF INTERFACE AND THE DIRECTIONAL DEPENDENCE OF PERMEATION IN PLASMA-GRAFTED COMPOSITE MEMBRANES

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Abstract—Composite membranes were prepared by grafting plasma-polymerized films onto the surface of nonporous poly (dimethylsiloxane) films. Gas permeabilities of the composite membranes were measured at 35℃, 1 atm for N_2, O_2, CO_2 and CH_4. The permeation properties of the composite membrane was analyzed using the series resistance model. There was a great interfacial resistance to CH_4 permeation through the composite membrane. The interfacial resistance was negligible for the other gases. The interfacial resistance seems to be a result of an interfacial layer caused by the interaction between the bulk two layers. For CH_4 gas, the permeation rate through the composite membrane was affected by the direction of flow. The directional dependence was negligible for the other gases.

Key words: Permeation Resistances, Composite Membranes, Plasma Film

INTRODUCTION

Application of plasma polymerization techniques to fabricate composite membranes has great advantages. Plasma films prepared by this method are ultra-thin, highly crosslinked, and adhere well to a variety of substrates. The thinness of the plasma film increases permeation fluxes and the crosslinked structure enhances permselectivities of the membrane [Yasude, 1985; Boenig, 1988; Yasuda, 1981].

A plasma treatment of polymers changes their surface properties such as wettability, contact angle and surface energy without affecting the bulk properties of the polymer [Youxian et al., 1991; Vargo et al., 1991]. Similarly, in the initial stage of plasma polymerization, the surface of a polymer substrate becomes activated and modified by the plasma, and an uniform plasma coating layer is produced as plasma polymerization proceeds.

Most permeation studies of plasma polymers have used porous polymer substrates, such as Celgard and Millipore, to support the plasma polymer films. In our previous study [Oh et al., 1995], permselective plasma films were produced by coating Celgard with plasma polymers of fluorine-rich, aromatic fluorocarbon compounds such as hexafluorobenzene (HFB) and pentafluoropyridine (PFP). The porous substrates usually do not affect the gas permeation properties of the composite membrane. Dense substrates, however, contribute to the overall permeabilities of the composite membranes and the interface between the dense substrate and the plasma polymer may also affect the permeation properties of the membrane.

In this study, composite membranes were prepared by grafting plasma polymers onto dense poly(dimethylsiloxane) [PDMS] films. We investigated the effect of plasma coating thickness on the permeability of composite membranes and the directional dependence of permeation through the composite membrane. The results were analyzed using the series resistance model. Deviations from the model fits are the measure of the permeation resistance of the interface between the bulk two layers.

EXPERIMENTAL

1. Materials

Non-porous PDMS was used as a substrate for the preparation of composite membranes. PDMS sheets with a nominal thickness of 0.01″ were supplied from Dow Corning Corp. [trade name : SILASTIC®]. The PDMS sheet was cleaned with mild soap and hot water, then rinsed with hot water followed by distilled water, and dried in the desiccator under vacuum for 24 hours before use.

The monomers used for plasma polymerization were pentafluoropyridine [PFP, 99+%] and pentafluorotoluene [PFT, 99%]. Both were purchased from Aldrich and were used as received.

2. Plasma Polymerization

Plasma polymerization was conducted in a microwave (2.45 GHz) powered plasma reactor. The reaction tube (34 cm i.d. and 40 cm long) is made of Pyrex glass, which is sealed at one end. The open end of the tube is fitted with a monomer inlet, vacuum pump and capacitance manometer. The schematic diagram is shown in Fig. 1. The experimental procedures of the plasma polymerization were the same as reported previously [Oh et al., 1995]. The reaction system was evacuated to 10^{-2} torr using a two stage rotary pump, and the reaction tube was exposed to Ar plasma for 10 minutes to eliminate water adsorbed on the surface of the tube. Then, a PDMS substrate (2×2 cm) was placed vertically in the reactor 2 to 3 cm outside from the glow region. The system was again evacuated to 10^{-2} torr, and equal molar ratio of monomer vapor and Ar were introduced into the reactor. Ar was used to sustain the plasma in the reactor. After the pressure and flow rate were determined and maintained at steady state, the microwave power was turned on and the plasma polym-

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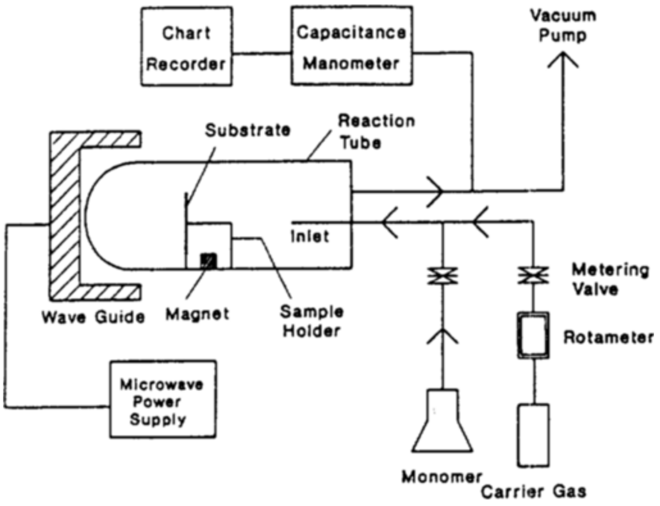

Fig. 1. Schematic diagram of the plasma polymerization system.

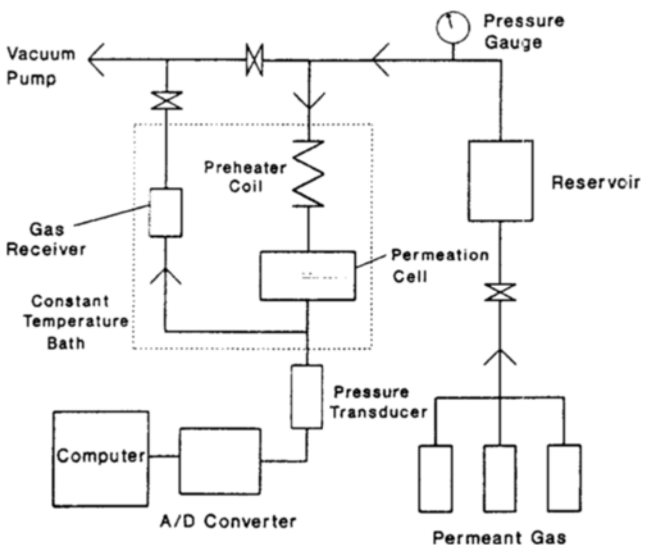

Fig. 2. Schematic diagram of the permeation system.

erization was conducted. The ranges of monomer flow rate and power input level were 2 to 3 SCCM and 30 to 50W, respectively.

3. Thickness Measurement

The thickness of the plasma coating layer was determined by depositing plasma polymer films onto glass slides (instead of PDMS) under the same conditions as used to make the permeation samples. The thickness of the film on the glass substrate was measured using a surface profilometer (Dektak IIA).

4. Gas Permeation

Composite membranes prepared by plasma polymerization were served for the measurement of gas permeabilities. A schematic diagram of the permeation system is shown in Fig. 2. The experimental procedures were the same as described previously [Oh et al., 1995]. The permeation cell divides the system into two parts by the charged membrane; the upstream high pressure side and downstream low pressure (vacuum) side. Once a sample is loaded into the permeation cell, the cell is placed into the constant temperature bath at 35℃ and both sides of the cell are evacuated below 0.1 torr using a two stage rotary pump for at least 2 hours; typically overnight. At the beginning of the measurement the upstream side of the system was filled with the penetrant gas and maintained at a level of 12 to 15 psia. The downstream side was isolated from the pump and the increase in pressure of the downstream side was monitored by the pressure transducer (MKS, Model 128A, 0-10 torr). The pressure buildup of the downstream side was always kept below 2 torr during the permeation measurement so that the pressure difference across the membrane be assumed equal to the upstream pressure. Data were collected using a personal computer via an analog/digital interface (Omega, Model WB-31) connected to the pressure transducer. The permeation rate was determined from the slope of the linear portion of the downstream pressure increase with time.

5. Estimation of Permeabilities

The overall permeability coefficient of the composite membrane, P_0 is defined by Eq. (1).

$$P_0 = \frac{QL_0}{\Delta p_0 A} \qquad (1)$$

In Eq. (1), Q is the permeation rate which is determined in the permeation measurement. L_0 and A are the overall thickness and effective permeation area of the membrane, respectively. Δp_0 denotes the total pressure drop across the membrane.

For an ideal composite membrane of two layers, 1 and 2, the series resistance model [Mohr and Paul, 1991] is used to describe the gas transport properties of the composite membrane as in Eq. (2).

$$\frac{L_0}{P_0} = \frac{L_1}{P_1} + \frac{L_2}{P_2} \qquad (2)$$

Where, $L_0 = L_1 + L_2$. In Eq. (2), P_1 and P_2 are the intrinsic permeability coefficients of layers 1 and 2, and L_1 and L_2 are their respective thicknesses. Each term in Eq. (2) represents the permeation resistance.

In the series resistance model, it is assumed that there is no permeation resistance of the interface between the two bulk layers of the composite membrane. If there is some resistance between the two layers, Eq. (2) can not be used directly. In order to consider the resistance, a lumped parameter R_{IF} can be introduced in Eq. (2), which gives Eq. (3).

$$\frac{L_0}{P_0} = \frac{L_1}{P_1} + \frac{L_2}{P_2} + R_{IF} \qquad (3)$$

We call R_{IF} the "interfacial resistance". If layers 1 and 2 denotes the PDMS layer and plasma coating layer, respectively, then a plot of (L_0/P_0) versus L_2 yields $1/P_2$ as the slope, and $(L_1/P_1 + R_{IF})$ as the intercept. Once P_0 and P_1 are determined, P_2 and R_{IF} can be estimated.

RESULTS

Fig. 3 and Fig. 4 are plots of (L_0/P_0) versus L_2 for the gases N_2, O_2, CO_2 and CH_4 in the composite membranes with PFP and PFT plasma coating layers, respectively. The thickness of PDMS substrates used was 0.292 mm (± 1%). The coating layer thickness was varied between 0.1 and 1 μm. Above a coating thickness of 1 μm, experimental data were not reproducible. This seems to be related to the cracking of the film with thicker plasma layers. The (L_0/P_0) data at zero coating thickness were those for the untreated PDMS membranes. Straight lines in the figures were obtained by least-square fits to the data points for each gas. In both

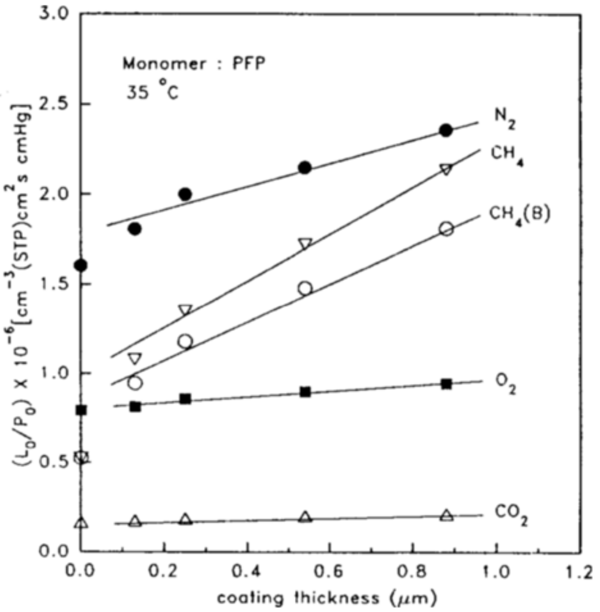

Fig. 3. Relationship between L_o/P_o and plasma coating layer thickness for composite membranes with PFP plasma coating layers.

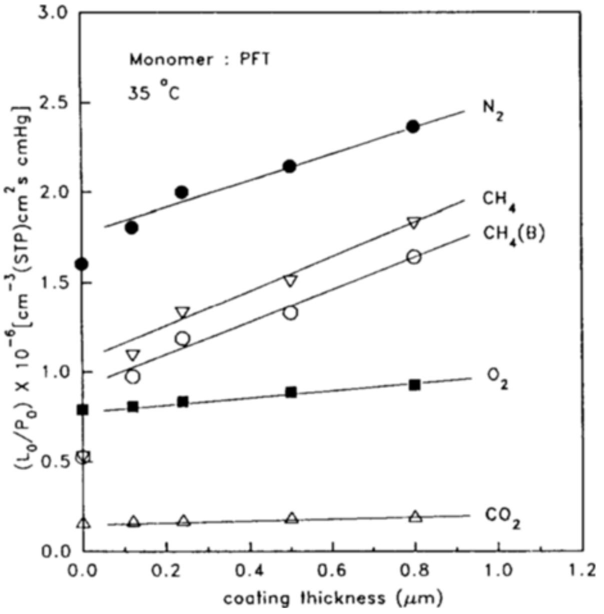

Fig. 4. Relationship between L_o/P_o and plasma coating layer thickness for composite membranes with PFT plasma coating layers.

figures two sets of data are shown for CH_4 : One for the permeation when the coating layer side is exposed to the high pressure, labeled CH_4, the other for the permeation when the PDMS side is exposed to the high pressure (i.e., the pressure gradient across the membrane is reversed), labeled CH_4(B). For the other gases, the changes in the permeabilities with the direction of flow were negligible.

In Fig. 3 and 4, extrapolation of the lines to $L_2=0$ for O_2 and CO_2 fits well with the (L_0/P_0) values of untreated PDMS. There is a small deviation for N_2 and a larger deviation for CH_4 in both composite membranes with PFP and PFT plasma coating layers.

Table 1. Gas permeabilities of the PDMS and plasma coating layer

Gas	$P \times 10^{10}$			P_1/P_2[b]	
	PDMS	Coating layer			
		PFP	PFT	PFP	PFT
CH_4	556	0.73	0.97	762	573
CH_4(B)[a]	556	0.90	1.05	618	530
N_2	182	1.46	1.20	125	152
O_2	369	5.99	4.91	62	75
CO_2	1763	19.92	21.70	89	81

·P has a unit of [cm^3(STP)cm/cm^2/sec/cmHg].

[a] CH_4(B) refers to the permeation when the PDMS side is exposed to the high pressure, and all the other cases refer to the permeation when the plasma coating layer side is exposed to the high pressure.

[b] Subscript 1 and 2 refer to the PDMS and plasma coating layer, respectively.

·PFP and PFP were the monomers used for plasma polymerization.

Table 2. Permeation resistances of each layer for composite membranes

Gas	Permeation resistance, $R_{i/F}$ [cm^{-3}(STP)cm^2 sec cmHg]$\times 10^{-5}$						
	PDMS	Coating layer		Interface		Total	
		PFP	PFT	PFP	PFT	PFP	PFT
CH_4	5.25	11.97	5.47	4.75	4.40	21.97	15.13
CH_4(B)	5.25	9.76	4.52	3.10	3.59	18.10	13.36
N_2	16.1	6.05	4.19	1.60	1.27	23.8	21.6
O_2	7.92	1.47	1.04	0.085	0.045	9.47	9.00
CO_2	1.66	0.44	0.23	0.03	0.013	2.14	1.90

·Thickness of PDMS : 0.0292 cm

·Thickness of PFP plasma coating layer : 0.88 μm

·Thickness of PFT plasma coating layer : 0.80 μm

Table 1 presents the permeability data of the PDMS and those of the plasma coating layers which are deduced from the slopes of the lines in Fig. 3 and 4. As shown in Table 1, the plasma coating layer showed 1 to 2 orders of magnitude lower permeability coefficients for the same gases than those of untreated PDMS. This result is reasonable since the plasma coating layer would have a dense, crosslinked structure.

Table 2 lists the permeation resistance values for the PDMS and plasma coating layer, the interfacial resistance and the total resistance of the composite membrane.

DISCUSSIONS

An interfacial resistance was found for some gases as shown in Table 2. The interfacial resistance was great for CH_4 and the resistances were negligible for O_2 and CO_2. The interfacial resistance appears to be a result of the formation of a third layer between the bulk PDMS and plasma coating layer in the composite membrane. Xu et. al. [Lin at al., 1993] have shown that CF_4 plasma treatment of poly (trimethylsilylpropyne) surface caused substantial changes in gas permeabilities of the polymer. Similarly, in the initial stage of the plasma polymerization the PDMS surface is exposed to the plasma and becomes activated and modified by the plasma. During the modification the PDMS surface would be incorporated with functional groups in the plasma and crosslinked because of its exposure to the plasma.

Negligible interfacial resistance for O_2 and CO_2 results from relatively large resistances of the PDMS layer as shown in Table

2. For the two gases the resistances of PDMS represent 80 to 90% of the total resistance of the composite membrane. If much thinner PDMS substrate is used, the resistances of the PDMS layer would decrease and the influence of the interfacial region be more apparent.

It is not clear why there is such a great interfacial resistance to CH_4 permeation in the composite membranes. The kinetic molecular diameter of gases [Breck, 1974] increases in the order of $d(CH_4)>d(N_2)>d(O_2)>d(CO_2)$. In Table 2, the permeation resistance of the plasma coating layer and interfacial region both increased as the diameter of gas molecules increased. Thus, it seems that the gas transport across the interface is primarily controlled by the size of the penetrant molecules, which is similar to the behavior of the plasma polymers [Oh et al., 1995; Oh, 1994].

The permeation resistance is inversely proportional to the permeability coefficient. In Table 1, the permeability coefficient of the plasma coating layer is much smaller for CH_4 than that of PDMS; the ratio of permeabilities for CH_4 is an order of magnitude greater compared to the other gases. It is very likely that the permeability of the interfacial region would be of similar magnitude to the plasma coating layer, since both layers show similar gas permeation behavior and have crosslinked structures. The smaller CH_4 permeability of the interfacial region would be partially responsible for the large interfacial resistance.

The permeability coefficient of a composite membrane with a mixture of polymer A and polymer B can be approximately represented as [Petropoulis, 1974]

$$P_o = v_A P_A + (1 - v_A) P_B \tag{4}$$

where, v_A is the volume fraction of polymer A. Eq. (4) predicts that the permeability of the composite ranges between the permeabilities of polymer A and B depending on the composition of polymers. The interface of the PDMS/plasma composite membrane is considered as a mixture of the materials of the two bulk layers. The permeability of the interfacial region may not be constant but show continuous, gradual changes with position since the composition of the composite changes with the position in the interfacial region. It is likely that broader region at the interface of the composite membrane would give an interfacial resistance to CH_4 permeation since the difference between CH_4 permeabilities of the PDMS and coating layer is greater compared to the other gases.

The permeabilities of the composite membrane was measured in both forward (plasma coating layer exposed to the high pressure) and backward (PDMS layer exposed to the high pressure) directions. As shown in Fig. 3 and 4, there was a significant directional dependence of permeation for CH_4. The directional dependence was negligible for the other gases. For the both composite membranes, the permeation rate of CH_4 in backward direction was 12 to 16% greater than those in forward direction. Schreiber et. al. [Urrutia et al., 1988] investigated the flow reversal effect for composite membranes composed of PDMS and a plasma coating layer from hexamethyldisiloxane and methylmethacrylate comonomers. They found that the permeabilities of O_2 and CO_2 increased 49% and 68%, respectively, when the PDMS was exposed to the high pressure compared to when the flow was reversed. In our study, the directional dependence was negligible for the two gases.

The flow reversal effect on the permeation of vapors was studied for composite membranes composed of two layers of traditional polymer films by several investigators [Petropulis, 1974; Urrutia et al., 1988; Stern et al., 1987]. Rogers [Rogers et al., 1957] has demonstrated that the pressure dependent permeability coefficient of at least one layer of the composite membrane is responsible for the directional dependence of permeation.

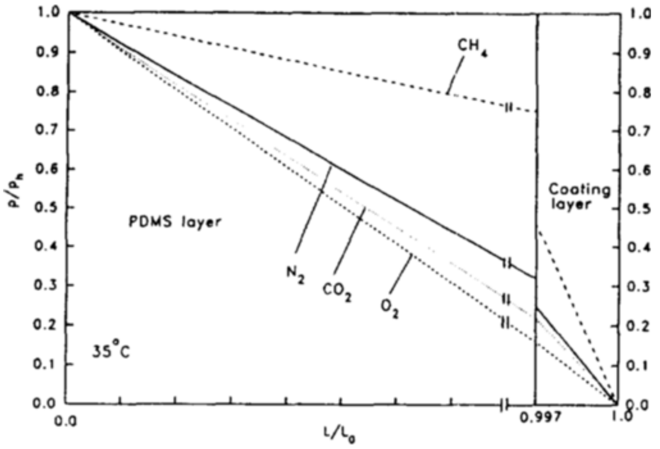

Fig. 5. Equilibrium pressure profile inside the composite membrane with a PFP plasma coating layer.

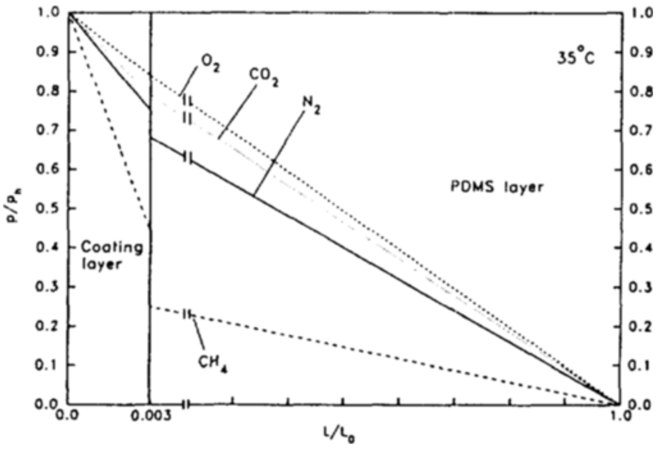

Fig. 6. Equilibrium pressure profile inside the composite membrane with a PFP plasma coating layer.

Gas permeabilities of PDMS are regarded as independent of pressure, since PDMS is a rubbery polymer. This has been shown by Stern et al. [Stern et al., 1987]. In our preliminary experiments, we measured the permeability of plasma films deposited on Celgard upto the maximum upstream pressure of 3 atm, and the pressure dependence of permeability of the plasma polymers was not observed. Then, the directional dependence may result from the pressure dependent permeability of the interfacial region.

Fig. 5 and 6 shows the pressure profile as a function of position in a PDMS (0.292 mm)/PFP (0.88 μm thick) composite membrane. Fig. 5 and 6 refer to the permeation in backward and forward direction, respectively. The thickness of the interfacial region was assumed zero in the figures. Dimensionless pressure in the ordinate of the figures are based on the upstream pressure (p_h). The advantage of plotting the pressure, instead of the concentration, is that for an ideal composite membrane (with no interfacial resistance) there is no discontinuity at the interface due to the difference in solubilities. Discontinuity at the interface, if any, indicate the contribution of interfacial resistance to permeation. In both Fig. 5 and 6, there is no discontinuity across the interface for O_2 and CO_2, a small discontinuity for N_2, and a relatively large discontinuity for CH_4.

It is noted in Fig. 5 and 6 that for CH_4 permeation the average pressure (p_{av}/p_h) at the interface is about 0.35 in the forward direction and about 0.6 in the reverse direction. It is impossible that such a small pressure difference causes pressure dependence of permeabilities of the interfacial layer. The flow reversal effect can not be explained with a pressure dependent permeability and requires more careful consideration.

CONCLUSIONS

Composite membranes were prepared by coating the surface of PDMS films with PFT and PFP plasma polymers. The gas permeation properties of the composite membrane are adequately described by the series resistance model for O_2, CO_2 and N_2. For CH_4, significant deviations from the series resistance model were observed and were attributed to an interfacial resistance. The interfacial resistance is believed to be a result of a interfacial region caused by the interaction between the PDMS and plasma coating layer. The great interfacial resistance for CH_4 may indicate that the interfacial layer is size selective in gas permeation since CH_4 has the largest molecular diameter of the penetrant gases used.

The permeation of CH_4 through the composite membranes was also found to be dependent of the direction of flow; The permeation rate of CH_4 was 12 to 16% greater when the PDMS was exposed to the high pressure side than when the plasma coating layer was exposed to the high pressure side. The directional dependence of permeation can not be easily explained with pressure dependent permeabilities.

ACKNOWLEDGEMENT

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NOMENCLATURE

A : effective permeation area [m^2]
L : membrane thickness [m]
P : permeability coefficient [cm^3(STP)cm/cm^2/sec/cmHg]
Q : volumetric flow rate of the penetrant passing through the membrane [cm^3(STP)/sec]
R_{IF} : interfacial resistance to gas permeation [cm^{-3}(STP)cm^2·sec·cmHg]
d : molecular diameter of permeant gases [A]
p : pressure of the penetrant in the membrane [cmHg]

Greek Letters

Δ : difference [-]
ν : volume fraction of the polymer [-]

Subscripts

h : upstream, high pressure side of the membrane
o : overall composite membrane
1 : layer 1 (PDMS layer) in the composite membrane
2 : layer 2 (plasma coating layer) in the composite membrane

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