

Gas Separation through Conductive Polymer Membranes. 2. Polyaniline Membranes with High Oxygen Selectivity

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Gas permeation experiments of O₂ and N₂ were performed with conducting polyaniline (PANi) composite membranes prepared by using a porous nylon membrane as a support. PANi composite membranes were easily obtained by a novel solvent welding process. Doping, dedoping, and redoping kinetics of PANi composite membranes were studied by calculating the [Cl]/[N] content using elemental analysis. After doping and dedoping processes, the permeability of a dedoped PANi membrane decreased while selectivity slightly increased, probably because of the changes in morphology of PANi. *d* spacing of the PANi film decreased from 4.89 to 3.67 Å after doping, dedoping, and redoping. As redoping continued, the degree of doping increased while the *d* spacing decreased, resulting in a dramatic increase in selectivity of a PANi membrane. The highest O₂/N₂ selectivity and permeability we obtained from PANi redoped for 2 h were 28 and 0.13 barrer, respectively. O₂/N₂ permeation experiments with different upstream pressure and temperature were carried out to study the permeation behavior of a PANi membrane.

Introduction

Molecular sieves are the materials that can separate molecules such as gases in an atomistic scale. Natural zeolite molecular sieves are well-known for catalysts and membranes. Carbon molecular sieves^{1,2} (CMS) are known to be made of amorphous carbons compared with carbons, diamonds, or graphite prepared by pyrolyzing polyimides that have a *d* spacing of around 3.65 Å, the value between the kinetic diameters of oxygen and nitrogen. Thus, the separation efficiencies of CMS membranes are remarkably improved, showing a selectivity toward oxygen, $\alpha(\text{O}_2/\text{N}_2)$, of ca. 11 and a permeability, $P(\text{O}_2)$, of 34.8 barrer.³ In contrast to inorganic or carbon molecular sieves having a controlled molecular size, organic polymeric materials are hardly known to be a molecular sieve. If one can prepare an organic molecular sieve (OMS) with high selectivity,⁴ then it has vast advantages over zeolite or carbon molecular sieves because of its easy processibility, thin film formability, and many other reasons. Among the possible organic materials for OMS, polyaniline doped with acidic dopants is a possibility because of a much smaller *d* spacing of 3.61 Å.⁵

After the report of Kaner et al.⁶ regarding the high oxygen selective polyaniline membranes, many researchers have attempted to reproduce an oxygen-selective PANi membrane and at the same time to acquire the high permeability. They reported that PANi, doped, undoped, and redoped with HCl, exhibited selectivity toward oxygen over nitrogen close to 30, which was a remarkable value known so far. The highest oxygen selectivity was reported to be about 11 for carbon

molecular sieve membranes pyrolyzed from polyimide.² However, Martin⁷ reported a PANi membrane showing a very low permeability value of 10^{-12} cm³(STP)·cm/cm²·s·cmHg close to the value of semicrystalline poly(ethylene terephthalate) (PET) and cellulose.⁸ They also reported that they obtained an oxygen selectivity of only 15 and had never obtained the $\alpha(\text{O}_2/\text{N}_2)$ of 30 as Kaner et al.⁹ originally reported. Since then, there have been a number of studies to reproduce the $\alpha(\text{O}_2/\text{N}_2)$ value of 30 as well as to improve the oxygen permeabilities.

Rebattet et al.¹⁰ reported from the electron spin resonance (ESR) investigations that polaron–oxygen interaction was the dominating mechanism for the oxygen permeability of a PANi membrane redoped with HCl using ESR. Later, they reported that doped, undoped, and redoped PANi gave about a 15% increase of permeability of H₂, CO₂, and O₂ gases and a 45% decrease of permeability of N₂ and CH₄ gases.¹¹ Mattes et al.¹² prepared asymmetric PANi hollow fibers in an attempt to increase the oxygen permeability by decreasing the thickness of the active skin and by fabricating into the hollow fiber membrane form. Martin et al.⁸ also reported that by reducing the thickness of the PANi membrane from 5 to 1 μm the membrane showed a remarkable increase of the total gas permeation rate, while the oxygen selectivity was also lowered because of pinholes formed on thin PANi membranes. Particularly the membrane thickness of around 3 μm was the threshold thickness for the permselectivity. The $\alpha(\text{O}_2/\text{N}_2)$ value was around 10 for a PANi membrane with 3 μm membrane thickness.

Doping with a large dopant such as dodecylbenzene-sulfonic acid failed to improve the membrane performance.¹³ The permeability increases greatly with the sacrifice of oxygen selectivity.¹⁴

The purpose of this study is to prepare the PANi membrane with *d* spacing between the backbone of the molecules which is close to the kinetic diameters of

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oxygen and nitrogen, so that only oxygen can permeate through the membrane while nitrogen cannot go into the PANi membrane.

Experimental Section

Materials. Aniline (Yakuri Pure Chemical) was dried with CaH_2 and distilled at reduced pressure. Ammonium peroxodisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, Junsei Chemical; minimum assay 95.0%) was used without further purification. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (dimethylpropyleneurea (DMPU), Aldrich; minimum assay 98%) and *N*-methylpyrrolidinone (NMP, Tedia Co., minimum assay 99.0%) were used as solvents without purification. A nylon membrane (Gelman Sciences, pore size 0.2 μm) was used as a support. A reagent-grade ammonia solution and hydrochloric acid were used in a doping, dedoping, and redoping procedure.

Polymer Synthesis. PANi was synthesized following the method of MacDiarmid et al.¹⁵ PANi is called leucoemeraldine when it is fully reduced. Fully oxidized PANi is called pernigraniline. When PANi was synthesized by the method of MacDiarmid et al., half-oxidized PANi (emeraldine base) (EB) was obtained. We used EB in our study. Aniline (0.3 mol) was dissolved in 200 mL of a 1 M HCl solution, and ammonium peroxodisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (0.3 mol) was separately dissolved in 200 mL of a 1 M HCl solution. An aniline solution was stirred and cooled in a circulation bath at -5°C , and the oxidant solution was slowly dropped into the aniline solution for 2 h. Then the reaction mixture was kept at cool conditions with stirring for 2 h. PANi hydrochloride salt was filtered from a reaction mixture and washed with distilled water. PANi salt was neutralized in 0.5 M ammonium hydroxide for 1 h to obtain the PANi base. The filtered PANi was washed with distilled water and dried in a vacuum at room temperature for 48 h.

Preparation of Composite Membranes. PANi powder was slowly added to 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) with constant stirring. The solution was filtered through a 0.2 μm syringe filter, cast on the glass plate, and dried in a vacuum oven at 60°C . Before the removal of the PANi film from the glass plate, the nylon membrane was attached to the PANi film, which was previously soaked with a 20 wt % aqueous NMP solution. The nylon-attached PANi film on the glass plate was again dried in a vacuum oven at 60°C to remove water and NMP. Water evaporates faster than NMP because of the lower boiling point. As water evaporates, the concentration of NMP increases. NMP located between the PANi surface and the nylon membrane dissolved the PANi surface. After evaporation of NMP, the nylon membrane was adhered and welded on the PANi film. The PANi composite membrane was peeled off from the glass plate and dried. The thickness of a PANi skin layer is about 5 μm .

Doping Process. Doping was carried out by immersing the PANi composite membrane in a 1 M HCl solution for at least 1 h to obtain emeraldine salt and dried at room temperature for 24 h. Dedoping was carried out with 1 M NH_4OH for at least 2 h to remove the chloride ion from the membrane and also dried at room temperature. A dedoped PANi membrane was mildly redoped by immersing in a 0.02 M HCl solution for a different period to control the degree of doping. Again the redoped membrane was washed with distilled

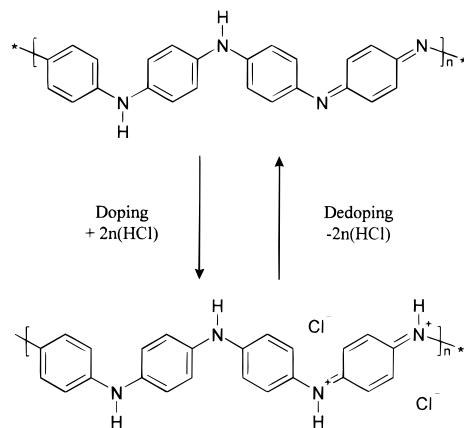


Figure 1. Doping and dedoping scheme of polyaniline.

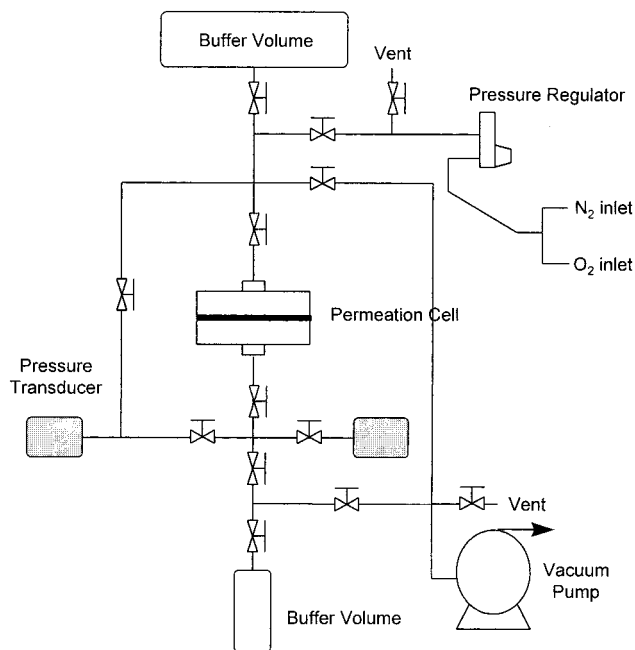


Figure 2. Single-gas membrane permeation apparatus.

water and dried. The scheme for doping and dedoping of PANi is shown in Figure 1.

Characterization. The weight-average molecular weight of PANi was determined by a light scattering method (Brookhaven model BI-9000AT).¹⁶ X-ray diffractometry (Rigaku Denki model RAD-C), FT-IR (Nicolet model Magna 550), and elemental analysis (Carbo Erba model EA 1110) were used to characterize the *d* spacing and degree of doping and redoping. The degree of doping (DD) is defined as the ratio of the molar concentration of chlorine and nitrogen, $[\text{Cl}]/[\text{N}]$. The thickness of a PANi membrane was 5–10 μm measured by a field emission scanning electron microscope (FE-SEM; JEOL model JSF 6340F).

Gas Permeation. The gas permeation measurements were conducted using the single-gas permeation method at a feed pressure of 200–1400 Torr and a feed temperature of 25–75 $^\circ\text{C}$. The single gas permeation apparatus used in this study is shown in Figure 2. Before the gas permeation measurements, both upper and lower sides were evacuated at <5 mTorr. The pressure versus time transient of the lower side equipped with a pressure transducer (MKS's Baratron type 146) was recorded on a personal computer. The slopes of the linear part of the transient pressure curves provide the

flux rates of permeant gases. The permeability coefficient for a permeant gas is determined by multiplying the flux rate by the film thickness and can be expressed as follows:

$$\frac{P}{l} = \frac{dp}{dt} \frac{273V}{760(273 + T)A} \frac{1}{\Delta P} \frac{1}{60} \quad (1)$$

where P/l = gas flux ($\text{cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$), dp/dt = pressure gradient during time t in a steady state (Torr/s), V = calibrated lower volume (124.8 cm^3), T = operating temperature ($^{\circ}\text{C}$), A = membrane area (14.5 cm^2), and ΔP = pressure difference between the upper and lower sides.

The permeability coefficient is expressed in barrer.

$$1 \text{ barrer} = 10^{-10} \frac{\text{cm}_{\text{STP}}^3 \cdot \text{cm}_{\text{polym.}}}{\text{cm}_{\text{polym.}}^2 \cdot \text{s} \cdot \text{cmHg}} \quad (2)$$

When a mixture of gases is separated, the ideal separation factor for components is defined as the ratio of permeability of each component as follows:

$$\alpha = P_A/P_B \quad (3)$$

Reproducibility and Minimum Detectable Quantity of the Data. We carried out these experiments over 200 times in 40 batches to confirm the reproducibility, meaning that, to obtain one data point, at least five specimens were studied. We checked the reproducibility in other laboratories using a similar time lag method. Two data indicated that the permeability and the selectivity were within quite good agreement.

To observe the transient change of permeability data, gas permeation experiments of selected samples were repeated seven times over 3 weeks. They did not show the remarkable transient change of permeability within the test period.

The guaranteed accuracy of the pressure transducer (from MKS) used in this study is 10^{-6} Torr. The leak rate of the gas separation apparatus is 0.4 mTorr/h. This means that the leak rate of our gas permeation equipment is equivalent to a permeability of 5.8×10^{-5} barrer. Therefore, we subtracted the leak rate from the permeation result and reported these results here.

The minimum detectable quantity¹⁷ of our apparatus can be calculated as follows:

$$\Delta x_{\min} = \bar{x}_1 - \bar{x}_b > t \cdot s_b \sqrt{\frac{N_2 + N_2}{N_1 N_2}} \quad (4)$$

where the subscript b refers to the blank determination, t is a statistical parameter which depends on the desired confidential level (95%), s_b can be expressed as $\{[\sum x_i^2 - (\sum x_i)^2/N_2]/(N_2 - 1)\}^{1/2}$, N_1 is the number of the actual measurements, and N_2 is the number of blank determinations (=leak rate). In this case, for a single actual measurement with five leak tests, the minimum detectable quantity of data can be calculated from eq 4 as follows:

$$\Delta x_{\min} > t(2.78) \cdot s_b (4.879 \times 10^{-5}) \sqrt{\frac{1+5}{1 \times 5}} = 1.45 \times 10^{-5} \text{ barrer} \quad (5)$$

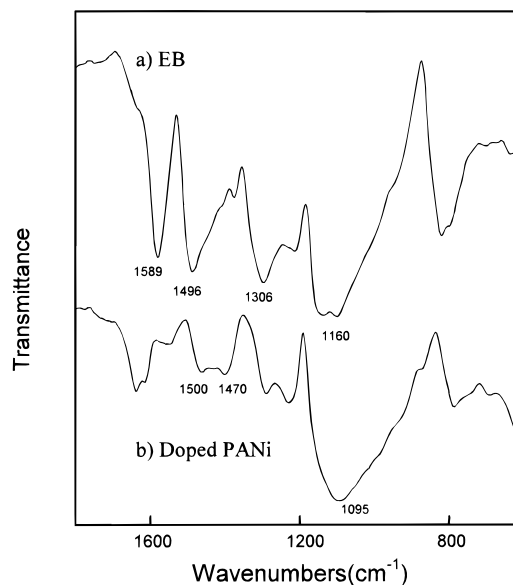


Figure 3. IR spectra of (a) emeraldine base and (b) doped PANi.

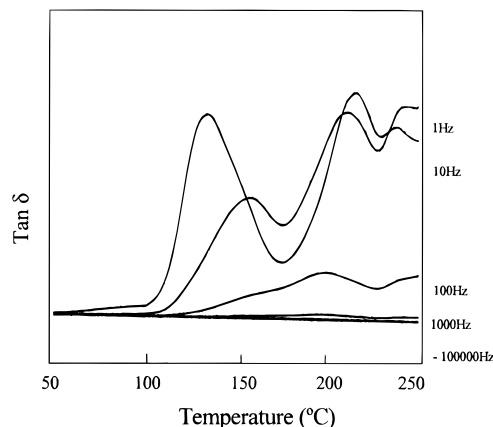


Figure 4. Dielectric analysis of an emeraldine base film.

Therefore, our reported permeation data are far beyond the minimum detectable quantity of our apparatus.

Results and Discussion

Preparation and Characterization. The weight-average molecular weight of PANi determined by a light scattering method was 340 000 Da.¹⁶ FT-IR spectra of EB and doped PANi powder are shown in Figure 3. The absorption bands of C–N stretching appear at 1306 and 1160 cm^{-1} . The absorption bands at 1589 and 1496 cm^{-1} are assigned to C=C stretching of the quinoid and benzenoid rings of PANi, respectively. After the doping process, the characteristic bands of doped PANi appear at 1095 and 1470 cm^{-1} .

Figure 4 shows the dielectric analysis patterns of an EB film. The peak at 207 $^{\circ}\text{C}$ measured at 1 Hz is regarded as the glass transition temperature (T_g) of the EB film. The peak at 135 $^{\circ}\text{C}$ indicates that solvent molecules remain in the base film (see later in Figure 8). This enables a solvent assay to escape from a hydrogen-bound site in PANi chains.

It is known that doping, dedoping, and redoping processes change the morphology of PANi. An optimum selectivity of a PANi membrane can be obtained by a controlled redoping. The doping, dedoping, and redoping

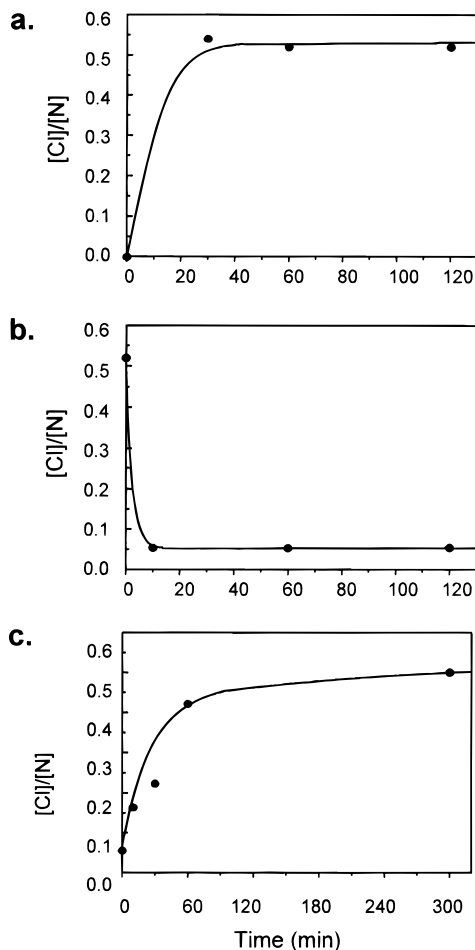


Figure 5. Doping and dedoping kinetics of PANi films: (a) doping in 1 M HCl; (b) undoping in 1 M NH_4OH ; (c) redoping in 0.02 M HCl.

kinetics of PANi films are shown in Figure 5. As the PANi base is doped with 1 M HCl, the DD reaches 0.5, meaning that half of the PANi is doped. The doping process is quite rapid. The DD reaches 0.5 within 0.5 h. Dedoping completes within 10 min with a DD of 0.05, while the DD remains 0.05 up to 5 h. Because we redoped PANi with 0.02 M HCl, the redoping rate was rather slow. By deliberately using a dilute acidic solution, we could easily control the DD.

If the material is crystalline in nature, the peak from the X-ray diffraction is sharp and the intensity is strong. However, when the material is amorphous, the peak is rather broad. In the case of the present PANi, as can be seen in the wide-angle diffraction (WAXD) patterns in Figure 6, PANi is regarded as a rather amorphous material. However, the WAXD pattern of an amorphous polymer is typically dominated by one broad peak associated with the center-to-center chain distance or d spacing. d spacing values are calculated from Bragg's equation, $n\lambda = 2d \sin \theta$ where θ is the angle for a peak in the patterns. Here, 2θ at the maximum intensity appearing at around 20° were used to calculate the d spacing, which was representative of the average openness degree within a material.

Changes in d spacing with doping, dedoping, and redoping were shown in Figure 7. The d spacing of the present doped PANi membrane (DD = 0.5) is 3.62 Å, which is much less than the kinetic diameter of N_2 . As the redoping time increases, the d spacing decreases

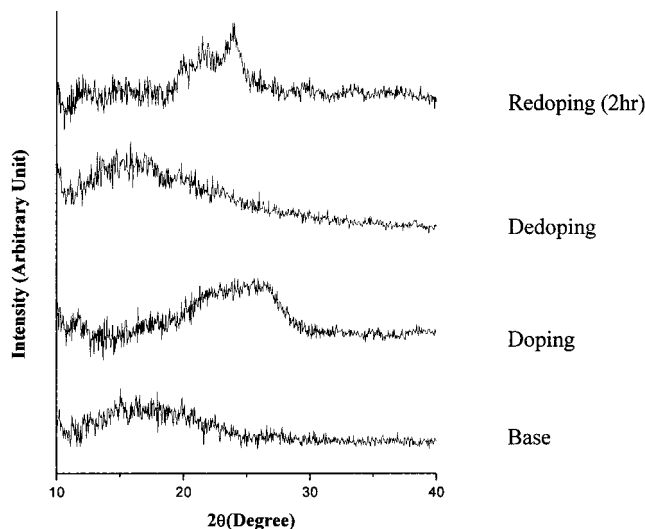


Figure 6. WAXD patterns of PANi films.

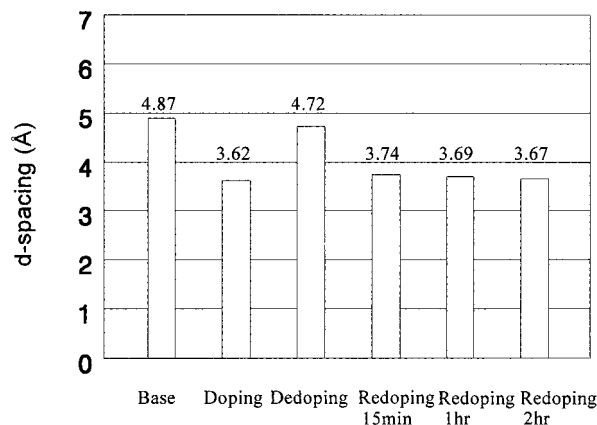


Figure 7. d spacing changes with doping, dedoping, and redoping.

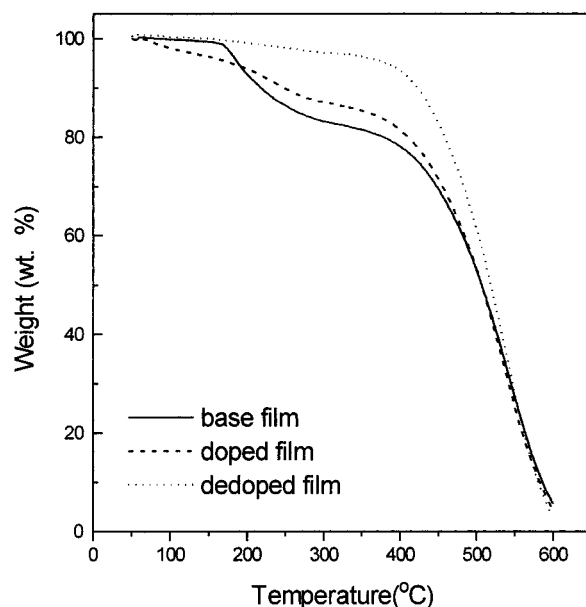


Figure 8. TGA thermograms of a base film and doped and redoped PANi films.

again and reaches 3.67 Å, which is close to the value of doped PANi (3.62 Å).

Figure 8 shows the result of TGA measurements of an EB film, a doped film, and a dedoped film. The EB film starts to lose its weight at about 164°C and reaches

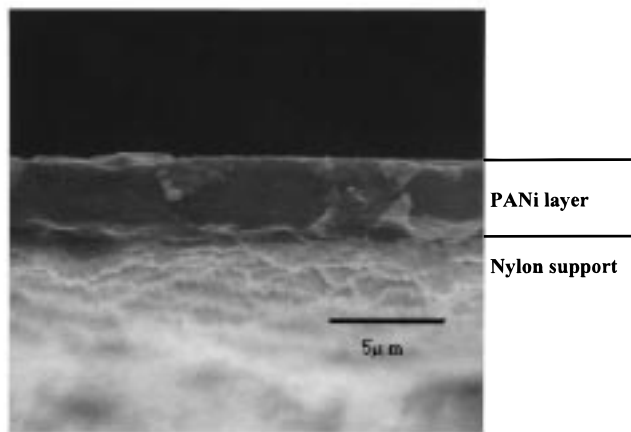


Figure 9. Scanning electron micrograph of a cross section of a PANi composite membrane.

77% residue at 400 °C, while the dedoped film loses only 8% of its original weight of a film at 400 °C. A drastic loss of weight for an EB film is due to an evaporation of solvent (DMPU), because the boiling point of DMPU is 146 °C. Therefore, it is evident that during the doping process a residual solvent in the PANi film could be removed. We obtained the same result from elemental analysis. The weight loss of the doped film at 240 °C is due to evaporation of dopant.

A scanning electron microphotography of a cross section of a PANi composite membrane is shown in Figure 9. A 5 μm PANi layer is clearly seen on top of the nylon support. There are no broken interfaces between PANi and nylon, proving that the welding process is an effective means to prepare the PANi composite membrane.

Gas Permeation Experiments. We prepared the composite membrane with an effective membrane thickness of 5 μm (Figure 9). As mentioned above, the d spacing of a doped PANi membrane is only 3.62 Å and could be an ideal perfect separation material for oxygen. Because the doped PANi membrane shows a d spacing between the kinetic diameters of oxygen (3.46 Å) and nitrogen (3.64 Å), the rigid backbone of the PANi chain, derived from a conjugated π bond, restricts its chain and permeant mobility.

Effects of redoping time, DD, and d spacing on the performance of PANi membranes are shown in Figure 10. As the redoping time increased, the permeability generally decreased and the selectivity increased because of the chloride ions which reduced the effective free volume and increased interchain forces.

The oxygen permeability value decreases from 0.28 to 0.13 barrer during the 2 h redoping process, while the selectivity increases from 8 to 28. Notice that the DD increases to 0.4 for the redoped period of an initial 2 h. Therefore, the DD and thus d spacing must have influenced the permeability and selectivity. In summary, because the redoping lasts a while, the d spacing and the permeability decrease while the DD and selectivity increase. Redoping clearly tightens up the molecule in PANi. Selectivity should increase as the d spacing of PANi approaches the value of the kinetic diameter of O₂. Again the doped PANi with a DD of 0.5 should be the separation membrane with maximum selectivity.

The reason we obtained such a high selectivity and separation performance can be explained by organic molecular sieve and composite membrane concepts. The

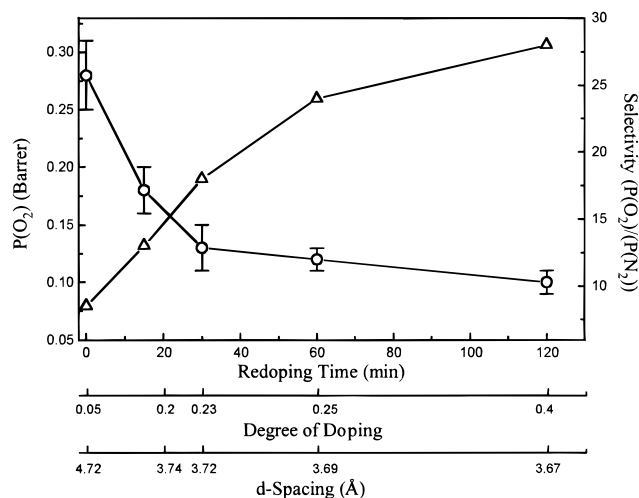


Figure 10. Effect of redoping time, degree of doping, and d spacing on the performance of PANi membranes.

effect of d spacing on the performance of PANi membranes is also shown in Figure 10. If we compare the kinetic diameter of permeating gases, 3.46 Å for O₂ and 3.64 Å for N₂, it is clear that the membrane having the d spacing between two values is regarded as an ideal separating membrane with unlimited selectivity. As the d spacing decreases, the oxygen and nitrogen permeability coefficients concurrently decrease. However, the decreasing rate of the nitrogen permeability coefficient is much faster than that of oxygen, so that the high selectivity values are obtained from the membrane with low d spacing values. The possible explanation for enhanced selectivity is that the smaller d spacing value enables a membrane to better discriminate between oxygen and nitrogen by the molecular sieving effect of PANi.

Maron et al.¹⁸ studied the local molecular structure of amorphous PANi by radial distribution function analysis of X-ray scattering data. They suggested that the doping process tended to develop more regular bond angles in an adjacent chain, causing the interchain spacing to become more regular. This means that doped PANi chains are packed regularly and effectively. This regular and closer PANi structure restricts particularly the nitrogen permeation.

We summarized the permeability and physical data for PANi membranes with the doping and redoping in Table 1. The EB membrane shows an oxygen permeability of 0.49 barrer and a α (O₂/N₂) of 7.2. As EB is doped with 1 M HCl, the DD reaches 0.5. The permeability of nitrogen through doped PANi was still too low to measure in our laboratory. The permeability of fully doped PANi is beyond the limit of measurement of our pressure transducer, indicating that it is lower than 10⁻⁴ barrer. Because fully doped PANi was impermeable to gases, the selectivity was not able to be determined. PANi redoped for 2 h with 0.02 M HCl showed an α (O₂/N₂) of 28 and a permeability of 0.13 barrer. The permeability of the present redoped PANi membrane is about the same as what Kaner et al. reported in 1991 with similar oxygen selectivity values.

In this study, the EB film has about a 4 times greater oxygen permeability coefficient than that of the literature value.¹⁹ Our membranes were not treated with the annealing. Therefore, some solvent molecules could remain compared with annealed membranes. The solvent in a polymer, particularly in an EB membrane, acts

Table 1. Permeability Data of a Composite PANi Membrane with Doping and Redoping Processes (5 μm)

	base	doped	dedoped	redoped		
				15 min	1 h	2 h
d spacing	4.87	3.62	4.72	3.74	3.69	3.67
degree of doping (DD) (Cl/N)	0.0	0.5	0.05	0.2	0.25	0.4
permeability of O ₂ (barrer)	0.49	<i>a</i>	0.28	0.17	0.12	0.10
selectivity ($P(\text{O}_2)/P(\text{N}_2)$)	7.2	<i>a</i>	8.5	13	24	28
O ₂ diffusion coefficient ^b D_{O_2} (10^{-8} cm ² /s)	1.029	<i>a</i>	0.253	0.075	0.058	0.056
N ₂ diffusion coefficient ^b D_{N_2} (10^{-8} cm ² /s)	0.230	<i>a</i>	0.053	0.012	0.008	0.007
diffusivity selectivity ($D_{\text{O}_2}/D_{\text{N}_2}$)	4.4	<i>a</i>	4.7	6.1	6.9	7.5
solubility selectivity ($S_{\text{O}_2}/S_{\text{N}_2}$) ^c	1.6	<i>a</i>	1.8	2.1	3.5	3.7

^a Not detectable. ^b Calculated from time lag data ($D = l^2/6\theta$). ^c Calculated as equal to (permeation selectivity)/(diffusion selectivity).

as a plasticizer because the solvent causes the polymer to be more flexible, resulting in a more permeable membrane than dedoped PANi. In the meantime, during the doping and dedoping processes where the solvent was removed, dopants in the PANi membrane were not completely detached from the doped PANi. Therefore, the permeability of a dedoped film was about 3 times lower than that of an EB film. Even though there is a decrease of permeability of a membrane, the doping and dedoping processes may be important to gain an optimal selectivity value before redoping is carried out.

The permeability is usually taken as the product of diffusivity and solubility. The ideal selectivity (permeability ratio) can also be expressed as a product of diffusivity selectivity, $D_{\text{O}_2}/D_{\text{N}_2}$, and solubility selectivity, $S_{\text{O}_2}/S_{\text{N}_2}$. Each diffusion coefficient and diffusional selectivity of various PANi membranes are shown in Table 1. As the redoping time increases, the diffusion coefficient decreases, while the diffusion selectivity and solubility selectivity increase. Our time lag experiments yielded diffusion selectivities of 4.4 for the EB membrane, 4.7 for the dedoped PANi membrane, and 7.5 for PANi redoped for 2 h. The increase of diffusion selectivity is attributed to the change of d spacing caused by the redoping process. These results indicate that the redoping process enhances diffusion selectivity.

Solubility selectivities, calculated from a ratio of permeation selectivity and diffusion selectivity, of various PANi membranes are also listed in Table 1. Solubility selectivities of EB, dedoped PANi, and redoped PANi (2 h) are 1.6, 1.8, and 3.7, respectively. Notice that the solubility selectivity of redoped PANi (2 h) is found to be 3.7, which is larger than that of other conventional polymers.²⁰ Pellegrino et al.²¹ measured the gas sorption isotherm of PANi. They reported that the O₂/N₂ solubility selectivity of a dedoped film (undoped) and an EB film were 3.8 and 1.8, respectively. Despite high solubility selectivity of PANi, their study indicated that the solubility selectivity resulted from the diffusional access of penetrants to the PANi membrane and therefore diffusion-controlled the permselectivity.

Rebattet et al. concluded that the polarons–oxygen interaction could explain the high selectivity values in PANi using the ESR measurements.¹⁰ However, they also reported that the sorption values of PANi–EB in oxygen and nitrogen were 8 and 4.5 cm³/cm³·cmHg at 1100 kPa and 298 K, respectively. Thus, $S_{\text{O}_2}/S_{\text{N}_2}$ was 1.8, which was in the range of values for normal polymers. This means that the diffusional selectivity, $D_{\text{O}_2}/D_{\text{N}_2}$, governs the permeability selectivity. Therefore, although the oxygen–polymer interaction is detected, the diffusion of oxygen through the intermolecular spacing dominates the total permeation behavior by a sieve mechanism.

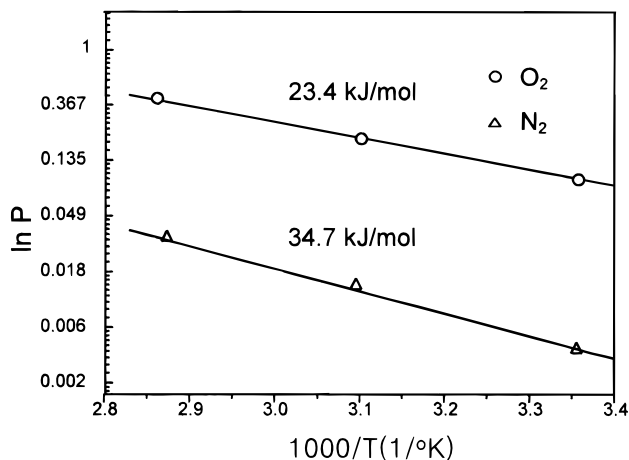


Figure 11. Effect of temperature on the performance of PANi membranes: Arrhenius plot of the permeation of O₂ and N₂.

Figure 11 presents an Arrhenius plot of permeation of O₂ and N₂. The temperature dependence of gaseous molecules in a polymeric membrane can be described by an Arrhenius expression

$$P = P_0 \exp(-E_p/RT) \quad (6)$$

where P_0 is a preexponential factor and E_p is the activation energy for gas permeation. The activation energies for oxygen and nitrogen permeation through redoped PANi membranes are 23.4 and 34.7 kJ/mol, respectively.

For polymer membranes, as the temperature increases, the permeability increases and the selectivity decreases because of the enlarged free volume due to thermal motion of polymer chains. The higher activation energy is an outcome of an additional energy required for the transient hole formation in the diffusional jump process of gas molecules. Gas molecules can jump through transient holes equal to or larger than its effective size in free volume.

Figure 12 shows the effect of pressure on the permeability. For glassy polymer membranes, as the pressure increases, the permeability slightly decreases and the selectivity increases because an increased upstream pressure causes compaction of free volume and makes permeant gases difficult to jump through the membrane.

Table 2 summarizes the data taken from the literature on PANi membranes and the data of the present study. Kaner et al. reported in 1991 the inconsistent selectivity and the permeability values using the same PANi membranes. Martin et al. and Rebattet et al. reported that the selectivity values of O₂/N₂ did not exceed 15, with the oxygen permeability values ranging between 0.14 and 0.3 barrer, depending on the prepara-

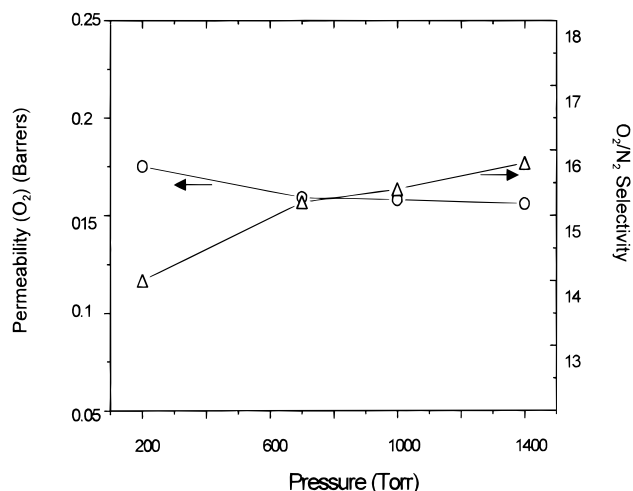


Figure 12. Effect of pressure on the performance of PANi membranes.

Table 2. Comparison of O₂ Permeability and Selectivity Data Appearing in the Literatures

researcher	treatment	barrer (O ₂)	$\alpha(O_2/N_2)$
Anderson ⁶	redoped	<i>a</i>	30
Martin ⁸	doped	0.164	14.8
Rebattet ¹¹	annealed	0.121	6.4
	doped	0.01	2.5
	undoped	0.15	9.4
	redoped	0.142	14.2
Chang ¹⁹	as-cast	0.12	<i>a</i>
	doped	0.016	<i>a</i>
	undoped	0.135	13.5
the present study	as-cast	0.5	7.2
	doped	0	<i>a</i>
	dedoped	0.28	8.5
	redoped	0.1	28

^a Not available.

tion conditions. The common points that should be noticed are the use of NMP as a solvent to dissolve PANi polymer powders for casting membranes. For doping and redoping processes, however, the doping level was somewhat different, indicating that, although they all used similar doping, undoping, and redoping procedures, the membrane morphologies of the films should have been different from each other.

Figure 13 shows the so-called Robeson's plot²² comparing the data from the literature and the present membranes. PANi redoped for 2 h is way beyond the upper limit. In this case a polyimide membrane is in that range. PANi membranes show along that limit with high selectivity and low permeability.

Conclusions

A PANi composite membrane was prepared with a nylon porous support membrane by solvent welding. The PANi composite membranes were doped, dedoped, and redoped with different DD levels. O₂/N₂ separation experiments with different upstream pressures (200–1400 Torr) and temperatures (25–75 °C) were carried out to study the permeation behavior of a PANi membrane. After the doping and dedoping processes, the permeability of a dedoped PANi membrane decreased and selectivity slightly increased because of changes in morphology of PANi. The *d* spacing decreased from 4.87 to 3.62 Å after the doping, dedoping, and redoping processes. As the redoping continued, the DD increased and *d* spacing decreased, while the selectivity of a PANi

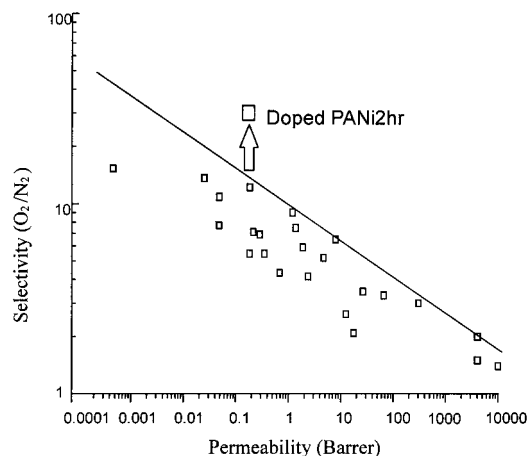


Figure 13. Robeson plot and performance of a PANi membrane.

membrane dramatically increased. An optimum condition to obtain the highest selective PANi membrane was doping, dedoping, and redoping for 2 h. The highest O₂/N₂ selectivity and oxygen permeability of redoped PANi (2 h) were 28 and 0.10 barrer, respectively. Time lag experiments yielded diffusion selectivities of 4.4 for the EB membrane, 4.7 for the dedoped PANi membrane, and 7.5 for PANi redoped for 2 h. The increase of diffusion selectivity is attributed to the change of *d* spacing caused by the redoping process. These results indicated that the redoping process enhanced the diffusion selectivity. High selectivity of redoped PANi is due to the smaller *d* spacing value that enables a membrane to better discriminate between oxygen and nitrogen by the molecular sieving effect of PANi.

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