Gas Permeation Properties of Conducting Polymer/Porous Media Composite Membranes I.

Kensuke KAMADA,* Jun KAMO, Akira MOTONAGA, Tadashi IWASAKI,
and Hiroshi HOSOKAWA

*Central Research Laboratories, Mitsubishi Rayon Co., Ltd.,
Ohtake, Hiroshima 739-06, Japan*

(Received March 8, 1993)

ABSTRACT: By means of chemical oxidative polymerization, micro-porous composite membranes were prepared with compositing conductive polymer, such as polypyrrole and poly(*N*-methylpyrrole), in the micro-pores of Vycor glass. Gas permeation rates through the membrane were measured mainly with O₂, N₂, and air as feed gases. The membrane showed high selective gas permeation for O₂ to give a separation factor $\alpha(\text{O}_2/\text{N}_2)$ greater than 3. From isothermal gas sorption experiments conducting polymers sorbed more amount of O₂ than N₂. The pore size distribution of the poly(*N*-methylpyrrole) composite membrane was evaluated by the BET method to have 2.1 nm average pore radius and more narrow distribution than that of Vycor. The experimental results in addition to the characteristic pressure dependence of gas permeation rate suggested that selective gas permeation occurred through the membrane with a mechanism of surface flow.

KEY WORDS Gas / Permeation / Conducting Polymer / Micro-Porous /
Membrane / Composite / Adsorption / Surface Flow /

Many studies have been reported on the mechanisms of gas permeation through membranes and improvements of membrane properties, such as gas permeation rate, selectivities, heat resistance and so on, because gas separation technology by membranes is more useful from the view point of energy consumption. There are, in general, three mechanisms for gas permeation through membranes.

- 1) Solution-diffusion flow through non-porous membranes.
- 2) Knudsen flow through porous membranes.
- 3) Surface flow through porous membranes.

Many polymers, through which gas molecules permeate with the first mechanism, have been investigated because they are easily made

into desirable shape and industrially important. In recent years, new synthetic polymer membranes, showing higher gas permeability than that of silicon membrane, have been found¹ and the mechanism of gas permeation is now under discussion. In general, the higher gas permeability these non-porous polymeric membranes have, the lower selectivity of gases they show. So it seems that there is a limit to obtain a high performance membrane having high permeability and high selectivity.

According to the second mechanism, it is well-known that gas permeability is very high, but selectivity is very low. It is no use to separate a gas mixture which contains gases having not so different molecular weights such as O₂ and N₂.

The membrane, through which gas molecules permeate with the third mechanism, is

* To whom correspondence should be addressed.

considered to have high permeability and high selectivity. Several studies²⁻⁵ on the surface flow have been reported, in which permeation of organic vapors such as ethylene, propylene, benzene, alcohols, through a porous membrane were investigated.

This paper reports O₂ and N₂ separation with the micro-porous membranes modified with conducting polymer to attain an effective separation by the third mechanism.

EXPERIMENTAL

Material

Reagent grade materials were used without further purification for chemical oxidative polymerization. As monomers, pyrrole, *N*-methylpyrrole and aniline, as oxidizing agents, ferric chloride (FeCl₃·6H₂O) and cerium nitrate·ammonium nitrate (Ce(NO₃)₄·2NH₄·NO₃) and as solvents, acetonitrile, ethanol and deionized water were used.

A micro-porous glass tube, Vycor #7930 (produced by Corning Glass Works), was used as a porous support to prepare the composite membrane on which the conducting polymer was polymerized. The outer and inner diameters of the tube were 7 mm and 4.8 mm, respectively. The cylindrical membrane was thus 1.1 mm in thickness and consisted of a porous structure having tortuous pores of *ca.* 2 nm average radius.

Chemical Oxidative Polymerization

Before the preparation of a composite membrane, chemical oxidative polymerization was investigated by mixing various monomers with oxidants in acetonitrile solution. Several drops of 0.1 mol·dm⁻³ oxidant solution were added to a 0.3 mol·dm⁻³ monomer solution in the test tube at room temperature. Except for the mixture of aniline and FeCl₃ solution, a powdery precipitate soon appeared upon mixing two solutions. In the case of the mixture of aniline and FeCl₃, yellow gel-like material appeared after 24 hours. For measurement of

gas sorption properties, polypyrrole and poly(*N*-methylpyrrole) were prepared by mixing 0.3 mol·dl⁻³ monomer and FeCl₃ solutions. The black precipitates were washed with water followed by methanol five times and dried at 60°C for five hours.

Preparation of Composite Membranes

Figure 1 shows the apparatus to prepare the composite membranes. At first, the Vycor glass was immersed and washed with solvent in the glass vessel for 10 min under degassing by vacuum and radiation of ultrasonic. After removing the solvent from the vessel, the Vycor glass was immersed in the oxidant solution for 5 min which contained a given oxidant in the same solvent. After discharging the oxidant solution from the vessel, the Vycor glass was immersed in the monomer solution. After 5 min, the monomer solution was discharged from the vessel. The two-step process mentioned above is one polymerization procedure and various composite membranes were prepared by repeating from three to six polymerization procedures. The composite membrane was washed with solvent for 10 min and dried at 50°C in vacuum for more than 5 hours.

The immersing and washing in preparing composite membrane were performed in the

Figure 1. Apparatus for preparation of composite membrane: 1, ultrasonic bath; 2, water; 3, glass vessel; 4, monomer or oxidant in solvent; 5, medium; 6, 3-direction cock; 7, aspirator; 8, vacuum gage.

glass vessel shown in Figure 1 while degassing the supporter by vacuum and radiation of ultrasonic. As polymerization proceeded, the color of Vycor glass turned from transparent to brown or black.

Isothermal Gas Sorption Measurement

The amounts of gas sorbed by polypyrrole and poly(*N*-methylpyrrole) were measured at 23°C by the gas sorption apparatus equipped with the electro micro-balance (manufactured by Chan Works). The pressure of test gases, O₂ and N₂, varied from 0 to 760 Torr (101 kPa).

Measurement of Pore Size Distribution

With Vycor glass and composite membrane of poly(*N*-methylpyrrole), pore size distribution, pore volume, and surface area were measured with OMNISORP® (manufactured by NIKKISO Co., Ltd.). N₂ gas volume sorbed and desorbed was measured by changing the pressure at the boiling temperature of N₂ and the data were analyzed by the BET method. The composite membrane for measurement was prepared by four polymerization procedures with 0.6 mol·cm⁻³ FeCl₃ and 0.6 mol·dm⁻³ *N*-methylpyrrole solutions of acetonitrile.

Measurement of Gas Permeation Rate (GPR)

GPR of the membranes was measured with GTR-10 (manufactured by YANAGIMOTO Co., Ltd.). The cell part attached to membrane was modified for our samples. As the membrane was pipe-type, both ends were connected to stainless steel tubes with adhesive, through which the test gas was introduced from one end and purged from the other. The test gas permeated the membrane from the inner side of the pipe to the outer side and was collected in the vacuum room. The collected gas was carried by carrier gas to gas chromatography for analysis. Effective membrane area for gas permeation was *ca.* 8.8 cm² calculated from the outer diameter of the pipe. Test gases were air, O₂, N₂, He, Ar, CO₂, and

the pressure of the feed gas was varied to 3 × 10³ Torr (400 kPa). The cell part was thermo-controlled in an oven and GPR was measured at 30°C. As the volume of gas permeated was analyzed by gas chromatography, GPRs of O₂ and N₂ could be determined in a time when air was used as the test gas.

In this study, GPR calculated according to eq 1 as cm³(STP)cm⁻²·s⁻¹·cmHg⁻¹.

$$\text{GPR} = Q/A \cdot \Delta P \quad (1)$$

where

Q, volume of gas permeated (reduced to standard temperature and pressure) per unit time.

A, membrane area calculated from outer surface of pipe.

ΔP , pressure difference of gas component between feed and permeated sides.

RESULTS AND DISCUSSION

Gas Sorption Properties

To understand the mechanism of gas permeation through the composite membrane, it is important to evaluate the gas sorption properties of the conducting polymer. The morphologies of polypyrrole and poly(*N*-methylpyrrole) prepared by chemical oxidative polymerization were observed with SEM shown in Photographs 1 and 2. Both polymers had an aggregated powdery structure consisting of *ca.* 0.5 μm primary particles.

Figure 2 shows isothermal gas sorption curves. The pressure dependence of curves was different from that of the Henry type as well as the Langmuir type. From the Figure, polypyrrole and poly(*N*-methylpyrrole) sorbed nearly the same amount of N₂, about 4.7 cm³(STP)/g-polymer at 1 atm. If molecules of N₂ are adsorbed with mono-layer on the surface of polymers which consist of spheres having 0.5 μm diameter, the amount of N₂ gas volume is roughly 1.85 cm³(STP)/g-polymer (assumed density of polymer, 1.5 g cm⁻³ and

Photograph 1. Scanning electron micrograph of polypyrrole powder: $\times 5000$.

Photograph 2. Scanning electron micrograph of poly(*N*-methylpyrrole) powder: $\times 5000$.

Figure 2. Isothermal gas sorption curves of conducting polymers: temp, 23°C; filled marks, polypyrrole; open marks, poly(*N*-methylpyrrole); (O), O₂, (Δ), N₂.

molecular area of N₂, 16.2 Å²). Thus the experimental value was 2.5 times larger than the estimated value for mono-layer adsorption and the difference was much larger with O₂ gas. It is considered that the gas molecules not only were adsorbed on the surface of the polymer but also dissolved the polymer at the experimental temperature, 23°C.

The amount of O₂ sorbed by polypyrrole was 16.8 cm³(STP)/g-polymer at 1 atm, approximately fifty times that of polydimethylsiloxane (PDMS) as roughly estimated from the solubility coefficient.⁶ Conducting polymers showed more affinity to O₂ than N₂. For polypyrrole, the ratio of O₂ volume sorbed at 1 atm to N₂ was 3.6, which was larger than the value (*ca.* 1.5⁶) for PDMS. These may be caused by special interactions, for example, magnetic interaction, between O₂ molecules and conjugated π -electrons of conducting polymers because O₂ molecules are paramagnetic compared to the diamagnetism of N₂ molecules.

GPR of Composite Membranes

There seems to be two principles to obtain a high performance composite membrane on applying the surface flow mechanism. One is an appropriate selection of micro-porous medium and the other, ingenious modification of the surface of pores. Average pore size, dis-

Table I. Characterization of membrane structures by the BET method

Item	Vycor glass	Composite membrane ^a
<i>C</i> value ^b	130	167
<i>V_m</i> (cm ³ g ⁻¹) ^b	38.0	43.4
Surface area (m ² g ⁻¹)	165	188
Prove volume (cm ³ g ⁻¹) ^c	0.384	0.250
Average pore radius (nm) ^d	2.2	2.1

^a Poly(*N*-methylpyrrole) composite obtained under the same conditions of No. 7 in Table III.

^b Calculated in the range of P/P_0 from 6×10^{-3} to 0.3.

^c Pore volume of pores having radius > 1 nm.

^d Peak radius of pore size distribution.

tribution, porosity, tortuosity, and thickness of medium are the main factors to influence the gas permeation properties of composite membrane. As it is our main purpose in this study to investigate the possibility separating O_2 and N_2 by surface flow through porous membrane, Vycor glass was chosen as the medium because it has been well characterized and has sharp pore size distribution. As shown in Table I and Figure 3, pore size distribution of the medium was very narrow and the average radius of pores was 2.2 nm.

Figure 3. Pore size distribution of micro-porous membranes: r_p , pore radius; dV/dr_p , derivative of pore volume by r_p ; (—), poly(*N*-methylpyrrole) composite membrane; (---), Vycor glass.

Horiguchi *et al.*² reported that Vycor glass adsorbed little N_2 at 0°C, 25°C, and 50°C. As shown in Table II, gas permeation through Vycor glass is dominated by Knudsen flow suggesting no selective gas adsorption. To make the surface of pores active to gases, it is important to coat the surface with a polymer which has affinity for gases as possible as uniformly and thinly without clogging the pores. For this purpose, it is necessary to intrude effectively monomer and oxidant into pores of the medium as small as 4.4 nm and to polymerize, which was done with the apparatus shown in Figure 1 under degassing by vacuum and radiation of ultrasonic. Solvents also had large influence on the intrusion of reactants and polymerization, affecting GPR of the composite membranes.

Table II shows the results of GRP along with other properties of composite membranes prepared by polymerizing pyrrole in various solvents. The electric resistance of membranes was measured with 1 cm apart on the surface of membrane and 1.1 mm apart across the membrane. In these experiments, GPR was measured separately with pure gases, O_2 and N_2 , and the separation factor $\alpha(O_2/N_2)$ was calculated from $GPR(O_2)/GPR(N_2)$. Vycor

Table II. Effects of solvents on the properties of polypyrrole composite membranes^a

Exptl. no.	Solv.	No. of Polymerization	Electric resistance ^b (kΩ)	GPR ^c		$\alpha(O_2/N_2)$
				O_2	N_2	
1	—	—	$> 3 \times 10^4$	1.8×10^{-5} , 2.0×10^{-5}		0.90
2	H ₂ O	3	$(4-7) \times 10^2$	1.3×10^{-5} , 1.4×10^{-5}		0.93
3	EtOH	3	$> 3 \times 10^4$	2.1×10^{-6} , 2.5×10^{-6}		0.84
4	CH ₃ CN	3	$(2-4) \times 10$ $(3-4) \times 10^2$	3.4×10^{-8} , 6.5×10^{-9}		5.2
5	CH ₃ CN	6	2-4 4-8	3.2×10^{-9} , 2.1×10^{-9}		1.2

^a Monomer (pyrrole) and oxidant ($FeCl_3 \cdot 6H_2O$) concn, $0.3 \text{ mol} \cdot \text{dm}^{-3}$.

^b Upper value, measured on surface; lower value, measured across membrane.

^c Test gases, O_2 and N_2 separately; feed gas pressure 2 atm ($2.02 \times 10^5 \text{ Pa}$), temp, 30°C; GPR unit, $\text{cm}^3 (\text{STP}) \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$.

Table III. Effects of monomers on the properties of composite membranes

Exptl. no.	Monomer	Conditions of composition ^a	Electric resistance ^b (k Ω)	GPR ^c		$\alpha(\text{O}_2/\text{N}_2)$
				O ₂	N ₂	
6	Pyrrole	A: 0.3M B: 0.3M C: 3	(2—4) $\times 10$ (3—4) $\times 10^2$	5.0×10^{-7} , 2.4×10^{-7}		2.1
7	<i>N</i> -Methyl pyrrole	A: 0.6M B: 0.6M C: 4	(17—30) $\times 10$ (15—20) $\times 10$	1.5×10^{-6} , 4.9×10^{-7}		3.1
8	Aniline	A: 0.4M D: 0.1M C: 4	$> 3 \times 10^4$ $> 3 \times 10^4$	8.4×10^{-9}	8.4×10^{-9}	1.0
9		A: 0.3M D: 0.3M C: 2	$> 3 \times 10^4$ $> 3 \times 10^4$	1.8×10^{-8}	5.9×10^{-9}	3.0

^a Solvent, CH₃CN; A, monomer concn; M denotes mol·dm⁻³; B, oxidant (FeCl₃·6H₂O) concn; C, no. of compositing; D, oxidant (Ce(NO₃)₄·2NH₄NO₃) concn.

^b Upper value and lower value mean the same in Table II.

^c Test gas, air; feed gas pressure, 2 atm; temp, 30°C.

glass (No. 1) and composite membranes, 2, 3, 5 showed no selectivity, suggesting that permeation of gases through the membrane was dominated by Knudsen flow, but 4 showed high selectivity.

Acetonitrile which has a high dipole moment and often used in electropolymerization as a solvent gave good results compared with other solvents. As the number of polymerization increased, GPR of the membrane decreased, but the separation factor did not always increase. So it is considered that there are ideal conditions for polymerization to prepare a high performance membrane.

To study the effects of monomers on the properties of membranes, composite membranes were prepared in acetonitrile with pyrrole, *N*-methylpyrrole and aniline. Table III shows the results and the conditions for polymerization. In this case, for measurement of GPR, air was used as feed gas and the volumes of O₂ and N₂ permeated were measured at the same time. As mentioned previously, aniline did not polymerize with

FeCl₃ as oxidant, Ce⁴⁺, which has a higher standard oxidation electrode potential than Fe³⁺, was used as oxidant.

All composite membranes prepared with the monomers showed selective permeation for O₂, but had different GPR with variation in polymerization conditions. The composite membrane of poly(*N*-methylpyrrole) showed excellent properties. The composite membrane of polypyrrole in Table III (No. 6) was prepared with the same conditions as in Table II (No. 4), but GPR and α were different. This might be caused partly by differences in test feed gas (pure gas or mixture gas), but mainly by small differences of polymerization conditions such as degree of degassing, amount of reactants and solvent adhered in discharging and etc.

Structure of Composite Membrane

The pore structures of membranes were evaluated from the BET method with the poly(*N*-methylpyrrole) composite membrane and Vycor for reference. Data were analyzed

according to eq 2.

$$P/V(P_0 - P) = 1/V_m \cdot C + [(C - 1)/V_m \cdot C](P/P_0) \quad (2)$$

where

P_0 , saturated vapor pressure of adsorbed gas (N_2).

P , equilibrium vapor pressure of adsorbed gas.

V , volume of gas adsorbed.

V_m , volume of gas adsorbed with mono-layer.

C , experimental constant.

For both samples, a linear relationship between $P/V(P_0 - P)$ and P/P_0 was obtained up to $P/P_0 = 0.30$. With the composite membrane, there is possibility that poly(*N*-methylpyrrole) absorbs N_2 gas. But in this experiments, the temperature of sorption was -196°C and data were analyzed by eq 2. It is considered that only adsorption occurred.

In Table I and Figure 3, the pore size distributions obtained by desorption curves of N_2 are shown. The medium and the composite membranes had narrow pore size distribution. The latter had a narrower distribution than the former, for smaller and larger pores in the medium vanished. This caused large decrease of the total pore volume of composite membrane, which was 65% of the medium, though the average pore sizes were not so different for the both membranes. The composite membrane had larger surface areas estimated by V_m than the medium, suggesting the surface of pores changed more unevenly by compositing with polymer.

The constant C in eq 2 is approximately expressed by eq 3.

$$C = \exp[(\lambda_1 - \lambda_L)/RT] \quad (3)$$

where

λ_1 , heat of adsorption with mono-layer.

λ_L , heat of liquefaction of gas.

R , gas constant.

T , temperature.

The composite membrane had greater C than the medium, which suggests increase of λ_1 in eq 3 with polymerization. This means interactions between surface of pore and N_2 molecules are large and N_2 molecules are more easily adsorbed.

Gas Separation Properties of Composite Membrane

To make clear the mechanism of gas permeation through composite membrane, GPRs of O_2 and N_2 were measured with varying pressure of feed gas (air) up to 3×10^3 Torr for the poly(*N*-methylpyrrole) composite membrane (No. 7). The results are shown in Figures 4 and 5. In general GPR of non-porous polymeric membranes, through which gas permeates above the glass transition temperature of polymer, was independent of the pressure of feed gas. But GPR of the composite membrane showed characteristic

Figure 4. GPR vs. feed gas (air) pressure for poly(*N*-methylpyrrole) composite membrane (No. 7); (○) GPR (O_2) and (△) GPR (N_2), broken line is GPR (O_2) calculated with silicon rubber (see the text).

Figure 5. O_2 content of permeated gas vs. feed gas (air) pressure: Membrane is the same as in Figure 4, broken line is O_2 content calculated with silicon rubber (see the text).

dependence on it. In the surface flow mechanism, GPR must be proportional to the product of the amount of gas adsorbed and surface diffusion constant. So large increase of GPR in a low pressure region may be caused by large pressure dependence of adsorption in this region as seen in Figure 2. The large increase of GPR in high pressure region may be caused by large surface diffusivity due to multilayer adsorption.

As $GPR(O_2)$ and $GPR(N_2)$ showed the same pressure dependence, the separation factor α was independent of air pressure as shown in Figure 5 and O_2 content of permeated gas reached 44%. The broken lines in Figures 4 and 5 show values for silicon rubber membrane. These are calculated from the permeability coefficient of O_2 and α ,⁷ if the thickness of silicon rubber were 1.1 mm equal to the composite membrane. The composite membrane had better properties for O_2 and N_2 gas separation from air than the silicon rubber membrane having the same thickness.

With another poly(*N*-methylpyrrole) composite membrane (No. 10), prepared by the same conditions as No. 7 in Table III, GPRs for various gases were measured with pure feed gases. The results are given in Figure 6. $GPR(O_2)$ and $GPR(N_2)$ of No. 10 are one order smaller than those of No. 7 which might

Figure 6. GPRs of various gases vs. feed gas pressure; membrane is poly(*N*-methylpyrrole) composite (No. 10): ($\square$) He; ($\bullet$) CO_2 ; ($\circ$) O_2 ; ($\blacktriangle$) Ar; ($\triangle$) N_2 .

be due by the same reasons mentioned previously for polypyrrole composite membranes. Compared with Figures 6 and 4 regarding $GPR(O_2)$ and $GPR(N_2)$, it is noted that the pressure dependence of GPR is somewhat different whether the feed gas is a mixture (Figure 4) or pure gas (Figure 6). This will be reported in detail in the following paper. From Figure 6, the ratios of GPR for each gas at 2 atm (1520 Torr) were 48.1:17.5:5.12:2.18:1.00 for $GPR(He):GPR(CO_2):GPR(O_2):GPR(Ar):GPR(N_2)$ respectively. The composite membrane showed high permeability especially for He and CO_2 , which could not be explained by Knudsen flow.

Mechanism of Gas Permeation through Composite Membrane

As shown in Table I and Figure 3, the composite membranes had the micro-porous structure similar to that of Vycor glass. The mechanism of gas permeation through a porous membrane is considered either Knudsen flow or surface flow. In the case of Knudsen flow, permeation coefficient, P , of the mem-

brane is proportional to $K/(M \cdot T)^{1/2}$, where K , M , T are the structural factor of membrane, molecular weight of the gas and temperature, respectively. Therefore, in this flow, the separation factor $\alpha(\text{O}_2/\text{N}_2)$ is $(28/32)^{1/2}$, or 0.94, which is nearly equal to the α of Vycor glass as shown in Table II (No. 1). Gas flow through Vycor glass is thus Knudsen flow.

The separation factor of composite membrane is higher than 3. This cannot be explained by the Knudsen flow mechanism. Thus, gas flow through the composite membrane may be dominated by surface flow and a high separation factor is produced by conducting polymer having an affinity for O_2 gas.

CONCLUSION

Micro-porous composite membranes were prepared with compositing conductive polymers in the micro-pores of Vycor glass. When air permeated the membranes, they showed selective gas permeation for O_2 . The mechanism of gas flow through the membrane was considered surface flow based on various experimental results, such as isothermal gas sorption, pressure dependence of GPR and

membrane structure obtained by the BET method. The composite membranes in this study showed high separation factor $\alpha(\text{O}_2/\text{N}_2)$, greater than 3, but GPRs were rather low because of the large thickness of membrane. The composite membrane has a great possibility to give a high performance membrane which would not be possible with synthetic polymers, if the composite membrane is as thinner as a few microns.

REFERENCES

1. T. Masuda, E. Isobe, and T. Higashimura, *Macromolecules*, **18**, 841 (1985).
2. Y. Horiguchi, R. R. Hudgins, and P. L. Silveston, *Can. J. Chem. Eng.*, **49**, 76 (1971).
3. M. Okazaki, H. Tamon, and R. Toei, *AIChE J.*, **27**, 262 (1981).
4. T. Okubo and H. Inoue, *AIChE J.*, **34**, 1031 (1988).
5. A. Yamasaki and H. Inoue, *Kagaku Kogaku Ronbunshu*, **14**, 609 (1988).
6. J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," 3rd ed, Wiley-Interscience, New York, N.Y., 1989, Chapter VI, p 435.
7. J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," 2nd ed, Wiley-Interscience, New York, N.Y., 1975, Chapter III, p 229.