Novel Polypyrrole composite membrane with high gas selectivity and permeability

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1.   Introduction

Gas separation membrane technology is useful for a variety of applications [1,2], such as hydrogen recovery from reactor purge gas, nitrogen and oxygen enrichment, water vapor removal from air, stripping of carbon dioxide from natural gas, etc. Although membrane separations are attractive because of low energy costs and simple operation, low permeabilities and/or selectivity often limit membrane applications [3,4]. Many researchers to overcome these limitation have attempted to makes increasing efficient surface area of membrane or/and decreasing thickness of selectivity layer vital for increasing flux without sacrificing selectivity. The currently investigated conductive polymers such as polypyrrole (Ppy) and polyaniline havepotential for use in a wide variety of electronic devices [5,6]. It has been show that these materials are prospective materials for use in gas separations due to very high gas separation efficiencies [7-9]. Current strategies for improving gas flux are largely directed towards to reducing the skin thickness of the membrane. Unfortunately, synthesis of defect-free ultrathin membrane "skins" is challenging. Strategies for forming the skins of these membranes include casting [10], in situ casting [11], in situ condensation of polymers and/or monomers at the porous support [12], and plasma polymerization [13]. In all of these methods, synthesis of defect-free skins with ultrathin layer is difficult.

To approach for achieving this goal, this study was perform to prepare the polypyrrole (PPy)/polydimethylsiloxane (PDMS) composite membrane with ultra-thin skin layer by novel method termed as chemically "Interfacial synthesis" and "monomer evaporization" having a suitable structure for gas separation because PPy active layer can be easily fabricated to ultar-thin layer by these methods. The fabrication of high-flux flat-PPy composite membranes requires deposition of an ultrathin, discriminating layer on a highly permeable support. Gas permeation experiments of O_2 and N_2 were performed with conducting PPy composite membranes prepared by using a PDMS as a highly permeable support. An "interfacial

methods" process easily obtained PPy composite membranes. PPy films as thin as ~200 nm effectively cover on underlying a highly permeable support. In order to understand the morphology of membranes, an investigation of the physical structure of the developed membranes has been carried out by scanning electron microscope(SEM). The polymerized films were characterized by X-ray photoelectron spectroscopy (XPS), FT-IR, wide-angle X-ray diffraction (WAXD) and Thermogravimetry (TGA) was carried out on a thermogravimetric analyzer, using high-purity nitrogen as purging gas.

2.   Experiments

Dense, homogenous, flat PDMS/Ppy composite membranes were prepared by interfacial synthesis methods. The process of the interfacial polymerization of pyrrole the first step, monomer (0.2 M) in the non-aqueous phase (n-hexane) and oxidizing agent (0.2 M) in the aqueous phase are allowed to form a film at the interface between the two immiscible phases. All the chemicals used were of reagent grade and were purchased from *Wako Chemicals, Japan*. A micro-porous stainless steel mesh (*400 Mesh, Nilaco, Japan*) or glass slide, acting as a substrate, was placed just below the interface. In the second step, monomer and dopant/oxidising agent dissolved in the two different phases, diffuse towards each other to yield a thin polymer skin at the interface. During the nucleation period, pyrrole was being oxidized to form a film. Within a few minutes, a thin film started to appear at the interface. At this point, removing the solutions over and below the film quenched polymerization. The film easily slides onto the placed mesh or glass slide; smooth and compact films could be obtained in a reproducible manner. We also found delaminated or folded patches of the film, which means that the film is mechanically integrated and flexible. It was seen that stirring inhibited both the nucleation and growth in the film formation. The collected film was allowed to dry prior to characterization.

Composite membranes were prepared by simply pouring a solution of PDMS in n-hexane on the surface of synthesized polypyrrole film and allowed to dry at either room temperature or in the oven at a preadjusted temperature. The thin film formed was carefully removed from the surface of the glass plate by simply washing with water and when necessary annealed 15min in an oven at the temperature of 70℃. The thin film formed was carefully removed from the surface of the glass plate and may be annealed overnight in an oven at a readjusted temperature.   Final thicknesses of the resulting composite membranes were in the range of 200~300 nm.

3.Resultsanddiscussion

The first parameter that was examined in this study was the effect of polymerization time on the film formation. Starting with a polymerization time from 5min, polymerization time

of pyrrole monomer was continuously increased. During the experiments, FeCl3 concentration (0.2M) and pyrrole concentration (0.2M) were kept constant. The increase of polymerization time relations a thickness of polypyrrole film, when we increased the PC composition in order to obtain thicker films, which may produce selective membranes, pyrrole amounts had also been increased to keep FeCl3 (oxidizing agent)/PPy ratio constant. A totalthickness of the prepared flat Ppy/PDMS composite membrane was about 280 m and thickness of polypyrrole as selective layer was from 100 to 600nm with pyrrole concentration (Fig. 1).

The effect of pyrrole concentrationon permeation is shown in Fig. 2, (A) and (B). Figure 2, (A) shows the film thickness dependence of the apparent permeation rate (P/L) of oxygen and ideal selectivity for oxygen to nitrogen in polypyrrole films deposited on the PDMS. PDMS itself is permselectivity to gases, the selectivity of pure gas permeates of N2 and O2through PDMS film were 2.0, which compared very well to that published in the open literate {14}. As shown in Fig. 2, (B) the oxygen permeation rate started to decrease with pyrrole concentrations (thickness of polypyrrole) and simultaneously the selectivity () started to increase. The values showed drastic changes in the vicinity of film thickness of 120~150 nm, and above a certain thickness, the values remained almost constant, irrespective of monomer concentration.
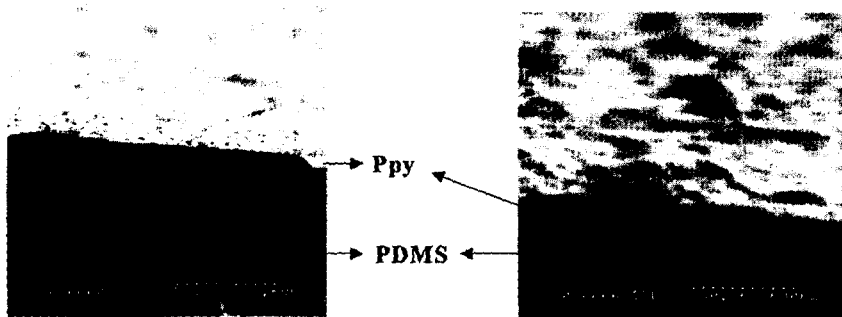

Fig. 1 The SEM image of flat polypyrrole/PDMS composite membrane after polymerizationfor30min.

Permeability obtained for these experiments were given in Fig. 3and the corresponding selectivity change at these condition were plotted in Fig. 3. Anologous selectivity and permeability coefficient versus polymerization rate were obtained for the composite membranes that yielded films thickness of 240nm ± 25nm of the polypyrrole layer coating on the PDMS support membrane surface. PPy/PDMS composite membrane showed that gas transport selectivity improved dramatically after the rate of polymerization down (increase with the concentration of ferrous chloride). Obtained permeability and selectivity for these experiments were given in Fig. 3. For example, for PPy2, compared with the polymerized membrane for PPy0.06, the O2 permeability coefficient in nearly 30 times lower than that for PPy2, while the P_{O2}/P_{N2} selectivity of former membrane is 218% higher than of the later membrane. Also, the

N_2 permeability is 57 times lower than those of polymerized membrane for PPy_2, the best performance of the PPy/PDMS composite membrane shown O_2/N_2 selectivity of 14.8 and permeability of 4×10^{-7} cm^3/cm^2 sec cmHg. In comparison with high polymerization rate, the permeability values of PPy/PDMS composite membrane decrease slight with decrease the rate of polymerization and significant improvement on the gas selectivity was observed.

Possible reason for this change in permeability and selectivity may be explained with the fact that, since the rate of polymerization decreased including ferrous chloride; possibility of forming pinhole diminishes, leading to denser structures.
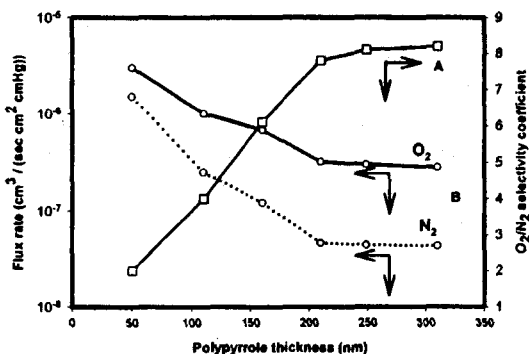

Fig. 2. Effect of polypyrrole film thickness of composite membrane on the O_2/N_2 selectivity coefficient (A) and the O_2 and N_2 permeability coefficient (B). free-standing films
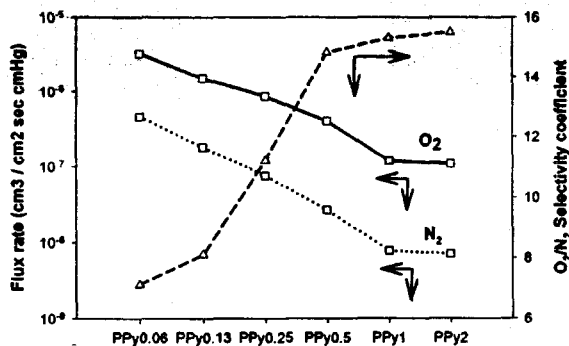

Figure 3. Effect of polypyrrole film thickness of composite membrane on the O_2/N_2 selectivity coefficient and the O_2 and N_2 permeability coefficient by the rate of polymerizations decrease.

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, $n = 2d$ sin where is the angle for a peak in the patterns. Here, 2 at the maximum intensity appearing at around 20were used to calculate the d spacing, which was representative of the average openness degree within a material. Changes in d spacing with the rate of polymerization were shown in Fig.4 (A) and (B). The d spacing of the present PPy membrane (DD = 0.5) is 4.62 , which is much high than the kinetic diameter of O_2. As the rate of polymerization increases, the d spacing decrease reaches 3.6 , which is close to the value of doped PPy film (3.67). If we compare the kinetic diameter of permeating gases, 3.46 for O_2 and 3.64 for N_2, 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.
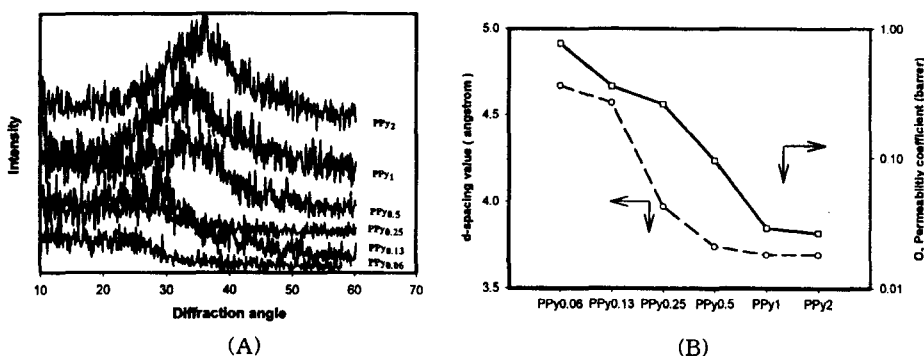

Figure 4. (A) XRD patterns of Ppy film with the rate of polymerization. (B) d spacing changes and oxygen gas Permeability coefficient of PPy/PDMS composite membrane with the rate of polymerizations. Thickness of Each PPy samples was 240 ±20nm

4.   Conclusion

The fabrication of high-flux composite membranes requires deposition of an ultrathin, discriminating layer on a highly permeable support. Gas permeation experiments of O_2 and N_2 were performed with conducting polypyrrole (PPy) composite membranes prepared by using a polydimethylsiloxane (PDMS) as a highly permeable support and polystyrene (PS) membrane. An "interfacial methods" process easily obtained PPy composite membranes. PPyfilms as thin as ~200 nm effectively cover on underlying a highly permeable support.

As the lower a rate of polymerizations, the permeability of a PPy/PDMS membrane decreased while selectivity slightly increased, probably because of the changes in morphology of PPy. PPy/PS composite membranes were studied by calculating Diffusivity and solubilityusing time-lags. d spacing of the PPy film decreased from 4.89 to 3.67 by decrease the rate of polymerization. As lower of the rate of polymerization continued, the $d$spacing decreased, resulting in a dramatic increase in selectivity of a PPy composite membrane. The

highest O_2/N_2 selectivity and permeability we obtained from PPy/PDMS composite membrane were 17 and 40 barrer, respectively. The so-called Robeson's plot comparing the data from the literature and the present membranes. All of the polymers exhibit gas separation performances below the upper bound limit. However, synthesized PPy/PDMS composite membranes are way above the upper limit.

5.Reference

1. J. M. S. Henis and M. K. Tripodi, *Science* **220**, 4592 (1983).

2. P. H. Abelson, *Science* **244**, 1421 (1989).

3. R. W. Spillman, *Chem. Eng. Prog.* **85**, 41(1989).

4. J. Haggin, *Chem. Eng. News* **68**, 22(1990).

5. T. J. Skotheim, Ed., *Handbook of Conducting Polymers* (Dekker, New York, 1986), vols. 1 and 2.

6. B. R. Saunders, R. S. Fleming, K. S. Murray, *Chem. Mater.* **7**,1082 (1995).

7. M. R. Anderson, B. R. Mattes, H. Reiss, R. B. Kaner, *Science* **252**, 1412 (1991).

8. R. V. Parthasarathy, C. R. Martin, *Nature* **369**, 298 (1994).

9. R. V. Parthasarathy, V. P. Menon, C. R. Martin, *Chem. Mater* **9**, 560 (1997).

10. J. D. Leroux, D. R. Paul, *J. Membr. Sci.* **74**, 233(1992)

11. R. Kesting, *Synthetic Polymeric Membranes: A Structural Perspective* (John Wiley & Sons: New York, 1985), pp. 224-236

12. S. Kuwabata, C. R. Martin, *J. Membr. Sci.* **91**, 1 (1994).

13. R. E. Kesting, A. K. Fritzsche, *Polymeric Gas Separation Membranes* (John Wiley & Sons: New York, 1993).

14. L. M. Robeson, *J. Membr. Sci.* **62**, 165 (1991).