Multilayer Ultrathin-Film Composite Membranes for Oxygen Enrichment

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ABSTRACT: Multilayer composite membranes were made of poly(4-methylpentene-1) (PMP), an ethyl cellulose (EC) + heptyl cellulose (HC) blend, polycarbonate (PC), polysulfone, poly(2,6-dimethylphenylene oxide), cellulose triacetate ultrathin films as selective layers, and polysulfone, poly(ether sulfone), and poly(sulfone amide) ultrafiltration membranes with a 10–45 nm pore size and 100–120 μm thickness as porous support layers. The effects of the ultrathin-film type and its casting solution concentration, operating pressure, temperature, as well as time on the oxygen-enriched air (OEA) flux and oxygen concentration in the OEA permeated in a single step through the composite membranes were investigated using a constant pressure–variable volume method. The OEA flux increases significantly with an increasing transmembrane pressure difference and operating temperature. The oxygen concentration in the OEA also increases with an increasing pressure difference but decreases slightly with an increasing operating temperature. In long-term tests, the oxygen-enrichment properties were maintained almost constant for as long as 170 h. The composite membranes consisting of the bilayer ultrathin film cast from a more dilute solution (0.11–0.26 wt %) on the porous support with a smaller pore size combine a higher oxygen-enriching ability and a higher stability than do those of monolayer and tetralayer ultrathin films. The maximum OEA flux and oxygen concentration produced at 20–75°C and a 500 kPa transmembrane pressure difference in a single pass across the PMP/98EC + 2HC bilayer and PC bilayer ultrathin-film composite membranes are 3.1×10^{-3} cm^3(STP)/s cm^2 and 50%, respectively. J Appl Polym Sci **66:** 2139–2147, 1997

Key words: composite membrane; ultrathin film; multilayer; oxygen enrichment; air separation; solution casting; operating condition; stability

INTRODUCTION

The market for oxygen-enriched air (OEA) is huge and membrane oxygen enrichment is simple and potentially energy efficient. As we know, the oxygen permeability P_{O_2} and oxygen over nitrogen separation factor P_{O_2}/P_{N_2}, generally vary inversely with one another. The P_{O_2} vs. the P_{O_2}/P_{N_2} relationship is summarized in Table I for a variety of selected polymeric materials having the potential to be industrially used on the basis of many of the latest reports.[1–17] Although P_{O_2} varies over 4 orders of magnitude, the P_{O_2}/P_{N_2} varies only from 2.5 to 14.4. For the range of reasonable P_{O_2}/P_{N_2}, namely, 3–5, the oxygen concentration through the polymer membranes will range from 35 to 50% in a single stage. It should be noted that the membranes with higher P_{O_2} (35–8000 Barrers) or

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Table I Intrinsic Oxygen over Nitrogen Permselectivity of Various Selected Polymer Membranes Having Industrial Applicability

Polymer	P_{O_2} (Barrer)[a]	P_{O_2}/P_{N_2}	Ref.
Polydi(trimethylsilyl)fumarate	8000	2.8	1
Polyvinylphenyldimethylvinylsilane	7400	4.4	2
Poly(*t*-butyltrimethylsilyl fumarate)	2300	3.8	1
Fluorinated polytrimethylsilyl propyne	1963	4.75	1
Block copoly(hydrostyrene-dimethylsiloxane-sulfone)	440	2.68	3
Polyvinyltrimethyl silane	300	4.0	4
Poly(*t*-butylacetylene)	300	3.0	5
Ethyl cellulose-*g*-dimethylsiloxane (65%)	188	2.95	6
4-vinylpyridine plasma-coated silicone	115	4.9	7
Block copoly(dimethylsiloxane carbonate)	100	2.5	1
Poly(2,6-dimethylphenylene oxide)-*g*-dimethylsiloxane)	46	4.1	8
Ethyl cellulose-*g*-dimethylsiloxane (40%)	44	3.93	6
Poly(4-methylpentene-1)-*g*-vinylpyridine (73%)	35.6	7.5	9
Poly(4-methylpentene-1)	32.3	4.0	1
Polymethylphenylsiloxane	30	3.1	10
Poly(4-vinylpyridine)	28	12.2	11
Poly(4-methylpentene-1)-*g*-4-vinylpyridine (89%)	26.4	11.1	9
Polybutadiene	19	3.0	1
Poly(2,6-dimethylphenylene oxide)	17	4.8	12
Ethyl cellulose	15	3.43	1
4-Vinylpyridine plasma-coated natural rubber	13.6	5.8	7
Polyvinylpyridine/polytrimethylsilyl propyne	12.2	8.5	13
Tetrabrominated hexafluoro polycarbonate	9.7	5.4	14
Polypyrrolone	7.9	6.5	14
Polyimide	7.85	6.2	14
Tetramethyl polycarbonate	5.6	5.1	14
Polystyrene	2.63	6.28	1
Polycarbonate	1.48	5.3	15
Polyestercarbonate	1.4	8.0	14
Tetrabrominated polycarbonate	1.4	7.5	14
Polysulfone	1.3	6.7	15
Poly[4-methylstyrene/1,2-bis(dimethyl silyl)ethane]	1.2	14.4	16
Polytriazole	1.2	9.0	17
Cellulose triacetate	1.0	5.2	12

[a] 1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg.

P_{O_2}/P_{N_2} (7.5–14.4) are generally made from the polymers with a complex molecular structure of graft/block copolymers or other modified polymers. Usually, these polymers are not easy to synthesize.

Recently, we discussed oxygen enrichment through a liquid crystalline heptyl cellulose (HC)-containing[18–29] or a low molecular weight liquid crystal-containing[30–35] ethyl cellulose (EC) thin-film composite membrane. Having considered the poor stability and relatively low separative ability of monolayer ultrathin-film composite membranes, here we present oxygen enrichment studies through the composite membranes containing multilayer ultrathin-film separative layers cast from the relatively simple polymers selected from Table I in an effort to understand the increased OEA flux, increased oxygen concentration, and higher operational stability at the same time over the monolayer composite membranes.[36]

EXPERIMENTAL

Materials

Poly(4-methylpentene-1) (PMP) pellets, designated as TPX MX-004 made by the Mitsui Petro-

chemical Co., was kindly supplied by Professor Guan-Wen Chen of the Chemistry Institute of Academia Sinica. Ethyl cellulose (EC) grains with a viscosity in ethanol/toluene of ca. 0.06 Pa-s were obtained from the Shantou Xinning Chemical Works of China. Heptyl cellulose (HC) was an experimental sample that was described in our earlier articles.[19,37] The intrinsic viscosity of the HC in chloroform was 0.26 dL/g. The HC was a gummy cholesteric liquid crystalline polymer showing fluidity even at room temperature. Polycarbonate (PC) pellets were purchased from the Second Organic Chemical Factory of Tianjin China. Polysulfone (PSF) particles with the intrinsic viscosity of 0.62 dL/g were from the Shanghai Shuguang Chemicals Works of China. Cellulose triacetate (CTA) was provided by Daicel Chemicals Industries Ltd. of Japan. The degree of substitution and the number-average degree of polymerization of the CTA are 2.7 and 315, respectively. Poly(2,6-dimethylphenylene oxide) (PPO) molding and extrusion pellets were obtained from BDH Chemical Ltd., Poole, England. DYC, a type of low molecular weight liquid crystal mixture, exhibiting a cholesteric liquid crystalline phase temperature range of 29–32°C, was purchased from the Second Chemical Reagent Factory of Tianjin China. A polysulfone (PSF) ultrafiltration membrane with 10–40 nm pores was kindly provided by Dalian Institute of Chemical Physics of China. The total thickness of the PSF layer, supported by a backing fabric, was ca. 120 microns. The air-permeation rate through the PSF membrane was ca. 0.05 cm^3(STP)/cm^2 s cmHg at 30°C. The poly(ether sulfone) (PES) ultrafiltration membrane with a 15–45 nm pore size and 120 micron thickness was supplied by Hangzhou Development Centre of Water Treatment Technology of China. The poly(sulfone amide) (PSA) ultrafiltration membrane with an average pore size of 15–25 nm and the molecular weight cutoff of 10,000 was provided by the Dalian Institute of Chemical Physics of China. The thickness of the PSA layer, supported by a backing fabric, was ca. 100 microns. All solvents used were reagent grade.

Membrane Fabrication

The polymer ultrathin films were prepared by pouring the casting solutions with polymer concentrations of 0.1–0.4 wt % onto dry glass plates and evaporating the casting solvents at room temperature for ca. 24 h. The glass plate covered with the ultrathin film was immersed in the distilled water, and several hours later, the ultrathin film separated from the glass plate and floated on the water surface. This monolayer ultrathin film had a thickness of 0.3–1 μm, which was estimated by an accurate thickness gauge made in China. The monolayer composite membrane was fabricated by laminating the ultrathin film on the porous polymer ultrafiltration membrane, i.e., by inserting underwater the flat porous membrane beneath the ultrathin film floating on the water surface and then lifting or picking up out of the water the porous membrane on which the ultrathin film was covered. A multilayer ultrathin-film composite membrane was fabricated by repeatedly using the same method.

Membrane-Enrichment Measurements

Oxygen-enrichment experiments were done using a constant pressure–variable volume method. Feed air was compressed air with an oxygen concentration of 20.9% from an air compressor. The permeate gas flux of the oxygen-enriched air (OEA) through the composite membranes in a single stage was determined by measuring the change in the volume of the OEA at a constant transmembrane pressure difference. The measurement of the oxygen concentration in the OEA permeated was performed on a 491 type industrial gas analyzer. The effective membrane area was 50 cm^2. The oxygen-enrichment characteristics of all the membranes described in this study were evaluated with the devices operating at a steady-state condition of temperature and pressure.

RESULTS AND DISCUSSION

Relationships between Oxygen Enrichment and Ultrathin Film/Porous Support

Table II summarizes the oxygen-enrichment data obtained for the bilayer and monolayer composite membranes with different ultrathin films supported on the PSF, PES, or PSA ultrafiltration membranes. When the ultrathin films are placed on the PSF support, the bilayer PC ultrathin-film composite membrane shows the highest oxygen concentration of 50% but the lowest OEA flux of 6.1×10^{-5} cm^3(STP)/s cm^2. The bilayer EC/PSF ultrathin-film composite membrane shows the

Table II Effect of Ultrathin Film on the Oxygen Enrichment through the Composite Membranes (Conditions: 30°C; 24 h Operating Time; 500 kPa Pressure Difference)

Ultrathin Film[a]		Porous Support	OEA Flux [cm^3 (STP)/s cm^2]	Oxygen Concentration (%)
Top Layer	Sublayer			
PC (0.33)	PC (0.33)	PSF	6.10×10^{-5}	50.0
EC (0.13)	PSF (0.37)	PSF	9.11×10^{-5}	49.1
PMP (0.21)	96EC + 4HC (0.36)	PSF	6.05×10^{-4}	43.2
No	96EC + 4HC (0.36)	PSF	7.81×10^{-4}	37.0
PMP (0.26)	98EC + 2HC (0.15)	PSF	9.07×10^{-4}	40.3
No	98EC + 2HC (0.35)	PSF	5.42×10^{-4}	39.6
PMP (0.18)	93EC + 7HC (0.24)	PSF	4.51×10^{-4}	39.7
93EC + 7HC (0.33)	93EC + 7HC (0.33)	PSF	3.63×10^{-4}	35.6
No	93EC + 7HC (0.33)	PSF	7.74×10^{-4}	32.6
CTA (0.19)	CTA (0.19)	PES	1.26×10^{-4}	41.3
No	CTA (0.32)	PSF	2.41×10^{-4}	35.7
PC (0.17)	PC (0.17)	PES	1.59×10^{-4}	37.9
PC (0.25)	PC (0.25)	PES	1.45×10^{-4}	36.5
PSF (0.22)	PSF (0.22)	PES	1.34×10^{-4}	38.5
PSF (0.17)	PSF (0.17)	PES	3.01×10^{-4}	36.8
PPO (0.3)	PPO (0.3)	PSA	5.25×10^{-4}	33.5
PMP (0.26)[b]	98EC + 2HC (0.15)[b]	PES	8.01×10^{-4}	39.1

[a] The casting solution concentration of the ultrathin films are given in the parentheses (wt %).
[b] The effective area of the PMP layer is only 10 cm^2 but the 98EC + 2HC layer has an effective area of 50 cm^2.

second highest oxygen concentration of 49.1% and the second lowest OEA flux of 9.11×10^{-5} cm^3(STP)/s cm^2, due to the highest P_{O_2}/P_{N_2} and the lowest P_{O_2} for the PC and PSF in the six kinds of polymers (PC, PSF, PMP, CTA, PPO, EC) being used here. It should be noted that the bilayer PMP/98EC + 2HC ultrathin-film composite membrane exhibits the highest OEA flux of 9.07×10^{-4} cm^3(STP)/s cm^2 and the higher oxygen concentration of 40.3% at the same time. Other PMP ultrathin film-containing bilayer composite membranes also have both a higher OEA flux and a higher oxygen concentration. Compared with the bilayer ultrathin-film composite membranes, the monolayer ultrathin-film composite membranes exhibit ca. a 1.2–2.0 times higher OEA flux but much lower oxygen concentration. Note that the 98EC + 2HC (0.35 wt % casting solution concentration) monolayer composite membrane shows both a lower OEA flux and lower oxygen concentration than those of the PMP (0.26 wt %)/98EC + 2HC (0.15 wt %) bilayer composite membrane. Generally, the composite membrane with the bilayer ultrathin-film cast from the more dilute solution shows higher oxygen-enrichment properties than those with the monolayerultrathin film cast from a more concentrated solution. It is unnecessary to fabricate trilayer or tetralayer ultrathin-film composite membranes because of the complexity of the membrane fabrication and the dramatic decrease of the OEA flux despite the higher oxygen concentration. For example, the 96PSF + 4DYC (0.22 wt %)/EC (0.13 wt %)/ 96PSF + 4DYC (0.22 wt %)/EC (0.13 wt %) tetralayer composite membrane on the porous PES exhibits an OEA flux of 1.63×10^{-4} cm^3(STP)/s cm^2 and the oxygen concentration of 41.3% at a 500 kPa pressure difference and at 27°C after a 32 h operating time. It can be seen that the composite membranes fabricated on the PES and PSA porous supports with a bigger pore size exhibit a lower oxygen concentration than on the PSF support. Generally, the composite membranes from the ultrathin film with the same thickness show a lower OEA flux on the PES and PSA supports than on the PSF support.

Relationship between Oxygen Enrichment and Casting Solution Concentration for Ultrathin Films

The effect of the casting solution concentration of EC + HC ultrathin film on the oxygen enrichment through the composite membranes with the PSF

Table III Effect of Casting Solution Concentration of EC : HC Ultrathin Films on the Oxygen Enrichment through Composite Membranes with the PSF Ultrafiltration Membrane as a Porous Support (Conditions: 20°C; 10 h Operating Time; 450 kPa Pressure Difference)

	EC : HC (wt %)									
	98 : 2	98 : 2	98 : 2	96 : 4	96 : 4	96 : 4	96 : 4	93 : 7	93 : 7	93 : 7
Solution concentration (wt %)	0.18	0.35	0.28	0.23	0.36	0.29	0.19	0.33	0.40	0.33
Ultrathin film layer number	2	1	1	2	1	1	1	2	1	1
OEA flux $\times 10^4$ (cm^3 (STP)/s cm^2)	3.15	2.87	6.51	3.13	4.23	13.0	27.7	1.95	4.25	5.26
Oxygen concentration (%)	38.9	39.62	29.0	38.0	37.4	27.6	26.8	35.9	35.7	32.5

support is presented in Table III for the monolayer ultrathin-film composite membranes. The OEA flux increases but the oxygen concentration decreases with decreasing of the casting solution concentration because the thickness of the ultrathin films decreases. The composite membranes from the bilayer ultrathin-film cast from a more dilute solution usually show a slightly lower OEA flux but a higher oxygen concentration than those from the monolayer film cast from a more concentrated solution. Additionally, the increase of the HC content in the ultrathin films will make the OEA flux higher but the oxygen concentration lower due to the fluidity of the cholesteric liquid crystalline HC even at room temperature.

Relationship between Oxygen Enrichment and Operating Temperature

The OEA flux and oxygen concentration through five types of composite membranes were investigated at 20–75°C and 500 kPa transmembrane pressure drop after a 4–144 h operating time. As shown in Figure 1, the OEA flux at 70°C is 4.0–4.8 times as high as is the OEA flux at 25°C, but the oxygen concentration at 70°C is 89–95% the size of the oxygen concentration at 25°C. Increasing the operating temperature gives rise to a strong increase in the polymer segmental motions, causing exponential increases in the molecular diffusion rates. Higher temperature tends to generate less discriminating gaps or free volume in the membranes. The OEA also becomes less condensable as the temperature increases. The net results of these changes are generally a higher OEA flux but lower oxygen concentration through the composite membranes. The slope of the OEA flux vs. temperature curves increases with increasing temperature, which is similar to that typically observed for homogeneous dense thick membranes and monolayer ultrathin-film composite membranes, but the oxygen concentration vs. temperature relationship differs from the results of the thick membranes and the monolayer ultrathin-film composite membranes. The slope of the oxygen concentration through the bilayer ultrathin-film composite membranes vs. operating temperature curves decreases with increasing temperature. In the whole temperature range of five types of ultrathin-film composite membranes, the bilayer PC ultrathin-film composite membrane exhibits the lowest OEA flux but the highest oxygen concentration (ca. 49.5% at 27°C). On the contrary, the PMP/96EC + 4HC bilayer ultrathin-film composite shows the highest OEA flux of 3.04×10^{-3} cm^3(STP)/s cm^2 and the third highest oxygen concentration of 39.3% at 71.5°C. This PMP/96EC + 4HC bilayer composite membrane should be considered to possess the best comprehensive performance of oxygen enrichment at an elevated temperature.

Relationship between Oxygen Enrichment and Pressure Difference

The effect of the varying operating pressure difference from 50 to 500 kPa or the pressure ratio from 0.67 to 0.17 on the OEA flux and oxygen concentration through the composite membranes is shown in Figure 2. The increase of the operating pressure difference from 100 to 500 kPa is found to increase both the OEA flux (7.1–10.4 times higher) and oxygen concentration (1.4–1.5 times higher). An increase in the OEA flux is caused by a significant acceleration in the rate of the OEA passing across the membranes with increasing pressure difference or reducing pressure ratio.

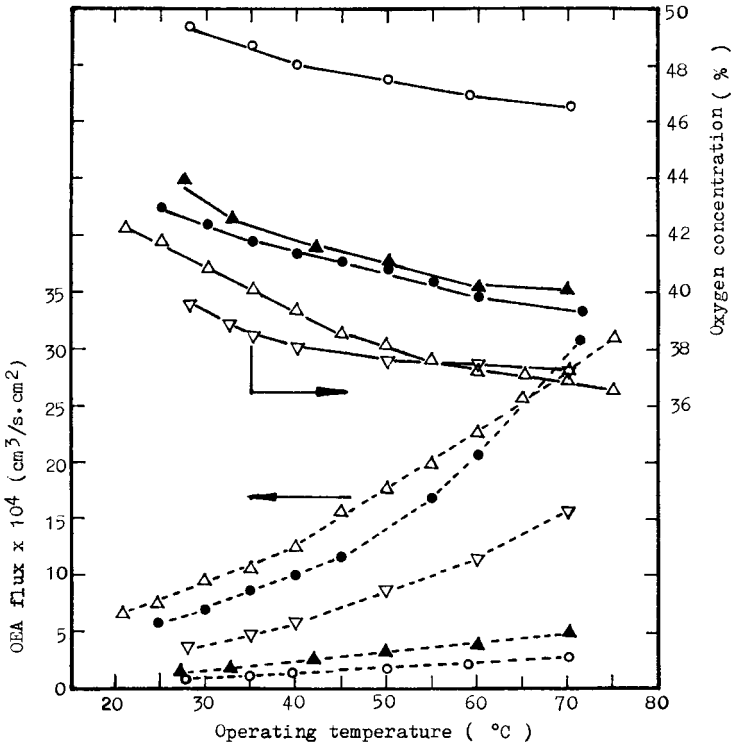

Figure 1 Effect of operating temperature on the OEA flux (dotted lines) and oxygen concentration (solid lines) at a 500 kPa pressure difference in a single stage through the composite membranes with the ultrathin films of the (○) bilayer PC cast from a 0.33 wt % solution after 24 h operating time (PSF support), (●) PMP (0.21 wt %)/96EC + 4HC (0.11 wt %) bilayer after 144 h operating time (PSF support), (△) PMP (0.26 wt %)/98EC + 2HC (0.15 wt %) bilayer after 24 h operating time (PSF support), (▲) bilayer CTA (0.19 wt %) after 4 h operating time (PES support), and (▽) monolayer CTA (0.1 wt %) after 24 h operating time (PES support).

The part of the increase in the OEA flux with the increasing pressure difference is simply a result of the standard permeation expression, although increasing the pressure difference would compress the membranes and then reduce the flux slightly. The compression could be localized between the ultrathin toplayer and the ultrathin sublayer, between the ultrathin sublayer and the porous support, as well as in the porous support. Such compressions would tend to increase the denseness of the ultrathin film but decrease the porosity in the support. Both of them would enhance the oxygen concentration to some extent. Note that the slope of the OEA flux vs. pressure curves increases slightly with increasing of the pressure difference, indicating that the pressure dependence of the OEA flux becomes stronger. On the contrary, the slope of the oxygen concentration vs. pressure curves decreases slightly with increasing of the pressure difference, suggesting that the pressure dependency of the oxygen concentration becomes weaker. This oxygen-enrichment properties vs. pressure relationship is akin to those typically observed for homogeneous dense thick membranes and monolayer ultrathin-film composite membranes. For a fixed transmembrane pressure difference of 500 kPa, the PMP/98EC + 2HC bilayer ultrathin-film composite membrane exhibits the highest OEA flux of 1.05 $\times$ 10^{-3} cm^3(STP)/s cm^2, while the PMP/96EC + 4HC bilayer ultrathin-film composite membrane exhibits an oxygen concentration of 42.3%. It can be inferred that the OEA flux might reach the higher value of ca. 2.5 $\times$ 10^{-3} cm^3/s cm^2 or the PMP/98EC + 2HC bilayer composite membrane at 27°C and the oxygen concentration might reach the higher value of 53% for the PMP/96EC + 4HC bilayer composite membrane at 32°C in a single stage under the transmembrane pressure difference of 1.0 MPa.

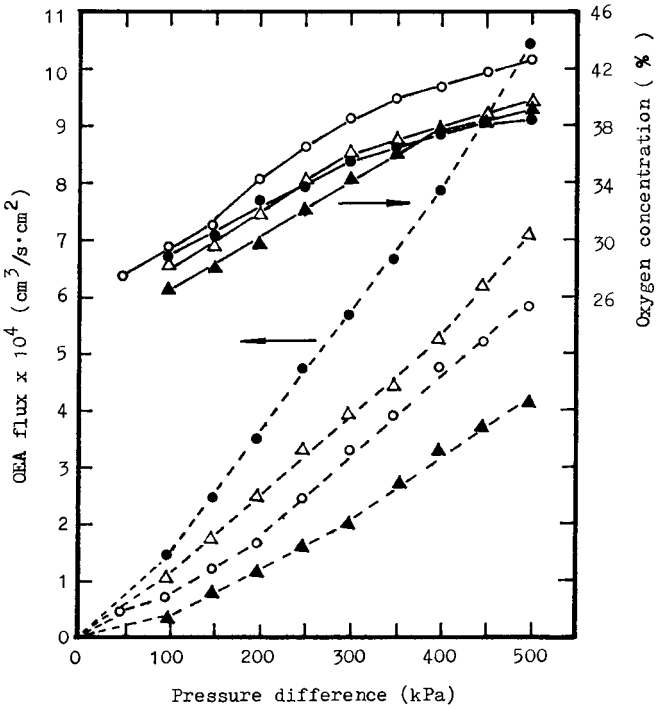

Figure 2 Effect of transmembrane pressure difference on the OEA flux (dotted lines) and oxygen concentration (solid lines) in a single step through the composite membranes with the ultrathin films of the (○) PMP (0.21 wt %)/96EC + 4HC (0.11 wt %) bilayer at 27°C after 24 h operating time (PSF support), (●) PMP (0.21 wt %)/96EC + 4HC (0.11 wt %) bilayer at 29°C (PSF support), (△) PMP (0.26 wt %) with the effective area of 10 cm^2/98EC + 2HC (0.15 wt %) at 27°C after 18 h operating time (PES support), and (▲) monolayer CTA (0.1 wt %) at 31°C after 3 h operating time (PES support).

Relationship between Oxygen Enrichment and Operating Time

Operating reliability is the most generally significant problem in membrane-based gas-separation processes. The variation of the OEA flux and oxygen concentration through seven types of ultrathin-film composite membranes with operating time is given in Figure 3. When the operating time is within 50 h, the decrease of the OEA flux and the increase of the oxygen concentration were observed only for the bilayer PSF ultrathin-film composite membrane, probably owing to the membrane compaction between the ultrathin film layers and the porous support layer. It is interesting that there are no significant changes in both the OEA flux and the oxygen concentration for the other six types of ultrathin-film composite membranes for the operating times of 100–170 h. The result demonstrated that a long-term oxygen enrichment might be carried out efficiently and stably in the ultrathin-film composite membranes.

CONCLUSIONS

Multilayer ultrathin-film composite membranes were fabricated and evaluated for their oxygen-enrichment properties. The oxygen-enriched air (OEA) flux and the oxygen concentration in the OEA permeated through the composite membranes are significantly influenced by the casting solution concentration, ultrathin film, porous support, operating temperature, transmembrane pressure difference, and operating time. The composite membranes which are composed of the bilayer ultrathin film cast from a more dilute solution (0.11–0.26 wt %) and the porous support with a smaller pore size combine high oxygen-

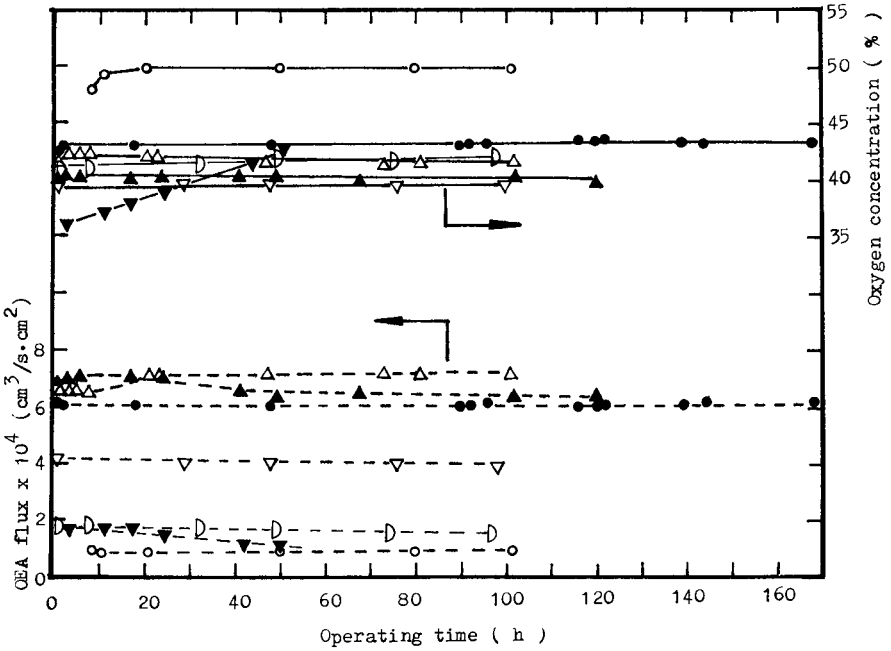

Figure 3 Effect of operating time on the OEA flux (dotted lines) and oxygen concentration (solid lines) at a 500 kPa pressure difference in a single stage through the composite membranes with the ultrathin films of the (○) bilayer PC (0.33 wt %) at 30°C operating temperature (PSF support), (●) PMP (0.21 wt %)/96EC + 4HC (0.11 wt %) bilayer at 29°C (PSF support), (△) PMP (0.26 wt %)/98EC + 2HC (0.15 wt %) bilayer at 25°C (PSF support), (▲) PMP (0.26 wt %)/98EC + 2HC (0.15 wt %) bilayer at 20°C (PES support), (▽) bilayer CTA (0.1 wt %) at 31°C (PES support), (▼) bilayer PSF (0.22 wt %) at 30°C (PES support), and (D) 96PSF + 4DYC (0.22 wt %)/EC (0.13 wt %)/96PSF + 4DYC (0.22 wt %)/EC (0.13 wt %) tetralayer at 27°C (PES support).

enrichment performance and high stability. The maximum OEA flux and oxygen concentration achieved at temperatures of 20–75°C and the transmembrane pressure difference of 500 kPa in a single pass through the multilayer ultrathin-film composite membranes are 3.1×10^{-3} cm^3-(STP)/s cm^2 and 50%, respectively. The OEA containing 35–50% oxygen through the multilayer ultrathin-film composite membranes might be used for the medical treatment of patients and for the improvement of the energy efficiency of many combustion processes.

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