Preparation of Defect-Free Asymmetric Membranes for Gas Separations

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ABSTRACT: A technique was developed to prepare defect-free, asymmetric, polymer membranes for gas separation. The preparation method eliminates the need for coatings, which are usually required to render asymmetric, polymer based, membranes gas selective. In this method, a casting solution containing a polymer, solvent, and salt additive is given a desired shape and immersed in a coagulation bath containing a nonsolvent. The nonsolvent is selected to have a low affinity for both the solvent and salt additive. After the complete coagulation of the membrane, the additive salt is leached out in a second bath. This leads to the formation of an asymmetric membrane that has a well-interconnected porous network. The fine membrane structure is preserved by solvent exchange before it is finally dried. Polyetherimide (PEI) (Ultem® 1000) membranes were prepared from casting solutions containing 23, 25, and 26.5% (wt) PEI, various amounts of lithium nitrate and N-methyl-2-pyrrolidinone (NMP). Membrane performance was determined for the separation of oxygen from air. The effects of polymer concentration, additive salt concentration and the drying process on oxygen permeance, and the actual separation factor of the membrane are discussed. The addition of a small amount of solvent to the coagulation bath improved the leaching of the salt additive and produced membranes with a more open structure. A polymer concentration of 23% produced membranes with the highest performance. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1471-1482, 1999

Key words: polyetherimide; air separation; asymmetric membrane; phase inversion; membrane preparation

INTRODUCTION

The selection of a suitable polymeric membrane material and the method of preparation play an important role in increasing the performance of gas separation membranes. The structure of the membrane, which is determined by the material properties of the polymer and the mechanisms of formation, must be optimized to produce a membrane that has a high permeance and separation factor for a component in a mixture. Composite or asymmetric membrane structures are used cur-

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rently for gas separations.¹ The desirable structural characteristics of an asymmetric membrane for gas separations are as follows:

- 1. Defect-free selective layer to avoid nonselective pore flow where gas transport occurs by viscous or Knudsen mechanisms.
- 2. The number of dead-ended pores should be minimized.
- 3. The number of selective pores, in which surface diffusion of permeate gas is predominant,² should be as large as possible.
- 4. The membrane should have a well-interconnected porous network structure to avoid high flow resistance.
- 5. The skin and overall cast film should be thin to obtain a high permeance.

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- 6. The substantial resistance of the membrane sublayer to gas transport should be as low as possible.
- 7. Macrovoid-free structure to avoid the formation of a weak layer under the skin or avoid the presence of nonselective pores.
- 8. High mechanical strength to avoid compaction under high-pressure operation.

The selection of a suitable polymeric membrane material depends on the required separation task. Glassy polymers have a rigid structure and a high glass transition temperature (T_{g}) . These properties make them suitable materials to form membranes with micropores having an excellent dimensional stability over a wide temperature range. Micropores are classified as pores or void volumes that are <2 nm in width.³ Glassy polymers are attractive materials to prepare membranes for the separation of permanent gas mixtures. This has been attributed to the flickering movement of the constituent polymer segments being moderated by the intrinsic rigidity of the polymer backbone that produces subtle sizeselective transient gaps through which gas molecules can jump. High mobility selectivity of transient gas molecules can be obtained in glassy polymers.⁴ Polyetherimide (PEI), one of these glassy polymers, is produced under the trade name Ultem[®] by General Electric, U.S.A. It is a high performance engineering amorphous thermoplastic resin.⁵ Ultem 1000 exhibits excellent mechanical, thermal, and electrical properties. Its chemical resistance is good but may be attacked by halogenated hydrocarbons, dipolar aprotic solvents, cresol, and concentrated acids and bases.^{6,7} The chemical structure of PEI is shown in Figure 1.⁸ The aromatic imide units provide stiffness and heat resistance, while the swivel groups such as -O and -C(CH3)₂ form flexible macromolecular chains that allow for good processability.⁶ The intrinsic permeabilities of oxygen and nitrogen for a dense PEI film, at 35°C, were reported by Barbari et al.⁹ as 0.4 and 0.05 barrers, respectively {1 barrer = 10^{-10} [cm³ (STP) cm/cm² s cm Hg]}. Permeabilities and selectivities at 35°C, for many glassy polymers, which can also be used for gas separation, have been reported elsewhere.⁴ The intrinsic selectivity of oxygen over nitrogen⁹ (at 35°C) for a dense PEI film is 7.6, which is higher than that for a dense polyethersulfone film (which is 5.7, reported by Wang et al.¹⁰) or for other glassy polymers reported by Koros et. al.⁴ Although PEI polymer has a lower gas permeability, its higher intrinsic selectivities for He/N₂,



Figure 1 Structure of a PEI repeat unit.

 CO_2/N_2 and O_2/N_2 makes this polymer an attractive membrane material.¹¹ However, membrane permeability can be increased by using a suitable preparation method that improves membrane morphology to obtain a high permeability without reducing membrane selectivity.

Once the polymeric material is selected, the appropriate preparation method must be determined. Generally, the following techniques or combinations of them are used in the preparation of asymmetric polymeric membranes: thermal phase inversion;¹² dry phase inversion;¹³ vapor phase inversion;¹⁴ and wet phase inversion.¹⁵ In all of these techniques, the resulting membrane structure will be affected by various formation mechanisms. These mechanisms involve one or several of the following basic processes: diffusion; evaporation; gelation; vitrification; crystallization; chemical reaction; phase conversion or separation; nucleation—growth; spinodal decomposition—coarsening; and coalescence.^{16–20}

BACKGROUND

Preparation Methods

The current industrial asymmetric membrane preparation techniques, for gas separations, are as follows: dry/wet phase inversion; phase inversion using Lewis acid : base complex solvents; and dual-bath methods.

Dry/wet Phase Inversion

In this method, a partial evaporation step is used to form the skin layer on the surface of the membrane, followed by immersion in a nonsolvent liquid medium to achieve an instantaneous phase inversion to form an interconnected open substructure.²¹

Phase Inversion by Using Lewis Acid : Base Complex Solvents²²

Relatively high amounts of nonsolvent can be added to the casting solution if the nonsolvent forms a Lewis acid:base complex with the casting solvent. The skin formation through an evaporation step or diffusion-driven process will be suppressed as a result of complex formation. Using an aqueous quench medium, a quick phase inversion occurs as a result of the rapid dissociation of the complex and the strong nonsolvent environment of the resulting Lewis acid-water-solvent combination. Highly porous and integrally skinned asymmetric membranes can be obtained. However, if these membranes are to be used in gas separations, a silicon rubber layer must be applied over the membrane to seal defects present in the skin layer of the membrane.

Dual-Bath Method

The dual-bath method has been developed to take the advantages of both the delayed phase inversion and the instantaneous phase inversion.²³ The concept of this method is to first shortly immerse the cast membrane into a nonsolvent bath to achieve a delayed phase inversion. Then, the cast film is immersed in a second nonsolvent bath to achieve an instantaneous phase inversion to form an interconnected open substructure in the support layer.

Mechanisms of Membrane Formation

The formation of a skin and the type of phase inversion play an important role in obtaining a structure required for gas separation membranes.

Skin Formation

An ultrathin skin layer is usually preferred to obtain a membrane with both a high permeate flux and separation factor. Two approaches can be used to form the skin layer: 1. A short evaporation is used to increase the polymer concentration in the top layer. This will play an important role in forming a dense skin layer. The evaporation process may be achieved by natural or forced convection.²⁴ However, highly volatile solvents such as chlorinated hydrocarbons are usually required; and 2. The formation of the dense skin film can be induced by a diffusion-driven process. This process occurs when the cast film is immersed in a nonsolvent liquid medium that has a thermodynamically poor interaction with the casting solvent. In this case, the onset of demixing is delayed, keeping the cast film as a viscous solution for a while during which the solvent diffuses easily from the outermost interface region of the cast film to the liquid quench medium. At the same time, the counter diffusion of the nonsolvent will

be delayed or reduced by the viscous nature of the casting solution. As a result of this multicomponent diffusion process, the rapid increase in the polymer concentration in the top layer of the cast film leads to the formation of a highly polarized gelled skin layer.^{1,15,16}

Type of Phase Inversion

The wet phase inversion process, which causes the asymmetric structure, can be divided into two types,²⁵ delayed phase inversion (membrane type I), and instantaneous phase inversion (membrane type II).

Delayed phase inversion. In the delayed phase inversion, the nonsolvent liquid medium and the solvent in the casting solution have a poor mutual affinity. A dense skin layer is induced by the previously described diffusion-driven process. In this situation, phase inversion proceeds slowly because of the dense top skin layer which suppresses the diffusion of the nonsolvent into the cast film, and the weak nonsolvent-solvent interaction which keeps the demixing process slow. Because this coagulation process is slow, the phase inversion will occur by nucleation and growth. The main disadvantages of type I membranes are a thick skin layer $(1 \ \mu m)$ and a closedcell structure that cause a very low permeate gas flux.¹

Instantaneous phase inversion. When the nonsolvent in the liquid coagulation medium has a strong thermodynamic interaction with the solvent in the casting solution, phase inversion is instantaneous. Because an instantaneous liquid–liquid demixing occurs, the rapid diffusion-driven process forms a very thin skin layer. A rapid phase inversion will occur and the membrane structure formed by the spinodal decomposition and coarsening processes. Generally, membranes formed by this mechanism have a very thin microporous skin layer and a finger or sponge-like open interconnected substructure.²⁶

The Proposed Method

As mentioned previously, the method used in membrane manufacture plays an important role in increasing the performance of an asymmetric membrane. The objective of this work was to prepare a membrane with a high separation factor and permeate gas flux from a single polymer without the need for a coating. It was proposed to achieve this by making a thin-skinned type I membrane having a well-interconnected porous network structure. The following materials and steps were proposed to manufacture this membrane.

To prepare the casting solution, PEI (Ultem 1000) was selected as a polymer because of its commercial availability and favorable characteristics. Anhydrous *N*-methyl-2-pyrrolidinone (NMP) was selected as a solvent because it is a powerful solvent for PEI compared with other solvents such as *N*,*N*-dimethylacetamide or dimethylformamide. When a more powerful solvent is used, a larger amount of the nonsolvent is imbibed in the coagulated polymer.²⁰ Therefore an improvement in the porosity of the polymeric structure is to be expected.

A nonsolvent medium having a thermodynamically moderate or poor interaction with the casting solvent was used in the coagulation bath. In such a case, there is a moderate delay time before the onset of demixing during which the diffusiondriven process forms the dense skin layer. A shorter delay time, before demixing in type I membranes, has been linked to the formation of a thinner skin layer.²³ Isopropyl alcohol was used to satisfy the above requirements.

To overcome the problem of the closed-cell structure often seen in type I membranes, lithium nitrate was added to the casting solution as a complexing agent. Lithium nitrate has a thermodynamically poor interaction with the isopropanol coagulant. The coagulation process is expected to occur without dissociation or leaching out of the additive salt. After a complete coagulation, the additive salt will then be leached out by using a nonsolvent having a good solubility for the salt. Methanol or water can be used to leach out the lithium nitrate. The final result of all these processes should be a skinned porous membrane having a well-interconnected open structure.

EXPERIMENTAL

Materials

Aromatic polyetherimide (Ultem 1000) was supplied by the General Electric Co. in pellet form and used after drying in an oven at 150° C for 8 h. Lithium nitrate (LiNO₃) from Fisher Scientific Co. (Ontario, Canada) was dried in the oven at 140°C for 8 h. Anhydrous 1-methyl-2-pyrrolidinone (99.5%, reagent grade) from Aldrich Chemical Co. (Milwaukee, WI). Methyl alcohol (microscopic grade), hexanes (reagent grade), and iso-

propyl alcohol were supplied from BDH Inc. (Ontario, Canada).

Membrane Preparation

Two sets of experiments were used to verify the concepts of the new preparation method. In a first set of experiments, issues surrounding the mechanisms involved in the preparation method were explored. In the second set of experiments, the effects of polymer and additive concentrations were examined.

In the first set, casting solutions of composition, shown in Table I, were cast at room temperature (22°C) under a dry nitrogen atmosphere onto a clean glass plate using a knife gap of 250 μ m. After 10 seconds, the film was immersed in a coagulation bath of isopropyl alcohol for 1 h. The film was then transferred to a leaching bath of methyl alcohol or water for 12 h. Finally, the film was solvent exchanged using hexane for 4 h followed by drying for 24 h at a temperature of 90°C, and under 725 mm Hg vacuum pressure. Before the water-wet membranes were dried, they were solvent exchanged using an isopropanol bath for 4 h followed by a hexane bath for 4 h. All baths were used under laboratory conditions, i.e., temperature of 22°C and atmospheric pressure.

In the second set of experiments, the casting solution compositions listed in Table II were studied. For the procedure described for case 11, Table I was used throughout the second set of experiments. After the membranes were solvent exchanged, they were tested for oxygen permeance and separation. They were then dried in a vacuum oven for 24 h at a temperature of 90°C, under a 725 mm Hg vacuum, and tested a second time for oxygen permeance and separation.

Membrane Testing

The average oxygen permeance (Po_2/ℓ) and oxygen separation factor, $\alpha O_2/N_2$ were determined for two or more coupons from each cast membrane. All permeation experiments were performed at a temperature of 22°C. A cross-flow test cell having a permeate surface area of 20 cm² was used. Tests were performed using standard compressed air (Air Products Co., Canada) at a pressure of 12.8 bar gauge. The permeate was discharged to atmosphere. An air feed flow rate of 400 L (STP)/min was used. The volumetric permeate gas flow rate was measured by a soap bubble flowmeter and the oxygen concentration in the permeate gas was determined using gas chromatography.

Case	Casting Solution 23% PEI in NMP with % LiNO ₃ /PEI Ratio (w/w)	Coagulation Bath	Mutual Affinity Between Solvent and Nonsolvent	Leaching Bath	Comments	Structure	Membrane Type
1	Without LiNO ₃	Water ^a or methanol ^b	Strong	—	High flux No oxygen selectivity	Open	II
2	3.3% LiNO ₃ / PEI (w/w)	Water ^a or methanol ^b	Strong	—	High flux No oxygen selectivity	Open	II
3	${f Without} {f LiNO_3}$	$\operatorname{Isopropanol}^{\mathrm{b}}$	Poor	Skip this step	No flux ^c	Closed	Ι
4	Without LiNO ₃	Isopropanol	Poor	$Methanol^{b}$	No flux ^c	Closed	Ι
5	Without LiNO ₃	Isopropanol	Poor	Water ^a	No flux ^c	Closed	Ι
6	3.3% LiNO ₃ / PEI (w/w)	$\rm Isopropanol^b$	Poor	Skip this step	No flux ^c	Open	Ι
7	3.3% LiNO ₃ / PEI (w/w)	Isopropanol	Poor	Methanol ^b	Membrane selective for O ₂ , with a reasonable flux	Open	Ι
8	3.3% LiNO ₃ / PEI (w/w)	Isopropanol	Poor	Water ^a	Membrane selective for O ₂ , with a reasonable flux	Open	Ι
9	$\begin{array}{c} \text{Without} \\ \text{LiNO}_3 \end{array}$	Isopropanol + 5% NMP (v/v)	Poor	$Methanol^{b}$	No flux ^c	Closed	Ι
10	3.3% LiNO ₃ / PEI (w/w)	Isopropanol + 5% NMP (v/v)	Poor	Skip this step	Membrane selective for O_2 , with a lower flux than in case 7 and 8	Open	Ι
11	3.3% LiNO ₃ / PEI (w/w)	Isopropanol + 5% NMP (v/v)	Poor	$Methanol^{b}$	Membrane selective for O ₂ , with best performance	Open	I

Table I Membrane Characteristics Using Various Coagulation Baths

Casting solutions were cast on a glass plate. After 10 sec, the glass plate was dipped in a coagulation bath (held at 22°C) for 1 h. The membrane was then transferred to a leaching bath (held at 22°C) for 12 h. Unless otherwise stated, all membranes were tested at an operating pressure of 6.9 bar gauge, and the permeate discharged to atmosphere.

^a Membranes were solvent exchanged with isopropanol for 4 h, then in hexane for 4 h and dried at 90°C in a 725 mmHg vacuum for 24 h. ^b Membranes were solvent exchanged using hexane for 4 h, then dried at 90°C in a 725 mmHg vacuum for 24 h.

^c There was no gas flux when feed pressure was increased to 27.6 bar gauge, permeate discharge to atmosphere.

Oxygen Permeance and Separation Factor $\alpha O_2/N_2$ Calculation²⁷

The oxygen permeance in the nitrogen and oxygen mixture through the membrane, $(Po_2\ell)$ can be

Table II Compositions of the Casting Solutions That Were Used to Produce Membranes in the Second Part of This Study

PEI Concentration in NMP, % (w/w)	LiNO ₃ /PEI, % (w/w)							
$23 \\ 25 \\ 26.5$	$1.1 \\ 1.1 \\ 1.1$	$1.6 \\ 1.6 \\ 1.6$	2.9 2.9 2.9	$3.2 \\ 3.2 \\ 3.2$	3.8 3.8 3.8	$4.7 \\ 4.7 \\ 4.7 \\ 4.7$		

defined in terms of the partial pressure difference of oxygen across a unit area of the membrane by using the following equation:

$$(Po_2/\ell) = \frac{Q_p y o_2 T_s}{\Delta P A_m T_a} \tag{1}$$

where Q_p is the volumetric flow rate of the permeate gas mixture at atmospheric pressure and temperature, $T_a = 295^{\circ}$ K, yo_2 is the mol fraction of oxygen in the permeate gas, A_m is the surface area of the membrane, $T_s = 273.16^{\circ}$ K is the standard temperature, and ΔP is the difference in the oxygen partial pressure across the membrane, which is given by the following equation:

$$\Delta P = P_{\rm f} x o_2 - P_{\rm p} y o_2 \tag{2}$$

where P_f and P_p are the absolute pressure in the upstream and downstream of the membrane respectively; xo_2 is the fraction of oxygen in the feed gas (standard air).

A similar equation can be used to calculate the nitrogen permeance in the oxygen/nitrogen mix-ture:

$$(PN_2/\ell) = \frac{Q_p(1 - yo_2)T_s}{[P_f(1 - xo_2) - P_p(1 - yo_2)]A_mT_a} \quad (3)$$

The permeance is typically expressed in units of GPU (Gas Permeation Unit), where:

$$1 \text{ GPU} = 1 \times 10^{-6} \frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^2 \sec \text{ cm Hg}} \qquad (4)$$

For standard air mixture permeating through the membrane, the actual separation factor of oxygen over nitrogen is given by the following equation:

$$\alpha(O_2/N_2) = \frac{[yO_2/(1 - yO_2)]}{[xO_2/(1 - xO_2)]}$$
(5)

RESULTS AND DISCUSSION

As mentioned previously, a first set of experiments was performed to explore the formation of the asymmetric membrane from the PEI, lithium nitrate, and NMP casting solution system. Table I contains a list of various casting solution formulations, coagulation, and leaching baths used to identify and discuss the concepts of the sequenced steps in the proposed preparation method.

Cases 1 and 2 in Table I illustrate the situation when the coagulation bath, water, or methanol has a strong mutual affinity with the solvent NMP. The coagulation process begins with an instantaneous liquid-liquid demixing (the membrane becomes opaque soon after immersion and lifts off rapidly from the glass plate). A solid phase is formed by spinodal decomposition and coarsening to produce an open cell structure (membrane type II).¹ Microscopic examinations of cross-sections of the membranes produced in cases 1 and 2 show the presence of a fingerlike sublayer structure. Type II membrane is usually classified as a microfiltration or ultrafiltration membrane according to its end application.¹⁶ Membranes of type II are usually not suitable for use directly as gas separation membranes unless a repair coating over the membrane is applied to seal the nonselective pores.²⁸ However, type II

membranes can be used for gas separations if a selective (defect-free) dense skin layer is formed. As it is observed elsewhere,²⁶ the higher the polymer concentration in the casting solution, the denser the resulting membrane. A dense skin can be formed by an increase in the polymer concentration in the outermost top layer of the cast film. In the dual-bath method, the skin formation is achieved by a diffusion-driven process, and in the dry/wet phase inversion method, by evaporation. The later method was further developed²⁴ by using forced convection instead of normal evaporation to produce a defect-free ultrathin-skinned asymmetric membrane suitable for gas separation.

Cases 3 to 11 in Table I illustrate situations in which the coagulation medium has low mutual affinity with the solvent NMP. In these cases, isopropanol was used as a coagulant. Upon immersion of the cast film in the coagulation bath, it is observed that the membrane lifts off the glass plate after 2 to 3 min. This slower release from the glass plate indicates a delayed phase inversion. In this case, a diffusion-driven process occurs before demixing to induce the formation of the skin layer. As the coagulation process continues, the solid phase is formed by the nucleation and growth to produce a closed cell structure (membrane type I).¹ Microscopic examinations of cross-sections of the membranes produced in cases 3 to 11 reveal the typical sponge-like structure often found in type I membranes. As can be observed in cases 3 to 6, a coagulation time of 1 h in isopropanol was sufficient to form a tight structure through which there was no gas flux even when the feed air pressure was increased to 27.6 bar gauge.

To obtain a reasonable gas flux through type I membranes, a complexing agent which has a thermodynamically poor interaction with the nonsolvent in the coagulation bath was added to the casting solution. The poor mutual affinity between isopropanol and lithium nitrate can be observed in case 6. Because the leaching process was skipped in case 6, the membrane still had a closed cell structure. This indicated that leaching of the lithium nitrate did not occur in the coagulation bath.

When a leaching bath of methanol or water was used as in cases 7 and 8, membranes suitable for air separation were produced. Lithium nitrate is very soluble in either water or methanol. Both membranes had a reasonable permeate flux and oxygen separation factor. This suggests that using two separate steps, coagulation followed by leaching, yields a membrane having a well-interconnected porous structure.

As seen in case 9, the addition of NMP to the coagulation bath did not open the structure of the membranes produced from the casting solution that did not contain lithium nitrate. When 3.3% (wt %) lithium nitrate was added to the casting solution and 5% of NMP (vol %) were added to the isopropanol bath, the partial leaching of the lithium nitrate in the coagulation bath was observed as in case 10, Table I. Comparing cases 6 and 10, the low permeate gas flux through the membrane in case 10 indicates that during coagulation in a bath containing 5% NMP in isopropanol, some lithium nitrate was leached out leaving a partially open structure. Therefore, the penetration of the nonsolvent into the coagulating membrane film improved the final removal of lithium nitrate from the membrane in the leaching bath.

The presence of NMP in the coagulation bath reduces the difference in chemical potential across the nascent skin layer. This causes a slower outflow of solvent from the cast film into the coagulation medium. The diffusion-driven transport is reduced as the content of the solvent increases in the coagulation bath. Then, the delay time before the onset of demixing will increase with a slower outflow of solvent giving a sufficient amount of time for the solvent to diffuse from the bulk of the casting solution to the depletion region under the skin layer. Therefore, the intermediate layer under the skin will have a moderate gradient in density, offering a good uniform support for the thin skin layer.

The strong mutual affinity between the NMP in the nonsolvent medium and the polymer will also affect the density of the resulting membrane. The presence of solvent in the imbibed quench medium has two effects, an increase in the amount of the coagulant required to achieve the polymer precipitation and an increase in the swelling effect, which forces the coagulant to imbibe inside the polymer film. Therefore, a total increase in the imbibed liquid into the nascent membrane will inherently lead to a decrease in density of the resulting skin layer and overall membrane.

Finally, as a result of this preliminary study, membranes produced using the technique described in case 11, Table I, show substantial promise as air separation membranes. The technique offers the possibility of forming type I, defect-free membranes that have good gas permeate flux. These membranes also have a strong mechanical structure because the formation of macrovoids was suppressed by the following: a delayed phase inversion, the addition of solvent to the coagulation bath,²⁹ and the addition of lithium nitrate to the casting solution. Huang and Feng^{20} have observed that the amount of nonsolvent required to precipitate the polymer is reduced when lithium nitrate is present in the casting solution.

Using the sequence of steps shown in case 11, Table I, a second set of experiments was performed based on the casting solutions described in Table II. The effect of polymer concentration, additive salt concentration, and the drying process on the performance of the membranes were studied before and after drying at 90°C under 725 mm Hg vacuum pressure for 24 h.

Effect of Initial Polymer Concentration in the Casting Solution

In the second set of experiments, three polymer concentrations were used to determine the effect of polymer concentration in the casting solution on the performance of the membranes. The relationship between log of the oxygen permeance and oxygen separation factor were plotted in Figure 2 for membranes produced from casting solutions shown in Table II. As shown in Figure 2(a,b), the highest productivity, defined as the highest simultaneous oxygen permeance and oxygen separation factor, was obtained for membranes produced from casting solutions containing 23% by weight PEI.

Changes in membrane morphology with decreasing polymer concentration in the casting solution can be explained by the following considerations:

- 1. In general, more dilute polymer solutions require greater amounts of non-solvent to precipitate the polymer.²⁰ Then a larger amount of imbibed non-solvent in the cast membrane leads to a more porous membrane structure.
- 2. In addition, the total thickness of the membrane decreases because the film shrinkage rate is higher due to increasing solvent outflow at lower polymer concentrations in the casting solution.²⁶
- 3. It is also reported elsewhere¹⁶ that the thickness of the dense top layer in type I membranes decreases with decreasing polymer concentration.

Therefore, a thinner skin layer of lower density, a thinner membrane film, and a high-poros-



Figure 2 Plot of the oxygen separation factor vs. the log of the oxygen permeance for the separation of air using membranes produced from casting solutions shown in Table 2; (a) before drying and (b) after drying a 90°C in a 725 mm Hg vacuum for 24 h. Open symbols, before drying; closed symbols, after drying.

ity sublayer structure all decrease the membrane resistance to gas flow leading to high oxygen permeance whereas the less substantial substructure resistance maintains a high oxygen separation factor.³⁰

Effect of Lithium Nitrate Concentration in the Casting Solution

For all dried membranes produced from casting solutions described in Table II, the oxygen permeance and the actual separation factor vs the ratio of LiNO_3 to PEI (% w/w) are shown in Figures 3 and 4, respectively. All trends in Figure 3 indicate that very little, if any, permeation occurs in the absence of lithium nitrate. This is in agreement with the preliminary work illustrated by cases 4, 5, and 9 listed in Table I. As shown in Figure 3, the oxygen permeance increases as the ratio of lithium nitrate in the casting solution increases. The rate of this increase is more pro-

nounced at the lower polymer concentration of 23% PEI than at the 25% and 26.5% PEI concentrations.

The following must be considered to explain the greater effect of the addition of lithium nitrate on the 23% PEI concentration:

- Decreasing PEI concentrations lead to an increase in membrane porosity and a thinner skin layer. Therefore, the leaching process is improved due to the easier penetration of the nonsolvent into the nascent membrane and an easier outflow of lithium nitrate. Most of the total additive lithium nitrate will be leached, leaving a well-interconnected porous structure. The magnitude of this effect will be accentuated at lower polymer concentrations as seen in Figure 3, the slope of the 23% PEI concentration is greater than that of the 25% and 26.5% PEI concentrations.
- For the same reason, the sublayer will be more open and have a higher porosity so that the substantial resistance of the substructure to gas transport will be very low or negligible. However, in Figure 3, the slope of the oxygen permeance vs lithium nitrate ratio seems to be nearly identical at the higher concentrations of 25% and 26.5% PEI. This would indicate that there is a limit to the enhancement of leaching and that there is a possibility that some lithium nitrate remains entrapped in the 26.5% PEI membranes.

As shown in Figure 4, the oxygen separation factor decreases as the amount of lithium nitrate increases in the casting solution. This decline is more pronounced at the lower polymer concentra-



Figure 3 Plot of the oxygen permeance vs. the $(\text{LiNO}_3/\text{PEI})$ ratio in the casting solution for air separation for dried membranes produced from casting solutions shown in Table 2. Legend as in Figure 2.



Figure 4 Plot of the oxygen separation factor vs. the $(\text{LiNO}_3/\text{PEI})$ ratio in the casting solution for air separation by using dried membranes produced from casting solutions shown in Table 2. Legend as in Figure 2.

tion. Therefore, at the 23% PEI concentration, only a small amount of lithium nitrate is required to produce a well-interconnected porous network structure. Increasing LiNO₃/PEI ratio to >2% leads to a more open structure, which causes a large increase in gas permeance accompanied by a large decrease in the oxygen separation factor. This decrease in the gas selectivity, due to increase in pore size, can be explained by an increase in viscous and Knudsen gas transport (nonselective mechanisms for separating O_2/N_2) with respect to the surface-diffusion which is a selective mechanism for separating oxygen from nitrogen.²

Above a LiNO₃/PEI ratio of 2%, the highest oxygen separation factor was obtained for a membrane produced from the 25% PEI casting solution. This indicates that LiNO₃ was still being leached out at the 25% PEI level. Increasing the lithium nitrate concentration above 2% makes the support layer more open, while maintaining a reasonable skin density until the LiNO₃/PEI ratio exceeds 4.7%.

As the polymer concentration increases to 26.5%, a more dense and thicker-skinned membrane is obtained. Leaching is more difficult leading to a decrease in the amount of lithium nitrate removed from the total amount of salt in the initial casting solution. A smaller number of pores and a less interconnected porous network structure will cause a significant resistance to gas transport, especially through the sublayer.

Effect of Drying

As mentioned previously membrane coupons were first tested after the solvent exchange step and then tested after drying. These results were initially plotted in Figure 2. As seen in Figure 2(a, b), the drying process caused an increase in the oxygen separation factor and a decrease in the oxygen permeance. A decrease in the residual NMP content in the membrane polymer and a change in the physical and microstructure properties of the membrane material can explain the change in membrane performance.

The increase in the trace amount of residual NMP in the membrane polymer leads to an increase in swelling, a depression in the T_g and a reduction in the polymer chain packing, especially in the skin layer. Therefore, NMP acts as a plasticizer that makes polymer segments flexible and decreases the intermolecular and intramolecular interactions between the polymer chains. These changes decrease the resistance of the polymeric film to gas transport so that a higher gas permeance can be obtained.

The permeation rate of both oxygen and nitrogen increases with increase in the opening of the membrane network structure achieved by a greater amount of lithium nitrate in the casting solution. Because the oxygen separation factor is proportional to both the mobility and solubility selectivities, the change in the separation factor can be explained by the change in these two selectivities.

In the presence of residual NMP, opening membrane structure by increasing the amount of lithium nitrate in the casting solution leads to the following: 1. An increase in the diffusion coefficient due to a structure of lower density and higher network connectivity causes a decrease in the mobility selectivity; 2. An increase in the specific surface area which contains the residual NMP enhances the solubility selectivity of oxygen. Oxygen has a higher critical temperature than nitrogen. This makes oxygen more condensable and hence more soluble than nitrogen in most media.⁴ In such a case, NMP acts as a liquid transport medium; and 3. An increase in the free fractional volume of the polymeric membrane causes an increase in the T_g .³¹ However, the presence of residual NMP causes a decrease in T_g . Both effects lead to a small overall change in T_{a} . Therefore, the rigidity of the membrane materials does not change significantly and hence the solubility selectivity remains high. For these reasons, the decrease in the mobility selectivity will be partially compensated by an increase in the solubility selectivity so that a gradual decrease in the oxygen separation factor with increasing oxygen permeate flux would be obtained, as shown in Figure 2(a). On the other hand, in the absence of residual NMP, increasing the opening of the membrane network structure leads to the following: 1. A decrease in the mobility selectivity due to an increase in the diffusion coefficient resulting from a structure of lower density and higher network connectivity; and 2. An increase in the glass transition temperature which is attributed to an increase in the rigidity of the membrane materials. Then, the solubility selectivity tends to be lower and the mobility selectivity becomes dominant. Therefore, a steep decrease in the separation factor with an increase in the oxygen permeate flux would be obtained as it is shown in Figure 2(b).

The rigidity of the final membrane material plays an important role in determining the slope of the correlation between the separation factor and the log of the oxygen permeance. As it is shown in Figure 2(a,b), the absolute value of the slope of the line increases with drying or with decreasing the polymer concentration in the casting solution. The increase in this slope can be attributed to an increase in the rigidity of the membrane material. In conclusion, the rigidity of the polymer increases when NMP is removed or when the free fractional volume of the polymer increases.

The effect of the drying process on the relationship between the gas permeate flux and the oxygen concentration in the permeate which corresponds to the oxygen separation factor is shown in Figure 5 for membranes produced from casting solutions containing 23% PEI. At a lower permeate flux (<7 GPU) where the membrane structure is less open, the mobility selectivity will dominate and be greatly affected by the increase in the packing density after the drying process due to the high initial packing density before drying. For instance, the highest oxygen concentration of 54.8% was obtained for a flux 2.4 GPU. At higher permeate flux (>7 GPU), where the membrane has a more open structure, the solubility selectivity will be enhanced by the presence of residual NMP leading to a moderate decrease in the total oxygen selectivity. For instance, at a permeate flux of 21 GPU through the membrane without drying, an oxygen concentration 34% was obtained in the permeate. However, the removal of the solvent and the nonsolvent is necessary to obtain a stable membrane.

A drying factor was defined as the absolute ratio of the increase in the oxygen separation factor divided by the decrease in the oxygen permeance for a given coupon. The drying factor vs. the ratio of $LiNO_3/PEI$ in the casting solution are



Figure 5 Plot of the permeance vs. the concentration of oxygen in the permeate for air separation by using dried membranes produced from casting solutions shown in Table 2.

plotted in Figure 6. Higher drying factors indicate greater improvement in membrane performance on drying. As can be observed in Figure 6, for all concentrations, the best improvement on drying was obtained at lower LiNO₃/PEI ratios. Reasonable fits were obtained for the 23% ($r^2 = 0.82$) and 25% ($r^2 = 0.82$) concentrations. The omission of one outlier at the 26.5% PEI concentration produced a similar fit. There seems to be a maximum improvement at a median concentration of 25% PEI. Explanations for this maximum are in good agreement with the results presented in Figure 4. As mentioned previously, LiNO₃ was still being leached out of the nascent membrane at the 25% PEI level. Above this level, LiNO₃ was more difficult to leach out leading to a denser skin, a smaller number of pores, and a less interconnected porous network structure.

CONCLUSIONS

- 1. A defect-free, asymmetric membrane having a skin of gradual density and a wellinterconnected porous structure can be produced for the separation of permanent gas mixtures, The proposed approach does not require an additional repair coating. Oxygen concentrations of >50% in the permeate were obtained for air separation.
- 2. When isopropanol is used as a coagulating agent for a casting solution containing PEI/LiNO₃/NMP, the coagulation process occurs without the leaching of lithium nitrate from the cast film.
- 3. The addition of NMP to the coagulation bath enhances the leaching of lithium ni-



Figure 6 The LiNO_3/PEI ratio in the casting solution vs. the drying factor. The drying factor is the absolute increase in the oxygen separation factor by the decrease in the oxygen permeance as a result of drying membranes produced from casting solutions shown in Table 2.

trate in the second bath yielding a more open membrane.

- 4. Membranes produced from casting solutions containing 23% PEI in NMP have higher performance (productivity) than the membranes produced from casting solutions in which the PEI concentration is greater than 23%.
- 5. The lithium nitrate concentration in the casting solution can be adjusted to produce membranes that have the desired oxygen permeance or oxygen separation factor. It was also found that the addition of lithium nitrate to the casting solution had a greater effect at lower polymer concentrations.
- 6. The highest selectivity was obtained for a membrane produced from casting solutions containing 23% PEI when the LiNO₃/PEI ratio was <2% (w/w), or from casting solutions containing 25% PEI when the LiNO₃/PEI ratio was above 2% (w/w).
- 7. The presence of residual solvent (NMP) in the PEI membrane improves the solubility selectivity, which maintains the oxygen separation factor high at a higher gas permeance of >7 GPU. This is useful to obtain higher productivity. Unfortunately, the performance of the membrane is not stable and the solvent is usually removed slowly during the running time.
- 8. The rigidity of the membrane increases on

drying at 90°C under vacuum. This increase causes a different effect on the performance of the membrane at different porosities. For instance, for testing membranes produced from casting solution that contained 23% PEI, the performance of the membrane was better before drying when the permeate flux was >7 GPU, whereas the performance of the membrane was better after drying when the permeate flux was <7 GPU.

 An increase in the LiNO₃/PEI ratio in the casting solution causes a decrease in the drying factor.

NOMENCLATURE

- A_m the active permeation surface area of the membrane (cm³)
- ℓ the effective thickness of the membrane (cm)
- P_f the absolute pressure at the upstream of the membrane (cm Hg)
- P_p the absolute pressure at the upstream of the membrane (cm Hg)
- P_{N_2} the nitrogen permeability [cm³ (STP) cm/cm² sec cm Hg]
- Po_2 the oxygen permeability [cm³ (STP) cm/cm² sec cm Hg]
- (P_{N_2}/ℓ) the nitrogen permeance $[cm^3 (STP)/cm^2 sec cm Hg]$
- (Po_2/ℓ) the oxygen permeance [cm³ (STP)/cm² sec cm Hg]
- Q_p the volumetric flow rate of the permeate gas mixture (cm³/sec)
- T_a the ambient temperature (°K)
- T_s the standard temperature (273.15°K)
- x0₂ the mol fraction of the oxygen in the feed gas mixture (mol/mol)
- yo₂ the mol fraction of the oxygen in the feed gas mixture (mol/mol)
- $\alpha(O_2/N_2)$ the actual separation factor for oxygen over nitrogen, dimensionless
- ΔP the oxygen partial pressure difference across the membrane (cm Hg)

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