

# Solid polymer electrolyte composite membranes for olefin/paraffin separation

Ingo Pinnau\*, Lora G. Toy<sup>1</sup>

*Membrane Technology and Research Inc., 1360 Willow Road, Suite 103, Menlo Park, CA 94025-1516, USA*

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## Abstract

Ethylene and propylene are produced in larger quantities than any other organic compound. Production of these olefins requires separation of the olefins from the corresponding paraffins. Distillation is currently used but this is an extremely energy-intensive process due to the very low relative volatility of the components. Previous studies have shown that facilitated transport membranes can have high selectivity for olefin/paraffin separation. However, four problems have limited the commercial application of facilitated transport membranes: (i) poor mechanical stability, (ii) the difficulty in preparing thin, high-flux composite membranes, (iii) the requirement of a water-vapor-saturated feed to provide mobility for the olefin-selective carrier, and (iv) poor chemical stability due to carrier poisoning. Solid polymer electrolytes are a novel class of facilitated transport membranes for olefin/paraffin separation. These membranes solve the first three problems listed above. Solid polymer electrolyte membranes are based on rubbery, polyether-based polymers containing a dissolved olefin-complexing metal salt. Solid polymer electrolyte composite membranes made from poly(ethylene oxide) loaded with silver tetrafluoroborate showed an ethylene/ethane selectivity of up to 240 and an ethylene permeance of  $8 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ s cmHg}$  with a *dry* feed gas mixture. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Ethylene and propylene are the most important chemicals used in the petrochemical industry. About 40 billion pounds of ethylene and 25 billion pounds of propylene are produced annually in the US, primarily for the production of polyethylene, polypropylene, styrene, ethylbenzene, ethylene dichloride, acrylo-

nitrile, and isopropanol [1]. An important step in the manufacture of olefins is large-scale separation of the olefin from the corresponding paraffin. Currently, this separation is carried out by distillation, which is highly energy-intensive due to the cryogenic temperatures required for the process. Distillation columns are often up to 300 feet tall and typically contain over 200 trays. With reflux ratios greater than 10, a very high energy input is required for the distillation process [1].

Membrane technology has been proposed as an alternative approach to the conventional distillation process for olefin/paraffin separation [1–10]. However, the permeabilities and olefin/paraffin selectivities of the conventional polymer membranes used in

\* Corresponding author. Tel.: +1-650-328-2228/ext. 113; fax: +1-650-328-6580.

E-mail address: ipin@mtrinc.com (I. Pinnau).

<sup>1</sup> Present address: Department of Chemical Engineering, North Carolina State University, Suite 3100 Partners II Building, Main Campus Drive, Raleigh, NC 27606, USA.

Table 1  
Solubility of silver salts in poly(ethylene oxide) [12]

Anion	Solubility
Cl <sup>-</sup>	Insoluble
Br <sup>-</sup>	Insoluble
I <sup>-</sup>	Insoluble
SCN <sup>-</sup>	Soluble
ClO <sub>4</sub> <sup>-</sup>	Soluble
CFSO <sub>3</sub> <sup>-</sup>	Soluble

membrane-based gas separation processes are generally too low for an economically viable process. The performance of polymeric membranes for ethylene/ethane separation is particularly poor. Currently, the best polymeric membranes exhibit ethylene/ethane selectivities of only 4–5 [7–9]. An alternative approach is to use facilitated transport membranes, which are highly olefin/paraffin selective and have sufficiently high olefin permeabilities [4–6,10]. However, current facilitated transport membranes are unstable under industrial operating conditions or require expensive downstream processing [3,4,10].

Our approach to improving facilitated transport membranes is based on recent work on solid polymer electrolytes made from rubbery, ether-based polymers containing dissolved metal ions. The bulk of the published work on polymer electrolytes has focused on rubbery poly(ethylene oxide)-based conductors of lithium (I) ions for applications in high-energy batteries [11–14]. In solid polymer electrolytes, both anions and cations are sufficiently mobile in the rubbery polymer matrix without the need of a solvent or plasticizer to promote conductivity [11,12]. As a result, dry polymer electrolyte films can exhibit conductivities up to 10<sup>-4</sup> S/cm [12]. Recent reports have shown that poly(ethylene oxide) can dissolve a wide variety of inorganic salts, including silver salts. Table 1 shows the solubility of silver salts in poly(ethylene oxide) in the solid state [12].

## 2. Background

### 2.1. Immobilized-liquid and solvent-swollen fixed-site carrier membranes

The most commonly used facilitated transport membrane types are: (i) immobilized liquid mem-

branes (ILMs) and (ii) solvent-swollen, fixed-site carrier membranes. ILMs are made by impregnating a microporous membrane with a solution containing the carrier. The carrier solution is held within the pores of the membrane by capillary forces [5,6,10]. Although ILMs have shown very high selectivity for the separation of olefins from paraffins, their mechanical and long-term stability is poor, because of solvent and carrier loss during high-pressure operation [4,5,10].

Nonporous, solvent-swollen fixed-site carrier membranes have been used to improve the mechanical stability of facilitated transport membranes. For example, LeBlanc et al. used a water-vapor-saturated sulfonated poly(phenylene oxide) cation-exchange membrane with an Ag<sup>+</sup> counter-ion carrier to separate ethylene/ethane mixtures [15]. Water-vapor-saturated poly(perfluoro sulfonic acid) [Nafion<sup>®</sup>] and crosslinked poly(vinyl alcohol) have also been used as polymer matrix materials for olefin-selective silver salts [16–23]. These water-swollen membranes exhibit excellent separation properties. However, unless water and/or plasticizers, such as glycerine, are present in the polymeric membrane matrix, tight ion-pairing of the silver salt occurs, resulting in very low mobility of the carrier species and, consequently, very low gas fluxes. As a result, fixed-site carrier membranes must be operated continuously in a water-vapor-saturated environment. The addition of water vapor to the feed and permeate stream and the required subsequent removal of water vapor from the olefin-rich permeate stream make the use of these membranes impractical for industrial applications.

Facilitated transport membranes differ from conventional polymer membranes by employing a carrier in the membrane that selectively forms a complex with one of the components in the feed gas. Gas permeation across a facilitated transport membrane takes place by two mechanisms: first, solution/diffusion of uncomplexed gas molecules, and second, diffusion of the carrier-gas complex. The second mechanism occurs only for gases that can react chemically with the carrier. The total flux of the membrane is the sum of the flux of the carrier-gas complex and the flux of the uncomplexed gas molecules [4].

Numerous complexing agents have been studied as carriers for facilitated transport membranes [4,10,24–27]. The carriers most commonly used for facilitated membranes for olefin/paraffin separation

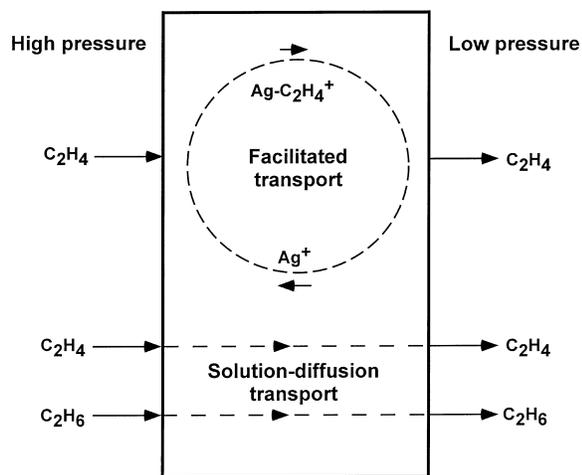


Fig. 1. Schematic representation of a liquid facilitated transport membrane containing a mobile silver salt carrier that reacts reversibly with ethylene.

are  $\text{Cu}^+$  and, particularly,  $\text{Ag}^+$ . The reaction of an olefin with a metal cation results from the interaction of the olefin  $\pi$ -orbital with the  $\sigma$ - and  $\pi$ -orbitals of the metal.

The mechanism by which facilitated transport takes place in a liquid membrane containing silver ions is illustrated schematically in Fig. 1 for the separation of ethylene/ethane mixtures. On the high-pressure side of the membrane, both ethylene and ethane are sorbed into the membrane. However, only ethylene forms a complex with the silver-ion carrier, providing significantly increased solubility of ethylene in the

membrane. Desorption of ethylene at the low-pressure side of the membrane leads to dissociation of the ethylene–silver complex. The ethylene flux of the membrane depends on the concentration of the silver ions and the equilibrium constant for the reaction between the silver ion and ethylene. Fig. 1 implies that the ethylene–silver complex is mobile and diffuses across the membrane acting as a shuttle for the transport of ethylene. However, it is far from clear that this mechanism occurs in solid polymer electrolyte membranes. We suspect that the increase in ethylene flux is due mostly to enhanced solubility of the ethylene in the membrane. The ethylene–silver ion complex is believed to be sufficiently labile for transport of the ethylene molecules hopping from site to site through the rubbery polymer matrix, as shown schematically in Fig. 2. This mechanism was previously suggested to describe facilitated transport in fixed-site carrier membranes [28,29].

## 2.2. Solid polymer electrolyte facilitated transport membranes

Solid polymer electrolytes, such as ether-based, rubbery polymers containing dissolved metal ions, are an alternative type of facilitated transport membrane [30–32]. This approach is based on previous studies using solid-state conductors based on lithium–poly(ethylene oxide) polymer electrolytes. In these systems, the salt dissolves in a polymer matrix in the solid state and dissociates into anions and cations. Interaction of the metal cation of the dissolved salt

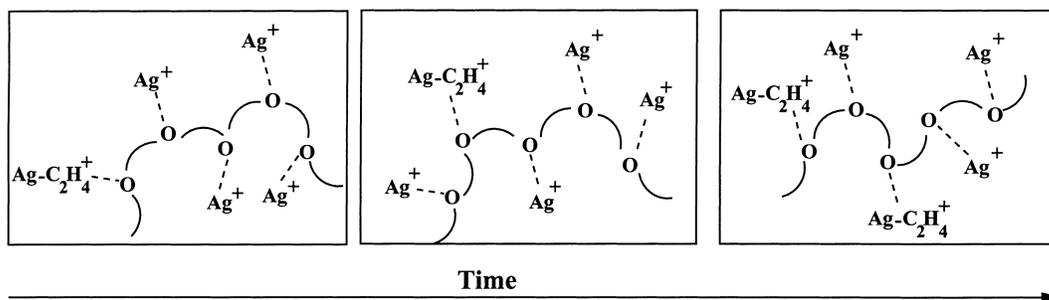


Fig. 2. Proposed transport mechanism of olefin molecules in an ether-based solid polymer electrolyte membrane (ether:silver-ion mole ratio = 1:1). Complexation results from coordination of the oxygen electron donor groups in the poly(ethylene oxide) backbone with  $\text{Ag}^+$  ions, cation–anion separation, silver–olefin complexation, and olefin transfer from chain to chain by hopping from site to site due to extensive thermal motions of the rubbery polymer matrix.

and electron donor pairs of heteroatoms in the polymer matrix, such as oxygen, can yield a conductive solid. Solvation of the cations by the heteroatoms of the polymer favors ion-pair separation in the salt.

The essential feature that distinguishes a solid polymer electrolyte from polymer/salt systems based on fixed-site carrier membranes is that ionic motions in a solid polymer electrolyte take place without a solvent or plasticizer being present. In solid polymer electrolytes, ionic transport relies on local polymer relaxation processes of flexible polymer chains [12]. To be an effective matrix for a solid polymer electrolyte membrane, a polymer should have two characteristics: (i) atoms with sufficient electron donor capacity to form coordinate bonds with metal cations and (ii) low barriers to bond rotation to provide sufficient segmental motion of the polymer chains. To date, rubbery poly(ethylene oxide) (PEO) homopolymer and PEO-based co-polymers as well as poly(phosphazenes) have been the most commonly used polymer matrixes for lithium-based high-energy batteries [11,12,33]. Because PEO forms polymer electrolyte complexes with a number of salts, including silver salts, it was selected as the preferred host material in this study. The selection of a suitable silver salt to promote facilitated transport in a solid polymer electrolyte membrane depends on the tendency of the  $\text{Ag}^+$  ion to interact with the olefin, which is sensitive to the anion-type and the rubbery polymer host.

One method of rationalizing the choice of a particular salt to be used is the hard–soft acid–base theory suggested by Pearson [12,34]. This theory predicts the stability of complexes formed between Lewis acids and bases. Acids and bases that are small, are highly electronegative, have low polarizability, and are difficult to oxidize are classified as *hard*, i.e. they hold their electrons tightly. *Soft* acids and bases have low electronegativity, tend to be large, are highly polarizable, and are easily oxidized, i.e. they hold their electrons loosely.

According to this theory, complexes are formed preferentially between hard acids and hard bases or between soft acids and soft bases. The  $\text{Ag}^+$  ion is characterized as a “soft acid” because of its low electronegativity and high polarizability [12]. On the other hand, ether-based polymers, such as PEO, have donor atoms (oxygen) with high electronegativity and low polarizability and are, therefore, “hard bases”. As a

result,  $\text{Ag}^+$  ions only interact weakly with the oxygen donor atoms of the PEO host polymer. Because of this weak acid–base interaction,  $\text{Ag}^+$  ions can also be complexed by olefin molecules in the rubbery PEO matrix.

The anion type is also of significant importance for complex formation between a salt and the host polymer. Poly(ethylene oxide) has negligible anion stabilization energy, implying that anion solvation is effectively absent in ether-based polymer electrolytes [12]. Large anions with relatively low lattice energies have little tendency to form tight ion pairs, and are, therefore, favorable for the formation of solid polymer electrolyte complexes. Examples of preferred anions for solid polymer electrolytes include:  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BF}_4^-$ , and  $\text{AsF}_6^-$  [12]. In this study, we report pure- and mixed-gas permeation properties of PEO– $\text{AgBF}_4$  solid polymer electrolyte membranes for olefin/paraffin separations.

### 3. Experimental

#### 3.1. Composite membrane preparation

Microporous support membranes were made from poly(ether imide) (Ultem<sup>®</sup> 1000, General Electric, Mount Vernon, IN) by a wet phase separation method. A solution of poly(ether imide) in a mixture of dimethylacetamide and an additive was cast onto a polyester non-woven support and precipitated in water. The resulting membrane was dried in an oven at 100°C. The nitrogen permeance of the microporous poly(ether imide) membrane was 0.05 cm<sup>3</sup>(STP)/cm<sup>2</sup> s cmHg.

Solid polymer electrolyte composite membranes were made from silver tetrafluoroborate [ $\text{AgBF}_4$ ] and poly(ethylene oxide) [PEO] (Aldrich, Milwaukee, WI). The weight-average molecular weight of the PEO was 900,000 g/mol. The PEO-based membranes were made from aqueous solutions in which both PEO and  $\text{AgBF}_4$  were readily soluble. The solutions were deposited onto the microporous poly(ether imide) support using a dip-coating process. For solvent removal, the membranes were dried in an oven under vacuum at 70°C for at least for 24 h. The resulting membranes consisted of a thin (~5 μm) polymer electrolyte layer on a microporous poly(ether imide) support, as shown in the electron photomicrograph in Fig. 3.

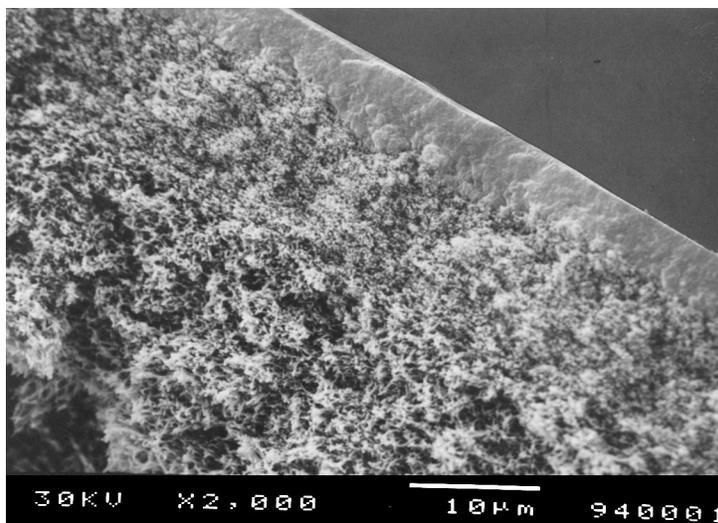


Fig. 3. Cross-section of a solid polymer electrolyte thin-film composite membrane. The membrane consists of a microporous poly(ether imide) support and a thin ( $\sim 5 \mu\text{m}$ ) poly(ethylene oxide)–silver tetrafluoroborate layer (80 wt.%  $\text{AgBF}_4$ ).

### 3.2. Characterization of gas permeation properties

The pure-gas permeation properties of the solid polymer electrolyte composite membranes were determined with ethane, ethylene, propane, and propylene at  $23^\circ\text{C}$ . The experiments were performed using the constant pressure/variable volume method at feed pressures between 50 and 500 psig; the permeate pressure was atmospheric (0 psig). Volumetric gas fluxes were determined with soap-bubble flowmeters. The membranes were also evaluated at feed pressures between 25 and 100 psig with a 50 vol.% ethane/50 vol.% ethylene mixture. The compositions of feed, residue, and permeate were determined with an online gas chromatograph equipped with an 80% Poropak N/20% Poropak Q column (Supelco, Bellefonte, PA). The ratio of permeate to feed flow rate, that is, the stage-cut, was always less than 1%. Under these conditions, the residue composition was essentially equal to the feed composition and concentration polarization effects were negligible.

The mixed-gas permeance of each gas component was calculated from the relationship

$$\left(\frac{P}{L}\right)_i = \frac{x_{2i} \times J}{(x_{1i} \times p_1) - (x_{2i} \times p_2)} \quad (1)$$

where  $(P/L)_i$  is the permeance ( $\text{cm}^3(\text{STP})/\text{cm}^2 \text{ s cmHg}$ ) of each component,  $J$  the total permeate flux ( $\text{cm}^3(\text{STP})/\text{cm}^2 \text{ s}$ ),  $p_1$  and  $p_2$  the feed and permeate pressures, respectively, and  $x_{1i}$  and  $x_{2i}$  the mole fractions of the gas components (olefin or paraffin) in the feed and permeate stream, respectively. The mixed-gas selectivity was calculated by

$$\alpha_{\text{paraffin}}^{\text{olefin}} = \frac{(P/L)_{\text{olefin}}}{(P/L)_{\text{paraffin}}} \quad (2)$$

## 4. Results and discussion

### 4.1. Pure-gas permeation properties of poly(ethylene oxide)/ $\text{AgBF}_4$ composite membranes

#### 4.1.1. Effect of $\text{AgBF}_4$ carrier concentration

To investigate the influence of the silver salt concentration on olefin/paraffin separation properties, solid polymer electrolyte composite membranes were prepared from 4 wt.% PEO solutions containing different concentrations of dissolved  $\text{AgBF}_4$ . The resulting membranes contained 33, 50, 67, and 80 wt.%  $\text{AgBF}_4$  in the polymer matrix, corresponding to ethylene oxide to silver mole ratios of 8:1, 4:1, 2:1, and 1:1, respectively. The PEO– $\text{AgBF}_4$  coatings on the

Table 2  
Effect of AgBF<sub>4</sub> carrier concentration on pure ethylene, ethane, propylene, and propane permeance of PEO/AgBF<sub>4</sub> composite membranes<sup>a</sup>

AgBF <sub>4</sub> content		Pressure-normalized pure-gas flux 10 <sup>-6</sup> cm <sup>3</sup> (STP)/cm <sup>2</sup> s cmHg)				Pure-gas selectivity	
wt.%	PEO:Ag mole ratio	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub>
0 <sup>b</sup>	–	0.55	0.46	0.89	0.36	1.2	2.5
33	8	0.18	0.10	0.22	0.11	1.8	2.0
50	4	1.6	<0.01 <sup>c</sup>	2.6	<0.01 <sup>c</sup>	>160	>260
67	2	10	<0.01 <sup>c</sup>	10	<0.01 <sup>c</sup>	>1000	>1000
80	1	55	<0.01 <sup>c</sup>	48	<0.01 <sup>c</sup>	>5500	>4000

<sup>a</sup> Feed pressure: 100 psig; permeate pressure: atmospheric (0 psig); temperature: 23°C.

<sup>b</sup> Pure PEO membrane.

<sup>c</sup> Gas flux too low (<10<sup>-8</sup> cm<sup>3</sup>(STP)/cm<sup>2</sup> s cmHg) to be accurately measured using the constant pressure/variable volume method.

microporous support were clear and showed no signs of dispersed salt crystals. The pure-gas permeation properties of the membranes were determined at 23°C with pure ethane, propane, ethylene, and propylene at a feed pressure of 100 psig. The pure-gas permeation properties of the PEO/AgBF<sub>4</sub> membranes as a function of silver salt content are summarized and compared to the properties of a pure PEO membrane in Table 2.

Pure poly(ethylene oxide) membranes exhibited poor performance for olefin/paraffin separation. The ethylene/ethane and propylene/propane selectivities of a pure PEO membrane were only 1.2 and 2.5, respectively. Composite membranes containing up to 33 wt.% AgBF<sub>4</sub> in the PEO matrix (PEO:AgBF<sub>4</sub> mole ratio = 8:1) also had poor olefin/paraffin separation properties. However, when the AgBF<sub>4</sub> concentration exceeded 50 wt.%, the complexation effect of the silver ions in the polymer membrane was clearly evident. The olefin flux now increased dramatically with increasing silver salt concentration. The pure ethylene and propylene permeances of membranes containing 80 wt.% silver salt were 50–100 times higher than those of a pure PEO membrane and 20-times higher than PEO membranes containing 50 wt.% AgBF<sub>4</sub>. These results have direct implications on the transport mechanism occurring in PEO-based solid polymer electrolyte membranes. Based on the pure-gas permeation properties, facilitated olefin transport occurred only in PEO membranes containing at least 50 wt.% dissolved AgBF<sub>4</sub>. This result suggests that the silver ions are not freely mobile in the rubbery polymer matrix. Therefore, we suggest that facilitated transport in solid polymer electrolyte membranes is likely

to occur by a hopping mechanism, wherein the olefin molecules move from silver–ether site to site across the membrane, similar to that suggested for fixed-site carrier membranes [28,29]. Based on this mechanism, the silver ions must be close enough to allow olefin molecules to diffuse from site to site. Accordingly, a threshold concentration of silver ions exists, below which no facilitation of olefin molecules occurs. This hypothesis is supported by our pure-gas permeation data in Table 2, which show that the ethylene and propylene fluxes increased dramatically for PEO membranes containing more than 50 wt.% AgBF<sub>4</sub>. Hence, the threshold concentration for facilitated olefin transport in PEO-based polymer electrolyte membranes appears to be around 50 wt.% AgBF<sub>4</sub>, which is equivalent to an ethylene oxide to silver mole ratio of 4:1. It is important to note that the pure-gas permeation properties were performed with *dry* gases and that the membranes contained neither solvents nor plasticizers. Previous fixed-site carrier membranes, such as Nafion–AgBF<sub>4</sub> or PVA–AgBF<sub>4</sub>, required either the addition of water vapor to the feed and/or permeate or the presence of a plasticizer in the polymer matrix to achieve any reasonable olefin flux. In solid polymer electrolyte membranes, we believe that the rubbery PEO matrix provides enough chain mobility for diffusion jumps by olefins from facilitation site to site beyond the required silver ion threshold, as discussed above.

As a result of the enhanced olefin facilitation effect at increased AgBF<sub>4</sub> concentration, the pure olefin/paraffin selectivity increased significantly at higher silver salt loadings. The pure-gas ethylene/ethane and propylene/propane selectivities of PEO membranes

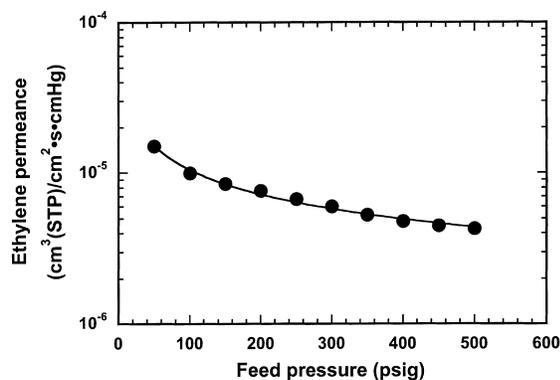


Fig. 4. Pure-gas ethylene permeance of a PEO/AgBF<sub>4</sub> (67 wt.% AgBF<sub>4</sub>) composite membrane as a function of feed pressure. Permeate pressure: atmospheric (0 psig); temperature: 23°C.

containing 80 wt.% AgBF<sub>4</sub> were about 5500 and 4000, respectively.

#### 4.1.2. Pressure stability of polymer electrolyte composite membranes

A major problem of previous facilitated transport membranes, specifically immobilized liquid membranes, is their poor pressure stability. High-pressure application of these membranes results in loss of carrier and/or water or plasticizer during operation, and, hence, severe loss in performance.

The pure-gas ethylene permeance of a solid polymer electrolyte composite membrane containing 67 wt.% AgBF<sub>4</sub> in PEO for feed pressures up to 500 psig is shown in Fig. 4. The PEO/AgBF<sub>4</sub> membrane was mechanically stable to at least 500 psig. The pure ethylene permeance decreased by a factor of 3.5 with increasing feed pressure, from  $1.5 \times 10^{-5}$  cm<sup>3</sup>(STP)/cm<sup>2</sup> s cmHg at 50 psig to  $4.3 \times 10^{-6}$  cm<sup>3</sup>(STP)/cm<sup>2</sup> s cmHg at 500 psig. This decrease in ethylene permeance resulted from partial saturation of the olefins with the available silver ions in the polymer electrolyte.

### 4.2. Mixed-gas permeation properties of poly(ethylene oxide)/AgBF<sub>4</sub> composite membranes

#### 4.2.1. Effect of AgBF<sub>4</sub> carrier concentration

The mixed-gas permeation properties of PEO membranes containing 50, 67, and 80 wt.% AgBF<sub>4</sub> were characterized with a 50/50 vol.% ethane/ethylene mixture at 23°C. The feed pressure was 100 psig;

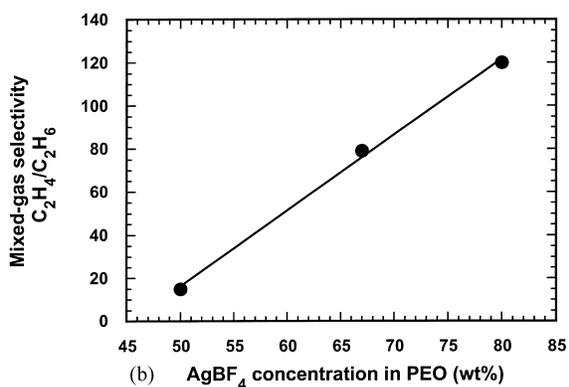
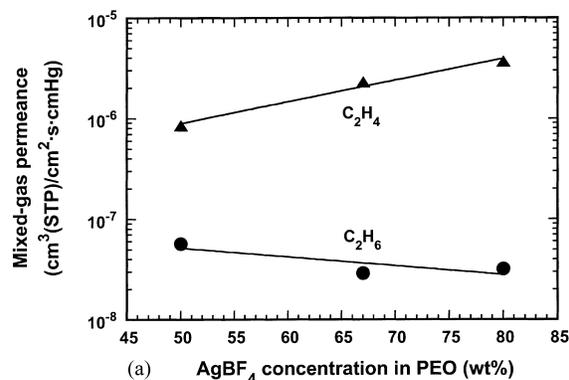


Fig. 5. Effect of solid polymer electrolyte composition on mixed-gas (a) ethylene and ethane permeance and (b) ethylene/ethane selectivity of poly(ethylene oxide)/AgBF<sub>4</sub> composite membranes. Feed composition: 50 vol.% ethylene/50 vol.% ethane; feed pressure: 100 psig; permeate pressure: atmospheric (0 psig); temperature: 23°C.

the permeate pressure was atmospheric (0 psig). The mixed-gas permeation properties of the PEO/AgBF<sub>4</sub> membranes for ethylene/ethane separation are shown in Fig. 5. Raising the AgBF<sub>4</sub> concentration from 50 to 80 wt.% increased the mixed-gas ethylene/ethane selectivity by eightfold, from 15 to 120. The improved selectivity with increasing silver content in the PEO membrane resulted from a significant increase in the mixture ethylene permeance and a concurrent decrease in the mixture ethane permeance (Fig. 5a). However, the selectivities (Fig. 5b) of the PEO–AgBF<sub>4</sub> membranes were significantly lower in the gas mixture than those obtained with pure gases (Table 2). The lower mixed-gas selectivities resulted from an increase in the ethane permeance over the

pure-gas values due to co-permeation of ethylene. Presumably, the high sorption level of ethylene increased the chain mobility of the host polymer, which led to an increase in ethane permeance through the PEO matrix of the membrane.

The properties of the PEO/AgBF<sub>4</sub> membrane are strongly dependent on the silver salt content. Provided that the AgBF<sub>4</sub> concentration is high enough (>50 wt.%), the silver ions dissolved in the PEO matrix simultaneously facilitate ethylene transport and hinder ethane transport. Further increases in carrier concentration improve the facilitated transport of ethylene, and, hence, the selectivity for ethylene over ethane. Because of its high ethylene permeance and ethylene/ethane selectivity, membranes containing 80 wt.% AgBF<sub>4</sub> were studied in more detail, as described below.

#### 4.2.2. Effect of feed pressure

The effect of feed pressure on the gas separation properties of PEO-based solid polymer electrolyte membranes containing 80 wt.% AgBF<sub>4</sub> was evaluated at feed pressures ranging from 25 to 100 psig, atmospheric permeate pressure (0 psig), and a stage-cut of less than 1%. The ethylene and ethane permeances and ethylene/ethane selectivity are shown as a function of feed pressure in Fig. 6a and b, respectively.

Raising the feed pressure from 25 to 100 psig resulted in a decrease of the ethylene/ethane selectivity from 260 to 120. This twofold reduction was caused by a decline in ethylene permeance and a simultaneous increase in ethane permeance. The decrease in ethylene permeance probably resulted from partial carrier saturation. On the other hand, the increase in ethane permeance resulted from increased chain mobility of the PEO matrix induced by the high sorption levels of ethylene. Although the ethylene/ethane selectivity and ethylene permeance decreased at higher feed pressures, the mixed-gas permeation properties of the PEO/AgBF<sub>4</sub> membrane remained extremely high for ethylene/ethane separation. The permeate ethylene concentration was relatively independent of feed pressure over the range of 25–100 psig and averaged about 99 vol.%.

#### 4.2.3. Stability of mixed-gas permeation properties

Mechanical and chemical instability are major concerns with conventional facilitated transport mem-

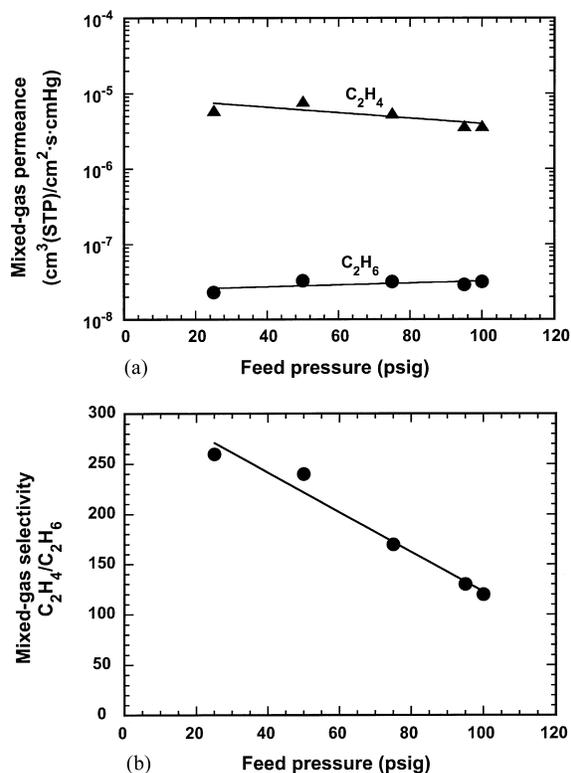


Fig. 6. Effect of feed pressure on mixed-gas (a) ethylene and ethane permeance and (b) ethylene/ethane selectivity of PEO/AgBF<sub>4</sub> composite membranes (80 wt.% AgBF<sub>4</sub>). Feed composition: 50 vol.% ethylene/50 vol.% ethane; permeate pressure: atmospheric (0 psig); temperature: 23°C.

branes. Therefore, the permeation properties of a PEO/80 wt.% AgBF<sub>4</sub> composite membrane were evaluated continuously for 16 h with a 50 vol.% ethylene/50 vol.% ethane gas mixture at a feed pressure of 50 and 0 psig permeate pressure. The mixed-gas permeation properties of the PEO/AgBF<sub>4</sub> membrane as a function of operating time are shown in Fig. 7. The degree of separation remained excellent and essentially stable over the 16 h operating period. The ethylene/ethane selectivity of 240 was essentially constant over the permeation period. However, the ethylene and ethane permeances decreased over time. During 16 h of continuous permeation, both ethylene and ethane permeances decreased to 50% of their original values. The loss in ethylene and ethane permeance may be a result of slow crystallization of the silver salt in the polymer electrolyte. In future work,

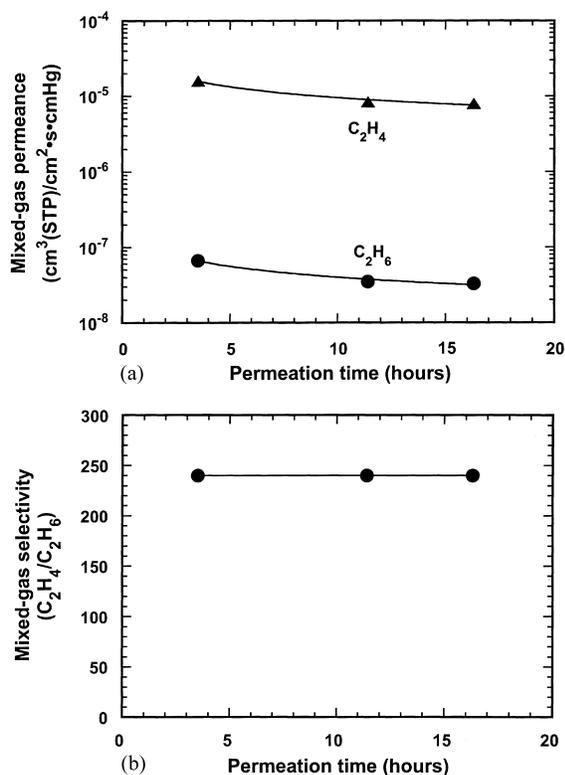


Fig. 7. Mixed-gas permeation properties a PEO/AgBF<sub>4</sub> composite membrane (80 wt.% AgBF<sub>4</sub>) as a function of permeation time: (a) ethylene and ethane permeance and (b) ethylene/ethane selectivity. Feed composition: 50 vol.% ethylene/50 vol.% ethane; feed pressure: 50 psig; permeate pressure: atmospheric (0 psig); temperature: 23°C.

we will investigate this hypothesis further using X-ray diffraction and FTIR.

## 5. Conclusions

High-flux, solid polymer electrolyte composite membranes were prepared by coating a solution containing poly(ethylene oxide) and silver tetrafluoroborate onto a microporous poly(ether imide) support. Formation of a polyether/silver salt complex resulted in the formation of a solid polymer electrolyte membrane. Permeation tests with pure gases showed a significant increase in ethylene and propylene permeance of PEO–AgBF<sub>4</sub> membranes with a silver

salt concentration of more than 50 wt.% over those of the pure PEO membrane, confirming that olefin transport results from interaction of the olefin with Ag<sup>+</sup> ions. In addition, the high carrier concentration also hinders paraffin transport. An increase in silver salt concentration in the polymer matrix increases the olefin permeance and olefin/paraffin selectivity. A PEO-based electrolyte membrane containing 80 wt.% AgBF<sub>4</sub> had a mixed-gas ethylene permeance of about  $1 \times 10^{-5}$  cm<sup>3</sup>/cm<sup>2</sup> s cmHg and an ethylene/ethane selectivity of 120–240. The solid polymer electrolyte composite membranes evaluated in this study had excellent mechanical properties. A PEO/67 wt.% AgBF<sub>4</sub> membrane was mechanically stable up to at least 500 psig.

The main advantage of solid polymer electrolyte membranes over previous types of facilitated transport membranes, such as immobilized liquid membranes or solvent-swollen fixed-site carrier membranes, is that they are mechanically stable and can be operated with a *dry* feed mixture. Furthermore, these membranes do not require incorporation of a solvent or plasticizer within the polymer/salt system. These solid polymer electrolytes can easily be made into thin-film composite membranes, thereby providing high gas fluxes. Therefore, solid polymer electrolyte composite membranes solve all the physical problems restricting the application of facilitated transport membranes to industrial applications. However, the practical use of this novel class of membranes is still limited by the poor chemical stability of currently available olefin carriers. For example, Ag<sup>+</sup> ions degrade easily if trace amounts of sulfur compounds, such as hydrogen sulfide, are present in the feed stream [4]. Furthermore, silver ions can react with acetylene to form an explosive silver acetylide salt. Hence, future work in facilitated transport membranes for olefin/paraffin separation should be directed towards the development of chemically stable olefin carriers.

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