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TUNABLE COMPOSITE MEMBRANES
FOR GAS SEPARATIONS

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J. P. Ferraris, K. J. Balkus, Jr. and I. H. Musselman

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Department of Chemistry
The University of Texas (Dallas)
P. O. Box 830688
Richardson, Texas 75083-0688

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Abstract:

Poly(3-octylthiophene), POT, membranes were selectively oxidized on one side using SbCl_5 solutions (15, 20, and 25% w/w in CH_3CN). Oxidation with a 25% SbCl_5 solution resulted in maximum decreases in permeability and increases in selectivity ($P_{\text{N}_2} = 3.1 \pm 0.2$, $P_{\text{O}_2} = 9.9 \pm 0.1$, $P_{\text{CH}_4} = 9.0 \pm 0.1$, $P_{\text{CO}_2} = 47.5 \pm 0.3$ Barrers, and $\text{O}_2/\text{N}_2 = 3.2 \pm 0.2$, $\text{CO}_2/\text{N}_2 = 15.3 \pm 0.9$, $\text{CO}_2/\text{CH}_4 = 5.3 \pm 0.3$). Oxidation of a 30% NaY/POT composite membrane with a 17% w/w SbCl_5 solution resulted in permeability values between the unmodified and oxidized POT membranes and selectivities similar to those of oxidized POT membranes ($P_{\text{N}_2} = 5.3 \pm 0.6$, $P_{\text{O}_2} = 16.7 \pm 1.8$, $P_{\text{CH}_4} = 15.3 \pm 1.2$, $P_{\text{CO}_2} = 80.1 \pm 3.7$ Barrers, $\text{O}_2/\text{N}_2 = 3.2 \pm 0.1$, $\text{CO}_2/\text{N}_2 = 15.2 \pm 0.8$, $\text{CO}_2/\text{CH}_4 = 5.3 \pm 0.2$).

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Executive Summary:

The increase in permselectivity realized upon oxidation of the conducting polymer, POT, is maintained with the addition of NaY zeolite. Simultaneously, owing to a preferential sorption-diffusion process of the gases in the NaY zeolite, this addition of zeolite increases the gas permeability of the membrane. Therefore, the strategy of combining polymer oxidation with zeolite incorporation, to prepare membranes for gas separations, is promising since gas permeability and selectivity can be increased simultaneously.

Introduction

The use of membrane technology for gas separations offers significant thermodynamic and economic advantages over distillation processes. Target separations of importance to the coal and energy fields include N_2/O_2 , $\text{H}_2\text{S}/\text{syngas}$ and CO_2/CH_4 . Current strategies for improving these separations are largely directed towards processable polymers with thin ($<500 \text{ \AA}$) skins. Unfortunately most polymeric materials that provide commercially viable permeation rates exhibit poor selectivities and *vice versa* and there are inherent limitations in gas permeability/permselectivity for pure polymers. Our strategy relies on modification of composite membranes, preferably *in situ*, to enhance the permselectivity while maintaining acceptable permeabilities. The composites consist of electroactive polymers (which can be switched from rubbery to glassy), filled with selective absorbents (zeolites) which are impregnated with metals or catalysts to effect facilitated transport. The project is multifaceted and involves the efforts of a polymer synthesis group, a microporous materials group, a microscopy group and a permeability measurements group, all working in concert. This report summarizes the results of our efforts for last quarter.

The separation properties of a composite membrane, formed by incorporating the polar, ionic NaY zeolite into the conducting polymer poly(3-octylthiophene) (POT), were reported last quarter. This quarter we determined the separation properties of the NaY/POT composite membrane following chemical oxidation. This combination of incorporating a zeolite to form a composite membrane and oxidizing the conducting polymer matrix was expected to enhance simultaneously the permeability and selectivity properties of the resulting NaY/POT composite membranes.

Experimental

Membranes of pure POT and composites with NaY zeolite (20%, 30%, and 40%, w/w) were prepared. POT membranes were oxidized with various concentrations of SbCl_5 dissolved in CH_3CN by dipping the membrane in the oxidant and also by selectively oxidizing one surface. Once the concentration and duration of the oxidant were optimized for a desirable improvement

in the separation properties, a 30% w/w NaY/POT composite membrane was oxidized with 17% w/w SbCl_5 on one side for 5 min. Its permeability properties were measured and surface and interior microstructures were characterized using OM, AFM, and SEM. The oxidized composite membranes were brittle and blue in color.

Results and Discussion

A. Oxidized POT Membranes:

POT membranes oxidized on both sides became brittle and difficult to handle. When selectively oxidized on one side, the membrane surface exposed to the oxidant developed a blue hue whereas that facing the glass plate retained its lustrous green color. These membranes were more flexible than the ones oxidized on both sides.

SEM and TMAFM were used to investigate the morphological changes brought about by the selective oxidation (one side) of POT membranes. SEM images of the membrane surface exposed to the oxidant (15% w/w SbCl_5) (top) showed scattered structures probably of the oxidant whereas those of the surface facing the glass substrate and not exposed to the oxidant (bottom) showed fewer particles. SEM images of the membrane surfaces oxidized with 20 and 25% w/w SbCl_5 solutions revealed similar deposits. SEM images of the cross-sections of POT membranes oxidized on one side with SbCl_5 showed a layer of polymer at the surface with a different morphology. The thickness of the seemingly oxidized layer differed slightly with SbCl_5 concentration. The average thicknesses of the layers for membranes oxidized with 15% SbCl_5 and 25% SbCl_5 were 3.00 and 2.79 μm respectively. TMAFM images of the oxidized surface revealed a rough structure with deposits. The RMS surface roughness increased with increasing oxidant concentration. The values of R_{RMS} were 19, 33, and 80 nm for membranes oxidized using solutions of 15, 20, and 25% w/w SbCl_5 , respectively. These values are higher than that measured for the unmodified POT membrane (10.1 nm).

Gas Separation Studies:

Unmodified POT membranes were oxidized selectively on one side for 5 min using solutions of 15, 20, and 25% w/w SbCl_5 in CH_3CN . Permeability and permselectivity data were acquired for these membranes (Table 1, Figs. 1 and 2). Compared to unmodified POT, the membranes

oxidized with 15% SbCl_5 showed a marked decrease in permeability and a slight/no increase in selectivity. Membranes oxidized with 20% SbCl_5 exhibited increases in permeability and selectivity. With 25% SbCl_5 , the permeabilities decreased and selectivities increased.

Table 1.
Permeability (in Barrers) and Permselectivity Data for POT Oxidized with SbCl_5
Dissolved in CH_3CN

	P_{N_2}	P_{O_2}	P_{CH_4}	P_{CO_2}	O_2/N_2	CO_2/N_2	CO_2/CH_4
15% w/w *	4.4 ± 0.1	11.7 ± 0.1	11.3 ± 0.1	55.1 ± 0.5	2.7 ± 0.0	12.6 ± 0.2	4.9 ± 0.1
20% w/w *	7.6 ± 0.1	24.7 ± 0.3	27.1 ± 0.4	123.5 ± 0.5	3.2 ± 0.0	16.2 ± 0.2	4.6 ± 0.1
25% w/w *	3.1 ± 0.2	9.9 ± 0.1	9.0 ± 0.1	47.5 ± 0.3	3.2 ± 0.2	15.3 ± 0.9	5.3 ± 0.3

*Errors associated with respective averages are the standard deviations of four runs with one membrane.

In unmodified POT, more segmental motion is allowed by the relatively unhindered rotation about the single bonds between the thiophene rings. Upon oxidation, double bonds are formed between thiophene rings, which restricts the rotation of the chain segments. In addition to the restricted rotation with oxidation, the polymer free volume becomes occupied partially by the dopant anion. The association of the dopant anion also increases the polarity of the polymer in the oxidized state, which increases the solubility of polar gases like CO_2 and N_2 and decreases the solubility of non polar gases like CH_4 . In addition, the solubility of gases N_2 , O_2 , and CO_2 increases and the solubility of CH_4 decreases with the increase in the concentration of the oxidant (Table 2).

Table 2. Diffusivity and Solubility for Oxidized POT Membranes

Test Gases	Diffusivity in $10^{-8} \text{ cm}^2 \text{ s}^{-1}$	Solubility in $\text{cm}^3 \text{ (STP) cm}^{-3}$
15% w/w SbCl₅		
N ₂	0.190 ± 0.071	0.014 ± 0.004
O ₂	0.377 ± 0.213	0.026 ± 0.021
CH ₄	0.183 ± 0.202	0.026 ± 0.031
CO ₂	0.474 ± 0.006	0.070 ± 0.001
20% w/w SbCl₅		
N ₂	0.026 ± 0.022	0.026 ± 0.002
O ₂	0.41 ± 0.269	0.028 ± 0.018
CH ₄	0.602 ± 0.395	0.019 ± 0.002
CO ₂	0.546 ± 0.406	0.076 ± 0.011
25% w/w SbCl₅		
N ₂	1.960 ± 2.60	0.031 ± 0.024
O ₂	0.100 ± 0.079	0.045 ± 0.016
CH ₄	0.366 ± 0.084	0.014 ± 0.004
CO ₂	0.545 ± 0.076	0.078 ± 0.008

Following chemical oxidation of POT membranes with 25% SbCl₅, the permeability values for N₂, O₂, CH₄, and CO₂ decreased by 44, 35, 47, and 24%, respectively. These results demonstrate that the fluxes of the larger gases, N₂ (3.64 Å) and CH₄ (3.8 Å), were reduced to a greater extent than those of the smaller gases, CO₂ (3.3 Å) and O₂ (3.46 Å), owing to partial filling of the free volume by the SbCl₆⁻ anion. These changes in permeabilities upon doping resulted in increases in membrane selectivity by 18, 38, and 43% for O₂/N₂, CO₂/N₂, and CO₂/CH₄, respectively.

B. Oxidized Composite Membranes:

Last quarter we reported that the permeability properties of POT membranes can be enhanced by the incorporation of NaY zeolites. We have also shown that chemical oxidation of the POT membranes leads to decrease in permeabilities and an increase in selectivities of gases. Oxidation of a 30% w/w NaY/POT composite membrane which has relatively good mechanical properties when compared to 40% NaY/POT composite membrane was chosen to investigate the effect of oxidation on composite membranes. A 25% w/w SbCl_5 which resulted in a maximum enhancement of selectivity, was scaled down to provide approximately same mole/mole ratio between the oxidant and the thiophene rings in the composite membrane oxidation.

Permeability data acquired for the oxidized composite membranes are presented in Table 3. The data are compared in Fig.3 and in Table 4 with those acquired from unmodified POT, 30% NaY/POT composite, and oxidized POT membranes. In comparison to the unmodified POT membranes, decreases in the permeabilities for N_2 (-8.3%) and CH_4 (-10.9%) and increases for O_2 (+10.4%) and CO_2 (+27.9%) were observed. With respect to the 30% NaY/POT composite membranes, decreases in permeability were observed for all gases except CO_2 (N_2 -27.3%, O_2 -12.7%, CH_4 -29.3%, CO_2 +10.2%). However, compared to the oxidized POT membranes, a substantial increase in the permeability of all gases was measured for the oxidized composite membrane (N_2 +20.3%, O_2 +30.0%, CH_4 +26.2%, CO_2 +30.9%).

Table 3.

**Permeability (in Barrers) and Permselectivity Data for 30% NaY/POT Composite
Membranes Oxidized with 17% SbCl_5 Dissolved in CH_3CN**

	P_{N_2}	P_{O_2}	P_{CH_4}	P_{CO_2}	O_2/N_2	CO_2/N_2	CO_2/CH_4
OxcompM₁ *	4.9 ± 0.1	15.4 ± 0.1	14.4 ± 0.2	77.5 ± 0.8	3.1 ± 0.0	15.8 ± 0.4	5.4 ± 0.1
OxcompM₂ *	5.7 ± 0.1	18.0 ± 0.1	16.1 ± 0.1	82.7 ± 0.5	3.2 ± 0.1	14.6 ± 0.4	5.1 ± 0.0
Grand Average**	5.3 ± 0.6	16.7 ± 1.8	15.3 ± 1.2	80.1 ± 3.7	3.2 ± 0.1	15.2 ± 0.8	5.3 ± 0.2

*OxcompM₁ and OxcompM₂ stand for oxidized composite membranes 1 and 2, respectively.

**Grand average is the average of two data sets obtained from OxcompM₁ and OxcompM₂ and the associated errors with the data are the standard deviations of the two averages.

Table 4. Comparison of Permeability Data of Oxidized-Composite POT Membranes with Respect to Other Types

Gas Studied	% Change with respect to Unmodified POT Membranes	% Change with respect to 30% NaY/POT Composite Membranes	% Change with respect to POT Membranes Oxidized with 25% w/w SbCl ₅
N ₂	– 8.6	– 27.4	+ 41.5
O ₂	+ 7.05	– 14.4	+ 40.7
CH ₄	– 14.0	– 29.8	+ 41.1
CO ₂	+ 25.9	+ 6.2	+ 68.6

Table 5. Comparison of Permeability Data of Modified POT Membranes with Respect to Unmodified POT Membranes

Gas studied	% Change of 30% NaY Composite Membranes with respect to Unmodified POT Membranes	% Change of POT Membranes Oxidized with 25% SbCl ₅ with respect to Unmodified POT Membranes
N ₂	+ 25.9	– 46.5
O ₂	+ 25.0	– 36.5
CH ₄	+ 22.4	– 49.4
CO ₂	+ 18.5	– 25.3

Combining the modification processes of polymer oxidation and zeolite incorporation resulted in mixed trends in permeability. Upon oxidation, the free volume of a polymer is reduced and the polarity of a membrane is increased thereby leading to a decrease in permeability and an increase in selectivity, respectively. However, mixing a zeolite, e.g. NaY, into a polymer facilitates the transport of gases through a composite membrane thereby increasing permeability. Relative to the unmodified membrane, the extent of the decrease in gas permeability (N_2 , CH_4) for the oxidized 30% NaY/POT composite membrane (Table 4) was less than for the oxidized POT membrane (Table 5). Although the free volume of the polymer decreased with oxidation, an increase in membrane polarity owing to polymer oxidation *and* to the presence of NaY zeolite apparently has facilitated the transport of gases. The increase in permeability was most pronounced for CO_2 , which, of all the gases studied, has the smallest kinetic diameter and the highest polarity. For the other gases (N_2 , O_2 , and CH_4), the increase in permeability realized by the 30% NaY/POT composite was not retained upon oxidizing the composite.

The diffusivity and solubility data obtained for the oxidized composite membranes (Table 6) show an increase in solubility with respect to unmodified and oxidized POT membranes, and a mixed change in diffusivities depending on the size and the nature of the test gases. Increase in solubility with respect to the POT membrane oxidized with 25% w/w $SbCl_5$, is more pronounced for CO_2 which is polar and a decrease in diffusivity is more pronounced for N_2 which is relatively larger when compared to CO_2 . The combined effect of these properties in the oxidized composite membranes may explain the permeability properties of the oxidized composite membranes.

Table 6. Diffusivity and Solubility for Oxidized Composite POT Membranes

Test Gases	Diffusivity in $10^{-8} \text{ cm}^2 \text{ s}^{-1}$	Solubility in $\text{cm}^3 \text{ (STP) cm}^{-3}$
N_2	0.013 ± 0.010	0.035 ± 0.002
O_2	0.647 ± 0.385	0.009 ± 0.009
CH_4	0.51 ± 0.237	0.020 ± 0.007
CO_2	0.335 ± 0.007	0.149 ± 0.003

The values of permselectivity acquired for the oxidized 30% NaY/POT composite membranes ($\alpha_{O_2/N_2} = 3.2 \pm 0.1$, $\alpha_{CO_2/N_2} = 15.2 \pm 0.8$, $\alpha_{CO_2/CH_4} = 5.3 \pm 0.2$) were similar to those measured for oxidized POT ($\alpha_{O_2/N_2} = 3.2 \pm 0.2$, $\alpha_{CO_2/N_2} = 15.3 \pm 0.9$, $\alpha_{CO_2/CH_4} = 5.3 \pm 0.1$) and greater than those measured for 30% NaY/POT ($\alpha_{O_2/N_2} = 2.7 \pm 0.0$, $\alpha_{CO_2/N_2} = 10.3 \pm 0.1$, $\alpha_{CO_2/CH_4} = 3.5 \pm 0.1$).

Conclusion

The increase in selectivity realized upon oxidation of the conducting polymer, POT, is maintained with the addition of NaY zeolite. Simultaneously, owing to a preferential sorption-diffusion process of the gases in the NaY zeolite, this addition of zeolite increases the gas permeability of the membrane as described above. Therefore, the strategy of combining polymer oxidation with zeolite incorporation, to prepare membranes for gas separations, is promising since gas permeability and selectivity can be increased simultaneously.

Continued work in this project includes studying the effect of incorporating other types of zeolites like X or A. NaY is ionic and preferentially facilitates the permeabilities of polar gases, such as CO₂. However, at high concentrations of zeolites (>30% w/w), the membranes tend to become brittle and difficult to handle. Therefore, incorporation of metals or metal complexes in the zeolites, which selectively and reversibly bind gases, may help to achieve facilitated transport at lower zeolite concentrations. Higher permselectivities of gases can be achieved by oxidizing the POT membranes with SbCl₅. However, SbCl₅ is extremely reactive and sensitive to moisture, which makes it necessary to perform the oxidation experiments in a glove bag or glove box. In addition, the oxidized membranes are not stable for long periods of time. Using other dopants may be a solution for these problems.

Figure 1. Permeabilities of Oxidized POT Membranes

Figure 2. Permselectivities of Oxidized POT Membranes

Figure 3. Permeability Comparison for Modified and Unmodified POT Membranes

Figure 4. Permselectivity Comparison for Modified and Unmodified POT Membranes