DOE/PC/94222-8

TUNABLE COMPOSITE MEMBRANES
FOR GAS SEPARATIONS

Progress Report

August 1996 - October 1996

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November 1996

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG22-94PC94222

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During this past quarter of project DE-FG22-94PC94222, continued significant progress was made in the synthesis and characterization of conducting polymer composite membranes for gas separations. Highlights from this funding period include:

- Fabrication of poly(dodecylthiophene), PDDT ($M_w = 250K$), membranes and characterization by light microscopy (LM), scanning electron microscopy (SEM) and atomic force microscopy (AFM).
- Permeability measurements for neutral and chemically oxidized PDDT membranes
- Extension of previous work on poly(octylthiophene)-zeolite (POT-NaY) composite membranes of different compositions.
- Preparation of tin(IV) sulfides to be incorporated as microporous, *electrically conducting*, additives in the composite membranes.
- Synthesis of poly(trioxynonylthiophene) and membrane fabrication and characterization.
- Talk entitled "Structure-Property Relationships in Poly(3-alkylthiophene) Membranes for Gas Separations" L. Li, I. H. Musselman, J. P. Ferraris, K. J. Balkus, L. Washmon, J. DeRouchey, S. J. Riley, presented at the 52nd American Chemical Society Southwest Regional Meeting, Houston, TX, October 17-19, 1996
- Talk entitled "Poly(3-alkylthiophene) Membranes for Gas Separation" I. H. Musselman, L. Washmon, D. Varadarajan, B. J. Tielsch, J. E. Fulghum, and published in the Proceedings of Microscopy and Microanalysis, 1996, G. W. Bailey, J. M. Corbett, R. V. W. Dimlich, J. R. Michael, N. J. Zaluzec, Eds., San Francisco Press, San Francisco, 1996, pp. 862-863 Minneapolis, MN, August 11-15, 1996.
- Poster entitled "Poly(3-alkylthiophene) Membranes for Gas Separation" I. H. Musselman, L. Washmon, D. Varadarajan, B. Tielsch, J. Fulghum, presented at the 212th American Chemical Society National Meeting, Orlando, FL, Aug. 25-29, 1996.

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Membranes of PDDT ($M_w = 250K$) were cast in a laminar flow hood recently installed in the Musselman laboratory. We had previously established that these films could be made with reproducible thicknesses and preliminary measurements indicated that they possessed permeability characteristics comparable to those made in the clean room. Films were oxidized using 3% w/w solutions of $SbCl_5$ in dry acetonitrile (AN). The films were then rinsed with AN and dried before being placed in the permeameter. Six membranes were tested in each state (neutral and oxidized). Tables 1 and 2 give the results.

The permeability and permselectivity values of *oxidized* membranes are quite uniform and the average permeability of these membranes is *higher* than that of neutral membranes although permselectivities are comparable. This may be caused by the morphology and/or structural changes upon oxidization and is currently under investigation.

Table 1 Permeability and Permselectivity Values for Neutral PDDT Membranes (MW = 249K)

Membrane	P N ₂	P O ₂	P CO ₂	a O ₂ /N ₂	a CO ₂ /N ₂
1	9.4 ± 0.2	21.8 ± 0.4	93.6 ± 0.2	2.3 ± 0.1	10.0 ± 0.2
2	8.7 ± 0.1	22.1 ± 0.4	98.0 ± 0.4	2.5 ± 0.1	11.2 ± 0.1
3	10.1 ± 0.5	19.0 ± 0.4	84.0 ± 0.4	1.9 ± 0.1	8.3 ± 0.4
4	7.8 ± 0.2	19.0 ± 0.5	82.8 ± 0.0	2.4 ± 0.1	10.6 ± 0.3
5	10.2 ± 0.5	19.5 ± 0.1	83.0 ± 0.6	1.9 ± 0.1	8.1 ± 0.4
6	10.3 ± 0.4	20.0 ± 0.2	87.6 ± 0.6	1.9 ± 0.1	8.5 ± 0.3
Grand Avg.	9.4 ± 0.9 (10%)	20.1 ± 0.9 (4%)	88.1 ± 1.0 (1%)	2.1 ± 0.2 (9%)	9.4 ± 0.7 (7%)

**Table 2 Permeability and Permselectivity Values
for Oxidized PDDT Membranes (MW = 249K)**

Membrane	P N ₂	P O ₂	P CO ₂	a O ₂ /N ₂	a CO ₂ /N ₂
1	10.1 ± 0.1	23.6 ± 0.2	109.1 ± 0.7	2.3 ± 0.0	10.8 ± 0.1
2	10.1 ± 0.1	23.8 ± 0.2	108.8 ± 0.5	2.4 ± 0.0	10.8 ± 0.1
3	12.0 ± 0.4	22.6 ± 0.2	102.0 ± 0.8	1.9 ± 0.1	8.5 ± 0.3
4	10.3 ± 0.2	21.5 ± 0.2	100.2 ± 0.7	2.1 ± 0.0	9.7 ± 0.2
5	10.8 ± 0.2	24.5 ± 0.6	113.0 ± 0.8	2.3 ± 0.1	10.5 ± 0.2
6	10.0 ± 0.2	22.8 ± 0.5	104.6 ± 1.7	2.3 ± 0.1	10.1 ± 0.5
Grand Avg.	10.6 ± 0.5 (5%)	23.1 ± 0.9 (4%)	106.3 ± 2.3 (2%)	2.2 ± 0.2 (8%)	10.1 ± 0.5 (5%)

A series of composite membranes of POT, containing a 20, 30 and 40% percent by weight NaY zeolite, were prepared according to the following procedures.

1. Dry zeolite (wt. depending upon loading required) was mixed with chloroform and sonicated for 5-10 min. (*XRD and SEM indicate no loss of zeolite crystallinity, See Figure 1*)
2. POT and additional chloroform were added and the mixture was stirred overnight to adequately disperse zeolite into the polymer.
3. The solvent was evaporated in air and the solids were resuspended in tetrachloroethylene at a concentration of 10 -12% solids.
4. Films were cast with casting bar onto a glass plate using 0.8-1.0 ml of the above described solution and then covered and left to dry.
5. The dry films were annealed under vacuum at 120 °C for 3 hr and then cooled to ambient temperature under vacuum.
6. Films were stored covered in a nitrogen-filled glovebox until permeability measurements were conducted.
7. After the permeability experiments, the membrane thicknesses were accurately determined using LM to correct the permeability results.

As presented in the recent Southwestern Regional ACS meeting, composite films with higher loadings of zeolite (>30%) exhibit improved selectivity and permeability. Films with lower loadings (20%) exhibit a slight decrease in selectivity. We attribute this effect to the zeolite acting as a filler or barrier, rather than facilitating gas absorption. Despite the general trends observed, data reproducibility to date has been a considerable problem and more systematic casting, annealing and permeability techniques are under investigation.

Figure 1: 40 % NaY / POT
Crystals are approx. 2 X 2 microns

A class of 2 and 3 dimensional tin chalcogenides have recently been discovered by UOP which exhibit some unique adsorption properties. For example, the layered tin(IV) sulfide designated SnS-1 readily adsorbs polar molecules such as CO_2 with the total exclusion of relatively non-polar molecules such as N_2 . The selective adsorption properties of these materials alone might be exploited in a facilitated transport process. However, these materials also have the advantage that they are semiconductors. Interestingly, the adsorption of hydrogen bonding molecules into these microporous materials results in an increase in bulk conductivity by several orders of magnitude. Therefore, these materials could also function as electrolytes in a conducting polymer composite membrane. They may also be ion exchanged with redox active metal complexes that selectively bind certain small molecules. Unlike the insulating zeolite host materials, the tin sulfides should render all the guest molecules electroactive.

Tin(IV) sulfide has been prepared according to the method of Ozin *et al* (*Chem. Mater.* 1995, 7, 245-8.) using the following procedure:

1. A 1:2:1:84 ratio of Sn:S: $n\text{Pr}_4\text{NOH}$ (TPAOH): H_2O was utilized in the synthesis.
2. Tin powder (325 mesh) and sulfur powder were mixed together in a high temperature Teflon reaction container (50 ml volume).

3. Water and TPAOH (1.0 M) were mixed in a plastic beaker and added to the Teflon reactor.
4. The reactor was then sealed in a Parr bomb and heated at 150 °C for 70 hours.
5. Following an overnight cooling period in a fume hood , the contents were filtered, washed with water, isopropanol, and a small amount of acetone.
6. Solids were then examined further with XRD and SEM.

We are currently refining our synthesis procedures to produce crystals with uniform and reproducible dimensions. An SEM micrograph of the products of one synthesis is given Figure 2.

Figure 2: SEM of crude product from tin (IV) sulfide synthesis. Large crystal is approximately 100 X 100 microns. Small spheres are metallic tin.