DOE/PC/94222-18

TUNABLE COMPOSITE MEMBRANES
FOR GAS SEPARATIONS

Final Report

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May 1999

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY
UNDER AWARD NUMBER DE-FG22-94PC94222--18

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Abstract:

Project DE-FG22-94PC94222 was conducted to prepare and assess conducting polymer composite membranes for gas separations. The (co) principal investigators who are all in the Chemistry department of the University of Texas at Dallas are:

- Dr. John P. Ferraris
- Dr. Kenneth J. Balkus, Jr.
- Dr. Inga Holl Musselman

Ten graduate students and six undergraduate students (including one UCR Summer Student), listed below, worked on the project which resulted (or will result) in five M. S. Theses and two Doctoral Dissertations. An automated, computer controlled permeameter was constructed with matching funds from UTD and results of the project enabled the PI's to attract additional funding from the State of Texas Advanced Technology program and Mobil Exploration Co. A second permeameter that included design improvements was constructed using DOE-PETC and this funding. This allowed increased throughput for the DOE project as well. In addition to the theses and dissertations, four refereed publications have appeared or been submitted, one referred abstract has been published, seven invited presentations and seven contributed presentations have been delivered.

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Executive Summary:

Accomplishments for Tunable Composite Membranes for Gas

Separations, DE-FG22-94PC94222

1. Construction of two custom-built, automated permeameters
2. First systematic studies of membranes based on polythiophene conducting polymers
3. First systematic studies of fabrication of defect-free membranes based on thiophene conducting polymers
4. First systematic studies of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of as-cast polyalkylthiophene-based membranes
5. First systematic studies of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of chemically doped polyalkylthiophene-based membranes
6. First systematic study of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of as-cast polyalkylthiophene-zeolite (NaY) composite membranes
7. First systematic study of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of doped polyalkylthiophene-zeolite (NaY) composite membranes
8. First systematic studies of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of as-cast polyalkyletherthiophene-based membranes
9. First systematic studies of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of composite membranes of poly(ethyleneoxide) and polyalkyletherthiophenes
10. First systematic studies of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of as-cast polyalkylesterthiophene-based membranes
11. First systematic studies of gas permeabilities and selectivities (N_2 , O_2 , CO_2 , CH_4) of polysulfone membranes containing the mesoporous molecular sieve, MCM-41

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/permeability for pure polymers. Our strategy relies on modification of composite membranes, preferably *in situ*, to enhance the permeability 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 final report summarizes the results of our efforts on the project.

Results and Discussion

Project DE-FG22-94PC94222 was conducted to prepare and assess conducting polymer composite membranes for gas separations. The (co) principal investigators who are all in the Chemistry department of the University of Texas at Dallas are:

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- Dr. Kenneth J. Balkus, Jr.
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Ten graduate students and six undergraduate students (including one UCR Summer Student), listed below, worked on the project which resulted (or will result) in five M. S. Theses and two Doctoral Dissertations. An automated, computer controlled permeameter was constructed with matching funds from UTD and results of the project enabled the PI's to attract additional funding from the State of Texas Advanced Technology program and Mobil Exploration Co. A second permeameter, which included design improvements, was constructed using DOE-PETC and this funding. This allowed increased throughput for the DOE project as well. In addition to the theses and dissertations the following presentations and publications emanated from this project.

Refereed Abstracts:

I. H. Musselman, L. Washmon, D. Varadarajan, B. J. Tielsch, J. E. Fulghum, "Poly (3-alkylthiophene) Membranes for Gas Separation", 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, Minneapolis, MN, August 11-15, 1996, pp. 862-863.

Refereed Publications:

I. H. Musselman, L. Li, L. Washmon, D. Varadarajan, S. J. Riley, M. Hmyene, J. P. Ferraris, K. J. Balkus, Jr., "Poly(3-dodecylthiophene) Membranes for Gas Separations", *J. Membrane Sci.* **152(1)**, 1-18 (1999).

B. Reid, F. A. Ruiz-Trevino, I. H. Musselman, K. J. Balkus, Jr., and J. P. Ferraris, "Gas Permeability Properties of Polysulfone Membranes Containing the Mesoporous Molecular Sieve, MCM-41, *Chem. Mater.* (1999), submitted.

I. H. Musselman, S. Madhugiri, K. J. Balkus, Jr., and J. P. Ferraris, "Poly(3-octylthiophene)/NaY Zeolite Composite Membranes for Gas Separations", *Chem. Mater.* (to be submitted).

B. Reid, V. H. M. Ebron, I. H. Musselman, J. P. Ferraris, and K. J. Balkus, Jr., "Poly 2-(3-thienyl)ethylacetate Membranes for Gas Separations", *Macromolecules* (to be submitted).

Invited Presentations:

I. H. Musselman, "Industrial Applications of (Atomic Force) Microscopy: Gas Separation Membranes and Corrosion of Steel", United Technologies Research Center, East Hartford, CT, June 6, 1996.

I. H. Musselman, "Industrial Applications of (Atomic Force) Microscopy: Gas Separation Membranes and Corrosion of Steel", University of Texas at Dallas, Solid State Physics Seminar, Dallas, TX, July 30, 1996.

I. H. Musselman, "Atomic Force Microscopy and Related Techniques: Introduction, Instrumentation and Application to Polymeric Materials", Minnesota Microscopy Society, St. Paul, MN, November 20, 1997.

I. H. Musselman, "Atomic Force Microscopy and Related Techniques: Introduction, Instrumentation and Application to Polymeric Materials", 3M Technical Forum, St. Paul, MN, November 21, 1997.

K. J. Balkus, Jr., "Recent Developments in the Application of Zeolites in Thin Films and Membranes", Exxon, Baytown, TX, December 1997.

I. H. Musselman, "Morphology of Poly(3-dodecylthiophene) Gas Separation Membranes", 215th American Chemical Society National Meeting, Dallas, TX, March 29 - April 2, 1998.

I. H. Musselman, "Atomic Force Microscopy and Related Techniques: Introduction, Instrumentation and Application to Polymeric Materials", Microscopy and Microanalysis '98, Atlanta, GA, July 12 - 16, 1998.

Contributed Presentations:

I. H. Musselman, L. Washmon, D. Varadarajan, B. Tielsch, J. Fulghum, "Poly(3-alkylthiophene) Membranes for Gas Separation", 212th American Chemical Society National Meeting Orlando, FL, August 25-29, 1996.

L. Li, I. H. Musselman, J. P. Ferraris, K. J. Balkus, L. Washmon, J. DeRouchey, S. J. Riley, "Structure-Property Relationships in Poly(3-alkylthiophene) Membranes for Gas Separations", 52nd American Chemical Society Southwest Regional Meeting, Houston, TX, October 17-19, 1996.

I. H. Musselman, L. Li, L. Washmon, S. J. Riley, J. P. Ferraris, K. J. Balkus, Jr., "Poly(3-alkylthiophene) Membranes for Gas Separations", NAMS '97, North American Membrane Society Ninth Annual Meeting, Baltimore, MD, May 31-June 4, 1997.

D. Smithhisler, K. Balkus, Jr., J. Ferraris, I. Musselman, S. Riley, "Poly-(3-alkylthiophene) / Molecular Sieve Composite Membranes for Gas Separations", NAMS '97, North American Membrane Society Ninth Annual Meeting, Baltimore, MD, May 31-June 4, 1997.

Sudha Madhugiri, Inga H. Musselman, Kenneth J. Balkus, Jr., John P. Ferraris, "Composite Membranes for Gas Separations", American Chemical Society Meeting in Miniature, Richardson, TX, April 16, 1999.

Brian Reid, Jody Neef, Inga Musselman, John Ferraris, Kenneth Balkus, Jr., "Gas Permselectivity of the Conductive Polymer MEH-PPV", American Chemical Society Meeting in Miniature, Richardson, TX, April 16, 1999.

V. H. M. Ebron, I. H. Musselman, J. P. Ferraris, K. J. Balkus, Jr., F. A. Ruiz-Treviño, "Poly 2-(3-thienyl)ethylacetate Membranes for Gas Separations", American Chemical Society Meeting in Miniature, Richardson, TX, April 16, 1999.

Graduate Students:

- Scott Riley: currently completing work on doctoral dissertation
- Brian Reid: currently completing work on doctoral dissertation
- Deepta Varadarajan
M.S. Thesis: Poly(3-alkylthiophene)s as Membranes for Gas Separation.
- Lisa Washmon
M.S. Thesis: Poly(3-alkylthiophene) Membranes for Gas Separation: A Structure/Property Study.
- Lin Li
M.S. Thesis: Poly(3-alkylthiophene) Membranes for Gas Separations - Fabrication, Gas Transport Studies and Characterization.
- Ziad Shaker (no degree awarded)
- Don Smithhisler (no degree awarded)
- Sudha Madhugiri
M.S. Thesis: Poly(3-octylthiophene)/NaY Zeolite Composite Membranes for Gas Separations
- Von Ebron
M.S. Thesis: Poly 2-(3-thienyl)ethylacetate Membranes for Gas Separations
- Rajkumar Juturu: currently working on doctoral dissertation

Undergraduate Students:

• Heather Carlson (UCR)	Karalyn Humphrey
• Jason DeRouchey	Betty Rostro
• Tana Langley	Sang Lam

Accomplishments for Tunable Composite Membranes for Gas Separations,
DE-FG22-94PC94222 (detailed abstracts appended)

1. Construction of two custom-built, automated permeameters
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Detailed Abstracts

1. Two computer-controlled permeameters were constructed and calibrated. The systems were modeled after ones designed at Los Alamos national Laboratories. Each system incorporates a pumping system, a thermostatted chamber that houses the test cell and attendant gas-handling systems, an electronics control rack and a data acquisition/analysis computer. One instrument has a Residual Gas Analyzer to enable the direct determination of membrane permselectivity toward gas mixtures. The instruments run under a LabView™ control program.

We designed and constructed an extensive program using G-Basic through LabView™ to run the permeameter. This program is capable of running up to 40 consecutive experiments with the use of up to eight different gases.

2. Polythiophenes represent a class of materials that are particularly promising for gas separations due to their redox properties that enable *in situ* and *ex situ* tunability of permeability/selectivity. Unlike polyaniline and poly(N-methylpyrrole), prior to our work, the permeability properties of polythiophenes received only cursory discussion in the literature. The rich derivative chemistry of these polymers and their ability to be both p- and n-doped provide tremendous flexibility in tailoring the membrane to the separation at hand. We have synthesized and for the first time studied several members of this family of polymers including poly(3-alkylthiophenes), poly(3-alkyletherthiophenes) and poly(3-alkylesterthiophenes), as as-cast, doped and composited membranes for gas separations.
3. The accurate and reliable measurement of the permeability of a polymer membrane depends on (1) knowing the thickness of the membrane and (2) being able to reproducibly cast membranes so that multiple measurements can be made. To this end, a reliable method for solution casting polythiophene-based membranes was developed. To assess the reproducibility of the casting technique, the membrane thickness and surface roughness were measured by light microscopy and TappingMode™ atomic force microscopy, respectively. Poly(3-octylthiophene) membranes were found to be of uniform thickness, $21.7 \pm 0.7 \mu\text{m}$, in the center 3.5 cm of the membrane. A similar measurement of thickness uniformity for poly(3-dodecylthiophene), PDDT. The average root-mean-square roughness value measured from four samples taken from the center portion of five identically prepared POT membranes was $0.7 \pm 0.1 \text{ nm}$. Based on these results the casting technique was determined to be reliable and reproducible.
4. Permeability studies of PDDT were conducted sequentially for the test gases N_2 , O_2 and CO_2 . The average permeabilities (P_{N_2} , P_{O_2} , P_{CO_2}) for each of 6 as-cast membranes

are reported as the mean values for 3 successive exposures to each test gas. A rubbery polymer at room temperature ($T_g = 253\text{ }^\circ\text{K}$), PDDT exhibited characteristically high permeabilities ($P_{N_2} = 9.4$ Barrers, $P_{O_2} = 20.2$ Barrers, $P_{CO_2} = 88.2$ Barrers) and low permselectivities ($O_2/N_2 = 2.2$, $CO_2/N_2 = 9.4$). The values of permeability and permselectivity are reproducible and the observed measurement error ($<10\%$) falls within the nonuniformity of PDDT membrane thicknesses ($<11\%$). Permeability measurements obtained for a second batch of as-cast PDDT with a lower molecular weight ($M_w = 139,000$, $M_n = 38,600$) yielded similar results.

Smooth, dense, uniformly thick membranes were solution cast from poly(3-octylthiophene) (POT) and their permeability properties were investigated for N_2 , O_2 , CH_4 , and CO_2 ($P_{N_2} = 5.8 \pm 0.4$, $P_{O_2} = 15.6 \pm 0.8$, $P_{CH_4} = 17.8 \pm 1.4$, $P_{CO_2} = 63.6 \pm 2.2$ Barrers), and selectivity properties were calculated ($O_2/N_2 = 2.7 \pm 0.2$, $CO_2/N_2 = 11.2 \pm 0.8$, $CO_2/CH_4 = 3.6 \pm 0.2$).

5. Permeability data were collected for PDDT membranes oxidized for 3 h in a glove bag using a 15% w/w solution of $SbCl_5$ in acetonitrile. Elemental analysis results revealed a 23% doping level for membranes oxidized in this manner. Compared to the as-cast PDDT membranes, a decrease in gas permeabilities of more than 45% was observed: $P_{N_2} = 3.5$ Barrers, $P_{O_2} = 10.5$ Barrers and $P_{CO_2} = 48.5$ Barrers. This decrease in permeability was accompanied by an increase in permselectivity: $O_2/N_2 = 3.0$, $CO_2/N_2 = 14.0$. The observed decrease in permeability and corresponding increase in permselectivity of PDDT with high levels of doping is caused by changes in diffusivity and solubility.

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 ($P_{N_2} = 3.1 \pm 0.2$, $P_{O_2} = 9.9 \pm 0.1$, $P_{CH_4} = 9.0 \pm 0.1$, $P_{CO_2} = 47.5 \pm 0.3$ Barrers, and $O_2/N_2 = 3.2 \pm 0.2$, $CO_2/N_2 = 15.3 \pm 0.9$, $CO_2/CH_4 = 5.3 \pm 0.3$).

6. NaY/POT composite membranes (20, 30, and 40% w/w zeolite) were prepared by stirring the polymer into a zeolitic suspension. Facilitated transport of gases (N_2 , O_2 , CH_4 , and CO_2) was observed for each of the zeolite loadings, the magnitude of which depended on the chemical nature of the gas and polymer/zeolite-penetrant interaction. Maximum facilitation was observed for 40% NaY/POT composite membranes (Facilitation ratio of $N_2 = 0.38 \pm 0.03$, $O_2 = 0.56 \pm 0.02$, $CH_4 = 0.13 \pm 0.01$, $CO_2 = 0.71 \pm 0.02$). An increase in the selectivity of gases was also observed for all zeolite loadings.

7. 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, $\text{O}_2/\text{N}_2 = 3.2 \pm 0.1$, $\text{CO}_2/\text{N}_2 = 15.2 \pm 0.8$, $\text{CO}_2/\text{CH}_4 = 5.3 \pm 0.2$).
8. Poly(trioxynonylthiophene (PTONT) was synthesized in several batches and its molecular weights as characterized by gel permeation chromatography ranged between 54K and 145K. PTONT from these batches formed membranes with the following permeability characteristics: ($P_{\text{N}_2} = 3.8$, $P_{\text{O}_2} = 7.5$, $P_{\text{CO}_2} = 100.8$ Barrers, $\text{O}_2/\text{N}_2 = 2.0$, $\text{CO}_2/\text{N}_2 = 26.6$).
9. Composites of PTONT and 25% 100K poly(ethyleneoxide), PEO, formed robust membranes. Permeability measurements on these membranes afforded the following results: ($P_{\text{N}_2} = 1.1$, $P_{\text{O}_2} = 2.7$, $P_{\text{CH}_4} = 2.5$, $P_{\text{CO}_2} = 45$ Barrers, $\text{O}_2/\text{N}_2 = 2.4$, $\text{CO}_2/\text{N}_2 = 40$, $\text{CO}_2/\text{CH}_4 = 15$. Note that the decrease in permeability and *increase* in permselectivity expected from incorporation of a glassy component (PEO) in the composite is observed.
10. Poly 2-(3-thienyl)ethylacetate (PAET) was synthesized and solution cast as thin films to form dense membranes. These membranes are mechanically robust and are redox active, holding out promise as gas separation materials. The permeability properties of PAET membranes were evaluated for N_2 (0.048 ± 0.008 Barrers), O_2 (0.24 ± 0.02 Barrers), CH_4 (0.081 ± 0.005 Barrers), and CO_2 (1.4 ± 0.1 Barrers). The corresponding selectivity values () were: $\text{O}_2/\text{N}_2 = 5.1$, $\text{CO}_2/\text{N}_2 = 29$, and $\text{CO}_2/\text{CH}_4 = 18$.
11. The all silica molecular sieve MCM-41 was incorporated into polysulfone at 10, 20 and 30% w/w. For all gases tested (N_2 , O_2 , CO_2 and CH_4) the permeability increased in proportion to the weight percent of MCM-41 present in the film. At the same time, calculated ideal selectivities remained almost constant irrespective of MCM-41 loading. The increases in permeability without a loss in selectivity suggests that using a mesoporous molecular sieve as the adsorbent additive reduces the formation of nonselective voids often found in similar composites.

Conclusions

This project was quite successful, with a number of firsts. Several families of thiophene polymers (polyalkylthiophenes, polyalkyletherthiophenes and polyalkylester-thiophenes) were synthesized and characterized. They were fabricated into membranes and their permeability/permeability properties with respect to test gases (N_2 , O_2 , CO_2 and CH_4) were determined in both as-cast and chemically modified configurations. Enhancements in permeability were obtained in the latter. Composites of these and other polymers with molecular sieves (NaY zeolite and MCM-41) were constructed and tested similarly. Permeability without concomitant loss of selectivity was demonstrated.

The grant contributed to several M.S. theses, two Doctoral dissertations and numerous publications and presentations. Several undergraduate students were also afforded the opportunity to work on a project of high technological importance. This grant also produced results that enabled the PIs to attract funding from other agencies (State and private) to expand the study of composite membranes for gas separations.