



01 May 1994

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Dunnegan, Chad, "Fixed Site Facilitated Transport of Oxygen and Nitrogen Through Plasma Polymer Films" (1994). *Opportunities for Undergraduate Research Experience Program*. 28.
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FIXED SITE FACILITATED TRANSPORT OF OXYGEN AND NITROGEN THROUGH PLASMA POLYMER FILMS

Chad Dunnegan
Chemical Engineering

ABSTRACT

A method of preparing plasma polymer films, in which metal chelate molecules are incorporated, is briefly outlined. The chemical reactivity of metal chelate molecules is preserved so that they may "facilitate" the transport of oxygen molecules through the membrane. The method for testing permeability of the films is presented and results are analyzed with respect to the dual mode sorption model, applied to fixed site facilitated transport.

INTRODUCTION

In the present study, low vapor pressure metal chelates were sublimed into a plasma and codeposited on to the substrates. The metal chelates are capable of reversibly binding oxygen, but not nitrogen, thereby highly promoting permselective transport of oxygen through metal chelate containing plasma polymer films. This highly promoting permselective transport is described as Fixed Site Facilitated Transport (FSFT).

The use of gas transport through membranes for the purpose of separation is appealing because of its efficiency from an energy standpoint. Separation of gas mixtures by permeation is based on differences in the diffusion coefficients of the gases. High selectivity, high flux, and good stability are potential advantages of the use of plasma polymer membranes capable of fixed site facilitated transport of one gas in a mixture.

This project focuses on a specific part of a larger research project being investigated by Dr. Nicholas Morosoff and Youngson Choe. The purpose of this project is to gain an understanding of the parameters involved in trying to reach a high permselectivity (O_2/N_2) through a plasma polymer film and to gain some relevant lab experience.

DIFFUSION, PERMEABILITY, AND PERMSELECTIVITY

Before description of the experiment occurs, some discussion of the physical phenomena involved in the study is in order. It has long been established that between gas mixtures with varying

relative concentrations of a particular species, a process results which tends to equalize their compositions. This process is called diffusion and, according to the solution-diffusion model, can be divided into four parts. These are: (1) sorption of the compound on to the surface, (2) solubilization of the permeant into the material, (3) diffusion of the permeant within the material to the opposite surface, and (4) release of the permeant from the sorbing material.

Both diffusion and solubility characteristics of the permeant in a material are incorporated in a measure of the permeant's permeability in that material. It has been shown that gases dissolving in rubber follow Henry's and Fick's law of diffusion:

$$C = k_D p \quad (1)$$

$$J = -D \frac{\Delta C}{\Delta x} \quad (2)$$

where C is the concentration of gas in the polymer in cm^3 gas (at STP)/ cm^3 of polymer, k_D is the solubility constant or Henry's law constant in cm^3 gas (at STP)/(cm^3 of polymer * cm Hg), p is the partial pressure of gas in cm Hg , and D is Fick's diffusion coefficient in $\text{cm}^2/\text{second}$. ΔC is the permeant concentration change across a thickness Δx .

Fixed gases (gases above their critical temperature) diffusing through rubbery polymers present fairly simple behavior [1]. For such a system the permeability is defined as:

$$J = \frac{P \Delta p}{l} \quad (3)$$

where P is the steady state permeability expressed in $\text{cm}^3(\text{STP})\text{cm}/(\text{sec} \cdot \text{cm}^2 \cdot \text{cm Hg})$, Δp is the pressure difference across the membrane, l is the thickness of the membrane, and

$$P = k_D D \quad (4)$$

where k_D is the adsorption coefficient (for sorption of the gas in the membrane), and D is Fick's diffusion coefficient. The above unit of permeability multiplied by 10^{-10} is currently referred to as the 'barrer' and is a common unit of permeability. These three constants can be obtained by measuring the permeation rate through an initially degassed membrane.

Permselectivity (or separation factor) has been widely used to characterize gas transport through membranes. The ideal selectivity between the permeants is expressed as the ratio of the two pure gas permeabilities in a membrane.

$$\alpha = \frac{P_A}{P_B} \quad (5)$$

A good gas separation should have both a high permeability and a high selectivity. Evidence has been provided that the most important parameter is the diffusion coefficient [2]. It has also been noted [3] that there is an inverse relationship between O_2/N_2 permselectivity and O_2 permeability. This results in an O_2/N_2 permselectivity ceiling of 9-10 for organic polymers.

CONVENTIONAL FSFT VS. PLASMA POLYMER FSFT

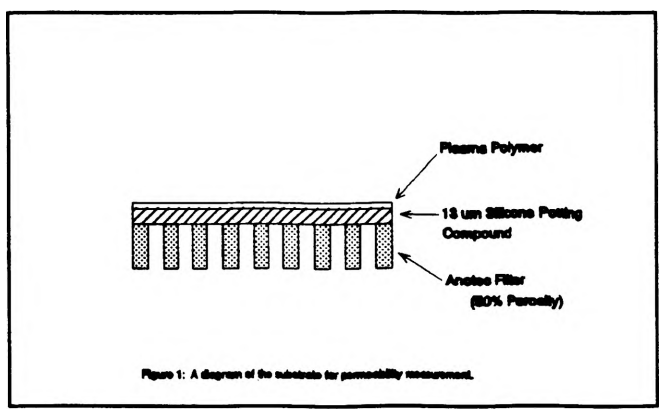
Improvements in the separation of O_2 from O_2/N_2 mixtures have been made by incorporating oxygen carriers into conventional polymer membranes. It has been shown that the use of immobilized synthetic transition metal chelates improve O_2/N_2 separation through permselective membranes [4]. O_2 binds to the metal complexes on one side of the membrane. O_2 -transition metal complexes diffuse through the membrane to the lower O_2 concentration. Finally, O_2 dissociates from the complex and evaporates from the membrane surface. This dual mode sorption model, it has been established, is indicated by a pressure dependence of the transport behavior. This pressure dependence is due to Langmuir mode by which sorption occurs. Henry's mode of transport through the matrix is pressure independent. These two postulates explain why such membranes are most effective at low pressures.

Conventional polymer FSFT membranes suffer from short lifetime problems due to diffusion of metal chelate complexes in the polymer matrices, and subsequent dimerization of the metal chelates. Plasma polymers have been introduced to overcome this obstacle in the hope of inhibiting this diffusion, thus preventing the dimerization, by means of increasing the degree of crosslinking of polymer structures.

APPARATUS AND TESTING

Plasma polymers were deposited onto Al_2O_3 membranes (Anodisc). The membrane pore size was 200 Å. Anodisc was used as a supporting substrate to withstand the high pressure gradient across the membrane since the plasma polymer films are extremely thin (800 - 2000 Å) and very brittle. The membranes were spin-coated with a two component silicone potting compound (RTV-615), vinylmethylpolysiloxane (VMPSiO), $d=0.98 \text{ g/cm}^3$, General Electric Silicones Inc.). Each membrane was weighed before and after application of the coatings. Membranes were spun at 7200 rpm for 4 minutes, then cured in an oven at 75 C for 15 hours. A cross

section of the composite filter is shown below:



Permeation studies were performed using trans-2-butene plasma polymer films to determine the separation abilities of the polymer prior to metal complex incorporation. Trans-2-butene plasma polymer films were deposited onto VMPSiO coated substrates. Complete coverage is obtained at a mass thickness of 9.5 ug/cm².

Permeability measurements were accomplished using the equipment schematically shown in Figure 2.

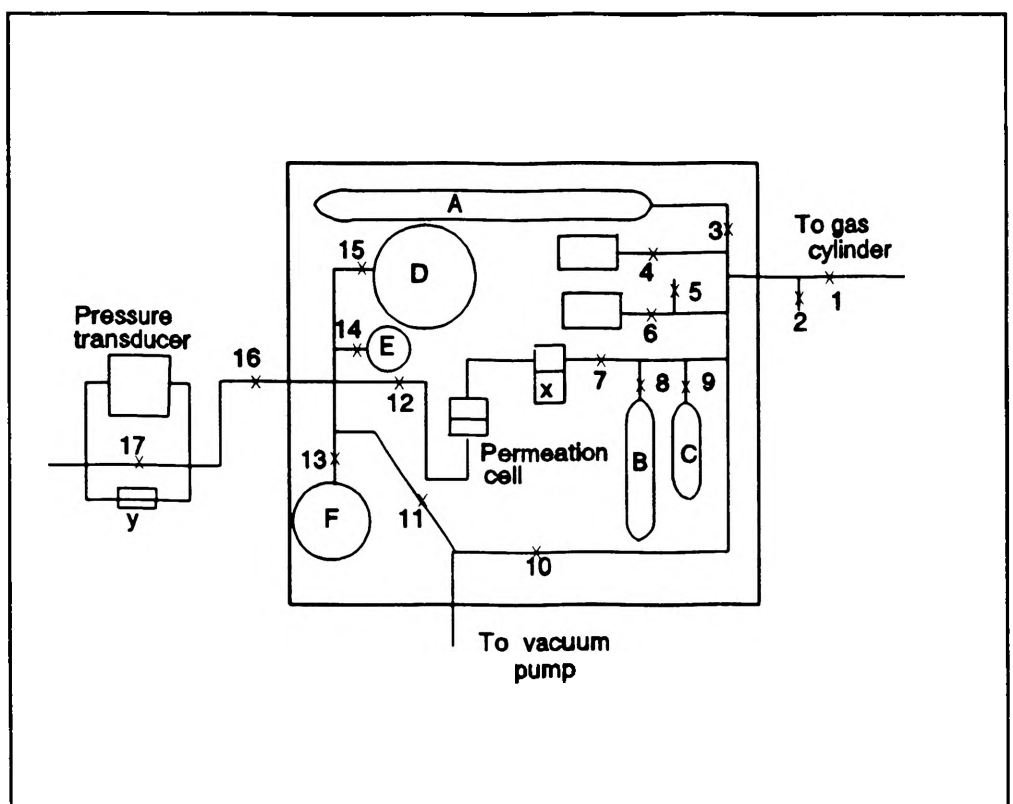


Figure 2: Permeability Measurement Apparatus

The upstream side consists of three feeding gas reservoirs connected via valves to the gas cylinder; the pressure was monitored by two Heise Baratron (a range of 0-1000 Torr and 0-1000 Torr) on a personal computer by A/D board and a Data Acquisition and Control System which was purchased from Strawberry Tree Computers, Inc. (Sunnyvale, CA). The downstream side has three receiving reservoirs and the pressure was monitored by a Heise Baratron that had a full range of 10 torr and sensitivity of +/- 0.001 Torr. The permeation cell used was a Millipore high pressure stainless steel 47 mm disc filter holder. The permeation cell consisted of a two part stainless steel housing, a perforated metal insert, and a porous metal support disk. The metal insert was placed inside the bottom half (low pressure side) of the cell and the porous metal support was placed on top of the insert. The membrane sample was set on top of the support disk. A lightly greased Silastic gasket sealed the membrane in the cell. Both sides were evacuated for 12 hours and filled with oxygen or nitrogen. Computer collection of pressure measurements on the low pressure side was then initiated, with pressure being recorded every 2 seconds for nitrogen or oxygen by a Data Acquisition and Control Program (Analog Connection ACJR™-12-8, Strawberry Tree Computers Inc., Sunnyvale, CA).

Permeation for the composite film was then calculated by the following equation:

$$P = \left(\frac{p_1}{t} \right) \frac{VL}{60ATp} \left(\frac{273}{76} \right) \quad (6)$$

where P is the composite permeability in $\text{cm}^3(\text{STP})\text{cm}/(\text{sec cm}^3 \text{ cm Hg})$, p_1/t is the slope of the low side pressure versus time graph in torr/minute, V is the volume of the low pressure side in mL, T is the temperature in Kelvin, A is the surface area of the membrane in cm^2 , L is the composite thickness in cm, and p is the pressure of the high pressure side gas in torr. To obtain the permeability of the plasma polymer layer alone, the following equation was applied

$$\frac{L}{P} = \frac{L_1}{P_1} + \frac{L_2}{P_2} \quad (7)$$

For the composite, the ideal selectivity is defined as:

$$\alpha = \frac{P(O_2)}{P(N_2)} \quad (8)$$

and for the plasma polymer, the ideal selectivity is defined as: where L is the composite thickness in cm, P is the composite permeability in barrers, L_1 is the plasma polymer layer thickness

$$\alpha_1 = \frac{P_1(O_2)}{P_1(N_2)} \quad (9)$$

in cm, L_2 is the VMPSiO coating layer thickness in cm, P_1 is the plasma polymer permeability in barrers, P_2 is the VMSiO coating layer permeability in barrer. All of the variables except P_1 were obtained experimentally or by direct measurement.

RESULTS

The ideal O_2/N_2 selectivity of VMSiO/trans-2-butene composite is plotted versus thickness of plasma polymer film in Figure 3. The maximum ideal O_2/N_2 selectivity is obtained at a thickness of 9.5 $\mu\text{g}/\text{cm}^2$. The ideal O_2/N_2 selectivity gradually decreases with increasing mass thickness of plasma polymer films. At 10 $\mu\text{g}/\text{cm}^2$ thickness of plasma polymer films, the average ideal O_2/N_2 selectivity is 3.8.

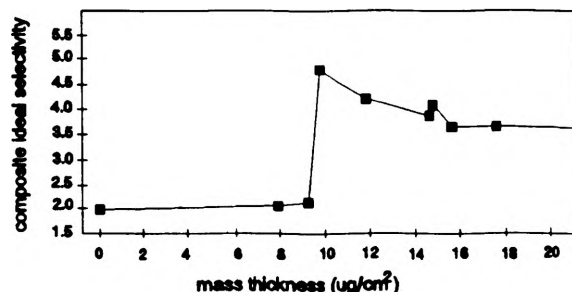


Figure 3: Selectivity vs. thickness (no chelate)

These results may be compared with those obtained by Choe for CoTPP/trans-2-butene plasma polymers. These films were deposited onto VMPSiO/ Al_2O_3 substrates, and successfully deposited with loadings up to 50%. The ideal O_2/N_2 selectivity of CoTPP/trans-2-butene plasma polymer film (or composite) is plotted versus mass thickness of the polymer film in figure 4. Complete coverage is obtained at a mass thickness of 8.5 $\mu\text{g}/\text{cm}^2$. The ideal O_2/N_2 selectivity of composite decreases with increasing mass thickness of the plasma polymer film, dropping from 8.8 to 6.3 as mass thickness increases from 8.5 to 17.5 $\mu\text{g}/\text{cm}^2$.

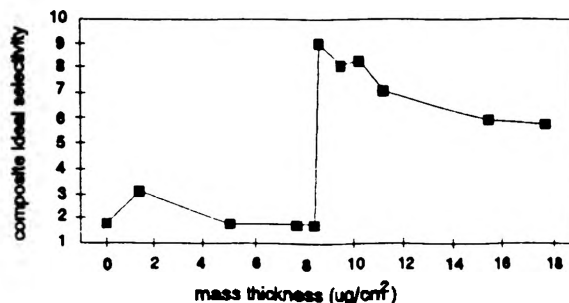


Figure 4: Selectivity vs. thickness (containing chelate)

Also shown in figure 5 are the time lags obtained for several 2% loaded plasma polymer films.

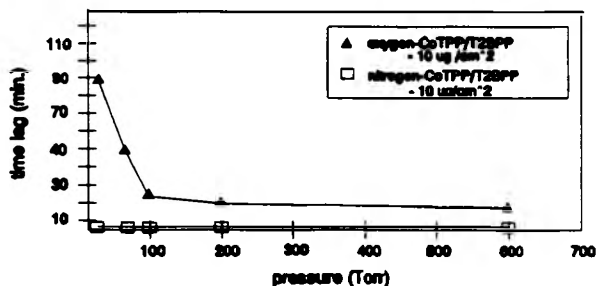


Figure 5: Time Lag vs. Pressure

Only for the combination of CoTPP and O₂ are pressure dependant time lags obtained. This is evidence of fixed site facilitated transport through CoTPP loaded film.

Trans-2-butene plasma polymer films containing CoTPP have ideal selectivities which are higher than trans-2-butene plasma polymers without the metal chelate. The ideal selectivity of CoTPP plasma has been shown to increase with increased film loading, up to 5% CoTPP in plasma polymer, for films of the same mass thickness (10-11 ug/cm³), as expected for fixed site facilitated transport. This is caused both by a decrease in nitrogen permeability and an increase in oxygen permeability. The permeability of nitrogen decreases as the concentration of the metal complex increases.

These phenomena can be explained by an increase in "tortuosity" with increasing CoTPP concentration. Large molecules such as CoTPP in the polymer matrix lengthen the path which solute molecules travel, resulting in smaller apparent diffusion coefficients. This effect is combatted in the case of oxygen, up to an optimum of about 5% loading, by the reversible bonding, and its facilitating effects, that occurs between oxygen and CoTPP.

For films with greater than 5% loading, the ideal O₂/N₂ selectivity of CoTPP/trans-2-butene plasma polymer film decreased with increasing % loading of CoTPP.

The dual mode sorption model, modified based on Barrer's four type diffusion model[5], is very important to explain the behavior described above.

$$J_A = - [D_{HH} + D_{DH} + D_{DH} \left(\frac{C_A}{C_T} \right) + D_A \left(\frac{C_{AO}}{C_{ABO}} \right) + D_{OH} \left(\frac{C_{AO}}{C_{ABO}} \right) C_B] \frac{dC_{AB}}{dx} \quad (10)$$

As the % loading of the metal chelate increases, the solute flux of the O₂ increases, but beyond the optimum % loading the solute flux begins to decrease.

Above about 20% loading, a different effect is introduced. Solubility tests of CoTPP loaded films indicate a lack of crosslinking, since the deposition rate is too high to build up enough crosslinks within the films. In these higher loaded films, N₂ permeability is higher than that of lower loaded films, resulting in decreasing ideal selectivities of composites with higher loading percents.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Nicholas C. Morosoff for his guidance and patience as his research advisor during the past year. The author would also like to thank Youngson Choe for his cooperation, time, patience, and friendship.

It should be noted that most of the results presented in this paper were achieved and compiled by Youngson. The amount of experimental work in which the author actually participated in constituted a very small part of Youngson's research in pursuit of his Ph.D.

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