FIXED SITE FACILITATED TRANSPORT IN COBALT CHELATE CONTAINING PLASMA POLYMERS

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Introduction

Separation of gas mixtures through conventional polymer membranes is based on differences in the diffusion coefficients for the gases [1]. This means of separation is, therefore, most effective for gases with an appreciable difference in molecular size. For gas mixtures of similar molecular size (e.g. O_2/N_2), separation on the basis of solubility differences would be more effective. Using a chemically reactive transition metal complex capable of reversibly binding one of the component but not the other would help achieve this separation. For example, a transition metal complex capable of reversibly binding O_2 but not N_2 could be used for separation. Transport which makes use of the preferential binding of a molecule to a metal chelate which is fixed in place in a polymer film is referred to as fixed site facilitated transport (FSFT) [2,3]. In this presentation we describe the preparation of plasma polymer films which contain cobalt (II) meso-tetraphenylporphyrin (CoTPP). These films have been shown to demonstrate FSFT for O_2.

Several publications describe theoretical models for the transport behavior through these membranes [4-7]. Paul and Koros [4] described a dual-mode sorption model to describe transport behavior through glassy polymers, based on the hypothesis that two diffusion coefficients are required to describe such transport. One diffusion coefficient, D_D, is associated with transport through the polymer matrix and one with microvoids in the matrix, D_H. This model is also applicable to FSFT membranes with the metal chelate taking the place of the microvoids as the Langmuir site. More recent models proposed by Fredrickson and Helfand, Barrer, and Noble modify the dual-mode sorption model to make it more physically realistic [5-7]. In addition, the more recent models provide a better fit to our experimental data.

Experimental

The plasma reactor used in this study has been described and depicted previously [8,9]. The reactor is a glass cylinder, 5.0 cm ID, with the RF power (13.56 MHz) inductively coupled to a coaxial 2.0 cm ID tube into which the monomer must diffuse. The RF power, at 7 to 12 Watts, was supplied with an RF Plasma Products 5S generator. A tantalum heating boat, which contains the metal chelate is located downstream of the monomer inlet, situated in an appendage which extends from the bottom of the reactor. The metal chelate complex is sublimed into the reactor, and is deposited simultaneously with a hydrocarbon plasma polymer on substrates placed on the ceiling of the reactor. The metal complex used in this study, Cobalt (II) meso-tetraphenylporphyrin (CoTPP) (Fig. 1), was delivered to the reactor at rates of 2 to 11.5 $\mu g \cdot cm^{-2} \cdot min^{-1}$. It is capable of reversibly binding O_2 but not N_2. Trans-2-butene (T2B), at flow rates of 0.3 to 0.4 sccm, was used to create the hydrocarbon plasma polymer. Substrates used were: glass for deposition rates, NaCl crystal fragments for FTIR, and substrates for gas permeability measurements.

Deposition rates were determined gravimetrically for deposition on the glass substrates. Infrared spectra were obtained by transmission on films deposited on NaCl crystal fragments with a Perkin-Elmer 1760-X FTIR spectrometer. The chelate mass content was obtained by comparing the absorbance of specific chelate FTIR bands for a plasma polymer of known mass thickness ($\mu g/cm^2$) with the absorbance of the same band for a sublimed metal chelate film of the same mass thickness [8]. Substrates for permeability measurements were Al_2O_3 filters consisting of 0.020 µm diameter pores (anodisc filters) onto which an approximately 13 µm thick silicone potting compound was formed (Fig.2). The silicone potting compound, which contained vinyl methyl polysiloxane, was spin coated onto the anodisc filter and cured at 74° C.

Permeation measurements were carried out using the permeation cell depicted in Fig. 3. The permeant was introduced (high pressure side) and was allowed to permeate through the membrane into a known volume (at the low pressure side). The rise in pressure was recorded and used to determine the permeability. To obtain the permeability of the plasma polymer/metal chelate layer alone, the following equation was applied:

$$\frac{L}{P} = \frac{L_1}{P_1} + \frac{L_2}{P_2} \qquad (1)$$

where L, L_1, and L_2 are the thicknesses of the composite, the silicone potting compound layer, and the plasma polymer/metal chelate layer, respectively; and P, P_1, and P_2 are the permeabilities of the composite, the silicone potting compound layer, and the plasma polymer/metal chelate layer, respectively. All variables in the equation except P_2 were obtained experimentally or by direct measurement.

To perform sorption measurements, CoTPP/T2B plasma polymer film was deposited on the surface of a gold-coated quartz crystal deposition monitor sensor. This crystal, along with the deposition rate monitor, was then placed in a chamber which was evacuated for 24 hours. Oxygen at a pressure of 100-5000 Torr was then introduced and the oxygen binding was monitored as a function of time.

Results and Discussion

We have previously shown that CoTPP can be incorporated in plasma polymer films with preservation of the ability to reversibly bind oxygen [10,11]. In some cases, we have observed FSFT of oxygen through such films. The evidence for this is presented below.

Ideal selectivity is defined as the ratio of the permeabilities of the two gases of interest. In this case, the ideal selectivity is defined as $\alpha = P(O_2)/P(N_2)$. The ideal selectivity of the composite (plasma polymer together with the silicone potting compound) is plotted versus nominal thickness of the plasma polymer film in Fig. 4. Complete coverage is obtained at a nominal mass thickness of 8.5 $\mu g/cm^2$. Figure 5 shows the ideal selectivities for both the composite and the plasma polymer as a function of the percent loading of CoTPP (which reversibly binds O_2 but not N_2) and NiTPP (which does not bind either component). The ideal selectivity increases for the CoTPP/T2B plasma polymer membranes, as expected for FSFT, up to 5% loading, but then decreases. The ideal selectivity for the NiTPP/T2B plasma polymer membranes remains fairly constant as a function of loading percent, indicating no FSFT, as expected. NiTPP does not reversibly bind O_2.

Permeability of both O_2 and N_2 as a function of the initial pressure of the permeant is shown in Fig. 6 for an 8.7 $\mu g/cm^2$ thick, 2% CoTPP loaded plasma polymer film. The permeability of O_2 initially decreases and then remains constant with increasing pressure. The permeability of N_2 remains fairly constant with pressure, and is a lower value than for O_2, consistent with the definition of FSFT (O_2 transport facilitated, but not N_2).

Time lag is defined as the time for permeation to reach steady state. This was determined by first exposing the CoTPP/T2B plasma polymer membrane to vacuum and then introducing O_2 on the high pressure side of the membrane. The time to reach steady state permeation was then determined from the pressure data. Time lag as a function of initial permeant pressure is shown in Fig. 7 for both O_2 and N_2 permeation through CoTPP-and NiTPP/T2B plasma polymer films at thicknesses of 8.7 and 10 $\mu g/cm^2$. Time lag decreases as pressure increases for O_2 permeation through the CoTPP/T2B plasma polymer films, rapidly at the lower pressures and then more gradually at the higher O_2 pressures, consistent with FSFT of O_2 through these membranes. The time lag for oxygen and nitrogen permeation through the NiTPP/T2B plasma polymer films and for N_2 permeation through the CoTPP/T2B plasma polymer film remains constant and at a low value as a function of pressure, consistent with no FSFT, as expected.

The parameters required for description of permeation by the Paul/Koros and Fredrickson/Helfand models were obtained from sorption and time lag data (see Fig. 7). These were then used to calculate permeability as a function of pressure. The results are compared with the experimental data in Fig. 6. The Fredrickson and Helfand model provided a better fit to the experimental data.

Experiments are in progress to determine the aspects of plasma polymer morphology and/or microstructure that permit FSFT to occur.

Conclusions

1. CoTPP has been incorporated into a plasma polymer film without compromising the ability of the metal to reversibly bind oxygen [10,11].

2. In some cases, such films exhibit pressure dependent sorption and permeability behavior indicative of FSFT of oxygen.

References

1. V.T. Stannett, W.J. Koros, D.R. Paul, and R.W. Baker, Adv. Polymer Sci., 32,69(1979).

2. H. Nishide, M. Ohyanagi, O. Okada, and E. Tsuchida, Macromol. 21,2910(1988).

3. M.S. Delaney, D. Reddy, and R.A. Wessling, J. Membr. Sci., 49,15(1990).

4. D.R. Paul and W.J. Koros, J. Polym. Sci.: Polym. Phys. Ed., 14,675(1976).

5. G.H. Fredrickson and E. Helfand, Macromol., 18,2201(1985).

6. R.D. Noble, J. Membr. Sci., 60,297(1991).

7. R.M. Barrer, J. Membr. Sci., 18,25(1984).

8. N.C. Morosoff, S.D. Clymer, J.M. Skelly, and A.L. Crumbliss, J. Appl. Polym. Sci.; Appl. Polym. Symp., 46,315(1990).

9. J.M. Skelly, A.L. Crumbliss, S.D. Clymer, V.T. Stannett, and N.C. Morosoff, Polymer Preprints, 32(2),36(1991).

10. J.M. Skelly, N.C. Morosoff, V.T. Stannett, and A.L. Crumbliss, Inorg. Chem., 32,1306(1993).

11. J.M. Skelly, N.C. Morosoff, V.T. Stannett, and A.L. Crumbliss, Chem. Mater., 6,227(1994).

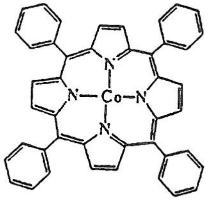

Figure 1. Structure of cobalt (II) meso-tetraphenylporphyrin (CoTPP).

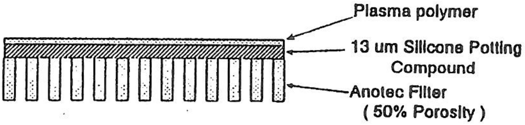

Figure 2. Diagram of the substrate used for the permeability measurements.

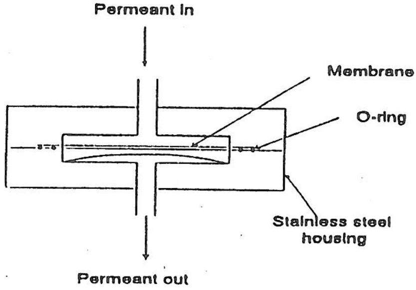

Figure 3. Schematic diagram of the permeation cell.

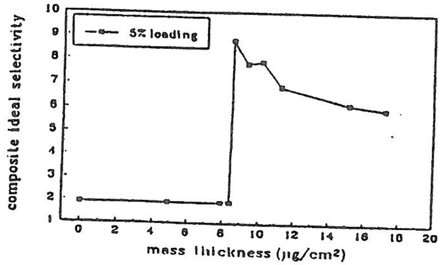

Figure 4. Composite (CoTPP/T2B plasma polymer plus silicone potting compound) ideal selectivity vs. mass thickness at 5 loading percent of CoTPP within the T2B plasma polymer film.

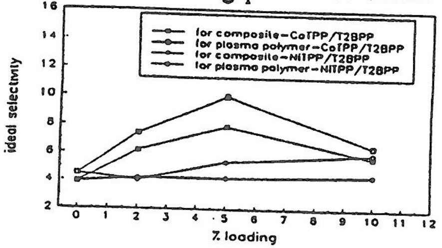

Figure 5. Ideal selectivities for both composite and plasma polymer vs. loading percent of CoTPP (CoTPP/T2B plasma polymer thickness = 10 μg/cm², initial O_2 (permeant) pressure = 600 Torr).

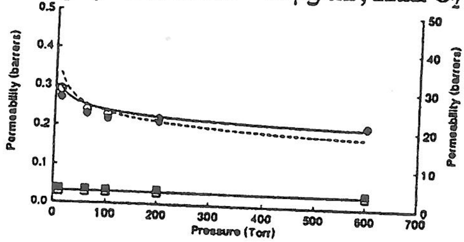

Figure 6. Permeabilities vs. initial permeant pressure for the composite (8.7 μg/cm², 2% CoTPP loaded T2B plasma polymer film on 13 μm thick silicone potting compound) using the right ordinate axis (N_2 ■, O_2 ●) and for the CoTPP/T2B plasma polymer film (N_2 □, O_2 O), derived from the composite values, using the left ordinate axis. Permeabilities of O_2 as a function of pressure calculated using the Fredrickson/Helfand (solid line) and Paul/Koros (dashed line) models use the left ordinate axis.

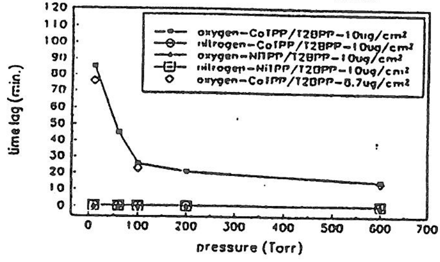

Figure 7. Time lag vs. O_2 and N_2 pressures.