

공기 분리용 열분해 탄소막

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Pyrolytic Carbon Membranes for Air Separations

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Abstract: Carbon molecular sieve (CMS) membranes were synthesized by the pyrolysis of polymeric precursors. The CMS materials had oxygen-nitrogen selectivities much higher than those observed for the polymeric precursors. Typically molecular sieving materials have diffusion selectivities much higher than polymeric materials. This has been identified as a result of higher *entropic selectivity* of the molecular sieving materials. A study of the development of molecular sieving properties as the polymeric precursor is pyrolyzed into a CMS material will offer us an insight into polymeric molecular structures needed for enhanced entropic selectivity membrane materials.

1. Introduction

Air separation into oxygen enriched 'permeate' and nitrogen enriched 'reject' streams typify current applications of gas separation membranes. Practical gas separation membranes need to be highly permeable to one of the mixture components while significantly rejecting the other component. Conventionally polymeric membranes have been used in these applications. Membrane materials must achieve a trade-off between permeability or (productivity) and permselectivity (or purity). Current knowledge permits tailoring glassy polymer structures to improve permeability and permselectivity simultaneously by introducing packing-inhibiting bulky groups on the polymer backbone to simultaneously hinder both segmental motion and

intersegmental packing. The benefits achievable using this simple concept seem to be approaching a limit as shown in the rather extensive trade-off curve for gas permeability and selectivity in Fig. 1. This is an adaptation of a similar figure published in 1991 [1]. In fact, the 'upper bound' line drawn in Fig. 1 still applies almost five years later. Molecular sieving materials like zeolites and carbon molecular sieves (CMS) lie above the upper bound for polymers on this trade-off curve. Understanding why polymeric membranes have been unable to achieve selectivities of the same order as zeolites or CMS is both scientifically and technologically interesting. Huge markets for O₂/N₂ separations alone justify focusing on approaches to achieve gas separation by advanced materials. Although zeolites and CMS are useful indicators of achievable limits for separation

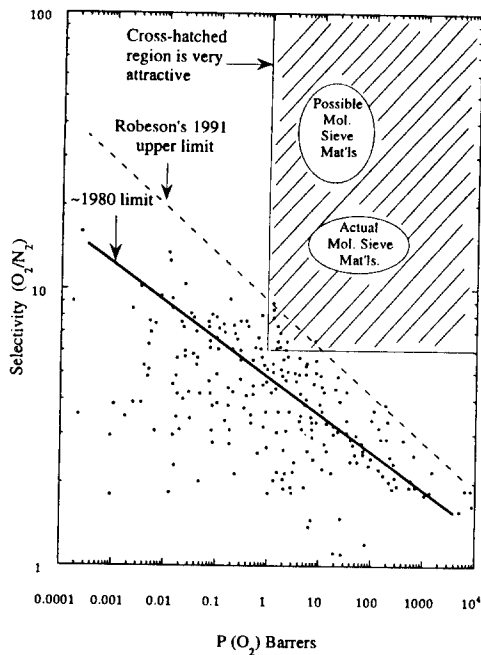


Fig. 1. Trade-off curve for permeability and permselectivity of oxygen-nitrogen mixture.

performance, practical hollow fiber membrane modules are likely to rely upon *polymeric* substrates due to economics, convenience, robustness and compatibility with existing manufacturing systems. The challenge, therefore, is to identify and introduce the key missing elements in polymeric materials to boost performance above the upper bound and approach that of the molecular sieving materials. The first step towards this objective is a study of molecular sieving membranes to identify the factors which lead to their improved transport performance over polymeric materials. CMS materials have typically been synthesized by the pyrolysis of polymeric materials in an inert atmosphere. CMS membranes for gas separation application have also been reported in literature which have been made by pyrolysis of low selectivity polymeric membranes in the form of flat sheets[2] and in the form of hollow fibers [3, 4]. In these studies the resulting CMS materials yielded much improved selectivities.

2. Background

Typically non-porous polymeric, CMS and zeolite media transport gases by a so called sorption-diffusion mechanism. Permeability of a penetrant in a membrane, defined as a pressure and thickness normalized flux $P_A = \frac{\text{Flux} \cdot \text{thickness}}{\Delta p}$, can be expressed as a product of a kinetic factor D , the diffusion coefficient and a thermodynamic factor S , the sorption coefficient[5]

$$P_A = D_A \cdot S_A \quad (1)$$

Following from Eq. 1, the permselectivity, $\alpha_{A/B}$, of practical gas separation membranes can be interpreted as a product of two terms: one related to the ratio of diffusivities of the two gases in the membrane and the second determined by the ratio of sorptivity of these gases in the membrane.

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \cdot \frac{S_A}{S_B} \quad (2)$$

The sorptivity selectivity, $\frac{S_A}{S_B}$, has proven difficult to adjust without seriously off-setting the diffusivity selectivity for non-porous polymeric membrane materials[5]. On the other hand, adjustment of the diffusivity selectivity has been the major tool used in moving from the 1980 limit to the 1991 (and current) limit depicted in Fig. 1. For O_2/N_2 separation, all of the materials that were compared, polymeric and molecular sieving, showed a sorption selectivity only between 0.7 and 2. It is the diffusivity selectivity which accounts for the vast differences in the permselectivity values in Fig. 1. A penetrant sorbed in a non-porous polymer matrix diffuses by executing a size-dependent jump. These jumps are moderated by the activation energy needed to create transient gaps of sufficient size to enable the jump to occur. In the rigid matrix of molecular sieving materials the molecules have to jump through narrow constricted regions of dimensions close to that of the diffusing gas molecule. Smaller penetrants require the localization of less activation energy. Size

dependent diffusion selectivity, therefore, favors the smaller of the two penetrants. This energetically biased selection process can be called 'energetic selectivity'. Most attention in the past has been focused on this energetic selectivity due to a better understanding of how to measure and tailor activation energies of diffusion in typical adsorbent and membrane materials.

2. 1. Entropic Selectivity

A comparison of the gas transport properties of the three different classes of materials shown in Fig. 1, namely, zeolite 4A, CMS and an upper bound polymer, revealed to us the importance of a phenomenon that is probably best referred to as 'entropic selectivity'[6]. Zeolite 4A and CMS have dissimilar chemical properties but have similar correlation between diffusivity and gas molecular diameters, thereby indicating that the barrier to diffusion is entirely due to repulsive forces involved in passing through the constricted regions of the micropores[7]. A rough analogy to the molecular sieving process can be drawn from the theory of diffusion of gases in glassy polymer matrices. In this case, as noted above, small gas molecules diffuse through openings occurring in the non-porous polymer matrix due to thermally induced local torsional motions of the polymer backbone[5].

Since diffusion is an activated process in both molecular sieving and polymeric media, the diffusion coefficient can be written as an Arrhenius relationship, viz.,

$$D = D_0 \exp\left[-E_d^\ddagger/RT\right] \quad (3)$$

where E_d^\ddagger is the energy of activation for the gas molecule to execute a diffusive jump from one cavity to another, D_0 is the temperature-independent pre-exponential term, T is the absolute temperature and R the universal gas constant. As observed in Table 1, there are relatively little differences in the exponential terms for polymers, zeolites and CMS; hence, the pre-exponential term D_0 accounts for the

substantial difference in the diffusivity selectivity for the three classes of materials. From the transition state theory the pre-exponential factor is [8]:

$$D_0 = e\lambda^2 \frac{kT}{h} \exp\left[\frac{S_d^\ddagger}{R}\right] \quad (4)$$

where, λ is the average diffusive jump length in the diffusion medium, S_d^\ddagger is the activation entropy of diffusion and k and h are the Boltzmann's and Planck's constants respectively. For the O_2/N_2 pair, the difference in the kinetic diameters of the two molecules is very small, hence it is expected that λ can be considered similar for both gases. The diffusivity selectivity for such a gas pair can be given by the following equation,

$$\frac{D_A}{D_B} = \underbrace{\exp\left[\frac{(S_{dA}^\ddagger - S_{dB}^\ddagger)}{R}\right]}_{\text{Entropic Selectivity}} \underbrace{\exp\left[\frac{-(E_{dA}^\ddagger - E_{dB}^\ddagger)}{RT}\right]}_{\text{Energetic Selectivity}} \quad (5)$$

or,

$$\frac{D_A}{D_B} = \exp\left[\frac{\Delta S_{A,B}^\ddagger}{R}\right] \exp\left[\frac{-\Delta E_{A,B}^\ddagger}{RT}\right] \quad (6)$$

In Eq. 6 the ' Δ ' terms refer to differences in activation quantities for oxygen and nitrogen. The diffusivity selectivity has been divided into an entropic and an energetic selectivity. From the values in Table 1, it can be seen that both energetic and entropic factors contribute significantly to the high values of diffusivity selectivities observed for zeolites and carbons. However, for the polymeric materials, the entropic factor is close to unity and its contribution to diffusivity selectivity is negligible. This observation is significant, since the glassy polymer considered in this study, a polypyrrolone[9], is one of the very best available in this generation and actually lies on the upper bound line at an overall O_2/N_2 selectivity of 6.5 and an oxygen permeability of 7.5 Barrers (1 Barrer = 10^{-10} cc(STP) cm/cm² sec cmHg). The entropic selectivity arises from oxygen retaining more degrees of freedom in the transition state than nitrogen. The polymer chains which are in constant thermal motion are incapable of

Table 1. Comparison of Diffusion Selectivities of Three Classes of Materials

Material	$\frac{D_{O_2}}{D_{N_2}}$ at 35°C	$E_{d_{O_2}} - E_{d_{N_2}}$ (kcal/mol)	$\exp\left[\frac{-\Delta E_{O_2, N_2}}{RT}\right]$ Energetic Effects	$\exp\left[\frac{-\Delta S_{O_2, N_2}}{R}\right]$ Entropic Effects
4A Zeolites	104	-1.2	7.1	104/7.1 = 14.7
Carbon Molecular Sieves ^a	25-45	-1.0	5.1	25-45/5.1 = 4.9-8.8
Upper bound poly-pyrrolone	5.1	-0.90 ^b	4.35	5.1/4.35 = 1.2

a [7]

b [11]

selectively restricting the motion of nitrogen in the transition state, thus resulting in a complete loss of entropic selectivity. The above observations imply that advanced membranes for O₂/N₂ separation must have markedly lower motions of the matrix for increased entropic selectivity.

The amorphous matrix of a CMS is obtained by pyrolyzing a polymer. Structural changes taking place at a molecular level lead to an increase in entropic selectivities. The accompanying improvements in permselectivities for O₂/N₂ separation will be studied as a material undergoes transformation from a flexible polymer matrix to a rigid carbon matrix.

3. Experimental

Dense, flat-sheet films of a hexa-fluoro isopropylidene substituted polyimide were pyrolyzed in a vacuum environment. The polyimide material and the temperature-time protocol used for our pyrolysis experiments was one optimized after extensive experimentation by Jones et al.[4]. In that work asymmetric hollow fiber polymer membranes were pyrolyzed to CMS membranes; however, to compute the entropic selectivity of materials, we need to separate out the diffusion coefficient from the measured flux/permeability values. For unambiguous results, homogeneous membranes with an accurate estimation of the thickness are required. Hence, symmetric, dense polymeric films were pyrolyzed in

this study to obtain high selectivity pyrolyzed membranes. Another aim of this study was to follow the development of these high selectivity membranes from the low selectivity polymer as the material is pyrolyzed. For this objective, the pyrolysis protocol was terminated at an intermediate step and these partially pyrolyzed membranes were tested for air separation properties.

3. 1. Pyrolysis

The soluble polyimide was cast into homogeneous, symmetric films from solution. Film thicknesses near 25-50 microns were typical. After careful drying to ensure complete removal of all solvent the films were placed on a flat quartz plate for support which was then placed in a quartz tube furnace. The furnace was then evacuated until the pressure was below 0.03 torr as read by a McLeod's vacuum gauge. The furnace was then isolated from the vacuum gauge and the heating cycle was started. The heating rate of the furnace was controlled by an Omega programmable temperature controller with PID control. At the beginning of the heating cycle a ramp rate of 13.3°C/min was used which was gradually reduced to a rate of 0.25°C/min as the final pyrolysis temperature of 550°C was approached. The membranes were held at this temperature for a period of two hours and then the furnace was allowed to cool gradually below 40°C. Before removing the pyrolyzed membranes (P) from the furnace, the pressure was read once again to confirm that no

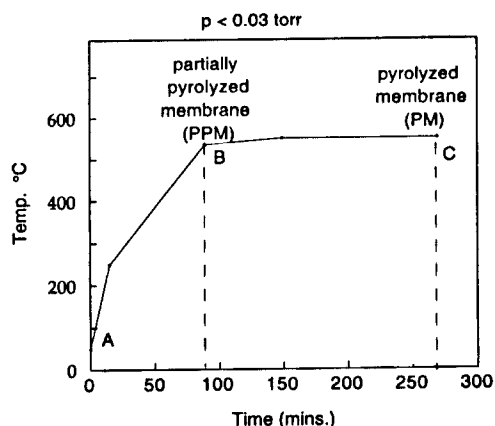


Fig. 2. Temperature-time profile for pyrolysis.

leaks had been caused during the course of pyrolysis. The partially pyrolyzed membranes (PP) were heated only till 535°C as shown in Fig. 2.

3.2. Permeation and Sorption

Polymer films and pyrolyzed membranes were tested for gas separation in a constant volume pressure rise cell with downstream pressures close to vacuum. The system is described in detail elsewhere [10]. High purity oxygen, nitrogen and dry compressed air were used as feed. Exposure to organics can lead to an irreversible loss of flux in the carbon membranes. To prevent exposure from vacuum pump oil vapors, a foreline trap with activated alumina adsorbent was attached to the inlet of the vacuum pump at all times.

Polymer precursors and CMS films were tested for permeation using pure oxygen and pure nitrogen. The relatively brittle pyrolyzed membranes were supported on top of a fritted metal disk on the downstream side of a stainless steel high pressure permeation cell. To prevent the brittle membranes from breaking due to the surface roughness of the metal disk, a highly porous ceramic Anotec[®] membrane was placed under the carbon membrane. The membrane was then sealed to the bottom of the cell using a 5-minute epoxy. The membrane thus sealed on the test cell was carefully evacuated at high tem-

peratures to ensure removal of all adsorbed gases from the pores of the carbon membrane. The permeate and the retentate stream compositions were analyzed using an on-line Gas Chromatograph for oxygen and nitrogen compositions. This allows us to calculate the flux of each component through the membrane and the O₂/N₂ selectivity.

4. Results and Discussion

The polymer precursor was a high permeability low selectivity glassy material with oxygen permeabilities of 32 Barrers and oxygen/nitrogen selectivities of 4.2. This makes the polymer fall at point A on the trade-off curve in Fig. 3.

The weight loss for the pyrolyzed membranes was 30~35% by wt. and a shrinkage of 35~45% in the area of the membranes was observed. There was an increase in the membrane thickness due to pyrolysis as well (a 15~35% increase in thickness of the membranes). Carbon membranes tested were typically 25~60 microns thick. The resulting membranes, both P and PP, had a smooth and glossy surface. Some membranes curl up at the edges to varying extents, however, they were flexible enough to be flattened on the permeation cell. This enabled us to seal the membranes to the test cell without causing any defects.

Asymmetry may arise in the membranes during the course of pyrolysis. Volatile pyrolysis products trying to escape from the membranes may form a porous structure in the membranes. This leads to some uncertainty about the thickness of the separating layer in the pyrolyzed membranes. Unusually high fluxes measured for the membranes, P and PP, lead us to believe that our membranes may have developed such an asymmetric porous structure. Table 2 shows an estimate of the permeabilities assuming the thicknesses of the separating layer, t , as different fractions of the total membrane thickness, h . These values for P and PP membranes are plotted in Fig. 3. Also, plotted are the results obtained by Jones depicted as region 'J'. There was uncertainty

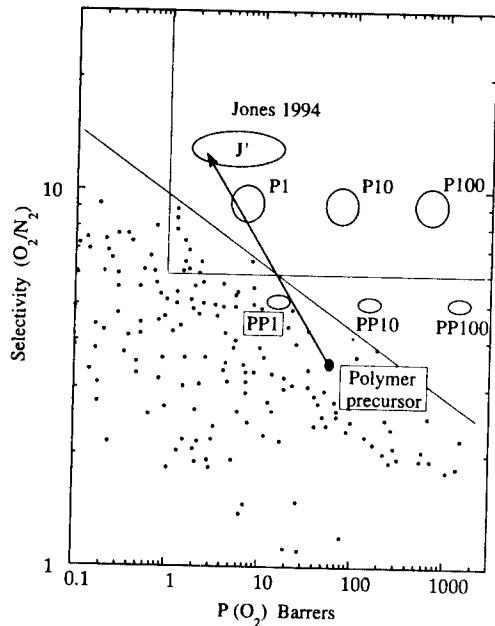


Fig. 3. Carbon membrane and polymer precursor data on the upper-bound curve.

in the thickness of the separating layer in that work as well, hence permeabilities have been estimated from the flux values using separating layer thicknesses ranging from 1000 Å to 5000 Å. This is a typical range of skin thicknesses in polymeric hollow fiber membranes.

Permeabilities calculated assuming that only 1% of the total P and PP membrane thicknesses are selective give data rather close to that obtained for the hollow fiber CMS membranes as shown in Fig. 3. This assumption may indeed be true as the precursor polymer films were supported on a non-porous quartz plate during pyrolysis. Presumably the volatile pyrolysis products would have lesser resistance to diffusion from the top surface of the membrane forming a more porous structure on the top with only a thin selective layer at the bottom surface.

The polymeric precursor falls well below the upper-bound curve as seen in Fig. 3. The material PP moves closer to the upper bound curve as the material goes through the pyrolysis protocol and with the completion of the protocol the performance

Table 2. Permselectivities and Permeability Estimates for Pyrolyzed Membranes

Polymer	P_{O_2} Barrers ^a	$\frac{P_{O_2}}{P_{N_2}}$
Polymer Precursor	28.5	4.22
PP (Partially pyrolyzed memb)		
$t=h$ (PP100)	1200~1400	5
$t=0.1h$ (PP10)	120~140	
$t=0.01h$ (PP1)	12~14	
P (Pyrolyzed memb)		
$t=h$ (P100)	600~1000	8~10
$t=0.1h$ (P10)	60~100	
$t=0.01h$ (P1)	6~10	

^a Barrers = 10^{-10} cc(STP) cm/cm² cmHg sec

t: thickness of the separating layer

h: total membrane thickness

of the material (estimated by the permeability/permeability properties) improves to place the material above the upper-bound curve with increasing selectivities. Recalling, from Fig. 2, the PP membranes were heated at 535°C which is close to the final pyrolysis temperature of 550°C. It would appear that most of the transformation in structure and the resulting improvement in performance arises in a small temperature range close to 550°C. We also notice that selectivities for membrane P were lower than those reported by Jones in an essentially similar study. The trend observed for membranes in this study, P and PP, indicates that selectivities will improve as we go further along the pyrolysis protocol with increasing temperatures and times. Extending the final temperature and/or the hold time at the final temperature beyond what we have been using presently would give us CMS materials with higher permselectivities to match those reported in work by Jones.

5. Conclusions

Molecular sieving materials like CMS and zeolites

have higher permselectivity values than polymers for gas separations due to an added contribution from entropic selectivity which is negligible in polymers. A study of amorphous carbon molecular sieves will prove valuable to gain an insight into what factors are responsible for this entropic selectivity in materials. It has been demonstrated that CMS membranes can be formed by the pyrolysis of polymeric precursors with a remarkable improvement in the performance properties. Further improvement in permselectivities could be achieved by increasing the temperature and time for pyrolysis. An asymmetry may develop in the membranes as a result of pyrolysis starting from symmetric polymeric precursors. This issue will be probed further to get an accurate estimate of the thickness of the selective layer in order to separate out the diffusivity term from the permeability data.

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