Macromol. Symp. ***188,*** *13–22 (2002)*

Gas Separation Membranes: Needs for Combined Materials Science and Processing Approaches

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Summary: Huge markets would exist for high volume gas separation membranes if more robust and higher selectivity membranes were economically available. Many of these markets include totally new paradigms, such as fuel cell driven vehicles and membrane reactors for hydrocarbon production. Other markets involve displacing entrenched large scale separations processes with more advanced versions of first generation "conventional" membranes. Existing materials and formation processes cannot exploit most of these opportunities, so basic research is needed. This research must occur with an awareness that competition to displace highly optimized conventional technologies such as absorption, cryogenic distillation and adsorption must consider economic as well as technical efficacy. Next generation membrane processes should, therefore, maintain attractive economics associated with current polymer-based membranes, while greatly extending performance properties. Several "contender" strategies based largely on polymers and specialized polymer processing approaches for achieving this ambitious goal will be considered in more detail.

Introduction and Background

Criteria for selecting a membrane for a given application are complex; nonetheless, durability, mechanical integrity under the operating conditions, productivity and separation efficiency are important stipulations that must be balanced against cost in all cases. The relative importance of each of these requirements varies with the application; however, selectivity (or separation efficiency) and permeation rate (or productivity) are clearly the most basic.

The so-called 'permeability" is the most commonly used parameter for describing mass transport through a membrane of thickness, ℓ, across which a driving force , ΔDF, is applied, viz.

$$\mathrm{P_i} = \frac{Flux\ of\ "i"}{\Delta DF/\ell} \qquad (1)$$

CCC 1022-1360/00/$ 17.50+.50/0

where the flux of component "i" is usually represented in terms of mols, or some closely related units and ΔDF is often simply equated to the difference in partial pressure of a component, eg. O_2) acting between the upstream and downstream membrane faces at points "1" and "2", respectively.

The ability of a membrane to achieve a separation of component "i" vs., "j" (eg. O_2 vs. N_2) is called "selectivity" or separation factor, α_{ij}. The separation factor is equal to the ratio of the mole fractions of component "i" and "j" at the downstream ("2") and upstream ("1") membrane faces, so:

$$\alpha_{ij} = \frac{y_{2i}/y_{2j}}{y_{1i}/y_{1j}} \qquad (2)$$

Under conditions where the downstream pressure is much lower than that in the upstream, α_{ij} can be simply approximated by the ratio of the permeabilities of component i vs. j, e.g.,

$$\alpha_{ij} = \frac{P_i}{P_j} \qquad (3)$$

In the absence of defects, the selectivity is independent of thickness and only a function of the material properties at the operating conditions. For a *given thickness*, the achievable flux (i.e., productivity) is only a function of the effective permeability of the selective layer. Clearly, therefore, the permeabilities of both the desired permeate gas, i, and the rejected gas, j, are of utmost importance in determining the effectiveness of the membrane. The productivity is a function of the material properties as well as the thickness of the barrier, and the lower the thickness, the higher the productivity.

The "Contender" Membrane Technologies

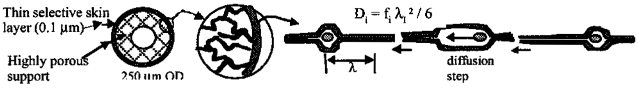
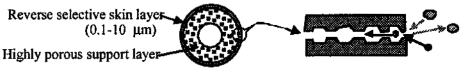
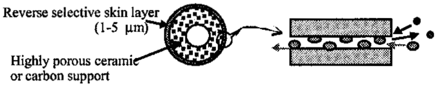
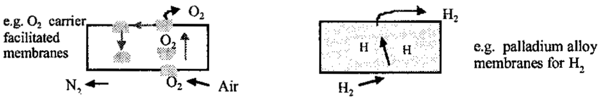
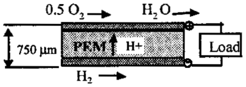
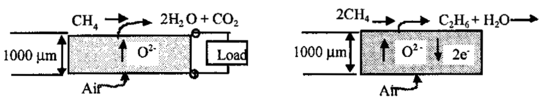
A membrane can be selective by various permeation mechanisms, and these can be broadly classified into three groups as described below.

"Simple" Sorption-Diffusion Membranes

These membranes are so named because transport occurs when gas molecules from the upstream gas phase first sorb into the membrane, then diffuse across it and finally desorb on the downstream gas phase side.

The membranes used in most commercial applications are polymeric solution-diffusion types [Figure 1A][1-5]. The membrane materials used in most separations are glassy polymers, which derive their selectivity primarily from their ability to separate gases based on subtle differences in penetrant size. Polymeric membranes tend to be more economical than other materials and thus dominate traditional gas separations. The low cost of polymeric membranes results from their ability to be easily spun into hollow asymmetric fibers or spiral wound modules, due to their segmental flexibility and

Figure 1: "Contender" technologies for large volume gas separation

Type	Features of Primary Gas Separation Membrane Types
A. Asymmetric polymeric solution-diffusion	
B. Molecular sieving (zeolite or carbon)	 (wide range of membrane sizes & morphologies)
C. "Reverse selective" surface diffusion	 (wide range of membrane sizes & morphologies)
D. Complexing & Reactive	
E. Proton exchange (PEM) (e.g. Nafion®)	
F. Solid Oxides	

solution processability. The main problems to be overcome in using polymeric membranes are the loss in performance stability at high temperature, high pressure and in the presence of highly sorbing components. The segmental flexibility of polymeric membranes that makes them economical to prepare, in fact, limits their discriminating ability for similarly sized penetrants [6].

Molecular sieving materials are an alternative to polymers. They rely primarily upon differences in molecular size to achieve separation. These membranes are ultra-microporous, with sufficiently small pores to exclude some molecules while allowing others to pass through (Figure 1B). On a laboratory scale, these membranes show extremely attractive permeation performance [7-8]. However, these membranes are still difficult to process, are fragile, and expensive to fabricate; thus, they are not commercially significant today except in niche applications.

In certain separations, it may be advantageous to permeate the larger sized penetrant and retain the smaller component. These separations can be potentially achieved using "surface selective flow" membranes [9-10] [Figure 1C]. The adsorbed molecules tend to create a hindrance to transport of smaller non-adsorbed species through the void space in the pores [11].

"Complex" Sorption-Diffusion Membranes

These membranes are similar to the "simple" sorption-diffusion membranes, but they involve additional phenomena as well as simple penetrant dissolution and diffusion [Figure 1D]. There can be further classified into two types: (i) facilitated transport for various gas types, and (ii) palladium and related alloys for hydrogen. Both facilitated transport and metal membranes have potential niche positions in the market; however, until issues relating to stability and cost are resolved, these membranes are unlikely to be used for large-scale gas separations.

Ion-Conducting Membranes

The most important ion conducting membranes are solid oxides (Figure 1F) and proton exchange (Figure 1E) types [12]. The solid oxides are permeable to oxygen ions and they can be further divided into two classes: mixed ionic electronic conductors and solid oxides. These membranes have exceptionally high selectivity and high fluxes compared to polymeric membranes and typically operate at high temperature (700 °C). There are, however, many problems that need to be resolved before large-scale membrane modules based on these materials can be manufactured. These problems include difficulties in proper sealing of the membranes as well as high sensitivity of membranes to the temperature gradients that can result in membrane cracking [13].

Proton exchange membranes [Figure 1E] are the mirror image of some solid oxide membranes described earlier for fuel cells, since they *only conduct protons* and not electrons and thus can potentially be used as power sources. Proton exchange membranes can be organic inorganic or in nature, but the most popular of these is Nafion®, a perfluoro sulfonic acid containing polymer. These membranes will play an increasingly important role in practical fuel cell applications. Generally, these applications do not involve large membrane areas for each specific application. Nevertheless, the potential market is likely to be very large when the product of the number of applications and the size of the membrane needed in each application is considered. The technical challenges are quite different in such fuel cell and more conventional large volume gas separation membranes that represent the majority of membrane-based gas separations. Therefore, proton exchange membranes will not be discussed further here. A separate detailed analysis of opportunities and challenges in this exciting fuel cell area of membrane applications would be valuable to motivate advances in this area as well.

Challenges in Large Scale Gas Separation Applications

The immediate challenges faced by current membrane technology can essentially be summarized into a few key areas. Achieving *higher permselectivity* for the relevant application with at least equivalent productivity is the first of these challenges. *Maintaining these properties* in the presence of complex and aggressive feeds is the second challenge. A third challenge in certain applications, e.g. hydrogen recovery, is *avoiding recompression of the desired product.* Materials exist that are technically capable of overcoming these three challenges outlined above; however, economic competitiveness with non-membrane alternatives is clearly at least as important as purely technical issues and inhibit their use for large-scale applications. For instance, inorganic non-polymeric membrane materials discussed earlier are capable of giving permselectivities that are five-fold to ten-fold higher than traditional polymeric materials. Moreover, these materials tend to be much less affected by aggressive feeds. Surface Selective Flow membranes are capable of recovering hydrogen without the need for recompression. However, it is not yet clear if these materials or purely molecular sieving zeolite or carbon materials, will become *truly economically feasible* for large-scale applications. Although improvements in manufacturing efficiency can reduce ultimate membrane and module costs, it is reasonable to expect finished modules based on ceramic, glass, carbon, zeolitic and other inorganic membranes to cost between one and three orders of magnitude more per unit of membrane area compared to polymeric membranes. This fact in no way suggests that such high performance materials are inappropriate to assist in expansion of membrane markets. It does, however, suggest that prudent first applications of such materials should target high value or *small niche applications* where cost per unit of membrane is secondary to performance. Examples might include sensors and high value-added specialty separations that are not feasible with membrane based alternatives.

The next section outlines strategies, which have the potential to overcome these challenges while maintaining viable economics.

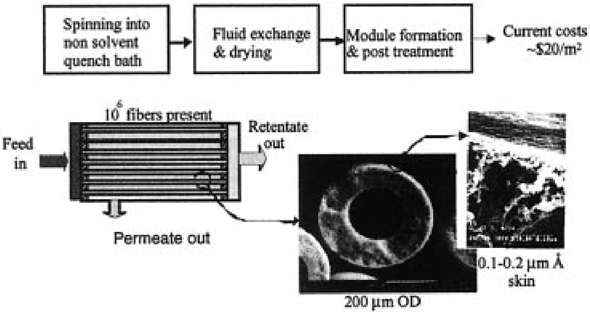
Strategies

Two important classes of materials that lie between conventional polymers and the high-performance materials noted above have been almost completely overlooked in terms of their potential to meet the challenges outlined in the preceding sections. These two classes are: crosslinked polymers and blends of molecular sieving domains in polymers, usually referred to as "mixed matrix" materials. Both of these types of materials are ideally suited for discussion at this conference. Such materials may offer the vehicles for capturing new high volume opportunities mentioned above that require higher selectivities, and the ability to maintain performance in demanding environments.

In order to understand why these schemes are so attractive compared to other options, one needs to examine the current process used to form commercial membranes [1]. Since the current membrane formation process has already been optimized at considerable expense one cannot deviate very significantly from it without significant economic penalty. The process is, however, quite flexible and offers considerable room for innovative adaptation. Both of the options noted above can benefit from existing economical processes for making membranes from conventional non-crosslinked polymers, so they are especially attractive.

As shown in schematically in Figure 2, the modern asymmetric membrane process (either fiber or spiral wound) first involves formulation and spinning or casting of a polymer solution (called a "dope) containing appropriate solvents and nonsolvents. This dope is formed into a nascent membrane and quenched in a nonsolvent (usually water). Subsequent solvent exchange and drying stops allow preservation of an ultrathin selective region on top of a highly porous open-cell support. This morphology maximizes productivities (see Eq(1)) while allowing selectivities equivalent to much thicker layers. High speed formation steps enabled by the desirable properties of polymers allow production of membrane modules at costs of $10-30/m^2. This economical cost makes membranes attractive to potential users.

Figure 2: Efficient asymmetric hollow fiber membrane manufacturing process (50 -100 m/min processing rates)



Crosslinkable Materials

Crosslinking of polymer structures can overcome one of the main challenges mentioned earlier, namely maintaining membrane properties in the presence of aggressive feeds. The crosslinked structure will not tend to placticize as readily, since the crosslinks prevent the material from swelling in the presence of plasticizing agents and promote chemical and thermal stability [14-17]. To implement the selectively crosslinked option, incorporating a crosslinkable functional group in the polymer backbone is an attractive approach since a polymer can then be spun into hollow fiber asymmetric fibers using the conventional formation process and crosslinked in a post-treatment step. Some recent data on crosslinked flat films formed using such an approach have showed the ability to maintain attractive transport properties under conditions where conventional materials typically plasticize and lose performance.

Mixed Matrix Materials

Besides crosslinkable materials, so-called "mixed-matrix" hybrid materials are capable of solving the first challenge, related to achieving higher selectivities, noted earlier. Mixed matrix materials comprising molecular sieve entities embedded in a polymer matrix offer the potential to combine the *processability* of polymers with the *superior gas separation* properties of rigid molecular sieving materials. Current asymmetric composite hollow fibers consist of an inexpensive porous polymeric support coated with a thin, higher performance polymer [18]. Similar in construction, mixed matrix composite (MMC) membranes could replace the thin, higher performance polymeric layer with a reasonable ($\leq$ 30-50 vol. %) sub-micron molecular sieving media, such as zeolites supported within an appropriate polymeric matrix. This could potentially be accomplished within much of the same cost infrastructure as used for the low performance conventional polymer. This approach has the potential to provide separation properties approaching those of high performance pure molecular sieve materials at a fraction of the cost [19].

While both of the above strategies are attractive, significant hurdles remain to be overcome in all cases. The crosslinking scheme needs to be tested on hollow fibers as all reported literature is on flat sheet membranes. Development of alternative crosslinking mechanisms is also required, as this will provide greater flexibility in implementation of this scheme. The mixed matrix work needs to be extended to polymers that are currently useful for gas separation. These materials are rigid and have issues with poor adhesion between the polymeric phase and the molecular sieving phase [20]. The extension of composite spinning to spinning with sieve materials is another significant challenge to the implementation of this scheme.

Conclusions

Exciting opportunities do indeed exist for large-scale gas separations using membranes; however, new material types are likely to be needed to fully benefit from these opportunities. Techniques must be developed to achieve and maintain finer control of transport under realistic operating conditions. Controlled crosslinking to achieve the final rigid structure after spinning of the asymmetric structure is one examples of such techniques. Hybrid structures like mixed matrices, especially when successfully coupled with such finer control methods, can open a new world of application areas. In all cases significant technical barriers exist to implementation. Overcoming these barriers along with continued efforts in molecular sieve, surface flow, and complexing/reactive approaches are needed in the next decade.

Acknowledgments

The authors gratefully acknowledge the support of the Department of Energy, DOE Grant DOE-FG03-95ER14538.

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