

EXPANDING THE LIMITS OF MEMBRANE-BASED GAS SEPARATION MATERIALS

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ABSTRACT

Gas separation science and technology is among the most rapidly growing areas involving membrane-based processes. Nitrogen enrichment of air, hydrogen recovery from a broad array of stream types, and removal of acid gases from natural gases are typical of the applications in this field. Great progress has been made in the discovery of guidelines for optimization of polymer structures with simultaneously high permeabilities and selectivities for these important gas pairs. The development of thin-skinned asymmetric hollow fibers have also provided structures with extremely high permeation fluxes. Especially in the case of O₂/N₂ separations, the rate of improvements in new polymeric materials for gas separations appears to be slowing to a halt. Evidence will be presented, however, that the practical tradeoff between membrane permeability and selectivity has *not* been reached.

The permselectivity of gas separation membranes that operate by a solution-diffusion mechanism can be interpreted as a product of two terms: one related to the relative solubility selectivities of the two gases in the membrane and the second determined by the relative diffusion coefficients of these gases in the membrane. The solubility-related term has proven difficult to adjust without introducing highly undesirable instability in the resultant membrane material. This is due primarily to a tendency for impurities in the process stream to reactively poison membranes which have the ability to selectively complex with the desirable permeant, e.g. oxygen in the O₂/N₂ system. On the other hand, the second term, related to diffusion selectivity, has been valuable for optimizing the current generation of membrane materials. Plots of O₂/N₂ selectivity vs. O₂ permeability of advanced polymers have been approaching an apparent "upper bound" tradeoff line; however, more rigid carbon molecular sieve membrane materials have not apparently been constrained by the same upper bound tradeoff line. This is somewhat surprising, since the diffusion process in both cases is "thermally activated" and a sorption-diffusion mechanism applies.

The mobility selection process operates on the basis of size and shape differences to allow control of the diffusion coefficient of molecule "A" compared to molecule "B". In the current generation of polymeric membranes, longer scale, but still local, segmental packing morphology is known to be important in determining membrane selectivity. This perspective helps to unify the field of carbon-based molecular sieve membranes and adsorbents with that of polymer-based membranes for gas separation. While advanced polymeric materials for gas separation have much in common with molecular sieve carbons, they still maintain more segmental level mobility. Distinctions also exist between more or less uniformly packing-disrupted materials such as polytrimethyl-silylpropyne (PTMSP) and complex polyimides or related families with long, flat, packable units connected by rigid-kinked joints.

Highly rigid polymers with properties similar to those of the molecular sieve carbons will be *difficult to dissolve* and the presence of flexible links in the backbone can be used to promote solubility in convenient processing solvents. Chemical and thermal curing steps can eliminate flexible links after rough membrane formation has occurred. While reactive treatments add complexity, such treatments are likely to be needed. In this case, the convenient solution-based membrane formation processes currently used can still be relied upon while also achieving a final molecular sieve-like selective skin environment. Fortunately, only the outermost region of the hollow fiber skin needs to be hyper-rigidified, so the bulk of the fiber can have its unmodified flexible polymeric backbone nature to allow convenient handling and module formation. The research project described here will explore ways of conveniently producing flat, extended backbone segments which can be processed to form a composite layer capable of reactive treatment to generate a molecular sieve environment for high performance separations.

The use of long, flat, packable polymer backbone segments with periodic packing disruptive elements appear to be the most attractive approach to mimicking the carbon molecular sieve environment. Moreover, introduction of packing disruptive elements promote polymer solubility and ease of membrane formation as well as providing for high productivity in the final membranes. A framework is suggested to help guide the evolution of the next generation of gas separation membranes based on the above perspective.