

Advanced Materials for Oxygen-Nitrogen Separation Membranes

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Replacement of thermal separation methods with membranes has great potential to reduce the energetic and environmental costs in a variety of industrial processes.¹ Membranes currently employed in industry involve organic polymers spun or cast into asymmetric fibers and sheets.² Unfortunately, pure polymer based membranes show an upper bound for selectivity and permeability, which Robeson illustrated³ in a 1991 compilation of hundreds of membrane performance data. On the other hand, purely inorganic materials such as zeolites and carbon molecular sieves possess better selectivity properties but are brittle and much too expensive to gain widespread use. Research on advanced hybrid or composite inorganic-organic materials is being carried out in order to develop membranes that take advantage of the processibility, mechanical stability, and low cost of organic polymers in addition to the high selectivity and chemical/thermal stability of inorganic materials.⁴⁻⁸ Three specific inorganic-organic materials will be covered in this talk and the relationship between their structure and membrane characteristics will be explored.

Separation in membranes is carried out by exploiting differences in properties such as size and affinity. The goal is to obtain a high permeability of one species and a high selectivity of that species over any other in the mixture. Transport can occur through several mechanisms,^{9, 10} depending on the type of material that is being used (see Figure 1). Solution-diffusion occurs in polymers and is based on the solubility and mobility factors, which favor the most condensible and smallest molecule, respectively. Molecular sieving occurs in carbon molecular sieves and zeolites and is based primarily on higher diffusion rates of the smallest species, while sorption level differences become important when size differences are slight. In the case of separations to yield nitrogen enriched and oxygen enriched streams, the similar size and chemical properties of the two molecules make the materials requirements for a separation membrane more strict, which calls for advanced materials can help solve this problem.

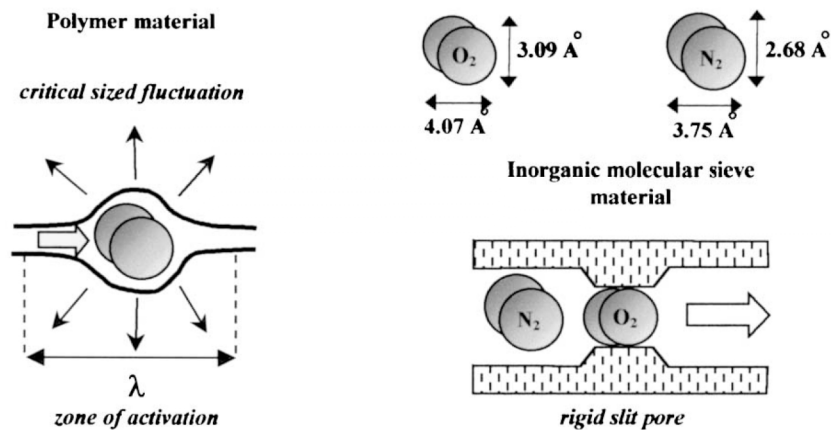


Figure 1¹⁰: Illustration of two simple transport mechanisms- solution-diffusion in polymers and molecular sieving in inorganic microporous materials with oxygen and nitrogen as an example. Hybrid and composite materials exhibit a combination of these and other mechanisms.

An alumina supported silica-polyimide composite membrane was synthesized by Bill Koros and coworkers by dispersing 100 Å diameter silica particles with the top layer of a porous alumina support.⁵ One of six glassy polymers was then deposited on the substrate surface and within the 200 Å diameter pores. Analysis of mixed gas transport properties was carried out and an increase in O₂/N₂ permselectivity and oxygen permeability compared to the corresponding bulk polymer membranes was observed for many of the membrane samples.^{11, 12} The resulting membranes surpassed the Robeson upper limit and also break into a region identified by the authors as industrially attractive. After characterizing the material, the authors hypothesized that the change in membrane properties from bulk 6FDA-IPDA was due to the formation of two distinct regions within the composite structure: 1) tightly packed chains through adsorption to silica particles and 2) packing disrupted regions between particles.⁵

Research on a polyimide-organosilicate hybrid was done by a group led by Eva Marand.¹³ A hybrid polyimide, 6FDA-6FpDA-DABA, was synthesized and coupled to one of three organosilicates via a silane linker. The sol-gel reaction was acid catalyzed, resulting in less crosslinking and smaller pore sizes within the silicate region than for a base catalyzed system. The final step in membrane formation consisted of either a curing process or an annealing process.^{4, 14} After recording single gas measurement data of the annealed samples, a slight decrease in O₂/N₂ selectivity and a large increase (200-500%) in oxygen permeability was observed.¹⁵ These membranes remained below the Robeson upper bound and outside of the industrially attractive region. The authors concluded that high temperature annealing resulted in a decrease in the organic character of the silicate and creation of a silica network, supported by TEM experiments, as well as chain rearrangement. The increase in permeation was attributed to changes in the free volume distribution and enhanced local segmental mobility of the chain ends resulting from removal of the sol-gel condensation and polymer degradation byproducts.⁴

A third material was investigated, again by Marand and coworkers,⁶ which showed possible advantages of O₂/N₂ selectivity contributions from both the inorganic and organic components. This material was formed by porous selective-flakes, layered aluminophosphate, with the same hybrid polymers, 6FDA-6FpDA-DABA, used in the second example. Single gas permeation measurements showed large increases in O₂/N₂ permselectivity and only slight decreases in oxygen permeability, which fell well above the Robeson upper limit and within the industrially attractive region. Structural analysis led the authors to hypothesize that the gain in membrane quality with respect to oxygen-nitrogen separation is due to solution-diffusion on the continuous polymer regions and adsorption selectivity and molecular sieving within the porous aluminophosphate regions.

In conclusion, impressive gains have been made in the performance of hybrid and composite inorganic-organic membranes in the past decade. These new materials will be crucial to the development of less energy intensive processes as the global population and commodity production expands in the next 10-15 years.

References

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