Materials & Materials Processing Opportunities to Enable Future Membranes Development

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Introduction

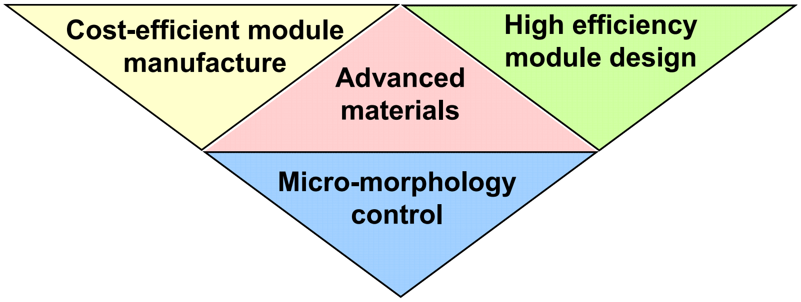
In 2003, the US comprised 4.8% of the world's population and was responsible for a disproportionate 25% of the world's energy consumption (DOE, 2004). The industrial sector was responsible for 33% of our energy consumption, followed by transportation (27%), residential (22%) and commercial (18%) areas. Within the industrial sector some processes such as raw material refining and polymer production intrinsically require high temperatures to occur economically. Discounting these special cases, a significant fraction of industrial processes are currently carried out using thermally-driven methods simply because installed capital investments provide inertia against change.

Replacing energy-inefficient separation processes requires confronting both materials and processing challenges to more broadly extend benefits available from first generation membranes. Indeed, despite many advantages, membranes have only recently emerged as a realistic platform for use in large scale processes. Since membrane technology is based on deceptively simple fundamentals, early work in this field overlooked the need to integrate four critical capabilities that are discussed below. The realization that membranes require treatment as a *cross-disciplinary specialty area* to allow this integration has enabled movement of the technology from the laboratory into commercial reality. It is critical to maintain this perspective in order to position membranes to economically handle aggressive feed streams that must be treated to significantly improve the efficiency of global energy use in separations. This improvement is especially important as the world population expands and emerging economies develop.

Background : Four Essential Elements in Membrane Technology Development

Figure 1 summarizes the four key elements needed to introduce any new type of membrane process, or even a new generation of the same type of membrane process (Koros, 2004). The figure also emphasizes a lesson learned in the introduction of early membranes for energy efficient separations: *interlinkage* between these elements is also crucial. Poor connectivity at *inter-linkage boundaries* between the four key elements can best be eliminated by viewing membrane technology holistically as an integrated sub-discipline within the chemical engineering paradigm.

Figure 1: Enabling technology elements required in synthetic membrane development



(i) Development of high efficiency modules with large amounts of area per volume was a necessary first step for the emergence of membranes in large scale separations. The numbers are impressive: hollow fiber modules can contain 10,000 m^2/m^3 of module, which is over 100 times larger than early plate and frame units (Baker, 2004). Such high efficiency modules provide the needed volumetric productivity to maintain compact system sizes for large scale applications with huge membrane area requirements.

(ii) Creation of advanced materials with tunable capabilities to separate molecularly similar components has been a second key factor in the emergence of membranes as a broadly applicable technology platform. Gels, rigid thermally stable polymers, amorphous carbons, ceramics, zeolites and metals provide a rich array of choices for forming functional high surface area units to perform separations (Kesting, 1985; Pinnau & Freeman, 1999; Pixton & Paul, 1994; Buxbaum, 1993; Langer & Peppas, 1993; Nair & Tsapatsis, 2003, Akin & Lin, 2002). These materials have applications running the gamut from processing of simple gases to complex bio-related feeds.

(iii) Development of sophisticated capability to control microscopic transport phenomena by tailoring of *morphology* at multiple levels within a membrane cross-section has been a less obvious third factor in the emergence of membranes. For instance, in the thickness dimension, a sub-micrometer ultrathin selective skin region is supported atop low resistance transition and microporous substrate layers. Within such an ultrathin top layer, additional structure with molecularly-selective and reactive features can exist. The scale of these critical features are truly molecular in nature and too fine to be imaged even with the highest resolution microscopy. The detailed functional elements present in a membrane vary greatly depending upon the particular application of interest. Recent examples of such morphology-engineering involves hybrid structures comprising *pre-assembled* micro or nano-scale functional entities dispersed in an engineered supporting matrix (Figoli et al., 2002; Mahajan & Koros, 2000). Such an approach allows efficient “off-line” engineering of the functional selective entities without compromising rapid economical production of large surface area modules.

(iv) The development of manufacturing methods to rapidly link the above three elements into economical devices with minimal defects is the critically important “final factor” responsible for commercially successful large scale membrane systems. Easily overlooked, this high speed processing capability is necessary to achieve cost-competitive modules (Eykamp, 1997). As new materials emerge, rethinking of the details in this “final factor” must also occur.

Discussion: Membrane Types and Terminology

Multiple phenomena, such as diffusion & fluid flow or diffusion & reaction often occur simultaneously in membrane processes. Focusing on the *key* function to be performed by a membrane usually allows considering secondary effects as details that can be addressed during optimization of the structure within the framework of Figure 1 for each application.

In use, synthetic membranes typically involve transport of components from an “upstream” side to a “downstream” side that is defined by the preferred direction of movement of a specified component. Although microscopic details differ between the various applications, description of the transport process for a component, *i*, across the membrane is possible in terms of the language of irreversible thermodynamics (Merten, 1966; Bird et al., 2002). This framework indicates that the flux of the *i*th component between upstream and downstream external phases is driven by the sum of the forces acting on the component. In principle, coupling of fluxes of one component to those of others may occur to complicate the description of transport. The negative gradient of chemical potential acting on component *i* as well as external forces such as electrical and pressure gradients under different conditions could all be at play in principle (Merten, 1966). In fact, an almost unlimited number of net driving force terms can be imposed on each penetrant between the upstream and downstream faces of a membrane. Fortunately, although coupling between effects can occur (Bird et al., 2002), a single driving force source, e.g., pressure, temperature, concentration, or voltage, is often sufficiently dominant in a given application to neglect the others.

Terminology for membrane types is summarized in Table 1 along with typical sources of driving forces used in each application and typical size discrimination limits. The resistance usually increases directly with the membrane thickness, so reducing thickness by some percentage generally increases flux by the same percentage. This generalization does have exceptions. For instance, reaction or complexation kinetics within the membrane or nonhomogeneous morphologies within the membrane may cause such exceptions in unusual cases (Cussler, 1997). Most practical membrane processes indicated in Table 1 are continuous steady state operations with a feed, permeate, and nonpermeate stream. Many types of membrane structures and modules exist, but the simple schematic in Figure 2 captures the essential

TABLE 1: Primary Synthetic Membrane Application Types & Key Characteristics

Function or Application (Abbreviation)	Typical Source of Driving Force	Size range of entities selectively rejected from feed*
Microfiltration (MF)	Trans-membrane pressure difference (10–25 psi)	100–20,000 nm
Ultrafiltration (UF)	Trans-membrane pressure difference (10–100 psi)	2–10 nm
Dialysis (D)	Trans-membrane solute concentration difference (1- 20 mg/dl)	1–4 nm
Nanofiltration (NF)	Trans-membrane pressure difference (100–500 psi)	0.5–2 nm
Reverse Osmosis (RO)	Trans-membrane pressure difference (100–1500 psi)	0.3–0.5 nm
Pervaporation (PV)	Trans-membrane fugacity difference (5-20 psi)	0.3–0.5 nm
Gas separation (GS) or Vapor separation (VS)	Trans-membrane pressure difference (10–1500 psi)	0.3–0.5 nm
Electrodialysis (ED)	Trans-membrane voltage difference (1-2 volt per membrane pair)	0.3–0.5 nm

* specific rejection depends upon details of selective layer morphology

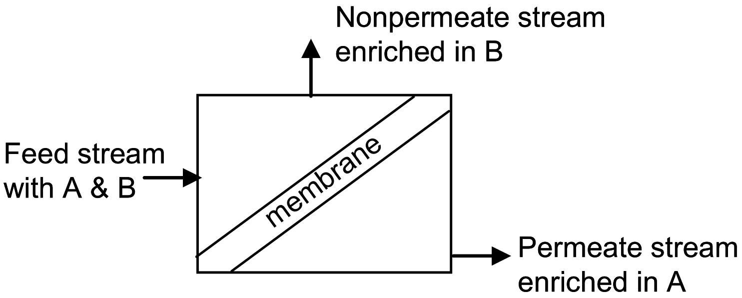


Figure 2: Idealized membrane process showing feed, nonpermeate and permeate streams. The most permeable (A) component is enriched in the permeate stream, while the least permeable is enriched in the nonpermeate stream. Actual membranes can be flat sheets, spiral wound units or hollow fibers.

features of all such processes. Since membrane processes involve separation of a permeated component A from a second, rejected component B, a measure of separation efficiency is useful. Due to the diversity of applications, many different measures of separation efficiency are used in the various membrane sub-areas in Table 1.

Selective restrictions to penetrant passage arise from interaction of the membrane with each permeating component. The membrane acts as a “Maxwell’s demon”, with the only apparent moving parts being the penetrants undergoing separation. The ability to minimize selective layer thickness without introducing defects relies upon the “micro-morphology control” element in Figure 1, so this topic impacts virtually all of the applications in Table 1.

Summary & Conclusions

Revolutionary energy savings are possible relative to competitive thermal options by introducing membrane processes for separations. Nevertheless, to achieve these savings, a large scale integrated systematic approach to greatly broaden the economical application of membranes to more aggressive feed streams. This information highlights the need for modeling and analysis that starts at megascale plant systems and ranges down to the molecular scale where most separations ultimately occur. Materials science is a critical component; however, technologies to engineer supermolecular membrane morphologies and economical modules are equally critical to build such an expanded platform.

In addition to its central role in advanced separation devices considered here, aspects of membrane technology impact fuel cells, advanced batteries used in hybrid vehicles and low cost flexible solar energy cells. Applying all of these related energy saving devices across the various sectors of society mentioned in the introduction of this article would motivate rational change toward energy efficiency. The special opportunities for synergistic combination of fuel cells and membrane separation technologies should be vigorously pursued to break the unnecessary current linkage between inefficacies in thermal energy conversion processes and separation processes. The US has taken action to promote the introduction of fuel cells, advanced batteries and solar cells; however, much less aggressive action is apparent to promote energy efficient separations. A concerted program focused on developing the membrane platform beyond its current state to enable rapid replacement of energy-inefficient separation processes is needed badly.

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