

Commentary

Design Next Generation Membranes or Rethink the “Old” Asymmetric Membranes?

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The first integrally-skinned asymmetric cellulose acetate (CA) membrane for water desalination were developed by Loeb and Sourirajan in the early 1960s at UCLA [1]. Asymmetric (or anisotropic) membranes can be classified into three structures (Figure 1): (i) integral-asymmetric with a porous skin layer, (ii) integral-asymmetric with a thin dense skin layer, and (iii) thin-film composite (TFC) membranes.

The process by Loeb-Sourirajan for making high flux, anisotropic integral-asymmetric with a dense skin layer membranes for desalination by reverse osmosis represents a milestone for the development of membrane technology. Indeed, it induced a change of level, from a laboratory scale to an industrial scale. These asymmetric CA membranes, significantly better than those existing at that time led to the fast commercialization of membrane desalination favoring the development of other pressure-gradient membrane operations such as ultrafiltration, microfiltration and providing the basis for modern gas separation technology [2].

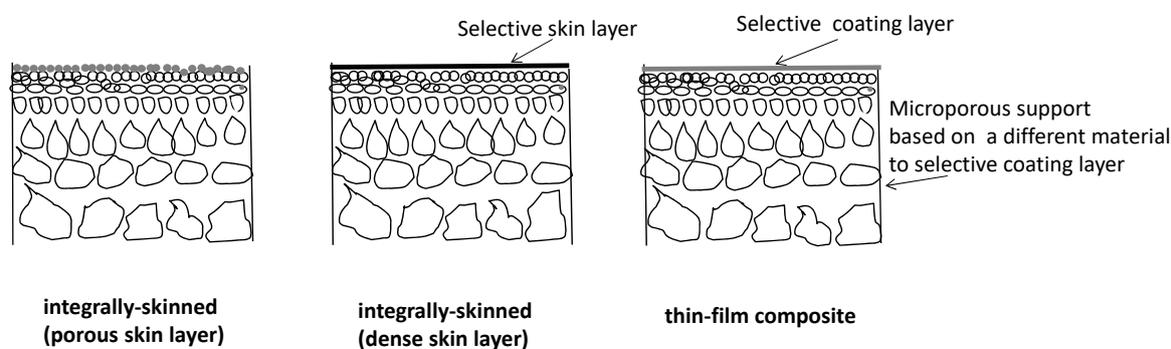


Figure 1. Schematic representation of asymmetric membrane structures.

By the mid-1980s, Cynara (now Natco), Separex (now Universal Oil Products, UOP) and Grace (now GCP) companies were active in the production of membrane plants for the treatment of natural gas (e.g., CO_2/CH_4 separation). The membrane modules were spiral wound (Grace, Separex) and hollow fiber (Cynara) and the membrane material was CA. The membrane gas separation industry is now 40 years old and the current industry standard for CO_2/CH_4 is still CA while in the other relevant applications i.e., O_2/N_2 , H_2/CH_4 , C_2/N_2 and C_3/CH_4 , the membrane materials used are more or less the same since a decade ago [3,4]. Why? For established membrane separations such as nitrogen from air, the answer is straightforward: there is no commercial driving force for the development of alternative materials. However, for other important gas separations, such as the treatment of natural gas by separation of CO_2/CH_4 , vapor/vapor mixtures, or olefin/paraffin separation, more selective, higher permeance membranes would either greatly improve the process or open new markets. For example, in the case of CO_2/CH_4 pairs, many interesting materials are more selective and permeable than CA,

but unfortunately they are characterized only as 100 μm thick films (which do not have problems of physical aging), made as a small stamp and with pure gas permeability data (ideal permeabilities) measured at low pressures. Indeed, when these new materials are characterized as thin membranes ($<100 \mu\text{m}$) with gas mixtures at real operating conditions (high operating pressures, temperature higher than $25 \text{ }^\circ\text{C}$, in presence of contaminants such as water, benzene, toluene, ethylbenzene, and xylenes, C2-C6 hydrocarbons), the separation performances of all of them change over time. Ideal permeabilities are a poor predictor of real performance for CO_2 separation from natural gas. CA membranes generally have a CO_2/CH_4 selectivity of *ca* 35–40 when measured with pure gas in ideal conditions. The selectivity drops to 15–20 by testing thin membranes with CO_2/CH_4 gas mixtures at high pressure and $50 \text{ }^\circ\text{C}$ and to 10–14 with real natural gas [5]. The phenomenon responsible for these negative changes is plasticization of the membrane material. Sorption of plasticizing components such as CO_2 and other hydrocarbons swells the polymer membrane, decreasing size selectivity (i.e., diffusion selectivity).

The phenomenon of plasticization, as well as physical aging, occurs in many high performance polymers, in particular when they are tested under realistic condition and as thin films. A relevant exception is represented by perfluoropolymers which are resistant to plasticization due to their atypical hydrocarbon solubility properties [6–12].

Industrial membranes have a selective layer thickness $<100 \mu\text{m}$, are made on large-scale production equipment and finding a promising material is only the first step.

Good predictors of real world membrane performance are tests with modules, not just membrane stamps and before this stage, it is mandatory to answer such questions such “(i) Is the data obtained with a thin membrane ($<1\text{-}\mu\text{m}$ -thick) or a film ($100\text{-}\mu\text{m}$ -thick)? (ii) Is the data measured under realistic process operating conditions (temperature, pressure, feed composition)? (iii) In experiments lasting more than a week, how does the membrane perform?” [13].

Rethinking industrial standard membrane materials not only by modifying them but also by investigating unexplored issues for performance optimization could offer an interesting alternative to the onerous investment in completely new materials, which before being commercialized require a long and not always successful path.

Regarding the specific application of natural gas treatment, not only CO_2 but also H_2S is another priority contaminant which corrodes processing and transporting equipment. Few studies have investigated the simultaneous removal of CO_2 and H_2S , prior studies being concentrated on low concentrations of H_2S due to its hazardous nature. The H_2S concentration in the gas reservoirs in the Middle East can reach 30 mol.%, along with a significant amount of CO_2 [14], so membranes of industrial interest for combined CO_2 and H_2S separation from CH_4 are a high priority topic. In the logic of rethinking polymeric membrane materials, facilely processed into thin-skinned hollow fiber asymmetric structures, Koros and co-workers [15] developed a novel method to modify CA—the mentioned above low cost industrial standard membrane material—to produce a material capable of separating aggressive acid gas feeds. The method consists of the modification of CA via grafting of vinyltrimethoxysilane (VTMS) to hydroxyl groups, followed by hydrolysis of the methoxy groups, with subsequent condensation of silanols to create a polymer network. The modified CA membrane had CO_2 and H_2S productivities more than 1 order of magnitude higher than neat CA, with higher $\text{H}_2\text{S}/\text{CH}_4$ selectivity than other glassy and rubbery polymers.

In a recent study, the same research group investigated combined CO_2 and H_2S separation performance of two polyimide membranes, i.e., 6FDA-DAM and 6FDA-DAM/DABA (3:2), attractive for a diverse range of gas separation and their ability to be facilely processed into thin-skinned hollow fiber asymmetric structures, i.e., to be tested as membrane modules [16]. Mixed gas permeation tests were performed using different mixtures of $\text{H}_2\text{S}/\text{CO}_2/\text{CH}_4$ in low and high H_2S concentration at pressures up to 46 bar. The study evidences how the relevant plasticization effect of the polyimides, in applications where H_2S is present, becomes a tool for performance optimization providing large performance benefits for $\text{H}_2\text{S}/\text{CH}_4$ separation.

The same concerns expressed above for membrane gas separation are valid for desalination and water purification membranes. The development of membrane desalination technologies relies on advances in membrane materials [17]. State-of-the-art commercial products include polymeric membranes [18], either CA-based asymmetric type or polyamide thin-film composite type [1,19]. Although molecular-level design approaches for desalination membranes represent an active area of research (nanotubes, two-dimensional nanosheets, aquaporins) [20] to identify candidates for next-generation desalination membranes, a particular issue for several of these materials is mechanical stability. In the particular case of two-dimensional nanosheets, such as nanoporous graphene, even though experimental studies have demonstrated their exceptional performance in water desalination predicted by theoretical calculations, the experimental studies to date are typically limited to micrometer-scale graphene flakes. As the stress of a selective membrane scales with $l^{-3/2}$ (where l is the membrane thickness), the atomically thin 2D membrane that is three orders of magnitude thinner than commercial membranes would undergo substantially larger stress [21]. Therefore the application of ultrathin 2D membranes for practical water treatment with sufficient mechanical strength and low cost is not a trivial task. A recent study by Yang et al. [22] reports a large-area graphene-nanomesh (GNM)/single-walled carbon nanotube (SWNT) hybrid membrane where the SWNT network supports the GNM, thus avoiding cracking of the atomically thin GNM.

Rethinking the performance of existing polymeric membranes, which, thanks to their stability and processability, continue to retain a dominant role in the global desalination market (as well as in membrane gas separation, as mentioned above), is the conceptual core of a recent study by Elimelech and co-workers [23] on modified cellulose triacetate (CTA) desalination membranes. The authors of this work emphasize how the actual effect of the polymer structure on water and salt transport in desalination membranes, critical to guiding membranes design, has not been well investigated. The desalination membranes investigated in the study are asymmetric CTA membranes treated in *p*-nitrophenol (PNP) solution, followed by water rinsing. The modified membranes were subsequently tested in a forward osmosis (FO) setup to evaluate the desalination performance. The modified membranes exhibit enhanced water/salt selectivity. PNP acts as a plasticizer in the CTA polymer, enhancing the chain mobility in the amorphous regions and swelling the crystalline domains, resulting in disruption of the molecular packing. Probably at the basis of the enhanced water/salt selectivity of the modified CTA membrane, there is the formation of smaller crystallites which results in a larger interfacial area between amorphous and crystallites regions. The results reported by Elimelech and co-workers [23] not only elucidate the structure–property–performance relationship of CTA desalination membranes, but also offer insight for the design of new asymmetric polymeric membranes.

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