



## Breaking separation limits in membrane technology

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### ABSTRACT

Membrane separation processes are efficient and sustainable alternatives to energy intensive distillation operations. In gas separations, polymeric membranes dominate the landscape of industrial applications and many improvements in performance hinge on the ability to tailor the chemistry of polymeric materials. The basic goal in membrane separations is to control the solubility and diffusivity of the chemical compounds in order to tailor the relative magnitude of the fluxes of the chemical species across the membrane. In this paper, we introduce a fundamentally new separation device that uses an anisotropic polymeric membrane to guide molecular transport to specific spatial locations. Our proposed separation device enables to manipulate the flux direction of compounds, in addition to the flux magnitude, thus adding a new tool to separate chemical species. We report unprecedented selectivities for O<sub>2</sub>/N<sub>2</sub> separation – up to two orders of magnitude larger than conventional membranes.

### 1. Introduction

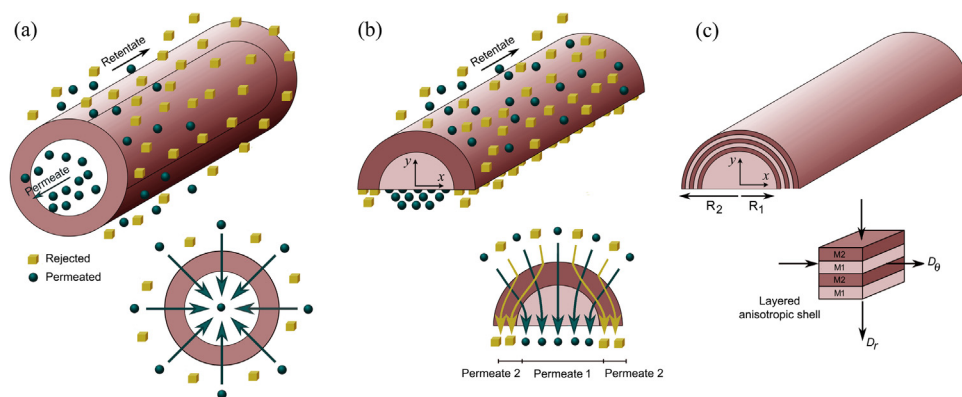
Membrane separation technologies are critically important for the development of sustainable industrial processes for global chemical production [1–4]. Separations based on membranes are less energy intensive than typical separation operations such as distillation and drying because membranes do not require phase changes [2–5]. Importantly, during the last decades, gas separation based on non-porous membranes have attracted considerable attention due to their low costs and improved efficiencies [5–8]. In non-porous membranes, separations are generally described by a solution-diffusion model involving a two-step mechanism: initial molecule absorption into the membrane followed by diffusive molecular transport under a chemical potential gradient [9]. The membrane efficiency for separating a binary mixture made of compounds *A* and *B* is generally measured by the ratio  $\alpha_{A/B}$  of the normalized fluxes with respect to the driving forces across the membrane (i.e. selectivity). The basic principle fueling most research on membrane separations is that large selectivities  $\alpha_{A/B}$  can be achieved by manipulating the diffusivity and solubility of compounds *A* and *B* such that the flux of *A* is increased while the flux of *B* is reduced [4–7,10–13]. An established approach to achieve such enhanced membranes is to tailor chemical and structural properties of the membrane material in order to affect the physical mechanisms that govern the diffusivities and solubilities of compounds *A* and *B* [4–6,13–16]. In the ideal case, the engineered material would yield a

membrane where the selectivity  $\alpha_{A/B}$  and the flux  $J_A$  of the compound of interest are both maximized. This principle has been successfully used for the design and fabrication of membranes that are at the commercial stage and also under research development [5–8]. Additionally, process engineering using multistage modules or internally staged permeators has been applied to increase the purity of the products [17–19].

Here we propose the development of a new class of separation processes by designing anisotropic membranes that can guide molecular transport to specific locations. We note that established approaches for mass separation assume that the membrane material is isotropic. This means that mass-flow cannot be “guided” in controlled ways to perform separations. In contrast, we propose rationally designed anisotropic membranes that purposely guide molecular diffusion to specific places and this translates into a completely new physical mechanism to improve current separation processes. Contrarily to conventional isotropic membranes, the use of anisotropic membranes allows controlling both *direction* and *magnitude* of the mass flux. Significantly, using our anisotropic design we found remarkable selectivities for O<sub>2</sub>/N<sub>2</sub> separations, up to two orders of magnitude higher than those obtained with the best available isotropic polymer.

We show in Fig. 1(b) how our separation device that controls the direction of mass flow using an anisotropic membrane operates significantly different from typical isotropic membranes such as planar, hollow fibers, or dual-layer hollow fiber membranes. In the isotropic case, membranes separate two compounds by selectively permeating

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**Fig. 1.** (a) Isotropic hollow fiber working for separation in countercurrent flow. The cylindrical membrane is highly selective for compound A (spheres) thus creating a permeate enriched in A. Inset shows the radial flux lines due to the cylindrical symmetry. (b) Proposed anisotropic membrane separation device consisting of an isotropic cylindrical core of radius  $R_1$  covered by an anisotropic cylindrical shell with internal radius  $R_1$  and external radius  $R_2$ . In this case, the two molecules (spheres and cubes) permeate in the membrane. The schematics show the ideal case where one compound (cubes) is directed around the core and the other compound (spheres) is focused towards the core. We are interested in collecting

towards the core. We are interested in collecting molecules A (spheres) at the core region ( $-R_1 < x < R_1, y = 0$ ). Inset shows the flux lines for the two compounds, which are bent as a consequence of the anisotropy of the shell. Simultaneous control of the flux trajectory for the two compounds is the basic principle of operation of the anisotropic membrane. (c) The anisotropic shell can be constructed using multilayer structures made of two isotropic materials  $M_1$  and  $M_2$  with mass resistances adding in series in the radial direction and in parallel in the azimuthal direction.

one compound through the membrane while rejecting the other one [Fig. 1(a)]. As a result, two streams with different compositions develop – a permeate enriched with the permeated compound and a retentate enriched with the rejected compound [7,9]. In contrast, the proposed separation device using an anisotropic membrane [Fig. 1(b)] is selective for one of the compounds by simultaneously guiding the molecules that have permeated into the membrane toward different locations on the “permeate” side. Three streams develop: the retentate and two permeate fractions, with compositions that depend on the effectiveness of the anisotropic membrane to reroute the different species. Also note that our separation device does not possess a hollow core but rather a solid material core, in contrast to hollow fiber membranes. Furthermore, separation processes in hollow fiber membranes occur under a one-dimensional radial concentration gradient [Fig. 1(a)], while our device requires a two-dimensional concentration gradient for operation [Fig. 1(b)]. It is important to highlight that control over flux direction as considered in this paper has already been proven both experimentally and theoretically for mass and heat diffusion but has not been used for gas separation [20–25]. A number of fundamental questions arise when considering anisotropic membranes for separation. What structural geometry would allow taking full control of the direction of mass flux and separation capabilities? How does an anisotropic membrane perform in comparison with a typical isotropic membrane? And how can we construct such anisotropic membrane considering that most currently available membrane materials are isotropic? In this paper, we address these questions in the context of gas separations and prove that anisotropic layered structures made of isotropic materials can be used to enhance the separation performance of typical isotropic membranes breaking the limits imposed by the conventional upper bound relation. Specifically, we discuss these findings in the case of  $O_2/N_2$  separation where we propose a structure/material design consisting of rationally arranged isotropic polymeric materials. Enhancing  $O_2/N_2$  gas separation is important since highly-efficient  $O_2/N_2$  separation has been challenging with current membrane materials. The large amount of tabulated data for the diffusion properties of  $O_2$  and  $N_2$  in different polymers facilitates material selection to achieve  $O_2$  and  $N_2$  anisotropic diffusion and separation. Clearly the proposed concept for separation can also be applied to other gas mixtures.

## 2. Methods

Diffusive transport processes in isotropic membranes are commonly described by Fick’s theory, which establishes that the flux  $J$  of species  $i$  across a planar membrane and the selectivity  $\alpha$  are given by

$$J_i = \frac{D_i S_i \Delta p_i}{L}, \quad \alpha_{A/B} = \frac{J_A / \Delta p_A}{J_B / \Delta p_B} = \left( \frac{D_A}{D_B} \right) \left( \frac{S_A}{S_B} \right) \quad (1)$$

where  $D_i$  is the diffusivity,  $S_i$  the solubility,  $\Delta p_i$  the driving force, and  $L$  the membrane thickness [1,13–16]. In contrast, in our proposed device, anisotropic material properties are engineered to obtain a specific functionality. This can be achieved by engineering the mass diffusivity tensor [21,26–30]

$$J_{(i)} = - \begin{bmatrix} D_{xx(i)} & D_{xy(i)} \\ D_{yx(i)} & D_{yy(i)} \end{bmatrix} \nabla C_{(i)} \quad (2)$$

In order to design separation processes using engineered anisotropic membranes, the first task is to define a suitable structural geometry. In the case of isotropic membranes, this selection is performed by considering that the system should fit standard module designs and be easy to manufacture and maintain [1,5,8]. In anisotropic membranes, however, it is also necessary to find a structural geometry that allows the easy collection of the permeate fraction of interest. Towards this end, we introduce a membrane separation device consisting of two concentric half-cylinders as shown in Fig. 1(b). The cylindrical core of radius  $R_1$  is made of an isotropic material  $I$  with solubility  $S_{I(i)}$  and diffusivity  $D_{I(i)}$  for compound  $i$ . On the other hand, the cylindrical shell with internal radius  $R_1$  and external radius  $R_2$  is made of an anisotropic material with solubility  $S_{II(i)}$  and tensorial diffusivity  $\bar{D}_{II(i)}$ . The role of the anisotropic shell is to manipulate the trajectory of the molecules of interest. For example, an ideal anisotropic shell for separation of a binary mixture should detour one compound around the core and focus the other compound towards the core [26,31]. The effectiveness of the anisotropic shell for separation will thus depend on the ability of the shell to differently promote the diffusion of the compounds along the radial and azimuthal directions. Note that in our proposed design, the permeate fraction enriched with the compound of interest is collected at the planar lower surface of the cylindrical core, i.e. at the line  $-R_1 < x < R_1, y = 0$ .

Our initial objective is to show how the anisotropic shell affects separation of a binary mixture of arbitrary compounds  $A$  and  $B$ . The diffusion of species  $i$  ( $A$  or  $B$ ) in the core and shell regions can be described using continuity and Fick’s law Eqs. (1) and (2), which yields the following differential equations for diffusion

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{I(i)}}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 C_{I(i)}}{\partial \theta^2} = 0 \text{ for the core} \quad (3)$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{II(i)}}{\partial r} \right) + \frac{l_{(i)}^2}{r^2} \frac{\partial^2 C_{II(i)}}{\partial \theta^2} = 0 \text{ for the shell} \quad (4)$$

where  $l_{(i)}^2 = D_{\theta(i)} / D_{r(i)}$ ,  $D_{\theta(i)}$  and  $D_{r(i)}$  are the azimuthal and radial

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