Towards large-scale application of nanoporous materials in membranes for separation of energy-relevant gas mixtures

Roberto Castro-Muñoz[a,b*], Kumar V. Agrawal[c*], Zhiping Lai[d*], Joaquín Coronas[e,f*]

(a) Tecnologico de Monterrey, Campus Toluca, Avenida Eduardo Monroy Cárdenas 2000 San Antonio Buenavista, 50110 Toluca de Lerdo, México
(b) Gdansk University of Technology, Faculty of Civil and Environmental Engineering, Department of Sanitary Engineering, 11/12 Narutowicza St., 80-233, Gdansk, Poland
(c) Institute of Chemical Sciences and Engineering (ISIC), École Polytechnique Fédérale de Lausanne, Sion, Switzerland
(d) Advanced Membrane and Porous Materials Center, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Kingdom of Saudi Arabia
(e) Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50018, Spain.
(f) Chemical and Environmental Engineering Department, Universidad de Zaragoza, Zaragoza 50018, Spain

Abstract

Membranes containing nanoporous materials (such as zeolites, metal-organic materials and 2D materials such as graphene derivatives) may allow more efficient separation of gas mixtures relevant to emerging energy technologies. For example, such membranes could be applied in the separation of gases containing mixtures of carbon dioxide (CO_2) and hydrogen (H_2). However, these membranes are currently at a relatively low technology readiness level. Hence, here we review the opportunities and challenges of applying these porous materials in practice and at scale in membranes for possible commercialization. Besides, we highlight the necessity of improvements in the porosity control of 2D materials and the decrease in the selective membrane skin layer when adapted in asymmetric membranes. In this latter point, we declare the main limitation of porous supports, as well as the further developments in the gutter layer and supports. Additionally, we review the main membrane module configurations and process requirements, declaring the most suitable configurations (e.g. spiral wound and hollow fiber modules) at scale with promising future for highly intensified membrane modules for applicability in CO_2 and H_2 separations. Finally, apart from the conclusions derived from this review, we outline key recommendations for the researchers in the field.

Keywords: Gas separation; porous materials; membrane modules; hollow fibers; challenges; hydrogen separation; CO2 separation.

1. Introduction

As the world seeks to move to greener energy technologies and to lower carbon footprints and emissions, a number of gas separation processes may become more important. For example, gas mixtures related to energy production include CO_2/N_2 (post-combustion carbon capture), CO_2/CH_4 (production of biomethane) and H_2/CO_2 (pre-combustion carbon capture). Current gas separation technology largely relies on thermally-driven processes, such as distillation, absorption and adsorption. Yet, there is evidence that some membrane-based separations applying concentration and pressure gradients may be more energetically efficient and environment-friendly than existing processes, and they could limit carbon dioxide emissions and reduce costs [1].

High-performance membranes for gas separation consist of a composite structure in which, ideally, an ultrathin film based on selective materials is placed on top of a mechanically robust porous support, constituting a thin-film composite (TFC) membrane (see **Fig. 1**)[2]. As of now, gas separation membranes are dominated by polymeric materials due to the fact that polymers can be rapidly processed into the TFC morphology. However, the gas separation performance from the polymeric membranes is limited by the intrinsic properties of the polymer determining gas sorption and diffusion, molecular solubility, the free volume between the polymeric chains, and chain stiffness [3–5]. Some of these properties have been improved with the so-called next-generation polymeric materials, e.g., polymers with intrinsic microporosity and thermally rearranged polymers. However, the free volume in the nanoporous polymer tends to reduce as a function of time which negatively impacts the gas permeance [6,7].

To improve the performance of gas separation membranes, nanoporous inorganic materials (e.g., zeolites, metal-organic frameworks or MOFs, and nanoporous two-dimensional materials) have been extensively investigated [8–11]. These materials with high porosity and thermal, chemical and mechanical robustness but mainly with pores in the range of sizes of common gas molecules can carry out molecular separations based on the relative size difference and adsorption affinity [12]. Besides their implementation as TFC membranes where a thin polycrystalline film acts as a selective layer, these materials can also be used as selective fillers for a target application, constituting the so-called mixed matrix membranes (MMMs), or when prepared as a thin film on a proper porous support, thin film nanocomposite membranes (TFN)[13]. These filler-polymer combinations could overcome the main limitations of the existing membrane technologies [14]: permeance-selectivity trade-off still far from commercial applicability, membrane reliability and long-term realistic operation. However, most of the reviews published, which timely report the current state of the art of membranes for gas separation, lack in revealing the drawbacks and challenges in the commercialization of membranes containing nanofillers (mainly zeolites, MOFs and 2D materials) for possible application at the industrial scale for H_2 and CO_2 separation. Therefore, this review examines the contribution of nanoporous materials to constitute membranes for the separation of energy-relevant gas mixtures. The main families of such materials are presented together with the limitations and possible improvements of the current membrane systems regarding their implementation in large-scale and more practical applications. Additionally, we declare the membrane requirements, membrane module configurations and the most suggested configuration (like hollow fibers) for these gas separation applications, giving an overview of the hybrid membrane concepts adapted in hollow fibers for the separation of CO_2 and H_2-containing mixtures.

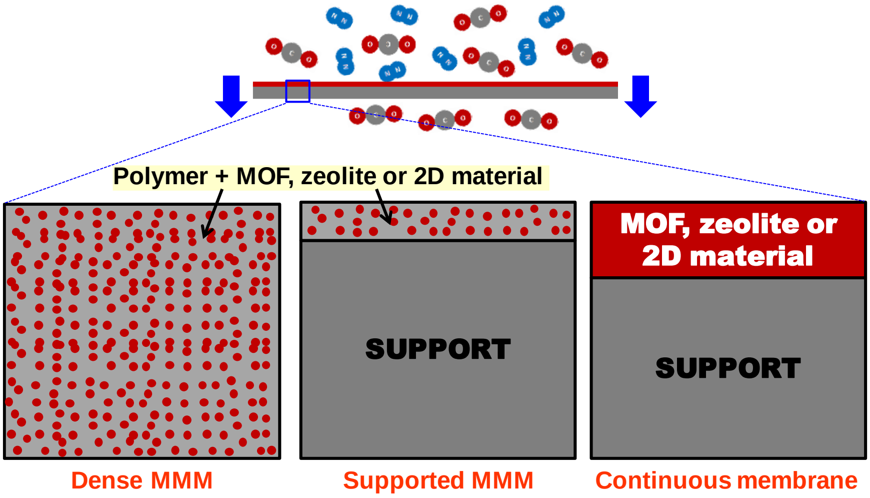


Fig. 1. Scheme of the different types of gas separation membranes involving nanoporous materials. The dense or supported (also known as TFC membranes) polymeric membranes can be MMMs (or TFN membranes) incorporating nanoporous fillers such as MOFs, zeolites, or others.

2. Zeolites and MOFs as main components of gas separation membranes

2.1. Opportunities of zeolites/MOFs for gas separation

Zeolites and MOFs are crystalline microporous materials, which in principle, provide a straightforward strategy to overcome the trade-off limit of polymeric membranes. That is, the uniform pore size offers precise molecular sieving to achieve high selectivity, while the highly porous structure allows fast transport of the smaller molecules to achieve high flux. If the pore size is adequately selected, zeolite/MOF membranes can differentiate molecules at a size difference of 0.02 nm or less [15]. Such clear-cut molecular sieving implies that almost every important pair of the gas system can be effectively separated.

The pore size of zeolite/MOF membranes is mainly determined by the framework structure. It can also be fine-tuned through ion exchange and surface modification [16]. The hybrid inorganic/organic MOF structures are much more diverse and easier for surface modification. Furthermore, the permanent porosity and the rigid framework structure can avoid the undesirable aging and plasticization effects observed for polymers [6]. Compared to MOF membranes, zeolite membranes are more stable in high temperatures, more resistant to organic solvents, and more robust in harsh conditions, providing unique opportunities for system integration with reactions to form innovative membrane reactors [17]. Recently, significant progress has also been achieved in preparing ultrathin zeolite/MOF membranes from their 2D nanosheets and further improving their membrane flux [18,19]. For example, ultrathin (<50 nm) zeolite (SAPO-34) nanosheets seeding layer allows the production of defect-free zeolite nanofilms (500–800 nm), which displayed an exceptional orientation and facilitated transport [20]. The performance was calculated as CO_2 permeance of ≈1.0×10^{-5} mol $(m^2 \ s \ Pa)^{-1}$, together with high CO_2/CH_4 and CO_2/N_2 selectivity of 135 and 41, respectively, in equimolar binary mixtures at room temperature. Thin membranes based on lamellar SAPO-34 zeolite nanosheets were also effective in separating CO_2/CH_4 (selectivity=102) with a permeance of 2.5×10^{-6} mol $(m^2 \ s \ Pa)^{-1}$ (approximately 7500 GPU) [21].

Fig. 2 shows H_2/CO_2 and CO_2/N_2 separation performance from the state-of-the-art zeolite/MOF membranes and their comparisons with the upper bound of polymeric membranes. As can be seen, zeolite/MOF membranes have had great success for the separation of H_2/CO_2 but much less for CO_2/N_2 when compared with polymer membranes. The reason is that in the H_2/CO_2 system the two transport properties that determine the membrane performance – diffusion and adsorption – often have opposite effects. That is, diffusion favours hydrogen because of its smaller kinetic size, but adsorption prefers CO_2 because of its higher quadrupole moment. Hence, to achieve a good H_2/CO_2 selectivity, the diffusion selectivity must be high. As said, zeolite/MOF membranes have a significant advantage over polymeric membranes in molecular sieving.

In contrast, in the system of CO_2/N_2, both diffusion and adsorption facilitate the transport of CO_2. Polymers can be easily grafted with a high density of functional groups to enhance CO_2 adsorption and thus can achieve comparable performance to zeolite/MOF membranes. In certain conditions when the CO_2 affinity is strong and the temperature is low, CO_2 may condense inside the pores due to the capillary condensation effect. This blocks the transport of other gases and turns the membrane to be CO_2 selective. Most of the membranes that work well for CO_2/N_2 are also suitable for CO_2/CH_4, and the selectivity is typically higher because CH_4 has a larger molecular size than N_2 [22], e.g., face-centred cubic (fcu)-MOF/polymer hybrid membranes have exhibited exceptional separation performance for energy-intensive separations considering distinct gas pairs, including H_2/CH_4, CO_2/N_2, CO_2/CH_4 and N_2/CH_4 [23].

Despite not yet reaching the same success as for H_2/CO_2 separation, MOF membranes still hold a great potential to separate CO_2/N_2. One way is to tune the pore size to enhance the molecular sieving. In this sense, the exploration of new MOF building blocks and different topological connections should be beneficial. Another way is to improve the density of functional groups inside the MOF channels to increase CO_2 adsorption. When looking at the history of zeolite development, most stable zeolites were discovered in the early stage. This is not surprising because zeolite synthesis is a dynamic process that tends to form the most thermodynamically stable state. This trend may also apply to MOF development and the MOF research community has grown to a substantial mass, but most of the reported MOF systems can hardly pass the stability criteria for practical applications [24]. Hence, starting from the stable MOF systems and conducting surface modification should be more efficient.

2.2. Challenges in commercialization

Membrane selectivity and permeance, membrane fabrication cost, long-term stability and process reproducibility determine the commercialization potential of a membrane system. The required selectivity is a process parameter that is determined by the separation task. It is also the main parameter that determines the process energy consumption. The higher the selectivity, the lower the energy consumption. Membrane permeance and fabrication cost determine the capital cost. Higher membrane permeance implies less membrane area, and thus can tolerate higher fabrication cost. For CO_2/N_2 separation, a selectivity of 30 and a permeance of 1000 GPU are the estimated polymeric membrane performances to make the process economically viable [25]. The fabrication cost of MOF/zeolite membranes is so far orders of magnitude higher than that of polymeric membranes. Hence, an equivalent improvement in permeance is required to make the process competitive. The membrane lifetime is another critical factor to determine the membrane cost. A typical lifetime is two years. The process reproducibility is a key parameter for product yield and quality control.

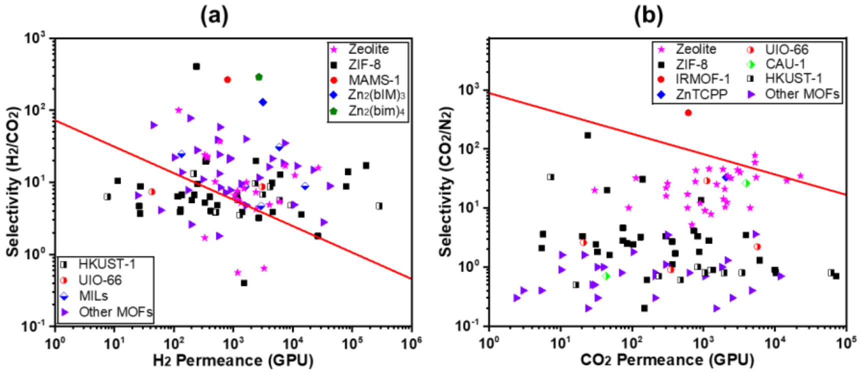
Factors, such as the need for robust support, lengthy and multi-step synthesis processes in batch mode, harsh synthesis conditions, such as high temperature and high pressure, and special care needed to handle the brittleness, make the fabrication cost of zeolite and MOF-based membranes much higher than that of polymeric membranes. These challenges encourage the implementation of low-cost polymeric supports and the development of fast, mild, and continuous fabrication processes, while the related cost disadvantage must be compensated by better membrane performance. For zeolite membranes, this can be compensated further by better long-term stability. For instance, high-silica zeolites are much more stable than their low-silica counterparts. Besides the Si/Al ratio, the amount of crystal surface defects and Brønsted acid sites are also key factors. A common approach to improve the hydrothermal stability is through surface modification using $SiCl_4$ or silane to eliminate the surface defects [26]. Compared to zeolites, MOFs are much weaker and more sensitive to moisture. Chemical modification to make the surface more hydrophobic is a helpful approach to improve stability [27]. However, most of the stability studies are examined only in weeks' time, which is too short to be practically meaningful. More comprehensive characterizations of the structure change (e.g., X-ray diffraction and microporosity) under relevant practical conditions in a much longer period (> 2 months) are highly demanded.

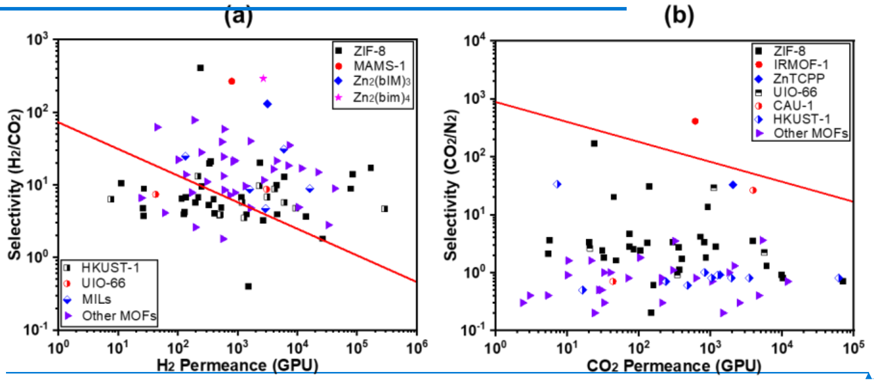
The process reproducibility of most zeolite and MOF membranes is still far below the satisfactory level. One of the major reasons is the presence of defects within the fabricated membranes. For zeolite membranes, most of the defects are introduced during the thermal treatment stage, when the organic structure-directing agents are removed [28]. MOF membranes have a similar issue when the organic solvent is removed from the structure. Some innovative methods using reactive agents, such as ozone, UV, and plasma, have shown good potential to activate the membrane without crack formation [29]. However, how to implement these approaches on large scale and at a low cost is still a big challenge. Reducing the membrane thickness can help expose the structure-directing agents to the reactive agents and remove them with less difficulty. Hence, the recent development in 2D membranes (see details in section 3)[30,31] will help to improve not only the membrane permeance but also the process reproducibility. Alternatively, surface coating using rubbery polymers, such as PDMS, has been widely used in polymeric membranes as an effective defect remedy method. it has also proved to be very helpful in MOF membranes [32]. Reducing the membrane permeance, this method is a necessary step in a commercial fabrication process to improve the membrane reproducibility because of its low cost and simplicity.

The commercialization of zeolite/MOF membranes will be also affected by the supports' geometry as it will subsequently determine the type of membrane modules. Most of the reported zeolite/MOF membranes in the academic literature are prepared on flat sheet supports because of their easy availability. However, all the commercial zeolite membranes so far are prepared on tubular supports. Tubular supports are more robust under pressure, easy to scale up and clean, but they are also very expensive (> 300 USD/m^2) and have a low packing density (30~50 m^2/m^3). Compared to tubular supports, hollow fibers (HFs) share a similar geometry but have a much higher packing density (see section 5), thus potentially reducing the overall cost substantially. Hence, future studies should focus more on how to integrate the membrane fabrication process more effectively with HF supports.

So far, there is no zeolite/MOF membrane commercialized for gas separations, but a number of zeolite membranes are on the commercialization roadmap, including those with the LTA, MFI, FAU, CHA, and DDR structures [33]. The most promising MOF membranes for commercialization are ZIF-8 and UiO-66 membranes, primarily because they are so far the most stable MOF structures [34]. Moreover, ZIF-8 is made from low-cost precursors and so has a cost advantage over many other MOFs. Many economical and simple membrane fabrication approaches have been developed, such as counter diffusion [35] and electrical field-induced growth [36–38] under the aqueous solutions. However, the process reproducibility is still low and the mechanical stability under the industrially relevant pressures (> 15 bar) has not been demonstrated.

Some zeolite membranes, such as LTA zeolite [39], have been successfully commercialized in liquid separation, which has certainly enhanced the confidence in overcoming the abovementioned challenges in gas separation. With more industrial experiences accumulated in zeolite membranes, it is expected that the production cost will be significantly reduced, and the membrane quality and process reproducibility will be greatly improved. As the syntheses of zeolite/MOF membranes share many common features, these signs of progress will certainly speed up the commercialization activities of the entire field in the near future.





Con formato: Español (España)

Fig 2. Separation performances of zeolite/MOF membranes and their comparisons with the upper bound of polymer membranes. (a) For H_2/CO_2 and (b) for CO_2/N_2. The red lines in the diagram represent the upper bound of polymeric membranes, where a membrane thickness of 100 nm is used to convert the permeance from the permeability database of polymeric gas separation membranes [40]. The data points of zeolite/MOF membranes are adapted from Ref.[41]

3. 2D nanoporous materials for gas separation membranes

3.1. Opportunities of 2D materials for gas separation

Nanoporous materials with a 2D morphology have the unique potential to constitute the thinnest selective layers ever imagined, down to the thickness of an atom, and therefore, can maximize the permselective gas flux reducing the needed membrane area and associated capital cost. Three distinct designs for selective layers can be achieved (**Fig. 3**): MMM where 2D materials constitute an ideal filler in a polymer matrix; stacked nanosheet membranes; and single-layer 2D film.

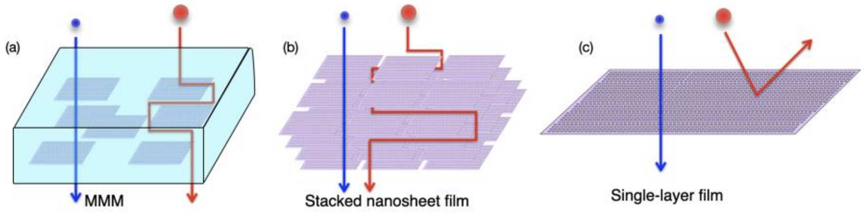


Fig 3. Design approaches for the selective layer from 2D materials and corresponding molecular pathways. a) MMM prepared by dispersing 2D nanosheets inside a polymeric filler. b) Stacked nanosheet film by the assembly of nanosheets. c) Macroscopic single-layer 2D film.

MMM prepared using nanoporous 2D nanosheets are extremely attractive due to the high aspect ratio and nanoscale thickness of the nanosheets. This is because a preferential orientation of the nanosheets in the matrix can be obtained, filler loading in the matrix can be maximized, and the overall film thickness can be minimized. The emergence of nanoporous 2D materials with high interphase compatibility with polymer (MOFs [42], g-C_3N_4 [43], covalent organic frameworks [44], etc.) have led to MMM yielding improved separation performances compared to the upper bound for polymeric materials. While membranes based on stacked 2D nanosheet films as the selective layer offer performance advantages over nanosheet-based MMM. The stacked nanosheet film offers a nanoporous pathway across the entire selective layer, improving the diffusivity of the gas molecules.

Oriented nanosheet films can be achieved by a scalable technique such as filtration on a porous support, and the film thickness can be easily regulated by the amount of suspension. The separation performance from the stacked nanosheet film is determined by the interplay between two transport pathways; one constituted by the nanosheet porosity and the other by the intersheet or packing gap between the nanosheets. This gap needs to be small enough to not become the primary transport pathway but also large enough so that the pore openings of the nanosheets are not blocked in the turbostatically-stacked film. Approaches modulating the gap, e.g., hot drop coating and reactive condensation of the nanosheets have yielded promising H_2/CO_2 separation performance from MOF nanosheets [18] and more recently from zeolite nanosheets [19]. Impervious nanosheets, such as graphene oxide [45] and MXenes [46], have also shown promising performance from their stacked films where gas transport takes place through the intersheet gap. For example, graphene oxide nanosheets assembled into laminar structures have displayed fast and CO_2 selective transport channels (CO_2/N_2: 91), along with exceptional operational stability [47]. Unfortunately, the intersheet gap and the gas transport in these films are sensitive to operating conditions including feed pressure and humidity [48,49], affecting the separation performance.

Synthesis of 2D nanosheets hosting CO_2-sieving nanopores will allow the realization of high-performance MMMs for CO_2 separation. A potential pathway is the exfoliation of a suitable layered precursor, such as zeolite hosting an 8-membered silicate ring. Layered SAPO-34 has been recently reported [21]. Recently, synthesis of 20-nm-thick SAPO-34 nanosheets have been also reported [20]. ~~Layered SAPO-34 has been recently reported [21], including its exfoliation to single-layer sheets [20].~~ Another promising material for this is ordered *g*-C_3N_4 such as poly(triazine imide) (PTI) which hosts 3.4 Å pores. Recently, PTI nanosheets have been prepared as single-layer nanosheets [43], however, the lateral size of exfoliated nanosheets was small (<50 nm), and the yield of exfoliated nanosheets was low. Synthesis of high-aspect-ratio *g*-C_3N_4 nanosheets with high yield would be highly beneficial in this respect.

Macroscopically-large 2D films, such as graphene and analogues, can be used to fabricate membranes with a selective layer that is just one atom thick. When a high density of gas-sieving pores is incorporated in graphene, extremely large permselective gas flux can be realized [50]. Molecular simulations predict permselective CO_2 permeance in the range of 10000-100000 GPU [51]. A CO_2 permeance of 10000 GPU has been recently demonstrated in combination with an attractive CO_2/N_2 selectivity (>20)[51,52]. This is mainly because of the extremely short diffusion path length of gases across the atom-thick pores of graphene [53]. Gas sieving can be obtained from nanopores hosting electron density gap comparable to that of the target gas molecules. For such nanopores, the flux of gas molecules can be modelled using the transition state theory and is determined by the energy barrier experienced by the molecule while crossing the

Con formato: Fuente: Sin Cursiva, Color de fuente:

Con formato: Color de fuente: Rojo

nanopore [54]. As a result, the relative size of the gas molecules with respect to the nanopore determines the gas pair selectivity.

There are three key challenges in developing size-sieving nanoporous graphene membranes: angstrom-scale pores have to be created with dimensions able to sieve the desired components (e.g., CO_2 or H_2); pore creation technique has to be precise to yield a narrow pore size distribution avoiding large nonselective pores; and the density of gas-permeable pores should be high enough (>0.1%) to outperform the conventional membranes. Meeting these requirements would realize membranes, which are highly permeable but also selective, overcoming the selectivity-permeability trade-off of conventional polymeric membranes. This will require the development of synthetic approaches where pore nucleation and expansion can be controlled, e.g., down to the removal of 10-16 carbon atoms per pore in the case of graphene for H_2- and CO_2-sieving [52].

The control of pore density (nucleation) and size (expansion), permitting maximization of gas flux and gas pair selectivity, will be highly beneficial. For CO_2/N_2 separation, exploiting the higher adsorption affinity of CO_2 by functionalizing with CO_2-philic groups is an attractive approach [55,56]. Although the field is in its infancy, attractive separation performance has been demonstrated for applications where large permeance is desired along with a moderate selectivity, e.g., post-combustion carbon capture. For instance, nanoporous graphene membranes prepared by controlled pore formation and/or functionalization have yielded CO_2 permeances of 10000 GPU along with an attractive CO_2/N_2 selectivity (above 20)[57]. Advances on the fundamental fronts

– especially mechanistic understanding of nanopore formation – are expected to further improve the separation performance toward improving the gas pair selectivity.

3.2. Challenges in commercialization

A challenge for MMM and stacked nanosheet films is to develop strategies to reduce their thickness down to that of the selective layer in TFC (<100 nm). For this, the development of low-cost, smooth, and porous polymeric support hosting asymmetric porous structure with nanometer-scale pore opening will be highly attractive. Such a support structure would allow the formation of a uniform thin film while avoiding pinhole defects. Nonsolvent-induced phase separation of polymer is a promising technique to produce such porous supports. In cases where high thermal stability is required, high-glass-temperature polymers, such as polybenzimidazole [58], are attractive.

In the case of single-layer 2D films such as nanoporous graphene film, a key challenge lies in developing synthetic methods that are conducive to scale-up. Large-area polycrystalline graphene films can be synthesized on a metal foil by chemical vapor deposition (CVD), a scalable method that can produce hundreds of meter squares of graphene, e.g., by a continuous roll-to-roll process [59] or by stacking the metal foil [60]. However, the CVD technique has to be optimized to yield graphene at a large scale with high enough quality for membranes, i.e., with an extremely low density of defects and contaminations. The cost of catalytic metal foil used for CVD of graphene needs to be reduced to or lower than 10

$/m^2. Alternatively, methodologies allowing the reuse of the foil for several rounds of synthesis can cut down the effective cost of foil.

For nanoporous single-layer graphene membrane, another critical challenge is the scalable incorporation of nanopores into an otherwise impermeable graphitic lattice. Direct synthesis of nanoporous graphene is highly attractive in this regard (top-down approach). Proof-of-concept for this has been demonstrated by lowering the CVD temperature [61,62] or by controlling the amount of carbon precursors for the synthesis of graphene [63]. For pore incorporation by post-synthetic etching (bottom-up approach), scalable chemical etching techniques involving gaseous etchants are highly attractive. Reactive gases can be exposed uniformly over the surface of graphene in simple setups. However, controlling pore nucleation and expansion at the Å-scale in an industrial-sized reactor is expected to be challenging for both top-down and bottom-up approaches. An improved mechanistic understanding of events, which control pore-size distribution, is needed to achieve a high pore density with a narrow size distribution.

From a membrane fabrication perspective, a crucial challenge is to develop methods for transferring the graphene film onto a porous support without inducing cracks or tears in the film. CVD graphene is synthesized on a substrate, and the transfer of graphene involves its isolation from the growth substrate. The mechanical stress generated during the isolation step is often high enough to generate macroscopic cracks in graphene, which deteriorates gas pair selectivity. Recently, crack-free centimeter-scale graphene membranes have been demonstrated by permanently reinforcing graphene with a gas-permeable layer, such as nanoporous carbon film [64], carbon nanotube film [65] and dense polymer films [52]. However, these methods require further improvement for the preparation of graphene membranes on low-cost and flexible support, such as those used for the preparation of polymeric TFC membranes.

4. Current technical limitations of asymmetric membranes presenting a selective layer with nanoporous materials

4.1. Asymmetric membranes for gas separation

In general, dense and thick polymeric membranes with no porous structure are mostly applied for characterization purposes or to test new membrane materials. Their single-gas permeability and ideal selectivity for a given mixture can be obtained with the so-called time lag system with the advantage of allowing the estimation of diffusivity and solubility parameters of the membrane [66]. However, this experimental setup is not very realistic, as in real-world applications mixtures of gases are used, including minor components such as moisture or H_2S, depending on the origin of the stream to be treated.

Instead, asymmetric membranes with a selective skin layer on top of a mechanically stable support constitute the perfect membrane structure, and one which could be ideal for commercial applications. The advantage of asymmetric membranes is that transport resistance is minimised and fabrication costs are reduced by using the minimum amount of selective material. This type of membrane supposes two in-series resistances to the gas transport and the contribution of the support has to be minimum so as not to penalize the function of the selective film [67]. As a consequence, the porosity of the support has to be as high as possible while providing an adequate activated surface to favour the deposition of the ultrathin film by certain coating techniques [2].

Sometimes an intermediate gutter layer is placed between the previous two layers. A gutter layer is an intermediate layer between the top selective layer and the surface of the membrane support. The gutter layer can modify the surface defects, plug the pores of membrane substrate and prevent the selective coating dispersion from penetrating deeply into the pores. It also provides a smooth surface bed for the top selective layer so that it is easier to spread a thinner layer than to coat directly on the relatively rough substrate. As a result, the gutter layer, even if it contributes to the whole transport resistance, can enhance the overall permeance of the membrane by an order of magnitude [68], having found that the gutter layer permeability should be 5-10 times higher than that of the selective layer to minimize the decrease in selectivity [69].

4.2. Limitation of support

In addition to conferring mechanical stability to the membrane, the support, in series with the skin layer, should minimally restrict the membrane transport. As an example, PEBA (poly (ether-block-amide)) type polymers, commercialized as Pebax®, are some of the most studied skin layers for CO_2 selective membranes.

Fig. 4 illustrates the expected effect of the membrane thickness on the permeance for elastomeric Pebax® 1657 membranes. From nine relevant studies, an average CO_2 permeability of 101±34 Barrer was obtained for Pebax®

1657 thick dense membranes (corresponding to CO_2/N_2 selectivities in the 36-89 range) [67,70–77]. The dotted line of negative slope is the calculation of permeance as a function of skin layer thickness from the value of 101 Barrer (dividing permeability by membrane thickness), implying negligible resistances from the support and gutter layer. Even if gas separation supports are highly permeable (ca. 200,000 GPU of CO_2) [78,79], in practice, the TFC membranes of only Pebax® 1657 (red squares) exhibit lower permeances than expected due to the negative contributions of both the support and the gutter layer. The deviation augments with decreasing selective layer thickness. The blue triangles in the plot correspond to Pebax® 1657 based MMMs, always with permeances above the expected, in line with the capacity of fillers to enhance the permeation of such membranes [80]. From this plot, we can conclude that as the skin layer thickness goes down to the nanometer dimension, the resistance of the support becomes more relevant suggesting its improvement in terms of porosity, thickness and mechanical strength. Moreover, MMMs can enhance the permeance beyond the thickness-related value.

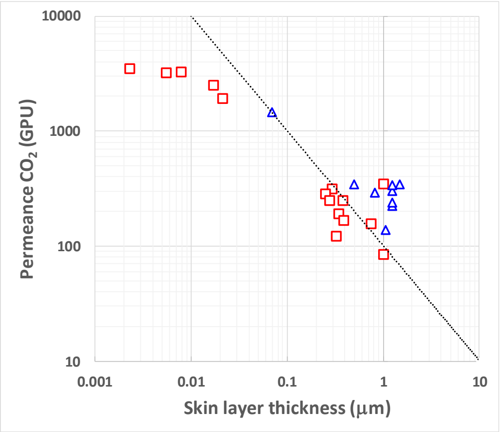


Fig. 4. CO_2 permeance as a function of the thickness of the Pebax® 1657 selective layer for different TFC membranes. The dotted line was obtained from the average of the permeabilities of nine different dense membranes [67,70–77]. The red squares and blue triangles correspond, respectively, to bare polymer [67,81–85] and to filler modified [69,85–87] TFC membranes of different thicknesses. These membranes are known as TFN membranes, i.e. TFC membranes incorporating porous particles. When the membrane thickness is 1 μm, a permeance of 1 GPU (1 GPU= $1 \cdot 10^{-6}$ $cm^3(STP) \cdot cm^{-2} \cdot cmHg^{-1} \cdot s^{-1}$) corresponds to a permeability of 1 Barrer.

4.3. Further developments in gutter layer and support

The highest permeance gas separation membrane ever reported, with 40,000 GPU of CO_2 and 10-12 CO_2/N_2 selectivity, was made of PDMS [79]. This membrane was 34 nm thick and prepared onto a glass substrate by spin coating, which was later detached using ethanol and thus transferred onto highly permeable PAN (polyacrylonitrile) ultrafiltration support; in this way, it was avoided the use of a gutter layer and the possible penetration of the PDMS within the substrate pores. Indeed, to extract the maximum performance of the selective layer, the resistances of the gutter layer and support have to be as negligible as possible.

The typical approach is to fill the support porosity with some liquid to avoid the penetration of the gutter material [78,88], but there are other interesting approaches such as the use of sacrificial gutter layers [67,89]. In this case, the sacrificial material should be removed without altering either the membrane separation properties or its attachment to the support. The PDMS membrane mentioned previously with the 40,000 GPU CO_2 permeance was first prepared by spin coating on a sacrifice layer of poly(4-hydroxystyrene)[79]. This was dissolved in ethanol and then the PDMS transferred to a PAN support maintaining its shape and mechanical strength. Even if it is true that the extrapolation of this methodology to a scalable industrial procedure and with more selective polymers than PDMS (this is more a gutter layer material than a desirable selective polymer, at least for CO_2 separation) may not be immediate, these results are quite encouraging. In fact, with this principle, a 70 nm thick polyetheramine-graphene oxide Pebax 1657 membrane has been prepared on a 75 nm thick PDMS gutter layer showing a CO_2 permeance of 1455 GPU together with a CO_2/N_2 selectivity of 68.1 [69]. In addition, one of the most promising membranes for CO_2 separation is the Polaris^{TM} one, made of a proprietary polymer presenting a gutter layer strategy and commercialized by Membrane Technology and Research, Inc., with up to 2000 GPU of CO_2 and CO_2/N_2 selectivity of 50 [90,91].

5. Membrane configurations and process requirements

To further improve the separation properties of thin layers, several microporous materials (like MOF) with exceptional molecular sieving ability are being filled in a composite (or MMM) layer onto HFs (see **Fig. 5**). However, a non-compelling physical and chemical compatibility among inorganic and organic phases in composites may compromise the result of enhanced separation performance. In the future, particular emphasis should be placed on the resulting structural changes to the membrane formulation when extrapolated from flat to HF configuration.

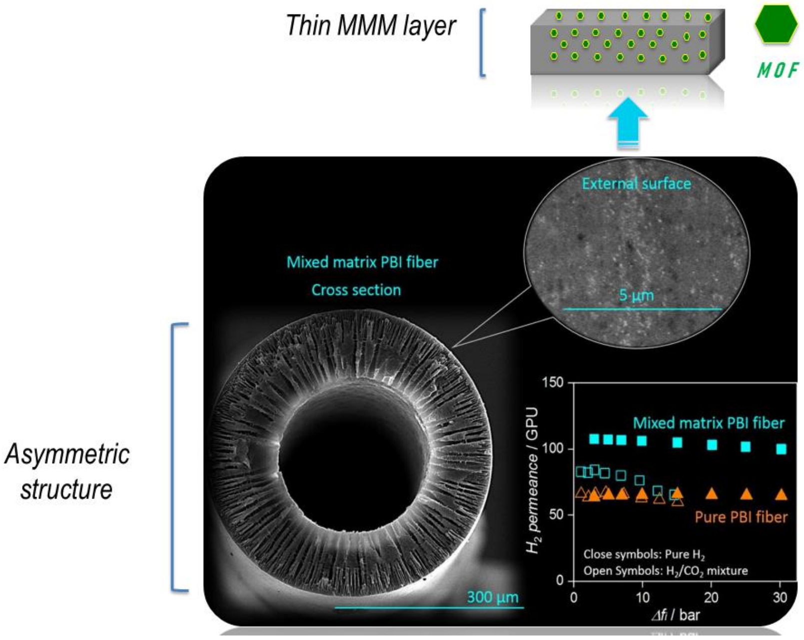


Fig. 5. Composite hollow fibre membranes for gas separation. Cross-section view of polybenzimidazole-10 wt.% ZIF-8 mixed matrix asymmetric hollow fibre for H_2/CO_2 separation [92].

Asymmetric membranes can be manufactured in a flat or a HF geometry and then packed into modules to reach high productivity for industrial applications. **Fig. 6** graphically illustrates the types of membrane module configurations, which typically refer to the geometry of the membrane and its position in space in relation to the flow of the feed fluid and of the permeate. HF [93] and spiral wound [87] are the membrane configurations providing the highest values of intensification in terms of membrane area per module volume (i.e., packing density). HF modules stand out as the most preferred due to their high packing density, varying from 500 up to 9000 m^2 m^{-3}, exceeding the reported densities for spiral-wound modules (ca. 1200 m^2 m^{-3}) and plate and frame modules (ca. 100–400 m^2 m^{-3}) [94]. HF membranes also have the benefit of being able to handle extremely high transmembrane pressure difference (approximately 70 bar), while the fabrication cost is around 5–20 times lower than the equivalent for spiral wound modules [95].

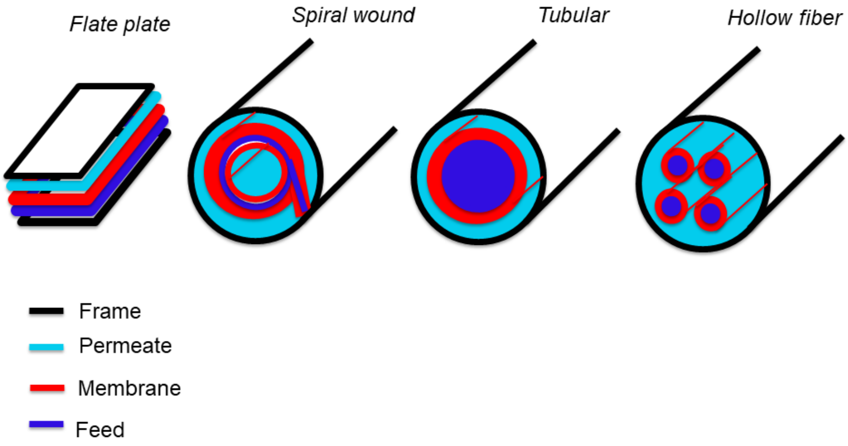


Fig. 6. Graphical depiction of the four types of membrane configurations.

Most commercially available membranes are manufactured as HF modules, while less than 20% correspond to spiral wound modules. Both are most suitable for gas separation applications [96], as they are relatively less prone to membrane fouling than flat sheet or tubular modules. In general, HF modules experience 25% more membrane surface shears promoting hydrodynamic pattern changes which consequently mitigate the deposition of foulants, e.g., when operating HF modules in cross-flow filtration mode, shear forces on the membrane occur thanks to bubbling, vibration, or particle scouring [97]. However, in the case of

HF modules, the feed gas requires further pre-treatment to mitigate severe fouling and plasticization, depending on the type of material. As for spiral wound modules, apart from being more resistant to plasticization, can be applied to a wider range of membrane materials compared with HFs [95]. To date, few spiral wound membranes for gas separation (at least for CO_2 and H_2-containing mixtures) have been documented [98–100].

Today, the production of HFs with a selective layer is still challenging for gas separation since gas molecules are sized in the Angstroms range [101], and are therefore very sensitive to any defect in the functional layer. The usage of an atomically thin layer with precisely controlled pores and chemical functionality is crucially needed to achieve true molecular sieving of gas molecules [102], as this separation mechanism is usually compromised by surface adsorption and condensation phenomena of the gas molecules in the membrane pores [103].

Forming ultrathin membranes into HF modules is an ongoing research challenge, but they still represent a promising way for efficient gas separation with scalable productivity and less economic expenditure [96]. Various ultrathin composite HF membranes for CO_2/H_2 separation have been successfully synthesized at lab scale (**Table 1)**. MOFs (such as ZIF-8, $Cu_3(BTC)_2$, MIL-53 and UiO-66-NH_2) are the most reported nanoporous fillers in composite HF fabrication due to their physical and chemical compatibility with polymer phases; however, such membrane modules are limited to small membrane sizes of 10-48 cm length.

Table 1. Various hollow fibre (HF) membrane concepts aimed at separating CO_2 and H_2 containing mixtures.

Composition	*Type of HF*	*Membrane/module size*	*Gas mixture*	*Operating conditions*	*Permeance in GPU (of faster gas)*	*Selectivity*	*Reference*
ZIF-8/Ultem®	Mixed matrix	6 fibers/ 20 cm length each	CO_2/N_2	45◦C, 6.8 bar	34	28	[104]
PTPESU	Asymmetric	10 fibers/ 15 cm length each	CO_2/N_2	25 ◦C, 3.5 bar	85.1	34	[105]
PBI/P84	Asymmetric	1 fiber/ 17 cm length	H_2/CO_2	180 °C, 6 bar	90	13.5	[106]
Pebax/PDMS/PAN	Composite	1 fiber/ 15-20 cm length	H_2/CO_2	25 °C, 2 bar	59.8	8.1	[107]
PVA/PPO	Thin film composite	10 fibers/ 10 cm length each	CO_2/N_2	25 °C, 2 bar	791	40	[108]
PDMS/PAN	Thin film composite	1 fiber/ 15 cm length	CO_2/N_2	25 °C, 3 bar	5000	11	[109]
sPPSU/PBI	Dual-layer	1 fiber/ 15 cm length	H_2/CO_2	90 °C, 14.2 bar	16.7	9.7	[110]
TNTs/PSf	Mixed matrix	10 fibers/ 20 cm length each	CO_2/N_2	25 °C, 3 bar	120	28.8	[111]
ZIF-8/PBI	Mixed matrix	1-22 fibers/ 18 cm length each	H_2/CO_2	150 °C, 7 bar	107	18	[92]

ZIF-8/Si_3N_4	Ceramic	1 fiber/ 10 cm length	H_2/CO_2	25 °C, 2.5 bar	2505	11.7	[112]
PDMS–$Cu_3(BTC)_2$/PSf	Asymmetric	1 fiber/ 15 cm length	CO_2/N_2	25 °C, 5 bar	109	31	[113]
PEI/Aminosilane functionalized MIL-53	Mixed matrix	10 fibers/ 48 cm length each	CO_2/N_2	35 °C, 5 bar	30.9	34.7	[114]
PIM/PDMS/PAN	Asymmetric composite	3 fibers/ 16 cm length each	CO_2/N_2	25 °C, 2 bar	483	22.5	[115]
Pebax® 2533-UiO-66-NH_2/PP	Mixed matrix	1 fiber/ 7-10 cm length	CO_2/N_2	25 °C, 2 bar	26	37	[116]

Abbreviations: PTPESU (poly trimethyl phenylene ethersulfone); PBI (polybenzimidazole); sPPSU (sulfonated polyphenylsulfone); PVA (poly (vinyl alcohol)); PDMS (polydimethylsiloxane); PAN (polyacrylonitrile); PPO (poly(p-phenylene oxide)); TNT (titania nanotube); PSf (polysulfone); PEI (polyetherimide); PIM (polymer of intrinsic microporosity); PEI (polyetherimide), PP (polypropylene).

Depending on the type of polymer (or dope solution composition) and preparation protocol, polymer composite HFs can display high permeation rates in gas separation performance. This is the case of PDMS/PAN thin composite, which has shown up to 5000 GPU permeance in CO_2/N_2 mixtures [109], while PIM/PDMS/PAN HFs displayed 483 GPU (with selectivity values of 22.5) towards similar gas mixture [115]. In this HF, a cross-linked PDMS gutter layer was introduced between the PIM selective layer and the PAN substrate, which was able to mitigate the detrimental solvent effects during the dip coating, permit PIM to adhere to it, and redistribute the gas transport across the membranes.

Compared with such HFs, PDMS–$Cu_3(BTC)_2$/PSf [113] and PEI/aminosilane functionalized MIL-53 [114] HFs offered better performance with CO_2/N_2 selectivities of 31 and 34.7, respectively, but with a decreased CO_2 permeance. ZIF-8 filled polyetherimide (Ultem® 1000) matrix was subsequently utilized for the fabrication of dual-layer asymmetric HF membranes via the dry jet-wet quench method [104]. The resulting MMM HFs showed a 20% increased permeance in CO_2/N_2 testing compared with the pristine HFs. In this regard, these few examples evidence that the involvement of inorganic materials, like MOFs, with superior gas molecular sieving nature, can enhance the CO_2/N_2 separation performance of polymer membranes [18]. Similarly, specific MOFs can be adapted in HFs presenting polymer or inorganic membrane supports for H_2/CO_2 mixture separation. For instance, ZIF-8 has contributed to a 65% increase in H_2 permeance at constant ideal selectivity in PBI HFs. Unlike pristine PBI HFs, filler incorporation into the PBI matrix contributed to a substantial increase in H_2 permeance from 65 GPU to 107 GPU, while the ideal H_2/CO_2 selectivity remained unchanged (ca. 18)[92]. Knowing the great advantages of ceramic materials in terms of high thermal and chemical stability in harsh environments, they have started to be applied as HF supports. As an example, ZIF-8 supported on silicon nitride ceramic HF exhibited improved permeation as high as 2,505 GPU, with H_2/CO_2 selectivity of 7.3 [112].

To date, most advances in composite polymer-based membranes containing either MOFs or zeolites have relied on the fabrication of flat sheet membranes, which have exhibited impressive performance surpassing polymer upper bound performance, e.g., MMMs based on ZIF-300 filled PEBA [117]. This is a result of engineered designs of the polymer and inorganic phases. Unfortunately, there is still limited research on HF membranes but studies show that they represent the most prominent membrane configuration for separating CO_2 and H_2-containing mixtures (see **Table 1**), at least in H_2/CO_2 and CO_2/N_2 mixture separations with scalable performances for possible industrial purposes [96]. Certainly, several factors should be considered when tailoring a HF membrane, such as inorganic and organic (i.e., polymer) phase properties, along with their compatibility with each other.

To some extent, the dope solution composition has a fundamental and decisive impact on the morphology and structure of prepared membranes and thus on gas separation performance. Therefore, particular emphasis must be placed on the fabrication parameters[118]; for instance, the dry-jet wet spinning process stands out as the most used method for HF preparation, where several variables, such as bore fluid composition, flow rates of dope and bore fluids, and air gap, are essential to obtain defect-free membranes. However, as for the selection of membrane material (both the support and the selective layer), the presence of humidity and impurities (e.g., H_2S)[88], as well as operating temperature and pressure, are also important for targeted separations.

Since most industrial separations demand large membrane areas (ca. 1000 – millions m^2), the major challenge impeding the industrialization of new membrane materials in HF configurations lies in producing membranes in a large quantity with high permeance and selectivity at a reasonable cost [119]. **Table 1** reports successful examples of new composite membranes in small HF modules; however, there is no report in which any of those membranes have been extrapolated to a large scale. Developing scalable methods to obtain reproducible permeance and selectivity in large HFs thus still remains highly challenging.

6. Conclusions and outlook

Current and future energy production processes involve the separation of CO_2 and H_2-containing mixtures. In this context, membrane technology seems to be the most suitable approach from the point of view of process simplicity, cost and sustainability. Besides, membranes based on or modified with nanoporous materials have demonstrated very good performance when separating CO_2/N_2, CO_2/CH_4 and H_2/CO_2 energy-related mixtures. Nevertheless, some limitations still remain to achieving the industrialization of membranes in this field, even if selectivity-permeance upper bounds have been surpassed with the help of many nanoporous materials.

For 2D materials, such as nanoporous graphene, control of pore size and porosity can still be enhanced by an improved mechanistic understanding of pore incorporation. The thickness decrease in the selective membrane skin layer would overcome issues like membrane activation and even the cost of relatively expensive nanoporous materials. However, large-scale, effective methods for transferring 2D films to porous supports without incurring defect formation are needed.

The ability to implement flat membrane procedures to process intensified spiral wound and HF membrane systems has to be improved. Moreover, some issues like support adequacy in terms of mechanical and diffusion resistances (requiring or not of a gutter layer), fabrication reproducibility and cost, mechanical robustness and long-term stability need attention to achieve commercially reliable membrane systems.

All these limitations suggest the concentration of efforts in two directions: more interdisciplinary work is needed combining chemistry, materials science and chemical engineering to extract the best of nanoporous materials when allied with the other membrane components; and more academic-industry collaboration is desired focussing on specific energy-relevant gas mixtures to be separated under realistic conditions.

Recommendations for the researchers in the field

For a possible real application, the gas mixtures must present contaminants (e.g., H_2S, CO), water and other gases, which strongly affect the membrane performance [120]; e.g., CO_2 and N_2 permeability can decrease as water occupies free volume in polymer membranes, while the N_2 permeability could increase in the presence of H_2S by improving the N_2 solubility or diffusion within specific polymers (e.g., PDMS) [120].

To date, most of the research has been done at a lab-scale, therefore, there is a need of extrapolating the performance to a larger scale (e.g., pilot scale), this is related to finding scalable fabrication methods with reproducibility in membrane performance. This may also imply the handling of operating conditions for better performance. For example, as for CO_2 separations, feed CO_2 concentration influence the separation performance (particularly gas flux) since there is different CO_2 partial pressure across the membrane.

In addition to this, when testing under zero transmembrane pressure using sweep gas, the non-selective viscous flow is minimized through the membrane defects resulting in enhanced selectivity. In realistic practical conditions, a non-zero downstream pressure exists, leading to higher solute concentrations in the membrane. This aspect should be also considered when testing the membrane performance.

References

[1] D.S. Sholl, R.P. Lively, Seven chemical separations, Nature. 532 (2016) 435–437.

[2] R. Castro-Muñoz, K. V. Agrawal, J. Coronas, Ultrathin permselective membranes: the latent way for efficient gas separation, RSC Adv. 10 (2020) 12653–12670. https://doi.org/10.1039/D0RA02254C.

[3] S. Kim, Y.M. Lee, High performance polymer membranes for CO 2 separation, Curr. Opin. Chem. Eng. 2 (2013) 238–244. https://doi.org/10.1016/j.coche.2013.03.006.

[4] R. Castro-Muñoz, M.Z. Ahmad, V. Fíla, Tuning of Nano-Based Materials for

Embedding Into Low-Permeability Polyimides for a Featured Gas Separation, Front. Chem. 7 (2020) 1–14. https://doi.org/10.3389/fchem.2019.00897.

[5] D.Q. Vu, W.J. Koros, S.J. Miller, Mixed matrix membranes using carbon molecular sieves, J. Memb. Sci. 211 (2003) 311–334. https://doi.org/10.1016/S0376-7388(02)00429-5.

[6] M.Z. Ahmad, R. Castro-Munõz, P.M. Budd, Boosting gas separation performance and suppressing the physical aging of polymers of intrinsic microporosity (PIM-1) by nanomaterial blending, Nanoscale. 12 (2020) 23333–23370. https://doi.org/10.1039/d0nr07042d.

[7] R. Castro-Muñoz, M. Zamidi Ahmad, M. Malankowska, J. Coronas, A new relevant membrane application: CO2 direct air capture (DAC), Chem. Eng. J. 446 (2022). https://doi.org/10.1016/j.cej.2022.137047.

[8] J. Dechnik, J. Gascon, C.J. Doonan, C. Janiak, C.J. Sumby, Mixed-Matrix Membranes, Angew. Chemie - Int. Ed. 56 (2017) 9292–9310. https://doi.org/10.1002/anie.201701109.

[9] Y. Shi, B. Liang, R.B. Lin, C. Zhang, B. Chen, Gas Separation via Hybrid Metal–Organic Framework/Polymer Membranes, Trends Chem. 2 (2020) 254–269. https://doi.org/10.1016/j.trechm.2020.01.002.

[10] A.R. Kamble, C.M. Patel, Z.V.P. Murthy, A review on the recent advances in mixed matrix membranes for gas separation processes, Renew. Sustain. Energy Rev. 145 (2021) 111062. https://doi.org/10.1016/j.rser.2021.111062.

[11] R. Castro-Muñoz, A. Cruz-Cruz, Y. Alfaro-Sommers, L.X. Aranda-Jarillo, E. Gontarek-Castro, Reviewing the recent developments of using graphene-based nanosized materials in membrane separations, Crit. Rev. Environ. Sci. Technol. 0 (2021) 1–38. https://doi.org/10.1080/10643389.2021.1918509.

[12] Y. Zhang, X. Feng, S. Yuan, J. Zhou, B. Wang, Challenges and recent advances in MOF-polymer composite membranes for gas separation, Inorg. Chem. Front. 3 (2016) 896–909. https://doi.org/10.1039/c6qi00042h.

[13] J. Müller, K.V. Peinemann, J. Müller, Development of facilitated transport membranes for the separation of olefins from gas streams, Desalination. 145 (2002) 339–345. https://doi.org/10.1016/S0011-9164(02)00433-2.

[14] G. Dong, H. Li, V. Chen, Challenges and opportunities for mixed-matrix membranes for gas separation, J. Mater. Chem. A. 1 (2013) 4610–4630. https://doi.org/10.1039/c3ta00927k.

[15] Z. Lai, M. Tsapatsis, Gas and organic vapor permeation through b-oriented MFI membranes, Ind. Eng. Chem. Res. 43 (2004) 3000–3007. https://doi.org/10.1021/ie034096s.

[16] X. Zhao, Y. Wang, D.S. Li, X. Bu, P. Feng, Metal–Organic Frameworks for Separation, Adv. Mater. 30 (2018). https://doi.org/10.1002/adma.201705189.

[17] H. Li, C. Qiu, S. Ren, Q. Dong, S. Zhang, F. Zhou, X. Liang, J. Wang, S. Li, M. Yu, Na+-gated water-conducting nanochannels for boosting CO2 conversion to liquid fuels, Science (80-.). 367 (2020) 667–671. https://doi.org/10.1126/science.aaz6053.

[18] Y. Peng, Y. Li, Y. Ban, H. Jin, W. Jiao, X. Liu, W. Yang, Metal-organic framework nanosheets as building blocks for molecular sieving membranes, Science (80-.). 346 (2014) 1356–1359.

[19] M. Dakhchoune, L.F. Villalobos, R. Semino, L. Liu, M. Rezaei, P. Schouwink, C.E. Avalos, P. Baade, V. Wood, Y. Han, M. Ceriotti, K.V. Agrawal, Gas-sieving zeolitic membranes fabricated by condensation of precursor nanosheets, Nat. Mater. 20 (2021) 362–369. https://doi.org/10.1038/s41563-020-00822-2.

[20] B. Wang, T. Wu, M. Yu, S. Li, R. Zhou, W. Xing, Highly Ordered Nanochannels in a Nanosheet-Directed Thin Zeolite Nanofilm for Precise and Fast CO2 Separation, Small. 16 (2020). https://doi.org/10.1002/smll.202002836.

[21] B. Wang, N. Wang, X. Li, R. Zhou, W. Xing, Exfoliation of lamellar SAPO-34 zeolite to nanosheets and synthesis of thin SAPO-34 membranes by a nanosheet-seeded secondary growth approach, J. Memb. Sci. 645 (2022)

120177. https://doi.org/10.1016/j.memsci.2021.120177.

[22] J. Zhao, S.H. Mousavi, G. Xiao, A.H. Mokarizadeh, T. Moore, K. Chen, Q. Gu, R. Singh, A. Zavabeti, J.Z. Liu, P.A. Webley, G.K. Li, Nitrogen Rejection from Methane via a “Trapdoor” K-ZSM-25 Zeolite, J. Am. Chem. Soc. 143 (2021) 15195–15204. https://doi.org/10.1021/jacs.1c06230.

[23] G. Liu, V. Chernikova, Y. Liu, K. Zhang, Y. Belmabkhout, O. Shekhah, C. Zhang, S. Yi, M. Eddaoudi, W.J. Koros, Mixed matrix formulations with MOF molecular sieving for key energy-intensive separations, Nat. Mater. 17 (2018) 283–289. https://doi.org/10.1038/s41563-017-0013-1.

[24] J.J. Low, A.I. Benin, P. Jakubczak, J.F. Abrahamian, S.A. Faheem, R.R. Willis, Virtual high throughput screening confirmed experimentally: Porous coordination polymer hydration, J. Am. Chem. Soc. 131 (2009) 15834–15842. https://doi.org/10.1021/ja9061344.

[25] H. Zhai, Advanced Membranes and Learning Scale Required for Cost-Effective Post-combustion Carbon Capture, IScience. 13 (2019) 440–451. https://doi.org/10.1016/j.isci.2019.03.006.

[26] N. Kosinov, V.G.P. Sripathi, E.J.M. Hensen, Improving separation performance of high-silica zeolite membranes by surface modification with triethoxyfluorosilane, Microporous Mesoporous Mater. 194 (2014) 24–30. https://doi.org/10.1016/j.micromeso.2014.03.034.

[27] X. Liu, Y. Li, Y. Ban, Y. Peng, H. Jin, H. Bux, L. Xu, W. Yang, Improvement of hydrothermal stability of zeolitic imidazolate frameworks, Chem. Commun. 49 (2013) 9140–9142. https://doi.org/10.1039/c3cc45308a.

[28] M. Navarro, E. Mateo, B. Diosdado, M. Tsapatsis, J. Coronas, Activation of giant silicalite-1 monocrystals combining rapid thermal processing and ozone calcination, RSC Adv. 5 (2015) 18035–18040. https://doi.org/10.1039/c4ra16284f.

[29] L. Wang, C. Zhang, X. Gao, L. Peng, J. Jiang, X. Gu, Preparation of defect-free

DDR zeolite membranes by eliminating template with ozone at low temperature, J. Memb. Sci. 539 (2017) 152–160. https://doi.org/10.1016/j.memsci.2017.06.004.

[30] M.Y. Jeon, D. Kim, P. Kumar, P.S. Lee, N. Rangnekar, P. Bai, M. Shete, B. Elyassi, H.S. Lee, K. Narasimharao, S.N. Basahel, S. Al-Thabaiti, W. Xu, H.J. Cho, E.O. Fetisov, R. Thyagarajan, R.F. Dejaco, W. Fan, K.A. Mkhoyan, J.I. Siepmann, M. Tsapatsis, Ultra-selective high-flux membranes from directly synthesized zeolite nanosheets, Nature. 543 (2017) 690–694. https://doi.org/10.1038/nature21421.

[31] K. Varoon, X. Zhang, B. Elyassi, D.D. Brewer, M. Gettel, S. Kumar, J. Lee, S. Maheshwari, A. Mittal, C. Sung, M. Cococcioni, L. Franxis, A. McCormick, K. Mkhoyan, M. Tsapatsis, Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane, Science (80-.). 334 (2011) 72–75.

[32] J. Yu, Y. Pan, C. Wang, Z. Lai, ZIF-8 membranes with improved reproducibility fabricated from sputter-coated ZnO/alumina supports, Chem. Eng. Sci. 141 (2016) 119–124. https://doi.org/10.1016/j.ces.2015.10.035.

[33] L. NGK INSULATORS, NGK's Large Ceramic Membrane to Be Used in Demonstration Test for CO2 Recovery from Associated Gas during Oil Production, (2019). https://www.ngk-insulators.com/en/.

[34] Y. Pan, Z. Lai, Sharp separation of C2/C3 hydrocarbon mixtures by zeolitic imidazolate framework-8 (ZIF-8) membranes synthesized in aqueous solutions, Chem. Commun. 47 (2011) 10275–10277. https://doi.org/10.1039/c1cc14051e.

[35] J. Yao, D. Dong, D. Li, L. He, G. Xu, H. Wang, Contra-diffusion synthesis of ZIF-8 films on a polymer substrate, Chem. Commun. 47 (2011) 2559–2561. https://doi.org/10.1039/c0cc04734a.

[36] R. Wei, H.Y. Chi, X. Li, D. Lu, Y. Wan, C.W. Yang, Z. Lai, Aqueously Cathodic Deposition of ZIF-8 Membranes for Superior Propylene/Propane Separation, Adv. Funct. Mater. 30 (2020) 1–7. https://doi.org/10.1002/adfm.201907089.

[37] G. He, M. Dakhchoune, J. Zhao, S. Huang, K.V. Agrawal, Electrophoretic Nuclei Assembly for Crystallization of High-Performance Membranes on Unmodified Supports, Adv. Funct. Mater. 28 (2018) 1–8. https://doi.org/10.1002/adfm.201707427.

[38] S. Zhou, Y. Wei, L. Li, Y. Duan, Q. Hou, L. Zhang, L.X. Ding, J. Xue, H. Wang, J. Caro, Paralyzed membrane: Current-driven synthesis of a metal-organic framework with sharpened propene/propane separation, Sci. Adv. 4 (2018) 1–8. https://doi.org/10.1126/sciadv.aau1393.

[39] I.G. Wenten, P.T. Dharmawijaya, P.T.P. Aryanti, R.R. Mukti, Khoiruddin, LTA zeolite membranes: Current progress and challenges in pervaporation, RSC Adv. 7 (2017) 29520–29539. https://doi.org/10.1039/c7ra03341a.

[40] A.W. Thornton, B.D. Freeman, L.M. Robeson, Polymer Gas Separation Membrane Database, (2012). https://research.csiro.au/virtualscreening/membrane-database-polymer-gas-separation-membranes/.

[41] M.R. Abdul Hamid, Y. Qian, R. Wei, Z. Li, Y. Pan, Z. Lai, H.K. Jeong, Polycrystalline metal-organic framework (MOF) membranes for molecular separations: Engineering prospects and challenges, J. Memb. Sci. 640 (2021) 119802. https://doi.org/10.1016/j.memsci.2021.119802.

[42] T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. Xamena, J. Gascon, Metal–organic framework nanosheets in polymer composite materials for gas separation, Nat. Mater. 14 (2015) 48–55.

[43] L.F. Villalobos, M.T. Vahdat, M. Dakhchoune, Z. Nadizadeh, M. Mensi, E. Oveisi, D. Campi, N. Marzari, K.V. Agrawal, Large-scale synthesis of crystalline g-C3N4 nanosheets and high-temperature H2 sieving from assembled films, Sci. Adv. 6 (2020) 1–9. https://doi.org/10.1126/sciadv.aay9851.

[44] Z. Kang, Y. Peng, Y. Qian, D. Yuan, M.A. Addicoat, T. Heine, Z. Hu, L. Tee, Z. Guo, D. Zhao, Mixed Matrix Membranes (MMMs) Comprising Exfoliated 2D

Covalent Organic Frameworks (COFs) for Efficient CO2 Separation, Chem. Mater. 28 (2016) 1277–1285. https://doi.org/10.1021/acs.chemmater.5b02902.

[45] H.W. Kim, E. Al., Selective Gas Transport Through Few-Layered Graphene and Graphene Oxide Membranes, Science (80-.). 342 (2014) 91–95. https://doi.org/10.1126/science.1236098.

[46] X. Sang, Y. Xie, D.E. Yilmaz, R. Lotfi, M. Alhabeb, A. Ostadhossein, B. Anasori, W. Sun, X. Li, K. Xiao, P.R.C. Kent, A.C.T. Van Duin, Y. Gogotsi, R.R. Unocic, In situ atomistic insight into the growth mechanisms of single layer 2D transition metal carbides, Nat. Commun. 9 (2018) 1–9. https://doi.org/10.1038/s41467-018-04610-0.

[47] J. Shen, G. Liu, K. Huang, W. Jin, K.-R. Lee, N. Xu, Membranes with Fast and Selective Gas-Transport Channels of Laminar Graphene Oxide for Efficient CO 2 Capture , Angew. Chemie. 127 (2015) 588–592. https://doi.org/10.1002/ange.201409563.

[48] J. Abraham, K.S. Vasu, C.D. Williams, K. Gopinadhan, Y. Su, C.T. Cherian, J. Dix, E. Prestat, S.J. Haigh, I. V Grigorieva, P. Carbone, A.K. Geim, R.R. Nair, Tunable sieving of ions using graphene oxide membranes, Nat. Nanotechnol. (2017) 1–6. https://doi.org/10.1038/nnano.2017.21.

[49] R. Castro-Muñoz, J. Buera-González, Ó. de la Iglesia, F. Galiano, V. Fíla, M. Malankowska, C. Rubio, A. Figoli, C. Téllez, J. Coronas, Towards the dehydration of ethanol using pervaporation cross-linked poly(vinyl alcohol)/graphene oxide membranes, J. Memb. Sci. 582 (2019) 423–434. https://doi.org/10.1016/j.memsci.2019.03.076.

[50] K. Celebi, J. Buchheim, R.M. Wyss, A. Droudian, P. Gasser, I. Shorubalko, J.-I. Kye, C. Lee, H.G. Park, Ultimate Permeation Across Atomically Thin Porous Graphene, Science (80-.). 344 (2014) 289–292. https://doi.org/10.1126/science.1249097.

[51] C. Sun, B. Wen, B. Bai, Application of nanoporous graphene membranes in

natural gas processing: Molecular simulations of CH4/CO2, CH4/H2S and CH4/N2 separation, Chem. Eng. Sci. 138 (2015) 616–621. https://doi.org/10.1016/j.ces.2015.08.049.

[52] S. Huang, S. Li, L.F. Villalobos, M. Dakhchoune, M. Micari, D.J. Babu, M.T. Vahdat, M. Mensi, E. Oveisi, K.V. Agrawal, Millisecond lattice gasification for high-density CO2- And O2-sieving nanopores in single-layer graphene, Sci. Adv. 7 (2021) 1–13. https://doi.org/10.1126/sciadv.abf0116.

[53] S.P. Koenig, L. Wang, J. Pellegrino, J.S. Bunch, Selective molecular sieving through porous graphene, Nat. Nanotechnol. 7 (2012) 728–732.

[54] Z. Yuan, A. Govind Rajan, R.P. Misra, L.W. Drahushuk, K.V. Agrawal, M.S. Strano, D. Blankschtein, Mechanism and Prediction of Gas Permeation through Sub-Nanometer Graphene Pores: Comparison of Theory and Simulation, ACS Nano. 11 (2017) 7974–7987. https://doi.org/10.1021/acsnano.7b02523.

[55] N. Li, Y. Tian, J. Zhang, Z. Sun, J. Zhao, J. Zhang, W. Zuo, Precisely-controlled modification of PVDF membranes with 3D TiO 2 / ZnO nanolayer : enhanced anti-fouling performance by changing hydrophilicity and photocatalysis under visible light irradiation, J. Memb. Sci. 528 (2017) 359–368. https://doi.org/10.1016/j.memsci.2017.01.048.

[56] B. Luan, B. Elmegreen, M.A. Kuroda, Z. Gu, G. Lin, S. Zeng, Crown Nanopores in Graphene for CO 2 Capture and Filtration, ACS Nano. (2022). https://doi.org/10.1021/acsnano.2c00213.

[57] K.J. Hsu, L.F. Villalobos, S. Huang, H.Y. Chi, M. Dakhchoune, W.C. Lee, G. He, M. Mensi, K.V. Agrawal, Multipulsed Millisecond Ozone Gasification for Predictable Tuning of Nucleation and Nucleation-Decoupled Nanopore Expansion in Graphene for Carbon Capture, ACS Nano. 15 (2021) 13230–13239. https://doi.org/10.1021/acsnano.1c02927.

[58] H. Zhang, Q. Xiao, X. Guo, N. Li, P. Kumar, N. Rangnekar, Y. Jeon, S. Al-thabaiti, K. Narasimharao, S.N. Basahel, B. Topuz, F.J. Onorato, C.W. Macosko,

K.A. Mkhoyan, M. Tsapatsis, Open-Pore Two-Dimensional MFI Zeolite Nanosheets for the Fabri- cation of Hydrocarbon-Isomer-Selective Membranes on Porous Poly- mer Supports, Angew. Chemie - Int. Ed. 300072 (2016) 7184–7187. https://doi.org/10.1002/anie.201601135.

[59] P.R. Kidambi, D.D. Mariappan, N.T. Dee, A. Vyatskikh, S. Zhang, R. Karnik, A.J. Hart, A Scalable Route to Nanoporous Large-Area Atomically Thin Graphene Membranes by Roll-to-Roll Chemical Vapor Deposition and Polymer Support Casting, ACS Appl. Mater. Interfaces. 10 (2018) 10369–10378. https://doi.org/10.1021/acsami.8b00846.

[60] Y.P. Hsieh, C.H. Shih, Y.J. Chiu, M. Hofmann, High-Throughput Graphene Synthesis in Gapless Stacks, Chem. Mater. 28 (2016) 40–43. https://doi.org/10.1021/acs.chemmater.5b04007.

[61] Z. Yuan, G. He, S. Faucher, M. Kuehne, S.X. Li, D. Blankschtein, M.S. Strano, Direct Chemical Vapor Deposition Synthesis of Porous Single-Layer Graphene Membranes with High Gas Permeances and Selectivities, Adv. Mater. 33 (2021). https://doi.org/10.1002/adma.202104308.

[62] P.R. Kidambi, G.D. Nguyen, S. Zhang, Q. Chen, J. Kong, J. Warner, A.P. Li, R. Karnik, Facile Fabrication of Large-Area Atomically Thin Membranes by Direct Synthesis of Graphene with Nanoscale Porosity, Adv. Mater. 30 (2018). https://doi.org/10.1002/adma.201804977.

[63] L.F. Villalobos, C. Van Goethem, K.J. Hsu, S. Li, M. Moradi, K. Zhao, M. Dakhchoune, S. Huang, Y. Shen, E. Oveisi, V. Boureau, K.V. Agrawal, Bottom-up synthesis of graphene films hosting atom-thick molecular-sieving apertures, Proc. Natl. Acad. Sci. U. S. A. 118 (2021) 1–10. https://doi.org/10.1073/pnas.2022201118.

[64] W.C. Lee, L. Bondaz, S. Huang, G. He, M. Dakhchoune, K.V. Agrawal, Centimeter-scale gas-sieving nanoporous single-layer graphene membrane, J. Memb. Sci. 618 (2021) 118745. https://doi.org/10.1016/j.memsci.2020.118745.

[65] Y. Yang, X. Yang, L. Liang, Y. Gao, H. Cheng, X. Li, M. Zou, A. Cao, R. Ma, Q. Yuan, X. Duan, Large-area graphene-nanomesh/carbon-nanotube hybrid membranes for ionic and molecular nanofiltration, Science (80-.). 1062 (2019) 1057–1062.

[66] H. Wu, J. Thibault, B. Kruczek, The validity of the time-lag method for the characterization of mixed-matrix membranes, J. Memb. Sci. 618 (2021) 118715. https://doi.org/10.1016/j.memsci.2020.118715.

[67] R. Selyanchyn, M. Ariyoshi, S. Fujikawa, Thickness Effect on CO 2 /N 2 Separation in Double Layer Pebax-1657®/PDMS Membranes, Membranes (Basel). 8 (2018). https://doi.org/10.3390/membranes8040121.

[68] M. Kattula, K. Ponnuru, L. Zhu, W. Jia, H. Lin, E.P. Furlani, Designing ultrathin film composite membranes: The impact of a gutter layer, Sci. Rep. 5 (2015) 1–9. https://doi.org/10.1038/srep15016.

[69] M. Jin Yoo, K. Hyun, J. Hyeok, T. Woo, C. Wook, Ultrathin gutter layer for high-performance thin- fi lm composite membranes for CO 2 separation, J. Memb. Sci. 566 (2018) 336–345. https://doi.org/10.1016/j.memsci.2018.09.017.

[70] L. Martínez-Izquierdo, M. Malankowska, J. Sánchez-Laínez, C. Téllez, J. Coronas, Poly(ether-block-amide) copolymer membrane for CO2/N2 separation: The influence of the casting solution concentration on its morphology, thermal properties and gas separation performance, R. Soc. Open Sci. 6 (2019). https://doi.org/10.1098/rsos.190866.

[71] V.I. Bondar, B.D. Freeman, I. Pinnau, Gas Transport Properties of Poly (ether-b-amide) Segmented, J. Polym. Sci. Part B Polym. Physics,. 38 (2000) 2051–2062.

[72] Y. Wang, H. Li, G. Dong, C. Scholes, V. Chen, Effect of Fabrication and Operation Conditions on CO2 Separation Performance of PEO-PA Block Copolymer Membranes, Ind. Eng. Chem. Res. 54 (2015) 7273–7283. https://doi.org/10.1021/acs.iecr.5b01234.

[73] J.H. Kim, S.Y. Ha, Y.M. Lee, Gas permeation of poly(amide-6-b-ethylene oxide) copolymer, J. Memb. Sci. 190 (2001) 179–193. https://doi.org/10.1016/S0376-7388(01)00444-6.

[74] V. Mozaffari, M. Sadeghi, A. Fakhar, G. Khanbabaei, A.F. Ismail, Gas separation properties of polyurethane/poly(ether-block-amide) (PU/PEBA) blend membranes, Sep. Purif. Technol. 185 (2017) 202–214. https://doi.org/10.1016/j.seppur.2017.05.028.

[75] R.S. Murali, S. Sridhar, T. Sankarshana, Y.V.L. Ravikumar, Gas Permeation Behavior of Pebax-1657 Nanocomposite Membrane Incorporated with Multiwalled Carbon Nanotubes, Ind. Eng. Chem. Res. 49 (2010) 6530–6538. https://doi.org/10.1021/ie9016495.

[76] B. Yu, H. Cong, Z. Li, J. Tang, X.S. Zhao, Pebax-1657 nanocomposite membranes incorporated with nanoparticles/ colloids/carbon nanotubes for CO2/N2 and CO 2/H2 separation, J. Appl. Polym. Sci. 130 (2013) 2867–2876. https://doi.org/10.1002/app.39500.

[77] D. Zhao, J. Ren, H. Li, X. Li, M. Deng, Gas separation properties of poly(amide-6-b-ethylene oxide)/amino modified multi-walled carbon nanotubes mixed matrix membranes, J. Memb. Sci. 467 (2014) 41–47. https://doi.org/10.1016/j.memsci.2014.05.009.

[78] S.D. Bazhenov, I.L. Borisov, D.S. Bakhtin, A.N. Rybakova, V.S. Khotimskiy, S.P. Molchanov, V. V. Volkov, High-permeance crosslinked PTMSP thin-film composite membranes as supports for CO2 selective layer formation, Green Energy Environ. 1 (2016) 235–245. https://doi.org/10.1016/j.gee.2016.10.002.

[79] S. Fujikawa, M. Ariyoshi, R. Selyanchyn, T. Kunitake, Ultra-fast, selective CO2 permeation by free-standing siloxane nanomembranes, Chem. Lett. 48 (2019) 1351–1354. https://doi.org/10.1246/cl.190558.

[80] B. Seoane, A. Dikhtiarenko, A. Mayoral, C. Tellez, J. Coronas, F. Kapteijn, J. Gascon, Metal organic framework synthesis in the presence of surfactants:

Towards hierarchical MOFs?, CrystEngComm. 17 (2015) 1693–1700. https://doi.org/10.1039/c4ce02324b.

[81] O. Selyanchyn, R. Selyanchyn, S. Fujikawa, Critical Role of the Molecular Interface in Double-Layered Pebax-1657/PDMS Nanomembranes for Highly Efficient CO2/N2Gas Separation, ACS Appl. Mater. Interfaces. 12 (2020) 33196–33209. https://doi.org/10.1021/acsami.0c07344.

[82] A. Car, C. Stropnik, W. Yave, K. Peinemann, Pebax ® / polyethylene glycol blend thin film composite membranes for CO 2 separation : Performance with mixed gases, Sep. Purif. Technol. 62 (2008) 110–117. https://doi.org/10.1016/j.seppur.2008.01.001.

[83] L. Wang, Y. Li, S. Li, P. Ji, C. Jiang, Preparation of composite poly(ether block amide) membrane for CO2 capture, J. Energy Chem. 23 (2014) 717–725. https://doi.org/10.1016/S2095-4956(14)60204-7.

[84] X. Ren, J. Ren, H. Li, S. Feng, M. Deng, Poly (amide-6-b-ethylene oxide) multilayer composite membrane for carbon dioxide separation, Int. J. Greenh. Gas Control. 8 (2012) 111–120. https://doi.org/10.1016/j.ijggc.2012.01.017.

[85] T. Li, Y. Pan, K.V. Peinemann, Z. Lai, Carbon dioxide selective mixed matrix composite membrane containing ZIF-7 nano-fillers, J. Memb. Sci. 425–426 (2013) 235–242. https://doi.org/10.1016/j.memsci.2012.09.006.

[86] P.D. Sutrisna, J. Hou, H. Li, Y. Zhang, V. Chen, Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fibre membranes, J. Memb. Sci. 524 (2017) 266–279. https://doi.org/10.1016/j.memsci.2016.11.048.

[87] P.D. Sutrisna, J. Hou, M.Y. Zulkifli, H. Li, Y. Zhang, W. Liang, D.M. D'Alessandro, V. Chen, Surface functionalized UiO-66/Pebax-based ultrathin composite hollow fiber gas separation membranes, J. Mater. Chem. A. 6 (2018) 918–931. https://doi.org/10.1039/c7ta07512j.

[88] J. Kim, Q. Fu, K. Xie, J.M.P. Scofield, S.E. Kentish, G.G. Qiao, CO2 separation

using surface-functionalized SiO2 nanoparticles incorporated ultra-thin film composite mixed matrix membranes for post-combustion carbon capture, J. Memb. Sci. 515 (2016) 54–62. https://doi.org/10.1016/j.memsci.2016.05.029.

[89] S. Karan, Z. Jiang, A. Livingston, Sub–10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation, Science (80-.). 348 (2015) 1347–1351.

[90] T.C. Merkel, H. Lin, X. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: An opportunity for membranes, J. Memb. Sci. 359 (2010) 126–139. https://doi.org/10.1016/j.memsci.2009.10.041.

[91] L.S. White, K.D. Amo, T. Wu, T.C. Merkel, Extended field trials of Polaris sweep modules for carbon capture, J. Memb. Sci. 542 (2017) 217–225. https://doi.org/https://doi.org/10.1016/j.memsci.2017.08.017.

[92] M. Etxeberria-Benavides, T. Johnson, S. Cao, B. Zornoza, J. Coronas, J. Sanchez-Lainez, A. Sabetghadam, X. Liu, E. Andres-Garcia, F. Kapteijn, J. Gascon, O. David, PBI mixed matrix hollow fiber membrane: Influence of ZIF-8 filler over H2/CO2 separation performance at high temperature and pressure, Sep. Purif. Technol. 237 (2020) 116347. https://doi.org/10.1016/j.seppur.2019.116347.

[93] Y. Zhang, Q. Shen, J. Hou, P. Sutrisna, V. Chen, Shear-aligned graphene oxide laminate/Pebax ultrathin composite hollow fiber membranes using a facile dip-coating approach, J. Mater. Chem. A. 5 (2017) 7732–7737. https://doi.org/10.1039/c6ta10395b.

[94] M. Mohammadi Ghaleni, M. Bavarian, S. Nejati, Model-guided design of high-performance membrane distillation modules for water desalination, J. Memb. Sci. 563 (2018) 794–803. https://doi.org/10.1016/j.memsci.2018.06.054.

[95] R.W. Baker, Future Directions of Membrane Gas Separation Technology, Ind. Eng. Chem. Res. 41 (2002) 1393–1411. https://doi.org/10.1021/ie0108088.

[96] Y. Ding, Perspective on Gas Separation Membrane Materials from Process

Economics Point of View, Ind. Eng. Chem. Res. 59 (2020) 556–568. https://doi.org/10.1021/acs.iecr.9b05975.

[97] E. Akhondi, F. Zamani, K.H. Tng, G. Leslie, W.B. Krantz, A.G. Fane, J.W. Chew, The performance and fouling control of submerged hollow fiber (HF) systems: A review, Appl. Sci. 7 (2017) 1–39. https://doi.org/10.3390/app7080765.

[98] K.K. Chen, W. Salim, Y. Han, D. Wu, W.S.W. Ho, Fabrication and scale-up of multi-leaf spiral-wound membrane modules for CO2 capture from flue gas, J. Memb. Sci. 595 (2020) 117504. https://doi.org/10.1016/j.memsci.2019.117504.

[99] Y. Han, W. Salim, K.K. Chen, D. Wu, W.S.W. Ho, Field trial of spiral-wound facilitated transport membrane module for CO2 capture from flue gas, J. Memb. Sci. 575 (2019) 242–251. https://doi.org/10.1016/j.memsci.2019.01.024.

[100] W. Salim, V. Vakharia, Y. Chen, D. Wu, Y. Han, W.S.W. Ho, Fabrication and field testing of spiral-wound membrane modules for CO2 capture from flue gas, J. Memb. Sci. 556 (2018) 126–137. https://doi.org/10.1016/j.memsci.2018.04.001.

[101] R. Castro-Muñoz, K.V. Agrawal, J. Coronas, Ultrathin permselective membranes: the latent way for efficient gas separation, RSC Adv. 10 (2020) 12653–12670. https://doi.org/10.1039/d0ra02254c.

[102] L. Wang, M.S.H. Boutilier, P.R. Kidambi, D. Jang, N.G. Hadjiconstantinou, R. Karnik, Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes, Nat. Nanotechnol. 12 (2017) 509–522. https://doi.org/10.1038/nnano.2017.72.

[103] R.W. Baker, B.T. Low, Gas Separation Membrane Materials: A Perspective, Macromolecules. 47 (2014) 6999–7013.

[104] Y. Dai, J.R. Johnson, O. Karvan, D.S. Sholl, W.J. Koros, Ultem ®/ZIF-8 mixed matrix hollow fiber membranes for CO 2/N 2 separations, J. Memb. Sci. 401–402 (2012) 76–82. https://doi.org/10.1016/j.memsci.2012.01.044.

[105] W.F. Yong, T.S. Chung, M. Weber, C. Maletzko, New polyethersulfone (PESU)

hollow fiber membranes for CO2 capture, J. Memb. Sci. 552 (2018) 305–314. https://doi.org/10.1016/j.memsci.2018.02.008.

[106] J. Sánchez-Laínez, M. Etxeberria-Benavides, O. David, C. Téllez, J. Coronas, Green Preparation of Thin Films of Polybenzimidazole on Flat and Hollow Fiber Supports: Application to Hydrogen Separation, ChemSusChem. 14 (2021) 952–960. https://doi.org/10.1002/cssc.202002700.

[107] H.Z. Chen, Z. Thong, P. Li, T.S. Chung, High performance composite hollow fiber membranes for CO2/H 2 and CO2/N2 separation, Int. J. Hydrogen Energy. 39 (2014) 5043–5053. https://doi.org/10.1016/j.ijhydene.2014.01.047.

[108] Z. Dai, J. Deng, L. Ansaloni, S. Janakiram, L. Deng, Thin-film-composite hollow fiber membranes containing amino acid salts as mobile carriers for CO2 separation, J. Memb. Sci. 578 (2019) 61–68. https://doi.org/10.1016/j.memsci.2019.02.023.

[109] C.Z. Liang, W.F. Yong, T.S. Chung, High-performance composite hollow fiber membrane for flue gas and air separations, J. Memb. Sci. 541 (2017) 367–377. https://doi.org/10.1016/j.memsci.2017.07.014.

[110] A. Naderi, T.S. Chung, M. Weber, C. Maletzko, High performance dual-layer hollow fiber membrane of sulfonated polyphenylsulfone/Polybenzimidazole for hydrogen purification, J. Memb. Sci. 591 (2019) 117292. https://doi.org/10.1016/j.memsci.2019.117292.

[111] A.K. Zulhairun, M.N. Subramaniam, A. Samavati, M.K.N. Ramli, M. Krishparao, P.S. Goh, A.F. Ismail, High-flux polysulfone mixed matrix hollow fiber membrane incorporating mesoporous titania nanotubes for gas separation, Sep. Purif. Technol. 180 (2017) 13–22. https://doi.org/10.1016/j.seppur.2017.02.039.

[112] J.W. Wang, N.X. Li, Z.R. Li, J.R. Wang, X. Xu, C.S. Chen, Preparation and gas separation properties of Zeolitic imidazolate frameworks-8 (ZIF-8) membranes supported on silicon nitride ceramic hollow fibers, Ceram. Int. 42 (2016) 8949–8954. https://doi.org/10.1016/j.ceramint.2016.02.153.

[113] A.K. Zulhairun, Z.G. Fachrurrazi, M. Nur Izwanne, A.F. Ismail, Asymmetric hollow fiber membrane coated with polydimethylsiloxane-metal organic framework hybrid layer for gas separation, Sep. Purif. Technol. 146 (2015) 85–93. https://doi.org/10.1016/j.seppur.2015.03.033.

[114] H. Zhu, X. Jie, Y. Cao, Fabrication of Functionalized MOFs Incorporated Mixed Matrix Hollow Fiber Membrane for Gas Separation, J. Chem. 2017 (2017). https://doi.org/10.1155/2017/2548957.

[115] C.Z. Liang, J.T. Liu, J.Y. Lai, T.S. Chung, High-performance multiple-layer PIM composite hollow fiber membranes for gas separation, J. Memb. Sci. 563 (2018) 93–106. https://doi.org/10.1016/j.memsci.2018.05.045.

[116] G. Li, W. Kujawski, K. Knozowska, J. Kujawa, Thin Film Mixed Matrix Hollow Fiber Membrane Fabricated by Incorporation of Amine Functionalized Metal-Organic Framework for CO2/N2 Separation, Materials (Basel). 14 (2021) 3366. https://doi.org/10.3390/ma14123366.

[117] J. Yuan, H. Zhu, J. Sun, Y. Mao, G. Liu, W. Jin, Novel ZIF-300 Mixed-Matrix Membranes for Efficient CO2 Capture, ACS Appl. Mater. Interfaces. 9 (2017) 38575–38583. https://doi.org/10.1021/acsami.7b12507.

[118] G. Li, W. Kujawski, R. Válek, S. Koter, A review - The development of hollow fibre membranes for gas separation processes, Int. J. Greenh. Gas Control. 104 (2021). https://doi.org/10.1016/j.ijggc.2020.103195.

[119] C.Z. Liang, W.F. Yong, T. Chung, High-performance composite hollow fi ber membrane for fl ue gas and air separations, J. Memb. Sci. 541 (2017) 367–377. https://doi.org/10.1016/j.memsci.2017.07.014.

[120] C.A. Scholes, G.W. Stevens, S.E. Kentish, The effect of hydrogen sulfide , carbon monoxide and water on the performance of a PDMS membrane in carbon dioxide / nitrogen separation, J. Memb. Sci. 350 (2010) 189–199. https://doi.org/10.1016/j.memsci.2009.12.027.