

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

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20

21 **Abstract**

22 **Membranes containing** nanoporous materials (such as zeolites, metal-organic
23 materials and 2D materials such as graphene derivatives) may allow more
24 efficient separation of gas mixtures relevant to emerging energy technologies.
25 For example, such membranes could be applied in the separation of gases

26 containing mixtures of carbon dioxide (CO₂) and hydrogen (H₂). However, these
27 membranes are currently at a relatively low technology readiness level. Hence,
28 here we review the opportunities and challenges of applying these porous
29 materials in practice and at scale in membranes for possible commercialization.
30 Besides, we highlight the necessity of improvements in the porosity control of 2D
31 materials and the decrease in the selective membrane skin layer when adapted
32 in asymmetric membranes. In this latter point, we declare the main limitation of
33 porous supports, as well as the further developments in the gutter layer and
34 supports. Additionally, we review the main membrane module configurations and
35 process requirements, declaring the most suitable configurations (e.g. spiral
36 wound and hollow fiber modules) at scale with promising future for highly
37 intensified membrane modules for applicability in CO₂ and H₂ separations.
38 Finally, apart from the conclusions derived from this review, we outline key
39 recommendations for the researchers in the field.

40

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

43

44 1. Introduction

45 As the world seeks to move to greener energy technologies and to lower carbon
46 footprints and emissions, a number of gas separation processes may become
47 more important. For example, gas mixtures related to energy production include
48 CO₂/N₂ (post-combustion carbon capture), CO₂/CH₄ (production of biomethane)
49 and H₂/CO₂ (pre-combustion carbon capture). Current gas separation technology
50 largely relies on thermally-driven processes, such as distillation, absorption and

51 adsorption. Yet, there is evidence that some membrane-based separations
52 applying concentration and pressure gradients may be more energetically
53 efficient and environment-friendly than existing processes, and they could limit
54 carbon dioxide emissions and reduce costs [1].

55

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

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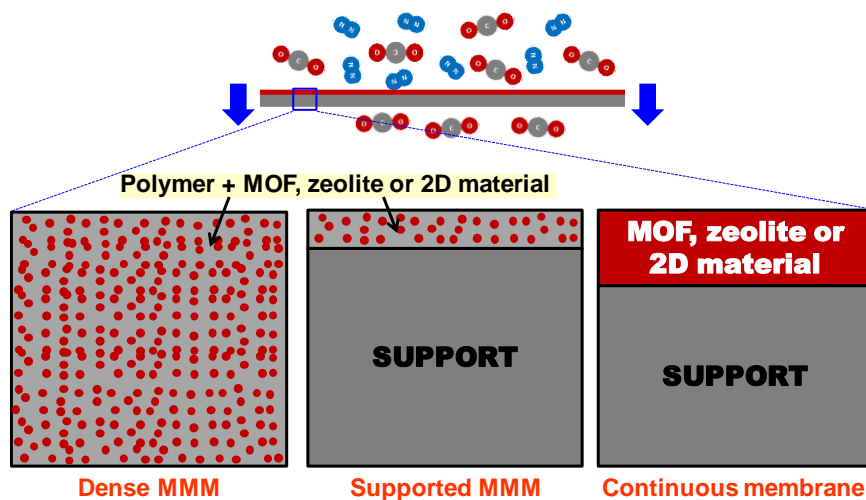
70 To improve the performance of gas separation membranes, nanoporous
71 inorganic materials (e.g., zeolites, metal-organic frameworks or MOFs, and
72 nanoporous two-dimensional materials) have been extensively investigated [8–
73 11]. These materials with high porosity and thermal, chemical and mechanical
74 robustness but mainly with pores in the range of sizes of common gas molecules
75 can carry out molecular separations based on the relative size difference and



76 adsorption affinity [12]. Besides their implementation as TFC membranes where
77 a thin polycrystalline film acts as a selective layer, these materials can also be
78 used as selective fillers for a target application, constituting the so-called mixed
79 matrix membranes (MMMs), or when prepared as a thin film on a proper porous
80 support, thin film nanocomposite membranes (TFN)[13]. These filler-polymer
81 combinations could overcome the main limitations of the existing membrane
82 technologies [14]: permeance-selectivity trade-off still far from commercial
83 applicability, membrane reliability and long-term realistic operation. However,
84 most of the reviews published, which timely report the current state of the art of
85 membranes for gas separation, lack in revealing the drawbacks and challenges
86 in the commercialization of membranes containing nanofillers (mainly zeolites,
87 MOFs and 2D materials) for possible application at the industrial scale for H₂ and
88 CO₂ separation. Therefore, this review examines the contribution of nanoporous
89 materials to constitute membranes for the separation of energy-relevant gas
90 mixtures. The main families of such materials are presented together with the
91 limitations and possible improvements of the current membrane systems
92 regarding their implementation in large-scale and more practical applications.
93 Additionally, we declare the membrane requirements, membrane module
94 configurations and the most suggested configuration (like hollow fibers) for these
95 gas separation applications, giving an overview of the hybrid membrane concepts
96 adapted in hollow fibers for the separation of CO₂ and H₂-containing mixtures.

97





98

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

103

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

105 *2.1. Opportunities of zeolites/MOFs for gas separation*

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

114

115 The pore size of zeolite/MOF membranes is mainly determined by the framework
116 structure. It can also be fine-tuned through ion exchange and surface modification
117 [16]. The hybrid inorganic/organic MOF structures are much more diverse and
118 easier for surface modification. Furthermore, the permanent porosity and the rigid
119 framework structure can avoid the undesirable aging and plasticization effects
120 observed for polymers [6]. Compared to MOF membranes, zeolite membranes
121 are more stable in high temperatures, more resistant to organic solvents, and
122 more robust in harsh conditions, providing unique opportunities for system
123 integration with reactions to form innovative membrane reactors [17]. Recently,
124 significant progress has also been achieved in preparing ultrathin zeolite/MOF
125 membranes from their 2D nanosheets and further improving their membrane flux
126 [18,19]. For example, ultrathin (<50 nm) zeolite (SAPO-34) nanosheets seeding
127 layer allows the production of defect-free zeolite nanofilms (500–800 nm), which
128 displayed an exceptional orientation and facilitated transport [20]. The
129 performance was calculated as CO₂ permeance of $\approx 1.0 \times 10^{-5}$ mol (m² s Pa)⁻¹,
130 together with high CO₂/CH₄ and CO₂/N₂ selectivity of 135 and 41, respectively, in
131 equimolar binary mixtures at room temperature. Thin membranes based on
132 lamellar SAPO-34 zeolite nanosheets were also effective in separating
133 CO₂/CH₄ (selectivity=102) with a permeance of 2.5×10^{-6} mol (m² s Pa)⁻¹
134 (approximately 7500 GPU) [21].

135
136 **Fig. 2** shows H₂/CO₂ and CO₂/N₂ separation performance from the state-of-the-
137 art zeolite/MOF membranes and their comparisons with the upper bound of
138 polymeric membranes. As can be seen, zeolite/MOF membranes have had great
139 success for the separation of H₂/CO₂ but much less for CO₂/N₂ when compared

140 with polymer membranes. The reason is that in the H₂/CO₂ system the two
141 transport properties that determine the membrane performance – diffusion and
142 adsorption – often have opposite effects. That is, diffusion favours hydrogen
143 because of its smaller kinetic size, but adsorption prefers CO₂ because of its
144 higher quadrupole moment. Hence, to achieve a good H₂/CO₂ selectivity, the
145 diffusion selectivity must be high. As said, zeolite/MOF membranes have a
146 significant advantage over polymeric membranes in molecular sieving.

147 In contrast, in the system of CO₂/N₂, both diffusion and adsorption facilitate the
148 transport of CO₂. Polymers can be easily grafted with a high density of functional
149 groups to enhance CO₂ adsorption and thus can achieve comparable
150 performance to zeolite/MOF membranes. In certain conditions when the CO₂
151 affinity is strong and the temperature is low, CO₂ may condense inside the pores
152 due to the capillary condensation effect. This blocks the transport of other gases
153 and turns the membrane to be CO₂ selective. Most of the membranes that work
154 well for CO₂/N₂ are also suitable for CO₂/CH₄, and the selectivity is typically higher
155 because CH₄ has a larger molecular size than N₂ [22], e.g., face-centred cubic
156 (fcc)-MOF/polymer hybrid membranes have exhibited exceptional separation
157 performance for energy-intensive separations considering distinct gas pairs,
158 including H₂/CH₄, CO₂/N₂, CO₂/CH₄ and N₂/CH₄ [23].

159

160 Despite not yet reaching the same success as for H₂/CO₂ separation, MOF
161 membranes still hold a great potential to separate CO₂/N₂. One way is to tune the
162 pore size to enhance the molecular sieving. In this sense, the exploration of new
163 MOF building blocks and different topological connections should be beneficial.
164 Another way is to improve the density of functional groups inside the MOF

165 channels to increase CO₂ adsorption. When looking at the history of zeolite
166 development, most stable zeolites were discovered in the early stage. This is not
167 surprising because zeolite synthesis is a dynamic process that tends to form the
168 most thermodynamically stable state. This trend may also apply to MOF
169 development and the MOF research community has grown to a substantial mass,
170 but most of the reported MOF systems can hardly pass the stability criteria for
171 practical applications [24]. Hence, starting from the stable MOF systems and
172 conducting surface modification should be more efficient.

173

174 *2.2. Challenges in commercialization*

175 Membrane selectivity and permeance, membrane fabrication cost, long-term
176 stability and process reproducibility determine the commercialization potential of
177 a membrane system. The required selectivity is a process parameter that is
178 determined by the separation task. It is also the main parameter that determines
179 the process energy consumption. The higher the selectivity, the **lower the** energy
180 consumption. Membrane permeance and fabrication cost determine the capital
181 cost. **Higher** membrane permeance implies less membrane area, and thus can
182 tolerate higher fabrication cost. **For CO₂/N₂ separation, a selectivity of 30 and a**
183 **permeance of 1000 GPU are the estimated polymeric membrane performances**
184 **to make the process economically viable [25].** The fabrication cost of MOF/zeolite
185 membranes **is** so far orders of magnitude higher than that of polymeric
186 membranes. Hence, an equivalent improvement in permeance is required to
187 make the process competitive. The membrane lifetime is another critical factor to
188 determine the membrane cost. A typical lifetime is two years. The process
189 reproducibility is a key parameter for product yield and quality control.



190

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

211

212 The process reproducibility of most zeolite and MOF membranes is still far below
213 the satisfactory level. One of the major reasons is the presence of defects within
214 the fabricated membranes. For zeolite membranes, most of the defects are



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

231

232 The commercialization of zeolite/MOF membranes will be also affected by the
233 supports' geometry as it will subsequently determine the type of membrane
234 modules. Most of the reported zeolite/MOF membranes in the academic literature
235 are prepared on flat sheet supports because of their easy availability. However,
236 all the commercial zeolite membranes so far are prepared on tubular supports.
237 Tubular supports are more robust under pressure, easy to scale up and clean,
238 but they are also very expensive (> 300 USD/m²) and have a low packing density
239 (30~50 m²/m³). Compared to tubular supports, hollow fibers (HFs) share a similar



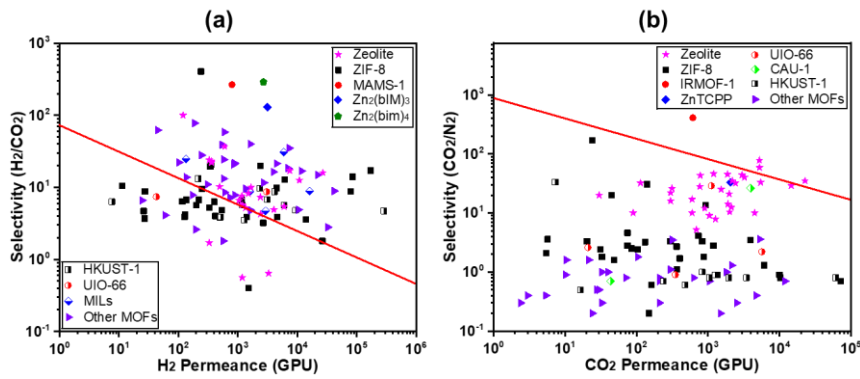
240 geometry but have a much higher packing density (see section 5), thus potentially
241 reducing the overall cost substantially. Hence, future studies should focus more
242 on how to integrate the membrane fabrication process more effectively with HF
243 supports.

244 So far, there is no zeolite/MOF membrane commercialized for gas separations,
245 but a number of zeolite membranes are on the commercialization roadmap,
246 including those with the LTA, MFI, FAU, CHA, and DDR structures [33]. The most
247 promising MOF membranes for commercialization are ZIF-8 and UiO-66
248 membranes, primarily because they are so far the most stable MOF structures
249 [34]. Moreover, ZIF-8 is made from low-cost precursors and so has a cost
250 advantage over many other MOFs. Many economical and simple membrane
251 fabrication approaches have been developed, such as counter diffusion [35] and
252 electrical field-induced growth [36–38] under the aqueous solutions. However,
253 the process reproducibility is still low and the mechanical stability under the
254 industrially relevant pressures (> 15 bar) has not been demonstrated.

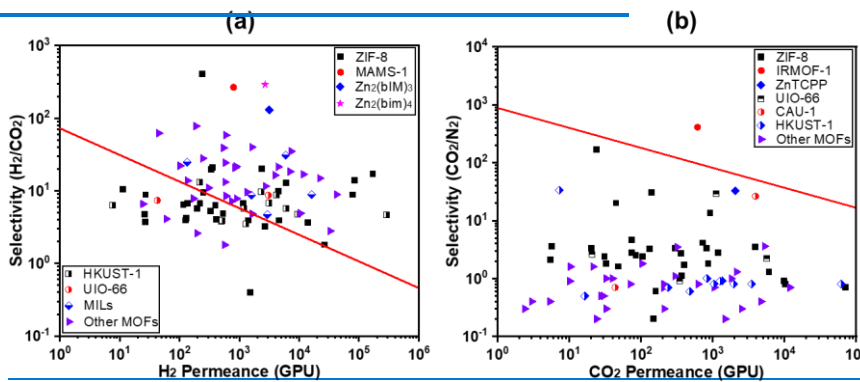
255

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





264



265

266 **Fig 2.** Separation performances of zeolite/MOF membranes and their
 267 comparisons with the upper bound of polymer membranes. (a) For H₂/CO₂ and
 268 (b) for CO₂/N₂. The red lines in the diagram represent the upper bound of
 269 polymeric membranes, where a membrane thickness of 100 nm is used to
 270 convert the permeance from the permeability database of polymeric gas
 271 separation membranes [40]. The data points of zeolite/MOF membranes are
 272 adapted from Ref.[41]

273

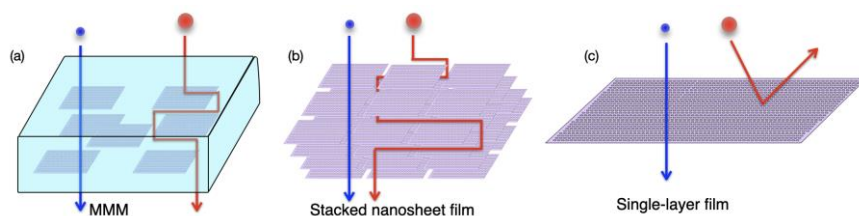
274 **3. 2D nanoporous materials for gas separation membranes**

275 *3.1. Opportunities of 2D materials for gas separation*

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276 Nanoporous materials with a 2D morphology have the unique potential to
277 constitute the thinnest selective layers ever imagined, down to the thickness of
278 an atom, and therefore, can maximize the permselective gas flux reducing the
279 needed membrane area and associated capital cost. Three distinct designs for
280 selective layers can be achieved (**Fig. 3**): MMM where 2D materials constitute an
281 ideal filler in a polymer matrix; stacked nanosheet membranes; and single-layer
282 2D film.

283



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

289

290 MMM prepared using nanoporous 2D nanosheets are extremely attractive due to
291 the high aspect ratio and nanoscale thickness of the nanosheets. This is because
292 a preferential orientation of the nanosheets in the matrix can be obtained, filler
293 loading in the matrix can be maximized, and the overall film thickness can be
294 minimized. The emergence of nanoporous 2D materials with high interphase
295 compatibility with polymer (MOFs [42], g-C₃N₄ [43], covalent organic frameworks
296 [44], etc.) have led to MMM yielding improved separation performances
297 compared to the upper bound for polymeric materials. While membranes based

298 on stacked 2D nanosheet films as the selective layer offer performance
299 advantages over nanosheet-based MMM. The stacked nanosheet film offers a
300 nanoporous pathway across the entire selective layer, improving the diffusivity of
301 the gas molecules.

302

303 Oriented nanosheet films can be achieved by a scalable technique such as
304 filtration on a porous support, and the film thickness can be easily regulated by
305 the amount of suspension. The separation performance from the stacked
306 nanosheet film is determined by the interplay between two transport pathways;
307 one constituted by the nanosheet porosity and the other by the intersheet or
308 packing gap between the nanosheets. This gap needs to be small enough to not
309 become the primary transport pathway but also large enough so that the pore
310 openings of the nanosheets are not blocked in the turbostatically-stacked film.
311 Approaches modulating the gap, e.g., hot drop coating and reactive condensation
312 of the nanosheets have yielded promising H₂/CO₂ separation performance from
313 MOF nanosheets [18] and more recently from zeolite nanosheets [19].
314 Impervious nanosheets, such as graphene oxide [45] and MXenes [46], have also
315 shown promising performance from their stacked films where gas transport takes
316 place through the intersheet gap. For example, graphene oxide nanosheets
317 assembled into laminar structures have displayed fast and CO₂ selective
318 transport channels (CO₂/N₂: 91), along with exceptional operational stability [47].
319 Unfortunately, the intersheet gap and the gas transport in these films are sensitive
320 to operating conditions including feed pressure and humidity [48,49], affecting the
321 separation performance.



322 Synthesis of 2D nanosheets hosting CO₂-sieving nanopores will allow the
323 realization of high-performance MMMs for CO₂ separation. A potential pathway
324 is **the** exfoliation of a suitable layered precursor, such as zeolite hosting **an** 8-
325 membered silicate ring. Layered SAPO-34 has been recently reported [21].
326 Recently, synthesis of 20-nm-thick SAPO-34 nanosheets have been also
327 reported [20]. Layered SAPO-34 has been recently reported [21], including its
328 exfoliation to single-layer sheets [20]. Another promising material for this is
329 ordered *g*-C₃N₄ such as poly(triazine imide) (PTI) which hosts 3.4 Å pores.
330 Recently, PTI nanosheets have been prepared **as** single-layer nanosheets [43],
331 however, the lateral size of exfoliated nanosheets was small (<50 nm), and the
332 yield of exfoliated nanosheets was low. Synthesis of high-aspect-ratio *g*-C₃N₄
333 nanosheets with high yield would be highly beneficial in this respect.

334

335 Macroscopically-large 2D films, such as graphene and analogues, can be used
336 to fabricate membranes with a selective layer that is just one atom thick. When a
337 high density of gas-sieving pores **is** incorporated in graphene, extremely large
338 permselective gas flux can be realized [50]. Molecular simulations predict
339 permselective CO₂ permeance in the range of 10000-100000 GPU [51]. A CO₂
340 permeance of 10000 GPU has been recently demonstrated in combination with
341 an attractive CO₂/N₂ selectivity (>20)[51,52]. This is mainly because of the
342 extremely short diffusion **path length** of gases across the atom-thick pores of
343 graphene [53]. Gas sieving can be obtained from nanopores hosting electron
344 density gap comparable to that of the target gas molecules. For such nanopores,
345 the flux of gas molecules can be modelled using the transition state theory and is
346 determined by the energy barrier experienced by the molecule while crossing the

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

349

350 There are three key challenges in developing size-sieving nanoporous graphene
351 membranes: angstrom-scale pores have to be created with dimensions able to
352 sieve the desired components (e.g., CO₂ or H₂); pore creation technique has to
353 be precise to yield a narrow pore size distribution avoiding large nonselective
354 pores; and the density of gas-permeable pores should be high enough (>0.1%)
355 to outperform the conventional membranes. Meeting these requirements would
356 realize membranes, which are highly permeable but also selective, overcoming
357 the selectivity-permeability trade-off of conventional polymeric membranes. This
358 will require the development of synthetic approaches where pore nucleation and
359 expansion can be controlled, e.g., down to the removal of 10-16 carbon atoms
360 per pore in the case of graphene for H₂- and CO₂-sieving [52].

361

362 The control of pore density (nucleation) and size (expansion), permitting
363 maximization of gas flux and gas pair selectivity, will be highly beneficial. For
364 CO₂/N₂ separation, exploiting the higher adsorption affinity of CO₂ by
365 functionalizing with CO₂-philic groups is an attractive approach [55,56]. Although
366 the field is in its infancy, attractive separation performance has been
367 demonstrated for applications where large permeance is desired along with a
368 moderate selectivity, e.g., post-combustion carbon capture. For instance,
369 nanoporous graphene membranes prepared by controlled pore formation and/or
370 functionalization have yielded CO₂ permeances of 10000 GPU along with an
371 attractive CO₂/N₂ selectivity (above 20)[57]. Advances on the fundamental fronts



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

375

376 *3.2. Challenges in commercialization*

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

386

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



396 \$/m². Alternatively, methodologies allowing the reuse of the foil for several rounds
397 of synthesis can cut down the effective cost of foil.

398

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

413

414 From a membrane fabrication perspective, a crucial challenge is to develop
415 methods for transferring the graphene film onto a porous support without inducing
416 cracks or tears in the film. CVD graphene is synthesized on a substrate, and the
417 transfer of graphene involves its isolation from the growth substrate. The
418 mechanical stress generated during the isolation step is often high enough to
419 generate macroscopic cracks in graphene, which deteriorates gas pair selectivity.
420 Recently, crack-free centimeter-scale graphene membranes have been

421 demonstrated by permanently reinforcing graphene with a gas-permeable layer,
422 such as nanoporous carbon film [64], carbon nanotube film [65] and dense
423 polymer films [52]. However, these methods require further improvement for the
424 preparation of graphene membranes on low-cost and flexible support, such as
425 those used for the preparation of polymeric TFC membranes.

426

427 **4. Current technical limitations of asymmetric membranes presenting a** 428 **selective layer with nanoporous materials**

429 *4.1. Asymmetric membranes for gas separation*

430 In general, dense and thick polymeric membranes with no porous structure are
431 mostly applied for characterization purposes or to test new membrane materials.
432 Their single-gas permeability and ideal selectivity for a given mixture can be
433 obtained with the so-called time lag system with the advantage of allowing the
434 estimation of diffusivity and solubility parameters of the membrane [66]. However,
435 this experimental setup is not very realistic, as in real-world applications mixtures
436 of gases are used, including minor components such as moisture or H₂S,
437 depending on the origin of the stream to be treated.

438

439 Instead, asymmetric membranes with a selective skin layer on top of a
440 mechanically stable support constitute the perfect membrane structure, and one
441 which could be ideal for commercial applications. The advantage of asymmetric
442 membranes is that transport resistance is minimised and fabrication costs are
443 reduced by using the minimum amount of selective material. This type of
444 membrane supposes two in-series resistances to the gas transport and the
445 contribution of the support has to be minimum so as not to penalize the function



446 of the selective film [67]. As a consequence, the porosity of the support has to be
447 as high as possible while providing an adequate activated surface to favour the
448 deposition of the ultrathin film by certain coating techniques [2].

449

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

461

462 *4.2. Limitation of support*

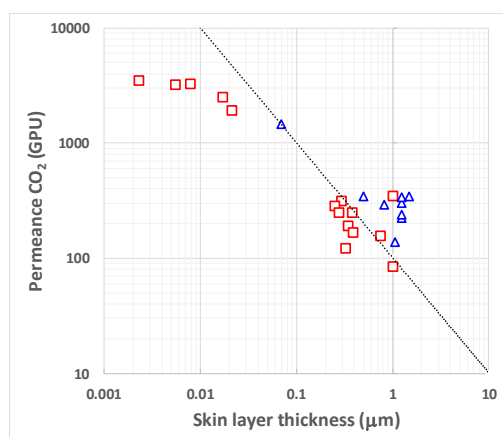
463 In addition to conferring mechanical stability to the membrane, the support, in
464 series with the skin layer, should minimally restrict the membrane transport. As
465 an example, PEBA (poly (ether-block-amide)) type polymers, commercialized as
466 Pebax[®], are some of the most studied skin layers for CO₂ selective membranes.

467

468 **Fig. 4** illustrates the expected effect of the membrane thickness on the
469 permeance for elastomeric Pebax[®] 1657 membranes. From nine relevant
470 studies, an average CO₂ permeability of 101±34 Barrer was obtained for Pebax[®]



471 1657 thick dense membranes (corresponding to CO₂/N₂ selectivities in the 36-89
472 range) [67,70–77]. The dotted line of negative slope is the calculation of
473 permeance as a function of skin layer thickness from the value of 101 Barrer
474 (dividing permeability by membrane thickness), implying negligible resistances
475 from the support and gutter layer. Even if gas separation supports are highly
476 permeable (ca. 200,000 GPU of CO₂) [78,79], in practice, the TFC membranes
477 of only Pebax® 1657 (red squares) exhibit lower permeances than expected due
478 to the negative contributions of both the support and the gutter layer. The
479 deviation augments with decreasing selective layer thickness. The blue triangles
480 in the plot correspond to Pebax® 1657 based MMMs, always with permeances
481 above the expected, in line with the capacity of fillers to enhance the permeation
482 of such membranes [80]. From this plot, we can conclude that as the skin layer
483 thickness goes down to the nanometer dimension, the resistance of the support
484 becomes more relevant suggesting its improvement in terms of porosity,
485 thickness and mechanical strength. Moreover, MMMs can enhance the
486 permeance beyond the thickness-related value.



487



488 **Fig. 4.** CO₂ permeance as a function of the thickness of the Pebax® 1657
489 selective layer for different TFC membranes. The dotted line was obtained from
490 the average of the permeabilities of nine different dense membranes [67,70–77].
491 The red squares and blue triangles correspond, respectively, to bare polymer
492 [67,81–85] and to filler modified [69,85–87] TFC membranes of different
493 **thicknesses**. These membranes are known as TFN membranes, i.e. TFC
494 membranes incorporating porous particles. When the membrane thickness is 1
495 μm, a permeance of 1 GPU (1 GPU= 1·10⁻⁶ cm³(STP)·cm⁻²·cmHg⁻¹·s⁻¹)
496 corresponds to a permeability of 1 Barrer.

497

498 *4.3. Further developments in gutter layer and support*

499 The highest permeance gas separation membrane ever reported, with 40,000
500 GPU of CO₂ and 10-12 CO₂/N₂ selectivity, was made of PDMS [79]. **This**
501 **membrane was 34 nm thick and prepared onto a glass substrate by spin coating,**
502 **which was later detached using ethanol and thus transferred onto highly**
503 **permeable PAN (polyacrylonitrile) ultrafiltration support; in this way, it was**
504 **avoided the use of a gutter layer and the possible penetration of the PDMS within**
505 **the substrate pores**. Indeed, to extract the maximum performance of the selective
506 layer, the resistances of the gutter layer and support have to be as negligible as
507 possible.

508

509 The typical approach is to fill the support porosity with some liquid to avoid the
510 penetration of the gutter material [78,88], but there are other interesting
511 approaches such as the use of sacrificial gutter layers [67,89]. In this case, the
512 sacrificial material should be removed without altering either the membrane

513 separation properties or its attachment to the support. The PDMS membrane
514 mentioned previously with the 40,000 GPU CO₂ permeance was first prepared
515 by spin coating on a sacrifice layer of poly(4-hydroxystyrene)[79]. This was
516 dissolved in ethanol and then the PDMS transferred to a PAN support maintaining
517 its shape and mechanical strength. Even if it is true that the extrapolation of this
518 methodology to a scalable industrial procedure and with more selective polymers
519 than PDMS (this is more a gutter layer material than a desirable selective
520 polymer, at least for CO₂ separation) may not be immediate, these results are
521 quite encouraging. In fact, with this principle, a 70 nm thick polyetheramine-
522 graphene oxide Pebax 1657 membrane has been prepared on a 75 nm thick
523 PDMS gutter layer showing a CO₂ permeance of 1455 GPU together with a
524 CO₂/N₂ selectivity of 68.1 [69]. In addition, one of the most promising membranes
525 for CO₂ separation is the Polaris™ one, made of a proprietary polymer presenting
526 a gutter layer strategy and commercialized by Membrane Technology and
527 Research, Inc., with up to 2000 GPU of CO₂ and CO₂/N₂ selectivity of 50 [90,91].

528

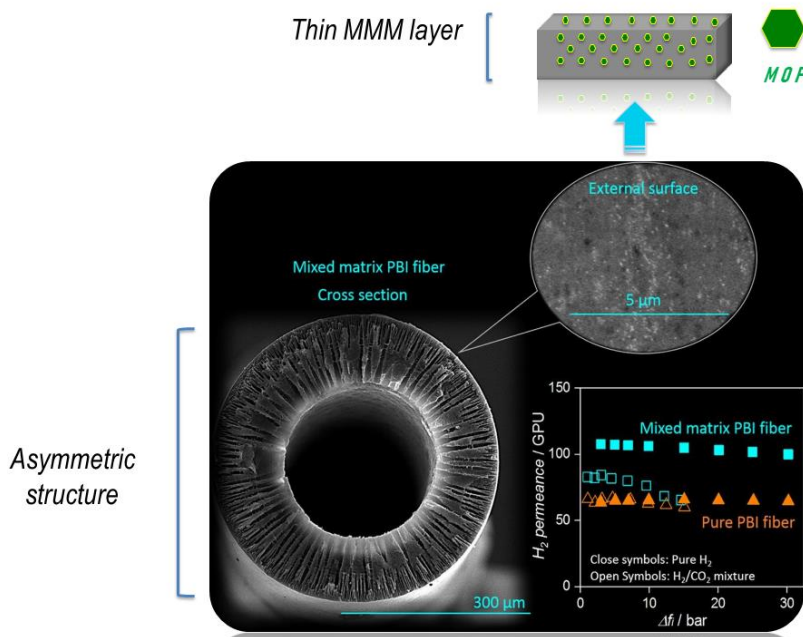
529 **5. Membrane configurations and process requirements**

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



538

539



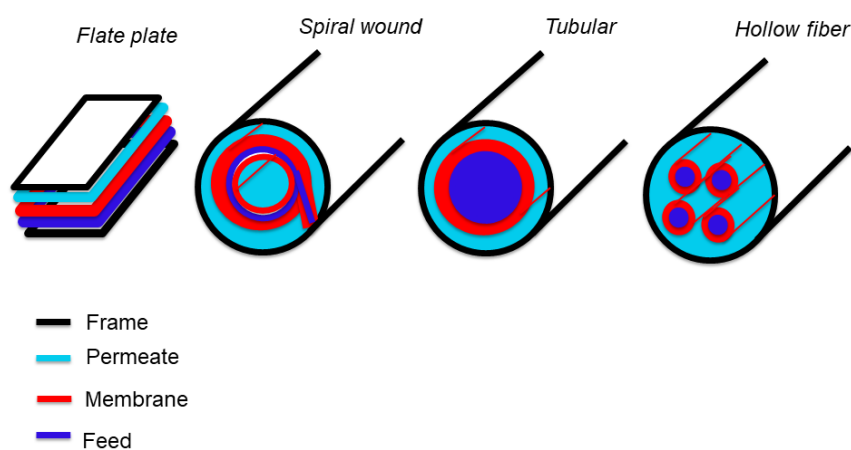
540

541 **Fig. 5.** Composite hollow fibre membranes for gas separation. Cross-section view
542 of polybenzimidazole-10 wt.% ZIF-8 mixed matrix asymmetric hollow fibre for
543 H₂/CO₂ separation [92].

544

545 Asymmetric membranes can be manufactured in a flat or a HF geometry and then
546 packed into modules to reach high **productivity** for industrial applications. **Fig. 6**
547 graphically illustrates the types of membrane module configurations, which
548 typically refer to the geometry of the membrane and its position in space in
549 relation to the flow of the feed fluid and of the permeate. HF [93] and spiral wound
550 [87] are the membrane configurations providing the highest values of
551 intensification in terms of membrane area per module volume (i.e., packing

552 density). HF modules stand out as the most preferred due to their high packing
553 density, varying from 500 up to 9000 m² m⁻³, exceeding the reported densities for
554 spiral-wound modules (ca. 1200 m² m⁻³) and plate and frame modules (ca. 100–
555 400 m² m⁻³) [94]. HF membranes also have the benefit of being able to handle
556 extremely high transmembrane pressure difference (approximately 70 bar), while
557 the fabrication cost is around 5–20 times lower than the equivalent for spiral
558 wound modules [95].



559
560 **Fig. 6.** Graphical depiction of the four types of membrane configurations.

561
562 Most commercially available membranes are manufactured as HF modules, while
563 less than 20% correspond to spiral wound modules. Both are most suitable for
564 gas separation applications [96], as they are relatively less prone to membrane
565 fouling than flat sheet or tubular modules. In general, HF modules experience
566 25% more membrane surface shears promoting hydrodynamic pattern changes
567 which consequently mitigate the deposition of foulants, e.g., when operating HF
568 modules in cross-flow filtration mode, shear forces on the membrane occur
569 thanks to bubbling, vibration, or particle scouring [97]. However, in the case of

570 HF modules, the feed gas requires further pre-treatment to mitigate severe fouling
571 and plasticization, depending on the type of material. As for spiral wound
572 modules, apart from being more resistant to plasticization, can be applied to a
573 wider range of membrane materials compared with HFs [95]. To date, few spiral
574 wound membranes for gas separation (at least for CO₂ and H₂-containing
575 mixtures) have been documented [98–100].

576

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

584

585 Forming ultrathin membranes into HF modules is an ongoing research challenge,
586 but they still represent a promising way for efficient gas separation with scalable
587 productivity and less economic expenditure [96]. Various ultrathin composite HF
588 membranes for CO₂/H₂ separation have been successfully synthesized at lab
589 scale (Table 1). MOFs (such as ZIF-8, Cu₃(BTC)₂, MIL-53 and UiO-66-NH₂) are the
590 most reported nanoporous fillers in composite HF fabrication due to their physical
591 and chemical compatibility with polymer phases; however, such membrane
592 modules are limited to small membrane sizes of 10-48 cm length.

593

594



Table 1. Various hollow fibre (HF) membrane concepts aimed at separating CO₂ and H₂ containing mixtures.

<i>Composition</i>	<i>Type of HF</i>	<i>Membrane/module size</i>	<i>Gas mixture</i>	<i>Operating conditions</i>	<i>Permeance in GPU (of faster gas)</i>	<i>Selectivity</i>	<i>Reference</i>
ZIF-8/Uitem®	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 composite	film 10 fibers/ 10 cm length each	CO ₂ /N ₂	25 °C, 2 bar	791	40	[108]
PDMS/PAN	Thin composite	film 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/Si₃N₄	Ceramic	1 fiber/ 10 cm length	H ₂ /CO ₂	25 °C, 2.5 bar	2505	11.7	[112]
PDMS-	Asymmetric	1 fiber/ 15 cm length	CO ₂ /N ₂	25 °C, 5 bar	109	31	[113]
Cu₃(BTC)₂/PSf							
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-NH₂/PP	Mixed matrix	1 fiber/ 7-10 cm length	CO ₂ /N ₂	25 °C, 2 bar	26	37	[116]

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



599 Depending on the type of polymer (or dope solution composition) and preparation
600 protocol, polymer composite HFs can display high permeation rates in gas
601 separation performance. This is the case of PDMS/PAN thin composite, which
602 has shown up to 5000 GPU permeance in CO₂/N₂ mixtures [109], while
603 PIM/PDMS/PAN HFs displayed 483 GPU (with selectivity values of 22.5) towards
604 similar gas mixture [115]. In this HF, a cross-linked PDMS gutter layer was
605 introduced between the PIM selective layer and the PAN substrate, which was
606 able to mitigate the detrimental solvent effects during the dip coating, permit PIM
607 to adhere to it, and redistribute the gas transport across the membranes.

608

609 Compared with such HFs, PDMS–Cu₃(BTC)₂/PSf [113] and PEI/aminosilane
610 functionalized MIL-53 [114] HFs offered better performance with CO₂/N₂
611 selectivities of 31 and 34.7, respectively, but with a decreased CO₂ permeance.
612 ZIF-8 filled polyetherimide (Ultem® 1000) matrix was subsequently utilized for the
613 fabrication of dual-layer asymmetric HF membranes via the dry jet-wet quench
614 method [104]. The resulting MMM HFs showed a 20% increased permeance in
615 CO₂/N₂ testing compared with the pristine HFs. In this regard, these few
616 examples evidence that the involvement of inorganic materials, like MOFs, with
617 superior gas molecular sieving nature, can enhance the CO₂/N₂ separation
618 performance of polymer membranes [18]. Similarly, specific MOFs can be
619 adapted in HFs presenting polymer or inorganic membrane supports for H₂/CO₂
620 mixture separation. For instance, ZIF-8 has contributed to a 65% increase in H₂
621 permeance at constant ideal selectivity in PBI HFs. Unlike pristine PBI HFs, filler
622 incorporation into the PBI matrix contributed to a substantial increase in H₂
623 permeance from 65 GPU to 107 GPU, while the ideal H₂/CO₂ selectivity remained



624 unchanged (ca. 18)[92]. Knowing the great advantages of ceramic materials in
625 terms of high thermal and chemical stability in harsh environments, they have
626 started to be applied as HF supports. As an example, ZIF-8 supported on silicon
627 nitride ceramic HF exhibited improved permeation as high as 2,505 GPU, with
628 H₂/CO₂ selectivity of 7.3 [112].

629 To date, most advances in composite polymer-based membranes containing
630 either MOFs or zeolites have relied on the fabrication of flat sheet membranes,
631 which have exhibited impressive performance surpassing polymer upper bound
632 performance, e.g., MMMs based on ZIF-300 filled PEBA [117]. This is a result of
633 engineered designs of the polymer and inorganic phases. Unfortunately, there is
634 still limited research on HF membranes but studies show that they represent the
635 most prominent membrane configuration for separating CO₂ and H₂-containing
636 mixtures (see **Table 1**), at least in H₂/CO₂ and CO₂/N₂ mixture separations with
637 scalable performances for possible industrial purposes [96]. Certainly, several
638 factors should be considered when tailoring a HF membrane, such as inorganic
639 and organic (i.e., polymer) phase properties, along with their compatibility with
640 each other.

641 To some extent, the dope solution composition has a fundamental and decisive
642 impact on the morphology and structure of prepared membranes and thus on gas
643 separation performance. Therefore, particular emphasis must be placed on the
644 fabrication parameters[118]; for instance, the dry-jet wet spinning process stands
645 out as the most used method for HF preparation, where several variables, such
646 as bore fluid composition, flow rates of dope and bore fluids, and air gap, are
647 essential to obtain defect-free membranes. However, as for the selection of
648 membrane material (both the support and the selective layer), the presence of

649 humidity and impurities (e.g., H₂S)[88], as well as operating temperature and
650 pressure, are also important for targeted separations.

651

652 Since most industrial separations demand large membrane areas (ca. 1000 –
653 millions m²), the major challenge impeding the industrialization of new membrane
654 materials in HF configurations lies in producing membranes in a large quantity
655 with high permeance and selectivity at a reasonable cost [119]. **Table 1** reports
656 successful examples of new composite membranes in small HF modules;
657 however, there is no report in which any of those membranes have been
658 extrapolated to a **large scale**. Developing scalable methods to obtain reproducible
659 permeance and selectivity in large HFs thus still remains highly challenging.

660

661 **6. Conclusions and outlook**

662 Current and future energy production processes involve **the** separation of CO₂
663 and H₂-containing mixtures. In this context, membrane technology seems to be
664 the most suitable approach from the point of view of process simplicity, cost and
665 sustainability. Besides, membranes based on or modified with nanoporous
666 materials have demonstrated very good performance when separating CO₂/N₂,
667 CO₂/CH₄ and H₂/CO₂ energy-related mixtures. Nevertheless, **some limitations**
668 **still remain to achieving the industrialization of membranes in this field, even if**
669 **selectivity-permeance upper bounds have been surpassed with the help of many**
670 **nanoporous materials.**

671

672 For 2D materials, such as nanoporous graphene, control of pore size and porosity
673 can still be enhanced by **an** improved mechanistic understanding of pore



674 incorporation. The thickness decrease in the selective membrane skin layer
675 would overcome issues like membrane activation and even the cost of relatively
676 expensive nanoporous materials. However, large-scale, effective methods for
677 transferring 2D films to porous supports without incurring defect formation are
678 needed.

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

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

691

692 ***Recommendations for the researchers in the field***

693 For a possible real application, the gas mixtures must present contaminants (e.g.,
694 H₂S, CO), water and other gases, which strongly affect the membrane
695 performance [120]; e.g., CO₂ and N₂ permeability can decrease as water
696 occupies free volume in polymer membranes, while the N₂ permeability could
697 increase in the presence of H₂S by improving the N₂ solubility or diffusion within
698 specific polymers (e.g., PDMS) [120].



699 To date, most of the research has been done at a lab-scale, therefore, there is a
700 need of extrapolating the performance to a larger scale (e.g., pilot scale), this is
701 related to finding scalable fabrication methods with reproducibility in membrane
702 performance. This may also imply the handling of operating conditions for better
703 performance. For example, as for CO₂ separations, feed CO₂ concentration
704 influence the separation performance (particularly gas flux) since there is different
705 CO₂ partial pressure across the membrane.

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

712

713

714

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