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# Membranes for $CO_2$ Capture and Separation: Progress in Research and Development for Industrial Applications

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$CO_2$ separation; carbon capture; membrane technology; membrane process; industrial application

## Abstract:

Industry interest in $CO_2$ capture and separation has grown almost exponentially over the past decades. This paper aims to promote membrane technology as a viable solution for this application and provide a reference for the industry seeking efficient $CO_2$ separation solutions. First, a brief summary of the basics of membrane material, effects of transport mechanisms, module configurations, and the separation conditions is presented as the basis for the discussion. Then, the latest advances in $CO_2$ separation membranes and processes in the context of industrial applications are outlined. Finally, challenges and gaps that hinder the implementation of membrane technology and future directions for membrane development from laboratory to industry are discussed.

**Highlights:**

* Progress in membranes for $CO_2$ capture and separation has been thoroughly reviewed;

* Membrane materials for $CO_2$ separation has been summarized;

* Industrial application of $CO_2$ separation membranes has been discussed;

* Future development of $CO_2$ separation membranes materials and membrane processes have been proposed.

**TOC:**

## 1. Introduction

Scientific evidence shows that the ever-growing greenhouse gas (GHG) emissions are irreversibly affecting the global climate, and the rate of change is accelerating. Except for apparently disappearing glaciers and ice caps, the world is witnessing more extreme weather, severe droughts, strong tropical cyclones, and frequent wildfires. Immediate actions are needed to reduce global GHG emissions and effectively mitigate the intensification of climate change [1, 2].

Carbon dioxide ($CO_2$) is commonly recognized as the dominant GHG, and burning fossil fuels (i.e., coal, oil, natural gas) for energy generation is by far the largest source of $CO_2$ emissions, accounting for nearly half of global $CO_2$ emissions. $CO_2$ emissions from the transport sector have caused almost one-quarter of the $CO_2$ emission worldwide, according to a report by IEA (International Energy Agency) in 2021[3], as indicated in **Figure 1**.

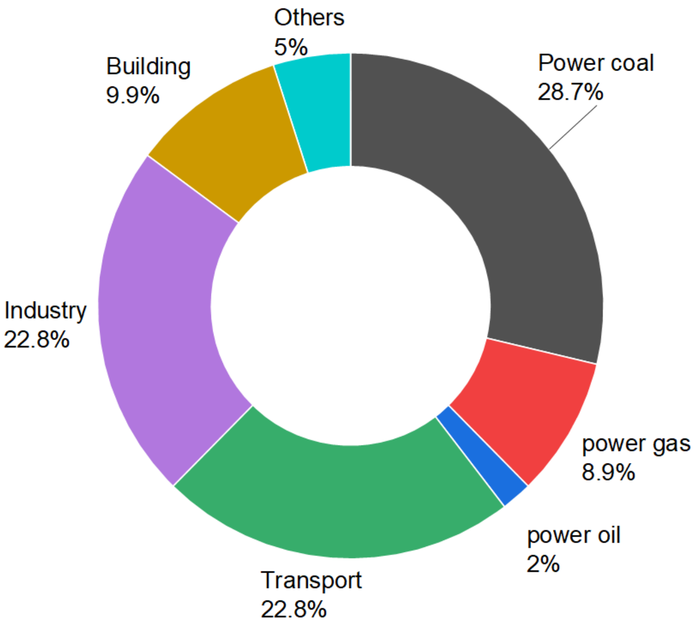

**Figure 1**. $CO_2$ emissions by sectors, reproduced from ref [3]

Over the past few decades, governments and science communities have been diligently tackling the challenges. An international framework has been developed to make laws and implement policies to address common issues, including United Nations Framework Convention on Climate Change (UNFCCC), Kyoto Protocol, and Paris Agreement. They have agreed on emission reduction targets, flexibility mechanisms, the 2-degree Scenario, and the 450 Scenario

[4] and proposed the carbon tax and $CO_2$ emissions credit trading as practical economic management instruments to implement the reduction strategies [5]. The net worth of the global carbon capture and storage market is expected to reach 6.13 × 109 $USD \cdot a^{-1}$ by 2027 [6], implying enormous opportunities for $CO_2$ separation technologies, especially membrane separation, an emerging technology with huge potential and many unexplored fields of applications.

In recent years, several high-quality review articles have been published and presented the research status of $CO_2$ separation membranes from different aspects[7-16], providing in-depth discussion and comprehensive information for researchers and engineers already knowledgeable in membrane separation. However, a critical reference for readers with an engineering background but outside the field is still missing. This paper aims to provide such a reference on $CO_2$ separation membrane systems for a broad readership, including new researchers and non-membrane experts. A research and development (R&D) roadmap is proposed to promote membrane technology for the industry seeking for efficient $CO_2$ separation solutions. As such, this review is presented with particular focus on membranes with industrial potentials, such as commercial membranes and membranes at the development stage close to industrial implementation. As a basis for discussion and to support our opinions, the fundamentals of membrane-based $CO_2$ separation and different aspects of membrane processes that make significant influences on separation results are briefly presented first. Some of the most important representative groups of membrane materials are selected from the literature to demonstrate the membrane improvement approaches and state-of-the-art membrane performances. The progress and advances in research and development of membranes for $CO_2$ capture and separation are also summarized. In addition to this, the contribution of machine learning techniques in the membrane industry is discussed from a big data perspective. Finally, challenges and potentials of membranes for industrial applications are discussed based on the above discussion.

### 1.1 Different sources of $CO_2$ and their separation conditions

As $CO_2$ produced from fossil fuel-based energy generation accounts for the most significant part of GHG emissions, implementing $CO_2$ capture and storage (CCS) in this sector is the most effective to achieve the internationally agreed emission reduction targets [17]. To date, great global efforts have been made to implement CCS in fossil fuel-fired power plants and other large-scale processes that cause large $CO_2$ emissions, such as cement manufacturing, iron and steel making, and oil and gas production. According to scientists, [18] however, the global response has been inadequate given the scale of the climate challenge; some sectors have only been partially or even not yet decarbonized. Therefore, it is essential to take different approaches for different $CO_2$-containing sources based on their compositions and separation conditions, so that the advantages of the capture technologies bring in economic and technical benefits to CCS. It is also critical to make it possible for $CO_2$ separation from sources that are currently overlooked, including those from small emission points in the agriculture and transport sectors[19].

**Table 1.** Representative industrial stationary $CO_2$ emission sources

| Sources | Processes | Common $CO_2$ content | 2nd key component<br>Impurities |
|---|---|---|---|
| Power plant: Post-combustion flue gas | Petroleum power plant | 6-10% | $N_2$<br>$NO_x$, $SO_x$, $O_2$ |
|  | Natural gas power plant | 4-8% |  |
|  | Coal power plant | 10-15% |  |
| Power plant: Pre-combustion | $H_2$ purification | 30-45% | $H_2$<br>CO, $CH_4$ |
| Iron & steel industry | Blast furnace | 20-27% | $N_2$<br>$H_2$, CO, $CO_2$, $H_2S$ |
|  | Basic oxygen Furnace | 16-42% | $N_2$<br>$H_2$, CO, $CO_2$, $H_2S$ |
| Cement industry | Precalciner | ~30% | $N_2$<br>HCs, volatiles ($K_2O$, $Na_2O$, S, Cl) |
|  | calcination | 14-33% |  |
| Natural gas industry | Acid gas removal | 4-20% | $CH_4$<br>$N_2$, $H_2S$, HHC |
| Biogas | Biogas upgrading | 30-50% | $CH_4$<br>$N_2$, $H_2S$, HHC |

**Table 1** presents an overview of the most common $CO_2$ emission sources summarizing gas compositions and typical impurities of selected $CO_2$-contained streams. $CO_2$ from power generation contributes the most to $CO_2$ emission. CCS in this sector is generally through three routes, i.e., oxy-fuel combustion, pre-combustion, and post-combustion [20], depending on where $CO_2$ is removed. The gas compositions and $CO_2$ separation conditions differ significantly in different capture routes, as presented in **Table 1**. Oxy-fuel combustion directly uses high-purity oxygen for combustion and produces high-purity $CO_2$. This route is energy-intensive since a large amount of energy is consumed in separating oxygen from the air [21].

A great example is the Aker Solutions (Norway) Zero Emission Underwater Power Station (ZEUS) [22], which produces electricity by burning natural gas and pure oxygen subsea and injecting the produced $CO_2$ directly back into the well. This route will not be discussed as there is no need to consider $CO_2$ separation. Pre-combustion capture removes $CO_2$ before the combustion, i.e., by converting a fossil-based fuel to syngas (a mixture of $CO_2$, CO, and $H_2$), through the integrated gasification combined cycle (IGCC). $CO_2$ is removed from the syngas, and the hydrogen-rich gas is used for combustion [23], usually for turbines or fuel cells. The advantages of pre-combustion capture include compacted system configuration and relatively low energy consumption for the $CO_2$ separation; the high-concentration $CO_2$ (30-45%) and the elevated pressures of the shifted syngas can provide a high driving force for $CO_2$ separation. The downside of the pre-combustion route is the high capital cost and relatively complicated system of the IGCC process. Recently, bio-hydrogen converted from biomass has been taken as an alternative to syngas, which has similar $CO_2$ concentration but much milder process conditions.

Post-combustion capture is the most applied carbon capture route in fossil fuel-based energy generation today, where $CO_2$ is removed from flue gas after combustion. This approach offers more advantages due to its flexible operation and potential to retrofit existing fossil fuel-based power plants or energy generation steps from large-scale industrial manufacturing sites, such as the cement industry, iron & steel production, and refinery plants. However, the large volume flow of flue gas at near atmospheric pressure and the low $CO_2$ partial pressure lead to a relatively low driving force for the separation.

Except for energy production, cement plants also consume a large amount of fossil fuel in the calcination process ($CaCO_3 \rightarrow CaO + CO_2$); Despite great efforts to improve efficiency, cement production remains the industry with the highest $CO_2$ emissions other than fossil-fuel-based power generation [24]. The iron & steel industry also contributes a considerable amount of $CO_2$ emission in the industry sector as both blast furnaces and basic oxygen furnaces, commonly used in the iron & steel industry, are energy-consuming [25]. Moreover, since the primary carbon input to the steelmaking process is coke utilized in the blast furnace process, as long as carbon is used to remove the oxygen from the iron ore, the overall $CO_2$ emissions reduction is limited.

$CO_2$ emission from the transport sector is also significant, and the ever-growing demand for transportation has intensified the contribution of $CO_2$ emissions from the transport sector with time. For on-road transport, using electric vehicles can shift $CO_2$ emissions from individual vehicles to energy generation by large point sources. However, for maritime conveyance, such as cross-ocean shipping, using batteries or non-fossil fuel as energy suppliers is not yet practical due to the current technical limitations in high-capacity batteries or alternative non-carbon fuels. On board CCS seems a must-have action. According to the International Maritime Organization (IMS) report [26], $CO_2$ capture must be implemented in ships to reach carbon-neutral fuel for maritime vessels and enable the long lifespan of current and planned fossil fuel-powered ships [27, 28].

Natural gas sweetening is the largest industrial $CO_2$ separation application today. $CO_2$ must be removed from raw natural gas to meet pipeline specifications and calorific value standards by natural gas sweetening [29, 30]. Given the large $CO_2$ volume, it is necessary to incorporate the removed $CO_2$ from natural gas sweetening into the CCS value chain. Biogas upgrading is another important $CO_2$ separation application to increase the calorific value of biogas as a qualified fuel. The biogas composition in different sources varies in the ranges of $CO_2$ (30-50%) and $CH_4$ (35-70%) [31]. Biogas is considered a promising renewable energy option and an important approach to achieving negative $CO_2$ emissions if the removed $CO_2$ from biogas is captured for further storage and utilization as part of the CCS value chain.

## 1.2 Technologies for $CO_2$ separation

Technologies for $CO_2$ separation typically include chemical absorption, adsorption, membrane separation, and cryogenic separation. Due to the wide variety of $CO_2$ sources with different $CO_2$ concentrations, properties of other gases, especially the critical 2nd component, and different separation conditions and the requirement of the final products, there is no all-in-one solution for $CO_2$ separation. It is wise to select an optimal technology based on economic and technical evaluations for different separation scenarios or to smartly combine two or more technologies to take advantage and avoid the limitations of individual technologies.

Among the current technologies, chemical absorption has received the most attention and is the most commercialized [32]. Chemical absorption typically involves a solvent which can reversibly react with $CO_2$ that give high $CO_2$ selectivity, for example, by using an aqueous solution of monoethanolamine (aq. MEA). However, chemical absorption has several drawbacks, including large-sized devices (due to the long residence time required) and hence high capital cost, high energy consumption for regenerating absorbents, and potential pollution due to degradation or the losses of solvents [19, 33]. Adsorption is an alternative technology to absorption, where solid adsorbents separate $CO_2$ based on gas-solid interactions. $CO_2$ separation is achieved through varying pressures and/or temperature, i.e., pressure swing adsorption (PSA) or temperature swing adsorption (TSA) [34]. Disadvantages of adsorption include the relatively low capacity (and thus the high recirculating load), high energy consumption for sorbent regeneration, and complicated pre-treatment to remove water vapor. Direct air capture (DAC) of $CO_2$ is also typically based on sorption. But due to the extremely low $CO_2$ concentration levels in the air, chemisorption materials are usually used in DAC processes [35]. DAC is an emerging technology developed to reach "negative emission," or it can be considered compensation for the distributed $CO_2$ emissions not viable to capture, e.g., from the agriculture and transport sectors.

Although the application is scarce, cryogenic separation is an alternative technology for $CO_2$ separation as well. A cryogenic process usually consists of two or three sequential steps of compression, cooling, expansion, and phase separation, where one or more species from the gas mixture, such as $CO_2$, are liquefied by cooling. This technology is often considered energy-intensive due to the use of compressor trains for cooling or high pressures. However, it may be taken as a stage in hybrid processes in combination with other technologies, such as the final step to liquefy $CO_2$ from the membrane process.

Membrane separation is an emerging technology for $CO_2$ separation. Membrane technology has some unique advantages, such as small and light systems, low capital cost, high modularity, and closed-loop. In addition, membrane separation of $CO_2$ requires no chemical additives or consequent potential pollutions and consumes no energy for regenerating solvents or sorbents; thus, it is widely recognized as an environmentally friendly "green" solution for $CO_2$ separation. Another attractive feature of membranes to the industry is the simplicity of the process and linear up-scaling. Moreover, compared with conventional technologies, membrane separation requires less investment and operational cost, especially when small to medium-scale operations are concerned. Thus, the threshold for setting up a membrane plant is relatively low. However, despite all the advantages, as a young technology, membranes for $CO_2$ capture and separation still lack industrial acceptance. Besides, the technology readiness level (TRL) of most membranes reported in the literature remains low (<5); there exits a significant gap between research and the industry needs.

**Table 2.** Pros and cons of different $CO_2$ separation technologies [36, 37]

| **Processes** | **Advantages** | **Disadvantages** |
|---|---|---|
| Chemical absorption | High product purity<br>Effective heat management<br>Large recovery rates<br>Mature technology | Large equipment size<br>High energy penalty due to regeneration<br>Loss/degradation of solvents and secondary pollution<br>Corrosion/Toxicity |
| Adsorption | Simple operation<br>Endurable in high pressure<br>High selectivity | Low recovery or purity of $CO_2$ in product<br>limited adsorbents available<br>High energy penalty for sorbent regeneration |
| Cryogenic separation | Good separation for large $CO_2$ quantity and high $CO_2$ concentration<br>Combination separation with $CO_2$ liquefaction | Energy-intensive<br>Complicated process<br>High-standard equipment materials required |
| Membrane separation | Small footprint<br>No chemical additives<br>No moving parts<br>Low capital cost | Moderate product purity<br>Multi-stage processes may be needed for high $CO_2$ recovery<br>TRL level is low |

The advantages and limitations of common $CO_2$ separation technologies are summarized in **Table 2**. It is worth noting that hybrid technologies have also been developed to combine the benefits of different separation principles, such as membrane absorption [16, 38] and DAC membranes [39-43]. These concepts are out of the scope and not included in the current paper.

### 1.3 Overview of $CO_2$ separation membranes

As a selective barrier, membranes separate a mixture based on one or more property differences of the components in the mixture, including differences in size, shape, chemical structure, or other chemical or physical properties. The driving force for a $CO_2$ separation membrane is, in almost all cases, the $CO_2$ partial pressure difference across the membrane, while the transport resistance is directly related to the gas transport mechanism and the morphology and configuration of the membrane. An illustrated in given in **Figure 2.**

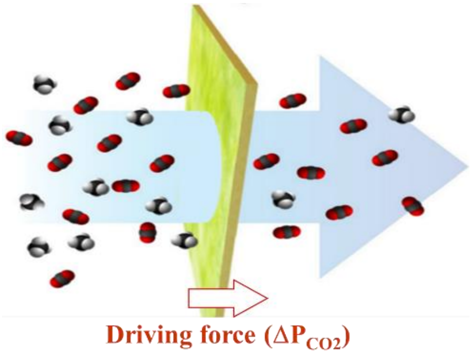

**Figure 2.** Gas transport through $CO_2$ separation membranes

Most gas separation membranes are polymeric membranes based on the solution-diffusion mechanism, which is intrinsically based on Fick's law (**eq. 1**).

$$J_i = -D_i \frac{dc_i}{dx} \qquad (1)$$

where $J_i$ is the flux of component $i$ [mol/(m$^2$ s)], $D_i$ is its diffusion coefficient [m$^2$/s] and $dc_i/dx$ is the concentration gradient for component $i$ over the length $x$ [mol/(m$^3$·m)].

Permeance is the driving force normalized flux, the most critical parameter to indicate the membrane permeation performance. Permeance for a given gas ($P_i/l$) can be defined by **eq. 2**.

$$\frac{P_i}{l} = \frac{J_i}{\Delta p_i} \qquad (2)$$

where $\Delta p_i$ is the partial pressure difference of $i$ across the membrane in [Pa] or [bar], and $l$ is the membrane selective layer thickness. Permeance reflects the gas flux of per unit membrane area in the unit [mol/(m$^2$ Pa s)], which is also often given in the unit GPU (1GPU=1 × 10$^{-6}$ cm$^3$ (STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$). When membrane materials are studied, the term permeability ($P_i$) in the unit of Barrer (1Barrer=1 × 10$^{-10}$ cm$^3$ (STP) cm$^{-1}$ s$^{-1}$ cmHg$^{-1}$) should be used for the performance evaluation, where the effect of membrane thickness is considered in the measurement.

Another critical parameter to assess a membrane is selectivity. Membrane selectivity in the literature is commonly expressed as ideal selectivity ($\alpha^*$), the ratio of the permeabilities of the gas pair $i$ and $j$ (**eq. 3**). When evaluating composite membranes that consist of several layers of materials or the performance of a membrane module, the term "separation factor" is more relevant. Separation factor (α) is the ratio of the mole fractions of key components in the permeate (*y*) and feed (*x*) flows, respectively, as expressed by **eq. 4**.

$$\alpha^{*}_{ij} = \frac{P_i}{P_j} \qquad (3)$$

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \qquad (4)$$

The concepts and definitions presented above are based on the book by Mulder.[44]

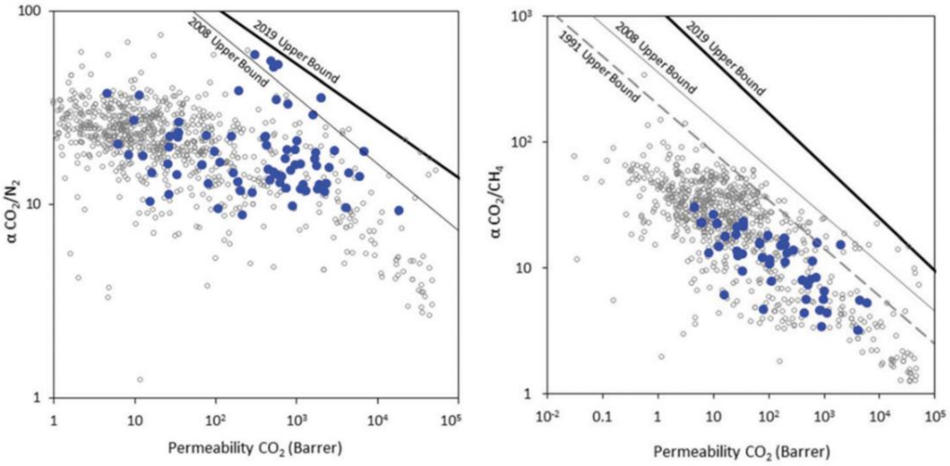

**Figure 3.** Robeson upper bound for $CO_2/N_2$ and $CO_2/CH_4$ gas pairs (Robeson plots from [45-48]; additional data from Ref. [49-53])

For most polymeric membrane materials, a trade-off between permeability and selectivity, the two major parameters to assess the separation performance of membrane materials, has been identified (**Figure 3**), indicating upper limits that constrain membranes' performances. This performance trade-off relationship, now well-known as the Robeson upper bound, was firstly published in 1991 [46]. In 2008, Robeson revisited the upper bounds by including new membrane materials that emerged during the years, showing significant moving up and forward in all upper-bound plots for the studied gas pairs. Several recent reports presented further shifts above the 2008 upper bounds [54], e.g., 2019 upper bounds [48]. These upper bounds have been used as the benchmark of state-of-the-art membranes, challenging membrane scientists to make breakthroughs, driving the membrane separation properties going up and forward to overcome the existing upper bounds; numerous new types of membrane materials and fabrication methods have been reported.

Over the past decade, industry interest in $CO_2$ separation membranes has nearly exploded due to the urgent need for CCS actions. Emerging new materials and nanotechnologies have resulted in intensive research in membrane optimization; many reported high-performance membrane materials have shown superior separation properties. Although membrane material properties make the most critical impact on separation, the overall performance also greatly depends on the membrane morphology, module configuration, and transport mechanisms. In general, gas separation membranes can be classified based on different aspects of their properties, such as the material type, pore size, transport mechanisms, membrane morphology, and module configurations. Table 3 summarizes the general classification of $CO_2$ separation membranes.

**Table 3**. Classification of $CO_2$ separation membranes based on different categories

| Membrane material | Morphology | Module configuration | Transport mechanism |
|---|---|---|---|
| - Polymeric | - Asymmetric | - spiral-wound | - solution-diffusion |
| - Inorganic | - Composite | - plate-and-frame | - facilitated transport |
| - Hybrid | | - hollow fiber | - molecular sieving |
| | | - tubular | |

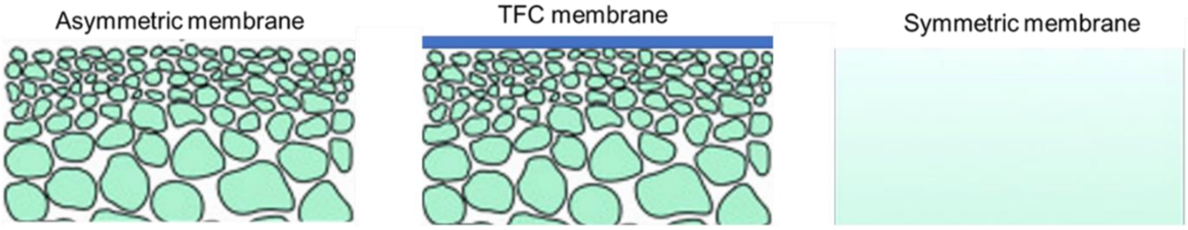

**Figure 4.** Scheme of an asymmetric membrane (a), a thin-film-composite membrane (b), and a symmetric thick film (c)

As indicated in the table, based on membrane morphology, gas separation membranes can be categorized into asymmetric and composite membranes **(Figure 4a and 4b)**. Due to a very high gas transport resistance, symmetric films (dense, thick membranes as shown in **Figure 4c**) are usually not applicable for gas separation applications. A typical asymmetric membrane (**Figure 4a**) has a dense skin layer for selective separation and a porous substrate to reduce the transport resistance while providing mechanical strength, in which a gradient in pore sizes along the depth of the membrane is formed through the controlled exchange/evaporation of solvent and nonsolvent (phase-inversion), and the membrane is made of the same polymeric material [55, 56].

**Figure 4b** presents a typical structure of a composite membrane, where a thin layer of selective material is deposited on an asymmetric porous substrate of a different material. A composite membrane can offer three key benefits compared to an asymmetric membrane. First, there is a broader choice of coating layer polymers, as mechanical performance requirements are no longer critical in composite membranes. However, only polymers suitable for making asymmetric structures and having the required mechanical strength may be used for asymmetric membranes. Furthermore, composite membranes allow the use of high-cost materials since the selective layers are thin, and the amount of material needed to form a thin layer is small, e.g., a few grams per square meter membrane. In addition, the selective layer thickness of composite membranes is much easier to control compared with an asymmetric membrane; ultra-thin selective layers can be readily fabricated in composite membranes, named as thin-film composite (TFC) [57-59]. These advantages make composite membranes more attractive for industrial applications. More basic concepts about membranes can be found from refs [59-61].

## 2. Transport Mechanisms in $CO_2$ Separation Membranes

Gas transport through a membrane is driven by partial pressure difference across the membrane through one or more different transport mechanisms. Solution-diffusion and facilitated transport (**Figure 5 (a, b)**) are two effective transport models in dense polymeric membranes, while in porous membranes or porous substrates of composite membranes, convective diffusion, Knudsen diffusion, molecular sieving, and sometimes, capillary condensation may be involved depending on the pore size ranges[44], as illustrated in **Figure 5 (c-d)**.

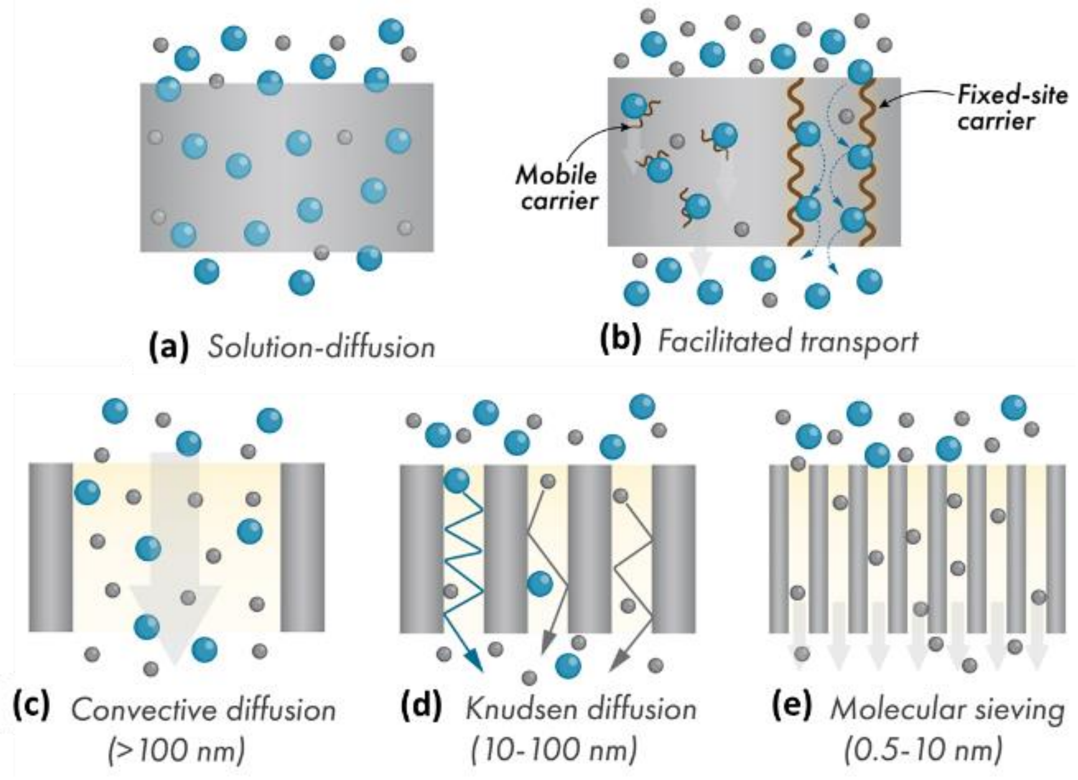

**Figure 5.** Gas transport mechanisms involved in gas separation membranes, reproduced from ref [29]

### 2.1 Solution-diffusion

Solution-diffusion is the most commonly applied gas transport model in dense polymeric membranes, in which gas permeability is a function of gas diffusivity (D) and solubility (S) in the membranes [44], as shown in **Eq. 5**.

$$P = D \times S \qquad (5)$$

The diffusivity of a gas in a polymer is associated with the gas kinetic diameters and the type and state of the polymer (glassy or rubbery state). Smaller gas molecules have high diffusivity and hence higher permeability in glassy polymers. The solubility of a gas in a polymer largely depends on the condensability and affinity of the gas in the polymer, where the gas condensability is directly related to its critical temperature. [44] Gases with higher critical temperatures generally show higher solubility and thus permeability, as shown in **Figure 6**.

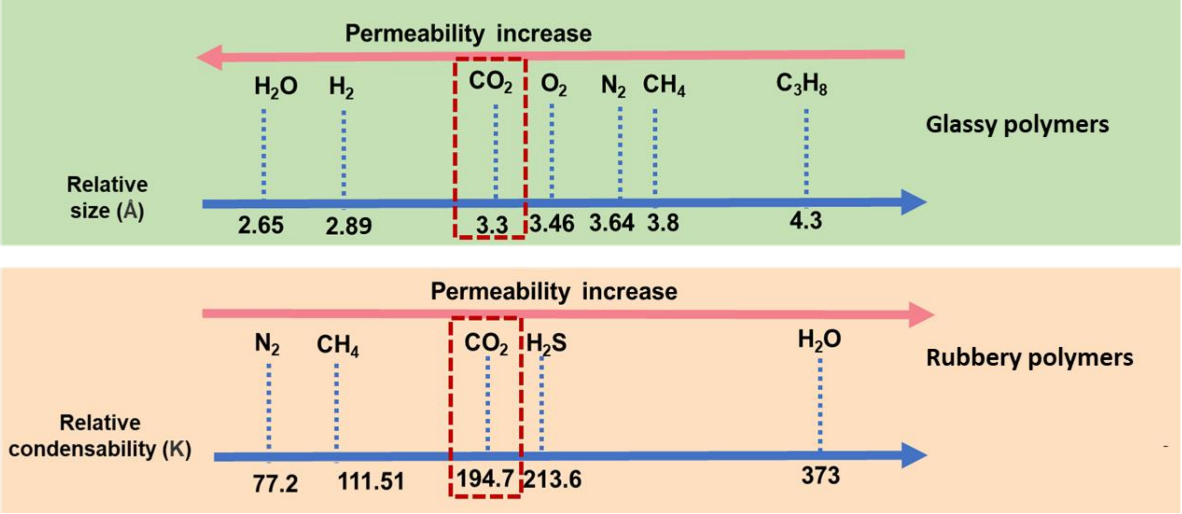

**Figure 6.** Representation of gas separation in glassy polymers and rubbery polymers. Reproduced from [62].

**Table 4**. Molecular size and critical temperature of common gases involved in $CO_2$ separation processes

| Gas molecule | $H_2$ | $CO_2$ | $N_2$ | $CH_4$ |
|---|---|---|---|---|
| Kinetic diameter(Å) | 2.89 | 3.3 | 3.64 | 3.8 |
| Critical temperature (K) | 33.3 | 304.2 | 126.1 | 190.7 |

**Table 4** summarizes the properties of the most common gases involved in $CO_2$ separation processes [63]. From the data listed, $CO_2$ has the highest critical temperature and exhibits the highest solubility in most polymers among the listed gases. The kinetic diameter of $CO_2$ is also smaller than $N_2$ and $CH_4$, so the diffusivity of $CO_2$ is higher, and it is possible to achieve $CO_2/N_2$ and $CO_2/CH_4$ separation based on solution-diffusion transport. On the other hand, $H_2$ has a higher critical temperature, hence much lower solubility compared to $CO_2$ ($S_{CO2}/S_{H2} >1$) but a much smaller kinetic diameter, hence much higher diffusivity ($D_{CO2}/D_{H2} \ll 1$). Thus, it is more challenging to separate $CO_2/H_2$ by solution-diffusion transport compared with other gas pairs.

## 2.2 Facilitated transport

As $CO_2$ is an acidic, reactive gas, $CO_2$ separation may greatly benefit from an additional transport path enhanced by reversible reactions of $CO_2$ with the membrane matrix. This reversible reaction-enhanced transport is called facilitated transport. [44] An illustration of the facilitated transport of $CO_2$ is presented in **Figure 7**.

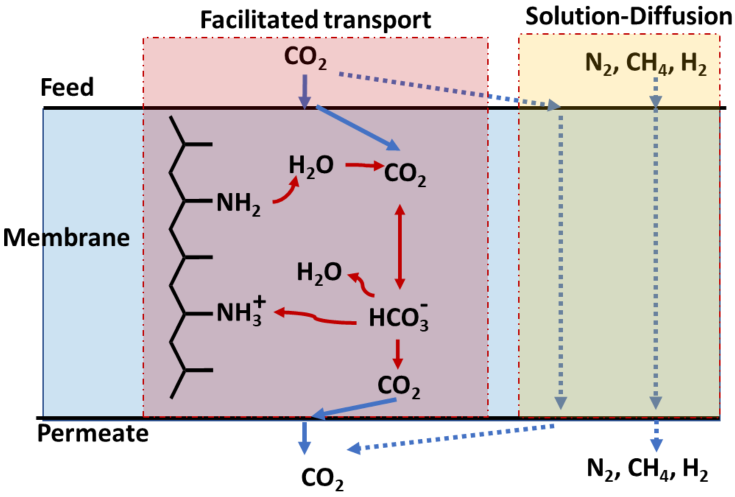

**Figure 7.** Scheme of $CO_2$ facilitated transport membranes

As seen in the figure, in addition to the solely physical solution-diffusion transport, chemical reactions of $CO_2$ with the reactive sites ($CO_2$-carriers) in a membrane provide an additional transport path, i.e., through the transport of one or more products or complex from the reversible reactions. Thus, the permeation of $CO_2$ is the sum of both solution-diffusion and facilitated transport, as expressed in **Eq. 6**.

$$J_{CO_2} = \frac{D_{CO_2}}{l}\Delta C_{CO_2} + \frac{D_{Carrier-CO_2}}{l}\Delta C_{Carrier-CO_2} \qquad (6)$$

where $D_{CO2}$ and $D_{carrier\text{-}CO2}$ are the diffusion coefficients of the Fickian diffusion and the facilitated transport-based diffusion, respectively.

Due to the additional reactive path by facilitated transport, this type of membrane can be highly $CO_2$ selective and simultaneously have high permeation of $CO_2$, overcoming the trade-off that limits most polymeric membranes. The facilitated transport effect is more significant for low $CO_2$ concentration or $CO_2$ partial pressures, as shown as red lines in **Figure 8**, in a similar polymer material with and without facilitated transport carriers, since the reversible reaction of $CO_2$ with carriers compensates for the low driving force (i.e., $CO_2$ partial pressure). However, facilitated transport may no longer be effective at high partial pressures when carrier saturation occurs[64] (shown in blue lines in **Figure 8**).

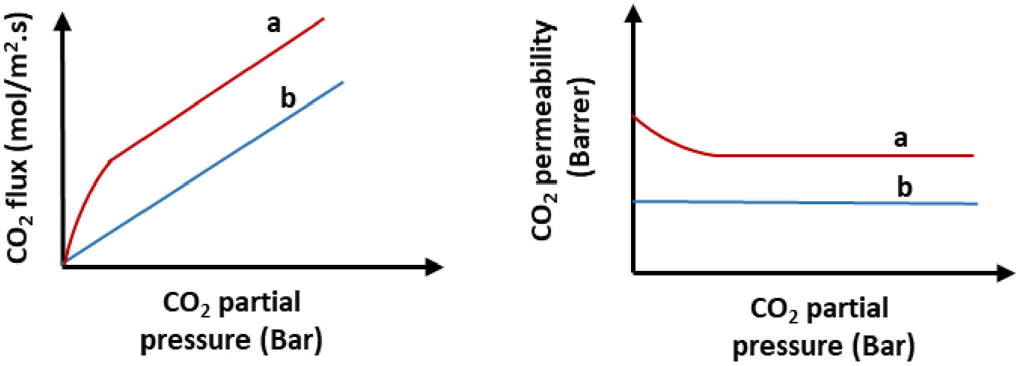

**Figure 8.** $CO_2$ flux and permeability as a function of $CO_2$ partial pressure for membranes based on facilitated transport (a, red line) and solution-diffusion transport (b, blue line).

Amine-based carriers are the most intensively studied in $CO_2$-selective facilitated transport membranes (FTMs). Amino groups (e.g., $-NH_2$) in FTMs can be covalently bound to polymer backbones, i.e., fixed to the polymer main chains as $CO_2$-carriers. This type of membrane is often referred to as fixed-site carrier (FSC) membrane [15, 65]. Small $CO_2$-philic or reactive molecules may also be added in membranes as carriers, like alkalines, amino acid salts, enzymes, and other additives that can enhance $CO_2$ transport, commonly categorized as "mobile carriers."

The reaction equations of primary amines with $CO_2$ are given in **Eqs**. (7) and (8). The weak basic amino group will initiate the reactions.

$$2RNH_2 + CO_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (7)$$

$$2RNH_2 + H_2O + 2CO_2 \leftrightarrow HCO_3^- + RNH_3^+ + RHNCOOH \qquad (8)$$

Primary amines (and also secondary amines) could react with $CO_2$ with or without the presence of water.[66] When water is not involved, the reversible reaction between $CO_2$ and the amines can be described by the zwitterion mechanism, which consumes 2 mols of amines to convert 1 mol of $CO_2$ into carbamate ions. In the presence of water, however, the reaction produces bicarbonates ($HCO_3^-$), reducing the amines needed to react with 1 mol $CO_2$. In this form, the transport will be changed from the transport of gas molecules through the solid polymer phase to ions transport through a highly water swollen polymeric matrix. Thus, the $CO_2$ permeation rate may be improved. Water is also involved in the reaction of tertiary amines with $CO_2$. It is reported that in tertiary amines or sterically hindered amines, the rotation of the C–N bond in the carbamate product is restricted by the surrounding bulky substituents. In the presence of water, the hindered carbamate can be easily hydrolyzed, forming bicarbonate, which presents a higher $CO_2$ loading capacity in the facilitated transport reactions [67, 68].

### 2.3 Transport mechanisms through porous membranes

The transport mechanisms of gasses through porous membranes are illustrated in **Figures 5 (c-e)**, including convective diffusion, Knudsen diffusion, and molecular sieving. One or more of the three transport mechanisms may apply within a gas separation membrane, depending heavily on the pore size and pore size distribution of the membrane as well as the size and mean free path of the gas molecules involved in the transport. Convective diffusion (bulk flow of fluid) will be in effect when the membrane pore size is much larger than the mean free path of the transporting molecules. Knudsen diffusion occurs when the pore size is smaller than the mean free path of gas molecules, where the diffusing gas molecules may collide more with the pore walls than with other molecules. [44] The selectivity by Knudsen diffusion depends on the square root of the ratio of gas molecular weights, $(M_i/M_j)^{1/2}$, so membranes by Knudsen diffusion are not possible to achieve $CO_2$ separation [69]. When a membrane has a pore size similar to the molecule size of the transported gases, molecular sieving takes over, where only molecules smaller than the pore size can pass through while larger molecules are stopped, leading to a high selectivity. Therefore, only molecular sieving may provide sufficient selectivity for $CO_2$ separation among transport mechanisms through porous membranes.

## 3. Membrane Materials for $CO_2$ Separation

### 3.1 General considerations in materials selection

The selection of materials for $CO_2$ separation membrane depends primarily on the separation properties of the material. Adequate separation performance is undoubtedly the first requirement to enable a membrane for industrial application, while considerations on other aspects, such as fabrication and upscaling, the membrane's stability and durability in real gas streams, and the cost, are equally important and should be taken into account from the beginning of the R&D activities.

$CO_2$ permeance and selectivity are the main factors that govern the process efficiency, so membrane materials with high $CO_2$ permeability are always desired to achieve high $CO_2$ flux, thus reducing the required membrane areas, while sufficient selectivity is needed to ensure the targeted $CO_2$ purity. As membranes of different materials and separation properties perform very differently in different gas streams under different process conditions, these aspects, such as feed gas composition, impurities, and operating conditions (e.g., gas flow rate, P, T), must be considered in the membrane material selection, often on a case-by-case basis.

Easiness of fabrication is another important consideration when selecting $CO_2$ separation membranes. Most polymeric membranes are solution-processible, and, in general, the fabrication cost is relatively low compared to inorganic membranes. However, if the potential for large-scale production is not considered in material selection at the beginning of the research stage, up-scaling membranes could be difficult due to material limitations or complicated fabrication procedures. Materials may not have industrial potential if they are not able to be fabricated into defect-free TFC membranes for further upscaling, such as some materials reported in the literature that can only be made as thick, coin-sized films. Another example is the not solution-processable materials, such as metal-organic frameworks (MOFs) membranes. Fabricating them into a selective membrane is usually through growing a continuous layer on a porous support, which is very complicated and hence more costly and easier to fail.

There are always undesired impurities in $CO_2$ –containing streams, such as $SO_x$ and $NO_x$ in flue gas and $H_2S$ and heavy hydrocarbon (HHC) in natural gas. The effects of impurities on membrane performance must be considered when selecting membrane materials and ensure that membranes have good resistance to impurities. In many cases, impurities negatively affect $CO_2$ separation by competitive sorption, while sometimes, irreversible reactions may happen between the impurities and membrane materials. Another problem in polymeric membranes is plasticization. Significant swelling of the membrane occurs when the membrane is subjected to highly soluble species like $CO_2$ and $CH_4$, especially at high pressures, and the consequently increased polymer chain mobility and free volume (i.e., space between the polymer chains) lead to the loss of membrane performance, e.g., increasing permeability of all gases, resulting in decreased selectivity [61]. Even worse, thinner membranes may be affected more by plasticization since the binding force of the molecular chain is smaller, and chain mobility is better in thin membranes. Thus, impurity effects and plasticization must be taken into account for $CO_2$ membrane separation, especially for processes operating at high pressures [8, 70].

Water vapor existing in flue gas is also a challenge for a large number of membranes, but membranes based on facilitated transport and some $CO_2$-philic polymers are exceptions. Harsh operating conditions like high temperature and pressure may also reduce membrane performances and mechanical strength. It is worth mentioning that, as water is a promotor to accelerate $CO_2$ transport in most FTMs, facilitated transport membranes are promising for $CO_2$ separation since almost all $CO_2$-containing gas mixtures are water vapor saturated. Moreover, plasticization is no longer a problem in FTM membranes as they are usually highly swollen by water in membrane matrices.

Another problem encountered by most polymeric membranes is aging, especially physical aging due to the non-equilibrium of polymer chains in the glassy state with inefficient packing or excess free volume, which will gradually lose over time and affect the membrane permeation. It is reported that physical aging has a greater effect on thin membranes and is more severe for membrane materials with high free volume [71, 72]. Thus, the long-term stability of membranes is a critical consideration for industrial applications. For instance, membranes and modules in a process are usually designed to be used for more than four years, but membrane materials are normally tested in the lab for a much shorter time. Thus, a test specifically carried out to evaluate the long-term stability under industrial conditions is necessary when selecting proper membrane materials.

### 3.2 Polymeric materials

Polymeric membranes are the most common membranes for $CO_2$ separation today. Up to now, over 90% of membranes for gas separation are polymeric membranes due to their good processibility and relatively lower cost. Commercial membranes currently used for $CO_2$ separation are mainly polymeric membranes, including cellulose acetate (CA), polysulfone (PSf), polyethersulfone (PES), and polyimide (PI). Several more types of polymeric membranes (e.g., membranes under trade names Polaris® and PolyActive™, and polyamine-based membranes) are undergoing pilot testing for further development for industrial applications [73, 74]. The separation performances of these commercial membranes are summarized in the Supporting Information (SI) file (**Table SI-1**) as reference [75]. Commercial PI is under the trade name Matrimid®. However, the trade-off between selectivity and $CO_2$ permeability makes polymeric membranes less advantageous. According to the data, the performances of the current commercial membranes are far below the 2008 upper-bounds, which creates a great opportunity for new membranes with better performance. There are several common approaches to improving membrane performance. The most applied approach has been to tailor existing polymeric materials for higher $CO_2$ solubility or diffusivity, such as by introducing functional groups or design polymers to form block copolymers with higher $CO_2$ affinity or synthesizing families of polymers with high fractional free volume (FFV). Moreover, given $CO_2$'s reactivity, reversible $CO_2$ reactions with membranes can be taken as an advantage to enable an additional facilitated transport path, such as by using polymers containing amino functional groups as carriers or introducing mobile carriers to enhance $CO_2$ transport. Combining polymers with inorganic phases or nano-dimensional additives to make hybrid membranes has also been taken as an effective approach for desired membrane properties.

### *3.2.1 $CO_2$-philic polymeric membranes*

As $CO_2$ is a polar gas with high condensability, $CO_2$ solubility in common polymers is considerably higher than that of other light gases (e.g., $H_2$, $N_2$, and $CH_4$), which favors the $CO_2$ separation. The $CO_2$ solubility can be further improved by introducing more polar function groups, such as ethylene oxide groups and ionic liquids, to the membranes.

Poly(ethylene oxide) (PEO) and its derivatives are one of the representative $CO_2$-philic polymer families widely studied for their strong dipole–quadrupole interactions with $CO_2$ molecules [76]. However, PEO polymers with low molecular weight normally show low mechanical strength, while PEO polymers with high molecular weight have a high tendency to form impermeable crystalline. Many methods have been developed to overcome the drawbacks of PEO-based materials, such as by forming block-copolymers [77, 78], creating cross-linked structures [79], or grafting PEO groups to other polymers [80] and making hybrid membranes with high liquid PEO loadings [81, 82].

Polyether block amide (or PEBA, under the tradename of PEBAX®) and PEOT/PBT multi-block copolymers (known as PolyActive$^{TM}$) are two of the most studied PEO-based polymers as $CO_2$ separation membrane materials. The cross-linking degree can be tuned by controlling the monomer ratios and/or UV treatment conditions[83]. With the addition of low molecular weight free PEO, $CO_2$ permeability of up to over 3000 Barrer with $CO_2/N_2$ selectivity over 50 were documented [84]. By introducing nanofillers into the mixture before crosslinking, $CO_2$

permeability of approximately 1000 Barrer with $CO_2/N_2$ selectivity of ~50 were also obtained [85].

Ionic liquids (ILs)-based membranes have also been widely studied for $CO_2$ separation in the past decades [86]. ILs are a class of low-temperature molten salts with large and asymmetric organic cations and organic or inorganic anions, exhibiting intrinsic advantages, including high $CO_2$ solubility. ILs are used as additives in hybrid membranes. Neutral (e.g., Pebax) [87-89], charged (e.g., Nafion) [90], and cross-linked (e.g., PEO) [91, 92] polymeric matrix have been investigated as hosting matrix for ILs. However, the long-term stability of most ionic liquids-based hybrid membranes is not sufficient.

Poly(ionic liquids) (PILs) membranes have been developed to address ILs-based membranes' stability issues. PILs can be either poly(ionene)s (charged groups constructed on the backbones) or poly(ionomer)s (ionic groups connected as a pendent group). Neat PILs usually present low $CO_2$ permeability, so PILs membranes often combined with unbonded ILs as additives [93, 94] to improve $CO_2$ transport. In some studies, ILs' charged groups are constructed onto polymer chains to form block copolymers [95, 96].

Even though many PEO-based and IL-based membranes present superior $CO_2$ separation performances, it is worth mentioning that a large amount of these data were based on self-standing membranes with a thickness of over 50 micrometers. To make these membranes into TFC membranes with a thickness lower than 1 μm could be challenging but it is a critical requirement for industrial applications.

### *3.2.2 Polymers with high free volumes*

Glassy polymers with high free volume exhibit extraordinary gas permeation properties, of which PIs, polymers of intrinsic microporosity (PIMs), Tröger's base polymers (TB polymer), and thermal-rearranged polymers (TR polymer) are the most researched membrane materials. Their chemical schemes are shown in **Figure 9**.

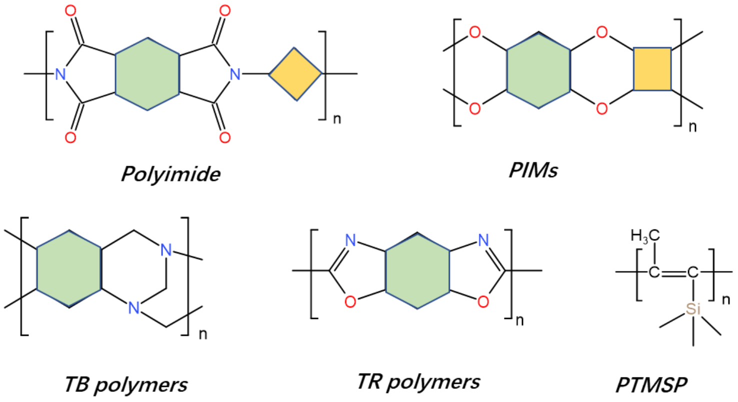

**Figure 9.** Representative high free volume polymers

PIMs are a type of porous organic polymers (POPs) firstly reported by Budd and McKeown in 2004 [97]. PIMs consist of highly inflexible and contorted molecular frameworks, providing abundant interconnected micropores (pore size <2 nm) and ultramicropores (pore size <0.7 nm) in the matrix [98, 99]. After around 20 years of development, more than 200 different PIMs have been synthesized [72], among which PIM-1 is the most intensively studied. Although neat PIMs already present ultrahigh $CO_2$ permeability (>6000 Barrers), the PIMs polymer chain holds the possibility of functionalization (e.g., grafting bulky groups onto polymeric chain [100] or crosslinking [101, 102]) to further improve the $CO_2$ separation performances [103]. Due to their extraordinary $CO_2$ separation performances, $CO_2$-related separation upper bounds were updated accordingly in 2019, using PIMs as model polymers [48].

TR polymers are a new class of polymers with rigid microporous structure formed of planar macromolecules from rod-like aromatic polymers bearing heterocyclic benzoxazole, benzimidazole, and benzothiazole rings through thermal rearrangement with aromatic PI, polyetherimide, or polyamide membranes [51, 104]. The pores in TR membranes can be fine-tuned in the range of 0.3–0.4 nm and 0.7–0.9 nm, resulting in TR-polymers with much better selective transport behaviors for small gas pairs [105, 106]. High $CO_2$ permeability (~5440 Barrer) and moderate $CO_2/CH_4$ selectivity(~40) were documented [107]. However, even though attempts have been made to fabricate TR polymer based hollow fiber membranes [108-110] and electrospun mat geometries [111], the thickness of most TR polymeric membranes prepared in the lab were in the range of tens of micrometers [112, 113].

Recently, Tröger's base (TB) polymers, a novel group of high free volume polymers with a bridged bicyclic diamine structure called Tröger’s base [114], have received great interest for fabricating $CO_2$ separation membranes [115-117]. Due to the possibility of introducing monomers with intrinsic microporosity into the polymeric chains, some TB polymers are named PIM-TB. As Tröger's base structure can also be introduced into PIs and PIMs polymeric chains, in many cases, co-PIs or co-PIMs with Tröger's base were obtained with high free volume [118-120].

PI is a glassy polymer used as a commercial membrane material in $CO_2/CH_4$ separation processes [121]. However, conventional PI membranes demonstrate low gas permeability with relatively high gas selectivity even at high operating pressures [62]. PI has been explored over the past decades [122] by introducing intrinsic microporous units into its polymer chains [123] or enhancing polymeric chain rigidity by crosslinking [123-125]. PI with intrinsic microporous units, named as PIM-PIs, exhibits $CO_2$ permeability much higher than conventional PI membranes with similar $CO_2/CH_4$ and $CO_2/N_2$ selectivities [126, 127].

In recent decades, new types of perfluoro polymers, such as Teflon™ AF, Hyflon™ AD, and Cytop™, were reported as membrane materials with high $CO_2$ permeability due to their high free volume elements but relatively low $CO_2$ selectivity [128]. For example, a $CO_2$ permeability of around 2200 Barrer was reported for a Teflon™ AF2400 membrane, with $CO_2$ selectivity of around 1, 4, and 5 over $H_2$, $N_2$, and $CH_4$, respectively [129]. Perfluoropolymers were considered not solvent-processible until organofluorine-type solvents were developed. With this solvent, perfluoro polymer-based membranes can be fabricated as composite membranes, exhibiting extremely high $CO_2$ permeance (>1000 GPU) [130]. Recently, Sandru et al. reported a modified AF2400 TFC membrane with an integrated transport mechanism to take advantage of the high free volume polymer’s high permeation rate and a grafted polyamine layer for $CO_2$-facilitated transport with high selectivity [131].

However, several drawbacks have to be addressed before the industrial exploitation of these super glassy polymers. For instance, TR polymers have low solubility in common solvents for membrane preparation, which, together with their high cost and the need for high thermal treatment temperatures, have been bottlenecks for their industrialization. PIM membranes and also perfluoro polymers exhibit other issues, such as moderate selectivity and low stability over time, i.e., severe physical aging, especially when the membrane is made in the TFC form [71, 132].

### *3.2.3 Facilitated transport membranes*

Facilitated transport membranes have been intensively studied for $CO_2$ separation. Both FSC and mobile carrier-based membranes have been developed to take advantage of $CO_2$ as an acidic, reactive gas. Some of the representative $CO_2$-facilitated transport carriers are shown in **Figure 10** [133, 134]. Several mathematical models have also been developed to characterize the facilitated transport effect in FTMs [135].

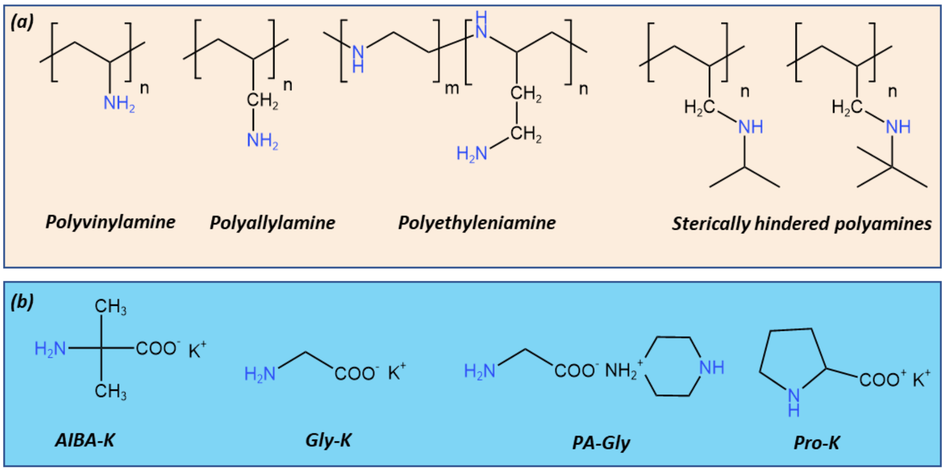

**Figure 10.** Representative fixed site carrier (a) and mobile carrier (b) in $CO_2$-facilitated transport membranes

Polyvinyamine (PVAm) is one of the representative amine-based polymers for FTMs. As the polymer with the highest content of primary amino groups, PVAm is a natural choice for FTMs to exploit the $CO_2$-amine chemistry. However, the firstly reported $CO_2$ permeance through PVAm membranes had been low (<10 GPU), not reflecting the facilitated transport effects[136, 137]. Later on, the presence of water was found critical as it is actively involved in the reaction to enhance $CO_2$ transport and achieve high $CO_2$ permeance [138, 139]. The strong dependence of FTMs' performance on the feed gas relative humidity (RH), or more precisely, water uptake in the membrane, was reported by Deng et al. [138, 139]. As water is involved in the $CO_2$-facilitated transport reactions and $CO_2$ transport in FTMs is enhanced by the water taken up within the membrane matrix, FTM membranes are usually made of hydrophilic polymers with a high degree of water swelling. For FTM membranes, separation under humid conditions must be ensured when designing a membrane module or a separation process.

PVAm membranes were documented with extraordinarily high $CO_2$ permeability and $CO_2/N_2$ selectivity under fully humid conditions[52]. PVAm can be blended with other compatible polymers (e.g., polyvinylalcohol (PVA)) to improve the membrane properties or embedding nano additives (e.g., nanocellulose, carbon nanotubes (CNT), graphene oxide (GO) and $TiO_2$) to further increase its gas separation properties [138, 140-143]. Wang and coworkers have developed PVAm-based copolymers as FSC membranes, such as by introducing functional groups into PVAm main chains, and both $CO_2$ permeability and selectivity with long-term stability were documented [144, 145].

Several types of amine-based FSC membranes using polymers other than PVAm have been investigated, including polyallylamine [146], polyethyleneimine [57, 147-149], and polyamidoamine (PAMAM) dendrimer . Tertiary amines were also utilized as fixed-site carriers in FTMs as they offer sterically hindering effects for higher facilitated transport efficiency and hence better $CO_2$ separation properties [150-154] (**Figure 10 (a)**).

Small $CO_2$-philic or reactive molecules **(Figure 10 (b))**, including amino acid salts, ionic liquids, mimic enzymes, and KOH, have been used as mobile carriers and added into a non-reactive hydrophilic polymer matrix, such as in PVA and PVP (polyvinyl pyrrolidone) membranes, to introduce $CO_2$-reactive effects [155-157]. Mobile carriers are often added to an FSC membrane for extra $CO_2$ facilitated transport effect to reinforce the $CO_2$ permeation properties [158-161]. Mobile carriers are found also increase gas diffusivities since these small molecules, typically organic molecules, usually plasticize the hosting polymer [12, 162-164]. It is worth mentioning that mobile carriers can also be attached to nanofillers embedded in polymeric membranes. By functionalizing the nanofillers, amine groups or other facilitated transport agents can be grafted onto the nanofillers, leading to improved $CO_2$ separation performances [133, 165].

A disadvantage of FTMs is the carrier saturation phenomenon at high $CO_2$ partial pressures, which will lead to the loss of the facilitated transport effect. It is thus not the best option to use FTMs for separations at elevated pressures. However, it has been reported that the facilitated transport effect is positively influenced by increasing membrane thickness [12, 166] or adding mobile carriers and nanofillers [140, 167]; thus, $CO_2$ separation can be achieved even at high $CO_2$ partial pressures. Moreover, for post-combustion $CO_2$ capture where the flue gas is at near ambient pressure with a $CO_2$ concentration of around only 3%–15%, i.e., at a low $CO_2$ partial pressure, FTMs could outperform other types of membranes.

### 3.3 Inorganic membranes

Compared to polymeric membranes, inorganic membranes show much better thermal stability that offers a much wider operation temperature window for $CO_2$ separation [168, 169]. As porous inorganic membranes separate gases based mostly on molecule sieving, high $CO_2$ selectivity may be achieved if the pore sizes of the membranes can be precisely tuned to be between the sizes of the gas pair, such as in zeolite, MOFs, and carbon molecular sieve (CMS) membranes. In particular, CMS membranes have attracted special attention for $CO_2$ separation [170, 171]. CMS membranes are typically prepared by carbonizing polymeric precursors such as PI, poly(phenylene oxide)(PPO), and cellulose derivatives. CA-based hollow fiber carbon membranes were fabricated successfully and tested for biogas upgrading, natural gas sweetening, and $H_2$ separation with excellent $CO_2$ separation performance [170]. However, CMS membranes are somewhat brittle and often suffer from aging issues and pore blockage of water vapor in humid gas streams (RH>30%). Module construction is also difficult due to the relatively brittle structures. Recently, Richter et al. [172] reported a high flux ceramic-supported carbon membrane with a $CO_2$ permeance of 220 GPU and $CO_2/CH_4$ selectivity of 30, which may be used as the membrane for natural gas sweetening against high pressures. Dai et al. [173]reported a CMS using Tröger’s base polymer as precursor, showing excellent $CO_2/H_2$ separation performance. New CMS membranes fabricated at a relatively low temperature that are more flexible and durable during module fabrication were also reported.[173, 174] There have been several reports on zeolite membranes and MOF membranes in for $CO_2$ separation based on molecular sieving [175-177], but not yet received industrial interest. Palladium (Pd)-based metallic membranes have also been investigated for $H_2/CO_2$ separation [178]. The most attracting part of Pd membranes is the extremely high $H_2$ selectivity as the result of the proton conductive transport mechanism. The main bottlenecks hindering the industrial application of Pd membranes are its high price and poor poison resistance [179]. Researchers have also attempted to apply Pd-based metallic membranes as membrane reactors for $H_2$ production with $CO_2$ capture for CCS [180, 181].

### 3.4 Hybrid membranes

Hybrid membranes, often referred to as mixed matrix membranes (MMMs) or nanocomposite membranes in the literature, can be fabricated by embedding various fillers in polymeric matrices [182]. MMMs consist of two materials governed by different transport mechanisms;

thus, such membranes have the potential to synergistically combine superior gas-separation performance of the porous inorganic filler phase with the easy processability of polymers. Some recently reported porous filler are shown in **Figure 11 (a)** [183, 184].

Nanocomposite membranes are usually made of polymeric membranes with dispersed nano-sized fillers. Based on the morphology, fillers can be nanoparticles (0D), e.g., fumed silica and TiO$_2$; nanofibers (1D), such as CNT and nanocellulose, and nanosheets (2D), e.g., graphene, GO, covalent organic framework (COF) (**Figure 11 (b)**), or 3D structured porous materials (MOF, Zeolites, PAF (Porous Aromatic Framework), etc.) [185-187].

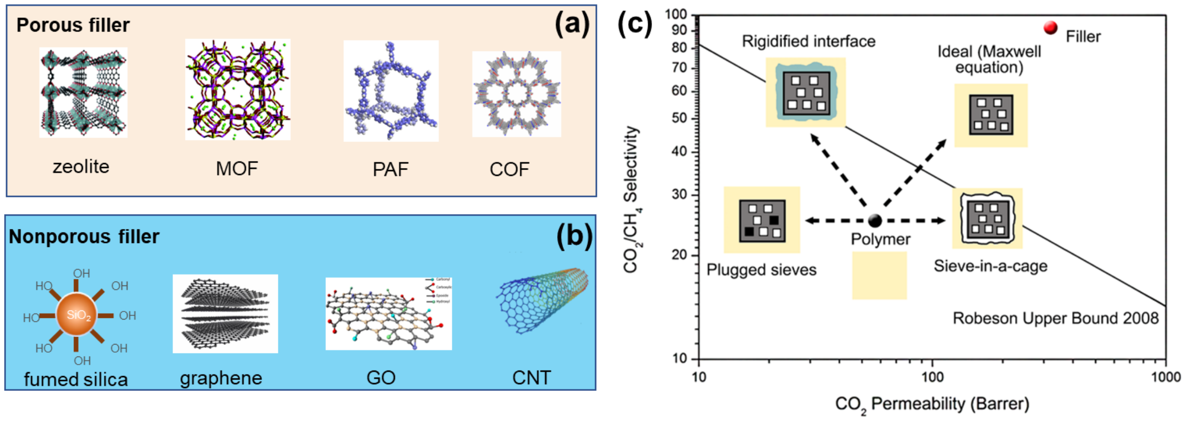

**Figure 11.** Commonly used porous (a) and non-porous nanofillers (b) in hybrid membranes, and the effect of filler-polymer interface conditions on separation performance (c). Reproduced from ref [188]

If good dispersion and interaction of the fillers with the polymer matrix are achieved (i.e., the ideal situation as shown in **Figure 11 (c)**), the presence of filler could significantly improve both CO$_2$ permeability and CO$_2$ selectivity of the hybrid membrane [142, 189-191]. However, the performance may not be improved as expected if non-selective microvoids are formed between fillers and the polymeric phase (shown as Sieve-in-cage in **Figure 11 (c)**); there will only be an increase in gas permeation with no effect on selectivity for the separation [188]. Rigidified interface and plugged sieves should also be avoided. It is critical to make the fillers and polymer compatible. Different functionalization methods have been applied to achieve ideal dispersion [192]. In some cases, a third compound was introduced to make three-phase hybrid membranes, such as CO$_2$-philic liquids (e.g., ILs), and the presence of the third compound significantly improves the compatibility between fillers and the polymer phase [193]. However, introducing a third compound may lead to other problems, like un-desired phase separation during membrane fabrication.

Most hybrid membranes fabricated in labs are self-standing films with thicknesses in the range of tens of micrometer. Reducing membrane thickness to minimize the membrane's resistance can be the bottleneck for the commercialization of most hybrid membranes since the minimum membrane thickness of the membrane depends on and is often limited by the size of the fillers or their agglomerations. In the past decades, lots of efforts have been dedicated to fabricating TFC membranes with a hybrid dense coating layer [194]. Nanocellulose and functionalized GO-based TFC membranes have been successfully fabricated and presented good $CO_2$ separation performances [141, 158, 195]. Due to the intrinsic advantages of 2D nano sheets in fabricating TFC membranes, 2D materials have been widely used in hybrid membranes for $CO_2$ separation [196-198]. Interestingly, Zhu et al. [199] developed a molecularly mixed composite membrane using soluble porous organic cages as fillers with perfect dispersion, while Chen et al. [200] reported a solid-solvent-processing approach to coat ultrathin and highly loaded MMMs, leading to a significant increase in $CO_2$ permeability and selectivity.

### 3.5 Effect of support substrates in composite membranes

Thin film composite membranes with a thin selective layer, preferentially < 1 µm, are desired for practical gas separation applications. The porous substrate in a TFC membrane is used to provide mechanical strength and structural integrity while preventing pore-filling by the dope solution during coating [58]. To prevent pore filling during coating, it is also common to add a gutter layer before coating the selective layer. Based on the resistance-in-series model, it is well-accepted that the permeability of the neat porous support should be at least 10 times higher than that of the resulting TFC membrane to ensure that over 90% of mass transfer resistance is generated from the selective layer [201]. Otherwise, the mass transfer resistance will gradually shift to the porous support, reducing the overall gas flux across the membrane [9].

The pore geometry, porosity, and surface pore size distribution can influence the overall performance of TFC membranes [9, 202]. It is desired to have porous substrates with high permeance ($>10^5$ GPU) [9], smooth surface (to reduce roughness and ensure ultrathin selective layer), good compatibility with the selective layer materials, and good solvent resistance. In addition, the membrane pore structure, i.e., finger type or sponge type, is an important feature to consider when selecting membrane substrates. The finger-type porous support may easily deform under pressure, so a sponge-type structure is preferred for processes at elevated pressures. PVDF (polyvinylidene difluoride), PSf and PES are the most accessible and commonly used polymeric porous substrates, while porous ceramics or stainless-steel films are commonly seen as substrates used for inorganic TFC membranes.

Please note that we have only discussed membrane materials attracted industrial interest to a certain extent. A more complete list of the most common membrane materials and their major applications in the literature can be found from several recent review articles on $CO_2$ separation membranes [7, 11, 12, 19, 57, 203-207].

## 4. Membrane Module Configurations

Membranes must be installed in modules to separate and leak-tight the feed side and permeate side streams to achieve the separation. A membrane module is also expected to protect membranes against mechanical damage and provide high productivity of the process, e.g., with a high ratio of membrane surface to module volume, often referred to as packing density. The main features of different membrane modules are summarized in **Table SI-2** [208], including plate-and-frame and spiral wound modules of flat sheet membranes and hollow fiber and tubular modules of tubular-shaped membranes[109].

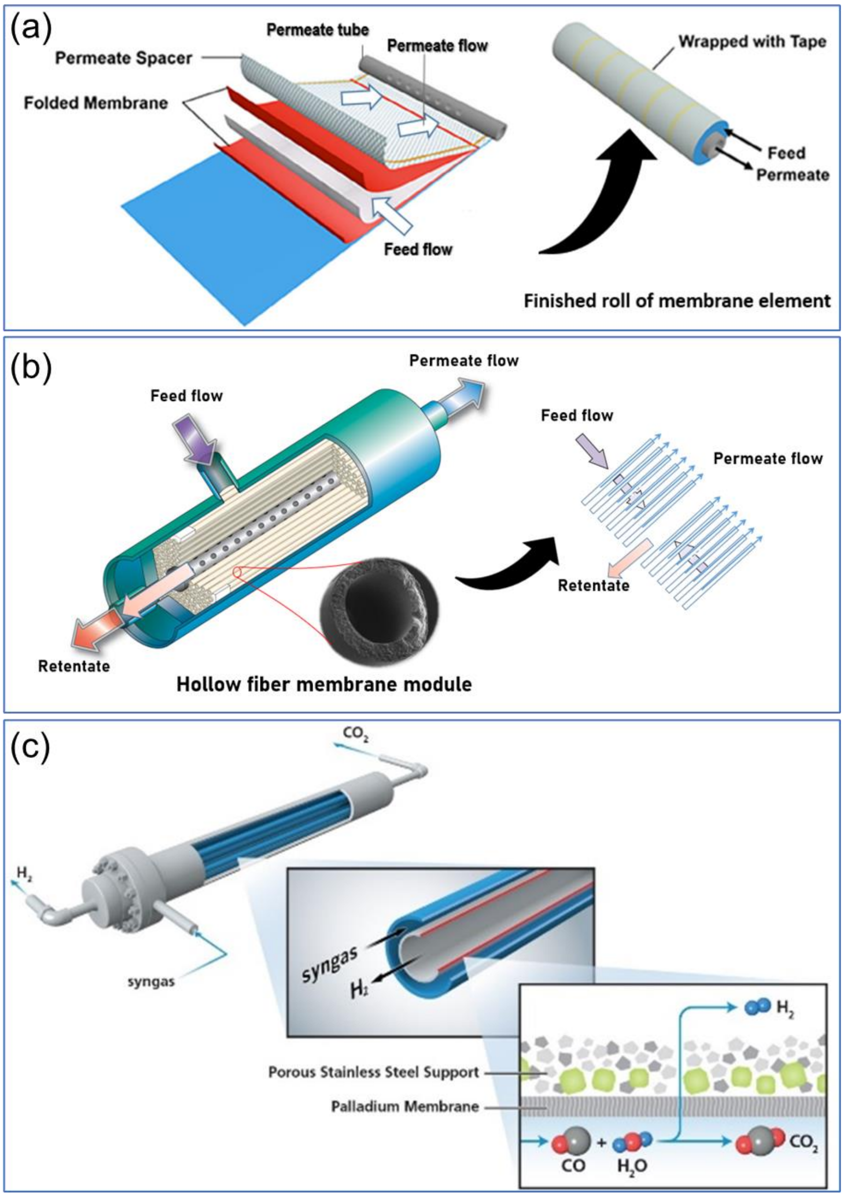

**Figure 12**. Sample spiral wound membrane module (a), hollow fiber membrane module with a central pipe (b), and Pd-based tubular membrane module (c). Reproduced from ref [31, 209, 210]

**Figure 12** presents the structures of the three most applied module configurations for $CO_2$ separation. Spiral wound modules (**Figure 12 (a))** are the most commonly used configuration for flat sheet membranes due to their higher packing density than plate-and-frame modules. Spiral wound modules have adjustable hydrodynamics, and optimizing the feed spacer can reduce boundary layers along the membranes and lessen the potential concentration polarization effect. Hollow fiber modules (**Figure 12 (b))** have the highest packing density of all configurations hence the lowest relative costs. Generally, it is easier to get higher (3-4 times) packing density in hollow fiber membrane modules than in spiral wound modules [211]. As hollow fiber membranes maximize the surface area per unit volume, they are particularly suitable for processing large-volume gas flows. Due to low packing densities, plate-and-frame configurations are found to be used only in a few pilot tests, while tubular membrane modules are only employed when the membrane materials are more suitable to be made into tubular forms, such as metallic or ceramic membranes, as seen in **Figure 12 (c)**.

Membrane separation performance is found to depend significantly on module configurations [212]. Besides the influences from packing density, flow patterns in different module configurations affect the concentration profile, boundary layer, pressure drop, and the consequent mass transfer efficiency in membrane modules and, eventually, the separation performance [213]. Gas transport in modules shows different flow patterns in different module configurations. Typically, cross-flow is the flow pattern in spiral wound membrane modules, and counter-current flow often applies in hollow fiber membrane modules [213].

When highly $CO_2$-permeable membranes are used, concentration polarization may occur, which may cause a decrease in the driving force and serious pressure drop along the membrane, undermining the module performance. Although counter-current flow gives a higher average driving force than cross flow for the same separation conditions [211], the better hydrodynamics in spiral wound modules makes them less suffered from concentration polarization issues. Nonetheless, the flow pattern in hollow fiber membranes can be optimized to reduce concentration polarization effects, such as using tangential flow directions for feed gas inlet or installing a central tube as the retentate gas outlet to change flow directions **(Figure 12 (b)**). It may be beneficial to take a double-ended flow as the permeate outlet or, sometimes, use a relatively lower packing density.

If FTMs are used, the water profile along the membranes is also critical and must be considered when optimizing the module configurations as water is involved in $CO_2$ facilitated transport in most FTM membranes [138, 214]. It is worth mentioning that gas separation performances of many conventional polymeric membranes based on solution-diffusion mechanism are also greatly influenced by RH, e.g., Nafion [90], Pebax [142, 215] and Nexar [216] membranes. Therefore, it is of critical importance to ensure sufficient RH inside the modules to maintain the overall module performances. Yang et al. [217, 218] reported a tanks-in-series approach in a modeling study for mass transfer in amine-based FTMs to predict the variations of water vapor contents, temperature, and pressures along the membrane module, as shown in **Figure**

**13**. Such models can be integrated into commercial software (e.g., Aspen HYSYS) for up-scaling membranes or more accurate performance estimation, particularly for FT membrane systems. In addition, the gas flow along membranes (e.g., along the length of hollow fibers) can be optimized according to the $CO_2$ concentration profile to avoid reverse transport and maximize the driving force.  With a proper design of hollow fiber membrane module configurations, the mass transfer coefficient may become higher than conventional spiral wound membrane modules [219]. Therefore, optimized hollow fiber membrane modules can be the most promising configuration in gas separation applications [220].

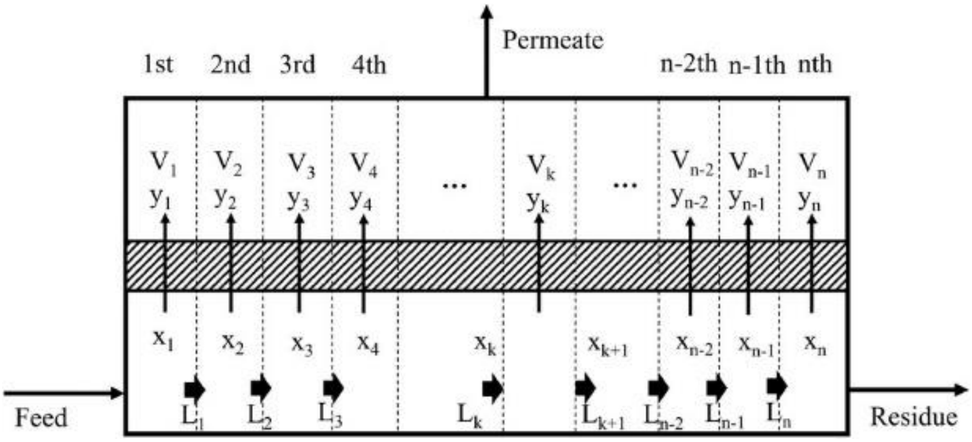

**Figure 13.** Schematic of the tanks-in-series approach along the membrane. Reproduced from [217, 218]

Pressure drop and leaking, especially at elevated temperatures and pressures, are also issues related to membrane modules. Pressure loss partly comes from the flow friction through the flow channels along the fiber or between the narrow spaces of flat sheet envelopes. Another part of the pressure drop is due to the loss of the permeated gas. As a result, the transmembrane pressure decreases along the membrane, reducing driving force and hence the overall performance. Hollow fiber membranes with the counter-current flow will suffer the most with the pressure drop. A smart design is to change the flow pattern to cross-flow, such as by introducing a central pipe for the feed outlet and forcing the flow direction of the feed (shell side) and permeate (the tube side) cross (**Figure 12 (b)**). However, with the shortened flow path, the stage-cut through the module may decrease, so the module diameter and the fiber length must also be optimized accordingly.

It is worth noting that, as $CO_2$ has a very high Joule-Thomson coefficient (1.11 K/bar), the Joule–Thomson effect takes place in $CO_2$ separation membranes and makes notable influence in temperature when the pressure drop across membranes is high [44]. Gas tends to expand from the high pressure side to the low pressure side, resulting in temperature drop under constant enthalpy [221, 222]. Thus, the temperature influence must be considered when the $CO_2$ permeation in a membrane is sensitive to temperature [223].

## 5. Process Design Considerations

A techno-economic feasibility study is always the first investigation before any new membrane can be applied in an industrial separation process, and process design is the basis for such a study. As the outcome, an optimized process design will be determined as the foundation of a new membrane process. Needless to say, $CO_2$ separation performance of the membrane plays the most critical role in the design of the membrane system. Based on the selected membrane material and its performance, considering the process conditions (e.g., P, T, feed $CO_2$ concentration and flow rate) and product requirements (purity and recovery), the design of a membrane system starts from determining the module configuration, stage design (e.g., single- or multi- stage), stage layout, and the option of internal recycling streams [37, 224]. For instance, in $CO_2$ capture processes, one-stage membrane separation is not usually sufficient to offer the desired $CO_2$ purity if the feed gas $CO_2$ concentration is low or the required product purity is too high. Thus, two-stage membrane processes, and if necessary, three or even four-stage membrane processes, should be designed, but two-stage membrane processes are more favorable since low operating cost and process complexity are always desired. For a multi-stage process, a cascade solution is typically used [225], where part of the flow is recycled to achieve the recovery rate or $CO_2$ purity in the final product stream. Two-stage membrane processes of two different cascade solutions and recycle streams are shown in **Figure 14** [36]. It is also beneficial to employ membranes of different performances at different stages [226, 227].

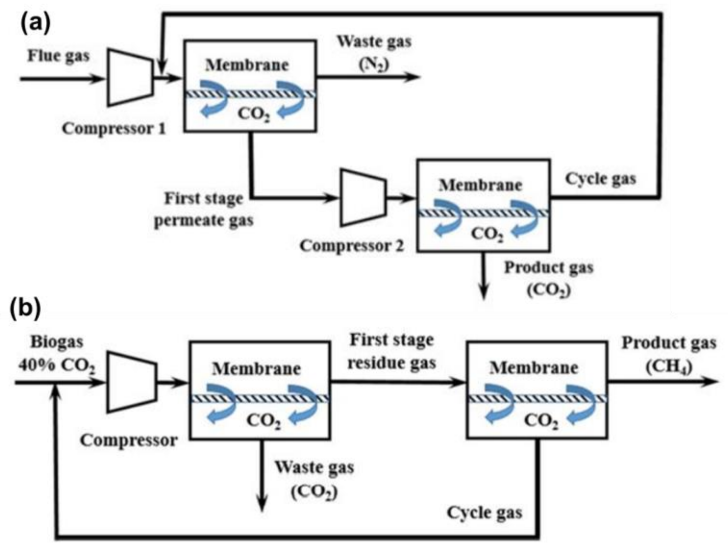

**Figure 14.** Process flow diagrams of the simulated two-stage $CO_2$ capture plant with a recycle stream in (a) 2nd stage for permeate stream and (b) 2nd stage for retentate stream. Reproduced from [36]

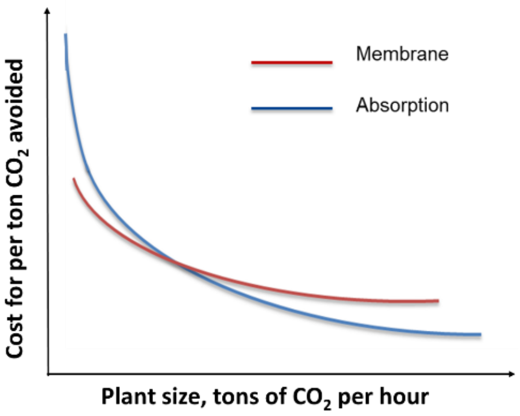

**Figure 15.** Qualitative comparison of $CO_2$ capture costs between membrane and absorption processes.

A general trend for the costs (per ton of $CO_2$ avoided) of various plant capacities, from small to large scale, is drawn based on the process simulation results in the literature[226, 228-234], showing the impact of plant capacity on $CO_2$ capture costs of the membrane-based and absorption-based processes, as presented in **Figure 15**. There exists a critical turn point when the trends presenting two technologies cross, indicating that when the plant size is below the critical capacity, i.e., a small to medium scale, the total cost using the membrane process becomes lower than that in an absorption process for per ton of $CO_2$ captured.

# 6. Industrial Applications

Membrane separation has been applied in industrial gas separation since the 1970s, such as to enrich oxygen, hydrogen separation in ammonia plants, and $CO_2$ removal from natural gas, but the market share for membranes has always been small. No application is there yet when $CO_2$ capture from flue gas is considered. However, especially in recent years, significant opportunities have been identified for $CO_2$ separation, thanks to the increased industrial acceptance of membrane technology and the demands for CCS actions. Membranes' unique advantages, such as compact system, low energy consumption, simple operation, and high modularity, leading to enormous technical, environmental, and economic benefits. The emerging membrane materials and fabrication techniques make membrane processes more competitive compared with other technologies.

In the past few decades, despite thousands of different membrane materials reported in the literature with $CO_2$ separation performance far above the Robeson upper bounds, sadly, only a few membrane materials have been applied in industrial processes or being developed towards industrial applications (e.g., performed pilot tests). Even for some membrane materials reported with superior separation performances, the costly synthesize route or challenges in fabricating lab-scale membranes into large scale or as asymmetric or TFC membrane forms may hinder their further development towards industrial applications. In fact, many membranes studied have been stopped at the lab scale with a test membrane area in the coin size range.

In this section, commercial membranes or membranes that undergo pilot studies are presented in the context of industrial $CO_2$ capture or separation processes. According to the key components of the separation, $CO_2$ separation applications can be grouped into three major types, namely $CO_2/CH_4$ separation, $CO_2/N_2$ separation, and $CO_2/H_2$ separation. Since industrial processes for $CO_2$ separation have very different process conditions, the requirements for membranes or issues to be considered in different applications vary significantly.

## 6.1 $CO_2/CH_4$ separation

### 6.1.1 Natural gas sweetening

Natural gas sweetening, or acid gas removal from natural gas, is by far the largest industrial application in membrane-based $CO_2$ separation, although membrane occupies only approximately 5% of the acid gas removal market where amine absorption technology has been dominating. Current key players in the $CO_2$ separation membrane market include Air Products, Honeywell UOP, Schlumberger, and MTR, Inc. (US), Air Liquide (France), Ube Industries (Japan) [235].

As one of the earliest commercial membrane materials since the 1950s, CA is still the most commonly used polymeric membrane today and is widely used for natural gas sweetening in industrial processes. Compared to the up-to-date gas permeation date in the literature, CA membranes display very low $CO_2$ permeability (~10 Barrer) and $CO_2/CH_4$ selectivity (~40 for single gas tests and ~20 for mixed gas tests) [236]. PI is another commercial membrane material (Matrimid) for $CO_2/CH_4$ separation, presenting a $CO_2/CH_4$ selectivity of between 30–60 [237]. PSf membranes have also been applied for $CO_2/CH_4$ separation, demonstrating permeability values of 20–40 Barrer and $CO_2/CH_4$ selectivity of 15–35 [238]. Even though these membrane materials exhibited relatively low $CO_2$ separation performances, their performances are reasonably stable over time, and to a certain extent, they show plasticization resistance. Since these membrane materials are available at low cost, their market shares in natural gas sweetening applications are assured. Information on the current commercially available gas separation membranes for natural gas sweetening applications is summarized in **Table SI-3** [239, 240].

Up to now, more than 20 large $CO_2$ membrane removal plants have been built over the world [241], such as the Cynara/Cameron plant in South East Asia and the Separex membranes in Spain (using UOP technology). A few smaller systems have also been developed. For instance, for offshore $CO_2$ separation systems, membrane technology has become a favorite choice due to the demands for small footprints and high environmental standards [242].

The problems of plasticization in this process are particularly severe because that natural gas sweetening is carried out under high pressures and both $CO_2$ and $CH_4$ cause plasticization, especially in the thin selective layers, resulting in less selective separation and hence more $CH_4$ loss from the process. Thus, the reduction of membrane selectivity must be considered when designing a process with potential plasticization issues.

### 6.1.2 Biogas upgrading

Biogas is a promising renewable fuel after being upgraded to bio-methane. Compared to natural gas, biogas has much higher $CO_2$ content in the feed, and the production capacity of biogas plants is much smaller. Due to the high $CO_2$ concentration and small to medium plant size, membrane separation is a comparatively cheap process with lower operating and capital costs and simpler and more compact membrane modules than other $CO_2$ separation technologies [243], as indicated in **Figures 16 (a)** and **(b)**. The energy demand is also much less for the membrane process.

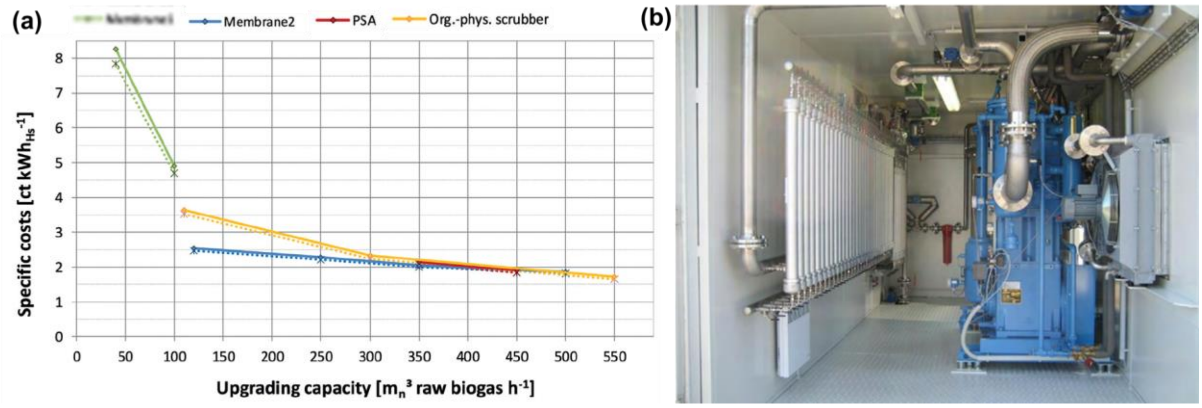

**Figure 16.** (a) Specific production costs of upgrading units in relation to capacity, reproduced from [232]; (b) Interior of a biogas upgrading membrane plant, reproduced from [244].

A large number of membrane materials have been reported for biogas upgrading, but commercial polymeric membranes for this process are still limited to CA, PSf, PEI, and PI, similar to membranes used for natural gas sweetening. Inorganic membranes, including carbon molecular sieves, zeolites, and silica membranes, were also reported for biogas upgrading applications, but no industrial application yet [245]. CMS hollow fiber membrane modules of a 2 $m^2$ area were made to test the membrane performance at the pilot plant with a capacity of processing 20 $Nm^3/h$ of biogas [246]. The techno-economical evaluation results show that in a multistage $CO_2/CH_4$ separation system, this carbon membrane consumed 22% less energy compared to commercial PI membranes.

Due to the limitation of either permeance and/or selectivity, multistage processes, 2-stage in most cases, are employed in membrane-based biogas upgrading processes to ensure high purity or low $CH_4$ losses [246] with one or both stages operate under elevated pressures. As raw biogas is produced at nearly ambient pressures, compressors become the major cost items of the biogas plants [228, 245, 246].

### 6.2 $CO_2/N_2$ separation

The process conditions of post-combustion flue gas, i.e., low $CO_2$ partial pressure, large and fully water-saturated flow, make it challenging for membrane separation. According to the literature[247], membranes with $CO_2$ permeance higher than 500 GPU and selectivity more than 40 may make membrane separation competitive with MEA absorption for $CO_2$ capture. Several other reports agree with this statement [248, 249] although they suggested different performance data as the threshold.

In the past decades, great efforts have been dedicated to developing membranes for $CO_2/N_2$ separation with $CO_2/N_2$ separation performances above the Robeson upper bounds. However, although numerous materials have been developed, only a small number of them were fabricated into TFC membranes with viable $CO_2$ flux [201], and even fewer were successfully developed to pilot scale [250].

Facilitated transport membranes have been successful in the development to pilot and demonstration scales. One example is the FTMs developed by the Norwegian University of Science and Technology (NTNU). Since 2011, pilot or pre-pilot tests based on FTM membranes have been carried out in several testing sites by NTNU with industrial partners (Air Products, etc.), including the Sines bituminous coal power station (Sines, Portugal) [74], the Tiller plant (Trondheim, Norway) [251], the Norcem cement factory (Brevik, Norway) [252], and the Colacem cement plant (Gubbio, Italy) [68, 253]. Flat sheet membrane modules were initially developed, but considering the large volume of flue gas, NTNU later changed its focus to hollow fiber membranes for higher packing density, as shown in **Figure 17a**. The fabricated membrane demonstrated good long-term stability over a testing period of up to 6 months [74]. The membrane also demonstrated excellent impurities resistance properties (e.g., SOx and NOx) [254]. NTNU's 2nd generation FTM membrane is under commercialization by Aqualung Carbon capture AS (Norway)[255].

Ohio state university (OSU) reported another effort of the field test for their FTMs containing both mobile and fixed-site amine carriers [256, 257] in spiral wound module configurations (**Figure 17c**). The $CO_2$ permeance of 1450 GPU with $CO_2/N_2$ selectivity of 185 was documented at 67 °C, and the module was demonstrated stable in a 500-h test. Tianjin University has also carried out pilot-scale projects of FTM membranes on $CO_2$ capture from flue gas. A membrane production facility with a productivity of 11000 $m^2/y$ was established

[258, 259]. A 3-stage membrane process using spiral wound modules was designed and installed for a $CO_2$ capture capacity of 50000 $Nm^3/y$. A $CO_2$ purity of up to 96.2% and a capture ratio of up to 81.3% were reported [258].

It is worth mentioning that, since FTMs are sensitive to $CO_2$ partial pressure in the feed, it is beneficial for the post-combustion flue gas conditions, i.e., low $CO_2$ concentration at near ambient pressure with a large volume [225]. As water vapor is involved in the facilitated transport mechanism, FTM membranes are also considered favorable for industrial applications because the pre-treatment step for water removal may be avoided. Nevertheless, no FTMs have yet been fully commercialized, mostly due to the remaining gap between pilot and industrial scale FTM membrane modules for high packing density and the issues in water management inside the FTM modules for optimal water profile to ensure sufficient facilitated transport effects.

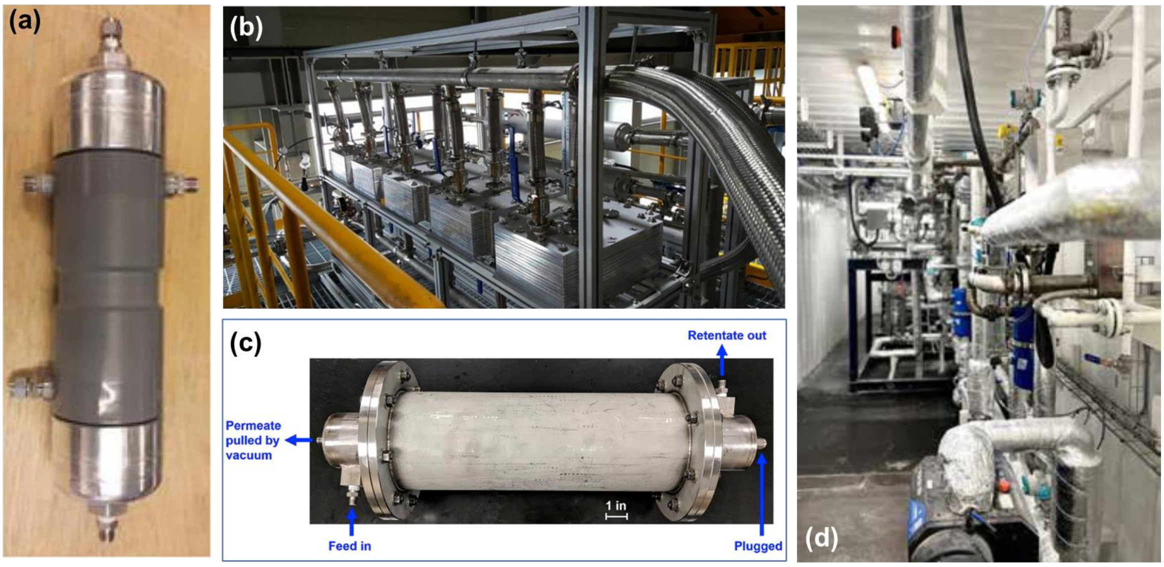

**Figure 17.** Membranes used in flue gas $CO_2$ capture pilot test. (a) Hollow fiber membrane module with a membrane area of 4.2 $m^2$ [251]; (b) plate and frame membrane module with a membrane area of 5.67 $m^2$ [260], (c) Spiral wound membrane module with a membrane area of 2.94 $m^2$ [261], and (d) Aqualung's hollow fiber membrane system installed at Nordkalk, Sweden[255].

Choi and coworkers have also performed a pilot test using hollow fiber membrane modules for flue gas $CO_2$ capture [262] by a 4-stage membrane process, in which $CO_2$ purity of 99.2% with a recovery of 91.5% was achieved using a polyethersulfone (PES) membrane with $CO_2$ permeance of only 60 GPU [262].

PolyActive membranes were tested in pilot scale for flue gas $CO_2$ capture in a plate-and-frame module, exhibiting $CO_2$ permeances of up to 1500 GPU with a $CO_2/N_2$ selectivity of > 55 at 20 °C [263]. It is claimed that the membrane can be manufactured into a 100 $m^2$ scale with reproducible separation performance [264]. Yoo et al. also performed a pilot test to study the defect effect of a GO-based hybrid membrane in a plate-and-frame module of nearly 6 $m^2$ (**Figure 17 b**) [260].

MTR is one of the pioneer companies in $CO_2$ capture pilot tests [248, 249]. Their first-generation Polaris membranes demonstrate $CO_2$ permeance of ~1000 GPU, while its second generation shows a doubled $CO_2$ permeance (~2000 GPU) with similar $CO_2/N_2$ selectivity (~50). In 2011, the 1st generation Polaris membrane as spiral wound modules was applied in a flue gas $CO_2$ capture pilot test with a scale of 1 ton of $CO_2$ per day, and later in 2015, it was extended to 20 tons of $CO_2$ per day [249]. This membrane presented good stability over 1000 h stability tests.

The reported pilot scale membranes and their performances can be found in **Table SI-4**. Some new polymeric membranes in the market with the potential for industrial $CO_2$ capture processes are listed in **Table SI-5** [247]. Overall, most of the tested membranes in the pilot test scale show reasonable stability and performance.

### 6.3 $CO_2/H_2$ separation

$CO_2/H_2$ separation is in most cases for pre-combustion $CO_2$ capture from syngas. Recently, $CO_2/H_2$ separation for bio-$H_2$ production has also been reported. Due to the significant differences in the properties of $CO_2$ and $H_2$, i.e., $H_2$ as a very small molecule has very high diffusivity while $CO_2$ is a highly condensable gas with very high solubility, the $CO_2/H_2$ separation through a membrane may be either $H_2$-selective [265, 266] or $CO_2$ selective [94], depending on the membranes' intrinsic properties. For $H_2$ selective membranes, high operation temperature is more favorable for higher $H_2$ diffusion that is enhanced at high temperatures [265, 267, 268], while for $CO_2$ selective membranes, low operation temperature is preferred as $CO_2$ solubility is higher at cold conditions except for FTM membranes; facilitated transport membranes show excellent performances even at elevated temperatures.[167]

#### 6.3.1 $CO_2$-selective membranes

$CO_2$-selective $CO_2/H_2$ separation membranes are mostly dense polymeric membranes showing high $CO_2$-philicity or $CO_2$-reactivity. PEO-based membranes are representative $CO_2$-selective membranes for $CO_2/H_2$ separation. $CO_2$-philic membranes without facilitated transport effect normally show low $CO_2/H_2$ selectivity (<30) [269]. Scholes et al. carried out $CO_2/H_2$ separation under pilot test conditions but with a lab-scale membrane area [270]. All the tested PDMS, Pebax, and cross-linked PEG membranes presented relatively low $CO_2/H_2$ separation performances under pre-combustion conditions.

However, if proper facilitated transport agents can be introduced into the membrane, high $CO_2/H_2$ may be achieved because that syngas is saturated with water vapor and the presence of water vapor is beneficial for $CO_2$ facilitated transport [67, 271]. For instance, by employing a sterically hindered amine membrane with facilitated transport carriers, Ho and coworkers reported a $CO_2/H_2$ selectivity of up to 300 with a $CO_2$ permeability of over 3000 Barrer [272]. With the same concept, FTMs with mobile carriers also present promising $CO_2/H_2$ selectivity [134].

In addition, a ceramic-carbonate dual-phase membrane consisting of a molten carbonate phase and metal or ceramic phase can be an interesting option for high-temperature $CO_2$ separation [273]. A high $CO_2$ flux with reasonably stable performance was obtained from dual-phase hollow fiber membranes [274].

### 6.3.2 $H_2$ selective membranes

$H_2$-selective membranes are one of the earliest industrialized membranes for $H_2$ recovery in ammonia plants [275]. However, obtaining high $H_2/CO_2$ selectivity is challenging due to the high $CO_2$ solubility in almost all polymers [276]. Glassy polymers with size-sieving ability generally exhibit $H_2$ selectivity over $CO_2$, such as high-free-volume, shape-persisting polymers. Polybenzimidazole (PBI) is a representative $H_2$ selective membrane material for $H_2/CO_2$ separation [277], which prefers higher operation temperature that favors $H_2$ diffusion but reduces $CO_2$ sorption, significantly improving the $H_2/CO_2$ selectivity [278]. In addition, embedding metal particles/wires with high $H_2$ solubility as nano additives to make hybrid membranes could promote $H_2$ transport through the membranes [279, 280]. O'Brien et al. [281] investigated the possibility of applying PBI-based hollow fiber membranes for $H_2/CO_2$ separation. The PBI membrane exhibited an $H_2/CO_2$ selectivity of over 40 and permeability of over 10 Barrer at 250 °C. A pilot-scale separation system of this membrane was designed, but no experimental results were reported on this work.

Inorganic membranes such as metallic membranes, microporous ceramic membranes, carbon molecular sieving membranes, and dense ceramic membranes have also been studied for $H_2/CO_2$ separation [282]. Compared to polymeric membranes, some inorganic membranes offer extremely high $H_2/CO_2$ selectivity due to unique transport mechanisms [283], such as the proton-conductive Pd-based membranes and molecular sieving CMS membranes. Besides, inorganic membranes could work at higher temperature conditions and handle high pressures. However, inorganic membranes are currently too expensive for industrial use for their high fabrication cost and not sufficient long-term stability performances.

Pd-base membranes are one of the most intensively studied $H_2$ separation membranes [284] as it only permeates $H_2$, giving almost infinite $H_2/CO_2$ selectivity, which could offer an $H_2$ purities of up to 99-99.995%, a purity impossible for any other membranes [285]. However, it is well-known that metallic $H_2$ separation membranes are sensitive to poisoning by components such as CO and $H_2S$; thus, a strict pre-treatment to remove these impurities is a must-have step to ensure long-term operation [286]. In recent years, three types of commercial Pd membranes have been applied in a 20 $Nm^3/h$ $H_2$ production plant, and all these membranes presented good stability over 1300 h [287]. In another study, Castro-Dominguez et al. [288] used a Pd multitube membrane module for coal-derived syngas separation. The module showed stable $H_2$ permeance of 16.2 $Nm^3\ m^{-2}\ h^{-1}\ bar^{-0.5}$ throughout 840 h. The produced $H_2$ purity was in the range of 98–99.87% [288]. It is also reported that SINTEF and industrial partners aim to upscale a Pd-based membrane for purifying 25-100 $Nm^3/h$ of $H_2$ in a pilot plant [289].

## 7. Big data and machine learning for $CO_2$ separation membranes

The integration of big data computing into the field of membrane science has been greatly facilitated by advancements in computer science. Machine Learning (ML) has emerged as a powerful computational tool capable of accurately forecasting the characteristics and functionalities of various materials [290, 291]. The combination of molecular simulation (MS) and ML has proven particularly valuable in the domain of $CO_2$ separation membranes. Recent studies have highlighted the impressive analytical capabilities of ML techniques, enabling swift exploration of a wide range of membrane materials and facilitating the identification of those with superior $CO_2$ separation properties.

However, despite promising results observed in laboratory settings, the industrial implementation of big data and ML remains limited. Only a small number of membranes have been successfully transitioned from ML models to practical applications in the laboratory, and even fewer have found their way in industry. This presents a significant gap between research and industrial production.

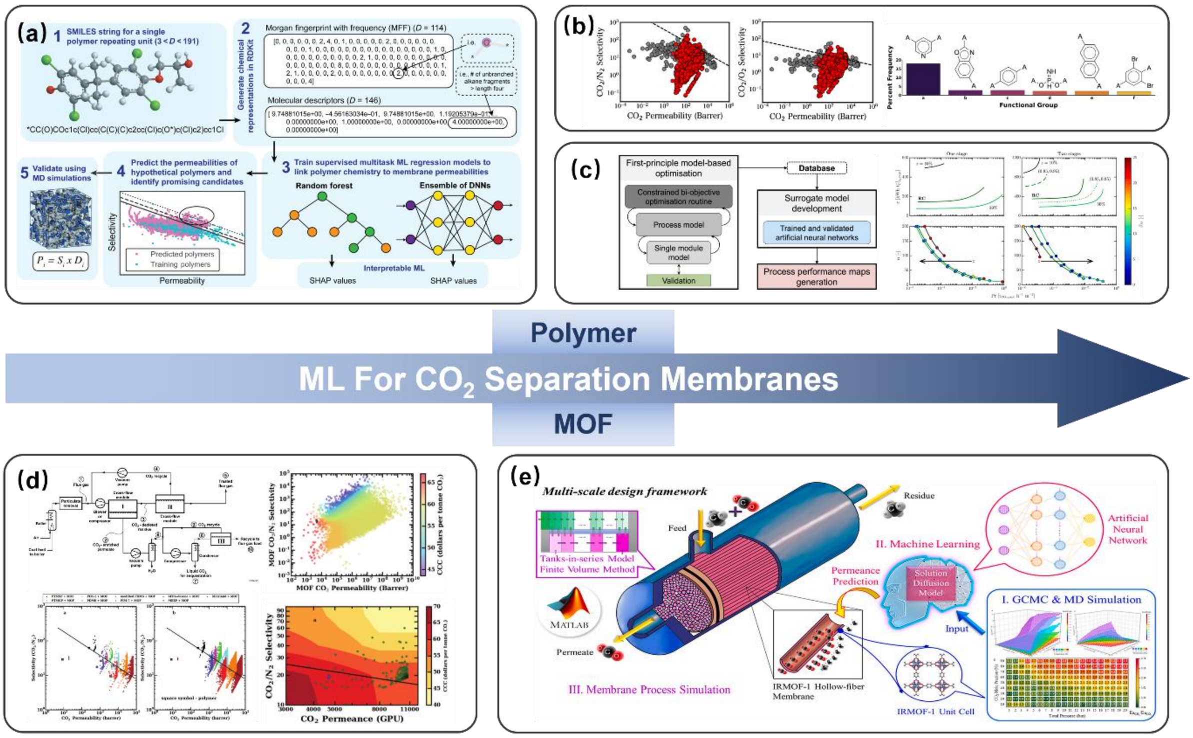

**Figure 18.** Overview of ML for $CO_2$ separation membranes. (a) Discovery of polymer membranes based on interpretable ML. (This illustration was published in [292], Copyright Sci. Adv.); (b) Design of polymer membranes based on ML and GA (reproduced from [293]), (c) a multi-objective optimization agent model based on ANN (adapted from [294]), (d) large-scale high-throughput screening of MOF-based MMMs considering economics (reproduced from Ref. [295] with permission from the Royal Society of Chemistry.), (e) Multiscale membrane processes with integrated MS, ML, and process modelling. (reproduced from [296])

### 7.1 ML for polymeric membranes

Polymer membranes are widely used in various industrial applications, and recent research has been focusing on enhancing their gas permeability properties. The abundance of structured data plays a crucial role in exploring the potential industrial applications of membranes.

To predict the gas permeability of millions of polymer materials, Yang et al.[292] employed chemical descriptors and ML models, such as deep neural networks and random forest models (**Figure 18a**). Remarkably, they discovered that a significant number of polymeric materials exceeded the latest upper limit set for the $CO_2/CH_4$ separation system. Additionally, characteristic contribution analysis and molecular dynamics simulations were used to identify the key factors influencing gas permeability.

In parallel, researchers at Caltech made an innovative discovery in the field of $CO_2$ separation membranes. Yasemin et al.[293] proposed a methodology that combines ML performance prediction and genetic algorithm-guided design for $CO_2$ separation membrane material design. By utilizing experimental permeability data for $CO_2$, $N_2$, and $O_2$, they developed ML models and employed genetic algorithms to identify 16,000 high-performance polymeric materials (**Figure 18b**). Notably, imines and polyethers emerged as promising candidates for $CO_2$ separation membranes based on these findings.

However, beyond the chemical structure of the polymeric materials, the process and operating conditions also play a crucial role in membrane performances. **Figure 18c** illustrates a comprehensive approach integrating density functional theory (DFT) simulation, ML, and process modeling as proposed by Antonio et al[294]. They developed a multi-objective optimization agent model based on artificial neural networks (ANN) to strike a balance between specific power consumption and productivity in $CO_2$ membrane separation processes. This data-driven methodology provides rapid and efficient optimization of process performance in less than 200 milliseconds.

Collectively, these studies highlight the significant contributions of ML and data-driven approaches in advancing the field of polymeric membranes-based $CO_2$ separation. By encompassing property prediction, material design, and process modeling, researchers are able to gain a comprehensive understanding of polymer membranes and optimize their performance for industrial applications.

### 7.2 ML for MOF-based membranes

In recent years, there has been growing interest in the industrial application of MOFs for $CO_2$ separation membranes. The exceptional porosity of MOFs has made them highly attractive for this purpose [297].To further advance the research on MOFs, data-driven approaches have been employed, particularly focusing on the combination of ML and MS [298-300]. One of the key areas of investigation is the evaluation of gas separation performance in membranes by utilizing ML techniques alongside MS [301]. This approach has allowed researchers to assess the viability of various MOFs with diverse synthetic and structural properties. Although the implementation of MOF-based membranes in industrial settings may require additional time, significant progress has been made at the laboratory stage.

Integrating MOFs into polymers as MMMs presents a promising option for industrial-scale applications. This approach considers factors such as cost, processing difficulty, and performance evaluation. To explore the vast number of potential MMMs, Samir et al. [295] conducted a high-throughput screening of over 100,000 MOFs. The experimental permeability of polymers combined with MOFs provided valuable data for the analysis, resulting in the identification of millions of potential MMM combinations. Additionally, economic optimizations were performed for different stages of membrane production, considering industrial conditions such as flow rate, capture fraction, pressure-temperature, among others. The outcome of these optimizations yielded numerous industrial MMM candidates that effectively balanced membrane performance and economic feasibility (**Figure 18d**).

Beyond economic considerations, ML techniques also offer significant contributions to multi-scale process modeling, ranging from the atomic level to full-scale plant operations. Xi et al.[296] demonstrated the integration of MS, ML, and process modeling to explore the industrial potential of MOF membranes at an atomic scale and the full workflow is shown in **Figure 18e**. By calculating membrane performance metrics, such as $CO_2$ adsorption isotherms and permeability, through MS, they obtained crucial data for analysis. This permeability prediction was then incorporated into an Artificial Neural Network (ANN) based model, specifically a tandem tank model of hollow fiber membrane separation processes. This integrated model dynamically predicted gas permeability and selectivity of IRMOF-1 membrane under varying operating conditions, allowing for higher recovery rates with smaller membrane areas.

In summary, the combination of ML, MS, and process modeling presents a promising pathway for the industrial application of MOF membranes. The ongoing efforts in large-scale screening, economic evaluation, and multi-scale modeling contribute to the advancement of this field, bringing it closer to the realization of efficient and cost-effective MOF-based membrane technologies.

## 8. Summary and Outlook

According to the literature, tremendous research efforts have been devoted to developing novel membrane materials with high $CO_2$ separation performances. The $CO_2/N_2$, $CO_2/CH_4$, and $CO_2/H_2$ separation upper bounds have been updated several times, pushing towards the upper right direction, falling into the zone where membrane technology is more competitive than chemical absorption. The noteworthy advances in new membrane materials and processes have made an enormous impact on membrane technology, providing valuable knowledge not only to academia but also to the industry. The industrial acceptance of membrane technology has significantly increased, and more and more commercial opportunities for $CO_2$ capture and separation by membranes have been identified. However, by now only a handful of membranes have been commercially applied and a few are undergoing upscaling toward industrial applications. Currently, most gas separation membranes reported in the literature have a TRL of <5, showing a big gap between research and industrial implementation of the technology. Following obstacles may have hindered new membranes from progressing further to a higher TRL level:

(1) A significant part of membrane materials research has focused too much on eye-catching concepts and compelling performance data without considering the possibility of membrane being fabricated into asymmetric or TFC forms or scaling up membranes to industrial scale. Some membrane materials may be too costly, or their fabrication procedures are too complicated and not reproducible, or prone to failure.

(2) A large amount of membrane performance data in the literature have been obtained using single gas testing, or better, in a simulated gas mixture without considering the effects of impurities in the real process gas streams and separation conditions (e.g., RH, T, and P). The stability and durability issues are overlooked. In addition, the performances of the up-scaled membranes may not be the same as their lab-scale performances. In this case, even membranes reported with excellent performances may

not be sufficient to meet the industry's separation requirements for high purity and recovery.

(3) The up-scaled module configuration may not be able to maintain the optimal flow condition, such as concentration polarization, pressure drop, and lack of water in FTM may make the module performance far below the membrane performance obtained in the lab.

(4) Currently big data and ML guided membrane processes are still far from industrial applications. Although data-driven models show great potential for material performance prediction and design, there are no good solutions to the problems of high-dimensional complex variables, material synthesizability, and integrated cross-scale modelling in membrane industrialization.

Membrane scientists and engineers from the industry are expected to work together to address the issues and bridge the gap between research and the industry needs. In addition to keeping the excellent research efforts in developing high performance membrane materials and effective fabrication techniques, it is crucial to enable and accelerate the implementation of existing membranes in the industrial applications, starting from promoting membranes in small to medium-sized processes, such as offshore CCS and carbon capture for shipping and cement manufacturing. There is no need to compete with absorption technology for its existing market but to explore new applications where the unique advantages of membranes can make them unrivaled. Stability and durability studies for different applications should be best started at an early stage, such as the material screening stage, when the potential to upscaling the membranes should be considered. Attention also needs to be paid to the optimization of membrane module configuration and flow patterns, such as with the aids from modeling and simulation studies.

Although there are still many challenges to be addressed, membrane technology is already part of the solutions to today's climate change problems, and will make an even greater contribution in the near future with the current advances and the foreseeable huge progress.

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# Supporting Information

# Membranes for $CO_2$ Capture and Separation: Progress in Research and Development for Industrial Applications

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Table **S1**. $CO_2$ separation performances of commercial $CO_2$ separation membranes [1]

| Membrane materials | Testing conditions | | | Performances | | |
|---|---|---|---|---|---|---|
| | T (°C) | P (bar) | $CO_2/N_2$ | *$P_{CO2}$ or $P_{CO2}/l$** | | Selectivity |
| PSf | RT | 4 | Single gas | 0.71 | Barrer | 1.6 |
| PSf | 25 | - | Single gas | 6 | Barrer | 38 |
| Matrimid® 9725 | 25 | 10 | Single gas | 6.2 | Barrer | 27.5 |
| Matrimid® 9725 | 35 | 9 | 50/50 | 4 | Barrer | 23 |
| Matrimid® 5218 | 30 | 2 | 10/90 | 8 | Barrer | 27 |
| Matrimid® 5218 (HF) | 35 | 4 | 55/45 | 16* | GPU | 28 |
| CA | - | 3 | Single gas | 401* | GPU | 32.92 |

*Please note that the listed data were collected from the literature with process conditions different from the industrial conditions, since performance data are usually treated as confidential by membrane vendors.

**Table S2.** Features of membrane module configurations for gas separation

| **Module type** | **Plate-and-frame** | **Spiral wound** | **Hollow fiber** | **Tubular** |
|---|---|---|---|---|
| **Packing density ($m^2/m^3$)** | 50-400 | 100-1500 | 500-10,000 | 30-500 |
| **Area per module ($m^2$)** | 2-30 | 10-50 | 50-500 | 2-30 |
| **Costs ($/$m^2$)** | 300-2000 | 50-500 | 10-100 | Material based |

*The costs are estimated based on market prices of similar products for other applications.

**Table S3.** Representative commercially available membranes for natural gas sweetening [2]

| **No.** | **Membrane trade name** | **Vendor/licensor** | **Membrane materials** | **Membrane module type** | **Website** |
|---|---|---|---|---|---|
| **1** | Z-TOP | MTR | perfluoro | SW | www.mtrinc.com |
| **2** | LPG-Sep | MTR | Polymeric | SW | www.mtrinc.com |
| **3** | Separex$^{TM}$ | UOP | CA | SW | www.uop.com |
| **4** | Medal | Air liquide | PI | HF | www.medal.airliquide.com |
| **5** | PrismTM | APCI | PSf | HF | www.airproducts.com |
| **6** | $CO_2$ separation membrane | UBE | PI | HF | www.ube.com |
| **7** | Nitrosep TM | MTR | polymeric | SW | www.metric.com |
| **8** | AIRRANE | AIRRANE | PSf | HF | http://www.airrane.com/ |
| **9** | CYNARA | Schlumberger | CA | HF | www.slb.com |
|  | Apura | -- | -- | SW | www.slb.com |
| **10** | SEPURAN® | EVONIK Industries | Fluoropolymer | HF | www.membrane-separation.com |
| **11** | -- | GAS RNG SYSTEMS | -- | HF | www.gasrng.com |
| **12** | -- | New point gas | CA | SW | www.newpointgas.com |
| **13** | UBE CO2 separator | UBE | -- | HF | www.ube.com |
| **14** | -- | fujifilm | -- | SW | www.fujifilmmembranes.com |

*HF: hollow fiber, SW: spiral wound, PF: plate-and-frame

**Table S4**. Representative membrane used in flue gas $CO_2$ capture pilot tests

| Membranes | Module configuration* | $CO_2$ permeance (GPU) | Selectivity | Membrane area ($m^2$) | Gas flow rate ($m^3$(STP)/h) | ref |
|---|---|---|---|---|---|---|
| PVAm | PF | 75-225 | 80-300 | 4.2-10 | 6–24 | [3] |
| GO-hybrid | PF | -- | -- | 5.67 | 30 | [4] |

| | | | | | | |
|---|---|---|---|---|---|---|
| PES | HF | 60 | 40 | -- | 30-40 | [5] |
| PVAm | HF | -- | -- | 8.4-18 | -- | [6] |
| PolyActive | PF | 1125 | 43-60 | 12.5 | 50-80 | [7] |
| FT membrane | SW | 1013 | 96 | 25 | 15–35 | [8] |
| Polaris | SW | 1000 | 50 | -- | 120-180 | [9] |
| FT membranes | SW | 1450 | 185 | 1.4-2.94 | -- | [10] |

**Table S5.** Representative commercially available $CO_2$ capture membranes for $CO_2/N_2$ separation [11]

| Membrane name | Manufacturer | $CO_2$ permeance(GPU) | $CO_2/N_2$ selectivity | polymer |
|---|---|---|---|---|
| Medal | Air liquids | -- | ~50 | PI |
| Prisim | Air products | 760 | 13, | PSf |
| Polaris gen 1 | MTR | 1000 | 50 | PE-PA block |
| Polaris gen 2 | MTR | 2000 | 49 | PE-PA block |
| PolyAcitve | Helmholtz-Zentrum | 1480 | 55 | PEO-PBT |
| Permselect | Permselect | 32.5 | 12 | PDMS |

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