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# $CO_2$ Capture and $H_2$ Purification: Prospects for $CO_2$-Selective Membrane Processes

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## Introduction

$CO_2$ capture from fuel and flue gases is widely believed to be the most important method to combat climate change. In this context, there are three technically plausible strategies (Figure 1): post-combustion capture, oxy-combustion, and precombustion capture.[1] In post-combustion capture (PCC), $CO_2$ has to be separated mainly from $N_2$, the major diluent in the air used for combustion of coal or natural gas, the two most commonly used fuels in thermal power plants. Other and minor components include water vapor, $O_2$, $SO_2$ and $NO_x$. In oxy-combustion, by using $O_2$ instead of air for combustion, an almost pure stream of $CO_2$ can be obtained for sequestration. The only significant separation challenge exists in producing the pure $O_2$ before fuel combustion. Although alternatives, including membranes, to the commercial cryogenic distillation are being studied in this context, they will not be a part of this discussion. In a newer approach to produce large-scale electricity, fossil fuels or biomass can be gasified into a cleaner gaseous fuel syngas ($CO + H_2$), which can then be used to produce electricity via gas turbines or fuel cells. To capture $CO_2$ before deriving energy and/or produce pure $H_2$ as a preferred fuel or chemical feedstock, the syngas can be subjected to a water-gas shift (WGS) reaction ($CO + \text{Steam} \rightleftharpoons CO_2 + H_2$). In precombustion capture (PrCC), $CO_2$ has to be separated from $H_2$. Other and minor components include water vapor, $H_2S$, and trace amounts of Ar, $N_2$, $NH_3$ and $CH_4$.[2]

Membrane separation, adsorption, and solvent absorption are the three main processes studied for the previous applications. Being the most well-developed of the three, solvent absorption has been analyzed in-depth by the Dept. of Energy (DOE).[2] For PCC using the state-of-the-art (SOTA) monoethanolamine process, the cost of electricity (COE) increase in a typical coal-based power plant is predicted to be about 85%. For PrCC in a coal-based integrated gasification combined cycle (IGCC) power plant, the Selexol-based physical solvent system is expected to increase the COE by about 39%. On the other hand, the economic targets set by DOE for the practical integration of $CO_2$ capture, compression and sequestration are 35 and 10%, respectively, for the conventional and IGCC power plants with 90% $CO_2$ recovery at a $CO_2$ purity of at least 95%.[2,3] It is obvious that the SOTA absorption processes are about two to four times more expensive than the set targets. This also represents an opportunity for new processes to emerge as sustainable $CO_2$ capture technologies. Membranes hold great potential for $CO_2$ capture due to numerous advantages including potentially lower energy consumption, operational simplicity, compactness, and ease of maintenance due to absence of moving parts. Both $CO_2$- and $H_2$- selective membranes have been shown to be promising for PrCC.[4,5]

Depending on the end goal, the $H_2$ purity and impurity constraints will be decided. Energy production via gas turbine, by itself, does not impose a stringent $H_2$ purity requirement. However, $H_2$ is an important chemical, used for hydrogenation and hydrotreating in refineries and chemical plants and production of ammonia, methanol, etc. Also, with greater emphasis on proton-exchange membrane (PEM) fuel cells for clean and efficient energy generation, the demand for ultra-high-purity ($<10-100$ ppm CO, $<10-100$ ppb $H_2S$)[6,7] $H_2$ can grow further. PEM fuel cells can be especially advantageous in on-board reforming for transportation and small scale off-shore power generation.

Industrially, high-purity $H_2$ is generally produced using pressure swing adsorption or amine scrubbing. Both these processes suffer from higher energy consumption due to

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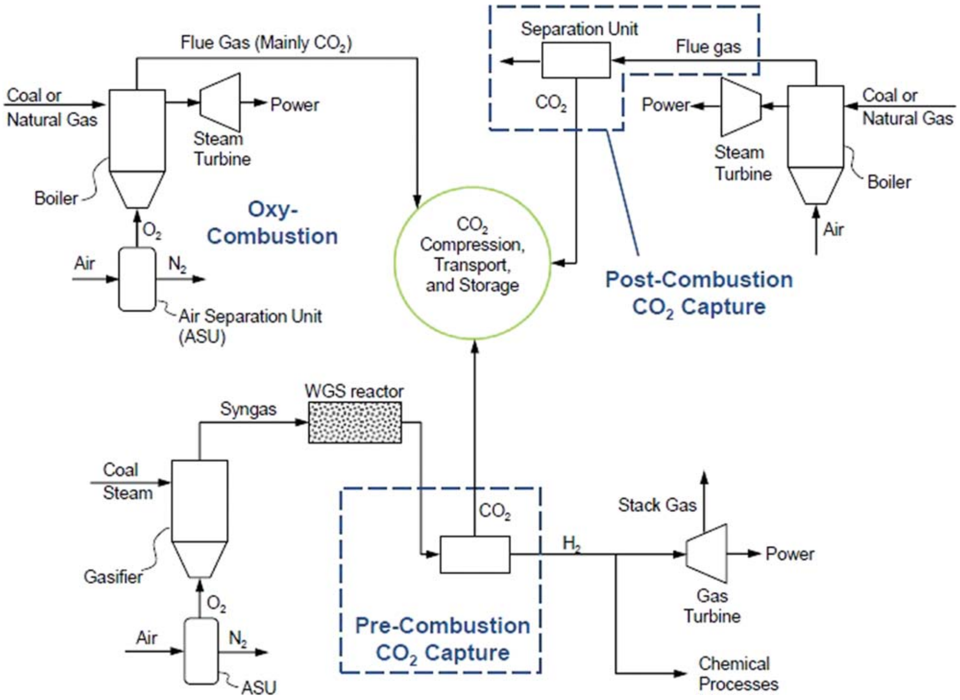

Figure 1. Strategies for $CO_2$ capture.

sorbent regeneration. Additionally, for the former, the $H_2$ recovery is generally less than 90%. Also, when producing pure $H_2$ is of a high priority, retaining $H_2$ at high pressure is energetically favorable. In this regard, a highly $CO_2$-selective membrane, while reducing the $H_2$ losses during separation, can also aid in reaching almost 100% CO conversion in an otherwise equilibrium-dominated low-temperature WGS reactor.

In the following discussion, an overview of the recent progress on important $CO_2$-selective membranes/membrane processes for all the above applications is presented. In addition, important considerations and directions for future research have been emphasized.

## Post-Combustion Carbon Capture

Several studies have looked at the technical and economic feasibility of membrane-based PCC.[8–11] Flue gas after desulfurization (FGD) in a typical coal-based power plant is humid and at close to 1 atm pressure and 50–60°C with $CO_2$ and $N_2$ concentrations at 10 – 15% and close to 70%, respectively.[2] The low $CO_2$ partial pressure of $0.1-0.15$ bar implies an inherently low driving force for $CO_2$ transport. In this context, it is important to recognize the important parameters describing the membrane performance, flux $J_i$ of component $i$ and membrane selectivity $\alpha_{i/j}$ of component $i$ over component $j$

$$J_i = \frac{P_i}{l}(p_f \times x_i - p_s \times y_i) \tag{1}$$

$$\alpha_{i/j} = \frac{P_i}{P_j} \tag{2}$$

where $P$ is the permeability, $l$ is the membrane (selective layer) thickness, $p_f$ is the feed pressure, $p_s$ is the permeate pressure, $x$ is the feed-side mole fraction, and $y$ is the permeate-side mole fraction. The permeance of component $i$ is given by $P_i/l$. A binary mixture of $i$ and $j$ for $CO_2$ and $N_2$, respectively, is assumed for simplicity. In a regime of limited pressure ratio ($p_f/p_s = 5 - 10$) such as for this application,[10,11] the pressure ratio affects not only the $CO_2$ flux but also the $CO_2$ purity due to its unequal effects on the fluxes of $CO_2$ and $N_2$. A lower pressure ratio at a given selectivity will reduce the $CO_2$ purity. Also, higher recoveries for $CO_2$ can further reduce its driving force and increase the membrane area. This can also reduce the $CO_2$ purity due to greater $N_2$ losses. It has been shown that 90% $CO_2$ recovery with a larger than 95% $CO_2$ purity are impossible in a single stage (without recycle) at practical pressure ratios of 5 – 10, generated by feed compression and/or permeate evacuation.[8,9]

To overcome this problem, simulation studies have used permeate staging and permeate/retentate recycling effectively to reach the desired recovery and purity goals.[9,10] Although such multistage processes can meet the process targets, they do not offer significant cost and energy savings over the SOTA amine process. More recently, however, researchers from Membrane Technology and Research (MTR), Inc. came up with an innovative design, using combustion air as sweep gas at 1 bar, to provide an almost "free" driving force for separation in a second membrane stage (Figure 2a).[10] The second stage is used to recycle and increase the $CO_2$ concentration in the flue gas entering the first stage that generates the $CO_2$ product stream. Using this process, it was argued that it is significantly more important to increase the $CO_2$ permeance for membrane area and cost reduction and increasing selectivity beyond 40 – 50 will not be useful due to the practical limit on obtainable pressure ratios. The necessity to have a positive driving force for $CO_2$ (Eq. 1) also means that $CO_2$ enrichment ($y_{CO_2}/x_{CO_2}$) is limited by $p_f/p_s$. In other words, higher selectivity can reduce the

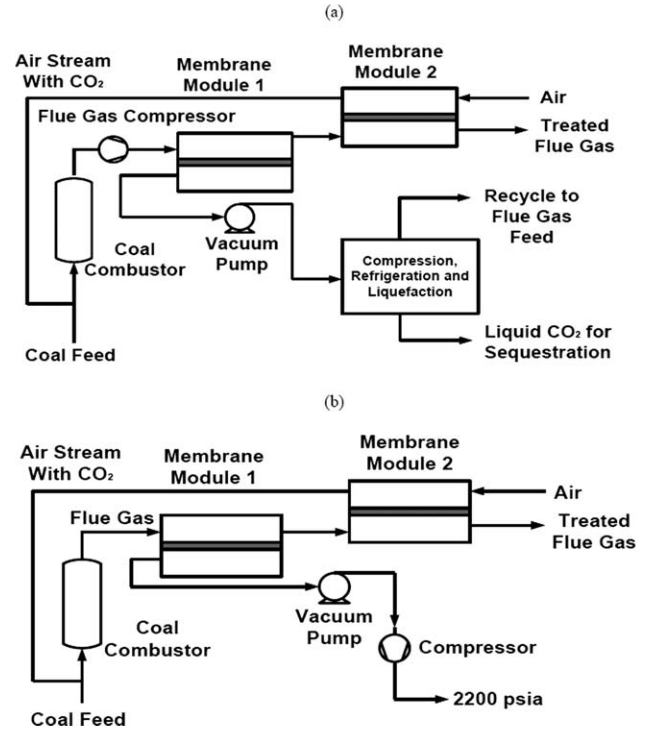

Figure 2. Membrane-based post-combustion capture processes (adapted from Ref. 10 and 11).

required pressure ratio but very high selectivities might not be useful. To reach $CO_2$ purity larger than 95%, they combined cryogenic distillation as an end step in a hybrid process. The optimum feed and first-stage permeate pressures were 2 bars and 0.2 bar, respectively. Although the economic analysis was not detailed, the air-sweep design was shown to be considerably more cost and energy-efficient than other schemes.

Other researchers have shown that a higher $CO_2/N_2$ selectivity (>100) is required to achieve high $CO_2$ purities (>90% purity).[8,9,11] Detailed economic analysis targeted toward achieving the DOE cost targets shows that a purely membrane-based simpler air-sweep process (Figure 2b) can achieve the targets at a $CO_2/N_2$ selectivity of about 150 and a $CO_2$ permeance of 3000 GPU (1 GPU = $3.35 \times 10^{-10}$ mol/(m$^2$.s.Pa)) at the flue gas feed pressure of about 1 atm.[11] There are also other considerations which demand a higher selectivity. The $CO_2/O_2$ selectivity is usually lower than the $CO_2/N_2$ value for any membrane. The ratio of the two depends on the specific membrane material. Higher $CO_2/O_2$ selectivities can reduce the $O_2$ losses in the second stages of the aforementioned processes. Curbing these losses will be important to maintain the minimum $O_2$ concentration at the boiler inlet (~18%), and help increase the $CO_2$ level before the first membrane stage. $CO_2$ concentrations approaching 20% or higher in the flue gas entering the first stage could help in reducing the overall costs more.[11]

It should be noted that although the aforementioned combination of transport properties has not yet been achieved, recent studies have shown that $CO_2$ permeances higher than 2000 GPU are attainable by some polymeric and inorganic membranes. Anyway, it is useful to look at the recent progress, advantages and disadvantages of different types of membranes. Figure 3 depicts the different molecular mechanisms by which $CO_2$-$N_2$ separation is achieved in these membranes.

### *Polymeric solution-diffusion membranes*

It is fairly well-accepted that gas transport through polymeric materials takes place by the solution-diffusion mechanism. The *i/j* selectivity can also be written as

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j} \tag{3}$$

where *S* is the solubility, and *D* is the diffusivity. The $CO_2$ and $N_2$ molecules are similar in their kinetic sizes at 3.3 Å and 3.6 Å, respectively.[12] The diffusivity selectivity ($D_{CO_2}/D_{N_2}$) is, therefore, not substantially different from 1. However, the quadrupole moment of the $CO_2$ molecule is about three times and polarizability about twice that of the $N_2$ molecule.[13,14] These factors combined with higher $CO_2$ condensability (critical temperatures: $CO_2$:304.1 K, $N_2$:126.2 K)[15] mean that the solubility selectivity ($S_{CO_2}/S_{N_2}$) is generally favorable (> 1) toward its preferential transport. To cross the well-known Robeson's upper bound on selectivity-permeability trade-off, two strategies were proposed by Freeman.[16] In the aforementioned context, the first is to increase $S_{CO_2}/S_{N_2}$. Polar ether linkage (—C—O—C—) can selectively interact with $CO_2$. In this way, block copolymers comprising of soft (rubbery) poly(ethylene oxide) (PEO) type segment and hard (glassy) segment like polyamide, polyester, etc. have been extensively studied. This approach can reduce crystallization of long polyether segments[15,17] with the hard segments also contributing to mechanical strength and film-forming ability. Blending with small poly(ethylene glycol) (PEG) type molecules and crosslinking can also reduce/avoid the polyether crystallization. The second strategy to cross the upper bound is to increase the chain stiffness while simultaneously increasing the interchain spacing or free volume. Some recent work on microporous glassy polymers has focused on this strategy.

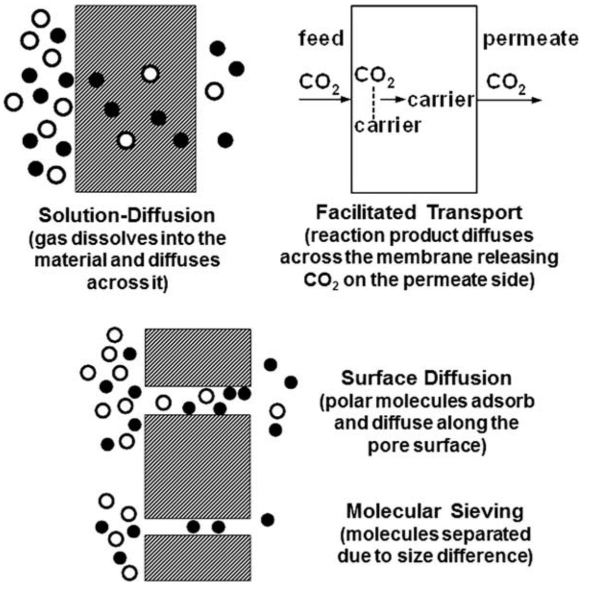

Figure 3. Mechanisms of gas transport through different membrane materials.

Pebax® and Polyactive® are the most commonly studied commercial block copolymers with polyamide and polybutyleneterephthalate hard segments, respectively. $CO_2$ permeability and $CO_2/N_2$ selectivity for these materials tend to be 100 – 150 Barrers (1 Barrer = $3.35 \times 10^{-16}$ mol-m/($m^2$.s.Pa)) and about 45, respectively, at 35°C.[15,18] Molecular reengineering of copolymers including subtle changes in chemistry and/or length of both hard and soft segments have produced from upto 50% to about four-fold rise in $CO_2$ permeability without a significant drop in selectivity.[18,19] Rubbery polyphosphazenes containing 2-(methoxy ethoxy) ethanol as a polar side chain have also shown comparable performances to that of commercial block copolymers.[20]

Adding amorphous polyether moieties can increase both the $CO_2$ solubility and the free volume. Blending block copolymers with PEG, PEG dimethyl ether and PDMS-PEG (PEG-grafted polydimethylsiloxane based oligomer with 80 wt % PEG) have all been attempted.[19,21] Blending Pebax®1657 with PEG in a 50:50 weight ratio doubled its $CO_2$ permeability with no drop in selectivity, while with PEG dimethyl ether, a less hydrogen bonding molecule with a bulkier end group, the $CO_2$ permeability increased eight-fold with the selectivity reducing slightly from 47 to 43 at 30°C.[21] A similar result has been obtained with PDMS-PEG.[19] The selectivity drop is presumably due to an excessive increase in the flexibility of the polymer matrix and related weakening of its size-sieving ability. Lin and Freeman synthesized highly crosslinked and branched network copolymers, based on poly(ethylene glycol) diacrylate and poly(ethylene glycol) methyl ether acrylate.[17] This method helped them to introduce more ether groups in the polymer, thereby obtaining a $CO_2$ permeability of about 570 Barrers with a selectivity of 41 at 35°C.

Poly(1-trimethylsilyl-1-propyne) (PTMSP), a glassy polymer with high-free volume is the most permeable polymer known. However, due to its unfavorably high interchain spacing, diffusivity selectivities are poor. Recently, Budd et al. reported an exceptionally high $CO_2$ permeability larger than 11,000 Barrers with a reasonable selectivity of greater than 25 at 23°C for PIM-1, a microporous polymer (PIM stands for "polymers of intrinsic microporosity").[22] There was no fast aging characteristic of high-free volume glassy polymers. More recently, Du et al. used click chemistry to convert the nitrile groups of PIM-1 to tetra-azole groups which can interact with $CO_2$. They obtained a $CO_2$ permeability of 2000 Barrers with a selectivity of over 40 at 25°C.[23]

All the work discussed previosuly explores pure material properties using thick films (several microns). To obtain a high permeance, the selective layer has to be much thinner. Although phase inversion has been successfully employed for glassy polymeric materials to fabricate integrally skinned structures, softer polymers are not amenable to this technique. Dip-coating is often employed to fabricate multilayer thin-film-composite (TFC) membranes. The technique requires working with dilute solutions. To reduce infiltration of polymer solution into the porous support and form a defect-free film, the approach of using an intermediate layer of highly permeable material like PDMS is well-known.[24,25] Using this approach, a $CO_2$ permeance larger than 2000 GPU has been achieved using block copolymers.[25,26] The intermediate layer approach requires the film to be formed on a dense hydrophobic PDMS surface. The coating solution with small molecules might have inferior film forming ability relative to that with only polymer at the same total solids concentration. Hence, there will be a trade-off between the small molecule content and the obtainable membrane thickness for blends. Similar and other inherent thin-film fabrication challenges exist for the crosslinking techniques too.

Thin-film-composite (TFC) membranes have conventionally been scaled up as spiral-wound modules due to ease of fabrication. General Electric (GE) is developing scalable coating methodologies for making TFC hollow fibers with a polyphosphazene selective layer.[27] Fiber diameters of about 100 $\mu$m or lower can result in a higher packing density than spiral-wound modules (2000 – 5000 $m^2/m^3$ vs. 1200 – 3400 $m^2/m^3$, respectively) in the case of no pressure drop issue, which can reduce the membrane cost per unit area.

The aforementioned materials have attractive properties like relatively high tolerance to impurities and water vapor, excellent film-forming properties and the ability to be easily fabricated into cost-effective compact modules. The biggest limitation, however, is their low selectivity. All the aforementioned selectivities drop to below 30 at the flue gas temperature of 50 – 60°C. Competitive sorption of impurities and water vapor and/or plasticization can lower the performance.[28,29] Lastly, some aging does occur in glassy polymer membranes, and it could be even faster in thin films.

### *Facilitated transport membranes*

In facilitated transport membranes, the $CO_2$ molecule reacts with carrier molecules in the membrane through a selective reversible chemical reaction by which its solubility is greatly enhanced. The nonreactive gases like $N_2$, $H_2$ and CO, etc. get transported purely by solution-diffusion. Consequently, high selectivities for $CO_2$/nonpolar gases can be readily achieved. The $CO_2$-carrier reaction product can diffuse through the membrane (small mobile carrier molecules) or $CO_2$ can "hop" from one site to another of a fixed-site carrier molecule. On the permeate side of the membrane with a relatively low $CO_2$ partial pressure in the gas phase, the $CO_2$-carrier reaction product can release $CO_2$ through the reverse reaction. Due to its acidic nature, $CO_2$ can react with amines and alkaline carbonate solutions. In the most common reactions, $CO_2$ gets hydrated, which is then converted into a bicarbonate ion by the base (Eqs. 4 and 6). $CO_2$ can also react with primary and secondary amines to form a carbonate ion (Eq. 5). Important reactions of amines and basic carbonate ion with $CO_2$ are shown here

$$CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons R\text{-}NH_3^+ + HCO_3^- \quad (4)$$

$$CO_2 + 2R\text{-}NH_2 \rightleftharpoons R\text{-}NH_3^+ + R\text{-}NH\text{-}COO^- \quad (5)$$

$$CO_2 + CO_3^{2-} + H_2O \rightleftharpoons 2HCO_3^- \quad (6)$$

As indicated by the aforementioned equations, water aids in the $CO_2$ uptake by the membrane which is made plausible by its presence in flue gas. The earliest facilitated transport membranes were fabricated in "immobilized" or "contained" liquid configurations. Important disadvantages of these membranes are the fabrication and stability challenges associated with reducing the membrane thickness and obtaining a higher productivity. In a more practical approach, the carriers can be part of a water-swollen polymer matrix. They can either be ions bounded by electrostatic forces to polyelectrolytes or ion-exchange polymers, be dispersed in a hydrophilic matrix or tethered to polymeric chains of a fixed site carrier molecule. More recent and promising work has focused on mobile small carriers and/or fixed-site carrier molecules that contain amino groups covalently bonded to the polymeric backbone.

Following the work of Ho[30,31] and using a highly hydrophilic blend of crosslinked poly(vinyl alcohol) (PVA) and polyallylamine (PAA), in which the potassium salt of 2-aminoisobutyric acid (AIBA-K) and potassium hydroxide (KOH) were dispersed as mobile carriers, Zou and Ho obtained a $CO_2$ permeability larger than 6000 Barrers with a selectivity higher than 1500 at 110°C.[32] Although the membrane was thick (30–60 $\mu$m), it can potentially be made much thinner by common coating techniques to obtain higher fluxes. Similar blends of pure PVA with polyethylenimine (PEI) or polyvinylamine (PVAm) have been used to obtained selectivities greater than 150 at room temperature.[33,34] In a more recent study,[35] Kim et al. synthesized a membrane with almost pure high-molecular-weight PVAm (molecular weight $>$ 340,000). The membrane was shown to have extraordinary separation properties with best $CO_2$ permeances and selectivities greater than 1000 GPU and 200, respectively at 35°C. The exceptional performance of this membrane warrants further research into this easily available commercial material.

Various researchers have also used polyamidoamine (PAMAM) dendrimers as carriers. Kai et al. used PAMAM dendrimer-impregnated chitosan intermediate layer on porous polysulfone to fabricate hollow fiber modules.[36] $CO_2/N_2$ selectivity of up to 170 was reported but the $CO_2$ permeance was less than 30 GPU at 25°C. Blends of the dendrimer with Pebax® or quaternary ammonium compounds with Pebax® have resulted in simultaneous increases in both permeability and selectivity.[28,37] Such blends are interesting from the point of view of alleviating the unfavorable selectivity-permeability trade-off in polymeric membranes.

These membranes based on reactive carriers are generally believed to be susceptible to poisoning by impurities and, therefore, require sulfur polishing before $CO_2$ removal. However, recent experimental trials have indicated that this might not absolutely be true. During field test at 35°C, a scaled up PVAm membrane showed long-term stability ($\sim$ 4 months) with exposure to $SO_2$ and $NO_x$.[38] Good stability in the presence of $SO_2$ has also been reported by Yuan et al. for a membrane with ethylenediamine dispersed in PVAm.[39]

Polymeric membranes based on facilitated transport potentially combine the fabrication ease of polymeric materials with the high selectivities offered by specific chemical reactions. One disadvantage is that the permeance may not increase proportionally with a reduction in thickness. There is a need, however, to increase the permeances as much as possible by reducing the thickness while also studying and improving the stability of thin membranes. More long-term stability studies in the presence of real flue gas conditions are needed for better evaluation.

### *Inorganic membranes*

Inorganic membranes studied for $CO_2/N_2$ separation are microporous in nature. In general, separation is achieved by either molecular sieving or selective surface diffusion through the pores or both. Molecular sieving is relatively ineffective due to the comparable sizes for $CO_2$ and $N_2$, and the permeances in pure molecular sieving are small.[13] In selective surface diffusion, $CO_2$ preferentially adsorbs and diffuses along a surface concentration gradient.[13] The pore area available for $N_2$ is then effectively reduced or, in some cases, blocked. Such microporous transport can comfortably cross the upper bound for polymeric materials. Zeolites, microporous silica and carbon are important materials in this context.

Zeolites are crystalline aluminosilicates with well-defined microporosity. Among them, Zeolite Y, because of its pore size of about 7 Å and Si/Al ratio of 1.5 – 3.8, is the most interesting candidate. Molecular dynamics (MD) simulations have indicated that pure NaY (zeolite Y with $Na^+$ as the counterion) crystal permeability is larger than $10^5$ Barrers with a $CO_2/N_2$ selectivity of greater than 200 at close to typical flue gas operating conditions,[13] which is the highest predicted performance among all zeolites. Experimentally, Kusakabe et al.[40] obtained a high $CO_2$ permeance higher than 3000 GPU at a selectivity larger than 35 at 35°C for a NaY membrane on porous alumina tube supports. They increased the selectivity to about 70 without much drop in permeance by exchanging the $Na^+$ with $Rb^+$ ions.[41] White et al. obtained extremely high selectivities of greater than 500 at a permeance of 300 GPU using a NaY membrane on flat alumina support.[42] $CO_2$ permeances larger than 2000 GPU with selectivities of 30–70 have been achieved at room temperature using even smaller pore or larger Si/Al ratio zeolites.[43,44] In a zeolite membrane, the crystals must be connected to form a polycrystalline thin film. The variations in literature data and differences between them and theoretical predictions are in part due to the difficulties in fabricating such a structure. Random orientation of zeolite crystals, intercrystalline interfacial resistance, and intracrystalline grain boundary resistance along with infiltration into the thick ceramic supports, could all reduce the permeance.[13,42]

Microporous silica membranes show useful combinations of $CO_2$ permeances and selectivities, but are susceptible to $SO_2$ poisoning and pore blockage by water at low temperatures as it might be the case with small pore zeolite membranes.[45] Some carbon membranes derived from pyrolysis of thermally resistant polymeric materials like polyimides etc. have also shown remarkably high $CO_2$ permeabilities but with relatively low selectivities.[46] However, they suffer from fabrication, reproducibility and scale-up issues similar to all other inorganic membranes. Defects can reduce the selectivity by allowing nonselective Knudsen or convective gas flow through them although coating an inorganic layer with PDMS has been successful in plugging defects.[47] From a fabrication point of view, the inorganic membranes are also plagued by the use of thick, brittle, less scalable, less compact and more expensive inorganic supports. However, novel approaches using flexible polymer and metal supports for inorganic selective layers can potentially deal with some of these issues.[44,48]

### *Mixed matrix membranes*

Mixed matrix membranes (MMMs) composed of inorganic particles dispersed uniformly in a continuous polymer matrix have attracted considerable attention for $CO_2$ separations. They can potentially realize a synergistic combination of advantages of polymers (easy processability, defect-free film formation, low cost) and inorganic materials (superior gas separation performance, mechanical strength, thermal stability). A recent review by Noble summarizes the usual design considerations in MMMs.[49] The Maxwell model is generally used to obtain a first-estimate of the permeability $P_{\mathrm{MMM}}$ of the MMM that is given by

$$P_{\mathrm{MMM}} = P_{\mathrm{c}} \frac{P_{\mathrm{d}} + 2P_{\mathrm{c}} - 2\phi_{\mathrm{d}}(P_{\mathrm{c}} - P_{\mathrm{d}})}{P_{\mathrm{d}} + 2P_{\mathrm{c}} + 2\phi_{\mathrm{d}}(P_{\mathrm{c}} - P_{\mathrm{d}})} \tag{7}$$

where $P_{\mathrm{d}}$ is the permeability of the dispersed inorganic phase, $P_{\mathrm{c}}$ is the permeability of the continuous polymeric phase, and $\varphi_{\mathrm{d}}$ is the volume fraction of the inorganic phase. The assumptions involved are (1) perfectly dispersed inorganic phase, (2) perfect adhesion between the two phases, and (3) no change in the inherent properties of the two phases. Generally, a microporous inorganic phase material has a higher selectivity and permeability than the polymer phase. Both $CO_2$ permeability and selectivity of the MMM should then increase relative to the polymeric material if there is a good match between the permeabilities of the two materials. Due to a combination of non-ideal effects like pore blockage by polymer chains and/or interfacial defects, etc. affecting the validity of the assumptions governing Eq. 7, the gains in transport properties are seldom close to ideal. In some cases, the nonideal effects could be the main contributors to the performance enhancement especially if the transport through the inorganic phase is small.

Bae et al. added 16 wt % of ZIF-90, a type of metal organic framework, into 6FDA-DAM polyimide and almost doubled the $CO_2$ permeability from 390 Barrers to 720 Barrers while also increasing the selectivity from 14 to 22 at 25°C.[50] However, for Ultem and Matrimid, polyimides with low permeabilities, the $CO_2$ permeability increased without an enhancement in the selectivity. More recently, for Pebax®1657, addition of ZSM-5 increased both the $CO_2$ permeability and $CO_2/N_2$ selectivity for the composite membrane relative to pristine Pebax®.[51]

Kim and Lee obtained simultaneous increases in both $CO_2$ permeability (~10%) and selectivity (~70%) for the Pebax®-silica system relative to pure Pebax® at room temperature. The reason was the $CO_2$ sorption increase brought about by the disruption in polymer chain packing and interaction between $CO_2$ and silica.[52] However, for PIM-1, addition of silica increased the permeability but with a significant drop in selectivity.[53]

In most of the aforementioned cases, to obtain a significant increase in membrane performance, the inorganic particle loading should be high enough. Thin MMMs with simultaneously high-inorganic loading and high productivity have not yet been demonstrated.

## Precombustion Carbon Capture and Hydrogen Purification

In PrCC, $CO_2$ has to be separated from $H_2$-containing streams. To produce large-scale electricity using gas turbines, the gasification is typically carried at very high pressures (>50 bars). From a membrane process point of view, higher pressure means larger driving force for separation. However, the challenging part is to separate $CO_2$ from $H_2$ (2.89 Å), which is a much smaller molecule than $N_2$ (3.6 Å). Both $CO_2$- and $H_2$-selective membranes with each type having its pros and cons have been considered for the aforementioned separation. Recent process modeling studies have used both these membrane types in different processes for carbon capture in an IGCC setup.[4,5]

Hot syngas after low-temperature WGS reaction is above 200°C, and at a pressure higher than 50 bars with close to 20–25% water vapor, 45% $H_2$, 30% $CO_2$, less than 1% CO, 0.5% $H_2S$, and smaller or trace amounts of $N_2$, Ar, $CH_4$, HCl and $NH_3$.[2] Frantz and Scherer studied the integration of both $CO_2$- and $H_2$-selective membrane processes in an IGCC power plant.[4] For purely membrane-based processes, using multistage operation, in order to be competitive with the SOTA absorption process, they concluded that a $H_2/CO_2$ selectivity higher than 50 or $CO_2/H_2$ selectivity larger than 150 are needed. Under the aforementioned operating conditions, these selectivity requirements are not met by any membrane reported in literature except for palladium membranes, which can permeate $H_2$ at infinite selectivity. However, these membranes suffer from serious poisoning in the presence of $H_2S$. Also, being inorganic, state-of-the-art palladium membranes cannot be fabricated into easily scalable, high-surface area/volume configurations. Considering a hybrid membrane/cryogenic separation process, Merkel et al. recently showed that the current polymeric $CO_2$- and $H_2$-selective membranes could give rise to comparable increases on the COE (~ 20%), which are lower than that obtained for the SOTA absorption process.[5]

Some of the important advantages of $CO_2$-selective membranes are summarized here:

1. Along with $H_2$, residual CO and $N_2$ in the syngas can be separated from $CO_2$. This can help to reach higher $CO_2$ purity in the stream to be sequestered.
2. Recovery target of 90% $CO_2$ is somewhat arbitrary and is more susceptible to change than the purity target of at least 95%. For a lower $CO_2$ recovery requirement, the amount of CO in the fuel stream will be higher due to a lower conversion in the WGS reactor. To tackle this, an additional combustion step will be needed after $CO_2$ capture for $H_2$-selective membranes. Since CO is retained by the fuel stream for $CO_2$-selective membranes, they can provide more flexibility on $CO_2$ recovery or CO conversion target for the WGS reactor.
3. Applying the same rationale to $N_2$, it can easily be concluded that they also provide greater flexibility on the purity of $O_2$ obtained from the air separation unit for the gasification. $H_2$- selective membranes cannot take too much nitrogen since it will have to be separated from $CO_2$ in an additional step before the capture. This flexibility can also reduce the energy consumption of the air separation unit.
4. Plasticization of polymeric solution-diffusion membranes due to high $H_2O$ and/or $CO_2$ partial pressures as in syngas can increase the $CO_2/H_2$ selectivity of rubbery $CO_2$-selective membranes while hampering the $H_2/CO_2$-selectivity of glassy $H_2$-selective membranes.

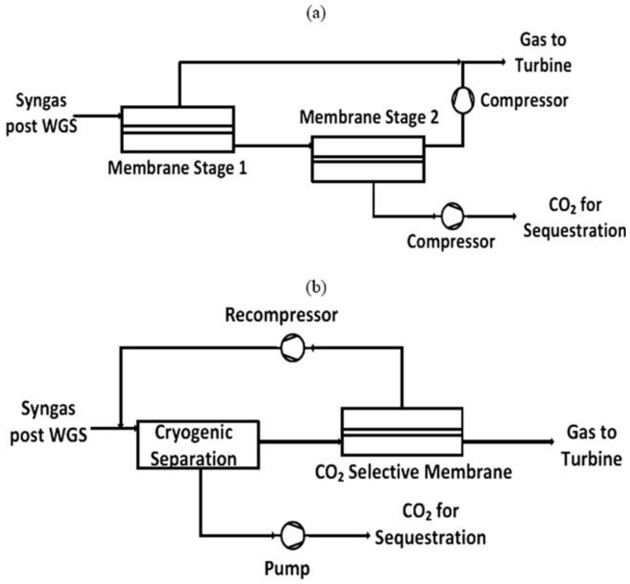

**Figure 4. $CO_2$-selective membrane processes for pre-combustion $CO_2$ capture ((b) adapted from Ref. 5).**

5. There is a greater scope to increase the reverse gas $CO_2/H_2$ selectivity by using facilitated transport membranes since they are not limited by the upper bound.

Although polymeric solution-diffusion $CO_2$-selective membranes cannot be operated at high temperatures, due to the lack of selectivity, other types of membranes, like those using a facilitated transport mechanism and a crosslinked heat-resistant matrix, can tolerate a higher-temperature operation.[30–32,54,55] $CO_2$-selective membrane processes for PrCC are shown in Figure 4. Figure 4a shows an example of a purely membrane-based process (high $\alpha_{CO_2/H_2}$), while Figure 4b shows a hybrid membrane-cryogenic separation process (low $\alpha_{CO_2/H_2}$). Although only one membrane stage is shown in Figure 4b, multistage operation can be used as shown in Figure 4a. High $CO_2/H_2$ selectivities can eliminate/reduce the energy consumed for permeate recompression and/or cryogenic separation.

In the case of electricity production by PEM fuel cells at lower pressures (1–6 bars), $H_2$ purification is a high priority. In this case, retaining $H_2$ at high pressure is more energy efficient, and using sweep gas (e.g., air) to provide the driving force for a $H_2$-selective membrane is not an option. On the other hand, a highly $CO_2$-selective membrane can be used advantageously. Steam or air can be used as sweep gas to provide driving force. For CO removal, as shown in Figure 5, the membrane can be used either as a stand-alone separation unit before the low-temperature WGS reaction or be integrated with WGS reaction in a $CO_2$-selective membrane reactor.[56–58] Both the configurations, if operated at low enough temperatures ($\leq$ 150°C), can achieve low CO levels (< 10–100 ppm) by shifting the WGS equilibrium forward due to the $CO_2$ removal while obtaining a hydrogen recovery of greater than 95%.[58] In the following subsections, an overview of the recent developments in $CO_2$-selective membranes, for PrCC and $H_2$ purification, is presented.

### *Polymeric solution-diffusion membranes*

The kinetic size of $H_2$ molecule is about 2.89 Å, which is considerably smaller than that of the $CO_2$ molecule (3.3 Å). As a result, $D_{CO_2}/D_{H_2}$ always favor $H_2$ permeation. Development of a polymeric membrane that retains $H_2$ molecules while permeating the larger $CO_2$ molecules is therefore difficult. The desired polymeric membrane is expected to maximize $S_{CO_2}/S_{H_2}$, while bringing $D_{CO_2}/D_{H_2}$ closer to one, i.e., reducing the size-sieving properties of the polymer matrix. In line with the earlier considerations and previously discussed polymeric materials, rubbery polymeric materials, based on the flexible polar ether groups, have been considered for this separation. PEO-containing polymers (e.g., crosslinked PEG diacrylate[59,60]), polymer blends with PEG,[61] and block copolymers of PEO-containing soft segment with polyamide,[62] polyimide,[63,64] polyurethane,[65,66] or polyester[67] as the hard segment have been generally considered for PrCC.

Pebax®1657, polyester-ether and polyurethane-ether provide $CO_2/H_2$ selectivities in the range of 7–13 at 35°C.[61,65,67] Blending with PEG type molecules is a relatively easy strategy to increase selectivity.[21,61] However, block copolymers look more promising from the stability point of view. By using PEO-containing copolyimide, Chen et al. recently obtained a higher selectivity of up to 22 with a $CO_2$ permeability of around 180 Barrers at 35°C.[64] As opposed to reduction, enhancement of $CO_2/H_2$ selectivity by plasticization was first shown by Lin et al.[59] They synthesized crosslinked PEG methyl ether acrylate using PEG diacrylate as crosslinker. The resultant copolymer contained abundant ethylene oxide units up to as high as 82 wt %, exhibiting an attractive selectivity of 31 accompanied by a $CO_2$ permeability of 410 Barrers at a feed pressure of 21 atm and a temperature of $-20$°C.[59] Although no effect of $CO_2$ partial pressure was found at 35°C, they obtained a 35% increase in selectivity at $-20$°C when the $CO_2$ partial pressure was increased from 1 to about 17 atm. The selectivity increase was also due to the

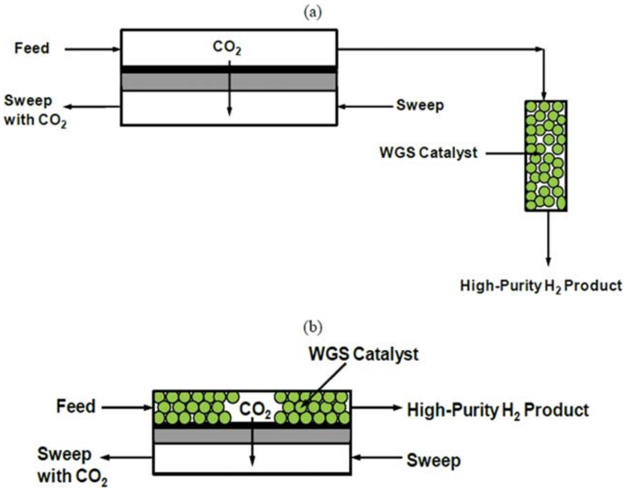

**Figure 5. $CO_2$-selective membrane processes for high-purity $H_2$ production (adapted from Ref. 56 and 57).**

**(a) $CO_2$-selective membrane + low-temperature WGS reactor. (b) $CO_2$-selective WGS membrane reactor.**

extremely low operating temperature of $-20$°C, at which the diffusion is slowed down, while the sorption of $CO_2$ vs. $H_2$ is increased relative to higher temperatures.

A downside to the use of rubbery polymeric materials for PrCC is the possibility of compression and free volume reduction during operation. Usually, the plasticization can help to reduce the effect of compression on the selectivity. However, if the $CO_2$ partial pressure is relatively low, as near the retentate end of a membrane module, the negative effects of compression may become important. Mechanical properties and stability of the above rubbery materials, under long-term exposure to high-pressure gradients, have yet to be verified. In this regard, the hard segment strength is important to resist compression at high pressures. Also, efforts have been made to increase the reverse selectivity of glassy materials, like Matrimid, by crosslinking with rubbery ether group containing crosslinkers, like PEO diamine.[63]

It should also be pointed out that most of the gas transport data in literature were measured at temperatures of about 30 – 35°C, the range of operating temperature for industrial $CO_2$ separation technologies such as pressure swing adsorption or SOTA absorption processes. The use of enhanced selectivity at lower temperatures must be balanced against the energy and cost penalty associated with the use of a refrigeration cycle.[63]

### *Facilitated transport membranes*

Membranes with higher $CO_2/H_2$ selectivities are desired to make membrane technology more competitive with conventional separation technologies in PrCC or in high-purity $H_2$ production. As discussed previously, early facilitated transport membranes were in the form of either supported liquid membranes or as improved ion-exchange membranes; both of which overcome the polymer upper bound on permeability and selectivity, but suffer from leakage of carriers, low resistance to high-pressure gradients, evaporative loss of solvents, and slow reaction kinetics. These issues have deterred their progress and commercialization though the emergence of dendrimers[68,69] and ionic liquids[70] as new, nonvolatile carriers has brought about significant improvements. Among water-swollen polymeric facilitated transport membranes, those based on a crosslinked hydrophilic matrix with fixed and/or mobile carrier molecules have shown good promise for both high and low pressure applications, because of better stability, mechanical properties and processing flexibility.

Such membranes have achieved remarkably high $CO_2/H_2$ selectivities at low pressures and temperatures greater than 100°C, close to PEM fuel cell operating conditions.[7,32,56–58,71,72] Ho and coworkers studied a series of amine carriers (e.g., PAA, PEI, AIBA-K, glycine-Li, and dimethylglycine-Li)[30–32,72] blended in a crosslinked PVA matrix. At a feed pressure of 2 atm and 110°C, the synthesized membrane containing PAA and AIBA-K demonstrated selectivity higher than 250 with a $CO_2$ permeability larger than 6000 Barrers.[32,57] Later, Zhao and Ho explored the amine steric hindrance effect in the solid membrane phase and established sterically hindered polyamines as a new group of high performance, stable fixed-site carriers.[71,72] The membrane with sterically hindered poly-N-isopropylallylamine exhibited significantly enhanced performance ($CO_2$ permeability larger than 6500 Barrers, selectivity higher than 300) and stability (more than 430 h) at 110°C and 2 atm.[72] At a higher temperature of 150°C, the facilitated transport membrane maintained selectivity higher than 80 accompanied with $CO_2$ permeability greater than 3500 Barrers.[32] As temperature was increased to 180°C, the selectivity dropped to 10–34.[32,72] Such selectivities are still comparable to conventional polymer membranes.

The aforementioned membranes are able to simultaneously and efficiently remove $H_2S$ from feed gas, which is attractive not only for $H_2S$ cleanup or fuel cell catalyst protection, but also for protecting the low-temperature WGS catalyst. The reversible $H_2S$-amine reaction (Eq. 8) involves only a proton transfer due to which it is much faster than the $CO_2$-amine reaction

$$H_2S + R\text{-}NH_2 \rightleftharpoons R\text{-}NH_3^+ + HS^- \qquad (8)$$

At 110–130°C, an $H_2S$ permeability as high as about three times that of $CO_2$ permeability was achieved using a simulated syngas feed consisting of 50 ppm $H_2S$, 1% CO, 17% $CO_2$, 45% $H_2$ and 37% $N_2$.[7] Using sweep gas, $H_2S$ in the retentate stream was thereby reduced to less than 10 ppb at a feed flow of 5 cc/min, indicating nearly complete removal of $H_2S$.[7] $H_2S$ removal can be integrated with the processes shown in Figure 5, as a step before WGS reaction.

The aforementioned membranes have also been exploited experimentally for CO clean-up.[56–58] A $CO_2$-selective WGS membrane reactor (effective membrane area of 343 $cm^2$) was set up and was able to convert 1% CO in the feed gas to less than 10 ppm in the hydrogen product stream, equivalent to nearly 100% CO conversion, at 150°C and 2 atm.[57,58] Another strategy is to use the $CO_2$-selective membrane as a stand-alone separation unit before a conventional low-temperature WGS reactor.[56] The membrane was operated at 120°C and 2 atm and could remove more than 99% of $CO_2$ from the feed stream before it entered the downstream WGS reactor, in which the reversible reaction was shifted forward to reduce the CO concentration to less than 10 ppm.[56]

At high pressures, the performance of such membranes is typically lower due to the characteristic "carrier saturation" phenomenon. As $CO_2$ partial pressure increases, its flux stops increasing proportionally at some point, because of a finite number of $CO_2$-reacting carriers that can be incorporated in the membrane. The viability of membranes at high pressures prevalent in PrCC is promising despite carrier saturation. Relying on efficient amine carriers, such as PAA and AIBA-K, the facilitated transport membranes synthesized by Ho's research group achieved a relatively high $CO_2/H_2$ selectivity larger than 85 and a $CO_2$ permeability greater than 1000 Barrers at 15 atm and at 106 – 110°C.[54,55] Development of $CO_2$-selective molecular gate membranes, using PAMAM dendrimers, has been conducted by the Research Institute of Innovative Technology for the Earth for several years. Recently, they modified conventional dendrimers with hydroxyl groups and demonstrated a very high selectivity of 1000 with a $CO_2$ permeability of over 1000 Barrers working with a pressurized syngas stream.[69]

The aforementioned membranes, despite excellent performance, have been questioned about their long-term stability. Persistent efforts by the membrane community in this direction have produced impressive improvements. The polyelectrolyte-salt blend membranes, consisting of poly(vinylbenzyltrimethylammonium fluoride) (PVBTAF) and cesium fluoride (CsF), showed no loss in $CO_2$ permeance and selectivities vs. $H_2$ and $CH_4$ at 23°C for more than 30 days.[73] The crosslinked PVAm membrane was stable for $CO_2/CH_4$ separation during a continuous operation of about 63 days.[74] Excellent stability of over 6 months was demonstrated by gel-supported liquid membrane, made of crosslinked poly(vinylalcohol-acrylate) gel containing aqueous $K_2CO_3$ solution and tested at 25°C and 1.2 atm.[75] Membrane stability at harsh conditions of high temperatures and high pressures has also been evaluated. In the work by Zhao and Ho, the membrane containing sterically hindered amines exhibited stable selectivity of 318 and $CO_2$ permeability of 3720 Barrers for more than 18 days at 110°C and 2 atm.[72] In a recent patent, the membrane synthesized by poly(vinylalcohol-acrylic acid) copolymer gel layer, containing 70 wt % cesium carbonate, showed stable performances (including $CO_2/H_2$ selectivity of over 100 and $CO_2$ permeance of 478 GPU) for more than 50 h at 160°C and 3.46 atm.[76]

Facilitated transport membranes provide superior selectivity with higher $CO_2$ permeability over polymeric membranes. Substantial progress has been demonstrated in improving the separation performance and durability at harsh operating conditions of industrial $CO_2/H_2$ separation. This type of membrane is moving into commercialization while continuous improvements are in progress. Carriers are directly responsible for the final separation performance; therefore, new carriers exhibiting higher reaction rate and/or absorption capacity along with better long-term stability are desired. Additionally, covalently/permanently bonding effective groups with matrix polymers, or approaches combining polymeric facilitated transport with inorganic particles could help in increasing the membrane stability. Optimization in terms of the amount of carriers vs. inert matrix polymer (if any), crosslinking degree, and membrane thickness is necessary in order to maximize the performance while maintaining a good stability.

### *Mixed matrix membranes*

For PrCC, the purpose of incorporating inorganic nanoparticles into the polymer matrix is ideally two-fold: (1) increasing membrane selectivity, and (2) improving mechanical and thermal stability of the membrane. The second point is important for membrane durability in practical operations. While enhanced mechanical strength can be readily achieved although inorganic nanofillers,[60,77] the concurrent change in gas transport properties is much more complex.

From a separation stand-point, the selection criteria for inorganic fillers and organic polymer host are clear, that is, both phases must preferably contain polar groups with $CO_2$ affinity. The inorganic particles, if porous, must have large pores to avoid molecular sieving effects. Most membranes reported in literature use polymeric materials with polar ether groups as the homogeneous phase. Typical fillers include fumed silica,[55,60,72] sol–gel silica,[77–81] polyhedral oligomeric silsequioxanes,[82] carbon nanotubes,[83,84] and carbon-silica microspheres.[85]

The addition of nanofillers can cause the following effects on the polymer phase: (1) an increase in $CO_2$ sorption within the hybrid matrix, (2) disruption in chain packing and consequent reduction in crystallization and increase in free volume, and (3) chain rigidification caused by covalent or non-covalent bonds with the filler material.[80,82] The first two effects typically can act together to increase the selectivity and permeability. The third one can decrease the free volume and increase the size-sieving properties of the polymer matrix and, therefore, is unfavorable.

Experiments are needed to determine the optimal filler loading for a given polymer-filler system. Desired nanofillers should be well dispersed in the polymer phase, so that they can contribute toward reducing polymer crystallization and increasing free volume. Within an optimal range of nanofiller loading, the polymer chain rigidification can prevent excessive plasticization,[77,78,80] which is beneficial for the mechanical properties of the membrane under high pressure gradients. Shao and Chung[77] used a crosslinked PEO/sol–gel silica system to obtain a $CO_2/H_2$ selectivity of about 13 with a $CO_2$ permeability of over 140 Barrers at 35°C. However, they observed a decline in transport properties as the amount of silica in the matrix increased. This is because the addition of excess fillers results in (1) unfavorable polymer chain rigidification and a consequent reduction in the free volume,[82] and (2) nonideal dispersion, e.g., aggregation, of nanofillers.[85]

The enormous potential of using carbon nanotubes (CNTs) as nanofillers in MMMs has been recognized for some time. CNTs constitute a unique tubular structure of rolled-up graphene walls with a nanoscale diameter and large aspect ratio. The pure carbon structure leads to the superlative mechanical and thermal properties in CNTs, and, thus, CNTs are considered ideal fillers for mechanical reinforcement of polymeric materials. Moreover, MD simulations have predicted that the gas transport through CNTs is orders of magnitude faster than in any other known filler material with nanopores due to the inherent molecular smoothness.[86] The graphene wall can also show preferential adsorption for one gas over the other. For instance, $CH_4/H_2$ selectivities of 10–20 through single-walled nanotube membrane have been predicted.[87] To fully utilize the exceptional properties of CNTs for gas transport, good dispersion and vertical alignment of open-ended CNTs within the polymer matrix is of utmost importance as demonstrated by experiments.[88,89]

Another type of MMM is prepared by randomly dispersing CNTs, acting as mechanical reinforcing fillers, in a polymer matrix.[83,84] Such an approach in combination with a polymeric facilitated transport membrane can potentially achieve both improved mechanical stability as well as excellent separation performance under high-pressure gradients. Ho's group has studied the effect of different inorganic fillers on improving membrane stability.[55,72,90] Xing and Ho incorporated sol–gel silica and fumed silica in crosslinked PVA/amine facilitated transport membranes and demonstrated improved stability at 107°C and 15 atm.[55] Zhao and Ho then exploited multiwalled CNTs to reinforce the mechanical strength of the same membrane. The initial work has shown considerable improvement in membrane stability compared to silica fillers.[90]

## Final Remarks

$CO_2$-selective membrane processes offer considerable promise as alternatives to SOTA absorption processes for $CO_2$ capture and $H_2$ purification. The challenges offered by different scenarios vary greatly. In PCC, the operating conditions are mild (close to ambient pressure and temperature), but driving force is limited. It is critical, therefore, to improve the membrane separation performance, both $CO_2$ permeance and $CO_2/N_2$ selectivity. Polymeric and inorganic membranes do offer high permeances, but have their pros and cons. The former suffer from low selectivities, while the latter are difficult to reproduce and scale up. MMMs can offer a good compromise, but issues related to thin-film fabrication need to be resolved. Polymeric facilitated transport membranes provide a good combination of selectivity and permeance, but have to be evaluated for their long-term stability in thin, highly productive configurations.

PrCC presents harsher operating conditions of high temperatures (100–200°C) and pressures (>50 bars). Other important challenge is to separate $CO_2$ from $H_2$, which is the second smallest gas molecule. Therefore, increasing membrane selectivity and evaluating and improving the operational stability will be critical to practical application. Again, polymeric solution-diffusion membranes offer low selectivities and need gas cooling before separation. Facilitated transport membranes offer higher selectivities, and, therefore, opportunities to reduce the energy consumption by reducing cooling requirements in a hybrid membrane-cryogenic separation process or decreasing the costs involved in permeate recompression and recycling. Both types of membranes can suffer from compression related stability problems at high pressures, and the mixed matrix approach can be creatively used to deal with these issues.

Lastly, as fuel cells are being developed as cleaner, more efficient and more localized electricity generating devices, highly $CO_2$-selective membranes operating at low pressures and higher than 100°C offer a unique approach to integrating $CO_2$ separation with WGS reaction. The resulting processes can convert/reduce CO down to less than 10 – 100 ppm. Membranes based on crosslinked hydrophilic polymer matrix with amine carriers for facilitated transport are tailor-made for such situations due to their high selectivities and low $H_2$ losses especially at low pressures. Moreover, due to their $H_2S$ removal capabilities, they offer a simultaneous means of CO, $CO_2$ and $H_2S$ cleanup.

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