

Current status and development of membranes for CO₂/CH₄ separation: A review

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ABSTRACT

Carbon dioxide (CO₂) is a greenhouse gas found primarily as a main combustion product of fossil fuel as well as a component in natural gas, biogas and landfill gas. The interest to remove CO₂ from those gas streams to obtain fuel with enhanced energy content and prevent corrosion problems in the gas transportation system, in addition to CO₂ implications to the climate change, has driven the development of CO₂ separation process technology. One type of technology which has experienced substantial growth, breakthroughs and advances during past decades is membrane-based technology. The attractive features offered by this technology include high energy efficiency, simplicity in design and construction of membrane modules and environmental compatibility. The objective of this review is to overview the different types of membranes available for use including their working principles, current status and development which form the primary determinants of separation performance and efficiency. The emphasis is toward CO₂/CH₄ separation, considering its substantial and direct relevance to the gas industry. To this end, discussion is made to cover polymeric gas permeation membranes; CO₂-selective facilitated transport membranes, hollow fiber gas–liquid membrane contactors, inorganic membranes and mixed matrix membranes.

The market for CO₂ separation is currently dominated by polymeric membranes due to their relatively low manufacturing cost and processing ability into flat sheet and hollow fiber configurations as well as well-documented research studies. While there have been immensely successful membrane preparation and development techniques with consequential remarkable performance for each type of membrane. Each type of membrane brings associated advantages and drawbacks related to the characteristic transport mechanism for specific application conditions. Inorganic membranes, for example, are very suitable for high temperature CO₂ separation in excess of 400 °C while all other membranes can be applied at lower temperatures. The recent emergence of mixed matrix membranes has allowed the innovative approach to combine the advantages offered by inorganic and polymeric materials.

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Abbreviations: 6FDA, 2,2'-bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride; -DAT, 2,6-diamino toluene; -DAM, Diaminomesitylene; -ODA/NDA, 4,4-diphenylene oxide/1,5-naphthalene; -mPDl, m-phenylene diamine; AIBA-K, 2-aminoisobutyric acid potassium salt; AMP, 2-amino-2-methyl-1-propanol; APTS, (γ-aminopropyl) triethoxysilane; CA, Cellulose acetate; CH₄, Methane; CMS, Carbon molecular sieve; CNT, Carbon nanotube; CO₂, Carbon dioxide; DABA, Diamino benzoic acid; DAMA, 2-(N,N-dimethyl) aminoethyl methacrylate; DEA, Diethanolamine; F2,4, Poly(vinylidene fluoride-co tetrafluoroethylene); FAU, Faujasite; FCM, Fixed carrier membrane; FTM, Facilitated transport membrane; HFP, Hexafluoropropylene; IEM, Ion-exchange membrane; LSM, Liquid support membrane; MCOC, Mixed conducting oxide ceramic; MDEA, Methyl-diethanolamine; MEA, Monoethanolamine; MMM, Mixed matrix membrane; MOF, Metal organic framework; MTMOS, Methyltrimethoxysilane; N₂, Nitrogen; NaOH, Sodium hydroxide; NIPS, Non-solvent induced phase separation; O₂, Oxygen; PAA, Poly(allylamine); PAI, Poly(amide-imide); PBI, Polybenzimidazole; PC, Polycarbonate; PDMC, Propyl monoester chain; PEI, Polyetherimide; PES, Polyethersulfone; PETEDA, Pentaerythritol tetraethylenediamine; PI, Polyimide; PP, Polypropylene; PSA, Pressure swing adsorption; PSf, Polysulfone; PTFE, Polytetrafluoroethylene; PTMOS, Phenyltrimethoxysilane; PVA, Poly(vinyl alcohol); PVAm, Polyvinyl amine; PVDF, Polyvinylidene fluoride; PVDF-HFP, Poly(vinylidene fluoride-co-hexafluoropropylene); RTILs, Room temperature ionic liquids; T_c, Critical temperature; T_g, Glass transition temperature; T_m, Melting temperature; TFE, Tetra-fluoroethylene; TIPS, Thermal induced phase separation; TIT, 2,2,4-trifluoro-5-tri-fluoromethoxy-1,3-dioxole; TMOS, Tetramethoxysilane; UV, Ultraviolet; SMM, Surface modifying macromolecules; SPBI, Sulfonated polybenzimidazole; SPEEK, Sulfonated poly(ether ether ketone); ZIF, Zeolitic imidazolate framework.

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1. Introduction

Carbon dioxide (CO₂) is the largest single contributor to global warming, with over 30 billion tonnes of global CO₂ emissions per year in the past five years (<http://CO2now.org/Current-CO2/CO2-Now/global-carbon-emissions.html>, 2011). CO₂ is commonly found in natural gas streams, biogas from anaerobic digestion, flue gas from fossil fuel combustion and product of coal gasification. The presence of CO₂ and other acid gases reduce the calorific value and make the gas streams become acidic and corrosive, which in turn reduces the possibilities of gas compression and the transport within the transportation systems. Pipeline specifications for natural gas usually require CO₂ concentrations below 2% (Othman et al., 2009). One major step to treat the various gas streams is to remove acid gas such as CO₂, H₂S and SO₂ before it is compressed and delivered. The separation of CO₂ from CH₄ is important in many industrial processes such as natural gas sweetening (e.g. CO₂ removal from high pressure methane in natural gas wells), biogas upgrading, oil recovery enhancement and landfill gas purification (Yang et al., 2008). On the other hand, highly concentrated CO₂ can also be produced from such separation processes rather than direct release into atmosphere contributing to the mitigation of

greenhouse gas emissions. By pumping and storing pure or highly concentrated CO₂ deep underground, sequestration may provide one feasible approach of treating the greenhouse gas emissions (Figuerola et al., 2008; Yang et al., 2008). Therefore, economic and effective techniques for CO₂ removal from CH₄ and capture at a wide range of CO₂ concentration levels and flow rates are highly desirable and have attracted great interest.

Conventional industrial methods employed for such purpose include chemical absorption by reactive solvents in e.g. packed towers, spray towers, venture scrubbers and bubble columns, pressure swing adsorption (PSA) and cryogenic separation (Basu et al., 2010). Regardless of the full maturity of the absorption process, the phase dispersion which occurs during the process frequently causes problems such as flooding, excessive loading, weeping, foaming and entrainment (Li and Chen, 2005; Wang et al., 2004c). Moreover, those conventional methods usually involve substantially complicated equipment, higher energy consumption and capital cost. As an alternative, membrane separation technology has shown promising features and accordingly, attracted increasing attention from the scientific community with research specialized in CO₂ capture due to its energy efficiency, simple process design, ease of scale-up and module construction as well as small footprint

(Bernardo et al., 2009; Li, 2008). This technology has proven its commercial availability for acid gas removal in the 1980s (natural gas purification) (Drioli and Barbieri, 2011). Over the years, tremendous progress in gas separation studies using membranes has been made toward membrane fabrication, improving chemical and physical properties of the membrane, process design and module configuration. However, it is worthwhile to note that although membrane technology is promising in gas separation, it is difficult to maintain the membrane performance in long-term operation. Most membranes do not have the resilience in practical industry conditions and quickly fail, which is one of the biggest challenges for their potential applications in industrial practice. Nevertheless, membrane-based technology has become a competitive separation process and has served as an efficient tool for CO₂/CH₄ separation.

Various membranes for CO₂/CH₄ separation are available. Based on the materials of the membranes, three major categories exist, e.g. polymeric membranes, inorganic membranes and mixed matrix membranes. Polymeric membranes can be further classified into three types based on their transport mechanism, e.g. gas permeation membranes, facilitated transport membranes as well as asymmetric microporous membranes used in a gas–liquid membrane contactor.

The primary objective of this review paper is to provide a comprehensive literature summary on the development of different membranes mainly used for CO₂/CH₄ separation processes. In this regard, the working principles, membrane development, associated limitations and approaches to address those limitations for all types of membranes are discussed. Comparisons between different types of membranes are made on their specific operating conditions, performances and cost. The future goals and directions are also suggested. This review is aimed at providing the necessary background information and general research directions to those who are involved or about to be involved in this field.

2. Dense polymeric membranes

2.1. Solution-diffusion model and gas transport in glassy polymers

Generally, the gas molecules are transported through non-porous polymeric membranes based on the principle of solution-diffusion mechanisms. In a solution-diffusion model, the selectivity is regulated by the polymer molecular structure that allows preferential passing of certain gas molecules based on their sizes, normally represented by their kinetic diameters. The kinetic diameters of CO₂ and CH₄ are 0.33 nm and 0.38 nm, respectively. On the other hand, the permeability is largely controlled by the gas solubility. The main parameter that determines the solubility is the ability of the penetrant gases to condense. CO₂ is more permeable than CH₄ due to the larger condensability, as indicated by the critical temperature (T_c), e.g. $T_{c,CO_2} = 304$ K, $T_{c,CH_4} = 191$ K (Lin and Freeman, 2004).

The gas transport in a nonporous membrane is represented by two coefficients, e.g. diffusivity coefficient (D) and solubility coefficient (S). The permeability coefficient, P_i can be expressed as:

$$P_i = D_i \times S_i, \quad (1)$$

where P_i is the permeability of component i through the membrane. The selectivity of component i with respect to component j is given by their permeability ratio as:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j} \right) \left(\frac{S_i}{S_j} \right), \quad (2)$$

where D_i/D_j represents the diffusivity selectivity and S_i/S_j represents the solubility selectivity.

For glassy polymers, the sorption and transport of penetrant molecules are usually described by the dual-mode sorption model, which consists of two types of sorption mechanisms, e.g. a Henry's law 'dissolved' mechanism (Equation 3) and a Langmuir 'hole-filling' mechanism [Equation (4)].

$$C_D = K_D f \quad (3)$$

$$C_H = \frac{C'_H b f}{1 + b f}, \quad (4)$$

where C_D is the gas concentration in the polymer due to dissolution within the polymer matrix, K_D is Henry's law solubility coefficient, f is the gas fugacity, C_H is the gas concentration in the microvoids 'frozen' in the polymer matrix, C'_H is the hole saturated constant and b is the Langmuir affinity constant which represents the ratio of the rate constant of gas adsorption and desorption in the microvoids or defects.

Thus, the total concentration of gas within the membrane can be expressed as Equation (5). The experimental investigation of the dual-mode sorption model has been reported by Wang et al. (Wang et al., 2002b).

$$C = K_D f + \frac{C'_H b f}{1 + b f}. \quad (5)$$

2.2. Experimental studies

Membranes have become an established technology in CO₂ removal since natural gas purification in 1980s (Drioli and Barbieri, 2011). Currently, most large-scale CO₂ separation setups are for natural gas purification, which were installed by installed by Kvaerner-GMS, Universal Oil Products and Cynara (Baker, 2004). Among the different types of membranes, industrial usage is dominated by polymeric membranes. A number of polymer materials have been utilized to fabricate dense polymeric membranes for gas permeation, such as polyimide (PI), cellulose acetate (CA), polysulfone (PSf), polyethersulfone (PES), and polycarbonates (PC). Different materials are suitable for different gas separation processes. Among those materials, PI and CA have been mainly used for CO₂/CH₄ separation commercially (Han and Lee, 2011). The pioneers for commercializing polyimide were DuPont (USA) and Ube Industries Ltd. (Japan) (Ohya et al., 1996). Polyimides membranes were initially used for hydrogen recovery, and now they have been modified to apply in the separation of CO₂ in various gas streams. CA was initially developed for the membrane reverse osmosis process by UOP and now has been commercialized and mostly used as gas permeation membranes in CO₂/CH₄ separation (Houde et al., 1996). The molecular structures of CA and PI-based polymers, as well as some other polymers used for CO₂/CH₄ separation are shown in Fig. 1.

The performances of polymeric membranes for CO₂/CH₄ separation are summarized in Table 1. PI membranes are ideal for CO₂/CH₄ mixture separation compared with other glassy polymers because of their good chemical, thermal and mechanical stability, spinnability (Kim et al., 1988b; Matsumoto and Xu, 1993) and high selectivity toward CO₂/CH₄ (Chung et al., 1994; Kim et al., 1988a; Koros et al., 1988; White et al., 1995). Among different aromatic polyimide materials, fluorinated polyimides containing 2,2'-bis (3,4'-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) have been identified as promising membrane materials as they exhibit excellent gas permeability and selectivity with respect to non-fluoropolyimides (Cao et al., 2002; Coleman and Koros, 1994; Koros and Fleming, 1993). This is most likely attributed to the presence of bulky $-\text{C}(\text{CF}_3)_2-$ group which hinders intrasegmental mobility and disrupts inter-chain packing and stiffens backbones (Kim et al., 1988b; Matsumoto and Xu, 1993). Thus, 6FDA-based polyimides have been intensively studied. On the other

Table 1
CO₂/CH₄ separation performance of polymeric membranes.

Membrane material	Membrane type	Pressure (bar)	Temperature (°C)	CO ₂ permeances/permeabilities		Selectivity (CO ₂ /CH ₄)	Test type ^d (CO ₂ vol%)	Ref.
				Value	Units ^{a,b,c}			
6FDA-BAPAF	Dense	30	21	24.6	GPU	22.78	S	Kim et al. (2003)
6FDA-DAP	Dense	30	21	38.57	GPU	77.82	S	Kim et al. (2003)
6FDA-DABA	Dense	30	21	26.3	GPU	46.96	S	Kim et al. (2003)
6FDA-1,5-NDA	Dense	10	35	22.6	Barrer	49	S	Wang et al. (2002b)
6FDA-durene/MPDA (50:50)	Dense	10	35	84.6	Barrer	29.9	S	Liu et al. (2003a)
6FDA-durene	Dense	10	35	458	Barrer	16.1	S	Liu et al. (2003a)
Matrimid® 5218	Dense	34.5	35	10	Barrer	35.71	S	Vu et al. (2003a)
Matrimid® 5218	Dense	1.1	20–25	28.5	GPU	50	M (not given)	Syrtsova et al. (2004)
Matrimid® 5218 (fluorinated)	Dense	1.1	20–25	18.7	GPU	93.5	M (not given)	Syrtsova et al. (2004)
Poly(dimethylsiloxane) PDMS	Dense	2–4	23	3800	Barrer	3.17	S	José et al. (2004)
Polycarbonate (PC)	Dense	20	30	2	Barrer	27.2	M (40%)	Sridhar et al. (2007a)
Polyamides	Dense	2	35	11	Barrer	36.3	S	Ghosal et al. (1995)
DMAEMA-PEGMEMA	Dense	2	35	24.3	GPU	12.5	S	Ji et al. (2010)
6FDA-DAT	Asymmetric	7	20	59	GPU	40	M (40%)	Cao et al. (2002)
6FDA-DAT	Asymmetric	2	35	55	GPU	60	M (40%)	Cao et al. (2003)
6FDA-DAT (crosslinked)	Asymmetric	2	35	32	GPU	55	M (40%)	Cao et al. (2003)
PSf	Asymmetric	5	25	80.7	GPU	40.2	S	Ismail et al. (1997)
Matrimid®	Asymmetric	15	20	11	GPU	67	M	Dong et al. (2010)
Matrimid®/P84 blend	Asymmetric	8	35	11.5	GPU	35	M (50%)	Visser et al. (2007)
Cellulose acetate	Asymmetric	8	35	2.5	GPU	20	M (50%)	Visser et al. (2007)
Cross-linked PI/PES	Dual layer	6	23	28.3	GPU	101	S	Liu et al. (2003b)
PBI/Matrimid® blend and PSf	Dual layer	10	35	4.81	GPU	41.81	S	Hosseini et al. (2010)
Matrimid®/PES	Dual layer	10	22	9.5	GPU	40	M (40%)	Jiang et al. (2004)

^a 1 GPU = 10⁻⁶ cc(STP) cm⁻² s⁻¹ cmHg⁻¹.

^b 1 Barrer = 10⁻¹⁰ cc(STP) cm cm⁻² s⁻¹ cmHg⁻¹.

^c Test type: Single gas experiment (S) and mixed gas experiment (M).

^d To convert values in GPU into mol m⁻² s⁻¹ Pa⁻¹ multiply the value by 5.95 × 10⁻⁴ (Ebner and Ritter, 2009).

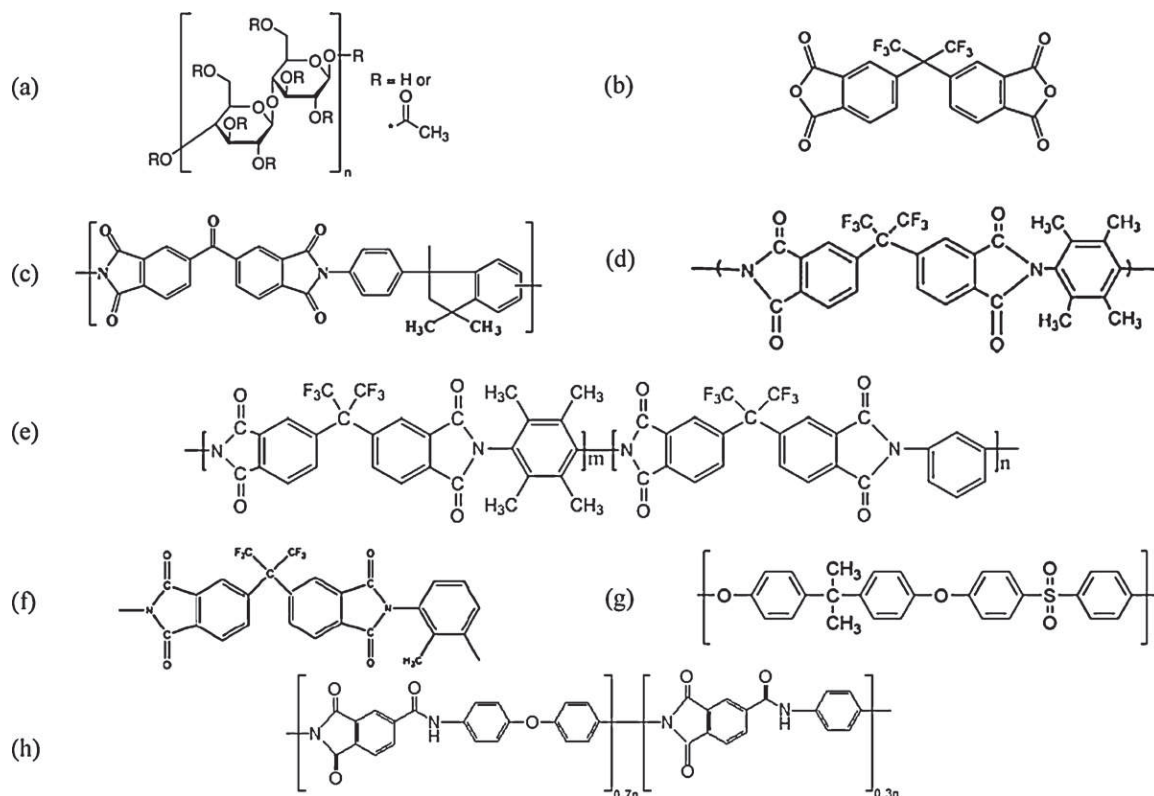


Fig. 1. Polymer molecular structure used for CO₂/CH₄ separation: (a) CA; (b) 6FDA; (c) Matrimid®; (d) 6FDA-durene; (e) 6FDA-durene-m-PDA; (f) 6FDA-DAT (g) PSf; (h) Torlon®.

hand, Matrimid®, produced by Ciba-Geigy, is also of great interest to fabricate CO₂/CH₄ separation membranes. However, Matrimid® is not as permeable as 6FDA-based polyimide membranes. Cross-linking is an effective method to enhance the separation properties of PI membranes. The 6FDA-based co-PI membrane cross-linked by ethylene glycerol showed improved CO₂/CH₄ selectivity (Hess and Staudt, 2007). Likewise, when Matrimid® membranes were soaked in and cross-linked by *p*-xylenediamine, the selectivity of CO₂/CH₄ of the modified membranes was improved compared to the neat Matrimid® membranes (Tin et al., 2003).

Dense membranes are usually formed by solvent evaporation in air during the phase inversion process. As a result, the formed membranes are usually thick and homogeneous. The permeability is mainly determined by the intrinsic property of the polymer material. On the other hand, asymmetric membranes can be fabricated by a solvent/non-solvent phase inversion process. Asymmetric membranes are normally composed of two parts, a thin selective layer with similar function as the dense film and a porous substrate. The porous substrate with no selectivity presents significantly higher permeance than the selective layer; the permeance and selectivity, in turn, are determined by the selective layer. The selective layer of asymmetric membranes tends to be significantly thinner than dense membranes. Therefore, it is expected to exhibit much smaller mass transfer resistance due to the greater reduction of the dense layer thickness and hence higher permeance. Various materials have been employed for the fabrication of asymmetric gas permeation membranes, including polyetherimide (PEI) (Wang et al., 1998), PSf (Ismail et al., 1999; Ismail and Shilton, 1998), 6FDA-durene (Wang et al., 2001), Matrimid® (Dong et al., 2010) and blend of PSf-PI (Rafiq et al., 2011a; Rafiq et al., 2011b).

In recent years, dual layer hollow fiber membrane technology has become an emerging technology which attracts great interest from membrane researchers. The dual-layer fabrication is performed by the co-extrusion technology that allows two polymer

solutions to be extruded simultaneously from a triple-orifice spinneret. The major advantage of this technology lies in the substantial cost reduction; since a high performance but expensive polymer is only required for the outer layer whereas an inexpensive material can be used as the inner support layer (Hosseini et al., 2010). Chung and his co-workers successfully developed the defect-free polymeric dual-layer hollow fiber membranes consisting of an ultrathin dense-selective poly(amide-imide) (PAI) (commercially known as Torlon®) layer and a PES supporting layer (Li et al., 2011). Mao et al. reported the fabrication of dual-layer CA/PSf hollow fiber membrane and its application for CO₂ separation (Mao et al., 2011). The permeance of dual layer membrane is greatly improved relative to the single layer membrane due to the reduced thickness of the separation layer. Similarly, interfacial polymerization is also used to form the selective layer in the separation of CO₂ from CH₄. The advantage of such a membrane is its very thin active layer in the order of 0.1–1 μm; resulting in a very small mass transfer resistance and enhanced permeance while maintaining reasonable rejection properties (Sridhar et al., 2007c). The typical membrane structure of dense film, asymmetric hollow fiber and dual layer hollow fiber membranes are shown in Fig. 2.

2.3. Limitations and improvements

2.3.1. Trade-off between permeability and selectivity

The current CO₂ separation membrane technologies are dominated by polymeric membranes due to their low cost (cheaper relative to inorganic membranes), excellent mechanical stability at high pressure, easy formability to both flat sheets and hollow fibers and straightforward scalability. Nonetheless, polymeric membranes normally suffer from either low permeability or low selectivity. An inverse relationship exists between the permeability and selectivity. A number of studies have reported the inverse relationship (Bahukudumbi and Ford, 2006; Wang et al., 2009; Wang

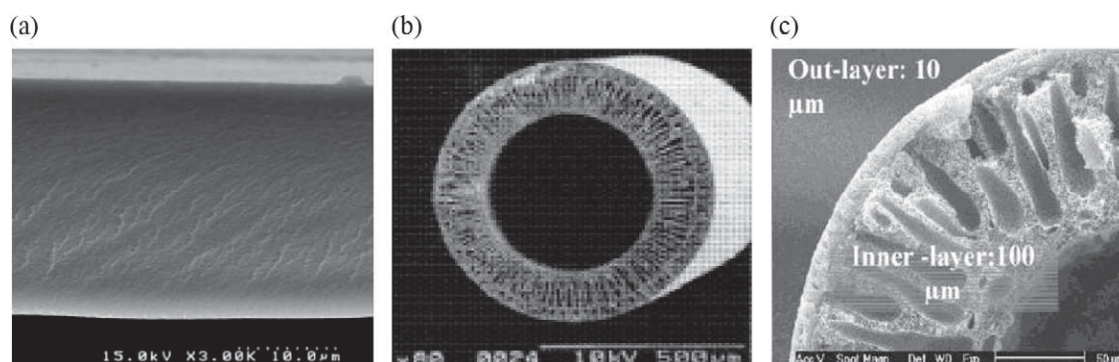


Fig. 2. Typical structures of (a) dense film; (b) asymmetric hollow fiber membrane and (c) dual layer hollow fiber membrane.

Source: Adopted from Ichwan and Son (2012); Liu et al. (2003b); Miltner et al. (2009).

et al., 2007a). This is shown graphically in Robeson's upper bound curve (Robeson, 1991, 2008), which is considered the benchmark in gas permeation membrane development. Fig. 3 shows the plot for the CO_2/CH_4 gas pair. It can be seen that only a minority of the membranes fall above or close to the curve.

2.3.2. Plasticization

Another issue, plasticization, is of particular concern for commercial CO_2/CH_4 separation where the CO_2 concentration in the feed stream is high. CO_2 -induced plasticization refers to a phenomenon where the CO_2 permeability increases as a function of pressure while the selectivity deteriorates (Ismail and Lorna, 2002). Acting as a plasticizer, the dissolved CO_2 swells the interstitial place among the polymer chains of the polymer matrix and causes permanent change in the polymer structure (Kesting and Fritzsche, 1993). Diffusion of penetrants is greatly increased during membrane plasticization due to the loosely packed chains, and simultaneously resulting in the deterioration of the separation performance. This phenomenon manifested into the observation of similar CO_2 permeances in the mixed gas and single gas permeation experiments and a higher CH_4 permeance in the mixed gas experiment relative to the single gas experiment;

due to the plasticization caused by CO_2 which leads to a loss of selectivity (Wang et al., 2002d).

There are several methods which have generally been utilized to suppress CO_2 plasticization, e.g. thermal treatment, cross-linking and polymer blending. Meanwhile, they are also considered effective to improve the membrane separation performance.

2.3.2.1. A: thermal treatment. Thermal molecular rearrangement e.g., the thermal decarboxylation of precursor polyimides between 350°C to 450°C can disrupt the polymer chain rigidity; change the chain structure and spatial location of rigid moieties (Park et al., 2007). As a result, free-volume element architecture can be tailored by controlling the degree of rearrangement and flexibility of the original chain. Due to the formation of unique cavity and the precise discrimination caused by the cavity coalescence constriction, both CO_2 permeability and CO_2/CH_4 selectivity can be greatly enhanced. Moreover, thermally rearranged polymers show dramatically reduced plasticization and can maintain high selectivity at high CO_2 concentration and high CO_2 partial pressure (Park et al., 2007). For some rigid polymers, such as polybenzimidazole (PBI), the structure is well packed due to the strong interactions between the polymer chains which lead to a very low gas permeability. Increasing

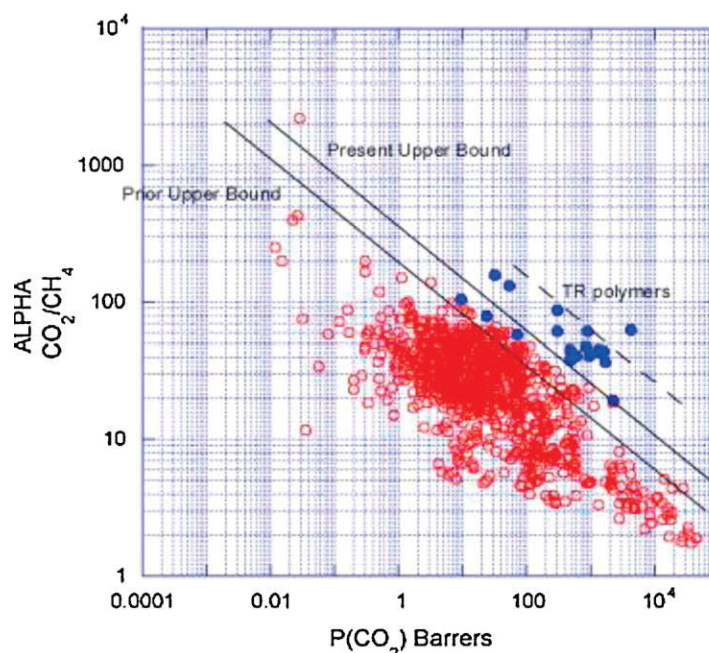


Fig. 3. Plot showing trade-off behavior and limit of CO_2/CH_4 gas permeation membranes.

Source: Adopted from Robeson (2008).

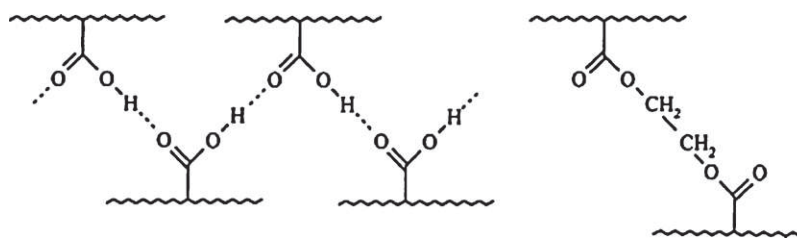


Fig. 4. Physical cross-linking by hydrogen bond between COOH (left side) and chemical cross-linking by free carboxylic acid groups with ethylene glycol (left side) of 6FDA-mPD/DABA (9:1).

Source: Adopted from Staudt-Bickel and Koros (1999).

the chain flexibility by thermal rearrangement greatly enhanced the fractional free volume and made the treated membrane highly permeable while maintaining the high selectivity by the molecular sieving capacity of the rigid matrix (Han et al., 2010). The performance of thermal treated PBI membranes is beyond the latest Robeson upper bound for CO₂/CH₄ separation (Robeson, 2008).

2.3.2.2. B: cross-linking. Cross-linking is an effective approach to suppress plasticization in CO₂ gas permeation membranes. Upon cross-linking, the molecular free volume between the polymer chains increases due to the presence of cross-linking agent which is beneficial for the improvement of the selectivity. Cross-linking can adjust membrane swelling when in contact with the feed mixture and hence, improves membrane chemical and thermal stability.

The cross-linking modification can be carried out by different methods, namely thermal treatment, ion beam, ultraviolet (UV) irradiation and chemical reaction (Ismail and Lorna, 2002). Among these methods, cross-linking via chemical reaction is considered the simplest, economically practical and most convenient method. *p*-Xylenediamine cross-linked 6FDA-ODA/NDA hollow fiber membranes showed a greatly reduced CO₂ plasticization and increased CO₂/CH₄ selectivity (Ren et al., 2003). The critical pressure of CO₂-induced plasticization was increased significantly from 70 psi up to 550 psi. 6FDA-2,6-DAT hollow fibers cross-linked by *p*-xylenediamine for 3 min showed favorable resistance to plasticization, enhanced CO₂/CH₄ selectivity but reduced CO₂ permeance due to tightening of the polymeric chains. Moreover, *m*-xylenediamine was found having a similar cross-linking effectiveness as *p*-xylenediamine.

Incorporation of polar groups in PI membranes, e.g. carboxylic acid (COOH[−]) groups can suppress plasticization; presumably due to the physical linking of hydrogen bonding between the carboxylic acid groups. 6FDA-mPD/DABA (9:1) containing COOH[−] groups showed less permeability; no plasticization until 14 atm relative to original 5 atm for the pure 6FDA-mPD membrane as well as enhanced selectivity. Further chemical cross-linking of such hydrogen-bond physical cross-linked 6FDA-mPD/DABA (9:1) with ethylene glycol significantly eliminated plasticization up to 35 atm pure CO₂ pressure. A 20% increase in selectivity was observed at a 10% degree of cross-linking with only a small loss of permeability (Staudt-Bickel and Koros, 1999). The physical and chemical cross-linking of 6FDA-mPD/DABA 9:1 is shown in Fig. 4.

2.3.2.3. C: polymer blending. Blending a polymer with high plasticization tendency with another that is hardly affected by the sorbed molecules can effectively stabilize the membrane from plasticization. Blending of Matrimid®/P84 (60:40 w/w) and Matrimid®/PSf (50:50 w/w) was studied. Both membranes were stabilized from plasticization. Meanwhile, Matrimid®/P84 exhibited better CO₂ separation performance with a significant increase in selectivity while Matrimid®/PSf showed deteriorated selectivity and permeability property (Bos et al., 2001). Similar phenomenon was also reported by Raymond et al. (Raymond et al., 1993) in which the

blend of PMMA/PSf membrane demonstrated decreased selectivity with increasing PSf concentration. In their report, the pure PMMA had the highest selectivity. Blending of sulfonated aromatic poly(ether ether ketone) (S-PEEK) in Matrimid® promotes the plasticization pressure. The permeability and selectivity for blend membranes, nonetheless is reduced. Further chemical cross-linking of the Matrimid® partly enhanced the selectivity with little loss of CO₂ permeability. Moreover, the resultant membrane showed increasing plasticization critical pressure well above 40 bar (Khan et al., 2011). Overall, the combination of polymer blending and cross-linking is considered useful to obtain membranes with high plasticization resistance and excellent gas separation properties.

3. Facilitated transport membranes

3.1. Carrier-mediated transport mechanism

In recent years, facilitated transport membranes (FTMs) are of interest because of their potential to achieve high selectivity without sacrificing permeability. This type of membrane is based on the reversible reactions between reactive carriers and CO₂ in the membranes. CO₂-reactive carriers incorporated in the membrane create the carrier-mediated CO₂ facilitated diffusion mechanisms in addition to the solution-diffusion mechanism of the gas permeation membranes. The carriers react with CO₂ dissolved on the feed side to form carrier-CO₂ complexes followed by the movement of the carrier-CO₂ complexes across the membrane and the release of CO₂ on the low pressure side along the direction of concentration driving force via the “hopping” mechanism suggested by Cussler (Cussler et al., 1989). The gas components which do not react with the carriers can only permeate through the membrane via the solution-diffusion process with most of them retained on the retentate side. As a result, higher CO₂ selectivity can be achieved while the permeability is also maintained. The facilitated transport mechanism is shown schematically in Fig. 5. Moreover, high CO₂ selectivity can also minimize the loss of primary gases such as methane through the permeate side. The carriers can be mobile carriers and fixed carriers and hence FTMs are available in the form of liquid support membranes (LSMs), ion-exchange membranes (IEMs) and fixed carrier membranes (FCMs).

3.2. Experimental studies

In FTMs, higher selectivity can be obtained by the additional carrier transport mechanism without reducing permeability. The diffusivity or permeability of CO₂ in a mobile carrier membrane is generally much higher than in a FCM (Cussler et al., 1989). LSM is one type of mobile carrier membrane which exhibits remarkably high selectivity (Kovvali and Sirkar, 2001; Scovazzo et al., 2004a,b; Teramoto et al., 2003). However, the disadvantage of LSMs is the membrane instability due to the volatility of the carrier solution (easy to evaporate and degrade) (Kovvali and Sirkar, 2003).

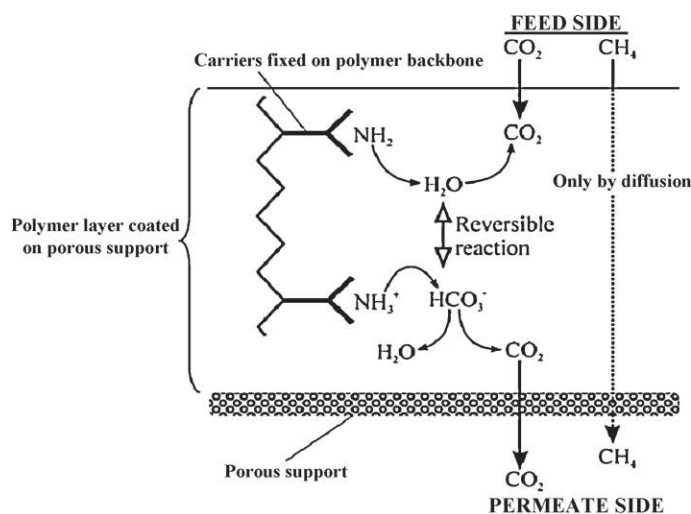


Fig. 5. A proposed mechanism of facilitated transport in fixed-site carrier membranes.

Source: Adopted from Kim et al. (2004).

IEMs have been developed as support materials for aqueous carrier agents to prepare FTMs. In IEMs, the ionic mobile carriers are retained inside the membranes by the attractive electrostatic force. The electrostatic force can reduce the carrier wash-out (Leblanc et al., 1980). The carrier leakage, however, still cannot be eliminated completely (Matsuyama et al., 1999; Pereira et al., 2001).

Table 2 summarized the permeability and selectivity of several FCMs for CO₂/CH₄ separation. By looking at Table 2, it can be seen that some membranes exhibited significantly larger selectivity than polymeric membranes as well as high CO₂ permeability. The FCM is also considered the most successful FTMs with the most stable configuration since the carriers are covalently bonded to the polymer matrix. CO₂ carriers which are usually in the form of polymers or small molecules containing amine groups are often incorporated by blending with the membrane polymers. However, very few polymer materials can be used as the polymer matrix in the FTMs due to incompatibility with amine carriers (Bai and Ho, 2009). Cross-linked poly(vinyl alcohol) (PVA) has been widely used as the polymer matrix in many studies due to its good compatibility with amine carriers, excellent thermal and hydrolytic stability, high hydrophilicity and good membrane forming property. Polyvinyl amine (PVAm) as the CO₂ carrier was blended with PVA and cast on a porous substrate (Deng et al., 2009). PVAm was fixed in the membrane matrix by the entanglement of the polymeric chains. The fixed amino groups in the PVAm facilitate the CO₂ transport whereas the PVA imparts its mechanical strength as a supporting network. Pentaerythritol tetraethylenediamine (PETEDA) dendrimer as the CO₂ carrier can also be blended with PVA polymer as the active layer of the composite membrane

(Wang et al., 2007b). Recently, Winston et al. was the first to employ sulfonated polybenzimidazole copolymers (SPBI) as a material for the membrane matrix (Bai and Ho, 2009). SPBI exhibited similar desired properties as PVA while SPBI is not soluble in water and hence can be fabricated via the phase inversion process by using water as the non-solvent, which is commonly used in industry. 2-aminoisobutyric acid potassium salt (AIBA-K) as the mobile carrier and polyethylenimine and poly(allylamine) (PAA) as the fixed carrier can also be blended with SPBI to synthesize a CO₂-facilitated transport membrane.

Many studies have been conducted to investigate the optimum operational conditions for CO₂ facilitated transport in FCMs. Similar to ion exchange membranes, CO₂ facilitated transport in the FCMs is enhanced in a water swollen membrane compared to a dry membrane e.g. the water swollen membrane exhibited higher permeability and selectivity (Bai and Ho, 2009; Kim et al., 2004; Zou and Ho, 2006). This is due to the fact that a higher water content inside the membrane resulted in the increased mobility of both mobile and fixed carriers and also increased the reaction rate of CO₂ with these carriers (Bai and Ho, 2009). This is particularly important when tri-substituted tertiary amine is used as the carrier. In a dry membrane, the facilitated transport of CO₂ is based on the interaction between amine moieties at the amine site, where CO₂ reacts with amine group to form zwitterions which then reacts with base (another amine site) (Danckwerts, 1979; Way and Noble, 1989). Nevertheless, for a tri-substituted tertiary amine, such as 2-(*N,N*-dimethyl) aminoethyl methacrylate (DAMA), no hydrogen atom is available to be displaced by CO₂. Therefore, the tertiary amine cannot directly react with CO₂. It is assumed that CO₂ is transformed into HCO₃[−] due to the interaction between CO₂ and water in a water swollen membrane. The tertiary amine carrier in the membrane, however, is not consumed during the reaction; it acts only as a weak base catalyst to enhance the CO₂ hydration reaction in a water-swollen membrane (Matsuyama et al., 1996; Yamaguchi et al., 1995). In this case, therefore, CO₂ transport is facilitated in the form of the small mobile ion HCO₃[−], which gives similar transport mobility as in a mobile carrier membrane.

3.3. Limitations and improvements

3.3.1. Carrier stability

For mobile carrier membranes, such as ILMs and IEMs, the loss of carriers by evaporation and degradation is detrimental to the long-term operation of those membranes. Continuing research in this area is exploring novel solvents which should have a higher solubility for CO₂, low vapour pressure, low viscosity and low or moderate hygroscopicity (Kovvali and Sirkar, 2002). Sirkar's group reported several different non-volatile solvents, such as carbonate-glycerol (Chen et al., 1999), glycine-Na-glycerol (Chen et al., 2000), dendrimer (Kovvali and Sirkar, 2001), and glycerol carbonate (Kovvali and Sirkar, 2002), which significantly reduced the evaporating loss

Table 2
CO₂/CH₄ separation performance of fixed-site carrier facilitated transport membranes.

Membrane material	Pressure (bar)	Temperature (°C)	CO ₂ permeances (GPU) ^{a,b}	Selectivity (CO ₂ /CH ₄)	Test type ^c (CO ₂ vol%)	Ref.
DMAEMA-AA on PSf support	0.011	26	816	255	S	Shen et al. (2006)
VSA-SA on PSf support	1.06	20	9.2	46.8	M (50%)	Wang et al. (2006)
PVAm/PEG blend	1.26	25	5.88	63	S	Yi et al. (2006)
PVAm on PSf hollow fiber	1.26	25	3.03	53	M (50%)	Dong et al. (2006)
PVAm on PSf support	2–4	25	3.11–3.7	700–1100	S	Kim et al. (2004)
PETEDA/PVA blend on PES support	2.48	20	69.4	33	M (10%)	Wang et al. (2007b)
PAAm/PVA blend on PSf support	1	25	26	58	M (10%)	Cai et al. (2008)

^a 1 GPU = 10^{−6} cc(STP) cm^{−2} s^{−1} cmHg^{−1}.

^b Test type: Single gas experiment (S) and mixed gas experiment (M).

^c To convert values in GPU into mol m^{−2} s^{−1} Pa^{−1} multiply the value by 5.95 × 10^{−4} (Ebner and Ritter, 2009).

of solvent. Teramoto et al. devised a “bulk flow liquid membrane” (Teramoto et al., 2004; Teramoto et al., 2003; Teramoto et al., 2001), in which the facilitated transport of CO_2 through a liquid membrane was accompanied by the permeation of carrier solution through the membrane. The carrier solution was mixed with the feed gas and continuously recycled to the feed side. The stability problem due to the evaporation of carrier was avoided because the membrane was always completely wetted and hence was able to maintain the selectivity.

IEMs, which are also known as polyelectrolyte membranes, are better than ILMs in terms of carrier stability because the carriers are contained in the membrane by the ionic strength via attractive electrostatic forces. Similarly, the use of non-volatile solvents for polyelectrolyte membranes can alleviate the solvent evaporation. Quinn et al. investigated a series of membranes consisting of molten salt or salt hydrates as the solvent and the evaporation was greatly reduced (Quinn et al., 1995, 2002; Quinn and Laciak, 1997; Quinn et al., 1997). Scovazzo et al. reported the use of various room temperature ionic liquids (RTILs) in the formation of ionic liquid membranes and the long-term solvent stability was demonstrated (Scovazzo et al., 2009; Scovazzo et al., 2004a,b; Scovazzo et al., 2002).

FCMs solved the carrier instability problem since the carriers are covalently bound to the membrane matrix. Although they counteract the carrier stability issue, the drawback of the FCMs lies in the permeability and selectivity which are much lower than those of the mobile carrier membranes. This is because the carriers can move inside the mobile carrier membranes freely, while in the FCMs case, the carriers are immobilized and can only move around its equilibrium positions (Cussler et al., 1989).

3.3.2. Feed preconditioning

For most FTMs, feed preconditioning by moisture is required to ensure the selectivity and membrane integrity, since water can increase the mobility of both mobile and fixed carriers and accelerate the reaction rate between the carriers and CO_2 . However, this limitation can be overcome in some applications where humidification preconditioning is not necessary, such as in the reforming process where H_2O is the participating component.

3.3.3. Carrier saturation phenomenon

Another issue is that most FCMs show decaying CO_2 permeance with increasing CO_2 partial pressure. At a low feed gas pressure, CO_2 permeance is high since most of the CO_2 is transported by CO_2 -carrier complexes and only a small portion of CO_2 is transported via the solution-diffusion mechanism. With the increase in feed gas pressure, CO_2 permeance reduces sharply as the contribution from the carrier-based transport decreases abruptly. When the feed gas pressure is high, the CO_2 permeation rate becomes severely limited as most of the carriers are saturated and CO_2 transport relies on the solution-diffusion mechanism only (Noble and Koval, 2006; Zhao et al., 2011). The carrier saturation phenomenon is the characteristic of FTMs which limits the use of FTMs at low CO_2 partial pressures.

4. Microporous hydrophobic membranes used in gas–liquid membrane contactor

4.1. Hollow fiber gas–liquid membrane contactor

Hollow fiber gas–liquid membrane contactor shows great potential for CO_2 separation when combined with the chemical absorbent process. In a membrane contactor, CO_2 absorption is achieved when the liquid absorbents are in contact with the gas streams flowing on the other side of the hollow fiber membranes, as illustrated in Fig. 6. The membrane contactor utilizes microporous

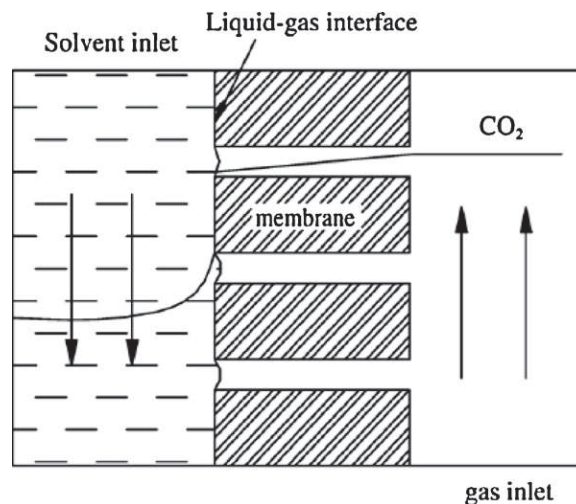


Fig. 6. CO_2 -membrane gas absorption principle.

Source: Adopted from Yan et al. (2007).

membranes to provide a large interfacial area to separate the liquid phase and the gas phase. Accordingly, the problems encountered in the conventional equipment such as flooding, foaming and entrainment can be avoided. Compared to the non-porous gas permeation membranes which have the selectivity advantage, the porous membranes in the membrane contactor are non-selective. The role of selectivity is fulfilled by liquid absorbents via physical absorption, chemical reaction or a combination of these two processes. Thus, membrane contactor provides a high permeation flux due to the lower mass transfer resistance and large interfacial area between the gas phase and liquid phase.

Hollow fiber membrane contactor offers several advantages over conventional techniques. The microporous hollow fiber membrane is the main element in a membrane contactor device, in which the membrane acts as a physical support and provides a large interfacial area between the contacting phases without phase dispersion, thus the gas phase and liquid phase can be manipulated independently. The compact modular structure of membrane contactors, in turn, provides the flexibility for scale up or down with much larger gas–liquid interfaces on a small foot-print so that the mass transfer efficiency can be enhanced significantly. In addition, the absorption membranes work at near atmospheric pressure (1 atm); enabling simple and low-cost construction. It has been reported that hollow fiber contactors are about 30 times more efficient for gas absorption than conventional equipment (Cussler, 1994). Consequently, the size of the absorber and stripper units can be reduced by 65% (Herzog, 2001), resulting in the potential cost reduction of up to 25% which is below the best available packed column technology (Dindore et al., 2005).

In the gas–liquid contacting process, the mass transfer resistance of gas diffusion from bulk gas phase to external membrane surface is negligible in comparison to other resistances (Dindore et al., 2004; Karoor and Sirkar, 1993; Rangwala, 1996). For physical absorption of CO_2 , the resistance associated with the liquid phase depends on the hydrodynamic condition which generally remains constant for a constant liquid flow rate (Mavroudi et al., 2006). On the other hand, the concentration of a particular gas in the bulk gas phase serves as the rate-limiting factor when the gas is absorbed by liquid via a chemical reaction. This phenomenon has been demonstrated by the experimental study on the simulation of CO_2 capture using both physical and chemical absorption by Zhang et al. (Zhang et al., 2006). In this study, when distilled water was used as the absorbent; the inlet CO_2 gas velocity had no significant influence on CO_2 flux. Increased liquid velocity, on the other hand, increased

Table 3CO₂ absorption flux of hollow fiber membrane contactors.

Membrane material	Liquid absorbent	Liquid velocity (m s ⁻¹)	Gas velocity (m s ⁻¹)	CO ₂ flux (mol m ⁻² s ⁻¹)	Test type ^{a,b} (CO ₂ vol%)	Ref.
PVDF	Pure water	0.15	0.06	1.0×10^{-3}	S	Ren et al. (2006)
PVDF	Pure water	1.5	0.07	2.0×10^{-4}	M (20%)	Atchariyawut et al. (2007))
PVDF	Pure water	1.5	0.07	2.5×10^{-3}	S	Atchariyawut et al. (2007)
PVDF	MEA	1.5	0.07	3.2×10^{-3}	S	Atchariyawut et al. (2007)
PVDF	NaOH	1.5	0.07	3.0×10^{-3}	S	Atchariyawut et al. (2007)
PVDF ^c	DEA	0.12	0.06	6.0×10^{-4}	M (20%)	Wang et al. (2005)
PP ^c	DEA	0.1	0.073	4.0×10^{-4}	M (20%)	Zhang et al. (2006)
PP ^c	MEA	0.1	0.211	5.8×10^{-4}	M (14%)	Yan et al. (2007)
PS ^c	Pure water	0.3	0.01	7.5×10^{-3}	S	Mansourizadeh and Ismail (2010a,b)
PEI ^d	Pure water	0.2	–	1.2×10^{-3}	S	Bakeri et al. (2010)
PAI ^e	Pure water	0.3	0.06	8.5×10^{-4}	S	Zhang et al. (2011)

^a Test type: Single gas experiment (S) and mixed gas experiment (M) (CO₂/CH₄).^b Gas mixture was CO₂/N₂.^c Gas mixture was CO₂/O₂/N₂.^d Feed gas pressure is 1 bar. No indication of feed gas pressure in other references, it is anticipated to be near atmospheric pressure.^e All the experiments were conducted at room temperature.

the CO₂ flux. Furthermore, when diethanolamine (DEA) was used as the chemical absorbent, CO₂ flux was affected significantly by the CO₂ velocity in the gas side while the liquid velocity had limited effect on CO₂ flux.

4.2. Experimental studies

Zhang and Cussler were the first to adapt hollow fiber membrane contactors to study CO₂ removal (Zhang and Cussler, 1985). Following their first trial, the performance of hollow fiber membrane contactor for CO₂ separation has been studied extensively (Al-Marzouqi et al., 2008; Asimakopoulou and Karabelas, 2006; Atchariyawut et al., 2006; He et al., 2009; Keshavarz et al., 2008; Li and Chen, 2005; Mavroudi et al., 2006; Rajabzadeh et al., 2009a; Ren et al., 2006; Rongwong et al., 2009; Sandru et al., 2010; Simons et al., 2009; Sridhar et al., 2007b; Wang et al., 2004b; Wang et al., 2004c; Yan et al., 2007; Zhang et al., 2006, 2008). Most of the studies have been conducted for CO₂ removal. However, most natural gas, biogas fields and other gas streams with high CO₂ content also have H₂S and other acid gases present, and removal of them is also necessary. Wang et al. reported the studies of removing H₂S by gas liquid membrane contactor (Wang et al., 2002a, 2004a). Lee et al. and Park et al. reported SO₂ removal in the hollow fiber membrane contactors (Lee et al., 2006; Park et al., 2008). Li and Chen reviewed absorption of CO₂ using chemical solvents in hollow fiber membrane contactors (Li and Chen, 2005). Recently, Mansourizadeh et al. did a comprehensive review about hollow fiber gas–liquid membrane contactors for acid gas capture (Mansourizadeh and Ismail, 2009). Currently, large pilot plant gas–liquid membrane contactor units have been developed by Kvaerner Oil & Gas and TNO Environment Energy and Process Innovation (Aresta, 2003; Feron and Jansen, 2002).

Table 3 provides a summary of CO₂ absorption flux for different membrane materials. Among various hydrophobic polymers, polypropylene (PP) and polytetrafluoroethylene (PTFE) are the most popular membrane materials. These materials have been used in membrane contactors (Wang et al., 2004b; Yan et al., 2007). However, since PTFE and PP membranes are usually produced by stretching or thermal methods, the relatively low porosity of PP and PTFE membranes impose a limit on the absorption flux. Consequently, the main advantage of the microporous hollow fiber membrane e.g. its high area-to-volume ratio has not been fully realized. In addition, PTFE and PP materials cannot be used to prepare asymmetric membranes via the phase-inversion method due to their insolubility in common solvents. Another hydrophobic material, polyvinylidene fluoride (PVDF) which has good chemi-

cal and thermal resistance, can be fabricated by the non-solvent induced phase separation (NIPS) method and hence the membrane structure can be tailored to meet the application requirements (Atchariyawut et al., 2006; Mansourizadeh and Ismail, 2010b, 2011a,b; Mansourizadeh et al., 2010). PVDF can also be fabricated by thermal induced phase separation (TIPS) (Rajabzadeh et al., 2009a; Rajabzadeh et al., 2008). PVDF membrane fabricated by TIPS with considerably different structures were compared and used in gas–liquid membranes for CO₂ separation (Rajabzadeh et al., 2009b).

However, it has been reported that the PVDF membrane cannot maintain long-term performance due to the wetting problem. One proposed reason is that the hydrophobicity of PVDF material is not sufficiently high to prevent liquid penetration into the membrane pores (Mavroudi et al., 2006). On the other hand, some less hydrophobic membranes such as PSf (Ismail and Mansourizadeh, 2010; Mansourizadeh and Ismail, 2010a) and PEI (Bakeri et al., 2010) are also investigated for CO₂ separation in the membrane contactor. However, the performance stability under long-term operating conditions is still subject to further investigations.

It is necessary to develop new highly hydrophobic membrane materials which can be processed using the phase-inversion method so the structure and morphology can be tailored. Alternatively, membrane surface modification may be conducted to improve the surface hydrophobicity. The strategies for overcoming the membrane wetting are discussed in detail in Section 3.3.

4.3. Limitations and improvements

4.3.1. Membrane wetting

Membrane wetting can be induced by chemical attack. The polymeric membranes in the membrane contactor generally have to be in direct contact with the liquid absorbents. The conventional absorbents include monoethanolamine (MEA), DEA, methyldiethanolamine (MDEA) and their mixtures, as well as sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP). The absorbents with a high CO₂ loading capacity are highly corrosive, which can induce change to the membrane morphology and eventually lead to the wetting of membrane pores (Kumar et al., 2002). Celgard® X40-200 and X50-215 polypropylene hollow fibers were observed to experience changes in their pore structure and surface roughness after being exposed to DEA aqueous solutions (Wang et al., 2004c). Commercially available porous polyolefin membranes were not compatible with MEA as evidenced by liquid seepage through the membranes during operation (Kumar, 2002). Falk-Pedersen and Dannström reported that poor performance of

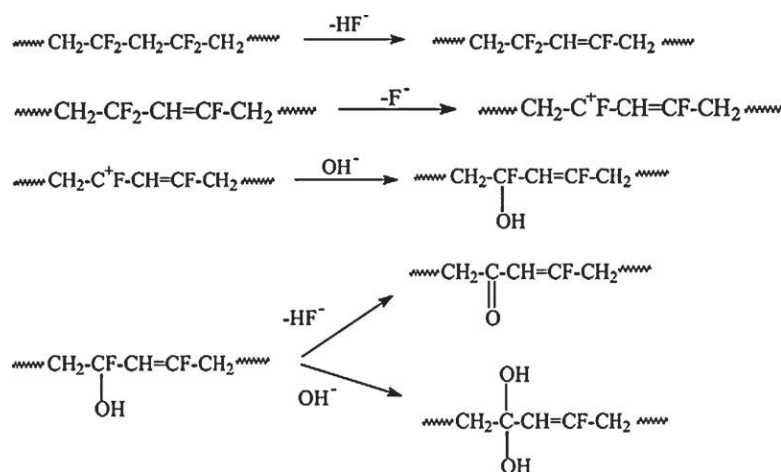


Fig. 7. Mechanisms of alkaline modification of PVDF.

Source: Adopted from Ross et al. (2001).

polypropylene and failure of polypropylene and polyethersulfone coated with polydimethyl siloxane after 7 days operation (Falk-Pedersen and Dannström, 1997). All these studies indicated that performance deterioration is associated with the wetting of the membranes used.

The membrane surface hydrophobicity must be improved to avoid wetting. Once the membrane pores are filled or even partially filled by the liquid, the mass transfer resistance will increase significantly due to the additional resistance from the stagnant liquid phase inside the pores. The breakthrough pressure or liquid penetrating pressure is widely used to characterize the membrane in terms of wetting resistance, above which the liquid can penetrate into the membrane pores, as represented by the Laplace–Young equation (Franken et al., 1987):

$$\Delta p = -\frac{4\sigma_l \cos \theta}{d_{\max}}, \quad (8)$$

where σ_l is the liquid surface tension, θ is the contact angle between the liquid and membrane surface, and $d_{\max}$ is the maximum pore diameter in the membrane. Equation (8) implies that, to obtain a high breakthrough pressure, the membrane has to be hydrophobic with a contact angle as high as possible and it should have a well-tailored surface pore structure, e.g. a relatively small maximum pore size and a narrow pore size distribution. Moreover, the membrane itself introduces an extra resistance to the mass transfer process. Thus, the membrane used should have a high overall porosity to minimize the membrane resistance. This can be controlled by changing the dope formula or adjusting the spinning conditions.

4.3.1.1. A: utilizing hydrophobic membranes. In general, two approaches can be adopted to obtain high membrane hydrophobicity. The first approach is to utilize hydrophobic materials with high chemical resistance for membrane fabrication. A copolymer of poly(vinylidene fluoride-co-tetrafluoroethylene) (F2,4) was fabricated by a phase inversion process by Feng et al. (Feng et al., 2004a; Feng et al., 2004b). The co-polymer of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is reported as a good candidate. The addition of an amorphous phase of hexafluoropropylene (HFP) into the main constituent VDF blocks modified the properties of the homopolymer e.g. increasing the fluorine content and making PVDF-HFP more hydrophobic than PVDF. Recently, Wang and her co-workers published a series of papers on the fabrication of PVDF-HFP asymmetric microporous membranes in both flat sheet and hollow fiber configurations (Feng et al., 2006; Shi et al., 2009;

Shi et al., 2007; Shi et al., 2008). Extensive studies have been performed to investigate various membrane preparation conditions. The rheology of dope solutions was studied which is essential to understand and control the pore size and its distribution. Moreover, the effects of process conditions such as coagulation temperature, air gap, spinning dope formulation and coagulant chemistry on membrane morphology and structure as well as their impact on pore size and its distribution in the resultant hollow fiber membranes were probed. Still, further studies are warranted to improve the pore structure and surface property of these membranes for CO_2 absorption.

4.3.1.2. B: surface hydrophobic modification. The second approach is to apply a more hydrophobic surface coating/modification layer on the existing hydrophobic membranes to protect the surface pores from wetting. A number of surface modification studies have been completed in which to increase the membrane hydrophobicity, given the availability of a variety of surface modification techniques. Gugliuzza et al. reported the surface coating of a thin layer of tetra-fluoroethylene (TFE) and 2,2,4-trifluoro-5-tri-fluoromethoxy-1,3-dioxole (TIT) (Hyflon AD X60) on PVDF membrane. The coated membrane exhibited strong hydrophobicity with a contact angle of 147° (Gugliuzza and Drioli, 2007). Kim et al. modified a PVDF flat sheet membrane surface by adding fluorinated surface modifying macromolecules (SMM) in the concentration range from 0 to 2 wt.% into the PVDF polymer matrix. The contact angle of modified PVDF membrane increased from original 75° to 90° with increasing SMM concentration (Kim et al., 2009). Similarly, Bakeri et al. recently reported the novel surface modification of PEI hollow fiber membrane using SMM as a dope additive. The membrane showed increased surface contact angle (Bakeri et al., 2012). A superhydrophobic PVDF film was fabricated by Zheng et al. via sodium hydroxide (NaOH) treatment and the enhancing chemical bath deposition method. The modified membrane exhibited superhydrophobicity and a self-cleaning property with the water contact angle and sliding angle of 157° and 1° , respectively (Zheng et al., 2010). They explained the mechanisms of alkaline modification of the PVDF film by using the mechanisms proposed by Ross et al. (Ross et al., 2001), as shown in Fig. 7. Two modification methods, e.g. plasma treatment and chemical treatment using a perfluoro-compound were reported by Yang et al. to treat commercial PVDF hollow fiber membrane. The modified PVDF membranes showed contact angles of 105° and 115° , respectively (Yang et al., 2011). PAI membrane was chemically modified from the original 76° to 117° by using perfluoro-compound (Fluorolink S10) for CO_2

Table 4Glass transition temperature T_g of polymers.

Polymer	T_g (°C)
Polytetrafluoroethylene	126
Polypropylene	–15
Polyethylene	–120
Polyther sulfone	230
Polysulfone	190
Polyvinylidene fluoride	–40
Polydimethylsiloxane	–123
Kapton polyimide	300

Source: Adopted from Mulder (1996).

absorption in a gas–liquid membrane contactor (Zhang et al., 2011). Very recently, a flat sheet PES membrane was modified by CF4 plasma treatment. The modification turned the hydrophilic PES membrane to a hydrophobic membrane with a contact angle above 120° (Wei et al., 2012).

4.3.2. Thermal stability

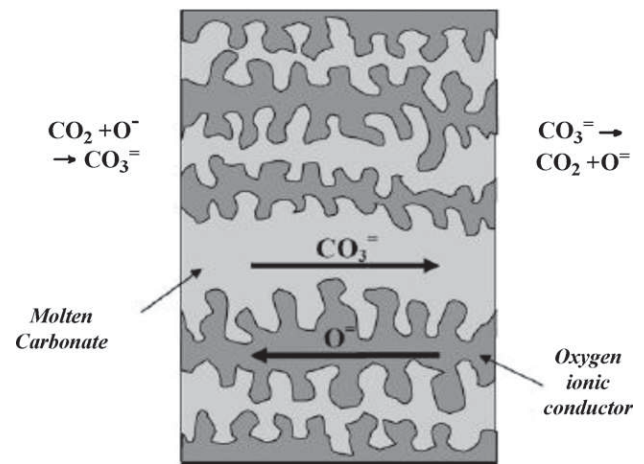
Thermal stability is an important property of a membrane. As most current membrane contactor studies are investigated at ambient temperature, the thermal stability of the membrane is less considered. However, this is important for industrial operations. Specifically, for CO₂ separation from flue gas, the gas stream is possibly above 100°, therefore a high membrane thermal stability is required. Otherwise, the membrane may deteriorate or even decompose under the high temperature. The extent of membrane change depends on its intrinsic property, e.g. glass transition temperature (T_g) for amorphous polymers or the melting point (T_m) for crystalline polymers. Over these temperatures, the membrane property will change significantly. Most polymers used for making membranes in a membrane contactor are amorphous, so T_g is commonly used. A list of T_g for different polymers is shown in Table 4. As can be seen from the table, PTFE has a much larger T_g compared to PP and PE and this feature contributes to its higher stability.

5. Inorganic membranes

5.1. Working principle

Inorganic membranes are useful for CO₂ separation under severe conditions (high temperature and pressure) when organic-based membranes are not functional. These membranes can be categorized into porous and non-porous types.

Porous inorganic membranes such as zeolites, which contain sub-nanometer pores, are favorable for CO₂ separation and removal from CH₄ because of their chemical resistance to CO₂ induced plasticization and superior selectivity to polymeric membranes (Li et al., 2005; Tomita et al., 2004; Zhu et al., 2006). Zeolites membranes normally consist of polycrystalline films of aluminosilicates loaded on porous supports (Li et al., 2005). CO₂ separation over CH₄ in zeolite is attributed to the favorable adsorption of CO₂ over CH₄ on most zeolites e.g. faujasite (FAU) and MFI types which normally decreases with increasing temperature (Othman et al., 2009; Zhu et al., 2006) as well as the molecular sieving mechanism due to their different molecular kinetic diameters with CO₂ of 3.30 Å and CH₄ of 3.80 Å. The selectivity of CO₂/CH₄ is quite dependent on the zeolite material composition. ZSM-5 with larger pores of 5.5 Å displayed a lower selectivity around 5 at room temperature (Poshusta et al., 1999). More promising membranes are made from SAPO-34 or DDR type zeolites having pores of 3.8 Å and 3.6 Å, respectively. SAPO-34 zeolite membrane on porous α-alumina supports exhibited the CO₂/CH₄ selectivity range from 86 to 171 with CO₂ permeabilities of 20,000–40,000 Barrer (Carreon et al., 2008). Himeno et al. synthesized a supported hydrophobic DDR

**Fig. 8.** Dual phase ceramic-carbonate membranes concept for CO₂ separation.

Source: Adopted from Anderson and Lin (2010).

zeolite membrane with CO₂ permeability of 2200 Barrer but with the selectivity up to 400 at room temperature (Himeno et al., 2007).

Other porous inorganic membranes such as silica and carbonized membranes are also available but less popular than zeolites. Both membranes normally separate CO₂ from other gases including CH₄ by molecular sieving principles e.g. silica has sub-nanometer sized pores which would pass different gases according to their sizes (De Vos and Verweij, 1998; Ogawa and Nakano, 2000; Raman and Brinker, 1995).

Non-porous inorganic membranes become attractive for high temperature applications (in excess of 400 °C) only when the amount of ionic defects in these membranes is significant enough to allow appreciable ionic movement and, therefore, high conductivity. This type of membrane is represented by a dual-phase membrane containing mixed conducting oxide ceramic (MCOC) and molten carbonate phases (Anderson and Lin, 2010; Li et al., 2009; Rui et al., 2009). Absolute CO₂/N₂ selectivity and very high CO₂ permeability have been demonstrated by these membranes which are unattainable previously by silica and zeolite membranes. This occurs because the adsorption in the micro-pores of these membranes becomes negligible at these temperatures, rendering their permeation to be limited only by the diffusivity which results in diminishing selectivity with increasing temperature (Anderson and Lin, 2010). The initial concept of this dual-phase membrane was originated from the initial dual-phase membrane trial which was composed of a metal (stainless steel) support infiltrated with a molten mixture of Li, Na and K carbonate (Chung et al., 2005). This membrane could separate CO₂ between 450 and 650 °C. Nevertheless, the stainless steel support is oxidized above 650 °C which further prompts the use of porous inorganic membrane as a support due to their high temperature stability. Basically, in this type of membrane, the carbonate ions are transported via the molten carbonate phase while the oxygen ions are transported via oxygen ionic conductor phase as depicted in Fig. 8. The transport through this membrane is driven by the CO₂ partial pressure difference between feed and permeate sides. In the feed side, the oxygen ions (O^{2–}) within the support react with CO₂ in the feed stream to form CO₃^{2–} which is then transported to the permeate side to form oxygen ions which remain on the solid phase all the time (Anderson and Lin, 2010). For example, a dual phase membrane of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3–δ} and 42.5Li₂CO₃/32.5Na₂CO₃/25K₂CO₃ (mol%) and Bi_{1.5}Y_{0.3}Sm_{0.2}O₃ and 43.5Li₂CO₃/31.5Na₂CO₃/25K₂CO₃ (mol%) only passed CO₂ and therefore showed absolute CO₂/Ar selectivity (higher than 225 which was the limit of detection in

the gas chromatograph) between 600 and 900 °C (Anderson and Lin, 2010).

To describe the high temperature CO₂/O₂ permeation characteristics of these dual-phase membranes, a theoretical model and equations have been developed by Lin and co-workers. The general case of CO₂ permeation with O₂ permeation can be simplified substantially into a single equation in the case of only CO₂ permeation without O₂ permeation (Rui et al., 2009). Using this model, the correlation between CO₂ flux with ionic and electronic conductivity of ceramic phase as well as oxygen permeation and volume fraction and tortuosity of each phase can be well explained (Rui et al., 2009). For example, CO₂ flux increases with increasing electronic conductivity and ionic conductivity (at low electronic conductivity) of the ceramic phase. O₂ flux also increases with increasing ionic conductivity and electronic conductivity of the ceramic phase. Also, the CO₂ flux for the case of CO₂/O₂ mixture as the feed is much higher than the pure CO₂ permeation case. Moreover, the CO₂ and O₂ fluxes of the ordered pore structure are larger than those for the disordered structure. Additionally, the CO₂ flux increases while O₂ flux decreases with increasing molten carbonate phase volume fraction when CO₂/O₂ permeates together. This is in opposite with the case for pure CO₂ permeation in which the CO₂ flux decreases with increasing molten carbonate phase volume fraction.

Lin and co-workers have also derived a very simple equation [Equation (6)] in the case of pure CO₂ permeation and oxygen ionic conductivity limiting case (e.g. oxygen ionic conductivity in the ceramic phase is much smaller than that of carbonate ions in molten carbonate). Equation (6) utilizes parameters only from the ceramic phase e.g. ε and τ are porosity and tortuosity of the ceramic support phase, respectively, and ϕ is the geometric correction factor of the support phase. R , T , σ_i , F , L correspond to ideal gas constant, temperature, Faraday's constant and the support thickness. P'_{CO_2} and P''_{CO_2} refer to carbon dioxide partial pressure in the feed and permeate sides:

$$F_{\text{CO}_2} = - \left(\frac{\varepsilon}{\tau} \right) \frac{RT\phi\sigma_i}{4(P'_{\text{CO}_2} - P''_{\text{CO}_2})F^2L} \ln \left(\frac{P'_{\text{CO}_2}}{P''_{\text{CO}_2}} \right). \quad (6)$$

Equation (6) fitted well the characteristics of dual-phase La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3- δ} and 42.5Li₂CO₃/32.5Na₂CO₃/25K₂CO₃ (mol%) system. The agreement between the experimental data and equation's results verified that CO₂ permeation mechanism is limited by the oxygen ionic conductivity of the support phase (Anderson and Lin, 2010).

5.2. Experimental studies

Table 5 provides a summary of the permeability and selectivity of several porous and non-porous inorganic membranes. Kusakabe and co-workers reported the use of NaY (FAU-type) zeolite membranes for CO₂/CH₄ separation and improve the selectivity and permeability of the membranes by ion-exchanging Na in Y zeolite with K (Hasegawa et al., 2002; Kusakabe et al., 1997). The occluded cations in the zeolitic structure affecting the sorption of CO₂ onto zeolite with study by Hasegawa et al. (Hasegawa et al., 2001) show that the CO₂ sorption into zeolite over N₂ (and therefore the CO₂ selectivity) is favored in the enhanced order of Na < Cs < K = Rb. Since both CO₂ and CH₄ molecules are much smaller than the FAU pores, separation with these membranes is mainly based on competitive adsorption. SAPO-34 zeolite membranes which are essentially a silicoaluminophosphate with the composition Si_xAl_yP₂O₂, where $x = 0.01 - 0.98$, $y = 0.01 - 0.60$, $z = 0.01 - 0.52$ and $x + z = y$, have also been prepared which have pores that are similar in size to CH₄; leading to higher selectivity to NaY zeolite (Li et al., 2005; Li et al., 2006). The selectivity and permeability of SAPO-34, nevertheless decrease in the presence of minor amounts of other gas components

such as water, N₂ and C₂–C₄ hydrocarbons (of interest in industry) with the percentage of hydrocarbon dominating the extent of decrease (Li et al., 2005). MFI type-zeolite e.g. silicalite-1 and ZSM-5 have also been studied due to the established synthesis knowledge, suitable channel opening size and thermal stability (Lovallo et al., 1998; Othman et al., 2009; Van Den Broeke et al., 1999; Zhu et al., 2006). Due to the negative effect of water on SAPO-34 zeolite from its hydrophilic nature which causes its strong affinity to water, zeolite membranes with hydrophobic properties e.g. DDR have been studied (Tomita et al., 2004; van den Bergh et al., 2008; Zhu et al., 2006). The interest in DDR zeolite membrane is also attributed to the contribution of molecular sieving mechanism since DDR zeolite membrane pores diameter size is in between the kinetic diameter of CO₂ and CH₄ (Othman et al., 2009). Another porous inorganic membrane e.g. silica membrane is also available which has been studied previously for CO₂/CH₄ separation and is not popular since its performance is inferior compared to zeolite (Raman and Brinker, 1995). In this type of membrane, templating strategy e.g. addition of organic component followed by its removal at calcinations is often used in combination with surface derivatization technique to reduce the pore sizes. Nonetheless, in this membrane, the trade-off between permeability and selectivity still dominates (De Vos and Verweij, 1998; Raman and Brinker, 1995). Carbonized membranes made by carbonizing polymer precursors at high temperature e.g. 700 °C and above have also been studied (Ogawa and Nakano, 2000).

For non-porous inorganic membranes, a promising dual-phase membrane concept consisting of MCOC and molten carbonate phases has recently been proposed and developed by Lin and co-workers as described in Section 2.4.1 (Anderson and Lin, 2010; Li et al., 2009; Rui et al., 2009). The dual-phase membranes are primarily targeted for applications to capture CO₂ in pre- and post-fuel combustion processes and as selective membranes in membrane reactors for CO₂–CH₄ dry reforming reactions; all of which offer heat integration opportunity.

5.3. Limitations and improvements

5.3.1. Limited applicability

Despite their superior selectivity and/or permeability at high temperatures and pressure when the organic-based membranes cannot operate, the major drawback of these membranes lies on their substantially higher cost and difficulty to scale up the membrane area without defects; especially accounting for their synthesis which involves high temperature processes and therefore, specialized equipment.

5.3.2. Poisoning gas effects on porous inorganic membranes

Moreover, the presence of other gas components such as water and hydrogen sulfide have also been reported to induce negative effects toward the CO₂ separation performance of zeolite membranes (Li et al., 2005). The research efforts to lessen the effect of water have focused around adjusting the surface properties of membranes, mostly by making the surface more hydrophobic (Zhu et al., 2006). Modifying the structure of zeolite by changing its cation e.g. by ion-exchanging Na in Y zeolite with K have been reported to improve the resistance of Fa-type zeolite to H₂S (Lee et al., 2005).

5.3.3. Low permeability of non-porous inorganic membranes

Non-porous inorganic membranes e.g. an oxygen ionic conductor-molten carbonate dual phase composite is attractive in terms of its absolute selectivity. Nevertheless, more improvements should be made in terms of its permeability which is relatively lower to its porous membrane counterpart.

Table 5
CO₂/CH₄ separation performance of inorganic membranes.

Membrane material	Membrane type	Pressure (bar)	Temperature (°C)	CO ₂ permeances		Selectivity (CO ₂ /CH ₄)	Test type ^c (CO ₂ vol%)	Ref.
				Value	Units ^{a,b}			
NaY zeolite (on porous alumina tube)	Porous		30	298.83	GPU	20	M (50%)	Kusakabe et al. (1997)
KY zeolite (on porous alumina tube)	Porous		30	2091.80	GPU	40	M (50%)	Hasegawa et al. (2002)
SAPO-34 zeolite (on porous stainless steel tube)	Porous	2.2	22	1045.9	GPU	120	M (50%)	Li et al. (2006)
SAPO-34 zeolite (on porous stainless steel tube)	Porous	2200	24	268.95 (130 ppm H ₂ O + 3% N ₂ + 3% C ₂ H ₄ + 1% C ₃ H ₈ + 0.2% n-C ₄ H ₁₀)	GPU	49 (130 ppm H ₂ O + 3% N ₂ + 3% C ₂ H ₄ + 1% C ₃ H ₈ + 0.2% n-C ₄ H ₁₀)	M (50%) + other gases	Li et al. (2005)
SAPO-34 zeolite (on porous stainless steel)	Porous	1.87	24	313.77 (no other gas), 257.29 (170 ppm H ₂ O), 300.9206 (3% C ₂ H ₄), 326.62 (1% C ₃ H ₈), 220.83 (0.2% n-C ₄ H ₁₀), 192.15 (130 ppm H ₂ O + 3% N ₂ + 3% C ₂ H ₄ + 1% C ₃ H ₈ + 0.2% n-C ₄ H ₁₀)	GPU	27 (no other gas), 27.36 (170 ppm H ₂ O), 25 (3% C ₂ H ₄), 23.64 (1% C ₃ H ₈), 19 (0.2% n-C ₄ H ₁₀), 16 (130 ppm H ₂ O + 3% N ₂ + 3% C ₂ H ₄ + 1% C ₃ H ₈ + 0.2% n-C ₄ H ₁₀)	M (50%) + other gases	Li et al. (2005)
MFI (on porous alumina disk)	Porous		170	26.89	GPU	8	S	Lovallo et al. (1998)
Silicalite ⁻¹	Porous	1.01	30	589.84	GPU	4.3	M (50%)	Zhu et al. (2006)
Silicalite ⁻¹	Porous	1	30	5755.22	GPU	2.4	M (50%)	Van Den Broeke et al. (1999)
Silicalite ⁻¹ (on porous alumina disk)	Porous	5	25	15.1	cc(STP)s ⁻¹ (no area information)	2.25	M (50%)	Othman et al. (2009)
H-ZSM-5 (on porous alumina tube)	Porous	0.27	27	5677.75 (Single gas permeation)	GPU	5.5	M (50%)	Poshusta et al. (1999)
Na-ZSM-5	Porous	5	25	14.7	cc(STP)s ⁻¹ (no area information)	6.29	M (50%)	Othman et al. (2009)
B-ZSM-5	Porous	5	25	14.58	cc(STP)s ⁻¹ (no area information)	8.19	M (50%)	Othman et al. (2009)

Table 5 (Continued)

Membrane material	Membrane type	Pressure (bar)	Temperature (°C)	CO ₂ permeances		Selectivity (CO ₂ /CH ₄)	Test type ^c (CO ₂ vol%)	Ref.
				Value	Units ^{a,b}			
DDR zeolite (on porous alumina tube)	Porous	02–5	24	199.22	GPU	220	M (50%)	Tomita et al. (2004)
DDR zeolite (on porous alumina tube)	Porous	02–5	100	99.61	GPU	100	M (50%)	Tomita et al. (2004)
DDR zeolite (on porous alumina disk)	Porous	1	27	209.18	GPU	400	M (50%)	van den Bergh et al. (2008)
DDR zeolite (on porous alumina disk)	Porous	5	27	239.06	GPU	500	M (50%)	van den Bergh et al. (2008)
Silica (on Membralox [®] tube)	Porous	1.38–5.52	25	2570	GPU	12.2	S	Raman and Brinker (1995)
Silica (derivatized, on Membralox [®] tube)	Porous	1.38–5.52	25	204	GPU	71.5	S	Raman and Brinker (1995)
Silica (on alumina disk)	Porous	1.5–4	25	750.06	GPU	326	S	De Vos and Verweij (1998)
Carbonized (polyamic acid)	Porous	1.6	100	5.71	GPU	70	M (15%)	Ogawa and Nakano (2000)
Stainless steel/molten carbonate (Li/Na/K ₂ CO ₃)	Non-porous	1.01	650	15.54	GPU	16	S	Chung et al. (2005)
Bi _{1.5} Y _{0.3} Sm _{0.2} O ₃ /molten carbonate (Li/Na/K ₂ CO ₃ , 43.5/31.5/25 mol%)	Non-porous		650	0.0011	cc(STP) cm ⁻² s ⁻¹	∞ (only CO ₂ pass)	CO ₂ /Ar (50%)	Li et al. (2009)
La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O _{3-d} /molten carbonate (Li/Na/K ₂ CO ₃ , 42.5/32.5/25 mol%)–0.375 mm	Non-porous		700	20.92	GPU	∞ (only CO ₂ pass)	CO ₂ /Ar (50%)	Anderson and Lin (2010)
La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O _{3-d} /molten carbonate (Li/Na/K ₂ CO ₃ , 42.5/32.5/25 mol%)–0.375 mm	Non-porous		900	146.43	GPU	∞ (only CO ₂ pass)	CO ₂ /Ar (50%)	Anderson and Lin (2010)

^a 1 GPU = 10⁻⁶ cc(STP) cm⁻² s⁻¹ cmHg⁻¹.^b Test type: Single gas experiment (S) and mixed gas experiment (M).^c To convert values in GPU into mol m⁻² s⁻¹ Pa⁻¹ multiply the value by 5.95 × 10⁻⁴ (Ebner and Ritter, 2009).

6. Mixed matrix membranes

6.1. Maxwell model

Mixed matrix membranes (MMMs), discovered by Kulprathipanja et al. at UOP (Kulprathipanja et al., 1988), offer another route for solution-diffusion transport type polymeric membranes. MMMs are heterogeneous membranes composed of an inorganic material such as zeolite or CMS, in the form of micro- or nano-scale particles embedded in the continuous polymeric matrix. According to Powell and Qiao (Powell and Qiao, 2006), the incorporation of nanoparticles has three major effects on the membrane permeability e.g. they can act as molecular sieves to alter the permeability, they can disrupt the membrane matrix structure to increase the permeability and they can also act as a barrier to reduce the permeability.

Maxwell model provides a simple and quantitative framework to predict gas permeability in mixed matrix materials with aspect ratio near unity (e.g. spherical particles) for the dispersed phase (Maxwell, 1973). According to two-phase Maxwell equation, the effective permeability in a MMM is as follows (Maxwell, 1973):

$$P_{eff} = P_c \left[\frac{P_D + 2P_c - 2\Phi_D(P_c - P_D)}{P_D + 2P_c + \Phi_D(P_c - P_D)} \right] \quad (7)$$

where P_{eff} is the effective permeability in mixed matrix material; Φ is the volume fraction and the subscripts D and C refer to the dispersed and continuous phase, respectively.

Other relations have also been proposed to describe the gas transport properties in MMMs, including three-phase Maxwell model (Mahajan and Koros, 2002a), Higuchi model (Higuchi, 1958), effective media theory and Bruggeman model (Banhegyi, 1986). Several studies have compared the predictions of these various models and the results have been quite similar (Mahajan, 2000; Petropoulos, 1985; Zimmerman et al., 1997). These models, however, are complicated in nature and the results do not provide significant improvement over the two-phase Maxwell equation. Therefore, the two-phase Maxwell equation has been widely used as the key theoretical framework to correlate the transport properties in a polymer matrix embedded with spherical inorganic particles.

6.2. Experimental studies

Although inorganic membranes can overcome the permeability and selectivity limitations of polymeric membranes on the small scale, manufacturing of inorganic membranes incurs large cost (a few orders of magnitude higher than polymeric membranes). Moreover, large-scale production of inorganic membranes requires reproducibility improvements. MMMs in principle combine size/shape selectivity of nanoporous materials with the processability and mechanical stability of polymers. By combining the advantages of inorganic and polymeric components, MMMs can be considered as an evolutionary approach to increase both permeability and selectivity. The gas permeability through a MMM depends on both the intrinsic molecular sieve properties of the inorganic filler and the polymer (Tantekin-Ersolmaz et al., 2000). The advantage of MMMs lies in the superior gas separation properties attributed to the molecular sieving ability of the molecular inorganic filler. Inorganic particles used in MMMs can be categorized into two groups, porous and non-porous e.g. porous zeolites, carbon molecular sieves (CMS), metal oxides and non-porous silica. The performance of some MMMs is listed in Table 6.

Zeolites are highly regarded as the frontier family of molecular sieve used in MMMs (te Hennepe, 1988; Hillock et al., 2008; Jia et al., 1991). Zeolites are microporous crystalline materials; they have three-dimensional uniform pore structures with

Table 6
CO₂/CH₄ separation performance of mixed matrix membranes.

Membrane material	Inorganic filler	Pressure (bar)	Temperature (°C)	CO ₂ Permeances		Selectivity (CO ₂ /CH ₄)	Test type ^d (CO ₂ vol%)	Ref.
				Value	Units ^{a,b,c}			
Cross-linkable polyimide (PDMC)	SSZ-13 zeolite (25%)	4.4	35	148	Barrer	38.9	S	Ward and Koros (2011)
PSf	MCM-41 silica (0%)	4	35	4.5	Barrer	23	S	Kim and Marand (2008)
PSf	MCM-41 silica (10%)	4	35	6.6	Barrer	23	S	Kim and Marand (2008)
PSf	MCM-41 silica (20%)		35	7.8	Barrer	23	S	Kim and Marand (2008)
PSf	MCM-41 silica (40%)	4	35	14.8	Barrer	15	S	(Kim and Marand, 2008)
Matrimid® 97 25	MOFs (0%)	4	35	10	GPU	18	M	Basu et al. (2011)
Matrimid® 97 25	[Cu ₃ (BTC) ₂] (30%)	10	35	17	GPU	23	M (35%)	Basu et al. (2011)
Matrimid® 97 25	ZIF-8 (30%)	10	35	22	GPU	20	M (35%)	Basu et al. (2011)
Matrimid® 97 25	MIL-53(Al) (30%)	10	35	19	GPU	22	M (35%)	Basu et al. (2011)
GFDA-DAM	MOFs (0%)	2	25	390	Barrer	24	M (35%)	Bae et al. (2010)
GFDA-DAM	ZIF-90 (15%)	2	25	720	Barrer	37	M (50%)	Bae et al. (2010)
Matrimid® 52 18	Carbon molecular sieve (CMS) (0%)	3.4	35	10	Barrer	35.71	S	Vu et al. (2003b,c)
Matrimid® 52 18	CMS (17%)	3.4	35	10.3	Barrer	44.78	S	Vu et al. (2003b,c)
Matrimid® 52 18	CMS (33%)	3.4	35	11.5	Barrer	47.92	S	Vu et al. (2003b,c)
Matrimid® 52 18	CMS (100%)	3.4	35	44	Barrer	200	S	Vu et al. (2003b,c)
Utem® 1000	Zeolites (0%)	7.8	35	13.8	GPU	39.6	M (20%)	Husain and Koros (2007)
Utem® 1000	Grignard treated zeolites (13.5%)	7.8	35	6.8	GPU	46.9	M (20%)	Husain and Koros (2007)

^a 1 GPU = 10⁻⁶ cc(STP) cm⁻² s⁻¹ cmHg⁻¹.

^b 1 Barrer = 10⁻¹⁰ cc(STP) cm cm⁻² s⁻¹ cmHg⁻¹.

^c Test type: Single gas experiment (S) and mixed gas experiment (M).

^d To convert values in GPU into mol m⁻² s⁻¹ Pa⁻¹ multiply the value by 5.95 × 10⁻⁴ (Ebner and Ritter, 2009).

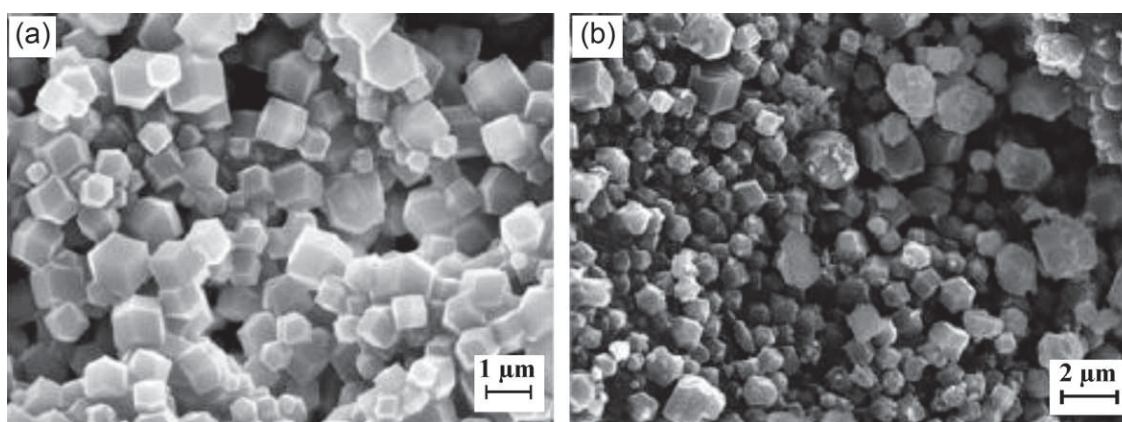


Fig. 9. SEM images of submicrometer-sized ZIF-90 particles; a) ZIF-90A synthesized using methanol as a nonsolvent; b) ZIF-90B synthesized using deionized water as a nonsolvent.

Source: Adopted from Bae et al. (2010).

interconnected tunnels and cages so gas molecules are sieved based on the size and shape (Derouane et al., 1992). With the addition of zeolite in the selective skin layer, the CO_2/CH_4 selectivity was improved around 50% more than the neat PSf/Matrimid[®] hollow fibers (Jiang et al., 2006).

Incorporation of CMSs has also been performed (Jha and Way, 2008; Vu et al., 2003a,b,c,d). CMSs are highly porous materials which allow high gas permeability yet their molecular sieving pore structure provides the discrimination of gas penetrants to yield high selectivity (Vu et al., 2002). Vu et al. (Vu et al., 2003c) examined the incorporation of CMS fiber into two polymer matrices Matrimid[®] 5218 and Ultem[®] 1000. For Matrimid[®] 5218-CMS, the selectivity of CO_2/CH_4 increased 45% with respect to the neat Matrimid[®] 5218 membrane. For Ultem[®] 1000-CMS, up to 40% enhancement in CO_2/CH_4 selectivity was observed with respect to the neat Ultem[®] 1000 membrane. In addition, carbon nanotubes (CNTs)-based MMM have also become an emerging research area. Very recently, Ismail et al. (Ismail et al., 2009) provided a comprehensive review on the past and recent development of CNTs-MMMs.

Metal oxide nanoparticles are another important type of inorganic particle due to its good affinity to CO_2 (Hu et al., 1997). Hosseini et al. (Hosseini et al., 2007) prepared the nanocomposite membrane by incorporating MgO nanoparticles into a Matrimid matrix followed by a 10-day silver ion treatment. The best CO_2/CH_4 separation performance was enhanced 50% relative to the neat Matrimid[®] membrane. The nanocomposite membrane was claimed to separate CO_2/CH_4 by a combination of a solution-diffusion mechanism in the polymeric matrix, size exclusion by silver coated MgO and the facilitated transport by the interaction between CO_2 and MgO/Ag.

Metal organic frameworks (MOFs), a class of nanoporous material containing a metal in the centre with various organic linkers to form a different type of dimensional structure with surface area, porosity, and tuneable pore structure, which has attracted great attention for gas separation recently (Bae et al., 2010). MOFs are expected to be more compatible with the organic phase than other inorganic fillers because the organic linkers in MOFs have better affinity with the polymer chains. ZIF-90 (zeolitic imidazolate framework-90) is an attractive MOF in CO_2 separation membrane application. ZIF-90 has a sodalite cage-like structure with 0.35 nm pore size; the SEM images are shown in Fig. 9. Moreover, the linker in ZIF-90 has carboxyl groups which have good affinity with CO_2 through a chemical non-covalent interaction. The incorporation of ZIF-90 in polyimide 6FDA-DAM membranes increased CO_2 permeability from 390 to 720 Barrer with enhanced CO_2/CH_4 selectivity

from 27 to 37, which indicated a defect-free MMM (Bae et al., 2010). ZIF-8 is also an attractive group of MOFs due to its facile synthesis coupled with its good chemical and thermal stability. Both enhanced CO_2 permeability and CO_2/CH_4 selectivity were observed for ZIF-8/Matrimid membranes (Ordoñez et al., 2010; Thompson et al., 2012).

Non-porous inorganic particles such as silica have been utilized in nanocomposite membranes. Unlike the porous inorganic fillers, non-porous inorganic fillers in glassy polymers could alter the polymer chain packing and results in a larger free volume; leading to a considerable enhancement in permeability (Ahn et al., 2008; Pinnau and He, 2001). Other studies reported the extra void at the interface between the polymer and silica agglomerates might also contribute to the enhancement of permeability (Ahn et al., 2008; Wang et al., 2006; Zou and Ho, 2006). Sadeghi et al. (Sadeghi et al., 2009) investigated the CO_2 and CH_4 transport properties in a composite membrane of polybenzimidazole (PBI) and silica. They found the incorporation of hydrated silica particles enhanced the solubility of condensable gases due to an increased number of polar OH groups in the polymer matrix. The dominant gas permeation mechanism changed from a diffusion mechanism in the neat PBI membrane to a solution mechanism in the hybrid membrane. It was also observed that the permeability decreased for non-condensable gas. This is related to the reduction of gas diffusivity in the polymer matrix caused by the restricted motion of gas molecules in the presence of silica particles.

6.3. Limitations and improvements

6.3.1. Dispersibility of fillers in the organic phase

One of the major challenges in the development of MMMs is the dispersibility of nano-sized inorganic particles in the polymer matrix. In general, the nano-particles disperse poorly in the polymer matrix and thus are liable to aggregate in the formed MMM. This tends to lead to the formation of numerous stress convergence points under the action of outside forces which will weaken the mechanical stability, especially at high inorganic filler concentrations (Yang et al., 2007). The addition of zeolites into a glassy polymer also often leads to the formation of defects at the interface between the zeolite and the polymer attributed to the poor compatibility between zeolites and the polymer matrix. The presence of defects can severely deteriorate the separation performance of the membrane. For instance, the MMM made by Matrimid[®]-zeolite showed much higher permeability with no improvement in selectivity relative to the neat Matrimid[®] membrane due to the formation of voids caused by the polymer chain delaminating away

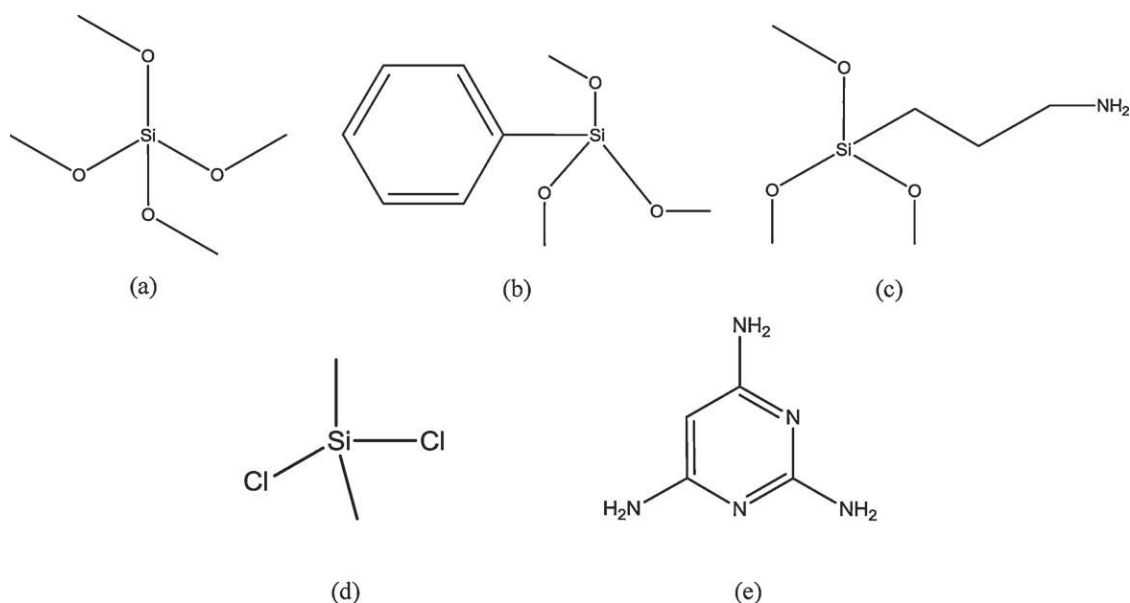


Fig. 10. Molecular structures of different silane coupling agents used in MMMs (a) TMOS; (b) PTMOS; (c) APTMS; (d) DCDMS and (e) TAP.

from the zeolite (Mahajan and Koros, 2000). This is to be expected due to the rigid nature of polymer chains. The rigid chains tend to cause shrinkage and stress during the phase inversion process to form the membrane (Mahajan and Koros, 2002b; Vankelecom et al., 1996). To eliminate the defects at the region between the bulk polymer and dispersed sieve phases, different modification techniques have been proposed and developed (Hillock et al., 2008; Jiang et al., 2006; Mahajan et al., 2002; Mahajan and Koros, 2000).

6.3.1.1. A: Chemical treatment. *p*-Xylenediamine/methanol soaking effectively removed the PSf-zeolite interface defects of the mixed matrix structure. The synthesized zeolites beta mixed matrix layer has a more uniform structure and improved attachment between the polymer matrix and the zeolites surface after *p*-xylenediamine treatment; most likely due to the hydrogen bonding mechanism. The selectivity increased by 50% relative to the neat membranes without zeolite. Hillock et al. (Hillock et al., 2008) modified the zeolites and polymer interface by cross-linking MMM so the mixed matrix was linked with the bulk polymer.

6.3.1.2. B: Priming. Prior to the addition of bulk polymer to the nanoparticles suspension, a small amount of polymer can be added to the nanoparticles solution to reduce the stress at the polymer-nanoparticle interface; defined as “priming”. “Priming” ensures an effective coating of polymer layer on the zeolites particles which prevent the aggregation of the zeolite particles due to the interaction between the coated zeolite and the bulk polymer. The polyimide 3:2 6FDA-DAM:DABA with a propyl monoester chain (PDMC) and zeolite SSZ-13 was used to fabricate MMM. The cross-linked PDMC membrane in combination with PDMC primed zeolite showed enhanced permeability and selectivity. The data was quite consistent with the trend of Maxwell model prediction; indicating a good adhesion between zeolite and polymer phase (Hillock et al., 2008).

6.3.1.3. C: Silane coupling effect. Silane coupling agents have also been used as an effective method to eliminate the interfacial void by enabling a chemical link between the zeolite phase and polymer matrix (Hillock et al., 2008; Mahajan and Koros, 2002a,b). Silanes can react with hydroxyl groups, amino groups and other functional groups from zeolite and/or the polymer matrix to enhance the

compatibility between the phase boundaries. Organosilicate was found to be covalently bonded to the PI matrix e.g. in the case of partially hydrolyzed tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS) or phenyltrimethoxysilane (PTMOS) (Hibshman et al., 2003). Silylation of zeolite by APTS ((γ -aminopropyl) triethoxysilane) also promotes the incorporation with PI films (Vankelecom et al., 1996). The structures of different silane coupling agents are shown in Fig. 10.

6.3.1.4. D: Selection of polymer material and inorganic fillers. The selection of polymer material and inorganic fillers are critical for MMMs. The choice of polymer material determines the intrinsic transport properties of the membrane. Inorganic fillers should be carefully chosen by their different sizes and shapes and the compatibility with the polymer matrix. The criteria normally includes one or more of (a) the average particle size in the nano-scale regime; (b) dispersibility in the polymer; (c) compatibility with the polymer used as the support and (d) particle composition and physical properties. Koros et al. (Mahajan and Koros, 2002a,b) demonstrated how to properly select the dispersed sieve phase and the continuous matrix phase and also explored novel approaches leading to formation of a successful MMM with well tightened interfacial region to prevent “non-selective leakage”.

7. Effect of process operational factors on membrane selection

Based on the operation pressure, membrane separation can be classified into two types e.g. high pressure gas separation and low pressure gas–liquid absorption.

Endowed with well-established modular design and energy efficiency, high pressure gas permeation membranes have been widely used in the CO₂ separation field, such as enhanced oil recovery where CO₂ is separated from a natural gas stream and re-injected into the oil well to enhance the recovery rates of oil and/or gas from a petroleum reservoir. The gas permeation membranes are suitable for use in enhanced oil recovery due to the high CO₂ concentration (>50%) and high pressure (up to 140 bar) encountered in these processes. Nevertheless, at elevated CO₂ pressure, CO₂ plasticization would occur and adversely affects the membrane separation performance, as discussed earlier in Section 2.3.2.

Table 7Comparison of different types of membranes for CO₂/CH₄ separation.

Polymer type	Membrane type	Energy consumption (pressure and temperature)	Permeability	Selectivity	Chemical absorbent	Cost
Polymeric	Gas permeation membrane	Normal-high	Low-good	Low-good	X	Normal-high
Polymeric	Facilitated transport membranes	Normal	Good	Good	X	Normal
Polymeric	Hollow fiber membrane contactor	Low	High	High	✓	Low
Inorganic	Inorganic membranes	High	High	High	X	High
Hybrid	Mixed matrix membranes	Normal-high	Good	Good	X	Normal-high

In the natural gas sweetening application, the feed gas is usually obtained directly from the gas well at a typical pressure of 20–70 bar and CO₂ content of less than 8%. The CO₂ content has to be reduced to around 2% to meet the pipeline specifications and requirements for transportation. Albeit the successful use of gas permeation membranes in enhanced oil recovery at relatively high CO₂ partial pressure, at a low CO₂ low partial pressure driving force, dense membranes and some porous inorganic membranes such as CMS are considered ineffective. This is primarily because of the substantial loss of hydrocarbon contained within the CO₂-rich permeate since more permeable polymers are less selective. The loss of hydrocarbon here renders the process economically unattractive.

On the other hand, a hollow fiber gas liquid membrane contactor in combination with acid gas absorption instead of dense membranes can achieve higher separation selectivity and therefore it is considered more attractive in natural gas sweetening applications; especially to minimize hydrocarbon losses in cases with low CO₂ concentrations. Numerous studies have been carried out using this membrane process in combination with chemical absorption for CO₂ separation; as discussed in Section 2.3. Nonetheless, most work was conducted at the low pressure membrane operation (≤ 2 bar), mainly because these reports are concerned with CO₂ separation from gaseous mixture in flue-gas applications which do not involve a pressurized gas stream (Marzouk et al., 2010). This is albeit the fact those microporous polymeric membranes are delicate in nature which hinders their usage in high pressure applications. Therefore, in the natural gas sweetening case which involves a high feed pressure operation, more studies on membrane contactor module construction, materials and operation condition are required to probe the potential of membrane gas–liquid contactors for use at elevated pressures. Currently, there is lack of systematic studies on high pressure membrane contactors with only two reported studies are available, one in 2004 by Versteeg et al. (Dindore et al., 2004) and another in 2010 by Marzouk et al. (Marzouk et al., 2010). These studies reported that the gas side pressure has a more prolonged effect on CO₂ flux for physical absorption than chemical absorption which renders physical absorption more attractive in elevated pressure relative to low pressure operations.

At high temperature and pressure, inorganic membranes are preferred considering their excellent thermal, mechanical and chemical stability, good erosion resistance and high pressure stability compared to conventional polymeric membranes. Moreover, inorganic membranes also offer the possibility for regeneration after fouling (by removing fouling components at high temperature or leaching fouling components) due to its relatively robust mechanical and chemical structure.

Generally, for all types of membranes, pore plugging is also a common issue. Pore plugging is not devised as a major problem in the laboratory-scale study where purified gas is used. Nonetheless, in industrial operations, gas feed normally contain particles which in most cases necessitate feed gas pre-treatment.

8. Membrane comparisons and future directions

The typical energy consumption (pressure/temperature), permeability, selectivity, chemical absorbent and cost of different

membranes types are compared in Table 7. This table provides an approximate picture on the overall cost and performance of each type of membrane. Dense polymeric membrane usually requires high pressure drops across the membrane due to the high mass transfer resistance by the dense membrane structure. Their permeability and selectivity have a trade-off relationship represented by the Robeson upper bound which served as a benchmark for future development. The facilitated transport membrane is usually operated at a low CO₂ partial pressure due to carrier saturation characteristics. This type of membrane has potential to attain relatively high selectivity without compensating CO₂ permeability by a carrier-mediated transport mechanism. Hollow fiber membranes and the acid gas absorption process are therefore integrated in a single piece of equipment. It works at ambient pressure and temperature with high permeability offered by the large gas–liquid interfacial area and high selectivity by the acid gas absorption process. Inorganic membranes show higher permeability, better selectivity, thermal and chemical stability compared with polymeric membranes. It also costs significantly more than polymeric membranes. Hybrid membranes have the potential to overcome individual deficiencies of the polymeric membrane and inorganic membranes; normally exhibiting high permeability and selectivity, given a compatible and homogeneous dispersion of inorganic phase in organic phase.

Membrane technology applications in CO₂/CH₄ separation processes show great potential for commercialization by substantial energy and cost savings. Each of the five different membranes considered here has its own specific features and advantages as demonstrated in either industrial applications or laboratory research. Each of them also has one or more associated limitations: dense polymeric membranes suffer from the trade-off between permeability and selectivity and CO₂-induced plasticization; FTMs suffer from the evaporation of solvent contained in the membrane pores (liquid membranes); the preconditioning of moisture to maintain their selectivity; gas–liquid membrane contactors suffer from pore wetting and morphology change due to the direct contact with chemical absorbents; inorganic membranes are limited to high temperature applications due to the expensive cost and relatively low reproducibility; MMMs suffer from poor dispersion of nanoparticles in the polymer matrix and phase separation due to incompatibility between the organic and inorganic phases. Future directions are therefore set based on these limitations and challenges each membrane technology faces as listed by the following goals.

8.1. Dense polymeric membranes

Most membrane materials do not have the resilience to industry conditions and quickly fail. Research into producing durable resilient materials is the main focus for industrial applications. The new generation of membranes must be able to maintain its durability in rigorous environments, e.g. good mechanical stability at high feed pressure/temperature and high resistance to plasticization, to ensure a long-term stable operation. Moreover, a highly permeable membrane with high selectivity for CO₂/CH₄

separation is required so that it can process large volumes of the feed gas.

8.2. Facilitated transport membranes

The goal is to develop a FTM that can maintain its permeability and selectivity without the preconditioning of moisture in the feed stream. CO₂ carrier stability in terms of degradation and evaporation should be improved, especially for mobile carrier membranes. The dependence of CO₂ partial pressure on CO₂ permeance should also be minimized.

8.3. Gas–liquid membrane contactors

To achieve a breakthrough in gas–liquid membrane contactor technology, the key opportunities are: (i) the development of novel membranes with excellent compatibility to the absorbents used, (ii) the utilization of new effective absorbents with low cost for regeneration. In this paper, we focus on the membrane aspect. A highly hydrophobic microporous hollow fiber membrane with a well-tailored pore structure which has prolonged stability against solvent-induced deterioration, membrane wetting and pore blocking is highly desired. On the other hand, the study of membrane contactor based on real flue gas, natural gas or biogas streams conditions is necessary because the absorption process can be affected significantly under elevated temperature and/or pressure (Mansourizadeh and Ismail, 2009).

8.4. Inorganic membranes

The goal is to develop porous inorganic membranes which can maintain permeability and selectivity during long-term operations in the presence of other gas components e.g. water, H₂S and C₂–C₄ hydrocarbons. More research on the non-porous inorganic membranes exhibiting absolute selectivity is also warranted with the aim to reduce the operating temperature to below 500 °C and enhance the permeability to reach the non-porous membrane performance. However, the high manufacturing cost and the difficulty in fabrication of large modules with a crack-free membrane surface area remain as the main challenges.

8.5. Mixed matrix membranes

The goal is to develop defect-free MMMs with enhanced permeability and selectivity; achieved most likely by eliminating the organic–inorganic phase separation problem and gas by-passing. The compatibility between polymer matrix and the fillers is crucial. In the case of glassy polymeric membranes, the membranes should also show stability against CO₂ plasticization in long-term operations.

9. Conclusions

This review paper provides comprehensive account on the membrane-based technology for the CO₂/CH₄ separation process, such as natural gas sweetening, biogas upgrading, and enhanced oil recovery, etc. Five different types of membranes are reviewed e.g. polymeric gas permeation membranes, FTMs, hollow fiber gas–liquid membrane contactors, inorganic membranes and MMMs. Current status and development as well as the associated problems and approaches taken for each type of the membrane are reviewed and discussed.

Polymeric membranes generally exhibit selectivity ~5–10 fold lower than those of inorganic membranes. These membranes, however, currently dominate the gas separation membrane market since they can be easily processed into both flat sheet and hollow

fiber configurations. In addition, their low manufacturing cost is of great interest for industrial applications. Inorganic membranes are attractive for CO₂ separation processes at high temperatures; considering their robust thermal, chemical and mechanical stability however, more studies need to be performed to improve the reproducibility and reliability and to reduce cost.

Hollow fiber membranes contactor is also promising for CO₂ separation in terms of simultaneous high flux and selectivity. Despite the current lack of systematic studies of a membrane contactor operated at elevated temperature, it is expected that such studies would be undertaken in the near future to enhance its application in important gas industries such as natural gas sweetening processes.

The key desirable properties for successful membranes, according to Koros (Freemantle, 2005), are high flux (permeability), selectivity, processability, stability and cost. In addition, the membrane lifetime, long-term permeability and selectivity, gas stream pre-treatment are crucial for the viability of large-scale industrial applications. Future research and development effort would ideally provide more durable membranes with improved performance which can be easily scaled up to fulfil these membranes potential in the CO₂ separation industry.

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