Combination of ionic liquids with membrane technology: A new approach for CO_2 separation

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ABSTRACT

This paper presents details of recent research progress on CO_2 separation membranes and membrane processes using ionic liquids (ILs) over the past few years, including supported ionic liquid membranes (SILMs), poly(ionic liquid) membranes (PILMs), poly(ionic liquid)–ionic liquid (PIL–IL) composite membranes, polymer-ionic liquid composite membranes, ion-gel membranes, and membrane absorption processes based on ILs. Descriptions of different approaches to membrane preparation, use of gas transport mechanisms, and state-of-the-art separation results are discussed in the context of breakthroughs and challenges. Furthermore, comprehensive assessment of recently improved membranes and possible future R&D prospective are also discussed.

Contents

1. Introduction

Increasing carbon dioxide (CO_2) emissions in the environment have contributed to global warming and climate change, which are issues of great concern today. Excessive greenhouse gases in the atmosphere are responsible for various environmental problems including enhancing heat stress, increasing severity of tropical storms, higher ocean acidity, rising sea levels, and the melting of glaciers, snow pack and sea ice, etc. [1]. In the foreseeable future, fossil fuels will continue to play a major role mainly in electrical power generation and industrial manufacturing in many countries. It has been reported by the International Energy Agency that the emission of the primary greenhouse gas, CO_2, increases by about 6% every year, due to the dependence of world economies on fossil fuels as an energy source [2]. CO_2 emissions from coal- or natural gas-fired power plant are the major contributors to greenhouse gas. A few other large point sources are energy intensive industries and parts of the manufacturing and construction sector, including cement manufacturing, iron and steel industry, oil refining, as well as ammonia production and fermentation.

Carbon capture and storage (CCS) has been widely acknowledged as an efficient and economical technique to regulate these emissions. The removal of CO_2 from post-combustion and pre-combustion flue gas has been the main focus in CCS. In recent years CO_2 capture from industrial processes such as cement industry and steel manufacturing has also attracted great attention [3,4]. Compared to the concept of CCS, CO_2 separation from natural gas has a much longer history with a large market [5], as CO_2 must be removed to increase the heating value of natural gas and to reduce corrosion in pipelines.

The feed gas conditions of CO_2 separation from various sources are different. For example, post-combustion flue gas has a low CO_2 concentration and low feed pressure, while natural gas or syngas have much higher CO_2 concentrations and feed pressures. In the past few decades, a large number of methods for CO_2 separation from various gas mixture streams having different thermodynamic and composition conditions have been investigated and developed, such as chemical and physical absorption [6–8], solid adsorption [9,10], membrane separation [11–15], chemical looping [16–18] and cryogenic separation [19]. New materials have emerged with applications in these technologies, including ionic liquids (ILs) [20–25], metal-organic frameworks [26,27], and gas hydrates [28,29]. Among them, membrane separation is considered as an emerging technology, which has the potential to be more environmentally friendly and energy saving, but yet not as mature as compared to the currently leading technology, i.e., amine absorption. Amine absorption occupies 90% of the market for CO_2 separation, while membrane technology has only around 10% of the share, which is mainly in the natural gas sweetening and biogas upgrading processes [30]. Membrane researchers have been making great efforts to develop more efficient and robust membranes for CO_2 separation from various sources at different separation conditions.

1.1. CO_2 separation membranes and membrane absorption processes

CO_2 separation is believed to have a large and ever-growing market due to the strong need to deal with global warming and rapidly-increasing energy consumption. However, membrane separation currently only occupies a small share in this market [30,31]. Membrane separation has been one of the most widely studied and fastest growing separation techniques of the century. Membrane separation processes have many advantages compared to traditional separation processes (e.g., absorption), such as lower capital and processing costs, smaller unit sizes, simpler operation, simpler up- and down-scaling, better energy efficiency, and much lower environmental impact. In addition, membrane separation is well recognized to be more environmentally friendly and less energy intensive. However, the cost of the separation using current commercial membranes is much higher than amine-based absorption mainly due to the limited membrane separation performance when using conventional membrane materials.

Innovative membranes are one of the most promising alternatives to meet the challenges, provided that membranes have both high CO_2 permeance and selectivity at the operating conditions for a given application. Only then will membranes have the potential to become economically competitive with the current industrial amine-based processes.

In the past few years, various membranes have been developed which targeted the attractive area above the so-called "Robeson upper bound", including mixed-matrix membranes (MMMs), thermal-rearranged membranes (TR-membranes), inorganic membranes (e.g. carbon membranes, metal-organic framework (MOF) membranes and zeolite membranes) and facilitated transport membranes. However, despite the numerous new materials synthesized and developed, few of them found successful commercial application in the gas separation market.

The combination of RTILs with membranes for CO_2 separation is a relatively new concept developed in the last 15 years [32,33]. Many different types of membranes and membrane processes containing ILs have been reported, including supported IL membranes (SILMs), polymerized ionic liquid (PIL) membranes, polymer/IL gel membranes, as well as membrane absorption using membrane contactors (MCs) using ILs as an absorbent. A comprehensive review on these research efforts is required to capture details of the progresses that have already been achieved. In recent years, a few review papers have been published concerning ILs and membranes, but they were not specifically focused on CO_2 separation [34–36]. This review mainly focuses on IL-based-membrane materials and membrane absorption processes for CO_2 separation from other light gases. Most of the latest results not included in previous reviews are listed and discussed. Moreover, some new IL-based membranes such as polymer/IL-based gel membranes, PIL–IL composite membranes, and MCs using ILs as absorbents are also highlighted in this review.

1.2. Ionic liquids (ILs) for CO_2 capture

An IL is a salt with an organic cation and an inorganic or organic anion, normally with a melting point below 100 °C. ILs have

a unique combination of physicochemical properties such as high CO_2 solubility (mole basis), high selectivity, low volatility and designable structure to adjust chemical/physical properties. The combination of these features can bring new opportunities in the use of IL-based membranes and processes in CO_2 separation applications, which are more energy efficient and environmentally friendly compared with the current commercial separation technologies. The use of ILs in membrane and membrane processes has been a research highlight in recent years.

Since ILs were proposed as a CO_2 separation medium in 2001 by Blanchard and co-workers [37], a large number of researchers have focused their attention on this application. By searching for the keywords "ionic liquid CO_2" and "ionic liquids membrane CO_2" in Web of Science, it was found that the number of publications of related research articles has increased dramatically over the past several years, as shown in Fig. 1.

CO_2 capture using IL-based solvents has also been extensively reviewed by several researchers in recent years [23–25,38,39], where ILs have been proposed as alternative solvents for CO_2 absorption [23,40]. Compared to traditional volatile organic solvents, ILs have many advantages such as negligible vapor pressure, non-flammability, higher thermal stability, ease of recycle with potentially lower demand for energy in the solvent regeneration step, etc. The disadvantages of ILs include high viscosity (especially in TSIL after CO_2 absorption), high production costs, unclear toxicities, and potential environment effects (i.e., they are non-biodegradable), which limit their further industrial application.

ILs can be classified into two categories: room-temperature ionic liquids (RTILs) and task-specific ionic liquids (TSILs, also called functionalized ILs). RTILs are also considered to be conventional ILs that demonstrate typical behavior of a physical solvent in that the solubility of gases in RTILs increase with gas pressure according to Henry's Law typically for gas pressures up to 10 bar. Henry's Law constant is widely used to represent gas solubility in RTILs [41]. Similar to other physical solvents, most RTILs show higher CO_2 solubility than other light gases such as N_2, CH_4, O_2 and H_2. Combining with other advantages, RTILs have been widely researched to separate CO_2 from flue gas, for natural gas sweetening, and for H_2 purification from syngas streams. Some commonly used IL cations and anions are listed in Fig. 2. More structures of ILs can be found in the Supporting information Table S1.

Although CO_2 shows high solubility in RTILs compared to other light gases, CO_2 absorption capacity can be further enhanced by introducing suitable moieties in the ILs (e.g., to generate TSILs or
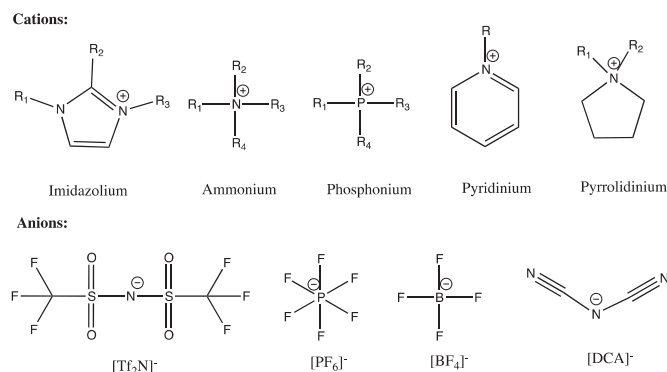

Fig. 2. Structures of commonly used RTIL cations and anions for CO_2 physisorption applications.

functionalized ILs). The CO_2 absorption ability of TSILs can reach up to three times that of corresponding alkyl-functionalized RTILs. After Bates et al. proposed to use the TSIL [NH_2p-bim][BF_4] (structure shown in Fig. 3) as a new absorbent for CO_2 separation in 2002 [20], various TSILs have been developed for CO_2 separation, including amino-acid-based TSILs [42], amine-based TSILs [43,44], and protic ILs [45]. Compared with conventional RTILs, which are physical solvents for CO_2 and prefer high pressure, TSILs are able to absorb CO_2 at low CO_2 partial pressure through a chemical reaction or chemical bonding (as shown in Fig. 3). If the partial pressure of CO_2 is further increased, there will be a steady increase in gas loading with an increase in pressure, providing evidence that both chemical and physical sorption are occurring at high applied CO_2 pressure [46]. The gas absorption capacities of some typical physisorption ILs and chemisorption ILs are listed in Table 1.

In spite of the attractive tunable properties of ILs, their high viscosities and relatively high production costs are two big challenges for ILs to be applicable on the industrial scale. Therefore, in order to integrate ILs into existing industrial processes, the combination of ILs with one or more non-IL components may be interesting to produce an optimal, IL-based hybrid solution amenable for use within an existing process. This approach may be more efficient than to design/synthesize new IL for desired properties. Up to now, most of the studies have been reported were related to the mixing of ILs with water [56], amines [58,59], or other organic compounds [60–62] to improve the CO_2 separation performance.

2. Supported ionic liquid membranes (SILMs)

A supported (or immobilized) liquid membrane (SLM) is a non-dispersive-type liquid membrane, in which the liquid-phase selective material is immobilized in the pores of a porous support by capillary forces. Generally, SLMs can be categorized into two major classes: flat-sheet SLMs and hollow-fiber SLMs. The advantages of SLMs include: (1) high interfacial area per unit volume for mass transfer, especially for hollow fiber supported membranes; (2) low solvent holding, which means an expensive but effective liquid can be used in SLMs and (3) more efficient in application over other liquid membrane techniques [63]. The primary drawback to SLMs is that over time the liquid phase evaporates or is pushed out of the membrane pores, resulting in a nonselective transport material. In addition, thick membranes will exhibit improved stability and reasonable lifetimes but lower gas flux [64].

Gas transport in an SLM involves three steps, as shown in Fig. 4: gas molecules from feed side dissolve in the liquid phase of the SLM, diffuse through the SLM, and release to the permeate side of
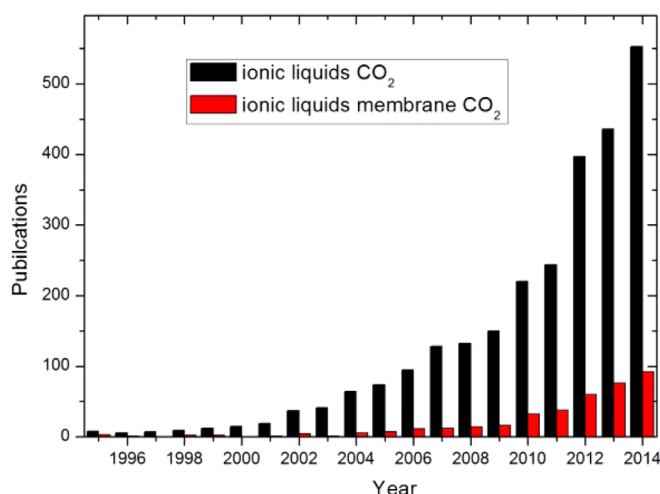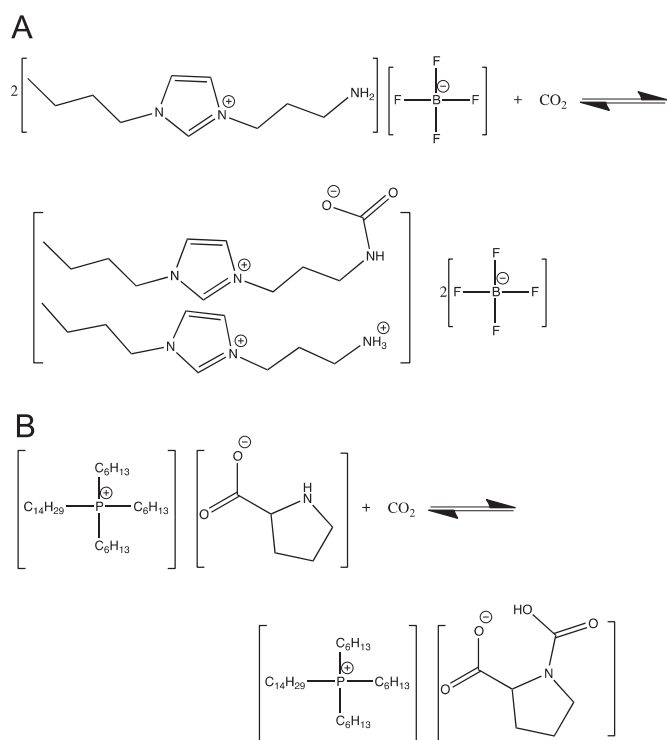

Fig. 1. Number of annual publications related to the search terms "ionic liquids membrane CO_2" over the past 20 years.
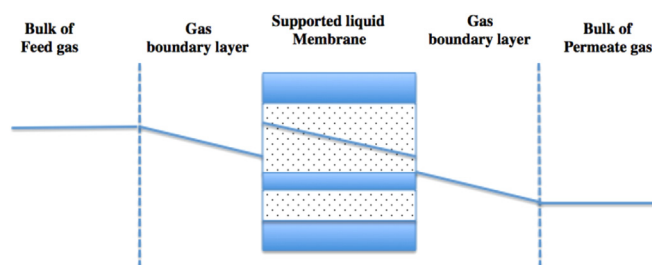
A

B

Fig. 3. Reaction schemes of CO_2 with (a) an amine-based TSIL and (b) an amino-acid-based TSIL, reproduced from Refs. [20,·47].

Fig. 4. Gas transport in SLMs.

2002 by Scovazzo et al. [32,33]. SILMs showed promising results for the separation of both CO_2/N_2 [68,69] and CO_2/CH_4 gas pairs [70]. The effects of different operational parameters (e.g., moisture, temperature) on the separation performance of these SILMs have been systematically investigated [71,72]. It has been found that in general, SILMs have long-term stability performance at low feed pressures but become unstable at high pressures. If the trans-membrane pressure difference exceeds the capillary forces holding the IL in the porous material, the SILM membrane may fail because the ILs will be pushed out of the porous support.

2.1. SILMs based on RTILs

In early studies on SILMs, most researchers focused on conventional ILs that utilized physical absorption. Gas transport in these membranes is based on a solution-diffusion mechanism, and their ideal selectivities are driven mainly by differences in the physical solubility of the gases in the IL. The diffusion coefficient of CO_2 and other relevant gases in ILs often differs by less than a factor of 2 [73]. Up to now, at room temperature, the highest CO_2 permeability for SILMs with RTILs was approximately 2000 Barrers, with a CO_2/N_2 selectivity of about 40. It should be noted that selectivity in this class can exceed 60 with permeability still in excess of 1000 Barrers [74,75]. It was also reported that for SILMs based on RTILs, the CO_2 feed partial pressure had little influence on the permeability and selectivity. Moreover, the permeability of gases normally increased with increasing temperature due to the strong temperature-dependency of the IL viscosity. Additionally, CO_2 solubility generally decreases dramatically with increasing temperature compared to other gases like CH_4 and N_2, leading to lower selectivity values at higher temperature. Therefore, a low operating temperature is favored for SILMs. Gas separation performances of some recently reported SILMs based on RTILs and the respective support materials are summarized in Table 2. Unless otherwise stated in the table (shown as (a)–(g)),

the SLM. Although faster transport of CO_2 could be obtained in SLMs, the large scale SLMs showed insufficient membrane stability due to the loss of liquid phase mainly by dislocation of the liquid in the membranes as the trans-membrane pressure difference increased. If an IL is used in SLMs, the membranes are called SILMs. Compared to traditional SLMs using amine-based aqueous solvents (such as diethylenetriamine (DETA), diaminoethane (DAE) [65], diglycolamine (DGA) and triethylene glycol (TEG) [66]), the usage of ILs as the liquid separating phase enhances the stabilization of the SLMs since ILs have negligible vapor pressure (lower possibility of volatile loss) and relatively high viscosity (resistance to blow-out by high pressure differentials) [67].

The most commonly used method of preparing SILMs is soaking a porous support in the desired IL for a few hours. As ILs have relatively high viscosity and negligible vapor pressure, application of vacuum is commonly used to remove gas bubbles in resulting membranes.

SILMs for CO_2 separation were reported for the first time in

Table 1
Gas absorption capacities of some physisorption ILs and chemisorption ILs at around 1 bar CO_2 pressure.

IL	Absorption type	Gas absorption capacity (mol/L)			
		CO_2	O_2	N_2	H_2
$[C_4mim][Tf_2N]$	Physisorption[a]	0.0780 [48]	–	–	0.0020 [48]
$[C_4mim][PF_6]$	Physisorption	0.0756 [49]	0.0039 [50]	–	0.0024 [50]
$[C_4mim][BF_4]$	Physisorption	0.0642 [51]	0.0032 [52]	0.0027 [52]	0.0021 [52]
$[C_8mim][Tf_2N]$	Physisorption	0.1069 [53]	–	–	–
$[C_2mim][eFAP]$	Physisorption	0.0864 [54]	–	–	–
$[N_{1114}][Tf_2N]$	Chemisorption	0.0815 [48]	–	–	0.0028 [48]
$[C_4mim][AC]$	Chemisorption	1.579 [55]	–	–	–
$[P_{66614}][Pro]$	Chemisorption	0.7613 [56]	–	–	–
$[P_{66614}][Ala]$	Chemisorption	0.9859 [57]	–	–	--
$[P_{66614}][Gly]$	Chemisorption	0.7156 [57]	–	–	–
$[MTBDH][TFE]$	Chemisorption	2.326 [45]	–	–	–
$[MTBDH][Im]$	Chemisorption	2.273 [45]	–	–	–

[a] CO_2 solubility values for physisorption ILs and chemisorption ILs were measured at 313 K and room temperature, respectively.

the data were obtained at single gas feed conditions of approximately 2 bar pressure at room temperature.

The support porous materials include polymeric and inorganic membranes. It is commonly accepted that the separation performance of SILMs is mainly due to the characteristics of the imbedded ILs rather than to the membrane support. However, it is interesting that some researchers have discovered interactions between ILs and support has influences on the states of the ILs in the support pores and the separation performance. Neves et al. reported that SILMs prepared with a hydrophobic support were more stable than those prepared with a hydrophilic membrane [94]. Furthermore, Scovazzo et al. reported that the CO_2 permeance of [C2mim][TfO] incorporated in a porous poly(ether sulfone) support was two times higher than the same IL impregnated within a hydrophobic PVDF membrane [91].

As a higher porosity usually leads to a higher IL content in the SILM, pore size is also one of the critical issues for membrane stability. Generally, membranes with a pore size of 100–200 nm are used to prepare SILMs. However, some researchers have also employed nanoporous inorganic membranes as the support to prepare SILMs [68,92,95]. The main motivation of developing SILMs using inorganic porous substrates is to enhance the high-temperature stability of the resulting membrane and reduce the possibility of swelling of the porous support by ILs in SILMs. Reported gas separation results for inorganic-support-based SILMs were in the same range as SILMs prepared with organic supports, but the former SILMs show excellent thermal and mechanical stability, which could be used in high-temperature applications.

According to the Young–Laplace equation, a smaller pore size will ensure better SILM stability, as a higher pressure is needed to push the ILs out of the pores. Interestingly, Banu et al. reported that both CO_2 solubility and diffusivity were enhanced in confined ILs when compared to values observed in unconfined ILs. Imidazolium-based ILs and Al_2O_3 membranes with an average pore size

Table 2
Supported ionic liquids membrane based on RTIL.

Support	IL	Gas permeability of SILM (Barrers)			Ref.
		CO_2	N_2	CH_4	
Hydrophilic PES	[P66614][Cl]	350 ± 20	24 ± 2	89	[33]
PES	[C6mim][Tf2N]	1200	–	–	[76][a]
Hydrophilic PTFE	[C2mim][Tf2N]	1702	73.6	–	[77]
	[C2mim][BF4]	968.5	21.8	–	
	[C2mim] [TfO]	1171.4	28.9	–	
hydrophilic PES	[C4mim][BF4]	460 ± 12	37 ± 2	56 ± 2	[78]
	[C4mim][PF6]	360 ± 15	26 ± 1	49 ± 2	
	[C6mim][BF4]	520 ± 11	45 ± 2	68 ± 3	
hydrophobic PVDF	Cyphos serials	487–642	11–20	76–113	[79]
PES	[Cnmim][Tf2N]	210–320	12–13	16–17	[80]
PVDF	[C4mim][BF4]	30–180	–	1.2–4	[81][b]
PES	[C2mim][TCB]	2040 ± 60	38 ± 4	–	[75]
	[C4mim] [TCB]	1755 ± 50	44 ± 3	–	
	[C2mim] [TCB]	1721 ± 80	38 ± 4	–	
Hydrophilic PTFE	[C2mim][TCB]	742	15.1	–	[82]
Hydrophilic PTFE	Binary mixture of ILs	142–445	2.3–8.7	–	[71]
PVDF	[C4mim][Tf2N] [C4mim][PF6]	6200	295	–	[83][c]
PVDF/PTFE	[C4mim][Tf2N] [C4mim][PF6]	956	–	–	[84][d]
Anodic alumina	[C2mim][TCB]	2040	38	–	[74]
Anodized alumina nanoporous membrane	[C2mim][Tf2N]	2640 ± 190	$12\,3 \pm 9$	–	[85]
	[C6mim][Tf2N]	1800 ± 400	150 ± 33	–	
Ceramic NL filtration membrane	[C2mim][TCM] [C4mim][TCM]	100–300	< 3	–	[86][e]
alumina membrane	Geminal IL	~300	–	18–28	[70][f]
mesoporous carbon	imidazolium-based ILs	90–180	2.5–5	–	[87]
PVDF	[C2mim][Ac] [C4mim][Ac] [Vbtma][Ac]	852–1100	25–28	–	[69]
ZIF-69ZIF-71	[C4mim][SCN]	42,795	8042	–	[88][g]
ZMOF	[C4mim][SCN]	27,584	370	–	
IRMOF-1	[C4mim][SCN]	40,188	3090	–	[89]
		Gas permeance (GPU)			
		CO_2	N_2	CH_4	Ref.
Porous γ-alumina discs (3–5 nm pore size)	dicationic ILs	0.93–0.98	0.04	0.03	[90]
hydrophilic-PVDF	[C2mim][DCA]	2.36			[91][h]
hydrophilic PES	[C2mim][Tf2N]	5.58			
	[C2mim][TfO]	4.88			
Porous Al_2O_3/TiO_2 tubes	[C2mim][Ac]	83.23 ± 3.29	2.52 ± 0.10	–	[68]
Nanoporous TiO2	[C2mim][Ac]	129.04 ± 3.89	4.16 ± 0.13	–	[92]
Electrospun PVP	[C6mim][BF4] [C6mim][PF6]	~15	~3	–	[93]

[a] Operating conditions: 37 °C, 15.7 psig.
[b] Operating conditions: 3 bar, 35 °C.
[c] Feed gas: mixture of 30/70 CO_2/N_2, flow rate 100 ml/min, trans-membrane pressure 0.21 atm.
[d] Wet feed stream at $T=333$ K.
[e] Feed gas: mixture of CO_2/N_2 in the range of 10–50% v/v CO_2.
[f] Operating conditions: 4535 °C, transmembrane pressure: 30 kPa.
[g] CO_2 partial pressure 100 kPa. Simulation results.
[h] CO_2/CH_4 gas mixture as feed gas.

of 20 nm were employed in their research. For the best case, a CO_2 permeability 15.7 times higher was observed for confined ILs compared with the bulk IL, which was believed due to the possible reorganization of the cation and anion at the pore surface and the consequent physical property changes of the ILs [96].

SILM separation performance was also tested under high-temperature conditions. Apparently, increasing temperature will enhance the diffusivity of CO_2, while the Henry's Law constant will increase (CO_2 solubility decrease) with temperature. Wickrama-nayake et al. prepared hollow-fiber SILMs using [C$_6$mim][Tf$_2$N] and two commercially available polymers (Matrimid® 5218, and Torlon 4000T) [97]. The results showed that CO_2 permeance increased by 4 times as the temperature increased from 37 °C to 200 °C, while the CO_2/H_2 selectivity decreased from 6 to 1. The decrease in selectivity may be due to the fact that gas diffusion dominates at high temperatures. In addition, the increasing temperature decreases the stability (i.e. by decreasing the surface tension) and the membranes may have formed pinholes. Similar correlation of CO_2 permeance and temperature phenomena was found for different gas pairs (CO_2/N_2 [98], CO_2/He [76]) and different IL species.

Kang et al. tried to enhance CO_2 transport in SILMs by incorporating small amounts of copper nanoparticles in different IL species. Their results showed that by adding only about 0.3 wt% copper nanoparticles in the ILs, both CO_2 permeance and CO_2/N_2 selectivity could be enhanced by about 30% and 100%, respectively [99,100]. Nevertheless, the CO_2 separation performance fell under the Robeson "upper bound" because of low CO_2/N_2 selectivity. Later, they added small amounts of graphene oxide to the system, and both permeability and selectivity were moderately enhanced [101].

Magnetic ILs (MILs) with different magnetic susceptibility values based on phosphonium cations were incorporated into hydrophobic and hydrophilic PVDF porous supports to give stable supported magnetic ionic liquid membranes for CO_2 separation [102]. The CO_2 permeabilities were in the range of 150–260 Barrers and the CO_2/N_2 selectivity values were in the range of 21–41. With an external magnetic field between 0 and 2 T applied to the SILMs, the CO_2 permeability was enhanced by up to 21.6% while the CO_2/N_2 selectivity remained similar [103].

It is worth mentioning that under the different measurement conditions, the use of different membrane supports as well as the presence of water or other impurities in the ILs greatly affect the SILMs gas permeation properties. Therefore, even for the same IL, big differences in observed gas permeability have been reported.

A modeling and theoretical study was reported by Camper et al. to predict the separation performance of the SILMs [104] in 2006. According to the most commonly used solution-diffusion model in membrane gas separations, the potential gas permeability and selectivity in RTIL-based membranes could be predicted from the gas solubility and diffusivity data of the ILs. In 2009, Scovazzo et al. developed models for predicting CO_2 selectivity and permeability according to the viscosity and molar volume of ILs, as shown below [77]:

CO_2 selectivity:

$$\alpha\left(CO_2/N_2\right) = \frac{2985}{(V_{RTIL})^{0.865}}$$

$$\alpha\left(CO_2/CH_4\right) = \frac{5483}{(V_{RTIL})^{1.09}}$$

CO_2 permeability:

$$P_{CO_2} = \frac{4953}{(\mu_{RTIL})^{0.388 \pm 0.03}}$$

where V_{RTIL} the molar volume of ILs in cm^3/mol and μ_{RTIL} is the viscosity in cP. This model indicates that the ILs species with

smaller molecular size and low viscosity tend to have both high selectivity and high permeability. In this paper, Scovazzo also made an "upper bound" for the SILMs (as shown in Fig. 5) to compare with the Robeson upper bound for polymeric membrane model.

As can be seen from Table 2, SILMs containing non-functionalized RTILs with lower viscosity and smaller molar volume will have better CO_2 selectivity and permeability. For example, the highest selectivity occurs with the smallest RTIL molar volumes (e.g., [C$_2$mim][BF$_4$]) and the highest CO_2-permeability occurs at low viscosity RTILs (e.g., [C$_2$mim][Tf$_2$N]). However, attempts to reduce the IL's molecular size/molecular weight face the challenge that the ILs may not be a liquid at near ambient temperature; thus, there may be little room for possible improvement in permeability for non-functionalized RTILs compared to those already reported in the literature. On the other hand, SILMs based on functionalized ILs might have more room for improvement. By properly choosing functional groups, there can be chemical interactions between the gas species and the ILs. Sometimes a facilitated transport mechanism can also be involved, therefore increasing CO_2 separation performances.

2.2. Functionalized IL-based SILMs

SILMs based on functionalized ILs, or TSILs have also been developed. Different from SILMs based on RTILs, in which the solution-diffusion model is commonly used to express the gas transport, in functionalized ILs-based SILMs, a facilitated transport mechanism is also normally involved for gas transportation. In this facilitated transport mechanism, first, the CO_2 molecules that dissolve on the feed side of the membrane can reversibly react with the facilitated transport carrier (e.g. amino groups in TSILs) and form CO_2 complexes (bicarbonates or carbamates) with/ without the presence of water vapor. Then these CO_2 complexes can diffuse through the membrane, and eventually CO_2 is dissociated and released on the permeate side of the membrane. Some latest results reported that water is needed when using amines in the IL membranes in facilitated transport. As an example, a proposed CO_2 facilitated transport involving water and HCO_3^- forming is shown in Fig. 6.

Amine groups are commonly used to functionalize ILs for facilitated CO_2 transport. Ideally, with water vapor in the feed stream, amine groups in the TSILs will help to form complexes with CO_2 (bicarbonates), thus offering both enhanced CO_2 permeability and selectivity over conventional non-functionalized
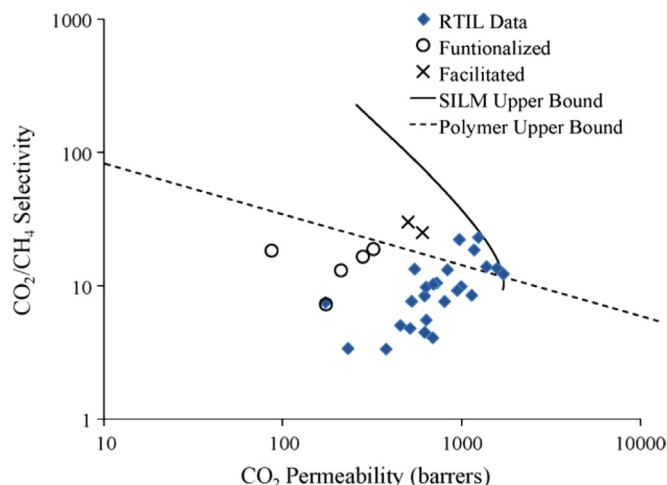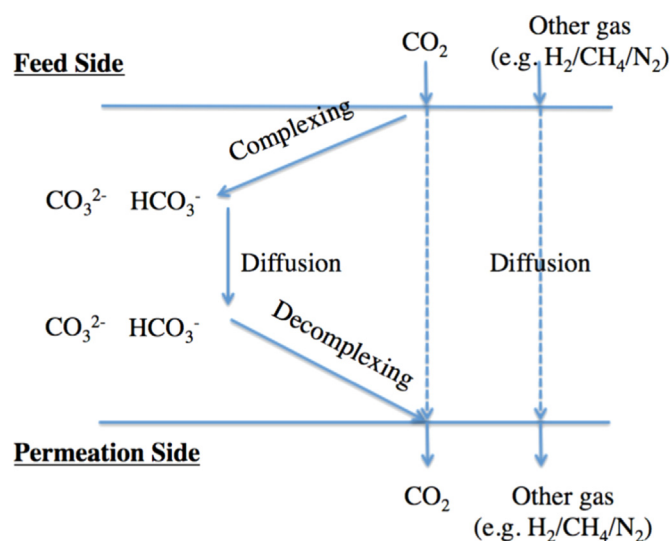

Fig. 5. Upper bound of SILMs for the CO_2/N_2 gas pair reported in 2009. Reproduced from Ref. [77].
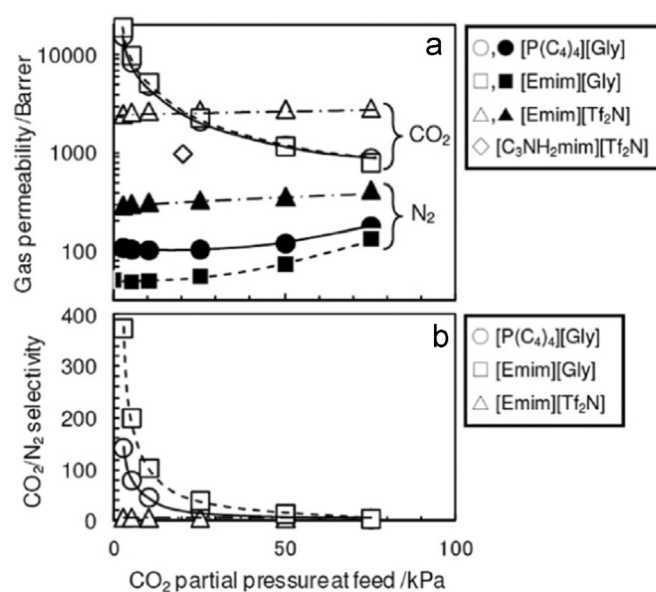
Fig. 6. Illustration of facilitated transport of CO_2 in a membrane. Adapted from Ref. [105].

Fig. 7. Effect of CO_2 partial pressure on CO_2 permeation properties for TSILs based (P4444Gly, C2mim Gly, C2NH2mim Tf2N) and RTILs based (C2mim Tf2N) SILMs. Reproduced from Refs. [112, 108].

RTILs. However, this kind of SILM typically only shows moderate enhancement in permeability/selectivity at high temperatures [105]. This phenomenon could be ascribed to CO_2 and TSIL forming a pseudo-polymeric ionic network and becoming extremely viscous, which reduces the diffusion of CO_2 [106]. Another explanation for this phenomenon is that CO_2 rapidly forms carbamate with the amine groups, leading to molecular Coulombic cross-linking and hindered diffusion [77]. The gas permeability values of some SILMs using TSILs are listed in Table 3.

Hanioka et al. developed TSIL-based SILMs that showed promising results at low CO_2 partial pressure (< 50 kPa) [112], but both the membrane selectivity and CO_2 permeance dramatically decrease as the CO_2 partial pressure increases, which is a typical feature of the facilitated-transport mechanism. At low CO_2 partial pressure, amino acid TSILs can facilitate the transport of CO_2 gas molecules, but as the CO_2 partial pressure increases, the carriers (in this case, the amino acid anions) become saturated and lose the facilitated transport effect [113].(Fig. 7).

Some amino acid-based TSILs were also employed in the SILMs by the same group from Kobe University [108]. Similar to the results they reported previously [112], CO_2 permeability and CO_2/N_2 selectivity were observed to rapidly decrease with increasing CO_2 partial pressure (0–80 kPa), but an ultra-high CO_2 permeability (8300 Barrers) and CO_2/N_2 selectivity (48) were obtained at optimized conditions. This membrane may be more appropriate for

post-combustion CO_2 capture, as the CO_2/N_2 mixture in these feeds have low CO_2 partial pressures and are processed at relatively high temperatures.

Besides amine-tethered TSILs, carboxylate-based TSILs represent another class of TSILs that exhibit good affinity with acidic gases [114,115]. Huang et al. investigated the performance of SILMs prepared from carboxylate-based ILs (including monocarboxylates and dicarboxylates) [109]. At low CO_2 partial pressures (0.1 bar), observed CO_2 permeability values ranged from 2147 to 2840 Barrers with permselectivities of CO_2/N_2 and CO_2/CH_4 of 178–265 and 98–221, respectively.

Acetate-based TSILs were also applied in SILMs for CO_2 separation. A CO_2 permeability of approximately 2000 Barrers was reported with a CO_2/N_2 selectivity of around 27 at 333 K [69]. The performance of [C2mim][Acetate]-based SILMs was tested for a CO_2/H_2 feed mixture at a temperature as high as 373 K. A CO_2 permeability of 3701 Barrers was obtained with a CO_2/H_2 selectivity of 20 [116]. Although these results are attractive for syngas separation, unfortunately, no stability data were reported. According to these results, it was concluded that ILs with small molar volume (leading to low H_2 solubility) that interact with CO_2 strongly (leading to high CO_2 solubility) might be the best

Table 3
Supported ionic liquids membrane based on TSIL.

Support	Functionalized IL or TSIL	Gas permeability of SILM (Barrer)			Ref.
		CO₂	N₂	CH₄	
PTFE	[C₃NH₂mim][TfO]	~1500	–	–	[107][a]
	[C₃NH₂mim][Tf₂N]	~1000	–	–	[122]
PTFE	[P₄₄₄₄][Gly]	~12,000	~200	–	[108][b]
PES	[N₂₂₂₄]₂[malonate]	2147	12	10.8	[109][c]
	[N₂₂₂₄]₂[maleate]	2840	10.7	12.8	
	[N₂₂₂₄][acetate]	~500	~10	~22	
PVDF	[P₆₆₆₁₄]₂⁺[CoCl₄]²⁻, [P₆₆₆₁₄]⁺[FeCl₄]⁻, [P₆₆₆₁₄]₂⁺[MnCl₄]²⁻ and [P₆₆₆₁₄]₃⁺[GdCl₆]³	147–259	2.7~10.9	–	[102,103]
	cholinium-based ILs	< 10	–	–	[110]
PVDF	[C₄mim][Tf₂N]+Carbonic anhydrase enzyme	~240	~4.8	–	[111]

[a] Dry gas, 0.1 bar, 40 °C.
[b] 20% humidified gas, 0.02 bar, 100 °C.
[c] Saturated humidified gas, CO_2 partial pressure: 0.1 bar, 40 °C, transmembrane pressure difference of 0.3 bar.

candidates for CO_2 separations from mixtures containing H_2. In another study, Albo et al. reduced the SILM thickness to about 500 nm, and the CO_2 permeance was observed to sharply increase to $(2.78 \pm 0.11) \times 10^{-8}$ mol/(m^2 s Pa) (about 80 GPU), with an ideal (i.e., single gas) CO_2/N_2 selectivity of 30.7 [68]. The stability was also tested and this membrane could hold the separation performance for about 25 h. Some researchers tried to functionalize ILs with CO_2-phlic groups such as nitrile/glycol group [90,117], but the results are not very promising.

It has been a concern that ILs (both RTILs and TSILs) have a certain degree of toxicity and are poorly biodegradable. Therefore, cholinium-based ILs were developed for use in SILMs for sustainable CO_2 capture [110]. The CO_2 separation performance of these membranes is not comparable to functionalized IL-based membranes (i.e., the CO_2 permeability is less than 10 Barrers), but it offers the idea of developing new biodegradable and environmental-friendly ILs for CO_2 capture.

The concept of removing CO_2 from flue gas streams using SILMs with a thermal-resistant enzyme that enhances the selective transport of CO_2 has also been investigated [111]. The rather small amount of enzyme (0.01 wt% of the IL) did enhance CO_2 permeability and selectivity by at least 20%. This improvement is not significant; however, these results illustrate the potential of using this approach to further enhance the performance of SLMs impregnated with the proper enzyme for CO_2 capture.

Very recently, Sun et al. used a mixture of PILs with RTILs in SILMs [118]. By introducing a small amount (5–20 wt%) of PIL particles in the RTILs, both the CO_2 permeability and CO_2/N_2 and CO_2/CH_4 selectivity were slightly increased. These researchers believed that the positive charge on the polymer chains can interact with the weakly acidic CO_2 gas, and thus serves as a CO_2 mobile carrier in SLMs via the facilitated transport mechanism to enhance CO_2 transport.

2.3. Stability of SILMs

Although the long-term mechanical/configurational stability of an SILM is improved compared to a SLM containing volatile organic solvents, it is still one of the most critical issues in the development of SILMs. Different methods to enhance the stability of SILMs have been studied [34,119,85]. Zhao et al. systematically investigated the liquid loss mechanism of SILMs [119], and they found that the liquid loss of SILMs could be attributed to two factors: membrane compression and IL extrusion from the large pores. Therefore, by choosing a proper size of porous support, the membrane system can tolerate a trans-membrane pressure up to 7.0 bar [85]. Several studies have investigated the long-term stability of SILMs. For example, Scovazzo et al. reported SILMs without the loss of performance over more than 100 days [91], and Hanioka et al. reported that their SILM showed 260 days of stable operation [112]. Most of the reported SILMs were prepared using microfiltration membranes and operated under relatively low trans-membrane pressures. As reducing the pore size will enhance SILM pressure resistance, nanofiltration membranes have also been investigated as porous supports for SILMs. Experimental results showed that ILs do not discharge from the nanofiltration membrane structure even under a trans-membrane pressure up to 10 bar, suggesting that SILMs based on nanofiltration supports may be used for practical applications at relatively high pressures.

In summary, IL-based membranes have been demonstrated to be capable of achieving gas separation via solution-diffusion or facilitated transport mechanisms. The solution-diffusion mechanism is mainly applied for RTIL-based SILMs. Different models can predict the performance of this kind of SILM. Compared to RTILs, functionalized ILs (aka TSILs) that have a facilitated transport effect are more promising as membrane materials, but the limitations of

high viscosity and low CO_2 partial pressure tolerance must be overcome. For both cases, the stabilization of the ILs in SILMs is the main challenge, especially in full-scale processes under real-world operating conditions. Reducing the membrane thickness to have a competitive gas permeance while maintaining membrane stability is another challenge.

3. Poly(ionic liquid) (PIL) membranes

PILs, or polymerized ionic liquids, refer to a subclass of polyelectrolytes prepared from polymerizable ionic liquid monomers. PILs possess many of the unique combination properties of ILs, such as ionic conductivity, thermal stability, tunable solution properties, and chemical stability, together with intrinsic polymer properties [120].

Initially, PILs were mainly considered to be a new type of polymer electrolyte, as PILs are polymers whose repeating unit bears an electrolyte group (cation or anion). In 2007, Tang et al. first observed that several imidazolium-based PILs unexpectedly exhibited significantly higher CO_2 absorption capacities than the corresponding IL monomers [121]. More importantly, when PILs were used as absorbents for CO_2 separation, they exhibited higher CO_2 sorption capacities and higher sorption and desorption rates than the corresponding ionic monomers [122–124]. These interesting results immediately attracted widespread attention and triggered "explosive" interest in the application of PILs for CO_2 separation [21,123,125–128]. The application of PILs as membrane materials has become one of the fast-growing fields in recent years.

Generally speaking, PILs can be synthesized via two basic strategies: direct polymerization of IL monomers and chemical modification of existing polymers. In each strategy, different polymerization techniques are involved, such as conventional and controlled radical polymerizations, ring-opening metathesis polymerization, step-growth polymerization, and polycondensation polymerization. More details about PIL synthesis strategies can be found in Refs. [129,·120].

Up to now, PILs with different structures have been developed for membrane applications, including homo-PILs (also called ionenes) synthesized by radical polymerization, block copolymers prepared by radical polymerization, followed a chemical modification process such as ion-exchange or grafting, as shown in Fig. 8(a) and (b). Alternating copolymers (e.g., polybenzimidazole, PBI) were also reported. Here, the benzimidazole unit was considered as a hypothetical monomer, and thus it could be considered as a homopolymer, as shown in Fig. 8(c). The copolymers with ionic groups in the main polymer chain are shown in Fig. 8 (d). Detailed structures of PILs can be found in the Supporting information Tables S2 and S3.

3.1. Homo-PIL membranes

In 2007, gas separation membranes made of homo-PILs were firstly reported by Bara et al. [130]. These membranes showed comparable results with traditional polymeric membranes. CO_2 permeabilities were 10–30 Barrers and CO_2/N_2 selectivities were around 30. Since then, these authors have intensively studied a large number of membrane materials composed of imidazolium-type polystyrene-, polyvinyl-, or polyacrylate-based PILs with various anions and containing alkyl chains of varying lengths and chemical compositions [131–135]. It is believed that the charged PILs chains form a tight and more stable matrix, which can prevent the membrane from excessive swelling and maintain the gas separation performances even at increased temperature and pressure conditions. Interestingly, Simons et al. found that the
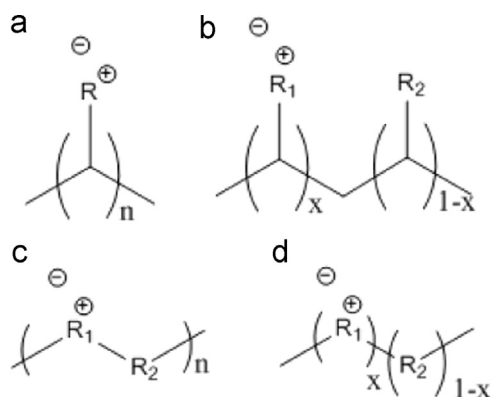
Fig. 8. Schematic illustrations of several common types of homo-PILs and copolymer-PILs: (a) ionenes; (b) grafted co-PIL; (c) alternating PIL-copolymer; (d) PIL-copolymer with ionic group in the main chain. R represents different organic groups.

permeability of CO_2 increases by more than 60% over a pressure range of 40 bar, noting that CO_2 is a strong plasticizer for the PIL materials [135].

Homo-PIL membranes normally show small CO_2 permeability values that are still orders of magnitude lower than analogous ILs and far below the 2008 Robeson Plot upper bound. Although the overall separation performances for homogenous homo-PIL membranes are not satisfactory for industrial applications, there are certainly many functional groups that can be incorporated into PILs. The designable structures of ILs give numerous possibilities to prepare new polymer materials with desired properties.

Homo-PILs were also prepared from highly thermally stable PBI [136–138]. The influences of polycation backbone variation, cation–anion variation on their physical properties were systematically investigated. According to experimental results, the polycation and anion play a crucial role in governing the gas permeation properties of these PILs, indicating further tuning of PIL structure and proper choice of an IL with a CO_2-philic anion may bring beneficial effects. It is worth noting that many of these PBI-based PIL membranes exhibited high CO_2/CH_4 selectivity values of around 69–98 at a pressure of 20 atm, which are higher than those of reported PILs and conventional polymers used as the gas separation membrane material. This phenomenon suggests no or little plasticization happening in the membranes from the absorbed CO_2. If the permeability could be further increased while the selectivity could be maintained at this range, this membrane will be promising material for natural gas sweetening, which involves high-pressure operating conditions.

Inspired by the structure of poly[1-(trimethylsilyl)-1-propyne] (PTMSP), Sakaguchi et al. synthesized high-free-volume polymers with ionic groups to enhance CO_2 gas separation selectivity [139]. By introducing the ionic groups into the poly(diphenylacetylene) polymer chain, the resulting membrane had a one order of magnitude reduction in CO_2 permeability but a doubled or even tripled selectivity. Similar to a PTMSP-like polymer, the permeability could profit from bulky counter anions as it prevents polymer chains from packing together.

Most of the PILs membranes reported were based on imidazolium-based PILs. In 2013, Tomé et al. developed pyrrolidinium-based PILs membranes for CO_2 separation [140]. Compared with imidazolium-based PILs, which involve a number of organic syntheses and purification steps at the monomer level as well as the requirement to control polymerization conditions, the pyrrolidinium-based PIL synthesis process was relatively easy and less expensive. The latter polymers can be synthesized by carrying out anion-exchange directly on commercially available poly(diallyldimethylammonium) chloride.

Homo-PILs based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were also reported by Cong and co-workers [141]. The overall performance of these membranes was not satisfactory with only one of the selected ILs slightly enhancing CO_2/N_2 selectivity with sacrificing of permeability. This effect was attributed to the incorporation of these ionic groups in the polymer dramatically reducing the CO_2 diffusion coefficient.

3.2. PIL-copolymer membranes

Although homo-PILs combine the many of the advantageous properties of ILs, the CO_2 permeability of homo-PILs membranes is typically relatively low. Homo-PILs materials were thus modified to have better gas separation performance. Incorporation of functional groups to PILs backbones or sidechains to prepare copolymer-PILs are effective ways of improving PIL properties, and many promising results have been found by this method. Normally PILs are brittle and mechanically weak; thus, copolymerization is an effective way to improve the mechanical properties and ensure the material can be tested in a flat-film module. As shown in Fig. 8, most of these co-polymers are block-copolymers (PIL-BCP).

The first IL-BCP was prepared by Hu et al. in 2006. Free-standing membranes were successfully prepared using two grafted copolymers, P[VBTMA][BF_4] and P[MATMA][BF_4] poly(ionic liquids), and their CO_2 separation performance as well as thermal stabilities were systematically investigated [128].

Later on, a co-PI-based PIL-BCP was synthesized by Li et al. [142,143]. Incorporation of ionic groups in the PI chain resulted in decreases in the polymer fractional free volume and increases in density, leading to gas permeability deduction and selectivity elevation compared with the pure PI material. In 2013, Gu et al. synthesized PIL-triblock copolymer by RAFT polymerization [144]. Free-standing membranes were successfully prepared, and they also mixed the polymer with ILs to prepare ion gel membranes. By introducing the nanoscale phase-separation of the two blocks in the PIL-BCP membrane, CO_2 diffusivity was enhanced by two magnitudes, and CO_2 permeability increased to up to 9300 Barrers [145] (as shown in Fig. 9). Although the selectivity of this PIL-BCP membrane is low (CO_2/N_2 selectivity lower than 10), it could be an excellent candidate for CO_2/light gas separations if the CO_2 selectivity could be improved by adding RTILs or other CO_2-selective additives such as amines, inorganic nanoparticles etc., or by tuning the different polymer blocks.

PIL-BCPs with really low permeability and selectivity were also reported by Adzima et al. [146]. The highlight point of their research was the PIL-BCP offered the possibility of cast thinner films on a porous support layer for preparing high-flux composite membranes. In 2013, Wiesenauer et al. proved this idea, and defect-free, supported composite membranes with nanostructured, ≤ 20 µm-thick top coatings were successfully fabricated with a PIL-BCP [147].

In the same year, Wiesenauer et al. developed a new type of imidazolium-based hydrophobic–ionic–hydrophilic ABC triblock copolymers, and supported composite membranes of these triblock copolymers were successfully fabricated with defect-free, ≤ 20 µm-thick top coatings [147]. The ABC triblock copolymers were found to phase-separate into different nanostructures in their pure melt states, resulting a CO_2 permeability of 2340 Barrers with CO_2/N_2 and CO_2/H_2 selectivities of 10.2 and 3.2, respectively. The same group also investigated the influence of the block length ratios, as well as incorporating added free IL and amines into these triblock CP system to explore the possibility of improving CO_2 permeability and selectivity for this ABC-BCP system.

Chi et al. incorporated IL groups to low-permeability poly(vinyl chloride) (PVC) to change the gas separation properties of the PVC [148]. Different IL groups were grafted to the Cl-sites via atom

transfer radical polymerization (ATRP). As usual, introducing of ILs groups to the polymer chain enhances the CO_2 permeability, with a slightly decreased CO_2/N_2 selectivity. The CO_2 permeability was further enhanced by introducing a small portion of free ILs. Their work demonstrated the possibility of developing CO_2-capture membranes from low-cost materials with good chemical and mechanical properties.

Cardo-based poly(ether ketone)s were also functionalized by alkyl imidazolium-based ILs and further applied for separation membranes [149]. The resulted membranes showed CO_2/N_2 and O_2/N_2 selectivites of 66.1 and 15.5, respectively. The CO_2/N_2 separation performance was not distinctive, but O_2/N_2 selectivity was extraordinarily high compared to traditional polymeric membranes [150].

Recently, a series of phenolate-containing polyelectrolytes were prepared via post-polymerization treatment of poly(4-vinylphenol) with ILs, and composite membranes with thicknesses between 4 and 9 μm on the top of cross-linked polysiloxane supports were prepared via solvent casting [151]. In the best case, the resulting composite membranes showed a CO_2 permeability of around 1200 Barrers with a CO_2/N_2 selectivity of 68, which exceeds the Robeson upper bound. If the membrane thickness could be reduced to less than 1 μm, this membrane will be promising for practical CO_2 separation.

Very recently, Ansaloni et al. investigated the influence of water vapor on the PIL membrane transport properties [152]. From their results, despite the hydrophobic nature of their polymer, the transport properties were positively affected by the presence of water vapor in the feed stream, which is a phenomenon commonly observed in hydrophilic polymers. Interestingly, as the hydrophobic nature of the polymer containing Tf_2N^- anion, the water uptake for both the homo-PIL and block co-PIL were lower than 2.5 wt% under 90% relative humidity condition, but a 80% and 40% enhancement of CO_2 permeability were observed with negligible effect on selectivity for the two polymers, respectively.

3.3. PIL–IL composite membranes

Another relatively easy way of improving PIL properties is blending free ILs with PILs to make PIL–IL composite membranes. As mentioned above, the earlier reported CO_2 permeabilities of homo-PIL membranes were in the range of 5–50 Barrers. (There are some exceptions, with proper functionalization of side group, some of the homo-PIL membrane can have a CO_2 permeability of about 130 Barrers [153]). The CO_2 permeabilities of the SILMs were in the range of 200–1700 Barrers. To further increase the CO_2 permeability of homo-PIL membranes, incorporation of a "free" (i.e., non-reactive) IL component into the PIL matrix to increase gas diffusivity was first proposed by Bara et al. [153]. Generally, the interactions between PILs and free ILs are considered to be much stronger than those between ILs and conventional uncharged polymers due to the additional Coulombic attractions present between IL and PIL [154] (as shown in Fig. 10). Thus, PILs serve as effective stabilizers, and PIL–IL composite membrane should remain stable under very high pressures. Simultaneously, the ILs serves as a plasticizer in the PIL matrix, which enhances the diffusivity of gas species. Because CO_2 diffuses much faster in the IL phase than in the solid PILs phase, it is assumed that most of the CO_2 permeability is governed by the amount of free IL in the PIL–IL composite membranes [155]. An increase of IL loading in the PIL matrix can lead to higher permeability without decrease or increase of selectivity. For example, it has been reported that incorporation of 20 mol% free IL in a PIL membrane yields a stable composite material with a CO_2 permeability increase of ~400%, with a 33% improvement in CO_2/N_2 selectivity relative to the analogous PIL membrane lacking any added IL [153]. These results

suggest that in PIL–IL composite membranes, the amount of free IL should be maximized to reach a higher permeability, while mechanical integrity should also be maintained.

The influence of the anions on gas separation performance of PIL–IL composite membranes was also investigated by Bara et al. [156]. Their results showed that the permeabilities of CO_2, N_2, and CH_4 in these PIL–IL composites increase by $2-5$ times relative to those in the neat PIL without a "free" IL component. PIL–IL composites with bigger IL molar volume shows higher CO_2 permeability. The effect of "free" IL cation substituent on gas separation performance of PIL–IL composite membranes was also tested by the same group [157]. The presence of IL in the PIL matrix had a larger influence on the diffusivity, though. It was reported that 20 mol% of "free" IL within the PIL matrix increases CO_2 permeability by 100–250% relative to the neat PIL membrane, while the CO_2/N_2 selectivity was reduced less than 20%.

PILs with different backbones (i.e., poly(ethylene), poly(styrene), and poly(acrylate)) and different functional cationic substituent (e.g., alkyl, fluoroalkyl, oligo(ethylene glycol), and disiloxane) were developed, and their gas separation performances as membranes were investigated by Carlisle et al. [133]. It is found that the longer n-hexyl group contributed to substantially higher CO_2 permeability than shorter alkyl chain sidegroups. The composite materials also followed a traditional trade-off in that the membranes with higher permeability have lower selectivity and vice-versa. Again, rather dramatic improvements in both CO_2 permeability and selectivity were observed upon blending 20 mol% IL in the PIL matrix.

As a result of the inherently strong ion–ion attractive interactions between the solid and liquid charged components, the PIL and IL can form miscible blends at a molecular level with IL loadings as high as 60 wt%. These membranes were mechanically stable at a trans-membrane pressure of 20 atm [158]. PILs–ILs homogenous composite membranes were also developed by the same group with CO_2/N_2 separation performance close to the 2008 "Robeson Upper Bound" [159].

The general procedure for preparing the aforementioned PIL–IL composite membranes is really straightforward, i.e. mixing them together, followed by casting the solution either on a porous substrate (composite membrane) or on a flat plate (self-standing membrane). Another easy way of preparing PIL–IL composite membranes is to blend together a cross-linkable IL monomers and non-reactive ILs, followed by UV-initiated radical cross-linking in situ [158,160].

McDanel and coworkers recently developed cross-linked ionic resins and gels from epoxide-functionalized imidazolium IL monomers [161]. Resulting materials have CO_2/N_2 and CO_2/CH_4 permeability and selectivity values near the Robeson upper bound. Interestingly, the membranes showed inverse CO_2/CH_4 diffusion selectivity ($D_{CO2} < D_{CH4}$), but this diffusivity selectivity is balanced by an increase in CO_2 solubility in the ionic resin. Thus the membrane still showed a CO_2/CH_4 permselectivity close to 20.

In a recent report, Zhou et al. fabricated thin-film composite (TFC) PIL–IL membranes with an active layer thickness of around 100 nm on porous substrates for the first time [162]. The resulting membranes showed a CO_2 permeance of 6100 ± 400 GPU and an ideal CO_2/N_2 selectivity of 22 ± 2. The membrane suggests that PIL–IL TFC composite membranes are promising for post-combustion CO_2 separation applications and could significantly reduce the cost for capturing CO_2 and make membrane-based CO_2 capture technology more competitive.

Overall, homo-PIL membranes normally show lower CO_2 permeability and selectivity, which are considered to be "not attractive" for industrial applications. However, many efforts have been made to incorporate functional groups onto PIL backbones or side-chains (block co-polymer) to enhance their separation performances.

Another way of improving gas separation performances is adding free ILs into the polymeric matrix. By designing new PIL materials and blending in free ILs with high permeability and selectivity, PIL–IL composite membranes have the potential to achieve excellent separation performance, although the results of most current PIL–IL composite membranes are still not satisfactory. Preparing thin-film membranes using PIL–IL composite materials on porous supports is also an approach.

4. IL-gel membranes

Physically gelled IL membranes have also been proposed, and different gas separation performances were investigated by Gin and Noble and co-workers [163,164]. IL-gel materials are attractive because they maintain liquid-like gas transport properties in a solid state, which is easier to handle and to prepare membrane modules for industrial applications.

Typically, an IL-gel membrane is prepared by mixing small amount of a low-molecular-weight organic gelator (LMOG, 2–5 wt%) with the chosen IL at elevated temperatures. When the samples were cooled down, a physical gel forms because of either hydrogen-bonding or/and van der Waals forces from the LMOG and IL to generate a dilute non-covalent network throughout the sample. Table 4 shows commonly used LMOGs and their corresponding ILs.

The physically gelled ILs retain relatively high permeability compared to the neat liquid IL (50–90%) (~500 Barrers) and also show improvements in burst pressure of SILMs prepared from them (up to 5 atm). Different from polymeric membranes that normally follow the permeability–selectivity trade-off illustrated by Robeson ([150,166,167]), the IL-gel membranes appear to suffer from a "flux–mechanical stability trade-off", which means increasing the weight fraction of the LMOG will improve the membrane mechanical stability but will sacrifice the permeability [164]. For example, increasing the LMOG loading from 20 mg/mL to 80 mg/mL, the storage modulus (E'), which represents the stiffness of the material, increases about 20 times. However, the CO_2 permeability decreases from about 640 Barrers to about 440 Barrers.

Physically gelled IL-based composite membranes with a thicknesses ranging from 10.3 to 20.7 μm were prepared by Bara et al. [164]. They also systematically investigated the effect of LMOG loading and operational temperatures on the separation performance of the gel membranes. Although the membranes showed a CO_2 permeance of only 50 GPU, which is far from industrial targets, they displayed superior thermal and mechanical stability even at 80 °C. If the thickness of the IL-gel active layer can be fabricated to less than 1 μm without defects, the resulting membrane will be more attractive and might be commercially viable.

Table 4
IL-Gel membrane.

LMOG	IL	Gas permeability (Barrers)		Ref.
		CO$_2$	N$_2$	
12-hydroxystearic acid	[C$_6$mim][Tf$_2$N]	650 ± 10	29 ± 1	[163]
Cyclo(L-β-3,7-dimethyloctylas- paraginyl-L-phenylalanyl)	[C$_6$mim][Tf$_2$N]	930 ± 20^a	–	[164]
	[C$_2$mim][Tf$_2$N]	690 ± 20^a	–	
Gelatin	[C$_2$mim][DCA]	482	72	[165]
	[C$_4$mim][DCA]	120	12	
	[BMPyr][DCA]	72	36	

^{a} LMOG loading: 20 mg/ml; N$_2$ permeability tested but not shown in the literature.

Couto et al. developed a gel membrane called an Ion-Jelly® membrane from a biodegradable biopolymer (gelatine) and RTILs [165]. Comparing with other gel membranes and SILMs, the Ion-Jelly® membranes showed much lower permeability and ideal selectivity for CO_2.

Although some of the separation performance of IL-gel membranes is promising, the number of LMOGs known to gel RTILs is limited, and the thermal stability of the IL-gel membrane is limited by the temperature at which the gel reversibly becomes a fluid (i.e., the gelation temperature). Therefore, new gelators that could gel IL with higher thermal stability and have the ability to gel functionalized RTILs with enhanced CO_2 affinity are required for further development of the IL-gel membrane platform.

5. Polymer-IL composite membranes

In addition to employing an LMOG to form an IL-gel, gel-like IL-based membranes have also been reported for gas separations (i.e., by blending a polymer with ILs to prepare polymer-IL composite membrane, in which the interactions between the polymer and ILs could be both physical and chemical). By choosing proper ILs, different polymers such as polyether–polyamide block-copolymer (Pebax), poly(vinylidene fluoride)-hexafluoropropylene P(VDF-HFP), poly(vinylidene difluoride) (PVDF) and PI can be used to form polymer-IL composite membranes. More details can be found in Table 5.

The most widely studied polymer for the preparation of polymer-based IL gel membranes is the uncharged copolymer PVDF-HFP. The structure of PVDF-HFP is shown in Fig. 11. Initially, polymer/IL gels were considered to be solid electrolytes, and research was mainly focused on the ion conductivity of the gels. Later, these types of materials were also found to be suitable for CO_2/light gas separations. Until now, several ILs have been applied to mix with PVDF-HFP to prepare membranes for gas separation applications.

Generally, mass transport in ILs is much faster than in solid polymer materials. Thus, higher gas fluxes and faster separation can be obtained in polymer/IL gel membranes with higher IL loadings. For example, by adding about 75 vol% of [C$_2$mim][TCB] to a PVDF matrix, CO_2 permeability was found to increase from about 400 Barrers to about 1800 Barrers, with a slight increase in both CO_2/H_2 and CO_2/N_2 selectivity [168]. For most cases, the membrane Young's modulus (i.e., the maximum breaking strength) and the melting temperature of the gel will dramatically decrease with increasing IL content in the membrane. This effect indicates that membrane mechanical strength and thermal stability are two issues that need to be considered for further application of these polymer-IL gel membranes.

The PVDF-HFP copolymer, a fluoroelastomer with the trade name of Viton, is commonly used as sealing O-rings in industry, denoting the desired slow gas transport properties of this material. Interestingly, the incorporation of ILs into the PVDF-HFP polymer matrix dramatically changes the transport properties of the material. The CO_2 permeability of the composite membrane is expected to be between that of the pure polymer and the neat added IL. However, the CO_2 permeability of the polymer-IL composite membrane with 70 wt% of [C$_6$mim][Tf$_2$N] was found to be almost thousand times higher than that of the pure polymer, and hundred times higher than that of the neat added IL [181]. It is believed that new transport channels were created between the polymer chains and the IL in generating this unexpected gas transport behavior.

Apparently, the permeability of different gas species (including CO_2, N_2, CH_4, H_2, and O_2) in PVDF-HFP-based polymer-IL gel membranes increases with increasing IL content. Friess et al. reported that CO_2 permeability increased by 3 orders of magnitude

Table 5
Polymer-IL composite membrane.

Polymer	IL	Gas permeability (Barrers)		Ref.
		CO_2	N_2	
PVDF-HFP	[C_2mim][BF_4]	400	6.7	[169][a]
PVDF-HFP	[C_2mim][Tf_2N] [C_6mim][Tf_2N]	212	14	[170][b]
PVDF-HFP	[C_2mim][Tf_2N]	533	18	[171][c]
PVDF-HFP	[C_2mim][Tf_2N]	545	23	[172][d]
PBI	[C_4mim][Tf_2N]	7	–	[173][e]
PI	[C_4mim][Tf_2N]	95	–	[173][e]
PI	[C_4mim][Tf_2N]	501 ± 50	18.4 ± 1.8	[174][e]
Pebax 1657	[C_4mim][TfO]	330	8	[175][f]
Pebax 2533	[C_4mim][TfO]	240	7	[175][f]
Pebax 1657	[C_2mim][BF_4]	350	7	[176][g]
PVDF	[C_2mim][TCB]	1778	43.3	[168][h]
SEOS	[C_6mim][Tf_2N] [C_6mim][BF_4] [C_6mim][PF_6]	–	–	[177][i]
SOS	[C_2mim][Tf_2N]	710	17	[178][j]
SMS	[C_2mim][Tf_2N]	840	35	[178][k]
PS–PIL–PS	[C_2mim][Tf_2N]	980	25	[178]
SOS	[C_2mim][Tf_2N]	740	19	[178]
SMS	[C_2mim][Tf_2N]	820	37	[178]
PS–PIL–PS	[C_2mim][Tf_2N]	1040	26	[178][l]
PVP	[P_{4444}][Gly] [P_{4444}][Ser] [P_{4444}][Lys] [P_{4444}][Pro]	6700	–	[179][m]
Tetra-PEG-NH_2 Tetra-PEG-NHS	[C2ImH][Tf_2N]	4000	400	[180][n]

[a] Membrane contains 50 wt% IL. Data were extrapolated from permeation experimental results at 35–45 °C using a CO_2/N_2 (50/50 v/v) mixture.

[b] Membrane contains 40 wt% of the [C_2mim][Tf_2N]/[Hdmim][Tf_2N] mixture (50/50 wt%), feed gas pressure 1 bar at 60 °C;

[c] Pure feed gas, pressure 1 bar, membrane contains 80 wt% IL;

[d] Pure feed gas, pressure 1 bar, membrane contains 80 wt% IL;

[e] Pure feed gas, membrane contains 40 wt% IL, temperature 200 °C;

[f] Pure feed gas at 35 °C; membrane contains 83 wt% IL;

[g] Pure feed gas at RT (25 °C), 1 bar, membrane contains 80 wt% IL, data estimated from literature graph;

[h] Pure feed gas at RT (25 °C), 2 bar, membrane contains 80 wt% IL, data estimated from literature graph;

[i] Pure feed gas at 35 °C and 2 atm, membrane contains 66.7 wt% IL;

[j] Permeances were reported, but exact membrane thicknesses were not offered, thus no permeability data;

[k] Pure feed gas, membrane contains 85 wt% IL;

[l] Mix gas permeation results (50/50 mol/mol mixture of CO_2/N_2), membrane contains 85 wt% IL;

[m] Mix gas permeation results for [P_{4444}][Pro]- PVP gel film, membrane contains 70 wt% ILs. Test temperature at 100 °C, mixed feed gas: CO_2/N_2 (2.5/97.5, volume ratio), Helium used as sweep gas, both feed-side and sweep-side pressures were atmospheric pressure, relative humidity=0%.

[n] Pure gas test at 100 °C, membrane contains 94 wt% IL, data estimated from literature graph.
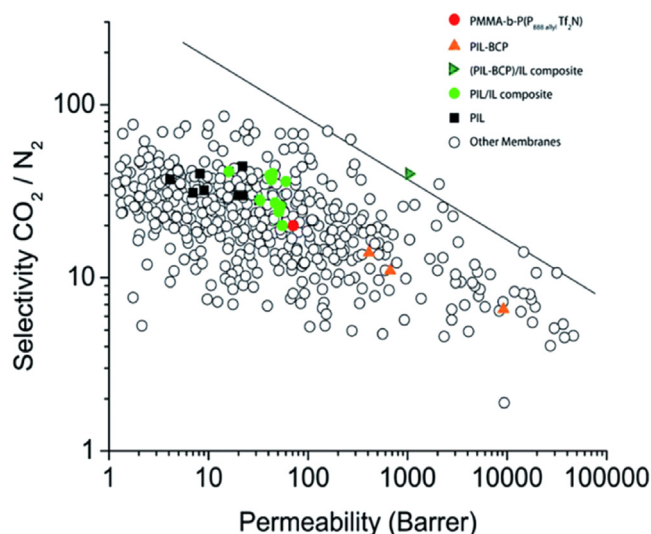
Fig. 9. Robeson plot comparing PILs, PIL–IL composites, ion gels, and PIL-BCPs. Reproduced from Ref. [146].

Fig. 10. Representation of PIL–IL composite. Red circles are free [C_2mim] cations, green circles are [Tf_2N] anions, and blue circles are polymer-bound imidazolium cations. Reproduced from Ref. [153]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with added IL in the polymer matrix [171]. For many gas pairs (e.g., CO_2/N_2, CO_2/CH_4, and O_2/N_2), the selectivities slightly decrease as the IL content increases. But interestingly, CO_2/H_2 selectivity has positive correlation with added IL content (i.e., it increases with
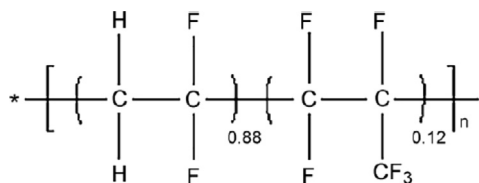
Fig. 11. Structure of PVDF-HFP.

higher IL loadings). A correlation of the transport properties with the Young's modulus of the resulting composite membrane material was innovatively proposed to explain this phenomenon as shown in Fig. 12. As Young's modules decreases (i.e., lower added IL content), the membrane switches from a diffusion-controlled region to a solubility-controlled region, which enhances CO_2/H_2 selectivity.

When high free volume polymers such as a 6FDA-TeMPD PI were used, the permeability of CO_2 first decreased with increasing IL content and then started to increase at a certain IL loading level [174]. A possible reason for this behavior is that the IL introduced to the polymer matrix first occupies the free volume in the pure PI, which reduces the CO_2 diffusion coefficient. However, as the IL content increases further, micro-sized domains of the IL are formed in the PI matrix. Thus, gases transport through these new domains is easier, leading to high permeability. It is worth mentioning that many of the polymer-IL gel membranes listed above are self-standing membranes. If high IL contents are desired, porous supports could be employed to offer mechanical strength. Yoon et al. prepared mechanically-stable composite membranes made with three different ion gels prepared by the self-assembly of IL/poly(styrene-*b*-ethylene oxide-*b*-styrene) (SEOS) triblock copolymer on the surface of a nylon support membrane [177]. Other block copolymer-based ion gel membranes have also been developed by Gu et al. [178]. Their membranes show favorable separation performance relative to the corresponding "upper bound" on the Robeson plots for both CO_2/N_2 and CO_2/CH_4 gas pairs.

Poly(ether-*b*-amide), a family of elastomeric multiblock copolymers commercially available with the trademark Pebax®, normally exhibits a high permeability to hydrocarbons and a high selectivity for CO_2 over many nonpolar gases (e.g., CO_2/N_2 and CO_2/H_2) [182–184]. In 2012, Bernardo et al. prepared an ion-gel membrane using Pebax® 2533 and Pebax® 1657 and added IL [175]. Gas permeation measurements showed that the permeability and selectivity of Pebax® 2533 were not notably affected by the addition of IL, whereas Pebax® 1657 showed a significant increase in gas permeability and a slight decrease of selectivity for most gas pairs with addition of IL. In 2014, ion-gel membranes were fabricated using Pebax® 1657 and [C_2mim][BF_4] by Rabiee et al. for CO_2 separations [176]. Similar to the trend reported in Ref. [171], the permeabilities of tested gases increases with increasing IL content, while the CO_2/H_2 selectivity of

the membrane was enhanced remarkably with a slight decrease in CO_2/N_2 and CO_2/CH_4 selectivity. The behavior suggests that solubility selectivity dominates at high IL content in these composite membranes.

Different from the straightforward method of mixing polymers with ILs to prepare ion-gels, polymeric ion-gels have also been prepared by blending reactive monomers with targeted ILs, followed with a free radical polymerization step. Ion-gel films containing amino acid ILs were successfully fabricated by Kasahara et al. [179]. Results showed both CO_2 permeability and CO_2/N_2 selectivity increased with increasing IL content. However, gas permeation tests were only performed with a low CO_2 feed partial pressure (2.5 kPa). As in a facilitated transport membrane, CO_2 permeability usually decreases with increasing CO_2 partial pressure. Thus, this kind of membrane is more attractive for low CO_2 partial pressure applications such as CO_2 capture from flue gas where CO_2 concentration is low.

Most polymer-IL composite membranes exhibit relatively poor mechanical and thermal stabilities at high temperatures. However, thermally stable polymer-IL composite membranes have been developed [173,180]. In Ref. [173], two thermally-stable polymers, poly(pyromellitimide-*co*-4,4′-oxydianiline) (PMDA-ODA PI) and polybenzimidazole (PBI) were mixed with [C_4mim][Tf_2N] to fabricate composite membranes (named CILPMs-composite IL/polymer membranes). These membranes could withstand 2–6 bar pressure gradients and temperatures as high as 100–200 °C. However, even at under high operating temperatures (200 °C), which is favored for transport of a small gas like H_2, the H_2 permeability is around 50 Barrers while the CO_2 permeability is only about 7 Barrers.

Very recently, Kenta et al. developed high-toughness polymer-IL composite membranes by blending a tetra-armed polymer network with ILs [180]. The resulting membranes were an ion-gel containing a large fraction of IL (94 wt%) that showed doubled CO_2 permeability and similar selectivity compared to neat ILs over high temperatures up to 100 °C. Therefore, it is anticipated that these two kinds of membranes hold significant potential for CO_2 separation applications at high temperatures.

Many PIL–IL composite membranes as well as polymer-IL composite membranes are referred to as "ion-gel" membranes because of the gel-like state of the membranes. Normally, adding ILs into either the charged PIL or traditional uncharged polymer matrix will swell the polymeric chains and thus enhance gas diffusion. Also, addition of CO_2-favorable ILs will enhance the CO_2 solubility. Many attractive properties of polymer-IL composite membranes have been reported, especially for IL-block copolymer composite membranes. Nevertheless, it is still a big challenge to find comparable polymers and ILs to prepare membranes without phase separation. In addition, preparing membranes with a thin active layer and good thermal stability is also critical.

6. Three-component mixed-matrix membranes (MMMs)

MMMs composed of polymer and inorganic/organic particles have been one of the most studied topics in membrane research. A wide range of polymers and solid fillers (e.g., zeolites [185,186], fumed silica [187,188], metal-organic frameworks (MOFs) [189–191], carbon nanotubes [192,193], carbon molecular sieves (CMS) [194], graphite [195] etc.) have been investigated in MMM fabrication. More state-of-the-art information on MMMs for CO_2 separations can be found in a recent review article by Rezakazemi et al. [196].

It is well-accepted that there is an interfacial layer presents in the MMM because of poor polymer/fillers adhesion or compatibility. The voids between the polymer matrix and fillers are
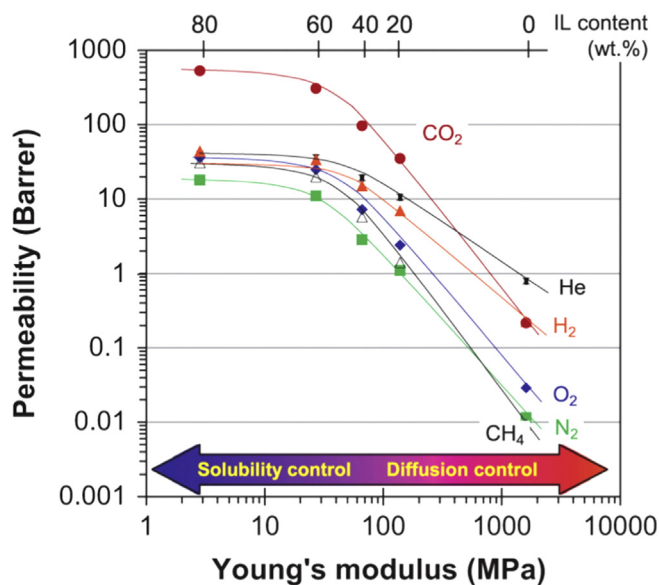

Fig. 12. Correlation of the gas permeability with Young's modulus of a PVDF-HFP-based polymer-IL gel membrane. Reproduced from Ref. [171].

normally non-selective, and thus MMMs typically show higher permeability with relatively lower selectivity compared to pure polymeric membranes. ILs offer a new possibility of improving the separation performance of MMMs, since ILs can increase the permeability of the polymer matrix and offer better interfacial wetting between the polymer matrix and inorganic particles [197]. This approach to MMMs was initially investigated by Hudiono et al. [198]. They confirmed that non-volatile IL coated on the surface of the SAPO-34 particles improved the compatibility between the ionic zeolite particles and the surrounding PIL matrix. In addition, the ILs created a selective layer around the SAPO-34 particles, which then increases the CO_2 permeability as well as CO_2/CH_4 and CO_2/N_2 selectivity. Moreover, the ILs plasticized the ionic PIL matrix, allowing the polymer chains to better interact with the ionic zeolite particle surfaces. All of these benefits allow the polymer matrix to be more flexible and better interact/adhere with the surface of zeolite particles without void formation, thus enhancing MMM gas separation performance. Noble further explained the behavior of these new IL-based three-component MMMs [199].

Hao et al. reported ZIF-8-incorporated membranes that exhibit significantly enhanced permeability for CO_2 than in PIL/IL membranes, while the CO_2/N_2 and CO_2/CH_4 selectivity were only slightly reduced [200].

Very recently, acetate-based ILs were used to improve the performance of microporous titanosilicate ETS-10/chitosan MMMs for CO_2/N_2 permeation, by addition of only small amount of ILs to the MMMs. Both permeability and selectivity were sharply enhanced. Most importantly, the added ILs increase the flexibility of the resulting MMMs, thus offering better processability [201].

ILs based three component MMMs has been demonstrated to improve the polymer/fillers adhesion or compatibility, and consequently enhance the gas separation performances of the MMMs. However, it is critical to find out the best combination of the host polymer and the selected ILs to avoid phase separation.

7. Membrane contactors using ILs as absorbents

CO_2 separation using membrane contactors is not new. In the 1980s, Cussler and Zhang first reported membrane absorption (i.e., a membrane contactor) for CO_2 capture [202,203]. Membrane absorption is a hybrid process that integrates the advantages of membrane separation and absorption, where liquid absorbents provide the selectivity and the porous/unselective membrane acts as the contacting interface between liquid and gas phases. Membrane contactors offer advantages such as determined interfacial area, independent control of gas and liquid flow rates, liner up-scaling, and avoidance of drop dragging. For most of the cases, membrane contactor is applied for CO_2 capture at relatively low pressure and temperature. Various aqueous absorbents have been investigated in membrane contactors for CO_2 capture [204–207], such as aqueous amine solutions, amino acid salt solutions, alkaline solutions, enzyme solutions, and ammonia solutions. Hydrophobic polymeric materials like polypropylene (PP) [208–211], polyvinylidenefluoride (PVDF) [212,213] and polytetrafluoroethylene (PTFE) [214,215] are commonly used as the membrane materials in membrane contactors to prevent pore wetting and maintain a high separation performance. In some cases, membranes with a highly permeable dense top layer have also been applied [216–225].

IL-based membrane contactors are currently a new concept that needs to be demonstrated. Compared with traditional absorbents, the excellent thermal stability of the IL component will enable higher temperature applications (e.g., syngas separation), and the negligible vapor pressure of the IL will sharply reduce solvent loss and regeneration energy. However, there are also many challenges for IL-based membrane contactors that still need to be overcome. The first challenge is the high viscosity of ILs, especially when the ILs are loaded with dissolved CO_2. Another challenge is that ILs have relatively low surface tension, which leads to easy membrane pore-wetting. In addition, the ILs are generally good solvents also for polymers, which means ILs may gradually dissolve some polymeric membranes or polymer-based sealing materials. Moreover, although ILs are commonly accepted as green solvents, the toxicity and potential environmental impact of many ILs are still not clear. The high price of ILs is also a drawback. So far, there are only a few reports on CO_2 capture using ILs in membrane contactors.

To develop the "zero solvent emission process" concept, ILs for the first time were used as an absorbent to capture SO_2 in a membrane contactor by Luis et al. [226]. Shortly after that, CO_2 capture using membrane contactors employing ILs as the absorbent were reported by the same group [227]. In their reports, a commercially available cross-flow membrane contactor offered by Liqui-Cel was used, and 1-ethyl-3-methylimidazolium ethylsulfate $[C_2mim][EtSO_4]$ was chosen as the IL solvent. Under their operating conditions, the observed separation factor ($K_{overall}\cdot a$) of the cross-flow contactors was similar to that of the parallel contactors, meaning that the overall mass transfer resistance showed little difference in the two modules. This group also compared the performance of different membranes in the membrane contactors using the same ILs [228]. In 2012, they systematically compared the separation of CO_2 by using 1-ethyl-3-methylimidazolium ethylsulfate $[C_2mim][EtSO_4]$ in parallel-flow and cross-flow membrane contactors [229]. Different from the results in [227], the overall mass-transfer coefficients were higher in the cross-flow membrane contactors than in the parallel-flow units. Compared with a traditional absorbent (e.g., 1 M aq. MDEA, Glycin salt), the overall mass-transfer coefficient of $K_{overall}$ with the ILs was still one to two orders of magnitudes lower. In their report, they claimed that the bottleneck step of the membrane absorption process was the slow interfacial chemical CO_2-IL reaction. Therefore, to enhance the membrane absorption process, high-reactivity ILs have to be used to increase the absorption rate.

Lu et al. investigated a membrane absorption/desorption process by employing two types of IL aqueous solutions [230,231]. They found that chemical-absorption ILs showed much higher CO_2 absorption capacity, but they were much more difficult to regenerate compared to the physical-absorption ILs.

The influence of temperature on membrane contactor separation performance was studied by Gómez-Coma et al. [232]. As expected, the mass-transfer coefficient of IL-containing membrane contactor is lower than that of membrane contactors using aqueous absorbents, presumably due to the high viscosity of ILs because the resistance in liquid phase is usually the main limitation to overall mass transfer. In addition, membrane contactors using chemical absorbents show better separation efficiency. According to their study, temperature is a key variable in the process, since increasing the operating temperature could reduce IL viscosity and also enhance the chemical reaction with CO_2.

To deal with the negative influence of the highly viscous chemisorption ILs, Jie et al. developed a pressure swing membrane absorption (PSMAB) process for pre-combustion CO_2 capture [233,234]. Their process is shown in Fig. 13. For safety, Helium gas was used instead of H_2 gas in their experiments.

Different from common membrane contactors discussed above, in the PSMAB process, the absorbent (i.e., a mixture of ILs and generation–zero poly(amido amine) (PAMAM) dendrimer) were kept stationary in the shell side of the membrane module. This PSMAB process was controlled by a 3-valve or 5-valve control system to simulate the flow of the liquid phase and to achieve the
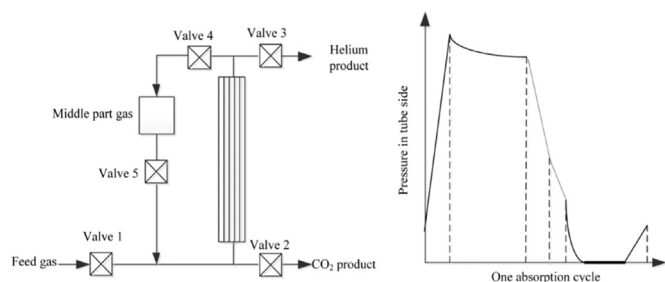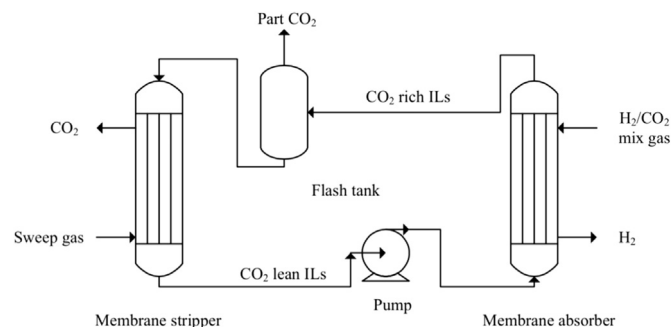
Fig. 13. Schematic diagram of the five-valve pressure swing membrane absorption process. Reproduced from Ref. [233].

Fig. 14. Illustration of a closed-cycle PSMAB process.

CO_2 absorption and desorption. The feed gas was introduced into tube side of the membrane module for a certain time. Because the absorbent preferably absorbs CO_2, the He-rich product was released from one side of the membrane module, and the CO_2-rich product was released from the opposite side of the membrane module. High temperature (about 100 °C) and high pressure (250 psig) were applied. Under optimized operation conditions, an 88.2% CO_2-enriched gas product and a He product with CO_2 concentration as low as 4.2–5.8% were produced. The effect of various parameters on the separation performances of this PSMAB process have also been intensively studied by the same group [235], including membrane module configuration design, solvent concentration, operating temperature, and operating pressure. However, as no energy consumption and operation cost data could be found from their report, it is hard to compare this process with other technologies.

Deng et al. also reported a PSMAB process using IL-based absorbents with relatively low viscosity. This is a continuous process in a closed loop with recirculation of the IL-based absorbents [236]. The membranes used in the membrane absorber and desorber are different. A schematic illustration of the process is shown in Fig. 14.

In this process, the syngas is first sent to the membrane absorber, in which the feed gas stream with a simulated pre-combustion syngas at elevated pressure (20 bar) and temperature (60–140 °C) flows counter-currently with the IL absorbents through the tube and shell sides of the membrane contactor, respectively. Purified H_2 is kept at elevated pressure, while the pressure of CO_2-enriched ILs is reduced to a low pressure (e.g., 3 bar) before it passes through the stripper. The released CO_2 is collected from one side of the stripper, and clean IL is recirculated to the absorber. Compared with post-combustion and oxy-combustion, CO_2 separation is relatively easier and cheaper in a pre-combustion process because of the higher operating pressure (about 20 bar) and higher CO_2 concentration (about 45%). This pressure swing process has high separation efficiency, and it is environmentally friendly and energy saving because the solvent has undetectable vapor pressure and high thermal and chemical stability. Also, the emission of solvent is negligible, and there is no solvent evaporation during the stripping/desorption step.

Some simulation and modeling of this process have also been studied [237]. The mass transfer of CO_2 through the membrane absorber was studied using 2D and 3D mathematic models. The influence of membrane parameters (e.g., diameter, length, thickness, porosity and pore size) and various process parameters (e.g., gas/liquid flow rates, operating temperature, and composition of the gas phase) on the mass transfer were investigated. Two-dimensional concentration/velocity distributions of the gas inside the lumen, through the membrane, and in the shell side were obtained. According to the results, membrane resistance has a significant contribution to mass transfer in the chemical absorption step. Membranes with high porosity and small thickness

could apparently reduce the membrane resistance and thus increase separation efficiency. Compared to porosity and thickness, membrane diameter and length have a relatively small influence on separation performance within a certain range.

To summarize, a CO_2 gas separation process using ILs as the absorbent in membrane contactors has many challenges but with great potential for being highly efficient and energy saving. The rapidly growing numbers of new IL-based absorbents reported with low viscosities, high absorption capacities and fast absorption rates, coupled with smart design of the processes and development of more compatible membrane materials offer a bright future to this young technology.

8. Conclusions and perspectives

The large number of publications relating to the use of ILs in membranes for CO_2 gas separations clearly shows that research in this field has grown dramatically over the last decade. This IL-based platform has opened a new door for exploring next-generation CO_2 separation membrane materials and membrane processes, which give a nearly infinite range of possibilities with respect to membrane design.

Some reported ILs-based membranes exhibit better separation performance than current commercial materials (e.g. cellulose acetate) [238]. The gas permeability is, however, relatively lower compared with the state-of-the-art highly permeable membrane materials (e.g. PTMSP, PMP, TR polymers and PIMs). Nevertheless, ILs based membrane materials are advantageous considering most of these highly permeable (high free volume) materials lead to serious physical aging over time, especially when the polymer is prepared as thin-film composite membranes. Many of these ILs based materials are very stable, easy to process with excellent film-forming properties. For example, although the intrinsic CO_2 permeability of a PIL–IL (poly(vinylhexylimidazolium bis(trifluoromethylsulfonyl)imide))-[C_2mim][Tf_2N] membrane is only around 600 Barrers, a thin-film composite membrane of this material with a 100 nm active top layer was reported with a CO_2 permeance of 6100 GPU while maintaining a good CO_2/N_2 selectivity. This IL-based membrane represents the state-of-the-art CO_2 separation membrane with the currently best separation performance. Furthermore, the nearly infinite combinations of cations and anions make it possible to design ILs with desired properties for the development of gas separation membranes with even better CO_2 separation performance.

Despite the rapid development of ILs-based membranes in recent years, there is still a big margin for the further improvement. In addition, research must be done to tackle the challenges associated with some of the IL-based membranes, such as the trade-off between the separation performance and mechanical strength. Thus, the following aspects deserve attention:

(1) Better understanding of structure-property relationship of ILs and the desired properties suitable for IL-based membranes (e.g. high CO_2 absorption capacity, low viscosity and fast absorption kinetics) to define new task-specific ILs as membrane materials;

(2) Development of PIL block-copolymer with different functional groups, preferably those lead to self-assembly or micro-phase separation, thus to enhance the gas separation performances [147];

(3) Developing PIL with robust mechanical strength, easy processing properties and strong interaction with free ILs;

(4) Preparation of thin-film composite membranes consisting of a thin IL-based layer (< 1 μm) on a porous/multilayer highly gas permeable support.

(5) Investigating the stability of ILs-based membrane at more-realistic operating conditions (i.e., elevated temperatures and mixed-gas feeds).

To conclude, the combination of ILs with membrane technology provides a new way to make membrane-based separations a more competitive technology in CO_2 separation. Although there are still many challenges that need to be addressed in order to transfer IL-based membranes from the laboratory to operation in the field, many novel materials, novel methods and interesting results have been documented in recent years to show the promise of this coupled approach.

Acknowledgments

Appendix A. Suplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2015.08.060.

References

[1] M.Z. Jacobson, Review of solutions to global warming, air pollution and energy security, Geochim. Cosmochim. Acta 73 (13) (2009), pp. A581–A581.

[2] IEA. CO_2 Emissions From Fuel Combustion Highlights 2014, 2014.

[3] M. Naranjo, D.T. Brownlow, A. Garza, CO_2 capture and sequestration in the cement industry, in: Proceedings of the 10th International Conference on Greenhouse Gas Control Technologies, 2011, vol. 4, pp. 2716–2723.

[4] D. Gielen, CO_2 removal in the iron and steel industry, Energy Convers. Manag. 44 (7) (2003) 1027–1037.

[5] A.H. Younger, Natural Gas Processing Principles And Technology – Part II (2004).

[6] M. Wang, A. Lawal, P. Stephenson, J. Sidders, C. Ramshaw, Post-combustion CO_2 capture with chemical absorption: a state-of-the-art review, Chem. Eng. Res. Des. 89 (9) (2011) 1609–1624.

[7] G.T. Rochelle, Amine scrubbing for CO_2 capture, Science 325 (5948) (2009) 1652–1654.

[8] B.A. Oyenekan, G.T. Rochelle, Energy performance of stripper configurations for CO_2 capture by aqueous amines, Ind. Eng. Chem. Res. 45 (8) (2006) 2457–2464.

[9] M.T. Ho, G.W. Allinson, D.E. Wiley, Reducing the cost of CO_2 capture from flue gases using pressure swing adsorption, Ind. Eng. Chem. Res. 47 (14) (2008) 4883–4890.

[10] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO_2 capture, Science 319 (5865) (2008) 939–943.

[11] C.E. Powell, G.G. Qiao, Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases, J. Membr. Sci. 279 (1–2) (2006) 1–49.

[12] E. Favre, Membrane processes and postcombustion carbon dioxide capture: challenges and prospects, Chem. Eng. J. 171 (3) (2011) 782–793.

[13] M.T. Ho, G.W. Allinson, D.E. Wiley, Reducing the cost of CO_2 capture from flue gases using membrane technology, Ind. Eng. Chem. Res. 47 (5) (2008)

[14] M.B. Hagg, A. Lindbrathen, CO_2 capture from natural gas fired power plants by using membrane technology, Ind. Eng. Chem. Res. 44 (20) (2005) 7668–7675.

[15] R. Bredesen, K. Jordal, A. Bolland, High-temperature membranes in power generation with CO_2 capture, Chem. Eng. Process. 43 (9) (2004) 1129–1158.

[16] M.M. Hossain, H.I. de Lasa, Chemical-looping combustion (CLC) for inherent CO_2 separations – a review, Chem. Eng. Sci. 63 (18) (2008) 4433–4451.

[17] A. Lyngfelt, B. Leckner, T. Mattisson, A fluidized-bed combustion process with inherent CO_2 separation; application of chemical-looping combustion, Chem. Eng. Sci. 56 (10) (2001) 3101–3113.

[18] J. Adanez, L.F. de Diego, F. Garcia-Labiano, P. Gayan, A. Abad, J.M. Palacios, Selection of oxygen carriers for chemical-looping combustion, Energy Fuels 18 (2) (2004) 371–377.

[19] M.J. Tuinier, M.V. Annaland, G.J. Kramer, J.A.M. Kuipers, Cryogenic CO_2 capture using dynamically operated packed beds, Chem. Eng. Sci. 65 (1) (2010) 114–119.

[20] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis, CO_2 capture by a task-specific ionic liquid, J. Am. Chem. Soc. 124 (6) (2002) 926–927.

[21] J.E. Bara, D.E. Camper, D.L. Gin, R.D. Noble, Room-temperature ionic liquids and composite materials: platform technologies for CO_2 capture, Acc. Chem. Res. 43 (1) (2010) 152–159.

[22] F. Karadas, M. Atilhan, S. Aparicio, Review on the use of ionic liquids (ILs) as alternative fluids for CO_2 capture and natural gas sweetening, Energy Fuels 24 (2010) 5817–5828.

[23] M. Ramdin, T.W. de Loos, T.J.H. Vlugt, State-of-the-art of CO_2 capture with ionic liquids, Ind. Eng. Chem. Res. 51 (24) (2012) 8149–8177.

[24] L. Zhang, J. Chen, J.X. Lv, S.F. Wang, Y. Cui, Progress and development of capture for CO_2 by ionic liquids, Asian J. Chem. 25 (5) (2013) 2355–2358.

[25] M. Hasib-ur-Rahman, M. Siaj, F. Larachi, Ionic liquids for CO_2 capture – development and progress, Chem. Eng. Process. 49 (4) (2010) 313–322.

[26] J.R. Li, Y.G. Ma, M.C. McCarthy, J. Sculley, J.M. Yu, H.K. Jeong, P.B. Balbuena, H. C. Zhou, Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks, Coord. Chem. Rev. **255** (15–16) (2011) 1791–1823.

[27] K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T. H. Bae, J.R. Long, Carbon dioxide capture in metal-organic frameworks, Chem. Rev. 112 (2) (2012) 724–781.

[28] N.H. Duc, F. Chauvy, J.M. Herri, CO_2 capture by hydrate crystallization – a potential solution for gas emission of steelmaking industry, Energy Convers. Manag. 48 (4) (2007) 1313–1322.

[29] H.J. Lee, J.D. Lee, P. Linga, P. Englezos, Y.S. Kim, M.S. Lee, Y.D. Kim, Gas hydrate formation process for pre-combustion capture of carbon dioxide, Energy 35 (6) (2010) 2729–2733.

[30] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: an overview, Ind. Eng. Chem. Res. 47 (7) (2008) 2109–2121.

[31] R.W. Baker, Future directions of membrane gas separation technology, Ind. Eng. Chem. Res. 41 (6) (2002) 1393–1411.

[32] P. Scovazzo, A.E. Visser, J.H. Davis, R.D. Rogers, C.A. Koval, D.L. DuBois, R. D. Noble, Supported ionic liquid membranes and facilitated ionic liquid membranes, Ionic Liquids 818 (2002) 69–87.

[33] P. Scovazzo, J. Kieft, D.A. Finan, C. Koval, D. DuBois, R. Noble, Gas separations using non-hexafluorophosphate $[PF_6]-$ anion supported ionic liquid membranes, J. Membr. Sci. 238 (1–2) (2004) 57–63.

[34] L.J. Lozano, C. Godínez, A.P. de los Ríos, F.J. Hernández-Fernández, S. Sánchez-Segado, F.J. Alguacil, Recent advances in supported ionic liquid membrane technology, J. Membr. Sci. 376 (1–2) (2011) 1–14.

[35] M.A. Malik, M.A. Hashim, F. Nabi, Ionic liquids in supported liquid membrane technology, Chem. Eng. J. **171** (1) (2011) 242–254.

[36] J.E. Bara, Ionic liquids in gas separation membranes, in: Eric M.V. Hoek, Volodymyr V. Tarabara (Eds.), Encyclopedia of Membrane Science and Technology, John Wiley & Sons, Inc, 2013, pp. 1–23 10.1002/9781118522318.emst048.

[37] L.A. Blanchard, Z.Y. Gu, J.F. Brennecke, High-pressure phase behavior of ionic liquid/CO_2 systems, J. Physical Chem. B 105 (12) (2001) 2437–2444.

[38] L.Y. Zhou, J. Fan, J.J. Wang, Capture of CO_2 by Ionic Liquids, Progress Chem. 23 (11) (2011) 2269–2275.

[39] X.P. Zhang, X.C. Zhang, H.F. Dong, Z.J. Zhao, S.J. Zhang, Y. Huang, Carbon capture with ionic liquids: overview and progress, Energy Environ.Sci. 5 (5) (2012) 6668–6681.

[40] M.S. Shannon, J.E. Bara, Reactive and reversible ionic liquids for CO_2 capture and acid gas removal, Sep. Sci. Technol. 47 (2) (2012) 178–188.

[41] Z.G. Lei, C.N. Dai, B.H. Chen, Gas solubility in ionic liquids, Chem. Rev. 114 (2) (2014) 1289–1326.

[42] H. Ohno, K. Fukumoto, Amino acid ionic liquids, Acc. Chem. Res. 40 (11) (2007) 1122–1129.

[43] S.H. Ren, Y.C. Hou, W.Z. Wu, S.D. Tian, W.N. Liu, CO_2 capture from flue gas at high temperatures by new ionic liquids with high capacity, RSC Adv. 2 (6) (2012) 2504–2507.

[44] C.M. Wang, Y. Guo, X. Zhu, G.K. Cui, H.R. Li, S. Dai, Highly efficient CO_2 capture by tunable alkanolamine-based ionic liquids with multidentate cation coordination, Chem. Commun. 48 (52) (2012) 6526–6528.

[45] C.M. Wang, H.M. Luo, D.E. Jiang, H.R. Li, S. Dai, Carbon dioxide capture by superbase-derived protic ionic liquids, Angew. Chem.-Int. Ed. 49 (34) (2010) 5978–5981.

[46] M.B. Shiflett, A. Yokozeki, Phase behavior of carbon dioxide in ionic liquids:

[emim][Acetate], [emim][Trifluoroacetate], and [emim][Acetate] plus [emim][Trifluoroacetate] mixtures, J. Chem. Eng. Data 54 (1) (2009) 108–114.

[47] B.E. Gurkan, J.C. de la Fuente, E.M. Mindrup, L.E. Ficke, B.F. Goodrich, E. A. Price, W.F. Schneider, J.F. Brennecke, Equimolar CO_2 absorption by anion-functionalized ionic liquids, J. Am. Chem. Soc. 132 (7) (2010) 2116.

[48] J. Jacquemin, P. Husson, V. Majer, M.F.C. Gomes, Influence of the cation on the solubility of CO_2 and H_2 in ionic liquids based on the bis(tri-fluoromethylsulfonyl)imide anion, J. Solut. Chem. 36 (8) (2007) 967–979.

[49] A.P.S. Kamps, D. Tuma, J.Z. Xia, G. Maurer, Solubility of CO_2 in the ionic liquid [bmim][PF6], J. Chem. Eng. Data 48 (3) (2003) 746–749.

[50] J. Jacquemin, P. Husson, V. Majer, M.F.C. Gomes, Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimida-zolium hexafluorophosphate, Fluid Phase Equilib. 240 (1) (2006) 87–95.

[51] W. Afzal, X.Y. Liu, J.M. Prausnitz, Solubilities of some gases in four im-midazolium-based ionic liquids, J. Chem. Thermodyn. 63 (2013) 88–94.

[52] J. Jacquemin, M.F.C. Gomes, P. Husson, V. Majer, Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric, J. Chem. Thermodyn. 38 (4) (2006) 490–502.

[53] A.H. Jalili, M. Safavi, C. Ghotbi, A. Mehdizadeh, M. Hosseini-Jenab, V. Taghikhani, Solubility of CO_2, H_2S, and their mixture in the ionic liquid 1-Octyl-3-methylimidazolium Bis(trifluoromethyl)sulfonylimide, J. Phys. Chem. B 116 (9) (2012) 2758–2774.

[54] D. Almantariotis, S. Stevanovic, O. Fandino, A.S. Pensado, A.A.H. Padua, J. Y. Coxam, M.F.C. Gomes, Absorption of carbon dioxide, nitrous oxide, ethane and nitrogen by 1-Alkyl-3-methylimidazolium C(n)mim, $n=2,4,6$) tris (pentafluoroethyl)trifluorophosphate ionic liquids (eFAP), J. Phys. Chem. B 116 (26) (2012) 7728–7738.

[55] M.B. Shiflett, D.J. Kasprzak, C.P. Junk, A. Yokozeki, Phase behavior of {carbon dioxide plus [bmim][Ac]} mixtures, J. Chem. Thermodyn. 40 (1) (2008) 25–31.

[56] B.F. Goodrich, J.C. de la Fuente, B.E. Gurkan, Z.K. Lopez, E.A. Price, Y. Huang, J. F. Brennecke, Effect of water and temperature on absorption of CO_2 by amine-functionalized anion-tethered ionic liquids, J. Phys. Chem. B 115 (29) (2011) 9140–9150.

[57] B.F. Goodrich, J.C. de la Fuente, B.E. Gurkan, D.J. Zadigian, E.A. Price, Y. Huang, J.F. Brennecke, Experimental measurements of amine-functionalized anion-tethered ionic liquids with carbon dioxide, Ind. Eng. Chem. Res. 50 (1) (2011) 111–118.

[58] M.B. Shiflett, A. Yokozeki, Liquid–liquid equilibria in binary mixtures con-taining fluorinated benzenes and ionic liquid 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide, J. Chem. Eng. Data 53 (11) (2008) 2683–2691.

[59] X.C. Zhang, F. Huo, Z.P. Liu, W.C. Wang, W. Shi, E.J. Maginn, Absorption of CO_2 in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Tris(pentafluoroethyl) trifluorophosphate ([hmim][FEP]): a molecular view by computer simula-tions, J. Phys. Chem. B 113 (21) (2009) 7591–7598.

[60] Z.F. Zhang, W. Wu, Z.M. Liu, B.X. Han, H.X. Gao, T. Jiang, A study of tri-phasic behavior of ionic liquid-methanol-CO_2 systems at elevated pressures, Phys. Chem. Chem. Phys. 6 (9) (2004) 2352–2357.

[61] Z.F. Zhang, W.Z. Wu, B. Wang, J.W. Chen, D. Shen, B.X. Han, High-pressure phase behavior of CO_2/acetone/ionic liquid system, J. Supercrit. Fluids 40 (1) (2007) 1–6.

[62] X.Y. Li, M.Q. Hou, Z.F. Zhang, B.X. Han, G.Y. Yang, X.L. Wang, L.Z. Zou, Ab-sorption of CO_2 by ionic liquid/polyethylene glycol mixture and the ther-modynamic parameters, Green Chem. 10 (8) (2008) 879–884.

[63] P.K. Parhi, Supported liquid membrane principle and its practices: a short review, J. Chem. 2013 (2013) 11.

[64] P. Bernardo, E. Drioli, G. Golemme, Membrane gas separation: a review/state of the art, Ind. Eng. Chem. Res. 48 (10) (2009) 4638–4663.

[65] M.H. Al Marzouqi, M.A. Abdulkarim, S.A. Marzouk, M.H. El-Naas, H. M. Hasanain, Facilitated transport of CO_2 through immobilized liquid membrane, Ind. Eng. Chem. Res. 44 (24) (2005) 9273–9278.

[66] A. Ito, S.H. Duan, Y. Ikenori, A. Ohkawa, Permeation of wet CO_2/CH_4 mixed gas through a liquid membrane supported on surface of a hydrophobic mi-croporous membrane, Sep. Purif. Technol. 24 (1–2) (2001) 235–242.

[67] P. Luis, T. Van Gerven, B. Van der Bruggen, Recent developments in mem-brane-based technologies for CO_2 capture, Progress Energy Combust. Sci. 38 (3) (2012) 419–448.

[68] J. Albo, T. Yoshioka, T. Tsuru, Porous Al_2O_3/TiO_2 tubes in combination with 1-ethyl-3-methylimidazolium acetate ionic liquid for CO_2/N_2 separation, Sep. Purif. Technol. 122 (2014) 440–448.

[69] E. Santos, J. Albo, A. Irabien, Acetate based supported ionic liquid membranes (SILMs) for CO_2 separation: influence of the temperature, J. Membr. Sci. 452 (2014) 277–283.

[70] N. Shahkaramipour, M. Adibi, A.A. Seifkordi, Y. Fazli, Separation of CO_2/CH_4 through alumina-supported geminal ionic liquid membranes, J. Membr. Sci. 455 (2014) 229–235.

[71] L.C. Tome, D.J.S. Patinha, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, CO_2 se-paration applying ionic liquid mixtures: the effect of mixing different anions on gas permeation through supported ionic liquid membranes, RSC Adv. 3 (30) (2013) 12220–12229.

[72] I. Cichowska-Kopczynska, M. Joskowska, B. Debski, J. Luczak, R. Aranowski, Influence of ionic liquid structure on supported ionic liquid membranes ef-fectiveness in carbon dioxide/methane separation, J. Chem. 2013 (2013) 10.

[73] R. Condemarin, P. Scovazzo, Gas permeabilities, solubilities, diffusivities, and diffusivity correlations for ammonium-based room temperature ionic liquids with comparison to imidazolium and phosphonium RTIL data, Chem. Eng. J. 147 (1) (2009) 51–57.

[74] S.M. Mahurin, J.S. Lee, G.A. Baker, H.M. Luo, S. Dai, Performance of nitrile-containing anions in task-specific ionic liquids for improved CO_2/N_2 se-paration, J. Membr. Sci. 353 (1–2) (2010) 177–183.

[75] S.M. Mahurin, P.C. Hillesheim, J.S. Yeary, D.E. Jiang, S. Dai, High CO_2 solubility, permeability and selectivity in ionic liquids with the tetracyanoborate anion, RSC Adv. 2 (31) (2012) 11813–11819.

[76] J. Ilconich, C. Myers, H. Pennline, D. Luebke, Experimental investigation of the permeability and selectivity of supported ionic liquid membranes for CO_2/He separation at temperatures up to 125 degrees C, J. Membr. Sci. 298 (1–2) (2007) 41–47.

[77] P. Scovazzo, Determination of the upper limits, benchmarks, and critical properties for gas separations using stabilized room temperature ionic liquid membranes (SILMs) for the purpose of guiding future research, J. Membr. Sci. 343 (1–2) (2009) 199–211.

[78] Y.Y. Jiang, Z. Zhou, Z. Jiao, L. Li, Y.T. Wu, Z.B. Zhang, SO_2 gas separation using supported ionic liquid membranes, J. Phys. Chem. B 111 (19) (2007) 5058–5061.

[79] P. Cserjesi, N. Nemestothy, K. Belafi-Bako, Gas separation properties of sup-ported liquid membranes prepared with unconventional ionic liquids, J. Membr. Sci. 349 (1–2) (2010) 6–11.

[80] J.E. Bara, C.J. Gabriel, T.K. Carlisle, D.E. Camper, A. Finotello, D.L. Gin, R. D. Noble, Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes, Chem. Eng. J. 147 (1) (2009) 43–50.

[81] Y.I. Park, B.S. Kim, Y.H. Byun, S.H. Lee, E.W. Lee, J.M. Lee, Preparation of supported ionic liquid membranes (SILMs) for the removal of acidic gases from crude natural gas, Desalination 236 (1–3) (2009) 342–348.

[82] L.C. Tome, C. Florindo, C.S.R. Freire, L.P.N. Rebelo, I.M. Marrucho, Playing with ionic liquid mixtures to design engineered CO_2 separation membranes, Phys. Chem. Chem. Phys. 16 (32) (2014) 17172–17182.

[83] P. Jindaratsamee, A. Ito, S. Komuro, Y. Shimoyama, Separation of CO_2 from the CO_2/N_2 mixed gas through ionic liquid membranes at the high feed con-centration, J. Membr. Sci. 423 (2012) 27–32.

[84] Y. Shimoyama, S. Komuro, P. Jindaratsamee, Permeability of CO_2 through ionic liquid membranes with water vapour at feed and permeate streams, J. Chem. Thermodyn. 69 (2014) 179–185.

[85] J.J. Close, K. Farmer, S.S. Moganty, R.E. Baltus, CO_2/N_2 separations using na-noporous alumina-supported ionic liquid membranes: effect of the support on separation performance, J. Membr. Sci. 390 (2012) 201–210.

[86] A.I. Labropoulos, G.E. Romanos, E. Kouvelos, P. Falaras, V. Likodimos, M. Francisco, M.C. Kroon, B. Iliev, G. Adamova, T.J.S. Schubert, Alkyl-methy-limidazolium tricyanomethanide ionic liquids under extreme confinement onto nanoporous ceramic membranes, J. Phys. Chem. C 117 (19) (2013) 10114–10127.

[87] S.H. Chai, P.F. Fulvio, P.C. Hillesheim, Z.A. Qiao, S.M. Mahurin, S. Dai, "Brick-and-mortar" synthesis of free-standing mesoporous carbon nanocomposite membranes as supports of room temperature ionic liquids for CO_2-N_2 se-paration, J. Membr. Sci. 468 (2014) 73–80.

[88] K.M. Gupta, Y.F. Chen, J.W. Jiang, Ionic liquid membranes supported by hy-drophobic and hydrophilic metal-organic frameworks for CO_2Capture, J. Phys. Chem. C 117 (11) (2013) 5792–5799.

[89] K.M. Gupta, Y.F. Chen, Z.Q. Hu, J.W. Jiang, Metal-organic framework sup-ported ionic liquid membranes for CO_2 capture: anion effects, Phys. Chem. Chem. Phys. 14 (16) (2012) 5785–5794.

[90] S.D. Hojniak, A.L. Khan, O. Holloczki, B. Kirchner, I.F.J. Vankelecom, W. Dehaen, K. Binnemans, Separation of carbon dioxide from nitrogen or methane by supported ionic liquid membranes (SILMS): influence of the cation charge of the ionic liquid, J. Phys. Chem. B 117 (48) (2013) 15131–15140.

[91] P. Scovazzo, D. Havard, M. McShea, S. Mixon, D. Morgan, Long-term, con-tinuous mixed-gas dry fed CO_2/CH_4 and CO_2/N_2 separation performance and selectivities for room temperature ionic liquid membranes, J. Membr. Sci. 327 (1–2) (2009) 41–48.

[92] J. Albo, T. Tsuru, Thin ionic liquid membranes based on inorganic supports with different pore sizes, Ind. Eng. Chem. Res. 53 (19) (2014) 8045–8056.

[93] S.J. Ho Seon Bang, Kang Yong Soo, Jongok Wona, Dual facilitated transport of CO_2 using electrospun composite membranes containing Ionic liquid, J. Membr. Sci. 479 (2015) 7.

[94] L.A. Neves, J.G. Crespo, I.M. Coelhoso, Gas permeation studies in supported ionic liquid membranes, J. Membr. Sci. 357 (1–2) (2010) 160–170.

[95] R.E. Baltus, R.M. Counce, B.H. Culbertson, H.M. Luo, D.W. DePaoli, S. Dai, D. C. Duckworth, Examination of the potential of ionic liquids for gas separa-tions, Sep. Sci. Technol. 40 (1–3) (2005) 525–541.

[96] L.A. Banu, D. Wang, R.E. Baltus, Effect of ionic liquid confinement on gas separation characteristics, Energy Fuels 27 (8) (2013) 4161–4166.

[97] S. Wickramanayake, D. Hopkinson, C. Myers, L. Hong, J. Feng, Y. Seol, D. Plasynski, M. Zeh, D. Luebke, Mechanically robust hollow fiber supported ionic liquid membranes for CO_2 separation applications, J. Membr. Sci. 470 (2014) 52–59.

[98] P. Jindaratsamee, Y. Shimoyama, H. Morizaki, A. Ito, Effects of temperature and anion species on CO_2 permeability and CO_2/N_2 separation coefficient through ionic liquid membranes, J. Chem. Thermodyn. 43 (3) (2011) 311–314.

[99] J.H. Lee, J. Hong, J.H. Kim, Y.S. Kang, S.W. Kang, Facilitated CO_2 transport membranes utilizing positively polarized copper nanoparticles, Chem. Commun. 48 (43) (2012) 5298–5300.

[100] J.H. Lee, I.S. Chae, D. Song, Y.S. Kang, S.W. Kang, Metallic copper incorporated ionic liquids toward maximizing CO_2 separation properties, Sep. Purif. Technol. 112 (2013) 49–53.

[101] I.S. Chae, J.H. Lee, J. Hong, Y.S. Kang, S.W. Kang, The platform effect of graphene oxide on CO_2 transport on copper nanocomposites in ionic liquids, Chem. Eng. J. 251 (2014) 343–347.

[102] J. Albo, E. Santos, L.A. Neves, S.P. Simeonov, C.A.M. Afonso, J.G. Crespo, A. Irabien, Separation performance of CO_2 through Supported Magnetic Ionic Liquid Membranes (SMILMs), Sep. Purif. Technol. 97 (2012) 26–33.

[103] E. Santos, J. Albo, C.I. Daniel, C.A.M. Portugal, J.G. Crespo, A. Irabien, Permeability modulation of supported magnetic ionic liquid membranes (SMILMs) by an external magnetic field, J. Membr. Sci. 430 (2013) 56–61.

[104] D. Camper, J. Bara, C. Koval, R. Noble, Bulk-fluid solubility and membrane feasibility of Rmim-based room-temperature ionic liquids, Ind. Eng. Chem. Res. 45 (18) (2006) 6279–6283.

[105] C. Myers, H. Pennline, D. Luebke, J. Ilconich, J.K. Dixon, E.J. Maginn, J. F. Brennecke, High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes, J. Membr. Sci. 322 (1) (2008) 28–31.

[106] K.E. Gutowski, E.J. Maginn, Amine-functionalized task-specific ionic liquids: a mechanistic explanation for the dramatic increase in viscosity upon complexation with CO_2 from molecular simulation, J. Am. Chem. Soc. 130 (44) (2008) 14690–14704.

[107] S. Hanioka, T. Maruyama, T. Sotani, M. Teramoto, H. Matsuyama, K. Nakashima, M. Hanaki, F. Kubota, M. Goto, CO_2 separation facilitated by task-specific ionic liquids using a supported liquid membrane, J. Membr. Sci. 314 (1–2) (2008) 1–4.

[108] S. Kasahara, E. Kamio, T. Ishigami, H. Matsuyama, Amino acid ionic liquid-based facilitated transport membranes for CO_2 separation, Chem. Commun. 48 (55) (2012) 6903–6905.

[109] K. Huang, X.M. Zhang, Y.X. Li, Y.T. Wu, X.B. Hu, Facilitated separation of CO_2 and SO_2 through supported liquid membranes using carboxylate-based ionic liquids, J. Membr. Sci. 471 (2014) 227–236.

[110] L.C. Tome, D.J.S. Patinha, R. Ferreira, H. Garcia, C.S. Pereira, C.S.R. Freire, L.P. N. Rebelo, I.M. Marrucho, Cholinium-based supported ionic liquid membranes: a sustainable route for carbon dioxide separation, Chemsuschem 7 (1) (2014) 110–113.

[111] L.A. Neves, C. Afonso, I.M. Coelhoso, J.G. Crespo, Integrated CO_2 capture and enzymatic bioconversion in supported ionic liquid membranes, Sep. Purif. Technol. 97 (2012) 34–41.

[112] S. Hanioka, T. Maruyama, T. Sotani, M. Teramoto, H. Matsuyama, K. Nakashima, M. Hanaki, F. Kubota, M. Goto, $CO(2)$ separation facilitated by task-specific ionic liquids using a supported liquid membrane, J. Membr. Sci. 314 (1–2) (2008) 1–4.

[113] A.S. Kovvali, H. Chen, K.K. Sirkar, Dendrimer membranes: a CO_2-selective molecular gate, J. Am. Chem. Soc. 122 (31) (2000) 7594–7595.

[114] G.N. Wang, W.L. Hou, F. Xiao, J.A. Geng, Y.T. Wu, Z.B. Zhang, Low-viscosity triethylbutylammonium acetate as a task-specific ionic liquid for reversible CO_2 absorption, J. Chem. Eng. Data 56 (4) (2011) 1125–1133.

[115] A. Yokozeki, M.B. Shiflett, C.P. Junk, L.M. Grieco, T. Foo, Physical and chemical absorptions of carbon dioxide in room-temperature ionic liquids, J. Phys. Chem. B 112 (51) (2008) 16654–16663.

[116] W. Shi, C.R. Myers, D.R. Luebke, J.A. Steckel, D.C. Sorescu, Theoretical and experimental studies of CO_2 and H_2 separation using the 1-Ethyl-3-methylimidazolium acetate ([emim][CH_3COO]) ionic liquid, J. Phys. Chem. B 116 (1) (2012) 283–295.

[117] S.D. Hojniak, I.P. Silverwood, A.L. Khan, I.F.J. Vankelecom, W. Dehaen, S. G. Kazarian, K. Binnemans, Highly selective separation of carbon dioxide from nitrogen and methane by nitrile/glycol-difunctionalized ionic liquids in supported ionic liquid membranes (SILMs), J. Phys. Chem. B 118 (26) (2014) 7440–7449.

[118] M.Z. Xiangjun Sun, Ruiqian Guo, Jujie Luo, Jinping Li, CO_2-facilitated transport performance of poly(ionic liquids) in supported liquid membranes, J. Mater. Sci. 50 (2015) 104–111.

[119] W. Zhao, G.H. He, F. Nie, L.L. Zhang, H.C. Feng, H.J. Liu, Membrane liquid loss mechanism of supported ionic liquid membrane for gas separation, J. Membr. Sci. 411 (2012) 73–80.

[120] D. Mecerreyes, Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes, Progress Polym. Sci. 36 (12) (2011) 1629–1648.

[121] J.B. Tang, M. Radosz, Y.Q. Shen, Poly(ionic liquid)s as optically transparent microwave-absorbing materials, Macromolecules 41 (2) (2008) 493–496.

[122] J.B. Tang, W.L. Sun, H.D. Tang, M. Radosz, Y.Q. Shen, Enhanced CO_2 absorption of poly(ionic liquid)s, Macromolecules 38 (6) (2005) 2037–2039.

[123] J.B. Tang, H.D. Tang, W.L. Sun, H. Plancher, M. Radosz, Y.Q. Shen, Poly(ionic liquid)s: a new material with enhanced and fast CO_2 absorption, Chem. Commun. 26 (2005) 3325–3327.

[124] J.B. Tang, H.D. Tang, W.L. Sun, M. Radosz, Y.Q. Shen, Low-pressure CO_2 sorption in ammonium-based poly(ionic liquid)s, Polymer 46 (26) (2005) 12460–12467.

[125] H.D. Tang, J.B. Tang, S.J. Ding, M. Radosz, Y.Q. Shen, Atom transfer radical polymerization of styrenic ionic liquid monomers and carbon dioxide absorption of the polymerized ionic liquids, J. Polym. Sci. Part A-Polym. Chem. 43 (7) (2005) 1432–1443.

[126] J.B. Tang, Y.Q. Shen, M. Radosz, W.L. Sun, Isothermal carbon dioxide sorption in poly(ionic liquid)s, Ind. Eng. Chem. Res. 48 (20) (2009) 9113–9118.

[127] A. Wilke, J.Y. Yuan, M. Antonietti, J. Weber, Enhanced carbon dioxide adsorption by a mesoporous poly(ionic liquid), ACS Macro Lett. 1 (8) (2012) 1028–1031.

[128] X.D. Hu, J.B. Tang, A. Blasig, Y.Q. Shen, M. Radosz, CO_2 permeability, diffusivity and solubility in polyethylene glycol-grafted polyionic membranes and their CO_2 selectivity relative to methane and nitrogen, J. Membr. Sci. 281 (1–2) (2006) 130–138.

[129] J.Y. Yuan, M. Antonietti, Poly(ionic liquid)s: polymers expanding classical property profiles, Polymer 52 (7) (2011) 1469–1482.

[130] J.E. Bara, S. Lessmann, C.J. Gabriel, E.S. Hatakeyama, R.D. Noble, D.L. Gin, Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes, Ind. Eng. Chem. Res. 46 (16) (2007) 5397–5404.

[131] J.E. Bara, C.J. Gabriel, E.S. Hatakeyama, T.K. Carlisle, S. Lessmann, R.D. Noble, D. L. Gin, Improving CO_2 selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents, J. Membr. Sci. 321 (1) (2008) 3–7.

[132] T.K. Carlisle, J.E. Bara, A.L. Lafrate, D.L. Gin, R.D. Noble, Main-chain imidazolium polymer membranes for CO_2 separations: An initial study of a new ionic liquid-inspired platform, J. Membr. Sci. 359 (1–2) (2010) 37–43.

[133] T.K. Carlisle, E.F. Wiesenauer, G.D. Nicodemus, D.L. Gin, R.D. Noble, Ideal CO_2/light gas separation performance of poly(vinylimidazolium) membranes and poly(vinylimidazolium)-ionic liquid composite films, Indus. Eng. Chem. Res. 52 (3) (2013) 1023–1032.

[134] J.E. Bara, E.S. Hatakeyama, C.J. Gabriel, X.H. Zeng, S. Lessmann, D.L. Gin, R. D. Noble, Synthesis and light gas separations in cross-linked gemini room temperature ionic liquid polymer membranes, J. Membr. Sci. 316 (1–2) (2008) 186–191.

[135] K. Simons, K. Nijmeijer, J.E. Bara, R.D. Noble, M. Wessling, How do polymerized room-temperature ionic liquid membranes plasticize during high pressure CO_2 permeation? J. Membr. Sci. 360 (1–2) (2010) 202–209.

[136] S.C. Kumbharkar, R.S. Bhavsar, U.K. Kharul, Film forming polymeric ionic liquids (PILs) based on polybenzimidazoles for CO_2 separation, RSC Adv. 4 (9) (2014) 4500–4503.

[137] R.S. Bhavsar, S.C. Kumbharkar, U.K. Kharul, Investigation of gas permeation properties of film forming polymeric ionic liquids (PILs) based on polybenzimidazoles, J. Membr. Sci. 470 (2014) 494–503.

[138] R.S. Bhavsar, S.C. Kumbharkar, A.S. Rewar, U.K. Kharul, Polybenzimidazole based film forming polymeric ionic liquids: synthesis and effects of cation-anion variation on their physical properties, Polym. Chem. 5 (13) (2014) 4083–4096.

[139] T. Sakaguchi, H. Ito, T. Masuda, T. Hashimoto, Highly CO_2-permeable and -permselective poly(diphenylacetylene)s having imidazolium salts: synthesis, characterization, gas permeation properties, and effects of counter anion, Polymer 54 (25) (2013) 6709–6715.

[140] L.C. Tome, M.A. Aboudzadeh, L.P.N. Rebelo, C.S.R. Freire, D. Mecerreyes, I. M. Marrucho, Polymeric ionic liquids with mixtures of counter-anions: a new straightforward strategy for designing pyrrolidinium-based CO_2 separation membranes, J. Mater. Chem. A 1 (35) (2013) 10403–10411.

[141] H.L. Cong, B. Yu, J.G. Tang, X.S. Zhao, Ionic liquid modified poly(2,6-dimethyl-1,4-phenylene oxide) for CO_2 separation, J. Polym. Res. 19 (2012) 2.

[142] P. Li, Q.C. Zhao, J.L. Anderson, S. Varanasi, M.R. Coleman, Synthesis of copolyimides based on room temperature ionic liquid diamines, J. Polym. Sci. Part A – polymer chemistry 48 (18) (2010) 4036–4046.

[143] P. Li, M.R. Coleman, Synthesis of room temperature ionic liquids based random copolyimides for gas separation applications, Eur. Polym. J. 49 (2) (2013) 482–491.

[144] Y.Y. Gu, T.P. Lodge, Synthesis and gas separation performance of triblock copolymer ion gels with a polymerized ionic liquid mid-block, Macromolecules 44 (7) (2011) 1732–1736.

[145] P.T. Nguyen, E.F. Wiesenauer, D.L. Gin, R.D. Noble, Effect of composition and nanostructure on CO_2/N_2 transport properties of supported alkyl-imidazolium block copolymer membranes, J. Membr. Sci. 430 (2013) 312–320.

[146] B.J. Adzima, S.R. Venna, S.S. Klara, H.K. He, M.J. Zhong, D.R. Luebke, M. S. Mauter, K. Matyjaszewski, H.B. Nulwala, Modular polymerized ionic liquid block copolymer membranes for CO_2/N_2 separation, J. Mater. Chem. A 2 (21) (2014) 7967–7972.

[147] E.F. Wiesenauer, P.T. Nguyen, B.S. Newell, T.S. Bailey, R.D. Nobleb, D.L. Gin, Imidazolium-containing, hydrophobic-ionic-hydrophilic ABC triblock copolymers: synthesis, ordered phase-separation, and supported membrane fabrication, Soft Matter 9 (33) (2013) 7923–7927.

[148] W.S. Chi, S.U. Hong, B. Jung, S.W. Kang, Y.S. Kang, J.H. Kim, Synthesis, structure and gas permeation of polymerized ionic liquid graft copolymer membranes, J. Membr. Sci. 443 (2013) 54–61.

[149] I. Kammakakam, H.W. Kim, S. Nam, H.B. Park, T.H. Kim, Alkyl imidazolium-functionalized cardo-based poly(ether ketone)s as novel polymer membranes for O_2/N_2 and CO_2/N_2 separations, Polymer 54 (14) (2013) 3534–3541.

[150] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (1–2) (2008) 390–400.

[151] M. Hammann, D. Castillo, C. Anger, B. Rieger, Highly selective CO_2 separation membranes through tunable poly(4-vinylphenolate)-CO_2 interactions, J. Mater. Chem. A 2 (39) (2014) 16389–16396.

[152] A. Luca, R.N. Jacob, Y. Yuesheng, A.E. Yossef, G. Marco Baschetti, Influence of water vapor on the gas permeability of polymerized ionic liquids

membranes, J. Membr. Sci. 487 (2015) 199–208 10.1016/j.memsci.2015.03.065.

[153] J.E. Bara, E.S. Hatakeyama, D.L. Gin, R.D. Noble, Improving CO₂ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid, Polym. Adv. Technol. 19 (10) (2008) 1415–1420.

[154] T.P. Lodge, Materials science – a unique platform for materials design, Science 321 (5885) (2008) 50–51.

[155] A.L. Miller, T.K. Carlisle, A.L. LaFrate, B.A. Voss, J.E. Bara, Y.C. Hudiono, B. R. Wiesenauer, D.L. Gin, R.D. Noble, Design of functionalized room-temperature ionic liquid-based materials for CO₂ separations and selective blocking of hazardous chemical vapors, Sep. Sci. Technol. 47 (2) (2012) 169–177.

[156] J.E. Bara, D.L. Gin, R.D. Noble, Effect of anion on gas separation performance of polymer-room-temperature ionic liquid composite membranes, Ind. Eng. Chem. Res. 47 (24) (2008) 9919–9924.

[157] J.E. Bara, R.D. Noble, D.L. Gin, Effect of "free" cation substituent on gas separation performance of polymer-room-temperature ionic liquid composite membranes, Ind. Eng. Chem. Res. 48 (9) (2009) 4607–4610.

[158] P. Li, K.P. Pramoda, T.S. Chung, CO₂ separation from flue gas using polyvinyl-(room temperature ionic liquid)-room temperature ionic liquid composite membranes, Ind. Eng. Chem. Res. 50 (15) (2011) 9344–9353.

[159] P. Li, D.R. Paul, T.S. Chung, High performance membranes based on ionic liquid polymers for CO₂ separation from the flue gas, Green Chem. 14 (4) (2012) 1052–1063.

[160] T.K. Carlisle, G.D. Nicodemus, D.L. Gin, R.D. Noble, CO₂/light gas separation performance of cross-linked poly(vinylimidazolium) gel membranes as a function of ionic liquid loading and cross-linker content, J. Membr. Sci. 397 (2012) 24–37.

[161] W.M. McDaniel, M.G. Cowan, T.K. Carlisle, A.K. Swanson, R.D. Noble, D.L. Gin, Cross-linked ionic resins and gels from epoxide-functionalized imidazolium ionic liquid monomers, Polymer 55 (16) (2014) 3305–3313.

[162] J.S. Zhou, M.M. Mok, M.G. Cowan, W.M. McDaniel, T.K. Carlisle, D.L. Gin, R. D. Noble, High-permeance room-temperature ionic-liquid-based membranes for CO₂/N₂ separation, Ind. Eng. Chem. Res. 53 (51) (2014) 20064–20067.

[163] B.A. Voss, J.E. Bara, D.L. Gin, R.D. Noble, Physically gelled ionic liquids: solid membrane materials with liquidlike CO₂ gas transport, Chem. Mater. 21 (14) (2009) 3027–3029.

[164] P.T. Nguyen, B.A. Voss, E.F. Wiesenauer, D.L. Gin, R.D. Nobe, Physically gelled room-temperature ionic liquid-based composite membranes for CO₂/N₂ separation: effect of composition and thickness on membrane properties and performance, Ind. Eng. Chem. Res. 52 (26) (2013) 8812–8821.

[165] R.M. Couto, T. Carvalho, L.A. Neves, R.M. Ruivo, P. Vidinha, A. Paiva, I. M. Coelhoso, S. Barreiros, P.C. Simoes, Development of Ion-Jelly (R) membranes, Sep. Purif. Technol. 106 (2013) 22–31.

[166] L.M. Robeson, B.D. Freeman, D.R. Paul, B.W. Rowe, An empirical correlation of gas permeability and permselectivity in polymers and its theoretical basis, J. Membr. Sci. 341 (1–2) (2009) 178–185.

[167] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, J. Membr. Sci. 62 (2) (1991) 165–185.

[168] H.Z. Chen, P. Li, T.S. Chung, PVDF/ionic liquid polymer blends with superior separation performance for removing CO₂ from hydrogen and flue gas, Int. J. Hydrog. Energy 37 (16) (2012) 11796–11804.

[169] S.U. Hong, D. Park, Y. Ko, I. Baek, Polymer-ionic liquid gels for enhanced gas transport, Chem. Commun. 46 (2009) 7227–7229.

[170] J.C. Jansen, G. Clarizia, P. Bernardo, F. Bazzarelli, K. Friess, A. Randova, J. Schauer, D. Kubicka, M. Kacirkova, P. Izak, Gas transport properties and pervaporation performance of fluoropolymer gel membranes based on pure and mixed ionic liquids, Sep. Purif. Technol. 109 (2013) 87–97.

[171] K. Friess, J.C. Jansen, F. Bazzarelli, P. Izak, V. Jarmarova, M. Kacirkova, J. Schauer, G. Clarizia, P. Bernardo, High ionic liquid content polymeric gel membranes: Correlation of membrane structure with gas and vapour transport properties, J. Membr. Sci. 415 (2012) 801–809.

[172] J.C. Jansen, K. Friess, G. Clarizia, J. Schauer, P. Izak, High ionic liquid content polymeric gel membranes: preparation and performance, Macromolecules 44 (1) (2011) 39–45.

[173] L.Z. Liang, Q. Gan, P. Nancarrow, Composite ionic liquid and polymer membranes for gas separation at elevated temperatures, J. Membr. Sci. 450 (2014) 407–417.

[174] S. Kanehashi, M. Kishida, T. Kidesaki, R. Shindo, S. Sato, T. Miyakoshi, K. Nagai, CO₂ separation properties of a glassy aromatic polyimide composite membranes containing high-content 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid, J. Membr. Sci. 430 (2013) 211–222.

[175] P. Bernardo, J.C. Jansen, F. Bazzarelli, F. Tasselli, A. Fuoco, K. Friess, P. Izak, V. Jarmarova, M. Kacirkova, G. Clarizia, Gas transport properties of Pebax (R)/room temperature ionic liquid gel membranes, Sep. Purif. Technol. 97 (2012) 73–82.

[176] Hesamoddin Rabiee, Ali Ghadimi, Toraj Mohammadi, Gas transport properties of reverse-selective poly(ether-b-amide6)/[Emim][BF₄] gel membranes for CO₂/light gases separation, J. Membr. Sci. 476 (2014) 286–302.

[177] I.N. Yoon, S. Yoo, S.J. Park, J. Won, CO₂ separation membranes using ion gels by self-assembly of a triblock copolymer in ionic liquids, Chem. Eng. J. 172 (1) (2011) 237–242.

[178] Y.Y. Gu, E.L. Cussler, T.P. Lodge, ABA-triblock copolymer ion gels for CO₂ separation applications, J. Membr. Sci. 423 (2012) 20–26.

[179] S. Kasahara, E. Kamio, A. Yoshizumi, H. Matsuyama, Polymeric ion-gels containing an amino acid ionic liquid for facilitated CO₂transport media, Chem. Commun. 50 (23) (2014) 2996–2999.

[180] F.T. Kenta, Makino, Kei Hashimoto, Takamasa Sakai, Mitsuhiro Kanakubo, Mitsuhiro Shibayama, CO₂ separation using high-toughness ion gel with tetra-armed polymer network, Chem. Lett. 44 (2014) 17–19.

[181] P. Uchytil, J. Schauer, R. Petrychkovych, K. Setnickova, S.Y. Suen, Ionic liquid membranes for carbon dioxide-methane separation, J. Membr. Sci. 383 (1–2) (2011) 262–271.

[182] L. Liu, A. Chakma, X.S. Feng, CO₂/N₂ separation by poly(ether block amide) thin film hollow fiber composite membranes, Ind. Eng. Chem. Res. 44 (17) (2005) 6874–6882.

[183] W. Yave, A. Car, S.S. Funari, S.P. Nunes, K.V. Peinemann, CO₂-philic polymer membrane with extremely high separation performance, Macromolecules 43 (1) (2010) 326–333.

[184] W. Yave, A. Car, K.V. Peinemann, Nanostructured membrane material designed for carbon dioxide separation, J. Membr. Sci. 350 (1–2) (2010) 124–129.

[185] T.W. Pechar, M. Tsapatsis, E. Marand, R. Davis, Preparation and characterization of a glassy fluorinated polyimide zeolite-mixed matrix membrane, Desalination 146 (1–3) (2002) 3–9.

[186] T.W. Pechar, S. Kim, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong, C. J. Cornelius, Fabrication and characterization of polyimide-zeolite L mixed matrix membranes for gas separations, J. Membr. Sci. 277 (1–2) (2006) 195–202.

[187] J. Ahn, W.J. Chung, I. Pinnau, J.S. Song, N.Y. Du, G.P. Robertson, M.D. Guiver, Gas transport behavior of mixed-matrix membranes composed of silica nanoparticles in a polymer of intrinsic microporosity (PIM-1), J. Membr. Sci. 346 (2) (2010) 280–287.

[188] M.C. Ferrari, M. Galizia, M.G. De Angelis, G.C. Sarti, Gas and vapor transport in mixed matrix membranes based on amorphous teflon AF1600 and AF2400 and fumed silica, Ind. Eng. Chem. Res. 49 (23) (2010) 11920–11935.

[189] B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, Functionalized flexible MOFs as fillers in mixed matrix membranes for highly selective separation of CO₂ from CH₄ at elevated pressures, Chem. Commun. 47 (33) (2011) 9522–9524.

[190] S. Basu, A. Cano-Odena, I.F.J. Vankelecom, MOF-containing mixed-matrix membranes for CO₂/CH₄ and CO₂/N₂ binary gas mixture separations, Sep. Purif. Technol. 81 (1) (2011) 31–40.

[191] T.H. Bae, J.S. Lee, W.L. Qiu, W.J. Koros, C.W. Jones, S. Nair, A high-performance gas-separation membrane containing submicrometer-sized metal-organic framework crystals, Angew. Chem.-Int. Ed. 49 (51) (2010) 9863–9866.

[192] S. Kim, L. Chen, J.K. Johnson, E. Marand, Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: theory and experiment, J. Membr. Sci. 294 (1–2) (2007) 147–158.

[193] Y.A. Zhao, B.T. Jung, L. Ansaloni, W.S.W. Ho, Multiwalled carbon nanotube mixed matrix membranes containing amines for high pressure CO₂/H₂ separation, J. Membr. Sci. 459 (2014) 233–243.

[194] D.Q. Vu, W.J. Koros, S.J. Miller, High pressure CO₂/CH₄ separation using carbon molecular sieve hollow fiber membranes, Ind. Eng. Chem. Res. 41 (3) (2002) 367–380.

[195] G. Clarizia, C. Algieri, E. Drioli, Filler-polymer combination: a route to modify gas transport properties of a polymeric membrane, Polymer 45 (16) (2004) 5671–5681.

[196] M. Rezakazemi, A.E. Amooghin, M.M. Montazer-Rahmati, A.F. Ismail, T. Matsuura, State-of-the-art membrane based CO₂ separation using mixed matrix membranes (MMMs): an overview on current status and future directions, Progress Polym. Sci. 39 (5) (2014) 817–861.

[197] Y.C. Hudiono, T.K. Carlisle, J.E. Bara, Y.F. Zhang, D.L. Gin, R.D. Noble, A three-component mixed-matrix membrane with enhanced CO₂ separation properties based on zeolites and ionic liquid materials, J. Membr. Sci. 350 (1–2) (2010) 117–123.

[198] Y.C. Hudiono, T.K. Carlisle, A.L. LaFrate, D.L. Gin, R.D. Noble, Novel mixed matrix membranes based on polymerizable room-temperature ionic liquids and SAPO-34 particles to improve CO₂ separation, J. Membr. Sci. 370 (1–2) (2011) 141–148.

[199] R.D. Noble, Perspectives on mixed matrix membranes, J. Membr. Sci. 378 (1–2) (2011) 393–397.

[200] L. Hao, P. Li, T.X. Yang, T.S. Chung, Room temperature ionic liquid/ZIF-8 mixed-matrix membranes for natural gas sweetening and post-combustion CO₂ capture, J. Membr. Sci. 436 (2013) 221–231.

[201] Md.M.L.-G. Clara Casado-Coterillo, Ángel Irabien, Synthesis and characterisation of ETS-10/acetate-based ionic liquid/chitosan mixed matrix membranes for CO₂/N₂ permeation, Membrane 4 (2014) 287–301.

[202] Q. Zhang, E.L. Cussler, Microporous hollow fibers for gas-absorption. 1. mass-transfer in the liquid, J. Membr. Sci. 23 (3) (1985) 321–332.

[203] Q. Zhang, E.L. Cussler, Microporous hollow fibers for gas-absorption. 2. mass-transfer across the membrane, J. Membr. Sci. 23 (3) (1985) 333–345.

[204] A. Gabelman, S.T. Hwang, Hollow fiber membrane contactors, J. Membr. Sci. 159 (1–2) (1999) 61–106.

[205] J.G. Lu, L.J. Wang, X.Y. Sun, J.S. Li, X.D. Liu, Absorption of CO₂ into aqueous solutions of methyldiethanolamine and activated methyldiethanolamine from a gas mixture in a hollow fiber contactor, Ind. Eng. Chem. Res. 44 (24) (2005) 9230–9238.

[206] J.G. Lu, Y.F. Zheng, M.D. Cheng, Membrane contactor for CO₂ absorption applying amino-acid salt solutions, Desalination 249 (2) (2009) 498–502.

[207] S.H. Yeon, K.S. Lee, B. Sea, Y.I. Park, K.H. Lee, Application of pilot-scale

membrane contactor hybrid system for removal of carbon dioxide from flue gas, J. Membr. Sci. 257 (1–2) (2005) 156–160.

[208] Y.X. Lv, X.H. Yu, S.T. Tu, J.Y. Yan, E. Dahlquist, Experimental studies on simultaneous removal of CO_2 and SO_2 in a polypropylene hollow fiber membrane contactor, Appl. Energy 97 (2012) 283–288.

[209] D. Demontigny, P. Tontiwachwuthikul, A. Chakma, Using polypropylene and polytetrafluoroethylene membranes in a membrane contactor for CO_2absorption, J. Membr. Sci. 277 (1–2) (2006) 99–107.

[210] C.A. Scholes, A. Qader, G.W. Stevens, S.E. Kentish, Membrane gas-solvent contactor pilot plant trials of CO_2 absorption from flue gas, Sep. Sci. Technol. 49 (16) (2014) 2449–2458.

[211] L. Wang, Z.H. Zhang, B. Zhao, H.W. Zhang, X.L. Lu, Q. Yang, Effect of long-term operation on the performance of polypropylene and polyvinylidene fluoride membrane contactors for CO_2 absorption, Sep. Purif. Technol. 116 (2013) 300–306.

[212] A. Mansourizadeh, A.F. Ismail, A developed asymmetric PVDF hollow fiber membrane structure for CO_2absorption, Int. J. Greenh. Control 5 (2) (2011) 374–380.

[213] A. Mansourizadeh, A.F. Ismail, Preparation and characterization of porous PVDF hollow fiber membranes for CO_2 absorption: Effect of different non-solvent additives in the polymer dope, Int. J. Greenh. Control 5 (4) (2011) 640–648.

[214] C.A. Scholes, M. Simioni, A. Qader, G.W. Stevens, S.E. Kentish, Membrane gas-solvent contactor trials of CO_2 absorption from syngas, Chem. Eng. J. 195 (2012) 188–197.

[215] S. Khaisri, D. Demontigny, P. Tontiwachwuthikul, R. Jiraratananon, Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor, Sep. Purif. Technol. 65 (3) (2009) 290–297.

[216] P.T. Nguyen, E. Lasseuguette, Y. Medina-Gonzalez, J.C. Remigy, D. Roizard, E. Favre, A dense membrane contactor for intensified CO2 gas/liquid absorption in post-combustion capture, J. Membr. Sci. 377 (1–2) (2011) 261–272.

[217] S. Heile, S. Rosenberger, A. Parker, B. Jefferson, E.J. McAdam, Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO_2 separation during biogas upgrading, J. Membr. Sci. 452 (2014) 37–45.

[218] V.V. Volkov, A.V. Bildukevich, G.A. Dibrov, V.V. Usoskiy, V.P. Kasperchik, V.P. Vasilevsky, E.G. Novitsky, Elaboration of composite hollow fiber membranes with selective layer from poly[1-(trimethylsylil)1-propyne] for re-generation of aqueous alkanolamine solutions, Pet. Chem. 53 (8) (2013) 619–626.

[219] G.A. Dibrov, V.V. Volkov, V.P. Vasilevsky, A.A. Shutova, S.D. Bazhenov, V.S. Khotimsky, A.V. de Runstraat, E.L.V. Goetheer, A.V. Volkov, Robust high-permeance PTMSP composite membranes for CO_2 membrane gas desorption at elevated temperatures and pressures, J. Membr. Sci. 470 (2014) 439–450.

[220] C. Makhloufi, E. Lasseuguette, J.C. Remigy, B. Belaissaoui, D. Roizard, E. Favre, Ammonia based CO2 capture process using hollow fiber membrane contactors, J. Membr. Sci. 455 (2014) 236–246.

[221] J.L. Li, B.H. Chen, Review Of CO_2 absorption using chemical solvents in hollow fiber membrane contactors, Sep. Purif. Technol. 41 (2) (2005) 109–122.

[222] Z. Cui, D. deMontigny, Part 7: a review of CO_2 capture using hollow fiber membrane contactors, Carbon Manag. 4 (1) (2013) 69–89.

[223] A. Mansourizadeh, A.F. Ismail, Hollow fiber gas-liquid membrane contactors for acid gas capture: a review, J. Hazard. Mater. 171 (1–3) (2009) 38–53.

[224] R.W. Yuan Zhang, Gas–liquid membrane contactors for acid gas removal: recent advances and future challenges, Curr. Opin. Chem. Eng. 2 (2) (2013) 7.

[225] P. Luis, B. Van der Bruggen, T. Van Gerven, Non-dispersive absorption for CO_2 capture: from the laboratory to industry, J. Chem. Technol. Biotechnol. 86 (6) (2011) 769–775.

[226] P. Luis, A. Garea, A. Irabien, Zero solvent emission process for sulfur dioxide recovery using a membrane contactor and ionic liquids, J. Membr. Sci. 330 (1–2) (2009) 80–89.

[227] J. Albo, P. Luis, A. Irabien, Carbon dioxide capture from flue gases using a cross-flow membrane contactor and the ionic liquid 1-ethyl-3-methylimi-dazolium ethylsulfate, Ind. Eng. Chem. Res. 49 (21) (2010) 11045–11051.

[228] J. Albo, P. Luis, A. Irabien, Absorption of coal combustion flue gases in ionic liquids using different membrane contactors, Desalin. Water Treat. 27 (1–3) (2011) 54–59.

[229] J. Albo, A. Irabien, Non-dispersive absorption of CO_2 in parallel and cross-flow membrane modules using EMISE, J. Chem. Technol. Biotechnol. 87 (10) (2012) 1502–1507.

[230] J.G. Lu, C.T. Lu, Y. Chen, L. Gao, X. Zhao, H. Zhang, Z.W. Xu, CO_2 capture by membrane absorption coupling process: application of ionic liquids, Appl. Energy 115 (2014) 573–581.

[231] Z. Wang, M.X. Fang, H. Yu, Q.H. Ma, Z.Y. Luo, Modeling of CO_2 stripping in a hollow fiber membrane contactor for CO_2 capture, Energy Fuels 27 (11) (2013) 6887–6898.

[232] L. Gomez-Coma, A. Garea, A. Irabien, Non-dispersive absorption of CO_2 in [emim][EtSO4] and [emim][Ac]: temperature influence, Sep. Purif. Technol. 132 (2014) 120–125.

[233] X. Jie, J. Chau, G. Obuskovic, K.K. Sirkar, Preliminary studies of CO_2 removal from precombustion syngas through pressure swing membrane absorption process with ionic liquid as absorbent, Ind. Eng. Chem. Res. 52 (26) (2013) 8783–8799.

[234] J. Chau, G. Obuskovic, X.M. Jie, K.K. Sirkar, Pressure swing membrane absorption process for shifted syngas separation: modeling vs. experiments for pure ionic liquid, J. Membr. Sci. 453 (2014) 61–70.

[235] X.M. Jie, J. Chau, G. Obuskovic, K.K. Sirkar, Enhanced pressure swing membrane absorption process for CO_2 removal from shifted syngas with den-drimer-ionic liquid mixtures as absorbent, Ind. Eng. Chem. Res. 53 (8) (2014) 3305–3320.

[236] L. Deng, Facilitated transport membranes and membrane contactors using ionic liquids for CO_2 capture, in: Proceedings of the 3rd Asian-Pacific Conference on Ionic Liquids and Green Processes, Beijing, China, 2012.

[237] Z. Dai, M. Usman, L. Deng, Numerical modeling of membrane contactor for pre-combustion CO_2 capture, in: The International Congress on Membranes and Membrane Processes, Suzhou, China, 2014.

[238] D.E. Sanders, Z.P. Smith, R.L. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: a review, Polymer 54 (18) (2013) 4729–4761.