



Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF
ENVIRONMENTAL
SCIENCES
www.jesc.ac.cn

Review

Recent advances in ionic liquids-based hybrid processes for CO₂ capture and utilization

Shaohan Lian¹, Chunfeng Song^{1,*}, Qingling Liu¹, Erhong Duan²,
Hongwei Ren^{2,*}, Yutaka Kitamura³

¹Tianjin Key Laboratory of Indoor Air Environmental Quality Control, School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China

²Pollution Prevention Biotechnology Laboratory of Hebei Province, School of Environmental Science and Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, China

³Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8572, Japan

ARTICLE INFO

Article history:

Received 2 March 2020

Revised 22 June 2020

Accepted 28 June 2020

Available online 27 July 2020

Keywords:

CO₂

Hybrid

Ionic liquids

Absorption

Adsorption

Membrane

Catalysis

ABSTRACT

CO₂ capture and utilization (CCU) is an effective strategy to mitigate global warming. Absorption, adsorption and membranes are methods used for CO₂ separation and capture, and various catalytic pathways have also been developed for CO₂ utilization. Although widely researched and used in industry, these processes are energy-intensive and this challenge needs to be overcome. To realize further optimization, novel materials and processes are continuously being developed. New generation materials such as ionic liquids (ILs) have shown promising potential for cost-effective CO₂ capture and utilization. This study reviews the current status of ILs-based solvents, adsorbents, membranes, catalysts and their hybrid processes for CO₂ capture and utilization. The special properties of ILs are integrated into new materials through hybridization, which significantly improves the performance in the process of CCU.

© 2020 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Global warming, as a result of greenhouse gas (e.g. CO₂) emissions, has become an urgent issue that requires significant mitigation. A special report "Global warming of 1.5°C" was published by Intergovernmental Panel on Climate Change (IPCC) in 2018, and stated that global temperatures were

already 1°C above pre-industrial levels and would reach 1.5°C in 2030. This continuous increase of global temperatures will effectively lead to climate deterioration and trigger a series of ecological and social problems (Li et al., 2019; Sun et al., 2018a).

CO₂ capture and utilization (CCU) has been widely recognized as an effective pathway to mitigate greenhouse gas emissions on a global scale. Until now, a number of technologies have been developed for CCU, such as absorption,

* Corresponding authors.

E-mails: chunfeng.song@tju.edu.cn (C. Song), renhongweirhw@126.com (H. Ren).

adsorption, cryogenic, membrane separation and biofixation, etc. (Song et al., 2018). CO₂ utilization has not only the ecological benefits of mitigating the greenhouse effect, but also produces intuitive economic value. For example, production of value-added chemicals by chemical or biological catalysis reactions are effective pathways for CO₂ utilization. However, there are some challenges in existing CCU technologies that need to be overcome for commercial application, such as the energy intensity, material stability, toxicity, corrosion and secondary pollution risk (Ren et al., 2018; Song et al., 2018).

In previous decades, many novel materials have been designed and applied to improve the efficiency of the CO₂ capture and utilization processes. Ionic liquids (ILs) are considered one of the most promising materials for such purposes. ILs are a class of room temperature molten salt composed of anions and cations (Walden, 1914). Compared with other liquids, ILs have several specific advantages, such as good chemical and thermal stability, extremely low saturated vapor pressure, and a wide electrochemical window (Fukaya et al., 2007; Gao et al., 2015; Huang et al., 2006). Most importantly, ILs can exhibit intensified properties via modification by functional groups, creating opportunities to design functional and green ILs.

To improve the environmental impact and reduce the synthesis costs of ILs, a new solvent, namely deep eutectic solvents (DES), with properties similar to ILs were developed (Abbott et al., 2003). With a lower melting point, they were formed by quaternary ammonium salt and amide compounds. Compared to ILs, DES have the advantage of a simple and fast synthesis process. DES are usually produced by a one-step synthesis of two or more substances; preparation is simple and less time consuming (Ruß and König, 2012). It should be noted that the melting point of DES is generally lower than the raw material for synthesizing it, which is very similar to ILs. DES is formed by hydrogen bonding between a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). The special nature of the structure offers great potential with respect to cost-effective CCU processes.

The aim of this work is to systematically summarize the application of ILs in different CCU processes and provide a comprehensive overview, in particular the ILs hybridization technology. The combination of ILs with other technologies (namely hybrid processes) can potentially take advantage of two or more standalone methods. Through integration of absorption, adsorption, membrane separation and catalytic conversion, some current bottlenecks in CCU of traditional processes have been overcome (e.g. reducing energy consumption, increasing capture and conversion efficiency). In addition to the current status, the opportunities and challenges faced by different technologies are also discussed.

1. Ionic liquids hybrid with absorption for CO₂ capture

Despite increased diversity in the global energy mix of late, fossil fuels remain the dominant energy source. There are three measures for CO₂ reduction in fossil fuel combustion processes: pre-combustion capture, oxy-fuel combustion, and post-combustion capture (Usman et al., 2016; Zhai and

Rubin, 2018). Among them, post-combustion capture is the most widely used technology, and using solvents for CO₂ absorption is a mature method for this. Alcohol ammonia solution (such as monoethanolamine,MEA) is currently the most widely used absorbent, but still faces the challenges of high regeneration energy consumption and large solvent loss (Bates et al., 2002; Ren et al., 2018; Yunus et al., 2012). Therefore, there is an urgent need for the development of new absorbents, and a large number of potential substances have been designed. Among them, ILs are considered to be one of the most promising substitutes for traditional absorbents due to their low solvent loss and strong absorption capacity (Kanakubo et al., 2016; Valencia-Marquez et al., 2017; Zhang et al., 2016b). Based on the composition of the absorbent, the integration of ILs and absorption (namely hybrid processes) is primarily divided into two types. One method is using ILs or ILs aqueous solution as solvent directly in absorption processes, including traditional ILs and new generation ILs – deep eutectic solvents (DES). The other method is a biphasic solvent, which is a mixture of ILs and other substances. The comparison of several generations of ILs absorbents is summarised in Table 1.

1.1. Ionic liquids

1.1.1. Traditional ionic liquids

In 1999, Blanchard et al. (1999) reported that CO₂ has high solubility in [BMIM][BF₄] ILs. Subsequently, a large number of studies investigated the application possibility of ILs in CO₂ absorption processes. The properties of ILs can be adjusted by changing the functional groups (such as amino groups) of the precursor to develop "task-specific" ILs for CO₂ capture. In previous studies, ILs based on imidazole or pyridine were often used for CO₂ capture (Yunus et al., 2012). Through the physical or chemical interaction between amino functional group and CO₂, the absorption properties of the prepared ILs are not lower than the conventional MEA solution. Bates et al. (2002) proposed to prepare "task-specific" ILs for CO₂ consisting of an imidazolium ion, which has a primary amine group. The functionalized ILs designed and synthesized were exposed to CO₂ for 3 hr and the level of capture reached 0.5 mol CO₂/mol ILs, which was similar to the MEA capture performance. Based on the mechanism of CO₂ capture by interaction with amine groups, ILs containing multiple amine sites have been developed. Among them, amino acids are widely used in the preparation of ILs due to their special chemical structure (Lv et al., 2016b). Sistla and Khanna (2015) have proven that the amino acids-based ILs with multiple amine sites have shown higher CO₂ absorption capacity than the ILs with only one primary amine group. Lv et al. (2016a) achieved a CO₂ solubility of 1.23 mol CO₂/mol ILs by introducing amine groups into the anion and cation of ILs simultaneously. The choline-amino acid ILs prepared by Bhattacharyya and Shah (2016) not only had low viscosity, but also had high CO₂ solubility of up to 1.62 mol CO₂/mol ILs. The mechanism of action between the amine group and CO₂ was also confirmed by density functional theory (DFT) calculation.

Several superbases have also been introduced into the preparation of ILs, and their basicity had a positive effect on CO₂ capture. Zhu et al. (2017) developed a new class of ILs con-

Table 1 – Comparison of several generations of CO₂ absorbents.

Absorbents	Advantages	Disadvantages	References
MEA	Low price	High volatility, corrosion, high energy consumption	Zhang et al., 2016b
Ils	Non-volatile, low corrosion, high solubility	Bio-toxicity, high price, high viscosity	Elhamarnah et al., 2019; Sarmad et al., 2017; Sistla and Khanna, 2015
DES	Non-volatile, low corrosion, high solubility, non-toxicity, low price, biodegradable nature	High viscosity	Huang et al., 2017; Ren et al., 2019; Zhang et al., 2018b
Biphasic solvents	Low energy consumption, low viscosity	Complex equipment	Hasib-ur-Rahman et al., 2012

MEA: monoethanolamine; Ils: ionicliquids; DES: deep eutectic solvents.

taining 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as a cation and substituted imidazole as anions. The addition of superbases makes the absorption capacity of ILs to CO₂ reach 1 mol CO₂/mol ILs. Xu (2017) demonstrated that the increase in the ability of ILs to absorb CO₂ is attributed to the strong alkalinity of DBU based ILs.

In addition to the influence of functional groups, the alkyl chain length and the anions also have a significant impact on the CO₂ absorption performance of ILs. Research results of Aki et al. (2004) show that increasing the alkyl chain length from butyl to octyl can increase CO₂ solubility. Sharma et al. (2012a, 2012b) studied the role of anions in the capture of CO₂ in amino-functionalized ILs. The order of CO₂ absorption of ILs containing different anions was as follows: BF₄⁻ < DCA⁻ < PF₆⁻ < TfO⁻ < Tf₂N⁻. Huang et al. (2018c) achieved a CO₂ absorption molar ratio of more than 2 by introducing anions at multiple reaction sites.

As a potential alternative to traditional organic alcohol ammonia solutions for CO₂ capture, cost control is a key concern. To explore the economic value and feasibility of ILs as an absorbent, Ma et al. (2018) investigated the difference of CO₂ capture and storage processes for flue gas from a power plant between an ILs-based process and a MEA-based process. The conclusions from the simulation showed that the ILs-based process was more economical for the entire process of CO₂ capture and storage, saving 30.01% on energy consumption and 29.99% in primary cost. Ma et al. (2017a) have also proved that the energy consumption in 1-butyl-3-methyl imidazolium trifluoroborate ([Bmim][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) based processes were lowered by 26.7% and 24.8% respectively than that in MEA-based processes. de Rivaet al. (2017) reduced the energy consumption of the ILs CO₂ capture process to 1.4 GJ/ton CO₂ through process optimization. The comparison of solubility and energy consumption in different ILs with aqueous ammonia or MEA CO₂ capture processes is listed in Table 2.

The use of ILs as a substitute for common absorbents in the CO₂ absorption process has significant advantages. The problem of solvent loss has been effectively solved due to the nature of the solvent itself. Furthermore, the cost control during flue gas capture is also very optimistic (Zhang et al., 2016b). However, there are still several problems that ILs need to overcome before large-scale commercialization of CO₂ capture can be achieved. Amino-functionalized ILs generally have a higher viscosity, resulting in a longer absorption process (Bhattacharyya and Shah, 2016; Zhang et al., 2020). Although

the high viscosity of ILs can be solved by increasing the water content (Navarro et al., 2019; Ziobrowski and Rotkegel, 2017), it will inevitably increase the volume accordingly. The cumbersome complexity of the preparation process also greatly limits large-scale applications. There is another problem that also cannot be ignored. Although the amino acid is used as a component of ILs to replace toxic substances such as imidazole, ILs can be considered as a green material to a certain extent, but the preparation process is still not sufficiently green.

1.1.2. Deep eutectic solvents

In order to overcome the problems encountered when ILs are applied for CO₂ capture, researchers developed DES for further optimization. Generally speaking, the raw materials used to synthesize DES exhibit desirable properties, such as biocompatibility, low-price, biodegradability, recyclability, non-toxicity (Liu et al., 2018a; Lv et al., 2016a; Sistla and Khanna, 2015). DES are considered economical alternatives to common ILs since they can be prepared simply with high-purity and cheap raw materials at a large-scale (Huang et al., 2017; Liu et al., 2017; Sze et al., 2014; Trivedi et al., 2016). When the compounds that constitute the DES are primary metabolites, namely, amino acids, organic acids, sugars, or choline derivatives, the DES are called natural deep eutectic solvents (NADES) (Paiva et al., 2014).

Originally, the raw material used to synthesize DES was choline chloride (ChCl) with other substances (Abbott et al., 2004; Chemat et al., 2016; Figueiredo et al., 2009; Leron et al., 2013; Leron and Li, 2013a, 2013b; Lin et al., 2014; Zhang et al., 2015). Dozens of combinations have been tried, and the ability of synthetic DES to capture CO₂ has been confirmed to be comparable to ILs, slightly higher than the normal absorption of MEA. It is worth mentioning that DES and ILs capture CO₂ by hydrogen bonding instead of alkaline, so the corrosion of metal containers is also much less than MEA (Ullah et al., 2015). In order to solve the problem of high viscosity, many DES based on hydrophilic polyols with a substance containing more nitrogen groups were synthesized. Ren et al. (2018) used L-arginine and glycerol to prepare hydrophilic NADES with strong ability to capture CO₂. The raw materials are completely biodegradable and can be consumed by humans. On the other hand, by preparing hydrates, the viscosity of the system is greatly reduced without loss of absorption capacity. The hydroxyl group of the polyol in DES is considered to be associated with the CO₂ reaction. The work of Cui shows that when hydroxyl of glycol and azide anions are present in DES simul-

Table 2 – Comparison of solubility and energy consumption in different capture processes.

Solvents	CO ₂ solubility (mol CO ₂ /mol solvents)	Energy consumption (GJ/ton CO ₂)	References
MEA	0.5	4.195	Oh et al., 2016; Zhang et al., 2016b
Aqueous ammonia	0.45	4.07	Yu and Wang, 2015
[Bmim][BF ₄]	0.444	2.63	Ma et al., 2017a
[Bmim][PF ₆]	0.513	2.70	Ma et al., 2017a
[Bmim][Ac]	0.498	3.2	Haghtalab and Kheiri, 2015; Shiflett et al., 2010
[Hmpy][Tf ₂ N]	0.2	0.991	Aghaie et al., 2018; Zhang et al., 2016b
[Bmim][Tf ₂ N]	0.681	1.194	Aghaie et al., 2018; Zhang et al., 2016b

[Bmim][BF₄]: 1-butyl-3-methyl imidazolium trifluoroborate; [Bmim][PF₆]: 1-butyl-3-methyl-imidazolium hexafluorophosphate; [Bmim][Ac]: 1-butyl-3-methyl-imidazolium acetate; [Hmpy][Tf₂N]: bis((trifluoromethyl)sulfonyl)imides; [Bmim][Tf₂N]: 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imid. The above five solvents are all ILs.

Table 3 – Comparison of CO₂ solubility based on different biphasic solvents.

Solvents	Phase composition after absorbing	Capabilities	References
ILs + DEA	Solid (CO ₂ rich) + Liquid	0.5 mol CO ₂ /mol DEA	Hasib-ur-Rahman et al., 2012
ILs + DMEE	Solid (CO ₂ rich) + Liquid	1.2 mol CO ₂ /mol ILs	Zhang et al., 2016a
ILs + Ethanol	Liquid (CO ₂ rich) + Liquid	~2.3 mol CO ₂ /mol ILs	Huang et al., 2018b

DEA: diethanolamine; DMEE: dimethylaminoethoxyethanol.

Table 4 – Comparison of CO₂ capabilities of ILs based adsorbents.

Adsorbents	Capabilities (mmol/g)	References
ILs + PMMA	~1.2	Uehara et al., 2019
ILs + SBA-15	2.15	Zhang et al., 2019
ILs + MCM-41	1.84	Wan et al., 2014
ILs + Mesoporous alumina	1.2	Wan et al., 2014
ILs + MCM-41	3.9 (5 MPa)	Nkinahamira et al., 2017
ILs + Titanate nanotubes	2.46	Yuan et al., 2017

PMMA: poly(methyl methacrylate).

Table 5 – Comparison of CO₂ separation capabilities of different supporting ionic liquid membranes (SILMs).

Types of ILs	Temperature (K)	Pressure (bar)	CO ₂ permeability	α_{CO_2/CH_4}	α_{CO_2/N_2}	References
[APTMS][Ac]	298	0.45	1100 Barrer	–	39	Santos et al., 2014
[Emim][Ac]	313	0.45	1329 Barrer	–	32	Santos et al., 2014
[C ₄ mim][Tf ₂ N]	373	0.7	734 Barrer	–	36	Abdelrahim et al., 2017
[DMAPAH][TFA]	303	0.2	1500 Barrer	68	90	Zhang et al., 2017e
[Emim][B(CN) ₄]	298	0.35	2040 Barrer	–	53	Mahurin et al., 2012
[Bmim][B(CN) ₄]	298	0.35	1755 Barrer	–	40	Mahurin et al., 2012
[BMIM][BF ₄]	298	1.4	47.3 GPU	68	153	Chen et al., 2018
[Vbtma][Ac]	298	10	23 GPU	41	–	Ilyas et al., 2017
[BMIM][BF ₄]	273	1.6	260 GPU	262	529	Ying et al., 2019b

[APTMS][Ac]: 3-(trimethoxysilyl)propan-1-aminium acetate; [Emim][Ac]: 1-ethyl-3-methyl imidazolium acetate; [C₄mim][Tf₂N]: 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide; [DMAPAH][TFA]: dimethylpropylenediamine methoxyacetate; [Emim][B(CN)₄]: 3-ethyl-1,2-dimethyl-1H-imidazol-3-ium bromide; [Bmim][B(CN)₄]: 3-butyl-1-methyl-1H-imidazol-3-ium bromide; [Vbtma][Ac]: vinylbenzyl trimethylammonium acetate; α_{CO_2/CH_4} : CO₂/CH₄ selectivity; α_{CO_2/N_2} : CO₂/N₂ selectivity; 1 GPU = 10⁻⁶ cm³ (STP)/(cm²·sec·cm Hg); 1 Barrer = 10⁻¹⁰ cm³ (STP)·cm·cm²/(sec·cm Hg).

taneously, CO₂ tends to react with hydroxyl groups to form carbonates rather than react with azide anions to form carbamates (Cui et al., 2019).

The use of DES to capture CO₂ is a relatively new concept compared to ILs, and many aspects of research remain at a theoretical stage. Yet, it still provides a promising approach to large-scale CO₂ capture.

1.2. ILs based biphasic solvents

ILs biphasic solvents are also considered a promising method for CO₂ capture. These solvents are typically composed of two or more solvents by hybridization. In the process of absorbing CO₂, the absorption liquid will have a distinct CO₂-poor phase and a CO₂-rich phase separation. Therefore, in the sol-

Table 6 – Comparison of gas separation capabilities of different poly ionic liquid membranes (PILMs).

Types of ILs	Temperature (K)	Pressure (bar)	CO ₂ permeability (Barrer)	α_{CO_2/CH_4}	α_{CO_2/N_2}	References
[P ₈₈₈ VB][Tf ₂ N]	298	—	186	—	15	Cowan et al., 2016
[Bmpy][TFSI]	298	1	11.8	—	35	Vollas et al., 2018
[C ₂ py][Tf ₂ N]	293	1	20	25	20	Tomé et al., 2015
[Voim][PF ₆]	293	1.2	18	—	70	Zhang et al., 2017a

[P₈₈₈VB][Tf₂N]: poly([(tri-8-alkyl)vinylbenzylphosphonium][bis(trifluoromethylsulfonyl)imide]); [Bmpy][TFSI]: 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonate)imide; [C₂py][Tf₂N]: 1-ethylpyridinium bis[(trifluoromethyl)sulfonyl]imide; [Voim][PF₆]: 1-vinyl-3-octylimidazolium hexafluorophosphate.

Table 7 – Comparison of gas separation capabilities of different mixed matrix membranes (MMMs).

Types of ILs in MMMs	Temperature (K)	Pressure (bar)	CO ₂ permeability	α_{CO_2/CH_4}	α_{CO_2/N_2}	References
[Bmim][BF ₄]	308	1	153 Barrer	—	64	Dai et al., 2019
[Emim][Tf ₂ N]	308	3.5	694 Barrer	12	20	Hao et al., 2013
[Emim][B(CN) ₄]	308	3.5	1062 Barrer	12	24	Hao et al., 2013
[Emim][BF ₄]	308	3.5	340 Barrer	17	29	Hao et al., 2013
[Emim][Tf ₂ N]	298	4	—	37.23	—	Nasir et al., 2018
[APMIm][Br]	298	4	900 GPU	—	45	Huang et al., 2018a
[Emim][Tf ₂ N]	298	3.75	7.24 GPU	20	19	Ahmad et al., 2017

[Emim][Tf₂N]: 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonate) amide; [APMIm][Br]: 1-(3-aminopropyl)-3-methylimidazolium bromide.

Table 8 – Comparison of the yield of ILs directly as a catalyst for catalytic cycloaddition.

ILs	Substrates	Yield (%)	References
[P ₄₄₄₄][bzim]	Propylene oxide	98.0	Goodrich et al., 2017
[N ₄₄₄₄][bzim]	Propylene oxide	80.0	Goodrich et al., 2017
[Urea-Im]I	Propylene oxide	97.0	Liu et al., 2016b
[Hmim]I	Propylene oxide	74.0	Liu et al., 2016b
[(HOCH ₂ CH ₂) ₃ NH]I	Propylene oxide	91.0	Liu et al., 2016a
[(HOCH ₂ CH ₂) ₃ NH]I	1,2-Epoxybutane	96.0	Liu et al., 2016a
PS-ImHI	Propylene oxide	98.1	Zhang et al., 2017b
PS-ImHI	Glycidyl phenyl ether	94.4	Zhang et al., 2017b
DEPzI	Propylene oxide	96.1	Ma et al., 2017b
DamPzI	Propylene oxide	89.9	Ma et al., 2017b
[TMTC ₂ H ₄ COOH]Br	Propylene oxide	99.0	Dai et al., 2017
[TMTC ₃ H ₆ OH]Br	Propylene oxide	98.0	Dai et al., 2017
DBPILs	Epichlorohydrin	92.0	Meng et al., 2019
[TMTC ₃ H ₆ OH]Br	1,2-Epoxybutane	99.2	Dai et al., 2017

[P₄₄₄₄][bzim]: tetrabutylphosphonium benzimidazolate; [N₄₄₄₄][bzim]: tetrabutylammonium benzimidazolate; [Urea-Im]I: urea derivative-based ionic liquids; [Hmim]I: 1-methylimidazolium iodide; PS-ImHI: immobilized imidazolium hydroiodide; DEPzI: 1,2-diethylpyrazolium iodide; DAmPzI: 1,2-diamylpyrazolium iodide; [TMTC₂H₄COOH]Br: [(CH₃NCH₃)₂CS(CH₂)₂COOH]Br; [TMTC₃H₆OH]Br: [(CH₃NCH₃)₂CS(CH₂)₃OH]Br; DBPILs: 1,8-diazabicyclo[5.4.0]undec-7-ene based bifunctional protic ionic liquids.

Table 9 – Performance comparison of ILs modified catalysts.

ILs	Catalysts	Substrates	Yield (%)	References
[HO ₂ CEtMlm]Cl	MIL-101-NH ₂	Propylene oxide	91.0	Wang et al., 2018
HEIMBr	Graphene oxide	Propylene oxide	99.0	Lan et al., 2018
Imidazolium-based	UiO-67	Epichlorohydrin	99.0	Ding et al., 2017
HPIL	EGDMA	Propylene oxide	99.5	Dai et al., 2016a
[2-Aemim][Br]	MIL-101-SO ₃ H	Epichlorohydrin	98	Sun et al., 2018b
TRILs	SBA-15	Propylene oxide	99	Cheng et al., 2013
TRILs	SBA-15	Epoxy ethane	99	Cheng et al., 2013

[HO₂CEtMlm]Cl: 1-carboxyethyl-3-methylimidazolium chloride; HEIMBr: 1-(2-hydroxyl-ethyl)-imidazolium-based ionic liquid; HPIL: hydroxyl-functionalized phosphonium-based ionic liquid; TRILs: 1,2,4-triazolium-based ionic liquids; EGDMA: ethylene glycol dimethacrylate.

vent regeneration process, only the CO₂-rich phase needs to be desorbed, which significantly reduces the energy consumption for regeneration.

The combination of alkanolamine and ILs is a typical phase change solvent (Iliuta et al., 2014). Hasib-ur-Rahman et al. (2012) used solvents composed of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide based ILs and diethanolamine (DEA) for CO₂ capture, and found that a distinct solid phase appeared in the absorption liquid after absorption of CO₂. DEA reacts with CO₂ to form a carbonate, which makes for easier separation of the two phases. Zhang et al. (2016a) designed a new solvent consisting of tetramethylammonium glycinate ([N₁₁₁₁][Gly]) and dimethylaminoethoxyethanol (DMEE), and also observed the appearance of solid-liquid two phases.

Huang et al. (2018a) prepared a highly efficient CO₂ phase separation solvent by simply blending amino functionalized ILs with water and ethanol. By adjusting the ratio of the three substances, the solvent separated into two phases after absorbing CO₂. The volume of the CO₂-rich phase was 1/3, and the loading of the CO₂-rich phase contributed to approximately 93% of the total solvent.

2. Ionic liquids hybrid with adsorption for CO₂ capture

As a common CO₂ capture technology, adsorption has some obvious advantages and disadvantages: (1) The adsorbent is easier to regenerate and consumes less energy than the absorbing liquid; (2) Hybridizing ILs with adsorbents can reduce the amount of ILs used and reduce costs; (3) When ILs hybridize with the adsorbent, it loses fluidity and avoids the disadvantage of the high viscosity of ILs; (4) The high affinity of ILs for CO₂ has the potential to enhance the performance of the adsorbent.

Generally speaking, there are two types of ILs hybrid adsorbents. One method is to introduce ILs into the adsorbent by impregnation. Uehara et al. (2019) prepared a CO₂ adsorbent by impregnation method through amino acid ILs 1-ethyl-3-methylimidazolium lysine ([EMIM][Lys]) hybrid porous silica material, which solved the gas mass transfer problem caused by large viscosity, the CO₂ capture capacities of ILs-impregnated (50 wt.%) poly(methyl methacrylate) (PMMA) was up to 1.2 mmol/g. Zhang et al. (2019) also introduced ILs into mesoporous silica by impregnation and revealed the interaction between CO₂ and ILs on the adsorbent by DFT calculation, indicating that the secondary amine group played an important role. Wan et al. (2014) prepared a series of CO₂ adsorbents based on different mesoporous materials by the impregnation method, MCM/ILs showed the best adsorption capacity (1.84 mmol/g). They proposed that the electrostatic interaction between mesoporous materials and ILs had a significant effect on the adsorption process. Cheng et al. (2016) loaded ILs onto molecular sieves by an impregnation method and compared the adsorption performance with unsupported ILs, proving that hybridization had significant advantages.

The second method is to attach ILs to the adsorbent by grafting. Nkinahamira et al. (2017) found that grafting qua-

ternary ammonium salt-based ILs onto the mesoporous material MCM-41 resulted in the loss of pores and reduced the amount of adsorption, but the presence of ILs significantly increased the adsorption selectivity. Similar trends have also been obtained by Zhu et al. (2014), who indicated that grafting produces good retention for ILs, which allows ILs to have a stable function as selective membranes during the adsorption process. Yuan et al. (2017) grafted amine-functionalized ILs to titanate nanotubes, demonstrating the improvement in adsorption performance of hybridization (up to 2.46 mmol/g).

Preparation of ILs into solid materials can also be used for CO₂ adsorption. Soll et al. (2013) prepared mesoporous adsorption materials for CO₂ adsorption through self-complexation of ILs, and proposed that the adsorption process occurs on the surface of the material and inside the copolymer matrix material. Ran et al. (2017) prepared solid poly-ILs by free radical polymerization for CO₂ adsorption, which has better adsorption performance than monomer ILs.

3. Ionic liquids hybrid with membranes for CO₂ capture

Membranes are a relatively mature separation technology and are widely used in CO₂ separation for flue gases and biogas purification. Permeability and selectivity are two critical and mutually antagonistic factors in membrane separation (Tomé and Marrucho, 2016). Generally speaking, there is a trade-off effect on the selectivity and permeability of the membrane. Therefore, much research focuses on the development of new materials or modifying membrane materials to improve selectivity under the premise of ensuring permeability for surpassing Robeson's upper-bound (Robeson, 2008).

Although ILs are significantly superior to traditional amine solutions in terms of CO₂ solubility, the disadvantages of high viscosity and slow mass transfer are difficult to overcome. It is evident that ILs can selectively absorb CO₂ from N₂ or CH₄ due to its affinity with CO₂ molecules (Anderson et al., 2007; Anthony et al., 2002), which gives potential for preparing CO₂ separation membranes going forward (Dai et al., 2016b). There are several advantages to hybridizing ILs to membranes. (1) Due to the selective absorption of CO₂ by ILs, the selectivity of membrane materials will be significantly improved. (2) The function of ILs is no longer to store CO₂ after absorption, but to diffuse it to the other side. Thus, the amount of ILs used in the whole process is greatly reduced, which solves the problem of complicated and expensive ILs preparation to some extent. (3) The membrane material is generally thin, and the concentration difference of the solute acts as a driving force for CO₂ transfer, so the disadvantage of slow diffusion of CO₂ in ILs is masked. As per existing forms of ILs in membrane materials, there are three types of hybridization patterns between ILs and membranes: (1) ILs are supported by inorganic materials; (2) Self-polymerized or mixed with polymers formed by self-polymerization; (3) Blended with other inorganic or organic phases. This section reviews the three types of ILs hybrid membranes mentioned.

3.1. Supported ionic liquid membrane

The supporting ionic liquid membrane (SILM) is a membrane technology that covers the ILs onto the solid support layer (such as anodized aluminum membrane, polycarbonate membrane, polyacrylonitrile membrane) to achieve gas separation. The separation process by ILs is roughly divided into three steps. In the first step, the gas molecules are absorbed by the surface layer of the liquid on the gas side. Secondly, the captured gas molecules diffuse inside the liquid layer to the other side under the action of a concentration gradient. Finally, the gas is desorbed on the side close to the support layer, passing through the pores of the support layer to the other side of the SLM. Not only are the capture and desorption achieved at the same time, but the solvent usage is also greatly reduced. For this reason, SILM is expected to have good application prospects.

Compared to ordinary liquid support membranes, the special properties of the ILs make them more suitable for the preparation of membrane materials. ILs have almost all non-volatile properties, meaning SILM has no problems related to shortened service life due to solvent volatilization as in ordinary SLM membranes. In addition, higher viscous activation energy, larger molecular volume, and complex hydrogen bonding networks make ILs more difficult to push into the pores of the support. The thermal stability of ILs are generally very good, providing the possibility to increase the operating temperature of the SILM (Mohammadi et al., 2018). The hybridization gives SILM potential in high temperature flue gas CO₂ separation processes (Raeissi and Peters, 2009).

In the SILM preparation process, ILs are typically not covered on the support, porous materials act as additives to form a selective layer with ILs. This combination not only helps the membrane separation performance, but also plays a role in fixing ILs. Doping porous materials in ILs can significantly improve the permeability of SILM. Karunakaran et al. (2017) prepared ultrathin membranes based on [EMIM][BF₄] ILs and graphene oxide for CO₂/N₂ separation, which surpassed the Robeson's upper bound. The most critical step in the preparation of the support membrane is to immobilize the ILs into the pores. There are two ways to implement this process. The first is to drop the ILs onto the surface of the membrane under vacuum filtration (Santos et al., 2014); the other is to autoclave the membrane with the surface covered by ILs (Ilyas et al., 2017). Ilyas et al. (2017) proved that membranes prepared by the second method are still stable under high pressures of up to 10 bar with no leaching of ILs observed. Lan et al. (2013) used hollow fiber membranes as supports to prepare SILM materials for CO₂ separation. The stability of the treated SILM by soaking and vacuum under high pressure (0.7 bar) was significantly improved. Based on the good thermal stability of ILs, the SILMs prepared by Abdelrahim et al. (2017) present good permeability and selectivity towards CO₂ against N₂ at high temperatures (up to 373 K), gas permeability increases with temperature with a decrease in the CO₂/N₂ selectivity.

After ILs are bound into the porous material, SILMs can be used for gas separation under humid conditions, and the selectivity will be significantly improved. Zhang et al. (2017e) believed that the presence of water provides an additional transport mechanism for CO₂ transfer, while N₂ and

CH₄ can only be delivered based on a dissolution-diffusion mechanism.

In order to further improve the stability and selectivity of the support membranes, the ILs-nanoconfined concept was proposed and used in the preparation process of SILM. Peng and his team (Chen et al., 2018, 2017b; Ying et al., 2019a, 2018) used 2D materials (such as WS₂, graphene oxide, MoS₂) to build membranes with 2D nanochannels, and the ILs were confined as a filler into the nanochannels. The membrane treated by the above method has high-temperature resistance, long-term durability, and high-pressure stability in addition to good separation effects. Liu et al. (2019) believed that 2D nanosheets provides a platform to build facilitating delivery channels for CO₂ in membranes. The combination also provides new ideas for the development of CO₂ separation membranes.

The separation performance of SILM can also be improved by other means. Hwang et al. (2016) found that applying additional electric fields can further improve the performance (by a factor of 2–5) of the hybrid membranes with nanoconfined ILs. The action of external forces causes the structure of ILs to reassemble, which changes the adsorption/desorption free energy, free volume and interaction energy of the IL. Alternatively, grafting amine groups can also provide a new direction for membrane upgrading (Jie et al., 2015), which is based on the affinity of amine groups with CO₂.

3.2. Poly ILs membranes

Although SILM has obvious advantages in CO₂ capture, their poor mechanical properties have affected large-scale utilization to some extent, and the stability of SILM membrane under high pressure is also a potential threat (Zhang et al., 2017a). Various means are used to keep ILs stable in the membrane at high transmembrane pressure differences. In addition to binding ILs into the nanochannels as mentioned above, it can also be solved by preparing the poly-ILs membranes or poly-ILs (PILs)/ILs membranes. Poly-ILs combine the high CO₂ affinity and stability of ILs, with the physical and mechanical properties of polymeric material (Nguyen et al., 2013). The processing of poly ILs membrane (PILM) is generally achieved by casting, which is completely different from the support membrane. The poly-ILs are fully dissolved in a volatile solvent, and then the ILs molecules self-assemble to form a thin membrane when the solvent is evaporated (Vollas et al., 2018).

In 2005, Tang et al. (2005) demonstrated that poly-ILs have higher absorption capacities and faster absorption/desorption rates than ILs monomers, and proposed poly ILs as a very promising membrane material. Polymer-formed ILs maintain the characteristics of having adjusting properties by changing the type of anion or cation (Bhavsar et al., 2012). A vast number of different types of poly-ILs were developed to prepare PILMs for CO₂ separation.

The membrane prepared by pure PILs is unsatisfactory in the performance of CO₂ separation. Therefore, the CO₂ separation membrane is prepared by a combination of PIL and free ILs. Vollas et al. (2018) prepared pyridinium based PILMs and PILs-ILs composite membranes, the separation performance of the composites membrane was significantly better than that of the pure membrane; Tomé et al. (2013) evaluated mem-

branes within a range of compositions, from pure ILs to pure poly-ILs, and founded that the addition of free ILs to the polymer system was the primary factor in the permeability and selectivity of the prepared composites.

Like pure ILs, the permeability and selectivity of the PILMs can also be adjusted (Jeffrey Horne et al., 2015). By changing the length of the alkyl chain, Cowan et al. (2016) prepared phosphonium-based PILM with high CO₂ permeability (186 barrers). The effect of different cations on membrane properties in composite membranes was studied by Tomé et al. (2015). The best CO₂ permselectivities were obtained when ammonium-based PILs were used as opposed to imidazolium or pyridinium, illustrating that the reaction sites theory when ILs are used as an absorption liquid is still established in the composites membrane. Nellepalli et al. (2019) evaluated the effect of the PILs based copolymers chemical structures in the stability of membranes, and imidazolium-based copolymers were proven to have great thermal stabilities (up to 300°C).

3.3. Ionic liquid-based composite membranes

ILs based composite membranes are membranes with good mechanical properties and separation properties prepared by using ILs as an additive and polymer as the matrix. According to the category of the component, it can be divided into two types. The first is crosslinked membranes composed of ILs and polymer, and the second is mixed matrix membranes composed of ILs, polymer, and inorganic porous material.

There are many choices for ILs crosslinked membranes. Cheng et al. (2017) introduced different CO₂ absorbents (MEA and ILs) into the Pebax membrane preparation process to prepare ILs blending membranes, and found that the increasing range of CO₂ permeability corresponded to the solubility of CO₂ in solvent. Halder et al. (2017) found that ILs composite membranes consisting of 1-ethyl-3-methyl imidazolium bis (trifluoromethylsulphonyl) imide [C₂mim][Tf₂N] and copolymer had very good performance for CO₂ separation (6650 barrer permeability and 20 selectivity of CO₂/N₂). Lu et al. (2016) developed polysulfone with 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][TFSI]) based membranes for CO₂ separation, and proposed that high selectivity was attributed to the high affinity between ILs and CO₂.

Mixed matrix membranes (MMMs) have been extensively studied due to the advantages of both inorganic membranes and polymeric membranes (Budhathoki et al., 2019; Cheng et al., 2019; Ding et al., 2019). The MMM consists of a dispersed particulate phase (filler) and a continuous polymer phase (polymer matrix) through the interaction between the filler and the matrix (Liu et al., 2018c). Due to the distinctive nature of ILs and the affinity of functionalized ILs for CO₂, ILs-based MMMs have received widespread attention. There are two main aspects to the introduction of ILs into MMMs. One is using ILs or materials modified by ILs as the main component of MMMs to improve the selectivity, the second is using ILs as a tool to fix the surface defects of membrane materials.

The selectivity of membranes can be effectively improved by blending a small amount of ILs with other polymers to prepare a membrane material (Lu et al., 2016). This combina-

tion is similar to the poly-ILs/ILs composite membranes mentioned above. Dai et al. (2019) found that the separation ability of membranes prepared by blending ILs with polymers can be further improved by humidification. Cheng et al. (2017) introduced different CO₂ absorbents into the Pebax membrane preparation process and found that an increasing range of CO₂ permeability corresponded to the CO₂ absorption capacity. However, this combination still faces low transparency problems. Hao et al. (2013) prepared room temperature ILs/zeolite imidazolate framework-8 (ZIF-8) mixed-matrix membranes for natural gas sweetening and post-combustion CO₂ capture.

In general, inorganic porous materials used in the synthesis of MMMs are silica, graphene oxide, zeolites, molecular sieves, and metal organic frameworks (Fam et al., 2018). Thus, the better dispersion of the porous material in the polymer matrix can give assurance to the membrane separation effect. Insufficient dispersion or aggregation will lead to defects that cannot be ignored on the film (Nasir et al., 2018). The degree of bonding between the filler and the matrix is another important factor affecting membrane performance (Hu et al., 2017; Hudiono et al., 2010). Huang et al. (2018a) used ILs modified graphene oxide (GO) as a filler and poly(ether-block-amide) (Pebax 1657) as a polymer matrix to prepare new MMMs. The hydrogen bond between ILs and Pebax led to a more uniform system, which was conducive to GO dispersion. Ahmad et al. (2017) also demonstrated the satisfactory dispersion of SAPO-34 particles with IL modification for 6 hr due to the improved polymer/filler interface morphology as shown by a scanning electron microscopy analysis.

Interface defects can also be improved by hydrogen bonding of ILs. Otherwise, defects can cause undesired gas to pass through the membrane. Ahmad et al. (2019, 2018) confirmed that the introduction of ILs to MMMs can enhance the selectivity and permeability by improving the compatibility between polymeric matrix (polysulfone) and inorganic filler (zeolite). Vu et al. (2019) used ILs-coated micron-sized ZIF particles to form MMMs with polymers, and ILs minimized the formation of non-selective interface defects as an interface binder.

4. Ionic liquids hybrid with catalysis for CO₂ utilization

The ultimate goal of CCU is not the capture of CO₂, but its utilization or storage. Only by converting CO₂ into valuable chemicals or for it to be consumed by photosynthesis can greenhouse gas production be effectively mitigated. CO₂ can be considered as a resource rather than a waste product as it can be catalytically reduced to simple organics such as methanol (Ganesh, 2014; Studt et al., 2014), formic acid (Moret et al., 2014) and methane (Swanson et al., 2012), and can also form more complex organics by cycloaddition reaction (Bobbink and Dyson, 2016). Considering the wide range of sources of CO₂, most of these reactions are economical (Lu et al., 2004). However, the chemical stability of CO₂ molecules is extremely strong. Utilizing CO₂ in a reaction to generate high-value chemicals requires a lot of energy to activate the molecules. Various catalysts have been developed to try to reduce the difficulty of this reaction and reduce energy

consumption (Song et al., 2017). ILs have played an important role in a variety of CO₂ conversion technologies (Zhang et al., 2014).

Cyclic addition reaction with epoxide to prepare cyclic carbonate is one of the most atomic economic reactions, and ILs have been extensively studied to catalyze such reactions (Goodrich et al., 2017; Yang et al., 2018). The activation of CO₂ and epoxide is the most critical step (Liu et al., 2016a). In addition, ILs also play an important role in the reaction of CO₂ with amines to form carbamates (Zhang et al., 2017b).

4.1. ILs catalyst

Compared with other catalysts (metal oxides, transition metal oxides, molecular sieves (Xie et al., 2013), alkali metal salts, quaternary ammonium salts, metal-organic frameworks (Zalomaeva et al., 2013), Lewis acids or bases) used for CO₂ conversion, functionally designed ILs not only spontaneously capture CO₂ molecules, but also activate CO₂ molecules efficiently (Song et al., 2017). The ILs used to catalyze the conversion of CO₂ mainly include for the following.

4.1.1. Amino-based ILs

Amino-based ILs can easily activate CO₂ molecules due to the affinity of the amine group for CO₂. Dual amino-functionalized ILs were prepared as efficient catalysts for carbonate synthesis from carbon dioxide and epoxide by Yue et al. (2017), and the plausible mechanism was proposed as follows. In the first step, the amine group of ILs activates the CO₂ molecule and the epoxide molecule through hydrogen bonding. Subsequently, the carboxyl group in ILs opens the ring of epoxide by nucleophilic attack. Finally, the intermediate product forms a cyclic carbonate. Liu et al. (2016b) developed a series of urea-based ILs with a good performance of CO₂ capture and outstanding catalytic activity for CO₂ conversion, indicating that the amino functional group plays a key role in these two processes. Meng et al. (2019) developed functional ILs with amine groups for CO₂ conversion reaction, showing great performance (92% yield of products) under mild conditions without any solvents, metal and co-catalyst.

4.1.2. Imidazolium-based ILs

Wang et al. (2017) used benzyl substituted imidazolium ILs to catalyze the cycloaddition of CO₂ with epoxides, and the conversion yield reached 94.89% under solvent-free conditions. It was proposed that the role of the hydrogen bonds and other noncovalent interactions were critical in the catalytic process. The same conclusion was also confirmed by Chen et al. (2017a). The hydrogen bond is confirmed to play a determining role in the catalytic activity by density functional calculations when the catalyst is an amino-functionalized imidazolium-based ILs.

4.1.3. Pyrazolium-based ILs and others ILs

The pyridine-based ILs and other ILs that catalyze the cycloaddition reaction of CO₂ with epoxides have also been extensively studied. Ma et al. (2017b) developed dialkylpyrazolium ILs as a novel catalyst for efficient fixation of CO₂, which presented excellent catalytic activity with a product yield of 96% and selectivity of 99% in benign conditions.

Hydroxyl-functionalized pyrazolium-based ILs prepared by Wang et al. (2019) had good suitability for most epoxides with satisfactory product yields. Shang et al. (2019) used a binary catalyst composed of morpholinium ILs and a metal salt to obtain more than 99% conversion and selectivity under mild conditions. Dai et al. (2017) used hydroxyl-and carboxyl-functionalized isothiouronium ILs as the catalysts for CO₂ conversion, the selectivity was up to 100% without any co-solvent and co-catalyst.

4.2. ILs-modified catalyst

With ILs as a homogeneous catalyst, the reaction of epoxides with CO₂ to form cyclic carbonates has the advantages of a high yield, no by-products and no solvent conditions (Sun et al., 2018b). However, the inherent homogeneous property of ILs makes them difficult to separate from the products (Jadhav et al., 2016). In order to improve stability and recyclability, the production of high-efficiency heterogeneous catalysts based on ILs by means of heterogeneity has become a more promising solution (Bobbink and Dyson, 2016; Dai et al., 2016a).

There are many options for hybridizing ILs to porous materials such as molecular sieves, zeolites, graphene oxide, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), etc. (Ding et al., 2017). The composite catalyst has both a high specific surface area of the porous material due to anti-agglomeration and a high catalytic activity of ILs, which makes the catalytic effect better. A series of molecular sieve SBA-15 supported 1,2,4-triazolium-based ILs were prepared by Cheng et al. (2013) and employed to catalyze the synthesis of cyclic carbonates from CO₂ and epoxides. An amino-functionalized imidazolium-based ILs was grafted into porous MOFs by Sun et al. (2018b), and the obtained composite catalyst exhibits a high catalytic activity for cyclizing CO₂ with epichlorohydrin under mild conditions without a co-catalyst. Lan et al. (2018) used multi-cationic ILs modified graphene oxide as a metal-free catalyst to promote CO₂ cycloaddition reaction. Compared to the combination of ILs and MOFs, the problem of heavy metal polluting in the environment when the catalyst life is exhausted is avoided. Metal-free composite catalyst can also be formed by immobilizing ILs on a polymer support. Zhang et al. (2017c) used polystyrene to immobilize ILs for catalytic CO₂ conversion, which can work continuously for in excess of 120 hr. Catalysts consist of imidazolium-based ILs and resin were prepared by Jadhav et al. (2016) and illustrated good catalytic activity. Dai et al. (2016a) successfully prepared a highly efficient catalyst by grafting ILs with polymer nanoparticles. The method of grafting ILs onto biopolymers was also used by Chen et al. (2014) in preparing catalysts to promote the cycloaddition reaction of CO₂ with epoxides. Wang et al. (2018) immobilized ILs on MIL-101-NH₂ to prepare acid-base bifunctional catalysts. Owing to the acid-base synergistic interaction of a Lewis base (-NH₂) and a Brønsted acid (-COOH), the novel catalyst exhibited high activity of up to 91%. Shi et al. (2018) developed a very novel approach in converting CO₂ to organic carbonates. A polyacrylonitrile fiber was used to make a support to fix ILs as a catalyst. Separation of the catalyst becomes more straightforward, even without filtration.

4.3. Application of ILs in CO₂ electrocatalytic conversion

Electrochemical reduction of CO₂ has also had a significant effect on offsetting climate change and the production of greenhouse gas emissions. As ILs can effectively absorb CO₂ and change the charge distribution on the surface of the molecule through hydrogen bonding, the introduction of ILs into the electrochemical reduction process has attracted considerable interest from researchers (Cruz et al., 2018). Iijima et al. (2018) modified the traditional Au electrode with ILs, changing the electron transfer in the reduction reaction and reducing the overpotential. This experimental design provided a new way to reduce the energy consumption of the reaction. For the electrochemical reduction of CO₂ process, ILs can improve the reaction by mixing with electrolytes in addition to modifying the electrode. Zhang et al. (2017d) introduced an imidazolyl-based ILs (1-ethyl-3-methylimidazolium dicyanamide) into the aqueous solution as an additive. Due to their special nature, the introduction of ILs not only improves the electrochemical reduction activity of CO₂ to formic acid, increasing the solubility of CO₂ in solution, but also inhibits the competitive hydrogen evolution reaction.

5. Challenges and prospects

Ionic liquids are identified as promising materials that have been widely used in CO₂ capture and conversion processes. Although the introduction of ILs significantly improves the CCU process, there are still significant improvements to be made. ILs face many challenges in becoming the new generation of green materials. Firstly, the majority of ILs used in the mature binding process are based on imidazole or pyridine-based. Such ILs have been proven to have non-negligible biological toxicity (Liu et al., 2018b; Wan et al., 2018; Xia et al., 2018; Zhang et al., 2018a). Although DES is considered to be an alternative to ILs with the advantages of good biocompatibility, low cost, and easy preparation, more efforts should be paid to CO₂ absorption. Currently few studies focus on the hybridization of DES with adsorption, membrane, and catalysis, etc.

In addition, considering the biocompatibility of DES as a new generation of ILs, the combination of DES and biology may be a promising development pathway for chemical absorption and microalgae conversion hybrid CCU. In this process, DES could be used to absorb CO₂ from flue gas, and then provided it as a nutrition source for microalgae. It should be noted that the development of CCU materials/processes based on ILs is still one of the most potential directions for CO₂ capture and utilization. Thus, the following aspects deserve attention: (1) To better understand the mechanism of action between ILs and different CCU materials, and provide further optimization of the structural design of functionalized ILs. (2) Explore the application of DES in CO₂ adsorption, membrane separation, and catalytic conversion to build a more environmentally friendly CCU process. (3) Carry out relevant research on the design and synthesis of functionalized DES for the hybrid process of chemical absorption and microalgae transformation.

6. Conclusions

This work reviews the application of hybrid ILs technology in CO₂ capture and utilization processes. Functional design can greatly increase the CO₂ affinity of ILs, which leads to ILs playing a key role in CCU processes. In addition, the special properties of ILs (extremely low saturated vapor pressure, chemical stability, and thermal stability) makes them have a wide application potential. Hybridization with other technologies has largely solved the disadvantages of ILs (large viscosity, complicated preparation process, high cost, etc.), and has provided significant optimization and improvement of the original process. For the absorption process, ILs can directly absorb CO₂ as a solution, or they can be mixed with other absorbents to synergistically absorb. For the adsorption process, ILs can modify the porous material to improve the adsorption effect by changing the pore size of the porous material and enriching the surface functional groups. For the membrane separation process, ILs can not only be used as the main component of the membrane material to prepare efficient separation membranes, but can also improve the separation performance by reducing the interface defects of the mixed matrix membrane as a repair agent. When ILs are used as catalysts or used to modify catalysts, their main role is to use their inherently high affinity to activate CO₂ molecules. In general, ILs have greatly promoted the development of CCU technology and will continue to have a profound impact.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was financially supported by the National Key Research and Development Program-China (No. 2017YFE0127200), National Natural Science Foundation of China (Nos. 21878228 and 31701526), Natural Science Foundation of Tianjin City (No. 17JCQNJC08500), Young Elite Scientists Sponsorship Program by Tianjin City (No. TJSQNTJ-2017-03) and International Cooperation Research centre of Carbon Capture in Ultra-low Energy-consumption (Tianjin).

REFERENCES

- Abbott, A.P., Boothby, D., Capper, G., Davies, D.L., Rasheed, R.K., 2004. Deep eutectic solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids. *J. Am. Chem. Soc.* 126, 9142–9147.
- Abbott, A.P., Capper, G., Davies, D.L., Rasheed, R.K., Tambyrajah, V., 2003. Novel solvent properties of choline chloride/urea mixtures. *Chem. Commun.* 70–71.
- Abdelrahim, M.Y.M., Martins, C.F., Neves, L.A., Capasso, C., Supuran, C.T., Coelhos, I.M., et al., 2017. Supported ionic liquid membranes immobilized with carbonic anhydrases for CO₂ transport at high temperatures. *J. Memb. Sci.* 528, 225–230.

- Aghaie, M., Rezaei, N., Zendehboudi, S., 2018. A systematic review on CO₂ capture with ionic liquids: current status and future prospects. *Renew. Sustain. Energy Rev.* 96, 502–525.
- Ahmad, N.N.R., Leo, C.P., Ahmad, A.L., 2019. Effects of solvent and ionic liquid properties on ionic liquid enhanced polysulfone/SAPO-34 mixed matrix membrane for CO₂ removal. *Micropor. Mesopor. Mater.* 283, 64–72.
- Ahmad, N.N.R., Leo, C.P., Mohammad, A.W., Ahmad, A.L., 2018. Interfacial sealing and functionalization of polysulfone/SAPO-34 mixed matrix membrane using acetate-based ionic liquid in post-impregnation for CO₂ capture. *Sep. Purif. Technol.* 197, 439–448.
- Ahmad, N.N.R., Leo, C.P., Mohammad, A.W., Ahmad, A.L., 2017. Modification of gas selective SAPO zeolites using imidazolium ionic liquid to develop polysulfone mixed matrix membrane for CO₂ gas separation. *Micropor. Mesopor. Mater.* 244, 21–30.
- Aki, S.N.V.K., Mellein, B.R., Saurer, E.M., Brennecke, J.F., 2004. High-pressure phase behavior of carbon dioxide with imidazolium-based ionic liquids. *J. Phys. Chem. B* 108, 20355–20365.
- Anderson, J.L., Dixon, J.K., Brennecke, J.F., 2007. Solubility of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: comparison to other ionic liquids. *Acc. Chem. Res.* 40, 1208–1216.
- Anthony, J.L., Maginn, E.J., Brennecke, J.F., 2002. Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B* 106, 7315–7320.
- Bates, E.D., Mayton, R.D., Ntai, I., Davis, J.H., 2002. CO₂ capture by task-specific ionic liquid. *J. Am. Chem. Soc.* 124, 926–927.
- Bhattacharyya, S., Shah, F.U., 2016. Ether functionalized choline tethered amino acid ionic liquids for enhanced CO₂ capture. *ACS Sustain. Chem. Eng.* 4, 5441–5449.
- Bhavsar, R.S., Kumbharkar, S.C., Kharul, U.K., 2012. Polymeric ionic liquids (PILs): effect of anion variation on their CO₂ sorption. *J. Membr. Sci.* 389, 305–315.
- Blanchard, L.A., Hancu, D., Beckman, E.J., Brennecke, J.F., 1999. Green processing using ionic liquids and CO₂. *Nature* 399, 28–29.
- Bobbink, F.D., Dyson, P.J., 2016. Synthesis of carbonates and related compounds incorporating CO₂ using ionic liquid-type catalysts: state-of-the-art and beyond. *J. Catal.* 343, 52–61.
- Budhathoki, S., Ajayi, O., Steckel, J.A., Wilmer, C.E., 2019. High-throughput computational prediction of the cost of carbon capture using mixed matrix membranes. *Energy Environ. Sci.* 12, 1255–1264.
- Chemat, F., Gnanasundaram, N., Shariff, A.M., Murugesan, T., 2016. Effect of L-arginine on solubility of CO₂ in choline chloride + glycerol based deep eutectic solvents. *Procedia Eng.* 148, 236–242.
- Chen, C., Ma, Y., Zheng, D., Wang, L., Li, J., Zhang, J., et al., 2017a. Insight into the role of weak interaction played in the fixation of CO₂ catalyzed by the amino-functionalized imidazolium-based ionic liquids. *J. CO₂ Util.* 18, 156–163.
- Chen, D., Wang, W., Ying, W., Guo, Y., Meng, D., Yan, Y., et al., 2018. CO₂-philic WS₂ laminated membranes with a nanoconfined ionic liquid. *J. Mater. Chem. A* 6, 16566–16573.
- Chen, D., Ying, W., Guo, Y., Ying, Y., Peng, X., 2017b. Enhanced gas separation through nanoconfined ionic liquid in laminated MoS₂ membrane. *ACS Appl. Mater. Interfaces* 9, 44251–44257.
- Chen, J., Jin, B., Dai, W., Deng, S., Cao, L., Cao, Z., et al., 2014. Catalytic fixation of CO₂ to cyclic carbonates over biopolymer chitosan-grafted quaternary phosphonium ionic liquid as a recyclable catalyst. *Appl. Catal. A Gen.* 484, 26–32.
- Cheng, J., Hu, L., Li, Y., Liu, J., Zhou, J., Cen, K., 2017. Improving CO₂ permeation and separation performance of CO₂-philic polymer membrane by blending CO₂ absorbents. *Appl. Surf. Sci.* 410, 206–214.
- Cheng, J., Li, Y., Hu, L., Zhou, J., Cen, K., 2016. CO₂ adsorption performance of ionic liquid [P₆₆₆₁₄][2-Op] loaded onto molecular sieve MCM-41 compared to pure ionic liquid in biohythane/pure CO₂ atmospheres. *Energy Fuels* 30, 3251–3256.
- Cheng, W., Chen, X., Sun, J., Wang, J., Zhang, S., 2013. SBA-15 supported triazolium-based ionic liquids as highly efficient and recyclable catalysts for fixation of CO₂ with epoxides. *Catal. Today* 200, 117–124.
- Cheng, Y., Zhai, L., Ying, Y., Wang, Y., Liu, G., Dong, J., et al., 2019. Highly efficient CO₂ capture by mixed matrix membranes containing three-dimensional covalent organic framework fillers. *J. Mater. Chem. A* 7, 4549–4560.
- Cowan, M.G., Masuda, M., McDanel, W.M., Kohno, Y., Gin, D.L., Noble, R.D., 2016. Phosphonium-based poly(ionic liquid) membranes: the effect of cation alkyl chain length on light gas separation properties and Ionic conductivity. *J. Membr. Sci.* 498, 408–413.
- Cruz, H., Jordão, N., Amorim, P., Dionísio, M., Branco, L.C., 2018. Deep eutectic solvents as suitable electrolytes for electrochromic devices. *ACS Sustain. Chem. Eng.* 6, 2240–2249.
- Cui, G., Lv, M., Yang, D., 2019. Efficient CO₂ absorption by azolide-based deep eutectic solvents. *Chem. Commun.* 55, 1426–1429.
- Dai, W., Yang, W., Zhang, Y., Wang, D., Luo, X., Tu, X., 2017. Novel isothiouronium ionic liquid as efficient catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides. *J. CO₂ Util.* 17, 256–262.
- Dai, W., Zhang, Y., Tan, Y., Luo, X., Tu, X., 2016a. Reusable and efficient polymer nanoparticles grafted with hydroxyl-functionalized phosphonium-based ionic liquid catalyst for cycloaddition of CO₂ with epoxides. *Appl. Catal. A Gen.* 514, 43–50.
- Dai, Z., Noble, R.D., Gin, D.L., Zhang, X., Deng, L., 2016b. Combination of ionic liquids with membrane technology: a new approach for CO₂ separation. *J. Membr. Sci.* 497, 1–20.
- Dai, Z., Ansaldi, L., Ryan, J.J., Spontak, R.J., Deng, L., 2019. Incorporation of an ionic liquid into a midblock-sulfonated multiblock polymer for CO₂ capture. *J. Membr. Sci.* 588, 117193.
- de Riva, J., Suárez-Reyes, J., Moreno, D., Díaz, I., Ferro, V., Palomar, J., 2017. Ionic liquids for post-combustion CO₂ capture by physical absorption: thermodynamic, kinetic and process analysis. *Int. J. Greenh. Gas Control* 61, 61–70.
- Ding, L.G., Yao, B.J., Li, F., Shi, S.C., Huang, N., Yin, H.B., et al., 2019. Ionic liquid-decorated COF and its covalent composite aerogel for selective CO₂ adsorption and catalytic conversion. *J. Mater. Chem. A* 7, 4689–4698.
- Ding, L.G., Yao, B.J., Jiang, W.L., Li, J.T., Fu, Q.J., Li, Y.A., et al., 2017. Bifunctional imidazolium-based ionic liquid decorated UiO-67 type MOF for selective CO₂ adsorption and catalytic property for CO₂ cycloaddition with epoxides. *Inorg. Chem.* 56, 2337–2344.
- Elhamarnah, Y.A., Nasser, M., Qiblawey, H., Benamor, A., Atilhan, M., Aparicio, S., 2019. A comprehensive review on the rheological behavior of imidazolium based ionic liquids and natural deep eutectic solvents. *J. Mol. Liq.* 277, 932–958.
- Fam, W., Mansouri, J., Li, H., Hou, J., Chen, V., 2018. Gelled graphene oxide-ionic liquid composite membranes with enriched ionic liquid surfaces for improved CO₂ separation. *ACS Appl. Mater. Interfaces* 10, 7389–7400.
- Figueiredo, M., Gomes, C., Costa, R., Martins, A., Pereira, C.M., Silva, F., 2009. Differential capacity of a deep eutectic solvent based on choline chloride and glycerol on solid electrodes. *Electrochim. Acta* 54, 2630–2634.
- Fukaya, Y., Iizuka, Y., Sekikawa, K., Ohno, H., 2007. Bio ionic liquids: room temperature ionic liquids composed wholly of biomaterials. *Green Chem.* 9, 1155–1157.

- Ganesh, I., 2014. Conversion of carbon dioxide into methanol - a potential liquid fuel: fundamental challenges and opportunities (a review). *Renew. Sustain. Energy Rev.* 31, 221–257.
- Gao, J., Cao, L., Dong, H., Zhang, X., Zhang, S., 2015. Ionic liquids tailored amine aqueous solution for pre-combustion CO₂ capture: role of imidazolium-based ionic liquids. *Appl. Energy* 154, 771–780.
- Goodrich, P., Gunaratne, H.Q.N., Jacquemin, J., Jin, L., Lei, Y., Seddon, K.R., 2017. Sustainable cyclic carbonate production, utilizing carbon dioxide and azolate ionic liquids. *ACS Sustain. Chem. Eng.* 5, 5635–5641.
- Haghtalab, A., Kheiri, A., 2015. High pressure measurement and CPA equation of state for solubility of carbon dioxide and hydrogen sulfide in 1-butyl-3-methylimidazolium acetate. *J. Chem. Thermodyn.* 89, 41–50.
- Halder, K., Khan, M.M., Grünauer, J., Shishatskiy, S., Abetz, C., Filiz, V., et al., 2017. Blend membranes of ionic liquid and polymers of intrinsic microporosity with improved gas separation characteristics. *J. Memb. Sci.* 539, 368–382.
- Hao, L., Li, P., Yang, T., Chung, T.S., 2013. Room temperature ionic liquid/ZIF-8 mixed-matrix membranes for natural gas sweetening and post-combustion CO₂ capture. *J. Memb. Sci.* 436, 221–231.
- Hasib-ur-Rahman, M., Siaj, M., Larachi, F., 2012. CO₂ capture in alkanolamine/room-temperature ionic liquid emulsions: a viable approach with carbamate crystallization and curbed corrosion behavior. *Int. J. Greenh. Gas Control* 6, 246–252.
- Hu, L., Cheng, J., Li, Y., Liu, J., Zhang, L., Zhou, J., et al., 2017. Composites of ionic liquid and amine-modified SAPO 34 improve CO₂ separation of CO₂-selective polymer membranes. *Appl. Surf. Sci.* 410, 249–258.
- Huang, G., Isfahani, A.P., Muchtar, A., Sakurai, K., Shrestha, B.B., Qin, D., et al., 2018a. Pebax/ionic liquid modified graphene oxide mixed matrix membranes for enhanced CO₂ capture. *J. Memb. Sci.* 565, 370–379.
- Huang, Q., Jing, G., Zhou, X., Lv, B., Zhou, Z., 2018b. A novel biphasic solvent of amino-functionalized ionic liquid for CO₂ capture: high efficiency and regenerability. *J. CO₂ Util.* 25, 22–30.
- Huang, Y., Cui, G., Wang, H., Li, Z., Wang, J., 2018c. Tuning ionic liquids with imide-based anions for highly efficient CO₂ capture through enhanced cooperations. *J. CO₂ Util.* 28, 299–305.
- Huang, Z., Jiang, B., Yang, H., Wang, B., Zhang, N., Dou, H., et al., 2017. Investigation of glycerol-derived binary and ternary systems in CO₂ capture process. *Fuel* 210, 836–843.
- Huang, J., Riisager, A., Wasserscheid, P., Fehrmann, R., 2006. Reversible physical absorption of SO₂ by ionic liquids. *Chem. Commun.* 4027–4029.
- Hudiono, Y.C., Carlisle, T.K., Bara, J.E., Zhang, Y., Gin, D.L., Noble, R.D., 2010. A three-component mixed-matrix membrane with enhanced CO₂ separation properties based on zeolites and ionic liquid materials. *J. Memb. Sci.* 350, 117–123.
- Hwang, H.J., Chi, W.S., Kwon, O., Lee, J.G., Kim, J.H., Shul, Y.G., 2016. Selective ion transporting polymerized ionic liquid membrane separator for enhancing cycle stability and durability in secondary zinc-air battery systems. *ACS Appl. Mater. Interfaces* 8, 26298–26308.
- Iijima, G., Kitagawa, T., Katayama, A., Inomata, T., Yamaguchi, H., Suzuki, K., et al., 2018. CO₂ reduction promoted by imidazole supported on a phosphonium-type ionic-liquid-modified Au electrode at a low overpotential. *ACS Catal.* 8, 1990–2000.
- Iliuta, I., Hasib-ur-Rahman, M., Larachi, F., 2014. CO₂ absorption in diethanolamine/ionic liquid emulsions - chemical kinetics and mass transfer study. *Chem. Eng. J.* 240, 16–23.
- Ilyas, A., Muhammad, N., Gilani, M.A., Ayub, K., Vankelecom, I.F.J., Khan, A.L., 2017. Supported protic ionic liquid membrane based on 3-(trimethoxysilyl)propan-1-aminium acetate for the highly selective separation of CO₂. *J. Memb. Sci.* 543, 301–309.
- Jadhav, A.H., Thorat, G.M., Lee, K., Lim, A.C., Kang, H., Seo, J.G., 2016. Effect of anion type of imidazolium based polymer supported ionic liquids on the solvent free synthesis of cycloaddition of CO₂ into epoxide. *Catal. Today* 265, 56–67.
- Jeffrey Horne, W., Andrews, M.A., Shannon, M.S., Terrill, K.L., Moon, J.D., Hayward, S.S., et al., 2015. Effect of branched and cycloalkyl functionalities on CO₂ separation performance of poly(IL) membranes. *Sep. Purif. Technol.* 155, 89–95.
- Jie, X., Chau, J., Obusovic, G., Sirkar, K.K., 2015. Microporous ceramic tubule based and dendrimer-Facilitated immobilized ionic liquid membrane for CO₂ separation. *Ind. Eng. Chem. Res.* 54, 10401–10418.
- Kanakubo, M., Makino, T., Taniguchi, T., Nokami, T., Itoh, T., 2016. CO₂ solubility in ether functionalized ionic liquids on mole fraction and molarity scales. *ACS Sustain. Chem. Eng.* 4, 525–535.
- Karunakaran, M., Villalobos, L.F., Kumar, M., Shevate, R., Akhtar, F.H., Peinemann, K.V., 2017. Graphene oxide doped ionic liquid ultrathin composite membranes for efficient CO₂ capture. *J. Mater. Chem. A* 5, 649–656.
- Lan, D.H., Gong, Y.X., Tan, N.Y., Wu, S.S., Shen, J., Yao, K.C., et al., 2018. Multi-functionalization of GO with multi-cationic ILs as high efficient metal-free catalyst for CO₂ cycloaddition under mild conditions. *Carbon* 127, 245–254.
- Lan, W., Li, S., Xu, J., Luo, G., 2013. Preparation and carbon dioxide separation performance of a hollow fiber supported ionic liquid membrane. *Ind. Eng. Chem. Res.* 52, 6770–6777.
- Leron, R.B., Caparanga, A., Li, M.H., 2013. Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T = 303.15–343.15K and moderate pressures. *J. Taiwan Inst. Chem. Eng.* 44, 879–885.
- Leron, R.B., Li, M.H., 2013a. Solubility of carbon dioxide in a eutectic mixture of choline chloride and glycerol at moderate pressures. *J. Chem. Thermodyn.* 57, 131–136.
- Leron, R.B., Li, M.H., 2013b. Solubility of carbon dioxide in a choline chloride-ethylene glycol based deep eutectic solvent. *Thermochim. Acta* 551, 14–19.
- Li, Y., Tao, H., Su, B., Kundzewicz, Z.W., Jiang, T., 2019. Impacts of 1.5 °C and 2 °C global warming on winter snow depth in Central Asia. *Sci. Total Environ.* 651, 2866–2873.
- Lin, C.M., Leron, R.B., Caparanga, A.R., Li, M.H., 2014. Henry's constant of carbon dioxide-aqueous deep eutectic solvent (choline chloride/ethylene glycol, choline chloride/glycerol, choline chloride/malonic acid) systems. *J. Chem. Thermodyn.* 68, 216–220.
- Liu, M., Li, X., Liang, L., Sun, J., 2016a. Protonated triethanolamine as multi-hydrogen bond donors catalyst for efficient cycloaddition of CO₂ to epoxides under mild and cocatalyst-free conditions. *J. CO₂ Util.* 16, 384–390.
- Liu, M., Liang, L., Li, X., Gao, X., Sun, J., 2016b. Novel urea derivative-based ionic liquids with dual-functions: CO₂ capture and conversion under metal- and solvent-free conditions. *Green Chem.* 18, 2851–2863.
- Liu, X., Gao, B., Jiang, Y., Ai, N., Deng, D., 2017. Solubilities and thermodynamic properties of carbon dioxide in guaiacol-based deep eutectic solvents. *J. Chem. Eng. Data* 62, 1448–1455.
- Liu, Y., Friesen, J.B., McAlpine, J.B., Larkin, D.C., Chen, S.N., Pauli, G.F., 2018a. Natural deep eutectic solvents: properties, applications, and perspectives. *J. Nat. Prod.* 81, 679–690.
- Liu, Y., Han, W., Xu, Z., Fan, W., Peng, W., Luo, S., 2018b. Comparative toxicity of pristine graphene oxide and its carboxyl, imidazole or polyethylene glycol functionalized products to daphnia magna: a two generation study. *Environ. Pollut.* 237, 218–227.

- Liu, Y., Liu, G., Zhang, C., Qiu, W., Yi, S., Chernikova, V., et al., 2018c. Enhanced CO₂/CH₄ separation performance of a mixed matrix membrane based on tailored MOF-polymer formulations. *Adv. Sci.* 5, 2–6.
- Liu, Y., Wu, H., Min, L., Song, S., Yang, L., Ren, Y., et al., 2019. 2D layered double hydroxide membranes with intrinsic breathing effect toward CO₂ for efficient carbon capture. *J. Memb. Sci.* 598, 117663.
- Lu, S.-C., Khan, A.L., Vankelecom, I.F.J., 2016. Polysulfone-ionic liquid based membranes for CO₂/N₂ separation with tunable porous surface features. *J. Memb. Sci.* 518, 10–20.
- Lu, X.B., Zhang, Y.J., Liang, B., Li, X., Wang, H., 2004. Chemical fixation of carbon dioxide to cyclic carbonates under extremely mild conditions with highly active bifunctional catalysts. *J. Mol. Catal. A Chem.* 210, 31–34.
- Lv, B., Jing, G., Qian, Y., Zhou, Z., 2016a. An efficient absorbent of amine-based amino acid-functionalized ionic liquids for CO₂ capture: high capacity and regeneration ability. *Chem. Eng. J.* 289, 212–218.
- Lv, B., Xia, Y., Shi, Y., Liu, N., Li, W., Li, S., 2016b. A novel hydrophilic amino acid ionic liquid [C₂OHHmim][Gly] as aqueous sorbent for CO₂ capture. *Int. J. Greenh. Gas Control* 46, 1–6.
- Ma, T., Wang, J., Du, Z., Abdeltawab, A.A., Al-Enizi, A.M., Chen, X., 2017a. A process simulation study of CO₂ capture by ionic liquids. *Int. J. Greenh. Gas Control* 58, 223–231.
- Ma, Y., Chen, C., Wang, T., Zhang, J., Wu, J., Liu, X., et al., 2017b. Dialkylpyrazolium ionic liquids as novel catalyst for efficient fixation of CO₂ with metal- and solvent-free. *Appl. Catal. A Gen.* 547, 265–273.
- Ma, Y., Gao, J., Wang, Y., Hu, J., Cui, P., 2018. Ionic liquid-based CO₂ capture in power plants for low carbon emissions. *Int. J. Greenh. Gas Control* 75, 134–139.
- Mahurin, S.M., Hillesheim, P.C., Yeary, J.S., Jiang, D., Dai, S., 2012. High CO₂ solubility, permeability and selectivity in ionic liquids with the tetracyanoborate anion. *RSC Adv.* 2, 11813–11819.
- Meng, X., Ju, Z., Zhang, S., Liang, X., von Solms, N., Zhang, X., et al., 2019. Efficient transformation of CO₂ to cyclic carbonates using bifunctional protic ionic liquids under mild conditions. *Green Chem.* 21, 3456–3463.
- Mohammadi, M., Asadollahzadeh, M., Shirazian, S., 2018. Molecular-level understanding of supported ionic liquid membranes for gas separation. *J. Mol. Liq.* 262, 230–236.
- Moret, S., Dyson, P.J., Laurenczy, G., 2014. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. *Nat. Commun.* 5, 4017.
- Nasir, R., Ahmad, N.N.R., Mukhtar, H., Mohshim, D.F., 2018. Effect of ionic liquid inclusion and amino-functionalized SAPO-34 on the performance of mixed matrix membranes for CO₂/CH₄ separation. *J. Environ. Chem. Eng.* 6, 2363–2368.
- Navarro, P., García, J., Rodríguez, F., Carvalho, P.J., Coutinho, J.A.P., 2019. Impact of water on the [C₄C₁im][Ac] ability for the CO₂/CH₄ separation. *J. CO₂ Util.* 31, 115–123.
- Nellepalli, P., Tomé, L.C., Vijayakrishna, K., Marrucho, I.M., 2019. Imidazolium-based copoly(ionic liquid) membranes for CO₂/N₂ separation. *Ind. Eng. Chem. Res.* 58, 2017–2026.
- Nguyen, P.T., Wiesnauer, E.F., Gin, D.L., Noble, R.D., 2013. Effect of composition and nanostructure on CO₂/N₂ transport properties of supported alkyl-imidazolium block copolymer membranes. *J. Memb. Sci.* 430, 312–320.
- Nkinahamira, F., Su, T., Xie, Y., Ma, G., Wang, H., Li, J., 2017. High pressure adsorption of CO₂ on MCM-41 grafted with quaternary ammonium ionic liquids. *Chem. Eng. J.* 326, 831–838.
- Oh, S.-Y., Binns, M., Cho, H., Kim, J.-K., 2016. Energy minimization of MEA-based CO₂ capture process. *Appl. Energy* 169, 353–362.
- Paiva, A., Craveiro, R., Aroso, I., Martins, M., Reis, R.L., Duarte, A.R.C., 2014. Natural deep eutectic solvents - solvents for the 21st century. *ACS Sustain. Chem. Eng.* 2, 1063–1071.
- Raeissi, S., Peters, C.J., 2009. A potential ionic liquid for CO₂-separating gas membranes: selection and gas solubility studies. *Green Chem.* 11, 185–192.
- Ran, H., Wang, J., Abdeltawab, A.A., Chen, X., Yu, G., Yu, Y., 2017. Synthesis of polymeric ionic liquids material and application in CO₂ adsorption. *J. Energy Chem.* 26, 909–918.
- Ren, H., Lian, S., Wang, X., Zhang, Y., Duan, E., 2018. Exploiting the hydrophilic role of natural deep eutectic solvents for greening CO₂ capture. *J. Clean. Prod.* 193, 802–810.
- Ren, H., Wang, X., Lian, S., Zhang, Y., Duan, E., 2019. Formation mechanisms of caprolactam-tetraalkyl ammonium halide deep eutectic and its hydrate. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 211, 189–194.
- Robeson, L.M., 2008. The upper bound revisited.. *J. Memb. Sci.* 320, 390–400.
- Ruß, C., König, B., 2012. Low melting mixtures in organic synthesis – an alternative to ionic liquids? *Green Chem.* 14, 2969–2982.
- Santos, E., Albo, J., Irabien, A., 2014. Acetate based supported ionic liquid membranes (SILMs) for CO₂ separation: influence of the temperature. *J. Memb. Sci.* 452, 277–283.
- Sarmad, S., Mikkola, J.-P., Ji, X., 2017. Carbon dioxide capture with ionic liquids and deep eutectic solvents: a new generation of sorbents. *ChemSusChem* 10, 324–352.
- Shang, Y., Gong, Q., Zheng, M., Zhang, H., Zhou, X., 2019. An efficient morpholinium ionic liquid based catalyst system for cycloaddition of CO₂ and epoxides under mild conditions. *J. Mol. Liq.* 283, 235–241.
- Sharma, P., Choi, S.H., Park, S.D., Baek, I.H., Lee, G.S., 2012a. Selective chemical separation of carbondioxide by ether functionalized imidazolium cation based ionic liquids. *Chem. Eng. J.* 181–182, 834–841.
- Sharma, P., Park, S.D., Park, K.T., Nam, S.C., Jeong, S.K., Yoon, Y.I., et al., 2012b. Solubility of carbon dioxide in amine-functionalized ionic liquids: role of the anions. *Chem. Eng. J.* 193–194, 267–275.
- Shi, X.-L., Chen, Y., Duan, P., Zhang, W., Hu, Q., 2018. Conversion of CO₂ into organic carbonates over a fiber-supported ionic liquid catalyst in impellers of the agitation system. *ACS Sustain. Chem. Eng.* 6, 7119–7127.
- Shiftlet, M.B., Drew, D.W., Cantini, R.A., Yokozeki, A., 2010. Carbon dioxide capture using ionic liquid 1-butyl-3-methylimidazolium acetate. *Energy Fuels* 24, 5781–5789.
- Sistla, Y.S., Khanna, A., 2015. CO₂ absorption studies in amino acid-anion based ionic liquids. *Chem. Eng. J.* 273, 268–276.
- Soll, S., Zhao, Q., Weber, J., Yuan, J., 2013. Activated CO₂ sorption in mesoporous imidazolium-type poly(ionic liquid)-based polyampholytes. *Chem. Mater.* 25, 3003–3010.
- Song, C., Liu, Q., Ji, N., Deng, S., Zhao, J., Li, Y., et al., 2018. Alternative pathways for efficient CO₂ capture by hybrid processes—A review. *Renew. Sustain. Energy Rev.* 82, 215–231.
- Song, Q.W., Zhou, Z.H., He, L.N., 2017. Efficient, selective and sustainable catalysis of carbon dioxide. *Green Chem.* 19, 3707–3728.
- Studt, F., Sharafutdinov, I., Abild-Pedersen, F., Elkjær, C.F., Hummelshøj, J.S., Dahl, S., et al., 2014. Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol. *Nat. Chem.* 6, 320–324.
- Sun, H., Wang, A., Zhai, J., Huang, J., Wang, Y., Wen, S., et al., 2018a. Impacts of global warming of 1.5 °C and 2.0 °C on precipitation patterns in China by regional climate model (COSMO-CLM). *Atmos. Res.* 203, 83–94.
- Sun, Y., Huang, H., Vardhan, H., Aguilera, B., Zhong, C., Perman, J.A., et al., 2018b. Facile approach to graft ionic liquid into MOF for improving the efficiency of CO₂ chemical fixation. *ACS Appl. Mater. Interfaces* 10, 27124–27130.

- Swalus, C., Jacquemin, M., Poleunis, C., Bertrand, P., Ruiz, P., 2012. CO₂ methanation on Rh/ γ -Al₂O₃ catalyst at low temperature: "In situ" supply of hydrogen by Ni/activated carbon catalyst. *Appl. Catal. B Environ.* 125, 41–50.
- Sze, L.L., Pandey, S., Ravula, S., Pandey, S., Zhao, H., Baker, G.A., et al., 2014. Ternary deep eutectic solvents tasked for carbon dioxide capture. *ACS Sustain. Chem. Eng.* 2, 2117–2123.
- Tang, J., Tang, H., Sun, W., Plancher, H., Radosz, M., Shen, Y., 2005. Poly(ionic liquid)s: a new material with enhanced and fast CO₂ absorption. *Chem. Commun.* 3325–3327.
- Tomé, L.C., Gouveia, A.S.L., Freire, C.S.R., Mecerreyres, D., Marrucho, I.M., 2015. Polymeric ionic liquid-based membranes: influence of polycation variation on gas transport and CO₂ selectivity properties. *J. Memb. Sci.* 486, 40–48.
- Tomé, L.C., Marrucho, I.M., 2016. Ionic liquid-based materials: a platform to design engineered CO₂ separation membranes. *Chem. Soc. Rev.* 45, 2785–2824.
- Tomé, L.C., Mecerreyres, D., Freire, C.S.R., Rebelo, L.P.N., Marrucho, I.M., 2013. Pyrrolidinium-based polymeric ionic liquid materials: new perspectives for CO₂ separation membranes. *J. Memb. Sci.* 428, 260–266.
- Trivedi, T.J., Lee, J.H., Lee, H.J., Jeong, Y.K., Choi, J.W., 2016. Deep eutectic solvents as attractive media for CO₂ capture. *Green Chem.* 18, 2834–2842.
- Uehara, Y., Karami, D., Mahinpey, N., 2019. CO₂ adsorption using amino acid ionic liquid-impregnated mesoporous silica sorbents with different textural properties. *Micropor. Mesopor. Mater.* 278, 378–386.
- Ullah, R., Atilhan, M., Anaya, B., Khraisheh, M., García, G., ElKhattat, A., et al., 2015. A detailed study of cholinium chloride and levulinic acid deep eutectic solvent system for CO₂ capture via experimental and molecular simulation approaches. *Phys. Chem. Chem. Phys.* 17, 20941–20960.
- Usman, M., Huang, H., Li, J., Hillestad, M., Deng, L., 2016. Optimization and characterization of an amino acid ionic liquid and polyethylene glycol blend solvent for precombustion CO₂ capture: experiments and model fitting. *Ind. Eng. Chem. Res.* 55, 12080–12090.
- Valencia-Marquez, D., Flores-Tlacuahuac, A., Vasquez-Medrano, R., 2017. An optimization approach for CO₂ capture using ionic liquids. *J. Clean. Prod.* 168, 1652–1667.
- Vollas, A., Chouliaras, T., Deimede, V., Ioannides, T., Kallitsis, J., 2018. New pyridinium type poly(ionic liquids) as membranes for CO₂ separation. *Polymers (Basel)* 10, 912.
- Vu, M.T., Lin, R., Diao, H., Zhu, Z., Bhatia, S.K., Smart, S., 2019. Effect of ionic liquids (ILs) on MOFs/polymer interfacial enhancement in mixed matrix membranes. *J. Memb. Sci.* 587, 117157.
- Walden, P., 1914. Molecular weights and electrical conductivity of several fused salts. *Bull. l'Academie Imp. des Sci. St.-petersbg.* 8, 405–422.
- Wan, M.M., Zhu, H.Y., Li, Y.Y., Ma, J., Liu, S., Zhu, J.H., 2014. Novel CO₂-capture derived from the basic ionic liquids orientated on mesoporous materials. *ACS Appl. Mater. Interfaces* 6, 12947–12955.
- Wan, R., Xia, X., Wang, P., Huo, W., Dong, H., Chang, Z., 2018. Toxicity of imidazoles ionic liquid [C₁₆mim]Cl to HepG2 cells. *Toxicol. Vitro.* 52, 1–7.
- Wang, T., Ma, Y., Jiang, J., Zhu, X., Fan, B., Yu, G., et al., 2019. Hydroxyl-functionalized pyrazolium ionic liquids to catalyze chemical fixation of CO₂: further benign reaction condition for the single-component catalyst. *J. Mol. Liq.* 293, 111479.
- Wang, T., Song, X., Luo, Q., Yang, X., Chong, S., Zhang, J., et al., 2018. Acid-base bifunctional catalyst: carboxyl ionic liquid immobilized on MIL-101-NH₂ for rapid synthesis of propylene carbonate from CO₂ and propylene oxide under facile solvent-free conditions. *Micropor. Mesopor. Mater.* 267, 84–92.
- Wang, T., Zheng, D., Ma, Y., Guo, J., He, Z., Ma, B., et al., 2017. Benzyl substituted imidazolium ionic liquids as efficient solvent-free catalysts for the cycloaddition of CO₂ with epoxides: experimental and Theoretic study. *J. CO₂ Util.* 22, 44–52.
- Xia, X., Wan, R., Wang, P., Huo, W., Dong, H., Du, Q., 2018. Toxicity of imidazoles ionic liquid [C₁₆mim]Cl to Hela cells. *Ecotoxicol. Environ. Saf.* 162, 408–414.
- Xie, Z., Zhu, M., Nambo, A., Jasinski, J.B., Carreon, M.A., 2013. Microwave-assisted synthesized SAPO-56 as a catalyst in the conversion of CO₂ to cyclic carbonates. *Dalt. Trans.* 42, 6732–6735.
- Xu, Y., 2017. CO₂ absorption behavior of azole-based protic ionic liquids: influence of the alkalinity and physicochemical properties. *J. CO₂ Util.* 19, 1–8.
- Yang, C., Liu, M., Zhang, J., Wang, X., Jiang, Y., Sun, J., 2018. Facile synthesis of DBU-based ionic liquids cooperated with ZnI₂ as catalysts for efficient cycloaddition of CO₂ to epoxides under mild and solvent-free conditions. *Mol. Catal.* 450, 39–45.
- Ying, W., Cai, J., Zhou, K., Chen, D., Ying, Y., Guo, Y., et al., 2018. Ionic liquid selectively facilitates CO₂ transport through graphene oxide membrane. *ACS Nano* 12, 5385–5393.
- Ying, W., Hou, Q., Chen, D., Guo, Y., Li, Z., Zhang, J., et al., 2019a. Electrical field facilitates selective transport of CO₂ through a laminated MoS₂ supported ionic liquid membrane. *J. Mater. Chem. A* 7, 10041–10046.
- Ying, W., Zhou, K., Hou, Q., Chen, D., Guo, Y., Zhang, J., et al., 2019b. Selectively tuning gas transport through ionic liquid filled graphene oxide nanoslits using an electric field. *J. Mater. Chem. A* 7, 15062–15067.
- Yu, J., Wang, S., 2015. Modeling analysis of energy requirement in aqueous ammonia based CO₂ capture process. *Int. J. Greenh. Gas Control* 43, 33–45.
- Yuan, J., Fan, M., Zhang, F., Xu, Y., Tang, H., Huang, C., et al., 2017. Amine-functionalized poly(ionic liquid) brushes for carbon dioxide adsorption. *Chem. Eng. J.* 316, 903–910.
- Yue, S., Wang, P., Hao, X., Zang, S., 2017. Dual amino-functionalized ionic liquids as efficient catalysts for carbonate synthesis from carbon dioxide and epoxide under solvent and cocatalyst-free conditions. *J. CO₂ Util.* 21, 238–246.
- Yunus, N.M., Mutalib, M.I.A., Man, Z., Bustam, M.A., Murugesan, T., 2012. Solubility of CO₂ in pyridinium based ionic liquids. *Chem. Eng. J.* 189–190, 94–100.
- Zalomaeva, O.V., Chibiryakov, A.M., Kovalenko, K.A., Kholdeeva, O.A., Balzhinimaev, B.S., Fedin, V.P., 2013. Cyclic carbonates synthesis from epoxides and CO₂ over metal-organic framework Cr-MIL-101. *J. Catal.* 298, 179–185.
- Zhai, H., Rubin, E.S., 2018. Systems analysis of physical absorption of CO₂ in ionic liquids for pre-combustion carbon capture. *Environ. Sci. Technol.* 52, 4996–5004.
- Zhang, C., Du, Z., Wang, J., Wang, J., Zhou, T., Li, B., et al., 2018a. Exposed zebrafish (*Danio rerio*) to imidazolium-based ionic liquids with different anions and alkyl-chain lengths. *Chemosphere* 203, 381–386.
- Zhang, K., Hou, Y., Wang, Y., Wang, K., Ren, S., Wu, W., 2018b. Efficient and reversible absorption of CO₂ by functional deep eutectic solvents. *Energy Fuels* 32, 7727–7733.
- Zhang, C., Zhang, W., Gao, H., Bai, Y., Sun, Y., Chen, Y., 2017a. Synthesis and gas transport properties of poly(ionic liquid)-based semi-interpenetrating polymer network membranes for CO₂/N₂ separation. *J. Memb. Sci.* 528, 72–81.
- Zhang, Q., Yuan, H.Y., Fukaya, N., Yasuda, H., Choi, J.C., 2017b. Direct synthesis of carbamate from CO₂ using a task-specific ionic liquid catalyst. *Green Chem.* 19, 5614–5624.
- Zhang, X., Su, D., Xiao, L., Wu, W., 2017c. Immobilized protic ionic liquids: efficient catalysts for CO₂ fixation with epoxides. *J. CO₂ Util.* 17, 37–42.
- Zhang, X., Zhao, Y., Hu, S., Gliege, M.E., Liu, Y., Liu, R., et al., 2017d. Electrochemical reduction of carbon dioxide to formic acid in

- ionic liquid [Emim][N(CN)₂]/water system. *Electrochim. Acta* 247, 281–287.
- Zhang, X.M., Tu, Z.H., Li, H., Li, L., Wu, Y.T., Hu, X.B., 2017e. Supported protic-ionic-liquid membranes with facilitated transport mechanism for the selective separation of CO₂. *J. Memb. Sci.* 527, 60–67.
- Zhang, F., Gao, K.X., Meng, Y.N., Qi, M., Geng, J., Wu, Y.T., et al., 2016a. Intensification of dimethylaminoethoxyethanol on CO₂ absorption in ionic liquid of amino acid. *Int. J. Greenh. Gas Control* 51, 415–422.
- Zhang, Y., Ji, X., Xie, Y., Lu, X., 2016b. Screening of conventional ionic liquids for carbon dioxide capture and separation. *Appl. Energy* 162, 1160–1170.
- Zhang, J., Yu, L., Gong, R., Li, M., Ren, H., Duan, E., 2020. Role of hydrophilic ammonium-based deep eutectic solvents in SO₂ absorption. *Energy Fuels* 34, 74–81.
- Zhang, S., Sun, J., Zhang, X., Xin, J., Miao, Q., Wang, J., 2014. Ionic liquid-based green processes for energy production. *Chem. Soc. Rev.* 43, 7838–7869.
- Zhang, W., Gao, E., Li, Y., Bernards, M.T., He, Y., Shi, Y., 2019. CO₂ capture with polyamine-based protic ionic liquid functionalized mesoporous silica. *J. CO₂ Util.* 34, 606–615.
- Zhang, Y., Ji, X., Lu, X., 2015. Chapter 3 - Choline-based deep eutectic solvents for mitigating carbon dioxide emissions. In: Shi, F., Morreale, B.B.T.-N.M. (Eds.), *Novel Materials for Carbon Dioxide Mitigation Technology*. Elsevier, Amsterdam, pp. 87–116.
- Zhu, J., Xin, F., Huang, J., Dong, X., Liu, H., 2014. Adsorption and diffusivity of CO₂ in phosphonium ionic liquid modified silica. *Chem. Eng. J.* 246, 79–87.
- Zhu, X., Song, M., Xu, Y., 2017. DBU-based protic ionic liquids for CO₂ capture. *ACS Sustain. Chem. Eng.* 5, 8192–8198.
- Ziobrowski, Z., Rotkegel, A., 2017. The influence of water content in imidazolium based ILs on carbon dioxide removal efficiency. *Sep. Purif. Technol.* 179, 412–419.