



## Recent advances in carbon dioxide capture and utilization with amines and ionic liquids

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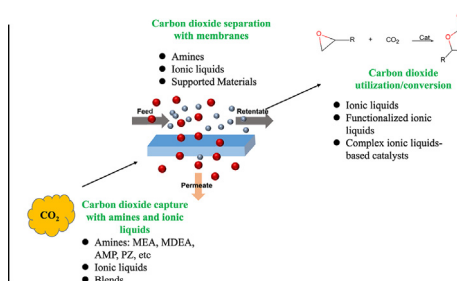
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### HIGHLIGHTS

- General methods for CO<sub>2</sub> capture and separation are discussed, particularly amine and ionic liquids-based solvent and materials.
- Ionic liquids used as catalysts for cycloaddition of CO<sub>2</sub> are summarized, which is beneficial for understanding the mechanism of CO<sub>2</sub> fixation.
- Future outlook for CO<sub>2</sub> capture, separation and conversion using amine and ionic liquids-based compounds is discussed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Global warming and climate change due to anthropogenic carbon dioxide (CO<sub>2</sub>) have aroused significant concerns at the global scale due to rapid economic growth in industries and other fields. Therefore, CO<sub>2</sub> capture, use, and storage have become particularly important. In this review, general background and methods for CO<sub>2</sub> capture and separation, in particular, on ionic liquids (ILs)-based solvents and materials, are discussed. Comprehensive surveys of ILs for CO<sub>2</sub> absorption are presented, which focused mainly on experimental researches, and then the concept is extended to functionalized absorbents and recent developments for CO<sub>2</sub> capture. Major advantages and disadvantages of amines-based and ILs-based absorbents are discussed in this review. Solutions of traditional amines (MEA, MDEA, DEA, AMP, PZ, etc.) and ILs (conventional ILs, functionalized ILs, etc.) are summarized. Moreover, research progresses on CO<sub>2</sub> separation are also introduced focusing mainly on amines and ILs-based membranes (e.g. supported amines membranes, SILMs). Furthermore, the fixation of CO<sub>2</sub> into cyclic carbonates catalyzed by ILs (pure ILs, complex catalyst system with ILs, supported ILs, etc.) is summarized, clearly explaining the mechanism of CO<sub>2</sub> fixation with ILs. Finally, exploration of some recent studies about CO<sub>2</sub> capture and conversion by ILs and challenges for further progress are presented and related suggestions are put forward.

## 1. Introduction

Global warming is a phenomenon caused by the concentration

increase of greenhouse gases (GHGs) in the atmosphere that causes drastic increase in temperature. In recent years, because of the rapid economic development and increment of human activities, global

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warming has become one of the greatest challenges faced worldwide, which has led to significant research attention on carbon dioxide (CO<sub>2</sub>) capture technologies. Therefore, carbon capture and storage (CCS) process has been regarded as a promising way to prevent CO<sub>2</sub> release in the atmosphere.

According to statistical data from international energy agency, energy-based activities lead to over two-thirds of GHGs emissions and more than 80% of CO<sub>2</sub> emission. Between 2000 and 2013, global CO<sub>2</sub> emissions increased at the rate of 2.6% per year [1]. Many reports provided the statistical data and effects and negative consequences of global warming. About 60% of the world is facing record-high temperatures every year. According to Global carbon project 2018, the actions for controlling and alleviating the emissions of anthropogenic CO<sub>2</sub> are becoming more and more urgent than ever before [2].

CO<sub>2</sub> capture methods such as absorption by liquid solvents, membranes, biological process, solid materials, etc. have been extensively studied in order to address the challenge of global warming. Among them, chemical absorption by alkanolamine solvents is the most mature commercial process that has been already used for CO<sub>2</sub> capture in a wide variety of industrial applications because of its high absorption efficiency and suitability for performance improvement of the power plant [3]. However, amine undergoes a strong chemical reaction with CO<sub>2</sub>; therefore, desorption process seems to be relatively difficult, thus resulting in high desorption cost and environment damage. Therefore, ionic liquids (ILs) have been proposed due to the favorable characteristics such as thermodynamic stability, nontoxicity, molecularly tunable, and nearly no vapor pressure [4]. However, ILs also have the drawbacks of high viscosity and high cost, which restrict their large-scale industry applications.

Despite years of study, the design of promising techniques for CO<sub>2</sub> capture still has a long way to go. Moreover, the reaction between absorbents and CO<sub>2</sub>, as well as the interaction between composite absorbents/solid materials and CO<sub>2</sub> need comprehensive explorations. More absorbents such as amines solutions, ammonia and porous solid materials can be considered. CO<sub>2</sub> absorption capacity is usually defined as follows.

$$Q(\text{absorption capacity}) = \frac{\text{CO}_2 \text{ absorbed/mol}}{\text{Absorbents/mol}} \quad (1)$$

Reducing the overall cost of CO<sub>2</sub> capture process is the most significant issue. In real process, CO<sub>2</sub> usually gets blended with other gases, thus taking into account only pure CO<sub>2</sub> capture strategies is unrealistic. Therefore, CO<sub>2</sub> separation process should also be taken into consideration. Absorption, adsorption, and cryogenics are major options for CO<sub>2</sub> separation [5]. Membranes are commonly applied in CO<sub>2</sub> separation process, and novel and advanced membranes modified with amines, ILs, or other materials are reported frequently due to their distinguished separation performance. The membranes for CO<sub>2</sub> adsorption have been developed early and steadily due to the low energy cost and commercial practical applications. In general, there are three steps for the permeation of CO<sub>2</sub> through a membrane [6]:

- (1) Adsorption of CO<sub>2</sub> on the higher pressure side of the membrane.
- (2) Diffusion of CO<sub>2</sub> through the membrane.
- (3) Desorption of CO<sub>2</sub> to the lower pressure side of the membrane.

Therefore, the gas separation performance depends on both absorption and desorption processes. More specifically, CO<sub>2</sub> separation process obeys solution-diffusion mechanism, and the permeability (P) of CO<sub>2</sub> through a membrane is connected with solubility (S) and diffusivity (D) [7]:

$$P = S \times D \quad (2)$$

Moreover, the ability of a membrane to separate gases can be measured based on selectivity ( $\alpha_{ij}$ ), which is related to the permeability of two species in the following manner:

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i}{D_j} \times \frac{S_i}{S_j} \quad (3)$$

In conclusion, permeability and selectivity are both related to gas species, interaction between gases and membranes, membrane's materials, or other features; and it has nothing to do with thickness of membranes. Till date, various absorbents and techniques for CO<sub>2</sub> capture, including absorption, adsorption, and membranes have been developed. For CO<sub>2</sub> capture, the major contradiction is how to balance the relationship between absorption and desorption, as well as environmental issues. For CO<sub>2</sub> separation with membranes, the main limitation is how to separate gases having fairly small differences in solubility and diffusivity with each other, and in the meantime pursue minimization of cost and environmental conservation. Consequently, the research on advanced absorbents and materials for enhancing CO<sub>2</sub> capture and separation comprehensively possesses enormous potential along with facing these challenges.

CO<sub>2</sub> conversion is another key to solve the greenhouse effect all over the world. Extensive research efforts have been devoted to the use of ILs, which can not only absorb CO<sub>2</sub> with high capacity, but also catalyze the cycloaddition of CO<sub>2</sub> with high activity, thus CO<sub>2</sub> conversion is comprehensively introduced in this review. Until now, several methods are available to convert CO<sub>2</sub> into high-value product, mainly forming C–O, C–N, C–H, and C–C bonds (cyclic carbonates, oxazolidinones, imidazolinone herbicides, etc). Among them, cyclic carbonate, polycarbonate, urea, and salicylic acid are the most widely produced materials in the industrial field. Cyclic carbonate is one of the most promising products obtained by direct coupling between CO<sub>2</sub> and epoxides, which has a great industrial interest and can be used in several fields. Owing to the toxicity and high cost of carbonyl chloride, CO<sub>2</sub> gradually replaced carbonyl chloride to be a new carboxylation reagent. Yield and selectivity of products are considered to be important assessment criteria for evaluating the catalytic performance of a catalyst. Turnover frequency (TOF) measures the catalytic reaction rate of a catalyst and represents the intrinsic activity of the catalyst. Fig. 1 presents the catalytic mechanism for the synthesis of cyclic carbonate. First, Lewis acid, usually hydroxyl groups or some metal cations, activates the

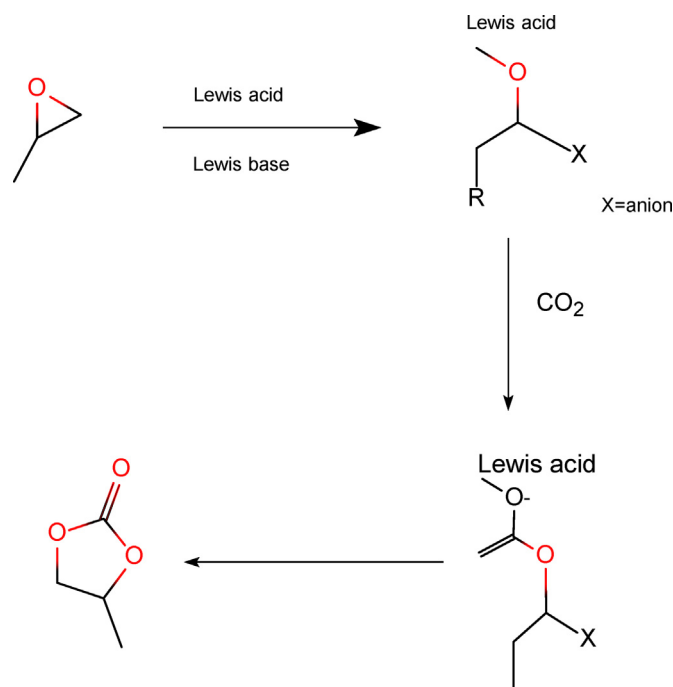


Fig. 1. Catalytic mechanism of the synthesis of cyclic carbonate from CO<sub>2</sub> and epoxide.

epoxide, and the anions ( $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , halogen anions, etc.) initiate a nucleophilic attack on carbon atom to display the ring-opening process, then  $\text{CO}_2$  is added to form the intermediate, and finally cyclic carbonate is regenerated.

In this review, conventional methods for  $\text{CO}_2$  capture are first discussed from the perspective of  $\text{CO}_2$  absorption capacity, environmental friendly nature, and cost effectiveness, taking into consideration amine solutions, inorganic solutions, ILs, etc. Then, amine and ILs supported membranes for  $\text{CO}_2$  separation are also introduced based on the separation performance and other characteristics.  $\text{CO}_2$  conversion catalyzed by ILs is presented at the same time. In general, their merits and demerits with respect to the whole perspective are discussed, primarily highlighting the history and development of ILs and their supported materials. Furthermore, this review also focuses on the fixation of  $\text{CO}_2$  into cyclic carbonate catalyzed by ILs or ILs-based materials to further understand the utilization of  $\text{CO}_2$  and the role of ILs in the reaction. By introducing some mature and immature methods for  $\text{CO}_2$  capture and conversion, a clear insight into the entire study of  $\text{CO}_2$  utilization chain, in particular, their differences and relationship can be obtained.

## 2. Research progress on carbon dioxide capture with amines and ionic liquids

Basic techniques for  $\text{CO}_2$  capture include absorption, adsorption, membranes, or others. In general, absorption process is related to a liquid absorbent for capturing or separating  $\text{CO}_2$ , which has quite a long history for  $\text{CO}_2$  capture. Amines and ammonia are the most representative sorbents because of their good  $\text{CO}_2$  absorption capacity; however, their use encounters high energy consumption and other issues. Adsorption is a promising technique using solid sorbents or liquid sorbents. Porous materials (e.g. zeolites, metal organic frameworks, and molecular sieves, etc.) are beneficial for adsorption process due to their appropriate surface structures. IL, in particular, conventional IL constitutes an important member of adsorption techniques likewise, and in this review ILs are discussed in detail. Membranes, which separate gases based on the rules of absorption, diffusion, and desorption, have many benefits over  $\text{CO}_2$  separation, for example low energy consumption and easy to blend with other absorbents. However, the stability, durability, and separation performance require further in depth investigation in the future. In general, amines absorb  $\text{CO}_2$  by chemical absorption and traditional ILs by physical absorption. Nonetheless, there are many exceptions, for example some task-specific ILs capture  $\text{CO}_2$  by reacting with it. Fig. 2 represents some major methods for  $\text{CO}_2$  capture and separation and their specific categories.

In this review,  $\text{CO}_2$  absorbents are analyzed and studied from the following considerations, and the advantages and disadvantages of common absorbents are listed in Table 1.

- ☐ Reaction rate;
- ☐  $\text{CO}_2$  absorption capacity;
- ☐ Renewable energy consumption and recovery rate;
- ☐ Environmentally friendly.

**Table 1**  
Advantages and disadvantages of methods of  $\text{CO}_2$  capture and separation [8].

Type of absorbents	Name	Advantages	Disadvantages
Amine solutions	MEA	Quick absorption	High recycling energy consumption, and easily undergoes oxidative degradation
Amine solutions	MDEA	High absorption capacity and low recycling energy consumption	Relatively slow absorption rate
Amine solutions	DEA	Quick absorption	High recycling energy consumption, and easily undergoes oxidative degradation
Amine solutions	AMP	High absorption capacity and absorption rate	High cost and immature technology
Amine solutions	PZ	High absorption rate	High cost, toxicity, and corrosion
Ionic liquids	Conventional ILs	Physical absorption, environmentally friendly, stable and tailorable	High cost and relatively low $\text{CO}_2$ absorption capacity because of high viscosity
Ionic liquids	Functionalized ILs	Chemical absorption, environmentally friendly, stable and tailorable	High viscosity, high cost, or other drawbacks
Inorganic solutions	Ammonia	High absorption efficiency and low recycling energy consumption	High volatility
Membranes	Amines-based membranes	Application: $\text{CO}_2$ separation	Lower rate of $\text{CO}_2$ absorption than MEA
Membranes	IL-based membranes	Decrease the viscosity of ILs	High cost

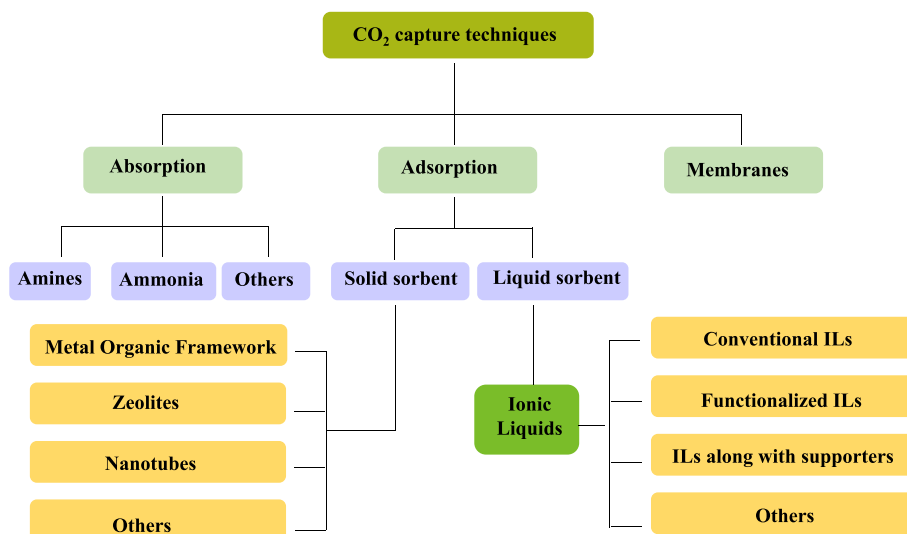


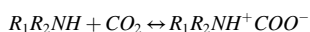
Fig. 2. Classification of  $\text{CO}_2$  capture techniques.

## 2.1. Amines and amine-based materials for carbon dioxide capture

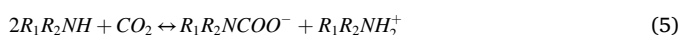
### 2.1.1. Amines

Chemical absorption especially using alkanolamines solutions to capture CO<sub>2</sub> dates back to 1930s and it has been proposed to be an effective applicable method for CO<sub>2</sub> capture since then. However, alkanolamines possess drawbacks such as high recycling energy consumption and corrosion. As a result, many other absorbents including various compounds and solid materials have been studied to overcome these issues; nonetheless, the merits of alkanolamines solutions in CO<sub>2</sub> capture cannot be neglected.

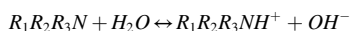
Usually alkanolamines can be sorted depending on how many alkyl groups are bonded to the nitrogen atom of amino group, which includes primary, secondary, and ternary amines. The reaction process of primary and secondary amine with CO<sub>2</sub> is represented as follows: (1) formation of zwitterion; (2) deprotonation of zwitterion, and formation of carbamate [8] (Eq. (4)):



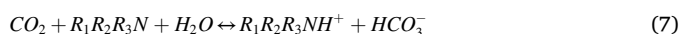
The overall reaction is (Eq. (5)):



According to Donaldson and Nguyen, the reaction of a ternary amine with CO<sub>2</sub> is different from that of primary and secondary amine, which does not form zwitterion. Ternary amine can only play a role in catalyzing the dissociation of water because it cannot react directly with CO<sub>2</sub> [9] (Eq. (6)).



The overall reaction equation is (Eq. (7)):



The most common alkanolamines include monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA). Besides, the sterically hindered amines or cyclic diamines such as 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) also display their unique advantages than traditional primary, secondary, and ternary amines. Table 2 presents the comparison of CO<sub>2</sub> absorption performance by typical aqueous amines.

Freguia et al. [14] reported that four primary and secondary amines showed prominent absorption capacity among 76 amines investigated, and MEA was found to be one of the most efficient absorbent for CO<sub>2</sub>. Moreover, MEA has been used in many commercial technologies such as Fluor Daniel technology and Econamine FG Plus. Abu-Zahra et al. [11] reported that energy saving could be realized by changing the concentration and operating pressure. In order to optimize the solvent loading and energy consumption, they investigated solvent concentration and operating pressure. The result exhibited that it was better to operate at low MEA loading of 0.3 with 40 wt% MEA solution and at 210 kPa, and the final energy consumption was 23% lower than that of the base. However, the corrosion and solvent degradation of higher-concentration MEA solution may limit its industrial applications.

Amines may result in the formation of undesirable byproducts in the process of oxidative degradation. In order to select energy-efficient CO<sub>2</sub> absorbent, Song et al. [12] measured the regeneration energy of CO<sub>2</sub> absorption of 30 wt% sodium glycinate (SG) solution and MEA by comparing enthalpy of reaction, and they found that MEA exhibited the lower regeneration energy. However, SG solutions displayed higher CO<sub>2</sub> absorption capacity than MEA, signifying a tradeoff between absorption capacity and regeneration energy.

**Table 2**

CO<sub>2</sub> absorption by aqueous amines experimental study.

Author	Year	System	Advantages	Disadvantages
Freguia et al. [14]	2003	76 amines including MEA	MEA is one of the most efficient absorbent for CO <sub>2</sub>	/
Kagimoto et al. [46]	2010	40 wt% MEA solution stripper operating pressure: 210 kPa	A minimum thermal solvent could be achieved	Corrosion and solvent degradation of higher MEA concentration
Song et al. [12]	2008	30 wt % sodium glycinate (SG) solution and MEA	MEA has the lower regeneration energy.	Undesirable byproducts
Benamor et al. [15]	2008	Aqueous DEA	High absorption rate due to their stabilizes of carbamates formation	0.5 mol CO <sub>2</sub> /mol amine
Rinker et al. [19]	2000	Mixture of DEA and MDEA	/	MDEA has nearly nothing to do with the deprotonation of the zwitterion
Sartori et al. [20]	1983	Hindered amines	Higher capacity and absorption rate than common amines like MEA	High viscosity or other drawbacks
Aroonwilas et al. [26]	1998	Sterically hindered amines such as AMP	The absorption ratio: 1 mol CO <sub>2</sub> /mol of amine Induce less corrosion than traditional amines	Lower rate of CO <sub>2</sub> absorption than MEA

Similarly compared to ILs, MEA possesses higher desorption energy consumption. Yang et al. [13] used MEA solutions blended with IL [bmim][BF<sub>4</sub>] to reduce energy consumption during desorption process. Owing to the oxidative degradation and high heat of reaction, pure MEA solutions had higher absorbent loss and energy consumption. Together with IL, they found that the energy consumption could decrease to 62.8% compared to pure amine solutions.

Apart from experimental research, it is also possible to calculate the operating parameters and costs by simulations. Modeling of CO<sub>2</sub> capture by aqueous MEA was carried out through thermodynamic model and rate model based on electrolyte-Non-Random Two Liquid (NRTL) equilibrium model, and the relationship among stripper pressure, rate of CO<sub>2</sub>, solvent circulation rate, steam requirements and steam consumption, and packing height were calculated to choose the operating parameters in economic and environmental ways [14].

Other than MEA, DEA and MDEA are also better choices in gas treating technology for their high CO<sub>2</sub> absorption capacity. Benamor et al. [15] demonstrated the kinetics of absorption process between CO<sub>2</sub> and DEA. As a secondary amine, the reaction of DEA with CO<sub>2</sub> obeys the above mentioned rules:

#### (1) Formation of zwitterion



#### (2) deprotonation of zwitterion and formation of carbamate



Compared to the heat of reaction of MEA (85.6 kJ mol<sup>-1</sup> CO<sub>2</sub>), DEA has a lower heat of reaction of 76.3 kJ mol<sup>-1</sup> CO<sub>2</sub>; therefore, the energy demand is lower than that of MEA, and shows higher cyclic capacity. Galindo et al. [16] studied the equilibrium loading of DEA, which was comparable to that of MEA, but DEA possessed lower absorption kinetics.



MDEA is also considered as a useful tertiary amine solution for CO<sub>2</sub> absorption because of low recycling energy consumption. Barzagli et al. [17] studied pure DEA and MDEA for CO<sub>2</sub> absorption, and found that MDEA has nearly similar kinetics and absorption capacity to those of DEA; nonetheless, MDEA displays lower absorption efficiency (74%) than DEA (71.3%).

As mentioned above, both MEA and DEA have been used for CO<sub>2</sub> capture for a long time because of high absorption rate due to stabilization of formed carbamates. Conversely, high solvent regeneration cost can be needed due to the stabilization of carbamates. Moreover, compared to some other types of amines, MEA and DEA possess the disadvantage of fairly low CO<sub>2</sub> loading, which is appropriately 0.5 mol CO<sub>2</sub>/mol amine. Moreover, MDEA different from the above mentioned two amines, is a type of tertiary alkanolamines and has the drawback of low reactivity owing to the formation of bicarbonates; however, the CO<sub>2</sub> absorption performance can reach 1 mol of CO<sub>2</sub>/mol of amine [18].

Till date, significant research efforts have been devoted to the study on blends of different absorbents, for example various types of amines. Barzagli et al. [17] also reported that the absorption efficiency of AMP-MDEA blends is higher than that of both pure AMP and MDEA solutions, which indicated that the amines mixture may sometime exhibit better performance. Mixture of DEA and MDEA for CO<sub>2</sub> absorption was studied by Rinker et al. [19]. When modelling the absorption process, they incorporated reversible reactions, coupling, as well as penetration theory. The absorption performance of pure DEA, pure MDEA, and blend of DEA and MDEA could be predicted via theoretical analysis.

Sartori et al. [20] reported that steric hindrance is a key factor during the reaction process between CO<sub>2</sub> and amines. A bulky substituent group can decrease the stability of carbamate; and therefore achieve higher CO<sub>2</sub> loadings. Hindered amines have higher capacity (20–40%) and absorption rate (up to 100%) than common amines such as MEA. However, they also have their own disadvantages. Studies indicate that complementing each other's advantages by mixing various amines might be a promising method.

PZ is a type of diamine which can effectively improve CO<sub>2</sub> absorption kinetics. Considering that aqueous PZ exhibits more than double of absorption rate than MEA, addition of PZ is a reasonable choice. However, the lower boiling point and higher viscosity limit its high concentration in the field of CO<sub>2</sub> capture, thus blends of amines might be a better choice [21]. Apart from CO<sub>2</sub> capture by chemical absorption via aqueous-based solvent, there are also studies focusing on regeneration parameters by evaluating absorption parameters. It turns out that piperidine (PIP) and PZ have better absorption-regeneration performance [22]. Taking this into account, researchers used modified approach to make their weaknesses irrelevant. Oyeneke et al. [23] reported that MEA/PZ and MDEA/PZ mixed systems possessed less energy consumption (22%) and better performance than 30 wt% MEA solution. Together with PZ, MEA could retain the advantages of high absorption efficiency and prevent high energy consumption. A dynamic model of CO<sub>2</sub> absorption rate based on experiment showed that combining with DETA, the activation energy becomes higher, thus DETA + MEA system could be affected by temperature than MEA system alone, leading to its improvement [24]. Similarly, Du et al. [25] studied CO<sub>2</sub> capture using tertiary amines blended with PZ and obtained promising CO<sub>2</sub> absorbents.

Recently, sterically hindered amines such as AMP have attracted significant attention due to their high CO<sub>2</sub> capacity. AMP possesses the same hindered form as MEA [26]; therefore, it can react with CO<sub>2</sub> and reach the absorption ratio at about 1 mol CO<sub>2</sub>/mol of amine, compared to MEA reaching capacity of only 0.5 mol CO<sub>2</sub>/mol of CO<sub>2</sub>. Besides, AMP can induce less corrosion than traditional amines. Unfortunately, AMP has lower rate of CO<sub>2</sub> absorption than MEA [24]. Although the absorption performance and energy consumption can be obtained by experiments and then compared, many studies focused on multiple-criteria analysis of carbon capture to deeply investigate the principle of amines absorbent. According to the ELECTROLYTE model of Aspen Plus, process data such as molar flows, composition, and operating pressure and

temperature, etc. can be obtained by carbon capture process simulation. The simulation result exhibited that pure amine solutions (MEA, DEA, MDEA, AMP) and their blends are good alternatives. However, considering the energy cost, blends such as 20% MEA with 10% AMP provided better performance in the CO<sub>2</sub> absorption process [27].

### 2.1.2. Amine-based materials

Silica materials (e.g. SBA-15, SBA-16, MCM-41, etc.) can act as promising and ideal support structures for CO<sub>2</sub> immobilized absorbents due to their high surface area. Ko et al. [28] found that double-walled silica nanotubes (DWSNTs) with amines could be a promising adsorbent for capturing CO<sub>2</sub>. Therefore, efficient CO<sub>2</sub> adsorption materials can be obtained by preparing amine-impregnated mesoporous silica sorbents. Watabe and Yogo [29] reported that the amine-based silica absorbents increased as much as 70 wt% amine than 50 wt% of traditional porous materials.

Moreover, blended amines-based silica sorbents also exhibited high CO<sub>2</sub> adsorption capacity for about 5.6–6.4 wt% and CO<sub>2</sub>/N<sub>2</sub> selectivity efficiency for 0.47–0.48. Primary amine (50%) and secondary amine (50%) are the most ideal choice [30]. Polyamine-modified fumed silica was designed for binary adsorption of CO<sub>2</sub> and H<sub>2</sub>S by Yoosuk et al. [31]. Among five categories of amines, PEI800 (polyethyleneimine with a molecular weight of 800) displayed the best compromise between CO<sub>2</sub> and H<sub>2</sub>S. Chen and Bhattacharjee [32] found that amine-based TS performed better when the amine loading reaching 70%, which signifies that amine-grafted TS exhibits superior comprehensive performance for CO<sub>2</sub> capture.

## 2.2. Ionic liquids and ionic liquid-based materials for carbon dioxide capture

### 2.2.1. Introduction to ionic liquids

CO<sub>2</sub> absorption by MEA or other amines has been widely used for a long time for they have demonstrated many advantages. Amines can achieve high absorption capacity; however, the cost and solvent degradation need to be taken into account because of the problems it may cause. Therefore, it is necessary to find a promising alternative to overcome corrosion and contamination. ILs commonly occur as liquid at room temperature and can be synthesized from the mixture of organic cations and various anions [33,34].

Conventional ILs through physical absorption capture CO<sub>2</sub> into spaces among ions, which illustrate that the absorption capacity is limited by spaces. ILs have the characteristics of intrinsic ionic conductivity, low volatility, high thermal stability, wide liquid range, non-flammability, and most importantly, they can be designed for specific application. These characteristics make ILs attractive for CO<sub>2</sub> absorption [35,36].

The most promising CO<sub>2</sub> capture technology must be energy-efficient; therefore, ILs are considered to be more potential absorbents than amines. According to Shiflett's study [37], there was nearly 16% decrease in the energy losses than commercial processes when the amines were blended with ILs. Certainly, ILs have some drawbacks and limitations, thus tremendous research efforts have been made in making the absorption capacity higher and viscosity lower.

### 2.2.2. Conventional ionic liquids

Blanchard et al. [38] synthesized the IL ([bmim][PF<sub>6</sub>]) and reported that CO<sub>2</sub> was highly soluble in [bmim][PF<sub>6</sub>]. ILs exhibited relatively high selectivity, thus the solubility of 0.6 mol CO<sub>2</sub>/mol IL could be achieved in the temperature range of 40–60 °C and at pressure of 0–9.5 MPa. This indicated the feasibility of ILs as CO<sub>2</sub> absorbent. By then, ILs have been considered as green and environmentally friendly alternatives to organic solvents because they possess lower risk of exposure and “tunability” of the solvent properties [39].

Furthermore, how ILs perform when absorbing CO<sub>2</sub> compared to the traditional absorbents such as MEA requires comprehensive discussion. CO<sub>2</sub> shows higher solubility in ILs than in other normal solvents; and

some properties such as heat capacity, density, and surface tension are better than those of conventional solvents [40]. ILs still have a relatively low absorption performance when facing organic amine solution because of the difference in absorption mechanism. However, ILs usually have the disadvantages due to its high viscosity and low absorption capacity [41], which result in slower CO<sub>2</sub> absorption kinetics [42]. To improve the solubility in ILs, it is necessary to evaluate the influence of ILs structure on CO<sub>2</sub> absorbing performance. Muldoon et al. [43] presented ILs containing fluoroalkyl chains and showed improvement in CO<sub>2</sub> solubility.

### 2.2.3. Functionalized ionic liquids

Functionalized ILs (or task-specific ILs) can achieve higher absorption performance according to the mechanism of CO<sub>2</sub> capture. By introducing suitable groups in IL, they can reach even higher absorption efficiency and lower cost than ever [44]. As mentioned above, the process between conventional ILs and CO<sub>2</sub> is physical absorption. In contrast, functionalized ILs were designed for not only physical absorption, but also chemisorption to react and bond CO<sub>2</sub> chemically by adding some moieties such as amines, so that ILs can increase their absorption capacity. Bates et al. [45] synthesized amino-functionalized IL, namely, TSIL (Fig. 3) and the absorption capacity could approach 0.5 mol CO<sub>2</sub>/mol TSIL, which is comparable to that of MEA. This ratio of CO<sub>2</sub> and ILs originate from amine deprotonation of a carbamic acid intermediate.

Researchers have been focusing on designing ILs with reduced viscosity and high absorption capacity, which can be initiated by designing functional ILs or different devices or structures to improve contact area or other factors affecting mass transfer coefficient. In order to overcome the drawbacks of traditional ILs, many researchers studied and designed different types of functionalized ILs for CCS process. Among these, amino acid-based ILs stand out because of their low toxicity and high absorption capacity toward CO<sub>2</sub>. Most notably, amino groups can be introduced to ILs to modify them chemically. Kagimoto et al. [46] synthesized different types of amino acid salts with relatively low density, which could be separated from water because of their hydrophobicity. Zhang et al. [47] synthesized tetrabutylphosphonium amino acid [P(C<sub>4</sub>)<sub>4</sub>][AA] and displayed rapid and reversible CO<sub>2</sub> absorption.

Amino acid-based ILs perform better than conventional ILs; however, the absorption capacity still needs to be improved. As mentioned above, the molar uptake of CO<sub>2</sub> per mole of TSIL approached 0.5, which is relatively low compared to former studies, and there are two approaches to solve the problems: the need of two molecules of amine to react with one molecule of CO<sub>2</sub>, and formation of solid or highly viscous products [48]. Another way out for capacity improvement is to design dual amino-functionalized ILs. Zhang et al. [49] used IL [aP<sub>4443</sub>][AA] for CO<sub>2</sub> absorption and found that the absorption capacity approached 1 mol CO<sub>2</sub> per mol IL.

### 2.2.4. Blends of ionic liquids and other compounds

Although amino ILs have promising reactivity toward CO<sub>2</sub>, they meet drastic increase in viscosity in the process of CCS, which exerts a negative effect on absorption process. Therefore, researchers are facing the

challenge about how to lower the viscosity and at the same time increase the absorption performance. ILs mixed with amine or other compounds can make up their own limitation and improve their function. Camper et al. [50] mixed RTILs and amines together for CO<sub>2</sub> capture without special design and found that they could be tailored to absorb CO<sub>2</sub> under different conditions when needed.

When amine-based anion-tethered IL was mixed with water and the influence of water and temperature was evaluated, the result indicated that the viscosity of the absorbents decreased, and CO<sub>2</sub> capacity also went down. This indicated that water may not be a good diluent for CO<sub>2</sub> absorbents [51]. Chen et al. [52] used [emim][Ac] as the diluent for AAILs to prevent the increase in the viscosity after CO<sub>2</sub> absorption. The CO<sub>2</sub> absorption rate in AAIL mixed with [emim][Ac] was dramatically improved compared to that in pure AAILs, which indicates that it is a type of effective absorbents for the CO<sub>2</sub> capture.

### 2.2.5. Reversible ionic liquids

Reversible ILs, based on amidinium or guanidinium alkylcarbonate salts, also show higher absorption capacity than conventional ILs. Heldebrant et al. [53] reported that reversible uptake of COS, CS<sub>2</sub>, and SO<sub>2</sub> could be achieved by ILs with o-alkylxanthate, o-alkylthiocarbonyl, and o-alkylsulfite anions (Fig. 4). The reversible ILs show reversible binding

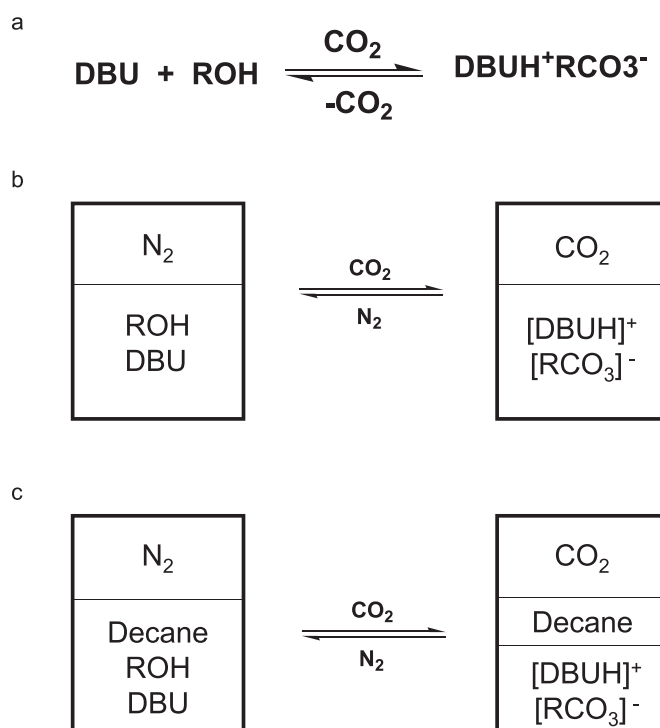


Fig. 4. The switching process of the solvents [54].

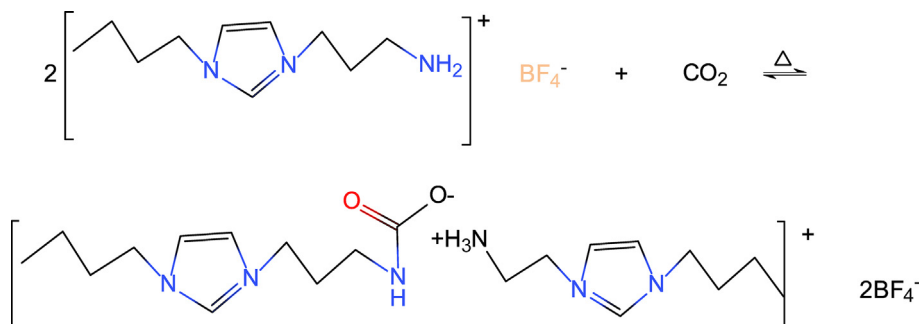


Fig. 3. Proposed reaction between TSIL and CO<sub>2</sub> [45].

and potential to act as sensors. Another similar study designed reversible nonpolar to polar ILs for CO<sub>2</sub> capture. They reported that a mixture of DBU and 1-hexanol could absorb CO<sub>2</sub> at normal pressure and temperature. The absorbent itself could be shifted reversibly to a different liquid in properties, but it has the disadvantage of significant increase in the viscosity of the liquid after reaction [54].

### 2.2.6. Polymeric ionic liquids

Polymeric ILs (PILs), are polyelectrolytes or polymers whose repeating unit bear an electrolyte group [55]. They show the properties of both ILs and polymer. Tang et al. [56] unexpectedly found that PILs behave better and faster toward CO<sub>2</sub> adsorption compared to room-temperature ILs, and the adsorption and desorption are reversible, which make it promising for CO<sub>2</sub> separation. Among three types of PILs, CO<sub>2</sub> adsorption capacity of PVBH is 0.305 wt% compared to 0.256 wt% of room-temperature IL [bmim][BF<sub>4</sub>]. By measuring cycles of CO<sub>2</sub> adsorption and absorption curve, apparently PILs are faster and better in CO<sub>2</sub> capture than RTILs in this situation. Tang et al. [57] also reported PILs with varied structures including cations, anions, backbones, and substituents, and investigated CO<sub>2</sub> capture capacity accordingly. They found that cation with short alkyl group, BF<sub>4</sub><sup>-</sup> anion, and polystyrene backbone were favorable structures for CO<sub>2</sub> capture. It was also observed and reported that poly([2-(methacryloyloxy) ethyl]trimethylammonium chloride) (poly([META]pCl<sup>-</sup>)), a type of PIL, displayed high CO<sub>2</sub>/N<sub>2</sub> selectivity. Apart from this, by testing anions such as BF<sub>4</sub><sup>-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, it was reported that anions had nearly nothing to do with CO<sub>2</sub> adsorption performance [58].

Various types of PILs have emerged as effective candidates. Xiong et al. [59] prepared imidazolium-based ILs and investigated their structures and properties (Fig. 5). The CO<sub>2</sub> adsorption capacity with the PILs they studied was relatively higher than those of IL monomers and many other PILs, which was three times as high as that of [bmim][PF<sub>6</sub>], and the adsorption equilibrium time of PILs-BF<sub>4</sub> was only about 20 min, compared to [bmim][PF<sub>6</sub>] for about 125 min.

Based on the anion effect on CO<sub>2</sub> adsorption, Bhavsar et al. [60] studied various PILs. Regarding diallyldimethylammonium chloride P [DADMA][Cl] (Figs. 6 and 7) as a precursor, they changed anions into types of carboxylates, sulphonates and inorganic. In contrast to the other two types, acetate anion P[DADMA][Ac] exhibited appreciable selectivity over CO<sub>2</sub> and N<sub>2</sub>.

Therefore, PILs display different CO<sub>2</sub> solubility when switching anions and cations. Shaligram et al. [61] reported the effects of substitution asymmetry on imidazole moiety of two types of polybenzimidazoles (PBI-Bul and PBI-HFA). Many new categories of PILs have emerged since then. Quaternary ammonium-based PILs have been reported, and it was found that the anion, rather than the cation, is chemically preferred for CO<sub>2</sub> capture as illustrated by electrostatic potential map [62].

Owing to the high viscosity and high amine loss and degradation during CCS process with amine solvents, one can combine supported structures to overcome these drawbacks. Wang et al. [63] used a PIL with quaternary ammonium ions attached to the polymer matrix for CCS process, and found that due to its unique feature, it could make up the thermodynamic behavior when absorbing CO<sub>2</sub> and thus achieving spontaneous cooling during CO<sub>2</sub> absorption. Table 3 summarizes the comparative analysis of CO<sub>2</sub> absorption/adsorption performance by

typical ILs.

## 3. Research progress on carbon dioxide separation with membranes

### 3.1. Supported amines membranes

It is well known that GHGs treatment is a worldwide public concern issue due to the adverse environmental issues; therefore, finding methods to reduce concentrations of GHGs have aroused extensive concern at the global scale. Besides removal of CO<sub>2</sub>, separation of CO<sub>2</sub> from natural gas is another example of CCS process. In order to enhance the mass transfer performance of amines, many relevant devices have been designed for CCS process. In the field of separation, membranes have been paid significant attention to due to their advantages for gas separation, as well as the enhancement in the limits of productivity and efficiency and stability under various conditions [7] (see Fig. 8).

Traditional membranes for gas separation have their own limitations and drawbacks, up to 90% of the common commercial membranes are made of less than ten membrane materials [66]. Porous materials have been considered as a strong candidate for CO<sub>2</sub> absorption and separation. Recently, amine-functionalized nanoporous materials have attracted significant research interest. They have advantages (e.g. high capacity, selectivity, fast kinetics, and low costs), which pure absorbents do not have. Moreover, stability and viscosity remain to be main bottleneck of membranes application. Yu et al. [67] developed various types of amine-silica membranes, and the results indicated that sterically hindered amines-based silica membranes showed faster kinetics for adsorption and desorption than unhindered amines. All the membranes displayed excellent molecular sieving at high temperatures except for CO<sub>2</sub>, making it possible for amine-based membranes holding back CO<sub>2</sub> and permeating other gases. After using various types of amines, they believed that TA-Si xerogel powders exhibited faster adsorption and desorption kinetics compared to PA-Si and SA-Si, which are not sterically hindered. The greatest merit of membranes is their excellent molecular sieving at high temperature and the separation index of TA-Si could reach as much as 0.34 mol m<sup>-1</sup> s<sup>-1</sup> at 35 °C.

Jindaratamee et al. [68] reported the use of liquid membranes of amine liquids with glycol compounds for the purpose of separating CO<sub>2</sub> from air. The emphasis and difficulty lie in how to absorb CO<sub>2</sub> when the concentration in air is only 400 ppm. As a result, the permeability coefficient of CO<sub>2</sub> through supported liquid membranes with MEA at 25 °C was 7.0 × 10<sup>-12</sup> mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1</sup>, and the membranes presented a 0.08 g-CO<sub>2</sub>/h recovery from air, sometimes could recover 92% CO<sub>2</sub>. Moreover, it could be concluded that the effects of amine concentration and types were apparent on the permeability of amine-supported membranes.

In order to improve CO<sub>2</sub>/CH<sub>4</sub> selectivity of mixed matrix membranes, Nguyen et al. [69] synthesized an amine-based hierarchical Ca-A zeolite and comprised into membrane polymers, which exhibited confirmed 53.3% enhancement for CO<sub>2</sub>/CH<sub>4</sub> selectivity. Poly(vinyl alcohol) (PVA), poly(ethylene glycol), or other types of polar compounds can interact with acidic gases which make them suitable materials for CO<sub>2</sub> separation membranes [70]. Francisco et al. [71] combined alkanolamines and PVA matrix together to separate CO<sub>2</sub> and N<sub>2</sub>. MEA, AMP, DEA, and MDEA were investigated and DEA stood out the best among four types of

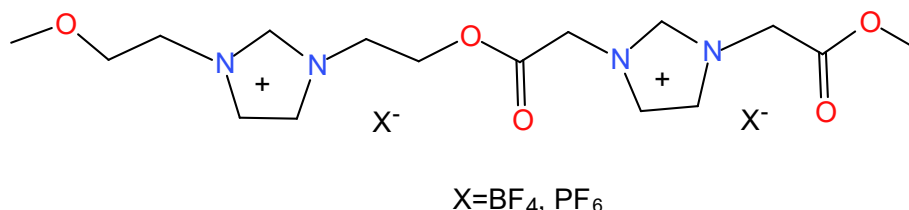


Fig. 5. Structural formula of the polymeric ionic liquids [59].

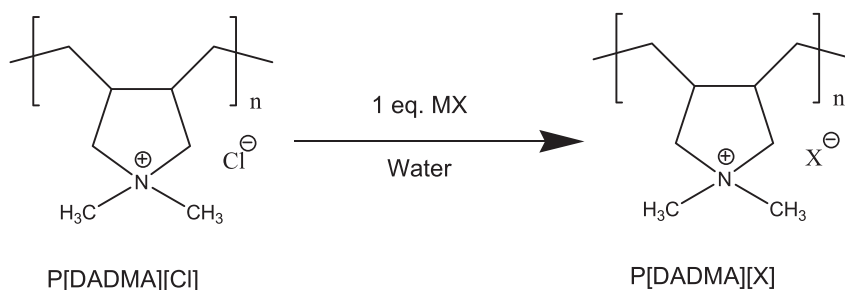


Fig. 6. Structural formula of P[DADMA][X] [60]. Copyright (2012) Elsevier.

$M = \text{Ag}^+, \text{Li}^+ \text{ or } \text{Na}^+;$

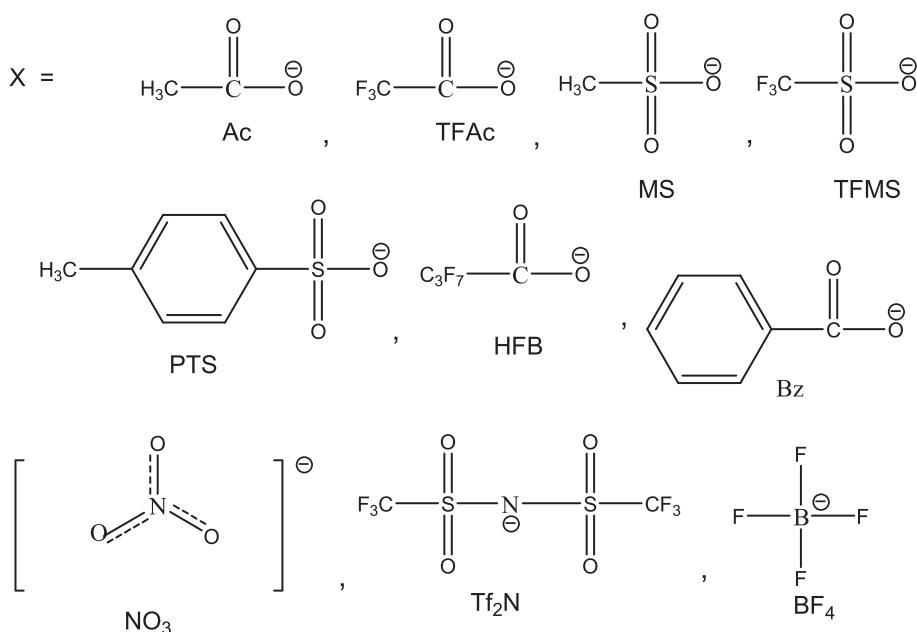


Fig. 7. Categories of tested anions [60]. Copyright (2012) Elsevier.

alkanolamines. Furthermore, amine content, feed pressure, and temperature were also studied in order to make it perform better. The experiments exhibited the best option for amine content, and the permeance of  $\text{CO}_2$  decreased with the increase in  $\text{CO}_2$  pressure rather than  $\text{N}_2$ .

Owing to superior performance of sterically hindered polyvinylamine, Tong et al. [72] introduced sterically hindered amines into polyvinylamine membranes, which exhibited 24% enhancement toward  $\text{CO}_2$  permeability and 14% on  $\text{CO}_2/\text{N}_2$  selectivity at  $57^\circ\text{C}$  compared to unmodified ones. Moreover, the results were further improved by increasing the temperature to  $102^\circ\text{C}$ , reaching a  $\text{CO}_2/\text{N}_2$  selectivity of 350 and  $\text{CO}_2/\text{H}_2$  of 162.

It is already known that amine-based membranes are promising alternatives for  $\text{CO}_2$  separation. Messaoud et al. [73] studied the influences of introducing primary and secondary amine functional groups into an organic-inorganic membrane. The results indicated that the primary amine membrane demonstrated the same  $\text{CO}_2$  permeance and a  $\text{CO}_2/\text{CH}_4$  selectivity of 70 compared to the four of the amine-free membranes. Among them, secondary amine membrane exhibited more than six times  $\text{CO}_2$  permeance and a  $\text{CO}_2/\text{CH}_4$  selectivity of 140.

Facilitated transport is the key for improving  $\text{CO}_2$  separation process, such as introduction of  $\text{CO}_2$ -facilitated transport fillers. Xin et al. [74] integrated PEI with abundant amine groups into titania fillers and realized  $\text{CO}_2/\text{CH}_4$  selectivity of 58 and that of  $\text{CO}_2/\text{N}_2$  of 64. Then, the influence factors on separation performance of amine-based PVAM

membranes were studied by Qiao and co-workers [75]. The  $\text{CO}_2/\text{H}_2$  separation performance was found to be worse with the increase of layer thickness, and stability of membranes showed no effect on separation process.

Undoubtedly, there are other factors in the real situation, for example, separation of  $\text{CO}_2$  from power plants using fossil fuels.  $\text{SO}_2$  serves as the minor contaminants and may significantly influence the polymeric membranes. Wu et al. [76] investigated  $\text{SO}_2$  interference on sulfonated PVA membranes and found that membranes at  $57^\circ\text{C}$  with  $\text{SO}_2$  at ppm level were stable and applicable for use in  $\text{CO}_2$  absorption from real gas. Moreover, Tong et al. [77] reported that how the water vapor affected the performance of amine-based membranes. Owing to highly hydrophilicity of membranes comprising 34% polyvinylamine and 66% sodium formate, they demonstrated high  $\text{CO}_2$  permeance and water vapor permeance. According to the experiment results, water vapor permeance had nothing to do with layer thickness and reduced linearly with the increase of layers' number. Therefore the resistance of water vapor was mainly governed by the substrate, and the dominant factor for separating  $\text{CO}_2$  was the selective layer.

### 3.2. Supported ionic liquid membranes

To improve mass transfer performance of ILs, many relevant devices have been designed for CCS process. Owing to the distinguished



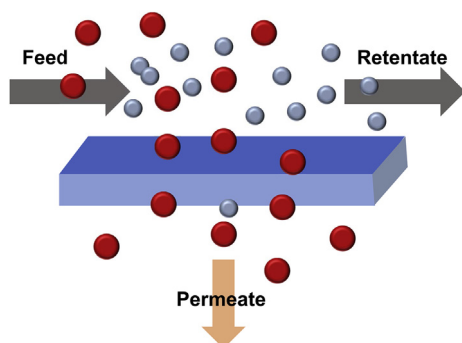
**Table 3**  
CO<sub>2</sub> absorption/adsorption by ionic liquids.

Author	Year	System	Performance	Operating conditions or others
Blanchard et al. [38]	1999	[bmim][PF <sub>6</sub> ]	Solubility: 0.6 mol CO <sub>2</sub> /mol IL	Temperature: 40–60 °C Pressure: 0–9.5 MPa Room temperature Pressure: 1 atm Time: 3 h Time: within 200 min
Bates et al. [45]	2002	Amino acid based ILs, TSIL	Solubility: 0.5 mol CO <sub>2</sub> /mol IL Disadvantages: high viscosity	
Zhang et al. [47]	2006	tetrabutylphosphonium amino acid [P(C <sub>4</sub> ) <sub>4</sub> ][AA]	Solubility: 1 mol CO <sub>2</sub> /mol IL of 1 wt% water	
Zhang et al. [49]	2009	[aP <sub>4443</sub> ][AA]	Solubility: 1 mol CO <sub>2</sub> /mol IL	Can be recycled for CO <sub>2</sub> uptake Temperature: 22 °C Pressure: 0.2 bar
Gurkan et al. [64]	2010	[P <sub>66614</sub> ][Pro] and [P <sub>66614</sub> ][Met]	Solubility: 1 mol CO <sub>2</sub> /mol IL	No viscosity increase after absorption Equilibrium Time: 20 min Temperature: 20 °C
Chen et al. [52]	2017	[emim][Ac] <sup>+</sup> AAIL	2.7 mol CO <sub>2</sub> /kg sorbents, rate of absorption enhanced	
Xiong et al. [59]	2012	Imidazolium-based polymeric ionic liquids	Sorption capacity: three times as high as [bmim][PF <sub>6</sub> ]	
An et al. [65]	2017	Hydroxypyridine-based ionic liquids	Capacity: 1.20 mol CO <sub>2</sub> per mol IL Viscosity: 193 cP	

characteristics of ILs, IL-based materials have become devisable task-specific materials and new alternatives for CO<sub>2</sub> separation. ILs can eliminate the problem associated with traditional membranes [78]. Besides, supported IL membranes can decrease the viscosity of ILs and the cost and improve the mechanical strength and separation performance [79]. Therefore, supported ionic liquid membrane (SILMs) is extremely preferred over conventional membranes in the field of gas separation.

The stability of SILMs depends on categories of ILs and features of membranes, in particular, hydrophilic and hydrophobic characteristics. Some researchers worked on effects of separation capacity due to external factors such as water or different functional groups, such as alkyl and hydroxyl. It was found that the presence of water in [bmim][BF<sub>4</sub>] enhanced membranes performance, and led to increase in CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity due to the decrease of viscosity with the increase of water content [80]. However, the permeability of CO<sub>2</sub> by SILMs is a function of viscosity. Permeability decreases with the increase of viscosity, which is consistent with experimental results [81]. For evaluating the influence of temperature, Myers et al. [82] used [H<sub>2</sub>NC<sub>3</sub>H<sub>6</sub>mim][Tf<sub>2</sub>N] to prepare SILMs and measured selectivity and permeability of the mixture of CO<sub>2</sub> and H<sub>2</sub>. The results indicated that selectivity increased with the increase of temperature from 37 °C to about 85 °C, and decreased with the further increase in temperature. CO<sub>2</sub> permeability dropped as temperature increased, which accords with Arrhenius behavior.

Various ILs-based membranes; however, result in different phenomena. Hanioka et al. [83] synthesized [C<sub>4</sub>mim][Tf<sub>2</sub>N], [C<sub>3</sub>NH<sub>2</sub>mim][Tf<sub>2</sub>N], and [C<sub>3</sub>NH<sub>2</sub>mim][CF<sub>3</sub>SO<sub>3</sub>] to prepare supported liquid membrane. The CO<sub>2</sub>/CH<sub>4</sub> selectivity decreased with temperature because high temperature prevented CO<sub>2</sub> from reacting with amine moiety. Though several theories and experimental studies based on SILMs exist, the stability of SILMs is still a non-ignorable issue. How to avoid the pressure drop pushing out the IL from the pores of membranes needs further investigation.



**Fig. 8.** Mechanism of membranes for CO<sub>2</sub> capture [7].

Specifically speaking, membranes are generally classified as inorganic, organic, and composite membranes. Each type of substrate has its own various structural characteristics and applicable conditions, for example following different transport mechanisms (Fig. 9). Basically, solution–diffusion polymer membranes possess high CO<sub>2</sub> permeance and lower CO<sub>2</sub>/N<sub>2</sub> selectivity due to the Robeson bound. However, facilitated transport membranes have both high permeance and selectivity. Polyallylamine, polyethylenimine, and polyvinylamine are usually considered as fixed carriers; and ethylenediamine, amino acid salts, and alkanolamines as mobile carriers. First, CO<sub>2</sub> reacts with amine carriers and then passes through the membrane, which enhances the solubility of CO<sub>2</sub>. The primary cause for some materials, for example zeolite, is that it follows both surface diffusion and molecular sieving mechanisms as explained by Chen and his partners [84].

### 3.2.1. Inorganic membranes

Despite good applicability of polymeric membranes, they are limited in industrial applications due to their low flux and a lack of high-temperature stability [85]. Inorganic membranes have many virtues, such as long term durability, high thermal stability (usually above 200 °C), chemical stability in wide pH, and high structural integrity [86], which in some cases can lead to disadvantage of polymeric membranes. Ceramic membranes, such as alumina and titania, are famous for high-temperature stability, and therefore caused extensive concern. Albo et al. [87] investigated [emim][Ac] immobilized in Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and exhibited a great potential in CO<sub>2</sub>/N<sub>2</sub> separation. In particular, CO<sub>2</sub> permeance can be achieved as high as  $2.78 \pm 0.11 \times 10^8 \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with  $\alpha(\text{CO}_2/\text{N}_2) = 30.72 \pm 0.86$ . They [85] also prepared nanoporous TiO<sub>2</sub> and SiO<sub>2</sub>-ZrO<sub>2</sub> membranes and combined with [emim][Ac] (a type of IL with high solubility for CO<sub>2</sub>), which outperformed the current state-of-the-art materials for CO<sub>2</sub>/N<sub>2</sub> separation.

Moreover, using ILs with different functions may aid in synthesizing specific membranes accordingly. Iarikov et al. [88] prepared IL membranes supported by  $\alpha$ -alumina inorganic supports with room temperature ILs for CO<sub>2</sub>/CH<sub>4</sub> separation. The IL-supported membranes could display CO<sub>2</sub> permeance from  $5 \times 10^{-10}$  to  $5 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , and reported a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 5–30. However, the performance under high pressure and temperature was still not satisfactory. In conclusion, despite inorganic membranes have the advantages of high selectivity and chemical stability, they have complex structures and high costs [7].

### 3.2.2. Organic membranes

Organic membranes, usually indicates polymeric membranes (polyamides, polyacrylates, polycarbonates, polysulfones, and polyimides, etc.), and they are the most widely studied SILM for CO<sub>2</sub> separation, owing to their high selectivity, low cost, and synthetic feasibility [89,90]. Therefore,

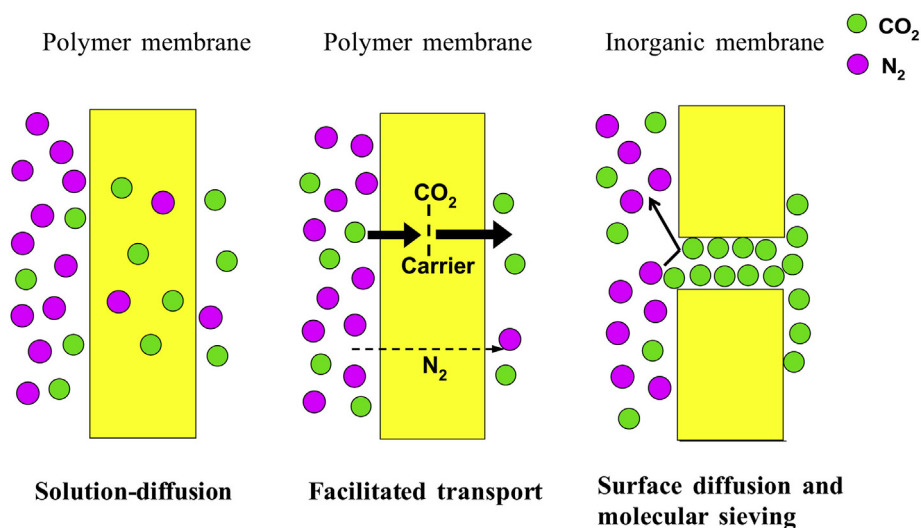


Fig. 9. Schematic illustration of CO<sub>2</sub>/N<sub>2</sub> transport mechanism [84]. Copyright (2016) Elsevier.

polymeric membranes are becoming more potential materials for gas separation than inorganic membranes. Mannan et al. [91] presented polyethersulfone (PES)/[emim][Tf<sub>2</sub>N] IL-polymeric membrane for CO<sub>2</sub>/CH<sub>4</sub> separation, which could maintain the selectivity and 30% improvement in separation compared to pure PES membrane under same conditions. Mohshim et al. [92] also blended IL [emim][Tf<sub>2</sub>N] (5 and 15 wt%, respectively) with polyethersulfone (PES), and the thermogravimetric analysis (TGA) indicated that CO<sub>2</sub> permeance was about 150% compared to that of pure PES membrane, and CO<sub>2</sub>/CH<sub>4</sub> selectivity also increased to 85%.

Task-specific ILs, in particular, amine functionalized IL can also be incorporated into polymeric membranes for CO<sub>2</sub> separation. Hanioka et al. [83] reported a functionalized IL-based polymeric membrane and showed high selectivity and stability. Among [C<sub>4</sub>mim][Tf<sub>2</sub>N], [C<sub>3</sub>NH<sub>2</sub>mim][CF<sub>3</sub>SO<sub>3</sub>], and [C<sub>3</sub>NH<sub>2</sub>mim][Tf<sub>2</sub>N], the latter two performed better toward CO<sub>2</sub>/CH<sub>4</sub> selectivity.

### 3.2.3. Composite membranes

Recently, the focus of SILMs has naturally shifted to composite membranes in order to achieve good selectivity and mechanical properties. Typically, mixed-matrix membranes are heterogeneous substances which contain inorganic and organic components. Owing to integrated benefits of both inorganic and organic membranes, mixed-matrix membranes have been focused upon for gas separation. Hudiono et al. [93] reported a mixed-matrix membrane involving three components of polymerizable ILs. The membrane combined the high permeability of ILs and stability of membranes together to fabricate gas separation membranes without defects.

To screen out better anions for supported IL mixed-matrix membrane, Fourier transform infrared (FTIR) spectroscopy and elemental analysis (CHN) technique can be used to figure out the anion effects. Mehrdad et al. [94] modified polyvinylchloride membranes with three anions, namely, bromide, thiocyanate, and tetra-fluoroborate. The experiments indicated that thiocyanate anion had better results on CO<sub>2</sub> separation. The increase of temperature was not conducive to membranes selectivity.

**3.2.3.1. Metal organic frameworks composite membranes.** Metal organic frameworks (MOFs) membranes, are emerging porous materials, which have high surface area and tunable pore size [95]. Ding et al. [96] integrated imidazolium-based poly ILs into the MOFs material MIL-101 for CCS process. The composite polyILs@MIL-101 displayed excellent CO<sub>2</sub> capture capability and could be beneficial for the cycloaddition of CO<sub>2</sub> (Fig. 10)..

Monteiro et al. [97] designed immobilization of ILs into MOFs to obtain [IL @MOF]@MatrimidU5218 mix matrix membranes. The membranes showed improvement towards CO<sub>2</sub>/N<sub>2</sub> separation. Building on atomistic simulation, the IL [bmim][SCN] supported with zeolite-like metal organic framework (ZMOF) was investigated to capture CO<sub>2</sub>/N<sub>2</sub>, and it exhibited higher permeability and selectivity than many other polymeric membranes [98]. To study the role of MOF-based IL membranes, Gupta et al. [99] synthesized isorecticular metal-organic frameworks (IRMOF)-1 supported IL membranes by atomistic simulation and found that at the same weight ratio of IL, the selectivity increased in the following sequence: [Tf<sub>2</sub>N] < [PF<sub>6</sub>] < [BF<sub>4</sub>] < [SCN], which illustrated the importance of anion effects on the properties of SILMs. Recently, Yao

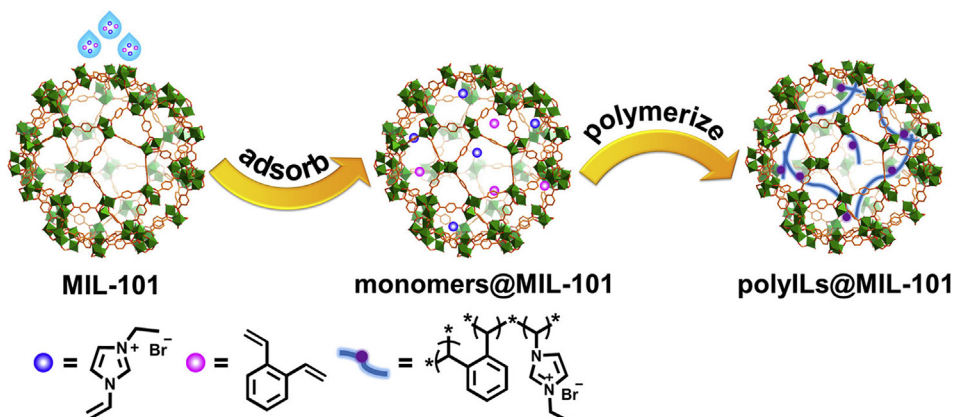


Fig. 10. Schematic illustration related with the preparation of polyILs@MIL-101 [96]. Copyright (2018) ACS.

et al. [100] employed nanometal organic frameworks as fillers for membranes and decorated with IL, and the membrane exhibited a highly selective adsorption for CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub>. Furthermore, the membrane was also proved to be an active catalyst for cycloaddition of CO<sub>2</sub> under a fairly low pressure.

In conclusion, mixed-matrix membranes exhibit the ability to combine advantages of both polymeric membranes and inorganic membranes, and porous materials are often used as supporters to increase the surface area of membranes. At the same time, it has also been demonstrated that mixed matrix membranes may face with problems that affect their various constituent phases [101].

**3.2.3.2. Molecular sieves.** Molecular sieves are considered as highly porous materials and their pore sizes are equipped with the same order as the sizes of gas molecules; therefore, it is possible to precisely separate exact types of gases. They possess high selectivity for gas separation [102].

Owing to the fascinating features of molecular sieves, numerous studies on membranes have been emerging since then. In 1997, Kita et al. [103] reported high CO<sub>2</sub>/CH<sub>4</sub> selectivity and permeability at 35 °C and 1 atm. It was found later that carbon molecular sieve (CMS) membranes comprising pyrolyzed polymeric precursor showed satisfactory air separation properties [104]. Li et al. [105] also investigated SAPO-34 membranes for separating CO<sub>2</sub>/CH<sub>4</sub> and the highest selectivity was 270 under low pressure.

Addition of ILs on molecular sieves may have a better effect on CO<sub>2</sub> separation. Yang et al. [106] used [NH<sub>3</sub>emim][BF<sub>4</sub>], [OHe-mim][BF<sub>4</sub>], and [HOEAm] to support onto molecular sieves, namely, NaY, USY, SAPO-34, and MCM-41. [NH<sub>3</sub>emim][BF<sub>4</sub>]/NaY was found to possess excellent CO<sub>2</sub> adsorption performance; however, the thermostability was good below 50 °C which cannot expound the strongpoint of ILs. Moreover, bad interfacial interaction between IL and molecular sieve further restricted development of this field.

However, molecular sieves are not considered as promising alternatives for membrane due to their complex surface [107]. However, integration of ILs with other materials can facilitate the overall performance of SILMs. Hu et al. [108] found that IL and amine-modified SAPO-34 composites could improve the separation process of CO<sub>2</sub>. Hudiono et al. [109] combined poly RTIL, SAPO-34, and membranes together and found an enhancement in CO<sub>2</sub>/CH<sub>4</sub> separation performance. Therefore, porous particles and ILs can enhance size-sieving ability of membranes and sometimes promote gas selectivity. Vu et al. [110] incorporated CMSs into mixed matrix membranes to study CO<sub>2</sub>/CH<sub>4</sub> selectivity, and it turned out that the introduction of CMSs showed 40% enhancement than pure composite membranes. Vu et al. [111] also reported that the composite membranes exhibited relatively stable properties in the existence of low-concentration toluene impurity, which could further realize optimization of industrial process for CO<sub>2</sub> separation. Table 4 lists typical SILMs for CO<sub>2</sub> separation.

#### 4. Cycloaddition of CO<sub>2</sub> to synthesize cyclic carbonate using ionic liquids

CO<sub>2</sub> is the most abundant and cheap C1 source in the world, and therefore, undoubtedly, development in CO<sub>2</sub> utilization, absorption, and reaction to synthesize high-value-added products is of great importance. In particular, cycloaddition of CO<sub>2</sub> into epoxides for the synthesis of cyclic carbonate is one of the most effective methods for the fixation of CO<sub>2</sub>, which can be used as polar solvents, electrolytes in secondary batteries, chemical intermediates, precursors for polycarbonates, etc. (see Fig. 11) [112]. Until now, numerous catalysts such as metal complexes [113], alkali metal salts [114], metal oxides [115], organic bases [116], and ILs are available for the CO<sub>2</sub> fixation process. However, the catalytic activity, extreme reaction conditions, need for co-catalysts, and recycle capacity still need to be solved. Nonetheless, ILs have gained extensive

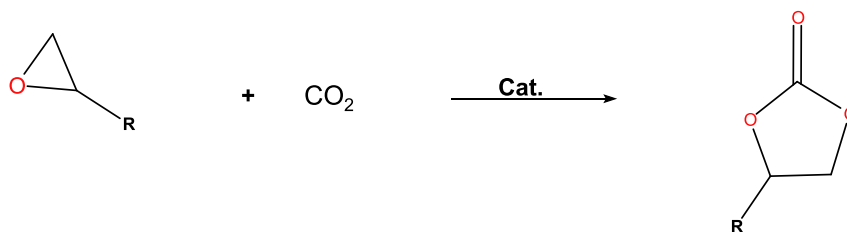
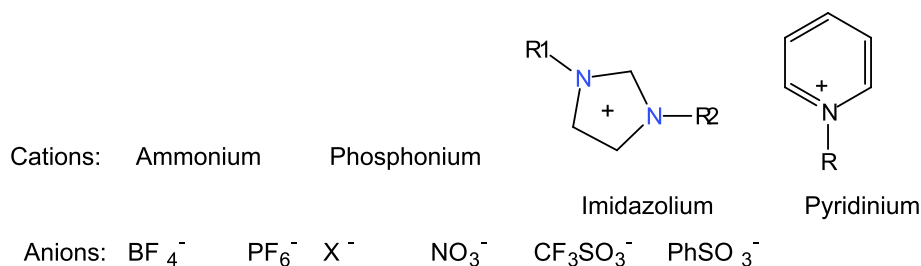
**Table 4**  
CO<sub>2</sub> separation by SILMs.

Author	Year	Category	System	Performances
Albo et al. [87]	2014	Inorganic	[emim][Ac] immobilized in Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	CO <sub>2</sub> permeance: $2.78 \times 10^8$ mol/(m <sup>2</sup> s Pa) $\alpha$ (CO <sub>2</sub> /N <sub>2</sub> ) = 30.72
Iarikov et al. [88]	2011	Inorganic	$\alpha$ -alumina membranes supported with RTILs	CO <sub>2</sub> permeance: $5 \times 10^{-10}$ to $5 \times 10^{-9}$ mol/(m <sup>2</sup> s Pa), CO <sub>2</sub> /CH <sub>4</sub> selectivity: 5–30
Mannan et al. [91]	2016	Organic/polymer	Polyethersulfone (PES)/[emim][Tf <sub>2</sub> N] ionic liquid-polymeric membrane	Maintain the selectivity and 30% improvement in separation than pure PES membrane
Mohshim et al. [92]	2013	Organic/polymer	[emim][Tf <sub>2</sub> N] with polyethersulfone (PES)	CO <sub>2</sub> permeance: 150% compared to pure PES membrane CO <sub>2</sub> /CH <sub>4</sub> selectivity: increases about 85%
Hudiono et al. [93]	2010	Composite/Mixed-matrix membrane	Poly(RTIL)-zeolite composite membranes	Addition of the ionic liquid increased the selectivity of the MMM
Gupta et al. [98]	2012	Composite/Mixed-matrix membrane	IRMOF-1 based ionic liquid membranes	Illustrates the importance of anion effects on the properties of SILMs
Yao et al. [100]	2017	Composite/Mixed-matrix membrane	Imidazolium-based Ionic Liquid Decorated UiO-66 Type NMOF	$\alpha$ (CO <sub>2</sub> /N <sub>2</sub> ) = 39.1 $\alpha$ (CO <sub>2</sub> /CH <sub>4</sub> ) = 25.1 (298 K, 10 bar, 50 wt %)
Hudiono et al. [93]	2011	Composite/Mixed-matrix membrane	Poly(RTIL)-SAPO-34 composite membrane	$\alpha$ (CO <sub>2</sub> /N <sub>2</sub> ) = 22 $\alpha$ (CO <sub>2</sub> /CH <sub>4</sub> ) = 81 Thickness: 155 $\mu$ m

research attention because of not only the advantages such as no vapor pressure and tailorable properties, but also selective dissolution into many materials. ILs can achieve clean transformation of CO<sub>2</sub> to cyclic carbonate, serving as both reaction media and catalysts, resulting in improvement in both reaction rate and selectivity of cyclic carbonate. Quaternary ammonium, phosphonium, imidazolium, and pyridinium cations are the mostly widely used cations as ILs catalysts. Early in 2001, Peng et al. [117] synthesized two types of imidazole IL, namely [bmim][PF<sub>4</sub>] and [bmim][Cl], to study the catalytic performance of cycloaddition of CO<sub>2</sub>. Accordingly, [bmim][PF<sub>4</sub>] exhibited high PO conversion under the reaction pressure of 2.5 MPa and temperature of 110 °C, and thus the possibility for ILs acting as catalysts was proposed for the synthesis of cyclic carbonate.

##### 4.1. Development of pure ionic liquids as catalyst

After the possibility of ILs as catalysts was known, many studies tended to focus on ILs and the rule of the catalytic activity due to their huge potential and characteristic of being tailorable. The common types of cations and anions used in ILs as catalysts for fixation of CO<sub>2</sub> are shown in Fig. 12. Kawanami et al. [118] synthesized series of 1-alkyl-3-methylimidazolium salts to be served as catalysts for cyclic carbonate synthesis. Among various anions, BF<sub>4</sub><sup>-</sup> displayed the most effective catalytic performance, and it was first proposed that the type of anion and the length of alkyl chain in the cation have decisive influence on the reaction. However, fairly low epoxide conversion was achieved attributed to the

Fig. 11. Reaction scheme for the cycloaddition of CO<sub>2</sub> into cyclic carbonate.Fig. 12. Anions and cations used in ionic liquids in the synthesis of cyclic carbonate from CO<sub>2</sub> [121].

non-nucleophilic nature of  $\text{BF}_4^-$  and high pressure even supercritical condition was needed in this reaction. Girard et al. [119] used [bmim][Br], [bmim][Cl], and [bmim][I] to catalyze CO<sub>2</sub> fixation reactions at 150 °C and 5 bar for 10 mol% of styrene oxide, 46% yield of cyclic carbonate was reported for [bmim][Cl] within 4 h. On the other hand, 99% yield was obtained for [bmim][Br] and [bmim][I] under same reaction time, which indicated the efficient catalytic activity of various halogenide anions and better performance than non-nucleophilic anions. Quaternary ammonium salts, which constitute another category of ILs, may also catalyze cycloaddition of CO<sub>2</sub> into cyclic carbonate. Calo et al. [120] reported excellent catalytic performance of butylammonium bromide and etrabutylammonium iodide under mild conditions, the bulkiness of the tetrahedral ammonium ion could lead to less electrostatic interaction with anions, which may explain the effective activity of quaternary ammonium salts.

The catalytic activity for fixation of CO<sub>2</sub> could be increased by synthesizing ILs with various types of anions and cations. It is worth further improving the performance by using synergistic effect between anions and cations, and therefore functionalized ILs were reported and studied (hydroxyl groups [122], amino groups [123], carboxylic groups [124], etc.). Cheng et al. [125] studied catalytic activity of hydroxyl-functionalized quaternary ammonium ILs for cycloaddition of CO<sub>2</sub>, by investigating effect of hydrogen bond. In order to figure out the mechanism of the positive effect on the fixation of CO<sub>2</sub>, they varied the number of hydroxyl groups in ammonium ILs from 0 to 4. In the absence of hydroxyl group, the yield of propylene carbonate (PC) could reach only 63% at the temperature of 120 °C and pressure of 1.5 MPa for 1 h. On the other hand, PC yield of 81, 88, and 92% could be achieved with one, two, and three hydroxyl groups, respectively, under the same operating conditions, which indicated the positive effect of hydroxyl group on the catalytic activity of quaternary ammonium ILs. The polarization of the oxygen atom through O–H bond together with nucleophilic activation of the carbon atom by the anion resulted in synergistic effect, and therefore led to the improvement of fixation of CO<sub>2</sub> to synthesize cyclic carbonate. Peng et al. [126] synthesized a range of multi-hydroxyl ILs as catalyst for the fixation of CO<sub>2</sub> without any co-catalyst or solvent. The catalyst system was proved to be promising for the cycloaddition of CO<sub>2</sub> because of the synergistic effects of hydroxyl groups and halogen anion. Moreover, the optimal operating conditions were 120 °C and 2 MPa for 3 h with a yield of 83.2% and high TOF of 33,300 h<sup>-1</sup>. Wang et al. [127] employed benzyl substituted imidazolium ILs as catalyst for fixation of CO<sub>2</sub> into cyclic carbonate in a solvent-free system. The high yield of cyclic

carbonate (94.89%) could be achieved at 130 °C and 2.0 MPa for 4 h. Moreover, they also found that the  $\text{Cl}^-$  anion displayed better catalytic performance than  $\text{PF}_6^-$  and  $\text{BF}_4^-$  due to the difference in nucleophilicity, and different electron-donating group in benzene ring also affected the catalytic activity, among which  $-\text{CH}_3$  performed better than the others ( $-\text{H}$ ,  $-\text{N}_2$ ,  $-\text{Cl}$ , etc.). Galvan et al. [128] synthesized various types of phosphonium salts [P<sub>881</sub>][A] to catalyze the cycloaddition of CO<sub>2</sub> to styrene oxide. The performance of each type of phosphonium salts was evaluated at 100 °C and ambient pressure, and acetate salts were proved to be more satisfactory. This study mainly discussed about how the anions affected catalytic performance; wherein the anion served as promoter of the ring-opening process and the cation could stabilize the intermediates via O–N system. Yang et al. [129] synthesized various types of Lewis basic ILs for formation of cyclic carbonate from CO<sub>2</sub>. The study showed that 1,8-diazabicyclo[5.4.0]undec-7-enium chloride ([HDBU][Cl]) displayed high yield (97%) and selectivity (>99%) of cyclic carbonate at 140 °C and 1 MPa at 2 h. Moreover, they also investigated the anion effect of various ILs (including  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{TF}_2\text{N}^-$ ,  $\text{AcO}^-$ ), and  $\text{OH}^-$  and some halide anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) exhibited excellent catalytic performance due to their good leaving ability and nucleophilicity, and Lewis basic cations (HDBU<sup>+</sup>) also performed well. Dai et al. [130] designed a series of isothiuronium ILs for the synthesis of cyclic carbonates from epoxide and CO<sub>2</sub>. The results exhibited that hydroxyl- and carboxyl-functionalized isothiuronium ILs displayed almost 100% yield and selectivity for propylene carbonate at 140 °C and 2.0 MPa for 2 h. The reason for using isothiuronium as cation was the synergistic effect caused by hydrogen bonding, and halide anion could promote the ring-opening process.

#### 4.2. Development of complex catalysts with ionic liquids

In order to further increase the catalytic performance for the fixation of CO<sub>2</sub> into cyclic carbonate, complex catalysts system has also been studied. The presence of Lewis acid compounds could enhance the performance of ILs as co-catalysts. Sun et al. [124] combined ILs with ZnBr<sub>2</sub>, which could afford 93% yield of cyclic carbonate at the temperature of 80 °C for 1 h, while only 6% SO yield could be achieved without zinc bromide. They proposed that the improvement is mainly attributed to the formation of bis(1-butyl-3-methylimidazolium) zinc tetrahalides. Apart from ZnBr<sub>2</sub>, Kossev et al. [131] reported a catalytic system with tetraalkylammonium or phosphonium halide and calcium chloride as co-catalyst of onium halides, which displayed excellent catalytic activity. Yang et al. [132] synthesized



DBU-based ILs with  $\text{ZnI}_2$  as co-catalyst, as catalyst for cycloaddition of  $\text{CO}_2$  to epoxides and also afforded high yield and selectivity under mild conditions ( $60^\circ\text{C}$ , 8 MPa, 8 h). Jasiak et al. [133] designed and synthesized imidazole IL with hydrogensulphate anion in zinc iodide solution for cyclic carbonate synthesis from  $\text{CO}_2$  and epoxide. The cocatalyst system displayed high yield and selectivity at  $120^\circ\text{C}$  and 2 MPa within 4 h.

A key obstacle in the study of ILs as catalysts is the recovery process after the reaction because of the high cost of ILs, as many types of ILs were used as homogeneous catalysts. Therefore, supported ILs were designed. Silica [134], porous polymers [135], and MOFs [136] could serve as supporters for ILs to achieve recycling after reaction. Xie et al. [137] grafted a type of ILs (1-glycidyl-butylimidazolium chloride) onto functionalized polymer spheres made of SBA-15 and silica gel. The yield of PC could reach as much as 95% catalyzed by this supported functionalized IL with the TOF of  $1693\text{ h}^{-1}$ , temperature of  $403\text{ K}$ , and pressure of 6 MPa at 8 h. The results showed that the polymer supports have a positive effect on the cycloaddition of  $\text{CO}_2$  because the TOF without polymer supports could only reach  $40.4\text{ h}^{-1}$  at the same operating conditions, which could be explained based on synergistic effects between supports and IL. Hu et al. [138] incorporated functionalized ILs with SBA-15 to realized cycloaddition of  $\text{CO}_2$ . Among all these different combinations,  $\text{Ti-SBA-15@ILClCH}_2\text{COO}$  (0.5) and  $\text{Al-SBA-15@ILClCH}_2\text{COO}$  (0.5) performed better with the yield of propylene oxide being above 95% at 0.5 MPa and  $110^\circ\text{C}$  at 3 h. It was demonstrated that supported carrier and anion sites of ILs acted as excellent accelerant for cycloaddition of  $\text{CO}_2$  into cyclic carbonates. Jayakumar et al. [139] synthesized cocatalyst-free hydroxyl functionalized IL-based polymers by radical copolymerization. The experimental results proved cooperative activation effect between hydroxyl group and IL. Owing to the high surface area and content of hydroxyl group, this specific type of IL-based catalyst could achieve yield of PC as much as 95% and TOF of  $188\text{ h}^{-1}$  at  $140^\circ\text{C}$  and 2 MPa. Cui et al. [140] studied nitrogen-rich porous organic polymers modified with imidazolium-based ILs to catalyze the reaction of  $\text{CO}_2$  cycloaddition. They believed that IL and polymers exerted synergistic effect on  $\text{CO}_2$  conversion. The  $\text{CO}_2$  adsorption capacity of IL-based polymers was approximately 1.5 times higher than that without IL. Moreover, the IL-based polymers performed well at the temperature of  $100^\circ\text{C}$  and atmospheric pressure of 24 h. Triazolyl groups of the nitrogen-rich porous organic polymers and the properties of IL simultaneously promoted the reaction process. Aprile et al. [141] synthesized covalently supported IL phase (mlc-SILP) based on bis-vinylimidazolium salts to use as catalysts for cycloaddition of supercritical  $\text{CO}_2$ . The novel catalysts

provided higher productivity than mesoporous SBA-15. Mlc-SILP exhibited higher catalytic productivity due to its multilayered IL phase, which resulted in higher loading ratio for ILs per unit supported materials. Han et al. [142] synthesized carbon nanotubes grafted with imidazole IL (CNT-ILs) and utilized them as heterogeneous catalysts for the cycloaddition of  $\text{CO}_2$  to produce cyclic carbonates. Compared to other supports such as silica and polymer, carbon nanotubes exhibited excellent catalytic reactivity toward the reaction of AGE and  $\text{CO}_2$  with a PC yield of 98.6% at  $110^\circ\text{C}$  and 1.82 MPa within 6 h. Xie et al. [143] reported a series of mesoporous poly(ILs)-grafted with bromide ions/zinc sites to test the catalytic performance toward cycloaddition of  $\text{CO}_2$ . Py-Im-6-Zn-5-SCD performed excellent due to the high density of nucleophile/electrophile, and this catalyst could be easily recovered and reused in the next turn. Specifically, the yield of PC could reach as high as 95% at  $30^\circ\text{C}$  and 30 bar for 18 h. Zhu et al. [144] studied  $\text{CO}_2$  fixation catalysis using immobilized ILs with hydroxyl and epoxy groups based on graphene oxide (Fig. 13). The catalytic performance of the functionalized graphene oxide was 95.6% for propylene oxide (PO) conversion and 99.4% for PC selectivity after 4 h, which was higher than those of simple ILs  $[\text{SmIm}][\text{I}]$ . Wu et al. [145] synthesized carboxymethyl cellulose (CMC) supported imidazolium ILs to be used as heterogeneous catalysts for  $\text{CO}_2$  fixation into cyclic carbonate. Among series of catalysts, the hydroxyl group functionalized ILs (HBimCl-NbCl<sub>5</sub>/HCMC) exhibited best catalytic activity (98.1% cyclic carbonate yield,  $130^\circ\text{C}$ , 1.5 MPa, 3 h) due to the synergistic effects between IL and Lewis acid.

#### 4.3. Recent advances in cycloaddition of carbon dioxide into cyclic carbonate

In recent years, mainly two key problems have been encountered for the further improvement of the reaction process via variation in operating conditions and total costs, namely, catalyst design and chemical process intensification. Guglielmo et al. [146] evaluated series of dicationic ionic liquids (DILs) applied in the fixation of  $\text{CO}_2$  to figure out the influence of the structure of ILs on catalytic activity. They found an increase in the observed rate constant and a negative effect in the presence of butyl substituent present on the imidazolium cations, on catalytic activity when imidazolium head groups possessed longer linker. Byun et al. [147] reported ILs as catalyst with homogeneity/heterogeneity switch for cycloaddition of  $\text{CO}_2$  by increasing alkyl chain length to achieve low temperature curing after homogeneous catalytic reaction.

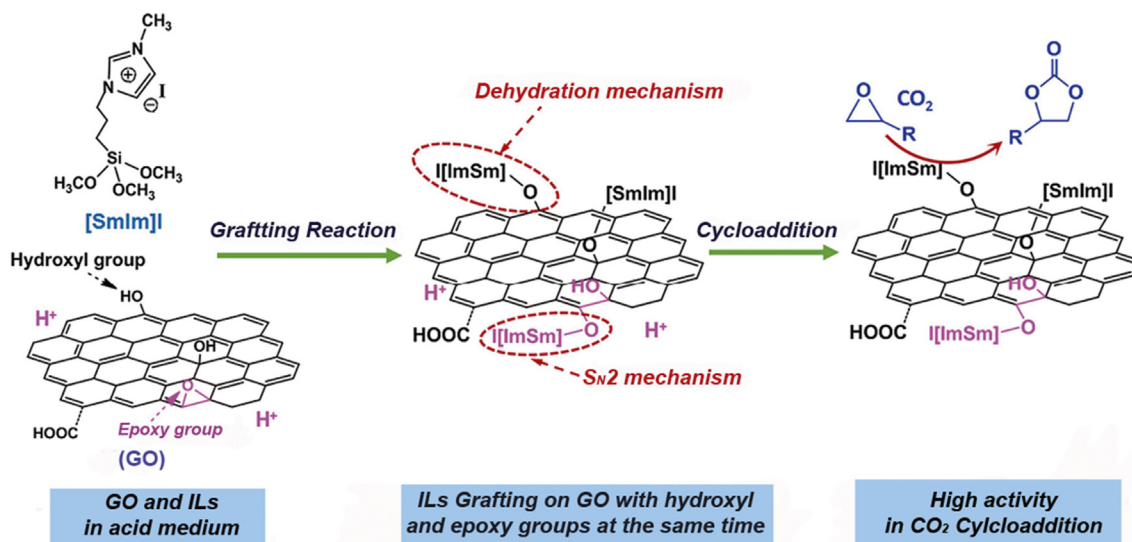


Fig. 13. The process for ionic liquids immobilization on GO sheets and catalyst cycloaddition of  $\text{CO}_2$  into cyclic carbonate [144]. Copyright (2018) Elsevier.



**Table 5**Cycloaddition of CO<sub>2</sub> for synthesis of cyclic carbonate catalyzed by ionic liquids.

Author	Catalyst	Temp./°C	Pressure/MPa	Time	Yield (%)	Reactor	Others
Girard et al. [119]	[bmim][Br], [bmim][Cl] [bmim][I]	150	0.5	4 h	99 99 46	Batch reactor	Catalytic activity: Br=Cl > I
Cheng et al. [125]	Hydroxyl-ammonium ILs	120	1.5	1 h	92	Batch reactor	Hydroxyl group is positive
Wang et al. [127]	Benzyl substituted imidazolium ILs	130	2.0	4 h	94.89	Batch reactor	Cl <sup>-</sup> > PF <sub>6</sub> <sup>-</sup> , BF <sub>4</sub> <sup>-</sup>
Sun et al. [124]	ILs/ZnBr <sub>2</sub>	80	3.0	1 h	93	Batch reactor	6% yield without ZnBr <sub>2</sub>
Xie et al. [137]	IL functionalized polymer spheres	130	6.0	8 h	95	Batch reactor	TOF of 1693 h <sup>-1</sup>
Zhao et al. [148]	Hydroxyl- ammonium ILs	180	3.5	14 s	99.8	Microreac-tion system	/

Microreaction system is one of the most potential technologies for intensification of chemical process due to the excellent mixing and mass/heat transfer performance and process safety. Zhao et al. [148] designed a microreaction system for fixation of CO<sub>2</sub> into cyclic carbonate, and 99.8% of PC yield could be achieved under the pressure of 3.5 MPa and 180 °C with the residence time of only 14 s, compared to several hours with traditional batch reactor.

Microreactor system also possesses the advantage of easy kinetics measurements. Reham et al. [149] carried out kinetic investigations of cycloaddition of styrene oxide catalyzed by ZnBr<sub>2</sub>/TBAB system in a continuous flow reactor, and 100% conversion of epoxide could be reached at 120 °C and 6.0 bar for 45 min.

Table 5 presents the typical results for the cycloaddition of CO<sub>2</sub> for synthesis of cyclic carbonate catalyzed with different type of ILs using various reactors.

## 5. Conclusion and outlook

The absorption performance of amines solutions, ionic liquid (ILs)-based absorbents as aqueous solutions, as well as porous materials and membranes were reviewed herein. Furthermore, discussion about the use of ILs as catalysts for cycloaddition of CO<sub>2</sub> into cyclic carbonate was presented. The major highlights for amines solutions and amine-immobilized materials include relatively high absorption capacity and kinetics, and the drawback lies in high desorption cost and pollution, resulting in hard regeneration. The reduction of the recycle cost and at the same time maintenance or even further improvement in absorption and separation performance is the key issue. The most obvious feature for ILs is low regeneration cost and tunable nature; however, at the same time, low absorption capacity and high viscosity are also noteworthy as drawbacks for CO<sub>2</sub> capture, but these characteristics make ILs more suitable for membranes than amines. Moreover, some studies reported consistency between excellent absorption solvents and ILs catalysts, but there also exists difference between ILs for absorbing CO<sub>2</sub> and catalyst reaction for CO<sub>2</sub> fixation. Consequently, more significant research efforts need to be devoted for finding the most practical solutions to capture, separate, and convert CO<sub>2</sub> into high-value products. For example, microreaction system possesses the characteristics of excellent mass/heat transfer performance, which can dramatically improve the TOF value and reduce the residence time. The primary issue is the balance relationship between absorption and desorption, stability and capacity, and cost and environment.

- 1) Material improvement. Both CO<sub>2</sub> adsorption and conversion are related closely with characteristics of adsorption solutions, catalyst, and their supported materials or co-catalysts. Various types of advanced compounds can be incorporated into adsorbents or catalysts to achieve better performance.
- 2) Process intensification. There would be barrier for material improvement; therefore, process intensification could be another way, such as microreaction process, supercritical process. High mass and heat transfer rate or unique characteristics can be reached by process intensification.

- 3) New application. Multiple materials and processes result in various applications, such as multifunctional and feature-rich materials, which can be applied in multiple fields and reach one plus one is greater than two results.

In the next decades, CO<sub>2</sub> separation and conversion will still be a great issue due to greenhouse effect. Many researchers will focus on this field, which will also let in the integration of newcomers such as biology, computer science, etc. CO<sub>2</sub> capture and conversion technologies will be used and updated to achieve more excellent performance, and be paid more attention on application which can benefit all humanity.

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