High Performing CO₂ Capture by Smart Strategies in Functionalized Ionic Liquids

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Functionalized ionic liquids (ILs) are the most promising approaches to achieve high performing CO₂ capture. This mini-review outlines some important progress for functionalized ILs in CO₂ capture. Amino-functionalized ILs exhibit high reactivity with CO₂, and their careful structural design is able to produce high absorption capacity of CO₂. The introduction of intra-molecular hydrogen bonding/proton transfer in amino-functionalized ILs is an attractive approach to avoid the formation of intermolecular hydrogen bonded networks generally occurred in traditional amino-functionalized ILs, thus resulting in enhanced absorption capacity of CO₂ and improved uptake rate. Non-amino anion-functionalized ILs such as substituted azolide or phenolate ILs show great potential for rapid and reversible uptake of CO₂ due to their lack of hydrogen bonding, controllable absorption enthalpy and excellent stability. However, there is still a long way to go to construct high performing systems based on functionalized ILs including high capacity of CO₂, rapid absorption kinetics and excellent cycling life. Smart strategies such as dual-tuning methods, multi-site cooperative interactions, and intra-molecular hydrogen bonding/proton transfer would promote the development of CO₂ capture in functionalized ILs significantly.

Keywords functionalized ionic liquids, smart strategies, high CO₂ capacity, rapid uptake kinetics, long cycling life

Introduction

Developing advanced materials or technologies for efficient, fast and reversible capture of post-combustion CO₂ is one of most important research activities for a sustainable environment. Among various approaches, ionic liquids (ILs), a class of low-temperature molten salts with melting point usually below 100 °C, have gained in popularity for the mitigation of CO₂ crisis by taking advantage of their unique properties including negligible vapour pressure, wide liquid temperature range, high stability, non-flammability, virtually unlimited tunability and excellent CO₂ affinity.^[1-3] The first report on physical solubility of CO₂ in the IL 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] demonstrated that the high pressure would result in high solubility of CO₂, for example, CO₂ uptake reached a molar ratio of 0.6 at 8 MPa.^[4] Much attention from academia then was paid to understanding and improving physical solubility of CO₂ in conventional ILs. However, to our best knowledge, the pure physical dissolution of CO₂ in conventional ILs at atmosphere pressure and room temperature is particularly low, only up to a molar fraction of 0.035 (gravimetric uptake capacity around 0.4%), which is almost impractical for industrialization.^[5]

Thus, smart design on the structure of ILs is highly desired for significant improvement of CO₂ uptake. Thanks to the first chemisorption of CO₂ in a task-specific IL,^[6] the progress on CO₂ capture technologies is being pushed to a large extent. This task-specific IL, 1-propylamine-3-butyl imidazolium tetrafluoroborate ([apbim][BF₄]), also called as functionalized IL, is prepared through attaching an amine group to the imidazolium cation, where absorption capacity of CO₂ could reach a molar

fraction of up to 0.5 under ambient conditions (Scheme 1). However, one significant disadvantage of this approach is its low absorption rate, associated with the relatively high viscosity of the IL after CO₂ absorption and formation of carbamate.^[7] Nevertheless, this pioneering work encouraged researchers to design smart strategies in functionalized ILs for high performing CO₂ capture.

Scheme 1 Proposed reaction between the first TSIL [apbim][BF₄] and CO₂.^[6]

Smart strategies including basicity tuning/dual tuning methods,^[8,9] multi-site cooperative interactions,^[10-12] and intra-molecular hydrogen bonding/intra-molecular proton transfer^[13,14] has been employed into ILs for CO₂ capture. For examples, Dai *et al.*^[8] investigated the relationship between the enthalpy of CO₂ absorption and the pK_a value in a series of non-amino functionalized ILs and concluded that it is possible to achieve both efficient CO₂ uptake and energy-saving release by simply tuning the basicity of the anion of IL. Wang *et al.*^[9] disclosed that conjugated ILs could reversibly capture high molar capacity of CO₂ through dynamic covalent carbon-oxygen bonds by

taking advantage of the dual-tuning roles of large π -conjugated anions. Cui and co-workers^[12] demonstrated a novel strategy based on cooperative interactions between CO₂ and multiple active sites in the pre-organized anion for highly efficient and reversible capture of low-concentration CO₂. Recently, Pan *et al.*^[13,14] established a series of amino-functionalized ILs for efficient CO₂ absorption as well as controllable viscosity change during the uptake process by creating intra-molecular hydrogen bonding or intra-molecular proton transfer. Therefore, the aim of this mini-review is to outline some typical advances in functionalized ILs for highly efficient, fast, and reversible capture of CO₂ in recent years.

High capacity of CO₂

Since the limit capacity of CO₂ in [apbm][BF₄] is only 0.5 mol per mol IL, much attention is paid on increasing the molar absorption capacity of CO₂ in amino-functionalized ILs towards equivalent molar ratio or beyond.^[15–26] One popular approach is to tether the amino group to the anion of IL such as trihexyl(tetradecyl)phosphonium methioninate ([P₆₆₆₁₄][Met]) and trihexyl(tetradecyl)phosphonium proline ([P₆₆₆₁₄][Pro]), and make the anion charge centre and amino group in close proximity (Scheme 2).^[15,16] As a result, a 1 : 1 stoichiometry of CO₂ uptake was obtained through formation of relatively stable carbamic acid. The introduction of more amino groups into the IL is a general method to further increase the molar absorption capacity. The naturally-occurring amino-acid anions containing an additional amine group (e.g., lysinate, asparaginate, glutamate) and trihexyl(tetradecyl)phosphonium cation ([P₆₆₆₁₄]) were used for the fabrication of functionalized ILs for beyond one molar absorption of CO₂.^[17–19] The cation effect was also studied by replacement of [P₆₆₆₁₄] with trihexyl(tetradecyl)-ammonium [N₆₆₆₁₄] when the anion was fixed as lysinate ([Lys]) anion.^[20] Surprisingly, the absorption capacity in [N₆₆₆₁₄][Lys] increased to 2.1 mol CO₂ per mol IL, exceeding 0.7 mol CO₂ per mol IL in comparison with [P₆₆₆₁₄][Lys]. This increase should relate to the difference in anion structures of corresponding IL-CO₂ adducts. However, the use of [P₆₆₆₁₄] cation would significantly decrease the gravimetric capacity of CO₂ due to its high molar mass.

Scheme 2 Reaction schematics of CO₂ with [P₆₆₆₁₄][Met] (top) and [P₆₆₆₁₄][Pro] (bottom).^[16]

Protic ILs, formed through proton transfer from a Brønsted acid to a Brønsted base, are able to be designed as flexible molecules with small molar mass and show potential on high uptake of CO₂. A mixture of strong organic bases and a wide variety of weak proton donors to attain protic ILs could produce rapid, reversible and equimolar capture of CO₂.^[27,28] Recently, the MacFarlane's group^[29,30] demonstrated several diamino protic ILs based on azolides as anions absorbed CO₂ to more than 20 wt% pointing towards equimolar absorption. The superior absorption capacity makes protic ILs receive considerable attention in CO₂ capture. However, the major drawback for protic ILs is the solvent degradation during the absorption-desorption cycles, resulting in rapid capacity decay of CO₂.

Imidazolium ILs are good platforms for high gravimetric capacity of CO₂. For example, Li *et al.*^[31] reported a new IL 1-hydroxyethyl-3-methylimidazolium lysine ([C2OHmim][Lys]) with an extremely high gravimetric uptake of 0.271 g CO₂ per g IL, however, it suffered from sluggish uptake rate of CO₂. Amino-functionalized IL-water blends could produce high gravimetric capacity of CO₂ as well as fast and reversible uptake of CO₂ if the structure of IL was carefully designed to a small scale because the IL can inhibit the evaporation of volatile solvent or solute and in turn, water containing the IL can remarkably decrease the viscosity of the system.^[32–36] The dual-functionalized IL, 1-(3-aminopropyl)-3-methylimidazolium glycinate ([APmim][Gly]) contains both amine and amino-acid groups, whose aqueous solution (0.5 M) exhibited high gravimetric capacity of CO₂ up to 19 wt%. Similarly, an aqueous solution of 1-(3-aminopropyl)-3-methylimidazolium lysinate ([APmim][Lys]) at the same concentration of 0.5 M achieved an even greater CO₂ absorption capacity of 26.7 wt%. Other types of IL-liquid blends such as IL-amine blend also were developed in light of the mature methods and theories for mixed amines.^[35,37,38]

The creation of multi-cooperative interactions in functionalized ILs is deemed to be one of the most promising approaches for highly efficient uptake of CO₂. The concept of cooperative interaction was firstly proposed by Wang *et al.*^[10] because both the negative oxygen site and adjacent nitrogen atom on the deprotonated hydroxypyridine anion can chemisorb CO₂ molecule, producing an ultra-high capacity of up to 1.6 mol CO₂ per mol IL. A new strategy for multi-molar absorption of CO₂ was reported by the activation of carboxylate groups in amino-acid ILs (Scheme 3).^[11] As shown in Figure 1a, the CO₂ capacity of [P₄₄₄₂]₂[IDA] is 1.69 mol per mol IL at 40 °C and 1 bar, indicating the presence of multi-site cooperative interactions. The theory calculations reveal the substituted acetate group of [IDA] anion can further interact with a second CO₂ very efficiently ($\Delta H_2 = -52.8 \text{ kJ} \cdot \text{mol}^{-1}$) after the amino group complexes with the first CO₂ ($\Delta H_1 = -89.0 \text{ kJ} \cdot \text{mol}^{-1}$) in contrast to that of [Gly] anion ($\Delta H_2 = -19.6 \text{ kJ} \cdot \text{mol}^{-1}$) (Figure 1b). The multi-site interactions between [IDA] and CO₂ were further verified by FT-IR and ¹³C NMR spectra (Figures 1c and 1d). In the IR spectra, the peak attributable to N-H stretch disappeared and simultaneously, two new characteristic peaks were observed at 1630 and 1423 cm⁻¹ attributable to NH-CO₂ and O-CO₂ interactions, respectively. In the ¹³C NMR spectra, two new resonances at 156.8 ppm and 163.5 ppm were observed, which could be assigned to NH-CO₂ and O-CO₂ carbon atoms, respectively. Therefore, the introduction of an electron-withdrawing acetate group could reduce the negative inductive effect of the amino group, while the other carboxylate group was simultaneously activated to interact with CO₂ efficiently (Figure 1). Thus, an extremely high absorption

Scheme 3 (a) Chemical structures of the anions and cations in amino-polycarboxylate-based ILs (APC-ILs) and (b) the proposed mechanism of CO₂ absorption by [P₄₄₄₂]₂[IDA] through multiple-site interactions.^[11]

Figure 1 (a) Absorption of CO₂ in five synthesized APC-ILs over time at 40 °C and 1 bar; (b) Multiple-site interaction of [IDA] and [Gly] anions with CO₂ by DFT calculation; (c) FTIR and (d) ¹³C NMR spectra of APC-IL [P₄₄₄₂]₂[IDA] before and after the capture of CO₂.^[11]

capacity of 1.69 mol CO₂ per mol IL was achieved. Furthermore, a new preorganization and cooperation strategy was developed for highly efficient and reversible capture of low-concentration CO₂ by imide-based ILs, giving rise to an extremely high gravimetric capacity of up to 22 wt% (1.65 mol CO₂ per mol IL) and excellent reversibility (16 cycles) from 10 vol% CO₂ in N₂.^[12]

Rapid uptake kinetics

Traditional amino-functionalized ILs exhibit high reactivity towards CO₂, however, they often encounter dramatic viscosity increase upon the uptake process due to the formation of a strong and pervasive hydrogen-bonded network.^[7] Thus, it is crucial to eliminate intermolecular hydrogen bonding in ILs during the capture process for a fast absorption rate of CO₂. Generally, there are two ways to tackle this issue. Firstly, a series of special means based on amino-functionalized ILs were developed to avoid the formation of an extensive hydrogen-bonded network, such as introducing electrostatic interaction or creating intramolecular hydrogen bonding/intramolecular proton transfer. Secondly, non-amino functionalized ILs such as azolide or phenolate ILs were designed in consideration of the lack of proton donor and acceptor in such systems.^[8,13]

Recently, Pan and co-workers^[13] designed a series of amino-functionalized ILs that possess equimolar and fast absorption of CO₂ by setting an amino group in the vicinity of negative oxygen atom in the pyridine anion (Scheme 4). Once CO₂ reacts with the amino group to form the carbamic acid, and subsequently the proton on carbamic acid can transfer to the negative oxygen group in the anion, resulting in enhanced CO₂ absorption capacity and improved uptake kinetics. For example, [P₆₆₆₁₄][2-NH₂-3-O-Py] could capture almost equimolar absorp-

tion capacity of CO₂ within only 25 min (Figure 2). In contrast to traditional amino-functionalized ILs, the viscosity of [P₆₆₆₁₄]-[2-NH₂-3-O-Py] has a remarkable decrease from original 1567 to 938 cP after the uptake of CO₂.^[13] The availability of intramolecular hydrogen bonding prevented the formation of extensive intermolecular hydrogen bonded network and contributed to greater anion asymmetry and disorder for the acceleration of the rotational and translational dynamics of IL, thus resulting in this viscosity decrease of around 40%. This finding endowed amino-functionalized ILs with new vitality toward practical application.

Scheme 4 Structures of the anions and cations used in creating amino-functionalized ILs.^[13]

Non-amino anion-functionalized ILs are another important approaches to make the viscosity of system controllable during the CO₂ capture in the absence of hydrogen bonded networks. Substituted azolides or phenolates are the popular options as the functionalized anions of ILs in view of their tunable absorption enthalpy and viscosity change during the CO₂ uptake process, providing an opportunity for high capacity and rapid up-take of CO₂ with low energy demand. Typically, Wang *et al.*

Figure 2 CO₂ absorption by amino-functionalized ILs as a function of time at 30 °C: [P₆₆₆₁₄][2-NH₂-3-O-Py] (■), [P₆₆₆₁₄]-[2-NH₂-4-O-Py] (●), [P₆₆₆₁₄][2-NH₂-6-O-Py] (▲), [P₆₆₆₁₄]-[3-NH₂-4-O-Py] (▼).^[13]

reported a class of non-amino anion-functionalized ILs such as azazolidine-functionalized ILs in order to achieve rapid CO₂ absorption kinetics (Scheme 5 and Figure 3).^[8] The absorption was almost complete in the first 10 min and no obvious viscosity change was observed. As example, the viscosities of [P₆₆₆₁₄][Pyr] and [P₆₆₆₁₄][Im] varied in a small range from 245.4 to 555.1 cP and 810.4 to 648.7 cP after the CO₂ absorption, respectively.^[8]

Scheme 5 Structure of anion and cation in azolide or phenolate functionalized ILs for CO₂ capture.^[8]

Figure 3 Rapid CO₂ absorption by some non-amino anion-functionalized ILs: $\diamond$ [P₆₆₆₁₄][Pyr], $\square$ [P₆₆₆₁₄][Im], ∇ [P₆₆₆₁₄][Triz], $\circ$ [P₆₆₆₁₄][Oxa], $\triangleleft$ [P₆₆₆₁₄][Tetz], $\triangle$ [P₆₆₆₁₄][PhO].^[8]

Long cycling life

The reversibility of IL is an important criterion for evaluating the CO₂ absorption performance of IL. A long cycling life of IL indicates the high stability of IL in CO₂ capture and release. The CO₂ absorption into and release from the IL in repeatedly cycles illuminates the sustainability for both the regeneration of absorbent and the CO₂ recycling performance, offsetting the relatively high cost of IL for practical application. As aforementioned, although amino-functionalized ILs and protic ILs exhibit high absorption capacity of CO₂, their stabilities during the recycling capture of CO₂ are a severe issue due to solvent degradation/oxidation or solvent loss during the absorption process. Therefore, the combination of phosphonium cations and non-amino functionalized anions could overcome this drawback.

With regard of the low stability of some anions such as phenolate and imidazolate during CO₂ uptake, Pan *et al.*^[9] designed a dual-tuning strategy to achieve both enhanced molar capacity of CO₂ and excellent cycling life by introduction of a large π -conjugated structure into the anion of IL (Scheme 6). The high molar capacity of CO₂ may be as a result of the strengthened dynamic covalent bonds through anion aggregation and the excellent reversibility originates from π -electron delocalization through charge dispersion. The desorption of [P₆₆₆₁₄][PNNPhO] was complete at 80 °C under N₂ atmosphere, while on the contrary, there is 0.17 mol CO₂ per mol IL residues remained for [P₆₆₆₁₄][PhO] under the same condition (Figures 4a and 4b). In contrast to the poor stability of [P₆₆₆₁₄][PhO], an excellent cycling reversibility in [P₆₆₆₁₄][PNNPhO] (up to 12 cycles) was observed during the CO₂ absorption and desorption (Figure 4c). Furthermore, thermogravimetric analysis (TGA) revealed that the release of CO₂ captured in [P₆₆₆₁₄][PNNPhO] began at 40 °C and was almost complete at 120 °C (Figure 4d), revealing an improved desorption performance as compared to [P₆₆₆₁₄][PhO]. However, the main disadvantages of these large π -conjugated ILs are the slow absorption kinetics and low gravimetric capacity of CO₂.

Scheme 6 Structure of anion and cation in large π -conjugated anion-functionalized ILs for CO₂ capture.^[9]

A class of tunable basic ILs such as $[P_{66614}][Triz]$ was developed for equimolar CO_2 capture as well as excellent reversibility. 25 cycles of CO_2 absorption and desorption demonstrate the CO_2 capture process by $[P_{66614}][Triz]$ is highly reversible (Figure 5).^[8] Moreover, the features of $[P_{66614}][Triz]$ also include desirable enthalpy of absorption, high absorption capacity, rapid absorption rate, offering an industrially attractive alternative for CO_2 capture. The replacement of $[P_{66614}]$ by a smaller molar weight cation such as tributyl(ethyl)phosphonium $[P_{4442}]$ may benefit for higher gravimetric capacity.^[12] Thus, the IL consist of an azolide anion and a phosphonium cation with small molecular mass provides an opportunity to meet the requirements of high performing CO_2 capture.

Figure 4 (a) Absorption kinetics of [P₆₆₆₁₄][PNNPhO] (■) and [P₆₆₆₁₄][PhO] (●) at 30 °C; (b) desorption kinetics of [P₆₆₆₁₄][PNNPhO] (■) and [P₆₆₆₁₄][PhO] (●) under N₂ purge at 80 °C; (c) 12 CO₂ absorption/desorption cycles in [P₆₆₆₁₄][PNNPhO], where CO₂ was absorbed at 30 °C and 1 bar for 150 min and desorbed at 80 °C under N₂ bubbling for 20 min; (d) TGA data of the ILs after CO₂ uptake: [P₆₆₆₁₄][PNNPhO] (black), [P₆₆₆₁₄][PCCPhO] (red), [P₆₆₆₁₄][PPhO] (blue), and [P₆₆₆₁₄][PhO] (dark cyan).^[9]

Figure 5 25 cycles of CO₂ absorption and desorption in [P₆₆₆₁₄][Triz]. CO₂ absorption was carried out at 25 °C for 20 min and desorption was performed at 80 °C under N₂ bubbling for 20 min.^[8]

Conclusions

Chemisorption of CO₂ by functionalized ILs is an appealing approach for high capacity and selectivity of CO₂. Careful structural design of ILs is essential to achieve desirable absorption enthalpy, favorable stability, fast reaction kinetics and excellent cycling life. In this mini-review, we discuss briefly some typical examples of the amino-functionalized ILs and non-amino anion-functionalized ILs for CO₂ capture. The traditional amino-functionalized ILs show high reactivity to CO₂, however, the uncontrollable viscosity change and high energy demand are the major obstacles to limit their practical application. The introduction of intramolecular hydrogen bonding or intramolecular proton transfer or electrostatic interaction in amino-functionalized ILs can avoid the formation of intermolecular hydrogen bonded networks and contribute to fast absorption kinetics of CO₂. Another promising approach is to develop non-amino anion-functionalized ILs such as substituted

azolides or phenolates for fast uptake of CO₂ due to the absence of proton donor and acceptor in these systems. High absorption capacity of CO₂ is one of the most important goals for ILs in CO₂ capture. The use of protic ILs or the introduction of multi-site cooperative interactions is an effective strategy to obtain high gravimetric capacity of CO₂. However, protic ILs are mostly faced with solvent loss or degradation problems during CO₂ uptake. Thus, the selection of phosphonium cations and non-amino functionalized anions to obtain a series of high stable aprotic ILs is much helpful to have a long cycling life during the CO₂ absorption and desorption process. Trihexyl-(tetradecyl)phosphonium [P₆₆₆₁₄] was used as the most common phosphonium cation due to its high stability, however, its large molar mass is against high gravimetric capacity. Therefore, a compromising strategy is required to achieve a commercially practical technology based on functionalized ILs.

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Author Contributions

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