



Ionic Liquids: Potential Materials for Carbon Dioxide Capture and Utilization

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The non-volatility, structure-tunability, and high CO₂ uptake capacity render ionic liquids (ILs) the most exciting materials for the carbon dioxide (CO₂) capture and fixation to value-added chemicals. The aim of this mini-review is to give a brief idea about the development of the potential ILs for CO₂ capture, the mechanism involved in the CO₂ binding and the application of ILs in the conversion of CO₂ to useful chemicals. The mechanisms and nature of interactions in between IL-CO₂ have been discussed in terms of the nature of cation, anion, presence of functional group, and the extent of interaction between the components of ILs. The fixation of CO₂ to linear and cyclic carbonates and electroreduction of CO₂ to carbon-rich fuels in ILs has been accounted in detail. At the end, future challenges in terms of commercializing the ILs for CO₂ capture and utilization technology are discussed.

Keywords: ionic liquid (IL), CO₂ capture, mechanism of CO₂-IL interaction, electrochemical reduction, dimethyl carbonate and faradaic efficiency

INTRODUCTION

Carbon dioxide (CO₂) emissions to the atmosphere give rise to negative environmental impacts as the release of it causes greenhouse effect leading to global warming (Ben-Mansour et al., 2016; Sanz-Perez et al., 2016). Apart from the anthropogenic activities, which account for the major release of the CO₂ into the environment, the energy gas resources, like natural or shale gas, syngas, and biogas, also contain a significant fraction of CO₂ lowering the heating value of gases, causing corrosion of equipment and demanding high energy cost during conversion and transportation (Huang et al., 2014; George et al., 2016). Therefore, developing technologies that can capture CO₂ have been of prime importance. One such technology is carbon dioxide capture and sequestration (CCS) where aqueous amine [typically monoethanolamine (MEA) and methyldiethylamine (MDEA)] are used as scavengers in CO₂ capture (Thitakamol et al., 2007). These solvents have several disadvantages such as high volatility, high cost, substantial energy consumption and corrosiveness and, therefore, designing new solvents is of prime importance (Shao and Stangeland, 2009). Ionic liquids (ILs) possess unique characteristics over the volatile organic compounds (VOCs) and have been explored in various chemical and biological applications (Steinruck and Wasserscheid, 2015). In the past decade, they were extensively studied as scrubbers of greenhouse gases (Zeng et al., 2017). The initial interests in these solvents emerged because of their negligible vapor pressure, high thermal stability, wide liquidus range, relative non-flammability, designability, and recyclability. The designability gives an extra edge to ILs over conventional scrubbers like MEA and MDEA and large number of potential ILs have been designed to achieve optimum CO₂ solubility. Of these,

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the representative class consists of imidazolium, pyridinium, pyrrolidinium, guanidinium and amine cations, and organic/inorganic (carboxylate, azolate, phenoxide, proline, thionate, halide, tetrafluoroborate, hexafluorophosphate, anion, etc (Zhang Y. Q. et al., 2009; Goodrich et al., 2011; Niedermaier et al., 2014). Contrary to the cation, the basicity of the anion was noted to influence more the CO₂ uptake in ILs. Process simulations showed that use of ILs in place of well-known MDEA can bring down the total electrical and thermal energy by 42.8 and 66.04%, respectively (Liu et al., 2016). The regeneration energy demand also decreased by 15% when IL (1-butylpyridinium tetrafluoroborate) was used in place of MEA (Mumford et al., 2015).

The major drawback of ILs as a scrubbing agent arises from their high viscosity which further increases upon CO₂ capture. For example, the viscosity of 3-aminopropyl tributylphosphoniumamino acid ([aP₄₄₄₃][AA]) and trihexyl(tetradecyl)-phosphonium isoleucinate ([P₆₆₆₁₄][Iso]) increased 3- and 200-fold, respectively, upon CO₂ capture (Liu et al., 2009; Gurkan et al., 2010a). However, the high viscosity of ILs can be lowered by incorporating ether functionality, imidazolate anion, addition of molecular solvents, and incorporating them on polymer membrane. The viscosity of trihexyl-(tetradecyl)phosphonium imidazolate ([P₆₆₆₁₄][Im]) was lowered upon CO₂ capture from 810.4 to 648.7 mPa.s because of the combined effect of physisorption and chemisorption (Wang et al., 2011). Similarly, the addition of ether functionality in ILs lowered the viscosity by 43% compared to non-functionalized ILs (Zeng et al., 2015). The addition of amine-based solvent in ILs also decreases viscosity exponentially without affecting the CO₂ uptake (Zhao et al., 2011).

The Carbon Capture Storage and Utilization (CCSU), which comprises all the efforts taken to reduce the CO₂ release in environment and its conversion to value-added products, has been worldwide accepted as the strategy to reduce the negative environmental effects of CO₂. Due to their dual nature, both as catalyst and solvent, ILs have been utilized in the conversion of CO₂ to useful organic moieties like, linear and cyclic carbonates, carbonmonoxide, methanol, formic acid/formates etc (Alvarez-Guerra et al., 2015). The electrochemical reduction of CO₂ is interesting as it operates at low temperatures and pressures. The electro-reduction of CO₂ requires an aqueous electrolyte medium which can absorb CO₂ and decrease the over-potential required to give rise to the CO₂⁻ radical anion in the presence of a metal cathode (Ag, Au, Pt, etc.) (Oh and Hu, 2013). Similarly, CO₂ can yield linear and cyclic carbonates at elevated temperatures and pressures. Thus, ILs serve the purpose because of the high CO₂ uptake efficiency (Xu et al., 2015).

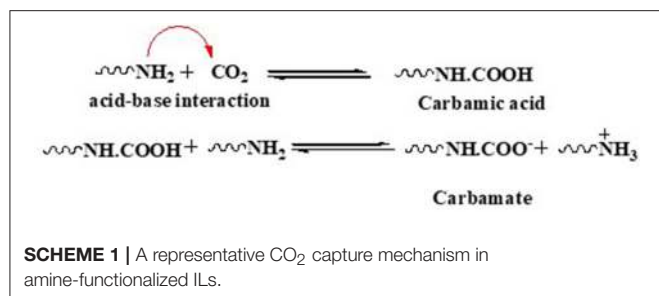
Ionic Liquids in Carbon Dioxide Capture

The pioneering work of Blanchard et al. showed for the first time that IL (1-butyl-3-methylimidazolium hexafluorophosphate, [BmIm][PF₆]) can be employed in CO₂ capture. Since then, plethora of research unraveling the mode and mechanism of CO₂ capture in conventional and functionalized ILs have been reported. In conventional ILs, the cation plays a minor

role and the basicity of the anion is observed to affect the CO₂ adsorption. Higher CO₂ uptake was attained in task-specific ILs despite their high viscosity. In this regard, superbase-derived ILs were tested for the optimum CO₂ uptake (Rebecca et al., 2015). Bates et al. (2002) reported semimolar CO₂ absorption in amino-functionalized ILs under ambient conditions. Gurkan et al. (2010b) succeeded in the equimolar absorption with amino acid-based ILs containing proline and methionine anions with phosphonium cation. Later, Wang et al. (2011) achieved equimolar absorption in ILs comprised of pyrazolate, imidazolate, triazolate, tetrazolate, indolate, and oxalate anion and phosphonium cation thus obtaining a linear correlation between the CO₂ capacity and basicity (pK_a) of ILs in DMSO. Multimolar CO₂ absorption (1.69 mol.mol⁻¹) was observed during the activation of carboxylic group in amino-functionalized ILs (Chen et al., 2016). The carboxylate group in the vicinity of NH- moiety stabilizes the CO₂ at the carbamic acid stage, thereby promoting the multimolar absorption. Similarly, a combined experimental and theoretical study on hydroxyl IL with phenolate anion showed 1.5 equivalent CO₂ uptake as both hydroxyl and phenoxide groups participated in the absorption (Vafaezadeh et al., 2015).

MECHANISMS OF CARBON DIOXIDE CAPTURE IN ILS

Besides the CO₂ uptake efficiency and selectivity, the mode of IL-CO₂ interaction also reveals important information in terms of selection of components and functionality for designing potential ILs. In [BF₄]- and [PF₆]-based ILs, an acid-base interaction was observed operating between the acetate anion and CO₂ (ATR-IR spectroscopy, Raman spectroscopy and DFT calculations) (Kazarian et al., 2000; Cabaco et al., 2011). Though acid-base interaction shed light on the interaction mechanism, it is not the sole reason for CO₂ uptake as the uptake efficiency doesn't follow the basicity order (Lei et al., 2014). The shortcomings of acid-base theory were later explained by the amount of free-volume in the IL system (Aki et al., 2004). The longer alkyl chain on cation and high anion fluorination increase the extent of free-volume and hence increase CO₂ solubility (Muldoon et al., 2007; Almantariotis et al., 2010). For example, 1-hexyl-3-methylimidazoliumtris(pentafluoroethyl) trifluorophosphate ([HmIm][FEP]) showed 70% higher CO₂ solubility than [HmIm][PF₆] because of the presence of six CF₂/CF₃ in [FEP] than [PF₆] and hence leads to larger free-volume (obtained by Monte Carlo and MD simulations) (Zhang X. C. et al., 2009). Apart from these, weak interactions such as hydrogen and halogen bonding were shown to affect the CO₂ uptake (Palomar et al., 2011; Zhu et al., 2011). The CO₂ capture mechanism in [HmIm][PF₆] and [FEP] showed the importance of electrostatic interaction in the CO₂ uptake in smaller and symmetrical [PF₆] anion whereas the van der Waals interaction has a key role in large and asymmetrical [FEP] anion (Zhang X. C. et al., 2009). In case of gas-[BmIm] cation complex, CO₂ interacts with cation by the formation of hydrogen bond on the C2 carbon (Zhao et al., 2015).



The amine-CO₂ interaction in ILs follows two mechanisms, namely semimolar and equimolar, depending on the presence of amine moiety on cation or anion in ILs (Bates et al., 2002). It is noted that ILs cation tethered with amine moiety follows semimolar mechanism while an equimolar mechanism operates if the amine is a part of the anion (Cao et al., 2016). A molar uptake plot clearly reveals the type of operative mechanism in a medium. In semimolar mechanism, CO₂ first reacts with amine moiety to form carbamic acid which further reacts with another molecule of amine to yield ammonium carbamate as the final product (Scheme 1). Thus, for one mole of CO₂, two moles of amine are required.

In equimolar mechanism, one mole of amine captures one mole of CO₂ and stabilizes the product as carbamic acid (Kasahara et al., 2016). Various studies have claimed multimolar absorption in ILs because of the presence of stabilizing group in the vicinity of NH₂- moiety of the amine (Luo et al., 2014).

Though amine-functionalized ILs improves CO₂ solubility in ILs, high viscosity and regeneration of ILs remain as challenges. To address these problems Wang et al. (2010) proposed non-amine functionalized superbases-derived protic ILs for equimolar CO₂ capture. Later, phenolic ILs were prepared from the phosphonium hydroxide and substituted phenols whereupon the effect of position and nature of substituents on the anion were correlated with the physicochemical properties and CO₂ uptake efficiency (Wang et al., 2012). Thus, cation-anion interaction strength affects the CO₂ uptake in phenolic ILs (Lee et al., 2016).

APPLICATIONS OF IONIC LIQUIDS IN CONVERSION OF CARBON DIOXIDE TO VALUE-ADDED PRODUCTS

IL-mediated conversion of CO₂ to value added products has been achieved through chemical, thermochemical, photochemical, biochemical, and electrochemical reduction methods (Barton et al., 2008; Chueh et al., 2010; Rosen et al., 2011; Chen et al., 2012; Costentin et al., 2012). Out of these methods, chemical and electrochemical reduction of CO₂ are the most attractive methods. In the chemical conversion method, epoxides and methanol were employed to convert CO₂ to cyclic and linear carbonates, respectively, via cycloaddition reactions. The electrochemical reduction of CO₂ is highly popular because of its higher conversion efficiency, product selectivity and its potential to store electrical energy from renewable energy sources like the sun (Spinner et al., 2012).

Conversion of CO₂ to Organic Carbonates

Organic carbonates have many industrial applications as green aprotic polar solvents, electrolytes for lithium-ion batteries as well as intermediates upon production of pharmaceuticals and polymers (Chaugule et al., 2017). This mini-review highlights recent findings in catalysis converting CO₂ to organic carbonates based on ILs under mild conditions (low temperature and pressure).

Five-Membered Ring Cyclic Carbonate

Traditional ILs-based catalysis for cyclic carbonates synthesis from CO₂ was reported first time in 2001 (Peng and Deng, 2001). In this study, a series of RTILs based on cations (BmIm⁺, BPy⁺) and anions (Cl⁻, BF₄⁻, PF₆⁻) acted as recyclable catalysts to produce propylene carbonate from propylene oxide and CO₂ in the absence of a solvent. Among them, [Bmim][BF₄] showed the highest catalyst activity with 100% yield under optimal conditions (110°C, 6 h, 2.5 MPa of CO₂, 2.5 mmol of [Bmim][BF₄] per 100 mmol of epoxide). Until now, numerous other ILs including new generations such as task-specific ILs were investigated for improving the production of cyclic carbonates under different experimental conditions (Chaugule et al., 2017).

Recently, a dual-IL system as a recyclable, efficient catalyst for cyclic carbonate synthesis under mild, solvent-free conditions was developed (Hu et al., 2018). In this study, [TMGH⁺][⁻O₂MMIm⁺]Br⁻ showed the best catalytic performance with 84% yield under optimal conditions (30°C, 12 h, 0.1 MPa of CO₂, 0.5 mmol of IL per 2 mmol of epichlorohydrin). The mechanism was also suggested, wherein a synergistic catalytic effect among carboxylate anion, bromide anion and the N-H bond of the iminium ion results in the cycloaddition of CO₂ and epoxide.

Moreover, to render the catalyst separation and reusability issues easier and practical in industry, the immobilization of ILs-based catalysts on recyclable solid supports has been widely studied (Chaugule et al., 2017). Several ILs such as [BmIm][X] (where X = Cl, Br, I) and [EpIm][X] were immobilized on commercial SiO₂ (pore size 6 nm, 35–70 μm) to yield efficient catalysts to produce cyclic carbonates under mild conditions (Martínez-Ferraté et al., 2018). Silica-supported [EpIm]Br was the best system reaching 99% conversion in just 30 min under optimal conditions (80°C, 5 bar of CO₂, 1.67 mmol of IL per 3.34 mmol of propylene oxide). This catalyst system was still active (79% conversion) when using a model gas mixture from an industrial exhaust (15% CO₂) instead of synthetic CO₂.

Dimethyl Carbonate

Recently, in the presence of different organic and inorganic bases, several imidazolium hydrogen carbonate ILs ([CnCmIm][HCO₃]) were used (recyclable catalyst and dehydrant) upon straightforward synthesis of dimethyl carbonate from CH₃OH and CO₂, at room temperature and 1 MPa of CO₂ (Zhao et al., 2017). Under optimal conditions, a combination between [BmIm][HCO₃] and Cs₂CO₃ in the presence of CH₂Br₂ solvent showed the highest conversion of CH₃OH (74%) and was easily reused.

Electrochemical Fixation of CO₂ in ILs

CO₂ is an abundantly available renewable C1 feedstock from various emission sources such as coal fired power plants, bio-refineries, crude oil processing industries etc (Friedlingstein et al., 2011). In the view of the negative impact of CO₂ on environment, its conversion to fuels and fine chemicals could be a way to eliminate the harmful effects of this greenhouse gas (Ansari and Park, 2012). The electrochemical and photochemical approaches were undertaken to convert CO₂ into useful chemicals such as methanol, carbon monoxide, ethylene, formic acid/formate, higher alcohols, alkanes etc. as well as important building blocks to synthesize various platform chemicals as well as polymers (Xiaoding and Moulijn, 1996). The electrochemical process involves cathodic reduction of CO₂ and anodic oxidation of solvent.

The centrosymmetric structure makes CO₂ electrically neutral though it has a bond dipole. **Scheme 2** shows steps through which CO₂ is reduced to various useful products, at different standard potentials (E⁰). The hydrogen formed in these reactions is an undesired major byproduct and should be avoided (Feng et al., 2018a). To eliminate H₂ from the process, a non-aqueous medium is required and room temperature ionic liquids (RTIL) are ideal in this regard.

Electrochemical Conversion of CO₂ to CO

RTILs as a dual medium were extensively explored in the electrochemical conversion of CO₂ to CO during the last decade. Rosen et al. (2011) studied electrochemical reduction of CO₂ to CO in 18% aqueous 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) and observed high Faradaic efficiency (96% for 7 h) with extremely low potential. The RTIL cation was noted to reduce the H₂ generation thereby assisting in the reduction of CO₂ to CO. Later, several ILs comprised of imidazolium, pyrrolidinium, ammonium, phosphonium cation and (bis(trifluoromethylsulfonyl)imide ([NTf₂]), tris(pentafluoroethyl)trifluorophosphate ([FAP]), and tetrafluoroborate [BF₄]) anion and role of substituents on the cationic core was investigated in the reduction of CO₂ to CO (Alvarez-Guerra et al., 2015; Lim and Kim, 2017). In all these

studies Au, Ag, Pt, and glassy carbon-based cathodes were used as electro-catalysts (Alvarez-Guerra et al., 2015). During the reduction, the IL cation coordinates with CO₂ molecule and forms CO₂⁻ radicals under negative electrode potential which subsequently form CO (Sun et al., 2014; Feng et al., 2018b).

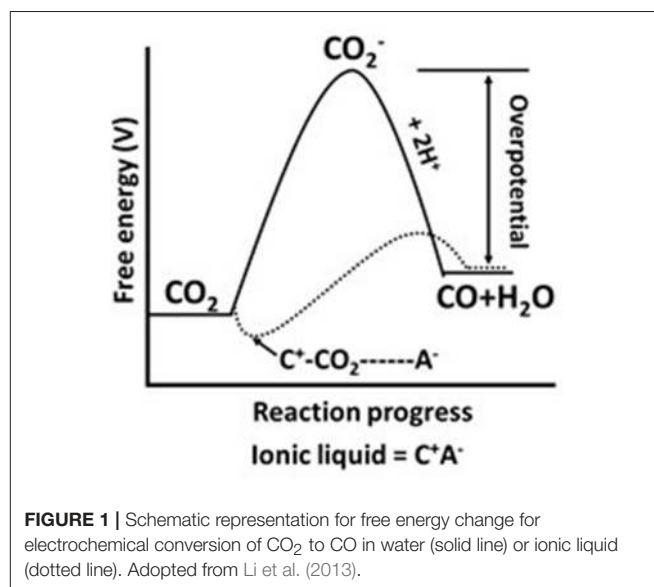
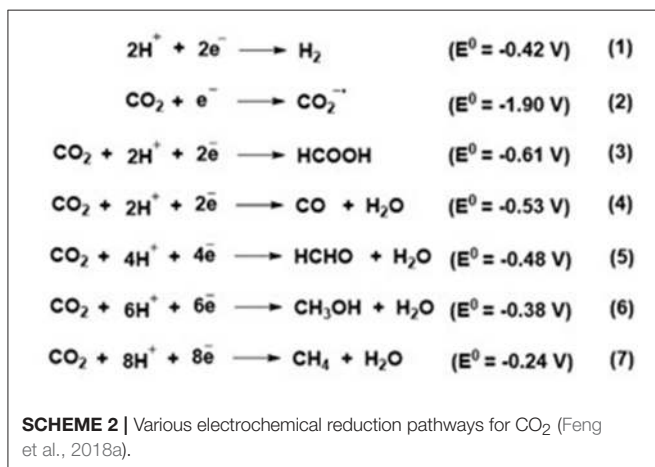
In other words, as shown in **Figure 1**, the electrochemical reduction of CO₂ to CO follow alternative path where the conversion proceeds with low overpotential compared with the case when there is an IL involved in the process. In reality, IL activates CO₂ molecule via formation of “cation-CO₂” intermediate through which the formation energy of CO₂⁻ radical anion decreases.

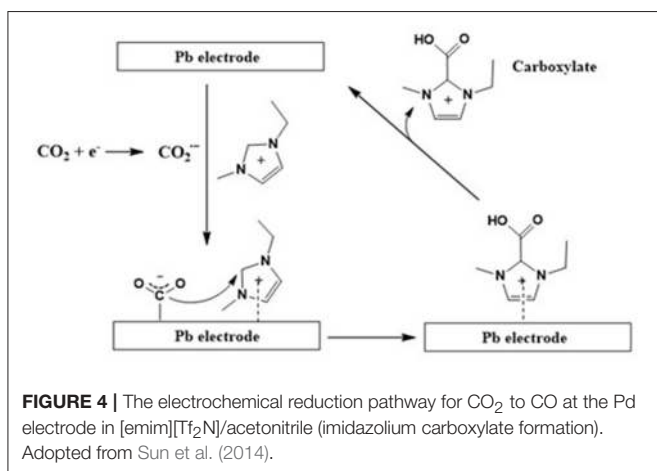
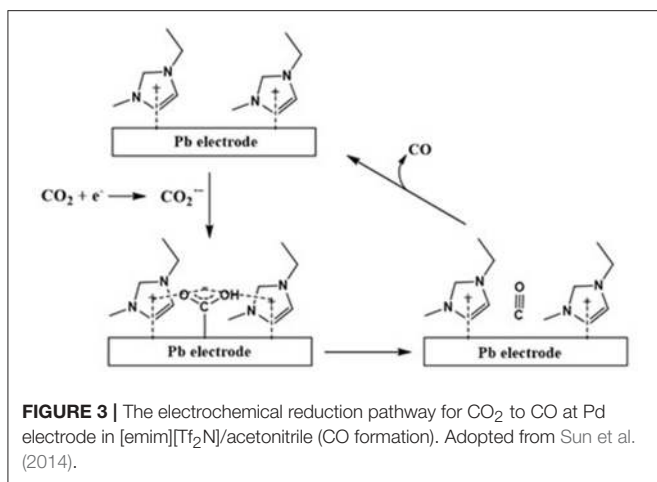
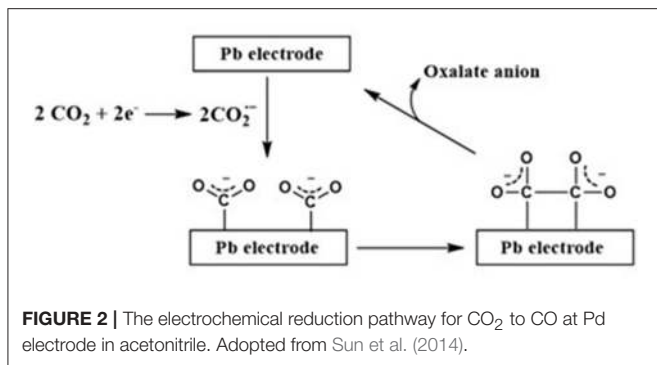
Alternatively, as shown in **Figures 2, 3**, Sun et al. (2014) proposed a mechanism for the electrochemical reduction of CO₂ to CO in the absence and presence of an IL at the Pd electrode in acetonitrile. In this case, based on the experimental evidence, the author proposed that the presence of an IL switches the course of electrochemical reduction of CO₂ where the IL favors the CO formation pathway instead of the undesirable oxalate anion formation.

As shown in **Figure 2**, the *in-situ* formed CO₂⁻ radical anion formed over the Pd electrode further dimerizes to an oxalate anion in the absence of an IL. On the other hand, as shown in **Figure 3**, the IL stabilizes CO₂⁻ and prevents its dimerization whereupon this stabilized CO₂⁻ further converts to CO molecule.

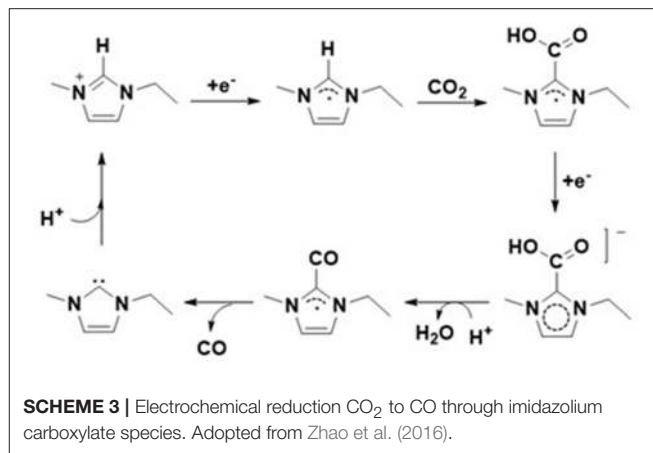
Additionally, it was also observed that along with CO formation, the imidazolium carboxylate formation pathway also exists (**Figure 4**). An earlier theoretical as well as experimental studies study performed by Zhao et al. (2016) claims that the formation of this carboxylate species deactivates the active sites on the imidazolium cation. However, these active imidazolium sites can be recovered by an addition of a proton source such as water.

Further, based on the density functional theory (DFT) as well as Raman and NMR spectroscopic techniques, Wang et al. (2015) also represented another alternative mechanism





for the formation of CO through electrochemical reduction of CO₂. The author proposed that in the presence of a proton source such as water, the *in-situ* formed carboxylate species can decompose into CO and the active imidazolium cation can be recovered (Scheme 3). In this case, the author reported that the imidazolium cation served as a co-catalyst as it provides its own acidic proton in the CO formation process. However, the role of this co-catalysis is limited to the having a proton source in the reaction medium to recover the imidazolium cation in the catalytic cycle.



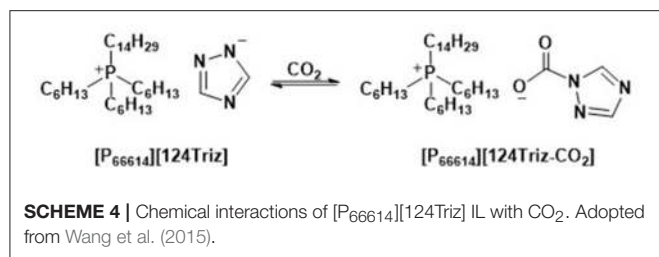
Hence, even though the formation of CO can be explained based on different mechanistic approaches, these studies indicate that ILs are playing an important role upon electrochemical reduction of CO₂ to CO.

Electrochemical Conversion of CO₂ to Formic Acid/Formate

The electrochemical conversion of CO₂ to formic acid was also undertaken by several workers. Watkins and Bocarsly (2014) used 1-ethyl-3-methylimidazolium trifluoroacetate ([Emim][TFA]) along with various metals as co-catalysts in the electrochemical conversion of CO₂ to HCOOH and found that iridium is an efficient catalyst. Hollingsworth et al. (2015) performed selective conversion of CO₂ to formate and syngas by an anion assisted electrochemical process. The IL consisting of tetraalkylphosphonium cation and 1,2,4-triazolate anion [P₆₆₆₁₄][1,2,4Triz] absorbed equimolar amount of CO₂ and assisted in the selective conversion of CO₂ to formate under extremely low applied electrode potential (−0.7 V vs. Ag⁺/Ag).

In a detailed study based on cyclic volumetric measurements for two different ILs, [P₆₆₆₁₄][1,2,4Triz] and [P₆₆₆₁₄][NTf₂], the author observed that the [1,2,4Triz][−] anion comprising IL were found more efficient compared to their [NTf₂][−] anion containing analogs upon electrochemical reaction of CO₂ to CO. In this case, in addition to physical interactions of the [P₆₆₆₁₄]⁺ cation with CO₂ (i.e., formation of [CO₂][−][P₆₆₆₁₄]⁺), the chemical interactions of the [1,2,4Triz][−] anion with CO₂ allowed for low-energy electrochemical reaction of CO₂ to CO (Scheme 4) compared to the case when the [P₆₆₆₁₄][NTf₂] IL was employed.

Zhang et al. (2017) studied CO₂ to formic acid conversion in the aqueous solution of 1-ethyl-3-methylimidazolium dicyanamide ([Emim][N(CN)₂]) using Sn powder electrode and noted that IL assisted in the electrochemical activation and conversion of CO₂ to HCOOH but also increased the solubility of CO₂ in the electrolyte system for maximum output. The 81.9% of Faradaic efficiency was achieved with 0.5 M [Emim][N(CN)₂] in water, under the potential of −1.2 V vs. reversible hydrogen electrode (RHE). Lu et al. (2017) first time introduced photo-electrochemical conversion of CO₂ to



HCOOH using functionalized IL such as 1-aminopropyl-3-methylimidazolium bromide ([NH₂C₃mim]Br) and the 94.1% faradaic efficiency was obtained for HCOOH conversion. The author claimed that the effective interaction of CO₂ with the IL cation facilitated the conversion of CO₂ to HCOOH. Recently, Huan et al. (2017) observed a cost-effective electro-reduction of CO₂ to HCOOH in [EMIM][BF₄] using a copper-based electrocatalyst as cathode achieving high Faradaic efficiency (87% for 8 h). Compared to the electrochemical reduction of CO₂ to CO, the electrochemical transformation of CO₂ to HCOOH or formate is still in its infancy in ILs and further addressing is required to understand the phenomena in detail.

Electrochemical Conversion of CO₂ to CH₃OH

Similar to electrochemical conversion of CO₂ to CO and HCOOH, formation of methanol by electrochemical conversion of CO₂ is another anticipated application and has been investigated extensively in ILs. Transformation of CO₂ to methanol via electrochemical activation of CO₂ has been performed recently by Han and coworkers (Sun et al., 2016). They used various bimetallic catalysts such as Mo-Bi, Mo-Ag, and Mo-Cu in [BmIm][BF₄]/acetonitrile solution. The synergic effect of Mo and Bi metals as bimetallic catalyst upon electrochemical CO₂-activation in 0.5 M solution of IL in acetonitrile gave 71.2% Faradaic efficiency in methanol formation. In bimetal Mo-Bi catalyst, Mo facilitates conversion of CO₂ to CO while Bi assists in the formation of H₂ and adsorption of *in-situ* formed CO and, therefore, increases the possibility of hydrogenation of CO₂ to CH₃OH.

Hence, RTILs play an important role in the electrochemical conversion of CO₂ to various value-added and industrially important products such as CO, HCOOH, and CH₃OH. Though

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several hypotheses have been introduced to investigate the role of RTILs in the electrochemical reduction of CO₂, none of them provide satisfactory information regarding the process. This could more be due to the complex structural and electronic nature of ILs at the IL-electrode interface than that of water. However, last but not least, ILs are proposed as a sustainable and green approach to activate and reduce the CO₂ to essential chemical moieties with minimum energy consumption rather than the existing thermochemical approach.

CONCLUSIONS AND OUTLOOK

The remarkable properties of ILs over the conventional volatile solvents, such as non-volatility and structure-tunability, make them suitable for applications involving CO₂ capture and fixation. The mini-review highlights the development in the CO₂ uptake since the inception of ILs in this area and further development in the last decade. The effects of cations, anions, and functional groups on the physicochemical properties and their impact on CO₂ uptake were reviewed, in both conventional and functionalized ILs. The forces involved in the CO₂ capture and mechanism were discussed in various types of ILs. Despite the exciting response, the lack of inexpensive and diverse ILs poses a problem in applying them on large scale. Moreover, the impact of ILs on environment, corrosion, toxicity, and long-term stability need to be addressed.

DATA AVAILABILITY

All datasets generated for this study are included in the manuscript and the supplementary files.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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