Ionic liquid-based electrolytes for CO₂ electroreduction and CO₂ electroorganic transformation

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ABSTRACT

CO₂ is an abundant and renewable C₁ feedstock. Electrochemical transformation of CO₂ can integrate CO₂ fixation with renewable electricity storage, providing an avenue to close the anthropogenic carbon cycle. As a new type of green and chemically tailorable solvent, ionic liquids (ILs) have been proposed as highly promising alternatives for conventional electrolytes in electrochemical CO₂ conversion. This review summarizes major advances in the electrochemical transformation of CO₂ into value-added carbonic fuels and chemicals in IL-based media in the past several years. Both the direct CO₂ electroreduction (CO₂ER) and CO₂-involved electroorganic transformation (CO₂EOT) are discussed, focusing on the effect of electrocatalysts, IL components, reactor configurations and operating conditions on catalytic activity, selectivity and reusability. The reasons for the enhanced CO₂ conversion performance by ILs are also discussed, providing guidance for the rational design of novel IL-based electrochemical processes for CO₂ conversion. Finally, the critical challenges remaining in this research area and promising directions for future research are proposed.

Keywords: ionic liquid, carbon dioxide, electrocatalysis, green synthesis, value-added fuels and chemicals

INTRODUCTION

Human society relies mainly on fossil fuels to meet the main energy demand since the industrial revolution. The use of fossil fuels as energy carriers and raw materials promotes the rapid development of society. However, the excessive exploitation of fossil fuels has given rise to the energy crisis and undesirable environmental changes [1,2]. The unrestrained combustion of these non-renewable fossil fuels also leads to a continuous increase of CO₂ concentration in the atmosphere, which is >400 ppm today and is estimated to triple by 2040 [3]. The excessive emission of CO₂ results in a series of environmental issues, such as global warming, rising sea levels and more extreme weather events. As a consequence, the utilization of abundant renewable energy is an urgent need and challenge for our society.

CO₂ is not only one of the main greenhouse gases but also an abundant, non-toxic, non-flammable and renewable C₁ resource. Producing fuels or chemicals using CO₂ is an attractive way to achieve a carbon-neutral energy cycle [4]. As illustrated in Scheme 1, CO₂ can be used as a feedstock to synthesize fuels and chemicals through the formation of various chemical bonds, such as C−H, C−C, C−O and C−N bonds [5,6]. CO₂ reduction represents an essential approach for CO₂ utilization, in which CO₂ could be transformed into many platform chemicals through the construction of C−H bonds, such as hydrocarbons, acids and alcohols [7−9]. In addition, using CO₂ as one of the reactants to synthesize valuable products is also an emerging strategy for CO₂ conversion. When CO₂ is used in carboxylation reactions, C−C bonds can be formed to produce valuable products, like carboxylic acids and organic carbonates [10,11]. The C−O or C−N bonds are established in CO₂ cycloaddition reactions with different substrates (e.g. epoxides, aziridines or propargylic amines) to synthesize cyclic carbonates and oxazolidinone derivatives [12,13].

Although the exploitation of CO₂ is particularly promising, the high thermodynamic stability and chemical inertness of CO₂ make it difficult to activate, posing a huge challenge for CO₂ conversion technology. In the past decades, a host of available pathways have been used to convert CO₂ into
Scheme 1. Value-added fuels and chemicals produced from CO2 transformation through the construction of various C—X bonds.

Figure 1. Some typical cations and anions of typical ILs for CO2ER and CO2EOT.
ionic conductivity, high gas solubility and chemical diversity and tailorable ability [29]. In recent years, ILs have been studied extensively as electrolytes in many electrochemical reactions [30]. Many studies on CO2 capture also use ILs as CO2 absorbents because of their high CO2 solubility [26,31]. Therefore, ILs are considered an appealing alternative to aqueous and organic electrolytes in CO2ER and CO2EOT. The high absorption capacity of CO2, high intrinsic ionic conductivity and wide electrochemical potential windows of ILs are beneficial for CO2 conversion. It was reported that ILs could reduce the initial barrier of CO2 conversion through lowering the formation energy of CO2•− intermediate. Moreover, the competing hydrogen evolution reaction (HER) could be suppressed in the presence of ILs, which might be favorable for improving the selectivity of CO2 conversion [25].

Over the past 10 years, we have witnessed heightened research activities and an increasingly deepened understanding of the electrochemical transformation of CO2 in IL-based electrolytes. Different high-quality review articles on the electrochemical transformation of CO2 are accessible, involving electrocatalysts, electrolytes and electrochemical devices. However, a timely and comprehensive review devoted to both the direct CO2ER and CO2EOT in IL-based electrolytes is lacking. Considering the rapidity of progress in this field, the recent advances in electrochemical transformation of CO2 in IL-based electrolytes catalyzed with heterogeneous catalyst systems are discussed in this review. The review will be carried out in the following three parts. The direct CO2ER into various platform chemicals in IL-based electrolytes will be presented in the first part. The second part will concentrate on the use of CO2 as a reactant to realize its electroorganic transformation into valuable products in IL-based electrolytes. We will discuss the involved ILs system, various types of applied electrocatalysts, electrochemical cells, products and reaction mechanisms. In addition, the challenges and perspectives for CO2ER and CO2EOT in the IL-based system will be outlined in the final section.

**CO2ER in IL-Based Electrolytes**

**Fundamentals of CO2ER**

CO2ER is a proton-coupled multielectron transfer process, commonly involving 2, 4, 6, 8, 12 or even more electron reaction pathways [7,18]. Diversified reduction products with various carbon oxidation states can be obtained in the reduction process, including carbon monoxide (CO), formic acid/formate (HCOOH/HCOO−), methanol (CH3OH), formaldehyde (HCHO), methane (CH4), ethylene (C2H4), ethanol (CH3CHOH), acetic acid/acetaf (CH3COOH/CH3COO−) and n-propanol (C3H7OH). The electroreduction pathways for converting CO2 into the above products and the thermodynamic potential are displayed in Equations (1)–(6) (CO2 reduction potentials vs. standard hydrogen electrode (SHE) at pH 7) [7]. In terms of thermodynamics, it is readily accessible to reduce CO2 to these desirable products. Nevertheless, these reactions generally suffer from sluggish kinetics and low efficiency, which is related to the complicated reaction mechanism [32].

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O} \quad E_0 = -0.52 \text{ V} \quad (1)
\]

\[
\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH} \quad E_0 = -0.61 \text{ V} \quad (2)
\]

\[
\text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E_0 = -0.51 \text{ V} \quad (3)
\]

\[
\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E_0 = -0.38 \text{ V} \quad (4)
\]

\[
\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E_0 = -0.24 \text{ V} \quad (5)
\]

\[
2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O} \quad E_0 = -0.34 \text{ V} \quad (6)
\]

\[
\text{CO}_2 + e^- \rightarrow \text{CO}_2^{•-} \quad E_0 = -1.90 \text{ V} \quad (7)
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E_0 = -0.42 \text{ V} \quad (8)
\]

According to the literature, the reaction of CO2ER can be conducted according to the following three steps [15]. The first step involves CO2 adsorption and activation, which is considered the most critical bottleneck in CO2ER. CO2 is a highly stable linear molecule with no electrical dipole, which makes CO2 adsorption on the catalyst surface difficult, and a large amount of energy is needed to activate CO2 [21]. As shown in Equation (7), transferring one electron to the CO2 molecule to form the key intermediate CO2•− will initiate up to −1.90 V vs. SHE, which contributes to the high overpotential and an undesired major by-product H2 (Equation (8)). After the formation of CO2•−, the multiple proton-coupled electron transfers occur and generate diverse reduction products. However, the small difference in thermodynamic potential
Equations (1)–(6) can result in low product selectivity. Finally, the products are desorbed from the catalyst surface [18].

The typical heterogeneous system for CO$_2$ER consists of anode and cathode compartments separated by a proton exchange membrane [25]. Both the CO$_2$ reduction reaction and HER take place at the cathode driven by electric energy over the catalyst. The oxygen evolution reaction (OER) occurs in the anode compartment. An efficient electrocatalyst can suppress HER to reduce the by-product of H$_2$. The common heterogeneous electrocatalysts can be classified into four groups: metals/ alloys, metal oxides and sulfides, metal-organic frameworks/complexes, and carbon-based materials. To better realize CO$_2$ER, many studies have been devoted to developing heterogeneous electrocatalysts by means of surface engineering, chemical modification, doping and nanostructured strategy to improve the catalytic efficiency of CO$_2$ER [15,33–35].

The electrolyte, especially in the cathode, also has an important influence on CO$_2$ER. A CO$_2$-containing electrolyte provides a source of CO$_2$, enabling sufficient CO$_2$ to be transported to the electrocatalyst surface. The electrolyte not only has close interactions with the electrocatalyst, adsorbed CO$_2$ molecule and intermediates, but also undertakes the role of transporting charge species [22,36]. Therefore, the electrolyte with high solubility for CO$_2$ and other reactants, appreciable electric conductivities and wide electrochemical potential widows, is conducive to CO$_2$ conversion. The lower proton concentrations of electrolytes are beneficial in suppressing the competing HER and reducing the unwanted side-product H$_2$ in the CO$_2$ conversion process. Different kinds of electrolytes have been used for CO$_2$ER, such as aqueous electrolyte, organic electrolyte and IL-based electrolyte [37]. Among them, IL-based electrolytes are particularly advantageous because they can lower the energy to form CO$_2$•– intermediate and show a suppression effect on the HER [38–41].

**CO$_2$ER in IL-based electrolyte**

In 2004, Zhao et al. reported the electroosynthesis of syngas by electrolysing supercritical CO$_2$ and water in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF$_6$) electrolyte for the first time [42]. In addition to CO and H$_2$, a small amount of HCOOH was also detected. In 2011, Rosen et al. found that in an electrocatalytic system with Ag cathode and 18 mol% 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF$_4$) solution electrolyte, the reduction of CO$_2$ to CO could be conducted for at least 7 h with Faradaic efficiency (FE) of 96% and the overpotential was below 0.2 V [39]. They claimed that the IL electrolyte could reduce the energy of the CO$_2$•– intermediate probably by complexation, thus lowering the initial reduction barrier and contributing to the improved activity. This report was marked as an important breakthrough in the development of IL electrolytes for CO$_2$ER, and since then the use of IL-based electrolyte in CO$_2$ER has received extensive interest and much related research has been published.

Several properties of ILs including their structures, conductivity, viscosity, CO$_2$ solubility, polarity and stability can influence catalytic performance. Therefore, the cations/anions, functional group or even the length of the alkyl chain of ILs should be considered when using them as the electrolyte. Up to now, the most commonly used class of ILs are imidazolium-based ILs [19,40,41,43].

**Applied electrocatalysts**

So far, a diversity of electrocatalysts has been developed for CO$_2$ER in ILs. Metals are the most widely studied working electrode materials, including noble metals, transition metals and post-transition metals [15,21,44,45]. The noble metals Au, Ag and Pd are the representative model catalysts for CO$_2$ER to produce CO. Zhu et al. reported the improved activity of Au nanoparticles in CO$_2$ER by using [Bmim]PF$_6$ as a more efficient COOH$^*$ stabilizer [46]. Pt was as the working electrode for CO$_2$ER was also studied in different IL-based electrolytes [47,48]. Martindale and Compton reported that CO$_2$ could be reduced into HCOOH in ILs bis(trifluoromethane)-sulfonimide (HNTf$_2$) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim]NTf$_2$) by using the pre-anodized Pt wire [48]. Considering the high cost and limited reserves of noble metals, earth-abundant and inexpensive transition metals such as Co, Cu and Mo have been considered as potential electrocatalysts for CO$_2$ER [18,49,50]. Huan et al. reported the first Cu-based material for reduction of CO$_2$ into HCOOH with high selectivity in [Emim]BF$_4$/H$_2$O electrolyte [51]. They proposed that ILs played a role in activating CO$_2$. The combination of nanostructured porous dendritic Cu-based electrocatalysts with [Emim]BF$_4$/H$_2$O electrolyte also contributed to the excellent activity and high selectivity for HCOOH, indicating the importance of the electrolyte. Post-transition metals have also been investigated, such as Bi, In and Sn [52–55]. For example, Rosenthal et al. demonstrated that CO$_2$ could be selectively reduced to CO with
a high FE of 95% by using a Bi-based electrocatalyst combined with imidazolium ILs, while HCOOH tended to be the product when Bi was combined with a bicarbonate aqueous electrolyte [56]. They claimed that the CO$_2$$^*$ intermediate at the electrode surface could be stabilized by the interface between Bi$^0$ and Bi$^{3+}$ sites, and imidazolium ILs might have a crucial influence in this pathway.

In addition, alloys, metal oxides and metal dichalcogenides are also promising electrocatalysts in IL-based electrolytes [43,57–59]. Sacci et al. reported that CO$_2$ could be reduced to CO at −1.65 V vs. standard calomel electrode (SCE) by using Cu-Sn thin-film alloys in an imidazolium-based IL electrolyte [60]. They proposed that the synergistic interactions of the Cu-Sn cathode and the imidazolium cation contributed to the low overpotential. By using bulk molybdenum disulphide (MoS$_2$) as the working electrode, CO$_2$ was converted into CO with high current density and low overpotential (54 mV) in [Emim][BF$_4$/H$_2$O electrolyte, and the tunable mixture of H$_2$ and CO (syngas) could be obtained by tuning the applied potentials (Fig. 2a–c) [61]. Moreover, this bulk MoS$_2$ catalyst showed significantly higher catalytic performance for CO$_2$ reduction than that of noble metals catalyst. Experimental and theoretical studies suggested that the Mo-terminated edges and the low work function of MoS$_2$ contributed to the high catalytic activity for CO$_2$ electroreduction. The two-dimensional (2D) nanoflake structures of different transition metal dichalcogenides (MoS$_2$, WS$_2$, MoSe$_2$) were also explored for CO$_2$ electroreduction in 50 vol% [Emim][BF$_4$/H$_2$O solution (Fig. 2d and e) [38]. WS$_2$ nanoflakes showed superior CO$_2$ electroreduction performance compared with the noble metal and other transition metal dichalcogenide catalysts with a high current density of 18.95 mA/cm$^2$ at a low overpotential of 54 mV. The carbon-based materials are also promising heterogeneous catalysts in CO$_2$ER. Sun et al. found that N-doped carbon (graphene-like) catalysts exhibited excellent activity and selectivity for CO$_2$ER to CH$_4$ by using [Bmim][BF$_4$ as the electrolyte [62].

**CO$_2$ER in ILs**

Imidazolium-based ILs are the most studied ILs for CO$_2$ER due to their high CO$_2$ capture ability [63]. Barrosse-Antle and Compton explored CO$_2$ER in 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]), which exhibited a high CO$_2$ solubility of 1520 mM [64]. The CO$_2$ in [Bmim][Ac underwent a chemically irreversible, one-electron transfer to the radical anion CO$_2$$^*$, and probably enabled the following formation of oxalate, CO and carbonate. CO$_2$ could be reduced into HCOOH on pre-anodized Pt electrode in [Emim][NTf$_2$ with HNTf$_2$ as the proton source [48]. Kumar et al. found that metal-free carbon nanofibre (CNF) catalysts were quite efficient for CO$_2$ER when [Bmim][BF$_4$ was used as the electrolyte [65]. It exhibited a negligible overpotential (0.17 V) for electroreduction of CO$_2$ to CO and much higher current density than that of Ag nanoparticles and bulk Ag film electrodes. Sun et al. reported that N-doped carbon (graphene-like) material/carbon paper electrodes could convert CO$_2$ into CH$_4$ in different
IL electrolytes including [Bmim]BF₄, [Bmim]PF₆, 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim]TfO), [Bmim]NTf₂ and 1-butyl-3-methylimidazolium dicyanamide ([Bmim]DCA) [62]. They found that the ILs containing fluorine showed higher total current densities than the ILs without fluorine probably due to the strong interactions between CO₂ and fluorine. In addition to the typical ILs with ‘common’ anions, Snuffin et al. designed and synthesized a novel IL 1-ethyl-3-methylimidazolium trifluorochloroborate ([Emim]BF₃Cl), which was used to dissolve and electrochemically reduce CO₂ [47]. With a Henry’s constant of 4.1 MPa at 1 atm, the CO₂ solubility was close to that reported in other ILs. A relatively positive reduction electrode potential of −1.8 V was recorded, and the current density reached 5.7 mA cm⁻². They proposed that the BF₃ could form a Lewis acid-base adduct BF₃-CO₂ with CO₂, which weakened the C=O bond and prompted the reduction of CO₂.

CO₂ER in IL-based binary/ternary media

Although there are many advantages in using ILs as electrolytes in CO₂ER, the relatively high cost and viscosity of ILs hinder their practical application. The use of IL-based mixtures such as binary/ternary media of ILs with water and/or organic solvents may provide an efficient medium for CO₂ER.

In 2012, Rosen et al. found that adding water into [Emim]BF₄ (relatively hydrophilic) led to an increase of CO FE over Ag nanoparticle cathode [66]. The CO FE reached nearly 100% with 89.5 mol% water and 10.5 mol% [Emim]BF₄, but the FE decreased at higher water concentrations probably due to the HER. In their following work, they studied the influence of water mole fraction in the electrolyte on CO₂ER by using a metal-free CNF cathode (Fig. 3) [65]. Similar results were observed with an Ag nanoparticle cathode. Significantly, the current density for CO₂ER to CO in 75 mol% water and 25 mol% [Emim]BF₄ was about five times higher than that in pure [Emim]BF₄ (Fig. 3b). They attributed these results to the decrease in pH and viscosity of [Emim]BF₄ when mixed with water. With the addition of water, the hydrolysis of [Emim]BF₄ led to a decrease in pH and a higher proton availability, thus accelerating the reduction of CO₂. The decrease in viscosity after adding water also resulted in lower mass transport resistance. In addition, they proposed that the [Emim]⁺ cation could inhibit the HER caused by water addition. These indicate that the ratio of ILs in binary medium has a significant effect on CO₂ER, and an optimum ratio is required to achieve an enhancement of CO₂ reduction. In IL1-ethyl-3-methylimidazolium trifluoroacetate ([Emim]TFA) with 33% water binary medium, CO₂ could be reduced to formate on In, Sn and Pb electrodes with high yield [52]. The peak charge on the voltammogram increased when 1 mL water was added into the ILs, but the peak charge decreased when the content of H₂O increased up to 2 mL. Adding water into ILs leads to a dramatic decrease in solution viscosity [67], re-
Figure 4. (a) Diffusion coefficients of CO2, H2O (overlapping), [Bmim]+ and [BF4]- as determined by PGSE-NMR. (b) Dynamic viscosity of [Bmim][BF4]/water mixtures. (c) Solubility of CO2 in [Bmim][BF4]/water mixtures. (d) pH of [Bmim][BF4]/water mixtures with a different composition saturated with CO2. (e) CVs measured at a sweep rate of 50 mV s⁻¹ with automatic IR-compensation. (f) The peak currents of CVs measured at different sweep rates. Adapted with permission from [68].

Resulting in the accelerated diffusion of CO2 to the electrode surface and the improvement of CO2ER. However, at higher water content, the CO2 content is lower and the favorable effect of lower viscosity on CO2 reduction no longer prevails. Besides, the HER process seemed to be enhanced at higher water content.

Rudnev et al. also conducted an in-depth study on the enhanced CO2ER in [Bmim][BF4]/water binary medium by using several electrochemical methods combined with pulsed-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) spectroscopy (Fig. 4) [68]. They found that after the addition of water, the onset potential was lowered and the peak current increased. It was attributed to the increased availability of the protons and the enhanced diffusion of reacting species due to lower viscosity. FE 95.6 ± 6.8% was achieved for CO in a 50 mol% 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][TFO])/H2O electrolyte.

When ILs were dissolved in common organic solvents, the resulting IL/organic solvent binary medium may also exhibit some favorable properties for CO2ER, such as lower viscosity, high CO2 solubility, ionic conductivity and low price [69]. DiMeglio et al. found that adding [Emim][BF4] into the CO2-saturated MeCN solution resulted in an increased FE of CO formation (93 ± 7%) compared with that without ILs (48 ± 13%) [56]. Moreover, it led to an almost 40-fold increase in current density. When [Bmim][BF4] and [Bmim][PF6] were used to replace [Emim][BF4], the FE reached 95 ± 6% and 90 ± 9% in [Bmim][BF4]/MeCN and [Bmim][PF6]/MeCN, respectively. Further, the current density was higher than that in the case of [Emim][BF4]/MeCN. They proposed that the proton source was most probably provided by deprotonation of the central imidazolium carbon of the cations of ILs. For example, the 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([Bmmim][BF4]) with a methyl substituent at the imidazolium 2-position showed lower current density than [Emim]- and [Bmim]-based ILs, which was likely attributed to the difficulty of deprotonation of [Bmmim][BF4].

Shi et al. reported CO2ER into CO in 1-butyl-3-methyl-imidazolium trifluoromethanesulfonates ([Bmim][CF3SO3])/propylene carbonate (PC) electrolyte with an Ag foil as a cathode [70]. Both [Bmim][CF3SO3] and PC exhibit high CO2 solubility. Commonly known, PC is a CO2 absorbent in industry and a common solvent used in organic electrochemistry. In this binary medium, Ag electrode showed a high FE of CO (90.1%) at −1.72 V (vs. Pt wire). Sun et al. found that Mo-Bi bimetallic chalcogenide electrocatalysts could efficiently catalyze the reduction of CO2 to CH3OH with a high FE of 71.2% and a current density of 12.1 mA cm⁻² in 0.5 M [Bmim][BF4]/MeCN [43]. The performance of CO2 electroreduction with Mo-Bi bimetallic chalcogenide/carbon paper electrode was also assessed in other common electrolytes/MeCN binary media, including [Bmim][PF6], 1-butyl-3-methylimidazolium perchlorate ([Bmim][ClO4]), [Bmim][NTf2], tetra-n-butylammonium tetrafluoroborate (TBABF4), tetraethylammonium hexafluorophosphate (TEAPF6) and tetraethylammonium perchlorate (TEAClO4). In TBABF4, TEAPF6 and TEAClO4-based binary media, CO was the main product while the liquid product CH3OH was not detected. Chen et al. developed N, P-co-doped carbon aerogels (NPCA) catalysts for CO2ER (Fig. 5) [71]. The FE attained for producing CO reached up to 99.1% with a partial current density of 143.6 mA cm⁻² by using 0.5 M [Bmim][PF6]/MeCN as an electrolyte, which is much higher than the catalytic performance in 0.5 M KHCO3 aqueous solution (65.3% for FE and 45.5 mA cm⁻² for current density). They attributed the significant
Figure 5. (a) Linear sweep voltammogram (LSV) curves over NPCA. (b) The FE(CO) for NPCA at different applied potentials. (c) The current density over NPCA compared with different catalysts. (d) Long-term stability of NPCA. Adapted with permission from [71].

performance advantage of [Bmim]PF$_6$/MeCN electrolyte to the high CO$_2$ solubility, lower reaction barrier via [Bmim-CO$_2$]$_{ad}$ complex formation, and the suppression of HER. The 0.1 mol L$^{-1}$ super basic tetra alkyl phosphonium IL [P$_{66614}$][124Triz] in MeCN has also been proved to be an effective medium for CO$_2$ER [72].

Zhu et al. investigated CO$_2$ER in IL/MeCN/H$_2$O ternary mixture electrolyte (Fig. 6) [53]. They found that the efficiency of CO$_2$ER on Pb or Sn cathodes could be significantly enhanced by adding a small amount of H$_2$O into [Bmim]PF$_6$/MeCN or [Bmim]BF$_4$/MeCN binary mixtures. By adjusting the composition of the ternary mixture, the performance and selectivity of CO$_2$ER could be modulated (Fig. 6a–c). They also conducted CO$_2$ER in ternary mixtures containing different IL components, including [Bmim]PF$_6$, [Bmim]BF$_4$, 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim]OTF), [Bmim]TFA, [Bmim]ClO$_4$, [Bmim]DCA, 1-butyl-3-methylimidazolium thiocyanate ([Bmim]SCN), 1-butyl-3-methylimidazolium nitrate ([Bmim]NO$_3$) and 1-butyl-3-methylimidazolium dihydrogen phosphate ([Bmim]H$_2$PO$_4$). Most of these IL/MeCN/H$_2$O ternary media displayed excellent performance for HCOOH formation. Notably, when [Bmim]PF$_6$ (30 wt%)/MeCN-H$_2$O (5 wt%) was used as electrolyte, the FE$s$ for HCOOH could reach 91.6% and 92.0% with a partial current density of 37.6 and 32.1 mA cm$^{-2}$ on a Pb and Sn cathode, respectively. Combined with electrochemical methods and small-angel X-ray scattering (SAXS) (Fig. 6f), they illustrated that the presence of an appropriate amount of H$_2$O in the ternary mixture resulted in higher solubility of CO$_2$, increased conductivity, decreased double-layer capacitance and lowered onset potential, which contributed to the high current density. Yang et al. reported that CO$_2$ could be converted into syngas on γ-In$_2$Se$_3$/carbon paper (CP) electrode in 30 wt% [Bmim]PF$_6$/65 wt%MeCN/5 wt% H$_2$O electrolyte [73]. They found that the composition of the electrolyte
could not only have a significant effect on the total current density, but also affect the ratio of CO/H₂ products. By adjusting the content of [Bmim]PF₆ (5–70 wt%) and H₂O (0–20 wt%), the CO/H₂ ratio could be tuned from 9 : 16 to 24 : 1 and 2 : 3 to 24 : 1, respectively.

Some of the representative examples for CO₂ electroreduction with different electrocatalysts in IL-based electrolytes have been summarized in Table 1. It can be seen that IL-based electrolyte affects the catalytic performance significantly.

**Mechanistic understanding of CO₂ER in IL-based electrolyte**

As shown above, many studies demonstrated that ILs were efficient media in CO₂ER with excellent catalytic reactivity and selectivity (Table 1). Moreover, the designability of ILs permits tailoring the electrolyte to achieve optimal conditions for CO₂ER. Therefore, a mechanistic understanding of IL-based electrolyte, especially the role of IL components, is important for the rational design of a new IL-based electrocatalytic system for CO₂ transformation.

In heterogeneous systems, CO₂ER occurs at the surface of electrocatalysts. Therefore, the understanding of the electrocatalyst-IL interface is imperative. In 2011, Rosen et al. reported that a 96% selectivity to CO was achieved in an 18 mol% [Emim]BF₄ solution with Ag cathode at a low overpotential, much higher than the 80% selectivity to CO in the absence of IL [39]. They proposed that IL could lower the energy of the (CO₂)⁻ intermediate, probably by the formation of a complex between the IL and (CO₂)⁻, resulting in a low-energy pathway for CO₂ conversion (Fig. 7a). They further used sum-frequency generation (SFG), an effective technique for probing the solid–liquid interface, to explore the molecular structures at electrode interfaces to figure out the cause of this selectivity enhancement (Fig. 7b and c) [74]. Pt electrode was used for these in situ spectroscopic examinations since it is almost inactive for converting CO₂ into CO, thus the enhancement in CO₂ conversion could be readily detected. The results demonstrated that the formation of CO was observed in the presence of [Emim]BF₄ and the formation of H₂ was suppressed compared with aqueous systems. The SFG spectrum of Pt catalyst in [Emim]BF₄ presented a CH₃ bending mode at ~1430 and a ring stretching mode at ~1570 cm⁻¹ (Fig. 7b), implying that a layer of [Emim]⁺ was located at the Pt electrode surface during electrolysis. The LSVs showed that no CO production was detected at a potential more negative than ~0.8 V in the absence of [Emim]⁺, indicating that the adsorbed [Emim]⁺ could reduce the overpotential. New species with a peak at 2348 cm⁻¹ appeared in LSV (Fig. 7c), which was presumed to be the formation of an [Emim-CO₂]⁺-BF₄ complex. Then, the generation of CO was started at ~0.25 V vs. SHE, which was a low-energy pathway. Finally, they proposed that the adsorbed cation was used as a cocatalyst for converting CO₂ to CO.

Quantum molecular dynamics simulations were used to reveal the role of ILs in observed high-CO₂ reduction reaction. Asadi et al. reported that the complex [Emim-CO₂]⁺ was most likely formed by the binding of CO₂ with [Emim]⁺ via the C4/S protons rather than through the C2 proton [61]. Moreover, the complex could be stabilized by H₂ bonding. In the CO₂ER, the complex [Emim-CO₂]⁺ could be potentially physisorbed at the negatively charged MoS₂ cathode. This created a close encounter between CO₂ molecules and MoS₂ surface, resulting in an increment of local CO₂ concentration near the cathode surface. Additionally, the existence of [Emim]⁺ was considered to reduce the reaction barrier for electrons transferring into CO₂. Lim et al. indicated that the cations and anions in ILs could stabilize surface-bound intermediates to form a suitable microenvironment, thereby lowering the energy barrier and improving the CO₂ reduction kinetics [48]. Thus, ILs were thought to play a crucial role in lowering the overpotential of CO₂ reduction.

It was reported that imidazolium-based ILs can interact with CO₂ by physical absorption, which can serve as both robust electrolytes and CO₂ activation promoters [75]. The kinds of anions have a significant effect on the CO₂ activation. The ILs containing fluorine such as [Bmim]BF₄, [Bmim]PF₆ and [Bmim]NTf₂ exhibited much higher activity than the ILs without fluorine, which is partly because fluorine has strong interaction with CO₂ [76]. Additionally, it leads to higher CO₂ solubility in the electrolyte, which can avoid mass transport limitation in the electrolysis [77].

**CO₂EOT with Organic Compounds in IL-Based Electrolytes**

CO₂ can also be utilized as a C1 synthon/building block to electrosynthesize valuable chemicals, which is another efficient pathway for CO₂ utilization [5]. By the electrochemical reactions with different substrates, like epoxides, alcohols, amines, aryl halides and olefins, CO₂ can be converted into various kinds of products, including cyclic carbonates, dialkyl carbonates, carbamates and carboxylic acids [78–81]. In particular, some reactions are
Table 1. The representative examples of CO\textsubscript{2} electroreduction with different electrocatalysts in IL-based electrolytes.

| IL-based electrolytes | Catalysts | Reaction conditions | Main products (FE, %) | Current density (mA cm\textsuperscript{-2}) | Ref. |
|-----------------------|-----------|---------------------|-----------------------|---------------------------------------------|------|
| [Emim]BF\textsubscript{4}/H\textsubscript{2}O (50 vol%)/50 vol% | WSe\textsubscript{2} nanoflakes | −0.164 V (vs. RHE) overpotential 54 mV | CO (24) | 18.95 | [38] |
| 18 mol% [Emim]BF\textsubscript{4}/H\textsubscript{2}O | Ag | −1.5 V (applied voltage), flow cell | CO (96) | — | [39] |
| 10.7 g [Bmim]PF\textsubscript{6} + 0.3 g H\textsubscript{2}O | Cu plank cathode | 318.2 K and 8.95 MPa CO\textsubscript{2}, cell voltage < 3.8 V\textsuperscript{a}, high pressure undivided cell | Syngas CO (38.1) + H\textsubscript{2} (50.6) | 20 | [42] |
| 0.5 M [Bmim]BF\textsubscript{4}/MeCN | Mo-Bi bimetallic | −0.70 V (vs. RHE) | CH\textsubscript{3}OH (71.2) | 12.1 | [43] |
| [Emim]BF\textsubscript{4}Cl | Pt disk working electrode | −0.573 V (vs. SHE), negligible overpotential | CO (98) | — | [47] |
| [Emim]BF\textsubscript{4}/H\textsubscript{2}O (92/8% v/v) | Porous dendritic copper | −1.55 V (vs. Fe\textsuperscript{3+}/Fe\textsuperscript{2+}) \textsuperscript{b} | Formate (87) | 6.5 | [51] |
| [Bmim]PF\textsubscript{6} (30 wt%)/MeCN\textsuperscript{-2}/H\textsubscript{2}O (5 wt%) | Pb | −2.30 V (vs. Ag/AgCl) | HCOOH (91.6) | 37.6 | [53] |
| [Bmim]PF\textsubscript{6} (30 wt%)/MeCN-H\textsubscript{2}O (5 wt%) | Sn | −2.30 V (vs. Ag/AgCl) | HCOOH (92.0) | 32.1 | [53] |
| 100 mM [Bmim][OTf]\textsuperscript{a} in MeCN | Bi nanoparticles | −2.0 V (vs. Ag/AgCl) | CO (96.1) | 15.6 | [54] |
| 20 mM [Emim]BF\textsubscript{4} in MeCN | Bi | −1.95 V (vs. SCE) \textsuperscript{d} | CO (95) | 5.51 | [56] |
| 4 mol%/96 mol% [Emim]BF\textsubscript{4}/H\textsubscript{2}O | MoSe\textsubscript{2} alloy monolayers | −1.15 V (vs. RHE) | CO (45.2) | 43 | [57] |
| 4 mol%/96 mol% [Emim]BF\textsubscript{4}/H\textsubscript{2}O | MoS\textsubscript{2} | −0.764 V (vs. SHE) | CO (98) | 65 | [61] |
| 0.1 M [P\textsubscript{66614}][124Triz]\textsuperscript{b}/MeCN | Ag | −1.72 V (vs. Pt wire) | CO (90.1) | 4.6 | [70] |
| 0.5 M [Bmim]PF\textsubscript{6}/MeCN | N,P-co-doped carbon aerogels | −2.4 V (vs. Ag/Ag\textsuperscript{+}) | CO (99.1) | 143.6 | [71] |
| 30 wt% [Bmim]PF\textsubscript{6}/65 wt% MeCN/5 wt%H\textsubscript{2}O | γ-In\textsubscript{2}Se\textsubscript{3}/CD\textsuperscript{b} | −2.3 V overpotential 220 mV | 0.05 mmol Formate (95) | — | [72] |

\textsuperscript{a}Cell voltage, \textsuperscript{b}ferrocene/ferrocenium, \textsuperscript{c}acetomitrile, \textsuperscript{d}standard calomel electrode, \textsuperscript{e}1-butyl-3-methylimidazolium triflic acid, \textsuperscript{f}propylene carbonate, \textsuperscript{g}trihexyltetradecylphosphonium 1,2,4-triazolate, \textsuperscript{h}carbon.
thermodynamically unfavorable without external energy, and thus the efficient reaction routes conducted by thermal catalysis are very limited. Using an electrochemical method to synthesize organic molecules has various advantages, such as mild conditions, high functional group tolerance and innate scalability and sustainability [82]. The general pathway of the CO2 EOT involves the generation of electro-induced radical/anion from CO2 and/or substrates, and then the radical/anion reacts with other substrates to yield various compounds. Several studies have further shown that ILs have a stabilization effect on the electro-induced CO2 molecule or substrates radical/anion. Combined with the high CO2 solubility and favorable electrochemical properties, ILs are considered as a green alternative reaction medium to volatile organic solvents for CO2 EOT [13,83]. In this section, we will review the use of CO2 as a reactant in IL-based reaction media for electrosynthesis of value-added chemicals.

**Electrosynthesis of organic carbonates**

Organic carbonates (especially cyclic carbonates and dialkyl carbonates) have attracted extensive attention owing to their wide usage as polar aprotic solvent, intermediate for polycarbonate and electrolyte in batteries [84,85]. Electrocatalytic fixation of CO2 to epoxides or alcohols to yield organic carbonates via C−O bond formation can avoid the use of toxic phosgene or CO, providing a green and atom economy pathway for the synthesis of organic carbonates.

Cyclic carbonate synthesis from CO2 and epoxides in pure ILs without additional supporting electrolyte and catalyst was reported by Deng and coworkers [78]. The reaction was performed in an undivided cell under mild conditions with a Cu working electrode and an Al or Mg rod sacrificed anode. The performance of cycloaddition of CO2 to different epoxide substrates (propylene oxide, epichlorohydrin and styrene oxide) was tested. The best performance was achieved by utilizing propylene oxide as substrate and [Bmim]BF4 as reaction media resulting in a 92% conversion and 100% selectivity to the desired product (cyclopropylene carbonate). CO2 underwent a one-electron reduction to generate the CO2− radical anion, and then reacted with the activated substrate to yield the corresponding cyclic carbonate. Wang et al. reported the electrosynthesis of cyclic carbonates from CO2 and diols in ILs in an undivided cell under mild conditions (1 atm, 50°C) [86]. When CO2 and 1,2-butanediol were used to synthesize butylene carbonate, the highest yield of 12% was achieved in [Bmim]BF4 with an Mg anode and a Cu cathode.

Zhang et al. found that the electrochemical activated CO2 in ILs could react with alcohol in the presence of an alkylation agent to generate dialkyl carbonates [79]. They found that CO2 was reduced to the anion radical CO2− in [Bmim]BF4 in an undivided cell. Especially, a more positive potential was
recorded than that in organic solvents, which possibly attributed to the stabilization effect from CO$_2$·-[Bmim]$^+$ ion-pairing. After adding CH$_3$I as the alkylating agent, the dimethyl carbonate (DMC) was obtained by the reaction of CO$_2$·-[Bmim]$^+$ with CH$_3$OH. Cathodic material screenings revealed that Cu and Ag were more efficient than Ti, Ni and stainless steel with good yields of 73% and 74%, respectively. Different alcohol substrates were screened and the results showed that primary alcohol and secondary alcohol gave 33%–73% yields toward corresponding carbonates, while tertiary alcohol and phenol were unreactive. Wu et al. reported the electrosynthesis of dialkyl carbonates from CO$_2$ and alcohols through electrogenerated N-heterocyclic carbenes [87]. With [Bmim]BF$_4$ as the solvent and N-heterocyclic carbenes precursor, 90% conversion and 96% selectivity of benzyl methyl carbonate were achieved from CO$_2$ and benzyl alcohol on Ti cathode. The other primary alcohols and secondary alcohols were also used as the substrates to react with CO$_2$ to give the corresponding dialkyl carbonates. Moreover, various electrode materials were investigated to improve the yield of DMC. The porous nanostructure composite electrode consisting of Cu skeletons and platinum shells and Ag-coated nanoporous Cu composites electrode gave a slight improvement with yields of 81% and 80%, respectively [88,89]. A 76% yield was obtained using an In electrode [90].

To avoid the use of toxic alkylating agent CH$_3$I, Yuan et al. proposed an IL-CH$_3$OK-methanol system for the synthesis of DMC [91]. The electrochemical conversion of CO$_2$ and CH$_3$OH was conducted in IL electrolyte with Pt as electrodes and CH$_3$OK as co-catalysts in an undivided four-neck bottle cell. They screened various ILs, including [Bmim]Br, [Emim]Br, [Bmim]Cl, [Bmim]OH, [Bmim]BF$_4$ and [Emim]BF$_4$. The highest yield of 3.9% for DMC with 88.4% selectivity was achieved in [Bmim]Br electrolyte. The anions of ILs were thought to have an important effect on the conversion. When ethanol was used as the substrate, diethyl carbonate was also synthesized in this electrochemical conversion process with a 0.4% yield. Instead of an undivided cell, a filter-press electrochemical cell with divided anodic and cathodic compartments was used in this IL-CH$_3$OK-methanol system to better investigate the behavior of DMC electrosynthesis from CO$_2$ [92]. Using a Nafion 117 membrane as the cationic exchange membrane, a 12.5% yield of DMC was obtained. A series of experiments were performed to study the influence of [Bmim]Br on the DMC electrosynthesis, and it revealed that [Bmim]Br might play a catalytic role in the process besides being used as an electrolyte. Nevertheless, further in-depth research is required to elucidate the reaction mechanism and ascertain possible specific roles of each components, especially CH$_3$OK and IL. The influence of the membrane (anion, cation exchange membrane and without the use of membrane) in this IL-CH$_3$OK-methanol system was investigated in the following work [93].

A [Bmim]Br-propylene oxide-methanol system was also developed to electrochemically convert CO$_2$ into DMC, achieving yields of 75.5% and 37.8% on Pt electrode in the related research [94,95]. Though a high yield was obtained, this route is inconsistent with the green pathway of CO$_2$ conversion due to the use of carcinogenic propylene oxide. To avoid the use of toxic additives and simplify the separation system, further work on the CO$_2$EOT to DMC without any additives was also conducted. However, the yield of DMC was not satisfactory. Different ILs and cathodes were screened. The maximum yield of DMC achieved with Pt-graphite electrode in 1-benzyl-3-methylimidazolium chloride([Bmim]Cl)-methanol-CO$_2$ system was only 3.8%. Considering the advantages of a basic medium in the absorption and activation of CO$_2$, the amino-functionalized ILs were also developed to generate DMC [96]. Using 1-(3-aminopropyl)-3-methylimidazolium bromide as an electrolyte, a 2.5% yield with 94.5% selectivity of DMC was obtained with graphite electrode without adding any additives.

Electrosynthesis of organic carbamates

Organic carbamates are important kinds of chemicals that have been extensively used as pharmaceuticals, agrochemicals and amine-protecting groups [97]. A phosgene-free process that uses CO$_2$ as a C synthon to construct C—N bonds by electrochemical methods provides a green synthetic route for organic carbamates [98]. Fero ci et al. reported the electrochemical fixation of CO$_2$ with amines in ILs to synthesize organic carbamates [80]. Electrolysis of CO$_2$-saturated [Bmim]BF$_4$ solution containing amines was conducted in a divided glass cell at 55°C. Then, the aliphatic or aromatic amines could react with the cathodic activation of CO$_2$ after adding EtI as an alkylating agent to yield corresponding carbamates. Cathodic material studies revealed that Pt cathodes were more efficient than Cu and Ni cathodes in the electrosynthesis of organic carbamates from CO$_2$ and amines, with a maximum yield up to 80%. The authors proposed that the nucleophilicity of amines had a strong influence on the yield of carbamates. The primary and
secondary aliphatic amines afforded carbamates with good yields of 73%–87%, while aniline showed a low yield of 38%.

**Electrocarboxylation**

Electrocarboxylation of CO$_2$ and organic compounds is an essential strategy for CO$_2$ fixation via the construction of C-C bonds. Moreover, the use of CO$_2$ as an alternative synthon to toxic and hazardous chemicals (e.g., phosgene and cyanides) provides a green route to synthesizing carboxylic acids and their derivatives. Different kinds of substrates, such as alkenes, alkynes, ketones and organic halides, undergo electrocarboxylation with CO$_2$ to yield corresponding carboxylated products. Some studies focused on using ILs as a reaction media to reduce the use of volatile solvents and enhance efficiency.

Lu et al. developed the electrocarboxylation of activated olefins in CO$_2$-saturated [Bmim]BF$_4$ solution in an undivided cell under mild conditions [99]. Electrochemically reduced ethyl cinnamate reacted with CO$_2$ to yield monocarboxylic acids as the main carboxylated product, as well as the by-product saturated esters. Screening on different cathodic materials (stainless steel, Ti, Cu, Ni) found that stainless steel was the most effective cathodic material, giving a 41% yield of monocarboxylic acid under optimized conditions (50°C, 1 atm CO$_2$). This method was extended to other olefins, achieving the corresponding monocarboxylic acid with moderate yields of 35%–55%. Yuan et al. performed the electrochemical dicarboxylation of aryl-substituted alkynes and CO$_2$ in an undivided cell with ILs as supporting electrolytes under room temperature [100]. Using styrene as a model molecule, the effects of various experimental parameters, including electrocatalysts, supporting electrolyte, CO$_2$ pressure and concentration of substrates, were investigated to obtain optimal reaction conditions. Screening on electrode materials indicated a significant dependence of the activity on both cathode and anode materials, in the order Pt > Ni > Cu > Cu-Sn alloy and Al > Mg > Zn. The supporting electrolyte also showed an important influence on the electrocarboxylation, as the yield of 2-arylsuccinic acids decreased depending on both cation and anion, in the order [Bu$_4$N]$^+$ > [Et$_4$N]$^+$ and Br$^-$ > Cl$^-$ > I$^-$. The electrolysis of styrene and CO$_2$ in 0.05 mol L$^{-1}$ n-Bu$_4$NBr-DMF solution on Ni cathode and Al anode gave a principal product 2-phenylsuccinic acid in high yield and selectivity (87%, 98%), accompanied by by-product 3-phenylpropionic acid. This method was extended to various aryl-substituted alkynes and gave the corresponding 2-arylsuccinic acids with yields of 50%–87%. They extended this method to electrocarboxylation of arylacetylenes [101]. The electrochemical dicarboxylation of phenylacetylene and its derivatives was conducted in a [Bu$_4$N]Br-DMF electrolyte system in an undivided cell with Ni cathode and Al anode, and the corresponding aryl-maleic anhydrides and 2-arylsuccinic acids were generated with high total yields of 82%–94%.

The electrocarboxylation of aromatic ketones with CO$_2$ in [Bmim]BF$_4$ in an undivided cell was reported by Feng and co-workers [102]. Various experimental parameters including temperature, electrode material, substrate concentration, current density, charge passed and working potential were screened to obtain the optimized conditions. The electrolysis of CO$_2$-saturated [Bmim]BF$_4$ solution containing a definite concentration of acetophenone or electron-donating substituted acetophenone was conducted with Pt cathode and Mg anode at 50°C, followed by adding the alkylating agent CH$_3$I to afford the corresponding α-hydroxy carboxylic acid methyl ester with yields of 56%–62%. The corresponding alcohols were obtained as the main by-products. Zhao et al. studied the influence of proton availability in ILs on product distribution of electrocarboxylation of acetophenone with CO$_2$ [103]. They revealed that dry 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BmPyrd]TFSI) with a low proton availability was an appropriate medium for this electrocarboxylation system to give 2-hydroxy-2-phenylpropionic acid with a good yield of 98%. The competing reactions are not conducive to the electrocarboxylation (Fig. 8) and some studies suggested that the product distribution depends strongly on the medium. In a following work, they further explored the influence of the nature of substrates and IL anions on the electrocarboxylation of aromatic ketones under CO$_2$ atmosphere [104]. A highest yield of 40.7% (2-(((1,10-biphenyl)-4yl)-2-hydroxy-2-phenylacetic acid) was achieved from electroreduction of 4-phenylbenzophenone in 1-butyl-2,3-dimethylimidazolium tris(pentafluoro ethyl)trifluorophosphate ([Bmim]FAP).

**Figure 8.** Competing reaction pathways for the electroreduction of aromatic ketones under a CO$_2$ atmosphere. Adapted with permission from [104].
Figure 9. (a) Electrocatalytic methylation of nitrobenzene with \( \text{CO}_2 \) and water over Pd\(_{2.2}/\text{Co–N/carbon} \) catalysts and (b) the possible pathway. Adapted with permission from [109].

Niu et al. reported the electrocarboxylation of benzyl chloride with \( \text{CO}_2 \) in [Bmim]BF\(_4\) in an undivided cell [105]. The Ag cathode exhibited a higher yield of phenylacetic acid than the Cu or Ni cathode, while the sacrificial anode showed no obvious effect on the yields. They proposed that the benzyl chloride underwent a cathodic reduction to Ph\(_2\)CH\(^{-}\), and then reacted with \( \text{CO}_2 \) through a nucleophilic reaction. The difference between the reduction peak potential of \( \text{CO}_2 \) and PhCH\(_2\)Cl was influenced by the cathode materials. A closer reduction potential at the Cu or Ni electrode than the Ag electrode could bring an interference of \( \text{CO}_2 \) reduction on the electrocarboxylation of PhCH\(_2\)Cl, resulting in the poor yields of phenylacetic acid.

The electrolysis of benzyl chloride in \( \text{CO}_2 \)-saturated [Bmim]BF\(_4\) with Ag cathode and Mg anode at 0.1 MPa \( \text{CO}_2 \) and 50°C, followed by adding anhydrous K\(_2\)CO\(_3\) and CH\(_3\)I, afforded the phenylacetic acid with a yield of 45%. They also found that the residual water had an unfavorable impact on this electrocarboxylation system, leading to the generation of undesirable toluene product. Hiejima et al. tried to promote the electrocarboxylation of \( \alpha \)-chloroethylbenzene in N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis[triﬂuoromethanesulfonyl]amide (DEME-TFSA) IL with compressed \( \text{CO}_2 \) [106]. The diffusion coefficient of \( \alpha \)-chloroethylbenzene was improved at high temperature and pressure. The promotion in the substrate diffusion might contribute to the increase of current efficiency. Tateno et al. tried to promote the electrocarboxylation by \( \alpha \)-chloroethylbenzene in N,N-diethyl-N-methylaniline as intermediates. H\(^{+}\) could be produced from water and act as a hydrogen source. Pd nanoparticles supported on Co-N/carbon were designed as the electrocatalysts, and 1-amino-ethylphosphonic acid was used as the co-catalyst. The N,N-diethylanilines were synthesized from the methylation of nitrobenzene and its derivatives, \( \text{CO}_2 \), and water under ambient conditions (Fig. 9) [109].

Electrosynthesis of methylanilines

N-methylation reaction is very important in the chemical industry. Various valuable products, including dyes, pesticides and perfumes can be obtained by using methylanilines as intermediates. H\(_2\) or PhSiH\(_3\) is generally used as the reducing agent for the N-methylation reaction of anilines under high temperature and pressure. Recently, Sun et al. developed an electrochemical strategy for the synthesis of N,N-diethylanilines from nitrobenzene and its derivatives, \( \text{CO}_2 \), and water under ambient conditions (Fig. 9) [109].

CONCLUSION AND PERSPECTIVE

Electrochemical conversion of \( \text{CO}_2 \) into high-value carbonaceous chemicals and fuels by \( \text{CO}_2 \)ER and \( \text{CO}_2 \)EOT provides a promising strategy for achieving \( \text{CO}_2 \) mitigation and relieving the dependence of our society on fossil fuels. With the high \( \text{CO}_2 \) solubility and good electrolyte properties, ILs have been extensively explored for \( \text{CO}_2 \) electrochemical conversion. Various types of ILs and IL-based mixtures have been studied, and imidazolium-based ILs are the most widely studied and used. The designability of ILs allows for the integration of functional ILs for \( \text{CO}_2 \) conversion to achieve an optimum transformation pathway.

\( \text{CO}_2 \)ER: Significant research progress has been achieved in IL-based \( \text{CO}_2 \)ER systems. A diversity of electrocatalysts have been exploited and have achieved excellent catalytic performance. Many studies showed that lower overpotential, and higher
current density and FE have been achieved in the presence of ILs. Experimental and theoretical studies have been conducted to figure out the reasons for the enhanced CO$_2$ER efficiency by ILs. It is suggested that the interactions of IL with CO$_2$ and reaction intermediates at the electrocatalyst surface contribute to the reduced activation energy and overpotential of CO$_2$ER. The cations and anions of ILs have been screened to optimize the CO$_2$ER efficiency. Imidazolium and pyrrolidinium cations have been proven to be very effective for enhancing CO$_2$ER kinetics. The catalytic performance is influenced by complex interactions at the electric double layer, rather than simply by the chain length of the imidazolium cation and CO$_2$ solubility. The cations of ILs play a multifunctional role in the electroreduction system, presumably acting as a co-catalyst, interacting with reaction intermediates, or changing the character of the interfacial double layer.

Despite the considerable progress achieved, challenges still exist in IL-based CO$_2$ER systems. The kinetically sluggish multiple-electron transfer process attributes to the large overpotential and low current density. The product selectivity and yield, especially for value-added C$_2$+ products, are still unsatisfactory for practical application. In addition, the actual role of ILs remains unclear. Optimized standard experimental systems and accurate fundamental theory are expected to be built in the future. Therefore, the development of more advanced IL-based systems is needed. The designability of ILs allows for optimizing electrocatalytic systems by adjusting various combinations of IL ions. The interplay between IL electrolyte and electrocatalysts can be engineered to facilitate CO$_2$ER. Furthermore, more research efforts devoted to reaction kinetics are required to clarify the characteristics and underlying mechanism of IL-based electrocatalytic systems, especially the interactions at electrocatalyst–IL electrolyte interface. Also, the common reaction at the anode compartment of CO$_2$ER is the OER; however, the OER as the anode reaction usually suffers from a large overpotential and generates a product with negligible economic value. Most recently, some studies have begun to explore alternative anode reactions for OER to lower the energy requirements for CO$_2$ER and yield a higher-value anode product; this may provide a quite beneficial approach for improving the economics of CO$_2$ER.

**CO$_2$EOT**: CO$_2$EOT in IL-based media could partially replace toxic reagents (e.g. CO and phosgene) and provide new routes to synthesizing a number of valuable chemicals, and the reaction was commonly conducted under mild reaction conditions. Therefore, it was considered as a green electrosynthesis methodology. We have reviewed recent advances in this area involving the reaction of CO$_2$ with different substrates, like epoxides, alcohols, amines, aryl halides and olefins with the participation of ILs. ILs have a stabilization effect on the electro-induced CO$_2$ molecule or substrates radical/anion intermediates, providing better control for succeeding reaction pathways and desirable products. The corresponding products of organic carbones, carboxylic acids are produced through electroreduction using CO$_2$ and the substrates. As important chemicals in industry, organic carbones (e.g. DMC) have received extensive research attention among these products. Various experimental parameters have been explored in order to achieve better catalytic performance, involving the IL components, electrocatalysts, electrolyte configurations and ion exchange membranes. Particularly, the electroreduction of DMC in IL-based media without additives has been carried out to avoid the use of toxic additives and simplify the separation system.

Although significant advances have been achieved in recent years, many challenges remain to be overcome. Firstly, the yield and selectivity of the products need to be improved for industrial application. The design of novel functional ILs and IL-based multi-component electrolytes could enhance CO$_2$ conversion. Secondly, detailed information about the reaction mechanisms and the role of ILs should be elucidated to improve the catalytic activity and conversion efficiency. Thirdly, the CO$_2$ conversion commonly studied in electrocatalytic systems is based on the formation of C–C, C–N and C–O bonds, which limits the development of this research area. Therefore, great research efforts should be devoted to the use of CO$_2$ as C1 synthon to prepare more diverse chemicals, especially functional organic materials by the construction of different kinds of C–X bonds, like C–Si, C–P and C–S bonds. Much research work needs to be done to develop new reactions that are thermodynamically unfavorable by thermal catalysis, which is a very promising strategy for CO$_2$ utilization.

In conclusion, electrochemical conversion of CO$_2$ into value-added fuels and chemicals is a promising and rapidly developing area. Many studies have shown that ILs offer great potential for CO$_2$ conversion technology. However, several critical challenges remain in this research area. Design of highly efficient catalyst-electrolyte-reactor systems, in-depth understanding of reaction mechanisms and the cooperative or synergistic effects of IL-based electrolytes and catalysts are crucial to tackling these...
challenges. Such research advances will promote the progress of industrialization of CO₂ utilization.

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