Electroreduction of carbon dioxide (CO$_2$) to value-added chemicals and fuels is a promising approach for sustainable energy conversion and storage. Many electrocatalysts have been designed for this purpose and studied extensively. The role of the electrolyte is particularly interesting and is pivotal for designing electrochemical devices by taking advantage of the synergy between electrolyte and catalyst. Recently, ionic liquids as electrolytes have received much attention due to their high CO$_2$ adsorption capacity, high selectivity, and low energy consumption. In this review, we present a comprehensive overview of the recent progress in CO$_2$ electroreduction in ionic liquid-based electrolytes, especially in the performance of different catalysts, the electrolyte effect, as well as mechanism studies to understand the reaction pathway. Perspectives on this interesting area are also discussed for the construction of novel electrochemical systems.

Introduction

Carbon dioxide (CO$_2$) is a major greenhouse gas. It plays a main role in global warming and leads to serious ecological and environmental problems. It is also a cheap, non-toxic, and abundant C1 feedstock for the production of alcohols, acids, and other value-added chemicals.$^1$ Recently, many technologies such as thermal, photochemical, and electrochemical methods have been used for CO$_2$ reduction. However, most thermal catalytic reactions are thermodynamically unfavorable and/or need harsh reaction conditions because CO$_2$ is thermodynamically stable and kinetically inert.$^2$ In photocatalytic reactions, the photocatalysts need to absorb light to generate electron-hole pairs with low reaction efficiency.$^3$ Among the numerous approaches, electrochemical reduction represents a promising approach owing to its high efficiency, simple operation, and mild conditions, providing potential opportunities for large-scale practical applications.$^4$–$^{11}$

Electrochemical reduction of CO$_2$ is a multi-electron/proton transfer process, which usually includes the following four steps: (1) CO$_2$ dissolution and adsorption on the catalyst surface, (2) one-electron reduction of CO$_2$ to CO$_2^-$ free radical, (3) further electron/proton transfer for the generation of the target product, and (4) desorption of the product into the electrolyte or gaseous product escape from the electrolyte. Therefore, the electrochemical reduction products can be controlled via changing reaction parameters such as the electrolyte, electrocatalyst, and applied voltage.$^{12}$–$^{15}$ However, an efficient and selective CO$_2$ reduction reaction is not trivial because of the chemical inertness of CO$_2$ molecules, and a large overpotential is often needed to improve the kinetically sluggish
reduction process. One resolution is to explore efficient electrochemical systems, including the catalyst and electrolyte, to boost the catalytic performance of CO₂ reduction.

Accordingly, the selection of the electrolyte is important in designing efficient electrochemical devices. The electrolyte provides a medium for the reduction process, including interactions among the electrode surface, reactants, and intermediates, which in turn influence the reaction pathway. Therefore, the type and composition of the electrolytes play important roles in the reduction reaction. So far, various electrolytes, such as aqueous electrolytes, organic electrolytes, and ionic liquids (ILs) have been applied in CO₂ reduction. Among them, ILs have attracted much attention as an electrolyte, and many catalytic reactions have been successfully carried out in this medium for green chemistry.

ILs are composed of cations and anions and have been proven to be a promising new class of environmentally benign solvents. They have also attracted extensive interest owing to their unique properties, such as nearly zero vapor pressure, high electrical conductivity, high electrical and thermal stability, and high gas solubility. In particular, their negligible vapor pressure, high ionic conductivity, and wide electrochemical windows make them excellent alternatives to conventional electrolytes in electrochemical applications. Moreover, ILs also exhibit excellent activity in the electroreduction of CO₂. They provide a medium for CO₂ reduction, and their strong absorption capacity for CO₂ promotes the CO₂ reduction reaction effectively. More importantly, the selectivity of CO₂ reduction can be significantly increased, and the hydrogen evolution reaction (HER) is suppressed in the presence of ILs. In recent years, electrochemical reduction of CO₂ has undergone significant progress in IL-based electrolytes.

In this review, we introduce the current progress of CO₂ electrocatalytic reduction in IL-based electrolytes. Various types of catalysts for producing the target products and the main factors for determining the efficiency are discussed. Moreover, some interesting results associated with the electrolyte effect and mechanism studies in understanding the reaction pathway are also described. Finally, the perspectives in this area are proposed for further study.

**Fundamentals of CO₂ Electroreduction in IL-Based Electrolytes**

**Typical Cell**

Typical CO₂ reduction cells in IL-based electrolytes are presented in Figure 1, including H-type cells and flow cells. In an H-type cell (Figure 1A), the cathode and anode are separated by a proton exchange membrane that only allows the transfer of corresponding ions. The membrane takes advantage of independent variation and prevents further oxidation of the products formed from CO₂ reduction. The oxygen evolution reaction and CO₂ reduction occur at the anode and cathode, respectively. In a flow cell (Figure 1B), the electrolyte is in a flow-through configuration to maximize the solubility of CO₂, to overcome mass transport limitations, and to suppress the HER in flow electrolyte.
Proposed Pathways for CO₂ Electroreduction

So far, the electroreduction of CO₂ can proceed via two-, six-, and eight-electron reduction pathways in IL-based electrolytes. CO₂ can reduce to species including carbon monoxide (CO), formic acid/formate (HCOOH/HCOO⁻/CO), methanol (CH₃OH), methane (CH₄), and acetic acid (CH₃COOH). From a thermodynamic perspective, the equilibrium potentials ($E^\circ$) of CO₂ reduction and HER are illustrated in Table 1. In CO₂ reduction, the rearrangement of a linear molecule to a bent radical anion (CO₂⁻) requires enormous energy, which occurs at −1.90 V versus the standard hydrogen electrode (SHE). Therefore, it is difficult to convert CO₂ to the desired product with high efficiency and selectivity by commonly used electrode materials in aqueous electrolytes, although the CO₂⁻ radical obtained is highly reactive and can form target products after several proton and electron transfer approaches. A more negative potential than $E^\circ$ is often needed to drive this reaction. In other words, the large overpotential is mainly attributed to the first step of CO₂ electroreduction.

ILs for CO₂ Electroreduction

The structures of typical ILs for electrochemical reduction of CO₂ are depicted in Table 2. In CO₂ reduction, the structure of ILs allows them to coordinate with CO₂, which promotes CO₂ adsorption on the catalyst surface and reduces the energy barrier for CO₂ activation. Hence, the current density and reaction selectivity can be improved. Rosen et al. found that in the presence of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄), the cell overpotential of CO formation from CO₂ electroreduction could be reduced to 0.17 V on a bulk Ag electrode. To date, many imidazolium-based ILs such as [Emim]BF₄, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄), and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF₆) have exhibited excellent performance in CO₂ electroreduction. So far, many achievements have been realized in CO₂ electroreduction with IL-based electrolytes. The major merits of IL as an electrolyte and co-catalyst for CO₂ electroreduction not only reflect its strong absorption capacity of CO₂ but also demonstrate that the IL can (i) suppress the competing HER, (ii) lower the reduction overpotential, and (iii) increase the selectivity for target products.

Catalysts for CO₂ Electroreduction in IL-Based Electrolytes

Various catalysts have been used in CO₂ reduction in IL-based electrolytes, ranging from homogeneous to heterogeneous catalysts. The interactions of CO₂ and/or imidazolium with catalysts play important roles in the efficiency of CO₂ reduction. The electrocatalysts and the applied potentials can significantly affect the current density and the selectivity of the target products. In general, different reduction products, such as CO, HCOOH/HCOO⁻, CH₃OH, CH₄, and CH₃COOH can be obtained by controlling the reaction conditions of CO₂ electroreduction.

Homogeneous Catalysts

The homogeneous catalysts are generally organic or organometallic compounds, which have intrinsic molecular structures. Therefore, they dissolve in the electrolytes to facilitate the electron and proton transformation during CO₂ reduction. Kubiak et al. summarized the mechanism of homogeneous electrocatalysts used for electroreduction of CO₂ in various electrolytes and elaborated on the electron sources of catalysts (Figure 2). In this case, the reduction of CO₂ and the homogeneous catalyst can occur simultaneously. Therefore, CO₂ reduction usually exhibits favorable kinetics with low overpotentials.
Owing to the unique properties of IL, homogeneous catalysts have been studied in various IL-based electrolytes. As an example, \( \text{fac-ReCl} \) (2,2'-bipyridine) (CO)\(_3\) was initially used as a homogeneous catalyst for electoreduction of CO\(_2\) to CO in 1-ethyl-3-methylimidazolium tetracyanoborate ([Emim]TCB) at a lower overpotential.\(^4\) The rate constant of the apparent CO\(_2\) reduction \((k_{\text{app}})\) in [Emim]TCB was up to 4,000 M\(^{-1}\)C\(_0\)1 s\(^{-1}\) at 25 ± 3°C. The authors proposed that the interaction between catalysts and [Emim]\(^{+}\) cations accelerated the dissociation of chloride and reduced the activation energy of CO\(_2\) reduction. In another study, the addition of [Bmim]BF\(_4\) to the aprotic electrolyte could serve as a proton source and promote in situ formation of Fe Porphyrin (FeTPP) conversion to [Fe\(^{0}\)TPP]\(^{2-}\) homogeneous catalyst at a less negative potential.\(^4\) Co-catalysis coupling of the IL and homogeneous catalyst for CO\(_2\) reduction exhibited a high faradaic efficiency (FE) of CO (93%) at low overpotential (670 mV) (Figure 3A).

Compared with the electrolytes without IL, the turnover number and turnover frequency (TOF) were both increased 4-fold in this system. Isaacs et al.\(^4\) investigated the catalytic activity of [M\(^{1+}\)(cyclam)Cl\(_2\)] \((M = \text{Ni}^{2+} \text{ and Co}^{3+}, \text{cyclam} = 1,4,8,11\text{-tetraazacyclotetradecane})\) homogeneous catalyst in [Bmim]BF\(_4\) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonfyl)imide ([Bmim]NTF\(_2\)) electrolytes. Interestingly, they observed that the diffusion coefficient and heterogeneous electron transfer rate of the complexes mainly depended on the anion of IL, which had excellent catalytic performance for CO formation in [Bmim]BF\(_4\). In addition, [Ni(cyclam)Cl\(_2\)] was proved to be an active catalyst (Figure 3B). When the applied potential was −1.4 V versus Ag/AgCl, only CO could be detected, and the TOF could reach 0.73 h\(^{-1}\). After 4 h electrolysis, the nuclear magnetic resonance (NMR) spectra of the electrolyte showed that the electrolysis reactions did not change the chemical structure of [Bmim]BF\(_4\), suggesting that [Bmim]BF\(_4\)

| Cations | Anions |
|---------|--------|
| [Emim]\(^{+}\) | [BF\(_4\)]\(^{-}\) |
| [Bmim]\(^{+}\) | [PF\(_6\)]\(^{-}\) |
| [Hmim]\(^{+}\) | X\(^{-}\) (Cl\(^{-}\), Br\(^{-}\), I\(^{-}\)) |
| [Bmpy]\(^{+}\) | [ClO\(_4\)]\(^{-}\) |
| [Bzmim]\(^{+}\) | [HSO\(_4\)]\(^{-}\) |
| [DBU-H]\(^{+}\) | [H\(_2\)PO\(_4\)]\(^{-}\) |
| [P\(_{6614}\)]\(^{+}\) | [NO\(_3\)]\(^{-}\) |

| [Ac\(^{-}\)] | [TFA\(^{-}\)] |
| [TFO\(^{-}\)] | [BF\(_4\)]\(^{-}\) |
| [SCN\(^{-}\)] | [DCA\(^{-}\)] |

| [NTf\(_2\)]\(^{-}\) | [TCB\(^{-}\)] |
| [FAP\(^{-}\)] | [124Triz\(^{-}\)] |
was stable during the reaction (Figure 3C). In addition, in situ infrared (IR) spectroscopy electrochemical experiments demonstrated that the existence of intermediary Ni(I) from the [Ni(cyclam)Cl2] catalyst can form a [Ni(cyclam)CO]+ complex and the by-product [Ni(CO)4], which may hinder the generation of CO (Figure 3D).

**Heterogeneous Electrocatalysts**

In contrast to the above-mentioned homogeneous electrocatalysts, heterogeneous electrocatalysts are low cost and easily recyclable for large-scale applications. The main mechanism of heterogeneous electrocatalysts for electroreduction CO2 in IL-based electrolytes is shown in Figure 4. In this case, CO2 reduction mainly occurs at the interface of the electrolytes and heterogeneous electrocatalysts because the electrocatalysts are usually solid and the electrolytes are solvents saturated with CO2. To date, many catalysts have been exploited, including metal catalysts, metal oxides, metal chalcogenides, and metal-free catalysts.

**Metal Catalysts.** Metal catalysts, such as Ag, Au, Bi, Cu, etc., have been studied extensively for CO2 electroreduction in IL-based electrolytes. In the CO2 reduction reaction, the binding energy between the intermediate and the catalyst surface plays a crucial role in the product distribution. Generally, some metals (e.g., Sn, Hg, Pb, In) can produce HCOO due to their weaker binding energy of CO2 intermediate; and some metals (e.g., Au, Ag, Zn, Pd) can bind COOH tightly, whereas the capability to bind CO intermediate is weak, and thus CO is the main product with these metals. Among them, Cu has moderate binding energy of *CO intermediate, which provides an opportunity to convert CO2 to more value-added chemicals with two or more carbon atoms. Cu and Cu-based catalysts as a special category are also be highlighted in this section.

**Noble Metal Catalysts.** Table 3 provides some results for CO2 electroreduction on noble metal catalysts in IL-based electrolytes. Rosen et al. reported the use of Ag catalyst for CO2 reduction in [Emim]BF4 aqueous solution. They found that IL can act as a homogeneous co-catalyst that improved the catalytic rate, which is ascribed to the extra stabilization of *COOH intermediate. The imidazolium cation can potentially form a complex with CO2 on the catalyst surface, which may minimize the free energy for the initial electron transfer to CO2 (Figure 5A). In their following work, they also explored the possible mechanism on a Pt catalyst via sum frequency generation (SFG). The results indicated that a layer of [Emim]+ on the catalyst surface is beneficial to form [CO2-Emim]+ complex by hindering the HER. By using nonresonant (NR) SFG measurements, they found that little CO was absorbed on the surface of Ag at a threshold potential of ~1.33 V versus Ag/AgCl (Figure 5B). When the applied potential shifted negatively, the increase in curvature suggested structural transition of IL driven by the variation of the potential within the double layer (Figure 5C). This suggests that the structural transition of IL and the low overpotential of CO2 reduction were closely related. Later, Dyson et al. investigated the effect of different imidazolium-based ILs for CO2 reduction (Figure 5D). In particular, their results showed that the C4 and C5 protons on the imidazolium ring were crucial for enhancing the reaction activity. In another study, trihexyltetradecylphosphonium 1,2,4-triazolide ([P66614]124Triz) was also used as a strongly basic tetraalkyl phosphonium IL to enhance the solubility of CO2 (Figure 5E). The promotion effect of the IL on CO2 reduction was also explored. In the reaction, CO2 could bind to a 1,2,4-triazole anion and was then reduced to HCOO at a low overpotential (0.17 V).
Au has also attracted wide attention because of the excellent performance of CO$_2$ conversion in IL-based electrolytes. An early report from Zhu et al. explored the catalytic activity of CO$_2$ reduction over Au nanoparticles in [Bmim]PF$_6$-based electrolyte. In the presence of IL, the intermediate COOH* could be stabilized efficiently on the Au catalyst. In a later study, electrochemical impedance spectroscopy was applied to determine the difference in interface character between 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim]CF$_3$SO$_3$)/propylene carbonate (PC) and tetrabutylammonium trifluoromethanesulfonate ([Bu$_4$N]CF$_3$SO$_3$)/PC over Au catalyst. The authors considered that [Bmim]$^+$ would be absorbed on the surface of the catalyst, resulting in the generation of IL film. During the reaction, the formation of [Bmim-CO$_2$]$_{(ad)}$ could be a benefit for decreasing the activation energy and overpotential of CO$_2$ electroreduction. Cuesta et al. combined in situ surface-enhanced infrared absorption spectroscopy in attenuated total reflection mode (ATR-SEIRAS) with cyclic
voltammetry (CV) to study the reason for the decreasing reduction potential of CO$_2$ in IL (Figure 6A). They attributed this to the lower coverage of the adsorbed layer formed upon CO$_2$ reduction, which led to a lower degree of dipole-dipole coupling. Then, the CO bands started decreasing at more positive potentials due to CO desorption from the surface. The catalytic ability of CO$_2$ was also studied on low-index Au(hkl) single crystal catalysts in eight ILs.$^{50}$ The Au(110) catalyst exhibited higher activity than Au(111) and Au(100) catalysts. The authors observed that the deactivation of Au(110) catalyst mainly originated from surface reconstruction by *in situ* scanning tunneling microscopy (STM) (Figure 6B).

Pt is another active catalyst for CO$_2$ reduction. As an example, Compton et al.$^{51}$ found electrochemical conversion of CO$_2$ to HCOOH can occur over anodized Pt wire in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim]NTF$_2$). The performance of ILs with cyano (–CN) or methoxy (–OCH$_3$) functionalized imidazolium cations was also evaluated as electrolytes for electrochemical reduction of CO$_2$ on Pt catalyst.$^{52}$ The results indicated that the addition of the functional groups in ILs can reduce the activated energy for the formation of CO$_2^-$ intermediate. Consistently, the Pt(110) single crystal catalyst also efficiently promoted electrochemical synthesis of HCOOH from CO$_2$ in [Emim]NTF$_2$ electrolyte.$^{53}$

**Post-transition Metal Catalysts.** Some examples of CO$_2$ electroreduction on post-transition metal catalysts in IL-based electrolytes are given in Table 3. Typically, Bi is an abundant, inexpensive, and non-toxic post-transition metal. It is widely probed in electrochemical conversion CO$_2$ to CO or HCOO$^-$ with IL-based electrolytes. Rosenthal et al.$^{64}$ reported pioneering work that utilized Bi film as the cathode for CO$_2$ reduction in acetonitrile containing TBAPF$_6$ and [Bmim]PF$_6$ as supporting electrolyte. In this system, the FE of CO could reach approximately 95% at a very low overpotential. In their following work, they also found ILs containing different cations as electrolytes affected the selectivity for CO$_2$ reduction over Bi cathodes (Figure 6C).$^{66}$ Recently, Zhu et al.$^{67}$ designed surface-activated Bi nanoparticles (NPs) for electrochemical reduction of CO$_2$ to CO in [Bmim]OTF/acetonitrile electrolyte. The FE of CO can reach 96.1%, and the mass activity for CO evolution (MA$_{\text{CO}}$) can achieve 15.6 mA mg$^{-1}$ over activated 36-nm Bi NPs (Figure 6D). Furthermore, the structure of Bi was studied during cathodic polarization in acetonitrile solution containing [Bmim]$^+$-based ILs.$^{75}$ The authors observed that the Bi$_2$O$_3$ layer on the Bi (001) films was reduced during the first CV scan, and Bi could gradually dissolve in lateral size in the CV scans between −1.5 V to −1.9 V versus Ag/AgCl (Figure 6E). The authors also found that the generation of a Bi···[Im]$^+$ complex was beneficial for CO$_2$ reduction.

CO$_2$ electroreduction on other post-transition metals, such as In, Sn, Pb, have also been studied. Rosenthal et al.$^{69}$ investigated the catalytic activity of Sn, Pb, Bi, and Sb, which were fabricated by the electrodeposition method. In their study, the electrochemical reduction
Table 3. Selected Examples of CO₂ Electroreduction on Metal Catalysts in IL-Based Electrolytes

| Catalysts          | Electrolytes | Potential (V) | Current Density (mA cm⁻²) | Main Products       | FE for Main Products (%) | References |
|--------------------|--------------|---------------|---------------------------|---------------------|--------------------------|------------|
| **Noble Metal Catalysts** |              |               |                           |                     |                          |            |
| Ag                 | 18 mol % [Emim]BF₄/H₂O | 1.5          | –                         | CO                  | 96                       | Rosen et al.²⁶ |
| Ag                 | 75 μM H₂O/[Emim]BF₄ | 3.25         | ~4                        | CO                  | –                        | Salehi-Khojin et al.²⁴ |
| Ag                 | 0.1 mol L⁻¹ [P₆₆₆₁₄] | –             | –                         | HCOOH (little amount HCHO) | 63                       | Hollingsworth et al.⁶⁰ |
| Ag                 | 0.02 M 1,3-diethyl-2-phenyl-imidazolium tetrafluoroborate/0.1 M TBAPF₆/7 mL acetonitrile | ~1.4         | 4.2                       | CO                  | ~100                     | Lau et al.⁴⁵ |
| Ag                 | 50 mol % [Emim]BF₄/H₂O (70%) | –             | –                         | HCOOH (little amount HCHO) | 63                       | Hollingsworth et al.⁶¹ |
| Ag                 | [Bmim]BF₄/H₂O | –             | –                         | CO                  | >90                      | Rudnev et al.⁷³ |
| Ag                 | [Bmim]BF₄/20% H₂O | –             | –                         | CO                  | >94                      | Rudnev et al.⁷⁴ |
| Ag                 | 1 M [EmimOH]Cl/2 M EG/PC | –             | –                         | CO                  | ~100                     | Vasiliyev et al.⁷⁵ |
| Rough Ag           | 8 mM [Poliim]BF₄/acetonitrile | ~2.5         | ~16.4                     | CO                  | 92                       | Zhang et al.⁶⁰ |
| Ag nanoflowers (flow cell with electrolyte flow-through rates of 100 mL min⁻¹) | [Emim]BF₄H₂O (92/8 v/v %) | –             | 36.6 (j CO) | CO | 75 | Vedharathinam et al.⁷⁶ |
| Ag, Au, or Pt      | 0.1 mol L⁻¹ [P₆₆₆₁₄] | –             | –                         | CO                  | 95                       | Martindale et al.⁵¹ |
| Au(110)            | [Bmim]BF₄ | –             | –                         | CO                  | 95                       | Fu et al.⁷⁷ |
| Au                 | 0.1 M [Bmim]BF₄/acetonitrile | ~1.7         | 8.6                       | CO                  | 98                       | Gonçalves et al.⁶⁵ |
| Au                 | 0.1 mol dm⁻³ [Bmim] OA-c/dimethyl sulfoxide/0.2 vol % H₂O | ~1.80        | ~10.1                     | CO                  | 78                       | Medina-Ramos et al.⁷⁵ |
| Pt                 | 50 mM H[NTF₄] | –             | –                         | HCOO⁻                | 78                       | Martindale et al.⁵² |
| **Post-transition Metal Catalysts** |              |               |                           |                     |                          |            |
| Bi                 | 20 mM [Emim]BF₄/acetonitrile/0.1 M TBAPF₆ | ~1.95         | 5.5 ± 1.2                | CO                  | 95 ± 6                   | DiMeglio et al.⁷⁴ |
| Bi                 | 300 mM [Bmim]OTF/acetonitrile | ~2.0         | 25 ± 2                   | CO                  | 87 ± 8                   | Medina-Ramos et al.⁷⁵ |
| Bi                 | 250 mM [Bmim]PF₆/acetonitrile/0.1 M TBAPF₆ | ~1.95         | 15 ± 2                   | CO                  | 84 ± 3                   | Atifi et al.⁶⁶ |
| Bi                 | 250 mM [DBU-H]PF₆/acetonitrile/0.1 M TBAPF₆ | ~2.0         | 27 ± 3                   | HCOO⁻                | 77 ± 5                   | Medina-Ramos et al.⁷⁵ |
| Bi                 | 100 mM [Bmim]OTF/acetonitrile | ~2.0         | 15.6 mA mg⁻¹ | CO                  | 96.1                     | Zhang et al.⁷⁷ |
| Sn                 | 0.5 M [Emim]N(CN)₃/H₂O | ~1.2         | ~0.3                     | HCOO⁻                | 81.9                     | Zhang et al.⁷⁸ |
| Sn                 | 100 mM [Bmim]OTF/acetonitrile | ~1.95        | 10.1 ± 2.1               | CO                  | 78 ± 5                   | Medina-Ramos et al.⁷⁵ |
| Sn                 | ~1.95 V versus SCE | 1.95 ± 1.9   | –                        | CO                  | 77 ± 5                   | Medina-Ramos et al.⁷⁵ |
| Pb                 | –             | –             | –                         | HCOO⁻                | 81 ± 5                   |            |

(Continued on next page)
of CO₂ was performed in acetonitrile/[Bmim]OTF electrolyte. Sn and Bi can efficiently catalyze CO₂ to CO with current densities of 5–8 mA cm⁻². In contrast, Pb and Sb cannot favor CO formation. They demonstrated that the IL can enhance the generation of CO by combining with an appropriate catalyst. In addition, Li et al.¹⁴ also found that in situ prepared In nanocrystals can efficiently catalyze CO₂ conversion to CO in IL-based electrolytes. Ha et al.⁶⁸ reported on [Emim]N(CN)₂ aqueous solution as the electrolyte to improve the solubility of CO₂ and inhibit the HER for efficient electroreduction of CO₂ to HCOOH over Sn powder catalyst. The maximum FE of HCOOH can reach 81.9% at −1.2 V versus RHE. In addition, acetonitrile and [Emim]TNF₂ solutions were used as the electrolyte for CO formation from CO₂ electroreduction using Pb as a catalyst.⁷¹ The authors also found that the ratio of acetonitrile and [Emim]TNF₂ changed the pathway of the reaction, reducing the formation of oxalate anion and enhancing CO generation. In addition, electroreduction of CO₂ over Pb or Sn cathodes was reported in ternary mixture electrolytes ([Bmim]PF₆ [30 wt %]/acetonitrile-H₂O) with a partial current density of 37.6 mA cm⁻² and FE of 91.6% for HCOO⁻.⁷⁰ Interestingly, the authors found that the existence of a small amount of H₂O can significantly enhance the efficiency of the reaction. In another example, In, Sn, and Pb catalysts were also applied in the electroreduction of CO₂ to HCOO⁻ in Table 3.

| Catalysts | Electrolytes | Potential | Current Density (mA cm⁻²) | Main Products | FE for Main Products (%) | References |
|-----------|--------------|-----------|---------------------------|---------------|--------------------------|------------|
| Sn        | 30 wt % [Bmim]PF₆/acetonitrile/5wt %H₂O | −2.3 V versus Ag/Ag⁺ | 32.1 ([HCOO⁻]³⁻) | HCOO⁻ | 92 | Zhu et al.⁷⁰ |
| Pb        | 0.1 M [Emim]TNF₂/0.1 M TEAP/acetonitrile | −2.34V versus Ag/AgNO₃ | 37.6 ([HCOO⁻]³⁻) | CO carboxylate | − | Sun et al.⁷⁵ |
| Pb        | 700 mM [Bmim] 124Triz'/acetonitrile/5 wt % H₂O | −2.4V versus Ag/Ag⁺ | 24.5 | HCOO⁻ | 95.2 | Feng et al.⁷² |
| Pb phytate | 12.8 wt % [Bmim]BF₄ /9.9 wt % H₂Oacetonitrile | −2.25 V versus Ag/Ag⁺ | 30.5 | HCOO⁻ | 92.7 | Wu et al.⁷⁵ |
| Sn        | [Bmim]PF₆/acetonitrile/1 mM In(acac)₃ | −1.34 V versus Ag | 30 | CO | 45 | Chen et al.⁷⁵ |
| Sn        | [Bmim]PF₆/acetonitrile/1 mM In(acac)₃ | −1.9 V versus SCE | −15 | HCOO⁻ | 99 | Ding et al.¹⁴ |

*Cell voltage.
¹Tetrabutylammonium hexafluorophosphate.
²Ferrocene/ferrocenium.
³-t-Butyl-3-methylimidazolium trifluoromethanesulfonate.
⁴Tetrabutylammonium hexafluorophosphate.
⁵-Decyl-3-methylimidazolium tetrafluoroborate.
⁶-t-Butyl-3-methylimidazoliumhydroxide chloride.
⁷Propylene carbonate.
⁸-(1,3-Dioxypropyl)-3-methylimidazolium tetrafluoroborate.
⁹CO partial current density.
¹₀Normal hydrogen electrode.
¹¹Partial current density.
¹²Pentafluorophenol.
¹³Tetraethylammonium bis(trifluoromethane)-sulfonimide.
¹⁴Saturated calomel electrode.
¹⁵-t-Butyl-3-methylimidazolium trifluoromethanesulfonate.
¹⁶[DBU] is 1,8-diazabicyclo[5.4.0]undec-7-ene.
¹⁷-t-Butyl-3-methylimidazolium dicyanamide.
¹⁸Reversible hydrogen electrode.
¹⁹HCOO⁻ partial current density.
²⁰Tetraethylammonium perchlorate.
²¹-t-Butyl-3-methylimidazolium 1,2,4-triazolide.
²²-Benzyl-3-methylimidazolium tetrafluoroborate.
²³Dimethylammonium dimethylcarbamate.
²⁴Cc⁺ is cobaltocenium.
²⁵Indium acetylacetonate.
²⁶CO₂ partial current density.
²⁷Tetraethylammonium perchlorate.
²⁸-t-Butyl-3-methylimidazolium 1,2,4-triazolide.
²⁹-t-Butyl-3-methylimidazolium hydroxide chloride.
³⁰HCOO⁻ partial current density.
1-ethyl-3-methylimidazolium trifluoroacetate ([Emim]TFA) aqueous solution. The excellent performance was attributed to the high CO$_2$ solubility in IL and the capacity of IL to stabilize the reaction intermediate.

**Cu-Based Catalysts.** Different hydrocarbons and alcohols have been obtained from direct conversion of CO$_2$ on Cu-based catalysts. Dendritic Cu nanomaterials were prepared for CO$_2$ electroreduction to HCOOH in IL-based electrolyte. It was discovered that the synergetic interaction between IL and the structure of the catalyst favors the generation of HCOO$^-$. Bimetallic nanomaterials have also been investigated to improve the catalytic performance by altering the degree of stabilization of key intermediates. On bimetallic Zn-Cu film,
the rate of syngas generation can reach 85 N μL (normal microliter) cm⁻² C⁻¹/170 N μL cm⁻² h⁻¹. In a recent study, Pd-Cu bimetallic aerogel was used as a catalyst for electrochemical conversion of CO₂ to CH₃OH in electrolytes composed of 25 mol % [Bmim]BF₄ and 75 mol % H₂O. The excellent performance of Pd-Cu aerogels can be attributed to the high porosity of aerogel and the special valence states of the two metals (Figures 7A–7D). The IL-based electrolyte can also adsorb and stabilize CO₂⁻⁻, which is favorable for CO₂ reduction. CuSn alloys can also efficiently reduce CO₂ in an IL-based electrolyte at low overpotential due to the synergistic effect between two metals.

In addition, Cu-doped catalysts have been explored in the reaction to enhance energy efficiency. For this purpose, Roy et al. investigated CO₂ electroreduction to CO on Cu-modified boron-doped diamond (BDD) in
100 mM [Emim]BF₄ aqueous solution. Compared with bare Cu, the Cu-modified BDD catalysts can inhibit the HER and enhance product selectivity (Figures 7E and 7F). N-based Cu(I)/C-doped boron nitride (BN-C) composites were also designed for electroreduction of CO₂ in [Emim]BF₄-LiI-H₂O electrolyte. The authors found that the current density could reach 13.9 mA cm⁻² with a high FE for acetic acid of 80.3%. The synergistic effect of Cu complex, substrate, and electrolyte favor the production of the desired product.

**Other Transition Metal-Based Catalysts.** Besides Cu, other transition metal (Mo, Co, Zn)-based catalysts have been tested in IL-based electrolytes. Xie et al.¹⁰⁴ carried out electroreduction of CO₂ on single Mo atoms loaded on N-doped graphene in 4 mol % [Emim]BF₄ aqueous solution, which can favor production of HCOO⁻. Zhang et al.⁸⁵ reported that the electrochemical reduction of CO₂ can be performed on a Cd catalyst derived from Cd(OH)₂ in [Bmim]PF₆/acetonitrile electrolyte. The FE for CO can reach 99.2% with a partial current density of 59.0 mA cm⁻². A Zn metal-organic framework (Zn-MOF) was also used as the cathode in [Bmim]BF₄ electrolyte for CO₂ reduction. The FE of CH₄ could reach 80% at a low overpotential of 0.14 V. Furthermore, electroreduction of CO₂ was studied over an indium tin oxide modified by cobalt 5,10,15,20 tetra- kis(4-aminophenyl)porphyrin (Co-TAPP) in [Bmim]BF₄. The results indicated that Co(I) porphyrin species, which promoted the reaction, were detected in an inert atmosphere rather than in the CO₂-saturated medium.

**Metal Oxides and Metal Chalcogenides.** So far, some attention have been given to CO₂ reduction on metal oxides and metal chalcogenides, such as MoO₂, SnO₂, and MoS₂. Chu et al.⁹⁸ synthesized low-density polyethylene from CO₂ electrochemical reduction over...
a nanostructured TiO2 catalyst in [Emim]BF4 aqueous solution. The current efficiency of low-density polyethylene was about 8%–14% at an applied potential of –1.50 V versus standard calomel electrode (SCE). Electro-reduction of CO2 was carried out over MoO2 with [Bmim] PF6/acetonitrile as electrolyte. The addition of IL in the electrolytes led to lower overpotential and improved the FE of CO. The electrocatalytic performance of commercial PbO2 was carried out in various catholytes composed of IL, H2O, and acetonitrile. The [Bzmmim]BF4 was considered to be the best IL for improving the FE of HCOOH. SnO2 nanosheets on N-doped porous carbon (SnO2@N-PC) were prepared for CO2 electroreduction to HCOOH in 0.5 M [Bmim]PF6 acetonitrile solution. The current density was 28.4 mA cm\(^{-2}\) with HCOOH FE of 94.1% at an overpotential of 0.31 V.

Metal chalcogenides can exist in many forms of stoichiometries and structures, therefore they have been widely studied in many fields including CO2 electrolysis. For example, titanium disulfide (TiS2) planes were synthesized for CO2 electroreduction to CO in IL-H2O-acetonitrile. The results revealed that cathodic energy efficiencies can be as high as 64% with a current density of 5 mA cm\(^{-2}\). Asadi et al. prepared molybdenum disulfide (MoS2) for CO2 electrochemical reduction. In the same electrolyte, N-doped MoS2 nanosheets and N-doped carbon nanodots (N-MoS2@NCDs) composite electrocatalyst were synthesized for CO2 reduction to CO. The good electrical conductivity provided by NCDs on the MoS2 surface can enhance electron transport. A series of Mo-Bi bimetallic chalcogenides (BMCs) were fabricated for CO2 electroreduction in [Bmim]BF4/acetonitrile. The FE of CH3OH was up to 71.2% and the total current density reached 12.1 mA cm\(^{-2}\). They found that IL played a crucial role in CO2 reduction with the stabilization of CO2 -. The synergistic effect of Mo and Bi favors the generation of CH3OH (Figure 8A). The flowerlike In2S3 was synthesized as an efficient electrocatalyst for CO2 reduction to HCOO- in IL-based electrolyte. The excellent catalytic activity was attributed to the special structure and large adsorption energy of intermediate COO- and OCHO-.

Metal-Free Catalysts. Metal-free catalysts can also act as potential electrocatalysts for CO2 reduction in IL-based electrolytes. According to a previous report, they have many intrinsic advantages that can enhance the performance of the reaction, such as excellent conductivity, high surface area, outstanding mechanical strength, and remarkable chemical stability. In addition, they are low cost and easily available in huge quantities. Although pure carbon nanocatalysts show low activity, heteroatoms can be easily introduced to adjust the chemical state and structure of the nanocatalysts to manipulate the active sites for CO2 reduction. Combining with IL, metal-free nanocatalysts are promising electrocatalysts. The catalytic performance of carbon nanofibers (CNFs) was explored in [Emim]BF4 and H2O mixture electrolytes. In this system, CO2 could be reduced to CO with high current density and low overpotential. The addition of H2O can instantly change the pH and viscosity of IL. The decrease in pH mainly originates from the generation of hydroxyl ions due to the hydrolysis of IL, which can promote the...
proton concentration and then improve the rate of CO2 reduction. It was reported that N-doped carbon (graphene-like) catalysts were efficient for the electrochemical reduction of CO2 when using IL as the promoter. The FE of CH4 could be as high as 93.5%, and the current density was 1.4 mA cm⁻² in [Bmim]BF₄/H₂O electrolyte.

**Electrolyte Effects**

**Comparison of IL, Aqueous Electrolytes, and Organic Electrolytes**

In aqueous electrolyte, the solubility of CO₂ is only 0.033 mol⁻¹ under ambient conditions (298 K, 1 atm), which leads to low conversion efficiency of CO₂ reduction. Therefore, the sluggish kinetics due to the formation of CO₂⁻ radical is the main energy barrier for the reaction. Consequently, adequate large overpotentials are usually required to drive this reaction. The other complicating factor is the HER, which is prevalent in aqueous media. As a competitive reaction, it can reduce the selectivity of the desired product. Moreover, most studies focus on weakly acidic or alkaline CO₂-saturated aqueous solutions consisting of inorganic salts (e.g., anions, HCO₃⁻, SO₄²⁻, Cl⁻, Br⁻, I⁻; alkali metal cations, K⁺ and Na⁺) and the catalytic activity and product selectivity.
are enhanced even though the exact mechanism is still under debate. Although there are still difficult issues with CO2 reduction, CO2 in aqueous electrolyte could undergo C–C coupling and be further reduced to multi-carbon products. Therefore, designing efficient catalysts for CO2 electroreduction in aqueous electrolytes can enhance the product selectivity and diversity of the product.

In organic electrolytes, the increased solubility of CO2 is accompanied by the poor conductivity of the electrolyte. At the same time, the volatilization of a large number of organic solvents also causes environmental problems. Therefore, organic solvent systems are mainly used in homogeneous catalysis or in the design of mixed electrolyte systems.

Compared with aqueous and organic electrolytes, ILs exhibit excellent activity in the electroreduction of CO2. They provide a medium for CO2 reduction, and their strong absorption capacity of CO2 promotes the reduction reaction effectively. More importantly, they can significantly increase the selectivity of products and inhibit the HER. However, a large proportion of ILs are expensive and have high viscosity. Therefore, synthesizing functionalized ILs with low viscosity, high CO2 absorption, and excellent stability is vital for CO2 reduction. In addition, most of the catalysts currently developed can only reduce CO2 to C1 product in IL-based electrolytes. This indicates that the reaction pathways in IL-based electrolyte are different from those in aqueous media. Therefore, it is also necessary to further study the mechanisms in IL-based electrolyte and design novel IL-based systems with high activity for multi-carbon products.

**Cation and Anion Effect of ILs**

Although many ILs are widely used, the promotion effect of the electrolyte remains unclear. To date, only a few studies have reported the electrolyte effect. This section discusses the recent progress in CO2 reduction systems concerning the cation and anion effect.

**Cation Effect.** Imidazolium cations have unique properties in CO2 reduction. In a recent study, Zhang et al. studied the CO2 reduction performance on an Ag electrode in acetonitrile solutions (0.1 M n-Bu4NPF6 as supporting electrolyte) containing 2.0 mM imidazolium, pyrrolidium, ammonium, phosphonium, or (trimethylamine)-(dimethylethylamine)-dihydroborate cations. They found that all these cations can enhance the kinetics of the reaction, but imidazolium and pyrrolidium are the most effective (Table 4). Rosenthal et al. found that the cation in ILs can change the selectivity of products over a Bi/IL interface. Selectively, CO was the main product in [Bmim]PF6, and the FE for HCOO– was higher in [DBU-H]PF6 (DBU, 1,8-diaza-bicyclo[5.4.0]undec-7-ene). These results indicated the interaction among the cation, catalyst, and CO2 plays an important role in the electroreduction of CO2. In addition, it was also reported that ILs with different imidazole rings had a vital influence on the catalytic activity of CO2 electroreduction. The hydrophobicity of ILs, which can be varied by the side cation chain length, was closely related to the solubility of CO2. At the same time, the stability of the imidazole ring-CO2 complex formed during CO2 reduction may be decreased by the steric bulkiness with increasing side chain length. Recently, Deng et al. used surface tension measurements and SFG spectroscopy to investigate the surface behavior at a liquid-air interface of 1-butyl-3-methylimidazolium methylsulfate ([Bmim]MS) aqueous solution.

| Additives | $E_{\text{applied}}$ (V) vs. Fe/Fe$^+$ | Charge @ H$_2$, CO, C$_2$O$_4^{2-}$, HCOO$^-$ | FE (%) |
|-----------|--------------------------------------|---------------------------------|--------|
| Without IL | 2.6$^b$ | 12.5 | 0.2 | 53.9 | 39.3 | 0.8 |
| 2.0 mM [C$_{10}$mim]BF$_4$ | 2.3 | 28.5 | 0 | 45.1 | 53.4 | 0.4 |
| 2.0 mM [C$_4$mpyr]BF$_4$ | 2.3 | 50.1 | 0 | 66.4 | 28.4 | 0.8 |
| Without IL + 1.0% H$_2$O | 2.3 | 15.3 | 87.4 | 9.5 | 3.5 |
| 2.0 mM [C$_{10}$mim]BF$_4$ + 1.0% H$_2$O | 2.3 | 61.8 | 1.8 | 70.4 | 27.1 | 0.4 |
| 2.0 mM [C$_4$mpyr]BF$_4$ + 1.0% H$_2$O | 2.3 | 50.2 | 0.4 | 58.4 | 42.6 | 0.8 |

Reproduced with permission from Zhu et al. Copyright 2016, ACS Publishers. $^a$H$_2$O content: 5.0 mM. $^b$This more negative potential was chosen to achieve a reduction rate that is comparable with that found in the presence of IL additive.
The results illustrated that the surface tension was mainly affected by the cations in ILs. Consistently, Dyson et al. also pointed out that different imidazolium rings are vital for efficient CO\textsubscript{2} reduction (Figure 5D).

**Anion Effect.** Anions in the imidazolium-based ILs also affect CO\textsubscript{2} reduction. Zhang et al. built an ionic microhabitat composed of an anion-functionalized IL [Bmim]\textsubscript{124}Triz, acetonitrile, and H\textsubscript{2}O for CO\textsubscript{2} electroreduction. Other ILs with different anions, such as BF\textsubscript{4}\textsuperscript{-}, PF\textsubscript{6}\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, and NTF\textsubscript{2}\textsuperscript{-}, were used for comparison. The authors found that [Bmim]\textsubscript{124}Triz promotes the solubility of CO\textsubscript{2} and bending linear CO\textsubscript{2} by forming the [124Triz]-CO\textsubscript{2} adduct. The activated CO\textsubscript{2} can be transferred into the catalyst surface easily, which can increase the generation of the target product (Figures 9A and 9B).

They also used computational results to validate the underlying mechanism of the super-basic IL. Interestingly, they found that the bond length in [Bmim]\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
The comprehensive effect of cation and anion was also investigated by Compton et al.\textsuperscript{107} They pointed out that the cation bound to the Ag surface allowed the CO\textsubscript{2} molecule to access the Ag surface before the process of desorption and an irreversible reduction of CO\textsubscript{2}. In addition, the anions in ILs may affect the local solvent structure other than the solubility of CO\textsubscript{2}. The electric double layer adjacent to the Ag surface can be occupied by cations and anions and allow CO\textsubscript{2} transport to the Ag surface before electron transfer occurs. Based on previous reports, we can summarize that the cations and anions in ILs play important roles in CO\textsubscript{2} electroreduction. They can interact with the reaction intermediates or change the properties of the electric double layer adjacent to the catalyst surface.

**Mechanism**

In general, the CO\textsubscript{2} electroreduction process is driven in imidazolium-based ILs. The importance of the effect of ILs on the activity toward CO\textsubscript{2} reduction was investigated by Lim et al.\textsuperscript{108}. In this work, the authors presented a combined experimental and theoretical study to investigate the promotion effect of ILs. Contrary to the previous concept, which assumed specific intermolecular coordination by ILs with the reaction intermediate, the authors figured out that the promotion effect was manifested by changing the reaction microenvironment. They found that the local coordinating environment of *COOH was nearly identical for aqueous and [Emim] BF\textsubscript{4}/H\textsubscript{2}O systems. A single H\textsubscript{2}O molecule bound to *COOH through a hydrogen bond (Figures 9C and 9E). However, considering that the H\textsubscript{2}O molecule served as a primary proton source, the local atomic geometry was responsible for the facile proton transfer.

In [Emim]BF\textsubscript{4}/H\textsubscript{2}O electrolyte, approximately one or two H\textsubscript{2}O and BF\textsubscript{4}\textsuperscript{−} molecules were closed to the adsorbed H\textsubscript{2}O molecule. Then, four [Emim]\textsuperscript{+} molecules surrounded an H\textsubscript{2}O-BF\textsubscript{4}\textsuperscript{−} complex via a strong cation-anion attraction (Figures 9D, 9F, and 9G). The combination of these complex noncovalent interactions in the mixed electrolytes formed an exotic microenvironment for *COOH with an alternating solvation shell structure. These three-dimensional atomic arrangements can result in [Emim]\textsuperscript{+} being in direct contact with the catalyst surface, surrounded by the key reaction intermediate. This phenomenon results in a significant polarization of the electron density on the catalyst surface. Then, plenty of metal electrons can be polarized toward the *COOH intermediate, which induces a strong local field effect at the catalyst interface and stabilizes the *COOH intermediate. Therefore, the electrical double-layer interface provided a suitable microenvironment for solvating the intermediate, which can be well preserved with the variations in chemical details because the solvation energy is dominated by the nonspecific interaction.

To further understand the CO\textsubscript{2} electroreduction pathway, Nakamura et al.\textsuperscript{109} figured out the possible intermediates and the transition states from CO\textsubscript{2} to CO in [Emim]BF\textsubscript{4} electrolyte. They stressed that the complex [Emim-COOH] generated during the reaction can be decomposed to CO. In the reaction pathway, H\textsubscript{2}O was a co-catalyst to facilitate proton transfer. The pathway to CO was thermodynamically more favored than that to HCOOH in IL-based electrolyte. As shown in Figure 10, there are many reaction pathways from [Emim]BF\textsubscript{4} and CO\textsubscript{2} to the final product CO. The thermodynamically favorable paths are marked by green arrows and unfavorable ones by red arrows. The black arrows represent the electron transfer from the electrodes. Although important progress has been made in electroreduction of CO\textsubscript{2} with IL-based electrolyte, research on the mechanism is still in its infancy, especially on understanding of the interaction between the liquid medium and the catalyst surface, which is important for the systematic design of efficient catalytic systems.

**Perspective**

ILs have shown promising applications in electroreduction of CO\textsubscript{2} due to their unique properties. To date, significant progress has been achieved in this interesting area. However, some related issues need to be solved.
(1) For IL-based electrolyte, large-scale application of CO$_2$ electroreduction has not been realized. On the one hand, the current density at high FE of the desired product is still low for industrial applications (a few hundred mA cm$^{-2}$ for industrial level). On the other hand, the high cost and high viscosity of ILs are also crucial factors to inhibit its large-scale application. Therefore, highly active, selective, and stable catalyst-electrolyte systems should be explored to promote commercial application, especially using renewable electricity. The design of novel electrochemical devices such as flow cells and gas-diffusion electrodes can overcome the poor mass transferability and increase the current density. Moreover, synthesizing functionalized ILs with low viscosity, high CO$_2$ absorption, and excellent stability can enhance the capacity of activating CO$_2$ molecules and achieve multiple reuse of the electrolyte.

Figure 10 A Schematic Flow of Reaction Intermediates
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Up to now, most of the catalysts that have been developed can only reduce CO$_2$ to C$_1$ products in IL-based electrolytes. The current density and FE for producing various products with two or more carbons are still not satisfactory because C–C coupling is involved. Therefore, it is interesting and important to explore novel catalyst-electrolyte systems with high activity for C–C coupling. Excellent catalysts with high potentials for the HER should be designed that can combine with ILs to provide a good three-phase contact interface for enhancing the selectivity toward multi-carbon products. While the electrocatalytic reduction of CO$_2$ and H$_2$O to produce valuable chemicals and fuels is of great importance, much attention should be given to investigations about new electrocatalytic reactions of CO$_2$ and organic compounds to synthesize more valuable chemicals. IL-based electrolytes may be more advantageous for this kind of reaction because ILs can dissolve both CO$_2$ and organic substances. Moreover, the interaction among ILs, CO$_2$, and organic reactants can be tuned by changing the structure of the IL, which may enhance catalytic activity and FE for a product, and even control the reaction pathways.

The interfacial properties and the mechanisms in IL-based electrolytes are still unclear. To further understand CO$_2$ reduction in IL-based electrolytes, comprehensive recognition of the theoretical and experimental mechanisms is needed. An in-depth study should also be carried out on the role of cations and anions in ILs and the microscopic mechanism of proton-electron transport and transfer. It is expected that combining in situ techniques with theoretical calculations can be used to address this issue.

Based on the above discussion, CO$_2$ electroreduction in IL-based electrolytes can be used to produce many value-added chemicals and feedstocks for fuels. The design of functionalized, low-toxicity, and easily prepared ILs will have broad application in CO$_2$ electroreduction. Although exploring efficient catalyst-electrolyte systems for CO$_2$ electroreduction is challenging, it should be given much attention because it is crucial for the development of this area.

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**Declaration of interests**

The authors declare no competing interests.

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