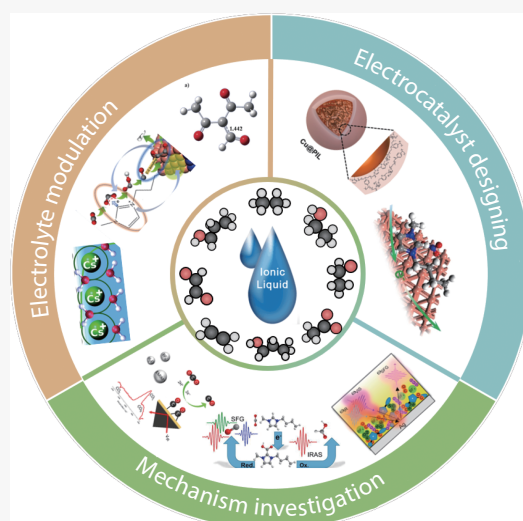


A perspective on electrochemical conversion of CO₂ to multicarbon chemicals in ionic liquids-based electrolytes

Minyang Dai, Yan Zhang, Wenpeng Ni*^{ID} and Shiguo Zhang*^{ID}

Carbon dioxide electroreduction (CRR) is a promising technology for both intermittent energy storage and emissions mitigation, but it faces challenges such as relatively high overpotential and poor selectivity. Introducing ionic liquids (ILs) into the CRR system has shown impressive activity for CO production, even in electrocatalysts that are primarily active for hydrogen evolution in aqueous electrolytes. However, converting CO₂ to high-value C₂₊ chemicals in IL electrolytes suffers from limitations in *CO coverage, proton accessibility, and specific stabilization effects on *COOH. In this perspective, we emphasize the modification of the steady-state adsorption of *CO and other intermediates to enhance the CO₂-to-C₂₊ conversion. More efforts need to be devoted to electrolyte modulation, involving the functional ILs design, the proton sources, and inorganic additive screening. It is also necessary to design effective electrocatalysts via developing a descriptor for C₂₊ selectivity, exploring the dynamic evolution of catalyst upon exposure to ILs, and constructing novel catalyst/ILs hybrids. Furthermore, developing a molecular understanding of the electrode/ILs interface and the bulk phase of IL-containing electrolytes could provide guidelines for designing an efficient electrochemical system for C₂₊ generation.



Electrochemical reduction of carbon dioxide (CRR) represents a promising option for storing intermittent renewable energy in chemical bonds. Through this process, a range of gaseous and liquid products can be produced, ranging from C₁ (carbon monoxide (CO), formic acid or formate (HCOO⁻), methane (CH₄), and methanol (CH₃OH)) to C₂ chemicals (acetic acid (CH₃COOH), ethanol (CH₃CH₂OH), ethylene (C₂H₄), and ethane (C₂H₆), and even C₃ fuel (propanol (n-C₃H₇OH)).^[1] A techno-economic analysis has revealed that the conversion of CO₂ into higher-value C₂₊ chemicals, such as CH₃CH₂OH and C₂H₄, has a more significant commercial potential due to their larger market size (> 80 million tons per year) and higher market price.^[2] However, the technology still faces significant hurdles in selectivity and energy efficiency during the multiple electron transfer process. To tackle these issues, most efforts have been devoted to designing Cu-based electrocatalysts via morphology and structure control (e.g., facet design, confinement, defect en-

gineering, bimetal strategy, and surface modification).^[3–4] Unfortunately, the production rate, multicarbon product (C₂₊) selectivity, and long-term stability of these developed catalysts remain problematic.

The efficiency of electrochemical reaction is also controlled by electrolyte, which not only provides a medium for mass transport but also shapes the characteristics of the interface, such as local electric field strength and pH.^[5–6] Therefore, there is a substantial interest in modulating C₂₊ selectivity via the regulation of electrolytes.^[7] For example, a higher local pH has been shown to be favorable for C₂₊ formation, as evidenced by the higher C₂H₄ selectivity in non-buffering electrolytes (KCl and K₂SO₄) and in high-concentration KOH solutions.^[8] Furthermore, the changes in electrolyte composition can prompt the formation of nanostructured Cu electrodes. In electrolytes containing I⁻, the presence of CuI crystals on Cu foil has been documented, facilitating the C-C coupling process. The introduction of Cs⁺ has been found to stabilize more Cu⁺ species on the Cu nanoparticles, thereby enhancing the selectivity of C₂₊ products.^[9] The adsorption of key intermediates for C₂₊ production, such as dipole *CO₂ and *OCCO, can be modulated by the electrostatic field in the electrochemical double layer (EDL).^[10] It has been reported that the local

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Received 15 February 2023; Accepted 28 June 2023; Published online

electric field strength can be adjusted by altering the radius of electrolyte cations, leading to improved faradaic efficiencies (FE) of C_2H_4 and C_2H_5OH with larger alkaline metal cations.^[11] Nonetheless, the conversion of CO_2 to C_{2+} chemicals in the aqueous electrolyte is still hindered by the fierce competing hydrogen evolution reaction (HER) and the mass transfer limitations of CO_2 .

Different from the aqueous electrolytes, organic solvent affords higher solubility of CO_2 than water and almost completely suppresses HER.^[12] More interestingly, the generation of valuable C_{2+} chemicals, such as oxalate, glycolic acid, and tartaric acid, which are not attainable in aqueous electrolytes, is feasible. Among various organic media, ionic liquids (ILs) have gained significant interest as a potential alternative to traditional solvents owing to their wide electrochemical window, negligible volatility, and chemical stability.^[13–14] Additionally, ILs can be employed as supporting electrolytes in binary systems with water/organic solvents or as catalyst surface modifiers to improve the activity of CRR.^[15–18] Benefiting

from the high CO_2 absorption capacity and potential co-catalysis effect, CO_2 electrolysis in IL-based systems showed an industrial production rate over metal (noble metal and post-transition metals), metal oxides, metal chalcogenides, and metal-free catalysts, especially for two-electron reduced products (CO and HCOOH).^[19–23]

In contrast to the widely studied C_1 products, the CO_2 -to- C_{2+} conversion in ILs system has received comparatively limited attention, as depicted in Figure 1. Our findings indicated that the formation of CH_3CH_2OH , C_2H_4 , and $n-C_3H_7OH$ is significantly impeded, even in the presence of Cu-based catalysts. This paper aims to understand the regulation of C_{2+} chemicals production in IL systems. We will first discuss the reasons for the low selectivity of C_{2+} products based on well-accepted modulation mechanisms of ILs for CRR. Subsequently, personal perspectives will be offered regarding strategies for improving C_{2+} selectivity, including electrolyte and catalyst design, and advancing our understanding of the underlying mechanism.

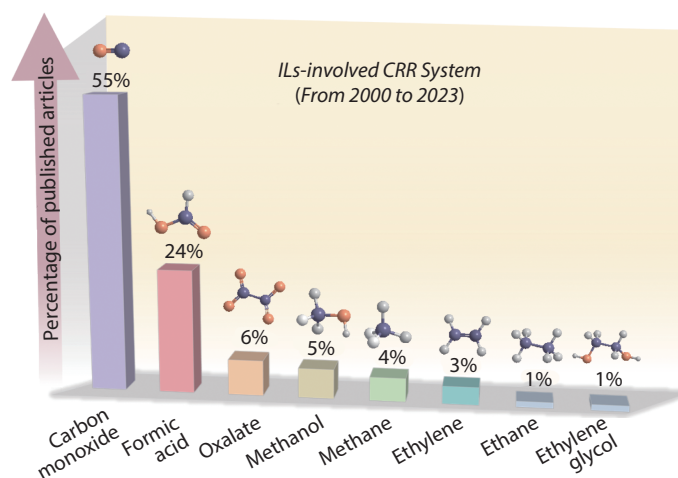


Fig. 1 Percentage of published articles on various CRR products in IL-containing systems.

Why are C_{2+} chemicals scarcely produced in IL-based systems?

Since Hori's group first reported on the generation of C_{2+} chemicals over a Cu catalyst, more than sixteen different hydrocarbons and oxygenated products have been detected in aqueous electrolytes.^[24] Despite various mechanisms being proposed, a steady-state adsorbed CO ($*CO$) is widely acknowledged as the main precursor for producing C_{2+} products through either CO dimerization or an insertion-type mechanism (Figure 2).^[25] On a Cu surface with a high CO coverage, C-C coupling between two adjacent $*CO$ was achieved through one proton-electron coupled step, yielding the intermediate $*COCO$ H, which subsequently transforms into $*CH_2CHO$. This intermediate then leads to the production of C_2H_4 , CH_3CH_2OH/CH_3CHO , or $n-C_3H_7OH$ via three parallel competitive pathways. In the case of CO insertion, protonation of $*CO$ gives two possible intermediates, $*CHO$ or $*COH$. The insertion of CO into $*CHO$ is energetically favored at more negative potentials, forming $*COCO$ H, which can produce glyoxal and glycol. $*COH$ can directly produce formaldehyde

after one proton-electron coupled step and CH_3OH after three proton-electron coupled steps, and highly reduced chemicals like CH_4 . On the other hand, the intermediate $*CH_2$ was also observed after the protonation of $*COH$. Interestingly, $*CH_2$ can further be protonated to give $*CH_3$, which undergoes a dimerization to generate C_2H_6 . Furthermore, the insertion of CO into $*CH_2$ theoretically forms $*CO-CH_2$, which may produce CH_3COO^- through base-catalyzed disproportionation of acetaldehyde. To sum up, the key to successful CO_2 -to- C_{2+} conversion lies in the steady-state adsorption of $*CO$ to ensure sufficient surface coverage, facial proton formation and smooth transfer, and precise control of the structure and stability of various protonated intermediates.

ILs can be used as effective additives to the electrolyte or as modifiers of the catalyst surface to significantly reduce the overpotential of CRR.^[26] Several mechanisms have been proposed to explain the improvement effect of ILs. Firstly, the high solubility of CO_2 in IL-based electrolytes significantly eliminates the limitation of the mass transfer of CO_2 .^[27] Secondly, covalent interaction between ILs and CO_2 or reduced intermediates could accelerate the kinetic rate of CRR

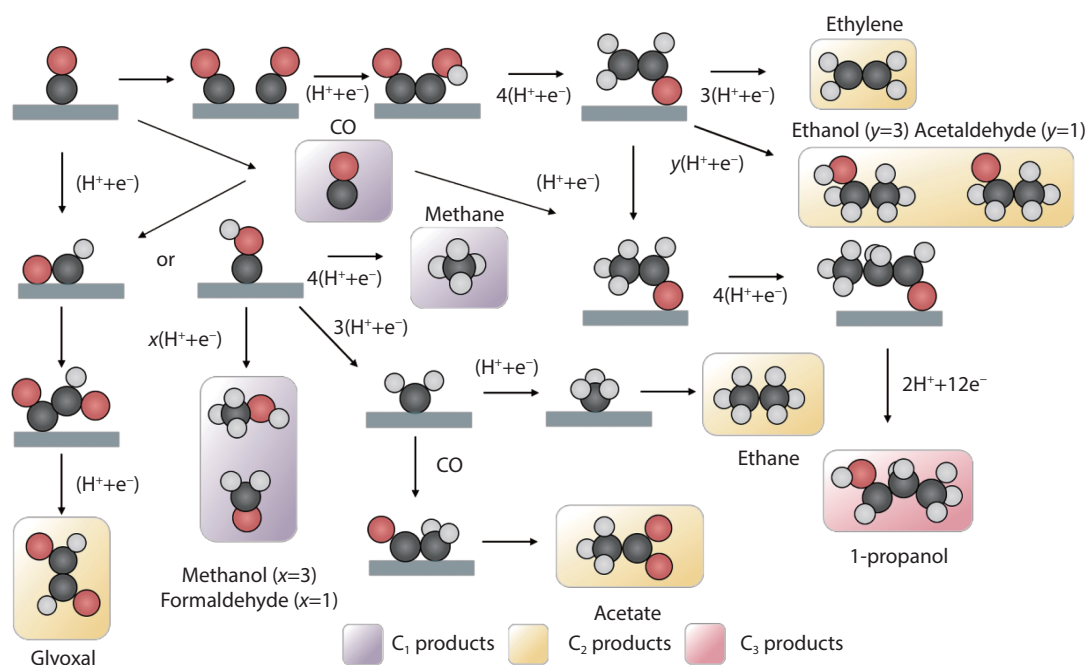


Fig. 2 Reaction pathways for CRR towards different products. (Black, C; red, O; grey, H; green, catalyst).

and guide the reaction pathways.^[28] For example, the active C2-H of the imidazolium ring can bond with $^*\text{COOH}$ via a carbene intermediate, resulting in the selective production of CO or HCOOH from the breakage of C-O bond or C-C bond, respectively (Figure 3a).^[29] Thirdly, the interfacial field-dipole interaction can stabilize certain intermediates of CRR, particularly for ILs that lack acidic C2-H sites (such as pyrrolidinium-, ammonium-, phosphonium-based ILs). The EDL containing

ILs cation with intermediate concentration exhibits a large gradient in electric field strength, which can stabilize polarized intermediates such as $^*\text{COOH}$ (Figure 3b).^[10] Fourthly, the ionic nature of ILs delivers an electrostatic stabilization effect toward ionic species via Coulomb interactions. The typical interaction between 1-butyl-3-methylimidazolium cation ([BMIm]⁺) and the CO_2 radical anion significantly reduced the onset potential of CRR. Fifth, the hydrophobic local environ-

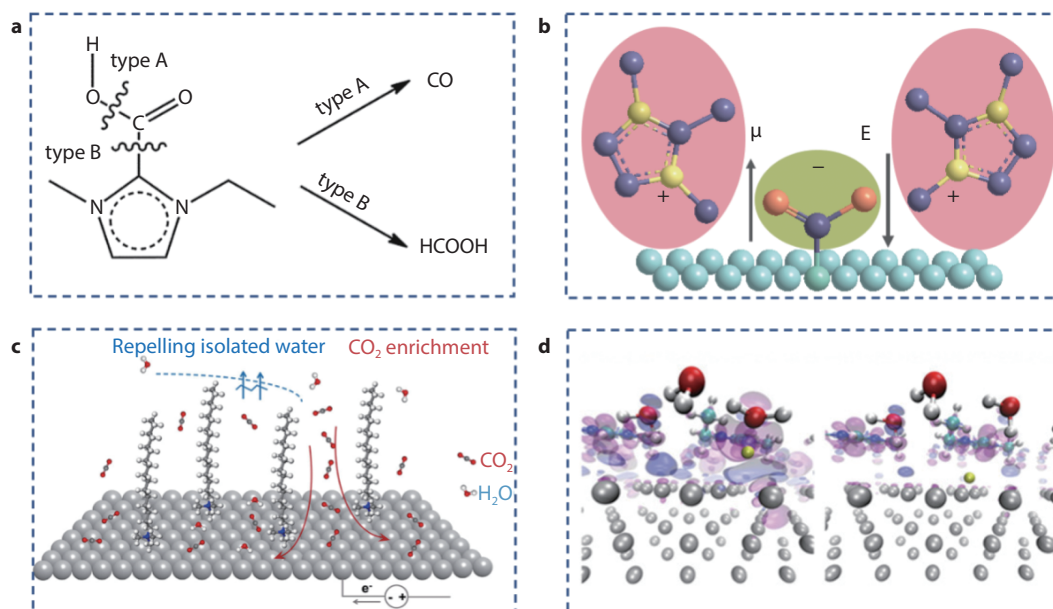


Fig. 3 **a** Covalent interaction between [EMIm] and intermediate $^*\text{COOH}$.^[29] Copyright 2015, RSC Publisher. **b** Stabilization of $\text{CO}_2^{\bullet-}$ by field-dipole interaction. **c** Configuration of CTAB at the electrified electrode–electrolyte interface.^[30] Copyright 2022, American Chemical Society. **d** Charge density isosurfaces for transition, and final states of the Volmer reaction on bare [EMIM]⁺-covered (bottom row) Ag(111). Magenta part represents an isosurface with a ρ value of $0.001 \text{ e } \text{\AA}^{-3}$ and blue corresponds to a ρ value of $-0.001 \text{ e } \text{\AA}^{-3}$. The yellow one is the H atom being transferred along the reaction path.^[31] Copyright 2017, American Chemical Society.

ment of ILs with long alkyl chains can repel the transfer of proton suppliers to catalyst surfaces, thereby suppressing the HER (Figure 3c).^[30] Meanwhile, the interfacial enriched cations can cause electrostatic repulsion with H^+ or H_3O^+ , decreasing the intrinsic activity of HER through thermodynamic control (Figure 3d).^[31]

Based on the preceding discussions, we propose some personal interpretations for the causes of the low selectivity towards C_{2+} in IL-based systems.

i) The primary factor is the low *CO coverage on the catalyst surface. This is because the high concentration of CO_2 in IL-based electrolytes results in most of the active sites being occupied by adsorbed CO_2 , leaving insufficient room for CO adsorption and making it challenging to achieve steady-state adsorption of CO in the IL electrolyte.

ii) The second factor is the limited proton accessibility in IL systems. To suppress HER, only a small amount of added water or H_3O^+ transferred from the anode part can act as a proton source. Furthermore, the density of H_2O molecules at the interface is lower than that of an aqueous electrolyte due to the local enrichment of ILs cations in the EDL. As a result, the limited proton formation and transfer do not meet the requirements for the production of C_{2+} involving multiple successive protonation steps.

iii) Finally, the specifically stabilizing effect of ILs on CO_2 reduction intermediates should not be overlooked. The covalent and non-covalent stabilization effects of ILs both rely on the structure of intermediates, such as the orientation of the dipole, the value of the dipole moment, and the polarizability. Almost all reported non-functional ILs only displayed a stabilization effect toward *COOH intermediate.^[32] Taking the field-dipole effect as an example, the structure-induced interfacial electric field stabilizes the *COOH by inducing intense electron polarization.^[10] While for *CO , neither the formation of the alternating solvation shell structure nor significant electron polarization is observed for catalyst surface with adsorbed CO . Although such specific stabilization for *COOH benefits CO formation, it is hard to achieve steady-state adsorption of *CO and maintain a high *CO coverage for further C-C formation or reduction to *CHO .

Strategies for improving C_{2+} products selectivity in ILs-based system

Electrolyte modulation

The electrolyte typically consists of ILs, proton donors, and other additives, and their types and concentrations can impact the apparent catalytic performance. Fortunately, ILs can be meticulously designed using sophisticated organic synthesis techniques. In order to optimize the efficiency of CO_2 -to- C_{2+} conversion, it is necessary to develop task-specific ILs system that can replace the commonly studied but non-functional ILs.^[33–35]

As shown in Figure 5a, the energy of intermediates over Cu (111) substrate is given as a function of field strength which corresponds to the following equation: $\Delta E = \mu\epsilon - \frac{1}{2}\alpha\epsilon^2 + \dots$. Here, μ is the dipole moment and α represents the polarizability, while ϵ denotes the electric field. The energy of the CO^* intermediate only slightly increases mildly with the increas-

ing of electric field strength, while that of *OCCO and *OCHO raised abruptly, which indicates that the stabilization effect of CO^* is much weaker than that of *CO_2 , *OCCO , and *OCCO (Figure 4a).^[36] Therefore, the first concern is improving the stabilizing ability of ILs toward *CO . Functional ILs interacting with *CO or increasing local CO concentration are applicable for improving C_{2+} selectivity. One potential candidate is ILs with carbanion, which affords a C-site for chemical interaction with CO , thereby delivering a superior CO solubility of up to $0.046 \text{ mol mol}^{-1}$ than traditional ILs such as BMIM-NTf₂ which could only capture $2 \times 10^{-3} \text{ mol CO}_2$ per IL with higher interaction energies (Figure 4b). Additionally, the recycling stability of these carbanion-functionalized ILs has been proved, and the captured CO is expected to be reactive for further conversion. Moreover, ILs with functional moieties, like amino groups, may provide the capping effect of stabilizing more Cu (1 0 0) for *CO adsorption and promoting the C-C coupling process (Figure 4c).^[37] Thus, the Cu/GDL exhibits higher selectivity of 61.39% towards C_2 (C_2H_4 and C_2H_5OH) by modifying amino-ionic liquids. Moreover, Dmitry et al. highlighted that substitution effects, charge delocalization, and availability are essential descriptors in determining the co-catalytic activity of ILs, which should be taken into account when designing novel functional ILs with optimized CO stabilization effects.^[32]

The synthesis of C_{2+} chemicals via multiple proton-involved reaction pathways necessitates efficient dissociation of proton sources and subsequent proton transfer. Currently, increasing the mass ratio of water in IL electrolytes is the most effective method for enriching the supply of protons.^[40] Nevertheless, the competing HER is activated with an increase in the amount of water.^[41] A wide range of proton donors like acid, phenol, or even protic ILs should be explored as promising alternatives to water in nonaqueous systems.^[42–44] The potential proton shuttling effect of ILs with aromatic N-heterocycles moieties, such as pyridine and imidazole, also should be considered. Based on the triple points model in a Pourbaix diagram, which considers the correlation between pK_a , pH, and applied potentials of CRR, it is possible to predict which ILs would facilitate proton transformation (Figure 4d).^[39]

It was anticipated that the electric field created by cations would stabilize not only *CO_2 but also those intermediate species such as *OCCO and *OCCO , which are subsequently reduced. Introducing electrolyte additives, specifically ionic compounds, can alter the microstructure of EDL, which in turn adjusts the electric field strength for stabilizing specific intermediates. In aqueous media, alkali cations have been shown to modulate the distribution of electric field in the EDL, impeding hydrogen evolution by hindering the migration of protons in the diffuse layer and improving selectivity for multicarbon products by promoting the stabilization of large dipole *OCCO intermediates.^[36,45–46] Among various alkali cations, Cs^+ has been found to exhibit the strongest dipole moment for interacting with *CO , *OCCO , and *OCCO , leading to the highest C_{2+} selectivity of 69.0%.^[9] This strategy can be extended to the IL system. Inorganic salt Lil has also been shown to have a similar effect by promoting acetic acid production in [EMIM]BF₄-water electrolyte, confirming the crucial role of inorganic promoters in the dimerization step. In

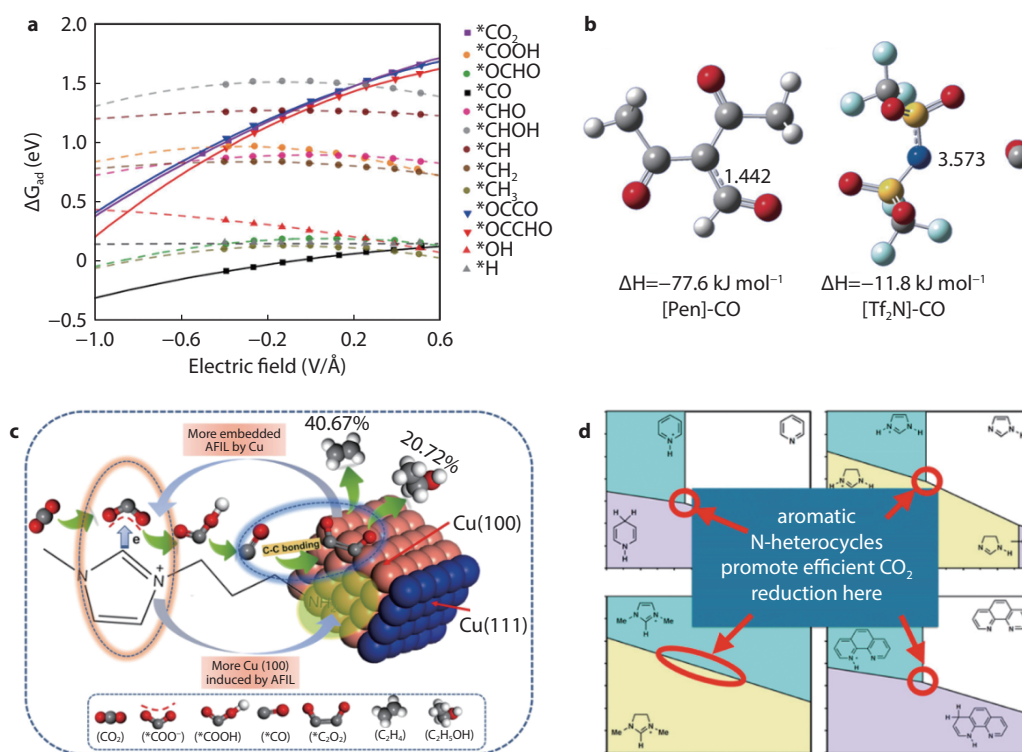


Fig. 4 **a** Field effect on various intermediates for CRR.^[36] Copyright 2017, American Chemical Society. **b** Optimized structures of [Pen]-CO and [Tf₂N]-CO.^[38] Copyright 2017, Wiley-VCH. **c** Scheme for the synergistic effect between Cu and AFIL on the possible pathway during the CRR to C₂.^[37] Copyright 2022, Elsevier Ltd. **d** Molecular Pourbaix diagrams for aromatic N-heterocycles.^[39] Copyright 2015, American Chemical Society.

addition to alkali cations, halide anions have also been investigated as an effective additive since they can restructure the catalyst and enhance the selectivity of C₂₊ products.^[47]

Electrocatalyst designing

Designing a competent cathode catalyst is imperative to achieve a sufficient CO₂ reaction rate and to attain excellent selectivity of the desired products. The influence of the microstructure of Cu-based catalysts has been well-established in aqueous electrolyte. Surface facet engineering, alloying, het-

eroatom doping, and nanostructuring have been demonstrated to achieve faradaic efficiency of C₂₊ products over 80.0%. However, most of the Cu-based catalysts reported in the ILs-based system exhibited inferior C₂₊ selectivity compared to those in the aqueous system due to the distinct interfacial microenvironment (Table 1).^[18, 48 - 53] Hence, further research efforts are needed to develop novel electrocatalysts and understand the relationship between the catalyst structure and electrochemical performance.

Table 1. CO₂ electroreduction system of Cu-based catalysts in ILs-based electrolytes.

Catalyst	Electrolyte	Main product	Faradaic efficiency (%)	Current density (mA cm ⁻²)	References
Cu porous dendrites	[EMIM](BF ₄)/H ₂ O	HCOOH	87	6.5	[48]
Cu-MOF	[BMIM]BF ₄ /MeCN/H ₂ O	HCOOH	98.2	102.1	[49]
Cu-PBA-2.2	[BMIM]BF ₄ /H ₂ O/MgCl ₂	HCOOH	93.1	4.5	[50]
Cu _{1.63} Se _{1/3}	[BMIM]PF ₆ /MeCN/H ₂ O	CH ₃ OH	77.6	41.5	[51]
Pd ₆₇ Cu ₃₃	[BMIM]BF ₄ /H ₂ O	CH ₃ OH	80	31.8	[52]
Ag ₂ S-Cu ₂ O/Cu	[BMIM]BF ₄ /H ₂ O	CH ₃ OH	67.4	122.7	[18]
Cu/BN-C	[EMIM]BF ₄ -LiI-water	H ₂ C ₂ O ₄	80.3	13.9	[53]

Identifying an appropriate activity descriptor is a practical way to screen effective catalysts. Various descriptors have been proposed over the past decades to correlate the physical properties of catalysts with C₂₊ selectivity. These descriptors include the adsorption energies of competed intermediates, the surface coordination number and d-band center.^[54-56] A volcano relationship has been established between *CO binding energy and overpotential of CRR, and the binding energy of *CO and *H separates Cu from other metals into the beyond CO group (Figure 5a).^[57] The *CH₃O

and *CH₂OH intermediate binding energy have also been investigated to differentiate between hydrocarbon and alcohol generation (Figure 5b). The variation of surface coordination number of catalysts can modify the adsorption geometry for the intermediate and determine its bonding strength on the active site. There is a linear scaling relationship between the surface coordination number of Cu and the binding energy of *CO, *CHO, and *CH₂O intermediates (Figure 5c).^[58] Additionally, the position of d-band center determines the interaction between adsorbents and catalyst, making it an effective pre-

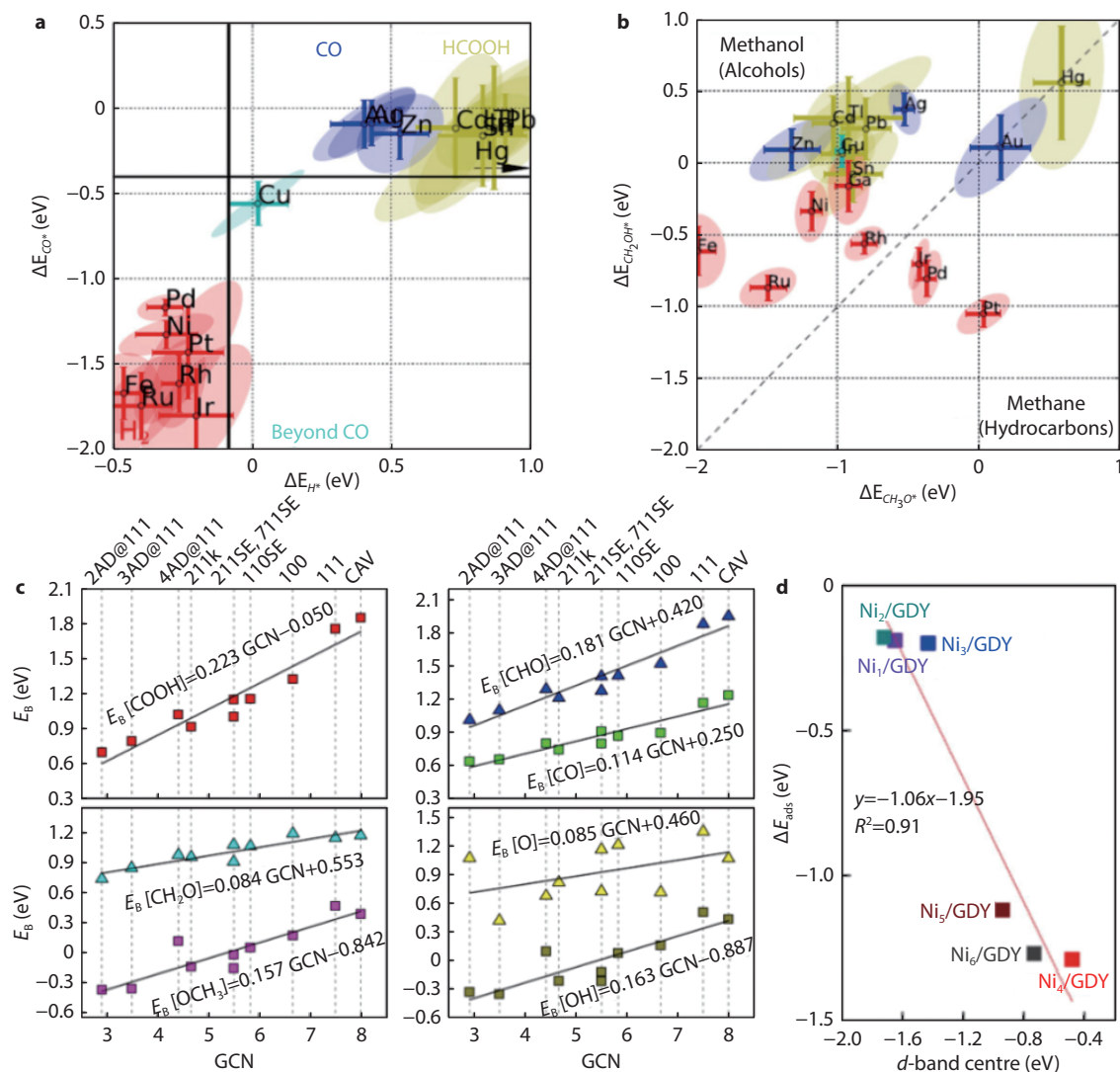


Fig. 5 Binding energies of **a** *CO and *H and **b** *CH₂OH and *CH₃O of various metals.^[57] Copyright 2017, Wiley-VCH. **c** The linear scaling relations between generalized coordination number (GCN) and binding energy of intermediates.^[58] Copyright 2016, American Chemical Society. **d** The variation of CO₂ adsorption energy with d-band center.^[59] Copyright 2022, Elsevier B.V. and Science Press.

dictor of electrochemical activity. For instance, Figure 5d demonstrates a strong linear relationship between the d band center of the Ni-based catalyst and the CO₂ adsorption energy. The interaction between the catalyst and CO₂ becomes stronger as the position of d-band center approaches the Fermi level.^[59] Nevertheless, these descriptors were mainly proposed in aqueous media. These descriptors enriched ILS cations under the applied bias or specific adsorbed ILS on the catalyst surface can change the adsorption strength of reaction intermediates, making the CRR activity different from that in aqueous electrolyte. For example, metallic Cu is thought to have the modest adsorption strength of *CO which drives its further reduction or dimerization. But in ILS-based electrolyte, the target product is mainly C₁ chemicals for Cu-based catalysts. We speculated that the adsorption strength of *CO is not strong enough to meet the C-C coupling. Developing a catalyst with stronger bonding ability towards CO is therefore necessary. Fe sites showed too stronger *CO adsorption to prevent the desorption of *CO, limiting the

kinetic rate for CO₂RR in aqueous system particularly under high overpotential. But in [Bmim]PF₆/MeCN/H₂O electrolyte, nitrogen-doped Fe₂O₃ gave C₂H₆ as the prominent C₂⁺ product, with an FE of 42% and current density of 32 mA cm⁻² at -2.0 V vs. Ag/Ag⁺.^[60]

Electrocatalysts are capable of undergoing an in situ reconstruction process during electrochemical reactions, which is mainly driven by variations in the applied bias and the local microenvironment. This process can lead to the formation of new active phase with higher intrinsic activity. This dynamic evolution phenomena have been observed in a wide range of materials, including metal alloys, metal oxides/phosphides/nitrides/borides, and metal-organic frameworks. In an ILS electrolyte, the potential structure variation of ILS, such as electrochemical reduction of cation and hydrolysis of anion, can generate different radicals that may interact with the reactive species on the catalysts. As a result, ILS can guide the reconstruction process of electrocatalyst, and even activate intrinsic inert materials like commercial carbon materials. Thus, un-

understanding the effect of the ILs structure on in situ structure variation of electrocatalysts is pregnant for constructing highly active catalyst toward the transformation of CO₂ into multicarbon products through a simple self-activation route.

Constructing catalyst/ILs hybrid is a promising approach to achieve highly efficient electrocatalyst for CO₂-to-C₂₊ conversion. This strategy has the potential to reduce the amount of ILs required and allows for the modification of the electronic properties of the catalyst. To illustrate, Sha and colleagues improved the selectivity of C₂H₄ by immobilizing [BMIM]NO₃ on a Cu electrocatalyst (Figure 6a and 6b).^[16] The catalysts are dispersed in the solution of ILs by continuous stirring and then the mixed catalysts can be obtained by centrifugation. The theoretical models of the IL@Cu and pure Cu was constructed for calculating *CO dimerization and *OCCO formation energies. Their results demonstrated that the strong interaction between nitrate groups of ILs and Cu atoms induces the electron transferring to [BMIM]NO₃, which reduced the energy barriers for *CO dimerization and achieved a maximum C₂H₄ faradaic efficiency of 77.3%. Additionally, poly(ionic liquids) have been used as catalyst modifiers to boost C₂₊ selectivity (Figure 6c). The Cu@PIL hybrids were obtained by adding Cu NPs in situ to a solution of IL monomer, cross linking reactants and initiators for polymerization. By adjusting the anion structure of PIL, a C₂H₄ selectivity of 29.0% was obtained with a high current density of 381 mA cm⁻² (Figure 6d), owing to the strong stabilization ability of Cl⁻ towards *CO, which promotes the C-C coupling process.^[61] According to the previous studies, the role of ILs in catalyst/ILs hybrid system can be summarized as follows. Firstly, the high CO₂ absorption ability of ionic liquids could enrich the CO₂ concentration in the vicinity of active sites for CRR and afford a moderate local CO₂ concentration which is beneficial for the C-C coupling process. Secondly, the cations of ILs, especially imidazolium cations, are supposed to stabilize the key intermediates, reducing the corresponding energy barriers

and accelerating the reaction rates. Lastly, the chemical environment and electric contribution around the active sites can be optimized via the interaction between ILs and catalysts, which can also reduce the energy barriers for rate-determining step of producing multicarbon like CO* dimerization.

Mechanism investigation

The CO₂-to-C₂₊ conversion involves a series of electron-proton transfer steps and multiple competing reaction routes, posing a significant challenge in elucidating the underlying reaction mechanisms. The complexity of the reaction is further amplified with the introduction of ILs, and most researchers still rely on the mechanisms proposed in aqueous media to explain the variations in electrochemical performance.^[18,51,62] Despite this, some attempts have been made to gain insight into the CRR mechanism in ILs systems by in situ spectroscopy techniques, which collect molecular information of solid-liquid interface. The formation of intermediate CO₂-Im IL complex and [BMIM]-2-carboxylic acid species have been confirmed using in situ sum-frequency generation spectroscopy and in operando Raman spectroscopy, respectively.^[28,63] Other techniques, such as in-situ surface-enhanced infrared absorption spectroscopy, have been used to track potential-dependent carboxylate radicals. However, some key issues must be resolved to clarify the C₂₊ formation routes in IL systems.

One primary concern pertains to comprehending the molecular-level intricacies of the EDL containing ILs cations. This is crucial since the complicated entangled structure, and electrostatic properties of ILs may render the EDL significantly different from that of aqueous systems. In this context, the type of anion also should be considered, particularly for those with specific adsorption ability on the catalyst surface. Additionally, uncovering the dynamic evolution of the ILs within the EDL under electric fields would help to acquire the interaction modes between ILs and catalyst surface adsorbed species

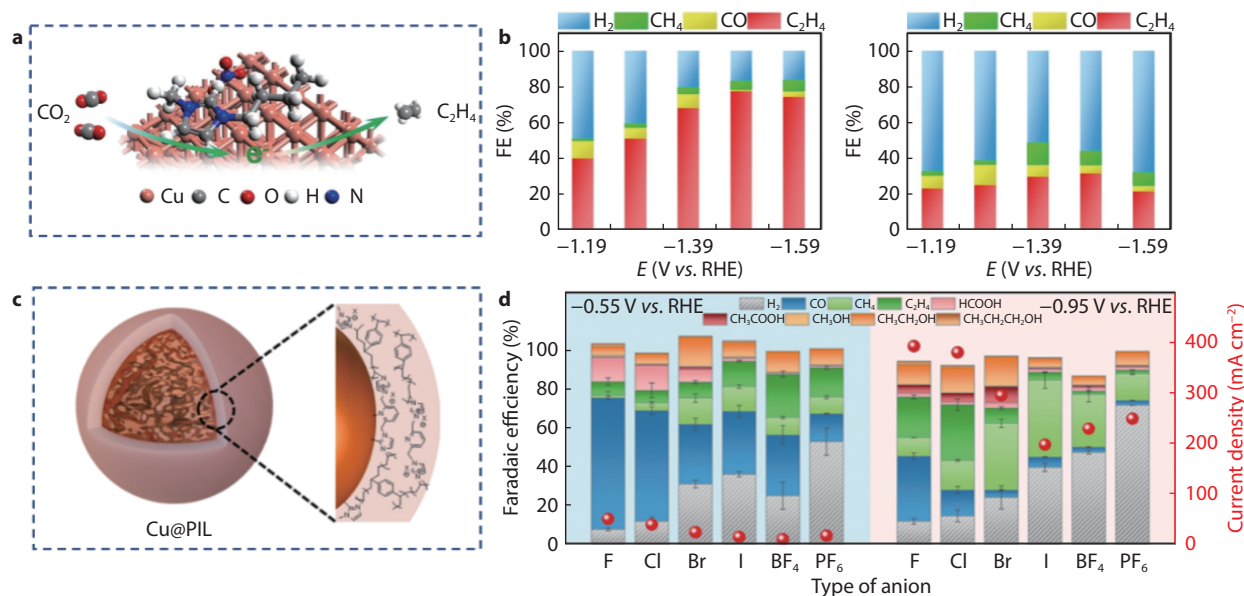


Fig. 6 a The model and b Faradaic efficiency of Cu and BMIMNO₃@Cu.^[61] Copyright 2021, Elsevier B.V. c The model and d Faradaic efficiency of Cu@PIL-X-1.2 with different anions.^[16] Copyright 2022, Elsevier Ltd.

cies, especially for *CO, *COH, and *CHO.

It is also essential to pay attention to the structure of the bulk phase of electrolytes. In aqueous electrolytes, the hydrogen-bond network governs the intermolecular interactions. While for the IL system, the interactions between ILs and solvent molecules (H₂O or other organic solvents) will change the mass transfer kinetics of CO₂ and proton sources. Consequently, this modifies the surface coverage of *CO and the protonation steps of CRR.

Conclusions

Ionic liquids (ILs) have demonstrated a great potential for promoting electrochemical CO₂-to-C₁ conversion by reducing overpotential and increasing faradaic efficiency. However, the generation of high-value C₂₊ chemicals still pose many challenges. Our analysis disclosed that the low selectivity for C₂₊ products is mainly rooted in insufficient *CO coverage, limited proton accessibility, and the specific stabilization effect of conventional ILs. To overcome these issues, significant efforts are required to modulate the electrolyte, design the electrocatalyst, and understand the mechanisms in the presence of ILs. So in our perspectives we proposed several strategies to provide directions for converting CO₂ to value-added C₂₊ chemicals, as outlined below:

i) Modulating the electrolyte by designing task-specific ILs with high CO capture abilities, screening efficient proton donors other than water, and introducing inorganic additives.

ii) Constructing reasonable descriptors that consider the adsorbed interface with ILs molecule and exploring other novel catalyst systems that involve the reconstruction of electrodes or the hybridization of catalyst and ILs.

iii) Conducting in situ investigations to probe the molecular microstructure of the electrode/ILs interface and the bulk phase of electrolyte, which will help to identify the interaction modes between reaction intermediates, solvent molecules, and ILs.

ACKNOWLEDGMENTS

This work was financially supported by the Intergovernmental International Science and Technology Innovation Cooperation Program of the National Key Research and Development Program (Grant No. 2022YFE0120200), the National Natural Science Foundation of China (Grant No. 21872046, 52072118, and 52102041), the Jiebang Guashuai Project of Hunan Province (Grant No. 2021GK1110), the Research and Development Plan of Key Areas in Hunan Province (Grant No. 2019GK2235), and the Natural Science Foundation of Hunan Province (Grant No. 2020JJ4174, 2022JJ40073).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

M. Y. Dai and Prof. S. G. Zhang initiated the project. Prof. Y. Zhang collected data and proposed the outline of the paper. M. Y. Dai and Dr. W. P. Ni wrote the manuscript together with

Prof. S. G. Zhang. All authors had approved the final version.

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Biographies

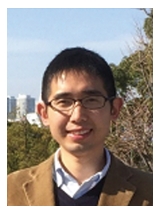


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