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Novel insights into CO₂ electroreduction in ionic liquids: CO₂ activation and selectivity tailored by ionic microhabitat

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Abstract: Electroreduction of carbon dioxide (CO₂) into high value added products is a potential solution to the CO₂ deduction and utilization. One major challenge is lacking of efficient system that can highly selectively reduce CO₂ to desirable products with low energy consumption. Ionic liquids (ILs) have been used as electrolytes for the electroreduction of CO₂, and it was proved CO₂-cation complex results in a low energy pathway. In this work, we build an ionic microhabitat (IMH) for CO₂ electroreduction, and designed a novel anion-functionalized IL [Bmim][124Triz] as reaction medium. The results showed that the IMH plays a key role in enhancing the performance of CO2 electroreduction, especially in dominating the product selectivity which is recognized as a great challenge in an electroreduction process. New insights into the role of IMH in higher CO₂ solubility, bending the linear CO₂ by forming [124Triz]-CO₂⁻ adduct, and transferring the activated CO₂ to the cathode surface easily, were revealed. The Faradaic efficiency for formic acid is as high as 95.2% with current density reached 24.5 mA cm⁻², this work will provide a promising way for designing robust and highly efficient ILs for CO₂ electroreduction.

The large amount emission of carbon dioxide (CO2) has raised serious environmental and social issues in the last hundred years.^[1] On the other hand, as one of the most abundant and cheap C1 resources, converting CO₂ to useful chemicals with the geographical, seasonal and intermittent energy (e.g., tied, wind, and solar) is an attractive solution to the global warming problems and energy crisis.^[2] Thus, works were emphasized towards the plentv of electrochemical conversion of CO₂ owing to its mild reaction conditions and easy implementation for practical applications.^[3] However, nearly all reduction systems investigated far still face great challenges, such as high reaction overpotential and low current density, especially the poor product selectivity. Hence, efforts are in great need to develop efficient reaction systems, which obtain both the fast reaction rate and high selectivity of CO₂ electroreduction.

Electrolytes undertake a crucial role in CO_2 dissolution, and a considerable amount of CO_2 in the electrolyte will

accelerate the electrochemical conversion efficiently. The CO₂ solubility in water is only 0.033 mol L⁻¹ under ambient conditions (298 K, 0.1 MPa). For CO₂ reduction in aqueous solution, it is crucial to suppress the hydrogen evolution reaction (HER), which is typically kinetically favored over CO₂ reduction reaction (CO₂RR). Furthermore, reducing CO₂ to fuel precursors (such as CO) or liquid chemicals at low overpotential, is a significant challenge due to the incredible stable structure of CO₂ molecule. Hence, tremendous energy is demanded to restructure the linear molecule to the non-linear [-CO₂]⁻ anion, which occurs at a very negative potential, that is, -1.9 V vs. NHE.^[4]

As a novel type of liquid salts, ILs consisting of cations and anions solely exhibit excellent CO₂ solubility,^[5] especially by functionalized ILs, such as amino-,[6] acetate-,[7] azolate-,[8] pyridine-,^[9] and amino acid-based ILs.^[10] Besides the reports on the ILs for CO₂ capture, ILs have also been used as electrolytes for CO2 electroreduction in recent years.[3d, 5e, 11] Their unique physicochemical properties, such as high intrinsic ionic conductivity and wide electrochemical potential windows,^[12] as well as high solubility of CO₂, are beneficial for CO₂RR.^[13] Previous report^[14] on CO₂ electro-reduction in an aqueous 1-ethyl-3-ethylimidazolium tetrafluoroborate ([Emim][BF₄]) solution with Ag as cathode, demonstrated that the overpotential for CO formation was decreased by 600 mV. This means that the imidazolium carboxylate complex can stabilize [·CO₂]⁻ radical anion and restrain their approaching, consequently, inhibit their dimerization to form oxalate, and lead to a low energy pathway for CO₂ reduction. Subsequently, the effects and mechanism for CO₂ reduction with the aid of conventional and functionalized ILs have been studied extensively.^[11b, 15] For instance, commercialized Pb and Sn electrodes were used to reduce CO2 into formic acid (HCOOH) in ILs/acetonitrile (MeCN)/H₂O ternary mixture along with high current densities (i.e., 37 and 32 mA cm⁻²),^[16] but these results were obtained only at very negative potentials. Recently, a high Faradaic efficiency for HCOOH on Ag electrode is acquired at low overpotential using functionalized phosphonium ILs,^[17] but the current density is less than 1 mA cm⁻². Additionally, previous research indicated an ambiguous role of the anions on CO2 electroreduction.^[18] The reduction of CO₂ at low overpotential with both high current density and Faradaic efficiency is a longstanding challenge.

In this work, we present an efficient CO₂ electroreduction microhabitat (Figure 1) based on a novel superbase IL 1-butyl-3-methylimidazolium 1,2,4-triazolide ([Bmim][124Triz]), and compared with other systems containing imidazolium ILs with different anions^[8]. The IMH

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provides an efficient environment for CO2 dissolve, activation and reduction. High efficiency of CO2 capture and conversion is achieved via an ionic microhabitat (IMH) in the novel IL reaction system, which means the nanoscale aggregates and chemical interaction in the ion of [124Triz]-CO2- result in a superior solubility of CO2 under ambient conditions. More notably, it shows that the stable CO₂ molecule is changed to a bent form (O-C-O bond angle of 136°) with a net negative charge (0.546 e) in the [124Triz]-CO₂ ion. As a result, it is expected to be favorable for CO_2 activation and $[\cdot CO_2]^$ stabilization. In addition, the IMH provides a facile route for the transferring of the activated CO_2^- to the cathode surface, which hence improves the current density and Faradaic efficiency of CO₂ electroreduction. Thus, the experimental results demonstrated that the superbase IL offers a low energy and high selective pathway for CO₂ electroconversion through an IMH.



Figure 1. Schematic representation of CO_2 electroreduction with the assistance of novel superbase IL [Bmim][124Triz].

The anion-functionalized superbase IL [Bmim][124Triz] was synthesized by neutralization of 1,2,4-triazole with a solution of 1-butyl-3-methylimidazolium hydroxide, which was acquired by the anion-exchange method.^[19] The absorption experiment of CO₂ was carried out by the apparatus shown in Supplementary Scheme 1, and the mole ratio of dissolved CO₂ in IL [Bmim][124Triz] was plotted in Figure S2. 0.726 mol CO₂ per mol IL was achieved at 298 K under ambient pressure. Previous reports indicated that the sufficient CO₂ in electrolytes will render the electrochemical conversion of CO₂ efficient.^[11a] In our work, we found that the solubility of CO₂ in the superbase IL is nearly 45 times higher than that in the conventional IL 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]).

We conducted the electrolysis experiments in a typical three-electrode system at 298 K and 0.1 MPa (See Supplementary Figure 3). The CO₂ reduction performance in ILs was examined by sweeping the applied voltage at a scan rate of 50 mV s⁻¹ from -1.0 V to -2.4 V versus Ag/Ag⁺ electrode. Firstly, the cyclic voltammetry (CV) results acquired in IL solutions which were saturated with N₂ (See

Supplementary Figure 4), and the results are consistent with previous reports of CV curves by using metal electrodes in dialkylimidazolium based ILs. Only small capacitive currents were observed in a wide potential window, and no additional reduction features associated with the reduction of the solvent or ILs were found in the cathodic CV range.

Pb was chosen to evaluate the influence of the anion on the catalytic activity of imidazolium-based ILs for CO₂ reduction to HCOOH (Figure 2). In agreement with previous reports, the potential that results in a current density of a 0.6 mA cm⁻² was selected as the onset potential for CO₂ reduction.^[20] As shown in Figure 2, the reduction current from circa -1.4 V to -1.8 V range was attributed to the reduction of H₂O to H₂, which is similar to a previous report.^[17] The cathodic feature from -1.78 V is related to the CO₂ reduction to HCOOH, which was validated by ¹H NMR quantification, and we found that in the potential range of CO₂ reduction, the reduction of water was suppressed to a large extent. Similar with the conventional ILs, the CV curves profiles in CO₂ purged aqueous of superbase IL, no new CV peaks were observed. However, compared with the conventional ILs, the onset potential of the CO₂ purged aqueous of [Bmim][124Triz] solution shifted anodically from -1.97 to -1.78 V (vs Ag/Ag⁺), which indicated that the reduction potential of carbon species was decreased significantly, and this positive effect of [Bmim][124Triz] on lowering the overpotential was ascribed to the formation of [124Triz]-CO2ion.



Figure 2. CV traces on Pb electrode in various CO₂-saturated electrolytes containing ILs in MeCN-H₂O (5 wt%) solution.

The effect of [Bmim][124Triz] content in the electrolyte on CO₂ reduction was investigated by using Pb electrode, and the CV traces were illustrated in Figure S4. The CV results showed that the polarization curves for CO₂ reduction were shifted slightly to more positive potentials with the increase of the [Bmim][124Triz] content in the MeCN-H₂O system, and the increased current densities were observed as a more negative potential was applied. Furthermore, we also investigated the effect of [Bmim][124Triz] content on Faradaic efficiency of the reduction products on Pb electrode

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at different applied potentials. In all cases, CO and H₂ were the only gas products formed on the cathode and O₂ on the anode, and HCOOH was the only liquid product. Other gaseous or liquid products may have been present at concentrations below the gas chromatography (GC) and ¹H-NMR detection limit. At a low IL content, the CV results demonstrated that the partial current density of CO increased dramatically with the IL content rising, yet the highest current density and Faradaic efficiency for HCOOH was obtained at the IL content of 700 mM in the MeCN-H₂O (5 wt%) mixture. Given this, the possible reason is that the intensive electrostatic attraction between anion and cation of the IL, which impedes the motion of the ions and slows down the charge transfer to the reaction species. Hence, the dominant products were switched to hydrogen in the reaction system.

The Faradaic efficiency of the major products from CO₂ electroreduction was measured by different ILs as the electrolytes, and controlled trials were carried out on Pb (Figure 3) electrode at an applied potential of -2.2 V (vs. Ag/Ag⁺) for 2 hours. Generally, high HCOOH selectivity was obtained in most IL systems, and the Faradaic efficiencies order of [Bmim][124Triz] > 1-butyl-3follow the methylimidazolium hexafluorophosphat ([Bmim][PF₆]) > [Bmim][BF₄] > 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][Tf₂N]) > 1-butyl-3methylimidazolium nitrate ([Bmim][NO₃]). Therein, we found that the anion plays a significant role in the observed catalytic selectivity, and the anion without fluorine, such as [Bmim][NO₃], yielded much lower Faradaic efficiency for HCOOH formation, while in [Bmim][124Triz] IL system, it exhibited the highest Faradaic efficiency of 95.2% (Figure 3b) and the current density reached as high as 24.5 mA cm⁻² (Figure 3a). This results indicate that the anion plays an important role in dominating the electrochemical reduction of CO₂ to HCOOH, and the reason may be attributed to the interaction differences between CO₂ and anions of ILs.

To investigate the durability of [Bmim][124Triz] under long-term bulk electrolysis conditions, the current density was measured as a function of time with different applied voltages (vs. Ag/Ag⁺). With no water in IL/MeCN, the current densities remained relatively constant in the beginning (Figure 3c). However, when the electrolysis proceeded further, the current densities fell rapidly, probably due to the [Bmim]⁺ species were consumed in the course of the bulk electrolysis (See Supplementary Scheme 1). Yet, when adding water to [Bmim][124Triz]/MeCN, the catalytic activity of [Bmim][124Triz]/MeCN-H2O (5 wt%) systems remained constant during all electrolysis period (Figure 3d), indicating that the inactive form of carbene was regenerated when a small amount water was present. Otherwise, carbene, the reduced species from imidazolium cation, can form an inactive complex with CO2,[18a] and then the catalytic action of imidazole ILs on CO2 electroreduction was deactivated significantly.



Figure 3. CO_2 electroreduction performances. (a) Partial current of HCOOH on Pb electrode, (b) Corresponding Faradaic efficiency for HCOOH, CO and H₂ in ILs/MeCN-H₂O (5 wt%), (c) Dependence of current density over time on Pb electrode at different applied potentials (vs Ag/Ag⁺) without and with water (d).

The mechanism of CO₂ reduction in [Bmim][124Triz] based reaction system can be described as follows in Equation 1 ~ 8 (See Scheme 1). All species involved CO₂ reduction were assumed to be adsorbed on the cathode surface. The clear evidences confirmed that the imidazolium cations as the electrode materials also play a dominant role in CO₂ electroreduction.^[21] The presented scheme is analogous to that proposed by Nakamura et al. according to the theoretical calculations.^[22] In the light of this reaction mechanism, imidazolium cations are reduced to neutral radicals, which in turn transfer the electrons to CO₂ and form a complex which can stabilize [.CO2] and prevent their dimerization to form oxalate. However, contrast to the conventional ILs, the overpotential of CO₂ reduction to HCOOH is lower in [Bmim][124Triz] solution, and the positive effect on lowering the overpotential is ascribed to the strong interaction between the anion of the IL and CO2. This mentioned catalytic mechanism reveals that the formation of carbene from the reduction of imidazolium leads to a rapid attenuation of current density during potentiostatic electrolysis. While, the inactive species can be reactivated when adding water into the system. Furthermore, the [124Triz]⁻ anion helps to maintain a high CO₂ content in electrolyte and transport CO₂ to the catalyst surface quickly, resulting in a superior performance for CO₂ electrochemical reduction to HCOOH.

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Chemically bound	
CO_2 + $[124Triz]$ $[Bmim]^+$ \longrightarrow $[124TrizCO_2]$ $[Bmim]^+$	(1)
$[124\text{TrizCO}_2] + 2\text{H}^+ + 2\text{e} \longrightarrow \text{HCOOH} + [124\text{Triz}]$	(2)
Physically bound	







$$H_{3}C_{N} \swarrow N \xrightarrow{C_{4}H_{9}} + H^{+} + e^{-} \longrightarrow H_{3}C_{N} \swarrow N \xrightarrow{C_{4}H_{9}} + HCOOH$$
(6)

Deactivation pathway:



Reactivation pathway:

 $H_{3}C_{N} \stackrel{\sim}{\longrightarrow} N \stackrel{C_{4}H_{9}}{\longrightarrow} + H^{+} \stackrel{H^{+}}{\longrightarrow} H_{3}C_{N} \stackrel{H}{\longrightarrow} N \stackrel{C_{4}H_{9}}{\longrightarrow} (with water) (8)$

Scheme 1. The possible pathways for CO_2 conversion into HCOOH with the help of [Bmim][124Triz].

Additionally, Quantum Chemical calculations were performed to evaluate the interaction between the anions and CO₂ (Table 1), and the lowest energy structures of the intermediates were shown in Figure S9-S13. A strong interaction with a high ΔE value (-206.5 kJ/mol) between [124Triz]⁻ and CO₂ is found, and the N···C bond length of 1.56 Å is approximate to that in the triazole ring of the anion (1.36 Å) (See supplementary Figure 9), resulting in a predictable bent CO₂ molecular with O-C-O bond angle of 136°. The calculation results indicate a rehybridization of CO₂ is from sp to nearly sp² character, and bond angle change to percentage π character of a hybridized orbital based on the Pauling correlation. In addition, the Gaussian calculation results for [124Triz]-CO2 complex species suggested that the CO₂ molecule in the complex is 75% sp² hybridized, retaining 25% of its sp character only. The carbon hybridization of CO2 in the complex is close to that in HCOOH, which will possibly facilitate the formation of HCOOH.



Table 1. Structure parameters for various species associated with the reduction of CO₂, calculated using the B3LYP/6-31++G (d,p) theoretical level.

species	CO ₂	∆ <i>E</i> (kJ/m	<0-C-
	Solubility ^[a]	ol) ^[b]	O(deg.) ^[b]
[NO ₃] ⁻ CO ₂	~0.1 ^[5e]	-37.14	172
[BF₄] ⁻ ····CO₂	0.0161 ^[5e]	-28.98	174
[Tf ₂ N] ⁻ ····CO ₂	0.0168 ^[5e]	-29.23	176
[PF ₆] ⁻ CO ₂	0.0308 ^[5e]	-24.79	175
[124Triz] ⁻ CO ₂	0.726	-206.5	136
[124Triz] ⁻ ····HCOOH		-274.1	126

^[a] The absorption was carried out at 298 K and 0.1 MPa in aqueous solution of ILs (mol CO₂ per mol IL). ^[b] These values represent a gasphase calculation using the B3LYP/6-31++G(d,p) basis set with no solvation model.

Furthermore, Natural Population analysis (NPA) was carried out to ascertain the change of charge distribution in the related species. For isolated [124Triz]⁻ anion, the N3 atom of triazole ring which presents the largest negative charge (See Supplementary Table 2) provides a chemical binding site with CO₂, therefore resulting in a charge distribution change of the total electron density of [124Triz]-CO₂⁻ ion (See Supplementary Figure 9). The negative charge value of [124Triz]⁻ decreases from -1 e to -0.454 e, while the net charge of neutral CO₂ molecule turns to -0.546 e. In this vein, we portrayed that the [124Triz]-CO₂⁻ anion proposed above provides a low energy pathway for CO₂ electroreduction.

Although it has been proved that the imidazolium cation on the electrode surface plays a key role in CO2 reduction at a low energy pathway. However, we found that the aforementioned CV curves in Figure 2 illustrates a notable enhancement of catalytic activity for CO₂ electroreduction in [Bmim][124Triz], and the increase of current density at low overpotential may be ascribe to the high CO_2 solubility and the stabilization of $[\cdot CO_2]^-$ in the superbase IL. Electrochemical impedance spectroscopy (EIS) can provide useful information about the properties of bulk electrolytes and the electrode interfaces. Hence, a Nyquist plot was obtained by running the experiment at an open circuit potential (Figure 4c). А simple equivalent circuit (LR)R(C(R(Q(RW)))) was then used to fit the acquired data of [Bmim][124Triz] (See supplementary Figure 7), and the charge transfer resistance (R_{ct}) was 41.8 Ω cm⁻², which was much lower than that in the conventional ILs (80.2 Ω cm⁻², 120.4 Ω cm⁻², 454.7 Ω cm⁻² and 802.8 Ω cm⁻²). This means that the electron transfer to the electrode surface in [Bmim][124Triz] is more facile, which can enhance the current density.^[23] Additionally, previous works presumed that the monolayer formed by ILs on the electrode surface plays a key role in CO_2 reduction and inhibiting H_2 formation on the cathode surface, and we found that the resistance of the absorbed film on the cathode surface $(R_{\rm f})$ was only 0.7 Ω cm⁻², it suggested that the reaction species can be easily transferred through the IL monolayer. These results provide sufficient supports to the excellent performance of CO₂ electroreduction in the superbase IL.

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Figure 4. The role of IL [Bmim][124Triz] in CO₂ capture, activation and reduction. (a) Dissolution of CO₂ in [Bmim][124Triz], (b) The formation of chemical bond between CO₂ and the anion of the superbase IL, (c) Nyquist plots for a Pb electrode in various electrolytes, (d) The activation and reaction of CO₂ at the electrode surface with the aid of [Bmim][124Triz].

Further computationally results were carried out to validate the underlying mechanism of the superbase IL, as shown in Figure 4. it can be seen that the C2H····CO₂ bond length in [Bmim]····CO₂···[124Triz] (2.30 Å) is much shorter than that in the conventional ILs ([Bmim][PF₆] (3.15 Å), [Bmim][BF₄] (2.93 Å), [Bmim][Tf₂N] (3.08 Å) and [Bmim][NO₃] (3.29 Å)) (See supplementary Figure S9-S13). This means the interaction between CO₂ and the superbase IL is much stronger than that between the CO₂ and the conventional ILs. Therefore, compared with the conventional ILs, during the potential static electrolysis, the fast transportation feasibility of activated CO_2 to the cathode surface in [Bmim][124Triz] medium caused by the anion most likely to account for the higher Faradaic efficiency of CO₂ reduction products. Based on the above analysis and previous reports, the novel reduction pathway of CO₂ with the help of the IMH is proposed and verified.

In summary, we put forward a novel insight for highly selective CO_2 electrochemical reaction by building an ionic microhabitat and revealed the underlying mechanism of the advanced performance. We proved that the ionic microhabitat of the IL plays a key role in CO_2 capture and conversion. Among the studied ILs, the superbase IL reaction system with [124Triz] anion exhibits an exceptionally high Faradaic efficiency for CO_2 electroreduction to HCOOH (95.2%) on Pb electrode at appreciable current density (24.5 mA cm⁻²). The H-bond between CO_2 and anion, and the chemical interaction between C atom of CO_2 and N3 atom of the [124Triz] anion makes a great change of configuration and electronic distribution of CO_2 molecule, which means that the anion can efficiently activate CO_2 and stabilize the [- CO_2] intermediate. Furthermore, the activated CO_2 can be easily transferred to the electrode surface, therefore leading to the

higher current density and Faradaic efficiency in potential static electrolysis, this subsequently result in a low energy and efficient pathway for CO_2 reduction. Our new finding will stimulate to develop more ILs to enhance this reaction and open a potential way for CO_2 utilization and the construction of a carbon neutral energy system.

Experimental Section

Materials

Experimental Details Materials and syntheses. [Bmim][124Triz] was synthesized by a reported method^[24] using a two step synthesis: Firstly, [Bmim][OH] was synthesized by an anion exchange resin from [Bmim][CI] (purity>99%). A column was packed with 600 mL ion exchange resin (Amberlite IRN-78, OH-form, from Sigma-Aldrich), and the resin was washed with absolute ethanol to wet it sufficiently and remove any air from the resin. 30 g of [Bmim][Cl] was mixed with 500 mL of ethanol and the mixed solution was poured into the column and flowed through the resin with one drop per 5~6 seconds. After ion exchange process, halide content of the mixture was below the detectable limit by AgNO3 testing, and the [Bmim][OH] in its ethanol mixture was measured by ¹H-NMR. With a 1:1 mol ratio, the desired amount of 124Triz was added into the solution and reacted with [Bmim][OH] at least 12 hours under ambient conditions and stirred. Conventional imidazolium ionic liquids, 1-butyl-3methylimidazolium chloride ([Bmim][Cl]), [Bmim][BF4], purity>99%, [Bmim][NO₃], purity>98%, [Bmim][PF₆], purity>99%, and [Bmim][Tf₂N], purity>99% in this study were purchased from Linzhou Keneng Tech Co., Ltd. All used ILs were purified and dried in vacuum oven at 333.15 K for 48 hours at least, the water content of the ILs was measured using a Metrohm 787 KF Titrino Karl Fischer and was found to be < 100 ppm, and finally obtained dry and pure ILs. Gasses used for absorption and electrochemistry reaction including H_2, N_2, CO_2 and CO were purchased from Beiwen and used as delivered.

Pb (purity>99.99%) electrode was purchased from Tianjin Aida Hensheng Technology Development Co. Ltd. Before each electrocatalysis test, the Pb electrode was polished with #800, #2000 and #5000 sandpaper sequentially, followed by washing with ethanol and acetone in an ultrasonic bath for 5 minutes, and finally rinsed with hyperpure water and then dried in N₂ atmosphere.

CO₂ absorption experiments

The CO₂ absorption solubility in the ILs was measured by a typical weighing method at room temperature and pressure^[9] (See Supplementary Figure 1). CO₂ was dried by calcium chloride before went through a glass container with an inner diameter of 8 mm, the glass container was immersed in a water bath to maintain the system temperature, the flow rate of CO₂ was 20 mL min⁻¹. The real-time amount of CO₂ absorbed in the ILs was obtained at intervals by an electronic balance (METTLER TOLEDO PL403) with an accuracy of 0.1 mg.

Electrochemical experiment setup and electrolysis measurements

An electrochemical workstation (CHI 660E, Shanghai CH instruments Co., China) was used for electrochemical experiments. Electrolysis measurements were carried out at room temperature (298 K) using a commonly used H-type cell (Figure S3), the cathode and anode compartments were separated by a proton exchange membrane (Alfa Nafion@117). The diameters of the cathode chamber and anode chamber were both 30 mm, and the volume of each chamber were about 40 mL. In

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a typical experiment, IL containing solution and H₂SO₄ aqueous solution (0.1 M) were used as cathodic and anodic electrolytes, respectively. The amount of electrolyte used was 30 mL in all the experiments. Before measurement, CO₂ was bubbled through the catholyte for 30 min under a steady follow of 30 mL min-1. Cyclic voltammograms (CVs) were recorded at working electrode in ILs/MeCN-H₂O mixture solution system, Pb as the working electrode and a platinum gauze as counter electrode, the reference electrode was 0.01 mol L⁻¹ Ag⁺/Ag formed by dissolving AgClO₄ in 0.1 M TBAP-MeCN and separated from the catholyte by a glass frit. The EIS experiments were carried out inside the two-compartment threeelectrode electrochemical cell by the same workstation, and the Nyquist plot for CO2 electroreduction in different ILs medium were collected and recorded at an open circuit potential and over a frequency of 100 kHz to 100 mHz with an amplitude of 5 mV. The obtained data from the EIS tests were fitted by using the Zview software, and the electrical equivalent circuit used for simulating the experimental impedance data is given in Supplementary Figure 6. Mild magnetic stirring was applied during the process for a better mixing. Controlled potential electrolyses were performed in ILs/MeCN-H₂O medium, and after a desired electrolysis time, the products were analyzed and quantified.

Products analysis and Calculations

Gaseous products were analyzed and quantified by gas chromatography (GC,Aglient 6820) with TCD and FID detector, and liquid products by Bruker Avance III 600 HD spectrometer in DMSO-d6 with phenol as internal standard. Briefly, the gas chromatograph, running N2 as a carrier gas, contained a 5A molecular sieve-packed column and havsep D column which were used together to separate CO₂, CO and hydrogen, after exiting the columns, the gas stream was first analyzed by a thermal conductivity detector (TCD) where hydrogen was detected. The gas stream then passed through a methanizer where CO and CO2 were converted to methane for immediate detection by a flame ionization detector (FID) where the carbon containing gas products were quantified. The peak areas for hydrogen, CO and CO₂ were compared to standards to find the concentration of each. The current efficiency was calculated as follows^[25]. Multiplication of this result by 100% expressed the current efficiency as a percentage, and total current density and Faradaic efficiency of the products were calculated on the basis of GC and NMR analysis. The obtained calibration curve of CO, H_2 and HCOOH are shown in supplementary Figure 7.

Quantum chemical calculations

All calculations were performed using the Gaussian 09 program package. For each set of calculations, we performed geometry optimization for each free anion, the free CO_2 molecule, each anion- CO_2 complex and each IL molecule- CO_2 complex at the B3LYP/6-31++G(d,p) theory level. Then, frequency calculations were performed to confirm that all the structures correspond to minima that without imaginary frequency.

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- M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* 2014, 114, 1709-1742.
- a) M. Y. He, Y. H. Sun, B. X. Han, *Angew. Chem. Int. Ed.* 2013, *52*, 9620-9633; b) C. Costentin, M. Robert, J.-M. Saveant, *Chem. Soc. Rev.* 2013, *42*, 2423-2436; c) J. Qiao, Y. Liu, F. Hong, J. Zhang, *Chem. Soc. Rev.* 2013, *43*, 631-675.
- [3] a) F. Urbain, P. Tang, N. M. Carretero, T. Andreu, L. G. Gerling, C. Voz, J. Arbiol, J. Ramon Morante, *Energy Environ. Sci.* 2017, 10, 2256-2266; b) J. Schneider, H. Jia, K. Kobiro, D. E. Cabelli, J. T. Muckerman, E. Fujita, *Energy Environ. Sci.* 2012, *5*, 9502-9510; c) E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazabal, J. Perez-Ramirez, *Energy Environ. Sci.* 2013, *6*, 3112-3135; d) M. Alvarez-Guerra, J. Albo, E. Alvarez-Guerra, A. Irabien, *Energy Environ. Sci.* 2015, *8*, 2574-2599; e) X. Chang, T. Wang, J. Gong, *Energy Environ. Sci.* 2016, *9*, 2177-2196.
 [4] a) E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem.*
 - a) E. E. Benson, C. P. Kubiak, A. J. Sathrum, J. M. Smieja, *Chem.* Soc. *Rev.* 2009, 38, 89-99; b) H. Mistry, A. S. Varela, C. S. Bonifacio,
 I. Zegkinoglou, I. Sinev, Y. W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser, B. R. Cuenya, *Nat. Comm.* 2016, *7*, 12123.
 - a) C. Wang, Y. Guo, X. Zhu, G. Cui, H. Li, S. Dai, *Chem. Commun.* 2012, *48*, 6526-6528; b) F. Ding, X. He, X. Luo, W. Lin, K. Chen, H. Li, C. Wang, *Chem. Commun.* 2014, *50*, 15041-15044; c) C. Wang, H. Luo, D.-e. Jiang, H. Li, S. Dai, *Angew. Chem. Int. Ed.* 2010, *49*, 5978-5981; d) L. A. Blanchard, D. Hancu, E. J. Beckman, J. F. Brennecke, *Nature* 1999, *399*, 28-29; e) S. Zeng, X. Zhang, L. Bai, X. Zhang, H. Wang, J. Wang, D. Bao, M. Li, X. Liu, S. Zhang, *Chem. Rev.* 2017, *117*, 9625-9673; f) E. D. Bates, R. D. Mayton, I. Ntai, J. H. Davis, *J. Am. Chem. Soc.* 2002, *124*, 926-927; g) X. P. Zhang, X. C. Zhang, H. F. Dong, Z. J. Zhao, S. J. Zhang, Y. Huang, *Energy Environ. Sci.* 2012, *5*, 6668-6681.
- [6] R. Vijayraghavan, S. J. Pas, E. I. Izgorodina, D. R. MacFarlane, *Phys. Chem. Chem. Phys.* **2013**, *15*, 19994-19999.
- [7] G. Gurau, H. Rodriguez, S. P. Kelley, P. Janiczek, R. S. Kalb, R. D. Rogers, *Angew. Chem. Int. Ed.* **2011**, *50*, 12024-12026.
 - C. M. Wang, X. Y. Luo, H. M. Luo, D. E. Jiang, H. R. Li, S. Dai, *Angew. Chem. Int. Ed.* **2011**, *50*, 4918-4922.

X. Luo, Y. Guo, F. Ding, H. Zhao, G. Cui, H. Li, C. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 7053-7057.

- [10] B. Gurkan, B. F. Goodrich, E. M. Mindrup, L. E. Ficke, M. Massel, S. Seo, T. P. Senftle, H. Wu, M. F. Glaser, J. K. Shah, E. J. Maginn, J. F. Brennecke, W. F. Schneider, *J. Phys. Chem. Lett.* **2010**, *1*, 3494-3499.
- a) W. Lu, B. Jia, B. Cui, Y. Zhang, K. Yao, Y. Zhao, J. Wang, Angew. Chem. Int. Ed. 2017, 56, 11851-11854; b) H. Tran Ngoc, P. Simon, G. Rousse, I. Genois, V. Artero, M. Fontecave, Chem. Sci. 2017, 8, 742-747; c) X. F. Sun, Q. G. Zhu, X. C. Kang, H. Z. Liu, Q. L. Qian, Z. F. Zhang, B. X. Han, Angew. Chem. Int. Ed. 2016, 55, 6770-6774; d) D. W. Yang, Q. Y. Li, F. X. Shen, Q. Wang, L. Li, N. Song, Y. N. Dai, J. Shi, Electrochim. Acta 2015, 189, 32-37.
- a) C. A. Gunawan, M. C. Ge, C. Zhao, *Nat. Comm.* 2014, *5*, 8; b) M.
 Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* 2009, *8*, 621-629; c) D. R. MacFarlane, M. Forsyth, P. C.
 Howlett, M. Kar, S. Passerini, J. M. Pringle, H. Ohno, M. Watanabe, F. Yan, W. Zheng, S. Zhang, J. Zhang, *Nat. Rev. Mater.* 2016, *1*, 15005.
- [13] a) B. C. M. Martindale, R. G. Compton, *Chem. Commun.* 2012, *48*, 6487-6489; b) L. Y. Sun, G. K. Ramesha, P. V. Kamat, J. F. Brennecke, *Langmuir* 2014, *30*, 6302-6308.
- [14] B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis, R. I. Masel, *Science* **2011**, *334*, 643-644.
- [15] a) E. E. L. Tanner, C. Batchelor-McAuley, R. G. Compton, J. Phys. Chem. C 2016, 120, 26442-26447; b) M. Asadi, K. Kim, C. Liu, A. V.

[5]

[8]

[9]

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Addepalli, P. Abbasi, P. Yasaei, P. Phillips, A. Behranginia, J. M.
Cerrato, R. Haasch, P. Zapol, B. Kumar, R. F. Klie, J. Abiade, L. A.
Curtiss, A. Salehi-Khojin, *Science* 2016, *353*, 467-470; c) J. Rosen,
G. S. Hutchings, Q. Lu, S. Rivera, Y. Zhou, D. G. Vlachos, F. Jiao, *ACS Catal.* 2015, *5*, 4293-4299; d) C. Cadena, J. L. Anthony, J. K.
Shah, T. I. Morrow, J. F. Brennecke, E. J. Maginn, *J. Am. Chem.*Soc. 2004, *126*, 5300-5308.

- [16] Q. Zhu, J. Ma, X. Kang, X. Sun, H. Liu, J. Hu, Z. Liu, B. Han, Angew. Chem. Int. Ed. 2016, 55, 9012-9016.
- [17] N. Hollingsworth, S. F. R. Taylor, M. T. Galante, J. Jacquemin, C. Longo, K. B. Holt, N. H. de Leeuw, C. Hardacre, *Angew. Chem. Int. Ed.* 2015, *54*, 14164-14168.
- [18] a) S. F. Zhao, M. Horne, A. M. Bond, J. Zhang, *J. Phys. Chem. C* **2016**, *120*, 23989-24001; b) L. Chen, S. X. Guo, F. W. Li, C. Bentley,
 M. Horne, A. M. Bond, J. Zhang, *Chemsuschem* **2016**, *9*, 1271-1278.
- [19] K. Fukumoto, M. Yoshizawa, H. Ohno, J. Am. Chem. Soc. 2005, 127, 2398-2399.

- [20] a) T. Nakagawa, C. A. Beasley, R. W. Murray, *J. Phys. Chem. C* **2009**, *113*, 12958-12961; b) L. Sun, G. K. Ramesha, P. V. Kamat,
 J. F. Brennecke, *Langmuir* **2014**, *30*, 6302-6308.
- [21] S.-F. Zhao, M. Horne, A. M. Bond, J. Zhang, J. Phys. Chem. C 2016, 120, 23989-24001.
- [22] S. Wang, J. Lin, X. Wang, Phys. Chem. Chem. Phys. 2014, 16, 14656-14660.
- [23] H. K. Lim, Y. Kwon, H. S. Kim, J. Jeon, Y. H. Kim, J. A. Lim, B. S. Kim, J. Choi, H. Kim, ACS Catal. 2018, 8, 2420-2427.
- [24] S. F. R. Taylor, C. McCrellis, C. McStay, J. Jacquemin, C. Hardacre, M. Mercy, R. G. Bell, N. H. de Leeuw, J. Solution Chem. 2015, 44, 511-527.
- [25] K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, *Energy Environ. Sci.* 2012, *5*, 7050-7059.

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We built an ionic microhabitat (IMH) for CO_2 electroreduction by using a superbase IL [Bmim][124Triz]. The anion plays a critical role in improving the selectivity and lowering the overpotential of CO_2 electroreduction by the [124Triz]- CO_2^- complex, and high selective reduction product, HCOOH was obtained. The method developed in this study opens a potential way for CO_2 utilization.

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Novel insights into CO₂ electroreduction in ionic liquids: CO₂ activation and selectivity tailored by ionic microhabitat