Molecular-level insight on CO2 electroreduction to formate facilitated by triazole ionic liquid interfacial microhabitat

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May 17, 2023

Abstract

The interfacial microhabitat induced by triazole ionic liquid ([124Triz]-) electrolyte can effectively enhance formate selectivity for electrochemical CO2 reduction reaction. However, the catalytic mechanism remains unclear. Herein, we combined molecular dynamics simulation and density functional theory to reveal the regulatory mechanism. The results showed that the dipolar interaction between CO2 and [124Triz]- cooperating the hydrogen bonds between [124Triz]- and H2O facilitate the accumulation of H atoms around C atoms of CO2. Meanwhile, the strong polar [124Triz]- induces negative electrostatic potential for the H atoms of H2O near anions. As a result, the negative H atoms are more likely to attack the positive C atoms of CO2, which results in a lower free energy of -0.10 eV for the formation of *HCOO intermediate and promotes the formation of formate. Thus, the [124Triz]- contributes to high formate selectivity owing to the combined effects of strong CO2-dipole interaction and hydrogen bonds with H2O.

Molecular-level insights on $\rm CO_2$ electroreduction to formate facilitated by triazole ionic liquid interfacial microhabitat

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ABSTRACT

The interfacial microhabitat induced by triazole ionic liquid (IL) electrolyte can effectively affect catalytic activity and enhance formate selectivity for electrochemical CO₂ reduction reaction (CO₂RR). However, the mechanism of triazole IL electrolyte promoting formate selectivity remains unclear, due to the limited understanding of the protonation reaction step. Herein, we combined molecular dynamics simulation and density functional theory to reveal the regulatory mechanism of the functionalized anion 1,2,4-triazolide ([124Triz]⁻) boosting formate selectivity. The results showed that the dipolar interaction between CO₂ and [124Triz]⁻ cooperating the hydrogen bonds between [124Triz]⁻ and H₂O facilitate the accumulation of H atoms around C atoms of CO₂. Meanwhile, the strong polar [124Triz]⁻ induces negative electrostatic potential for the H atoms of H₂O near anions. As a result, the negative H atoms are more likely to attack the positive C atoms of CO₂, which results in a lower free energy of -0.10 eV for the formation of *HCOO intermediate and promotes the formation of formate, comparing with the free energy of 0.43 eV in the electrolyte with [NTf₂]⁻. Thus, the functionalized anion [124Triz]⁻ contributes to high formate selectivity owing to the combined effects of strong CO₂-dipole interaction and hydrogen bonds with H₂O. This work provides a significant guidance for designing high-performance CO₂RR electrolytes in the future.

 $\mathbf{Keywords:} \mathrm{CO}_2$ electroreduction, interfacial microhabitat, ionic liquids, formate selectivity, catalytic mechanism

Highlights:

- The mechanism of the [124Triz]⁻ boosting formate selectivity were revealed.
- The [124Triz]⁻ induces different proton microhabitat and facilitates the accumulation of protons around C atoms of interfacial CO₂.
- The [124Triz]⁻ results in a low free energy of -0.10 eV for the formation of *HCOO intermediate.
- A significant guidance for designing the functionalized ionic liquids electrolyte boosting formate selectivity were proposed.

INTRODUCTION

In recent years, the electrochemical CO₂ reduction reaction (CO₂RR) has been generally recognized as a viable alternative to achieve carbon utilization, due to the advantage of mild temperature and pressure conditions, taking advantage of renewable or distributed energy.^{1, 2}Nevertheless, the high thermodynamic stability of CO₂ and the CO₂RR process involves multiple proton-electron transfer, which leads to poor energy utilization efficiency and product selectivity.³ Novel electrolytes can facilitate lowering overpotentials and improving target product selectivity.^{4, 5} For CO₂RR, electrolytes play a significant role in providing local reaction microhabitat at the electrode/electrolyte interface, affecting the catalytic activity of CO₂RR *via* an electronic polarization effect on reaction intermediates, changing the proton donor for the multistep proton-electron transfer reaction, and has been widely concerned in recent years.^{6, 7}

Hence, some novel functionalized electrolytes have been gradually studied for CO_2RR . Ionic liquid (IL) electrolytes have shown significant advantages in efficient dissolution and activation of CO_2 , reducing the overpotential and improving the target product selectivity for CO_2RR .^{4, 8, 9}For example, Rosen et al.⁴ demonstrated that 1-ethyl-3-ethylimidazolium tetrafluoroborate ([Emim][BF₄]) aqueous solution with Ag electrode reduced overpotentials by 600 mv for the formation of CO. Lim *et al*.⁸ further proved that the four [Emim]⁺ around a H₂O-[BF₄]⁻ complex formed an exotic interfacial microhabitat around *COOH on the Ag electrode in the [Emim][BF₄] electrolyte, which induced increase of the electron density on the electrode surface to stabilize the *COOH intermediate and decrease the overpotential.

Regarding product selectivity, the CO_2RR involves multiple proton-electron transfer, and extensive studies have realized that ILs can promote CO_2 activation for the first electron transfer process, as follows, CO_2 + e⁻ - CO_2^{-} .¹⁰⁻¹² However, the next protonation steps ($CO_2^{-} + H^+ - *COOH$, $CO_2^{-} + H^+ - *HCOO$) for C1product (CO, formate) were shown to be more related to the product selectivity.^{13, 14}Sargent et al.¹³ showed that the hydration layer around interfacial CO_2 had an important impact on the formation of *COOH and *HCOO intermediates, which proves the intermediates of CO and formate, respectively. They have pointed that the proton of *COOH intermediate mainly came from the surrounding H₂O molecules, while the proton of HCOO*intermediate mainly originated from the surface proton in aqueous solution. The results indicated that the interfacial proton microhabitat proved to be very important for the CO/formate selectivity. Similarly, our previous experimental work¹⁵ also found that the functionalized anion (1,2,4triazolide [124Triz]⁻) exhibited better formate selectivity (95.2%) and current density (24.5 mA cm⁻²) with same Pb electrodes and cation (1-butyl-3-methylimidazolium [Bmim]⁺), comparing to conventional anions (trifluoromethanesulfonate [NTf₂]⁻, hexafluorophosphate [PF₆]⁻, tetrafluoroborate [BF₄]⁻, nitrate [NO₃]⁻). However, the effects of interfacial microhabitat induced by IL electrolytes on the protonation reaction step for CO₂RR remains obscure.

Therefore, we combined the molecular dynamics simulation (MD) and the density functional theory (DFT) method to reveal the catalytic mechanism of the interfacial microhabitat for enhancing the formate selectivity. We have compared the effects of strong polar anions ([124Triz]⁻) and conventional anions on the formate selectivity for CO₂RR with same cation ([Bmim]⁺) and Pb electrode. We have focused on the effect of different IL electrolytes on interfacial proton microhabitat and protonation reaction step for CO₂RR. The results showed that [124Triz]⁻ effectively promoted the protons surround the C atoms of interfacial CO₂, meanwhile, resulted in a lower free energy of -0.10 eV for the *HCOO intermediate formation, which facilitates improving the formate selectivity. The mechanism provides guidance in designing functional electrolytes for CO₂RR in the future.

SIMULATION METHODS

2.1 MD Simulation Details

In this work, we have built the sandwich structure of Pb (111)-ILs/H₂O/CO₂ models with different kinds of ILs at different voltages, including [Bmim][124Triz], [Bmim][NTf₂], to acquire the regulatory mechanism for IL interfacial microhabitat enhancing the formate selectivity. Due to the fact that CO_2RR occurs on the surface of the negative electrode, we mainly analyzed the interfacial microhabitat near the negative electrode as shown in Figure 1a. The distance between two electrodes was determined by pressure, while the periodic condition was used only in dimensions x and y.

The numbers of molecules in different systems are shown in the Table S1. The three-point model and SPC/E model were used to describe the CO_2 and H_2O molecule, respectively.^{16, 17} The revised OPLS-AA force field has been used to describe the $[Bmin]^+$ and $[NTf_2]^-$, which have been successfully used to predict its structural and dynamic properties.¹⁸ For the functionalized anion $[124Triz]^-$, we have adopted a generalized AMBER force field.¹⁹ First, $[124Triz]^-$ was optimized using Gaussian 09 at the B3LYP/6-311g level. Then, we fitted the electrostatic potential (ESP) generated from the above calculations to acquire the atom charges of $[124Triz]^-$ according to the method of one-conformation two-step restraint ESP.²⁰⁻²² The force field parameters of $[124Triz]^-$ were provided in Table S2 and S3. The nonbonded vdW parameter of Pb was derived from the force field developed by Heinz *et al.*²³, which has been widely used to describe the nonbonded interactions of the vdW and Coulombic interactions, respectively. The mixed LJ parameters were used according to the Lorentz-Berthelot combination rule, $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. The cutoff was set to 1.3 nm in this work. The particle-mesh Ewald method was used to calculate the long-range Coulomb interactions.

The constant potential method (CPM) was used here to simulate the electric field of the electrode, where the atomic charges of the electrode could fluctuate to realize the constant external potential.²⁴ The distance between two electrodes have equalized for 5 ns, with Newton's equation integrated by the verlet algorithm with a time step of 1.0 fs. The systems were then relaxed in the NVT ensemble for 5 ns at U= ± 1.5 V, ± 2.0 V and ± 2.5 V. After the systems were fully equilibrated, a 20 ns trajectory of the NVT ensemble was collected to analyze the structures and thermodynamic properties of the systems, which was updated every 100.0 fs. An additional simulation with a smaller step of 0.5 fs and the velocity information was stored every 0.5 fs for the vibrational spectra of the H₂O. Temperature and pressure were set at 300.0 K and 1 atm via the Berendsen method. All MD simulations in this work were performed by using the large-scale atomic/molecular massively parallel simulator (LAMMPS).²⁵

2.2 DFT Calculation Details

In this work, the Vienna ab initio simulation package (VASP) software was used to calculated the CO₂ activation and conversion.²⁶ We have built a 5×5 unit cell with 3 layers for the Pb (111) surface, while the bottom layer was fixed. The vacuum thickness was employed to 15 Å to prevent the interaction between neighboring periodic structures. In the calculation process, the Perdew-Burke-Emzerhof (PBE) functional method²⁷ was used here to optimize the structures and calculate the electronic properties. We used a $3\times3\times1$ Γ -centered Monkhorst-Pack k-points sampling and an energy cutoff of 400 eV. The convergence criteria of energy and atomic force were 10^{-5} eV, 0.05 eV/Å for the ions relax, respectively. Long-range electrostatic interactions were performed using the Grimme method in DFT-D3 for the vdW correction of the molecules and surfaces. In this work, the electronic energies were calculated with reference to the computational hydrogen electrode.²⁸ All the Gibbs free energies were calculated through the following equation:

$\Delta G = \Delta E + \Delta E_{ZPE} - T \Delta S$

where ΔE , ΔE_{ZPE} and ΔS illustrates the changes of the electronic energy, the zero-point energy, and the entropy at 300.0 K, respectively.

In addition, in order to calculate the interactions between the anions and CO_2 , H_2O , we optimized the structures with Gaussian 09 at the B3LYP/6-311++g(d, p) level. All the atom charges were analyzed by Natural Bond Orbital (NBO) method, and the ESPs results were analyzed based on the optimized structures. The 3D-optimized structures in this study were observed by Gaussview 6.0 visualization program.

2.3. Data availability and reproducibility statement

The input files included complete information on the force fields and other simulation settings for the molecular simulation calculation at different voltages, which were provided in the supplementary material. The simulation time is long enough to ensure the accuracy of calculation. After the systems were fully equilibrated, a 20 ns trajectory of the NVT ensemble was collected to analyze the structures and thermodynamic properties of the systems. The Figure 2, 3, 5, 6, and 7 were acquired based on subsequent trajectory files. All input and output files for Gaussian calculations were also provided in the supplementary materials. Optimized structures and NBO charges for figure S2, S4 and 8c can directly obtained from the output files. Interaction energy data for figure S2 and S4 were also tabulated in Excel. All input and output files for Vasp calculations were also provided in the supplementary materials. The specific ACF.dat file for Bader charge for Figure 4 were provided, and the total charges for each ion/molecule have also been statistically sorted out in Excel. The free energy data in Figure 8 were also tabulated and calculated in Excel.

RESULTS AND DISCUSSION

3.1 Interfacial Solvation Structure in IL Electrolytes

In order to analyze the interfacial solvation structure of IL electrolytes, we defined the density distribution of all the molecules along the Z direction, perpendicular to the surface of the electrode, ρ (r). The ρ (r) is the ratio of the local density along the z-axis at the position r to the corresponding bulk density. Furthermore, the geometric center of the imidazole ring and triazole ring, the N atom of $[NTf_2]^-$, the C atom of the CO₂ and the O atom of the H₂O were represented the $[Bmim]^+$, $[124Triz]^-$, $[NTf_2]^-$, CO₂ and H₂O, respectively. As shown in Figure 2a, the results showed that the first solvation layer near the negative electrode interface was composed of CO₂, H₂O, and $[Bmim]^+$, while $[NTf_2]^-$ was far away from the electrode surface for the $[Bmim][NTf_2]$ electrolyte. The distribution of cations and anions are mainly affected by electrostatic interactions of the charged electrode.²⁹⁻³¹ The density distributions of cations ($[Bmim]^+$) and anions ($[NTf_2]^-$) increased and decreased with the increase of voltages, respectively. Additionally, we found that CO₂ could accumulate significantly near the electrode surface, which was beneficial to improve the current density of CO₂RR. Especially, it can be seen that the density distributions of interfacial CO₂ increase with the increase of interfacial $[Bmim]^+$, while the electrode voltages range from -1.5 V to -2.5 V. As a result, we considered the $[Bmim]^+$ had stronger interactions with CO₂ than $[NTf_2]^-$.

Regarding the [Bmim][124Triz] electrolyte, the cations and anions showed the same distribution with $[Bmim][NTf_2]$ electrolyte, while the cations were close to the electrode surface and the anions were far away from the electrode surface due to electrostatic repulsion. As show in Figure 2b, the layering behavior of cations and anions significantly aggravated with the increase of voltages, which was consistent with previous work.²⁹⁻³¹ However, CO₂ molecules and H₂O molecules showed entirely different solvation structure in [Bmim][124Triz] electrolyte, comparing to the [Bmim][NTf₂] electrolyte. A smaller amount of H₂O molecules appeared on the electrode surface for [Bmim][124Triz] electrolyte, which could effectively weaken the H₂O decomposition and inhibit hydrogen evolution reaction (HER). The result was consistent with our previous experimental work.¹⁵ Regarding the CO_2 molecules, the number of interfacial CO_2 decreased with a voltage ranging from -1.5 V to -2.5 V, which was consistent with the [124Triz]⁻. It was entirely different from the $[Bmim][NTf_2]$ electrolyte. Therefore, we inferred that $[124Triz]^-$ had a stronger interaction with CO₂ than [Bmim]⁺. We further proved this result by DFT calculations. As shown in Figure S2, we have calculated the interaction energies of [Bmim]⁺, [124Triz]⁻, [NTf₂]⁻ with CO₂. The binding energies are -21.96, -60.60 and -14.88 kJ/mol for [Bmim]⁺, [124Triz]⁻ and [NTf₂]⁻, respectively. There exists strong CO₂-dipole interaction between $[124 \text{Triz}]^-$ and CO₂. This result proved that the interaction energies between the ions and CO₂ were in the order of $[124 \text{Triz}]^- > [\text{Bmim}]^+ > [\text{NTf}_2]^-$. According to the radial distribution functions (RDFs), g(r), between the anions and the C atoms of CO_2 in the interfacial microhabitat, Figure 3 showed that the C atoms of CO_2 also had a close connection with [124Triz]⁻ due to the strong polar interaction, especially the N4 atom, comparing with the $[Bmim][NTf_2]$ electrolyte.

3.2 Activation Effect of Interfacial CO₂ in IL Electrolytes

In addition to the interfacial solvation structure, DFT calculations were also performed here to elucidate the activation effect of different IL electrolytes on the Pb (111) surface. The Bader charge analysis and the charge density difference are shown in the Figure 4. The Bader charge analysis can confirm the exact electron number of each atom. The charge density difference can intuitively acquire the electron transfer between different fragments, which can provide the information of charge gains and losses of interfacial CO₂ molecules. As shown in Figure 4a, the charge of the C and O atoms in CO_2 were 1.892, 7.070 and 7.092, respectively, the total charge of CO_2 were 16.054. Comparing the initial charge of CO_2 in Table S4, it showed that interfacial CO_2 only acquired an additional 0.054 e in [Bmim][NTf₂] electrolyte. Similarly, there is almost no charge transfer between interfacial CO_2 and other segments according to the charge density difference, which illustrates little activation effect on interfacial CO_2 . However, [Bmim][124Triz] electrolyte showed a completely different behavior. As shown in Figure 4b, the total charges of CO_2 reached 16.360, which were more abundant than $[Bmim][NTf_2]$ electrolyte. The abundant charge of CO₂ molecule promotes its activation. It can clearly see that the angle of CO_2 has been bent from 180.00° to 135.75°, the length of bond has been stretched from 1.17 Å to 1.25 Å and the C atom of CO_2 was bound to the N4 atom of [124Triz]⁻. These phenomena indicated that CO_2 was significantly activated in the [Bmim][124Triz] electrolyte. More importantly, the results showed that the extra charges of interfacial CO₂ mainly originated from [124Triz]⁻ according to the charge density difference. In conclusion, [Bmim][124Triz] electrolyte promotes the CO₂ activation and conversion by changing the charge distributions in the interfacial microhabitat.

3.3 Proton Distribution around Interfacial CO₂

The above results have shown that [Bmim][124Triz] electrolyte could promote the reaction of $CO_2 + e^- - CO_2^-$, and facilitate the activation of interfacial CO_2 . However, the CO_2 activation in different IL electrolytes could not explain the improvement of the formate selectivity for CO_2RR . The formate selectivity mainly depends on the competitive effect on the protonation reaction step, $CO_2^- + H^+ - *COOH$, $CO_2^- + H^+ - *HCOO$, while the *COOH intermediate can be reduced to *CO and C_{2+} products, and the *HCOO favors the formation of formate.³² From the perspective of intermediate configuration, the main difference between the two intermediates is the CO_2 hydrogenation position. The *COOH is the oxygen hydrogenation step and the *HCOO is the carbon hydrogenation step. Therefore, the local proton microhabitat of the interfacial CO_2 is significantly important for the product selectivity of CO_2RR . Similarly, several studies have indicated that H_2O served as the main proton source in a realistic reaction environment, compared to ILs.³³ Therefore, we have focused on the distribution of H atoms of H_2O around the C and O atoms of interfacial CO_2 in different IL electrolytes.

As shown in the Figure 5a, the RDFs displayed that the H atoms of H_2O exhibited a close peak with the O atoms of CO_2 in the [Bmim][NTf₂] electrolyte. However, the proton showed a high peak with C atoms of CO_2 for [Bmim][124Triz] electrolyte in the Figure 5b. The results illustrated that the protons mainly distributed around the O and C atoms of interfacial CO_2 in [Bmim][NTf₂] and [Bmim][124Triz] electrolyte, respectively. The high proton concentration around O atoms of interfacial CO_2 facilitates the formation of the *COOH intermediate. However, more protons surrounded the C atoms of interfacial CO_2 in [Bmim][124Triz] electrolyte, which was conducive to generate *HCOO intermediate. Therefore, the different local interfacial microhabitats contribute to the different product selectivity for CO_2RR in IL electrolytes. Similarly, as shown in Figure S3, we have found the same results with voltage ranging from -1.5 V to -2.5 V.

3.4 Hydrogen Bonds (HBs) between Anions and H₂O

According to the previous analysis, a strong interaction between $[124\text{Triz}]^-$ and CO₂ was existed. However, how could $[124\text{Triz}]^-$ regulate the distribution of H₂O around interfacial CO₂ still confused? We speculated whether $[124\text{Triz}]^-$ also had a strong interaction with H₂O. Therefore, the binding energy between the anions and H₂O were calculated here. Figure S4 showed that the binding energies for $[\text{NTf}_2]^-$ and $[124\text{Triz}]^$ with H₂O were -40.21 and -66.26 kJ/mol, respectively. The results proved that $[124\text{Triz}]^-$ had a stronger interaction with H₂O. Furthermore, the reduced density gradient (RDG) of $[124\text{Triz}]^-\text{H}_2\text{O}$, $[\text{NTf}_2]^-\text{H}_2\text{O}$ based on optimized geometries was analyzed. As shown in Figure S4d, the blue, green and red regions indicate HBs, vdW and repulsive interactions (steric effects), respectively.^{34, 35} The most negative $sign(I_2)r$ value of -0.045 indicated that there existed strong HB interactions between $[124\text{Triz}]^-$ and H₂O.

According to the previous literature, HBs are directional interaction that play an important role in regulating the orientation distribution of the electrolyte.^{31, 36} To further quantify the strength of HB between different anions with H₂O, the corresponding continuous HB time correlation function $(\text{TCF})S_{HB}(t)$ between anions and H₂O and its lifetime t (ps) were calculated here. The related equation can be seen in the Supporting Information. The Figure 6a and 6b have shown the schematics of the HB definition between the H atoms of the H₂O molecule (as the donor) and the electronegative atoms of the anions (as the acceptor). HBs between anions and H₂O are defined if the distance between the two atoms, R, is less than 3.5 A, the angle of ϑ , is less than 30°. The details of the HB definition were discussed in Figure S5. As shown in Figure 6c, the HB TCFs between [NTf₂]⁻H₂O declined very rapidly. The average lifetimes in the interfacial region was 3.21 ps. However, for the HBs between [124Triz]⁻ and H₂O, Figure 6c showed that the TCFs declined slowly, and the lifetime reached 94.13 ps, respectively. The longer lifetime means stronger HB strength. Therefore, the results indicated that the HB strength between [124Triz]⁻-H₂O was significantly stronger than [NTf₂]⁻-H₂O.

As an important tool, vibrational spectra have also been widely used to characterize the strength of HBs of H_2O molecules. (Definition can be seen in Supporting Information). Related studies have shown that the enhanced HBs promoted molecules associating stronger, reducing the energy of the systems and leading to the red shift of the O-H stretching vibration frequency (including the symmetric stretching vibration mode).^{37, 38} As a result, the vibrational spectra of interfacial H_2O molecules in different IL electrolytes were calculated in this work. As shown in Figure 6d, the vibrational spectra of interfacial H_2O in the [Bmim][NTf₂] electrolyte has undergone a 30 cm⁻¹ blue shift, comparing with the [Bmim][124Triz] electrolyte. It was indicated that the HB strength between [NTf₂]⁻ and H_2O was weaker than [124Triz]⁻ H_2O pair, which was consistent with the previous results of HB strength.

Furthermore, the different HB strength between anions and H_2O also influences the interfacial microhabitat. The RDFs between the anions and the H atoms of H_2O were shown in the Figure 7. It showed that the highest peak of $[NTf_2]^-$ was less than 1.5, while the peak of N4 atom of $[124Triz]^-$ reached 14. The results demonstrated the $[124Triz]^-$ showed a close connection with H_2O . According to the above result, the C atoms of CO_2 were also close to the N4 atom of $[124Triz]^-$. Therefore, it was confirmed that the N4 atom of $[124Triz]^-$ interacted with the H atoms of H_2O and the C atoms of CO_2 , which can shorten the distance between them and promote the accumulation of H atoms around C atoms of CO_2 . Therefore, the special proton microhabitat induced by $[124Triz]^-$ was conducive to generate the *HCOO intermediate and enhance the formate selectivity.

3.5 Catalytic Mechanism of IL electrolytes

In addition to the effects of the proton distribution around the interfacial CO_2 , the influence of anions on the reaction pathway was further explored. For the formate selectivity, the essence is the competition the formation of the *COOH and *HCOO intermediates. Therefore, the free energy diagrams for the formation of two types of intermediates were explored. Based on the above discussion, it was demonstrated that the H_2O was important for CO_2RR . Xiao and coworkers³³ pointed out that H_2O can serve as a strong proton donor for the first protonation step in the C1 pathways of CO₂RR, leaving adsorbed *OH on the surface. Therefore, H_2O was also taken into consideration for the protonation step in this work. As shown in Figure S6, the free energy for the formation of the *COOH and *HCOO intermediates on the Pb (111) surface were 1.15 eV and -0.01 eV, respectively. All the optimized structures can be seen in Figure S7-9. Azuma. et al 39 pointed out that the *HCOO intermediate dominates on the Pb (111) surface, which reflects the rationality of our DFT calculations. However, the results showed that the free energy for the formation of *COOH and *HCOO intermediate was 1.56 eV and 0.43 eV on the Pb (111)@[NTf₂]⁻ surface, respectively. Although the reaction path of the *HCOO intermediate still dominated, the free energy for the formation of *HCOO has increased by 0.44 eV, comparing to the Pb (111) surface. Furthermore, as shown in Figure 8b, the free energy for the formation of *COOH and *HCOO intermediates was 1.15 eV and -0.10 eV for Pb (111)@[124Triz] surface, respectively. The free energy for the formation of the *HCOO was 0.09 eV lower than the Pb (111) surface. Therefore, $[124 \text{Triz}]^2$ promoted the formation of *HCOO for CO₂RR and the high formate selectivity.

How could the free energy for the formation of the *HCOO decrease? A deeper understanding was obtained based on the NBO charge and ESP results between the anions and H_2O . The red and blue regions represent negative and positive ESPs, respectively. As shown in Figure 8c, the charges of O atoms and H atoms of H₂O around $[NTf_2]^-$ were -0.958 e, 0.479 e and 0.470 e, respectively. The total charge was -0.009 e. Similarly, both the H atoms of H₂O showed a moderate ESPs near the $[NTf_2]^-$. However, the charges of the O and H atoms of H_2O near $[124Triz]^-$ were -0.994 e, 0.432e and 0.502 e, with a total charge of -0.06 e. The H_2O acquired more charge from $[124 \text{triz}]^-$ than $[\text{NTf}_2]^-$, especially the H atom close to N4 atom of $[124 \text{Triz}]^-$, which gained more electrons and showed more negative ESPs. Therefore, the negative H atoms were easier to attack the positive C atoms of CO_2 and form the *HCOO intermediate. In summary, the reaction pathway involved with the $[124 \text{Triz}]^-$ can be seen in Figure 8d. It showed that $[124 \text{triz}]^-$ activated CO₂ to $[124 \text{Triz}-\text{CO}_2]^-$. At the same time, the $[124 \text{triz}]^-$ interacted with surrounding H₂O through HBs and transferred electrons to H atoms, which made it easier to attack the C atoms of CO_2 , promoting the formation of *HCOO intermediate, thus improving the formate selectivity. Therefore, a clear cognition of strong polar anions [124Triz]⁻ boosting the formate selectivity for CO₂RR was obtained. The anions with strong CO₂-dipole interaction and HBs with H_2O can contribute to the formation of formate, which provides a guidance for designing functional electrolytes for CO_2RR in the future.

CONCLUSION

In this work, the mechanism of functionalized IL ([Bmim][124Triz]) electrolyte enhancing the formate selectivity for CO₂RR was revealed by combining MD and DFT calculations. By analyzing the interfacial microhabitat in different IL electrolytes, we have demonstrated that [124Triz]⁻can shorten the distance between H atoms of H₂O and C atoms of interfacial CO₂ due to the N4 atom of [124Triz]⁻ forming strong HBs with H atoms of H₂O and dipolar interaction with C atoms of interfacial CO₂, thus promoting the accumulation of H atoms around C atoms of interfacial CO₂. But for conventional IL electrolyte ([Bmim][NTf₂]), the H atoms mainly surround the O atoms of interfacial CO₂ molecules. In addition to increase the proton concentration near the C atoms of interfacial CO₂, the strong polar [124Triz]⁻ induces electron polarization and transfers more electrons to the H atom of H_2O for the $[124\text{Triz}]^-H_2O$ pair, showing negative electrostatic potential. Therefore, the negative H atoms are likely to attack the positive C atoms of CO₂, resulting in a lower free energy of -0.10 eV for the formation of *HCOO intermediate, comparing with the free energy of 0.43 eV in the electrolyte with $[\text{NTf}_2]^-$, which promotes the formate formation and boosts the formate selectivity. In summary, the polar anions with strong CO₂-dipole interaction and HBs with H₂O co-facilitate the formation of formate. This work provides a guidance for designing new functional electrolytes for CO₂RR.

ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (2020YFA0710200), the National Natural Science Foundation of China (U22A20416, 22122814 and 22278400) and State Key Laboratory of Multiphase complex systems, Institute of Process Engineering, Chinese Academy of Sciences (No. MPCS-2022-A-03). Sincerely appreciate Prof. Suojiang Zhang (IPE, CAS) for his careful academic guidance and great support.

NOTES

The authors declare no competing financial interest.

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Figure Captions

Figure 1. (a) The schematic of Pb (111)-[Bmim][124Triz]/H₂O/CO₂ system and the region of CO₂RR interfacial microhabitat. (b) Atomic structures of CO₂, H₂O, [NTf₂]⁻, [124Triz]⁻, Pb and [Bmim]⁺.

Figure 2. The solvation structure of the CO₂RR interfacial microhabitat. The density distribution of the different ions and molecules along the z-axis in (a) [Bmim][NTf₂] and (b) [Bmim][124Triz] electrolytes at different voltages, respectively.

Figure 3. RDFs between the C atoms of CO₂ with different atoms of anions in the interfacial microhabitat in (a) [Bmim][NTf₂], (b) [Bmim][124Triz] electrolytes.

Figure 4. Bader charges and charge density difference of interfacial CO_2 in (a) [Bmim][NTf₂] (b) [Bmim][124Triz] electrolyte. The yellow and green isosurfaces represent electron accumulation and depletion with charge densities of -0.001 and + 0.001 e Bohr⁻³, respectively.

Figure 5. RDFs of H atoms of H₂O molecules around C and O atoms of interfacial CO₂ in the (a) [Bmim][NTf₂], (b) [Bmim][124Triz] electrolyte.

Figure 6. Schematic illustrations for the definitions of HBs between (a) $[NTf_2]^-H_2O$, (b) $[124Triz]^-H_2O$. (c) Continuous TCFs $S_{HB}(t)$ and the average lifetime *t* for the $[NTf_2]^-H_2O$ and $[124Triz]^-H_2O$ in the interfacial region. (d) Vibrational spectra for interfacial H₂O $S_{H2O}(t)$ in $[Bmim][NTf_2]$ and [Bmim][124Triz] electrolytes.

Figure 7. RDFs between the H atoms of H₂O with different atoms of anions in the interfacial microhabitat in (a) [Bmim][NTf₂], (b) [Bmim][124Triz] electrolytes.

Figure 8. Calculated free energy diagrams for CO_2 conversion to HCOO and COOH on (a) Pb $(111)@[NTf_2]^-$ and (b) Pb $(111)@[124Triz]^-$ surface, respectively. (c) The optimized geometrics and ESPs of $[124Triz]^-H_2O$ and $[NTf_2]^-H_2O$ pairs. (d) Reaction mechanism schematic of CO_2RR to formate based on $[124Triz]^-$ electrolyte.



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