Electrocatalytic reduction of CO_2 in neat and water-containing imidazolium-based ionic liquids

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Summary

Energetically efficient electrochemical reduction of CO_2 would offer the possibility of storing electricity from renewables in the form of fuels and other valuable chemicals. It may also help mitigate the increase of atmospheric CO_2 associated with global warming. However, the process suffers from a low energy efficiency due to the large overpotentials required. In aqueous electrolytes, the competing hydrogen evolution reaction also decreases the faradaic efficiency (which contributes to the low energy efficiency of the process). Recent claims of high faradaic efficiency and low overpotentials for the reduction of CO_2 in room temperature ionic liquids (RTILs) and RTIL-water mixtures have spurred considerable research. Here, we offer a critical review of those claims and of recent work aimed at understanding the details of this important reaction in these non-conventional electrolytes.

1. Introduction

In the energy landscape, the CO_2 reduction reaction (CO_2RR) is often envisioned as a carbon-neutral method to drive the conversion of globally significant quantities of carbon dioxide into fuels or other useful chemicals. As such, it has been proposed as a procedure to store excess renewable energy from wind or solar. Although currently electrochemical CO_2 conversion technologies are not ready for large-scale industrial implementation, their use is feasible provided there is a large enough market demand for products, low cost energy input, and energetic efficiency. The CO_2RR could provide specialty and commodity chemicals which have large market demand, and industrial scale current density of CO_2 electroreduction to CO has been achieved recently by Zhuang and co-workers [1]. Currently, the major challenge is reducing energy input costs, that is, reducing the overpotential required to ignite the reduction of CO_2 [2,3]. In addition, the CO_2RR is also an excellent model in fundamental studies of electrochemical reactions, because it involves multiple steps and the reaction conditions greatly affect its activity and selectivity. Therefore, it is certainly worth pursuing a deeper understanding of this reaction, so that we may tune the reaction parameters optimally to achieve the desired outcome.

The CO_2RR is energetically inefficient in aqueous systems because large overpotentials of more than 1 V are required. In addition to the decrease in energy efficiency directly associated to these large overpotentials, an additional decrease is typically produced by the competing hydrogen evolution reaction (HER), which decreases the faradaic efficiency for the generation of reduced-CO_2 products (although parasitic generation of H_2 during the CO_2RR is not necessarily bad because, if happening at sufficiently low overpotentials, production of syngas is an attractive option). By contrast, room-temperature ionic liquids (RTILs) have wide electrochemical windows (ca. 3-8 V) [4,5] and do not display hydrogen evolution. Therefore, the use of RTIL electrolytes enables the study of electrochemical reactions over a large potential range without disturbance from electrolyte decomposition. One additional advantage of RTILs for the CO_2RR is increased CO_2 solubility (about 3 times higher than in water). But the most interesting fact is that amine based RTILs appear to lower the required overpotential for the CO_2RR. This is probably the main reason why research on electrocatalytic reduction of CO_2 in RTILs is appealing. Nevertheless, despite important efforts, the origin of the allegedly low overpotential and the overall reaction mechanism remain open questions. We review here the recent experimental and theoretical advances in the field, and suggest future work to improve our understanding of the CO_2RR in imidazolium-based RTIL systems.

2. Low overpotentials

When discussing low-energy pathways of CO_2RR, the overpotential refers, by definition, to the deviation of the applied potential from the equilibrium potential of CO_2RR to the product of interest in the working medium. If that equilibrium potential is not known, as is the case for most relevant processes in RTILs, an upper limit to the overpotential applied can be estimated by comparing the applied cell voltage with ΔG of the overall reaction, if all the reactants and the products are in the gaseous state. Reaction 1 shows the overall reaction for decomposition of CO_2 into CO and O_2, which is the overall reaction of an electrolyser reducing CO_2 to CO in the cathode and oxidising H_2O to O_2 in the anode.

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO}(g) + {}^{1}\!/_{2}\,\mathrm{O_2}(g) \qquad \Delta G^{\mathrm{o}} = -1.33\ \mathrm{V} \qquad (1)$$

Some claims in the literature of low overpotentials for the CO_2RR in RTILs are based on comparing the onset potential of the reaction with the equilibrium potential in aqueous medium, or even with the open-circuit potential of the system. Such claims are wrong and misleading. The first report of a low overpotential for the CO_2RR in RTILs [6] correctly compared the applied voltage in a CO_2 electrolyser with the minimum voltage required for the reaction (1.33 V) as described above, but the reported overpotential of 0.17 V is impossibly low. Formation of CO at the Ag cathode occurred at a cell potential of 1.5 V, i.e., at an overall overpotential of

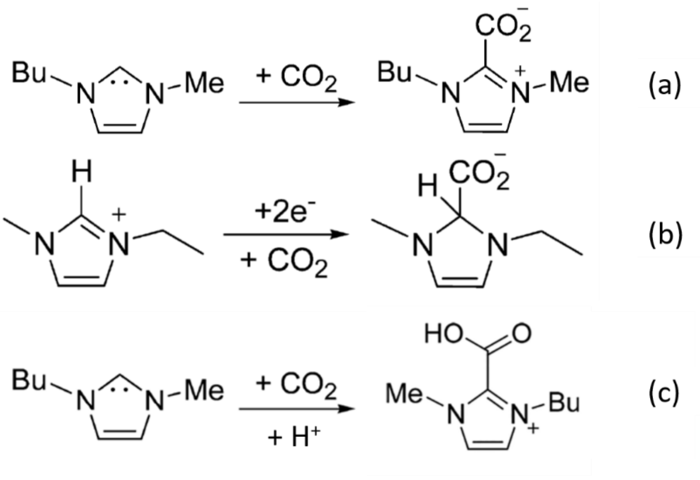
0.17 V (which must include the overpotential at the cathode and that at the anode). This cannot be correct if the anodic reaction was, as the authors claim, oxygen evolution on Pt in 0.1M H_2SO_4 (making Reaction 1 the overall cell reaction), because that alone requires an overpotential of at least 0.3-0.4 V. So, the only way that the overall overpotential could have been 0.17 V is if CO_2 was being reduced to CO at a potential more positive than the corresponding equilibrium potential, which is impossible. Most likely, a parasitic oxidation reaction was happening at the anode at a potential considerably lower than that needed for oxygen evolution, so the overall reaction and ΔG were different to Reaction 1.

The same group seem to have realised this mistake in a later publication, which reported CO_2R onset at an overpotential of ca. 0.67 V [7]. This would correspond to an overpotential for the CO_2RR to CO of ca. 0.3 V, which is remarkably low compared to the reaction in aqueous media. They achieved this by modifying an anion-conductive membrane with an imidazolium group to mimic the co-catalytic effect in RTILs. The setup was able to operate with a current density of > 100 mA cm^{-2} at a cell potential of 3 V, with > 90% selectivity to CO. Furthermore, maximising the contact area between the ionomer and the Ag catalyst more than doubled the current density, which emphasises the co-catalytic role of imidazolium [7].

Other reports have explored the activity of alternative catalysts and produced interesting information, despite occasional claims of low overpotential based on flawed reasoning. For example: MoS_2 and Nb-doped MoS_2 show a higher turnover frequency for CO than Ag nanoparticles in an imidazolium RTIL–water mixture [8,9]; Sun et al. [10] achieved 93.5% faradaic efficiency to CH_4 using an N-doped carbon electrode, with a current density six times that of a Cu electrode in similar conditions; Zhu et al. showed that Pb and Sn electrodes catalyse the reduction of CO_2 to HCOOH at 95% faradaic efficiency in an acetonitrile/water/RTIL system [11]; Kunene et al. demonstrated that Rose's metal ($Bi_{50}Sn_{22}Pb_{28}$) promotes conversion of CO_2 to CO at up to 95% faradaic efficiency in MeCN electrolyte with millimolar concentrations of RTIL as an additive [12]; and Grills et al. [13] employed a homogeneous Re catalyst and achieved a faradaic efficiency of 88 ± 10% in conversion of CO_2 to CO. In summary, there has been considerable effort testing different materials and conditions. This being clearly important, the greatest potential for progress lies in improving our mechanistic understanding of the electrocatalytic reduction of CO_2 in RTIL-based systems.

2.1 What is the mechanism accounting for the reduced overpotential?

The claims of CO_2 reduction at low overpotentials in RTILs have prompted a considerable amount of work in the last five years focusing on understanding the reaction mechanism and the origin of the alleged low overpotential. Rosen et al. [6] initially proposed that the decrease in the overpotential was due to the stabilisation of the $CO_2^{\bullet -}$ intermediate (generated after the first, rate-determining, electron transfer) through complexation with the electrogenerated imidazolium carbene at the 2-position (Scheme 1a). This adduct has indeed been detected [14–16], but evidence suggests that it is a by-product rather than an intermediate in the path to CO or formate. Other reports [15,17] suggest an alternative intermediate involving a tetrahedral carbon at the C2-position (Scheme 1b), formed by coupling between the electrogenerated EMIM radical (as opposed to the carbene) and $CO_2^{\bullet -}$. Kemna et al. [18] instead argue that the key intermediate in the reduction of CO_2 to CO and formate on Pt electrodes is a C2-carboxylic acid adduct (Scheme 1c), to which they assigned an infrared absorption at 1670 cm^{-1}.



Scheme 1. Formation of possible CO_2-imidazolium adducts at the C2-position via (a) carbene-CO_2 coupling to give a zwitterion, (b) radical-radical coupling to give a tetrahedral carboxylate as in ref. [15], and (c) carbene-CO_2 coupling with a proton transfer to give a cationic carboxylic acid as in ref. [18].

According to other authors, interaction of the $CO_2^{\bullet-}$ radical at the C2-position of the imidazolium ring may not be all-important for the enhancement effect. Lau et al. [19] examined structure-activity relationships of imidazolium salts with different substituents and found that the C4- and C5-protons are vital for co-catalysing CO_2R (Fig. 1). They propose that hydrogen bonding between these protons and adsorbed $CO_2^{\bullet-}$ stabilises the latter and may account for the reduced overpotential of CO_2R in imidazolium based RTILs. Interestingly, the authors observed highest activity for CO generation when using a phenyl-substituted imidazolium cation at C2-position (cation 2a in Fig. 1a), which probably excludes formation of an adduct as in Scheme 1. In addition, when all three positions (C2, C4 and C5) were substituted by methyl (cation 3a in Fig. 1a), the imidazolium based cation still had a co-catalytic effect (the onset potential of CO_2R was shifted positively by ca. 0.2 V compared with no imidazolium cation present, see Fig. 1b). This co-catalytic effect emphasises that imidazolium-based cations act as promoters of CO_2 electroreduction despite not forming an EMIM-CO_2 complex.

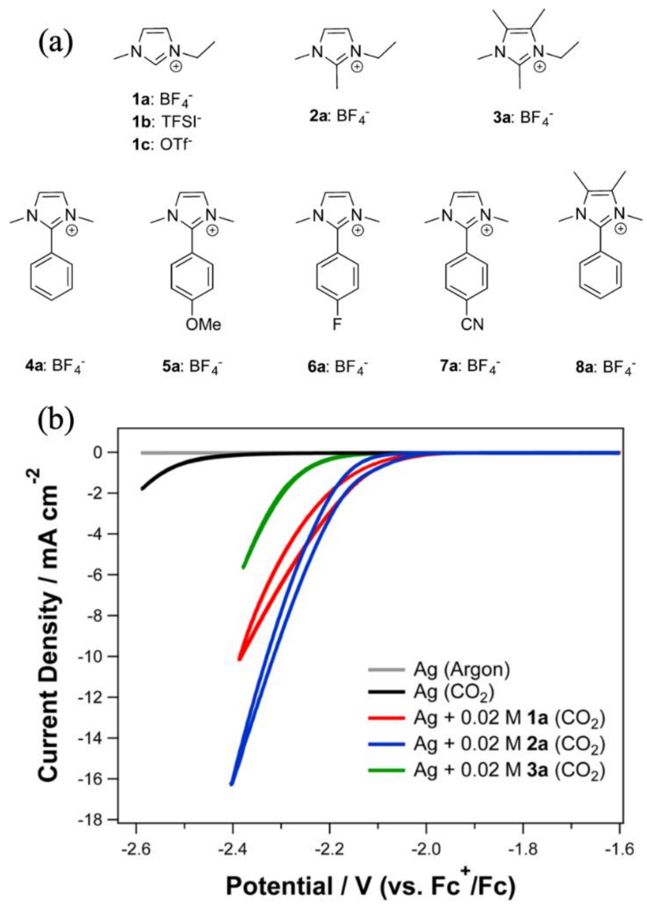


Figure 1. (a) Chemical structures of imidazolium salts studied; (b) Effect of adding different cations (1a, 2a, 3a) on the electrochemical reduction of CO_2 in dry acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBA PF_6) as supporting electrolyte. Reprinted with permission from ref. [19]. Copyright (2016) American Chemical Society.

Tanner et al. [20] also claim that formation of the imidazolium-CO_2 complex is unlikely to play a significant role in the overall reaction, because the choice of cation influences the potential at which the maximum CO_2RR current occurs. Moreover, they showed that the imidazolium-based enhancement of the CO_2RR is greatest for silver cathodes and suggest a mechanism in which a purely chemical step is followed by an electron transfer rate-determining step (usually denoted chemical-electrochemical, CE), involving desorption of the RTIL cation before the electron transfer to CO_2. Recent results by Montiel et al. [21] also suggest that the C2 position on the imidazolium ring does not play a key role in the CO2RR. These authors noted that the

CO_2 reduction activity of Pt nanoparticles was unaffected when using an imidazolium RTIL with a methyl group at the C2-position.

In situ spectroscopy is a powerful tool that can improve our mechanistic understanding. So far, spectroscopic experiments have not been able to provide unambiguous evidence supporting any of the mechanisms mentioned above in imidazolium-based RTILs, because different conditions have yielded different results. Braunschweig et al. [22] detected a sum-frequency generation (SFG) active vibrational mode at 2355 cm^{-1} (Figure 2a and b) and attributed it to an interfacial [CO_2-EMIM] complex. The authors claim that this complex forms at remarkably positive potentials and reduces the potential barrier for CO_2 reduction in EMIM[BF_4] on Pt. Interestingly, the vibrational frequency is higher than that of solvated CO_2 (2343 cm^{-1}), which implies that the C=O bond is strengthened as a result of this interaction. The lack of spectral bands around 1550-1700 cm^{-1} means that neither the carboxylates nor the carboxylic acid shown in Scheme 1 were detected. An absorbance centred at 2052-2028 cm^{-1} was assigned to adsorbed CO generated by reduction of CO_2. However, the spectra suggest that the CO coverage increases at positive potentials and decreases at negative potentials, which is a strange behaviour for the product of an electrochemical reduction.

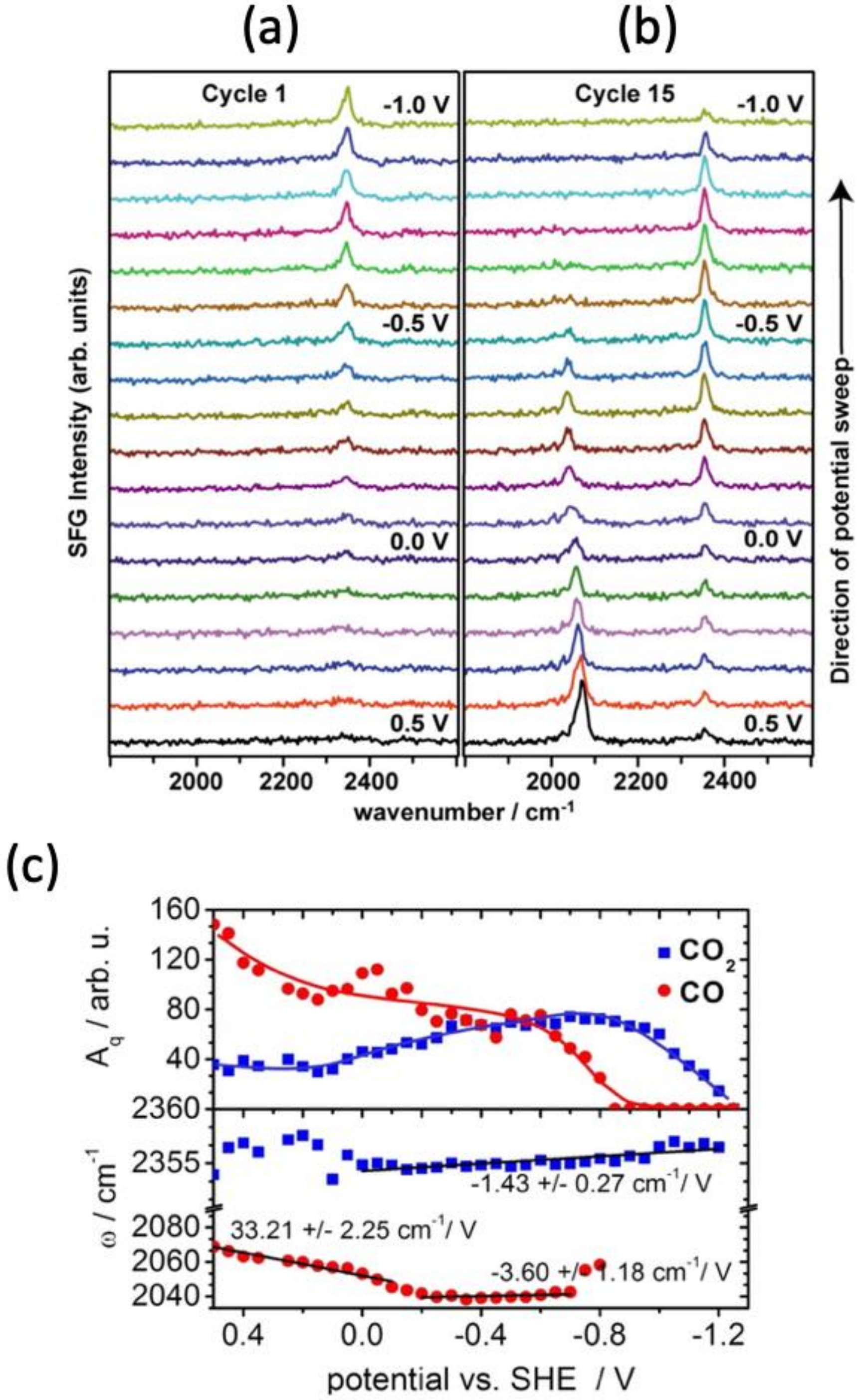


Figure 2. SFG spectra showing interfacial CO_2 and adsorbed CO at a Pt / EMIM[BF_4] interface during the first (a) and 15th (b) potential cycles at 5 mVs^{-1} during the electroreduction of CO_2; (c) integrated absorbance of CO_2 and CO (top panel) and Stark tuning rate of CO and CO_2 (bottom panel). Reprinted from [22], Copyright (2017), with permission from Elsevier.

In comparison, an ATR surface-enhanced infrared absorption (SEIRA) study on Au in 18 mol% EMIM[BF_4] [23] showed that CO was the main adsorbed product of the CO_2RR in these conditions too (Figure 3). However, in this case the IR absorption of CO followed the expected trend for the product of an electrochemical reduction (**Error! Reference source not found.**3c, bottom panel). The integrated absorbance of the band corresponding to solvated CO_2 tracked the current (**Error! Reference source not found.**3c, middle panel). Furthermore, there were no bands attributable to interfacial CO_2. or EMIM-CO_2 complexes. This work also showed that two populations of water were present in the mixture, one with an OH stretching absorbance at ca. 3610 cm^{-1} and another, more bulk-like water, at 3400 cm^{-1}. Both populations are initially brought towards the interface during a negative-going potential sweep, but the high-frequency water gets consumed or removed from the interface at −1.3 V, when the CO_2RR is apparently transport limited. This may be an indication that the high-frequency water is favoured as proton donor in the reduction of CO_2 to CO, perhaps because it offers a stabilisation effect on the $CO_2^{\bullet-}$ radical.

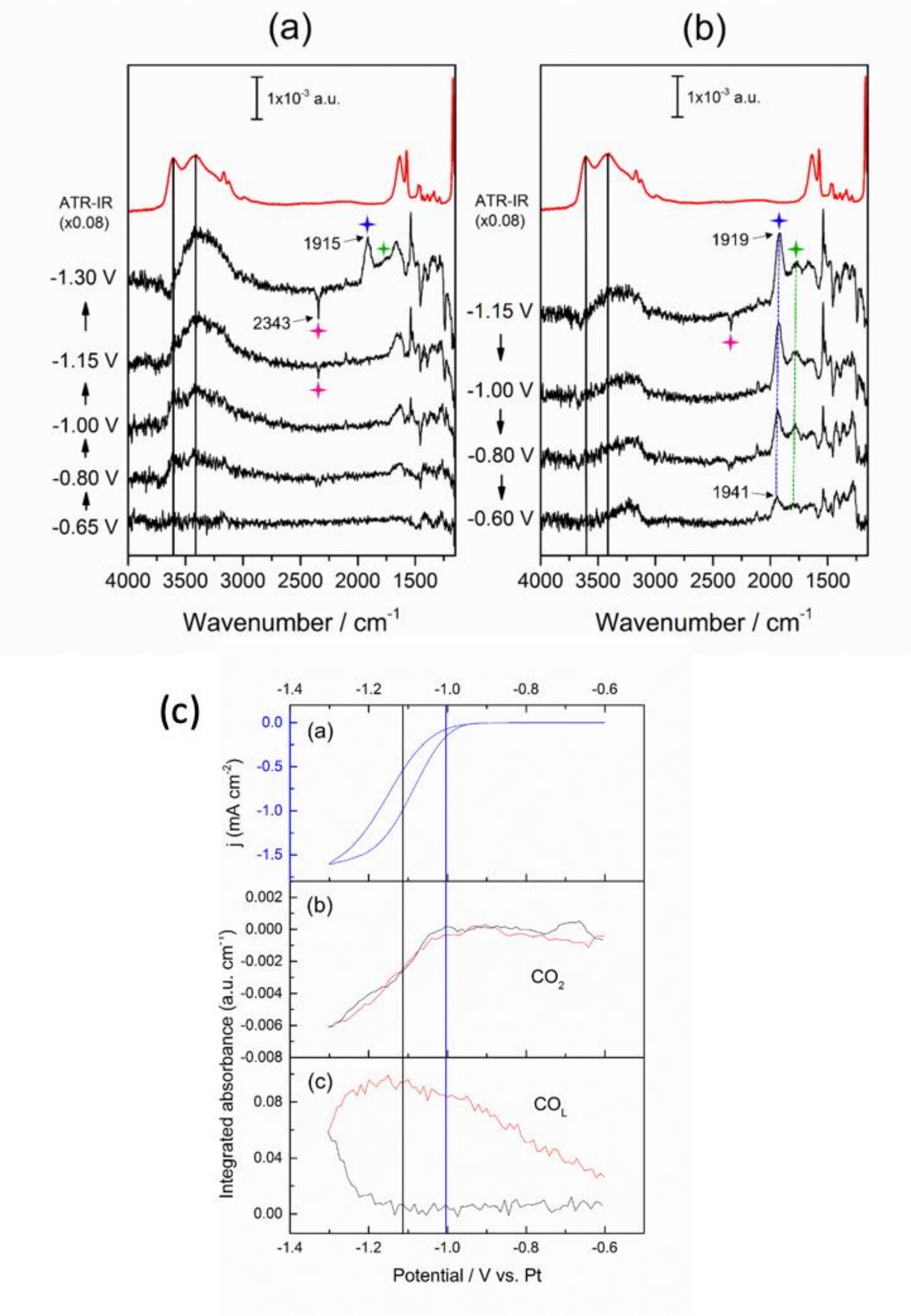


Figure 3. ATR-SEIRA spectra of Au in an EMIM BF_4 / H_2O mixture (18% mol / mol) collected during negative-going (a) and positive-going (b) potential sweeps at 0.5 mVs^{-1}. The highlighted bands correspond to solvated CO_2 (magenta star), linearly bound CO (blue star) and bridge-bonded CO (green star). The IR spectrum of the same mixture is shown in red. (c) CV recorded simultaneously with ATR-SEIRA spectra (top panel), potential dependence of the integrated absorbance of CO_2 (middle panel) and linearly bound CO (bottom panel). Reprinted with permission from ref. [23]. Copyright (2018) American Chemical Society.

The organisation and potential-dependent structural rearrangements of RTILs at electrified interfaces must also play an important role in electrocatalytic reactions. An SFG study [24] found that a structural transition in the RTIL may control the onset of the CO_2RR on polycrystalline Ag in EMIM[BF_4] containing 0.3 mol% water. The authors observed a minimum in the non-resonant SFG signal precisely at the onset potential of the CO_2RR with different curvatures on either side, suggesting a change in the structure of the interface. The potential at which the minimum occurred also coincided with a change in the Stark shift of adsorbed CO on Ag, which indicates a change in the interfacial electric field. Interestingly, the structural transition occurred regardless of whether CO_2 was present, *i.e.*, it must be a property of the RTIL itself. The same authors found that the addition of more water shifted both the non-resonant SFG minimum and the threshold potential for the CO_2RR to less negative potentials [25]. In addition, the faradaic efficiency of CO_2 reduction to CO increased dramatically, reaching > 90% at 90 mol% water.

Several other studies have confirmed that the presence of water enhances the CO_2RR in RTILs [8,10,21,26–28]. This is not surprising because most pathways of the CO_2RR require transfer of protons as well as electrons, and water is a good proton donor. The enhancement may also in part be attributable to changes in the product distribution of imidazolium reduction: one report [29] showed that adding protons to neat 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide shifted the equilibrium between the imidazolium radical and the carbene towards the former, which could play a part in the CO_2RR mechanism (Scheme 1b). The obvious downside of adding water to RTIL systems is hydrogen evolution. However, some reports suggest that imidazolium cations may suppress the HER even at water concentrations as high as 90 mol% [27,28]. In contrast, one study [23] reports significant hydrogen evolution occurring simultaneously to the CO_2RR in 82 mol% water and 18 mol% EMIM[BF_4]. Feaster et al. [30] found that the addition of 0.1M [EMIM]Cl to acidic aqueous electrolyte suppressed HER activity by 10-75% on transitional metal catalysts, whereas no suppression occurred in basic electrolyte. The authors argue that this happens because $EMIM^+$ displaces interfacial H_3O^+, but not interfacial H_2O.

In addition to the experimental work discussed above, theoretical calculations have also attempted to determine the key intermediate of the CO_2RR in RTIL based systems. Wang et al. [31] focused on electrochemical reduction of CO_2 in aqueous solutions of EMIM[BF_4]. They optimised all possible intermediate structures of EMIM-CO_2 complexes on C2-position in the aqueous solutions by using density functional theory (DFT) method, and the solvation environment was treated by implicit water solvation model. Then they calculated Gibbs free energies of all intermediates and found a thermodynamically favourable reaction pathway. In this reaction pathway, the $EMIM^+$ is reduced before the formation of EMIM-CO_2 complexes, and hydrogen in the C2-position is considered to be the proton donor to form the key intermediate, $[EMIM\text{-}COOH]^-$. However, based on calculated redox potentials in the thermodynamic pathway, an applied potential of -2.4 V vs. SHE is needed to make all steps exergonic, which is much more negative than the experimental onset potentials (-0.25 vs. SHE) [28]. The authors attributed this discrepancy to the absence of the electrode surface in their calculations. In addition, the implicit solvation model is most likely incapable of accurately describing chemical environments for ionic-liquid ions such as $EMIM^+$ and BF_4^-.

Besides interactions between EMIM and $CO_2^{\bullet-}$, double layer effects can also play an important role in the CO_2RR and these can be investigated using computational methods. Due to the complexity of RTIL/electrode interfaces, simulation models often need to be reasonably simplified. Nørskov and co-workers [32,33] studied using DFT the effect in the CO_2RR of substituting K^+ for $EMIM^+$ at the electrochemical interface. The atomistic interface model consists of a four-layer 3×3 slab of Ag electrode and the electrolyte including several explicit water molecules, CO_2 and co-adsorbate (K^+ or $EMIM^+$). By comparing the computed adsorption energies of CO_2 on Ag(111) with cation and water molecules in the vicinity with those under vacuum with an applied electric field, they found that cations in the vicinity of CO_2 have a significant stabilizing effect on adsorbed CO_2 on weakly adsorbing metals such as Ag, and that this effect is not due to specific chemical bonding but to the interfacial electric field. By using a microkinetic model combined with calculated free energies of all intermediates from CO_2 to CO, they demonstrated that, when the electric field is considered, the formation of *CO, instead of the formation of *COOH, is the rate-determining step. They further used the reaction rates obtained from the kinetic model to calculate polarization curves at different pH, which reasonably agree with experimentally measured polarization curves. Their calculation indicates that electric field effects or explicit interface structures are important to reproduce realistic environments for CO_2 electroreduction and need to be included in simulation models.

With the aim of explicitly simulating double layer effects at the interface, Kim and co-workers [34] developed a multi-scale model, (DFT in classical explicit solvent, DFT-CES), in which the Ag electrode and adsorbates $*CO_2$ and *COOH were treated quantum mechanically while the electrolytes having the same composition of the EMIM[BF_4]/water mixture as experiment were described using classical force fields. The efficient method allows for sufficient simulation time to equilibrate the interface structures, especially for bulky ions like $EMIM^+$ and BF_4^-. They calculated the free energies of adsorbed intermediates $*CO_2$, *COOH and *CO in both aqueous solution and EMIM[BF_4]/water mixtures, and found that in the latter the overpotential for the reduction of CO_2 to CO can be decreased by 0.31 V compared with the aqueous solution. The main difference between the aqueous solution and the EMIM[BF_4]/water mixture occurred at the first proton-coupled electron transfer (PCET) step, namely, the formation of *COOH. By investigating the local coordinating environment of *COOH, they found that the promotion effect of RTILs on the CO_2RR was the result of the collective participation of both cations and anions. Due to the strong cation-anion electrostatic attraction, the combination of non-covalent interactions between water, BF_4^- and $EMIM^+$ forms a micro-environment at the interface, and makes $EMIM^+$ directly contact the metal surface around *COOH (Figure). This local electric field effect, similar to that mentioned above in the work of Nørskov and co-workers [32,33], can help stabilise adsorbates. To further separate the polarization effect of the metal electrode, they performed a non-self-consistent DFT-CES calculation, in which the electronic polarization of the Ag electrode in response to the adjacent electrolytes was not included, and found that the thermodynamic overpotential was about 0.14 eV higher than that obtained in the self-consistent DFT-CES simulations.

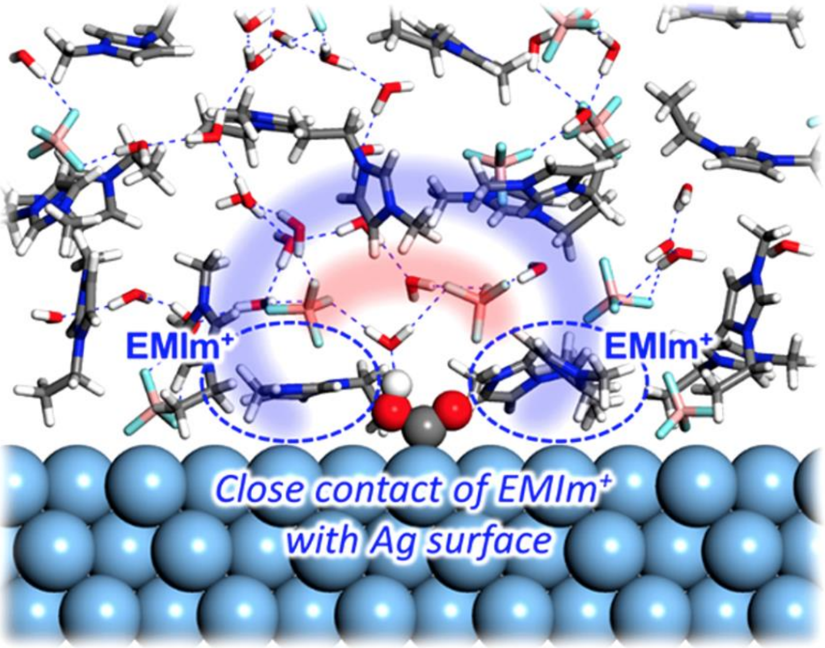


Figure 4. Side view of the overall molecular structure around *COOH in the 20:80 EMIM-BF_4/water mixed electrolyte. The $EMIM^+$ cations are located quite close to the Ag surface by *COOH. Reprinted with permission from ref. [34]. Copyright (2018) American Chemical Society.

3. Conclusion and outlook

Thanks to the efforts made by many researchers in the past few years, we start to have a basic understanding of CO_2 electroreduction in RTIL-based electrolytes. Although the overall reaction mechanism remains largely unknown, the contributions to the observed decrease in overpotential can be roughly divided into the following categories: (i) chemical interactions between $EMIM^+$ cation and $CO_2^{\bullet-}$ radical, (ii) double-layer effects and (iii) effects due to the composition and structure of the electrode surface. In this review, we have summarized recent relevant work analysing these contributions, but unfortunately, many of the hypotheses launched still lack direct evidence to reach solid conclusions. In order to obtain such evidence, we believe that an increase in experimental studies focusing on the effect of the electrode's composition and structure and on electric double-layer effects is needed. Similarly, there is a need for computational work aimed at quantifying the contribution of the chemical interaction of the RTIL with the $CO_2^{\bullet-}$ radical as well as of double-layer effects to the decreased overpotential, because of the excessive computational cost of simulating the full electrochemical cell.

More specifically, we suggest the following research avenues (in some of which we are already working or planning work):

(i) Identifying the chemical nature and the environment of the key reaction intermediate. The very negative equilibrium potential of the CO_2 / $CO_2^{\bullet-}$ couple [35,36], which is mainly due to the unstable structure of the $CO_2^{\bullet-}$ radical in water, is thought to be the main responsible for the high overpotential of the CO_2RR. However, until now CO_2^{-} has eluded detection in situ using vibrational spectroscopy. On the contrary, electrogenerated $CO_2^{\bullet-}$ was detected both in aqueous and organic electrolytes using ultraviolet reflectance spectroscopy 47 years ago [37]. Similar experiments in RTILs would confirm that the species is generated and should provide information about the effects of the environment on the species. Thanks to the enormous instrumental advances since 1973, it should also be possible to use this type of techniques to monitor its rate of formation and consumption and to study how it is affected by the environment. Equilibrium potentials of unstable radicals, *e.g.*, of the CO_2/ $CO_2^{\bullet-}$ redox couple, can be conveniently computed, thereby determining the thermodynamic overpotential of the reaction [38–41]. We have recently developed computational approaches for the redox potential calculations in RTILs, such as the computational Ag/AgCl reference electrode [42] and a multiscale simulation method for electrolytes including bulky ions such as $EMIM^+$ and BF_4^-. Future coupling of experimental and computational studies to understand the formation and reactivity of the $CO_2^{\bullet-}$ radical could lead to a qualitative leap in our understanding of the CO_2RR in RTILs, but also in other, more conventional media.

(ii) Computational and experimental work aimed at understanding double-layer effects in RTILs. Following recent work in aqueous media [43], a combination of vibrational spectroscopy and computational methods can provide a wealth of information on the effect of the size and, eventually, structure of RTIL cations on the intensity of the interfacial electric field, as well as providing insight into other aspects of double layer structure, like potential-induced changes in the orientation or concentration of ions at the interfaces, all of which can have pronounced influence on the CO_2RR. The quantum mechanics/molecular mechanics (QM/MM) approach of Kim and co-workers [34] suggests that multiscale modelling could be a feasible approach for this problem, however, how to apply the electrode potential in the simulation is a challenge. Recently, Dufils et al. [44] reported a method that combines a polarizable electrode with a finite field method to reproduce the electrochemical interface with constant potential. This success points the way for our future choice to apply the electrode potential in the multiscale simulation.

(iii) Experimental work with single-crystal electrodes in RTILs aimed at understanding the role of surface structure and surface composition. This is a formidable challenge, due to the need of ultraclean conditions when working with this kind of electrodes and the well-known presence of impurities in RTILs [21,45,46], the levels of which can vary from one batch of product to the next. An additional problem in the case of neat RTILs is the absorption of water (from the atmosphere or from a gas being bubbled through the liquid), which acts as an impurity and can obscure relevant voltammetric features [21].

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Even though the claimed overpotential is too small to be real, this is the first claim of enhanced faradaic and energy efficiency of CO2RR in RTILs and probably trigered all the research done afterwards.

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