Water-in-salt environment reduces the overpotential for reduction of CO$_2$ to CO$_2^-$ in ionic liquid/water mixtures

Xiao-Hui Yang$^a$, Marco Papasizza$^{b,†}$, Angel Cuesta$^{b,c,*}$ and Jun Cheng$^{a,d,*}$

$^a$ State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

$^b$ Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, AB24 3UE, Scotland, UK.

$^c$ Centre for Energy Transition, University of Aberdeen, AB24 3FX, Scotland, UK.

$^d$ Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM), Xiamen, China.

† Current address: Sweetch Energy, 6 Rue Pierre Joseph Colin, 3500 Rennes, France.

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ABSTRACT: We report a combined computational and experimental work aimed at estimating
the equilibrium potential for the electroreduction of CO₂ to CO₂⁻ (widely accepted to be the first
and overpotential-determining step) and at throwing new light on the reason behind the lower
overpotentials for CO₂ reduction in imidazolium-based ionic liquid/water mixtures. First, we
obtained an eighty-picosecond ab-initio molecular dynamics trajectory of the CO₂⁻ solvation
structures in an 18% EMIM-BF₄/water mixture, which delivered no evidence of interaction
between EMIM⁺ and CO₂⁻. Second, using the Fc⁺/Fc couple as the non-aqueous reference, we
calculated the equilibrium potential of the CO₂/CO₂⁻ couple in the mixture and aligned it with the
aqueous SHE scale, proving that the equilibrium potential of CO₂/CO₂⁻ in the mixture is about
0.3 V less negative than in the aqueous medium. We then looked for the origin of this catalytic
effect, by comparing the computed vibrational spectra with experimental FTIR spectra. This
revealed the presence of two water populations in the mixture, namely, bulk-like water and water
in the vicinity of EMIM-BF₄. Finally, we compared the hydrogen bonding interactions between
the CO₂⁻ radical and H₂O molecules in water and in the mixture, which showed that stabilization
of CO₂⁻ by water molecules in the EMIM-BF₄/water mixture is stronger than in the aqueous
medium. This suggests that water in EMIM-BF₄/water mixtures could be responsible for the low
overpotentials reported in this kind of electrolytes.

1. Introduction

The electrocatalytic reduction of CO₂ to hydrocarbons has great potential for large-scale
applications. Recently, CO₂ electroreduction to CO at industrial-scale current density has been
achieved,¹⁻⁴ which provides hope that the large-scale conversion of CO₂ to hydrocarbons using
Cu cathodes is also feasible.⁵,⁶ According to Weber’s⁷ approximate technoeconomic analysis,
there is a huge market for hydrocarbons and other commodity chemicals obtained from CO$_2$ electroreduction. However, this technology still faces challenges to become economically viable, one of the most important being the large overpotentials required.

According to our current understanding of the mechanism of CO$_2$ reduction to CO or HCOOH, the large energy difference between the linear CO$_2$ and the bent CO$_2^-$ intermediate is the main responsible for the activation barrier.$^{8,9}$ Therefore, stabilizing CO$_2^-$ would reduce the overpotential required for CO$_2$ electroreduction. Over the past decades, great success has been achieved in developing low overpotential electrochemical cells for electrochemical conversion of CO$_2$ to CO. Among the most outstanding is the system reported by Rosen et al.$^{10}$ in 2011, which employs an EMIM-BF$_4$/H$_2$O mixture (EBH mixture) as electrolyte and exhibits a claimed total overpotential of 0.17 V. Please note that this is the cell overpotential and should, therefore, be the sum of the anodic and cathodic overpotentials for oxygen evolution and CO$_2$ reduction, respectively, plus ohmic losses. As we have discussed in a recent review,$^{11}$ because oxygen evolution on Pt (the anode material used by Rosen et al.) in 0.1 M H$_2$SO$_4$ (the electrolyte in the anode compartment) alone requires an overpotential of at least 0.3-0.4 V, the reported overpotential of 0.17 V is impossibly low. The same group reported later a more reasonable onset cell overvoltage of 0.67 V,$^{12}$ which would correspond to a still remarkably low overpotential for the electroreduction of CO$_2$ to CO of ca. 0.3 V. Such low overpotential was attributed to the stabilization of the CO$_2^-$ radical resulting from the first electron transfer in an EMIM-CO$_2$ complex.$^{10}$ However, this explanation remains controversial ten years after it was first proposed,$^{11,13-24}$ because there is still no evidence for the explanation provided by Rosen et al., no matter how sophisticated the control experiments or complex theoretical calculations attempted.
In experiment, the CO$_2^-$ radical was first detected during, and therefore confirmed as a key intermediate in, the electrocatalytic reduction of CO$_2$ by Bewick and co-workers$^{25}$ in 1973. This was later confirmed by others,$^{26}$ and the equilibrium potential of the CO$_2$/CO$_2^-$ couple was determined in 1989.$^{27,28}$ Not much has been done since in terms of detection of the CO$_2^-$ radical and characterization of its thermodynamic and kinetic properties, mainly due to its instability in water, which often forces experiments in solvents of low proton availability.$^{29}$

Computational methods allow to study reactions involving unstable radicals$^{19,30-35}$ like CO$_2^-$ without having to design sophisticated experiments. Another advantage of computational methods is that the reaction environment can be fully controlled, and quantifying the contribution of each component becomes feasible.$^{36}$ However, calculations of equilibrium potentials of redox couples (such as CO$_2$/CO$_2^-$) in non-aqueous solutions are difficult, even more in mixtures like EMIM-BF$_4$/H$_2$O solutions. Conventional implicit solvation models$^{37-43}$ face challenges in describing the charged solute (for example, the CO$_2^-$ radical) in non-aqueous mixtures because of strong electrostatic interactions at the boundary between the solute and the implicit solvent. Even if explicit solvent molecules are included in the vicinity of the solute to compensate for the electrostatic effects, the calculation of cavitation energies is still questionable, not to mention the accuracy of parameterizations in describing the mixture solution. Therefore, there is a need to study CO$_2$ reduction in an explicitly described, consistent chemical environment as a prerequisite to completely understanding the electrocatalytic reduction of CO$_2$.

Ab initio molecular dynamics (AIMD) can explicitly describe both solutes and solvents at the same level of electronic structure theory, and thus the chemical environment is naturally consistent with experiments. By combining AIMD with free energy perturbation (FEP) methods, Cheng, Sprik and co-workers$^{30,44}$ have developed a thermodynamic scheme that can calculate
equilibrium potentials of any redox couples in any solution with respect to the computational SHE (in water) or Ag/AgCl (in non-aqueous solution). As a remarkable low overpotential for the CO₂ electroreduction was reported by Rosen et al. in an 18 mol% EBH mixture, a rational option is to study the same electrolyte used in those works. Therefore, by using this method, we can calculate the CO₂/CO₂⁻ equilibrium potential in that EBH mixture. To quantify the decrease in overpotential in the EBH mixture, we need to compare the CO₂/CO₂⁻ equilibrium potential in the EBH mixture with that in water in the same potential reference scale. Since the equilibrium potential of ferrocenium/ferrocene (Fc⁺/Fc) in 18 mol% EBH mixture with respect to SHE in water has been reported, we can calculate the CO₂/CO₂⁻ equilibrium potential with respect to the Fc⁺/Fc reference in the EBH mixture, and then align it with the SHE scale in water. By using this approach, we can directly compare the equilibrium potentials of CO₂/CO₂⁻ in aqueous medium with that in the 18 mol% EBH mixture.

In this work, we combined computation and experiment to study the reduction of CO₂ to CO₂⁻ in the EBH mixture. First, we performed AIMD of both CO₂⁻ and CO₂ in the 18 mol% EBH mixture, investigating their solvation structures and exploring the existence of EMIM-CO₂ or CO₂⁻ complexes. Then, we calculated the equilibrium potentials of the CO₂/CO₂⁻ and Fc⁺/Fc redox couples with respect to the computational Ag/AgCl (aCl⁻ = 1) reference electrode (cAgCl) in the EBH mixture. As the experimental equilibrium potential of Fc⁺/Fc against the Ag/AgCl electrode in ionic liquids has been reported, we were able to verify our computational results. Next, we aligned the CO₂/CO₂⁻ equilibrium potential in the 18 mol% EBH mixture with the SHE in water and compared with the CO₂/CO₂⁻ equilibrium potential in pure water, which revealed a clearly less negative equilibrium potential in the EBH mixture. Because the overpotential for the reduction of CO₂ is mainly attributed to the thermodynamic overpotential required to generate
the CO\textsuperscript{2−}, this difference must result in a clearly lower overpotential in the EBH mixture. Finally, we compared computational vibrational frequencies of all the electrolyte media used in the AIMD study with experimental FTIR spectra, which allowed us to conclude that the hydrogen bond interactions between water molecules and CO\textsuperscript{2−} in the EBH mixture are stronger than in the aqueous medium. The strong hydrogen bond interactions help stabilize the CO\textsuperscript{2−} radical and thus reduce the overpotential required for CO\textsubscript{2} electroreduction.

2. Method

2.1 Computational methods

The method for the calculation of equilibrium potentials has been described in detail in previous publications\textsuperscript{30,44,45,47}. In this work, the equilibrium potentials were initially calculated against the cAgCl. For the convenience of the reader, we summarize below a few key points. The detailed derivation process can be found in the Supporting Information.

The free energy changes for the electron transfer or particle solvation reactions are calculated with a combination of the free energy perturbation (FEP) theory and the thermodynamic integration (TI) method. In this method, a thermodynamic path (η from 0 to 1) between two states is connected by a linear combination through a coupling parameter, where the two ends of the path (η = 0 and 1) correspond to the initial and final states, respectively. Thus, the free energy change (ΔA) is obtained using the TI method,

\[ ΔA = \int_{0}^{1} d\eta \langle ΔE \rangle_\eta, \]

where \( \langle ΔE \rangle_\eta \) is the ensemble average of the potential energy difference between the initial \( (E_0) \) and final \( (E_1) \) states at a fixed configuration \( (ΔE = E_1 - E_0) \).\textsuperscript{44}
Using the TI method in Eq. 1, the free energy of oxidation (reduction) from $X^-$ to $X$ ($X$ to $X^-$) can be obtained by reversibly removing (inserting) an electron from the AIMD simulation under periodic boundary conditions (PBC). However, directly inserting an electron in a PBC system charges the system, and renders the reference for the electrostatic potential uncertain. A computational Ag/AgCl ($a_{\text{Cl}^-} = 1$) reference electrode (cAgCl) is developed to recover the potential reference under PBC and align it to the experimental Ag/AgCl ($a_{\text{Cl}^-} = 1$) reference electrode. For a specific oxidation reaction $X^-/X$ with respect to the cAgCl, its full reaction is

$$X^-(\text{aq}) + \text{AgCl}(s) \rightarrow X(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag}(s),$$

and the corresponding equilibrium potential ($U_{X^-/X}^{\text{Ag/AgCl}}$) can be obtained by

$$U_{X^-/X}^{\text{Ag/AgCl}} = (\Delta A_{X^-/X} + \Delta \Delta G_{\text{Cl}^-}^{\text{g.o}} - \Delta A_{\text{Cl}^-} + \Delta A_{\text{LJ}} - \Delta E_{\text{Cl}^-})/e_0. \quad (3)$$

Where $\Delta A_{X^-/X}$, $\Delta A_{\text{Cl}^-}$, and $\Delta A_{\text{LJ}}$ are oxidation free energy of $X^-/X$, desolvation free energy, and formation energy of the Lennard-Jones cavity, respectively. All free energies ($\Delta A$) in this work are obtained by using the Eq. 1. The $\Delta \Delta G_{\text{Cl}^-}^{\text{g.o}} = -1.3\text{eV}$ is the standard Gibbs free energy of formation of the gas phase chloride anion, and $\Delta E_{\text{Cl}^-}$ is the total energy of $\text{Cl}^-$ in the gas phase.  

### 2.2 Modelling setup

In this work, we performed three AIMD simulations. To investigate the solvation structure of $\text{CO}_2^-$ and calculate the $\Delta A_{\text{CO}_2^-/\text{CO}_2}$ for the equilibrium potential calculation, the $\text{CO}_2/\text{CO}_2^-$ model in 18 mol% EBH mixture is conducted (Figure 1a). We also simulated the Fc/Fc$^+$ model (Figure 1b) and the $\text{Cl}^-$ solvation model (Figure 1c) in 18 mol% EBH mixture to compute the equilibrium potential of Fc/Fc$^+$ with respect to cAgCl. Additionally, the equilibrium potentials of $\text{CO}_2/\text{CO}_2^-$...
and Fc/Fc⁺ with respect to cAgCl in a dilute aqueous solution (hereafter referred to as aqueous medium) were also calculated. **For the reader's convenience, we summarise the key parameters of the calculations below.** Details can be found in the Supporting Information.

![Figure 1.](image)

**Figure 1.** Snapshots of the simulations with solvated CO₂⁻ (a), ferrocenium (b), and chloride (c) in the 18 mol% EMIM-BF₄/H₂O mixture. Solutes are displayed using the ball-and-stick model, while the liquorice model presents the electrolyte molecules. Atoms are color coded as follows: purple is Fe, grey is C, red is O, yellow is Cl, white is H, blue is N, pink is B, and green is F. The electrolyte consists of 6 EMIM-BF₄ ion-pairs and 26 water molecules.

All AIMD simulations were performed with the open-source CP2K program. The density functional implementation in the CP2K/Quickstep section is based on the hybrid Gaussian plane wave (GPW) scheme. In this work, we employed the BLYP functional, the Goedecker-Teter-Hutter (GTH) pseudopotentials (core electrons in each element can be found in Table S2), TZP2P-GTH (models of CO₂/CO₂⁻ and Cl⁻ solvation) and DZVP-GTH (Fc/Fc⁺ model) basis sets, and 400 Ry of the plane wave density cut-off. **The dispersion correction was also applied in all calculations using the Grimme D3 method.** The free energy differences ∆A were recomputed at the hybrid functional level of theory (HSE06) using the trajectories generated by BLYP functionals, leading to an effective hybrid level of accuracy in the equilibrium potentials.
The simulation boxes are cubic cells with $L = 13.39$ (models of CO$_2$/CO$_2^-$ and Cl$^-$ solvation) and 13.8 Å (Fc/Fc$^+$ model). All boxes include 6 EMIM-BF$_4$ ion-pairs and 26 water molecules, plus 1 reactant molecule (e.g., CO$_2^-$, Cl$^-$ or Fc$^+$) corresponding to the ambient density. The canonical (NVT) ensemble underwent Langevin molecular dynamics in this work and the temperature of the system was 300 K. To accelerate AIMD simulations, one of the AIMD families, the second-generation Car-Parrinello based molecular dynamics (SGCPMD) was used to sample configurations.\textsuperscript{54} SGCPMD performs almost identical dynamics when compared with Born-Oppenheimer molecular dynamics (BOMD) but at a smaller computational cost.\textsuperscript{55} Furthermore, in the CO$_2$/CO$_2^-$ model, we replaced all the hydrogen atoms in this simulation with deuterium atoms and set the time step to 1 fs. \textbf{The production runs of the SGCPMD simulations were about 80 ps after more than 10 ps equilibration.} To validate the electronic structures described by the SGCPMD simulation, a 20 ps conventional BOMD trajectory with time step $\tau=0.5$ fs was also obtained. Based on the results of CO$_2$/CO$_2^-$ simulation, the vertical energy difference was converged within 20 ps. Therefore, for the Fc/Fc$^+$ and Cl$^-$ solvation simulations, a timestep of 0.5 fs was used, and the production period of SGCPMD was reduced to about 20 ps after 10 ps equilibration.

\subsection*{2.3 ATR-IR}

Absorption infrared spectra were recorded using a Nicolet iS50R FT-IR spectrometer equipped with a liquid N$_2$-cooled mercury cadmium telluride (MCT) detector and a homemade attenuated total reflectance (ATR) accessory, using unpolarized light. Differential spectra are reported in absorbance units and calculated as $-\log \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} \right)$, where $R_{\text{reference}}$ and $R_{\text{sample}}$ are the background and sample spectra, respectively. ATR absorption infrared spectra of EBH mixtures
were recorded by simply covering the surface of a Si prism with a liquid film of the mixture, using the spectrum of the dry Si prism as background. Both the background and sample spectra consisted of 100 interferograms with a spectral resolution of 4 cm$^{-1}$.

3. Results and discussion

3.1 CO$_2^-$ solvation structures
**Figure 2.** Comparison of solute-electrolyte radial distribution functions (RDF) for CO$_2$ (black line) and CO$_2^-$ (red line) in 18 mol% EMIM-BF$_4$/water mixture. Graphs on the left show the distance between the C atom in CO$_2$ or CO$_2^-$ and the C2 (a), C4&C5 (c), N1&N3 (e) sites of EMIM$^+$, while graphs on the right side illustrate hydrogen bonding interactions between O atoms in CO$_2$ or CO$_2^-$ and H2 (b) and H4&H5 (d). The radial distribution function between O atoms in CO$_2$ or CO$_2^-$ and H atoms in water (Hw) is shown in (f). The bin size for the evaluation of the distribution function is of 0.1 Å.

The CO$_2^-$ radical complexation has been proposed as the possible reason behind lower overpotentials for CO$_2$ reduction in EMIM-BF$_4$. Therefore, we carefully investigated the solvation of both CO$_2^-$ and CO$_2$ in the 18 mol% EBH mixture. After 80 ps AIMD simulation and 20 ps BOMD simulation, we found no evidence of interaction between CO$_2^-$ and EMIM$^+$, *i.e.*, EMIM$^+$-CO$_2^-$ complexes involving stable chemical bonds are not formed. However, this does not exclude the stabilization of CO$_2^-$ through hydrogen bonding interactions and other electrostatic interactions. Figure 2 shows radial distribution functions (RDF) in the mixture solvent between C and O atoms of both CO$_2^-$ and CO$_2$ and all the possible active sites on EMIM$^+$ (namely, C2/H2, C4/H4 and C5/H5, See Support Information for notations) as well as hydrogen atoms in water. Nitrogen atoms (N1 and N3) in EMIM$^+$ were also included in order to investigate the distance between CO$_2^-$ or CO$_2$ and the EMIM$^+$ imidazole ring. According to Figures 2(a), (c) and (e), reduction of CO$_2$ to CO$_2^-$ results in an increase of the coordination number of EMIM$^+$ around the solute, while the distance between EMIM$^+$ and the C atom of the solute remains constant. This implies that there is no specific interaction between the C atom of CO$_2^-$ and EMIM$^+$, as the increase of the coordination number can simply be explained by the electrostatic attraction between CO$_2^-$ and EMIM$^+$. In contrast, Figures. 2(b) and (d), show that reduction of CO$_2$ to CO$_2^-$
results in a decrease of the distance between the oxygen atoms and the H4/H5 sites, which seems in agreement with Lau et al.’s conclusion that H4 and H5 help stabilize the CO$_2^-$ radical. However, the maximum lies at $r_{O-H4&H5} = 2.5$ Å, indicating that there is no interaction between them. Interestingly, the maximum at $r_{O-Hw} = 1.8$ Å, characteristic of hydrogen bonding, appearing in Fig. 2(f) upon reduction of CO$_2$ to CO$_2^-$ implies that water molecules in the mixed solvent must play an important role in stabilizing the radical. An intuitive view of the interactions between water molecules and CO$_2^-$ is presented in Figure 3(a).

**Figure 3.** (a): A snapshot of CO$_2^-$ solvation structure in the EMIM-BF$_4$/water mixture. The yellow region is the excess electron density in the CO$_2^-$ model. The figure inside the left circle is the enlarged view of the central region close to CO$_2^-$, and the blue dashed lines are hydrogen bonds formed in this snapshot. A few molecules have been removed in the enlarged figure for a clear view of the hydrogen bond networks between CO$_2^-$ and electrolyte molecules. (b): CO$_2^-$-water binding times obtained from AIMD trajectories in water and in EBH.

Figure 3(a) suggests the formation of hydrogen bonds between CO$_2^-$ and water molecules in the EBH mixture. In principle, it might seem that a similar situation would arise in aqueous solutions. In fact, our simulations reveal that the total number of hydrogen bonds around the
solute is the same in pure water and the EBH mixture. Nevertheless, based on the simulation trajectories, in the EBH mixture CO$_2^-$ forms stable hydrogen bonds with specific water molecules which do not exchange with other water molecules. In contrast, although hydrogen bonds were also formed in the aqueous medium, these do not correspond to specific water molecules interacting with CO$_2^-$, but are continuously being exchanged with other water molecules in the bulk. The CO$_2^-$-water binding time obtained from trajectories in Figure 3(b) proved that the dynamics of water molecules in the EBH are about four times slower than in water. The consequence of these slow dynamics is that CO$_2^-$ forms stable hydrogen bonds with specific water molecules which do not exchange with other water molecules.

3.2 Equilibrium potentials

Based on the solvation structure in Figure 3, a direct catalytic contribution of the EBH to CO$_2$ reduction is quite doubtful. A reduction in overpotential could, however, also stem from the observed change in solvation for EBH mixtures vs. aqueous environment discussed above. To compare the equilibrium potential of the CO$_2$/CO$_2^-$ in EBH mixture with that in water, we need to compute both in at the same reference potential scale. Using Eq. 3 and Eq. S14, we calculated the equilibrium potentials of CO$_2$/CO$_2^-$ and Fc/Fc$^+$ redox couples in the 18 mol% EBH mixture with respect to cAgCl in different levels of density functional theory (DFT) approximation, and computed band edges of the electrolyte. Band edges of the electrolyte, which are the valence band maximum (VBM) and the conduction band minimum (CBM), can be calculated from the average energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the mixture, respectively. Results of vertical energy gaps $\langle \Delta E \rangle_\eta$ and the corresponding thermodynamic integrations $\Delta A$ are presented in Figure 4(a), and all values required in Eq. 3 and Eq. S14 can be found in Tables S5-S8 in the Supporting
Information. In Figure 4(b), we summarize all equilibrium potentials and band-edge positions of the 18 mol% EBH mixture with respect to cAgCl under different DFT approximations. The CBM is 0.3 V more positive at the generalized gradient approximation (GGA) level of theory than with the hybrid functional HSE06, which also shifts the CO₂/CO₂⁻ and Fe⁺/Fc equilibrium potentials positively by about 0.1 V. The VBM of the mixture is about 1 V more negative at the GGA level of theory than with hybrid functional HSE06, which is caused by the delocalization error of DFT at GGA level.

Figure 4. (a) Time accumulation averages of the vertical energies (〈ΔE〉ₜ, left column) and the corresponding thermodynamic integrations (ΔΔ, right column) obtained in this work. Three models from top to bottom are CO₂/CO₂⁻ model, Cl⁻ solvation model, and Fe⁺/Fc model. (b) Equilibrium potentials of CO₂/CO₂⁻, Fe⁺/Fc and band-edge positions of the 18mol% EBH mixture with respect to the cAgCl under different DFT approximations. The GGA level BLYP functional is on the left, and the right is the hybrid level HSE06 functional.

We then calculated the equilibrium potentials of CO₂/CO₂⁻ and Fe/Fc with respect to cAgCl in the aqueous medium, and report all equilibrium potentials in Table 1. Results obtained
in the aqueous medium can be directly compared with the experiment, and the error is about 0.1 V. This error is within our computational uncertainty, and thus implies that the DFT approximations made result in negligible errors in the computation of \( \text{CO}_2/\text{CO}_2^- \) and \( \text{Fc}/\text{Fc}^+ \) equilibrium potentials. However, verifying equilibrium potentials in the EBH mixture is a challenge, because (1) there are few experimental values of the equilibrium potential of \( \text{Fc}/\text{Fc}^+ \) in this EBH mixture, and (2) the reference electrode employed in those experiments cannot be directly compared to \( \text{cAgCl} \). Nevertheless, we still attempted to roughly verify the equilibrium potentials in the EBH mixture, even if with a few approximations.

**Table 1.** Equilibrium potentials of the \( \text{CO}_2/\text{CO}_2^- \) and \( \text{Fc}/\text{Fc}^+ \) redox couples with respect to \( \text{cAgCl} \) in both aqueous medium and 18 mol\% EBH mixture.

<table>
<thead>
<tr>
<th></th>
<th>CO(_2/\text{CO}_2^-) vs. Fc/Fc(^+) (unit in V)</th>
<th>Fc/Fc(^+) vs. cAgCl (unit in V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous medium</td>
<td>Exp. -2.30(^a)</td>
<td>Exp. 0.18(^a)</td>
</tr>
<tr>
<td>Aqueous medium</td>
<td>Cal. (BLYP) -2.40(^b)</td>
<td>Cal. (BLYP) 0.29(^c)</td>
</tr>
<tr>
<td>18 mol% EBH mixture</td>
<td>Cal. (BLYP) -2.28</td>
<td>Cal. (BLYP) 0.20</td>
</tr>
<tr>
<td>18 mol% EBH mixture</td>
<td>Cal. (HSE06) -2.27</td>
<td>Cal. (HSE06) 0.11</td>
</tr>
</tbody>
</table>

\(^a\)Experimental results adopted from CRC handbook.\(^{56}\)

\(^b\)The computational results of CO\(_2/\text{CO}_2^-\) in pure water were adopted from Cheng et al’s work.\(^{30}\)

\(^c\)Computational details of Fc/Fc\(^+\) equilibrium potential in pure water are provided in section S4 in the Supporting Information.
The equilibrium potential of the Fc/Fc\(^+\) redox couple is often used as reference in several non-aqueous electrolytes (IUPAC recommendations). However, the stability of the Fc/Fc\(^+\) redox couple fails in the presence of water, which prevents its use in aqueous solutions. Please note that the Fc/Fc\(^+\) equilibrium potential has to depend on the solvent, as the (electro)chemical potential of the species involved in the electrochemical equilibrium will be different. For example: in aqueous solution, the Fc/Fc\(^+\) equilibrium potential versus the aqueous SHE is 0.40 V,\(^{56}\) while in non-aqueous electrolytes, a considerable higher equilibrium potential (ca. 0.65 V) with respect to the aqueous SHE has been reported.\(^ {46}\)

Rosen et al.\(^ {10}\) used an Ag/Ag\(^+\) electrode immersed in CH\(_3\)CN (ANE) as their reference state. They reported the potential of the ANE in the 18 mol% EBH mixture to be 0.631 V against the aqueous SHE, and an Fc/Fc\(^+\) equilibrium potential in the same EBH mixture of -5.5 mV with respect to ANE. This yields an Fc/Fc\(^+\) equilibrium potential in 18 mol% EBH mixture of 0.625 V vs. aqueous SHE, which we use to convert the equilibrium potential of CO\(_2/\)CO\(_2^−\) in the EBH mixture to the aqueous SHE scale. We summarize the potential alignment result in Figure 5, where the scale on the left corresponds to the potential vs. Fc/Fc\(^+\) in EBH. The scales on the right side of Figure 5 correspond to the aqueous SHE and cAgCl. By definition, the cAgCl is the same as the experimental AgCl reference electrode, and thus the alignment between cAgCl and SHE uses the experimental value of 0.222 V vs. SHE (\(a_{Cl^-} = 1\) in the definition of cAgCl). Please note that scales in different electrolytes cannot be aligned unless a reference state is measured on both scales. Fortunately, we know that the Fc/Fc\(^+\) equilibrium potential in 18 mol% EBH mixture is 0.625 V with respect to the aqueous SHE scale. This allows to align the Fc/Fc\(^+\) scale in EBH with the SHE scale in water in Figure 5. We can now locate the position of the CO\(_2/\)CO\(_2^−\)
equilibrium potential using Table 1. The equilibrium potential of \( \text{CO}_2/\text{CO}_2^- \) vs. \( \text{Fc/Fc}^+ \) is -2.27 V in the EBH mixture and is -2.40 V in water.

![Graph showing potential alignments](image)

**Figure 5.** A schematic view of potential alignments between the \( \text{Fc/Fc}^+ \) reference state in 18 mol% EBH mixture and the aqueous SHE scale. The alignment between \( \text{cAgCl} \) and SHE uses the experimental value of 0.222 V vs. SHE (\( a_{\text{Cl}^-} = 1 \) in the definition of \( \text{cAgCl} \)). The \( \text{Fc/Fc}^+ \) equilibrium potentials in 18 mol% EBH mixture is 0.625 V with respect to the aqueous SHE.\(^{10}\)

If we refer the \( \text{CO}_2/\text{CO}_2^- \) equilibrium potential to the aqueous SHE scale, we obtain a value of -1.65 V in the EBH mixture (Figure 5), which is about 0.3 V lower than in water, in very good agreement with the experimental overpotential reduction reported by Rosen *et al.*\(^{12}\) Please note that we use the computational result of the \( \text{CO}_2/\text{CO}_2^- \) equilibrium potential in water (-2.4 V in Table 1) instead of the experimental value (-2.3 V in Table 1), because the difference between two computational results should be more accurate due to error cancellations. Together with the result in Section 3.1 we can conclude that the stabilization of the \( \text{CO}_2^- \) radical by hydrogen bonding with water molecules in the 18 mol% EBH mixture, and not the formation of
EMIM-CO$_2$ complexes, is responsible for the reported decrease of the overpotential of CO$_2$ electroreduction of about 0.3 V.

3.3 Water in EBH mixtures

Please note that the conclusion above excludes any additional catalytic contribution from the electrode, and thus the only possible way to stabilize the CO$_2^-$ radical in the EBH mixture is the hydrogen bond interaction between the oxygen of CO$_2^-$ and the hydrogen of H$_2$O. In a recent spectroelectrochemical study of the electrocatalytic reduction of CO$_2$ to CO on Au electrodes in an 18 mol% EBH mixture, Papasizza and Cuesta$^{14}$ identified two water populations characterized by O-H stretching frequencies centred at 3610 and 3400 cm$^{-1}$, respectively. They identified these as water with a low degree of hydrogen bonding in an EMIM-BF$_4$-rich environment (3610 cm$^{-1}$) and bulk-like water (3400 cm$^{-1}$), and suggested that these two types of water might play different roles during the electrocatalytic reduction of CO$_2$. It is consistent with common sense that, in the EBH mixture, the large EMIM$^+$ and BF$_4^-$ ions disrupt the hydrogen bond network and separate water molecules into isolated populations with different behaviour. This is also confirmed by our simulation trajectories.

Inspired by the snapshot in Figure 3, we took a closer look at the solvation structure around CO$_2^-$ and identified five types of water in the EBH mixture as illustrated in Figure 6(a). Water molecules are separated based on their hydrogen bonding interactions with other molecules. In Figure 6(a), water #1 and water #5 both have a H atom interacting with an O atom in the CO$_2^-$ radical, and we identify the corresponding O-H stretching mode in water as $\nu_{OH-OC}$. In water #5, the other H atom interacts with the O atom in water #2. We identify the corresponding O-H stretching mode as $\nu_{OH-OH}$. In contrast, the other H atom in water #1 hardly
interacts with other molecules and is therefore identified simply as $\nu_{\text{OH}}$. Accordingly, the two O-H stretching modes in water #2 are both $\nu_{\text{OH-OH}}$. In water #3, one of the H atoms interacts with a F atom in BF$_4^-$, and this O-H stretching mode is identified as $\nu_{\text{OH-F}}$. Water #4 is water in an EMIM-BF$_4$-rich environment and has therefore none of its two hydrogen atoms is hydrogen bonded to any other atom. Both of its O-H stretching modes are identified as $\nu_{\text{OH}}$ in Figure 6(a).

**Figure 6.** (a): An illustration of the CO$_2^-$ solvation structure in the EBH mixture. Five types of water molecules are marked by #1 to #5. (b): Experimental ATR infrared absorption spectra of EMIM-BF$_4$/H$_2$O mixtures with increasing water content. The y-axis corresponds to the mol% of EMIM-BF$_4$. (c): Computed power spectra of the three possible O-H stretching modes ($\nu_{\text{OH-OH}}$, $\nu_{\text{OH-F}}$, and $\nu_{\text{OH}}$) corresponding to the three possible different environments in 18 mol% EMIM-BF$_4$/water mixtures.
The ATR infrared absorption spectra of EBH mixtures with increasing concentration of water shown in Figure 6(b) confirm the correctness of the assignment in our previous work\textsuperscript{14} of the bands at 3610 and 3400 cm\textsuperscript{-1} to water with a low degree of hydrogen bonding in an EMIM-BF\textsubscript{4}-rich environment and bulk-like water, respectively. The peak at 3607 cm\textsuperscript{-1}, and a smaller one at ca. 3550 cm\textsuperscript{-1} which disappears for mixtures with less than 20% EMIM-BF\textsubscript{4}, are absent in 100% EMIM-BF\textsubscript{4} and are the only bands present in the region characteristic of O-H stretching modes when the ionic liquid content is between 82 and 49%, confirming that this must correspond to water molecules in an EMIM-BF\textsubscript{4}-rich environment with very few, if any, hydrogen bonds with other water molecules. The band at 3607 cm\textsuperscript{-1} in Figure 6(b) is consistent with the O-H stretching mode with a low degree of hydrogen bonding, \textit{i.e.}, $\nu_{\text{OH}}$ in Figure 6(a). Since water #1 has this O-H stretching mode with a low degree of hydrogen bonding, we calculated its power spectrum by using the velocity autocorrelation function (VACF) method on top of AIMD trajectories, and present the result in Figure 6(c) (red line). The peak around the 3642 cm\textsuperscript{-1} indicates that our assignment is consistent with the experimental transmission spectra. As a verification, the experimental band at 3560 cm\textsuperscript{-1} is consistent with the $\nu_{\text{OH-F}}$ stretching mode of water #3 computed at 3562 cm\textsuperscript{-1}, as is the experimental trend that this band only exists when the EMIM-BF\textsubscript{4} content is high. The typical bulk-water OH stretching band around 3400 cm\textsuperscript{-1}, with a shoulder around 3300 cm\textsuperscript{-1} which becomes clearer as water content increases, only appears with mixtures containing less than 40% ionic liquid. Its intensity increases with increasing water content. We attribute this band to bulk-like water with a structure and degree of hydrogen bonding similar to liquid water. The results are consistent with the spectrum of $\nu_{\text{OH-OH}}$ in Figure 6(c). The band corresponding to the H-O-H bending mode of water appears at a lower frequency around 1610 cm\textsuperscript{-1} in the mixtures with low water content. Its frequency increases
towards 1640 cm\(^{-1}\) with increasing water concentration, which is also consistent with an increase in the degree of hydrogen bonding. Interestingly, in Figure 6(c), we found the same trend of the H-O-H bending mode from 1610 cm\(^{-1}\) to 1680 cm\(^{-1}\). Please note that, although we have focused our discussion of the computational power spectrum on the O-H stretching modes (e.g., \(\nu_{\text{OH}}\) or \(\nu_{\text{OH}}-\text{F}\)), the spectrum contains all the vibrational information in water, including the vibrational frequencies of the H-O-H bending mode, which are therefore also present in Figure 6(c). The computed vibrational frequencies of the H-O-H bending mode, from lower to higher degree of hydrogen bonding interactions, are 1609 cm\(^{-1}\)(\(\nu_{\text{OH}}\)), 1634 cm\(^{-1}\)(\(\nu_{\text{OH}}-\text{F}\)), and 1676 cm\(^{-1}\)(\(\nu_{\text{OH}}-\text{OH}\)), respectively.

![Diagram](image)

**Figure 7.** (a): An illustration of the CO\(_2^-\) solvation structure in the EBH mixture. Five types of water molecules are marked by #1 to #5. (b)-(f): Computed power spectra in the O-H stretching
region of water types #1 to #5 (black lines). The spectra corresponding to each one of the specific OH vibrations of water types #1 to #5 are illustrated with red and blue lines.

To study how the CO$_2^-$ radical is stabilized by water molecules, we focus on the five types of water molecules in the EBH mixture described above, and calculated their corresponding power spectra in Figures 7(b)-(f). In each one of Figures 7(b) to (f), we include the total power spectrum of water (black lines) and the computed spectrum of each of the O-H stretching modes of each specific type of water (red and blue lines). Based on the results in Figures 7(b) and (f), the O-H stretching mode $\nu_{\text{OH-OC}}$ due to the hydrogen bonding interaction between water #1 and #5 with the CO$_2^-$ radical in the EBH mixture is 3450 cm$^{-1}$. The hydrogen bonding interaction between water and the BF$_4^-$ anion is weaker, and thus the O-H stretching mode $\nu_{\text{OH-F}}$ is 3562 cm$^{-1}$. The wavenumber of the O-H stretching mode is further increased if the H atom in water hardly interacts with other molecules, *i.e.*, has a low degree of hydrogen bonding interactions, and the corresponding value of $\nu_{\text{OH}}$ is higher than 3600 cm$^{-1}$. The spectrum of $\nu_{\text{OH-F}}$ in Figure 7(d) shows two peaks at 3562 cm$^{-1}$ and 3618 cm$^{-1}$, respectively. This is due to the occasional break of the hydrogen bond between the H atom in water #3 and the F atom in BF$_4^-$, leading to an increase in the wavenumber, which becomes similar to $\nu_{\text{OH}}$. 
Figure 8. Computed power spectra of the $\nu_{\text{OH}\text{--OC}}$ (black lines) and $\nu_{\text{OH}\text{--OH}}$ (blue lines) modes in the 18 mol% EBH mixture (a) and in pure water (b) of CO$_2^-$. We also calculated the power spectrum of an aqueous solution containing CO$_2^-$ (Figure 8(b)), where $\nu_{\text{OH}\text{--OH}}$ and $\nu_{\text{OH}\text{--OC}}$ correspond to the same vibrational modes as in the EBH mixture (see Figure 6(a)). Comparing with the power spectrum of CO$_2^-$ in EBH (Figure 8(a)), the $\nu_{\text{OH}\text{--OC}}$ blueshifts from 3450 cm$^{-1}$ to 3494 cm$^{-1}$ in pure water. Here, our computation captures the shift of the $\nu_{\text{OH}\text{--OC}}$ due to interaction with different electrolytes. The lower wavenumber of $\nu_{\text{OH}\text{--OC}}$ in EBH suggests that hydrogen bonding interactions between water molecules and the CO$_2^-$ radical are stronger in the EBH mixture than in pure water. We believe that this enhanced hydrogen bonding between water molecules and the CO$_2^-$ radical is responsible for the stabilization of CO$_2^-$ in the EBH mixture, reducing the overpotential of CO$_2$ electroreduction by 0.3 V.

4. Conclusions
Our work shows that the solvation structure of the CO$_2^-$ radical in the EBH mixture does not reveal any interaction between CO$_2^-$ and EMIM$^+$ that might account for a stabilization of the radical intermediate and, therefore, a decrease of the apparent activation energy. We found, however, stable hydrogen bonding with specific water molecules in the EBH mixture. In order to quantitively confirm whether the overpotential decrease in the EBH mixture can be attributed to the reduction of the potential required for electroreduction of CO$_2$ to CO$_2^-$, the equilibrium potential of this redox couple was calculated with respect to the Fc$^+/Fc$ in the same electrolyte. We then converted the reference state from the Fc$^+/Fc$ in EBH mixture to the aqueous SHE scale and found a positive shift of approximately 0.3 V of the CO$_2$/CO$_2^-$ equilibrium potential in the EBH mixture as compared to the aqueous medium. Finally, we compared experimental and computed vibrational spectra of water in aqueous solution and in the EBH mixture, with CO$_2^-$ present in both cases, which suggested that hydrogen bonding between water molecules and CO$_2^-$ in in the EBH mixture is stronger than with water in the aqueous medium. This enhancement of the hydrogen bonding interactions renders the CO$_2^-$ intermediate more stable in the EBH mixture, thus accounting for the overpotential decrease for CO$_2$ electroreduction of about 0.3 V.

Our studies confirm that the EBH mixture lowers the overpotential for CO$_2$ reduction by shifting the CO$_2$/CO$_2^-$ equilibrium potential positively, although the catalytic effect is not due to the formation of EMIM-CO$_2$ complexes and might instead be connected to a stabilization through hydrogen bonding of the CO$_2^-$ radical inside a water cage in a water-in-salt environment. Improved catalysis by stabilization of unstable radicals in a suitable cage might be a general feature in catalysis, as suggested by recent reports involving aldehyde reduction$^{57}$ and reports of anti-Arrhenius kinetics in the electroreduction and electrooxidation, respectively, of CO$_2$ and CH$_4$ in gas hydrates at sub-zero temperatures.$^{58}$ Our results are also consistent with very recent
reports on the relevance of electrostatic stabilization of the CO$_2^-$ radical for the electrochemical reduction of CO$_2$.\textsuperscript{2,59–61}

This is also the first time that equilibrium potentials in non-aqueous solution have been calculated in the actual chemical environment and directly compared with experiments to reveal eventual catalytic effects of the solvent excluding effects from other components. Because the computational methods used herein can be applied to any redox couple in any solution, this can be a new protocol for studying homogeneous catalysis. The calculated equilibrium potentials can then be referred to practical reference scales, such as cAgCl or Fe$^+/$/Fc, which can greatly enhance the synergy between computation and experiment and lead to improved understanding of electrocatalytic reactions, especially in non-aqueous solutions.\textsuperscript{62–68}

AUTHOR INFORMATION

Corresponding Author

Jun Cheng - State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China; Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM), Xiamen, China;
Email: chengjun@xmu.edu.cn

Angel Cuesta - Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, AB24 3UE, Scotland, UK; Centre for Energy Transition, University of Aberdeen, AB24 3FX, Scotland, UK;
Email: angel.cuestaciscar@abdn.ac.uk
ASSOCIATED CONTENT

The following files are available free of charge.

Method of the potential shift $V_0$ correction, computational data of all equilibrium potentials calculations in both EBH mixture and pure water, atom labelling of EMIM-BF$_4$, RDF results in EBH mixture and validation of Fc$^+/Fc$ vs cAgCl in EBH mixture. (PDF)

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https://doi.org/10.3390/nano9020304.

For Table of Contents Only
(Supporting information)

Water-in-salt environment reduces the overpotential for reduction of CO$_2$ to CO$_2^-$ in ionic liquid/water mixtures

Xiao-Hui Yang$^a$, Marco Papasizza$^{b,†}$, Angel Cuesta$^{b,c,*}$ and Jun Cheng$^{a,d,*}$

$^a$ State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

$^b$ Department of Chemistry, School of Natural and Computing Sciences, University of Aberdeen, AB24 3UE, Scotland, UK.

$^c$ Centre for Energy Transition, University of Aberdeen, AB24 3FX, Scotland, UK.

$^d$ Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM), Xiamen, China.

$^†$ Current address: Sweetch Energy, 6 Rue Pierre Joseph Colin, 3500 Rennes, France.

KEYWORDS: electrochemical reduction of CO$_2$, room temperature ionic liquid, $ab$ $initio$ molecular dynamics, absorption infrared spectra, hydrogen bond networks
**S1. Computational methods**

**S1.1 Thermodynamic integration.**

The free energy changes for the electron transfer or particle solvation reactions are calculated with a combination of the free energy perturbation (FEP) theory and the thermodynamic integration (TI) method. In FEP theory, two states can be connected by a linear combination through a coupling parameter, \( \eta \) (\( \eta \in [0,1] \)). Thus, a thermodynamic path (\( \eta \) from 0 to 1) between two states is constructed, where the two ends of the path (\( \eta = 0 \) and 1) correspond to the initial and final states, respectively. Thus, a fictitious hybrid energy state can be written as

\[
E_\eta = (1 - \eta)E_0 + \eta E_1, \tag{S1}
\]

where \( E_0 \) and \( E_1 \) are the potential energy of the initial and final states, respectively. The free energy change (\( \Delta A \)) is obtained exactly using the TI method,

\[
\Delta A = \int_0^1 d\eta \langle \Delta E \rangle_\eta, \tag{S2}
\]

where \( \langle \Delta E \rangle_\eta \) is the ensemble average of the energy difference between the reactant and product states at a fixed configuration (i.e., vertical energy gap \( \Delta E = \frac{\partial E_\eta}{\partial \eta} = E_1 - E_0 \)).

**S1.2 Free energy calculations.**

We use a generic redox couple \( X^-/X \) to represent the computation of electron-transfer free energies. Using the TI method in eq. S2, the free energy of oxidation (reduction) from \( X^- \) to \( X \) (\( X \) to \( X^- \)) can be obtained by reversibly removing (inserting) an electron from the AIMD simulation under periodic boundary conditions (PBC). However, directly inserting an electron in a PBC system charges the system, and renders the reference for the electrostatic potential uncertain. This electrostatic potential uncertainty is due to the standard Ewald summation under PBC. The electrostatic potential of the charged system has a potential shift \( V_{0,X^-/X} \) compared to the neutral system, and thus the oxidation free energy \( \Delta A_{X^-/X} \) obtained from eq. S2 does not correspond to the adiabatic ionization free energy (AIP\(_{X^-}\)), by a difference equal to \( q_{X^-/X} \cdot V_{0,X^-/X} \). The AIP\(_{X^-}\) can therefore be obtained from eq. S3, where \( q_{X^-/X} = -1 \) is the total charge difference between the initial and final states.

\[
\text{AIP}_{X^-} = \Delta A_{X^-/X} - q_{X^-/X} \cdot V_{0,X^-/X} \tag{S3}
\]

**S1.3 Computational Ag/AgCl (\( a_{Cl^-} = 1 \)) reference electrode (cAgCl).**

A computational Ag/AgCl reference electrode is developed to recover the potential reference under PBC. For a specific oxidation reaction \( X/X \) with respect to the cAgCl, its full reaction and the corresponding equilibrium potential (\( U_{X^-/X}^{Ag/AgCl} \)) are

\[
X^-(aq) + AgCl(s) \rightarrow X(aq) + Cl^-(aq) + Ag(s) \tag{S4a}
\]
\[ U^{\text{Ag/AgCl}}_{X^-/X} = \Delta G/e_0. \] (S4b)

The overall reaction in eq. S4a is composed of two half-reactions, the anodic reaction and the cathodic reaction. The anodic reaction is the oxidation of the solvated species \( X^- \) to \( X \), thus the electrode reaction and the corresponding absolute equilibrium potential of \( X^-/X \) \( (U^{\text{abs}}_{X^-/X}) \) are

\[ X^- (\text{aq}) \rightarrow X(\text{aq}) + e^- (\text{vac}). \] (S5a)

\[ U^{\text{abs}}_{X^-/X} = \text{AIP}_{X^-}/e_0. \] (S5b)

Where the \( \text{AIP}_{X^-} \) is considered as the electronic work function of an electron bound in solvated \( X^- \), and is obtained from the computation by using the TI method (eq. S3). The cathodic reaction and the corresponding absolute electrode potential \( (U^{\text{abs}}_{\text{Ag/AgCl}}) \) are

\[ \text{AgCl}(s) + e^- (\text{vac.}) \rightarrow \text{Cl}^- (\text{aq}) + \text{Ag}(s). \] (S6a)

\[ U^{\text{abs}}_{\text{Ag/AgCl}} = (\Delta G_{\text{Cl}^-}^{\text{E.o}} - W_{\text{Cl}^-})/e_0. \] (S6b)

Where \( \Delta G_{\text{Cl}^-}^{\text{E.o}} = -1.3 \text{eV} \) is the standard Gibbs free energy of formation of the gas phase chloride anion, and \( W_{\text{Cl}^-} \) is the work function of \( \text{Cl}^- \).

This \( W_{\text{Cl}^-} \) is the energy of extracting a solvated \( \text{Cl}^- \) from the electrolyte to the gas phase, and can be obtained from computation by using the TI method, \( i.e., \) a chloride ion is reversibly inserted and removed. In practice, the \( \text{Cl}^- \) is not directly removed but replaced by a dummy, in order to preserve the location for the subsequent insertion of the \( \text{Cl}^- \). The dummy should have zero interactions with electrolytes. However, if no restraints are applied on the dummy, it could overlap with solvent molecules, and thus the subsequent insertion of the \( \text{Cl}^- \) cannot have a logical configuration. To avoid the overlap between inserted \( \text{Cl}^- \) and solvent molecules, we apply a repulsive potential between the dummy and solvent molecules. Same as the above-described calculation of oxidation free energy in eq. S3, reversibly inserting and removing the chloride ion in the system under PBC also lead to a potential shift \( (V_{0,\text{Cl}^-}) \) in the charged system compared to the natural system. Therefore, the desolvation free energy \( (\Delta A_{\text{Cl}^-}) \) obtained from eq. S2 also has a corresponding potential shift \( (q_{\text{Cl}^-} \cdot V_{0,\text{Cl}^-}) \), and \( q_{\text{Cl}^-} = -1 \) is the total charge difference between the initial and final states. In addition, due to the repulsive potential applied to the dummy, a cavity is formed around the dummy. The formation energy of this cavity \( (\Delta A_{\text{LJ}}) \) is then obtained by using the TI method in eq. S2. Please note that the work function of \( \text{Cl}^- \) corresponds to transferring it from the electrolyte to the gas phase, not to removing it altogether. Therefore, the total energy of \( \text{Cl}^- \) in the gas phase \( (\Delta E_{\text{Cl}^-}) \) needs to be added back. In summary, the equation to calculate the work function is

\[ W_{\text{Cl}^-} = \Delta A_{\text{Cl}^-} - \Delta A_{\text{LJ}} + \Delta E_{\text{Cl}^-} - q_{\text{Cl}^-} \cdot V_{0,\text{Cl}^-}. \] (S7)

After substituting the \( W_{\text{Cl}^-} \) in eq. S6b and the \( \text{AIP}_{X^-} \) in eq. S5b by eqs. S7 and S3, respectively, the equation to calculate the equilibrium potential of \( X^-/X \) with respect to the cAgCl is
\[ e_0 U_{X^-/X}^{Ag/AgCl} = \Delta H_{X^-} + \Delta G_{CI^-}^{E,0} - W_{CI^-} \]
\[ = \Delta A_{X^-/X} + \Delta_f G_{CI^-}^{E,0} - \Delta A_{CI^-} + \Delta A_{LJ} - \Delta E_{CI^-} + (q_{CI^-} \cdot V_{0,CI^-} - q_{X^-/X} \cdot V_{0,X^-/X}) \]

(S8)

If the \( \Delta A_{X^-/X} \) and \( \Delta A_{CI^-} \) are obtained in the same computational setup (e.g., unit-cell dimensions, number of solvent molecules, and density functional approximations), the corresponding potential shift \( q_{X^-/X} \cdot V_{0,X^-/X} \) and \( q_{CI^-} \cdot V_{0,CI^-} \) are the same.4 In this case, the last term \( (q_{CI^-} \cdot V_{0,CI^-} - q_{X^-/X} \cdot V_{0,X^-/X}) \) in eq. S8 is zero, and thus the resulting equation for the equilibrium potential calculation of X/X with respect to the cAgCl is

\[ e_0 U_{X^-/X}^{Ag/AgCl} = \Delta A_{X^-/X} + \Delta_f G_{CI^-}^{E,0} - \Delta A_{CI^-} + \Delta A_{LJ} - \Delta E_{CI^-}. \]

(S9)

**S1.4 Correction of potential shift \( V_0 \)**

The potential shift \( q \cdot V_0 \) in eq. S8 is a correction term with respect to vacuum. It can be cancelled if the same computational setup is used in simulation. Alternatively, this potential correction term can also be interpreted by employing the electrostatic potential of bulk solvent \( \varepsilon \). Taking the calculation of \( \Delta A_{X^-/X} \) as an example, the corresponding potential shift is \( q_{X^-/X} \cdot V_{0,X^-/X} \). If a constant \( C \) can be employed as the potential difference between vacuum and the potential in this unit-cell where the solvent electrostatic potential is zero \((\varepsilon^0 = 0)\), the potential correction can be replaced by

\[ q_{X^-/X} \cdot V_{0,X^-/X} = q_{X^-/X} (C + (\varepsilon_{X^-} - \varepsilon^0)) \]

(S10)

Where the \( \varepsilon_{X^-} \) represents the electrostatic potential of bulk solvent when the simulation net charge is not zero. Similarly, in the calculation of \( \Delta A_{CI^-} \), the potential correction can be replaced by

\[ q_{CI^-} \cdot V_{0,CI^-} = q_{CI^-} (C + (\varepsilon_{CI^-} - \varepsilon^0)) \]

(S11)

Therefore, the last term \( (q_{CI^-} \cdot V_{0,CI^-} - q_{X^-/X} \cdot V_{0,X^-/X}) \) in eq. S8 is

\[ q_{CI^-} \cdot V_{0,CI^-} - q_{X^-/X} \cdot V_{0,X^-/X} = q_{CI^-} \cdot \varepsilon_{CI^-} - q_{X^-/X} \cdot \varepsilon_{X^-}. \]

(S12)

Where \( q_{X^-/X} = -1 \) and \( q_{CI^-} = -1 \) are the total charge difference between the initial and final states. Substituting the above eq. S12 into eq. S8, and the equilibrium potential of X/X redox couple against the Ag/AgCl \((a_{CI^-} = 1)\) reference electrode is:

\[ e_0 U_{X^-/X}^{Ag/AgCl} = \Delta A_{X^-/X} + \Delta_f G_{CI^-}^{E,0} - \Delta A_{CI^-} + \Delta A_{LJ} - \Delta E_{CI^-} + (q_{CI^-} \cdot \varepsilon_{CI^-} - q_{X^-/X} \cdot \varepsilon_{X^-}) \]
\[ = \Delta A_{X^-/X} - \Delta A_{CI^-} + \Delta A_{LJ} - \Delta E_{CI^-} + \Delta_f G_{CI^-}^{E,0} + e_0 (\varepsilon_{X^-} - \varepsilon_{CI^-}) \]

(S13)

**S2. Fe/Fe\(^+\) gas phase ionization energies**
To evaluate the energy difference derived by DFT approximations in equilibrium potential calculations, the ionization energy (IP) of Fc/Fc⁺ in the gas phase were calculated and validated with well accepted experimental results. Table S1 shows ionization energies of Fc/Fc⁺ with different basis sets and functionals, basis sets like double-ζ basis with polarization function (DZVP-MOLOPT-SR-GTH), triple-ζ basis with two sets of polarization functions (TZP2P-MOLOPT-SR-GTH) and quadruple-ζ basis with polarization function (Ahlrichs-def2-QZVP) were employed. Core electrons were also represented by the Goedecker-Teter-Hutter (GTH) pseudopotentials in calculations with a notation “Yes”, while the calculation with “all electrons” means no pseudopotential is employed in the calculation. Here, the 2s, 2p electrons of C, the 3s, 3p, 3d, 4s electrons of Fe were treated as valence electrons.

Table S1. Calculated ionization potentials of Fc/Fc⁺ in the gas phase. ∆E is the difference with the experimental value. The experimental value is adopted from the NIST Chemistry WebBook.⁵

<table>
<thead>
<tr>
<th>Functionals / basis sets / pseudopotentials</th>
<th>Total energy (Hartree)</th>
<th>IP (eV)</th>
<th>ΔE_{Fc/Fc⁺} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLYP / DZVP / Yes</td>
<td>-185.924</td>
<td>-185.690</td>
<td>6.373</td>
</tr>
<tr>
<td>BLYP / TZV2P / Yes</td>
<td>-185.938</td>
<td>-185.700</td>
<td>6.457</td>
</tr>
<tr>
<td>HSE06 / DZVP / Yes</td>
<td>-186.197</td>
<td>-185.964</td>
<td>6.336</td>
</tr>
<tr>
<td>HSE06 / TZV2P / Yes</td>
<td>-186.206</td>
<td>-185.971</td>
<td>6.397</td>
</tr>
<tr>
<td>B3LYP / TZV2P / Yes</td>
<td>-186.038</td>
<td>-185.812</td>
<td>6.147</td>
</tr>
<tr>
<td>BLYP / QZVP / all_electrons</td>
<td>-1650.924</td>
<td>-1650.680</td>
<td>6.637</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td></td>
<td>6.71</td>
</tr>
</tbody>
</table>

According to the results in Table S1, ionization energies can be properly calculated at GGA level with large basis set employed without pseudopotentials. Due to the limitation of computational cost, our DFTMD simulations were performed with pseudopotentials and the basis set is DZVP. Therefore, the ionization energy difference ΔE_{Fc/Fc⁺} was directly added in eq. S13, and the final equation to calculate the Fc/Fc⁺ equilibrium potential was replaced by:

\[ e_0 U_{Fc/Fc⁺}^{Ag/AgCl} = \Delta A_{Fc/Fc⁺} - \Delta E_{Fc/Fc⁺} - \Delta A_{Cl⁻} + \Delta A_{Li} - E_{Cl⁻} + \Delta G_{Cl⁻}^{Gr} + e_0(\varepsilon_{X⁺} - \varepsilon_{Cl⁻}) \]

(S14)
**S3. Modelling setup**

**Table S2.** Computational setup of the three models in this work.

<table>
<thead>
<tr>
<th>Models</th>
<th>Box size L (Å)</th>
<th>Electrolytes</th>
<th>Basis sets</th>
<th>Pseudopotentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂/CO₂⁻</td>
<td>13.39</td>
<td>6 EMIM-BF₄ and 26 water molecules</td>
<td>TZV2P-GTH</td>
<td>1s electrons of B, C, N, O, F</td>
</tr>
<tr>
<td>Fe/Fc⁺</td>
<td>13.80</td>
<td>6 EMIM-BF₄ and 26 water molecules</td>
<td>DZVP-GTH</td>
<td>1s, 2s, and 2p electrons of Fe</td>
</tr>
<tr>
<td>Cl⁻ solvation</td>
<td>13.39</td>
<td>6 EMIM-BF₄ and 26 water molecules</td>
<td>TZV2P-GTH</td>
<td>1s electrons of B, C, N, O, F</td>
</tr>
</tbody>
</table>

**Table S3.** Parameters used in Langevin dynamics during the SGCPMD.

<table>
<thead>
<tr>
<th>Models</th>
<th>Gamma (fs⁻¹)</th>
<th>Noisy gamma of each thermo region</th>
<th>( EMIM-BF_4 )</th>
<th>Water</th>
<th>Solute</th>
<th>( EMIM-BF_4 )</th>
<th>Water</th>
<th>Solute</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂/CO₂⁻</td>
<td>1.00E-03</td>
<td>2.00E-04</td>
<td>2.00E-04</td>
<td>2.20E-04</td>
<td>2.20E-04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe/Fc⁺</td>
<td>1.00E-03</td>
<td>2.00E-04</td>
<td>2.00E-04</td>
<td>2.00E-04</td>
<td>2.00E-04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻ solvation</td>
<td>1.00E-03</td>
<td>2.00E-04</td>
<td>2.00E-04</td>
<td>2.00E-04</td>
<td>2.00E-04</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**S4. Fe/Fc⁺ equilibrium potential in aqueous solution**

The Fe/Fc⁺ equilibrium potential with respect to the computational Ag/AgCl \( (a_{\text{Cl}^-} = 1 \text{ M}) \) reference electrode was calculated by employing Equation S5. Free energies such as \( \Delta A_{\text{Fc/Fc}^+} \), \( \Delta A_{\text{Cl}^-} \) and \( \Delta A_{\text{LJ}} \) are obtained by employing the thermodynamic integration approach. Here energies related to the work function of Cl⁻, \( W_{\text{Cl}^-} \), was adopted from previous work, and the setup inconsistency was corrected by recalculating free energy differences. Thus, the only term that needs to be calculated is the oxidation free energy of Fe/Fc⁺.

**S4.1 Computational details.** The simulation box for Fe/Fc⁺ was cubic cell with size at \( L = 12.80 \text{ Å} \), including 62 water molecules and 1 Fc/Fc⁺ solute. Canonical (NVT) ensemble underwent Langevin molecular dynamics in this work and the temperature of the system was 300 K. Time step of this simulation was 0.5 fs and the cut-off energy of the finest grid level of plane wave density was set to 400 Ry. The SGCPMD simulation was performed with the BLYP functional for the exchange correlation approximation, double-\( \zeta \) basis with polarization functions (DZVP-MOLOPT-SR-GTH).
standard basis set, Goedecker-Teter-Hutter (GTH) pseudopotentials and the van der Waals correction with Grimme D3 method. The production periods of DFTMD simulations are ~6 ps after more than 2 ps equilibration.

**S4.2 Fc/Fc* vs. cAgCl in aqueous solution.** The molecular dynamic simulation of Fe/Fc* in aqueous solution was carried out for about 6 ps, and the energy convergence was shown in the Figure S1 below.

**Figure S1.** Time accumulation averages of the vertical energies (a, b and c) and thermodynamic integration path (d) for Fe/Fc* redox couple oxidation reaction in aqueous solution. Three integration points (η = 0, 0.5, 1) are presented in (a, b and c), respectively. The picture (d) is the averaged vertical energy difference ⟨ΔE⟩η as a function of the coupling parameter η.

The free energy of ΔA_{Cl}− in previous work is obtained with the basis set TZV2P, and the value is about 0.43 eV compared to the DZVP basis set. Therefore, the ΔA_{Cl}− is 407.54 eV in this work and the formation energy of cavity in the simulation is the same as in the previous work ΔA_{LJ} = 0.21 eV. Electrostatic potentials of both ε_{Fc+} and ε_{Cl−} were cumulatively averaged from the edges of the simulation box. Once the total energy of gas phase chloride E_{Cl}− = −407.45 eV is obtained to yield the potential of Fe/Fc* vs. Ag/AgCl in aqueous solution (Table S4).
Table S4. Summary of free energies used in Equation S5 and the equilibrium potential of Fc/Fc\(^+\) vs. Ag/AgCl (a_{Cl}^- = 1 M) in water. \(eU_{Fc/Fc}^{Ag/AgCl}\) is the calculated equilibrium potential while \(eU_{exp}\) is the result in experiment. Error of this calculation is \(\Delta U_{error}=0.1\) eV.

<table>
<thead>
<tr>
<th>(\Delta A_{Fc/Fc^+})</th>
<th>(\varepsilon_{Fc^+})</th>
<th>(\Delta A_{Cl^-})</th>
<th>(\varepsilon_{Cl^-})</th>
<th>(\Delta A_{LJ})</th>
<th>(eU_{Fc/Fc}^{Ag/AgCl})</th>
<th>(eU_{exp})</th>
<th>(\Delta U_{error})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>0.69</td>
<td>407.54</td>
<td>-0.11</td>
<td>0.21</td>
<td>0.28</td>
<td>0.18</td>
<td>0.10</td>
</tr>
</tbody>
</table>

S5. Chemical structure of EMIM-BF\(_4\).  

![Chemical structure of EMIM-BF\(_4\).](image)

Figure S2. Atom labelling used in this work. The EMIM\(^+\) is the cation on the left, and BF\(_4\)\(^-\) is the anion on the right hand.

S6. Free energy calculations in the EBH mixture.

The equilibrium potentials of Fc/Fc\(^+\) and CO\(_2^-\)/CO\(_2\) with respect to cAgCl in the EBH mixture were calculated by employing Equations S5 and S4, respectively. Helmholtz free energies \(\Delta A\) were obtained by employing the TI approach, which requires the averaged vertical energy gap \(\langle \Delta E \rangle_\eta\).

S6.1. Calculation of \(\Delta A_{CO_2^-/CO_2}\). The oxidation free energy of CO\(_2^-\)/CO\(_2\) redox couple, \(\Delta A_{CO_2^-/CO_2}\), was firstly calculated at GGA level with BLYP functional and TZV2P basis sets, then \(\Delta A_{CO_2^-/CO_2}\) at HSE06 level with the same basis set was obtained by recalculating the vertical energy difference. Table S5 below shows all calculated vertical energies for the oxidation free energy of CO\(_2^-\)/CO\(_2\).
Table S5. Summary of vertical energy gap $\langle \Delta E \rangle_\eta$ and the corresponding thermodynamic integrations $\Delta A_{\text{CO}_2/\text{CO}_2}$ calculated in this work.

<table>
<thead>
<tr>
<th>CO$_2$/CO$_2$ with TZV2P basis set</th>
<th>$\eta$</th>
<th>BLYP</th>
<th>HSE06</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.60</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>-2.47</td>
<td>-2.51</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>-2.59</td>
<td>-2.63</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-2.79</td>
<td>-2.83</td>
</tr>
<tr>
<td>$\Delta A_{\text{CO}_2/\text{CO}_2}$</td>
<td>-2.21</td>
<td>-2.16</td>
<td></td>
</tr>
</tbody>
</table>

S6.2. Calculation of $\Delta A_{\text{Cl}^-}$. The solvation free energy of Cl$^-$ in the mixture solvent, $\Delta A_{\text{Cl}^-}$, was firstly calculated at GGA level with BLYP functional and TZV2P basis sets, then $\Delta A_{\text{Cl}^-}$ at different functionals and different basis sets were also obtained by recalculating the vertical energy difference. Table S6 below shows all energies corresponding to the calculation of Cl$^-$ work function.

Table S6. Summary of vertical energy gap $\langle \Delta E \rangle_\eta$ and the corresponding thermodynamic integrations $\Delta A_{\text{Cl}^-}$ calculated in this work. Total energies of Cl$^-$ in the gas phase were also included.

<table>
<thead>
<tr>
<th>Cl dummy with</th>
<th>TZV2P basis set</th>
<th>DZVP basis set</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta$</td>
<td>BLYP</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>408.43</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>407.12</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>405.79</td>
</tr>
<tr>
<td>$\Delta A_{\text{Cl}^-}$</td>
<td>407.14</td>
<td>408.43</td>
</tr>
<tr>
<td>$E_{\text{Cl}^-}$</td>
<td>-408.12</td>
<td>-409.29</td>
</tr>
</tbody>
</table>

S6.3. Calculation of $\Delta A_{\text{Fc}/\text{Fc}^+}$. The oxidation free energy of Fc/Fc$^+$ redox couple $\Delta A_{\text{Fc}/\text{Fc}^+}$, was firstly calculated at GGA level with BLYP functional and DZVP basis sets, then $\Delta A_{\text{Fc}/\text{Fc}^+}$ at HSE06 level with the same basis set was obtained by recalculating the vertical energy difference. Table S7 below shows all calculated vertical energies for the oxidation free energy of CO$_2$/CO$_2$.
Table S7. Summary of vertical energy gap $\langle \Delta E \rangle_\eta$ and the corresponding thermodynamic integrations $\Delta A_{F_c/F_c^+}$ calculated in this work.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>BLYP</th>
<th>HSE06</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.28</td>
<td>0.24</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.26</td>
<td>-0.29</td>
</tr>
<tr>
<td>1</td>
<td>-0.62</td>
<td>-0.65</td>
</tr>
<tr>
<td>$\Delta A_{F_c/F_c^+}$</td>
<td>-0.23</td>
<td>-0.26</td>
</tr>
</tbody>
</table>

S6.4. Calculation of $\Delta A_{LJ}$. The last one that requires thermodynamic integral calculation is the formation energy of the cavity $\Delta A_{LJ}$ in the electrolyte. This formation energy calculation was carried out in the classical molecular dynamics, and forcefields employed in this simulation were borrowed from Ghoshdastidar et al.’s work, and little difference were confirmed when employing OPLS/AA parameters. The derivative of the potential energy in this work was calculated by using the finite difference method. Here, the range of $\sigma$ was changed from 0 to 3.5 Å, and averaged $\langle dE/d\sigma \rangle_\sigma$ at different integration points $\sigma$ are presented in Figure S3, and the integration value is $\Delta A_{LJ} = 0.14$ eV.

![Graph](image)

**Figure S3.** The averaged derivative of the potential energy surface $\langle dE/d\sigma \rangle_\sigma$ as a function of the finite distance $\sigma$. Integration of the plot from $\sigma = 0$ to 3.5 Å yields the formation energy of the cavity, $\Delta A_{LJ}$. Integration points $\sigma$ smaller than 1.5 Å were ignored because the derivative result is less than $10^{-4}$ eV, thus the actual integration starts from 1.5 Å.
**S7. Equilibrium potential results in EBH mixture.**

**Table S8.** Equilibrium potentials of CO$_2$/CO$_2$ and Fc/Fc$^+$ redox couples in the 18mol% EBH mixtures with respect to cAgCl. $\Delta \varepsilon_{\text{bulk}} = (\varepsilon_X - \varepsilon_{\text{Cl}^-})$ is the electrostatic potential difference between two simulations.

<table>
<thead>
<tr>
<th>Energy</th>
<th>GGA/BLYP</th>
<th>Hybrid/HSE06</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO$_2$/CO$_2$ vs. cAgCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta A_{\text{Cl}^-}/d$</td>
<td>407.14</td>
<td>408.43</td>
</tr>
<tr>
<td>$\Delta A_{\text{LJ}}$</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>$E_{\text{Cl}^-}$</td>
<td>-408.12</td>
<td>-409.29</td>
</tr>
<tr>
<td>$\Delta A_{\text{CO}_2/\text{CO}_2}$</td>
<td>-2.21</td>
<td>-2.16</td>
</tr>
<tr>
<td>$\Delta \varepsilon_{\text{bulk}}$</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>$eU_{\text{Ag}/\text{AgCl}}^{\text{CO}_2/\text{CO}_2}$</td>
<td>-2.10</td>
<td>-2.16</td>
</tr>
<tr>
<td><strong>Fc/Fc$^+$ vs. cAgCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta A_{\text{Cl}^-}/d$</td>
<td>406.89</td>
<td>408.14</td>
</tr>
<tr>
<td>$\Delta A_{\text{LJ}}$</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>$E_{\text{Cl}^-}$</td>
<td>-407.45</td>
<td>-408.64</td>
</tr>
<tr>
<td>$\Delta A_{\text{Fc}/\text{Fc}^+}$</td>
<td>-0.23</td>
<td>-0.26</td>
</tr>
<tr>
<td>$\Delta E_{\text{Fc}/\text{Fc}^+}$</td>
<td>0.34</td>
<td>0.37</td>
</tr>
<tr>
<td>$\Delta \varepsilon_{\text{bulk}}$</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>$eU_{\text{Ag}/\text{AgCl}}^{\text{Fc}/\text{Fc}^+}$</td>
<td>0.18</td>
<td>0.11</td>
</tr>
</tbody>
</table>
S8. Validation of $\text{Fc}^+/\text{Fc}$ vs cAgCl in EBH mixture.

The computed $\text{Fc}^+/\text{Fc}$ equilibrium potential with respect to the computational Ag/AgCl reference electrode in the 18 mol% EMIM-BF$_4$/water mixture is 0.2 V at the GGA level and 0.1 V using the hybrid functional HSE06. This is in good agreement with the experimental value of 0.156 ± 0.010 V reported by Ohsaka and co-workers, measured with a homemade Ag/AgCl wire immersed in the pure (i.e., dry and chloride-free) EMIM-BF$_4$. Because our computational Ag/AgCl reference electrode is calculated for activity of chloride 1, we have corrected Ohsaka’s and co-workers’ value assuming that, in their case, the activity of Cl$^-$ is determined by the solubility product of AgCl, as follows:

\[
U_{\text{Au/sol}}^{\text{Ag/AgClwire}} = U_{\text{Au/sol}}^{\text{Ag/AgCl}} - \frac{RT}{F} \ln a_{\text{Cl}^-} \\
\approx U_{\text{Au/sol}}^{\text{Ag/AgCl}} - \frac{RT}{2F} \ln K_{sp} \tag{S15}
\]

Where the $K_{sp}$ is the solubility product of AgCl in the mixture, $R$ is ideal gas constant, $T$ is the temperature in Kelvin and $F$ is the Faraday constant. Kakiuchi et al. reported the solubility of AgCl in 1-Methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide ([OMIM]$^+$[TFSA$^-$]), to be 6.3x10$^{-5}$ mol L$^{-1}$ at room temperature, about 5 times more soluble than in water. If the solubilities of AgCl in EMIM-BF$_4$ and OMIM-TFSA are assumed to be similar, the potential of Ohsaka’s and co-workers’ “homemade Ag/AgCl wire” with respect to our computational Ag/AgCl ($a_{\text{Cl}^-} = 1$ M) reference electrode is about 0.25 V. An additional difference is that our simulations correspond to an 18 mol% EMIM-BF$_4$/water mixture as opposed to dry EMIM-BF$_4$. If we ignore this difference, the experimental $\text{Fc}^+/\text{Fc}$ equilibrium potential of 0.156 V measured by Ohsaka and co-workers corresponds to -0.09 V in our computational Ag/AgCl ($a_{\text{Cl}^-} = 1$ M) scale. The result of our simulation (0.1 V), is therefore about 0.2 V more positive.

Considering the various approximations involved in the computation, and errors to the approximate value of the $K_{sp}$ difference between the two different mixtures, this is an acceptable error. To better illustrate the source of the 0.2 V error, here, we list the specific approximations as follows.

1. The solubility of AgCl in pure EMIM-BF$_4$ was not found. Thus, we use the solubility of AgCl in pure [OMIM]$^+$[TFSA$^-$]. In this step, we assume the solubility difference between two ionic liquids, EMIM-BF$_4$ and [OMIM]$^+$[TFSA$^-$], is small.

2. After having the solubility of AgCl in pure ionic liquid, we assume that the activity of Cl$^-$ can be obtained from the solubility product in such a low concentration of Cl$^-$, as shown in Eq. S15.

3. In this way, we concluded that our result is about 0.2 V positive compared to the experiment. However, please note that the chemical potential difference between the 18 mol% EBH mixture and pure EMIM-BF$_4$ is not considered yet. The solubility of AgCl in the [OMIM]$^+$[TFSA$^-$] is about 5 times larger than water, and thus if the water content increases, this error is reduced.
4. We know that the experimentally measured Fc/Fc⁺ is 0.4 V in water, while it is 0.625 V in EBH, and about 0.68 V in pure EMIM-BF₄. Therefore, not only the chemical potential of Cl⁻ is different in pure EMIM-BF₄ and EBH mixture, but also the equilibrium potential of Fc/Fc⁺ changes if the water content increases.

In practical equilibrium potential calculations, none of the above assumptions are included, and thus the error should be much smaller than 0.2 V.

S9. References


