

Protic Imidazolium Ionic Liquids for Electroreduction of CO₂

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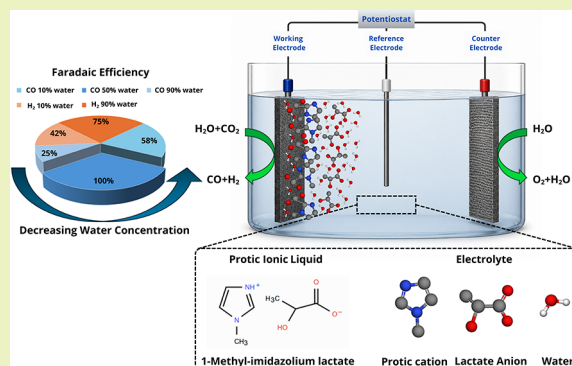
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ABSTRACT: Protic ionic liquids characterized by permutable protons have important applications in electrochemistry. This work represents an unprecedented report of the use of such electrolytes for CO₂ electroreduction (ECR) into CO at 10 bar and near room temperature (45 °C) on zinc electrodes. It was observed that when protic ILs are synthesized from strong acids, the competition with the hydrogen evolution reaction increases. In contrast, the use of softer acids in the synthesis significantly enhances CO production. Imidazolium-based protic ILs were chosen due to their known high CO₂ solubility and consequently their potential to increase reaction productivity. The electrolytes were electrochemically characterized, their conductivities and diffusion coefficients were determined, and their performance was compared. Despite the aqueous nature of the electrolyte, remarkably, 100% Faradaic efficiencies were obtained with [HMIM][Lac] containing 50 wt % water. The performance of the aqueous protic 50 wt % [HMIM][Lac] electrolyte surpassed the performance of the non-protic 50 wt % [EMIM][OTf] electrolyte. Furthermore, among the investigated water concentrations, the maximum CO production for the protic 50 wt % [HMIM][Lac] (177 μmol/cm²) is of the same order as the magnitude of 90 wt % [EMIM][OTf] (271 μmol/cm²), an almost pure IL, more expensive, and less sustainable electrolyte. The non-fluorinated bio-based lactate anion concurs to the higher sustainability of the process. Hydrophilic protic ILs are thus promising as electrolytes for ECR.

KEYWORDS: protic ionic liquids, electrochemical CO₂ reduction, carbon capture and utilization, electrolytes, syngas



1. INTRODUCTION

The possibility of generating sustainable fuels and chemical building blocks from electrochemical CO₂ reduction (ECR) coupled with renewable energy sources is the subject of extensive research. ECR technology depends on many parameters, one of the most significant being the nature of the electrolyte. While aqueous electrolytes have been the focus of most studies, the use of ionic liquids (ILs) as electrolyte components remains an emerging and rapidly expanding field of investigation.

The tunable properties of ILs make them suitable candidates for a variety of electrochemical applications, including ECR. Additionally, some IL families exhibit excellent CO₂ solubility, which is crucial for efficient CO₂ reduction processes. These properties, combined with their tunable nature—where the cation and anion combinations can be customized—make ILs highly promising for integrating CO₂ capture with conversion processes, leading to potentially economically viable solutions. To the best of our knowledge, the first report of ILs being used for ECR dates back to 2004.¹ In this pioneering work, a water-saturated, hydrophobic 1-ethyl-3-methyl-imidazolium tetrafluoroborate IL ([BMIM][PF₆]) was employed to generate syngas at high pressure, acknowledging that CO₂ solubility in ILs is pressure-dependent.

To address the challenges posed by the higher viscosities of ILs in comparison to aqueous electrolytes, several studies explored the dissolution of hydrophobic ILs in organic solvents such as acetonitrile. These mixtures were then tested as electrolytes for ECR.^{2,3} Additionally, a smaller number of studies have focused on hydrophilic ILs dissolved in organic solvents^{4,5} or even ternary mixtures consisting of ILs, organic solvents, and water, further complicating the issue of electrolyte recycling.

Despite the promising applications of ILs in ECR, the mechanism by which ILs promote the reduction of CO₂ remains incompletely understood. A deeper understanding of this mechanism is essential for the development of more efficient IL-based electrolytes. Several proposed mechanisms are outlined in the literature, each contributing to the current understanding of IL-mediated CO₂ reduction.

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Rudnev et al.⁶ investigated the use of ILs as the sole electrolyte component for CO₂ reduction and suggested that the co-catalyst effect is a result of a synergistic interaction between the chemical properties of the IL (outer sphere mechanism) and those of the catalytic material (inner sphere mechanism). This effect appears to be specific to certain combinations of ILs and electrode materials. These findings align with those of Tanner et al.,⁷ who explored the influence of electrode material, cation, and anion on CO₂ reduction to CO in pure hydrophobic ILs and in the hydrophilic IL [BMIM][BF₄]. They observed that variations in peak potentials from cyclic voltammograms of different cations (0.4 V) were much smaller than those seen for variations in electrode materials (1.5 V). Tanner and colleagues suggested that the process likely involves a chemical step, such as the binding of the cation to the surface of a silver electrode, followed by desorption, allowing CO₂ to arrive at the electrode to be irreversibly reduced. This supports the idea of an inner sphere mechanism on the silver electrode, while the desorption process from the electrode's double layer can be viewed as part of the outer sphere mechanism.

Hanc-Scherer et al.⁸ investigated CO₂ electroreduction in pure hydrophobic IL [EMIM][NTf₂] on a platinum electrode. When a proton source is not available, they concluded that the catalytic activity could be explained by the formation of an adduct [EMIM-CO₂][−], which involved the reduction of both the EMIM⁺ cation and CO₂. When a proton source was introduced in the form of [H⁺][NTf₂][−], formic acid (HCOOH) formation was observed, with a concomitant inhibition of EMIM⁺ reduction. The availability of protons is thus an important factor in defining the reaction pathway.

Subsequent studies have investigated CO₂ electroreduction in ILs dissolved in anhydrous organic solvents. For example, Sun et al.⁹ found that replacing the supporting electrolyte tetraethylammonium perchlorate with [EMIM][NTf₂] in anhydrous acetonitrile led to enhanced CO₂ reduction to CO, rather than the formation of oxalate anions, and decreased the overpotential at a Pb electrode. Further, increasing the concentration of [EMIM][NTf₂] led to the formation of carboxylate species, with CO₂ being covalently linked to the imidazolium ring along with CO.

Lau et al.¹⁰ attributed the catalytic activity of imidazolium ILs to the stabilization of the high-energy intermediate CO₂[−], which forms hydrogen bonds with the C4-H or C5-H positions of the imidazolium cation. These interactions were observed to involve anions such as tetrafluoroborate (BF₄[−]), tetrafluoromethanesulfonate (OTf[−]), and bis(trifluoromethanesulfonyl)imide (TFSI[−]) in solutions containing 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile.

Neyrizi et al.¹¹ examined the effect of imidazolium cations on the electroreduction of CO₂ in anhydrous acetonitrile, correlating the acidity of the C2-H carbon by varying the functionality of the cation in the N1 and N2 positions. Their study demonstrated that the reaction involved a concerted electron–proton transfer to the electrode-adsorbed CO₂ intermediate determining the reaction rate.

Liu et al.¹² highlighted the importance of collective ion correlations and their organization in reactivity, using an electrolyte consisting of EMIMBF₄ in acetonitrile with TBA BF₄ as a supporting electrolyte and small amounts of water. Their findings indicated that the maximum reactivity occurred when the electrified interface exhibited the strongest shielding effect, stabilizing charged or polar intermediates via electric fields.

Further work by Noh et al.¹³ demonstrated that the rate of CO₂ reduction is controlled by the initial entropic state of the electrolyte, which depends on the applied potential and the organization of cations at the electrochemical interface. Thus, cation organization is crucial in influencing the reaction rate.

Although a significant body of work has focused on IL-based electrolytes for ECR, the number of IL structures explored remains limited. To expand the range of ILs used in ECR, Messias et al.¹⁴ investigated hydrophilic picolinium-based electrolytes for CO₂ reduction at pressures above atmospheric levels. They concluded that predicting the influence of water on reactivity is challenging, as several parameters—such as conductivity, viscosity, CO₂ solubility, and the local concentration of IL at the electrode surface—have a decisive contribution.

In this work, a new class of ILs as constituents of electrolytes for CO₂ reduction are investigated systematically. Namely, imidazolium protic ILs were chosen due to their known high CO₂ solubility. The use of these solutions in ECR, to our knowledge, is here described for the first time. As they are characterized by active or permutable protons, they show great potential for specific applications such as ECR, in which proton transfer plays a role in the reaction mechanism.¹⁴ In Figure 1, the chemical structures of protic ionic liquids employed in this work are depicted.

2. MATERIALS AND METHODS

2.1. Materials and Reagents

Following an optimized synthetic procedure, the protic ionic liquids 1-methyl-imidazolium formate [HMIM][For], 1-methyl-imidazolium acetate [HMIM][Ac], and 1-methyl-imidazolium lactate [HMIM][Lac] were synthesized in our lab.^{15–18} 1-Ethyl-3-methyl-imidazolium trifluoromethanesulfonate was purchased from Iolitec with a purity of >99%. Before use, it was dried overnight under vacuum.

1-Methyl-imidazole (TCL, >99%), acetic acid (Merck Emplura, 99.8%), formic acid (Sigma Aldrich, 99%), and lactic acid (BDH, 75%) were used for the preparation of ILs without further purification. ¹H-NMR spectra were obtained at room temperature in DMSO on a Bruker AMX400 equipment. Chemical shifts are reported downfield in parts per million (ppm). Elemental analysis was performed with a Thermo Finnigan instrument, Series: Flash EA 1112 by Laboratório de Análises at LAQV-REQUIMTE.

Carbon dioxide (N45 purity 99.995%) and nitrogen (99.999 purity), both from Air Liquide, were employed.

2.2. Preparation of Protic Ionic Liquids

The following protic ILs were derived from strong acids: 1-methyl-imidazolium hydrogen sulfate [HMIM][HSO₄], 1-methylimidazolium methanesulfonate [HMIM][CH₃SO₃], tetramethylguanidinium hydrogen sulfate [TMGH][HSO₄], pyridinium hydrogen sulfate [H-Pyr][HSO₄], and 4-picolinium hydrogen sulfate [H(4)PIC][HSO₄]. These ILs were prepared by addition of 1 equivalent of sulfuric acid (H₂SO₄) and mesylic acid (CH₃SO₃H) in acetonitrile solution. These solutions were stirred overnight at room temperature. The final products were obtained in quantitative yields after evaporation of acetonitrile and drying under vacuum.^{19,20} ¹H-NMR chemical shifts (ppm) of the prepared ILs are presented below.

[HMIM][HSO₄]. ¹H-NMR (400 MHz, DMSO) δ: 9.05 (s, 1H), 7.69 (m, 2H), 6.89 (s, 1H), 3.87 (s, 3H) ppm.

[HMIM][CH₃SO₃]. ¹H-NMR (400 MHz, DMSO-d₆) δ: 9.043 (s, 1H); 7.67 (d, 2H, *J* = 12 Hz); 3.87 (s, 3H); 3.39 (s, 1H); 2.33 (s, 3H) ppm.

[PyrH][HSO₄]. ¹H-NMR (400 MHz, D₂O) δ: 8.77 (m, 2H), 8.62 (m, 1H), 8.07 (m, 2H) ppm.

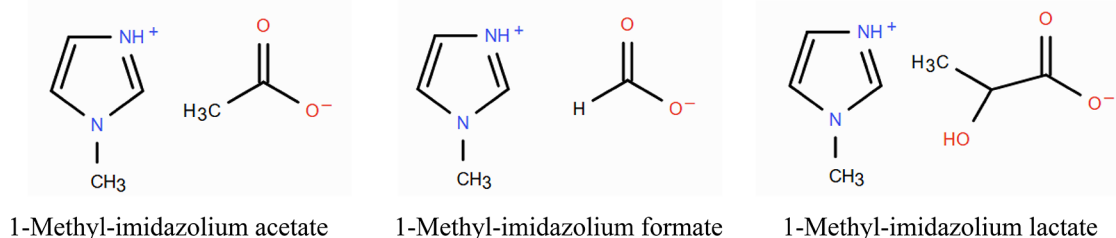


Figure 1. Chemical structures of the protic ionic liquids employed in this work.

[4-picH][HSO₄]. ¹H-NMR (400 MHz, CDCl₃) δ: 14.37 (s, 1H), 8.47 (m, 2H), 7.66 (m, 2H), 2.31 (s, 3H) ppm.

[TMGH][HSO₄]. ¹H-NMR (δ, CDCl₃, 400 MHz): 2.81 (s, 1H), 1.61 (s, 12H), 0.91 (s, 2H) ppm.

The following protic ILs were derived from softer acids: 1-methyl-imidazolium formate [HMIM][For], 1-methyl-imidazolium acetate [HMIM][Ac], and 1-methyl-imidazolium lactate [HMIM][Lac]. They were prepared by neutralization of the Brønsted acids (formic acid, acetic acid, and lactic acid) with 1-methyl-imidazole.^{15–18} These solutions were stirred overnight at room temperature, using ethanol (EtOH) as a solvent. The final products were obtained in quantitative yields after evaporation of ethanol and drying under vacuum. ¹H-NMR chemical shifts (ppm) of the prepared ILs are presented below.

[HMIM][Ac]. ¹H NMR (400 MHz, DMSO-d) δ: 1.91 (s, 3H), 3.65 (s, 3H), 6.89 (t, 1H), 7.11 (t, 1H), 7.58 (s, 1H) ppm.

[HMIM][For]. ¹H NMR (400 MHz, DMSO-d) δ: 3.67 (d, 3H), 6.98 (dd, 1H), 7.18 (dq, 1H), 7.76 (m, 1H), 8.23 (dd, 1H), 10.21 (s, 1H) ppm. Viscous colorless liquid obtained in quantitative yield.

[HMIM][Lac]. ¹H NMR (400 MHz, DMSO-d) δ: 1.24 (d, 3H), 3.65 (s, 3H), 4.04 (q, 1H), 6.91 (t, 1H), 7.12 (s, 1H), 7.63 (s, 1H) ppm. Viscous colorless liquid obtained in quantitative yield.

2.3. Electrochemical Measurements

2.3.1. Cyclic Voltammetry. An undivided high-pressure cell with a three-electrode system described in detail elsewhere was used.²¹ In brief, it consists of a high-pressure cell with a glass beaker containing an electrolyte volume of 5 cm³ enclosed in a 50 cm³ stainless steel cylindrical high-pressure vessel. Cathode: zinc foil, ca. 1.3 cm²; sacrificial anode: ca. 1.3 cm² zinc foil; quasi reference electrode: Ag rod. The voltammograms were recorded by a PGSTAT128N-Autolab 84469 potentiostat in a potential range from −0.5 V to −2.5 V vs Ag/Ag⁺ at 45 °C, 10 bar pressure of CO₂ or N₂ and at a scan rate of 50 mV/s. Aqueous solutions of ILs with different concentrations were tested as electrolytes.

2.3.2. Electrolysis. Galvanostatic electrolysis was undertaken employing the facility described in Section 2.3.1. CO₂ was introduced into the cell at 10 bar. After about 1 h at 45 °C, the electrolyte was saturated in CO₂, and the experiment was started under stirring. The gaseous reaction mixture was analyzed by gas chromatography using an Agilent Micro GC 3000 with a TCD detector. The sampling and analysis procedure is described elsewhere.²¹

2.3.3. Electrochemical Impedance Spectroscopy. The same conditions and setup for cyclic voltammetry and electrolysis were used, with the exception of the counter electrode that was a commercial IrO₂-based electrode so that the results could be easily transferred to a two chamber membrane electrolyzer.²² Detailed description can be found elsewhere.¹⁴ The Nyquist plots were measured at fixed potentials in the range of −1.2 V to −1.8 V vs Ag/Ag⁺ with an AC amplitude of 5 mV at frequencies from 100 kHz down to 50 mHz. Data was analyzed with the software ZView.

3. RESULTS AND DISCUSSION

ILs liquid at room temperature and pressure and hydrophilic were selected to avoid difficulties with additional phase

formation with different CO₂ solubilities and physical and chemical properties such as viscosity, conductivity, and thermal stability. Aiming at an industrial application, the simplicity of a single phase electrolyte would also be desirable. Protic ILs derived from strong acid anions (1-methyl-imidazolium hydrogen sulfate [HMIM][HSO₄], 1-methyl-imidazolium methanesulfonate [HMIM][CH₃SO₃], tetramethylguanidinium hydrogen sulfate [TMGH][HSO₄], pyridinium hydrogen sulfate [H-Pyr][HSO₄], 4-picolinium hydrogen sulfate [H(4)PIC][HSO₄]) and weak acid anions ([HMIM][For], [HMIM][Ac], and [HMIM][Lac]) were synthesized to evaluate their performance. In the latter case, carboxylic acid anions with different chain lengths were tested to also evaluate the influence of this parameter in the electrochemical reaction.

3.1. Cyclic Voltammetry Characterization

During the cyclic voltammetry analysis, the onset potentials (E_{onset}) were defined as the potential at which current density reaches −1 mA cm^{−2}.²³ From Table 1, it is possible to observe that for the [HMIM] cation, the onset potential does not vary significantly with the change of anions. However, when compared with the [EMIM][OTf] in a N₂ atmosphere, the onset potential is substantially less negative.

It was also examined how the different water compositions affect voltammograms. In Figure 2, the voltammograms of the dry ILs in N₂ and CO₂ atmospheres are compared with the electrolytes under investigation. The study of the [EMIM][OTf] based-electrolyte was presented in a previous work,¹⁴ where it was observed that the E_{onset} diminishes with augmenting water content except for the case of 90 wt % water content. The oxidation peak in both atmospheres in the voltammograms of dry [EMIM][OTf] was attributed to the oxidation of the reduced [EMIM] cations. When water was added up to a concentration of 10 wt %, the oxidation peak in the CO₂ atmosphere increased and is related to a clear reduction process that involves the [EMIM] cation, CO₂, and water. 50 wt % water composition yielded the highest current densities. In the case of [HMIM][For] electrolyte (Figure 2a), an oxidation peak is only visible in the voltammogram with 90 wt % water at −0.92 V vs Ag/Ag⁺ (QRE). E_{onset} does not vary considerably with water content (Table S1, Supporting Information); for a water composition of 50 wt %, a small reduction peak is identified at −0.76 V vs Ag/Ag⁺ (QRE). No further peaks are observed for other water compositions.

For the [HMIM][Ac] based electrolyte (Figure 2b), E_{onset} does not change considerably with water content (Table S1, Supporting Information). The electrolyte containing 50 wt % water yields the highest current densities for applied potentials more negative than −1.3 V vs Ag/Ag⁺ (QRE).

Table 1. Onset Potentials for Dry Ionic Liquids

IL	E_{onset} (V) vs Ag/Ag ⁺			
	[EMIM][OTf]	[HMIM][For]	[HMIM][Ac]	[HMIM][Lac]
Dry IL in N ₂	−1.69	−0.91	−1.11	−1.22
Dry IL in CO ₂	−1.30	−0.94	−1.13	−1.22

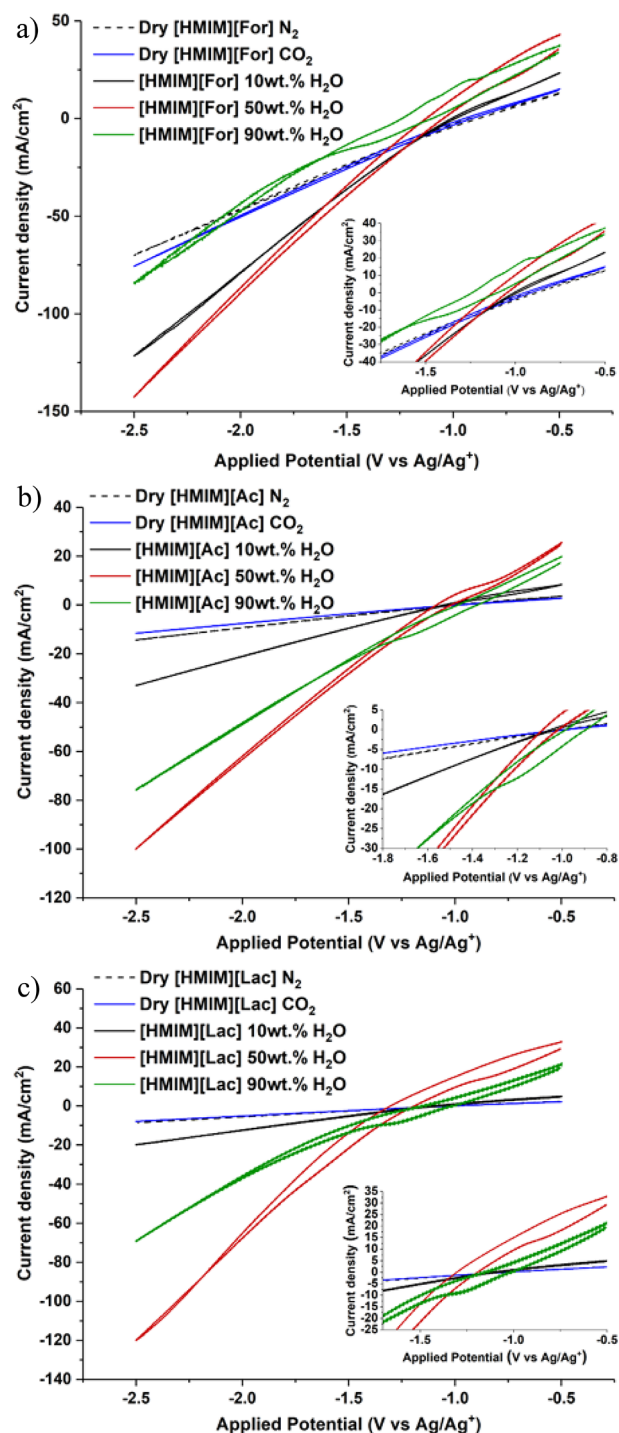


Figure 2. Comparison of voltammograms: (a) [HMIM][For], (b) [HMIM][Ac], and (c) [HMIM][Lac].

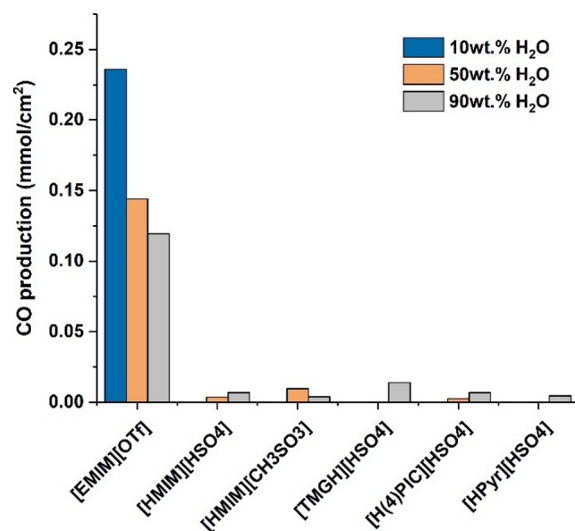
However, for less negative applied potentials, reduction current densities are higher for the electrolyte containing 90 wt % water. No oxidation peaks are identified in all the water compositions selected.

For the [HMIM][Lac] electrolytes (Figure 2c), E_{onset} shows similar values for all water contents, −1.2 V vs Ag/Ag⁺ (QRE), except for 90 wt % water that exhibits a more positive E_{onset} at −1.03 V vs Ag/Ag⁺ (QRE). An irreversible reduction peak is observed at −0.74 V and −1.27 V vs Ag/Ag⁺ (QRE) for 50 wt % and 90 wt % water, respectively. For applied potentials, more negative than −1.35 V vs Ag/Ag⁺ (QRE), the maximum current densities are obtained with the electrolyte containing 50 wt % water. However, for less negative applied potentials, reduction current densities are higher for the electrolyte containing 90 wt % water.

3.2. Electrochemical Reduction of CO₂

Initially, five protic ionic liquids with a strong acid as the anion were studied. In Figure 3, CO productions are plotted for the different electrolyte solutions. Applied current density was in the range of −3 to −7.7 mA/cm², and 50C of charge was passed. It can be verified that the productions are significantly lower when compared to [EMIM][OTf]. It is important to consider that the pH of all the electrolytes is around 1.5 at atmospheric pressure, while the pH of the [EMIM][OTf] electrolyte is around 5.5 and/or 6.5. In these conditions of lower pH, the competition by the hydrogen evolution reaction is predominant. For this reason, more detailed characterization was not undertaken.

Then, ILs based on [HMIM] cations combined with soft acids as anions were investigated. In Figure 4, the production of H₂ and CO is plotted for the electrolyte solutions. For [EMIM][OTf] and [HMIM][Ac] based-electrolytes, the increase of water content corresponds to a lower production of CO. However, for the [HMIM][For] and [HMIM][Lac], the figure shows that higher CO production is obtained with 50 wt % water, with production values of 9.24×10^{-2} and 1.77×10^{-1} mmol/cm², respectively. Figure 4b shows that for the [HMIM][Lac], only CO is produced, and no electrolytic

Figure 3. CO productions with different electrolytes: [EMIM][OTf], [HMIM][HSO₄], [HMIM][CH₃SO₃], [TMGH][HSO₄], [H(4)PIC][HSO₄], and [HPyr][HSO₄].

H₂ is produced during this electrolysis. To evaluate the influence of the cation, electrolysis is carried out with lactic acid. The results showed that only hydrogen was produced. This demonstrated that the ionic liquid is crucial for CO₂ reduction.

The differences among selectivities in terms of anion contribution may be probably explained by the difference in hydrogen bonding between water molecules and the anions and self-association of the anions. As lactic acid is a stronger acid than acetic acid ($pK_a = 3.86$ vs 4.76 at 25°C and atmospheric pressure), the deprotonation extent will be higher. Consequently, the hydrogen bonding of water molecules with lactate anion will also be higher than that of the acetate anion, resulting in a better shielding of the cathode toward HER by the lactate anion. Formic acid is a compact smaller molecule ($pK_a = 3.75$), where self-association will exist in greater extent, creating a less efficient barrier for HER. Thus, in more dilute solutions, the IL [HMIM][Ac] exhibits the lowest selectivity. In more concentrated solution, water does not compete so effectively for hydrogen bond formation, with the carboxylic moiety of formate resulting in an increased competition of HER.²⁴

For 10 wt % water, CO production increases with chain length of the protic ILs. This is not the case for the other water compositions. [HMIM][Ac] presents the lowest production.

The selectivity of the electrochemical reaction is measured by the Faradaic efficiency (FE), and the calculation is described in detail in the Supporting Information. The production of H₂ by a chemical pathway due to the corrosion of zinc in acid medium during the stabilization period before electrolysis is started explains the Faradaic efficiencies above 100% detected. This problem can be overcome when the system is run in continuous mode with the cathode under a negative potential. CO and H₂ were the only gaseous products detected. From Table 2, it can be observed that [HMIM][Lac] achieved 100% selectivity for CO production with 50 wt % water content. The lower selectivity for CO production was obtained with [HMIM][For] at 10 and 90 wt % water and [HMIM][Ac] at 90 wt % water with FE values of 12.41%, 13.07%, and 10.04%, respectively.

3.3. Electrochemical Impedance Spectroscopy Analysis

Charge transfer, double layer effects, and diffusion phenomena occurring in CO₂ electroreduction can be interpreted by means of electric circuit elements. In Nyquist plots, electrolyte resistance can be derived from high frequency region – resistor R₀. Charge transfer resistance and double layer can be assessed from data in the medium frequency region – RC elements, where capacitor C is generalized to a fractional order capacitor. Diffusion phenomena can be evaluated in the low frequency region by the Warburg elements – W. The phenomena under study were selected to be represented by an equivalent circuit depicted in Figure 5.

Figure 6 shows the Nyquist plots obtained for the different ILs with the three compositions of water for an applied potential of -1.2 V vs Ag/Ag⁺ (QRE). Tables 3, 4, and 5 report the fitting parameters for 10, 50, and 90 wt % water, respectively. A good agreement with experimental results was achieved. The error is higher for the [EMIM][OTf]-based electrolyte with 10 wt % water that presents the highest value of chi-squared. The results can be interpreted by the presence of two time constants for all the electrolytes tested. When the water concentration increases for the [HMIM][For]-based electrolyte, no diffusional components are found after fitting

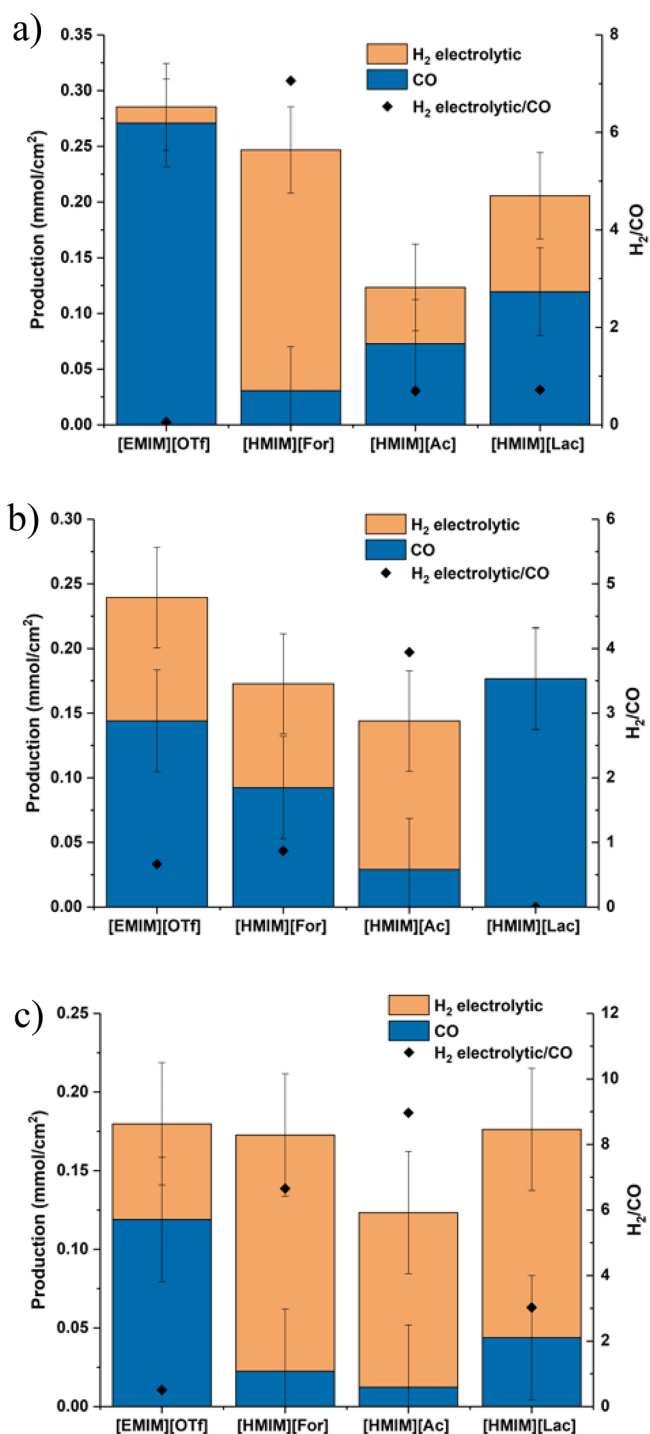


Figure 4. Hydrogen and CO productions for water concentrations of (a) 10 wt %, (b) 50 wt %, and (c) 90 wt %.

the EIS data, implying that mass transfer of species is not the limiting factor. The [HMIM][Ac]-based electrolyte shows one diffusional component when water concentration increases. The [HMIM][Lac]-based electrolyte shows a diffusional component for 50 wt % water. This component is not observed when the water concentration increases to 90 wt %. In contrast to these situations, in [EMIM][OTf]-based electrolytes, when water concentration increases, diffusional components become more pronounced, and the results for 90 wt % water are well

Table 2. CO Production and Faradaic Efficiencies

Ionic Liquid	[H ₂ O] (wt %)	CO (mmol/cm ²)	FE CO (%)
[EMIM][OTf]	10	2.71×10^{-1}	87.35
[HMIM][For]	10	3.06×10^{-2}	12.41
[HMIM][Ac]	10	7.29×10^{-2}	59.09
[HMIM][Lac]	10	1.20×10^{-1}	58.13
[EMIM][OTf]	50	1.44×10^{-1}	60.21
[HMIM][For]	50	9.24×10^{-2}	53.49
[HMIM][Ac]	50	2.91×10^{-2}	20.23
[HMIM][Lac]	50	1.77×10^{-1}	100.00
[EMIM][OTf]	90	1.19×10^{-1}	49.73
[HMIM][For]	90	2.26×10^{-2}	13.07
[HMIM][Ac]	90	1.24×10^{-2}	10.04
[HMIM][Lac]	90	4.38×10^{-2}	24.86

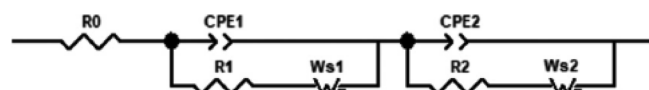


Figure 5. Equivalent circuit model selected. R0 electrolyte resistance; R1, R2 charge transfer resistances; CPE1, CPE2 fractional order capacitors; Ws1, Ws2 Warburg elements.

described by the equivalent circuit in Figure 5 with two Warburg elements Ws.

Observing the resistance of the electrolyte R0 for all the IL-based electrolyte studied, it is possible to conclude that the protic ILs possess a different response compared to [EM-IM][OTf]. For the [EMIM][OTf]-based electrolytes, R0 increases when the water content is 90 wt %. On the contrary, [HMIM][Lac] presents a pronounced decrease in R0 when the water content increases. The [HMIM][Lac] with 10 wt % water shows the highest electrolyte resistance of 272.3 Ω decreasing to 40.25 and 24.4 Ω for 50 wt % and 90 wt % water, respectively. [HMIM][Ac] and [HMIM][For] exhibit the lowest R0 for 50 wt % water, with a resistance of 11.52 Ω for [HMIM][For], which is the lowest among the electrolytes studied.

A deviation from real capacitance indicated by the coefficient of the constant phase element n1 has been justified by the ionic liquid reduced and/or adsorbed on the cathode. This behavior was observed for all the IL-based electrolytes at all water compositions studied, except for the [HMIM][Lac] with 10 wt % and 50 wt % water.

In [HMIM][For]-based electrolytes, R1 does not change significantly when water concentration increases from 10 wt % to 50 wt % but increases for the water concentration of 90 wt %. For [HMIM][Ac]-based electrolytes, R1 decreases when the water content increases to 50 wt % and increases again for the water concentration of 90 wt %. In [HMIM][Lac]-based electrolytes, R1 decreases when the water content increases to 50 wt % and increases significantly for the water concentration of 90 wt %. [EMIM][OTf]-based electrolytes still show a different trend: R1 increases for the water concentration of 50 wt % and decreases for the water concentration of 90 wt %. The lowest values of R1, 0.47 Ω and 0.51 Ω , correspond to the electrolytes consisting of [HMIM][Lac] and [HMIM][Ac] with 50 wt % water, respectively.

In [HMIM][For] and [HMIM][Lac]-based electrolytes, R2 increases significantly when the water content is 90 wt %. In [HMIM][Ac]-based electrolytes, R2 increases slightly with the increase in water concentration. [EMIM][OTf]-based

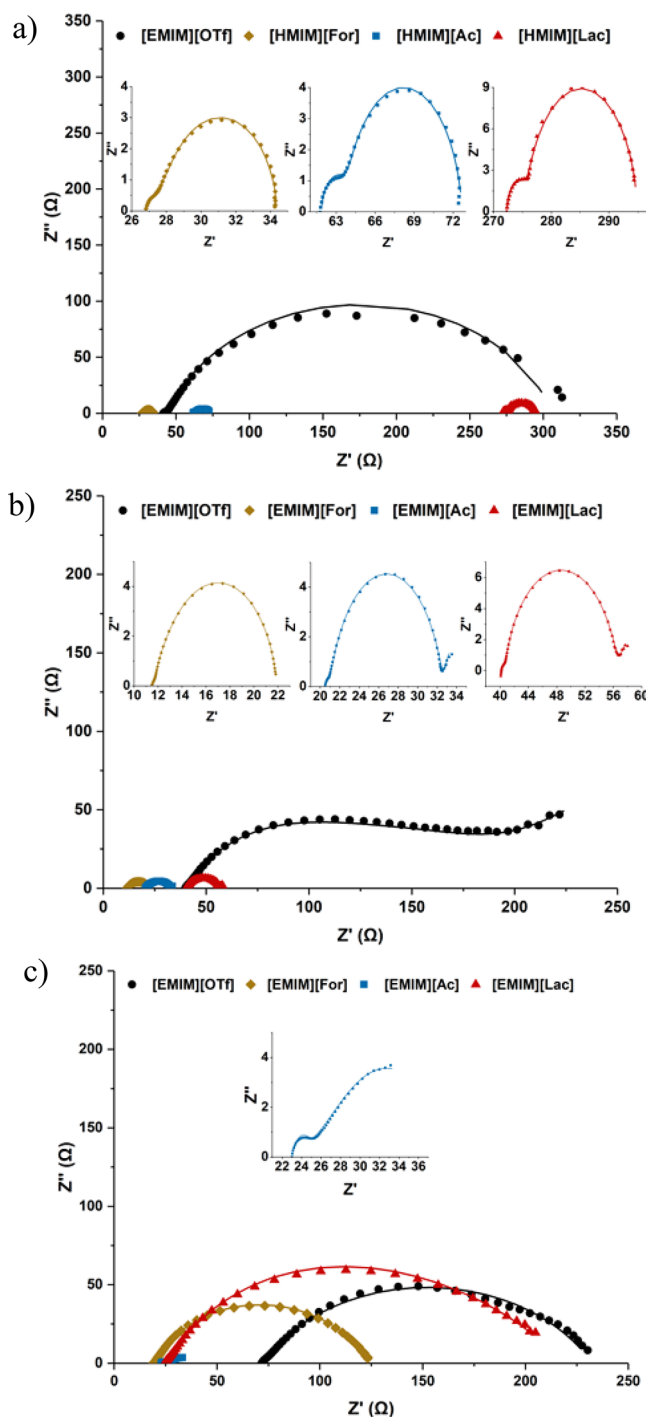


Figure 6. EIS experimental data on the Zn cathodes at -1.2 V vs Ag/Ag^+ (QRE) for the different compositions of water: (a) 10 wt %; (b) 50 wt %; (c) 90 wt %; continuous line: fitted data.

electrolytes show an opposite trend: R2 decreases significantly with increasing water concentration. [HMIM][For] exhibits the lowest R2, 6.18 Ω , for the water concentration of 10 wt %.

Summing up (Figure 7), an increase in the resistance (R1 and R2) is observed for 90 wt % water compositions in all the protic IL-based electrolytes, which will enhance the competition of hydrogen formation reaction explaining the high selectivity for hydrogen production obtained in the electrolysis. In the case

Table 3. Results of EIS Fittings According to the Equivalent Circuits at -1.2 V vs Ag/Ag^+ (QRE) for the Different Ionic Liquids with 10 wt % Water

Ionic Liquid	[EMIM][OTF]	[HMIM][For]	[HMIM][Ac]	[HMIM][Lac]
Chi-squared	2.63×10^{-3}	2.15×10^{-4}	1.55×10^{-4}	5.15×10^{-5}
R_0/Ω	41.62	26.80	61.87	272.3
$Q_1/\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	1.71×10^{-4}	1.80×10^{-3}	9.84×10^{-5}	9.50×10^{-5}
n_1	0.71	0.69	0.95	0.99
R_1/Ω	3.59	1.41	1.93	3.41
$Q_2/\Omega^{-1} \text{ s}_n \text{ cm}^{-2}$	1.59×10^{-4}	8.53×10^{-4}	9.88×10^{-4}	9.19×10^{-4}
n_2	0.81	0.95	0.93	0.95
R_2/Ω	260.7	6.18	8.89	19.15

Table 4. Results of EIS Fittings According to the Equivalent Circuits at -1.2 V vs Ag/Ag^+ (QRE) for the Different Ionic Liquids with 50 wt % Water

Ionic Liquid	[EMIM][OTF]	[HMIM][For]	[HMIM][Ac]	[HMIM][Lac]
Chi-squared	3.36×10^{-4}	2.40×10^{-4}	1.37×10^{-4}	5.78×10^{-5}
R_0/Ω	39.62	11.52	20.56	40.25
$Q_1/\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	3.23×10^{-4}	7.22×10^{-3}	6.01×10^{-4}	1.76×10^{-4}
n_1	0.89	0.65	0.85	1
R_1/Ω	54.41	1.65	0.51	0.47
$Q_2/\Omega^{-1} \text{ s}_n \text{ cm}^{-2}$	2.39×10^{-3}	9.14×10^{-4}	1.28×10^{-3}	1.02×10^{-3}
n_2	0.56	0.91	0.85	0.88
R_2/Ω	124.3	8.76	11.50	15.68
$W_{S_2}\text{-R}/\Omega$	120		6.14	10.34
$W_{S_2}\text{-T/s}$	15.19		23.22	56.84
$W_{S_2}\text{-P}$	0.56		0.72	0.55

Table 5. Results of EIS Fittings According to the Equivalent Circuits at -1.2 V vs Ag/Ag^+ (QRE) for the Different Ionic Liquids with 90 wt % Water

Ionic Liquid	[EMIM][OTF]	[HMIM][For]	[HMIM][Ac]	[HMIM][Lac]
Chi-squared	3.12×10^{-4}	5.49×10^{-4}	3.10×10^{-4}	6.84×10^{-4}
R_0/Ω	71.27	19.04	22.85	24.4
$Q_1/\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	2.97×10^{-4}	5.18×10^{-3}	1.37×10^{-4}	3.67×10^{-4}
n_1	0.63	0.54	0.94	0.92
R_1/Ω	10	28.47	1.20	68.19
$W_{S_1}\text{-R}/\Omega$	106.7			
$W_{S_1}\text{-T/s}$	0.0034			
$W_{S_1}\text{-P}$	0.5			
$Q_2/\Omega^{-1} \text{ s}_n \text{ cm}^{-2}$	1.86×10^{-4}	3.82×10^{-4}		1.10×10^{-3}
n_2	1.14	0.85		0.63
R_2/Ω	20	78.45		125.2
$W_{S_2}\text{-R}/\Omega$	25.13		15.27	
$W_{S_2}\text{-T/s}$	0.21		1.65	
$W_{S_2}\text{-P}$	0.50		0.32	

of the [HMIM][Lac] with 50 wt % water, the results show that the resistance (R_1 and R_2) is lower compared to those with 10 wt % and 90 wt % water. This observation is in agreement with the electrolysis showing the higher CO production for the [HMIM][Lac] with 50 wt % water.

EIS data was also used to calculate the average conductivity of the different electrolytes through equation (1). The results are presented in Table 6,

$$\sigma = \frac{2d}{R_0 \times A} \quad (1)$$

where A is the geometrical area and d is the distance between

the electrodes. The [HMIM][For] electrolyte shows the highest conductivity for all the water compositions, reaching 100.20 mS/cm at 50 wt % water compositions. Meanwhile, [HMIM][Lac] shows the lowest conductivity of 3.87 mS/cm at 10 wt % water composition.

Diffusion coefficients were also calculated using equation (2) when the necessary EIS data was available,

$$D = \frac{\lambda^2}{\tau} \quad (2)$$

where λ is the Debye length and τ is $W_{S_2}\text{-T}$ derived from Zview fitting software.

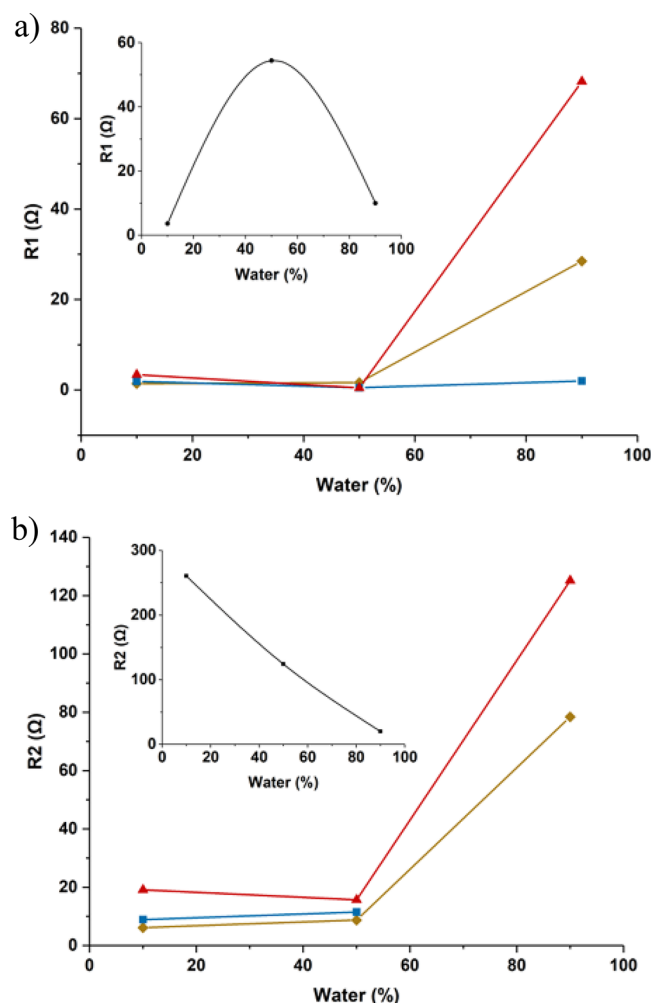


Figure 7. Charge transfer resistance: (a) R1; (b) R2; [EMIM][OTf] (black), [HMIM][For] (golden), [HMIM][Ac] (blue), and [HMIM][Lac] (red).

Table 6. Calculated Conductivities for the Different Electrolytes

IL	Water %	Conductivity (mS cm ⁻¹)
[HMIM][Ac]	10	20.65
[HMIM][Ac]	50	62.72
[HMIM][Ac]	90	38.67
[HMIM][For]	10	48.12
[HMIM][For]	50	100.20
[HMIM][For]	90	60.64
[HMIM][Lac]	10	3.87
[HMIM][Lac]	50	22.60
[HMIM][Lac]	90	45.66

The formal Debye length calculated from the full ion concentration is extremely short, about 0.1 nm or even smaller, which is shorter than an ion diameter and therefore not a useful description of the actual screening in ILs. The use of effective screening length seems more appropriate than calculated by the standard dilute-solution Debye–Hückel theory. Values of about 1–10 nm were calculated.²⁵ Assuming a Debye length of 10 nm for the 50 wt % and 1 nm for the 90 wt % water

compositions, the calculated diffusion coefficients are presented in Table 7.

The values calculated by the classical Debye–Hückel theory (see the Supporting Information) would be 8.11×10^{-22} and 7.42×10^{-20} for [HMIM][Ac] with 50 wt % and 90 wt % water compositions, respectively, and 3.45×10^{-22} for [HMIM][Lac]. These very low diffusion coefficients, showing very restricted ionic species mobility, probably due to the bulky IL-complex, support the hypothesis of the formation of a film of adsorbed IL or IL derived species at the surface of the electrode.²⁶ For [HMIM][Ac], where data is available, when water concentration increases to 90 wt %, the diffusion coefficient increases one order of magnitude as a consequence of less extensive IL film formation at the surface of electrode.

Comparing the values of the diffusion coefficients of [HMIM][Lac] and [EMIM][OTf], it can be verified that the values for the 50 wt % composition are three orders of magnitude higher, contributing to the enhanced performance of CO₂ electroreduction observed for the former electrolyte.

4. CONCLUSIONS

The investigation into the electrochemical performance of protic ionic liquids (ILs) in CO₂ reduction has revealed several important insights. It was observed that when protic ILs are synthesized using strong acids, the reaction medium becomes highly acidic. This increased acidity leads to a significant enhancement in the competition with hydrogen formation, resulting in lower carbon monoxide production. The enhanced HER activity in strongly acidic environments tends to dominate the electrochemical process, thereby limiting the efficiency of CO₂ reduction to CO. This trend is consistent with previous findings in the literature where acidic media have been reported to inhibit CO production due to the preferential evolution of hydrogen. In contrast, when protic ILs are prepared using softer acids, the reaction medium becomes less acidic, which allows for a more favorable environment for CO₂ reduction. Under these conditions, there is a noticeable increase in CO production, suggesting that the acidity of the medium influences critically the efficiency of CO₂ electroreduction. Specifically, ILs such as [HMIM][Ac] exhibited a trend similar to that of [EMIM][OTf], where CO production decreased with an increase in water content. This observation aligns with previous studies that suggest that water can influence the ionic conductivity and solvation properties of ILs, thereby affecting the reaction kinetics. Results confirm the striking effect of water not only as a modulator of proton availability but also of surface composition, since it is evident that apart from the effect on conductivity, lowering viscosity and improving ion mobility, water also contributes to reducing the electrostatic interaction between the cation and the anion, which affects surface composition. Remarkably, protic ILs such as [HMIM][For] and [HMIM][Lac] exhibited significantly higher CO production at a 50 wt % water content. This behavior highlights the importance of understanding the interaction between the IL structure and water content, as well as the influence of these factors on reaction pathways. Notably, [HMIM][Lac] demonstrated 100% selectivity for CO production, with a faster kinetics, according to RC values found by EIS in the high frequency domain and adjudicated to cathode charge transfer processes, with CO production levels only slightly lower than those of [EMIM][OTf] with 10 wt % water.

Table 7. Estimated Diffusion Coefficients for the IL-Based Solutions

Ionic Liquid	Potential (V)	Water (%)	D_1 ($\text{m}^2 \text{s}^{-1}$)	D_2 ($\text{m}^2 \text{s}^{-1}$)
[EMIM][OTf]	−1.2	50		2.09×10^{-21}
[EMIM][OTf]	−1.2	90	5.72×10^{-17}	1.07×10^{-18}
[HMIM][AC]	−1.2	50		4.31×10^{-18}
[HMIM][AC]	−1.2	90		1.52×10^{-17}
[HMIM][Lac]	−1.2	50		1.76×10^{-18}

Data also shows that for a higher water content, 90 wt %, a slower response is exhibited, suggesting that excess water is probably associated with CO_2 depletion at the electrode surface, which can be related to inhibition of the CO_2 capture mechanism by the IL. These findings are particularly interesting because they suggest that the introduction of water, at pre-defined ratios, is based on a balance required to ensure sufficient CO_2 solubility while controlling the proton concentration at the surface. This seems to be related, according to the obtained results for the case of 100% CO selectivity, to diffusional phenomena, which may be considered critical in controlling selectivity and the HER reaction. In this case, protons provided by water must be used for hydrogenation of intermediates and not for H_2 formation, so that CO_2 reduction as prevalent to HER implies the presence of a barrier to proton transport and adsorption. In the related EIS data and used model, this manifest itself as a finite length Warburg element, associated with a cathode mass transfer process, which dominates the low frequency domain of the EIS spectrum, which is sensitive to water content. It is suggested that this could be the consequence of the existence of a thin interfacial layer on the surface of the electrode, probably by imidazolium cations, affecting surface composition for preventing water and protons from accessing active sites.

The exact mechanisms behind these trends remain unclear and warrant further investigation. While it is evident that the choice of acid used in the synthesis of protic ILs significantly impacts the electrochemical performance, the interactions between the IL cations, anions, and water content are complex and not fully understood. Future studies should focus on understanding the precise influence of water in shaping the solvation and conductivity properties of protic ILs, as well as their effect on the electrochemical interfaces during CO_2 reduction.

It should be highlighted that the performance of the aqueous protic 50 wt % [HMIM][Lac] electrolyte surpasses the performance of the non-protic 50 wt % [EMIM][OTf] electrolyte. Furthermore, among the investigated water concentrations, the maximum CO production for the protic 50 wt % [HMIM][Lac] is of the same order as the magnitude of the 90 wt % [EMIM][OTf], an almost pure IL, more expensive, and less sustainable electrolyte. The non-fluorinated bio-based lactate anion concurs to the higher sustainability of the process. Currently, a direct cost comparison between the two ILs is not possible. Contrary to [EMIM][OTf], [HMIM][Lac] is not produced commercially. However, the cost per kg of [HMIM][Lac] is estimated as 2 times lower than the cost of [EMIM][OTf]. The use of [HMIM][Lac] instead of [EMIM][OTf] seems thus to be preferable. Additionally, optimizing the concentration of the [HMIM][Lac]-based electrolyte and exploring a broader range of protic ILs with different cation and anion

combinations could provide further insights into the design of more efficient electrolytes for sustainable CO_2 reduction that can surpass the CO productivity of [EMIM][OTf].

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.6c06152>.

Determination of the number of moles formed during electrolysis, calculation of Faradaic efficiencies, onset potentials and oxidation reduction peaks of the electrolytes, potential profiles of CO_2 reduction, calculated conductivities for the studied electrolytes, diffusion coefficients derived from classical Debye–Hückel theory (DOCX)

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Notes

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