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# Role of Ionic Solvents in the Electrocatalytic CO<sub>2</sub> Conversion and H<sub>2</sub> Evolution Suppression: from Ionic Liquids to Deep Eutectic Solvents

Alejandro Leal-Duaso,<sup>a,b</sup> Yanis Adjé,<sup>a</sup> Carlos M. Sánchez-Sánchez<sup>a\*</sup>

[a] Dr. Carlos M. Sánchez-Sánchez, Dr. Alejandro Leal-Duaso, Mr. Yanis Adjé  
Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques (LISE)  
4 place Jussieu, F-75005 Paris, France  
E-mail: carlos.sanchez@sorbonne-universite.fr

[b] Dr. Alejandro Leal-Duaso  
Universidad de Zaragoza, Programa Margarita Salas  
Calle Pedro Cerbuna, E-50009 Zaragoza, Spain

**Abstract:** The ionic solvents, including both ionic liquids (ILs) and deep eutectic solvents (DES), are deeply studied for their potential in the carbon dioxide (CO<sub>2</sub>) capture and its further electrochemical conversion using different electrocatalysts. The aim of this review is to present and critically compare the role of ILs and DES in the activation of the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) and suppression of the hydrogen evolution reaction (HER). Therefore, the most relevant advances in the use of these ionic solvents in CO<sub>2</sub>RR, either as neat reaction medium or as electrolyte in molecular solvents, have been summarized and discussed. A special focus has been made on comparing the current density, overpotential, faradaic efficiency and products selectivity of the CO<sub>2</sub>RR in the presence of the ionic solvents and relating those results with their chemical composition. Herein, the most recent strategies reported in the literature based on the use of either DES or ILs for enhancing the electrocatalytic CO<sub>2</sub> conversion are reviewed, and some new perspectives based on immobilized ILs at the electrode are discussed.

## 1. Introduction

The causes and effects of the current climate change are well known nowadays, and relevant efforts are being developed during the last years in order to minimize the anthropogenic carbon footprint and mitigate the consequences of carbon dioxide (CO<sub>2</sub>) emissions contributing to this global warming. As a consequence, and related to the availability of this affordable C<sub>1</sub> source, the capture and chemical conversion of CO<sub>2</sub> is one of the most relevant scientific issues nowadays.<sup>[1–3]</sup>

In this context, different physical and chemical processes have been applied for the sequestration and conversion of CO<sub>2</sub> into high-value chemicals or fuels (usually known as “Carbon Capture and Utilization” –CCU– technologies).<sup>[4,5]</sup> The transformation of this stable molecule into other C<sub>1</sub>, C<sub>2</sub> or even C<sub>2+</sub> compounds finds direct application in many industrial or energetic applications.<sup>[6]</sup> Therefore, thermal, chemical, biochemical, and photochemical reduction strategies have been explored for activating and converting the CO<sub>2</sub> molecule, producing various reduction products with very different results.<sup>[7,8]</sup> More recently, and thanks to the possibility of using renewable energy, the electrochemical catalytic reduction of carbon dioxide (CO<sub>2</sub>RR) has emerged as an

efficient pathway for its chemical conversion.<sup>[9–18]</sup> This strategy opens the door to the production of a wide range of products, tuning the selectivity with respect to the previously described processes, in a more sustainable way.<sup>[19]</sup>

Unfortunately, the efforts in reducing the utilization of fossil-based fuels as a part of the reduction of the global CO<sub>2</sub> emissions, sharpen the current energetic crisis. The renewable energies, outstanding solar, wind and hydrothermal, are expected to contribute to the global production of sustainable electricity. Nevertheless, the intermittence and variability of this kind of energies make necessary the development of energy storage systems such as batteries and also energy vectors. It is in this context where the CO<sub>2</sub>RR reaction has been described as “*one of the most viable and economical methods to store renewable energy by producing sustainable fuels, feed-stock chemicals, commodity chemicals, intermediates and task-specific products*”.<sup>[20]</sup> However, along with the CO<sub>2</sub>RR reaction, the hydrogen evolution reaction (HER) appears as one of the main competitive (often concomitant) process limiting the CO<sub>2</sub>RR performance. This competition between the electrochemical reduction of both CO<sub>2</sub> (CO<sub>2</sub>RR) and H<sub>2</sub>O/H<sup>+</sup> (HER) triggers a decrease in the energetic efficiency of the CO<sub>2</sub> conversion, as well as reduces the selectivity of the reaction products and, thus, its further industrial applicability.

This is the general framework for the present review article, where the state-of-the-art of the role and effects of the different types of ionic solvents at the electrical double layer are evaluated, and critically compared for both the CO<sub>2</sub>RR and the competitive HER, with the aim of pointing new directions for the enhancement in the performance of the CO<sub>2</sub> electrocatalytic conversion.

## 2. Ionic Solvents: Types and Features

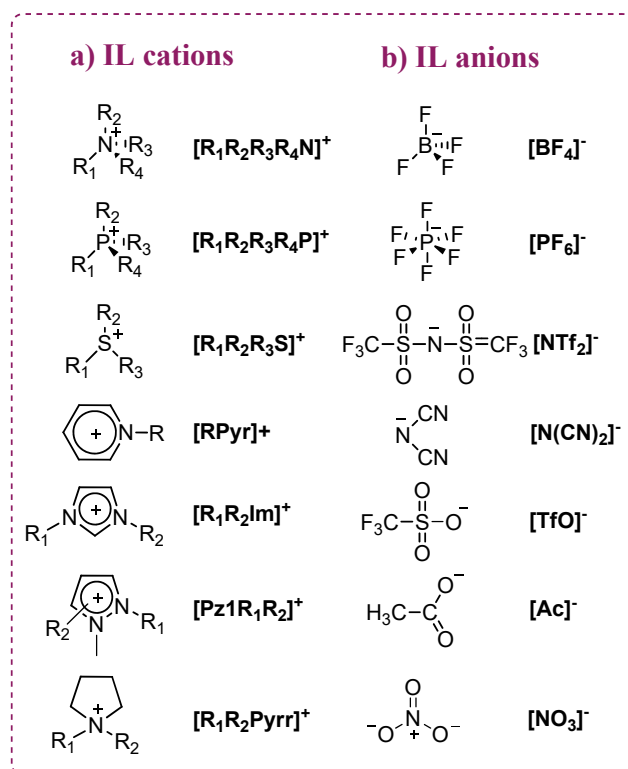
In general, the ionic solvents, *i.e.* stable liquids at room temperature (or at least below 100 °C) including ions in their own composition, can be classified in two main families: Ionic Liquids (ILs) and Deep Eutectic Solvents (DES).<sup>[21]</sup>

On the one hand, ILs can be defined as liquids exclusively composed by ions, namely an organic cation and an inorganic or organic anion, displaying a melting point below 100 °C (or room temperature). This low melting point in ILs is a consequence of their low trend to crystallize due to the weak cation-anion interactions and the high structural asymmetry in the cation.<sup>[22]</sup> The first example of the formation of an ionic liquid was described by Walden in 1914, reporting a melting point of 12 °C for the ethylammonium nitrate ([EtNH<sub>3</sub>][NO<sub>3</sub>]).<sup>[23]</sup> Nevertheless, this first generation of ammonium-based ILs presented the disadvantage of being highly reactive with water, generating corrosive hydrogen

## REVIEW

chloride (HCl) as a product. For this reason, those first ILs were essentially abandoned until the development of a new generation of liquids, still hygroscopic, but air and water stable, by Wilkes et al. during the decade of 1990.<sup>[24]</sup> Since then, diverse combinations of cations and anions have been successfully explored, extending a list of almost one thousand potential ionic solvents.<sup>[23]</sup>

Different families of ILs can be described based on their chemical composition. In general, it is very common to distinguish them into two types of ILs depending on whether the cation presents or not an acidic proton able to build up hydrogen bonds in the medium. Respectively, they are known as protic ionic liquids (PILs) and aprotic ionic liquids (AILs).<sup>[25]</sup> Otherwise, ILs are usually named and grouped by the chemical structure of the cation present in their composition (see Figure 1a). In the structure of conventional ILs, it is common to find the presence of the cations tetralkylammonium  $[R_1R_2R_3R_4N]^+$ , tetralkylphosphonium  $[R_1R_2R_3R_4P]^+$ , trialkylsulphonium  $[R_1R_2R_3S]^+$ , *N*-alkylpyridinium  $[RPyr]^+$ , *N,N'*-dialkylimidazolium  $[R_1R_2Im]^+$ , polyalkylpyrazolium  $[Pz1R_1R_2]^+$ , and *N,N'*-dialkylpyrrolidinium  $[R_1R_2Pyr]^+$ . All these cations present in their structure various R substituents, outstanding methyl (M), ethyl (E), butyl (B), octyl (O) and benzyl (Bz) chains. Moreover, a wide range of anions have also been reported for their combination with the above listed cations in the formation of ILs (Figure 1b). Among them, tetrafluoroborates  $[BF_4]^-$ , hexafluorophosphates  $[PF_6]^-$ , bis(trifluoromethylsulfonyl)imides  $[NTf_2]^-$ , dicyanamides  $[N(CN)_2]^-$ , triflates  $[TfO]^-$ , acetates  $[Ac]^-$ , nitrates  $[NO_3]^-$ , and different halides  $[X]^-$  are present.



**Figure 1.** Structure of the most commonly used cations and anions present in ILs composition.

On the other hand, DES constitute a differentiated family of ionic solvents, with a particular structural composition. Although DES were initially defined as binary or ternary eutectic mixtures

between hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD), nowadays, DES are better considered to be “a mixture of Lewis and Brønsted acids and bases which significantly reduce the freezing point compared with those of the components”.<sup>[26]</sup> In general, the generation of a network of hydrogen bonds between the acid/HBD component present in the DES with the anion of the salt disrupts the crystallinity of the latter, triggering a variable decrease in the melting point of the eutectic mixture with respect to their pure components separately.<sup>[27]</sup> Thus, only a specific molar ratio composition (expressed as mol HBA: mol HBD) allows the formation of a stable solvent. This eutectic ratio between the ionic (HBA) and the non-charged (HBD) components is the main difference of DES with respect to ILs, which in contrast are exclusively composed by ions.

The first example of eutectic solvent phenomenon was described in 2003 by the combination of two solids, choline chloride ( $HOCH_2CH_2N^+(CH_3)_3Cl^-$ , ChCl) and urea ( $H_2NCONH_2$ ) in a molar ratio (1:2). The resulting liquid mixture displayed a melting temperature of 12 °C, which is significantly lower than the melting points of their individual components, ChCl and urea (302 °C and 134 °C, respectively).<sup>[28]</sup> It was in 2004 when Abbott et al. introduced the term DES for describing mixtures of quaternary ammonium chlorides with a series of different carboxylic acids.<sup>[29]</sup> Since then, up to five types or generations of DES have been described (Table 1).

Type-I and type-II DES are composed by a quaternary ammonium salt (commonly ChCl) and a metal halide or a hydrated metal halide, respectively. These first generations of DES correspond to air-sensitive fluids including metallic ions in their composition, what can be an advantage or drawback depending on the final application of the solvent.<sup>[26]</sup> Otherwise, type-III DES are the most numerous (in terms of publications, examples of solvents and applications). Type-III DES are composed by the mixture of a solid quaternary ammonium or phosphonium salt and a metal-free HBD, the versatility in the composition and properties of these DES is increasing continuously. In general, the most utilized ammonium salt is ChCl, because of being a very accessible, non-toxic and bio-based compound, highly demanded as additive in alimentary industry.<sup>[27]</sup> Regarding the metal-free HBD component, a really massive amount of non-charged organic compounds have been successfully incorporated in the formation of type-III DES. Among them, we can mention diverse types of alcohols, urea and its derivatives, amines, mono-, di- and tricarboxylic acids, sulphonic acids, and sugars and complex carbohydrates. An additional generation is the type-IV DES, with intermediate characteristics to the type-II and III DES, since they are composed of a hydrated metal halide in the role of HBA and a metal-free HBD component. Finally, hydrophobic type-V DES represent the most recent family of DES described in the literature.<sup>[30]</sup> They are formed by the combination of an organic HBA and a long-chain carboxylic acid in the role of HBD. Despite using as HBA several substituted tetraalkylammonium halides, most of their HBA are neutral molecules as menthol or thymol, so these resulting DES cannot be considered as ionic solvents, since no ions are present in their composition.

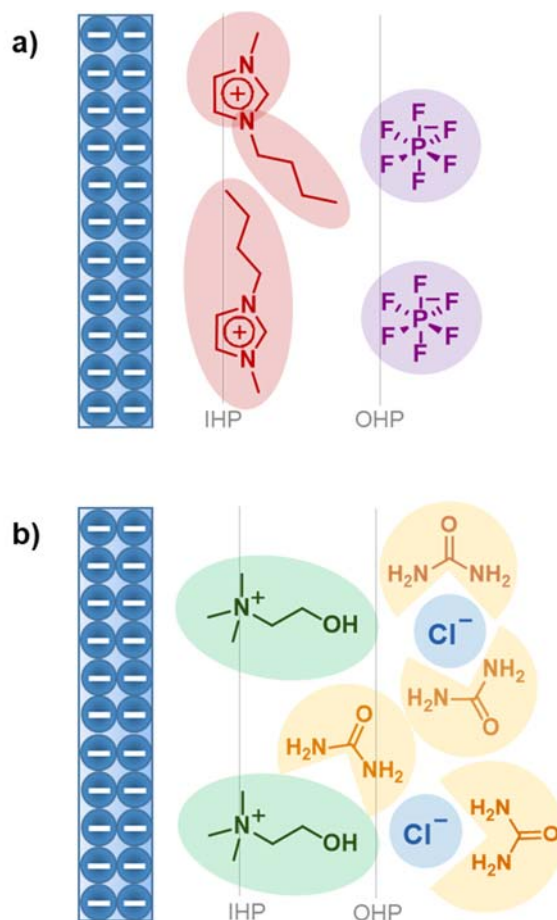
**Table 1.** Structure and examples for the five types of Deep Eutectic Solvents.

DES type and example (name)	Acceptor (HBA/base)	Donor (HBD/acid)	Viscosity (mPa·s) <sup>a</sup>

Type-I DES	Quaternary ammonium salt	Metal halide (MX <sub>n</sub> )	
ChCl-ZnCl <sub>2</sub> (1:2)	Choline chloride	Zinc chloride	85000
Type-II DES	Quaternary ammonium salt	Hydrated metal halide (MX <sub>n</sub> ·yH <sub>2</sub> O)	
ChCl-CrCl <sub>3</sub> ·6H <sub>2</sub> O (1:1, <i>chromeline</i> )	Choline chloride	CrCl <sub>3</sub> ·6H <sub>2</sub> O	2346
Type-III DES	Quaternary salt	Alcohols, urea, carbohydrates, amines, acids...	
ChCl-Urea (1:2) ( <i>reline</i> )	Choline chloride	Urea	750
ChCl-EG (1:2) ( <i>ethaline</i> )	Choline chloride	Ethylene glycol (EG)	37
Type-IV DES	Metal halide (MX <sub>n</sub> )	Alcohols, urea, amides...	
AlCl <sub>3</sub> -AA (1:1)	AlCl <sub>3</sub>	Acetamide (AA)	60
Type-V DES	Organic HBAs	Carboxylic acids, alcohols	
TBAC-DA (1:2)	Tetrabutylammonium chloride (TBAC)	Decanoic acid (DA)	265
Menthol-OA (1:1)	Menthol	Octanoic acid (OA)	15

<sup>a</sup> Viscosity values determined at 298 K.

Both ILs and DES are ionic solvents able to present similar features and properties, but their composition and chemical structure are completely different. The most evident difference is that ILs are entirely composed of ions, while DES contain an important proportion of neutral molecules ( $\geq 50$  mol%), which directly impacts on the distribution of charged species and oriented dipoles existing at the electrode/solution interface. This is described in the schematic representation of the electrode/electrolyte interface shown in Figure 2, comparing the electrical double layer (EDL) at a negatively-polarized cathode in the presence of a neat imidazolium-based IL (Figure 2a) and a neat choline chloride-based type-III DES (Figure 2b). In the case of the neat IL, mainly electrostatic interactions appear between its cations and anions. But interestingly, depending on the applied negative potential at the electrode, the main plane of the imidazolium cationic rings within the EDL is oriented parallel or perpendicular to the cathode surface.<sup>[31]</sup> In the case of the neat DES, the choline cation and the chloride anion constitute an ionic pair through strong electrostatic interactions. Simultaneously, the non-charged HBD molecule (urea) “sequesters” the chloride anion by formation of hydrogen bonds.<sup>[27]</sup> For this reason, when the electrode is negatively polarized, the choline cations and chloride anions are rearranged in the EDL, but neutral urea molecules mainly remain attached to the chloride ions, with the exception of some of them that might be directly adsorbed on the electrode surface.



**Figure 2.** Schematic representation of the electrical double layer at a negatively-polarized cathode in a) neat imidazolium-based IL [BMIm][PF<sub>6</sub>], and b) neat choline chloride-based type-III DES ChCl-urea (1:2).

In summary, ionic solvents share many of their chemical-physical and electrochemical properties, but significant differences can be also found. Recently, the electron-transfer kinetics in ChCl-EG (1:2) was evaluated and compared with different ILs and molecular solvents.<sup>[32]</sup> The electron-transfer rate constant measured in this DES is close to the one reported for molecular solvents. In contrast, ILs exhibit a considerably slower electron transfer rate. Among the common characteristics, both ILs and DES are solvents presenting low melting point, low volatility and moderate ionic conductivity.<sup>[15,33,34]</sup> Regardless, one of the main positive aspects of both ILs and DES is that they can be fully considered as design-solvents. This is due to the possibility of designing the solvent by just choosing the appropriate cation and anion (in the case of ILs) or the individual components of the mixture (in the case of DES), thus adjusting the solvent properties for a specific application (“task-specific” ionic solvents).<sup>[35,36]</sup> Moreover, while it is true that the estimated number of possible DES is greatly higher than those of ILs (ca.  $10^6$  vs.  $10^3$ ), DES variability comes mostly from the neutral HBD component, since most of the used DES contains only ChCl as HBA component. Nevertheless, this should not be a limitation for using DES in electrochemical applications, since despite maintaining constant the HBA component, the modification of the HBD completely modify the resulting properties of the global ionic solvent.

A very relevant aspect for the use of ionic solvents in the electrochemical CO<sub>2</sub>RR relies on their interesting properties as reversible absorbents for the CO<sub>2</sub> capture. It has been proved that both ILs and DES present an elevated CO<sub>2</sub> absorption capacity, and thus a moderate-high CO<sub>2</sub> solubility.<sup>[37–40]</sup> This constitutes one important advantage for these ionic solvents to enhance the CO<sub>2</sub>RR performance, since the CO<sub>2</sub> availability at the electrode surface is much greater than in aqueous solution. For instance, the reported CO<sub>2</sub> solubility in the most commonly used choline chloride-based DES is in the interval of 0.28–0.60 mol<sub>CO<sub>2</sub></sub>·L<sup>−1</sup> at 298 K and 1 atm, which is much higher than the solubility offered in aqueous media (0.03 mol<sub>CO<sub>2</sub></sub>·L<sup>−1</sup> at 298 K and 1 atm) and similar to the one displayed by organic molecular solvents (usually 0.16–0.27 mol<sub>CO<sub>2</sub></sub>·L<sup>−1</sup> at 298 K and 1 atm). During the last decades, 30–50 wt% monoethanolamine (MEA) aqueous solutions have been industrially used for the CO<sub>2</sub> capture, mainly thanks to the reversible chemical formation of carbamates.<sup>[34,39]</sup> Recently, amine-based DES containing in their composition different di- and monoethanolamines,<sup>[41,42]</sup> functionalized-DES possessing CO<sub>2</sub> affinity groups,<sup>[43]</sup> as well as imidazole-based DES,<sup>[44]</sup> have been developed for enhancing the CO<sub>2</sub> capture capacity with respect to traditional MEA solutions.<sup>[20,45]</sup> This is because these novel DES are able to display both a chemical reaction and additional Van der Waals interactions with CO<sub>2</sub>, which notably enlarge the amount and efficiency of the mechanisms for the CO<sub>2</sub> capture, with respect to the use of molecular solvents or imidazolium-based ILs.<sup>[39]</sup>

In general, most of the ILs present lower volatility (negligible vapor pressure) and higher thermal stability than DES.<sup>[34,46]</sup> However, ILs are starting to be critically evaluated during the last decade due to some drawbacks including their high cost and limited availability, the presence of impurities (notably affecting to the performance and reproducibility of the electrochemical processes) and their moderate ecotoxicity.<sup>[47]</sup> In contrast, most of the DES come from renewable sources, being much more sustainable in their preparation and origin of their components.<sup>[48]</sup> Moreover, DES present a simpler and more effective solvent preparation, which allows to reach a higher solvent purity than in the case of ILs. Regarding to the bio-based origin of many of the DES components, its relevance is not only related to the possibility of having a solvent whose entirely composition comes from a renewable source, but also the interest in valorizing raw bio-compounds with high importance from a circular economy point of view.<sup>[49]</sup> For instance, some of the most used DES components, such as urea, glycerol or ChCl, are widely available with low cost because there is no enough industrial demand for them at present, despite their numerous described applications. Just to show some figures, urea is an industrial raw material with a huge worldwide production (ca. 180 million tons per year), glycerol is a concomitant byproduct in the synthesis of biodiesel from vegetable oils with an overall production of ca. 3 million tons per year, and ChCl is a bio-based food additive produced in more than 200,000 tons per year.<sup>[27]</sup>

DES are usually biodegradable, non-toxic, non-flammable and easily available at a low cost.<sup>[27,50,51]</sup> An additional advantage for the use of DES in electrochemical applications, with respect to ILs, is related to the large presence of structural chloride anions in solution, which provides an ideal environment for reaching a very stable reference potential by only using a Ag/AgCl wire as a reference electrode, without any additional chlorides-containing aqueous solution. This avoids adding any internal soluble redox

reference compound in the DES for properly establishing the reference potential as happens in the case of ILs. Thus, the use of DES has been described in the literature like a low-cost, benign and more sustainable alternative to ILs for their catalytic and electrochemical applications.<sup>[26,48,52,53]</sup> Nevertheless, it is noteworthy to mention that a new generation of bio-based ILs, coming from protein, sugar or lignin sources, is currently in development. But their properties and applicability has been barely evaluated till date, neither for catalysis nor in electrochemistry.<sup>[48]</sup>

In general, ionic solvents present a wide electrochemical potential window, which has been considered as one of the main advantages for performing the CO<sub>2</sub>RR in neat ILs (both as reaction solvent and supporting electrolyte).<sup>[54–57]</sup> Nevertheless, the non-negligible viscosity of many of these ionic solvents can represent a severe limitation for using them as neat solvents in electrochemical applications, since mass transfer processes are hindered. Notably, viscosity varies enormously depending on the specific composition of each ionic solvent. For instance, imidazolium-based ILs containing the anion [NTf<sub>2</sub>]<sup>−</sup> present much lower viscosity (32–45 mPa·s at 298 K) than the ones containing the anions [BF<sub>4</sub>]<sup>−</sup> (ca. 100 mPa·s at 298 K), [PF<sub>6</sub>]<sup>−</sup> (>200 mPa·s at 298 K) or [Ac]<sup>−</sup> (>400 mPa·s at 298 K). This variability is even greater for the case of DES, overcoming the viscosity range of ILs (see Table 1). Fortunately, this issue of viscosity of the ionic solvents results minimized in the case of using them as a supporting electrolyte in a molecular solvent, as will be also discussed in the next sections.

### 3. CO<sub>2</sub>RR vs. HER: Competitive Electrochemical CO<sub>2</sub> Conversion and H<sub>2</sub> Production

During the last decade and by means of the use of renewable electricity, the electrochemical CO<sub>2</sub>RR appears as a promising tool for achieving the conversion of this stable molecule into high value-added fuels and chemicals under ambient conditions and with the aim of a net zero greenhouse gas emissions economy.<sup>[16]</sup> Nevertheless, the CO<sub>2</sub>RR presents several issues whose solution would allow to take a relevant step forward in CO<sub>2</sub> conversion: Firstly (i), a limitation in both the catalytic activity and the products selectivity is usually present due to the low availability of highly efficient and/or selective cathode materials for CO<sub>2</sub>RR. Secondly (ii), the availability of CO<sub>2</sub> on the electrode surface is often limited by the low solubility of this gas in the commonly used aqueous media. Finally (iii), and no less important, the formation of undesired products such as H<sub>2</sub> coming from the competitive HER, which diminishes the faradaic efficiency for CO<sub>2</sub>RR. Moreover, the competition CO<sub>2</sub>RR vs. HER triggers a notable increase in the cathode overpotential, which diminishes the energetic efficiency for CO<sub>2</sub>RR. Different strategies have been proposed to enhance the efficiency of CO<sub>2</sub>RR vs. HER, which include modifying the electrode/electrolyte interface on both sides, at the electrode surface and in the electrolyte composition. Therefore, it is essential to further research in the development of more active and selective cathode materials, as well as in the increase on the CO<sub>2</sub> availability during the CO<sub>2</sub>RR, and diminish the concurrence HER by modifying the electrolyte composition.<sup>[58]</sup>

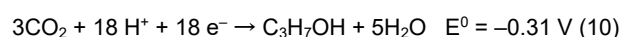
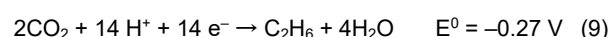
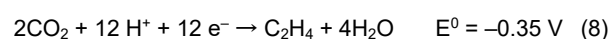
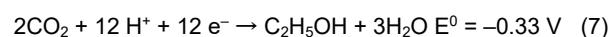
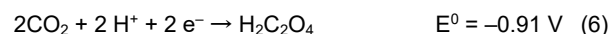
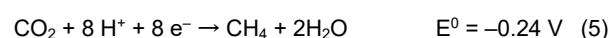
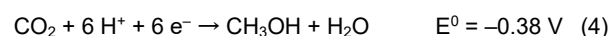
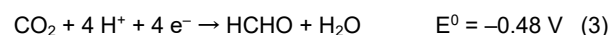
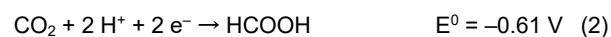
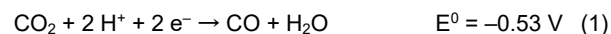
The CO<sub>2</sub>RR occurs through a series of different chemical and electrochemical steps, including the adsorption and activation of

the CO<sub>2</sub> molecule, the proton-coupled electron transfer and the product desorption at the active sites on the cathode surface.<sup>[9]</sup> The CO<sub>2</sub>RR vs. HER selectivity can be controlled by the stabilization of the different CO<sub>2</sub>RR reaction intermediates, playing the catalyst, as well as the ionic species in solution, a major role for that purpose.<sup>[59,60]</sup> A wide range of transition metals have been already studied as both molecular complexes and heterogeneous electrocatalytic materials for CO<sub>2</sub>RR.<sup>[61,62]</sup> Among them, silver, platinum, tin, copper, as well as copper and tin alloys, some mixed oxides and nitrogen-doped carbon materials have shown very different activity, product selectivity and scalability perspectives for CO<sub>2</sub>RR.<sup>[14,61–65]</sup> Moreover, the cations present in the electrode/electrolyte interface play also a major role controlling the CO<sub>2</sub>RR vs. HER selectivity. For instance, it has been recently reported that the presence or absence of a high concentration of potassium cations (K<sup>+</sup>) in acidic aqueous solution was able to modify the selectivity CO<sub>2</sub>RR vs. HER from (0:100) (in [K<sup>+</sup>] = 0 M) to (50:50) (in [K<sup>+</sup>] = 3 M) on copper electrodes.<sup>[60]</sup> Therefore, the electrolyte in solution is receiving a notably attention nowadays.<sup>[12,16,58]</sup> This field is usually known as electrolyte engineering and is based on the modification of the electrochemical interface through the addition of different electrolytes or dissolved species in order to tune the electrocatalytic properties of the electrode material by designing the most suitable double layer structure. In this context, the utilization of ionic solvents, which are able to act either as the reaction medium (solvent + electrolyte), or just as an electrolyte dissolved in molecular solvents thanks to the anions and cations present in their composition, has been proposed as an additional strategy of electrolyte engineering for enhancing the CO<sub>2</sub>RR vs. HER selectivity. In particular, this electrolyte engineering strategy involving the use of ionic solvents, such as ILs and DES, is discussed in detail in the present review article, paying special attention to their impact on CO<sub>2</sub>RR and HER performance. Notably, the understanding of the nature and structure of the EDL formed at the boundary phase between electrode and electrolyte represents a key issue in most electrocatalytic reactions, not only for fundamental science, but also for the proper design of industrial-scaled processes. However, the CO<sub>2</sub>RR studies are in most of the cases still in the level of the fundamental research, and an industrial implementation is widely required. Thus, this review article deals specifically with the role that ionic solvents play for the CO<sub>2</sub>RR activation, together with the HER suppression, and their possible future industrial implementation.

Electrochemical HER can be inhibited through different mechanisms. For instance, the modification of the electrode surface in order to increase its hydrophobicity has been proved to limit the availability of protons on it, and thus to hinder the HER occurrence. In this way, the addition of both cationic surfactants,<sup>[66,67]</sup> or hydrophobic polymers,<sup>[68]</sup> allows a remarkable HER inhibition. Otherwise, the adsorption of Cl<sup>−</sup> ions on a zinc cathode has been reported for blocking the HER, facilitating the electron transfer process, which leads to higher faradaic efficiencies for the CO<sub>2</sub>RR.<sup>[69]</sup>


Regarding the selectivity of the possible products from the CO<sub>2</sub>RR reaction, many different compounds can be obtained depending on the catalyst, supporting electrolyte, number of involved electrons and applied potential.<sup>[70,71]</sup> The thermodynamic potentials for the various CO<sub>2</sub>RR products and also the H<sub>2</sub> production are shown in Equations 1–11 (determined at pH 7 in aqueous solution expressed in volts versus a standard hydrogen




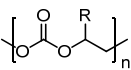

electrode (SHE)). It is possible to distinguish between the generation of C<sub>1</sub> products (Equations 1–5), such as carbon monoxide (CO), formate/formic acid (HCOO<sup>−</sup>/HCOOH), formaldehyde (HCHO), methanol (CH<sub>3</sub>OH) and methane (CH<sub>4</sub>), and the formation of C<sub>2</sub> and C<sub>2+</sub> products (Equations 6–10), for instance oxalate/oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), ethylene (C<sub>2</sub>H<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>) and longer alkyl-chain alcohols (C<sub>3</sub>H<sub>7</sub>OH, etc.).



Depending on the main product obtained from the CO<sub>2</sub>RR, the scaling up of the process can be industrially interesting for valorizing the CO<sub>2</sub> molecule in different direct applications, for instance the generation of alcohols for fuel cells, or for the large-scale preparation of high-value platform molecules such as formic acid or formaldehyde, among others. Table 2 gathers some examples of the main chemicals produced from some of the CO<sub>2</sub> reduction processes at industrial scale. Alternatively, the direct CO<sub>2</sub>RR can be industrially combined with other chemical processes in order to generate more complex products, such as copolymers and polymers, pharmaceutical products or even fine chemicals.

**Table 2.** Some of the main chemicals produced from CO<sub>2</sub>RR products at industrial-scale.

Product	Chemical structure	Applications
Carbon monoxide	CO	Synthesis gas
Formic acid		Industrial formulations
Formaldehyde		Composites

		
Methane	CH <sub>4</sub>	Energy
Methanol	CH <sub>3</sub> OH	Fuel cells
Urea		Cosmetics
Ethylene carbonate		Solvent, batteries
Copolymers		Polymers industry
Salicylic acid		Fine chemicals

#### 4. Ionic Liquids as Solvents and/or Electrolytes in CO<sub>2</sub>RR vs. HER

ILs have been extensively used as excellent modulators of the electrochemical interface in order to tune the electrocatalytic properties of both molecular and heterogeneous electrocatalysts. Physical-chemical properties of the ILs, such as viscosity, conductivity or surface tension, alongside the interactions with reaction intermediates, profoundly influence the CO<sub>2</sub>RR vs. the HER selectivity.<sup>[11,12,72,73]</sup>

Ionic solvents (including both ILs and DES) can play a dual role: (i) as neat solvent and supporting electrolyte simultaneously, and (ii) only as supporting electrolyte mixed with molecular solvents (H<sub>2</sub>O, acetonitrile, organic carbonates, etc.). As neat solvents, ILs create a stable local environment for reactions to occur and facilitate ions transport.<sup>[74,75]</sup> Their appeal lies in their conductivity, low volatility, high chemical and thermal stability, and wide electrochemical window.<sup>[15,76]</sup> Notably, the interaction between ILs and CO<sub>2</sub> plays a vital role in CO<sub>2</sub> absorption capacity and conversion.<sup>[77]</sup> The main drawback comes from the limited mass transfer rate in highly viscous fluids. Conversely, when ILs are mixed with molecular solvents like water or acetonitrile, they primarily act as supporting electrolytes. The molecular solvent provides then the solvation environment for reactants, while the IL enhances both ionic conductivity and reaction intermediates stability. This combination often results in a more efficient CO<sub>2</sub>RR. Moreover, the solubility of CO<sub>2</sub> is different for each reaction medium, which tunes the availability of CO<sub>2</sub> on the electrode surface, and thus the catalytic activity, as well as the concurrence of the competitive HER.<sup>[40]</sup> Consequently, the aim of the majority

of works studying the performance of neat ILs in the CO<sub>2</sub>RR is to develop a more efficient, safe (in comparison with the case of volatile and flammable molecular solvents), and alternative solvent to the use of water and organic solvents.<sup>[57,78]</sup>

The pioneer work of Rosen *et al.* reported in 2011 the use of the IL [EMIm][BF<sub>4</sub>] as supporting electrolyte in aqueous solution (18 mol%) for the CO<sub>2</sub>RR over an Ag electrode, achieving 96% of faradaic efficiency to CO and lowering the overpotential, due to the decrease in the free energy of the CO<sub>2</sub> reduction intermediate.<sup>[79]</sup> Since then, a wide series of different ILs, where mainly [EMIm][BF<sub>4</sub>] and [BMIm][BF<sub>4</sub>] stand out, have been studied to convert CO<sub>2</sub> into value-added products.<sup>[15,72]</sup> To comprehensively summarize this field, Table 3 gathers a selection of the most representative examples of the utilization of different types of ILs, both as neat solvent and as supporting electrolyte, for the CO<sub>2</sub>RR. As can be observed from Table 3, both molecular and heterogeneous metallic electrocatalysts have been used in the presence of ILs in various electrochemical setups for the production of many different CO<sub>2</sub> reduction products (CO, HCOOH, CH<sub>3</sub>OH, oxalate, polyethylene, etc.). The most relevant electrocatalytic performance metrics, including selectivity, current density and main product faradaic efficiency, are included in Table 3. In many cases, the impact of ILs enhancing CO<sub>2</sub>RR is accompanied by the inhibition or suppression of the HER. For instance, in the case of employing a rhodium molecular catalyst in solution (Table 3, entries 5 & 6), the introduction of an imidazolium-based IL was found to significantly enhance the catalytic activity and selectivity, promoting the CO<sub>2</sub> reduction to formate while suppressing the HER.<sup>[80]</sup> This effect can be observed in both acetonitrile (entry 5) and aqueous (entry 6) solutions. In particular, Figure 3(a–c) evaluates the role of imidazolium cations in the electrolyte by adding either tetrabutylammonium ([TBA]<sup>+</sup>) or [EMIm]<sup>+</sup> in aqueous solution. Comparing by cyclic voltammetry the current vs. potential response for CO<sub>2</sub>RR (green plots in Figure 3(a–b)), no significant difference is observed. However, comparing the current vs. potential response for HER (black plots in Figure 3(a–b)), an evident decrease in current density for HER is displayed in the case of [EMIm]<sup>+</sup> in comparison with [TBA]<sup>+</sup> for a given potential, as summarized in Figure 3c. Thus, the major role of the imidazolium cation in this case seems to be linked to the inhibition of HER, which indirectly provides an improvement in CO<sub>2</sub>RR activity. Analogously, a relevant role of the IL anion was reported in CO<sub>2</sub> conversion to CO vs. HER on metallic heterogeneous catalysts such as Ag foil (Table 3, entry 17).<sup>[76]</sup> Figure 3d shows the impact of fluorinated anions (as triflate or tetrafluoroborate) in imidazolium-based ILs favoring CO production (red bars) in contrast with acetate anions favoring the HER (blue bars). In this work, the IL [BMIm][SO<sub>3</sub>CF<sub>3</sub>] in acetonitrile solution displays the highest faradaic efficiency for CO (>95%), while exhibiting the lowest H<sub>2</sub> production.

**Table 3.** Catalytic activity, selectivity and main experimental conditions of a selection of neat ILs and ILs as electrolyte in solution for CO<sub>2</sub>RR.

Entry	Solvent	Cell type	Catalyst	Main product	Cathode Potential (V)	Current density  (mA·cm <sup>-2</sup> )	Faradaic Efficiency (FE, %)	Ref.
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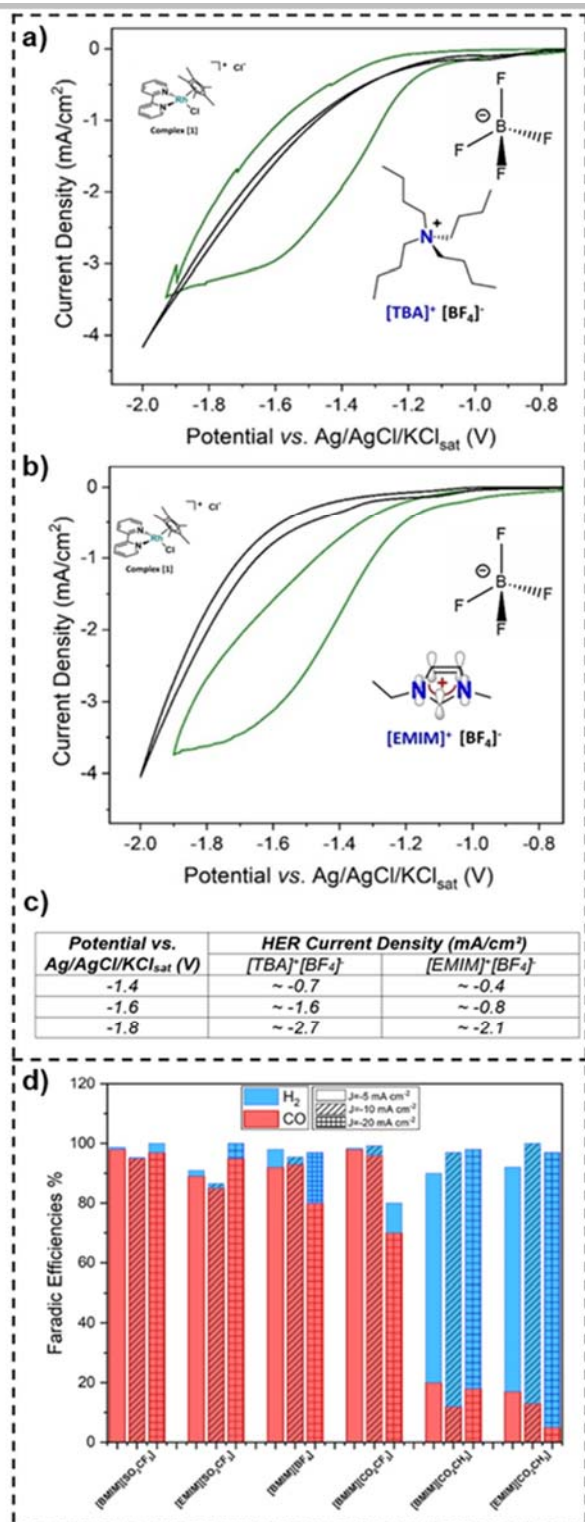
<i>Neat ILs</i>								
1	[EMIm][BF <sub>4</sub> ]	Single compartment cell	N-doped carbon nanofibers	CO	−0.57 vs. SHE	3.5	98.0	[81]
2	[EMIm][Tf <sub>2</sub> N]	Two-compartment cell	Pt	HCOOH				[82]
3	[BMIm][BF <sub>4</sub> ]	Single compartment cell	Co porphyrin complex <sup>a</sup>	CO	−0.8 vs. Ag/AgCl		64.9	[83]
4	[BMIm][BF <sub>4</sub> ]	Two-compartment cell	N-doped carbon nanomaterials	CH <sub>4</sub>	−1.4 vs. SHE		93.5	[84]
<i>ILs as electrolyte</i>								
5	[EMIm][BF <sub>4</sub> ] (0.5 M) in ACN <sup>b</sup> , 5% v/v H <sub>2</sub> O	Two-compartment cell	Rh complex <sup>c</sup>	HCOOH	−1.83 vs. Fc <sup>+</sup> /Fc		91.0	[80]
6	[EMIm][BF <sub>4</sub> ] (0.5 M) in H <sub>2</sub> O	Two-compartment cell	Rh complex <sup>c</sup>	HCOOH		3.33	49.0	[80]
7	[EMIm][BF <sub>4</sub> ] (10.5 mol%) in H <sub>2</sub> O	Flow cell	Ag nanoparticles	CO			99.0	[85]
8	[EMIm][BF <sub>4</sub> ] in H <sub>2</sub> O (92/8% v/v)		Ag-coated Al foam	CO	−1.8 vs. Pt	36.6	75.0	[86]
9	[EMIm][BF <sub>4</sub> ] in H <sub>2</sub> O, (92/8% v/v)		Nanostructured Cu	HCOOH	−1.55 vs. Fc <sup>+</sup> /Fc		83.0	[87]
10	[EMIm][BF <sub>4</sub> ] in H <sub>2</sub> O, (50/50% v/v)	Two-compartment cell	Nanostructured TiO <sub>2</sub>	LDPE <sup>d</sup>	−1.50 vs. SCE		14.0	[88]
11	[BMIm][Cl] in H <sub>2</sub> O (80/20% v/v)	Two-compartment cell	Ag foil	CO	−1.5 vs. SCE	ca. 2.4	>99	[89]
12	[BMIm][BF <sub>4</sub> ] (25 mol%) in H <sub>2</sub> O		Pd <sub>83</sub> Cu <sub>17</sub> aerogel	CH <sub>3</sub> OH	−2.1 vs. Ag/Ag <sup>+</sup>	31.8	80.0	[90]
13	[BMIm][BF <sub>4</sub> ] in H <sub>2</sub> O (1 : 3)	Two-compartment cell	Sn/CuO	CH <sub>3</sub> OH	−2.0 vs. Ag/Ag <sup>+</sup>	67.0	88.6	[91]
14	[BMIm][PF <sub>6</sub> ] in ACN <sup>b</sup> /H <sub>2</sub> O (30/65/5 wt%)	Two-compartment cell	Pd <sub>3</sub> Bi nanostructured	CO	−2.0 vs. Ag/Ag <sup>+</sup>	7.1	87.7	[92]
15	[BMIm][PF <sub>6</sub> ] in ACN <sup>b</sup> /H <sub>2</sub> O (30/65/5 wt%)	Two-compartment cell	Sn foil	HCOOH	−2.3 vs. Ag/Ag <sup>+</sup>	32.1	92.0	[72]
16	[BMIm][PF <sub>6</sub> ] in ACN <sup>b</sup> /H <sub>2</sub> O (30/65/5 wt%)	Two-compartment cell	Cu <sub>1.63</sub> Se <sub>(1/3)</sub> nanostructured	CH <sub>3</sub> OH	−2.1 vs. Ag/Ag <sup>+</sup>	41.5	77.6	[93]
17	[BMIm][SO <sub>3</sub> CF <sub>3</sub> ] (0.3 M) in ACN <sup>b</sup>	Two-compartment cell	Ag foil	CO	−1.8 vs. Ag/AgCl	5	>95	[76]
18	[BzMIm][BF <sub>4</sub> ] in ACN <sup>b</sup> /H <sub>2</sub> O (14.6/73.7/11.7 wt%)		PbO <sub>2</sub>	HCOOH	−2.3 vs. Ag/Ag <sup>+</sup>	40.8	95.5	[94]
19	[TBP][4-MF-PhO] <sup>e</sup> in ACN <sup>b</sup>	Two-compartment cell	Pb foil	C <sub>2</sub> O <sub>4</sub> <sup>2−</sup>	−2.6 vs. Ag/Ag <sup>+</sup>		93.8	[95]

<sup>a</sup> Cobalt tetrakis(4-aminophenyl)porphyrin complex. <sup>b</sup> Acetonitrile. <sup>c</sup> [Rh(2,2'-bipyridine)(pentamethylcyclopentadienyl)Cl]Cl. <sup>d</sup> Low density polyethylene. <sup>e</sup> [Tetrabutylphosphonium][4-(methoxycarbonyl)phenol].

**Figure 3.** Cyclic voltammograms on a glassy carbon electrode in a) 0.1 M [TBA][BF<sub>4</sub>] and b) 0.1 M [EMIm][BF<sub>4</sub>] aqueous solutions, containing 0.1 M acetate buffer and 1 mM Rh complex. Measurements conducted under argon (black plot) and under CO<sub>2</sub> (green plot) at a scan rate of 0.01 V·s<sup>−1</sup>. c) HER current density values at a given potential from black plots in Figures 3a & 3b. d) Faradaic efficiency of CO and H<sub>2</sub> from CO<sub>2</sub> electrolysis

on Ag-foil cathode at different applied current densities in 0.3 M ILs acetonitrile solutions. Adapted from refs. [80] and [76] (CC-BY 4.0 Wiley-VCH GmbH and Springer Nature Ltd).





All these findings highlight the complexity in interpreting the role of ILs in CO<sub>2</sub>RR, emphasizing the challenges associated with concomitant HER suppression. Nevertheless, ILs offer an evident set of advantages in CO<sub>2</sub>RR, thus position them as promising contenders for advancing electrochemical CO<sub>2</sub> conversion technologies. Moreover, ILs seem to play an additional role modulating the products selectivity (C<sub>1</sub>, C<sub>2</sub> and C<sub>2+</sub>) in the CO<sub>2</sub>RR.

#### 4.1. CO<sub>2</sub>RR in ILs for the Production of C<sub>1</sub> Compounds

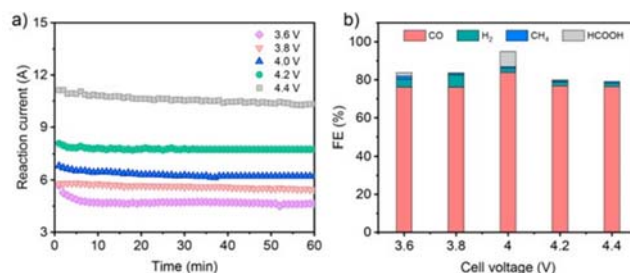
Different C<sub>1</sub> products have been yielded during the electrocatalytic CO<sub>2</sub>RR in the presence of ILs, being the conversion of CO<sub>2</sub> either to CO or HCOOH the most deeply studied CO<sub>2</sub>RR pathways in the presence of ILs, as can be observed from Table 3. ILs have been mainly used in solution only as electrolyte, to avoid drawbacks such as the transport limitations associated with viscosity and cost. Nevertheless, some interesting results have been also obtained using neat ILs (Table 3, entries 1–4). In these cases, the CO<sub>2</sub> solubility is much higher than in aqueous solution, which enhances the CO<sub>2</sub>RR performance. For instance, different catalytic materials have led to the formation of multiple C<sub>1</sub> products, including CO, CH<sub>4</sub> and HCOOH, with faradaic efficiencies as higher as 98%, in the presence of neat imidazolium-based ILs.<sup>[81–84,96]</sup>

Apart from CO and HCOOH, another interesting C<sub>1</sub> product from CO<sub>2</sub>RR is methanol (CH<sub>3</sub>OH), a clean and versatile fuel. Traditionally plagued by inefficiency and low selectivity, CO<sub>2</sub> conversion to CH<sub>3</sub>OH saw a breakthrough in the work from Guo et al. (Table 3, entry 13).<sup>[91]</sup> This electrocatalyst was featured by dispersing Sn atomic sites anchored on defective CuO, in the presence of the IL [BMIm][BF<sub>4</sub>] as electrolyte in aqueous solution. By means of this combination of catalyst and electrolyte, an outstanding faradaic efficiency to methanol of 88.6% was achieved within a current density of 67 mA·cm<sup>-2</sup>. The synergy between the Sn atomic sites, adjacent oxygen vacancies created by H-plasma treatment, and also the CuO support improved double-layer capacitance and CO<sub>2</sub> adsorption capacity, as well as reduced the interfacial charge transfer resistance.

Industrial ILs implementation for CO<sub>2</sub>RR in flow cell systems with an electrode active area of 495 cm<sup>2</sup> has been recently reported by Yuan et al.<sup>[97]</sup> For instance, Figure 4 shows an imidazolium-IL in acetonitrile solution containing 5 wt% H<sub>2</sub>O under the optimum operating conditions (E<sub>cell</sub> = 4 V), which displays 83.9% FE to CO, while HER was effectively suppressed (only 2% FE<sub>H<sub>2</sub></sub>).

**Figure 4.** CO<sub>2</sub>RR in 0.1 M [BMIm][BF<sub>4</sub>]/ACN/5 wt% H<sub>2</sub>O. a) Evolution of CO<sub>2</sub>RR current during electrolysis at different cell potentials. b) Effect of cell voltage on selectivity. Reprinted with permission from ref. [97]. Copyright 2022 Elsevier Ltd.

With the same aim, Feng et al. demonstrated the remarkable impact of a 1,2,3-trialkyl-imidazolium IL ([BMMIm][BF<sub>4</sub>]) in a flow cell,<sup>[98]</sup> not only by increasing the faradaic efficiency for CO production and the current density (234 mA·cm<sup>-2</sup>), but also by decreasing the overpotential of the CO<sub>2</sub> conversion to CO.



#### 4.2. HER Suppression in the Presence of ILs

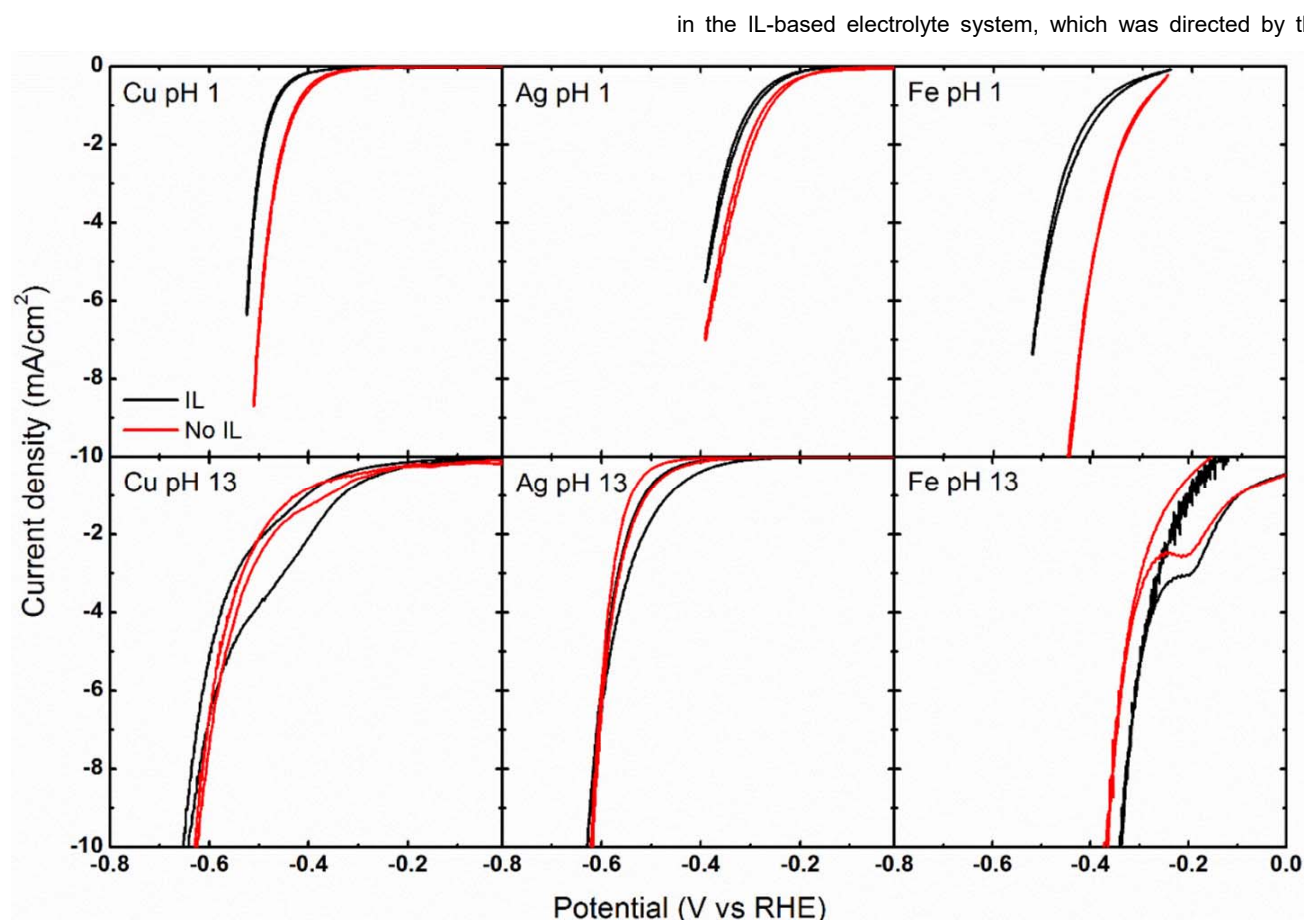
In general, the presence of ILs as electrolyte in molecular solvents notably diminishes the reduction potential for CO<sub>2</sub>RR and also helps to suppress the competitive HER. In particular, the impact

of a low concentration of imidazolium-based ILs (0.1 M) on the HER activity on several transition metal electrocatalysts was reported by Feaster et al.<sup>[99]</sup> The studied cathode materials were selected on the basis of their different product selectivity: Fe towards HER, Ag for enhancing CO production and Cu towards  $C_2$  products. In all three cases, it was demonstrated that the addition of 0.1 M [EMIm][Cl] to an acidic aqueous solution suppressed HER activity by between 10% and 75 % (Figure 5, upper panel), whereas barely no HER suppression occurred in basic medium (Figure 5, lower panel), which introduces the solution pH as an additional parameter to understand the role of ILs in  $CO_2$ RR. The authors attributed this pH-dependent behavior to the fact that the [EMIm]<sup>+</sup> cation displaces the interfacial  $H_3O^+$  from the electrode surface, but not the interfacial neutral  $H_2O$  molecules. This is a relevant factor for potential application of ILs in acidic  $CO_2$  electrolysis.<sup>[60,99,100]</sup>

Regarding the different mechanisms for the HER suppression mediated by ILs, there are two main hypotheses reported in the literature: (i) the modification of the electrode surface by ILs, which increases its hydrophobicity, and (ii) the electrostatic interactions provoked by the presence of IL ions within the EDL.

(i) Wang et al. performed the reduction of an imidazolium-based IL on Cu electrode, reporting the formation of an [EMIm]<sup>+</sup> layer, which played the role of an active catalytic site for  $CO_2$ RR on the electrode surface.<sup>[101]</sup> This made possible to limit the HER thanks to the inhibition of the proton adsorption by the adsorbed [EMIm]<sup>+</sup> layer. Further parallel density functional theory (DFT) calculations revealed that this cation plays a key role in the catalytic enhancement of the  $CO_2$ RR by a Re complex in acetonitrile.<sup>[102]</sup> In the same frame, Cuesta and col. in situ monitored the  $CO_2$ RR in a 18% [EMIm][BF<sub>4</sub>]/H<sub>2</sub>O mixture on Au electrodes.<sup>[78]</sup> The modification of the EDL structure during  $CO_2$ RR was studied by highly-sensitive attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS). By increasing cathodic polarization potential, IR absorption bands corresponding to [EMIm]<sup>+</sup> become more intense, suggesting a different reorientation of [EMIm]<sup>+</sup> within the EDL when  $CO_2$  is present. Banerjee et al. also enhanced the  $CO_2$ RR by modifying EDL by increasing the concentration of cationic surfactants with long hydrocarbon tails.<sup>[67]</sup> This accumulation of hydrophobic cations at the EDL decreased the local dielectric constant and effectively lowered the available protons for HER.

**Figure 5.** Cyclic voltammograms recorded on Cu, Ag, and Fe electrodes using both basic and acidic aqueous electrolytes, and in the presence and absence of 0.1 M [EMIm][Cl]. Reprinted with permission from ref. [99]. Copyright (2017) American Chemical Society.



(ii) On the other hand, Lim et al. have pointed out the electrostatic effect promoted at the metal/IL interface as responsible for facilitating the  $CO_2$ RR and suppressing the HER.<sup>[103]</sup> Those authors found a significant polarization of the metal electron density on the catalyst surface toward the key  $COO^{\bullet-}$  intermediate

charge effect of the [EMIm]<sup>+</sup> cation on the metal surface. This induces a strong local electric field effect at the EDL interface, which stabilizes the  $COO^{\bullet-}$  intermediate via field-dipole interaction. Ren et al. have also confirmed the role of the [BMIm]<sup>+</sup> cation in the  $CO_2$ RR intermediates stabilization over Ni-N

catalyst,<sup>[104]</sup> by minimizing the energy barrier of the rate-limiting reaction step from 1.49 to 0.80 eV. Interestingly, Ni–N hosts can overcome some of the major drawbacks of ILs, including viscosity, moderate conductivity, low diffusion and cost, by confining the ILs within nanoporous. All these features lead to a faradaic efficiency for CO production over 98% with the HER practically suppressed.<sup>[104]</sup> In this case again, the presence of [BMIm]<sup>+</sup> on the Ni–N surface induces a strong local electric field effect at the EDL interface, and thus stabilizes the COO<sup>•−</sup> intermediate *via* field-dipole interaction.

In conclusion, most of the works described in the literature are devoted to the use of imidazolium-based ILs.<sup>[57,79,105,106]</sup> However, other alternatives such as pyrrolidinium,<sup>[106,107]</sup> and pyrazolium-based ILs have also been mentioned.<sup>[108]</sup> For example, fully-substituted pyrazolium cations display enhanced CO<sub>2</sub>RR, through the stabilized pyrazolium–CO<sub>2</sub> adduct formation and the effective modification of the EDL. Nevertheless, imidazolium ILs are in general the most active ones favoring CO<sub>2</sub>RR and suppressing HER. This is most probably because the aromatic ring present in imidazolium-ILs is able to notably stabilize the CO<sub>2</sub> anion-radical intermediate *via* hydrogen bond interactions, which effectively reduces the overpotential associated to CO<sub>2</sub>RR, but also allows to tune the EDL.<sup>[98,109]</sup> Moreover, the impact of ILs in the CO<sub>2</sub>RR performance can be modulated by introducing specific functional groups (for instance –OH) or also by modifying the location and accessibility of the surface charges.<sup>[108]</sup>

## 4.3. CO<sub>2</sub>RR in ILs for the Production of C<sub>2</sub> and C<sub>2+</sub> Compounds

In the realm of electrocatalytic CO<sub>2</sub> reduction to produce C<sub>2</sub> and C<sub>2+</sub> products, ILs have emerged as a compelling choice because of their customizable acidity and alkalinity, their electrochemical properties and designable structures.<sup>[97,109,110]</sup>

Ethylene (C<sub>2</sub>H<sub>4</sub>), in particular, holds economic and industrial interest, and for its production Cu stands as the preferred catalytic material due to reasonable high faradaic efficiency and C<sub>2</sub>H<sub>4</sub> selectivity. In this way, Ummireddi et al. presented a significant advance in the electrochemical CO<sub>2</sub>RR on Cu by adding ammonium-based cations for promoting the selective production of ethylene.<sup>[111]</sup> The strategical modification of the binding strength of the critical COO<sup>•−</sup> intermediate, successfully favored the pathway to ethylene over formate, while additionally inhibiting the HER. For it, various ILs, including imidazolium, pyrazolium, pyrrolidinium, and tetralkylammonium cations, were investigated. Among them, the tetraethylammonium cation exhibited the most promising results, showing high CO<sub>2</sub>RR selectivity to C<sub>2</sub>H<sub>4</sub> production and minimal HER activity. DFT calculations further elucidated that this outcome can be attributed to the moderate stabilization of the COO<sup>•−</sup> intermediate, as well as to a reduction in the hydrogen binding energy, underlining the mechanism behind the enhanced CO<sub>2</sub>RR to C<sub>2</sub>H<sub>4</sub> with a simultaneous HER

suppression. Oxalate (C<sub>2</sub>O<sub>4</sub><sup>2−</sup>) is another industrially-relevant C<sub>2</sub> product generated in the CO<sub>2</sub>RR using ILs.<sup>[112–114]</sup> For instance, the use of a phosphonium-based IL ([TBP][4-MF-PhO]) in acetonitrile solution has already allowed 93.8% faradaic efficiency for oxalate production on a Pb foil (Table 3, entry 19).<sup>[95]</sup>

The CO<sub>2</sub>RR process to generate C<sub>2+</sub> products, mainly long alkyl-chain alcohols, involves multiple intermediate steps and complex intermediates, requiring a multi-proton/electron transfer process and C–C coupling steps.<sup>[115]</sup> In general, Cu-based catalysts are widely studied for the formation of C<sub>2+</sub> products due to their ability to perform C–C coupling reactions. However, the adsorption strength for the \*CO intermediate directly affects the products distribution on Cu-based catalysts, with strong \*CO adsorption leading to catalyst poisoning, and weak \*CO adsorption generating CO as the main product. Additionally, the C–C coupling reaction is a proton reductive process, making the protons supply critical. A too high concentration of protons promotes the undesired HER, while a low concentration is not enough for \*CO hydrogenation process. Therefore, it is essential to consider not only the effect of \*CO adsorption strength on the catalyst, but also the proton supply.<sup>[115]</sup>

Some global techno-economic studies for the use of ILs in CO<sub>2</sub>RR at industrial scale can be found in the literature, even including a full life cycle assessment (LCA) analysis for evaluating the environmental impact.<sup>[77,116]</sup> In general, techno-economic analysis show that the electrochemical conversion of CO<sub>2</sub> to CO is the main profitable route at present time, together with the production of methanol. Finally, just mention that some drawbacks associated with cost, viscosity or ecotoxicity, could limit the direct scaling up of some IL-based electrolytes in the CO<sub>2</sub>RR.

## 5. Deep Eutectic Solvents as Solvents and/or Electrolytes for CO<sub>2</sub>RR

DES present a wide range of physical-chemical properties, which are similar to those in ILs. Thus, their use in CO<sub>2</sub>RR has being studied since the first works of Verma et al. (in 2016, using a DES as electrolyte),<sup>[117]</sup> and Vasilyev et al. (in 2019, using a DES both as solvent and electrolyte).<sup>[118]</sup> Moreover, as it has been described in the introduction, customized DES might display an exalted capacity of absorption/desorption for CO<sub>2</sub>. Therefore, the interest in the design and development of energy-efficient and non-toxic integrated systems based on DES for combining both the capture and conversion of CO<sub>2</sub> is attracting increasing attention. Moreover, the techno-economic analysis shows a lower cost of DES with respect to the use of ILs for CO<sub>2</sub>RR.<sup>[116]</sup>

**Table 4.** Catalytic activity, selectivity and main experimental conditions of a selection of neat DES and DES as electrolyte in solution for CO<sub>2</sub>RR.

Entry	Solvent	Cell type	Catalyst	Main products	Current density  (mA·cm <sup>−2</sup> )	Faradaic Efficiency (FE, %)	Ref.
<i>Neat DES</i>							

1	ChCl-Urea (1:2) <sup>a</sup>	Two-compartment cell	Ag disc	CO	0.1	15.8	[118]
2	ChCl-EG (1:2) <sup>b</sup>	Two-compartment cell	Ag disc	CO	0.4	78.0	[118]
3	1 M ChCl in EG	Two-compartment cell	Ag disc	CO	0.94	71.1	[118]
4	ChCl-EG (1:2) <sup>b</sup>	Two-compartment cell	Au sheet	CO	1.1	81.8	[119]
5	[BMIm][Cl]-EG (1:2)	Two-compartment cell	Ag disc	CO	0.88	95.8	[118]
<b>DES solutions</b>							
6	2 M ChCl-Urea (1:2) in H <sub>2</sub> O	Flow reactor	Ag nanoparticles	CO	11.6	94.1	[117]
7	2 M ChCl in H <sub>2</sub> O	Flow reactor	Ag nanoparticles	CO	27.6	78.0	[117]
8	ChCl-Urea (1:2) + H <sub>2</sub> O (15 vol%)	Two-compartment cell	Ag disc	CO	0.6	59.0	[118]
9	ChCl-Urea (1:2) + H <sub>2</sub> O (50 wt%)	Two-compartment cell	Ag foil	CO		96.0	[120]
10	1 M ChCl - 2 M EG in H <sub>2</sub> O	Two-compartment cell	Ag disc	CO	2.3	23.3	[118]
11	1 M ChCl - 2 M EG in ACN <sup>c</sup>	Two-compartment cell	Ag disc	CO	7.0	98.8	[118]
12	MEAHCi-MEA (1:1) in H <sub>2</sub> O <sup>d</sup>	Two-compartment cell	Ag foil	CO	15.4	54.5	[20]
13	MEAHCi-DEA (1:1) in H <sub>2</sub> O <sup>e</sup>	Two-compartment cell	Ag foil	CO	12.6	59.0	[20]
14	MEAHCi-MDEA (1:1) in H <sub>2</sub> O <sup>f</sup>	Two-compartment cell	Ag foil	CO	10.5	71.0	[20]
15	MDEAHCi-MDEA (1:1) in H <sub>2</sub> O	Two-compartment cell	Zn foil	CO, H <sub>2</sub>		34.0	[20]
16	MDEAHCi-MDEA (1:1) in H <sub>2</sub> O	Two-compartment cell	Cu foil	CO, H <sub>2</sub>		10.0	[20]

<sup>a</sup> ChCl: Choline Chloride. <sup>b</sup> EG: Ethylene Glycol. <sup>c</sup> ACN: acetonitrile. <sup>d</sup> MEAHCi-MEA: Monoethanolamine hydrochloride-methylethanolamine. <sup>e</sup> MEAHCi-DEA: Monoethanolamine hydrochloride-diethanolamine. <sup>f</sup> MEAHCi-MDEA: Monoethanolamine hydrochloride-methyldiethanolamine.

In the present section, the role of DES in CO<sub>2</sub>RR as either solvent/electrolyte or only supporting electrolyte is discussed in detail. Despite of the interest that the use of DES for CO<sub>2</sub>RR has awakened in the scientific community, a limited number of publications devoted to this topic are available in the literature at present. Nevertheless, interesting conclusions can be already made in order to offer perspectives and clues for expanding the room of DES in CO<sub>2</sub>RR. With this aim, Table 4 summarizes some of the most representative examples of the use of neat DES, as well as aqueous and organic DES solutions, in CO<sub>2</sub>RR.

### 5.1. CO<sub>2</sub>RR in DES for the Production of C<sub>1</sub> Compounds

As can be seen from Table 4, most of the works published so far studying the activity of CO<sub>2</sub>RR in DES (both as solvent and electrolyte) involve the use of a silver catalyst at the cathode. As a consequence, the main C<sub>1</sub> product obtained in the CO<sub>2</sub>RR has been CO.

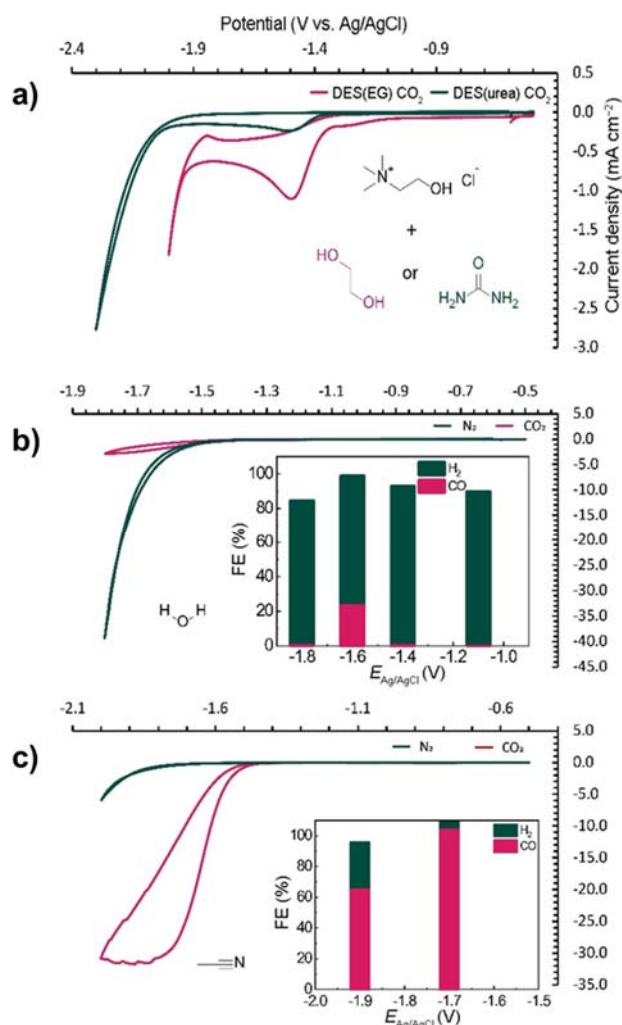
The first reported attempt of applying a DES for CO<sub>2</sub>RR was carried out by Verma et al. by studying the activity of the DES ChCl-urea (reline) as electrolyte in aqueous solution (entry 6 in Table 4).<sup>[117]</sup> Despite the high viscosity of this DES (750 mPa·s at 298 K), a faradaic efficiency of 94.1% to CO production was obtained using Ag nanoparticles in an electrochemical flow reactor. This first example reveals that the high viscosity issue of

some of these ionic solvents can be mostly circumvented in the case of using them as electrolytes in aqueous solution. In this case, the great increase in the faradaic efficiency to CO (with respect to using conventional supporting electrolytes) can be attributed to the stabilization of the rate-limiting COO<sup>•-</sup> intermediate by the tetralkylammonium cation present in the ChCl-HBA component of the DES.<sup>[117]</sup> This is demonstrated by the high CO production (FE = 78%) achieved with the sole presence of the ChCl in aqueous solution (entry 7 in Table 4). Interestingly, the addition of a second electrolyte together with ChCl-Urea (1:2) for increasing the medium conductivity allowed to improve the CO<sub>2</sub>RR performance. Thus, addition of potassium chloride (KCl 1.5 M, keeping constant the total electrolyte concentration in 2.0 M), increased two times the current density on the CO<sub>2</sub> conversion to CO and kept simultaneously a high faradaic efficiency of 85.1%.<sup>[117]</sup>



**Figure 6.** Cyclic voltammograms recorded on Ag electrode for CO<sub>2</sub>RR in a) neat ChCl-urea (green plot) and ChCl-EG (red plot) DES, b) 1 M ChCl and 2 M EG in aqueous solution, c) 1 M ChCl and 2 M EG in acetonitrile solution. Insets: FEs obtained during potentiostatic electrolysis in presence of CO<sub>2</sub> in each case. Adapted from ref. [118] (CC-BY 2019 Wiley-VCH GmbH).

The DES reline was not applied as neat reaction medium (thus as both solvent and supporting electrolyte) for the CO<sub>2</sub>RR until the work of Vasilyev et al.<sup>[118]</sup> Herein, two choline-based DES were



studied (Figure 6a), ChCl-urea (reline) and ChCl-EG (ethaline), together with a novel imidazolium chloride DES, [BMIm][Cl]-EG. The results were significantly different for each studied DES, as it could be expected a priori due to the different physical-chemical and electrochemical properties of these solvents. For instance, in the case of using ChCl-urea as neat DES, a peak attributed to the CO<sub>2</sub> reduction was found in the CV experiments (see green plot in Figure 6a). However, the corresponding chronoamperometric analysis revealed that neat ChCl-urea displayed a low CO<sub>2</sub>RR performance, with current densities lower than 0.1 mA·cm<sup>-2</sup> and a faradaic efficiency for CO production of 15.8% (Table 4, entry 1). The authors proposed that the higher viscosity of the DES reline (see the value above) triggers the faster depletion of CO<sub>2</sub> at the cathode surface, which facilitates the competing HER and even the reduction of the electrolyte.<sup>[118]</sup> Alternatively, the CO<sub>2</sub> conversion to CO was noticeably higher when using the ChCl-EG

as neat DES, which displays much lower viscosity (37 mPa·s at 298 K) and thus higher conductivity (7.6 mS·cm<sup>-1</sup>). In the fundamental analysis by CV and chronoamperometry, the CO<sub>2</sub> reduction peak showed more than one order of magnitude of difference in the current density (with respect to the ChCl-urea DES, Figure 6a in red). Furthermore, in the potentiostatic electrolysis, a faradaic efficiency for CO of 78%, more than 5 times higher than in the case of using neat ChCl-urea, and a current density of 0.4 mA·cm<sup>-2</sup> were achieved (Table 4, entry 2). This improvement in faradaic efficiency and current density was proved to be mainly linked to the presence of the ChCl in ethylene glycol solution (Table 4, entry 3) and thanks to the stabilization of CO<sub>2</sub>RR intermediates. Therefore, it is clear that limitations in the mass transport due to the viscosity of the solvent can discourage the application of viscous neat DES such as reline or glyceline to the CO<sub>2</sub>RR. Fortunately, at least five possible strategies to overcome this issue have been proposed in the literature, including: (i) better design of the electrochemical cell or electrodes configuration and surface,<sup>[118]</sup> (ii) utilization of more active electrocatalysts,<sup>[20]</sup> (iii) introduction of gas-diffusion electrodes for helping to the slow diffusion of CO<sub>2</sub>,<sup>[118]</sup> (iv) electrolyte engineering strategies,<sup>[117]</sup> and (v) their application as supporting electrolytes dissolved in non-viscous molecular solvents.<sup>[117,118]</sup> Following strategy (v), both Verma et al. and Vasilyev et al. works, showed a great increase in the CO<sub>2</sub>RR performance by using aqueous solutions of DES.<sup>[117,118]</sup> For instance, in the case of the viscous ChCl-urea DES, the faradaic efficiency to CO increased from 15.8% to 59% just by increasing the amount of water in solution (see Table 4, entries 1 and 8, respectively). This increase in the catalytic activity is a consequence of the great reduction in the medium viscosity that lead to a facilitated mass transport. The introduction of the water molecules disrupts the strong hydrogen-bond network of the pure DES, facilitating the transport of the dissolved CO<sub>2</sub>, reaction intermediates and ions at the cathode surface. Nevertheless, in a mostly aqueous medium the higher availability of protons can lead to a parallel increase in the faradaic efficiency for H<sub>2</sub> production, due the competitive HER. More recently, Garg et al. achieved a faradaic efficiency for CO<sub>2</sub> conversion to CO of 96% by using a selective silver catalyst at the cathode and an aqueous solution of ChCl-urea (50 wt%) (Table 4, entry 9).<sup>[120]</sup> In this case, and with respect to the previous studies using aqueous solutions of DES, the increase in the product selectivity is explained by the authors based on the surface restructuring underwent by the Ag foil electrode. Initially, the dissolution of silver oxide layers on the electrode surface takes place (thanks to the powerful metal-solubilizing ability of the highly chloride concentrated DES), followed by the electrodeposition of silver nanoparticles back on the cathode surface. As a consequence of this dissolution/deposition process, low-coordinated silver atoms are generated on the cathode surface, increasing the surface area and facilitating the adsorption of choline cations and urea at the cathode surface. This notably reduces the HER, and enhances the CO<sub>2</sub>RR.<sup>[120]</sup>

In order to increase the catalytic activity in the CO<sub>2</sub>RR, but reducing at the same time the competitive HER by reducing the availability of proton at the cathode surface, non-aqueous solutions of DES have been also proposed with excellent results. For instance, instead of using ChCl-EG aqueous solutions (Figure 6b and entry 10 in Table 4), the dissolution of this DES in acetonitrile (Figure 6c and entry 11 in Table 4) allowed to increase the current density during the CO<sub>2</sub> electrolysis from 0.4 in neat ChCl-EG to 7.0 mA·cm<sup>-2</sup>, as well as the faradaic efficiency

towards CO from 78% to 98.8% (see Figure 6c vs. 6a & 6b).<sup>[118]</sup> This is due to the facilitated mass transport in these organic media, and also to the higher CO<sub>2</sub> availability at the surface electrode, since the CO<sub>2</sub> solubility in organic solvents such as acetonitrile can be up to eight times higher than in aqueous solutions.

In all the above described cases, the enhancing in the performance on the CO<sub>2</sub>RR was mainly attributed to the presence of the vicinal hydroxyl group in the structure of the cation choline present as the HBA component of the DES. In fact, Vasilyev et al. found a shift in the reduction onset potential of 600 mV when comparing the CO<sub>2</sub>RR in the presence and in the absence of ChCl. Therefore, it seems that, at least in the case of the ChCl-based DES, the quaternary ammonium salt (HBA) is responsible to reduce the overpotential required thanks to the stabilization of the COO<sup>•-</sup> intermediate during the electro-reduction of CO<sub>2</sub>.<sup>[118]</sup>

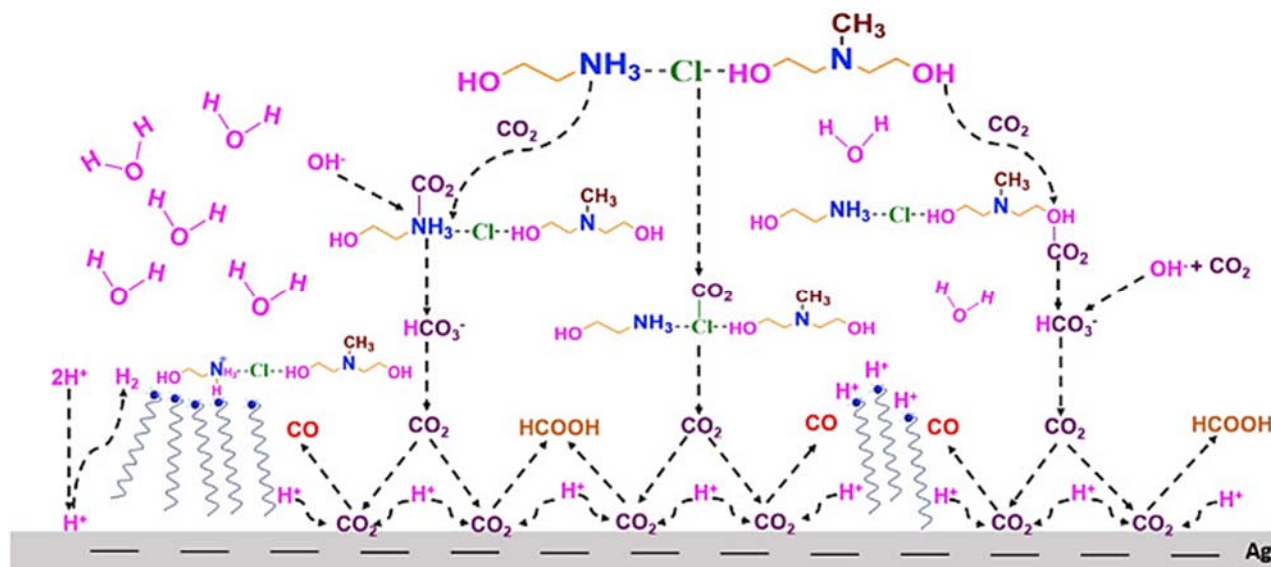
Novel DES are continuously appearing in the literature. For instance, [BMIm][Cl]-EG (Table 4, entry 5) provides a faradaic efficiency for CO production of almost 96%, despite displaying a viscosity similar to that of the neat ChCl-EG (36.9 and 40.1 mPa·s at 294 K, respectively). This enhancement in the faradaic efficiency from 78% to 96% could only be attributed to the role of the different cation present in the DES (choline versus imidazolium). Moreover, tetrabutylammonium chloride (TBAC)-based DES, containing citric acid, fructose and diethanolamine as the HBD, has been recently evaluated for CO<sub>2</sub>RR.<sup>[121]</sup> Interestingly, these DES that include in their composition a more hydrophobic ammonium salt, but no the proximal hydroxyl group, displayed poorer results than ChCl-based DES in the electro-reduction of CO<sub>2</sub>, supporting the key role played by the vicinal hydroxyl group in choline cation.

According to the proposed idea of developing an integrated system for the in situ capture and conversion of CO<sub>2</sub> by using highly-efficient CO<sub>2</sub>-capture DES based on amines, Ahmad et al. have recently studied the CO<sub>2</sub>RR facilitated by ethanolamine-based DES in aqueous solution (Table 4, entries 12–16). The studied HBD components were methylethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). In this case, the presence of the ionic solvent as electrolyte enhances the CO<sub>2</sub> conversion to CO and in some extent to formate on silver, zinc and copper cathodes.<sup>[20]</sup> It is interesting to mention that those DES were proved to enhance CO<sub>2</sub>RR activity, thanks to the occurrence of a synergistic mechanism with nano-size metallic agglomerate dispersion formed by a dissolution/deposition process at the electrode surface together with bicarbonate formation that enhance the CO<sub>2</sub>RR with respect to the use of the pure amine alone. But what is even more interesting here, is that both components of the DES, i.e. both HBD and HBA, had an impact on the performance of the CO<sub>2</sub>RR. For instance, regarding the HBD component, in the case of using a silver catalyst (Table 4, entries 12–14), the concentration of amine in the medium allowed to modify the products selectivity, since the faradaic

efficiency towards CO increased inversely to the MDEA concentration (up to 71%, see Table 4, entry 14). Furthermore, the DES containing the amine MDEA as HBD showed a 33% higher FE<sub>CO</sub> value than the one containing MEA as HBD (Table 4, entry 12). This was attributed to the basicity difference of the DES, leading to a different stabilization of the CO<sub>2</sub>RR intermediates.<sup>[20]</sup> Regarding the HBA component, the highest faradaic efficiency was provided by the DES containing the cation MEAHCl, much higher than for DEAHCl, possibly because the presence of an additional OH group in DEAHCl lowers the dielectric constant and basicity of the DES that reduces the CO<sub>2</sub> absorption and thus the CO<sub>2</sub>RR performance. In all the cases, the use of an amine-base DES allowed to achieve much higher CO<sub>2</sub>RR performance than in the case of using the corresponding pure amine. This could be probably related to the massive chloride ions concentration in the case of the DES, which facilitates the transport of CO<sub>2</sub> to the cathode surface as has been recently proposed in the case of silver cathodes (Figure 7).<sup>[20]</sup>

As a conclusion of these results, it becomes possible to design and tune the composition of the DES for optimizing the CO<sub>2</sub>RR performance. Alternatively to the use of silver cathodes, the performance of these ethanolamine-based DES as electrolytes in CO<sub>2</sub>RR was also evaluated using zinc and copper electrodes (Table 4, entries 15 & 16).<sup>[20]</sup> In these cases, lower faradaic efficiencies to CO were achieved (34% FE<sub>CO</sub> for zinc in MDEAHCl-MDEA solution and 10% FE<sub>CO</sub> for copper in MEAHCl-MDEA or MDEAHCl-MDEA solutions), since other products were formed, mainly H<sub>2</sub> coming from HER. The authors explained that using an amine-based DES in the presence of a copper electrode represents a more complex situation, since the formation of a Cu-amine complex on the cathode surface notably favors the competitive HER.

As can be observed from Table 1, mainly type-III DES have been applied for CO<sub>2</sub>RR so far. This can be explained from the availability, renewable origin and general stability/easy handling of this specific type of DES. Nevertheless, the utilization for CO<sub>2</sub>RR of other types of DES, such as type-IV DES as neat solvent and/or electrolyte, or type-I and type-II DES only as electrolyte (due to their high viscosity) should be encouraged as well, since the presence of metallic ions provided by the solvent has been already proved to display a co-catalytic role in diverse catalytic reactions.<sup>[26]</sup> Recently, Halilu et al. have studied the use of transition-metal-based DES, such as ZnCl<sub>2</sub>-ethanolamine (1:4) and CoCl<sub>2</sub>-ethanolamine (1:4), for the CO<sub>2</sub> capture and its electrochemical conversion using single-atom Ag as electrocatalyst.<sup>[122]</sup> The authors analyze for the first time mechanistic aspects as the CO<sub>2</sub> coordination mode to the metal and propose that the metallic DES component forms a compact layer at the interface, while the COO<sup>•-</sup> intermediate remains in the diffuse layer.



**Figure 7.** Mechanism for the production of CO on Ag electrode using a MDEA-based DES. Reprinted with permission from ref. [20]. Copyright 2021 Elsevier Ltd.

Finally, it is noteworthy to mention that all the above described works carry out the CO<sub>2</sub>RR in electrochemical cells with electrodes separation (such as H-type or U-type divided cells), mainly due to the risk of electro-oxidation at the anode of the reaction products or even the eutectic solvent components. In this context, the work of Verma et al. proved the feasibility of using a flow reactor for carrying out the CO<sub>2</sub>RR using a DES with high efficiency (~95% FE to CO).<sup>[117]</sup> Nevertheless, more research is still required to be able to implement industrial scaled CO<sub>2</sub>RR processes involving the use of DES.

## 5.2. CO<sub>2</sub>RR in DES for the Production of C<sub>2+</sub> Compounds

Although the DES have already being successfully used in CO<sub>2</sub>RR for the generation of C<sub>1</sub> products with a relatively high efficiency, C<sub>2+</sub> products are still limited in terms of efficiency using these ionic solvents. As can be seen from Table 4, CO has been the main product reported in the literature so far. Moreover, the mechanism explaining the formation of CO and the concurrence of side HER has being already investigated (Figure 7). In this context, copper-based catalysts have been barely studied for CO<sub>2</sub>RR using DES, which means that the role of DES in the generation of C<sub>2+</sub> products is still unexplored. This is probably due to the fact that the first example of DES for the CO<sub>2</sub>RR did not appear until 2016 (2019 for the case of using a neat DES). Very recently, it has been proved that the design of the Cu-based electrocatalyst, for instance by tuning the growth of specific crystallographic planes using ionic solvents, has allowed to promote the CO<sub>2</sub>RR to C<sub>2</sub> products such as ethanol and ethylene.<sup>[123]</sup> Apart from the relevance of ionic solvents in the cathodic material synthesis, they are able to stabilize ionic metallic species in solution. This is particularly relevant in the case of DES, thanks to the large amount of chloride anions present in their composition. This fact represents a key point in the modulation of the CO<sub>2</sub>RR selectivity, in particular in the case of Cu cathodes. Unfortunately, no enough data are available yet to

draw conclusions about the performance of DES for the production of C<sub>2</sub> and C<sub>2+</sub> from CO<sub>2</sub>RR.

## 6. Further Strategies using Ionic Solvents for Enhancing CO<sub>2</sub>RR

Among the different ionic solvents described in this work, imidazolium-based ILs, mainly acting as supporting electrolyte mixed with molecular solvents to avoid drawbacks associated with mass transfer limitations due to high viscosity, were identified as excellent modulators of the electrochemical interface. Thus, the presence of a low concentration of imidazolium-based ILs in solution significantly enhances the catalytic activity and selectivity of CO<sub>2</sub>RR by promoting the CO<sub>2</sub> conversion and simultaneously suppressing the HER. Nevertheless, the solubility of most ILs in molecular solvents is limited and adding species in solution provokes additional difficulties to separate the CO<sub>2</sub>RR liquid products from them. According to this, it would be very interesting to immobilize a layer of imidazolium-based ILs on the cathode surface to overcome the present limitation of adding them in solution. Interestingly, several strategies to carry out the immobilization of very different imidazolium-based ILs onto the surface of the electrode have been recently proposed in the literature.

### 6.1. Enhanced CO<sub>2</sub>RR vs. HER by Surface Immobilized ILs

An advanced strategy for controlling the activity and selectivity of electrocatalysts for CO<sub>2</sub>RR lies in molecular modification of the electrode surface. This recent approach includes the immobilization of ILs onto the surface of the electrode material, which enhances the stability and selectivity of the CO<sub>2</sub>RR, as well as reduce the impact of the ILs drawbacks. Table 5 summarizes some of the most recent studies on ILs attached to the electrode surface for CO<sub>2</sub>RR.

**Table 5.** Catalytic activity, selectivity and main experimental conditions of a selection of surface-immobilized ILs for CO<sub>2</sub>RR.

Entry	Immobilized IL	Electrolyte	Cell type	Cathode	Products	Cathode Potential (V)	Current density  (mA·cm <sup>-2</sup> )	Faradaic Efficiency (FE, %)	Ref.
1	[BMIm][NO <sub>3</sub> ]	0.1 M KHCO <sub>3</sub>	Two-compartment cell	IL@Cu	C <sub>2</sub> H <sub>4</sub>	−1.19 vs. RHE	16.0	39.7	[124]
2	[BMIm][NO <sub>3</sub> ]	0.1 M KHCO <sub>3</sub>	Two-compartment cell	IL@Cu	C <sub>2</sub> H <sub>4</sub>	−1.49 vs. RHE	34.2	77.3	[124]
3	Poly(ionic liquid)	1 M KOH	Flow reactor	Cu <sup>0</sup> @PIL@Cu <sup>I</sup>	C <sub>2</sub> +	−0.85 vs. RHE	400	76.1	[125]
4	Poly(ionic liquid)	1 M KHCO <sub>3</sub>	Flow reactor	Cu <sup>0</sup> @PIL@Cu <sup>I</sup>	C <sub>2</sub> +		400	48.0	[125]
5	[OMIm][Cl] <sup>a</sup>	0.1M KHCO <sub>3</sub>	Two-compartment cell	Cu <sub>2</sub> O/ILGS-400 <sup>b</sup>	C <sub>2</sub> +	−1.15 vs. RHE	11.0	62.4	[109]
6	[OMIm][Cl]	1 M KOH	Flow reactor	Cu <sub>2</sub> O/ILGS-400	C <sub>2</sub> +	−1.10 vs. RHE	123.1	78.5	[109]
7	[PVBBI][TFSI]	H <sub>2</sub> O/[EMIm][BF <sub>4</sub> ] (10% v/v)	Single compartment cell	PS-b-[PVBBI][TFSI]/Re@HPC <sup>c</sup>	CO	−1.85 vs. Fc/Fc <sup>+</sup>	0.5	23.0	[126]
8	None	H <sub>2</sub> O/[EMIm][BF <sub>4</sub> ] (5% v/v)	Single compartment cell	Re@HPC	CO	−1.85 vs. Fc/Fc <sup>+</sup>		70.0	[126]
9	[EMIm][BF <sub>4</sub> ]	0.05 M H <sub>2</sub> SO <sub>4</sub> + 3 M KCl	Flow reactor	CuNP-EMIm	C <sub>2</sub> +		200.0	53.0	[100]
10	[EMIm][BF <sub>4</sub> ]	0.1 M H <sub>2</sub> SO <sub>4</sub>	Flow reactor	CuNP-EMIm	C <sub>2</sub> +		100.0	15.0	[100]

<sup>a</sup> 1-Octyl-3-methylimidazolium chloride. <sup>b</sup> ILGS: Ionic Liquid functionalized Graphite Sheets. <sup>c</sup> Hydrophobic Polystyrene-block-[poly(vinylbenzylimidazolium) with a butyl-substituted imidazolium][trifluoromethanesulfonimide]/Rhenium-based molecular complex on Hierarchical Porous Carbon material (HPC).

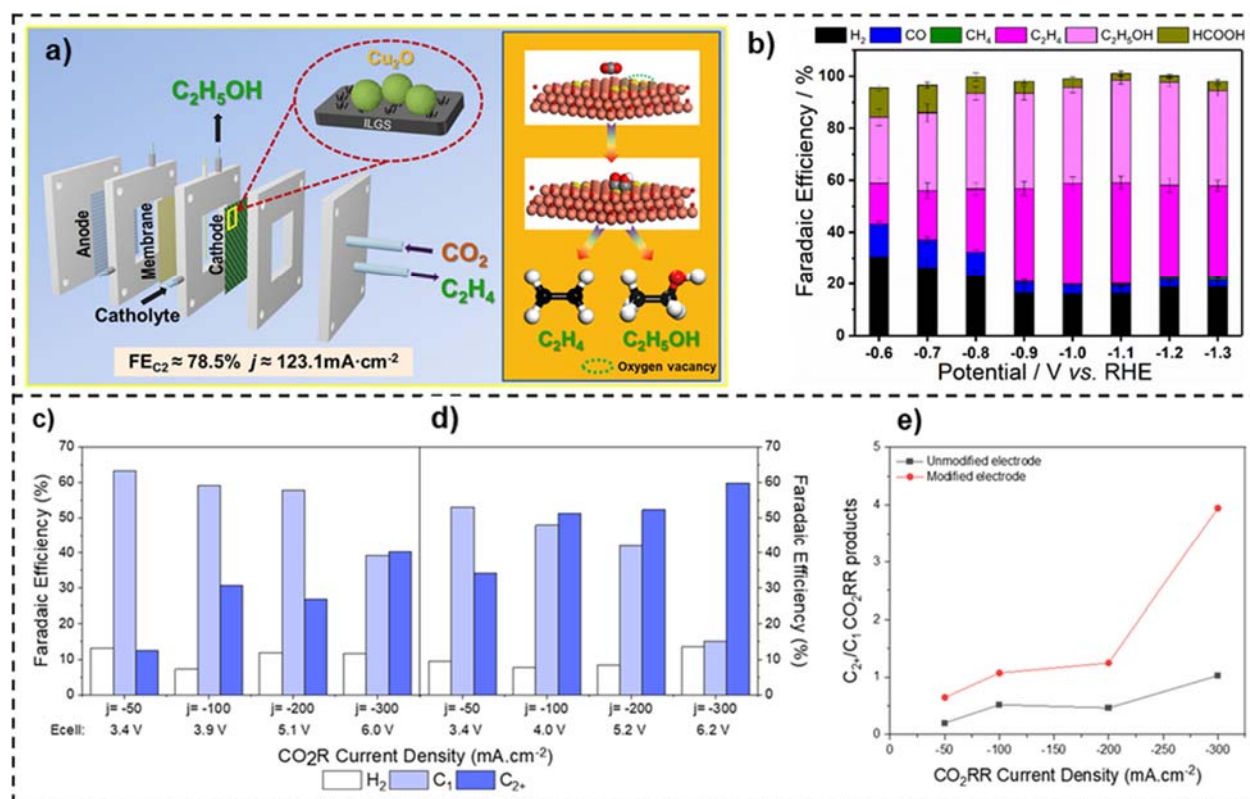
Sha et al. conducted a study aiming to enhance the CO<sub>2</sub>RR to ethylene (C<sub>2</sub>H<sub>4</sub>) by anchoring the IL [BMIm][NO<sub>3</sub>] on copper electrocatalysts by impregnation and subsequent electrolysis.<sup>[124]</sup> Then, the CO<sub>2</sub>RR was studied in 0.1 M KHCO<sub>3</sub> aqueous solution and the catalyst synthesized in presence of [BMIm][NO<sub>3</sub>] was named as IL@Cu. Remarkably, the faradaic efficiency to C<sub>2</sub>H<sub>4</sub> over IL@Cu exceeded 40% over a wide potential range spanning from −1.19 V to −1.59 V, reaching a maximum faradaic efficiency of 77.3% at −1.49 V (Table 5, entries 1 & 2) in contrast with 31.2% obtained on bare Cu electrocatalyst under equivalent conditions. Nevertheless, only moderate current densities were reached in this study (<40 mA·cm<sup>-2</sup>). Notably, the competitive HER was effectively suppressed, which was attributed by the authors to the increased CO<sub>2</sub> concentration at the electrode-solution interface facilitated by the hydrophobic chains in [BMIm][NO<sub>3</sub>], thus enhancing the selectivity towards CO<sub>2</sub> conversion.

A poly(ionic liquid) (PIL)-based Cu<sup>0</sup>–Cu<sup>I</sup> tandem catalyst for the CO<sub>2</sub>RR towards C<sub>2</sub> products successfully reached industrially relevant current densities (>100 mA·cm<sup>-2</sup>) at high faradaic efficiency (Table 5, entries 3 and 4).<sup>[114]</sup> This (PIL)-based Cu<sup>0</sup>–Cu<sup>I</sup> catalyst was synthesized by in situ polymerization of imidazolium-pyridine-imidazolium tridentate IL monomer in the presence of Cu nanoparticles and further addition of Cu<sup>I</sup> by impregnation. Then,

the CO<sub>2</sub>RR was studied in 1 M KOH and 1 M KHCO<sub>3</sub> aqueous solutions and the catalyst synthesized was named as Cu<sup>0</sup>@PIL@Cu<sup>I</sup>. The highly alkaline solution (Table 5, entry 3) favors C–C coupling reaction and suppresses more efficiently HER. Nevertheless, very limited carbon utilization can be reached under those conditions due to the abundant formation of carbonates from CO<sub>2</sub>.

In another study conducted by Wang et al., an enhanced CO<sub>2</sub>RR to C<sub>2</sub> products was achieved by the assistance of the IL 1-octyl-3-methylimidazolium chloride ([OMIm]Cl) in the synthesis of quasi-spherical Cu<sub>2</sub>O particles with rough surface.<sup>[109]</sup> In this approach, [OMIm]<sup>+</sup> cation played a key role as like-surfactant in inhibiting the growth of crystal planes in Cu<sub>2</sub>O nanoparticles. Those particles were synthesized supported on ionic liquid-functionalized graphite sheets (ILGS) and were named as Cu<sub>2</sub>O/ILGS composite material. Remarkably, when moving from an H-cell configuration (Table 5, entry 5) to a flow reactor configuration (Table 5, entry 6), a notable enhancement in the current density and faradaic efficiency towards C<sub>2</sub> products was observed. This catalyst demonstrated exceptional electrocatalytic performance, boasting a high faradaic efficiency for C<sub>2</sub> products (78.5%) and achieving commercial-level current density (123.1 mA·cm<sup>-2</sup>) over a 100-hour period in a flow reactor (Figure 8a).





**Figure 8.** a) Enhanced CO<sub>2</sub>RR to C<sub>2</sub> products in a flow reactor through Cu<sub>2</sub>O nanoparticles synthesized in the presence of [OMIm]Cl b) FE of all different products obtained from CO<sub>2</sub>RR in a flow reactor over Cu<sub>2</sub>O/ILGS-400 at different potentials. Adapted with permission from ref. [109]. Copyright 2022 Elsevier Ltd. c) and d) Faradaic Efficiency for H<sub>2</sub>, C<sub>1</sub> and C<sub>2</sub><sup>+</sup> products from acidic CO<sub>2</sub> electrolysis in a flow reactor as a function of applied current density using as cathode: (c) the unmodified Cu electrode or (d) the CuNP-EMIm and e) C<sub>2</sub><sup>+</sup>/C<sub>1</sub> products ratio vs. applied current density from acidic CO<sub>2</sub> electrolysis in a flow reactor. Reprinted with permission from ref. [100]. Copyright (2023) American Chemical Society.

Additionally, it is important to highlight the effective suppression of the HER as shown in Figure 8b. Further investigation via in situ Raman spectroscopy and DFT calculations corroborated the distinctive Cu<sub>2</sub>O structure role in strengthening the adsorption of intermediates (CO<sub>2</sub><sup>-</sup>, CO\*) and subsequently facilitating C–C coupling reactions.

Grammatico et al. explored the potential of a polymer based on imidazolium poly(ionic liquid) deposited on top of a molecular rhenium catalyst drop casted on a conductive porous carbon material for CO<sub>2</sub> conversion to CO.<sup>[126]</sup> Different block copolymer ionic liquids (BCPILs) were synthesized through controlled-radical polymerization and nucleophilic post-substitution to introduce imidazole moieties. However, the faradaic efficiency for CO production when the poly(ionic liquid) was deposited on the electrode BCPIL/Re@HPC (Table 5, entry 7) was significantly lower than the one on the raw catalyst Re@HPC (Table 5, entry 8). This highlights the present need of developing controlled immobilization methods of ILs to reach enhanced CO<sub>2</sub>RR results. Following this goal, Vichou et al. have recently reported a remarkable innovation for enhancing acidic CO<sub>2</sub> electrolysis (pH ≤ 1) through the electrodeposition of an imidazolium-based IL layer on Cu nanoparticles (CuNP-EMIm).<sup>[100]</sup> This molecular modification allows to control the CO<sub>2</sub>RR selectivity by directing it towards the production of C<sub>2</sub> products, notably ethylene and ethanol as is demonstrated by comparing the electrolysis results reported in Figures 8c (bare CuNP) and 8d (CuNP-EMIm). This

achievement is particularly noteworthy as it is accomplished at industrially relevant current densities under highly acidic pH conditions (Table 5, entry 9). Furthermore, CuNP-EMIm cathode is able to provide for the first time a moderate CO<sub>2</sub> conversion yield in a cation free acidic solution (0.1 M H<sub>2</sub>SO<sub>4</sub>, entry 10 in Table 5). This illustrates a possible future strategy for circumventing the need for using a large concentration of cations in solution in order to inhibit HER in acidic electrolytes. Thus, the immobilization of a positively charged imidazolium cation on the electrode surface mimics the role of imidazolium cations in solution.

## 7. Summary and Outlook

The capture and conversion of CO<sub>2</sub> by electrochemical reduction in one of the most relevant scientific issues nowadays. In this context, ionic solvents, including ILs and DES, present great potential in both CO<sub>2</sub> capture and electrochemical conversion using different catalytic cathode materials. Highly-efficient CO<sub>2</sub>-capture DES based on amines have been already synthesized. Some of these amine-base DES achieved much higher CO<sub>2</sub>RR performance than the corresponding pure amine. For this reason, the interest on combining both the capture and conversion of CO<sub>2</sub> using DES is attracting increasing attention. However, only a limited number of publications devoted to this topic are available in the literature at present. Further research is needed to fully

understand the potential of these ionic solvents in CO<sub>2</sub>RR, especially for the case of DES, and to optimize their use in scaled-up applications. Nevertheless, previously reported techno-economic and LCA analysis have already shown the industrial feasibility of using ionic solvents for the production of C<sub>1</sub> products.

ILs are different from DES because they are entirely composed of ions, while DES contain an important proportion of neutral molecules. This fact controls the distribution of charged species and oriented dipoles existing at the electrode/electrolyte interface. Moreover, ILs present moderate ecotoxicity in contrast with bio-based origin of DES, which makes them more compatible with circular economy principles. Nevertheless, both ILs and DES are considered as design-solvents, which offers a very large number of available ionic solvents. The non-negligible viscosity of DES and ILs represent a severe limitation for using them as neat solvents in CO<sub>2</sub>RR. This issue results minimized in the case of using them as a supporting electrolyte in a molecular solvent. Thus, results on CO<sub>2</sub>RR using neat ILs and DES, as well as aqueous and organic ILs and DES solutions are reviewed here. Particular attention is paid to the role that ionic solvents play for the CO<sub>2</sub>RR activation and simultaneous HER suppression. The most representative examples of both ionic solvents with molecular catalysts and heterogeneous electrocatalytic materials for CO<sub>2</sub>RR are discussed.

It is demonstrated that the addition of ILs in solution enhances the current density and faradaic efficiency for CO<sub>2</sub>RR products, as well as reduces its required overpotential. ILs tune the catalytic properties on both molecular and heterogeneous electrocatalysts, and particular attention is focused on the role at the EDL interface of the cation present in the IL. In particular, imidazolium-based ILs are the most active ones favoring CO<sub>2</sub>RR and simultaneously suppressing HER. This is most probably because the aromatic ring present in imidazolium is able to stabilize the CO<sub>2</sub>RR intermediates more efficiently than non-aromatic ILs. Two main hypotheses are proposed for explaining the role of ILs suppressing HER: (i) the increase in hydrophobicity at the electrode surface, and (ii) the electrostatic interactions between IL cations and protons within the EDL. The impact of imidazolium-based ILs on suppressing HER is pH-dependent, which favors the use of ILs for CO<sub>2</sub> electrolysis mainly in acidic solution. Moreover, ILs play an additional role modulating the products selectivity (C<sub>1</sub>, C<sub>2</sub> and C<sub>2+</sub>) in the CO<sub>2</sub>RR. Thus, further research at the EDL interface by situ/operando techniques is necessary to fully understand the CO<sub>2</sub>RR activation and HER suppression mechanisms.

The ionic component of DES, and particularly the cation, controls the EDL interface and thus, the CO<sub>2</sub> conversion performance, as the IL cation does. However, mostly tetralkylammonium cations, and particularly choline cation, are used in DES so far. Choline-based DES significantly enhance CO<sub>2</sub>RR by reducing the overpotential required for CO<sub>2</sub>RR, which is attributed to the stabilization of CO<sub>2</sub>RR intermediates, since almost the same performance is achieved by the sole presence of ChCl in aqueous solution. For this reason, future developments need to increase the limited number of different cations studied in DES at present.

The production of C<sub>2</sub> and C<sub>2+</sub> compounds from CO<sub>2</sub>RR takes place almost exclusively on Cu catalyst. ILs present a relevant effect enhancing the C–C coupling reaction and improving selective production of C<sub>2</sub>H<sub>4</sub>, as well as inhibiting HER. In contrast,

Cu-based catalysts have been barely studied for CO<sub>2</sub>RR using DES, since most reports are on Ag cathodes, as a consequence, the main product reported is CO.

Immobilization of ILs onto the surface of the cathode represents a novel strategy to enhance CO<sub>2</sub>RR vs. HER, which allows to keep the advantages of ILs in solution, meanwhile the impact of ILs drawbacks is limited. An imidazolium-based IL layer on Cu was able to provide for the first time a moderate CO<sub>2</sub> conversion yield in a cation free acidic solution (only presence of protons), which represents a future strategy for circumventing the need of using a large concentration of cations in solution in order to inhibit HER in acidic electrolytes. But the addition of ILs onto the catalyst does not always provide an enhanced CO<sub>2</sub>RR activity, which highlights the present need of developing methods for the controlled immobilization of ILs to effectively enhance CO<sub>2</sub>RR and suppress HER.

Finally, the implementation of ILs for CO<sub>2</sub>RR in flow cell systems with high electrode active area have been already reported, but mainly novel approaches, like the immobilization of ILs at the cathode surface allow to achieve industrially relevant current densities for CO<sub>2</sub>RR. For this reason, we believe immobilized ILs at the electrode surface should concentrate future efforts in research to develop efficient and sustainable electrochemical CO<sub>2</sub> conversion technologies.

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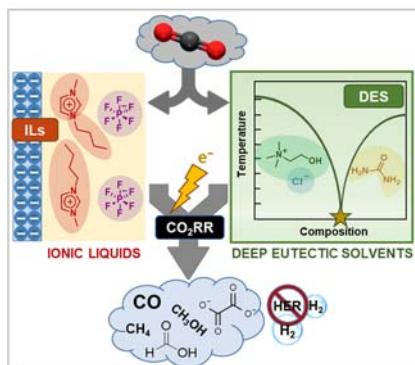
**Keywords:** CO<sub>2</sub> electroreduction • Hydrogen Evolution • Ionic Solvents & Electrolytes • Ionic Liquids • Deep Eutectic Solvents

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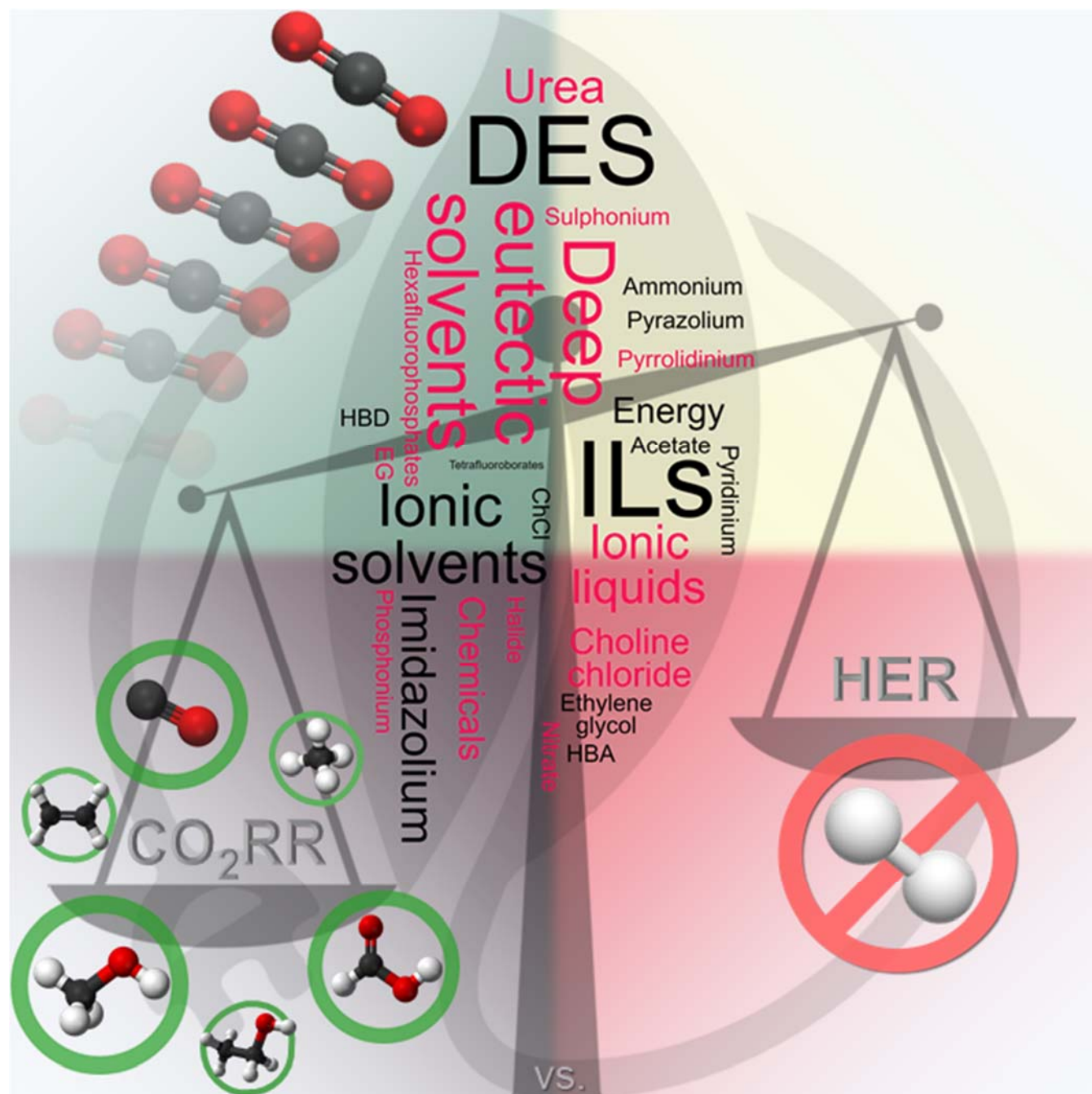
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## Entry for the Table of Contents



Ionic liquids (ILs) and deep eutectic solvents (DES) represent a large set of ionic solvents only recently available for electrochemical applications. These ionic solvents allow both capture and conversion of pollutant gases such as carbon dioxide ( $\text{CO}_2$ ). The non-negligible viscosity of DES and ILs might be considered as a drawback, but it is minimized in the case of using them as supporting electrolyte in a molecular solvent. Moreover, immobilization of ionic solvents onto the surface of the electrode represents a novel strategy for keeping the advantage of ionic solvents in solution, but limiting their drawbacks. ILs are different from DES because they are entirely composed of ions, while DES contain an important proportion of neutral molecules. The ions present in ILs and DES composition modify the electrode/electrolyte interface and play a relevant role either enhancing or inhibiting different electrochemical reactions such as in the case of carbon dioxide reduction reaction ( $\text{CO}_2\text{RR}$ ) and hydrogen evolution reaction (HER), respectively. In contrast, no significant role of ILs or DES has been reported regarding the product selectivity in  $\text{CO}_2\text{RR}$ , giving as a result the formation of all types of products  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_{2+}$ .





### Author biographies

**Alejandro Leal-Duaso** received his Ph.D. degree with international mention in 2020 from the University of Zaragoza (Spain), under the supervision of Prof. J. I. García and Prof. E. Pires. His research is mainly focused on the development and study of deep eutectic solvents, as well as in the sustainable preparation of novel nanostructured catalysts. Currently, he obtained a Margarita Salas fellowship from the Spanish Government for developing a 2-years postdoctoral stage at Sorbonne Université in Paris (France).



**Yanis Adjex** graduated with a master's degree in Chemical Engineering from Sorbonne University (Paris) in 2021. He is currently enrolled in a PhD program supervised by Dr. Carlos M. Sánchez-Sánchez, which is focused on the immobilization of ionic liquids at the electrode surface for inhibiting H<sub>2</sub> evolution reaction and thus, boosting the electrode performance of environmentally relevant electrochemical reactions such as nitrate or carbon dioxide reduction reactions. His academic focus aligns with his commitment on advancing sustainable engineering practices and contributing to the evolution of clean energy technologies.



**Carlos M. Sánchez-Sánchez** is an Associate Scientist at National Center for Scientific Research (CNRS) working at Sorbonne Université in Paris (France) and holds a PhD in Chemistry from the University of Alicante (Spain). He accumulates a senior degree of expertise in electrocatalysis and scanning electrochemical microscopy (SECM). His current research interest is in the development of highly active and selective catalysts for carbon dioxide and nitrate electroconversion, through the modulation of the electrode/electrolyte interface, by paying particular attention to the role of ionic liquids at the electrical double layer.

