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Ionic liquids in the electrochemical valorisation of CO_2

Manuel Alvarez-Guerra, Jonathan Albo, Enrique Alvarez-Guerra, Angel Irabien

Broader context

Climate change mitigation and transition to energy systems less dependent on fossil fuels are great challenges in the 21st century. Converting carbon dioxide into useful products (the so-called Carbon Capture and Utilisation, CCU) is an attractive strategy that can complement Carbon Capture and Storage (CCS). Particularly, the CO_2 valorisation by electrochemical routes is receiving increasing attention as a way to obtain chemicals with added-value and as a promising option to chemically store renewable energy from intermittent sources like solar or wind, thus reducing our reliance on fossil fuels. On the other hand, ionic liquids (ILs) are a family of compounds with unique properties that have led to their consideration as interesting alternative, more effective solvents in many applications, including in electrochemistry. Therefore, the growing interest in the electrochemical valorisation of CO_2 has resulted in different innovative attempts, including the use of ILs in order to improve the performance of these electrochemical approaches. This review aims to specifically address the use of ILs in the electrochemical process of CO_2 valorisation, offering a complete overview of the state-of-the-art to both inform readers and encourage further research efforts in this challenging field.

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Ionic liquids in the electrochemical valorisation of CO_2

Manuel Alvarez-Guerra [a, *], Jonathan Albo [b], Enrique Alvarez-Guerra [a],
Angel Irabien [a]

[z] *Department of Chemical and Biomolecular Engineering. ETSIIT. University of Cantabria. Avda. Los Castros, s/n. 39005, Santander, Spain.*

[b] *Department of Chemical Engineering, University of the Basque Country (UPV/EHU). Apdo. 644, 48080 Bilbao, Spain.*

**E-mail: alvarezgm@unican.es*

Abstract

The development of electrochemical processes for using captured CO_2 in the production of valuable compounds appears as an attractive alternative to recycle CO_2 and, at the same time, to store electricity from intermittent renewable sources. Among the different innovative attempts that are being investigated to improve these processes, the application of ionic liquids (ILs) has received a growing attention in recent years. This paper presents a unified discussion of the significant work that involves the utilisation of ILs for the valorisation of CO_2 by means of electrochemical routes. We discuss studies in which CO_2 is used as one of the reactants to electrosynthesise value-added products, among which dimethyl carbonate has been the focus of particular attention in the literature. Approaches based on the electrochemical reduction of CO_2 to convert it into products without the use of other carbon-based reactants are also reviewed, highlighting the remarkable improvements that the use of ILs has allowed in the CO_2

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electroreduction to CO. The review emphasises on different aspects related with process design, including the nature of ILs anions and cations that have been used, the working conditions, the electrocatalytic materials, the electrode configurations, or the design of electrochemical cells, as well as discussing the most relevant observations, results and figures of merit that the participation of ILs has allowed to achieve in these processes. Several conclusions are finally proposed to highlight crucial challenges and recommendations for future research in this area.

1. INTRODUCTION

1.1. The problem of CO_2

The increase in the concentration of carbon dioxide (CO_2) in the atmosphere since preindustrial times due to anthropogenic emissions has been considered as a major contributor to the greenhouse effect and global warming [1]. According to the latest Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), about two-thirds of the total greenhouse gas emissions in 2010 were CO_2 emissions related to the combustion of fossil fuels [2]. Fossil fuels (i.e. oil, coal and natural gas) represented 81.7% of the total primary energy supply in the world in 2012, while renewable energies only accounted for 13.5% [3]. Although the ultimate goal for many countries is to phase out fossil fuels in heat and power production, as well as in the transport sector, future estimations indicate that the shift to renewable energy sources is slow and that the world energy supply will still rely on fossil fuels in the next decades [4, 5]. Therefore, CO_2 emissions have to be reduced urgently, but in a context of an increasing world energy consumption that will still be highly dependent on fossil fuels [3]. This represents a complex challenge that has to be met. Consequently, different mitigation strategies are

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being considered, seeking to reduce the extent of climate change by reducing CO_2 emissions or increasing their removal from the atmosphere [6]. Among these strategies, the capture of CO_2 from flue gases of combustion processes and its subsequent storage for long-term isolation from the atmosphere ("Carbon Capture and Storage", CCS) [7-9] has gained significant attention. In fact, CCS has been suggested as a key climate change technology that is currently in the process of being demonstrated worldwide [10]. However, CCS technology development has progressed slower than anticipated in large scale demonstration [5]. New funding for CCS demonstration projects peaked in 2008, when several governments supported CCS technology demonstration as part of economic stimulus plans, but since then, additional funding has been limited [11].The lack of a positive public opinion to CO_2 storage, which has already been detected recently in some projects may also hamper its implementation. Although long-term CO_2 storage requires intervention of authorities through the application of strict penalties or economic support and subsidies [10], the IEA (International Energy Agency) considers that the deployment of CCS in both power and industry is critical to address climate change [5]. In this way, in the IEA BLUE Map Scenario (which assumed that global energy-related CO_2 emissions are reduced to half their levels by 2050 compared to 2007 levels), the use of CCS accounted for 19% of the emissions reduction, where 58% of the CO_2 captured would come from power generation, 21% from industry and 24% from fuel transformation [12]. More recently, the main focus of IEA Energy Technology Perspectives (ETP) 2014 is the 2ºC Scenario (2DS), which aims to achieve the ambitious goal of limiting global temperature rise to 2ºC and sets the target of cutting energy-related CO_2 emissions by more than half in 2050 compared with 2011; in the 2DS, CCS is also considered as crucial for realising deep emission cuts in the industrial

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sector, providing around one quarter of the cumulative reductions needed to achieve the 2DS goals [5].

In this context, while CCS technologies are being developed with the focus of capturing and storing CO_2 in huge quantities [13], processes for converting captured CO_2 into useful and valuable products (the so-called “Carbon Capture and Utilisation”, CCU) are being developed in parallel [14]. Although it has been argued that the potential of CCU is still limited because the current global demand for products does not have the capacity to sequester enough CO_2 emissions to contribute significantly to meeting the carbon reduction targets [10, 14], it has also been recognised that exploiting part of the captured CO_2 to generate value from it as raw material for chemical synthesis of for use as fuel can complement its storage [13]. Therefore CCU appears as an innovative and attractive option that has started to draw attention worldwide [14]. Currently, important research efforts are being carried out to develop CCU processes [15, 16] which may allow its conversion into valuable chemicals by means of, e.g. chemical [17-19], electrochemical [20-27], photocatalytic [28-31] or biological [32-35] transformations.

Apart from the attractive possibility of obtaining useful chemicals from CO_2, the electrochemical valorisation has been suggested in the literature as an excellent future option to store energy from renewable sources which is intermittent and difficult to predict accurately, such as solar or wind energy [36]. In this way, processes for the electrochemical conversion of CO_2, coupled to renewable energy sources, could allow the valorisation of captured CO_2 obtaining value-added products, and at the same time, could also make it possible to store electrical energy in chemical form. Because electricity is difficult to store on a large scale, its production has to closely follow demand and to adapt to fluctuations. Nevertheless, renewable energies such as solar and wind are intermittent and not able to follow closely the demand (i.e. wind does not blow

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constantly, while solar energy cannot be produced during the night or with cloudy weather). Therefore, the reliable integration of renewables is complex and, according to the IEA, perhaps the most disputed and misunderstood factor in sustainable electricity supply [37].

1.2. Ionic liquids

Ionic Liquids (ILs) are organic salts composed solely of ions (cations and anions), which are liquids below 100 ºC. Many of them are liquids even at room temperature, so they are also called “room-temperature ionic liquids” (RTILs). As opposed to an ionic solution, which is a solution of a salt in a molecular solvent, the term “ionic liquid” should be literally understood as a liquid that consists entirely of ions [38]. Heating normal salts, such as NaCl (melting point 801ºC) to high temperature produces also a liquid, which consists entirely of ions, but this is considered a molten salt and not defined as an ionic liquid [39] . An essential feature of ILs is that they exhibit a very wide liquidus range (i.e. a very wide span of temperatures between the melting and boiling points). With the exception of some liquid polymers, no molecular solvent can match the liquidus range of ILs [40]. Although ILs and traditional molten salts share this fundamental feature of possessing a wide liquidus range, they differ in where the liquidus range is in the scale of temperature. Moreover, in contrast to molten salts, which form tight ion pairs in the vapour phase, the reduced Coulombic interactions between ions energetically restricts the ion pair formation required for volatilisation of ILs leading to little measurable vapour pressures [40].

In the last decades, ILs have received rising interest in multiple fields of chemistry and chemical technologies due to their useful properties in these contexts, which include immeasurably low vapour pressure [41], high thermal stability and excellent solvation

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ability for a wide range of compounds [42]. Moreover, ILs ideally designed to fulfil a specific task (i.e. “task-specific” or “functionalised” ILs) can be created by choosing certain anionic and cationic components which incorporate functional groups designed to impart to them particular properties or reactivities [43]. In spite of the fact that ILs have some solubility in water, and hence, it is necessary to assess their potential toxicity to the aquatic environment [44-47], their negligible vapour pressure eliminates the problems associated with polluting emissions to the atmosphere. Consequently, ILs are considered attractive replacements for volatile organic solvents in many applications, including in electrochemistry [40, 48-50]. Some of the most commonly used ILs are illustrated in Figure 1.

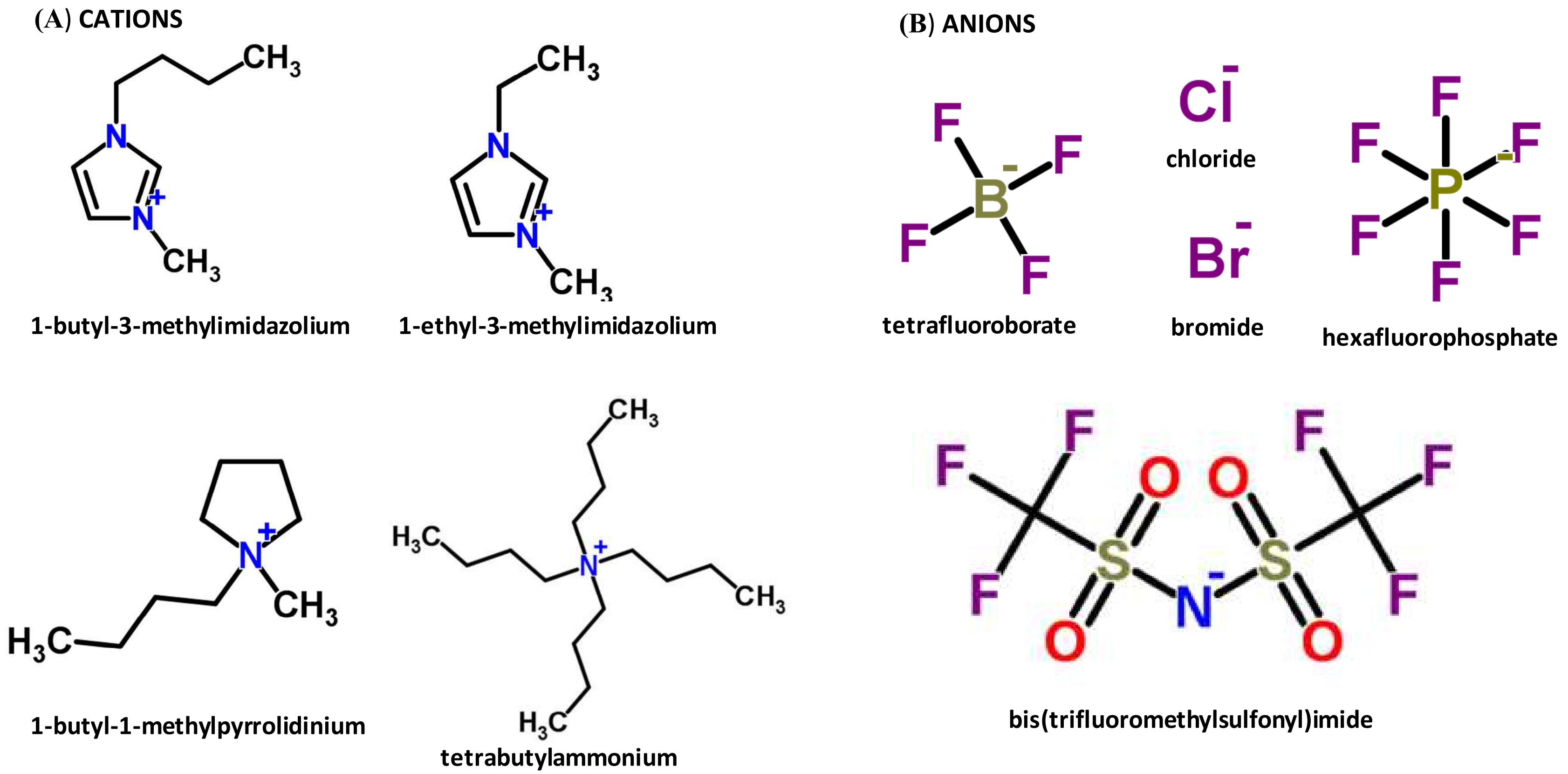

Figure 1. Structures of some common ionic liquid cations (A) and anions (B). (Obtained using Chemspider, owned by the Royal Society of Chemistry: http://www.chemspider.com/)

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1.3. Suitability of ionic liquids for CO_2 capture & conversion

The possibility of either converting the CO_2 into products or of simply sequestering the CO_2 involves the need to separate it from the gas mixtures of the sources of emission. Therefore, it has been highlighted that capture of CO_2 from flue gases of conventional coal- and natural-gas-fired power plants is likely to be an important component of the energy portfolio in the next decades [51]. The most mature and applied technology for the post-combustion capture of CO_2 from flue gas streams is cyclic chemical absorption/ desorption using aqueous solutions of monoethanolamine (MEA) [52, 53]. However, amine-based processes have many disadvantages and limitations, including those related to the corrosive and volatile nature of amines, and especially, the high energy consumption required to release the captured CO_2 in the regeneration step [54-56].

In recent years, ILs have also been proposed as alternative, more effective or next-generation solvents for CO_2-selective separation processes [57-59].

Substitution of the absorption liquid (usually volatile and toxic aqueous amine solutions) by a solvent with low vapour pressure like ILs has been proposed as way to perform process intensification of CO_2 capture from post-combustion flue gases at industrial scale [60, 61]. Therefore, ILs for CO_2 capture have been the focus of intense research activity, as shown in several recent reviews on this subject (see e.g. [51, 55, 56, 62-66]).

An interesting advantage is that both the selectivity and solubility of CO_2 in ILs can be readily “tuned” by tailoring the structures of cation and/or anion, offering an unprecedented control over solvent composition and functionality [57]. Although when encountering wet flue gases some selectivity problems may be found with ILs with highly basic anions that absorb large quantities of water [10], ILs show inherently high selectivity for CO_2 over other components in the post-combustion flue gas mixture and their capacity can be dramatically enhanced by incorporation of amine functional

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groups to chemically capture CO_2 [51]. Furthermore, many ILs exhibit, due to their chemical structure, a high affinity towards CO_2, which make them additionally interesting solvents for CO_2 capture processes [67-69]. The high solubility of CO_2 in ILs suited to this specific task will facilitate electrochemical CO_2 valorisation because, as already mentioned, ILs show desirable properties as media for electrochemical reactions.

Several references can be found in the literature that explain in detail the properties of ILs as electrochemical solvents and describe their many applications in the field of electrochemistry (see e.g. [70-78]). The viscosities of ILs, which are usually 1-3 orders of magnitude higher than those of conventional solvents, are probably their major drawback in electrochemistry [73]. However, ILs have many advantages when employed as a solvent in electrochemical experiments [71]. Especially, their inherent redox-robustness, generally possessing a wide electrochemical window (i.e. a wide potential difference between the oxidation and reduction reactions of the molecules/ions that constitute the solvent [75]), is a usual common property of ILs which is highly desirable for applying them as electrochemical solvents [73]. It should also be emphasised that the conductivity of ILs, which is another feature of vital importance, is generally similar to that of conventional nonaqueous solvents with added inorganic electrolytes, but ILs offer the advantage that this property is intrinsic to the pure IL and does not require the addition of a separate salt [70]. Besides, those ILs containing metals in their anion (also known as magnetic ionic liquids (MILs)), have shown interesting properties as a reaction media for various catalytic reactions, as well as for electrochemical devices (i.e. flow battery systems, anti-glare rear, information displays, etc.), where reversible oxidation/reduction processes involve changes in colour or magnetic properties [79].

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1.4. Aim and structure of the review

In recent years a renewed interest in the electrochemical valorisation of CO_2 has been observed, with a rapidly growing number of studies focussed on different innovative attempts. The ILs are a family of compounds with unique properties, so their use, as well as in other fields and even in other electrochemical applications, has also been explored for the electrochemical valorisation of CO_2. Different previous reviews have mentioned some studies that utilise ILs in the electrochemical conversion of CO_2 [67, 80-83]. However, there is a lack of a comprehensive work that specifically discusses and unifies the literature on this particular topic. According to the increasing attention that this field has attracted recently, a work which, expanding previous reviews and incorporating the abundant relevant recent literature, could offer a complete overview on the state of the art of the use of ILs in the electrochemical valorisation of CO_2, taking into consideration the types of ILs used, configuration of electrodes and electrochemical cells, operating conditions, or the effect that the ILs have had on the performance of electrolyses for CO_2 valorisation, would be of great interest.

Therefore, to fill this gap, this review article presents a unified discussion of relevant studies that involve the utilisation of ILs for the electrochemical valorisation of CO_2. The review has been divided in two main parts. Approaches in which CO_2 is used as one of the reactants to electrosynthesise valuable products with the participation of ILs will be reviewed and discussed in the first part (section 2). Then, the second part (section 3) will deal with the use of ILs in direct electrochemical approaches to convert CO_2 without other carbon-based reactants. In both parts, key aspects that will deserve special attention in the discussion include the nature of ILs anions and cations that have been used; the products that have been obtained in the different studies; which conditions, electrocatalytic materials, electrode configurations and types of cells have

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been utilised; and the most relevant observations, results and figures of merit that the participation of ILs has allowed to achieve in these processes. The codes used in this paper to designate the different ILs are listed in Table 1. Besides, a final section will include some concluding remarks, highlighting as well crucial challenges that will have to be tackled in the vibrant area of research of innovative processes for the electrochemical valorisation of CO_2.

(TABLE 1 HERE)

2. USE OF ILS IN ELECTROSYNTHESIS OF VALUABLE COMPOUNDS USING CO_2 AS REACTANT

2.1. Summary of studies

Relevant studies which involve the use of ILs in CO_2 electrochemical valorisation approaches in which CO_2 is used as one of the reactants, together with other substrates, to synthesise chemicals of interest [84-110], are summarised in Table 2. This Table is focused on showing, for each study, the substrates and products of the electrosynthesis application, the specific ILs used in the reaction media, the operating conditions that were studied, the nature and characteristics of electrodes investigated, and the type of electrochemical cell used, together with a brief description of relevant observations and results reported in each study.

(TABLE 2 HERE)

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2.2. Discussion and trends

Types of products. It is important to emphasise that Table 2 focusses on studies that have carried out electrolyses that involve the use of ILs as media to conduct electrochemical reactions of different substrates with CO_2 to synthesise valuable compounds. Among these products, several studies have focussed on synthesising organic carbonates (especially dimethylcarbonate, DMC) from alcohols and CO_2 [84, 89-91, 94, 97-99, 101, 102, 106, 108, 109]. Various references whose aim is the synthesis of different carboxylic acids can also be found [86-88, 92, 93, 105], such as phenylacetic acid [92], 2-phenylpropionic acid [93], 2-hydroxy-2- phenylpropionic acid [107], fatty acids [105] or 2-arylsuccinic acids [87, 88]. Other approaches that have also been reported include the synthesis of organic carbamates [85, 96], the pharmaceutical intermediate 6-aminonicotinic acid [95], or 1-phenylethanol [100].

Most used ILs. Examination of Table 2 reveals that imidazolium-based ILs have been, by far, the most researched class of ILs for CO_2 electrochemical valorisation applications, and, particularly, the ILs 1-butyl-3-methylimidazolium tetraflouroborate ([BMIm][BF_4]) [84-86, 89-92, 94-96, 98, 99, 101-104, 106], and to a lesser extent, 1-butyl-3-methylimidazolium bromide ([BMIm][Br]) [90, 91, 97, 106, 108-110] or 1-ethyl-3-methylimidazolium tetraflouroborate ([EMIm][BF_4]) [84, 90, 91, 96].

Applied electrode materials. Regarding the materials that have been used as electrodes, the different works reported have studied the conversion of CO_2 in ILs using metallic electrodes. As can be noticed in Table 2, the most studied metals as working electrodes in these processes have been Cu, Pt and Ni. It is worth mentioning that the results of many of the references pointed out that electrochemical synthesis reactions

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between substrates and CO_2 in an IL-medium are also strongly dependent upon the nature of the cathode material, which usually resulted in great differences in the yields of the desired products depending on the metal used as cathode (see e.g. [86-89, 92, 95, 98, 103-106]).

Operating conditions. Table 2 also reveals that the different electrochemical conversions of CO_2 in ILs have been carried out under mild conditions. Most studies have been performed at ambient temperature and pressure. An increase in the current efficiencies achieved has been reported using higher CO_2 pressures, due to the fact that the solubility of the CO_2 in the IL increased with increasing pressure [93]. However, it is important to emphasise that the influence of the temperature on these processes is more complex, because temperature can have an effect on both the viscosity of the IL and the solubility of CO_2 in the IL medium. Lower temperature leads to an increase in the solubility of CO_2 in the IL, which is favourable to the electrosynthesis; on the other hand, decreasing the temperature also usually leads to an increase of viscosity that causes mass transport within solution to be slower, and therefore is unfavourable to the performance of the process. The combination of these two opposite influences explains that the different works that investigated the effect of temperature, usually in a range between 20-30ºC and 60-75ºC (Table 2), came to the same conclusion that the optimum temperature resulted to be an intermediate value of the range studied (usually 50 or 55ºC) [86, 89, 92, 94, 95, 98].

Types of electrochemical cells. Most of the studies that are summarised in Table 2 have been performed in small undivided cells and with small electrode areas (usually in the order of a few cm^2). Few works have used divided cells [85, 96, 103, 104], and only very

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recently, the use of filter-press flow-by type cells has been reported [109, 110], specifically to study the performance of the electrosynthesis of DMC (Figure 2).

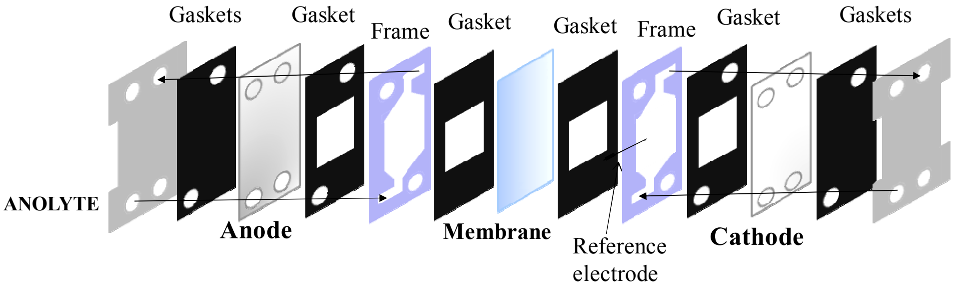

Figure 2. Scheme of the filter-press electrochemical cell with cathodic and anodic compartment separated by a membrane. Reprinted from ref. [110].

2.3. Electrosynthesis of dimethylcarbonate (DMC)

As already mentioned, DMC is clearly the most studied product of electrosyntheses that involve the use of ILs, particularly among the most recent works, which reveal the increasing interest in this compound. Methanol and CO_2 are the common substrates used in all the references found in the literature (Table 2). Figure 3 shows the yields reported in different studies, graphically organised according to the other compounds and the ILs involved in the electrosynthesis.

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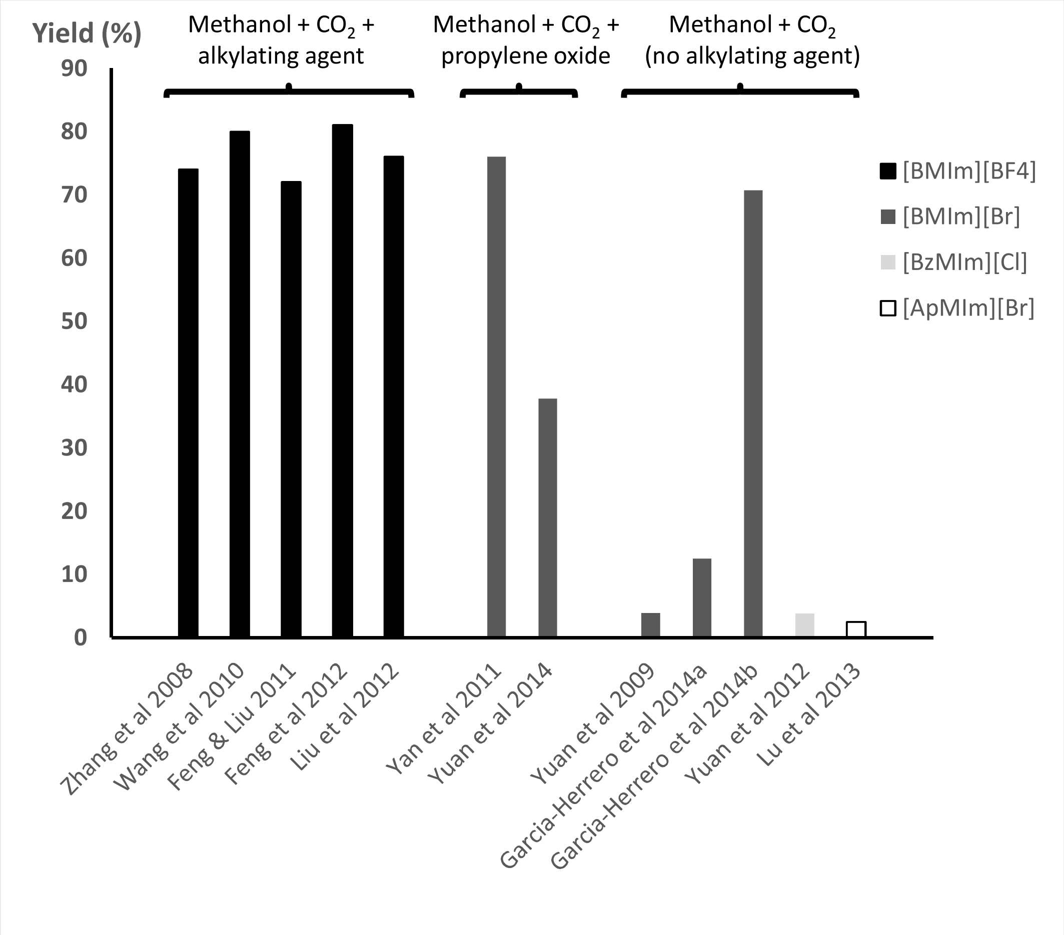

Figure 3. Yields of DMC (based on limiting reactant) reported in different studies, organized according to the reactants used and the ILs involved. Data from refs. [89-91, 94, 97, 99, 101, 102, 106, 108-110].

Most of the initial works that studied the electrosynthesis of DMC involved the use of the IL [BMIm][BF$_4$] [89, 94, 99, 101, 102] with electrodes mainly based on Cu. Yields of 74% [89] and 72% [99] have been reported using a Cu working electrode, while 76% yield was obtained with an In electrode [102]. Slight improvements were achieved when electrodes based on nanoporous Cu were used: Wang et al. [94] reported 80% yield with a working electrode prepared by depositing Ag on nanoporous Cu, and Feng et al. [101] achieved 81% yield with a porous nanostructured electrode where Pt was deposited over Cu skeleton. However, in all these works that used [BMIm][BF$_4$] the high yields of DMC

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were achieved after adding methyl iodide (CH_3I) as alkylating agent in the final steps of the electrosynthesis, which is a carcinogenic compound.

Other works have used methanol, CO_2 and propylene oxide to synthesise DMC using the IL [BMIm][Br] and Pt electrodes achieving yields of 76% [97], or more recently, of 37.8% [108]. Although both works avoided the use of CH_3I, propylene oxide is also a carcinogenic and mutagenic compound. Attempts that do not involve the use of such problematic species have also been reported, but at the expense of achieving much lower yields in DMC. The ILs used in these attempts implied the participation of a methylimidazoilum-based cation with a halide anion (Br^- or Cl^-), using either Pt or graphite electrodes [90, 91, 106, 109]. In ref. [91], using only methanol, CO_2 and the IL 1-benzyl-3-methyl imidazolium chloride ([BzMIm][Cl]), with graphite electrodes, DMC was synthesised with a maximum yield of 3.8%. However, although DMC was obtained without the use of any other additives, the preparation of the IL proposed involved the use of benzyl chloride, which is a compound classified as carcinogenic. More recently, also using graphite as electrodes, the synthesis of the amino-functionalised IL 1-(3-aminopropyl)-3-methylimidazolium bromide ([ApMIm][Br]) and its use for electrosynthesis of DMC has been proposed, giving maximum yields of 2.5% [106].

Finally, works that have studied the electrosynthesis of DMC from methanol and CO_2 with Pt electrodes, adding only CH_3OK and the IL [BMIm][Br], can also be found [90, 109, 110]. Yuan et al. [90] studied this synthesis in a small cell in excess CO_2, reporting a 3.9% yield and suggesting that CH_3OK acted as a co-catalyst and [BMIm][Br] as an electrolyte. Further work on the system methanol-CO_2-CH_3K-[BMIm][Br] has recently been carried out using a filter-press electrochemical reactor with anodic and cathodic compartments divided by a Nafion membrane, achieving a yield in DMC of 12.5% in excess methanol [109]. The influence of the membrane was then explored in a subsequent

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work, in which new results using different anion exchanged membranes were reported [110]. Interestingly, although similar results of DMC concentration were achieved after 48 h, the evolution with time was different when comparing both types of membranes; using the best performing anion exchange membrane tested (fumasep FAB-PK-130), the concentration of DMC did not increase strongly during the first hours as happened with the Nafion membrane, but it increased slowly and progressively throughout the experiment. Apart from reporting the first results found in the literature of DMC electrosynthesis from CO_2 and methanol using a filter-press cell configuration, these works also suggested that the IL [BMIm][Br] is not merely an electrolyte, but it must play a catalytic role in the electrosynthesis of DMC. However, further more in-depth research is needed to clarify the reaction mechanism, and particularly, to ascertain the possible specific role of the IL that is involved in this electrosynthesis.

3. USE OF ILs IN ELECTROREDUCTION OF CO_2 WITHOUT OTHER CARBON-BASED REACTANTS

3.1. Summary of studies

Table 3 gives an overview of relevant studies that have used ILs in CO_2 electroreduction processes to convert it directly into products (i.e. without the use of other carbon-based reactants) [111-129]. Similar to Table 2, for each of the references Table 3 summarises the IL involved, the desired product to be obtained, the operating conditions and the characteristics of the electrodes and cells used for the electrolyses, together with a brief summary of the main observations and figures of merit reported to assess the performance.

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(TABLE 3 HERE)

3.2. Discussion and trends

Types of products. A first look at Table 3 reveals that the use of ILs in the electrochemical reduction of CO_2 has been studied in processes to obtain only a few different types of products. In 2008, Chu et al. [112] reported the production of low-density polyethylene (LDPE) with 8-14% current efficiency by bubbling CO_2 gas in a mixture of IL [EMIm][BF_4] and water. Some references can be found related to the formation of N-heterocyclic carbene-CO_2 (NHC-CO_2) adducts by electrolysis on [BMIm][BF_4] bubbling CO_2, where the NHC-CO_2 adduct can then be used as latent catalyst for organocatalysed reactions[115] or may be utilised to catch and release CO_2 cyclically and in mild condition [130]. Very recently, an interesting investigation where the electrochemical CO_2 reduction with the participation of ILs yielded formate was carried out by Watkins and Bocarsly [123] in a medium formed by the IL 1-ethyl-3-methylimidazolium trifluoroacetate ([EMIm][TFA]) with 33% water as cosolvent. The [EMIm][TFA] was considered especially due to its high storage capacity for CO_2, which is largely unaffected by water. In this IL, the authors proposed that the mechanism did not involve the C-2-bound carboxylate intermediate suggested in other studies [113], but they proposed instead the direct CO_2 reduction at the In electrode to yield formate. Higher current density and lower electrode potential for electrolysis, in comparison to aqueous systems, were reported, which was attributed to a stabilising effect of the IL [EMIm][TFA] on the CO_2 intermediate and the increased solubility of CO_2 in the matrix [123].

Since the majority of works using ILs has CO as product, this CO_2 electroreduction will be specifically discussed in subsection 3.3. below.

Most used ILs. Table 3 shows that species within the family of imidazolium-based ILs have clearly been the most investigated type of ILs. Especially, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF_4]), followed by 1-butyl-3-methylimidazolium tetraflouroborate ([BMIm][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]), have been, by far, the most widely used ILs in the electroreduction of CO_2.

Applied electrode materials. Metals of different nature have been the materials widely used as working electrodes for studying the electroreduction of CO_2 with the participation of ILs. It is interesting to note in Table 3 that many studies have employed a configuration in which the metal catalysts are deposited over a carbon support (e.g. [113, 114, 116, 118, 119, 122, 125]). Bismuth-based CO evolving electrocatalysts, in which this metal is electrodeposited onto a glassy carbon electrode, have been recently studied [118, 125]. Ag nanoparticles painted on a graphite gas diffusion layer were the cathodes in studies that involved the use of [EMIm][BF_4] [113, 114, 116], while Au nanoparticles painted on carbon paper were used in matrix of [BMIm][PF_6] [119].Interesting recent works on CO_2 electroreduction to CO report better performance than noble metal catalysts (like Ag or Au) using molybdenum disulphide (MoS_2) [128] (superior performance that was attributed to the metallic character and high d-electron density of the Mo-terminated edges of MoS_2), and using non-metallic carbon nanofibre heterogeneous catalysts [117].
Although the vast majority of studies have been carried out with metal-based heterogeneous electrocatalysts, Grills et al. [124] very recently explored the effect of ILs

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on the electrochemical reduction of CO_2 to CO with a homogeneous Re catalyst (*fac*-ReCl(2,2′-bipyridine)-$(CO)_3$, whose electrocatalytic activity for the selective reduction of CO_2 to CO was already known in organic solvents like acetonitrile). In this work, in which the authors indicate that it is the first example of ionic liquid-enhanced electrocatalytic CO_2 reduction with a homogenous catalyst, the use of 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIm][TCB]) as both the solvent and the electrolyte resulted in 0.45V lower overpotential for the electrocatalytic reduction of CO_2 to CO with the Re catalyst compared to in acetonitrile containing 0.1M [TBA][PF_6]. Although the experiments showed that the IL helped to abate the activation energy for the CO_2 reduction reaction, the roles of $[EMIm]^+$ and $[TCB]^-$ still have to be clarified [124].

Operating conditions. As can be seen in Table 3, almost all the studies on the electrochemical reduction of CO_2 using ILs have been carried out at ambient conditions of temperature different temperatures and pressures have been reported. Zhao et al. investigated the effect of CO_2 pressure on CO_2 electroreduction, working with high pressures of up to 10 MPa, and reporting that the Faradaic efficiency of CO increased considerably as the pressure was increased [111]. This enhanced efficiency at higher pressures was attributed to the fact that the solubility of CO_2 in the IL [BMIm][PF_6] increased with increasing pressure, and at the same, the viscosity of the IL decreased more significantly as more CO_2 was dissolved, which both were factors that favour the reduction of CO_2 [111].

Types of electrochemical cells. Regarding the type of electrochemical cell, Table 3 shows that most of the works have studied the electroreduction of CO_2 using a two-

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compartment cell divided by a Nafion cation-exchange membrane to separate the cathodic and anodic compartments [113, 114, 116, 118, 119, 122, 125, 129]. Although some of them have used a classic H-type cell, the use of a flow cell, i.e. a filter-press or sandwich style reactor that allows the circulation of the catholyte and the anolyte through its own compartment (Figure 4) has also been reported [113, 114, 116].

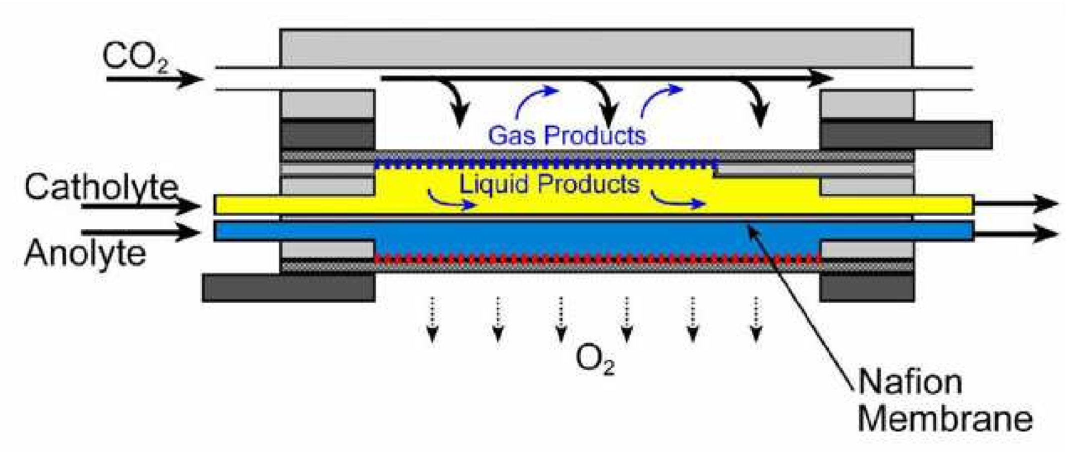

Figure 4. Schematic of electrochemical flow cell with catholyte and anolyte channels separated by a Nafion membrane. Reprinted from ref. [116]

3.3. CO_2 electroreduction to CO

The electroreduction of CO_2 to CO has clearly been the most studied route in which ILs have been used, particularly since the publication in 2011 of the work by Rosen et al. [113]. This paper reports the promising results of an electrocatalytic system based on a flow cell with a silver cathode that was able to reduce CO_2 to CO at very low overpotentials (i.e. below 0.2V more than the equilibrium potential) for at least 7 h with Faradaic efficiencies greater than 96% using an IL electrolyte (aqueous solution 18mol% [EMIm][BF_4]). In a subsequent work, these authors indicate that, according to

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in situ spectroscopic studies, the IL [EMIm][BF_4] had the effect of suppressing hydrogen formation and enhancing CO_2 conversion [131], proposing that the IL provided a low-energy pathway for CO_2 conversion to CO at low overpotential via formation of an adsorbed CO_2-EMIm complex (Figure 5).

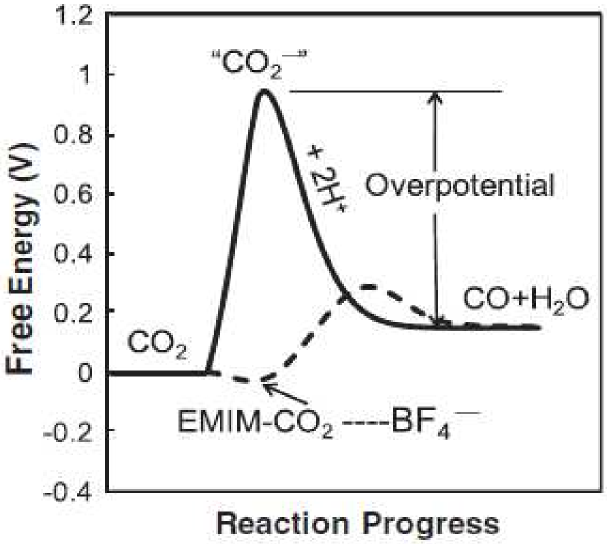

Figure 5. A schematic of how the free energy of the system changes during the reaction $CO_2 + 2H^+ + 2e^- \leftrightarrow CO + H_2O$ in water or acetonitrile (solid line) or IL [EMIm][BF_4] (dashed line). Reprinted from ref. [113].

These ideas of Rosen et al. [131] have been recently supported by investigations where the formation of CO is also attributed to the interaction between CO_2 and the cation $[EMIm]^+$ at the electrode surface [129]. When trying to explain how the mechanism of CO_2 electroreduction switch from oxalate anion to CO at a Pb electrode when using [EMIm][NTf_2], this study suggests that the cathode surface is covered with both $CO_2^{-\bullet}$ and the imidazolium cations, which stabilise the $CO_2^{-\bullet}$ and prevent close approach of two $CO_2^{-\bullet}$, hence inhibiting their dimerization to form oxalate and allowing the formation of CO [129] (Figure 6). These results are in agreement with Rosen et al.'s study

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[131], and, interestingly, they also suggest that after $CO_2^{-\bullet}$ coordinates with $[EMIm]^+$, the formation of an imidazolium carboxylate appears as a competing pathway to the $CO_2^{-\bullet}$ conversion to CO, as represented in Figure 6.

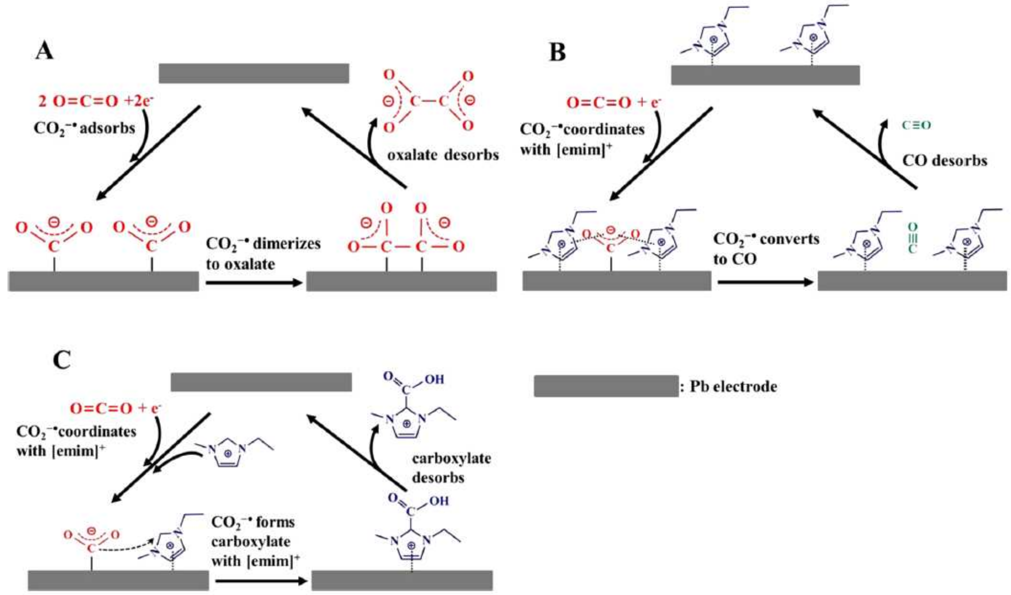

Figure 6. Reaction pathways for the electrochemical reduction of CO_2 in the (A) absence and (B, C) presence of $[EMIm][NTf_2]$ at a Pb electrode in acetonitrile. Reprinted from ref. [129]

Following the work of Rosen et al. [113], several studies have also used the IL $[EMIm][BF_4]$ in the catholyte for CO_2 reduction to CO, either in mixtures with water [114, 117, 128], as dried pure IL [116], in acetonitrile [118] or even diluted in methanol [120]. Some of these recent works have carried out further studies to confirm the role of the $[EMIm][BF_4]$ in the CO_2 reduction mechanism to CO. For example, Kumar et al. [117] report that dissolved CO_2 and $[EMIm]^+$ form an intermediate complex $[EMIm\text{-}CO_2]$ which adsorbs on reduced carbon atoms of carbon nanofibre catalyst and will re-oxidise these carbon atoms to their initial state and form CO as product. Very recently [128],

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quantum molecular dynamics simulations also revealed that the $[EMIm]^+$ cation forms a complex $[EMIm\text{-}CO_2]^+$ with CO_2 stabilised by hydrogen bonding, which reacts with water in neutral solution (forming either $[EMIm–HCO_3]$ or $[EMIm–CO_3]^-$ complexes) and that in acidic environment remains stable; furthermore, the $[EMIm\text{-}CO_2]$ complexes could potentially physisorb at the negatively charged cathode (bulk molybdenum disulphide in this study), suggesting that the presence of $[EMIm]^+$ cations around CO_2 molecules could reduce the reaction barrier for electrons passing into CO_2 [128].

ILs with the anion $[BF_4]^-$ have been the most widely studied in the CO_2 electroreduction to CO, not only with $[EMIm]^+$ cation ($[EMIm][BF_4]$, as already stated) [113, 114, 116-118, 120, 128], but also with cation $[BMIm]^+$ in the IL $[BMIm][BF_4]$ [118, 122, 125-127]. The deprotonation of the central imidazolium carbon of the $[EMIm]^+$ and $[BMIm]^+$ ILs has been suggested as the most likely source of protons to drive the $2e^-/2H^+$ conversion of CO_2 to CO [118]. Several works have also studied the use of $[BMIm][PF_6]$ [118, 119, 125], which some authors hypothesise that could serve as both a promoter for CO_2 activation at the catalyst and the supporting electrolyte in the catholyte solution [125]. Using density functional theory calculations, the major fraction of the overpotential of the CO_2 reduction into CO was attributed to the need of energetically stabilise the key reaction intermediate COOH*, and in this sense, the $[BMIm][PF_6]$ would act as a more efficient COOH* stabiliser [119].

Various studies that have compared the performance of CO_2 electroreduction to CO using different ILs have been recently published. For example, Medina-Ramos et al. [125] performed controlled potential electrolysis experiments to compare the behaviour of CO_2 saturated solutions of acetonitrile containing $[PF_6]^-$, $[BF_4]^-$, $[Cl]^-$, $[Br]^-$, or $[OTf]^-$ salts of $[BMIm]^+$ using a bismuth catalyst modified glassy carbon electrode. Although each of these ILs surveyed displayed selectivities for CO production higher than 74% and partial current densities for CO ranging from 17 to 30 mA cm^{-2}, the best results

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were obtained with [BMIm][PF_6], [BMIm][BF_4], and particularly, with [BMIm][OTf], which is also one of the least expensive commercially available $[BMIm]^+$ ILs. However, the solutions containing $[BMIm]^+$ halides gave the lowest efficiencies and slowest kinetics of the ILs studied, which was attributed to the fact that [BMIm][Br] and [BMIm][Cl] are more hygroscopic than the other ILs surveyed, and the presence of water in the electrolyte may lead to the formation of other CO_2 reduction products apart from CO, such as formate [125]. Another interesting comparison was carried out by Zhou et al. [126], who examined a series of aqueous solutions of ILs with different cation and anion structures, reporting that CO_2 reduction on Ag electrode did not occur in aqueous solutions of quaternary ammonium ILs (such as [TEA][BF_4] or [TBA][BF_4]) but it did occur in imidazolium IL solutions (such as [BMIm][BF_4], [BMIm][Cl] or [MOEMIm][BF_4]). Specifically, the best results were achieved with [BMIm][Cl]; on the one hand, the significant effectiveness of $[Cl]^-$ containing IL for the CO_2 electroreduction to CO was explained due to the stronger H-bond formed by Cl^- with the hydrogen from H_2O molecules, which might decrease the binding strength with the surface of Ag cathode and hence might result in an enhanced inhibition of hydrogen evolution reaction; on the other hand, the relatively strong H-bond of imidazolium cation with water would promote the elimination of O from CO_2; therefore, the anion $[Cl]^-$ and $[BMIm]^+$ cation were suggested as the most effective combination for CO_2 reduction to CO probably due to the dominating water-cation and water-anion interactions in aqueous [BMIm][Cl], although they also admit that great research efforts are still needed to fully understand the reaction mechanism [126].

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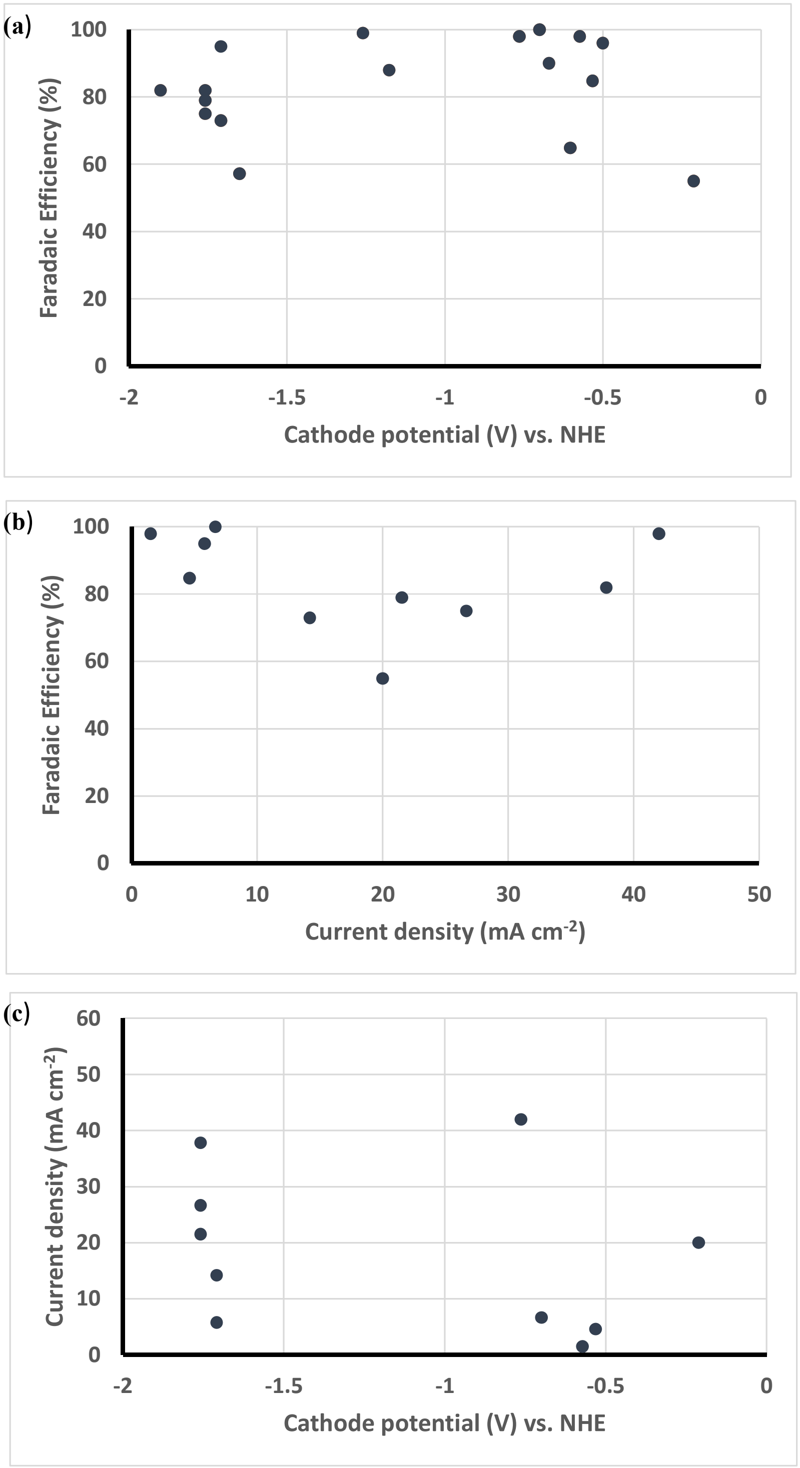

Figure 7. Summary of results of studies for CO_2 electroreduction to CO with ILs. Data from refs. [100, 113, 114, 117-122, 124-129]. (a) Faradaic efficiencies for CO as a function of the cathode potential (vs. NHE, Normal Hydrogen Electrode). (b) Faradaic efficiencies for CO vs. current density. (c) Current density vs. cathode potential (vs. NHE)

Figure 7 summarises the Faradaic efficiencies for CO and current densities against the cathode potential, as well as the relationship between Faradaic efficiency and current density, obtained in works that have carried out electrolyses for the conversion of CO_2 to CO with the aid of ILs. It should be noted that the data used for these plots have been taken from studies where different variables, such as the nature of the catalyst, configuration of the electrode and cell, type of electrolytes and ILs used, or working conditions, are not consistent and may influence the results. Moreover, some of the listed in Table 3 could not be included because they did not report some of these data. In any case, Figure 7 reveals that several studies have achieved very high Faradaic efficiencies, close to 100%, at cathode potentials between -0.5 and -0.77 V vs. NHE (Figure 7a). However, it is noteworthy that the total current densities achieved in these electrolyses have been low, even for studies with lower Faradaic effiencies than 100% (Figure 7b) or for cathode potentials of up to -1.7 V vs NHE (Figure 7c). Therefore, these low current densities reported, far from the values of hundreds of mA cm^{-2} that are considered to be required for the viability of a CO_2 electroreduction process [132], represent an important issue to address, which is usually attributed to limitations due to CO_2 diffusion. In this sense, for example, Shi et al. [121] very recently reported the conversion of CO_2 into CO in an IL/ organic solvent electrolyte solution. The conventional organic solvent propylene carbonate (PC) was used to dilute the IL 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate ([BMIm][CF_3SO_3]) with the aim of overcoming the problem of the low current density of CO_2 electroreduction because of restrained CO_2 diffusion in ILs owing to their high viscosity [121], and the cathodic current densities of CO_2 reduction measured in cyclic voltammetry studies were much

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higher in [BMIm][CF_3SO_3]/PC solution than those detected in [BMIm][CF_3SO_3] catholyte.

3.4. Other studies on CO_2 electroreduction

Although they have not performed electrolytic tests and therefore they have not been included in Table 3, it should be emphasised that some other works have carried out fundamental electrochemical studies with interesting results on the use of ILs for electroreduction of CO_2. For example, Barrosse-Antle and Compton [133] studied the electrochemical reduction of CO_2 in 1-butyl-3-methylimidazolium acetate ([BMIm][Ac]) with Pt electrode (10 μm diameter) in a “T-cell” at ambient temperature and pressure, and reported that CO_2 is reduced to the radical anion $CO_2^{-\cdot}$ and that probable follow-up chemistry includes the formation of oxalate, CO and carbonate. They also found the diffusion coefficient of CO_2 in this IL to be lower than it would be expected in the case of simple physical absorption of CO_2, which suggested chemical complexation of CO_2 in the IL [BMIm][Ac] [133]. Subsequent work of Compton group focussed on studying the reaction of CO_2 and protons from strong acid bis(trifluoromethane)-sulfonimide (H[NTf2]) in the IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][NTf_2]) or 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPyrr][NTf_2]), at mild conditions of room temperature (298 K) and pressure (1 atm), with pre-anodised Pt microelectrode in a glass T-shaped cell [134]. From the study of cyclic voltammograms, the proposed reaction is between reduced CO_2 and activated H on Pt, giving as final products formic acid and H_2; although good yield of formic acid is suggested, concentrations or efficiencies that could be obtained were not reported [134]. However, Martindale and Compton point out that the advantage over the equivalent reduction in aqueous solution is that the radical

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anion is significantly more stabilised in the IL medium and so survives for a longer period, which could provide considerably greater control over subsequent reaction pathways and may open possibilities for developing processes with higher efficiencies to the desired product. Finally, it is also worth mentioning that Snuffin et al. [135] reported the design and synthesis of an IL 1-ethyl-3-methyl-imidazolium trifluorochloroborate ([EMIm][BF_3Cl]) that contains a novel anion (BF_3Cl^-). Using a pre-polished Pt disk (2 mm diameter), cyclic voltammograms showed a reduction peak at about -1.8V that yielded a current density of 5.7 mA cm^{-2}. The authors suggested that this anion may catalyse the CO_2 reduction by forming a Lewis acid-base adduct BF_3-CO_2, although the chemical reactions of CO_2 fixation following the electrochemical reduction were still under investigation [135].

4. CONCLUDING REMARKS AND FUTURE PERSPECTIVES

Climate change mitigation and the transition to energy systems less dependent on fossil fuels are some of the great challenges in the 21st century. The deployment of CCS is currently considered to be crucial for capturing and storing CO_2 in the large quantities required to contribute significantly to achieve carbon reduction targets. In parallel, CCU technologies can complement CO_2 storage and generate value from part of the captured CO_2 by converting it into useful products. Particularly, the development of electrochemical processes for CO_2 valorisation appears as an interesting possibility. Apart from the possibility of obtaining useful chemicals from CO_2, the electrochemical valorisation has been suggested in the literature as an excellent future option to chemically store intermittent energy from renewable sources such as solar or wind

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energy. Moreover, CO_2 electrochemical conversion processes can be carried out at mild conditions.

For all of these reasons, in recent years a renewed interest in the electrochemical valorisation of CO_2 has been observed, with a rapidly growing number of studies focussed on different innovative attempts. The ILs are a family of compounds with unique properties, so their use, as well as in other fields and even in other electrochemical applications, has also been explored for the electrochemical valorisation of CO_2. This review focusses on giving an overview of the use of ILs both in the CO_2 electroreduction and in approaches for the electrosynthesis of valuable compounds in which CO_2 is used as one of the reactants. The ILs studied, the operating conditions (pressure, temperature, electrolytes, potentials applied, way of supplying CO_2, etc.), the nature and characteristics of the electrodes, and the types of electrochemical cells, together with the most remarkable findings and figures of merit reported in relevant studies on the electrochemical valorisation of CO_2 that involve ILs, are summarised and presented in comprehensive tables to help readers easily find the information.

Different ILs have been considered, but the most studied ones have clearly been imidazolium-based ILs, especially [BMIm][BF_4], [EMIm][BF_4], or [BMIm][Br]. Regarding the electrosynthesis of value-added chemicals by employing ILs, organic carbonates, and in particular DMC, have been the focus of increasing attention. Interesting approaches to synthesise DMC from methanol and CO_2 using ILs but without the addition of problematic alkylating agents like CH_3I have been proposed. However, great research efforts are needed to clarify the reaction mechanism and the role of the ILs involved in this electrosynthesis, which would help to achieve the increase in the yields of DMC that is required for further development of these processes. Approaches for the electroreduction of CO_2 with the aid of ILs, particularly

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to convert it to CO, have been more thoroughly studied, reaching a higher level of development than approaches for the electrosynthesis of other products like DMC, although still only at a lab scale. As discussed in this review, CO_2 has been successfully reduced to CO using ILs at very low overpotentials when compared to the theoretically required ones, which encourages the need to continue exploring the use of ILs in electrochemical processes for converting CO_2 in other products of interest.

The different studies reviewed in this paper show that the application of ILs can help improving the electrochemical valorisation of CO_2. However, the maturity of the technology for the electrochemical conversion of CO_2 is still far from practical application. Despite the encouraging results reported in recent investigations, there are several technical challenges that have to be overcome. The rates of formation of the product (measured by the current density at which the process can be operated), the reaction efficiencies and the products yields achieved in these electrochemical routes have to be improved. Together with attempts to increase catalytic activity, product selectivity and stability by exploring innovative electrocatalysts and optimised electrode /reactor configurations, the use of novel compounds like ILs can also help to achieve the significant advances that are currently required to develop processes for the electrochemical efficient production of useful products by valorisation of CO_2.

Promising results reviewed in this paper on studies where the use of ILs (alone or in mixtures with water or other solvents) has allowed improving the performance of CO_2 electrovalorisation approaches support this idea. It can then be concluded that ILs can play a beneficial role in these electrochemical processes, although deeper research is still necessary to fully explore their possibilities. Despite the fact that some attempts to have an insight into the electrochemical conversion of CO_2 can be found in the literature, the level of understanding of the CO_2 reaction mechanisms, pathways and

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intermediates involved in the production of useful chemicals is not enough. Particularly, the role of the ILs in many of the CO_2 electrochemical approaches in which they have been tested is far from being clear. Therefore, a greater knowledge on a molecular level could also guide the design efforts along paths that will lead to "task-specific" ILs that could be especially suited for the electrochemical conversion of CO_2. Finally, apart from the considerable research required to overcome current limitations, once the technical feasibility of these processes is demonstrated, it is important to realise that other important aspects of the electrochemical valorisation of CO_2 must not be disregarded and will have to be analysed in a systematic manner. In this way, the cost-effectiveness and a holistic view of the sustainability of CO_2 electrovalorisation approaches will have to be carefully assessed considering the entire life cycle, in order to ensure a favourable economic balance, social acceptance and a positive environmental profile.

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Ionic liquids in the electrochemical valorisation of CO_2

Manuel Alvarez-Guerra, Jonathan Albo, Enrique Alvarez-Guerra, Angel Irabien

Tables

Table 1. Codes and names used for ILs in this paper.

Table 2. Studies about electrosynthesis of valuable compounds using CO_2 as reactant that involve the use of ILs.

Table 3. Studies about electroreduction of CO_2 to obtain value-added products that involve the use of ILs.

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Table 1. Codes and names used for ILs in this paper.

Code	Name
[AcMIm][Cl]	1-acetic acid-3-methylimidazolium chloride
[ApMIm][Br]	1-(3-aminopropyl)-3-methylimidazolium bromide
[BMIm][BF_4]	1-butyl-3-methylimidazolium tetraflouroborate
[BMIm][Br]	1-butyl-3-methylimidazolium bromide
[BMIm][CF_3SO_3]	1-butyl-3-methyl-imidazolium trifluoromethanesulfonate
[BMIm][Cl]	1-butyl-3-methylimidazolium chloride
[BMIm][OH]	1-butyl-3-methylimidazolium hydroxide
[BMIm][OTf]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[BMIm][PF_6]	1-butyl-3-methylimidazolium hexafluorophosphate
[BMMIm][BF_4]	1-butyl-2,3-dimethylimidazolium tetrafluoroborate
[BMMIm][Cl]	1-butyl-2,3-dimethylimidazolium chloride
[BMPyrd][NTf_2]	1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)imide
[BMPyrr][NTf_2]	1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[BPy][BF_4]	butylpyridinium tetrafluoroborate
[BzMIm][Cl]	1-benzyl-3-methyl imidazolium chloride
[DEME][TFSA]	N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis- (tri-fluoromethanesulfonyl)amide
[EMIm][BF_3Cl]	1-ethyl-3-methylimidazolium trifluorochloroborate
[EMIm][BF_4]	1-ethyl-3-methylimidazolium tetraflouroborate
[EMIm][Br]	1-ethyl-3-methylimidazolium bromide
[EMIm][$EtSO_4$]	1-ethyl-3-methylimidazolium ethylsulfate
[EMIm][NTf_2]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[EMIm][TCB]	1-ethyl-3-methylimidazolium tetracyanoborate
[EMIm][TFA]	1-ethyl-3-methylimidazolium trifluoroacetate
[MMMIm][NTf_2]	trimethylimidazolium bis(trifluoromethylsulfonyl)imide
[MOEMIm][BF_4]	1-(2-methoxyethyl)-3-methylimidazolium tetrafluoroborate
[MPPyrr][NTf_2]	1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[TBA][BF_4]	tetrabutylammonium tetrafluoroborate
[TBA][Br]	tetrabutylammonium bromide
[TBA][Cl]	tetrabutylammonium chloride
[TBA][I]	tetrabutylammonium iodide
[TBA][PF_6]	tetrabutylammonium hexafluorophosphate
[TEA][BF_4]	triethylammonium tetrafluoroborate
[TMPA][TFSA]	N,N,N-trimethyl- N-propylammonium bis- (tri-fluoromethanesulfonyl)amide

Table 2. Studies about electrosynthesis of valuable compounds using CO_2 as reactant that involve the use of ILs

Ref.	Substrates	ILs	Products of electrochemical synthesis	Electrolysis operating conditions	Electrodes	Cell	Other observations
Yang et al. 2002 [84]	Epoxides (propylene oxide, epichlorohydrin, styrene oxide) and CO_2	$[BMIm][BF_4]$, $[EMIm][BF_4]$, $[BMIm][PF_6]$, $[BPy][BF_4]$.	Cyclic organic carbonates	Ambient T & P. Reaction time typically 24 h. Continuous bubbling of CO_2 throughout the reaction	Cu working electrode. Mg or Al rod as sacrificed anode	Undivided cell	Best performance was achieved with $[BMIm][BF_4]$ using propylene oxide as substrate (92% conversion, 100% selectivity, 87% current efficiency)
Feroci et al. 2007 [85]	Amines and CO_2. C_2H_5I was added as an alkylating agent	$[BMIm][BF_4]$	Organic Carbamates (and alkylated amines as byproducts)	1 atm CO_2, 55ºC Continuous bubbling of CO_2	Cathode: Cu, Pt or Ni. Anode: Pt. Ag wire as quasireference electrode. Spiral electrodes, apparent area 0.8 cm^2	Divided glass cell (volume of catholyte & anolyte 1 mL). Anolyte and catholyte were separated through a G-5 glass septum.	Maximum chemical yield of carbamate (80%) was obtained using a Pt cathode
Wang et al. 2007 [86]	Activated olefins (e.g. ethyl cinnamate) and CO_2	$[BMIm][BF_4]$	Monocarboxylic acids (principal product), accompanied by saturated esters.	1 atm CO_2; 25, 40, 50 or 60ºC	Metallic ring cathode: stainless steel, Ti, Cu or Ni. Mg rod sacrificial anode.	Undivided cell	Optimal temperature was 50ºC. Reaction yields and selectivity were particularly dependent on the nature of the electrodes; highest yield of monocarboxylic acid: SS (41%) > Ti (35%) > Cu (30%) > Ni (26%).
Yuan et al. 2008 [87]	Aryl-substituted alkenes (mainly styrene and derivatives) and CO_2	Mixture of [TBA][Br] and dried DMF solvent	2-arylsuccinic acids	4 MPa CO_2 pressure, room temperature	Cathode: Ni plate (2 cm x 3 cm x 0.02 cm) Anode: Al plate (2 cm x 3 cm x0.05 cm). Other cathodes (Pt, Cu, Cu-Sn alloy) and anodes (Mg or Zn) were also tested.	High-pressure stainless-steel undivided cell	Moderate to good yields (50-87%) and high selectivity (98%) were achieved. Among the different cathodes and anodes investigated, the optimal results for reaction of styrene and CO_2 were with Ni (or Pt, but it is much less available than Ni) as cathode and Mg or Al as anode (selectivity 98%, yield 85-87%)
Yuan et al. 2008 [88]	Arylacetylenes (phenylacetylene and derivatives) and CO_2	Mixture of [TBA][Br] and dried DMF solvent	Aryl-maleic anhydrides and 2-arylsuccinic acids	3 MPa CO_2 pressure, room temperature	Cathode: Ni sheet (2 cm x3 cm x0.02 cm) Anode: Al plate (2 cm x3 cm x0.05 cm). Other cathodes (Pt, Ag, Cu, Zn, stainless	High-pressure stainless-steel undivided cell	The products were obtained with excellent total yields (82-94%). For reaction of phenylacetylene and CO_2, Ni cathode gave best results, with excellent total yields of 93% (with Al anode) and 87% (with Mg anode).

					steel, Cu-Sn alloy) and anodes (Mg) were also tested.		
Zhang et al. 2008 [89]	Alcohols and CO_2. Alkyl iodides (CH_3I or C_2H_5I) were added as alkylating agent	[BMIm][BF_4]	Organic carbonates (e.g. DMC)	1 atm CO_2; 25, 35, 45, 55, 65 or 75ºC. Continuous bubbling of CO_2	Cathode: Cu, Ag, stainless steel, Ti or Ni (8.0cm^2) Mg sacrificial anode Reference electrode: Ag/AgI electrode	Undivided glass cell	The yield of DMC decreased in the order Cu ≈ Ag > SS >Ti > Ni. Best yields with Cu and Ag cathodes (73 and 74% of DMC), at an optimum temperature of 55ºC. Primary and secondary alcohols were converted in good yields, whereas tertiary alcohol and phenol were unreactive.
Yuan et al. 2009 [90]	Methanol and CO_2. CH_3OK was added as co-catalyst	Imidazolium-based ILs: [BMIm][Br], [EMIm][Br], [BMIm][Cl], [BMIm][OH], [BMIm][BF_4], [EMIm][BF_4].	DMC	Ambient pressure, temperature in the interval 273-323 K. Solution was saturated with CO_2 by gentle bubbling (ca. 2–3 bubbles s^{-1}). The reaction was carried out for 48 h at 5.5V.	Cathode and anode: both Pt	Undivided four-neck bottle cell	[BMIm][Br] gave the best, but low (3.9%) yield of DMC after 48 h of reaction time and at 303 K. This low yield was attributed to the bulk hydrogen production in the cathode. CH_3OK was found to play a key role in the synthesis of DMC, enhancing the reduction of CO_2.
Yuan et al. 2012 [91]	Methanol and CO_2	[BzMIm][Cl]. Other ILs used: [BMIm][Cl], [BMIm][OH], [BMIm][Br] [BMIm][BF_4], [EMIm][BF_4], [EMIm][Br].	DMC	Atmospheric pressure, temperature in the interval 283-313 K. Solution was saturated with CO_2 by gentle bubbling (ca. 2–3 bubbles s^{-1}, about 5.0-7.5 mg min^{-1}). Electrolysis was carried out at 4.0V constant potential for 60 h.	Graphite as cathode and platinum as anode. Other cathodes were also studied: Pt, glass-carbon and Cu. Working electrode surface area= 0.2826 cm^2.	Undivided four-neck bottle cell	Maximum yield (3.77%) and selectivity (51.8%) for DMC were obtained using [BzMIm][Cl], with graphite cathode, after 60 h at 293 K. The suggested reaction mechanism was totally different from that proposed in their previous work [90]: "electrochemical synthesis of DMC is mainly based on the activation of methanol on the electrode surface, and CO_2 merely participates in the chemical reaction with the methoxide anion adsorbed on the electrode surface"
Niu et al. 2009 [92]	Benzyl chloride and CO_2	[BMIm][BF_4]	Phenylacetic acid (principal product), accompanied by dimer 1,2-biphenylethane.	0.1 MPa CO_2 pressure; 30, 40, 50, 60 or 70ºC	Cathode: Ag cylinder (8 cm^2). Mg rod sacrificial anode. Other cathodes (Cu, Ni) and anodes (Al, Zn) were also tested.	Undivided cell	The effect of different electrodes was investigated: much higher yields with Ag cathode (45%) than with Cu and Ni (5 and 7%). No differences observed among the use of Mg, Al and Zn as sacrificed anode. Best temperature was 50ºC.

Hiejima et al. 2010 [93]	α-chloroethylbenzene and high-pressure CO_2	[DEME][TFSA]	2-phenylpropionic acid	0.1, 3, 5 or 8 MPa pressure, 25 or 40 ºC	Working electrode: Pt plate (2x1 cm^2). Counter electrode: Mg rod (diameter 6.4 mm) sacrificial anode. Quasi-reference electrode: Pt wire (diameter 0.5 mm)	High-pressure vessel	Current efficiency (low under ambient conditions) drastically increased with temperature and pressure (maximum 65% at 40ºC and 8 MPa), which was mainly explained by the increase of the diffusion coefficient of the reactant in the IL. Experiments with other ILs gave worse results: the reaction system did not work in [TMPA][TFSA], and the yields of undesired byproducts increased appreciably in [BMIm][TFSA]
Wang et al. 2010 [94]	CO_2. At the end of electrolysis, methanol first, and finally 3-fold molar CH_3I, were added.	[BMIm][BF_4]	DMC	Ambient pressure; 20, 30, 40, 50, 60 or 70 ºC.	Working electrode: silver-coated nanoporous copper (NPC-Ag). Ag or NPC cathode material were also tested but gave remarkable lower yield of DMC. Counter electrode: Pt foil. Reference: Ag wire	Undivided cell	80% yield of DMC was obtained under the optimal reaction conditions (temperature= 50ºC, -1.7V vs. Ag).
Feng et al. 2010 [95]	2-amino-5-bromopyridine and CO_2. $PhCH_2Br$ was used as esterification agent; 6-ANA was finally obtained by hydrogenation of the ester in CH_3OH with 10% Pd/C catalyst	[BMIm][BF_4]	6-aminonicotinic acid (6-ANA)	Ambient pressure, 25, 50 or 75 ºC. CO_2 was bubbled for 30 min after bubbling Ar gas for 30 min.	Ringed Ag cathode (area 3 cm^2). Sacrificial Mg rod anode (diameter 0.5 cm). Reference: Ag wire. Cu, Ni and stainless steel were also investigated as cathode, and Al as anode.	Undivided cell	6-ANA was obtained in 75% yield and 100% selectivity under optimised conditions (Ag cathode/ Mg anode, 50ºC, -1.9V vs. Ag., 0.01 mol L^{-1} of substrate concentration, 2.0 F mol^{-1} passed charge)
Feroci et al. 2011 [96]	Amines, CO_2 and O_2. C_2H_5I was also added as alkylating agent.	[BMIm][BF_4] and other imidazolium-based ILs	Organic carbamates	60ºC. Continuous O_2 and CO_2 bubbling. Time of electrolyses between 3.5 and 10 h.	Cathode (surface area ca. 1 cm^2): C, Cu, Pt, Ni, Pb. Anode (0.8 cm^2): flat Pt spiral (99.9%). Ag quasi reference	Two compartment home-made glass cell. The anolyte (1 mL) and catholyte	Superoxide ion $O_2^{\cdot -}$ is electrochemically generated by selective reduction of O_2, which reacts with CO_2 yielding the carboxylating $C_2O_6^{2-}$ anion. Good electrochemical efficiency with a reasonable time of electrolysis (4 h) was

					electrode.	(2 mL) were separated by a glass disk	achieved in [BMIm][BF_4] using a Cu cathode.
Yan et al. 2011 [97]	Methanol, CO_2 and propylene oxide (PO)	[BMIm][Br]	DMC	Ambient pressure, temperature in the interval 293-313 K. Solution was saturated with CO_2 by gentle bubbling (ca. 2–3 bubbles s^{-1}). Electrolysis time: 48 h, supplying 5.5V via the 2 electrodes	Cathode and anode: both Pt. Graphite and glass-carbon electrodes were also used, achieving worse results	Undivided four-neck cell	The effect of various conditions was studied. Under the optimal operation conditions for the system (303K, reaction time 48h, methanol/PO molar ratio 11.5:1, and amount of IL 0.059 mol), the conversion and yield (calculated on the basis of PO) were 97% and 75.5%, respectively, with a selectivity to DMC of 77.8%.
Wang et al. 2011 [98]	Diols (mainly 1,2-butanediol) and CO_2. CH_3I and anhydrous K_2CO_3 were added to esterify the reaction mixture.	[BMIm][BF_4]. [BMIm][PF_6] was also studied, with worse results.	Cyclic organic carbonates (mainly butylene carbonate)	Mild conditions: 1 atm CO_2; 40, 45, 50, 55 or 60ºC. Potentiostatic electrolysis	Metallic ring cathode: Ni, Ag or Cu. Mg rod sacrificial anode.	Undivided cell	The influence of reaction conditions (electrode materials, electrolysis potential, temperature, diol concentration and composition of IL) were investigated. Highest yield obtained at optimized conditions was 12% carbonate, achieved with Ni cathode, at 50ºC, -1.7 V electrolysis potential, and using 1,2-butanediol concentration of 0.10 mol L^{-1}. Carbonate yield maintained ca. 12 % for 6 cycles of reuse of IL.
Feng & Liu 2011 [99]	CO_2. At the end of electrolysis, methanol (0.12M) first, and finally 5 fold molar CH_3I, were added.	[BMIm][BF_4]	DMC	Potentiostatic electrolyses at 55ºC until 1 F of charge passed. Prior to every experiment, the solution was bubbled with CO_2 under stirring for 0.5 h to be saturated. Continuous CO_2 flow was kept throughout the electrolyses.	Working electrode: ringed Cu electrode (area =5 cm^2). Counter electrode: Mg rod (d=0.5 cm), placed down the middle of the ringed Cu cathode. Reference electrode: Ag^+/AgCl	Undivided cell with a gas inlet and outline	The effect of the applied potential on the Faradaic efficiency was studied in the range -1.8V to -2.3V. Maximum Faradaic efficiency and yield of DMC was 72.3% at -1.9V.
Zhao et al 2011 [100]	Acetophenone and CO_2	[BMIm][BF_4]	1-phenylethanol	Potentiostatic bulk electrolysis at 25ºC. A slow stream of CO_2 (to provide a constant supply of the reactant)	Glassy carbon beaker cathode; Mg sacrificial anode; silver wire quasi-reference electrode	Undivided cell	Unexpectedly, 97% yield of 1-phenylethanol (with 65% conversion of acetophenone) was obtained, instead of the anticipated 2-hydroxy-2-phenylpropionic acid

				was applied during the electrolysis (P=1 atm). Duration of electrolysis was about 10 h.			
Feng et al. 2012 [101]	CO_2. At the end of electrolysis, methanol (0.12M) first, and finally 3 fold molar CH_3I, were added.	[BMIm][BF_4]	DMC	Potentiostatic electrolyses at -2.2 V (vs. Ag) at 25ºC until 1 F of charge passed. Prior to every experiment, the solution was bubbled with CO_2 under stirring for 30 min to be saturated	Working electrodes: 1) Pure Pt. 2) NPC-Pt film (area=1cm^2) (i.e. Three-dimensional porous nanostructure composite electrode of copper skeletons and platinum shells, NPC-Pt) Counter electrode: Mg rod (d=0.5cm). Ag wire was used as quasi-reference electrode	Undivided cell with a gas inlet and outline	Cyclic voltammogram studies indicated that nanoporous structure of NPC-Pt electrode can increase the active centers where the reduction of CO_2 occurred, compared to pure Pt electrode. Pure Pt and NPC-Pt electrodes were compared in potentiostatic electrolyses: higher and more stable current density (3.2 mA cm^{-2}) obtained at NPC-Pt; higher yield of DMC finally formed on NPC-Pt (81% vs. 64% on pure Pt); current efficiency kept constant at 83% on the NPC-Pt after 5 cycles, compared to 64% of the pure Pt.
Liu et al. 2012 [102]	CO_2. After electrolysis, methanol, and finally CH_3I as alkylation agent (3-fold excess), were added.	[BMIm][BF_4]	DMC	Mild conditions; 30, 40, 50, 60 or 70 ºC. Prior to each test, [BMIm][BF_4] was bubbled with CO_2 for 30 min to be saturated. Constant potential was applied (-1.5, -1.7, -1.9 or -2.1 V) and continuous CO_2 flow was kept throughout the tests	In electrode (area= 1 cm^2) Magnesium rod (d=0.5 cm) sacrificial anode	Standard undivided glass cell	The influence of temperature, working potential and charge passed on the yield of DMC was studied. Maximum yield was 76%, obtained under a charge consumption of 1.0 F mol^{-1}, with a potential of -1.7V and at 40ºC.
Wu et al. 2012a [103]	CO_2 and diols (mainly styrene glycol). CH_3I and anhydrous K_2CO_3 were then added to esterify the reaction mixture.	[BMIm][BF_4]. Other alkylimidazolium ILs were also studied, with worse results.	Cyclic carbonates (mainly styrene carbonate)	Mild reaction conditions: 1 atm CO_2 and temperatures from 30 to 60ºC. Galvanostatic conditions	Working electrode: Ti, Cu, Stainless steel (SS), Pt, Ni, glassy carbon (GC)	Two-compartment cell divided by cation-exchange membrane	The synthesis of the cyclic carbonates from CO_2 and diols was suggested to be carried out via electrogenerated N-heterocyclic carbenes. Best yield of 60% for styrene carbonate (based on styrene glycol) was obtained using Ti, at 40ºC, when the passed charge reached 1.5 F mol^{-1}, at current density of 18.9 mA cm^{-2}, and with stirring time of 2h. The yield decreased depending on the cathode material in this order:

							Ti>Cu>SS>Pt>Ni>GC.
Wu et al. 2012b [104]	CO_2 and alcohols (mainly benzyl alcohol). CH_3I and anhydrous K_2CO_3 were then added to esterify the reaction mixture.	[BMIm][BF_4]. Other ILs ([BMIm][PF_6] and [BMMIm][BF_4]) were also studied, with worse results.	Dialkyl carbonates (mainly benzyl methyl carbonate)	Mild reaction conditions: 1 atm CO_2 and temperatures from 20 to 60ºC. Galvanostatic conditions	Working electrode: Ti, Cu, Stainless steel (SS), Pt, Ni	Two-compartment cell	The dialkyl carbonates were synthesised via electrogenerated N-heterocyclic carbenes (NHCs), where the IL acted as NHC precursor. Best results for synthesis of benzyl methyl carbonate from CO_2 and benzyl alcohol (92% conversion and 96% selectivity) were obtained using Ti, at 40ºC, with 2.0 F mol^{-1} of charge passed, at current density of 18.9 mA cm^{-2}, and with stirring time of 2.5 h. Under these optimised conditions, other primary alcohols were converted into the corresponding dialkyl carbonates with conversions ~90% and selectivities 95-97%; secondary alcohols were also converted into dialkyl carbonates with selectivities 93-95% but low conversions (24-27%); and for tertiary alcohol and phenol, no carbonate was detected.
Matthesen et al. 2013 [105]	CO_2, DMF or MeCN as solvent, and conjugated linoleic acid methyl esters (CLAME). Other different conjugated dienes were also studied	[TBA][Br], [TBA][I] or [TBA][PF_6]. [MPPyrr][NTf_2] & [BMIm][BF_4] were also used as solvents for the electrocarboxylation of CLAME, but gave no product	Dicarboxylated products, fatty triacid methyl esters (e.g. 9,12-Carboxy-10-octadecenoic acid trimethyl ester)	Galvanostatic experiments at room temperature. Atmospheric pressure or CO_2 pressure of 3, 5, 10 or 20 bar. CO_2 was charged into the cell to the desired pressure or continuous bubbling was kept during the whole test.	Ni (or Ta, Pt, Cu, SS) cylindrical cathode mesh (wet surface area of 10 cm^2). Central sacrificial Mg or Al anode rod (wet surface area of 4 cm^2)	Stainless-steel (SS) undivided cell	A yield of 79% and a current efficiency of 53% were achieved by at room temperature by supplying 3 F mol^{-1} at 3 mA cm^{-2} to a 0.2 mol dm^{-3} concentration of CLAME, while bubbling CO_2 at atmospheric pressure, at the best experimental parameters found for the reaction: Ni as cathode, Mg as anode, MeCN as solvent and TBABr as supporting electrolyte.
Lu et al. 2013 [106]	Methanol and CO_2	[ApMIm][Br]. Other ILs used: [BMIm][OH], [BMIm][Br] [BMIm][BF_4], [AcMIm][Cl]	DMC	Ambient conditions. Atmospheric pressure, temperature in the interval 0-50ºC. Solution was saturated with CO_2 by gentle bubbling (ca. 2–3 bubbles s^{-1}). Electrolysis was carried	Graphite as cathode and platinum as anode. Other cathodes were also studied: Pt, glass-carbon and Cu.	Undivided four-neck bottle cell	Best performance (2.5% yield and 94.5% selectivity for DMC after 60 h) was obtained with graphite using [ApMIm][Br], which was attributed to the basicity of the functionalized IL. Increasing temperature beyond 20ºC and reaction time beyond 60h decreased conversion and selectivity.

				out at 3.5V cell voltage for 60 h.			
Zhao et al. 2014 [107]	Acetophenone and CO_2	[BMMIm][BF_4] or [BMPyrd][NTf_2]	2-hydroxy-2-phenylpropionic acid	Potentiostatic bulk electrolysis at 22ºC with [BMPyrd][NTf_2] or 50ºC with [BMMIm][BF_4]. A constant stream of CO_2 flowed through the cell during the electrolysis (P=1 atm)	Glassy carbon cylindrical tube cathode; Mg sacrificial anode; silver wire quasi-reference electrode	Undivided cell	A 98% yield of 2-hydroxy-2-phenylpropionic acid was obtained with dry [BMPyrd][NTf_2]; water promoted undesirable reactions. Using dry [BMMIm][BF_4] the product yields were 15% 2-hydroxy-2-phenylpropionic, 60% 1-phenylethanol and 25% dimers.
Yuan et al 2014 [108]	CO_2, Methanol and propylene oxide (PO)	[BMIm][Br]	DMC	Solution was saturated with CO_2 by gentle bubbling (ca. 2–3 bubbles s^{-1}) at ambient pressure after blowing nitrogen for 30 min. Different potentials (from 5 to 7.5V) and different temperature (273 to 313K) were used. The effect of reaction time and of the amount of IL were also studied.	Pt electrodes	One compartment cell	The optimum values of cell voltage and temperature were 5.5V and 303K. Yield of DMC increased rapidly with reaction time, achieved a maximum (37.8%), at 48h, but beyond 48h, it fell sharply.
Garcia-Herrero et al. 2014a [109]	Methanol and CO_2. CH_3OK was added as co-catalyst	[BMIm][Br]. Tests with [EMIm][$EtSO_4$] were also done with worse results.	DMC	CO_2 was bubbled into the electrolyte of the working compartment until saturation. Electrolytes were circulated with a flow rate of 20 mL min^{-1}. A 1.2 V potential between working and reference electrodes was applied for up to 48h at 303K. The influence of the composition of the reaction medium was	Pt/Nb plate (99.5% Pt) electrodes with a surface area of 10 cm^2 each. Leak-free Ag/AgCl 3.4 M KCl reference electrode.	Flow-by filter-press cell. Anodic and cathodic compartments separated by a Nafion 117 cation exchange membrane	First study of CO_2 electrovalorisation to DMC using a divided cell. The simultaneous presence of both CH_3OK and [BMIm][Br] was found to be required to obtain DMC. The results suggest that [BMIm][Br] is not merely an electrolyte, but it plays a catalytic role in the electrosynthesis. Best results were obtained with 5% CH_3OK, 15% [BMIm][Br] and 80% methanol (wt %). The evolution of the DMC conc. with time revealed that after 18h it no longer increased but fluctuated around 15 mmol L^{-1} (1.4 g L^{-1}). A final yield of 12.5% (based on

				also studied.			CO_2) was obtained.
Garcia-Herrero et al. 2014b [110]	Methanol and CO_2. CH_3OK was added as co-catalyst	[BMIm][Br]	DMC	CO_2 was bubbled until saturation. In undivided configuration, tests were also carried out using constant CO_2 bubbling and molecular sieves 3A as dehydrating agents. Electrolytes were circulated with a flow rate of 20 mL min^{-1}. 1.2 V between working and reference electrodes (average cell potential of 3.5V) was applied for up to 48h at 303K.	Pt/Nb plate (99.5% Pt) electrodes with a surface area of 10 cm^2 each. Leak-free Ag/AgCl 3.4 M KCl reference electrode.	Flow-by filter-press cell, with two different configurations: undivided cell or divided cell with anodic and cathodic compartments separated by 6 different anion exchange membranes.	The use of constant bubbling and molecular sieves only gave slight improvements during the first hours. A similar DMC concentration to that achieved with the Nafion membrane was obtained after 48 h using the best performing anion exchange membrane tested. Regardless of which membrane is used, an additional resistance seems to be introduced. A final concentration of 85 mmol L^{-1} (yield of 70.71% based on CO_2) was obtained up to 48 h without membrane, which involves a six-fold increase regarding the previous work with Nafion membrane.

Notes:
[DMF]: N,N-Dimethylformamide
DMC: dimethylcarbonate
H[NTf$_2$]: acid bis(trifluoromethane)-sulfonimide
MeCN: acetonitrile

Table 3. Studies about electroreduction of CO_2 to obtain value-added products that involve the use of ILs

Ref.	ILs	Products	Electrolysis operating conditions	Electrodes	Cell	Other observations
Zhao et al. 2004 [111]	[BMIm][PF_6],	Syngas (CO + H_2) and trace amount of formic acid	Supercritical CO_2 was charged into the cell at different high pressures (in the range 7.3 – 10.6 MPa). Electrolyses were conducted galvanostatically with a current density of 20 mA cm^{-1} at 318.2 K. Different amount of water was added in the system	Cu (>99.99%) plank cathode (geometric area of 2.0 cm^2). Pt (>99.99%) plank anode (geometric area of 2.0 cm^2). Pt wire quasi-reference electrode with a diameter of 0.3mm.	High pressure undivided cell: Teflon-lined stainless steel cell of 30 mL. Cathode and anode were in parallel with a distance between them of 3 mm.	FE for CO increases (from about 20 to 55%) and for H_2 decreases (from about 60 to 40%) as the CO_2 pressure is increased (from about 7.3 to 10.6 MPa). As the amount of water added is smaller, the FE for CO is larger and the FE for H_2 decreases.
Chu et al. 2008 [112]	[EMIm][BF_4]	Low-density polyethylene (LDPE)	Ambient temperature and pressure. CO_2 was bubbled into the catholyte (mixture of [EMIm][BF_4] and water (1:1 v/v)) for 0.5 h.	Cathode: nanostructured nsTiO_2 film electrode (area 10 cm^2). Anode: Pt foil (area 10 cm^2). Reference electrode: aqueous SCE	Divided H-type cell. A cationic film (0.18-mm thickness) was used as the diaphragm.	FE for LDPE production of 8-14%. In the proposed reaction mechanism, the role of [EMIm][BF_4] is to maintain a high concentration of CO_2 at the electrode surface.
Rosen et al. 2011 [113]	[EMIm][BF_4]	CO (desired) and H_2 (undesired) on the cathode; O_2 on the anode	CO_2 flows at a rate of 2.5 sccm at 22ºC. In the cathode compartment, 18 mol% [EMIm][BF_4] in water flows at 0.5 mL min^{-1}. In the anode compartment, 100 mM aqueous H_2SO_4 also flows at 0.5 mL min^{-1}. Experiments were carried out at constant voltage on the cell.	Silver cathode (electrochemical surface area of 6 cm^2): Sigracet® graphite gas diffusion layer in which 10 mg of Ag nanoparticles ink was painted. Pt anode (electrochemical surface area of 500 cm^2): 10 mg of Platinum Black nanoparticles painted on same Sigracet® paper.	Flow cell. A Nafion 117 membrane was placed between the anode and the cathode to isolate the anode from the IL.	Formation of gaseous CO was first observed at an applied voltage of 1.5 V, just slightly above the minimum (i.e., equilibrium) voltage of 1.33 V. FE of CO formation was always greater than 96% at any applied cell 22potential between 1.5 and 2.5V. Hydrogen formation was always less than 3% of the FE. The system continued producing CO for at least 7 h at FEs greater than 96%. The energy efficiency of the process was 87% at low voltage (1.5V) and dropped as voltage increased.
Rosen et al. 2013 [114]	[EMIm][BF_4]	CO	CO_2 flowed at a rate of 2.5 sccm at 22ºC. All liquids (catholyte: mixtures of [EMIm][BF_4] and water;	Cathode: Sigracet® graphite gas diffusion layer in which 10 mg of Ag nanoparticles ink	Flow cell. A Nafion 117 membrane was placed between the	The FE to CO increased when water was added to the dry [EMIm][BF_4] electrolyte, reaching nearly 100% at 89.5 mol% water. The [EMIm][BF_4]

			anolyte: 0.1 M H_2SO_4) flowed through the cell at 0.5 mL min^{-1}. Cell potential was held at 2.5V.	was painted onto an area of 1.5 cm^2. Anode: 5 nm Pt black nanoparticles painted on the same Sigracet® paper.	anode and the cathode to isolate the anode from the IL.	could inhibit the H_2 evolution expected upon water addition, even at high water concentrations.
Feroci et al. 2013 [115]	[BMIm][BF_4]	Adduct NHC-CO_2	Electrolyses under galvanostatic control. Cell was kept at 60ºC. CO_2 was bubbled into the catholyte for 15 min.	Electrodes were flat Pt spirals, 99.9%; surface areas: ca 1.0 cm^2 for the cathode and 0.8 cm^2 for the anode	Two-compartment home-made glass cell, in which anolyte and catholyte were separated by a glass disk	The NHC-CO_2 adduct was obtained by simple bubbling of CO_2 in pre-electrolysed [BMIm][BF_4]. The NHC-CO_2 adduct can be used as latent catalyst that release NHC (N-heterocyclic carbenes) upon thermal or ultrasound activation; the released NHC can be used as reagent or as catalyst in classical chemical reactions; it was successfully employed in two exemplifying organocatalyzed reactions: the benzoin condensation and the oxidative esterification of cinnamaldehyde with benzyl alcohol.
Salehi-Khojin et al. 2013 [116]	[EMIm][BF_4]	CO	Both electrolytes (catholyte: dried [EMIm][BF_4]; anolyte 0.5M H_2SO_4) were pumped at 0.5 mL min^{-1}. CO_2 flows at a rate of 7 sccm at 25ºC. Different cell potential was applied: 2.75, 3.00, 3.25V. At each cell potential, the cell was allowed to reach steady state for 200 s, after which the gaseous products and unreacted CO_2 were collected for analysis.	Cathode: Ag nanoparticles of 200, 70 or 40 nm painted onto Sigracet® carbon paper (5 mg cm^{-2}). Anode: Pt black (5 mg cm^{-2}) painted onto Sigracet® carbon paper.	Flow cell. A Nafion 212 membrane was used to separate the catholyte and anolyte.	Highest current density of CO in the flow cell (almost 4 mA cm^{-2}) was observed at 3.25V with 40 nm nanoparticles. Voltammetry studies with different Ag nanoparticles (200, 70, 40, 5 and 1 nm) showed that the catalytic activity increased with decreasing particle size until 5 nm, but the activity decreased when using even small nanoparticle size (1 nm). This volcano effect was attributed to changes of the binding energy of key intermediates as the particle size decreases.
Kumar et al. 2013 [117]	[EMIm][BF_4]	CO	Chronoamperometry experiments at -0.573 V vs. SHE were carried out for 9h in pure IL. Water mole fraction in	Working electrode: metal-free carbon nanofibres (CNFs) with 1x0.5 cm^2 surface area.	Three-electrode electrochemical cell	The polyacrylonitrile-based heteroatomic CNFmetal-free catalyst exhibited negligible overpotential (0.17V) for CO_2 to CO and more than an

			the electrolyte was varied from 0 to 100% H_2O mole fraction)	The performance with CNFs was also compared with Ag nanoparticles painted onto Sigracet® graphite layer with 1 cm^2 surface layer. Conunter-electrode: 25x8 mm^2 Pt, gauze 52 mesh with 99.9% metal basis. Reference electrode: Ag wire (0.5 mm diameter, annealed, 99.9% metal basis)		order of magnitude higher current density compared with Ag catalyst under similar experimental conditions. At a constant potential of -0.573V (vs. SHE), the FE for CO formation was 98%. When the influence of water mole fraction was studied, the highest current density in CV experiments was obtained for a $[EMIm][BF_4]$ solution 75 mol% water and 25 mol% $[EMIm][BF_4]$ (~15 mA cm^{-2}, approximately five times higher compared with pure $[EMIm][BF_4]$)
DiMeglio & Rosenthal 2013 [118]	$[EMIm][BF_4]$, $[BMIm][BF_4]$, $[BMIm][PF_6]$ or $[BMMIm][BF_4]$	CO	Controlled potential electrolysis (CPE) experiments were performed at an applied potential -1.95 V vs. SCE for a CO_2- saturated solution of MeCN containing 0.1 M $[TBA][PF_6]$ as supporting electrolyte and 20 mM IL.	Working electrode: Bi^0/Bi^{3+} material electrodeposited onto an inert glassy carbon electrode substrate. Counter electrode: platinum gauze (99.9%). Ag/AgCl reference electrode (1.0 M KCl)	Single-compartment electrochemistry cell with three-electrode configuration. Gas-tight two-compartment cell divided by a Nafion 212 membrane	In CPE with the single-compartment cell, using $[EMIm][BF_4]$, FE of nearly 95% for CO with an average partial current density for CO of 3.77 mA cm^{-2} were observed; similar FEs were obtained using $[BMIm][BF_4]$ or $[BMIm][PF_6]$ but the current densities for CO production were slightly higher (5.51 or 4.82 mA cm^{-2}, respectively). In the two-compartment cell, electrocatalytic conversion of CO_2 to CO was coupled to water oxidation, showing initial current densities of approx. 9 mA cm^{-2} with a FE of 52% for CO, using $[BMIm][PF_6]$ as IL; permeation of the Nafion membrane by water caused a gradual decrease to j_{tot}=0.25 mA cm^{-2} with a FE of 39% for CO, although extended CPEs of over 12 h showed no additional decay in j.
Zhu et al. 2013 [119]	$[BMIm][PF_6]$	CO	Experiments in aqueous 0.5M $KHCO_3$ saturated with CO_2 at	Working electrode: Monodispersed 4, 6, 8,	Conventional gas-tight two-	The CO_2 reduction activity was size-dependent. The 8 nm Au NPs showed

			25ºC. Each compartment contained 50 mL electrolyte. Before the experiment, the catholyte was saturated with CO_2 by bubbling CO_2 gas for at least 30 min.	10 nm Au Nanoparticles (NPs). A C-Au paste (20 mg of C-Au NPs, 3 mg of PVDF and a few drops of *N*-methyl-2-pyrrolidone), in which [BMIm][PF_6] was added, was painted onto carbon paper (Toray TGP-H-060). Counter electrode: 99.9% Platinum wire Reference electrode: Ag/AgCl (4.0M KCl)	compartment H-cell, separated by Nafion 212 membrane	the maximum FE (up to 90% at -0.67V vs. reversible hydrogen electrode, RHE). Using density functional theory (DFT) calculations, this behaviour was attributed to the presence of dominated edge sites on the 8 nm NP surface, which eases the adsorption/ stabilisation of key reaction intermediates for the CO_2 reduction into CO and inhibits hydrogen evolution reaction. Au NPs embedded in a matrix of [BMIm][PF_6] exhibited even higher reaction activity (3 A·g^{-1} mass activity) and selectivity (97% FE) at −0.52 V (vs. RHE).
Shi et al. 2013 [120]	[EMIm][BF_4]	CO	[EMIm][BF_4]/methanol mixture with 1:1 volume ratio. Potentiostatic electrolysis at -1.95V for 2h, with CO_2 bubbled through the cell continuously.	Working electrode: Ag sheet (99.99%, 2x2 mm^2). Counter electrode: graphite rod (99.99%, 5 mm diameter). Reference electrode: SCE	Three electrodes system (not clear if a divided or an undivided cell is used)	Current density reached 14.2 mA cm^{-2} after 1000 s and remained stable until 7200 s electrolysis, with a FE of CO formation of 73%
Shi et al. 2014 [121]	[BMIm][CF_3SO_3]	CO	Cathode compartment (120 mL) filled with a CO_2 saturated solution of [BMIm][CF_3SO_3] diluted in the organic solvent propylene carbonate (PC) (49 vol% IL solution). Anode compartment (80 mL) filled with 0.1M H_2SO_4 aqueous solution. Potentiostatic electrolysis during 3h at ambient temperature and -1.72 V vs. Pt wire (which was the cathodic limiting potential detected in the catholyte).	Cathode: Ag sheet (99.99%, 2.5x2.5 mm^2). Anode: graphite rod (99.99%, 5 mm diameter). Quasi-reference electrode: Pt wire.	Electrolysis cell with two compartments separated by a Nafion 117 ion-exchange membrane	The FE of CO_2 formation, initially as high as 90.1%, gradually decayed to 84.8% after 180 min electrolysis, while FE of H_2 formation increased from 8.6 to 13.5%. These variations in the FEs were attributed to the increase of water in the catholyte (caused by the water naturally produced in the CO_2 reduction, and the water transferred from the anode across the ion-exchange membrane. The current density was stabilised at around 4.6 mA cm^{-2} during the 3h electrolysis. The high FEs of CO formation obtained were attributed to the high solubility of CO_2 in the nonaqueous electrolyte.

Ganesh et al. 2014 [122]	[BMIm][BF_4]	CO	Controlled potential electrolysis (applied voltage -2.5V vs ref. electrode). Catholyte: acetonitrile + 0.1 M $TBAPF_6$ + 20 or 50 mM [BMIm][BF_4]. Anolyte: 1M NaPi (sodium phosphate buffer) + 0.1M $Co(NO_3)_3$ or 0.1M $NaClO_4$. High purity CO_2 gas (99.99%), was sparged at a constant flow rate of 20 scc/min into catholyte.	Cathode: 50 wt.% Cu-doped TiO_2 thin film deposited on conductive FTO-coated soda-lime glass substrate ("50CDTT electrode"). Anode: Pt rod. Reference electrode: $Ag/AgNO_3$+ 0.01 M $TBAPF_6$ in acetonitrile	Custom-made two-compartment all-glass gas-tight electrochemical cell, with Nafion membrane to separate anodic and cathodic compartments	Faradaic efficiencies to CO of 82% and CO selectivity of ≈ 96% were obtained when the "50CDTT electrode " was pre-reduced in an aqueous electrolyte solution comprising 0.2 M acid-phthalate buffer(pH = 3.5) solution + 0.1 M NaCl under Ar atmosphere for 20 min at −2000 mV, and employed as a cathode in conjunction with [BMIm][BF_4] (50 mM) in acetonitrile. Liquid products formed could not be identified.
Watkins & Bocarsly 2014 [123]	[EMIm][TFA]	Formate	Bulk electrolyses were conducted until 20C of charge had passed. Throughout electrolysis the headspace of the solution (2 mL of [EMIm][TFA] and 1 mL of water) was purged with CO_2. Applied potential varied between -1.55V and -2.15V vs. Ag/AgCl	Working electrode: indium electrode (surface area ≈ 2 cm^2), which was prepared by pressing indium shot (99.9%) into a foil and pressing a copper wire into one side of the foil. Lead and tin electrodes were also investigated. Counter electrode: unfritted zinc foil (99.99%) Reference electrode: Ag/AgCl (3M NaCl)	Degassed 5 mL two-necked flask	Voltammetry results showed that the addition of a water co-solvent lowered the overpotential for the reduction of CO_2 as well as increased the rate of CO_2 reduction. In bulk electrolyses with indium electrode, a maximum FE for formate of around 90% was found at -1.95V.Tin showed very similar behaviour to that of indium; lead required a higher potential for CO_2 reduction although efficiencies rose to 100% with an applied potential of -2.15V. Yields for formate of up to 3 mg h^{-1} cm^{-2} were reported for [EMIm][TFA] with 33% water as cosolvent.
Grills et al. 2014 [124]	[EMIm][TCB]	CO	Controlled potential electrolysis for over 20h at -1.8V vs $Fc^{+/0}$ and 25±3ºC under a CO_2 atmosphere, of [EMIm][TCB] (2 mL) containing 2 mM of *fac*-ReCl(2,2′-bipyridine)-$(CO)_3$ and 50 mM of water	In standard three-electrode cell: ultramicro disc electrode (carbon fiber) or disc electrode (glassy carbon, 3 mm diameter) as a working electrode, a Pt wire as a counter	Standard three-electrode cell for voltammograms. Custom-made air-tight electrochemical cell for bulk electrolysis experiments	First example of IL-enhanced electrocatalytic CO_2 reduction with a homogenous catalyst: *fac*-ReCl(2,2′-bipyridine)-$(CO)_3$. In cyclic voltammograms, [EMIm][TCB] was observed to decrease in 0.45V the potentials required for *fac*-ReCl(2,2′-bipyridine)-$(CO)_3$ to catalyze

				electrode, and a reference electrode of Ag/$AgNO_3$ (0.01 M) in [TBA][PF_6] (0.1 M) MeCN solution. In the custom-made air-tight cell: glassy carbon disc working electrode (3 mm diameter), a platinum coil counter electrode immersed in wet (50 mM H_2O) IL, & the same ref. electrode		the selective reduction of CO_2 to CO compared with CH_3CN as a solvent. In bulk electrolysis experiments, CO was obtained with a selectivity of > 98% and FE of 88± 10%.
Medina-Ramos et al. 2014 [125]	[BMIm][PF_6], [BMIm][BF_4], [BMIm][Cl], [BMIm][Br], or [BMIm][OTf]	CO	Controlled potential electrolysis (CPE) experiments were performed at an applied potential of -2.0V vs SCE for CO_2- saturated solutions of MeCN containing 300 mM IL.	Working electrode: Bi-CO evolving catalyst (Bi-CMEC) electrodeposited (either ex-situ or in-situ) onto a glassy carbon electrode substrate. Counter electrode: platinum gauze (99.9%). Ag/AgCl reference electrode (1.0 M KCl)	Gas-tight two-compartment cell divided by a Nafion 212 membrane	In CPE experiments with Bi-CMEC deposited ex-situ, FEs from 74 to 87% for CO with partial current densities for CO that ranged from 17 to 31 mA cm^{-2} were obtained using the ILs tested, with energy efficiencies above 70%; best results were observed with $[BF_4]^-$, $[PF_6]^-$ and $[OTf]^-$. In CPE experiments with in-situ generated Bi-CMEC (using an organic soluble Bi^{3+} precursor) and [BMIm][OTf], reduced FE (approx. 75%) and partial current densities for CO (approx. 20 mA cm^{-2}) were obtained compared to when the Bi-CMEC was deposited ex-situ. The rate of CO production ranged from 0.1 to 0.5 $mmol \cdot cm^{-2} \cdot h^{-1}$ at an applied overpotential of ~250 mV for a cathode with surface area equal to 1.0 cm^2.
Zhou et al. 2014 [126]	[BMIm][BF_4], [TEA][BF_4], [MOEMIm][BF_4],	CO	Controlled potential electrolysis (CPE) experiments were conducted in pure ILs or their aqueous	Cathode: Ag, Cu, Pt or Au (areas about 1.6 cm^2) Anode: Pt Reference: SCE	Glass cell with proton exchange membrane	Best results were obtained with Ag metal and [BMIm][Cl] with 20wt.% water: >99% selectivity (FE > 99%) in the electroreduction of CO_2 to CO. With

	[TBA][BF_4], [BMIm][Cl], [TBA][Cl], [BMMIm][Cl] or [BMIm][Br]		solution under a slow stream of CO_2 (30 $mL \cdot min^{-1}$) for 10 h under atmospheric pressure at 25ºC, at -1.5V (vs. SCE)			increasing water content in [BMIm][Cl], selectivity for CO decreased significantly, and low proton concentration favored CO formation with higher selectivity. CO_2 reduction on Ag electrode did not occur in aqueous solutions of quaternary ammonium ILs (e.g. [TEA][BF_4] or [TBA][BF_4])
Quezada et al. 2014 [127]	[BMIm][BF_4]	CO	Electrolysis was performed for 4 h at -0.8V vs. Ag/AgCl	Working electroe: optically transparent indium tin oxide, on whose surface a conducting polymer of cobalt 5,10,15,20 tetrakis(4-aminophenyl)porphyrin (Co-TAPP) was grown (area 1.5 cm^2). Counter-electrode: Pt wire (8 cm^2). Ag/AgCl reference electrode.	Undivided glass electrochemical cell	CO was the only reaction product detected by gas chromatography, with a FE of 64.9%. At times longer than 200 min there was a decrease in the CO produced, which was probably related to redisolution of the CO from gas phase to the IL medium.
Asadi et al. 2014 [128]	[EMIm][BF_4]	CO (or tunable mixture of H_2 and CO (syngas))	Aqueous solutions of [EMIm][BF_4] with different water mole fractions were used as electrolytes. In the chrono-amperometry experiments, CO_2 concentration was kept constant with bubbling high-purity CO_2 in solution along with mixing during experiment.	Working electrode: bulk molybdenum disulphide (MoS_2). Conunter-electrode: Pt gauze 52 mesh. Reference electrode: Ag wire	Custom made two-compartment three-electrode cell where the compartments were separated by a physical barrier using a glass frit	MoS_2 showed superior performance than noble metal catalysts (e.g. Ag, Au), with a high current density and low overpotential (54 mV) in the IL. CO_2 is converted at MoS_2 into a tunable mixture of H_2 and CO ranging in each component from 0 to ~ 100% depending on the applied potentials between -0.2 and -0.764V vs. reversible hydrogen electrode (RHE). A CO_2 reduction *j* of 65 mA cm^{-2} with FE to CO of ~98% was obtained at -0.764V vs. RHE, and even a higher j of 130 mA cm^{-2} was observed at this potential using vertically aligned MoS_2. Water mole fraction affected the

						catalytic activity of the MoS_2 catalyst, reaching the maximum j in the 4 mol% [EMIm][BF_4] aqueous solution.
Sun et al. 2014 [129]	[EMIm][NTf_2], or [MMMIm][NTf_2]	CO	Electrolysis at an applied potential of -2.25 V (vs Ag/$AgNO_3$) for up to 3 hr were performed in CO_2 saturated 0.1M [EMIm][NTf_2] in acetonitrile solution. The electrolyte was kept saturated with CO_2. 10 mL and 5 mL of electrolyte solution were used in the cathodic and anodic compartment, respectively.	Working electrode: Pb sheet (99.998%) with geometrical surface area of 2.0 cm^2. Counter-electrode: 25 x 25 mm Pt gauze (99.9%, 52 mesh). Reference electrode: Ag/$AgNO_3$	Two-compartment, three electrode glass cell, divided by a Nafion 117 membrane	[EMIm][NTf_2], when used as the supporting electrolyte in acetonitrile, decreased the reduction overpotential at a Pb electrode by 0.18 V as compared to tetraethylammonium perchlorate as the supporting electrolyte. In electrolysis using 0.1M [EMIm][NTf_2] in acetonitrile, CO and an imidazolium - carboxylate species were the predominant products and the formation of oxalate was suppressed. FE of the CO was ~ 45% and that of the carboxylate was ~50%, with an amount of product formed of ~35 µmol of CO and ~90 µmol of carboxylate. In tests with [MMMIm][NTf_2], for 1 h electrolysis at -2.25 V (vs Ag/$AgNO_3$), an even higher FE of 57.2% for CO was obtained.

Notes:
FE: Faradaic efficiency
j: current density
MeCN: acetonitrile
SCE: Saturated Calomel Electrode

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Ionic liquids in the electrochemical valorisation of CO_2

Manuel Alvarez-Guerra, Jonathan Albo, Enrique Alvarez-Guerra, Angel Irabien

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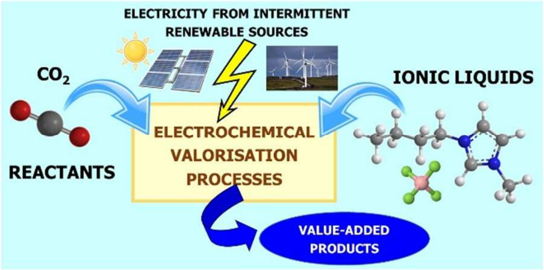
Graphical abstract



Textual abstract

This work reviews the use of ionic liquids in electrochemical approaches for the valorisation of CO_2 into value-added products, highlighting the beneficial role that ionic liquids can play to improve CO_2 electrovalorisation processes.