



Review Article

Use of CO₂ for electrosynthesis

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**Abstract**

A review of the main ideas related to the capture and valorization of CO₂ by using electrochemical processes is presented. The advantages of using an electrode-controlled potential that provides the possibility of reducing CO₂ to non-fossil carbon-based fuels, or of using this atmospheric pollutant in organic synthesis processes that rely on electrocarboxylation steps are outlined. The implications of a reduction in atmospheric CO₂ emissions in the global climate change emergency, while at the same time finding alternative and clean ways of producing valuable fuels and chemicals, are emphasized. Particular attention is paid to the powerful role that ionic liquids can play as ideal solvents and electrolytes in such electrochemical reactions. A general description of the advantages that these liquids have for the solubilization and the support of the electrochemical reduction of CO₂ is presented.

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Introduction

As the increasing concentration of greenhouse gases in the atmosphere is triggering a global climate change, a clear need exists to control the level of atmospheric carbon dioxide, by far the most important anthropogenic pollutant with greenhouse effects. CO₂ accumulated in the atmosphere at an average rate of 1.4 ppmv per year between 1959 and 2006 and roughly 2.0 ppmv per year between 2006 and 2020, with a current (March 2023)

average atmospheric CO₂ concentration of 421 ppmv [1], the highest in the last 800,000 years [2–4].

Atmospheric CO₂ levels can be reduced by replacing the current massive consumption of fossil fuels with the use of alternative sources of energy, but also by capturing and removing the molecule from the atmosphere while, at the same time, finding ways for its chemical valorization [5]. Several means of atmospheric CO₂ removal, such as reforestation, soil carbon sequestration in croplands and grasslands, carbon capture and storage [CCS], enhanced weathering (alkalinity enhancement), ocean fertilization, are currently being proposed and/or tested [6,7], although a clear worldwide use of any of them is not yet underway.

Post-combustion CCS technologies of flue gases in traditional gas or coal-fired power plants or in industrial facilities such as cement kilns, or iron and steel production can be visualized as chain technologies created to: i) separate CO₂ from industrial gas sources, ii) transport it to a storage location and iii) secure long-term isolation from the atmosphere [8–10].

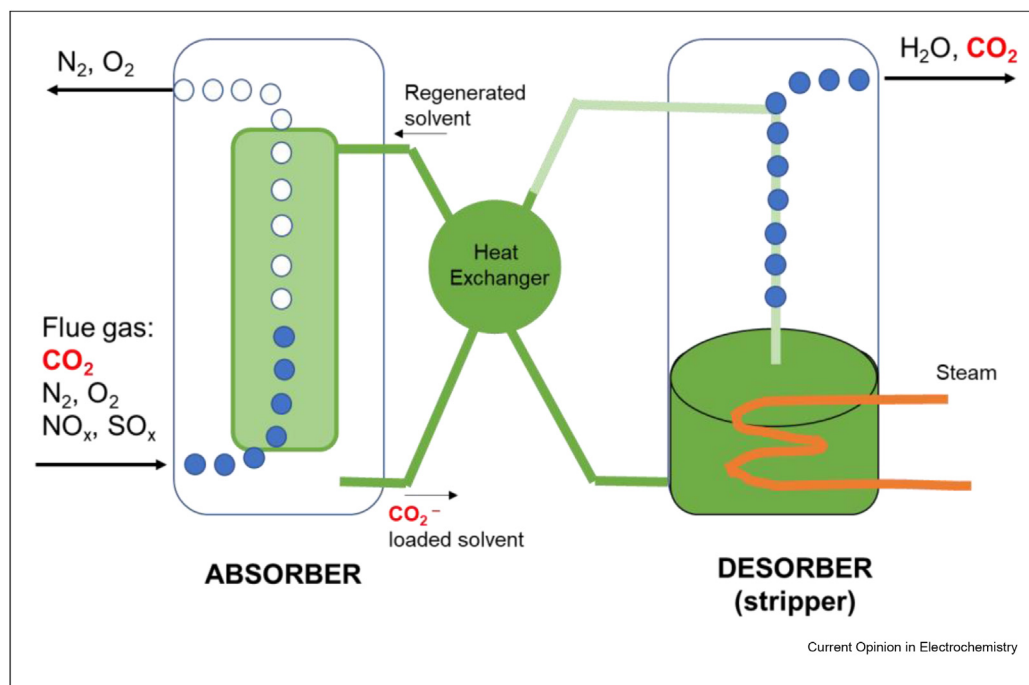
Currently available CO₂ capture strategies

Chemical absorption by aqueous amine-based solvents appears to be the most promising short-term solution for CO₂ capture [11]. Large-scale processes using an aqueous solution of monoethanolamine (MEA) and diethanolamine (DEA) with overall efficiencies above 90% already exist. Once captured, the CO₂ is liberated in higher concentrations by steam stripping. This kind of process is called amine scrubbing [12] (Figure 1).

Unfortunately, implementation of these CO₂ capture systems has been limited due to the costs associated with the high energy consumption during amine regeneration, as well as to solvent degradation, and corrosion [13].

Ionic liquids (ILs) have been proposed as viable alternatives to amines as CO₂ absorbers [14,15]. Indeed, ionic liquids have extremely low volatility and many of them can solubilize large amounts of carbon dioxide. Ramdin et al. [14] have provided a very extensive review of the advantages and problems of using ionic liquids for the purpose of capturing carbon dioxide. They are also electrical conductors, and ideal absorbers/solvents for

Figure 1

CO₂ capture from flue gas by an aqueous amine system.

the electrochemical capture and transformation of CO₂ described in this review [15].

Metal organic frameworks (MOFs) are also a most promising class of adsorbents, especially for gas separation applications. MOFs have extraordinary surface areas, ultra-high porosity, and flexibility to tune their porous structure and their surface functionalities due to the potential modification of their organic ligands. Many MOFs have carbon dioxide capture capabilities ranging from 4 to 26 mmol g⁻¹ [16–18], although they also present several drawbacks like low thermal stabilities, the use of complex and costly ligands, and the difficulties of large-scale production.

Of all the different CO₂ capture approaches, the biologically based one seems to be especially attractive since CO₂ can be converted by photosynthesis into organic matter by using sunlight as a source of energy. In particular, algae can convert CO₂ into organic compounds more efficiently than other terrestrial plants, being a promising source of biofuels or food. This alternative, while valuable, still requires further research and development [19,20].

CO₂ as feedstock for production of fuels and chemicals

CO₂ conversion into fuels is considered the best alternative in CO₂ utilization. Methane, methanol, *syngas*, and alkanes are some of the compounds that can be

produced from CO₂. Hydrogenation of CO₂ offers the possibility of recycling CO₂, storing H₂, producing a liquid fuel, and storing excess green electric energy (e.g., solar, wind, biomass) by transforming it into non-fossil carbon-based fuel sources that help reduce the use of fossil fuels [21–23].

In addition to synthetic fuels, CO₂ can be used as a feedstock to produce a large array of fine chemicals, the most important applications being the production of urea, inorganic carbonates, polyurethane, acrylic acid and acrylates, polycarbonates and alkylene carbonates [24,25].

The present review provides a description of the state of the art of a group of new CO₂ capture processes based on the use of electrochemical reactions that reduce CO₂ to other carbon-containing molecules with potential benefits. The great features of electrochemistry as a method of synthesis of materials, being a clean, powerful and easy-to-control way of carrying out chemical processes, are highlighted, and its potential for a large-scale effective removal of atmospheric CO₂ is emphasized.

Electrochemical valorization of CO₂

Electrochemical reduction of CO₂ in aqueous and non-aqueous conventional electrolytes

Electrochemical reduction or activation of CO₂ can produce a number of valuable products, such as oxalic acid, CO, formic acid, methane, methanol, ethane,

ethylene, ethanol, as well as other hydrocarbons and oxygenates.

The electrochemical reduction of CO₂ usually requires high overpotential ($\eta > 1$), due to the energy requirements of the single electron reduction of CO₂ into the CO₂^{•-} anion radical, which depend on electrolytic media and electrode. With gold electrodes, the value of electrochemical carbon dioxide reduction occurs at -1.9 V (vs standard hydrogen electrode, SHE), determined in 0% of water content electrolyte media [26]. The electrochemical CO₂ reactivity and selectivity obtained is strongly dependent on the type of electrocatalytic material and solvent employed, so highly active and selective electrocatalyst are necessary to reduce the activation energy of the reaction and to enable an energetically efficient process.

In *aqueous environments*, it is reported that the target products of the CO₂ electrochemical reduction processes can be tuning depending on the nature of the electrode, being mainly formate/HCOOH derivatives on Cd, In, Sn and Pb; CO on Au, Ag, Pd, and Zn; and alcohols and more valuable hydrocarbon on Cu cathodes [27–30]. The relationship between the binding energies of key intermediates and the free energy of the catalyst surface determines the main product yielded. The use of fully or partially oxidized metals can also improve selectivity and activity under more favorable conditions, such as low overpotential [27,30]. Finally, the use of electrocatalyst nanostructures affects the CO₂ reduction reaction activity and product selectivity by modifying the morphology, size, shape, and grain boundary [31–33]. In this sense, the design of those nanostructured cathodes can also incorporate different metals for improving its performance [29].

Another drawback in progress of carbon dioxide electroreduction is the low solubility of carbon dioxide in aqueous electrolytes (c.a. 33 mM at normal room temperature and pressure) [34]. There are two types of strategies have been developed to enhance the efficiency of the process; (i) the utilization of gas diffusion electrodes (GDEs), as already used in fuel-cell technology, and (ii) the use of non-aqueous electrolytes.

GDEs are porous electrodes with a catalyst layer in contact with the electrolyte. Due to the high CO₂ mass transport and reduced diffusion lengths within the catalyst layer, GDEs can achieve current densities higher than those of traditional electrodes [35]. Recent developments in GDE technology have increased carbon dioxide reduction efficiencies. Ma *et al.* incorporated multi-walled carbon nanotubes (MWCNT) in the Ag catalyst layer of gas diffusion electrodes and reported a current density up to 350 mA cm⁻², with 95% faradaic efficiencies towards the formation of CO [36].

The second strategy mentioned above would be the use of *non-aqueous solvents* as electrolytes. Organic solvents usually dissolve gases much better than water, and in inert electrodes the CO₂ reduction products are normally oxalate and CO when the solvent is dry, although the presence of water promotes the appearance of formate [37]. The reduction of CO₂ begins with the formation of the carbon dioxide radical anion, which can dimerize leading to a C₂⁺ product, oxalate, avoiding proton-assisted multiple-electron-transfer processes (Figure 2, equation 1) [26,38,39]. Depending on the experimental conditions as well as the cathode material a primary competitive reaction is through a nucleophilic coupling radical anion CO₂^{•-} with CO₂ (ads), leading to CO and CO₃²⁻ (Figure 2, equation 3-4). Hence, in the case of Fe, Cr, Mo, Ni and Ti electrodes substantial amounts of oxalic acid and CO are obtained. For Ni, Pd, Pt, Cu, Ag, Au, Cd and Sn cathodes the main product obtained is CO; whereas C₂ product is yielded for Pb, Tl, and Hg electrocatalytic materials [40].

On the other hand, another approach related to the conversion of CO₂ to high value-added molecules, in aprotic organic solvents, considers its incorporation in larger chemical structures by using electrochemistry. In that respect, electrochemical carboxylation is one of the most useful methods for CO₂ fixation to organic molecules, because it is a mild and easy-to-handle process [41].

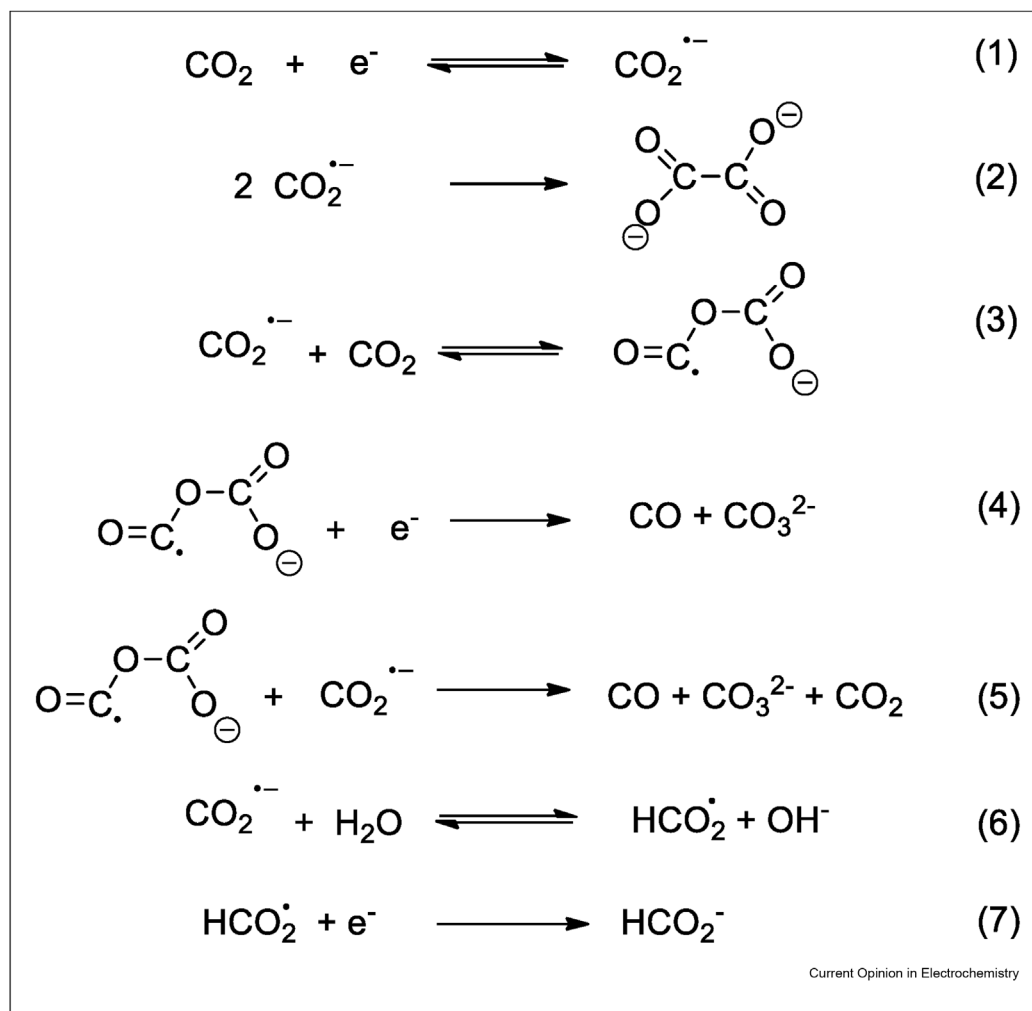
Electrochemical carboxylation of CO₂ in organic aprotic electrolytes

The general mechanism of electrochemical carboxylation involves the reduction of a substrate, and/or CO₂, leading to the formation of the corresponding radical anion, and the reaction between the radical anion and the substrate (or the CO₂) to render the carboxylate anion [41]. Figure 3a shows different types of substrates that feature carbon-carbon double bonds and that can be employed in the synthesis of the corresponding carboxylic acid through an electrocarboxylation process [42].

By using a one-compartment cell equipped with a Pt cathode and an Mg anode in DMF, Senboku *et al.* have successfully accomplished the electrochemical carboxylation of several flavones at the C2-position, producing flavanone-2-carboxylic acids with moderate to good yields [43].

Following the achievements obtained in the electrocarboxylation of styrene derivatives [44], Jiang *et al.* have studied the electrochemical carboxylation of phenylacetylene with CO₂ [45]. An unsaturated aryl-maleic anhydride was the main product under anhydrous conditions, while saturated 2-arylsuccinid acid could also be obtained as a major product in the presence of H₂O.

Figure 2

Proposed mechanism of CO₂ electroreduction in organic electrolytes.

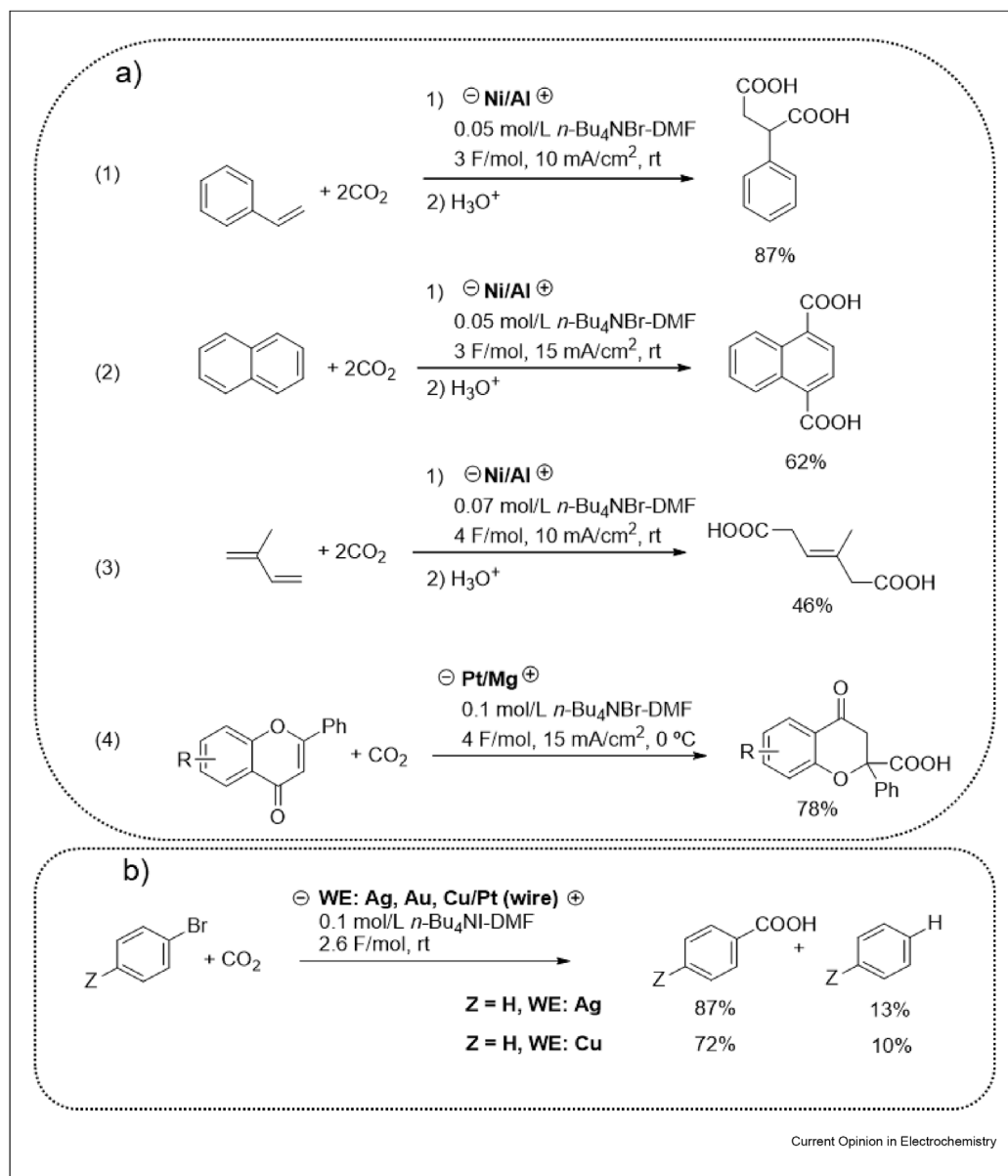
Organic halide electrocarboxylation has also been widely studied, using silver in the electrochemical reduction of arylethyl chlorides [46], or showing that the direct CO₂ reduction at Ag and Cu working electrodes occurs at more negative potentials than the reduction potentials of a series of bromobenzenes (ArBr), allowing the selective reduction of ArBr in CO₂-saturated DMF [47–49]. It was also shown that hydrodebromination yielding ArH is always in competition with the desirable carboxylation reaction (Figure 3b).

For halobenzonitriles, after a four-electron reduction process and two electrocarboxylic processes, it is possible to carry out the friendly synthesis of phthalate derivatives that can potentially be used for making plastic polymers [50]. The use of benzyldisulfide [51] and benzyl phenyl thioethers also allows to reversibly

capture or to tune the CO₂ reactivity [52] after a S–S or C–S electrochemical bond cleavage reaction, respectively. Note that more sophisticated carboxylated products, such as pharmaceutical derivatives [53–56] or molecular switches [57] can be obtained following similar routes. Finally, it is worthy to remark that there are also other kind of molecules which can be used as substrates for electrocarboxylations reactions, such as pseudo-halides, imines, ketones and aldehydes. In this sense, Zhang et al. summarized recent advances in electrochemical carboxylation based on those substrates for the synthesis of fine chemicals [58].

Nevertheless, the volatility and toxicity [59], the low electric conduction of aprotic solvents and the addition of large quantities of supporting electrolytes represent an obstacle for their use as solvents in many electrochemical reactions.

Figure 3



a) Various examples of olefins for the electrocarboxylation process **b)** Electrochemical synthesis of benzoic acid derivatives in DMF using different cathodes through electrocarboxylation processes.

Electrochemistry of CO₂ in ionic liquids: capture and electrocarboxylation processes

In order to avoid the use of volatile and toxic solvents, and simplify separation, electrocarboxylation in CO₂-saturated room-temperature ionic liquids have been developed. Ionic liquids (ILs), as electrically conducting “organic” solvents which have moderate conductivities and high CO₂ absorption capacity, represent a good compromise for that kind of processes.

The modular nature of ILs means that they can be submitted to many structural modifications, making

them an attractive choice of solvent in many important chemical processes [15,60].

Room-temperature ionic liquids (RTILs) have received a lot of attention as potential “green” and “customizable” solvents. RTILs have better properties than aprotic solvents: a) very large liquid range (e.g. BMIM TFSI: –89–450 °C as compared to EtOH: –114 to 78 °C), b) good solvency for a wide range of inorganic, organic and polymeric materials, c) Brønsted, Lewis and Franklin acidity, hydrogen-bonding ability, π–π interactions, etc. d) neglectable vapor pressure, e) water

impurities do not restrict their industrial applications, f) thermally stable up to 200 °C., and g) relatively cheap and easy to prepare. Moreover, RTILs have intrinsic ionic conductivity at room temperature and a wide electrochemical window (electrochemical stability in the range of 4.0–5.7 V [61].

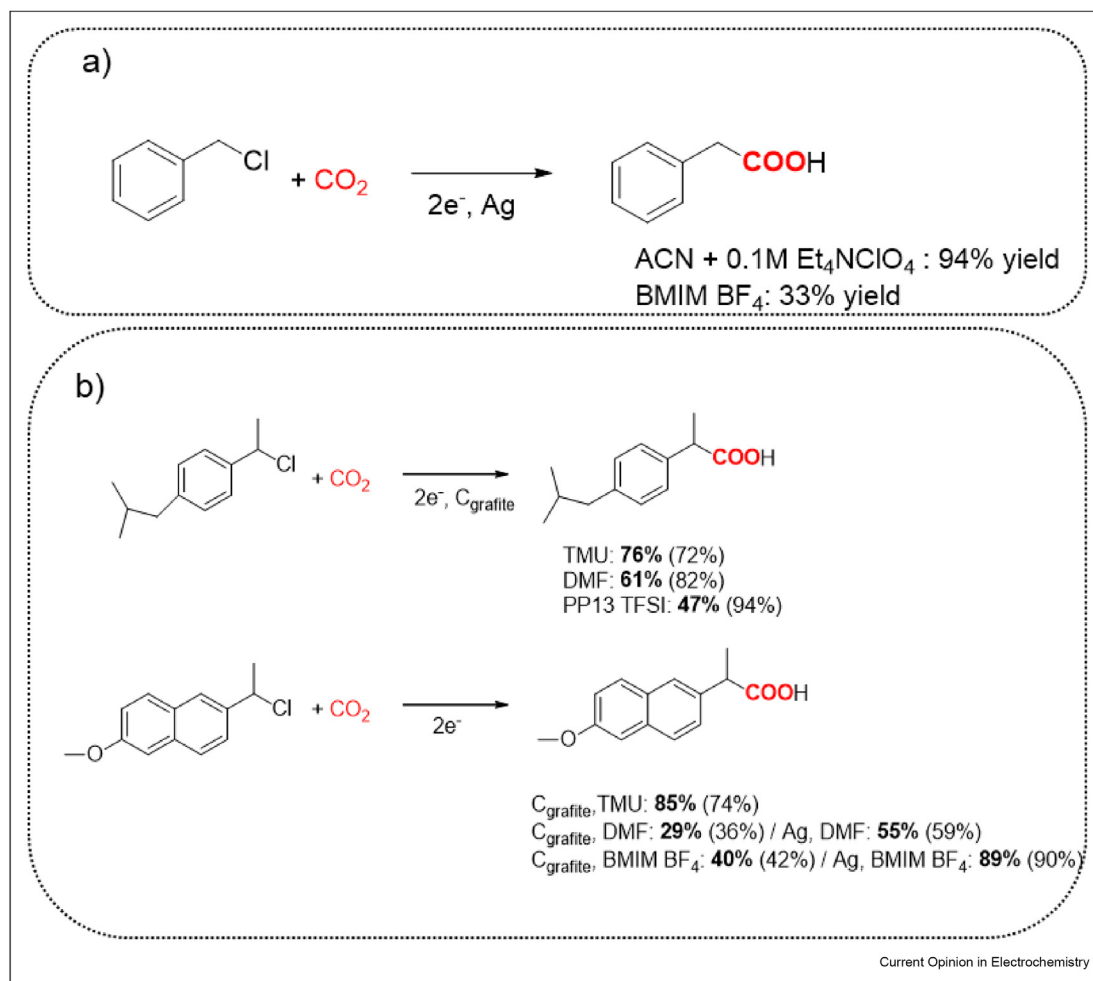
Nevertheless, there are two common drawbacks to ILs: (a) mass transport rates (reported as diffusion coefficients) are smaller by a factor of between 10 and 100 in all IL media (compared to molecular solvents), due to the viscous nature of the media; and (b) the heterogeneous electron-transfer rate constants can be smaller by as much as two orders of magnitude for processes controlled by outer-sphere dynamics [62].

Ionic liquids are appealing solvents (compared to alkanolamines) for carbon dioxide capture in flue-gas from coal-fired power plants because of their low volatility, and potential to be recycled. However, even though

solubility of CO₂ in ionic liquids is relatively high, best absorption capacities at low post-combustion partial pressures are lower than 5 mol%. Therefore, IL-based functional deep eutectic solvents (DESS) and other combinations with functional CO₂-philic groups have been created, to increase the molar absorption capacity of these materials [63,64].

Zhao et al. used an ionic liquid as electrolyte for the electrochemical reduction of high-pressure CO₂, obtaining *syngas* as the electrolysis product [65]. Different reviews of electrochemical transformation of carbon dioxide in ionic liquids within the framework of capture and sequestration are already available [15,66], showing that the trend has been to move from less abundant substances, such as noble metals, to more commonly available metals and materials. Rosen et al. [67], described that some ionic liquids can significantly lower the overpotential of CO₂ reduction, and proposed that some ILs may stabilize the CO₂ anion that is formed

Figure 4



a) Electrocarboxylation reaction of benzyl chloride in acetonitrile and BMIM BF₄ under almost the same experimental conditions b) electrochemical synthesis for ibuprofen and naproxen extracted to references [54,71,72].

in the first step of the electrochemical reaction, through formation of a complex, thus decreasing the activation barrier and the overpotential. Compton *et al.* discovered that the ionic liquid 1-butyl-3-ethylimidazolium acetate showed an abnormally high solubility of carbon dioxide due to the formation of molecular complexes [68], making it clear that in order to facilitate the electrochemical reduction process, carbon dioxide capture should be a physical absorption (as seen for CO₂ mixing in most ionic liquids), rather than chemical absorption, which potentiated the extent of capture at the expense of down-stream transformation and separation.

Isse *et al.* showed that benzyl chloride could be carboxylated, driving its electrochemical reduction in CO₂-saturated acetonitrile with yields c.a 90% using Ag as working electrode [47]. Lu *et al.* showed that it was possible improve that electrocarboxylation, in terms of toxicity and sustainability, by using an RTIL (BMIM BF₄) as solvent-electrolyte media [69], which could be recycled and reused four times (Figure 4a). Senboku *et al.* demonstrated that electrochemical carboxylation of organohalides was successfully achieved with reasonable yields in ionic liquids [70]. Description of sustainable and highly efficient chemical routes for synthesizing useful compounds using CO₂ as a C1 symptom through electrocarboxylation reactions for the synthesis of NSAIDs in ILs has been also recently described. Controlled potential electrolysis of 1-chloro-(4-isobutylphenyl)ethane and 2-(1-chloroethyl)-6-methoxynaphthalene in CO₂-saturated ionic liquids solutions obtains ibuprofen [71] and naproxen [72]. In those latest cases a comparison between the use of organic aprotic solvents containing 0.1 M of supporting electrolyte and ionic liquids as electrolytes can be done [54]. For the electrochemical synthesis of ibuprofen, in both electrolytes moderate yields were obtained using carbon graphite cathodes, although a greater conversion rate was seen for the piperidonium ionic liquid. In the case of the electrochemical obtention of naproxen, the use of ionic liquids allows to improve the yield from c.a. 85% to 90% and conversion rates from 74% to 90% compare to conventional electrolytes, as well as the suitability of the process (Figure 4b) [54].

This methodology offers a “green” way for the synthesis of different carboxylic acids that could potentially displace their petrochemical sources in a future. Finally, it is remarkable that the electrocarboxylation approach is a low-cost alternative for countries where electricity prices are below 4 cents per kWh and for processes with at least 60% of electrochemical conversion efficiencies [73]. Hence, apart from the technical challenges of using electrochemistry for manufacturing marketable products as well as reducing electricity price between 2 and 4 times by using renewable energy sources, this methodology offers a “green” way for the synthesis of different high added value carboxylic derivatives that

could potentially displace the petrochemical processes in a future.

Conclusions

The capture and valorization of CO₂ in protic-, organic- or IL-based electrochemical processes, either by direct CO₂ reduction to valuable fuels and chemicals, or by electrocarboxylation of organic molecules, is a promising field of research that can help to tackle the control and reduction of the increasing levels of atmospheric CO₂ while generating alternative green fuels and chemicals and bringing solutions to the pressing global emergency of climate change. The use of aqueous electrolytes allows to move from the obtention of SYNGAS (CO + H₂) to hydrocarbons by using either noble metals (such as Au, Ag or Pd) or Cu electrodes, respectively. Whereas, the use of organic electrolytes allows to tune from the conversion of CO₂ into oxalate, formate or carbonate derivatives into electrocarboxylated high added-value products. Finally, ionic liquids are considered one of the most advantageous electrolytes for such applications, and although their high cost has been considered a disadvantage, the enormous potential for structural customization due to the huge number of possible combinations between different cations and anions, together with a wide liquid temperature range, high thermal stability, and extremely low volatility, could allow the design of green, low-cost, low-viscosity solvents with high CO₂ absorption capacity that could pave the way for an effective integration of CO₂ capture with CO₂ conversion, while also contributing to a removal of atmospheric CO₂.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Data availability

Data will be made available on request.

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- * of special interest
- ** of outstanding interest

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