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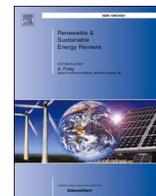
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Electrocatalytic CO₂ conversion to C₂ products: Catalysts design, market perspectives and techno-economic aspects

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ABSTRACT

The energy crisis caused by the incessant growth in global energy demand joint to its associated greenhouse emissions motivates the urgent need to control and mitigate atmospheric CO₂ levels. Leveraging CO₂ as carbon pool to produce value-added products represents a cornerstone of the circular economy. Among the CO₂ utilization strategies, electrochemical reduction of CO₂ conversion to produce fuels and chemicals is booming due to its versatility and end-product flexibility. Herein most of the studies focused on C₁ products although C₂ and C₂₊ compounds are chemically and economically more appealing targets requiring advanced catalytic materials. Still, despite the complex pathways for C₂₊ products formation, their multiple and assorted applications have motivated the search of suitable electrocatalysts. In this review, we gather and analyse in a comprehensive manner the progress made regarding C₂₊ products considering not only the catalyst design and the electrochemistry features but also techno-economic aspects in order to envisage the most profitable scenarios. This state-of-the-art analysis showcases that electrochemical reduction of CO₂ to C₂ products will play a key role in the decarbonisation of the chemical industry paving the way towards a low-carbon future.

1. Introduction

The constant growth in global energy demand has entailed a massive consumption and excessive depletion of fossil fuels, leading to an energy crisis as well as a health crisis due to greenhouse gas emissions, responsible for climate change and global temperature increase. The atmospheric CO₂ level (one of the main greenhouse gases contributors) has also increased, reaching a value of 416.47 ppm (May 2020) [1] and is forecast to reach up to 570 ppm by 2100 [2], while the safety limit is estimated at 350 ppm [3]. As a result, there is an urgent need to control and mitigate these emissions by pursuing low-carbon alternatives including CO₂ capture, sequestration, and utilization [1]. Indeed, research efforts are focused on the use of CO₂ as carbon pool, given its potential to become genuine feedstock to produce value-added products hence turning a problem into a virtue.

Nonetheless, conversion of CO₂ is an arduous task given its high

thermodynamic stability due to the two strong equivalent C=O linear bonds; bonds that possess a much higher bonding energy (750 kJ mol⁻¹) than that of other carbon bonds (C-H, 411 kJ mol⁻¹; C-C, 336 kJ mol⁻¹; C-O, 327 kJ mol⁻¹) [4]. Therefore, a suitable CO₂ transformation route must overcome these energy barriers requiring high energy input, preferably coming from carbon-neutral sources, as well as the use of an active catalyst or high pressures and temperatures [5–7]. Among all the possible techniques to convert CO₂, including thermochemical, electrochemical, photochemical and biological processes [1,7–9], electrochemical reduction of CO₂ has attained a growing interest due to its multiple possible uses in the energy sector and chemical industries, producing value-added fuels and chemicals at mild conditions and in a carbon-neutral way [10–12].

Electrochemical reduction of CO₂ allows tuning the selectivity of the value-added products obtained [13]. Traditionally, research on electrocatalytic reduction of CO₂ has mainly focused on the formation of C₁

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products (such as CO, formate and methanol) since these simple $2e^-$ transfer reactions are kinetically more favourable [14,15]. However, the production of C_{2+} species would be rather interesting from the application perspective [16]. C_{2+} alcohols contain higher energy densities, lower toxicity and corrosiveness compared to methanol, being more suitable as blending or even pure fuels in existing internal combustion engines; and short-chain alkanes can be directly injected into gas-distribution grids enhancing the calorific value of natural gas or biogas. They can also be regarded as entry platform chemicals for current value chains, e.g. light olefins for the production of polymers [9, 17]. Moreover, and taking acetate as an example, its direct production from the electrochemical reduction of CO_2 is a more efficient and effective process in terms of energy and steps compared to the traditional industrial multistep process from fossil fuels, besides more environmentally friendly from a CO_2 emissions point of view [14].

However, C_{2+} products reaction pathways are complex and strongly influenced by the catalyst surface, electrode materials, reaction medium (buffer strength and electrolyte solution), design of electrochemical cell or working conditions such as temperature, pH or pressure and concentration of CO_2 [18,19]. The high C–C coupling activation energy required joint to its bond formation competition with C–H and C–O bond formations limit the efficiency towards C_{2+} products. The later along with the overpotential gap between the essential CO intermediates formation and that of C_{2+} species are the main impediments in the practical application of CO_2 reduction to C_{2+} species in commercial electrolyzers. Indeed, these aspects are regarded as the major bottlenecks accounting for the low energy efficiency of C_{2+} products compared to C_1 counterparts [19,20]. Still the commercial appetite and their extraordinary added value makes necessary to strengthen the research efforts towards direct CO_2 to C_{2+} products.

In order to achieve the practical viability and implementation of this technology, higher efficiency and energy requirements as well as lower operational costs must be met. Electricity plays a key role in the profitability of the CO_2 reduction reaction (CO_2RR), being the main factor in the operational costs [21,22]. Nonetheless, one of the advantages of the electrochemical reduction of CO_2 is that it can be approached as an efficient way to store all excess electrical green energy (generated from unpredictable and intermittent sources such as wind and solar) as transportable chemicals and fuels [23]. Regarding the efficiency requirements, commercial electrolyzers require current densities above 200 mA cm^{-2} as well as long-term durability catalysts [21,24,25]. For these reasons, research on the development of efficient catalysts is encouraged.

Recently, several efforts have been made to obtain suitable electrocatalysts, able to improve catalytic activity and selectivity by controlling their chemical states, size, morphology, surface defects, crystal facets, porosity or by creating heterostructures [6,20,26–28]. Generally, catalysts explored for the electrochemical reduction of CO_2 are based on metals. While formic acid is the main product using Sn, Pb, In, Hg or Bi as catalysts; Zn, Ag, Au and Pd have been found to be selective towards CO [10,23,29]. In the case of C_{2+} products, Cu has demonstrated a unique ability to facilitate C–C coupling, although it is not a selective catalyst since numerous C_1 – C_3 hydrocarbon and oxygenate products have been observed on Cu surface [19,30].

In this scenario and given the research gaps and motivation for this appealing CO_2 conversion route, herein we analyse the recent advances and efforts in the electrochemical CO_2 reduction to C_{2+} products. Beyond summarising the fundamental aspects for the development of a suitable catalyst as well as the mechanistic pathways of the most industrially desired C_{2+} species, this review makes emphasis on key aspects to design highly selective electrocatalysts. Additionally, as a very important aspect not frequently addressed in electrocatalysis literature, we bring techno-economical requirements into discussion targeting potential industrial implementation.

2. Fundamental aspects of electrochemical CO_2 conversion

Electrocatalytic CO_2 reduction is especially appealing due to the wide variety of important products derived from it and their multiple advantages. The process can be carried out in neutral pH, at room temperature and atmospheric pressure and it can be controlled by the reaction temperature and the electrode potential. The chemical consumption can be minimised since electrolytes can be completely recycled and the intermittent renewable energy can be converted into stable chemical energy. Moreover, the system is modular, compact and easy to scale-up [8,9,13,31]. However, despite all the advantages, some drawbacks must be overcome for the technology to fully take off at commercial level. The activation of the very stable CO_2 molecule is the first step in its electrochemical reduction and requires high overpotential. In fact, the formation via single-electron transfer of $CO_2^{\bullet-}$ radical intermediate ($E = -1.9\text{ V vs. SHE}$) is considered as the rate-determining step on most transition metal-based catalysts [3,32]. In general, heterogeneous electrocatalytic reactions take place at the catalyst surface-electrolyte interface [33], so the main CO_2 electroreduction process could be simplified as follows: CO_2 chemisorption and bond forming interaction on the catalyst surface, electron and/or proton transfers leading to C–H, C–O bonds or C–C coupling; and product species rearrangement and desorption from the catalyst surface into the electrolyte [3,20,34]. While formate and CO generation from C–O and C–H has been further studied and can be achieved upon implementing the right electrocatalyst at low overpotential [32], hydrocarbon or alcohol production is a more complex task. A summary of the most accepted activation routes for the electrochemical CO_2 reduction to C_{2+} products is given in Fig. 1 [12,19,20,32].

Due to the multiple reaction pathways that can be conducted in parallel and competitive ways as well as more complex pathways that are not elucidated yet, a wide-ranging product distribution is generally obtained. The reaction pathways and, consequently, product distributions strongly depend on the electrocatalyst. Noble metals (Ag, Au and Pd) have been found as high selective catalysts for C_1 products like CO and formic acid, while activity towards more than $2e^-$ products such as methanol and methane has been obtained with Cu-based catalysts [12]. Besides the choice of a selective electrocatalyst, product distribution can be also adjusted by tuning external parameters such as the electrode characteristics (surface, morphology, facets, ...), operation conditions (applied overpotential, electrolyte, anodic reaction) or the cell design itself.

2.1. Electrolyte

In general, electrolytes should provide stable pH at bulk, good ionic conductivity and moderate to high CO_2 solubility [22]. The type, concentration and composition of electrolytes have been found to affect CO_2 electrochemical reduction. One of the most common and favourable electrolytes is alkaline aqueous solution because it stands lower overpotential than its neutral counterpart [22,35], helps to suppress the hydrogen evolution reaction (Eq. (1)) and provides a high conductivity which reduces ohmic losses [35]. Hydrogen evolution reaction (HER) (equation (1)) is the main competing reaction to CO_2 reduction. Due to the proton insufficiency on the catalyst surface, a basic media helps to suppress this undesired reaction boosting CO_2 electrochemical reduction products [35,36].



In the study of Verma et al. [37] it was observed with different alkaline aqueous solutions higher current densities as increasing the solutions concentrations and through electrochemical impedance spectroscopies demonstrated the decrease of the cell resistance due to the ionic conductivity increase while increased the concentrations. Moreover, as Gabardo et al. reported [35], a 240-mV positive shift of the onset potential was achieved while using a 10 M KOH solution as electrolyte

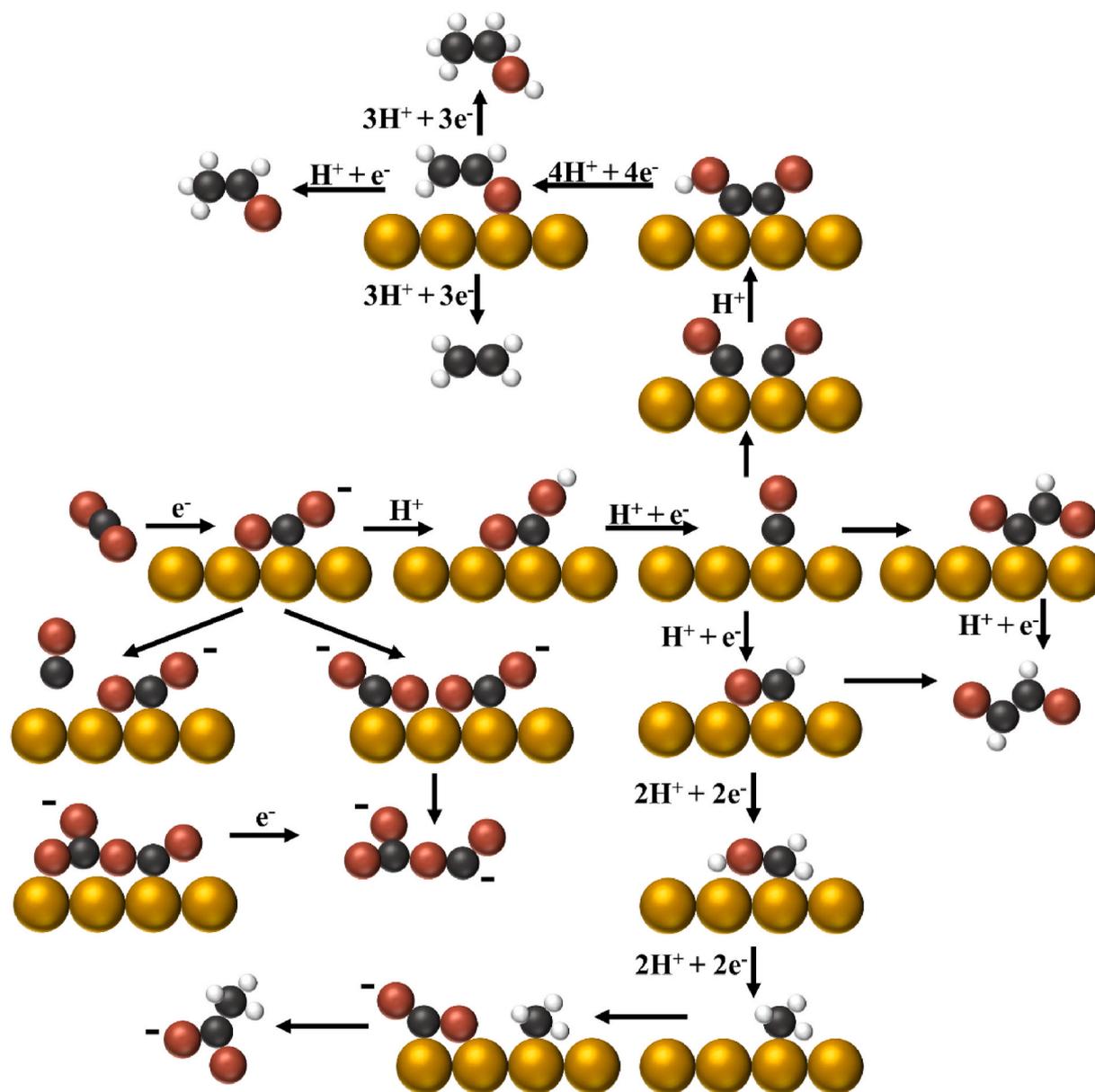


Fig. 1. Electrochemical CO₂ reduction reaction pathways to C₂ products [12,19,20,32].

instead of a 1 M KOH one.

The CO₂ solubility can be increased using organic solvents instead of water solutions as electrolytes. Although CO₂ is a nonpolar molecule, it possesses an appreciable polarizability and an ability to accept hydrogen bonds from suitable donor solvent [38]. Most of the organic electrolytes are polar solvents and allow the electrochemical CO₂ reduction in a wider potential window [20]. The use of an aprotic solvent (such as acetonitrile or dimethylformamide) enables the *CO-CO dimerization while CH₄ production is favoured in a protic solvent. Nonetheless, electrochemical CO₂ reduction can be tuned by adding protic compounds to aprotic solvents in order to facilitate the generation of H-containing products [20]. Some research on the use of ionic liquids (added to aqueous or organic solvents) has been made looking for a higher conductivity and hence, a decrease in overpotential [39–41]. Ionic liquids (ILs) could be proper electrolytes since they have good thermal stability, high CO₂ solubility, wide electrochemical window, low vapor pressure and partially HER inhibition [20,42]. However, ILs also present some drawbacks concerning their high cost, the environmental toxicity embedded in their production, liquid products

extraction struggling [43] or cathodic corrosion [44]. The latest works where ILs has been used as electrolyte are summarised in Table 1. Cathodic catalysts can suffer from deactivation due to the presence of trace impurities (metal ions or organics) coming not only from noble metal anodic catalysts dissolved because of operating conditions [45], but from the electrolyte, being the main deactivation cause in Cu, Ag and Au catalysts [46]. However, deactivation due to impurities can be avoided if a pre-electrolysis with a sacrificial electrode or an irreversible coordination between metal ions and a chelating agent (e.g. ethylenediaminetetraacetic acid) are conducted [46].

2.1.1. pH

As depicted in Fig. 1, the formation of C₂₊ products through different reaction pathways depends on the protonation process. The protonation transfer can affect the product distribution in electrochemical CO₂ reduction, therefore, pH near the catalyst electrode surface, bulk pH, and local pH were found to affect the final product distribution [6].

Due to the consumption of protons near the electrode surface as a result of proton and water reduction, a local pH (usually more alkaline

Table 1Latest works where an ionic liquid has been used as electrolyte for CO₂RR.

IL	Electrolyte	Catalyst	Major product	FE (%)	Potential	Current density (mA·cm ⁻²)	Ref.
[BMIM]BF ₄	[BMIM]BF ₄ :H ₂ O 1:3	Atomically dispersed Sn catalysts on defective CuO	Methanol	88.6	-2.0 V vs. Ag/Ag ⁺	67	[47]
	[BMIM]BF ₄ :CH ₃ CN:H ₂ O 30:65:5 (wt %)	Mn-N ₃ (SAC) embedded in g-C ₃ N ₄	CO	>90	0.62 V (overpotential)	29.7	[48]
	[BMIM]BF ₄ :CH ₃ CN:H ₂ O 30:65:5 (wt %)	I treated porous N-doped carbon	CO	~100	-2.2 V vs. Ag/Ag ⁺	38.2	[49]
	0.1 M [BMIM]BF ₄ /PC	Ag	CO	98.5	-1.9 V vs. Fc/Fc ⁺	8.2	[50]
	[BMIM]BF ₄ aqueous solution	Pd-Cu bimetallic aerogel	Methanol	80	-2.1 V vs. Ag/Ag ⁺	31.8	[51]
[BMIM]Otf	100 mM TBAPF ₆ and 100 mM [BMIM]Otf in CH ₃ CN	Bi-based CO	CO	90	-2.05 V vs. SCE	20	[52]
[BMIM]PF ₆	[BMIM]PF ₆ :CH ₃ CN:H ₂ O 30:65:5 (wt %)	Porous ZnO nanosheets with OH group	CO	97.8	-2.0 V vs. Ag/Ag ⁺	44.3	[53]
	0.5 M [BMIM]PF ₆ in CH ₃ CN	Atomic In anchored on N-doped carbon	CO	97.2	-2.1 V vs. Ag/Ag ⁺	39.4	[54]
	0.1 M [BMIM]PF ₆ and 0.1 M TEAPF ₆ in CH ₃ CN	CoPc-DrGO	CO	93.1	-2.6 V vs. Ag/Ag ⁺	122	[55]
[Bu ₄ N]BF ₄	0.1 M [Bu ₄ N]BF ₄ /PC	Ag	CO	85	-1.9 V vs. Fc/Fc ⁺	2.7	[50]
[BZMIM]BF ₄	[BZMIM]BF ₄ : CH ₃ CN:H ₂ O 14.7:73.6:11.7 (wt%)	PbO ₂	Formic acid	95.5	-2.3 V vs. Ag/Ag ⁺	40.8	[56]
[EMIM]BF ₄	[EMIM]BF ₄ :NaHCO ₃ 90:10 (%v/v)	Nanoporous Au films	CO	96.6	-0.55 V vs. RHE	4.5	[57]
	[EMIM]BF ₄ :H ₂ O 92:8 (%v/v)	3D Ag nanoflower coated Al foam	CO	75	-1.8 V vs. Pt	36.6	[58]
[EMIM][OTf]	[EMIM][OTf]:CH ₃ CN:H ₂ O 81:14:5 (wt%)	PbSn alloy sheets	Formate	91	-1.95 V vs. Ag/AgCl	7.7	[59]
TBAPF ₆	100 mM TBAPF ₆ and 100 mM [BMIM]Otf in CH ₃ CN	Bi-based CO	CO	90	-2.05 V vs. SCE	20	[52]
TEAPF ₆	0.1 M [BMIM]PF ₆ and 0.1 M TEAPF ₆ in CH ₃ CN	CoPc-DrGO	CO	93.1	-2.6 V vs. Ag/Ag ⁺	122	[55]
[TEA][4-MF-PhO]	0.9 M [TEA][4-MF-PhO] in CH ₃ CN	Pb	Oxalic acid	86	-2.6 V vs. Ag/Ag ⁺	9.03	[60]

than bulk pH) can be generated [32]. This difference in pH is caused by mass transport limitations [61] and depends on the operation conditions: current density, bulk pH, types of cations or anions, and on the electrode morphology [6,32,61]. Providing the adequate electrolyte with the right pH is a key factor to control the reaction pathway and the stability of the reaction intermediates [19,62]. As an example, it has been reported that selectivity towards ethylene on Cu electrocatalysts can be fine-tuned by modifying the buffering capacity. At high local pH, ethylene production through *CO-CO dimerization pathway is both kinetically and thermodynamically favourable, whereas the C₁ pathway is suppressed [63,64].

2.1.2. Ions effect

In accordance with pH effect, H⁺ and OH⁻ concentration has been shown to influence both, the activity and selectivity of the electrochemical CO₂ reduction. Comparing several electrolytes containing potassium precursors (KCl, K₂SO₄, KClO₄), phosphate buffer and KHCO₃ aqueous solution diluted and concentrated, it was found that diluted KHCO₃ KCl, K₂SO₄, KClO₄ solutions favoured the formation of C₂H₄ and alcohols [65,66]. The presence of OH⁻ anions produced from electrochemical reactions provokes a pH increase in the electrocatalyst surface enhancing C₂ selectivity by suppressing HER [63,67]. Concentrated electrolytes (concentrated KHCO₃ and phosphate buffer) are capable of neutralising this OH⁻ anions. The local pH does not differ from the bulk pH and CH₄ formation is favoured [65].

Besides H⁺ and OH⁻ ions, the electrolyte cations and anions nature was also reported to have a significant effect on product selectivity. Increasing size of alkali cation from Li⁺ to Cs⁺ usually leads to higher electrochemical CO₂ reduction rates and higher C₂/C₁ products. This behaviour was attributed to differences in the local pH and changes in the electrochemical potential in the outer Helmholtz plane (OHP) due to the cation size [68]. The presence of hydrated alkali metal cations located at the edge of the Helmholtz plane stabilises the adsorption of surface intermediates such as *CO₂, which is the intermediate precursor to the formation of C₂ products through C-C coupling. Slighter cations are strongly hydrated, hindering cation-specific adsorption on the

electrode surface [12]. Larger cations are more energetically favoured at the OHP than smaller ones, hence an increase in cation size typically leads to a large cations coverage [68].

The influence of halide anions on electrochemical CO₂ reduction has also been studied. The halide adsorption on the catalyst surface affects to the activity, selectivity, and the electronic structure, depending on the halide size and its concentration [69,70]. It has been reported that adsorbed halide anions could limit the proton adsorption, inhibiting HER [71]. While using Cu as electrocatalyst, halides are able to stabilize the *CO intermediate through the formation of a covalent Cu-halide interaction [69]. Due to this increase in *CO population on the catalyst surface, adding Cl⁻, Br⁻ and I⁻ to the electrolyte can lead to an increase in CO selectivity and hence a large methane production [69], or a lower overpotential and an increase in CO₂ reduction rate while keeping C₂-C₃ faradaic efficiencies [70]. Among the mentioned halides, KI electrolyte led to the highest *CO formation on the catalyst surface and then, the highest C₂ selectivity [72].

2.2. Pressure and temperature effects

Working at higher pressures encompasses the possibility of operating at higher temperatures and an increase in the CO₂ solubility according to Henry's law [73]. This increase favours the adsorption of CO₂ species on the catalyst surface due to the higher CO₂ concentration in the electrolyte [22], and some works have reported higher current densities by increasing CO₂ partial pressure [73,74]. Therefore, changing the CO₂ partial pressure can tune the relative surface coverage and hence, the stability of CO₂ reduction intermediates and the product selectivity [35]. The combination of both, an increase in the reaction pressure and a highly alkaline environment could improve CO selectivity and energy efficiency reaching industry relevant current density values [35]. Nevertheless, working at high pressures imposes some drawbacks since an unbalanced pressure could result in drying the catalyst surface or flooding of the catholyte causing operational issues [22].

Regarding the temperature effect, it has rarely been studied and most studies were conducted at ambient temperature. An increase of

temperature implies a lower CO₂ solubility, so the undesired HER will prevail over the CO₂ reduction process. Moreover, the temperature increase is also limited by the possible membrane degradation, the operational window is rather narrow, although it could be widened if coupled with a pressurised system [22]. In general, higher temperatures lead to higher currents since ionic conductivity increases and the diffusion coefficient also rises, thus the CO₂ transport is more efficient [75]. The CO₂ solubility problem could be overcome while supplying CO₂ and water vapor in a gas phase electrolyser provided with a proper gas diffusion electrode (GDE). That way, the reaction kinetics would be enhanced due to the higher temperature and would compensate the poor solubility [22,75]. Nonetheless, further studies of temperature effects should be conducted in order to achieve the optimal operation conditions and assess its economic viability.

The effects of pressure and temperature strongly depend on the cell design, i.e., their permissible and adequate values are certainly disparate if a gas phase system or a liquid phase system is used, and additional studies are needed. However, and considering the limited available studies, it could be stated that slightly higher than ambient conditions of pressure and temperature would be favourable in terms of product selectivity and reaction rate [22].

2.3. Overpotential

The energy barrier between the onset potential and the standard reduction potential, the overpotential, is highly dependent on the working electrode. The different ranges of the applied overpotential can affect the preferable pathways to form C–C coupling. The *CO–COH coupling is dominant at high overpotentials, while the *CO–CO dimerization is favoured at low overpotentials [6,19].

2.4. Anodic reaction

Up-to-date, CO₂ cathodic reaction has usually been coupled with anodic water oxidation since water electrolysis is a well-known process without mass transport limitations, and all accomplishments and knowledge achieved in water electrolyzers can be adapted to CO₂ electrolyzers [76]. However, oxygen evolution reaction (OER) requires a high overpotential that limits the energy efficiency of the whole electrolyser (OER can consume up to 90% electricity in CO₂RR [77]) and

oxygen gas could corrode and oxidise metallic catalysts or cell components [22]. Replacing this reaction for another with lower cell voltage requirements and providing high-value anodic products while maintaining a free of emissions process could be of interest. The work of Vass et al. [76] reviews and summarises different interesting alternatives to the widely used OER, including the CO₂RR coupled with an already existing technology, the use of industrial waste as sacrificial agents or the production of raw and fine chemicals [78–80]. In the case of Li et al. [77], possible anodic oxidation reactions have been summarised and classified attending to the desired cathodic and/or anodic products. Some of the valued-added anode processes that have been lately paired up with CO₂RR are summarised in Table 2. Moreover, first techno-economic analysis have shown promising results concerning CO₂RR coupled with organic compounds oxidation [81], achieving an electricity consumption save up to 53% in the case of the glycerol oxidation [78]. Notwithstanding, the complexity of coupling CO₂ cathodic reaction with these anodic reactions in terms of operation conditions, cell design and structure, product separation is still a challenge that requires further research (see Table 3).

2.5. Cell design

Significant efforts and improvements have been made on developing a suitable electrocatalytic reaction system that enhances the electrochemical CO₂ reduction reaction [13,22,25]. As represented in Fig. 2, electrochemical reaction systems can be categorised into H-cell systems, flow cell systems and microfluidic reactors.

H-type cells are widely used because of their simple assembly, operation and products separation, their versatile configurations and low cost. In this system, working and reference electrodes are fixed in the cathodic reaction chamber while counter reaction is fixed in the anodic one. Both chambers are prefilled with the electrolyte and work without recycling. Their main disadvantage is the low CO₂ solubility in the liquid electrolyte, which limits the current density [98], as well as the large distance between electrodes [99]. Moreover, selectivity towards C₂₊ products has always been diminished in favour of HER [13]. For all mentioned above, H-type cells are a suitable batch reactor for studying and comparing different electrocatalysts and products in lab-scale, although they do not fit in further industrial applications.

The main component of the flow cell systems is the membrane-

Table 2
Latest value-added anodic processes paired up with CO₂RR.

Anodic reaction	Equation	Electrolyte	Anodic catalyst	Anodic main product	Ref.
Methanol oxidation	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	0.5 M KOH	Pd/MnFe ₂ O ₄ NSs	CO ₂	[82]
	$CH_3OH + 4OH^- \rightarrow HCOOH + 3H_2O + 4e^-$	1 M KOH	Ni-MOF NSs	HCOOH	[83]
		1 M KOH	Ni(OH) ₂ /Ni foam	HCOOH	[84]
		1 M KOH	CuONS/CF	HCOOH	[85]
		1 M KOH	NiCo-MOF	HCOOH	[86]
Ethanol oxidation	$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$	0.5 M NaHCO ₃	Pt mesh – TEMPO	Acetic acid	[87]
	$CH_3CH_2OH + OH^- \rightarrow CH_3COO^- + 2H_2$	4 M KOH	Nanostructured Pd@Ti	Acetate	[88]
Isopropanol oxidation	$C_3H_8O \rightarrow C_3H_6O + 2H^+ + 2e^-$	0.5 M NaHCO ₃	Pt mesh – TEMPO	Acetone	[87]
1,2-propanediol oxidation	$C_3H_8O_2 + H_2O \rightarrow C_3H_6O_3 + 4H^+ + 4e^-$	0.5 M KHCO ₃ /0.5 M K ₂ CO ₃	ACT-TEMPO	Lactic acid	[89]
Glycerol oxidation	$C_3H_8O_3 + 2OH^- \rightarrow C_3H_6O_3 + 2H_2O + 2e^-$	0.5 M HCO ₃ ⁻ /CO ₃ ²⁻	STEMPO	Glyceraldehyde	[90]
	$C_3H_8O_3 + 8OH^- \rightarrow 3HCOOH + 5H_2O + 8e^-$	2 M KOH	CoSe ₂ /CC	Formic acid	[91]
Benzyl alcohol oxidation	$PhCH_2OH \rightarrow PhCHO + 2H^+ + 2e^-$	0.5 M acetate/0.5 M Na ₂ SO ₄	Nano-ITO	Benzaldehyde	[92]
1-phenylethanol oxidation	$C_8H_{10}O \rightarrow C_8H_8O + 2H^+ + 2e^-$	0.5 M NaHCO ₃	Pt mesh – TEMPO	Acetophenone	[87]
4-methoxybenzyl alcohol oxidation	$C_8H_{10}O_2 \rightarrow C_8H_8O_2 + 2H^+ + 2e^-$	0.5 M NaHCO ₃	Pt mesh – TEMPO	4-methoxybenzaldehyde	[87]
Ammonia oxidation	$2NH_3 \rightarrow N_2 + 6H^+ + 6e^-$	5 M KOH	Pt	N ₂	[80]
Urea oxidation	$(NH_2)_2CO + H_2O \rightarrow CO_2 + N_2 + 6H^+ + 6e^-$	5 M KOH	Ni	N ₂ , CO ₂	[80]
HMF oxidation	$HMF + 4OH^- \rightarrow FFCA + 4H_2O + 4e^-$	0.5 M KHCO ₃	NiO NPs	FFCA, FDCA	[93]
	$HMF + 6OH^- \rightarrow FDCA + 6H_2O + 6e^-$				
NaCl oxidation	$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^-$	0.5 M NaCl	RuO ₂ /Ti	ClO ⁻	[94]
SO ₃ ²⁻ oxidation	$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^-$	0.3 M Na ₂ SO ₄	IrO ₂ -Ta ₂ O ₅ /Ti	SO ₄ ²⁻	[95]
Chlor-alkali reaction	$2Cl^- \rightarrow Cl_2 + 2e^-$	1 M HCl	Ru-based DSA	Cl ₂	[96]
		KCl saturated	DSA	Cl ₂	[79]
Organic pollutants removal	<i>p</i> -nitrophenol oxidation	0.5 M KCl	Ti/SnO ₂ -Sb	–	[97]

Table 3
Most important characteristics and findings of the techno-economic analysis available in the literature.

Ref.	Aim of the study	C ₂ product targeted	Economic parameter evaluated	Main findings
[244]	Identifying potential CO ₂ reduction profitable products	Ethylene Ethanol	Price to reach profitable scenarios	Key performance targets are Faradaic Efficiency (90%), Cell Voltage (<1.8 V), Current Density (>300 mA cm ⁻²), and Stability (>80 000 h).
[24]	Evaluate the techno-economic feasibility of producing different C ₁ –C ₂ chemicals	Ethylene Ethanol	Gross margin (difference between revenues and costs divided revenues)	Carbon monoxide and formic acid are the most economically viable products. Ethanol and ethylene could reach profitability if co-produced with the two previously mentioned.
[243]	Economic evaluation of 100 ton/day plant for various CO ₂ reduced products	Propanol Ethanol Ethylene	Net present value	To reach profitability, improvement in performances is needed: 300 mA cm ⁻² and 0.5 V overpotential at 70% Faradaic efficiency.
[251]	Reduce CO ₂ losses to crossover and carbonate formation, trough analysing the costs of different alternatives	Ethylene	Cost analysis	Current lab scale scenario: 5800–7800 \$/ton Optimistic scenario: 1200–3800 \$/ton
[119]	Review different alternatives for CO ₂ utilization, giving some estimations for electrocatalytic CO ₂ reduced products.	Propanol Ethanol Ethylene	Levelized cost per ton of product from CO ₂ reduction	Assuming very optimistic scenario (electrolyser cost of \$500/kW, energy conversion efficiency of 60%, Faradaic efficiency of 90%, electricity cost of 2 ¢/kWh, and CO ₂ cost of 30\$/ton), ethylene, propanol and ethanol can be competitive with current prices.

electrode assembly (MEA), where the electrodes are assembled to the solid polymer electrolyte or membrane, which acts a separation barrier of the chambers and is in charge of ion transportation between them. Depending on the type of ion transported, membranes can be cation exchange membrane (CEM), i.e., protons are transported from the anolyte to the cathodic chamber; anion exchange membrane (AEM), where hydroxide ions are transported from the anode to the cathode or the combination of both, bipolar membrane (BPM).

According to the way of feeding the CO₂ into the cell, two cell systems can be distinguished: gas phase and liquid phase electrolyser. In the former type, a humidified gaseous CO₂ stream can be directly used as feedstock at cathode, enhancing this way mass diffusion and production rates [13]. The use of this cell design has also been reported to increase

CO selectivity [100], to improve partial current density and stability for formate production [101], and to selectively generate C₂₊ products [14, 102].

In the liquid phase electrolyser, liquid electrolyte is in both electrodes. For that reason, the system can be pressurised and CO₂ can be fed without further humidification [35]. In general, these flow cells have shown a better electrochemical CO₂ reduction performance compared with H-type cells, mainly due to the enhanced CO₂ diffusion and the local gas-electrolyte-catalyst interface [13].

Microfluidic cells are an attractive alternative electrolyser configuration where, in some cases, the membrane is replaced by a thin gap between the electrodes filled with flowing electrolyte stream. The CO₂ molecules are easily diffused into the electrode-electrolyte interface. Besides avoiding issues related to membrane degradation and cost, its absence allows wider pH and reaction temperature windows [103]. However, the existence of crossover could result in the products oxidation at some extent, although a multichannel design, a nanoporous separator [104] or a dual-electrolyte system [105] could solve this problem.

2.6. Electrode surface and morphology

The electrode surface and morphology has been reported to strongly affect in the activity and selectivity on the electrochemical CO₂ reduction. Formation of defect sites, nano or complex structures, subsurface oxygen or crystal facets (schemed in Fig. 3) are the dependant factors [13,32].

2.6.1. Defect sites

The formation of defect sites from vacancies or grain boundaries has been pointed out as the responsible of increasing activity and selectivity in electrochemical CO₂ reduction [106,107]. Grain boundaries can alter the surface properties of particles, generating active sites and inducing a large surface catalytic area [26]. These modifications of the particles and the catalyst surface can lead to a lower energy barrier for CO₂ reduction or to an enhancement of CO adsorption and the C–C bond formation with a consequent stabilization of C₂ intermediates and higher selectivity for this C₂₊ products [107,108].

2.6.2. Structure

Several efforts have been made to create nanostructured catalysts more active and selective than bulk or foil electrocatalysts. It was found that roughened Cu electrodes could provide a high local pH, which promotes C₂H₄ generation over CH₄ [109,110]. Catalyst structure is capable of controlling C₂₊ products selectivity by tuning the pore size and depth of nanostructures such as nanowire arrays, nanofoams, nanoparticles or nanocubes [111–113]. Smaller and deeper pores increase ion concentration and intermediates residence times, enhancing C₂₊ products selectivity. Moreover, intermediates can be confined into the nanostructure generating long chain molecules [26,114].

2.6.3. Facets

Besides physical factors, the intrinsic catalyst properties could also affect the activity and selectivity [19] and several studies have proved the strong facet dependence on electrochemical CO₂ reduction product selectivity [6,19]. As an example, it has been observed in Cu catalysts that Cu(100) favours selectivity towards ethylene and the C–C coupling improving C₂₊ products selectivity while Cu(111) favours the methane and formate formation [67,115,116].

2.6.4. Oxidation states

The electrocatalyst performance could also be adjusted by tuning the oxidation states via oxide-derived materials. Using again the copper catalysts as an example, it was observed that Cu oxidation states can easily change during electrochemical reaction conditions and oxide-derived catalysts enhance the activity and selectivity towards C₂₊

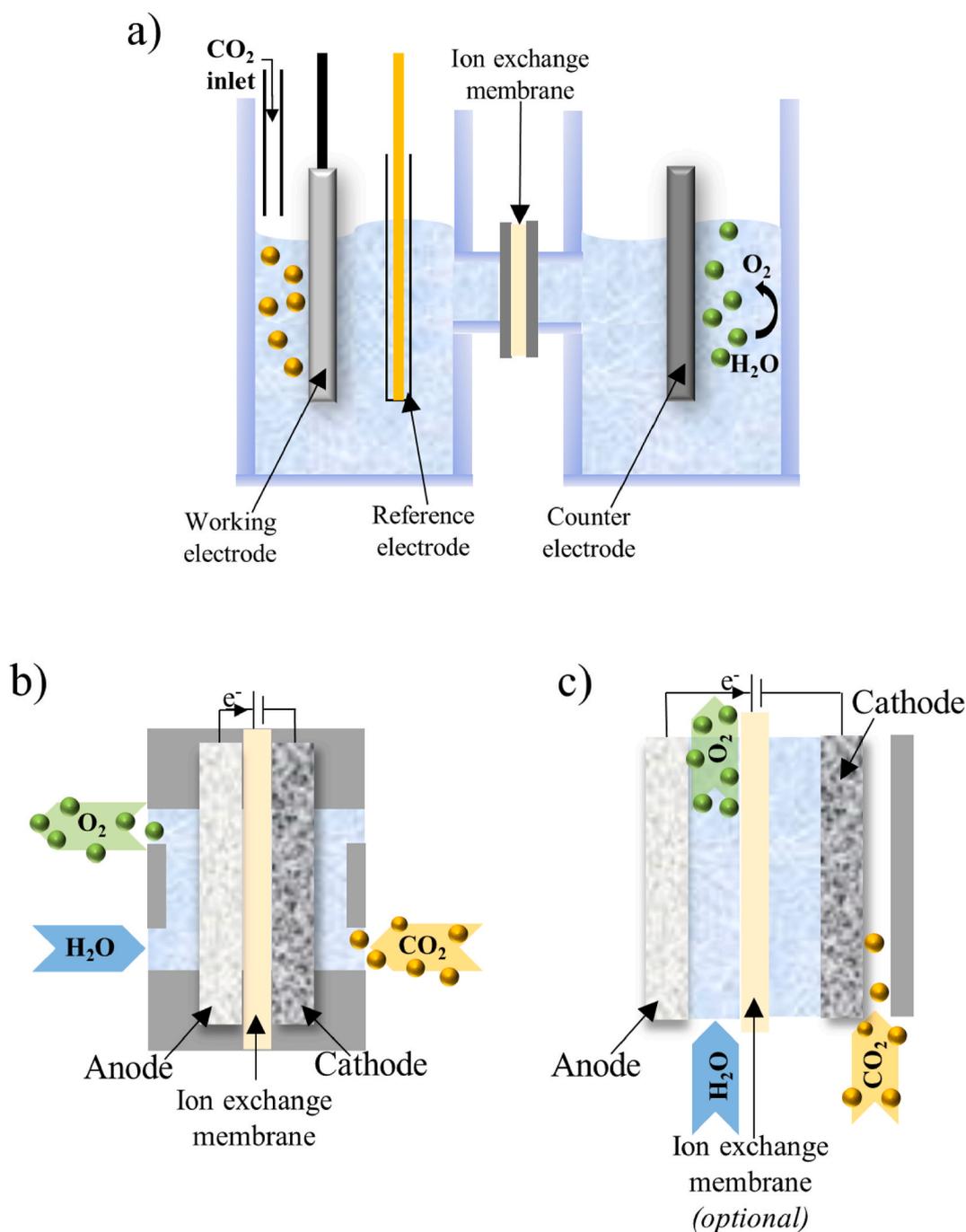


Fig. 2. Electrochemical reaction systems: a) H-cell, b) flow cell, c) microfluidic cell.

products [6,19]. The presence of residual oxygen, subsurface oxygen or oxidized copper states favours the stabilization of the intermediates thus enhancing C–C coupling [117,118].

3. Product distribution based on electrocatalyst design

As mentioned before, due to the multiple possible reaction pathways, numerous products can be originated. However, product distribution can be tuned by designing an active and selective electrocatalyst. The complex formation of C₂₊ products is gaining attention due to their higher energy density and economic value [119], and several research projects are currently focused on their production [120–122]. The numerous and assorted applications, where these products can be valuable, are summarised in Fig. 4. The search of a catalyst with

adequate electronic properties to be selective for the C–C coupling is vital to generate species with one or more C–C bonds. Among metals, copper has been found particularly active for the formation of C₂₊ compounds, although a few non copper-based catalysts such as heteroatom-doped carbon materials [123], NiP [124], NiGa [125] or PdAu [126] have shown significant formation of C₂₊ species. In the following subsections we will discuss the catalysts design to successfully facilitate the production of key C₂ and C₂₊ products which are highly appealing for the chemical industry and whose electrochemical production might result in a game-changing approach.

3.1. CO₂ to oxalate/acetate

3.1.1. Oxalate. Oxalate or oxalic acid is the simplest dicarboxylic

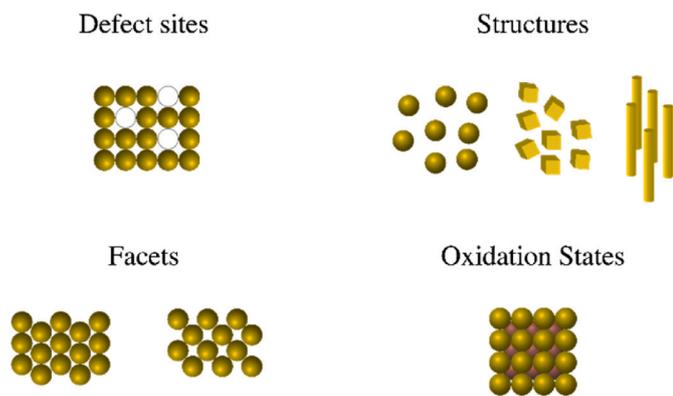


Fig. 3. Electrode surface and morphology factors that affect to the electrochemical performance.

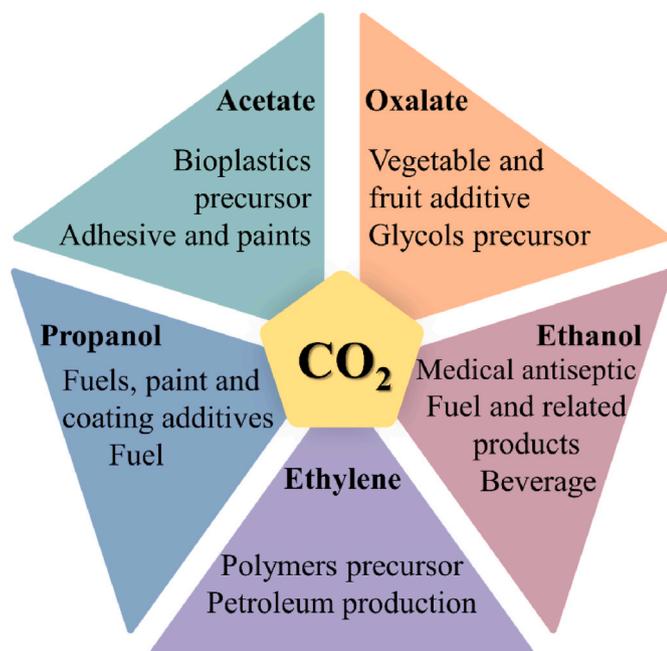


Fig. 4. Main applications of C_{2+} products.

acid widely used in the chemical industry in applications such as pharmaceuticals and textiles manufacturing, rare earth extraction, oil refining or metal processing [127–130]. Oxalate is a precursor to glycols, which are in turn precursors to valuable synthetic materials [131, 132]. Some research has been done concerning the beneficial effect of its application to improve quality of some vegetable and fruits and to extend their storage time and prevent its early degradation [133–135] and its role in the recovery of valuable metal ions from lithium-ion batteries [136,137]. Regarding current investigations, oxalic acid effect is being subject of study in a treatment to a honeybee's disease [138].

The electrochemical CO_2 reduction products strongly depend on both the chemical nature of the electrode and the reaction medium. In a protic solvent as water, formate would be the main product [139,140]. Since the solubility of CO_2 in aqueous solutions is really low (about 30 mM), water molecules would be available nearby the electrode surface and HER would be favoured. In fact, only hydrogen is yielded while water is the only component of the electrolyte, the charge transfer proceeds favourable to water [141]. Using aprotic solutions that provide a higher solubility (about 240 mM in acetonitrile as an example [141]) as solvents would lead to CO_2^{*-} intermediate disproportionation to

carbon monoxide and carbonate or dimerization to oxalate ions [139]. Besides their higher CO_2 solubility, aprotic nonaqueous solvents such as acetonitrile, dimethyl formamide, dimethyl sulfoxide or propylene carbonate have been widely used because of their large cathodic window and the inhibition of HER [130,142].

In this aprotic medium, CO and carbonate were reported as the major products using metals such as Pt, Pd, In, Zn, Sn or Au as catalysts, while oxalic has been reported as the major product using a Pb, Sn or Hg electrode [143,144].

It is known that the first and primary step on the electrochemical CO_2 reduction is the formation of the intermediate radical ion CO_2^{*-} , a charge and mass-transfer controlled reaction that must be conducted at a sufficiently cathodically polarized electrode. In a nonaqueous aprotic medium, two main competitive pathways have been repeatedly described in literature: nucleophilic coupling of CO_2^{*-} with nearby CO_2 , that could produce CO and carbonate, or oxalate through ECE mechanism; and the purely dimerization of two radical ions following an EC mechanism, which would also lead to an oxalate anion production [131, 140,141,143,145–147]. Dimerization reaction is more favourable at high concentrations of CO_2^{*-} radical anions while the reductive disproportionation of CO_2 could be conducted at low CO_2^{*-} concentrations [148]. The reaction mechanism for oxalate production is depicted in Fig. 5.

Lead has traditionally been chosen as the working cathode due to its high HER overpotential and its low cost, which favours CO_2 reduction [143,144,147,149]. In nonaqueous medium, oxalate has been reported as the main product and oxalate faradaic efficiencies (FEs) exceeding 80% were registered from the very early studies [143,144]. The work of Eneau-Innocent et al. studied the role of Pb electrode in a propylene carbonate electrolyte [142]. Propylene carbonate large electrochemical window, CO_2 solubility and relative low toxicity made this aprotic solvent suitable for the electrochemical reduction. It was found that Pb electrodes are very selective towards oxalate via direct dimerization route. In situ IR spectroscopy measurements revealed that unstable intermediate CO_2^{*-} radical ions evolve quickly to adsorbed $Pb-CO_2^{*-}$, which dimerizes, and oxalate is finally desorbed.

Some studies have also explored Pb or stainless steel electrodes coupled with sacrificial anodic electrodes in order to easily remove oxalate product from the electrochemical system [130,147,148]. Zinc has been widely used as a sacrificial anode because it produces zinc cation which fast reacts with oxalate anion towards insoluble zinc oxalate, preventing the further reduction or oxidation reaction of oxalate anion [147]. Lv et al. achieved a 96.8% FE for producing oxalate in 0.1 M tetrabutylammonium perchlorate in acetonitrile with a lead cathode and a zinc sacrificial anode [147]. Such a high efficiency was a result of a combination of two factors: water total elimination and low temperature

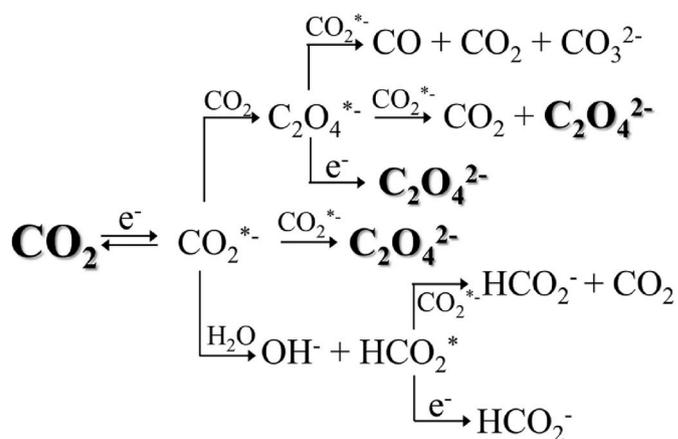


Fig. 5. Electrochemical CO_2 reduction reaction pathways to oxalate generation [139,140,145].

(5 °C), as shown in Fig. 6. As observed in the reaction mechanism (Fig. 5), the presence of water in the electrochemical CO₂ reduction negatively affects to oxalate selectivity (see Fig. 6) [60]. Therefore, in this study [147], the electrochemical system was subjected to a pre-electrolysis and CO₂ desiccation process in order to remove possible trace of water from the electrolyte and from CO₂. It was found a decrease up to 40% in oxalate FE where 1.25 v/v% of water was added to the electrolyte solution, confirming the interferences of water in electrochemical CO₂ reduction. In the case of temperature effect, solubility of CO₂ increases while decreasing the temperature, enhancing CO₂ availability on the electrode surface for its reduction.

The advantages of incorporating ILs as electrolytes were also explored for oxalate production in Pb electrodes. A novel aromatic ester anion functionalized IL of 4-(methoxycarbonyl) phenol tetraethylammonium ([TEA][4-MF-PhO]) was designed based on catalytic and

stability properties of aromatic esters and quaternary ammonium salts, respectively [60]. DFT calculations were performed in order to investigate the interaction between aromatic ester anion of [4-MF-PhO]⁻ and CO₂ revealing the ability of the anion with phenoxy and ester double active sites to bend the stable CO₂ molecule to CO₂^{*}. H⁺ cations provided by anolyte were combined with the anion-radical generating [4-MF-PhO-COOH]⁻ that eventually dimerized to oxalic acid (Fig. 6). High partial current densities (9.03 mA cm⁻²) and acceptable FEs (86%) obtained on Pb electrode in [TEA][4-MF-PhO]-acetonitrile electrolyte assert the integration of IL in this aprotic electroreduction systems for oxalate production and open a potential path of research and improvement.

Besides all progress related to Pb or stainless steel electrodes, cathodic materials such as metal organic frameworks (MOFs), metal-complexes or carbon supported metals have also been explored to perform the electrochemical CO₂ reduction to oxalate [132,150–152]. Metal organic frameworks are porous materials with a crystalline ordered structure capable of storing CO₂, which have also presented attractive features such as high porosity or thermal stability and adjustable chemical functionality [153–155]. They are indeed an emerging family showing promising features for electro and thermal catalysis [156] and their careful implementation in CO₂ to oxalate process merits further studies.

Shentil Kumar et al. coated Cu-BTC on a glassy carbon electrode to prove it as an efficient electrocatalyst for the oxalate production from CO₂ [151]. The electrochemically synthesized MOF was capable of sequestering and electro reducing CO₂ simultaneously. The electrochemical reduction can be conducted inside the pores through heterogeneous electron transfer between the MOFs and the previously adsorbed and compressed CO₂ molecules, generating a 90% pure oxalic acid with a FE of 51%.

Silver was also tested as cathodic catalyst in a carbon-silver hybrid configuration [150]. Babassu coconut, an important Brazilian vegetation that has been previously used for nanocarbon production [157], has been hydrothermally carbonised in the presence of silver nitrate solution, obtaining the Ag@C catalytic system (see Fig. 7). Comparing the results obtained with this system with those in absence of silver nanoparticles, it can be concluded that silver nanoparticles enabled the charge transfer for the CO₂ reduction besides enhancing the electrocatalytic activity. Moreover, synthesis with longer residence times resulted in larger deposits of silver particles that influenced the size of the carbon spheres and increased oxalic acid production.

As opposed to the previous works, Paris et al. reported the use of a Cr–Ga electrode supported on glassy carbon to produce oxalate in a KCl aqueous solution electrolyte [158]. This catalytic system consisted of a Cr₂O₃–Ga₂O₃ thin alloy film and, whereas neither Cr₂O₃ nor Ga₂O₃ films alone could produce oxalate, the alloy of the two oxides led to oxalate FE of 59% at a pH of 4.1. Organic solvent or those with low proton availability reported the production of the oxalate dianion; however, in this aqueous system, a combination of monoanionic and dianionic species was generated. The Cr–Ga system originates a more appealing product distribution since protonated oxalates are more desired species from an industrial point of view [158].

Oxalate was obtained at a more positive potential than that required for CO₂^{*} intermediate generation, i.e., this process provides a CO₂^{*} independent and lower energetic pathway than those previously reported (Fig. 5). This low energetic reaction pathway could involve a C₁ product as oxalate precursor, and experiments feeding CO, formate, methanol or their combinations instead of CO₂ were conducted. It was observed that CO-methanol combination did lead to oxalate production. Labelling experiments showed that carbon atoms oxalated derived from CO, although both methanol and CO are required for its production. Results obtained from this report encourage additional studies to advance in oxalate production in aqueous solutions [158].

3.1.2. Acetate. As already mentioned, the traditional synthesis of acetic acid involves a three-step energy-intensive process (methane or

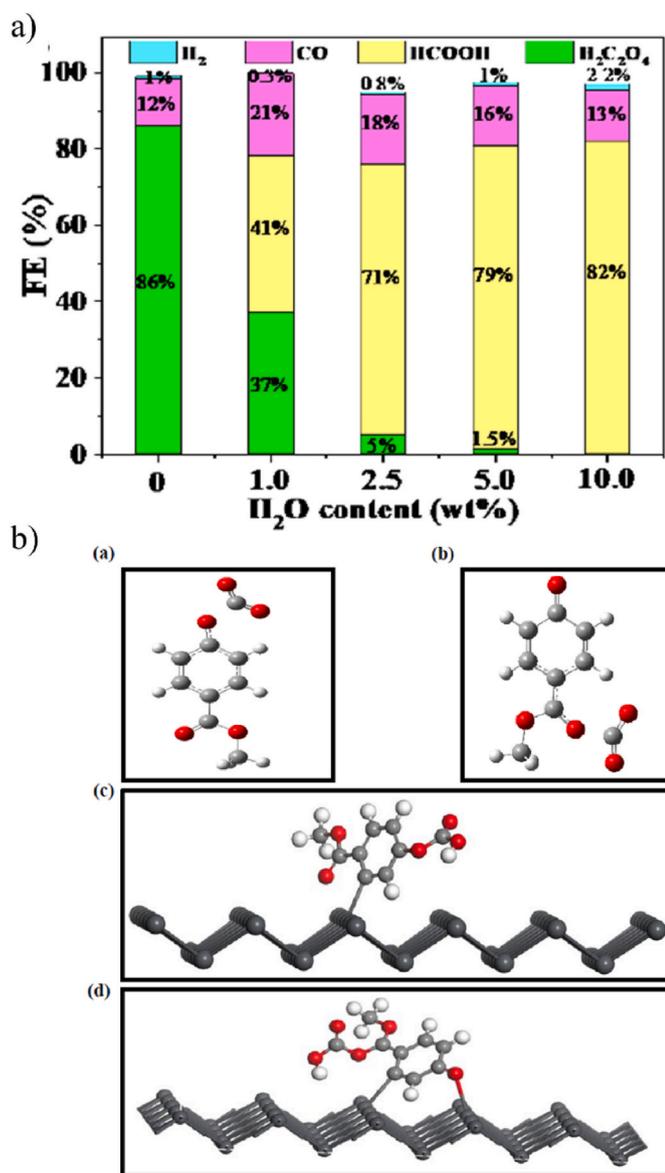


Fig. 6. a) The effect of H₂O on the faradaic efficiency of CO₂ reduction products in the IL electrolyte at -2.6 V (Vs. Ag/Ag⁺); b) The function of IL anion of [4-MF-PhO]⁻ on CO₂ capture, activation, and transformation. Interaction between CO₂ and aromatic ester anion with (a) phenolic and (b) ester groups. (c) and (d) The activation and reaction of CO₂ at the Pb electrode surface with the aid of [4-MF-PhO]⁻ and H⁺. Reprinted with permission from Ref. 60. Copyright © 2020 Wiley-VCH GmbH.

believed to be generated by the formation and adsorption of CO and H⁺ species, which would generate CH₂ that, in turn, could react with CO and be hydrated until acetic acid generation [89]. In the second work, due to the ANH groups of polyaniline catalyst and the use of methanol as electrolyte, H atoms are generated on the electrode surface and then transferred to the CO₂ molecules generating formic acid that could be attacked by the methanol and form acetic acid [167].

Although copper-based catalysts are the most suitable for C₂+ products from CO₂, bulk copper catalysts face limitations (poor selectivity, high energy input, low activity) that must be overcome tuning these copper catalysts. More selective catalysts can be generated with smaller nanoparticles, defect sites, core-shell structures, oxidation states or heteroatomic doping [168]. In that sense, several tuned copper-based catalysts have reported high faradaic efficiencies toward acetic acid or acetate.

The choice of a suitable support could be a key to improve bulk copper performance. The incorporation of conducting polymers such as polyaniline have been proved to decrease the electrochemical CO₂ reduction overpotential [167]. Cu₂O nanoparticles, with oxygen species to easily adsorb CO₂ and Cu⁺ ions promoting CO₂ reduction as active sites, were dispersed in a polyaniline matrix. This configuration led to a

synergistic effect which allows the generation of acetic acid as the main product with an efficiency of 63% [167].

Boron-doped diamond (BDD) has been widely used in electrochemical application due to its adequate characteristics for those purposes [169]. Although it is able to produce formaldehyde on its own under ambient conditions [89], as support of copper particles, it resulted in a selective electrode to acetic acid generation. Acetic acid was not observed while using copper or BDD as electrodes separately [89]. Same behaviour was observed in an electrocatalyst based on copper nanoparticles supported on carbon nanotubes (CNTs), achieving a production of acetic acid with a selectivity close to 60% [16].

Pure titanium oxide does not present activity in the electrochemical CO₂ reduction process itself [170], but its ability to control the local pH and its good conductivity make nanotubular TiO₂ array (TNA) a suitable support. In the work of Zang et al. TNA was applied as the support of a modified polyoxometalate Cu catalyst [168]. Polyoxometalates (a type of transition metal oxygen anion clusters) were induced to modify the local electronic and protonic environment of Cu nanoparticles conforming a Mo₈ modified cubic fragmented Cu submicron particles on TNA (Mo₈@Cu/TNA) catalytic system. The skeleton structure and SEM images of the catalytic system can be observed in Fig. 9.

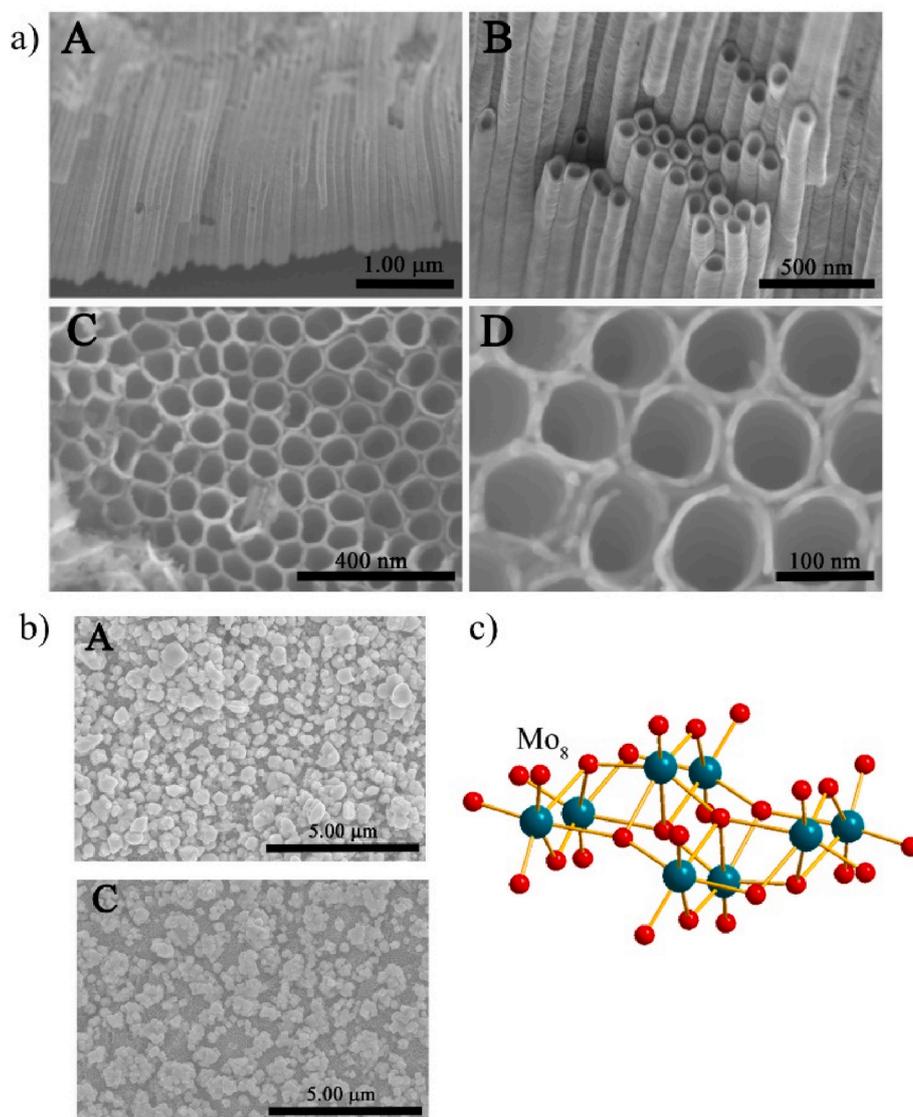


Fig. 9. a) SEM of TiO₂ nano tube array (TNTA); A, B: side views; C, D: top views. b) SEM of the obtained Cu/TNTA, (A) Cu/TNTA, (C) Mo₈@Cu/TNA. c) Polyoxometalate skeleton structure of Mo₈. Reprinted with permission from Ref. 168. Copyright © 2020 Elsevier B.V.

Acetate is originated following the single carbon coupling pathway (schemed in Fig. 8), i.e., CO₂ molecules were coupled with formed *CH₃. Experiments on mechanism investigation showed the synergistic effects of Cu planes and polyoxometalate cluster promoting the generation of the intermediate *CH₃ tuning the selectivity towards acetate. Moreover, Mo oxide clusters modified Cu catalyst obtaining a fragmented Cu surface rich on grain boundaries. Ag was selected as metal to substitute Cu, but in view of selectivity and FE obtained while using Ag instead of Cu, these control experiments just served to highlight the synergistic effect between Cu surface and Mo oxides.

Wang et al. also incorporated Ag in the electrocatalyst, but combined with Cu, forming clusters (~ 6 nm) of Cu and Ag on the surfaces of electropolymerized films, (Cu)_m, (Ag)_n/polymer/GCE [171]. The increase in the acetate formation as Ag was added to the nanoparticles evidenced the important role of surface metal composition. As observed in Fig. 10, it is believed that the presence of Ag could modified reaction mechanism although is still uncertain. Ag catalysts are able to promote CO₂ reduction to CO [172], so Ag sites could facilitate the CO formation that would be further captured on neighbouring Cu sites for C–C bond formation and later acetate production (Fig. 10).

N-doped systems also represent an appealing family of materials for electrochemical CO₂ conversion. Indeed, they are chemically and active stable compounds that present an overpotential for HER higher than most reported electrocatalysts [173]. This way electrochemical CO₂ reduction could be conducted suppressing H₂O reduction and hence, enhancing the selectivity for the desired product [174]. Boron nitride (BN) promotes the CO₂ chemisorption in the presence of electrons, thus the role of a C-doped BN as support of a Cu(I) complex Cu(I)/BN-C for acetic acid production was evaluated achieving a FE of 80.3% [160]. The support and the catalyst complex behaviours were evaluated separately, finding that bulk BN is not active for CO₂ reduction, but BN-C can generate large amounts of formic acid since N-doped carbon materials can absorb CO₂ and stabilize CO₂* [175]. The high selectivity to acetic acid is then related to a synergistic effect between catalyst complex and BN-C. CO₂ is first adsorbed and converted into CO₂* due to BN-C and then protonated and reduced into methanol that would generate the desired acetic acid via C–C coupling with the help of the Cu metal center [160].

Due to the observed proper characteristics of N-doped materials, N-doped nanodiamond supported on a Si rod array (NDD/Si RA) (schemed in Fig. 11) was tested for electrochemical CO₂ reduction showing high

efficiency, fast kinetics and good selectivity towards acetate [123]. As observed in Fig. 11, an increase in the N content led to an enhance in acetate and formate production rates due to the defects sites presence and the carbon atoms polarized by the N doping [176]. Defects sites and polarized carbon atoms may promote CO₂ adsorption and CO₂*- stabilization and rod array structure provides a large surface area that facilitates electron transfer. The combination of all these effects would explain the promising results obtained [123].

As mentioned before, Cu-based catalysts have shown excellent performance on electrochemical CO₂ reduction and high selectivity towards C₂₊ products, although they are not the only ones and, as in the case of the N-doped nanodiamond catalyst, modified Fe, Mn, Au, Pd or In metals have demonstrated its activity and selectivity towards acetic acid [15, 177–180].

Fe oxyhydroxide nanostructures (Ferrihydrite-like clusters, Fh-FeOOH) were also supported on N-doped graphitic materials (Fe/N-C), and FE values were up to 97% with a high selectivity to acetic acid [177]. Results supporting the same clusters on O-doped carbon were not so encouraging, revealing the favourable Fe–N interaction. N-dopants allowed the stabilization of Fe(II) species instead of Fe₀ (as in the case of using O-dopants) that promotes HER. Acetic acid formation was attributed to the presence of these Fe(II) species adjacent to N sites, while Fe(II) species are believed to reduce HCO₃⁻ species, N sites enable the C–C coupling.

Indium metal favours the formation of C₁ products, although modifying its electronic properties inducing transitions metal oxygen anion clusters such as polyoxometalate (which has also reported beneficial effects modifying Cu electrodes) [168] can tune its selectivity towards C₂₊ products. Li et al. [180] and Zha et al. [15] works have incorporated polyoxometalates as electrolyte to assist In for the electrochemical CO₂ reduction. As expected, the electrocatalytic performance of In resulted in the formation of hydrogen and formic acid as the only products. The addition of SiW₁₁Mn to the electrolyte gave a result the appearance of acetic acid as well as hydrogen and formic acid, according to ion chromatography, gas chromatography and mass spectrometry analyses [180]. The presence of SiW₁₁Mn reduced the overpotential and enriched In₀ species since it enabled the re-reduction of elemental In.

In the case of adding SiW₉V₃ to the electrolyte, the reaction mechanism was investigated through IR monitoring experiments and gas chromatography [15]. Control experiments (electrolyte without adding SiW₉V₃, and SiW₉V₃ electrolyte without In metal as catalyst) reported

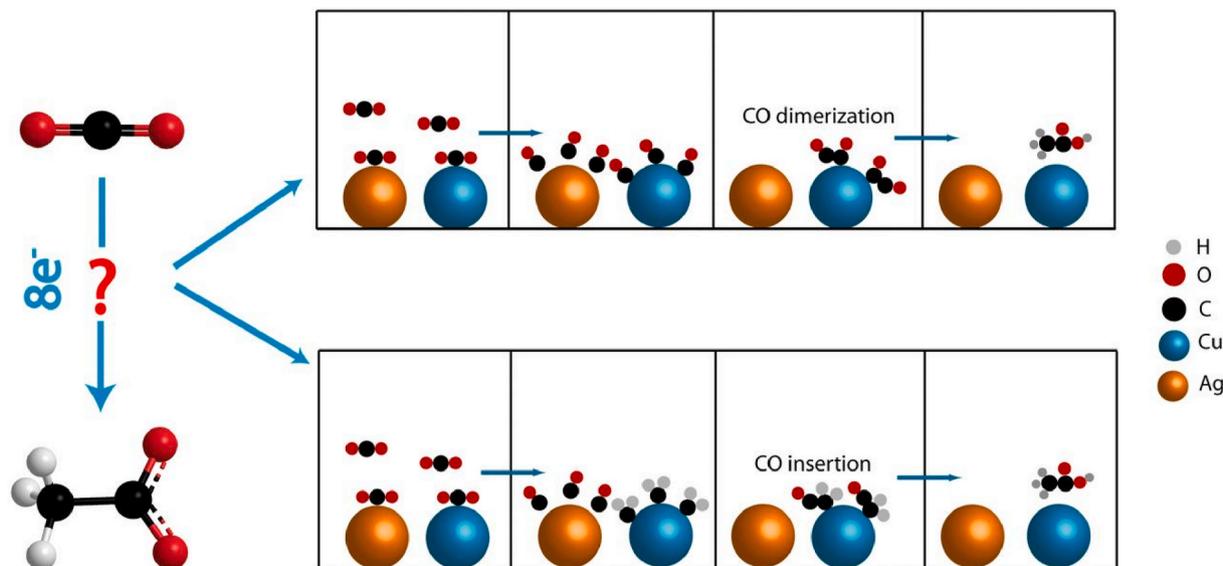


Fig. 10. Possible reaction mechanism for CO₂ reduction to acetate on (Cu)_m, (Ag)_n/polymer/GCE electrodes. Reprinted with permission from Ref. 171. Copyright © 2018 National Academy of Sciences.

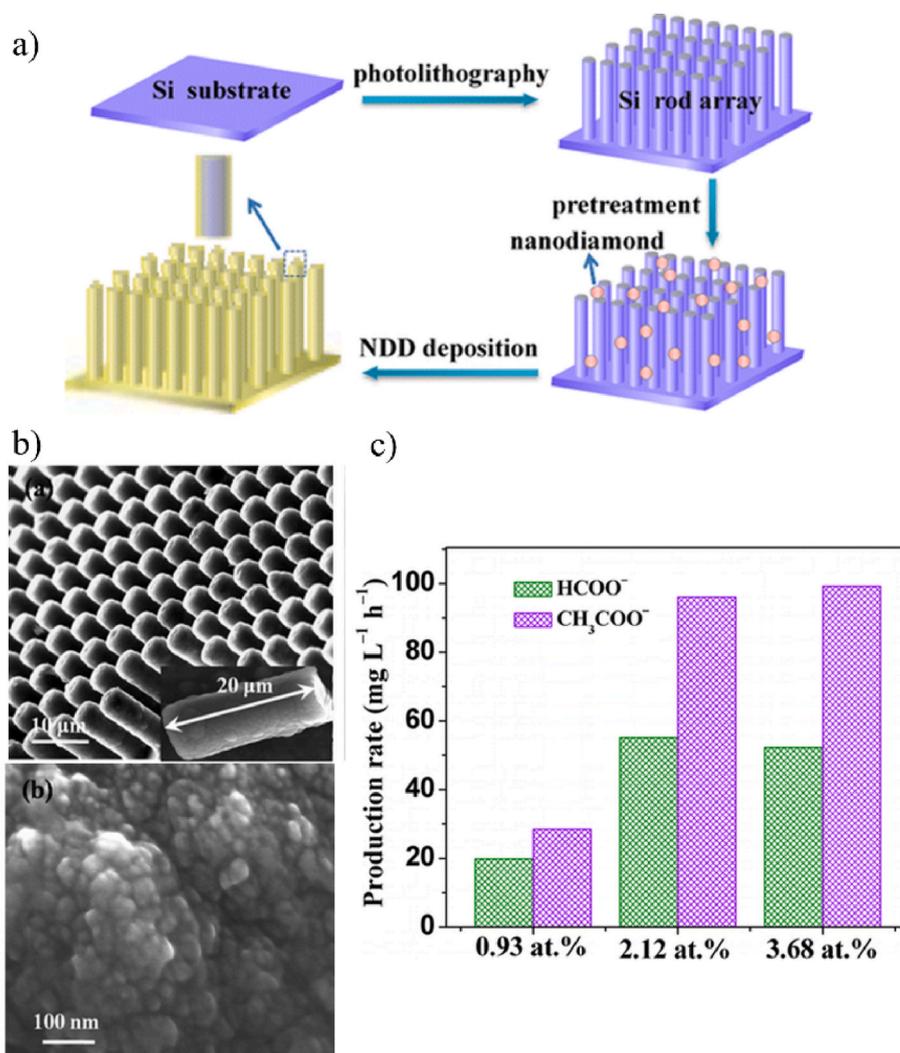


Fig. 11. a) Scheme of the NDD/Si RA preparation process, b) SEM images of NDD_L/Si RA. c) Acetate and formate production rates of acetate and formate on NDD_L/Si RA electrodes with different N contents (0.93, 2.12, and 3.68 atom %) at -1.0 V. Reprinted with permission from Ref. 123. Copyright © 2015 American Chemical Society.

that SiW₉V₃ was necessary for the acetic acid formation (as in the previous case using SiW₁₁Mn) and In for the CO₂ reduction since the first step on the mechanism was the In-facilitated formation of In-CO₃⁻ (instead of CO₂^{*} intermediate). Besides, XPS spectra indicated that the V-center of SiW₉V₃ participates in the electron transfer process decreasing the overpotential, i.e., V-center efficiently catalyses the reduction of CO₂. Faradaic efficiencies in this system reached values up to 96% with nearly 96% selectivity towards acetic acid.

3.2. CO₂ to ethylene

The synthesis of C₂₊ products from CO₂, such as ethylene or ethanol, is of high importance due to the essential role of these products in the chemical and energy industry [119,181–183]. Ethylene is widely used as a building block in the production of many raw materials such as polyethylene, ethylene oxide, vinyl acetate, and ethylene glycol. Usually, ethylene is obtained from steam cracking of naphtha under harsh production conditions (800–900 °C). Although steam cracking is the industry standard for ethylene production, it presents different disadvantages. This process is non-catalytic and non-selective and is high energy and capital intensive, yielding into many by-products which require extensive separations and purification [184,185]. In recent years, the ethylene electrochemical synthesis from CO₂RR is gaining

attention since this approach offers mild conditions and an environmental pathway for ethylene production [186,187]. However, the use of CO₂RR for the highly selective production of compounds of economic interest such as ethylene is still a challenge [186]. Concerning the catalyst, in the electrochemical environment of this reaction, i.e., abundant protons and negative electrode polarization, different catalytic behaviours have been observed: Ni, Fe, Pt, and Ti cathodes preferentially produce H₂ over CO/CO₂ production. Post-transition metals such as Pb, In, Sn, and Tl mostly produce formates. Additionally, Ag, Au, Pd and Zn reduce CO₂ only to CO. On the other hand, Cu possess the outstanding ability to reduce CO₂ or CO to CH₄, C₂H₄, C₂H₅OH, and a variety of products [188–190].

Copper catalysts have been extensively explored in the electrocatalytic synthesis of ethylene. It has been proved that tuning the intermediates' stabilities can favour a desirable reaction pathway and by consequence, improve the selectivity [190–192] However, the mechanistic pathway for the formation of ethylene over Cu catalyst is still under academic discussion [19]. While the C–C coupling of two carbenes (*CH₂) has been proposed as the determinant step for the synthesis of the C₂ product from CO₂RR over Cu catalyst [193], more recent, studies concluded that C₂ product formations are more attributed to CO dimerization.

Different theoretical and experimental studies have supported that

the CO dimerization pathway is the limiting step for ethylene production [192]. As shown in Fig. 12, in the CO dimerization, $^*CO + ^*CO$ (Fig. 12a), $^*C_2O_2^-$ intermediate can exist either from carbon and oxygen atoms from $^*C_2O_2^-$ intermediate, which are bounded to the catalyst surface in a bridging mode (Fig. 12b) or by the $^*C_2O_2^-$ intermediate which is bounded to the surface by two C atoms (Fig. 12c). However, both ways proceed to further protonation of the $^*C_2O_2^-$ intermediate giving place to more stable intermediates such as $^*CO-COH$ (Fig. 12d) of *COCHO [194]. Alternatively, Goodpaster et al. proposed that while at low overpotential, the formation of the C-C bond takes place in a reaction of two *CO bounded to the surface, at higher overpotential, the reaction between *CO and *CHO (Fig. 12e and f) is favoured as a result of the larger activation barrier to the formation of the CO dimer [195]. This intermediate is followed by the reaction with *CO to form *COCHO (Fig. 12g) and finally ethylene formation [164,165].

Copper has been selected as an ideal catalyst in the electrochemical conversion of CO_2 due to the thereof mentioned characteristics. Its reaction performance has been widely explored in CO_2RR by controlling morphology [113], grain boundaries [166], facets [196], oxidation states [197], molecule decoration [188–190], and dopants [198]. Among these methods, the design of Cu metallic nanostructures for C_2+ products seems more promising due to the simple synthesis and the easy study of the structure-activity relationship of the catalyst. For instance, Roberts et al. showed that modifying the structure of the copper surface is a novel pathway to improve ethylene efficiency and selectivity. These authors obtained nanotubes-covered copper (CuCube) surface with high selectivity and low overpotential to ethylene formation, but also probed the effect of (100) sites in the C-C coupling as a strategy to target multicarbon products [199].

Recently Zhang et al. reported the design of Cu nanosheets as an electrocatalyst for ethylene synthesis from CO_2RR . These nanosheets (Fig. 13a) present defects in the size of 2–14 nm, which were observed to be strengths in the adsorption, enrichment, and confinement for reaction intermediates and hydroxyl ions on the catalyst. As shown in Fig. 13b, the maximum FE reached with these copper nanosheets was up to 83.2%, which is the highest value among all the studied electrocatalysts to date [200].

Louidice et al. explored the effect of shape and size of Cu nanocrystals (NCs) in ethylene production. They explored crystal cube and

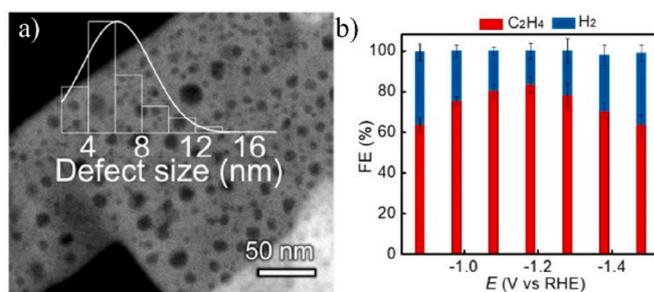


Fig. 13. a) HAADF-STEM images of n-CuNS and size distribution of the nanodefects b) Faradaic efficiencies of C_2H_4 and H_2 at different applied potentials for n-CuNS. Reprinted with permission from Ref. 200. Copyright © 2020 American Chemical Society.

spheres of Cu NCs, observing an increase in the activity as the crystal size decreased [116].

The modification of oxidative copper states has also been proved to be an alternative to enhance the selectivity and efficiency of C_2+ products [197,201]. Anodized-copper was investigated in CO_2RR as a tool to improve ethylene selectivity. It was observed that compared with a Cu foil, this anodized-Cu catalyst presented a two-fold improvement [202]. But most importantly, the selectivity continued stable over 40 h of the experiment. As it is observed in Fig. 14a, the catalyst performance remained stable, retaining an average of 38.1% FE for ethylene production. In this experiment, it was also observed the electrochemical treatment of the as-synthesized catalyst as a critical parameter in the ethylene selectivity (Fig. 14b). When the material was exposed to electrochemical reduction treatment at mild biased potential, the species were observed to suffer a reduction, quickly decreasing the ethylene selectivity. Meanwhile, when the treatment was performed at highly biased harsh conditions, the catalyst presents much extended durability for selectivity C-C coupling. These observations give evidence of the relationship between Cu-O-containing surface states and the durability of ethylene production, which are of high importance to develop new strategies for controlling selectivity and durability of O-Cu catalyst for electrochemical synthesis of ethylene [202].

The Cu-based alloys such as Ag-Cu, Au-Cu, Au-Pd, and Cu-Pt have

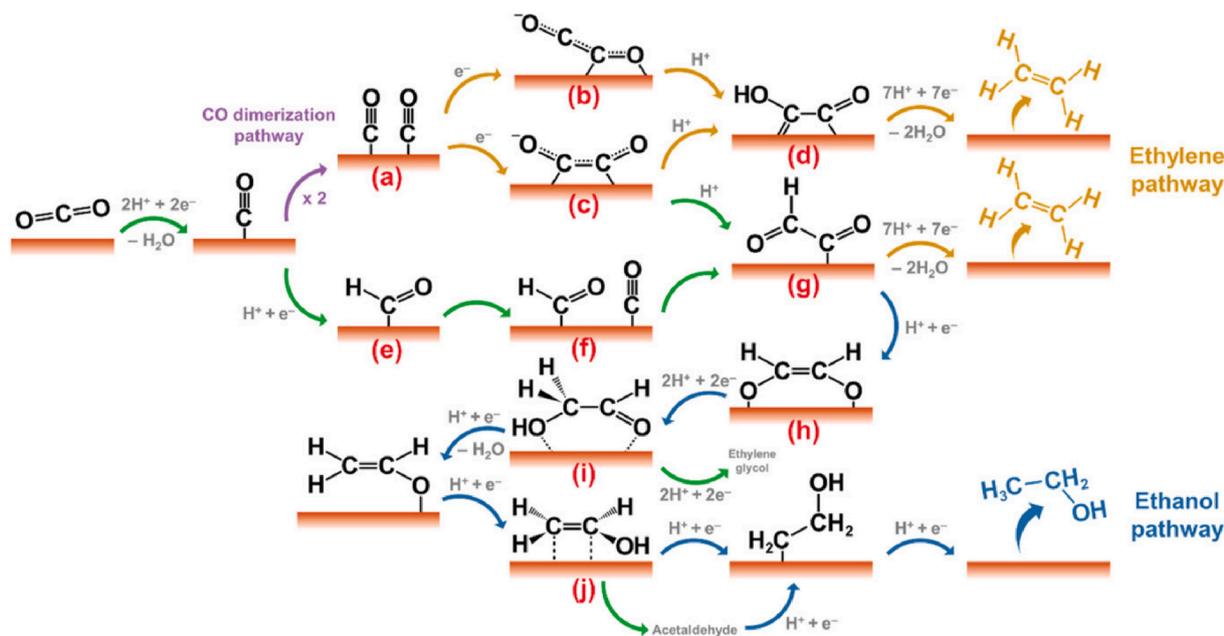


Fig. 12. Ethylene and ethanol formation. The brown and blue arrows indicate ethylene pathways and ethanol pathways. Reprinted with permission from Ref. 6. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

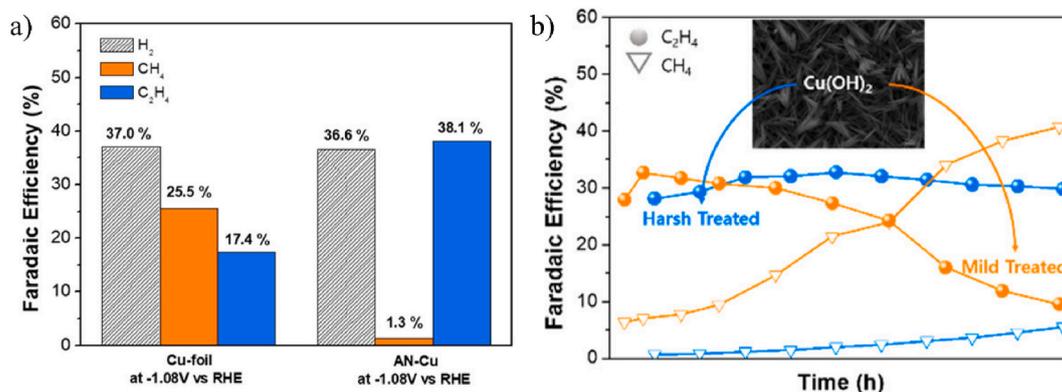


Fig. 14. a) Faradaic efficiencies of H₂, CH₄, and C₂H₄ at -1.08 V vs. RHE, b) Effect of the catalyst treatment in the FE of CH₄ and C₂H₄. Reprinted with permission from Ref. 202. Copyright © 2018 American Chemical Society.

been demonstrated to present a high efficiency in the C₁ production via stabilization of the intermediates [203,204]. However, the effect of these alloys in the production of C₂₊ hydrocarbons seem to be more complex [205]. For instance, Chang et al. reported an atomically dispersed Cu–Ag bimetallic catalyst where it was observed that Cu-rich zones preferred the production of hydrocarbons. In contrast, Ag-rich zones are dominated by CO. These experiments highlighted the importance of the atomic ratio for CO₂RR electrocatalysts [206]. Similar

studies using Cu–Ag alloys from additive-controlled electrodeposition showed that Ag sites were believed to act as a promoter for CO formation during the electrocatalytic CO₂ reduction, helping the C–C coupling in the neighbouring Cu due to the availability of CO intermediate [207].

Molecular distribution in Pd–Cu catalyst has also proved to play an important role in improving the selectivity of C₂₊ compounds. For instance, Ma et al. demonstrated that a phase-separated Pd–Cu catalyst offered an ethylene selectivity up to 50% compared with its disordered

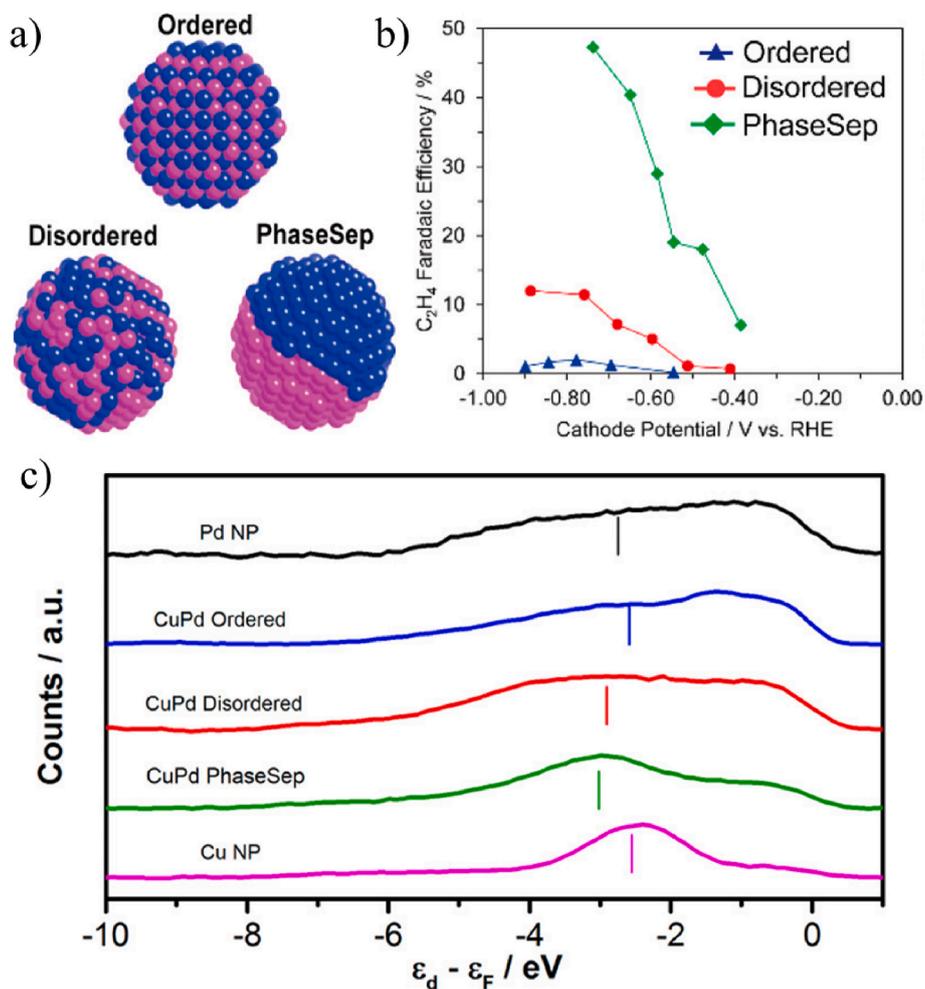


Fig. 15. a) Structures of the different prepared CuPd nanoalloys, b) Faradaic efficiencies for C₂H₄ formation using bimetallic Cu–Pd catalysts with different structures and c) Surface valence band photoemission spectra of CuPd nanoalloys corresponding to Fermi level. Reprinted with permission from Ref. 208. Copyright © 2016 American Chemical Society.

and ordered counterparts (Fig. 15a and b) [208]. Since according to the d-band theory, typically, lower d-band center transition metals show weaker binding on the in-situ generated intermediates on the metal surface [209]. The Pd–Cu alloy exhibited a similar catalytic activity and selectivity for CO that the ones obtained with Cu nanoparticles (NPs). It offered a wide d-band difference (Fig. 15c) which helps to conclude that the geometry and structure effect may play a more important role than the electronic effect for enhancing the selectivity of hydrocarbons in phase-separated Cu–Pd alloys case [208].

The nature of the electrocatalytic CO₂ reduction imposes the need of catalysts with specific active sites for the reactants adsorption and the further transformation of multiple intermediates, thus makes primary importance the increasing of specific active sites in the design of catalyst. As discussed in the oxalate section, MOFs have emerged as an alternative to act as both, as electrocatalysts or precursors to derive in different heterostructured catalysts due to their extraordinary properties and could be useful for electrochemical ethylene production from CO₂. In fact, from an electrochemical point of view, the permanent porosity, ultrahigh surface area, coordinatively unsaturated metal sites, adjustable pore size, and active sites homogeneous dispersion makes them highly attractive for this kind of reactions [210].

Post-synthesis modification of MOFs is a strategy of high relevance in the design of electrocatalysts since it could assemble the functional metal fractions such as metal porphyrin and metal complex that would enhance the CO₂ reduction in MOFs, particularly in those with

coordinatively unsaturated metal sites, which interact with CO₂ working as Lewis acid [29,211,212]. Cu-BTC (HKUST-1), which presents open metal sites, has been widely studied in the CO₂RR due to its structural features that enhance the catalytic performance. Nam et al. reported the strategy involving the MOF-regulated Cu cluster formation (Fig. 16a) as a tool to optimize the selectivity of ethylene in comparison with MOF-based active carbon. They obtained an efficiency of up to 45% (Fig. 16b) [213].

MOFs derivatives such as metal oxides, porous carbons, carbides, phosphides, and nitrides have appeared to overcome the main limitations of MOFs related to the poor stability and conductivity in electrochemical reactions [214–217]. For instance, Zheng et al. studied N-doped nanoporous carbon obtained from ZIF-8 for ERC, emphasizing the calcination temperature in the reaction and the mechanism. According to the catalytic performance, higher pyrolysis temperature resulted in a higher activity with a maximum FE for CO formation of 95.4% [218].

The design of atomically dispersed metals in activated carbon (AC) has also been a powerful tool in the electrochemical conversion of CO₂. As shown in Fig. 17, Guan et al. boosted the CO₂ electroreduction to CH₄ and C₂H₄ by tuning the neighbouring single-copper sites in a doped-AC showing the Cu-coping concentration as a tool to direct the selectivity to the desired product. For instance, they showed that at a Cu high concentration, the distance between Cu-N_x species was close enough to enable C–C coupling and, by consequence, produce C₂H₄. In contrast, a

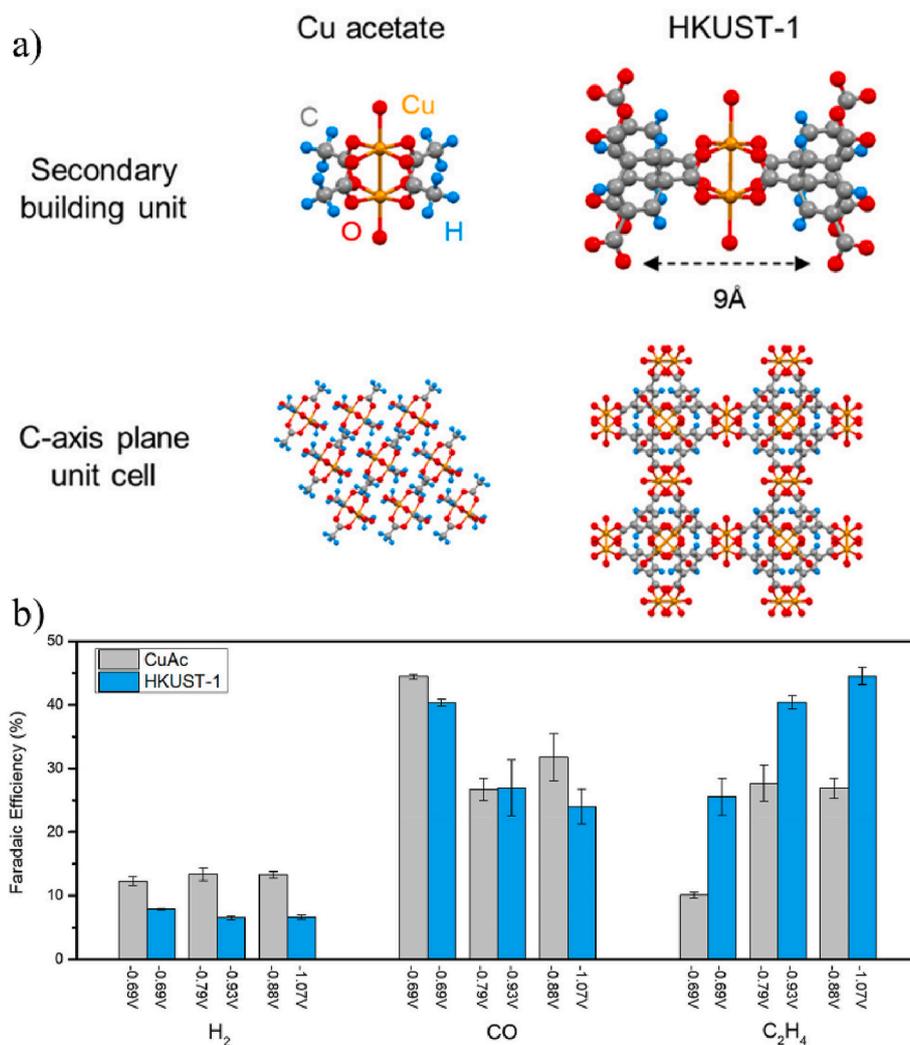


Fig. 16. a) Schematic Comparison of paddle-wheel structured HKUST-1 vs. CuAc. Structural investigations of as-fabricated HKUST-1, b) CO₂RR activities of CuAc (200 °C 1 h calcined), and HKUST-1 (250 °C 3 h calcined). Reprinted with permission from Ref. 213. Copyright © 2018 American Chemical Society.

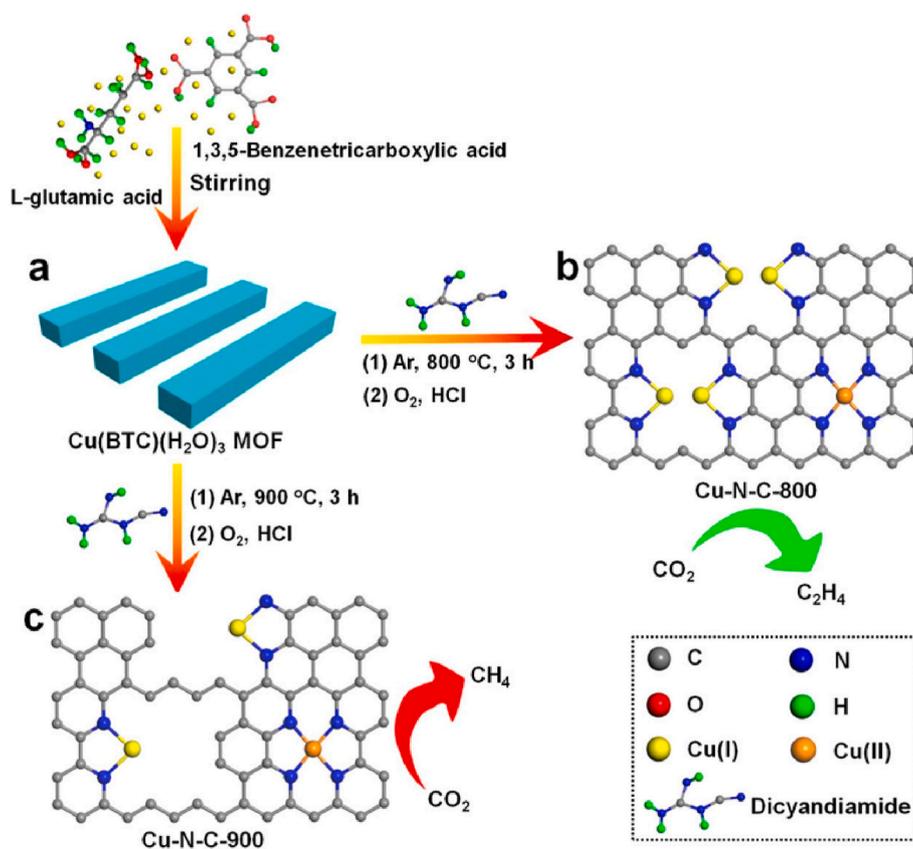


Fig. 17. Scheme of Cu-N-C-T catalysts synthesis process: a) Cu(BTC) (H₂O)₃ MOF precursor, b) Cu-N-C-800 synthesized by pyrolysis of Cu(BTC) (H₂O)₃ MOF and dicyandiamide at 800 °C, (c) Cu-N-C-900 derived from the pyrolysis of Cu(BTC) (H₂O)₃ MOF and dicyandiamide at 900 °C. Reprinted with permission from Ref. 219. Copyright © 2020 American Chemical Society.

Cu concentration lower than 2.4% mol, the distance between species was larger to the formation of CH₄ was favoured [219].

3.3. CO₂ to C₂₊ alcohols

The electrocatalytic conversion of CO₂ to higher-value hydrocarbons beyond the C₁ products is an area of extraordinary importance for applications such as transportation, fuels, energy storage, and the chemical industry [220]. With a worldwide production of ca. 88.5 Mt/y and a projection of US\$105.2 billion by 2025, ethanol is an important organic chemical for the biofuel and food industries [221,222]. For instance, approximately 80% of global ethanol produced is used as fuel, followed by food, pharmaceutical, and cosmetics applications [223].

In recent years, electrochemical production of ethanol has been proposed as a green route to obtain this high-value chemical. As observed in Fig. 12, the electrochemical production of ethanol takes place in a similar pathway to ethylene, where the C-C coupling activity is considered a critical step in ethanol production, similarly to other C₂₊ products. Garza et al. proposed an ethanol pathway over Cu catalyst where it was observed that *COCHO intermediate (Fig. 12g) is the key to determinate the selectivity between ethylene and ethanol [165]. The glyoxal can be reduced to acetaldehyde and ethanol (Fig. 12h), followed by a further reduction to glycolaldehyde (Fig. 12i) and ethylene glycol/vinyl alcohol (Fig. 12j) or acetaldehyde, and finally to ethanol [164, 189].

The main goal for CO₂RR to ethanol is to improve selectivity at high conversion rates, which are influenced by the catalyst and the process conditions. By far, Cu-based catalysts have been the most studied to catalyse CO₂RR for ethanol production [201,224,225]. In this sense and similarly to ethylene, different strategies have been studied to enhance ethanol selectivity in Cu-based catalysts, such as nanoparticle

morphology [226,227], oxidation states [228], and Cu-based alloys [208,229]. For instance, Duan et al. studied the crystallinity of Cu nanoparticles as a driven parameter in the ethanol selectivity, observing that amorphous nanoparticles enhance the adsorption of CO₂ at room temperature, which plays a key role in the CO₂RR [230].

Several studies have demonstrated the strong relationship between product selectivity of CO₂RR and the crystal facets of Cu [231]. For example, Cu(100) increases the selectivity for ethylene, while in Cu (111) catalyst, methane is the main hydrocarbon product [67,115,116, 232]. Jiang et al. developed and studied an efficient nanocube-shaped catalyst with significant improvement in C₂₊ selectivity. It was reported that Cu(100) and (211) facets favour ethanol and other C₂₊ products over Cu(111) via dimerization of *CO to form *OCCHO and the subsequent proton-electron transfer and surface hydrogenation to form *OCCHO [196].

The oxidation states of copper can vary among Cu₀, Cu⁺, and Cu²⁺, and their states change reversibly during electrochemical reaction conditions. Copper oxide-based catalysts improve the activity and selectivity of C₂₊ products. Generally, copper oxide-based catalysts are synthesized by the growing of Cu₂O from Cu-based precursors followed by high-temperature treatment and consequently reducing Cu₂O to form Cu₀ sites. However, the elucidation of the pathways of this enhancement toward C₂ formation is still under debate [19]. Tentatively, the enhancement of the selectivity for ethanol of such catalyst could be attributed to (i) the presence of residual oxygen atoms close to the surface that favour the modification of the electronic structure of Cu atoms and the increase of the CO binding energy, which by consequence promotes C-C couplings [233]; (ii) the strong adsorption of H₂O molecules due to the presence of residual Cu⁺ which may work synergically with Cu₀ sites. These H₂O molecules favour the CO₂ conversion to CO [117,118]. For instance, Handoko et al. reported a mechanistic study

electroreduction of CO₂ to ethanol and other C₂₊ hydrocarbons on Cu₂O-derived films. They synthesized Cu₂O films with five different morphologies and proved a relationship between the crystal size and the selectivity to C₂ products being able to reach a FE of c. a. 20% in middle-sized particles [234].

A wide variety of morphologies of copper oxide-based materials has been reported as a determinant factor to enhance ethanol production. For instance, Daiyan et al. reported the synthesis of nanowires of Cu₂O/CuO/Cu foam (Fig. 18a) that exhibited a FE for ethanol formation of 31% [235]. Also, 3D dendritic Cu–Cu₂O/Cu catalyst (Fig. 18b) were synthesized and proved a FE up to 39.2% attributed to the high density of exposed active sites and favourable Cu₂O:Cu ratio [220].

Copper alloys have attracted considerable attention as a strategy to change the composition of Cu single crystal catalysts via combining it with a secondary metal able to produce H₂ (i.e., Fe, Ni, Ag, Au, and Pd) and to tune the activity and selectivity through optimization of the binding strength of the key intermediates on the surface of the catalyst [6]. For instance, Shen et al. described the synthesis of submicron arrays based on the alloy CuAu reaching a FE up to 29%. It showed the critical role of Cu:Au ratio content in the selectivity ethanol/ethylene [236]. Interestingly, in the same way as metal ratios, the phase distribution of the metal involved in the alloys has been proved to be a determinant factor in directing the selectivity to ethylene or ethanol. As observed in Fig. 19a, which shows the ethanol/ethylene selectivity in an Cu/Ag catalyst, the selectivity is three times higher in the catalyst with phase blended, probably related to the effect of the dopant in the surrounding Cu atoms but also to the effect of Ag–Cu biface boundaries that suppresses the HER and favours the formation of mobile CO on Ag sites and its further reaction to a residual intermediate on Cu sites (Fig. 19b and c) [225].

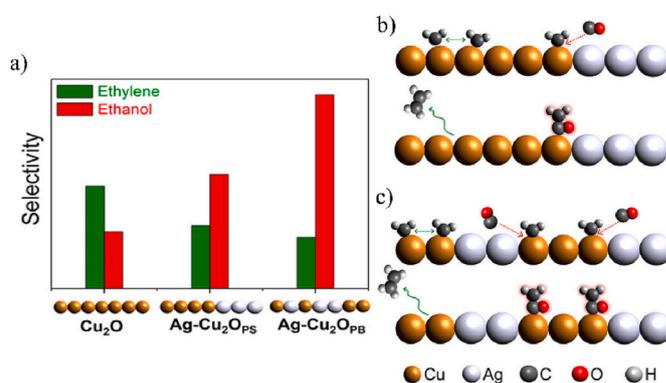


Fig. 19. a) Ethylene and ethanol selectivity in Cu/Ag catalyst. Possible CO-insertion reaction mechanism scheme: CO transfer from one metal site that weakly binds CO (Ag) to another site that binds residual C₁ intermediate species (Cu) for the case of b) Ag–Cu₂O_{PS} and c) Ag–Cu₂O_{PB}. Reprinted with permission from Ref. 225. Copyright © 2017 American Chemical Society.

In the last decade, MOFs, and especially those formed by Cu metal ions or clusters, have served as active electrocatalyst in CO₂RR but also as precursors for highly dispersed Cu over N-doped carbon catalysts [237,238]. For instance, Zhao et al. synthesized a porous Cu/C catalyst consisting of Cu₂O and metal Cu particles embedded in a porous carbon matrix through the pyrolysis of Cu-based MOF (HKUST-1) (Fig. 20). A maximum FE for ethanol production of 34.8% at a potential of –0.5 V was obtained using this selective catalyst [239].

The electrochemical reduction of CO₂ to C₃₊ products remains a challenge. Among the C₁–C₃ alcohols, n-propanol possesses the highest

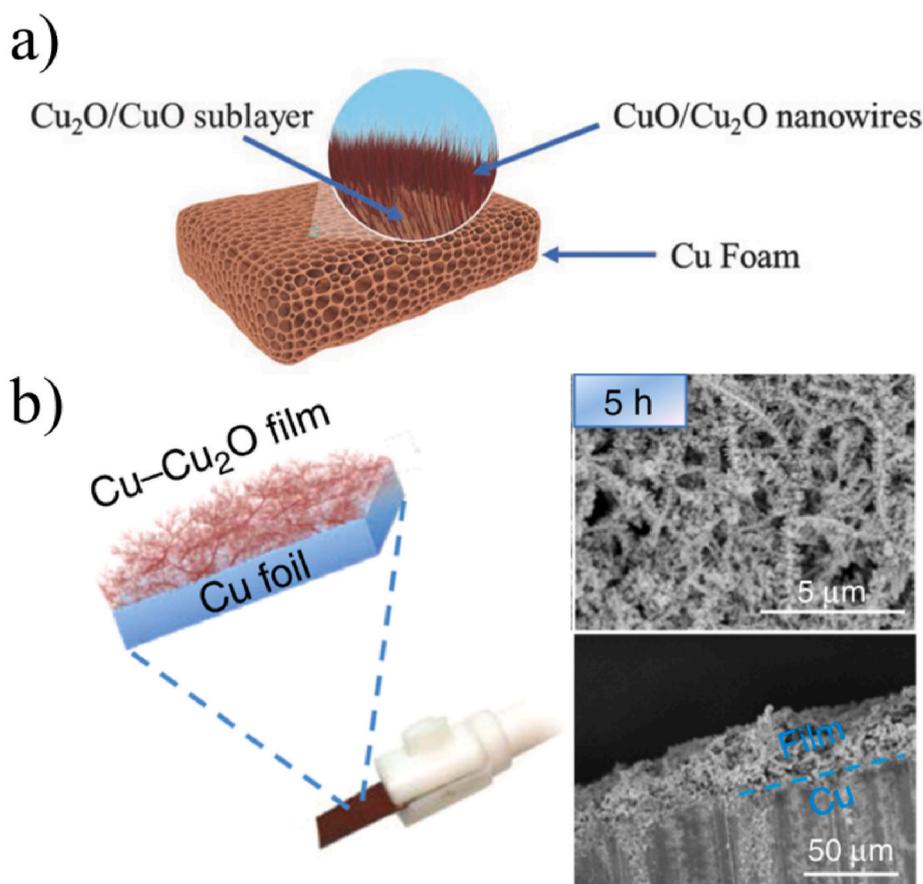


Fig. 18. a) Scheme of Cu sandwich electrode. Reprinted with permission from Ref. 203. Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) Scheme of 3D dendritic catalyst and SEM images of the catalyst. Reprinted with permission from Ref. 220. Copyright © 2019, Qinggong Zhu et al.

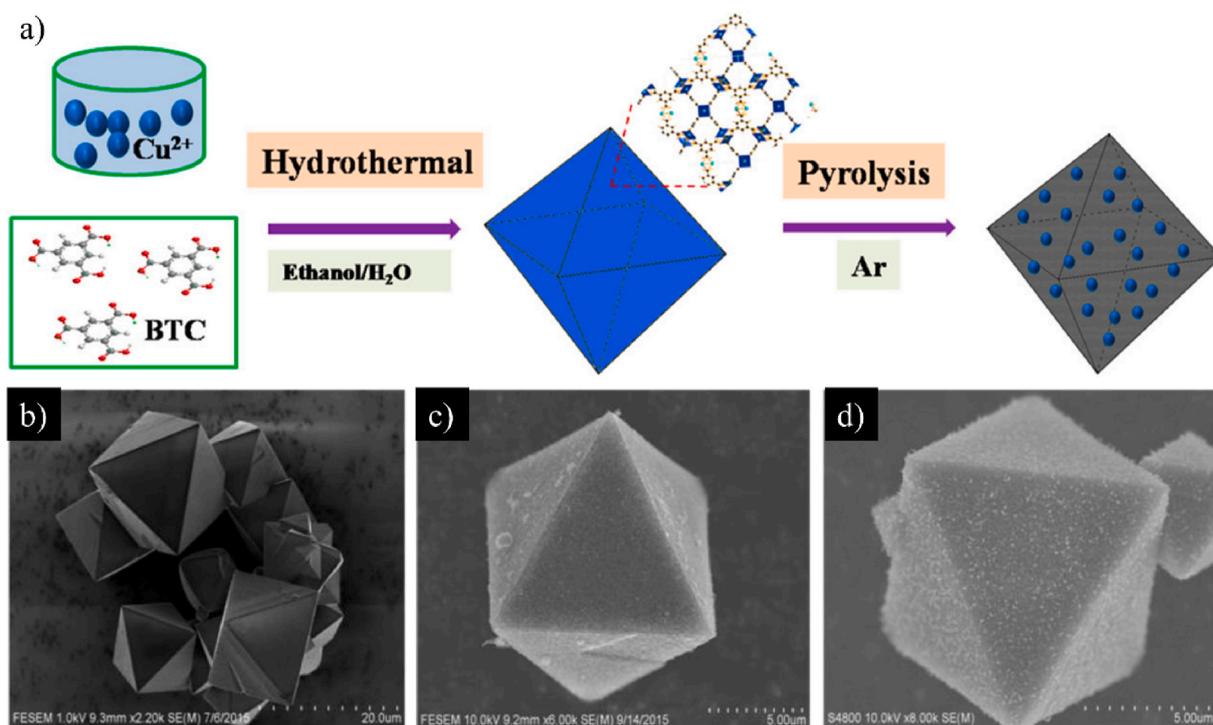


Fig. 20. a) Scheme of synthesis of HKUST-1 and Cu/C electrocatalyst and b) SEM image of HKUST-1 crystals, c) SEM image of Cu/C catalyst treated at 900 °C, and d) SEM image of Cu/C catalyst treated at 100 °C. Reprinted with permission from Ref. 239. Copyright © 2017 American Chemical Society.

energy-mass density (30.94 kJ/g) and an octane number up to 118 [240, 241]. These relevant properties make the efficient and green production of n-propanol a target point nowadays.

The n-propanol production by a CO₂ reduction reaction has been only observed in Cu-based catalysts. It has been hypothesized the pathways for n-propanol production as a result of the transformation of acetaldehyde into vinyl alcohol by a tautomerization equilibrium [227, 242]. As observed in Fig. 21, the adjacent intermediates CO and *CH₂ are inserted into *CH₃-CH in a similar way. Then, the reduction to propionaldehyde (CH₃-CH₂-CHO) and, consequently, to n-propanol takes place [20].

Ren et al. reported a mechanistic study to n-propanol electrosynthesis via the design of nanocrystals agglomerates with unprecedented catalytic activity. The defect sites generated in the catalyst surface was responsible for the improved activity of the Cu nanocrystals and, hence, the n-propanol formation [227].

4. Market perspective and techno-economic aspects

In contrast with the previous sections, in which each product has been reviewed separately, here we give a general overview of the market aspects and techno-economic analysis carried out to date. The market size of the targeted products is critical from both a commercial perspective and CO₂ utilization potential. In this vein, Fig. 22 presents the approximate market size of the C₂-products here considered [243–249]. As shown, for example, propanol and acetic acid market sizes are very low in comparison with other potential CO₂ utilization routes. For instance, other relevant CO₂ utilization alternatives such as CaCO₃ production, have a market sizes one hundred times higher than propanol and acetic acid (116 Mton/a market size) [250]. Nonetheless, their production from CO₂ should not be dismissed as the production capacities may fit with the capacities of small-medium CO₂ emitters. A fair example of these emitters is biogas upgrading, that could achieve the category of negative CO₂ emissions technology if propanol or acetic acid are produced from the CO₂ contained in this bio-resource. Oxalic acid is a very interesting C₂ product from a utilization perspective since it is

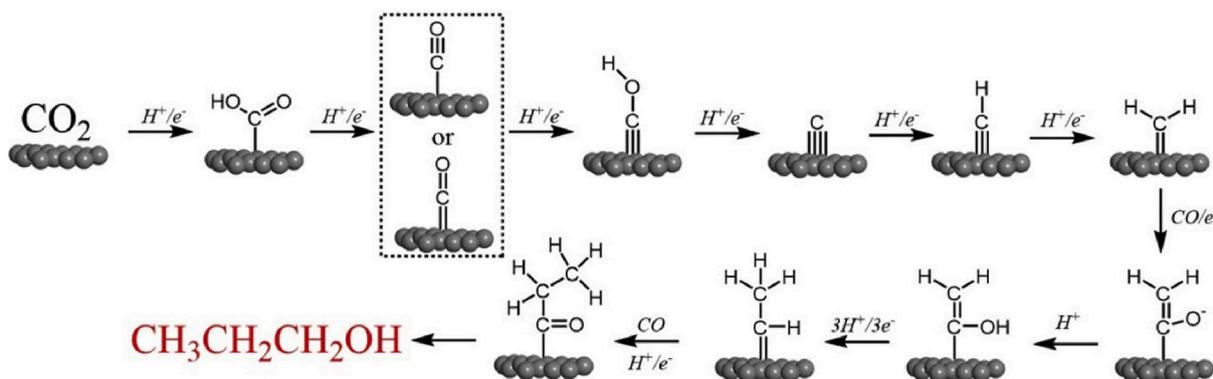


Fig. 21. Possible pathway to n-propanol production via CO₂ reduction reaction. Reprinted with permission from Ref. 20. Copyright © 2018 Elsevier Ltd.

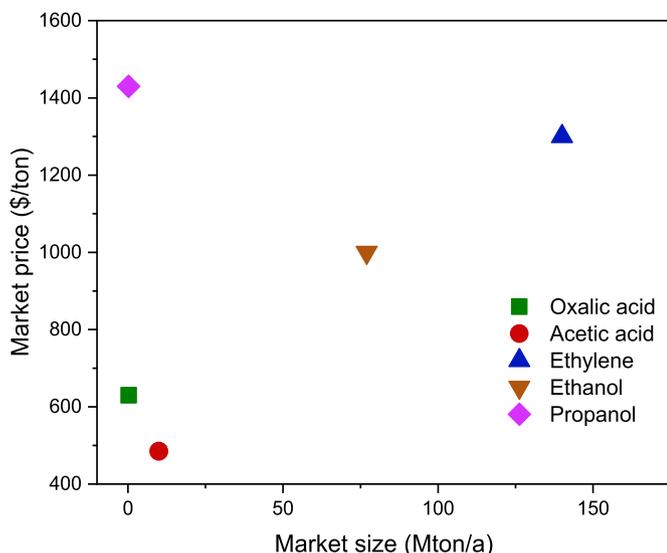


Fig. 22. Market size vs market price for C_2 products [213–219].

demand by pharmaceuticals, textiles manufacturing, rare earth extraction, oil refining or metal processing industries. Nonetheless, worldwide oxalic acid production is above 0.230 Mton/a [249], which places oxalic acid in the same range than propanol and acetic acid. Therefore, this option cannot provide an alternative for CO_2 utilization of large emitters. Ethylene and ethanol present market sizes considerably greater, and as explained in previous sections, the production of these chemicals is crucial for the end-products consumed by our society nowadays.

On the other hand, Fig. 22 also presents the market prices for the products studied. From a market price point of view, ethanol, ethylene and propanol are the most attractive products to be achieved via CO_2 electrocatalytic reduction. Although rapidly booming, CO_2 utilization technologies are currently far from being competitive with traditional technologies, hence focusing on products with elevated market prices could be a good strategy to balance economic performance. Following this reasoning, the production of oxalic and acetic acid from CO_2 would be difficult to become economically profitable with the current market prices in the short term. However, the growing projection for CO_2 emission taxes along with the ongoing commitments to pursue a net-zero emissions opens the possibility for the viable production of all these chemicals using electrochemical routes.

Concerning techno-economic works carried out to date, only a few studies are reported in literature. Economic assessment of CO_2 electrocatalytic reduction are scarce probably because of the complexity of the analysis and the lack of reliable commercial scale data. In this sense, this criticism aims to be an encouraging call for experts in techno-economic and profitability evaluations. Focusing on the works performed, Table 1 gathers the most important characteristics and findings of the techno-economic analysis available in the literature. Perhaps the most impacting study carried out to date was performed by Jouny et al. [243] In this work, authors present the end-of-life net present value (NPV) of a 100 ton/day plant for various CO_2 reduced products: propanol, formic acid, carbon monoxide, ethanol, ethylene and methanol. From the products targeted in their study, here we focus on propanol, ethanol and ethylene. Under the current conditions, authors conclude that the production of these C_2 -products from CO_2 is not profitable. Nevertheless, the result could be reverted if reasonable electrocatalytic performance benchmarks are achieved. In agreement with these authors, these performances must be 300 mA cm^{-2} and 0.5 V overpotential at 70% FE. Another very important work was presented by Kibria et al. [244]. In their work, a techno-economic analysis was carried out with the aim of ensuring the economic viability of the process by the identification of

profitable CO_2 electrocatalytic reduced products as well as the performance targets that should be met to achieve it. As in the previous discussed work, this study includes parameters such as current density, energy and faradaic efficiencies, and stability. The most interesting point of this work is the prices predicted for ethanol and ethylene to achieve profitable scenarios. According to these authors analysis, ethanol price should achieve 1400 \$/ton to get a net present value equal to zero (revenues equal to costs at the end of the plant life). In comparison with the current market price for ethanol (around 1000 \$/ton, see Fig. 22), the difference is 40%. This fact shows the great technological challenge that we face to make electrocatalysis economically attractive in the context of direct CO_2 conversion to C_2 products. In the same study, a price of 1700 \$/ton is predicted for ethylene to be a profitable alternative. Again, in comparison with current market prices (approximately 1300 \$/ton), the threshold needed is remarkably higher. Interestingly, the authors present a sensitivity analysis based on a tornado plot, revealing that current density is the main parameter with room for improvement for all the products considered.

5. Final remarks and outlook

The transition towards sustainable modern societies relies on the implementation of disruptive technologies for CO_2 utilization. Among these technologies, electrocatalytic CO_2 conversion to added value products will play a major role given its advantages compared to traditional thermal catalysis. In particular, the fact the electrochemical reactions can take place at very mild conditions represents a major bright side of this approach. So far, most of the academic works are focused on the conversion of CO_2 to C_1 products since the reaction is “electrochemically cheaper”. Nevertheless, the production of C_2 and C_{2+} is more appealing for the chemical industry given the broad market applications of these advanced products. Herein, challenges on the catalysts design to achieve high faradaic efficiencies and end-product selectivity are identified as the main bottlenecks for the electrochemical CO_2 conversion to C_2 and C_{2+} compounds. Among the different studied heterogeneous catalysts, Cu-based formulations outstand showcasing the best activity/selectivity balance. However, in many cases their performance is still below the threshold to be considered as commercially viable options. In this sense, new formulations of advanced materials including multi-alloy systems, N-doped catalysts, optimized porous MOFs structures among many others are under development showing promising results. In this sense, our review provides an end-product guided perspective of the progress within catalyst design to deliver C_2 and C_{2+} from electrochemical CO_2 conversion routes. Beyond offering an illustrative analysis for experts and a straightforward starting point to newcomers in the field, our work would also like to emphasize the need to strengthen the research efforts within the catalysis and energy communities in the conversion of CO_2 to advanced products. More precisely we advocate for a C_2 and C_{2+} production using a new generation of advanced electrocatalytic materials.

Along with the catalysts design and electrochemical processes considerations, market studies are crucial to ascertain the viability of the CO_2 electrochemical conversion routes. Our analysis indicates that products with a broad market such as ethanol, ethylene and propanol are worth exploring in the short term while electrochemical production of other key products such as oxalic and acetic acids are not yet economically appealing. Still, progress on catalyst design pushing forward products selectivity and overall CO_2 conversion will certainly help to make these options also viable. In any case, the production of advanced products using CO_2 as carbon pool and electrocatalysts design seem to share a common destiny whose convergence will result in a remarkable contribution to decarbonise the chemical industry, opening new routes for the desired low-carbon future.

Author contributions

The authors equally contributed to this work.

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 paper.

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