



CO₂ electrochemical reduction: A state-of-the-art review with economic and environmental analyses

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ABSTRACT

The electrochemical reduction of carbon dioxide is an emerging strategy to reduce emissions, allowing the storage of renewable energy and the electrification of the chemical industry according to the principle of carbon dioxide utilization. Valuable fuels and chemical commodities can be obtained by ensuring a closed carbon loop and the main important products are carbon monoxide, formic acid, methanol, methane, ethylene, ethanol, and propanol. Inside this context, here, we explore the state-of-the-art of carbon dioxide electrolysis technologies, showing that efforts have been put into the development of reactor cell architectures and catalysts able to provide high selectivity and efficiency. New insights are currently about the study of reaction mechanisms, optimization of cell design, and development of more performing electro-catalysts. Moreover, an overview of economic and environmental studies based on carbon dioxide electrochemical reduction is conducted in this work and a preliminary screening based on the levelized production cost and climate change impact of several products obtained through carbon dioxide electrochemical reduction is proposed for a large-scale plant. Today, carbon monoxide and formic acid are the primary carbon dioxide reduction product targets from an economic point of view. In the future, production costs are expected to decrease, and other low-carbon products could be competitive with market prices. Renewable energy sources and carbon dioxide with a low carbon footprint contribute to an environmentally friendly electrochemical production process.

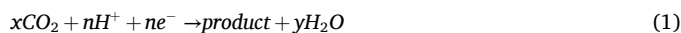
1. Introduction

In the last few decades, carbon dioxide (CO₂) emissions and atmospheric concentration have increased, achieving respectively values of 34.81 billion tonnes and 413 ppm in 2020, with negative consequences on the environment such as the phenomena of global warming and climate change (NOAA, 2021). Due to the effect of this high value of emissions, it is very important their reduction and to achieve this aim, CO₂ capture (from air and point sources) for its utilization and/or storage has been developed. For the utilization route, in addition to the biochemical (biological reactions through bacteria convert CO₂ in other compounds), thermo-catalytic (catalysts are used to activate the reaction synthesis from CO₂) and photo-catalytic (photoactive catalysts are used under sunlight to convert CO₂ into organic products) conversion technology, CO₂ electrochemical reduction (CO₂ER) has been proposed in the literature as a promising CO₂ utilization strategy, according to the electrification trend of the chemical industry (e.g. the replacement of thermal and chemical energies by electrical energy) (Garg et al., 2020;

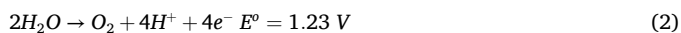
Sánchez et al., 2019).

Compared to other solutions, the electrochemical route is the most promising alternatives available for CO₂ reduction, as it does not require high temperatures or high pressures for an efficient reduction, uses water as a source of protons, and allows a greater product selectivity than that obtained with other reduction methods. In addition to having a greater operational flexibility, it can be easily installed in places with a difficult access and/or the availability of cheap energy. However, this method has still considerable challenges such as low CO₂ solubility, mass transfer limitations, low catalyst stability, and technology commercialization (Wiranarongkorn et al., 2023).

In a CO₂ electrolyser at ambient temperature, CO₂ is reduced to different products at the cathode side via a CO₂ reduction reaction (CO₂RR), as in Eq. (1), while H₂O is oxidized at the anode side according to the oxygen evolution reaction (OER), as in Eq. (2).



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Overall, the reaction involves multiple steps with the transfer of multiple protons and electrons and electricity is provided to allow the electrolytic reaction to produce fuels or chemical commodities. In addition to main products (carbon monoxide, formic acid, methanol, methane, ethylene, ethanol, and propanol), up to 16 different CO₂-based compounds, including glyoxal, ethylene glycol, acetaldehyde, propionaldehyde, etc. have been reported in the literature (Jouny et al., 2018). However, these additional products are mainly reported as trace amounts.

A CO₂-closed loop is ensured when the process is powered by green electricity and the CO₂ emitted from each end product is captured, as in Fig. 1, to be used in the electrochemical cell. In this way, emissions from the usage stage of CO₂-based products are captured so that no emissions are outside the carbon cycle also because renewable and green electricity is used for the cell. Nowadays, this is of particular importance because, it is imperative to exploit renewable energies and have processes with net negative CO₂ emissions (EIA, 2019).

For the electrochemical reduction of CO₂ there are advantages and disadvantages. Among advantages there is the decarbonization of society, the operation under ambient pressure, the easy scale-up due to its modularity, the possibility to tune the selectivity by controlling the catalyst, and any source of electricity (renewable and non-renewable) can be used to drive the process (Agarwal et al., 2011; 2017; Lu and Jiao, 2016).

On the other hand, among disadvantages, there are some thermodynamic and kinetic limitations. For example, CO₂ activation is the limiting step and CO₂ is a very stable molecule, therefore a substantial input of energy is needed. However, despite its high thermodynamic stability, the presence of an electric field is known to facilitate the activation of CO₂ through electrostatic effects. Additional disadvantages are: high costs for the increased energy consumption, it is difficult to simultaneously achieve high efficiencies and selectivities by minimizing costs and the complexity of the separation section (Jouny et al., 2018; Liang et al., 2020; Garg et al., 2020). According to these considerations, to overcome these obstacles, many efforts have been put into developing efficient catalysts.

Currently, CO₂ER electrolyzers are still not mature at an industrial scale, but recent studies show their potential development at that level although the most critical issue is the structural design of the electrolyzer (Ma et al., 2021). There are only demonstrations at the pilot scale, except for solid oxide electrolyzers used by Haldor Topsoe already at a commercial scale and by Shell actually under construction (van Bavel et al., 2020; Qi et al., 2021; Welch et al., 2020; Küngas et al., 2017;

CERES, 2022). The SOEC plant, located in the Herning (Denmark), is scheduled to be operational by 2025 with a capacity of 500 MW and a size of 23000 m². For the other electrochemical systems, data at a smaller scale are present. When CO is produced, the current density can range between 0.4 A/cm² and 0.7 A/cm² while the selectivity can be between 90 % and 99 % (Yuan et al., 2023). For formate production current density and selectivity are respectively 0.7–0.9 A/cm² and 91–93 %, while for ethylene production current density and selectivity can vary between (Yuan et al., 2023).

Different factors influencing the reaction environment have been investigated in the literature, such as temperature, pressure, potential, current density and electrolyte composition (Gao et al., 2019; Liang et al., 2020). It has been found that current density and voltage potential have a positive effect on product selectivity. Moreover, at a higher cell voltage there is a higher current density (Yuan et al., 2023). However, at a higher current density the energy efficiency decreases (Yuan et al., 2023). Electrolyte concentration can have a negative or positive effect on product selectivity and current density (Yuan et al., 2023). Temperature and pressure have different effects on CO₂ER, but more systematic studies are needed to better understand the effects on CO₂ER under high temperature and atmospheric pressure conditions (Zong et al., 2023).

Most of the recently published work on CO₂ER has been focused on the development of new catalysts, electrolyser system architectures, economic and environmental analyses as well as on understanding reaction mechanisms in order to improve performances and efficiencies as explained below in this paper (de Salles Pupo and Kortlever, 2019; Lin et al., 2020; Garg et al., 2020; Qiao et al., 2014; Ma et al., 2021; Senocrate and Battaglia, 2021; Lu and Jiao, 2016; Hatsukade et al., 2014; Somoza-Tornos et al., 2021; Yang and Li, 2021; Hernandez-Aldave and Andreoli, 2020).

New insights for CO₂ER have been achieved for reaction mechanisms. Li et al. (2023) proposed a new reaction pathway for the electrochemical reduction of CO₂ to oxalate by using an aromatic ester-functionalized ionic liquid ([N2222][4-MF-PhO]). In their proposal, CO₂ does not have electrons from the electrode directly, but the anion of the ionic liquid, [4-MF-PhO]⁻, works as a catalyst and electron transporter due to a lower Gibbs free energy barriers and higher selectivity compared with the formation of oxalate on the electrode surface. A mechanism of reaction for CO₂ reduction to copper single-atom alloy catalysts was suggested by Liu et al. (2023) finding that increasing the coverage of *CO on the catalyst leads to relocation of the active site, resulting in improved activity of C₂ products.

In this work, we first and critically introduce the main products that can be obtained via CO₂ER. Next, we give an overview of different electrolysis devices used for the reduction of CO₂ with future perspectives, figures of merit (current density, Faradaic efficiency, energetic efficiency and stability) and suggested electrocatalysts. In other sections, we analyze the literature research about the life cycle assessment (LCA) and economic analysis of CO₂ER systems. At the end, as the innovative point of this paper, we propose an economic screening of the main products obtained at a large-scale with the electrochemical reduction of CO₂ for the current and future (2050) years as well as a global sensitivity analysis (GSA) to find significant factors for the levelized production cost. For the same CO₂-based products an environmental analysis is also presented to evaluate the climate change impact.

2. Main products obtained from CO₂ER

Depending on the number of electrons and protons transferred per molecule of CO₂ during its reduction, several compounds can be obtained by CO₂ER, as reported in Fig. 2, where the current industrial production methods are also shown.

For 2 exchanged electrons, carbon monoxide (CO) and formic acid (HCOOH) can be obtained. For 6 exchanged electrons, methanol (CH₃OH) can be obtained while for 8 electrons, methane (CH₄) could be

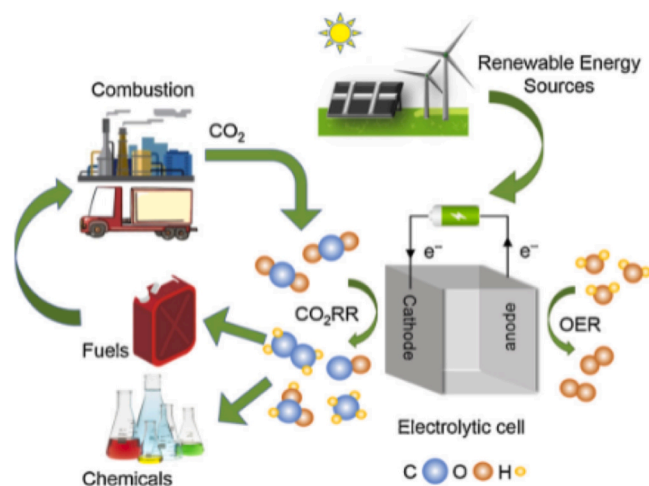


Fig. 1. A schematic diagram of CO₂ER (Reproduced with the permission of Liang et al. (2020)).

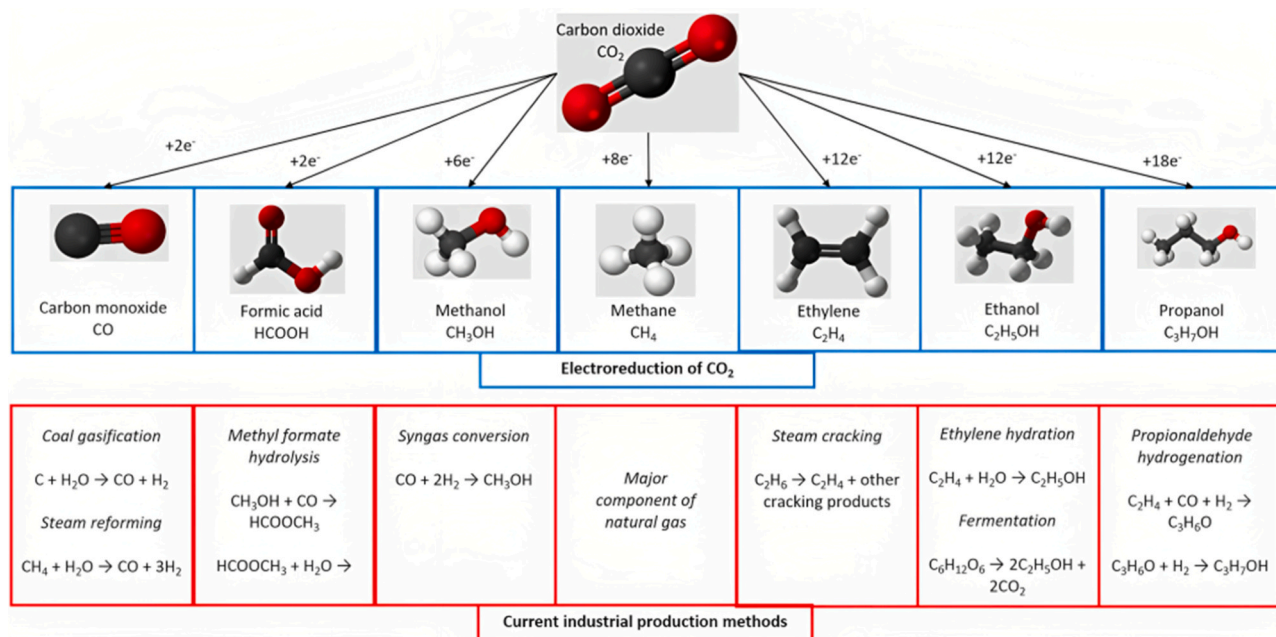
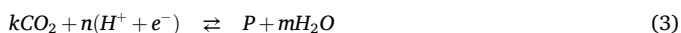


Fig. 2. Main products from CO₂ER and the respective current industrial production method.

produced. Ethylene (C₂H₄) and ethanol (C₂H₅OH) can be produced when 12 electrons are exchanged. The exchange of 18 electrons can produce propanol (C₃H₇OH).

For these main products, Table 1 shows the half-cell electrochemical reactions and the respective thermodynamic electrode potential versus the standard hydrogen electrode (V vs SHE) under standard conditions (298 K, 1 atm, pH 0), evaluated from the standard Gibbs free energies for aqueous solutions (Jouny et al., 2018). The values of standard potentials are in a narrow range of $-0.25\text{ V} - 0.169\text{ V}$ and hence it is difficult to achieve a high product selectivity (Garg et al., 2020). The equilibrium standard potential suggests the thermodynamic propensity of the reaction and does not provide information about the kinetics, such as the reaction rate or mechanism, which also depend on the catalytic properties of a given electrode material. In particular, the standard electrode potential is a measure of the tendency of a species to gain electrons (be reduced), measured under standard conditions. Generally, a more positive value of this parameter suggests a higher propensity for a reduction reaction to occur, so that the reduction reaction occurs with difficulty at more negative values of equilibrium standard potential.

It is important to underline that for the overall process the cell potential (e.g. the difference between the potential of cathode and anode) must be considered to verify the spontaneity of the overall reaction that is according to the following equation (see Eq. (3)) (Kortlever et al., 2015a):



The value of k, n and m coefficients are reported in Table 2 for each product P: propanol is the compound with the highest consumption of

Table 1
Electrochemical reduction reactions of CO₂ (Jouny et al., 2018).

Reaction	Potential (V vs SHE)
$\text{CO}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$	-0.106
$\text{CO}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCOOH}_{(\text{l})}$	-0.250
$\text{CO}_{2(\text{g})} + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{CH}_3\text{OH}_{(\text{l})} + \text{H}_2\text{O}_{(\text{l})}$	0.016
$\text{CO}_{2(\text{g})} + 8\text{H}^+ + 8\text{e}^- \rightleftharpoons \text{CH}_4_{(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$	0.169
$2\text{CO}_{2(\text{g})} + 12\text{H}^+ + 12\text{e}^- \rightleftharpoons \text{C}_2\text{H}_4_{(\text{g})} + 4\text{H}_2\text{O}_{(\text{l})}$	0.064
$2\text{CO}_{2(\text{g})} + 12\text{H}^+ + 12\text{e}^- \rightleftharpoons \text{C}_2\text{H}_5\text{OH}_{(\text{l})} + 3\text{H}_2\text{O}_{(\text{l})}$	0.084
$3\text{CO}_{2(\text{g})} + 18\text{H}^+ + 18\text{e}^- \rightleftharpoons \text{C}_3\text{H}_7\text{OH}_{(\text{l})} + 5\text{H}_2\text{O}_{(\text{l})}$	0.095
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$	0

Table 2

Stoichiometric coefficients for the overall reaction of CO₂ reduction and the required minimum work.

	k	n	m	Minimum work (kWh/mole of product)
Carbon monoxide	1	2	1	0.07
Formic acid	1	2	0	0.08
Methanol	1	6	1	0.19
Methane	1	8	2	0.23
Ethylene	2	12	4	0.37
Ethanol	2	12	3	0.38
Propanol	3	18	5	0.55

CO₂ per mole of product. Carbon monoxide, formic acid, methanol and methane have the lowest consumption of CO₂ per mole of the product, hence the lowest reduction of this emission is ensured producing these compounds while propanol ensures the highest CO₂ reduction.

However, from an energetic point of view, as reported in Table 2, at standard conditions, propanol has the highest minimum work (0.55 kWh/mole product) required for the electrolysis process. Here the minimum work is evaluated from the Gibbs free energy, known the cell potential and using the correlation as $\Delta G = -nFE$, with n the number of exchanged electrons, F the Faradaic constant and E the cell potential (Kazmi et al., 2022). A trade-off between the energy consumption (in term of minimum required work) and emission reduction (in term of CO₂ consumption per mole of product) should be considered when selecting the best target compound.

3. Figures of merit for electrolyzers

Figures of merit are used to describe the performance of an electrochemical process and include current density, Faradaic efficiency (FE), energetic efficiency (EE), and stability. These figures of merit are described below. An ideal and efficient electrolyser should have high values for the parameters here defined, however, the increase of cell voltage to improve the current density causes a decrease in the energy efficiency (Gao et al., 2021). Nevertheless, high current densities should be ensured at the expense of energetic efficiency as a trade-off between costs and effectiveness.

3.1. Current density

The current density measures the electrochemical reaction rate per geometric area of the electrode (i.e. the geometric area and not the real surface area, which can be greater due to roughness) (Kibria et al., 2019). It is also defined as the ratio between the current and the electrode area (Hamann et al., 2007). This parameter is affected by catalyst loading, utilization of the catalyst, transport rate of reactants and products to and from the electrode and higher values of current density are preferred because they minimize the electrolyser dimensions and CAPEX.

3.2. Faradaic efficiency

The Faradaic efficiency or current efficiency is provided by the following relation (see Eq. (4)) (Dutta et al., 2024; Lv et al., 2014):

$$\varepsilon_{\text{Faradaic}} = \frac{z \cdot n \cdot F}{Q} \quad (4)$$

where z is the number of required electrons to produce a given product, n the number of moles of the given product, F the Faraday's constant (96,485 C/mol electrons), and Q the total charge passed. It is also defined as the ratio between the charge used for the production of a given product and the total charge passed (Gao et al., 2021). This

parameter measures the selectivity of the electrochemical reaction towards a specific product: higher values are preferred because reduce the need for additional separation units that increase CAPEX and OPEX. Generally, in aqueous electrolytes, the electrochemical reduction of CO_2 occurs simultaneously with the HER limiting the Faradaic efficiency of CO_2 reduction.

3.3. Energetic efficiency

The energetic efficiency is defined by the following relation (see Eq. (5)) (Hamann et al., 2007):

$$\varepsilon_{\text{energetic}} = \frac{E^0 \cdot \varepsilon_{\text{Faradaic}}}{E^0 + \eta} \quad (5)$$

with E^0 being the thermodynamic voltage, η the total overpotential and $\varepsilon_{\text{Faradaic}}$ the Faradaic efficiency. It is the ratio between the energy stored in the desired product and the total energy input needed to synthesize it: higher energy efficiencies mean a small energy penalty for the production of the desired product.

3.4. Stability

Stability describes the variation of current density, Faradaic and energetic efficiency with time due to the deactivation of catalyst and/or

Table 3
Main catalysts for carbon dioxide electrochemical reduction.

Catalyst	Product	Faradaic efficiency (%)	Cell voltage (V vs RHE)	Reference
Metal				
<i>Noble metal</i>				
Au	Carbon monoxide	90	-0.67	Zhu et al. (2013, 2014)
Ag	Carbon monoxide			Hatsukade et al. (2014)
<i>Non noble metal</i>				
Zn	Carbon monoxide	>55		Luo et al. (2019)
Cu	Ethylene, methane, alcohols			Tang et al. (2012)
<i>Oxides</i>				
Cu_2O	Carbon monoxide/ formate	40 %/33 %		Li and Kanan (2012)
Ag_2O	Carbon monoxide			Ma et al. (2016)
SnO_2	Formic acid	87		Li et al. (2017)
TiO_2	Ethanol			Huo et al. (2017)
IrO_2/NiO	Formic acid			Bashir et al. (2015); Jiwanti et al. (2020)
ZnO	CO	91.6		Luo et al. (2020)
Cu_2O	Ethylene	77		Liu et al. (2022)
Bimetallic				
Au-Cu				
Cu-In	Carbon monoxide	90		Rasul et al. (2015)
Cu-Sn/Cu-Pd	Carbon monoxide			Sarraz et al. (2016)
Cu-Ag	Ethylene	76		Jiang et al. (2018)
Au-Pt	Carbon monoxide			Ma et al. (2017)
Au-Pd	Formate			Hahn et al. (2015)
Pd-Pt	Formate	88		Kortlever et al. (2015b)
Cu-Al	Ethylene	80		Zhong et al. (2020)
Cu-Al	Formic acid, carbon monoxide	33–44/17–26		Zeng et al. (2022)
PbCu	Formate	96	-0.8	Li et al. (2022)
Sb SA/NC	Formate	94	-0.8	Jiang et al. (2020)
$\text{ZrO}_2/\text{Cu-Cu}_2\text{O}$	Ethylene	62.5		Guo et al. (2022)
Metal chalcogenide				
Transition metal chalcogenides				
Non-metal				
C tuned by N, F, S, B	Carbon monoxide	up to 85		Wu et al. (2016)
S doped by N	Carbon monoxide			Pan et al. (2019)
Nb-N-C	Carbon monoxide	up to 90		Gao et al. (2022)
Molecular				
Carbon nanotubes	Carbon monoxide	92		Zhang et al. (2017c)
Cu/CeO ₂ nanotubes	Ethylene	78.3	-0.7	Tian et al. (2022)
CR-MOF	Formate	90		Tufa et al. (2020)
$\text{In}_2\text{O}_3@/\text{In-Co PBA}$	Formate	85	-0.96	Zhai et al. (2022)
Covalent organic frameworks	Carbon monoxide			Liu et al. (2018)

degradation of the overall cell. Better stability allows the reduction of maintenance and replacement costs as well as downtime during operation, playing, in this way, an important role in the scale-up of the process (Lin et al., 2020). The electrolyser stability should be investigated at a time scale of thousands of hours of operation.

4. Electrocatalysts for CO₂ reduction

The main catalysts for CO₂ electrochemical reduction are developed to produce CO, formic acid and ethylene, as shown in Table 3, where the main investigated catalysts are those based on metals. A short overview of these used catalysts is here reported.

4.1. Metal catalysts

4.1.1. Noble metals

Several noble metals are used for CO production, as they show good activity and low overpotentials but, they are expensive and are therefore rarely used in catalytic reactions. The main noble metals for CO formation are gold (Au) and silver (Ag) (Tufa et al., 2020). Among them, Au is the most active and investigated metal for the electrochemical conversion of CO₂ to CO and good conditions could be obtained by using a nanostructured morphology that reduces the reaction overpotential significantly (Hansen et al., 2013). Zhu et al. (2013, 2014) found that the highest selectivity of CO₂ reduction to CO is obtained with Au nanoparticles with a size of 8 nm (the measured FE was 90 % at −0.67 V vs RHE).

On the other hand, the metallic Ag has also been suggested due to its lower cost and higher selectivity compared to the Au surface. However, a higher overpotential is needed due to the high activation energy barrier of the initial electron transfer for the stabilization of COOH* intermediate (Rosen et al., 2015). In Hatsukade et al. (2014), the optimal selectivity of CO production from CO₂ER with Ag electrodes was measured at an applied voltage between −1 and −1.2 V vs RHE, with an overpotential in the range of 0.9–1.1 V. This limitation could be overcome by using nanostructured Ag with low coordinate sites that could help the CO₂ activation decreasing the activation energy barrier (Lu et al., 2014). Regarding the selectivity of Ag catalyst, it has been found that facets have also an important role in the selectivity of CO₂ER for CO production better results were obtained on Ag(110) compared to Ag(111) and Ag(100) (Hoshi et al., 1997).

4.1.2. Non noble metals

In addition to noble metals, non noble metals are used for CO production and among them, Zinc (Zn) is an important catalyst due to its intrinsic advantages, such as abundance on Earth, economic viability, and high selectivity for CO production. However, bulk Zn electrodes demonstrate poor performance in CO₂ER, as they generally exhibit low CO partial current density and have considerable overpotentials limiting their application (Hori, 2008). However, porous Zn prepared with an electrodeposition method was able to achieve a FE value higher than 55 % at an overpotential of 0.5 V (Luo et al., 2019). Overall, although Zn is an abundant and low-cost metal, there are few studies on the development of a selective and stable Zn catalyst at low overpotential (Zhang et al., 2018; Quan et al., 2015).

Non noble metals are used for the production of other chemical compounds in addition to CO and among them, Copper (Cu) has been extensively explored in recent decades for CO₂ reduction. This catalyst is able to reduce CO₂ to several chemicals such as ethylene, methane and alcohols, due to the suitable binding strength of intermediates like CO, COH and CHO on its surface during CO₂ reduction (Tang et al., 2012; Peterson and Nørskov, 2012). Cu-based catalysts are extraordinary at converting CO₂ into various forms of liquid and gaseous products: in Kuhl et al. (2012), 16 hydrocarbon and oxygenate products were obtained at different potentials by using a Cu catalyst for CO₂ electrochemical reduction. However, the activity degradation is remaining

challenges for practical application and great efforts are still needed to reduce the overpotential, optimize the selectivity, and stability.

Generally, the surface morphology, size, crystal orientation and roughness of this catalyst could significantly improve activity and selectivity (Ma et al., 2015; Kas et al., 2014; Sen et al., 2014). In Tang et al. (2012), Cu nanoparticles showed an improved selectivity for carbon monoxide and ethylene, especially at lower sizes due to a stronger binding strength for key intermediates as H and COOH. In addition to that, Ma et al. (2017) reported that the length and density of Cu nanowires can tune the selectivity of hydrocarbon products: higher values improve the catalytic selectivity to ethane obtained from the intermediate (CH₃CH₂O) or CH₃ dimerization. On the other hand, the importance of roughness is reported by Sen et al. (2014): a high surface roughness enhances the production of HCOOH, H₂ and CO while a small amount of C₂H₄, C₂H₆, CH₄ and C₃H₆ was detected. Another factor influencing the final product formation is the crystal orientation of the Cu surface. Hori et al. (1995) found that Cu (100) favors ethylene production while Cu (111) promotes CH₄ formation.

4.1.3. Metal oxides

Metal-oxide-based electrocatalysts have gradually got attention due to their decent energy efficiency and selectivity for CO₂ electroreduction, although the instability is still a big problem. The use of metal oxide was an attempt to enhance the CO₂ adsorption to the electrode surface facilitating the C-C coupling, so that the HER is suppressed and a better selectivity is obtained (Jiwanti et al., 2021). In addition, metal oxide could also stabilize the intermediate for CO₂ products (Chu et al., 2018). For these reasons, different oxide derived metals have been investigated for the electrochemical reduction of CO₂. The main analyzed metal oxides are those based on the main investigated metals, as below described.

Li and Kanan (2012) studied the electrochemical reduction of CO₂ on Cu₂O obtaining CO and HCCOH with a FE of 40 % and 33 % respectively at −0.5 V vs RHE. The reduction reaction was favored by the formation of CO₂ intermediate and by the high density of grain boundary surfaces providing active sites. In this context, Frese et al. (1991) reported an enhanced methanol production directly on Cu₂O catalysts in comparison to the standard bulk Cu. Good performances are reported in other works: the same catalyst achieved a maximum C₂⁺ Faradaic efficiency of 77.0 ± 0.3 % at a conversion rate of 513.7 ± 0.7 mA/cm² in a neutral electrolyte (Liu et al., 2022).

Another analyzed catalyst is the oxide derived Au nanocatalyst, producing CO with 96 % of FE and only 0.24 V of overpotential (Chen et al., 2012). Here, better performances are associated with the high density of grain boundaries (Feng et al., 2015).

Ag₂O is another oxide derived metal used for CO₂ER to CO production (Ma et al., 2016): the catalyst is able to produce CO with 80 % of FE at an overpotential of 0.49 V. In this case, a better performance compared to the polycrystalline form is due to the stability of the *COOH intermediate.

SnO₂ is a metal oxide used for the electrochemical reduction of CO₂ to formic acid with 87 % of efficiency at 0.88 V of overpotential in Li et al. (2017). Other similar catalysts are TiO₂ (Huo et al., 2017) for ethanol production, IrO₂ (Jiwanti et al., 2020) and NiO (Bashir et al., 2015) for formic acid formation.

ZnO-derived catalysts are highly selective and stable, showing a selectivity to CO higher than 90 % and more than 18 h stability (Luo et al., 2020). The great potential of ZnO-derived catalysts for industrial applications was demonstrated in a flow reactor, where 91.6 % Faradaic efficiency for CO at a current density of 200 mA/cm² can be achieved at −0.62 V vs. RHE.

4.2. Bimetallic catalysts

Bimetallic catalysts have been investigated in the literature for CO₂ER to minimize costs and improve performances. The introduction

of another element affects the electronic structure of the host materials, which can modulate the binding strength of intermediates with the metal surface.

The most investigated are those based on Cu. Kim et al. (2014) studied an Au-Cu catalyst finding different product distributions at different compositions, due to the changed degree of stabilization of intermediates at the catalyst surface. On the other hand, the use of a Cu-In catalyst was proposed by Rasul et al. (2015) for CO production with 90 % of FE at 0.39 V of overpotential. Among these class of catalysts, Cu-Sn and Cu-Pd have been investigated for CO₂ER to CO showing a higher catalytic selectivity at a lower overpotential (Sarfratz et al., 2016; Li et al., 2016a). In addition, Ren et al. (2016) prepared a CuZn catalyst finding that the increase of Zn improves the selectivity towards ethanol production (29.1 % of FE for ethanol was measured at −1.05 V vs RHE on Cu₄Zn). Moreover, Jiang et al. (2018) found that Cu-Ag was able to achieve 76 % of FE for ethylene and other C₂⁺ products. On the other hand, Zhong et al. (2020) described that Cu-Al electrocatalysts, identified using density functional theory calculations in combination with active machine learning, efficiently reduce CO₂ to ethylene with a high Faradaic efficiency (80 %). The same catalyst was investigated to reduce CO₂ to CO and formic acid by Zeng et al. (2022); nanostructured Cu-Al materials were able to convert CO₂ to CO and HCOOH with good efficiency. The catalysts were synthesized via a green microwave-assisted solvothermal route, and were composed of Cu₂O crystals modified by Al. Other, Cu-based bimetallic catalysts have been investigated. In Li et al. (2022), the as-prepared Pb single-atom alloyed Cu catalyst (Pb₁Cu) exhibited near unity selectivity towards HCOOH and impressive stability, providing the prospect of industrial production of HCOOH from CO₂.

Non-Cu binary catalysts have been proposed in the literature for the electrochemical reduction of CO₂ and among non-Cu binary catalysts, AuPt, AuPd and Pd-Pt have been mostly investigated. Ma et al. (2017) found that in the AuPt catalyst an increase in selectivity and activity for CO formation is due to the electronic effect of Au content. In Hahn et al. (2015) it is reported that AuPd showed more activity and selectivity for formate production while both pure Au and Pd metals had negligible amounts of the same compound. For the same product, Kortlever et al. (2015b) obtained a high FE (88 %) at −0.4 V vs RHE by using a Pd₇₀-Pt₃₀ binary catalyst.

Other bimetallic catalysts have been studied for CO₂ER. Jiang et al. (2020) discovered that an Sb single atom (SA) material consisting of Sb-N₄ moieties anchored on N-doped carbon (NC) nanosheets (named Sb SA/NC) could serve as a CO₂RR catalyst to produce formate with high efficiency. Sb SA/NC exhibited a formate Faradaic efficiency of 94.0 % at −0.8 V vs. RHE. As additional catalyst, the bimetallic Cu–Zr catalyst (denoted as ZrO₂/Cu-Cu₂O) with a Cu/Zr molar ratio of 7/1 could achieve a 62.5 % Faradaic efficiency of ethylene with a high current density of 24 mA/cm² at −1.28 V (vs. RHE) in 0.1 M KCl electrolyte (Guo et al., 2022).

4.3. Metal chalcogenide catalysts

Transition metal chalcogenides (TMC) have been investigated for CO₂ER for their abundance and easy synthesis method and their performance is strongly related to active edge sites that can control the reaction selectivity. Among these metals, WSe₂, MoSe₂, WS₂, and MoS₂ NFs exhibited more than 90 % of CO selectivity with current densities above 130 mAcm^{−2} (Xu et al., 2017). Edges sites can be increased through the doping of transition metals (Ta, Nb, etc.), reducing the binding energy of intermediates and enhancing the product formation (Abbasi et al., 2017).

4.4. Non-metal catalysts

Non-metal catalysts have been considered for CO₂ER due to the low cost and easy structural modifications for a better activity and selectivity

(Sun et al., 2016; Wang et al., 2016). Among these catalysts, the most commonly used are doped carbon catalysts, in fact, pure carbon catalysts are not promising due to their very low ability to adsorb CO₂ intermediates. However, their efficiency can be improved with the tuning of heteroatoms such as nitrogen (N), fluorine (F), sulfur (S) and boron (B) (Tufa et al., 2020). In this context, Wu et al. (2016) reported up to 85 % of FE at −0.47 V vs RHE for CO production by using graphene foam catalyst doped by N, which creates lower energy for *COOH intermediates, more favorable for CO formation. Moreover, Srekanth et al. (2015) used boron-doped graphene for the electrocatalytic reduction of CO₂ to formic acid obtaining a FE of 66 % at an overpotential of −1.4 V vs. RHE. In addition, B and N doped nanodiamond enabled a 93.2 % of selectivity towards ethanol at −1 V vs RHE (Liu et al., 2017). Another investigated non-metal catalyst is the S, N doped nanoporous carbon material, which showed a good CO production efficiency (selectivity 91 % at a current density of 2 mA/cm²) (Li et al., 2016b; Pan et al., 2019). On the other hand, the Nb-N-C atomic catalyst demonstrated aqueous CO₂ER activity with CO Faradaic efficiency up to 90 % (Gao et al., 2022). Other metal free catalysts for CO₂ER are: g-C₃N₄/MWCNTs, CN-MWCNT, C-NF for CO production with a selectivity of 89.6 %, 70 %, 70 % and 90 % (Xie et al., 2018; Lu et al., 2016b; Zhong et al., 2017; Pan et al., 2019).

4.5. Molecular catalysts

Molecular catalysts are other promising solutions for the CO₂ electrochemical reduction because improved performances can be obtained by tuning the ligand position with advanced organic synthesis methods (Elgrishi et al., 2017). However, molecular catalysts generally have low stability with a lifetime of a few hours, and their recyclability deserves attention as well (Zhang et al., 2019).

Different molecular catalysts have been investigated in the literature and the most commonly used materials are carbon nanotubes (CNT), metal organic frameworks (MOFs), covalent organic frameworks (COFs). Among them, carbon nanotubes substrate bearing Cobalt(II) phthalocyanine (CoPc) efficiently catalyzed the reduction of CO₂ to CO with a FE of 92 % at −0.63 V vs. RHE (Zhang et al., 2017c). Similarly, Choi et al. (2019) developed a 3D Fe-porphyrin graphene hydrogel (FePGH) for an efficient electroreduction of CO₂ to CO achieving a FE up to 95 % at 0.39 V vs RHE. In Tian et al. (2022) hollow Cu/CeO₂ nanotubes synthesized via the self-templated method displayed a high faradaic efficiency of 78.3 % for the electrochemical reduction of CO₂ into ethylene in flow cell at a low applied potential of −0.7 V vs. RHE

Metal organic frameworks have received huge attention as catalysts for CO₂ER, due to their topology and structure that can be tuned at a molecular level (Tufa et al., 2020). The copper rubeanate MOF (CR-MOF) showed an excellent activity with a potential of 0.2 V and high selectivity of HCOOH (90 %) at −1.6 V vs. RHE. In Zhai et al. (2022), In₂O₃@In-Co PBA exhibited excellent performances with Faradaic efficiency of 85 % for formate at a potential of −0.96 V vs. RHE and with current density of 31.5 mA/cm² at −1.32 V vs. RHE, surpassing most of the reported indium-based catalysts.

In addition, amine linkage covalent organic frameworks can improve the reaction process increasing the CO conversion efficiency from 13 % to 53 % at −0.70 V and from 43 % to 80 % at −0.85 V in comparison with bare Ag electrode (Liu et al., 2018).

Other molecular catalysts for CO₂ER are: Co-phthalocyanine, perfluorinated cobalt phthalocyanine, PorCu, ZnPor, Fe triphenyl porphyrin and CoPc-py/CNT for CO production (Zhang et al., 2018; Maurin and Robert (2016); Morlanés et al., 2016; Weng et al., 2016; Wu et al., 2017) and Ir Pincer for formate production (Kang et al., 2014).

4.6. New insights for electrocatalysts

New research has led to new efficient catalysts with high selectivity and durability. Nam et al. (2023) synthesized the TA-ZnS electrocatalyst

(a Zn-based material) that is able to achieve around 83 % of CO Faraday efficiency under the potential of -1.9 V vs Ag|AgCl, in stable conditions and repressing the hydrogen evolution reaction. The size and morphology of the catalyst have an important role in the overall efficiency and recent studies showed that considering nano-sized materials instead of macro-sized ones increase the number of superficial active sites so that metal nanoparticles, nanocubes and nanostructured (layered double hydroxides, MOFs, etc.) catalysts have been investigated (Serafini et al., 2023). Progress has also been carried out in the design and development of nanostructured Cu, Cu-based complexes (including nonmetallic elements), Cu-based bimetallic catalysts (including Cu and other metals), and carbon-based Cu-free catalysts for the production of C_2 and C_{2+} at high activity and selectivity (Chen et al., 2021). New strategies to improve activity and selectivity has been figured out. In Zeng et al. (2023) coating a hydrophobic polymer polytetrafluoroethylene on Cu, the Faradaic efficiency to ethylene production increases and achieves a value of 70.2 % due to a stronger CO_2 adsorption and CO^* binding. Moreover, in Zeng et al. (2022), the addition of Sb on Cu allows to reduce energy barriers for the formation of key intermediate, improve CO desorption and stabilize Cu surface for the catalyst, ensuring selectivity and activity for CO production.

Recent studies have been conducted on proposing porous metal oxides as catalysts for CO_2 ER due to their better performances on mass transfer and lifetime. New insights have been achieved understanding the relation between different factors (e.g. material composition, phase transition, structural change during the reaction, etc.) encouraging their use for the electrochemical reduction of CO_2 (Zhang et al., 2023).

5. Electrolysers for CO_2 reduction

CO_2 ER cells are classified in batch or continuous operation. Continuous cell reactors can be classified as basic, proton exchange membrane, microfluidic and solid oxide electrolysers and each of them is characterized by advantages and disadvantages as described below. Overall, flow continuous reactors (basic, proton exchange membrane, microfluidic) have different configurations in the gas diffusion electrode, influencing physical characteristics and performance. In particular, the microfluidic reactor has current density and mass transport higher than proton exchange membrane and basic schemes but, with a lower efficiency on the separation of products. In addition, among all flow reactors, only solid oxide electrolysers work at high temperatures (up to 1000 °C) ensuring high current density and an operation at a larger scale, against other configurations working at ambient temperature and with a lower technology readiness level (TRL).

5.1. Electrolyser reactors

CO_2 can be fed into the electrolytic cell as a gas phase or dissolved in an electrolyte to be reduced at the catalyst surface. Among these two options, practical limitations such as low solubility (30 mM in H_2O at 1 bar) and diffusivity, make the option of aqueous CO_2 reduction commercially unviable (Hernandez-Aldave and Andreoli, 2020; Weiss, 1974). However, the increase of pressure or the reduction of temperature could improve technical performance but, hamper commercial viability. On the other hand, in the first case, gas diffusion electrodes (GDEs) are used, allowing a higher current density due to high CO_2 mass transport and reduced diffusion lengths, which could ensure the scale-up and commercialization. In addition, this kind of system is characterized by a simple cell design and a higher resistance towards the metallic contamination present in electrolytes (Liu et al., 2019). However, GDEs have limited durability with performance degrading after several operating hours and a poor stability is due to the weak mechanical adhesion between each element and catalyst deactivation (Birdja et al., 2019; Burdyny and Smith, 2019; Yang and Li, 2021).

Generally, a GDE is composed of a gas diffusion layer (GDL), which is a porous structure between a catalyst layer (CL) and a gas flow channel.

Inside this structure, the GDL offers abundant CO_2 supply to the catalyst with a much shorter diffusion pathway and at the same time, due to its low resistance, allows the transportation of electrons, protons and products from the CL to the electrolyte (Ma et al., 2021). In particular, the hydrophobic (avoiding the penetration of electrolyte into the gas flow channel and blocks reactions causing flooding phenomena) GDL can be a single macroporous layer or substrate, or a double layer (consisting of a microporous layer with carbon fiber to suppress electrolyte flooding and a macroporous layer with carbon powder working as a gas diffuser). Regarding this last option, a schematic diagram of a GDE with a double layer is reported in Fig. 3: the gas flow channel is in contact with the macroporous layer, at the top of which the microporous layer is present with the catalyst layer and after, the electrolyte.

The operating principle of a liquid-feed and gas-feed CO_2 electrolyser is shown in Fig. 4.

In the first case there is a diffusion-limited problem because, a diffusion layer of 50 μm is produced during the operation: CO_2 diffuses from the electrolyte bulk to the electrode surface where catalytic nanoparticles are supported on a solid non porous substrate. On the other hand, in the gas-feed electrolyser, CO_2 diffuses from the bulk of GDE to the catalytic layer, producing a shorter diffusion layer of 50 nm near the catalyst. This causes a CO_2 concentration gradient delivering CO_2 to the catalyst in a faster way compared to the first case: the transportation of CO_2 on the catalyst is facilitated and higher catalytic surface areas are ensured, allowing higher current density and lower overpotential but similar selectivities compared to the previous case (Jiang et al., 2018; Dinh et al., 2018; Jeon et al., 2018; Hoang et al., 2018). Moreover, the shorter diffusion path ensures the CO_2 -saturated electrolyte layer on the catalyst, preventing the HER and avoiding the reaction of CO_2 with the hydroxide in the electrolyte (Seifitokaldani et al., 2018).

Generally, according to the operation, CO_2 electrolysers are structured as H-cells or flow cells if a batch operation or a continuous operation is respectively present. A comparison between the two kinds of systems is reported in Table 4.

5.1.1. H-type electrochemical cell reactors

A schematic diagram of an H-type electrochemical cell, commonly used in the lab-scale, is reported in Fig. 5a. In this scheme, two compartments, called sections or chambers and representing the anode and cathode, are connected by an ion-exchange membrane, providing an H shape. In the cathode, a reference and working electrode are inserted: the former ensures the possibility of potential control, while in the latter the CO_2 reduction occurs. In the anode, a counter electrode is present allowing voltage or current control (Endrodi et al., 2017). As additional element of the H-cell scheme, a capillary tube or a glass frit is used to feed CO_2 in the cathode through bubbles on the working electrode. Moreover, a gas chromatographer (GC) measures gas phase compositions at the outlet while liquid products are identified through a proton nuclear magnetic resonance (PNMR) or a high-performance liquid chromatography (HPLC).

Despite some advantages (ease of assembly, facile modification and reproducibility, low costs), there are some disadvantages of this batch reactor type such as: mass transport limitations, poor mixing, high cell electrical resistance, low CO_2 conversion and current density and metallic contamination present in the electrolyte that all contribute to ensure a low system efficiency (Hernandez-Aldave and Andreoli, 2020; Senocrate and Battaglia, 2021; Hori, 2008). However, H-cell reactors are convenient for a small scale and can be used for experiments in the lab.

The limitations of H-cell electrolysers are overcome by flow cell reactors, characterized by a higher mass transfer and mixing, better control of temperature, heat and electrolyte residence time, so that they are more suitable for the industrial scale (Hernandez-Aldave and Andreoli, 2020; Bevilacqua et al., 2015; Weekes et al., 2018). Then, the thermodynamics and kinetics are improved in continuous reactors due to a higher CO_2 concentration on the catalyst surface, a shorter transmission

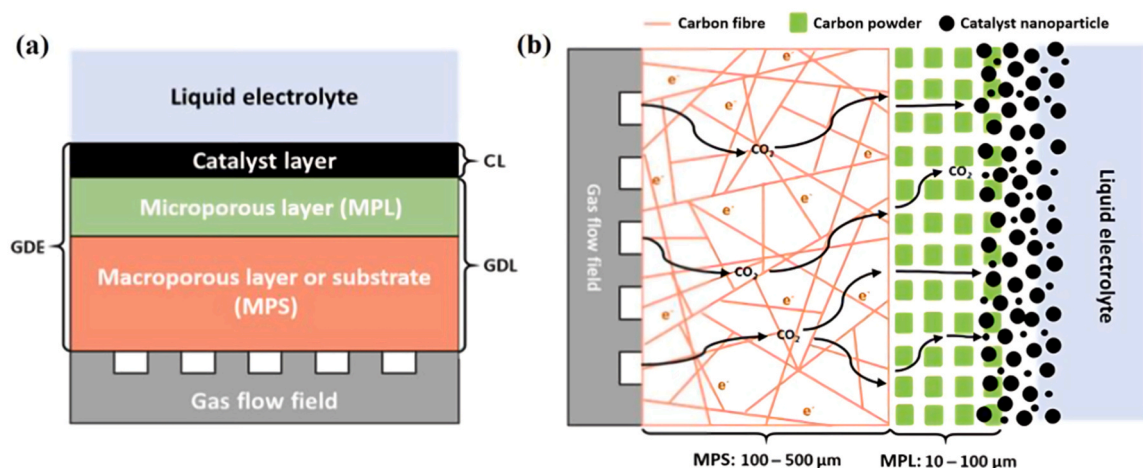


Fig. 3. Schematic diagram of GDE with a double layer: a) stacked structure; b) elements on it (Hernandez-Aldave and Andreoli, 2020).

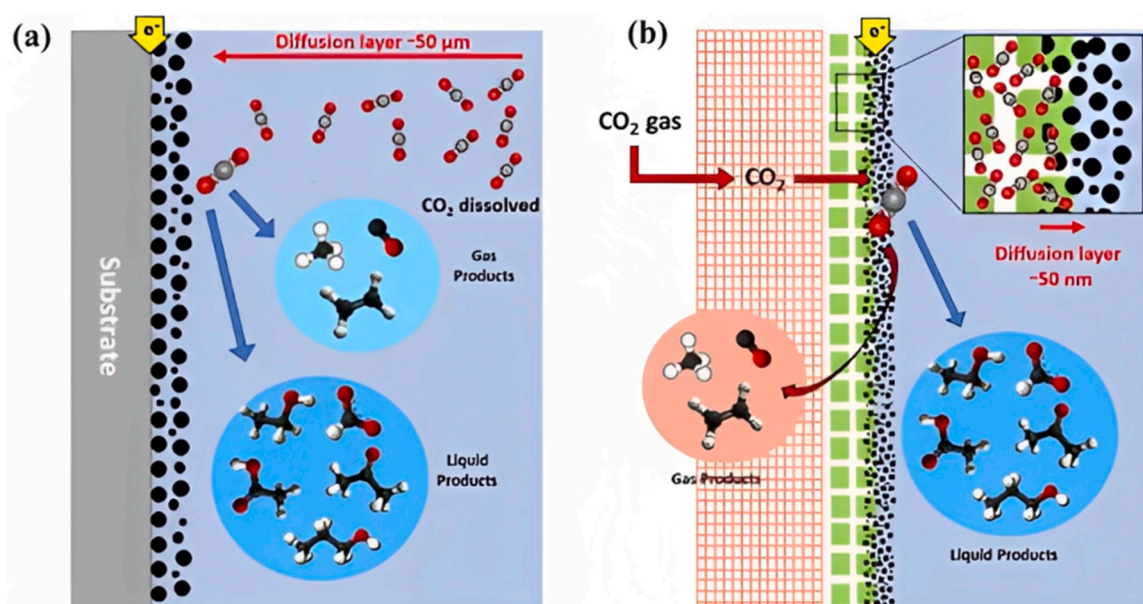


Fig. 4. Operating principle of (a) liquid-feed and (b) gas-feed CO_2 electrolyser (Hernandez-Aldave and Andreoli, 2020).

path and a suitable gas diffusion layer (Ma et al., 2021).

5.1.2. Flow cell reactors

Generally, unlike a batch H-cell reactor, a flow cell electrolyser can work without a reference electrode or seldom with two reference electrodes to monitor the electrode potential of both half-cells (Endrodi et al., 2017).

Flow cell reactors are classified into basic flow, polymer electrolyte membrane (PEM), micro-fluid and solid oxide (SOE) electrolyser.

The basic reactor is so-called because other configurations are derived from it. A schematic diagram of a basic gas feed flow cell reactor is reported in Fig. 5b, where three different compartments are present: one for the CO_2 gas flow, one for the catholyte and the other one for the anolyte, each of which is fed by a pump to ensure a constant flow. In this scheme, cathode and anode channels are separated by an ion-exchange membrane to avoid the crossover of products between the compartments. The cathode compartment and CO_2 flow channel are divided by a GDE, while a traditional non-porous electrode is used in the anode section and a reference electrode is inserted in the cathode section.

There are two ways for CO_2 to reach the catalyst layer in a basic flow cell reactor: flow-by and flow-through (Duarte et al., 2019; Park et al.,

2021; De Mot et al., 2020). In the first case, CO_2 , flowing alongside the electrode reaches the catalyst by diffusion, establishing CO_2 and product gradient concentrations inside the GDE. On the other hand, in the second case, CO_2 is forced to flow with diffusion and convection through the GDE, causing the formation of gas bubbles in the catholyte resulting in an ohmic drop. In this way, CO_2 and product gradient concentrations are not produced in this option but, electrolyte crystallization (crystallization of hydroxide and bicarbonate salts) in the porous layer of the GDL is reported (Hernandez-Aldave and Andreoli, 2020). For this last reason, the flow-by case is suitable for long-term operations.

In PEM electrolyzers, also called membrane electrode assembly (MEA) electrolyzers, a GDE is used as anode and cathode, both separated by an ion-exchange membrane, as illustrated in Fig. 5c. The stack GDE/membrane/GDE is known as membrane electrode assembly and polymer electrolyte membranes can be: cation exchange membranes (CEMs), anion exchange membranes (AEMs) or bipolar membranes (BPMs) (Weekes et al., 2018; Endrodi et al., 2017). In this scheme, overall, anode and cathode are composed of a GDE, current collector and flow plate. Hence, unlike the basic flow cell configuration, in this case, the catalyst layer is in contact with the membrane and so no liquid electrolyte is used and no separation is present between electrode and

Table 4
Description of electrolyzers for CO₂ electrochemical reduction.

Reactor configuration		Characteristics	Advantages	Drawbacks
Batch reactor	H-cell	Two chambers separated by an ion-exchange membrane, with a reference, working and counter electrode	Convenient in lab-scale experiments	Poor mass transfer and mixing
			Suitable for the study of half-cell reactions	High cell resistance
Flow reactor	Basic	- A compartment for the CO ₂ gas flow, anolyte and catholyte. - Anode and cathode sides are separated by an ion-exchange membrane. - A gas diffusion electrode in the cathode. - A reference electrode in the cathode side	Possibility screening of electrocatalysts	Low CO ₂ conversion and current density
			Commercial available	Metallic contamination from electrolytes
			Easy of assembly and reproducibility	Not easy identification of liquid products
			Low costs	Difficulty to use in large-scale application (limited electrode surface area and large distance between electrodes)
	PEM	- A gas diffusion electrode for the anode and cathode sites separated by an ion-exchange membrane. - No liquid electrolyte and separation between gas diffusion electrodes and membrane. - No reference electrode (A working and counter electrodes are used)	Mass transport and mixing better compared to the H-cells	High cell voltage and low energy efficiency
			Current density and Faradaic efficiency higher compared to the H-cells	The way to supply CO ₂ to the catalyst is critical
			Potential for industrial applications	Cell design is critical
	Microfluid	- Two gas diffusion electrodes separated by a thin layer of electrolyte with a micro-reference electrode	Diffusion path shorter than that of H-cells	High Ohmic drop and low energy efficiency
			Relatively easy scale-up and pressurization	pH imbalance between anode and cathode favoring the HER
			Existing know-how (similarity to water electrolyzers)	Cost and stability of membranes
SOE	- A cathode, an anode and a solid-oxide electrolyte	Mass transport and mixing better than the H-cells	Drying of membranes	
		Potential for industrial applications	Additional resistance or product crossover due to membrane	
		Cell resistance an Ohmic loss lower compared to the basic cell (higher energy efficiency)	Strong corrosion at high overpotential	
		Compact structure		
SOE	- A cathode, an anode and a solid-oxide electrolyte	Reduced risk of catalyst poisoning due to impurities in the electrolyte		
		Current density and mass transport higher than PEM	Less effective separation of products from electrodes	
		Fast screening of catalysts	Lower liquid product concentration	
		Better control of flooding at electrodes	Not easy pressurization	
SOE	- A cathode, an anode and a solid-oxide electrolyte	Decrease of ohmic losses	Possibility of product re-oxidation	
		Avoidance of high membrane cost		
		Flexibility in operating conditions		
		Less decrease of pH		
SOE	- A cathode, an anode and a solid-oxide electrolyte	Longer operation times (about 500 h)	High operating temperatures (500–1000 °C)	
		Decrease in overpotential	Specific electrodes are needed	
		Increase in charge transfer	Impurities of gas feed cause the electrode passivation	
		High current density due to high temperatures	Carbon deposition	
SOE	- A cathode, an anode and a solid-oxide electrolyte	Commercial scale only for CO production	Metal particles oxidation	
			Cell degradation	
				Low current efficiency

membrane (this is referred to as a ‘zero-gap’ arrangement). This configuration decreases cell resistance and ohmic losses compared to the basic configuration (Ma et al., 2021).

A PEM reactor works without a reference electrode, but only with a counter and working electrodes (Liang et al., 2020). The main disadvantage of this reactor configuration is that the finite ion transport rates across the membrane can induce a significant pH imbalance between catholyte and anolyte, favoring the hydrogen evolution reaction and not CO₂ reduction (Endrodi et al., 2017). Other problems of a PEM electrolyzer are the drying of the ion-exchange membrane with a detrimental effect on the ion transport capabilities, the cost and stability of membranes (Nwabara et al., 2020; Sánchez et al., 2019). On the other hand, advantages of this reactor configuration are: relatively easy scale-up and pressurization being similar to PEM water electrolyzers, the possibility of different configurations with a straightforward stack construction, the existing know-how due to similarities with water electrolyzers and the reduced risk of catalyst poisoning due to impurities in the electrolyte (Sánchez et al., 2019; Ma et al., 2021).

To further decrease the cell potential, microfluidic reactors have

been developed (Lin et al., 2020). The use of a microfluidic reactor for CO₂ reduction has been proposed by Whipple et al. (2010), while other studies are about the screening of electrocatalysts and operating conditions (Sánchez et al., 2019). Fig. 5d shows a schematic diagram of a microfluidic electrolyzer for CO₂ reduction: two electrodes as GDEs are separated by a thin layer (< 1 mm) of a liquid electrolyte in a laminar flow (Liang et al., 2020; Weekes et al., 2018). In this scheme, the catalyst on the cathode side favors the CO₂ reduction while the catalyst on the anode side promotes the oxygen evolution reaction (Ma et al., 2021). In addition, the electrolyte can be managed in order to change operating conditions and water management issues (cathode flooding and anode dry-out) (Liang et al., 2020).

Compared to a traditional PEM, this configuration ensures a higher current density because it eliminates problems related to the mass transfer and neutralization between catholyte and anolyte caused by crossover or mixing (Park et al., 2021). Moreover, unlike the other reactors, this configuration works without a membrane, relying on the diffusion of the gaseous products to divide reduction and oxidation products (Weekes et al., 2018). For this reason, there is a less effective

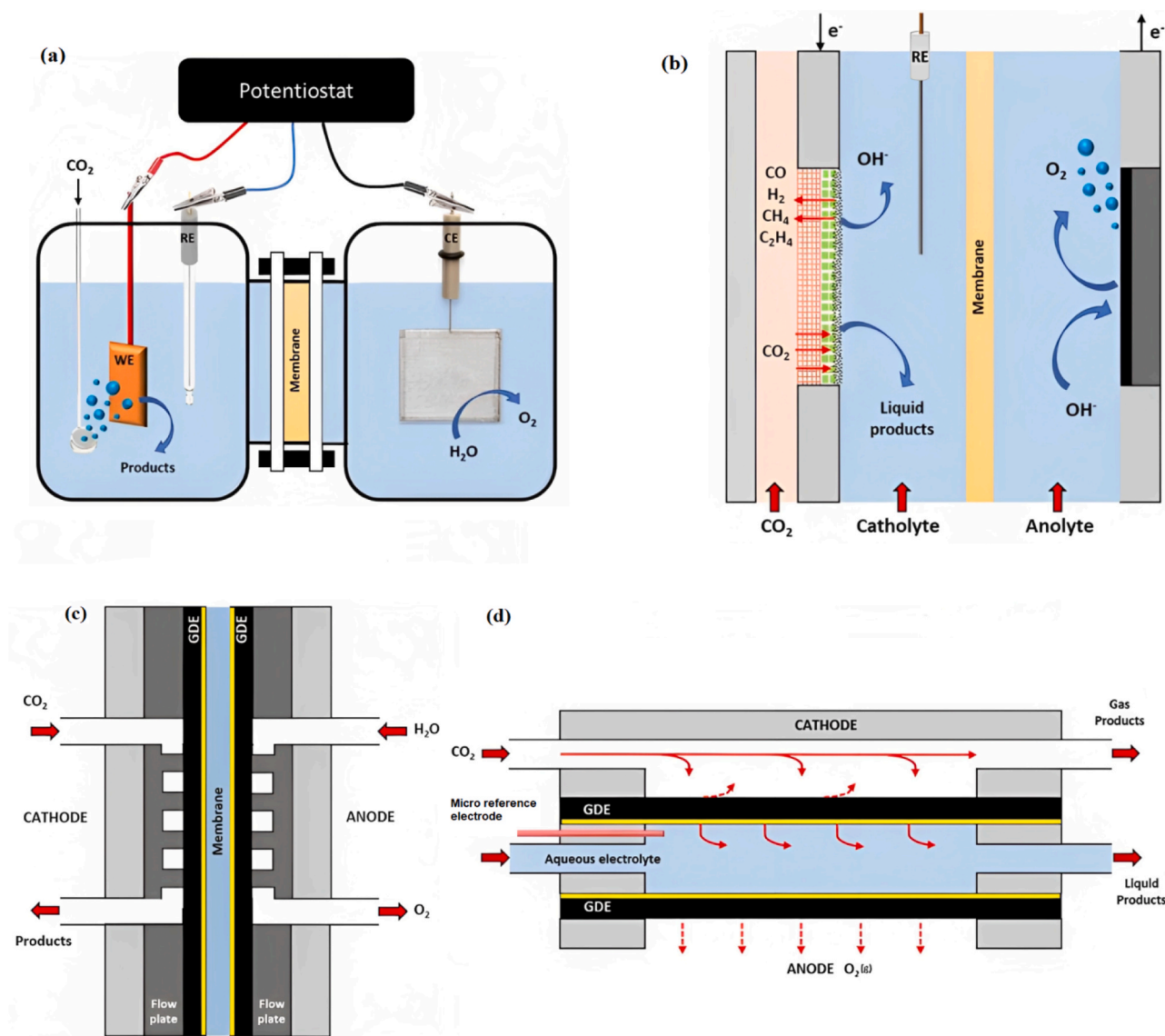


Fig. 5. Schematic diagram of a) H-cell electrolyser, b) basic gas feed flow cell electrolyser, c) polymer electrolyte membrane electrolyser, d) microfluid electrolyser (Hernandez-Aldave and Andreoli, 2020).

separation of products from electrodes and the possibility of product crossover, potentially decreasing energy efficiency and productivity (Sánchez et al., 2019; Yang and Li, 2021).

A micro reference electrode is inserted in the electrolyte allowing the measurement of individual electrode potential while, the pressure sensitivity (i.e. difficulty in pressurisation) of microfluidic cells limits their potential industrialization and scale-up (Hereijgers et al., 2016). Some advantages are the fast screening of catalysts under various operating conditions, better control of flooding at electrodes and the decrease of ohmic losses by working without a physical barrier as a membrane (Sánchez et al., 2019; Lin et al., 2020; Leonard et al., 2020). The use of a costly membrane is also avoided (Ma et al., 2021), while ongoing challenges for this kind of reactor is a dual electrolyte system to improve performances and avoid the crossover from cathode to anode of liquid products that could be oxidized (Lu et al., 2016a).

In SOEs, electrodes and electrolytes are in the solid phase (the second one is a layer of solid oxide). SOEs have been investigated for CO₂ reduction since last decades due to the high temperature operation (500–1000 °C), longer operation times (about 500 h), decrease in overpotential, increase in charge transfer and the possibility of CO₂ and H₂O co-electrolysis (Bidrawn et al., 2008; Sánchez et al., 2019). Higher

temperatures could ensure high current density due to the improved kinetics (Zhang et al., 2017a).

Generally, the solid electrolyte can be oxygen ion conducting or proton conducting. In the former case, the electrolyte transports oxygen ions formed at the cathode, through the CO₂ reduction, to the anode where are oxidized to oxygen gas. On the other hand, in the second case, the water is oxidized in the anode, producing oxygen and protons that cross through the protonic conductor layer and react with CO₂ in the cathode (Zhang et al., 2017b).

Carbon deposition, metal particles oxidation, and cell degradation are potential problems of this process (Zhang et al., 2017b), as also reported in reviews on CO₂ reduction using SOEs conducted by Zhang et al. (2017a). The first commercial plant based on a SOE cell for CO₂ reduction was proposed by Haldor Topsoe: the plant is able to produce 10–100 Nm³/h of high purity CO (Küngas et al., 2017). SOE cells are unique to have a commercial scale but only CO is obtained: no catalysts have been developed for the production of other compounds.

New insights are present for flow cell reactors. Regarding the electrolytic cell design, several novel flow channel design, such as spiral flow channel, corrugated flow channel, bionic flow channel, and multiple flow channel combinations, have been suggested to improve the

uniformity of the fluid flow distribution, enhancing local mass transfer, CO₂ conversion with reduced pressure drop (Yuan et al., 2023). Improvements on GDE engineering have been achieved by proposing MOF-modified GDEs that are able to increase CO₂ concentration near the catalytic active site, thereby enhancing CO₂ER performances. In the work conducted by Nam et al. (2022), the use of a GDE structure of C/Cu/MOF/PTFE allows to have 48 % of ethylene selectivity at a production rate of 1000 mA/cm² and not the same selectivity on the C/Cu/PTFE GDE at a production rate of 400 mA/cm².

5.2. Future perspectives of electrolyser reactors

CO₂ gas feed flow electrolysers with GDE, ensuring higher current densities, have a greater potential for future developments, although more is needed to understand and do to make CO₂ER industrially viable (Jhong et al., 2013). Future research should be focused on the scalability of these kinds of reactors, material and system design as well as on operating conditions (Vennekoetter et al., 2019; Pérez-Rodríguez et al., 2016).

New GDE materials and configurations are needed in order to ensure industrial operations (current densities above 1 A/cm², Faradaic efficiency higher than 80 %, cell potential lower than 3 V and time operations more than 30,000 h) (Jouny et al., 2018). The material properties of each element of a GDE have an effect on the transportation of reactants and products inside the electrolyser, influencing their accumulation or depletion and then the performance of the cell (Liu et al., 2019).

A trade-off between porosity, hydrophobicity (water management), components and structure of GDE as well as feed should be evaluated to avoid electrolyte flooding and electrolyte deposition respectively in the flow-by and flow-through configurations. Focusing the attention on the GDE, the GDL is an important component of the electrolyser, and it is necessary to further study the integration with the catalyst layer to improve CO₂ reduction performance. The developing of super-hydrophobic GDL materials to replace the commonly used carbon fiber GDL to maintain its stability can be a future focus.

Other important points to be considered and improved in future studies are the following: production rate, stability, CO₂ utilization efficiency, energy efficiency, liquid product cross-over (Yang and Li, 2021). In this context, strategies that increase the current density could improve production rates. Approaches to reduce the CO₂ cross-over (bicarbonates produced at the cathode site and migrated to the anode) are required to decrease downstream separation costs and improve the membrane stability. As additional future studies, in order to achieve long term operation, it is important to discover a catalyst that is stable for the extended use or that can be regenerated at a low cost. Regarding catalysts, strategies on introducing active sites such as defects engineering (e.g., grain boundary, heteroatom doping, anion vacancies, etc.), and surface engineering (e.g. size effect) can facilitate the reaction process. In addition, catalysts with a CO₂ adsorption capacity improving the mass transfer and increasing conversion efficiency are suggested for future research. It is also important to have a stable membrane that can remain undamaged by swelling and/or dehydration. For example, a membrane with a polymer matrix mixed with nanofillers could allow high ion mobility and mechanical stability (Tufa et al., 2020). The electrolyte is an important factor to be considered in order to increase the efficiency of CO₂ER systems: the exploration of an acidic electrolyte or ionic liquid-based electrolyte to avoid crystallization and precipitation of inorganic salts is suggested (Yuan et al., 2023).

Among electrolysers using GDEs, PEMs are the most promising for practical applications analyzing carefully current density, Faradaic efficiency, energy efficiency and stability (Gao et al., 2021). A PEM electrolyser is, in fact, used to produce jet fuel by the Twelve company (Twelve, 2021). It is evident that with continued in-depth research and development to optimize and improve the electrolyser configuration, industrial scale CO₂ electrolysis for clean fuel and value-added

chemicals will be realized in the near future (Ma et al., 2021).

6. Economic profitability of CO₂ER process

6.1. Literature studies

Economic analyses about the CO₂ electrochemical reduction to different compounds have been carried out in the literature, as reported in Table 5. These analyses are based on different assumptions and so there is a difficulty with comparing the results directly, however, among different products, only CO, formic acid and oxalic acid are the most economically viable products but only under certain conditions.

An economic analysis for the electrochemical process producing CO has been conducted by Lee et al. (2021), proposing a new cell that, without a catholyte compartment, enables reduction of Ohmic losses and energy consumption. The authors found a production cost (584 \$/tonCO) lower than that obtained by the methane steam reforming and suggested by the market (600 \$/tonCO) and better conditions are ensured by increasing the current density and energy efficiency.

In Xing et al. (2023), it is reported that the production cost for CO and formate for the eCO₂RR process is about 378 \$/ton_{product}, which is much lower than the cost of a CO₂ utilisation plant (835 \$/ton_{product}) but higher than that of conventional fossil fuel-derived technology at 315 \$/ton_{product}.

Orella et al. (2020) performed an economic study to evaluate the production cost of CO, formate, methane, ethylene and ethanol. Assuming an electricity cost of 0.03 \$/kWh, only CO has a production cost lower than the current selling price.

The best conditions for CO and formic acid production via CO₂ER are underlined in the work of Jouny et al. (2018). Here, among propanol, formic acid, CO, ethanol, ethylene, methanol, only CO and formic acid have a positive Net Present Value (NPV) in all analyzed cases and assumptions, although the electricity price has the highest impact on it.

A more detailed analysis was conducted by Rumayor et al. (2019a) evaluating the economic feasibility of formic acid production via CO₂ electrochemical reduction and comparing it with the conventional route (hydrolysis of methyl formate). Results show that the alternative production way is suggested only with favorable (lower cost of renewable energy and emission trading systems) and optimal operating (100 % of FE, current density of 300 mA/cm²) conditions and not under the current market conditions. Moreover, a Faradaic efficiency of 90 % could decrease the operating costs from 1.62 \$/kg of formic acid to 0.19 \$/kg of formic acid, while the lowest operating cost obtained for the conventional route is 0.24 \$/kg of formic acid.

At the same value of Faradaic efficiency (with an energy conversion efficiency of 70 % and electricity price of 0.04 \$/kWh), a promising production cost of formic acid (108 \$/ton vs 570 \$/ton of the traditional route) was reported by De Luna et al. (2019) through the use of an electrolyser system.

A favorable price was reported by Boor (2020), for oxalic acid production via CO₂ electrochemical reduction. Based on many simplifications and assumptions (Faradaic efficiency of 80 % and a current density of 120 mA/cm²) the suggested cost is 0.87 \$/ton of oxalic acid compared to 1 \$/ton of oxalic acid that is the market value. Here, the Faradaic efficiency and current density are the most important parameters that make the process unviable.

In particular conditions, ethylene and ethanol may have a production cost lower than the market price. In Kibria et al. (2019), a CO₂ cost of 40 \$/ton, an electricity cost of 0.02 \$/kWh, a cell voltage of 1.8 V, a Faradaic efficiency of 90 % and a current density of 500 mA/cm² ensure a convenient price for CO, formate, ethylene and ethanol.

Despite the results of the previous research, a few positive results have been reported in the literature through an economic analysis of the CO₂ER process for formic acid production by Agrawal et al. (2011) and Norouzi et al. (2021). In the former study, a negative NPV is reported over a 10 year lifespan, if the CO₂ price is ignored. In the second case

Table 5
Literature studies about the economic analysis of CO₂ER.

References	Parameter evaluated in the economic analysis	CO ₂ based-product	Comparison with the conventional process	Parameters assumed in the economic analysis	Results
Pappijin et al. (2020)	Capex, Opex, Gross margin	Ethylene	Yes (conventional process: steam cracking of naphtha)	Selectivity = 70 %, Conversion = 50 % CO ₂ = -30 euro/metric ton Electricity = 35 euro/MWh, production = 10 ⁵ Metricton/year	CO ₂ ER has a higher CAPEX and OPEX, but a lower gross margin vs the conventional route
Spurgeon and Kumar (2018)	Production cost	(1) CO and subsequent Fischer–Tropsch conversion of syngas to diesel fuel (CO ₂ –CO–FTL) (2) ethanol in one step (CO ₂ –C ₂ H ₅ OH) (3) CO and subsequent reduction to ethanol in two steps (CO ₂ –CO–C ₂ H ₅ OH) (4) formic acid (CO ₂ –HCOOH)	Yes	(1) cell voltage = 1.8 V, current density = 400 mA/cm ² , FE = 98 % (2) cell voltage = 2.3 V, current density = 250 mA/cm ² , FE = 28 % (3) cell voltage = 1.8 V, current density = 400 mA/cm ² , FE = 98 % (4) cell voltage = 3.5 V, current density = 140 mA/cm ² , FE = 94 %	production cost of (1) 18.9 \$/gge vs 2.12–3.19 \$/gge of the market value production cost of (2) 55.3 \$/gge vs 2.1–2.55 \$/gge of the market value production cost of (3) 49.8 \$/gge vs 2.1–2.55 \$/gge of the market value production cost of (4) 1.16 \$/kg vs 0.4–0.6 \$/kg of the market value
Rumayor et al. (2019a)	NPV	Formic acid	Yes (conventional process: hydrolysis of methyl formate)	Current density = 200 mA/cm ² , Cell potential = 4.3 V FE = 42.3 %, Formic acid = 21 w/w % Current density = 300 mA/cm ² , Cell potential = 1.48 V FE = 100 %, Formic acid = 85 w/w %	CO ₂ ER has a NPV < 0 vs 16.9 M€ of the conventional route
Lee et al. (2021)	Production cost	CO	Yes (conventional process: steam methane reforming)	Cell potential = 2.2 V, FE = 93.2 %, current density = 209.7 mA/cm ²	CO ₂ ER has a production cost of 584 \$/tonCO vs 600 \$/tonCO of the market value
Herron and Maravelias (2016)	Production cost	Methanol	Yes	Current density = 33 mA/cm ² , FE = 60 %	CO ₂ ER has a production cost of 5.79 \$/kg vs 0.44 \$/kg of the market value
Adnan and Kibria (2020)	Levelized production cost	Methanol	Yes	Current density = 0.3 A/cm ² , Cell voltage = 2.5 V, CO ₂ conversion = 50 %, Faradaic efficiency = 50 %	CO ₂ ER to methanol is competitive with the market only in optimal operating conditions
Moreno-Gonzalez et al. (2021)	Production cost	Syngas	Yes (conventional process: reverse water gas shift)	Current density = 0.2 A/cm ² , FE to CO ₂ = 95 %, FE to H ₂ = 5 %, cell voltage = 3 V	CO ₂ ER has a production cost of 1.3 \$/kg vs 1.1 \$/kg of the conventional route
Orella et al. (2020)	Production cost	CO, Formate, Methane, Ethylene, Ethanol	Yes	Electricity cost = 0.03 \$/kWh	In the CO ₂ ER only CO have a lower cost than that of the market
Rumayor et al. (2019a)	Utility costs	Formic acid	Yes (conventional process: hydrolysis of methyl formate)	FE = 90 %	In the CO ₂ ER the cost of utilities ranged between 0.16 €/kg and 1.40 €/kg of FA vs 0.21–0.43 €/kg of FA of the conventional route
Kibria et al. (2019)	Production cost	CO, Formate, Ethanol, Ethylene	Yes	CO ₂ cost = 40 \$/ton, electricity cost = 0.02 \$/kWh, cell voltage = 1.8 V, FE = 90 %, current density = 500 mA/cm ²	The CO ₂ ER route has a production cost lower than that of the market
De Luna et al. (2019)	Production cost	Ethylene, CO, Formic acid	Yes (conventional process: fossil fuel derived)	FE = 90 %, electricity cost = 0.04 \$/kWh, energy efficiency = 70 %	Production cost of ethylene in CO ₂ ER is 1100 \$/ton vs 600–1300 \$/ton of the conventional route Production cost of CO in CO ₂ ER is 200 \$/ton vs 150 \$/ton of the conventional route Production cost of formic acid in CO ₂ ER is 108 \$/ton vs 570 \$/ton of the conventional route

(continued on next page)

Table 5 (continued)

References	Parameter evaluated in the economic analysis	CO ₂ based-product	Comparison with the conventional process	Parameters assumed in the economic analysis	Results
Boor (2020)	Production cost	Oxalic acid	Yes	Current density = 120 mA/cm ² , FE = 80 %	In CO ₂ ER the production cost is of 0.87 \$/ton vs 1 \$/ton of the market value
Xing et al. (2023)	Production cost	CO, formate	Yes		CO and formate have a production cost of 378 \$/ton, lower than that of CO ₂ utilization plant (835 \$/ton) but higher than that of conventional plant (315 \$/ton)
Norouzi et al. (2021)	Exergo-economic	Formic acid	No	Anode = IrO ₂ Current density = 140 mA/cm ² FE = 94 % Cell voltage = 3.28 V	Exergy rate cost and flow rate cost of 0.21 \$/kWh and 2.280 × 10 ⁻² \$/s.
Agarwal et al. (2011)	NPV	Formate/Formic acid	No		NPV < 0 over a 10 lifespan
Jouny et al. (2018)	NPV	Propanol, Formic acid, CO, Ethanol, Ethylene, Methanol	No	Current density = 200 mA/cm ² , cell voltage = 2.3 V, selectivity = 90 %, electricity price = 0.05 \$/kWh, lifetime = 20 year, production rate = 100 ton/day, CO ₂ price = 70 \$/ton Current density = 300 mA/cm ² , cell voltage = 2 V, selectivity = 90 %, electricity price = 0.03 \$/kWh, lifetime = 20 year, production rate = 100 ton/day, CO ₂ price = 40 \$/ton	Only CO and Formic acid have NPV > 0 Propanol, Formic acid, CO, Ethanol, Ethylene have NPV > 0

study, an exergo-economic analysis was carried out considering different anolyte solutions (DSA/O₂, IrO₂, KOH, Amberlite IR120) for the cell: the use of an IrO₂ anode decreases the exergy rate cost and the flow rate cost to 0.21 \$/kWh and 2.280 × 10⁻² \$/s.

In Spurgeon and Kumar (2018) the following routes were analyzed: (i) CO via CO₂ER and subsequent Fischer–Tropsch conversion of syngas to diesel fuel (ii) ethanol in one step via CO₂ER (iii) CO via CO₂ER and subsequent reduction to ethanol (iv) formic acid via CO₂ER. However, under specific assumptions all production routes were not competitive with the traditional ones due to the high values of capital costs influenced by the current density, Faradaic efficiency, and cost per electrode area.

Other CO₂-based compounds have been analyzed from an economic point of view, showing their non favorable production of this innovative route.

CAPEX, OPEX and gross margins (e.g. the difference between revenues and feedstock cost) for ethylene production were evaluated by Pappijin et al. (2020). The CO₂ER route was compared with the traditional way of ethylene production via the steam cracking of naphtha in different case studies (high selectivity, high conversion, high CO₂ value, free electricity and current operating conditions). Results show that the electrochemical process has higher CAPEX, caused by the expensive electrode materials combined with limited economies of scale due to the modular character of the electrochemical cells.

Another compound obtained from CO₂ER is methanol. Herron and Maravelias (2016) found a production cost of 5.79 \$/kg of methanol, which is 13 times higher than the industrial selling price (0.44 \$/kg of methanol). The main cost is the solar electricity for the electrolyser (63 % of the total cost). In the process, the Faradaic efficiency is 60 % and the current density is up to 33 mA/cm². Adnan and Kibria (2020) reported that only in optimistic scenario, methanol production via CO₂ER is competitive with the market ensuring a production cost of 430 \$/ton.

Higher production costs for syngas production via CO₂ER were obtained in the work of Moreno-Gonzalez et al. (2021). The authors found a price of 1.3 \$/kg of syngas compared to 1.1 \$/kg of syngas when the reverse water gas shift is used despite a high value of Faradaic efficiency for CO.

Some of the above discussed works have been conducted at the lab-scale with relatively low current density and low energy efficiency. Then, there is the need in future research to understand the operation of CO₂ electrolysis at industrial scale with higher current densities and using CO₂ streams with impurities (SO_x, NO_x, etc.) (Somoza-Tornos et al., 2021). Moreover, due to the high variabilities in the production cost reported by different studies there is the need to further examine the assumptions used for the techno-economic assessment.

6.2. Economic analysis

An economic analysis, evaluating the production cost of the main CO₂-based products discussed in Section 2, is reported here for an economic screening, suggesting more promising compounds in comparison with the market price. The economic analysis was conducted considering the scheme for a CO₂ER plant at a large-scale proposed by Jouny et al. (2018), with the aim to have an estimation of the production cost at the industrial level.

For this reason, in this analysis, the current density, Faradaic efficiency, cell potential difference and CO₂ conversion were fixed as in Jouny et al. (2018), where current values of these parameters are proposed. Then, these figures of merit are assumed constant for all products, as reported in the literature in Jouny et al. (2018). According to this work, the cell works with alkaline conditions, because these conditions are used by the best bench scale CO₂ electrolyser. Moreover, the use of nonprecious metals at the anode allows a comparison with alkaline water electrolyzers. For these reasons, the current density was set at 0.3 A/cm² for all products, while the cell voltage is different for each

Table 6

Levelized costs of products obtained via CO₂ER at different electricity costs (Park et al., 2021) and comparison with the market price (Jouny et al., (2018), Methanex (2021), Global Petrol Price (2021), Factiva (2021)) (current density 0.3 A/cm², Faradaic efficiency 90 %, CO₂ conversion 50 %).

	Electricity from biomass (\$/kWh) 0.078 Levelized cost (\$/kg)	Electricity from geothermal (\$/kWh) 0.087 Levelized cost (\$/kg)	Electricity from hydro (\$/kWh) 0.056 Levelized cost (\$/kg)	Electricity from PV (\$/kWh) 0.081 Levelized cost (\$/kg)	Electricity from wind offshore (\$/kWh) 0.136 Levelized cost (\$/kg)	Electricity from wind onshore (\$/kWh) 0.063 Levelized cost (\$/kg)	Electricity from fossil fuels (\$/kWh) 0.213 Levelized cost (\$/kg)	Market price (\$/kg)
Pure CO	0.74	0.79	0.61	0.75	1.07	0.65	1.57	0.72
Formic acid	0.76	0.79	0.68	0.77	0.97	0.71	1.24	0.88
Methanol	1.54	1.65	1.25	1.57	2.31	1.34	3.32	0.62
Methane	3.29	3.56	2.55	3.37	5.19	2.78	8.05	2.02
Ethylene	2.99	3.24	2.33	3.06	4.71	2.54	7.29	1.02
Ethanol	1.98	2.12	1.58	2.02	3.00	1.70	4.37	0.77
Propanol	2.30	2.47	1.85	2.35	3.48	1.99	5.04	1.71

Table 7

Levelized costs of products obtained via CO₂ER for 2050 at different electricity costs (IEA, 2021) and comparison with the market price (Irena and methanol institute (2021), Gorre et al. (2019), Neuwirth and Fleiter (2020)) (current density 2 A/cm², Faradaic efficiency 90 %, CO₂ conversion 70 %).

	Electricity from PV (\$/kWh) 0.022 Levelized cost (\$/kg)	Electricity from wind offshore (\$/kWh) 0.045 Levelized cost (\$/kg)	Electricity from wind onshore (\$/kWh) 0.039 Levelized cost (\$/kg)	Electricity from fossil fuels (\$/kWh) 0.105 Levelized cost (\$/kg)	Market price (\$/kg)
Pure CO	0.34	0.47	0.43	0.84	-
Formic acid	0.52	0.59	0.57	0.80	-
Methanol	0.71	1.00	0.92	1.79	0.25–0.63*
Methane	1.23	1.97	1.76	4.09	0.89–2.32
Ethylene	1.12	1.78	1.59	3.69	0.88–3.73**
Ethanol	0.85	1.25	1.14	2.30	-
Propanol	1.01	1.47	1.34	2.67	-

* renewable methanol

** including production via steam cracker, electrolysis, methane pyrolysis

case study and about 2 V. In addition, Faradaic efficiencies of 90 % have been demonstrated for numerous CO₂ reduction products and were assumed for these cases. The CO₂ conversion was set at 50 % because it could be achieved by a well-designed electrolyser.

The economic analysis was conducted for a system producing 100 ton/day of a product as in large-scale chemical production, with a process scheme consisting of an electrolyser unit, a gas separation unit (PSA) and a distillation unit when CO₂ liquid products are considered. These assumptions are based on a developed scheme reported in the literature (Jouny et al., 2018): in particular, capital costs were evaluated as in Jouny et al. (2018) while operating costs were according to the Peter and Timmerhaus (1991) method (the methodology is reported in more detail in the Supplementary Material).

Results are reported in Table 6, where levelized costs based on different electricity sources (from biomass, geothermal energy, hydro energy, PV, wind offshore, wind onshore and fossil fuel that are renewable and non renewable sources) are compared with the market

Table 8

Factors chosen for the global sensitivity analysis for each product obtained via CO₂ER.

	Factor	Distribution type	Lower bound	Upper bound
1	Electricity price from biomass (\$/kWh)	Uniform	0.058	0.285
2	CO ₂ price (\$/ton)	Uniform	15	25
3	Faradaic efficiency (%)	Uniform	80	100
4	CO ₂ conversion (%)	Uniform	30	70
5	Current density (A/cm ²)	Uniform	0.1	0.5
6	Electrolyser cost (\$/m ²)	Uniform	549	2198

price: only CO and formic acid show some promising conditions through their electrochemical production at the current operating conditions.

In fact, for both products, the production cost is lower than that of the market (0.72 \$/kg of CO and 0.88 \$/kg of formic acid) in all cases with the exception when electricity from offshore wind energy and fossil fuels are used (CO production via CO₂ER by using electricity from offshore wind energy is 1.07 \$/kg of CO and 1.57 \$/kg of CO is fossil fuel is used as electricity source; formic acid production via CO₂ER by using electricity from offshore wind energy is 0.97 \$/kg of formic acid and 1.24 \$/kg of formic acid if electricity from fossil fuels is used). CO production cost via CO₂ER with electricity from biomass, geothermal energy, hydro energy, PV and onshore wind energy is respectively of 0.74 \$/kg of CO, 0.79 \$/kg of CO, 0.61 \$/kg of CO, 0.75 \$/kg of CO and 0.65 \$/kg of CO. Formic acid production cost via CO₂ER with electricity from biomass, geothermal energy, hydro energy, PV and onshore wind energy is respectively of 0.76 \$/kg of formic acid, 0.79 \$/kg of formic acid, 0.68 \$/kg of formic acid, 0.77 \$/kg of formic acid, 0.71 \$/kg of formic acid. On the other hand, methanol, methane, ethylene, ethanol, and propanol productions via CO₂ER are not economically favorable compared to the market in all investigated cases.

The same analysis is reported for the future (considering a 2050 scenario). In this case, the electrolyser capital cost was assumed to be 4080 \$/m² (IRENA, 2020). For operating conditions, the current density was set at 2 A/cm² while, CO₂ conversion at 70 % (IRENA, 2020; Jouny et al., 2018). The input CO₂ price was reduced to 11 \$/ton from the current 25 \$/ton (METI, 2021). Other assumptions were unchanged. Results are reported in Table 7 (for some products the future market price is missing in the existing literature).

A comparison between Tables 5 and 6 shows that in the future the

Table 9

Total Sobol sensitivity index of each factor for each product obtained via CO₂ER (1 = Electricity price from biomass; 2 = CO₂ price; 3 = Faradaic efficiency; 4 = CO₂ conversion; 5 = Current density; 6 = Electrolyser cost).

	Carbon monoxide	Ethanol	Ethylene	Formic acid	MeOH	Methane	Propanol
Stot[1]	0.8057	0.9018	0.9049	0.8089	0.9043	0.9075	0.9016
Stot[2]	1.43·10 ⁻⁵	2.67·10 ⁻⁶	5.46·10 ⁻⁶	1.76·10 ⁻⁶	2.51·10 ⁻⁶	3.10·10 ⁻⁶	2.70·10 ⁻⁶
Stot[3]	0.0513	0.0609	0.0598	0.0510	0.0603	0.0617	0.0609
Stot[4]	0.1306	0.0200	0.0184	0.1296	0.0193	0.0114	0.0200
Stot[5]	0.0108	0.0145	0.0143	0.0096	0.0136	0.0159	0.0147
Stot[6]	0.0061	0.0082	0.0080	0.0054	0.0077	0.0089	0.0082

production cost of compounds from CO₂ER decreases. Moreover, methane and ethylene could be also competitive with the market due to a lower cost compared to the expected range. The lowest expected cost of methane from CO₂ER is 1.23 \$/kg of methane while for ethylene the lowest expected cost from CO₂ER is 1.12 \$/kg of ethylene.

For the same systems analyzed above for the current economic screening, a global sensitivity analysis (with the methodology reported in the [Supplementary Material](#)) was conducted in order to find significant factors for the total levelized cost. For the sensitivity analysis, the considered factors are the electricity price (from biomass), CO₂ price, Faradaic efficiency, CO₂ conversion, current density and electrolyser cost that with a uniform distribution have upper and lower bounds as in [Table 8](#). The upper and lower bounds for the electricity price are set according to [Park et al. \(2021\)](#), the CO₂ price is reported as in [IEA \(2021\)](#) while, the range of other inputs was set as in [Jouny et al. \(2018\)](#).

The results are reported in [Table 9](#), showing the total order Sobol sensitivity index value for each factor and each CO₂-based product. A value higher than 0.05 makes the input significant for the total levelized cost ([Zhang et al., 2015](#)) so that the electricity price and Faradaic efficiency influence the cost in all products. CO₂ conversion is significant only for the cost of CO. Due to a higher value of the index, the electricity price has the highest influence on the production cost and therefore its reduction reduces significantly total costs. Economic incentives and political actions should be done with the aim to reduce the electricity price allowing the economic profitability of this new carbon dioxide conversion process. In addition, continuous research is required to improve the selectivity (in terms of Faradaic efficiency) and CO₂ conversion with the aim to decrease production costs.

7. Life cycle assessment of CO₂ER process

7.1. Literature studies

The LCA of the CO₂ electrochemical reduction has been reported in several studies, as documented in [Table 10](#). Different methodologies were used and different assumptions were made during the modelling stage, so that different results were obtained among the considered studies.

Most of the environmental investigations consider formic acid and formate production and improved performances compared to the conventional route are obtained especially when renewable electricity and optimal conditions are implemented.

In [Banu et al. \(2023\)](#) a LCA (cradle-to-gate) for formic acid production was carried out considering experimental lab data in the inventory. Results are respectively 3.27 kgCO_{2eq}, 4.28·10⁻³ kgSO_{2eq}, 2.12·10⁻² kgP_{eq}, 3.85·10⁻¹¹ kgCF_{11eq} and 8.35 m³ for climate change, terrestrial acidification, freshwater eutrophication, ozone depletion and water depletion for 1 kg formic acid produced.

In [Thonemann \(2020\)](#), a LCA for formic acid production was conducted and compared to the traditional CO₂ hydrogenation route. Results show that hydrogenation performs better in most indicators, but the investigated alternative route is promising in terms of climate change and human health when the German electricity grid or electricity from wind energy are used.

However, [Rumayor et al. \(2019b\)](#) found that only the renewable

electrical energy pathway is able to ensure a global warming potential (GWP) and abiotic depletion potential (ADP) value lower than that of the conventional route. The cradle-to-gate analysis was conducted using the GaBi tool with the CML2001 methodology.

Overall, optimal operating conditions allow better environmental performances in formate production via CO₂ER. In [Dominguez-Ramos et al. \(2015\)](#) the first LCA study on the CO₂ER to formate is reported. Here, a very optimistic scenario (Faradaic efficiency of 100 %, extractive distillation and solar energy) reduces CO₂ emissions up to 41 % compared to the conventional process, although the current state of technology is not suggested from an environmental point of view.

Also, [Paulillo et al. \(2021\)](#) developed a LCA of CO₂ER with ionic liquid ([P66614][124Triz]), at a lab scale. The authors found that the recycling rate of unreacted reagents is the most important parameter and only with its value of 99.9 % the electrochemical reduction of CO₂ to formate can be competitive with the traditional process, based on the hydrolysis of methyl formate.

Another product investigated for the LCA is ethylene oxide in [Rondin et al. \(2022\)](#): negative emissions of up to -0.5 kgCO_{2eq}/kg_{product} were obtained under optimized process conditions regarding energy and conversion efficiency and using biogenic CO₂. In contrast, emissions exceeded the fossil benchmark when the European grid mix was applied.

Other non-comparative LCA studies about formic acid production through the CO₂ER have been carried out by [Thonemann and Schulte \(2019\)](#) and [Norouzi et al. \(2021\)](#). In the former, the authors, analyzing different reactor configurations, found that the flow-through reactor has a GWP value lower than that of the batch reactor and three-compartment cell. In the second, an exergo-environmental analysis was conducted considering different anolytic solutions (DSA/O₂, IrO₂, KOH, Amberlite IR120). Results show net negative CO₂ emissions in all investigated cases.

In addition to formic acid and formate, other compounds are obtained by CO₂ electrochemical reduction and their production has been analyzed using LCA.

Among ten potential products (carbon monoxide, formic acid, formaldehyde, methane, methanol, ethylene, ethane, ethanol, oxalic acid, and propanol) according to [Rob et al. \(2020\)](#), carbon monoxide, formic acid, formaldehyde, and n-propanol are attractive as they give both positive specific GHG reduction and positive gross operating margin (e.g. revenues less direct operating costs), based on the current market in South Korea.

With the aim to improve the electrochemical process performance, [Yu et al. \(2021\)](#) compared the simple CO₂ electrochemical reduction to formate and CO with the bi-carbonate conversion to the same products. Results show a lower environmental impact for the second mentioned option (total GHG emissions for formate and CO production from bi-carbonate are respectively -0.5238 and -0.6287 tonCO_{2eq}/tonCO₂ injection of carbon-based fuels).

Ethylene production has been investigated by [Khoo et al. \(2020\)](#) and [Pappijn et al. \(2020\)](#). In [Khoo et al. \(2020\)](#) small and large-scales are considered with a functional unit of 1 gr and 1 ton of ethylene, respectively. Results show a GWP of 0.98–3.7 grCO_{2eq} for the small-scale setup and 0.65–3.0 tonCO_{2eq} for the large-scale model. On the other hand, in the second research, an environmental analysis was conducted considering energy consumption and electricity emission factors (which for

Table 10
LCA literature studies on CO₂ER.

References	LCA typology	Used software	CO ₂ based product	Functional unit	Comparison with the conventional route	Assumed parameters	Results
Thonemann (2020)	Cradle-to-gate		Formic acid	1 kg of formic acid	Yes (conventional route: CO ₂ hydrogenation)		The hydrogenation performs better in most indicators, but the electrochemical route shows promising results in terms of impacts on climate change and human health. These results are valid when electricity is taken from Germany grid or wind energy.
Dominguez-Ramos et al. (2015)	Cradle-to-gate		Formate	1 kg of HCOO-	Yes (Conventional route: From formic acid or sodium formate)		Better performance of CO ₂ ER only with optimistic conditions (100 % FE, extractive distillation, and a solar photo-voltaic-powered electrolyzer) (GWP 41 % lower than that of the conventional process)
Kibria Nabil et al. (2020)	Cradle-to-gate		Carbon monoxide, formic acid, methane, methanol, ethylene, ethanol, n-propanol, acetic acid	1 kg of product (but 1 kg CO + 0.216 kg H ₂)	Yes (Conventional route: thermochemical and incumbent processes)	FE = 90 % Electricity emission factor = 0.17 kgCO _{2eq} /kWh	Syngas, ethylene, and n-propanol are the most compelling products in terms of GWP
Pappijn et al. (2020)	Cradle-to-gate (but no separation and purification)		Ethylene	1 ton ethylene	Yes (Conventional route: naphtha cracking)	Ideal electrolyzer (100 % of conversion and selectivity) Electricity emission factor for natural gas, solar, wind = 490, 48, 12 kgCO ₂ /MWh	The electroreduction of CO ₂ needs to be powered by green electricity in order to obtain an overall negative net CO ₂ balance.
Rumayor et al. (2019b)	Cradle-to-gate	GaBi	Methanol	1 kg of methanol	Yes (Conventional route: from natural gas and direct CO ₂ hydrogenation)	FE = 45.7 %, Current density = 6.93 mA/cm ² , Overall cell voltage = 2.335 V	Worse conditions in terms of GWP for CO ₂ ER due to the high steam required in the distillation section (methanol purification)
Rumayor et al. (2019a)	Cradle-to-gate	GaBi	Formic acid	1 kg of formic acid	Yes (Conventional route: hydrolysis of methyl formate)	FE = 90 %	GWP, ADP fossil are lower than conventional route only with electricity from renewable energy
Paulillo et al. (2021)	Cradle-to-gate	Gabi	Formate	1 kg of formate	Yes (Conventional route: via hydrolysis of methyl formate obtained from fossil fuels)	FE = 95 %	The recycling rate of unreacted reagents is the most significant parameter. The system needs to attain a 99.9 % recycling rate to be competitive with the conventional process
Wyndorps et al. (2021)			Ethylene	1 kg of ethylene	Yes (Conventional route: via hydrogenation reaction)		CO ₂ ER to ethylene could reduce GHG emissions over the H ₂ -based pathway by up to 44 %
Rodin et al. (2022)	Cradle-to-gate	Gabi	Ethylene oxide	1 kg of ethylene oxide	Yes	Cell voltage up to 10 V, current density of 150–200 mA/cm ² , cell area = 300 cm ²	Negative emissions of up to –0.5 kg CO _{2eq} /kg product are obtained under optimized process conditions regarding energy and conversion efficiency and using biogenic CO ₂
Khoo et al. (2020)	Cradle-to-gate		Ethylene	1 gr/1 ton ethylene	No		With the use of renewable energy sources to power CO ₂ ER processes, a potential net 0.98–3.7 g CO _{2eq} is achievable in the small-scale setup; 0.65–3.0 tCO _{2eq} is achievable in the large-scale model

(continued on next page)

Table 10 (continued)

References	LCA typology	Used software	CO ₂ based product	Functional unit	Comparison with the conventional route	Assumed parameters	Results
Roh et al. (2020)	Cradle-to-gate		Carbon monoxide, formic acid, formaldehyde, methane, methanol, ethylene, ethane, ethanol, oxalic acid, and propanol	1 ton of the main product and X ton of oxygen as byproduct	No		Carbon monoxide, formic acid, formaldehyde, and n-propanol are attractive products as they give both positive specific GHG reduction and positive gross operating margin.
Thonemann and Schulte (2019)	Cradle-to-gate	openLCA	Formic acid	1 kg of formic acid	No	FE = 90 % Total cell voltage = 3.5 V Current density = 2.5 kA/m ²	GWP of batch reactor and three-compartment cell configurations are higher than those of the flow-through reactor
Yue et al. (2021)	Cradle-to-gate	openLCA	Formate and CO	1 ton CO ₂ injection of carbon-based fuels	No		The (b)carbonate-to-chemicals process can obtain more positive environmental impacts compared to gaseous CO ₂ -to-chemicals conversion.
Norouzi et al. (2021)	Cradle-to-gate		Formic acid		No		Negative net CO ₂ emission for all analyzed cases and a reduction of resources consumption
Banu et al. (2023)	Cradle-to-gate	GaBi	Formic acid	1 kg of formic acid	No		3.27 kgCO _{2eq} (climate change), 4.28•10 ⁻³ kgSO _{2eq} (terrestrial acidification), 2.12•10 ⁻² kgP _{eq} (freshwater eutrophication), 3.85•10 ⁻¹¹ kgCFC-11 _{eq} (ozone depletion), 8.35 m ³ (water depletion)

Northwestern Europe, for natural gas, solar and wind are equal to respectively 490, 48, and 12 kg CO_{2eq}/MWh). Results show that only with renewable electrical energy the alternative production route is competitive with the traditional one based on cracking of naphtha. However, CO₂ emissions related to the product separation and purification steps are not taken into account in this calculation.

A LCA on carbon monoxide, formic acid, methane, methanol, ethylene, ethanol, propanol and acetic acid production was conducted by Nabil et al. (2021) considering a single or two steps (CO₂ to CO in solid oxide electrolysis cell followed by CO electroreduction in the alkaline flow cell) of CO₂ electroreduction. The system boundaries involve CO₂ capture, conversion and product separation (without considering the disposal of products). A lower environmental impact is present in the two-step route and CO, ethylene, n-propanol are the most compelling products in terms of GWP. Here, the environmental analysis was done evaluating the energy consumption and considering an electricity emission factor.

Worse conditions were obtained for methanol production via CO₂ER in Rumayor et al. (2019b), due to the high steam requirement in the distillation section because no process integration is considered, although solar electricity is used. 949 tonCO_{2eq}/ton methanol are emitted by the electrochemical system.

According to the above literature analysis, further research should be performed to determine which method is more suitable for the assessment of CO₂ER. The number of analyzed indicators is scarce: the GWP is widely used by the LCA community, so that future studies should tackle the inclusion of a combination of midpoint and endpoint indicators. A clearer system boundary should be defined for a better comparison of this research and, as for the economic analysis, studies at a large-scale are useful.

7.2. Environmental analysis

A LCA for the main CO₂-based products obtained via the electrochemical reduction is reported here and the analysis was conducted according to four phases: goal and scope definition, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation (ISO 14040, 2009; ISO 14044, 2006). Among these phases, goal and scope definition, LCI and LCIA stages are discussed in the Supplementary Materials, while the interpretation phase as a discussion of results is reported in this section.

Results are shown in Fig. 6 where the climate change impact is reported for the electrochemical processes at different electricity sources (wind and solar energies and mix grid, this last with a carbon intensity of 0.0935 kgCO_{2eq}/MJ, located in the UK) and for the conventional processes taken from SimaPro, based on the Ecoinvent database (Ecoinvent, 2018) (the combustion of heavy heating oil for carbon monoxide, direct hydration of ethylene for ethanol, steam cracking of hydrocarbons for ethylene, hydrolysis methyl formate for formic acid, up grading of biogas for methane, reforming of natural gas for methanol, catalytic hydrogenation of propionaldehyde for propanol).

For the CO₂ feedstock two different values (-0.5 kgCO_{2eq} and -0.8 kgCO_{2eq} per kg of CO₂) of carbon footprint were taken into account (Nabil et al., 2021).

7.2.1. LCA results for formic acid

From the reported results, it is evident that the production of formic acid through CO₂ER is always promising compared to the conventional route also when electricity from mix grid is used for the electrolyser due to a lower value of climate change impact. For the CO₂ feedstock with a carbon footprint of -0.5 kgCO_{2eq}/kgCO₂ the climate change impact for formic acid production via electrochemical reduction is 31.7 kgCO_{2eq}/ton of formic acid, 283 kgCO_{2eq}/ton of formic acid and 1970 kgCO_{2eq}/ton of formic acid when wind, solar energies and grid are respectively used.

On the other hand, for a CO₂ feedstock with a carbon footprint of

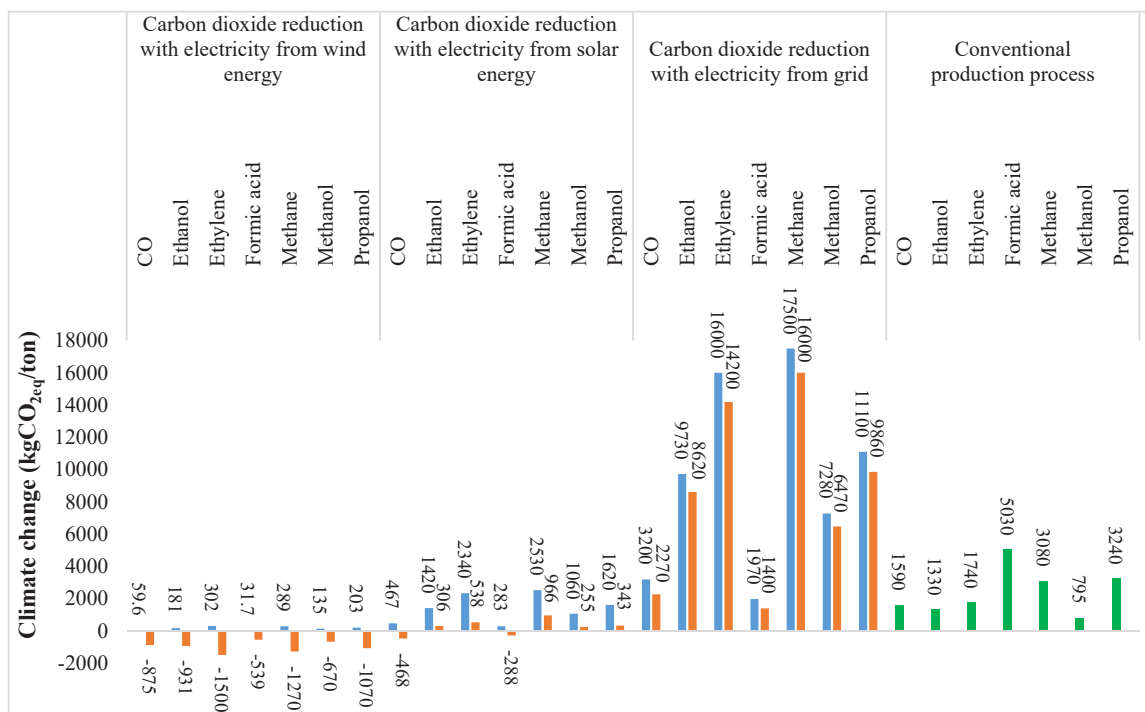


Fig. 6. Climate change impact for products obtained via CO₂ER at different electricity sources and carbon footprints of CO₂ with a comparison with the conventional process (blue bar=carbon footprint of CO₂: $-0.5 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$; orange bar= carbon footprint of CO₂: $-0.8 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$).

$-0.8 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$ the climate change impact for the innovative formic acid production is $-539 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of formic acid, $-288 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of formic acid and $1400 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of formic acid when wind, solar energies and grid are respectively used. The conventional formic acid production has a climate change impact value of $5030 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of formic acid (Ecoinvent, 2018).

7.2.2. LCA results for methane and propanol

Methane and propanol are preferred over the respective BAU processes when renewable electricity is used. These results are in agreement with those obtained by Rumayor et al. (2019b). For a carbon footprint of $-0.5 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, the climate change impact of CO is respectively $59.6 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of CO and $467 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of CO when wind energy and solar energy are used for the electricity. On the other hand, for a carbon footprint of $-0.8 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, CO has $-875 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of CO and $-468 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of CO respectively when wind and solar energies are used for electricity. These values are clearly lower than that of conventional process ($1590 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of CO) and of electrolytic process moved by electricity grid. Regarding methane, results show that for a carbon footprint of $-0.5 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, the climate change impact of methane is respectively $289 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of methane and $2530 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of methane if wind and solar energies are used for electricity. Considering a carbon footprint of $-0.8 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, methane has an environmental impact of $-1270 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of methane when wind energy is used for electricity and $966 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of methane when solar energy is used for electricity. These values are lower than that of the conventional process ($3080 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of methane) and CO₂ER moved by electricity grid. For the propanol synthesis it is obtained that for a carbon footprint of $-0.5 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, the environmental impact is of $203 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of propanol and $1620 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of propanol when wind and solar energies are respectively used for electricity. When the carbon footprint is of $-0.8 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$ the climate change impact is of $-1070 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of propanol and $343 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of propanol respectively for electricity moved by wind and solar energy. Also in this case, for both carbon footprints propanol synthesis has a lower environmental impact

compared to that of the conventional one ($3240 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of propanol) and that based on CO₂ electrochemical reduction using grid electricity.

7.2.3. LCA results for ethanol and ethylene

Ethanol and ethylene production via electrochemical reduction of CO₂ are promising compared to the traditional pathways when renewable electricity from wind and solar energies and when lower values of carbon footprint for CO₂ are almost used. For ethanol, considering a carbon footprint of $-0.5 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, the climate change impact is $181 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethanol when wind is used for the electricity. This value is lower compared to that obtained when ethanol is produced through CO₂ER using electricity from solar energy ($1420 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethanol), grid electricity ($9730 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethanol) and through the conventional process ($1330 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethanol). On the other hand, for a carbon footprint of $-0.8 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, the environmental impact of ethanol production is $-931 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethanol, $306 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethanol and $8620 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethanol respectively when CO₂ER using wind and solar energies and grid electricity are used. For ethylene, considering a carbon footprint of $-0.5 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, the CO₂ER process moved by wind energy has an environmental impact of $302 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethylene that is lower compared to that obtained when the CO₂ER uses solar energy for electricity ($2340 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethylene) and grid electricity ($16,000 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethylene) and that of the conventional process ($1740 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethylene). On the other hand, for a carbon footprint of $-0.8 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, ethylene production through CO₂ER has an environmental impact of $-1500 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethylene, $538 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethylene and $14,200 \text{ kgCO}_{2\text{eq}}/\text{ton}$ of ethylene respectively for an electricity moved by wind energy, solar energy and grid.

7.2.4. LCA results for methanol

The use of the alternative production of methanol is not suggested when electricity from grid and solar energy are used and with higher values of carbon footprint for CO₂ feedstock. In fact, for a carbon footprint of $-0.5 \text{ kgCO}_{2\text{eq}}/\text{kgCO}_2$, the climate change for methanol

production through CO₂ER using wind energy is 135 kgCO_{2eq}/ton of methanol while the environmental impact for the same process using solar energy and grid energy is respectively of 1060 kgCO_{2eq}/ton of methanol and 7280 kgCO_{2eq}/ton of methanol. The conventional process has 795 kgCO_{2eq}/ton of methanol. When the carbon footprint of CO₂ is -0.8 kgCO_{2eq}/kgCO₂, the electrochemical conversion of CO₂ is favorable also if electricity from solar energy is used. In fact, the climate change for CO₂ER using wind and solar energy for electricity and grid electricity is respectively of -670 kgCO_{2eq}/ton of methanol, 255 kgCO_{2eq}/ton of methanol, 6470 kgCO_{2eq}/ton of methanol.

7.2.5. Overall considerations for LCA results

Overall, these results show that, as suggested in Pappijn et al. (2020), in the most cases only renewable electricity (mostly electricity from wind energy) and particular CO₂ sources (ensuring a very low value of carbon footprint for CO₂) should be used to have a negative value of GWP for the CO₂ER process ensuring a strong climate change mitigation. It is not only important to develop an innovative process but also to have alternative renewable energy sources and CO₂ with a low environmental impact. Nabil et al. (2021) report that global warming impact of electrochemical route is highly sensitive to the electricity emission intensity and is compelling over incumbent routes only when coupled with low emission intensity (<0.25 kgCO_{2eq}/kWh).

It is important to underline that in this analysis a negative value of climate change impact does not mean a removal of CO₂, because a cradle-to-gate analysis has been conducted (Muller et al., 2020).

8. Conclusions

In this critical state-of-the-art, we investigated the CO₂ electrolyzers proposed in the literature. Continuous flow cell reactors are the most promising and are classified into basic flow, PEM, micro-fluid and SOE electrolyzers. Among these systems, SOEs are currently at a commercial scale for CO production, while other systems are at a pilot scale but ongoing research could take them to an industrial scale in the next years because important steps in this direction have been made with encouraging results.

Electrocatalysts for CO₂ER were reviewed and according to the state-of-art were classified in terms of metals, bimetallic catalysts, metal chalcogenides, non-metal catalysts and molecular catalysts. The current research is looking for new electro-catalysts, understanding the mechanism of reaction and developing more efficient cell designs.

The economic and the environmental impacts are important aspects for the application of this new strategy and hence a literature analysis on LCA and economic studies was conducted in this overview followed by our evaluation of production cost and climate change for a large-scale plant at different electricity sources.

Results of our economic analysis show that today, only CO and formic acid electrochemically produced have the potential for a leveled cost lower than the current market price. In the future (in 2050), the production costs of these compounds produced via CO₂ER can decrease so that other products can be economically competitive. In the economic analysis, electricity price, Faradaic efficiency and CO₂ conversion have a significant influence for the reduction of the production cost and more effort should be done to find their optimal values.

Moreover, to enable the economic future of these processes, the focus of research must eventually shift to large-scale applicable and affordable materials. A trade off among all operating conditions must be evaluated in the future to ensure the optimal economy of the process. Finding a robust and selective electrocatalysts for CO₂ reduction to individual products could really help the achievement of these objectives because separation costs will be reduced. In this context, a close and interdisciplinary collaboration between academia and industry is suggested to ensure progress of this technology.

Regarding the environmental analysis, results show that only formic acid production has a climate change lower than that of traditional

process in all investigated case studies. For other products, the use of a renewable energy and CO₂ with a low carbon footprint ensure better performances of the alternative process compared to the conventional one. So that, in a future work, it is important to increase the energy efficiency of the process in order to reduce the electricity consumption and hence the environmental burden, in addition to benefits on the economic point of view.

CRedit authorship contribution statement

Anna Hankin: Writing – review & editing. **Grazia Leonzio:** Writing – original draft, Investigation, Data curation, Conceptualization. **Nilay Shah:** Writing – review & editing.

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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.cherd.2024.07.014](https://doi.org/10.1016/j.cherd.2024.07.014).

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