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Treball Final de Grau

Bibliographic study on the electroreduction of CO₂ using Cu-Metal cathodes.

Estudi bibliogràfic sobre l'electroreducció del CO₂ mitjançant càtodes Cu-Metall.

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En primer lloc, vull agrair a la Dra. Maria Sarret Pons i a la Dra. Teresa Andreu Arbella, com a tutores del meu treball final de grau, la seva dedicació i acompanyament durant tots aquests mesos, i per tots els bons consells donats.

D'altra banda, vull agrair tot el suport rebut per la meva família, parella i amigues durant aquests cinc anys, per creure en mi en tot moment i motivar-me en moments menys fàcils.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)



Take urgent action to combat climate change and its effects.

This UN statement has been used as a guide to include this work in the climate action goal. This bibliographic report aims to study the reaction of CO₂ reduction to reduce greenhouse gas emissions and avoid worsening climate change. In this process, CO₂ is used as a raw material to obtain carbon products of interest.

As a result of increasing greenhouse gas emissions into the atmosphere, alarming environmental changes have occurred. Among them, the increase in the world average temperature of 1.1°C stands out, as well as the melting ice and, consequently, the rise in sea level. Therefore, it is necessary to take a variety of technological measures and adopt changes in human behaviour to counteract these harmful environmental changes.

Regarding the objectives for the climate action goal, education and awareness of humanity, the incorporation of new measures and the use of other processes to avoid fossil resources could favour the reduction of these greenhouse effect emissions and avoid the evolution of climate change:

Target 13.1 Strengthen resilience and adaptive capacity to climate-related hazards and natural disasters in all countries.

Target 13.2 Integrate climate change measures into national policies, strategies and planning.

Target 13.3 Improve education, awareness-raising and human and institutional capacity on climate change mitigation, adaptation, impact reduction and early warning.

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1. SUMMARY

CO₂ is a gas released from the burning of fossil fuels that has a major impact on the greenhouse effect and worsening climate change. This is why, in recent years, studies have been carried out on possible new processes to reduce these emissions.

The CO₂ reduction reaction is a process that allows the use of CO₂ as a raw material to obtain products of interest, such as alcohols and hydrocarbons. The main objective of CO₂ electroreduction is the study of different metal catalysts and working parameters, such as current density, applied potential and faradaic efficiency, to obtain the most efficient CO₂ conversion. Also, reaction conditions such as temperature or pH must be considered, as they can influence the selectivity and efficiency of the products. Different experimental studies have used various metals as catalysts, but only Cu and its alloys have shown good results in the conversion of this gas. Apart from the experimental studies, theoretical studies have been carried out to be able to expand the investigation of this process without having any type of limitation. This fact has made it possible to analyse the current challenges and the future perspectives in this field. Even so, these studies cannot end without an economic and environmental analysis to see the economic profitability and the impact on the environment of this process.

Therefore, the study of the different Cu alloys and the working conditions, together with the economic and environmental viability, to achieve the most efficient conversion of CO₂ and achieve the reduction of the emissions of this gas, are the objectives of this work.

Keywords: CO₂ Electroreduction, Copper alloys, Faradaic efficiency

2. RESUM

El CO₂ és un gas que s'allibera en les crema de combustibles fòssils i que té un gran impacte en l'efecte hivernacle i en l'empitjorament del canvi climàtic. És per això que, en els anys més recents, s'han dut a terme estudis sobre possibles nous processos que permetin reduir aquestes emissions.

La reacció de reducció del CO₂ és un procés que permet la utilització del CO₂ com a matèria primera per a l'obtenció de productes d'interès, com alcohols i hidrocarburs. El principal objectiu de l'electroreducció del CO₂ és l'estudi de diferents catalitzadors metàl·lics i paràmetres de treball, com la densitat de corrent, el potencial aplicat i l'eficiència faradaica, per obtenir la conversió del CO₂ més eficient. També, cal tenir en compte les condicions de reacció, com la temperatura o el pH, ja que poden influir en la selectivitat i eficiència dels productes. Diferents estudis experimentals han utilitzat diversos metalls com a catalitzadors, però només el Cu i els seus aliatges han mostrat bons resultats en la conversió d'aquest gas. A part del estudis experimentals, s'han realitzat estudis teòrics per poder ampliar la investigació d'aquest procés sense tenir cap tipus de limitació. Aquest fet, ha permès analitzar els actuals reptes i, també, les perspectives futures en aquest camp. Tot i així, aquests estudis no poden acabar-se sense fer un anàlisi econòmic i mediambiental per tal de veure la rendibilitat econòmica i l'impacte en el medi ambient d'aquest procés.

Per tant, els objectius d'aquest treball són l'estudi dels diferents aliatges de Cu i de les condicions de treball, juntament amb la viabilitat econòmica i mediambiental, per aconseguir la conversió més eficient del CO₂ i aconseguir la disminució de les emissions d'aquest gas.

Paraules clau: Electroreducció CO₂, Aliatges de coure, Eficiència faradaica

3. INTRODUCTION

During the last decades, anthropogenic CO₂ emissions have been increasing due to the burning of fossil fuels, such as oil, natural gas, and coal, which are used for energy production [1]. CO₂ contributes to the increase in the greenhouse effect, which causes important problems, such as the melting of glacial masses, the rise in sea level causing flooding in coastal areas, desertification of fertile areas and many other environmental impacts. That is why, relatively recently, they have begun to investigate and study different processes that allow the reduction of CO₂ emissions and the possibility of converting this gas into other products of interest, such as alcohols and hydrocarbons, through different chemical reactions.

CO₂ is a linear molecule with two double bonds that connect carbon to two oxygen atoms. This molecule has higher binding energies than a normal carbonyl bond, but when subjected to suitable reducing conditions it can be reduced to simpler products by the CO₂ reduction reaction (CO₂RR) [2]. It is one of the chemical processes currently receiving the most attention, as it allows for the easy and controllable closure of the CO₂ production cycle [3]. This process converts CO₂ into useful chemicals and fuels using electricity (Table 3.1). However, it should be noted that, as a reduction process of CO₂ in an aqueous solution, it could compete with the hydrogen evolution reaction (HER), causing a decrease in energy efficiency [4]. For this reason, the presence of a catalyst is necessary to increase the reaction rate.

Table 3.1. Standard electrochemical potentials for CO₂ and proton reduction at 25°C and 1 atm [5].

Reaction	E° / V vs. RHE
CO ₂ + e ⁻ → CO ₂ ^{•-}	-1.48
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.10
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.19
CO ₂ + 4H ⁺ + 4e ⁻ → HCHO + H ₂ O	-0.06
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	+0.03
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	+0.17
2CO ₂ + 12H ⁺ + 12e ⁻ → C ₂ H ₅ OH + 3H ₂ O	+0.09
2CO ₂ + 12H ⁺ + 12e ⁻ → C ₂ H ₄ + 4H ₂ O	+0.08
2CO ₂ + 14H ⁺ + 14e ⁻ → C ₂ H ₆ + 4H ₂ O	+0.14
2H ⁺ + 2e ⁻ → H ₂	0.00

Selectivity depends on how CO_2 molecules are initially absorbed on the electrocatalyst surface (Figure 3.1). To obtain CO, the carbon of the adsorbed CO_2 molecule binds to the catalyst surface while oxygen reacts with water to form the $^*\text{COOH}$ intermediate. This adsorbed intermediate is then reduced to $^*\text{CO}$ which is eventually desorbed from the electrode giving rise to the product CO [6]. In the case of the formation of HCOOH , the two oxygen atoms of the CO_2 molecule are attached to the catalyst surface so that carbon can be hydrogenated to giving rise the desired product. The formation of C_1 , C_2 , and other hydrocarbons compounds has a common intermediate, $^*\text{CO}$. Depending on the catalytic properties and surface orientation of the catalyst, protonation of $^*\text{CO}$ can lead to two intermediates, $^*\text{CHO}$ and $^*\text{COH}$. Both intermediates, through a series of electron transfer reactions, protonation, and reductions can generate methane CH_4 as the final product. Also, through the reaction of $^*\text{CHO}$, it can be protonated to give methanol CH_3OH . On the other hand, the intermediate $^*\text{CH}_2$, if it undergoes another protonation, leads to $^*\text{CH}_3$ which, together with another molecule, can give rise to the dimer C_2H_6 . Finally, the formation of two other products, C_2H_4 and $\text{CH}_3\text{CH}_2\text{OH}$, is carried out through the dimerization of $^*\text{CO}$ and subsequent reactions of protonation and electron transfer. Bibliographic studies found that 2e- transfer products (HCOOH , CO) are formed at lower overpotentials, while higher e- transfer products (CH_4 , C_2H_4) are formed at higher overpotentials [7]. [8].

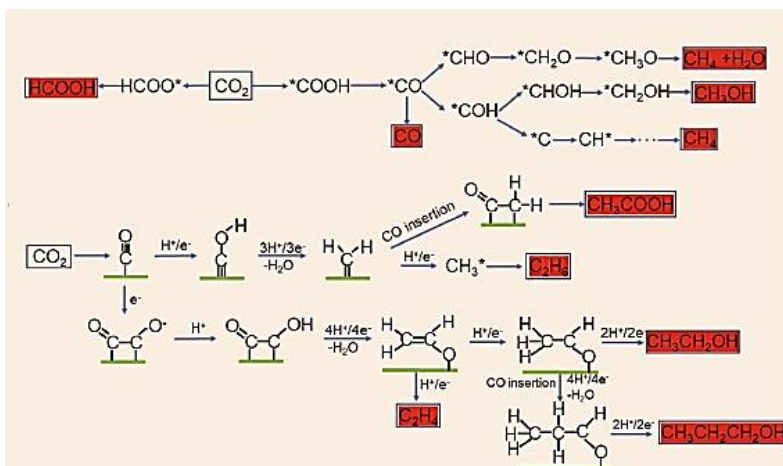


Figure 3.1. Reaction pathways for the reduction of CO_2 to C_1 and C_2 products [6].

After studying different metals, copper has been of great interest due to its electrocatalytic characteristics. Copper (Cu) is a transition metal and both the pure form and its alloys have been used for thousands of years due to their chemical, mechanical and electrical properties. It is one of the most abundant metals in the earth's crust, it is found in the form of minerals, such as oxides and sulfides, and it is easily obtained. In addition, it presents great ductility and malleability, which allows easy work on it. As copper gained importance in daily life, its alloys began to be studied to achieve better results. Some of these alloys are bronze, copper and tin alloy; brass, an alloy of copper and zinc; cupronickel alloys, copper and nickel alloys; and many more. The main properties of these alloys are resistance to corrosion and oxidation, since they produce protective films; and greater hardness, since they prevent breakage when used and increase their ductility; or even decorative [9]. Little by little, over the years, interest in copper and its possible applications has increased and varied significantly, from its use in parts for ships or the manufacture of weapons, to the use of nanoparticles in industrial processes.

Until now, copper alloys have been the catalysts with the greatest interest in this field since they present remarkable faradaic efficiency for the C-C coupling. It allows the formation of carbon-carbon bonds and, therefore, the formation of hydrocarbons and C₂₊ oxygenated compounds [10]. It is crucial to be able to obtain the best possible durability and stability of these compounds to be able to develop practical and cost-effective processes that allow the electroreduction of CO₂ on a large scale.

4. OBJECTIVES

The main objective of this work is to carry out a bibliographic study and analysis on the CO₂ reduction reaction and the obtaining of its main products. To carry it out, different points must be considered:

- Investigate the different Cu-Metal cathodes used so far in CO₂RR and compile the different products that can be obtained in each case and with what faradaic efficiencies.
- Do a short search of the current trends used in the study of the reaction at a theoretical level.
- Carry out a brief economic study of the feasibility of the process at an industrial level.

5. METHODS

To carry out the study of copper alloys, a bibliographic search was made using the SciFinder database from Chemical Abstracts Service (CAS). Initially, the keyword "Copper alloy" was searched to see in which year publications on the topic began and in which period there was an increase. As can be seen in Figure 5.1, the number of publications related to copper alloys grows exponentially over the years. Then, using the filtering tool, articles were divided by year to study the initial function and production of these alloys. Starting from the year 1836, the year of the first published article, until the year 2000, it was observed that copper alloys with other metals (M: Ni, Al, Zn, Sn...) were mainly used to prevent corrosion of metals and protect them from air, sea, and other external agents; furthermore, their production was essentially through electrodeposition.

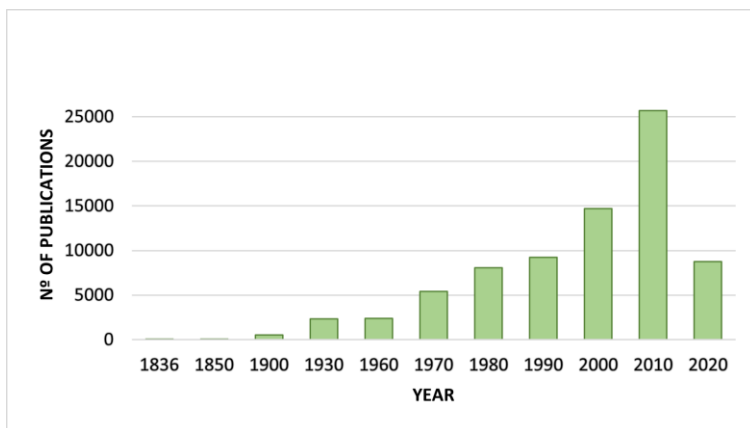


Figure 5.1. Number of publications for copper alloys every 10 years.

Once it was seen that, in the most recent years, between the years 2000 and 2023, the number of publications was greater, articles related to copper alloys for the electroreduction of CO_2 were searched. The keywords "copper alloy" and " CO_2 electroreduction" were used using the Boolean operator "and". As can be seen in Figure 5.2, the number of publications per year also grows exponentially and the number of articles obtained was lower, but the topic to be dealt with was much more specific and indicated for this study.

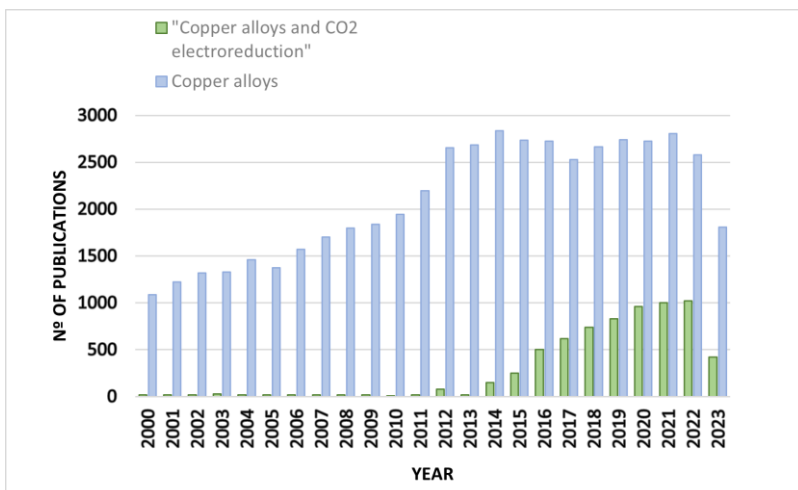


Figure 5.2. Number of publications for copper alloys vs. copper alloys and CO_2 electroreduction.

Once the more general articles on the electroreduction of CO_2 were found, other databases, "SpringerLink" and "Elsevier", were used to search for different metals that could be alloyed with copper to be used as electrocatalysts. In this case, the keywords "Metal-copper alloy" and " CO_2 electroreduction" were used, where "Metal" could be zinc, silver, gold, tin, nickel etc. From these articles it was possible to make a more specific study of each alloy, considering its composition, structure, faradaic efficiency, applied potential or used electrolyte.

Finally, in the same databases, a search was made for articles on theoretical calculations and on economic and environmental feasibility. The keywords "Computational methods" and "Economic and environmental analysis" were used together with " CO_2 Electroreduction" using the Boolean operator "and".

6. RESULTS AND DISCUSSION

6.1. FIRST USES OF Cu-METAL ALLOYS

As previously mentioned, copper is a metal that has been used in many applications for thousands of years, and its world production has increased significantly in recent decades thanks to the development of new extraction techniques.

Around the 1960s and 1970s, both copper and its main alloys, such as CuSn, CuZn or CuNi, were used to prevent corrosion of metal parts. As can be seen in Table 6.1, the method for obtaining these alloys was variable, but the most common, due to its cost and effectiveness, was electrodeposition. This process consists of the deposition of the metallic alloy on a substrate using an electrolytic solution and electric current; in addition, it allows to control the chemical composition and some of its properties.

Table 6.1. Function and obtaining of some copper alloys.

Alloy	Function	Method	Reference
Cu - Ni	Anticorrosive	Electrodeposition	[11], [12]
Cu - Al	Anticorrosive	Electrodeposition	[13], [14]
Cu - Sn	Protective, protective-decorative, and antifriction coating	Electrodeposition	[15]
Cu - Cd	Anticorrosive	Electrodeposition	[16]
Cu - Zn	Anticorrosive	Electrodeposition	[17]
Cu - Pb	Antifriction material	Casting method	[18]

Over the years, new applications for its use have appeared, as is the case of this bibliographical study on the electroreduction of CO₂ with copper catalysts. For this process, the use of nanoparticles has been proposed since they present advantages over bulk catalysts. Through synthetic processes, a wide range of compositions, sizes and shapes can be prepared, thus making it possible to study the performance of these catalysts by controlling the active sites [19].

6.2. CO₂ ELECTROCHEMICAL REDUCTION PROCESS

The electrochemical CO₂ reduction process, as mentioned above, is the reaction in which CO₂ is reduced to chemicals using electrical energy. This interacts with the CO₂ and the components of the solution, resulting in an exchange of electrons called current density (j). This parameter represents the number of transferred electrons passing through the electrolyte and the electrode per unit area per unit time. That is, it reflects the kinetic speed of the electrochemical transformation [20].

$$j = \frac{i}{A} \quad \begin{array}{l} j = \text{current density (A/m}^2\text{)} \\ i = \text{electric current (A)} \\ A = \text{surface (m}^2\text{)} \end{array}$$

Therefore, the current density influences the obtaining of another important parameter in this process, the faradaic efficiency. It is defined as the percentage of electrons consumed to produce a specific product, that is, it reflects the selectivity for a certain product.

$$FE = \frac{\alpha n F}{j t} = \frac{\alpha n F}{Q} \quad \begin{array}{l} \alpha = \text{transferred electron number} \\ n = \text{mole number of a given product} \\ F = \text{Faraday's constant (96500 C/mol)} \\ Q = \text{amount of charge for a specific reaction (C)} \\ j = \text{current density (mA/cm}^2\text{)} \\ t = \text{time (s)} \end{array}$$

This process is carried out inside an electrolytic cell, which is divided into several compartments, thus separating the cathode and anode by means of a membrane to avoid the mixing of the electroreduction products. In addition, a polymeric electrolyte or an electrolytic solution is placed in each compartment that allows the diffusion of the ions [21]. To carry out the

CO₂ reduction reaction, different cell configurations have been used and it must be considered that there are various design factors that affect the cell performance for CO₂RR as seen in Figure 6.1.

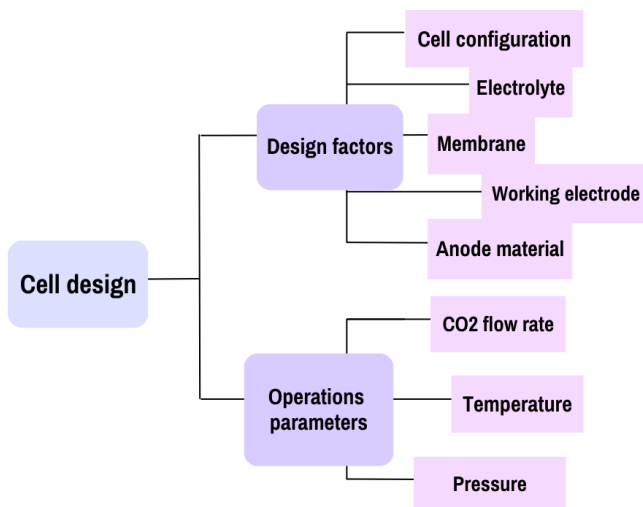


Figure 6.1. Summary of some factors affecting the cell design of the CO₂RR.

To fully understand the concepts mentioned in Figure 6.1, a short description of the main elements related to design factors will be given below.

6.2.1. Cell configuration

The conventional H-type cell (Figure 6.2) consists of two compartments and three electrodes. The cathode compartment contains the working electrode and the reference electrode, where the CO₂ reduction reaction takes place; while in the anode compartment it contains the counter electrode or auxiliary electrode that is used to close the electrical circuit. As mentioned, the compartments are divided by a membrane, which prevents the CO₂RR products from being oxidized during the reaction, but they are connected by a channel through which the electrolytic solution passes, which allows the transport of ions and, therefore, the transport of charge. In addition, CO₂ gas is continuously bubbled into the cathode compartment to ensure electrolyte saturation and removal of residual air. The reaction is started by applying an external voltage or current, and the formation of gaseous and liquid products is analysed by gas chromatography, liquid chromatography or proton nuclear magnetic resonance [22],[23].

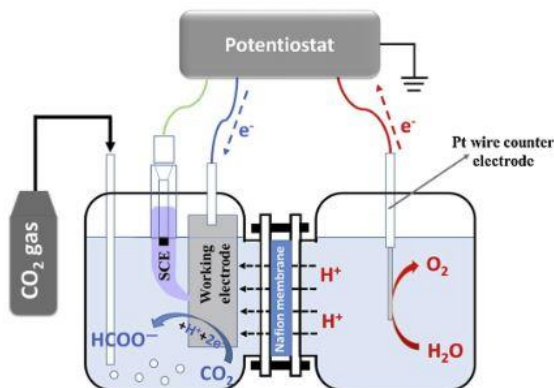


Figure 6.2. Conventional H-type cell configuration [24].

The conventional H-type cell, however, presents a limitation, which is the low solubility of CO_2 in aqueous electrolytes at room temperature and pressure, thus giving an inefficient result of CO_2RR [25].

Another limitation of the conventional H-type cell is the low concentration of some products obtained after the reaction due to the small size of the electrode and the large volume of electrolytic solution. In this case, it is suggested [26] to modify the structure of the conventional H cell for a Sandwich type H cell (Figure 6.3), in which the electrode is larger, and the electrolyte solution is smaller in volume. In this case, the working electrode is placed parallel to the auxiliary electrode and an anion exchange membrane is placed between the two compartments to prevent oxidation of the products obtained.

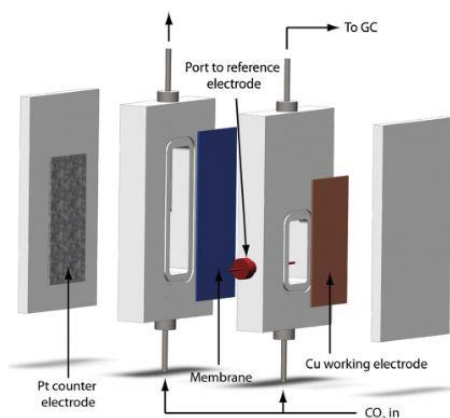


Figure 6.3. The configuration of Sandwich H-type cell [27].

Another type of cell used is the filter press cell (Figure 6.4) which consists of two compartments separated by an electrolytic membrane. An anolyte is fed to the anode, and a catholyte and the pumped CO₂ are fed to the cathode. This type of cell allows the operation of a continuous process in which both the catholyte and the anolyte pass through the cell once. Also, GDE is generally used as it features a larger surface area compared to the other electrodes [28], [29].

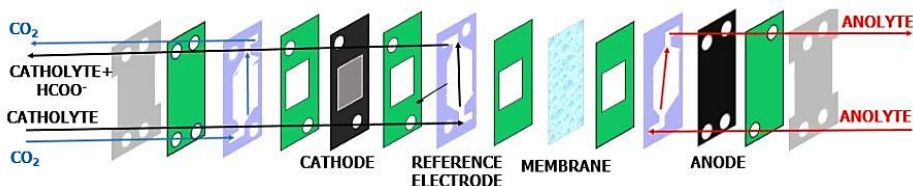


Figure 6.4. Filter press cell configuration [29].

Finally, another type of cells used to carry out the CO₂RR are the flow cells, and there are two types. First, polymer electrolytic membrane (PEM) flow cells (Figure 6.5) are reactors that can be used at an industrial level. Generally, a membrane is placed between the cathodic and anodic compartments to prevent the products from crossing over. In addition, a gas diffusion electrode (GDE) is usually used in the cathode compartment, since it allows a higher concentration of CO₂ in this compartment, thus making the reaction rate higher and increasing the efficiency of the cell [21]. This PEM cell presents an advantage, since it allows obtaining a high faradaic efficiency (FE), that is, a high selectivity of CO₂ reduction to the desired product. As a second type of this type of cell, there is the membraneless flow cell (Figure 6.6) that consists of two GDEs separated by an electrolyte stream. CO₂ is fed into the cathode side and is directly reduced, while oxygen is released from the anode side. Even so, there are some limitations that affect the performance of the cell, such as the low diffusivity of CO₂ in the porous electrode or the effect of hydrogen dilution, which is due to the accumulation of H₂ gas near the reactive surface within the GDE thus decreasing the concentration of CO₂ [30].

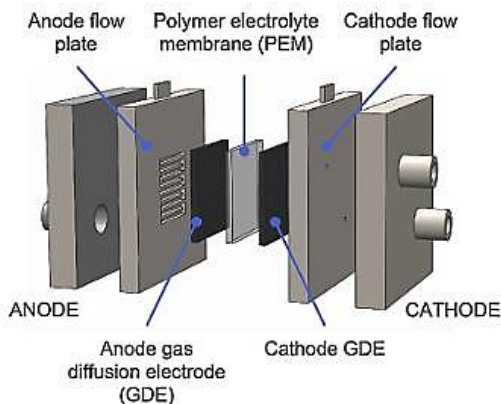


Figure 6.5. PEM cell configuration [27].

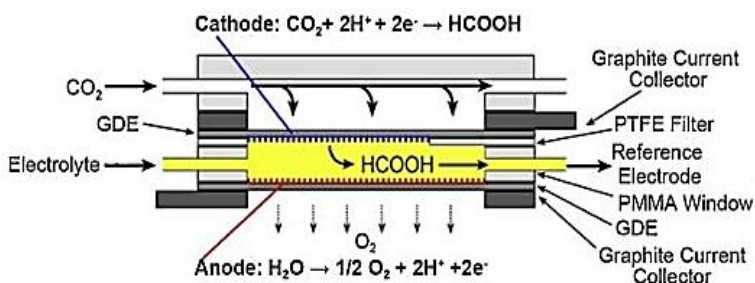


Figure 6.6. A Schematic diagram of the microfluidic reactor for CO₂ conversion [27].

Therefore, the configuration of the cell used is important to obtain good cell performance as it affects the efficiency of mass transport, the scalability of the process and, importantly, the sustainability of the operation, which advantages and disadvantages of cell types are summarized in Table 6.2. In addition, it must be considered that it also affects the FE of obtaining the desired product, as well as the energy of the cell. For example, the conventional type H cell has various limitations, including the limitation of mass transport, which do not allow its use in certain processes. On the other hand, the flow cell presents a good FE for the formation of the product and can operate continuously with low internal resistance, which allows better results during its use. On the other hand, the filter press cell can operate in a continuous mode in which anolyte and catholyte pass through the cell only once, but the reuse of electrolytes should be investigated to reduce costs in the process.

Table 6.2. Advantages and disadvantages of the different cell configurations [21].

Cell	Configuration	Advantages	Disadvantages
Static cell	Conventional H-cell	<ul style="list-style-type: none"> · Suitable for catalyst testing. · Easy to operate. 	<ul style="list-style-type: none"> · Poor mass transfer. · Difficult to control temperature and pressure. · Low product concentration. · Not suitable for industrial application.
	Sandwiched H-cell	<ul style="list-style-type: none"> · Low electrolyte volume · Easy to quantify product due to its high concentration. 	<ul style="list-style-type: none"> · The configuration is restricted to flat shape electrode.
Flow cell	Filter press cell	<ul style="list-style-type: none"> · Continues operation. · High product production rate can be achieved. 	<ul style="list-style-type: none"> · Relatively high energy consumption. · Restricted to flat shape electrode.
	Polymer electrolyte	<ul style="list-style-type: none"> · Can operate with liquid catholyte or humidified CO₂. · Allow zero-gap arrangement, which might result in better CO₂ conversion efficiency. · Continuous operation. · Low internal resistance. · Can be scaled up without a reduction in the FE. 	<ul style="list-style-type: none"> · The pH should be carefully controlled. · Flooding of GDE with liquid electrolyte. · Resistance due to the existence of the membrane. · Membrane re-usability and cost.
	Microfluidic	<ul style="list-style-type: none"> · Does not require use of membrane. · Continuous operation. · Electrolyte characteristics can be easily controlled. · Reduced water flooding and dry-out issue. 	<ul style="list-style-type: none"> · Accumulation of hydrogen gas near the cathode. · Steep CO₂ gradient, which increases the mass transport resistance. · Electrolyte flow rate should be carefully controlled. · Relativity high energy requirement.

6.2.2. Electrolyte

An electrolyte is a substance whose main function is to transfer charge between the electrodes and the catalyst during the CO₂ reduction process. It has an important role in the entire reduction process since it influences the HER, the rate of production of the desired product, the energy efficiency of the cell, the FE, etc. In addition, the electrolyte can improve the performance of the cell, so characteristics and properties, such as pH [31], must be considered and controlled to maximize performance. For example, increasing the concentration of the KHCO₃ solution from 0.1 M to 1 M causes the FE of the HCOOH to drop from 80% to 40% [32]. Electrolytes can be classified into aqueous and non-aqueous, and their concentration must be investigated in each study to avoid affecting the solubility of CO₂.

Aqueous electrolytes consist of salts, such as Na⁺, K⁺, Cl⁻, and HCO₃⁻, dissolved in a solvent, usually water. Commonly, they are the most used since they have a high electroconductivity in water, which facilitates the CO₂RR process. In most of the studies developed for the CO₂RR, aqueous solutions with HCO₃⁻ instead of other anions, such as SO₄²⁻ or ClO₄⁻, are used and are known for their high yield to obtain the desired product, such as for example HCOOH. This is because it provides enough dissolved CO₂ at the interface between the electrode and the electrolyte, thus obtaining a higher FE for the product. The cations are also important when it comes to achieving good results in obtaining the desired product (Figure 6.7). It has been observed that the larger the cation, the lower the faradaic efficiency obtained as a function of the current density used [33].

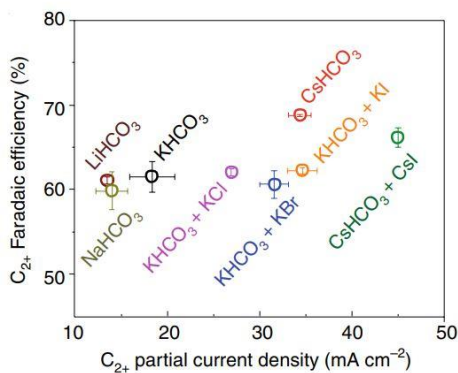


Figure 6.7. FE and partial current densities of C₂₊ products obtained from a catalyst in different electrolytes [34].

On the other hand, non-aqueous electrolytes can also be used for the CO₂ reduction reaction. They are characterized by their higher CO₂ solubility, compared to aqueous ones, so there is less mass transport limit. However, non-aqueous electrolytes give rise to low faradaic efficiency, thus limiting their industrial application, but they can suppress HER due to their low proton concentration [35]. In addition, ionic liquids used as electrolytes have limitations in preparation, price, and toxicity [36].

6.2.3. Membrane

Membranes are another important part of electrolytic cells and are used to separate the anodic and cathodic compartments preventing the reduction product obtained from being oxidized again in the anodic compartment. Still, there are cells, such as microfluidic cells, that do not require the use of a membrane. Three types of membranes are used for CO₂RR: the cation exchange membrane (CEM) (Figure 6.8 a) is a monopolar membrane with a fixed negative charge that allows the passage of cations and prevents the passage of anions; the anion exchange membrane (AEM) (Figure 6.8 b) is a positively charged membrane that allows the passage of anions and prevents the passage of cations; and the bipolar membrane (BPM) (Figure 6.8 c) is a selective membrane towards anions and cations [37], [38]. Both cation and anion exchange membranes are inexpensive, easy to manufacture, and have a long service life; however, they suffer from electrolytic contamination, product crossover, and a high pH gradient across the membrane. Fortunately, these problems are avoided by using a BPM, since it can maintain constant pH through its selective transport of anions and cations. Although, despite having good features and providing good results, it has drawbacks, such as high price, short lifespan, and low stability.

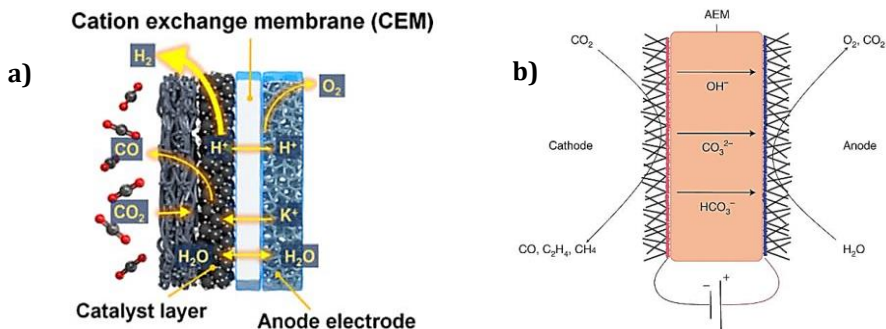


Figure 6.8. a) Cation exchange membrane for CO₂ [39]; b) Anion exchange membrane for CO₂ [40].

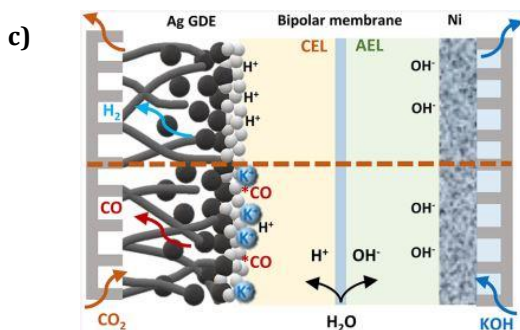


Figure 6.8. c) Bipolar membrane [41].

6.3. COPPER ALLOYS AS ELECTROCATALYTIC CATHODES

To carry out the CO_2RR process, copper alloys have been proposed to improve the catalytic activity and the selectivity of CO_2 reduction by allowing adjustment of the intermediate binding force to the surface, thus improving the reaction kinetics. Specifically, nanoparticles offer an ideal platform to study this effect due to their advantages over bulk catalysts. Through synthetic processes, a wide range of compositions, sizes, and shapes can be prepared, enabling the performance of these catalysts to be studied while controlling active sites. They are promising candidates because smaller particle size leads to larger surface areas, meaning there are many more active sites per mass or volume, providing better electrical conductivity [19],[42]. However, it must be considered that when additional metals are added to catalysts, as compared to those containing only one metal, changes in the electronic properties of the central metal or in the arrangement of atoms in active sites may occur. This, in turn, can influence the adsorption energy and the geometry of the intermediate. Therefore, the activity and selectivity of the catalysts may change [6].

Furthermore, it has been observed that, depending on the second metal in the alloy, there is a higher affinity for hydrogen or oxygen, resulting in different reduction products. Therefore, we can classify secondary metals based on two factors: the affinity for hydrogen (H) and the affinity for oxygen (O). A metal with a high affinity for H refers to one that binds hydrogen more strongly than copper, while a metal with a high affinity for O refers to one that binds oxygen more strongly than copper. Next, metals are then classified based on their affinity for hydrogen and oxygen (Figure 6.9).

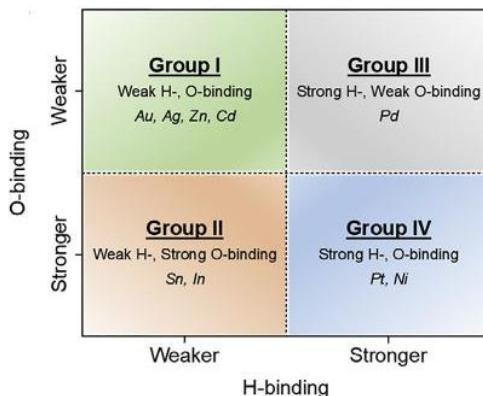


Figure 6.9. Classification of metals into different groups with respect to Cu, based on their O and H affinities [7].

6.3.1. Group 1

The metals that belong to group 1 are characterized by presenting, in comparison with copper, a lower affinity for both oxygen and hydrogen. These tend to bind more strongly to the intermediate *COOH, leaving free the *CO that is obtained as the final product [7]. The metals that are part of this group are Au, Ag, Zn and Cd. A summary of some products obtained from different studies with different characteristic values is presented in Table 6.3.

- **Cu – Au alloys:**

Gold (Au) is a *d*-block metal with low affinity for both H and O. It has been extensively studied for alloying with copper and used as a catalyst in CO₂RR since it was experimentally demonstrated that a higher content of Au favours the production of CO over other possible products [43].

The catalyst consists of Cu-Au nanoparticles deposited in a monolayer and has allowed for the study of CO₂ reduction activity, as well as comparison of selectivity and activity based on the metallic composition of the catalyst (Au₃Cu, AuCu, AuCu₃). It has been observed that pure Cu nanoparticles exhibit minimal activity, but as the concentration of gold increases, the activity also increases until it reaches a maximum point that corresponds to Au₃Cu. Just as it has been observed that an increase in Au favours the production of CO, it has been observed that in the case of ethylene and methane, the faradaic efficiency (FE) decreases [42]. After conducting a comprehensive investigation into the effect of the Cu-Au stoichiometric ratio in bimetallic catalysts,

the electrochemical results indicated that alloys with higher Cu content produced multiple reduction products, while higher Au content simultaneously improved CO formation and suppressed other pathways [42]. In addition, it was found that by increasing the degree of atomic ordering and stabilization of *COOH intermediates in gold-copper alloys, the selectivity of CO₂ to CO reduction can be adjusted with a faradaic efficiency (FE) of 80% [44].

- **Cu – Ag alloys:**

Silver (Ag) is another metal with a low affinity for both H and O and it has been shown that an alloy with a higher silver content gives rise to CO as a product. On the other hand, if the alloy has a higher Cu content, there is greater selectivity towards hydrocarbons [3],[7]. Both electronic and geometric effects played a crucial role in the catalytic activity of the examined alloy. In particular, the binding energy of *CO at Ag active sites was found to be lower compared to that of Cu, favouring *CO desorption with increasing silver content. In addition, it was possible to adjust the binding strength of the intermediates by modifying the atomic arrangement of the active sites [7].

More recently, several Cu-Ag catalysts deposited at the Cu nanowire interface with high selectivity towards methane (CH₄) were developed. CO₂ reduction is generally performed in a three-electrode system of an H-type electrolytic cell. As can be seen in Figure 6.2, the typical cell includes a working electrode, a counter electrode, a reference electrode, and a membrane for exchange of ions to separate the cathode and anode reactions [3]. With this cell it was shown that the catalyst with composition Cu₉Ag₁ obtained a FE of 72% for CH₄ and a FE of 21% for C₂H₄. On the other hand, varying the composition of the catalyst to Cu-Ag, the selectivity towards methane formation was maintained; but in the alloy with CuAg composition (1:1) the main formation product was CO [45],[5].

In another study [46], the authors reported on the morphological effect of Ag on CO production. For a Cu-Ag catalyst with nanoporous Ag, a FE of 90% was obtained, whereas for Ag nanoparticles, a FE of 40% was achieved. Later, these authors aimed to improve the production of CO by preparing a Cu-Ag catalyst with dendritic morphology through electrodeposition. This technique is a simple and cost-effective process that allows for control over the composition and shape of the catalyst. After the study, it was concluded that the catalyst with a composition of Cu₄₃Ag₅₇ exhibited the highest catalytic activity towards CO (Figure 6.10) [47].

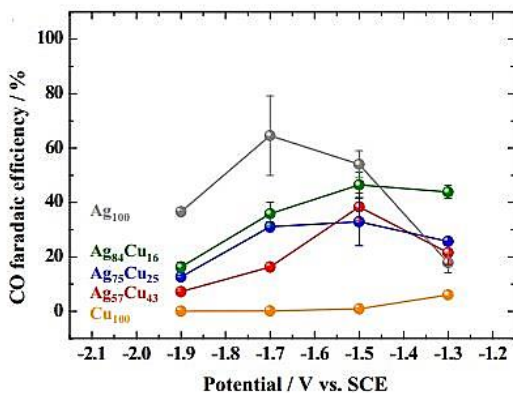


Figure 6.10. Faradaic efficiencies of Ag, Ag–Cu and Cu dendrite catalysts for (a) CO production [47].

• Cu – Zn alloys

Zinc (Zn) has also been studied to form a copper alloy and be used as a catalyst for CO₂ reduction. In this case, it is interesting because it is not a precious metal and therefore reduces costs and decreases its toxic characteristics. It is a metal that has high selectivity for CO in CO₂RR and low activity in the hydrogen evolution reaction, therefore, it can suppress it. In a recent study it has been seen that, apart from obtaining CO as a product, obtaining the C₂H₄ hydrocarbon is favourable (Figure 6.11) when the catalyst is based on a surface of porous nanostructures, since it retains the intermediates, thus giving the possibility of obtaining the final product. In this case, a FE of 33.3% was obtained for CO and a FE of 46.6% for CH₃CH₂OH using an H-type cell [6].

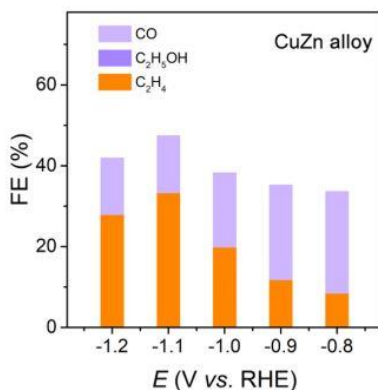


Figure 6.11. FE values for CO₂RR on CuZn alloy at different potentials [48].

Table 6.3. Summary of products obtained using group 1 copper alloys.

Metal Alloy	Structures	Alloy	Electrolyte	Potential	Product	Ref.
Au	Nanowires	CuAu	0,1 M KHCO ₃	-0.77 V vs. RHE	CO 80%	[44]
	Nanoparticle	CuAu	0,5 M KHCO ₃	-0.30 V vs. RHE	CO 96%	[43]
	Nanowire	CuAu ₃	0,1 M KHCO ₃	-0.50 V vs. RHE	C ₂ H ₅ OH 48%	[49]
	Nanoparticles	o-AuCu	0,1 M KHCO ₃	-0.8 V vs. RHE	CO 80%	[50]
Ag	Nanowires	AgCu	1 M KOH	-0.70 V vs. RHE	C ₂ H ₄ 60%	[6], [51]
	Nanoparticle	Cu _{0,86} Ag _{0,14}	1 M KHCO ₃	-0.67 V vs. RHE	C ₂ H ₅ OH 41%	[6], [52]
	Nanowires	Cu ₉ Ag ₁	0,1 M KHCO ₃	-1.17 V vs. RHE	CH ₄ 72%	[5], [53]
	Nanoporous	CuAg	0,5 M KHCO ₃	-0.50 V vs. RHE	CO 90%	[46]
	Nanodimers	AgCu	0,1 M KHCO ₃	-1.1 V vs. RHE	C ₂ H ₄ 40%	[54]
Zn	Nanoporous	CuZn	0,1 M KHCO ₃	-1.10 V vs. RHE	CO 33,3%	[6], [48]
	Nanoparticles	Cu ₅ Zn ₈	0,1 M KHCO ₃	-0.80 V vs. RHE	C ₂ H ₅ OH 46,6%	[6]
	Nanofibers	CuZn	0,5 M NaHCO ₃	-1.05 V vs. RHE	HCOOH 48,6%	[5]
	Nanofoam	Zn ₉₄ Cu ₆	0,5 M KHCO ₃	-0.9 V vs. RHE	CO 90%	[55]
Cd	Nanofibers	CuCd	0,5 M NaHCO ₃	-1.05 V vs. RHE	HCOOH 70,5%	[5], [56]

6.3.2 Group 2

In this case, the metals belonging to this group have, in comparison with copper, a higher affinity for oxygen and a lower affinity for hydrogen. They are characterized by presenting a weak adsorption of the intermediate *COOH after the first reaction stage; that is why the main product of CO₂RR is formic acid (HCOOH). Within this group we can find the metals In, Sn, Hg, Pb... A summary of some products obtained from different studies with different characteristic values is presented in Table 6.4.

- **Cu – Sn alloys:**

Tin (Sn) is a metal present in catalysts used for CO₂ reduction, and it has been shown experimentally that it limits the formation of products reduced to 2e⁻. It was seen that a Cu-Sn material was more selective to produce CO with a FE of 90% (Figure 6.12) [57]. On the other hand, the use of tin (IV) oxide on the catalyst surface to produce Cu-SnO₂ nanoparticles was proposed, obtaining up to a FE of 93% for CO. In this case, it has been seen that the thickness of Sn deposited on the catalyst surface influences the selectivity of the final product. A greater thickness of the Sn layer favours the production of HCOOH, while a lesser thickness leads to the production of CO [58].

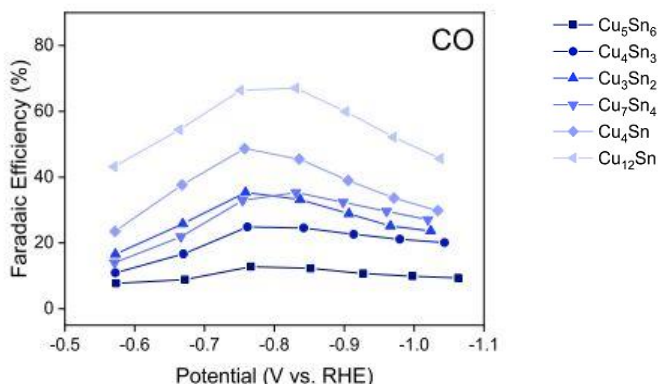


Figure 6.12. Electrochemical performance of various Cu-Sn alloy catalysts in 0.1 M KHCO₃ electrolytes; measured FE toward CO [59].

- **Cu – In alloys:**

When it was decided to alloy indium (In) to be used as an electrocatalyst for CO₂RR, it was seen that the results of the Cu-In catalyst were very selective for obtaining CO, with a FE of 90% using a flow cell [60]. In another study [61], a catalyst with active sites on CuIn was designed from CuInO₂. After electroreduction of the catalyst at the appropriate current density, faradaic efficiencies of 63% for CO and 31% for HCOOH were obtained.

Table 6.4. Summary of products obtained using group 2 copper alloys.

Metal Alloy	Structures	Alloy	Electrolyte	Potential	Product	Ref.
Sn	SnO ₂ nanoparticles	CuSn	0,5 M KCl	-1.80 V vs. RHE	HCOOH 90%	[4], [62]
	Cones	CuSn	0,1 M KHCO ₃	-0.60 V vs. RHE	CO 82,7%	[6], [63]
	Nanoparticles	Cu ₃ Sn	0,1 M KHCO ₃	-1.0 V vs. RHE	C ₂ H ₅ OH 64%	[6]
	SnO ₂ nanoparticles	CuSn	0,5 M KHCO ₃	-0.70 V vs. RHE	CO 93%	[64]
	Nanoparticles	CuSn/Sn	1 M KHCO ₃	-0.7 V vs. RHE	HCOOH 84,1%	[65]
	Particles	Cu ₆ Sn ₅ /Sn	1 M KOH	-1.0 V vs. RHE	HCOOH 86,7%	[66]
	Nanocones	CuSn	0,1 M KHCO ₃ + 0,3 M KCl	-1.1 V vs. RHE	HCOOH 90,4%	[67]
Porous	Cu _{6,26} Sn ₅	0,1 M KHCO ₃	-1.1 V vs. RHE	HCOOH 97,8%	[68]	
In	Nanoparticles	CuIn	0,1 M KHCO ₃	-0.60 V vs. RHE	CO 90%	[69]
	Nanoparticles	CuIn	0,1 M KHCO ₃	-0.50 V vs. RHE	HCOOH 30%	[57]
	Nanoparticles	Cu _{11,5} In _{88,5}	0,1 M KHCO ₃	-1.1 V vs. RHE	HCOOH 85%	[70]

6.3.3. Group 3

Group 3 metals have a higher affinity for both oxygen and hydrogen. However, despite obtaining small amounts of hydrocarbons and alcohols on these metal surfaces, these alloying elements tend to favour the competitive hydrogen evolution (HER) reaction. Within this group are the metals Pd, Ni, Pt, Co... A summary of some products obtained from different studies with different characteristic values is presented in Table 6.5.

- **Cu – Pd alloys:**

Palladium (Pd) is a metal with great potential to form part of the copper alloy to be used as an electrocatalyst for the CO reduction reaction. It has been seen that when the Pd content is higher in the CuPd alloy, the main product that is formed is CO. Even so, Pd can generate, apart from the CO, the HCOOH as a reduction product. The formation of one or the other depends on the microstructure of the material, the applied potential, and the composition of the alloy [6]. Specifically, for ordered Cu-Pd nanoparticles, a FE for C₁ products, more specifically CO, of 80% was obtained; on the other hand, for C₂ products, such as C₂H₄, a FE around 60% was obtained.

It was suggested to investigate the synthesis and characterization of bimetallic catalysts with different characteristics, structures, and atomic compositions, to analyse their influence and selectivity on CO₂ reduction. Three samples were studied (Figure 6.13): disordered phase CuPd, ordered phase CuPd and phase separated CuPd. The results indicate that for cathode potentials more positive than -0.3 V_{vs. RHE}, the faradaic efficiency for CO was similar for the three samples. However, for cathode potentials more negative than -0.3 V_{vs. RHE}, the CO faradaic efficiency of ordered CuPd was higher, while that of phase separated CuPd was lower. As for the C₂ products, the results were reversed, with a higher faradaic efficiency of 63% for phase separated CuPd and a lower efficiency of 5% for ordered CuPd. On the other hand, for the CH₄ selectivity, the disordered phase presented a higher faradaic efficiency. Furthermore, a study of the catalyst was carried out with two different compositions, Cu₃Pd and CuPd₃, and it was observed that as the Cu concentration increased, so did the faradaic efficiency of the C₂ products [71].

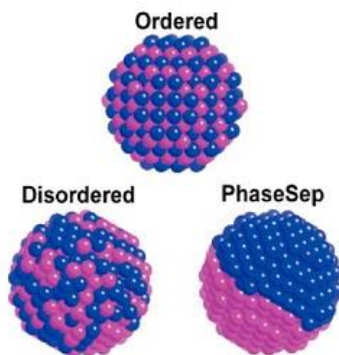


Figure 6.13. Physical characterization of bimetallic Cu–Pd catalysts with different atomic mixing patterns: ordered, disordered, and phaseseparated [71].

- **Cu – Ni alloys:**

Nickel is an interesting metal that has also been extensively studied to form an alloy with copper and have the role of a CO₂ electrocatalyst. It is able to promote the production of hydrocarbons, but only at high electric potentials. Even so, the greater affinity of CO towards Ni compared to Cu, could improve the kinetics of the C-C coupling process, which determines the reaction rate, and favouring the obtaining of C₂ products. However, the Cu-Ni alloys studied so far have only seen improvements towards obtaining C₁ products. The use of Cu-Ni nanowires, with different atomic compositions, as CO₂RR electrocatalysts was analysed. It was observed that, in a specific potential range, faradaic efficiencies close to 100% were obtained for the main reduction product, HCOOH. In addition, a FE of 16% was obtained for C₂H₅OH, and a FE of 24% for C₂H₄ [72].

- **Cu – Pt alloys:**

Platinum (Pt) has also been studied to be alloyed with Cu to give rise to electrocatalysts for CO₂RR, but in this case, they have not been so widely used due to their high affinity for the competing HER reaction; therefore, the main product obtained is H₂. Still, another study showed that when the Pt content was high, the dominant reaction was HER; but, when Cu predominated, more intermediate *CO was formed, giving rise to a greater production of CH₄. Cu-Pt nanocrystals with the appropriate atomic proportions gave rise to a FE for CH₄ greater than 20% [73].

Once some of the products with the highest faradaic efficiency of the different copper alloys have been summarized, it is possible to comment on the distinctive features of each group. First, as previously mentioned, alloying elements belonging to group 1 present CO as a reduced product with higher FE because it is less strongly bonded. However, other products, such as C₁ and C₂, are also obtained with a lower FE. As for group 2, it is characterized by presenting a metal with a greater affinity for oxygen compared to copper. The product obtained with the highest FE is HCOOH, although there are other varieties of products. Finally, in group 3, despite obtaining different products, hydrocarbons and alcohols tend to be formed in small amounts because HER is favoured.

Taula 6.5. Summary of products obtained using group 3 copper alloys.

Metal Alloy	Structures	Alloy	Electrolyte	Potential	Product	Ref.
Ni	Nanowires	CuNi	0,5 M NaHCO ₃	-0.56 V vs. RHE	CO 100% C ₂ H ₄ 24%	[72]
	Nanowires	CuNi	0,5 M NaHCO ₃	-0.77 V vs. RHE	C ₂ H ₅ OH 16%	[72]
	Nanowires	CuNi	0,5 M NaHCO ₃	-0.97 V vs. RHE	C ₂ H ₄ 24%	[72]
Pd	Nanoparticles	CuPd	0,1 M KHCO ₃	-0.90 V vs. RHE	CO 87%	[6], [74]
	Nanoparticles	Cu ₁₈ Pd ₇₂	0,1 M KHCO ₃	-0.30 V vs. RHE	HCOOH 96%	[6], [75]
	Nanodendrites	Cu ₃₀ Pd ₇₀	0,1 M KHCO ₃	-0.30 V vs. RHE	HCOOH 99,4%	[5], [76]
	Mesoporous	Pd ₇ Cu ₃	0,1 M KHCO ₃	-0.8 V vs. RHE	CO 80%	[77]
	Particles	Pd ₈₅ Cu ₁₅ /C	0,1 M KHCO ₃	-0.9 V vs. RHE	CO 86%	[70]
	Nanosheets	CuPd	0,1 M KOH	-0.6 V vs. RHE	CO 71%	[70]
Pb	Nanoparticles	CuPb	0,5 M KHCO ₃	-0.9 V vs. RHE	HCOOH 96%	[6]
	Nanofibers	CuPb	0,1 M KHCO ₃	-1.05 V vs. RHE	HCOOH 58,7%	[5], [56]
Ga	Nanoparticles	CuGa ₂	0,5 M KHCO ₃	-0.30 V vs. RHE	CH ₃ OH 77,3%	[78]
	Nanoparticles	CuGa ₁₇	0,1 M KHCO ₃	-1.20 V vs. RHE	CH ₄ 52%	[79]

6.4. IMPROVEMENT OF EFFICIENCY, SELECTIVITY AND DURABILITY OF CATALYST

To obtain the best results in the CO₂ reduction reaction, there are different strategies that allow improving the efficiency and selectivity of the products obtained [4].

The catalytic performance of our material is influenced by the size of its particles, as this allows for a diverse distribution across its surface, thus creating key active sites where the CO₂ molecule or its intermediates can be absorbed. For example, a study was carried out to analyse how different particle sizes affect the catalytic activity of an Au nanoparticle. The results demonstrated that a size of 8 nm was optimal for 90% catalytic efficiency for CO at 0.60 V vs. RHE (Figure 6.14 a) [80].

The morphology of the catalyst is also an important aspect to consider when obtaining the highest possible efficiency in our reaction. In this case, the effect of Cu nanowire morphology on CO₂RR performance in aqueous solutions was investigated. For example, they made variations in the length and density of these nanowires and observed, among other aspects, that it was possible to control the formation of hydrocarbons at a fixed potential. Thinner samples were found to result in lower faradaic efficiency at all potentials (Figure 6.14 b) [81], [82].

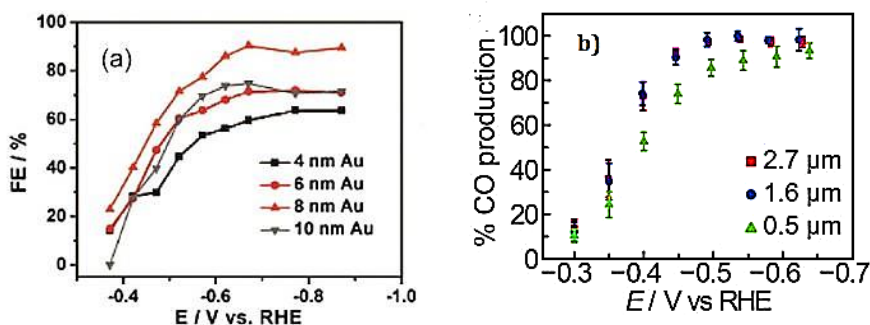


Figure 6.14. a) Potential-dependent FEs of Au NPs on carbon for electrocatalytic CO₂ reduction^[4]. b) Potential-dependent CO FE on different thickness Au catalysts ^[82].

Another strategy that improves the efficiency of our reaction are the modifications that can be made to the surfaces of our catalyst. For example, in one study it was shown that a treatment that first oxidizes the metal and then reduces it improves the performance of these electrodes by creating new active sites. It was reported that the nanostructured silver resulting from silver oxide was capable of reducing CO₂ to CO with a FE of 80% at a moderate overpotential of 0.49 V vs. RHE (Figure 6.15) [83]. Finally, it was observed that the selectivity of the reduced products obtained could be adjusted by varying the atomic composition of the bimetallic materials used as reaction catalysts.

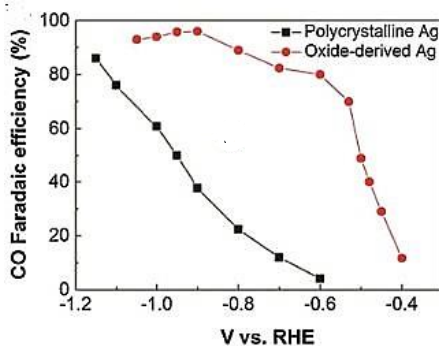


Figure 6.15. Potential-dependent CO FE of polycrystalline Ag and oxide-derived Ag [83].

In addition to considering efficiency and selectivity, it is crucial to consider the durability of catalysts for their long-term practical application. In general, catalysts tend to deactivate after several hours of use, which was initially attributed to poisoning and loss of active sites on surfaces. After various studies it was confirmed that certain CO₂RR intermediates can decrease the catalytic performance and that metallic or organic impurities in the electrolyte or anode can cause poisoning and blockage of the active sites during the reaction. To address this problem and prolong the durability of catalysts, various strategies have been proposed, such as metal doping, surface coating, and loading of a specific supported material [84].

6.5. COMPUTATIONAL METHODS

Computational methods are theoretical tools that have been very useful to further explore and understand the complex aspects of the CO₂ reduction reaction considering kinetic and thermodynamic models. For example, they facilitate detection and information about all active sites on the surface and reaction intermediates. Most of these studies are recent and over the years various effects have been incorporated, which will be briefly explained below.

Theoretical calculations have allowed the estimation of catalytic activities with fast and accurate results. This is thanks to the use of the Density Functional Theory (DFT) and the Computational Hydrogen Electrode (CHE) model, since they allow calculations on an atomic scale and, therefore, the study of a great possibility of novel materials and active sites [85]. Using these two methods it has been possible to examine reaction pathways from CO to products C₁ and C₂ through lower overpotentials. The computational model of the hydrogen electrode (CHE) is a model that implies the correction, a posteriori, of the standard constant charge, so it allows considering the potential of the electrode. It is a model that, when used in conjunction with DFT calculations, provides a picture of possible reaction pathways and redox reaction potentials.

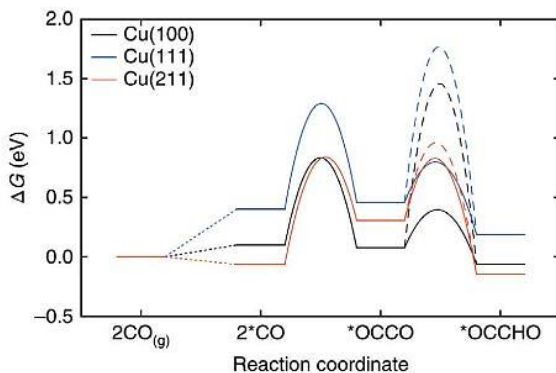


Figure 6.16. Free energy diagram of C-C coupling and the subsequent hydrogenation step on different Cu facets [40].

In the first DFT-based studies, the adsorption energies for Cu surfaces were analysed in different facets and the activation barriers were examined for each possible transition state from CO₂ to the desired product. The study authors found that, for example, for methane with a Cu (111) facet, $^*\text{CO}$ is more easily hydrogenated to $^*\text{COH}$ than to $^*\text{CHO}$ [86]. On the other hand, for the Cu (100) facet, the $^*\text{CHO}$ pathway is kinetically favoured (Figure 6.16). Therefore, the kinetics

of the elementary steps influence the reaction pathways. A new challenge currently being worked on is the formation of multiple C-C bonds, forming C₃ products and larger products such as n-propanol. Until now, the FE obtained for this type of compound have been < 3%.

- **Scaling relations**

The scaling relationships are linear correlations between the absorption energies of the intermediates and are effective for synthesizing DFT-based catalytic models. The scaling relationships have been extensively studied as they allow the implementation of additional constraints to improve the optimization of current catalysts. Also, recent studies have investigated the possibility of breaking scaling relationships for better results. Alloying, addition of promoters, introduction of *p*-block dopants, and creation of low coordination sites are some of the suggested strategies to break these scaling relationships [85].

- **Effect of structure and pH**

During the CO₂RR process there are different factors that alter the reaction mechanisms, such as pH, structural sensitivity, and ionic effects. In addition, as mentioned in previous sections, it has been shown that certain characteristics of the products obtained depend not only on the chosen catalyst material, but also on its surface structure [87]. Furthermore, it has been noted that pH plays a crucial role in the mechanism of electrochemical reduction of carbon dioxide (CO₂RR). It is assumed that during each stage of this process, sequential transfers of coupled electrons and protons occur to allow the application of the CHE model [88]. However, it is important to highlight that the CHE model cannot capture the effects of pH, since the adsorption energies of all intermediates change proportionally.

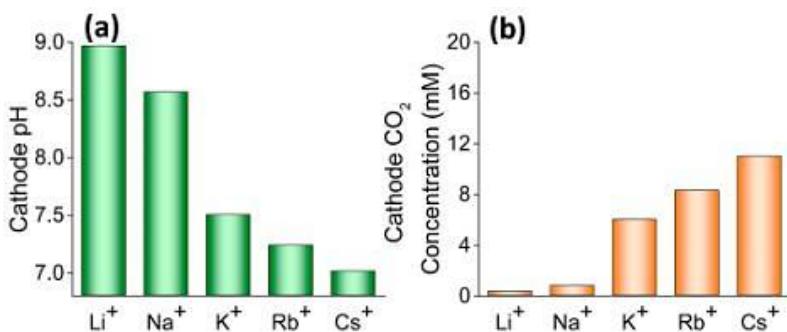


Figure 6.17. Values of (a) cathode pH, (b) cathode CO₂ concentration for some CO₂RR products in CO₂-saturated 0.1 M MHCO₃ (M = Li, Na, K, Rb, Cs) electrolyte [89].

A pioneering experimental study^[90] has been carried out that has shown that it is possible to improve the production of multicarbon species by using alkaline cations. The inclusion of larger cations can increase the selectivity towards certain products, such as C₂H₄. As can be seen in Figure 6.17, the effects of cations on CO₂RR are satisfactorily explained by the higher CO₂ concentrations in the vicinity of the cathode and the lower local pH observed with increasing cation size.

When factoring the effects of cations into computational models, there are two possible approaches: implicit and explicit. In a previous study^[91], an implicit method was used to model the effects of cations, by applying a general electric field instead of individual point charges. The electric field interacts with the adsorbed intermediates, modifying the adsorption energies according to the dipole moment of each species. On the other hand, another study^[92] used an explicit approach by considering the effects of cations using a specific model, combined with DFT calculations to account for the impact of adsorbed ions. In this way, it was observed that some ions favour the improvement of selectivity towards a particular pathway.

The computational studies are mainly based on the DFT calculations for the CO₂RR, which provides a great deal of detail about the catalytic activity of the materials. However, these calculations are often computationally expensive. One promising alternative is machine learning algorithms, which offer a different approach to electrocatalyst selection and design by leveraging an extensive library of pre-existing data from previous research. Through an initial training process, trends present in previously documented results are detected and examined. Then, through statistical analysis, it is possible to predict with some degree of accuracy new selective materials for a desired product, without the need to carry out new DFT calculations. In this way, the process of discovery and optimization of materials for CO₂RR is streamlined.

6.6. ECONOMIC AND ENVIRONMENTAL ANALYSIS

As has been explained throughout this bibliographic study, CO₂ can be electrochemically reduced to various products with similar potentials. So which CO₂ reduction product should be targeted for marketing? The answer depends, in large part, on the economy, the supply and demand of certain products, and also on general and production costs and rates. To deal with the economic issue, a techno-economic study of the conversion of CO₂ into the different products must be carried out to see if they are profitable processes [24].

Table 6.6 shows the market price (\$/kg) of the main CO₂ reduction products. Also, the price per electron (\$/electron) must be considered, since the electrical energy needed to drive the reduction of CO₂ will vary and, therefore, the electrical costs of this process. Finally, the annual global production quantities of each product also should be taken into account [93].

Table 6.6. Market price and annual global production of major CO₂ reduction products in 2016 [93].

product	number of required electrons	market price (\$/kg)	normalized price (\$/electron) × 10 ³	annual global production (Mtonne)
carbon monoxide (syngas)	2	0.06	0.8	150.0
carbon monoxide	2	0.6	8.0	
formic acid	2	0.74	16.1	0.6
methanol	6	0.58	3.1	110.0
methane	8	0.18	0.4	250.0
ethylene	12	1.30	3.0	140.0
ethanol	12	1.00	3.8	77.0
<i>n</i> -propanol	18	1.43	4.8	0.2

There are a few things to note about this table. First, in the case of carbon monoxide (CO) it can be observed its division into two by-products, synthesis gas and pure CO, since most of the CO produced industrially is in the form of synthesis gas (it contains variable amounts of carbon monoxide (CO) and hydrogen (H₂)). Syngas is a fuel that is manufactured from coal, oil or its derivatives by different methods. This gas is used as an intermediate in the production of synthetic natural gas, and to produce methanol and ammonia.

Second, formic acid is a clear example of how the relationship between supply and demand affects annual production and costs. Although it has the highest price per electron, its annual production is one of the lowest due to its limited industrial use. On the other hand, methane stands out for having the highest annual production and the lowest normalized market price. In this case,

methane plays an important role as a source of energy and heating in homes. Continuing with the products, n-propanol has a low annual production due to the difficulties involved in its production. However, if efficient production were achieved through CO₂RR, it could become a highly demanded product. Finally, of all the products, ethylene presents the highest costs due to the large amount of electricity needed per kg of product. These high costs, along with the large amount of raw material required, contribute to the low profitability of ethylene relative to other products (Figure 6.18).

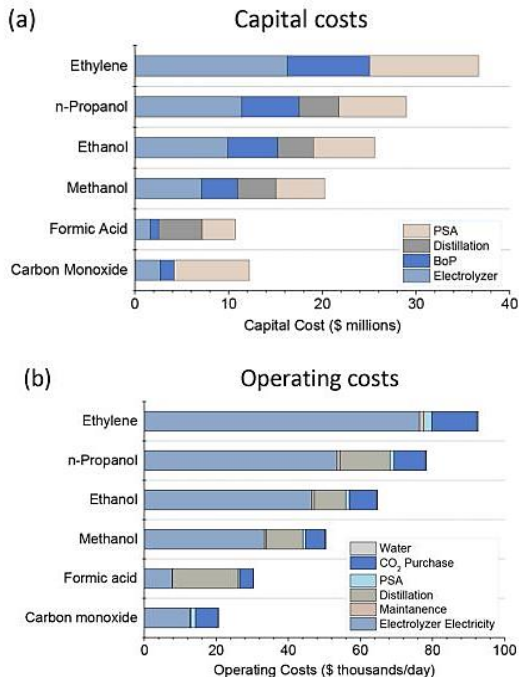


Figure 6.18. a) Capital and b) operating costs for various products under optimistic case assumptions in 2016 [93].

A point to keep in mind is the capture of CO₂ from the atmosphere or from chemical installations. Currently, it is a high-cost process, approx. 70\$/ton of CO₂ by chemical absorption with amine [94], and is the main barrier to the incorporation of CO₂ into power plants. Furthermore, a problem to consider is the presence of other combustion products, such as SO_x and NO_x, which can interfere with the performance of this process. Still, through solvent and process design improvements, the cost could be significantly reduced, and stable and efficient conversions

obtained. Also, it is worth noting the costs of the electrochemical cells, of the separation processes once the indicated product is obtained and, in addition, additional costs, such as transportation and storage, of the products of interest. Therefore, although the CO₂ reduction reaction is an innovative and promising process to reduce CO₂ emissions, it is a process that may be feasible and cost-effective at the laboratory level but nowadays expensive at the industrial level.

Although the CO₂ reduction reaction is a process to reduce emissions and obtain benefits from this gas it must serve as a net CO₂ sink avoiding CO₂ emissions and it must be socially acceptable. As for the social issue, although there is very little knowledge, there is a high initial acceptance of the technologies for the use of CO₂ to obtain products of interest. Regarding the environmental perspective, life cycle assessment studies have been carried out to see and evaluate the possible environmental impacts caused by this process.

Life Cycle Assessment (LCA) is a tool that allows to assess the impact of materials and energy flow on the environment throughout the life cycle of a process. After the LCA study, the main advantage of the electrochemical reduction technique is the use of CO₂ as raw material to replace fossil fuels thus reflecting a reduction in CO₂ emissions per Kg of product [95]. However, CO₂RR has some disadvantages compared to conventional industrial processes. First, the preparation of many of the electrode materials is complex and cannot be mass produced; this means that there will be sub-processes in the preparation of the raw material, giving rise to more substances that are difficult to degrade and a greater impact on the ecosystem. Second, questions remain about the lifetime and stability of electrode materials. And finally, CO₂RR consumes much more energy per kg of product than conventional processes. For example, the consumption to produce 1 kg of formic acid using CO₂RR is 4.351 MJ/kg product, while the energy consumption to produce 1 kg of formic acid using a conventional process is 0.552 MJ/kg product.

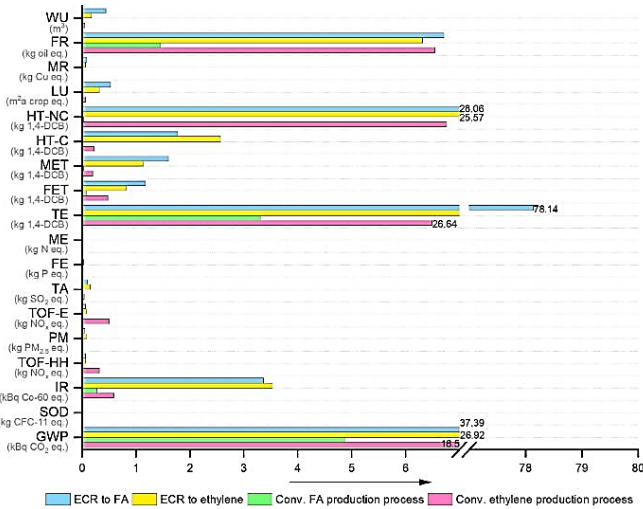


Figure 6.19. Environmental impact of electrocatalytic CO₂ reduction process and conventional process to produce acid formic and ethylene [95].

Figure 6.19 shows a comparison of the environmental impacts of four study routes, two using conventional methods and two using CO₂RR. In both processes, significant results were observed in aspects of fossil resources (FR), non-carcinogenic human toxicity (HT-NC), terrestrial ecotoxicity (TE) and global warming potential (GWP). Regarding the indicator of ionizing radiation (IR), the CO₂RR process presents higher values compared to the conventional process.

7. CONCLUSIONS

In this study, a bibliographical investigation has been carried out focused on the innovative process of electrocatalytic reduction of carbon dioxide to obtain products of interest, such as alcohols and hydrocarbons. Through this process want to reduce CO₂ emissions that cause so many environmental problems.

Mainly, the research is based on the study of metallic catalysts that allow obtaining products efficiently. Until now, only copper and its alloys have been able to form carbon-carbon bonds and give rise to C-C coupling products with remarkable faradaic efficiency. Even so, it has been seen that depending on the metal alloyed with copper and the composition and structure used, different products and different faradaic efficiencies are obtained.

Secondly, apart from the experimental studies, theoretical studies are carried out that allow the investigation to be expanded without any type of limitation. For example, they have made it possible to study all the active sites and intermediate products that are produced during the CO₂ reduction reaction, or the influence of pH in obtaining the products. These studies allow us to analyse the current challenges and the future prospects in this area.

The last key point of this study is the economic issue at the industrial level. The first experimental investigations have been carried out at the laboratory level, where CO₂ uptake is easy, the cost of metals is low due to the small amount needed to carry out the process, and the energy used is minimal. The economic problem appears when these experiments must be carried out at an industrial level, since costs increase, and CO₂ capture is not an easy task. It has also been seen that the products C₁ and C₂ are more economical due to the lower transfer of electrons and, therefore, the lower energy expenditure. Even so, research continues to obtain the best alloys and conditions to obtain carbonated products through an economically profitable CO₂RR process.

- **Final remarks**

If I had to give my opinion on which copper alloys have promise as catalysts to achieve a profitable and efficient process, I would consider the economic point. Although noble metals have proven to be very good catalysts and make it possible to obtain C_1 and C_2 products with very good FE, the costs of these metals are extremely high. In this way, if this cost can be reduced to the maximum with the use of metals that present great selectivity and good faradaic efficiency but lower cost, higher economic costs such as the cell and the energy consumed can be compensated. Therefore, if I had to choose a catalyst, I would say Cu-Zn and Cu-Ni alloys, since they have also been shown to be promising in obtaining C_3 products and more.

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12. ACRONYMS

AEM	Anion Exchange Membrane
BPM	Bipolar Membrane
CAS	Chemical Abstracts Service
CEM	Cation Exchange Membrane
CHE	Computational Hydrogen Electrode
CO₂RR	Dioxide Carbon Reduction Reaction
DFT	Density Functional Theory
FE	Faradaic Efficiency
FR	Fossil Resources
GDE	Gas Diffusion Electrode
GWP	Global Warning Potential
HER	Hydrogen Evolution Reaction
HT-NC	Non-Carcinogenic Human Toxicity
IR	Ionizing Radiation
LCA	Life Cycle Assessment
PEM	Polymer Electrolytic Membrane
RHE	Hydrogen Reference Electrode
TE	Terrestrial Ecotoxicity

