




Review

Progress in Electrodeposited Copper Catalysts for CO₂ Conversion to Valuable Products

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Abstract: Carbon capture, utilisation and storage (CCUS) is a key area of research for CO₂ abatement. To that end, CO₂ capture, transport and storage has accrued several decades of development. However, for successful implementation of CCUS, utilisation or conversion of CO₂ to valuable products is important. Electrochemical conversion of the captured CO₂ to desired products provides one such route. This technique requires a cathode “electrocatalyst” that could favour the desired product selectivity. Copper (Cu) is unique, the only metal “electrocatalyst” demonstrated to produce C₂ products including ethylene. In order to achieve high-purity Cu deposits, electrodeposition is widely acknowledged as a straightforward, scalable and relatively inexpensive method. In this review, we discuss in detail the progress in the developments of electrodeposited copper, oxide/halide-derived copper, copper-alloy catalysts for conversion of CO₂ to valuable products along with the future challenges.

Keywords: carbon capture utilisation and storage; CCUS; CCS; copper; carbon dioxide electroreduction; electrodeposition; oxide-derived copper



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1. Introduction

1.1. Background

Carbon capture, utilisation and storage (CCUS) is a culmination of technologies aiming to capture carbon dioxide (CO₂) from anthropogenic sources and either convert it into useful products or store it long-term in geological formations. It is considered as a key strategy for carbon abatement that can aid in meeting the Paris Agreement targets. Global greenhouse gas (GHG) emissions have continued to rise, amounting to 51.3 gigatonnes (Gt) of equivalent carbon dioxide emissions (CO₂e) in 2021, compared to 48.1 GtCO₂e in 2015 [1,2]. Of the 51.3 GtCO₂e in 2021, 74% (38.2 Gt [2]) were specific to CO₂ emissions, with the vast majority of annual CO₂ emissions arising from the combustion of fossil fuels and industrial processes.

In a broader context, one of the main strategies to reduce CO₂ emissions is to electrify processes that use fossil fuels directly and to generate electricity from net-zero renewable sources. While this strategy is suitable for many industries and is likely to play a key role in a future net-zero world, there is a variety of emissions sources that cannot yet be abated by this approach [3]. A circular carbon economy could be achieved by generating commodity chemicals from CO₂ emissions through this approach. Synergistic capture benefits can

then be obtained if the produced chemicals are value-added commodities. CO₂ capture has accrued several decades of development. However, despite significant investments all the way up to pilot or large-scale demonstration projects [4,5], complete deployment of post-combustion capture technologies has been limited by the high energy requirements of the process.

The concept to combine carbon capture with utilization has gained significant interest in recent years [6–11]. The conversion of CO₂ through the electrochemical route enables the production of a variety of molecules containing one, two, three or more carbon atoms (C₁, C₂ or C₃ products, etc.), which also involve a varying number of electron transfers to obtain desired products. These chemicals serve important roles as precursors to plastics, such as polyethylene, as well as a variety of specialist chemicals used in paints, cosmetics, antifreeze and medical/sterilisation applications [12]. For many of these applications, the CO₂ that was reduced can be considered sequestered or quasi-sequestered owing to the long-term use of the corresponding products. Importantly, some of these molecules could also be used as fuels, fuel additives and precursors to synthetic fuels. This is important because in addition to the issues of difficult-to-abate sectors (such as cement, metal processing industries) and the time-consuming transition to renewables, a significant drawback to the complete adoption of renewables is the issue of intermittence in the energy they provide. Therefore, the ability to use fuels in a circular system that minimises net emissions provides a way to overcome the intermittency of renewable resources.

Conversion of CO₂ is a key reaction, central to the CCUS approach. Following CO₂ capture, the loaded capture medium is processed via several unit operations to create high concentration/purity CO₂ gas, which is then fed to the electrochemical cell for conversion to desired products. The use of electrochemical cells has been the primary approach considered for the development of electrocatalysts for CO₂ electro-reduction. The development of gas-fed electrolyzers (GFE) for ethylene or C₂₊ generation has shown remarkable progress in terms of activity and selectivity towards ethylene, with operational current densities (j) exceeding 100 mA/cm² and faradaic efficiencies over 70% [13–15].

GFEs are typically made of three different compartments as shown in Figure 1. A gas diffusion electrode (GDE) on the cathode side separates the fed gas from the electrolyte, which can be a single phase (liquid or solid ion exchange membrane) or an assembly of both. A conventional non-porous/porous electrode usually serves as the anode. A GDE consists of flow fields, porous gas diffusion layer(s), catalyst layer with the porous layer structure sandwiched between the flow field and catalyst layer. CO₂ is transported to the catalyst layer through the gas diffusion layer from the gas side of the electrolyser (cathode) and is shown in Figure 1. Gas products are directed to the gas side of the electrode (cathode side) while the liquid ones stay in the electrolyte solution [16].

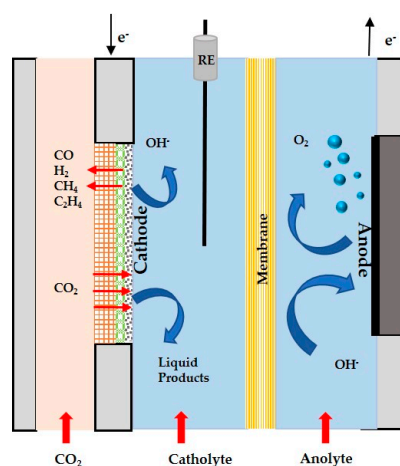


Figure 1. Figure representing the schematic diagram of the conventional gas-fed electrolyzer with three different compartments. Adapted with permission from [16].

The use of GDE in a GFE allows high CO₂ local concentrations on the surface of the electrocatalyst, suppressing unwanted, non-carbon related, side reactions such as a hydrogen evolution reaction (HER). However, high selectivity towards carbon reaction comes at the expense of low CO₂ conversions as significant excess of non-reacted CO₂ is fed to the electrolyser. All literature on GFEs have reported CO₂ conversions below 40%, with the top values obtained at the expense of lower faradaic efficiencies or current densities [6,17,18].

One technological option gaining interest to enhance carbon utilization is to feed CO₂ in a liquid stream, directly from the capture media [19,20]. The CO₂ is transferred into the cell in a liquid (intensely through introduction of amine-based solvents or purely aqueous) phase, where provision of adequate CO₂ is necessary for reaction at the electrocatalyst–electrolyte interface. However, the high concentration of water in the capture media induces HER. It is important to develop electrode architectures that contribute to the control of water access to the electrocatalyst active sites, while avoiding hydrogen evolution.

Copper (Cu) was recognized as one of the catalysts that could serve as an effective electrode to produce C₂ products such as ethylene. Cu is claimed to be the only pure metal with considerable faradaic efficiencies (FEs) capable of converting CO₂ to products involving more than two electron transfers (commonly referred to as “>2 e⁻ products”). In addition, the capacity to electrochemically convert CO₂ to beneficial hydrocarbons such as ethylene, ethane and alcohols is of significant interest. As a result, considerable research efforts were devoted to better understand the reactivity of Cu and how it might be tailored to achieve higher selectivity, stability and efficiency.

While there are different methods reported to prepare active Cu electrocatalysts, such as wet chemistry, drop casting, airbrushing or sputtering [15,21], electrodeposition methods have been regarded as straightforward when it comes to operation and scalability when it comes to the synthesis and production of catalysts. Additionally, high-purity metal deposits are more cost-effective than wet chemical synthesis. In contrast to the easy electrodeposition procedure, wet chemical methods necessitate the utilisation of severe operating conditions, chemicals, lengthy stages and a significant labour effort.

1.2. Objectives and Review Methodology

This review aims to provide an overview of current developments in electrodeposition-based, Cu-containing materials that are effective catalysts for carbon dioxide conversion into C₂ chemicals such as ethylene and ethane by providing a comprehensive overview of the current state of knowledge. This is expected to provide a reference for the synthesis of an electrocatalyst that is capable of operating with high CO₂ reduction selectivity, even under flooded conditions, with low faradaic efficiency for hydrogen evolution. This review also focuses on the importance of electrodeposition as a simple and economic method for synthesising copper-based catalysts for conversion of CO₂ while summarising the progress in the electrodeposited metals for CO₂ conversion to valuable compounds. Table 1 lists the key reviews that were published covering the period 2019–2022 and provides a summary of the topics covered, with a focus on CCUS. According to Table 1, published reviews on the creation of catalysts focusing on the electrodeposition method as a flexible way to build catalysts for electrochemical CO₂ conversion are limited, indicating the significance of the current study. Besides the progress in electrodeposition, the review also emphasizes other key aspects such as choice of electrolyte (aqueous, non-aqueous), catalyst morphology and the test cell configurations (electrolyser, H-cell).

There are five sections to the review (Sections 2–6 of the paper). Section 2 provides the main principles and insights of electrodeposited copper for electrochemical CO₂ reduction (hereinafter referred to as “ECR”). Section 3 focuses on the advancements of oxide-derived copper and halide-derived copper-based catalysts, as well as their performance in ECR. Section 4 provides a brief overview of electrodeposited copper alloys. Section 5 summarises the current state of knowledge and future difficulties linked with the requirement to produce copper electrocatalysts with precise orientation in order to achieve C₂ product

yield and selectivity. The final section (Section 6) summarises the findings and provides concluding remarks, emphasising the future roadmap.

Table 1. Key reviews published during 2019–2022 along with their summaries.

Year	Author	Summary
2019	Chen et al. [22]	Reviewed the role of ionic liquid (IL) as a solvent, electrolyte, CO ₂ absorbents, CO ₂ activating agents, catalysts or co-catalysts and their contribution towards the conversion of CO ₂
2019	Nitopi et al. [23]	Reviewed different aspects of the complex interplay associated with copper-based catalysts and their mechanisms towards formation of products via electrochemical CO ₂ conversion covering the experimental and theoretical elements.
2020	Pérez-Sequera et al. [24]	Reviewed works that employed carbon that has been doped with boron, fluorine, nitrogen and sulphur to electroreduce CO ₂ , with a focus on the synthesis processes and the electrochemical performance of the resultant materials.
2020	Nguyen et al. [25]	Reviewed developments in catalysts and their design strategies (nano structuring, alloying, doping) for the electrochemical conversion of CO ₂ to CO.
2020	Garg et al. [26]	Reviewed the impact of design and operating conditions related to electrolyser configurations, choice of electrolytes, structure of electrode and their relation to the reaction conditions at catalyst sites in a CO ₂ electrolyser and the efficiency of the process.
2020	Zhao et al. [27]	Reviewed activities in copper catalysts with different morphologies and forms (metallic, oxide-derived, halide-derived), covering different electrolytes (aqueous, non-aqueous) along with the catalysts' electrochemical performance towards the CO ₂ reduction.
2020	Fan et al. [28]	Discussed the mechanisms and the function of the catalysts with dendritic nature, emphasising the need to combine in situ spectroscopic techniques with computational simulations that confirmed the nature of these active sites and provided insights into the mechanisms associated with dendrite morphology-based catalysts.
2020	Yang et al. [29]	Reviewed the progress in CO ₂ electroreduction involving ILs with different catalysts and their mechanism in IL-based electrolytes.
2020	Cui et al. [30]	Reviewed three research areas on electrochemical CO ₂ reduction in ionic liquids (ILs) including (i) the adsorption of CO ₂ by ILs, (ii) the electrolytes composed of ILs and (iii) the electrode modification in ILs.
2021	Yang et al. [31]	Summarised the most recent developments in structural modification of metals that catalyse the CO ₂ conversion, including size, crystal facets and phase composition, grain structure, surface, interface and modification of ligands.
2021	Masel et al. [32]	Reviewed the state-of-the-art CO ₂ electrolyzers from an industrial perspective, highlighting the catalyst developments associated with CO ₂ conversion to CO, formic acid. Future perspectives and catalyst design strategies associated with C ₂ , C ₂₊ products were provided.

Table 1. *Cont.*

Year	Author	Summary
2020	Li et al. [33]	Reviewed developments of in situ studies to monitor the reaction intermediates and catalyst evolution during the electrochemical conversion of CO ₂ process with a future prospective suggestion.
2021	Xiao et al. [34]	Reviewed the tailored copper electrocatalyst architectures for electrochemical CO ₂ conversion and their correlation between the architecture and selectivity towards the formation of C ₂ products.
2021	Liang et al. [35]	Reviewed different types of electrocatalysts including noble metals and their derived compounds, transition metals and their derived compounds, organic polymer and carbon-based materials for the electrochemical conversion of CO ₂ . Discussed the major products formed in relation to the faradaic efficiency, current density and onset potential along with the reaction mechanisms.
2021	Yu et al. [36]	Reviewed approaches in catalyst engineering focusing on composition, size, crystal facet, surface and interface effects towards the electrochemical conversion of CO ₂ to C ₂ , C ₂₊ products.
2021	Luo et al. [37]	Reviewed the performance of gas diffusion electrodes coated with different catalysts towards CO ₂ reduction to multi carbon products and their operating life time along with future prospects for advancing the electroreduction of CO ₂ .
2021	Li et al. [38]	Reviewed advances in the catalysts coated onto the gas diffusion layer and their electrochemical performance as a cathode in a CO ₂ electrolyser. The influence of altering the wettability of the gas diffusion layer towards improving the cathode performance along with their challenges and opportunities for development was also reviewed.
2022	Woldu et al. [39]	Reviewed advances in the activity and selectivity of CO ₂ reduction to C ₂₊ products over different Cu-based catalysts such as metallic copper, oxide-derived copper and halide-derived copper covering the facet-dependant surface oxide relationships.
2022	Sargeant et al. [40]	Reviewed the electrochemical conversion of CO ₂ in organic solvents, ionic liquids, solid electrolytes and brines.
2022	Ruiz-López et al. [41]	Reviewed progress on C ₂ , C ₂₊ products produced from the electrochemical route considering the catalyst design, electrochemistry and techno-economic aspects.
2022	Miao et al. [42]	Provided a general overview on the progress and prospect of electrodeposition-type catalysts in CO ₂ reduction.

2. Electrodeposition of Copper

2.1. Key Concepts

Copper (Cu) is a unique substance with exceptional physical, chemical, electrical and electrochemical characteristics, to mention but a few. Since the year 2000, there has been substantial study of copper electrodeposition, with almost 2500 published papers during this time period. Figure 2a depicts the number of research publications published on copper electrodeposition for various purposes, and Figure 2b depicts the breakdown of electrodeposited copper utilised in applications such as fuel cells, catalysis, temperature sensors and photovoltaics. This research has shown a variety of possible ways for tailoring the characteristics of copper-based catalysts for use in the CO₂ electroreduction process to produce valuable compounds.

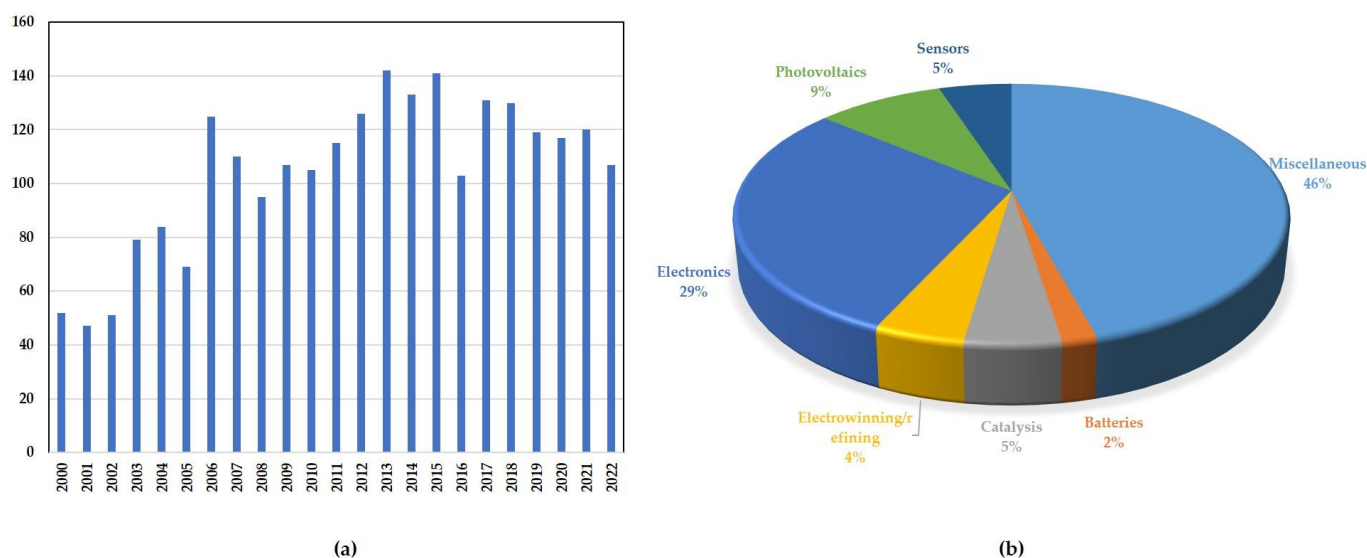


Figure 2. (a) Breakdown of the number of papers published on copper electrodeposition from 2000 till December 2022. Data taken from a search of the Scopus database with different key words: electrodeposition; copper; carbon capture, electrochemical reduction of carbon dioxide, carbon capture utilisation and storage. (b) Applications of electrodeposited copper that were reported from 2000 till December 2022. Data taken from a search of the Scopus database.

Cu has the unique capability to produce a variety of hydrocarbons, aldehydes and alcohols when used as an electrocatalyst for the electroreduction of CO_2 . Metallic copper exhibits a face-centred cubic (fcc) crystal structure and the preferential exposure of certain Cu $\{hkl\}$ faces has been studied primarily for its ability to increase the FE of C_{2+} products in general and to specifically tune the FE towards certain C_{2+} products. It has been suggested that in order for the electroreduction to be economically viable, an FE of 80–90%, a current density in excess of 300 mA cm^{-2} , a cell voltage of less than 1.8 V and system stability in excess of 80,000 h are required [41,43].

Single crystal studies by Hori et al. [44] of two low index Cu facets (Cu $\{110\}$ and Cu $\{111\}$) demonstrated an increased FE for methane (CH_4) compared to planar polycrystalline Cu as well as increased ethylene (C_2H_4) suppression resulting in very low FE for ethylene (C_2H_4). The same studies demonstrated an FE for $>2 e^-$ transfer products in excess of 90% at 5 mA cm^{-2} for Cu $\{100\}$. These studies also reported increased CH_4 suppression with a 10:1 $\text{C}_2\text{H}_4:\text{CH}_4$ ratio and a 50% FE for ethylene (C_2H_4) on Cu $\{711\}$ compared to 40.4% C_2H_4 FE and a 4:3 ratio on Cu $\{100\}$ all at potentials between -1.34 and -1.40 V vs. the reference hydrogen electrode (RHE) [45–48].

Cu faceting has also been a useful technique to improve the theoretical understanding of electroreduction of CO_2 [40,42]. However, there is still a significant lack of understanding and consensus regarding the mechanisms by which various products are formed through the ECR, and this is a major drawback in the efforts for rational catalyst design to maximise the effectiveness of the CCUS process. While monolithic blocks of single crystals have a low geometric surface area and are not suitable for use as electrocatalysts, experimental observations on single crystal facets have provided validation for only certain theoretical approaches and thus helped to reduce the number of possible mechanisms. The ECR typically takes place at the electrode–electrolyte interface. Therefore, the activity of the catalyst and product selectivity are strongly associated with the binding strength between the catalyst surface (typically metal) and the adsorbed intermediates. For example, for ethylene formation on Cu $\{100\}$, three pathways to C–C coupling have been proposed and are thought to be dependent on the overpotential being applied [26], however, in the low overpotential scenario there is disagreement on the subsequent reaction pathway taken to produce C_2H_4 [26]. The performance of the catalyst is influenced by the mode

of co-ordination (carbon, oxygen, mixed) between the chemisorbed CO₂ and the catalyst. Research showed that these coordination modes are typically influenced by the:

- Type of the electrocatalyst—size and orientation, surface morphology, crystal structure and phase composition, oxidation state (valency).
- Supporting electrolyte—pH, concentration, anion, cation and its associated electrical fields, and could be interchanged.
- Electrical field.

2.2. Key Insights

The high activation overpotentials required to activate the CO₂ reactant seriously limit the efficacies of CO₂ electroreduction. Particularly when employing aqueous media, the (parasitic) water splitting process superimposes the electroreduction of CO₂ conversion, greatly lowering the overall CO₂ conversion efficiency. The numerous studies reported on the subject, as can be seen in Table 1, demonstrated that the co-ordination modes could be interchanged and had a significant influence on the electrochemical reduction of CO₂ and product selectivity. Recognizing the significance of the chemisorption step, many ways for improving the electrochemical CO₂ reduction process have been investigated. The emphasis was on increasing active catalyst sites, electrochemical surface area, surface defects, surface area (chemical)-pore volume ratios and producing binary metal co-catalysts. One of the effective strategies for improving CO₂ conversion performance is to synthesise the catalyst using electrodeposition because it provides the flexibility to obtain a catalyst that meets the aforementioned criteria and may influence the mode of co-ordination between the chemisorbed CO₂ and the catalyst.

Cu-based catalysts are recognized for their exceptional capacity to bind the intermediates formed during the electrocatalytic process in a balanced way, hence lowering the overpotentials. In addition, these catalysts have the unique capability to bind CO₂ and protonate CO that is adsorbed to CHO*(C-O-H) or COH*(H-C=O) intermediates. The Cu catalysts also possess the capability of producing a variety of hydrocarbon products such as C₁ (e.g., formate, formic acid, methane) and C₂ (e.g., ethane, ethylene, ethanol) but with low product selectivity. Some of the pioneering works by Hori et al. [44,45,47–49] clearly demonstrated a favourable efficient C-C coupling (C₂ pathway) on single crystal Cu catalysts with a {1 0 0} textured surface. On the contrary, methane (C₁ pathway) was shown to be the preferred hydrocarbon reaction product on Cu {1 1 1}-type surfaces. In a similar vein, research by Sargeant et al. [40] showed that Cu with a {1 0 0} composition could achieve faradaic efficiency (FE) for C₂₊ products up to 90% at a partial current density of 520 mA cm⁻² (0.67 V against reversible hydrogen electrode, RHE). Full cell test results conducted in an electrolyser with a membrane electrode assembly configuration resulted in C₂₊ conversion efficiencies of 37% and accomplished C₂H₄ product selectivity during the course of 65 h of operation at a current density of 350 mA cm⁻².

There is, however, a need for a careful approach when looking at single crystal studies, largely related to the potential for catalyst restructuring to occur. Due to the reactivity and mobility of copper, the electrocatalyst is highly susceptible to a variety of in situ and ex situ factors that can cause restructuring of the single electrodes and affect electrochemical performance and characterization (including the electrolyte media, and oxidation through air exposure). This phenomenon was shown by Hori et al. [48], highlighting the dependence of the electrode pretreatment used on the results obtained on Cu {1 1 1} and Cu {1 1 0} single crystals. In addition, the study also discussed the possibility of Cu restructuring under certain reaction conditions, which could potentially influence the Cu catalysts' performance towards ECR in terms of activity and selectivity. This was further examined by Eren et al. [50], who reported on the restructuring of Cu {1 1 1} to a highly textured surface when exposed to low CO partial pressures in a vacuum.

Cu nanoparticles could be an ideal electrocatalyst owing to their high electrochemical surface area, significant roughness factors often expressed as a ratio between the electrochemical surface area and geometrical surface area. Through proper control of the

electrodeposition parameters (deposition overpotential, electrolyte concentration, metal precursor, current density, etc.) and electrolyte conditions, it is possible to attain a catalyst with different morphologies such as dendritic, cubic, columnar and so on.

Gonclaves et al. [51] obtained Cu nanoparticles with three morphologies on copper substrates by varying the potential in the range between -0.55 and -1.15 V (vs. SCE). Dendrites with different sizes, varying strengths and thickness were reported with increasing cathodic potentials up to -1.05 V while deposition at higher potentials displayed a transition in morphology to honeycomb and 3D-foam-like structures. The study highlighted the Cu dendritic growth dependence on the deposition potential and its influence on the hydrogen evolution. Cu 3D-foams and honeycomb structure catalysts developed at higher deposition potentials (>-1.05 V vs. SCE) indicated better C_2 product (C_2H_4 , C_2H_6) yield than the dendritic ones with significant suppression of C_1 product (CH_4) formation, signifying the role of electrodeposition on the catalyst structure and electroreduction of CO_2 . Besides deposition potential, the study also demonstrated the influence of electrolyte concentration and the choice of substrate on the morphological features of the copper. Increasing the electrolyte (H_2SO_4) concentration in the range 0.5 – 1.5 mol L^{-1} was shown to promote higher hydrogen gas evolution during deposition and resulted in the formation of porous electrode structures. The authors also demonstrated the influence of metal precursor (copper sulfate, $CuSO_4$) concentration in relation to the porous Cu catalyst structures. It was shown that increasing the metal precursor concentration (from 0.15 to 0.2 g L^{-1}) accelerated the rate of deposition, favouring faster reduction of copper relative to the hydrogen gas evolution which influenced the size of the pores and wall thickness of the porous structures formed. The porous structures formed by varying the electrolyte conditions were shown to exhibit high electrochemical surface area, to facilitate rapid transport of gas and liquid and to favour C_2 product selectivity. Besides the above-mentioned factors that influence the electrodeposition process, the choice of substrate and additives such as triazoles, pyrrolidones and tetraalkyl halides has a direct influence on the catalyst morphology and its growth orientation.

Different types of electrodeposition baths are available for copper electrodeposition, including cyanide copper, pyrophosphate copper and acid copper. Although cyanide copper solution is still used in many commercial plating processes, the relatively high toxicity problem further limits its application. As a consequence, the acid copper bath is becoming more attractive for copper deposition. Within the group of acidic copper solutions, sulfuric acid (H_2SO_4) and sulfate-based ($CuSO_4$) solutions are most popular in industrial applications as well as in academic research. Attempts were also made with different anions such as phosphates and nitrates. Zhao et al. [52] studied the effect of phosphate ligands in relation to the morphological transition from particles to branched structures and the product selectivity was investigated in detail. By modifying the electrode with phosphate ligands, it has been demonstrated that phosphate anions could be combined with free Cu(II) to produce complexes that could compete with the electrodeposition process at the identified deposition potentials and allow dendrites to take the place of aggregates. For comparison purposes, deposition was also performed on copper foils in the absence of phosphate ions. The morphology of the deposited Cu was transformed from particles to hexagonal plates and to branched 3D structures by varying the applied voltage and phosphate concentrations. As compared to Cu foil (FE 33%), the modified electrodes containing phosphate species showed greater selectivity for HCOOH production from the electrochemical reduction of CO_2 (FE 80%).

Scholten et al. [53] reported on the electrodeposition of copper nanodendrites on silver and platinum substrates employing copper sulfate as the metal precursor. Prior to deposition, the substrates were pretreated using plasma treatment in an oxygen environment for different time intervals. The results of the electrodeposited copper on the treated substrates exhibited a dendritic morphology with different properties. Copper dendrites deposited on pretreated platinum produced substantial amounts of hydrogen, whereas copper dendrites deposited on pretreated silver produced carbon monoxide. The study

found that the substrate and its treatment had a direct association between the roughness, surface morphology and catalytic performance of copper deposits, as well as product selectivity and method of deposition. The substrate treatment not only changes the deposition morphology, but it also suppresses the hydrogen evolution process.

Table 2 lists the works that reported on the electrodeposition of copper with different morphologies performed via potentiostatic or constant voltage mode along with the deposition conditions and their catalytic performance towards electroreduction of CO₂.

Table 2. Table lists the works that reported on the electrodeposition of copper obtained via potentiostatic mode.

Substrate	Electrolyte	Deposition Conditions	Morphology	Major Product (s)	FE _{C₂H₄} , %	Reference
Copper mesh	0.15 M CuSO ₄ ·5H ₂ O + 0.5 H ₂ SO ₄	−0.55 V vs. SCE until a final deposition charge of 25 C cm ^{−2} was reached	Dendritic with different size and thickness	CH ₄ , C ₂ H ₄	5	[51]
Copper mesh	0.15 M CuSO ₄ ·5H ₂ O + 0.5 MH ₂ SO ₄	−0.65 V vs. SCE until a final deposition charge of 25 C cm ^{−2} was reached	Dendritic with different size and thickness	CH ₄ , C ₂ H ₄	10	[51]
Copper mesh	0.15 M CuSO ₄ ·5H ₂ O + 0.5 MH ₂ SO ₄	−0.85 V vs. SCE until a final deposition charge of 25 C cm ^{−2} was reached.	Dendritic with different size and thickness	C ₂ H ₄	8	[51]
Copper mesh	0.15 M CuSO ₄ ·5H ₂ O + 0.5 M H ₂ SO ₄	−1.05 V vs. SCE until a final deposition charge of 25 C cm ^{−2} was reached	Dendritic with different size and thickness	C ₂ H ₄	8	[51]
Copper mesh	0.15 M CuSO ₄ ·5H ₂ O + 1.5 M H ₂ SO ₄	−1.15 V vs. SCE until a final deposition charge of 25 C cm ^{−2} was reached	Honey comb	C ₂ H ₄	8	[51]
Copper foil	0.15 M CuSO ₄ ·5H ₂ O + 1.5 M H ₂ SO ₄	−1.15 V vs. SCE until a final deposition charge of 25 C cm ^{−2} was reached	Honey comb	C ₂ H ₄ , C ₂ H ₆	10	[51]
Copper foil	0.2 M CuSO ₄ ·5H ₂ O + 1.5 MH ₂ SO ₄	−1.15 V vs. SCE until a final deposition charge of 25 C cm ^{−2} was reached	3D foam	C ₂ H ₄ , C ₂ H ₆	9	[51]
Copper sheet	0.025 M CuSO ₄ ·5H ₂ O + 1 M H ₂ SO ₄	−0.3 V (vs. Ag/AgCl) for 300 s	Spheres of Cu nanoparticles	CH ₄ , C ₂ H ₈	43	[54]
Copper sheet	0.25 M CuSO ₄ ·5H ₂ O + 1 M H ₂ SO ₄	−0.3 V (vs. Ag/AgCl) for 300 s	Densely populated larger cubes	CH ₄ , C ₂ H ₈	28	[54]
Copper mesh	CuSO ₄ ·5H ₂ O + H ₂ SO ₄	−1.1 V vs. RHE	Dendritic with different size and thickness *	HCOO [−] , C ₂ + alcohols (ethanol, n-propanol)	49.2	[55]
Carbon paper	Cu(NO ₃) ₂ + H ₂ SO ₄	−0.3 V (vs. Ag/AgCl) for 1800 s	Tiny particle with rich grain boundary	C ₂ H ₄ , C ₂ H ₅ OH	73	[56]
Carbon paper	Cu(NO ₃) ₂ + H ₂ SO ₄	−0.3 V (vs. Ag/AgCl) for 1800 s	Uniform lattice-oriented particles without grain boundaries	C ₂ H ₄ , C ₂ H ₅ OH	49	[56]
Copper plate	CuSO ₄ ·5H ₂ O + H ₂ SO ₄	12 V	Porous and dendritic #	H ₂ , HCOOH	20	[57]
Carbon paper	CuSO ₄ ·5H ₂ O + H ₂ SO ₄	0.3 V vs. Ag/AgCl	Smooth and flat #	C ₂ H ₄ , C ₂ H ₅ OH	40.67	[58]

* Potentiostatic deposition followed by thermal annealing. # IL-modified Cu foam.

Cu prepared on electropolished Cu foils through the electrochemical anodization route displayed a predominant {1 0 0} facet with cubic morphology with C₂H₄ as the major product and a FE of 45%. Electrodeposited Cu nanocubes with {1 0 0} facet on carbon paper (Toray, Tokyo, Japan) with different cube sizes (80 nm–1.2 μm) were obtained by Grosse et al. [59], but the product selectivity was low with 20% FE. The study highlighted not only the morphological instability of the Cu cubes, and change in surface roughness during

operation, but also indicated that the size dependency and formation of sub-surface oxygen play a critical role in the formation of C_{2+} products.

Although nanoparticles have a large active surface area and are therefore very active, the need for a binder to attach the particles to an electrode limits their activity and stability. High porosity Cu metal foams might be able to provide a high surface area catalyst without the need for a binder. However, the most common methods for producing Cu metal foams are electrodeposition utilising hydrogen bubbles as the template or metallization on a foam substrate. The architectures of the foam substrates that can be used to create metal foams are expensive and constrained by the availability of foam substrates and their structures. While the hydrogen bubble templating method has the advantages of being straightforward and inexpensive, the rapid rate of deposition under potentiostatic conditions during foam synthesis and the active hydrogen bubble evolution limit the tunability of the film structure and may adversely affect film stability, especially at high catalyst loading. Moreover, H_2 is the primary byproduct resulting from the electroreduction of CO_2 using Cu foam-based catalysts with FE in the range 50–90%, restricting the overall efficiency of ECR to desired products by 10–50%.

To alleviate the hydrogen (H_2) gas evolution, one of the effective strategies is to employ carbon-based materials owing to their excellent electron transfer and interaction capabilities. This could be achieved via the introduction of defects either extrinsic (through surface functionalisation, heterodoping, electrochemical activation) or intrinsic through post-treatment. Ma et al. [60] synthesised 3D vertical graphene on carbon paper combining a plasma enhanced chemical vapour deposition and an argon-based post treatment, deposited copper nanoparticles via pulsed galvanostatic electrodeposition. For comparison, copper was electrodeposited onto 3D vertical graphene and 2D graphene without post treatment. The results reported a better Cu dispersion on the post-treated vertical 3D graphene with good stability. The authors observed that the 3D vertical structures could provide more anchoring sites for Cu while the argon-based post-treatment generated intrinsic defects that could alter the electron accessibility to Cu active sites, thereby suppressing the hydrogen gas evolution.

Carbon materials such as pure graphite, carbon nano tubes (CNTs) and graphene oxide (GO) were explored and often contain metallic impurities, with Cu being one among them besides nickel (Ni) and iron (Fe). The presence of these impurities influences the electrochemical properties and often alters the electrochemical reduction of CO_2 , resulting in inconsistent product yields. Ager et al. [61] investigated the role of metallic impurities in carbon supports towards the electrochemical reduction of CO_2 , comparing the performance of the supports before and after removal of the metallic impurities. The authors utilized the benefits of electrodeposition by depositing copper onto the treated carbon supports and demonstrated FE up to 40% with methane as the major product. The study highlighted the significance of introducing surface defects in carbon supports and the potential role of electrodeposition as a versatile tool to produce a highly active Cu catalyst on defect-engineered carbon supports (such as graphene) for electrochemical reduction of CO_2 . Research works were also devoted towards producing ethylene with electrodeposited catalysts supported on doped carbon supports such as nitrogen-stacked graphene sheets and resulted in FE up to 27%. Though the novel carbon-based materials are reported to play a key role in promoting the CO_2 reduction reaction, they are prone to electrochemical corrosion owing to the fact that the product selectivity is tested at significantly high potentials (>-0.9 V vs. RHE), thereby limiting the stability and durability of the catalyst. Table 3 presents some of the key works carried out on the electrodeposition of copper on carbon-based supports.

Table 3. Works reported on the electrodeposition of copper obtained on different composite-based substrates.

Substrate	Electrolyte	Mode of Deposition	Morphology	Major Product (s)	FE _{C₂H₄} , %	Reference
3D vertical graphene	0.02 M CuSO ₄ ·5H ₂ O + 0.15 M lactic acid	Pulsed galvanostatic	nanoparticles		~3	
3D vertical graphene-argon treated	0.02 M CuSO ₄ ·5H ₂ O + 0.15 M lactic acid	Pulsed galvanostatic	nanoparticles	formate	~6	Ma et al. [60]
2D graphene	0.02 M CuSO ₄ ·5H ₂ O + 0.15 M lactic acid	Pulsed galvanostatic	nanoparticles		NA	
Pure graphite	0.01–2 ppm CuSO ₄ ·H ₂ O + 0.1 M NaHCO ₃	Potentiostatic deposition	nanoparticles		N.D.	
Carbon nanotubes (CNTs)	2 ppm CuSO ₄ ·H ₂ O + 0.1 M NaHCO ₃	Potentiostatic deposition	nanoparticles	methane	N.D.	Ager et al. [61]
Graphene oxide (GO)	2 ppm CuSO ₄ ·H ₂ O + 0.1 M NaHCO ₃	Potentiostatic deposition	nanoparticles		N.D.	
nitrogen-doped Graphene sheet stacks	0.05 M–1.25 M CuSO ₄ ·5H ₂ O aqueous solution	Pulse mode	Dendritic, needles	ethylene	27%	Lesnicenoks et al. [62]

Current density and deposition time are additional process parameters that influence the morphology and the materials deposited on a given substrate. As a consequence, the ECR performance of the materials produced utilising different electrodeposition methods are divergent. Additives are often introduced into the electrodeposition bath with the objective to either control or transform the surface morphology and structure. Hoang et al. [63] reported on the galvanostatic or constant current deposition of copper from an electrolyte containing copper sulfate and sulfuric acid employing three different additives: (i) 3,5-diamino-1,2,4-triazole (DAT), (ii) dodecyltrimethylammonium bromide (DTAB) and (iii) thonzonium bromide (ThonB). The results included different morphologies (dots, wires, films). The authors observed a controlled morphological feature when 3,5-diamino-1,2,4-triazole (DAT) is introduced into the electrodeposition bath. The results showed that the additive could act as an inhibitor which could not only control the morphology of copper but also resulted in high specific surface area with a porous structure. CuDAT-wire samples were reported to exhibit the best CO₂ reduction activities favouring C₂H₄ product formation with FE up to 40% at −0.5 V vs. RHE and C₂H₅OH as the other product with 20% FE. Jeon et al. [64] attempted a single step electrodeposition to produce highly defective prism-shaped Cu catalysts, employing copper sulfate solution, while varying concentrations of the Janus Green B additive in the range 0.4–2.0 mM. The authors demonstrated that the additive could not only act as a crystal modifier to produce prism-shaped Cu morphological structures but also had the capability to induce the preferential deposition of Cu ions. Cu with prism-shaped structures were shown to exhibit high ECR activity favouring C₂H₄ production with an excellent stability over at least 12 h.

Chen et al. [56] introduced an inert polymer polyvinylpyrrolidone (PVP) as an additive in the electrodeposition of copper and reported on the method development focusing on the grain control and growth of copper electrodeposition. The results showed that PVP could influence the kinetics of copper electrodeposition through selective adsorption on the copper surface and increasing the nucleation rate while decreasing the crystal size. In comparison with Cu electrocatalysts that were deposited in the absence of PVP, grain boundary-rich Cu obtained with the addition of PVP exhibits higher C₂ product selectivity (FE = 70%) in the range of ~1.0 to ~1.3 V (vs. RHE). Table 4 lists the works that reported employing different additives during the electrodeposition of copper with differ-

ent morphologies performed via different modes of deposition, along with the deposition conditions and their catalytic performance towards electroreduction of CO₂.

Table 4. Works that reported on the electrodeposition of copper employing different additives.

Substrate	Additive	Deposition Media	Mode of Deposition	Morphology	Dominant Facet (hkl)	Test Electrolyte and Cell Type	Product(s)	Performance	Reference
CP	PVP	6.5 mM Cu(NO ₃) ₂ + 0.5 g PVP + 50 mL ultra-pure water	Potentiostatic	Grain boundary rich	{111}	1 M KOH saturated with 5 mL min ⁻¹ of CO ₂ and flow cell	C ₂ H ₄ , C ₂ H ₅ OH	FE of 70–73% in a potential range between –1.0 and –1.3 V vs. RHE	[56]
Au	DAT	0.1 M CuSO ₄ ·5H ₂ O + H ₂ SO ₄ + 10 mM DAT	Galvanostatic	Dot	{111}	1 M KHCO ₃ and H-Cell	C ₂ H ₄ , C ₂ H ₅ OH	CuDAT-wire samples exhibited the best CO ₂ reduction activities with an FE for C ₂ H ₄ product formation reaching 40% at –0.5 V vs. RHE, 20% for C ₂ H ₅ OH at –0.5 V vs. RHE	[63]
Au	DAT	0.1 M CuSO ₄ ·5H ₂ O + H ₂ SO ₄ + 10 mM DAT	Galvanostatic	Wire	{111}				
Au	DAT	0.1 M CuSO ₄ ·5H ₂ O + H ₂ SO ₄ + 10 mM DAT	Galvanostatic	Amorphous	{111}				
Au	DTAB	0.1 M CuSO ₄ ·5H ₂ O + H ₂ SO ₄ + 10 mM DTAB	Galvanostatic	Smooth	{111}				
Au	ThonB	0.1 M CuSO ₄ ·5H ₂ O + H ₂ SO ₄ + 10 mM ThonB	Galvanostatic	Smooth	{111}				
CP	DAT	0.1 M CuSO ₄ ·5H ₂ O + H ₂ SO ₄ + 10 mM DAT	Galvanostatic	Agglomerates -		1 M KOH and Flow electrolysis cell	C ₂ H ₄ , C ₂ H ₅ OH	The FE for C ₂ H ₄ production for the CuDAT-wire catalyst reaches and maintains a maximum value of ~40% at a potential of –0.5 V vs. RHE for C ₂ H ₄ , when tested in a flow electrolysis cell. Around 20% of FE is achieved for C ₂ H ₅ OH at –0.5 V vs. RHE	[63]
Cu foil	Janus Green B	0.25 M CuSO ₄ ·5H ₂ O + 0.3 M H ₃ BO ₃ + 0.4–2.0 mM Janus Green B	Galvanostatic	Prism shape	{111}, {200}	0.1 M KHCO ₃ Two-compartment electrochemical cell	C ₂ H ₄	FE of 27.8% C ₂ H ₄ at 1.1 V vs. RHE	[64]

Au—gold; CP—carbon paper; DAT—3,5-diamino-1,2,4-triazole; DTAB—dodecyltrimethylammonium bromide; PVP—poly vinyl pyrrolidone; ThonB—hexadecyl [2-[(4-methoxyphenyl)-methylpyrimidin-2-yl amino] ethyl]dimethyl azanium bromide (thonzonium bromide)).

Though additives have been shown to influence surface morphology during the deposition process, the addition of surfactants, complexing agents, polymers and structure-directing agents as additives during the production of electrodeposited Cu electrodes still necessitates laborious procedures to remove them completely from the electrodeposited catalyst surface, allowing them to be used as pure catalysts. Furthermore, the position of the small additive molecules often detach from the catalyst surface affecting the reaction characteristics, altering the co-ordination of C-O, contaminating the electrolyte and resulting in detachment of catalyst particles from the electrode surface, hence affecting their long-term stability. Therefore, it is important to develop either an eco-friendly water-soluble additive or a template-free electrodeposition process with preferred orientation to achieve the desired performance towards CO₂ electroreduction.

3. Electrodeposition of Oxide-Derived Copper

In addition to modifying the shape and growth direction of Cu, reducing surface oxide phases is thought to be a promising method for boosting the availability of weakly coordinated surface sites and is a significant factor affecting the activity and product selectivity of ECR. The benefits of obtaining reduced surface oxide phases through activation

of Cu catalysts (also termed as oxide-derived (OD) Cu) extend beyond CO₂ conversion and include electroreduction of CO as well. Dutta et al. [65] evaluated the performance of mesoporous Cu foams developed by template-assisted electrodeposition towards C₂ product formation (C₂H₄ and C₂H₆), and observed FE up to 55%. To obtain mesoporous (high surface area) metal foams with controlled porosity, the authors combined the reduction of Cu surface oxides via activation with a novel electrodeposition strategy proposed by Shin et al. [66,67] and variation of the experiment parameters (pH, concentration of metal ions, and time). After being emerged from the plating bath, these Cu foams were reported to undergo rapid surface oxidation. The oxide-derived Cu foam mesoporous catalysts formed in this manner were demonstrated to be potential catalysts with superior selectivity towards C₂ product formation at reasonably low overpotentials.

According to some research, additives could indeed form complexes with metals to participate in the ECR process while tailoring the surface morphology of the metal catalysts. Extensive studies on the electrodeposition of Cu₂O films involving surfactants, complexing agents such as sodium dodecyl sulphate, lactic acid and their combinations are significantly performed and well established [68,69]. Though the formation of {1 1 1} and {1 0 0}-oriented films has previously been studied, reports on the {1 1 0}-oriented films revealed that the Cu₂O films with {1 1 1} are stable in a limited electrolyte pH range [70–72]. Kas et al. [73] attempted to reproduce Cu₂O films with preferential {1 1 0} orientation and was successful, but observed a difference in the orientation of the films with increased thickness. This was attributed to the change in pH (from 9 to 12) and copper metal ion concentration during the electrodeposition process. The authors also found that lactic acid as a supporting electrolyte at higher pH and the molar ratio of lactic acid to copper ions played a critical role in obtaining Cu₂O films with orientations along the {1 1 1} direction with low current densities and they are reproducible. Similar work was carried out by Ren et al. [74] from an electrodeposition bath containing lactic acid, caustic soda, copper sulfate and obtained oxide-derived copper polyhedrons which displayed an FE of 34–39% at –0.99 V vs. RHE for C₂H₄ and 9–16% for C₂H₅OH.

Besides oxide-derived copper, there is another class of Cu-based catalysts (termed as “halide-derived Cu”). These catalysts are potentially derived from halide anions such as fluoride, chloride, bromide, iodide and a Cu cation. Halide-derived Cu catalysts are reported to have greater stability than the oxide-derived ones owing to their significant electronegativity difference between halides (Cl[–], Br[–], I[–], F[–]) and oxygen which can generate Cu⁺ species [27]. These are shown to influence the binding energies and coordination and play an important role towards C₂₊ products formation. For instance, Kwon et al. [75] reported an enhancement in faradaic efficiency for C₂ products such as ethylene and ethyl alcohol when copper foil was previously electrochemically cycled in the presence of potassium cations and different halide anions (X = F[–], Cl[–], Br[–], I[–]). The authors demonstrated the significance of the halide-derived Cu by comparing the results of the oxide-derived Cu that were obtained without the presence of halide anions. Physical characterisation data confirmed the formation of halide-derived Cu cubes at pH > 4 and their transformation to oxide-derived copper in neutral and basic solutions. In summary, oxide-derived Cu and halide-derived Cu were reported to exhibit superior catalytic activity for C_n (n = 2–4) products owing to either the morphology transformation to cubes or the presence of monovalent copper cations (Cu⁺). However, the problem associated with this type of catalyst is the stability, durability and transformation with change in pH.

4. Electrodeposition of Copper Alloys

Though Cu is known to bind CO₂ and protonate CO that is adsorbed to CHO*(C–O–H) or COH*(H–C=O) intermediates, these catalysts yield different spectra of C₂, C₂₊ products, and are often affected by the potentials that are being applied to the copper electrodeposited on substrates. The electrodeposition of copper alloys enhances the performance of CO₂ electroreduction due to synergistic effects among copper and other substances. Table 5 lists the summary of the works that include Cu-alloys employing electrodeposition. As can

be seen from the table, most of the research works focus on the combination of alloying copper with oxophilic materials such as bismuth (Bi). Studies by Zhao et al. [27] and Li et al. [76] showed that combining Cu with Bi could inhibit the competitive hydrogen evolution reaction in the electroreduction of CO₂ but favoured C₁ product selectivity (typically formates) up to FEs of >90%. Similarly, studies on Cu-In bimetallic catalysts were reported to yield formates with an FE of 87.4%. The combination of Cu with metals such as Ag and Pd were reported to favour C₂ product selectivities with FEs reaching up to ~45% at −1.0 V (vs. RHE) with good stability and durability. However, the alloying metals are expensive and are listed under the critical raw materials category in the UK and the EU. The search for potential binary catalysts based on Cu that could catalyse the CO₂ reaction towards producing C₂ products deserves detailed research. Furthermore, the influence of different metal active sites in the binary alloy catalyst systems and their contribution towards improving C₂ product selectivity requires deeper research and better theoretical guidance.

Table 5. Works that reported on the electrodeposition of copper alloys.

Substrate	Alloy	Deposition Media	Mode of Deposition	Morphology	Test Electrolyte and Cell Type	Product(s)	FE, %	Reference
Cu foil	Cu ₁₀ Zn	0.3 M CuSO ₄ ·5H ₂ O + 2.3 M lactic acid + 10 mM ZnCl ₂ + NaOH (for adjusting the pH from 9.6 to 12.0)	Galvanostatic	Spherical	0.1 M KHCO ₃ and H-Cell	C ₂ H ₄	4.52 at −1.05 V	[77]
	C ₂ H ₅ OH					6.38 at −1.05 V		
	C ₂ H ₄					10.75 at −1.05 V		
	Cu ₄ Zn		Galvanostatic	Spherical		C ₂ H ₅ OH	29.1 at −1.05 V	
	Cu ₂ Zn		Galvanostatic	Spherical		C ₂ H ₄	1.85 at −1.05 V	
						C ₂ H ₅ OH	11.65 at −1.05 V	
Carbon Paper	CuAg	0.1 M CuSO ₄ ·5H ₂ O + 1 mM Ag ₂ SO ₄ H ₂ SO ₄ + 10 mM DAT	Galvanostatic	Film	1 M KOH and flow electrolyser	C ₂ H ₄	23.5 at −0.72 V	[78]
				Wire		1 M KOH and flow electrolyser	C ₂ H ₅ OH	
						C ₂ H ₄	51.8 at −0.71 V	
						C ₂ H ₅ OH	16.9 at −0.71 V	
Cu foil	Cu ₁₅ Ag ₈₅	20 mM CuSO ₄ + 2 mM Ag ₂ SO ₄ + 1.5 M H ₂ SO ₄ + 0.1 M Na ₃ C ₆ H ₅ O ₇	Galvanostatic	Foam	CO ₂ -saturated 0.5 M KHCO ₃ electrolytes and electrolysis cell	C ₂ H ₄	36.56 at −1.1 V	[79]
Cu foam	CuSn	0.2 M SnSO ₄ + 1.5 M H ₂ SO ₄	Galvanostatic	Nanoparticles	0.5 M KCl solution purged with 5% N ₂ /CO ₂ and H-cell	HCOO [−]	90.0 ± 2.7 at −1.14 V	[80]
ionic Cu foil	CuSn	0.2 M CuSO ₄ ·5H ₂ O + 0.7 M H ₂ SO ₄ + 0.15 M Na ₃ C ₆ H ₅ O ₇ + 0.03 mM C ₁₈ H ₂₉ NaO ₃ S + 0.6 M SnCl ₂ ·2H ₂ O	Galvanostatic	3D core-shell porous structures	N ₂ -saturated KHCO ₃ and electrolysis cell	HCOO [−]	100 at −0.9 V	[81]
Cu foil	CuPb	0.01 M Pb(ClO ₄) ₂ ·xH ₂ O + 0.1 M HClO ₄	Potentiostatic	-	0.1 M KHCO ₃ saturated with CO ₂ and two-compartment electrochemical cell	HCOO [−]	70.5 ± 0.7 at −1.05 V	[82]
Cu foil	CuIn	5 mM CuSO ₄ ·5H ₂ O + 20 mM In ₂ (SO ₄) ₃ + 1.5 M H ₂ SO ₄	Galvanostatic	Smooth	0.5 M KHCO ₃ saturated with CO ₂ and H-cell	HCOO [−]	96.8 at −1.0 V	[83]
Carbon Paper	CuPd	0.1 M CuSO ₄ ·5H ₂ O + 1 mM PdSO ₄ + 0.1 M H ₂ SO ₄	Galvanostatic	Tetrahedron structures	CO ₂ -saturated 0.1 M KCl solution and H-cell	C ₂ H ₄	45.2 at −1.2 V	[84]
Cu foam	CuBi	4 μmol Cu(NO ₃) ₃ ·3H ₂ O + 4 μmol Bi(NO ₃) ₃ ·5H ₂ O + 20 μmol Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O + 20 μmol CH ₄ N ₂ O + 4 μmol C ₁₀ H ₁₆ N ₂ O ₈ + 20 μmol CHNaO ₂	Potentiostatic	Needle-like structure	0.5 M KHCO ₃ saturated with CO ₂ and H-cell	HCOO [−]	94.4 at −0.97 V	[85]

5. Summary and Future Challenges

Most of the reviewed research works reported that Cu and its derived oxides demonstrated the ability to reduce CO₂ electrochemically to C₂ hydrocarbons and oxygenates. With copper-based catalysts, a range of C₂-based reduction products, including C₂H₄, C₂H₈

and C_2H_5OH , could be produced due to the comparatively low binding energy for most carbon-containing chemical intermediates. Results from literature showed a substantial enhancement in FE but with poor product selectivity. Particle size and crystal facet orientation majorly influence the Cu catalyst activity and product selectivity towards ethylene and other C_{2+} products. Research emphasised that metallic Cu with cubic surface morphology, nano-crystalline in nature with dominant $\{1\ 0\ 0\}$ facets are essential towards improving the electrochemical reduction of CO_2 and its associated product selectivity. Cu $\{1\ 0\ 0\}$ was reported to be the ideal Cu metal catalyst facet that could facilitate the formation of the $CHO^*(C-O-H)$ species, a critical early intermediate for the production of C_2H_4 . On the contrary, Cu $\{1\ 1\ 1\}$ was reported to preferentially stabilize $COH^*(H-C=O)$ intermediates and favoured the formation of CH_4 .

Most of the studies were performed using copper catalysts synthesised by other wet chemical methods such as polyol, modified polyol, chemical reduction and in alkaline saturated environments with limited studies on electrodeposition. In electrodeposition, copper sulfate pentahydrate and sulfuric acid is the most commonly used electrolyte which produced metallic copper with $\{1\ 1\ 1\}$ facets with needle, wire and dendritic-like morphologies when deposited using potentiostatic and galvanostatic methods. Few studies reported on $Cu(NO_3)_2$ and chloride-based precursors and lactic acid, sodium hydroxide or potassium chloride as potential supporting electrolytes for the electrodeposition of copper and its derived oxides or halides.

Studies on the combination of electrodeposited copper catalysts and post-combustion capture media containing amines are very limited and scarce. While most of the efforts were devoted towards development and testing of copper catalysts in gas GFE, new approaches to reduce and convert the CO_2 directly from capture media are still in the early stages [86]. In addition to the catalyst size and crystal facet-dependent effects, the valence state of the copper has an influence on the conversion of CO_2 to ethylene and C_{2+} products.

Oxide-derived Cu catalysts have also shown significant enhancement of the electrochemical reduction of CO_2 . This was accomplished either by creating a positive interaction between metallic copper (Cu (0)) and oxidised (Cu(+1)) species by producing mixed valence states, or a combination of both.

Additives such as 3,5-diamino-1,2,4-triazole (DAT), Janus Green B and poly vinyl pyrrolidone (PVP) played a vital role towards influencing the morphological features during the electrodeposition of copper, whereas they achieved FE up to 40% with C_2H_4 , C_2H_5OH as the major reduction products with predominant $\{1\ 1\ 1\}$ orientation exhibiting needle, wire and dendritic-like morphologies. Few studies reported on copper with high index facets that favour the formation of C_2 , C_{2+} products with possible dynamic catalyst restructuring similar to low index faceted Cu catalysts. However, the high surface energy combined with their lack of in situ investigation about the surface reconstruction of high index faceted copper under real-time reaction conditions pose a challenge. Under specific reaction conditions, metallic Cu(0) is recognised to be the most catalytically active site. Nevertheless, the presence of a specific oxidation state of Cu species was reported to increase the selectivity of C_2 , C_{2+} products. Studies that reported on oxide-derived Cu electrodes indicated that the oxygen centres of copper oxide (Cu_2O) surfaces could serve as strong binding sites, govern reactivity and influence the product distribution substantially. The sensitivity of the electrocatalytic performance resulting from the variations in the initial and final state of Cu catalyst forms (before and after electrochemical reduction of CO_2) plays a critical role in the formation of C_2 , C_{2+} products and therefore requires a detailed understanding and consideration

The crystal surfaces of different forms of catalysts (metallic, oxide-derived, halide-derived) were reported to show tremendous impact on the selectivity of CO_2 . However, obtaining a single facet-enclosed Cu for a greater selectivity of CO_2 reduction towards C_2 , C_{2+} products still remains a challenge. Most of the reviews discussed the progress and developments in the copper catalysts with different forms (metallic, oxide, halide) towards the electrochemical conversion of CO_2 . However, reviews focusing on the influence of

catalyst synthesis methods and testing of copper catalysts in amine-based carbon capture chemistries are very scarce. Non-aqueous systems such as ionic liquids have gained researchers' attentions in the electrochemical reduction of CO₂ owing to their capability towards tailoring the electrode structure, voltammetry properties and sensitivity of the method (through reduction of background current) (Table 1). However, the studies involving copper-based catalysts are very limited.

Though there are significant works reported on the electrodeposition of copper and its derived oxides, no clear comparison on the measured activity/performance has been reported. Most of the works reported on the test performance of the catalysts with different roughness factors under different electrolyte (type, concentration, pH) and electrochemical test conditions. Furthermore, copper electrodes were tested at different potentials and test conditions. These resulted in different rates of mass transport limitations with different kinetic overpotentials, which hinders further commercialisation. Thus, it is important to design and optimise the copper catalyst architecture in terms of size, facet orientation, valence state, product selectivity and stability in the chosen phase changing solvents (PCSs) to enable it to function effectively when integrated as a component into the gas-fed electrolyser (GFE) [87].

Among the electrodeposited copper alloys identified and explored so far, Cu with critical raw materials such as Ag and Pd was reported to be promising in terms of producing C₂ products. The search for potential binary Cu-alloy catalysts based on non-critical raw materials (CRMs) and low toxicity that could catalyse the CO₂ captured from phase-changing solvents such as amines towards producing C₂ products, deserves detailed research.

In addition, most of the works that reported on the electrodeposition of copper and its oxides and alloys utilized either potentiostatic, galvanostatic or pulse modes. However, no detailed research has been reported on the different modes of deposition (such as square voltammetry, programmed electrodeposition) and the combination with other synthesis methods such as polyol or modified polyol synthesis to achieve the desired orientation of copper ($\{1\ 0\ 0\}$). Clearly, these directions deserve attention. In addition, the influence of an external field such as a magnetic field on controlling the orientation of copper during electrodeposition is not well recognized. Other methods, such as hydrothermal synthesis, have been used for the development of Cu-based [88,89] and transition metal-based [90,91] catalysts for CO₂ reduction.

Similarly, copper sulphide (CuS) is known to be a good electrode material and its use in this application is an interesting area of research as a future direction owing to its excellent physical, electronic and chemical properties. While most of the synthesis of CuS materials with various morphologies were obtained by wet chemical methods such as hydrothermal and solvothermal, studies on the electrodeposition of CuS materials are scarce [92–94]. Exploring the synthesis of CuS hierarchical structures via template free electrodeposition would be an interesting area of research towards producing C₂, C₂₊ products via electrochemical reduction of CO₂. The referenced works provide a useful set of references regarding this method, although the current review focuses on electrodeposition.

To overcome the limitations associated with copper catalysts in GFEs, efforts were devoted to improve the dispersion of electrodeposited Cu on novel carbon-based materials such as graphene and doped graphene as catalyst supports. Dedicated research was also carried out on understanding the role of trace metal impurities that are often present in the carbon-based materials utilizing electrodeposition of copper, with enhanced performance of CO₂ reduction. However, the influence of different metal active sites in the binary Cu-alloy catalyst systems incorporated through electrodeposition on treated (or) cleaned (or) activated carbon-based supports and their contribution towards improving C₂ product selectivity requires deeper research and better theoretical guidance.

In addition, optimization of other device components (catalyst supports, ion-exchange membrane, electrolyte) and operating conditions (flow rate, temperature, pressure, etc.), as well as testing the tolerance to more realistic conditions is expected to accelerate the development of the CCUS technologies. For instance, utilising the CO₂ captured from an

upstream process to convert into ethylene is expected to not only dilute the CO₂ stream with potential contaminants (e.g., from sources such as industrial flue gases) but to also contribute to the global ethylene production, decarbonisation and circular economy.

6. Conclusions

The electrochemical reduction of CO₂ to chemicals and fuels has the potential to provide products with added value while minimising the greenhouse effect caused by CO₂ emissions. The manufacture of multi-carbon (C₂, C₂₊) molecules such as ethylene, ethane, hydrocarbons and oxygenates is critical for industrial applications. So far, copper, its oxides (Cu₂O) and halide-derived copper have demonstrated their capacity to catalyse the C-C bond coupling during the electrochemical reduction of CO₂ with significant efficiency and considerable kinetic viability, yielding a wide spectrum of C₂ products in aqueous electrolytes. Nonetheless, the low product selectivity associated with Cu and Cu₂O-based catalysts remains the primary technical difficulty for the widespread implementation of ECR technology. The conversion of captured CO₂ in an electrolyser necessitates a careful and well-thought-out electrocatalyst architecture. According to the literature, rational design of a Cu catalyst architecture has a significant impact on the adsorption energetics of important intermediates, their reaction pathways and successfully increasing the electrocatalytic CO₂ reduction to C₂H₄. The essential techniques to obtain high ethylene selectivity are size management, surface porosity construction, preferential crystal facet exposure and valence state manipulation.

Furthermore, an examination of the most recent research papers listed in the literature reveals that significant experimental investigations on the creation of Cu and Cu₂O-based catalysts have been conducted. Although the results showed enhanced performance towards ECR, these studies were performed using catalysts synthesised via wet chemical methods and in CO₂ saturated solutions, still indicating poor C₂ product selectivity and catalyst chemical stability. To overcome the critical limitations associated with wet chemical synthesis methods such as addition of complexing agents, templates, surfactants and requirement of tedious filtering and washing, electrodeposition is seen as a versatile technique to synthesise copper catalysts with tailored facets.

An innovative catalyst design with a preferential crystal facet orientation and with a mechanistic insight of the catalyst architecture–performance relationships is believed to be a potential way forward towards commercialization of ECR technologies. Combining upstream post-combustion carbon capture with CO₂ conversion using electrodeposited copper catalysts can be viewed as a beneficial approach to global commercialization, and could overcome the limitations of poor product selectivity and catalyst stability in post-combustion carbon capture solutions.

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