Tailoring gas-phase CO$_2$ electroreduction selectivity to hydrocarbons at Cu nanoparticles

I Merino-Garcia, J Albo and A Irabien

Department of Chemical and Biomolecular Engineering, University of Cantabria, Avenida de los Castros s/n, 39005 Santander, Cantabria, Spain

E-mail: merinoi@unican.es

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Abstract

Copper-based surfaces appear as the most active catalysts for CO$_2$ electroreduction to hydrocarbons, even though formation rates and efficiencies still need to be improved. The aim of the present work is to evaluate the continuous gas-phase CO$_2$ electroreduction to hydrocarbons (i.e. ethylene and methane) at copper nanoparticulated-based surfaces, paying attention to particle size influence (ranging from 25–80 nm) on reaction productivity, selectivity, and Faraday efficiency (FE) for CO$_2$ conversion. The effect of the current density and the presence of a microporous layer within the working electrode are then evaluated. Copper-based gas diffusion electrodes are prepared by airbrushing the catalytic ink onto carbon supports, which are then coupled to a cation exchange membrane (Nafion) in a membrane electrode assembly. The results show that the use of smaller copper nanoparticles (25 nm) leads to a higher ethylene production ($1148 \mu$mol m$^{-2}$ s$^{-1}$) with a remarkable high FE (92.8%), at the same time, diminishing the competitive hydrogen evolution reaction in terms of FE. This work demonstrates the importance of nanoparticle size on reaction selectivity, which may be of help to design enhanced electrocatalytic materials for CO$_2$ valorization to hydrocarbons.

Keywords: CO$_2$ electroreduction, Cu nanoparticles, hydrocarbons, reaction selectivity, ethylene

(1Some figures may appear in colour only in the online journal)

1. Introduction

The continuous rise of carbon dioxide (CO$_2$) emissions into the atmosphere led to an increase of 6 ppm in CO$_2$ concentration between 2015 and 2017 (406.42 ppm) [1]. This represents an unprecedented 2 years record for the National Oceanic and Atmospheric Administration, which has been reporting the rate of CO$_2$ growth since 1960. It is therefore crucial to reduce CO$_2$ emissions in order to mitigate the negative effects of global warming. In this context, the utilization of CO$_2$ represents an attractive alternative to reduce our reliance on fossil fuels for energy and chemical synthesis, helping also to palliate global warming effects [2].

The electrochemical reduction technology is particularly interesting for CO$_2$ utilization, since it allows the storage of intermittent renewable energy in the form of chemical bonds [3]. The slow kinetics of the reaction, the high energy requirements and market limitations, among others, are, however, issues that limit the practical application of this technology [4].

Among the different products obtained from the electroreduction of CO$_2$ (e.g. carbon monoxide, formic acid, alcohols or hydrocarbons) at different conditions [5–7], the formation of hydrocarbons such as ethylene (C$_2$H$_4$) or methane (CH$_4$) is appealing due to their several applications in the chemical industry as raw materials, energy vectors and fuels [3]. However, the overpotential of these reactions is too large, which makes these processes energetically inefficient [8]. Besides, the limited productivity rates hinder the CO$_2$-to-hydrocarbons electrochemical reaction, which is mainly associated with the catalytic material applied.

Up to date, only copper (Cu)-based electrocatalysts seem to be able to electroreduce CO$_2$ to hydrocarbons with modest
reaction rates and efficiencies [9], in which controlling the selectivity to hydrocarbons and reducing the overpotential of the reaction are nowadays two of the most scientific challenges [10]. In this regard, several authors have focused their research on evaluating different aspects of Cu-based catalytic materials such as surface structure, morphology and particle size, showing a dramatic influence on reaction performance [10–14]. For instance, Hori et al [11, 12] analyzed the effect of Cu facets on hydrocarbons selectivity, demonstrating that Cu (111) facets favored the formation of CH₄. In contrast, Cu (100) facets were favorable for the production of C₂H₆ at the same conditions, which can be explained as differences in the chemisorption characteristics of the surfaces [10]. This significant dependence of CO₂ reduction selectivity on surface structure may explain the differences in product formations on electrodeposited Cu and Cu film-based electrocatalysts. On the other hand, the morphological effect has also been studied by using polycrystalline Cu and Cu meshes with mesopores of different width and depth at the nanometre scale [13]. As narrowing and decreasing the pore width and depth the Faraday efficiency (FE) to CH₄ significantly decreased. As a consequence, the FE to C₂-products (i.e. C₂H₄ and C₂H₆) was enhanced at these conditions. As summary, both local pH and mass flow can be affected by morphology, enhancing C–C coupling reaction and extending retention times of key reaction intermediates. Furthermore, particle size analyzes have been carried out for different electrocatalytic reactions such as the oxygen reduction reaction [15] and the electrocatalytic CO oxidation [16], among others. The first study on particle size effect for the electrochemical reduction of CO₂ at Cu nanoparticles in a liquid–liquid reactor configuration was developed by Reske and coworkers in 2014 [10]. The product selectivity was evaluated in the size range of 2–15 nm. The authors suggested that very small particles (<3 nm) should be avoided for the production of hydrocarbons due to the increase in the strength of the binding of products (i.e. CO) and intermediate species, favoring the formation of H₂ and CO. However, at the intermediate particle size level (i.e. 5–15 nm) hydrocarbon formation was favored owing to the weaker CO and H bonding. Accordingly, similar trends were observed with Cu nanoparticles on different supports [14]. The C₂H₄/CH₄ ratio was highly influenced by the particle size. Larger ratios were observed for smaller particles. Nevertheless, the FE to CH₄ was slightly increased as improving the size of the Cu nanoparticles.

Furthermore, different electrochemical reactor configurations have been reported for the conversion of CO₂ [17, 18]. Among them, the use of membrane reactors allows the separation of cathode and anode compartments, involving an easier separation of reduction products and avoiding their re-oxidation [17, 19]. Moreover, mass transfer limitations in the process have led to apply gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs), in which the contact and the transport of ionic species are enhanced [20–23], promoting CO₂ transformation into more reduced products such as hydrocarbons. Besides, the introduction of CO₂ directly as gas is an interesting alternative, which allows avoiding issues related to the low solubility of CO₂ in water [9, 24–26].

Overall, the aim of this work is to evaluate the influence of Cu nanoparticle size (ranging from 25–80 nm) on reaction productivity, selectivity and FE for the continuous gas-phase CO₂ electroreduction to hydrocarbons. As far as the authors know this is the first attempt in the literature to evaluate the effect of electrocatalyst size in gas-phase CO₂ electroreduction systems, although the effects of Cu nanoparticle size in the range 2–15 nm on the catalytic electroreduction of CO₂ has been previously evaluated in liquid-phase-based systems [10]. Consequently, this study may contribute to a better understanding of the performance of the process at a larger Cu nanometre size range (25–80 nm). The performance of the Cu-GDE system is tested using a filter-press type electrochemical membrane reactor in continuous operation. The effect of the current density (j) applied and the presence of a diffusion microporous layer (MPL) within the working electrode structure is also analyzed. The obtained results may provide new insights in the development of highly active catalytic materials for CO₂-to-hydrocarbons electrochemical reactions.

2. Experimental details

2.1. Cu-GDE preparation and characterization

Table 1 summarizes the main technical features of the electrocatalytic materials evaluated in the present study. Cu nanoparticles (NPs) with different particle size were provided by Sigma-Aldrich. Regarding the manufacturing process of the different GDEs, a Toray paper was used as carbon support (TGP-H-60, Toray Inc.). The catalytic layer was prepared by air-brushing a catalytic ink composed by a mixture of Cu NPs, a Nafion solution (5 wt%, Alfa Aesar, copolymer polytetrafluoroethylene) as binder, and isopropanol (IPA) (AcroSeal, Extra Dry 99.5% purity) as vehicle, with a 70:30 Cu/Nafion mass ratio and 3 wt% of solids (Cu + Nafion). The final mixture was agitated in an ultrasound bath for at least 30 min. Under these conditions, Cu GDEs with a geometric surface area (A) of 10 cm² and a Cu loading (L) of 0.5 mg cm⁻² were obtained. The assembly of the membrane (Nafion 117) with the Cu-GDE in a MEA was completed at 323 K and 80 bar using a filter press (Carver, Inc.).

The MPL ink includes Vulcan carbon powder (VXC72R, Cabot, carbon black) and polytetrafluoroethylene, PTFE (Sigma-Aldrich, 60 wt% dispersion in H₂O) with a 70:30

| Nomenclature | Size (nm) | Purity (%) |
|--------------|-----------|------------|
| Cu25         | 25        | —          |
| Cu40–60      | 40–60     | >99.5      |
| Cu60–80      | 60–80     | >99.5      |
Vulcan/PTFE mass ratio. The mixture was then diluted to 3% in IPA and agitated in an ultrasonic bath. This solution was air-brushed onto the Toray paper and the obtained MPL layer was sintered at 623 K for 30 min.

The Cu-based GDEs were electrochemically characterized by cyclic voltammetry (CV) tests in a three-electrode undivided cell, in which a CO2 saturated-based 0.1 M potassium bicarbonate (KHCO3) aqueous solution was used as electrolyte. A graphite rod and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. Small pieces of Cu-GDEs (Cu NP = 25 nm, 40–60 nm and 60–80 nm) were used as working electrodes. The resulting j was normalized to the geometric area of the electrode. The applied potential was controlled using a MSTAT4 system (Arbin Instruments) and the samples were cycled five times from 0 V versus Ag/AgCl to −2 V versus Ag/AgCl.

2.2. CO2 electroreduction tests

The experimental setup to perform the gas-phase CO2 electroreduction has been described in our previous study [9]. The core of the filter-press type electrochemical reactor is the MEA, which serves as working electrode and separates the cathode and anode compartments. A dimensionally stable anode [DSA/O2Ir-MMO (mixed metal oxide) on platinum] and a leak-free Ag/AgCl were used as counter and reference electrodes, respectively. Humidified CO2 was fed to the cathode compartment at a flow rate, Qg, of 18 ml min−1 cm−2 and a 0.1 M KHCO3 aqueous solution was used as anolyte. The CO2 reduction experiments were conducted at galvanostatic conditions (j = 7.5, 15, 30 mA cm−2) using an AutoLab PGSTAT 302 N potentiostat. All experiments were carried out at ambient conditions. Gas reduction products were analyzed using a four-channel gas microchromatograph (3000 micro GC, Inficon) equipped with a thermal conductivity detector. Gas samples were measured every 5 min for 45 min, with three replicates for each experiment to obtain an averaged reaction rate, r (μmol m−2 s−1), selectivity, S, defined as the ratio between rCH4 and rX, with x being CH4 and H2, and FE, for each product.

3. Results and discussion

3.1. CV tests

Figure 1(a) shows the current–voltage responses after 5 electrochemical scans for the Cu NP based-GDEs (i.e. 25 nm, 40–60 nm and 60–80 nm) and that response for the Toray paper for comparison. Additionally, to further analyze the catalytic activity for CO2 electroreduction, figure 1(b) reveals the CV results for the Cu25-GDE in the absence of CO2 (under N2 saturation).

Figure 1(a) displays similar trends for all the Cu-based electrodes tested, even though higher activities can be clearly observed when decreasing Cu nanoparticle size (from 60–80 to 25 nm). The main characteristic of the CV voltammograms is the difference between the starting potentials for the reduction process as a function of each material tested, which may be initially associated with the particle size influence on reaction mechanisms [10], involving different pathways and reaction intermediates. For instance, larger Cu particle-based GDEs (i.e. 60–80 and 40–60 nm) presented a similar CO2 reduction peak (starting at around −0.9 V versus Ag/AgCl). However, Cu25-based GDEs reached an onset potential of about −0.8 V versus Ag/AgCl. The highest catalytic activity of the Cu25-based electrode (continuous-red line) might be related to an increase in the fraction of under-coordinated sites, such as defects, edges and corners on the electrode surface due to the smaller size of the Cu NPs, which might involve an increased reaction selectivity to more reduced species [14]. Figure 1(b) demonstrated the reduction of CO2 molecule, as the activity increased in comparison to that curve under N2 conditions.
Figure 2. Time evolution for $E$ and $r$ in the production of $\text{C}_2\text{H}_4$ (circles) and $\text{CH}_4$ (triangles) at Cu25-based GDE, $j = 15$ mA cm$^{-2}$.

3.2. Gas-phase CO$_2$ electroreduction

Figure 2 shows the time evolution for the potential ($E$) and the reaction rate ($r$) in the continuous gas-phase CO$_2$ electrochemical conversion to $\text{C}_2\text{H}_4$ and $\text{CH}_4$ at the GDE-based electrode (Cu25; $L = 0.5$ mg cm$^{-2}$) when applying a constant current of $j = 15$ mA cm$^{-2}$. Besides $\text{C}_2\text{H}_4$ and $\text{CH}_4$, CO and $\text{H}_2$ were also detected.

As shown in the figure, steady state conditions can be reached after 15 min of operation, when $E$ remains constant ($E$ averaged at $-2.1$ V versus Ag/AgCl with a deviation of 5%), although the fact that CO$_2$ is directly fed as gas to the cathodic compartment also provokes fluctuation in the voltage owing to the presence of bubbles. It is also worth noting that the evolution of $E$ with time for the other materials (i.e. Cu40–60 and Cu60–80) shows a similar pseudo-stable behaviour after 15 min. The $r_{\text{C}_2\text{H}_4}$ and $r_{\text{CH}_4}$ behave similarly, which may indicate the suitability of the Cu25-based electrode for the production of $\text{C}_2\text{H}_4$ and $\text{CH}_4$ after 45 min, even though material deactivation might occur at longer reaction times [21]. Future research efforts should include long-term stability test, which is essential to analyze the technical feasibility of the gas-phase CO$_2$ electroreduction process.

3.2.1. Particle size effect. Table 2 and figure 3 show the main results for the continuous gas-phase CO$_2$ reduction in the filter press electrochemical cell as a function of the Cu particle size.

From the results, a significant production of $\text{C}_2\text{H}_4$ was achieved at lower particle sizes, $\text{CH}_4$, CO and $\text{H}_2$ were also observed over the entire Cu NP size range. In addition, lower rates for liquid-phase products such as $\text{CH}_3\text{OH}$ ($r < 0.5$ $\mu$mol m$^{-2}$s$^{-1}$) and $\text{C}_2\text{H}_5\text{OH}$ ($r < 2.4$ $\mu$mol m$^{-2}$s$^{-1}$) were detected with a FE $< 0.5\%$. Previous findings in the group demonstrated that Cu60–80 are able to electroreduce CO$_2$ to CH$_4$, also producing $\text{H}_2$ and CO in a wide range of applied potentials (i.e. from $-2.4$ to $-1.8$ V versus Ag/AgCl) and catalytic loadings (i.e. from 0.25 to 1.5 mg cm$^{-2}$) in a MEA configuration [9]. The highest CH$_4$ production was achieved at 0.5 mg cm$^{-2}$ and $-2$ V versus Ag/AgCl ($j = 7.5$ mA cm$^{-2}$). However, $\text{C}_2\text{H}_4$ was not detected at this Cu NP size level (60–80 nm), in contrast to those results obtained in the present report when reducing particle size (i.e. Cu40–60 and Cu25). The absence of $\text{C}_2\text{H}_4$ at the largest Cu NP size tested (Cu60–80) may be associated with the lower presence of corners, specific crystal orientation surfaces, edges and defects in the electrocatalyst than those presented when reducing particle size [14, 27]. The presence of edge sites may represent key sites which facilitate the adsorption and stabilization of CO$_2$ reduction reaction intermediates towards C–C coupling [28]. In contrast, the lower presence of these parameters at the largest particle size tested seems to be beneficial for CH$_4$ formation, at least in terms of FE. Consequently, it is crucial to identify which structural parameters in electrocatalysts for CO$_2$ electroreduction are able to control the selectivity of the reaction to multicarbon products.

The best values for $\text{C}_2\text{H}_4$ production were reached when using Cu25, in which a rate of $r = 1148$ $\mu$mol m$^{-2}$s$^{-1}$ and a FE of 92.8% were obtained. In the same manner, the optimum CH$_4$ production rate was achieved at this particle size level ($r = 37.6$ $\mu$mol m$^{-2}$s$^{-1}$ with a FE of 2%). This change in reaction performance compared to larger Cu NPs (i.e. 60–80 nm) also entails a decrease in the FE to H$_2$ and CO. In addition, the $S_{\text{C}_2\text{H}_4}$/$S_{\text{CH}_4}$ was enhanced when decreasing the Cu particle size ($S_{\text{C}_2\text{H}_4}$/$S_{\text{CH}_4} = 3.1$ at Cu25) due to the presence of defects in the material in comparison to larger Cu particles ($S_{\text{C}_2\text{H}_4}$/$S_{\text{CH}_4} = 0.99$), whereas the highest $S_{\text{C}_2\text{H}_4}$/$S_{\text{H}_2}$ was reached at Cu40–60 ($S_{\text{C}_2\text{H}_4}$/$S_{\text{H}_2} = 51.2$), in which CH$_4$ formation was considerably reduced in comparison to the Cu25 performance ($S_{\text{C}_2\text{H}_4}$/$S_{\text{CH}_4} = 30.5$). Thus, the most active material for the reduction of CO$_2$ was Cu25, in agreement with the higher reduction response observed from CV profiles (figure 1). The literature shows that the formation of hydrocarbons from CO$_2$ can be suppressed at very small NPs (i.e. 2–15 nm) due to the reduction of catalytic active surface area as discussed by Reske et al in 2014 [10], where the formation of syngas was preferred over the formation of hydrocarbons. The authors suggested that very small (i.e. $<3$ nm) Cu catalysts should be avoided for the formation of hydrocarbons from CO$_2$ electroreduction.

It is also worth noting that similar potentials are required to reach a current $j = 7.5$ mA cm$^{-2}$ at Cu60–80 and Cu40–60 ($-2.2$ V versus Ag/AgCl and $-2.5$ V versus Ag/Cl,
respectively). Nevertheless, a considerable decrease in the voltage needed is observed at Cu25 (∼1.7 V versus Ag/AgCl), which may involve lower energy consumptions to perform the CO2 reduction reaction. These findings can be explained by alteration of energetic barriers for the different intermediates involved when decreasing Cu NP size, which may imply changes in product distribution (i.e., more reduced species can be obtained with higher rates).

3.2.2. Current density influence. Previous findings in our group demonstrated the possibility to modulate product yields with the applied current density [20, 29]. Thus, the performance of the system is evaluated at different current density levels in an attempt to enhance hydrocarbon yields. Table 3 and figure 4 summarize the productivity, selectivity and efficiency values at the Cu25-based GDEs as a function of the applied j.

As shown in table 3 and figure 4, the product distribution, rates and process efficiency are correlated with the current applied to the system. In this regard, the production of H2 gained importance when increasing j, involving a reduction in the FE in the E to C2H4 (from 92.8% to 86.8%) and CH4 (from 2.0%–0.3%), as well as in reaction selectivity (Sc2H4/CH4). This effect might be explained by the consumption of the additional current in producing H2 (with only two electrons exchanged required) through the hydrogen evolution reaction instead of producing hydrocarbons from CO2 electroreduction at higher j levels. Similarly, r to CH4 is negatively affected by j, with r = 37.6 μmol m⁻² s⁻¹ and r = 3.5 μmol m⁻² s⁻¹ for j = 7.5 mA cm⁻² and j = 30 mA cm⁻², respectively. Additionally, the Sc2H4/CH4 value goes from 30.5 to 212 when increasing the current from j = 7.5 mA cm⁻² to j = 30 mA cm⁻², respectively. On the other hand, CO productivity and efficiency were slightly improved at higher j probably because of the simplicity of the CO2-to-CO reaction (two electrons exchanged).

To sum up, applying a current density of j = 7.5 mA cm⁻², which allows achieving the highest C2H4 production (r = 1148 μmol m⁻² s⁻¹, FE = 92.8 and Sc2H4/CH4 = 3.1) with lower energy requirements (E = −1.7 V versus Ag/AgCl), resulted in an improved gas-phase CO2 electroreduction. This results may be taken into consideration when designing future applications for gas-phase CO2 electroreduction processes.

3.2.3. Microporous layer evaluation. As discussed above, mass transfer limitations usually affect selectivity, productivity and efficiency in CO2 electroreduction processes. Therefore, the use of a carbon MPL between the catalytic layer and the Toray carbon support may help to alleviate these limitations, favoring the transport of species (i.e., CO2 and intermediates) in the filter-press cell. Table 4 shows the results for the presence/absence of a MPL within the Cu25-based working electrode at the optimal current density level (j = 7.5 mA cm⁻²).

Similar C2H4 formation rates were obtained in the presence and absence of the MPL (considering experimental standard deviation). The same can be said for the FE to C2H4. In the same manner, CO and H2 production was not affected neither by the presence of an additional porous layer. Conversely, a decrease in CH4 reaction rate (involving a significant increase in Sc2H4/CH4) and FE was observed when using the MPL within the working electrode. The results may indicate that the presence of the MPL favored the electro-chemical reduction of CO2 to more reduced products (Sc2H4/CH4 = 628 versus Sc2H4/CH4 = 30.5 in its absence) with an insignificant effect on the C2H4/H2 ratio. This finding can be probably associated with an improved transport of CO2 through the working electrode.

Another advantage of the MPL seems to be the energy consumption, reaching voltage values of −1 and −1.7 V versus Ag/AgCl, for the presence and absence of the MPL, respectively. This can be justified by increases in the electrode
conductivity, which is a key factor for an efficient CO₂ valorization system.

3.2.4. Final remarks. Table 5 shows a summary of the \( r \) and FE to C₂H₄ and CH₄ (and other subproducts) from literature, paying attention to electrochemical reactor configuration (i.e. G: gas; L: liquid), electrocatalytic materials and process conditions.

As observed, this work reports the highest productivity values for C₂H₄ (\( r_{\text{C}_2\text{H}_4} = 1148 \mu\text{mol m}^{-2}\text{s}^{-1} \)) and one of the highest for CH₄ (\( r_{\text{CH}_4} = 37.6 \mu\text{mol m}^{-2}\text{s}^{-1} \)) achieved so far, which denotes the relevance of the work. Besides, the highest FE to C₂H₄ has been also reached with this study (92.8%) at Cu25-based GDEs. However, higher FE to CH₄ have been reported in literature for G-L and L-L systems (up to 76%). It is also worth noting that several researchers have detected long-chain hydrocarbons at different Cu-based catalytic materials (i.e. electrodeposited Cu, oxide-derived Cu, Cu + glycine, etc), with higher FEs to C₂H₆ (e.g. 43%). In any case, most of the systems are more selective to H₂, which should be reduced if we intend to increase the formation of hydrocarbons.

To sum up, further advances are needed to improve the key parameters for the electroreduction of CO₂ to hydrocarbons (i.e. \( r \), \( S \), FE, energy consumption, etc) in order to get closer to real applications. The authors recommend focusing future research on the development of alternative catalytic materials (i), reactor configurations (ii) and ion-exchange membranes (iii). Additionally, a deeper understanding on reaction mechanisms (iv) is required to better understand the behaviour of the system.

(i) Alternative catalytic materials. Highly active electrocatalysts should be developed in order to boost \( r \) and FEs to hydrocarbons. In this regard, particle size, crystal orientation and catalyst shapes need to be controlled, owing to their influence on the selectivity of the electrochemical reaction. In addition, the combination of other metals with Cu (i.e. multimetallic electrocatalysts) may imply changes in reaction pathways and intermediates, involving a reduction of the overpotential and the competitive hydrogen evolution reaction. The application of new catalyst structures, such as metal organic frameworks may also be interesting due to their tunable structure.

(ii) Reactor configurations. Electrochemical reactors have an essential role in the progress of CO₂-valorization processes because of mass transfer limitations, which limits the widespread use of the technology. CO₂ solubility issues should also be taken into account. These limitations may be overcome by the application of GDEs and MEAs. Therefore, the possibility of suppressing the liquid phase from the electrochemical systems (i.e. G-L and G-G configurations) are attractive, even though big efforts are still required to make progresses in this field.

(iii) Ion-exchange membranes. Highly conductive cation exchange membranes are needed to carry out the electrochemical CO₂ reduction to hydrocarbons because of the high number of protons involved in the reaction. Therefore, the development of alternative conductive membrane materials is required in order to replace the costly Nafion membranes.

(iv) Mechanisms understanding. The key determining step in CO₂ reduction to hydrocarbons processes seems to be the protonation of adsorbed CO to obtain CHO. On the one hand, the pathway for the formation of CH₄ at Cu surfaces involves further protonation steps of adsorbed CHO, in which OCH₃ adsorbed is finally protonated to produce CH₄, with different intermediates involved depending on the crystal orientation and lattice of the electrocatalytic material applied, among others. On the other hand, the formation of C₂H₄ requires C–C bonding and adsorbed CH₃O species seems to be key intermediates for further dimerization to obtain C₂H₄. In any case, the reaction pathway is still unclear and further research efforts are required in this regard.

![Figure 4. FE and \( r_{\text{CH}_4} \) at different \( j \) on Cu25-based MEAs. Color codes for FEs (columns): light to dark shading (C₂H₄, H₂ and CH₄, respectively).](image-url)
### Table 5. \( r \) and FE at CO₂ reduction systems with Cu-based electrodes.

| Reactor type | Catalyst | \( E \) (V versus Ag/AgCl) | \( FE \) (%) | \( r \) (\( \mu \)mol m\(^{-2}\) s\(^{-1}\)) | Reference |
|--------------|----------|-----------------------------|-------------|---------------------------------|-----------|
| G-L          | Cu NP 25 nm | −1.7 | 4.9 | <0.1 | 2.0 | 92.8 | 37.6 | 1148 | CH₃OH, CH₃CHO, HCOOH (traces) | This work |
| G-L          | Cu-SPE \(^a\) | −1.95 | — | — | 9.0 | 10.0 | — | — | — | [24] |
| G-L          | Cu gauze | −3.01 | — | — | 9.1 | 69 | — | — | — | [30] |
| G-L          | Cu-SPE \(^a\) | −1.45 | 86.8 | 2.6 | <0.1 | 8.8 | — | — | HCOOH | [31] |
| G-L          | Cu/C | — | 79 | 0.3 | 4.5 | — | — | — | HCOOH, CH₃CHO | [32] |
| G-L          | Cu₂O/C | 2.5\(^b\) | 45 | — | 30 | 5 | — | — | CH₃OH | [33] |
| G-L          | Cu₂O/C | 2.5\(^b\) | 20 | Low | 10 | — | — | — | CH₃OH, C₂H₆ | [34] |
| G-L          | Cu/C | −1.8\(^b\) | — | — | Low | Low | — | — | 0.007 | Alcohols | [26] |
| G-L          | Cu/CNFs | — | — | — | — | — | — | 0.001 | CO, alcohols, CH₃CHO | [35] |
| G-L          | Cu NP | −2.0 | 41.5 | 3.22 | 4.5 | — | 4.4 | — | — | [9] |
| L-L          | Electropolished Cu | −1.65 | 20.5 | 1.3 | 33.3 | 25.5 | — | — | Alcohols, HCOOH | [36] |
| L-L          | Cu (110) | −1.75 | 18.8 | — | 49.5 | 15.1 | — | — | Alcohols, HCOOH | [37] |
| L-L          | Cu foil | −4.0 | Low | 17 | 60 | 15 | — | — | HCOOH | [38] |
| L-L          | Cu (100) | −1.6 | 6.8 | 0.9 | 30.4 | 40.4 | — | — | HCOOH | [12] |
| L-L          | CuBr–Cu mesh | −2.4 | 9.3 | 2.4 | 5.8 | 79.5 | — | — | C₂H₆ | [39] |
| L-L          | Cu foil | −3.0 | 17.9 | 3.2 | 70.5 | 3.1 | — | — | HCOOH | [40] |
| L-L          | Polished Cu | −1.9 | 40 | 7 | 19.4 | 18.7 | — | — | — | [41] |
| L-L          | Cu foil | −1.35 | 52 | <2% | 40 | 10 | — | — | HCOOH, alcohols, CH₃CHO | [42] |
| L-L          | Cu NP | −1.3 | 28 | 33 | 2 | 35 | — | — | C₂H₆ | [43] |
| L-L          | Cu mesh | −1.9 | Balance | 5 | 15 | 8 | — | — | — | [44] |
| L-L          | Polypyrrol coated Cu | −3 V\(^d\) | Not analyzed | 15.1 | 25.5 | 3.1 | — | — | HCOOH, CH₃COOH | [45] |
| L-L          | Cu layers on Pt | −1.2 | Balance | 33 | 7 | — | — | — | [46] |
| L-L          | Cu foil | −1.35 | 45 | 30 | — | 30 | — | — | — | [47] |
| L-L          | Electropolished Cu | −2.2 | 5 | 2.5 | 60 | 20 | — | — | — | [14] |
| L-L          | Cu foil | −1.3 | 20 | 3 | 57 | 20 | — | — | — | [10] |
| L-L          | Cu nanoneedles | −1.4 | 18 | — | 14 | 6 | — | — | HCOOH | [48] |
| L-L          | Cu nanofoam | −1.7 | 60 | 7.5 | 0.2 | 1.3 | — | — | HCOOH, C₂H₆ | [49] |
| L-L          | Cu NP | −1.55 | 25 | — | 76 | — | — | — | [50] |
| L-L          | Deposited Cu₂O | −1.3 | Balance | 3 | 5 | 37.5 | — | — | C₂H₆ | [51] |
| L-L          | Cu₂O over Cu | −1.19 | 39 | Low | Low | 39 | — | — | HCOOH, C₂H₆, C₂H₅OH | [52] |
| L-L          | Cu₂O-derived Cu | −1.2 | 18 | Low | Low | Low | — | — | — | [53] |
| L-L          | Cu mesocrystals | −1.19 | 60 | 2 | 2.7 | 27.2 | — | — | — | [54] |
| L-L          | Cu₂O reduced to Cu | −1.8 | 24 | Low | 2 | 44 | — | — | — | [27] |
| L-L          | Electropolished Cu | −1.4 | 30 | — | 28 | — | — | — | C₂H₆ (43%) | [55] |
| L-L          | Cu foil | −1.6 | 15 | 1 | 70 | 15 | 62 | 5 | 250\(^e\) | HCOOH, C₂H₆ (35%) | [57] |
| L-L          | Oxide-derived Cu | −1.0 | 15 | 15 | — | 20 | — | 250\(^e\) | HCOOH, C₂H₆ | [56] |
| L-L          | Cu foil | −1.2 | 15 | 1 | 60 | 20 | 10 | 6 | HCOOH | [58] |
| L-L          | Cu foil + glycine | −1.9 | — | — | 30 | 25 | — | — | C₂H₆, C₂H₅OH | [59] |
| L-L          | Cu + graphene oxide | −1.5 | 50 | Low | 40 | Low | — | — | HCOOH | [60] |
Table 5. (Continued.)

| Reactor type | Catalyst | $E$ (V versus Ag/AgCl) | $r$ (μmol m$^{-2}$ s$^{-1}$) |
|--------------|----------|------------------------|-----------------------------|
| L-L          | Cu foil  | −1.65                  | 140$^a$                     |
| L-L          | Cu$_5$O–CuBr films | −2.1                   | —                           |
| L-L$^f$      | Cu sheet | −1.6                   | 250$^g$                     |
| L-L          | Cu mesh  | −1.9                   | —                           |
| L-L          | Cu films | −1.6                   | —                           |
| L-G          | Cu deposit | —                      | —                           |
| G-G          | Cu felt  | 3.9$^b$                | —                           |

Note:
$^a$ Solid polymer electrolyte.
$^b$ Unknown reference electrode.
$^c$ μmol s$^{-1}$.
$^d$ Pb(Hg)x/PbSO$_4$/SO$_2^{2-}$ reference electrode.
$^e$ ppm cm$^{-2}$ h$^{-1}$.
$^f$ CO$_2$ (70%)-O$_2$ (30%) inlet.
$^g$ ppm.

4. Conclusions

This work presents innovative results on the continuous production of hydrocarbons (i.e. ethylene and methane) from gas-phase CO$_2$ electroreduction at Cu-based electrodes including different nanoparticles sizes (ranging from 25–80 nm). Cyclic voltammetry tests showed that Cu 25 nm based electrodes displayed an improved performance in comparison to larger Cu particles (i.e. 40–60 nm and 60–80 nm), which can be explained by an increase in the fraction of under-coordinated sites when decreasing particle size.

The highest ethylene production (1148 μmol m$^{-2}$ s$^{-1}$) was achieved at the lowest particle size level tested (i.e. 25 nm), with a FE of 92.8%. When increasing Cu particle size (i.e. 40–60 nm and 60–80 nm) the productivity and the FE to C$_2$H$_4$ was negatively affected, involving also higher over-potentials. Conversely, ethylene/methane ratio was enhanced at the 40–60 nm based electrodes (51.2), although the hydrogen evolution was also improved (ethylene/hydrogen ratio = 0.99) compared to that obtained at the lowest particle size level (3.1). In addition, similar ethylene rates were achieved in the whole current density range (7.5–30 mA cm$^{-2}$), while the FE to ethylene decreased. Finally, the use of a MPL led to higher ethylene/methane ratios with an insignificant effect on ethylene/hydrogen ratios, which means that the presence of the MPL favors the electrochemical reduction of CO$_2$ to more reduced products.

Overall, the productivity, selectivity and efficiency of the gas-phase CO$_2$ electroreduction to hydrocarbons are highly dependent on the Cu particle size. Other aspects such as crystal orientation and shape, among others, should be considered in future research for an efficient CO$_2$ electroreduction to hydrocarbons process.

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ORCID iDs

I Merino-García https://orcid.org/0000-0003-3240-5400

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