

Tailoring gas-phase CO₂ electroreduction selectivity to hydrocarbons at Cu nanoparticles

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Abstract. Copper-based surfaces appear as the most active catalysts for CO₂ 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 CO₂ electroreduction to hydrocarbons (i.e. ethylene and methane) at copper nanoparticulated-based surfaces, paying attention to particle size influence (ranging from 25 nm to 80 nm) on reaction productivity, selectivity, and Faraday efficiency for CO₂ 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 (1242 $\mu\text{molm}^{-2}\text{s}^{-1}$) with a remarkable high Faraday efficiency (91.2 %) and, diminishing, at the same time, the competitive hydrogen evolution reaction. This work demonstrates the importance of nanoparticle size on reaction selectivity, which may be of help to design enhanced electrocatalytic materials for CO₂ valorization to hydrocarbons.

Keywords: CO₂ electroreduction, Cu nanoparticles, hydrocarbons, reaction selectivity, ethylene

1. Introduction

The continuous rise of carbon dioxide (CO₂) emissions into the atmosphere led to an increase of 6 ppm in CO₂ concentration between 2015 and 2017 (406.42 ppm) [1]. This represents an unprecedented 2-years record for the National Oceanic and Atmospheric Administration (NOAA), which has been reporting the rate of CO₂ growth since 1960. It is therefore crucial to reduce CO₂ emissions in order to mitigate the negative effects of global warming. In this context, the utilisation of CO₂ 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 CO₂ utilisation, 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 CO₂ (e.g. carbon monoxide, formic acid, alcohols or hydrocarbons) at different conditions [5-7], the formation of hydrocarbons such as ethylene (C₂H₄) or methane (CH₄) is appealing due to their several applications in the chemical industry as raw materials, energy vectors and fuels [3]. The overpotential of these reactions is too large, which makes these processes energetically inefficient [8]. Besides, the limited productivity rates hinder the CO₂-to-hydrocarbons electrochemical reaction, which is mainly associated to the catalytic material applied.

47 Up to date, only copper (Cu)-based electrocatalysts seem to be able to electroreduce CO₂ to
48 hydrocarbons with modest reaction rates and efficiencies [9], in which controlling the selectivity
49 to hydrocarbons and reducing the overpotential of the reaction are nowadays two of the most
50 scientific challenges [10]. In this sense, several authors have focused their research on
51 evaluating different aspects of Cu-based catalytic materials such as surface structure,
52 morphology and particle size, showing a dramatic influence on reaction performance [10-14].
53 For instance, Hori et al. [11-12] analysed the effect of Cu facets on hydrocarbons selectivity,
54 demonstrating that Cu (111) facets favoured the formation of CH₄. In contrast, Cu (100) facets
55 were favourable for the production of C₂H₄ at the same conditions, which can be explained as
56 differences in the chemisorption characteristics of the surfaces [10]. This significant dependence
57 of CO₂ reduction selectivity on surface structure may explain the differences in product
58 formations on electrodeposited Cu and Cu film-based electrocatalysts. On the other hand, the
59 morphological effect has also been studied by using polycrystalline Cu and Cu meshes with
60 mesopores of different width and depth at the nanometre scale [13]. As narrowing and
61 decreasing the pore width and depth the Faraday efficiency (*FE*) to CH₄ significantly decreased.
62 As a consequence, the *FE* to C₂-products (i.e. C₂H₄ and C₂H₆) was enhanced at these
63 conditions. As summary, both local pH and mass flow can be affected by morphology,
64 enhancing C-C coupling reaction and extending retention times of key reaction intermediates.
65 Furthermore, particle size analyses have been carried out for different electrocatalytic reactions
66 such as the oxygen reduction reaction [15] and the electrocatalytic CO oxidation [16], among
67 others. The first study on particle size effect for the electrochemical reduction of CO₂ at Cu
68 nanoparticles in a liquid-liquid reactor configuration was developed by Reske and coworkers in
69 2014 [10]. The product selectivity was evaluated in the size range of 2 nm to 15 nm. The
70 authors suggested that very small particles (< 3 nm) should be avoided for the production of
71 hydrocarbons due to the increase in the strength of the binding of products (i.e. CO) and
72 intermediate species, favouring the formation of H₂ and CO. However, at the intermediate
73 particle size level (i.e. 5 nm to 15 nm) hydrocarbon formation was favoured owing to the
74 weaker CO and H bonding. Accordingly, similar trends were observed using Cu nanoparticles
75 on different supports [14]. The C₂H₄/CH₄ ratio was highly influenced by the particle size.
76 Larger ratios were observed for smaller particles. Nevertheless, the *FE* to CH₄ was slightly
77 improved as increasing the size of the Cu nanoparticles.

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

87 Overall, the aim of this work is to evaluate the influence of Cu nanoparticle size (ranging from
88 25 nm to 80 nm) on reaction productivity, selectivity and *FE* for the continuous gas-phase CO₂
89 electroreduction to hydrocarbons. As far as the authors know this is the first attempt in the
90 literature to evaluate the effect of electrocatalyst size in gas-phase CO₂ electroreduction
91 systems, although the effects of Cu nanoparticle size in the range 2-15 nm on the catalytic
92 electroreduction of CO₂ has been previously evaluated in liquid-phase-based systems [10].
93 Consequently, this study may contribute to a better understanding of the performance of the
94 process at a larger Cu nanometer size range (25-80 nm). The performance of the Cu-GDE
95 system is tested using a filter-press type electrochemical membrane reactor in continuous
96 operation. The effect of the current density (*j*) applied and the presence of a diffusion

97 microporous layer (MPL) within the working electrode structure is also analyzed. The obtained
98 results may provide new insights in the development of highly active catalytic materials for
99 CO₂-to-hydrocarbons electrochemical reactions.

100 2. Experimental details

101 2.1. Cu-GDE preparation and characterization

102 Table 1 summarises the main technical features of the electrocatalytic materials evaluated in the
103 present study. Cu nanoparticles (NPs) with different particle size were provided by Sigma-
104 Aldrich. Regarding the manufacturing process of the different GDEs, a Toray paper was used as
105 carbon support (TGP-H-60, Toray Inc.). The catalytic layer was prepared by air-brushing a
106 catalytic ink composed by a mixture of Cu NPs, a Nafion solution (5 wt %, Alfa Aesar,
107 copolymer polytetrafluoroethylene) as binder, and isopropanol (IPA) (AcroSeal, Extra Dry 99.5
108 % purity) as vehicle, with a 70:30 Cu/Nafion mass ratio and 3 wt% of solids (Cu + Nafion). The
109 final mixture was agitated in an ultrasound bath for at least 30 min. Under these conditions, Cu
110 GDEs with a geometric surface area (*A*) of 10 cm² and a Cu loading (*L*) of 0.5 mgcm⁻² were
111 obtained. The assembly of the membrane (Nafion 117) with the Cu-GDE in a MEA was
112 completed at 323 K and 80 bar using a filter press (Carver, Inc., United States).

113 **Table 1.** Electrocatalytic Cu materials applied.

Nomenclature	Size (nm)	Purity (%)
Cu25	25	-
Cu40-60	40-60	>99.5
Cu60-80	60-80	>99.5

114 The MPL ink includes Vulcan carbon powder (VXC72R, Cabot, carbon black) and
115 polytetrafluoroethylene, PTFE (Sigma-Aldrich, 60 wt% dispersion in H₂O) with a 70:30
116 Vulcan/PTFE mass ratio. The mixture was then diluted to 3 % in IPA and agitated in an
117 ultrasound bath. This solution was air-brushed onto the Toray paper and the obtained MPL layer
118 was sintered at 623 K for 30 min.

119 The Cu-based GDEs were electrochemically characterised by cyclic voltammetry (CV) tests in a
120 three-electrode undivided cell, in which a CO₂ saturated-based 0.1 M potassium bicarbonate
121 (KHCO₃) aqueous solution was used as electrolyte. A graphite rod and an Ag/AgCl electrode
122 were used as counter and reference electrodes, respectively. Small pieces of Cu-GDEs (Cu NP=
123 25 nm, 40-60 nm and 60-80 nm) were used as working electrodes. The resulting *j* were
124 normalised to the geometric area of the electrode. The applied potential was controlled using a
125 MSTAT4 system (Arbin Instruments) and the samples were cycled five times from 0 V vs.
126 Ag/AgCl to -2 V vs. Ag/AgCl.

127 2.2. CO₂ electroreduction tests

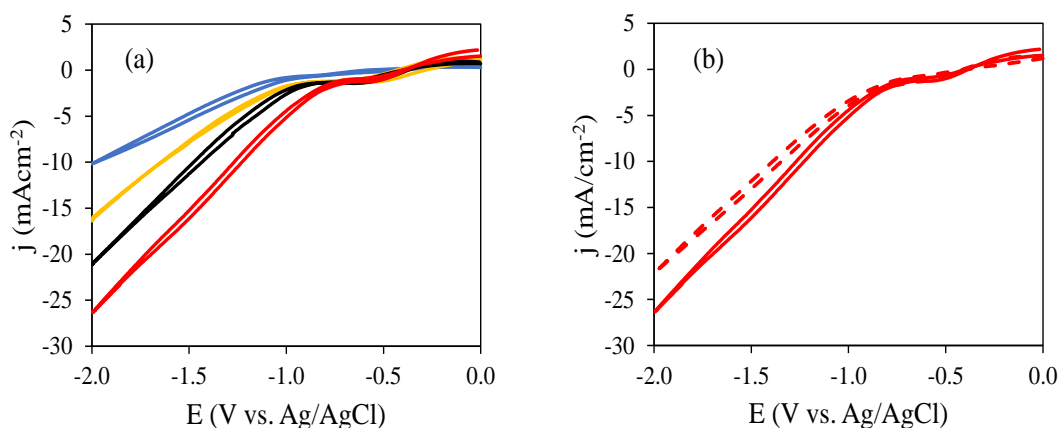
128 The experimental setup to perform the gas-phase CO₂ electroreduction has been described in
129 our previous study [9]. The core of the filter-press type electrochemical reactor is the MEA,
130 which serves as working electrode and separates the cathode and anode compartments. A
131 dimensionally stable anode [DSA/O₂(Ir-MMO (Mixed Metal Oxide) on Platinum)] and a leak-
132 free Ag/AgCl were used as counter and reference electrodes, respectively. Humidified CO₂ was
133 fed to the cathode compartment at a flow rate, *Q_g/A*, of 18 mLmin⁻¹cm⁻² and a 0.1 M KHCO₃
134 aqueous solution was used as anolyte. The CO₂ reduction experiments were conducted at
135 galvanostatic conditions (*j*=7.5, 15, 30 mAcm⁻²) using an AutoLab PGSTAT 302N potentiostat.
136 All experiments were carried out at ambient conditions. Gas reduction products were analyzed
137 using a four-channel gas microchromatograph (3000 micro GC, Inficon) equipped with a

138 thermal conductivity detector (TCD). Gas samples were measured every 5 min for 45 min, with
139 three replicates for each experiment to obtain an averaged reaction rate, r ($\mu\text{molm}^{-2}\text{s}^{-1}$),
140 selectivity, S , defined as the ratio between $r_{\text{C}_2\text{H}_4}$ and r_x , with x being CH_4 and H_2 , and FE , for
141 each product.

142 3. Results and discussion

143 3.1. Cyclic voltammetry tests

144 Figure 1.a. shows the current-voltage responses after 5 electrochemical scans for the Cu NP
145 based-GDEs (i.e. 25 nm, 40-60 nm and 60-80 nm) and that response for the Toray paper for
146 comparison. Additionally, to further analyse the catalytic activity for CO_2 electroreduction,
147 figure 1.b. reveals the CV results for the Cu25-GDE in the absence of CO_2 (under N_2
148 saturation).



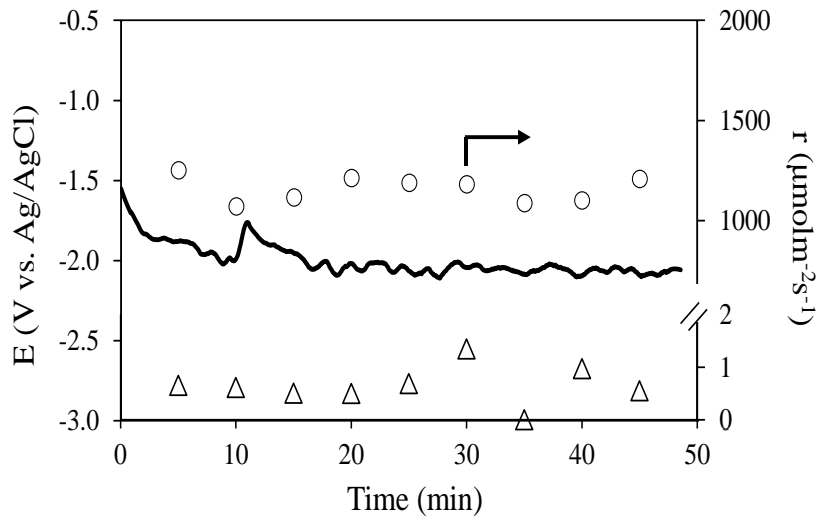
149

150 **Figure 1.** Cyclic voltammograms for: (a) Cu-GDEs in CO_2 -saturated 0.1 M KHCO_3 aqueous
151 electrolyte. Colour codes: Toray paper (blue), Cu25 (red), Cu40-60 (black), Cu60-80 (yellow)
152 and, (b) Cu25-GDE in CO_2 (continuous-red line) and N_2 (dotted-red line) saturated 0.1 M
153 KHCO_3 solution.

154 Figure 1.a. displays similar trends for all the Cu-based electrodes, even though higher activities
155 can be clearly observed when decreasing Cu nanoparticle size (from 60-80 nm to 25 nm). The
156 main characteristic of the CV voltammograms is the difference between the starting potentials
157 for the reduction process as a function of each material tested, which may be initially associated
158 with the particle size influence on reaction mechanisms [10], involving different pathways and
159 reaction intermediates. For instance, larger Cu particle-based GDEs (i.e. 60-80 and 40-60 nm)
160 presented a similar CO_2 reduction peak (starting at around -0.9 V vs. Ag/AgCl). However,
161 Cu25-based GDEs reached an onset potential of about -0.8 V vs. Ag/AgCl. The highest catalytic
162 activity of the Cu25-based electrode (continuous-red line) might be related to an increase in the
163 fraction of under-coordinated sites, such as defects, edges and corners on the electrode surface
164 due to the smaller size of the Cu NPs, which might involve an increased reaction selectivity to
165 more reduced species [14]. Figure 1.b. demonstrated the reduction of CO_2 molecule, as the
166 activity increased in comparison to that curve under N_2 conditions.

167 3.2. Gas-phase CO_2 electroreduction

168 Figure 2 shows the time evolution for the potential (E) and the reaction rate (r) in the continuous
169 gas-phase CO_2 electrochemical conversion to C_2H_4 and CH_4 at the GDE-based electrode (Cu25;
170 $L=0.5 \text{ mgcm}^{-2}$) when applying a constant current of $j=15 \text{ mA/cm}^2$. Besides C_2H_4 and CH_4 , CO
171 and H_2 were also detected.



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Figure 2. Time evolution for E and r in the production of C_2H_4 (circles) and CH_4 (triangles) at Cu25-based GDE. $j=15 \text{ mAcm}^{-2}$.

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As shown in the figure, steady state conditions can be reached after 15 min of operation, when E remains constant (E averaged at $-2.1 \text{ V vs. Ag/AgCl}$ 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 $r_{C_2H_4}$ and r_{CH_4} behave similarly, which may indicate the suitability of the Cu25-based electrode for the production of C_2H_4 and 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 analyse the technical feasibility of the gas-phase CO_2 electroreduction process.

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3.2.1. Particle size effect

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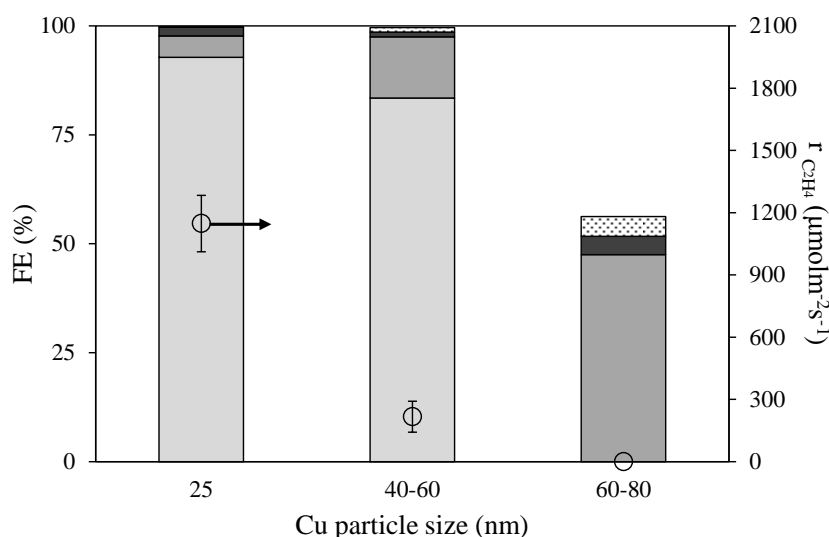
Table 2 and figure 3 show the main results for the continuous gas-phase CO_2 reduction in the filter press electrochemical cell as a function of the Cu particle size.

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Table 2. r and FE at Cu-based-GDEs as a function of the Cu NP size. $j=7.5 \text{ mAcm}^{-2}$.

Cu NP (nm)	E (V vs. Ag/AgCl)	r ($\mu\text{molm}^{-2}\text{s}^{-1}$)				S		FE (%)			
		H_2	CO	CH_4	C_2H_4	$S_{C_2H_4/CH_4}$	$S_{C_2H_4/H_2}$	H_2	CO	CH_4	C_2H_4
25	-1.7	366.6 ± 20	4.5 ± 1.3	37.6 ± 5.2	1148 ± 136	30.5	3.1	4.9	<0.1	2.0	92.8
40-60	-2.5	218.8 ± 7.0	16.7 ± 0.3	4.23 ± 0.5	216.7 ± 75	51.2	0.99	14.0	1.1	1.1	83.4
60-80	-2.2	184.7 ± 31	17.6 ± 1.8	4.1 ± 0.5	-	-	-	47.5	4.5	4.17	-

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191

192 **Figure 3.** *FE* and $r_{C_2H_4}$ as a function of Cu NP size at $j=7.5 \text{ mAcm}^{-2}$. Colour codes for *FEs*
 193 (columns): light to dark shading (C_2H_4 , H_2 and CH_4 , respectively), and dotted points (CO).

194 From the results, a significant production of C_2H_4 was achieved at lower particle sizes. CH_4 , CO
 195 and H_2 were also observed over the entire Cu NP size range. In addition, lower rates for liquid-
 196 phase products such as CH_3OH ($r < 0.5 \mu\text{molm}^{-2}\text{s}^{-1}$) and C_2H_5OH ($r < 2.4 \mu\text{molm}^{-2}\text{s}^{-1}$) were
 197 detected with a *FE* $< 0.5 \%$. Previous findings in the group demonstrated that Cu60-80 are able
 198 to electroreduce CO_2 to CH_4 , also producing H_2 and CO in a wide range of applied potentials
 199 (i.e. from -2.4 V to -1.8 V vs. Ag/AgCl) and catalytic loadings (i.e. from 0.25 mgcm^{-2} to 1.5
 200 mgcm^{-2}) in a MEA configuration [9]. The highest CH_4 production was achieved at 0.5 mgcm^{-2}
 201 and -2 V vs. Ag/AgCl ($j=7.5 \text{ mAcm}^{-2}$). However, C_2H_4 was not detected at this Cu NP size level
 202 (60-80 nm), in contrast to those results obtained in the present report when reducing particle
 203 size (i.e. Cu40-60 and Cu25). The absence of C_2H_4 at the largest Cu NP size tested (Cu60-80)
 204 may be associated with the lower presence of corners, specific crystal orientation surfaces,
 205 edges and defects in the electrocatalyst than those presented when reducing particle size [14,
 206 27]. The presence of edge sites may represent key sites which facilitate the adsorption and
 207 stabilisation of CO_2 reduction reaction intermediates towards C-C coupling [28]. In contrast, the
 208 lower presence of these parameters at the largest particle size tested seems to be beneficial for
 209 CH_4 formation, at least in terms of *FE*. Consequently, it is crucial to identify which structural
 210 parameters in electrocatalysts for CO_2 electroreduction are able to control the selectivity of the
 211 reaction to multicarbon products.

212 The best values for C_2H_4 production were reached when using Cu25, in which a rate of $r=1148$
 213 $\mu\text{molm}^{-2}\text{s}^{-1}$ and a *FE* of 92.8 % were obtained. In the same manner, the optimum CH_4
 214 production rate was achieved at this particle size level ($r=37.6 \mu\text{molm}^{-2}\text{s}^{-1}$ with a *FE* of 2 %).
 215 This change in reaction performance compared to larger Cu NPs (i.e. 60-80 nm) also entails a
 216 decrease in the *FE* to H_2 and CO. In addition, the $S_{C_2H_4/H_2}$ was enhanced when decreasing the Cu
 217 particle size ($S_{C_2H_4/H_2}=3.1$ at Cu25) due to the presence of defects in the material in comparison
 218 to larger Cu particles ($S_{C_2H_4/H_2}=0.99$), whereas the highest $S_{C_2H_4/CH_4}$ was reached at Cu40-60
 219 ($S_{C_2H_4/CH_4}=51.2$), in which CH_4 formation was considerably reduced in comparison to the Cu25
 220 performance ($S_{C_2H_4/CH_4}=30.5$). Thus, the most active material for the reduction of CO_2 was
 221 Cu25, in agreement with the higher reduction response observed from CV profiles (figure 1).
 222 The literature shows that the formation of hydrocarbons from CO_2 can be suppressed at very
 223 small NPs (i.e. 2-15 nm) due to the reduction of catalytic active surface area as discussed by
 224 Reske et al. in 2014 [10], where the formation of syngas was preferred over the formation of

225 hydrocarbons. The authors suggested that very small (i.e. <3 nm) Cu catalysts should be
 226 avoided for the formation of hydrocarbons from CO₂ electroreduction

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

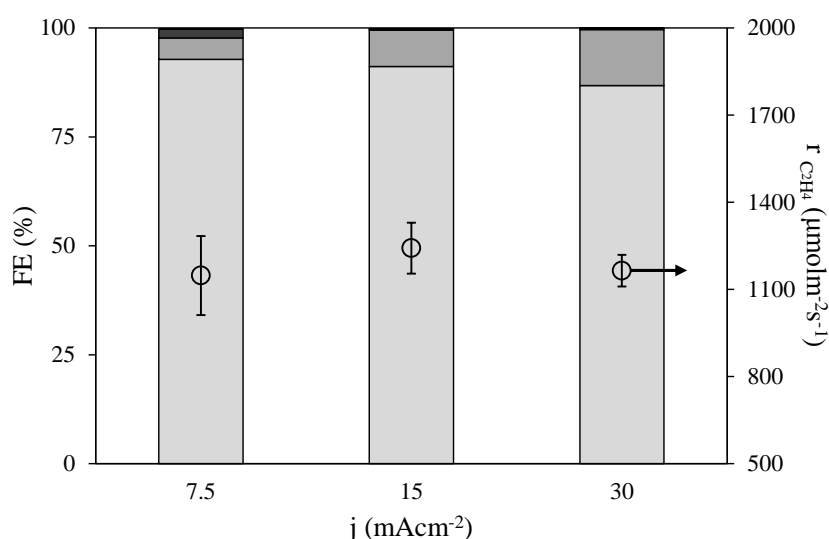
234 3.2.2. Current density influence

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

240 **Table 3.** r and FE at Cu25-based-GDEs. $j = 7.5 - 30 \text{ mAcm}^{-2}$.

j (mAcm ⁻²)	E (V vs. Ag/AgCl)	r (μmolm ⁻² s ⁻¹)				S		FE (%)			
		H ₂	CO	CH ₄	C ₂ H ₄	S _{C₂H₄/CH₄}	S _{C₂H₄/H₂}	H ₂	CO	CH ₄	C ₂ H ₄
7.5	-1.7	366.6 ± 20	4.5 ± 1.3	37.6 ± 5.2	1148 ± 136	30.5	3.1	4.9	<0.1	2.0	92.8
15	-2.1	682.4 ± 22	9.5 ± 7.3	4.8 ± 4.4	1242 ± 88	259	1.8	8.4	<0.15	0.2	91.2
30	-3.4	1034 ± 11	9.9 ± 8.0	5.5 ± 3.4	1165 ± 54	212	1.1	12.8	<0.15	0.3	86.8

241



242

243 **Figure 4.** FE and $r_{\text{C}_2\text{H}_4}$ at different j on Cu25-based MEAs. Colour codes for FEs (columns):
 244 light to dark shading (C₂H₄, H₂ and CH₄, respectively).

245 As shown in table 3 and figure 4, the product distribution, rates and process efficiency are
 246 correlated with the current applied to the system. In this regard, the production of H₂ gained

247 importance when increasing j , involving a reduction in the FE to C_2H_4 (from 92.8% to 86.8%)
 248 and CH_4 (from 2.0 to 0.3), as well as in reaction selectivity ($S_{C_2H_4/H_2}$). This effect might be
 249 explained by the consumption of the additional current in producing H_2 (with only two electrons
 250 exchanged required) through the hydrogen evolution reaction instead of producing
 251 hydrocarbons from CO_2 electroreduction at higher j levels. Similarly, r to CH_4 is negatively
 252 affected by j , with $r=37.6 \mu\text{molm}^{-2}\text{s}^{-1}$ and $r=5.5 \mu\text{molm}^{-2}\text{s}^{-1}$ for $j=7.5 \text{ mAcm}^{-2}$ and $j=30 \text{ mAcm}^{-2}$,
 253 respectively. Additionally, the $S_{C_2H_4/CH_4}$ value goes from 30.5 to 212 when increasing the current
 254 from $j=7.5 \text{ mAcm}^{-2}$ to $j=30 \text{ mAcm}^{-2}$, respectively. On the other hand, CO (two electrons
 255 exchanged) productivity and efficiency were slightly improved at higher j probably because of
 256 the simplicity of the CO_2 -to- CO reaction (two electrons exchanged).

257 To sum up, applying a current density of $j=7.5 \text{ mAcm}^{-2}$, which allows achieving the highest
 258 C_2H_4 production ($r=1148 \mu\text{molm}^{-2}\text{s}^{-1}$, $FE=92.8$ and $S_{C_2H_4/H_2}=3.1$) with lower energy
 259 requirements ($E=-1.7 \text{ V}$ vs. $Ag/AgCl$), resulted in an improved gas-phase CO_2 electroreduction.
 260 This results may be taken into consideration when designing future applications for gas-phase
 261 CO_2 electroreduction processes.

262 3.2.3. Microporous layer evaluation

263 As discussed above, mass transfer limitations usually affect selectivity, productivity and
 264 efficiency in CO_2 electroreduction processes. Therefore, the use of a carbon MPL between the
 265 catalytic layer and the Toray carbon support may help to alleviate these limitations, favouring
 266 the transport of species (i.e. CO_2 and intermediates) in the filter-press cell. Table 4 shows the
 267 results for the presence/ absence of a MPL within the Cu25-based working electrode at the
 268 optimal current density level ($j=7.5 \text{ mAcm}^{-2}$).

269 **Table 4.** r and FE at Cu25 and MPL-Cu25-based-GDEs. $j=7.5 \text{ mAcm}^{-2}$.

MPL	E (V vs. $Ag/AgCl$)	r ($\mu\text{molm}^{-2}\text{s}^{-1}$)				S		FE (%)			
		H_2	CO	CH_4	C_2H_4	$S_{C_2H_4/CH_4}$	$S_{C_2H_4/H_2}$	H_2	CO	CH_4	C_2H_4
No	-1.7	366.6 ± 20	4.5 ± 1.3	37.6 ± 5.2	1148 ± 136	30.5	3.1	4.9	<0.1	2.0	92.8
Yes	-1.0	364.7 ± 22	5.6 ± 0.6	1.3 ± 0.4	816 ± 428	628	2.2	6.9	<0.15	<0.1	92.8

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271 Similar C_2H_4 formation rates were obtained in the presence and absence of the MPL
 272 (considering experimental standard deviation). The same can be said for the FE to C_2H_4 . In the
 273 same manner, CO and H_2 production was not affected neither by the presence of an additional
 274 porous layer. Conversely, a decrease in CH_4 reaction rate (involving a significant increase in
 275 $S_{C_2H_4/CH_4}$) and FE was observed when using the MPL within the working electrode. The results
 276 may indicate that the presence of the MPL favoured the electrochemical reduction of CO_2 to
 277 more reduced products ($S_{C_2H_4/CH_4}=628$ vs. $S_{C_2H_4/CH_4}=30.5$ in its absence) with an insignificant
 278 effect on the C_2H_4/H_2 ratio. This finding can be probably associated to an improved transport of
 279 CO_2 through the working electrode.

280 Another advantage of the MPL seems to be the energy consumption, reaching voltage values of
 281 -1 V and -1.7 V vs. $Ag/AgCl$, for the presence and absence of the MPL, respectively. This can
 282 be justified by increases in the electrode conductivity, which is a key factor for an efficient CO_2
 283 valorisation system.

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285

287 Table 5 shows a summary of the r and FE to C_2H_4 and CH_4 (and other subproducts) from
 288 literature, paying attention to electrochemical reactor configuration (i.e. G: gas; L: liquid),
 289 electrocatalytic materials and process conditions.

290 **Table 5.** r and FE at CO_2 reduction systems with Cu-based electrodes.

Reactor type	Catalyst	E (V vs. Ag/AgCl)	FE (%)				r ($\mu\text{molm}^{-2}\text{s}^{-1}$)		Other	Ref.
			H_2	CO	CH_4	C_2H_4	CH_4	C_2H_4		
G-L	Cu NP 25 nm	-1.7	4.9	<0.1	2.0	92.8	37.6	1148	CH_3OH , C_2H_5OH (traces)	This work
G-L	Cu-SPE ¹	-1.95	---	---	9.0	10.0	---	---	---	[24]
G-L	Cu gauze	-3.01	---	---	9.1	69	---	---	---	[30]
G-L	Cu-SPE ¹	-1.45	86.8	2.6	<0.1	8.8	---	---	HCOOH	[31]
G-L	Cu/C	---	79	0.3	4.5	---	---	---	HCOH, CH_3OH	[32]
G-L	Cu_2O/C	2.5 ²	45	---	30	5	---	---	CH_3OH	[33]
G-L	Cu_2O/C	2.5 ²	20	Low	10	---	0.005 ³	---	CH_3OH , C_2H_6	[34]
G-L	Cu/C	-1.8 ²	---	Low	Low	---	0.007	---	Alcohols	[26]
G-L	Cu/CNFs	---	---	---	---	---	0.001	---	CO, Alcohols, CH_3CHO	[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	---	---	C_2H_6	[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, CH_3CHO	[42]
L-L	Cu NP	-1.3	28	33	2	35	---	---	C_2H_6	[43]
L-L	Cu mesh	-1.9	Balance	5	15	8	---	---	---	[44]
L-L	Polypyrrol coated Cu	-3 V ⁴	Not analysed	15.1	25.5	3.1	---	---	HCOOH, CH_3COOH	[45]
L-L	Cu layers on Pt	-1.2	Balance	---	33	7	---	---	---	[46]
L-L	Cu foil	-1.35	45	---	30	---	---	---	---	[47]

L-L	Electrode posited Cu NP	-2.2	5	2.5	60	20	---	---	---	[14]
L-L	Cu foil	-1.3	20	3	57	20	---	---	---	[10]
L-L	Cu nanoneed les	-1.4	18	---	14	6	---	---	HCOOH	[48]
L-L	Cu nanofoa m	-1.7	60	7.5	0.2	1.3	---	---	HCOOH, C ₂ H ₆	[49]
L-L	Cu NP	-1.55	25	---	76	---	---	---	---	[50]
L-L	Deposited Cu ₂ O	-1.3	Balanc e	3	5	37.5	---	---	C ₂ H ₆	[51]
L-L	Cu ₂ O over Cu	-1.19	39	Low	Low	39	---	---	HCOOH, C ₂ H ₆ , C ₂ H ₅ OH	[52]
L-L	Cu ₂ O- derived Cu	-1.2	18	Low	Low	Low	---	---	HCOOH, C ₂ H ₆ (30 %), C ₂ H ₅ OH,	[53]
L-L	Cu mesocrys tals	-1.19	60	2	2.7	27.2	---	---	HCOOH	[54]
L-L	Cu ₂ O reduced to Cu	-1.8	24	Low	2	44	---	---	---	[27]
L-L	Electrode posited Cu	-1.4	30	---	28	---	---	---	C ₂ H ₆ (43 %)	[55]
L-L	Cu foil	-1.6	15	1	70	15	62	5	---	[56]
L-L	Oxide- derived Cu	-1.0	15	15	---	20	---	250 ⁵	HCOOH, C ₂ H ₆ (35 %)	[57]
L-L	Cu foil	-1.2	15	1	60	20	10	6	HCOOH	[58]
L-L	Cu foil+glyc ine	-1.9	---	---	30	25	---	---	C ₂ H ₆ , C ₃ H ₈	[59]
L-L	Cu + graphene oxide	-1.5	50	Low	40	Low	---	---	HCOOH	[60]
L-L	Cu foil	-1.65	---	---	45	2	---	---	HCOOH	[61]
L-L	Cu ₂ O- CuBr films	-2.1	81	---	---	17	---	---	C ₂ H ₆	[62]
L-L ⁶	Cu sheet	-1.6	30	Low	10	30	250 ⁷	140 ⁷	---	[63]
L-L	Cu mesh	-1.9	---	5	10	37	---	---	---	[13]
L-L	Cu films	-1.6	21	5	4	40	---	---	---	[64]
G-G	Cu deposit	---	---	---	0.11	1.7	---	---	C ₂ H ₆	[65]
G-G	Cu felt	3.9 ²	---	---	0.12	---	---	---	Long- chain Hydrocarb	[66]

291 Notation: ¹solid polymer electrolyte, ²unknown reference electrode, ³ $\mu\text{mol s}^{-1}$, ⁴Pb(Hg)x/PbSO₄/SO₄²⁻ reference
292 electrode, ⁵ppm $\text{cm}^{-2}\text{h}^{-1}$, ⁶CO₂ (70 %)- O₂ (30 %) inlet, ⁷ppm.

293 As observed, this work reports the highest productivity values for C₂H₄ ($r_{\text{C}_2\text{H}_4}=1148 \mu\text{molm}^{-2}\text{s}^{-1}$)
294 and one of the highest for CH₄ ($r_{\text{CH}_4}=37.6 \mu\text{molm}^{-2}\text{s}^{-1}$) achieved so far, which denotes the
295 relevance of the work. Besides, the highest *FE* to C₂H₄ has been also reached with this study
296 (92.8 %) at Cu25-based GDEs. However, higher *FEs* to CH₄ have been reported in literature for
297 G-L and L-L systems (up to 76 %). It is also worth noting that several researchers have detected
298 long-chain hydrocarbons at different Cu-based catalytic material (i.e. electrodeposited Cu,
299 oxide-derived Cu, Cu+glycine, etc.), with higher *FEs* to C₂H₆ (e.g. 43 %). In any case, most of
300 the systems are more selective to H₂, which should be reduced if we intend to increase the
301 formation of hydrocarbons.

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

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

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

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

327 iv) Mechanisms understanding. The key determining step in CO₂ reduction seems to be the
328 protonation of adsorbed CO to obtain CHO. On the one hand, the pathway for the formation of
329 CH₄ at Cu surfaces involves further protonation steps of adsorbed CHO, in which OCH₃
330 adsorbed is finally protonated to produce CH₄, with different intermediates involved depending
331 on crystal orientation and lattice, among others. On the other hand, the formation of C₂H₄
332 requires C-C bonding and adsorbed CH₂O species seems to be key intermediates for further
333 dimerization to obtain C₂H₄. In any case, the reaction pathway is still unclear and further
334 research efforts are required in this regard.

335

336

337 4. Conclusions

338 This work presents innovative results on the continuous production of hydrocarbons (i.e.
339 ethylene and methane) from gas-phase CO₂ electroreduction at Cu-based electrodes including
340 different nanoparticles sizes (ranging from 25 nm to 80 nm). Cyclic voltammetry tests showed
341 that Cu 25 nm-based electrodes displayed an improved performance in comparison to larger Cu
342 particles (i.e. 40-60 nm and 60-80 nm), which can be explained by an increase in the fraction of
343 under-coordinated sites when decreasing particle size.

344 The highest ethylene production (1148 μmolm⁻²s⁻¹) was achieved at the lowest particle size level
345 tested (i.e. 25 nm), with a Faraday efficiency of 92.8 %. When increasing Cu particle size (i.e.
346 40-60 nm and 60-80 nm) the productivity and the Faraday efficiency to C₂H₄ was negatively
347 affected, involving also higher overpotentials. Conversely, ethylene/methane ratio was enhanced
348 at the 40-60 nm-based electrodes (50.4), although the hydrogen evolution is also improved
349 (ethylene/hydrogen= 0.99) compared to those obtained at the lowest particle size level (3.1). In
350 addition, similar ethylene rates were achieved in the whole current density range (7.5 mAcm⁻² to
351 30 mAcm⁻²), while the Faraday efficiency to ethylene decreased. Finally, the use of a
352 microporous layer led to higher ethylene/methane ratios with an insignificant effect on
353 ethylene/hydrogen ratios, which means that the presence of the MPL favours the
354 electrochemical reduction of CO₂ to more reduced products.

355 Overall, the productivity, selectivity and efficiency of the gas-phase CO₂ electroreduction to
356 hydrocarbons are highly dependent on the Cu particle size. Other aspects such as crystal
357 orientation and shape, among others, should be considered in future research for an efficient
358 CO₂ electroreduction to hydrocarbons process.

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