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Engineering copper nanoparticle electrodes for tunable electrochemical reduction of carbon dioxide

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ABSTRACT

The electrochemical conversion of CO2 catalyzed by copper (Cu)-based materials is widely reported to produce different valuable molecules, and the selectivity for a specific product can be achieved by tuning the characteristics of catalytic materials. Differing from these studies on materials, the present work focuses on the engineering of gas diffusion electrodes in order to properly modify the selectivity, particularly by changing the Cu nanoparticle catalyst loading of the electrodes. Low catalyst loadings (< 0.25 mg cm−2) favor CH4 production, and intermediate (~1.0 mg cm−2) loadings shift the selectivity toward C2H4. Eventually, larger values (>2.0 mg cm−2) promote CO production. Detailed analyses reveal that both bulk and local CO generation rates, and charge transfer mechanism are responsible for the observed loading-dependent selectivity. The present work provides a new strategy for steering the CO2RR selectivity by simple electrode engineering beyond material development.

1. Introduction

The reduction of CO2 into useful fuels and chemicals through electrochemical means is both economically and environmentally appealing. This innovative technology has the potential to establish a sustainable carbon cycle and combat climate changes, while also storing renewable energy [1,2]. Despite over a decade of global efforts by chemists, physicists, and engineers, commercializing this process is difficult due to the complex mechanism of CO2 reduction reaction (CO2RR), which results in a variety of products like carbon monoxide (CO), formic acid (HCOOH), methane (CH4), ethylene (C2H4), ethanol (C2H5OH) and methanol (CH3OH) [3–9]. Among them, CO and HCOOH can be obtained with very high selectivity (> 90%), and the use of gas diffusion electrodes is a key factor to go beyond the state-of-the-art performance and the stability issue is the main challenge for commercialization [10]. Instead, state-of-the-art methods for electrochemical CO2 conversion to some products such as CH4, C2H4 and C2H5OH still call for electrocatalysts to enhance the selectivity by improving the CO intermediate production and blocking hydrogen formation [10,11].

Nonetheless, these products are significant for various industries. For instance, CH4, which makes up the largest part of natural gas, provides 24% of the world’s energy and has a well-established system for storage, transportation, and consumption [12,13]. C2H4, on the other hand, is widely used in the production of materials such as ethyleneglycol, ethylene oxide, and polyethylene, which is produced mainly through the steam cracking of naphtha and natural-gas-derived ethane in the current industries. However, this process requires a lot of energy and results in a considerable amount of CO2 emissions [14]. The production of these molecules through electrochemical reduction of CO2 has high economic and environmental significance, but still poses challenges in terms of catalytic materials and processes. Copper (Cu) has been found to be a unique catalyst among the studied metals, capable of directing the selectivity of CO2RR towards C1 and C2 chemicals. Studies suggest that the selectivity of Cu catalysts for C1 and C2 products, particularly hydrocarbons, can be controlled through various methods, such as surface engineering, coordination control, modification of the catalyst/electrolyte interface, and process design. This includes techniques such as manipulating particle size [15], surface roughness [16,17], facet [18], oxidation state [19–22], grain boundary [23], Cu coordination number [24], local pH [25], controlling CO2 availability [12] and using tandem catalysis [26,27]. The size of Cu nanoparticles shows dramatic effects on the catalytic activity and selectivity of the catalysts during CO2 electroreduction, with remarkable enhancement in the production of CH4 and
CO with decreasing Cu particle size [15]. Studies have shown that the roughness of a surface has a significant impact on the selectivity of CO₂ reduction towards C₂ products. This is because roughness causes the confinement of gaseous intermediates like CO within mesopores, which is key in determining the selectivity. Theoretical and experimental studies have found that the Cu (111) facet affects the pathways for generating CH₄ during CO₂ reduction, while the Cu (100) facet directs the C–C coupling step for the production of C₂ products. Additionally, the composition of the Cu catalyst surface plays a crucial role in determining the selectivity and activity towards CH₄ or CH₂ [28]. The exact nature of the active site of the catalyst, specifically the ratio of Cu oxidation species (Cu⁺) to metallic species (Cu⁰), is still a matter of debate. Nevertheless, several studies have shown that the ratio of Cu⁺ to Cu⁰ can significantly influence the selectivity between CH₄ and CH₂ under the same conditions. Cu⁰ sites tend to favor the hydrogenation of CO into CH₄, while Cu⁰/Cu⁺ hybrid sites tend to promote the dimerization of CO into C₂H₂. Different coordination numbers of Cu were found to have different hydrocarbon selectivity, with low coordination numbers promoting the production of CH₂.

In this study, instead of focusing on material properties, we demonstrate that it is possible to tune the selectivity of CO₂RR towards C₂ and C₂ products by simply modifying the catalyst loading on the electrodes. This strategy was partially studied on copper-based catalysts such as copper phosphate [29] and copper(II) phthalocyanine/carbon catalysts [24]. In the former work, the copper phosphate is reduced to metallic Cu nanoparticles at low loading condition, favoring *CO hydrogenation to CH₂ production, while metallic Cu nanoparticles decorated with Cu₃(PO₄)₂ are produced at high Cu₃(PO₄)₂ loading condition, promoting the dimerization of *CO to C₂H₂ formation. Hence, the effect of catalyst loading is actually considered to be the effect of the surface composition of derived catalysts in this literature work. In the latter work, carbon particles are used to isolate and prevent the agglomeration of low coordination number Cu clusters formed during the in-situ reduction of a copper(II) phthalocyanine, enhancing the *CO hydrogenation and boosting the selectivity toward CH₄. Strictly speaking, this literature work can be considered to have a focus on a composite catalyst of Cu clusters and carbon nanoparticles with various Cu/C ratios. On the contrary, in the present study, commercial Cu nanoparticles (NPs) are the only composition of the catalyst layer beyond a 17 wt.% of Nafion, and only the Cu NPs loading varies for different electrodes. The Cu NPs gas diffusion electrodes (GDE) were then tested in a flow reactor with highly alkaline electrolyte and a gaseous CO₂ feed. This setup ensures a high rate of CO₂ diffusion and shortens the distance between the CO₂ gas and the catalyst layer, allowing to obtain industrially-relevant current densities larger than 1 A cm⁻² at cell voltages lower than 4.0 V. The electrodes demonstrated a controlled selectivity towards CH₄, C₂H₆ and CO, which was likely due to the combination of the bulk and local CO generation rates on the electrode and at the active sites, respectively.

2. Experimental

2.1. Materials

The following materials were obtained from Merck: Copper nanoparticles of 25 nm size (CAS Number: 7440-50-8), copper nanoparticles with a size range of 40–60 nm (CAS Number: 7440–50–8), a 5 wt% solution of Nafion® 117 (CAS Number: 31,175–20–9), isopropanol (CAS Number: 78-68-8), and potassium hydroxide with a purity of 84 wt% or greater (CAS Number: 1310–58–3). They were used as received, unless otherwise indicated.

2.2. Preparation of the electrodes

The method used to create the electrodes is extremely crucial and has a significant impact on their electrochemical performance [30,31]. In this study, a straightforward drop-casting approach was employed to place Cu NPs on a carbon gas diffusion layer (GDL) substrate, which allows for precise control over the catalyst quantity. Electrodes with varying Cu loadings of 0.25, 0.5, 1.0, 2.0, and 3.0 mg cm⁻² were created, all with a consistent 17 wt.% Nafion content in the dry electrode. Two different sized Cu NPs, 25 nm and 50 nm, were examined. The electrodes featuring 25 nm NPs are labeled as Cu25_x and those with 50 nm NPs are referred to as Cu50_x, where x represents the respective catalyst loading of 0.25, 0.5, 1.0, 2.0, or 3.0. A standard preparation involves thoroughly mixing a specific quantity of Cu NPs, Nafion solution, and 150 µL of isopropanol through sonication. The resulting homogeneous mixture was then applied to a GDL (SIGRACET 28BC, SGL Technologies) and left to dry at room temperature for an entire night to eliminate the solvents.

2.3. Physical and chemical characterizations of Cu NPs and prepared electrodes

Morphological characteristics of the samples were obtained through Field emission scanning electron microscopy (FESEM Supra 40, Zeiss, Oberkochen, Germany) equipped with Oxford EDS microanalysis (Liquid-N₂ cooled Si(Li) detector). X-ray diffraction (XRD) patterns of the samples were acquired with a PANalytical X Pert Pro-diffractometer (Cu-Kα radiation, 40 kV and 30 mA) equipped with an X’Celerator detector.

2.4. Electrochemical tests and product analysis

The electrochemical performance of the electrodes was initially evaluated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. These tests were conducted in a flow cell configuration (Scheme S1a), using a CH760D potentiostat at room temperature. A Pt wire served as the counter electrode, while a Ag/AgCl (3 M Cl⁻) electrode acted as the reference. The working electrode was the Cu NP-coated GDL electrode with an active area of 0.25 cm². A 1.0 M KOH aqueous solution that was purged with argon (Ar) was used as the electrolyte. CV measurements were carried out over a potential range from 0.6 V to −0.6 V relative to the reversible hydrogen electrode (RHE) at a scan rate of 100 mV s⁻¹. After that, all potentials mentioned in this work are expressed in terms of RHE and adjusted according to the Nernst equation: E (V vs. RHE) = E (V vs. Ag/AgCl) + E_Ag/AgCl + 0.059 * pH, where E_Ag/AgCl is the standard potential of the reference electrode, E (V vs. Ag/AgCl) is the applied potential against the reference electrode, pH is the pH value of the electrolyte, and E (V vs. RHE) is the reported potential. Furthermore, CV tests were also conducted over a narrow potential range of 0.036 V to 0.236 V at scan rates of 5, 10, 20, 30, 40, 50, 60, 80, and 100 mV s⁻¹ to estimate the double layer capacitance (C_dl) of the electrode. The EIS measurements were performed over a frequency range of 10⁻¹ – 10⁻⁷ Hz with an AC signal of 10 mV of amplitude at −0.4 V in 1.0 M KOH electrolyte, in order to gain insight into the electrical properties of the electrodes and the electrode/electrolyte interface.

The CO₂ electrolysis was performed using a chronopotentiometry (CP) method with a CH760D potentiostat. The performance of all electrodes was evaluated based on the selectivity of CO₂RR in a 1.0 M KOH electrolyte using a flow cell configuration, as shown in Scheme S1a and discussed in detail in our previous work [32]. Additionally, the Cu25_1.0 electrodes were further tested in a two-electrode setup (Scheme S1b) at various current densities in a 1.0 M KOH electrolyte, using a commercially available iridium-coated titanium plate (Ir-MMO) as the anode and an as-prepared Cu electrode as the cathode. The quantification of gaseous products was done using a micro gas chromatograph (µGC) equipped with two Rt-Molsieve 5A and Rt-Q-Bond columns, and a micro thermal conductivity detector (TCD) for each module. A high-performance liquid chromatograph (HPLC) was also used to analyze the liquid products. The HPLC was equipped with a ReproSil column and an ultraviolet-visible (UV–Vis) detector that was set at 210 nm, with a mobile phase of 9.0 mM H₂SO₄ and a flow rate of
1.0 mL min\(^{-1}\). The faradaic efficiency (FE) was calculated using Eq. (1), which involves dividing the amount of charge required to produce a specific number of moles (\(N\)) of a product by the total charge consumed during the corresponding reduction period (\(Q\))

\[
\text{FE} = \frac{nNF}{Q} \times 100\%
\]

(1)

where \(n\) is the mole of electrons required to obtain one mole of this product (\(n = 2\) for CO, HCOO\(^{-}\) and H\(_2\); \(n = 12\) for C\(_2\)H\(_4\) and C\(_2\)H\(_5\)OH; \(n = 8\) for CH\(_4\) and CH\(_2\)COO\(^{-}\)), and \(F\) is the Faraday constant that is 96,485 C mol\(^{-1}\).

The energy efficiency (EE) for a specific product was calculated using Eq. (2),

\[
\text{EE} = \frac{E_{\text{anode}} - E_{\text{cathode}}}{\text{cell voltage}} \times \text{FE}
\]

(2)

where \(\text{FE}\) is the faradaic efficiency of this product in percentage, \(E_{\text{anode}}\) is the equilibrium potential (V vs. RHE) of water oxidation, \(E_{\text{cathode}}\) is the equilibrium potential (V vs. RHE) of CO\(_2\) reduction to a specific product [33].

3. Results and discussion

3.1. Study of physical and chemical properties of Cu NPs and electrodes

FESEM has been performed on the commercial Cu nanoparticles in order to confirm the morphology of the samples. As shown in Fig. 1, the particles have expected average sizes, 25 nm and 50 nm, respectively, as indicated in datasheet of the commodities. The nanoparticles agglomerate, and form secondary particles that are much bigger.

The morphology of the 25 nm and 50 nm electrodes has also been studied, as shown in Figures S1 and S2, respectively. The Cu NPs agglomerations are more visible at higher loadings, and they are distinguishable from carbon black nanoparticles of the microporous layer of GDL (Figure S3). At the lowest loading of 0.25 mg cm\(^{-2}\), many carbon black particles with a uniform size are observed, as can be seen from EDX mapping on Cu25_0.25 in Figure S4. With increasing the loading, the Cu agglomerations dominate the electrode surface at loadings ≥1.0 mg cm\(^{-2}\), which can be observed by EDX mapping on Cu25_1.0 in Figure S5. XRD analysis has been conducted on the as-prepared electrodes with 3.0 mg cm\(^{-2}\). The electrodes with the highest loading were used for XRD measurements in order to obtain better signal of the catalyst layer. As displayed in Figure S6, both Cu25 and Cu50 electrodes show intensive diffraction peaks associated with metallic Cu, and only a small fraction of cuprous oxide (Cu\(_2\)O) is also observed due to the oxidation of Cu in air.

3.2. Study of electrochemical properties of Cu electrodes

Before conducting any experiments, the prepared electrodes underwent a stabilization process in which they were subjected to 30 cycles from 0 V to −0.6 V relative to the reversible hydrogen electrode (RHE) with a scan rate of 100 mV s\(^{-1}\). As shown in Figure S7, at the end of the process, the CV curves become stable, meaning that the surface oxide is mainly reduced to metallic Cu. The metallic Cu is the main active phase under the CO\(_2\)RR potentials, which are more negative than −0.6 V. Concisely, this process aims to reduce the little oxide on the surface in order to obtained the double layer capacitance of the Cu electrodes with metallic surface, which should be the real surface under the CO\(_2\)RR conditions. After stabilization, cyclic voltammetry tests were conducted at various scan rates of 5–100 mV s\(^{-1}\) in a potential range where no electrochemical reactions take place, to calculate the double-layer capacitance.

Fig. 1. FESEM images of Cu25 (a and b) and Cu50 (c and d) nanoparticles.
capacitance ($C_{dl}$) of the electrode. [34,35]. The $C_{dl}$ is estimated by plotting the geometric current densities against scan rates and finding the slope of the linear fit. The calculated $C_{dl}$ values for the Cu25_0.25, Cu25_0.5, Cu25_1.0, Cu25_2.0, and Cu25_3.0 electrodes were found to be 1.4, 2.1, 2.7, 7.4, and 7.8 mF cm$^{-2}$ respectively, as shown in Fig. 2 for the Cu25_1.0 electrode. According to the literature [36], an ideally flat Cu foil has a $C_{dl}$ value of 28 µF cm$^{-2}$, and the electrochemical active surface area (ECSA) of the electrodes can be obtained via dividing the $C_{dl}$ values by 28 µF cm$^{-2}$. This method is widely used to evaluate the ECSA of Cu electrodes [34,37], despite the obtained ECSA values are not totally precise, since the $C_{dl}$ of the ideally flat Cu slightly varies in different electrolytes [38]. However, this method is valid to compare different electrodes in the same work. The calculated ECSA are 50, 75, 96, 264 and 278 cm$^2$ for each geometric unit (cm$^2$) of Cu25_0.25, Cu25_0.5, Cu25_1.0, Cu25_2.0 and Cu25_3.0 electrodes, respectively. Similarly, the evaluated $C_{dl}$ values and ECSA of the Cu25_0.25, Cu50_0.5, Cu50_1.0, Cu50_2.0 and Cu50_3.0 electrodes, respectively, corresponding to ECSA of 43, 71, 107, 125 and 307 cm$^2$ for each geometric cm$^2$. In general, the ECSA of the Cu25 electrode is slightly higher than that of the Cu50 one at the same loading, and the ECSAs increase with increasing the Cu loading for both Cu25 and Cu50 samples. This is due to the fact that smaller particles potentially have a higher surface-to-mass ratio compared to larger ones, and a higher loading has more particles available for building the electrolyte/catalyst interface.

The electrochemical behaviors of the Cu electrodes were analyzed by conducting CV experiments in a 1.0 M KOH electrolyte that was purged with Ar. Fig. 3a and 3b present the voltammograms of the Cu25 and Cu50 electrodes, respectively. In the potential range between 0.25 and 0.6 V, peaks related to the redox reactions of Cu species are observed [39]. The cathodic scan reduces Cu oxide species to metallic Cu, while the anodic scan re-oxidizes Cu to Cu oxides. The intensity of the redox peaks increases as the loading of Cu NPs increases, as expected. Within the potential range of -0.2 to -0.6 V, only hydrogen evolution reaction (HER) is observed due to the Ar purging of the electrolyte during measurement. The activity of the Cu NPs increases with a rise in the catalytic activity of the Cu NPs on the electrode, can be obtained. As active surface area (ECSA), the specific current density, which reflects current density also rises. By dividing the current by the electrochemical interface.

EIS was also conducted to analyze the electrochemical characteristics of the Cu electrodes in an Ar-purged 1.0 M KOH electrolyte. Fig. 4a and 4b display Nyquist plots of the impedance of Cu25 and Cu50 electrodes, respectively. The impedance spectra of all samples are dominated by the charge transfer process, which has a much greater resistance than the high-frequency charge transport process [40]. Moreover, for both sets of electrodes, as the loading increased, the impedance values decreases, which aligns with the trend observed in the CV measurements (Fig. 3a and 3b) where the larger the current, the lower the impedance. By using the equivalent circuit shown in the inset of Fig. 4 (5), the charge transfer resistance ($R_{ct}$) values were obtained and displayed in Fig. 4c and 4d for Cu25 and Cu50 electrodes, respectively. As expected, the $R_{ct}$ values decrease with increasing NPs loading. However, when the charge transfer time constant ($\tau$) values were calculated by multiplying the $R_{ct}$ values by the corresponding $C_{dl}$ values [3], it is observed (as shown in Fig. 4c and 4d) that the trend of $\tau$ exhibits a minimum. This indicates that the charge transfer mechanism is dominated by capacitive effects [41], which slow down the reduction process at high loadings. The minimum $\tau$ value is found to be at a loading of 0.5–1.0 mg cm$^{-2}$ for Cu25 electrodes, implying that these electrodes have faster faradaic processes. For Cu50 electrodes, the $\tau$ value increases with increasing catalyst loading, except for the lowest loading of 0.25 mg cm$^{-2}$.

3.3. CO$_2$RR tests and product distribution on various Cu electrodes

The activity of the Cu electrodes was compared through CO$_2$ electrolysis performed at constant cathodic current densities of 200 and 267 mA cm$^{-2}$ in a 1.0 M KOH electrolyte. Figures 5a and 5b depict the typical time-potential curves at current densities of 200 mA cm$^{-2}$ and 267 mA cm$^{-2}$ for the Cu25_0.5 electrodes, respectively. All other electrodes exhibit similar curves, with potentials that are comparably negative as the current density increases. Figures 5c and 5d present the distribution of gas products as a function of time at current densities of 200 and 267 mA cm$^{-2}$, respectively. CO$_2$RR, while HER is found to dominate and increase over time.

The selectivity of different Cu25 electrodes in a 1.0 M KOH at current densities of 200 and 267 mA cm$^{-2}$, taking into account both gas and liquid products, is presented in Figs. 5a and 5b, respectively, and the detailed data are listed in Table S1. At both current densities, the selectivity for C$_2$H$_4$ rises as the catalyst loading increases from 0.25 to 1.0 mg cm$^{-2}$ and then decreases as the loading increases further, which is in contrast to the trend of H$_2$ production. The selectivity of CO increases with increasing Cu loading, becoming the dominant product at

![Fig. 2. Determination of $C_{dl}$ in Ar-purged 1.0 M KOH: (a) representing voltammograms on Cu25_1.0 electrode; (b) current density as function of scan rate.](image-url)
higher loadings (≥ 2.0 mg cm⁻²). On the other hand, CH₄ is prominently formed at the lowest loading and quickly decreases with increasing Cu loading. To comprehend the changes in selectivity, the equivalent geometric (bulk) CO generation and dimerization rates are calculated and normalized (local) by the ECSA at various current densities. The equivalent bulk CO generation and dimerization rates on all Cu25 electrodes at 200 and 267 mA cm⁻² are presented in Fig. 5c and 5d, respectively. At both current densities, a notable increase in the CO generation rate can be observed as the Cu loading increases from 0.25 to 1.0 mg cm⁻², followed by a quasi-plateau. The CO dimerization rate is also observed to increase with the increase in the CO generation rate at relatively low loadings (≤ 1.0 mg cm⁻²), which is reasonable given that a higher CO concentration promotes CO dimerization [42, 43]. At higher loadings, the CO dimerization rate decreases, even though the CO generation rate does not show any decrease. Most of the formed CO tends to release rather than undergo further dimerization. To shed light on the local CO concentration on the active sites, the CO generation and dimerization rates were normalized by the ECSA value for each Cu25 electrode, as shown in Fig. 5e and 5f for current densities of 200 and 267 mA cm⁻², respectively. The local CO generation rate at the active sites is relatively lower at high loadings (> 1.0 mg cm⁻²), which may explain the decrease in the CO dimerization rate and the increase in CO release. It is noteworthy that the highest CH₄ selectivity is observed at the lowest catalyst loading, which could be due to the high dispersion of Cu NPs on the carbon black layer of the GDL. This results in more distanced active sites, suppressing CO dimerization and promoting its hydrogenation, representing a new approach for improving CH₄ selectivity and differing from the methods described in previous studies. According to a study by Xu et al. [24], a low coordination Cu catalyst, which was created by distributing Cu clusters on a GDL, resulted in CH₄ formation even with high pH electrolytes. Bai et al. [19] synthesized two copper catalysts with well-controlled and distinct surface structures that showed unique adsorption configurations of CO intermediates. On low coordination Cu⁰ sites, bridge-adsorbed CO intermediates are more likely to be hydrogenated and reduced to CH₄, while on local Cu⁰/Cu⁺ sites, bridge-adsorbed and linear-adsorbed CO molecules coexist and tend to form C₂H₄. Zhang et al. [21] showed that the selectivity between CH₄ and C₂H₄ can be controlled by adjusting the composition of Cu surface species on gas-diffusion electrodes. A higher Cu⁺⁺/Cu⁰ ratio leads to better selectivity for CH₄ (65.4%) through the hydrogenation of *CO, while a low Cu⁺⁺/Cu⁰ ratio results in higher selectivity for C₂H₄ (80.1%) through C–C coupling. The selectivity for C₂H₄ increases and the selectivity for CH₄ decreases as the proportion of Cu oxide species decreases. Zhou et al. [44] stabilized cationic Cu ions in a CeO₂ matrix, which significantly increased the selectivity for CH₄ by improving the adsorption stability of *CO intermediates. In this study, the observed loading-dependent selectivity provides an easy way to prepare electrodes for producing specific products. To maximize CH₄ formation, a more advanced method such as ultrasonic spray coating should be used to create homogeneous electrodes with very low Cu NP loading.

The Cu50 electrodes display a higher selectivity for C₂H₄ compared to Cu25 electrodes when the catalyst loading is less than 1.0 mg cm⁻² (Fig. 6a and 6b, Table S2), with a much lower selectivity for CH₄ at 0.25 mg cm⁻². Higher CH₄ selectivity was obtained at lower loadings than
0.25 mg cm$^{-2}$ (data not shown). Low FE values are maintained for all loadings in the HER process, and the CO selectivity consistently increases as the catalyst loading increases at both current densities. With respect to the Cu25 NPs electrodes, the trend of selectivity change with loading remains the same for the Cu50 NPs ones, despite the significant differences in their behaviors. Fig. 6c and 6d depict the equivalent CO generation and dimerization rates on different Cu50 electrodes at 200 and 267 mA cm$^{-2}$, respectively. At both current densities, the CO generation rate steadily increases as the Cu loading increases from 0.25 to 3.0 mg cm$^{-2}$, while the CO dimerization rate shows an opposite trend. The CO generation and dimerization rates are normalized by the ECSA value of each Cu50 electrode in Fig. 6e and 6f at 200 and 267 mA cm$^{-2}$ to understand the CO concentration at the active sites. It is observed that the local CO generation at the active sites decreases at high loadings, leading to a corresponding decrease in the CO dimerization rate.

Additionally, it’s worth mentioning that, for Cu25 electrodes, the trend of the local CO dimerization rate is in line with the charge transfer time constant that was discussed earlier in Fig. 3. In other words, the larger the local dimerization rate, the shorter the time constant. This holds true for Cu50 electrodes as well, except for the smallest loading of 0.25 mg cm$^{-2}$. This correlation supports the idea that the slower flow of charges from the electrode decelerates the further reduction of CO near the catalytic sites, hindering the formation of C$_2$ products. A comprehensive examination was carried out on the Cu25_1.0 electrodes in a two-electrode configuration across a range of current densities from 150 to 1200 mA cm$^{-2}$. Fig. 7a displays the product distribution at all current densities, and Table S3 lists the detailed data. The CO selectivity decreases as the current density increases, while CH$_3$CH$_2$OH production generally increases with an increase in current density and reaches 19% at 1200 mA cm$^{-2}$. FE$_{\text{C}_2\text{H}_4}$ attains desirable values (> 35%) at current densities above 300 mA cm$^{-2}$, with a peak of 46% when a current density of 600 mA cm$^{-2}$ is used. At all the studied current densities, the selectivity for CH$_3$COO$^-$, HCOO$^-$, and CH$_4$ remains low (< 5%), and FE$_{\text{H}_2}$ remains below 20%. It’s worth noting that the selectivity for C$_2$ products improves with increasing current density (Fig. 7b), resulting in an increase in the C$_2$/C$_1$ product ratio.

The selectivity for C$_2$ products is nearly 60% at high current densities of 800–1200 mA cm$^{-2}$, at relatively low cell voltages less than 4.0 V, as shown in Fig. 7d. As seen in Fig. 7c, there is a significant correlation between the current density and the CO generation rate, as well as the
CO dimerization rate. A higher current density leads to a faster generation of CO and, as a result, a higher local concentration of CO, which results in a higher dimerization rate and $C_2$ selectivity. The cell voltage increases with an increase in the current density, as a result of a higher overpotential for both anodic and cathodic reactions, as well as a larger ohmic voltage drop, as shown in Fig. 7d. It is worth noting that the cell voltages are relatively lower compared to those reported in the literature for similar current densities and selectivity [37], indicating that the
Cu\textsubscript{25.1.0} electrodes can produce C\textsubscript{2} products with a relatively higher energy efficiency (EE). The values of EE are calculated through Eq. (2) and reported in Figure S9. It is noticed that the EE for C\textsubscript{2} products in the two-electrode configuration is around 15–20\% at current densities higher than 200 mA cm\textsuperscript{-2}, which is much higher than the 10\% reported in simile work at comparable current densities [37] and especially at high current densities > 500 mA cm\textsuperscript{-2} [45].

A stability study has been performed on the Cu\textsubscript{25.1.0} electrodes at

![Graph showing selectivity, equivalent bulk CO generation and dimerization rates, and ECSA-normalized equivalent CO generation and dimerization rates for Cu\textsubscript{25.1.0} electrodes at different loadings.](image-url)
The potential is almost constant, while the selectivity is not stable at each current density, and a higher current density leads to a lower stability in the product distribution. The performance is characterized by a changeover in the selectivity from the CO\textsubscript{2} RR to the HER, indicating that the stability issue is more related to the flooding of the electrode. In the literature, it is widely reported that the flooding of the GDL electrodes is typically observed in the first several hours of electrolysis, resulting in a significant decline in the selectivity for CO\textsubscript{2} RR products [46,47]. When the GDL electrode is flooded, the liquid electrolyte fulfilled a part of the initially hydrophobic pores, not only compromising CO\textsubscript{2} diffusion to active sites on the catalyst surface, but also causing salt precipitation and further choking the pore irreversibly. Recently, the durability has emerged as one of the critical issues to be resolved before further commercialization of CO\textsubscript{2} conversion and it attracts much attention. Leonard et al. [48] reported that the flooding phenomenon could be associated with the total charge passed through the electrodes. A longer electrolysis and a higher current density can cause more severe flooding, due to more OH\textsuperscript{-}/CO\textsubscript{2} interaction. However, Jouny et al. [49] also observed GDL electrode flooding for CO reduction reaction using KOH as electrolyte where no OH\textsuperscript{-}/CO\textsubscript{2} interaction exists. In this case, the flooding is considered to be related to the condensation of water vapor. Yang et al. [50] sustained that the applied potential plays a critical role in the flooding advent of GDL electrodes. CO\textsubscript{2}RR usually requires high overpotentials, which induce HER on the GDL carbon support and impact the wetting properties of the originally hydrophobic GDL. From this point of view, the operating of CO\textsubscript{2} electrolysis in a low overpotential range, enabled by implementation of high-performance catalytic materials, could improve the stability of CO\textsubscript{2}RR.

4. Conclusion

In this work, two families of electrodes fabricated from Cu NPs of different sizes (25 and 50 nm) and characterized by various loadings (between 0.25 and 3.0 mg cm\textsuperscript{-2}) were tested as CO\textsubscript{2} RR catalysts. Both classes of electrodes show a variation in selectivity as the loading changes. CH\textsubscript{4} is found to be the main reduction product at very low loadings, while CO is prevalent at higher loadings. For intermediate values (0.5 to 1.0 mg cm\textsuperscript{-2}), the highest selectivity toward C\textsubscript{2}H\textsubscript{4} is observed. This behavior can be explained by considering that for very low loadings, the presence of small density NPs, with relatively large distance between active sites, makes the dimerization of CO less likely, favoring instead its hydrogenation toward CH\textsubscript{4} production. By increasing the loading, the higher rate of bulk CO generation makes the dimerization more likely, thus increasing the C\textsubscript{2}H\textsubscript{4} production. However, EIS analysis reveals that with further increase in NP loading, the influence of capacitance becomes dominant, thus slowing down the flow of charges from the electrode. This limits the further reduction of CO produced near the active sites, thus making it the main product at higher loadings. Cu25\textsubscript{1.0} electrodes were further tested at different current densities up to 1200 mA cm\textsuperscript{-2} in order to maximize the C\textsubscript{2}H\textsubscript{4} production.
production. $F_{\text{C2H4}}$ values higher than 35% are obtained over the studied current density range, with a maximum of 46% at 600 mA cm$^{-2}$.

Both CO generation and dimerization rates raise with increasing current, so that the selectivity toward C$_2$ products shows the same trend. This result, together with the relatively low cell voltage ($<4.0$ V), reveals that the Cu$_{25}$ electrodes are capable of producing C$_2$ molecules with good energy efficiency.

CRediT authorship contribution statement

Juqin Zeng: Conceptualization, Methodology, Validation, Visualization, Supervision, Investigation, Writing – original draft, Writing – review & editing. Manlio Mignosa: Investigation, Data curation, Validation, Writing – review & editing. Nicolò B.D. Monti: Investigation, Writing – review & editing. Adriano Sacco: Visualization, Supervision, Methodology, Writing – review & editing. Candido F. Pirri: Resources, Project administration, Visualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Supplementary materials


References


Fig. 8. Long-term CO$_2$RR on Cu$_{25}$ electrodes: 300 mA cm$^{-2}$ (a) voltage as a function of time and (b) product distribution as a function of time; 600 mA cm$^{-2}$ (c) voltage as a function of time and (d) product distribution as a function of time.