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Production of methanol from CO₂ electroreduction at Cu₂O and Cu₂O/ZnO-based electrodes in aqueous solution

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Abstract

In this study, we examine the performance of Cu₂O and Cu₂O/ZnO surfaces in a filter-press electrochemical cell for the continuous electroreduction of CO₂ into methanol. The electrodes are prepared by airbrushing the metal particles onto a porous carbon paper and then are electrochemically characterized by cyclic voltammetry analyses. Particular emphasis is placed on evaluating and comparing the methanol production and Faradaic efficiencies at different loadings of Cu₂O particles (0.5, 1 and 1.8 mg·cm⁻²), Cu₂O/ZnO weight ratios (1:0.5, 1:1 and 1:2) and electrolyte flow rates (1, 2 and 3 ml·min⁻¹·cm⁻²). The electrodes including ZnO in their catalytic surface were stable after 5 hours, in contrast with Cu₂O-deposited carbon papers that present strong deactivation with time. The maximum methanol formation rate and Faradaic efficiency for Cu₂O/ZnO (1:1)-based electrodes at an applied potential of -1.3 V vs. Ag/AgCl were $r = 3.17 \times 10^{-5} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $FE = 17.7 \%$, respectively. Consequently, the use of Cu₂O-ZnO mixtures may be of application for the continuous electrochemical formation of methanol, although further research is still required in order to develop highly active, selective and stable catalysts for CO₂ electroreduction to methanol.

Keywords: CO₂ valorisation, electrochemical reduction, methanol, Cu₂O/ZnO-based electrodes, stability.

- **Introduction**

The large scale consumption of fossil fuels for the production of energy has raised CO₂ levels up to 400 mg·L⁻¹ over the last century. These high atmospheric CO₂ concentrations are linked to severe environmental problems, such as the undesirable effects of global warming. Therefore, decreasing the atmospheric CO₂ concentration has become a critical issue for a sustainable development and various governments worldwide have signaled their concern by increasing their investment in research to address this issue.

There are different approaches to mitigate CO₂ emissions from the use of fossil fuels, including its capture and subsequent storage [1-3] or its conversion into valuable chemicals [4-6]. In view of the vastness of CO₂ supplied in the atmosphere, this gas can be considered as a potential source of C1 feedstock for the production of chemicals and fuels. However, and due to its thermodynamic stability and its relative kinetic inertness, a preliminary activation is required. At this regards, the use of electrochemical methods for the conversion and reduction of CO₂ appears as an interesting strategy [7-9]. In addition, this technology coupled to a renewable energy source, such as wind or solar, could generate carbon neutral fuels or industrial chemicals that are conventionally derived from petroleum.

The electrochemical route of CO₂ reduction is known to produce a variety of useful products, which mainly depend on the catalyst materials, and the reaction medium employed [10]. The major reduction products are carbon monoxide (CO), formic acid (HCOOH), formaldehyde (CH₂O), methanol (CH₃OH), oxalic acid (H₂C₂O₄), methane (CH₄), ethylene (CH₂CH₂) or ethanol (CH₃CH₂OH) [9-11]. Among these possible reduction products, CH₃OH, with relatively high energy density and stable storage properties, is regarded as a feasible approach and recent progress has been made in developing new solutions to enhance its yield and efficiency in the electrochemical reduction of CO₂ [7, 12]. Besides, CH₃OH can be used as a feedstock for the production of liquid fuels such as dimethyl ether (DME), synthetic gasoline and several organic compounds [13]. Although CH₃OH is effectively produced in hydrogenation reactions using syngas and CO₂ feeds (400–800 K, 2–12 MPa) [14], the aqueous electrochemical process operates at room temperature and offers a convenient method

to store electrical energy without increasing CO₂ emissions.

Since the transformation of CO₂ to CH₃OH requires six electrons, the reduction reaction is considered to be kinetically slow; hence, new and more active and selective catalytic materials are required in order to make this conversion route of technical interest with minimal energy input. Unfortunately, among the many electrocatalytic materials previously investigated for CO₂ reduction, none of them are both efficient and selective, and the most common products are CO and HCOOH, which are not as readily used as fuels as hydrocarbons or alcohols are [10]. Among the studied materials, copper (Cu), molybdenum (Mo) and ruthenium (Ru), as well as their mixtures and oxidized forms [11, 15-30], have been reported to be the most active materials for the electrochemical transformation of CO₂ to CH₃OH. Cu is the only known material capable of producing mixtures of chemicals potentially interesting for industrial applications at high reaction rates over sustainable periods of time [31-34]. Particularly, Cu oxide surfaces (i.e. Cu₂O) present both intermediate hydrogen overpotentials and CO adsorption properties, which allows higher CH₃OH yields in aqueous solutions to be produced [15-17, 21, 22, 35]. For example, Chang et al. [35] deposited Cu₂O particles onto a carbon cloth electrode and carried out cyclic voltammetry measurements for CO₂ reduction. The results demonstrated the notable catalytic ability of the Cu₂O-catalyzed carbon clothes for electrochemical CH₃OH formation. Besides, current density was slightly decreased initially and then, stabilized at -4.32 mA·cm⁻² for an overall experimental time of 4 hours. Lately, Le et al. [17] reported CH₃OH production rates as high as 11.9 x 10⁻⁵ mol·m⁻²·s⁻¹ and Faradaic efficiencies up to 38 % in 0.5 M KHCO₃ at electrodeposited cuprous thin films electrodes for an applied potential of -1.45 V vs. Ag/AgCl (10 min. reaction). They suggested that the production of CH₃OH may be associated with the presence of Cu(I) species. However formation rates tend to diminish at longer reaction times (>30 min) and are accompanied with CH₄ generation, due to the partial reduction of the oxide electrodes.

In this work, electrodes based on Cu₂O with different loadings (0.5, 1 and 1.8 mg·cm⁻²) and Cu₂O-ZnO mixtures with different weight ratios (1:0.5, 1:1 and 1:2) were evaluated towards CO₂ electroreduction to CH₃OH. The main objectives of the present study were as follows:

- to electrochemically characterize, by cyclic voltammetry measurements, the so prepared Cu₂O and Cu₂O/ZnO-based electrodes;
- to evaluate the performance of a filter-press electrochemical cell for the continuous electroreduction of CO₂ to CH₃OH at the Cu-based cathodes;
- to analyse the effect of the Cu₂O catalytic loading and the Cu₂O/ZnO weight ratio in the catalytic surface, as well as the electrolyte flow rate (1, 2 and 3 ml·min⁻¹·cm⁻²) on the electrochemical formation of CH₃OH; and finally,
- to evaluate the stability of the developed electrodes at longer reaction times.

As previously state, the technological key challenge necessary to develop a CO₂ electroreduction industrial plant for CH₃OH formation seems to be the development of more active and selective electrocatalysts able to reduce CO₂ molecule to CH₃OH at low overpotentials, at high current densities and without the formation of unwanted by-products. These results are a step forward in the way of study CO₂ valorisation processes and devices in continuous operation.

- **Materials and methods**

- *Preparation and characterization of the electrodes*

Cu₂O based electrodes (area, A= 10 cm²) were manufactured by airbrushing a catalytic ink onto a porous carbon paper type TGP-H60 (Toray Inc.). This catalytic ink was formed by a mixture of Cu₂O particles (Sigma Aldrich, particle size < 5 μm, 97% purity) as electrocatalyst, Nafion[®] dispersion 5 wt.% (Alfa Aesar) as binder and isopropanol (IPA) (Sigma Aldrich) as vehicle, with a 70/30 catalyst/Nafion mass ratio and a 3% solids (catalyst + Nafion) percentage; this mixture was sonicated for 15 minutes. The Cu₂O electrodes with different catalytic loadings, *L*, were prepared by simple accumulation of layers and complete IPA evaporation. This last fact was verified by constant weight after each catalytic loading. Cu₂O-ZnO (< 45 μm, 99.5% purity, ACROS organic)-based electrodes were similarly prepared. The composition of the Cu₂O-ZnO mixtures together with the material loading is presented in Table 1. All electrodes were dried at ambient conditions for 24 hours and rinsed with deionised water before use. A scanning electron microscope (SEM, HITACHI S-3000N) was

used to characterise the different electrodes.

Table 1. Composition and metal loading of the prepared Cu₂O-ZnO electrodes

Electrode	Cu ₂ O : ZnO weight ratio	Catalytic loading, <i>L</i> (mg·cm ⁻²)
Cu ₂ O (0.5)	1 : 0	0.5
Cu ₂ O (1)	1 : 0	1
Cu ₂ O (1.8)	1 : 0	1.8
Cu ₂ O/ZnO (1:0.5)	1 : 0.5	1.5
Cu ₂ O/ZnO (1:1)	1 : 1	2.0
Cu ₂ O/ZnO (1:2)	1 : 2	3.0

- *Electrochemical cell and experimental conditions*

The electrochemical behaviour of the electrodes was evaluated using cyclic voltammetry at a scan rate of 50 mV·s⁻¹. A CO₂ saturated 0.5 M KHCO₃ (Panreac) aqueous solution was used as electrolyte in a standard three-electrode electrochemical cell equipped with a glassy carbon as the counter electrode and a Ag/AgCl (sat. KCl) as reference electrode. Portions (about 1 cm² geometric area) of the prepared electrodes were cut and used as working electrodes. An AutoLab PGSTAT 302N potentiostat (Metrohm, Autolab B.V.) was used in all the electrochemical experiments. The potentials ranged from 0 to -1.8 V vs. Ag/AgCl.

The continuous electrochemical reduction of CO₂ to CH₃OH production was carried out using a filter-press electrochemical cell (Micro Flow Cell, ElectroCell A/S) at ambient conditions. A Nafion 117 cation exchange membrane was used to separate the cathode and anode compartments. A platinised titanium electrode was used as the anode and an Ag/AgCl (sat. KCl), assembled close to the cathode, was used as reference electrode. The prepared Cu₂O and Cu₂O/ZnO-catalyzed carbon papers were employed as the working electrodes. The experimental setup has been described in detail previously [4-6].

A 0.5 M KHCO₃ aqueous solution is used as both, catholyte and anolyte. Prior to the experiments, the aqueous electrolyte was saturated with CO₂ by bubbling for 20 minutes (25 °C, pH= 7.6). Then, CO₂ was bubbled continuously in the catholyte side

during the experimental time. The electrolytes were pumped to the cell by two peristaltic pumps (Watson Marlow 320, Watson Marlow Pumps Group). All the experiments were performed at potentiostatic conditions (i.e. at a constant voltage of -1.3 V vs. Ag/AgCl). The experimental time was 90 minutes. Liquid samples (10 ml) were taken every 15 minutes from the catholyte tank placed at the outlet of the electrochemical cell. The CH₃OH formation in each sample was analysed by duplicate in a headspace gas chromatograph (GCMS-QP2010 Ultra Shimadzu) equipped with a Flame Ionization Detector (FID). Compounds were separated on a DB-Wax 30 m x 0.25 mm x 0.25 μ m column, with an injection and detector temperature of 250 °C and 270 °C, respectively. Helium was used as a carrier gas at a flow rate of 50 ml·min⁻¹. An average concentration was obtained for each point from the performance of three replicates with an experimental error less than 16.4 %.

The performance of the process is evaluated by the rate of CH₃OH production, r (i.e. CH₃OH obtained per unit of cathode area and time), and the Faradaic efficiency, FE (i.e. selectivity of the reaction for the production of CH₃OH). FE is calculated assuming that six electrons are required per molecule of CH₃OH according to the following equation:

$$(1)$$

where z is the theoretical number of e⁻ exchanged to form the desired product, n is the number of moles produced, F is the Faraday constant ($F= 96,485 \text{ C}\cdot\text{mol}^{-1}$) and q is the total charge applied in the process.

- **Results and discussion**

- *SEM characterization of the electrodes*

Figure 1a and 1b show the SEM images for Cu₂O (1) and Cu₂O/ZnO (1:1)-supported carbon papers, respectively. As can be seen from the figures, the Cu₂O crystals show a tetragonal bipyramid morphology and a particle size of about 4 μ m, which is higher than those particles sizes reported for air-oxidized (particle size: ~1 μ m) and electrodeposited cuprous oxide-based electrodes (~2 μ m) [17].

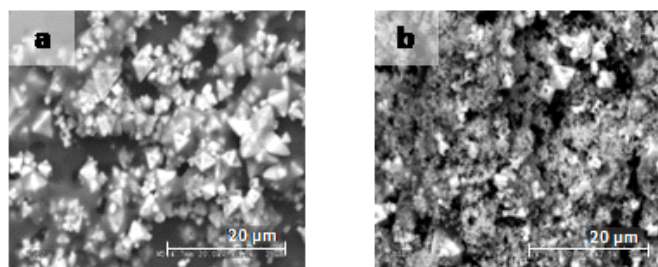


Figure 1. SEM micrographs of (a) Cu_2O (1) and (b) $\text{Cu}_2\text{O}/\text{ZnO}$ (1:1)-based electrodes

For a comparative analysis, representative SEM images of Cu_2O -supported carbon papers at different loadings (0.5, 1 and $1.8 \text{ mg}\cdot\text{cm}^{-2}$) and $\text{Cu}_2\text{O}/\text{ZnO}$ -based electrodes at different weight ratios (1:0.5, 1:1 and 1:2) are presented in Figure 2.

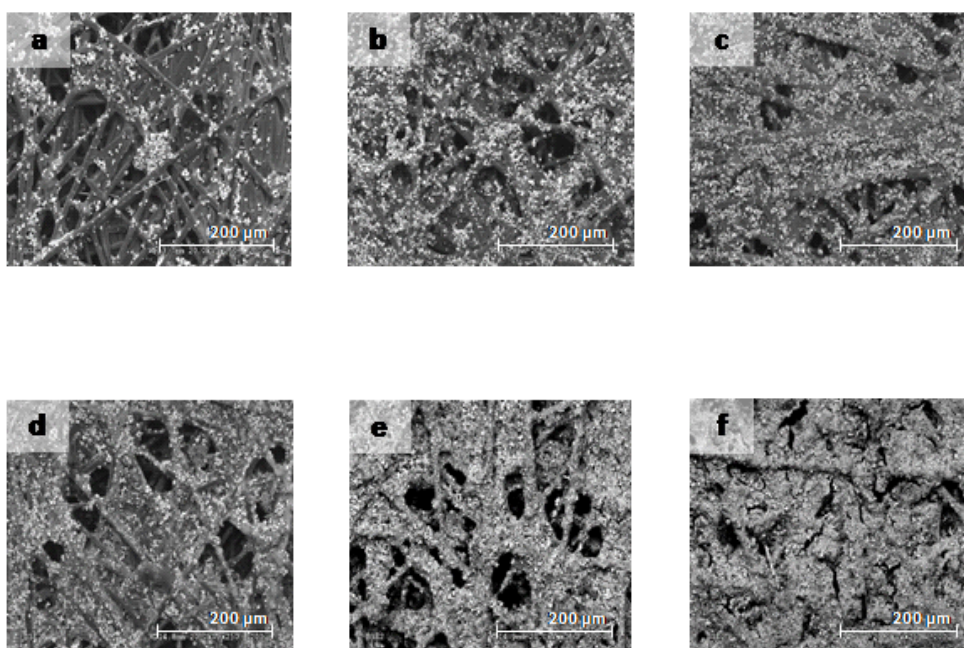


Figure 2. SEM images of Cu_2O -based electrode surfaces with (a) 0.5, (b) 1 and (c) $1.8 \text{ mg}\cdot\text{cm}^{-2}$ catalytic loading deposited on carbon supports and $\text{Cu}_2\text{O}/\text{ZnO}$ -based electrode surfaces with (d) 1:0.5; (e) 1:1 and (f) 1:2 weight ratios

As observed, airbrushing the Cu_2O or $\text{Cu}_2\text{O}/\text{ZnO}$ inks rendered a relatively uniform coverage of the Toray fibers. It can be inferred that the dispersion of the particles by air-brushing minimizes the agglomeration of the catalyst in the carbon support [36] and

thus the electrodes are expected to present an improved catalytic response because of the high surface to volume ratio, although other factor such as size, shape, nature and bulk/surface composition of the particles may greatly affect the electrode performance [21, 35, 37]. However, it is worth noting that for higher loadings an evident decrease of porosity in the substrate is observed and a massive and compact layer is formed.

- *Cyclic voltammetric characterization*

To examine the electrochemical behaviour of the prepared materials, Figure 3 and 4 show the cyclic voltammetric responses of the different electrodes in CO₂-saturated 0.5 M KHCO₃ aqueous solution after 5 scans, and where current densities, j , were normalized to the geometric area of the electrodes. Besides, Figure 5a and b show, respectively, the current-potential curve for Cu₂O (1) and Cu₂O/ZnO (1:1) electrodes with and without CO₂ (in Ar saturated solution).

Figure 3a reports the voltammetric profiles obtained for the Cu₂O-based electrodes at different loadings (0.5, 1 and 1.8 mg·cm⁻²). An oxidation-reduction contribution is observed between -0.2 and 0 V, which depends on the catalytic loading. However, the main characteristic of the voltammograms is a reduction process, starting at around -0.8 V vs. Ag/AgCl, which may be associated with the reduction of CO₂ molecule on the catalyst surface if we compare the current potential-curve in the absence or the presence of CO₂ (Figure 5a and b), where the partial formation/decomposition of the oxides on the electrode surface may also occur. However, at more negative potentials than -1.2 V the reduction response can be mainly attributed to CO₂ reduction, as observed in Figure 5a and b.

Very remarkable changes are observed when ZnO is incorporated into the electrodes (Figure 3b), which denotes the synergic effect of Cu₂O and ZnO in the reduction response. Figure 4a and 4b shows the characteristic voltammetric responses of the different Cu₂O/ZnO based electrodes at different weight ratios. The responses are compared to an electrode prepared by airbrushing ZnO (1 mg·cm⁻²) and Cu₂O/ZnO-based electrodes at different loadings of Cu₂O (0.1, 0.5 and 1 mg·cm⁻²). Again, the results obtained suggest that the presence of ZnO results beneficial in the reduction response. Furthermore, an oxidative peak appears at around -1.0 V in the reverse scan, which may be tentatively assigned to the transition of remaining Zn to ZnO. However,

the peak remains after the fifth scan, and so it could be related to the formation of oxidized subproducts in the CO_2 reduction reaction.

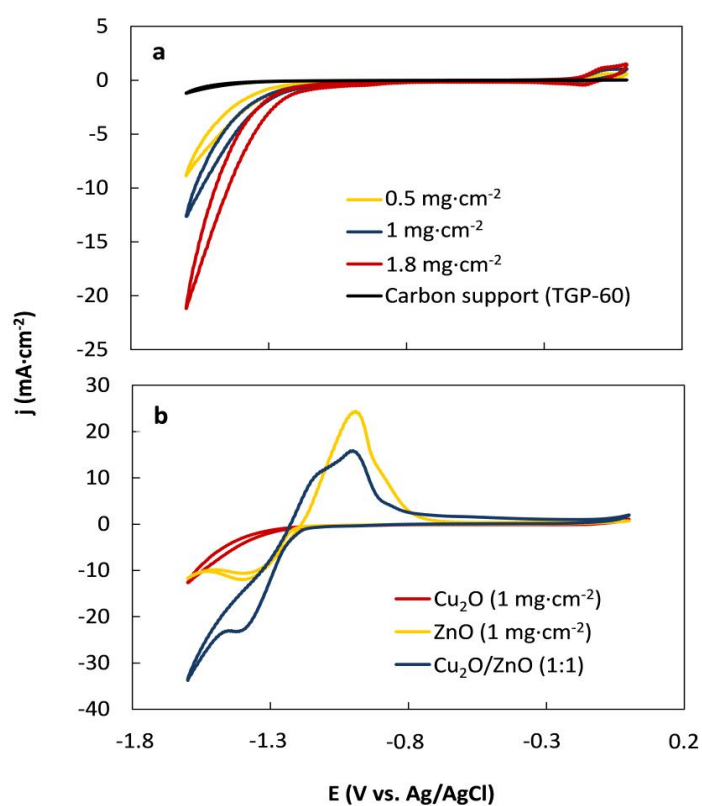


Figure 3. Cyclic voltammetric responses for (a) Cu₂O-based electrodes (at different loadings) and; (b) Cu₂O (1), ZnO (1) and Cu₂O/ZnO (1:1)-based electrodes in the CO₂ saturated 0.5 M KHCO₃ solution

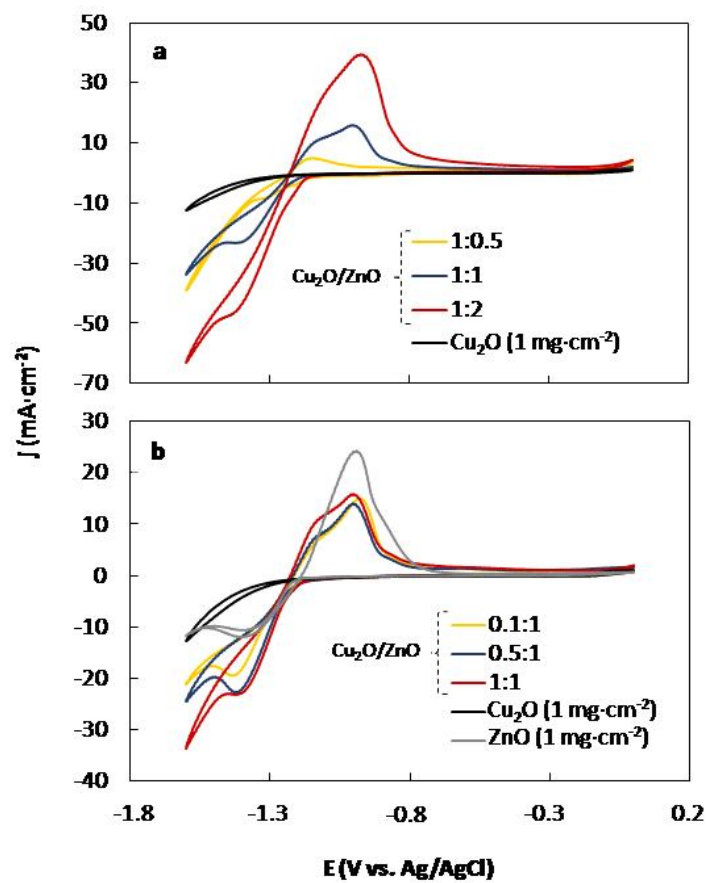


Figure 4. Cyclic voltammetric responses for Cu₂O/ZnO-based electrodes for (a) Cu₂O (1)/ZnO (different loadings) and; (b) Cu₂O (at different loadings)/ZnO (1) in the CO₂ saturated 0.5 M KHCO₃ solution

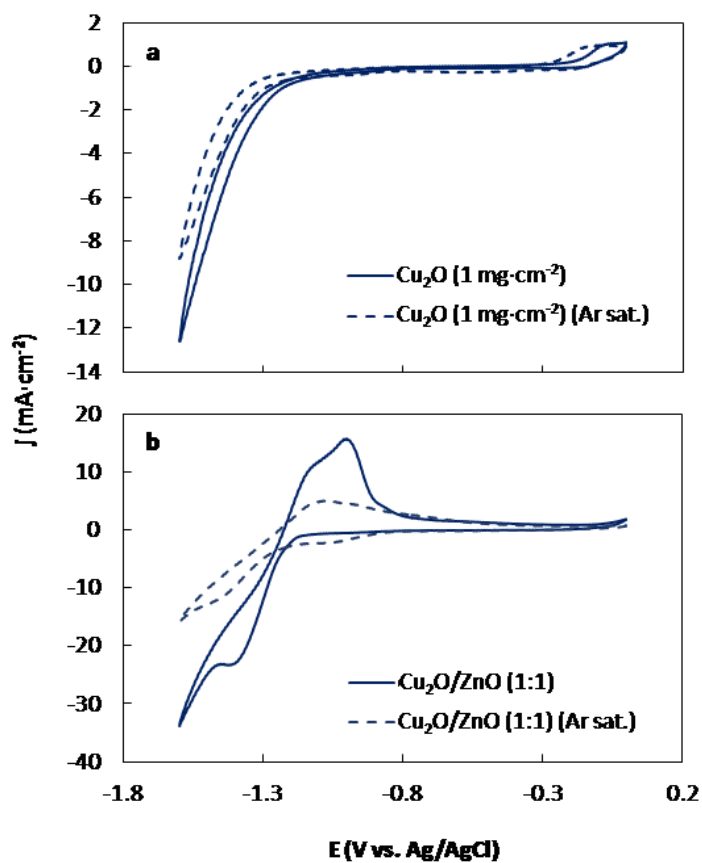


Figure 5. Cyclic voltammetric responses for (a) Cu_2O (1) and (b) $\text{Cu}_2\text{O}/\text{ZnO}$ (1:1)-based electrode in a CO_2 (—) and Ar (---) saturated 0.5 M KHCO_3 solution

- *Filter-press electrochemical performance*

Figure 6 shows an example for the time evolution of the current density, j , and Faradaic efficiency, FE , for the CO_2 electroreduction to CH_3OH at Cu_2O (1) electrode in the filter-press electrochemical reactor at ambient conditions.

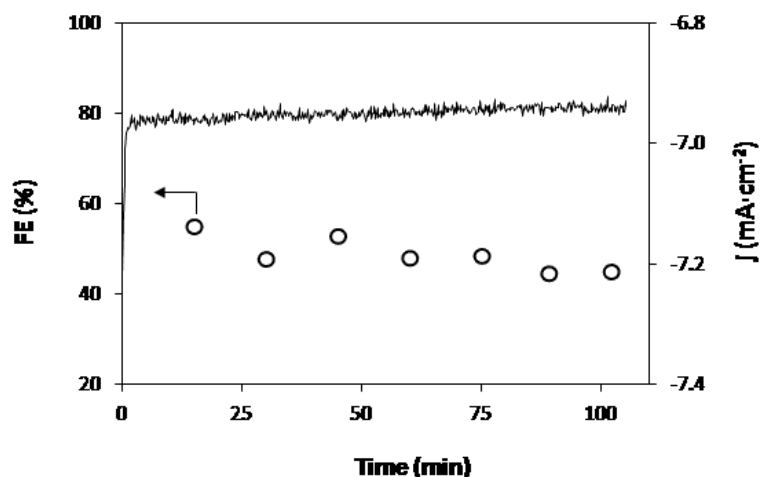


Figure 6. Time evolution of the current density, j (-) and Faradaic efficiency, FE (○) for CH_3OH formation at -1.3 V vs. Ag/AgCl

As shown in Figure 6, pseudo-stable values were reached after 25 minutes of operation at -1.3 V vs. Ag/AgCl . The current remains almost stable over the course of the 90 minutes of operation, indicating only little deactivation of the electrode. The fluctuations in current density can be explained as bubbles begin to form on the electrode surface at -1.3 V vs. Ag/AgCl applied potential. Preliminary experiments showed that, for more negative cathode potentials than -1.3 V vs. Ag/AgCl , a clear formation of bubbles was observed, due to the production of hydrogen. The formation of hydrogen not only competes with the CO_2 electroreduction to form CH_3OH , but also affects the electrode stability because of the detachment of the metal particles from the cathode surface during the hydrogen gas evolution. In this sense, a recent study demonstrated that the Faradaic efficiency of the reaction to CH_3OH decreased from 2.5% to 1% when the cathode potentials was shifted from -1.35 V to -1.75 V vs. Ag/AgCl , respectively, at Cu-based electrodes [22], in good agreement with previous findings with oxidized Cu surfaces [14, 16]. Consequently, according to the maximum reduction responses from the cyclic voltammetries, before a massive formation of bubbles was observed, a constant potential of -1.3 V vs. Ag/AgCl was applied in the

all tests carried out in this study.

The obtained values for the rate of CH₃OH formation, r , and Faradaic efficiency, FE , for Cu₂O-based electrodes with different metal loadings are summarized in Table 2. Besides, for a proper interpretation of the electrocatalytic activity of the different materials, r is initially normalized by the total charge, in coulombs (C), passed to the system, q (r^q) and then by the total mass of the catalyst in mg, m (r_m^q). The results are compared to those obtained in a filter-press electrochemical cell equipped with a Cu plate at -1.3 and -1.5 V vs. Ag/AgCl applied potentials.

Table 2. Rate of CH₃OH production and Faradaic efficiency for Cu₂O-based electrodes at different loadings in comparison to a Cu plate. $E = -1.3$ V vs. Ag/AgCl. Electrolyte flow/area ratio (Q/A) = 2 ml·min⁻¹·cm⁻²

Electrode (loading)	Curr. dens. j (mA·cm ⁻²)	Charg e q (C)	CH ₃ OH conc. (mg·L ⁻¹)	Rate, r (10 ⁻⁵ mol·m ⁻² ·s ⁻¹)	Normalized rate x 10 ⁸		FE (%)
					r^q (r·C ⁻¹)	r_m^q (r ^q ·mg ⁻¹)	
Cu ₂ O (0.5)	1.35	72.9	0.53	0.54	7.41	1.48	24.5
Cu ₂ O (1)	6.93	374.2	5.85	6.08	16.25	1.62	45.7
Cu ₂ O (1.8)	8.23	444.4	6.19	6.44	14.50	0.81	42.7
Cu plate	10.83	584.8	0.73	0.87	1.49	-	4.6
	16.56 ^a	894.2	0.92	2.30	2.57	-	3.6

^a Experiment performed at $E = -1.5$ V vs Ag/AgCl

The results obtained indicate that the Cu₂O electrode containing 1 mg·cm⁻² shows the highest rate of CH₃OH formation, both normalized to the total charge applied to the system (r^q), as well as to the total catalyst mass deposited in the electrode (r_m^q). In addition, this electrode also displays the highest FE (~45%). Interestingly, these values are remarkably higher than those obtained with the Cu plate, independently of the applied potential. This fact is in good agreement with previous findings where surfaces with copper oxides have shown higher activity for the reduction of protons than the Cu (0) sites for CO₂ electroreduction to CH₃OH, as demonstrated by Frese et al. [15] where the electrochemical performance of Cu-based electrodes (i.e Cu foil, Cu foil thermally oxidized in air and air-oxidized Cu electrodeposited on anodized or air-oxidized Ti foil) was compared, or as recently reported by Lan et al. [23], where a larger amount of CH₃OH was obtained for Cu(core)/CuO(shell) catalysts in 1 M KHCO₃ at -1.72 V vs. Ag/AgCl than that amount obtained at a Cu foil.

Among the Cu₂O-based electrodes, Table 2 clearly indicates that when the catalytic loading is increased from 0.5 to 1 mg·cm⁻², a remarkable increase (more than two fold) in the charge normalized rate formation is observed. This improvement is still present when this formation rate is normalized to the total Cu₂O mass deposited although, obviously, is clearly reduced. Therefore, in term of efficiency, the electrode containing 1 mg·cm⁻² is clearly superior to that containing 0.5 mg·cm⁻². Interestingly, when the metal loading is increased to 1.8 mg·cm⁻², both the r^q and FE remain relatively constant, while the r_m^q resulted importantly reduced. This finding may suggest the existence of an important degree of particle agglomeration, which hinders the removal/accessibility of the reactants and products to the available catalytic surface area. Consequently, a Cu₂O loading of 1 mg·cm⁻² seems to be optimal for the reaction under study. It is also worth noting that the highest efficiency obtained in the present work, ($FE= 45.7\%$) outperformed the current best selectivity values reported at electrodes based on Cu₂O particles electrodeposited on stainless steel ($FE= 38\%$) [17] or for Cu₂O particles deposited on carbon papers in a solid polymer electrolyte cell ($FE= 20\%$) [22]. The improvement observed in the present work may be attributed to the promoting effect of Cu(I) species for CO₂ reduction, the electronic structure of the Cu₂O particles, as well as to the effect of the electrochemical cell configuration. Furthermore, previous works found that no liquid phase products other than CH₃OH were formed at copper oxide surfaces with predominantly H₂ and trace amounts of CO in the gas phase [17, 35]. In this work, trace amounts of ethanol were also detected in the liquid phase.

The performance for the Cu₂O/ZnO-based electrodes at different weight ratios (1:0.5, 1:1 and 1:2) is similarly presented in Table 3.

Table 3. Rate of CH₃OH production and Faradaic efficiency for Cu₂O/ZnO-based electrodes at different weight ratios. $E= -1.3$ V vs. Ag/AgCl. $Q/A= 2$ ml·min⁻¹·cm⁻²

Electrode (weight ratio)	Curr. dens. j (mA·cm ⁻²)	Charge q (C)	CH ₃ OH conc. (mg·L ⁻¹)	Rate, r (10 ⁻⁵ mol·m ⁻² ·s ⁻¹)	Normalized rate x 10 ⁸		FE (%)
					r^q (r·C ⁻¹)	r_m^q (r ^q ·mg ⁻¹)	
Cu ₂ O/ZnO (1:0.5)	8.85	477.9	3.73	4.93	10.32	0.69	25.2
Cu ₂ O/ZnO (1:1)	10.64	574.6	3.05	3.17	5.52	0.28	17.7
Cu ₂ O/ZnO (1:2)	27.98	1510.9	1.11	1.15	0.73	0.03	2.3

The results reported in Table 3 show that the formation rate of CH₃OH (r^q and r_m^q), as

well as the *FE* of the reaction, were considerably lower at Cu₂O/ZnO-based electrodes than at those electrodes prepared with Cu₂O particles. The values for efficiency and CH₃OH production suffered a clear decrease when increasing ZnO loading from 0.5 to 1 mg·cm⁻². Further increase in ZnO content led to an almost inactive electrode for the formation of CH₃OH. These results are somehow unexpected if we consider the enhancements for the formation of hydrocarbons (i.e. CH₂CH₂ and CH₄) when mixing Cu₂O with Zn particles to form a particle-press electrodes [37]. In the present work, the lower catalytic activity of Cu₂O/ZnO-based electrodes could be firstly attributed to the partial coverage of Cu₂O particles (~4 μm), which is supposed to be the active material for CH₃OH formation, by the ZnO particles (<45 μm). In a previous work, Zn particles mixed with CuO and Cu₂O powders were pressed for fabricating a disk plate electrode in order to evaluate the characteristic of copper oxide catalysts for the electrochemical reduction of CO₂ [37]. The results demonstrated that without copper oxide, only HCOOH and CO were formed. The same result was previously obtained when using polycrystalline ZnO (sintered powder) in carbonate electrolytes, which showed only CO and HCOO⁻ as products along with the partial reduction of ZnO (Zn formation) at -1.4 V vs. Ag/AgCl [38]. Therefore, the lower efficiencies obtained for CH₃OH in this work as the load of ZnO particles increased probably have more to do with the promoting effect of Zn for the formation of unwanted products, instead of CH₃OH.

- *Influence of electrolyte flow in the electrochemical cell*

In an attempt to improve the CO₂ electroreduction performance of the process, additional experiments were carried out at different electrolyte flow/area ratios (*Q/A*) for the electrodes prepared with Cu₂O particles (1 mg·cm⁻²) onto the carbon support at an applied potential of -1.3 V vs. Ag/AgCl. The results are again compared to those obtained for a Cu plate. Figure 7 shows the comparative results at a *Q/A* of 1, 2 and 3 ml·min⁻¹·cm⁻².

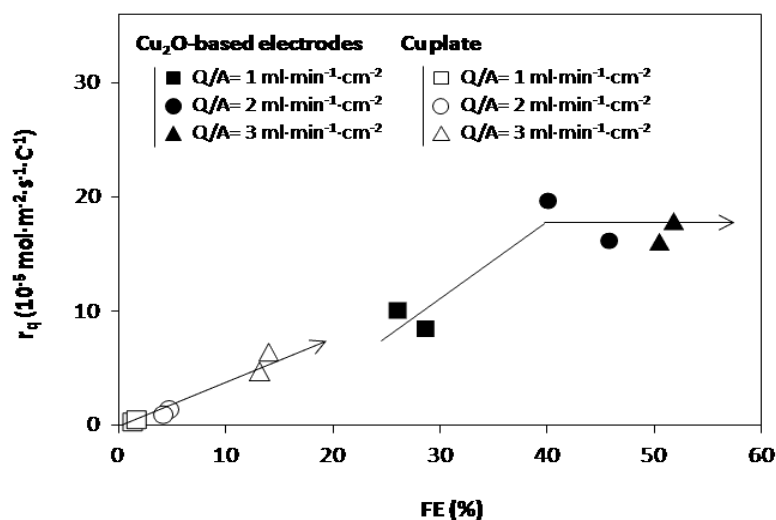


Figure 7. r_d and FE for Cu_2O (1) at different flow/area ratios (Q/A). The results at a Cu plate electrode are included for comparison

In general, the formation of CH_3OH and efficiency of the reduction process can be further enhanced when increasing Q/A , probably because the reaction is limited by the external mass transfer in the system. Interestingly, an increase in Q/A from 2 to 3 $\text{ml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ did not significantly improve the r_d performance, although the FE was slightly enhanced to values around 50%. In any case, the beneficial effect of increasing electrolyte flow led also to a reduction in CH_3OH concentration in the solution (i.e. from 5.85 to 3.87 $\text{mg}\cdot\text{L}^{-1}$) when increasing the Q/A ratio from 2 to 3 $\text{ml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ with Cu_2O -based electrodes. Therefore, using lower Q/A ratios generated a concentrated product, although CH_3OH yield is lower, then an optimal compromise between these two factors must be reached. On the other hand, the performance for CO_2 electroreduction at the Cu plate can be still enhanced at $Q/A=3\text{ ml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$, which means that the process is still limited by the external supply of mass for electroreduction. Probably, further increases in catholyte flow would finally lead to dragging effects that may produce a decrease in process performance [4].

- *Stability of the prepared electrodes*

The stability of the Cu_2O -based electrodes is critical for the industrial application of these materials in the electrochemical conversion of CO_2 to CH_3OH . In general, the

working life of Cu₂O catalysts could be enhanced mainly by two mechanisms: (a) preventing the electrode degradation by keeping homogeneity in the metal particle dispersion with time and, (b) avoiding the poisoning or blocking of the Cu₂O crystallites surfaces. Figure 8a and Figure 8b show the temporal evolution for the charge normalized rate of CH₃OH formation, r^q , and efficiency, FE , in the 0.5 M KHCO₃ electrolyte solution for 5 hours at Cu₂O (1) and Cu₂O/ZnO (1:1) electrodes.

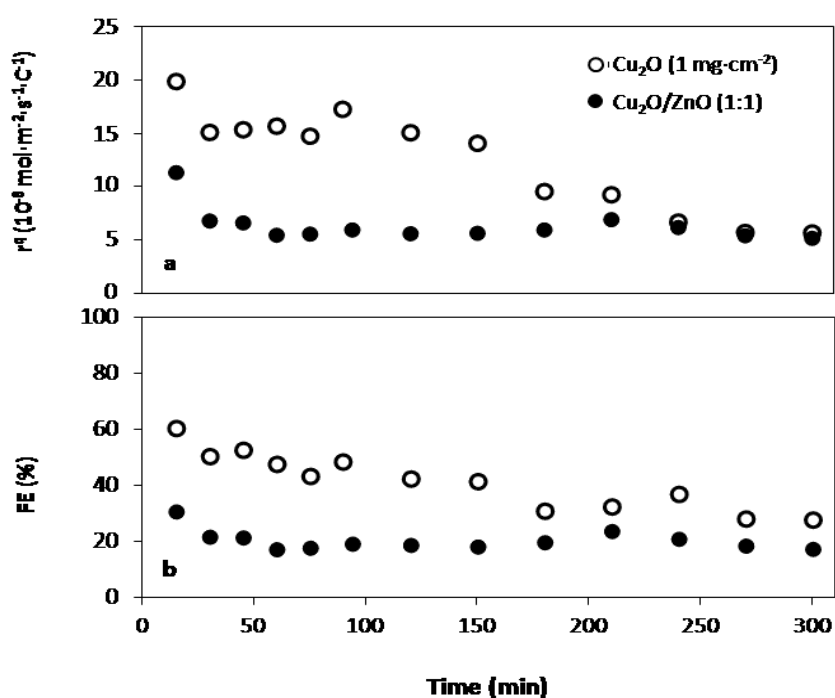


Figure 8. Time-dependence on (a) r^q , and (b) FE at Cu₂O (1) (○) and Cu₂O/ZnO (1:1)-based electrodes (●) in a 0.5 M KHCO₃ solution at -1.3 V vs. Ag/AgCl

As observed, both the charge normalized rate of CH₃OH formation, r^q , and efficiency, FE , at the Cu₂O-based electrode tend to diminish at longer reaction times (>90 minutes), with a reduction of 71.4 % and 59.7 %, respectively, in comparison to the initial experimental values ($r^q = 19.9 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{C}^{-1}$; $FE = 60.6\%$). Precisely, the r^q drops from 19.9 to $5.7 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{C}^{-1}$ after 5 hours of operation. The loss of activity at the Cu₂O-based electrodes may be associated with the detachment of metal particles at longer operation times [35], the reduction or blocking of the active copper oxides active sites produced by intermediate species formed in the CO₂ reduction reaction [17, 38], and also probably related by the crystallization of Cu₂O catalyst,

which may be accelerated by water produced along with CH₃OH [39]. Moreover, the agglomeration of particles and probable defects in the surface region occurred during the preparation of the electrodes would likely assist tunnelling and thus destabilize the Cu₂O surface [15], which may be the cause of the shortcoming of electrochemical CO₂ reduction performance.

On the other hand, for Cu₂O/ZnO (1:1) electrodes, an initial decrease in r^A and FE can be observed, followed by values with nearly negligible fluctuations during the whole measurement (5 hours). The results indicated that Cu₂O/ZnO-based electrodes present better stability than the Cu₂O-deposited carbon papers during CH₃OH formation, as well as a longer stability period than those electrodes prepared by brush-painting the Cu₂O particles onto carbon clothes [35] and Cu₂O thin films electrodeposited on stainless steel electrodes applied for the electroreduction of CO₂ to CH₃OH [17]. Probably, Zn does more than just provide a surface for the Cu, but also stabilizing Cu atoms and remove impurities, which can deactivate the catalyst in the long run, as it is already demonstrated for the industrial Cu-Zn catalysts for CH₃OH production [39, 40]. Previous reports hypothesized that the stability of Cu-ZnO species may be a key factor for maintaining catalytic activity, since ZnO strengthen the Cu-CO⁻ link, increasing the selectivity to alcohols, and stabilizing Cu in the hydrogenation reaction [21, 38, 41, 42].

Finally, Table 4 compares the production of CH₃OH, r , and efficiency, FE , at Cu₂O (1) and Cu₂O/ZnO (1:1)-based electrodes prepared in this study with previous results reported in literature for Cu-based surfaces, when different supporting electrolytes and cell configurations are applied [11, 15-23].

Table 4. Comparison of the rate of CH₃OH production, r , and Faradaic efficiency, FE , at the prepared Cu₂O and Cu₂O/ZnO-based electrodes, in comparison to other Cu-based materials reported in literature

Electrode	Electrolyte/Cell Configuration	E vs. Ag/AgCl (V)/ j (mA·cm ⁻²)	Rate, r (10 ⁻⁵ mol·m ⁻² ·s ⁻¹)	Faradaic eff., FE (%)	Ref.
Cu ₂ O(1 mg·cm ⁻²)-carbon paper	0.5M KHCO ₃ / Two compart. (Nafion)	-1.30/6.93	6.08	45.7	This work
Cu ₂ O/ZnO(1:1)-carbon paper		-1.30/10.64	3.17	17.7	
Electropolishing Cu foil	0.1M KHCO ₃ / Two compart. (AMV Selemion)	-1.35/~10	-	~0.13	[11]
Pre-oxidized Cu (1 h, 130 °C)	0.5M KHCO ₃ / Undivided	-0.01/0.069	0.28	~240 ^b	[15]
Pre-oxidized Cu (17 h, 130 °C)		-1.50/7.1	2.36 ^a	-	
Anodized Cu foil		-1.20/1.4	2.78 ^a	~120 ^b	
Pre-oxidized Cu-TiOx (300 °C)		-1.0/0.74	2.25 ^a	~180 ^b	
Pre-oxidized Cu-TiOx (500 °C)		-0.40/0.30	3.33 ^a	~30 ^b	

(La _{1.8} Sr _{0.2} CuO ₄)-carbon GDE	0.5M KOH/Two compart.(Nafion)	-2.25 to -2.55/180	-	2	[16]
Air-furnace oxidized Cu	0.5M KHCO ₃ / Undivided cell	-1.45/~10	0.03 ^a	2	[17]
Anodized Cu foil (Elect. oxidized)		-1.35/~5	0.56 ^a	20	
Cu ₂ O electrodeposited-steel		-1.05/~5	11.9 ^a	38	
Cu ₈₈ Sn ₆ Pb ₆ alloy foil	2M HCl/Two compart. (Nafion)	-0.60/0.24	1.06 ^{a,c}	34.3	[18]
	1.5M HCl-0.17M BaCl ₂ /Two compart. (Nafion)	-0.60/0.41	0.176 ^{a,c}	36.3	
(Cu _{63.9} Au _{36.1})-nanoporous Cu film	0.5 M KHCO ₃ / Two compart. H-type	-0.95/~0.85	-	15.9	[19]
Electroplating Cu-carbon paper	SPE (Nafion)/ Two compart.	-/11.1	-	0.54	[20]
	SPE (SPEEK)/ Two compart.	-/8.9	-	0.44	
Cu nanocluster-ZnO (1010)	0.1M KHCO ₃ / Two compart. (Nafion)	-1.40/~12	0.425 ^a	2.8	[21]
Cu nanocluster (111)		-1.40/~12	0.02 ^a	0.1	
Electrodeposited Cu ₂ O-carbon paper	SPE (CMI-7000)/ Two compart. (MEA)	-2 ^d /~3.7	-	5	[22]
	SPE (AMI 7001)/ Two compart. (MEA)	-2 ^d /~2.4	-	20	
Cu/CuO nanopowder-carbon GDE	1M KHCO ₃ / Two compart. (Nafion 117)	-1.35/17.3	-	2.5	[23]

^a Calculated from reported data

^b Apparent *FE* (justified in terms of chemical and electrochemical CO₂ reduction)

^c Data for total CO₂ reduction to various products (including CH₃OH)

^d Reference electrode not provided

The performance of the electrodes prepared in this work (Cu₂O and Cu₂O-ZnO based electrodes) were comparable to those previously reported for Cu and oxidized Cu materials, although the prepared electrodes did not outperform the extraordinary high apparent *FE* values (i.e. >100%) found in literature for thermally oxidized Cu surfaces (where obviously both chemical and electrochemical steps must be involved in the CO₂ reduction process) [15], or the high CH₃OH formation rates reached at electrodes based on Cu₂O electrodeposited on stainless steel, $r = 11.9 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at -1.05 V vs. Ag/AgCl [17]. Nevertheless, the electrodes prepared with Cu₂O-ZnO mixtures (at 1:1 weight ratio) present a relatively high formation rate ($r = 3.17 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) and Faradaic efficiency (*FE* = 17.7 %), as well as a stable behaviour for as long as 5 hours of experimental time, which may suggest the use of these materials for CO₂ electrochemical valorisation processes in continuous operation.

Further advances are still required in order to develop catalyst materials with optimal performance for practical applications. The authors believe that the breakthrough is in the development of new complex catalysts and catalyst assemblies, including hybrid metal catalysts (which can account for an electrochemical synergic effect) and nanostructures and MOFs-based electrocatalysts (which may provide higher specific

surface area and more active sites available). With continued research efforts, new catalysts materials with higher catalytic activity and product selectivity, as well as acceptable stability for the electrochemical conversion of CO₂ to CH₃OH will be developed.

- **Conclusions**

The continuous electroreduction of CO₂ to methanol under ambient conditions was investigated at Cu₂O-based electrodes in a CO₂-saturated KHCO₃ aqueous solution. The electrodes were prepared by airbrushing the Cu₂O particles at different loadings (0.5, 1 and 1.8 mg·cm⁻²) and Cu₂O-ZnO mixtures at different weight ratios (1:0.5, 1:1 and 1:2). The materials were electrochemically characterized by cyclic voltammetric analyses in a standard three-electrode electrochemical cell at potentials ranging from 0 to -1.8 V vs. Ag/AgCl. The results indicated that the CO₂ electroreduction behaviour depends on the loading of Cu₂O particles deposited. Interestingly, in presence of ZnO, a synergetic effect seems to take place during the electrochemical reduction process.

Furthermore, the Cu₂O and Cu₂O/ZnO-based electrodes were tested as cathodes in a filter-press electrochemical cell for the continuous reduction of CO₂ to methanol. The results showed that increases in Cu(I) content in the electrode produces a remarkable increase in methanol production and efficiency when increasing catalytic loading from 0.5 to 1 mg·cm⁻², although further increases in catalyst loading have a negligible influence on the electrode performance. The methanol production and efficiency of the reaction was further enhanced when increasing electrolyte flow due to external mass transfer limitations in the system. The stability tests demonstrated that Cu₂O/ZnO (1:1)-based electrodes present negligible fluctuations during 5 hours, in contrast with Cu₂O-deposited carbon papers, which suffered loss of activity with time. Therefore, and despite their initial lower activity, the use of Cu₂O/ZnO-based electrodes could be beneficial for the formation of methanol from CO₂ electroreduction processes. The stable rate of methanol formation at Cu₂O/ZnO (1:1)-based electrodes was $r = 3.17 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ with a Faradaic efficiency of 17.7 %; which is significantly higher than those formation rates obtained at Cu plates.

There are still several issues that need to be tackled for this technology to achieve widespread use, although, with continued and extensive efforts, the technology of CO₂

electroreduction to methanol will probably become practical and economically feasible in the near future.

Acknowledgement

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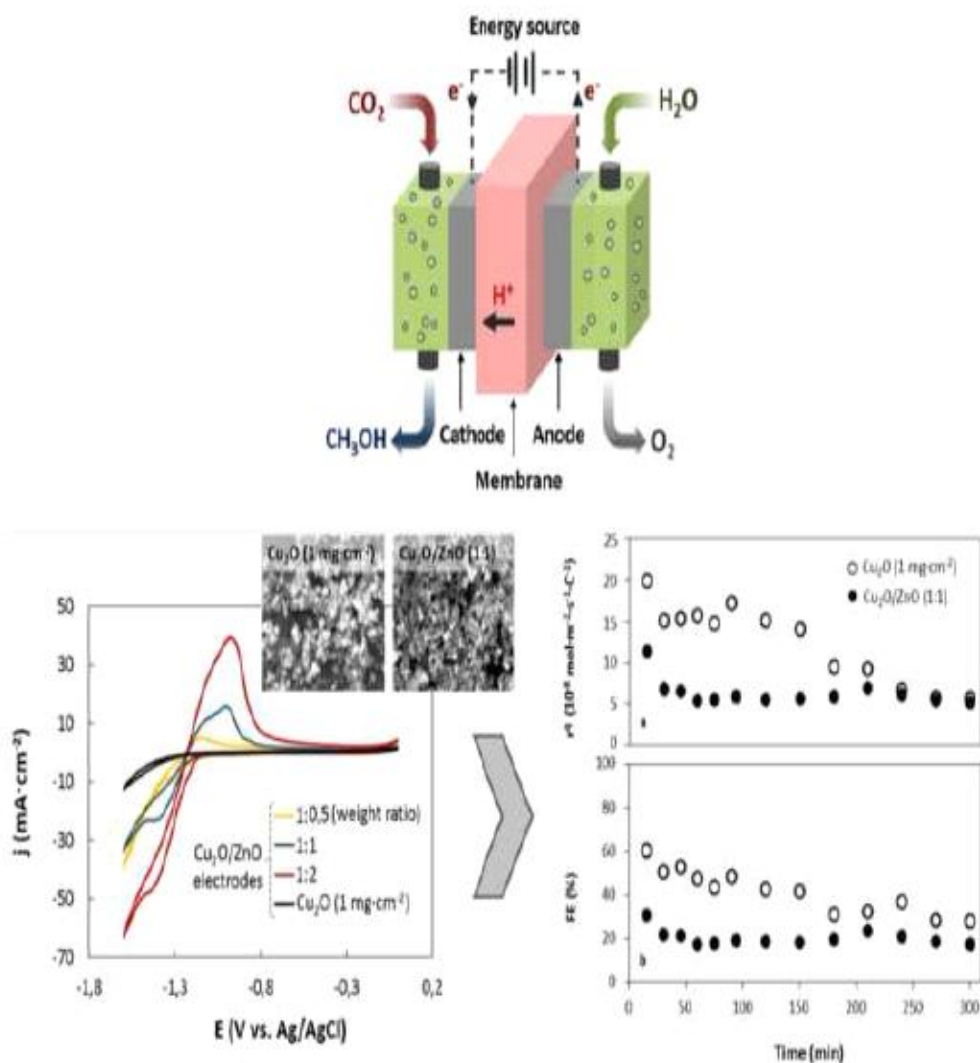
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GRAPHICAL ABSTRACT



HIGHLIGHTS

Highlights

- Cu-based electrodes are tested for the continuous electroreduction of CO₂ to CH₃OH
- Cu₂O and Cu₂O/ZnO-based electrodes are used at different loadings and

weight ratios

- Increases in Cu(I) in the electrode result in an enhanced formation of CH₃OH
- The electrodes with ZnO in the catalytic surface are stable for 5 hours
- The influence of electrolyte flow reveals mass transfer limitations in the system