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Bimetallic Cu-based hollow fibre electrodes for CO₂ electroreduction

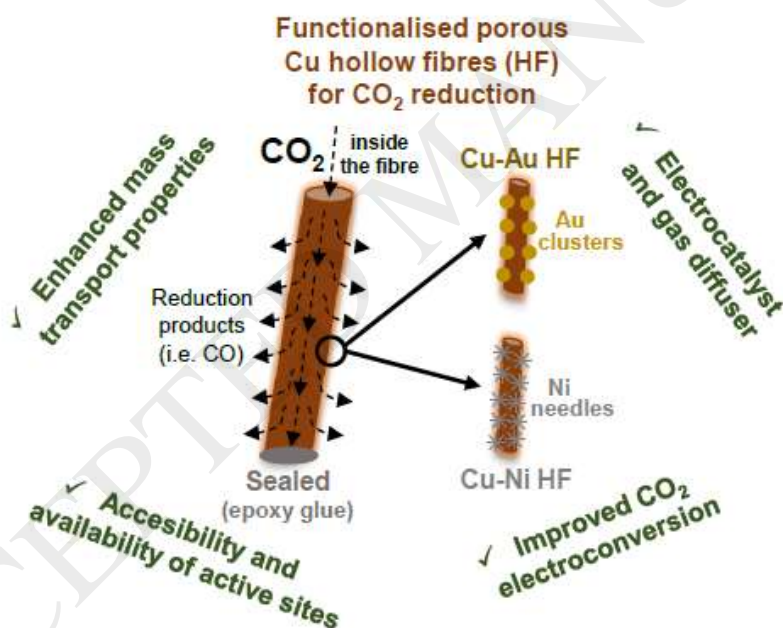
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Graphical abstract



Highlights

- Porous Cu-based hollow fibre electrodes were synthesised for CO₂ electroconversion
- Cu hollow fibres were functionalised with Au and Ni via electrodeposition technique
- Preliminary results in cell showed promising results in terms of faraday efficiency
- This work may provide new insights for developing highly efficient electrocatalysts

Abstract

The electrochemical reduction of CO₂ represents an attractive alternative to both, satisfy the increasing energy demand, and to help closing the carbon cycle. However, the energy required

for CO₂ activation and the subsequent multiple number of proton-coupled electron transfer steps involved, makes this process very challenging. Besides, catalytic material limitations are hampering the application of this technology in the short term. Consequently, in this work we synthesise, characterise and preliminarily evaluate bimetallic Cu-based hollow fibre electrodes with a compact three-dimensional geometry to overcome mass transfer limitations and to enhance the electrochemical conversion of CO₂. The Cu hollow fibres are functionalised with Au in an attempt to tune the binding energy of the CO* intermediate, which appears to be key in the reduction of CO₂. The Cu fibres are also functionalised with Ni, aiming to decrease the reaction overpotential, resulting in beneficial energy efficiency. The so prepared Cu-based porous hollow fibre electrodes are obtained by spinning and electrodeposition procedures. The materials are then characterised by scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction analyses and cyclic voltammetry tests. Finally, preliminary results of CO₂ electroreduction in a divided three-electrode cell are reported. The results show the potential of highly active, bimetallic hollow fibre-based electrocatalysts for enhanced conversion of CO₂ into value-added products, and deposition of particles should be performed with care, not to effect pore characteristics and thus mass transfer properties.

Keywords: Electrochemistry, CO₂ electroconversion, Cu-based hollow fibre electrodes, climate change.

1. Introduction

The continuous accumulation of carbon dioxide (CO₂) in the atmosphere is considered one of the most important challenges of the 21st century owing to its impact on the undesirable effects of global warming [1]. Therefore, significant strategies must be taken into consideration in order to palliate the consequences of climate change. In this context, the possibility to electrochemically convert CO₂ into value-added products while using renewable energy sources (e.g. solar or wind-based energies) is appealing, because of different environmental benefits such as the possibility of storing intermittent renewable energy in chemical bonds [2]. Furthermore, the continuous burning of fossil fuels for the synthesis of chemicals might be considerably reduced owing to the electrochemical conversion of CO₂ into value-added products at room temperature, facilitating a closed carbon cycle at the same time. Nevertheless, the high energy requirements for the activation of CO₂, the slow kinetics of the electrochemical reaction as well as the low production rates achieved so far usually limit the practical application of this technology in the short term [3].

Moreover, the availability of cheap, active, efficient, selective and stable electrocatalytic materials for CO₂ electrovalorisation is still limited [4]. In this regard, different electrocatalysts have been applied in CO₂ electroreduction processes [5], in which copper (Cu)-based surfaces are among the most studied materials because of

their ability to perform the electrocatalytic conversion of CO₂ into fuels [6].

Nevertheless, the reported productivities, selectivities and efficiencies are still far from practical applications [7]. In this respect, good adsorption and mass transfer properties are often the main features required for Cu-based electrodes to achieve an enhanced electrocatalytic conversion of CO₂. Moreover, the competitive hydrogen evolution reaction needs to be controlled in order to improve the selectivity of the process [8].

In this context, the design of Cu-based hollow fibre (HF) electrodes is particularly appealing due to the multiple advantages that can be found in this kind of materials such as their porous and three-dimensional structure, which may improve the accessibility to catalytic active sites as well as its availability. Besides, the possibility of improving the diffusion of reactants and products represents an attractive opportunity for CO₂ electroreduction processes since the hollow fibre can act as both gas diffuser and electrocatalyst.

Furthermore, the combination of metals to prepare multimetallic electrocatalysts appears to be an attractive owing to the possibility of tuning the adsorption properties of intermediate species. In addition, the utilization of metals that bind specific reaction intermediates (i.e. CO*) may involve an enhanced CO₂ electroreduction, because the binding energy of the intermediate may be tuned, which might affect reaction mechanisms and the reaction overpotential, among others [9]. Several researchers have also demonstrated that these alterations in the adsorption properties when using different Cu-based bimetallic materials also involve changes in the selectivity of the CO₂ reduction reaction [10,11]. Nevertheless, further work is needed to deepen the understanding of the influence of different parameters such as composition ratio, particle size and morphology, among others [12].

Therefore, the aim of this work is to prepare, characterise and preliminary evaluate bimetallic Cu-based HFs electrodes for an enhanced CO₂ electroreduction. The Cu HFs are then functionalised with Au (i.e. Cu-Au HFs) and Ni (i.e. Cu-Ni HFs) in an attempt to improve the adsorption of reaction intermediates and to decrease the reaction overpotential, which is essential in terms of energy efficiency. Thus, this study represents an innovative approach to evaluate the application of bimetallic three-dimensional Cu-based hollow fibre electrocatalysts for CO₂ electroconversion. The effect of the HFs composition (i.e. Cu, CuO, Cu-Au and Cu-Ni HFs) on the catalytic activity of the materials is then discussed. Finally, the most active Cu-based HF electrodes are evaluated in a cell in terms of Faraday efficiency (FE), as a function of the applied potential (E). This study is expected to provide new insights for developing innovative working electrodes for CO₂ electroreduction processes.

2. Experimental details

The electrocatalytic Cu HFs are prepared according to the procedure developed by Kas et al. [4]. In brief, Cu powder (Skyspring nanomaterials, particle size= 1-2 μm ; purity= 99 %) as catalyst precursor, N-methylpyrrolidone (NMP, Sigma Aldrich, 99.5 wt%) as solvent, and polyetherimide (PEI, General Electric, Ultem 1000) as polymer are mixed with a weight percent of 71 %, 22 % and 7 %, respectively. The catalyst precursor is first added to the NMP solution, followed by continuous agitation in an ultrasonic bath for 30 min. The addition of PEI is carried out afterwards and the resulting mixture is finally heated (at 60 $^{\circ}\text{C}$) and stirred for, at least, 2 h. The solution is then stirred overnight and then, vacuum is applied for approximately 1 h. The spinning process (spinneret with inner and outer diameters of 0.8 mm and 2 mm, respectively) is performed at room temperature using a stainless steel vessel. A coagulation bath is utilised to collect the fibres once the mixture is pressed through the spinneret while deionized water is pumped (30 mlmin^{-1}) through the bore of the spinneret. The distance between the spinneret outlet and the coagulation bath level (i.e. air gap) is set at around 1 cm. The obtained Cu HFs are kept into the coagulation bath for 24 h in order to remove NMP traces. After the drying step at room temperature for 1 day, the fibres are thermally treated at 600 $^{\circ}\text{C}$ for 3 h to remove traces of PEI as well as for Cu sintering, resulting in a porous CuO HF. Finally, the oxidised HFs are reduced by hydrogenation (4 % H_2) at 280 $^{\circ}\text{C}$ in Ar atmosphere for 1 h, using a tube furnace.

The functionalisation of the Cu HFs is carried out through electrodeposition experiments in inert atmosphere while flowing N_2 gas through the hollow fibre. An undivided three-electrode cell (working electrode: Cu HF; counter electrode: Pt wire; reference electrode: Ag/AgCl 3M NaCl) is used to obtain the bimetallic electrocatalysts. A solution of HAuCl_4 (0.1 g/L) and 0.5 M H_2SO_4 (1:1 v/v) is used for Au electrodeposition at -0.9 V vs. Ag/AgCl for 10 min (current density of about 116 mAcm^{-2}). On the other hand, an aqueous solution 50 mM of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is used as electrolyte to functionalise Cu HFs with Ni at -1 V vs. Ag/AgCl for 15 min (current density of 2.5 mAcm^{-2}).

Different techniques are applied to physico-chemically characterise the catalytic materials. Scanning electron microscope (SEM) images are collected using a Zeiss Merlin HR-SEM with an acceleration voltage of 20 V – 30 kV. X-ray diffraction (XRD) analyses are performed to evaluate the chemical composition of the materials using a Bruker D2 Phaser diffractometer, equipped with a Cu-K α radiation source and operated at 30 kV and 10 mA. Besides, SEM-Energy dispersive X-ray spectroscopy (EDX) images are also collected. On the other hand, the electrochemical

characterisation of the materials is carried out through cyclic voltammetry (CV) analyses using an undivided three-electrode cell, in which a Cu-based HF, a Pt wire and a Ag/AgCl-based electrode are applied as working, counter and reference electrodes, respectively. A CO₂-saturated (CO₂) 0.1 M KHCO₃ solution (pH 6.8) is utilized as electrolyte to fill the cell. A potential ranging from 1.5 V vs. Ag/AgCl to -1.5 V vs. Ag/AgCl with a voltage ramp of 20 mV/s is applied to the working electrode to analyse the electrochemical activity.

The performance of the process is evaluated through preliminary CO₂ reduction experiments, which are conducted in a divided three-electrode cell (see figure 1) that is composed by the HF as working electrode (3.5 ± 0.5 cm), a Pt mesh as the counter electrode and a Ag/AgCl 3M NaCl as the reference electrode. The CO₂ electroreduction experiments are performed at room temperature (20 °C). A Nafion 212 membrane divides the cell compartments, whereas a CO₂-saturated 0.1M KHCO₃ solution is used as electrolyte. The hollow fibre electrode is connected to a stainless steel tube using conductive silver glue. Then, epoxy glue is applied on the top of silver glue to avoid the contact of the conductive silver glue with the electrolyte. The potentiostat clamp is then connected to the stainless steel tube. On the top of this tube, CO₂ is directly supplied into the fibre. The CO₂ flow rate is 20 mlmin⁻¹, which flows inside the material and is forced to cross the porous structure. For that purpose, the fibre is sealed at the bottom with epoxy glue. The influence of the applied potential is studied from -1.0 V vs. Ag/AgCl to -1.5 V vs. Ag/AgCl. It is worth noting that the reactor is purged with CO₂ (30 min) before measurements to saturate the electrolyte. The experiments are conducted for around 20 min, when steady state conditions are achieved. In addition, the reactor is also purged between potential changes. A gas chromatograph (GC) installed online downstream the cell and equipped with thermal conductivity detector (TCD) is used for the detection of H₂ and CO.

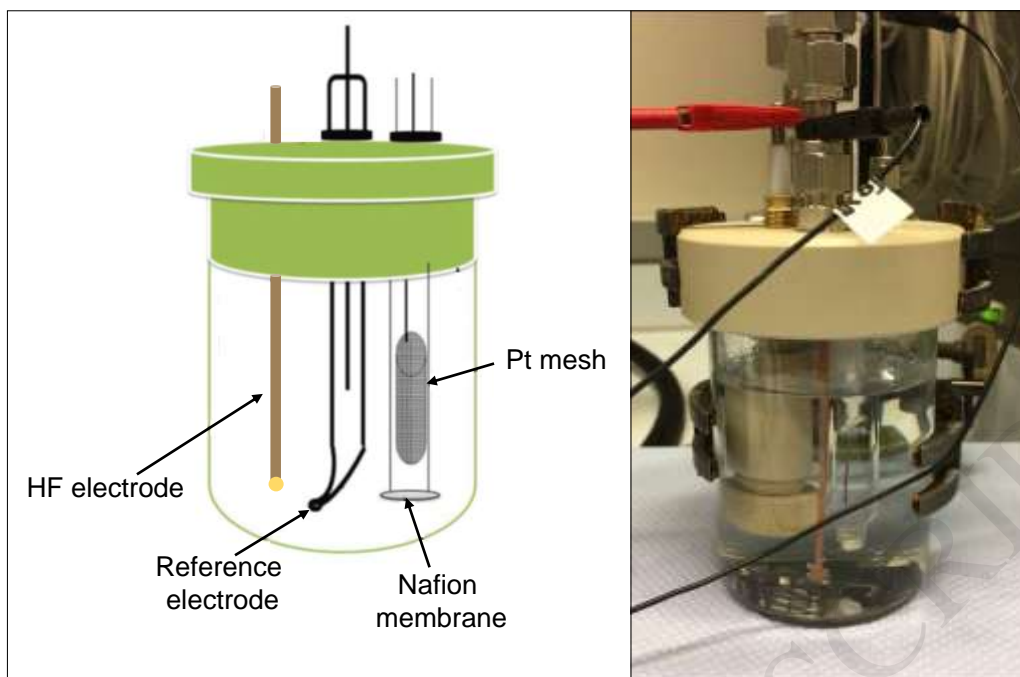


Fig. 1. Electrochemical cell.

3. Results and discussion

Physico-chemical characterisation of the Cu-based HF electrodes

Fig. 2 shows different SEM images of the Cu HF electrodes. The porous structure of the fibres is demonstrated in Fig. 2a-d, where voids can be clearly observed. Besides, Fig. 2c reveals that the sintering of Cu particles has been successfully carried out and the Cu HF electrodes are formed by interconnected and aggregated Cu particles that form a three-dimensional porous structure. The so prepared Cu HF electrodes are obtained with inner and outer diameters of approximately 1.3 mm and 1.6 mm, respectively (Fig. 2a). This porous-based three-dimensional electrocatalyst might therefore enhance the accessibility to catalytic active sites and also improve the diffusion of CO_2 in comparison with the use of two-dimensional working electrodes.

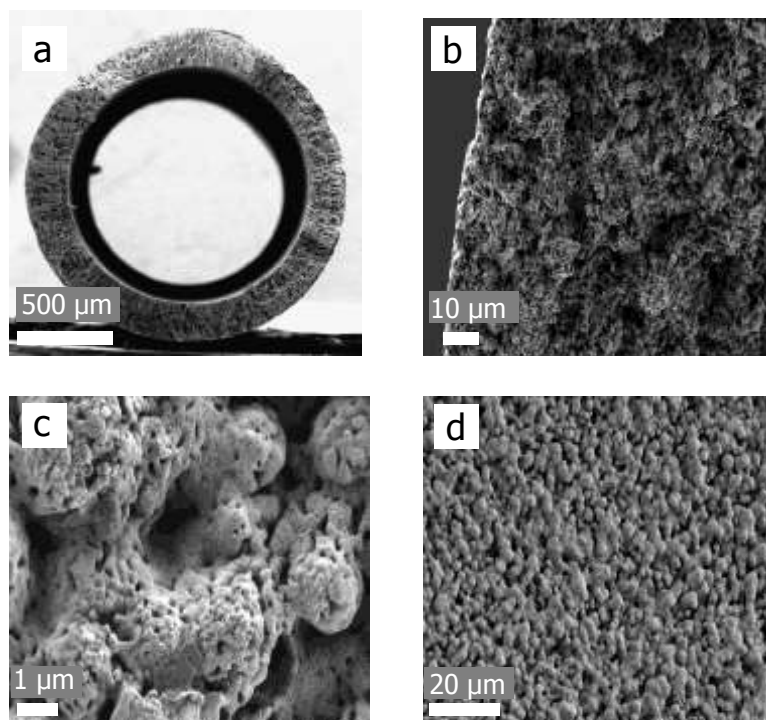


Fig. 2. SEM images of Cu HFs: a) [4] and b) Cross section, scale bars = 500 μm and 10 μm , respectively. c) External surface, scale bar = 1 μm . d) Inner surface, scale bar = 20 μm .

Fig. 3 displays the SEM images of the Cu-Au HFs, which evidences the presence of Au clusters within the electrocatalytic material (bright areas) as well as the presence of oxides that can be observed in Fig. 3c (black parts). This fact denotes the fast oxidation of the Cu-Au HF in the presence of air. Overall, the electrodeposition of gold has been successfully performed, even though further characterisation techniques need to be applied to conclude that we are able to synthesise bimetallic Cu-Au HF electrodes.

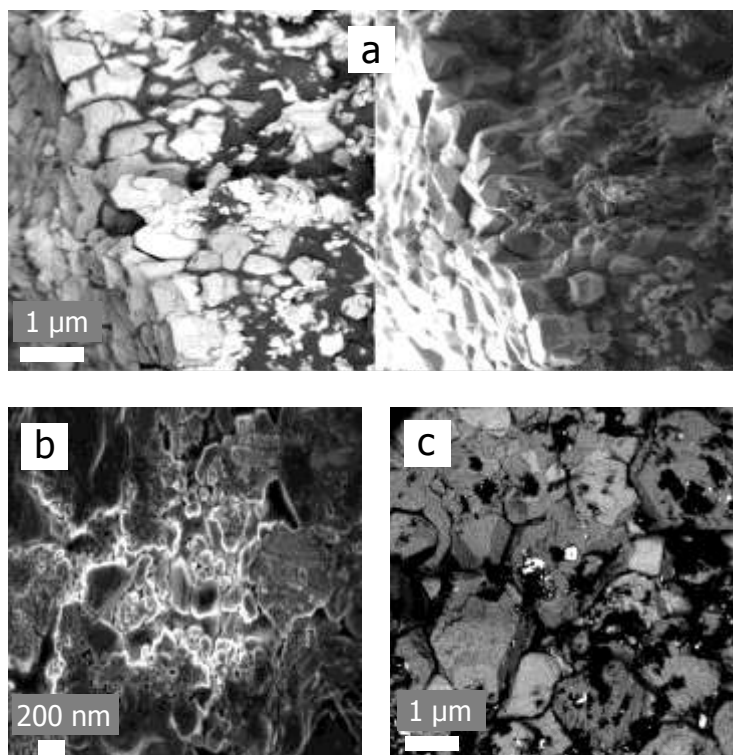


Fig. 3. SEM images of Cu-Au HFs: a) Cross section, scale bar = 1 μm . b) External surface, scale bar = 200 nm. c) Inner surface, scale bar = 1 μm .

Fig. 4 shows the SEM images of the Cu HF fibers electrodeposited with Ni. The presence of Ni as needle-like structures in the surface of the porous electrocatalyst can be clearly observed. The high porosity of the materials is remarkable, which may improve the diffusion of reactants and products through the fibre.

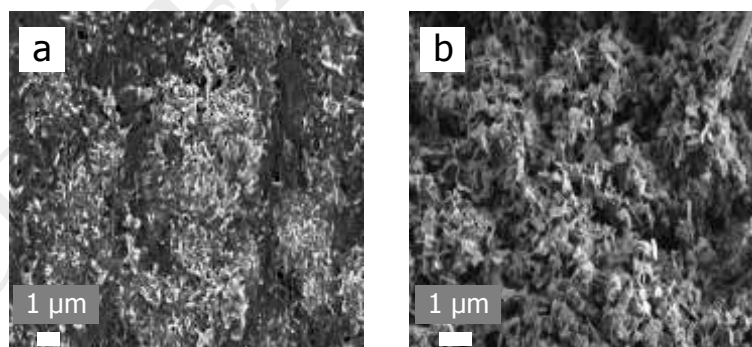


Fig. 4. SEM images of Cu-Ni HFs: a) External surface, scale bar = 1 μm . b) Inner surface, scale bar = 1 μm .

To further determine the composition of the Cu-based HF electrodes, different XRD measurements have been carried out. Fig. 5 shows the XRD patterns for the different Cu materials obtained during the synthesis of Cu HFs (i.e. the calcined HF and the final reduced HF), including the Cu powder response. If we compare the resulting

patterns, the same Cu crystal orientations can be clearly observed in both Cu powder and reduced HF (Cu 111, Cu 200 and Cu 220), which demonstrates the successful synthesis of this porous material. Besides, the presence of CuO is proven after the calcination step, which is converted into pure Cu after the reduction process.

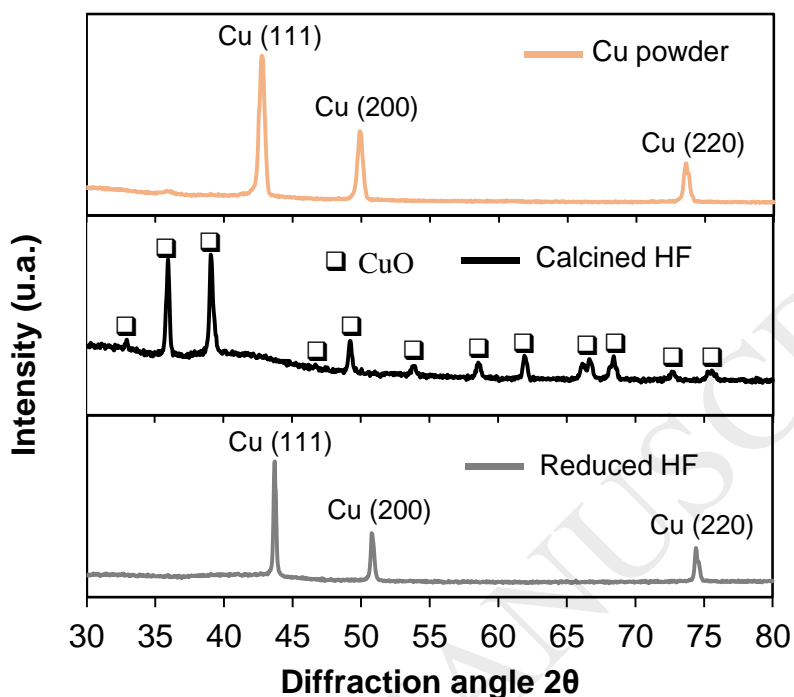


Fig. 5. XRD patterns for Cu powder, calcined HF and reduced HF.

The same procedure has been followed to analyse the XRD response associated with the functionalised HF electrodes. Fig. 6 displays the XRD diagrams for Cu-Au HF (Fig. 6a, where the XRD pattern for Cu HF has been also included for comparison) and Cu-Ni HF (Fig. 6b). On the one hand, Fig. 6a reveals the presence of the Cu structures (Cu 111, Cu 200 and Cu 220) identified in the Cu HF, as well as four specific Au crystal orientations (Au 111, Au 200, Au 220 and Au 311), which confirms the presence of gold in the functionalised HF electrodes. On the other hand, Fig. 6b shows that the XRD response of Cu and Ni is practically equal in terms of diffraction angle. Therefore, the utilisation of other characterisation techniques is needed to demonstrate that the material is composed by Cu and Ni. Consequently, an EDX analysis (Fig. 7) of the outer surface of the Cu-Ni HF is carried out, demonstrating thus the presence of both Cu and Ni structures, as observed by SEM. Overall, XRD and EDX analyses demonstrate that the electrodeposition has been successful.

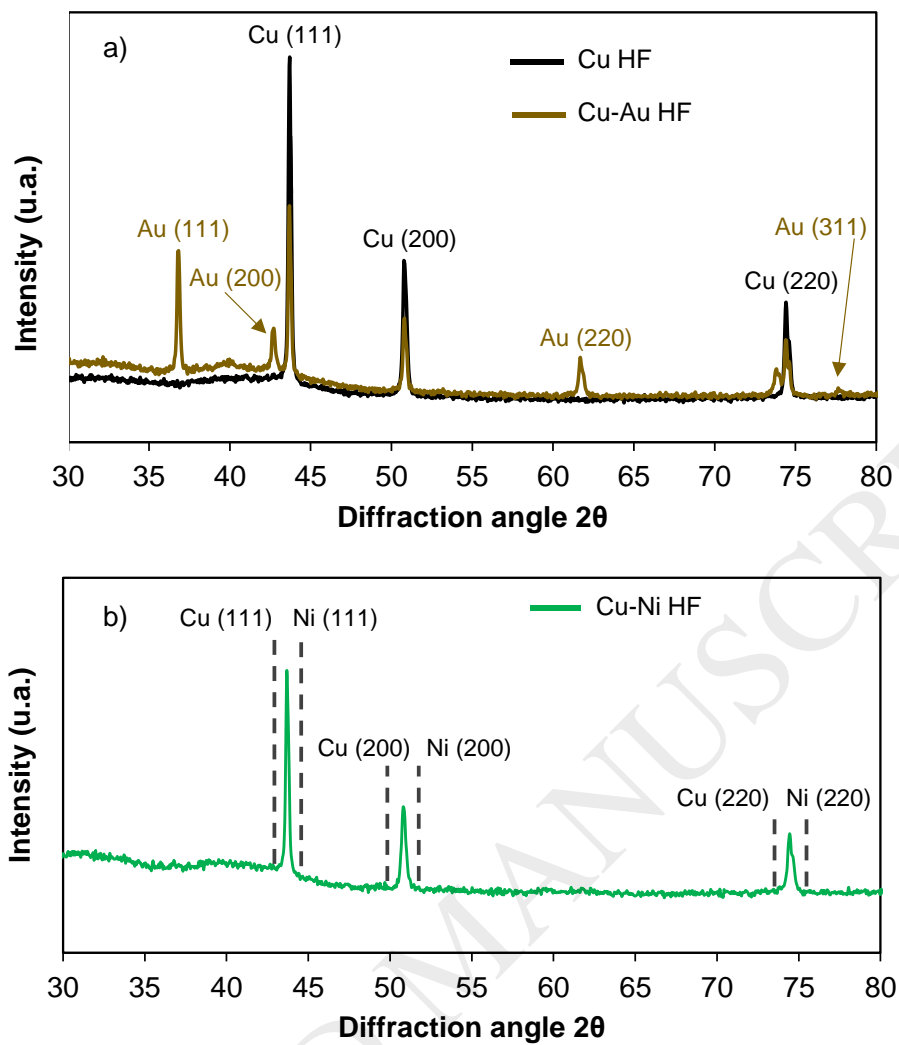


Fig. 6. XRD patterns for a) Cu-Au HF and b) Cu-Ni HF.

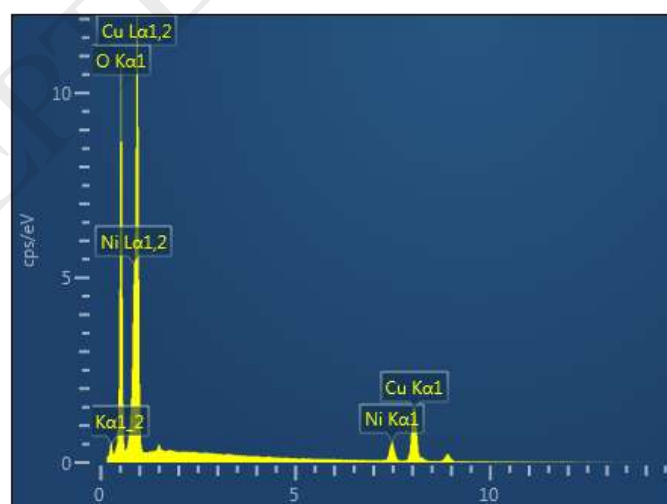


Fig. 7. EDX analysis of the Cu-Ni HF outer surface.

Electrochemical characterisation of the Cu-based HF electrodes in the presence of CO₂

Fig. 8 shows the current-voltage responses for the materials (i.e. Cu, CuO, Cu-Au and Cu-Ni HFs electrodes). The calcined HFs (CuO) reach an unnoticeable current-voltage response compared to those voltammograms obtained for the reduced (Cu HFs) and functionalised fibre electrodes (Cu-Au and Cu-Ni HFs), which might be related to lack of conductivity of the fibre after the calcination step [13]. If we analyse the voltammetric profiles of the most active electrocatalytic materials (i.e. Cu HF and bimetallic HF), it can be seen that the highest response at -1.5 V vs. Ag/AgCl is achieved for the Cu HF electrodes, which might be initially related to reduction of surface oxides, followed by an enhanced production of H₂ and CO (syngas) as reported by Kas et al. [4], who previously electroreduced CO₂ to syngas at low applied potentials using Cu HFs electrodes. The lower current densities observed for the bimetallic HF electrodes can be associated with the electrodeposition procedures used for the synthesis of the Cu-Au and Cu-Ni bimetallic fibres. It is plausible to assume the copper oxide has been reduced at the negative potentials applied for the deposition of Ni and Au. The lower current densities observed in the range of -1.0 to -1.5 V vs Ag/AgCl could be due to differences in resistance, or pore dimensions, creating *sub-optimal* supply of CO₂. Kas et al. [4] have previously demonstrated that the current density is a function of CO₂ flow rate and supply.

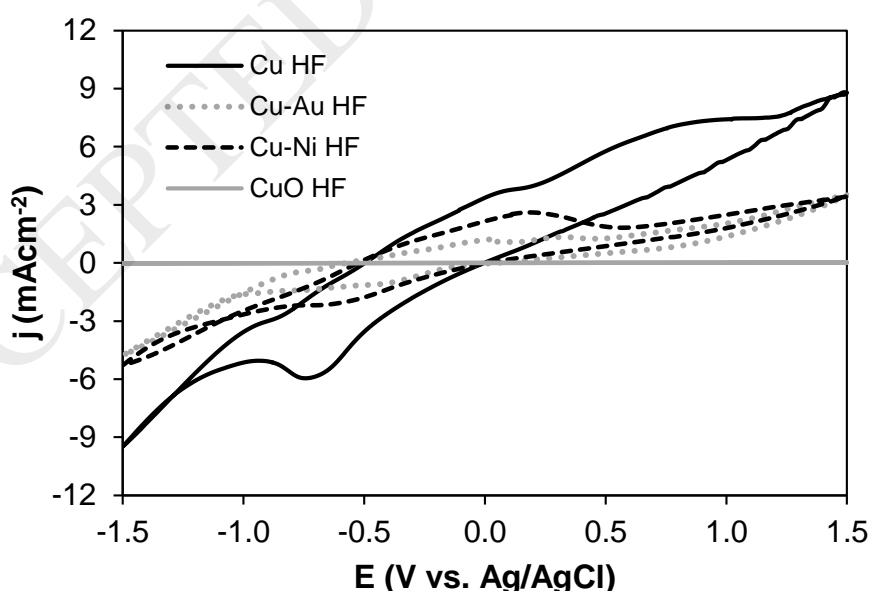


Fig. 8. CVs for Cu HF (black line), CuO HF (grey line), Cu-Au HF (grey dotted line) and Cu-Ni HF (black dotted line). The CVs were recorded in a CO₂-saturated 0.1 M KCHO₃ aqueous solution.

Preliminary CO₂ reduction experiments in cell

In order to evaluate the effect of Au and Ni on the selectivity and FE of reduction of CO₂, four types of HF electrodes synthesised in this study (i.e. CuO, Cu, Cu-Au and Cu-Ni HFs) were evaluated at a potential ranging from -1.0 V to -1.5 V vs. Ag/AgCl. The results are shown in Table 1. It is important to point out that the use of CuO HF does not lead to any CO₂ reduction product, which is in accordance with the low current-voltage response observed in the CV analyses of Fig. 7.

Table 1. FE results from CO₂ electroreduction at Cu-based HF electrodes as a function of the applied potential.

Electrocatalyst	E = -1.0 V			E = -1.25 V			E = -1.5 V		
	FE (%)		j (mAcm ⁻²)	FE (%)		j (mAcm ⁻²)	FE (%)		j (mAcm ⁻²)
	CO	H ₂		CO	H ₂		CO	H ₂	
Cu HF	43.2	11.3	2.2	66.1	8.6	6.6	63.2	11.8	12.7
Cu-Au HF	27.8	9.7	1.8	64.7	10.7	4.3	67.2	12.9	8.0
Cu-Ni HF	45.7	39.6	2.2	76.3	7.4	6.8	77.5	9.3	13.6

The preliminary results suggest that the optimal potential range for the production of CO is from -1.25 V to -1.5 V vs. Ag/AgCl. An improved FE to CO can be observed with Cu-Ni HF at -1.25 V and -1.5 V vs. Ag/AgCl, including a higher current density level compared to those values obtained for Cu and Cu-Au HF electrodes, which may indicate the proton assisted electron transfer to CO₂ is promoted by the presence of Ni particles on the Cu HFs. This is in agreement with the lower FE efficiency towards hydrogen in the presence of Ni. The FE does not close to 100%: the formation of formate and alcohols is very likely, and should account for the missing percentage. Analysis of formate and alcohols is presently performed in further characterizing the behaviour of bimetallic hollow fibres. On the contrary, the utilisation of Cu-Au HF electrodes presents similar results in terms of FE to those reached at Cu HF electrodes, although the overall current density is lower. This might again be due to the plate-like, and irregular deposition of Au, which might reduce the number of effective pores through which CO₂ is provided to the reactive interface of Cu(Au), CO₂, and electrolyte. Moreover, the obtained current density values, especially for Cu-Ni HF at -1.5 V vs. Ag/AgCl (13.6 mAcm⁻²), are of relevance when compared with previous

reports on the electrochemical conversion of CO₂ at Cu-based electrodes. For instance, a current density ranging from 0.7 mAcm⁻² to 7.5 mAcm⁻² (as a function of different applied potentials) was obtained for CO₂ electroreduction at Cu-based gas diffusion electrodes [14]. Besides, different Cu-based solid polymer electrolytes were applied in a membrane electrode assembly configuration for CO₂ electroconversion, where current densities ranged from 3.3 mAcm⁻² to 11.1 mAcm⁻² [15]. The innovative materials developed in the present study allow working at applied potentials ranging from -1 V to -1.5 V vs. Ag/AgCl, which are lower than those required for CO₂ electroconversion at Cu-based surfaces such as Cu nanoparticles and Cu nanofoams with applied voltages of -2.0 V vs. Ag/AgCl [14], -2.2 V vs. Ag/AgCl [16] and -1.7 V vs. Ag/AgCl [17], respectively. This denotes the interest in further developing hollow fibre electrode configurations for an improved CO₂ conversion with lower energy penalty.

In short, the preliminary results show differences in performance as compared to fibres made entirely out of copper. The advantages observed in terms of FE to CO, and enhanced current density when using Cu-Ni HF electrodes can likely be associated with a synergic effect between Cu and Ni in the CO₂ conversion pathway. However, further work is required to improve the performance of the deposition process of metallic particles on the copper fibres, with focus on control of size and distribution of particles, and study of the effect of changes in the pore dimensions and associated gas flow characteristics on performance.

4. Conclusions

This study reports the synthesis, characterisation and preliminary evaluation of innovative electrode materials for the electroreduction of CO₂. Cu-based hollow fibre electrodes are prepared with a porous and three-dimensional geometry, acting as both gas diffusers and working electrodes. These materials are then functionalised with Au and Ni through electrodeposition experiments to get bimetallic hollow fibre electrodes with potential to enhance the electroconversion of CO₂.

SEM images show the well-defined porous structure of the materials. Besides, the bimetallic Cu-Au and Cu-Ni hollow fibre images demonstrated the presence of Au and Ni in the form of clusters and needles, respectively. Deposition is further characterised by XRD and EDX analyses. Cyclic voltammetry analyses reveal a promising catalytic activity of Cu, Cu-Au and Cu-Ni HFs. The differences in activity at -1.5 V vs. Ag/AgCl might be related to changes in reaction mechanisms owing to the presence of metallic components, while for Au inferior pore characteristics and associated inferior mass transfer properties might be the cause of lower current densities.

Overall, this research work should be of help for developing active and efficient electrocatalytic materials for CO₂ electrovalorisation processes.

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