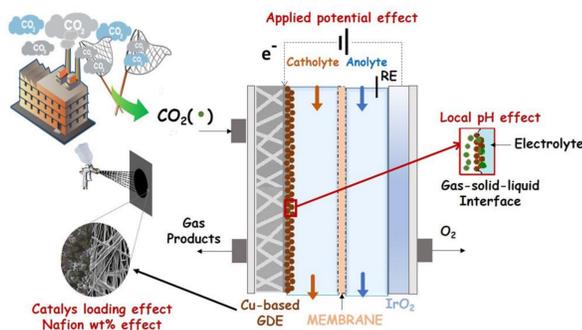


OVERVIEW

In the context of climate change and carbon management, electrochemical CO₂ reduction represents a promising solution¹. In this work, a **porous and conductive support** has been employed, where the catalyst has been manually deposited.

CuZnAl-based² catalysts obtained via **co-precipitation** method

The physical-chemical properties of the catalytic materials employed have been investigated through different characterization techniques.



Several variables have been assessed in order to find the most promising conditions leading to a **higher C₁₊ products formation**.

Catalyst loading, Nafion content, Applied potentials, Electrolyte concentration, presence of metal oxides

The outcome of the work has revealed that the **binder content** has affected the spectrum of obtained products. A **preliminary model³** has been implemented, which confirmed the role of a **high local pH** in promoting **salts formation⁴**.

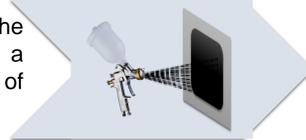
MATERIALS AND METHODS

The molar concentration of nitrates used as precursors were the following: Cu:Zn:Al=0.6M:0.3M:0.1M **CuZA-06-03-01**, Cu:Zn=0.6M:0.3M **CuZ-06-03**, Cu=0.6M **Cu-06**. CuZn and Cu catalysts were also synthesized in order to evaluate the contribution of **Al- and Zn- oxides**.

A catalytic ink consisting of **Cu-based catalyst** nanoparticles, conductive carbon support (**Vulcan XC 72R**), **Nafion dispersion** and **isopropyl alcohol** was prepared



By means of an **airbrusher**, the catalytic ink was deposited onto a **carbon paper** support. A GDE of 10.2 cm² was obtained



Electrochemical tests performed at ambient conditions in a continuous flow cell.

3-Electrodes system

W.E.: CuZnAl-based GDE

R.E.: Ag/AgCl

C.E.: Ir-MMO plate



INVESTIGATION HIGHLIGHTS

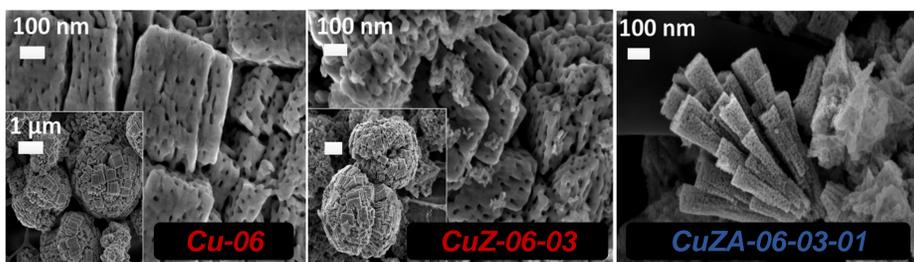


Fig. 1 FESEM images of the Cu-based electrocatalysts

A novel **nano-pyramidal** structure was highlighted in the **CuZA** catalyst (Fig. 1); spherical microparticles made-up of **rectangular-section** structures were shown by **Cu** and **CuZ** materials.

Table 1 Physical-chemical properties

Catalyst	BET surface area, m ² g ⁻¹	Total pore volume, cm ³ g ⁻¹	EDS, atomic ratio	Crystallite size, nm (11-1) CuO
Cu-06	18.4	0.11	Cu/O 1:1	17
CuZ-06-03	55.16	0.23	Cu/Zn 60:40	7
CuZA-06-03-01	101.65	0.37	Cu/Zn/Al 60:30:10	9

The incorporation of metal oxides allowed to increase the **surface area** and had an effect on the growth of the final crystals, reducing the **crystallite sizes** (Table 1).

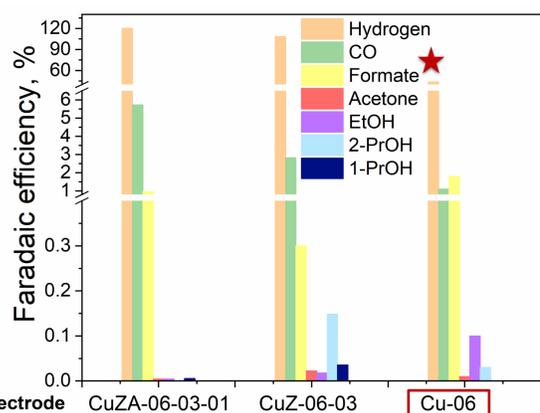


Fig. 2 Faradaic efficiencies of gaseous and liquid products at -1.5 V vs Ag/AgCl applied potential for different catalysts

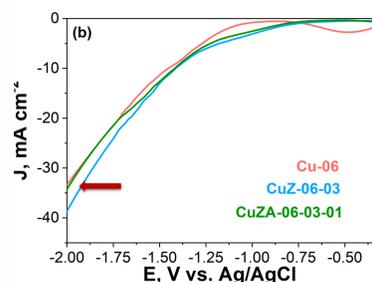


Fig. 3 Linear sweep voltammetry of the tested catalysts

In view of the good performance (Figs. 2 and 3), **Cu-06** was selected to evaluate the effects of Nafion content and applied potential. Indeed, current densities up to **35 mA cm⁻²** were reached and the **FE toward H₂** was hindered (★).

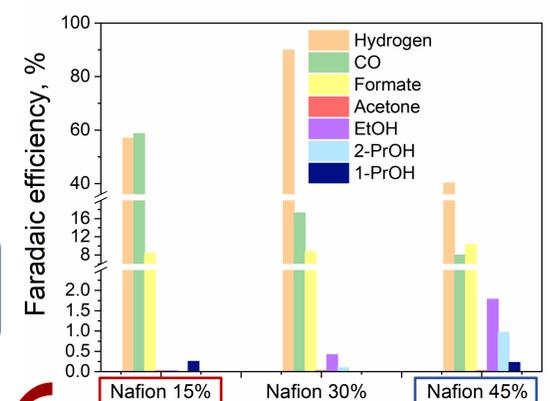
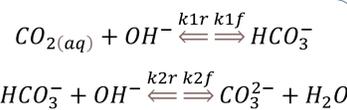


Fig. 4 Faradaic efficiencies of gaseous and liquid products at -1.5 V vs Ag/AgCl for Cu-06 with different Nafion content

A **lower** Nafion content has led to increase CO selectivity; whereas, a **higher** Nafion content has promoted C₁₊ production.

Effect of local pH highlighted in our work

An enhanced formation of liquid products has been correlated to a lower pH increase.

↑pH, ↑hydration of CO₂ to carbonate and bicarbonate species

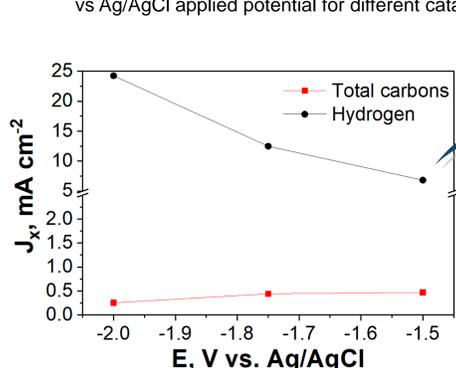


Fig. 5 Effect of applied potential on partial current densities

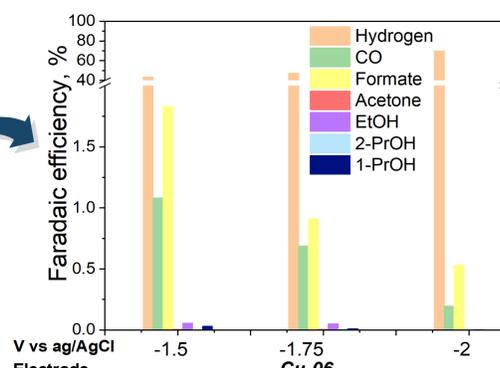


Fig. 6 Faradaic efficiencies of gaseous and liquid products

The highest FE and current density to H₂ were reached at **-2 V vs Ag/AgCl** (Figs. 5 and 6), whereas the efficiencies towards CO and liquid products decrease at the most negative potentials. The **management of gases transport** through the gas-diffusion-electrode represents a **challenge**.

CONCLUSIONS

The research work shows that C-C coupling was not promoted at high overpotentials, as expected from literature and previous experiments in liquid-phase conditions. This finding focuses attention on mass transfer limitations throughout the porous structure of the electrode, where a triple-phase-boundary should be formed. Moreover, the liquid crossover – affected by electro-wetting – was found to severely impacts the GDE performance, by hindering CO₂ diffusion towards the active sites and favouring HER. The Nafion content had a relevant effect in the selectivity of the process. The effect of local pH has been visualized in salts deposition.

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