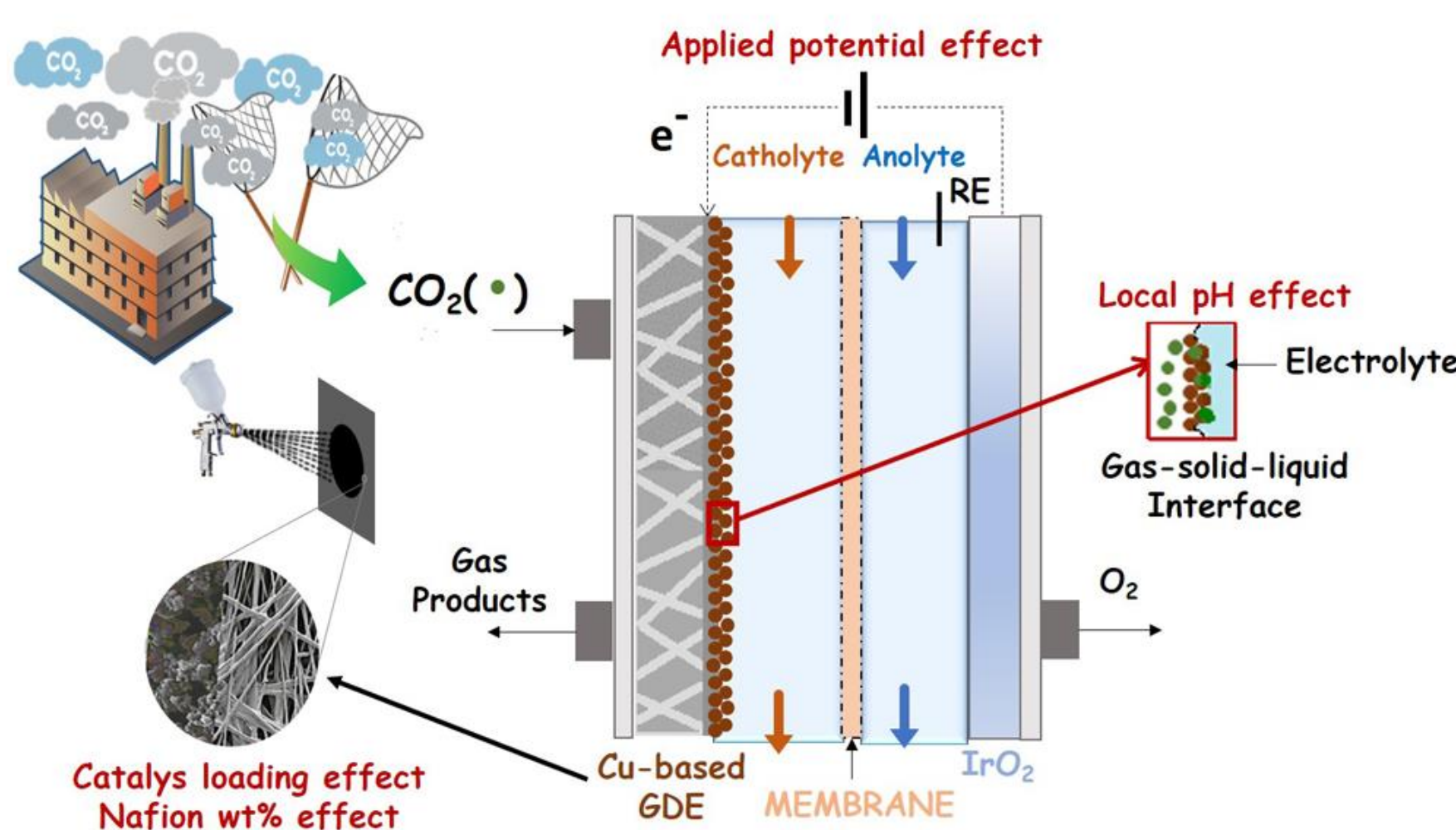


## OVERVIEW

In the context of climate change and carbon management, electrochemical CO<sub>2</sub> reduction represents a promising solution<sup>1</sup>. In this work, a **porous and conductive support** has been employed, where the catalyst has been manually deposited.

**CuZnAl-based<sup>2</sup> 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 C<sub>1+</sub> 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 model<sup>3</sup>** has been implemented, which confirmed the role of a **high local pH** in promoting **salts formation<sup>4</sup>**.

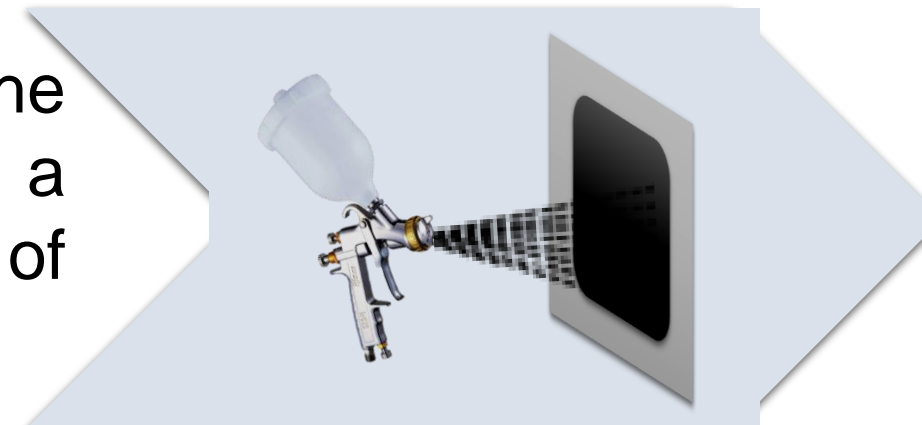
## MATERIALS AND METHODS

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 cm<sup>2</sup> was obtained



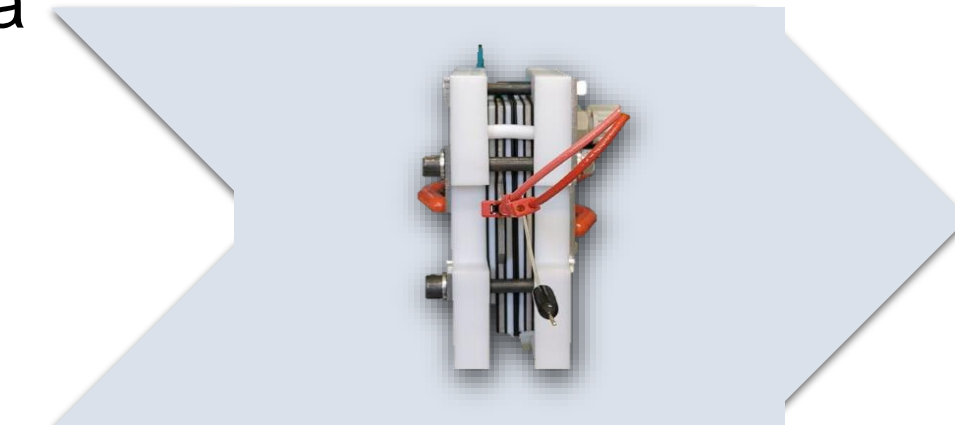
Electrochemical tests performed at ambient conditions in a continuous flow cell.

**3-Electrodes system**

W.E.: CuZnAl-based GDE

R.E.: Ag/AgCl

C.E.: Ir-MMO plate



## INVESTIGATION HIGHLIGHTS

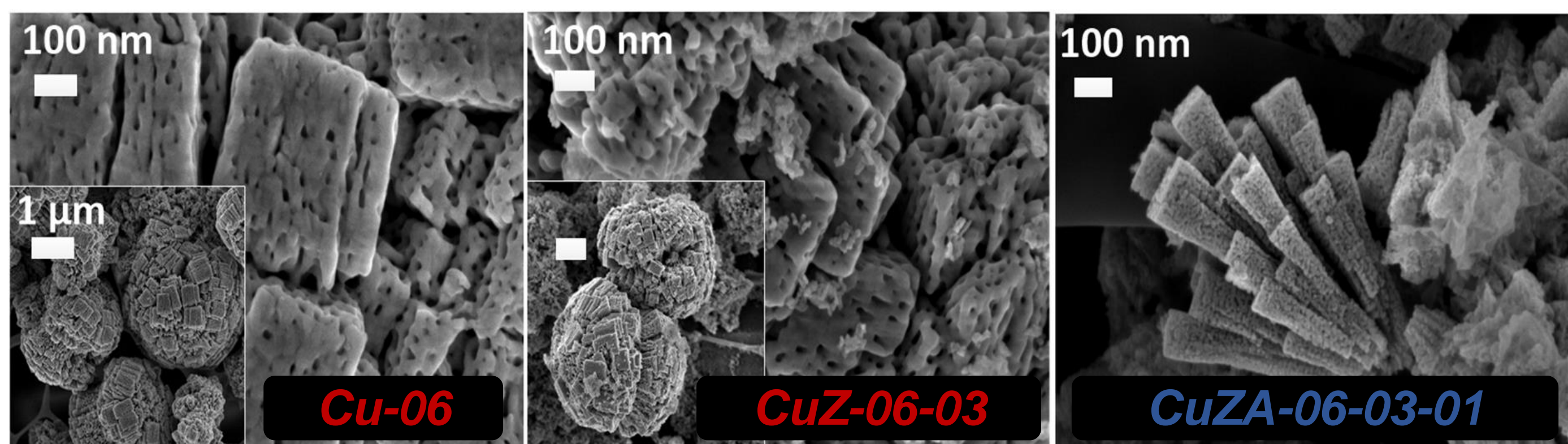


Fig. 1 FESEM images of the Cu-based electrocatalysts

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 <sup>2</sup> g <sup>-1</sup>	Total pore volume, cm <sup>3</sup> g <sup>-1</sup>	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).

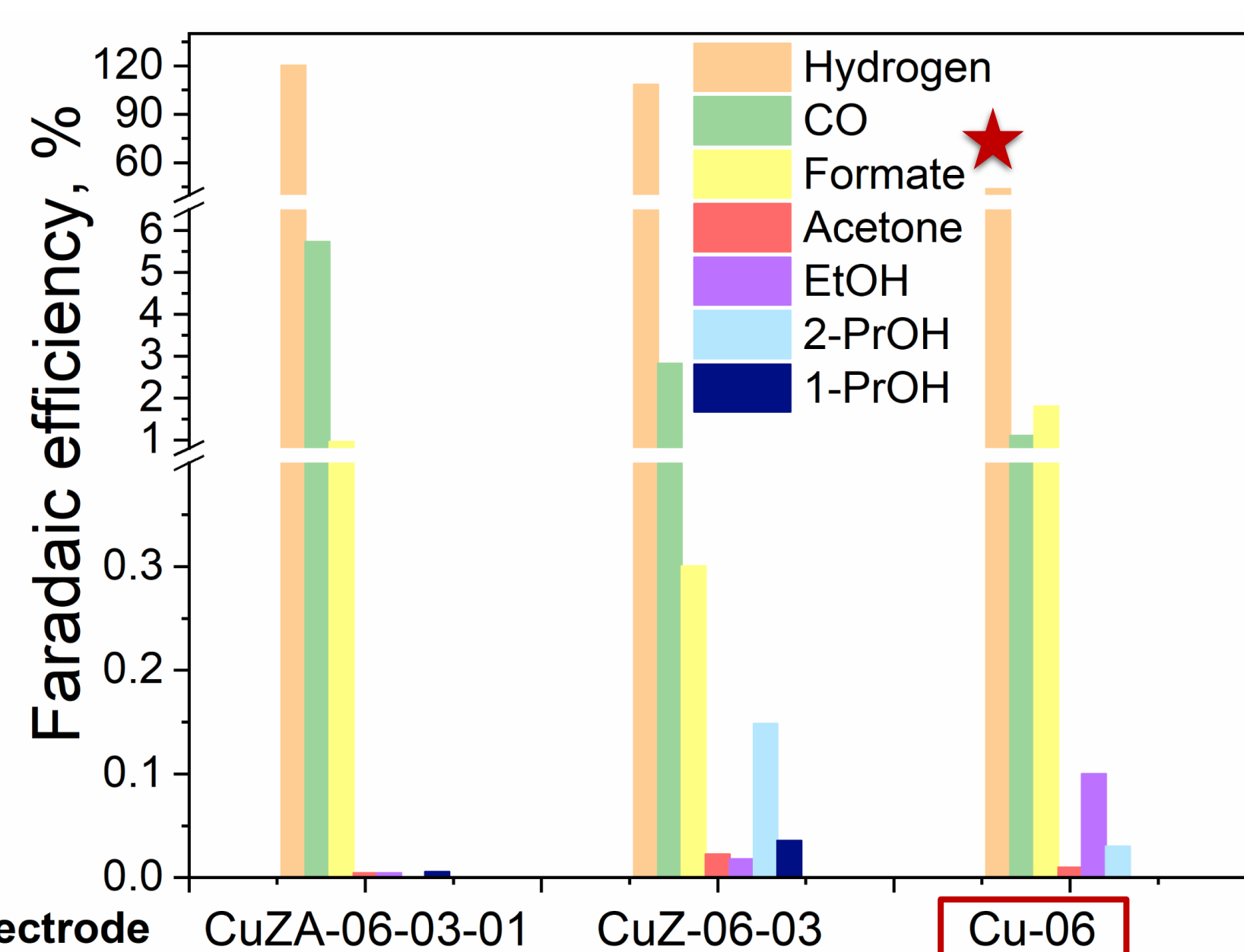


Fig. 2 Faradaic efficiencies of gaseous and liquid products at -1.5 V vs Ag/AgCl applied potential for different catalysts

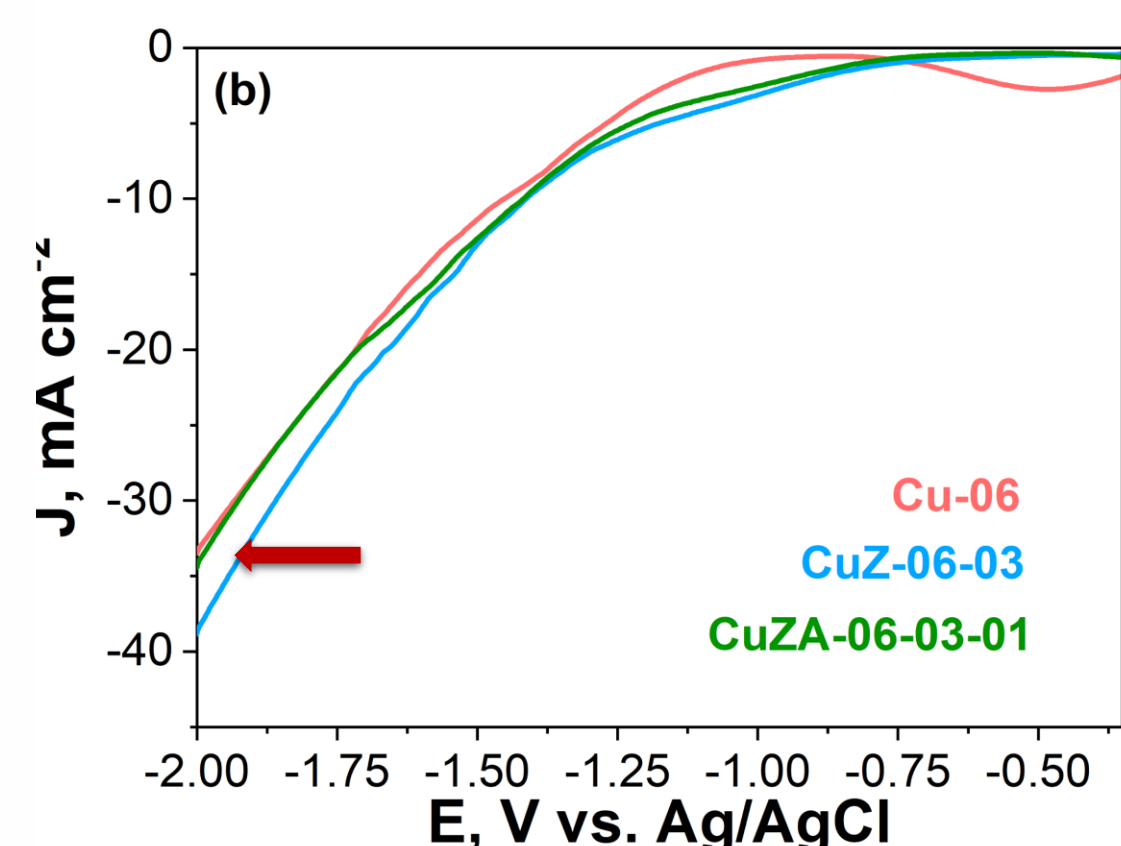


Fig. 3 Linear sweep voltammetry of the tested catalysts

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<sup>-2</sup>** were reached and the **FE toward H<sub>2</sub>** was hindered (★).

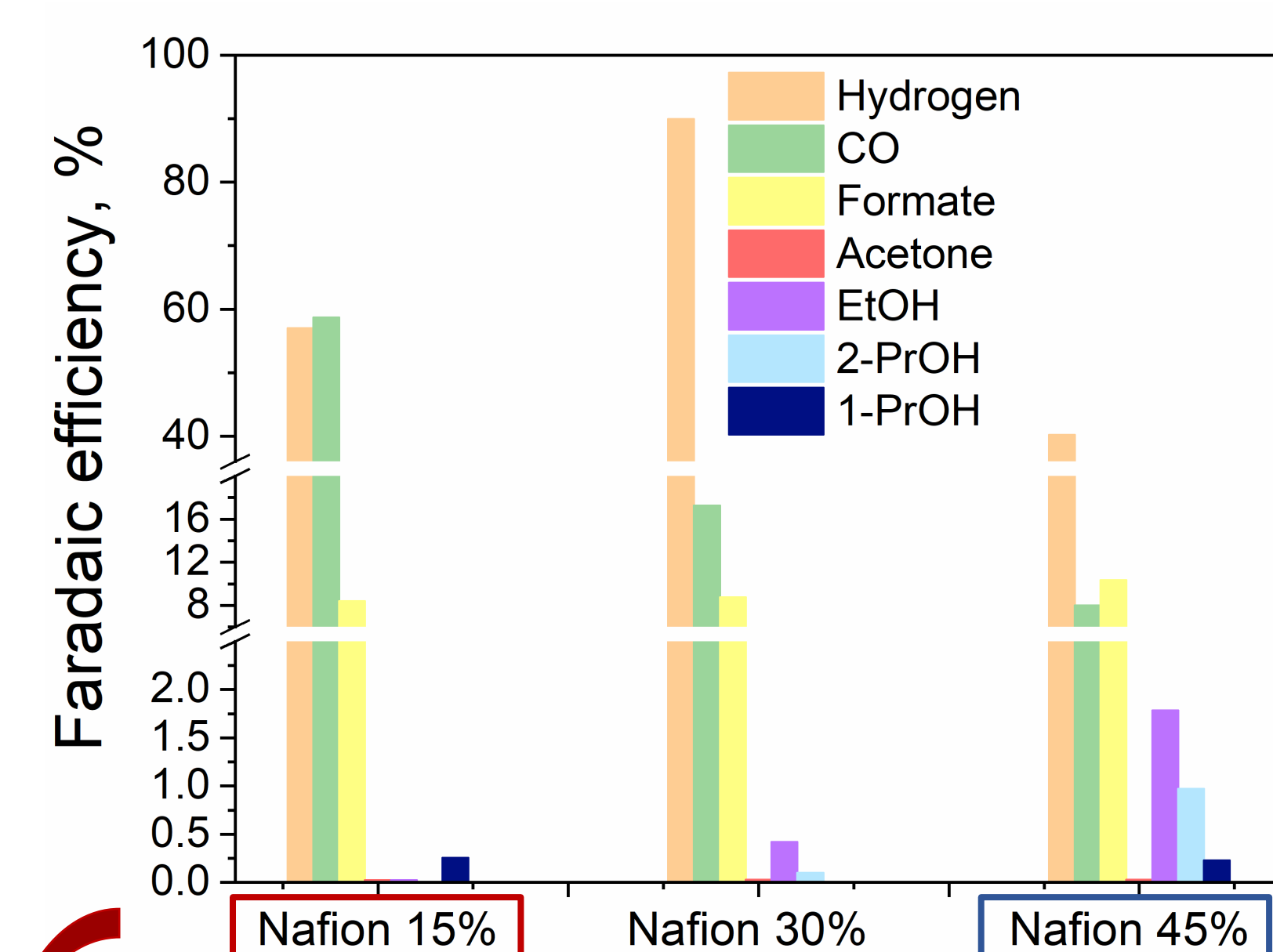
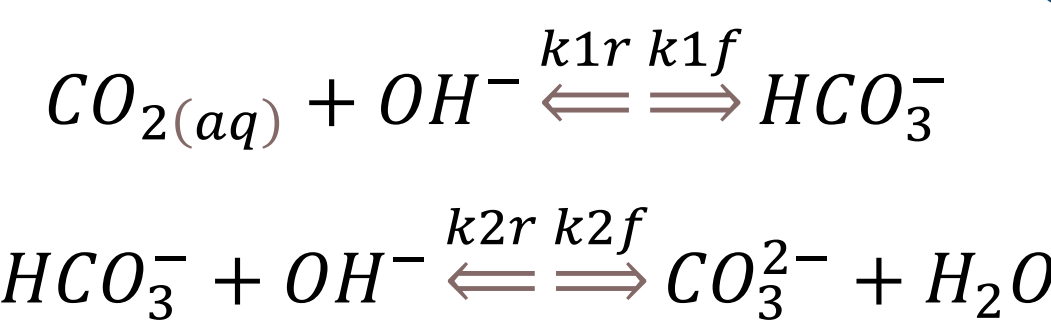


Fig. 4 Faradaic efficiencies of gaseous and liquid products at -1.5 V vs Ag/AgCl for Cu-06 with different Nafion content

A **lower** Nafion content has led to increase CO selectivity; whereas, a **higher** Nafion content has promoted C<sub>1+</sub> 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 CO<sub>2</sub> to carbonate and bicarbonate species

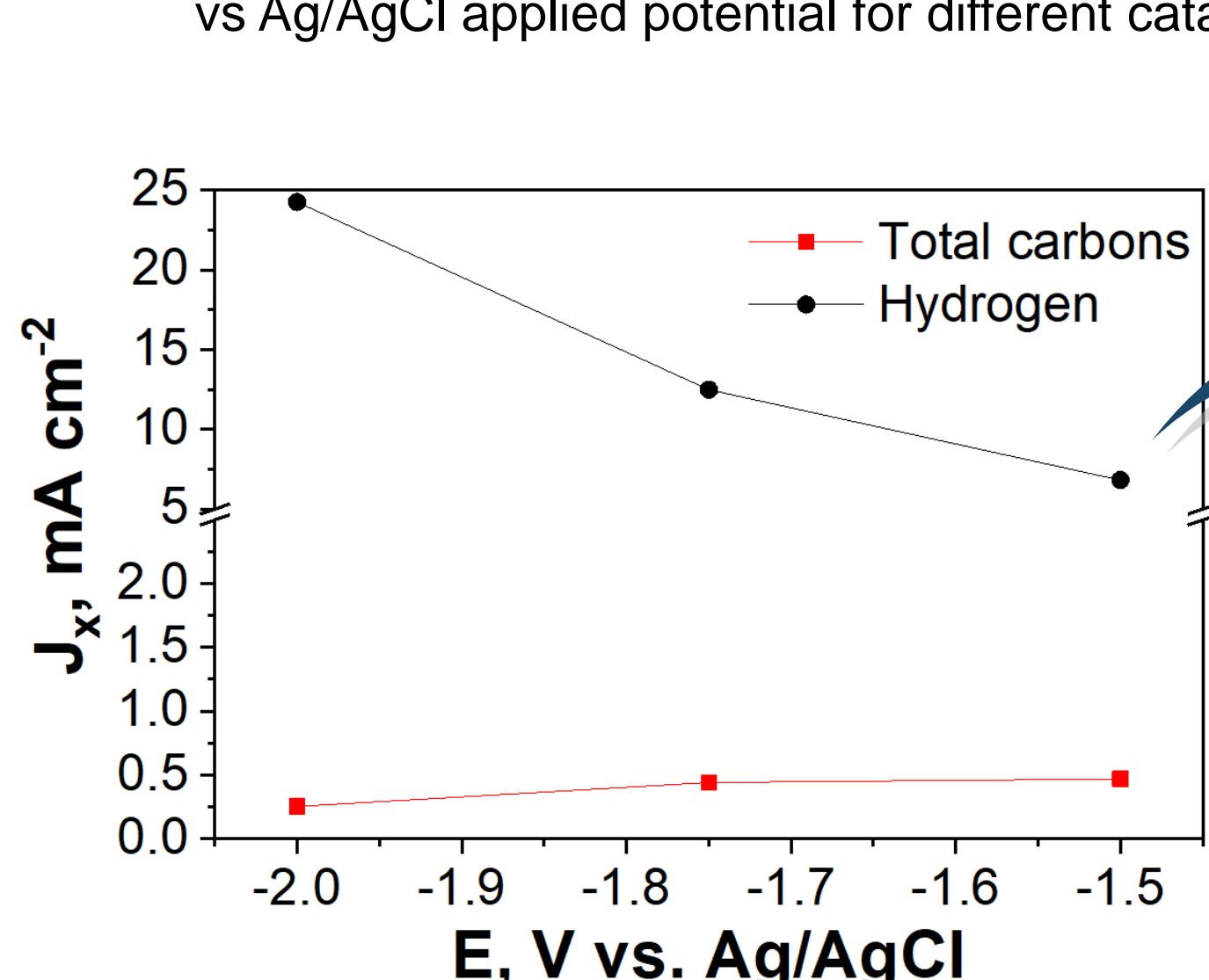


Fig. 5 Effect of applied potential on partial current densities

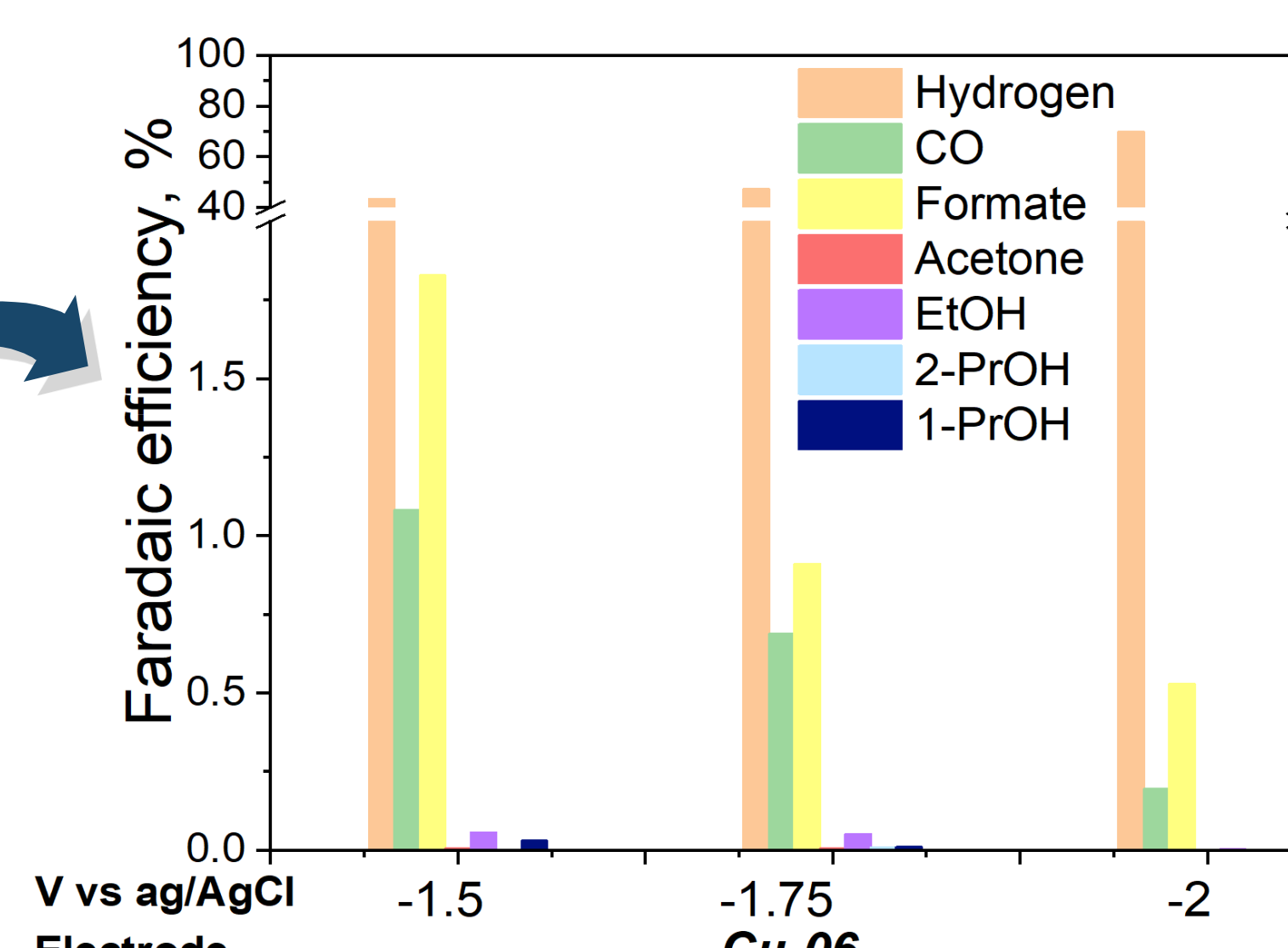


Fig. 6 Faradaic efficiencies of gaseous and liquid products

The highest FE and current density to H<sub>2</sub> 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 CO<sub>2</sub> 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.

## REFERENCES AND ACKNOWLEDGEMENTS

- H. Guzmán, F. Salomone, E. Batuecas, T. Tommasi, N. Russo, S. Bensaid and S. Hernández, *Chem. Eng. J.*, **2020**, 127973. DOI:10.1016/j.cej.2020.127973.
- H. Guzmán, N. Russo and S. Hernandez, *Green Chem.*, **2021**, 23(5), 1896-1920. DOI:10.1039/d0gc03334k.
- J. J. Lv, M. Jouny, W. Luc, W. Zhu, J. J. Zhu and F. Jiao, *Adv. Mater.*, **2018**, 30, 1-8. DOI:10.1002/adma.201803111
- H. Guzmán, F. Zammillo, D. Roldán, C. Galletti, N. Russo and S. Hernández, *Catalysts*, **2021**, 11(4), 482. DOI:10.3390/catal11040482.

The financial support of the SUNCOCHEM project (Grant Agreement No 862192) of the European Union's Horizon 2020 Research and Innovation Action programme is acknowledged.