

Cite this: *Mater. Adv.*, 2024,  
5, 2377

# CeO<sub>2</sub>-promoted Cu<sub>2</sub>O-based catalyst sprayed on the gas diffusion layer for the electroreduction of carbon dioxide to ethylene†

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The development of efficient and selective catalysts for the carbon dioxide reduction reaction (CO<sub>2</sub>RR) is crucial for sustainable energy and chemical synthesis. In this work, CeO<sub>2-y</sub> (y = C (cubic) and R (rod)) was incorporated into Cu<sub>2</sub>O nanocube electrocatalyst as a promoter for ethylene (C<sub>2</sub>H<sub>4</sub>) production. The results demonstrate that the catalyst with a loading of 5 wt% crystalline CeO<sub>2-C</sub> exhibits competitive activity and stability for ethylene production compared to pristine Cu<sub>2</sub>O. Under optimized reaction conditions of −250 mA cm<sup>−2</sup> current density and 1 M KOH electrolyte, the Cu<sub>2</sub>O–5CeO<sub>2-C</sub> catalyst achieved a faradaic efficiency (FE) of ~53% for C<sub>2</sub>H<sub>4</sub> production, while maintaining stability over a period of 120 minutes. In contrast, non-promoted Cu<sub>2</sub>O exhibited a lower FE for C<sub>2</sub>H<sub>4</sub> (~38%) and experienced partial deactivation after 45 minutes. The characterization of the catalysts before and after the reaction revealed that the interaction between Cu<sub>2</sub>O and CeO<sub>2-C</sub> creates intrinsic sites (Cu<sup>x</sup>–CeO<sub>2-x</sub>; Cu<sup>x</sup> = Cu<sup>2+</sup>, Cu<sup>+</sup>, and Cu<sup>0</sup>) for the binding of CO<sub>2</sub> and H<sub>2</sub>O molecules. Moreover, the Cu<sub>2</sub>O–5CeO<sub>2-C</sub> catalyst outperforms other reported systems in terms of FE and partial current density for C<sub>2</sub>H<sub>4</sub> production. It requires a lower potential (−0.98 V vs. RHE) to operate at the same electrolyte concentration. This finding highlights the promising nature of Cu<sub>2</sub>O–5CeO<sub>2-C</sub> as an efficient and cost-effective catalyst for C<sub>2</sub>H<sub>4</sub> production.

Received 15th November 2023,  
Accepted 19th January 2024

DOI: 10.1039/d3ma01009k

rsc.li/materials-advances

## Introduction

The electrochemical carbon dioxide reduction reaction (CO<sub>2</sub>RR) has attracted enormous interest due to its mild reaction conditions and potential to be used for renewable electricity storage via the production of synthetic fuels. Particularly, the CO<sub>2</sub>RR to ethylene (C<sub>2</sub>H<sub>4</sub>) aiming at high current densities and faradaic efficiencies (FE) is intensively studied because of the extremely high industrial value and the need to transition away from fossil fuel C<sub>2</sub>H<sub>4</sub> production.<sup>1</sup> Copper-based (Cu,<sup>2–4</sup> CuO<sup>5–8</sup> and Cu<sub>2</sub>O<sup>9–14</sup>) electrodes are proven to be the most used heterogeneous catalysts that tend to produce hydrocarbons and oxygenate compounds with competitive activity. However, as multi-step electron and proton transfer processes are involved in C<sub>2</sub>H<sub>4</sub> formation, hydrogen (H<sub>2</sub>) and other by-products such as

methane (CH<sub>4</sub>) will inevitably be produced during electrolysis. Therefore, the design of efficient catalysis systems specific for the CO<sub>2</sub>RR to ethylene with both high selectivity and high FE as well as low overpotential is highly desirable.

Various catalyst design strategies have been reported to effectively regulate the selectivity of the CO<sub>2</sub>RR.<sup>15–17</sup> Notably, by altering the electronic structure of Cu-based catalysts by the addition of a second metal<sup>18–20</sup> or metal oxide promoter<sup>21</sup> phase provides a significant improvement for C<sub>2</sub>H<sub>4</sub> production. Ceria (CeO<sub>2</sub>) is widely used as a catalyst, support and promoter for a variety of heterogeneous catalytic reactions involving the hydrogenation of CO<sub>2</sub><sup>22</sup> due to its acid–base and unique redox properties of oxygen storage and release.<sup>23</sup> The size and shape modification, surface/face reconstruction, and faceting of ceria at the nanoscale level can offer an important tool to govern activity and stability in these reactions.<sup>24</sup> Furthermore, strong interaction between noble metals and ceria leads to their higher dispersion, electronic modifications and enhanced catalytic activity.<sup>25</sup>

Recently, the implementation of CeO<sub>2</sub> as a support material for the CO<sub>2</sub>RR has been investigated by some researchers. For instance, a high methane (CH<sub>4</sub>) faradaic efficiency (up to ~54% at −1.2 V vs. RHE) over Cu/CeO<sub>2-x</sub> nanocrystalline heterodimers was reported by S. Varandili *et al.*<sup>26</sup> In another

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ma01009k>



study, Cu/CeO<sub>2</sub> carbon nanofiber (Cu/CeO<sub>x</sub>@CNF) catalysts synthesized by an electrospinning method were explored by X. Zong *et al.*<sup>27</sup> In this case, their optimized Cu/CeO<sub>x</sub>@CNF<sub>S-2</sub> catalyst exhibited a high CO faradaic efficiency (up to ~59% at -0.6 V vs. RHE) at a high current density of 100 mA cm<sup>-2</sup>. Most recently, Zhao *et al.*<sup>28</sup> have that the Cu electrode coating with CeO<sub>2</sub> nanoparticles largely enhanced the C<sub>2+</sub> product selectivity during CO<sub>2</sub> electroreduction. The FE and partial current density of C<sub>2+</sub> products on the CeO<sub>2</sub>-Cu electrode achieved in a gas-tight H-type electrolytic cell with 0.1 M KHCO<sub>3</sub> was 61% and 8.45 mA cm<sup>-2</sup> at -1.05 V vs. RHE, respectively. In that study, 1.5 mg cm<sup>-2</sup> was found to be the optimal CeO<sub>2</sub> coating. The improved CO<sub>2</sub>RR selectivity and activity of CeO<sub>2</sub>-Cu were attributed to the interface between Cu and CeO<sub>2</sub>, which promotes C-C coupling towards C<sub>2+</sub> production products. The CO<sub>2</sub>RR to C<sub>2+</sub> has also been evaluated over a CuO modified 20 wt% CeO<sub>2</sub> catalyst using a flow cell at 1 M KOH. Under those conditions, the reported faradaic efficiency of the C<sub>2+</sub> products was ~75.2% at a current density of 1.21 A cm<sup>-2</sup>. S. Yan *et al.*<sup>29</sup> revealed that CeO<sub>2</sub> and Cu and the subsurface Cu<sub>2</sub>O coexisted in CeO<sub>2</sub>/CuO during the CO<sub>2</sub>RR and two competing pathways for C-C coupling were promoted separately, of which hydrogenation of \*CO to \*CHO is energetically favoured.

In terms of the CO<sub>2</sub>RR to C<sub>2</sub>H<sub>4</sub>, the stabilization of Cu<sup>+</sup> within a CuO-CeO<sub>2</sub> interface has been reported by S. Chu *et al.*<sup>30</sup> They suggested that tuning the CuO/CeO<sub>2</sub> interfacial interaction permits dramatic suppression of proton reduction and enhancement of CO<sub>2</sub> reduction. The C<sub>2</sub>H<sub>4</sub> faradaic efficiency (up to ~50% at -1.1 V vs. RHE) was obtained over an optimised CuO/30 wt% CeO<sub>2</sub> using a liquid H-type cell with continuous CO<sub>2</sub> bubbling in 0.1 M KHCO<sub>3</sub> electrolyte. Lately, the effect of exposed facets of CeO<sub>2</sub> (cubes (100), rods (110), and octahedral (111)) has also been investigated under similar reaction conditions by S. Chu *et al.*<sup>31</sup> In the CeO<sub>2</sub>-supported Cu nanoparticles, they found that CeO<sub>2</sub> changed the oxidation state of Cu atoms towards Cu<sup>+</sup> at the CuO-CeO<sub>2</sub> interface. This fact was mainly identified on the Cu/CeO<sub>2</sub>(110), flowed by Cu/CeO<sub>2</sub>(100) and Cu/CeO<sub>2</sub>(111). The existence of Cu<sup>+</sup> species was supposed to be likely the adsorption and active sites for CO<sub>2</sub> activation followed by further C-C coupling to yield C<sub>2</sub>H<sub>4</sub>. The FE towards C<sub>2</sub>H<sub>4</sub> was ~39% on the Cu/CeO<sub>2</sub>(110) at a mild overpotential of 1.13 V. In another study performed on a flow-cell at high current density and under 1 M KOH, Ce-doped Cu nanoparticles (Ce-Cu NPs) were reported to be highly selective to C<sub>2</sub>H<sub>4</sub>. A high faradaic efficiency (FE) of C<sub>2</sub>H<sub>4</sub> close to 53% at a current density of 150 mA cm<sup>-2</sup> was achieved using a Ce/(Cu + Ce) precursor ratio = 10%. J. Shan *et al.*<sup>32</sup> suggested that the high performance, which is 2.8 times higher than Cu nanoparticles under the same conditions, is due to the shrinking of the particle sizes due to Ce doping resulting in more catalytic active sites with oxygen defects. It seems that the proximity of the Ce atoms can boost the local electronic distribution on the Cu nanoparticles. Under similar reaction conditions, anchoring CeO<sub>2</sub> quantum dots on to the CuO surface has been evaluated by S. Wang *et al.*<sup>33</sup> Their optimal catalyst consisting of 100 wt% CeO<sub>2</sub> and 50 wt% CuO achieved a high faradaic efficiency of

~50% for ethylene with a partial current density of 197 mA cm<sup>-2</sup>, attributed to the CuO/CeO<sub>2</sub> interfaces that simultaneously stabilize Cu<sup>+</sup> and key intermediates.

Despite these advances in CuO supported CeO<sub>2</sub> electrocatalysts for CO<sub>2</sub>RR to C<sub>2</sub>H<sub>4</sub>, the role of the CeO<sub>2</sub> as a promoter using Cu<sub>2</sub>O instead of CuO has not been investigated yet. Recent studies have revealed that the Cu<sub>2</sub>O phase provides a higher selectivity to ethylene compared to CuO.<sup>34</sup> Furthermore, the economic viability of most large-scale chemical processes relies on the use of simple and low-cost catalytic materials. Therefore, the implementation of CeO<sub>2</sub> as a promoter instead of bulk support is a practical way to design cost-effective electrocatalytic materials. In this line, the promoter content optimization into Cu<sub>2</sub>O can provide a highly active-stable, and low-cost electrocatalytic formulation for C<sub>2</sub>H<sub>4</sub> production.

Here, we developed a CeO<sub>2</sub>-promoted Cu<sub>2</sub>O-based catalyst sprayed on a carbon-based gas diffusion layer for the CO<sub>2</sub>RR to C<sub>2</sub>H<sub>4</sub>. A series of Cu<sub>2</sub>O-*x*CeO<sub>2</sub> were synthesized by the simple liquid phase reduction method. The influence of CeO<sub>2</sub> crystallinity and promoter loading (*x* = 5-20 wt%) was studied under relevant reaction conditions (current density (*j*) = -[50-300] mA cm<sup>-2</sup>, 1 M KOH, and flow of CO<sub>2</sub> (*F*<sub>CO<sub>2</sub></sub>) = 200 mL min<sup>-1</sup>). Furthermore, the influence of the KOH concentration (0.1-3 M) and electrolyte type (KOH, KCl, and KHCO<sub>3</sub>) over the optimized Cu<sub>2</sub>O-5CeO<sub>2</sub> GDE was investigated to identify the best reaction components. Lastly, its stability was additionally tested under the selected reaction conditions (*j* = -250 mA cm<sup>-2</sup>, electrolyte = 1 M KOH, and *F*<sub>CO<sub>2</sub></sub> = 200 mL min<sup>-1</sup>). The physico-chemical properties responsible for catalyst performance were studied using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman and photoelectron spectroscopy (XPS).

## Experimental section

### Chemicals and reagents

All chemical reagents used were of analytical grade without further treatment. Copper(II) sulfate [CuSO<sub>4</sub>, 99%] and Nafion<sup>®</sup> perfluorinated resin solution (5 wt% in a mixture of lower aliphatic alcohols and water, 45% water) were purchased from Sigma Aldrich. Cerium(III) nitrate hexahydrate [Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.5%] was purchased from Thermo Scientific. L(+)-Ascorbic acid [C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, 99%] was purchased from Acros Organics. Sodium hydroxide [NaOH, 97%], potassium hydroxide [KOH], and ethanol absolute [C<sub>2</sub>H<sub>6</sub>O, 99.8%] were purchased from Fisher Scientific. Ultrapure water was provided by Milli-Q Millipore source (18.2 MΩ cm, 20 °C).

### Preparation of the catalysts

The promoter phase, CeO<sub>2</sub>, was first synthesized using a hydrothermal method. In a typical synthesis, 3.25 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 15 mL of deionized water to obtain cerium nitrate aqueous solution. Then, a NaOH aqueous solution was prepared in a Teflon-lined steel reactor using 9 g



of NaOH and 50 mL of deionized water. The cerium nitrate aqueous solution was later added dropwise into the NaOH aqueous solution. After magnetic stirring for 30 min, the reactor was sealed and heated at two different temperatures of 80 °C and 240 °C for 24 h to obtain rod (R) and cubic (C) ceria particles, respectively. After cooling down to room temperature, the resulting precipitate was separated by centrifugation (4000 rpm for 5 min) and washed three times with excess ethanol, followed by drying in an oven overnight at 80 °C.

The series of CeO<sub>2</sub>-promoted Cu<sub>2</sub>O (Cu<sub>2</sub>O-*x*CeO<sub>2-*y*</sub>; *x* = 5, 10, 15 and 20 wt% and *y* = rod (R) and cubic (C) shape) samples were synthesized using a simple liquid phase reduction method. CuSO<sub>4</sub> (0.2689 g) and the respective amount of the promoter (CeO<sub>2</sub>) were dissolved into 50 mL of distilled water under sonication for 30 min and later by magnetic stirring for 30 min. Sequentially, 0.8 g NaOH was dissolved in 50 mL of distilled water and added to the mixture dropwise. In the next step, 0.7045 g of C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> as a reducing agent, was added to the mixture and kept constantly stirring for 30 min. Then, the CeO<sub>2</sub>-promoted Cu<sub>2</sub>O catalysts were centrifuged at 4000 rpm for 5 min and washed three times with excess ethanol. Finally, they were dried overnight in an oven at 80 °C. A non-promoted Cu<sub>2</sub>O was also synthesized using the same procedure.

### Preparation of gas diffusion electrode (GDE)

The GDE usually consists of a gas diffusion layer (GDL) on which a catalytic layer is deposited. The carbon-based GDL (Freudenberg H23C6) was used as the support. A catalytic ink was formulated by mixing 20 mg of the as-prepared catalyst, 0.5 mL of ethanol absolute and 140 μL of Nafion<sup>®</sup> perfluorinate. The ink deposition on the GDL was performed using the spray coating technique. The catalyst loading mass was fixed to 1 ± 0.05 mg cm<sup>-2</sup> according to the previous control test, see Fig. S11 (ESI<sup>†</sup>). After the catalyst deposition, GDEs were dried at room temperature. The GDEs were denoted as Cu<sub>2</sub>O, Cu<sub>2</sub>O-5CeO<sub>2-C</sub>, Cu<sub>2</sub>O-10CeO<sub>2-C</sub>, Cu<sub>2</sub>O-15CeO<sub>2-C</sub>, Cu<sub>2</sub>O-20CeO<sub>2-C</sub>, CeO<sub>2-C</sub>, Cu<sub>2</sub>O-5CeO<sub>2-R</sub>, and CeO<sub>2-R</sub>. Fig. S12 (ESI<sup>†</sup>) shows a systematic representation of the catalyst and GDE preparation.

### CO<sub>2</sub> electroreduction set-up

The electrocatalytic tests were carried out using a compact H-type electrochemical cell.<sup>35</sup> The cell is shown in Fig. S13 (ESI<sup>†</sup>), and included a current collector made of stainless steel with a built-in spiral flow field, which connected the cathode compartment and the GDE of the cell and guaranteed homogeneous distribution of the inlet reactants. In the first series of experiments, the influence of the promoter phase (CeO<sub>2</sub>) was investigated using a CO<sub>2</sub> flow rate of 200 mL min<sup>-1</sup>, which was adjusted by a manual flow meter (FR2000, Key Instruments). The working gas diffusion electrodes had a projected area of 1 cm<sup>2</sup> to the 1 M KOH aqueous electrolyte, while a platinum square mesh of 1 × 1 cm<sup>2</sup> was used as the counter electrode, located at the anode compartment and separated from the catholyte compartment by a proton exchange membrane (PEM, Nafion<sup>®</sup> 115) and immersed in 1 M KOH aqueous electrolyte. The total volume of the electrolyte was 150 mL. The reference

electrode was an Hg/HgO (1 M NaOH) electrode. The potential values were then translated into RHE (reversible hydrogen electrode) voltages by using eqn (1) and verified by a hydrogen reference electrode (Hydroflex<sup>®</sup> (M-v01-0071)).

$$E(\text{vs. RHE}) = E\left(\text{vs. } \frac{\text{Hg}}{\text{HgO}}\right) + 0.14 \text{ V} + 0.059 \text{ V} \times \text{pH} \quad (1)$$

For each electrode, the faradaic efficiency (FE) was evaluated by varying the current density from -50 to -300 mA cm<sup>-2</sup> ( $\Delta j = -50 \text{ mA cm}^{-2}$ ) and using cronopotentiometry (PGSTAT204, Metrohm-Autolab). At each current density, the presence of gas products from the cathode outlet stream was examined for 5 minutes. During this time, the volume of the outlet products was measured and then analysed using an on-line gas chromatography (Shimadzu GC 2030) equipped with a Porapak Q 80/100 column. The gases (H<sub>2</sub>, CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) were detected using a thermal conductivity detector (TCD) and a flame ionization detector (FID).

After the identification of the most promising Ce-promoted copper-based GDE, the influence of the KOH concentration (0.1 M-3 M) and electrolyte type (KCl, KOH, KHCO<sub>3</sub>) over the optimized Cu<sub>2</sub>O-5CeO<sub>2-C</sub> GDE was additionally investigated to find the most effective electrolyte conditions. Finally, a stability test was performed at the selected reaction conditions ( $j = -250 \text{ mA cm}^{-2}$ , electrolyte = 1 M KOH,  $F_{\text{CO}_2} = 200 \text{ mL min}^{-1}$ ).

The FE<sub>X</sub> of the X obtained products, such as C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>, were estimated by using the following equation (eqn 2):

$$\text{FE}_X = \frac{Q_X}{Q_{\text{Total}}} = \frac{n_X N_X F}{Q_{\text{Total}}} \quad (2)$$

where  $Q_X$  and  $Q_{\text{Total}}$  are the charge passed to produce product X and the total passed charge (C) during CO<sub>2</sub>RR,  $n_X$  represents the electron transfer number of product X,  $N_X$  is the product amount (mol) of X measured by the GC, and  $F$  is the Faraday constant (96 485 C mol<sup>-1</sup>).

### Catalyst characterization

The series of catalysts sprayed on the carbon-based gas diffusion layer were characterized by different physico-chemical techniques like scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman and photoelectron spectroscopy (XPS).

The surface morphology and elemental composition were investigated using a JEOL JSM-7200F high-resolution SEM equipped with an EDX detector (Oxford instruments) and AZtecEnergy software. Prior to EDX analysis, catalysts were fixed over an aluminium holder. Elemental analysis was carried out at 20 kV and restricted to Cu, Ce, and O to avoid inconsistent results. TEM images were recorded on a FEI Tecnai T12 electron microscope operating at 120 kV. The powder samples were dispersed by ultrasound in ethanol. Suspension drops were deposited on a holey carbon-coated copper grid of 300 mesh and then dried in air.

The crystal structure of the catalysts was examined using a Bruker type XRD D2 Phaser diffractometer. X-ray powder



diffraction patterns were acquired by applying a Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), a voltage of 40 kV, and a current of 40 mA. Continuous scans were collected over the  $2\theta$  range of  $10^\circ$  to  $80^\circ$ . The crystalline phases present in the samples were identified by comparison with reference patterns available in the JCPDS database. The crystallite sizes of the main Cu $^x$  species (Cu $_2$ O, CuO and Cu $^0$ ) and cerium oxide (CeO $_2$ ) were estimated using the Scherrer's equation at  $2\theta = 36.46^\circ$  for Cu $_2$ O (111),  $38.76^\circ$  for CuO (111),  $43.32^\circ$  for Cu (111), and  $28.53^\circ$  for CeO $_2$  (111);  $D = (K\lambda/\beta \cos \theta)$ , where  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width of the diffraction line at half maximum (FWHM), and  $\theta$  is the Bragg angle.

Raman measurements were recorded on a Raman spectrometer (Horiba LabRAM HR800) equipped with a CCD detector, using a laser with a wavelength of 532 nm as the excitation source. The Raman spectra were obtained using a x50LWD objective with an incident power of 0.1 mW (5 acquisitions, 60 s of exposure time).

X-ray photoelectron spectroscopy (XPS) experiments were performed in a PHI 5500 Multitechnique System (from Physical Electronics) with a monochromatic X-ray source (Al K $\alpha$  1486.6 eV).

## Results and discussion

### Characterization

SEM images displayed in Fig. SI4 (ESI $^\dagger$ ) evidenced that the formation of particles with cubic-like morphology was achieved for both the active phase (Cu $_2$ O) and promoter phase (CeO $_2$ -c) prepared at  $240^\circ\text{C}$ . In the case of CeO $_2$ -r prepared at  $80^\circ\text{C}$ , its morphology was not possible to identify by SEM because the particle sizes were below the detection limits. When the electrocatalysts were synthesised in the presence of CeO $_2$ -c, a catalytic system composed of particles with a cubic shape was also achieved for the series of CeO $_2$ -c-promoted Cu $_2$ O-based catalyst. Furthermore, EDX analysis performed over all catalysts proved the presence of their main components (Cu, Ce, and O). As a representative example, the EDX elemental mapping image exhibited in Fig. 1 demonstrated the experimental composition (82 wt% Cu, 5 wt% Ce, and 13 wt% O) and interaction between the cubic particles of the Cu $_2$ O-5CeO $_2$ -c catalyst.

A summary of the elemental composition of all the as-prepared catalysts is shown in Table 1. The experimental composition of the CeO $_2$  promoter phase falls within the range of 6–21 wt%  $\pm 1$ , which closely matches the theoretical values. On the other hand, a slight difference in the elemental composition was mainly identified between the two synthesized promoters (CeO $_2$ -r (81 wt% Ce and 19 wt% O) and CeO $_2$ -c (83 wt% Ce and 17 wt% O)), suggesting the possible presence of different oxidation state of cerium (Ce $^{3+}$  and Ce $^{4+}$ ) over these samples. Therefore, the used temperature for the synthesis of CeO $_2$  nanoparticles can be a key parameter for the generation of Ce $^{3+}$  and Ce $^{4+}$ .

The cubic-like morphology of the CeO $_2$ -c promoter (Fig. 2(a)) and pristine Cu $_2$ O (Fig. 2(b)) was additionally confirmed by

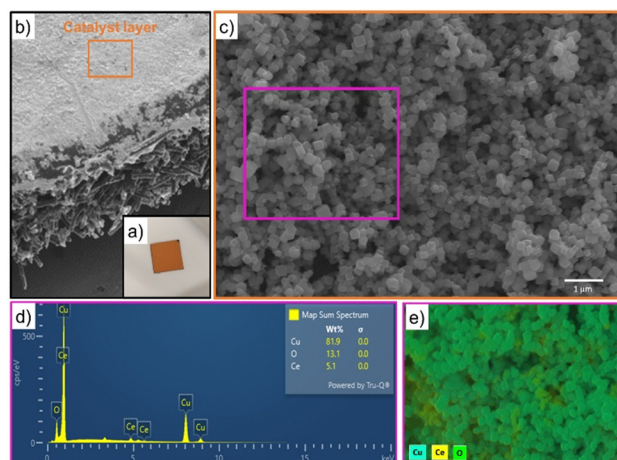


Fig. 1 Surface morphology and elemental composition analysis for the Cu $_2$ O-5CeO $_2$ -c GDE. (a) Image of the as-prepared GDE. (b) SEM image showing the catalyst layer and the carbon-based GDL. (c) SEM image of the electron micrograph region, (d) EDX spectrum, (e) and distribution of Cu, Ce and O in elemental mapping.

Table 1 Elemental composition of the catalysts

Sample	Elemental composition		
	Cu	Ce	O
			[wt% $\pm 2$ ]
Cu $_2$ O	89	—	11
Cu $_2$ O-5CeO $_2$ -c	82	5	13
Cu $_2$ O-10CeO $_2$ -c	75	9	16
Cu $_2$ O-15CeO $_2$ -c	70	12	18
Cu $_2$ O-20CeO $_2$ -c	62	17	21
CeO $_2$ -c	—	83	17
CeO $_2$ -r	—	81	19
Cu $_2$ O-5CeO $_2$ -r	81	4	15

TEM. Regarding the CeO $_2$ -r, rod-like morphologies with particle sizes of  $\sim 8$  nm and irregular length can be identified, see Fig. SI5 (ESI $^\dagger$ ). Between cubic particles, the main difference observed was the size. The cubic CeO $_2$ -c particles ( $\sim 29$  nm)

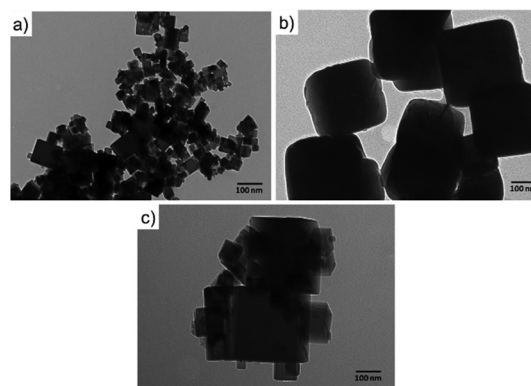


Fig. 2 TEM images of the (a) CeO $_2$ -c, (b) Cu $_2$ O, and (c) Cu $_2$ O-5CeO $_2$ -c catalysts.



were smaller than cubic  $\text{Cu}_2\text{O}$  particles ( $\sim 165$  nm). The interaction between the  $\text{CeO}_{2-\text{C}}$  and  $\text{Cu}_2\text{O}$  particles was clearly detected over a series of  $\text{Cu}_2\text{O}-\text{CeO}_{2-\text{C}}$  catalysts. Fig. 2(c) is an example of the strong  $\text{Cu}_2\text{O}-\text{CeO}_2$  interaction achieved over the  $\text{Cu}_2\text{O}$  catalyst promoted by 5 wt%  $\text{CeO}_{2-\text{C}}$ . For this  $\text{CeO}_{2-\text{C}}$ -promoted  $\text{Cu}_2\text{O}$  catalyst, a decrease in the  $\text{Cu}_2\text{O}$  particle sizes was found, suggesting that the addition of  $\text{CeO}_2$  during the synthesis inhibits the growth of  $\text{Cu}_2\text{O}$  particles. The average particle sizes estimated for  $\text{CeO}_{2-\text{C}}$  and  $\text{Cu}_2\text{O}$  were 43 nm and 160 nm, respectively.

The XRD patterns of the  $\text{CeO}_{2-\text{C}}$  promoter, pristine  $\text{Cu}_2\text{O}$  and the series of  $\text{CeO}_{2-\text{C}}$ -promoted  $\text{Cu}_2\text{O}$  are shown in Fig. 3. The XRD profiles confirmed the phase purity of the polycrystalline  $\text{CeO}_2$  (JCPDS: 00-034-0394) and  $\text{Cu}_2\text{O}$  (JCPDS: 00-005-0667). For the  $\text{CeO}_{2-\text{C}}$  sample, the high-intensity reflections are observed at  $2\theta = 28.53, 33.09, 47.48, 56.33, 59.08, 69.41, 76.69,$  and  $79.04^\circ$  corresponding to the  $\text{CeO}_2$  (111), (200), (220), (311), (222), (400), (331), (420) lattice planes. On the other hand, the diffraction peak at around  $2\theta = 29.61, 36.46, 42.34, 61.42,$  and  $73.56^\circ$  represent the  $\text{Cu}_2\text{O}$  (110), (111), (200), (220), and (311) lattice planes. Over the series of  $\text{Cu}_2\text{O}-\text{CeO}_{2-\text{C}}$  catalysts,  $\text{CeO}_2$  and  $\text{Cu}_2\text{O}$  reflections were identified at a similar  $2\theta$  position, but with differences in their relative intensity, in agreement with the composition. With higher  $\text{CeO}_2$  content, the intensity of the reflections of  $\text{CeO}_2$  increased, while the reflections of  $\text{Cu}_2\text{O}$  were decreased. Compared to  $\text{CeO}_{2-\text{C}}$  promoter, the XRD profiles of  $\text{CeO}_{2-\text{R}}$  suggested that the sample appeared to be composed of small particles. Only four reflections were identified for the  $\text{CeO}_{2-\text{R}}$ . As can be seen in Fig. S16 (ESI<sup>†</sup>), the reflections related to  $\text{CeO}_2$  phase in the  $\text{Cu}_2\text{O}-\text{CeO}_{2-\text{R}}$  were under the detection limit. These reflections were identified at  $2\theta = 28.53, 33.09, 47.48, 56.33^\circ$  and associated to the  $\text{CeO}_2$  (111), (200), (220), (311) lattice planes.

On the other hand, Raman spectroscopy analysis was additionally performed over the most promising fresh samples ( $\text{CeO}_{2-\text{C}}$ ,  $\text{Cu}_2\text{O}$ , and  $\text{Cu}_2\text{O}-5\text{CeO}_{2-\text{C}}$ ) taking into consideration that the formation of defective sites can be interpreted by the alteration in M–O vibration frequency after  $\text{CeO}_2$  introduction to the  $\text{Cu}_2\text{O}$  structure. Fig. 4 proved that the fluorite-type cubic

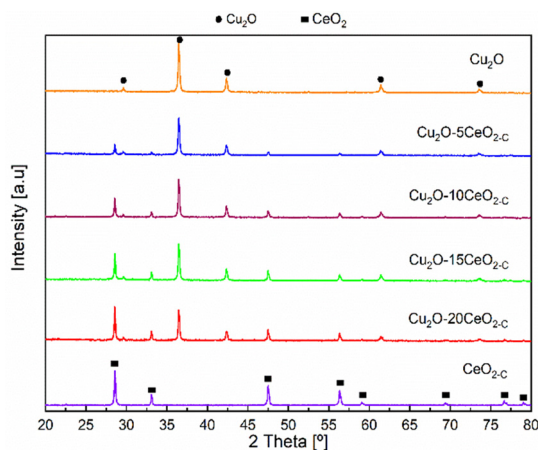


Fig. 3 XRD Patterns of the catalysts.

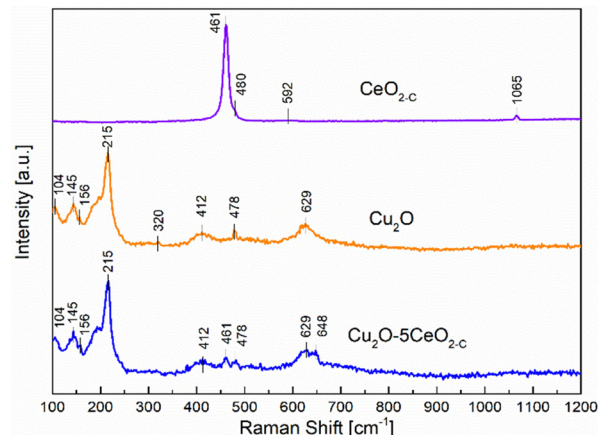


Fig. 4 Raman spectrum of  $\text{CeO}_{2-\text{C}}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}-5\text{CeO}_{2-\text{C}}$  catalysts.

crystal structure of ceria in the  $\text{CeO}_{2-\text{C}}$  sample exhibits one first-order Raman active fundamental mode located at  $461\text{ cm}^{-1}$ .<sup>36</sup> This  $\text{F}_{2g}$  mode was associated with the symmetric vibrations of oxygen ions around  $\text{Ce}^{4+}$  ions in octahedral  $\text{Ce}-\text{O}_6$ .<sup>37</sup> The bands at  $480$  and  $592\text{ cm}^{-1}$  were attributed to the oxygen vacancies due to the presence of reduced  $\text{Ce}^{3+}$  cations ( $\text{Ce}^{3+}\text{O}_6$ )<sup>38</sup> and the vacancy-interstitial Frenkel-type oxygen intrinsic defects in pure ceria,<sup>39</sup> respectively. Additionally, solid-state phonons assigned to second-order features  $2\omega\text{R}(X)$  were observed at  $1065\text{ cm}^{-1}$ .<sup>40</sup>

In the non-promoted  $\text{Cu}_2\text{O}$  sample, the most intense Raman peak identified at  $215\text{ cm}^{-1}$  was related to the second-order overtone  $2\Gamma_{12}^-$ .<sup>41</sup> The remaining Raman bands were assigned as follows: an inactive mode  $\Gamma_{12}^-$  at  $104\text{ cm}^{-1}$ , an IR active mode  $\Gamma_{15}^{(1)}$  (LO) at  $145\text{ cm}^{-1}$ , a fourth order overtone  $4\Gamma_{12}^-$  at  $412\text{ cm}^{-1}$ , and an IR active mode  $\Gamma_{15}^{(1)}$  (TO) at  $629\text{ cm}^{-1}$ .<sup>42-44</sup> In addition to the prominent peaks observed for  $\text{Cu}_2\text{O}$ , a weak band was also observed at  $320\text{ cm}^{-1}$ , which corresponds to the  $\text{A}_g$  mode of  $\text{CuO}$ .<sup>45</sup> On the other hand, the introduction of  $\text{CeO}_2$  into the  $\text{Cu}_2\text{O}$  structure induced the formation of a new extrinsic  $\text{MO}_8$  site capable of delivering oxygen under reducing conditions, *i.e.* part of a Frenkel defect.<sup>46</sup> This new Raman peak identified over the  $\text{Cu}_2\text{O}-5\text{CeO}_{2-\text{C}}$  catalyst located at  $648\text{ cm}^{-1}$  can be probably an effect of the strong interaction between  $\text{Cu}^+$  and  $\text{Ce}^{3+}$  cations.<sup>47</sup> Furthermore, the presence of the  $\text{CuO}$  phase was not identified in comparison with the  $\text{Cu}_2\text{O}$  sample, implying that  $\text{CeO}_2$  avoids overoxidation of  $\text{Cu}_2\text{O}$  and preserves the  $\text{Cu}(i)$  oxidation state.

The surface elemental composition and chemical state of the fresh  $\text{CeO}_{2-\text{C}}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}-5\text{CeO}_{2-\text{C}}$  samples were examined by X-ray photoelectron spectroscopy. The survey scan in Fig. S17 (ESI<sup>†</sup>) shows the presence of C, Cu, Ce and O. The C 1s peak at  $284.4\text{ eV}$  was used as a reference peak for calibration of all the spectra. The high-resolution XPS spectra of Cu 2p are presented in Fig. 5. The peaks at  $932.1\text{ eV}$  and  $951.9\text{ eV}$  were linked to  $\text{Cu}^+ 2p_{3/2}$  and  $\text{Cu}^+ 2p_{1/2}$ , respectively. Furthermore, characteristic shoulder peaks can also be resolved at  $934.8$  and  $954.8\text{ eV}$ , which were associated with  $\text{Cu}^{2+} 2p_{1/2}$  and  $\text{Cu}^{2+} 2p_{3/2}$ , respectively. The presence of satellite peaks at the binding



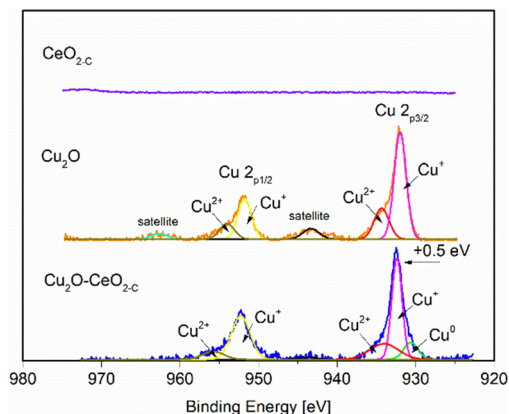


Fig. 5 Cu 2p XPS spectra of  $\text{CeO}_{2-\text{C}}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}-5\text{CeO}_{2-\text{C}}$  catalysts.

energies of 943.4 indicated that Cu(I) was the major valence state for Cu species.<sup>48</sup>

The peaks of the  $\text{Cu}_2\text{O}-5\text{CeO}_{2-\text{C}}$  nanocomposites shift in the direction of high binding energy compared with that of the  $\text{Cu}_2\text{O}$  nanocrystals. The difference between the two peaks is 0.5 eV from the binding energy, which indicates that there is an electronic exchange between  $\text{Cu}_2\text{O}$  and  $\text{CeO}_2$ . In particular, the  $\text{Cu}^0$  phase was identified in the  $\text{Cu}_2\text{O}-5\text{CeO}_{2-\text{C}}$  sample, suggesting that  $\text{CeO}_2$  promotes the reduction of  $\text{CuO}$ . Regarding the  $\text{CeO}_2$  phase (see Fig. S18, ESI<sup>†</sup>), peaks at 881.9, 888.1, 897.9,

899.8, 901.8, and 916.1 eV were only detected in the Ce 3d spectrum of the  $\text{CeO}_2$  sample, corresponding to the binding energies of  $\text{Ce}^{4+} 3d_{5/2}$ ,  $\text{Ce}^{3+} 3d_{5/2}$ ,  $\text{SU}_1$ ,  $\text{Ce}^{4+} 3d_{3/2}$ ,  $\text{SU}_2$ , and  $\text{Ce}^{3+} 3d_{3/2}$ , respectively.<sup>49</sup> Fig. S19 (ESI<sup>†</sup>) depicts the high-resolution O 1s spectra of the different catalysts. The characteristic peaks resolved in the binding energy range of 534.6 to 526.3 eV were assigned to lattice oxygen ( $\text{O}_{\text{lat}}$ ) and oxygen vacancies ( $\text{O}_{\text{Vs}}$ ).<sup>50,51</sup> Compared to  $\text{Cu}_2\text{O}$ , the relative proportion of oxygen vacancies was higher for the  $\text{Cu}_2\text{O}-5\text{CeO}_2$ . The  $\text{O}_{\text{Vs}}$  are renowned for their possession of weakly bound electrons, serving as exceptional Lewis base sites for  $\text{CO}_2$  adsorption. These electrons contribute to the formation of the  $\text{CO}_2^{\bullet-}$  intermediate by providing electron donation.<sup>52,53</sup> Therefore, this indicates that the  $\text{Cu}_2\text{O}-5\text{CeO}_2$  exhibits the strongest ability for  $\text{CO}_2$  adsorption and subsequent electrochemical reduction.

### $\text{CO}_2\text{RR}$

**$\text{CeO}_2$  loading.** Fig. 6 illustrates the influence of  $\text{CeO}_{2-\text{C}}$  loading on a series of  $\text{Cu}_2\text{O}$ -based gas diffusion electrodes (GDEs). During the  $\text{CO}_2$  electroreduction reaction in 1 M KOH, the main products detected across all GDEs were  $\text{C}_2\text{H}_4$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{H}_2$ . Within the evaluated range of current densities ( $-50$  to  $-300 \text{ mA cm}^{-2}$ ), the faradaic efficiencies for  $\text{C}_2\text{H}_4$  production were consistently higher in the  $\text{CeO}_{2-\text{C}}$ -promoted  $\text{Cu}_2\text{O}$ -based GDEs compared to the non-promoted

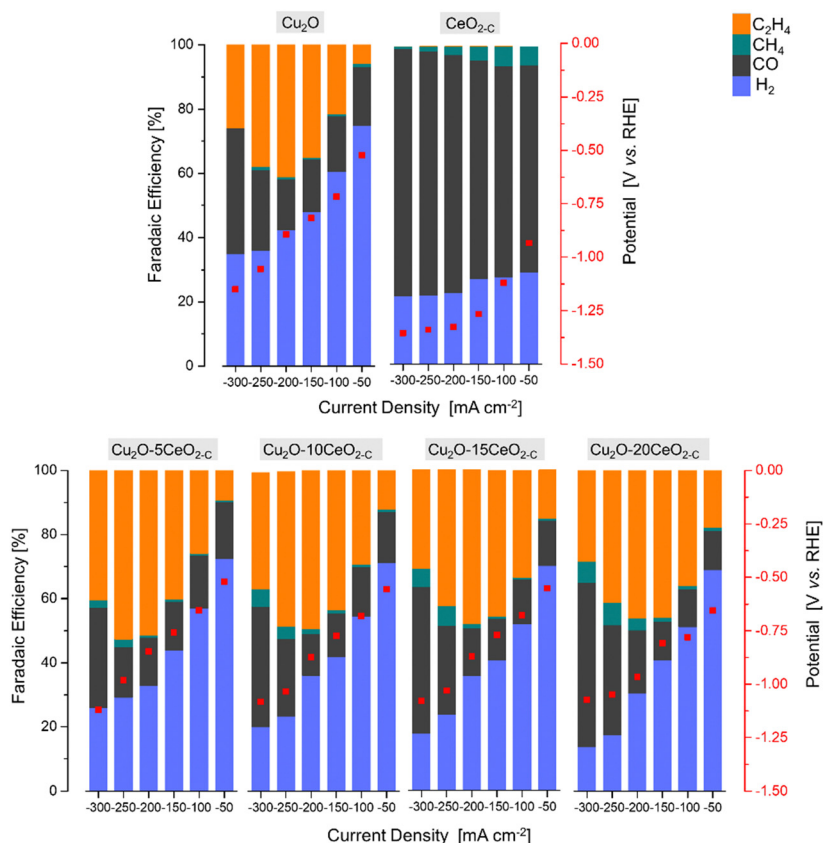


Fig. 6 The faradaic efficiency [%] and potential [V vs. RHE] as a function of the current density [ $\text{mA cm}^{-2}$ ] over the series of  $\text{Cu}_2\text{O}$ -based GDEs.



Cu<sub>2</sub>O GDE. This indicates that the incorporation of the CeO<sub>2-C</sub> promoter phase is beneficial for enhancing C<sub>2</sub>H<sub>4</sub> formation during the CO<sub>2</sub>RR.

The product formation on the CeO<sub>2-C</sub> electrode starts at approximately  $-0.93$  V vs. RHE, see Fig. 6. The achieved faradaic efficiencies (FEs) for C<sub>2</sub>H<sub>4</sub> were lower compared to the FEs for other sub-products such as H<sub>2</sub>, CO, and CH<sub>4</sub>. The maximum FE<sub>C<sub>2</sub>H<sub>4</sub></sub> observed for this electrode was 0.6% at  $-1.34$  V vs. RHE, and this was achieved at a high current density ( $j = -250$  mA cm<sup>-2</sup>). In contrast, when the current densities exceeded  $-150$  mA cm<sup>-2</sup>, a noticeable increase in FE<sub>CO</sub> ( $>75%$  at  $-1.33$  V vs. RHE) and a decrease in FE<sub>CH<sub>4</sub></sub> ( $<3%$  at  $-1.33$  V vs. RHE) were observed. Comparing with the CeO<sub>2-C</sub> electrode, the Cu<sub>2</sub>O electrode exhibited a maximum FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of approximately 41% at  $-0.87$  V vs. RHE, which was achieved at a current density of  $-200$  mA cm<sup>-2</sup>. The onset potential for C<sub>2</sub>H<sub>4</sub> formation (approximately  $-0.52$  V vs. RHE) was lower compared to the CeO<sub>2-C</sub> electrode.

The observed behaviour of faradaic efficiencies (FEs) for the Cu<sub>2</sub>O–CeO<sub>2-C</sub> series indicates that a lower amount of the CeO<sub>2</sub> promoter is favoured to enhance C<sub>2</sub>H<sub>4</sub> production. In this case, the potential at which C<sub>2</sub>H<sub>4</sub> formation starts ranged between  $-0.52$  and  $-0.67$  V vs. RHE. It is noteworthy that the maximum FEs for C<sub>2</sub>H<sub>4</sub> were shifted towards lower current densities due to the increased CeO<sub>2</sub> loading. Furthermore, the FE<sub>CO</sub> and FE<sub>CH<sub>4</sub></sub> increased, while FE<sub>H<sub>2</sub></sub> decreased with both increasing CeO<sub>2</sub> loading and current density. Among the Cu<sub>2</sub>O–CeO<sub>2-C</sub> electrodes, Cu<sub>2</sub>O with 5 wt% of CeO<sub>2-C</sub> was determined to be the optimum electrode for C<sub>2</sub>H<sub>4</sub> production. It achieved a maximum FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of approximately 53% at  $-0.98$  V vs. RHE, at a current density of  $-250$  mA cm<sup>-2</sup>.

To investigate the influence of the CeO<sub>2</sub> particle morphology, a CO<sub>2</sub>RR test was conducted using rod-like ceria particles (CeO<sub>2-R</sub>) with the optimized promoter content of 5 wt% (previously found for cubic-like ceria particles, CeO<sub>2-C</sub>), under the same reaction conditions (1 M KOH,  $j = -50$  to  $-300$  mA cm<sup>-2</sup>). Fig. SI10 and SI11 (ESI†) revealed that the FEs for C<sub>2</sub>H<sub>4</sub>

formation are dependent on the shape of the promoter particles.

In the CeO<sub>2-R</sub> promoter electrode, the main products observed were CO, H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>, similar to the CeO<sub>2-C</sub> promoter. However, compared to CeO<sub>2-C</sub>, the CeO<sub>2-R</sub> electrode required a more negative potential ( $-0.94$  V vs. RHE) to initiate C<sub>2</sub>H<sub>4</sub> formation. Furthermore, the maximum FE for C<sub>2</sub>H<sub>4</sub> ( $\sim 0.15%$  at  $-1.26$  V vs. RHE) over CeO<sub>2-R</sub> was detected at a current density of  $-150$  mA cm<sup>-2</sup>. This suggests that the rod-like ceria morphology is less favourable for C<sub>2</sub>H<sub>4</sub> production, as a higher potential was achieved at relatively low current densities. Regarding the FEs for other subproducts, CeO<sub>2-R</sub> exhibited a lower FE for CO and higher FE for H<sub>2</sub> and CH<sub>4</sub> compared to CeO<sub>2-C</sub>, as shown in Fig. SI10 (ESI†).

On the other hand, the combination of Cu<sub>2</sub>O with CeO<sub>2-R</sub> did not have a positive effect on enhancing the faradaic efficiency for C<sub>2</sub>H<sub>4</sub>, see Fig. SI11 (ESI†). The maximum FE<sub>C<sub>2</sub>H<sub>4</sub></sub> achieved over the Cu<sub>2</sub>O–CeO<sub>2-R</sub> electrode was only  $\sim 50%$  at  $-0.90$  V vs. RHE. This low faradaic efficiency can be attributed to the insignificant promotion of CO<sub>2</sub> and H<sub>2</sub>O activation by the presence of CeO<sub>2-R</sub>, as shown in Fig. SI9 (ESI†). Therefore, the results suggest that CeO<sub>2-C</sub> promotes more suitable activation of both CO<sub>2</sub> and H<sub>2</sub>O molecules, which is crucial for ensuring the selective formation of C<sub>2</sub>H<sub>4</sub>. It should be noted that the optimum catalyst exhibits a low cathodic polarization compared to pristine Cu<sub>2</sub>O (Fig. SI12, ESI†) attributed to the local CO formation at the CeO<sub>2-C</sub> promoter and simultaneous CO<sub>2</sub> and CO electroreduction. Thus, the combination of Cu<sub>2</sub>O with CeO<sub>2-C</sub> demonstrates improved performance in terms of FE<sub>C<sub>2</sub>H<sub>4</sub></sub> compared to Cu<sub>2</sub>O–CeO<sub>2-R</sub>.

**Electrolyte.** The influence of three different electrolytes, namely KOH, KCl, and KHCO<sub>3</sub>, was investigated on the optimized Cu<sub>2</sub>O–5CeO<sub>2-C</sub> catalyst while maintaining a constant electrolyte concentration of 1 M and varying the current density ( $j = -[50-300]$  mA cm<sup>-2</sup>). In terms of C<sub>2</sub>H<sub>4</sub> production, the KOH electrolyte exhibited higher C<sub>2</sub>H<sub>4</sub> faradaic efficiencies ( $\geq 9%$  at  $-0.52$  V vs. RHE) at all tested current densities, except for 50 mA cm<sup>-2</sup>. The selectivity trend for C<sub>2</sub>H<sub>4</sub> among the

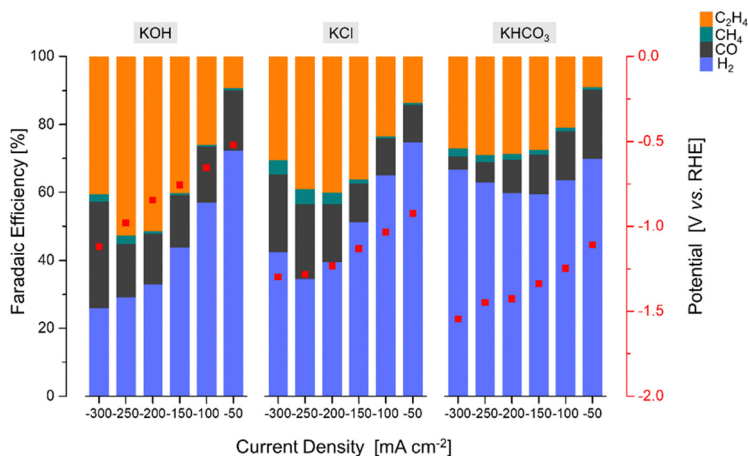


Fig. 7 The faradaic efficiency [%] and potential [V vs. RHE] as a function of current density [mA cm<sup>-2</sup>] over the Cu<sub>2</sub>O–5CeO<sub>2-C</sub> GDE using different electrolytes.



different electrolytes was observed as follows:  $\text{KOH} > \text{KCl} > \text{KHCO}_3$ , as shown in Fig. 7. As the current density increased, the preferential occurrence of the hydrogen evolution reaction was observed in the electrolytes based on  $\text{KCl}$  and  $\text{KHCO}_3$ . Overall,  $\text{KHCO}_3$  exhibited the most negative potentials ( $> -1.10$  V vs. RHE) compared to the other evaluated electrolytes. Therefore, the selection of the electrolyte is crucial for the  $\text{CO}_2$  reduction reaction on  $\text{Cu}_2\text{O}-5\text{CeO}_{2-c}$  gas diffusion electrodes, with alkaline  $\text{KOH}$  conditions enabling preferential  $\text{C}_2\text{H}_4$  production.

**KOH concentration.** As the electrolyte pH also plays an important role in the  $\text{CO}_2\text{RR}$  to  $\text{C}_2\text{H}_4$ , the influence of the  $\text{KOH}$  concentration was evaluated by varying the current density ( $j = -[50-300]$   $\text{mA cm}^{-2}$ ). Fig. 8 demonstrates that the electrochemical activity is highly dependent on the concentration of  $\text{KOH}$ . Notably, the lowest faradaic efficiencies for  $\text{C}_2\text{H}_4$  production ( $\geq 18\%$  at  $-0.60$  V vs. RHE) were observed at the selected  $\text{KOH}$  concentration of  $0.1$  M. In contrast, there was an expected decline in the preference for the hydrogen evolution reaction with increasing concentration ( $> 1$  M). Similarly, at higher current densities ( $> 250$   $\text{mA cm}^{-2}$ ), the hydrogen evolution reaction became even less preferred. Concerning the potentials, more negative values ( $-1.05$  V vs. RHE) were achieved with the increase of the  $\text{KOH}$  concentration. Particularly,  $\text{CO}$  and  $\text{CH}_4$  were the main products promoted at those high negative potential values.

**Stability test.** The stability of  $\text{Cu}_2\text{O}-5\text{CeO}_{2-c}$  and  $\text{Cu}_2\text{O}$  catalysts shown in Fig. 9 was used to evaluate the effect of the promoter phase. The tests were conducted under the optimized reaction conditions of  $j = -250$   $\text{mA cm}^{-2}$  and  $1$  M  $\text{KOH}$  electrolyte, which were found to yield the most promising results for the  $\text{CeO}_{2-c}$ -promoted  $\text{Cu}_2\text{O}$  gas diffusion electrode (GDE). Under these selected conditions, the  $\text{Cu}_2\text{O}-5\text{CeO}_{2-c}$  electrode exhibited a higher  $\text{FE}_{\text{C}_2\text{H}_4}$  ( $\sim 53\%$  at  $-0.98$  V vs. RHE) and maintained its stability over a period of 120 minutes. The faradaic efficiencies for other byproducts ( $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ ) remained constant throughout the reaction (see Fig. SI13, ESI†).

In contrast, when using non-promoted  $\text{Cu}_2\text{O}$ , the initial  $\text{FE}_{\text{C}_2\text{H}_4}$  reached a maximum value of approximately  $38\%$  at

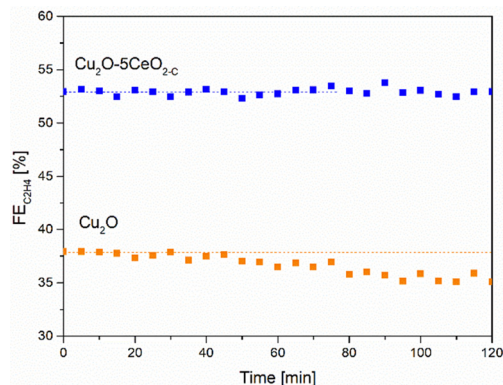


Fig. 9  $\text{C}_2\text{H}_4$  FE [%] as a function of the time [min] over the  $\text{Cu}_2\text{O}-5\text{CeO}_{2-c}$  GDE. Reaction conditions: electrolyte =  $1$  M  $\text{KOH}$  and  $j = -250$   $\text{mA cm}^{-2}$ .

$-1.05$  V vs. RHE but experienced partial deactivation after 45 minutes. The FE for  $\text{C}_2\text{H}_4$  on the  $\text{Cu}_2\text{O}$  electrode decreased by approximately  $5\%$ . Notably, the FEs for  $\text{CO}$  and  $\text{H}_2$  increased as the FE for  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$  decreased on  $\text{Cu}_2\text{O}$  (see Fig. SI14, ESI†).

Consistently with these experimental findings, the  $5$  wt%  $\text{CeO}_{2-c}$ -promoted  $\text{Cu}_2\text{O}$  demonstrated enhanced performance compared to the non-promoted  $\text{Cu}_2\text{O}$  electrode in terms of ethylene production, aligning with the results obtained from linear sweep voltammetry (see Fig. SI15, ESI†). The  $\text{Cu}_2\text{O}-5\text{CeO}_{2-c}$  electrode exhibited a more positive onset potential than  $\text{Cu}_2\text{O}$ , indicating that it was the most active catalyst for the  $\text{CO}_2\text{RR}$ .

XRD measurements were also conducted on the  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}-5\text{CeO}_{2-c}$  gas diffusion electrodes at different reaction times ( $t = 0$  (before reaction: fresh),  $5$  and  $120$  min (after reaction: used)) to investigate the surface copper species during the stability test. In both the fresh and used electrodes, reflections at  $18.15$ ,  $25.67$ , and  $52.74^\circ$  were attributed to the carbon phase (JCPDS:  $00-047-0787$  and  $00-026-1076$ ) of the carbon-paper support (see Fig. SI16, ESI†). Prior to sample activation ( $t = 0$  min), characteristic reflections associated with the  $\text{Cu}_2\text{O}$

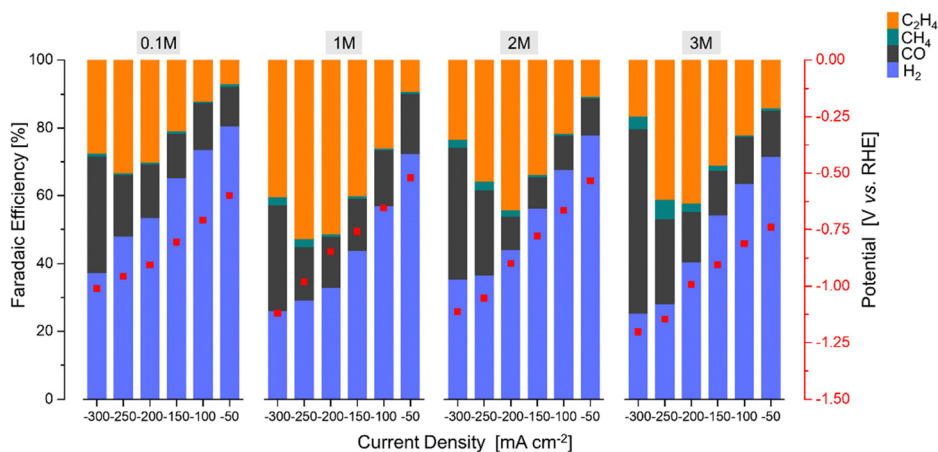


Fig. 8 The faradaic efficiency [%] and potential [V vs. RHE] as a function of the current density [ $\text{mA cm}^{-2}$ ] over the  $\text{Cu}_2\text{O}-5\text{CeO}_{2-c}$  GDE using different  $\text{KOH}$  concentrations.





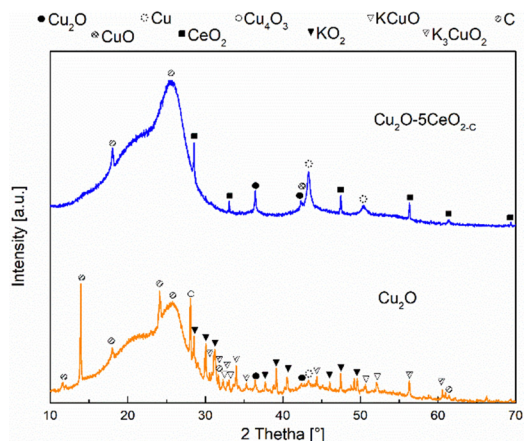


Fig. 10 XRD patterns of the  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}-5\text{CeO}_2$  GDEs at the reaction time of 120 minutes.

phase were observed in both  $\text{Cu}_2\text{O}$  (see Fig. SI17, ESI†) and  $\text{Cu}_2\text{O}-5\text{CeO}_2$  (Fig. SI18, ESI†) electrodes. Additionally,  $\text{CeO}_2$  was detected on the  $\text{Cu}_2\text{O}-5\text{CeO}_2$  electrode.

After a reaction time of 5 min, the intensity of reflections corresponding to  $\text{Cu}_2\text{O}$  decreased in both gas diffusion electrodes, and two new phases,  $\text{CuO}$  (JCPDS: 01-078-0428) and metallic  $\text{Cu}^0$  (JCPDS: 00-004-0836), were identified. A similar behaviour was observed for the intensity of the reflections related to the  $\text{CeO}_2$  phase in the  $\text{Cu}_2\text{O}-5\text{CeO}_2$  electrode. However, two new phases,  $\text{Cu}_4\text{O}_3$  (JCPDS: 00-033-0480) and  $\text{K}_3\text{CuO}_2$  (JCPDS: 00-038-0971), were specifically identified in the  $\text{Cu}_2\text{O}$  electrode.

At a total reaction time of 120 min (see Fig. 10), the reflections corresponding to  $\text{CuO}$  phases disappeared, and the intensity of reflections related to  $\text{Cu}_2\text{O}$  and  $\text{Cu}^0$  decreased. Additionally, new reflections were observed in the  $\text{Cu}_2\text{O}$  electrode, which were associated with the  $\text{KCuO}$  (JCPDS: 01-076-2437) and  $\text{KO}_2$  (JCPDS: 01-084-1972) phases. In contrast, the reflections of  $\text{Cu}_2\text{O}-5\text{CeO}_2$  remained like those identified at 5 min, indicating that  $\text{CeO}_2$  promoted the stability of the main copper species ( $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ , and  $\text{Cu}^0$ ) involved in the  $\text{CO}_2\text{RR}$ . These identified copper species were consistent with those detected through cyclic voltammetry measurements (see Fig. SI19, ESI†).

According to XRD analysis, the crystallite size of the main  $\text{Cu}^x = \text{Cu}^{2+}$ ,  $\text{Cu}^+$ , and  $\text{Cu}^0$  species were modified after the reaction, see Table SI1 (ESI†). The increase of the  $\text{Cu}_2\text{O}$  crystallite size for the non-promoted  $\text{Cu}_2\text{O}$  catalyst was 15%, while for the  $\text{Cu}_2\text{O}-5\text{CeO}_2$  it was 1%. For  $\text{Cu}_2\text{O}-5\text{CeO}_2$ , the  $\text{CeO}_2$  crystallite sizes were also slightly increased by 8%. Furthermore, the crystallite size corresponding to the  $\text{Cu}$  phase (20 nm) was higher for the  $\text{Cu}_2\text{O}$  sample. Therefore, the poor stability of the  $\text{Cu}_2\text{O}$  catalyst can result in the increase of the crystallite sizes of the main copper species.

Additionally, SEM-EDS analysis was performed after the reaction to verify the catalyst composition, see Table SI2 (ESI†). Besides the main elements ( $\text{Cu}$ ,  $\text{Ce}$ , and  $\text{O}$ ), the potassium ( $\text{K}$ ) phase was also detected on the surface of both used catalysts. However, a clear modification of the catalyst composition was identified for used  $\text{Cu}_2\text{O}$ . In this catalyst, the  $\text{Cu}$  phase decreased by 55% compared to its fresh estate. This behaviour

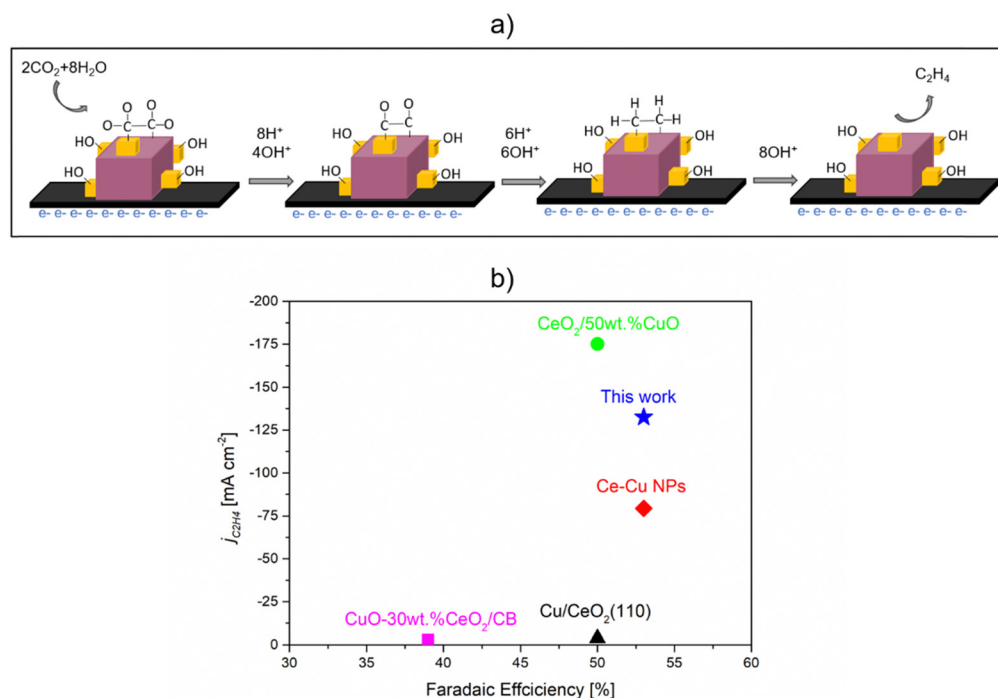


Fig. 11  $\text{CO}_2\text{RR}$  to ethylene over  $\text{Cu}_2\text{O}-5\text{CeO}_2$  GDE. (a) Plausible mechanism of  $\text{CO}_2\text{RR}$  to  $\text{C}_2\text{H}_4$ . (b) Performance comparison with similar catalytic system reported in the literature. 0.1 M  $\text{KHCO}_3$  was used for  $\text{CuO}-30 \text{ wt}\% \text{CeO}_2/\text{CB}$ <sup>31</sup> and  $\text{Cu}/\text{CeO}_2(100)$ ,<sup>31</sup> while 1 M  $\text{KOH}$  was used for  $\text{CeO}_2/50 \text{ wt}\% \text{CuO}$ ,<sup>33</sup>  $\text{Ce}-\text{Cu}$  NPs,<sup>32</sup> and  $\text{Cu}_2\text{O}-5 \text{ wt}\% \text{CeO}_2$  (this work).



can be related to the presence of the new KOx and KCuOx phases (see Fig. SI20, ESI†), in agreement with post-catalysis XRD results. Regarding the used Cu<sub>2</sub>O–5CeO<sub>2</sub>, its composition was slightly modified, suggesting that CeO<sub>2-C</sub> (see Fig. SI21, ESI†) inhibits the formation of potassium species, which are negative for ethylene production.

Based on the electrochemical and catalyst characterization conducted before and after the reaction, it can be concluded that the interaction between Cu<sub>2</sub>O and CeO<sub>2</sub> creates intrinsic sites (Cu<sup>x</sup>–CeO<sub>2-x</sub>; Cu<sup>x</sup> = Cu<sup>2+</sup>, Cu<sup>+</sup>, Cu<sup>0</sup>) for the binding of CO<sub>2</sub> and H<sub>2</sub>O. The proposed mechanism, illustrated in Fig. 11(a), suggests that CO<sub>2</sub> can be adsorbed around the Cu<sup>x</sup>–CeO<sub>2-x</sub> interface and reduced to \*CO on the CeO<sub>2-x</sub> site. This step is crucial as CO serves as the key intermediate for the production of C<sub>2+</sub> products.<sup>30,33</sup> Subsequently, \*CO can undergo further reduction to C<sub>2</sub>H<sub>4</sub> through enhanced \*CO–\*CO coupling, which occurs on Cu<sup>x</sup> = Cu<sup>2+</sup>, Cu<sup>+</sup>, and Cu<sup>0</sup> sites, with the assistance of H<sup>+</sup> species derived from adsorbed H<sub>2</sub>O on Cu<sup>+</sup>–CeO<sub>2-x</sub> sites.<sup>30,54</sup> Therefore, the improved and stable FE<sub>C<sub>2</sub>H<sub>4</sub></sub> achieved with the Cu<sub>2</sub>O–5CeO<sub>2-C</sub> catalyst supports the assertion that CeO<sub>2-C</sub> plays a significant role in the CO<sub>2</sub>RR. It promotes the formation of Cu<sup>x</sup>–CeO<sub>2-x</sub> sites, which govern the activity, selectivity, and stability of C<sub>2</sub>H<sub>4</sub> production by synergistically activating CO<sub>2</sub> and H<sub>2</sub>O molecules.

The performance comparison with catalysts shown in Fig. 11(b), in terms of faradaic efficiency (FE) and partial current density, indicates that Cu<sub>2</sub>O–5CeO<sub>2-C</sub> is a promising catalytic system for C<sub>2</sub>H<sub>4</sub> production. Compared to other reported catalytic systems, Cu<sub>2</sub>O–5CeO<sub>2-C</sub> demonstrates a high FE for C<sub>2</sub>H<sub>4</sub> (FE<sub>C<sub>2</sub>H<sub>4</sub></sub> ~ 53%) at a high partial current density ( $j_{\text{C}_2\text{H}_4} = 132 \text{ mA cm}^{-2}$ ). Additionally, one of the most significant advantages of Cu<sub>2</sub>O–5CeO<sub>2-C</sub> is that it requires a lower potential (–0.98 V vs. RHE) than the reported CeO<sub>2</sub>/50 wt% CuO system (–2.3 V vs. RHE) to operate at the same electrolyte concentration of 1 M KOH.<sup>33</sup>

## Conclusions

This study investigated the influence of CeO<sub>2</sub> promotion on the catalytic performance of Cu<sub>2</sub>O-based catalysts for the electrochemical reduction of CO<sub>2</sub>. The addition of the CeO<sub>2-C</sub> promoter phase was found to enhance the formation of C<sub>2</sub>H<sub>4</sub>, a valuable commercial product, during the CO<sub>2</sub>RR compared to the non-promoted Cu<sub>2</sub>O catalyst. The characterization techniques, including SEM, TEM, XRD, Raman spectroscopy, and X-ray photoelectron spectroscopy, provided valuable insights into the structural and compositional properties of the catalysts.

The results indicated that the synthesized catalysts exhibited well-defined morphologies, with cubic-like particles for Cu<sub>2</sub>O and CeO<sub>2-C</sub>, and rod-like morphologies for CeO<sub>2-R</sub>. The XRD analysis confirmed the phase of Cu<sub>2</sub>O and CeO<sub>2</sub>, while Raman spectroscopy revealed characteristic peaks for both materials and a new peak indicating the interaction between Cu<sup>+</sup> and Ce<sup>3+</sup> cations. X-ray photoelectron spectroscopy further confirmed the presence of different copper oxidation states in the Cu<sub>2</sub>O-based catalysts.

The electrochemical evaluation of the catalysts demonstrated that the CeO<sub>2-C</sub>-promoted Cu<sub>2</sub>O-based gas diffusion electrodes (GDEs) exhibited higher faradaic efficiencies for C<sub>2</sub>H<sub>4</sub> production compared to the non-promoted Cu<sub>2</sub>O GDE. The optimal loading of CeO<sub>2-C</sub> for maximum C<sub>2</sub>H<sub>4</sub> production was determined to be 5 wt%. The proposed Cu<sub>2</sub>O–5CeO<sub>2-C</sub> GDE demonstrates enhanced and stable C<sub>2</sub>H<sub>4</sub> production through the interaction of Cu<sub>2</sub>O and CeO<sub>2</sub>, creating active sites (Cu<sup>x</sup>–CeO<sub>2-x</sub>; Cu<sup>x</sup> = Cu<sup>2+</sup>, Cu<sup>+</sup>, Cu<sup>0</sup>) for the CO<sub>2</sub>RR. It exhibits high faradaic efficiency (FE<sub>C<sub>2</sub>H<sub>4</sub></sub> ~ 53%) and partial current density ( $j_{\text{C}_2\text{H}_4} = 132 \text{ mA cm}^{-2}$ ) at a low potential (–0.98 V vs. RHE) with 1 M KOH electrolyte, making it a promising catalyst. As an important fact, the FEs for C<sub>2</sub>H<sub>4</sub> in the Cu<sub>2</sub>O–5CeO<sub>2-C</sub> GDE were found to be influenced by the type of electrolyte and its concentration.

These findings highlight the potential of CeO<sub>2</sub> promotion in improving the selectivity and activity of Cu<sub>2</sub>O-based catalysts for the CO<sub>2</sub>RR. The study contributes to the understanding of the structure–property relationship in CO<sub>2</sub> electrochemical conversion and provides a foundation for further development of more efficient catalysts.

## Conflicts of interest

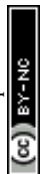
There are no conflicts to declare.

## Acknowledgements

This work was funded by AEI projects PID2019-108136RB-C33 and CNS2022-135235 (MCIN/AEI/10.13039/501100011033 and NextGenerationEU/PRTR). A. A. acknowledges the support from the Margarita Salas grant from the European Union – Next Generation EU through the Universitat de Barcelona.

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