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Tuning The CuO Catalyst Properties for an Optimal H_2:CO Ratio

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This study reports the design and engineering of CuO-based electrocatalysts synthesized via a facile hydrothermal approach to optimize the H_2:CO syngas ratio in CO_2 electrocatalytic reduction. This process offers a sustainable alternative to traditional methods by operating under mild conditions, reducing greenhouse gas emissions, and enabling the use of renewable energy. Three CuO-based electrocatalysts, synthesized by the same hydrothermal method but with different precursors, were used to prepare innovative gas-diffusion electrodes and tested in an optimized compact electrochemical flow-by reactor. Unlike conventional devices with liquid anode and cathode compartments separated by a membrane, this reactor features an additional gas chamber adjacent to the cathode liquid compartment, forming a triple gas/solid/liquid interface that enhances the local CO_2 concentration at the electrode surface. The study demonstrates that introducing different salts (e.g., Li^+ or Na^+) during synthesis enables significant modifications to the structural properties of the CuO catalysts, leading to different product distributions in CO_2 electroreduction. The optimal H_2:CO ratio, suitable for Fischer-Tropsch or methanol synthesis, can be modulated introducing Li^+ or of Na^+ salt in the synthetic CuO route, as well as by fine-tuning the operating conditions, such as the cell potential and current density. The performance differences among the catalysts were elucidated through electrochemical characterizations, including measurements of capacitance, resistance and electrochemical active area (ECSA), as well as through the analysis of hydrophilicity properties of the electrode surface.

1. Introduction

Syngas, a mixture composed of carbon monoxide and hydrogen in different stoichiometric ratios, can be used to produce pharmaceuticals, intermediates (e.g., ammonia, methanol), plastics, solvents, and fertilizers. Currently, the most efficient technologies for syngas synthesis include coal gasification and natural gas reforming through the mediation of a catalyst and the main disadvantage of these processes is the high temperatures and pressures required (Gao et al., 2023). The possibility of varying the H_2/CO mixture ratio during the electrochemical process, for example by tailoring the active sites of the catalyst or through engineering the electrochemical reactor (Ampelli et al., 2023b), as well as by choosing the best operating conditions, represents an attractive route to perform Fischer-Tropsch or methanol processes. Methanol, a valuable intermediate in the synthesis of several chemicals and e-fuels and used as energy carrier (Sarvestani et al., 2024), can be synthesized through the main reaction (eq.1), followed by the secondary reaction (eq.2).

$$CO + H_2 \rightarrow CH_3OH \qquad \Delta H = -90.7 \text{ kJ/mol} \qquad (1)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H = -49.4 \text{ kJ/mol} \qquad (2)$$

CO_2 utilization, as shown by equation n.2, can directly contribute to reducing the greenhouse effect (Marchese et al., 2021) and consequently, an electrochemical reduction approach can also be a valuable tool. This strategy, until now, has led to low faradaic efficiencies and furthermore, additional costs must also be accounted for downstream separation processes.

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Electrochemical CO_2 reduction is currently considered a green approach for producing chemical feedstock and liquid fuels, making it a valuable tool for carbon recycling and energy storage, especially if driven by renewable sources, such as sunlight (Ampelli et al., 2023a). The CO_2 molecule is one of the most stable carbon-based molecules, and its activation, via the formation of the $CO_2^{\cdot-}$ radical anion intermediate, requires considerable effort to produce carbon-based chemicals.
The selectivity and faradaic efficiency of these processes are often low because the formation of carbon-based compounds competes with the unavoidable parasitic hydrogen evolution reaction (HER). Among the various available catalysts, copper currently appears to be the only one capable of producing long-chain carbon compounds (C1-C3), although selectivity and yields remain low despite several efforts (Giusi et al., 2022a). Carbon monoxide (CO) production, for those materials that allow low HER yields, seems to be the most readily achievable product, as it requires only two-electron transfer process (Poon et al., 2022). Materials such as silver (Ag), and gold (Au), preferentially reduce CO_2 to CO, while simultaneously exhibiting low yields in HER (Leonzio et al., 2024). By fine-tuning the material properties, it is possible to optimize the presence of active sites both for CO_2 reduction reactions and HER, not limiting the search for materials solely to gold or silver. Palladium, for example, despite being known to be easily poisoned by CO (with which it bonds strongly), has been considered a promising candidate for the electrochemical production of syngas with a 1:1 H_2/CO ratio (Sheng et al., 2017), but a sustainable approach should require the use of more available materials.
In this paper, we propose the synthesis of two CuO-based electrocatalysts obtained through the same hydrothermal procedure but introducing two different cations, such as Li^+ (from LiOH) and Na^+ (from NaOH), and comparing their electrochemical performance in the CO_2 reduction reaction. These two synthesized materials were compared with a commercial CuO catalyst used as a reference material.
The synergy of the various chemical and physical properties of the materials can produce H_2:CO mixtures with a different ratio, highlighting that engineering the surface properties is as important as the choice of the catalytic material itself, without the need to use expensive and critical raw elements (Tabassum et al., 2022).

2. Materials and Methods

2.1 CuO-based catalysts

The CuO (Li-modified) catalyst was synthesized via a facile hydrothermal treatment by dissolving 1 mmol of $CuCl_2$ and 3 mmol of LiOH in 20 mL of H_2O. The resulting solution, stirred for 30 minutes, was then transferred to a 50 mL Teflon autoclave and heated to 180°C for 2 hours with a ramp of 5°C min^{-1}. The autoclave was then cooled to room temperature, and the black precipitate centrifuged and washed three times with H_2O and ethanol to remove the impurities. The resulting solid was then dried overnight at 70°C in a vacuum oven.

The CuO (Na-modified) catalyst was synthesized with the same synthetic strategy as the CuO (Li-modified) material but replacing the LiOH salt with 20 mL of 2M NaOH.

The CuO (reference) sample was purchased from "Merck©" and its purity was ≥ 99% (ACS reagent).

The working electrodes were prepared by depositing the catalyst (obtained as a solid) through spray-coating on a carbon gas-diffusion layer (GDL, Sigracet® 36BB, supplied by Ion Power). This technique consists of the deposition, using an airbrush, of the catalytic material (in the form of an ink) on the pre-heated carbon substrate to allow the solvent to evaporate and fix the catalytic material on its surface.
The ink was obtained by mixing a certain amount of the catalysts with 50 µL of 5% Nafion® perfluorinated solution and 10 mL of 2M 2-propanol for 20 minutes under sonication, until a stable suspension was obtained. The catalysts were deposited on GDL until a loading of 0.5 mg cm^{-2} was achieved.

2.2 X-Ray diffraction (XRD) analysis

The purity of the electrocathodes and their crystallographic structure was analysed by X-ray diffraction crystallography (XRD). The crystallinity of all materials was demonstrated by the presence of well-defined peaks (Figure 1). Our synthesized samples show more defined and narrow peaks than the commercial sample, thus evidencing a higher crystallinity degree. The main detected peaks corresponding to (110), ($\bar{1}$11), (111), ($\bar{1}$12), ($\bar{2}$02), (020), (202), ($\bar{1}$13), ($\bar{3}$11), (113), ($\bar{2}$20), and (311) crystallographic planes were observed at 32.8°, 35.7°, 39.0°, 46.5°, 48.9°, 53.6°, 58.6°, 61.7°, 66.6°, 68.2°, 72.7°, and 75.2°, proving that CuO was the only phase present in all materials.

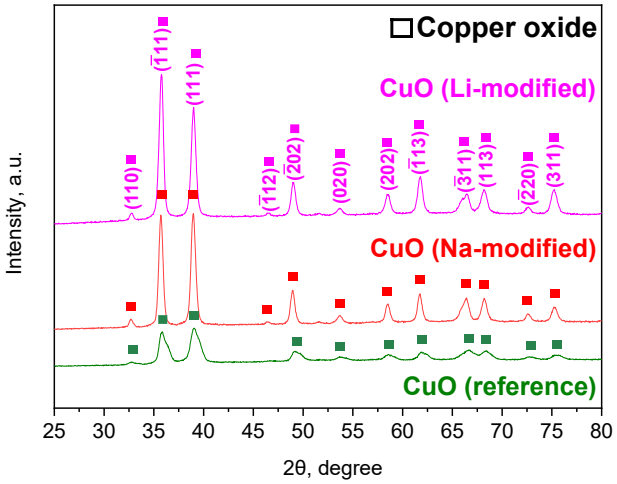

Figure 1: XRD patterns for CuO (Li-modified), CuO (Na-modified) and CuO (reference).

2.3 Morphology analysis

The morphological analysis of the three materials was conducted through the scanning-electron microscopy (SEM) and the images are presented in Figure 2. While the CuO (reference) material presents spherical particles with a diameter range between 0.40 and 1.7 µm, the introduction of two different salts (Li^+ and Na^+) via the same synthetic process in the two other samples CuO (Li-modified) and CuO (Na-modified), did not lead to significant changes in the morphology, which in both cases correspond to interconnected nanoplates. The latter are known to exhibit a high density of active sites compared to different particle shapes (Hecker et al., 2023). The sample substituted with Li^+ presents nanoplates with maximum length of about 5 µm, slightly longer compared to the sample substituted with Na^+ (3 µm).

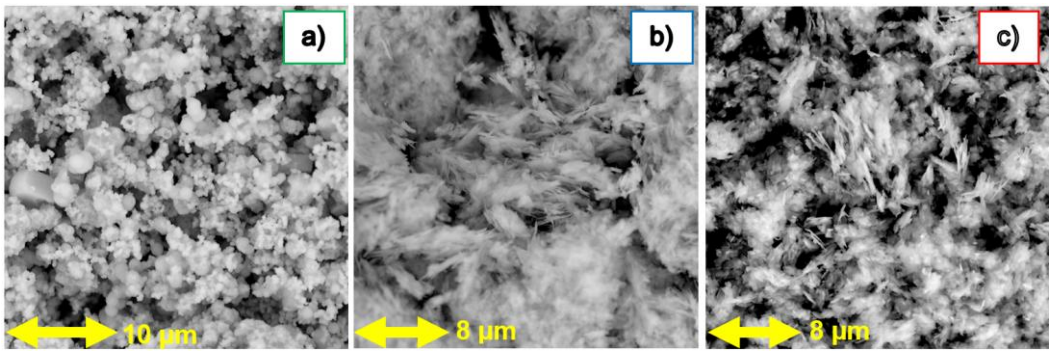

Figure 2: Scanning electron microscopy for a) CuO (reference); b) CuO (Na-modified) and c) CuO (Li-modified).

2.4 Electrochemical device

Electrochemical tests were conducted in an innovative homemade flow-by electrochemical reactor, made of Plexiglas to facilitate internal inspection. This reactor consists of two liquid chambers, an anode and a cathode, and a gas chamber adjacent to the cathode chamber, where CO_2 is continuously fluxed. This configuration allows for the formation of a triple gas/solid/liquid interphase, which has the following advantages: *i)* improved diffusion of CO_2 to the active sites of the catalytic material; *ii)* increased local availability of CO_2, which would otherwise be limited by its maximum concentration in the aqueous electrolyte (Giusi et al. 2023b); *iii)* separation of gaseous and liquid products, with the former collected from the gas chamber outlet and the latter taken from the liquid reservoirs at the end of the tests. The two liquid chambers were separated by a proton-exchange membrane (Nafion® NR324), which serves to separate the reaction environments (allowing operation with different electrolytes and pH), preventing mixing of formed products, improving safety issues, and facilitating proton (H^+) transport from the anode to the cathode chamber, where they participate in the CO_2 reduction reactions (in addition to HER). Two solutions of 0.1 M $KHCO_3$ and 1 M KOH were employed as catholyte and anolyte, respectively, and were recirculated continuously in the chambers with a peristaltic pump at a flow rate of 10 mL min^{-1} for the entire test duration. The 0.1 M $KHCO_3$ catholyte was pre-saturated for 30 minutes with CO_2 before all tests to achieve a final pH of 6.8, while an additional CO_2 flow (20 mL min^{-1}) was maintained in

the cathode reservoir (in addition to the gas chamber) to limit pH variation during the test due to proton consumption and to keep the solution saturated with CO_2. The electrodes used as anode and cathode had an active area of about 5 cm^2. During the tests, the produced gases were sampled periodically (every 5 minutes) and analysed using Gas Chromatography (MicroGC GCX Pollution Analytic Equipment), while the liquid samples were taken at the end of the tests and analysed using Ion Chromatography (IC, column organic acids) to detect organic acids and Gas Chromatography-Mass Spectrometry (GC-MS, equipped with a Stabilwax column and He as the carrier gas) to check for the formation of alcohols such as methanol, ethanol, and other organic compounds.

3. Results and Discussion

3.1 CO_2 Reduction tests

The CO_2 reduction tests were conducted through the application of the following electrochemical protocol*: i*) capacitance measurement through double layer technique*; ii)* running of chrono voltammetry cycles (CVs) up to the potential set for the test (see point *iv*), for the stabilization of the material and evaluation of the onset-potential. *iii*) resistance measurement through electrochemical impedance spectroscopy (EIS); *iv*) running of chrono-amperometry tests (CAs) at increasing potentials.

3.1.1 Chronoamperometry tests

The CAs were conducted from -0.2 up to -1 V vs RHE, depending on the current densities achieved for the various catalysts (which exhibited different conductivities), and each test lasted 1 hour. For example, for the CuO (Li-modified) sample, the maximum potential reached was -0.6 V vs RHE, since the current densities achieved were already comparable to those observed at lower potentials for the other two electrodes. While for the CuO (reference) and CuO (Na-modified), the H_2:CO ratio varied from 3.5 to 4 for the first and from 4 to 5 for the second (depending on the applied potential), the CuO (Li-modified) sample presents significantly lower values, ranging from a minimum of 1.3:1 to 1.8:1 for the highest potential. In industrial methanol synthesis, a mixture of CO, CO_2, and H_2 is typically used, characterized by the M module, defined as $(H_2\text{-}CO_2)/(CO+CO_2)$, whose optimal value is equal to 2. In practice, slightly higher ratios are often employed to enhance process efficiency, shifting the equilibrium toward the methanol production, improving reaction kinetics, and preventing the catalyst deactivation due to coke formation (Hankin et al., 2017). This last step is the real test for evaluating performance in the CO_2 reduction, in terms of current density, productivity and faradaic efficiency (Figures 3a, b and c).

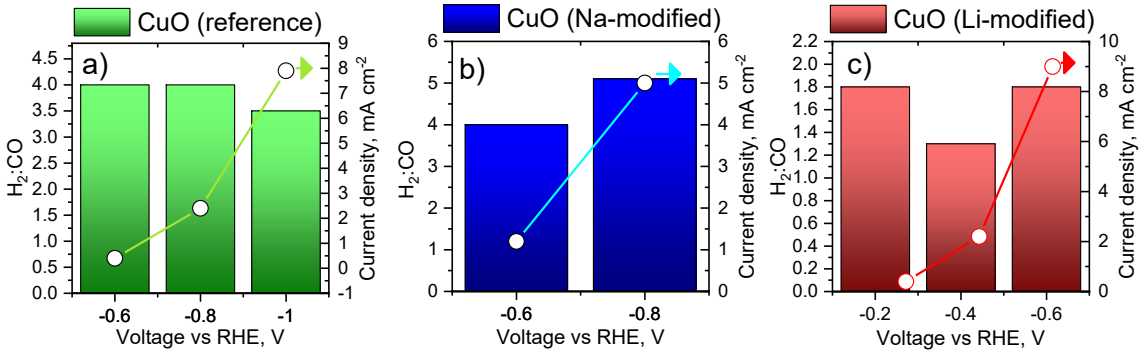

Figure 3: H_2:CO ratio and current density profiles vs. applied voltage for a) CuO (reference); b) CuO (Na-modified) and c) CuO (Li-modified).

3.1.2 Electrochemical and catalytic properties

The investigated chemical and physical properties of our materials are reported in Table 1. The electrochemical active surface area (ECSA) was obtained by dividing the double layer capacitance (C_{dl}) by the specific capacitance (C_s). The former was obtained through an electrochemical method (double layer) consisting of several chrono voltammetry cycles performed around the open circuit potential (OCP) value (to provide only non-faradaic charge transfer processes) at different scan rates. The CuO (Li-modified) sample showed a higher ECSA than the two other samples, equal to 60 cm^2, compared to 31 cm^2 and 45 cm^2 for the CuO (Na-modified) and CuO (reference), respectively. Contact angle measurements with water droplets were also carried out, highlighting how the modification with Li^+ resulted in a higher contact angle than the Na^+ modified material (which could not be measured, due to its high hydrophilicity), but lower than CuO (reference). The combination of the higher ECSA, increased capacitance and lower hydrophilicity can explain the remarkable difference in terms of

H_2:CO ratio among the various samples. The onset potential measurements (from the CVs curves) also confirmed the results from the wettability tests, indicating that the hydrophilicity follows the following order: *1*) CuO (Na-reference); *2*) CuO (Li-reference), and *3*) CuO (reference). The higher hydrophilicity, related to the presence of different functional groups (for example OH^-) can be associated with a superior capacity to bind water molecules, activating it and promoting the HER reaction more than the CO_2 reduction reactions. Additionally, the contribution of the sample morphology must also be taken in account, since for example the lower hydrophilicity of the (CuO-Li modified) sample may be the key to explaining the lower H_2:CO ratio, as the reduction of CO_2 to CO can be favoured compared to HER, due to the reduced interaction with water molecules. The titration of OH^- surface groups with nitric acid instead highlighted a higher concentration of acidic sites in the sample modified with Li^+ compared to the others (Figure 4, a). The capacitance profile (normalized to ECSA) and the H_2:CO ratio, as a function of the various materials, are reported in Figure 4, b. The CuO (Li-reference), which provides the lowest H_2:CO ratio, exhibits lower normalized capacitance than the CuO sample modified with Na^+ but comparable to the CuO (reference). While this data may explain the differences in performance between the two Na and Li samples, i.e. the greater hydrophilicity observed in CuO (Na-reference) influencing interfacial water absorption and double layer capacitance, these factors may not fully explain the differences relative to the CuO (commercial) sample. In the latter case, the morphology (different from the two synthesized samples, which are similar) and, therefore, the concentration of active sites could be more decisive.

Table 1: ECSA, capacitance and contact angle measurements for the three investigated CuO electrodes.

Catalysts	ECSA, cm^2	Capacitance, µF	Contact angle, °C
CuO (reference)	45	3802	130
CuO (Na-modified)	31	3751	Not measurable
CuO (Li-modified)	60	4950	111

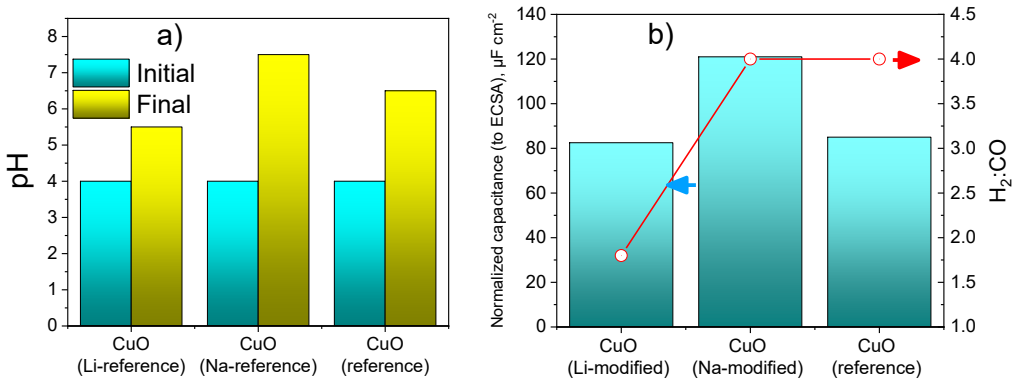

Figure 4: a) Titration with nitric acid; b) Normalized capacitance (to ECSA) and H_2:CO ratio for the different materials.

It was demonstrated that the introduction of Li^+ (instead of Na^+) resulted to a significant change in the material physical properties, specifically by increasing its hydrophobicity, leading to a lower H_2:CO ratio ranging from 1.3:1 to 1.8:1 (depending on the applied potential), suitable for the second step production of liquid fuels via Fischer-Tropsch process. On the contrary, a higher H_2/CO ratio can be obtained with Na^+, thus more suitable for methanol production. The electrochemical tests were supported by various chemicals analysis and electrochemical characterizations, which revealed significant changes among the three materials in terms of capacitance, electrochemically active surface area (ECSA) and resistivity. An analysis of hydrophilic properties and wettability was conducted through the titration of the surface hydroxyl groups with nitric acid and through contact angle measurements, indicating that the CuO (Li-modified) material was more hydrophobic than the Na-modified CuO (and slightly less than the CuO-commercial one). This evidence, in combination with higher ECSA and double-layer capacitance, can explain the different results.

4. Conclusions

This study has demonstrated that optimising the chemical and physical properties of the electrocatalyst is more critical for enhancing performance in CO_2 electrocatalytic reduction than the choice of the material itself. By varying the properties of the same material (CuO), such as hydrophilicity, capacitance, and conductivity, it was possible to modulate the H_2:CO ratio, which is important for subsequent processes like methanol synthesis or Fischer-Tropsch process, involving higher temperatures and pressures and using and iron and cobalt-based

catalysts (Jeske et al., 2021). The introduction of Li^+ during hydrothermal synthesis resulted in a H_2:CO ratio (about 1.8:1) close to the stochiometric ratio required for the methanol synthesis (2:1), whereas a higher ratio was observed for the sample synthesized with Na^+ and for the commercial CuO sample, thus more suitable for direct industrial application. Analysis of the chemical and physical properties, using both chemical and electrochemical methods, confirmed that their combination accounts for the significant difference in product distribution. The ability to vary the H_2:CO ratio by adjusting only the synthesis parameters or operating conditions is an easy and sustainable way to avoid the use of expensive materials with a high environmental impact, making the overall process scalable and economically efficient.

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