



CO₂ conversion to synthetic fuels using flow cell reactor over Cu and Ag based cathodes

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Received: 28 February 2024 / Accepted: 22 April 2024
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Abstract

As a result of electrochemical conversion of carbon dioxide (CO₂), value-added chemicals like as synthetic fuels and chemical feedstocks can be produced. In the current state of the art, copper-based materials are most widely used being the most effective catalysts for this reaction. It is still necessary to improve the reaction rate and product selectivity of CuOx for electrochemical CO₂ reduction reaction (CO₂RR). The main objective of this work was synthesized and evaluate the copper oxide electrocatalyst combined with silver (CuO 70% Ag 30%) for the conversion of carbon dioxide into synthetic fuels. The catalysts have been prepared by the oxalate method and assessed in a flow cell system. The results of electrochemical experiments were carried out at room temperature and at different potentials (-1.05 V–0.75 V vs. RHE in presence of 0.1 M KHCO₃) and gas and liquid chromatographic analysis are summarized. The CuOx-based electrodes demonstrated the selective of ~25% at -0.55 V for formic acid (HCOOH) and over CuO -Ag and selective of ethylene at ~20% over CuOx at -1.05 V. Other products were formed as ethylene, ethanol, and propanol (C₂H₄, EtOH, PrOH) at more positive potentials. On the other hand, carbon monoxide, acetate, ethylene glycol, propinaldehyde, glycoaldehyde and glyoxal (CO, CH₃COO, C₂H₆O₂, C₃H₆O, C₂H₄O₂, C₂H₂O₂) have been formed and detected. Based on the results of these studies, it appears that the formation of synthetic fuels from CO₂ at room temperature in alkaline environment can be very promising.

Keywords CO₂ conversion · Flow electrochemical cell · Synthetic fuels · Copper oxide · No critical raw catalyst

Introduction

There is an urgent need for technological solutions to remove carbon dioxide (CO₂) from the atmosphere to combat global warming, which is caused by an increase in the amount of carbon dioxide that is being emitted into the atmosphere. Innovative solutions are essential to achieving global energy and climate change goals [1]. It is essential that both existing technologies and those not yet on the market are deployed as soon as possible. During this decade, major efforts must be made in the area of innovation as well as deployment of these new technologies in order to bring them to market in time. By next twenty years it is expected that most of the CO₂ emissions from the world's

energy sector will be reduced using new technologies that are readily available today [2–8]. To reduce CO₂ emissions, and to store renewable energy, it is necessary to use renewable energy to convert carbon dioxide and water into synthetic fuels and chemical feedstocks [9, 10]. An abundance of evidence suggests that carbon dioxide can be converted into organic compounds using electrochemical cells with active electrocatalysts at the cathode of the cells [11–13]. However, the carbonaceous synthetic fuels can be applied in several energy technologies like combined heat and power systems [14, 15]. There has been considerable interest in the development of novel, structured materials from non-noble and non-critical raw materials in recent years [16–18]. There are a wide variety of electrocatalysts that can be used for the CO₂RR, and reduction products are highly dependent on the electrocatalyst used [19, 20]. In electrochemical CO₂RR, three steps are involved, which begin with the adsorption of carbon dioxide on catalyst surfaces. A second step in carbon dioxide reduction involves activating and reducing CO₂ molecules. Generally, electron transfer is the

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rate-determining step in creating CO₂ intermediates, since it imposes a high energy barrier. Finally, the catalyst surface is recovered for further reactions after desorption of products. As an important intermediate in carbon dioxide reaction reduction, CO₂ plays a significant role in determining how final products are distributed [21, 22]. It should be noted that copper-based catalysts perform differently depending on the state of oxidation of the catalyst. There is a direct relationship between the catalytic performance of an electrocatalyst and its structure and active site. Other study by Zheng et al. [23], examined the connection between the fundamentals of the reaction and the effectiveness of electrocatalysts in their critical assessment of CO₂ reduction to C₂ products by focusing on the fundamentals of the reaction. During a comprehensive discussion of the mechanistic aspects of the C₂ reactions under electrocatalytic conditions, copper-based catalysts are discussed in terms of both mechanics and practical aspects under electrocatalytic conditions. The authors also visualized the roadmap for generating C₂ products by demonstrating the advantages of integrating theoretical calculations, surface characterization, and electrochemical measurements into one process. Concerning Gao et al. [24], have been demonstrated that selected geometries and compositions of catalysts in combination with a carefully selected electrolyte are responsible for the enhanced selectivity of C₂₊ in the reaction. As it is known, copper-based catalysts exhibit different performance for carbon dioxide reduction depending on their oxidation state. Hori et al., investigated in aqueous inorganic electrolytes the acid-base equilibrium between bicarbonate and CO₂ reactant involving H⁺ (CO₂ (g) + H₂O (l) + H₂CO₃ (aq) + H⁺ (aq)), whereas reduction entails protonation. As a result, H⁺ concentration on the surface of catalysts plays an important role in determining their product selectivity. The C₂H₄ is favored when the electrolyte concentration is low (0.1 M) whereas CH₄ and H₂ are favored when the electrolyte concentration is high [25]. However, there is a limitation on the carbon dioxide conversion rate of electrocatalysts due to their structure and oxidation state, but it is possible to optimize their electrocatalytic performance. In general, surface vacancies are also important factors that influence electrochemical performance. Copper catalysts are one of the most commonly used electrocatalysts in electrochemical CO₂ reduction [26–29] by multiple electron transfer reactions. To achieve high efficiency in CO₂ reduction, however, it is necessary to have a sufficient number of active sites. It can electrochemically convert CO₂ into different products, such as hydrocarbons and alcohols, due to its electrochemical properties [11, 30–32]. Selectivity of the products is directly related to the active copper species and the morphology, however, an irregular surface structure can be present on the catalyst surface, where wires, particles, and aggregates can be

distributed in a nearly random manner. Despite this severe heterogeneity, multiple factors still support the hypothesis that high FE values are determined by local pH levels and the surface of the catalyst is covered with Cu species [33], under the surface of the catalyst, oxygen levels are monitored. The reduction of carbon dioxide involves a set of steps described as follows: dissolution, adsorption, activation, multiple electron/proton transfers, as well as desorption of carbon products from the catalyst after it has been activated. The temperature can also affect carbon dioxide solubility in aqueous solutions, as reported by several researchers [34, 35]. CO₂ reduction efficiency and selectivity depend also on electrodes and reactor design in addition to the catalyst itself. Special attention should be given to the synthesizes and materials used for carbon dioxide conversion. A simple method was used to synthesize nanoparticles copper - based materials that are most widely used being the most effective catalysts for carbon dioxide reduction. With the utilization of copper nanoparticles synthesized via the oxalate method, in this work we demonstrate the selectivity CO₂ conversion to multi carbon compounds in a flow cell at room temperature. We report the effect of Ag in combination with CuO at different potentials (-0.75, -0.85, -0.95, -1.05 V vs. RHE in 0.1 M KHCO₃), the liquid phase outlet streams were collected and analyzed using gas and liquid chromatography.

Materials and methods

Cleaning procedure

There was a 12 - hours soak required before each experiment was conducted for all glassware and the PEEK H-cell in an acid solution containing 0.5 M H₂SO₄ and 1 g / L KMnO₄ was conducted. To remove any remaining manganese oxide, the glassware and H - cell were rinsed and soaked in a solution of H₂O₂ and H₂SO₄. A subsequent rinse with ultrapure water was performed along with three boils in Milli - Q before the glassware and H - cell were cooled down ($\geq 18.2 \text{ M } \Omega \text{ cm}$) ultrapure water [36].

Electrode preparation

Copper oxide powder (CuO or CuO -Ag) was drop-cast onto a graphite disk. Beforehand, an ink of the respective powder was prepared by mixing 1 mg cm⁻² of powder mixed with isopropanol. The ink was then dried in ambient air for at least 30 min. The resulting electrode was partially used as the working electrode. It is worth mentioning that the electrode was reduced by sweeping the potential from -0.1 V to -1.0 V for 20 cycles at a scan rate of 50mV/s.

Electrolysis

All electrolysis experiments in this study were conducted using a custom-made PEEK H - type cell. The working electrode was used as mentioned before (3.2. Electrode preparation). The counter electrode was a dimensionally stable anode (DSA), while the reference electrode was a leak-free mini HydroFlex® hydrogen electrode (Gaskatel) [36]. An anion-exchange membrane (Selemion AMVN, AGC) was used to facilitate the separation of the working electrode and the counter electrode compartment. The compartments were filled with 6 mL of electrolyte. CO₂RR was carried out in 0.1 M CO₂ - saturated KHCO₃ (pH=6.8) electrolyte. CO₂ gas flow the purge was conducted continuously over test into the electrolyte at a rate of 15 mL / min. All potentials (-0.75, -0.85, -0.95, -0.105 V vs. RHE in 0.1 M KHCO₃) were controlled using an Ivium potentiostat (Ivium Technologies). During the experiment, impedance spectroscopy (EIS) was utilized to determine the resistances, and 85% ohmic drop compensation was applied (graph not shown). A sample of the gas was taken every 10 min during the experiment and analyzed using a Micro-GC (Agilent), which was equipped with two thermal conductivity detectors (TCD). One TCD was equipped with a CP-SIL 5B column to separate CO₂, CH₄, and C₂H₄, while the other TCD used a combination of MS5A and CP - PORABOND Q columns to separate H₂, O₂, N₂, CH₄, and CO. Liquid products were analyzed using high-performance liquid chromatography (HPLC, Shimadzu) with an Aminex HPX-87 H column from BioRad, equipped with a refractive index detector (RID).

Synthesis of catalysts

A copper-based cathodes electrocatalyst was synthesized according to the procedure described previously in the paper [37]. It involved dissolving copper nitrate in distilled water and neutralizing it with NaOH in order to mix copper nitrate with oxalic acid at pH 6.5. The molar ratio of the metal and chelating agent was 10. After forming a metal complex, hydrogen peroxide was applied at 80 ° C to decompose it, resulting in a precipitate, which was filtered, washed, and dried at 100 ° C for 24 h. The raw powders were subsequently calcined at 350 ° C for 120 min. The Ag catalyst was impregnated onto CuO and was successively treated in diluted 5% H₂ / 95% He atmosphere to form metallic silver nanoparticles. On the prepared catalyst, ball milling at 160 rpm was performed during 24 h on the 70% CuO and 30% Ag specimens.

Physicochemical characterisation

Using a D 8 Advance diffractometer, the structure and crystallinity of the cathode electrocatalyst were determined (Bruker AXS, Germany) equipped with Ni β - filtered Cu - Kα radiation ($\lambda = 1.5406 \text{ \AA}$), for the purpose of this experiment, the following parameters were used: 2θ range 20–100 °, 40 kV and 40 mA, scan step of 0.03° s⁻¹. To obtain the micrographs, scanning electron microscopy (SEM) were used to obtain a series of images from the sample in an Apreo SEM (Thermo Fisher Scientific) with an acceleration voltage of 15 kV and an electron beam current of 0.4 nA. Electrode chemical composition was investigated by energy dispersive X - Ray spectrometry (EDX) using an Oxford Instruments X -Max N 150 Silicon Drift detector coupled to the Apreo SEM. EDX data processing was carried out with the Pathfinder™ X - ray Microanalysis software v 1.3. A chemical composition of the electrode has been calculated using the chemical compositions of ten different regions on the electrode. To determine the surface chemical composition of the samples as well as the chemical environment of the samples, X-ray photoelectron spectroscopy (XPS) was used. A Physical Electronics GMBH PHI 5800-01 spectrometer was used for this analysis (Physical Electronics GmbH, Munich, Germany), which was equipped with a monochromatic Al - Kα source (1486.6 eV) and a 300 W power beam.

Results and discussion

The copper oxide catalyst was prepared by oxalate method as active phase with small particles as a way of increasing the number of active sites on the surface of the cathode catalyst by maximizing their concentration. Both catalysts were subjected to a preliminary study to determine phase purity and morphology. X-ray diffraction studies prove that the obtained CuO is a face-centered cubic phase in agreement with standard powder diffraction. A comparison of the crystal reflection of CuO and CuO-Ag specimens is shown in Fig. 1, along with typical patterns for CuO (JCPDS card n° 05–0661) and metallic Ag for reference (JCPDS card n° 04 -0783). No phase impurities were present in the diffractogram and Scherrer equation applied to the FWHM of CuO and Ag peaks showed that, and the crystallite size was determined to be 8 nm (CuO) and 17 nm (Ag). Other investigation was conducted by SEM analyses (Fig. 2) of powders supported carbon papers. It is intended to illustrate the morphology of CuO and Ag electrocatalysts and indicating that there is little agglomeration between the crystallites of CuO. To determine the elements in the sample, elemental

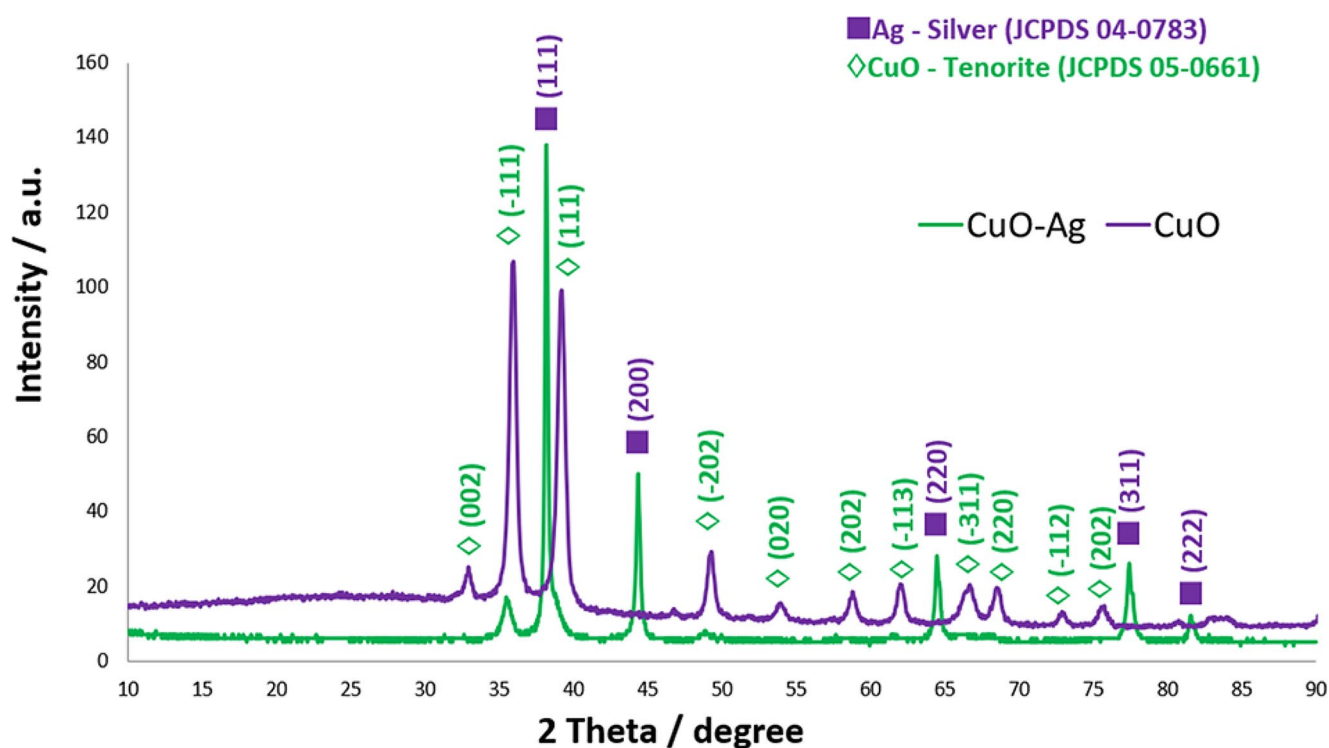


Fig. 1 XRD patterns copper oxide and silver sample (CuO -Ag) and copper oxide sample CuO catalysts

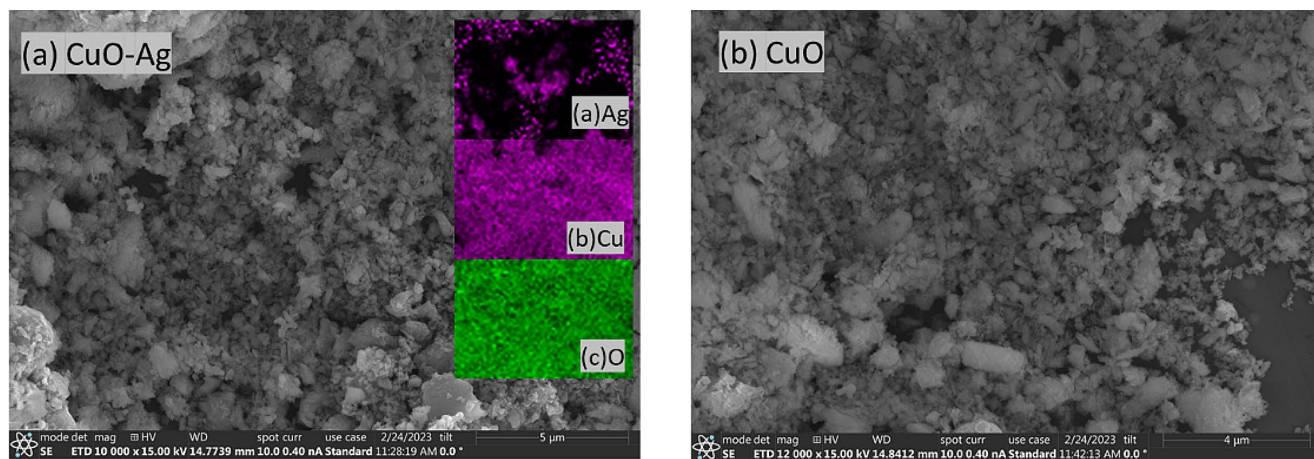


Fig. 2 SEM images of copper oxide and silver sample CuO -Ag (a) and copper oxide sample CuO (b) catalysts prepared by oxalate method

analysis was performed the presence of Ag was confirmed by EDX (Fig. 2a).

In the following analysis regarding the scanning electron microscopy (SEM), the images showed in the Fig. 2, representing the CuO nanoparticles with basically spherical and clustered morphology combined with silver with predominant tetrahedron structure.

XPS spectra of Ag and CuO to determine their surface valence state. Figure 3 shows the Survey of CuO -Ag and CuO. Copper oxide and silver surface atomic ratios derived from XPS were similar to those obtained from XRD, with

slight oxide enrichment. To determine the atomic composition of the surface, an XPS analysis was conducted. As can be seen in Fig. 3, both catalysts showed an enhanced signal from carbon. As a support for the powder analysis, carbon paper was used during electrode assembly. The atomic composition was 0.67% silver, 18.32% copper, 36.6% oxygen, 44.7% carbon for sample (a) and 25.62% copper, 45.24% oxygen, 29.14% carbon for sample (b). There were no signs of contamination on the surfaces of the materials examined.

In Fig. 4, the spectra of Ag 3d (a) and Cu 2p (b) are reported. The binding energy position of Ag 3d 5/2 (

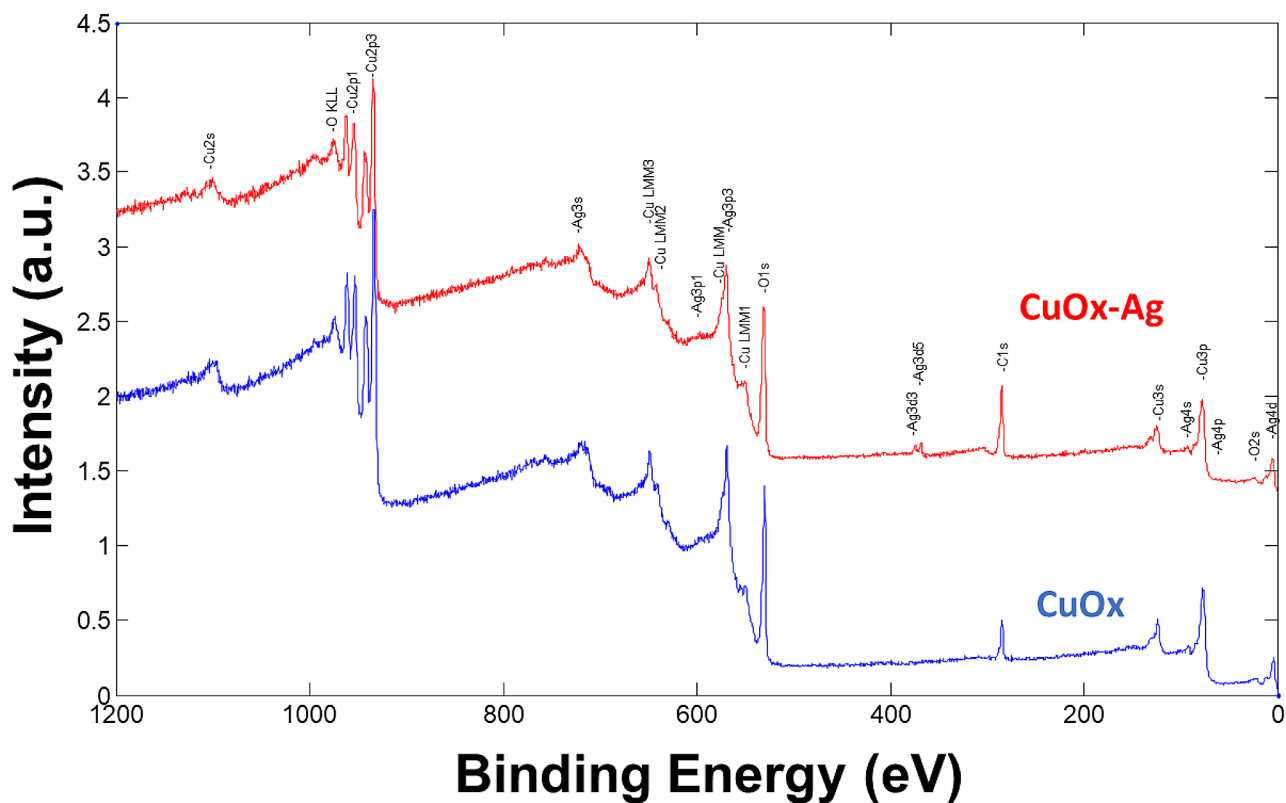


Fig. 3 Survey XPS spectra of CuOx - Ag and CuOx

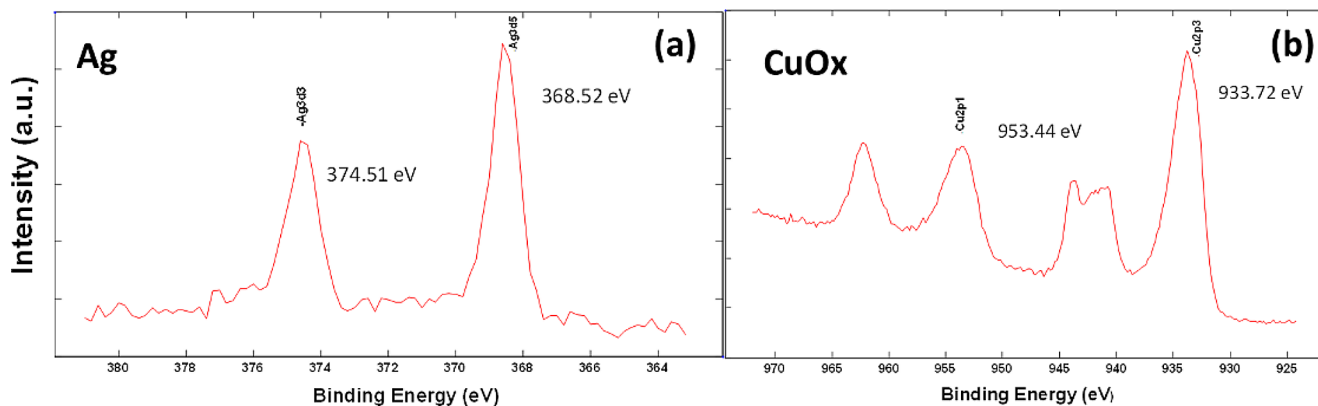


Fig. 4 Evaluation of the electronic state for Ag (a) and CuOx (b)

368.52 eV) and 3d 3/2 (374.51 eV) (Fig. 4a) proves the metallic state of silver (Ag^0) at the surface of the catalyst [38]. The spectrum of Cu 2p (Fig. 4b) consists of two spin-orbit components at binding energies of 933.72 eV (2p 3/2) and 953.44 eV (2p 1/2) and two Cu²⁺ shake-up satellites. Spectral shapes and peak positions indicate the presence of Cu (II) species at the surface of CuO - Ag catalyst, in addition to being consistent with the structure of cupric oxide (CuO) [16, 39, 40].

The Fig. 5. shows the results in a flow cell in a 0.1 M KHCO_3 solution, two different cathodes were evaluated for electrochemical carbon dioxide reduction reactions. Two main formulations of catalysts have been developed as a result of the synthesis of oxalate, copper oxide (CuO) and copper oxide mixed with silver (CuO -Ag 70% : 30%). The CO_2 reduction reaction over two different cathodes was investigated at different potentials -0.75 , -0.85 , -0.95 , -0.105 V vs. RHE. The composites exhibit good catalytic

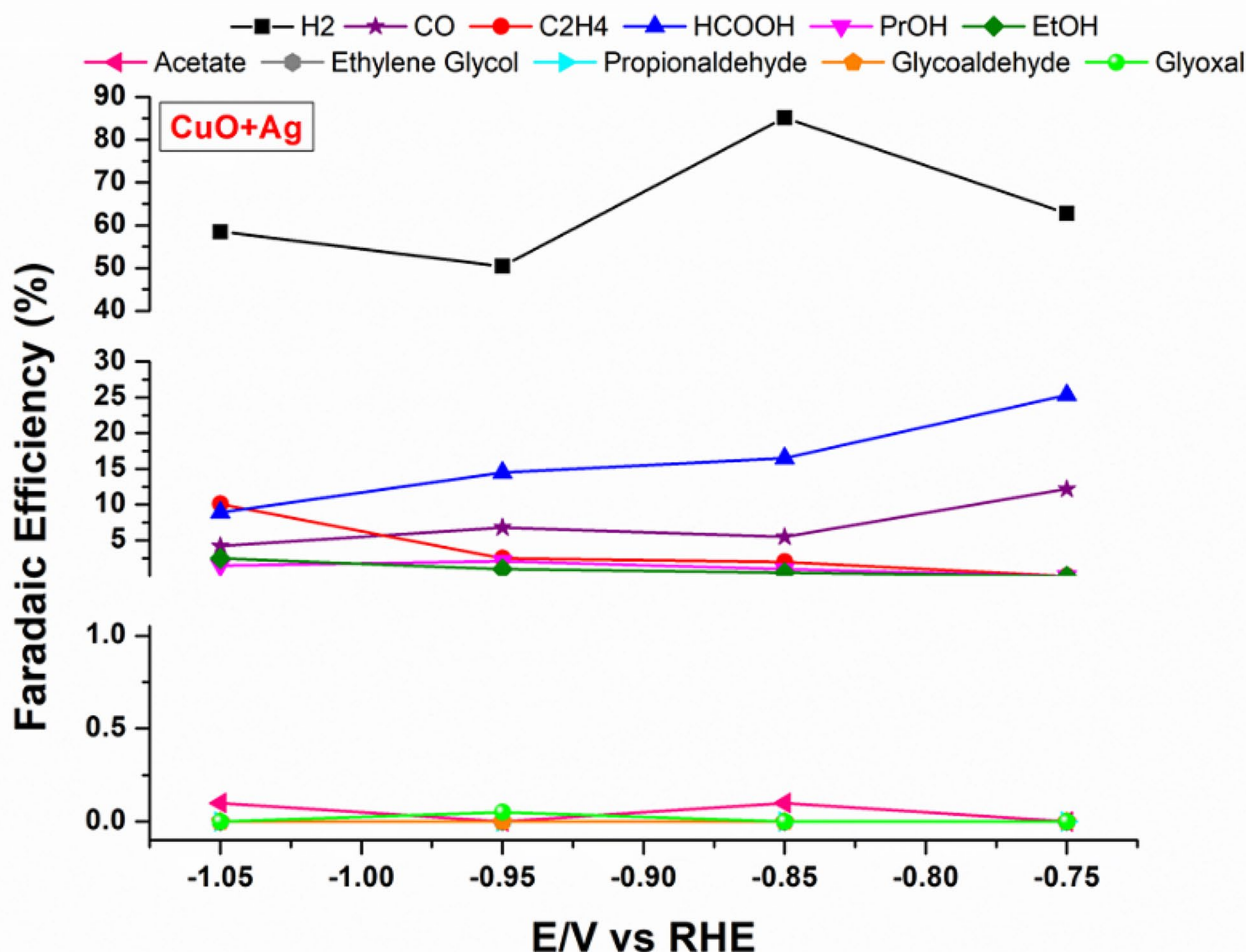


Fig. 5 Selectivity Faradaic efficiency (FE %) for copper oxide mixed with silver catalyst (CuO -Ag)

activity due to their synergistic properties provided by their electronic and geometric structures. It was observed that the selectivity increased for hydrogen (H₂) and formic acid (HCOOH) formation at -0.85 V over CuO - Ag. Following, C₂₊ products were formed ethylene, ethanol, and propanol (C₂H₄, EtOH, PrOH) at -0.75 V. On the other hand, carbon monoxide, acetate, ethylene glycol, propionaldehyde, glycoaldehyde and glyoxal (CO, CH₃COO, C₂H₆O₂, C₃H₆O, C₂H₄O₂, C₂H₂O₂) have been detected in poor concentration. In comparison to the materials investigated by Jeon et al. [41], in a full flow single cell the electrocatalytic performances of Cu Ag combination catalysts of varying compositions was identified. The authors observed that at 2.2 V voltage, C₂H₄ faradaic efficiency appears to be 1.5 times higher in the Cu₉₀ Ag₁₀ than the bare Cu and has a higher current density in C₂H₄ relative to the bare Cu. The authors observed the synergistic effect between Cu and Ag, the Cu₉₀ Ag₁₀ exhibits improved performance due to the appropriate ratio between Cu and Ag between the two alloys.

On the investigated electrodes containing only CuOx, Fig. 6, ethylene formation (~20% of C₂H₄) occurred at -1.05 V vs. RHE compared than composite catalyst CuO - Ag (~10% of C₂H₄). In the experiments acetate formation seems increased at the -0.85 V potential range basically only for both copper oxide catalysts and the conversion decreased for hydrogen. Poor FEs were observed for the CuOx electrodes at more reductive potentials.

According to Kim et al. [11], it is possible to form at low overpotential C₂-C₃ products using a combination of Cu nanoparticles. The redox mechanisms during electrochemical operation result in enhanced selectivity for C₂ products from copper catalysts essentially based on copper oxide. In particular, the state of oxidation of Cu and the shape of its surface determines the selectivity and productivity. It is important to note that the carbon dioxide reaction involves the transfer of multiple protons as well as multiple electrons (2 electrons, 4 electrons, 6 electrons, or 8 electrons). Despite the challenges that remain, Cu-based electrocatalysts will

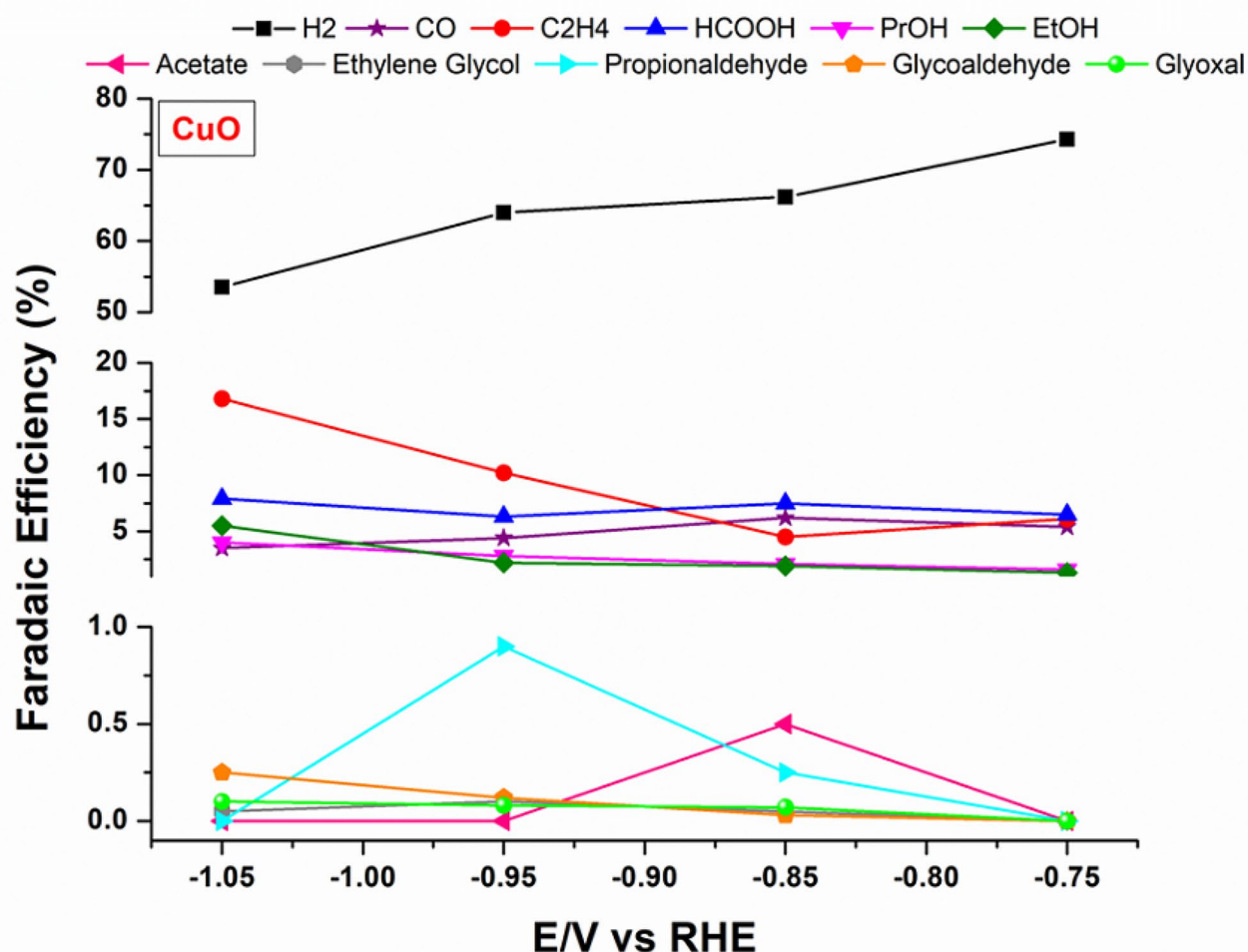


Fig. 6 Selectivity Faradaic efficiency (FE %) for tenorite copper oxide catalyst (CuO)

continue to receive considerable attention in the literature for targeted practical applications.

Conclusions

Clearly, there has been a lot of progress made on electrochemical carbon dioxide reduction reactions by the development of new electrocatalytic materials that are both more efficient and more stable, or by developing new methodologies that prevent electrochemical carbon dioxide reduction reactions from occurring within the first place. Although some advances have been made in understanding how the reaction works, there is still a lot to be understood about its mechanism. In this work two different cathodes were synthesized by oxalate method and evaluated for carbon dioxide conversion in a flow cell configuration. By enhancing CO₂ reduction, Ag can mitigate the H₂ evolution reaction, thereby providing a competitive advantage over

carbon-based fuels at more negative potentials. Two different cathodes were evaluated for CO₂RR in an alkaline environment. Using the CuO_x and CuO-Ag composite catalysts, C₂₊ products (C₂H₄, EtOH and PrOH), in 0.1 M KHCO₃ have been formed. These results appear very promising for alternative and innovative green fuel production from CO₂ conversion over copper oxide catalysts prepared by the oxalate method.

Declarations

Acknowledgements The authors acknowledge the financial support provided by the EU H2020 LOTERCO2M project “CRM-free Low Temperature Electrochemical Reduction of CO₂ to Methanol” Grant Agreement number: 761093 and by the EU H2020 GREEN DEAL “ECO2FUEL” project “Large-scale low temperature electrochemical CO₂ conversion to sustainable liquid fuels” Grant Agreement number: 20 101037389. Dr Sabrina C. Zignani acknowledges financial support from the CNR - Short Term Mobility 2022 program. The authors also acknowledge the Prof. Dr. Marc T. M. Koper and Dr. Alisson H. M. da Silva for the support during the experiments in the laboratory at

Leiden University.

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