



Alkaline electrolysis using CuO_x cathode for the conversion of carbon dioxide into liquid fuels

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Abstract

Electrochemical reduction of CO_2 is an effective method for storing intermittent renewable energy. This could result in fuel additives and chemical feedstocks such as alcohols. A challenge of electrochemical alcohol production is the transfer of electrons and protons, as well as the formation of C–C bonds. As of now, copper-based materials are the most commonly used and effective catalysts. Although CuO_x is considered a promising catalyst for electrochemical CO_2 reduction reactions (CO₂RR), significant improvements in product selectivity are still needed. This paper presents some results obtained using copper oxide as a cathode, combined with 33% of ionomer, nickel iron as anode, and membrane Fumatech as electrolyte. As a result of physico-chemical experiments, morphological measurements of the cathode, electrochemical experiments carried out with a complete zero-gap cell operating under alkaline conditions, and gas-chromatographic (GC) analyses of the cathode outlet stream, we determined that methyl formate, ethanol, and propanol were mainly obtained at a rate of $116.3 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ during operation at 2.2 V.

Keywords Green fuels · CO_2 reduction · Zero-gap electrochemical cell · Carbonaceous fuels · CRM-free catalyst

Introduction

To combat global warming caused by increasing carbon dioxide (CO_2) emissions into the atmosphere, technological solutions for their removal are urgently needed [1, 2]. One of the greatest technological challenges of our time is the production of fuels and chemicals from carbon dioxide [3, 4]. It is possible to achieve this goal using electrochemical processes at room temperature and pressure [5, 6]. By using renewable energy to feed an electrochemical cell, carbon dioxide and water can be converted into “green fuels”, reducing CO_2 emissions and storing renewable energy [3, 7]. Through a mechanism involving electron transfer, an electrochemical cell containing an active electrocatalyst at the cathode reduces CO_2 into organic products. It is currently challenging to control which products could be achieved through this mechanism. Several reduction products can be formed in aqueous and non-aqueous based electrochemical

devices, including methanol, formic acid, methane, and carbon monoxide [8, 9]. Due to the fact that one of the most promising electrochemical cells uses alkaline conditions, novel, hierarchical materials made of non-noble and noncritical raw materials (CRM-free) have recently gained attention [10, 11]. Among the most commonly used electrocatalysts for electrochemical CO_2 reduction in alkaline conditions is copper, which electrochemically converts CO_2 into more than 30 products, including hydrocarbons and alcohols [9, 12–19]. Specific studies evidenced that Cu-based electrocatalysts can enhance CO dimerization to promote the formation of C₂ products [18, 20–24]. According to the literature, product distribution is influenced by morphology and the exposed face of Cu, although applied potential and electrolytes also play an important role [20, 25, 26]. While CO_2 is being reduced, copper catalysts produce ethylene rather than ethanol or *n*-propanol [10, 27]. In a specific experiment conducted using Cu-based electrocatalysts, Roy et al. reported that *n*-propanol might be one of the most important C₃ products [28]. Consequently, there is a great deal of motivation to develop Cu-derived oxide electrocatalysts so that C₂ or higher products can be produced with high Faradaic efficiency.

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Moreover, alkaline conditions improve oxygen evolution kinetics because less energy is required in comparison with acidic conditions. In addition, CO_2 solubility in alkaline conditions could contribute to its easier reduction, since the reaction involves a lower order of reaction [29, 30]. In spite of this, alkaline electrolytes suffer from several disadvantages, including a lower ionic conductivity than H^+ electrolytes and the need to recirculate caustic solutions [31–34]. The purpose of this manuscript is to examine the role of CuO_x mixed with carbon in the cathodic reduction of CO_2 in a single cell of 5 cm^2 and under different cell potentials to evaluate the quality of products and the efficiency of their production [35–38]. Experiments were conducted at 1.8 V and 2.2 V cell voltages with 1 M KOH circulating on the anode as a refilling electrolyte, while the liquid phase in the outlet stream from the cathode was collected and analysed with gas chromatography (GC).

Materials and methods

Copper-based cathode electrocatalyst was prepared by the oxalate method (Patent WO2004049491), described in detail in our previous paper [19]. In brief, Cu nitrate was dissolved in distilled water and mixed with a solution of oxalic acid neutralized with NaOH at pH 6.5. The metal and chelating agent were mixed at a molar ratio of 10. The metal complex was formed and then decomposed at $80 \text{ }^\circ\text{C}$ with hydrogen peroxide to obtain a precipitate. This precipitate was then filtered, washed, and dried at $100 \text{ }^\circ\text{C}$ for 24 h. Afterward, the raw powders were calcined at 350 degrees Celsius for 120 min, then milled for 6 h with Ketjenblack (KB 600) carbon in the ratio 70:30 (metal oxide:carbon).

As part of the physicochemical characterization of the cathode electrocatalyst, transmission electron

microscopy was used to study the morphology of the material at nanoscale magnification (TEM-FEI CM12 fitted with a LaB6 filament). The structure and crystallinity of the cathode electrocatalyst were determined using a D8 Advance diffractometer (Bruker AXS, Germany) equipped with Ni β -filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), based on the following experimental parameters: 2θ range 20° – 100° , 40 kV and 40 mA, scan step of $0.03^\circ \text{ s}^{-1}$.

A complete cell architecture was used to conduct electrochemical experiments. First, anode and cathode inks were prepared. The anode for all electrochemical experiments was NiFeO_x , which has already been thoroughly characterized and described in our previous paper [11]. The inks contained 33 wt% anionic ionomer (i.e. Fumatech) and 67 wt% electrocatalyst. These materials were dispersed and sonicated in ethanol for 30 min before being used to manufacture electrodes by spray coating technique. Gas diffusion layer (GDL) purchased from Sigracet was used as support for the cathode and nickel felt purchased from Bekaert for the anode. This procedure resulted in a total catalyst loading of 2.5 mg cm^{-2} for the anode and 6 mg cm^{-2} for the cathode. A Fumatech (FAA3-50) anion exchange membrane was used as a polymer electrolyte [39]. After anode and cathode electrodes were cold assembled with electrolyte in the middle, the membrane electrode assembly (MEA) was completed.

A setup cell with an active area of 5 cm^2 is shown in Fig. 1. This apparatus was designed for electrolysis of CO_2 in an alkaline environment with 1 M KOH recirculated at the anode, as described in this paper. Figure 1a illustrates the inlet and outlet streams of each electrode, in addition to the wire connections and materials placed within the housing. The cryogenic system shown in Fig. 1c was used to collect liquid from the cathode side.

In this setup, a nickel housing maintained at $50 \text{ }^\circ\text{C}$ was used to conduct electrochemical experiments on MEAs. A

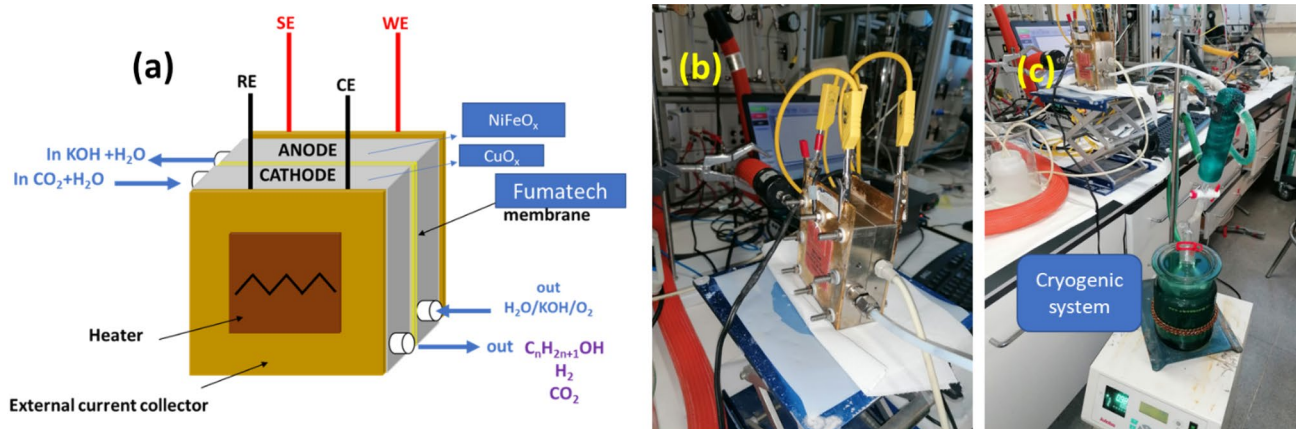


Fig. 1 Setup for electrochemical cell testing. **a** Cell housing, **b** connection between test bench and cell housing, **c** cryogenic system for capturing the cathode outlet stream

peristaltic pump was used to circulate a KOH solution (1 M) at a rate of 5 ml min^{-1} in the anode compartment. The cathode was fed with humidified CO_2 at a rate of 50 ml min^{-1} after being preheated to cell temperature. Keithley power supply equipment (Tektronix, Rome, Italy) was used to conduct electrochemical investigations (polarization curves versus current density, I – V curves) and chronoamperometry. A gas chromatographic analysis of the cathodic outlet was performed during endurance testing to identify electrochemically produced organic soluble species. For this purpose, the liquid was entrapped in a vial maintained in a cryogenic apparatus at a temperature below 1°C . These analyses were performed using a GC model Agilent 7890 A. The instrument included a capillary column (30 m by 0.53 mm by 0.2 m film thickness), model Supelcowax 10 (Merck KGaA, Darmstadt, Germany) connected directly to a flame ionization detector. Helium was used as a carrier gas for eluting the analytes. To determine the “sensitivity factors” of each compound, the GC was calibrated with standards before use.

Results and discussion

Figure 2 shows the XRD spectrum of fresh CuO_x/KB used as a cathode in electrochemical experiments. There are typical crystal reflections of cuprite (Cu_2O —JCPDS card no. 05-0667), tenorite (CuO —JCPDS card no. 05-0661), and metallic copper (Cu —JCPDS 04-0836). A semi-quantitative determination of the weight fraction of each phase was performed using native software on XRD equipment. As a result, 30.4 wt% of cuprite, 51.1 wt% of tenorite, and 18.5 wt% of metallic copper were found. Results from an XRD spectrum showed no apparent impurities.

Fresh cathode electrocatalyst morphology was investigated using a TEM. As can be seen in Fig. 3, the

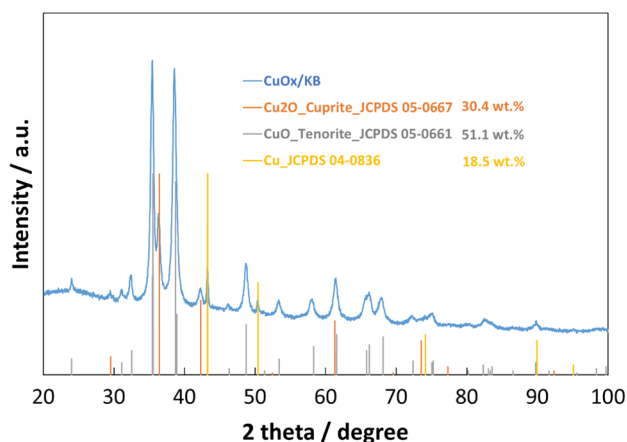


Fig. 2 XRD pattern of the cathode electrocatalyst prepared by the oxalate method

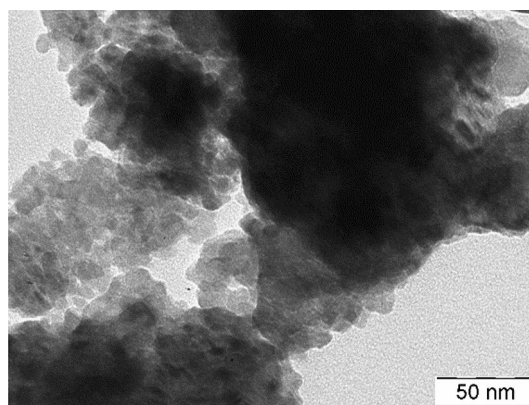


Fig. 3 TEM image of the fresh cathode

nanoparticles were well dispersed on the Ketjenblack support. In spite of this, regions with a high particle density exhibit significant agglomeration, which could lead to larger particles. It is very likely that the high copper oxide content of the electrocatalyst (70 wt%) caused the particle distribution observed by microscopy.

Using an I – V curve for a preliminary diagnosis, the fresh cell showed a linear dependence of V from current density at potentials higher than 1.8 V, mainly due to ohmic constraints (Fig. 5). Under these conditions, the fresh cell appeared to be stable as well as barely affected by activation constraints. Consequently, the cathodic outlet stream was measured at 1.8 V, where I – V profiles significantly changed, and at 2.2 V, where best performance was obtained. The first chronoamperometry test was conducted at 1.8 V (Fig. 4a). Cell performance was quite poor at this voltage, allowing a current density of approximately 90 mA cm^{-2} , which rapidly dropped to approximately 30 mA cm^{-2} . In the liquid collected from the cathode stream after 6 h, methyl formate, ethanol, and propanol were detected (Fig. 4c). The current density was approximately 200 mA cm^{-2} when the cell was placed at 2.2 V. It took approximately 1 h for the cell to achieve steady state behaviour around a current density of 530 mA cm^{-2} . Chromatographic analysis of the liquid collected from the cathode outlet stream showed a significant increase in methyl formate and propanol, whereas the signal of ethanol remained substantially unchanged (Fig. 4c). It was in agreement with findings from two previous studies published by Kim et al. [10] and Ting and collaborators [27].

Table 1 summarizes the gas-chromatography results for the cathode’s outlet stream. These data demonstrated a significant improvement in the products at 2.2 V, partly due to an additional hour of liquid collection. However, most of this improvement can be attributed to the significant increase in current density by cell operation at 2.2 V. On the other hand, despite a one order of magnitude increase in current density, liquid product formation and relative composition

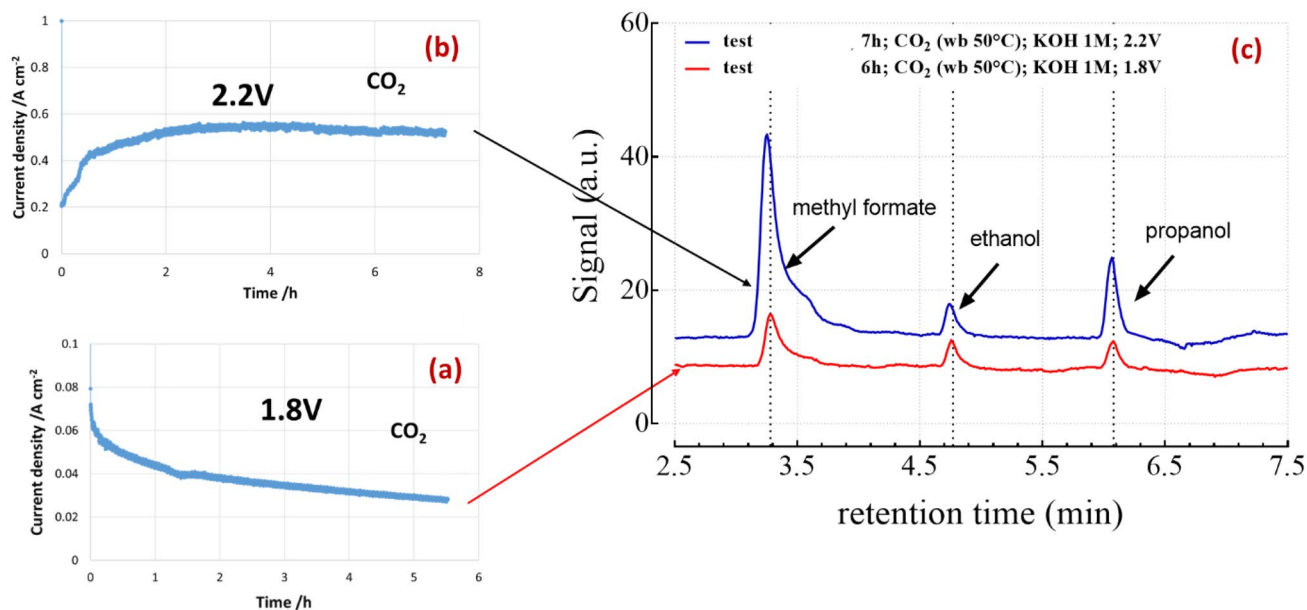


Fig. 4 Chronoamperometric tests at 1.8 V (a) and 2.2 V (b) and corresponding liquid-phase analyses of cathode outlet streams (c)

Table 1 Distribution of products in electrochemical experiments at 1.8 V and 2.2 V

Operative conditions	Product formation rate ($\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$)			Product yield ($\mu\text{mol g}_{\text{cat}}^{-1}$)			CO_2 consumption rate ($\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$)
	Methyl formate	Ethanol	Propanol	Methyl formate	Ethanol	Propanol	
6 h @ 1.8 V	13.3	2.5	1.8	79.7	15.2	10.8	37.0
7 h @ 2.2 V	103.2	4.5	8.6	722.4	31.8	60.5	241.4

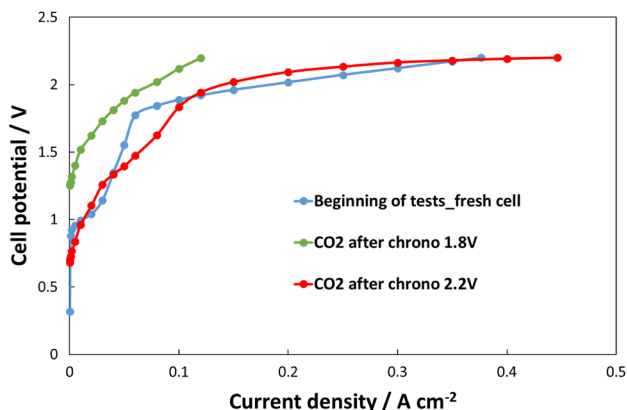


Fig. 5 A comparison of polarization curves measured at various experimental moments

did not increase as expected. According to the literature, electrochemical reduction of CO_2 in an alkaline environment results in intermediates such as carbon monoxide (Eq. 1), formic acid (Eq. 2), and ethene (Eq. 3). However, upon combination, or through other means of di- or trimerization, other C2+ final products can be observed. This

aspect was highlighted in a study by Ai et al. [40], where these results were theoretically predicted and experimentally confirmed. Based on these preliminary results, a complex mechanism involving intermediates and secondary reactions was observed in the cell, which depended on the voltage and partial pressure of species.

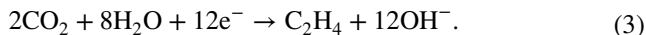
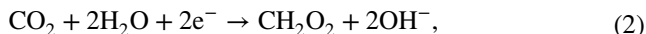


Figure 5 illustrates a comparison of characteristic current–voltage curves collected at various cell life moments.

At the beginning of durability tests, there was a very low open circuit potential (OCP) and significant activation overpotential (blue curve). A moderate increase in current density was observed between approximately 1 V and 1.77 V (i.e. 4 mA cm^{-2} and 50 mA cm^{-2} , respectively). This feature of the curve and slightly improved performance with increased cell potential could be attributed to the multiple Cu oxidation states. Above 50 mA cm^{-2} ,

the curve feature was quite smooth and controlled by the ohmic mechanism. The electrolysis products were investigated at 1.8 and 2.2 V based on this specific cell behaviour (Fig. 4 and Table 1).

After 6 h of testing at 1.8 V, the characteristic curve (green curve) was determined. This led to an OCP value of 1.25 V in this case. Based on the results of this test, the cell performance was significantly depleted due to high ohmic constraints, probably as a result of partial reoxidation of metallic Cu, or Cu-based reactive sites were occupied by intermediates. In both cases, cathodic electronic percolation could have been adversely affected. After the cell was placed at 2.2 V, its performance gradually improved. As a result of the test, the characteristic I – V curve (red curve) showed the OCP dropping to around 700 mV. In the region where the current density was approximately 30 mA cm^{-2} , the I – V curve was mainly influenced by the activation energies of the processes involved. Despite significant ohmic constraints up to 1.94 V, this cell showed very promising results above this value.

Conclusions

Our study investigated the feasibility of electrolysis CO_2 in an alkaline environment to produce liquid added value synthetic fuels. To make this approach feasible, we developed a CRM-free cathode based on a CuO_x electrocatalyst for its use in an alkaline zero-gap cell. Experimental results showed that using the oxalate method, we achieved a mixture of Cu-based structures having oxidizing states from 0 to 2. This specimen had a strong tendency to agglomerate. Electrochemical tests combined with liquid effluent analyses confirmed some results reported in the literature concerning the promotion of intermediates that can lead to secondary reactions producing liquid organic fuels. Our findings indicated that the recommended operating cell potential for this device should be above 1.9 V because of the high current density achievable and the quality of products.

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Data Availability This study included data to support its findings.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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