

PAPER

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2024, 8, 3104Recycling spent batteries to green innovation:
a CuCo-based composite as an electrocatalyst for
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The reuse of solid and gaseous waste is necessary to achieve a significant advance toward more sustainable and eco-friendly processes. It is a challenge in the electronic industry, where the materials are generally expensive and toxic (if disposed of in nature), requiring strategies for maximum material recovery. Here, we report a strategy to recycle lithium-ion batteries (LIBs), preparing a copper–cobalt composite catalyst designed to operate in electrochemical CO₂ reduction to hydrocarbons. The proposed method allows fast and easy electrodeposition of a thin layer of spherical Cu/Co nanoparticles over a conductive substrate. The electrodes were assessed for their CO₂ reduction activity at different potentials (−0.13, −0.33, and −0.53 V vs. RHE). As a result, we achieved different products such as methanol, acetic acid, ethanol, and hydrogen with selectivity according to the applied potential. The highest production and faradaic efficiency for C₁₊ compounds were for methanol, reaching 103 μmol mg_{cat}^{−1} and 65% after 3 h of reaction at an applied potential of −0.13 V vs. RHE. A proposed scheme, based on *in situ* FTIR spectra using D₂O, suggests that CO₂ initially undergoes one-electron reduction, forming *CO_{ads}, which acts as a stable intermediate on the Cu surface. The Cu surface predominantly drives the reaction despite its higher amount in the CuCo-based composites. From that, various pathways can arise from the protonation of the intermediate, leading to the production of C₂₊ alcohols in smaller quantities or C₁ alcohols in larger quantities and intensity.

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Introduction

Recently, the United Nations established global goals for sustainable development that address changes in energy and climate.¹ Recently, the United Nations established global goals for sustainable development, which address changes in energy and climate.¹ In this sense, electrification is a cost-effective means of preventing or reducing greenhouse gas (GHG) emissions, which helps mitigate the consequences of climate change since it is one of the most cost-effective energy transitions.¹ Lithium-ion batteries (LIBs) have emerged as one of the most viable strategies for modern civilization to reduce the amount of directly produced CO₂. Batteries are a promising alternative to combustion-powered transport vehicles, which account for nearly 18% of total CO₂ emissions.² However, the metal used in the manufacture of these electronic devices causes severe

environmental damage if disposed of in nature or not correctly recycled.^{3,4}

There are two industrial ways to recycle spent LIBs: the pyrometallurgical and hydrometallurgical processes.⁵ The latter is the primary method for recycling LIBs because it allows the recovery of metal ions under mild conditions, and its resulting solution can be harnessed through precipitation, extraction, or electrodeposition methods.^{6–8} Electrochemical recycling *via* electrodeposition is a promising strategy for separating and recovering metals from multi-component mixtures. It is a viable and controlled process to produce metal films, alloys, and multilayer deposits.^{7,9}

Copper and cobalt are some of the metals found in used LIBs that hold exciting applications for supporting the achievement of global sustainable development goals, as they can contribute to reducing CO₂ emissions by their use as building blocks for making value-added molecules.^{10,11} Currently, copper is the only metal capable of producing alcohols and dimerizing carbon molecules to produce C₂₊ compounds in an aqueous reaction related to the intermediate binding strength between CO₂ molecules and the active copper sites.^{12,13} Simultaneously, cobalt-based catalysts have shown promising results for CO₂ conversion, being an alternative to metals such as Au, Ag, Pd, or In.^{14–16} Recently, Wang's group reported that incorporating cobalt nanoparticles on single-layer nitrogen-doped graphene boosted the selective hydrogenation of

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CO₂ to methanol, obtaining 71.4% methanol under mild conditions.¹⁷ Kim's group reported the potential of a Co-based catalyst for direct CO₂ hydrogenation at a mild temperature of 270 °C, achieving high-yield C₅₊ (21.1%) even during long-term catalytic reactions (up to 1425 h).¹⁸

Bimetallic Cu/Co materials are promising electrocatalysts based on the synergism between the copper and cobalt particles, associated with the percentage of each metal, which drives the direction of the reactions. It may form mainly CO, CH₄, >C₂₊, and alcohol. Guo *et al.* observed a faradaic efficiency (FE) of 97.4% for CO, using Cu/Co bimetallic catalysts.¹⁹ Bernal *et al.* investigated the product selectivity of Cu/Co toward CO, HCOOH, and H₂ by varying the size and composition of catalysts. They attested that small Co contents enhance Cu/Co NPs activity, while increasing particle size favors the CO₂RR over the HER.²⁰ Grote *et al.* produced Cu–Co NPs with composition-dependent product selectivity, which demonstrated good selectivity for ethylene and alcohol synthesis when the Co content was maintained within the range of 5–15%.²¹ Zhang *et al.* confirmed the potential of this catalyst using density functional theory (DFT) methods to investigate the main pathways for alcohol production on bimetallic Cu/Co sites through syngas (CO/H₂) conversion. According to the authors, the insertion of Co into copper-based catalysts can accelerate the whole reaction system by inserting CO and CHO on the surface or even by the decomposition of CH_xO and CH_xOH, which is necessary for the formation of higher alcohol precursors.²²

Although the literature extensively explores copper- and cobalt-based materials as promising catalysts for the production of alcohols and C₂₊ compounds, there are few reports on the use of lithium-ion batteries (LIBs) as raw materials for such catalysts.²³ Recent studies have indicated that the graphite anode present in discarded batteries can serve as a promising alternative carbon support for copper catalysts in CO₂ conversion and the degradation of organic contaminants.^{24,25} However, both of them have not explored the potential metal ions in the cathode.

Thus, in our present study, we have effectively produced a catalyst by using a direct method that includes ion leaching, followed by filtration to eliminate carbon powder, and electrodeposition at ambient temperature. Notably, the copper and cobalt used in this catalyst were exclusively obtained from discarded lithium-ion batteries. Our approach adequately fits three pillars of circular economy, *i.e.*, use of waste, straightforward synthesis method, and application for low-carbon production of chemicals (*i.e.*, CO₂ conversion to methanol at room temperature). Since the thermocatalytic process, commonly operating above 300 °C, is still the commercial route for methanol production, low-temperature routes are desirable in the context of energy efficiency for this product.²⁶ Our results reveal the potential utilization of the suggested technique and material in advancing the understanding of a sustainable economy founded on environmentally friendly chemistry.

Experimental methods

Leaching of metals from spent Li-ion batteries

The material based on Cu/Co was prepared from waste cell phone lithium-ion batteries. Following the procedure described by

Nascimento *et al.*,²⁷ the lithium-ion batteries were dismantled piece by piece. The copper current collector underwent a cleansing process with distilled water to eliminate lithium salts. Subsequently, it was cut into smaller pieces and immersed in a beaker containing aqua regia solution (HCl : HNO₃ – 3 : 1 v/v). The mixture was stirred magnetically at 60 °C for 2 hours to ensure complete leaching of copper and cobalt ions, resulting in a solution. This solution was then filtered to remove any solid residues (Fig. 1).

Electrodeposition of the Cu/Co composites

The spent LIBs were reused by reducing the metal ions from leaching liquor to form a thin film of metal nanoparticles on fluorine oxide (FTO) coated glass substrates by electrodeposition.²⁸ Firstly, the leaching liquor was ultrasonically cleaned in deionized water, isopropanol, deionized water, acetone, and then ethanol for 10 min each. The pH of the leaching liquor was adjusted to 2.7 with NaOH pellets to promote the proper nucleation of the metal nanoparticles on the substrate surface and then H₃BO₃ was added up to a concentration of 0.1 M to stabilize the pH during the electrodeposition.²⁸ The nucleation and growth of nanoparticles were achieved by an electrodeposition method using a potentiostat (Metrohm Autolab PGSTAT30N), a homemade three-electrode cell containing an FTO-substrate (1 cm² active area), Pt mesh, and Ag/AgCl (3 M KCl) as the working, counter, and reference electrodes, respectively, and leaching liquor as electrolyte. The electrodeposition process was carried out in multiple steps under potentiostatic conditions. Initially, a potential of –0.6 V was applied, followed by 0.07 V vs. RHE, as illustrated in Fig. 1. It allows a controlled and selective growth of the copper and cobalt particles on the substrate surface. After the electrochemical procedure was complete, we discovered a brown electrode that had been repeatedly cleaned with ethanol and dried with nitrogen gas. Following electrodeposition, the weight of the film was found to be around 0.173 mg cm^{–2}.

Structural characterization

The phase and crystallinity of the prepared film were characterized using an X-ray diffractometer (XRD; Shimadzu, XRD-

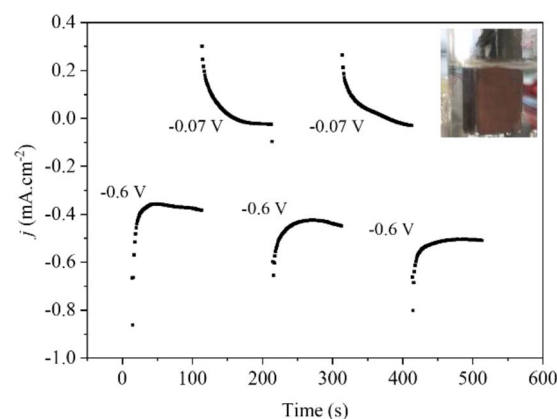


Fig. 1 Chronoamperometry curves of electrodeposition of the spent LIBs at different deposition potentials on the FTO surface.

600) with primary monochromatic high-intensity Cu K α ($\lambda = 1.541 \text{ \AA}$) radiation. The morphology and the chemical composition of deposited materials were investigated using a scanning electron microscope (SEM; JEOL, JSM-6510) coupled with an energy dispersive spectrometer (EDS; Thermo Scientific) analysis. The quantitative analysis of copper and cobalt electrodeposited was performed by flame atomic absorption spectroscopy (FAAS; PerkinElmer, PinAAcle 900T). The flame was composed of synthetic air (10 mL) and acetylene (2.5 mL) at a wavelength of 324.75 nm. X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe II) was performed with incident radiation Al K α . Surveys and high-resolution spectra were recorded using a pass energy of 0.8 and 0.1 eV, respectively. CasaXPS software was used for data analysis, and the C 1 s peak was employed as a calibration reference.

Electrochemical study

All the electrocatalytic reactions were carried out at ambient temperature and pressure using a potentiostat (Metrohm Autolab PGSTAT30N). A homemade three-electrode electrochemical H-cell containing two compartments separated by a cationic exchange membrane was used (Nafion 117). The working and reference (Ag/AgCl, 3 M KCl) electrodes were set on the cathode side, and a counter electrode (platinum mesh) was set on the anode side of the H-cell. 0.1 M Na₂SO₄ (Sigma-Aldrich, 99.9%) (pH 7.8) aqueous solution was used as the electrolyte. Before each assay, that solution was saturated with N₂ (99.99% purity) or CO₂ (99.99% purity) gas for 15 min to remove the oxygen gas from the cathodic chamber.

After this saturation period, the cell was hermetically closed, and the gaseous products generated at the end of the reaction were collected using a gas-tight syringe (Hamilton) and analyzed on a gas chromatograph (Thermo Trace 1310) equipped with a Carboxen 1010 PLOT capillary column. Argon (99.999%) was used as the carrier gas. The liquid product was measured on a Bruker 600 MHz NMR spectrometer in water suppression mode. After electrolysis, a 540 μL electrolyte was collected and combined with 60 μL of a standard solution comprising D₂O (Sigma-Aldrich), DMSO (Sigma-Aldrich, 99.8%), and 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (TSPd₄) (Sigma-Aldrich).

ATR-IR spectra were collected with a 6700 Nicolet Fourier transform infrared spectrometer equipped with a mercury cadmium telluride (MCT) detector and a VeeMAX ATR apparatus (Pike Technologies) set at a 60° reflection angle. For each spectrum, 64 scans at a resolution of 4 cm⁻¹ were typically obtained. The background was obtained at open circuit potential (OCP) after 15 min of continuous CO₂ purge in the system. A purge of CO₂ was kept constant during all the chronoamperometry measurements up to -0.33 V vs. RHE. The spectra are presented in absorbance mode with positive and negative peaks, showing an increase and decrease in the signal, respectively. In all experiments, the working electrode was pressed against a CaF₂ prism to form a thin layer, 0.1 M Na₂SO₄ in D₂O was used as a supporting electrolyte, and a Pt mesh was used as an auxiliary electrode. The potential applied to the working electrode was controlled with an Autolab potentiostat (Metrohm).

Results and discussion

Structural characterization

Table 1 shows the elemental concentrations of the ions found in the leached and electrodeposited liquor. These results reveal an ion concentration of 1918.7 mg L⁻¹ in liquor, and 85.68% and 14.32% for Cu and Co, respectively. On the other hand, to determine the deposited elements and their concentration on the substrate surface, a film of the liquor was prepared by electrodeposition²⁸ and then immersed in an acid solution to leach from the electrodeposited material. The elements observed were similar to those found in the leached liquor, but in 30 $\mu\text{g L}^{-1}$ amounts, and 77.08 and 22.92% for Cu and Co, respectively. The reduction in the Cu/Co ratio observed at the electrode compared to the liquor can be attributed to the higher frequency of applying the potential -0.6 V vs. RHE compared to the potential -0.07 V vs. RHE. It indicates that at more negative potentials, despite the copper concentration being six times higher, the deposition kinetics of cobalt are more pronounced.²⁹ However, it is essential to note that this electrochemical approach effectively maintains the original composition of the liquor on the substrate surface, with only a negligible reduction of ions. As a result, the leading solution can be reused efficiently, given the chosen electrochemical conditions of potential and reaction time.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the FTO glass substrate covered with the spent Li-ion battery. The pattern shows that the prominent peaks are the same as those observed for the pure FTO background located at 2θ of 28°, 34°, 38°, 52°, and 65°, corresponding to the (110), (101), (200), (211), and (301) planes, respectively. However, additional diffraction peaks are observed at 43°, 50°, and 55°, indicating the existence of mainly metallic Cu particles (PDF 03-065-9026). The low intensity of the peaks indexed to copper and cobalt electrodeposited particles indicates that the electrodeposition method led to the formation of thin films of metal nanoparticles.³⁰ Furthermore, the absence of prominent peaks indexed to cobalt (metal or oxide) suggests that any Co precipitates existing in the prepared samples must either be consistent with the Cu matrix or too small,³¹ making phase identification unclear. This finding agrees with atomic absorption analysis, which reveals that Cu/Co has a higher fraction of copper species than the cobalt species.

Fig. 3 shows the micrographs of the surface of the pure and Cu/Co nanoparticle-coated FTO substrates. The surface topography of the pure substrate (Fig. 3a) reveals that the FTO layer on the glass surface has a structure similar to a pyramidal

Table 1 Quantitative analysis via AAS of the metal ions from the spent battery in the leached and electrodeposited liquor

Ion source	Total		Copper		Cobalt	
	mg L ⁻¹	%	mg L ⁻¹	%	mg L ⁻¹	%
Liquor leaching	1918.7	100	1644	85.68	274.7	14.32
Electrodeposited	0.03	100	0.0232	77.08	0.0068	22.92

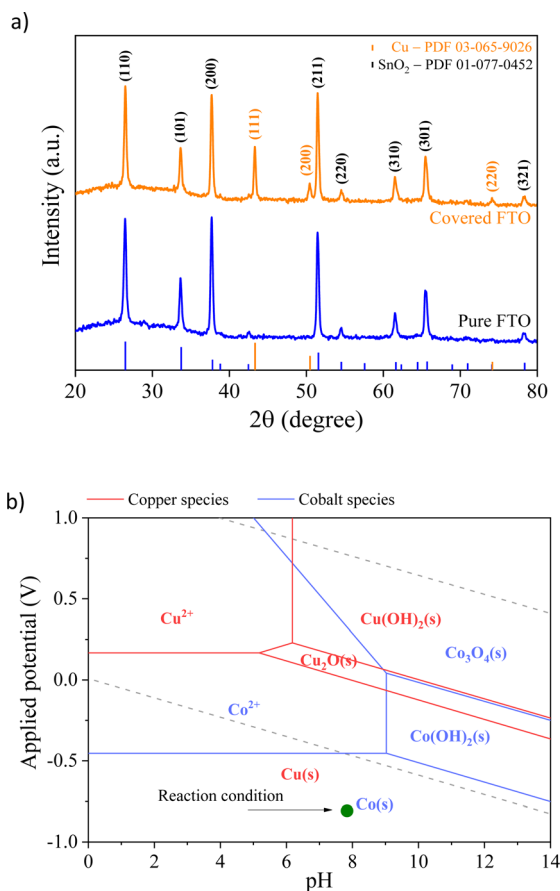


Fig. 2 (a) XRD patterns of the pure substrate (FTO) and covered spent LIB particles; (b) superposition of Pourbaix diagrams for Cu and Co, indicating the expected produced phases.

shape.³² On the other hand, the electrodeposited particles on the substrate surface show a quasi-spherical morphology, with an average size of 0.27 μm (270 nm), homogeneously distributed over the substrate surface, and a relatively uniform film thickness of 2.64 μm . Moreover, elemental microanalysis confirms that these are nanoparticles of a bimetallic composed of copper and cobalt, in agreement with AAS and XRD data, demonstrating that the proposed synthesis method from spent batteries *via* electrodeposition is an efficient way to produce spherical Cu/Co composites at the nanoscale.

XPS measurements were carried out to understand the chemical surface of the electrodeposited material on the FTO substrate (Fig. 4). Cu 2p has two significant peaks between 934 and 952 eV in the high-resolution spectra (Fig. 4a), ascribed to Cu 2p_{3/2} and Cu 2p_{1/2}.³³ The observed peaks were deconvoluted into two peaks at 933.25 and 931.4 eV attributed to Cu 2p_{3/2} as well as 954.7 and 952.5 eV attributed to Cu 2p_{1/2}, which are ascribed to the coexistence of Cu²⁺ and Cu⁰/Cu⁺ species on the electrode.³⁴ The Co 2p core level XPS spectra of the prepared material display two prominent peaks ranging from 810 to 774 eV, corresponding to the Co 2p_{3/2} and Co 2p_{1/2} core levels (Fig. 4b).³⁵ These signals were deconvoluted into two components each and were verified as a signal assigned to Co²⁺ and the

satellite of Co oxide species. The difference in Co²⁺ between the 2p_{3/2} (780.4 eV) and 2p_{1/2} (796.05 eV) signals reaches 15.64 eV (Fig. 4b), which coincides with elemental cobalt spectra, implying the presence of Co species.³⁶ Furthermore, the strong signal of satellite peaks belongs to Co²⁺ at 785.42 and 801.9 eV, confirming that cobalt species exist mainly as CoO.³⁵ However, the noisy signal of the analysis does not clarify the presence of other cobalt species but confirms its low content in the electrodeposited material.

Electrocatalytic CO₂ reduction

To identify the electrochemical redox properties of Cu/Co composites, cyclic voltammetry (CV) was performed in 0.1 M Na₂SO₄ with a scan rate of 25 mV s⁻¹. The CV curve of the Cu/Co composite in saturated N₂ electrolyte (Fig. 5a) shows two pairs of redox peaks between 0 and 1.0 V (vs. RHE). The redox peaks A1 and C1 can be associated with the oxidation and reduction of copper, respectively. On the other hand, the redox peaks A2 and C2 are related to the oxidation and reduction of cobalt, respectively.^{37,38} These redox peaks confirm the presence of copper and cobalt species in the prepared electrode, which supports the Pourbaix diagram depicted in Fig. 2b. The reversible profile indicates that the prepared electrode is stable even under structural stress promoted by the electrical stimulus induced by applied external potential.

The CO₂RR process on Cu/Co electrodes was evaluated using linear scan voltammetry (LSV) curves in N₂ and CO₂-saturated electrolytes, as illustrated in Fig. 5b. It is possible to observe that the initial potential's current (0.67 V) is higher in the N₂ atmosphere. This current is associated with the surface oxidation of copper. Subsequently, the cathodic peak detected at 0.18 V in N₂-saturated solutions is attributed to the reduction of copper oxide.³⁹ Conversely, this reduction feature is not evident under CO₂-saturated conditions, suggesting that this process may have been hindered by the adsorption of CO₂ on the electrode. Starting from the onset potential at -0.03 V there is similarity in the presence and absence of CO₂. One broad cathodic peak ensues, accompanied by an exponential increase in current in both electrolytes. The

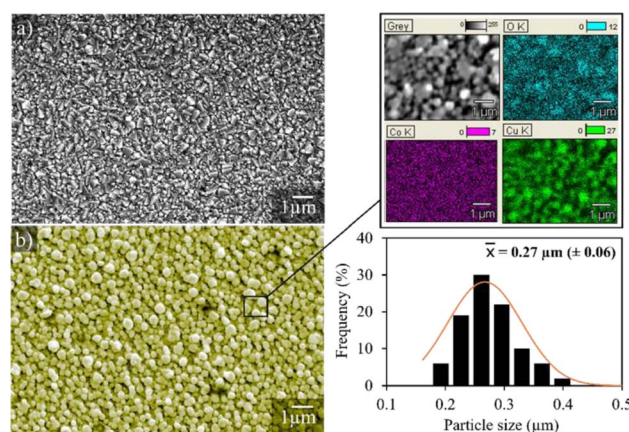


Fig. 3 Representative images of the pure FTO substrate (a) and the FTO coated with Cu/Co particles (b).



Fig. 4 High-resolution XPS spectra of Cu 2p (a) and Co 2p (b).

shoulder peak is ascribed to copper oxide reduction, while the exponential current is associated with water reduction to produce hydrogen gas. Up to ~ -0.33 V (vs. RHE), the cathodic current in the presence of CO₂ surpasses that observed under the N₂-saturated conditions, indicating the simultaneous occurrence of the CO₂RR and H₂ production. It indicates that under saturated CO₂ and low applied potential, the Cu/Co deposited on the FTO surface selectively acts towards the CO₂RR. However, as the applied potential increases, the hydrogen evolution reaction (HER) may become the predominant faradaic process within the studied potential range.

Chronoamperometry analysis (Fig. S1†) was performed further to investigate the performance of Cu/Co catalysts in the CO₂RR. As shown in Fig. 6a and b, the CO₂RR was performed within the potential range from -0.13 V to -0.53 V (vs. RHE), which decreased the oxygenated liquid products (methanol, acetic acid, acetone, and ethanol). At the same time, the increase in the HER indicates that liquid products are predominantly formed at the lower negative applied potential. Ethanol was the main product at -0.13 V (vs. RHE) with a production of ~ 63.52 $\mu\text{mol mg}^{-1}$ and a selectivity of 75% during the first two hours of the reaction. After three hours of reaction, the cathodic current density increased. In contrast, the ethanol production had been entirely surpassed, leading to

other liquid products, yielding methanol (103.03 $\mu\text{mol mg}^{-1}$), acetic acid (38.54 $\mu\text{mol mg}^{-1}$), and acetone (2.77 $\mu\text{mol mg}^{-1}$) with a FE of 65.5%, 32.7%, and 4.7%, respectively. It indicates a change in the reaction mechanism since methanol, the main product in the last hour, is from the formation pathway of ethanol, *i.e.*, acetic acid and acetone may be associated with ethanol previous formation. On the other hand, the methanol should be directly formed by CO₂, supposing that ethanol C–C bond breakage is not expected under these conditions. Furthermore, only H₂ traces were detected at this potential, confirming the high selectivity for the CO₂RR over the HER. At -0.33 V (vs. RHE), the main product was acetic acid with a maximum yield of 48.30 $\mu\text{mol mg}^{-1}$ with 52% selectivity, in addition to the increase in acetone yield reaching up to 10.94 $\mu\text{mol mg}^{-1}$. At the highest potential tested, the liquid products severely decreased, while the H₂ formation increased from -0.33 to -0.53 V (vs. RHE), reaching a maximum selectivity (92%) at -0.53 V.

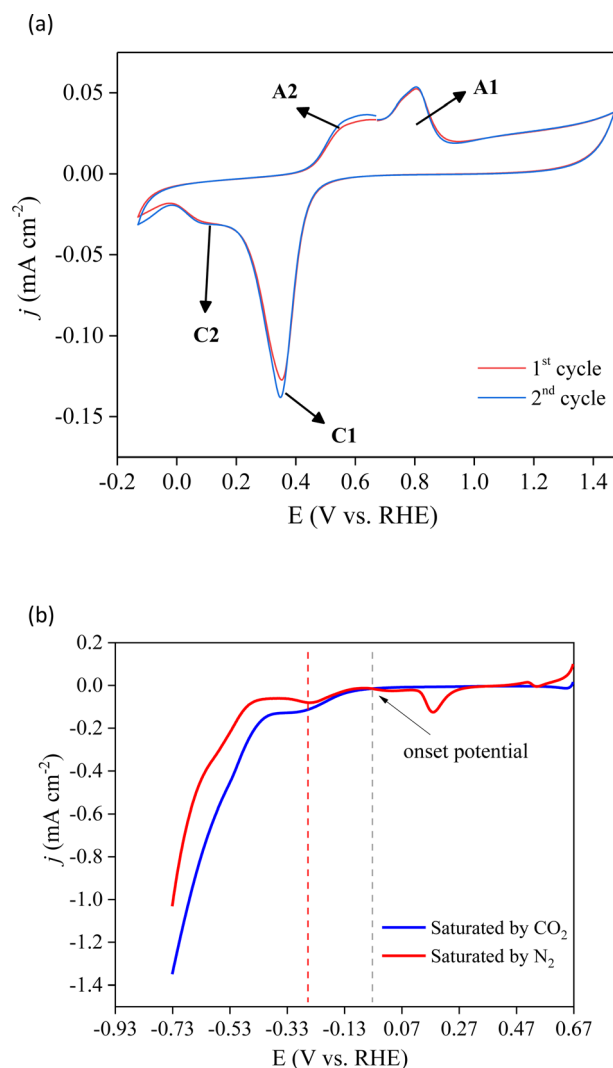


Fig. 5 Cyclic (a) and linear (b) voltammetry of the prepared Cu/Co electrode in 0.1 M Na₂SO₄ under CO₂ and N₂ atmospheres at 25 mV s⁻¹.

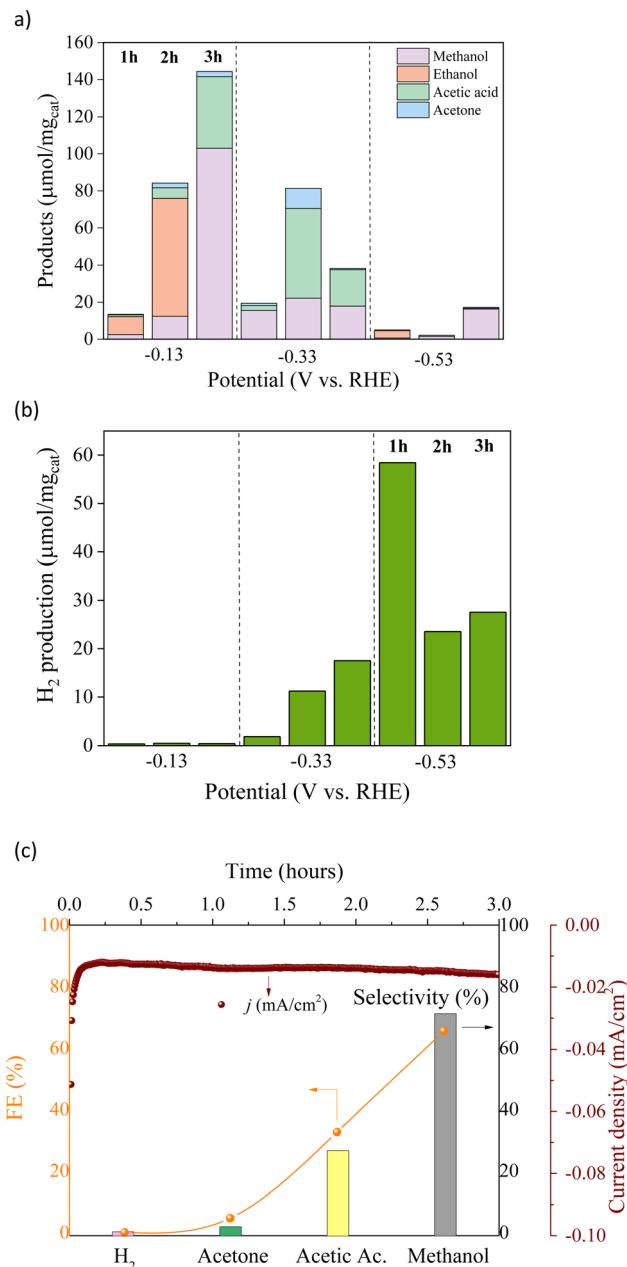


Fig. 6 Electroreduction of CO_2 to (a) liquid oxygenated products and (b) hydrogen at different applied potentials. (c) Selectivity, faradaic efficiency (FE), and current density of CO_2 reduction at -0.13 V (vs. RHE) for 3 hours.

In situ electrochemical ATR-IR spectral measurements were carried out on the Cu/Co composite at different applied potentials in 0.1 M $\text{Na}_2\text{SO}_4 + \text{D}_2\text{O}$ under CO_2 -saturated conditions (Fig. 7). It aimed to examine the reaction intermediates and provide information about the electrocatalytic mechanism during CO_2 conversion. The reaction pathway and intermediates of the CO_2 catalytic reactions can be proposed based on the intensity and direction of the peaks, with positive peaks indicating chemical generation and negative peaks suggesting consumption. Upon applying potentials, distinct bands corresponding to various species were observed. These species

included dissolved CO_2 in the liquid, adsorbed CO , carbonate anions in the solution, and OH deformation.⁴⁰ The reverted band intensity increased at $2400\text{--}2280\text{ cm}^{-1}$ in response to the applied potential, indicating increased CO_2 consumption during the CO_2RR process.⁴¹ At the same time, there is a slight peak at 1541 cm^{-1} and another at 2842 cm^{-1} , attributed to the deformation of interfacial water molecules and OH adsorption on the surface, respectively. These results agree with electrocatalytic tests that indicate an increase in the catalytic process due to water molecule breakdown at high applied potentials. This result is supported by bicarbonate anions in D_2O and well-defined bands at 1630 and 1367 cm^{-1} . Furthermore, the presence of bicarbonate anions in D_2O can be visualized (1630 and 1367 cm^{-1}).⁴² However, the decrease of these signals with increasing potential, associated with an increase in the intensity of the inverted peak suggesting the consumption of the metal-coordinated carbonate (M-CO_3) at 1106 cm^{-1} , demonstrates the interaction of the CO_2 -derived species with the surface of the prepared material, resulting in the production of

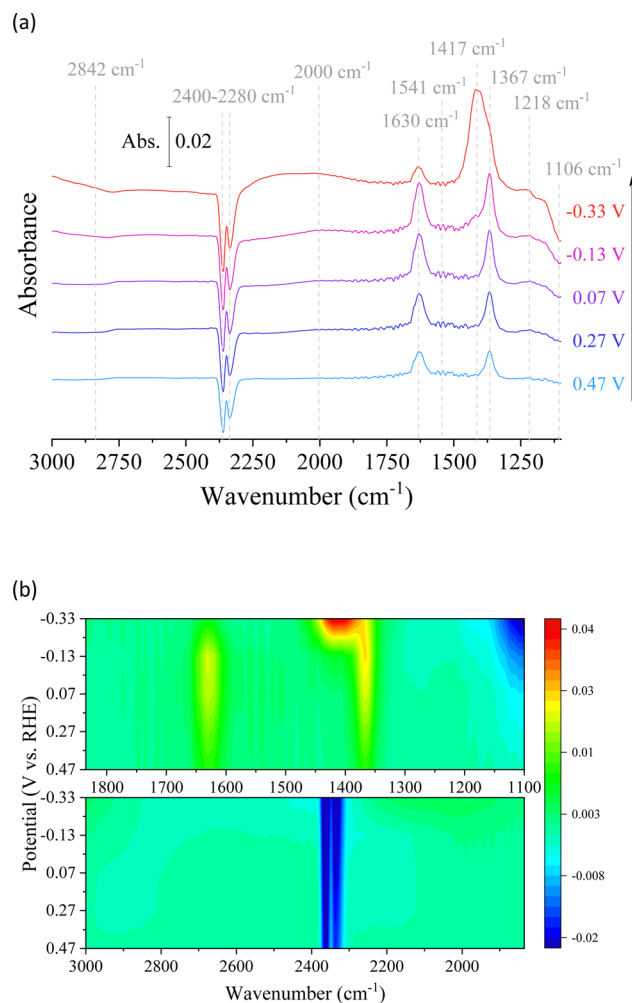


Fig. 7 *In situ* FTIR spectra were obtained during chronoamperometry at different potentials in 0.1 M $\text{Na}_2\text{SO}_4 + \text{D}_2\text{O}$ under saturated CO_2 conditions. (a) Spectra with attributed peaks and (b) 3D spectra with evidence of peak changes.

exhibited the same trends previously discussed. After two hours of reaction, ethanol selectivity was approximately 75%, while methanol production was minimal since the ethanol pathway differs from the methanol pathway. The increase in methanol (71%) and acetic acid (27%), related to the $^*\text{COH}$ intermediate, and no ethanol production during the last 3rd hour support the possible reaction pathway of the CO_2RR suggested above. An investigation was carried out to assess the integrity of the Cu/Co-based material that was produced. The same conditions as those described above were used for the experiment, applying -0.13 V vs. RHE for 24 hours. After the reaction was completed, it was observed that the current remained relatively stable (Fig. 9a), suggesting a potential lack of degradation in the electrode. In order to confirm this observation, XRD analysis (Fig. 9b) was carried out, which showed that there were no structural changes in the catalyst before and after the reaction, indicating that the method of synthesizing nanoparticles based on Cu/Co could be an interesting alternative for catalytic processes.

Conclusions

In summary, we have successfully demonstrated the preparation of electrocatalysts to selectively act on the CO_2RR from spent lithium-ion batteries (LIBs). The prepared Cu/Co composite was electrodeposited uniformly on the surface of a FTO substrate, containing regular particle sizes with a high copper loading. Electrocatalytic tests under neutral conditions reveal a potential dependence and selectivity of the conducted reactions since the best condition was the application of -0.13 V (vs. RHE) , achieving yields of methanol ($103.03\text{ }\mu\text{mol mg}^{-1}$), acetic acid ($38.54\text{ }\mu\text{mol mg}^{-1}$), and acetone ($2.77\text{ }\mu\text{mol mg}^{-1}$) with a FE of $\sim 65\%$, 32.7% , and 4.7% , respectively, and completely suppressing the HER. *In situ* FTIR experiments reveal that the possible reaction mechanism for the production reveals that copper is the principal catalytic agent. Furthermore, cobalt may imply other reaction pathways, such as blocking the formation of intermediates that would lead to formic acid formation, thus leading to higher efficiency, at low applied potentials, in the production of CH_3OH . Finally, the importance of these studies for reusing solid and gaseous wastes to reduce environmental and economic problems by converting CO_2 into valuable chemicals and storing renewable energy is worth noting.

Author contributions

Jean Cruz: conceptualisation, investigation, methodology, writing – original draft, and writing – review and editing. Ricardo Marques: methodology, validation, and writing – original draft. Gelson da Silva: conceptualisation, investigation, methodology, visualization, writing – original draft, and writing – review and editing. Lucia Mascaro: conceptualisation, funding acquisition, writing – review and editing, supervision, and project administration. Caue Ribeiro: conceptualisation, funding acquisition, methodology, writing – original draft, writing – review and editing, supervision, and project administration.

Conflicts of interest

There are no conflicts to declare.

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