Selectivity control of Cu nanocrystals in a gas-fed flow cell through CO$_2$ pulsed electroreduction.

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ABSTRACT: In this study, we have taken advantage of a pulsed CO$_2$ electroreduction reaction (CO$_2$RR) approach to tune the product distribution at industrially-relevant current densities in a gas-fed flow cell. We compared the CO$_2$RR selectivity of Cu catalysts subjected to either potentiostatic conditions (fixed applied potential of -0.7 V$_{RHE}$) or pulsed electrolysis conditions (1 s pulses at oxidative potentials ranging from $E_{in} = 0.6$ V$_{RHE}$ to 1.5 V$_{RHE}$, followed by 1 s pulses at -0.7 V$_{RHE}$), and identified the main parameters responsible for the enhanced product selectivity observed in the latter case. Herein, two distinct regimes were observed: (i) for $E_{in} = 0.9$ V$_{RHE}$ we obtained 10% enhanced C$_3$ product selectivity (F.E. C$_{3}$H$_{6}$ = 43.6% and F.E. C$_{3}$H$_{4}$OH = 19.8%) as compared to potentiostatic CO$_2$RR at -0.7 V$_{RHE}$ (F.E. C$_{2}$H$_{4}$ = 40.9% and F.E. C$_{2}$H$_{5}$OH = 11%), while (ii) for $E_{in} = 1.2$ V$_{RHE}$, high CH$_4$ selectivity (F.E. CH$_4$ = 48.3% vs. 0.1% at constant -0.7 V$_{RHE}$) was observed. Operando spectroscopy (XAS, SERS) and ex-situ microscopy (SEM and TEM) measurements revealed that these differences in catalyst selectivity can be assigned to structural modifications and local pH effects. The morphological reconstruction of the catalyst observed after pulsed electrolysis with $E_{in} = 0.9$ V$_{RHE}$, including the presence of highly defective interfaces and grain boundaries was found to play a key role in the enhancement of the C$_3$ product formation. In turn, pulsed electrolysis with $E_{in} = 1.2$ V$_{RHE}$ caused the consumption of OH$^-$ species near the catalysts surface, leading to an OH$^-$-poor environment favorable for CH$_4$ production.

1. Introduction

The electrochemical CO$_2$ reduction (CO$_2$RR) driven by electrical energy from renewable sources has attracted attention as an environment-friendly path to convert the undesired greenhouse gas into feedstock chemicals and fuels. Among the metal catalysts used for CO$_2$RR, copper-based catalysts are of particular interest due to their unique capability to transform CO$_2$ into various hydrocarbons and alcohols with high energy density such as CH$_4$, C$_2$H$_6$, and C$_2$H$_5$OH. However, controlling the selectivity toward a specific product remains the main challenge in this field. Different approaches to address this issue have been explored, such as controlling the morphology of the catalyst and exposed facets, tuning the electrolyte composition, and incorporating secondary metals.

Apart from these strategies, applying periodic oxidative potentials during the CO$_2$RR was also shown to be an efficient way to steer the selectivity of Cu catalysts towards certain desired products. By choosing the proper values of cathodic and anodic potentials and pulse lengths, the production of CO, CH$_4$, C$_2$H$_6$, and C$_2$H$_5$OH could be enhanced. For example, experiments with millisecond pulses have shown that the selectivity of a polycrystalline Cu foil toward syngas (H$_2$ and CO) can be improved, which was attributed to a modification of the Cu surface morphology by successive oxidation and reduction. In another study employing a Cu(100) single crystal, pulsed electrolysis was applied to periodically to regenerate Cu(I) species, resulting in a significantly enhanced selectivity for ethanol when highly defective Cu(I)/Cu(0) interfaces were available. Several other studies have also reported the generation of unusual products such as methanol during pulsed CO$_2$RR, with a concomitant increase in the C$_2$ selectivity (e.g., C$_2$H$_4$, C$_2$H$_6$, and propanol), in comparison to that achieved under potentiostatic electrolysis conditions. In the former examples, the selectivity trends observed in H-type cells at low current densities were assigned to the modification of the local chemical environment and concentrations of OH$^-$ and CO adsorbates on the Cu surface. These results are supported by theoretical studies showing that pulsed electrolysis causes changes in the local pH and CO$_2$ concentration.

Although the pulsed electrolysis has shown remarkable results for controlling the catalyst selectivity, the majority of data available originate from experiments conducted in an H-type cell configuration. However, the current density of CO$_2$RR in an H-type cell can only reach a few tens of mA/cm$^2$ due to the low solubility of CO$_2$ in the electrolyte and the resulting mass transfer limitations. In addition, single crystals that were previously discussed are less attractive for commercial applications due to the limited possibilities to scale up the process and the high catalyst
cost. In this regard, a gas-fed flow cell configuration with a gas diffusion electrode (GDE) in an alkaline electrolyte provides an attractive alternative for industrial utilization. It features the three-phase boundary of CO₂ gas/liquid/solid interface, can achieve high current density (over 200 mA/cm²),^27,30 and allows using nanoparticulate catalysts. However, practical feasibility of such a system depends on gas-fed flow cell characteristics. Harsh experimental conditions associated with high current densities are expected to affect the chemical and physical properties of the catalysts. Consequently, *operando* studies in the flow cell configuration are required to shed light on the correlation between the pulsed CO₂RR parameters and the observed selectivity trends.

Previous studies of pulsed CO₂RR in H-type cells have reported that oxidative potentials are beneficial for hydrocarbon and alcohol production. Here we extend such studies to a flow cell configuration and high current densities, using highly active shape-selected Cu₅O nanocube (Cu NC) catalysts. Herein we demonstrate that pulsed electrolysis in a gas-fed flow cell configuration enables the efficient control over the product selectivity, allowing us to switch from C₅ (C₅H₁₀ and C₅H₁₀OH) to C₂ (CH₄) product formation by tuning the value of the applied anodic potential (Eₓ). To that end, we also apply higher pulsed potentials than in previous studies. Such high oxidative pulsed potentials can potentially lead to transient oxidation of CO₂RR products, which might have discouraged previous studies of exploring larger potential ranges. However, here we will show that oxidation of C₅ CO₂RR products during pulsing is negligible for the chosen potential range (up to ±1.2 V vs. RHE) and that the changes in F.E. are likely related to interfacial pH and catalyst changes. Cyclic voltammetry, *operando* X-ray absorption fine structure spectroscopy (XAS), *ex situ* scanning electron microscopy (SEM), and *ex situ* transmission electron microscopy (TEM) measurements allowed us to extract correlations between the catalytic properties and the structure and chemical state of the catalyst.

2. Experimental

2.1. Preparation of Cu NCs and electrodes

Cu NCs were prepared by modifying a previously reported recipe. In a typical synthesis, a diluted alkaline solution containing Cu ions was prepared by adding 8 mL of a CuSO₄·6H₂O solution (0.1 M) and 28 mL of a NaOH solution (1 M) to 732 mL of ultrapure water at room temperature. After stirring for 10 seconds, 32 mL of an L-ascorbic acid solution (0.25 M) were added to the mixture. The solution was then further stirred for 13 min. The solution was centrifuged and washed several times with water and ethanol.

To prepare the electrodes on a GDE, the catalysts ink was made by dispersing 0.5 mg of the catalyst powder with a ~22 wt% of Nafion (relative to the total loading, Sigma-Aldrich) in 1 ml methanol. The ink was then ultra-sonicated for 30 min. The as-prepared ink was spray-coated on the microporous layer (MPL) of a gas diffusion electrode (GDE, Sigracet 39bb) using an airbrush. The loading was determined by weighing the GDE before and after the spray coating, and was found to be roughly 0.25 mg/cm².

2.2. Electrochemical measurements for CO₂ reduction reaction

Electrochemical CO₂ reduction experiments were performed in a gas-fed flow cell configuration (*Figure S1*). The flow cell consisted of three-compartment for CO₂, gas, catholyte, and anolyte. A catalyst deposited on the GDE working electrode was positioned between the CO₂ gas and the catholyte chamber, with the catalyst side of the GDE facing the electrolyte. The catholyte and anolyte chambers were equipped with a leak-free Ag/AgCl reference electrode (Innovative Instruments) and a platinum mesh counter-electrode (MaTeCK). An anion exchange membrane (Fumasep FAA-PK-130) was mounted between the catholyte and the anolyte chamber. Gaseous CO₂ was passed behind the gas diffusion layer at a constant flow 10 scm by means of a mass flow controller (Bronkhorst). Note that since a fraction of CO₂ gas is converted into products, the flow rate at the outlet of the CO₂ gas chamber was re-measured by a volumetric digital flow meter (Agilent ADM 1000) and used for the Faradaic efficiency calculations. An aqueous solution of 1 M KOH (pH 13.7, Acros-Organics) was used as an electrolyte, as well as phosphate buffer (pH 7.4 and pH 6.4, Sigma-Aldrich) and citric acid (pH 5, Sigma-Aldrich) for auxiliary experiments. The electrolytes were circulated in both compartments by a dual-channel peristaltic pump (FAUST PLP980) at a constant flow controlled by the pump’s rotation speed, which was set to 10 RPM. The electrochemical experiments were performed using a potentiostat (Autolab PGSTAT302N). The Ohmic resistance was determined by electrochemical impedance spectroscopy (EIS). The potential values after IR compensation were converted to the reversible hydrogen electrode (RHE) reference scale using $E = (E_{Ag/AgCl} + 0.242 V + 0.059 V × pH - IR)$.

The gas products were quantified by gas chromatography (GC, Agilent 7890B) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). The GC was directly connected to the CO₂ gas chamber of the flow cell for online analysis. The formic acid and acetate concentrations were analyzed by high-performance liquid chromatography (HPLC, Shimadzu Prominence) equipped with a NUCLEOgel® SUGAR 810 column and refractive index detector (RID). The alcohols and aldehyde concentrations were quantified with a liquid GC (L-GC, Shimadzu 2010 plus) equipped with a fused silica capillary column and FID detector. The details of Faradaic efficiency calculation are given in Supplementary Information (*Supplementary Note 1*).

2.3. *Ex-situ* characterization

The surface morphology and structure of the catalysts were investigated using SEM (Thermo Fisher Scientific, Apreo SEM) and TEM (JEOL Ltd, ARM200F). Samples for TEM were prepared by coating a nickel grid (400 mesh
with a lacy carbon film, PLANO GmbH) with the catalyst dispersed in Hexane before and after CO₂RR.

2.4. Operando characterization

The high surface-to-volume ratio in these (initially cubic) nanostructured catalysts enhances the contribution of the active surface sites to the signal yielded by sample-averaging spectroscopic techniques. This is instrumental for operando tracking the changes in the morphology and chemical state of the catalysts during the CO₂RR using methods like X-ray absorption spectroscopy (XAS).

Operando XAS measurements were performed at the P64 beamline of PETRA-III synchrotron (Hamburg, Germany). Time-resolved quick X-ray absorption fine structure (QXAFS) spectra were collected in fluorescence mode. A home-made flow cell was used to acquire the XAS spectra under reaction conditions. In the operando flow cell, the Kapton window was installed to allow X-rays to illuminate the catalyst on the GDE from the back and collect the emitted fluorescence (Figure S2). All samples were measured in air and under operando conditions corresponding to potentiostatic and pulsed electrolysis. The details of the XAS data acquisition and processing, as well as schematics of the flow cell employed are given in the Supplementary Information (Supplementary Note 2).

Operando surface-enhanced Raman spectroscopy (SERS) was carried out with a Raman spectrometer (Renishaw, In-Via Reflex) coupled with an optical microscope (Leica Microsystems, DM2500M) together with a motorized stage for sample tracking (Renishaw, MS300 encoded stage). Calibration of the system was performed using a Si(100) wafer (520.5 cm⁻¹). A near-infrared laser (Renishaw, RL785, λ = 785 nm, P_max = 500 mW) served as excitation source. The backscattered light was Rayleigh-filtered and the Raman scattering was collected in the range of 100-1200 cm⁻¹ with a grating of 1200 lines mm⁻¹ and directed to a CCD detector (Renishaw, Centrus). For the operando measurements, the excitation source was focused on the surface of the sample and Raman scattering signals were collected with a water immersion objective (Leica microsystems, 63x, numerical aperture 0.9) protected from the electrolyte with a Teflon film (DuPont, film thickness of 0.013 mm) wrapped around the objective. The collection of each spectrum was performed with 5 s of exposure time. The Raman data were processed using the Renishaw WiRE 5.2 software. The spectra were baseline-subtracted using the polynomial feature of 8th order and cosmic rays were removed.

3. Results and Discussion

We first measured the cyclic voltammetry (CV) of Cu NCs in KOH electrolyte to establish the relevant potential values for the pulsed CO₂RR conditions. As shown in Figure 1a, we observed two distinct anodic peaks at 0.9 V and 1.2 V vs. RHE in the CV curves. To identify these two oxidation peaks, we tracked the chemical state of the catalyst by means of XAS (see Supplementary Note 3 and Figures S3-S4). XAS data revealed that these CV peaks can be assigned to the formation of Cu₂O and CuO, respectively, which is in good agreement with the literature.39 We note, however, that according to XAS, the formation of Cu(I) species starts at potentials as low as 0.6 V, but is significantly faster at higher potentials. Furthermore, oxidation of Cu to Cu(II) state starts at ca. 1.0 V, but even at these high potentials, the formation of new Cu(I) species is still significant and surpasses that of Cu(II) species. We attribute that, in part, to the instability of Cu(II) under the given reaction conditions, which results in leaching of Cu(II), and to the partial re-reduction of Cu(II) back to Cu(I) (see Supplementary Note 3).

![Figure 1](image_url)

Figure 1. (a) Cyclic voltammogram of the Cu NCs obtained at a scan rate of 1 mV/s in the 1 M KOH electrolyte. (b) The F.E. and current density of Cu NCs under potentiostatic conditions at -0.7 V vs. RHE in the flow cell.

Based on the CV data we selected the pulsed electrolysis conditions. Specifically, a 1s pulse at an anodic potential (E_a) was followed by a 1s pulse at a cathodic potential (E_c), and the sequence was repeated for 30 min. The E_a was varied from 0.6 V to 1.5 V vs. RHE, while holding the E_c value for CO₂RR at -0.7 V vs. RHE. All potentials mentioned in the text are referenced vs. RHE, unless stated otherwise. Next, as a control experiment, the selectivity of the Cu NCs under potentiostatic conditions (at -0.7 V for 30 min) was examined (Figure 1b).
It was observed that the current density under these conditions was -254 mA/cm², and the main products were C₂ products, in particular, C₂H₄ (F.E. of 40.9%) and C₂H₅OH (F.E. of 11%), which is consistent with previous studies.³² This control experiment serves as a standard for comparing and analyzing the upcoming results of the pulsed electrolysis.

The current densities and F.E. data for the potentiostatic (reference) and pulsed electrolysis with different values of the anodic potential (Eₐn) are shown in Figure 2. All catalytic activity data were collected after 30 min of CO₂RR at the given conditions. Similar high current densities as observed under potentiostatic conditions were also obtained under the pulsed CO₂RR with Eₐn less than 1.0 V. Nevertheless, further increase in the Eₐn value (≥ 1.0 V vs. RHE) results in a remarkable reduction of the current density by ca. 30 % as compared to that under potentiostatic conditions. The F.E. of the pulsed electrolysis also showed different selectivity trends depending on the Eₐn value. The F.E. at Eₐn = 0.6 V showed a similar selectivity toward C₂ products as observed under potentiostatic conditions. Nonetheless, upon increasing the Eₐn value to 0.9 V, the C₂ product selectivity increased and achieved a total C₂ F.E. of 63.6% (with a F.E. for C₂H₄ of 44% and a F.E. for C₂H₅OH of 20%), which is about 10% higher than that of potentiostatic CO₂RR for the same cathodic potential of -0.7 V. Interestingly, a further increase in the anodic potential does not result in an improved selectivity to C₂ products. Instead, at Eₐn = 1.0 V, the C₂ product selectivity declines, and the CH₄ product selectivity is enhanced. At Eₐn values over 1.0 V, CH₄ was the main reaction product, and achieved a maximum of 53.9 % F.E. at Eₐn =1.5 V.

The formation of Cu oxide species between ~0.8 V and ~1.5 V in the regular CV in Figure 1 and the changes in the F.E. in Figure 2 are closely correlated. Figure S5 shows the total amount of Cu oxide on the surface, estimated from the CVs by peak integration, and the CH₄ FE as a function of the applied potential. The close similarity between these two trends is striking and suggests a close link between the
Cu oxide formation and CH₄ production. A detailed discussion is given in Supplementary Note 4. The amount of Cu oxide during the 1 s pulses will be substantially less than during the CV (with a scan rate of 1 mV s⁻¹). However, an incremental time interval of 1 s will lead to an incremental amount of Cu oxide of the total amount, and we hypothesize that the qualitative trend in Figure S5 will be the same. However, to accurately characterize the oxidation state of Cu under these reactive conditions operando spectroscopic methods are needed, as shown below.

Figure 3. Current density (top) and F.E. (bottom bargraph) of the pulsed electrolysis with E_an = 0.9 V and 1.2 V and the cathodic pulse E_ca = -0.7 V. The arrows indicate that the same samples pre-treated using pulsed electrolysis were subsequently measured at a constant potential of −0.7 V vs. RHE. The activity and selectivity data reported are an average of at least three different measurements on analogously prepared fresh independent samples and the error is estimated as the standard deviation.

To that end, we investigated whether the differences in catalyst activity and selectivity are attributed to dynamic changes in the catalyst structure and composition under pulsed CO₂RR conditions, or whether they are associated with irreversible changes in the catalyst morphology. To this end, we first run the pulsed electrolysis with either E_an = 0.9 V or 1.2 V for 30 min, and then exposed these samples to potentiostatic conditions at −0.7 V. Interestingly, as shown in Figure 3, the results obtained in these two cases showed a completely different behavior. In the case of the treatment with E_an = 0.9 V pulses, the enhanced C₂ selectivity was maintained even after the pulses were interrupted and the same catalytic properties were measured under potentiostatic conditions. This result indicates that the enhancement in C₂ production induced by the pulsed pre-treatment can be assigned to irreversible changes in the catalyst morphology. Nevertheless, in the case of the pre-treatment with E_an = 1.2 V pulses, the CH₄ selectivity observed under the pulsed electrolysis was suppressed after the pulses were stopped, and C₂ chemicals reappeared as the main CO₂RR products. In addition, we observed that the current density, partially suppressed under the E_an = 1.2 V pulsed conditions, recovered the level attained under potentiostatic electrolysis with a fresh catalyst. This allows us to conclude that the suppression of C₂ products formation, decrease in current density and enhancement in CH₄ selectivity under pulsed CO₂RR with E_an values above 1.0 V all are results of dynamic and reversible changes induced by the pulsed reaction conditions.

We further elucidated the respective roles of irreversible changes in the Cu NC morphology and that of dynamic (and reversible) changes in the Cu NC structure on their catalytic properties under pulsed CO₂RR conditions. To that end, we performed ex-situ SEM and TEM measurements of samples in their as-prepared state and after the potentiostatic and pulsed electrolysis (Figure 4), as well as time-resolved operando XAS (Figure 5) and operando SERS measurements (Figure 6).

Regardless of the electrolysis mode, the SEM images showed that the well-defined cubic shape (31 ± 4 nm in size) of the as-prepared samples changed after the reaction. In particular, the samples exposed to the pulsed electrolysis evolved into irregularly-shaped agglomerates larger than those found in samples treated under potentiostatic CO₂RR. The TEM images illustrate more clearly the morphological differences among the three sample types after the reaction. The sample exposed to potentiostatic CO₂RR conditions transformed into agglomerates that have Cu NCs stacked on each other. The agglomerated Cu NCs also partially preserved their cubic shapes. This shape stability is consistent with observations by Buonsanti et al. who reasoned that maintaining the shape after CO₂RR is a consequence of the lower potentials required in the gas-fed flow cell (ca. −0.7 V vs. RHE) as compared to the H-type cell configuration, where typically −1.0 to −1.1 V vs RHE are used.

On the other hand, the sample after pulsed electrolysis with E_an = 0.9 V did not show a structure consisting of agglomerated cubes. Instead, the NCs had reconstructed into larger particles. At E_an = 1.2 V, we also observed Cu₂O particles on the surface of the Cu catalysts in some cases (Figure S6), but it cannot be unambiguously attributed to the effect of pulsed electrolysis due to the samples being transferred in air. Nevertheless, it is clear that the Cu reconstruction under pulsed conditions was more significant under these conditions as compared to the potentiostatic treatment and lead to the creation of catalyst particles with a rougher surface. Figure 7 compares scanning TEM and energy dispersive X-ray spectroscopy (EDX) maps of the potentiostatic sample, and the pulsed electrolysis samples treated with E_an = 0.9 V and 1.2 V respectively. The maps suggest a higher oxygen content in the pulsed samples, but we were not able to collect higher signal-to-noise maps due to the presence of the Nafion binder.
Operando XAS provides further details about the changes in the catalyst structure under different CO\textsubscript{2}RR regimes. Changes in the Cu K-edge X-ray absorption near-edge structure (XANES) and Fourier-transformed (FT) extended X-ray absorption fine structures (EXAFS) spectra for fresh Cu NCs exposed to pulsed reaction conditions with $E_{\text{an}} = 0.9$ V are shown in Figure 5a and b. Raw EXAFS data, as well as the corresponding plots for potentiostatic CO\textsubscript{2}RR and pulsed reaction conditions with $E_{\text{an}} = 1.2$ V are shown in the Supplementary Information, Figure S8. In all cases we observe that Cu, which in the fresh samples is predominantly in the Cu(I) state, is gradually reduced, as indicated by a characteristic shift of the absorption edge to higher energies and a change in the XANES features (Figure 5a), as well as the decrease of the peaks in the FT-EXAFS spectra at ca. 1.5 and 3 Å (phase uncorrected) that correspond to the Cu\textsubscript{2}O-like phase.

At the same time, a new peak in the FT-EXAFS develops at ca. 2 Å (phase uncorrected), corresponding to Cu-Cu bonds in metallic Cu. In order to extract quantitative information, we performed linear combination analysis (LCA) of the XANES spectra (Figure 5c), as well as fitting of the EXAFS data (Figure S9-S11).

As shown in Figure S12, both approaches provide good agreement regarding the changes in the concentrations of metallic and oxidized Cu species. The small discrepancies observed in some cases in the Cu(0) concentration are attributed to disorder effects in the EXAFS data.

We observe that the transformations in the catalyst’s oxidation state under potentiostatic CO\textsubscript{2}RR conditions and in the pulsed regime with $E_{\text{an}} = 0.9$ V proceed in qualitatively similar way, although the reduction is slower in the latter case. Note here that the time-resolution of our XAS experiment (ca. 5 s per spectrum in this case) is not sufficient to track the changes in the catalyst oxidation state during the individual 1 second long potential pulses. Nevertheless, the average oxidation state of the Cu NCs after ca. 1500 s of potentiostatic CO\textsubscript{2}RR conditions at -0.7 V and under pulsed CO\textsubscript{2}RR (with $E_{\text{an}} = 0.9$ V and $E_{\text{ca}} = -0.7$ V) is practically the same. This finding is different from the one reported in a recent operando XAFS study on another oxide-derived catalyst under pulsed reaction conditions, where an increase in the average catalyst oxidation state was reported under pulsed conditions with $E_{\text{an}} = 0.5$ V. We attribute this difference to the much shorter oxidative pulse lengths employed in our study (1 s here vs. 10 s in Ref.[37]), and to the much higher current densities achieved in our flow cell setup during the cathodic pulse, resulting in a faster catalyst reduction. Moreover, irreversible changes in the catalyst morphology seem to diminish the re-oxidation efficiency of our catalyst. To demonstrate this, in Figure 6 we show the results of XANES analysis for an additional experiment, where longer pulses (60 s) with the same $E_{\text{an}}$ and $E_{\text{ca}}$ values were applied. The increased pulse length allows us in this case to directly track the time-dependent changes in the catalyst composition and structure using operando QXAFS. The obtained results support that the periodic application of $E_{\text{an}} = 0.9$ V potential results in a significant re-oxidation of the catalyst (Figure 6a). The generated cationic Cu species, however, are removed as soon as the cathodic potential pulse is applied, and, more importantly, the reduction of the Cu NCs is clearly much faster than the oxidation (Figure 6b).
Figure 5. Time-dependent Cu K-edge (a) XANES and (b) Fourier-transformed (FT) EXAFS spectra showing the reduction of Cu NCs under pulsed CO$_2$RR with 1 s pulses and $E_{an} = 0.9$ V. (c) Results of linear combination fitting of XANES spectra for Cu NCs under potentiostatic CO$_2$RR and under pulsed reaction conditions with 1 s pulses and $E_{an} = 0.9$ and 1.2 V. Spectra for metallic Cu, Cu$_2$O, CuO and Cu(OH)$_2$ were used as references for the LCA fitting. The Cu(II) concentration reported is the sum of CuO and Cu(OH)$_2$ contributions. Weights of the other components are shown in Figure S1a2.

Moreover, the amount of oxide generated during each pulse of the anodic potential decreases for each subsequent pulse. The latter is assigned to the irreversible changes in the catalyst morphology taking place during the pulsed protocols. In particular, our TEM data (Figure 4) revealed an increase in the NC size during the pulse treatments, which has also associated a decrease in the current density due to the smaller surface area available (Figure S1b6). This reconstructed NC morphology is also expected to affect the oxidation state. Prior literature reports revealed that differently oriented Cu surfaces display different oxidation kinetics. Our [100] nanocubes are transformed during the pulse electrolysis into rougher morphologies with likely distinct oxidation dynamics. While extrapolation of the results collected with 60 s pulses to the case with 1 s pulses should be done with caution, in both cases we observe very similar trends in the sense that the role of the periodically regenerated oxide species diminishes with time, in line with the irreversible changes previously revealed.

The situation is remarkably different when pulses with higher $E_{an}$ value are applied. First, under 1 s pulses at $E_{an} = 1.2$ V the reduction of the Cu$_2$O phase initially present is much faster than under 1 s pulses with $E_{an} = 0.9$ V. Moreover, unlike in the potentiostatic and pulsed CO$_2$RR cases with lower $E_{an}$ values, for $E_{an} = 1.2$ V the pulsed reaction conditions result in the formation of a small fraction of Cu(II) species (Figure 5c). The Cu(II) species, however, are not stable under these conditions, and are either dissolved (see Supplementary Note 3) or converted back to Cu(I) species. Indeed, after ca. 200 s under pulsed CO$_2$RR with $E_{an} = 1.2$ V, the contribution of Cu(II) decreases to practically zero, while a significant enhancement in the population of Cu(I) species is present. The concentration of Cu(I) species is ca. 20%, which indicates the formation of a thick oxide layer. The conversion of Cu(I) first to Cu(II), and then back to Cu(I) species is also supported by the EXAFS fitting results, which demonstrate an increase in the Cu-O bond length during the first 100 s under pulsed CO$_2$RR conditions, and then its decrease back to the original value (Figure 5b13), in agreement with the difference in Cu-O bond length in CuO and Cu$_2$O oxides (1.937 Å and 1.836 Å, respectively). The QXAFS results collected under 60 s pulses (Figure 6) confirm the trends in the dataset with 1 s pulses. In particular, the periodic application of an anodic potential drives oscillations in the Cu(I) concentration, while the contribution of Cu(II) species is detectable only during the first few potential cycles (Figure 6c). Moreover, unlike what is observed in the case of $E_{an} = 0.9$ V, under $E_{an} = 1.2$ V pulses, the average concentration of Cu(I) does not decrease with time.
Figure 6. Periodic oxidation and reduction of pre-reduced Cu NCs under 60 s pulses with $E_{an} = -0.7$ V and $E_{an} = 0.9$ V and 1.2 V. (a) Time-dependency of the Cu(0), Cu(I) and Cu(II) concentrations, as obtained from LCA-XANES. XANES spectra corresponding to metallic Cu, Cu$_2$O, CuO and Cu(OH)$_2$ were used as references. Weights corresponding to CuO and Cu(OH)$_2$ are shown separately (green and purple circles, respectively). The sequence of applied potential pulses is also shown in (a). (b,c) Zoomed-in regions of (a), corresponding to the first three pulses with (b) $E_{an} = 0.9$ V and (c) 1.2 V.

Instead, in this regime the prolonged exposure to pulsed conditions suppresses the catalyst reduction under cathodic potential, and minimizes the difference between catalyst reduction and oxidation rates. Indeed, as visible in Figure 6a, the changes in the Cu(0) concentration profile during reductive/oxidative pulses with $E_{an} = 1.2$ V are more symmetric after 10 cycles than during the first few cycles, and also more symmetric than those observed under pulses with $E_{an} = 0.9$ V.

Complementing bulk-sensitive XAS data, operando SERS measurements provide an important insight into the surface speciation under CO$_2$RR at high current densities and different pulse protocols. Figure 7 shows Raman spectra acquired under open circuit potential (OCP) and during the potentiostatic and pulsed CO$_2$RR. Under OCP, the characteristic bands of Cu$_2$O were observed at 624 cm$^{-1}$, 523 cm$^{-1}$ as well as at 144 cm$^{-1}$.

Under potentiostatic conditions at -0.7 V, these bands vanished. Meanwhile, new bands appeared at 530 cm$^{-1}$ and 368 cm$^{-1}$. These bands are associated with the presence of *OH and *CO on the Cu surface, and this finding is thus in line with previous Raman studies carried out for oxide-derived Cu nanostructures in an alkaline electrolyte. Under the pulsed electrolysis conditions, the adsorbed *CO band was detected, regardless of the $E_a$ value, suggesting that *CO could serve as an intermediate for the production of hydrocarbons. Note here that the time resolution of the SERS measurements (5 s per spectrum) does not allow us to track the changes in the adsorbate coverage during each individual pulse, and therefore it only provides information about the average state of the catalyst surface. In contrast to the results for *CO, the adsorbed *OH band showed a strong dependency on the $E_{an}$ value. The pulsed electrolysis treatment with an $E_{an}$ value below 0.8 V had no significant influence on the intensity of this band. However, increasing the anodic potential to $E_{an} = 0.9$ V and higher resulted in a noticeable decrease of this band’s intensity, paralleled by the appearance of bands related to the Cu$_2$O phase. These Cu$_2$O bands were more pronounced at $E_{an}$ values over 1.0 V. Therefore, in a good agreement with the operando XAFS data, SERS data also indicated that the pulsed electrolysis at high $E_{an}$ values resulted in the accumulation of Cu$_2$O species. An important finding from SERS is that the band of absorbed *OH reduced significantly in intensity when Cu$_2$O was accumulated, suggesting that the formation of Cu$_2$O consumed the *OH species on the Cu surface.
This is a reasonable assumption, considering that in the alkaline electrolyte Cu$_2$O is produced under the anodic potential by the reaction of metallic Cu with OH ions (Cu + OH$^{-}$ → Cu$_2$O + H$_2$O). From this observation, we infer that the local pH near the surface of the Cu NCs must transiently decrease during the pulsed electrolysis.

Based on the XAS, SERS and microscopy results, we have observed that the effect of the pulsed electrolysis in the flow cell configuration on the selectivity for either C$_2$ products or CH$_4$ depends strongly on the $E_{an}$ value. For $E_{an}$ values below 0.9 V, the enhanced C$_2$ selectivity can be attributed to irreversible changes in catalyst morphology, namely, to the creation of a defective surface with large defective interfaces and grain boundaries under harsh pulsed conditions. These defect sites appear to facilitate the C$_2$ product formation. Previous studies in H-type cells have demonstrated that the presence of defects, specific facets, and grain boundaries on the Cu surface promotes the C-C coupling required for C$_2$ product generation.$^{5,8,45-47}$ It should be noted that the pulse electrolysis treatment employed here does not only affect the catalyst morphology, chemical state and local pH around the active motifs, but that the oxidative potentials might also result in the oxidation of alcohols, aldehyde, and formate to generate more carbonaceous intermediates (including CO$^{*}$) which are key intermediates to C$_2$ products, particularly C$_2$H$_4$. The latter effect was however discarded as the main contributor for the selectivity trends obtained since the enhanced C$_2$ selectivity remained after the pulse treatment was interrupted and the same sample was subsequently measured under potentiostatic conditions (constant negative applied potential). This indicates that irreversible changes in the sample morphology taking place during the pulse treatment are mainly responsible for the improved C$_2$ selectivity detected.

In the case of pulses with $E_{an} = 1.2$ V, where CH$_4$ is produced as the main product, XAS and SERS point to the formation of a Cu$_2$O layer that cannot be fully removed during the cathodic pulse. The low conductivity of the Cu$_2$O shell formed on the surface of the metallic Cu NCs is likely responsible for the decrease in the current density$^{48}$ observed in Figure 2. Strikingly, this Cu$_2$O layer suppresses the formation of C$_2$ products, yet, appears to enhance the formation of CH$_4$. This result is intriguing, since normally metallic Cu is considered to be the active site for methane formation. Given that our operando SERS data still display the presence of bonds between metallic Cu and *CO adsorbrates under pulsed condition, this result implies that metallic Cu and Cu$_2$O coexist on the catalysts surface during pulsed electrolysis. Therefore, we postulate that the active sites for CH$_4$ production are still metallic Cu species, and that the enhancement in CH$_4$ selectivity obtained for $E_{an} = 1.2$ V can be attributed to a pH effect. In general, it is well-known that the CH$_4$ production in CO$_2$RR is greatly affected by the local pH.$^{49}$ The matching trends (Figure S5) of the total amount of Cu oxide generated during cyclic voltammetry (Figure 1) and the change in F.E. (Figure 2) as a function of the applied potential indicate an interfacial change beyond a simple change of the active surface site (see Supplementary Note 4 for a detailed discussion). In fact, our operando SERS data revealed the consumption of OH species due to the regeneration of Cu$_2$O species during the anodic pulse. This condition would lead to local OH-consumption, resulting in a rapid decrease in the local pH near the surface of the catalyst. The locally reduced pH may make the reaction pathway favorable toward CH$_4$ production. To test this, we used different buffer electrolytes as a control and found that a weak acidic environment indeed produced CH$_4$ as the main product instead of C$_2$ products (Figure S14). Interestingly, we also observed that the use of a weak acid as an electrolyte increased the H$_2$ selectivity. This observation is different from the pulsed electrolysis where the effective suppression of H$_2$ production takes place, which is likely due to the low proton concentration (ca. 10$^{-5-7}$ mol/L) in the bulk KOH electrolyte. Given that H$_2$ production is regarded as a competing reaction to CO$_2$ reduction, these results highlight that the pulsed electrolysis is an effective way to produce CH$_4$, while suppressing H$_2$ production. Furthermore, the complex interactions taking place at the electrolyte-catalyst interface are likely strongly influenced by the presence of the binder/Nafion, which is currently largely overlooked in the literature and requires further research.

The application of large oxidative potentials during the pulse protocol deserves special attention. In general, applying large oxidative potentials can lead to oxidation of CO$_2$RR products which would strongly impact our local pH interpretation above. In particular, a decreasing F.E. for C$_2$ products at the expense of an increasing CH$_4$, FE could indicate C-C fission during the oxidative pulse. To test this possibility, we studied the oxidation behavior of ethanol by recording gas chromatograms during pulsed electrolysis with oxidative pulses ≤ 1.2 V with our flow cell in the presence of only N$_2$ gas (Figure S15). For the whole potential...
range, we did not detect any ethanol oxidation products (CO, CH₄ or CO₂) above the background levels. Together with the near 100% F.E. observed in Figure 2 (calculated by only accounting for the cathodic currents), this result strongly suggests that C-C fission does not occur under the conditions tested here, likely because of a high activation energy (for a more detailed discussion see Supplementary Note 5).

Lastly, stability tests of potentiostatic and pulsed electrolysis were carried out for 10 hours (Figure S16 and S17). We observed that the selectivity obtained under the given pulsed condition was maintained during the reaction. However, it should be noted that the system stability was guaranteed when the electrolyte was periodically refreshed, otherwise a continuous decrease in the current density was observed during the reaction (Figure S18). The latter is explained by the gradual transformation of KOH to carbonate, resulting in the reduction of the electrolyte conductivity. Indeed, the change in the selectivity caused by this transformation was more pronounced under the pulsed conditions of CH₄ production, which is sensitive to the change of the local pH (Figure S6c). For practical commercial applications of the pulsed electrolysis, further work is still required to address this issue, ensuring thus long-term productivity and techno-economic feasibility. Nonetheless, the pulsed electrolysis appears to be a promising strategy to achieve tunability in the CO₂RR selectivity at high current densities.

4. Conclusion

In summary, we have explored the effect of a pulsed CO₂ electroreduction procedure on the selectivity of Cu NC catalyst in a gas-fed flow cell configuration. Our results demonstrate that the hydrocarbon selectivity can be effectively controlled and that one can switch between C₁ and C₂ product formation by properly choosing the pulsing conditions. *Operando* spectroscopy and *ex situ* microscopy measurements revealed that such selectivity trends can be assigned to different factors. The irreversible changes in the morphology of the Cu NCs observed after pulsed electrolysis with \( E_{\text{on}} = 0.9 \) V was found to play a key role in the enhancement of the C₂ product formation. Meanwhile, the OH-poor environment achieved at \( E_{\text{on}} = 1.2 \) V was found to be responsible for the higher selectivity toward CH₄.

We believe that our findings provide new strategies for controlling the selectivity of Cu catalysts for the electrochemical CO₂ conversion at high current density, and new insight into the fundamental processes governing the catalyst properties in the flow cell configuration. While our study was focused on the effect of the anodic potential (\( E_{\text{on}} \)) in the pulsed conditions, we expect that further flexibility in steering the CO₂ reduction product distribution can be achieved by tuning other parameters of the pulsed protocol employed, such as the cathodic potential (\( E_{\text{on}} \)) and the respective pulse lengths, offering new opportunities for the selective production of the desired products according to the industrial demand.

**REFERENCES**

1. Whipple, D. T.; Kenis, P. J. A., Prospects of CO₂ utilization via direct heterogeneous electrochemical reduction. *J. Phys. Chem. Lett.* 2010, 1, 3451-3458.
2. Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G. O.; Perez-Ramirez, J., Status and perspectives of CO₂ conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. *Energy Environ. Sci.* 2013, 6, 3121-3135.
3. Kuhl, K. P.; Cave, E. R.; Abram, D. N.; Jaramillo, T. F., New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* 2012, 5, 7050-7059.
4. Hori, Y., Electrochemical CO₂ reduction on metal electrodes. In modern aspects of electrochemistry, Vayenas, C.; White, R.; Gamboa-Aldeco, M., Eds. Springer New York: 2008; Vol. 42, pp 89-189.
5. Li, Y.; Cui, F.; Ross, M. B.; Kim, D.; Sun, Y.; Yang, P., Structure-sensitive CO₂ electroreduction to...
hydrocarbons on ultrathin 5-fold twinned copper nanowires. *Nano Lett.* **2017**, *17*, 1312-1317.

(6) Mistry, H.; Varela, A. S.; Bonifacio, C. S.; Zegkinoglou, I.; Sinev, I.; Choi, Y. W.; Kisslinger, K.; Stach, E. A.; Yang, J. C.; Strasser, P.; Roldan Cuenya, B. Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. *Nat. Commun.* **2016**, *7*, 12123.

(7) Loiudice, A.; Lobaccaro, P.; Kamali, E. A.; Thao, T.; Huang, B. H.; Ager, J. W.; Buonsanti, R. Tailoring copper nanocrystals towards C2 products in electrochemical CO2 Reduction. *Angew. Chem. Int. Ed.* **2016**, *55*, 5789-5792.

(8) Jeon, H. S.; Kunze, S.; Scholten, F.; Roldan Cuenya, B., Prism-shaped Cu nanocatalysts for electrochemical CO2 reduction to ethylene. *ACS Catal.* **2018**, *8*, 531-535.

(9) Singh, M. R.; Kwon, Y.; Lum, Y.; Ager, J. W.; Bell, A. T., Hydrolysis of electrolyte cations enhances the electrochemical reduction of CO2 over Ag and Cu. *J. Am. Chem. Soc.* **2016**, *138*, 13006-13012.

(10) Gao, D.; Scholten, F.; Roldan Cuenya, B., Improved CO2 electroreduction performance on plasma-activated Cu catalysts via electrolyte design: Halide effect. *ACS Catal.* **2017**, *8*, 5112-5120.

(11) Varela, A. S.; Ju, W.; Reier, T.; Strasser, P., Tuning the catalytic activity and selectivity of Cu for CO2 electroreduction in the presence of halides. *ACS Catal.* **2016**, *6*, 2136-2144.

(12) Rasul, S.; Anjum, D. H.; Jedidi, A.; Minenkov, Y.; Cavallo, L.; Takanabe, K., A highly selective copper-indium bimetallic electrocatalyst for the electrochemical reduction of aqueous CO2 to CO. *Angew. Chem. Int. Ed.* **2015**, *54*, 2146-2150.

(13) Morales-Guio, C. G.; Cave, E. R.; Nitopi, S. A.; Feaster, J. T.; Wang, L.; Kuhl, K. P.; Jackson, A.; Johnson, N. C.; Abram, D. N.; Hatsuakde, T.; Hahn, C.; Jaramillo, T. F., Improved CO2 reduction activity towards C2 products on Cu(i) alcohols on a tandem gold on copper electrocatalyst. *Nature Catal.* **2018**, *1*, 764-771.

(14) Yin, G.; Sako, H.; Gubbala, R. V.; Ueda, S.; Yamaguchi, A.; Abe, H.; Miyachi, M., A Cu-Zn nanoparticle promoter for selective copper dioxide reduction and its application in visible-light-active Z-scheme systems using water as an electron donor. *Chem. Comm.* **2018**, *54*, 3947-3950.

(15) Hu, H.; Tang, Y.; Hu, Q.; Wan, P.; Dai, L.; Yang, X. J., In-situ grown nanoporous Zn-Cu catalysts on brass foils for enhanced electrochemical reduction of carbon dioxide. *Appl. Surf. Sci.* **2018**, *445*, 281-286.

(16) Feng, Y.; Li, Z.; Liu, H.; Dong, C.; Wang, J.; Kulinich, S. A.; Du, X., Laser-prepared CuZn alloy catalyst for selective electrochemical reduction of CO2 to Ethylene. *Langmuir* **2018**, *34*, 13544-13549.

(17) Jeon, H. S.; Timoshenko, J.; Scholten, F.; Sinev, I.; Herzog, A.; Haase, F. T.; Roldan Cuenya, B., Operating insight into the correlation between the structure and composition of CuZn nanoparticles and their selectivity for the electrochemical CO2 reduction. *J. Am. Chem. Soc.* **2019**, *141*, 19879-19887.

(18) Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Norskov, J. K.; Jaramillo, T. F.; Chorkendorff, I., Progress and perspectives of electrochemical CO2 reduction on copper in aqueous electrolyte. *Chem. Rev.* **2019**, *119*, 7610-7672.

(19) Strain, J. M.; Gulati, S.; Pishgar, S.; Spurgeon, J. M., Pulsed electrochemical carbon monoxide reduction on oxide-derived copper catalyst. *ChemSusChem* **2010**, *3*, 3028-3033.

(20) Kumar, B.; Brian, J. P.; Atla, V.; Kumari, S.; Bertram, K. A.; White, R. T.; Spurgeon, J. M., Controlling the product syngas H2:CO ratio through pulsed-bias electrochemical reduction of CO2 on copper. *ACS Catal.* **2016**, *6*, 4739-4745.

(21) Aran-Ais, R. M.; Scholten, F.; Kunze, S.; Rizo, R.; Roldan Cuenya, B., The role of in situ generated morphological motifs and Cu(i) species in C2 product selectivity during CO2 pulsed electrosynthesis. *Nature Energy* **2020**, *5*, 317-325.

(22) Kimura, K. W.; Casebolt, R.; Cimada DaSilva, J.; Kauffman, E.; Kim, J.; Dunbar, T. A.; Pollock, C. J.; Suntivich, J.; Hanrath, T., Selective electrochemical CO2 reduction during pulsed potential stems from dynamic interface. *ACS Catal.* **2020**, *10*, 8632-8639.

(23) Le Duff, C. S.; Lawrence, M. J.; Rodriguez, P., Role of the adsorbed oxygen species in the selective electrochemical reduction of CO2 to alcohols and carbonyls on copper electrodes. *Angew. Chem. Int. Ed.* **2017**, *56*, 12909-12924.

(24) Yano, J.; Yamasaki, S., Pulse-mode electrochemical reduction of carbon dioxide using copper and copper oxide electrodes for selective ethylene formation. *J. Appl. Electrochem.* **2008**, *38*, 1721.

(25) Kimura, K. W.; Fritz, K. E.; Kim, J.; Suntivich, J.; Abruna, H. D.; Hanrath, T., Controlled selectivity of CO2 reduction on copper by pulsing the electrochemical potential. *ChemSusChem* **2011**, *4*, 1781-1786.

(26) Gupta, N.; Gattrell, M.; MacDougall, B., Calculation for the cathode surface concentrations in the electrochemical reduction of CO2 in KHCO3 solutions. *J. Appl. Electrochem.* **2006**, *36*, 161-172.

(27) Burdyny, T.; Smith, W. A., CO2 reduction on gas-diffusion electrodes and why catalytic performance must be assessed at commercially-relevant conditions. *Energy Environ. Sci.* **2019**, *12*, 1442-1453.
(28) Weekes, D. M.; Salvatore, D. A.; Reyes, A.; Huang, A.; Berlinguette, C. P., Electrolytic CO₂ Reduction in a Flow Cell. Acc. Chem. Res. 2018, 51, 910-918.

(29) Hoang, T. T. H.; Verma, S.; Ma, S.; Fister, T. T.; Timoshenko, J.; Frenkel, A. I.; Kenis, P. J. A.; Gewirth, A. A., Nanoporous copper-silver alloys by additive-controlled electrodeposition for the selective electroreduction of CO₂ to ethylene and ethanol. J. Am. Chem. Soc. 2018, 140, 5791-5797.

(30) Zhang, J.; Luo, W.; Zuttel, A., Self-supported copper-based gas diffusion electrodes for CO₂ electrochemical reduction. J. Mater. Chem. A 2019, 7, 26285-26292.

(31) Dinh, C.-T.; Burdyny, T.; Kibria, M. G.; Seifi-kaldani, A.; Gabardo, C. M.; Garcia de Arquer, F. P.; Kiani, A.; Edwards, J. P.; De Luna, P.; Bushuyev, O. S.; Zou, C.; Quintero-Bermudez, R.; Pang, Y.; Sinton, D.; Sargent, E. H., CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 2018, 360, 783-787.

(32) Moller, T.; Scholten, F.; Thanh, T. N.; Sinew, I.; Timoshenko, J.; Wang, X.; Jovanov, Z.; Gliech, M.; Roldan Cuenya, B.; Varela, A. S.; Strasser, P., Electro-catalytic CO₂ reduction on CuOx nanocubes: Tracking the evolution of chemical state, geometric structure, and catalytic selectivity using operando spectroscopy. Angew. Chem. Int. Ed. 2020, 59, 17974-17983.

(33) Ke, W.-H.; Hsia, C.-F.; Chen, Y.-J.; Huang, M. H., Synthesis of ultrasmall CuO nanocubes and octahedra with tunable sizes for facet-dependent optical property examination. Small 2016, 12, 3530-3534.

(34) Liu, K.; Smith, W. A.; Burdyny, T., Introductory guide to assembling and operating Gas diffusion electrodes for electrochemical CO₂ reduction. ACS Energy Lett. 2019, 4, 639-643.

(35) Giri, S. D.; Sarkar, A., Electrochemical study of bulk and monolayer copper in alkaline solution. J. Electrochem. Soc. 2016, 163, H252-H259.

(36) De Gregorio, G. L.; Burdyny, T.; Louidace, A.; Iyengar, P.; Smith, W. A.; Buonsanti, R., Facet-dependent selectivity of Cu catalysts in electrochemical CO₂ reduction at commercially viable current densities. ACS Catal. 2020, 10, 4854-4862.

(37) Lin, S.-C.; Chang, C.-C.; Chiu, S.-Y.; Pai, H.-T.; Liao, T.-Y.; Hsu, C.-S.; Chiang, W.-H.; Tsal, M.-K.; Chen, H. M., Operando time-resolved X-ray absorption spectroscopy reveals the chemical nature enabling highly selective CO₂ reduction. Nat. Commun. 2020, 11, 3525.

(38) Lian, X.; Xiao, P.; Yang, S.-C.; Liu, R.; Henkelman, G., Calculations of oxide formation on low-index Cu surfaces. J. Chem. Phys. 2016, 14, 044711.

(39) Bagger, A.; Aran-Ais, R. M.; Haldin Stenlid, J.; Campos dos Santos, E.; Arnarson, L.; Degn Jensen, K.; Escudero-Escribano, M.; Roldan Cuenya, B.; Rossmeisl, J., Ab initio cyclic voltammetry on Cu(111), Cu(100) and Cu(110) in acidic, neutral and alkaline Solutions. ChemPhysChem 2019, 20, 3096.

(40) Deng, Y.; Handoko, A. D.; Du, Y.; Xi, S.; Yeo, B. S., In situ Raman spectroscopy of copper and copper oxide surfaces during electrochemical oxygen evolution reaction: Identification of CuII oxides as catalytically active species. ACS Catal. 2016, 6, 2473-2481.

(41) Mandal, L.; Yang, K. R.; Motapothula, M. R.; Ren, D.; Lobaccaro, P.; Patra, A.; Sherburne, M.; Batista, V. S.; Yeo, B. S.; Ager, J. W.; Martin, J.; Venkatesan, T., Investigating the role of copper oxide in electrochemical CO₂ reduction in real time. ACS Appl. Mater. Inter. 2018, 10, 8574-8584.

(42) Zhao, Y.; Chang, X.; Malkani, A. S.; Yang, X.; Thompson, L.; Jiao, F.; Xu, B., Speciation of Cu surfaces during the electrochemical CO reduction reaction. J. Am. Chem. Soc. 2020, 142, 9735-9743.

(43) Jiang, S.; Klingan, K.; Pasquinii, C.; Dau, Holger, New aspects of operando Raman spectroscopy applied to electrochemical CO₂ reduction on Cu foams. J. Chem. Phys. 2019, 150, 041718.

(44) Chen, X.; Henckel, D. A.; Nwabara, U. O.; Li, Y.; Frenkel, A. I.; Fister, T. T.; Kenis, P. J. A.; Gewirth, A. A., Controlling speciation during CO₂ reduction on Cu-alloy electrodes. ACS Catal. 2020, 10, 672-682.

(45) Aran-Ais, R. M.; Gao, D.; Roldan Cuenya, B., Structure- and electrolyte-sensitivity in CO₂ electroreduction. Acc. Chem. Res. 2018, 51, 2906-2917.

(46) Reske, R.; Mistry, H.; Behafarid, F.; Roldan Cuenya, B.; Strasser, P., Particle size effects in the catalytic electroreduction of CO₂ on Cu nanoparticles. J. Am. Chem. Soc. 2014, 136, 6978-6986.

(47) Verdaguer-Casadevall, A.; Li, C. W.; Johansson, T. P.; Scott, S. B.; McKeown, J. T.; Kumar, M.; Stephens, I. E. L.; Kanan, M. W.; Chorkendorff, I., Probing the active surface sites for CO reduction on oxide-derived copper electrocatalysts. J. Am. Chem. Soc. 2015, 137, 9808-9811.

(48) Hajimammadov, R.; Bykov, A.; Popov, A.; Juhasz, K. L.; Lorite, G. S.; Mohl, M.; Kukovecz, A.; Huuhtanen, M.; Kordas, K., Random networks of core-shell-like Cu-CuxO/CuO nanowires as surface plasmon resonance-enhanced sensors. Sci. Rep. 2018, 8, 4708.

(49) Varela, A. S.; Kroschel, M.; Reier, T.; Strasser, P., Controlling the selectivity of CO₂ electroreduction on copper: The effect of the electrolyte concentration and the importance of the local pH. Catal. Today 2016, 260, 8-13.

(50) Dinh, C.-T.; García de Arquer, F. P.; Sinton, D.; Sargent, E. H., High Rate, Selective, and stable electroreduction of CO₂ to CO in basic and neutral media. ACS Energy Lett. 2018, 3, 2835-2840.
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