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Insights into autonomously formed oxygen-evacuated Cu$_2$O electrode for the selective production of C$_2$H$_4$ from CO$_2$

Dahee Kim, Seunghwa Lee, Joey D. Ocon, Beomgyun Jeong, Jae Kwang Lee, Jaeyoung Lee

In-situ transformation of bulk Cu$_2$O to a Cu$_2$O-derived bulk structure with oxygen-vacated sites, with the oxide layer still on the surface, resulted to highly active, stable, and selective production of ethylene from carbon dioxide.
Insights into autonomously formed oxygen-evacuated Cu$_2$O electrode for the selective production of C$_2$H$_4$ from CO$_2$

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Electrochemical conversion of carbon dioxide (CO$_2$) to small organic fuels ($e.g.$, formate, methanol, ethylene, ethanol) is touted as one of the most promising approaches in solving the problems of climate change and energy security. In this study, we report the highly efficient electrochemical reduction of CO$_2$ using cuprous oxide (Cu$_2$O) electrodes to produce ethylene (C$_2$H$_4$) primarily. During CO$_2$ electrolysis with an electrodeposited Cu$_2$O on a carbon electrode, we observe the transformation of compact metal oxide layer to a metal oxide structure with oxygen-vacated sites at the bulk region, where the notable electrocatalytic process towards selective production of C$_2$H$_4$ occurs. In contrast with previous studies, our results clearly indicate that the Cu$_2$O remains at the surface of the catalyst and it efficiently catalyzes the conversion process of CO$_2$ at low overpotential, exhibiting high selective faradic efficiency of over 20 % towards C$_2$H$_4$ formation even in long-term electrolysis.

Introduction

Of late, the control of greenhouse gas emissions in the atmosphere is critical in averting the myriad of issues surrounding global warming. While carbon dioxide (CO$_2$) from fossil fuel combustion is one of the primary greenhouse gases, it has the potential also to be a feed for the production of hydrocarbons. To this end, researchers are still exploring for ways to solve the climatic CO$_2$ challenge and utilize its abundance to synthesize valuable chemicals via different conversion technologies ($e.g.$, thermo-, photo-, electrochemical).

In particular, the electrocatalytic reduction of CO$_2$ to useful organic compounds has received great attention due to the relatively simpler process, with highly controllable operation. By passing current on an electroactive surface ($e.g.$, metals, metal oxides), it is possible to break the strong carbon-oxygen bonds in CO$_2$ to form various small organic molecules. The process requires a considerable amount of electrical energy because of its non-spontaneous tendency and thus, the development of a highly efficient electrocatalyst is needed to overcome this drawback.

In the electrolytic CO$_2$ reduction, superior catalytic activity and product selectivity are strongly dependent on the type of catalyst used. For instance, formate (HCOO$^-$) is primarily formed on electrocatalysts such as Sn, Pb, and Hg, which exhibit negligible carbon monoxide (CO) adsorption. The Au and Ag electrodes mainly convert CO$_2$ to CO. Cu is analogous to the metals with weak CO adsorption, but is considered to be an unique catalyst for production of monovalent and divalent hydrocarbons. Based on the above observations in previous studies, CO adsorption is undoubtedly an important step, since CO molecules are considered as key intermediates during CO$_2$ electroreduction.

Among these metals, great effort has been recently focused on Cu electrodes because of its unique electrocatalytic behaviour in enabling adsorbed CO to further react to more reduced organic molecules, such as methane (CH$_4$), ethylene (C$_2$H$_4$), methanol (CH$_3$OH), and ethanol (C$_2$H$_5$OH).

In addition, recent studies have shown that the oxidation state of Cu influences its electrocatalytic properties. For example, Chang et al. studied CO$_2$ electroreduction with Cu$_2$O-catalyzed carbon cloth, with CH$_3$OH as the only confirmed reaction product, while the Faradaic efficiency was not reported. In another study, Faradaic efficiencies of 7.5 % and 6.8% for CH$_4$ and C$_2$H$_4$, respectively, were observed using an electrode based on Cu$_2$O/Zn. Furthermore, Le and co-workers suggested that Cu (I) species might play a key role for the selective catalysis of CH$_3$OH from their experiments using Cu$_2$O electrodes. The latest studies on Cu$_2$O electrodes, a recent study reported that the Cu$_2$O layer could contribute to the fabrication of highly active Cu electrodes. Kanan’s group suggested that Cu$_2$O layers formed by annealing are fully reduced to Cu particles during CO$_2$ electroreduction and these Cu particles efficiently catalyze the reduction process at relatively lower overpotentials. In addition, it was shown that
formate (HCOO\(^{-}\)) was produced at lower overpotentials on the Cu electrode, which was prepared by a combined process of high‐temperature annealing and electroreduction.\(^{17,18}\)

Summarizing previous reports on the usage of Cu$_2$O catalyst in an electrolytic reduction of CO$_2$, the catalyst itself was completely covered into Cu metal during the reduction process.\(^{15,16}\)

In this paper, we compared the activity of Cu and Cu$_2$O to figure out how the Cu$_2$O behaves as a catalyst for CO$_2$ conversion. We tried to understand the enhanced selectivity of in‐situ formed specific structure of Cu$_2$O towards C$_2$H$_4$ formation. Finally, we provide new insights on the structural transformation of Cu$_2$O for CO$_2$ electrolysis.

### Experimental

All electrochemical experiments were carried out using a three‐electrode assembly, with a commercial Ag/AgCl electrode. Pt plate (1 cm$^2$) was used as counter electrode. The working electrode was fabricated by electrodepositing Cu or Cu$_2$O at room temperature on a GDE (TPGH‐060, Toray). Deposition of metal catalysts on GDE was carried out by constant potential electrolysis using a potentiostat/galvanostat (PGSTAT‐302N, Autolab). A polycrystalline copper electrode was prepared by applying -0.3 V (vs. Ag/AgCl) for 10 min in a 0.01 M CuSO$_4$ solution (> 99%, Sigma‐Aldrich) in diluted sulfuric acid. Additionally, Cu$_2$O nanoparticles were deposited at -0.5 V (vs. Ag/AgCl) for 10 min from a 0.5 M CuSO$_4$‐containing lactic acid and 5.0 M NaOH solution. An optimized procedure to fabricate the electrodes was used, following a previous study on the electrodeposition of Cu and Cu$_2$O.\(^{19}\)

The H‐type electrolytic cell used for CO$_2$ electrolysis is shown in Figure S1. A cation exchange membrane (Nafion N117, Dupont) separated the cathode compartment from the anode compartment, while a Pt mesh (4 cm$^2$) was used as the counter electrode. The electrolyte was made from ultrapure water and reagent‐grade potassium bicarbonate (KHCO$_3$, Sigma‐Aldrich), with a catholyte volume of 300 mL. Further, the electrolyte was saturated using high purity CO$_2$ (99.999 %) via bubbling for 40 min at 5 °C. Linear sweep voltammetry (LSV) measurements were carried out to examine the catalytic activity for CO$_2$ electroreduction, while bubbling Ar and CO$_2$ on the electrodes. Subsequent CO$_2$ reduction experiments were performed at a chosen potential between -0.9 V and -2.5 V (vs. Ag/AgCl) for 30 min. After optimizing the operating conditions, long‐term electrolysis was done at -1.9 V (vs. Ag/AgCl) for 2 h to ascertain the stability of the catalyst. In order to compare the relative surface roughness of Cu$_2$O and Cu electrode, Cyclic voltammetry (CV) was performed in 0.1 M HClO$_4$ with Ar gas bubbled. Chronopotentiometry experiment was also performed on Cu electrode at 80 mA for 1 h to check the dependence of current density which might cause higher local pH.

Gas‐phase products generated during CO$_2$ electrolysis were analysed using gas chromatography (GC) with thermal conductivity detector (TCD) and gas chromatography‐mass spectrometry (GC‐MS). The dissolved products in the electrolyte were quantified by high performance liquid chromatography (HPLC, Alliance 2690) analysis of the electrolyte after the electrolysis. The crystalinity and morphology of the electrodes were analyzed by X‐ray diffraction (XRD, Rigaku Miniflex II), a field‐emission scanning electron microscope (FE‐SEM, Hitachi, S‐4700) and high resolution transmission electron microscope (HR‐TEM, Tecnai‐F20 Ultra twin). The surface composition was identified via the Auger electron spectra obtained using an X‐ray photoelectron spectroscopy (XPS, VG Multilab 2000). During the XPS sample preparation, the electrodes were rinsed with deionized water and dried immediately by blowing air to prevent the formation of copper hydroxide on the surface. The electrodes were then instantly vacuum‐packed and placed in an Ar‐filled glove box.

Depth profiling of Cu$_2$O and Cu electrodes were performed using Auger electron spectroscopy (AES, Perkin Elmer, SAM 4300) with differentially pumped ion source controller (Physical Electronics, model 11‐065). The surface of electrodes was sputtered by Ar ions of 3 keV energy with a starting pressure of 10$^{-6}$ bar. The base pressure was increased to 1.2×10$^{-7}$ bar during the sputtering. For the excitation Auger electrons, an 5 keV electron beam was irradiated on the surface of samples and monitored beam current was 300 nA.

### Results and discussion

After preparing the electrodes, the surface morphology and the crystal structures were characterized. Figure 1 shows the X‐ray diffractograms of as‐prepared Cu$_2$O and Cu electrodes before applying the cathodic potential. Several dominant Cu$_2$O and Cu phases on the electrode were observed. Inset images display the surface structure showing nano‐sized Cu$_2$O and Cu catalyst particles uniformaly placed on the GDE surface. Hence, the two different electrodes were prepared as desired.

![Figure 1. X‐ray diffractograms of the electrodeposited Cu (black) and Cu$_2$O (red) electrocatalysts on GDE. Insets show the SEM images of (a) Cu$_2$O and (b) Cu catalyst.](image-url)
In order to compare the electrocatalytic activity between Cu$_2$O and Cu, LSV curves were obtained. The electrode potential was swept at 10 mV s$^{-1}$ with an initial open-circuit voltage in the 0.5 M KHCO$_3$ electrolyte saturated with Ar and CO$_2$. As shown in Figure 2, hydrogen evolution reaction (HER) slowly begins at around -0.9 V at Cu$_2$O and -1.1 V at Cu under the Ar-saturated condition (inset of Figure 2). The cathodic currents in the sufficient CO$_2$ condition were notably smaller than in Ar gas, in potentials ranging from HER through -2.1 V. Suppression of HER during CO$_2$ electroreduction was generally attributed to the adsorbed CO molecules on the electrode surface$^{11,13}$. The difference in the reduction current measured in Ar-purged electrolyte and the current measured in CO$_2$-saturated electrolyte should be considered as the indication of CO$_2$ reduction. This transition could be confirmed by product analysis, which will be discussed in the next paragraphs. With the Cu$_2$O reduction to Cu taking place simultaneously during CO$_2$ electrolysis, moreover, further detailed understanding is needed to determine the Faradaic efficiencies at given potentials.

![Figure 2](image2.png)

**Figure 2.** Linear sweep voltammograms for the electrodeposited Cu$_2$O (red) and Cu (black) electrode in 0.5 M KHCO$_3$ purged with Ar (dashed line) and CO$_2$ (solid line). Electrocatalytic CO$_2$ reduction began on Cu$_2$O at around -0.9 V with (a) Ar and (b) CO$_2$ gas purging, while CO$_2$ reduction in Cu were observed at around -1.1 V with (c) Ar and (d) CO$_2$ gas purging. Inset graph focuses on the potential region where the reactions occurred and the overpotential difference between the two electrodes. The scan rate was set at 10 mV s$^{-1}$ in all the experiments.

The Faradaic efficiencies of the reaction products during the CO$_2$ electroreduction were used to evaluate and compare the electrocatalytic activity between Cu$_2$O and Cu electrodes at a fixed potential for 30 min. Various electrolysis products from CO$_2$ electroreduction were observed and the product distribution is displayed in Figure S2. It was observed that the Cu$_2$O electrode required less overpotential of ~0.2 V to convert CO$_2$ to its reduction products than that of metallic Cu electrode, in good agreement with a previous study.$^{11}$ As shown in Figure S2, both Cu$_2$O and Cu electrodes showed similar trends in the oxygenate formation in the less negative potential region. CO and HCOO$^-$ were the dominant species, when excluding the hydrogen, which is predominantly produced during CO$_2$ electrolysis in the potential ranges.$^{11,13}$ In addition, the remainder of faradaic efficiency was allotted for the reduction of Cu$_2$O to Cu in the less negative potential ranges where applied potential for activation of CO$_2$ electrolysis was deficient.

![Figure 3](image3.png)

**Figure 3.** Faradaic efficiencies for the production of CH$_4$ (■), C$_2$H$_4$ (○), and CO (▲) Cu$_2$O and (b) Cu at different reduction potentials. CO$_2$ electrolysis was performed for 30 min at each potential in a CO$_2$ saturated 0.5 M KHCO$_3$ solution. Relatively lower overpotentials were required for CO$_2$ electrolysis on Cu$_2$O than at Cu and each electrode has varying selectivities for the production of hydrocarbons.

CO formation in the highly negative potential region suppressed the HER (Figure S2), as noted in the rise in Faradaic efficiencies of CH$_4$ and C$_2$H$_4$ and simultaneous decrease in CO as it was further converted to hydrocarbons (Figure 3).$^{11,13}$ This observation supports the proposed mechanism for the formation of hydrocarbons via CO molecules as intermediate species.$^{11,20}$ When the selectivity for C$_2$H$_4$ production was compared between two electrodes, the Faradaic efficiency in Cu$_2$O electrode was more than twice higher than that of Cu electrode. As discussed previously, earlier studies on CO$_2$ reduction have demonstrated only favorable CH$_3$OH production with Cu$_2$O electrode.$^{14-16}$ On the other hand, a notable selectivity towards C$_2$H$_4$ formation was observed on Cu$_2$O electrodes in our
experimental results. Hence, it was expected that a transformation of Cu$_2$O electrode during the electrolytic process could lead to different CO$_2$ conversion routes such as results of Li et al. and Qiao et al., showing the favorable HCOO$^-$ production.$^{17,18}$

Long-term CO$_2$ electroreduction was carried out to fully confirm the electrocatalytic activity trends of Cu$_2$O and Cu electrodes in C$_2$H$_4$ production. Following the above results, the electrolysis was performed at the optimal potential of -1.9 V for 2 h. During long-term electrolysis, the Cu electrode exhibited an average current density of 8.5 mA cm$^{-2}$, while Cu$_2$O electrode demonstrated an average current density of 10 mA cm$^{-2}$ (Figure S3). As seen in Figure 4, the Faradaic efficiency of CH$_4$ for Cu electrode changed from 52 % to 25 %, while the Faradaic efficiency of C$_2$H$_4$ decreased from 7 % to 3 %. In contrast, electrocatalytic activity for hydrocarbon formation over Cu$_2$O electrocatalysts remained high even after the 2 h electrolysis, with the Faradaic efficiencies towards CH$_4$ and C$_2$H$_4$ production at 2.5 % and 22 %, respectively. Furthermore, by multiplying the total current density in Figure S3 at a given potential by the faradaic efficiency towards each product, the distribution of partial current density can be plotted with respect to the electrolysis time (Figure S4). Considering other state of the art catalysts such as copper nanofoams showing faradaic efficiency for HCOOH of around 35 % and nanocrystalline copper for the production of liquid fuels with a faradaic efficiency of around 40 %, our catalyst’s activity and selectivity are comparable with these previous studies.$^{21,22}$ In addition, R. Reske et al. analyzed the particle size effects of Cu nanoparticles and their results showed a maximum Faradaic efficiency for CH$_4$ and C$_2$H$_4$ at 55 % and 20 %.$^{23,24}$

![Figure 4. Faradaic efficiencies for the production of C$_2$H$_4$ (■) and CH$_4$ (□) on (a) Cu$_2$O (bottom) and (b) Cu catalyst (top) during CO$_2$ with respect to the electrolysis time. Both of two gas phase products were collected and analyzed at each marked time.](image)

From these experimental observations, one can assume that Cu$_2$O does not enhance all CO$_2$ reduction reactions, but only the reactions that form the heavier hydrocarbons in the more cathodic potential region. For a better understanding of the electrocatalytic behavior depending on the type of electrode, additional experiments were performed. First, CV was obtained on both of two electrodes following the procedure in previous reports to measure their capacitance (Figure S5).$^{17,22}$ In order to quantify the surface roughness of Cu$_2$O relative to Cu, we have assigned a surface roughness factor of 1.0 for the Cu electrode. As seen in Figure S5, Cu$_2$O has higher surface roughness factor than Cu at almost three times the latter’s value. Although the electrode property based on the difference of particle size could increase the current efficiency at low overpotential region, surface area is not considered as the main contributor in the product distribution such as a C$_2$H$_4$/CH$_4$ ratio during CO$_2$ electrolysis.$^{17,22,23}$ Previous reports have also suggested that the enhanced selectivity for C$_2$H$_4$ might have been a result of the increased total current density causing higher local pH in the vicinity of the electrode.$^{11,13}$

Hence, further experiment was carried out to investigate the dependence of current density, which might cause higher local pH. CO$_2$ electrolysis was performed on the Cu electrode at a constant current of 10 mA cm$^{-2}$, same as that of Cu$_2$O at -1.9 V (Figure S3). This should verify if the relationship between high current density and product selectivity is correct, with the same product distribution expected from both Cu and Cu$_2$O electrodes at high current densities. However, Figure S6 showed that a significant difference in the products was not observed, compared with that of Cu electrode at constant potential of -1.9 V in Figure 4. As the above results support our earlier hypothesis on the maintained selectivity of the Cu$_2$O electrode, we then characterized and analyzed the structure and morphology of the two cathodes by SEM, TEM, XRD, XPS, and AES.

Figure S7 shows the SEM images of Cu$_2$O and Cu electrodes, before and after CO$_2$ electrolysis. In the case of as-deposited Cu electrode, Cu nanoparticles with individual particle sizes of up to 160 nm were formed on the carbon substrate (Figure S7a). CO$_2$ electrolysis on the Cu electrode, however, could lead to deactivation of the surface active sites.$^{12,20,24}$ Previous studies have reported that adsorption of amorphous carbon and impurities in the electrolyte might have caused the catalytic activity degradation in Cu electrodes.$^{12,24-27}$ Interestingly, the Faradaic efficiency of ca. 20% for the CH$_4$ production at Cu electrode in this study was kept for longer than 2 h, suggesting that another factor should have been accounted for the decline in activity. As observed in SEM (Figure S7b), Cu nanoparticles agglomerated into larger particles after CO$_2$ electrolysis up to 5 µm, possibly explaining the catalyst deactivation as suggested by other researchers as well.$^{20,24}$

In contrast, the morphological structure Cu$_2$O nanoparticles were almost unchanged after electrolysis, as seen in Figure S7c-d. This structural feature in Cu$_2$O, which prevents the decrease of catalytic active sites, supports the superior electrocatalytic stability of Cu$_2$O than that of Cu during CO$_2$ electroreduction. In addition, we observed the electrode materials using HR-TEM before and after CO$_2$ electrolysis. Our observations from HR-TEM, however, showed that there is not much difference between the particle morphology of the two electrodes. As
shown in Figure S8, the particles seem to agglomerate, in agreement with our observation in SEM.

The Cu$_2$O electrode’s structural durability was identified, we observed that after applying reduction potential for a few minutes, characteristic Cu peaks appeared in the X-ray diffractograms, indicating simultaneous reduction of Cu$_2$O during CO$_2$ electrolysis. As already introduced in previous studies, Cu$_2$O phases were changed into metallic Cu under the electrolytic reduction condition.$^{15-18}$ Moreover, the superior electrocatalysis was specifically attributed to the Cu$_2$O-derived Cu electrode upon application of cathodic potential.$^{17,18}$

![Figure 5](image1)  
**Figure 5.** (a) X-ray diffraction patterns and (b) Auger spectra of Cu$_2$O electrocatalysts in as-prepared Cu$_2$O, and in 10 min, 1 h, and 2 h after electrolysis. Shaded areas in the Auger spectra indicate the binding energies of the most intense components of the Auger peaks (Cu$^{1+}$ and Cu$^0$).

In our case, despite the electrochemical reduction of Cu$_2$O to Cu, SEM and TEM images did not show any noticeable surface morphological changes while the Faradaic efficiency towards C$_2$H$_4$ production was favorably kept high even after 2 h. This could be attributed to a particular characteristic of the transformed Cu$_2$O electrode during electrolysis. According to the XRD patterns of Cu$_2$O with respect to the electrolysis time (Figure 5a), Cu$_2$O (111) peak is barely visible on the as-used electrodes. The ex-situ X-ray diffractograms indicate that Cu$_2$O catalysts were not totally converted to Cu but obviously remained even after the phase changes caused by the applied cathodic potential for CO$_2$ electroreduction. The peak intensity decrease is most likely a result of increasing oxygen vacancy in the Cu$_2$O structure as the electrolysis occurs.$^{28}$

Figure 5b shows the Cu LMM Auger spectra indicating the oxidation state of the electrode surface up to 10 nm of depth.$^{29}$ The intense peak of Cu$_2$O was observed at 570.05 eV, together with a less intense peak corresponding to Cu at 568.15 eV (Figure S9).$^{30}$ The Auger spectra confirmed the presence of Cu$_2$O on the electrode surface after the electrolysis and that the oxide layer was unchanged during electrolysis. This provides evidence to the fact that the surface layer of the as-used Cu$_2$O remained while the bulk Cu$_2$O was reduced to Cu. The structure remained Cu$_2$O on the outmost surface more densely might be possible because bulk phase reduction occurs easier than surface reduction in energy level calculations.$^{31,32}$

To further study the structural transformation of Cu$_2$O during CO$_2$ electrolysis, elemental depth profiling of the electrodes was performed using AES. Figure 6 exhibits the relative atomic concentration of O to Cu of each electrode as a function of the electrode depth. As already explained from the XRD and Auger spectra analyses above (Figure 5), complete reduction of the Cu$_2$O to metallic Cu did not occur. As shown in the concentration profile of oxygen in the as-deposited Cu (Figure 6a), a native oxide layer with a thickness of almost 2.5 nm is present.$^{33-35}$ Identifying the thickness of the native oxide layer is crucial in showing the thickness of the oxide in the Cu$_2$O electrode at the onset of electrolysis.

![Figure 6](image2)  
**Figure 6.** Auger depth profiles showing the atomic content of oxygen in Cu$_2$O of (a) as-deposited Cu electrode, Cu$_2$O electrodes after CO$_2$ electrolysis for (b) 10 min (dotted line) and (c) 2 h (solid line), and (d) as-deposited Cu$_2$O electrode.

For instance, the oxygen depth profile of as-deposited Cu$_2$O in Figure 6d demonstrates a decreasing amount of oxygen and then an almost constant oxygen amount at a depth around 20 nm. The oxygen concentration profile indicates that electrode structure is that of Cu$_2$O before electrolysis. Upon applying the cathodic potential, however, the oxygen depth profile changed, showing a decrease in the oxygen content for samples under electrolysis for 10 min and 2 h (Figure 6b-c). This provides another evidence on the partial conversion of Cu$_2$O nanoparticles to metallic Cu nanoparticles. Nevertheless, an oxide layer thicker than the native oxide still exists in the surface of the catalyst. In addition, both as-used Cu$_2$O electrodes exhibited similar depth profiles, regardless of the length of exposure in the reducing conditions of CO$_2$.


electrolysis. For these reasons, it is believed that the Cu$_2$O electrode partially maintained its initial structure, especially in the bulk phase, and the transformed structures were built with sites where oxygen atoms were removed. The new catalyst structure, with the oxide layer on top of the sub-surface Cu$_2$O-derived Cu at the bottom, contributed greatly to the sustained high activity and good selectivity for C$_2$H$_4$ formation. The structural transformation of the Cu$_2$O electrode, as ascertained in AES depth profiling is crucial in the high conversion rates for the production of Cu$_2$O from CO$_2$.

To summarize the discussions above, bulk and surface-sensitive techniques (i.e. XRD, AES) demonstrated the partial reduction of Cu$_2$O to metallic Cu. In addition, there is a strikingly similar structural feature between the two as-used Cu$_2$O electrodes after electrolysis in terms of their oxygen concentration profiles. Thus, giving us an insight on the possible role of Cu$_2$O catalysts for the selective C$_2$H$_4$ production from CO$_2$ electrolysis. On the basis of these experimental results, the Cu$_2$O electrode during electrolysis can be pictured as having an oxide layer on top of metallic Cu with a lot of oxygen-vacated sites from the restructuring of the crystal structure during CO$_2$ reduction. With the formation of the oxygen-vacated sites on the metallic Cu layer, along with the presence of the oxide layer, the electrode is able to maintain its high turn-over rate for C$_2$H$_4$ formation. Our results strongly suggest a new role of the Cu$_2$O layer, not only as a starting material for making an oxide-derived Cu catalysts, but as the active layer during CO$_2$ electrolysis, a view that is in stark contrast with previous works.17,18

A key question in the structural transformation of Cu$_2$O is how the Cu$_2$O particles maintained its activity during CO$_2$ electrolysis. This interesting situation could be explained from first-principle calculations using density functional theory (DFT) on copper oxide reduction.31,32,36 Furthermore, in some cases of reduction of CuO and Cu$_2$O with H$_2$, not all Cu$_2$O powders were completely reduced to metallic Cu, leaving a residue of the starting oxide material when exposed to H$_2$ for more than 60 min.31 They reported that the partial reduction of Cu$_2$O grains was attributed to the coating protection by the Cu film, which was quickly reduced, leaving oxygen trapped within the structure.31

Maimaiti et al. found that loss of the subsurface oxygen is initially thermodynamically favorable in copper oxide reduction and showed that the reduction of CuO to Cu at the surface is more energetically difficult than in the bulk phase.32 Oxygen-vacancy structures in Cu$_2$O (111) were also studied and their usefulness for CO$_2$ adsorption as active sites was demonstrated.36

In addition, the partial depletion of Cu$_2$O electrode might have resulted from following reactions:

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (1)$$

$$\text{CO}_2(\text{g}) + 6\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{CH}_4 + 8\text{OH}^- \quad (2)$$

$$2\text{CO}_2(\text{g}) + 8\text{H}_2\text{O} + 12\text{e}^- \rightarrow 2\text{CH}_4 + 12\text{OH}^- \quad (3)$$

Hydroxide ions (OH$^-$) are generated at the electrode surface during CO$_2$ electroreduction. There is an instantaneous pH rise in the local region just close to the surface layer as active sites.24,25,37 Under the electrolytic conditions, the reduction of Cu$_2$O to metallic Cu can be suppressed.14,38,39 Recent literature suggested that Cu$_2$O shows prominent stability even after applying the cathodic potential in alkaline media for oxygen reduction reaction.40,41 As a result, the uniquely structured Cu$_2$O electrodes leads to selective C$_2$H$_4$ formation - but not CH$_4$ formation – and the structure is maintained during CO$_2$ electrolysis owing to the hydroxide molecules (equation 1-3) promoting the locally alkaline state.

Conclusions

The superior electrocatalytic behaviour in CO$_2$ electrolysis of the electrodeposited Cu$_2$O electrode was demonstrated, with the catalyst exhibiting low overpotential and high selectivity towards C$_2$H$_4$ formation over other reaction products. Contrary to a number of earlier studies, Cu$_2$O was only partially reduced, leaving an oxide layer on top of the bulk Cu$_2$O-derived Cu layer. Using bulk and surface-sensitive analytical techniques, we demonstrated the decrease in the oxygen concentration of the Cu$_2$O electrode during electrolysis, resulting to the formation of oxygen-vacated structures, which are randomly distributed in the Cu$_2$O structure-derived bulk layer. The in-situ formed structures play a critical role in maintaining the high reactivity of the electrode for C$_2$H$_4$ production. Hence, the surface oxide coverage and the oxide-derived metallic layer are both key in the selective CO$_2$ catalysis towards large oxygenate molecules. While we have provided in-depth analysis on the oxide transformation during CO$_2$ reduction, more fundamental studies are needed to elucidate the atomic reorganization of the surface and bulk oxide layers and to understand its role in forming the CO$_2$-active sites. Our route to providing a highly active and stable CO$_2$ catalyst, however, is highly advantageous, because the extra oxide reduction step in preparing the electrode is no longer necessary. This will be important in preparing industrially-relevant catalysts for converting CO$_2$ into high value chemicals using renewable energy sources.

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Notes and References

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
Electronic Supplementary Information (ESI) available: Schematic diagram of the H-type cell, Faradaic efficiencies for all products at different applied potentials, Current density profiles of CuO and Cu during electrolysis for 2 h, Partial current densities during CO2 electrolysis of CuO and Cu, Cyclic voltammograms for the measurement of the surface roughness factor, Potential profile during CO2 electrolysis on Cu electrode at a constant current density of 10 mA cm\(^{-2}\) for 1 h, SEM images of CuO and Cu electrodes before and after CO2 electrolysis, TEM images of CuO and Cu electrodes before and after CO2 electrolysis, Auger spectra of CuO and Cu electrodes before and after CO2 electrolysis for 2 h. See DOI: 10.1039/b000000x/

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