This document is the accepted manuscript version of the following article:
Permyakova, A. A., Herranz, J., El Kazzi, M., Diercks, J. S., Povia, M., Mangani, L. R., ... Schmidt, T. J. (2019). On the oxidation state of Cu₂O upon electrochemical CO₂ reduction: an XPS study. ChemPhysChem. <https://doi.org/10.1002/cphc.201900468>

On the Oxidation State of Cu₂O upon Electrochemical CO₂ Reduction: an XPS Study

Dr. Anastasia A. Permyakova,^{[a],‡} Dr. Juan Herranz,^{[a],‡,} Dr. Mario El Kazzi,^[a] Justus S. Diercks,^[a] Dr. Mauro Povia,^[a] Léa Rose Mangani,^[a] Michael Horisberger,^[b] Dr. Alexandra Pătru,^[a] and Prof. Dr. Thomas J. Schmidt^[a,c]*

^[a]Electrochemistry Laboratory, Paul Scherrer Institut

Forschungsstrasse 111, 5232 Villigen PSI, Switzerland

^[b]Laboratory for Scientific Developments and Novel Materials, Paul Scherrer Institut

Forschungsstrasse 111, 5232 Villigen PSI, Switzerland

^[c]Laboratory of Physical Chemistry, ETH Zurich

HCI G 215, Vladimir-Prelog-Weg 1-5/10, 8093 Zurich, Switzerland

*Corresponding author: juan.herranz@psi.ch; ‡these authors contributed equally to this work

Abstract

The encouraging selectivity of copper oxides for the electroreduction of CO₂ into ethylene and alcohols has led to a vivid debate on the possible relation between their *operando* (sub-)surface oxidation state (i.e., fully reduced or partially oxidized) and this distinct reactivity. The high roughness of the Cu-oxides used in previous studies on this matter adds complexity to this controversy, and motivated us to prepare *quasi*-planar Cu₂O thin films that displayed a CO₂-reduction selectivity similar to that of oxide-derived copper catalysts reported in previous studies. Most importantly, when the *post-mortem* thin films were transferred for characterization in an air-free environment, X-ray photoelectron spectroscopy measurements confirmed their complete reduction in the course of the CO₂-reduction reaction. Thus, our results indicate that the selectivity of the Cu-oxides featured in previous studies stems from their enhanced roughness, while highlighting the importance of controlled sample transfer upon *post-mortem* characterization with *ex situ* techniques.

Introduction

The electrochemical reduction of carbon dioxide to added-value chemicals is gaining attention as a means to valorize CO₂ while decreasing its emissions and environmental impact.^[1] Despite this interest, the large overpotentials and poor selectivities displayed by most CO₂-reduction electrocatalysts represent a major obstacle for the development of an implementable technology, which would additionally require a rigorous assessment of the CO₂-reduction products with the greatest marketability potential.^[2] In this regard, some studies have suggested that CO₂-electroreduction to formate or H₂/CO mixtures (i.e., syngas) may be cost-competitive when performed using Sn- or Au-based catalysts implemented in electrode/cell configurations allowing

to draw currents $> 100 \text{ mA}\cdot\text{cm}^{-2}$.^[3–5] On the other hand, the production of ethylene or methanol using the same setups would lead to estimated production costs ≈ 2 -fold above current market values^[3,4] – a price gap that could be significantly narrowed by substituting the copper catalysts considered in the above studies^[3,4] with copper oxides,^[6] which display enhanced selectivities and stabilities for CO₂-to-ethylene/-methanol reduction.

These distinct properties have motivated a significant research effort to understand the factors that induce the CO₂-reduction selectivity of these oxides, which customarily consist of nanostructured, high surface area catalysts with a cuprous oxide (Cu₂O) composition.^[6–10] Specifically, a vivid debate is currently ongoing regarding the oxidation state of this initial Cu₂O in the course of the CO₂-reduction reaction. On the one hand, the latter takes place at potentials $\ll 0$ volts vs. the reversible hydrogen electrode (V_{RHE}) that are well below the Cu₂O/Cu⁰ equilibrium (at $\approx 0.5 V_{\text{RHE}}$),^[11] and from which the *operando* reduction of the initial oxide would be expected – an extent that has been predicted by several computational studies^[12,13] and experimentally demonstrated using *in situ* X-ray diffraction^[14] and Raman spectroscopy,^[10,15] as well as *post-mortem* secondary ion mass spectrometry (SIMS).^[16] On the other hand, and in clear conflict with those works, a greater number of recent studies implementing *in situ* or *post-mortem* X-ray absorption, photoelectron or electron energy loss spectroscopies (XAS, XPS, EELS) have concluded that the initial oxide does not get completely reduced in the course of the CO₂-reduction process. Moreover, those same works additionally assigned the enhanced selectivity for ethylene/alcohols production displayed by these catalysts to the presence of remnant oxide within their (sub-)surface.^[9,17–26]

The validation of these conflicting lines of thought is complicated by the high surface roughness intrinsic to these Cu₂O catalysts, since their eventual reduction to Cu⁰ would translate into an abundance of [100](-stepped) analogous domains^[27–29] and/or in a high surface pH^[28–31] that would

justify the CO₂-to-ethylene selectivity displayed by these materials. Additionally, their correspondingly large content of surface grain boundaries prone to re-oxidation upon contact with trace amounts of oxygen^[13,16] (e.g., during sample transfer for *post-mortem* characterization) could cause the apparent presence of remaining (sub-)surface oxides asserted in the above studies.^[9,17–26] Thus, to suppress the ambiguous effects of the surface roughness on the oxide's selectivity and *post-mortem* oxidation state, in this work we prepared quasi-planar, low-roughness Cu₂O thin films (TFs) and used them as CO₂-reduction electrocatalysts. As we will show in the following, these TFs displayed a product selectivity similar to that of oxide-derive copper catalysts,^[31] and *post-mortem* characterization through XPS (implementing an air-free transfer) confirmed their complete reduction to Cu⁰. Thus, our results indicate that the unique ethylene selectivity of Cu-oxides is a result of their enhanced roughness, and suggest that the often-reported presence of (sub-)surface oxides in these materials may stem from their re-oxidation upon air contact during transfer for (or in the course of) *post-mortem* characterization.

Experimental Section

Thin film sample preparation. – Copper oxide thin films were fabricated by reactive DC magnetron sputter deposition according to the procedure described in detail in Ref. 32. The target was a metallic Cu disk (99.99 wt. % in purity – Umicore AG) with a diameter of 75 mm and 6 mm in thickness. The substrate for electrochemical investigations was a silicon wafer (Si(100), type n, P-doped – PB-Technik AG). A ≈ 4 nm thick Ti interlayer was first deposited by DC magnetron sputtering, followed by a ≈ 20 nm Ag interlayer used to improve the adhesion of the final Cu₂O thin film (TF) on the substrate. Discharge was conducted at 200 W and a back-pressure of $5 \cdot 10^{-7}$

mbar attained by dosing a 50:50 mixture of O₂ in Ar. Samples with two different film thicknesses (≈ 100 nm vs. ≈ 1 μ m) were obtained by controlling the deposition time. The thickness of the resulting films was determined using a stylus profilometer (Veeco Dektak-8).

Materials.— Potassium chloride (≥ 99.999 %, Merck), caesium carbonate and potassium bicarbonate (≥ 99.999 vs. ≥ 99.95 %, respectively – Sigma Aldrich) were used without further purification. All electrolytes were prepared by dilution of the above salts in ultrapure water (18.2 M Ω ·cm, Elga Purelab Ultra). Copper foil (≥ 99.999 % metals basis, 1.00 mm in thickness) was purchased from Goodfellow Cambridge Ltd. Fine polishing MicroPolish Alumina suspension (0.05-0.3 μ m) and polishing cloth (MasterTex, PSA, 8 IN) were purchased from Buehler. Carbon dioxide, nitrogen, argon and hydrogen gases (all 6.0 quality) were purchased from Carbagas.

Preparation of the polycrystalline copper electrode.— For the preparation of the polycrystalline copper benchmark electrode (Cu_{poly}), Cu-foil was cut into 2.5×2.5 cm² pieces, polished with alumina suspension down to 0.05 μ m on a polishing cloth, and subsequently cleaned by sonication in 2-propanol (99.9 %, Chromasolv Plus for HPLC, Sigma Aldrich) and ultrapure water (18.2 M Ω ·cm, Elga Purelab Ultra) for 30 min. Finally, the copper foil was electropolished in concentrated phosphoric acid (≥ 85 wt. % in H₂O, 99.999+ % metals basis, Sigma Aldrich) for 5 min at a potential of 2.0 V vs. a copper foil counter electrode, followed by rinsing in ultrapure water and drying under nitrogen.

CO₂-Electroreduction measurements.— All electrochemical CO₂-reduction tests were performed in 0.1 M CsHCO₃ electrolyte solution, which was obtained by bubbling 0.05 M Cs₂CO₃ with pure CO₂ for 1 h at 1 bar until a pH of 6.8 was attained. CO₂ electrolysis was performed at ambient pressure in a gas-tight custom-made parallel plate electrochemical cell made of polyether ether

ketone (PEEK) and fitted with o-rings.^[33,34] The cell configuration is designed to ensure a uniform potential distribution across the surface of the working electrode by placing the counter electrode (platinum foil) parallel to the working electrode.^[33,34] The geometric surface area of both electrodes was 1.00 cm². To separate anodic and cathodic compartments and prevent the oxidation of CO₂-reduction products, an anion exchange membrane (Selemion[®] AMV, AGC Inc.) was placed in between. Both anodic and cathodic compartments contained small electrolyte volumes (2 vs. 1.8 mL, respectively) to ensure high concentrations of liquid products and therefore decrease the detection limits. An Ag/AgCl electrode (LF-1, Harvard Apparatus GmbH) was used as the reference. Data were converted to a reversible hydrogen electrode (RHE) potential (E) scale using the Equation:

$$E \text{ (V vs. RHE)} = E \text{ (V vs. Ag/AgCl)} + 0.197 \text{ V} + pH \cdot 0.0591 \text{ V}$$

where pH refers to the pH of the CO₂-saturated electrolyte solution (i.e., $pH = 6.8$ – see above). Before conducting CO₂ electrolysis, the electrolyte was purged with CO₂ for at least 15 min to ensure complete CO₂ saturation. During electrolysis, CO₂ was constantly bubbled through the electrolyte at a flow rate of 5 sccm controlled by a mass flow controller (Bronkhorst). For each measurement the solution resistance was determined using electrochemical impedance spectroscopy at the open circuit potential applying a 10 mV perturbation (1 MHz to 10 Hz). Before the cyclic voltammetry (CV) and chronoamperometry (CA) measurements, the potentials were partially corrected for the corresponding IR-drop by setting the Biologic SP-300 potentiostat to 85 % software compensation.

Product analysis.— Gas products analysis was carried out with a gas chromatograph (GC – 8610C, SRI Instruments) equipped with a packed HaySep D column and a packed MolSieve 5A column.

A flame ionization detector (FID) equipped with a methanizer was used to detect hydrocarbons with argon as the carrier gas. A thermal conductivity detector (TCD) was used to detect hydrogen with argon as the carrier gas. Calibration of the GC was carried out using four calibration gas mixtures in argon prepared by Carbagas. *Online* gaseous product GC-analysis was carried out after CO₂ passed through the cell directly into the gas sampling loop. For all experiments, gas analysis was performed after 30 min of continuous electrolysis to obtain the faradaic efficiencies of the various products.

Charge-neutral liquid products (e.g., ethanol) were analyzed by collecting aliquots of the electrolyte after electrolysis from the cathode chamber, using the GC's split/splitless injector and Innopeg capillary column. On the other hand, formate was analyzed on diluted electrolyte samples using ionic chromatography (IC, Metrohm 882 Compact IC plus and 863 Compact Autosampler) with a detection limit of < 1 ppb. Liquid products' calibration of the GC and IC devices was carried out using calibration liquid mixtures with products concentrations ranging from 0.1 to 10 or 100 to 10,000 ppm for IC vs. GC, respectively.

Air-free transfer of post-CA samples to ultra-high vacuum (UHV).— To avoid contact with air, a custom-made, gas-tight chamber allowing sample transfer without air intrusion^[35] and the electrochemical cell described above were placed inside a glovebox (SICCO V 1982-08) that was constantly purged with N₂ and equipped with an O₂-sensor (O2-BTA by Vernier Software & Technology). Once the O₂-content inside the glovebox reached a value ≤ 0.2 vol. %, the electrochemical test was performed and, with the glovebox still closed, the cell was disassembled and the sample was recovered and transferred inside the gas-tight transfer chamber. The latter was then closed, taken out of the glovebox and directly transported and quickly mounted (in < 2 min) in the transfer port of the UHV-setup used for Ar-sputtering and X-ray photoelectron spectroscopy

(cf. below), where the transfer chamber was opened only once a back-pressure $\leq 10^{-4}$ mbar was reached.

Ultra-high vacuum characterization. – XPS measurements were performed at $\approx 2 \cdot 10^{-9}$ mbar in a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) using focused monochromatized Al K_{α} radiation (1486.6 eV) with a beam size of $\approx 500 \mu\text{m}^2$. The spectrometer was pre-calibrated by performing measurement on a clean silver surface, whereby the Ag 3 $d_{5/2}$ peak was aligned to a binding energy of 368.25 eV with a full width at half-maximum of 0.78 eV at a pass energy of 30 eV. All survey spectra were recorded with a dwell time of 50 ms, using a pass energy of 50 eV and in 0.5 eV binding energy steps; for spectra acquired in a narrow energy span, these last parameters accounted to 30 and 0.05 eV, respectively. All recorded spectra were energy-calibrated by aligning the Cu 2 $p_{3/2}$ peak to a binding energy of 932.5 eV.^[36]

Argon sputtering was performed in a separated chamber directly connected in UHV to the XPS station and with a back pressure of $\approx 2 \cdot 10^{-9}$. A leak valve (Kurt J. Lesker Company) was used to dose Ar (6.0 quality – Carbagas AG) until a pressure of $\approx 9 \cdot 10^{-6}$ mbar was reached. Sputtering for the stipulated time was then completed using an IQE 11/35 ion source (SPECS GmbH) operated at a voltage of 3 kV.

X-ray diffraction (XRD). – Grazing incidence XRD measurements were performed using a Smartlab Rigaku diffractometer set in parallel beam mode. The diffractometer's Cu K_{α} X-ray source was operated at 200 mA and 45 kV and placed at 0.3° with respect to the sample's surface. A graphite Göbel mirror was used to make the beam parallel and remove the Cu- K_{β} radiation. A $2 \times 0.3 \text{ mm}^2$ spot size was projected on the sample using a 2 mm slit placed after the Göbel mirror.

The data were acquired between 2θ values of 20 and 90 °, moving the SC70 detector at a rate of 1 ° min⁻¹.

Scanning electron microscopy (SEM).— SEM measurements were performed in a Carl Zeiss Ultra55 scanning electron microscope, using the in-lens detector at an acceleration voltage of 3 kV and a working distance of $\approx$ 4.5 mm.

Results and Discussion

Initial properties and CO₂-electroreduction performance of Cu₂O thin films.— Cuprous oxide TFs $\approx$ 100 nm in thickness were deposited on Si(100) wafers with a $\approx$ 20 nm thick Ag adhesion interlayer using magnetron sputtering (cf. Experimental Section for details). As revealed by the SEM image in Figure 1A, the resulting samples displayed a low roughness surface topography convenient to our purposes. To quantify this asseveration, pieces of the silicon wafer covered with the Cu₂O TF were cut and mounted in a three-electrode electrochemical cell^[33] filled with CO₂-saturated 0.05 M Cs₂CO₃, and were submitted to cyclic voltammetry (CV) measurements at various scan rates, from which a double layer capacitance of $\approx$ 16 $\mu\text{F}\cdot\text{cm}_{\text{geom}}^{-2}$ (at 0.4 V_{RHE}) was estimated (cf. Figs. 2A and 2C). Assuming the conversion capacitance of $\approx$ 30 $\mu\text{F}\cdot\text{cm}_{\text{surface}}^{-2}$ customarily used to estimate the roughness factor (RF) of Cu-based catalysts in this potential window^[29,31] would lead to a below-unit RF of only $\approx$ 0.5 $\text{cm}_{\text{surface}}^2\cdot\text{cm}_{\text{geom}}^{-2}$. On the other hand, this seemingly low roughness may be affected by imprecisions in the above normalization capacitance,^[29,31] which stems from measurements on reduced, Cu⁰ samples with an oxidation state different from that of the initially oxidized Cu₂O TF used herein. On the basis of observations for reduced vs. oxidized Pt, Ir and Ru surfaces,^[37,38] surface oxidation reportedly leads to a $\approx$ 2-fold

decrease of the intrinsic double layer capacitance; this would in terms translate in a lower conversion capacitance (i.e., $\approx 15 \mu\text{F}\cdot\text{cm}_{\text{surface}}^{-2}$) leading to an RF closer to the unit value expected for the *quasi*-flat surface observed by SEM.

Figure 1. Scanning electron micrographs of the as-deposited, ≈ 100 nm thick Cu_2O thin film (A) and of the same sample after 30 minutes of chronoamperometric CO_2 -reduction at $-1.0 V_{\text{RHE}}$ in CO_2 -saturated $0.05 \text{ M Cs}_2\text{CO}_3$ (B).

Having assessed the TF's initial topography and roughness, grazing angle XRD measurements confirmed the exclusive presence of crystalline Cu_2O domains in its bulk (cf. Fig. 3A). This characterization was complemented by XPS measurements, whereby the survey scan in Figure S1 confirmed the exclusive presence of copper, oxygen and adventitious carbon on the TF surface. Most importantly, the $\text{Cu L}_{3\text{M}_{4.5}\text{M}_{4.5}}$ Auger spectrum in Figure 3B consisted of a broad peak located at a binding energy of ≈ 570 eV (corresponding to a kinetic energy of ≈ 916.5 eV). Interestingly, this energy position is precisely in-between the values reported for Cu_2O and CuO

(at kinetic energies of ≈ 916 vs. ≈ 917 eV, respectively),^[39] and therefore suggests the simultaneous presence of both oxides on the film's surface. This was confirmed by the satellite peaks observed at binding energies of ≈ 935 , ≈ 945 , ≈ 963 and ≈ 975 eV in the corresponding core level Cu 2p XPS displayed in Figure S2, which are assignable to CuO.^[40]

Figure 2. Cyclic voltammograms recorded at various scan rates on the ≈ 100 nm thick Cu_2O thin film prior to and after 30 minutes of chronoamperometry (CA) at $-1.0 \text{ V}_{\text{RHE}}$ in CO_2 -saturated $0.05 \text{ M Cs}_2\text{CO}_3$ (A vs. B). Corresponding plots of the currents at $0.4 \text{ V}_{\text{RHE}}$ as a function of the scan rate (C), whereby the slopes of the linear fits lead to pre- vs. post-CA capacitance values of ≈ 16 vs. $\approx 480 \mu\text{F}\cdot\text{cm}_{\text{geom}}^{-2}$, respectively.

Figure 3. Grazing angle X-ray diffractograms (A) of the ≈ 100 nm thick Cu_2O thin film as-prepared and after 30 minutes of chronoamperometry (CA) at $-1.0 V_{\text{RHE}}$ in CO_2 -saturated $0.05 \text{ M Cs}_2\text{CO}_3$ ('Before CA' vs. 'After CA', respectively), along with reference diffraction peaks of Cu_2O and Cu^0 standards (COD card numbers 1000063 and 4105040). Note that the intensities of the Cu_2O diffraction peaks at $\approx 30^\circ$, $\approx 53^\circ$ and $\approx 77^\circ$ have been multiplied 5- or 10-fold to allow for a clearer assignment. Corresponding Cu $L_{3M_{4,5}M_{4,5}}$ Auger spectra (B), whereby post-CA samples were transferred to ultra-high vacuum for XPS analysis in contact with air ('After CA, air') or by disassembly of the electrochemical cell inside a N_2 -filled glovebox and transport in a gas-tight transfer chamber ('After CA, N_2 '). Comparison among the Cu $L_{3M_{4,5}M_{4,5}}$ Auger spectra of the post-CA sample transferred in the absence of air ('After CA, N_2 ') and of Ar-sputtered polycrystalline copper foil (Cu_{poly}), along with the difference of both spectra (C).

Following this initial characterization, the CO₂-electroreduction performance of this ≈ 100 nm Cu₂O/Si(100) TF-wafers was determined in the same electrochemical cell^[33] used for the above CV measurements and filled with CO₂-saturated 0.05 M Cs₂CO₃ (if connected to a gas chromatography for products' analysis – see above Experimental Section for details). Figure 4A displays the Faradic efficiencies (FEs) obtained in chronoamperometric (CA) tests at potentials ranging between -0.8 and -1.1 V_{RHE} (see Figs. S3 and S4 for the corresponding, overall and product-specific currents, respectively). Upon comparison with previous results using the same electrolyte and cell configuration,^[31] the TF's limited efficiency for ethylene production (maxing at ≈ 20 %) and relatively large H₂-yields (≈ 40 to ≈ 60 %) are comparable to those observed for a thermally-produced copper oxide (cf. the OD-Cu sample in Ref. 31) – a consistency that also extends to the minor selectivities for ethanol, CH₄ and CO, but that does not apply to the TF's increase in HCOO[−]-yield with potential, more similar to the trend reported for Cu_{poly} in the same study.^[31] These difference among samples are highlighted in Figure 4B, which summarizes the FEs at -1 V_{RHE} displayed by the Cu₂O TF and Cu_{poly}; chiefly, the product distribution for the latter, polycrystalline sample is in very good agreement with the results in Ref. 31 (i.e., using the same electrolyte and cell configuration). In the case of the Cu₂O TF, though, the observed ethylene and methane yields are comparatively lower than on Cu_{poly}, and appear to be offset by a greater selectivity for H₂-evolution.

Figure 4. Potential-dependent Faradaic efficiencies (FEs) of the ≈ 100 nm Cu_2O thin film in independent, 30 minute long chronoamperometric tests in CO_2 -saturated 0.05 M Cs_2CO_3 (A). Comparison of the Faradaic efficiencies at -1.0 V_{RHE} for the ≈ 100 nm cuprous oxide thin film ($\text{'Cu}_2\text{O TF'}$) and a polycrystalline copper ($\text{'Cu}_{\text{poly}}'$) sample (B).

Post-CA roughness and bulk composition of the Cu_2O thin films.— To shed light on the reasons for this product selectivity, the surface topography of a Cu_2O TF sample after CA at -1 V_{RHE} was inspected with SEM; the corresponding images displayed in Figure 1B unveil the appearance of numerous cracks that were not present on a Cu_{poly} sample submitted to the same electrochemical protocol (cf. Fig. S5). Interestingly, this surface morphology change at CO_2 -reduction potentials is qualitatively consistent with previous observations for Cu-catalysts,^[7,8,10,41,42] and has recently been suggested to be triggered by surface-adsorbed CO produced as a CO_2 -reduction intermediate.^[43] Moreover, the specific appearance of cracks in the TF is likely related to the reduction of the initial Cu_2O to Cu^0 in the course of CO_2 -electroreduction (cf. discussion below),

which would imply a $\approx 15\%$ contraction of the TF's lattice (on the basis of the face centered cubic lattice constants of 4.27 vs. 3.62 Å reported for Cu₂O vs. Cu⁰, respectively)^[44,45] that would trigger the film's in-plane fracture. Most importantly, *post*-CA CV measurements equivalent to those performed on the as-prepared TF yielded a double layer capacitance value of $\approx 480\text{ }\mu\text{F}\cdot\text{cm}_{\text{geom}}^{-2}$ (cf. Figs. 2B and 2C) that translates into a roughness factor of $\approx 16\text{ cm}_{\text{surface}}^2\cdot\text{cm}_{\text{geom}}^{-2}$ when considering the conversion capacitance of $\approx 30\text{ }\mu\text{F}\cdot\text{cm}_{\text{surface}}^{-2}$ quoted above for Cu⁰ (i.e., relying on the reduction of the TF's surface – *vide infra*). Interestingly, this *post*-CA RF value is comparable to those reported in Ref. 31 for a series of thermally- or electrochemically-prepared oxide-derived copper catalysts, but remains ≈ 2 - to ≈ 6 -fold below the (*post*-CA) factors determined for plasma-activated Cu materials.^[18,26] Moreover, this relatively large roughness may explain the TF's enhanced H₂-evolution activity, concomitant with the selectivity for this by-product displayed by rough Cu⁰-samples with an abundance of low-coordinated surface sites (i.e., edges, corners and kinks).^[46-49] Finally, this operando enhancement of the film's RF also undermined our original purpose to decouple the effect of this variable and the (sub)surface's oxidation state on the catalyst's selectivity; nevertheless, as it will be shown below, the subsequent characterization of the *post*-CA TF did serve to unambiguously assess the (sub)surface's state following CO₂-reduction.

In this regards, our first effort to verify the possible reduction of the cuprous oxide TF upon CO₂-electroreduction consisted of characterizing the *post*-CA TF again through grazing angle XRD. The resulting diffractogram, plotted in Figure 3A, discloses that the initial Cu₂O did indeed get reduced to Cu⁰ in the course of the CO₂-reduction process; however, the low-intensity, broad peak at a 2θ -value of $\approx 37^\circ$ indicates the presence of Cu₂O in this *post-mortem* sample, either due to the incomplete electrochemical reduction of the initial oxide and/or due to its *post*-CA oxidation

upon contact with air in the course of the XRD measurement (lasting 70 min – see Experimental Section for details).

Post-CA TF oxidation state assessed through (depth profiling) XPS.— Trying to discriminate these effects with the aid of XPS, an equivalent Cu₂O TF sample (i.e., having undergone CA at -1 V_{RHE}) was rapidly disassembled from the electrochemical cell and transferred in ≈ 2 min to ultra-high vacuum (UHV) for analysis. The corresponding Cu L₃M_{4,5}M_{4,5} Auger and 2p spectra displayed in Figures 3B and S1 confirm the presence of copper oxide on this *post*-CA TF; specifically, the Cu L₃M_{4,5}M_{4,5} Auger in Figure 3B (more sensitive than core level Cu 2p spectra for discriminating among Cu₂O and Cu⁰)^[39,40] featured the general shape observed for the initial Cu₂O TF, along with two shoulders at binding energies of ≈ 568 and ≈ 565 eV assignable to Cu⁰. Additionally, the Cu 2p spectrum featured in Figure S2 still displayed small contributions of the CuO-satellites discussed above.

While these results may appear to suggest the incomplete reduction of the initial Cu₂O TF in the course of the CO₂-reduction reaction, they could still be affected by the air-induced oxidation of the sample during cell disassembly and/or upon fast transfer to UHV, as previously proven in Ref. 36; thus, an equivalent TF was prepared keeping the electrochemical cell inside an N₂-filled glovebox, whereby the post-CA sample was mounted inside a portable, gas-tight transfer chamber that has previously been validated for the XPS-study of air-sensitive battery materials (see Experimental Section for details).^[35] The survey scan acquired on this air-free transferred sample and displayed in Figure S1 only features peaks assignable to Cu, O, and adventitious carbon, along with a minor Cs contribution arising from the supporting electrolyte used in the electrochemical CO₂-reduction measurement (*vide infra*). Most importantly, the Cu 2p XPS and L₃M_{4,5}M_{4,5} Auger spectra following CA and this air-free transfer (cf. Figs. S2 and 3B, respectively) do not display

any signs of the oxides discussed above, and instead match the spectrum of Cu^0 reported in previous literature.^[21,36,39] To further verify this assignment, Figure 3C displays a comparison between this *post*-CA, air-free transfer spectrum and the one recorded on a sputter-cleaned Cu_{poly} reference sample; chiefly, the good overlay among spectra (only displaying minor background differences that cannot be assigned to remnant oxide) unambiguously confirms the complete reduction of the sample's surface in the course of CO_2 -electroreduction.

Motivated by these results, we proceeded to Ar-sputter this *post*-CA TF as to study the possible presence of Cu-oxides in its sub-surface, which has recently been linked to the distinct product selectivity of oxide (derived) CO_2 -reduction electrocatalysts.^[17-26] The corresponding XPS spectra appear plotted in Figure 5; sputtering for only 1 min led to the complete disappearance of the Cs 3d and O 1s peaks initially present on the as-transferred surface and related to deposits of the electrolyte salt,^[36] while no other changes were observed after an additional 4 min of sputtering. When the cumulative sputtering time reached 15 min, though, the recorded spectrum displayed an additional couple of peaks at ≈ 370 eV that can be assigned to the TF's Ag adhesion interlayer,^[50] indicating sputtering along the complete TF thickness and proving the negligible presence of oxygen within the sample (i.e., below the XPS's detection limit of ≈ 1 at. %). This asseveration is fully consistent with the corresponding Cu $\text{L}_{3\text{M}_{4,5}\text{M}_{4,5}}$ Auger spectra (see inset in Fig. 5), which are identical for all sputtering durations and the as-transferred (i.e., non-sputtered) sample and therefore confirm the TF's complete reduction to Cu^0 along the film's bulk thickness during CO_2 -electroreduction.

Chiefly, these observations were excellently reproduced on a thicker, $\approx 1 \mu\text{m}$ Cu_2O TF, which displayed a CO_2 -reduction product selectivity similar to that of the ≈ 100 nm sample (cf. Fig. S6) and matching properties upon UHV characterization (see XPS spectra in Fig. S7). This lack of

sensitivity of the products' distribution to the thickness of the oxide layer is further proof of the negligible role of this oxide phase on the CO₂-reduction mechanism,^[13] and is consistent with previous online electrochemical^[51] and ¹⁸O secondary ion^[15] mass spectrometry studies that have suggested that the latter reaction is only triggered once the oxide is reduced to Cu⁰.

Figure 5. Depth-profiling X-ray photoelectron spectra of the ≈ 100 nm Cu₂O thin film subjected to 30 minutes of chronoamperometry at -1.0 V_{RHE} in CO₂-saturated 0.05 M Cs₂CO₃, following disassembly of the electrochemical cell in a N₂-filled glovebox and transport to ultra-high vacuum in a gas-tight transfer chamber (cf. ‘After CA, N₂’ sample in Figures 3B and 3C). XP spectra were recorded just after transfer (‘0 min’) or following Ar-sputtering (at $\approx 9.10^{-6}$ mbar and 3 kV) for 1, 5 or 15 min. The inset displays the corresponding Cu L₃M_{4,5}M_{4,5} Auger spectra. Note the presence of Cs and O signals exclusively on the surface of the as-transferred, non-sputtered sample (‘0 min’), as well as the detection of the TF’s Ag adhesion layer after 15 min of sputtering.

On the other hand, as highlighted in Table 1, our observations are in stark disagreement with numerous studies postulating the presence of residual Cu-oxide within the catalyst's (sub-)surface in the course of CO₂-electroreduction.^[9,17-26] While we cannot pinpoint the specific cause(s) that may have led to this inconsistency, the *post-mortem* samples in Refs. 9 and 17 were reportedly exposed to air (and thus oxidized) prior to their characterization. Contrarily, previous *post-mortem* XPS^[21] and EELS^[22,23] measurements seemingly implementing minimized air contact upon sample transfer still reported a partial oxidation of the catalysts following CO₂-electroreduction. Assuming a comparable level of exposure to residual O₂ in those studies^[21-23] and this work, whereby Cu₂O TFs are univocally proven to get reduced to Cu⁰, the partial oxidation of the *post-mortem* samples reported in Refs. 21–23 may be tentatively assigned to their enhanced reactivity^[13,16] with residual O₂. Such a behavior could in terms be caused by the extremely large surface roughness and corresponding abundance of highly reactive, low-coordinated surface sites in those materials (featuring RFs $\approx$ 2- to $\approx$ 6-fold larger than that of the post-CA TF).^[16,18,26] Nevertheless, this relation among surface oxidation and roughness factor does not appear to be univocal; specifically, as showcased in Table 1, samples with a roughness factor as high as $\approx 44 \text{ cm}_{\text{surface}}^2 \cdot \text{cm}_{\text{geom}}^{-2}$ have been reported to be absent of sub-surface oxides following CO₂-electroreduction (see Ref. 24), whereas the latter oxide was detected in the subsurface of catalysts with similar or even lower RFs.^{21,26} Thus, further efforts should be devoted to clarify the effect of other parameters (like the catalyst support²⁵ or the addition of anionic species to the electrolyte²⁴) on the reported presence of these (sub-)surface Cu-oxides, ideally minimizing possible artifacts introduced upon sample transfer by substituting *post-mortem* characterization techniques with *in situ* / *operando* ones.

Table 1. Summary of qualitative literature results (including those derived from this study) regarding the detection of Cu-oxides in the catalyst's (sub)surface in the course of or just after electrochemical CO₂-reduction, as derived from *in situ* or *post-mortem* characterization techniques and specifying whether sample transfer involved contact with air for the latter kind. Note that for all fields the dash symbol ('-') refers to information that was not specified in the cited manuscript, whereas 'NA' stands for 'not applicable' (i.e., as in the case of air contact upon *in situ* characterization), and that for selected electrochemical (EC) protocols and transfer conditions the relevant technique is reported between parenthesis.

Catalyst	EC protocol	Roughness factor [cm _{surface} ² ·cm _{geom} ⁻²]		Characterization technique	Air-contact upon transfer*	(Sub)surf. Cu-oxide†	Ref.
		Before EC	After EC				
Cu ₂ O NPs on C-based GDE	10 min to 2 h @ – 1.9 V vs. Ag/AgCl	2.4	–	<i>Post-mortem</i> , depth-profiling XPS and AES	Yes	Yes	9
1.7 μm thick Cu ₂ O film on Cu	200 s @ – 0.99 V vs. RHE	4.7	–	<i>In.situ</i> Raman spec.	NA	No	10
Polycrystalline Cu w/ surface oxide layer	Potential scan from 0.65 to – 0.3 V vs. RHE	–	–	<i>In situ</i> GI-XRD	NA	No	14
Various Cu ₂ O/Cu nanomaterials	10 s @ – 1.0 mA·cm ⁻² (Raman)	–	–	<i>In situ</i> Raman spec., <i>post-</i> <i>mortem</i> XRD	NA (Raman) Yes (XRD)	No	15
¹⁸ O-enriched Cu ₂ O/Cu nanocubes	10 min to 5 h @ – 1.0 V vs. RHE	22	21	<i>Post-mortem</i> SIMS	Yes	No	16
Cu ₂ O/Cu nanoparticles	5 h @ – 1.6 V vs. RHE	–	–	<i>Post-mortem</i> XPS and XAS	Yes#	Yes	17
Various plasma- treated Cu- electrodes	1 h @ – 0.91 V vs. RHE (EDS)	≤ 90	–	<i>Post-mortem</i> EDS, <i>in situ</i> XAS	Yes (EDS)	Yes	18
Thermally oxidized Cu(111)	NA§	–	–	<i>In situ</i> XPS	NA	Yes	19
Plasma-treated Cu nanocubes	1 h @ – 1.0 V vs. RHE	≤ 36	–	<i>Post-mortem</i> XPS and EDS	No (XPS) Yes (EDS)	Yes	21
Electrochemically oxidized, polycrystalline Cu	<i>E</i> -cycling down to – 0.73 V vs. RHE	–	–	EELS	No	Yes	22
Electrochemically oxidized Cu nanoparticles	55 min @ – 1.15 V vs. RHE	–	–	STEM-EELS	No	Yes	23
Various plasma- treated Cu- electrodes	1 h @ – 1.0 V vs. RHE	≤ 44	–	<i>Post-mortem</i> XPS and EDS	No (XPS) Yes (EDS)	No	24
Electrodeposited Cu-nanocubes	1 h @ – 1.1 V vs. RHE	–	–	<i>Post-mortem</i> XPS, <i>in situ</i> XAS	No (XPS)	Yes/No ^Ω	25
Various plasma- treated Cu- electrodes	1 h @ – 1.0 V vs. RHE	–	≤ 44 ^Φ	<i>Post-mortem</i> XPS,	No (XPS) Yes (EDS)	Yes	26

Cu ₂ O thin films	30 min @ – 1.0 V vs. RHE	≈ 1	≈ 16	Post-mortem, depth-profiling XPS	No	No	This work
------------------------------	--------------------------------	-----	------	--	----	----	--------------

*Specifies whether the sample experienced contact with air upon transfer from the electrochemical test to *post-mortem* characterization (i.e., it does not apply to *in situ* measurements). †Refers to the qualitative observation of copper oxide in the catalyst's (sub)surface upon *post-mortem* or *in situ* characterization. #Unclear whether the XAS-measurements were truly *in situ* or performed just after CO₂-reduction (i.e., *post-mortem*); in the latter case the samples were reportedly dried with an air-gun. §In situ near ambient pressure XPS measurements at a CO₂ (and in some cases H₂O) pressure of 0.7 Torr, but without potential control. ¶Positive detection of (sub)surface oxide reported for nanocubes supported on Cu-foil, whereas no oxide was detected when the support was a carbon paper. ΦSample-dependent values reported after 1 h of CO₂-reduction at –1.0 V vs RHE, whereby the roughness of a sample with ≈ 25 cm_{surf}²·cm_{geom}^{–2} after 1 h reportedly decreased to ≈ 12 cm_{surf}²·cm_{geom}^{–2} after 30 h of reaction.

Conclusions

In summary, when implementing proper means of sample transfer, our XPS results monitoring the Cu Auger spectra of *post-mortem*, low roughness TF electrodes provide clear proof of the complete reduction of the initial Cu₂O surface and bulk in the course of CO₂-reduction. As such, our conclusions agree with those of recent computational^[13] and experimental^[15,16,31] studies by the Ager and Bell groups, and indirectly suggest that the product selectivity of oxide-derived Cu-catalysts is linked to their great roughness and corresponding abundance of ethylene-selective surface domains. Ultimately, our work additionally highlights the importance of careful sample transfer for drawing meaningful conclusions upon *post-mortem* surface characterization using *ex situ* techniques,^[2] as well as the need for a continued development of *operando* characterization tools that can circumvent these limitations.^[52]

Acknowledgments

This work was supported by the Competence Center Energy & Mobility Switzerland (CCEM-CH), Swiss Electric Research, Innosuisse and the Swiss Competence Center for Energy Research Heat & Electricity Storage (SCCER-HaE). The authors are thankful to Mr. Christian Marmy and Mr. Adrian Heinritz for technical support. AAP greatly acknowledges the Danish Agency for Science, Technology and Innovation for financial support through the CITRIS visiting scholarship at University of California, Berkeley, and expresses her gratitude to Prof. Alexis T. Bell, Dr. Peter Lobaccaro and Dr. Ezra L. Clark for sharing their knowledge on CO₂ reduction and the parallel plate electrochemical cell. JH greatly acknowledges the Swiss National Science Foundation for financial support through Ambizione Energy grant PZENP2_173632. TJS thanks Innosuisse and the Swiss Competence Center for Energy Research Heat & Electricity Storage.

References

- [1] D. T. Whipple, P. J. A. Kenis, *J. Phys. Chem. Lett.* **2010**, *1*, 3451–3458.
- [2] J. Herranz, J. Durst, E. Fabbri, A. Patru, X. Cheng, A. A. Permyakova, T. J. Schmidt, *Nano Energy* **2016**, *29*, 4–28.
- [3] S. Verma, B. Kim, H.-R. Jhong, S. Ma, P. J. A. Kenis, *ChemSusChem* **2016**, *9*, 1972–1979.
- [4] J. Durst, A. Rudnev, A. Dutta, Y. Fu, J. Herranz, V. Kaliginedi, A. Kuzume, A. A. Permyakova, Y. Paratcha, P. Broekmann, T. J. Schmidt. *Chimia* **2015**, *69*, 769–776.
- [5] A. Patru, T. Binniger, B. Pribyl, T. J. Schmidt, *J. Electrochem. Soc.* **2019**, *166*, F34–F43.

- [6] K. W. Frese, *J. Electrochem. Soc.* **1991**, *138*, 3338–3344.
- [7] M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, J. C. Flake, *J. Electrochem. Soc.* **2011**, *158*, E45–E49.
- [8] C. W. Li, M. W. Kanan, *J. Am. Chem. Soc.* **2012**, *134*, 7231–7234.
- [9] D. Kim, S. Lee, J. D. Ocon, B. Jeong, J. K. Lee, J. Lee, *Phys. Chem. Chem. Phys.* **2015**, *17*, 824–830.
- [10] D. Ren, Y. Deng, A. D. Handoko, C. S. Chen, S. Malkhandi, B. S. Yeo, *ACS Catal.* **2015**, *5*, 2814–2821.
- [11] N. De Zoubov, C. Vanleughenaghe, M. Pourbaix in *Atlas of Electrochemical Equilibria in Aqueous Solutions* (Ed.: M. Pourbaix), Pergamon Press, Oxford, **1966**, pp. 384–392.
- [12] X. Nie, G. L. Griffin, M. J. Janik, A. Asthagiri, *Catal. Commun.* **2014**, *52*, 88–91.
- [13] A. J. Garza, A. T. Bell, M. Head-Gordon, *J. Phys. Chem. Lett.* **2018**, *9*, 601–606.
- [14] S. B. Scott, T. V. Hogg, A. T. Landers, T. Maagaard, E. Bertheussen, J. C. Lin, R. C. Davis, J. W. Beeman, D. Higgins, W. S. Drisdell, C. Hahn, A. Mehta, B. Seger, T. F. Jaramillo, *ACS Energy Lett.* **2019**, *4*, 803–804.
- [15] L. Mandal, K. R. Yang, M. R. Motapothula, D. Ren, P. Lobaccaro, A. Patra, M. Sherburne, V. S. Batista, B. S. Yeo, J. W. Ager, J. Martin, T. Venkatesan, *ACS Appl. Mater. Interfaces* **2018**, *10*, 8574–8584.
- [16] Y. Lum, J. W. Ager, *Angew. Chem. Int. Ed.* **2018**, *57*, 551–554.

- [17] S. Lee, D. Kim, J. Lee, *Angew. Chem. Int. Ed.* **2015**, *127*, 14914–14918.
- [18] H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser, B. Roldan Cuenya, *Nat. Commun.* **2016**, *7*, 12123.
- [19] M. Favaro, H. Xiao, T. Cheng, W. A. Goddard III, J. Yano, E. J. Crumlin, *Proc. Nat. Acc. Sci.* **2017**, *114*, 6706–6711.
- [20] H. Xiao, W. A. Goddard III, T. Cheng, Y. Liu, *Proc. Nat. Acc. Sci.* **2017**, *114*, 6685–6688.
- [21] D. Gao, I. Zegkinoglou, N. J. Divins, F. Scholten, I. Sinev, P. Grosse, B. Roldan Cuenya, *ACS Nano* **2017**, *11*, 4825–4831.
- [22] A. Eilert, P. Cavalca, F. S. Roberts, J. Osterwalder, C. Liu, M. Favaro, E. J. Crumlin, H. Ogasawara, D. Friebe, L. G. M. Pettersson, A. Nilsson, *J. Phys. Chem. Lett.* **2017**, *8*, 285–290.
- [23] F. Cavalca, R. Ferragut, S. Aghion, A. Eilert, O. Diaz-Morales, C. Liu, A. L. Koh, T. W. Hansen, L. G. M. Pettersson, A. Nilsson, *J. Phys. Chem. C* **2017**, *121*, 25003–25009.
- [24] D. Gao, F. Scholten, B. Roldan Cuenya, *ACS Catal.* **2017**, *7*, 5512–5120.
- [25] P. Grosse, D. Gao, F. Scholten, I. Sinev, H. Mistry, B. Roldan Cuenya, *Angew. Chem. Int. Ed.* **2018**, *57*, 6192–6197.
- [26] D. Gao, I. T. McCrum, S. Deo, Y.-W. Choi, F. Scholten, W. Wan, J. G. Chen, M. J. Janik, B. Roldan Cuenya, *ACS Catal.* **2018**, *8*, 10012–10020.
- [27] Y. Hori, I. Takahashi, O. Koga, N. Hoshi, *J. Phys. Chem. B* **2002**, *106*, 15–17.

- [28] K. J. P. Schouten, Z. Qin, E. Pérez Gallent, M. T. M. Koper, *J. Am. Chem. Soc.* **2012**, *134*, 9864–9867.
- [29] F. S. Roberts, K. P. Kuhl, A. Nilsson, *Angew. Chem. Int. Ed.* **2015**, *54*, 5179–5182.
- [30] R. Kas, R. Kortlever, H. Yilmaz, M. T. M. Koper, G. Mul, *ChemElectroChem* **2015**, *2*, 354–358.
- [31] Y. Ref, B. Yue, P. Lobaccaro, A. T. Bell, J. W. Ager, *J. Phys. Chem. C* **2017**, *121*, 14191–14203.
- [32] A. Rabis, D. Kramer, E. Fabbri, M. Worsdale, R. Kötz, T. J. Schmidt, *J. Phys. Chem. C* **2014**, *118*, 11292–11302.
- [33] K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, *Energy Environ. Sci.* **2012**, *5*, 7050–7059.
- [34] P. Lobaccaro, M. R. Singh, E. L. Clark, Y. Kwon, A. T. Bell, J. W. Ager, *Phys. Chem. Chem. Phys.* **2016**, *18*, 26777–26785.
- [35] G. Ferraresi, C. Villevieille, I. Czekaj, M. Horisberger, P. Novak, M. El Kazzi, *ACS Appl. Mater. Interfaces* **2018**, *10*, 8712–8720.
- [36] W. Kautek, J. G. Gordon II, *J. Electrochem. Soc.* **1990**, *137*, 2672–2677.
- [37] W. G. Pell, A. Zolfaghari, B. E. Conway, *J. Electroanal. Chem.* **2002**, *532*, 13–23.

- [38] N. Danilovic, R. Subbaraman, K.-C. Chang, S. H. Chang, Y. J. Kang, J. Snyder, A. P. Paulikas, D. Strmcnik, Y.-T. Kim, D. Myers, V. R. Stamenkovic, N. M. Markovic, *J. Phys. Chem. Lett.* **2014**, *5*, 2474–2478.
- [39] D. Tahir, S. Tougaard, *J. Phys.: Condens. Matter* **2012**, *24*, 175002.
- [40] M. C. Biesinger, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, *Appl. Surf. Sci.* **2010**, *257*, 887–898.
- [41] Y.-G. Kim, J. H. Baricuatro, A. Javier, J. M. Gregoir, M. P. Soriaga, *Langmuir* **2014**, *30*, 15053–15056.
- [42] M. Rahaman, A. Dutta, A. Zanetti, P. Broekmann, *ACS Catal.* **2017**, *7*, 7946–7956.
- [43] C. M. Gunathunge, X. Li, J. Li, V. J. Ovalle, M. M. Waegle, *J. Phys. Chem. C* **2017**, *121*, 12337–12344.
- [44] M. E. Straumanis, L. S. Yu, *Acta Cryst.* **1969**, *A25*, 676–682.
- [45] M. Heinemann, B. Eifert, C. Heiliger *Phys. Rev. B* **2013**, *87*, 115111.
- [46] D. Reyter, M. Odziemkowski, D. Bélanger, L. Roué, *J. Electrochem. Soc.* **2007**, *154*, K36–K44.
- [47] R. Reske, H. Mistry, F. Behafarid, B. Roldan-Cuenya, P. Strasser, *J. Am. Chem. Soc.* **2014**, *136*, 6978–6986.
- [48] A. Loiudice, P. Lobaccaro, E. A. Kamali, T. Thao, B. H. Huang, J. W. Ager, R. Buonsanti, *Angew. Chem. Int. Ed.* **2016**, *55*, 5789–5792.

- [49] J. Huang, N. Hörmann, E. Oveisi, A. Loiudice, G. L. de Gregorio, O. Andreussi, N. Marzari, R. Buonsanti, *Nat. Commun.* **2018**, *9*, 3117.
- [50] P. Prieto, V. Nistor, K. Nouneh, M. Oyama, M. Abd-Lefdil, R. Díaz, *Appl. Surf. Sci.* **2012**, *258*, 8807–8813.
- [51] R. Kas, R. Kortlever, A. Milbrat, M. T. M. Koper, G. Mul, J. Baltrusaitis, *Phys. Chem. Chem. Phys.* **2014**, *16*, 12194–12201.
- [52] M. Povia, J. Herranz, T. Binniger, M. Nachtegaal, A. Diaz, J. Kohlbecher, D. Abbott, B.-J. Kim, T. J. Schmidt, *ACS Catal.* **2018**, *8*, 7000–7015.

Table of Contents

XPS of *post-mortem* Cu₂O thin film electrodes characterized following an air-free transfer to ultra-high vacuum unveils their complete transformation into Cu⁰ in the course of CO₂-electroreduction.

Keywords

Catalysis, co-electrolysis, electrochemistry, energy conversion, photoelectron spectroscopy.