**In-situ Studies of Copper-based CO₂ Reduction Electrocatalysts by Scanning Transmission Soft X-ray Microscopy**

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**Abstract**

A micro-fluidic enabled electrochemical device has been developed to investigate electrochemically active materials under reaction conditions using *in-situ* scanning transmission soft X-ray microscopy (STXM). *In-situ* STXM measurements at the Cu 2p edge were conducted on electro-deposited Cu catalysts under electrochemical CO₂ reduction (CO₂R) conditions. The study provides detailed, quantitative results about the changes in the morphology and chemical structure (oxidation state) of the catalyst particles as a function of applied electrode potentials. The initially electrochemically deposited Cu particles contain both Cu(0) and Cu(I). As an increasingly cathodic potential is applied, the Cu(I) species gradually converted to Cu(0) over the potential range of +0.4 to 0 V versus the reversible hydrogen electrode (V_RHE). During this process, Cu(I) particles of various sizes are converted to metallic Cu at different reaction rates and at slightly different electrode potentials, indicating a degree of heterogeneity in the electrochemical response of discrete particles. At CO₂R relevant potentials, only metallic Cu is observed, and the morphology of the particles is fairly stable within the spatial resolution limits of STXM (~ 40 nm). We also prepared a working electrode with relatively thick Cu-based electro-deposits. The spatially resolved chemical analysis by STXM identified that Cu-oxide species can persist under CO₂R conditions, but only when the catalyst particles are electronically isolated from the working electrode and therefore are catalytically irrelevant. Thus, *in-situ* STXM is presented as a technique to gain advanced morphological and spatially-resolved chemical structure insight into electrochemically active materials, which was used to provide improved understanding regarding Cu electrodes under CO₂ reaction conditions.

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1. Introduction
Carbon dioxide electroreduction (CO$_2$R) is a promising route to generate valuable fuels and chemical feedstocks through the electrochemical conversion of CO$_2$ into hydrocarbon, alcohol, and carbonyl products.[1-3] With electricity generated by renewable energy resources such as wind and solar, electrochemical CO$_2$ reduction has the potential to become a sustainable approach to produce carbon-based chemicals and fuels, which could replace conventional petrochemical processes, thereby reducing greenhouse gas emissions and helping to protect the global environment. Among the different catalysts studied, copper (Cu) is known as the only material that can uniquely convert CO$_2$ into valuable multi-carbon products (C$_{2+}$) in appreciable quantities.[4-6] Unfortunately, despite much progress in recent years, the poor conversion efficiency, limited control of product distribution, and low stability of Cu-based electrocatalysts limit large-scale application of CO$_2$R.[7-8]

Improved understanding of Cu catalysts during electrochemical CO$_2$R is crucial for the development of high-performance, selective and practical electrocatalysts, yet there remains debate over the nature of active site structure(s) and their evolution under reaction conditions. For example, the presence of oxidized Cu (either Cu(I) and Cu(II) species) or subsurface oxygen during electro-reduction has been suggested to improve CO$_2$R activity and steer the selectivity towards C$_2$, products such as ethanol and ethene.[9-11] However, other studies have refuted the presence of non-zero-valent Cu species under the electrochemically reducing conditions required for the reaction.[12-14] Morphological changes of Cu electrocatalysts during the CO$_2$R process have also been demonstrated, leading to rapid restructuring of catalytic structures which correlate with observed changes in activity and selectivity.[15,16] Overall, the morphology and chemical structures present in Cu catalysts change as a direct function of the local reaction environment and applied potential, which draws into question the suitability of using ex-situ characterization techniques to study Cu catalyzed CO$_2$R processes. This has motivated the development and application of in-situ/operando spectroscopy, microscopy and spectro-microscopy techniques to provide real-time and same-position characterization of working catalysts under electrochemical reaction conditions.[17-18]

In this work, we have used in-situ soft X-ray scanning transmission X-ray microscopy (STXM) [19-28] to characterize Cu electrocatalysts in a micro-chip electrochemical cell designed to achieve electrolyte flow under applied electrochemical potentials which closely resemble the conditions experienced by Cu particles in a laboratory-scale CO$_2$R reactor. STXM is a synchrotron-based spectro-microscopic technique that can simultaneously provide microscopic imaging of catalyst morphologies alongside spatially resolved (sub-50 nm spatial resolution) [29, 30] spectroscopic characterization through near edge X-ray
absorption fine structure (NEXAFS) spectroscopy [29] to enable quantitative, chemically selective imaging. This can overcome some of the limitations of techniques such as in-situ diffraction [31] or in-situ X-ray absorption spectroscopy [32-34] measurements that provide only bulk-averaged characterization and no morphological insight, or in-situ electron microscopy [35, 36] that only provides region-specific morphological characterization and no insight into local chemical structures owing to the difficulty of performing high-resolution electron energy loss spectroscopy in the presence of a liquid electrolyte. By utilizing a microfluidic-based flow electrochemical micro-chip reactor, in-situ STXM was conducted to characterize the morphology and chemical structure(s) present in electrodeposited Cu particles as catalysts under electrochemical CO2 reduction conditions as a function of time and electrode potential. The micro-fluidic based electrochemical device enabled controllable electrolyte flow and could achieve an aqueous electrolyte thickness < 2 μm [27, 28] to enable soft X-ray transmission-mode measurements. In-situ STXM measurements provided a detailed quantitative evaluation of the particle evolution as a function of local chemical environments and applied potential. In this study the electrodeposited Cu particles are initially comprised largely of Cu(I) species that convert to metallic Cu (denoted as Cu metal or Cu(0)) at potentials ~0.2 V more positive than the onset of CO2R. Significant changes in the particle morphology accompany the reduction of Cu-oxide species into metallic Cu. We also identify conditions where Cu-oxide species persist under reducing electrochemical CO2R conditions and find that it is due to electronic isolation of the Cu particles from the working electrode when thick electro-deposits are used. However, we find no evidence of kinetically or diffusion trapped Cu-oxide species in catalytically relevant particles with electronic connectivity to the electrode. Overall, in-situ STXM has enabled spectro-microscopic insight into the behavior of Cu catalysts under CO2R conditions. The techniques reported here can be readily translated to other electrochemical materials/processes to gain insight into the morphology and spatially resolved chemical structures present in electrochemically active materials.

2. Results
2.1 Electrochemical CO2 reduction evaluation.
The catalytic performance of electrodeposited Cu nanoparticles for CO2 reduction in CO2-saturated 0.1 M KHCO3 was evaluated in a custom-built 2-compartment electrolyte membrane separated cell that has been reported previously [37, 38] (Fig. S-1a), with results displayed in Fig. 1. Details for catalyst electrode synthesis, experimental details, catalytic efficiency and product distribution measurements are presented in Section 6.1. At an electrode potential of -0.4 V_RHE, the deposited Cu sample showed a current density of -0.18 mA/cm2 (Fig. 1a) with the majority of current going towards the production of H2 with a Faradaic efficiency of 86% (Fig. 1b). Small amounts of other products (CO, hydrocarbons and
alcohols) were detected, suggesting that CO$_2$R reactions have started to occur but with slow kinetics at this electrode potential. When the potential reached -0.6 V$_{RHE}$, the overall current density increased to -0.83 mA/cm$^2$ and there was a larger amount of CO$_2$R products (29% Faradaic efficiency) compared with at -0.4 V$_{RHE}$. At -0.8 V$_{RHE}$, the formation of CO$_2$R products dominated and the Faradaic efficiency for H$_2$ production was only 25%. This shows that the CO$_2$R reactions started to increase the overall reaction rate from -0.6 V$_{RHE}$ and became the main electrochemical reactions at more negative potentials. In general, electrochemical CO$_2$R on Cu does not occur at appreciable rates at potentials more positive than ca. -0.65 V$_{RHE}$.[37] In this case, it is important to note that the Cu particles were electro-deposited on Au, a well-known CO$_2$ to CO catalyst, to mimic the electrode configuration used for in-situ STXM measurements. It is the presence of Au that likely underlies the CO$_2$R products formed, as Au can produce CO electrochemically that can either be released as a product or subsequently reduced to alcohols and carbonyls by Cu at potentials as positive as -0.4 V$_{RHE}$[39] via a tandem catalytic reaction scheme.[40, 41]

![Figure 1](image.png)

**Figure 1.** Evaluation of activity and selectivity for electrochemical CO$_2$ reduction by electrodeposited Cu catalysts in CO$_2$-saturated 0.1 M KHCO$_3$ in a custom-built 2-compartment membrane separated cell. (a) Overall geometric current density. (b) Faradaic efficiency towards various products under -0.4, -0.6 and -0.8 V$_{RHE}$.

### 2.2 In-situ STXM experiments in micro-fluidic electrochemical in-situ device

All in-situ STXM experiments were conducted using a novel micro-fluidic electrochemical in-situ device, which differs in several significant ways from existing commercial electrochemical liquid devices. ([Fig. 2](image2.png), the details are discussed in Section 6.2) [27, 28] This in-situ micro-fluidic device is a major improvement compared to our previously reported 3D-printed device,[23]. It is more reliable with respect to electrolyte handling and can provide an electrolyte layer thickness of ~1.6 µm with a continuous flow of 25 µL/h, which provides good ionic conductivity while being thin enough for STXM studies at the Cu 2p edge ([Section S-5, Fig. S-5](image3.png)). The two inlet and two outlet flow channels facilitate changing the electrolyte in
minutes (rather than hours when using single inlet/outlets) and are very useful for reducing the inner pressure and removing air or gaseous product bubbles. The light weight of the device, due to the fabrication of components using plastic and polymers rather than steel, improves the stability and reduces vibration in STXMs when the sample is scanned. The in-situ micro-chip design includes a working electrode (WE), reference electrode (RE) and counter electrode (CE) that are all observable and measurable within the silicon nitride window area (Fig. 2b, 2c), as opposed to many in situ electrochemical micro-chip design that only provide visibility of the working electrode. Imaging all three electrodes is useful for being able to track unexpected electrochemical phenomena and to gain a holistic picture of all electrochemical processes occurring within the system. Fig. 2d is a picture of the device inside the ambient STXM microscope at the Canadian Light Source (CLS) spectromicroscopy beamline, 10ID-1.

To ensure the local chemical environment present at the surface of the working electrode in our in-situ device closely mimics the conditions at the working electrode of the 2-compartment membrane separated cell used for CO₂R activity/selectivity evaluation, cyclic voltammetry (CV) of electrodeposited Cu particles in the two-compartment cell was collected and compared with the CV of electrodeposited Cu (prepared using the same methods) from the in-situ device (Fig. S-1). Qualitatively, the CV behavior was the same for the two cells, indicating a similar electrochemical reaction environment. Quantitatively the currents from the micro-chip electrode cell were several orders of magnitude lower, which is due to the reduced dimensions (geometric electrode area of ~2200 µm² in the in-situ cell versus 5.7 cm² in the reactor). Ultimately, the measurements reported here demonstrate that the electro-deposited Cu catalysts have a very similar electrochemical response and thus similar local reaction environments in our in-situ STXM micro-chip reactor as in the two compartment cell used for CO₂R activity/selectivity evaluation. This ensures that the morphological changes and chemical states (oxidation states) observed and mapped by STXM spectro-microscopy are catalytically relevant.
Figure 2 Microfluidic-based flow electrochemical device for in-situ STXM experiments. Schematics describing (a) in-situ device consisting of 3 parts: a machined printed circuit board (PCB), a polydimethylsiloxane (PDMS)/glass microfluidic cell equipped with the electrochemical in-situ chips (PDMS cell) and a poly(methyl methacrylate) backplate (PMMA plate) (b) in-situ chips consisting of 2 parts: base chip E containing 3 micro-Au-electrodes and spacer chip F with a pre-deposited 1 µm spacer defining the height of the electrolyte flow channel within the micro-chip setup. (c) 3 micro-Au-electrodes region on base chip E. The Si₃N₄ window area is 240 µm wide and 100 µm high. The thickness of the Si₃N₄ windows are 100 nm (base chip E) and 50 nm (spacer chip F). The areas used for STXM studies (dark circles on working and counter electrodes) are 20 µm diameter and have a coating consisting of 5 nm Cr and 15 nm Au. (d) Photo of the device inside the CLS ambient STXM.

2.3 In-situ STXM of electrodeposited Cu particles

Cu particles were electrodeposited from a 5 mM CuSO₄/KCl solution onto the Au working electrode of
the custom-designed *in-situ* STXM device using multiple CV scans as described in section 6.4. The deposition of Cu-based particles was confirmed by measuring STXM transmission images at 933.5 eV, the peak Cu 2p X-ray absorption energy for both Cu(I) and Cu(0) species. As shown in Fig. 3a, the electrodeposited Cu typically consisted of particles ranging in size from tens of nm to ~0.8 µm, distributed across the Au-coated working electrode. After Cu particle deposition, a four-energy (4-E) Cu 2p STXM stack was recorded at a region showing well-defined Cu particles (see inset of Fig. 3a) to identify the composition of the electrodeposited Cu particles. This STXM stack measurement probes the catalyst at four specific photon energies which were carefully chosen to directly identify and map the oxidation states present in the Cu-based particles while enabling significantly accelerated measurements versus recording a stack measurement at closely spaced energy values across the Cu 2p edge. The stack was fit using the reference spectra of Cu(0) and Cu(I) (Fig. 3b) to generate component maps for each species (Fig. 3c, Fig. 3d, Fig. S-7). The component maps were then combined, using rescaling within each color, to generate color-coded component maps such as the one shown in Fig. 3e. The intensity scales in Fig. 3c and 3d indicate the thickness in nm of the indicated species. To verify the analyses, spectra of the Cu(0) and Cu(I) regions were extracted and compared with reference spectra (Fig. S-8). The extracted spectra from Cu(0) and Cu(I) regions correctly showed that each species was the dominant component.

**Figure 3. Illustration of STXM investigation of in-situ electrodeposited copper particles.** (a) transmission image at 933.5 eV. (b) Cu 2p X-ray absorption spectra of Cu(0) (Cu metal) and Cu(I) from Cu₂O. Quantitative component maps of (c) Cu(0), and (d) Cu(I), derived from fitting reference spectra to a 4-E stack. (e) Color coded composite (rescaled) of the Cu(0) (red) and Cu(I) (green) maps.
3.3 Quantitative in-situ STXM on Cu particle during CO₂R

After electrodeposition of the Cu particles, the electrolyte was changed from 5 mM CuSO₄/KCl to CO₂ saturated 0.1M KHCO₃ (Section 6.5). Chronoamperometry holds at various potentials (+0.4, +0.2, +0.1, 0, -0.1, -0.2, -0.4, -0.6 Vₚ) were applied in sequence, with a 30 s hold at +0.4 Vₚ applied between each new electrode potential to ensure the catalyst was in the same starting state. Fig. 4a plots the current density obtained from chronoamperometry as a function of applied potential during the in-situ STXM measurements. Fig. 4b depicts the electrode potential profile used throughout the process. At each applied potential, two STXM images (image 1 and 2 at 933.5 eV, ~3 mins for each), a fast 4-energy STXM stack scan (4-E stack, 920, 933.5, 937 and 960 eV, ~7 mins) and a complete Cu 2p STXM stack scan (full stack, 53 energies from 920 to 965 eV, ~30 min) were conducted. Collecting two STXM images, one at the start of the measurements and one at the end, enabled us to track the morphological changes that occurred over the course of the measurements. The results from the 4-E stack and the full stack showed the evolution of the morphology and oxidation state of the Cu particles on different time scales, with the 4-E stack covering the first ~3-10 min of the measurements and the full stack covering ~10-40 min after the specified electrode potential was applied.

Figure 4 in-situ STXM studies of Cu particles as a function of potential. (a) Average current at various potentials during chronoamperometric measurements in the in situ device. (b) Illustration diagram to show the STXM measurements at each applied potential.

Figure 5 presents the results collected following this protocol on the Cu particles under CO₂R conditions, including STXM images 1 and 2 alongside colour-coded composite maps of the Cu(0) and Cu(I) species obtained from analysis of the 4-E and the full stacks at potentials ranging from +0.4 to -0.6Vₚ. The complete STXM results are presented in Section S-8, Fig. S-9. The morphology and oxidation states of the Cu particles were observed during different time periods (0-3, 3-10, 10-40, 40-43 min) under various potentials. From +0.4 to +0.2 Vₚ, the Cu(I) particles reduced in size by an extent proportional to their original size. It is easiest to observe the changes of large Cu(I) particles in region A1 (outlined by a blue
square on the 4-E color coded map at +0.4 \( V_{\text{RHE}} \)). The particles in this region were inter-connected at +0.4 \( V_{\text{RHE}} \), but at +0.2 \( V_{\text{RHE}} \) became smaller in size and more discrete from the Cu agglomerates. For the very small Cu(I) particles outside region A1, it was hard to observe size reduction due to the limited spatial resolution. Furthermore, no apparent particle size reduction occurred at the Cu(0) particles. The structural shrinking of Cu(I) particles has been similarly reported by other researchers,[42] most likely arising due to the structural contraction from removal of the oxygen atoms in Cu-oxide. Moreover, from +0.4 to +0.2 \( V_{\text{RHE}} \), the amount of Cu(I) present in the particles was reduced to a certain extent. After applying a more reducing potential of +0.1 \( V_{\text{RHE}} \), conversion of most of the Cu(I) to metallic Cu(0) was observed, with Cu(I) species found to reduce over a timescale of minutes, as seen by comparing the slightly higher portion of Cu(I) particles present in the 4-E stack (collected over the first 3-10min of measurement) versus the full stack measurement (collected over the first 10-40min of measurement). These results show that not all of the Cu(I) species convert to metallic Cu at the same time, despite the fact that all particles are nominally experiencing the same applied electrode potential. The Cu(I) species that remained at +0.1 \( V_{\text{RHE}} \) continued to reduce in size when the electrode potential was reduced to 0 \( V_{\text{RHE}} \). No Cu-oxide species were observed after several minutes at this electrode potential. Ultimately, these results demonstrate that the reduction of Cu(I) happens at various times and electrode potentials for different particles, but at electrode potentials from 0 to -0.6 \( V_{\text{RHE}} \), only Cu(0) species remain. In addition, after complete reduction to Cu(0) species, the Cu particles largely maintained the same micro-structure during ~43 mins of CA at -0.6 \( V_{\text{RHE}} \) under CO\(_2\)R conditions.
Due to the use of OD1 spectra (Fig. 3b), the thickness of the Cu(0) and Cu(I) particles was determined and could be used along with the lateral area to calculate the volume of the Cu(0) and Cu(I) species. Section S-9, Fig. S-10 shows an example of the calculation of the volume of Cu(0) and Cu(I) at +0.4 V_RHE from the full stack results. The calculated volumes at each potential are shown in Table S-2. The volume of Cu species under various potentials from +0.4 to -0.6 V_RHE were calculated by the same method, with results shown in Table S-3. The volume ratios of Cu(0) and Cu(I) at different time periods after specific potentials were applied are displayed in Fig. 6a. The Cu(0) particles maintain the same oxidation state at -0.2, -0.4 and -0.6 V_RHE (Fig. 5, Fig. S-9), and the volume ratios were calculated from the full stack (10-40 min) at these three electrode potential values. At +0.4 V_RHE, the Cu particles were relatively stable, with a composition of 43(±4)% Cu(0) to 57(±6)% Cu(I) during the first 3-10 min of measurement, and 40(±4)% Cu(0) to 60(±6)% Cu(I) during the first 10-40 min of measurement. When the potential was reduced from +0.4 to 0 V_RHE, the Cu(I) fraction gradually decreased to < 1%. At all potentials more negative than 0 V_RHE, the Cu particles consisted of pure Cu(0) within the measurement precision (>99% Cu(0)).
Figure 6. Quantitative analysis of composition from Cu 2p spectroscopy. (a) Percentage volume composition of Cu(I) and Cu(0). (b) Average spectra of the particles from the 53-energy full stacks at various potentials.

The calculated volumes presented in Fig. 6a are consistent with the STXM component thickness maps shown in Fig. 5 and Fig. S-9. The volumes and volume ratios of Cu(0) and Cu(I) quantitatively show the transition from Cu(I) to Cu(0) during the electrochemical process. Moreover, this can also be straightforwardly confirmed by examining the average spectrum of all the Cu particles at each of the potentials, as shown in Fig. 6b. These spectra show that, over the potential sequence, and particularly between +0.2 and 0 V$_{\text{RHE}}$, the particles change from primarily Cu(I) to completely metallic Cu(0).

3. Discussion

Our in-situ STXM results show that the initially formed, mixed oxidation state Cu particles are converted to exclusively metallic Cu(0) between +0.4 and 0 V$_{\text{RHE}}$ — electrode potentials that are several hundred millivolts more positive than where the CO$_2$R reaction commences. During this reduction process, changes of morphology and oxidation states of the Cu particles were observed during different time periods (0-3, 3-10, 10-40, 40-43 min). Our results show that conversion of some portions of the Cu(I) to Cu(0) is a relatively slow process, continuously occurring over the time period of a few minutes to tens of minutes as the chronoamperometric electrode potential holds are applied. At each potential between +0.4 and 0 V$_{\text{RHE}}$, the Cu(I) particles gradually reduced in size and converted to Cu(0) particles. Moreover, some of the Cu(I) particles completely disappeared during this process rather than converting to metallic Cu, showing there are other reactions in addition to Cu(I)/Cu(0) conversion (see region A1 in Fig. 5).
Furthermore, some predominantly Cu(I) particles reduced to metallic Cu at different rates at the same electrode potential or did not reduce fully until more negative electrode potentials were applied (Fig. 5), suggesting each Cu particle can have significantly different electrochemical responses even under the same applied reaction conditions. These observations show complicated conditions that can be encountered when characterizing Cu-based CO₂R catalysts. Others studies have characterized the Cu materials during the CO₂R process using different in-situ spectroscopic techniques, and found results similar to Fig. 6b, whereby Cu(I) decreases and Cu(0) increases as the potential is decreased.[4, 42] However, the use spectro-microscopy in this study gave quantitative oxidation state analysis and mapping at a sub-50 nm spatial scale, thereby probing the process of Cu(0)/Cu(I) conversion and CO₂R with both morphological and chemical information.

At potentials lower than -0.4 V\textsubscript{RHE} where CO₂R occurs, only Cu(0) species were observed, which we identify as the active site for CO₂R. The Cu(0) particles were stable during the CO₂R reactions with no detectible changes in oxidation state and morphology of particles within the spectral sensitivity and spatial resolution of STXM (~40 nm). According to the calculated Cu compositions (Fig. 6a) the particles are >99% Cu(0) at electrode potentials below 0 V\textsubscript{RHE}. This strongly supports the viewpoint that there are no significant amounts of non-zero-valent Cu species under the electrochemical reducing conditions for CO₂R reaction.[12-14, 42] The results and capabilities of the in-situ STXM technique brought us to question the assertion across the literature that non-zero-valent Cu species can persist under CO₂R conditions and impact the catalytic processes.[12-14] While every CO₂R catalyst, electrode and reactor leads to different local chemical reactive environments, we aimed to probe the conditions upon which Cu-oxide species may exist under the CO₂R conditions employed in our in-situ setup. To accomplish this, in our early in-situ studies, [27] we prepared a working electrode where we did not limit the amount of Cu that was electro-deposited, leading to the formation of micrometer scale deposits extending off the surface of the working electrode that may more closely mimic the thicker catalyst layers used in CO₂R flow cells or membrane electrode assemblies. A typical STXM image of this electrode is shown in Fig. 7a. Upon application of potentials of +1.3 and +0.7 V\textsubscript{RHE}, the system consisted of a mixture of Cu(0), Cu(I) and Cu(II) species, as expected for Cu-based particles under these electrochemical potentials.[43]

Interestingly, after applying a negative electrode potential of -0.5 V\textsubscript{RHE}, a CO₂R relevant electrode potential, a significant portion of Cu(I) species remained in the electrode structure. More details of these measurements are provided elsewhere.[27] Under these electrochemically reducing conditions the Cu-oxide species persisted, particularly at locations that extended away from the Au-based working electrode. These regions of the catalyst layer remained unresponsive to changes in electrode potential. In contrast,
Cu particles in close proximity to the underlying Au-based working electrode were found to interchange between the metallic Cu(0) and Cu-oxide states as a function of electrode potentials that were more negative and more positive than the reversible potential of the Cu(0)/Cu(I) redox pair, respectively. This persistence of Cu-oxide species at potentials as low as -0.5 V\textsubscript{RHE} contrasts the results shown in Fig. 3, whereby all Cu species were in metallic form at potentials more negative than 0 V\textsubscript{RHE}. This observation, combined with the lack of electrochemical response observed for the thick catalyst layer regions, led us to conclude that the Cu-oxide species under CO\textsubscript{2}R conditions persist because they are electronically isolated from the electrode and therefore have no relevance on electro-catalytic performance.

![In-situ STXM to show the electronic isolated Cu materials](image)

**Figure 7. In-situ STXM to show the electronic isolated Cu materials.** (a) STXM image (935 eV) for the electrodeposited Cu materials on the whole WE. (b-d) Cu oxidation state maps of Cu(0) (red), Cu(I) (green) and Cu(II) (blue) at +1.3, +0.7 and -0.5 V\textsubscript{RHE}. More details are in [27].

The results presented in this work exemplify one of the significant advantages of in-situ STXM over bulk averaged measurement techniques (such as non spatially resolved X-ray absorption spectroscopy) that have shown the presence of oxidized Cu species under CO\textsubscript{2}R conditions,[13,14] but cannot provide spatial distinction between regions containing metallic Cu and/or Cu-oxide to validate whether the Cu is electronically active or electronically isolated. The question then arises if small amounts of Cu-oxide can persist under electrochemical CO\textsubscript{2}R conditions by being either kinetically or diffusion trapped within the particles. We believe Cu oxides cannot persist if they are electronically active, since other in-situ microscopic techniques, such as (scanning) transmission electron microscope (TEM or STEM) [15, 16, 44] have shown that the nanoscale morphology Cu-based particles can rapidly evolve under CO\textsubscript{2}R conditions, rendering it very difficult for subsurface Cu-oxide species to remain protected/entrapped at conditions
where, thermodynamically, they are unlikely to persist. However, based on the limitation in spatial resolution (sub-50 nm) of *in-situ* STXM used in this work, it is difficult to effectively monitor the nanoscale re-construction and evolution of Cu particles during CO2R reactions, a key limitation of current STXM capabilities. This has motivated us to pursue improving the spatial resolution of *in-situ* soft X-ray spectromicroscopy by applying spectro-ptychography which can provide similar chemical mapping to STXM but ~3 times better spatial resolution. In our recent *in-situ* spectro-ptychography study we tracked chemical changes and the morphological evolution of a single Cu catalyst particle under CO2R conditions, demonstrating the ability to significantly improve upon the spatial resolution limits of STXM and advanced the technique even further beyond the state-of-the-art measurements reported in the present work.

4. Conclusions

*In-situ* STXM measurements on electrodeposited Cu particles provided detailed, quantitative insight into the morphology and spatially resolved chemical structures present in these catalysts under electrochemical CO2R conditions. At electrode potentials from +0.4 to 0 V_RHE, predominantly Cu(I) particles converted to metallic Cu. Differences were observed in the electrode potential and/or the rate (time) it took for the particles to become metallic, suggesting that discrete Cu particles have a high degree of heterogeneity in terms of their electrochemical response. However, at CO2R relevant potentials more negative than 0 V_RHE, all of the particles were observed to completely reduce into metallic Cu within the experimental precision of the measurements (>99%) and minimal particle reconstructions were observed within the spatial resolution capabilities (~40 nm) of the technique. By preparing electrodes with relatively thicker Cu-based electro-deposited catalyst layers, we show that a significant portion of the Cu-species can remain in oxidized form at potentials as low as -0.5 V_RHE. These Cu-oxide regions in the catalyst layer were found to remain unresponsive to electrode potential, indicating that they were electronically isolated from the underlying working electrode substrate. Thus, we highlight an advantage of *in-situ* STXM over bulk-averaged *in-situ* measurement techniques in that it can provide spatial and spectroscopic distinction between particles that are electronically connected to the electrode and those that are isolated, rendering them electro-catalytically irrelevant. In this sense, *in-situ* STXM, enabled by our custom designed micro-fluidic electrochemical device, provides a means for achieving advanced understanding of the morphology and spatially resolved chemical structures present under CO2R electrochemical conditions. Our results identify metallic Cu as the active species. *In-situ* STXM is suitable for electrocatalysis and energy storage (battery) research. The spatial resolution and other capabilities of the technique can be further improved through technological innovations, such as spectro-ptychography and more rapid data acquisition to better follow electrochemically induced changes.
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6. Methods
6.1 Catalysis performance characterization.
The activity and selectivity of the Cu particles used in this work towards electrochemical CO$_2$R was tested. Cu particle coated working electrodes were prepared by electrodepositing a solution of 5mM CuSO$_4$ and 5mM KCl on an Au coated graphite foil by running three cycles of cyclic voltammetry (CV) from 0 V to +0.4 V versus reversible hydrogen electrode (VRHE) with a scan rate of 20 mV/s. This is identical to the process used to prepare Cu catalysts in the in-situ STXM cell. The electrodeposited Cu electrode was used as the working electrode for electrochemical CO$_2$ reduction and tested in a custom-built 2-compartment electrolyte membrane separated cell that has been reported previously.[37, 38] (Fig. S-1a) The geometric area of the working electrode was 5.7 cm$^2$. The electrolyte compartments of the working and counter electrode were filled with CO$_2$ saturated 0.1M KHCO$_3$ (5 mL). CO$_2$ was flowed continuously through the catholyte and anolyte chambers at 20 sccm throughout the course of the experiment. A Pt foil was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The Ag/AgCl reference electrode was calibrated versus a home-made reversible hydrogen electrode (RHE), and the reported potentials are versus RHE. The catholyte and anolyte chambers were separated by an ion exchange membrane (Selemion AMV, AGC Inc). Catalysts were tested by chronoamperometric measurements at various electrochemical potentials, -0.2, -0.4, -0.6 - 0.8V$_{\text{RHE}}$. The effluent gas from the catholyte compartment was fed to a gas chromatograph (GC) and the collected electrolyte was tested using nuclear magnetic resonance (NMR) for liquid product identification and quantitation to determine Faradaic efficiencies. CV was conducted to check the potentials of Cu oxidation and reduction peaks in CO$_2$ saturated 0.1M KHCO$_3$ in the 2-compartment membrane cell. (Fig. S-1a).
6.2 *In-situ* microfluidic-based electrochemical device.

**Figure 1** presents the microfluidic-based flow electrochemical device used for *in-situ* flow electrochemical STXM experiments. The *in-situ* device consists of a machined printed circuit board (PCB), a polydimethylsiloxane (PDMS)/glass cell equipped with the electrochemical *in-situ* chips (PDMS cell) and a poly(methyl methacrylate) (PMMA) backplate (PMMA plate) ([Fig. 2a](#)). The microfluidic PDMS cell contains four flow tubes and micro-fluidic channels shown as dotted lines on PDMS cell, which serve as two inlets and two outlets to connect to the assembled *in-situ* micro-chip reactor ([Fig. 2b](#), Norcada Inc, Edmonton, Canada, [https://www.norcada.com](https://www.norcada.com)). The flow tubes can be connected to one or more fluid circulation devices (we use syringe pumps, but pressure pumps could also be used) to establish a stable flow of one or more electrolytic fluids to the *in-situ* chips. Electrochemical reactions can then be performed by applying suitable potentials to the 3 electrodes on base chip E ([Fig. 2c](#)), which are connected to a potentiostat through the PCB traces and a 4-pin connector on the PC board. Spacer chip F ([Fig. 2b](#)) has a pre-deposited 1 µm spacer defining the height of the electrolyte flow channel within the micro-chip setup. The working electrode, counter electrode and reference electrodes on base chip E are all Au ([Fig. 2c](#)). The darker circles on the working electrode and counter electrode are regions that have been thinned out to reduce X-ray absorption arising from the electrode thickness. The Au reference electrode acts as a pseudo reference electrode, such that all potentials measured are V versus the Au pseudo-reference (V\text{Au}). The open circuit potential (OCP) was stable (~ -0.045 ± 0.01 V\text{Au}) in CO₂ saturated 0.1M KHCO₃ with electrodeposited Cu on the Au working electrode ([Fig. S-2d](#)). External CV measurements conducted in a 2-compartment cell using a calibrated Ag/AgCl electrode ([Fig. S-1e](#)) enabled us to convert from potentials measured relative to the Au pseudo reference electrode to V\text{RHE} using the well-defined Cu redox peaks. The calibration yielded a value of: V\text{RHE} = V\text{Au} + 0.40. All potentials reported in this work are relative to RHE, unless stated otherwise.

When the *in-situ* device is assembled, the PDMS/glass cell is kept in place in the machined PCB frame by a PMMA plate. Electrical connections between the on-chip electrodes and Cu traces on the PC board are made using Cu clips soldered to the PCB traces. For the experiments, the *in-situ* microfluidic-based flow electro-chemical device is connected to a potentiostat ([Emstat4](#), PalmSens) or Ivium PocketStat, [https://www.ivium.com/instruments/](https://www.ivium.com/instruments/) to control potential and monitor current while one or more of the fluid lines is connected to a syringe pump (New Era, [https://www.syringepump.com/](https://www.syringepump.com/)) to establish a stable electrolyte flow rate, typically 10 – 50 µL/hour.

6.3 *In-situ* device setup and mounting in STXM.
First, the electrolytes used in *in-situ* experiments are prepared and loaded into 1 mL syringes. Bubbles are removed by pushing/withdrawing the syringe. The syringe with the electrolyte is connected to the *in-situ* device using Tefzel tubes (Idex, www.idex-hs.com) with inner diameter of 0.040” and outer diameter of 1/16”) [NB improved performance was found after these experiments by using a narrower 0.010” ID tubing]. The syringe plunger is pushed manually to fill the tubes with electrolyte. Then the filled tubing is connected to the assembled *in-situ* device and the syringe plunger is placed into the syringe pump. A flow rate of 25 µl/hr for 10 min is used to slowly fill the *in-situ* device with electrolyte. The filling process is always conducted under an optical microscope, in order to confirm that the electrolyte completely fills the window region.[Fig. S-2]. Once the 3-electrode region (Fig. 2c) is filled with the electrolyte, the *in-situ* device is connected to the potentiostat. The open circuit potential should be close to ~ +0.355 V RHE and stable within ± 0.01 V, confirming proper connections and electrochemical activity. These procedures verify good electrical connections and steady electrolyte flow with no problems such as liquid leaking, channel blocking due to bubbles or cable disconnection.

Then the *in-situ* device is loaded into the STXM. First, the connections to potentiostat and syringe pump are disconnected to simplify device insertion into the STXM. The *in-situ* device, connected only to the electrolyte tubing, is moved with caution from the optical microscope to the STXM chamber and inserted through a 4.5” flange. Note, since these measurements were first made, the fluid line and electrical connections have been modified to be implemented on a 2.75” conflat flange, which enables compatibility with most modern STXMs. In the chamber, the *in-situ* device is mounted in the 3-pin sample kinematic holder and then the potentiostat and syringe pump are re-connected. The syringe pump is turned on with a flow rate of 25 µl/hr to keep a stable electrolyte flow through the *in-situ* device. The electrolyte tubes and potentiostat cables are organized in the STXM chamber and stabilized using Kapton tape to attach them to a suitable position in the chamber to avoid interfering with STXM operations such as sample scanning.

After the *in-situ* device is loaded in the STXM, the air in the tank is replaced with He gas by displacing the air at a slow rate (~10 min). After achieving a plateau in X-ray transmission, the He gas flow is stopped and the STXM chamber is closed. Note that this procedure is routine at the CLS ambient STXM, but not possible at some other facilities, due to a minimum pressure requirement. STXM imaging was used to locate the SiNx window (240 µm x 120 µm) and to make sure there are no bubbles in the 3-electrode area that occasionally occur in the process of moving and loading the *in-situ* device into the STXM. The signal from X-rays transmit through the SiNx windows and electrolyte is measured and compared with the incident X-ray intensity measured in one of the holes in the *in-situ* device (Fig. 2d) in order to evaluate the absorption (optical density, OD), which in most spectral regimes is dominated by
absorption by the water. Comparison to the known X-ray transmission properties of the SiNₓ windows and water allows determination of the thickness of the electrolyte, which was between 2 and 5 µm, depending on the spacer used (0.5, 1, 1.5 µm), syringe pump flow rate, and ID of the electrolyte tubing. A thin electrolyte layer (as thin as ~1.6 µm) can be achieved. In this work a 1 µm spacer was used. If the electrolyte layer is thick (>4 µm), X-ray cannot transmit through the electrolyte and STXM cannot be performed. After the liquid thickness is measured, electrochemical experiments are performed on the 3-electrode area through the control of potentials and current using potentiostat.

6.4 Electro-deposition of Cu catalyst particles.
Copper nanoparticles were electrodeposited from a mixture solution of 5mM CuSO₄ and 5mM KCl on to the Au working electrode of the in-situ micro-chip cell. The electro-deposition solution concentrations and conditions were chosen based on previous reports [15, 16] to target particles in the range of 300 – 500 nm diameter that are relevant for CO₂R and STXM measurements. After setting up the in-situ device as described in Section 6.3, the electro-deposition was carried out by performing three cyclic voltammetry cycles between 0 and +0.4 V_rhe with a scan rate of 20 mV/s. This is the same protocol as used in preparing the electrode for the catalyst performance measurements described in Section 6.1. The as-deposited Cu particles are then characterized using STXM to gain insight into the morphology and chemical structure (i.e., oxidation state) distributions (see Section S-3, Fig. S-3). STXM measurements at this step should be as fast as possible because some Cu particles will slowly disappear by dissolution into the 5mM CuSO₄ / KCl electrolyte which has a measured pH of 6.1. This could be caused by slow conversion of Cu(I) to Cu(II) in the mildly acidic environment under open circuit potential conditions (ca. +0.36 V_rhe under in-situ conditions) as Cu(I) is not stable at lower pH values [48], followed by Cu(II) dissolution into the electrolyte. This phenomenon has been observed several times in our in-situ experiments.

Once a region with particles of suitable thickness (50 – 200 nm) and size (50 – 600 nm) is identified and oxidation states determined, the CuSO₄/KCl electrolyte is displaced by CO₂ saturated 0.1 M KHCO₃ for subsequent in-situ STXM experiments under CO₂R conditions. In the CO₂ saturated 0.1 M KHCO₃ electrolyte, the Cu particles are more stable as the pH is close to neutral (pH 6.8). Therefore, changing the electrolyte from CuSO₄/KCl to CO₂ saturated 0.1 M KHCO₃ is done as fast as possible to avoid loss of the deposited Cu particles.

6.5 In-situ STXM under CO₂R conditions
The CO₂ saturated 0.1 M KHCO₃ is prepared just before the in-situ STXM experiments by bubbling CO₂
gas into 0.1 M KHCO₃ solution for 20 mins in a septum sealed vial. After Cu *in-situ* electrodeposition (Section 6.4) the electrolyte is changed to CO₂ saturated 0.1 M KHCO₃. Deionized water is first used to flush the CuSO₄/KCl out of the *in-situ* micro-chip device. Then the CO₂ saturated 0.1 M KHCO₃ electrolyte is continuously filled using a 25 µl/hr flow rate. Changing the electrolyte takes around 20 mins. After electrolyte changes, there is no STXM-detectible Cu²⁺ signal in the electrolyte. *In-situ* STXM measurements were conducted using a series of chronoamperometry (CA) potential sequences. Before all measurements, CA at +0.4 V RHE was applied for 30 s (to ensure the catalyst was always in the same starting state) followed by a cathodic step to the electrode potential at which STXM was conducted. STXM measurements were conducted sequentially (with the +0.4 V RHE for 30s in between each) at +0.4, +0.3, +0.2, +0.1, 0, -0.2, -0.4 and -0.6 V RHE. The CA current-time plots are presented in Fig. S-4. During CA at each potential, the current was continuously recorded and several STXM measurements were made in sequence. The sequence consisted of: (1) STXM image at 933.5 eV; (2) 4-energy stack measurement that enabled differentiation between the different oxidation states of Cu present in the materials; (3) 53-energy Cu 2p stack; and (4) STXM image at 933.5 eV for comparison with the first STXM image measured. In all this took ~43 m at each potential which enabled time-dependent monitoring of morphology and chemical structure changes to the Cu particles under controlled electrode potentials. Potentials more negative than -0.6 V RHE were not applied as bubble formation would render the STXM measurements unstable. Gas generation by CO₂R to gas phase products or water reduction to H₂ occasionally created large bubbles which occupied the 3-electrode region, leading to a disconnection of the working electrode that stopped the electrochemical reactions. Generally, electrode potentials less negative than -0.6 V RHE did not generate gas bubbles in the *in-situ* setup. Following CA potentials and STXM measurement, CVs were collected (Fig. S-1c).

### 6.6 STXM measurements and analysis

STXM imaging and spectroscopy were performed using the spectro-microscopy beamline (SM) 10ID-1 at the Canadian Light Source (CLS, Saskatoon, Canada). Details of the STXM [49], beamline [50] and operating procedures for ambient STXM [29] have been presented elsewhere. Briefly, the monochromatic X-ray beam was focused to a ~40 nm spot by a Fresnel zone plate (ZP). The sample was positioned at the focal point of the X-ray beam. Images were measured by (x,y) raster scanning the sample while recording the transmitted X-ray intensity pixel by pixel in a single photon counting mode using a phosphor/photomultiplier single X-ray counting detector. The energy scale was calibrated by recording Ne 1s spectra of Ne gas.[51]

Four types of STXM measurements were used in this work: STXM point scan, STXM image, STXM full
The **STXM point scan** measures the transmission spectrum at one or more points on a sample over a user specified photon energy range. In this work, point scans at the Cu 2p edge from 920 to 965 eV were measured at the position of one of the holes drilled through the *in-situ* device to obtain the incident X-ray \((I_o)\) signal (**Fig. S-5a, b**). The difference in the X-ray intensity between the \(I_o\) spectrum and that measured through the electrolyte in the cell corresponds to the X-ray absorption by the SiNx windows and the electrolyte (**Fig. S-5c**). If the material composition and density is known, the net X-ray absorption, given by \(\text{OD} = -\ln(I/I_o)\), is directly related to the thickness. After subtracting the OD of 150 nm SiNx, the remaining OD can be considered from the X-ray absorption of the electrolyte. The electrolyte is mostly water so the X-ray absorption properties of H\(_2\)O in the 900 – 1000 eV range were used to calculate the thickness of electrolyte in the window region, which was \(~1.6\ \mu\text{m}** (**Section S-5, Fig. S-5d**). **STXM images** at a single photon energy were measured by scanning the sample while recording the transmitted X-ray intensity pixel by pixel. A **STXM full stack** involved a sequence of STXM images collected at various photon energies (also known as stacks [29]) to provide spatially resolved spectroscopic information about the sample. In this work, a 53 energy Cu 2p stack spanning 920 to 965 eV (taking a total of \(~30\ \text{min}\)) was used. A **STXM 4-energy stack** (4-E stack, \(~7\ \text{min}\)) was also used to conduct chemical speciation of the sample in accelerated fashion. It measured images at 920 (pre-edge), 933.5 (Cu(I)&Cu(0)), 937 (Cu(I)) and 960 eV (post-edge), and provides the same spectroscopic information as STXM full stack (**Fig. S-6**). Further details of the STXM measurements are presented in **Table S-1**.

All STXM data was analyzed using aXis2000 software,[52] The images in a stack typically drift by a few hundred nm over a 40-80 eV scan range. Therefore the stacks were aligned to \(~2\ \text{nm}\) registry using a Fourier cross-correlation method. The transmission signal \((I)\) of the aligned stack was converted to optical density (OD) using the Beer Lambert Law: \(\text{OD}(x,y) = -\ln(I(x,y)/ I_o)\), where \(I(x,y)\) is the X-ray intensity transmitted though the \((x,y)\) point on the sample, and \(I_o\) is the incident X-ray intensity measured off the sample but where the X-rays transmit through all other parts of the X-ray path (optics, windows, zone plate, detector) and the sample support (the electrolyte and 150 nm of SiNx window). After OD conversion, the Cu 2p X-ray absorption spectra (XAS) of selected areas (many pixels, which are not necessarily contiguous, but with similar Cu L\textsubscript{3} spectra) were extracted from the STXM stacks using methods described in greater detail below.

A fitting procedure, based on the singular value decomposition (SVD) matrix method [53], was used to analyze the stacks. The SVD routine fits the NEXAFS spectrum at each pixel to a user-identified set of reference spectra, which can be derived from the spectroscopy of pure reference compounds (external) or
to spectra extracted from the measured stack (internal). The result of a SVD fitting is a set of component maps (spatial distributions), one for each component, along with the residual of the fit.[29] For quantitative analysis, the external reference spectra are converted to an absolute intensity scale, optical density per nm (OD1) [30], by scaling the spectrum such that the intensity in the pre-edge and far-continuum (>30 eV above the edge) match the elemental response for 1 nm thickness of the known composition and density of the reference material. The latter are calculated using parameters from the Centre for X-ray Optics database [https://henke.lbl.gov/optical_constants/]. The gray scale of the component maps derived using OD1 reference spectra is an estimate of the thickness of that component at each pixel in the region analyzed. To confirm the validity of the spectro-microscopy fitting procedure, spectra are extracted from specific areas of a stack, identified based on morphology and / or spectral similarity and then subjected to a spectral curve fitting procedure using SVD. When reference spectra on OD1 intensity scales are used in a SVD curve fit, the gray scale of the component maps of each spectral component is an estimate of the average thickness in nm of that component in the area from which the spectra were extracted.

References:


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