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Stability of residual oxides in oxide-derived Cu catalysts for electrochemical CO₂ reduction investigated with ¹⁸O labeling

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Abstract: Oxide-derived (OD) Cu catalysts have high selectivity towards the formation of multi-carbon products (CₓCᵧ) for aqueous electrochemical CO₂ reduction (CO₂R). It has been proposed that a large fraction of the initial oxide can be surprisingly resistant to reduction and that these residual oxides play a crucial role in promoting the formation of CₓCᵧ products. We investigate the stability of residual oxides by synthesizing ¹⁸O enriched OD Cu catalysts and testing them for CO₂R. These catalysts maintain a high selectivity towards CₓCᵧ products (~60%) for up to 5h in 0.1 M KHCO₃ at -1.0 V vs RHE. However, secondary ion mass spectrometry measurements show that only a small fraction (< 1%) of the original ¹³O content remains, showing that residual oxides are not present in significant amounts during CO₂R. Furthermore, we show that OD Cu reoxidizes rapidly in the absence of a reducing potential, which could compromise the accuracy of ex-situ methods for determining the true oxygen content.

Electrochemical reduction of CO₂ (CO₂R) into chemical fuels and feedstock, powered by renewable electrical energy has been proposed as a strategy to mitigate rising greenhouse gas emissions. [1–3] Two main challenges in this area of research are improving the product selectivity and reducing the overpotentials required to drive CO₂R. [2,4,5] “Oxide-derived” Cu (OD Cu) catalysts have attracted much attention because they exhibit higher selectivity towards potentially valuable multi-carbon products (e.g. ethanol and ethylene) with lower overpotential requirements. [6–10] OD Cu catalysts are formed by oxidizing Cu and subsequently reducing it. Recently, it has been proposed that residual oxides are responsible for its remarkable catalyst properties. [11–13] Using ex-situ energy dispersive X-ray spectroscopy (EDS), Cuenya and co-workers reported that a large fraction of the initial oxide can be resistant to reduction even under strongly reducing potentials typically used for CO₂R. [11,12] They proposed that the presence of Cu on the surface was important for the formation of CₓCᵧ products. [12] Muller and co-workers studied an OD Cu catalyst with ambient pressure x-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) and they found a small amount of oxygen residing in the subsurface, possibly modifying the electronic structure of the catalyst and creating active sites with higher CO binding energy. [14]

First principles calculations performed by Goddard and co-workers found that the presence of oxygen in the subsurface would generate a mix of Cu⁺ and Cu²⁺ on the surface. These could then work with adsorbed CO₂ and aid in CO₂R activation by forming chemisorbed CO₂, which is the first step on the CO₂R. [15] In a separate report, they investigated a partially reduced copper oxide matrix consisting of a mix of Cu⁺ and Cu²⁺ regions. [16] They showed that Cu⁺ and Cu²⁺ ions work synergistically to promote CO₂ dimerization and suppress Cu⁺ pathways, thereby boosting catalyst selectivity.

However, a few aspects of this emerging picture of the role of residual oxides in controlling the activity of OD Cu are puzzling. (1) Cu nanomaterials have been shown to readily oxidize, which could create difficulties in performing accurate ex-situ quantification of the oxygen content. [17–19] (2) Moisture and oxygen are shown to cause corrosion (oxidation) of Cu and exposure to both is difficult to avoid. Corrosion might also be exacerbated in a porous, high surface area material such as OD Cu. (3) OD Cu possesses a high density of grain boundaries, which are known to accelerate the oxidation process by serving as nucleation sites and as pathways where diffusion can occur at a faster rate. [20–23] It is therefore possible that upon removal of reducing potential, Cu rapidly reoxidizes and as a result, the O content characterized ex-situ would not be representative of the actual case during CO₂R.

To address these concerns, we employed ¹⁸O isotope labeling in order to confirm the presence/absence of residual oxides in OD Cu during CO₂R. [18] Enriched OD Cu catalysts were synthesized by oxidation/reduction cycling in H₂O/¹⁸O following the procedure of Nilsson and co-workers (see SI for full details). [24] These OD Cu catalysts (OD₁₈ Cu) were then tested for CO₂R for various times and the residual ¹⁸O content was analyzed ex-situ using secondary ion-mass spectrometry (SIMS). This ex-situ method allows us to determine what the “in-situ” oxygen content of the catalyst is during operation as any subsequent reoxidation of the catalyst would not result in ¹⁸O enrichment above the natural isotopic abundance of 0.2 atomic %.

Figure 1a shows the electrochemical oxidation and reduction process used to generate OD₁₈ Cu by sweeping to an anodic potential and then to a cathodic potential in an electrolyte consisting of 0.1 M KHCO₃ and 32 mM of KCl in H₂O/¹⁸O. Working electrodes were 1 μm thick Cu films deposited on Si, and oxidation results in formation of Cu₂O/¹⁸O nanocubes on the surface. Reduction results in loss of the cubical morphology and formation of a porous oxide-derived layer (roughness factor ~22), which is approximately 100 nm thick. Additional characterization, including electroactive surface area, additional SEM images, Raman spectroscopy, x-ray photoelectron
spectroscopy and x-ray diffraction are available in the SI (Figures S1 to S8).

Figure 1. (a) Electrochemical oxidation and reduction procedure for generating OD18 Cu. The blue box highlights the oxidation stage and the green box highlights the reduction stage. SEM images are shown as insets (scale bars: 0.5 µm) (b) Faradaic efficiency to C\textsubscript{2}/C\textsubscript{3}, C\textsubscript{1} and hydrogen for OD\textsubscript{18} Cu, Cu film and Cu foil (70 min tests). Average current densities are given in parenthesis (full data in Tables S2 to S5). (c) 5 h long CO\textsubscript{2}R with OD\textsubscript{18} Cu. Graph shows current density (black line) and faradaic efficiency to ethylene (red squares) vs time. See Figure S9 for faradaic efficiency to other gas products. Error bars are standard deviations from 3 repeat experiments.

The product distributions obtained by operating OD\textsubscript{18} Cu catalysts at -1.0 V vs RHE with CO\textsubscript{2} saturated 0.1 M KHCO\textsubscript{3} in H\textsubscript{2}\textsuperscript{16}O electrolyte for 70 mins are shown in Figure 1b along with results from the unmodified Cu film and a Cu foil. As expected, OD\textsubscript{18} Cu has a higher selectivity towards C\textsubscript{2}/C\textsubscript{3} products (60.1%) and lower selectivity towards C\textsubscript{1} products (6.5%) relative to planar Cu controls. Values obtained here are in good agreement with what has been reported for OD Cu in the literature (Table S6). During long-term testing (5 h) the gas product distribution was relatively stable, with a stable ethylene selectivity of ~34% throughout (Figures 1c and S9).

Next, CO\textsubscript{2}R was performed under identical conditions for 10 mins, 30 mins, 1 hr and 5 hrs with fresh samples of OD\textsubscript{18} Cu. After CO\textsubscript{2}R, the samples were rinsed with copious amounts of DI water, dried and then quickly stored in a N\textsubscript{2} glove box. The residual \textsuperscript{18}O and \textsuperscript{16}O contents of these samples, as well as a freshly prepared sample (0 mins) were determined ex-situ using SIMS (Figure 2). Also, a control sample was prepared by oxidation and reduction in H\textsubscript{2}\textsuperscript{16}O electrolyte and tested for CO\textsubscript{2}R for 1 hr (OD\textsubscript{16} Cu 1 hr).
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Figure 2. (a) $^{18}$O and (c) $^{16}$O content of OD Cu catalysts with different CO$_2$R durations measured by SIMS. Note the different scales in (a) and (c). For ease of viewing, the results for 30 mins and 1 hour are omitted in (a) and (c) but are available in Figures S17 and S18. (b) shows the percentage of the initial $^{18}$O that remains in OD18 Cu after CO$_2$R (see SI for calculation details).

As seen from Figure 2a, the OD18 Cu sample has $^{18}$O content on the order of $10^{22}$ atoms/cc, which is the same order of magnitude as the atomic density of Cu. However, after CO$_2$R has been carried out, the $^{18}$O content drops drastically. Figure 2b shows the percentage of the initial $^{18}$O that remains after CO$_2$R (details of calculation in SI) in the top ~100 nm layer (estimated thickness of the oxide-derived layer). Surprisingly, only <1% of the original $^{18}$O remains after CO$_2$R and, in fact, the $^{16}$O content drops to the same order of magnitude as the control sample, OD16 Cu 1 hr, which was not enriched with $^{18}$O. However, the control sample is due to its natural abundance of 0.2 atomic %.) This means that the oxide layer is completely reduced, as would be expected since the applied potential typical of CO$_2$R is >1 V negative of the standard reduction potential of Cu$_2$O. There therefore cannot be a large concentration of oxygen remaining in the catalyst under CO$_2$R conditions. Another possibility is that during CO$_2$R, $^{18}$O atoms that leave as a result of reduction are replaced instantly via oxidation, with $^{16}$O taking its place. However this is unlikely as the oxidation step is thermodynamically unfavorable because of the highly reducing potentials applied.

Intriguingly even after CO$_2$R, the $^{16}$O content in OD Cu does not change and actually increases (Figure 2c). In fact, contents after CO$_2$R are on the order of $10^{22}$ atoms/cc, suggesting that samples have been heavily oxidized. However, in our experimental process, care was taken to ensure that exposure to ambient air was as minimal as possible. We therefore considered the possibility that reoxidation of OD Cu occurs rapidly, as soon as the reducing potential is turned off. In-situ Raman spectroscopy measurements by Yeo and co-workers on Cu$_2$O films revealed that application of a potential of -0.99 V vs RHE resulted in loss of the characteristic Cu$_2$O Raman peaks, and they concluded that complete reduction to metallic Cu$_0$ had taken place. Surprisingly, once the potential was removed, Cu$_2$O peaks began to appear again after 60 s and by 120 s had become very distinct, meaning that rapid reoxidation of OD Cu had taken place. In this work, in-situ Raman spectroscopy was also carried out (Figure S10) and similar observations were made.

To further emphasize the rapid oxidation of OD Cu, a freshly prepared OD16 Cu sample was soaked in H$_2^{18}$O (with 0.1 M KHCO$_3$) for 3 mins and then rinsed immediately with DI water. SIMS measurements revealed that the $^{18}$O content in this sample (blue trace) indeed rises by an order of magnitude. To further investigate the reoxidation process, CO$_2$R was carried out on an OD16 Cu sample in H$_2^{18}$O electrolyte (0.1 M KHCO$_3$) at -1.0 V vs RHE for 3 mins. This sample was then washed with DI water and the $^{18}$O content in this sample was similarly analyzed ex-situ using SIMS (Figure 3, red trace). Surprisingly, this sample showed a very high incorporation of $^{18}$O, with concentrations on the order of $10^{22}$ atoms/cc, meaning that a large degree of reoxidation had occurred. We emphasize that the $^{18}$O content is not simply due to trapped H$_2^{18}$O in these porous catalysts. This is evidenced by Raman peak shifts of Cu$_2$O consistent with isotopic substitution (Figure S11a). Taken together, all these results highlight the difficulty of ex-situ measurements of the oxygen content, since OD Cu can be rapidly reoxidized.

As seen from Figure 2a, the OD18 Cu sample has $^{18}$O content on the order of $10^{22}$ atoms/cc, which is the same order of magnitude as the atomic density of Cu. However, after CO$_2$R has been carried out, the $^{18}$O content drops drastically. Figure 2b shows the percentage of the initial $^{18}$O that remains after CO$_2$R (details of calculation in SI) in the top ~100 nm layer (estimated thickness of the oxide-derived layer). Surprisingly, only <1% of the original $^{18}$O remains after CO$_2$R and, in fact, the $^{16}$O content drops to the same order of magnitude as the control sample, OD16 Cu 1 hr, which was not enriched with $^{18}$O. However, the control sample is due to its natural abundance of 0.2 atomic %.) This means that the oxide layer is completely reduced, as would be expected since the applied potential typical of CO$_2$R is >1 V negative of the standard reduction potential of Cu$_2$O. There therefore cannot be a large concentration of oxygen remaining in the catalyst under CO$_2$R conditions. Another possibility is that during CO$_2$R, $^{18}$O atoms that leave as a result of reduction are replaced instantly via oxidation, with $^{16}$O taking its place. However this is unlikely as the oxidation step is thermodynamically unfavorable because of the highly reducing potentials applied.

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Finally, we consider the reasons for the rapid reoxidation of OD Cu. Firstly, Cu nanomaterials are known to be easily oxidized due to numerous highly reactive undercoordinated atoms on the surface. Secondly, previous studies have shown that grain boundaries can act as nucleation sites for oxide growth as well as provide channels for diffusion to take place at a faster rate (compared to diffusion through the bulk lattice). OD Cu has a high density of grain boundaries, which could explain why OD Cu can reoxidize so quickly via exposure to ambient air and moisture (see Schematic 1). Comparatively, Cu with fewer grain boundaries (Cu film) does not oxidize as quickly, as illustrated by our Cu Auger LMM measurements (Figure S8).

In conclusion, the stability of residual oxides was investigated by 18O isotope labeling. OD enriched Cu catalysts were synthesized and CO2R was performed with them. The residual 18O content was then analyzed ex-situ with SIMS and it was found that only <1% of the original 18O content remained in the samples. We therefore conclude that residual oxides are unstable in our OD Cu catalysts during CO2R. We believe that the 18O content selectivity exhibited by these catalysts is most likely due to a high density of grain boundaries as previously proposed by Kanan and co-workers. We also confirm that these catalysts can rapidly reoxidize due, possibly, to the numerous grain boundaries present in the material. The rapid reoxidation process could compromise the accuracy of ex-situ methods for determining the true oxygen content of the catalyst during CO2R conditions.

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Keywords: CO2 reduction • Roper oxides • Electrocatalysis • oxide stability • isotopic labeling

Figure 3. 18O content in OD16 Cu 1 hr. OD16 Cu with CO2R for 3 mins in H218O electrolyte and OD16 Cu that was soaked in H218O for 3 mins. The 18O content was also analyzed (Figure S11b).

Figure 4. High GB density Cu Rapid GB facilitated diffusion of oxygen Oxidized Cu

Scheme 1. Rapid reoxidation of OD Cu occurs because oxygen diffusion and oxide nucleation can be facilitated by grain boundaries.

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In this work, we show that residual oxides in oxide-derived Cu catalysts are not stable under strongly reducing potentials during electrochemical CO\textsubscript{2} reduction. This is demonstrated with the use of \textsuperscript{18}O labelled oxide-derived Cu catalysts. Instead we find that the surface is rapidly reoxidized in the absence of a reducing potential.

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Stability of residual oxides in oxide-derived Cu catalysts for electrochemical CO\textsubscript{2} reduction investigated with \textsuperscript{18}O labeling