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Permalink
https://escholarship.org/uc/item/64w0850n

Journal
Angewandte Chemie (International ed. in English), 57(2)

ISSN
1433-7851

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Publication Date
2018

DOI
10.1002/anie.201710590

Peer reviewed

Stability of residual oxides in oxide-derived Cu catalysts for electrochemical CO$_2$ reduction investigated with ^{18}O labeling

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Abstract: Oxide-derived (OD) Cu catalysts have high selectivity towards the formation of multi-carbon products (C$_2$/C$_3$) for aqueous electrochemical CO$_2$ reduction (CO$_2$R). 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 C$_2$/C$_3$ products. We investigate the stability of residual oxides by synthesizing ^{18}O enriched OD Cu catalysts and testing them for CO$_2$R. These catalysts maintain a high selectivity towards C$_2$/C$_3$ products (~60%) for up to 5h in 0.1 M KHCO$_3$ at -1.0 V vs RHE. However, secondary ion mass spectrometry measurements show that only a small fraction (< 1%) of the original ^{18}O content remains, showing that residual oxides are not present in significant amounts during CO$_2$R. 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 CO$_2$ (CO$_2$R) 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 CO$_2$R.[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.[6–13]

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 catalytic properties.[11,12,14] 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 CO$_2$R.[11,12] They proposed that the presence of Cu$^+$ on the surface was important for the formation of C$_2$/C$_3$ products.[12] Nilsson 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.[15]

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 Cu^0 on the surface. These could then work with adsorbed H$_2$O and aid in CO$_2$ activation by forming chemisorbed CO$_2$, which is the first step of CO$_2$R.[16] In a separate report, they investigated a partially reduced copper oxide matrix consisting of a mix of Cu^0 and Cu$^+$ regions.[17] They showed that Cu$^+$ and Cu^0 regions could act synergistically to promote CO dimerization and suppress C$_1$ 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.[18,19] (2) Moisture and oxygen are known 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.[20–24] It is therefore possible that upon removal of a reducing potential, Cu rapidly reoxidizes and as a result, the O content characterized *ex-situ* would not be representative of the actual case during CO$_2$R.

To address these concerns, we employed ^{18}O isotope labeling in order to confirm the presence/absence of residual oxides in OD Cu during CO$_2$R. ^{18}O enriched OD Cu catalysts were synthesized by oxidation/reduction cycling in H$_2$^{18}O following the procedure of Nilsson and co-workers (see SI for full details).[25] These OD Cu catalysts (OD18 Cu) were then tested for CO$_2$R for various times and the residual ^{18}O 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 ^{18}O 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 KHCO$_3$ and 32 mM of KCl in H$_2$^{18}O. Working electrodes were 1 μm thick Cu films deposited on Si, and oxidation results in formation of Cu$_2$^{18}O 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-

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ray diffraction are available in the SI (Figures S1 to S8).
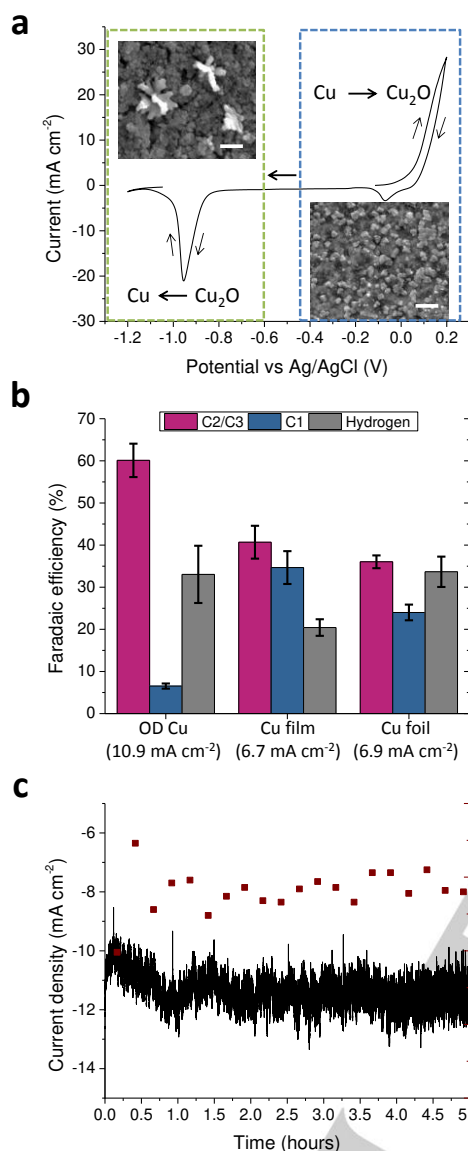

Figure 1. (a) Electrochemical oxidation and reduction procedure for generating OD18 Cu. The blue box highlights the oxidation stage and the green box highlights the reduction stage. SEM images are shown as insets (scale bars: 0.5 μm) (b) Faradaic efficiency to C_2/C_3, C_1 and hydrogen for OD Cu, Cu 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_2R with OD18 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 OD18 Cu catalysts at -1.0 V vs RHE with CO_2 saturated 0.1 M $KHCO_3$ in $H_2^{16}O$ electrolyte for 70 mins are shown in Figure 1b along with results from the unmodified Cu film and a Cu foil. As expected, OD18 Cu has a higher selectivity towards C_2/C_3 products (60.1%) and lower selectivity towards C_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 an ethylene selectivity of ~34% throughout (Figures 1c and S9).

Next, CO_2R was performed under identical conditions for 10 mins, 30 mins, 1 hr and 5 hrs with fresh samples of OD18 Cu. After CO_2R, the samples were rinsed with copious amounts of DI water, dried and then quickly stored in a N_2 glove box. The residual ^{18}O and ^{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 $H_2^{16}O$ electrolyte and tested for CO_2R for 1 hr (OD16 Cu 1 hr).
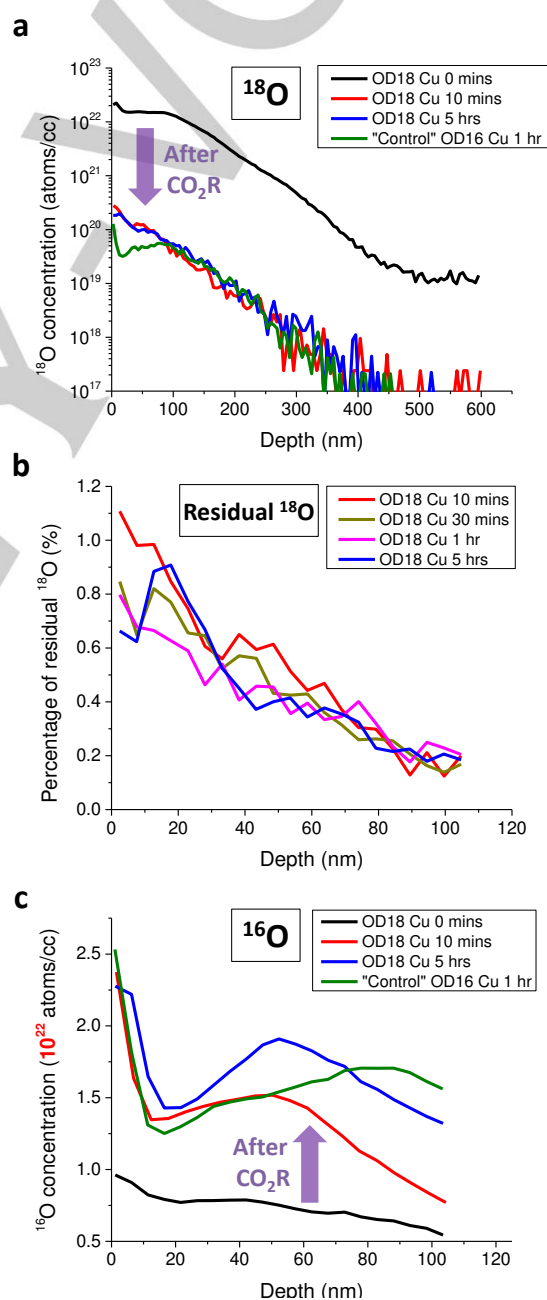
Figure 2. (a) ^{18}O and (c) ^{16}O content of OD Cu catalysts with different CO_2R durations measured by SIMS. Note the different scales in (a) and (c). For ease of viewing, the results for 30 mins and 1 hour are omitted in (a) and (c) but are available in Figures S17 and S18. (b) shows the percentage of ^{18}O that remains in OD18 Cu after CO_2R (see SI for calculation details)

As seen from Figure 2a, the OD18 Cu 0 mins has ^{18}O content on the order of 10^{22} atoms/cc, which is on the same order of magnitude as the atomic density of Cu, showing successful incorporation of ^{18}O into the catalyst structure. However, after CO_2R has been carried out, the ^{18}O content drops drastically. Figure 2b shows the percentage of the initial ^{18}O that remains after CO_2R (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_2R and, in fact, the ^{18}O content drops to the same order of magnitude as the control sample, OD16 Cu 1 hr, which was not enriched with ^{18}O. (We note that the ^{18}O in 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_2R is >1 V negative of the standard reduction potential of Cu_2O. There therefore cannot be a large concentration of oxygen remaining in the catalyst under CO_2R conditions. Another possibility is that during CO_2R, ^{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_2R, the ^{16}O content in OD18 Cu does not change and actually increases (Figure 2c). In fact, ^{16}O contents after CO_2R 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_2O films revealed that application of a potential of -0.99 V vs RHE resulted in loss of the characteristic Cu_2O Raman peaks, and they concluded that complete reduction to metallic Cu^0 had taken place.[6] Surprisingly, once the potential was removed, Cu_2O 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 (Figure 3, blue trace) indeed rises by an order of magnitude. To further investigate the reoxidation process, CO_2R 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). Startlingly, 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_2O 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.
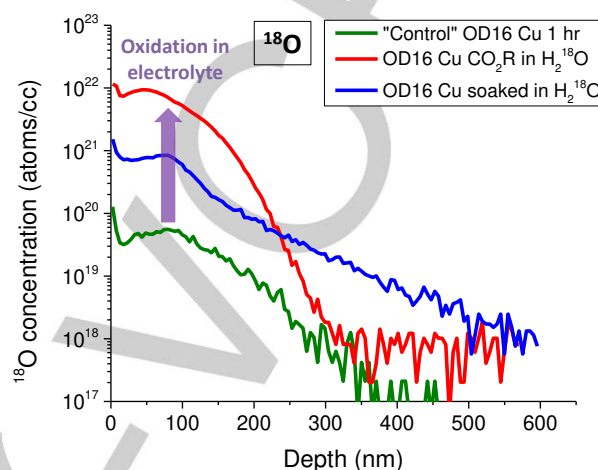

Figure 3. ^{18}O content in OD16 Cu 1 hr, OD16 Cu with CO_2R for 3 mins in $H_2^{18}O$ electrolyte and OD16 Cu that was soaked in $H_2^{18}O$ for 3 mins. The ^{16}O content was also analyzed (Figure S11b).

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.[19] Secondly, previous studies have shown that grain boundaries can act as nucleation sites for oxide growth as well as provide channels diffusion can take place at a faster rate (compared to diffusion through the bulk lattice).[20–24] OD Cu has a high density of grain boundaries,[8,27,28] 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).
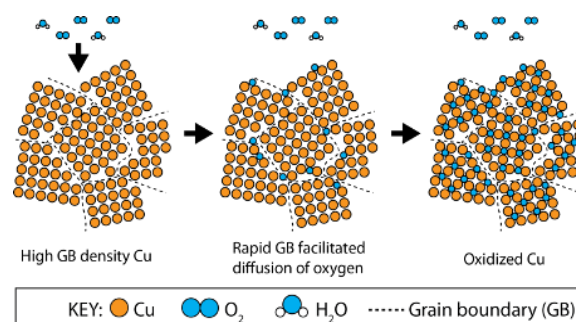
Scheme 1. Rapid reoxidation of OD Cu occurs because oxygen diffusion and oxide nucleation can be facilitated by grain boundaries.

In conclusion, the stability of residual oxides was investigated by ^{18}O isotope labeling. ^{18}O enriched oxide-derived Cu catalysts were synthesized and CO_2R was performed with them. The residual ^{18}O content was then analyzed *ex-situ* with SIMS and it was found that only <1% of the original ^{18}O content remained in the samples. We therefore conclude that residual oxides are unstable in our oxide-derived Cu catalysts during CO_2R. We believe that the high C_2/C_3 product selectivity exhibited by these catalysts is more likely due to a high density of grain boundaries as previously proposed by Kanan and co-workers[28,29]. We also show 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 CO_2R conditions.

Acknowledgements

Keywords: CO_2 reduction • copper oxides • electrocatalysis • oxide stability • isotope labeling

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Layout 2:

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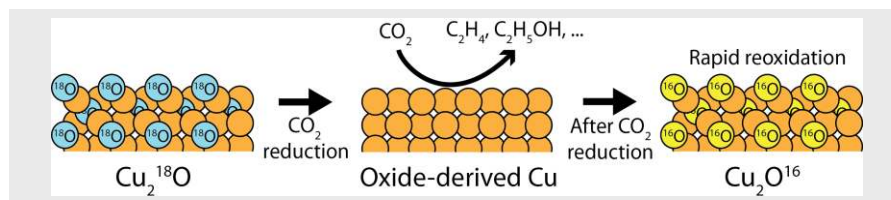
In this work, we show that residual oxides in oxide-derived Cu catalysts are not stable under strongly reducing potentials during electrochemical CO$_2$ reduction. This is demonstrated with the use of ^{18}O labelled oxide-derived Cu catalysts. Instead we find that the surface is rapidly reoxidized in the absence of a reducing potential.

Yanwei Lum, Joel W. Ager

Stability of residual oxides in oxide-derived Cu catalysts for electrochemical CO$_2$ reduction investigated with ^{18}O labeling