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Absence of Oxidized Phases in Cu under CO Reduction Conditions

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Abstract
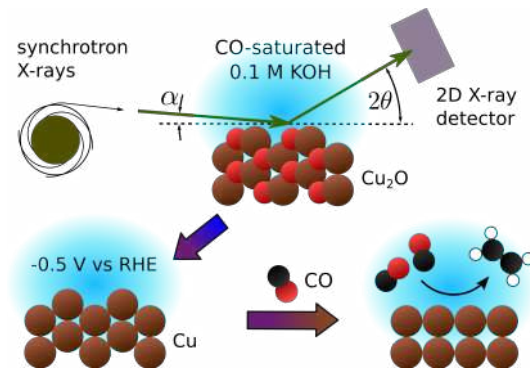
The surface structure and oxide content near the surface of copper electrodes under CO and CO_2 reduction conditions are debated. By live-monitoring Cu and Cu_2O Bragg peaks from the surface of a polycrystalline Cu electrode while scanning from open-circuit potential to CO reduction potentials, we show that the near-surface region is fully converted to the metallic phase at approximately $+0.3$ V vs RHE.

Copper can catalyze the electrochemical reduction of CO_2 and CO to multi-carbon fuels with significant activity and Faradaic efficiency,[1,2] and copper-based gas-diffusion electrodes for reduction of CO_2 and CO to ethylene in alkaline electrolyte are approaching technological viability.[3,4] However, uncertainty about the atomic structure of the electrode surface and near-surface region under reaction conditions remains a challenge to the development of more active and selective electrodes materials.

Importantly, the presence of oxygen is a matter of debate. Despite the high equilibrium potentials for reduction of bulk oxidized phases of copper ($U^\circ_{RHE} > 0.4V$, see Table S1), several studies have reported signs that oxygen is present near the surface of copper electrodes under reaction conditions ($U^\circ_{RHE} < 0V$),[5,6] and density functional theory (DFT) calculations have indicated that subsurface oxygen may promote CO_2/CO reduction activity.[6,7] Other experiments and calculations have indicated that subsurface oxygen is not stable under the cathodic reaction conditions,[8–10] and recent comparisons have shown that, when properly normalized, the intrinsic CO and CO_2 reduction activity on copper-based electrodes does not depend on the initial oxidation state.[2,11]

In addition to the debate over the presence of oxygen under reaction conditions, *in-situ* scanning tunneling microscopy (STM) studies have indicated that copper surfaces are dynamic under reaction conditions.[12,13] Additional *in-situ* methods averaging over a macroscopic sample area can help to confirm and better understand these effects.

We used *in-situ* grazing incidence X-ray diffraction (GIXRD) with synchrotron radiation to probe the structure of a polycrystalline copper thin film under CO reduction conditions 0.1 M KOH (pH≈13), using a three-electrode setup with a flow cell and techniques described in detail elsewhere.[14] By varying the incident angle (α), GIXRD diffractograms were taken at probe depths of ≈2.5 nm ($\alpha = 0.15°$) and ≈20 nm ($\alpha = 0.20°$). Product quantification is out of the scope of this study, but has been described elsewhere for polycrystalline copper under the same CO reduction conditions.[2]

Figure 1a shows typical GIXRD diffractograms of a polycrystalline Cu film in CO-

saturated 0.1 M KOH electrolyte, taken at the surface-sensitive incident angle of $\alpha = 0.15°$ before (+0.65 V vs RHE) and after (-0.4 V vs RHE) reduction. The first potential is near the measured open-circuit potential (OCP, typically ≈ 0.7 V vs RHE, see Figure S1), and CO reduction is significant at the latter potential.[2] The broad $Cu_2O(111)$ peak centered at $2\theta = 16.9°$ in the pre-reduction diffractogram, attributed to the native oxide formed while the sample is exposed to air and/or at OCP, disappears in the post-reduction diffractogram. In contrast, the metallic Cu peaks, most noticeably Cu(111) at $2\theta = 20.1°$, grow in the post-reduction diffractogram. The large width of the $Cu_2O(111)$ peak in the pre-reduction diffractogram indicates that the oxide phase is less crystalline than the metallic phase (≈ 5 nm crystallites compared to ≈ 15 nm, see Figure S2). No peaks for other oxidized Cu phases such as CuO or $Cu(OH)_2$ were observed in these experiments. The pre- and post-reduction diffractograms in Ar-saturated electrolyte look similar to those in CO (Figure S3). The high pH likely plays a role in the formation of long-range order in the Cu_2O phase at OCP, since Cu_2O diffraction peaks have not been observed at OCP at lower pH.[14]

Figure 1b shows the live reduction of a fresh sample in Ar-saturated electrolyte. The GIXRD data are shown as a heat map indicating intensity as a function of 2θ on the vertical axis in the top panel and time on the horizontal axis, with the concurrent electrochemical potential (U, swept at -10 mV/s) and current density (J) in the bottom panel. The $Cu_2O(111)$ peak disappears and the Cu(111) peak becomes more intense at approximately t=40 s, when the potential is between 0.4 and 0.3 V vs RHE.

The reduction of electrodes in Ar and CO are compared in Figure 1c. The normalized integrated intensities for the Cu(111) and $Cu_2O(111)$ GIXRD peaks during this experiment are plotted against electrode potential in the upper panel of Figure 1c, with the current density in the lower panel. (The heat map for the sample reduced in CO is shown in Figure S4.) For both samples, the $Cu_2O(111)$ peak disappears and the Cu(111) peak grows to maximum intensity between 0.4 and 0.3 V vs RHE, just cathodic of the standard reduction potential of Cu_2O (Table S1). Interestingly, whereas the cathodic current wave coincides
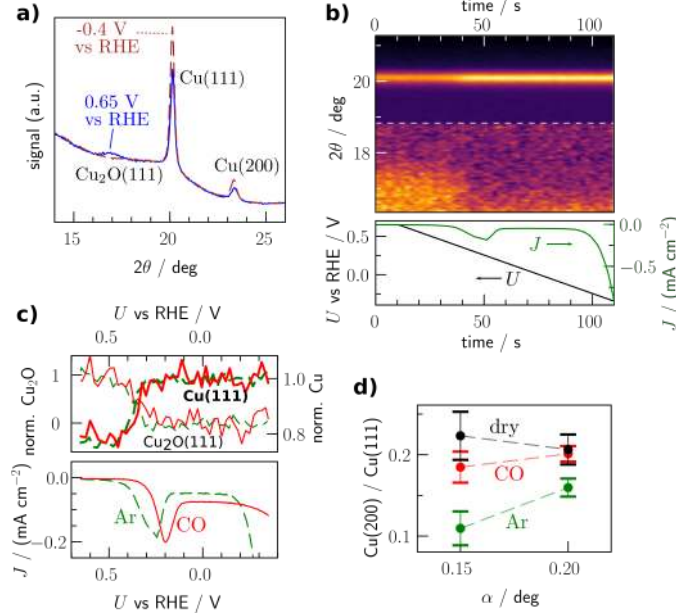
Figure 1: ***In-situ* GIXRD of polycrystalline Cu electrodes.** a) Diffractograms at incident angle $\alpha = 0.15°$ of a Cu sample in CO-saturated 0.1 M KOH before ($U = 0.65$ V vs RHE) and after ($U = -0.4$ V vs RHE) reduction of the surface. b) Live monitoring of diffraction signal ($\alpha = 0.15°$) during reduction of a sample in Ar-saturated electrolyte, with the coinciding potential (U) and current (J) in the bottom panel. c) Integrated Cu(111) and Cu$_2$O(111) Bragg peaks in the top panel and current in the bottom panel during reduction of samples in Ar-saturated (green, dashed lines) or CO-saturated (red) electrolyte. d) The ratio of the integrated Cu(200) and Cu(111) peaks for dry samples and reduced samples in Ar or CO-saturated electrolyte, as a function of incident angle. Points and error bars represent means and standard deviations, respectively.

with the change in XRD peak intensity for the sample reduced in Ar-saturated electrolyte, the current lags the change in peak intensity by 50 to 100 mV for the sample reduced in CO-saturated electrolyte. This might indicate an electrochemical reduction mechanism involving a step in which CO acts as a chemical reducing agent, as CO is known to reduce copper oxides in thermal catalysis,[15] but more studies are necessary to confirm the effect.

The increase in the Cu(111) peak intensity is especially informative: while the scattering signal from a non-crystalline oxidized copper phase might not be discernible from the background scattering signal from the electrolyte, a significant portion of such a phase within the attenuation depth of 2.5 nm ($\approx$12 monolayers) would reduce the intensity of the Cu(111) peak. Since the metal peak abruptly increases in intensity while the potential is $\approx$0.4 to

0.3 V vs RHE without any subsequent change, significant content of any oxidized phase of Cu at potentials relevant for CO reduction seems highly unlikely, as the content of such a phase would have to remain constant from about +0.3 to -0.5 V vs RHE. This rules out a significant sub-stoichiometric oxide, crystalline or amorphous, though we cannot rule out minute amounts of oxygen dissolved in the metallic Cu phase.

Given the low penetration depth, the ratio of peak intensities in GIXRD can be influenced by the surface faceting of a polycrystalline sample, as illustrated in the Supplementary Information (Figure S5). Figure 1d shows the ratio of the integrated intensity of the Cu(200) Bragg peak to that of the Cu(111) peak as a function fo incidence angle. The results are grouped into dry samples, reduced samples (-0.4 or -0.5 V vs RHE) in Ar-saturated electrolyte, and reduced samples in CO-saturated electrolyte. While this ratio is similar in Ar and CO prior to reduction (Figure S6), at the small incidence angle ($\alpha = 0.15°$) the Cu(200) peak increases relative to the Cu(111) peak in the post-reduction diffractogram for samples in CO saturated electrolyte. The ratios converge at $\alpha = 0.20°$, confirming that the difference is due to a surface phenomenon. Compared to the dry samples, the Cu(200)/Cu(111) ratio is actually lower at $\alpha = 0.15°$ for both the Ar and CO samples. This is consistent with the STM observation of polycrystalline Cu electrodes which reconstruct first to (111) and then to (100),[12] and evidences the promotion by CO of the reconstruction to (100)-like surfaces. The CO-promoted transformation to (100)-like surfaces helps explain why polycrystalline Cu electrodes show high selectivity for CO reduction to ethylene, similar to stepped (100) surfaces.[1] Small shifts of peak centers ($\Delta 2\theta \approx -0.02°$) were also observed during the reduction (Figure S6), possibly reflecting hydrogen-induced expansion.[13]

In this study, we used *in-situ* grazing-incidence X-ray diffraction (GIXRD) to examine changes in the surface composition and morphology of polycrystalline copper under CO reduction conditions. We showed that the $Cu_2O(111)$ diffraction peak disappears during the cathodic scan at about 0.3 V vs RHE while the Cu(111) peak simultaneously increases to its maximum intensity, with no further increase at more cathodic potentials, demonstrating

that the oxide is fully reduced to the metallic phase at potentials relevant to CO reduction. Compared to other studies which also show the reduction of oxidized copper phases prior to the onset of CO or CO_2 reduction by means of *in-situ* x-ray absorption spectroscopy[16] and Raman spectroscopy,[10] our results stand out for the high time resolution and the surface-sensitivity enabled by the grazing incidence configuration. We also provided preliminary GIXRD evidence of preferential surface faceting guided by electrochemical environment, in agreement with STM studies.[12] Taken together, these results help explain why the intrinsic CO reduction activity of copper-based electrodes is largely invariant regardless of the structure or oxidation state of the precursor.[2] Surface roughening caused by these faceting changes and transient structures such as undercoordinated sites present during the reconstruction may also contribute to copper's CO reduction activity.

Supporting Information: Experimental details and additional GIXRD data and analysis.

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grant.

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