Supporting information

Morphological stability of copper surfaces under reducing conditions

Stefan J. Raaijman*,‡, Nakkiran Arulmozh†*,‡, Marc T.M. Koper*,*

*aLeiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

*m.koper@chem.leidenuniv.nl

‡These authors contributed equally.
1. Blank reproducibility spherical single crystal

The effectiveness of surface recovery via H$_2$/O$_2$ annealing near the melting point of a copper spherical single crystal after having been oxidized at $+0.70$ V for 1 minute is depicted in Figure S1. In black, the blank as obtained prior to surface oxidation is depicted, and in red the blank obtained after recovering the surface via annealing after it had been oxidized. Comparison of the two blank CVs shows that facet distribution is very similar, although the red line exhibits a larger density of {111} terrace sites as evidenced by increased charge near $+0.1$ V (OH-adsorption) and also near $+0.45$ V (O-adsorption).

![Figure S1. Blank CV (0.1 M NaOH, $\nu =$ 50 mV s$^{-1}$) reproducibility after a pre-oxidation + cathodization experiment (+0.70 V / -1.75 V, 1 min each) after the crystal was annealed in a H$_2$/O$_2$ flame close to the melting point for 30 minutes.](image)

2. Time-dependent voltammetry changes in 0.1 M KHCO$_3$ during CO2RR

The evolution of the cyclic voltammogram of a copper surface after being subjected to CO2RR at -0.75 V in 0.1 M KHCO$_3$ for varying amounts of time is depicted in Figure S2. Clear changes are observed as reaction time is increased, indicated by the arrows in the figure. These changes correspond well with voltammetric changes observed after applying reducing conditions in both 0.5 M KHCO$_3$ and 10 M NaOH (main text).
Figure S2. Blank CV (0.1 M NaOH, \(v = 50 \text{ mVs}^{-1}\)) development for a polycrystalline copper electrode as a function of reaction time during CO2RR at -0.75 V in 0.1 M KHCO\(_3\) electrolyte under continuous CO\(_2\) bubbling. Voltammograms obtained after 1, 5, 15 and 30 minutes are compared to the initially obtained blank CV in red, green, blue, purple and black, respectively.

3. **Anisotropy of halide-induced roughening**

Proof of the anisotropic nature of oxidation and reduction of copper in halide-containing solution is provided in Figure S3, where a SEM image depicting the overall surface of a spherical single crystal post-treatment is provided. Various distinct regions are present on the surface, with their periodicity matching that of the three basal planes in an FCC lattice.
4. Possible morphological change-directed options for decreasing area

Assuming that the CV changes discussed in the main text (a decrease in the overall number of active sites, but little change in the relative abundance of the various individual types of sites) are the result of changes in morphology, the following surface restructuring-driven mechanisms can be envisioned.

E.g., one could assume that we start with a rough surface that undergoes considerable restructuring in such a manner that mesoscale and nanoscale deposits change their geometrical shapes towards such geometries that exhibit lower surface area to volume rations (i.e., spheres). This phenomenon could explain a decrease in overall sites; however, such an explanation is rather unreasonable. Especially when we consider that the electrodes employed in this work are prepared by melting a copper wire into a droplet and allowing it to solidify resulting in a (near) spherical bead which intrinsically has a low roughness factor and low surface area to volume ratio, owing to surface-tension directed surface energy minimization effects.

Another theory that might explain a decrease in area would be to (literally) shrink the electrode radius, and thus decreasing the geometric surface area, via copper dissolution. This explanation is equally unreasonable as the former, considering the large amount of dissolution that would be required. Also, dissolution has been reported to be absent at the negative potentials we employ.\(^1\)
CV evolution for CORR in 10 M NaOH various potentials

Cyclic voltammetry studies were also employed to investigate the effect of adding CO during cathodization in 10 M NaOH electrolyte. Furthermore, to guarantee that actual reduction of CO would occur, the applied potential was lowered from -1.75 V to both -0.75 V (Figure S4) and -0.40 V (Figure S5). The former potential (-0.75 V) was chosen as it is equal to the potential we used for our CO2RR studies, whereas the latter (-0.40 V) was chosen to see if the presence of CORR intermediates plays a significant role considering that -0.40 V is close to the onset of the CORR in alkaline media meaning its rate of reduction is much decreased. The changes in voltammetry are virtually identical to what is observed when we apply -1.75 V in 10 M NaOH without CO present in both cases, though the rate at which the CV changes is somewhat slower in when applying -0.40 V in the presence of CO.

Figure S4. Blank CV (0.1 M NaOH, v = 50 mVs⁻¹) evolution after conducting CORR experiments in 10 M NaOH electrolyte with active CO bubbling at -0.75 V for various reaction times.
Figure S5. Blank CV (0.1 M NaOH, $v = 50$ mVs$^{-1}$) evolution after conducting CORR experiments in 10 M NaOH electrolyte with active CO bubbling at -0.40 V for various reaction times.

5. Electrode deactivation during CO2RR

Deactivation of the catalytic activity of the roughened spherical single crystal used for SEM studies into the long-term morphological stability of copper under CO2RR conditions (1 hour at -0.75 V in 0.5 M KHCO$_3$ electrolyte under constant CO$_2$ bubbling) is depicted in Figure S6, in the form of decreasing current response of the system with constant potential.
Figure S6. Time-dependent current deactivation of roughened copper spherical single crystal surface during CO2RR conditions (-0.75 V in 0.5 M KHCO$_3$ during active CO$_2$ bubbling).

6. Absence morphology changes after long-term CO2RR but resulting presence impurities

Identical-location SEM + EDX experiments were conducted for multiple locations on a nitric acid-cleaned polycrystalline surface as discussed in the main text. Proof that the same observations discussed there hold also for other locations on the crystal is provided in the form of SEM micrographs before and after CO2RR (-0.75 V in saturated KHCO$_3$ for ca. 5 hours) with accompanying EDX signals for two other locations on the crystals in Figures S7 and S8.

Figure S7. Surface morphology and elemental analysis results before and after ca. 5 hours of CO2RR at -0.75 V in saturated KHCO$_3$ solution under constant CO$_2$ (g) purging for a different location than discussed in the main text with different mesoscopic morphology on a nitric acid-cleaned polycrystalline bead electrode. Panels a and c represent the EDX spectrum a) prior to and c) after CO2RR, whilst b) and d) represent the accompanying SEM micrographs, respectively.
Figure S8. Surface morphology and elemental analysis results before and after ca. 5 hours of CO2RR at -0.75 V in saturated KHCO$_3$ solution under constant CO$_2$ (g) purging for a different location than discussed in the main text with again different mesoscopic morphology on a nitric acid-cleaned polycrystalline bead electrode. Panels a and c represent the EDX spectrum a) prior to and c) after CO2RR, whilst b) and d) represent the accompanying SEM micrographs, respectively.

References

1. Speck, F. D.; Cherevko, S., Electrochemical copper dissolution: A benchmark for stable CO2 reduction on copper electrocatalysts. *Electrochem Commun* **2020**, *115*, 106739.