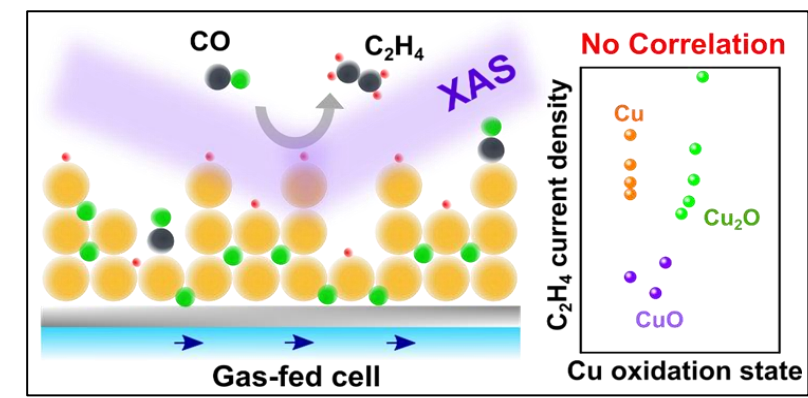


Correlating Oxidation State and Surface Area to Activity from *Operando* Studies of Copper CO Electroreduction Catalysts in a Gas-Fed Device

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Abstract: Oxide-derived Cu catalysts exhibit a remarkable selectivity towards multi-carbon products for the electrochemical CO reduction reaction (CORR), but the exact role of oxide remains elusive for explaining the performance enhancements. Here, we used *operando* X-ray absorption spectroscopy (XAS) coupled with simultaneous measurements of catalyst activity and selectivity by gas chromatography (GC) to study the relationship between oxidation states of Cu-based catalysts and activity for ethylene (C_2H_4) production in a CO gas-fed cell. *Ex-situ* characterization from microscopic techniques suggests that the changes in C_2H_4 activity and selectivity may arise from a morphological transformation that evolves into a more active structure.



Results and Discussion

Cu, Cu_2O , and CuO were electrodeposited on carbon gas diffusion layers (GDLs) as electrocatalysts for CORR. Faradaic yields of C_2H_4 and H_2 were monitored by in-line GC, while oxidation states were simultaneously monitored by *operando* XAS. It was found that C_2H_4 Faradaic yields were greatest when the bulk catalyst was fully reduced to the metallic state.

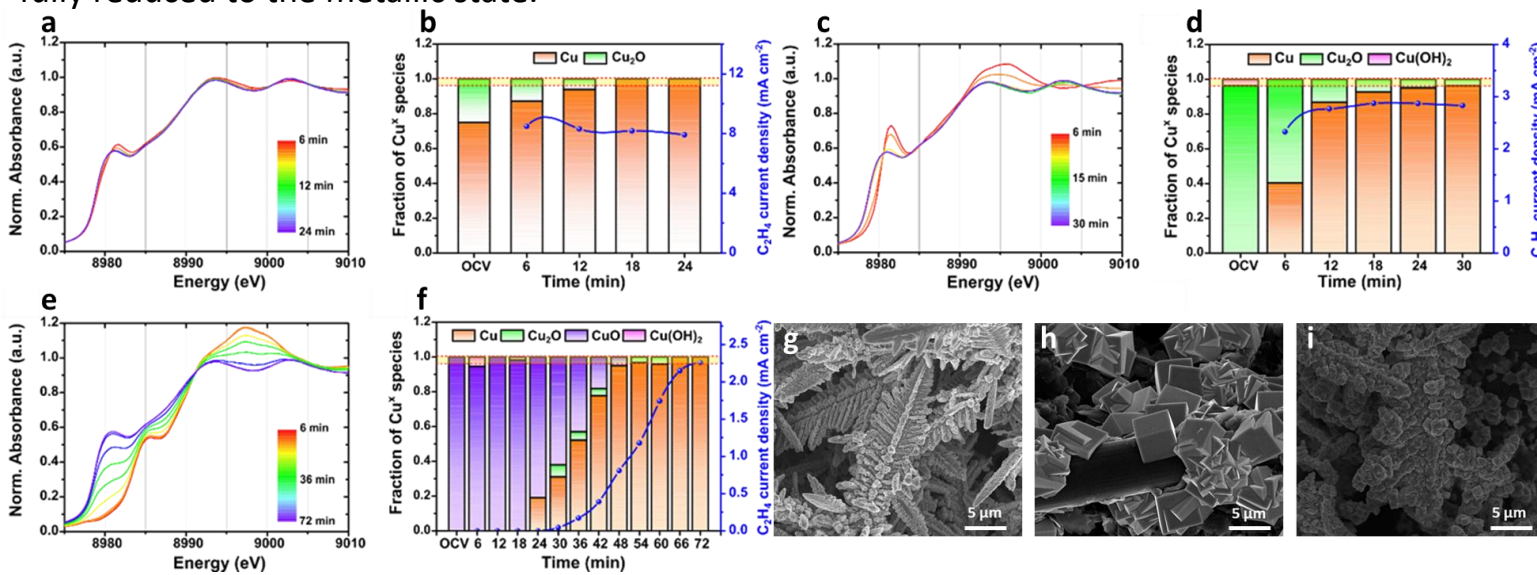


Figure 1. *Operando* XAS and corresponding current densities for Cu (a, b), Cu_2O (c, d), and CuO (e, f). SEM images of as deposited Cu (g), Cu_2O (h), and CuO (i).

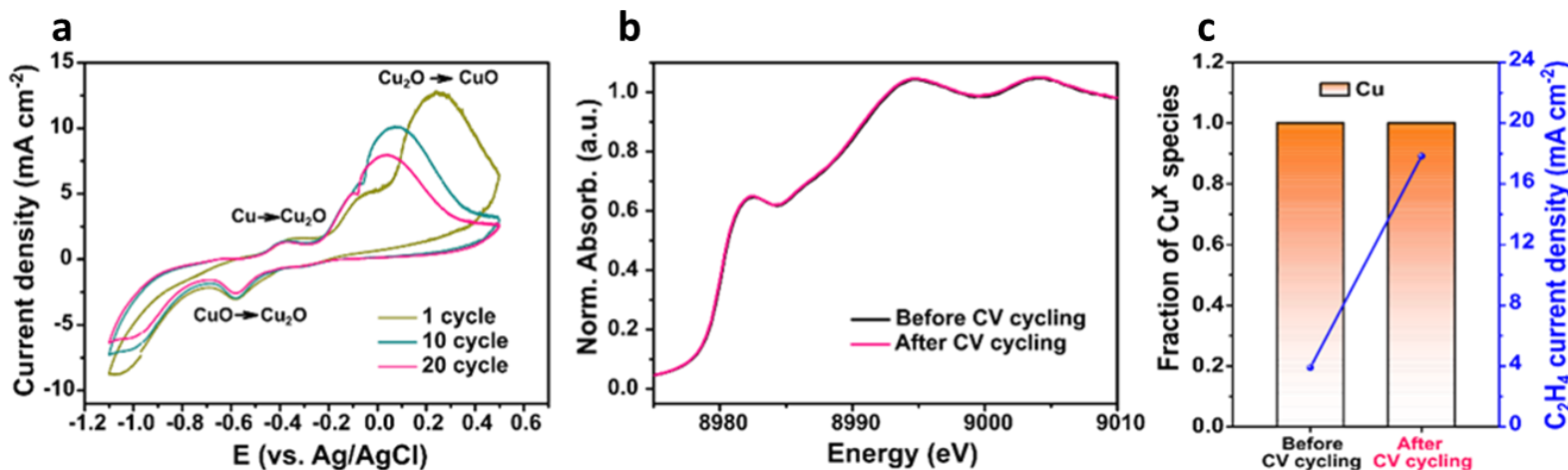


Figure 2. CV scans of Cu-GDE (a) resulted in no observable change of oxidation state for Cu (b) but resulted in enhanced C_2H_4 current densities (c).

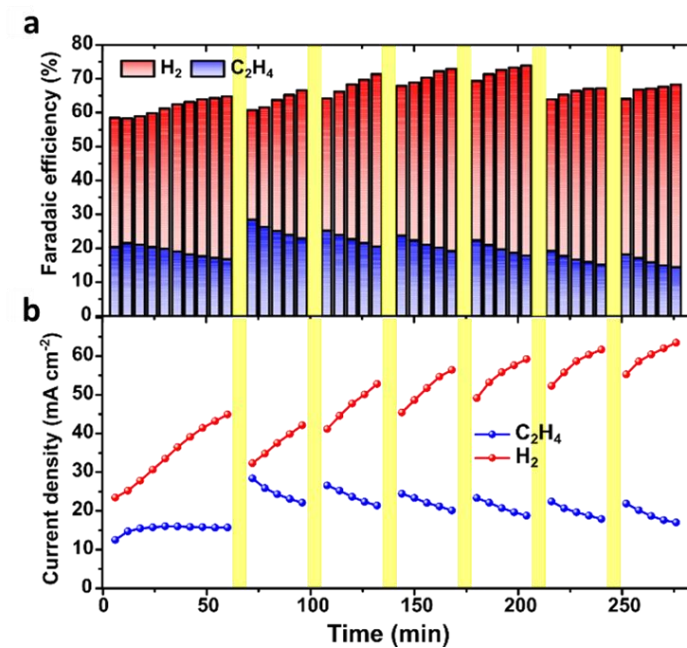


Figure 4. Faradaic efficiency (a) and current density (b) of Cu-GDE during bulk electrolysis with oxidation cycles. Yellow shaded regions indicate oxidation cycles

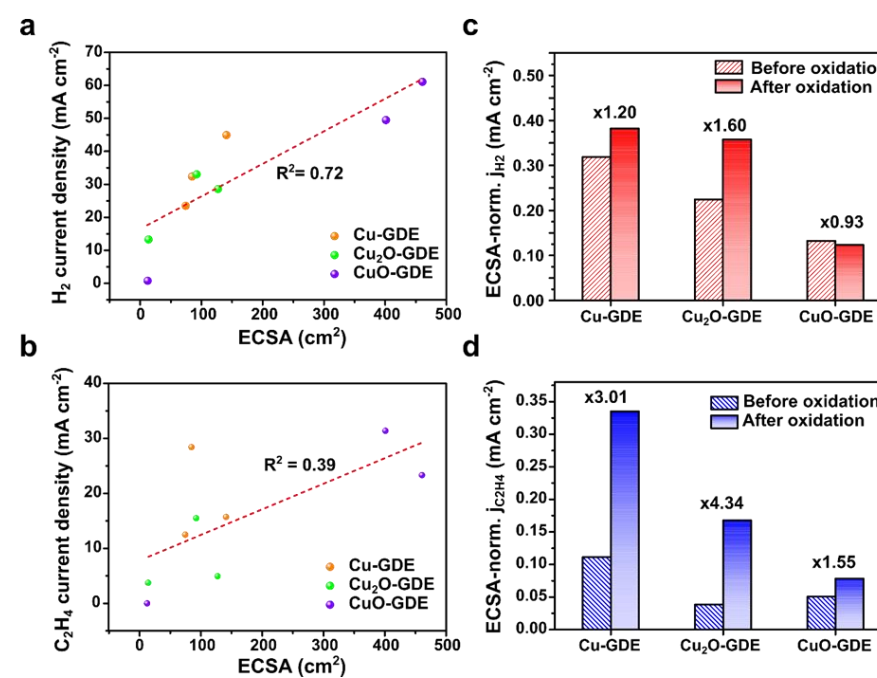


Figure 5. H_2 (a) and C_2H_4 (b) partial current density of Cu catalysts as a function of ECSA estimated by EDLC. Normalized current densities by ECSAs for each Cu catalyst for H_2 (c) and C_2H_4 (d) before and after electrochemical oxidation.

Conclusions

Combining data from XANES fitting and synchronized product analysis, we found that the C_2H_4 activity and selectivity increased as the oxides were reduced to metallic Cu^0 . By introducing an electrochemical oxidation process, which improved CORR performance, we successfully proved that the oxidation states and specific ion species do not correlate with the activity or selectivity of Cu catalysts. An electrochemical oxidation-reduction process was utilized as a regeneration method that restored the original catalyst activity and selectivity in the GDE cell without requiring cell disassembly.

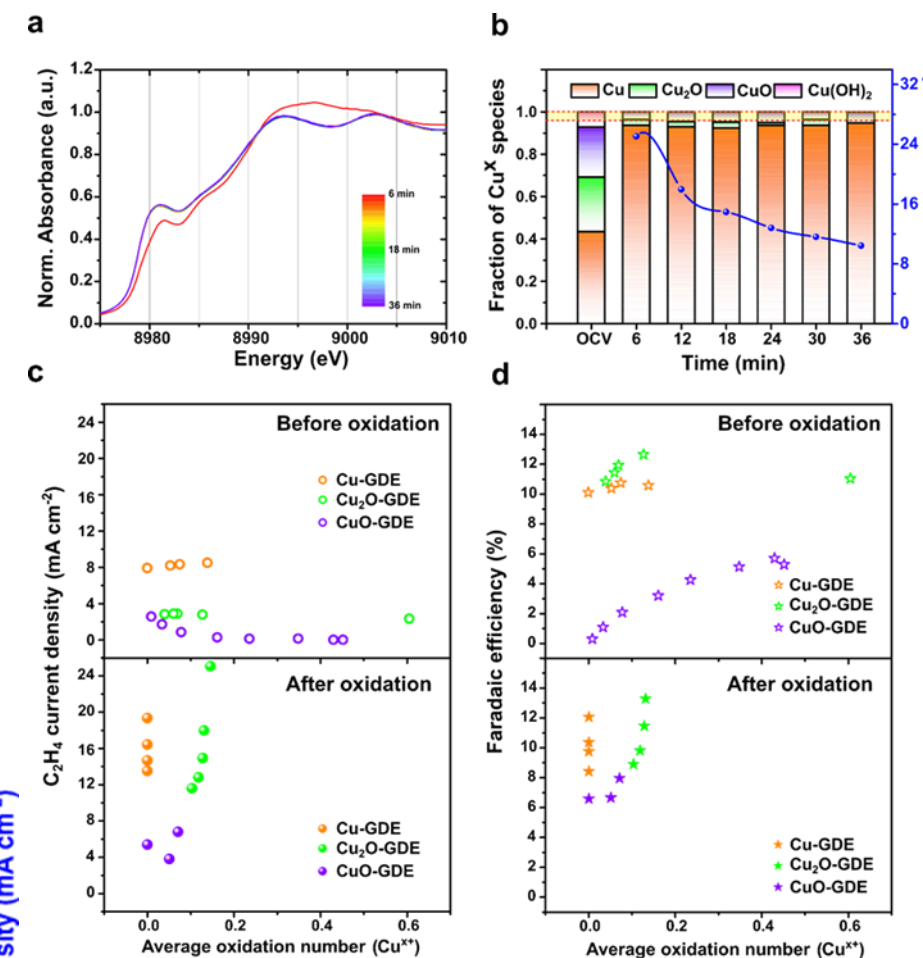


Figure 3. Cu K-edge XANES spectra of Cu_2O -GDE after applying anodic potential at 1.5 V vs. Ag/AgCl for 5 min (a). The calculated fraction of Cu oxidation states of Cu_2O -GDE after electrochemical oxidation (b). C_2H_4 partial current density (c) and Faradaic efficiency (d) of Cu catalysts as a function of Cu oxidation states before and after electrochemical oxidation.

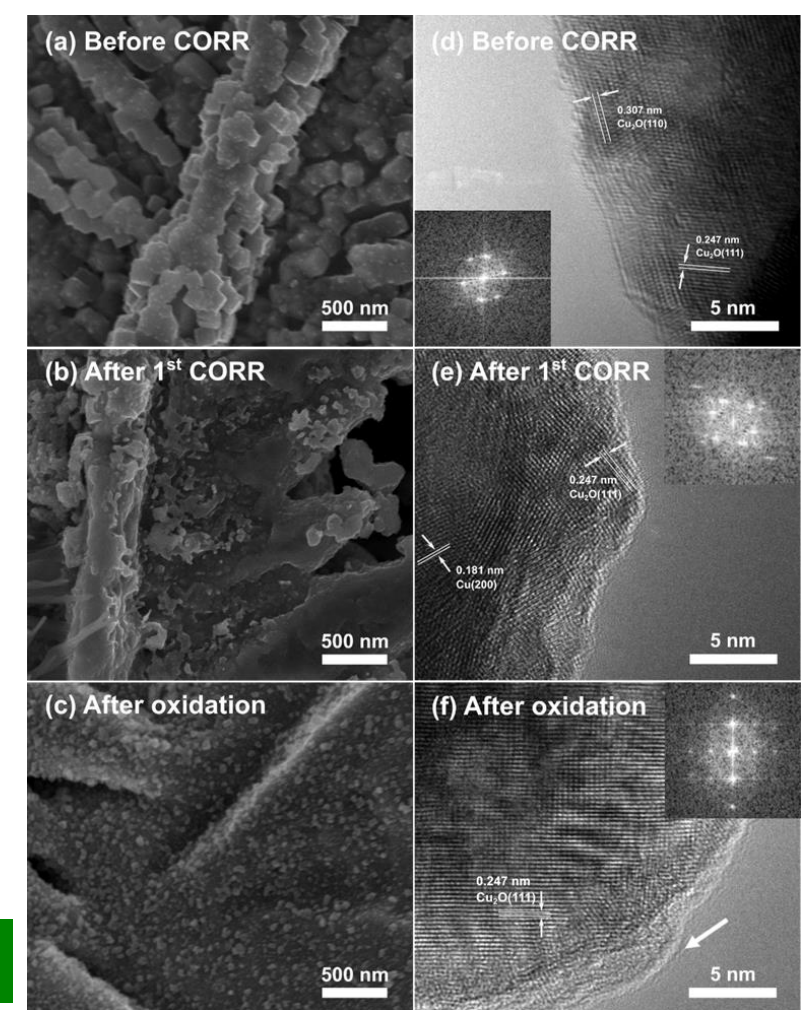


Figure 6. Ex-situ electron microscopy images of Cu as deposited (a, d), after first bulk electrolysis (b, e), and after oxidation (c, f).