Comparing FEFF9 XANES Simulations of Copper with Subsurface Oxygen to *Operando* Grazing Incidence XAS of Copper Thin Films During Electrochemical CO_2 Reduction

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The electrochemical reduction of carbon dioxide to fuels and useful chemicals with renewably-produced electricity could both reduce the atmospheric CO_2 concentration and provide a sustainable alternative to fossil fuels. Among the transition metals, only Cu catalyzes the electroreduction of CO_2 to highly reduced multicarbon products, such as C_2H_4, at a significant rate. It has been suggested that subsurface O atoms may contribute to the enhanced CO_2 electroreduction observed in nanostructured copper derived from oxidized precursors. Using a custom electrochemical cell with pumped electrolyte flow, we collected *operando* grazing incidence XANES and EXAFS spectra in fluorescence mode at the Cu K-edge on a Cu thin film electrocatalyst during CO_2 reduction. The highly metallic Cu K-edge XANES spectra observed at reducing potentials prompted us to use FEFF9 to simulate the XANES spectrum of Cu(111) both with and without approximately 5% subsurface O in an interstitial site between the 1st and 2nd atomic layers. The FEFF simulations show that, while Cu atoms directly bonded to O have significantly different K-edge XANES spectra, their contribution to the overall grazing incidence XANES spectrum is small and subtle. Until we correct for self-absorption in our *operando* grazing incidence XANES spectra, we cannot conclude that subsurface O is either present or absent in the Cu thin films that were probed during CO_2 electroreduction. However, the results of the FEFF simulations suggest that it may be possible to distinguish the grazing incidence K-edge XANES spectrum of entirely metallic Cu from that of Cu with subsurface O.