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Operando Grazing Incidence XAS of Polycrystalline Cu Thin Films During Electrochemical CO_2 Reduction

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Abstract

Using a custom cell, we have collected *operando* grazing incidence x-ray absorption spectra (GIXAS) in fluorescence mode at the Cu K-edge on polycrystalline Cu thin film electrodes during electrochemical CO_2 reduction (CO_2R). At potentials relevant to CO_2R, our *operando* GI-XANES spectra show that the Cu surface is highly reduced and no bulk Cu oxide phase is present. However, this is not conclusive evidence of the absence of subsurface oxygen during CO_2R, because XANES simulations in FEFF9 indicate that a small amount of subsurface oxygen in Cu(111) may not be detectable with Cu K-edge GIXAS. Analysis of the *operando* GI-EXAFS spectra is ongoing and may provide additional insights.

Introduction

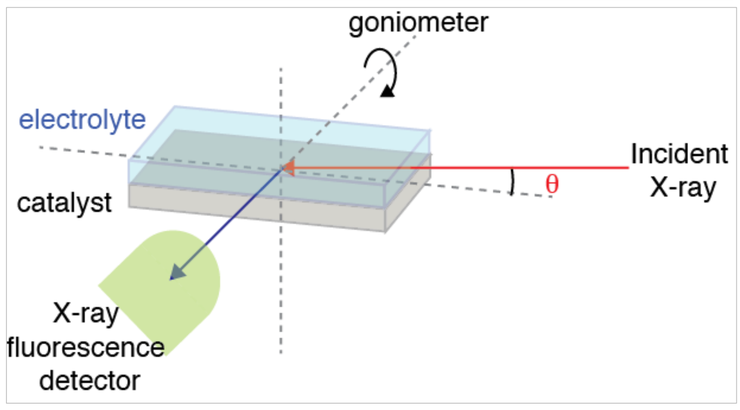


Image courtesy of Dr. Walter Drisdell

- At grazing incidence, x-rays probe the top 2-4 nm of Cu thin films.
- Our electrochemical flow cell collects *operando* GIXAS by minimizing electrolyte scattering and removing gas bubbles from the WE surface.

Outlook

- With our custom cell, we can collect *operando* GIXAS spectra at absorption edges above 8.0 keV and at current densities above 10.0 mA/cm^2 in aqueous electrolyte.
- No bulk Cu oxide is detected in the top 2-4 nm of polycrystalline Cu thin films at potentials relevant to CO_2R.
- GIXAS spectra can be simulated for proposed surface structures.

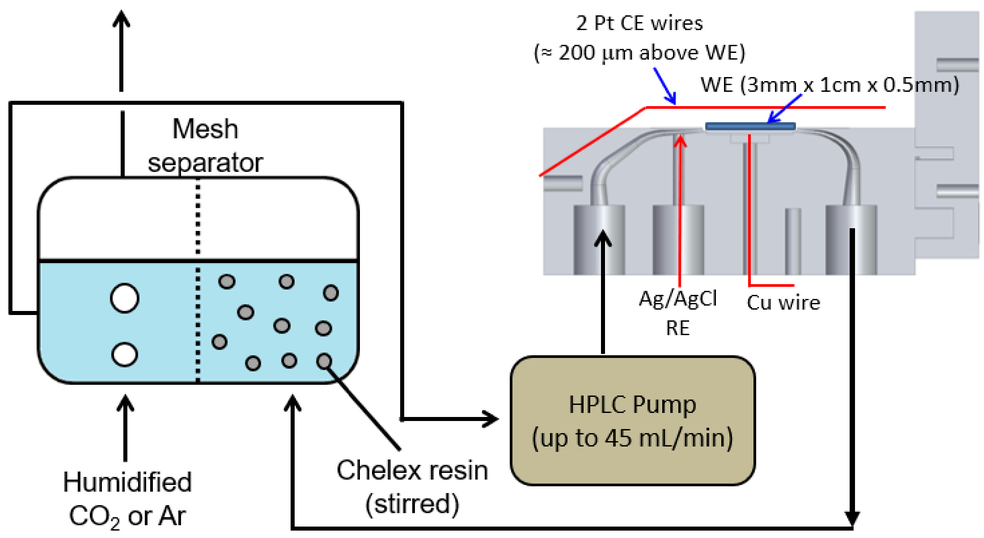
Acknowledgments

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993.

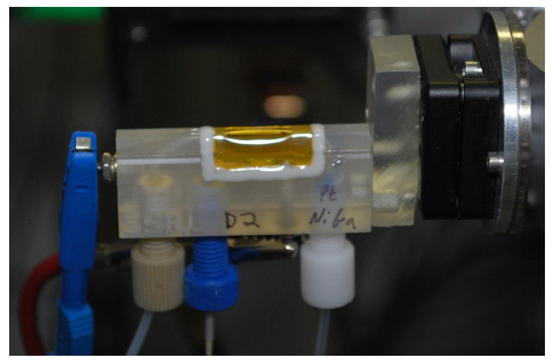
Operando Cu K-edge GIXAS spectra were collected at Beamline 11-2 at the Stanford Synchrotron Radiation Lightsource. In addition, we thank the Stanford Nanocharacterization Laboratory for use of their facilities.

Results, Highlights, and Accomplishments

Custom Electrochemical Cell

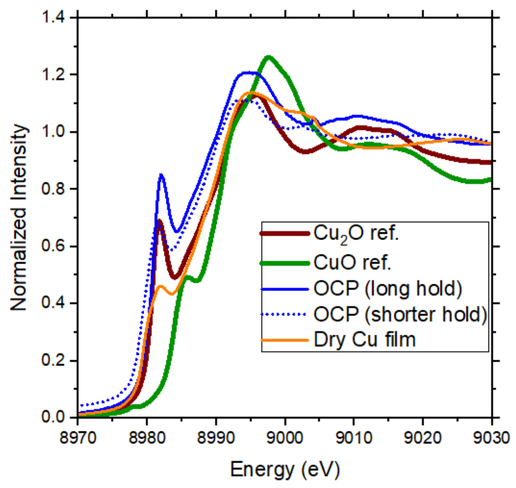


- 3-D printed cell
- 50-nm Cu and 3-nm Cr on n-type Si(100) substrate
- Back contact with In/Ga eutectic and Ag epoxy



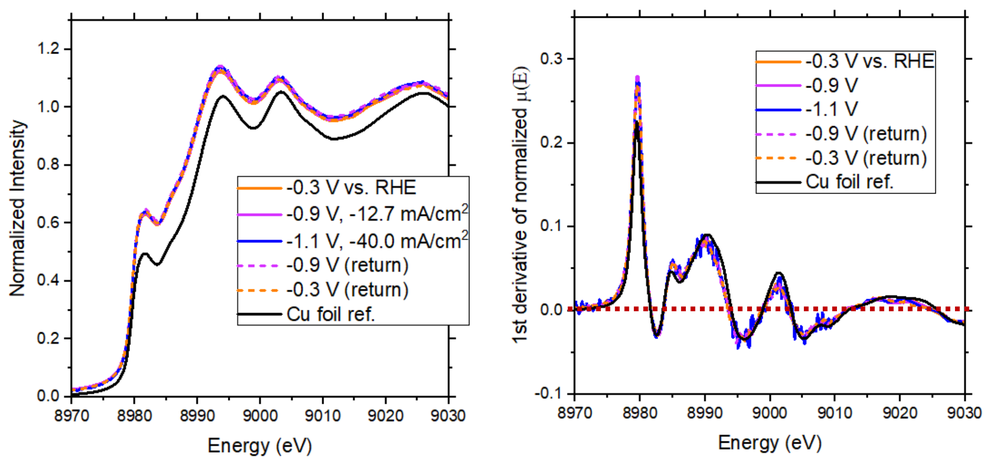
Images courtesy of Dr. Ryan Davis and Dr. Jeremy Feaster

Operando Grazing Incidence Cu K-edge XANES

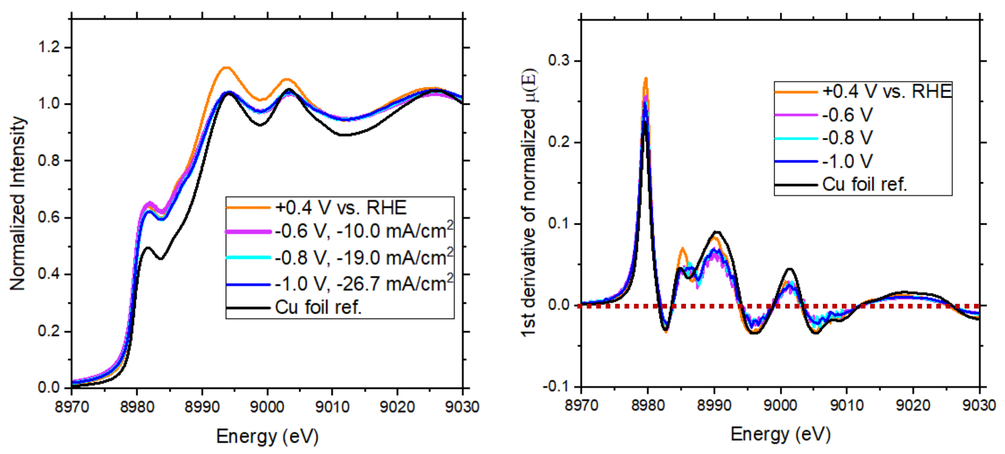


- Oxide peaks are present at grazing incidence on the dry film and at open-circuit.
- GI-XANES is highly reduced at cathodic potentials.
- 1st derivative of XANES also shows Cu is highly reduced.

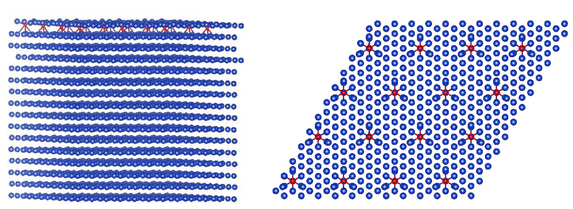
CO_2-sparged 0.1 M $KHCO_3$ (pH 6.8)



Ar-sparged 0.1 M potassium phosphate (pH 6.8)



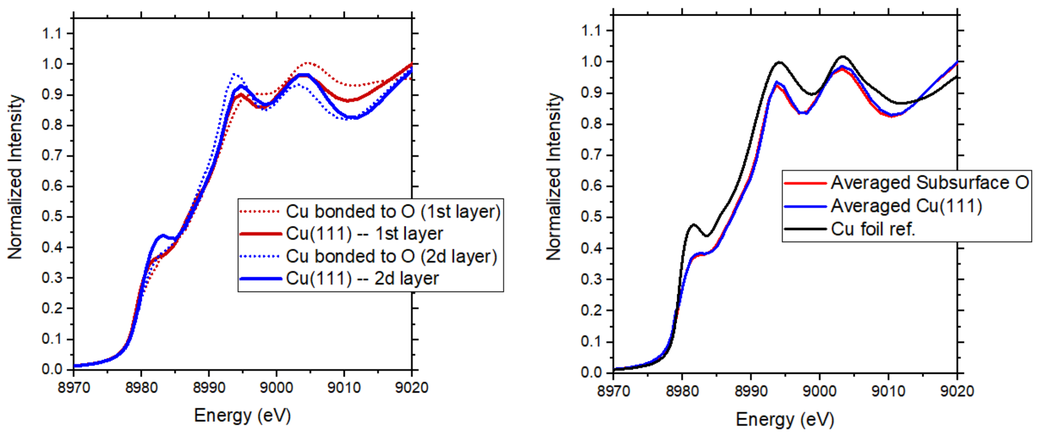
FEFF9 GI-XANES Simulations for Subsurface O in Cu(111)



Structures courtesy of Meredith Fields

Cu(111) with ≈5% subsurface O in an interstitial site between the top 2 layers (which strengthens CO binding).

- Only Cu atoms directly bonded to O have a significantly different K-edge XANES spectrum.
- **After averaging the contributions of all Cu atoms, the effect of subsurface O is very small.**



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