

# An Electrochemical Surface Science Perspective of Operando Structure-Activity-Selectivity Correlations in Electrocatalysis

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## Abstract

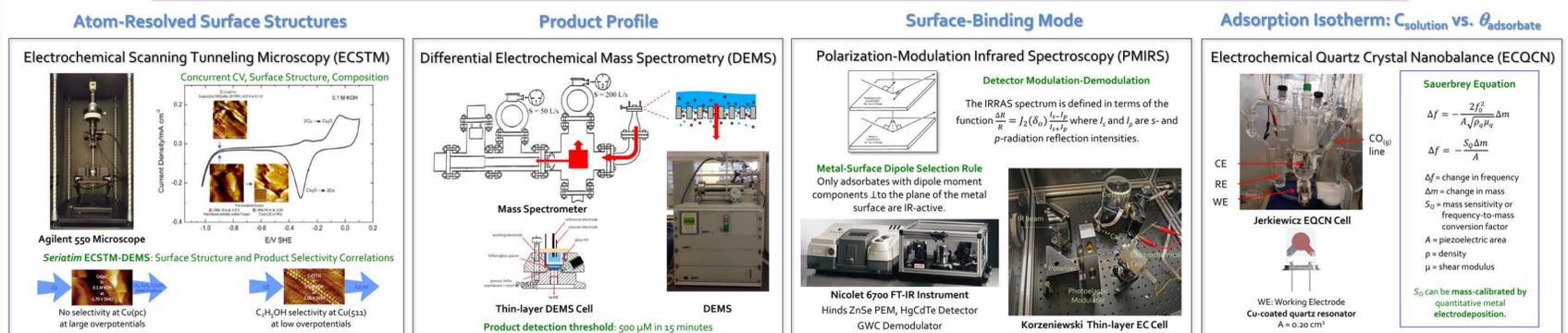
Electrocatalysis – the action of a heterogeneous catalyst under electrochemical conditions – is a surface-mediated process. Activity and selectivity are dependent upon the composition and the crystallographic structure of the electrode surface, the nature of the reactant-catalyst interactions, and the applied electrode potential. The *surface science approach* to electrocatalysis entails the scrutiny of surfaces with well-defined structure and composition *before, during, and after* the reaction of interest so that unambiguous correlations can be drawn. The merits of the often slow and invariably rigorous electrochemical surface science protocols are showcased herein for CO<sub>2</sub> reduction studies. Systematic investigations are built upon copper, the sole monometallic electrocatalyst for the production of a variety of energy-rich molecules. The development and the *seriatim* implementation of *operando* tools have led to the discovery of (i) the potential-driven surface reconstruction of polycrystalline Cu into a (100)-terminated surface; (ii) the relative stability of the low-index facets of Cu; (iii) the atomic details of the chemisorption of CO on Cu(100) under different electrolytic environments; and (iv) the specific surface structure selective for the formation of ethanol, C<sub>2</sub>H<sub>5</sub>OH, in alkaline medium.

## Introduction

Structure-composition-activity relationships underpin the principles of rational design for new electrocatalysts. The reliability of these correlations in CO<sub>2</sub>R rests on the careful curation of data that embrace (i) delineation of bulk-vs-surface composition; (ii) acquisition of atomically resolved surface structures instead of gross morphological analysis; and (iii) determination of reliable electrochemically active surface area that allows calculation of accurate current densities. The idiosyncratic surface chemistry of Cu has necessitated the tenets of electrochemical surface science, elevating the efforts from mere "model" studies to *operando* inquiries of "real world" surfaces.

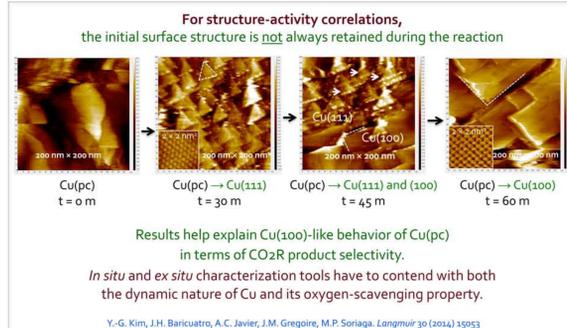
## Accomplishments and Highlights

### Seriatim Implementation of Operando ECSTM, DEMS, PMIRS, and ECQCN



### Operando Studies of Electrocatalytic Surface Structure, Activity, and Product Selectivity

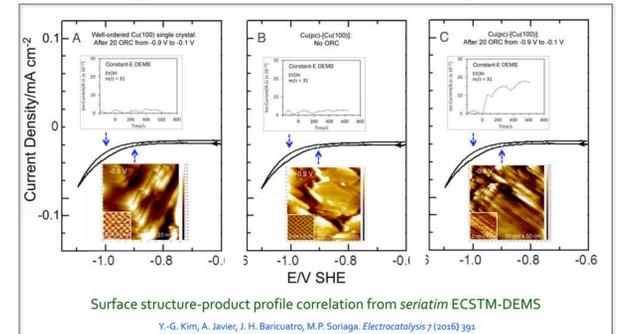
#### "Real World" Electrocatalysts: Surface Reconstruction of Cu(pc) at CO<sub>2</sub>R Conditions



#### Surface Chemical Considerations: Cu is an O<sub>2</sub> Scavenger No CO adsorption on Cu at Room T

- The search for better-than-Cu catalysts for CO<sub>2</sub>R is best anchored to the ascription of specific surface properties (structure and composition) to performance metrics (current density, product selectivity).
- Intrinsic activity and selectivity of a catalyst primarily rely on surface transactions rather than distal events in the bulk solution.
- The "non-nobility" of Cu necessitates *operando* characterization methods in CO<sub>2</sub>R studies.
- The hallmark of a true *operando* method in electrochemical surface science is the contemporaneous determination of surface characteristics and reaction rate.
- Applied potential is the primary driving force of CO adsorption on Cu at room temperature.
- Cu is zerovalent under CO<sub>2</sub>R conditions.

#### Discovery of an Ethanol-Selective Cu(511) Surface Electrogenerated from Oxidation-Reduction Cycles (ORC)



## Team



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<sup>†</sup>M.P.S. passed away on July 17, 2019. John C. Hemminger (UC-Irvine) has served generously the team in M.P.S.'s stead

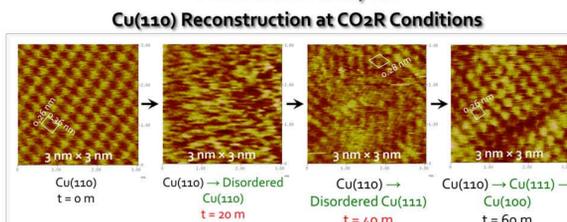
## Outlook

The electrochemical surface science of CO<sub>2</sub>R and COR provides a template for future atomic-level studies of novel electrocatalytic systems. The examples shown here demonstrate the need for the development of *operando* methods suitable for the unique surface chemistry of the catalytic material and analyte.

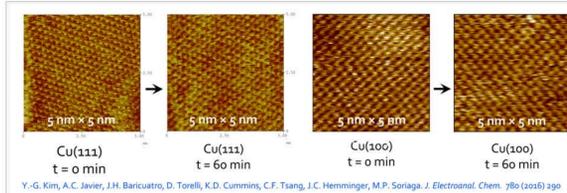
## Acknowledgments

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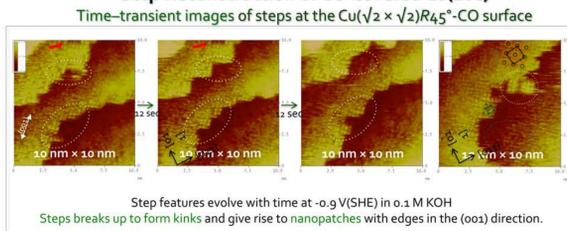
#### Model Electrocatalysts: Cu(110) Reconstruction at CO<sub>2</sub>R Conditions



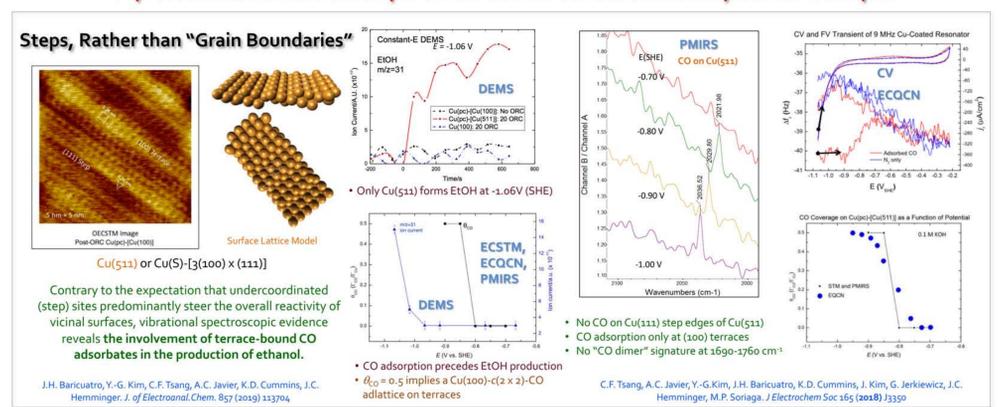
#### Cu(111) and Cu(100) Surfaces are Stable at -0.9 V/0.1 M KOH



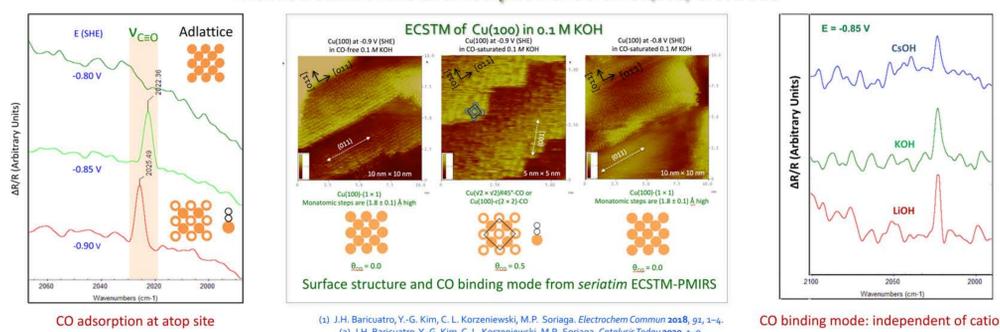
#### Step Reconstruction of CO-covered Cu(100)



#### Unprecedented Seriatim Quadruple Combination of Surface-Sensitive Operando Techniques



#### Atomic Details of the Chemisorption of CO on Cu(100) Electrode



## Generalizations, Implications, and Prospects

- CO<sub>2</sub>R, in the context of artificial photosynthesis, is an interfacial problem that can be compartmentalized, at first approximation, as an investigation of the electrical double-layer region.
- The nature of the catalytic surface dictates the extent of applicability of *ex situ* and *in situ* characterization methods as approximations of *operando* counterparts. Oxophilic surfaces like Cu are best examined during, rather than before and/or after, the reaction. The possibility of surface reconstruction places a caveat on any structure-activity correlation from *ex situ* and *in situ* analyses.
- Multihyphenated analytical techniques implemented in *seriatim* mode are powerful tools for the interrogation of electrode surfaces under authentic electrocatalytic conditions.
- Progress in the mechanistic understanding of electrocatalytic reactions requires the development of *operando* methods that address both the short surface residence time and very low submonolayer coverages of intermediates.