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Cu-Sn Bimetallic CO_2 Reduction Catalysts: Assembling the Puzzle of How Composition, Structure, Morphology and Speciation Affect Activity and Selectivity

Laura C. C. Pardo Perez[1], Alexander Arndt[1], Sasho Stojkovikj[1] and Matthew T. Mayer[1]

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Abstract

In the field of electrochemical reduction of CO_2 (CO_2ER) Cu and oxide derived OD-Cu electrocatalysts have been widely studied due to their unique capability to produce high added value products, such as CO, hydrocarbons and alcohols, albeit with relatively low selectivity.[1] Cu-M bimetallic catalysts are a promising approach to break scaling relations among key intermediates and modulate the CO_2ER selectivity. In the past 5 years, several studies on the CO_2ER activity of Cu-Sn bimetallic catalysts have demonstrated remarkably high selectivities towards CO[2,3] or formate.[4,5] In general, comparison of several studies employing various Cu-Sn stoichiometries shows that Sn-poor catalysts are typically selective towards CO production, while Sn-rich catalysts favor formate ($HCOO^-$). However, the specific optimal compositions leading to high activity towards CO or formate vary significantly among reports. [6–8] Furthermore, the mechanistic origins of the selectivity differences among Cu-Sn catalysts remains a topic of debate.

Trends in product selectivity have been ascribed to aspects including composition, lattice effects,[7] charge redistribution among metals in alloy structures,[9] oxidation states,[4,8] and the resulting effects on adsorption strength of key intermediates (e.g. *COOH, *OCHO, *CO, *H) directing selectivity among H_2, CO and $HCOO^-$. A comparison of the relevant literature has allowed us to establish common trends in CO_2ER activity of Cu-Sn of various morphologies, synthetic procedures and speciation (Oxide derived vs Alloy materials) and identify points of controversy and key open questions that might help unifying the understanding of the activation of CO_2 on Cu-Sn bimetallics. At the center of the debate is the persistence of oxidized metal sites during CO_2ER and the precise nature of the active site. A major challenge in this regard, is the complex dependence of catalyst structure and composition with applied electrochemical bias.

In this context, we explore X-ray spectroscopies as powerful tools to investigate the chemical environment and oxidation state of metal sites Sn and Cu in bimetallic electrocatalysts. By correlating diverse X-ray spectroscopy methods (soft and hard X-ray absorption (XAS) techniques, as well as X-ray photoelectron spectroscopy (XPS)), complementary information can be obtained on the chemical environment of metal sites in an electrocatalyst bulk and surface. We report our study on the dependence of structure and composition on applied electrochemical potential in Sn-functionalized Cu catalysts, achieved by combining *in situ* hard XAS, *ex situ* soft-XAS and XPS toward building a more complete picture of this model catalyst system.

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