

# Comparative Spectroscopic Study Revealing Why the CO<sub>2</sub> Electroreduction Selectivity Switches from CO to HCOO<sup>-</sup> at Cu–Sn- and Cu–In-Based Catalysts

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**ABSTRACT:** To address the challenge of selectivity toward single products in Cu-catalyzed electrochemical CO<sub>2</sub> reduction, one strategy is to incorporate a second metal with the goal of tuning catalytic activity via synergy effects. In particular, catalysts based on Cu modified with post-transition metals (Sn or In) are known to reduce CO<sub>2</sub> selectively to either CO or HCOO<sup>-</sup> depending on their composition. However, it remains unclear exactly which factors induce this switch in reaction pathways and whether these two related bimetal combinations follow similar general structure–activity trends. To investigate these questions systematically, Cu–In and Cu–Sn bimetallic catalysts were synthesized across a range of composition ratios and studied in detail. Compositional and morphological control was achieved via a simple electrochemical synthesis approach. A combination of operando and quasi-in situ spectroscopic techniques, including X-ray photoelectron, X-ray absorption, and Raman spectroscopy, was used to observe the dynamic behaviors of the catalysts' surface structure, composition, speciation, and local environment during CO<sub>2</sub> electrolysis. The two systems exhibited similar selectivity dependency on their surface composition. Cu-rich catalysts produce mainly CO, while Cu-poor catalysts were found to mainly produce HCOO<sup>-</sup>. Despite these similarities, the speciation of Sn and In at the surface differed from each other and was found to be strongly dependent on the applied potential and the catalyst composition. For Cu-rich compositions optimized for CO production (Cu<sub>85</sub>In<sub>15</sub> and Cu<sub>85</sub>Sn<sub>15</sub>), indium was present predominantly in the reduced metallic form (In<sup>0</sup>), whereas tin mainly existed as an oxidized species (Sn<sup>2/4+</sup>). Meanwhile, for the HCOO<sup>-</sup>-selective compositions (Cu<sub>25</sub>In<sub>75</sub> and Cu<sub>40</sub>Sn<sub>60</sub>), the indium exclusively exhibited In<sup>0</sup> regardless of the applied potential, while the tin was reduced to metallic (Sn<sup>0</sup>) only at the most negative applied potential, which corresponds to the best HCOO<sup>-</sup> selectivity. Furthermore, while Cu<sub>40</sub>Sn<sub>60</sub> enhances HCOO<sup>-</sup> selectivity by inhibiting H<sub>2</sub> evolution, Cu<sub>25</sub>In<sub>75</sub> improves the HCOO<sup>-</sup> selectivity at the expense of CO production. Due to these differences, we contend that identical mechanisms cannot be used to explain the behavior of these two bimetallic systems (Cu–In and Cu–Sn). Operando surface-enhanced Raman spectroscopy measurements provide direct evidence of the local alkalization and its impact on the dynamic transformation of oxidized Cu surface species (Cu<sub>2</sub>O/CuO) into a mixture of Cu(OH)<sub>2</sub> and basic Cu carbonates [Cu<sub>x</sub>(OH)<sub>y</sub>(CO<sub>3</sub>)<sub>y</sub>] rather than metallic Cu under CO<sub>2</sub> electrolysis. This study provides unique insights into the origin of the switch in selectivity between CO and HCOO<sup>-</sup> pathways at Cu bimetallic catalysts and the nature of surface-active sites and key intermediates for both pathways.

**KEYWORDS:** CO<sub>2</sub> electroreduction, Cu nanostructures, in situ spectroscopy, bimetallic catalysts, electrodeposition

