**QXAFS Study of Chemical and Structural Transformations in Copper-Zinc Nanocatalysts during the Optimized Pulsed CO2 Electrocatalytic Reduction toward Ethanol**

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Electrocatalytic CO2 reduction reaction (CO2RR) converts CO2 into value-added chemicals and fuels, and is an attractive pathway for closing the carbon cycle.1 Copper‑based nanocatalysts are commonly used for CO2RR due to their unique ability to convert CO2 into more complex hydrocarbons, but the distribution of reaction products is hard to control.2 A commonly used strategy for tuning the catalysts selectivity is to combine copper with a secondary CO-producing metal such as zinc.3 Furthermore, recently it was proposed that one can steer the chemical state and structure of the Cu catalyst’s surface (and, hence, its selectivity) by periodically applying oxidative potentials during the CO2RR.4 However, the bimetallic catalysts experience structural, compositional, and morphological changes when exposed to CO2 reduction and oxidizing conditions.2 These transformations affect their catalytic properties, but the atomistic details of this process remain largely elusive. *Operando* X-ray absorption spectroscopy (XAS) is one of a few techniques that can provide direct insight into the evolution of working catalysts.5 For bimetallic materials, XAS is especially attractive, since this element-specific method probes the catalyst’s local structure from the perspective of both metals.6

In this study, we used the QXAFS (quick X-ray absorption fine structure) method to track the time-dependent changes of ZnO-decorated Cu2O nanocubes (30 nm) under CO2RR and oxidizing conditions. Particular attention was devoted to studies of the potential‑dependent behavior of the catalysts. By combining QXAFS with cyclic voltammetry scans, we identified the main structural and chemical changes taking place in the CuZn catalysts under CO2RR and anodic conditions, and the corresponding potential values. In particular, the formation of metallic Zn and a ZnCu alloy was observed, each of these phases having unique reduction and oxidation potentials. This information was used to design pulsed reaction protocols that ensured enhanced selectivity of our catalyst toward ethanol production.

The presented approach is thus a powerful tool to gain a detailed mechanistic understanding of how the bimetallic catalyst adapt on an atomic- and nanoscale to the reactive environment. The obtained knowledge allows us to design an optimized reaction protocol for CO2RR, making it a competing net-zero approach for energy transformation and storage.

References

1. Y. Hori, A. Murata, R. Takahashi, J. Chem. Soc., Faraday Trans. 1 85, 2309 (1989).
2. A. D. Handoko, F. Wei, B. S. Yeo, Z. W. Seh, Nat. Catal. 1, 922 (2018).
3. H. S. Jeon, J. Timoshenko, F. Scholten, I. Sinev, A. Herzog, F. T. Haase, B. Roldan Cuenya, J. Am. Chem. Soc. 141, 19879 (2019).
4. H. S. Jeon, J. Timoshenko, C. Rettenmaier, A. Herzog, A. Yoon, S. W. Chee, S. Oener, U. Hejral, F. T. Haase, B. Roldan Cuenya, J. Am. Chem. Soc. 143, 7578 (2021).
5. J. Timoshenko, B. Roldan Cuenya, Chem. Rev. 121, 882 (2021).
6. S. Bordiga, E. Groppo, G. Agostini, J. A. van Bokhoven, C. Lamberti, Chem. Rev. 113, 1736 (2013).