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Understanding the Structure-Properties Relationship in Nanocatalysts for CO2 Electroreduction using Time-Resolved XAS and Advanced Data Analysis

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Electrochemical CO₂reduction to valuable chemical feedstocks and fuels, powered by the energy from renewable sources, is an attractive possibility for the CO₂ minimization in the atmosphere (e.g., at industrial sites where concentrated CO₂ is available) but a suitable catalyst is needed. Currently Cu-based catalysts are the only ones that can convert CO₂ with significant yield to energy dense C₂₊ products, such as ethylene and ethanol. Nonetheless, the distribution of possible reaction products for CO₂ reduction reaction (CO₂RR) over Cu catalysts is broad, and the selectivity of the catalyst is hard to control. Atomistic details of the CO₂RR and the nature of active states also remain debated due to the coexistence and transformations under reaction conditions of multiple copper species. To address these questions, X-ray absorption fine structure spectroscopy (XAFS) has been used for decades [1]. Nonetheless, new exciting possibilities are enabled by the recent development in the instrumentation and data analysis approaches. The former allow now operando quick XAFS (QXAFS) studies with subsecond time resolution. Thus, the evolution of the catalyst structure and composition under realistic working conditions can be directly tracked for the first time. Moreover, QXAFS method provides also a direct insight into the catalyst dynamics under non-equilibrium reaction conditions, which have been recently proposed as an attractive way to steer the catalyst functionality by dynamically controlling the catalyst's surface composition and structure [2]. On the other hand, the breakthrough developments in data science provide now the possibility to employ machine learning methods for the interpretation of XAFS data, allowing quick analysis of disordered, heterogeneous structures of working electrocatalysts [3,4,5].
Here we demonstrate the potential of QXAFS method and machine learning-based data analysis on an example of studies of Cu-based catalysts under potentiostatic and dynamic (pulsed) CO₂RR conditions. In particular, our approach allows us to explain the different selectivity trends for shape-selected Cu₂O nanocubes (NCs) exposed to pulsed CO2RR with different pulse durations [2], to understand the dynamics of NCs oxidation state under pulsed and static CO₂RR in gas-fed cell at high current densities [6], and to track the fast alloying/dealloying processes and their link to oxidation/reduction processes in Zn-decorated Cu₂O NCs [5]. The compelling evidences about the nature of the catalyst active states, obtained from *operando* time-resolved XAFS coupled with advanced data analysis approaches allow us to decouple the contributions of different species coexisting in working catalysts to the CO₂RR selectivity, and provide guidelines for the further optimization of catalytic systems and reaction protocols.

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