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Insights on the Restructuring of Copper Complexes During Electrochemical Reduction of Carbon Dioxide

Rafael L. Romano^a, Kotaro Sasaki^b, Fabio H. B. Lima^{a,*}

^a São Carlos Institute of Chemistry, University of São Paulo
Av. Trabalhador São-Carlense, 400, São Carlos, São Paulo, Brazil

^b Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973, United States

*e-mail: fabiohbl@iqsc.usp.br

The electrochemical reduction of carbon dioxide (ERCO₂) stands out as a promising CO₂ utilization technology that enables the production of valuable fuels and chemicals. However, important drawbacks for its practical applications lie on the high required overpotentials and poor selectivity, making the rational design of active, selective and stable electrocatalysts a key step towards large scale ERCO₂ usage.^[1] In the past few years, copper complexes and other Cu-based molecular electrocatalysts have gained substantial attention due to their well-defined structure and high ERCO₂ selectivity, and efforts have been directed towards understanding the correlation between catalytic performance, catalyst structure and identity of the active sites. Indeed, several studies revealed that many copper-based molecular electrocatalysts exhibited restructuring under CO₂ reduction conditions, undergoing changes in Cu oxidation state and coordination number, which significantly affected their catalytic properties. Interestingly, evidences of reversible restructuring have been reported.^[2] In the present study, the restructuring phenomena and the electrocatalytic properties of the copper complexes [Cu(bzimpy)Cl₂] and [Cu(pyrben)₂(NO₃)]NO₃ were evaluated during ERCO₂. Here, *bzimpy* and *pyrben* are the water-insoluble organic ligands 2,6-bis(2-benzimidazolyl)pyridine and 2-(2-pyridyl)benzimidazole, respectively. Quantitative product analyses revealed that both complexes are highly selective for CO₂ reduction, with [Cu(bzimpy)Cl₂] exhibiting a Faradaic Efficiency of ~ 45% towards C₂ products (ethylene, ethanol and acetic acid) at -1.24 V vs. RHE (Figure 1(a)). In-situ X-ray Absorption Spectroscopy experiments evidenced that the Cu complexes undergo structural changes under ERCO₂ conditions (Figure 2(b)), with Cu²⁺ being reduced to nanostructured Cu⁰ species, the real active sites. Lead underpotential deposition (Pb-UPD) characterization suggests that the Cu⁰ structures formed at -1.24 V present a dominant contribution of the (100) orientation, which is in line with the high C₂ products selectivity.

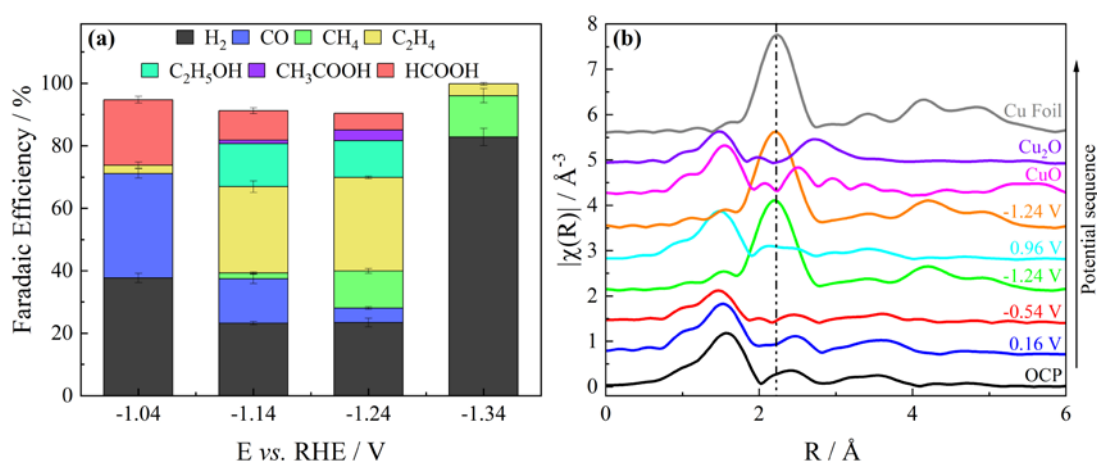


Figure 1: (a) Faradaic Efficiencies for CO₂ reduction products obtained with [Cu(bzimpy)Cl₂]. (b) FT-EXAFS spectra of [Cu(bzimpy)Cl₂] obtained at different applied potentials. Electrolyte: CO₂-saturated 0.1 mol L⁻¹ K₂SO₄ solution (pH = 4.2).

References:

- [1] NITOPI, S. *et al.* Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chemical Reviews*, **119**, 7610–7672, 2019.
- [2] WENG, Z. *et al.* Active sites of copper-complex catalytic materials for electrochemical carbon dioxide reduction. *Nature Communications*, **9**, 415, 2018.