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Durability Enhancement in CO_2 Electrocatalysis *via* Copper Complex Restructuring

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The electrocatalytic reduction of carbon dioxide ($ERCO_2$) enables the production of valuable fuels and chemicals. However, the development of CO_2 electrolyzers is hindered mainly by the poor selectivity and stability of the $ERCO_2$ catalyst [1]. In recent years, copper complexes and other Cu-based molecular catalysts have attracted significant interest due to their well-defined structures and high selectivity. Research efforts have focused on understanding the relationship between the catalyst structure or active site and selectivity. Studies have shown that many copper-based molecular electrocatalysts undergo restructuring under CO_2 reduction conditions, experiencing changes in Cu oxidation state and coordination number that greatly influence their catalytic behavior [2]. In the present study, the restructuring process and the electrocatalytic activity and selectivity of the copper complexes $[Cu(bzimpy)Cl_2]$ and $[Cu(pyrben)_2(NO_3)]NO_3$ (*bzimpy* and *pyrben* are the water-insoluble ligands 2,6-bis(2-benzimidazolyl)pyridine and 2-(2-pyridyl)benzimidazole, respectively) were investigated for the $ERCO_2$. *In-situ* X-ray Absorption (XAS) and Electron Paramagnetic Resonance (EPR) Spectroscopy experiments evidenced that the copper complexes undergo structural changes under $ERCO_2$ conditions, with Cu^{2+} being reduced to nanostructured Cu^0 species (the real active sites). Quantitative product analyses revealed that both complexes are highly active for CO_2 reduction, with $[Cu(bzimpy)Cl_2]$ exhibiting faradaic efficiency of *ca.* 45% towards C_2 products (ethylene, ethanol and acetic acid) at -1.24 V *vs.* RHE. Interestingly, and contrarily to what was observed for $[Cu(pyrben)_2(NO_3)]NO_3$ and for regular carbon-supported copper nanoparticles or Cu^{2+} ions anchored on carbon powder (taken as blanks), the $[Cu(bzimpy)Cl_2]$ catalyst presented a reversible restructuring behavior. After potential excursions to potentials slightly higher than the Cu^{2+}/Cu^0 equilibrium, the initial catalyst structure (N-coordinated Cu^{2+}) was restored, as evidenced by EPR and in-situ XAS and, after negative polarization, the activity was reestablished for the $ERCO_2$. This cycle was repeatedly several times, and the same initial structure and CO_2 reduction activity was obtained. These findings may guide the future synthesis of more stable catalysts, enabled by the reversible restructuring capability, offering new opportunities for the development of more durable carbon dioxide electrolyzers.

References

[1] POPOVIĆ, S. et al. *Stability and Degradation Mechanisms of Copper-Based Catalysts for Electrochemical CO2 Reduction*. Angewandte Chemie - International Edition, v. 59, n. 35, p. 14736–14746, 2020.
[2] WENG, Z. *et al.* Active sites of copper-complex catalytic materials for electrochemical carbon dioxide reduction. *Nature Communications*, **9**, 415, 2018.