Visualising active species in CO_2 electroreduction

Yu Yang[1], Yaohui Shi[2], Fengwang Li[1]*

[1]School of Chemical and Biomolecular Engineering and ARC Centre of Excellence for Green Electrochemical Transformation of Carbon Dioxide, The University of Sydney, NSW 2006, Australia

[2]Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China

*Corresponding author. Email: fengwang.li@sydney.edu.au

Abstract

Understanding the evolution of Cu-based catalysts during electrochemical CO_2 reduction (ECR) remains challenging. The study by Lim et al. in *Joule* devises an *operando* scanning transmission X-ray microscopy to investigate the dynamic phase transformations of Cu catalysts and reveals that Cu^{2+} species play a crucial role in enhancing C–C coupling. The findings inform the authors an approach to dynamically redirect the oxidation state of Cu, achieving, as a result, higher selectivity and efficiency for ECR catalysis.

Main

Electrochemical CO_2 reduction (ECR) is a promising technology for achieving net-zero carbon emissions and developing sustainable energy systems.[1] As one of the most promising non-precious metal catalysts for ECR, Cu-based catalysts can uniquely facilitate the formation of multi-carbon (C_{2+}) products such as ethylene and ethanol.[2]

Previous studies demonstrated that the selectivity of Cu-based catalysts is correlated with the oxidation state of copper species.[3] During ECR, the dynamic evolution of Cu oxidation states, including Cu^0, Cu^+, and Cu^{2+}, plays a critical role in modulating key reaction steps such as *CO adsorption and C–C coupling.[4] For example, it has been suggested that partially oxidized Cu species (e.g., Cu^+) enhance *CO adsorption, thereby promoting C–C bond formation,[5] while metallic Cu (Cu^0) facilitates the hydrogenation of adsorbed intermediates.[6] Nevertheless, there are few approaches to provide *in-situ*, real-time information on the dynamics of these diverse Cu states.

Traditional methods, such as bulk-averaged spectroscopy and *ex-situ* imaging, often fail to capture the real-time dynamics and spatial heterogeneity of Cu oxidation states at the nanoscale, limiting the comprehensive understanding of temporal evolution of Cu oxidation states during ECR and its relationship with the selectivity for C_{2+} products.

Advanced techniques with high spatial and temporal resolution are essential. In this context, *operando* scanning transmission X-ray microscopy (STXM) has emerged as a promising tool, allowing the tracking of catalysts' real-time chemical and morphological changes with exceptionally high sensitivity.[7] By leveraging such innovative methods, Lim and co-workers reported their study in a recent *Joule* publication,[8] aiming to provide new insights into the dynamic phase evolution of Cu-based catalysts during ECR. The findings bridge the knowledge gap between catalyst structure and performance.

Operando STXM enabled the authors to track Cu-based catalysts' chemical and morphological evolution in real-time, unveiling the critical role of oxidized copper species (Cu^{+} and Cu^{2+}) in enhancing catalytic activity. This advanced technique serves two crucial functions: (1) it provides exceptional sensitivity for mapping various oxidation states of Cu, revealing a significant correlation between the dynamic evolution of Cu^{2+} species on the metallic Cu catalyst surface and enhanced C–C coupling; and (2) it proposes an electrochemical redirection method of low- to high-activity catalysts by inducing Cu^{2+} phases.

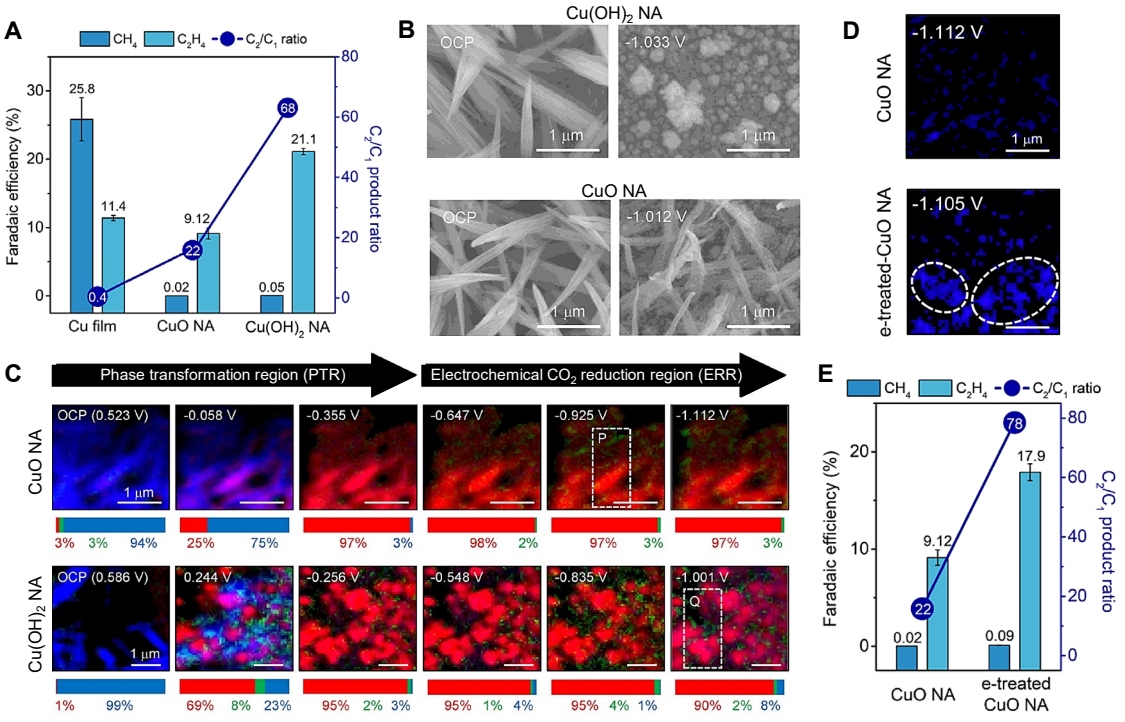

Figure 1. CO_2 reduction performance and chemical composition images of the Cu-based electrocatalysts during ECR

(A) FE and C_2/C_1 gaseous product ratio for CuO NA and $Cu(OH)_2$ NA at –1.0 V_{RHE} in an H-type cell.
(B) SEM images of $Cu(OH)_2$ NA and CuO NA at specific potential (OCP and –1.0 V_{RHE}).
(C) Operando chemical composition mapping images of the CuO NA and $Cu(OH)_2$ NA electrocatalysts at the phase transformation and electrochemical CO_2 reduction regions.
(D) Cu^{2+} phase images of e-treated CuO NA and CuO NA at –1.0 V_{RHE}. The intensity of the Cu^{2+} phase in the images was magnified 25-fold after eliminating the noise level.
(E) Faradaic efficiencies and C_2/C_1 product ratios of the CuO NA and e-treated CuO NA electrocatalysts at approximately –1.0 V_{RHE}.

To investigate the correlation between the morphological changes and evolution of the minor oxidized species during ECR, the authors compared $Cu(OH)_2$ nano-needle array ($Cu(OH)_2$ NA) with CuO NA, which has an identical Cu^{2+} oxidation state and similar shape to $Cu(OH)_2$ NA as confirmed by Raman spectroscopy, X-ray absorption spectroscopy (XAS), and scanning electron microscopy (SEM). When operating under ECR conditions in an H cell, $Cu(OH)_2$ NA and CuO NA catalysts exhibit significant differences in product selectivity and post-reduction morphology. The Faradaic efficiency (FE) ratios of the C_2/C_1 products reveal that higher C–C coupling selectivity was achieved on $Cu(OH)_2$ NA (67.8) than on CuO NA (22) (Figure 1A). Meanwhile, SEM images showed that $Cu(OH)_2$ NA undergoes pronounced structural changes

while CuO NA retains its initial needle-like morphology (Figure 1B), suggesting that the evolution in $Cu(OH)_2$ NA during ECR is crucial in promoting multi-carbon product formation.

To understand the mechanisms underlying these differences, the researchers first excluded the influence of electrochemical surface area (ECSA) and grain size, then employed *operando* STXM at the Cu L_3-edge with a spatial resolution of 50–75 nm to investigate changes in the local Cu oxidation state and morphology simultaneously (Figure 1C). By tracking the distribution of copper oxidation states at the nanoscale, they revealed that $Cu(OH)_2$ NA forms Cu^0 nano-agglomerates surrounded by Cu^+ and Cu^{2+} localized at the edges of the Cu^0 domains during ECR. In contrast, CuO NA showed minimal formation of Cu^{2+} species, correlating with its reduced ability to facilitate C_2 production. These observations suggest that the presence and distribution of Cu^{2+} species are critical factors in determining the selectivity and efficiency of copper-based catalysts for ECR.

The authors proposed that the observed Cu^{2+} species in $Cu(OH)_2$ NA were thermodynamically stabilized by copper (II) carbonate hydroxide species ($Cu^{2+}_x(CO_3)_y(OH)_z$) that dynamically persisted under ECR, as demonstrated through long-term *operando* STXM test and complementary *in-situ* surface-enhanced Raman spectroscopy (SERS). Using $Cu^{2+}_x(CO_3)_y(OH)_z$ as the model for Cu^{2+}-containing phases, density functional theory (DFT) calculations reveal that Cu^{2+} significantly lowers the energy barrier for *CO dimerization, a key step in ethylene formation. Besides, Cu^{2+} species can also stabilize carbonyl oxygen of *COOH (or $*CO_2$), enhancing the local $*CO/CO_2$ concentration near the cathode, potentially accelerating the C–C coupling activity.

Building on these insights, the researchers developed a method to enhance C_2 selectivity by introducing Cu^{2+} species into the catalyst structure. This redirection process partially reduced CuO NA to Cu_2O phase under negative potentials, followed by spontaneous re-oxidation at open-circuit potential (OCP). During this process, Cu^+ dissolves into the electrolyte as Cu^{2+} ions, which re-deposit onto the catalyst surface, creating Cu^{2+} motifs, denoted as e-treated CuO NA catalysts (Figure 1D). This approach significantly improved C_2 selectivity, with the modified CuO NA achieving nearly double the FE for ethylene compared to its unmodified counterpart (Figure 1E). This finding underscores the potential of dynamic phase engineering to optimize catalyst performance.

While this study provides promising insights into the spatiotemporal evolution of copper-based catalysts during ECR using *operando* STXM, limitations of the technique and mechanism studies warrant further improvement and exploration.

The STXM reactor employed in this study closely resembles an H-cell configuration, which inherently operates at low current densities due to high internal resistance and low CO_2 availability. However, the performance and structural evolution of ECR catalysts can vary substantially between different cells or current densities, due to the discrepancy in the local reaction environment, mass transport dynamics, and pH distribution.[9] Therefore, Cu-based catalysts' structural evolution and reaction mechanisms in flow cells and membrane electrode assembly (MEA) systems require further investigation, coupled with technical advancements in *operando* techniques to accommodate these configurations.

While this study demonstrates the important role of Cu^{2+} in promoting C_2 selectivity, it also acknowledges that Cu^{2+} is not the only active site for C_2 product formation. For example, C_2

products can still be generated in ECR when Cu^{2+} species are absent, as observed in the CuO NA catalyst. The inherent heterogeneity of active sites in copper-based catalysts complicates the establishment of clear links between catalytic performance and structure. For instance, introducing Cu^{2+} at OCP has limited control over the amount of Cu^{2+} formed during ECR turnovers, making it challenging to determine the optimal concentration of Cu^{2+} for C^2 production. This limitation hampers the rational design of highly efficient catalysts based on the Cu^{2+}-induced mechanisms proposed in this study.

Despite limits existing in the techniques, this work provides new insights into the dynamic evolution of Cu-based catalysts during ECR, emphasizing the critical role of Cu^{2+} species in enhancing C_2 selectivity. Using *operando* STXM, the researchers precisely tracked real-time morphological and compositional changes in copper catalysts with a ~50 nm spatial resolution. The findings reveal that stabilising Cu^{2+} species by forming $Cu^{2+}_x(CO_3)_y(OH)_z$ phases promotes C–C coupling and multi-carbon product formation by lowering the energy barrier for *CO dimerization and enhancing the local *CO/CO_2 concentration. Moreover, the study highlights the potential of dynamic phase engineering, demonstrating how the deliberate introduction and stabilization of Cu^{2+} motifs can transform low-activity catalysts into highly selective systems for ECR.

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Declaration of interests

The authors declare no competing interests.

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