**Operando** Electrochemical Liquid-Cell Scanning Transmission Electron Microscopy (EC-STEM) Studies of Evolving Cu Nanocatalysts for CO₂ Electroreduction

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**ABSTRACT:** The design and synthesis of nanocatalysts with well-defined sizes, compositions, and structures have revolutionized our accessibility to tunable catalyst activity and selectivity for a variety of energy-related electrochemical reactions. Nonetheless, establishing structure-(re)activity correlations requires the understanding of the dynamic evolution of pristine nanocatalysts and the identification of their active states under operating conditions. We previously communicated the *operando* observation of Cu nanocatalysts evolving into active metallic Cu nanograins for CO₂ electroreduction (Yang et al. Nature 2023, 614, 262–269). Here, we expand our discussion to the technical capabilities and further research applications of *operando* electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM), which enables quantitative electrochemistry while tracking dynamic structural evolution of sub-10 nm Cu nanocatalysts. The coexistent H₂ bubbles, often disruptive to *operando* spectroscopy, are an effective approach to create a thin-liquid layer that significantly improves spatial resolution while remaining electrochemically accessible to Cu nanocatalysts. *Operando* four-dimensional (4D) STEM in liquids provides insights into the complex structure of active polycrystalline metallic Cu nanograins. With continuous technical developments, we anticipate that *operando* EC-STEM will evolve into a powerful electroanalytical method to advance our understanding of a variety of nanoscale electrocatalysts at solid/liquid interfaces.

**KEYWORDS:** Operando, EC-STEM, 4D-STEM, CO₂RR, Dynamic evolution, Cu nanocatalysts

**INTRODUCTION**

Electrocatalysis is the cornerstone of sustainable electrochemical energy technologies with the potential to significantly mitigate the environmental impacts of fossil fuels. Although conventional *ex situ* characterizations provide a baseline understanding, many nanoscale electrocatalysts undergo significant structural transformation under electrochemical reactions, which calls for the use of *operando/in situ* methods.1–3 In particular, the dynamic evolution of highly active Cu nanocatalysts under the CO₂ reduction reaction (CO₂RR) conditions requires nanoscale time-resolved analytical techniques.4 Cu nanocatalysts (sub-10 nm) were previously reported to selectively convert CO₂ to multiscarbon (Cₙ) products at lower overpotentials (−0.8 vs reversible hydrogen electrode, RHE), than bulk Cu counterparts.5 In our recent work, a suite of *operando* electron microscopy and X-ray methods was employed to identify the structure of the active sites in Cu nanocatalysts as “Cu nanograins”.6 At CO₂RR operating potentials, the hydrogen evolution reaction (HER) accounts for a significant fraction of the Faradaic efficiency.

The H₂ bubbles, generated along with the CO₂RR, often pose a significant challenge for *operando* vibrational spectroscopy and X-ray absorption spectroscopy that require a stable liquid thickness for background subtraction in spectroscopic analysis.7 Electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM) cells have a liquid thickness of 500 nm or thicker at different locations of the cell due to the bulging out of the SiN₄ windows in order to adjust to the pressure difference between the liquid cell and the TEM chamber.8 With such a thick liquid layer, the spatial resolution of STEM imaging in liquids is severely compromised, which makes it particularly challenging to resolve sub-10 nm features at a beam dose below the threshold of affecting electro-
The thick liquid also poses a formidable challenge to the use of electron diffraction for structural information in liquids. Our previous studies introduced the “thin-liquid” strategy enabled by H₂ bubbles electro-generated during cathodic corrosion, which enabled the first four-dimensional (4D) STEM diffraction imaging in liquids. In this operando EC-STEM study, we take advantage of the coexistent H₂ bubbles formed during the CO₂RR to create a thin-liquid layer, which significantly improves spatial resolution for resolving dynamic evolution at the nanometer scale. 4D-STEM diffraction imaging is readily accessible in thin-liquid films to provide structural information on the polycrystalline metallic Cu nanograins. In the end, we identified several key aspects that are required to enable more quantitative electrochemistry in EC-STEM, so that this fast-growing technique can make significant contributions to the vast energy materials community, in general, and the electrocatalysis community, in particular.

RESULTS AND DISCUSSION

Operando EC-STEM enables quantitative electrochemistry and simultaneous tracking of the dynamic evolution of nanoscale electrocatalysts under operating conditions (Figure 1a). The electrochemical liquid cell is composed of a liquid layer with a 500 nm spacer in between two silicon nitride (SiNₓ) windows (each is about 50 nm thick). The three-electrode system includes an electron-transparent and electrochemically inert glassy carbon working electrode (WE) with a thickness of ~50 nm and geometric area of ~2,500 μm² (Figure 1b). The Pt counter electrode (CE) with a large area of 0.29 mm², relative to the WE, enables a rapid polarization in response to the applied potential on the WE. The circular CE can establish a symmetrical electrical field and uniform current density around the WE and is positioned sufficiently far away from the WE to minimize the effects of electrochemical reactions of the CE on the WE. Given the sub-micrometer electrolyte, it is challenging to accommodate a standard RE such as Ag/AgCl in the KCl solution with a salt bridge within the liquid cell. Pt serves as a pseudo-RE for its chemical stability, wide potential window, and facile nanofabrication.

A 7 nm Cu nanoparticle NP ensemble was deposited on the glassy carbon WE for electrochemical measurements in CO₂-saturated 0.1 M KHCO₃. The as-synthesized NP ensemble rapidly oxidizes to Cu₂O after brief air exposure prior to electrochemical reactions. The cyclic voltammetric (CV) profile of the 7 nm Cu NP ensemble shows well-defined reduction and oxidation peaks, corresponding to Cu₂O reduction to Cu and Cu reoxidation to Cu₂O, respectively (Figure 2a). The electroreduction peak of the NP ensemble is located at ~0.35 V vs RHE, which is consistent with the reduction peak of NP ensembles measured in a standard electrochemical H-cell at ~0.45 V vs RHE (Figure S1a). The discrepancy may come from the uncertainty in potential conversion given that the potential of the Pt pseudo reference electrode (pseudo-RE) is estimated to be 0.8 ± 0.1 V vs the
The chronoamperometric (CA) profile of the Cu NP ensemble at 0 V vs RHE simulates the operating conditions near the hydrogen evolution reaction (HER) with a steady-state current of about $-10 \text{ nA}$ (Figure 2b). The CA profile at $-0.8 \text{ V vs RHE}$ simulates the optimal CO$_2$RR potential for C$_2$ formation on a 7 nm NP ensemble and shows a stable current plateau of about $-100 \text{ nA}$ (about $-4 \text{ mA/cm}^2$ by normalizing the current to the geometric area of the WE). This is within the same order of magnitude as the operating current density in a realistic electrochemical H-cell (about $-14 \text{ mA/cm}^2$) at $-0.8 \text{ V vs RHE}$ (Figure S1b). The ohmic resistance was measured to be $20-30 \text{ k}\Omega$ in the 0.1 M KHCO$_3$ electrolyte with electrochemical impedance spectroscopy (EIS). Given the $\sim100 \text{ nA}$ operating current in EC-STEM, the iR drop was estimated to be $2-3 \text{ mV}$, a negligible value when compared to the operating potential. In summary, these electrochemical measurements indicate that operando EC-STEM is capable of delivering a reversible hydrogen electrode (RHE). The chronoamperometric (CA) profile of the Cu NP ensemble at 0 V vs RHE simulates the operating conditions near the hydrogen evolution reaction (HER) with a steady-state current of about $-10 \text{ nA}$ (Figure 2b). The CA profile at $-0.8 \text{ V vs RHE}$ simulates the optimal CO$_2$RR potential for C$_2$ formation on a 7 nm NP ensemble and shows a stable current plateau of about $-100 \text{ nA}$ (about $-4 \text{ mA/cm}^2$ by normalizing the current to the geometric area of the WE). This is within the same order of magnitude as the operating current density in a realistic electrochemical H-cell (about $-14 \text{ mA/cm}^2$) at $-0.8 \text{ V vs RHE}$ (Figure S1b). The ohmic resistance was measured to be $20-30 \text{ k}\Omega$ in the 0.1 M KHCO$_3$ electrolyte with electrochemical impedance spectroscopy (EIS). Given the $\sim100 \text{ nA}$ operating current in EC-STEM, the iR drop was estimated to be $2-3 \text{ mV}$, a negligible value when compared to the operating potential. In summary, these electrochemical measurements indicate that operando EC-STEM is capable of delivering a reversible hydrogen electrode (RHE).
comparable reaction rate (current density) at a comparable driving force (applied potential; overpotential), relative to standard electrochemical measurements.

Operando EC-STEM under CO$_2$RR relevant conditions makes use of the electrogenerated H$_2$RR bubbles to generate a thin-liquid layer with significantly enhanced spatial resolution. With linear sweep voltammetry (LSV) from 0.4 to around 0 V vs RHE, H$_2$ gas bubbles are formed (Figure S2). An initial potential below the open circuit potential (OCP) at about 0.6 V vs RHE was chosen in order to start with a reducing current and avoid undesirable structural changes due to oxidation from Cu$_2$O to CuO at more positive potentials. As the LSV reaches around 0 V vs RHE, the thick liquid layer is displaced, and dynamic particle aggregation is clearly resolved (Figure S2c).

In an effort to determine the thickness of the thin-liquid layer, low-loss electron energy loss spectroscopy (EELS) was performed and analyzed based on Beer's law (Figure S3). The thickness of the dry SiN$_x$ windows was measured to be about 100 nm, which is consistent with the combined thickness of two layers of 50 nm-thick SiN$_x$ windows. The total thickness of the thin-liquid layer and the SiN$_x$ windows was measured to be 200 ± 15 nm (Table S1). Thus, the estimated thickness of the thin-liquid layer is about 100 nm. Assuming that the liquid layer has the same thickness below and above the H$_2$ bubbles within the cell, the liquid covering the WE is about 50 nm thick. It should be noted that both CA profiles at 0 and −0.8 V vs RHE were acquired after H$_2$ bubble formation (Figure 2b). The stable current plateau with mA/cm$^2$-level current density at −0.8 V vs RHE suggests that the hydrophilic glassy carbon WE, covered with a thin-liquid layer, remains electrochemically accessible to the CO$_2$RR instead of drying out after forming H$_2$ bubbles.

With electrochemical measurements and liquid thickness quantification established, operando EC-STEM imaging was performed to investigate the dynamic morphological changes of Cu NPs under CO$_2$RR relevant conditions. Figure 3 provides an overview of the transformation of the 7 nm Cu NP ensemble under applied potentials. The high-angle annular dark-field detector (HAADF) STEM image shows that the as-synthesized 7 nm Cu NPs are monodisperse and self-assembled in a hexagonal packing on the carbon substrate (Figure 3a). The interparticle distance was estimated to be ∼1 nm based on our previous resonant X-ray scattering study. After the LSV scan from 0.4 to 0 V vs RHE, the operando EC-STEM image in Figure 3b captures both the remaining 7 nm Cu NPs on the left and the initial aggregation into loosely connected Cu nanograins (Figures S4, S5). No beam damage was observed at a low beam dose of ∼50 e$^-$/nm$^2$ per image frame (dose rate of ∼12.5 e$^-$/nm$^2$ s$^-$$^o$). Under CO$_2$RR relevant conditions (∼0.8 V vs RHE), those newly formed Cu nanograins undergo further aggregation/coalescence and reach a steady-state structure of closely packed Cu nanograins (∼100 nm, Figures 3, 4a). Detailed analysis of operando EC-STEM movies of dynamic evolution can be found in our recent work.$^9$

With the thin-liquid strategy, this study can go beyond conventional STEM imaging and enable 4D-STEM diffraction imaging in liquids. The 4D-STEM data set is captured on an electron microscopy pixel array detector (EMPAD) with single electron sensitivity and fast readout speed which are crucial for low-dose electron diffraction in beam-sensitive liquids.$^{1,15}$ 4D-STEM diffraction imaging was acquired at an estimated beam dose of ∼2,000 e$^-$/nm$^2$ (a dose rate of ∼6 e$^-$/nm$^2$ s$^-$$^o$). The HAADF-STEM image shows that irregular Cu nanograins (50–100 nm) are formed at −0.8 V vs RHE under CO$_2$RR relevant conditions (Figure 4a). A virtual bright-field (BF) STEM image was reconstructed by integrating the (000) transmitted spot of the 4D-STEM data set which shows the granular features of those Cu nanograins (Figure 4b). Two representative diffraction patterns were selected to show the different orientations of the Cu nanograins (Figure 4c,d). Some regions of the Cu nanograins show highly polycrystalline diffraction patterns like the one in Figure 4d. A false-color dark-field 4D-STEM composite image (Figure 4e), extracted from three diffraction spots (1 (red), 2 (green), and 3 (blue)) in Figure 4c, shows crystal domains matching crystal orientations of those three diffraction spots. The magnified composite image and corresponding virtual BF-STEM image (Figure 4fg), as well as diffraction patterns in Figure 4hl, better illustrate that multiple Cu nanograins with different crystal orientations can exist within each particle.

In summary, this study illustrates the electrochemical capability of operando EC-STEM and presents the application of the “thin-liquid” strategy enabled by electrogenerated H$_2$ bubbles under CO$_2$RR conditions. The pristine 7 nm Cu NP ensemble undergoes a dramatic structural transformation into an active state of polycrystalline metallic Cu nanograins (50–100 nm). Operando electrochemical 4D-STEM structural analysis provides a glimpse into the complex nature of active metallic Cu nanograins under CO$_2$RR conditions. Future work on quantifying grain sizes and density may provide additional insights into how to tune the structure of Cu nanograins for more effective C–C coupling reactions. This study points out the need for operando methods to investigate active sites of electrocatalysts instead of relying on conventional ex situ methods, especially for highly reactive Cu nanocatalysts.$^{22,24}$ We would also like to point out several future directions that are required to make operando EC-STEM more accessible to the broad energy materials community.

(1) Quantification of applied potentials. A rigorous calibration of the potential of the Pt pseudo-RE in different electrolyte environments will be instrumental to benchmark electrochemistry in operando EC-STEM. The uncertainty of the Pt pseudo-RE potential values (∼0.1 V) is less than an issue for electrochemical reactions such as the CO$_2$RR, N$_2$ electroreduction, or oxygen evolution reaction (OER) that require significantly large overpotentials to operate. However, a stable RE with an uncertainty below 10 mV will be required to study electrochemical reactions that are highly sensitive to small changes in overpotentials, in particular, hydrogen oxidation/evolution reactions (HOR/HER) and the oxygen reduction reaction (ORR) for fuel cells. In comparison, a commercial RE electrode, such as Ag/AgCl or Hg/HgO, can connect to the liquid cell externally and serve as a stable potential reference point with a stability of the order of 1 mV.$^{25,26}$ We anticipate that the incorporation of a more stable RE will be critical to enable more quantitative electrochemistry, so that EC-STEM can evolve into a reliable operando electrochemical technique, like operando X-ray absorption spectroscopy, that can be widely and readily used by
Improvement of spatial resolution without forming bubbles. How can we expand operando EC-STEM to electrochemical reactions that do not generate H₂ bubbles, such as the HOR and ORR as well as in most battery applications? There is a need to push the technical limit of nanofabrication for a pristine liquid layer thickness on the order of 100 nm and thinner SiNₓ windows.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c06542.

Experimental methods (NP synthesis, operando EC-STEM and 4D-STEM measurements); Figures S1–S5 and Table S1, additional electrochemical, EC-STEM and EELS measurements (PDF)

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Notes

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**DEDICATION**

We dedicate this work to Prof. Héctor Abruná’s 70th birthday and over 40 years of contributions to Operaendo Electron Microchemistry.

**REFERENCES**


