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Cu-Induced Redox Stabilization of Zn in Electrodeposited ϵ -CuZn₄ during CO₂ Electroreduction

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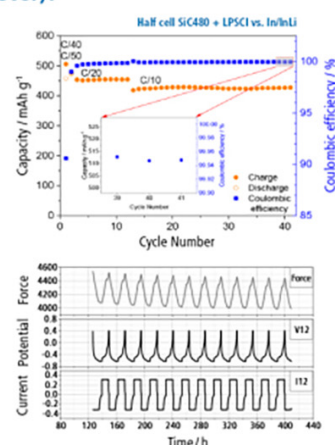
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Erratum: Cu-Induced Redox Stabilization of Zn in Electrodeposited -CuZn₄ during CO₂ Electroreduction [J. Electrochem. Soc. **173**, 054504 (2026)]

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Cu-Induced Redox Stabilization of Zn in Electrodeposited ϵ -CuZn₄ during CO₂ Electroreduction

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The electrochemical reduction of CO₂ (CO₂RR) to carbon monoxide (CO) represents a promising approach for converting a readily available carbon feedstock into valuable fuels and chemicals. While Zn is a low-cost, Earth-abundant CO₂RR catalyst with high CO selectivity, it has sluggish oxide reduction kinetics and poor activity at low overpotentials. In this work, we explored the intermetallic alloy ϵ -CuZn₄ as a Zn-rich model system to investigate how Cu incorporation alters Zn's surface chemistry and electrochemical behavior. Both Zn and ϵ -CuZn₄ films were synthesized via direct electrochemical deposition onto gas diffusion electrodes and characterized under conditions relevant to gas-fed CO₂ electrolysis. Electrochemical measurements reveal that Cu incorporation enhances catalytic activity and selectivity while significantly improving stability at low overpotentials. In situ X-ray absorption spectroscopy shows that Cu promotes rapid oxide reduction, circumventing Zn's sluggish reduction kinetics and limited stability at low overpotentials. Complementary to X-ray absorption fine structure, density functional theory and Bethe-Salpeter equation simulations reveal that Cu incorporation shifts the Zn d-band center and delocalizes Zn d-states, altering adsorption energetics in a way that enhances CO₂-to-CO conversion.

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Electrochemical reduction of CO₂ is a promising route to sustainable fuels and chemicals.^{1–4} Among the various products generated, carbon monoxide (CO) is particularly attractive due to its high energy density and commercial value as a key component in syngas for the Fischer-Tropsch reaction and methanol synthesis.^{5–7} Noble metals such as silver and gold are well-established for producing CO due to their high activity and selectivity.^{8–13} However, their high cost and limited availability hinder large-scale deployment. Consequently, low-cost and Earth-abundant materials are favored as catalysts for CO₂RR to valuable chemicals and fuels.^{14,15}

Toward that end, Zn offers high CO selectivity (up to 80% Faradaic efficiency) and low material cost,^{16–19} but overcoming the low current densities it delivers, even at high overpotentials, remains challenging. Strategies such as (nano)structuring, including nanoparticles,²⁰ dendrites,¹⁸ and multilayered architectures,²¹ have yielded performance gains, but do not overcome Zn's sluggish oxide reduction kinetics and poor activity at low overpotentials. Recognizing the limits of (nano)structuring, recent strategies have shifted toward alloying Zn with other Earth-abundant metals to unlock higher activity. Among these, Cu–Zn alloys offer enhanced activity and selectivity for CO₂RR by favorably altering the electronic structure of the catalyst, lowering the activation energy of the COOH intermediates and weakening CO binding, thereby facilitating CO production.^{5,22} However, many reported Cu–Zn catalysts are phase-separated composites, which introduce potential catalyst instability.^{23–25} Considerable progress on understanding these issues has been achieved via in situ X-ray absorption fine structure (XAFS) studies, which track oxide reduction and alloy restructuring, often over the course of several hours.^{23–25} Furthermore, several studies have successfully synthesized solid-solution Cu–Zn alloys, yet these materials typically lack long-range atomic ordering, making it difficult to isolate how specific structural

motifs impact reactivity.^{23–26} Together, the limitations of phase-separated composites and disordered solid solutions highlight the need for model systems with atomic-scale structural precision. Intermetallic compounds, with their well-defined atomic ordering, remain underexplored yet offer a promising route to isolate how Zn's surface chemistry and local environment influence catalytic behavior.²³

In this work, we investigate ϵ -CuZn₄, an ordered intermetallic phase, as a model Zn-rich catalyst to understand how atomic-scale Cu incorporation modulates Zn's behavior during CO₂ reduction. The ordered structure of ϵ -CuZn₄ offers a defined Zn-rich environment, distinguishing it from solid-solution or phase-segregated Cu–Zn materials. This enables the retention of Zn's intrinsic CO selectivity while allowing systematic investigations of how Cu alters catalytic function. To enable a stable supply of CO₂ to the electrode surface during CO₂ electroreduction, we directly synthesize ϵ -CuZn₄ and Zn films onto gas diffusion electrodes via electrochemical deposition, yielding high-surface-area catalysts through a scalable fabrication route. In situ XAFS measurements are employed to explore the structural evolution of the films and evaluate the stability of the intermetallic ϵ -CuZn₄ under catalytic conditions. Valence band X-ray Photoelectron Spectroscopy (XPS) measurements isolate the electronic influence of Cu incorporation and results are validated by density functional theory (DFT) simulations. Finally, theoretical simulations of the X-ray response using the Bethe-Salpeter equation (BSE) approach reveal how Cu coordination perturbs the local Zn environment, providing atomistic insight into how intermetallic ordering influences catalytic performance.²⁷

Results and Discussion

Electrodeposition was used to synthesize Zn- and Cu–Zn-based catalysts directly onto gas diffusion layers (GDL), following the method previously developed.²⁸ Briefly, the GDL substrate was immersed in an aqueous plating bath containing 0.006 mol L^{−1} CuSO₄, 0.023 mol L^{−1} ZnSO₄·7H₂O, 0.118 mol L^{−1} glycine (C₂H₅NO₂), and 0.033 mol L^{−1} Na₂SO₄, with the pH adjusted to

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9.5. Deposition of ϵ -CuZn₄ or Zn was carried out from baths containing both Cu and Zn precursors or Zn alone, respectively, by applying a constant potential of -1.4 V vs Hg/HgO for 1600 s. The counter electrode (graphite rod or Pt wire) was separated from the plating bath by a porous ceramic frit to minimize contamination and suppress hydrogen crossover.

The crystal structures of the resulting materials were assessed by X-ray diffraction (XRD). The XRD pattern for the material obtained from the bath containing only Zn ions displayed a dominant peak near $2\theta = 43.3^\circ$ from the (101) reflection of Zn, along with additional peaks that match the standard diffraction pattern for hexagonal Zn (Fig. 1a). The Cu-Zn alloy showed a major peak near $2\theta = 43.6^\circ$ which was assigned to the (1 $\bar{1}$ 1) reflection of ϵ -CuZn₄ with multiple additional reflections that are consistent with the expected pattern for the ϵ -CuZn₄ intermetallic phase (Fig. 1a). This confirms that ϵ -CuZn₄ and Zn, which crystallize in the hexagonal P6₃/mmc space group, are produced directly by electrodeposition. Scanning electron microscopy (SEM) images showed that Zn and ϵ -CuZn₄ adopted distinct morphologies, each exhibiting unique structural features. The top-down SEM for ϵ -CuZn₄ showed tightly packed ridges and clusters resulting in highly rough irregular topography, while the Zn sample had a folded sheet-like structure with sharp and elongated features that form an interconnected, porous network (Figs. 1b, 1c). While the top-down SEM images do not directly measure sample porosity, the revealed topologies suggest that more macroscopic porosity is present in the rough, ridged ϵ -CuZn₄ than in the tightly bound folds of the Zn. Cross-sectional SEM was performed to obtain information about the internal morphology of the deposition. Images of Zn (Fig. 1d) depict that the density of the sheets increases towards the base of the deposit, this is likely a reflection of a depletion gradient of the Zn²⁺ ions or pH gradient being established over the course of the deposition. Interestingly, the presence of Cu(SO₄) in the solution seems to regulate the change in density observed for the Zn deposit, thus the deposited ϵ -CuZn₄ had a more uniform dendritic structure that blossomed from nuclei having formed on the carbon-based GDL (Fig. 1e). Cu deposited quickly at the start of the process. This promoted the formation of the ϵ -CuZn₄ phase, which may have

subsequently been regulated by the deposition of zinc. Without this regulation, a Zn-rich layer would likely have formed as the deposit grew thicker.

Elemental mapping by top-down energy-dispersive X-ray spectroscopy (EDS) was used to evaluate the spatial composition of the ϵ -CuZn₄ deposit (Figs. 1f and S1 and S2). The atomic fractions for Cu and Zn in ϵ -CuZn₄ were measured to be 0.22 ± 0.03 and 0.78 ± 0.03 , respectively, (where the $\pm$ is the standard deviation of three measurements (Fig. S1)). A line scan through the deposit showed a slight enrichment of Cu (≈ 0.25) at the base of the deposit (Fig. 1f), however this is less noticeable from the 2D map (Fig. S2). This can be explained by the preferential deposition of Cu over Zn at the beginning of deposition since Cu must reach mass-transport limited deposition. Throughout the bulk of the deposit a stoichiometric ratio of ≈ 0.22 is measured. At the tip of the deposit, Cu was slightly enriched as well. Likely, upon removal of the electrode following deposition, the residual solution will contain Cu ions that can galvanically displace Zn. XPS following 2 min of Ar sputtering to remove native oxide reveals metallic Cu and Zn with a Cu fraction of 0.2 ± 0.05 (Fig. S3). Although XRD indicated a phase-pure material, elemental analysis revealed sensitivity of the deposit to post-deposition handling, underscoring differences between bulk-averaged and surface-sensitive probes. As a result, the catalytically active surface under reaction conditions may deviate from ideal bulk termination. Accordingly, structure–activity relationships discussed here should be interpreted as reflecting the behavior of a Cu-modified Zn-rich intermetallic environment rather than a perfectly stoichiometric surface. Electrode preparation could benefit from further studies on fabrication methodology.

To evaluate the catalytic activity and selectivity of the electrodeposited ϵ -CuZn₄ and Zn for CO₂ electroreduction, we tested the materials with a gas diffusion electrode at the cathode in 1 mol L⁻¹ KOH with a flow rate of 3 mL min⁻¹ of CO₂ into the flow field behind the carbon-based gas diffusion layer. During CO₂ reduction, both Zn and ϵ -CuZn₄ generate H₂ and CO as major products, but ϵ -CuZn₄ demonstrates a higher activity and selectivity for CO across all tested potentials compared to Zn. For ϵ -CuZn₄, the average Faradaic efficiency (FE) for CO was above 80% in the potential

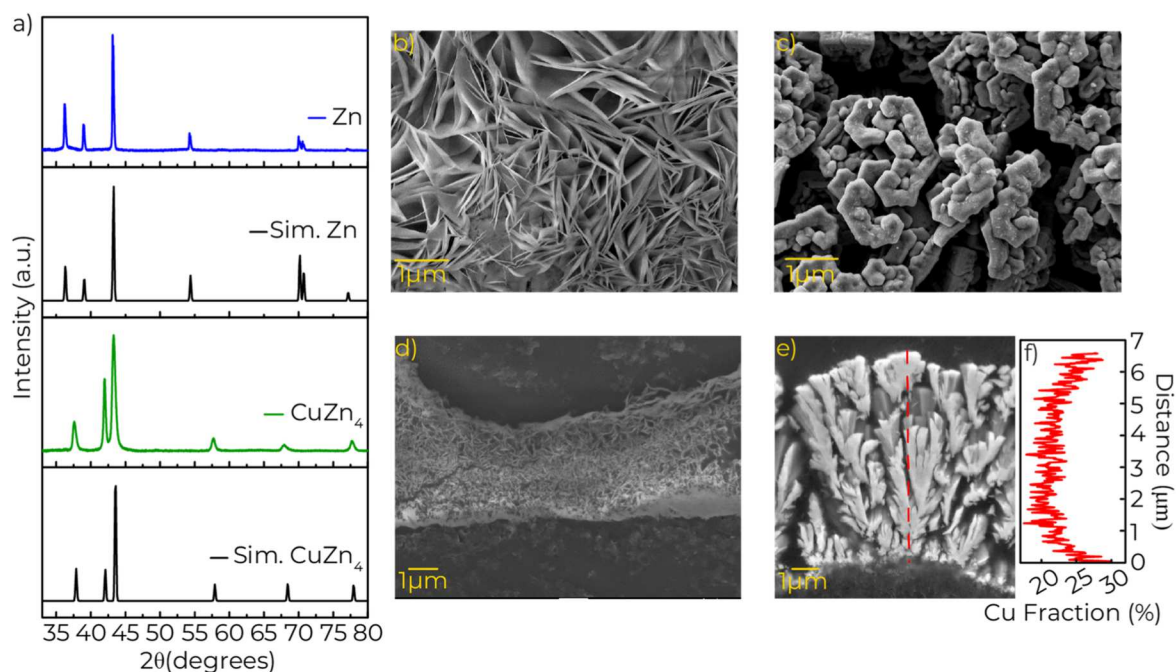


Figure 1. Characterization of electrodeposited Zn and ϵ -CuZn₄ on carbon-based gas-diffusion layers. (a) X-ray diffraction of the as-deposited Zn and ϵ -CuZn₄ compared to simulated patterns (ICSD: 25286 and 103157, respectively). (b), (c) top-down and (d), (e) cross-sectional SEM images of (b), (d) Zn and (c), (e) ϵ -CuZn₄. (f) EDS line scan indicated by the red dashed line in (e) of Cu and Zn. Quantitative EDS analysis indicates an average atomic fraction of ≈ 0.22 for Cu and ≈ 0.78 for Zn (Fig. S1).

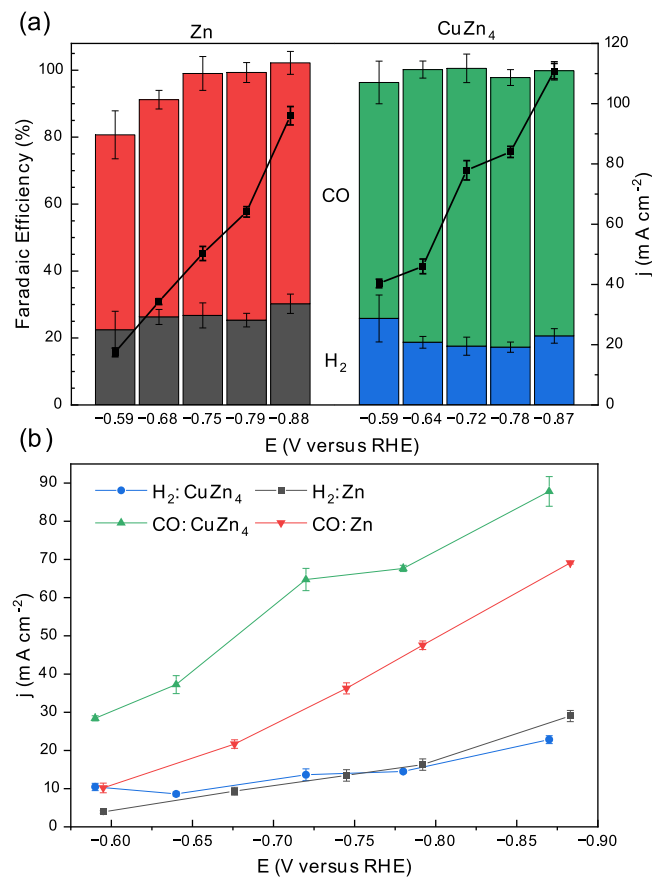


Figure 2. Electrochemical CO₂ reduction activity of Zn and ε-CuZn₄. (a) The Faradaic efficiency for H₂ and CO (bars, left axis) and total current density (scatter, right axis) for Zn and ε-CuZn₄. (b) Partial current density for H₂ and CO for Zn and ε-CuZn₄. All potentials reported in this figure are *iR*-corrected.

range of -0.64 V to -0.87 V vs the reversible hydrogen electrode (RHE), with a maximum FE_{CO} of 83% at -0.72 V vs RHE (assume throughout). Furthermore, approximately 71% FE_{CO} was maintained at -0.59 V (Fig. 2a). Compared to ε-CuZn₄, Zn exhibited an average FE_{CO} of $\approx 72\%$ between -0.75 V and -0.88 V, whereas this decreased to 65% at -0.676 V and further to 58% at -0.595 V (Fig. 2b). Low-overpotential conditions provide a sensitive regime for comparing CO₂ reduction behavior, as small changes in surface chemistry and reaction pathways can strongly influence selectivity and competing reactions. Interestingly, ε-CuZn₄ maintains $>70\%$ FE_{CO} even near -0.59 V, displaying its improved intrinsic activity and ability to suppress competing HER at lower driving forces. This performance enhancement at modest overpotentials highlights a potential advantage of the intermetallic structure for energy-efficient CO₂ electroreduction.

Zn showed a higher selectivity towards H₂ compared to ε-CuZn₄. The total FE values were less than 100% at -0.595 V (a total FE of $\approx 80\%$) and -0.68 V (a total FE of $\approx 91\%$) (Fig. 2a). ε-CuZn₄ exhibited total Faradaic efficiencies typically between $>80\%$ across the investigated potential range, consistently higher than Zn under identical conditions (Fig. 2a). This phenomenon suggests possible instability of the Zn catalyst compared to the ε-CuZn₄ alloy. Analysis of the catholyte via nuclear magnetic resonance spectroscopy (NMR) revealed that no liquid products were present after electrolysis with Zn, suggesting that the missing FE for voltages > -0.7 V could be due to charge consumption associated with Zn oxidation–reduction processes and corrosion reactions expected near the Zn stability boundary in the Pourbaix diagram under the CO₂ electrolysis conditions. While these electrochemical measurements reveal distinct CO₂ reduction behavior for Zn and ε-CuZn₄, they do

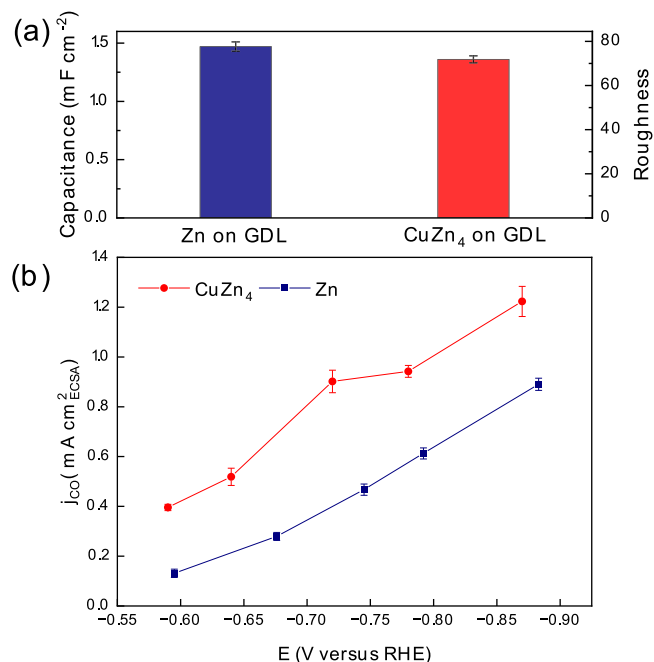


Figure 3. Roughness and specific activity of Zn and ε-CuZn₄. (a) Double layer capacitance as measured by cyclic voltammetry (Fig. S4) for Zn and ε-CuZn₄ and the corresponding roughness after normalizing using flat Zn sheet with a capacitance of $20 \mu\text{F cm}^{-2} \pm 1 \mu\text{F cm}^{-2}$. (b) Specific activity towards CO after accounting for electrochemical roughness.

not directly resolve the oxidation state or structural evolution of the catalysts under reaction conditions.

To provide more insight into the kinetics of the reaction, we evaluated the geometrically normalized partial current density of CO and H₂. ε-CuZn₄ shows higher CO partial current densities across all tested voltages, with the highest CO partial current density reaching -88 mA cm⁻² at -0.87 V (Fig. 2b). ε-CuZn₄ outperforms Zn, which only reaches its maximum CO partial current density of -69 mA cm⁻² at -0.88 V (Fig. 2b). Therefore, the CuZn₄ demonstrates improved rates for conversion of CO₂ to CO compared to elemental Zn across all the potentials tested.

Double layer capacitance measurements were used to approximate the electrochemically active surface area (ECSA) of the ε-CuZn₄ and Zn deposits. Cyclic voltammetry was conducted over a series of scan rates within a non-Faradaic region (Fig. S4). The double layer currents were plotted and fit to a linear curve to determine the capacitance (Fig. 3a). A Zn foil served as the standard to find the sample roughness and was subject to the same cyclic voltammetry conditions. Although normalization by double-layer capacitance partially accounts for geometric surface area, the markedly different morphologies of Zn and ε-CuZn₄ preclude complete separation of structural and electronic contributions. Accordingly, the enhanced activity of ε-CuZn₄ should be interpreted as arising from the combined effects of Cu-induced electronic modification and morphology. Both Zn and ε-CuZn₄ demonstrated nearly 80× the capacitance relative to the Zn foil. The denser yet finer features of the sheet-like Zn resulted in capacitance of $1.47 \text{ mF cm}^{-2} \pm 0.05 \text{ mF cm}^{-2}$, larger than the $1.36 \text{ mF cm}^{-2} \pm 0.04 \text{ mF cm}^{-2}$ produced by the thicker dendritic ε-CuZn₄ deposit. Normalizing the geometric current density towards CO by the roughness factors (≈ 78 and ≈ 72 , found using double layer capacitance, see supporting information) for Zn and ε-CuZn₄, respectively, showed that ε-CuZn₄ displayed higher activity across all tested potentials. While the highest ECSA normalized activities are $\approx -1.2 \text{ mA cm}^{-2} \text{ ECSA}$ and $\approx -0.9 \text{ mA cm}^{-2} \text{ ECSA}$ for ε-CuZn₄ and Zn, respectively, near ≈ -0.87 V; the largest gap in activity is at the lowest overpotential of ≈ -0.59 V, where ε-CuZn₄ ($\approx 0.4 \text{ mA cm}^{-2} \text{ ECSA}$) is 3× higher than Zn ($\approx 0.13 \text{ mA cm}^{-2} \text{ ECSA}$).

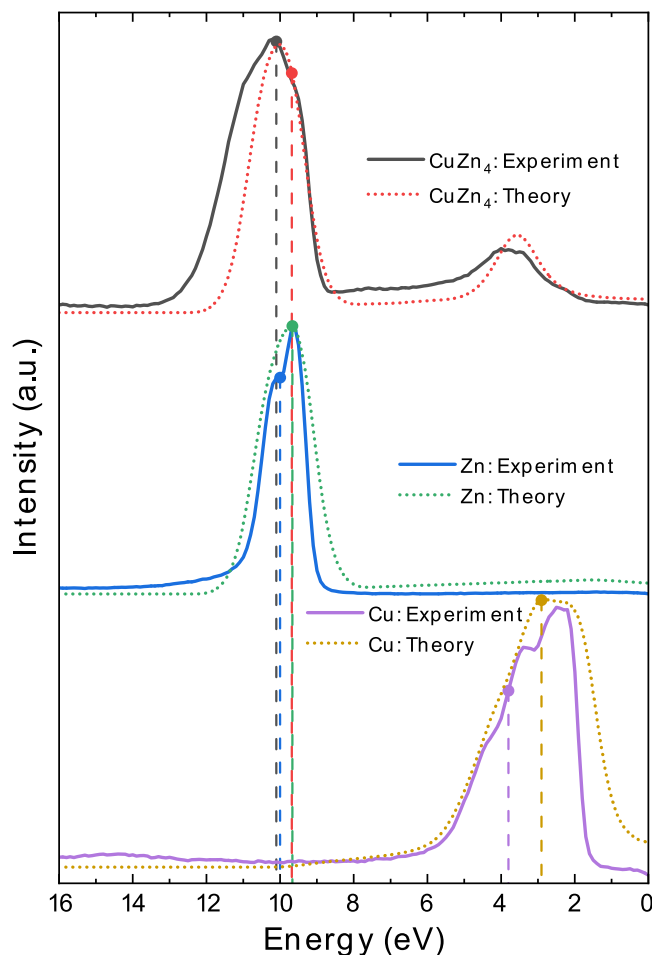


Figure 4. Comparison of experimentally measured and computationally simulated valence band spectra for ϵ -CuZn₄, Cu, and Zn. The experimental spectra were collected via X-ray Photoelectron Spectroscopy (XPS).

While the higher specific activity towards CO formation is one clear benefit of the ϵ -CuZn₄ deposit compared to Zn, an additional benefit appears to be the redox behavior of the deposit during catalytic testing. The Faradaic efficiency of the lowest overpotential for Zn under steady-state conditions does not reach unity, $\approx 20\%$ of the charge passed is unaccounted (Fig. 2a). The Pourbaix diagram indicates that Zn is close to its corrosion boundary in a 1 mol L⁻¹ KOH solution at pH 14 when poised at ≈ -0.59 V vs the Standard Hydrogen Electrode (SHE). At this potential, the reduction of any ZnO could be a prolonged process and could be further inhibited by non-Faradaic chemistry induced by the introduction of CO₂ or from the local microenvironment (namely OH⁻ production) during electrolysis. In fact, SEM images collected after CO₂ electrolysis at -0.6 V show that the Zn reconstructs to particles (Fig. S5a) from its initial nanosheet state (Fig. 1b), while the ϵ -CuZn₄ generally maintains its structure (Fig. S5b). Therefore, the introduction of Cu to make ϵ -CuZn₄ has a multifaceted benefit. First, Cu stabilizes Zn by weakening its oxophilicity. Second, Cu can act as a site to stabilize adsorbed COOH, the intermediate at the likely potential determining step in CO₂RR.²⁹ This is consistent with a computational study by Wang et al. which found stronger adsorption of COOH on a Zn-Cu bimetallic catalyst relative to Zn and attributed this to a synergistic electronic effect involving Cu-C and Zn-O interactions from neighboring metal sites.⁵

XPS valence band results (Fig. 4) reveal that ϵ -CuZn₄ likewise possesses valence-band states at energies similar to bulk Cu and can therefore play a similar role here. The multiple discrete bands in the experimental data could reflect the difference in the density of states for atoms at the surface vs the bulk of the material. Interestingly, the

Zn valence band center is upshifted in ϵ -CuZn₄ relative to Zn, leading to a final benefit of Cu incorporation. Based on work by Norskov et al., the d-band shift in ϵ -CuZn₄ suggests weaker CO binding which would increase CO₂-to-CO conversion efficiency by facilitating reactant desorption and limiting CO poisoning.³⁰ This is consistent with the results of Baek et al. which showed that alloying copper with zinc shifts the d-band center, weakening CO binding.²² It is also consistent with the increased specific activity for ϵ -CuZn₄ after roughness correction already shown in Fig. 3b. Finally, agreement between the measured and simulated valence band XPS results in Fig. 4 further validate both successful construction of the desired intermetallic phase and appropriate simulation of its electronic structure.

Electrochemical mass spectrometry (EC-MS) was used (see the SI for experimental details and Fig. S6) to track the time-dependent CO₂RR selectivity of Zn and ϵ -CuZn₄. The time-dependent measurements (Figs. 5a, 5b) demonstrates the stark contrast in catalytic selectivity between Zn and ϵ -CuZn₄. Within the first ≈ 80 s ϵ -CuZn₄ reaches a total FE $> 90\%$ while Zn is limited to 60%. Linear scan voltammetry (LSV) further supports the notion that Zn selectivity does not reach 100% until potentials < -0.75 V. The LSV for both samples demonstrates that the plateau or slight decrease in the CO selectivity is at least in part due to the onset of water splitting (Figs. 5c, 5d).

While the above measurements define the CO₂ reduction behavior of each electrocatalyst, in situ spectroscopic measurements are needed to verify the chemical phase and underlying electronic behavior of the materials during reaction. In-situ X-ray absorption spectroscopy shows that ϵ -CuZn₄ rapidly stabilizes Zn in a metallic state during CO₂ electroreduction, whereas elemental Zn exhibits delayed oxide reduction and pronounced redox dynamics. Toward that end, in situ X-ray absorption fine structure (XAFS) measurements were conducted using a modified GDE cell and beamline 6-BM at the National Synchrotron Light Source II (Fig. S7, see experimental section in SI for details). This technique was selected due to the relevant information it can reveal in two distinct spectral regions. First, the X-ray absorption near-edge structure (XANES) accesses details of the electronic structure and is thus able to act as a fingerprint of the materials present and a probe of the ongoing redox chemistry. Further, the extended X-ray absorption fine structure (EXAFS) accesses the local atomic structure, including coordination numbers and bond distances, of particular relevance to chemical bonding studies in catalysis.^{31–33}

As an experimental control, both ϵ -CuZn₄ and Zn deposits were measured under Ar gas (Fig. S8). For the Zn system, Zn atoms are present in a metallic state from the first XANES scan as indicated by the consistent position and shape of spectral features including a shoulder at ≈ 9665 eV, a white line at ≈ 9772 eV, and additional features higher in energy. Spectra from all deposits show signs of self-absorption as indicated by the stretching of features toward a normalized absorption of unity. This is expected as the deposits are concentrated in the element of interest and moderately thick, nevertheless, features are still sufficiently discernible for the present purposes. Moreover, as the XANES spectra did not reveal time-dependent changes, all spectra were averaged prior to EXAFS analysis. With regard to the EXAFS region, the magnitude of the Fourier transform is dominated by a peak at 2.2 Å (not phase corrected) which is highly indicative of a Zn-Zn bond, rather than the presence of an oxide which is observed at shorter bond lengths. For the ϵ -CuZn₄ system, the Zn K-edge XANES was also tracked as a function of time. Similarly, the XANES spectra did not reveal time dependence, yet the spectra revealed several key differences relative to the Zn standard. Namely, new features are observed at ≈ 9667 eV and at ≈ 9676 eV, or on the low and high energy sides of the white line. This is consistent with previous Zn K-edge measurements that Timoshenko et al. reported for a Cu₃₀Zn₇₀ alloy.²⁴ Lastly, the EXAFS region of ϵ -CuZn₄ showed only metallic Zn-Zn/Cu coordination, confirming the absence of oxide species. Overall, these results suggest successful synthesis of the desired phase and its existence under the control conditions.

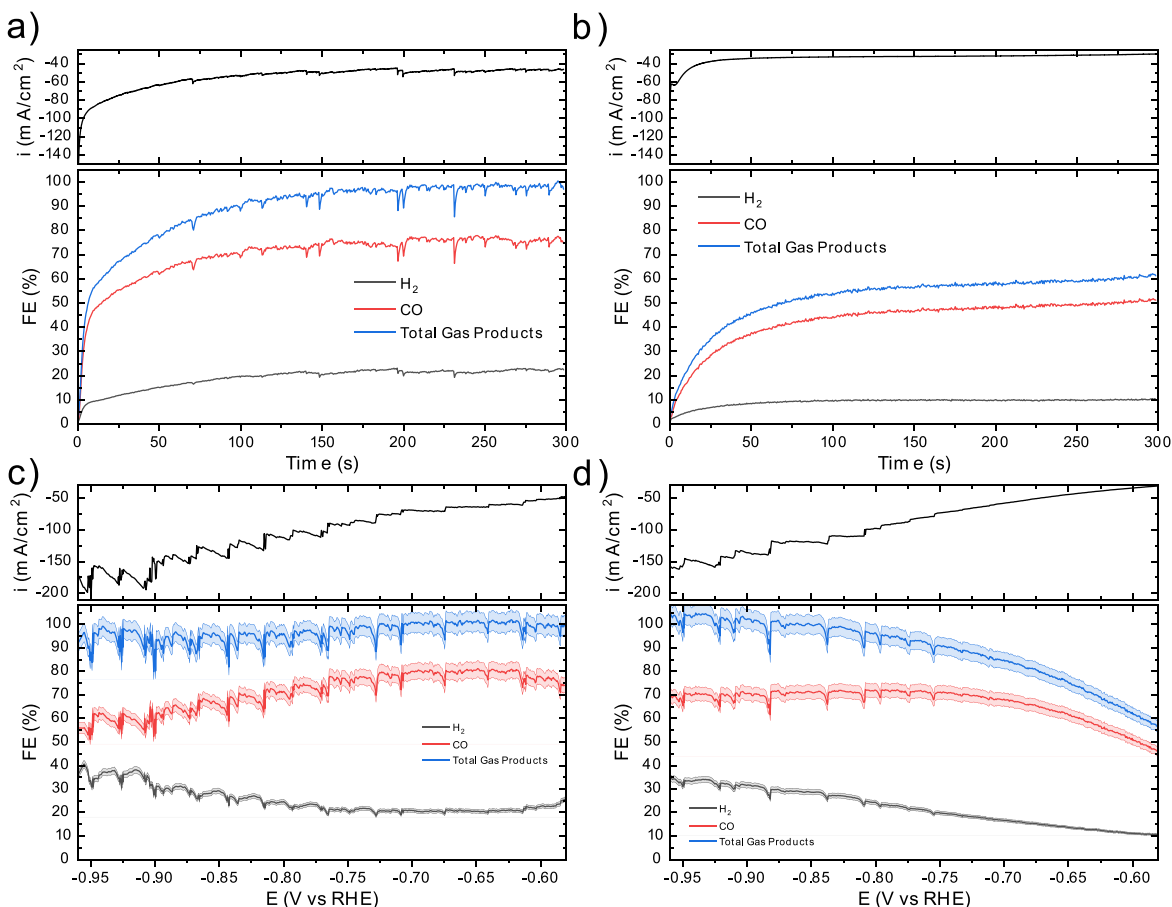


Figure 5. (a), (b) Time dependent selectivity (at -0.6 V) and (c), (d) potential dependent selectivity (at 1 mV s^{-1}) of (a), (c) $\epsilon\text{-CuZn}_4$ and (b), (d) Zn as measured by electrochemical mass spectrometry (EC-MS).

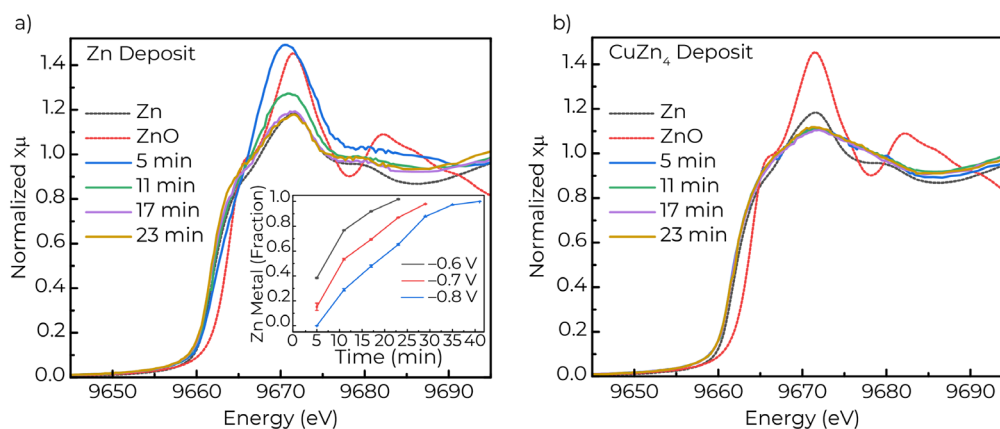


Figure 6. Zn K-edge XANES spectra collected during CO_2 electrolysis at -0.6 V for (a) Zn and (b) $\epsilon\text{-CuZn}_4$. Durations in the legend are measured from the start of electrochemical control to the start of the XANES scan. The inset of (a) represents the fraction of Zn atoms in the Zn deposit present in a metallic phase as calculated by linear combination analysis of the Zn K-edge XANES.

The results collected under inert gas were in sharp contrast to the behavior of the Zn deposit during CO_2 RR, where the chemical state of the Zn varied throughout the reaction (Fig. 6a). In the first scan under CO_2 RR, the Zn deposit exhibited an intense white line feature similar to that observed in ZnO, suggesting that the material possesses an oxidic component. While this spectrum does not exhibit the shoulder at ≈ 9665 eV and post-white line feature at ≈ 9682 eV, which are characteristic of ZnO, it should be noticed that those features are not required for oxidic zinc species and their absence has been similarly reported in studies of nanoparticle ZnO phases.³⁴

Regardless, the absence of this behavior in the Ar control experiments would suggest the source of the Zn deposit's instability is a decrease in oxide reduction kinetics from the presence of $\text{CO}_2(\text{aq})$ or its adsorbed intermediates, and/or an increase in OH^- near the electrode surface due to higher current densities during CO_2 reduction. Counter to expectation, going to higher overpotentials prolongs the time it takes for the ZnO in the Zn deposit to reduce, indicating a likelihood that the OH^- concentration gradient is the culprit behind the prolonged oxide reduction (Fig. 6a inset). Linear combination fitting to two phases was supported by the presence of

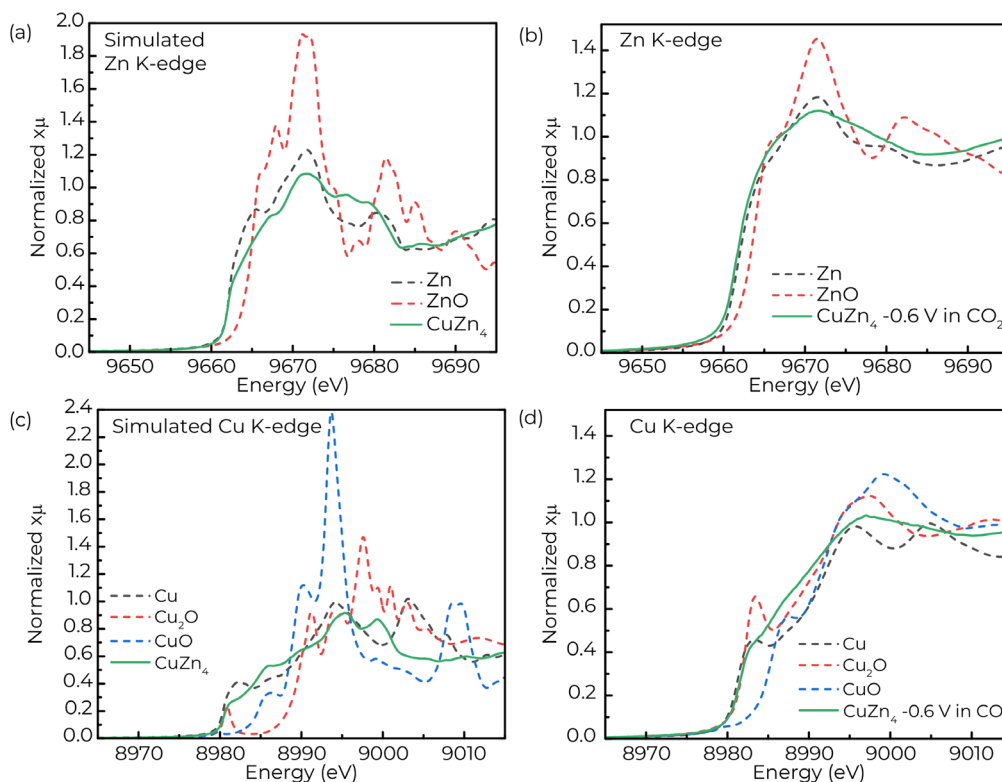


Figure 7. Theoretical (a), (c) spectra compared to (b), (d) experiment of the (a), (b) Zn and (c), (d) Cu K-edge of ϵ -CuZn₄ alongside metal and oxide spectra for comparison. For the experimental result, the ϵ -CuZn₄ was at -0.6 V with 3 ml min^{-1} CO₂ flowing through the GDE.

apparent isosbestic points at ≈ 9666 eV and ≈ 9688 eV, consistent with a direct transition between oxidic and metallic Zn species. This behavior contrasts with Timoshenko and Jeon's *operando* studies, which reported rapid reduction of Cu but very slow Zn evolution and Cu-Zn alloying under CO₂RR, showing that the stability of ordered intermetallic phases fundamentally differs from the alloy dynamics observed in that work.^{23,24} The delayed reduction of oxidic Zn observed by in situ XANES is consistent with the lower CO selectivity and increased non-Faradaic charge consumption observed for Zn at low overpotentials. Taken together with the absence of detectable liquid products by NMR, these *operando* XANES results further support assignment of the diminished Faradaic efficiency of Zn at low overpotentials to Zn oxidation–reduction processes rather than to unaccounted reaction products.

Exposure of the ϵ -CuZn₄ deposit to CO₂RR conditions revealed the material was consistently metallic but with an electronic structure distinct from pure Cu or Zn. Time-resolved Cu K-edge XANES spectra are shown in Fig. S9 for the CuZn₄ deposit at each potential. Here, there are noticeable inflection points at ≈ 8982 eV and ≈ 8996 eV which roughly align with the shoulder and white line features of metallic Cu. However, there is an additional shoulder feature at ≈ 8988 eV and clear broadening of the white line feature on the high energy side (≈ 9000 eV). This feature has been observed in other Cu-Zn alloys, suggesting successful formation of the desired phase.²⁴ Indeed, our Cu K-edge simulation found similar behavior, with the features around 8988 eV and 9000 eV exhibiting stronger intensity in ϵ -CuZn₄ than Cu metal. The underlying cause for these features is the interaction between Cu-Zn which was also observed in DFT calculations of the electronic density of states using QUANTUMESPRESSO shown in Fig. 4.³⁵ The copper and zinc d-bands shift to lower energy in ϵ -CuZn₄ which manifest as higher energy in the valence band XPS measurement. The d-electrons of zinc are also more delocalized, being broadened by the interaction with Cu. Finally, as the ϵ -CuZn₄ did not appear to vary across the timescales studied here, the XAFS measurements were averaged for each

potential and are presented in Fig. S10. No clear spectral differences between potentials were observed at the Cu K-edge or Zn K-edge, revealing a stable metallic structure. In contrast, the rapid stabilization of metallic Zn in ϵ -CuZn₄ under reaction conditions correlates with its higher CO selectivity and suppressed parasitic processes across the same potential range

Time-resolved measurements of the Zn K-edge XANES are shown in Fig. 6b. In contrast to Zn, the ϵ -CuZn₄ spectra are stable in an apparently metallic state and exhibit a shoulder at ≈ 9667 eV, as observed in the Ar control discussed above. A smaller white line intensity compared to the deposited Zn is also apparent, suggesting an interaction between Cu and Zn due to the addition of Cu. This is in agreement with the XAS calculation using the OCEAN code which found a reduction in intensity at the white line (Fig. 7).²⁷ Moreover, the calculation found the interaction between copper and zinc in ϵ -CuZn₄ leads to an additional feature at around ≈ 9676 eV. In all, the reduction at the white line, and rising shoulder and post-white line feature which are due to the interaction between Cu and Zn can be understood as representing two groups of Zn atoms contributing to the spectral shape. Namely, as Cu is a minor species in ϵ -CuZn₄, the Zn atoms strongly interact with the Cu atom they neighbor, as well as Zn atom sites further away from Cu atoms with an electronic structure more closely resembling metallic Zn. This is confirmed by the Zn K-edge X-ray response where the spectral feature of the Zn site with no immediate Cu neighbors exhibits similar feature to the one in monometallic Zn (Fig. S11). Taken together, alloying Cu with Zn shifts the electronic structure of Zn, stabilizing it during CO₂ reduction and preventing oxidation at low overpotentials.

Conclusions

In this work we demonstrated the electrochemical deposition of Zn and ϵ -CuZn₄ directly onto a gas-diffusion electrode for use in CO₂ electrolysis. The addition of Cu to the deposit boosts the electrochemical activity and selectivity for production of CO, but the

primary benefit lies in improving catalyst stability at low overpotentials. In situ X-ray absorption spectroscopy reveals that ϵ -CuZn₄ stabilizes Zn against the formation of oxidic species and enables more rapid oxide reduction during CO₂ reduction, in contrast to elemental Zn, which exhibits delayed oxide reduction. These differences are consistent with Zn's narrow electrochemical stability window suggested by the Pourbaix diagram and with the missing charge observed for Zn at low overpotentials. This instability may be attributed to chemical gradients in the cell—particularly the buildup of OH[−] as a byproduct of hydrogen evolution and CO₂RR.

ϵ -CuZn₄ thus serves as a Zn-rich intermetallic model system to examine how Cu incorporation influences Zn redox behavior during CO₂ electroreduction. While the specific activity of ϵ -CuZn₄ is not directly transferable to disordered Cu–Zn alloys or commercial brass, the results show that Cu incorporation in a Zn-rich environment can suppress oxidic character, accelerate oxide reduction, and tune adsorption energetics, effects that can be broadly interrogated using in situ X-ray absorption spectroscopy.

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