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Perspective

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Overcoming copper stability challenges in CO_2 electrolysis

Jesse Kok[1,3], Petru P. Albertini[2,3], Jari Leemans [2], Raffaella Buonsanti [2] & Thomas Burdyny [1]

Abstract

Copper and copper-based catalysts can electrochemically convert CO_2 into ethylene and higher alcohols, among other products, at room temperature and pressure. This approach may be suitable for the production of high-value compounds. However, such a promising reaction is heavily burdened by the instability of copper during CO_2 reduction. To date, non-copper catalysts have also failed to supplant the activity and selectivity of copper, leaving CO_2-to-C_2 electrolysis in the balance. In this Perspective, we discuss copper catalyst instability from both the atomistic and the microstructure viewpoint. We motivate that increased fundamental understanding, material design and operational approaches, along with increased reporting of failure mechanisms, will contribute to overcoming the barriers to multi-year operation. Our narrative focuses on the copper catalyst reconstruction occurring during CO_2 reduction as one of the major causes inducing loss of C_2 activity. We conclude with a rational path forward towards longer operations of CO_2-to-C_2 electrolysis.

Sections

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Introduction

To decrease global CO_2 emissions, our society must transition from a fossil fuel-based energy economy to a renewable energy-based one. However, complete avoidance of fossil fuels is extremely challenging because of our societal dependence on hard-to-abate carbon-based goods directly derived from them. Currently, the larger carbon chains of crude oil are hydrocracked into smaller molecules and distilled into various products streams, including smaller C_1–C_6 base chemicals that make up everyday chemical products (such as plastics or detergents). The associated emissions and market value of the industry are substantial; for example, ethylene (C_2H_4) production reached 225 Mtons in 2022, with an estimated value of more than 150 billion euros[1]. However, such markets also provide an environmental and economic motivation to shift to a non-fossil carbon feedstock and production process. The largest-scale alternative carbon source is CO_2.

The routes from CO_2 to small-molecule base chemicals are quite limited, however, and include water electrolysis combined with thermochemical processes (such as reverse-water gas shift and Fischer–Tropsch), CO_2 electrolysis and biomass routes. Among these options, the electrochemical reduction of CO_2 (CO_2RR) stands out for its ability to achieve over 50% selective conversion of CO_2 into ethylene and higher alcohols in a single step, unlike the multistep routes required for the other options. Unfortunately, CO_2 electrolysis is at an earlier stage of development compared to these other options, and thus, technical and economic challenges must be overcome for its industrial implementation.

Within the literature, the technical and economic viability of CO_2 electrolysis is linked to performance metrics such as current density (reaction rate), cell voltage, selectivity and stability[2,3]. Deterministic targets for each performance metric remain uncertain, yet current literature performance metrics are approaching anticipated industrial targets. Although current density and selectivity metrics are at sufficient levels (>250 mA cm^{-2} and >50% faradaic efficiency for ethylene), improvements in cell voltage and stability are needed to achieve industrial implementation of CO_2RR[4]. Stability is particularly problematic, with 40,000–60,000 h of operation required for electrolyser capital expenditures to be justifiable against operating expenditures[4,5]. These time frames contrast the currently achievable 1–200 h of ethylene or alcohol production observed in the literature. CO_2 electrolysers face several stability challenges, including flooding and salt precipitation, as well as possible membrane stability issues. However, one of the key unresolved challenges, both fundamentally and practically, is maintaining the stability of the copper electrocatalyst on the cathode. Copper and copper-based catalysts have been extensively studied for CO_2RR applications since the 1980s owing to their unique ability to reduce both CO_2 and CO into multi-carbon (C_{2+}) compounds. Despite numerous attempts to use other metals, alloys, nanostructures and non-metal catalysts for C_{2+} product formation, no other catalysts have matched the combined activity, selectivity and scalability of copper. As a result, copper remains the most promising option for the direct conversion of CO_2 to ethylene and higher alcohols.

Problematically, copper is highly prone to morphological restructuring in short operational periods (in most cases, 1–10 h), resulting in an inability to maintain ethylene and alcohol production for the multi-year timescales needed for industrial implementation[6–9]. Although copper stability is a long-observed problem, efforts to better understand its degradation mechanisms and achieve longer stability have intensified only recently. Two key observations offer promise to overcome stability issues. The first observation is the existence of a CO_2RR-dependent degradation pathway between copper and adsorbed carbon monoxide intermediates (*CO) that make copper species have a higher surface mobility and a higher tendency to dissolution–redeposition[10–13]. The second observation is that the push towards the use of membrane electrode assemblies (MEAs), targeted because of their higher achievable current densities and efficiencies, also came with an unexpected increase in operational lifetimes (100 s of hours). These longer lifetimes reflect an unexpected catalytic trend as reaction rates increase, suggesting that more industrial cell configurations enhance operational stability. Given the absence of practical alternatives to copper catalysts for the conversion of CO_2 to C_{2+} products, we posit that these recent developments should be leveraged to focus on enhancing copper stability for multi-year operation.

In this Perspective, we provide a framework to address the stability of copper electrocatalysts for the conversion of CO_2 to C_{2+} products. We begin by unifying what is known about copper instability at the atomistic level. We identify copper dissolution, migration and redeposition as key successive degradation steps that need to be subverted to maintain stability. This overview on the fundamental mechanisms behind copper instability leads to atomistic solution approaches such as compositional tuning, coating and controlled redeposition that can be used to stabilize copper atoms and lattices during CO_2RR. We then zoom out to analyse how atomistic dissolution and redeposition processes manifest as microscopic and macroscopic restructuring, which ultimately results in a loss of ethylene and alcohol production. Our argumentation is supported by a literature analysis of the longest-performing copper systems, which highlights the effects of current density, voltage distribution and confinement on catalyst layer restructuring. We highlight some of the open fundamental questions remaining in each sub-section. We then provide a forward-looking outlook detailing how this field can advance towards achieving practical multi-year copper stability. Achieving this goal will require efforts from the entire community to report material and operational failures, analyse the factors behind them, and develop accelerated testing protocols to evaluate long-term stability strategies.

Mechanistic insight into copper instability

Copper remains a unique CO_2RR electrocatalyst owing to its optimal binding energies towards key intermediates that enable the reduction of CO_2 to C_{2+} products[14]. However, copper-based electrodes suffer from reconstruction during operation, which is a common phenomenon in heterogenous catalysis[14,15]. This reconstruction leads to changes in product selectivity, which can be either desirable[10,16,17] (for example, improving C_{2+} production) or not[18–21] (for example, suppressing C_{2+} and hydrogen evolution reaction (HER) promotion).

These changes generally occur over different timescales and are strongly influenced by catalyst features, including particle size and morphology. For instance, small (7 nm) spherical Cu nanocrystals (NCs) transform during the start-up phase – that is, the potential ramping from open-circuit potential (OCP) to operational cathodic potential – into highly disordered materials that favour C_{2+} products[16]. The improved C–C coupling has been ascribed to the presence of defects and grain boundaries in what is often referred to as the 'scrambled catalyst'[10,17]. By contrast, cubic Cu NCs preserve their morphology and, thus, can sustain ethylene production for a few hours before undergoing severe reconstruction, which comes with increased HER and loss of ethylene selectivity[6,18,19]. These examples suggest that all copper-based catalysts restructure but on different timescales. Although restructuring might initially lead to catalytic improvement, the selectivity

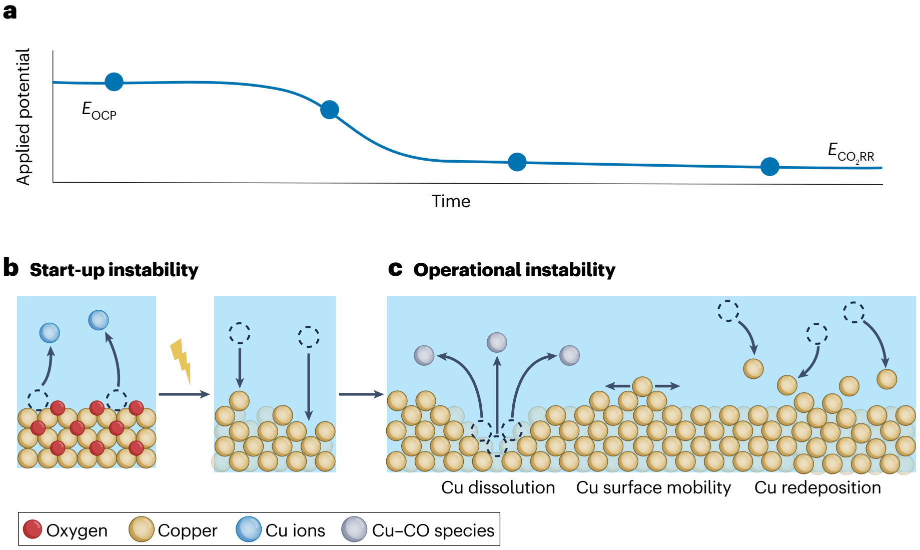


Fig. 1 | Atomistic picture of the copper intrinsic instability from start-up to operating CO_2RR applied potential and during CO_2RR. a, The applied voltage evolves from open-circuit potential (E_{OCP}) to the electrochemical reduction of CO_2 (CO_2RR) operating cathodic potential (E_{CO_2RR}) over time. **b**,**c**, Copper undergoes dissolution and redeposition both during the start-up phase (panel **b**) and during CO_2RR operation (panel **c**) at constant cathodic potential along with surface diffusion. The copper species dissolving at OCP and under CO_2RR are different. The soluble copper species at OCP are Cu ions from the unstable copper oxide whereas the soluble copper species under CO_2RR conditions are induced by the binding of CO intermediates to the copper surface.

will eventually shift away from C_{2+} products given long enough timescales, unless the restructured morphology is intrinsically stable or deliberately stabilized.

A challenge exists in understanding the broad variability of reported operating times when linking copper instability to C_{2+} product formation. For example, although some copper-based electrodes operate stably for hundreds of hours[22], others fail within a few hours[18,23,24]. These discrepancies do not imply that reconstruction occurs in only some cases, but they rather indicate that the reconstruction process can be influenced by various intrinsic and extrinsic factors which allow selectivity to fade or to be maintained. Intrinsic factors might include initial size, shape and oxidation state, which also determine the preferred product selectivity, whereas extrinsic factors might include operational conditions.

Achieving stable operation over thousands of hours for the production of ethylene and higher alcohols first requires addressing a fundamental question: what are the intrinsic atomic-scale processes that drive the restructuring of copper?

Considerable efforts have been dedicated to identifying the processes and elemental steps leading to copper electrode reconstruction, focusing on those occurring during the early stages of operation (Fig. 1). These steps can be broadly classified into a start-up instability phase, owing to the oxidation and reduction of copper, and an operational instability phase, which occurs during CO_2RR. In both phases, copper species migrate, through dissolution–redeposition cycles and surface diffusion, from the copper catalyst to the surrounding electrolyte or ionomer environment. This migration provides the foundation for reconstruction.

Instability during start-up phase

Several reports have clarified that copper already suffers from instability in the start-up phase, which occurs at OCP and during the transition from OCP to the operating CO_2RR potential[19,25–27]. For example, in situ transmission electron microscopy (TEM) on the aforementioned spherical 7-nm Cu NCs has revealed that degradation starts at OCP. During this phase, the copper surface gets passivated by cuprite (Cu_2O), and the oxide layer is then dissolved in the electrolyte as Cu ions[12]. This process was also confirmed for other morphologies, such as polycrystalline copper and Cu NCs using online inductively coupled plasma-mass spectrometry (ICP-MS)[12,28]. Upon application of a cathodic potential, any remaining Cu_2O gets reduced to metallic Cu, and electrodeposition of the Cu ions that were dissolved at OCP occurs[19,27] (Fig. 1). Both processes contribute to the copper reconstruction during the start-up phase.

The influence of start-up instability on copper reconstruction has been further evidenced through studies that carefully bypass copper oxidation at OCP by applying a cathodic potential during immersion into the electrolyte[25,26]. In these conditions, the reconstruction of mass-selected Cu NCs and polycrystalline copper is greatly reduced. The extent of surface oxidation might impact the reconstruction behaviour when reaching higher cathodic potential[24]. In line with this suggestion, it was shown that Cu electrodes with higher surface-to-volume ratio experience the most rapid changes into scrambled catalysts with higher density of grain boundaries[10] (Fig. 2a). The faster reconstruction of smaller NCs at cathodic potentials was tentatively assigned to a change in surface energy linked with more pronounced surface oxidation at OCP[10,24]. Thus, the period of time that a copper catalyst sits inside an electrochemical cell before CO_2RR contributes to the extent of dissolution and possible restructuring that will follow. Furthermore, higher surface area and porous copper nanostructures will have a greater degree of dissolution during OCP than systems with lower surface-to-volume ratio.

Based on this evidence, oxide-derived copper (OD-Cu) electrodes should experience a greater extent of reconstruction than metallic copper electrodes. Indeed, OD-Cu cubic NCs undergo fast morphological changes, with rapid loss of edges and corners together with surface roughening and formation of secondary copper particles, within the first hour, whereas no major reconstruction is observed during the same timescale for their metallic counterpart[16,17,24]. As scrambled catalysts derived from 7-nm Cu NCs transform into single-crystal Cu_2O cubes upon re-oxidation[3–5], one might expect a reversible transformation of these Cu_2O cubes back to scrambled catalysts and, thus, to C_{2+} product generation. Interestingly, performance and reconstruction behaviour different from what is expected were observed when starting from these post-electrolysis Cu_2O nanocubes[10]. Thus, although

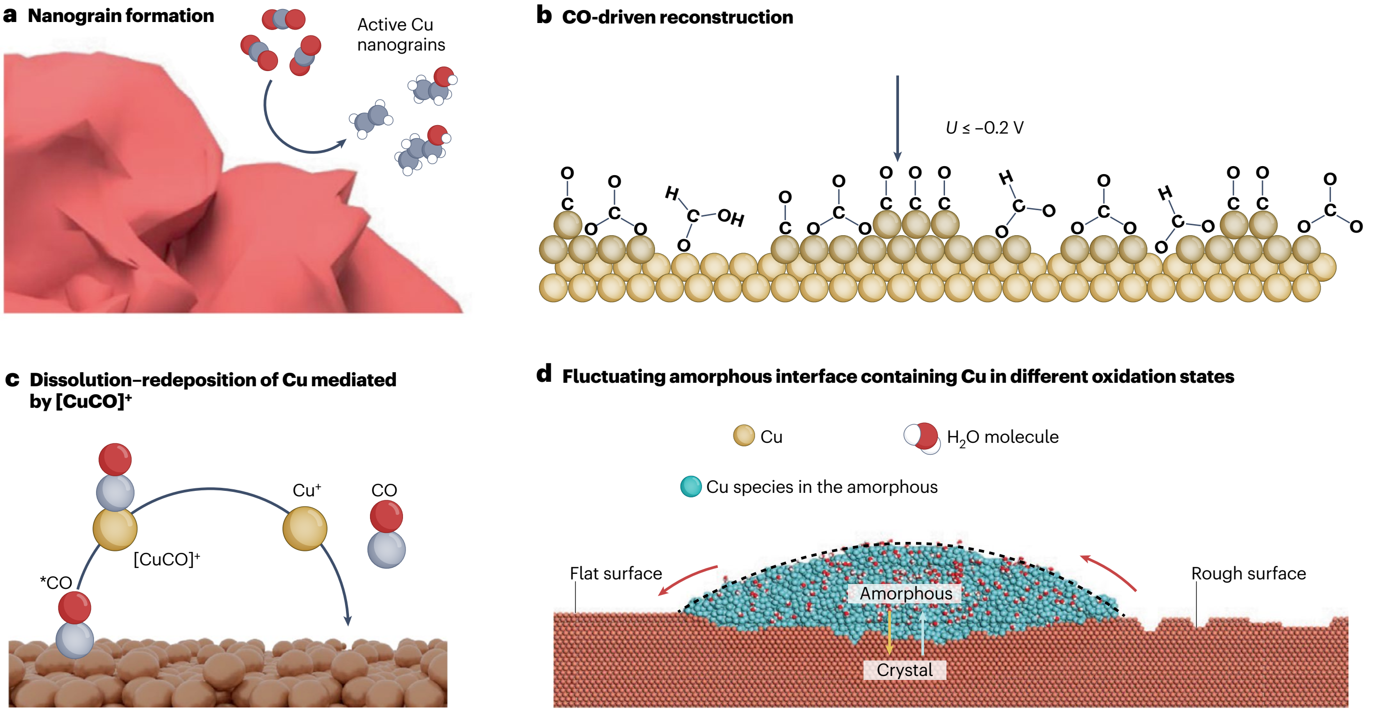


Fig. 2 | Experimental evidence corroborating the atomistic picture of the intrinsic copper instability during CO_2RR. a, The formation of nanograins on 7-nm spherical Cu nanocrystals (NCs) as a result of the electrochemical reduction of CO_2 (CO_2RR), as learned from 4D scanning transmission electron microscopy. **b**, The CO-driven reconstruction of a Cu surface during CO_2RR, as learned from in situ scanning tunnelling microscopy images and Raman spectroscopy. **c**, The dissolution and redeposition of Cu mediated by Cu(I)–carbonyl complexes ($[CuCO]^+$), as learned from the detection of Cu(I) intermediates by ultraviolet–visible spectroscopy using dimethylphenantroline as an optical probe and theoretical calculations. **d**, The formation of an amorphous interface containing Cu in a mix of 0 and +1 oxidation states as a result of CO_2RR. The amorphous state was captured by in situ transmission electron microscopy along with electron energy-loss spectroscopy characterization. Panel **a** adapted from ref. 10, Springer Nature Limited. Panel **b** adapted from ref. 11, CC BY 4.0. Panel **c** reprinted from ref. 12, Springer Nature Limited. Panel **d** adapted from ref. 13, Springer Nature Limited.

oxidation–reduction (redox) reactions are a major contributor to reconstruction, a missing link still exists between the oxidation state of the copper electrode and its influence on the reconstruction pathways and/or kinetics of reconstruction. Overall, some nuanced aspects of the copper morphology, initial oxidation state and operating procedures explain why stability reports have high variability.

Instability during operation

Despite the link between surface oxidation and restructuring, start-up redox processes alone are not sufficient to describe the changes occurring during operation observed for both Cu and OD-Cu (refs. 18,19). Indeed, the progressive conversion of polycrystalline copper foil to surfaces terminated by (111) — and later on by (100) — facets was observed using electrochemical scanning tunnelling microscopy[29–31]. Complementary to the start-up phase instability, a dissolution–redeposition process was identified during CO_2RR operation using in situ TEM on Cu NCs. This process leads to Ostwald ripening, wherein smaller NCs dissolve and larger ones form[27]. It was proposed that solution-based Cu transient intermediates drive the observed reconstruction during CO_2RR operating conditions when Cu is fully metallic[27]. The findings establish that copper migration, through dissolution–redeposition and surface diffusion, is a main bottleneck for stability under cathodic bias, thus posing a fundamental challenge to achieving stable Cu electrocatalysis beyond just the instability at start-up.

Adsorbed intermediates have a crucial role during the CO_2RR as a complementary driving force to the voltage-driven redox processes[18,32–35]. It was suggested that both CO_2 and applied voltage have a role in the reconstruction of Cu NCs[32], with adsorbed *CO driving the reconstruction[32]. Calculations predicting the equilibrium shape (Wulff construction) of cubic Cu NCs under applied voltage also confirmed the role of *H and *CO adsorbates in their reconstruction[18]. Similar conclusions on the importance of coordinated CO were drawn for Cu_2O NCs and polycrystalline copper foils[34,35]. More decisive evidence has only recently been gathered owing to the development of more advanced multi-modal characterization approaches[11–13]. For example, in situ scanning tunnelling microscopy combined with surface X-ray diffraction and Raman spectroscopy revealed that the dynamic and irreversible surface restructuring of copper near the onset potential of CO_2 is linked to the early formation of adsorbed *CO intermediates[11] (Fig. 2b). These studies demonstrate that copper migration is triggered by *CO intermediates leading to the surface diffusion of Cu atoms.

Further insights into the chemical nature of the solution-based Cu transient intermediates, which drive the dissolution and redeposition of Cu NCs at the CO_2RR cathodic potential, were provided[12]. These solution-based transient intermediates are short-lived. These intermediates were detected by ICP-MS, using dimethyl phenanthroline as a fluorophore, indicating the presence of Cu in the +1 oxidation state in the soluble transient intermediates. Density functional theory indicated that Cu(I)–carbonyl complexes ($[CuCO]^+$) can exist under CO_2RR conditions and be involved in the dynamic dissolution–redeposition equilibrium[12] (Fig. 2c). This critical dissolution–redeposition process drives continuous restructuring as long as CO_2RR is active, as evidenced by atomic resolution in situ liquid TEM[13]. Indeed, copper nanowire catalysts undergo surface amorphization with a mix of 0 or +1 oxidation states, which is supposedly the intermediate solid-state phase of the dissolution–redeposition process[13] (Fig. 2d).

Overall, a consensus on the importance of CO-induced surface reconstruction through Cu migration during CO_2RR operation has emerged, with both continuous dissolution–redeposition and surface diffusion occurring in the early stages of operation. Similar to the link between *CO binding energy and product selectivity, we expect different *CO binding energies and binding modes to affect restructuring pathways or kinetics.

Future steps

Studies that link product selectivity to restructuring pathways and/or kinetics become even more critical at longer time scales, wherein product accumulation can lead to additional degradation pathways depending on the catalyst selectivity. For example, poisoning owing to carbon species deposition on methane-producing catalysts has been sporadically proposed across the literature[36]. However, these studies have yet to be validated by in situ characterization and performed in industrially relevant devices.

In addition, the impact of CO residence time, co-feeding of CO in tandem systems, or direct CO reduction reaction on the reconstruction process should be investigated[37]. Understanding the interactions between CO and Cu surfaces in greater detail becomes even more critical knowing that CO_2-to-CO reduction and further CO reduction occur on different active sites[38]. Additionally, direct CO electrolysis is much more stable than CO_2 electrolysis, indicating that deeper complexities, including the reaction environment (such as pH or carbonate levels), might contribute to the destabilization of copper induced by the *CO intermediate.

Interactions between CO and Cu are, thus, not only a function of the catalytic surface and reaction pathways towards the final products but are also greatly affected by the microenvironment[39,40]. Ions should have an important role in modulating the reconstruction given their critical role in the activity and selectivity during CO_2RR[41]. For example, the presence of alkali cations in the electrolyte has been shown to influence the surface amount of Cu^{1+} during pulsed electrolysis[42]. Complementary, for Au(111), it was shown that the nature of the alkali cation impacts the extent of structural evolution[43]. The impact of alkali cations on the reconstruction is still unclear, with only one study pointing towards an alkali-induced cathodic corrosion[44]. We expect pH to also impact the dissolution–redeposition equilibrium. From the Pourbaix diagram of Cu, which plots the electrochemical potential as a function of pH, one might expect that accumulation of hydroxide ions near the surface impedes the dissolution of copper-based transient species, thus limiting Cu dissolution.

In our opinion, further efforts should be dedicated to systematically study the influence of ions or other electrolyte species on reconstruction.

Atomistic approaches to copper stability

Catalyst degradation and consequent loss of selectivity and/or activity is one of the most important challenges in catalysis[45]. Although a plethora of solutions have been proposed for thermal catalysis, fewer options exist for electrocatalysis and even less for CO_2RR[46]. Degradation in Pt-based proton exchange membrane fuel cells has been studied[47], and although some similarities can be drawn to address Cu instability in CO_2RR, system-specific solutions are necessary. Generally, chemical and material approaches to catalyst stability aim at stabilizing and/or regenerating the catalytic active sites to maintain the desired reactivity during operation, thus providing intrinsic stability. The chemical and material approaches suggested so far to address intrinsic copper instability consist of compositional tuning, coatings and in situ regeneration (Fig. 3a), each of which aims at preventing or counteracting restructuring. However, all of these approaches come with specific drawbacks and/or open questions.

Compositional tuning

Compositional tuning aims to stabilize CO_2RR-active Cu atoms by increasing their dissociation energy and keeping them within the lattice structure. Specifically, alloying Cu with an element M that possesses a higher oxophilicity and lower electronegativity should reduce the tendency of Cu to oxidize at OCP and promote the formation of heteroatomic Cu–M bonds, which have higher dissociation energies than Cu–Cu bonds. These effects should hamper Cu dissolution or mobility, thus improving Cu structural stability. Metals that match these criteria are early 3*d* metals, such as Sc and Ti, and *p*-group metals, such as Al, Ga, In and Bi.

Although numerous studies on metal-doped and alloyed materials exist, only a few studies have focused on assessing the stability of these new materials compared to pristine Cu (refs. 11–13,34,38,39). These few studies are promising and corroborate the proposed hypothesis. For example, CuGa-alloyed NCs demonstrated superior structural stability and methane selectivity for up to 20 h, whereas pristine Cu NCs degraded in less than 2 h (ref. 48) (Fig. 3b). In addition, oxidic copper sites, which hinder Cu mobility and render reconstruction-resistant catalysts, are stabilized for both Al–Cu/Cu_2O and $SrCuO_2$ catalysts[49,50].

Overall, there are ample opportunities to explore compositional effects to stabilize Cu active sites during CO_2RR. Guidelines for studying the stability of bimetallic copper and copper oxide catalysts should be developed, along with criteria to control selectivity towards targeted products. However, tuning stability and selectivity in alloys across their large compositional space is challenging and is a drawback of this strategy.

Coatings

Coatings have also been explored to confer stability in CO_2RR. An ideal coating for Cu in CO_2RR and, even more generally, in the context of any electrocatalyst should possess several characteristics. First, it should allow electron transport during electrocatalytic processes, which is especially important if the coating is applied before deposition on the electrode. It should also possess sufficient mechanical strength to withstand eventual gas bubble evolution during catalysis. It should be porous to allow ions, reactant and product diffusion without poisoning the catalytic sites. Porosity might also be beneficial to confine the diffusion of the Cu–CO species, thus favouring their redeposition closer to the original site. Finally, the synthesis of the coating should occur under conditions that do not damage the catalyst itself. Ideally, the synthesis method should also enable extensive tunability of the main structural features of the coating itself (such as thickness and porosity). This tunability is eventually crucial to identify the features that enable optimal performance.

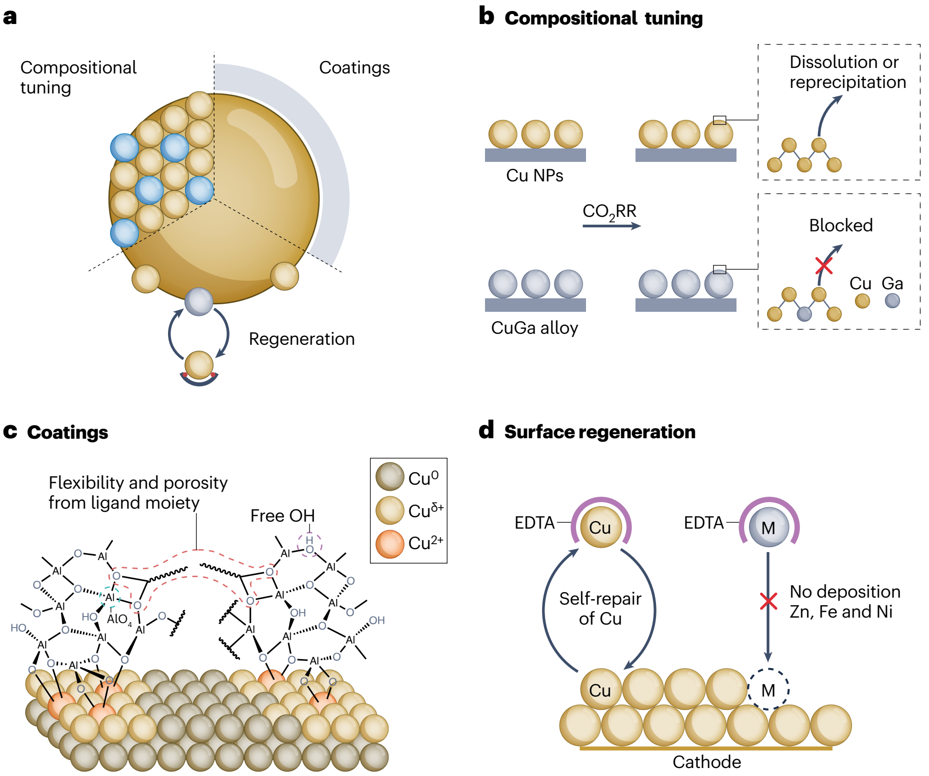


Fig. 3 | Chemical and material approaches to increase copper intrinsic stability. a, Overview of chemical and material approaches. **b**, The first approach is compositional tuning. For example, alloying Cu with Ga hinders Cu reconstruction as Ga possesses a higher oxophilicity and lower electronegativity than Cu. These properties reduce the tendency of Cu to oxidize at open-circuit potential and promote the formation of heteroatomic Cu–Ga bonds, which have higher dissociation energies than Cu–Cu bonds, thereby hampering Cu dissolution or mobility. **c**, The second approach involves the use of coatings. For example, oxide hybrid alumina coatings lock in place the oxidation state of the Cu surface during the electrochemical reduction of CO$_2$ (CO$_2$RR) and restrict Cu mobility in close proximity of the surface; altogether, these effects hinder Cu reconstruction. **d**, The final approach is surface regeneration. One potential strategy to enable surface regeneration is through the use of metal-chelating ethylenediaminetetraacetic acid (EDTA) molecules. These molecules prevent the deposition of metal ion impurities, which poison the Cu surfaces and modify its selectivity. Similar molecules could be used to regenerate Cu sites in the future. NP, nanoparticle. Panel **b** adapted with permission from ref. 48, American Chemical Society. Panel **c** adapted from ref. 65, CC BY 4.0. Panel **d** adapted with permission from ref. 72, American Chemical Society.

Carbon coatings. Given the above criteria, coating copper with a layer of carbon is a clear option because of the high electrical conductivity of carbon. As one example, copper nanoparticles coated with graphitic carbon can achieve 180 h of stability with higher selectivity towards ethylene while preserving their shape and electrochemical surface area[51]. Similarly, copper nanowires coated with graphene oxide shell demonstrate superior structural stability compared to their uncoated counterpart, preserving their (111) facets that are selective for methane[20].

However, the mechanism behind this improved stability remains elusive. Carbon coatings have generally been thought of as a mechanical barrier preventing both catalyst particle agglomeration and contact with the electrolyte[52]. However, whether this mechanism holds in the case of surface mobility or dissolution–redeposition processes is unclear. Does the mechanical shielding mechanism fully describe the effect of carbon coating? The limit of this mechanism was raised in Pt nanoparticles in fuel cells[53], in which the carbon shell was revealed to also act as a sacrificial agent. Additionally, it was shown that porosity has a role in preventing Pt dissolution while allowing reactant diffusion. Indeed, despite its critical importance, the impact of carbon coatings on mass diffusion, including on the diffusion path of dissolved species and the retention time of intermediates, is often overlooked and remains to be investigated. The impact of carbon coating on surface energetics and an atomistic picture of the interface with copper catalysts are also missing. Finally, the hydrophobic character of carbon coating might have a role in its selectivity and activity, which deserves consideration[54].

Oxide coatings. Oxide coatings have also been investigated to improve Cu stability during CO$_2$RR. These oxide coatings typically have a high binding energy at the interface with the catalyst, which provides resistance against dissolution of the catalyst under working conditions. To provide such stabilization, oxides that do not reduce to metals during catalytic operations are necessary. These coatings also induce an electronic effect, which provides a means to tune the reactivity. Generally, metal oxides possess excellent electrochemical and chemical stability, a diverse material chemistry, and tunable electronic properties[55,56]. These features render metal oxides as ideal coatings to design highly active, selective and durable catalysts. One issue for metal oxide shells is their generally low electrical conductivity. However, this challenge can be addressed by using ultrathin shells (typically less than 5–10 nm) of amorphous oxides, which allow electron tunnelling through their intrinsic oxygen vacancies, dangling bonds, undercoordinated atoms and short-range order[57,58]. Pairing metal oxides with a metal catalyst during CO$_2$RR was initially used as a strategy to enhance selectivity through the tuning of the binding energy of intermediates[53,59], with CeOx being one of the figureheads in this context[60–62]. Interactions between copper and metal oxides have only recently been recognized as a means to enhance copper stability. Thermodynamics suggest that metal oxide coatings, beyond simply acting as a mechanical barrier, improve the surface adhesion energy of metal particles through interfacial bonding, thus conferring superior stability against dissolution[63,64]. Aluminium oxide, silicon oxide and cerium oxide were all identified as promising candidates to create reconstruction-resistant catalysts[65–68]. Hybrid coatings that include amorphous oxides and embedded organic ligands have also been proposed to improve the stability of electrocatalysts against structural reconstruction during CO$_2$RR[65] (Fig. 3c).

Although ignored in the case of carbon coatings, the impact of metal oxide coatings on copper surface speciation has been more systematically investigated using operando measurements. For instance, operando X-ray absorption spectroscopy of Cu@AlOx aluminium oxide-coated NCs (that is, Cu NCs coated with aluminium oxide) has revealed the locking of a fraction of oxidic copper through the creation of the reduction-resistant $Cu^{\delta+}$–O–Al bond at the interface[65]. Similarly, CuOx@CeOx preserves between 10% and 20% Cu^{1+} depending on the CeOx content[66]. Thus, a link emerges between the enhanced structural stability conferred to copper by the oxide coating and the inhibition of the CO_2RR start-up redox process through the formation of reduction-resistant Cu–O–M bonds. For porous oxide shells, not all the surface atoms will directly bind to the oxide. However, neighbouring electronic effects might still occur, which render these copper atoms more strongly bound to the surface and, thus, more resilient against dissolution. Neighbouring active sites are still strongly influenced by the metal oxide, resulting in a change of electronic behaviour with a partial positive charge[69]. Similarly, induced electronic effects occur in Cu@AlOx, which enhance the intrinsic activity of the copper atoms neighbouring the Lewis acidic alumina[65].

The porous oxide shells can be envisioned to confine soluble $[CuCO]^+$ near the surface through spatial, steric or electrostatic effects. This limited diffusion during dissolution might favour the redeposition of the transient intermediates back to the initial surface site, thus enabling stability during operation through active site regeneration. Although no direct evidence has been gathered so far, a similar mechanism has been proposed for copper clusters in zeolites, wherein Cu ions are electrostatically trapped by the alumino-silicate support[70].

Similar to carbon coating, the effect of confinement on the mass transport and retention time of intermediate species remains unresolved. Moreover, design rules for oxide coatings remain elusive, owing to a lack of systematic investigation for different oxides. However, besides the superior structural stability that they award, metal oxides may serve as electronic regulators, fine-tuning electronic effects and guiding selectivity in catalysis. Such concept was introduced in thermal catalysis but remains unexplored in the electrocatalytic field[71]. Although oxides and coatings mitigate Cu deactivation, they inevitably introduce trade-offs, including increased ohmic losses, as well as hampered ionic conduction and catalyst selectivity.

Regeneration

The in situ regeneration of the Cu active sites is a very appealing and intriguing strategy towards improving the operational stability of CO_2RR. Rather than immobilizing and stabilizing Cu atoms in the catalytic surface, dynamically stable active sites would be created by deliberately manipulating the dissolution and redeposition cycle during operation. One chemical approach to realize such in situ regeneration is through the tuning of the microenvironment using organic chelating agents. These molecules alter the solubility and reduction rate of oxidic copper species and, thus, drive electrodeposition to preferentially grow surfaces with the desired selectivity. Here, one can envision the creation of dynamically active stable sites as an ultimate goal of such an approach, which remains to be demonstrated. Metal-chelating molecules can influence the operational stability of methane production, as demonstrated with ethylenediaminetetraacetic acid (EDTA)[72,73] (Fig. 3d). However, an atomistic proof of the in situ regeneration of the active sites is still missing. Although electrolyte additives and surface ligands are generally used to tune selectivity[74–83], their potential to control catalyst stability and surface evolution remains largely underexplored.

In conclusion, different chemical and material design strategies are being considered to stabilize copper catalytic sites during CO_2RR. We highlight that examples for each strategy remain scarce and are only tested in H-cells, which leaves plenty of space for further developments. The material platforms developed, besides offering invaluable fundamental insights into catalyst design, remain to be evaluated in more industrially relevant conditions. Interestingly, the strategies discussed above focus mainly on either mitigating Cu degradation or promoting in situ catalyst regeneration. However, ex situ regeneration of the deactivated catalyst could also be explored, using strategies such as redox post-treatment, chemical etching or overcoating the deactivated catalyst with additional Cu.

The overall number of studies dedicated to assessing stability and providing an atomistic mechanistic understanding remains limited, especially in industrially relevant electrolyser configuration. Increasing efforts are essential to identify the most promising strategy that both enhances the stability of electrocatalysts in CO_2RR and enables control over their selectivity.

System-level approaches to copper stability

In the preceding sections, emphasis was placed on intrinsic copper stability and the atomistic dissolution, migration and redeposition processes that result in copper surface restructuring. Here, we describe how these atomistic processes result in an entire reorganization of the in-plane and through-plane copper catalyst layer within hours of operation. We then detail system-level approaches that are used to inhibit product selectivity changes and extend stability to >100 h.

The described atomistic phenomena can be translated to the nanoscale and microscale, as exemplified by individual copper particles measuring 0.01–1 µm. Copper atoms will dissolve from a larger nanoparticle during CO_2RR or diffuse along the interconnected copper surfaces (Fig. 4a). The dissolved species can either be redeposited on the same nanoparticle, resulting in morphological changes at the particle level, or can migrate to a different part of the catalyst layer. These dissolution–migration–redeposition processes are occurring across the catalyst layer wherever CO_2RR is taking place (Fig. 4b), which results in a continuous dynamically regenerating concentration of dissolved copper species. Although a greater understanding of the composition and transport mechanism of the Cu complex leaving the double layer would be useful to circumvent dissolution altogether, for our discussion, it is sufficient to assume that the Cu complex enters the bulk electrolyte.

At this point, we speculate that Cu redeposition follows classical electrodeposition principles wherein an aqueous metal species is electrochemically redeposited on the cathode[84]. Electrodeposition is notably influenced by species concentration, electrode morphology and the applied reduction potential, which means that each of these factors will influence the restructuring of copper over time as it is continuously dissolved and redeposited. Positively charged copper complexes will then be redeposited more favourably in the direction of the greatest potential and protruding surfaces, leading to a preferential copper migration direction over time (Fig. 4c). The porosity and original catalyst layer structure is also expected to influence the changes. For the gas-diffusion electrode (GDE) configuration (Fig. 4), copper migrates towards the direction of the current collector which is at the highest potential[85–87].

Experimentally, such restructuring manifests as a decrease in faradaic efficiency for C_{2+} products over time. Although much emphasis has been placed on how restructuring may impact selectivity owing to nanomorphology effects (such as changes in facets or reductions in surface area), we hypothesize that on a GDE, the microstructure

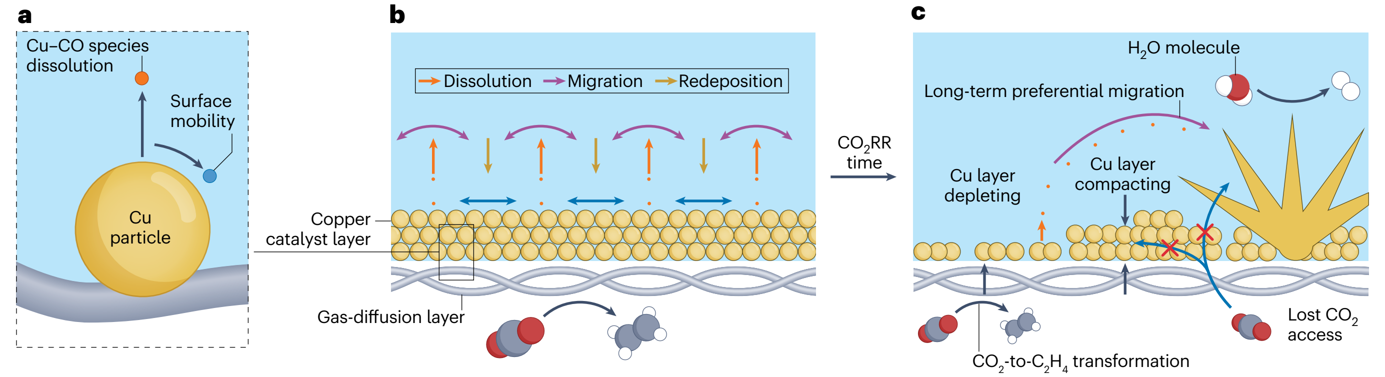


Fig. 4 | Linking atomistic dissolution effects to long-term microscale copper restructuring. a, Cu dissolution and surface mobility processes occurring at the scale of a Cu nanoparticle deposited on a gas-diffusion layer. **b**, Visualization of the dissolution–migration–redeposition and surface mobility occurring across an entire Cu catalyst layer immediately after the electrochemical reduction of CO_2 (CO_2RR) has begun. **c**, How continuous and sequential Cu restructuring leads to microscale changes in a Cu catalyst layer is illustrated here. Restructuring can cause Cu depletion and compaction and can create large microstructures, all of which negatively impact CO_2-to-C_2 products.

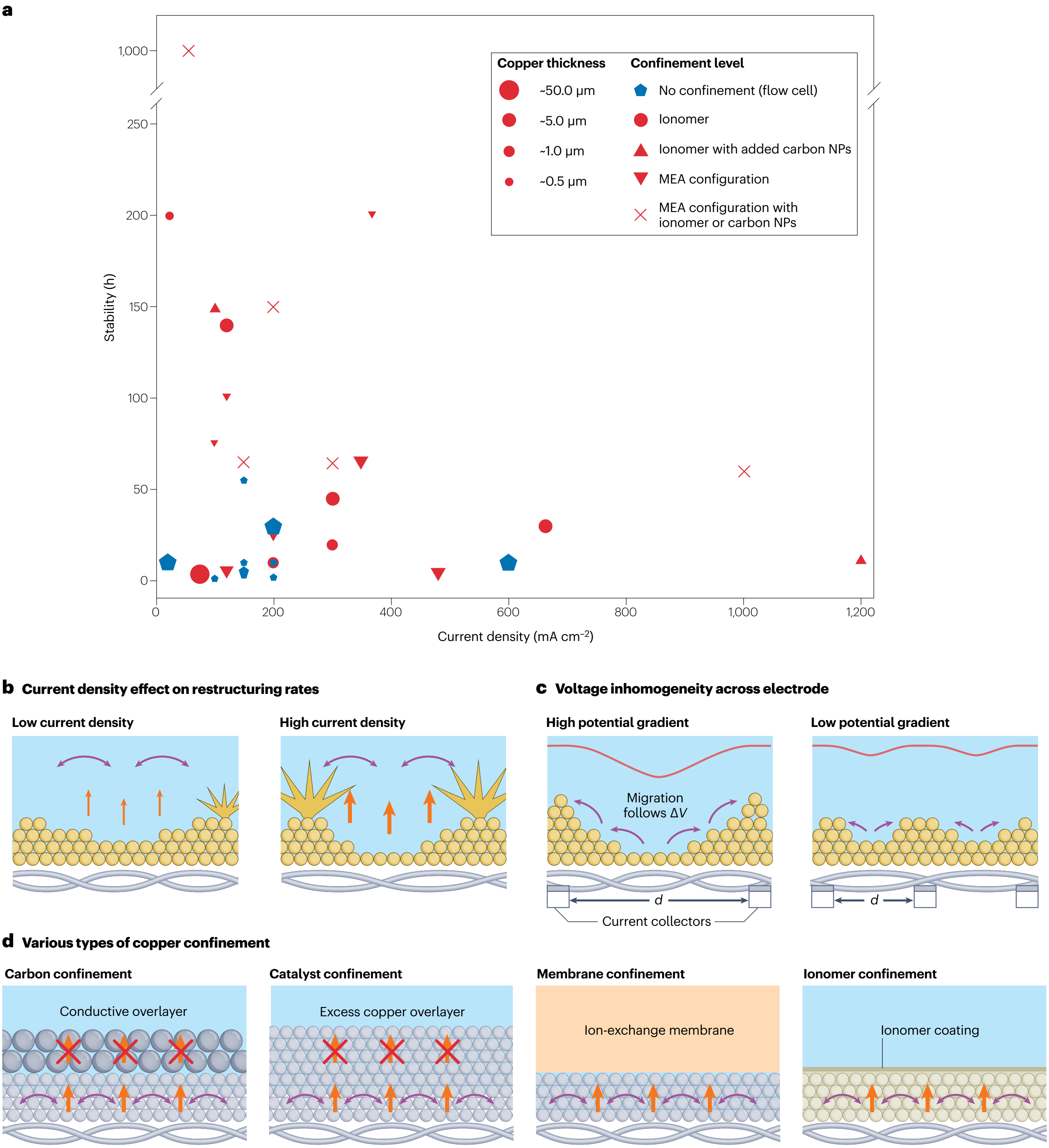
is greatly impacted by restructuring, which subsequently lowers C_{2+} selectivity. For example, as copper migrates towards regions of higher potential, areas of lower potential become copper-depleted (Fig. 4c). As the catalyst surface area decreases, the geometric current density also declines[86], which means that these areas will contribute less to CO_2RR over time. Meanwhile, catalyst accumulation can reduce porosity, blocking CO_2 access and favouring the HER over CO_2RR at similar electrode potentials in neutral pH conditions[88,89]. Lastly, as larger microstructures protruding into the electrolyte are too far away from the gas–liquid interface to be reached by CO_2, they will further act as HER sites. The combined effects of copper depletion and the formation of denser copper regions lead to decreased C_{2+} selectivity and increased HER activity over time. The issue of copper stability then becomes more complex, extending beyond surface reactivity alone. Even if individual copper sites remain active for CO_2RR to ethylene or ethanol, instability in the overall copper microstructure prevents sustained selectivity for the desired reaction.

The stability of the copper microstructure is particularly alarming if 40,000–60,000-h operation is to be achieved. Although the migration distance of an individual copper complex upon a single dissolution–redeposition cycle may be small, continuous cycling results in very clear morphological changes and macroscopic copper migration spanning several centimetres per hour for exposed copper in a flow-cell configuration[85–87]. At a system level, efforts must then be undertaken to either block, inhibit or reverse the in-plane and through-plane migration of copper complexes during CO_2RR. In the past few years, extensive experimental work on copper catalysts at elevated reaction rates has been carried out across a wide range of system configurations and catalyst deposition processes. Many of these experiments show copper stabilities with 100-fold enhancements as compared to aqueous testing environments, indicating that the microscale dissolution–migration–redeposition processes have been hindered.

Overall, copper catalyst stability has been evaluated across a range of current density, catalyst layer thickness and catalyst configuration (here noted as confinement for reasons described later)[16,22,23,85,90–109] (Fig. 5a). Stability is often assessed by the ethylene faradaic efficiency and/or the sum of C_{2+} products. In the literature, catalyst failure was observed in only a few cases, marked by a severe change in product selectivity with time. For these cases, we have defined stability as the point wherein the targeted product experienced an unrecovered decay in selectivity of over 5%. In the absence of clear catalyst failure, stability was reported based on the operational time. To maintain a clear focus on copper, studies involving nitrogen-doped or phosphorus-doped catalysts[110,111], halide-stabilized intermediates[112,113], or tandem or molecular catalyst systems were excluded[114,115]. Furthermore, only continuously operated CO_2RR experiments are shown, and CO reduction (CORR) and pulsed electrolysis are excluded. Notably, copper exhibits greater overall stability under CORR conditions than CO_2RR[116–120], but it is outside of the scope of this Perspective. Pulsed electrolysis[121] is discussed at the end of this section. Finally, it is critical to note that the reported stabilities do not represent the maximum achievable values, as most studies terminated operation before substantial faradaic efficiency degradation was observed. The pH environment of copper, as previously explained, is also correlated to catalyst lifetime, with more alkaline environments achieving higher stability[85,105]. Higher current density operation would also increase catalytic surface pH, which could aid in achieving greater stability than when using H-cell systems with lower current density. However, as the literature does not report surface pH, we have not explicitly included pH within Fig. 5a.

Fig. 5 | Elucidating the more stable production of C_{2+} products on copper catalysts in industrial system configurations. a, Compilation of the longest stable demonstrations of the electrochemical reduction of CO_2 (CO_2RR) to multi-carbon (C_{2+}) on purely copper catalysts. Marker size and type indicate the size of the catalyst layer and cell configuration, respectively. The works used as data points in the figure are tabulated in Supplementary Table 1. Here, stability is defined as the operating time wherein C_{2+} selectivity deviated by less than 5% over the reported period. **b**, The effects of current density on catalyst layer restructuring owing to reaction rate-dependent dissolution and redeposition mechanisms. **c**, The effects of variable electrode voltages on the long-term migration of copper-species from low to high potential regions **d**, Various types of copper confinement that discourage the in-plane migration of dissolved copper species, thus enhancing overall catalyst layer stability. MEA, membrane electrode assembly; NP, nanoparticle.

A clear inverse relationship exists between reported copper catalyst stability and current density, with increasing reaction rates correlating with decreased catalyst lifetime (Fig. 5a). From a microscopic catalyst lifetime perspective, we argue that increased current densities have a twofold penalty on copper stability. First, any copper dissolution related to CO_2RR reaction mechanisms tends to proportionally increase with current density (Fig. 5b). Second, voltage inhomogeneity at high current densities causes dissolved Cu complexes to be redeposited



unevenly. As electrons travel through the GDE and catalyst layer from the current collector, some voltage is lost owing to ohmic resistance. At elevated current densities, these ohmic losses are higher and voltage disparity increases (Fig. 5c). Decreasing the distance between current collectors can reduce voltage inhomogeneity but will not eliminate them entirely, implying that a preferential copper migration direction tends to always exist.

From the above argumentation, we can then further examine the reports included in Fig. 5a to explore how the restructuring processes have been effectively reduced. A clear trend emerges from comparing cases with physically confined layers – achieved through the deposition of additional materials such as ionomers or carbon layers, or by compressing the catalyst layer in a MEA (Fig. 5a, red markers) – and unconfined layers (Fig. 5a, blue markers). These physically confined catalyst layers consistently enable higher current densities and greater stabilities than their unconfined counterparts. However, for some of the seemingly unconfined cases, thick catalyst layers might effectively provide a 'confinement' effect near the gas–liquid interface, wherein CO_2RR activity is highest.

In all confinement cases (Fig. 5d), we anticipate that stability of the copper microstructure is enhanced by limiting the in-plane mobility of dissolved Cu complexes compared to exposed copper in a flowing catholyte. Migration to higher-potential regions then occurs at a slower pace, and copper particles have higher tendency to be redeposited closer to their dissolution location. Confinement also limits the growth of large nanostructures and keeps copper closer to the gas–liquid interface for longer operating times. Finally, in systems with conductive overlayers[86,109] and excess copper loadings, increased catalyst layer conductivity reduces voltage inhomogeneity. Collectively, these factors promote more stable CO_2 conversion to C_{2+} products by preventing the degradation of the microstructure. Any confinement of the catalyst layer will also restrict movement of anionic species, thus resulting in a higher expected surface pH than that of an equally unconfined catalyst.

To achieve confinement, the first strategy involves depositing a carbon and/or graphite layer on top of a copper catalyst layer or using an excessively thick catalyst layer. Such a result is often achieved by spray-depositing a mixture containing an evaporative solvent (such as isopropanol), a cation exchange ionomer (such as Nafion), and carbon nanoparticles on an already deposited copper layer[92,93,98]. The addition of carbon and graphite, originally introduced to improve conductivity when using non-conductive polytetrafluoroethylene (PTFE) as a gas-diffusion layer[93], has proven essential for maintaining ethylene selectivity over longer operation times. A similar effect is observed when thicker catalyst layers are deposited on PTFE substrates[32]. As the electrolyte penetration depth of CO_2 from a gas–liquid equilibrium at elevated current densities is typically limited to ~1 µm (refs. 122,123), the majority of the catalyst layer beyond this depth remains inactive for CO_2RR. We speculate that thick catalyst layers exceeding 5 µm enhance stability by providing confinement that limits copper mobility every dissolution–redeposition cycle[16,99,102,120].

The second confinement strategy is through the use of ionomers. Ionomers are typically used as a binding material to keep deposited nanoparticles adhered to the electrode support, but they indirectly promote stability in a few ways. Similar to carbon or catalyst confinement, ionomers obstruct the movement of the dissolved copper species, limiting migration for each dissolution–redeposition cycle. Additionally, functional groups within ionomers can further restrict movement through charge resistance. For example, in the presence of a cation exchange ionomer, dissolved species experience an extra electrostatic force that drives them back towards the electrode after dissolution. Such an approach has been demonstrated in a strongly acidic environment, resulting in 30 h of consistent C_{2+} production at 663 mA cm^{-2} (ref. 103). Similar approaches also showed extended stability[92,101]. In addition, no change in copper particle size or ethylene faradaic efficiency was reported when Nafion was integrated into the catalyst layer after 5 h of CO_2RR[124]. By contrast, the absence of Nafion resulted in larger copper particle formation with time, indicating restructuring. Although the use of specific binders could also influence the local pH of the catalyst layer, these effects are not discussed here.

The final confinement strategy involves MEA configurations, in which the copper cathode is compressed against an ion-exchange membrane. Such confinement provides similar benefits to the approaches above and often achieves the best combinations of stability and current density[95,97,98,101,104] (Fig. 3). Within an MEA, the copper GDE is confined by a membrane, restricting migration to the in-plane direction, which is more physically constrained. Many MEA systems also incorporate carbon overlayers and ionomers. Another clear benefit of MEAs is that their potential distribution is more uniform in comparison to most flow cell designs. MEAs typically use stainless-steel endplates with narrow flow field channels (~1 mm) that are compressed against a conductive carbon gas-diffusion layer. This current collection distance (Fig. 5c, right) is around 1 mm for MEA cells, compared to 1–3 cm in flow cells using PTFE-based gas diffusion layers. The resulting ohmic drop across the GDE and catalyst layer is then substantially reduced, lowering the spatial potential gradient of the electrode. The migration driving force is, thus, greatly reduced, probably contributing to the much longer stabilities observed in MEA systems.

Although further targeted research is warranted to show direct evidence of the suggested restructuring mechanism, existing studies separately demonstrate the benefits of voltage homogeneity[86,90], local pH control[105] and confinement[91,93] in limiting restructuring and subsequently extending catalyst lifetime. These parameters collectively support catalyst stability when switching from an H-cell to an MEA configuration.

Although this Perspective has so far primarily focused on continuous electrolysis, it is also critical to consider pulsed electrolysis (that is, intentional copper oxidation and reduction cycles as a strategy to enhance copper lifetimes). During pulsed electrolysis, the cathode potential is periodically changed from a CO_2-reducing potential to a more anodic potential such that copper is oxidized – either electrochemically or chemically – to copper oxide (Cu_xO). A reducing potential is then reapplied, causing Cu_xO to convert back to Cu. Both strategies have demonstrated substantial improvements in operational lifetimes, with increases of 10-fold to 100-fold compared to continuous operation[85,94,121,125].

Building on the processes described earlier (Figs. 1 and 4), we hypothesize that pulsed electrolysis may enable longer catalyst lifetimes by counteracting the preferential migration of copper towards the current collectors. Specifically, the reincorporation of oxygen into a copper lattice during oxidation results in anodic dissolution as copper makes room for oxygen[8,15,27,28,126–128]. As long as the oxidative process is maintained, the dissolved Cu^{d+} species that leach during the oxidation step are then free to diffuse throughout the aqueous environment of the catalyst layer. These copper species are redeposited only upon reapplying a reductive current. Thus, unlike the preferential migration of copper towards the current collectors during CO_2RR, during an oxidative pulse, dissolved copper species can freely diffuse away from the current collectors. If the anodic pulse or OCP is held for long enough, the dissolved Cu^{d+} species would even form a roughly homogeneous concentration throughout the catalyst layer and be redistributed roughly evenly across the electrode area. However, if OCP is held for too long, dissolution can persist depending on the local pH[28]. Hence, although pulsing has been demonstrated to extend and recover C_{2+} product selectivity, a greater understanding of the underlying mechanisms and limitations is needed. Furthermore, the ability to apply either of the pulsing methods at scale is unclear.

Outlook

Within this Perspective, we have outlined state-of-the-art data and investigations in copper stability during CO_2 reduction at both the atomic scale and microscale. Fundamental studies connecting these two length scales remain limited but are essential to identify and develop solutions that extend catalyst operations from hundreds to thousands of hours. Thus, we believe that any bold claim of revolutionary new directions and strict protocols for accelerated stress tests aimed at reaching 40,000–60,000-h lifetimes are premature, as knowledge is still missing.

Towards this goal, we advocate for stability performance metrics to receive the same emphasis as those of efficiency, selectivity and current density. Below, we outline recommendations to advance copper stability efforts with the aim of creating a framework for discussions in the community.

The first recommendation is to increase the reporting of stability tests across the literature, with greater consistency in testing conditions and reporting protocols[129]. We suggest running these tests at the upper bound of current densities. Although performance may be categorized at current densities spanning 100–500 mA cm^{-2}, stability tests are often performed at the lower current bounds. Running longer duration tests at higher current densities also requires circumventing other cell stability issues, such as salt precipitation and GDE flooding. Salt precipitation can be mitigated through strategies such as using Cs^+ cations or operating at higher temperatures. We encourage adopting such best practices to improve assessment of copper stability at the top of the current density range[130–132].

The second recommendation is to provide information on when and why operation actually fails. We believe that this information is crucial for developing rational stress-testing protocols and designing accelerated stability tests for CO_2RR. Such a testing protocol is outlined in Fig. 6 and motivated by equivalent alkaline water electrolysis testing. Notably, many experiments included in Fig. 5a appear to be voluntarily stopped, probably owing to challenges of occupying potentiostat and gas chromatographs for extended periods of time. Thus, we are left with an incomplete understanding of actual catalyst failure points relative to long-lifetime (40,000 to 60,000 h) targets.

Identifying early failure indicators can accelerate the assessment of mitigation strategies. One indicator would be to monitor carbon monoxide production, as carbon monoxide selectivity decays either before or together with ethylene[23,85,91,94,95,104,106]. With a drop in carbon monoxide production over time, less C–C coupling can occur towards the formation of ethylene, ethanol and other C_{2+} products. The rate of decay in carbon monoxide during the first hours of stability tests can then be a direct indication of the expected lifetime of the copper cathode. Unfortunately, most studies do not share the faradaic efficiency profile of the other gas and/or liquid products during the reported stability tests, and as previously mentioned, few run their systems to failure. For example, 85% of the studies included in Fig. 5a do not show clear failure.

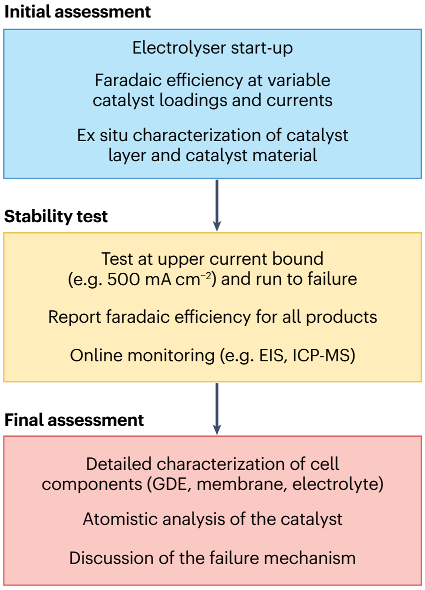


Fig. 6 | Testing catalyst stability in CO_2 electrolysis. A three-stage laboratory-scale standard protocol is suggested here to probe and understand the stability of copper catalysts in CO_2 electrolysis applications. EIS, electrochemical impedance spectroscopy; GDE, gas-diffusion electrode; ICP-MS, inductively coupled plasma-mass spectrometry.

Along these lines, more post-mortem analysis of failed systems — including cell components and catalyst layers at both the microscale and atomistic level — is needed, particularly for systems that operate for 100 s of hours. Although operando X-ray scattering and imaging techniques would be ideal, they are not accessible to all. Thus, at a minimum, post-mortem scanning electron microscopy or detailed cross-sectional analysis of the copper catalyst layer can help to visualize structural reconstruction, providing valuable information into why the catalyst performed well over extended periods and what ultimately led to its failure. Such analysis is crucial to understand the relevant length scale involved in selectivity failure, thus enabling the development of more appropriate solutions.

We also advocate for greater fundamental understanding of how atomistic copper instability impacts microscale reconstruction. Modelling the diffusion processes involved inside and outside the double layer and how they are impacted by the initial catalytic material, operating conditions, electrolytes and product evolution from the reactor are interesting directions to pursue. These studies, aimed at bridging length scales and timescales, should be accompanied by solutions wherein atomistic and system-level approaches are merged to enhance stability.

A final recommendation is to probe deeper into the comparable differences in stability between CO_2 and CO electrolysis and derive strategies to benefit from the latter. Studies of CORR stability were excluded from our discussion, as were tandem catalyst designs that aim to promote CO_2 to CO on one catalyst, followed by CORR on a copper catalyst. The use of a cobalt phthalocyanine complex adsorbed on copper has been shown to enhance C_{2+} product formation and stability[133,134]. This result suggests that stability improvements originate from the copper electrode undergoing a shift from primarily CO_2 electrolysis to CO electrolysis.

In closing, copper is an unstable but uniquely promising electrocatalyst for producing valuable ethylene and higher alcohols in a single step. With continued collective efforts, we believe that stable copper operation is possible.

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Author contributions

T.B. and R.B. conceptualized the article. J.K., P.P.A., J.L., R.B. and T.B. researched data for the article. All authors wrote the initial draft and contributed to the discussions of its content. The manuscript was revised in a collaborative manner.

Competing interests

The authors declare no competing interests.

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