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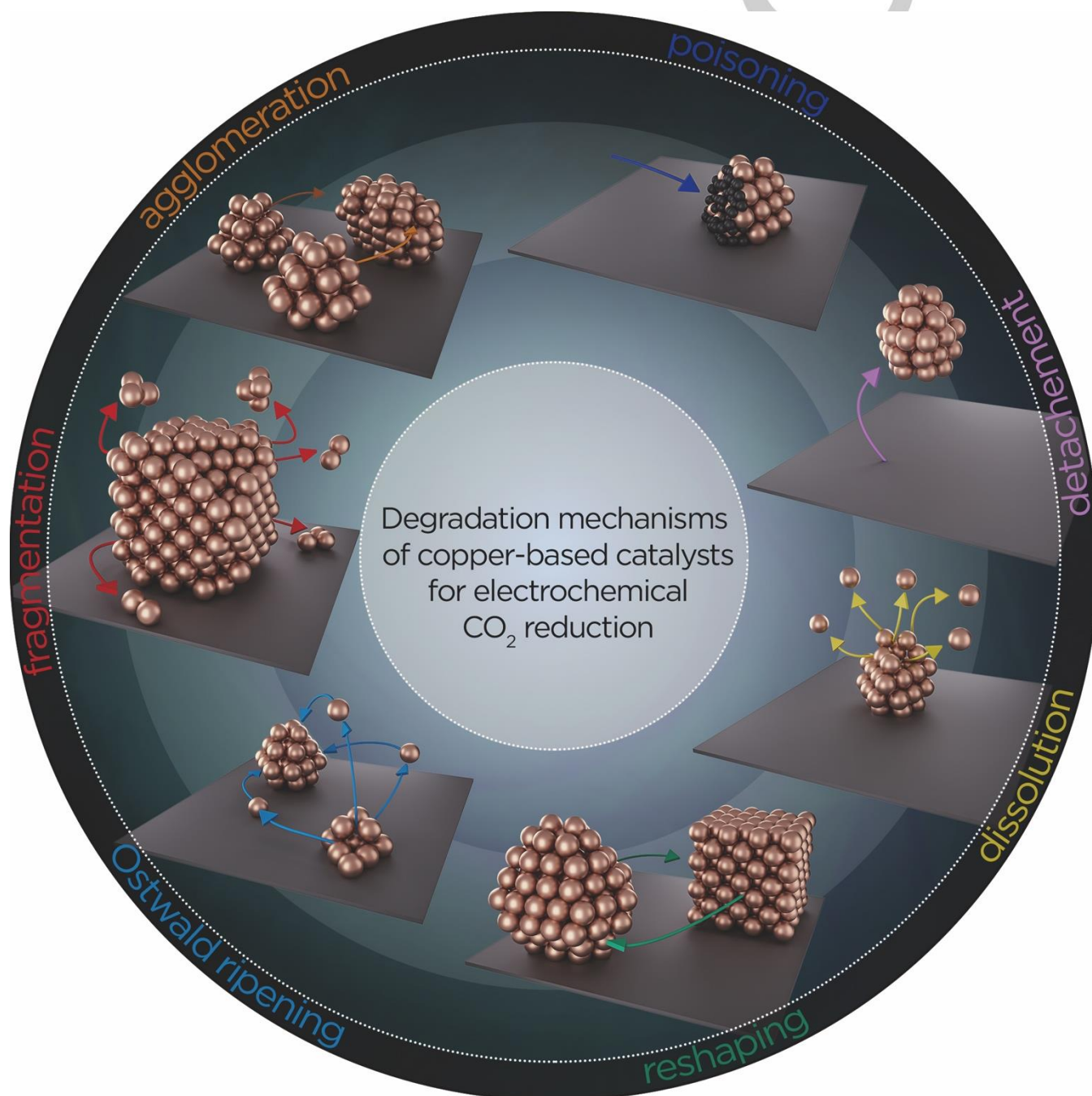
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Stability and degradation mechanisms of copper-based catalysts for electrochemical CO₂ reduction

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Up to date, copper is the only monometallic catalyst that can electrochemically reduce CO₂ into high value and energy-dense products, such as hydrocarbons and alcohols. In recent years, great efforts have been directed towards understanding how its nanoscale structure affects activity and selectivity for the electrochemical CO₂ reduction reaction (CO₂RR). Furthermore, many attempts have been directed to improve these two properties. Nevertheless, to advance towards applied systems, the stability of the catalysts during electrolysis is of great significance. This aspect, however, remains less investigated and discussed across the CO₂RR literature. In this mini-review, the recent progress on understanding the stability of copper-based catalysts is summarized, along with the very few proposed degradation mechanisms. Finally, our perspective on the topic is given.

1. Introduction

In the recent years, the electrochemical CO₂ reaction reduction (CO₂RR) to chemical fuels and other energy-dense products, powered by renewable energy, has become one of the most intriguing challenges in the field of electrocatalysis.^{[1],[2],[3]} Indeed, in addition to long term energy storage, it has the potential to mitigate the rising greenhouse gas emissions. Compared to other possible CO₂ utilization technologies, including thermal CO₂ hydrogenation,^{[4],[5]} some of the unique advantages of CO₂RR are the mild operating conditions (e.g., room temperature and ambient pressure), the possibility to obtain different reaction products by tuning the reaction conditions (e.g., applied potential, nature of electrode material and electrolyte, mass transport, etc.), the aforementioned ability to directly store excess of renewable electricity in chemical bonds. Despite the huge promise of CO₂RR, its technological implementation is still limited by the activity and selectivity of catalysts for products that go beyond CO.^{[1]-[3],[6]} Based on the current state-of-the-art, CO₂RR electrocatalysts can be divided into three major groups: metallic, non-metallic, and molecular catalysts.^{[1],[2]} The structural simplicity, easy handling, and robustness make monometallic catalysts especially attractive for fundamental studies and also for the eventual implementation in an electrolyzer.^[6] Hori and co-workers categorized single metal surfaces in four groups according to the main CO₂RR products^[7]:

- 1) Pb, Hg, In, Sn, Cd, and Ti (major product HCOO⁻)
- 2) Au, Ag, Zn, Pd, Ga (major product CO)
- 3) Cu and Cu alloys (produce hydrocarbons and alcohols)
- 4) Ni, Fe, Pt, Ti (produce hydrogen and are inactive for CO₂-RR)

Copper is one of the few metallic catalysts that can electroreduce CO₂ to hydrocarbons and alcohols with decent efficiency.^[2,8,9] However, recently the development of new families of catalysts, non-copper containing catalysts, have shown the ability to electroreduce CO₂ to C₂₊ products but with low product yields, limiting these catalysts for further use.^[10] The uniqueness of Cu as CO₂RR electrocatalyst has been explained by the fact that it is the only metal that has negative adsorption energy for CO* (an important CO₂RR intermediate) and positive adsorption energy for H* (an intermediate in the competitive hydrogen evolution reaction; HER).^[3] Besides, the CO* binding energy on Cu has an intermediate value, which provides a balance between activation of CO₂ and hydrogenation of CO*, the latter being a key step towards hydrocarbons. While Cu has the unique ability to produce products beyond CO, studies show that polycrystalline copper foils generate more than 16 different species, which represents a huge challenge for their separation.^[11] Pioneering work by Hori et al. in 1985 has evidenced the importance of facet-dependent selectively using Cu single crystal, where CO₂ reduction to methane and ethylene on Cu(111) and Cu(100), respectively, was shown.^[12-14] To date, many studies have focused on modifying the structure of copper catalysts to increase their activity/selectivity toward energy-dense products, including single crystals and nanoparticles.^[3]

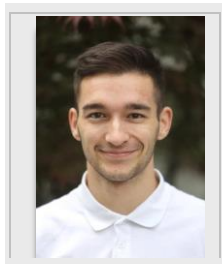
At the same time, commercial applications of CO₂RR require a catalyst with high performance, i.e., high faradic efficiency and current density for one specific product; which are also stable for long-term operation.^[6] Nevertheless, the structural stability of the catalysts under CO₂RR conditions has been given considerably less attention in comparison to activity/selectivity issues. While stable operation times up to 150 hours have been reported^[15], some of the Cu-based catalysts show performance loss already after a few tens of minutes of operation^[16,17]. In general, studies on the degradation mechanisms, which would explain catalyst failures and this being more helpful, are rare compared to the works done in other relevant electrochemical reactions, like oxygen reduction and evolution reactions^[18-20]. We note that a systematic and critical overview of the stability of Cu-based catalysts for CO₂RR is generally lacking.

The aim of this minireview is to summarize the current status and recent advances in understanding the stability mechanisms and deactivation of state-of-the-art Cu-based catalysts for CO₂RR, including some of the proposed mitigation strategies to enhance durability. Correlations between product selectivity and evolution of catalyst structure are also discussed. The importance of reporting stability data for CO₂RR catalysts is explained and a general protocol for testing the stability of CO₂RR catalysts is proposed. Finally, we stress the importance of tracking changes in the size/structure/morphology of the Cu-catalysts during electrolysis, as this is known to govern their activity and selectivity.

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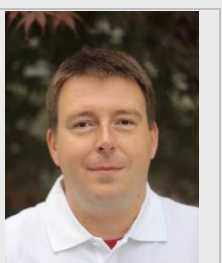
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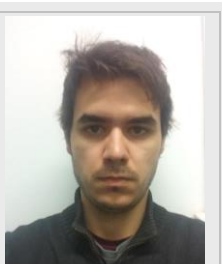
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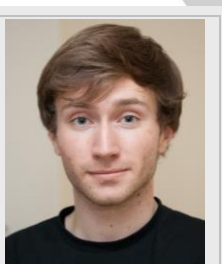
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reaction.

2. Structural and compositional stability of Cu-based electrocatalysts

2.1. Meso- and nano-structured films

Nanostructured Cu films have attracted much attention as catalysts for CO₂RR due to their superior performance compared to the polycrystalline copper foil.^[3] Some of the characteristic features that contribute towards their distinct catalytic behavior include high surface area, numerous edge/low-coordinated sites, grain boundaries, and porosity. However, the complexity of nanostructured catalysts makes it challenging to gain insights into the contribution of each structural feature to the overall improvement in CO₂RR performance. Furthermore, morphological transformations can occur during operation and they must be taken into account.

Mesoporous (pore size 2 nm to 50 nm) and macroporous (pore size above 50 nm) Cu electrodes have been shown to exhibit improved selectivity towards C₂ products compared to Cu foil.^{[18],[21]} This behavior was attributed to a dominant (100) surface texture as well as to the temporal trapping of intermediates within the pores. Thus, for stable ethylene production, these two features must be retained. The longest stability reported so far is by Peng et al.^[22], where a porous Cu layer, formed by chemical dealloying of a thermally treated electrodeposited Zn, is shown to be stable for up to 8 hours.

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Ren et al. have reported that the anodization process of Cu nanoparticles (Cu-NPs) to $\text{Cu}(\text{OH})_2$ and Cu_2O , which are then reduced back to Cu^0 nanocrystals (Cu-NCs) during CO_2RR (as an *in-situ* reconstruction event) is beneficial for their selectivity towards n-propanol^[23]. The Cu NCs showed remarkable stability in producing n-propanol over 12 hours compared to the initial Cu-NPs. The authors explained this improved behavior as a low propensity toward methane formation that can supposedly decompose into graphitic carbon, which then blocks the catalyst surface.^[24–27] Thus, suppression of this route minimizes the poisoning, which is the deactivation of the catalyst.^[28] We note that poisoning effects of the reaction intermediates are still not completely elucidated in literature,^[17,24] hence future studies on this particular topic are necessary.

Another example where oxidation/reduction cycles result in a more active catalyst is provided by Li et al.^[16] Here the authors investigated modified Cu-based electrodes prepared by annealing of Cu foil in the air at various temperatures and then electrochemically reducing the resulting oxidized copper layers. They showed that this oxide-derived Cu exhibits much better CO_2RR performance in terms of activity and selectivity towards ethylene and ethanol than polycrystalline Cu electrodes, which produce a mixture of CO and formic acid at the same potentials.^[29] Figure 1 illustrates that the annealed sample exhibits higher activity (J_{tot}), CO_2 conversion efficiency and selectivity for formic acid along with more stable performance compared to the untreated copper. Regarding the compositional changes of the catalyst during electrolysis, through various techniques, including X-ray Diffraction Analysis (XRD) and X-Ray Photoelectron Spectroscopy (XPS), performed after operation, the authors demonstrate that the Cu_2O layer on annealed Cu electrode is mostly reduced during CO_2RR . However, they do not completely rule out the presence of a thin metastable Cu_2O layer or other surface-bound Cu^+ species during electrocatalysis.

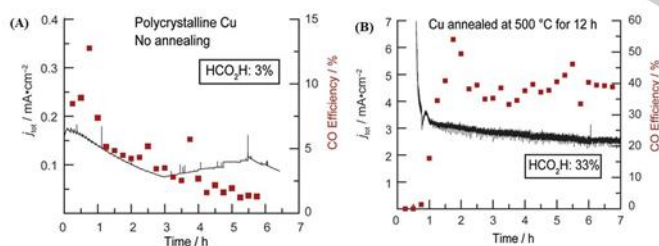


Figure 1. CO_2 reduction electrolysis data for untreated polycrystalline Cu (A) and for oxide-derived Cu (B) collected at -0.5 V vs RHE.^[16] Copyright 2012, American Chemical Society.

Importantly, surface reconstruction during electrolysis might be beneficial and eventually leading to more active or selective catalysts.^[30] In this context, Chen et al.^[31] have studied *in situ* formed copper mesocrystals as catalysts for high selectivity towards ethylene production. An in-depth analysis evidenced the presence of Cu(100) facets and steps that were identified to be essential for the selective reduction of CO_2 to C_2H_4 . Most importantly, the copper mesocrystals displayed stable catalytic activity towards C_2H_4 formations for more than 6 hours. Unfortunately, no data for longer times were provided. Another important parameter that can lead to deactivation of copper electrodes during CO_2RR is the presence of electrolyte impurities and blocking species.

To cite one example, Hori et al. noticed the poisoning or deactivation of copper electrodes after observing a decline in hydrocarbon yields and the prevalence of the hydrogen evolution after a 10-30 min after the start of the CO_2 electrolysis.^[13,17] The deactivating/poisoning species were classified into three groups: 1) heavy metals impurities contained in the chemicals; 2) small amounts of organic substances in water, which are very difficult to remove even after distillation; 3) the CO_2RR intermediate species. One of the most common electrolyte across the literature, namely a 0.1M KHCO_3 aqueous solution, does contain 0.02-0.05 ppm of heavy metals such as Fe, Zn, Pb, which can all deactivate copper surface if deposited. Therefore, electrolyte purification, for example, by irreversibly coordinating them *in situ* with ethylenediaminetetraacetic acid (EDTA) or *ex-situ* with a solid-supported iminodiacetate resin, must be performed to avoid such source of deactivation of the copper catalysts.^[32] As a second example, Dunwell et al. observed that transition-metal-cations from the anode can reach the cathode side even when an anion exchange membrane is utilized and contaminate the cathode surface.^[33] This migration can be significant especially for long operation time. One of the possible solutions is to use a carbon-based electrode as the anode, however, the latter is not particularly stable at oxidative potential, so other options must be found.

2.2 Shape-controlled Cu nanoparticles

Up to date, various synthesis approaches have been used to synthesize shape-controlled Cu nanoparticles, most common being colloidal chemistry and electrochemical deposition.^{[34],[35]} The aim of these studies was to investigate the structure-activity/selectivity relations of the CO_2RR , also referred to as »facet-effect«. ^[31,36] Primarily, single-crystal work done by Hori et al.^[14] showed that a different product selectivity is observed depending on the surface orientation of the copper electrode. It was found that Cu(100) produces primarily C_2H_4 , while Cu(111) surfaces predominantly form CH_4 . Further increment of the C_2H_4 production is promoted by the introduction of (111) or (110) steps to the (100) basal plane, leading to the increased $\text{C}_2\text{H}_4/\text{CH}_4$ ratio. Moreover, the authors observed that (110) electrode preferably promote high yield of CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$, and CH_3COOH but with a very low yield of CH_4 .^[14] These high-indexed crystal series promoted the dimerization of CO^* , which has a lower activation barrier on Cu(100) comparing to Cu(111) surface, as shown later by Montoya et al.^[37] Furthermore, a group led by Koper^[38–40] has done few studies to provide evidence on a mechanism on how C_2 species may be formed on Cu(100) electrodes. The authors showed, both, theoretically and experimentally, that pathway for ethylene production occurs via an electron-mediated dimerization reaction of two adsorbed CO molecules. Across the literature, particular emphasis has been given to copper nanocubes, which have shown remarkable selectivity toward C-C bond mostly due to the presence of the {100} facets. Size-dependent studies and calculations have pointed at the importance of the interface between {100} facets and {110} edges for C-C coupling.^[38,41] Unfortunately, the main drawback of these shape-controlled nanoparticles is their deactivation due to the loss of initially well-defined facets and decrease in size under reaction conditions.^[30,34,42,43]

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Grosse et al. have investigated the dynamic morphological transformations of ~100 nm cubes by *operando* electrochemical atomic force microscopy (EC-AFM). Concomitantly with the morphological changes, the reduction of initially present CuO_x species was made via *operando* X-ray absorption techniques. Figure 2A shows the change of copper cubes during the electrochemical reduction of CO_2 . Evident reconstruction was observed even when exposing the cubes to air before the electrochemical reaction. In general, corners and edges had a greater tendency towards degradation than the flat facets. The authors also investigated the product selectivity over time, in terms of faradaic efficiency towards CO_2RR and HER (Figure 2B). Larger cubes possessed higher FE towards CO_2RR , which was assigned to their improved morphological stability, most likely due to a larger ratio of flat surface sites to corners and edges (Figure 2B). Independently of size, there was an overall decrease in the FE for CO_2RR and an increase in HER over time. This could be attributed to the possible re-deposition as small Cu clusters and nanoparticles on the support and/or on the Cu cubes, as observed in other studies.^[42,43] This would then, in principle, lead to the formation of isolated low-coordinated sites favoring HER over CO_2RR .^[44]

The detachment of small clusters from the copper surface during CO_2RR was revealed using transmission electron microscopy (TEM) analysis by Huang et al.^[42] Here, the authors used well defined and monodispersed copper nanocubes (CuNC) synthesized *via* colloidal techniques to give further insights into their degradation mechanism. They found that the predominant degradation pathway, while CO_2RR is occurring, is a potential-induced fragmentation into Cu nanoclusters, which are 2-4 nm in size.^[42] The stability investigation was performed by stopping the reaction at defined times and collecting the reacted CuNCs for microscopy analysis. The morphological evolution of CuNCs shows that as the reaction proceeds, there is an increasingly pronounced disintegration of individual cubes, which eventually leads to coalescence (Figure 3A). After 12 h, the CuNCs are glued together and no single pristine CuNC is observed. Furthermore, the electrocatalytic performance of the CuNCs was investigated to observe possible alterations in catalytic behavior during long-term electrolysis. Figure 3B shows a slight decrease in FE for CO_2RR and an increase in HER after 6 h of the reaction, while the total current density remains stable for 12 h from the compensation of these two effects. 3D electron tomography (Figure 3C) evidences that the CuNCs undergo a pitting process, leaving tiny pinholes at the edges of the cube. This result is consistent with the theoretical findings that the edge/facet interface is the most active for C-C coupling.^[45]

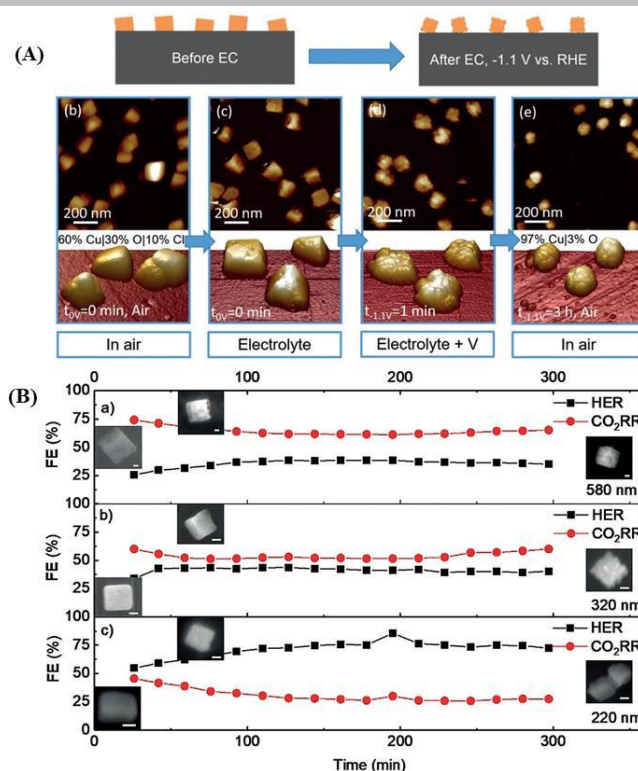


Figure 2. (A) (a) Schematic illustration of the morphological change of electrodeposited Cu cube catalysts; (b) AFM images of Cu cubes deposited on highly oriented pyrolytic graphite (HOPG) acquired in air, (c) and EC-AFM measurements in a CO_2 -saturated 0.1M KHCO_3 at OCP, (d) at -1.1 V vs. RHE for 1 minute, (e) after 3 h and after drying the electrolyte (e); (B) FE for CO_2RR and HER at -1.05 V vs. RHE recorded during 5 h for different Cu cube sizes (sizes shown on right side of picture). SEM images of typical Cu cubes are shown after different reaction times. The size of the scale bars is 100 nm.^[34] Copyright 2018, Wiley - VCH.

Moreover, additional experiments were performed to investigate the effect of CO_2 adsorption and applied negative potential separately. DFT calculations of the surface energy of different Cu facets under applied potential were performed and thermodynamically stable shapes were predicted using the Wulff construction. All results pointed to the role of the negative potential as the main driving force of the observed morphological changes. A similar degradation mechanism was also observed for Ag and Pd nanoparticles.^[42] The observed fragmentation differs from the degradation mechanisms more commonly observed in nanocatalysis, such as dissolution/re-deposition, coalescence, and Ostwald ripening.^[19] Instead, it resembles the phenomenon of cathodic corrosion reported for noble and non-noble metals under high cathodic potentials.^[46,47]

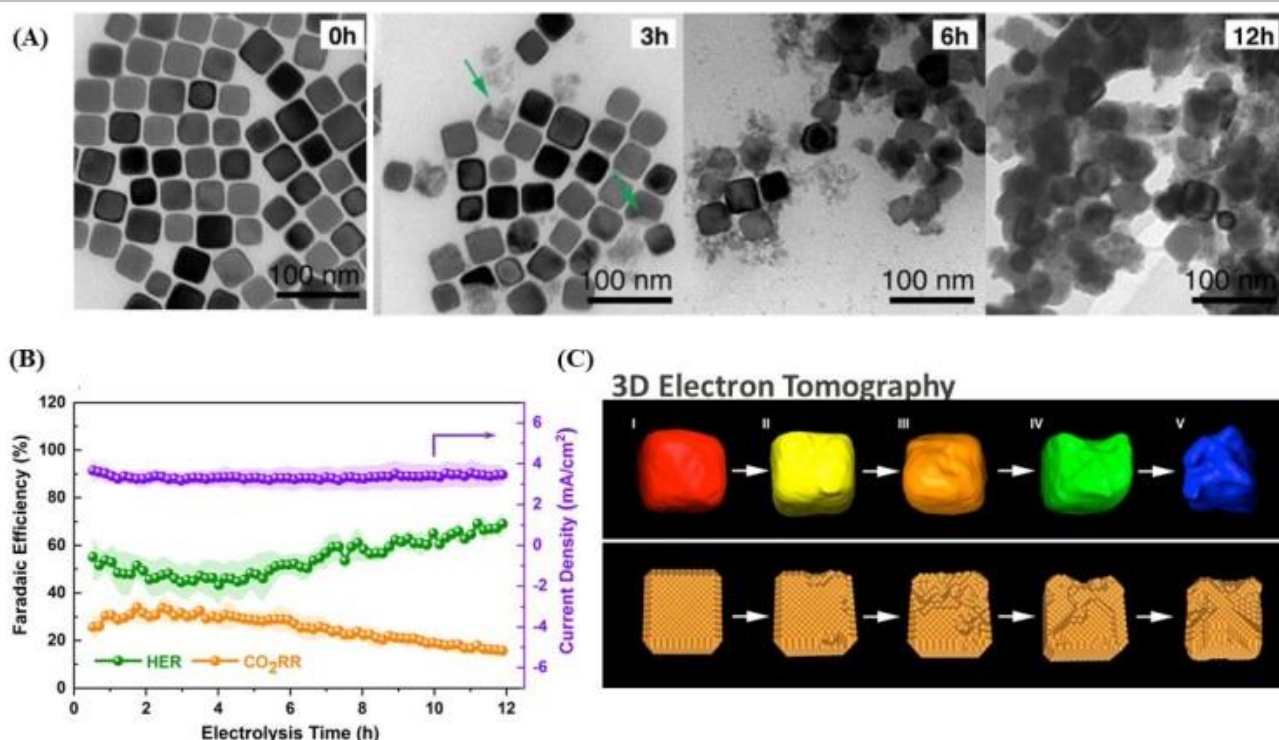


Figure 3. (A) Morphological evolution of CuNCs during electrolysis. (B) Time dependence of the FE and current density for 41 nm CuNCs. (C) 3D electron tomography of a random CuNCs at different stages during a 12 h of CO₂RR. (Electrolyte: 0.1M KHCO₃; chronoamperometric regime at -1.1 V vs. RHE).^[42] Copyright 2018, Nature Publishing Group

Interestingly, the onset of cathodic corrosion for Pt was shown to be as low as -0.5 V vs. RHE^[48], which is well within the potentials commonly applied during CO₂RR. The proposed mechanism for cathodic corrosion involves the formation of metastable metal anions that spontaneously oxidize to form small metal nanoparticles.

In addition to the two studies discussed above, Cu surface modification has been observed in other examples, which do not all involve CO₂RR conditions.^[49,50] Thus, fragmentation can be considered as one of the steps leading to the reconstruction and eventually the formation of Cu facets, which is known to affect the selectivity towards high-value CO₂RR products. Nevertheless, more insights into the corrosion mechanism could be gained with emerging electrochemical *in-situ* microscopy^[51] and *operando* techniques to detect mass losses (i.e. electrochemical quartz crystal microbalance coupled with ICP-OES^[52] and ICP-MS).^[53,54]

In situ transformations of Cu nanoparticles for CO₂RR are attracting increasing attention. As mentioned for the thin films, the morphological evolution of the catalyst in the initial stages of CO₂RR could even lead to an increase in activity/selectivity over time, rather than performance degradation. For example, Kim *et al.* have reported that the evolution of an ensemble of Cu nanoparticles induced highly selective CO₂RR toward C₂-C₃ products^[55]. They found that densely packed 6 nm spherical Cu nanoparticles undergo a structural transformation into electrocatalytically active cubic particles (Figure 4 A, B). SEM analysis confirmed that this change occurs as early as 7 minutes from the start of electrolysis. The authors observed high C₂-C₃ selectivity (~50%) at -0.75 V vs. RHE and demonstrated stable performance for 10 h (Figure 4C). A recent study by Osowecki *et*

al.^[56] revealed that CO₂ reduction intermediates play a capital role in Cu NC reconstruction. They emphasized that both in CO₂ and argon electrolysis, the sintering process occurs, most probably via the particle migration and coalescence process. However, under argon, clusters never form individual crystalline grains larger than the starting material or any spherical shapes.

In contrast to the aforementioned examples, recent work from Jung *et al.* shows that having well-defined facets might not be the only way to improve the FE towards C₂ and C₃ products.^[43] The authors demonstrate that fragmentation of a Cu₂O catalyst into small (2-4 nm) densely packed nanoparticles in the initial stages of CO₂RR could enhance selectivity toward ethylene production during the long-term electrolysis (Figure 5A). However, colloiddally synthesized Cu particles of similar size were found to be mainly active for HER, consistently with the previous work^[44].

This control experiment suggests that the presence of a large number of grain boundaries (Fig 5B) is likely responsible for the enhanced ethylene selectivity. Figure 5C shows TEM images with selected area (electron) diffraction (SAED) pattern before and after 10h of CO₂RR. The fragmented nanoparticles were barely visible on the carbon support, because of the small size and low contrast differences. Through additional experiments, the authors demonstrated that CO₂RR conditions are needed for the fragmentation. A similar effect was observed for CO reduction to C₂ and C₃ products, where fragmented Cu are prepared by *in-situ* reduction of CuO and the degree of fragmentation is controlled. The higher density of grain boundaries results in an increase in catalyst selectivity for C₂- and suppression of HER.^[57]

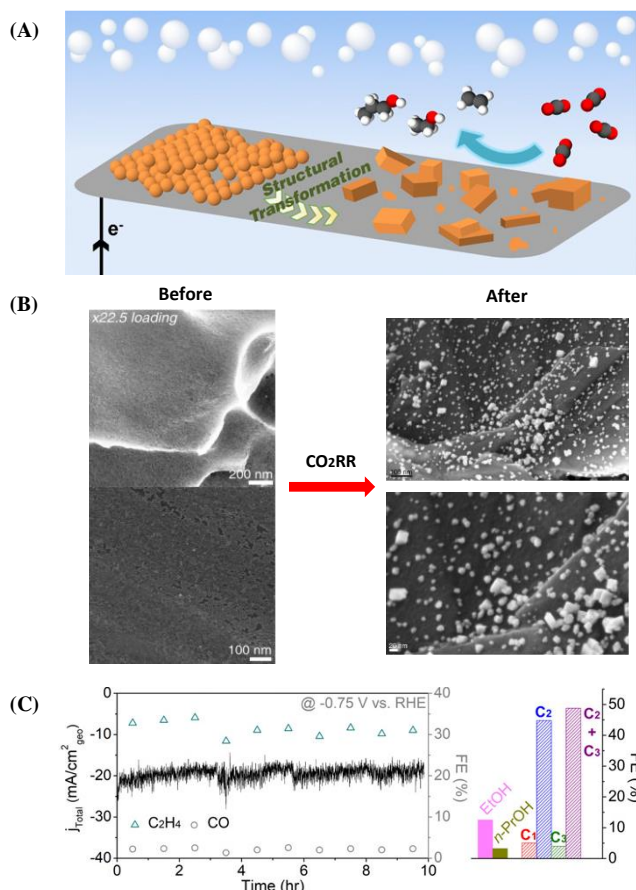


Figure 4. (A) Schematic of the structural transformation of Cu nanoparticles ensembles. (B) SEM image comparison nanoparticle loaded carbon-paper working electrode before and after 1 h of electrolysis in 0.1M KHCO₃ at -0.81 V vs. RHE (C) Long-term electrolysis at -0.75 V vs. RHE of transformed Cu ensembles with faradaic efficiencies for C₂H₄ and CO formation. The column graph summarizes C₁, C₂ and C₃ product FEs for the 12 h experiment.^[55] Copyright © 2019 National Academy of Sciences.

2.3 Compositional effect in Cu nanoparticles

In addition to the structure, the tuning of composition is crucial for catalytic selectivity as mixing different types of functionalities within the same catalyst allows to modify the binding energies of reaction intermediates on surfaces and break what is usually referred to as »scaling relationships«.^[58] The latter often represents a major limitation in activity and selectivity for single-site catalysts. Multicomponent catalysts for CO₂RR have only recently commenced to populate the recent literature and they include bimetallic electrodes, high-entropy alloys^[59], metal/metal oxide interfaces, metal/polymers.^[60–63] Because the data on stability are scarce, these catalysts are not discussed in this review.

Instead, in the context of compositional effects, oxide-derived (OD)-Cu surfaces have been at the center of interest in CO₂RR because of their improved selectivity towards C₂ products.^[8,16] Various *ex-situ* techniques (ambient-pressure X-ray photoelectron spectroscopy, atomic emission spectroscopy, TEM, etc) have been used to investigate the catalyst structure after CO₂RR and have shown residual oxygen.^[64–68] However, these *ex-situ* investigations of the surface/subsurface oxidation state of copper are prone to systematic error due to a tendency of Cu to rapidly oxidize at open-circuit voltage when the

reductive potential is cut off.^[69] More recently, *in-situ* grazing incidence X-ray diffraction measurements have asserted the complete reduction of a polycrystalline Cu₂O thin film to Cu under CO reductive conditions.^[70] The authors recognize that the presence of subsurface oxygen or amorphous oxide cannot be excluded. Indeed, the identification of a small amount of oxygen remains a challenge for *operando* techniques. In a recent study, isotopic oxygen labeling in OD-Cu catalyst revealed that less than 1% of the original O¹⁸ content remains after the CO₂RR, which suggests a complete reduction of the surface oxides during CO₂RR and its reformation on the cell shutdown, thus no major impact is expected on the electrochemical performance.^[65] However, the role of subsurface oxygen remains quite controversial in the community.

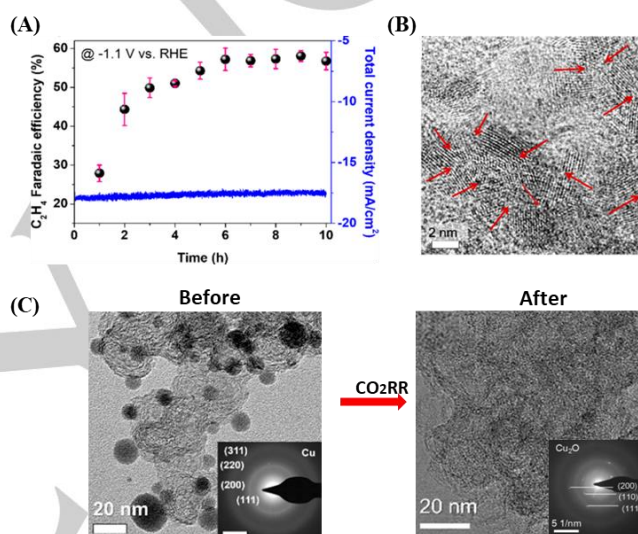


Figure 5. (A) Increase of electrocatalytic selectivity toward C₂H₄ formation during 10h of CO₂-RR (B) marked grain boundaries between Cu nanoparticles and (C) TEM images with SAED patterns comparison before and after 10 h of CO₂RR^[43] Copyright 2019, American Chemical Society.

3. Mitigation Strategies – Towards Stable Electrocatalysts

In addition to contributing towards a rational design of catalysts, understanding the mechanisms of catalyst deactivation opens up the development of strategies to prevent these processes and even to direct catalyst reconstruction towards better performing structure. Some efforts towards the stabilization of Cu-based catalysts have already been made.

The main strategy of these studies has been to preserve the morphology in order to maintain the reaction selectivity. A very effective approach is particle confinement, which was used to stabilize platinum and silver nanoparticles against coalescence and agglomeration.^[71] Li *et al.*^[72] showed that wrapping Cu nanowires with graphene oxide prevents structural changes and the loss of methane-selective sites (Figure 6A). Vanrenterghem *et al.*^[73] have reported a similar way for the prevention of coalescence/agglomeration of metallic nanoparticles by physical separation of the Ag nanoparticles with vertically oriented graphene.

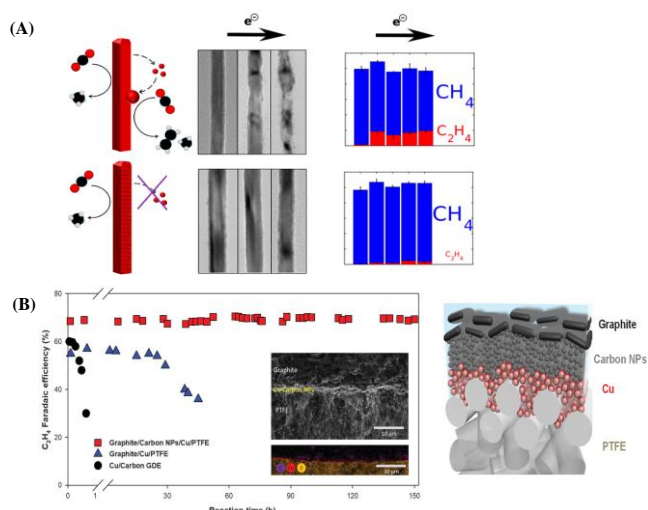


Figure 6. (A) Schematic representation for the correlation between morphology and selectivity. Transformed Cu nanowires without (up) and with (down) protective graphene oxide wrapping.^[72] Copyright 2017, American Chemical Society (B) Long term performance test of CO₂ electroreduction to ethylene on gas diffusion electrode showing stable high selectivity of the graphite/carbon NPs/Cu/PTFE electrode compared with that of a traditional carbon-based gas diffusion electrode (GDE). Schematic illustration of the graphite/carbon NPs/Cu/PTFE electrode (right) ^[15] Copyright 2018, American Association for the Advancement of Science.

Guntern *et al.*^[74] have recently shown increased morphological stability of the Ag nanoparticles when covered with an aluminum-based MOF. The authors demonstrated that the synthesis method is generally applicable to other metal nanoparticles, thus offering a new way for the enhanced selectivity and stability of electrocatalysts. Another factor worth considering is the effect of surface-bound organic molecules during the CO₂RR. Colloidal synthesis of nanocatalyst requires the use of ligands to control their shape and size. These ligands are not always removed prior to electrocatalysis and can play an important role in stabilizing the catalyst shape. The desorption of trioctylphosphine oxide ligand during the initial stages of CO₂RR was confirmed by attenuated total reflection – Fourier transformed infrared spectroscopy and XPS for various sizes of Cu cubes.^[42] When the ligands were intentionally removed by N₂ plasma before the CO₂RR, the catalyst morphological changes were accelerated.^[42] Common ligands such as thiols or amines are readily electrodesorbed, which leads to sintering and coagulation of Au, Pd, and Ag nanoparticles.^[74,75] Strongly bound carbene based ligands were instead shown to stabilize the morphology of these electrocatalysts, leading to enhanced stability for selective CO formation.^[76]

4. Concluding remarks and perspective

CO₂RR has been attracting increasingly more attention in the last few decades as it offers the possibility of producing valuable chemicals and high energy-density fuels while recycling CO₂ and storing renewable energy. Many intriguing nanoscale structure-activity and structure-selectivity relationships have been discovered up to date. However, in order to bring the process closer to the commercial and applied level, it is necessary to further enhance the catalyst stability, in addition to the activity/selectivity. In this mini-review, we have discussed

previous studies focusing on the stability of Cu-based catalysts with the aim to highlight this critical issue that has been underestimated so far in the vast literature related to CO₂RR. Generally speaking, most works on Cu-based catalysts report stability in a range comprised from 5 to 15 hours, which is far away from commercial applications.⁷ One of the few exceptions is represented by the 150 hours of stable operation when copper catalysts are assembled in a gas-diffusion electrode (GDE).^[15] This example suggests that one additional possibility for the stability might come from a synergistic interplay between catalyst design and system engineering (Figure 6B). Moreover, in part devoted to shape-controlled nanoparticles, morphological transformation correlated to electrocatalytic performance are presented. The degradation mechanisms mentioned in this review and proposed so far are sketched in Figure 7. Yet, in-depth studies are still to come, which will then shed more light on the local atomic-scale effect and overall real-life feasibility of these CO₂RR catalysts. Finally, a standardized protocol for assessment of the electrocatalyst stability for CO₂RR should be established, which should rely on parameters such as electrode type, electrolyte, electrolysis time/potential and favored product. Implementation of this protocol would enable benchmarking of the catalysts in a straightforward manner.

In our perspective, we suggest that future studies should be directed towards the following three topical areas:

(i) Developing advanced electron microscopy tools

While X-ray measurements, including absorption and scattering techniques, provide ensemble information, electron microscopy allows us to observe local morphological, structural and compositional changes of Cu nanostructures at the nano- and at the atomic-scale.^[51,77,78] As such, it is highly complementary to X-ray characterization. Electron microscopy techniques like identical location and in-situ liquid TEM should be further developed in the context of CO₂RR where, for instance, challenges with bubbles forming on the TEM grid will occur, especially if the latter is constructed of some active material like gold. The acquired knowledge should then be coupled with theory and computer simulations. In order to find a strategy for successful mitigation of catalyst degradation during CO₂RR, it is necessary to have a physical model and a deeper fundamental knowledge of the reconstruction mechanism.

(ii) Establishing accelerated degradation tests and protocols for stability assessment

A useful perspective on data acquisition and standard protocols to evaluate the activity and selectivity of CO₂RR catalysts has recently been published.^[33] The next step is now to develop degradation protocols to benchmark catalyst stability. Long-lasting tests under real operation conditions, such as those performed by Siemens for 1200 hour⁷, are not realistic for academic institutions. Accelerated tests are needed. These tests should be developed based on the identified driving forces for catalyst degradation and/or reconstruction. Considering the very few studies and the limited current knowledge on this topic, it is difficult to identify the conditions at this moment. However, the community should keep this in mind and reconvene at due time.

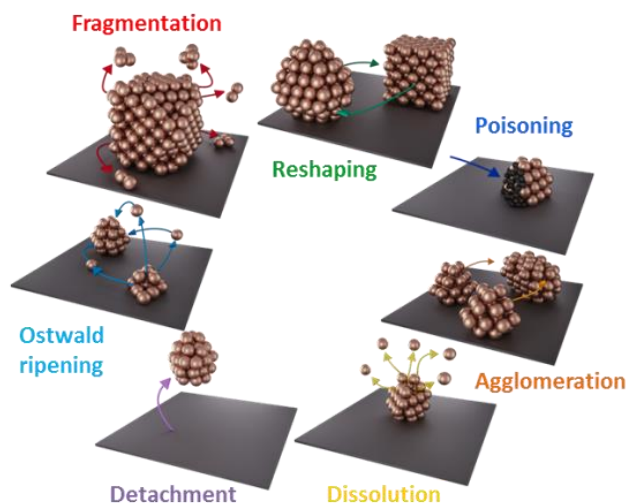


Figure 7. Summary of nanoscale degradation mechanism of Cu-based nanostructures during CO₂RR are: detachment, dissolution, Ostwald ripening^[51]; reshaping^[65], fragmentation^[43]; agglomeration^[42]; poisoning^[17,28]. They cause the change of active surface area, structure, and morphology of copper electrocatalysts, which directly affects activity and selectivity.

We propose to have standardized tests in all CO₂RR related publications that would include one test to simulate start-stop conditions and one test to evaluate stability under load experienced by the electrolyzer. We suggest 12-24 hr under optimal conditions with on-line gas product distribution (every hour) to evaluate stability under load. For start-stop operation, we propose 1h electrolysis quantifying gas products, followed by 200-1000 CV cycles from OCV to operating potential at 50-100 mV/s with subsequent 1h electrolysis quantifying gas products. In addition, morphological characterization before/after (SEM; TEM) should be done in any type of protocol, as well as additional characterization methods (case-specific) if available.

(iii) Investigating synergism between catalyst degradation mechanisms and electrolyzer design

The use of carbon-based gas diffusion layers (GDL) and the assembly of catalysts into a membrane electrode assembly (MEA) are attracting increasing attention as the community moves towards gas-fed electrolyzers.^[15,79–82] The latter can reach commercially relevant current densities by bypassing the solubility limit of CO₂ in aqueous electrolytes and shortening the diffusion paths for the reaction to occur. This type of electrolyzer typically operates at lower overpotentials and higher local pH conditions as opposed to a traditional H-cell. These differences represent a challenge when translating catalyst degradation and preventive strategies developed in the well-controlled environment of an H-cell to gas-fed electrolyzers. Furthermore, engineering issues, like the GDL flooding, should be considered as well as degradation of the GDL itself. Overall, when it comes to GDE and MEA, the knowledge of the parameters influencing catalyst and device stability is even less explored compared to the H-cell configuration, where the catalysts are deposited on flat glassy carbon supports. Future efforts must be directed towards understanding the effects of catalyst loading, catalyst distribution in the GDL, nature of the electrolyte, electrolyte flow rate, type of electrolyte (liquid or solid), potential, current, etc. Special attention should be dedicated also to the development of ad-hoc *in-situ* and *operando* tools and techniques. In GDL and

MEA one of the challenges is that the primary active catalyst surface is no longer easily accessible to surface characterization techniques, as in the case of flat carbon supports. Studies performed for fuel cells can be a great source of inspiration in terms of cell design for spectroscopic techniques.^[83] Environmental scanning electron microscopy studies could be performed similarly to what attempted for batteries.^[84,85] Newly emerging synchrotron techniques, such as X-Ray ptychography and microscopy, are also potentially interesting in the context of CO₂RR.^[85,86]

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Keywords: electrocatalysts • electrochemical CO₂ reduction • copper nanoparticles • stability • degradation

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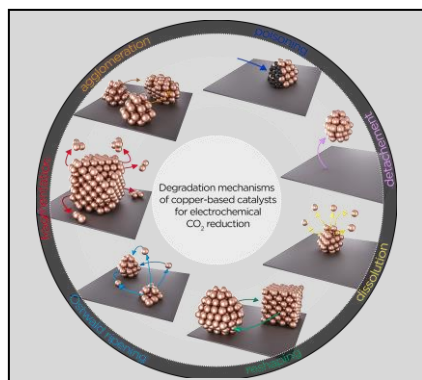
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Entry for the Table of Contents

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Recently CO₂ electroreduction reaction gained in its popularity. Cu is still the only monometallic catalyst that can effectively produce interesting molecules, such as hydrocarbons and alcohols. Many breakthroughs have been on the so-called structure-activity and -selectivity relationships. However, the stability of Cu-based electrodes and the nanoscale degradation mechanisms are still in its infancy. This aspect is in our opinion, the next grand challenge.

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