

Accepted Article

Title: Reconstruction of Copper Nanoparticles at Electrochemical CO₂ Reduction Reaction Conditions Occurs via Two-step Dissolution/Redeposition Mechanism

Authors: Stefan Popovic, Marjan Bele, and Nejc Hodnik

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemElectroChem* 10.1002/celc.202100387

Link to VoR: <https://doi.org/10.1002/celc.202100387>

ARTICLE

Reconstruction of Copper Nanoparticles at Electrochemical CO₂ Reduction Reaction Conditions Occurs via Two-step Dissolution/Redeposition Mechanism

Stefan Popovic^[a, b], Marjan Bele^[a], Nejc Hodnik^{*[a, b]}

[a] SP, Popović ; dr. MB, Bele; prof. NH, Hodnik
Department of Materials Chemistry,
National Institute of Chemistry
Hajdrihova 19, 1000 Ljubljana, Slovenia
E-mail: nejc.hodnik@ki.si

[b] SP, Popović ; prof. NH, Hodnik
University of Nova Gorica
Vipavska 13, 5000 Nova Gorica, Slovenia

Abstract: Copper is still the monometallic electrocatalyst of choice for electrochemical reduction of CO₂ (ERC) when added-value products, such as hydrocarbons and alcohols, are desired. However, severe morphological and structural changes are observed upon exposure to the ERC operation conditions. One of the pending questions in the community is what is the mechanism behind this reconstruction. In this study, pulse-electrodeposited copper nanoparticles were exposed to different ERC relevant reductive potentials and tracked with identical location scanning electron microscopy (IL-SEM). This approach provides information on the morphological and structural history and subsequent change of Cu nanoparticles and with that a deep insight into the reconstruction events. With this evidence, we could interpret the observed structural changes as two separate electrochemical processes occurring one after another, namely copper dissolution from pre-oxidized native nanoparticles and subsequent (electro) redeposition of the dissolved copper species in a form of new smaller Cu fragments.

Introduction

Anthropogenic impact on the environment has drastically increased since the beginning of society's industrialization and modernization. In favor of that, the early sixties of the last century can be considered as the start of an impetuous increase of atmospheric CO₂. Up to date, the enormous increase of CO₂ has triggered different strategic decisions and efforts to limit the temperature increase below 2 °C above pre-industrial levels, declared by the Paris Agreement.^[1] Electrochemical reduction of CO₂ (ERC) has emerged as a prospective strategy for the conversion of CO₂ to value-added products. Copper is the only monometallic electrocatalyst that converts CO₂ to fuels and feedstocks such as hydrocarbons and oxygenates.^[2,3] Recently, while researchers' efforts have been devoted to the activity/selectivity of ERC, the stability of the Cu-based catalysts has gained a lot of attention.^[4] Since nanoscale electrocatalysts' activity and selectivity are highly affected by the structural changes via so-called structure-property relationships^[5,6], understanding this phenomenon and the development of approaches to control it is of paramount importance. So far, copper-based catalysts have been observed to be highly

susceptible for restructuring while exposed to the applied bias of the ERC.^[7–10] Since nanostructured copper surfaces are prone to oxidation when exposed to the ambient air, water-based electrolyte immersion,^[11] a local pH increase,^[12] presence of undercoordinated atoms and grain boundaries^[13] it is expected that copper oxide is present on the surface before ERC.^[14,15] Oxide-derived copper (OD-Cu) catalysts are proposed to have high catalytic performance, however, the interpretation of this increase is still not settled. To this point, the mechanism governing their morphological evolution, namely reconstruction, is thus very important for the interpretation of their electrochemical activity. Up to date, there have been different approaches to understand and reveal the process of the reconstruction and degradation mechanisms of nanostructured copper-based catalysts under ERC relevant conditions.^[7–9,11,15–18] Despite the multidisciplinary approaches that were employed to study Cu-based catalysts' reconstruction under ERC conditions, either through *ex-situ*^[7,16,18] and *in-situ* or *operando*^[11,17,19,20] methods, there is still an active debate in the community regarding their actual mechanisms.

Huang et al.^[7] studied the disintegration of individual Cu nanocubes (Cu NCs) by using transmission electron microscopy (TEM). They observed pronounced truncation of Cu NCs during ERC and recognized potential-driven fragmentation into Cu nanoclusters as the main degradation pathway. Since Osowiecki et al.^[21] reported the timelines behavior of sintering and declustering of small Cu (7nm) nanospheres, there have been a few studies of small Cu nanoparticles whose morphological evolution enhances the catalytic performance.^[8,22] However, the physicochemical background of the process remains unclear. Not directly related to the restructuring of Cu, however very informative, Luna et al.^[15] showed that the nature of the morphology of sol-gel Cu₂(OH)₃Cl catalysts depends on the negative applied bias. It was shown to occur through electro-redeposition of the dissolved and redeposition of copper from a sol-gel precursor. Depending on an applied bias a broad range of nanostructures of varying sharpness emerged. Recently, copper surface dissolution was shown to be the main process that governs the reconstruction of nanostructured Cu-based catalysts.^[11,12] Vavra et al.^[11] revealed dissolution/redeposition as the main degradation mechanism in the initial stages of ERC.

ARTICLE

Nevertheless, the *in-situ* liquid TEM with all its limitations (e.g., beam-induced radiolysis effects)^[23,24] provides only low-resolution morphological changes of the of Cu-based catalyst. Even though the *ex-situ* characterization cannot probe the nature of catalytic sites^[14], it is still common and very useful to observe and follow morphological changes. Identical location scanning electron microscopy (IL-SEM) has stood out as a very efficient tool for electrocatalyst research in the past decade.^[25] It allows observation of the same site (down to single-nanoparticle) before and after electrochemical treatment. This provides direct evidence of the structural changes since the history of the site is known. Unlike in random imaging where always statistical analysis (with certain uncertainty) needs to be made to elucidate structural events. It is recognized as one of the valuable characterization tools for investigating the degradation process as it is a non-destructive and non-invasive method. Since Hodnik et al.^[26] firstly reported the method in 2012, IL-SEM has been employed successfully in different fields of electrocatalysis and beyond. Afterward, Kinumoto et al.^[27] showed morphological changes that occur on a Pt/C catalyst for polymer electrolyte fuel cell. They classified the degradation behavior of Pt nanoparticles as disappearance, precipitation, migration, coalescence, and transformation. To our best knowledge, Rahaman et al.^[18] firstly employed the IL-SEM method to investigate and identify the morphological evolution of electrodeposited Cu dendritic catalysts during ERC. IL-SEM analyses showed that subsequent thermal annealing of dendritic electrodeposited Cu promotes the formation of nanodendritic Cu, which exhibits a tendency toward the production of multicarbon alcohols. Moreover, the group led by Peter Broekmann employed IL-SEM investigation in several studies to follow structural and compositional stability of different types of catalysts for ERC.^[28–31]

In the present study, IL-SEM is used for the first time to track the reconstruction process of pulse-electrodeposited copper nanoparticles (ED Cu NPs) with defined shapes at ERC relevant conditions. With full awareness of the limitations and advantages of the IL-SEM^[32,33], a two-step ED Cu NPs dissolution/redeposition reconstruction mechanism is confirmed. Upon exposure to the reductive potentials, Cu-oxide reduction triggers severe cathodic dissolution which is followed by the local (electro) re-deposition of dissolved Cu in form of small fragments.

Results and Discussion

Figure 1 shows SEM images of typical as-synthesized Cu NPs used for IL-SEM degradation studies. Particle morphologies range from spherical to shaped half-micron particles. It needs to be emphasized that Cu particles of particular interest for ERC mainly contain grain boundaries^[34], facets^[35,36], high roughness^[37], defects^[38], which have been shown to improve ERC performance towards C₂₊ product formation. In the present study, a structurally and morphologically distinct set of Cu NPs can be considered as an ideal specimen as it allows observation of different structure-stability relationships in one measurement. Besides, NPs size optimally facilitates IL-SEM observation (i.e., resolution) and can therefore serve as a model system for studying the reconstruction process during ERC-relevant conditions. Potential-dependent and time-dependent reconstruction of the ED Cu NPs were studied by following morphological changes during ERC electrochemical treatment by the IL-SEM method.

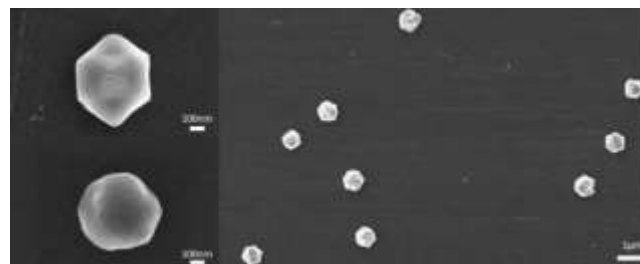


Figure 1. Representative SEM micrographs of as-synthesized pulse-electrodeposited Cu nanocrystals on glassy carbon rotational disk electrode (GC-RDE)

Since the nature of *ex-situ* study, starting Cu nanoparticles are in an oxidized form most likely due to exposure to the air, as well as the aqueous electrolyte.^[11] Thus, we can safely consider the surface of NPs to be composed of Cu_xO as a starting material prior to ERC. The same was also observed in other studies.^[39] Figure 2 shows the morphological evolution of the same Cu-based nanoparticle before and after exposure to the negative applied potential of -0.7 V_{RHE}. ERC was performed in 0.1 M KHCO₃ for 20 min in the chronoamperometry regime. The native particle gets severely fragmented and shrinks in a size of approximately 20 % (~100 nm) after 20 min of electrolysis. At the first stage, oxidation at open circuit potential (OCP) is accompanied by some relatively small dissolution of copper after immersing the electrode in an electrolyte.^[11,12] This can already change the structure of nanoparticles and provide a source of Cu ions in the electrolyte. After application of ERC reductive potentials, CuO_x reduction triggers aggressive cathodic dissolution, which releases additional Cu ions into the electrolyte.^[12] Subsequently, the negative potential is sufficient to drive the process of Cu electrodeposition. This phenomenon can be observed in a form of a variety of copper fragments with a particular size and shape redeposited on the glassy carbon substrate onto the native Cu particles. Moreover, the redeposited fragments can be perceived around the vicinity of Cu particle in-focus (Figure S1). We observed the electrodeposited fragments in the range of 20–40 nm, predominantly on the top of the native particle and its surrounding. Interestingly, it can be perceived that to some degree redeposited fragments are cuboidal shape, previously reported to occur in the reconstruction process for small 7 nm Cu NPs, which showed unique ERC activity.^[8] However, close inspection and also repeatable measurements reveal that the presence of cubic fragments is not constant and sometimes even only undefined shape fragments are observed. (Figure S2.) This is a proof that the re-deposition process is highly complex and affected by many local and bulk parameters like local Cu ion concentration, presence of nucleation sites, effective local pH and potential, etc.^[40] This observed sensitivity is typical for electrodeposition in general where it is known that reaction conditions need to be optimized and under complete control if the process is to be reproducible.^[41] Consequently, this gives another argumentation that reconstruction for ED Cu NPs includes the (electro) re-deposition process, and not through the solid-phase reshaping or cathodic corrosion.^[42] Surface migration, agglomeration of the particles weren't noticed during measurements, most likely due to a large size of native Cu-based NPs. Some detachment was observed, however, we believe this is not a consequence of degradation but merely due to random

ARTICLE

mechanical stress as a result of handling and immersion of the electrode. We note that with the IL-SEM experiment we can claim that pristine Cu nanoparticles do not reconstruct but rather shrink on the account of newly formed Cu particles. Therefore the question of what is the source of the formed fragments is in our case clear as we observe the changes that occur on the same particles. This would not be possible with random subjective imaging where the history of the nanoparticles' presence, size, structure, and morphology is not known.

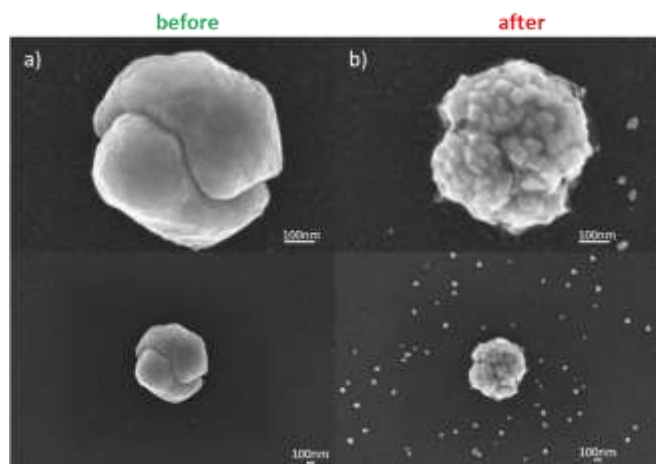


Figure 2. Ex-situ IL-SEM micrographs of electrodeposited Cu nanoparticles a) before and b) after electrochemical treatment at $-0.7V$ vs. RHE for 20min in $0.1M$ $KHCO_3$ saturated with CO_2 . While redeposition occurs all over the electrode, most of the 20-40nm fragments redeposit on top of the big particle.

According to the literature, applied potential and presence of the ERC reaction intermediates are the two factors that mainly influence the morphology change and reconstruction of Cu-based catalysts.^[16] Since the applied potential alone can drive the reconstruction of copper surfaces^[7], there is an option to exempt one of those two factors. With the attention to understand the reconstruction process of ED Cu NPs without the presence of ERC intermediates, even though they are suggested to not be crucial for reconstruction, we conducted the experiments in Ar-saturated $0.1M$ $KHCO_3$ at $-0.7V_{RHE}$, where no reaction intermediates from ERC are expected since we omitted the CO_2 source (Figure S3). The particles remain in their shape, without truncation, and redeposition can be observed. The slightly different behavior can be attributed to the intermediates' role in the ERC reaction. Additionally, the IL-SEM study was performed at the $0 V_{RHE}$ in CO_2 -saturated $0.1M$ $KHCO_3$ to follow the reconstruction process when both previously mentioned parameters are excluded. The particle is noticeably reconstructed, truncated, and the partial cracking is observable. Since the potential is sufficient for CuO_x reduction (Figure S4) we propose that morphological changes come from oxide reduction and dissolution. In our opinion, cracking could occur from subsequent re-oxidation when exposed to the air. Since the redeposition potential is proposed as the important morphology "shaping" parameter^[15], we could observe only a few redeposition fragments at the identical location after 20min (circled in Figure 3). This is presumably because of the relatively low overpotential for Cu

redeposition and the presence of smaller nanoparticles that are most likely below the detection of the SEM (few nm in size). This experiment proves that indeed Cu-oxide reduction is the main driving mechanism of the reconstruction of native Cu particles. The formation of new Cu fragments is, however, dependent on the applied reductive potential. To understand the time-dependent behavior of redeposition and mainly to confirm the dissolution/redeposition mechanism as the main reconstruction process, a two-step experiment was developed. We employed the sequential time-dependent *ex-situ* approach presented in Figure 4 where we performed two consecutive exposures to ERC for 20 and 30 minutes and took SEM images at each step. If the degraded sample reached a steady-state then further ERC exposure would not affect it anymore. However, as the re-oxidation occurs upon exposure to ambient conditions between the electrochemistry experiment and microscopy analysis again, Cu-oxide grows. This is then a decisive factor in triggering even more copper dissolution *via* Cu-oxide reduction-induced transient dissolution. This is in line with our hypothesis on the dissolution/redeposition mechanism. Therefore the proposed two-step experiment shows how re-oxidation and subsequent transient dissolution of copper affect the morphological change and reconstruction of the native and newly formed Cu nanoparticles.

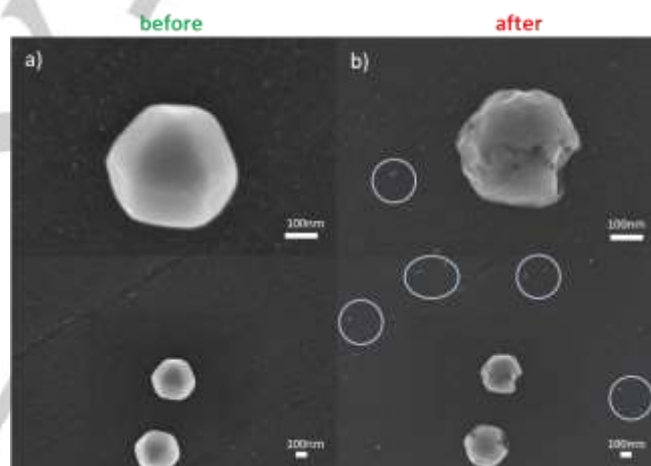


Figure 3. Ex-situ IL-SEM micrographs of electrodeposited Cu nanoparticles a) before and b) after electrochemical treatment at $0 V_{RHE}$ for 20min in CO_2 saturated $0.1M$ $KHCO_3$.

The result of the first step in Figure 4 is in accordance with the one shown in Figures 2 and 3. Thus, the electrolysis of as-synthesized ED Cu NPs, under the previously mentioned conditions, for 20 min at a potential of $-0.7 V_{RHE}$. Exhibits some copper dissolution that occurs already when exposed to the electrolyte (OCP) and mostly after oxide reduction^[11,12]. Subsequent redeposition in the form of small (shaped) fragments follows. In the second step, we show how additional exposure to air and subsequent re-oxidation of the copper surface further affect the final change in morphology.

ARTICLE

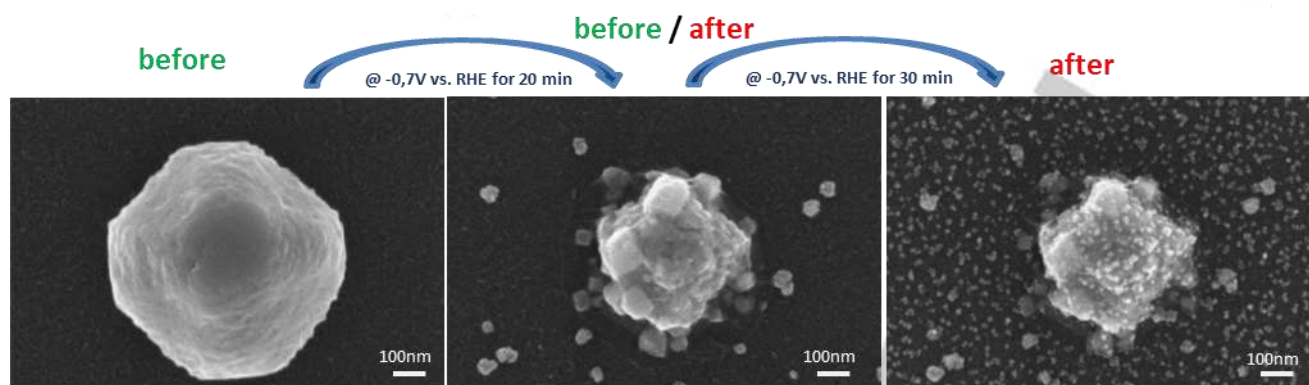


Figure 4. *Ex-situ* IL-SEM approach proving the dissolution/redeposition as the main degradation pathway. Two-step approach - electrochemical treatment of the Cu NPs at $-0.7V_{RHE}$ for 20 min and subsequent 30 min. IL-SEM micrograph taken after each electrochemical treatment

The electrolysis is performed for an additional 30 min at the same potential. The pronounced reconstruction occurs, however to all of the Cu particles. Compared to the first electrolysis step we now observe the formation of even smaller fragments of Cu redeposition and less damage to the native Cu particle. The number of redeposited fragments noticeably increases, which indicates that there are more nucleation sites present on the surface or local conditions are altered in some other way. The observed effect is following the fact that the sample was again exposed to air enabling additional oxidation, which later served as an additional source of copper for redeposition through transient dissolution/redeposition mechanism. These results can be useful as an insight into the reconstruction of copper catalysts during the proposed standardized measurements for ERC in the form of start/stop conditions.⁴ Our results are not consistent with the Rahaman et al.¹⁸ where IL-SEM experiments carried out after ERC on a pristine dendritic electrodeposited Cu catalyst showed no signs of reconstruction upon 6h. It might be that in their case Cu in dendritic morphology is less prone to re-oxidation and subsequent reconstruction/fragmentation. Besides, we can see from Figures 2 to 4 that different shapes of native Cu-oxide particles degrade in the same manner. Therefore we presume that the shape is not the determining factor and does not play a critical role.

Conclusion

In this study, we demonstrated the morphological evolution of pulse-electrodeposited Cu nanoparticles upon exposure to the ERC conditions by identical location scanning electron microscopy (IL-SEM) technique. The IL-SEM approach provided the high-resolution analysis down to a single-particle before and after electrochemical treatment. We observed the shrinkage of the native ED Cu NPs and the formation of new small Cu fragments and referred it to as the two-step dissolution/redeposition mechanism.¹¹ Moreover, the potential-dependent study proved that the role of the main driving force, namely the applied reductive potential, was to reduce the Cu-oxide, which triggered aggressive Cu transient dissolution and

subsequent potential-dependent redeposition of Cu.^{7,21} The two-step experiment showed that re-oxidation provoked additional restructuring and formation of even smaller fragments. Our study confirms that the dissolution/redeposition mechanism is responsible for the severe Cu-catalyst restructuring observed and debated in the literature. The same mechanism will most likely govern the restructuring of any other non-noble and potentially also some noble metal nanoparticles if exposed to first (oxidative) ambient and then to the reductive aqueous electrochemical conditions. Our study also provides a practical notice of Cu-based catalysts' severe restructuring each time the ERC electrolyzer will be exposed to the start/stop conditions.

Experimental Section

Electrodeposited copper nanoparticles (ED Cu NPs) were prepared by pulse electrodeposition (P-ED) method from 10 mM copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5 H_2O$, Sigma Aldrich, USA) solution in a standard three-electrode electrochemical cell. Glassy carbon rotating disk electrodes (GC-RDE) were employed as a substrate for the synthesis of ED Cu NPs. During the electrodeposition, 10 mM $CuSO_4 \cdot 5 H_2O$ electrolyte was constantly bubbled with Ar and GC-RD electrodes were rotated with 1600 rpm. Platinum rod and Ag/AgCl_{Sat.KCl} served as a counter and a reference electrode, respectively. For all electrochemical experiments, potentiostat/galvanostat (Biologic SP300, USA) was used to control the potential. Before deposition, GC-RDE substrates were polished on a cloth pad (1.0 μm Alumina suspension, Buehler, USA), rinsed with Mili-Q water, and 3 times ultrasonicated in ultrapure Mili-Q water to remove all the alumina residual. The P-ED method was optimized with a different pulse and relaxation time duration, as well as a various number of pulses. Cu NPs selected for further investigation were synthesized with 6 consecutive pulses of 500 ms at $-0.3V$ vs. Ag/AgCl with the 30s of open circuit potential (OCP) relaxation in-between. The schematic representation of the P-ED method is shown in Figure 6A.

ARTICLE

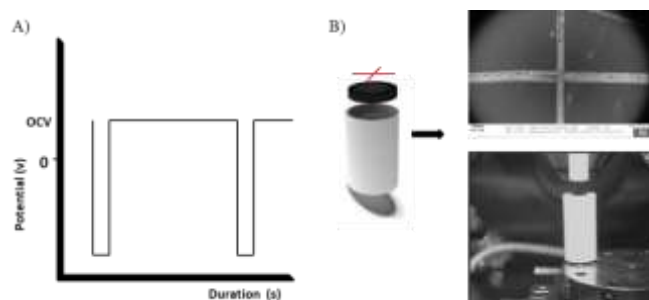


Figure 6. A) Schematic representation of pulse electrodepositon method with appropriate pulse and relaxation time range; B) Facilitating tracking of an identical location with scratched GC substrates with corresponding SEM micrograph and RDE under a microscope.

Electrodeposited Cu NPs on GC-RDE were used as a working electrode in a standard glass three-electrode electrochemical cell to perform ERC measurements. Standard three-electrode cell and RDE setup (OrigaLys, France) were used to facilitate and accelerate the degradation of copper-based catalysts. Platinum rod and Ag/AgCl_{Sat} KCl were employed as a counter and reference electrode, respectively. During the electrolysis, carbon dioxide (CO₂, 99,998% Messer, Austria) was constantly bubbled through 0.1M potassium bicarbonate (KHCO₃, 99,7% Honeywell, USA) to avoid depletion of CO₂ source. Electrolyte solutions were prepared with 18.2 MΩ Mili-Q water. Chronoamperometry regime was used for electrochemical measurements with a different time range, which will be emphasized for each sample in section 3. Potentiostatic electrochemical impedance measurements were done before each experiment and corresponding hardware IR compensation (85%) was employed during the chronoamperometry regime. The potential was controlled using potentiostat/galvanostat (Biologic SP 300, USA) and is given versus RHE (Reversible Hydrogen Electrode). RHE potential was calculated by using Equation 1.

$$\text{Equation 1: } E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0,059\text{pH} + E_{\text{Ag/AgCl}}^0$$

where $E_{\text{Ag/AgCl}}^0 = 0.199\text{V}$ and pH of the CO₂-saturated 0.1M KHCO₃ was 6.8.

All IL-SEM micrographs are obtained using a scanning electron microscope (FE-SEM Zeiss SUPRA 35VP) with an accelerating voltage of 3 or 5 keV and an InLens detector. Moreover, the working distance used for obtaining SEM micrographs was from 4-5mm. To ensure good electrical contact between the RDE electrode and the SEM stage, we used a home-made SEM "holder" which screw-spring construction provides a connection of GC substrate and SEM stage. To facilitate the observation of identical locations inside the SEM, the GC substrates were scratched prior to the Cu NPs deposition with a diamond cutter; marked with a red cross, and shown with SEM image and position inside the microscope in Figure 6B.

Acknowledgements

This study was supported by the Slovenian Research Agency for the research programme P2-0393 and project N2-0106.

Keywords: IL-SEM • copper • carbon dioxide • electrocatalysis • reconstruction

[1] R. S. Haszeldine, S. Flude, G. Johnson, V. Scott, *Philos. Trans. R.*

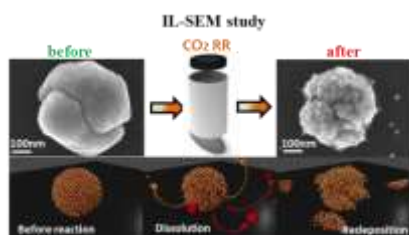
- Soc. A Math. Phys. Eng. Sci.* **2018**, DOI 10.1098/rsta.2016.0447.
- [2] C. S. Chen, A. D. Handoko, J. H. Wan, L. Ma, D. Ren, B. S. Yeo, *Catal. Sci. Technol.* **2015**, DOI 10.1039/c4cy00906a.
- [3] M. Gattrell, N. Gupta, A. Co, *Energy Convers. Manag.* **2007**, DOI 10.1016/j.enconman.2006.09.019.
- [4] S. Popović, M. Smiljanić, P. Jovanović, J. Vavra, R. Buonsanti, N. Hodnik, *Angew. Chemie - Int. Ed.* **2020**, DOI 10.1002/anie.202000617.
- [5] Y. Hori, I. Takahashi, O. Koga, N. Hoshi, *J. Mol. Catal. A Chem.* **2003**, 199, 39–47.
- [6] S. A. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, K. Albert, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, J. K. Nørskov, et al., *Chem. Rev.* **2018**, DOI 10.1021/ACS.CHEMREV.8B00705.
- [7] J. Huang, N. Hörmann, E. Oveisi, A. Loidice, G. L. De Gregorio, O. Andreussi, N. Marzari, R. Buonsanti, *Nat. Commun.* **2018**, 9, 1–9.
- [8] Y. Li, D. Kim, S. Louisia, C. Xie, Q. Kong, S. Yu, T. Lin, S. Aloni, S. C. Fakra, P. Yang, *Proc. Natl. Acad. Sci. U. S. A.* **2020**, 117, 9194–9201.
- [9] H. Jung, S. Y. Lee, C. W. Lee, M. K. Cho, D. H. Won, C. Kim, H. S. Oh, B. K. Min, Y. J. Hwang, *J. Am. Chem. Soc.* **2019**, 141, 4624–4633.
- [10] P. Grosse, D. Gao, F. Scholten, I. Sinev, H. Mistry, B. Roldan Cuenya, *Angew. Chemie - Int. Ed.* **2018**, DOI 10.1002/anie.201802083.
- [11] J. Vavra, T. Shen, D. Stoian, V. Tileli, R. Buonsanti, *Angew. Chemie Int. Ed.* **2020**, DOI 10.1002/anie.202011137.
- [12] F. D. Speck, S. Cherevko, *Electrochem. commun.* **2020**, DOI 10.1016/j.elecom.2020.106739.
- [13] Y. Lum, J. W. Ager, *Angew. Chemie - Int. Ed.* **2018**, 57, 551–554.
- [14] J. J. Velasco-Velez, J. J. Velasco-Velez, R. V. Mom, L. E. Sandoval-Diaz, L. J. Falling, C. H. Chuang, D. Gao, D. Gao, T. E. Jones, Q. Zhu, et al., *ACS Energy Lett.* **2020**, DOI 10.1021/acsenerylett.0c00802.
- [15] P. De Luna, R. Quintero-Bermudez, C. T. Dinh, M. B. Ross, O. S. Bushuyev, P. Todorović, T. Regier, S. O. Kelley, P. Yang, E. H. Sargent, *Nat. Catal.* **2018**, 1, 103–110.
- [16] W. T. Osowiecki, J. J. Nussbaum, G. A. Kamat, G. Katsoukis, M. Ledendecker, H. Frei, A. T. Bell, A. P. Alivisatos, *ACS Appl. Energy Mater.* **2019**, 2, 7744–7749.
- [17] R. M. Arán-Ais, R. Rizo, P. Grosse, G. Algara-Siller, K. Dembélé, M. Plodinec, T. Lunkenbein, S. W. Chee, B. R. Cuenya, *Nat. Commun.* **2020**, DOI 10.1038/s41467-020-17220-6.
- [18] M. Rahaman, A. Dutta, A. Zanetti, P. Broekmann, *ACS Catal.* **2017**, DOI 10.1021/acscatal.7b02234.
- [19] T. Möller, F. Scholten, T. N. Thanh, I. Sinev, J. Timoshenko, X. Wang, Z. Jovanov, M. Gliech, B. Roldan Cuenya, A. S. Varela, et al., *Angew. Chemie - Int. Ed.* **2020**, DOI 10.1002/anie.202007136.
- [20] G. H. Simon, C. S. Kley, B. Roldan Cuenya, *Angew. Chemie Int. Ed.* **2020**, DOI 10.1002/anie.202010449.
- [21] W. T. Osowiecki, J. J. Nussbaum, G. A. Kamat, G. Katsoukis, M. Ledendecker, H. Frei, A. T. Bell, A. P. Alivisatos, *ACS Appl. Energy Mater.* **2019**, DOI 10.1021/acsaem.9b01714.
- [22] D. Kim, C. S. Kley, Y. Li, P. Yang, *Proc. Natl. Acad. Sci.* **2017**, DOI 10.1073/pnas.1711493114.
- [23] N. Hodnik, G. Dehm, K. J. J. Mayrhofer, *Acc. Chem. Res.* **2016**, 49, 2015–2022.
- [24] B. Ambrožič, A. Prašnikar, N. Hodnik, N. Kostevšek, B. Likozar, K.

ARTICLE

- Ž. Rožman, S. Šturm, *Chem. Sci.* **2019**, *10*, 8735–8743.
- [25] N. Hodnik, S. Cherevko, *Curr. Opin. Electrochem.* **2019**, *15*, 73–82.
- [26] N. Hodnik, M. Zorko, M. Bele, S. Hočevar, M. Gaberšček, *J. Phys. Chem. C* **2012**, DOI 10.1021/jp303831c.
- [27] T. Kinumoto, H. Nishihira, M. Matsuoka, N. Eguchi, T. Tsumura, M. Toyoda, *Electrochemistry* **2015**, *83*, 12–17.
- [28] R. Erni, K. Kiran, M. Rahaman, A. Dutta, J. Drnec, P. Broekmann, **2020**, *68*, DOI 10.1016/j.nanoen.2019.104331.
- [29] A. Dutta, C. E. Morstein, M. Rahaman, A. Ceden, P. Broekmann, **2018**, DOI 10.1021/acscatal.8b01738.
- [30] P. Moreno-garc, N. Schlegel, A. Zanetti, A. Ceden, A. Dutta, M. Rahaman, P. Broekmann, **2018**, DOI 10.1021/acsami.8b09894.
- [31] Y. Hou, R. Erni, R. Widmer, M. Rahaman, H. Guo, **2019**, 3189–3198.
- [32] Y. Hou, N. Kovács, H. Xu, C. Sun, R. Erni, M. de J. Gálvez-Vázquez, A. Rieder, H. Hu, Y. Kong, M. Liu, et al., *J. Catal.* **2021**, *394*, 58–66.
- [33] M. Zorko, B. Jozinović, M. Bele, N. Hodnik, M. Gaberšček, *Ultramicroscopy* **2014**, *140*, 44–50.
- [34] C. W. Li, M. W. Kanan, *J. Am. Chem. Soc.* **2012**, DOI 10.1021/ja3010978.
- [35] M. Jin, G. He, H. Zhang, J. Zeng, Z. Xie, Y. Xia, *Angew. Chemie - Int. Ed.* **2011**, *50*, 10560–10564.
- [36] A. Loiudice, P. Lobaccaro, E. A. Kamali, T. Thao, B. H. Huang, J. W. Ager, R. Buonsanti, *Angew. Chemie - Int. Ed.* **2016**, *55*, 5789–5792.
- [37] R. Kas, R. Kortlever, H. Yilmaz, M. T. M. Koper, G. Mul, *ChemElectroChem* **2015**, *2*, 354–358.
- [38] W. Tang, A. A. Peterson, S. Varela, Z. P. Jovanov, L. Bech, W. J. Durand, S. Dahl, K. Nørskov, I. Chorkendorff, **2012**, *4*, 76–81.
- [39] P. Grosse, A. Yoon, C. Rettenmaier, S. W. Chee, B. R. Cuenya, *J. Phys. Chem. C* **2020**, *124*, 26908–26915.
- [40] H. Liu, F. Favier, K. Ng, M. P. Zach, R. M. Penner, *Electrochim. Acta* **2001**, *47*, 671–677.
- [41] L. P. Bicelli, B. Bozzini, C. Mele, L. D'Urzo, *Int. J. Electrochem. Sci.* **2008**, *3*, 356–408.
- [42] B. Vanrenterghem, M. Bele, F. R. Zepeda, M. Šala, N. Hodnik, T. Breugelmans, *Appl. Catal. B Environ.* **2018**, *226*, 396–402.

ARTICLE

Entry for the Table of Contents



Copper is still the first choice as a catalyst for electrochemical conversion from CO₂ to high-value-added products. The lack of its stability is one of the major issues towards implementation in an electrolysis device. Identical location scanning electron microscopy (IL-SEM) is employed to reveal the dissolution/redeposition degradation mechanism of electrodeposited Cu nanoparticles.

Institute and/or researcher Twitter usernames: [@Electrocatalyst](#)