# **Real-time Monitoring Reveals Dissolution/Redeposition Mechanism in Cu Nanocatalysts during the Initial Stages of the CO<sub>2</sub> Reduction Reaction**

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# ABSTRACT

Size, morphology and surface sites of electrocatalysts have a major impact on their performance. Understanding how, when, and why these parameters change under operating conditions is of uttermost importance for designing stable, active, and selective catalysts. Here, we study the reconstruction of a Cu-based nanocatalysts during the startup phase of the electrochemical CO<sub>2</sub> reduction reaction by combining results from electrochemical in-situ transmission electron microscopy with operando X-ray absorption spectroscopy. We reveal that dissolution followed by redeposition, rather than coalescence, is the mechanism responsible for the size increase and morphology change of the electrocatalyst. Furthermore, we point out the key role played by the formation of copper oxides in the process. Understanding of the underlying processes opens a pathway to rational design of Cu electro (re)deposited catalysts and to stability improvement for catalysts fabricated by other methods.

## **INTRODUCTION**

The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is a promising strategy to recycle waste CO<sub>2</sub> by converting it into fuels and chemical feedstock while storing renewable energy.<sup>[1–3]</sup> Copper is at the center of attention in the CO<sub>2</sub>RR research, as it is the only single metal catalyst able to drive the reaction towards multielectron reduction products, beyond CO and formate. While 16 different products are generated on polycrystalline copper foil, all the recent record selectivities and activities have been achieved with copper-based nanoparticle (NP) catalysts by tuning their composition and/or structure at the nanoscale, along with the electrolyte and the reactor design.<sup>[4–8]</sup>

In addition to monitoring activity and selectivity, the study of catalyst reconstruction processes is of uttermost importance for building an unambiguous understanding of structure/properties relations. Thus far, few examples of copper catalyst reconstruction at steady-state operation have been reported in the literature and they evidence the tremendous impact of the observed changes on the catalyst activity and selectivity. <sup>[9–12]</sup> Changes occurring during the startup phase of the catalytic process often lead to the formation of the active form of the catalytic material, whereas morphological and compositional changes occurring during steady-state operation are generally connected to catalyst deactivation.<sup>[13–16]</sup> Overall, developing a comprehensive understanding of catalyst modifications under various conditions, including steady-state and transient (i.e. startup and shutdown) operations is vital in the field of catalysis.

Some insights can be extracted by comparing the catalyst before and after the reaction,<sup>[16–18]</sup> but overall, the knowledge of the mechanism driving copper catalyst reconstruction under CO<sub>2</sub>RR conditions is still very limited. The development of in-situ and operando tools, including transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS), is essential in understanding such phenomena. While in-situ and operando X-ray scattering and absorption are becoming increasingly common in CO<sub>2</sub>RR,<sup>[19]</sup> in-situ microscopy studies remain

scarce with few examples employing in-situ atomic force microscopy <sup>[20,21]</sup> and, only recently, some studies based on in-situ electron microscopy.<sup>[22–24]</sup> For example, the electrodeposition of 200-300 nm Cu<sub>2</sub>O cubes on Pt electrode and their subsequent fast deterioration under reducing conditions has been observed with in-situ TEM.<sup>[22]</sup> In-situ electrochemical scanning electron microscopy has been instead used to describe the reconstruction process of electrodeposited copper under CO<sub>2</sub>RR conditions. <sup>[24]</sup> While these studies highlight the potential of in-situ electron microscopy to study catalyst changes during operation, great care must be taken in interpretation such data. Indeed, in a TEM the Cu deposition can be readily driven by the electron beam <sup>[25]</sup> and additional limitations arise from the requirement of extremely thin and electron transparent electrochemical cells.<sup>[26]</sup>

Spherical Cu NPs are not particularly selective towards a certain product.<sup>[9]</sup> However, various studies have shown that they transform into a catalyst that is more selective towards C-C coupling during the initial stages of CO<sub>2</sub>RR.<sup>[17,27,28]</sup> Recently, ex-situ microscopy and in-situ XAS have revealed that the active catalyst is constituted by disordered aggregates, which was in line with in-situ TEM observations .<sup>[23]</sup> However, the chemistry driving the activation process remains still to be elucidated.

Herein, we use in-situ TEM to study the reconstruction of spherical Cu NPs during the startup phase of CO<sub>2</sub>RR in order to gain deeper insights into the underlying mechanisms of the catalyst activation process. We designed and microfabricated electrochemical chips with glassy carbon working electrode specifically for in-situ TEM under CO<sub>2</sub>RR conditions, which allows for monitoring of the immediate shape, size and crystal structure of the catalyst by imaging and diffraction techniques in real-time. The controlled electron dose during the experiments and the improved resolution of this purpose-built chips provide access to details of the reconstruction process that were not accessible before. Complementary operando XAS then supplies important insights into the oxidation state of the Cu catalysts, which corresponds well with the in-situ electron diffraction data. Our results reveal that the catalyst reconstruction process during the

startup phase is caused by nucleation of larger NPs from Cu ions dissolved in solution at open circuit voltage. We propose that the growth of these secondary NPs continues via the dissolution and redeposition of the initial catalysts. By resolving the individual NPs during this morphological transformation, we exclude the process of migration and coalescence.

#### **RESULTS AND DISCUSSION**

The as-synthesized catalyst consists of spherical metallic Cu NPs. Figure 1a reports a representative high resolution TEM (HRTEM) image of a few of them. In the corresponding FFT (Figure 1b) the d-spacing is assigned to Cu {111} planes, which confirm their metallic nature. Figure 1c then depicts the electrochemical chip design adopted specifically for the insitu CO2RR TEM experiments. The ability to perform CO2RR inside the confined volume of the micro-cells used for in-situ TEM demands the suppression of the hydrogen evolution reaction and the elimination of the intrinsic activity of the supporting electrode for CO<sub>2</sub>RR.<sup>[29,30]</sup> These requirements rule out the use of typical metals used for current collectors in micro-cells, such as platinum or gold. Glassy carbon or carbon felt is typically used as the supporting electrode for CO<sub>2</sub>RR nanoparticle catalysts due to its good conductivity, low chemical reactivity, large overpotential for HER and minimal activity for CO<sub>2</sub>RR. Inspired by the stable electrodes used in bulk cells, we modified the in-situ TEM electrochemical chips to feature a true glassy carbon working electrode that provides a suitable support for the nanoparticle catalyst. The fabricated thin layer carbon working electrode exhibits glass-like behavior, good conductivity and high charge transfer resistance, resembling the behavior of its bulk counterpart (Figure S1). The large area of the working electrode facilitates the catalyst loading, that can be performed simply by dropcasting. The potential of the working electrode is measured in-situ with a Pt-pseudoreference electrode, whose potential has been externally calibrated (Figure S2), allowing us to report all potentials versus the reference hydrogen electrode (RHE).



Figure 1. Characterization of the as-prepared catalyst. a) HRTEM image of a few Cu NPs from an as-synthesized sample prepared and analyzed in oxygen-free conditions. b) FFT of the highlighted particle in a) where d-spacing corresponds to Cu  $\{111\}$  planes. c) Optical micrograph of the electrochemical chip fabricated for the in-situ TEM during CO<sub>2</sub>RR. d) Low magnification HAADF-STEM image of the catalyst loaded on the electrode in air before introducing the electrolyte for the in-situ TEM experiment. e) Rotational average of a SAED pattern of the catalyst in d) with reflections assigned to Cu<sub>2</sub>O. f) Schematic cross-section of the cell operating inside the microscope. RE, WE and CE abbreviate reference electrode, working electrode and counter electrode respectively.

A representative low-magnification image of the NPs loaded on the working electrode in air before introducing the electrolyte is reported in **Figure 1d**. Spherical NPs with the size of 6.7  $\pm$  0.9 nm are observed. The rotational average of a selected area electron diffraction (SAED) pattern (**Figure 1e**) indicates that they are Cu<sub>2</sub>O. The NPs are synthesized as metallic Cu; however, they gradually oxidize when exposed to air and/or when immersed in the CO<sub>2</sub>RR electrolyte (for more details see **Figure S3, S4, S5**). Schematic cross-section through the imaging region in **Figure 1f** illustrates the cell geometry. The in-situ cell is a three-electrode configuration with glassy carbon working electrode Pt reference and counter electrolyte layer, which are ideal for imaging. Using the developed setup, we studied the morphological and compositional changes of the catalyst during its activation stage. We first performed a potential sweep (linear sweep voltammetry - LSV) in order to simulate a gradual cell startup. Next, we monitored the catalyst during the first minute of its operation under a constant applied cathodic potential in a chronoamperometry (CA) experiment. We focused on the initial stage of the process because the change of selectivity towards ethylene occurs within the first few minutes of operation,<sup>[27]</sup> aiming to capture the structural and morphological transformation accounting for this process. The operating potential of -0.8V vs RHE was chosen based on previous electrochemical experiments performed by us and by other groups.<sup>[17,27,31]</sup>

We first observed the morphological evolution of the catalyst during LSV, data are reported in **Figure 2** and **Sup. Movie 1**. By gradually sweeping the potential from open circuit voltage (OCV), of around 0.5 V vs RHE, to cathodic values, we can correlate the morphology of the catalyst to the immediate applied potential. After introduction of the CO<sub>2</sub> saturated electrolyte in the micro-cell, the contrast and resolution reduce due to increased inelastic electron scattering from the liquid layer. Still, the pristine Cu NPs can be resolved in areas where they are loaded as a multilayer (**Sup. Movie 1**). The in-situ TEM experiments were performed in a conventional transmission mode as opposed to a scanning mode to minimize the local electron dose and, in consequence, to avoid catalyst modification due to irradiation effects (**Figure S6, S7**). We found that while the STEM imaging mode does provide good contrast, the high local electron dose of the condensed beam induces rapid changes to the catalyst (**Figure S8**).

Representative snapshots of the morphological evolution of the catalytic NPs at specific potentials are depicted in **Figure 2a.** The corresponding LSV recorded in-situ is shown in **Figure 2b.** No changes are observed between 0.5 V vs RHE (OCV) and 0.1 V vs RHE. Nucleation of larger particles occurs between 0.1 V and 0 V vs RHE. The original 7 nm Cu NPs and these newly formed larger particles will be referred to as "primary" and "secondary" NPs, respectively. The nucleation of the secondary particles is well reflected in the statistical data in

**Figure 2c** as the total number of secondary particles abruptly increases along with an increase in the mean particle diameter. The primary particles in this experiment have low contrast and cannot be reliably analyzed. Spikes in the mean particle diameter between 0.4 and 0.1 V vs RHE (red curve in **Figure 2c**) correspond to the few primary particles picked up in certain frames. The nucleation of the secondary particles coincides with the reduction feature in the LSV around 0 V vs RHE, where Cu ions are reduced to metallic Cu.<sup>[32]</sup> The secondary particles grow to average diameter of about 14 nm. When the potential is swept even more negative to reach the operational value of -0.8 V vs RHE, additional nucleation and growth of secondary particles take place. This process is illustrated in **Figure S9**. The overall catalyst morphology after LSV corresponds qualitatively to an ex-situ experiment reported in **Figure S10**, providing evidence that the electron beam and reduced reaction volumes are not interfering with the reconstruction process.



Figure 2. In-situ TEM documenting the catalyst morphological evolution during the cell startup. a) Representative TEM images from Supplementary Movie 1 depicting the nucleation of larger secondary NPs during the LSV. Electron dose rate:  $35 \text{ e}^{-nm^{-2}s^{-1}}$ . b) LSV recorded during the in-situ experiment. c) Total number of the formed secondary particles (black line) along with their mean equivalent circular diameter (red line) with its standard error (pink) as a function of the immediate applied potential.

A complementary experiment was performed in a region with higher signal to background ratio

that ultimately provided enhanced resolving power for tracking the transformation of individual

primary particles into secondary ones (Figure 3 and Supplementary Movie 2). We note that the total cell thickness is usually not homogeneous across the imaging area (Figure S9), due to membrane bulging and/or possible air trapped in the probed area.<sup>[33]</sup> In this experiment the potential is first swept from OCV to -0.25V vs RHE (between -12 s and 0 s) which is followed by a chronoamperometry experiment at -0.25V for 60s (Figure 3d). The onset of secondary particle nucleation around 0V vs RHE is consistent with the previous experiment, but the particle growth is slower due to the amount of Cu ions locally available to undergo reduction. The secondary particles in this case nucleate more densely and grow to a lower final size, yet with the above-mentioned considerations we can qualitatively translate the observed process back to the bulk cell. Figure 3a shows an overview of the process. A magnified series of images in Figure 3b, reveals that some of the primary particles grow into secondary particles. By following the process on a single particle level (Supplementary movie 2), it is evident that this growth is not caused by particle coalescence, but is instead mediated by soluble Cu species. In turn, some of the primary particles visibly shrink in size and disappear between 30 s and 60 s (Figure 3c). In the plot of area weighted particle size distribution (Figure 3e), the decrease in the population of the primary nanoparticles (arrow I) is accompanied by the increase in population of the secondary particles (arrow II). From a statistical analysis of the full image sequence, we conclude that the mean particle size remains constant (Figure 3f), which, in this initial stage, is not surprising as the effect of dissolution of the smaller primary particles is compensated by the growth of a fewer secondary particles. This process is better demonstrated by looking at the standard deviation of the lognormal particle size distribution, which steadily grows from 1.9 nm to 2.7 nm during the experiment. By resolving individual particles during this process, we see that the evolution of primary to secondary particles goes through a solution intermediate state. This is indicative of a process similar to Ostwald ripening, where dissolution of smaller primary particles feeds the growth of the bigger secondary particles, assisted by the applied potential in our case.

When the electrodes were analyzed immediately after the cell disassembly, we identified a mixture partially oxidized primary and secondary particles (**Figure S3**). After full re-oxidation of the catalyst, we observed the formation of distinct, single crystal Cu<sub>2</sub>O cubes (**Figure S4**), which were previously identified as an ex-situ signature of the catalyst active for C-C coupling.<sup>[23]</sup>



Figure 3. In-situ TEM documenting the catalyst morphological evolution under constant applied potential. a) Sequence of TEM images taken from Supplementary movie 2 at given times during the experiment. Red and blue frames correspond to magnified images b) and c) respectively. b) Magnified images depicting the secondary particle growth process (red). c) Magnified images depicting the shrinking process of the primary particles (blue) Electron dose rate:  $35 \text{ e}^{-nm^{-2}s^{-1}}$ . d) Electrochemical data recorded in-situ during the experiment. e) Evolution of the area weighted particle size distribution. Arrow I highlights the decrease in population of primary particles, whereas arrow II points to the gradually increasing population of secondary particles. f) Mean circular equivalent diameter (black line)  $\pm$  its standard error (grey) and a standard deviation of the fitted lognormal distribution. The constant potential applied during this experiment is -0.25 V vs RHE.

In addition to the morphological changes imaged in real-time, we monitored the structural transformation of the catalyst by recording in-situ SAED patterns under similar electrochemical

conditions. Figure 4a depicts diffractograms at selected potentials of 0.4 V vs RHE (OCV) corresponding to Cu<sub>2</sub>O. Diffractograms at -0.1 V and -0.8 V vs RHE correspond to metallic Cu. Representative diffraction patterns of the two structures are shown in Figure 4b,c and the full dataset is reported as a color map in Figure 4d. Individual components were extracted from the dataset (Figure 4e) and synchronized to the immediate applied potential during the LSV (Figure 4f). The onset of this process is at 0.2 V vs RHE and reduction into metallic Cu is mostly completed at a potential of -0.1 V vs RHE. The metallic Cu reflections are becoming more intense and narrower with increasingly negative potentials, indicating an increase of the Cu crystallite size (details in Figure S11). The reduction of the initial Cu<sub>2</sub>O to Cu correlates with the onset potential for the growth of secondary NPs described above.



Figure 4. In-situ SAED documenting the catalyst structural evolution during the initial stages of  $CO_2RR$ . a) Diffractograms at selected potentials reported as rotational averages of the respective electron diffraction patterns in panel b) and c). d) Time-resolved diffractograms synchronized with the electrochemical experiment. Diffractograms at selected potentials are horizontal cross-sections from the dataset. e) Fractions of Cu and Cu<sub>2</sub>O components extracted by MCR-ALS. f) LSV recorded during the experiment.

To complement and validate the in-situ TEM data, we performed a similar experiment at a synchrotron beamline with a standard H-cell in fluorescence configuration (Figure S12). An

overview of the X-ray absorption near edge structure (XANES) data acquired during a CO<sub>2</sub>RR/LSV experiment is given in Figure 5. The Cu K-edge spectra at the selected potentials of 0.4 vs RHE (OCV) and -0.8 V vs RHE are displayed in Figure 5a and 5b, respectively. Notably, they match the Cu<sub>2</sub>O and Cu metal standards, as displayed below each spectrum. The time-resolved intensity map in Figure 5c was extracted into its individual components by multivariate curve resolution using alternating least-squares (MCR-ALS). Individual component fractions as a function of the applied potential are reported in Figure 5d. The LSV measured during the experiment is shown in Figure 5e. Prior to 0.1 V vs. RHE, the Cu catalyst exists in its oxidized form. At around 0.1 V a reduction feature appears in the LSV. Concomitantly, the Cu<sub>2</sub>O component starts to decrease and the concentration of metallic Cu increases. The reduction feature reaches its minimum around -0.1 V vs. RHE and this corresponds to a composition of about 50% Cu metal and 50% Cu<sub>2</sub>O. At the operating potential of -0.8 V vs. RHE ca. 95% of the catalyst is reduced to its metallic state. By the end of the LSV scan to -1.1 V vs. RHE, the catalyst is entirely reduced to its metallic form. Overall, the XAS experiment confirms the structural evolution of the particles observed by the in-situ SAED. The slower kinetics of the catalyst reduction compared to the TEM cell are ascribed to a high catalyst loading, which was required to collect enough signal to resolve the Cu absorption edge.



Figure 5. Operando XAS monitoring the oxidation state of the catalyst during the initial stages of  $CO_2RR$ . a) and b) Cu K-edge spectra at the indicated potentials along with the reference spectra from Cu foil and Cu<sub>2</sub>O pellet. c) Time resolved intensity map of the Cu K-edge during the CO<sub>2</sub>RR/LSV experiment. d) Concentration profile expressed as ratio of Cu<sup>0</sup> to Cu<sup>+</sup> components obtained by MCR-ALS on the operando dataset. e) LSV curve acquired during the experiment.

The insights gained from the in-situ experiments all together enable us to separate the restructuring process of the primary Cu NPs (**Figure 6a**) into three subsequent stages, namely catalyst exposure to electrolyte at OCV (**Figure 6b**), cell startup (**Figure 6c**), and cell operation (**Figure 6d**).



**Figure 6. Schematic illustration of the catalyst reconstruction process.** a) depicts the as-synthesized metallic Cu NPs, b) is the catalyst oxidization and Cu ion dissolution into the electrolyte, c) shows the dissolved ions that redeposit onto the catalyst while applying the reducing potential, and d) shows the dissolution of the smaller particles into transient species, of unknown nature to date, that feeds the growth of larger nanoparticles under constant applied potential during the cell operation.

In the first stage, the Cu catalyst is immersed in the CO<sub>2</sub>RR electrolyte at OCV and undergoes spontaneous oxidation to Cu<sub>2</sub>O accompanied by Cu ion dissolution into the electrolyte.<sup>[34]</sup> The presence of Cu ions in the electrolyte was verified by elemental analysis. The solution was filtered (pore size of around 0.7 nm) to remove any detached NPs prior to inductively coupled plasma-mass spectroscopy (**Table S1**). The data reveal that 4.8 % of the total catalyst mass was already dissolved after only 5 min of catalyst immersion. This process is in agreement with predictions based on the Cu Pourbaix diagram<sup>[32]</sup> where coexistence of Cu<sub>2</sub>O, Cu<sup>+</sup> and Cu<sup>2+</sup> is expected at pH 8. Notably, the measured amounts of dissolved Cu is several orders of magnitude higher than experimental equilibrium concentrations for dissolution of Cu<sub>2</sub>O and CuO.<sup>[35]</sup> The large surface-to-volume ratio of the NP ensemble and the presence of undercoordinated Cu atoms at their surface most likely account for such increased dissolution.<sup>[36]</sup>

In the second phase, corresponding to the cell startup, a cathodic potential is applied, which causes reduction of the aqueous Cu ions back onto the working electrode. This results in an apparent growth of a subpopulation of particles, forming the metallic Cu secondary particles. The process starts right at the onset of the reduction feature in the LSV at 0.1 V vs RHE. The LSV features are well resolved in the XAS experiment and are also apparent in the imaging insitu TEM experiments at similar potentials. This is accompanied by the Cu<sub>2</sub>O primary NPs being reduced back to metallic Cu, as determined in both SAED and XAS experiments. Additional copper ions are likely released into the electrolyte during the lattice rearrangement of primary particles. Release of aqueous ions upon reduction of the respective oxide has been reported previously for Cu and other noble metal catalyst such as Ru, Ir, Rh, Pd, Pt and Au.<sup>[34,37–39]</sup>

In the third phase, the catalyst is under constant applied potential, which is meant to simulate the cell operation. At this point, the catalyst is fully reduced to its metallic  $Cu^0$  state, yet the particle size distribution continues to change. We observe further growth of the subpopulation

of larger secondary particles. The growth process is accompanied by size reduction and eventual disappearance of the smaller primary particles. While the primary particles are mobile, no coalescence is observed. The process is rather similar to Ostwald ripening, and the net reduction of surface free energy is a plausible driving force for the observed process to occur. The nature of the transient Cu species formed under the reducing conditions is yet unclear. Dissolution of aqueous Cu<sup>+</sup> and Cu<sup>2+</sup> ions under the reducing conditions is unlikely, but the highly alkaline local pH under operation might drive dissolution of metallic Cu to Cu(OH)2<sup>-</sup>. <sup>[32,[34,40]</sup> A similar process of anomalous dissolution of Cu under cathodic polarization in acidic media has been studied and its chemical conjugation to oxygen reduction reaction was suggested as an explanation.<sup>[41,42]</sup> Another possibility is the migration of negatively charged transient Cu<sup>-</sup> species in a water depletion layer close to the electrode surface; a process referred to as cathodic corrosion.<sup>[43]</sup> This process was observed on Pt electrodes at potentials as high as -0.5 V vs RHE.<sup>[44]</sup> Finally, while previous observations on the same or similar nanocatalysts suggest that the CO<sub>2</sub> reduction intermediates are not crucial for the reconstruction process to occur <sup>[16,17]</sup>, their role in the formation of the transient Cu species should also be assessed. Obtaining experimental evidence for these transient species is non-trivial and would likely require development of advanced electrochemical in-situ spectroscopic techniques.

#### CONCLUSIONS

We have studied the activation process of spherical Cu NPs (~7nm) as catalysts for CO<sub>2</sub>RR during the initial stages of the reaction (startup and constant applied potential) by combining in-situ imaging and diffraction methods in TEM with operando XAS. Initially, the evolution of these primary NPs towards larger secondary NPs is correlated with the reduction of aqueous Cu ions. It is demonstrated that Cu ions are generated by the chemical dissolution of the Cu<sub>2</sub>O phase under open circuit conditions. It is further proposed, that additional Cu ions are released into the electrolyte during reduction of Cu<sub>2</sub>O phases to metallic Cu. While the role of Cu surface

oxides on CO<sub>2</sub>RR has been debated across the literature,<sup>[24,45-48]</sup> we clearly identify its role during reconstruction of Cu-based catalysts, which offers a novel outlook on the subject. Subsequently, the reconstruction process continues under constant applied reducing potential, despite the absence of oxidized phases. This secondary process is also mediated by transient soluble Cu species, whose exact nature is yet unknown.

The dissolution of Cu nanocatalysts at OCV might negatively impact long-term intermittent operations. However, the observed phenomena are expected to be less pronounced for larger NPs with lower surface-to-volume ratio, that are a more attractive choice for CO<sub>2</sub>RR because of suppressed activity for HER.<sup>[9,10]</sup> Furthermore, the development of strategies aimed at preventing dissolution, i.e. the introduction of tailored interfaces with oxides or carbon, might help to overcome this issue. <sup>[49–51]</sup> Finally, future studies on the facet-dependence of the proposed mechanism are interesting and foreseen in the near future.

By advancing the understanding of the mechanisms underlying copper catalyst reconstruction during its activation process, we contribute towards establishing a framework to understand catalyst transformations towards more active forms, a subject which remains underexplored in the context of CO<sub>2</sub>RR. Using such analytical tools that monitor the dynamics of the catalyst transformations will aid towards the rational design of electro (re)deposited catalysts, and will help in explaining the processes responsible for catalyst deactivation in later stages.

#### ASSOCIATED CONTENT.

The Supporting Information are available free of charge and contain additional experimental details, rendering of the cells, TEM data and supplementary movies.

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## REFERENCES

- S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo, I. Chorkendorff, *Chem. Rev.* 2019, *119*, 7610–7672.
- [2] D. Gao, R. M. Arán-Ais, H. S. Jeon, B. Roldan Cuenya, Nat. Catal. 2019, 2, 198–210.
- [3] Y. Y. Birdja, E. Pérez-Gallent, M. C. Figueiredo, A. J. Göttle, F. Calle-Vallejo, M. T. M. Koper, *Nat. Energy* 2019, 4, 732–745.
- [4] C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. García de Arquer, A. Kiani, J. P. Edwards, P. De Luna, O. S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton, E. H. Sargent, *Science* 2018, *360*, 783–787.
- [5] F. P. G. de Arquer, C.-T. Dinh, A. Ozden, J. Wicks, C. McCallum, A. R. Kirmani, D.-H. Nam, C. Gabardo, A. Seifitokaldani, X. Wang, Y. C. Li, F. Li, J. Edwards, L. J. Richter, S. J. Thorpe, D. Sinton, E. H. Sargent, *Science* 2020, *367*, 661–666.
- [6] Y. Wang, Z. Wang, C.-T. Dinh, J. Li, A. Ozden, M. Golam Kibria, A. Seifitokaldani, C.-S. Tan, C. M. Gabardo, M. Luo, H. Zhou, F. Li, Y. Lum, C. McCallum, Y. Xu, M. Liu, A. Proppe, A. Johnston, P. Todorovic, T.-T. Zhuang, D. Sinton, S. O. Kelley, E. H. Sargent, *Nat. Catal.* 2020, *3*, 98–106.
- [7] M. Luo, Z. Wang, Y. C. Li, J. Li, F. Li, Y. Lum, D.-H. Nam, B. Chen, J. Wicks, A. Xu, T. Zhuang, W. R. Leow, X. Wang, C.-T. Dinh, Y. Wang, Y. Wang, D. Sinton, E. H. Sargent, *Nat. Commun.* 2019, 10, 1–7.
- [8] Y. Pang, J. Li, Z. Wang, C.-S. Tan, P.-L. Hsieh, T.-T. Zhuang, Z.-Q. Liang, C. Zou, X. Wang, P. De Luna, J. P. Edwards, Y. Xu, F. Li, C.-T. Dinh, M. Zhong, Y. Lou, D. Wu, L.-J. Chen, E. H. Sargent, D. Sinton, *Nat. Catal.* 2019, *2*, 251–258.
- [9] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, P. Strasser, *J. Am. Chem. Soc.* **2014**, *136*, 6978–6986.
- [10] A. Loiudice, P. Lobaccaro, E. A. Kamali, T. Thao, B. H. Huang, J. W. Ager, R. Buonsanti, *Angew. Chem. Int. Ed.* **2016**, *55*, 5789–5792.
- [11] P. Iyengar, J. Huang, G. L. De Gregorio, C. Gadiyar, R. Buonsanti, *Chem. Commun.* 2019, 55, 8796–8799.
- [12] S. Popović, M. Smiljanić, P. Jovanovič, J. Vavra, R. Buonsanti, N. Hodnik, *Angew. Chem. Int. Ed.* n.d., *n/a*, DOI 10.1002/anie.202000617.
- [13] D. S. Su, B. Zhang, R. Schlögl, Chem. Rev. 2015, 115, 2818–2882.
- [14] C. Spöri, J. T. H. Kwan, A. Bonakdarpour, D. P. Wilkinson, P. Strasser, Angew. Chem. Int. Ed. 2017, 56, 5994–6021.
- [15] H. Mistry, A. S. Varela, S. Kühl, P. Strasser, B. R. Cuenya, Nat. Rev. Mater. 2016, 1, 16009.
- [16] J. Huang, N. Hörmann, E. Oveisi, A. Loiudice, G. L. De Gregorio, O. Andreussi, N. Marzari, R. Buonsanti, *Nat. Commun.* 2018, 9, DOI 10.1038/s41467-018-05544-3.
- [17] 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.
- [18] 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, DOI 10.1021/jacs.8b11237.
- [19] A. D. Handoko, F. Wei, Jenndy, B. S. Yeo, Z. W. Seh, Nat. Catal. 2018, 1, 922–934.
- [20] P. Grosse, D. Gao, F. Scholten, I. Sinev, H. Mistry, B. Roldan Cuenya, Angew. Chem. Int. Ed. 2018, 57, 6192–6197.

- [21] Y.-G. Kim, J. H. Baricuatro, A. Javier, J. M. Gregoire, M. P. Soriaga, *Langmuir* 2014, 30, 15053–15056.
- [22] 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, *11*, 3489.
- [23] 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. 2020, 117, 9194–9201.
- [24] J.-J. Velasco-Velez, R. V. Mom, L.-E. Sandoval-Diaz, L. J. Falling, C.-H. Chuang, D. Gao, T. E. Jones, Q. Zhu, R. Arrigo, B. Roldan Cuenya, A. Knop-Gericke, T. Lunkenbein, R. Schlögl, ACS Energy Lett. 2020, 2106–2111.
- [25] M. den Heijer, I. Shao, A. Radisic, M. C. Reuter, F. M. Ross, APL Mater. 2014, 2, 022101.
- [26] S. Hwang, X. Chen, G. Zhou, D. Su, Adv. Energy Mater. 2020, 10, 1902105.
- [27] D. Kim, C. S. Kley, Y. Li, P. Yang, Proc. Natl. Acad. Sci. 2017, 114, 10560-10565.
- [28] K. Manthiram, B. J. Beberwyck, A. P. Alivisatos, J. Am. Chem. Soc. 2014, 136, 13319– 13325.
- [29] J. D. Benck, B. A. Pinaud, Y. Gorlin, T. F. Jaramillo, PLoS ONE 2014, 9, e107942.
- [30] R. Girod, N. Nianias, V. Tileli, *Microsc. Microanal.* 2019, 25, 1304–1310.
- [31] G. L. De Gregorio, T. Burdyny, A. Loiudice, P. Iyengar, W. A. Smith, R. Buonsanti, *ACS Catal.* **2020**, *10*, 4854–4862.
- [32] B. Beverskog, I. Puigdomenech, J. Electrochem. Soc. 1997, 144, 3476–3483.
- [33] N. de Jonge, M. Pfaff, D. B. Peckys, in *Adv. Imaging Electron Phys.* (Ed.: P.W. Hawkes), Elsevier, **2014**, pp. 1–37.
- [34] F. D. Speck, S. Cherevko, *Electrochem. Commun.* 2020, 115, 106739.
- [35] D. A. Palmer, J. Solut. Chem. 2011, 40, 1067–1093.
- [36] J. Leitner, D. Sedmidubský, O. Jankovský, *Materials* 2019, 12, DOI 10.3390/ma12203355.
- [37] S. O. Klemm, A. A. Topalov, C. A. Laska, K. J. J. Mayrhofer, *Electrochem. Commun.* 2011, 13, 1533–1535.
- [38] A. A. Topalov, I. Katsounaros, M. Auinger, S. Cherevko, J. C. Meier, S. O. Klemm, K. J. J. Mayrhofer, Angew. Chem. Int. Ed. 2012, 51, 12613–12615.
- [39] S. Cherevko, A. R. Zeradjanin, A. A. Topalov, N. Kulyk, I. Katsounaros, K. J. J. Mayrhofer, *ChemCatChem* 2014, 6, 2219–2223.
- [40] K. Yang, R. Kas, W. A. Smith, J. Am. Chem. Soc. 2019, 141, 15891-15900.
- [41] V. Kreizer, I. K. Marshakov, N. M. Tutukina, I. D. Zartsyn, 2003, 39, 4.
- [42] I. V. Kreizer, I. K. Marshakov, N. M. Tutukina, I. D. Zartsyn, Prot. Met. 2004, 40, 23– 25.
- [43] Yu. I. Yanson, A. I. Yanson, Low Temp. Phys. 2013, 39, 304–311.
- [44] T. J. P. Hersbach, A. I. Yanson, M. T. M. Koper, Nat. Commun. 2016, 7, 12653.
- [45] H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser, B. R. Cuenya, *Nat. Commun.* 2016, 7, 12123.
- [46] R. M. Arán-Ais, F. Scholten, S. Kunze, R. Rizo, B. Roldan Cuenya, Nat. Energy 2020, 5, 317–325.
- [47] Y. Lum, J. W. Ager, Angew. Chem. Int. Ed. 2018, 57, 551–554.
- [48] S. B. Scott, T. V. Hogg, A. T. Landers, T. Maagaard, E. Bertheussen, J. C. Lin, R. C. Davis, J. W. Beeman, D. Higgins, W. S. Drisdell, C. Hahn, A. Mehta, B. Seger, T. F. Jaramillo, I. Chorkendorff, ACS Energy Lett. 2019, 4, 803–804.
- [49] Y. Li, F. Cui, M. B. Ross, D. Kim, Y. Sun, P. Yang, Nano Lett. 2017, 17, 1312–1317.
- [50] F. D. Speck, F. S. M. Ali, M. T. Y. Paul, R. K. Singh, T. Böhm, A. Hofer, O. Kasian, S. Thiele, J. Bachmann, D. R. Dekel, T. Kallio, S. Cherevko, *Chem. Mater.* 2020, DOI 10.1021/acs.chemmater.0c02048.

[51] J. Fu, Q. Yue, H. Guo, C. Ma, Y. Wen, H. Zhang, N. Zhang, Y. Zheng, J. Zheng, B.-H. Chen, ACS Catal. 2018, 8, 4980–4985.