Facet-Dependent Selectivity of Cu Catalysts in Electrochemical CO₂ Reduction at Commercially Viable Current Densities

Gian Luca De Gregorio, Thomas Burdyny, Anna Loiudice, Pranit Iyengar, Wilson A. Smith, and Raffaella Buonsanti*

ABSTRACT: Despite substantial progress in the electrochemical conversion of CO₂ into value-added chemicals, the translation of fundamental studies into commercially relevant conditions requires additional efforts. Here, we study the catalytic properties of tailored Cu nanocatalysts under commercially relevant current densities in a gas-fed flow cell. We demonstrate that their facet-dependent selectivity is retained in this device configuration with the advantage of further suppressing hydrogen production and increasing the faradaic efficiencies toward the CO₂ reduction products compared to a conventional H-cell. The combined catalyst and system effects result in state-of-the-art product selectivity at high current densities (in the range 100−300 mA/cm²) and at relatively low applied potential (as low as −0.65 V vs RHE). Cu cubes reach an ethylene selectivity of up to 57% with a corresponding mass activity of 700 mA/mg, and Cu octahedra reach a methane selectivity of up to 51% with a corresponding mass activity of 1.45 A/mg in 1 M KOH.

KEYWORDS: electrochemical CO₂ reduction, nanocatalyst, structural selectivity, copper, gas-diffusion electrolyzer

Although in the last decades several advances have been recorded in the field of renewable energy, these sources are discontinuous and the energy generated cannot easily be stored for long periods of time.1−3 In this scenario, the electrochemical CO₂ reduction reaction (CO₂RR) represents an appealing process that can be conveniently integrated with various renewable energy systems for producing carbon-based chemical feedstocks and fuels.4,5 However, this method must satisfy several requirements in order to become an economically valuable solution. At present, CO₂RR suffers from poor efficiency due to the CO₂ thermodynamic stability and to the reaction kinetic impediments, which result in the need for a large overpotential to activate and convert this molecule to more energy-dense products.6−8

Among the transition metals, copper is the only one capable of driving CO₂RR toward longer chain hydrocarbons and alcohols at reasonable faradaic efficiencies (FEs).9−16 Several studies highlight that the obtained reduction products depend on multiple factors, including the environmental pH,14,15 the nature of the electrolyte,17−19 the applied potential,10,20 the diffusion mechanism of CO₂,21,22 as well as the chemical and morphological characteristics of the catalyst itself.23,24 These conclusions have been mostly obtained by experiments performed in the traditional H-cell, where CO₂ is dissolved in an aqueous electrolyte (the most common being 0.1 M KHCO₃) and the catalysts are primarily deposited on flat glassy-carbon electrodes.25 While these testing conditions can provide valuable information about the intrinsic activity of different catalytic materials, current densities are limited by the low catalyst loading allowed on the flat electrode and, more importantly, by the low solubility of CO₂ in water and the long CO₂ diffusion pathway to the catalyst surface.21,22,26

Recently, several studies have performed CO₂RR in gas-fed reactors capable of sustaining high current densities with acceptable faradaic efficiencies.21,22,26,27 Using this approach, a very high surface area porous catalyst layer can be employed, so that CO₂ mass limitations to this surface are greatly reduced, resulting in substantially higher current densities at lower overall potentials.28,29 Several architectures have been proposed and realized to achieve these goals, including flow cell configurations based on gas-diffusion electrodes (GDE).26,30−32 With this design, conversion efficiencies for ethylene up to 70% at a potential of −0.55 V vs RHE (reversible hydrogen electrode) and current densities up to 300 mA/cm² have been reported in the presence of a highly concentrated alkaline electrolyte (10 M KOH).33

Received: January 18, 2020
Revised: March 8, 2020
Published: March 27, 2020

© 2020 American Chemical Society

This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.
Investigations on Cu single crystals in an H-cell have revealed that the (100) surface is more selective for C2H4, whereas the Cu (111) surface is more selective toward CH4 under CO2RR conditions.34−37 Nanoparticle-based studies, including our own, have also demonstrated that such facet-dependent structural selectivity is maintained down to the nanoscale and can be further tuned through size effects.38−42 Decade-long studies on nanocatalysts for the oxygen reduction reaction, however, have evidenced that tests under idealized conditions do not predict the catalytic activity and stability under conditions relevant for commercial-scale reactors.43,44 For this reason, the impressive performance in fundamental studies has never been reproduced into a membrane electrode assembly used in fuel cells.45,46

When we consider the development of catalysts for CO2 electrolysis, the intrinsic nature of the reaction warrants a similar degree of scepticism. In particular, in order to reach substantial current densities due to the mass transport limitations of CO2 in aqueous electrolytes, a catalyst must be incorporated into either a GDE or a membrane electrode assembly. Under these conditions, the catalyst layer now functions as a porous electrode due to the electrolyte/ion pathway on one side of the catalyst and the CO2 diffusion pathway on the other.47 Such configurations are then expected to provide more surface area and reach higher current densities at lower applied potentials, which can impact not only potential-dependent product formation but also the restructuring and stability of facets on metal surfaces. Further, as current densities are increased, the reaction environment becomes substantially different from those achievable within controlled H-cell systems.48 Indeed, multiphysical transport modeling of mesostructured silver electrodes has already shown that the improved selectivity toward CO compared to flat silver electrodes is purely a result of mass transport effects.49 Similar effects to those described above could play a role when faceted Cu nanoparticles are integrated into a GDE. A recent study of (100) faceted Cu nanoparticles in alkaline gas diffusion electrolyzers has revealed that the systems were similarly selective toward ethylene as in an H cell.46 Nevertheless, an increased local pH as a result of high current densities in a GDE would also promote formation of ethylene,15,28,50 and so a definitive mechanism for the apparent similarity in selectivity is still not clear. Therefore, assessing various shaped Cu nanoparticles in different electrode architectures can help to provide further insights to the influences of surface facets, surface area, and the reaction environment on catalytic selectivity.

Having this in mind, we sought to directly compare the facet-dependent activity and selectivity of differently shaped Cu nanoparticles at much higher current densities than those achievable in an H-cell. By making this direct comparison, we can determine if the observed performance is maintained or altered in a GDE configuration compared to an aqueous H-cell and thus provide meaningful insights to the CO2 reduction community that will shed light on an open debate.

Cu nanocrystals (NCs) of different shapes were synthesized according to colloidal methods previously reported by our group (see Experimental Section).38,39,47 Figure 1 provides an overview of the morphological and structural characterization of the NCs. Figure 1a−c reports the transmission electron microscopy (TEM) images of the as-obtained Cu spheres of 6 nm (Cushp), Cu cubes of 44 nm (Cucub), and Cu octahedra of 150 nm (Cuoaa), which all possess high uniformity in size and shape. These structures were chosen as they were found to be separately optimally selective for ethylene, methane, and a mixture of C1−C2 products, respectively, in H-cell tests.38−42 X-ray diffraction (XRD) patterns in Figure 1d show the characteristic preferential orientation for the Cucub and Cushp which is along the (100) and (111) directions, respectively, whereas the Cushp’s exhibit both orientations and a peak ratio closer to the bulk copper reference. More extensive characterization of the same NCs is reported in our previous work.38,39,47 The as-synthesized NCs were spray-coated or drop-casted onto the GDL to form the gas diffusion electrode (GDE), as described in the Experimental Section. No particular difference was observed between the two deposition techniques upon optimization (Figure S1). Figure 1e and 1f reports representative in-plane scanning electron microscopy (SEM) images of the Cushp and Cushp NCs deposited on the GDL for the highest loadings used in this work, revealing a high degree of coverage.

The catalytic performance of the as-prepared GDEs was tested in a gas-fed flow cell with 1 M KOH as the supporting electrolyte (Experimental Section, Table S1). This setup was
reproduced from previous literature, and the alkaline electrolyte was chosen because of the reported record FE toward ethylene of 36% and 66% with partial current densities of 150 and 184 mA/cm² in KOH 1 and 10 M, respectively, at an applied potential of around −0.55 V vs RHE.28,33 Figure 2 reports the faradaic efficiencies (FEs) obtained for the three NCs in the gas-fed flow cell along with the partial mass activities and current densities normalized by the electrochemically active surface area (ECSA) at three representative values of iR-corrected potentials. The current densities normalized by the geometric area are shown in Figure S3; the corresponding CO₂ conversion efficiencies and cell voltages are reported in Figure S4.

At a current density of 100 mA/cm² at −0.69 V vs RHE, Cuₙₐₚₚ NCs produce 28% CO and 20% ethylene. At a higher current density (200 mA/cm², −0.79 V vs RHE), the FE for CO drops to 16%. Concomitantly, ethylene becomes the main CO₂RR reaction product (FE ≈ 31%), which suggests that more CO molecules undergo coupling. Finally, when the Cuₙₐₚₚ’s are investigated at 300 mA/cm² and −0.86 V vs RHE, HER increases (FE ≈ 43%), CO further decreases (FE ≈ 4%), as well as C₂H₄ decreases (FE ≈ 25%). The mass activities in Figure 2b follow the same described trend. Overall, the behavior of the Cuₙₐₚₚ (Figure 2a and 2b) resembles that of polycrystalline copper tested in a similar device configuration.21,29–31,33

When turning to the Cuₙₐₜₜ’s, they exhibit a much higher selectivity toward ethylene compared to the spheres across all of the potentials (Figure 2a). This result points at the fact that the exposed (100) facets do play a role in directing selectivity, even under these more extreme conditions. Specifically, conversion of CO₂ to C₂H₄ ranges from 55% at 100 mA/cm² and −0.65 V vs RHE to around 60% at 200 mA/cm² and −0.70 V vs RHE. Finally, at 300 mA/cm² and −0.75 V vs RHE, the observed conversion to ethylene is ~57%. The corresponding ethylene mass activities are reported in Figure 2c and vary between 200 and 700 mA/mg, higher than the mass activities of the other products across the whole potential range. These efficiencies overcome those previously reported for randomly shaped Cu NCs in 1 M KOH, which were 36% at −0.58 V vs RHE at a similar ethylene partial geometric current density (150 mA/cm²) and with lower ethylene mass activities of around 176 mA/mg.28

As for the Cuₙₒₘₚ’s, methane is the main hydrocarbon product, in line with the presence of the exposed (111) facets. The highest FE of ~53% is obtained at 100 mA/cm² and −0.91 V vs RHE, with the corresponding lowest H₂ production (FE ≈ 22%). Ethylene is also present as a product but only with an ~10% conversion efficiency at this current density, giving a methane:ethylene ratio of almost 5:1 compared to the roughly 1:20 ratio for the Cuₙₐₜₜ’s. At the higher current densities and potentials (200 mA/cm² and −0.93 V vs RHE; 300 mA/cm² and −0.96 V vs RHE), HER increases substantially and a general decrease of C₁ and C₂ products is observed, most likely due to the reaction entering a CO₂-depleted regime. Yet, methane does still remain the major CO₂RR product with FE
around 40%. The mass activities in Figure 2d are consistent with the selectivity trend, i.e., the methane and hydrogen current densities are higher than those for CO and ethylene across the whole potential range. To the best of our knowledge, the catalyst’s mass activity toward methane is the largest reported to date and varies from 1.00 to 2.5 A/mg for potentials in the range from $-0.91$ to $-0.96$ V vs RHE.

Figure 3. (a) Cross-sectional SEM images of 440 $\mu$g/cm$^2$ Cu$_{\text{nc}}$ NCs loaded on the GDL together with a magnification of the same. (b) EDX colored map cross-section of Cu$_{\text{nc}}$ for different loadings: 100, 250, and 440 $\mu$g/cm$^2$ from left to right. (c) In-plane SEM images of the samples in b with an inset of the same at higher magnification.

Figure 4. (a) Geometric current density vs $iR$-corrected potentials in 1.0 M KOH for Cu$_{\text{nc}}$ NCs on a GDL at varying loading. (b–d) Corresponding C$_2$H$_4$, CH$_4$, and H$_2$ faradaic efficiencies. Error bars indicate the standard deviation of three independent samples.
Compared to the results obtained from the same NCs tested in an H-cell (Figure S5), the major CO₂RR products are preserved yet the hydrogen production is lower in the gas-fed flow cell at all potentials. The high alkaline conditions may explain this result as the CO₂ reduction reaction remains constant on the SHE scale while the hydrogen evolution reaction does not. As CO₂ will interact with the alkaline electrolyte over time, it is also important to ensure that these changes do not impact the conclusions made over the length of the experiment. For this reason, the pH of the bulk electrolyte was measured before and after the experiment as shown in Table S3. As the pH remains highly alkaline even at the end of the experiment, the slow degradation of the KOH electrolyte with CO₂ was not considered as a factor in these specific experiments.

Considering the notable differences in CH₄ vs C₂H₄ activity obtained with the faceted NCs, the following discussion will only focus on the Cuₙcob and Cuₙoh NCs and dive further into the influences of catalyst loading and operating conditions for these two catalysts.

Catalyst loading has been shown to affect the electrochemical performance due to the reconstruction of the deposited particles as well as by affecting transport at the mesoscale. Furthermore, it is unknown whether the whole amount of catalyst loaded onto a GDL, or only part of it, reacts with CO₂. For these reasons, it is important to investigate the effect of increasing catalyst loading on CO₂ depletion and availability while maximizing the electrochemically active surface area to reduce applied potentials. It is worth noting that reductive stripping of the native ligands from the catalyst surface occurs (Figure S6). Therefore, similar to what was concluded in comparative experiments done in an aqueous H-cell, the ligands do not have any major impact on the electrochemical performance.

Figures 3, 4, and S7 summarize the results related to the effect of loading for the Cuₙcob, while those for the Cuₙoh are reported in the Supporting Information (Figures S8–S10). Figure 3a shows a representative cross-sectional SEM image for the Cuₙcob NCs deposited on the GDL with a loading of 440 μg/cm², and Figure 3b illustrates the cross-section energy-dispersive X-ray spectroscopy (EDX) colored maps for the same NCs at different loadings. The images evidence that the as-deposited NCs are uniformly distributed through the whole GDL thickness as proved by the presence of a NC layer on the fibers of the backing paper support.

In Figure 3b, one can notice that a surface layer builds up on the top of the GDL. Figure 3c shows the top-down SEM images of Cuₙcob NCs with the same loadings of Figure 3b. As the loading increases, the Cuₙcob's form an increasingly more compact layer on the top of the GDL. Very similar observations were made for the Cuₙoh NCs, though formation of such a compact top layer occurred at lower loadings (200 μg/cm²) than the Cuₙcob NCs (440 μg/cm²), most likely because of the bigger NC size (Figures S8 and S9).

The CO₂RR performance of the Cuₙoh and of the Cuₙcob NCs was evaluated at loadings in the range of 50–1000 μg/cm² (Figures 4, S7, S10, and S11 and Tables S4 and S5). Figure 4a shows that the required potential can be driven down at higher loading as the catalytic surface area increases. At lower current densities, the Cuₙcob NCs exhibit similar slopes for all loadings, indicative of a similar level of intrinsic activity. As the current increases above 100 mA/cm², the slope also changes. Such change is more pronounced for 440 and 1000 μg/cm², which are higher loadings than those utilized in Figure 2 (250 μg/cm²). The deviation from a linear dependence of the current density on the potential in this high-current/high-loading region is likely a combined result of mass transport effects and changes in overall activity due to modifications of the local environment. Similar observations were made for the Cuₙoh (Figure S10), though with even more drastic effects. Indeed, above 200 μg/cm², which is when the thick top layer forms, only vigorous gas bubbling from hydrogen production was observed on the GDE surface (Figures S8 and S9).

To gain further understanding about the accessibility of the electrolyte to the NCs, EDX analysis of the potassium through the GDE thickness was performed (Figure S12). It is reasonable to assume that the presence of potassium indicates a wetted electrode and that, therefore, all of the NCs are in the condition to be potentially active. We found that the increasing loading is accompanied by a decreasing concentration of potassium in the GDE up to the point of not detecting any potassium inside when the top compact layer forms. These results suggest that the top compact layer effectively prevents the electrolytes from penetrating into the pores, thus effectively impeding the reaction between CO₂ and water.

In agreement with this compositional analysis, the ECSA for the Cuₙoh notably increases with a loading of up to 440 μg/cm² while the change becomes less significant between 440 and 1000 μg/cm² (Figure S2). Instead, the results for the Cuₙoh evidence that 50 μg/cm² is already enough to maximize the active surface area, which we speculatively assign to the bigger size of the octahedra (Figure S2).

When analyzing the product selectivities at different loadings (Figure 4b–d), the FE of the intermediate loadings (250 and 440 μg/cm²) show an overall more moderate potential dependence. On the contrary, for the lower and higher loadings (50, 100, and 1000 μg/cm²), the FE of CH₄ and FE of H2 decrease and increase, respectively, while going from lower to higher potentials (Figure 4b–d). For the samples with the lower loading, the HER increase is accompanied by increased methane as well (Figure 4d).

In order to explain the observed product distribution, various effects need to be considered. First, there are the aforementioned mass transport resistances. For the 1000 μg/cm² sample, the increased HER and decreased ethylene can be justified in terms of mass transport limitations, causing CO₂RR to be replaced with HER as current densities increase. Nevertheless, between 200 and 250 mA/cm² HER slightly decreases for both 440 and 1000 μg/cm², while polarization curves show already a decreasing slope. Thus, mass transport limitations cannot be the only explanation. Mass transport limitations also do not explain the increased CH₄ at higher potential for the lower loadings.

One could then consider the effect of polarization. It has been reported that at high overpotentials (<=0.8 V vs RHE), C₂H₄ and CH₄ can form simultaneously from the common intermediate *COH on both Cu(100) and Cu(111) facets. This behavior however has not been observed during experiments in alkaline media. We speculate that the negative potential applied to the system to meet the set current density at such low catalyst loadings (lesser exposed surface area) makes CH₄ more favorable than C₂H₄ at these potentials. However, polarization effects do not justify the high methane production of the 100 μg/cm² compared to the 250 and 440 μg/cm² for similar applied potentials (~0.77 V for...
200 mA/cm², −0.75 V for 300 mA/cm², and −0.76 V for 250 mA/cm²).

If we plot the FEs versus the applied potential (Figure S13), it becomes clear that another factor to consider is the optimal electrode potential range for a given product, which indeed changes for different loadings. These data contribute to explain the observations above. Finally, the contribution of the GDL itself to the high hydrogen evolution rate (FE ≈ 60%) in the low loadings may be considered as well (Figure S14).

The same effects (i.e., mass transport limitations, polarization effects, optimal potential range, substrate effects) explain the observed behavior for different loadings of CuohNCs (Figure S13).

Finally, catalyst and device stability is as important as activity and selectivity. TEM and XRD analyses show that the morphological stability of the CuohNCs is preserved up to 6 h, and it is accompanied by stable ethylene production (Figures S15 and S16). These initial data point at an improvement of the intrinsic stability compared to what we previously observed in an H-cell.22 The lower potentials needed in the gas-fed flow cell (−0.76 to −0.65 V vs RHE with respect to the −1.1 V vs RHE in the H-cell) are one possible reason for the observed behavior. On the contrary, Cuoh did not show high stability (Figures S17 and S18). In the case of the more stable Cuoh after 6 h, the entire device stops operating because of GDL flooding, thus suggesting that engineering solutions to achieve device stability for a longer time are crucial before continuing to further investigate the parameters contributing to catalyst stability.21,56,57

In summary, this study presents the integration of collooidally synthesized NCs in a gas-fed flow cell with optimal morphologies for high ethylene and methane conversion efficiencies and production rates. We observed that the Cuoh NCs are highly selective toward C₂H₄. Cuoh are selective toward CH₄ and Cuoph are not selective toward any specific product. Loading experiments demonstrated that an optimal amount of catalyst must be deposited in order to achieve the best performance in terms of activity and selectivity. In particular, the catalyst layer should uniformly cover the GDL without clogging the porous structure. The latter results in a limited mass diffusion operational regime and promotes the subsequent evolution of hydrogen. Future modeling will help to understand mass transport in more detail.45,58

Overall, integration of the Cu NCs in the gas-fed flow electrolyzer enabled achievement of remarkable performance for ethylene and methane in a low-concentration alkaline electrolyte. Initial tests have revealed that these selectivities are preserved also in different electrolytes (Figure S19, Tables S6 and S7). Specifically, ethylene mass activities between 200 and 700 mA/mg in a potential range between −0.65 and −0.75 V vs RHE with a selectivity of ~57% were obtained in 1 M KOH. The methane current densities were exceptionally large and varied from 1.45 to 2.5 A/mg in the potential range from −0.93 to −0.96 V vs RHE with selectivities between 51% and 41% in 1 M KOH. The latter is a very interesting fundamental result which illustrates the power of catalyst design even in gas-fed electrolyzers, as activity toward methane is expected and has generally been shown to be suppressed under high bulk and local pH conditions.15,28,33

Experimental Section; sketch of the gas-fed flow cell used in this work and schematic representation of the NC-based electrode; in-plane SEM images of Cuoh NCs drop casted and spray coated with a loading of 100 μg/cm²; faradaic efficiency for the Cuoh, Cu phosphorus, and Cuoh NCs in the gas-fed flow cell; cyclic voltammetry at different scan rates on Cuoh 50 μg/cm² in KHC₄O₃ 0.1 M, plot of capacitive current vs scan rate for Cuoh 50 μg/cm², Cuoh 250 μg/cm², and Cuoph 200 μg/cm², and estimated ECSA vs NCs loading for Cuoh and Cuoph roughness factors and electroactive area for different Cu samples; partial current densities normalized by the geometric area vs potential for Cuoph (200 μg/cm²), Cuoh (250 μg/cm²), and Cuoh (50 μg/cm²) measured in 1 M KOH; faradaic efficiencies and total CO₂ consumption versus the applied cell voltage; bulk pH values measured before and after the electrochemical measurements for the three NCs tested in 1 M KOH; faradaic efficiencies for Cuoph, Cu phosphorus, and Cuoh NCs measured in the H-cell at different potentials, and comparison of CO₂RR vs HER selectivity for the three NCs measured at different potentials in the H-cell and in the flow cell; FTIR analysis performed on the GDE before and after the chronopotentiometric measurements; faradaic efficiencies in 1.0 M KOH for Cuoh NCs at different loadings at 100, 200, and 300 mA/cm² current densities, and highlight of the liquid products; in-plane SEM images of the Cuoh NCs deposited on the GDL at different loadings; cross-section SEM images of Cuoh NCs at 200 μg/cm² loading at different magnifications, cross-section EDX map of the copper element; in-plane and cross-section SEM-EDX images for the 1 mg/cm² Cuoh NCs loading, and corresponding cross-section SEM-EDX images; faradaic efficiencies in 1.0 M KOH for Cuoh NCs at different loadings at 100, 200 and 300 mA/cm² current densities, geometric current density as a function of applied potential in 1.0 M KOH electrolyte for Cuoh NCs at varying loadings, CH₄, H₂, C₂H₄, and CO faradaic efficiencies in 1.0 M KOH for Cuoh NCs at different loadings in the current density range 100–300 mA/cm²; FEs vs iR-corrected potential for different loadings of Cuoh; linear plots of geometric current density as a function of applied potential in 1.0 M KOH electrolyte for Cuoh NCs and Cu phosphorus NCs at varying loadings; cross-section SEM of the GDE loaded with different amounts of Cuoh NCs, and EDX spectra in the energy range of the potassium peak; CH₄, C₂H₄ and H₂ faradaic efficiencies vs iR-corrected potentials for different loadings of Cuoh, CH₄, C₂H₄, and H₂ faradaic efficiencies vs iR-corrected potentials for different loadings of Cuoh, carbon GDL substrate measured in 1.0 M KOH at different applied currents; faradaic efficiency for the Cuoh and Cu phosphorus NCs in the gas-fed flow cell in 1.0 M KOH at different applied currents and different loadings; applied potentials and mass activities for the Cuoh and Cu phosphorus NCs in the gas-fed flow cell in 1.0 M KOH at different loadings; ethylene faradaic efficiency for Cuoh NCs tested in the flow cell at...
Author Contributions
G.L.D. designed and carried out all of the experiments and analyzed the data. T.B. provided assistance in the electrochemical experiments and data analysis. A.L. performed the XRD, SEM, TEM experiments and analyzed the data. P.I. synthesized the Cuoh nanocrystals. W.A.S. contributed to discussion and supervision. R.B. designed and supervised the entire project. All authors discussed the results and assisted during manuscript preparation.

Notes
The authors declare no competing financial interest.

Acknowledgments
R.B. acknowledges funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement no. 715634-HYCAT). W.A.S. acknowledges funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement no. 759743-WUTANG). P.I. was financially supported by Gazzat S.A. The authors thank Seyyedeh Behnaz Varandili for performing inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements to determine sample concentration.

References
(1) Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. Nat. Mater. 2017, 16, 16.
(2) Kondratenko, E.-V.; Mal, G.; Baltrusaitis, J.; Larrazabal, G. O.; Perez-Ramirez, J. Status and perspectives of CO2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. Energy Environ. Sci. 2013, 6, 3112.
(3) Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical Energy Storage for Green Grid. Chem. Rev. 2011, 111, 3577.
(4) De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S. A.; Jaramillo, T. F.; Sargent, E. H. What would it take for renewably powered electrolysers to displace petrochemical processes? Science 2019, 364, eaav3506.
(5) Vasileff, A.; Zheng, Y.; Qiao, S. Z. Carbon Solving Carbon’s Problems: Recent Progress of Nanostructured Carbon-Based Catalysts for the Electrochemical Reduction of CO2. Adv. Energy Mater. 2017, 7, 1700759.
(6) Dutta, A.; Rahaman, M.; Luedi, N. C.; Mohos, M.; Broekmann, P. Morphology Matters: Tuning the Product Distribution of CO2 Electroreduction on Oxide-Derived Cu Foam Catalysts. ACS Catal. 2016, 6, 3804.
(7) Mistry, H.; Varela, A. S.; Bonifacio, C. S.; Zegkinoglou, I.; Sinev, I.; Choi, Y.-W.; Kisslinger, K.; Stach, E. A.; Yang, J. C.; Strasser, P.; Cuena, B. R. Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. Nat. Commun. 2016, 7, 12123.
(8) Roberts, F. S.; Kuhl, K. P.; Nilsson, A. High selectivity for ethylene from carbon dioxide reduction over copper nanocube electrocatalysts. Angew. Chem., Int. Ed. 2015, 54, 5179.
(9) Bagger, A.; Ju, W.; Varela, A. S.; Strasser, P.; Rossmeisl, J. Rossmeisl, Electrochemical CO2 Reduction: A Classification Problem. ChemPhysChem 2017, 18, 3266.
(10) Kuhl, K. P.; Cave, E. R.; Abram, D. N.; Jaramillo, T. F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. Energy Environ. Sci. 2012, 5, 7050.
(11) Peterson, A. A.; Abdil-Pedersen, F.; Studt, F.; Rossmeisl, J.; Norskov, J. K. How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels. Energy Environ. Sci. 2010, 3, 1311.
(12) Horii, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. Electrochemical process of CO selectivity in electrochemical reduction of CO2 at metal electrodes in aqueous media. Electrochim. Acta 1994, 39, 1833.
(13) Horii, Y.; Kikuchi, K.; Suzuki, S. Production of CO and CH4 in electrochemical reduction of CO2 at metal electrodes in aqueous hydrogen carbonate solution. Chem. Lett. 1985, 14, 1695.
(14) Liu, X.; Schlexer, P.; Xiao, J.; Yi, J.; Wang, L.; Sandberg, R. B.; Tang, M.; Brown, K. S.; Peng, H.; Ringe, S.; Hahn, C.; Jaramillo, T. F.; Norskov, J. K.; Chan, K. pH effects on the electrochemical reduction of CO2 towards C2 products on stepped copper. Nat. Commun. 2019, 10, 32.
(15) Schouten, K. J. P.; Pérez-Gallent, E.; Koper, M. T. M. The influence of pH on the reduction of CO and CO2 to hydrocarbons on copper electrodes. J. Electroanal. Chem. 2014, 716, 53.
(16) Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; Seger, B.; Stephens, I. E. L.; Chan, K.; Hahn, C.; Norskov, J. K.;...
J. K.; Jaramillo, T. F.; Chorkendorff, I. Progress and Perspectives of Electrochemical CO2 Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* 2019, 119 (12), 7610.

Gao, D.; McCrum, I. T.; Deo, S.; Choi, Y.-W.; Scholten, F.; Pan, W.; Chen, J. G.; Janik, M. J.; Roldan-Cuenya, B. Activity and Selectivity Control in CO2 Electroreduction to Multicarbon Products over CuOx Catalysts via Electrolyte Design. *ACS Catal.* 2018, 8, 10012.

Resasco, J.; Chen, L. D.; Clark, E.; Tsai, C.; Hahn, C.; Jaramillo, T. F.; Chan, K.; Bell, A. T. Promoter Effects of Alkali Metal Cations on the Electrocatalytic Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* 2017, 139, 11277.

Lum, Y.; Yue, B.; Lobaccaro, P.; Bell, A. T.; Ager, J. W. Optimizing C–C Coupling on Oxide-Derived Copper Catalysts for Electrochemical CO2 Reduction. *J. Phys. Chem. C* 2017, 121, 14191.

Hori, Y.; Takahashi, I.; Koga, O.; Hoshi, N. Electrochemical reduction of carbon dioxide at various series of copper single crystal electrodes. *J. Mol. Catal. A: Chem.* 2003, 199, 39.

Iyengar, P.; Huang, J.; De Gregorio, G.; Gadjiar, C.; Buonsanti, R. Size dependent selectivity of Cu nano-octahedra catalysts for the electrochemical reduction of CO2 to CH4. *Chem. Commun.* 2019, 55, 8796.

Louiudce, A.; Lobaccaro, P.; Kamali, E. A.; Thao, T.; Huang, B. H.; Ager, J. W.; Buonsanti, R. Tailoring Copper Nanocrystals towards C2 Products in Electrochemical CO2 Reduction. *Angew. Chem., Int. Ed.* 2016, 55, 5789.

Huang, J.; Mensi, M.; Oveisi, E.; Mantella, V.; Buonsanti, R. Structural Sensitivities in Bimetallic Catalysts for Electrochemical CO2 Reduction Revealed by Ag–Cu Nanodimers. *J. Am. Chem. Soc.* 2019, 141, 2490.

Lamithram, K.; Beberwyck, B. J.; Alivisatos, A. P. Enhanced electrochemical methanation of carbon dioxide with a dispersible nanocopper catalyst. *J. Am. Chem. Soc.* 2014, 136, 13319.

Reske, R.; Mistry, H.; Behafarid, F.; Roldán Cuenya, B.; Strasser, P. Particle size effects in the catalytic electroreduction of CO2 on Cu nanoparticles. *J. Am. Chem. Soc.* 2014, 136, 6978.

Kim, C.; Dionigi, F.; Beermann, V.; Wang, X.; Moller, T.; Strasser, P. Alloy Nanocatalysts for the Electrochemical Oxygen Reduction (ORR) and the Direct Electrochemical Carbon Dioxide Reduction Reaction (CO2RR). *Adv. Mater.* 2019, 31, 1806517.

Strasser, P.; Gleich, M.; Kuehl, S.; Moeller, T. Electrochemical processes on solid shaped nanoparticles with defined facets. *Chem. Soc. Rev.* 2018, 47, 715.

Suter, S.; Haussener, S. Optimizing Mesosctructed Silver Catalysts for Selective Carbon Dioxide Conversion into Fuels. *Energy Environ. Sci.* 2019, 12, 1668.

Wang, Y.; Shen, H.; Livi, K. J. T.; Raciti, D.; Zong, H.; Gregg, J.; Onadeko, M.; Wan, Y.; Watson, A.; Wang, C. Copper Nanocubes for CO2 Reduction in Gas Diffusion Electrodes. *Nano Lett.* 2019, 19, 8461.

Strach, M.; Mantella, V.; Pankhurst, J. R.; Iyengar, P.; Louiudce, A.; Das, S.; Corrinboeuf, C.; van Beek, W.; Buonsanti, R. Insights into Reaction Intermediates to Predict Synthetic Pathways for Shape-Controlled Metal Nanocrystals. *J. Am. Chem. Soc.* 2019, 141, 16312.

Wang, L.; Nitopi, S. A.; Bertheussen, E.; Orozov, M.; Morales-Guiom, C. G.; Liu, X.; Higgins, D. C.; Chan, K.; Norskov, J. K.; Hahn, C.; Jaramillo, T. F. Electrochemical Carbon Monoxide Reduction on Polycrystalline Copper: Effects of Potential, Pressure, and pH on Selectivity toward Multicarbon and Oxygenated Products. *ACS Catal.* 2018, 8 (8), 7445.

Ma, M.; Clark, E. L.; Dalsgaard, S.; Therkildsen, K. T.; Chorkendorff, I.; Seger, B. J. Insights into the Carbon Balance for CO2 Electroreduction on Cu using Gas Diffusion Electrode Reactor Designs. *Energy Environ. Sci.* 2020, 13, 977.

Kim, D.; Kley, C. S.; Li, Y.; Yang, P. Copper nanoparticle ensembles for selective electroreduction of CO2 to C2–C3 products. *Proc. Natl. Acad. Sci. U. S. A.* 2017, 114, 10560.

Mistry, H.; Behafarid, F.; Reske, R.; Varela, A. S.; Strasser, P.; Roldán Cuenya, B. Tuning Catalytic Selectivity at the Mesoscale via Interparticle Interactions. *ACS Catal.* 2016, 6, 1075.

Huang, J.; Hörmann, N.; Oveisi, E.; Louiudce, A.; De Gregorio, G.; Andreussi, A.; Marzari, N.; Buonsanti, R. Potential-induced nanoclustering of metallic catalysts during electrochemical CO2 reduction. *Nat. Commun.* 2018, 9, 3117.
(53) Manthiram, K.; Surendranath, Y.; Alivisatos, A. P. Dendritic assembly of gold nanoparticles during fuel-forming electrocatalysis. J. Am. Chem. Soc. 2014, 136, 7237.

(54) Xiao, H.; Cheng, T.; Goddard, W. A.; Sundararaman, R. Mechanistic Explanation of the pH Dependence and Onset Potentials for Hydrocarbon Products from Electrochemical Reduction of CO on Cu (111). J. Am. Chem. Soc. 2016, 138, 483.

(55) Varela, A. S.; Kroschel, M.; Reier, T.; Strasser, P. Controlling the selectivity of CO2 electroreduction on copper: The effect of the electrolyte concentration and the importance of the local pH. Catal. Today 2016, 260, 8.

(56) Verma, S.; Hamasaki, Y.; Kim, C.; Huang, W.; Lu, S.; Jhong, H.-R. M.; Gewirth, A. A.; Fujigaya, T.; Nakashima, N.; Kenis, P. J. A. Insights into the Low Overpotential Electroreduction of CO2 to CO on a Supported Gold Catalyst in an Alkaline Flow Electrolyzer. ACS Energy Lett. 2018, 3, 193.

(57) Liu, K.; Smith, W. A.; Burdyny, T. Introductory Guide to Assembling and Operating Gas Diffusion Electrodes for Electrochemical CO2 Reduction. ACS Energy Lett. 2019, 4, 639.

(58) Moosavi, S. M.; Niffeler, M.; Gostick, J.; Haussener, S. Transport characteristics of saturated gas diffusion layers treated with hydrophobic coatings. Chem. Eng. Sci. 2018, 176, 503.