The effects of currents and potentials on the selectivities of copper toward carbon dioxide electroreduction

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Copper electrodes have been shown to be selective toward the electroreduction of carbon dioxide to ethylene, carbon monoxide, or formate. However, the underlying causes of their activities, which have been attributed to a rise in local pH near the surface of the electrode, presence of atomic-scale defects, and/or residual oxygen atoms in the catalysts, etc., have not been generally agreed on. Here, we perform a study of carbon dioxide reduction on four copper catalysts from −0.45 to −1.30 V vs. reversible hydrogen electrode. The selectivities exhibited by 20 previously reported copper catalysts are also analyzed. We demonstrate that the selectivity of carbon dioxide reduction is greatly affected by the applied potentials and currents, regardless of the starting condition of copper catalysts. This study shows that optimization of the current densities at the appropriate potential windows is critical for designing highly selective copper catalysts.
The reduction of carbon dioxide (CO₂) to fuels and chemical feedstocks using renewable electricity has the potential of becoming a key component in the development of a sustainable carbon cycle. This process requires selective, efficient, and stable electrocatalysts before it can be implemented in the industrial scale. Among the metal electrocatalysts studied, copper is the only metal that can reduce CO₂ to significant amounts of hydrocarbons and oxygenates. Of these products, methods to selectively form formate (HCOO⁻), carbon monoxide (CO), methane (CH₄), ethylene (C₂H₄), and ethanol (C₂H₅OH) have been extensively pursued.

To understand how these products are formed on copper, Peterson and Nørskov modeled the reduction of CO₂ on Cu(211) surface (a stepped surface) using density functional theory (DFT). As the applied potential became more negative, CO₂ was first reduced to HCOO⁻ and CO, from −0.41 V vs. RHE (reversible hydrogen electrode) onward. C₂H₂ and CH₄ were the next major products and evolved at potentials negative to −0.71 V vs. RHE. These theoretical predictions are consistent with the findings reported earlier by Hori et al. on a polycrystalline Cu surface, where HCOO⁻ and CO were produced first, followed by CH₃ and CH₄. Interestingly, when Cu single-crystal surfaces were studied using chronopotentiometry at −5 mA cm⁻² in 0.1 M KHCO₃ electrolyte, the selectivity between C₂H₂ and CH₄ changed. Cu(100) and Cu(111) were, respectively, found selective for C₂H₂ and CH₄ formation. Further optimization of C₂H₂ production could be achieved by using stepped-Cu(100) surfaces. For example, the faradaic efficiency (FE) of C₂H₂ reached 50%, while CH₄ was suppressed to 5% on a Cu(S)-[4(100)×(111)] electrode polarized at −5 mA cm⁻² (−0.94 V vs. RHE). Oddly and still without an explanation, the selectivity of neither C₂H₂ nor CH₄ seemed to improve significantly on stepped-Cu(111) surfaces.

Besides the Cu(100) single-crystal series, some oxide-derived Cu catalysts have also shown a propensity for C₂H₂ and C₂H₅OH production. For example, we have found that at −0.99 V vs. RHE, Cu films reduced from μm-thick CuO could catalyze the reduction of CO₂ in 0.1 M KHCO₃ electrolyte to C₂H₂ with FEs = 34−39%, while the FEs of CH₄ were minimized to <1%⁹. Interestingly, thick oxide-derived Cu films, which do not appear to have very different morphological and chemical differences as the aforementioned C₂-selective catalysts, have also been independently reported to be selective toward the formation of CO and HCOO⁻⁵,⁶. The selective reduction of CO₂ to CH₄ on Cu surfaces has been relatively less studied. Recently, Manthiram et al. reported that 7 nm-sized Cu nanoparticles dispersed on a glassy carbon electrode could catalyze the formation of CH₄ with an average FE of 80% in 0.1 M NaHCO₃ at −1.25 V vs. RHE.⁷

Based on characterizations of the catalysts presented to the above reports, the underlying causes for the selective reduction of CO₂ to various products on Cu catalysts have been attributed to factors such as morphology, particle sizes, crystallite sizes and facets (for example, Cu(100))¹⁸, grain boundaries, strains,⁹ presence of residual oxygen (or Cu+²⁵,¹⁰,²¹), and rise in local pH at the surface of the electrode. However, the effect of applied potential on the selectivity of these catalysts, as shown earlier by Peterson and Nørskov has been largely neglected or sidestepped in these important works.¹²

Here, we address this inadequacy by studying a series of Cu catalysts (metallic film and oxide-derived films) with different roughness factors for the electroreduction of CO₂. We find that the selectivities of CO₂ reduction toward HCOO⁻/CO, C₂H₂, and CH₄ are observed to occur at different potential windows, as long as the mass transport limitation of CO₂ is not reached. Furthermore, this finding can be used to explain the selectivities exhibited by a range of Cu single-crystal surfaces and nanostructures. We also discuss the role of oxide in oxide-derived Cu catalysts for the enhanced formation of CO, HCOO⁻, and C₂H₄.

**Results**

**Characterization of the catalysts.** The copper catalysts were prepared via electrodeposition. By tuning the pH of the electrolyte and the deposition time, four different films were deposited (Supplementary Figure 1). These catalysts were characterized by scanning electron microscopy (SEM), selected area electron diffraction (SAED, with transmission electron microscopy, TEM), and Raman spectroscopy (Fig. 1). As shown by their SAED patterns, 10 min depositions using pH = 10.5 electrolyte led to the formation of metallic Cu films (Cu-10), while the other three catalysts deposited using pH = 13.2 electrolyte for 1 min, 10 min, and 60 min were all CuO (termed as CuO-1, CuO-10, and CuO-60, respectively). The morphologies of the four films before and after CO₂ reduction were revealed by SEM. The surface of Cu-10 consisted of μm-sized particles before reduction (Fig. 1a). The surfaces of CuO-1, CuO-10, and CuO-60 were covered with 10−100 nm particles, though the nanoparticles of CuO-60 agglomerated as μm-sized particles (Fig. 1b–d). After reduction, there was no significant morphology change for all four catalysts (Fig. 1e–h). The roughness factors (RFs) of post-reduced Cu-10, CuO-1, CuO-10, and CuO-60 were estimated by the double layer capacitance method to be 1.4, 5, 48, and 186, respectively (Supplementary Figure 2 and Supplementary Table 1).

The Raman spectra of the three CuO films exhibited peaks at 293, 308, 338, and 610 cm⁻¹, which could be assigned to signals from CuO (Fig. 1i)²²,²³. According to the Pourbaix diagram of the Cu₂H₂O system, the three CuO samples would be reduced to the metallic state under CO₂ reduction potentials, i.e., potentials more negative than −0.50 V vs. RHE (all potentials cited in this work are referenced to the RHE).²⁴ This was further verified by operando Raman spectroscopy of the catalysts (representative data for CuO-60 in Fig. 1j). Upon application of an electrochemical potential of −0.50 V vs. RHE, the 293, 338, and 610 cm⁻¹ peaks of CuO disappeared within 140 s. From 140 s onward, three bands at 280, 360, and 2090 cm⁻¹ appeared. These can be, respectively, assigned to the restricted rotation of bound CO, the Cu-CO stretching and C=C-O stretching modes.²⁵–²⁷ These bands were also observed on CuO-60 at more negative potentials from −0.60 to −0.80 V (Supplementary Figure 3), where hydrocarbons such as C₂H₄ were formed with appreciable quantities (FE_{ethylene} = 3−19%). This observation is consistent with previous reports that indicates CO is a key intermediate formed during the reduction of CO₂ to hydrocarbons on Cu catalysts.²⁸ The appearance of Cu-CO signals only after the CuO signals have disappeared indicates that the active sites for CO₂ reduction are likely to be metallic Cu. The reduction of oxide is also indicated by the chronoamperogram, which showed a reduction peak in the first 100 s (Fig. 1j).

**The effects of limiting currents and applied potentials on CO₂ reduction activity.** The electrochemistry of our four catalysts toward CO₂ reduction was assessed using 60 min chronocoulometry in aqueous 0.1 M KHCO₃ electrolyte. A three-electrode setup was used and the products were quantified using gas chromatography and high performance liquid chromatography.²⁹

The total current density and CO₂ reduction current density are presented in Fig. 2a, b. In general, the total current densities exhibited by the catalysts correlated positively with the latters’ roughness factors and with the overpotentials applied. However, the CO₂ reduction current densities on the four catalysts exhibited parabolic-like trends against the applied potentials,
with maxima of about $-20$ mA cm$^{-2}$. These maxima corresponded to total current densities of about $-40$ mA cm$^{-2}$. Beyond the limiting total current density, the CO$_2$ reduction current densities decreased and the selectivity toward H$_2$ production increased. The limiting CO$_2$ current can be attributed to the mass transport limitation of CO$_2$ to the electrode, as CO$_2$ has a poor solubility in aqueous electrolytes (~34 mM at 25 °C). Additionally, as the total current increased with applied overpotentials, there will also be a buildup of OH$^-$ near the electrode surface, i.e., an increase in local pH. This will cause a decrease in local concentration of CO$_2$ near the electrode surface, resulting in the fall in CO$_2$ reduction currents. The findings are supported by numerical simulations of the concentrations of CO$_2$ and local pH values at the Cu surface (using Cu-10 as the model; Supplementary Figure 4). As the simulated current increased to $-90$ mA cm$^{-2}$, the local pH increased from a bulk value of 6.8 to 11.5, while the local CO$_2$ concentration fell from 34 mM to 6.5 mM.

The FE of major CO$_2$ reduction products are presented in Fig. 2c–e (Supplementary Tables 2–5). We found that a slightly roughened metallic Cu surface (Cu-10, RF = 1.4) exhibited excellent CH$_4$ selectivity at $-1.2$ V with FE$_{\text{methane}}$ of 62%. The oxide-derived Cu surfaces (CuO-1, RF = 5; CuO-10, RF = 48, and CuO-60, RF = 186) were generally more selective for CH$_4$ and C$_2$H$_5$OH (up to total FE of 48%) \cite{9,19}. Interestingly, CuO-1 also exhibited a good selectivity toward CH$_4$ at $-1.15$ V with a FE of 40%. This observation appears unusual as oxide-derived Cu films are hitherto not known to be selective toward the formation of CH$_4$ \cite{5,9}. We also note that the roughest sample, CuO-60, gave relatively high selectivities for CO and HCOO$^-$ at low overpotentials (FE$_{\text{CO}}$ = 46% at $-0.50$ V and FE$_{\text{formate}}$ = 35% at $-0.60$ V).

Another observation is that the catalytic selectivity toward the formation of different products was only observed in specific potential ranges. At potentials more positive than $-0.7$ V, CO and HCOO$^-$ (maximum total FE = 75% at $-0.55$ V) were significantly formed. From $-0.8$ to $-1.1$ V, C$_2$H$_4$ and C$_2$H$_5$OH were produced in great quantities by all the CuO catalysts. As the overpotential increased further (more negative than $-1.1$ V), CH$_4$ was selectively produced (high CH$_4$ selectivity on Cu-10 at $-1.15$ V and CuO-1 at $-1.2$ V). Only small amounts of CH$_4$ were produced using CuO-10 and CuO-60. This is likely because their total current density exceeded the limiting current density of $-40$ mA cm$^{-2}$ after the potential reached more negative to $-1.1$ V, which caused significant decrease of the CO$_2$ concentration near the electrode.

**Fig. 1** Material characterization of four catalysts. SEM images and SAED patterns (inserts) of (a) Cu-10, (b) CuO-1, (c) CuO-10, and (d) CuO-60 catalysts before reduction; SEM images of (e) Cu-10, (f) CuO-1, (g) CuO-10, and (h) CuO-60 catalysts after reduction; (i) Raman spectra of Cu oxide surfaces collected ex situ and (j) operando Raman spectroscopy with the simultaneously obtained chronoamperogram of CuO-60 during CO$_2$ reduction in 0.1 M KHCO$_3$ at $-0.5$ V vs. RHE. Scale bars: 1 μm for SEM (a–g) and 5 nm $^{-1}$ for SAED (inserts of a–d)
Proposed mechanism for the formation of major C₁ and C₂ products. Considering the electrocatalytic properties of different Cu catalysts and the DFT calculations reported in the literature, we propose a mechanism for the formation of major C₁ and C₂ products (Fig. 3). After one proton and one electron transfer, CO₂ could be reduced to either *OCHO or *COOH intermediate. Further reduction of *OCHO and *COOH lead to the respective formation of HCOO⁻ and CO. The presence of *CO as an intermediate species of CO₂ reduction is demonstrated by our operando Raman spectroscopy results in Fig. 1j and Supplementary Figure 3. In agreement with previous studies, our results indicate that the potential-dependent profile of HCOO⁻'s faradaic efficiency does not exactly follow that of CO on CuO-60 (Fig. 2e)⁴–⁶. This indicates that CO and HCOO⁻ may not have been formed through the same *COOH intermediate⁴,⁶. This finding is consistent with recent DFT calculations, which shows that the activities of a range of metallic catalysts toward HCOO⁻ formation correlate better with their binding energies to *OCHO intermediate⁶. *CO could be further reduced to CH₄, or undergo C=C coupling with another *CO to form C₂H₄ and C₂H₅OH. It is notable that to-date copper is the only metal electrode capable of facilitating these value-added reactions at reasonable rates as *CO is optimally bonded to it (Cu resides near the top of the volcano plot⁴.⁶. We have also recently proposed a CO-insertion mechanism for the formation of C₂H₅OH in a CO rich environment¹¹. The different energy barriers in the multiple pathways to form CO₂, HCOO⁻, C₂H₄, C₂H₅OH, and CH₄ could be the reason why these products were observed at different potential windows (Fig. 2c–e)⁶.

Discussion

On the basis of the preceding results, we propose here that the effects of tuning the morphology of a Cu catalyst may not solely lie in creating catalytically active sites (as commonly believed)⁹,⁹–¹¹, but also affects its roughness so that the material operates with a suitable current density at a particular potential. Here, we discuss this proposition in conjunction with previous works (Fig. 4, Supplementary Tables 6 and 7). In Hori’s classic work, a constant current of −5 mA cm⁻² was applied during CO₂ reduction on all the Cu single crystals¹⁴,⁴². Under these conditions, Cu(100) and Cu(111) were, respectively, more selective for C₂H₄ and CH₄ formation. Introducing (110) atomic steps to Cu(100) terraces to create high index surfaces was shown to further enhance C₂H₄ selectivity. These studies suggest that surface crystallography is paramount in the control of product selectivity. However, two recent CO₂ reduction studies performed at various potentials (<−0.30–−1.25 V by our group and −0.89–−1.15 V by Hahn et al.) revealed that Cu(100) could also reduce CO₂ to CH₄ with FE of 30–44% at about −1.1 V (Fig. 4a)²,⁴. It is remarkable that the enhanced selectivities for CH₄, C₂H₄, and HCOO⁻ formation (the formation of CO is generally <15% in these studies) on all the surfaces studied are most pronounced in distinct potential ranges. At potentials negative or equal to −1.1 V, CH₄ selectivity was enhanced and the faradaic efficiency of C₂H₅OH suppressed to <10%, including on Cu(111). High faradaic efficiencies (FE) of HCOO⁻ were observed at potentials more positive to −0.9 V on single crystals, especially on Cu(110). These evidences indicate that the applied potential is a crucial factor for...
the selectivities of different Cu single crystals. The corollary is that
the frequently generalized statement ‘enhanced CH₄ selectivity
using Cu(111)’ or ‘enhanced C₂H₄ selectivity using Cu(100)’ is
only true under specific conditions⁵,⁴⁴, ⁴².

Besides Cu single crystals, we found that the selectivities of 20
other copper catalysts including metallic nanoparticles, oxide-
derived nanoparticles, nanorods, etc. were also greatly affected by
the applied potentials (Fig. 4b). To achieve a high selectivity of
CH₄ on catalysts, such as isolated Cu nanoparticles⁴, polycrystalline Cu⁴,¹³, as well as Cu-10 in this study, the applied
potential was always more negative than −1.1 V (solid circles).
Note that these catalysts have relatively smooth surfaces and as
such, do not exhibit current density that exceeds −40 mA cm⁻²
(the limiting current density) at negative potentials −1.2 V. For
catalysts that favor C₂H₄ formation, such as CuO films⁸–¹⁰ Cu
nanoparticles¹⁵ Cu nanocubes,³¹,⁴⁰,⁴⁶,⁴⁷ Cu nanocrystals³⁵ and
CuO films in this study, the optimum potential range was from
−0.9 to −1.1 V (solid squares). CO and HCOO⁻ selectivity were
usually observed on rough and thick oxide-derived Cu films at
potentials positive to −0.7 V⁵,⁶,⁸,¹⁰,⁴⁵,⁴⁸.

Hence, the top three regions in Fig. 4b (from left to right) indicates the most suitable potential ranges for the selective formation of CH₄, C₂H₄ and CO/HCOO⁻, which are, respectively, about −1.1 V, −0.9 V to −1.1 V, and >−0.9 V. It is notable that
outside their suitable potential windows, these products are
usually produced with FE <15% (hollow shapes in the bottom
three regions of Fig. 4b). For example, the FE of C₂H₄ using
ethylene-selective catalysts were <11% at potentials negative to
−1.1 V or positive to −0.8 V (hollow squares). We note here that
the selectivities of some catalysts could not be clearly defined at
the potentials interfacing two potential windows, such as at
−0.90 V. For instance, apart from catalyzing the reduction of CO₂
to C₂H₄ at −0.90 V (FE = 15%), CuO-1 could also catalyze the
formation of HCOO⁻ with an appreciable faradaic efficiency of
~20%. However, its selectivity toward HCOO⁻ is lower compared
with that of the thicker films (HCOO⁻ forms at a FE of 35 % on
CuO-60 at −0.60 V).

The potential windows highlighted in Fig. 4 are applicable to
reports where the surfaces of the catalysts were particulate or
planar, the electrolysis cell was similar to the design of Kuhl et al⁴
and the electrolyte was aqueous 0.1 M KHCO₃ or other similar electrolytes (such as 0.1 M NaHCO₃). Studies using significantly
different cell designs,⁹ gas diffusion electrodes,¹⁰ nanoneedles, or
nаноfoams²⁶ may exhibit different potential ranges for a specific
product since these systems may have higher limiting current
densities. The use of KOH or KCl electrolytes¹⁶,³⁵ may introduce
other effects such as high local pH, and thus, do not fit properly
in the above-defined regions.

The aforementioned potential windows (Fig. 4) also show that
the DFT predictions made by Peterson and Nørskov on how
potentials affect product selectivity is not only applicable to Cu
(211) surfaces¹², but can also be applied to a variety of Cu
catalysts such as Cu single crystals, oxide-derived Cu and Cu
nanostructures, as long as mass transport limitation of CO₂ has
not been reached.

It is interesting that CuO-1, an oxide, exhibited a surprisingly
high faradaic efficiency of CH₄ (Fig. 2c). In fact, from −0.95 to
−1.15 V, the FE of CH₄ on CuO-1 (3–40%) and Cu-10 (2–54%)
are comparable. This observation is remarkable because oxidized
Cu catalysts are known for their propensity to reduce CO₂ to C₂
products, rather than to CH₄⁵⁻⁸⁻¹⁰. Hence, this result indicates that
the presence of oxide is not the most crucial factor in determining
selectivity between CH₄ and C₂H₄. We further note that an
electropolished Cu surface would be oxidized once exposed to air
(which is almost inevitable during sample transfer) and yet, this
catalyst is known to produce high FE of CH₄ at negative
potentials (Fig. 4b)⁴.

An insight could also be gained from the selectivities exhibited
by oxide-derived Cu catalysts reported by many groups, including
Kanan, Baltrusaitis, and ours⁵,⁶,⁸,⁹,¹³,⁴⁸. These films have been
reported selective toward the reduction of CO₂ to either HCOO⁻
or C₂-H₄ products. This behavior is intriguing if we consider that
the chemical identities and morphologies (in the nanometer scale)
of these films do not appear very different⁸. For example, using a
thick layer of Cu oxide (prepared by annealing a Cu foil at 500 °C for 12 hours), Kanan et al. reported FE of 47% for CO
and 39% for HCOO⁻ at −0.35 and −0.55 V, respectively. C₂H₄
was formed at a maximum FE of only ~5% at −0.95 V⁵. The
production of C₂H₄ is, thus, notably lower than that on a
polycrystalline Cu surface (FE = 23% at −0.97 V) and our oxide-
derived Cu films (34–39% at −0.99 V)⁹.¹³. The fact that Kanan’s
Cu sample exhibited rather low selectivities toward C₂H₄ seem to
contradict with observations made by Baltrusaitis et al. and our
group. We propose here a simple explanation for this observation:
apart from the slightly different electrolytes used, we highlight that
the high total current density (about −25 mA cm⁻²) exhibited by Kanan’s annealed Cu at −0.95 V will result in a
lower local concentration of CO₂ near the electrode surface. This
will cause an overall lowering of the FE for CO₂ reduction and
consequently, a decreased formation of C₂H₄ at −0.95 V. Our
observation indicates that thick oxide films will not be suitable for
C₂H₄/C₂H₅OH formation, once their roughness factors exceed the
optimum⁹.

Schouten and Koper have measured the onset potentials
required for the formation of CH₄ and C₂H₄ during CO reduc-
tion on Cu(100) and Cu(111) electrodes.⁵²,⁵³ It was shown that
C₂H₄ could be formed at ~400 mV lower overpotential compared
to CH₄ on Cu(100) in pH = 7 electrolyte. C₂H₄ was further
proposed to be formed via a CO dimerization pathway on Cu
(100). Although this study had revealed the potential-dependence
of C₂H₄ formation on Cu(100), we draw here a more general
trend of how the electrochemical potential affects the selectivity of
CO₂ reduction for a wide range of Cu surface structures. The
effect of limiting current density on selectivities is also addressed
here.
Finally, our work highlights how we could design Cu catalysts with various selectivities—it is critical to control the surface roughness such that the limiting current density lies in the suitable potential window for CH4, C2H4, or CO/HCOO−. In order to achieve a high selectivity of CH4 formation, the catalyst should be relatively smooth so that the limiting current density is not exceeded at the very negative applied potentials needed (i.e., more negative than −1.2 V). With a roughness factor of 1.4, Cu-10 catalyst exhibits both high faradaic efficiency (62%) and high partial current density (−18 mA cm−2) of CH4, making it among the best catalysts toward CH4 formation7. For C2H4 and C2H4OH selectivity, the catalyst should have a slightly roughened surface so that the intermediates are stabilized and its CO2 reduction current density is maximized at regions from −0.9 V to −1.1 V. To obtain a high faradaic efficiency of CO or HCOO−, the catalysts should be thick and rough oxide-derived films with high RFs. We note here that though smooth surfaces such as Cu(110), polycrystalline Cu, and Cu-10 could catalyze the reduction of CO2 to HCOO− or CO at more negative potentials, their selectivities are not comparable with those exhibited by thick Cu oxide films at less negative potentials13,43.

In this work, we prepared four Cu-based films by electrodeposition, and showed that they exhibited different selectivities toward CO2 reduction at different potential ranges. We highlight how limiting currents and applied potentials affect the selectivity of CO2 reduction reactions. This helps to rationalize the selectivity of different Cu catalysts, not only in this work, but also from many other reports. A FE of ~40% of CH4 observed on CuO-1 film at −1.15 V contradicts with a proposition that Cu2+ or subsurface oxygen-modified Cu is the preferred catalyst for CH4 selectivity. This study strongly shows that optimization of CO2 reduction current densities at the appropriate potential windows is critical for forming the type of product needed, and thus provides us with insights into how highly selective Cu catalysts could be rationally designed.

**Methods**

**Preparation of electrocatalysts.** The substrates were mechanically polished Cu discs (99.99%, Goodfellow) with an exposed geometric surface area of 0.865 cm2. Two aqueous deposition electrolytes, A and B were prepared, for the depositions of metallic and oxide films, respectively.

Electrolyte A was prepared by first dissolving tartaric acid (Alfa Aesar, 99%) in deionized water (18.2 MΩ cm, Barnstead Type 1). CuSO4·5H2O (GCE, 99%) was then added. The solution was then cooled and continuously stirred in an ice water bath while NaOH (Chemiboc, 99%) was slowly added. The final pH of the solution was 10.5, with the concentrations of tartaric acid, CuSO4·5H2O and NaOH at, respectively, 0.2, 0.2, and 0.8 M. The deposition of CuO-10 was carried out in a two-electrode setup with a Pt wire as the counter electrode and the acquisition time was 10 seconds for each spectrum. A dry objective (Olympus MP Plan N, 50x, numerical aperture = 0.75) and a water immersion objective (Olympus LUMFL 60x, numerical aperture = 1.00) were, respectively, employed for ex situ and operando Raman spectroscopy. The morphology of the catalysts were characterized by SEM (JEOL JSM-6710F, 5 kV). Their electrochemical-active surface areas were determined by their cyclic voltammograms performed in a non-faradaic region from −0.05 V to 0.05 V vs. RHE. The scan rates were 50, 100, 150, 200, 250, 300, 350, and 400 mV s−1.

Electrochemical reduction of CO2. CO2 electroreduction was performed in a custom built three-electrode electrochemical cell15. The reference and counter electrodes, respectively, were a Ag/AgCl (saturated KCl, Pine) and a coiled Pt wire. The cathodic and anodic compartments were separated by an anion exchange membrane (Asahi Glass). Both compartments were filled with CO2-saturated 0.1 M
Number of electrons used for producing $X$

**Numerical simulations of local pH and CO$_2$ concentration.** Numerical simulations were performed with MATLAB 8.5 to calculate the local pH and how the concentration of CO$_2$ near the electrode changed as a function of current density. The electrode was taken to be planar (1-D model). The resulting bulk concentration of CO$_2$, HCO$_3^-$, CO$_3^{2-}$, and H$^+$ diffusion coefficients, and rate constants were taken from the work of Gupta et al., along with the boundary conditions. The diffusion layer thickness was assumed to be 36 μm. The normalized current density (against the electrochemical-active surface area) and the FE were used for calculations. Only the effect of diffusion and surface reaction were considered in this model. The Cu-10 surface was simulated as it has a small roughness factor of 1.4, and, thus, its surface is close to planar.

**Data availability.** The data that support the findings of this study are available from the corresponding authors.

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Author contributions

D.R., and B.S.Y. conceived the idea and designed the experiments. D.R., and J.F. ran the electrochemistry measurements. D.R. characterized the samples. B.S.Y. supervised the project. All the authors analyzed the data and contributed to the final manuscript.

Additional information

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