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Surface Reconstruction of Polycrystalline Cu Electrodes in Aqueous KHCO$_3$ Electrolyte at Potentials in the Early Stages of CO$_2$ Reduction

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Abstract

The reconstruction of the Cu(pc) polycrystalline surface at potentials that correspond to the early stages of CO$_2$ reduction in 0.1 M KHCO$_3$ was investigated by electrochemical scanning tunneling microscopy (ECSTM) at −0.90 V (SHE). A kinetically hindered surface reconstruction of the topmost layers of Cu(pc) into the (100) face was observed, reminiscent of the transformation previously reported at the same electrode potential in 0.1 M KOH. Evidently, the same reconstructed surface, Cu(pc)-[Cu(100)], can be generated in either 0.1 M KHCO$_3$ (pH 8) or 0.1 M KOH (pH 13). In addition, only minimal structural disruption was observed when the reconstructed surface was transferred from KHCO$_3$ to KOH electrolyte, and vice versa, provided the solution exchange was executed potentiostatically at −0.90 V. The structural convergence toward the same (100) facet regardless of pH or supporting electrolyte strongly suggests that the Cu(pc) → Cu(pc)-[Cu(100)] surface reorganization is a general phenomenon driven primarily by the rather negative potential applied on the electrode.

Keywords Surface reconstruction of Cu(pc) under CO$_2$-reduction potentials · *Operando* electrochemical scanning tunneling microscopy · Electrochemical CO$_2$ reduction · Cu(pc) to Cu(pc)-[Cu(100)] surface reconstruction

Introduction

The ability of elemental copper to catalyze the electrochemical conversion of CO$_2$ into economically valuable products such as hydrocarbons and oxygenates is unmatched by other single-metal catalysts that generate only carbon monoxide, in either the pure (CO) or hydrous (HCOOH) form [1–4]. The electrochemical reduction of CO$_2$ into C$_1$–C$_2$ products is notably endergonic [5–7], and the associated current densities for the Cu-catalyzed transformations register in the lower end of

the mA/cm^2 scale [3]. The search for an electrocatalyst simultaneously more active and better product-selective than Cu poses a steep challenge: A set of "heuristic rules,"[1] extracted solely from experimental results, for the production of hydrocarbons and oxygenates [8, 9], must be transcended especially when the target is the preferential formation of "energy-rich" molecules more chemically reduced than CO.

Reactivity-structure correlations traditionally underpin the rational design and optimization of catalysts. Single-crystal electrodes represent model surfaces whose well-defined structure and composition can be tracked, at the atomic level, before and after the catalytic reaction. For instance, it has been shown that CO$_2$ reduction (CO$_2$R) at Cu(111) electrode surfaces

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[1] With regard to the generation of pure and oxygen-substituted hydrocarbons, (i) no metal displays better activity than Cu. (ii) Alloys do not enhance activity but may improve selectivity. (iii) Catalytic activity can be increased, but at the expense of selectivity and vice-versa. (iv) It is best if $\Delta G_{H,ads}$ and $\Delta G_{CO,ads}$ were not too different from one another; for Cu, the ratio of $\Delta G_{H,ads}$ to $\Delta G_{CO,ads}$ is close to unity. (v) Selectivity can be regulated by an atomic-level control of surface structure. (vi) Under CO$_2$R conditions, surfaces may undergo surface reconstructions that can alter both activity and selectivity.

gives, at certain potentials, methane as the favored product on Cu(111); at Cu(100) electrodes, ethylene is the dominant product [10, 11]. The yields are invariably low because product exclusivity remains elusive. *Operando* electrochemical scanning tunneling microscopy (ECSTM) has revealed that the surfaces of Cu(111) and Cu(100) correspond to the nominal crystallographic orientation prior to and at the onset of CO_2R [12]. The case is, however, drastically different for Cu(110) and polycrystalline Cu, Cu(pc); the physical attributes of the latter are more proximate to those of "real-world" catalysts. In the case of Cu(pc), under CO_2R potentials in 0.1 M KOH (pH 13) solution, a still-undetermined number of topmost layers undergoes surface reconstruction to form a well-ordered (100) facet [13]. The dynamic nature of the Cu(pc) surface in KOH under *operando* conditions has provided the impetus of the present investigation, viz., to ascertain whether the same surface reorganization also transpires in $KHCO_3$, a widely employed supporting electrolyte in the CO_2R corpus. It is of fundamental importance to determine the generality or specificity of the phenomenon of the surface reconstruction of Cu under CO_2R potentials.

Experimental

The experimental procedures have been described in detail elsewhere [14] and will only be summarized here. Surface visualization studies by electrochemical scanning tunneling microscopy (EC-STM) were conducted using a Nanoscope E microscope (Digital Instruments, Veeco, Santa Barbara, CA) that had been refurbished (Advanced Surface Microscopy, Inc., Indianapolis, IN) and equipped with a built-in three-electrode potentiostat. A Pt counter electrode and a miniature leakless Ag/AgCl (3.4 M KCl) reference electrode (Innovative Instruments, Inc., Tampa, FL) were fitted inside an STM electrochemical cell custom-crafted from Kel-F (Emco Industrial Plastics, Inc., Cedar Grove, NJ). A 99.99%-pure polycrystalline Cu disk, 1.0 mm in thickness and 10 mm in diameter (GoodFellow, Coraopolis, PA), served as the working electrode. Potentials are referenced to the standard hydrogen electrode (E_{SHE}), for direct correlation to thermodynamic free-energy changes. The interconversion between the E_{SHE} and E_{RHE} scales is given by the equation: $E_{SHE} = E_{RHE} - 0.059$ pH.

The STM tips were prepared by an electrochemical etch of a 0.25 mm diameter tungsten wire (Sigma-Aldrich, St. Louis, MO) in 0.6 M KOH at 15 VAC. All images were acquired after 1-h polarization at − 0.9 V; a high-resolution scanner was employed in constant-current mode without post-scan operations.

A two-step cleaning sequence of the Cu working electrode, prior to use, was employed: a mirror-finish metallographic polish with a suspension of polycrystalline diamond (Buehler, Lake Bluff, IL) at a grain size of 0.05 μm, followed by a 10-s electropolishing in 85% H_3PO_4 (Sigma-Aldrich) at 2.0 V with a Pt counter electrode. The electrode was then ultrasonicated in, and later rinsed with, deaerated Nanopure water. The polished sample was not thermally annealed.

Analytical-grade $KHCO_3$ and KOH (Sigma-Aldrich) were used to prepare 0.1 M of the electrolyte solutions. The 0.1 M $KHCO_3$ solution was deaerated for at least 1 h in ultrahigh purity N_2 (Airgas, Radnor, PA); 0.1 M KOH was treated identically. Voltammetric scans were carried out at a scan rate of 50 mV/s; the reported voltammograms represented results from the 10th potential cycle.

Results and Discussion

Previous work on *operando* electrochemical scanning tunneling microscopy (ECSTM) depicted a dramatic reconstruction of the polycrystalline Cu surface, in alkaline solution, into the (100) facet after a constant-potential hold at − 0.9 V [13]. The same potentiostatic protocol is revisited in N_2-purged 0.1 M $KHCO_3$ at a pH of 8. The tableau of ECSTM images in Fig. 1 captures the temporal evolution of the polycrystalline electrode surface. After 2 h, multiple domains collectively formed wide regions with right-angular corners such as those marked by broken lines. On the third hour, further surface-atom rearrangement gave rise to a square adlattice indicative of a Cu(100) surface. The results were reminiscent of the Cu(pc) → Cu(pc)-[Cu(100)] transformation in 0.1 M KOH; the acquisition of atomically resolved images smaller than 10 nm × 10 nm was, however, onerous.

Cyclic voltammetry of the reconstructed surface, Cu(pc)-[Cu(100)], in 0.1 M $KHCO_3$ bubbled with N_2 was initiated at − 0.9 V to avoid disruption of the long-term potential hold. Figure 2 superimposes the voltammograms of the pre- and post-reconstructed Cu(pc) electrodes. The steady-state current-potential profile of the Cu electrode, prior to reconstruction, was consistent with the well-documented reduction-oxidation signatures of Cu in alkaline conditions [15]. Two distinct voltammetric features render support to the visual narrative chronicled by ECSTM: (1) Among the low-index facets of Cu, the (100) surface has been reported to manifest the lowest overpotential for the hydrogen evolution reaction (HER) [16]. Hence, Cu(pc)-[Cu(100)] in Fig. 2 is not unexpected to manifest a positive shift in the onset potential of HER. Such nuanced difference in electrochemical behavior corroborates the geometric evidence from ECSTM, which clearly points to the monocrystallinity of the reconstructed surface. (2) The area of the peak at ca. − 0.20 V, ascribed to the cathodic reduction of Cu(I) oxide to zerovalent Cu [14], was found to decrease after the reconstruction. The result implies a decrease in the electrochemically active surface area of

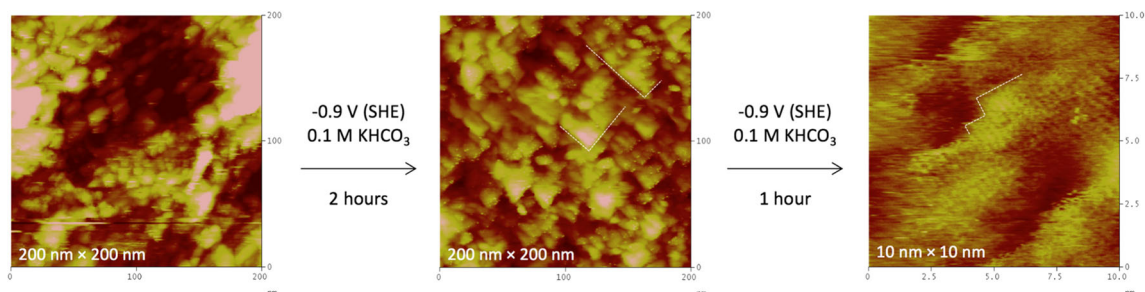## Reconstruction of Cu(pc) in 0.1 M KHCO₃ at -0.9 V (SHE)

Fig. 1 Electrochemical scanning tunneling microscopy images of polycrystalline Cu, Cu(pc), acquired during a constant-potential hold at − 0.90 V in N₂-purged 0.1 M KHCO₃. Dashed lines are provided as visual guide

the Cu electrode; that is, the topographic homogeneity of the polycrystalline Cu surface improved after reconstruction.

The Cu(pc)-[Cu(100)] sample originally prepared in N₂-purged 0.1 M KHCO₃ was further examined in N₂-purged 0.1 M KOH. Although the applied potential was nominally kept at − 0.90 V during the replacement of the electrolyte solution, perturbations in the local electric field of the Cu electrode were inevitable as the bulk pH changed from 8 to 13 and the ionic environment transitioned from HCO₃⁻-rich to predominantly OH⁻. Thus, the initial wide-scale ECSTM image in Fig. 3 revealed irregularly shaped domains with symmetry properties indecipherable from those of a pure (100) surface. Indications of surface-atom reorganization were noticeable after 30 min: narrow regions emerged with straight edges parallel to each other. After an hour, atomically resolved images of the Cu(100) square adlattice were unambiguously discernible from an area of 2.5 nm × 2.5 nm at numerous locations on the surface.

The facile structural reversion in 0.1 M KOH was consistent with the resemblance of the cyclic voltammograms

recorded before and after the 1-h polarization at − 0.90 V (Fig. 4). Only a slight decrease (ca. 16%) in the peak area after the potential hold was evident for the Cu₂O-to-Cu cathodic reaction at ca. − 0.40 V. The restoration of the (100) facet was also marked by a marginally small shift in the HER onset potential.

Juxtaposition of the voltammograms for the two Cu(pc)-[Cu(100)] samples, one prepared in N₂-purged 0.1 M KHCO₃ (Fig. 2) and the other regenerated in deaerated 0.1 M KOH (Fig. 4), reveals a pH-dependent shift of the onset potential of HER. For instance, to achieve a current density of − 0.1 mA cm⁻², an applied potential of ca. − 0.8 and − 1.0 V was needed, respectively, at pH 8 and pH 13. The negative shift of the onset potential of HER in alkaline media qualitatively agreed with the Nernstian pH correction of − 0.059 V (13– 8) = − 0.30 V, although the observed shift was much smaller at − 0.20 V. Such deviation may emanate, in part, from the fact that the bulk pH often differs substantially from the more crucial pH at the electrical double-layer region [17]. Furthermore, the variable baseline asymmetry, typical of

Fig. 2 Cyclic voltammogram of polycrystalline Cu, Cu(pc), in N₂-purged 0.1 M KHCO₃, before and after a constant-potential hold at − 0.90 V for at least 3 h. Scan rate = 50 mV/s
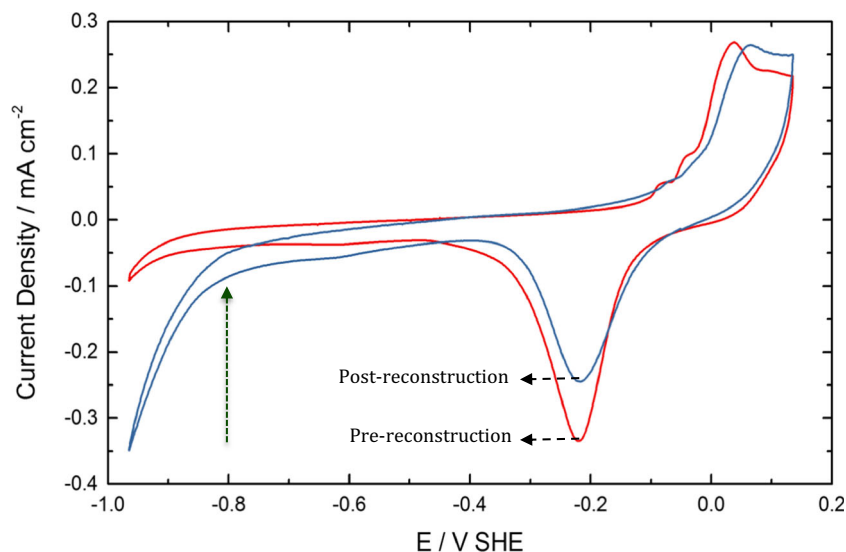
Cu(pc)-[Cu(100)] from KHCO₃ Transferred to 0.1 M KOH at -0.9 V (SHE)
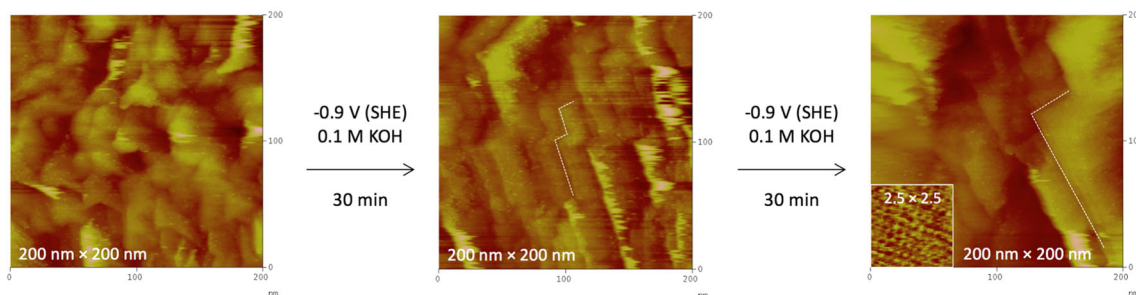

Fig. 3 Electrochemical scanning tunneling microscopy images of Cu(pc)-[Cu(100)] acquired at a constant potential of − 0.90 V in 0.1 M KOH. The reconstructed surface was initially prepared in 0.1 M KHCO₃. Dashed lines are provided as visual guide

many voltammetric scans in alkaline medium, precludes a precise comparison of onset potentials under these conditions.

It may be noted that, at − 0.9 V, the potential at which the ECSTM images were acquired, the extent of HER, albeit still incipient, was more pronounced in 0.1 M KHCO₃ than in 0.1 M KOH. In 0.1 M KHCO₃, the applied potential was competitively channeled between HER and surface reconstruction, and the resultant rate of the latter process was consequently more sluggish than that in alkaline solution. The reconstructed surfaces in both electrolyte systems, however, still converged to the same structure, i.e., Cu(pc)-[Cu(100)]. At potentials not far removed from the onset of the electrochemical reduction of CO_2, the polycrystalline-to-monocrystalline transformation of the Cu electrode surface remained unaffected by the change in supporting electrolyte from the bicarbonate system at pH 8 to the strongly alkaline medium at pH 13. These results demonstrated that the surface reconstruction of Cu under the present experimental conditions was unaffected by the presence of supporting electrolyte ions in solution, viz., OH^-, HCO_3^-, CO_3^{2-}, H_3O^+, and K^+. The accumulated evidence indicates that the surface reconstruction of polycrystalline Cu is a general phenomenon driven primarily by the negative potential applied on the electrode.

Summary

The polycrystalline surface of copper, Cu(pc), in N₂-purged 0.1 M KHCO₃ underwent surface reconstruction at a constant potential of − 0.90 V (SHE), near the onset of the electrochemical reduction of CO_2. Atomic-level visualization from electrochemical scanning tunneling microscopy (ECSTM) depicted a kinetically hindered formation of the (100) facet, a surface-atom rearrangement similar to that previously reported in CO₂-free 0.1 M KOH. Nuances in the voltammetric features rendered additional support to the polycrystalline-to-monocrystalline surface transformation. The reconstructed Cu surface generated at pH 8 in 0.1 M KHCO₃ can be subsequently examined electrochemically and structurally at pH 13 in 0.1 M KOH, with minimal disruption, as long as the electrolyte exchange is executed potentiostatically at −0.90 V. At near-neutral-to-alkaline conditions, ions such as OH^-, HCO_3^-, CO_3^{2-}, K^+, and H_3O^+ exert essentially no influence on the reorganization process. The Cu(pc) → Cu(pc)-[Cu(100)] surface reconstruction under CO₂ reduction potentials is a general phenomenon driven primarily by the rather negative applied potential.

Fig. 4 Cyclic voltammogram of Cu(pc)-[Cu(100)] in 0.1 M KOH, before and after a constant-potential hold at − 0.90 V for at least 1 h. The reconstructed surface was initially prepared in 0.1 M KHCO₃. Scan rate = 50 mV/s. Experimental details are described in the text
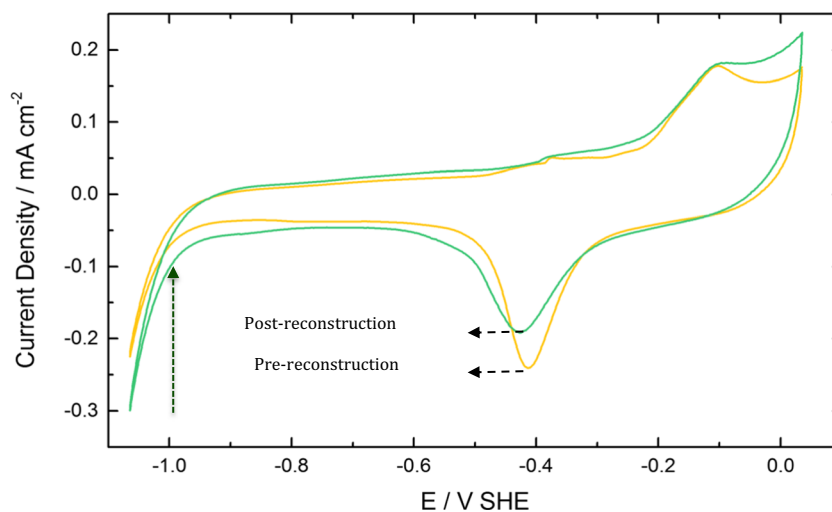
References

1. Y. Hori, in *Modern Aspects of Electrochemistry*, ed. by C. G. Vayenas, R. E. White, M. E. Gamboa-Aldeco. Electrochemical CO_2 Reduction on Metal Electrodes (Springer, New York, 2008), p. 89

2. M. Gattrell, N. Gupta, A. Co, A review of the aqueous electrochemical reduction of CO_2 to hydrocarbons at copper. J. Electroanal. Chem. **594**(1), 1–19 (2006)

3. K.P. Kuhl, E.R. Cave, D.N. Abram, T.F. Jaramillo, New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. Energy Environ. Sci. **5**(5), 7050 (2012)

4. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C.P. Kubiak, Photochemical and photoelectrochemical reduction of CO_2. Annu. Rev. Phys. Chem. **63**(1), 541–569 (2012)

5. C. Shi, K. Chan, J.S. Yoo, J.K. Nørskov, Barriers of electrochemical CO_2 reduction on transition metals. Org. Process. Res. Dev. **20**(8), 1424–1430 (2016)

6. J.H. Montoya, A.A. Peterson, J.K. Nørskov, Insights into C-C coupling in CO_2 electroreduction on copper electrodes. ChemCatChem **5**(3), 737–742 (2013)

7. A.J. Garza, A.T. Bell, M. Head-Gordon, Mechanism of CO_2 reduction at copper surfaces: pathways to C_2 products. ACS Catal. **8**(2), 1490–1499 (2018)

8. M.P. Soriaga, J.H. Baricuatro, A.C. Javier, Y.-G. Kim, K.D. Cummins, C.F. Tsang, J.C. Hemminger, N.N. Bui, J.L. Stickney, in *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry*, ed. by K. Wandelt. Electrochemical Surface Science of CO_2 Reduction at Well-Defined Cu Electrodes: Surface Characterization by Emersion, Ex Situ, In Situ, and Operando Methods (Elsevier Inc., Oxford, 2017), p. 1

9. Y.-G. Kim, A. Javier, J.H. Baricuatro, M.P. Soriaga, Seriatim ECSTM-DEMS of Cu-catalyzed reduction of CO in alkaline solution: Operando correlation of electrode-surface atomic structure with product selectivity. Curr. Top. Catal. **13**, 1 (2017)

10. Y. Hori, I. Takahashi, O. Koga, N. Hoshi, Selective formation of C_2 compounds from electrochemical reduction of CO_2 at a series of copper single crystal electrodes. J. Phys. Chem. B **106**(1), 15–17 (2002)

11. K.J.P. Schouten, Z. Qin, E.P. Gallent, M.T.M. Koper, Two pathways for the formation of ethylene in CO reduction on single-crystal copper electrodes. J. Am. Chem. Soc. **134**(24), 9864–9867 (2012)

12. Y.-G. Kim, A. Javier, J.H. Baricuatro, D. Torelli, K.D. Cummins, C.F. Tsang, J.C. Hemminger, M.P. Soriaga, Surface reconstruction of pure-Cu single-crystal electrodes under CO-reduction potentials in alkaline solutions: a study by seriatim ECSTM-DEMS. J. Electroanal. Chem. **780**, 290–295 (2016)

13. Y.-G. Kim, J.H. Baricuatro, A. Javier, J.M. Gregoire, M.P. Soriaga, The evolution of the polycrystalline copper surface, first to Cu(111) and then to Cu(100), at a fixed CO_2RR potential: a study by operando EC-STM. Langmuir **30**, 15053 (2014)

14. Y.-G. Kim, A. Javier, J.H. Baricuatro, M.P. Soriaga, Regulating the product distribution of co reduction by the atomic-level structural modification of the Cu electrode surface. Electrocatalysis **7**, 1 (2016)

15. Y.-G. Kim, M.P. Soriaga, Cathodic regeneration of a clean and ordered Cu(100)-(1×1) surface from an air-oxidized and disordered electrode: an operando STM study. J. Electroanal. Chem. **734**, 7–9 (2014)

16. Y. Huang, A.D. Handoko, P. Hirunsit, B.S. Yeo, Electrochemical reduction of CO_2 using copper single-crystal surfaces: effects of CO* coverage on the selective formation of ethylene. ACS Catal. **7**(3), 1749–1756 (2017)

17. M.R. Singh, Y. Kwon, Y. Lum, J.W. Ager, A.T. Bell, Hydrolysis of electrolyte cations enhances the electrochemical reduction of CO_2 over Ag and Cu. J. Am. Chem. Soc. **138**, 13006 (2016)