J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

CO_2 Reduction at Low Overpotential on Cu Electrodes Resulting from the Reduction of Thick Cu_2O Films

Christina W. Li and Matthew W. Kanan*

Department of Chemistry, Stanford University, 337 Campus Drive, Stanford, California 94305, United States

Ⓢ *Supporting Information*

ABSTRACT: Modified Cu electrodes were prepared by annealing Cu foil in air and electrochemically reducing the resulting Cu_2O layers. The CO_2 reduction activities of these electrodes exhibited a strong dependence on the initial thickness of the Cu_2O layer. Thin Cu_2O layers formed by annealing at 130 °C resulted in electrodes whose activities were indistinguishable from those of polycrystalline Cu. In contrast, Cu_2O layers formed at 500 °C that were $\geq\sim3$ μm thick resulted in electrodes that exhibited large roughness factors and required 0.5 V less overpotential than polycrystalline Cu to reduce CO_2 at a higher rate than H_2O. The combination of these features resulted in CO_2 reduction geometric current densities >1 mA/cm^2 at overpotentials <0.4 V, a higher level of activity than all previously reported metal electrodes evaluated under comparable conditions. Moreover, the activity of the modified electrodes was stable over the course of several hours, whereas a polycrystalline Cu electrode exhibited deactivation within 1 h under identical conditions. The electrodes described here may be particularly useful for elucidating the structural properties of Cu that determine the distribution between CO_2 and H_2O reduction and provide a promising lead for the development of practical catalysts for electrolytic fuel synthesis.

Closing the anthropogenic carbon cycle by using renewable energy to convert CO_2 and H_2O into fuel requires efficient CO_2 reduction catalysts.[1−4] Materials that catalyze electrochemical CO_2 reduction are longstanding targets because they would enable direct electrolytic fuel synthesis powered by a renewable electricity source.[5] Researchers over the past three decades have identified several materials that are capable of reducing CO_2 electrochemically in aqueous solutions,[6−8] but none are efficient and stable enough for practical use. Polycrystalline Cu has been the focus of most CO_2 reduction studies because it is one of the best available catalysts and is capable of producing hydrocarbon products. Although mechanistic studies have yielded valuable insights into the CO_2 reduction pathways on Cu,[7,9−13] the principal shortcomings of this electrode have not been addressed. Most significantly, the energetic efficiency of Cu is limited by the large overpotential (>0.7 V) required for CO_2 reduction to outcompete H_2O reduction.[14] In addition, Cu electrodes rapidly lose their CO_2 reduction activity unless stringently purified electrolytes are used,[7] a requirement that is not compatible with scalable fuel synthesis.

Achieving efficient Cu-catalyzed CO_2 reduction requires preparing Cu particles whose surfaces have active sites that are different from those on the surface of a polycrystalline Cu electrode. Electrochemical reduction of metal oxides provides one possible route to metal particles with altered surface structures.[15−17] Researchers have previously used electrochemical methods including potential cycling and anodic pulses to form and subsequently reduce oxides on Cu electrodes. These treatments have resulted in increased hydrogen evolution activity in alkaline electrolytes[18] and altered product selectivity at high overpotential in CO_2 reduction electrolyses.[19−21] While these studies provide evidence of altered electrocatalytic properties, substantial improvements to the energetic efficiency of CO_2 reduction have not been observed. Researchers have also used copper oxide electrodes directly in CO_2 reduction electrolyses. The oxides were reduced to Cu^0 in situ during CO_2 reduction catalysis, but only transient changes in the CO_2 product distribution attributed to oxide catalysis were observed.[22,23] Here we show that the CO_2 reduction properties of Cu^0 electrodes resulting from copper oxide reduction vary widely depending on the properties of the initial oxide layer. Reduction of thick Cu_2O layers formed by high temperature annealing results in electrodes that catalyze energy-efficient CO_2 reduction and are stable to the deactivation phenomena that plague bulk metal electrodes.

Electrodes were prepared by electropolishing pieces of polycrystalline Cu foil (99.9999%) in 85% phosphoric acid and subsequently annealing the electrodes in air at selected temperatures for variable amounts of time. The activities of these electrodes were compared to that of a polycrystalline Cu electrode in controlled potential electrolyses performed in CO_2-saturated 0.5 M $NaHCO_3$ electrolyte ("$NaHCO_3/CO_2$") in a two-compartment electrolysis cell. The headspace of the cathodic chamber was continuously purged with CO_2 into the sampling loop of a gas chromatograph (GC) to enable periodic quantification of the gas-phase products. The solution-phase products were quantified by NMR analysis of the electrolyte at the conclusion of the electrolyses.

Figure 1 shows the total geometric current density (j_{tot}) vs time, the faradaic efficiency (FE) for CO vs time and the overall FE for HCO_2H for the polycrystalline Cu electrode and several of the annealed electrodes at −0.5 V vs the reversible hydrogen electrode (RHE; all potentials are referenced to this electrode). The polycrystalline Cu electrode exhibited a j_{tot} of ~100 μA/cm^2, a FE for CO that declined from 10% at the start of the

Received: February 2, 2012
Published: April 16, 2012

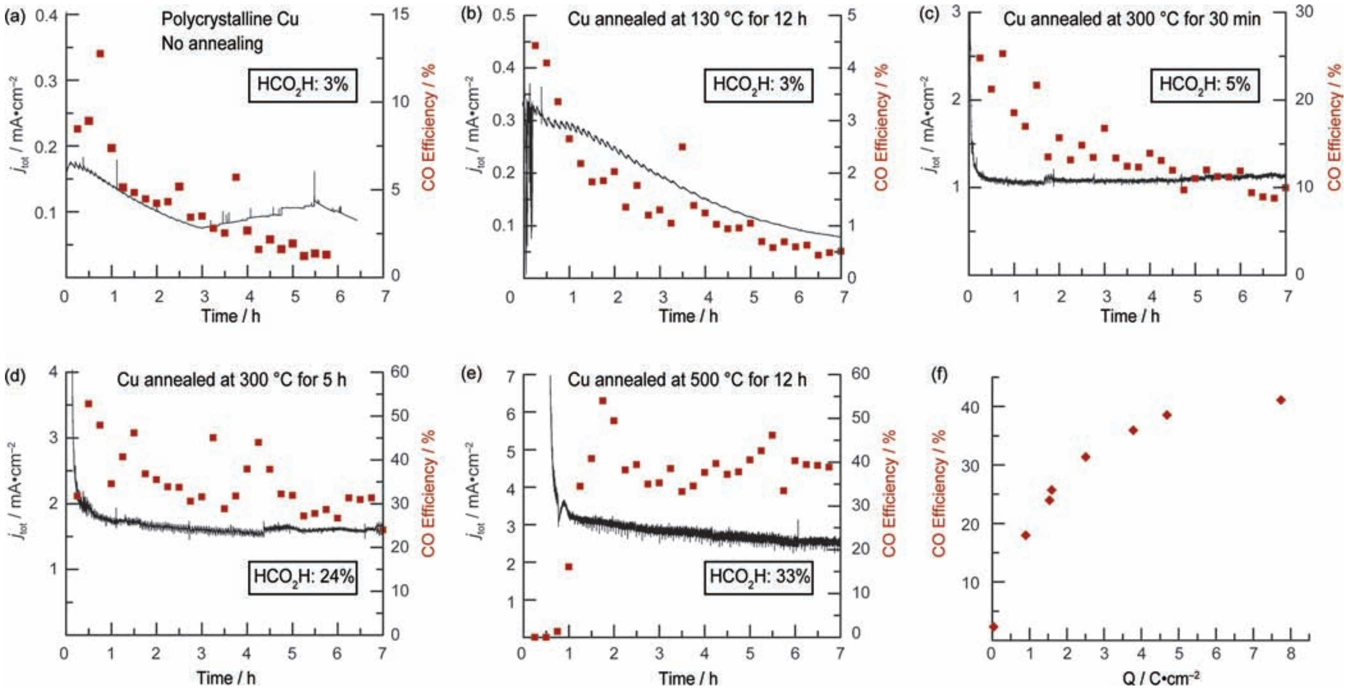

Figure 1. CO_2 reduction electrolysis data at −0.5 V vs RHE for polycrystalline Cu and several annealed electrodes. (a−e) Total current density vs time, faradaic efficiency (FE) for CO vs time and total FE for HCO_2H for electrodes with progressively thicker initial Cu_2O layers. (f) Average FE for CO vs amount of charge required to reduce the Cu_2O layer per electrode area.

electrolysis to <2% over the course of 7 h and a FE for HCO_2H of 3%. The majority of the current, >90%, was due to H_2 evolution. These values are consistent with the previously measured activity for Cu in $KHCO_3$ electrolytes.[7] Annealing Cu at 130 °C, the temperature used to prepare Cu_2O electrodes for most previous studies,[22,23] had very little effect on the activity under these conditions. The electrode annealed at 130 °C for 12 h exhibited a j_{tot} of 10 mA/cm^2 during the first 4 s in which the thin Cu_2O layer was reduced. Subsequently, the j_{tot} and FEs were very similar to those of the polycrystalline electrode (Figure 1b).

In contrast to these results, the electrodes annealed at higher temperatures exhibited larger j_{tot} values and improved CO_2 reduction FEs upon reduction of the Cu_2O layer. The electrode annealed at 300 °C for 30 min exhibited an initial j_{tot} of 10 mA/cm^2 for 2 min as the Cu_2O was reduced and subsequently a stable j_{tot} of 1.0 mA/cm^2. The FE for CO was 25% during the first hour of electrolysis before declining to 10% over 7 h; the FE for HCO_2H on the reduced electrode was 5%. Further improvements were obtained by starting with a thicker Cu_2O layer. After Cu_2O reduction of the electrode annealed at 300 °C for 5 h, j_{tot} reached a stable value of 1.3 mA/cm^2, the FE for CO reached 35% and the FE for HCO_2H was 24% (Figure 1d). Annealing at 500 °C for 12 h resulted in an even thicker Cu_2O layer and a stable j_{tot} of 2.7 mA/cm^2. This electrode produced CO with ~40% FE and HCO_2H with 33% FE. Notably, the FE for CO was maintained at 40% throughout the electrolysis, indicating not only efficient but also stable activity for CO_2 reduction on this surface.

A plot of the average CO FEs for the annealed electrodes vs the amount of charge passed per electrode area (Q) in the Cu_2O reduction is shown in Figure 1f. The FEs increased with the amount of charge passed until reaching a plateau at 30−40% for $Q \geq \sim 5$ C/cm^2. Assuming bulk density of Cu_2O on the electrode, 5 C/cm^2 corresponds to a ~3 μm-thick layer. Together, these results demonstrate that a threshold thickness of the initial Cu_2O layer is required to achieve both efficient and stable CO_2 reduction catalysis for the electrode resulting from Cu_2O reduction.

Based on these results, electrodes prepared by annealing Cu at 500 °C for 12 h were selected for further characterization and CO_2 reduction studies. Figure 2 shows the scanning electron microscopy (SEM) images, X-ray diffraction (XRD) patterns, and high-resolution Cu 2p X-ray photoelectron spectroscopy (XPS) spectra for a Cu electrode after this annealing procedure and after subsequent CO_2 reduction electrolysis. After annealing, the SEM showed a dense array of rods with 100−1000 nm diameters on the electrode surface. These rods are the outermost portion of a thick Cu_2O layer coating the electrode, as evidenced by the large Cu_2O peaks and the near complete suppression of the Cu^0 peaks in the

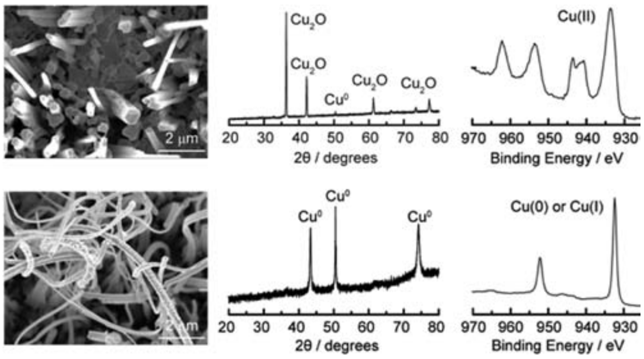

Figure 2. Top: SEM image (left), XRD pattern (middle), and XPS spectrum (right) of a Cu electrode after annealing at 500 °C for 12 h. Bottom: analogous data for the same electrode after CO_2 reduction electrocatalysis at −0.5 V vs RHE.

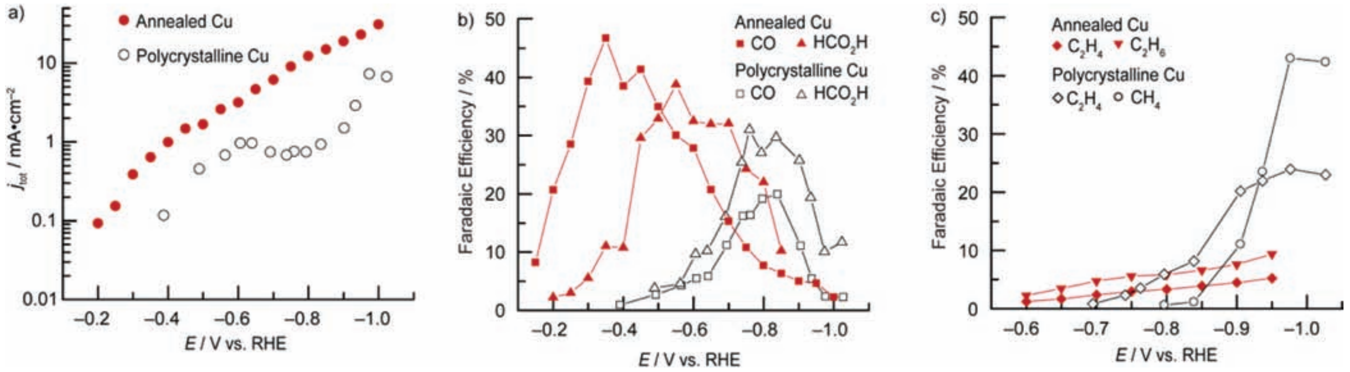

Figure 3. Comparison of the electrocatalytic activities of polycrystalline Cu and Cu annealed at 500 °C for 12 h. (a) Total current density vs potential. (b) Faradaic efficiencies for CO and HCO_2H vs potential. (c) Faradaic efficiencies for CH_4, C_2H_4 and C_2H_6 vs potential. Data for polycrystalline Cu is literature data (ref 14) obtained in 0.1 M $KHCO_3/CO_2$.

XRD pattern. The characteristic Cu^{2+} satellite peaks in the XPS spectrum are consistent with the presence of a thin (<10 nm) CuO layer coating the Cu_2O. Following CO_2 reduction electrolysis, SEM indicated that the rod morphology was intact, but smaller particles (∼20 nm) were embedded within the rods (Figure 2 and Figure S3). Only Cu^0 peaks were observed in the XRD pattern. The Cu 2p XPS spectrum indicated the presence of Cu^0 or Cu^{1+},[24] but the peaks associated with Cu^{2+} in the spectra prior to electrolysis were absent. Together, these results indicate the complete reduction of the Cu_2O layer, although we cannot rule out the presence of a thin, metastable Cu_2O layer or other surface-bound Cu^{1+} species during electrocatalysis.

The electrochemically active surface area of a reduced electrode that had been annealed at 500 °C for 12 h was determined by measuring the double layer capacitance in 0.1 M $HClO_4$ after CO_2 reduction electrolysis (Figure S5).[25] The capacitance was 13.9 mF/cm^2, which is 480× larger than the capacitance of 29 μF/cm^2 measured for a polycrystalline Cu electrode. This roughness factor is considerably larger than the difference in j_{tot} between the two electrodes (∼30×) (Figure 1), consistent with the difference in FEs between the two electrodes.

The presence of 100−1000 nm rods observed in Figure 2 is not necessary for efficient CO_2 reduction. Electrodes annealed at temperatures ≥500 °C for variable amounts of time exhibited very different morphological features on this length scale, but nonetheless comparable FEs for CO_2 reduction at −0.5 V (Figure S2). These results suggest that the CO_2 reduction efficiency of electrodes annealed at high temperatures is associated with a Cu particle surface or grain boundary structure that forms when suitably thick Cu_2O layers are electrochemically reduced.

To further characterize the effect of high temperature annealing on the CO_2 reduction activity of Cu, we measured the partial current densities for the reduction products at a variety of potentials between −0.2 and −1.0 V in $NaHCO_3/CO_2$ using an electrode that had been annealed at 500 °C for 12 h (hereafter referred to as "annealed Cu"). The total current densities and faradaic efficiencies for the major products are shown in Figure 3. Attempts to collect the corresponding data under identical conditions with polycrystalline Cu were unsuccessful due to the rapid degradation of catalytic activity. Instead, optimal data from previous studies with polycrystalline Cu at several potentials in 0.1 M $KHCO_3$ are included for comparison.[7]

The annealed Cu electrode exhibits a high efficiency for CO_2 reduction at remarkably low overpotentials. A peak faradaic efficiency of ∼45% for CO production is obtained at potentials ranging from −0.3 to −0.5 V, corresponding to 0.19−0.39 V of overpotential for this product (Figure 3b). By comparison, essentially no CO_2 reduction to CO is observed for polycrystalline Cu in this potential range; the maximum efficiency for CO with polycrystalline Cu is 20%, which requires −0.8 V (η = 0.69 V). Similarly, annealed Cu attains a peak faradaic efficiency for HCO_2H production of 33% at potentials ranging from −0.45 to −0.65 V (η = 0.25−0.45 V), whereas polycrystalline Cu requires −0.7 to −0.9 V (η = 0.5−0.7 V) to attain a comparable faradaic efficiency (Figure 3b).

At relatively negative potentials (<−0.6 V), annealed Cu catalyzes the reduction of CO_2 to ethylene and ethane (Figure 3c). In contrast, polycrystalline Cu produces only ethylene and methane at high overpotential. Previous work on Cu single crystals has shown that the ratio of ethylene to methane can be boosted by introducing (111) steps in the (100) basal plane.[26] However, methane was never fully suppressed and no ethane was observed in these studies.[27] These results indicate that the surface structures of the Cu particles produced by Cu_2O reduction are distinct from the structures of the high index faces of Cu. We also note that no methanol was detected among the reduction products for annealed Cu at any potential examined here, in contrast to what has been reported for CO_2 reduction catalysis with Cu electrodes annealed at lower temperatures.[22,23]

The faradaic efficiencies for the hydrocarbon products on annealed Cu are low and H_2 is the major product at high overpotentials. This difference relative to the lower overpotential regime most likely reflects the mass transport limitations at the high current densities observed (>10 mA/cm^2) rather than the intrinsic selectivity of the electrode. Improvements in mass transport by using a flow cell[28] or gas diffusion electrode[29] are expected to enable substantially higher CO_2 reduction current densities without large overpotential increases.

To obtain insight into the mechanistic pathway(s) for CO_2 reduction with annealed Cu, a plot of overpotential vs the log of the partial current density for CO production (a Tafel plot) was extracted from the data described above. The data are shown in Figure 4 along with Tafel data for polycrystalline Cu extracted from previous reports.[7] The plot for annealed Cu is linear over the range of overpotentials from 0.05 to 0.3 V with a slope of 116 mV/decade. This slope is consistent with a rate-

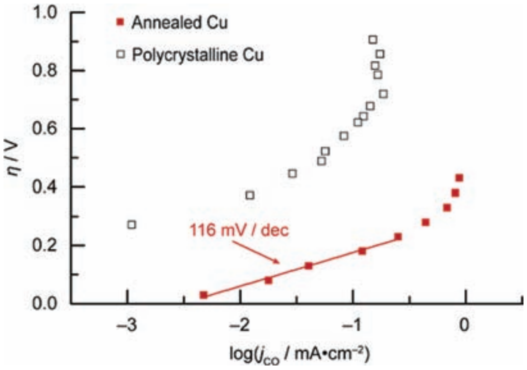

Figure 4. CO partial current density Tafel plots for polycrystalline Cu and for Cu annealed at 500 °C for 12 h. Data for polycrystalline Cu is literature data (ref 14) obtained in 0.1 M $KHCO_3/CO_2$. Data for annealed Cu were collected in 0.5 M $NaHCO_3/CO_2$.

determining initial electron transfer to CO_2 to form a surface-adsorbed $CO_2^{\bullet -}$ intermediate, a mechanism that is commonly invoked for metal electrodes.[9] A similar slope is evident in the plot for polycrystalline Cu. The dramatic difference in FE between the two electrodes suggests that the Cu surfaces formed by reducing thick Cu_2O layers enable formation of the $CO_2^{\bullet -}$ intermediate while suppressing H_2O reduction.

In summary, our results show that Cu particles prepared by reducing μm-thick Cu_2O films catalyze the reduction of CO_2 to CO and HCO_2H with high faradaic efficiencies at exceptionally low overpotentials and produce C2 hydrocarbons to the exclusion of CH_4 at high overpotentials. Electrodes with these characteristics can readily be prepared with high surface areas, enabling >1 mA/cm^2 geometric current densities for CO_2 reduction at <0.4 V overpotential and measurable CO_2 reduction current densities at <0.1 V overpotential, levels of activity that were previously inaccessible with metal electrodes under comparable conditions. Furthermore, CO_2 reduction with these electrodes is resistant to deactivation for at least several hours, a marked improvement over the rapid deactivation of polycrystalline Cu under identical conditions. We anticipate that elucidation of the surface structures of the Cu particles formed by reducing thick Cu_2O layers will provide crucial insights into the structural requirements for preferential CO_2 reduction and the formation of C2 products. In addition, this synthetic approach may prove useful for preparing additional electrocatalysts for CO_2 reduction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

mkanan@stanford.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Stanford University and the Precourt Institute for Energy for support of this work. C.W.L. gratefully acknowledges an NSF Predoctoral Fellowship.

■ REFERENCES

(1) Olah, G. A.; Prakash, G. K. S.; Goeppert, A. *J. Am. Chem. Soc.* **2011**, *133*, 12881.

(2) Cook, T. R.; Dogutan, D. K.; Reece, S. Y.; Surendranath, Y.; Teets, T. S.; Nocera, D. G. *Chem. Rev.* **2010**, *110*, 6474.

(3) Centi, G.; Perathoner, S. *Catal. Today* **2009**, *148*, 191.

(4) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.

(5) Bell, A. T.; Gates, B. C.; Ray, D., U.S. Department of Energy. Basic Research Needs: Catalysis for Energy (PNNL-17214). Report from a workshop held August 6−8, 2007, Bethesda, MD, http://www.sc.doe.gov/bes/reports/ list.html.

(6) Hori, Y.; Kikuchi, K.; Suzuki, S. *Chem. Lett.* **1985**, 1695.

(7) Hori, Y. In *Modern Aspects of Electrochemistry*; Vayenas, C. G., White, R. E., Gamboa-Aldeco, M. E., Eds.; Springer: New York, 2008; Vol. *42*, p 89.

(8) Chen, Y.; Kanan, M. W. *J. Am. Chem. Soc.* **2012**, *134*, 1986.

(9) Gattrell, M.; Gupta, N.; Co, A. *J. Electroanal. Chem.* **2006**, *594*, 1.

(10) Dewulf, D. W.; Jin, T.; Bard, A. J. *J. Electrochem. Soc.* **1989**, *136*, 1686.

(11) Schouten, K. J. P.; Kwon, Y.; van der Ham, C. J. M.; Qin, Z.; Koper, M. T. M. *Chem. Sci.* **2011**, *2*, 1902.

(12) Peterson, A. A.; Abild-Pedersen, F.; Studt, F.; Rossmeisl, J.; Nørskov, J. K. *Energ. Environ. Sci.* **2010**, *3*, 1311.

(13) Durand, W. J.; Peterson, A. A.; Studt, F.; Abild-Pedersen, F.; Nørskov, J. K. *Surf. Sci.* **2011**, *605*, 1354.

(14) Hori, Y.; Murata, A.; Takahashi, R. *J. Chem. Soc., Farad. Trans. 1* **1989**, *85*, 2309.

(15) Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J. M. *Nature* **2000**, *407*, 496.

(16) Zhang, D. W.; Chen, C. H.; Zhang, J.; Ren, F. *J. Mater. Sci.* **2008**, *43*, 1492.

(17) Han, W. K.; Choi, J. W.; Hwang, G. H.; Hong, S. J.; Lee, J. S.; Kang, S. G. *Appl. Surf. Sci.* **2006**, *252*, 2832.

(18) Reyter, D.; Odziemkowski, M.; Belanger, D.; Roue, L. *J. Electrochem. Soc.* **2007**, *154*, K36.

(19) Augustynski, J.; Kedzierzawski, P.; Jermann, B. *Stud. Surf. Sci. Catal.* **1998**, *114*, 107.

(20) Yano, J.; Yamasaki, S. *J. Appl. Electrochem.* **2008**, *38*, 1721.

(21) Tang, W.; Peterson, A. A.; Varela, A. S.; Jovanov, Z. P.; Bech, L.; Durand, W. J.; Dahl, S.; Nørskov, J. K.; Chorkendorff, I. *Phys. Chem. Chem. Phys.* **2012**, *14*, 76.

(22) Frese, K. W. *J. Electrochem. Soc.* **1991**, *138*, 3338.

(23) Le, M.; Ren, M.; Zhang, Z.; Sprunger, P. T.; Kurtz, R. L.; Flake, J. C. *J. Electrochem. Soc.* **2011**, *158*, E45.

(24) Larson, P. E. *J Electron Spectrosc.* **1974**, *4*, 213.

(25) Waszczuk, P.; Zelenay, P.; Sobkowski, J. *Electrochim. Acta* **1995**, *40*, 1717.

(26) Hori, Y.; Takahashi, I.; Koga, O.; Hoshi, N. *J. Phys. Chem. B* **2002**, *106*, 15.

(27) The production of ethane has been reported in one previous study of an electrode described as a copper electrodeposit, but no further details about the catalyst were provided. See: Goncalves, M. R.; Gomes, A.; Condeco, J.; Fernandes, R.; Pardal, T.; Sequeira, C. A. C.; Branco, J. B. *Energy Convers. Manag.* **2010**, *51*, 30−32.

(28) Whipple, D. T.; Finke, E. C.; Kenis, P. J. A. *Electrochem. Solid St.* **2010**, *13*, D109.

(29) Hara, K.; Sonoyama, N.; Sakata, T. *Stud. Surf. Sci. Catal.* **1998**, *114*, 577.