Operando scanning tunneling microscopy first revealed that application of a CO$_2$-reduction potential to a Cu(pc) electrode in 0.1 M KOH resulted in the reconstruction of the selvedge to an x-layer stack of well-ordered Cu(100) terraces, Cu(pc)-s([Cu(100)]. Subsequent Cu-→Cu$_2$O oxidation-reduction cycles between −0.90 V and 0.10 V SHE converted the reconstructed region to a stepped Cu$_3$O-[3(100) × (111)], or Cu(511), surface. Differential electrochemical mass spectrometry showed that reduction of CO produced only CH$_3$CH$_2$OH at the lowest overpotential. Later application of STM and surface infrared spectroscopy uncovered a potential, above which no CO adsorption occurs. In this study, electrochemical quartz crystal nanobalance was combined with STM and DEMS as a precondition to the acquisition of CO coverages as continuous functions of concentration and potential; in heterogeneous catalysis, surface coverage are important since the reaction rate is functions of those quantities. Also equally critical is the knowledge of the packing arrangement at the onset of the reaction because, if "CO dimers" were indeed the precursors to C$_2$ products, reduction can only be initiated when the adlayer consists of closely packed CO; otherwise, dimerization will not transpire if the molecules were far apart. The results indicate that the catalysis lags the adsorption, and starts only when CO adsorption is saturated.

Operando scanning tunneling microscopy first revealed that application of a CO$_2$-reduction potential to a Cu(pc) electrode in 0.1 M KOH resulted in the reconstruction of the selvedge to an x-layer stack of well-ordered Cu(100) terraces, Cu(pc)-s([Cu(100)]. Subsequent Cu-→Cu$_2$O oxidation-reduction cycles between −0.90 V and 0.10 V SHE converted the reconstructed region to a stepped Cu$_3$O-[3(100) × (111)], or Cu(511), surface. Differential electrochemical mass spectrometry showed that reduction of CO produced only CH$_3$CH$_2$OH at the lowest overpotential. Later application of STM and surface infrared spectroscopy uncovered a potential, above which no CO adsorption occurs. In this study, electrochemical quartz crystal nanobalance was combined with STM and DEMS to enable side-by-side, side-to-end, or end-to-end dimerization. From the potential-induced surface reconstruction of a pre-oxidized, medium, provided the original work is properly cited. [DOI: 10.1149/2.0451815jes] © The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0451815jes] © The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0451815jes] © The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0451815jes]
Preparation of Cu(511) for DEMS.—Differential electrochemical mass spectrometry has been described elsewhere, and only aspects related to the preparation of the Cu(511), surface are outlined here. A 99.99%–pure polycrystalline Cu disk (Goodfellow, Corapolis, PA), 1.0 cm in diameter and 0.15 mm in thickness, was metallographically polished and electropolished for 10 s in 85% phosphoric acid solution (Sigma-Aldrich, St. Louis, MO) at 2.1 V against a 99.8%–pure graphite rod (Alfa Aesar, Ward Hill, MA). After a thorough rinse in Nanopure water, a potential of −0.9 V (vs. SHE) was applied to the Cu electrode in a N2-saturated 0.1 M KOH solution (Sigma-Aldrich) for 2 hours to convert the initially disordered polycrystalline surface to well-ordered Cu(100) single-crystal layers. This was followed by multiple monolayer-limited oxidation-reduction cycles (ORC) between 0.1 V and −0.9 V to induce surface reconstruction from Cu(pc)-(Cu(100)) to Cu(pc)-(Cu(511)). With a protective layer of 0.1 M KOH electrolyte, the Cu(511) electrode was then placed inside the DEMS cell pre-filled with a CO-bubble-saturated solution of 0.1 M KOH. The potential was held for 600 s each at preselected values of −1.07 V, −1.02 V, −0.97 V, −0.92 V, −0.77 V, and −0.67 V, as the ion current for m/z = 31 (ethanol) was monitored by an HPR-20 quadrupole mass spectrometer (Hidden Analytical, Warrington, England) equipped with a secondary electron multiplier detector set at a voltage of 950 V and an emission current of 300 μA. The ethanol MS signals at 600 s were plotted as a function of applied potential. The base peak of ethanol at m/z = 31 is shared by methanol but the correct peak assignment is ensured by the congruence of the ratio of the analytical signals at m/z plotted as a function of applied potential. The base peak of ethanol for m/z = 31 was shared by methanol but the correct peak assignment is ensured by the congruence of the ratio of the analytical signals at m/z plotted as a function of applied potential.

EQCN.—A quartz crystal nanobalance (QCN) was used to measure, under electrochemical reaction conditions, the changes in the frequency, Δf, of a quartz resonator when variations in mass (Δm) transpire at the surface. The EQCN data were acquired with a Seiko-EG&G QCA922 analyzer (Bio-logic, Knoxville, TN) interfaced to a Bio-Logic SP-200 potentiostat. The EQCN cell, reminiscent of classic H-cells, was constructed from Pyrex glass, Figure 1, based on a design by the Jerkiewicz group at Queen’s University. The bottom part of the main compartment held the resonator, doubled as the working electrode, in a horizontal configuration. A gold wire served as the auxiliary electrode. The reference electrode, located in the outer compartment, was a reversible hydrogen electrode (RHE) brought in close proximity to the working electrode by a Luggin capillary. Potentiostatic electrochemical impedance was performed at 100 kHz to determine the uncompensated solution resistance, Ruc, of the resonator-electrode was an AT-cut quartz crystal with 9-MHz resonance frequency, coated on both sides with ca. 300 nm-thick Cu; it was mounted onto a PTFE holder so that only one side would be in contact with the solution. The EQCN cell was set on a platform suspended by bungee cords inside a custom-built Faraday enclosure that insulated against electromagnetic fields. The entire cage was itself mounted on a solid-rubber stage for vibration isolation. The pre-treatment of the Cu film electrode prior to the EQCN measurements were as described above, but potentiostatic (e.g., CO preadsorption at −1.06 V) and cyclic voltammetric (CV) operations (e.g., between 0.1 V to −0.9 V) were such that the Cu(pc) surface would have been reconstructed to Cu(511), as later confirmed by an ethanol-product-elektronically compensated, akin to the corrections made to the DEMS spectra. In this work, however, the EQCN data were directly converted to θCO, by calibration with PMIRS data on Cu(pc)-(Cu(511)). For example, θCO at −0.9 V and at E ≥ −0.8 V were found to be 0.50 and 0.0, respectively; consequently, the EQCN coverage data at these potentials were made equivalent to the STM-PMIRS values. In this context, it will be mentioned that non-PM IRS data for CO chemisorbed on pristine Pt(100) and Pt(511) single crystals showed essentially identical coverages.

Results and Discussion

The formation of surface-reconstructed interfacial layers of Cu(100) and Cu(511) from polycrystalline Cu(pc) anodically oxidized at 0.1 V in CO-free 0.1 M KOH is illustrated in the step-scan operando STM images in Figure 2. Inset A shows a 200 nm × 200 nm ECSTM image of the Cu(pc) electrode after a 30-s reduction at −0.9 V; the existence of a disordered, still oxidized, surface is evident. Inset B shows the same surface after 60 m at −0.9 V; at

Figure 1. Picture of the electrochemical quartz-crystal nanobalance. One of the CO ports is for direct sparging of CO into the solution, the other is for CO circulation in the head space. CE: Pt counter electrode. RE: SHE reference electrode. WE: Cu-film electrode on quartz crystal resonator.
this stage, surface reconstruction has already resulted in well-ordered wide terraces of (100) orientation. When the latter surface is subjected to multiple ORC between 0.1 V and −0.9 V, further reconstruction ensues to yield a stepped surface, Cu(S)-(3(100) × (111)), or Cu(511). It will be noted that, at potentials more positive than −0.7 V, disordered surface Cu$_2$O starts to form that prevents the observation of atomic-level images; but it is remarkable that, when the potential is returned to −0.9 V, the well-ordered, oxide-free Cu(100) or Cu(511) structures are immediately restored. It is not known accurately at this time how many of the reconstructed monocrystalline layers are formed.

Figure 3 overlays a triad of DEMS plots from various Cu surfaces during the electrocatalytic reduction of CO in 0.1 M KOH. Evidently, only the electrochemically generated Cu(511), in red trace, produces ethanol at −1.06 V (SHE). CH$_3$CH$_2$OH and other reduced products such as ethylene, C$_2$H$_4$, and methane, CH$_4$, are produced on Cu surfaces at onset potentials ca. 150 mV more negative, than the potential applied in the present experiment. The overpotential reported here for CH$_3$CH$_2$OH production on Cu(511) is by far the lowest among the other hydrocarbon and oxygenated products formed on Cu(pc).

Unlike on pristine Cu(100) surfaces, distinct atomic-level STM images could not be obtained on Cu(511) when CO is adsorbed. But that cannot be taken to signify the absence of adsorbed CO since, as described in the previous paragraph, both the DEMS and PIRMS data, and, in the same vein, the IR spectra of CO on Pt(100) and Pt(511), indicate otherwise. The possibilities exist that: (i) because of the low-overpotential activity at Cu(511), the initial reduction, regardless of how minute, already renders the images indistinct, an effect analogous to what is observed even before the actual onset of bulk Cu$_2$O formation, or, (ii) the limited (3-atom) width of the Cu(100) terraces, hemmed in by the likely more reactive Cu(111) steps, mitigates the formation of stable well-ordered sub-nanometer structures.

The current-potential curve for Cu(511) in 0.1 M KOH is shown in Figure 4 along with the total-frequency-variation transients $\Delta f_r$ vs. E when CO is preadsorbed on the surface (at −1.06 V), and when only N$_2$ is present in solution; it is clear from the CV that, at E > −0.4 V, the Cu$\leftrightarrow$Cu$_2$O reaction becomes predominant. It should first be noted that, while the frequency-Transient plot for N$_2$ shows no hysteresis, that for CO can only be started from −1.06 V and initially traversed in the positive direction. Given the Sauerbrey equation, $\Delta f = -Cf \Delta m$, where $\Delta m$ is the mass change, $A$ the piezoelectric area, and $C_f$ the frequency-to-mass conversion factor, it can be inferred that the decrease in $\Delta f$ (i.e., the increase in $\Delta m$) at E > −0.7 V for N$_2$ is due to the formation of Cu$_2$O; for CO, the weight increase is the net change given the desorption of CO and the creation of Cu$_2$O. The irreversibility of the CO frequency-Transient plot is a result of the fact that the desorbed CO becomes unrecoverable: When a nmol of CO, the quantity initially adsorbed on 1 cm$^2$ of Cu, is released to 50 mL of solution, the volume of the EQCN cell, a concentration of 20 nM is produced, too minute to rekindle adsorption.

Figure 2. Combined cyclic voltammetry and scanning tunneling microscopy that illustrate the preparation of the stepped Cu(511) surface via the potentiostatic surface reconstruction of Cu(pc) at E < −0.9 V in 0.1 M KOH, followed by oxidation-reduction cycles between −0.9 V and 0.1 V. The geometric area of the single crystal was 1.0 cm$^2$. The potential sweep rate was 50 mV s$^{-1}$. Experimental parameters: Bias voltage = −300 mV. Tunneling current: low-resolution images: 2 nA; high-resolution images: 5 nA.

Figure 3. Differential electrochemical mass spectrometry of a 0.1 M KOH solution saturated with CO at −1.06 V SHE. Black: Reconstructed Cu(pc)-[Cu(100)] without prior oxidation-reduction cycles. Blue: Pristine Cu(100) bulk single-crystal after twenty oxidation-reduction cycles (ORC). Red: Reconstructed Cu(pc)-[Cu(511)] after multiple ORC from −0.9 V to 0.1 V. The lines do not imply any theoretical fit but serve as visual guides. The DEMS signals shown were only for m/z = 31, the base peak for CH$_3$CH$_2$OH. The fragment ratio for m/z = 31 and m/z = 45 corresponded to that of a CH$_3$CH$_2$OH standard, but the ion-current plots for m/z = 45 are not reported here.

Figure 4. Cyclic voltammograms (CV) and frequency variation $\Delta f_r$ (FV) transients of Cu-coated resonator in 0.1 M KOH, with (red trace) and without (blue trace) CO preadsorption at −1.06 V, followed by bubbling the electrolyte and purging the headspace with N$_2$ under the same potential-hold. The black arrows indicate the initial direction of the scan. The difference between the $\Delta f_r$ transients in the upper and lower red trace was used to extract the CO coverage at a given potential from Equation 1 as described in the text. Potential scan rate: 20 mV s$^{-1}$. 

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are obvious but need to be emphasized: (i) the adsorption of CO
with the ethanol ion-current DEMS spectrum. Two major differences
between the results of this study and those of previous investigations
are intermediates in and precursors to the formation of ethanol, a
C2 product. In such an event, it would not be illogical to invoke the
necessity of saturation coverage since that is the only situation
in which the surface-coordinated, vertically oriented CO molecules
would become much more susceptible toward adsorption; consequently, any
surface site vacated by an outgoing ethanol would be immediately
occupied by CO. As a result, θCO remains constant at 0.5.

It is not possible to extract correct kinetic parameters from the
limited data of the present study. Nevertheless, it may be qualitatively,
but confidently, conjectured from the results that, in the mechanistic
progression of (i) reactant adsorption, (ii) multi-step surface reactions,
and (iii) product desorption, the rate-determining step lies within the
second stage such as, perhaps, the postulated formation of a “CO dimer”.

Summary

Operando electrochemical quartz-crystal nanobalance was com-
combined with scanning tunneling microscopy and differential elec-
rochemical mass spectrometry to investigate the potential-dependencies
of the adsorption of CO and its low-overpotential selective reduction
to CH3CH2OH at a stepped Cu(511) surface; the latter was prepared
from the potentiostatic surface reconstruction of Cu(pc) at E < −0.9 V
in 0.1 M KOH, followed by monolayer-limited oxidation-reduction
cycles between −0.9 V and 0.1 V. The results indicate that the elec-
trocatalytic reduction lags the adsorption process and, in fact, does
not start until maximum CO adsorption is attained. The latter may indirectly suggest that the formation of “CO dimers”
is involved in the production of ethanol, since such dimers would most likely not be
formed if the CO coverage (θCO) in the adsorbed layer is much lower
than 0.5; that is, the distance between the CO admolecules would be
too large to effect dimerization.

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