

# Surface Hydride Formation on Cu(111) and Its Decomposition to Form H<sub>2</sub> in Acid Electrolytes

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**ABSTRACT:** Mass spectrometry and Raman vibrational spectroscopy were used to follow competitive dynamics between adsorption and desorption of H and anions during potential cycling of three low-index Cu surfaces in acid electrolytes. Unique to Cu(111) is a redox wave for surface hydride formation coincident with anion desorption, while the reverse reaction of hydride decomposition with anion adsorption yields H<sub>2</sub> by recombination rather than oxidation to H<sub>3</sub>O<sup>+</sup>. Charge imbalance between the reactions accounts for the asymmetric voltammetry in SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and Cl<sup>-</sup> electrolytes with pH 0.68–4.5. Two-dimensional hydride formation is evidenced by the reduction wave prior to H<sub>2</sub> evolution and vibrational bands between 995 and 1130 cm<sup>-1</sup>. In contrast to Cu(111), no distinct voltammetric signature of surface hydride formation is observed on Cu(110) and Cu(100). The Cu(111) hydride surface phase may serve to catalyze hydrofunctionalization reactions such as CO<sub>2</sub> reduction to CH<sub>4</sub> and should be broadly useful in electro-organic synthesis.



he interaction of H with Cu surfaces has been studied as a model system for chemisorption and catalysis.<sup>1–13</sup> Important proton-coupled electron-transfer reactions are known to proceed on Cu surfaces, with great interest focused on its ability to produce various multicarbon hydrocarbon and oxygenate products during electrocatalytic reduction of  $CO_2$ .<sup>11,14-16</sup> Despite numerous investigations, the origin of its unique catalytic performance remains unclear. For example, surprisingly high faradaic efficiency for CO<sub>2</sub> products on Cu electrodes is reported in acid electrolytes even though the high hydronium concentration might be expected to favor hydrogen evolution.<sup>17</sup> Indeed, the role of surface and subsurface H in hydrogenation reactions remains a subject of fundamental interest in electrodeposition and electro-organic synthesis.<sup>18</sup> Accordingly, an understanding of the complex reactions involved in hydrogenation of CO<sub>2</sub> and other molecules requires measurements of the potential-dependent interactions between hydrogen and Cu.

Herein, mass spectrometry and Raman spectroscopy are used to examine the competitive adsorption and desorption dynamics between H and anions on three low-index Cu surfaces. Evidence is presented of molecular hydrogen produced at positive potentials, i.e., >0 V vs RHE, on a Cu(111) electrode in acid electrolytes. The hydrogen originates from reductive proton adsorption and absorption to form a near-surface hydride phase, which subsequently decomposes to Cu<sup>0</sup> and molecular H<sub>2</sub> when polarized to more positive potentials. This phenomenon is unique to Cu(111) and accounts for the unexplained voltammetric charge asymmetry associated with anion adsorption.

A recent advance in electrochemical mass spectrometry (EC-MS) provides submonolayer sensitivity for gas-generating

reactions with time resolution on the order of 1 s.<sup>25,26</sup> The method was recently used to study H<sub>2</sub> evolution from polycrystalline Cu in alkaline media.<sup>27</sup> Surprisingly, some H<sub>2</sub> was generated at potentials positive of the reversible hydrogen electrode. The unanticipated phenomenon was attributed to a hydroxide displacement reaction where adsorbed hydrogen atoms combine and desorb as molecular H<sub>2</sub> as opposed to oxidative desorption as H<sub>3</sub>O<sup>+.27</sup> In the present work, EC-MS was applied to examine competitive adsorption and desorption of H and various anions on the three primary low-index surfaces of Cu. In parallel with the mass spectrometry study, vibrational spectroscopy using shell isolated nanoparticle enhanced Raman spectroscopy (SHINERS) was used to examine Cu(111) under near identical conditions, revealing previously unresolved features that are central to understanding the role of H in Cu surface chemistry.<sup>28,29</sup>

Voltammetry for three single-crystal Cu surfaces in 0.1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> (Figure 1a-c) reveals a monotonic increase in the hydrogen evolution (HER) current at negative potentials and onset of Cu dissolution at the positive limit. For Cu(111) a unique reduction wave at -0.35 V with a corresponding oxidation wave at +0.08 V are evident with significant charge asymmetry between them. In contrast, the other Cu surfaces reveal a comparatively flat pseudocapacitive response prior to

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Figure 1. Voltammetry (top row) and mass spectrometry data (bottom row) for Cu single-crystal electrodes in 0.1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub>. The third voltammetric cycle is shown in the top row. The MS signals are background-subtracted and calibrated for H<sub>2</sub> production (see Figure S1).

the hydrogen evolution reaction where Cu(100) is the most active. Simultaneously, the H<sub>2</sub> produced is monitored by the intensity of its 2 atomic mass unit (amu) mass spectrum (Figure 1d-f). The  $H_2$  signal increases with the reduction current at negative potentials, with detection lagging the voltammetric current by ~3.5 s because of diffusional transport across the nominal 100  $\mu$ m thin-layer cell. For Cu(110) and Cu(100), the rise and fall of the mass spectrometry signal follows the HER response. In contrast, for Cu(111) the decreasing HER on the positive voltammetric scan is followed by an additional  $H_2$  mass spectrometry peak (Figure 1d) that corresponds to potentials at or above 0 V<sub>RHE</sub>, denoted by the colorized time stamps (Figure 1d-f). Closer examination of the EC-MS H<sub>2</sub> signal against potential demonstrates that reductive H<sub>2</sub> generation (Figure 2) begins only after the reduction wave, indicating the majority of charge up to this juncture goes to adsorption and absorption of H. Integration of the second 2 amu peak (i.e., "anodic"  $H_2$ ) and averaging across three cycles indicate that ~0.15 nmol of  $H_2$  (0.77 nmol of  $H_2/$  $cm^2$ ) was produced, equating to removal of 1.54 nmol of H/  $cm^2$  or 0.52 monolayer H from the Cu(111) surface. Examination of polycrystalline Cu similarly revealed a second, albeit smaller, 2 amu peak in EC-MS, ascribed to H recombination on a subset of (111) oriented grains (Figure S2).

This phenomenon was not specific to sulfuric acid and was observed for Cu(111) in SO<sub>4</sub><sup>2</sup>, ClO<sub>4</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and Cl<sup>-</sup> electrolytes with pH 0.68–4.5. As in Figure 1, the cathodic H charging wave always precedes nonfaradaic H<sub>2</sub> production on the positive-going sweep. Stronger anion adsorption stimulates H recombination with the "anodic" H<sub>2</sub> peak potential, referenced to SHE, increasing from Cl<sup>-</sup> to SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> (Figures S3 and S4). "Anodic" H<sub>2</sub> production was also evident in unbuffered SO<sub>4</sub><sup>2-</sup> electrolytes with a pH of 4.5 (Figure S5) where oxide and hydroxide adsorption must be considered.

To better understand the voltammetric features and "anodic" hydrogen production, Cu(111) was examined by Raman spectroscopy. Spectra for Cu(111) in 0.1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> (Figure 3a) correspond to the initial set of potential step experiments, while the second set (Figure 3b) was



Figure 2. First two voltammetric cycles for Cu(111) in 0.1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> (top) while monitoring the 2 amu mass spectrum (bottom).

collected in the same manner but after 50 continuous voltammetric cycles. The potential was stepped in the negative direction from 0.14 V in 25 mV increments to -0.36 V and then reversed. At the positive limit the Raman peaks at ~950 cm<sup>-1</sup> and ~1220 cm<sup>-1</sup> are associated with adsorbed SO<sub>4</sub><sup>2-</sup>, while at more negative potentials these bands attenuate while Cu–H stretches and/or hydride phonon modes appear between 990 and 1130 cm<sup>-1</sup> (see Tables S1 and S2).

Coincident with the disappearance of the  $SO_4$  modes, the broadband Cu–H modes develop between -0.125 and -0.260 V punctuated by maxima at 1030 and 1130 cm<sup>-1</sup> with a neighboring single band at 990 cm<sup>-1</sup>. The spectral features overlap singular modes observed in vacuum studies of Cu(111)-H as well as the broadband phonon states of chemically prepared, stoichiometric and nonstoichiometric,



Figure 3. SHINERS Raman spectra (633 nm source) for Cu(111) in 0.1 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> at different potentials (a) after an initial excursion and (b) following 50 cycles. (c) Peak intensities for the sulfate and H-modes.



Figure 4. (a) First two voltammetry cycles for Cu(111) in 0.1 mol  $L^{-1}$  HClO<sub>4</sub> while monitoring (b) the 2 amu mass spectrum. (c) Raman spectra for the specified potentials.

metastable wurtzite hydride (Table S1).<sup>2-4,6,30,31</sup> DFT calculations indicate H adsorption in 3-fold hollow sites with absorption into subsurface sites likely at higher coverages.<sup>1,5</sup> Most relevant of all, ECSTM reveals  $(4 \times 4)$ -xH reconstruction of Cu(111) under conditions almost identical to the present study.<sup>12</sup> The charge associated with the reduction wave exceeds that of a 3-fold hollow H-saturated

monolayer (1.2 ML versus 0.67  $ML_{sat'd}$ ), consistent with the presence of subsurface H giving rise to the buckled nature of the (4 × 4)-xH hydride surface.

The potential dependence of the transition from the  $SO_4^{2-}$  adlayer to the Cu–H surface phase is tracked by the integrated intensity for selected vibrational bands (Figure 3c). The potential-dependent shift and decrease in the 1220 cm<sup>-1</sup>



Figure 5.  $H_2$  generation as a function of the negative potential vertex. Voltammetry (top row) and 2 amu mass spectrometry (bottom row) for Cu (111) in 0.1 mol L<sup>-1</sup> HClO<sub>4</sub>.

sulfate band approaches background levels below -0.16 V but returns, albeit more slowly, when the potential was stepped positive of -0.16 V, consistent with its desorption and adsorption, respectively.<sup>32</sup> The sharp decrease in  $SO_4^{2-}$  modes below -0.125 V is accompanied by the increase in the 1060 cm<sup>-1</sup> Cu-H mode. Development of the 1120 cm<sup>-1</sup> band trails the increase of the 1060 cm<sup>-1</sup> peak by  $\sim$ 50 mV. This suggests the 1060 cm<sup>-1</sup> band is associated with H adsorption while the 1120 cm<sup>-1</sup> band is related to subsurface H, similar to an early vacuum study where the higher wavenumber mode developed only at higher coverages.<sup>2</sup> The lag may also be related to the ECSTM observations that the  $(4 \times 4)$ -xH reconstruction forms only following H saturation of the surface.<sup>12</sup> Analogous Raman experiments with a deuterated electrolyte provide further support for the hydride assignment (Figure S6). Negative of -0.250 V, the 1060 and 1120 cm<sup>-1</sup> peaks continue increasing simultaneously, reaching a maximum on the return path at -0.2 V. As the potential increases further, the Cu-H modes sharply decrease above -0.125 V with  $SO_4^{2-}$ adsorption. The 1060 cm<sup>-1</sup> peak merges with the spectral background while the 1120 cm<sup>-1</sup> peak settles to a plateau that overlaps with the potential regime where "anodic" H<sub>2</sub> evolves from the surface. The differing time scale of the EC-MS and Raman experiments makes analysis of the remnant 1120 cm<sup>-1</sup> peak challenging. It could be the result of more extended polarization at negative potentials or may involve overlap with bisulfate adsorption (see Table S1) or perhaps reaction and buildup of stray organic material on the hydride surface.

To circumvent the ambiguity between possible overlap of  $SO_4^{2-}$ ,  $HSO_4^{-}$ , and H vibrational bands on Cu(111), experiments were performed in 0.1 mol L<sup>-1</sup> HClO<sub>4</sub>, where significant anion chemisorption is not expected. Voltammetry (Figure 4) reveals the H deposition wave has two components marked by the inflection near -0.275 V and peak at -0.310 V followed by the much smaller oxidation peak near 0.15 V on the return sweep. The associated charge increments for the reduction and oxidation waves are  $-361 \,\mu\text{C/cm}^2$  and  $+83 \,\mu\text{C/cm}^2$ , the difference ( $-278 \,\mu\text{C/cm}^2$ ) being close to 1 monolayer equivalent of H ( $284 \,\mu\text{C/cm}^2$ ). Integration of the

second H<sub>2</sub> mass spectrometry peak yields 1.38 nmol/cm<sup>2</sup> of  $H_{2}$ , corresponding to 2.76 nmol/cm<sup>2</sup> or 0.94 monolayer of H. In the absence of strong anion adsorption, the deposited H is largely removed before the second charging cycle begins. At the positive potential limit, a single Raman peak is evident at 930 cm<sup>-1</sup> for the dominant symmetric  $v_s(ClO_4^{-})$  stretch of the solvated ion. Stepping negative of -0.160 V, the Cu-H modes arise with at least three distinguishable features with the broadband envelope and local maxima being the same as in sulfuric acid, while the isolated peak at 990  $cm^{-1}$  is substantially larger. When the potential is stepped back to potentials positive of -0.160 V, the Cu-H modes decrease slowly and eventually merge with the background at the upper potential limit (Figure S7). The slow kinetics of removal are consistent with EC-MS voltammetry that indicate CuH decomposition is still underway at the positive potential limit.

Further evidence that the reduction wave on Cu(111) leads to formation of a 2D hydride layer is garnered by adjusting the negative voltammetric limit while monitoring its impact on "anodic" H<sub>2</sub> evolution. As the vertex is decreased in 50 mV steps from -0.2 to -0.4 V (Figures 5 and S8), the second "anodic" H<sub>2</sub> mass spectrometry peak is correlated to the depth of the reduction wave explored and is distinct from conventional H<sub>2</sub> evolution generated at potentials negative of -0.350 V.

Summarizing, EC-MS and voltammetry reveal adsorption of a monolayer equivalent of H per Cu atom on Cu(111) prior to the onset of the hydrogen evolution reaction. The hydride surface phase exhibits broadband vibrational modes between 1030 and 1120 cm<sup>-1</sup> along with a singular band at 990 cm<sup>-1</sup>. The surface phase subsequently decomposes at positive potentials to form H<sub>2</sub> by Tafel recombination. The charge imbalance between these two reactions accounts for the asymmetric voltammetry observed for Cu(111) in a wide range of acid electrolytes. Exploration in different electrolytes reveals that anion adsorption stimulates H recombination with stronger anion-metal interactions leading to decomposition of the hydride phase and "anodic" H<sub>2</sub> generation at more negative potentials. The observation of Cu-hydride on Cu(111) does not preclude the existence of similar hydride phases on other Cu surfaces. Rather, the hydride vibrational signature combined with detection of nonfaradaic hydrogen recombination, unique to Cu(111) under these conditions, enabled clear resolution of the Cu-hydride formation and decomposition occurring at potentials relevant for many hydrogenation reactions.

The implication of surface and subsurface H in catalysis of proton-coupled electron-transfer reactions on Cu has received sparse attention. Vacuum studies of CO adsorption on Cu(111) indicate subsurface H suppresses CO adsorption, an important intermediate in CO<sub>2</sub> reduction.<sup>6</sup> The hydride surface detailed herein likely accounts for the enhanced hydrofunctionalization of Cu(111) in the reduction of CO<sub>2</sub> to CH<sub>4</sub> compared to the other low-index surfaces.<sup>14,15,33</sup> More generally, the Cu(111) surface hydride phase is expected to be useful in electro-organic synthesis in a manner analogous to the established utility of ligand modified Cu–H in homogeneous catalysis.<sup>19,20</sup>

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c03131.

Experimental methods; preparation of Cu(*hkl*) crystals; EC-MS measurements and calibration (Figure S1); operando SHINERS measurements; EC-MS voltammetric data for polycrystalline Cu in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (Figure S2) and Cu(111) in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 1 mmolL<sup>-1</sup> NaCl, 0.1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>, and 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> (Figures S3-S5); H vibrational modes on Cu(111) in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; literature reports of Cu(111)-H and CuH vibrational modes (Table S1); literature reports of relevant sulfuric and perchloric acid vibrational modes (Table S2); SHINERS for Cu(111) in 0.1 mol  $L^{-1}$   $D_2SO_4$  (Figure S6); integrated CuH broadband intensity (980-1180 cm<sup>-1</sup>) as a function of potential (Figure S7); EC-MS voltammetry in 0.1 mol  $L^{-1}$  HClO<sub>4</sub> as a function of the negative vertex potential (Figure S8); and references (PDF)

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#### **Author Contributions**

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#### Notes

Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

The authors declare no competing financial interest.

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