#### Supporting Information (SI)

# Grazing Incidence X-Ray Diffraction: Identifying the Dominant Facet in Copper Foams that Electrocatalyze the Reduction of Carbon Dioxide to Formate

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#### pH Measurements

In general, the pH (and pKa) of solutions decrease as temperature increases due to increased ionization. The buffering capacity of a bicarbonate/CO<sub>2</sub> solution, consisting of amphoteric bicarbonate (HCO<sub>3</sub><sup>-</sup>), dissolved CO<sub>2</sub>, carbonic acid (H<sub>2</sub>CO<sub>3</sub>), carbonate (CO<sub>3</sub><sup>2-</sup>), hydroxide (OH<sup>-</sup>), hydronium (H<sub>3</sub>O<sup>+</sup>), and H<sub>2</sub>O in equilibrium, reduces the temperature dependence of pH.<sup>1</sup> The increase in pH with temperature for the equilibrium HCO<sub>3</sub><sup>-</sup>(aq)  $\rightleftharpoons$  CO<sub>2</sub>(g) + OH<sup>-</sup>(aq) follows Le Châtelier's principle: as temperature increases, the concentration of CO<sub>2</sub> decreases, and the equilibrium shifts rightward. This concept is similar to the increase in bulk pH observed when KHCO<sub>3</sub> concentration is increased, which is caused by a rightward shift in equilibrium for HCO<sub>3</sub><sup>-</sup>(aq) + H<sub>2</sub>O(I)  $\rightleftharpoons$  H<sub>2</sub>CO<sub>3</sub>(aq) + OH<sup>-</sup>(aq).<sup>2</sup>

Temperature also affects the performance of pH meter electrodes. For example, the response of an ideal pH meter electrode is defined by the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln a_{H^{+}} \approx E^{\circ} + 1.98 \times 10^{-4} \cdot T \log [H^{+}]$$
(1)

where *E* is the potential between the sensing and internal reference electrodes, *E*° is the standard potential of the pH meter electrode, *R* is the ideal gas constant (i.e., 8.314 J mol<sup>-1</sup> K<sup>-1</sup>), *n* is the number of electrodes or ion valency (in this case, n = 1), *F* is the Faraday constant (i.e., 96,485 C mol<sup>-1</sup>), *T* is the solution temperature in degrees Kelvin, and  $a_{H_{+}}$  is the activity of a proton (H<sup>+</sup>) in solution. From the  $1.98 \times 10^{-4} \bullet T$  term in Eq 1, an ideal Nernstian slope of 59.2 mV is obtained at 25 °C. This slope decreases as temperature decreases because of increased ionization (*vide supra*), which in turn causes measured pH and true pH to diverge. This change in slope is accounted for when pH meters capable of automatic temperature compensation (ATC) are used.

#### **Unit Conversion for Activation Energy**

Molar activation energy in units of kJ mol<sup>-1</sup> was converted to molecular free energy in units of eV as follows:

$$\frac{x\,kJ}{mol} \times \frac{1000\,J}{1\,kJ} \times \frac{1\,mol}{6.02\,\times\,10^{23}\,e} \times \frac{1\,e}{1.602\,\times\,10^{-19}\,C} = y\,eV$$
(2)

$$1 V = \frac{1 J}{1 C} = \frac{1 eV}{e}$$
(3)

# **Calculation of Faradaic Efficiency, Voltage Efficiency, Energy Efficiency, and Production Rate** Current or faradaic efficiencies of each product produced were determined from the measured concentration of product divided by the concentration calculated from the number of coulombs passed during electrolysis. Sample Calculations for the Faradaic Efficiency (FE), Voltage Efficiency (VE), Energy Efficiency (EE), and Production Rate (PR) of Formate as a representative product of CO<sub>2</sub> reduction at copper foams are as follows:

Cathodic half-cell reaction:

(1) 
$$CO_2(g) + H_2O(I) + 2e \rightarrow HCOO^-(aq.) + OH^-(aq.)$$

$$E_{C}^{0}$$
 = - 0.63 V vs. SHE at pH 6.8

Anodic half-cell reaction:

(2) 
$$H_2O(I) \rightarrow 2H^+ + \frac{1}{2}O_2(g) + 2e^ E_A^0 = 0.831 \text{ V vs. SHE at pH 6.8}$$

Thermodynamic cell voltage for  $H_2O/H^+$ ,  $O_2 \parallel CO_2/HCOO^-$  system:

(3)  $E_{cell}^0 = E_A^0 - E_C^0 = 0.831 - (-0.63 \text{ V}) = 1.461 \text{ V}$ 

The formula to calculate current efficiency (4) and a sample calculation (5) are:

(4) 
$$CE = \frac{j_{Formate}}{j_{Total}} = \frac{q_{Formate}}{q_{Total}} = \frac{C_{Formate}V_{Solution}nF}{j_{Total}At}$$

$$CE = \frac{\frac{mol}{L} * L * \frac{mol e^{-}}{mol} * \frac{C}{mol e^{-}}}{\frac{C}{s * cm^{2}} * cm^{2} * s}$$
(5)

(6)  
$$CE = \frac{0.00271 \frac{mol}{L} * 0.008L * 2 \frac{mol e^{-}}{mol} * 96485 \frac{C}{mol e^{-}}}{0.004 \frac{C}{s * cm^{2}} * 1.0 cm^{2} * 3600 s}$$

(7) CE = 0.29 or 29%

The formula to calculate voltage efficiency (8) and a sample calculation (9) are:

$$VE = \frac{E_{Cell}^{0}}{E_{cell}}$$

(9) 
$$VE = \frac{1.461 V}{2.354 V} = 0.62 \text{ or } 62\%$$

The formula to calculate energy efficiency (10) and a sample calculation (11) are:

(10) EE = CE \* VE

(11) EE = 0.29 \* 0.62 = 0.18 or 18%

The formula to calculate the rate of production of formate (12) and a sample calculation (13) are:

(12) 
$$PR = \frac{CEj_{Formate}}{nF}$$

$$PR = \frac{0.29 * 0.004 \frac{C}{s * cm^2}}{2 \frac{mol \ e^-}{mol} * 96485 \frac{C}{mol \ e^-}} = 6.0113 * 10^{-9} \frac{mol}{s * cm^2} = 21.64 \frac{\mu mol}{cm^2 * hn}$$
(13)

#### **Preparation of XRD Samples**

To minimize oxidation of the Cu foam surface to  $Cu_2O^3$  or possibly CuO (Figure S1) and to demonstrate repeatability of the diffraction experiments, a fresh Cu foam sample was fabricated immediately prior to each XRD experiment. The surface was then protected by dipcoating in ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) – the concentration of O<sub>2</sub> is ca. 210,000 ppm in air, 196 ppm in CH<sub>3</sub>CH<sub>2</sub>OH, and 28 ppm in H<sub>2</sub>O.<sup>4</sup> While the concentration of O<sub>2</sub> is higher in CH<sub>3</sub>CH<sub>2</sub>OH than in H<sub>2</sub>O, Cu foams dip-coated in H<sub>2</sub>O consistently showed diffraction patterns corresponding to Cu<sub>2</sub>O (JCPDS 00-005-0667, Figure S1). Apparently CH<sub>3</sub>CH<sub>2</sub>OH is more effective than H<sub>2</sub>O at protecting Cu foams from adventitious oxidation, which may be due to the difference in wettability of Cu by these solvents (e.g., measured contact angles on planar Cu: H<sub>2</sub>O = 65.7(1)° vs. CH<sub>3</sub>CH<sub>2</sub>OH = <10°).



**Figure S1.** Example  $\theta$ -2 $\theta$  (i.e., Bragg-Brentano) XRD patterns of a Cu foam (a) dip-coated in H<sub>2</sub>O before the experiment in which oxidation of the surface to Cu<sub>2</sub>O (no CuO) was visible and (b) dip-coated in CH<sub>3</sub>CH<sub>2</sub>OH. The diffractograms are zoomed in for clarity. Red labels show the peak locations for Cu<sub>2</sub>O (JCPDS 00-005-0667).



**Figure S2.** (a) and (b)  $\theta$ -2 $\theta$  (i.e., Bragg-Brentano) XRD and (c) thru (f) GIXRD patterns for  $\theta$  = 8.0° to 1.0° of Cu foams electrodeposited onto a Cu substrate. Right ordinates are normalized to the intensity of the Cu(111) peak. See Figure 2 for GIXRD pattern for  $\theta$  = 0.5°.



**Figure S3.** (a) and (b)  $\theta$ -2 $\theta$  (i.e., Bragg-Brentano) XRD and (c) thru (f) GIXRD patterns for  $\theta$  = 8.0° to 1.0° of Cu foams electrodeposited onto a Mo substrate. Dominant texture of the Mo substrate was Mo(200). Right ordinates are normalized to the intensity of the Cu(111) peak wherever possible. Red labels show the peak locations for polycrystalline Cu (JCPDS 00-004-0836) and polycrystalline Mo (JCPDS 00-004-0809).



**Figure S4.** (a) and (b) (i.e., Bragg-Brentano) XRD and (c) thru (f) GIXRD patterns for  $\theta = 8.0^{\circ}$  to 1.0° of Cu foams electrodeposited onto a Pt substrate, which was more polycrystalline than the Mo substrate. Right ordinates are normalized to the intensity of the Cu(111) peak wherever possible. Red labels show the peak locations for polycrystalline Cu (JCPDS 00-004-0836) and polycrystalline Pt (JCPDS 00-004-0802).

#### **Preparation of Goniometer Samples**

To minimize oxidation of the Cu foam surface to  $Cu_2O^3$  or possibly CuO (Figure S1) and to demonstrate repeatability of the contact angle measurements, a fresh Cu foam sample was fabricated immediately prior to each goniometer experiment. The surface was then protected by dip-coating in ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, *vide supra*). As expected from highly roughened and highly porous Cu foams,<sup>5</sup> a droplet of H<sub>2</sub>O immediately wet the surface (Figure S5).



**Figure S5.** Contact-angle of  $H_2O$  on the surface of a Cu substrate before (a) and after (b) electrodeposition of Cu foam. Insets are photographs of the Cu substrate. After wrapping Cu substrate with Kapton tape, an area of ~1 cm<sup>2</sup> was left exposed for electrodeposition of Cu foam (darkened area).

## **Surface Analysis**

In support of GI-XRD experiments, HR-TEM was used to confirm that Cu(111) facets dominate the surface of Cu foams (Figures 1e and S6).



**Figure S6.** HR-TEM of a Cu foam electrode showing multiple grains and lattice fringes that reveal a lattice distance of 2.07(2) Å. Copper metal has face-centered cubic geometry and thus, this lattice distance corresponds to the distance between Cu (111) planes (2.08 Å) as calculated from lattice spacing ( $d = \sqrt{3}a/3$ , where *a* corresponds to the lattice parameter for a cubic unit cell).

## Summary of Results for Copper Foam Electrocatalysts

Previously we reported a maximum FE for HCOO<sup>-</sup> of 37% with an overall current density of ca. -4 mV cm<sup>-2</sup> at a modest -1.5 V (vs. Ag/AgCl) (Figure S7b).<sup>6</sup> Updates to the electrochemical system to improve mass transport and use of 100% iR compensation yields a similar FE at a lower overpotential (i.e., -1.3 V) (Figure S7a). A comparison of current density supports a juxtaposition of this data (*cf.* Figure S7c green and Figure S7d green). In contrast, the FE of HCOO<sup>-</sup> at -1.2 V should not be juxtaposed with the original 34(6)% at -1.3 V due to a difference in current density.



**Figure S7.** Comparison of FE by product ((a) and (c)) and corresponding chronoamperograms ((b) and (d)) from this work and reference 6. Data for (a) and (b) are taken from reference 6 and replotted.



#### **Product Analysis**

**Figure S8.** Example GC traces from the (a) FID) and (b) TCD channels *in operando* from electrocatalytic reduction of  $CO_2$  at Cu foams at -1.3 V and 22°C (red) juxtaposed with calibration standards (blue and black). All traces were taken at least 1 hour after the start of electrocatalysis. Asterisk (\*) indicates valve switching.



**Figure S9.** Example <sup>1</sup>H NMR spectrum of liquid products from CO2RR experiments. Phenol and DMSO were added as internal standards. Spectrum was taken post-electrocatalysis at -1.3 V and 22°C. Acetone and acetate (indicated with an asterisk) are suspected to be residuals from washing of NMR tubes and not products as suggested by Kuhl et al.<sup>7</sup>

# **Notes and References**

- 1. D. W. Oxtoby, H. P. Gillis and A. Campion, *Principles of Modern Chemistry*, Cengage Learning, Boston, MA, 8th edn., 2016.
- 2. A. S. Varela, M. Kroschel, T. Reier and P. Strasser, *Catal Today*, 2016, **260**, 8-13.
- 3. A. Dutta, M. Rahaman, N. C. Luedi and P. Broekmann, ACS Catal, 2016, 6, 3804-3814.
- 4. J. Tokunaga, *J Chem Eng Data*, 1975, **20**, 41-46.
- 5. B. Han, X. Wang, J. Zheng, S. Liang, K. Xiao, J. Yu, Z. Qian and X. Huang, *Langmuir*, 2019, **35**, 15009-15016.
- 6. S. Sen, D. Liu and G. T. R. Palmore, *ACS Catal*, 2014, **4**, 3091-3095.
- 7. K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Energy Environ Sci.*, 2012, **5**, 7050-7059.