

Investigation into the Re-Arrangement of Copper Foams Pre- and Post-CO₂ Electrocatalysis

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Experimental details

Electrocatalysis experiments: CH440c (CH Instruments, USA) and Ivium-n-stat (Ivium Technologies B. V., Netherlands) potentiostat instruments were used for electrochemical measurements and electrolysis. Ivium-n-stat was used for electrochemical impedance spectroscopy for ohmic drop measurements, which was measured at a sinusoidal potential frequency of 10 kHz with 5 mV amplitude centered on the electrolysis potential (-1.6 to -1.4 V vs Ag/AgCl) just before electrolysis. A total of 85% of the measured ohmic drop was compensated for using the potentiostat control software; the remaining 15% (R_u) was manually adjusted for during data treatment using Ohm's law. Due to variations in ohmic drop and current between experiments, the actual potential difference also varied from run to run. A three-electrode setup was used with a leak-free reference electrode based on Ag/AgCl in 3.4 M KCl (+0.210 V vs SHE; Innovative Instruments Inc., USA), and the counter electrode was a 2.5 cm × 5 cm piece of platinum mesh electrode (99.9% Goodfellow, UK). Potentials are converted to the reversible hydrogen electrode (RHE) scale using eq 1.

$$E_{\text{RHE}} \text{ (V)} = E_{\text{Ag/AgCl(3.4M)}} \text{ (V)} + 0.210 \text{ V} + (0.059 \text{ V} \times \text{pH}) + iR_u \quad (1)$$

The pH was measured at the start of the experiment, after bubbling CO₂ but prior to starting electrocatalysis. The pH of the CO₂-saturated bicarbonate solution was found to be 6.8.

For 35 minute electrolysis experiments a custom-made H-cell was used, constructed as described previously.¹ The cell was filled with 3.5 mL electrolyte on the cathode side and 40

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mL electrolyte on the anode side. Carbon dioxide gas was flowed into the electrolyte and maintained at a constant rate of 40 mL/min during electrolysis using a mass flow controller GFC5-010058 (Cole-Parmer, USA). Gas inlet and outlet streams were added to the cell to allow CO₂ to enter and escape while keeping the internal pressure of the cell at ambient levels. To take a gaseous measurement 2.5 mL of experimental gas exhaust was injected in the GC, of which 0.4 mL was analyzed.

Gaseous products were quantified using Agilent 7820A gas chromatograph (Agilent Technologies, UK) equipped with a thermal conductivity detector and flame ionization detector coupled to a methanizer, with argon used as the carrier gas. The following gaseous products of CO₂ electrolysis were quantified; hydrogen, carbon monoxide, methane, ethylene and ethane as well as oxygen, nitrogen and carbon dioxide. The method was also able to quantify propane, butane, pentane and hexane but these peaks were not present or near the limits of detection. The GC had two columns, HP-PLOT Q which separates hydrocarbons and CO₂, followed by HP-PLOT 5A (molecular sieve) column which separate other permanent gases. The two columns were connected by valves which could be programmed to be run in series or bypass mode. The sample peak areas were compared to calibration gases (Calgaz, USA), and quantified according to the equation below. Single point calibration was used to quantify product concentration. Linearity between hydrogen and ethylene concentration and peak area was tested using two mass flow controllers connected to a source of calibration gas and argon carrier gas, the two were mixed before injection into the GC sampling tube.

$$\text{Faradaic Efficiency} = \frac{nFP_s c_c V}{1000P_c C_T}$$

Faradaic efficiency is given in decimals, n is the number of electrons needed to reduce CO₂ to a given product, F is the Faraday constant (96485 Cmol⁻¹), P_s and P_c are the peak areas of the sample and the calibration gas respectively, c_c is the calibration gas concentration in

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mol dm^{-3} , v is the total volume of gas flowed through the electrolysis cell during electrolysis in cm^3 and C_T is the total charge passed through the system during electrolysis in Coulombs.

Characterization details

Characterization of copper foams made in the presence of varying HCl concentrations

Copper foams that formed in the presence of 4 mM HCl (CF-4H) have the thinnest average wall width of 19.3 μm , whereas foams made with 73 mM HCl (CF-73H) have the widest average wall width of 29.0 μm . The 18 mM HCl foams (CF-18H) are in the middle, 26.2 μm . The pore size also varies with HCl concentration. The smallest average pore size, 38.1 μm , is observed for CF-4H. CF-18H has the largest pores, average diameter 58.6 μm , ranging from 36.5 to 70.3 μm . In contrast, CF-73H is less homogeneous than CF-18H with pore diameters ranging from 24.3 μm to 70.9 μm (these values are based on 8 measurements per foam).

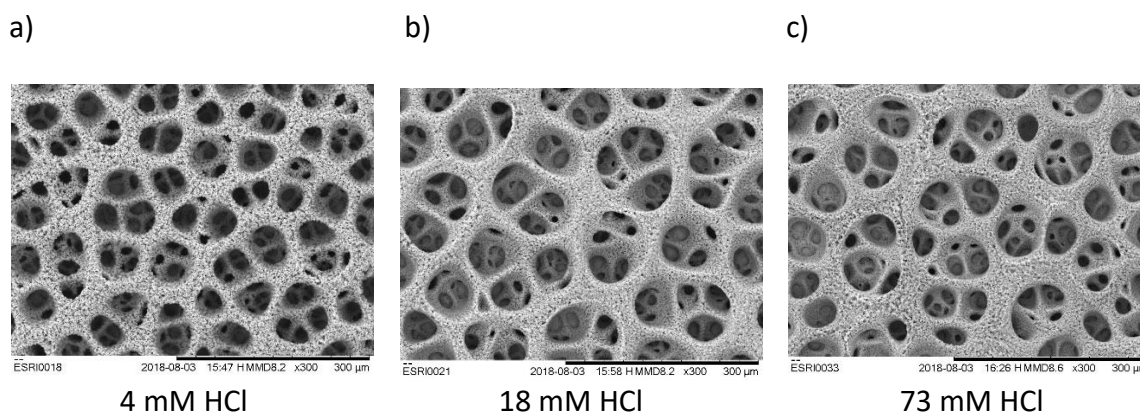


Figure S1. SEM images of the copper foams made in the presence of various concentrations of added HCl. a) CF-4H, b) CF-18H, c) CF-73H. The black bar at the bottom of the pictures represents 300 μm .

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Table S1. Summary of the wall widths and pore sizes of various copper foams.

Copper Foam	Wall Width (μm)	Pore Size (μm)
CF-4H	19.3	38.1
CF-18H	26.2	58.6
CF-18H-100U	18.2	44.1
CF-73H	29.0	47.6

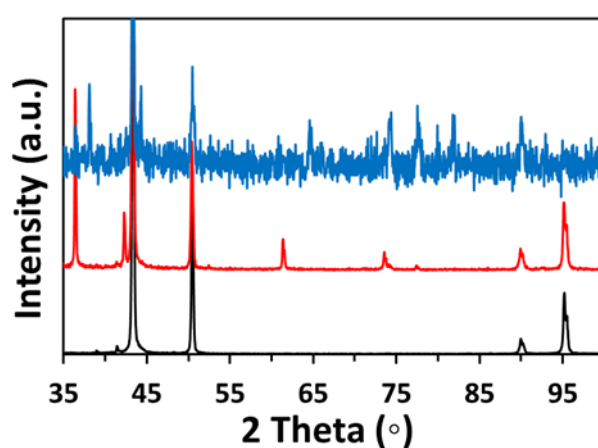


Figure S2. XRD of plain copper disc (black), CF-18H on copper disc (red), CF-18H on a carbon tab (blue).

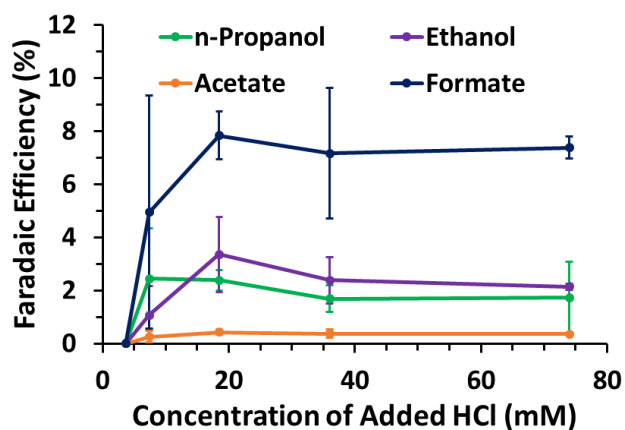


Figure S3. Faradaic efficiencies of liquid products (%) vs the concentration of added HCl into the copper foam deposition bath (mM). Electrocatalysis experiments carried out at -0.81 V vs RHE in 0.1 M KHCO_3 electrolyte.

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Table S2. Table summarizing the faradaic efficiencies of the gaseous products from electroreduction catalysis of CF-18H at -0.81 V vs RHE.

	Run 1	Run 2	Run 3	AVG
Ethylene (%)	3.67	4.82	4.06	4.18
Ethane (%)	1.40	2.81	4.87	3.03
CO (%)	4.89	3.90	2.54	3.78
H ₂ (%)	56.60	59.96	52.84	56.47

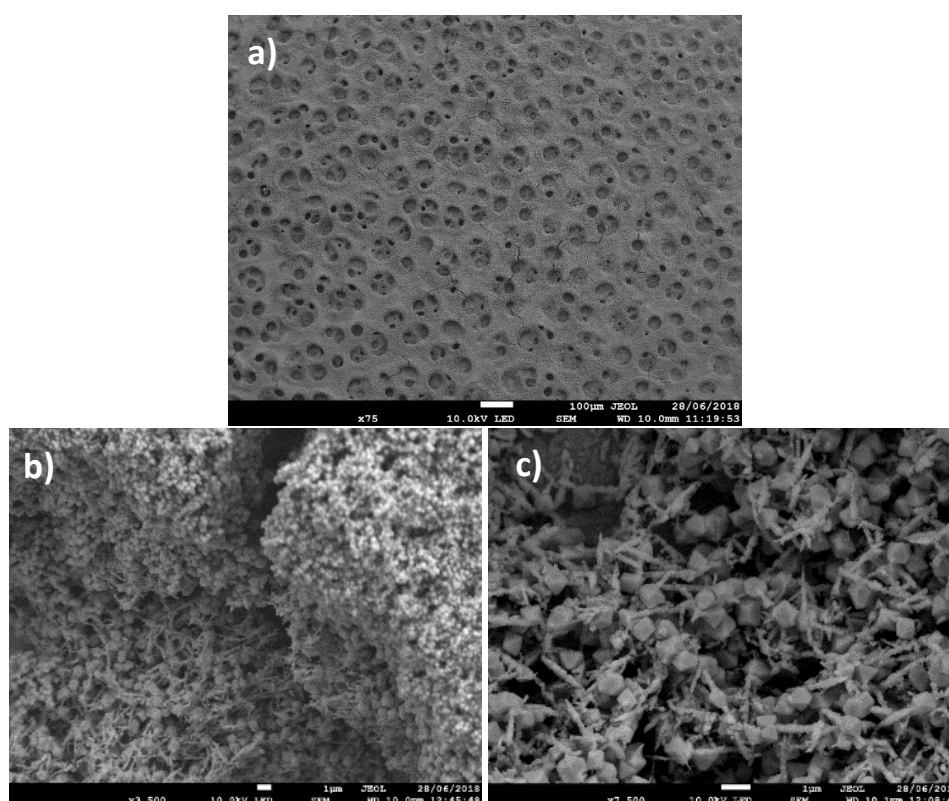


Figure S4. SEM of CF-18H-100U. a) x75 magnification, b) x3,500 magnification of one of the “cracks” depicting the change in structure with depth. c), cuboctahedra structures interspersed with dendrites from a site below the “crack”.

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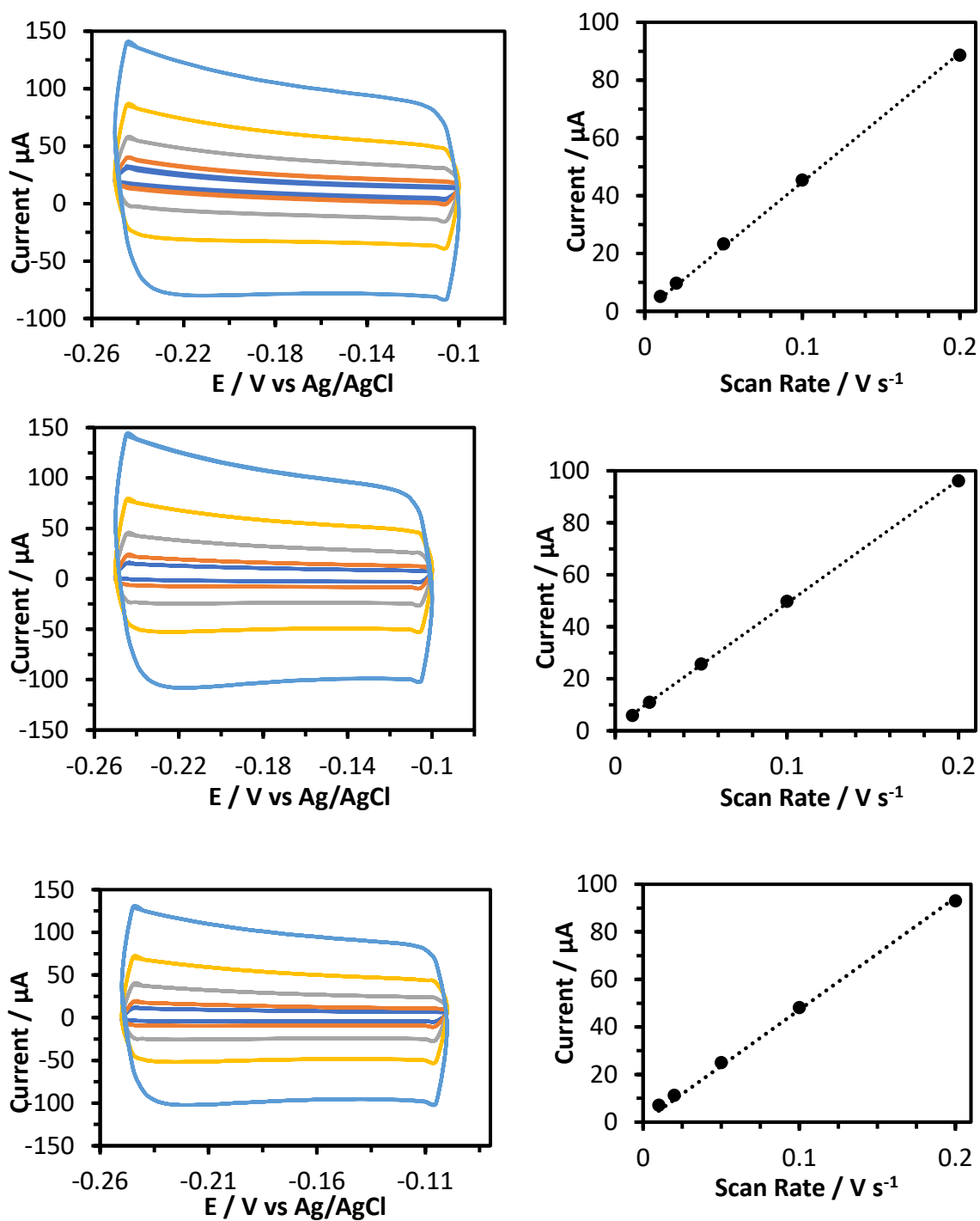


Figure S5. Cyclic voltammograms of copper foams in argon saturated 0.1 M HClO_4 at 0.01, 0.02, 0.05, 0.1 and 0.2 V s^{-1} . Left – cyclic voltammograms. Right – shows the sum of charging and discharging current as a function of scan rate. Top to bottom, CF-18H, CF-18H-100U, CF-18H-DCU.

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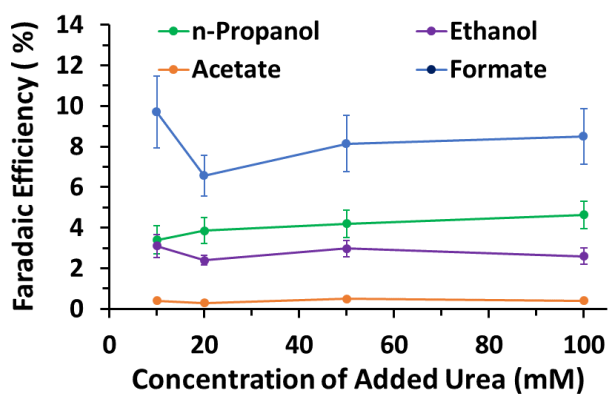


Figure S6. Faradaic efficiencies of liquid products (%) vs the concentration of added urea into the copper foam deposition bath (mM). Electrocatalysis experiments carried out at -0.82 V vs RHE in 0.1 M KHCO_3 electrolyte. Error bars are the standard deviation from 3 measurements. The error bars on acetate are too small to depict.

Table S3. Current density calculations for CF-18H and CF-18H-100U at -0.83V vs RHE.

	CF-18H	CF-18H-100U	
Potential vs RHE	-0.83	-0.83	V
Avg Coulombs	4.36	5.58	C
Avg current	0.002	0.003	A/s
Avg current	2.08	2.66	mA/s
Diameter of disc	0.30	0.30	cm
Radius of disc	0.15	0.15	cm
Area	0.07	0.07	cm^2
Current density	29.37	37.61	mA/cm^2
Partial current density for <i>n</i> -propanol	0.98	1.85	mA/cm^2

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Table S4. Summary of the percentage faradaic efficiencies of all products from the CF-18H and the CF-18H-100U copper foams.

	CF-18H					CF-18H-100U				
Voltage (V)	-0.70	-0.75	-0.83	-0.93	-1.05	-0.70	-0.75	-0.83	-0.93	-1.05
Hydrogen	41.93	54.24	56.47	68.17	74.30	47.61	66.29	69.21	76.21	90.91
CO	14.40	5.49	3.78	2.42	1.71	9.20	7.40	4.60	3.90	0.88
Formate	12.17	6.90	6.13	3.37	2.67	24.73	5.79	5.92	3.09	2.42
Methane	---	---	---	---	0.37	---	---	---	---	0.70
Ethanol	---	1.38	2.79	0.87	2.51	---	1.75	3.19	1.07	1.51
Acetate	---	0.43	0.32	0.17	0.14	---	0.23	0.70	0.12	0.07
Ethylene	---	3.54	4.18	9.70	11.67	1.50	2.50	4.00	5.60	8.00
Ethane	---	1.92	3.03	2.39	0.69	1.30	2.40	2.80	1.20	0.00
<i>n</i> -Propanol	---	1.51	3.34	1.64	1.77	---	2.23	4.93	1.31	0.89
<i>i</i> -Propanol	---	0.79	0.68	0.87	0.74	---	---	---	0.11	---
C3 Product total	---	2.30	4.02	2.50	2.51	---	2.23	4.93	1.43	0.89
C2 Products	---	7.27	10.32	13.13	15.01	2.80	6.87	10.68	7.99	9.58
C2+C3 products	---	9.57	14.34	15.68	17.51	2.80	9.10	15.61	9.42	10.47
C1 Products	26.57	12.39	9.91	5.79	4.75	33.93	13.19	10.52	6.99	4.00

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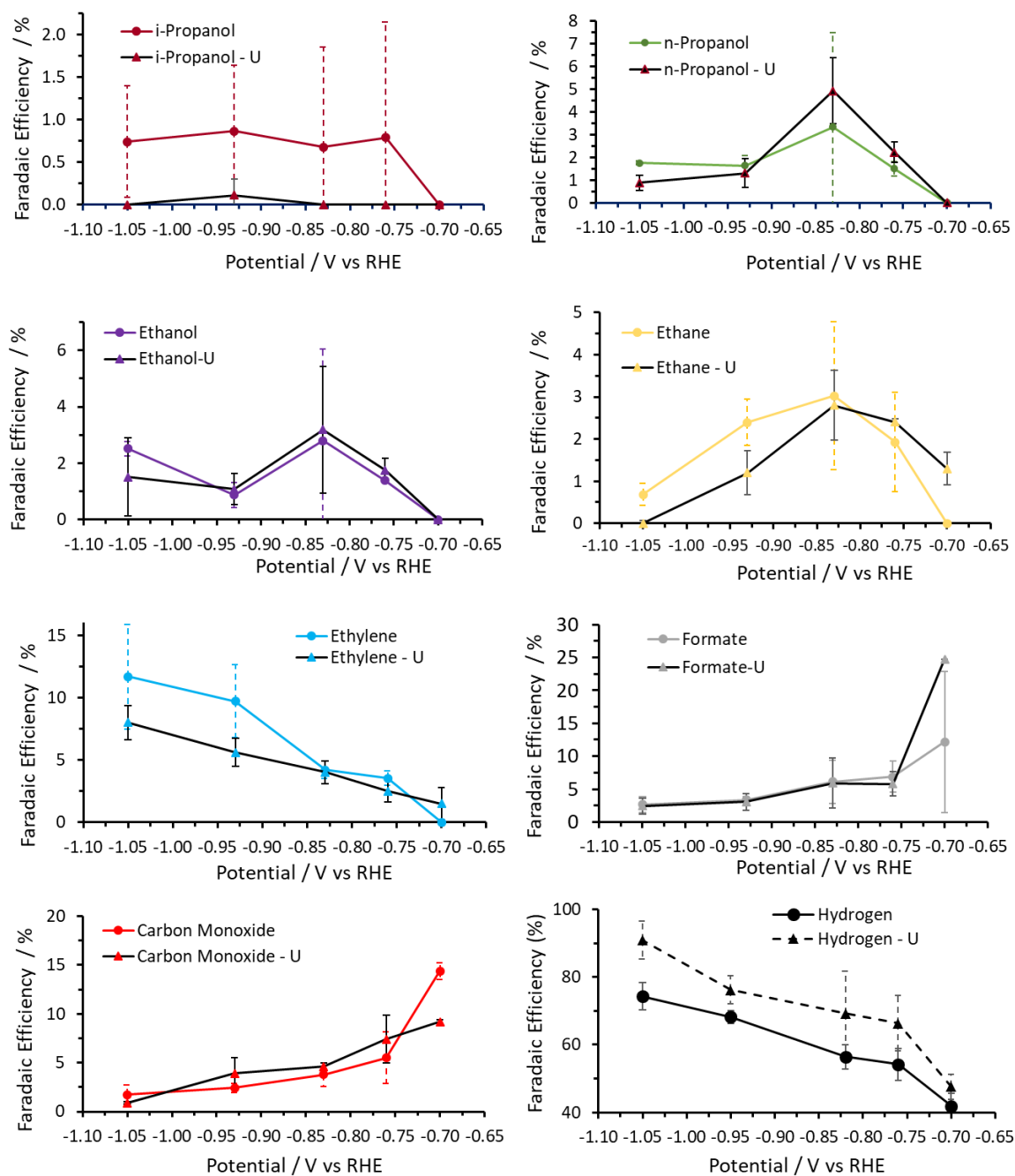


Figure S7. Faradaic efficiency for observed products on CF-18H and CF-18H-100U plotted vs potential, corrected to RHE. The error bars are the standard deviation from three independent measurements. Data for acetate are provided in Figure 8 of the manuscript.

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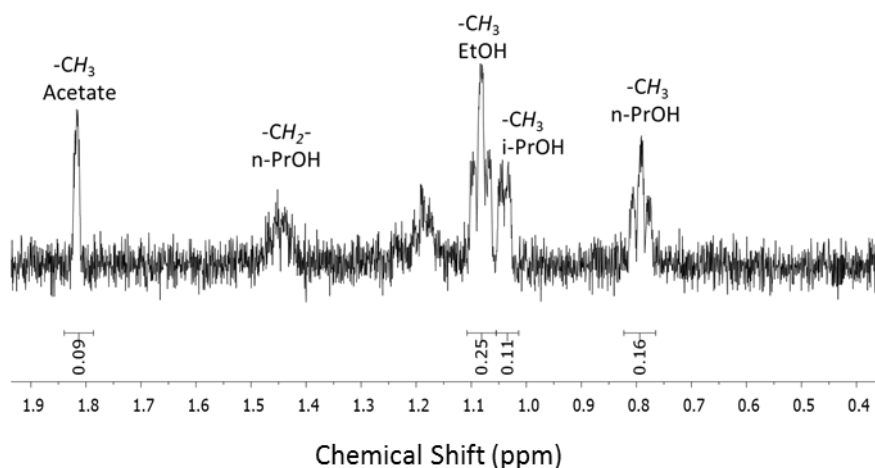


Figure S8. Representative NMR spectrum depicting the peaks attributed to *n*-PrOH, *i*-PrOH, EtOH, and acetate. CF-18H at -0.83 V vs RHE. The broad peak at 1.2 ppm could be due to diethyl ether but this peak alone is not enough to report the electroreduction of CO_2 to diethyl ether so no such claim has been made.

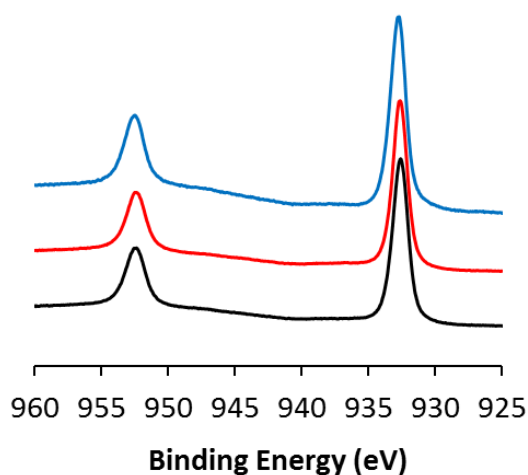


Figure S9. Copper 2p signal from CF-18H (black), CF-18H-100U (red), CF-18H-DCU (blue) after 35 minutes of electrolysis at -0.83 V vs RHE.

References

1. S. Ahn, K. Klyukin, R. J. Wakeham, J. A. Rudd, A. R. Lewis, S. Alexander, F. Carla, V. Alexandrov and E. Andreoli, *ACS Catalysis*, 2018, **8**, 4132-4142.