

# Copper-based Electrocatalyst for Hydrogen Evolution in Water

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## S1. General

### S1.1 Phosphate buffer preparation

$\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$  were  $\geq 99\%$  AR grade purchased from commercial suppliers and used without further purification. Water was either single-distilled, RO, or milli-Q, and was always milli-Q for the large cell.

1 M pH 7 phosphate buffer solution was made by first preparing separate 1 M aqueous solutions of (a)  $\text{KH}_2\text{PO}_4$  (13.61 g to 100 mL, approximate pH = 4.2) and (b)  $\text{K}_2\text{HPO}_4$  (17.42 g to 100 mL, approximate pH = 9.2), then mixing 1 M  $\text{KH}_2\text{PO}_4$  (40 mL) with 1 M  $\text{K}_2\text{HPO}_4$  (60 mL) and monitoring with a pH meter, if needbe adjusting the pH to a stable reading of 7.0 by adding more of either solution as required.

### S1.2 Reference electrode preparation

$\text{Bu}_4\text{NPF}_6$  (99 %, for electrochemical analysis) used in the MeCN studies in the small cell, including for the 0.01 M  $\text{AgNO}_3|\text{Ag}$  reference electrode, was purchased from Sigma Aldrich and used without further purification. Acetonitrile was HPLC grade and freshly distilled over  $\text{CaH}_2$ .  $\text{AgNO}_3$  was AR Grade from Fisher Scientific. Silver wire (99.99%, 0.5 mm) was purchased from surepure.com (6373). Teflon heat shrink tubing (MF-2027) and porous glass frits (MF-2064) were purchased from BASi (basinc.com). KCl was AR Grade ( $>99.8\%$ , UNIVAR) or better and used without further purification.

The **0.01 M  $\text{AgNO}_3|\text{Ag}$  reference electrode** (only used in the small cell for acetonitrile experiments) was prepared prior to each experiment, using a fresh solution of 0.01 M  $\text{AgNO}_3$  and 0.1 M  $\text{Bu}_4\text{NPF}_6$  in dry MeCN each time. After each experiment the reference electrode was thoroughly rinsed with dry MeCN before being stored in dry MeCN in a sealed container to prevent the porous glass frits from drying out.

The **reference  $\text{Ag}|\text{AgCl}|\text{sat. KCl}$  electrodes** were prepared by roughening a  $\sim 10$  cm length of silver wire in conc. nitric acid for 10 s, followed by rinsing with RO water then soaking in RO water for up to an hour. Alternatively, the silver wire was sanded and then soaked in ammonia solution for several hours before cleaning with RO water as above. The roughened silver wire was coated with AgCl by partly submerging it in saturated KCl solution and applying an anodic

current (the silver wire is acting as the working electrode in this setup) of approximately +20  $\mu\text{A}$  overnight (or more current for a shorter time if needed), which results in a white to grey coloured coating of AgCl forming on the wire. A Pt wire or plate was used as the counter electrode, with the reference connection either to the counter electrode or another Ag|AgCl reference electrode (which allows monitoring of the newly forming reference's potential over time). This step could be done with the silver wire in a sealed tube filled with saturated KCl solution (ideally with a few KCl crystals present to maintain saturation), with an air-tight electrical connection out of the tube. A porous glass frit was fitted on the end using Teflon heat-shrink tubing ensuring there was no or minimal air in the sealed tube/new reference electrode. After forming the AgCl layer on the wire, the new Ag|AgCl|sat. KCl reference electrode was stored in saturated KCl solution and allowed to equilibrate for a day before use. The electrode was always stored in a saturated KCl solution between use.

The reference potentials of the Ag|AgCl reference electrodes were checked against either an internal standard (see section S2.2 and Figure S3) or by measuring open circuit potentials (OCP) against 'master' Ag|AgCl reference electrodes and/or a SCE electrode before and after experiments to ensure they were in good order and hadn't drifted over the course of an experiment. The 'master' reference electrodes were always stored in sat. KCl and never used experimentally. The OCP was simply checked by connecting two reference electrodes sitting in the same sat. KCl solution to a multimeter and measuring the voltage (or alternatively by using a potentiostat and doing an OCP experiment), which was usually <11 mV different to the expected value, though it would occasionally drift over a long experiment to be up to 20 mV from expected, at which point the electrode would be replaced.

### S1.3 Stability of $[\text{Cu}^{\text{II}}\text{L}^{\text{Et}}]\text{BF}_4$ (**1**) in phosphate buffer (pH 7) solution (no applied potential)

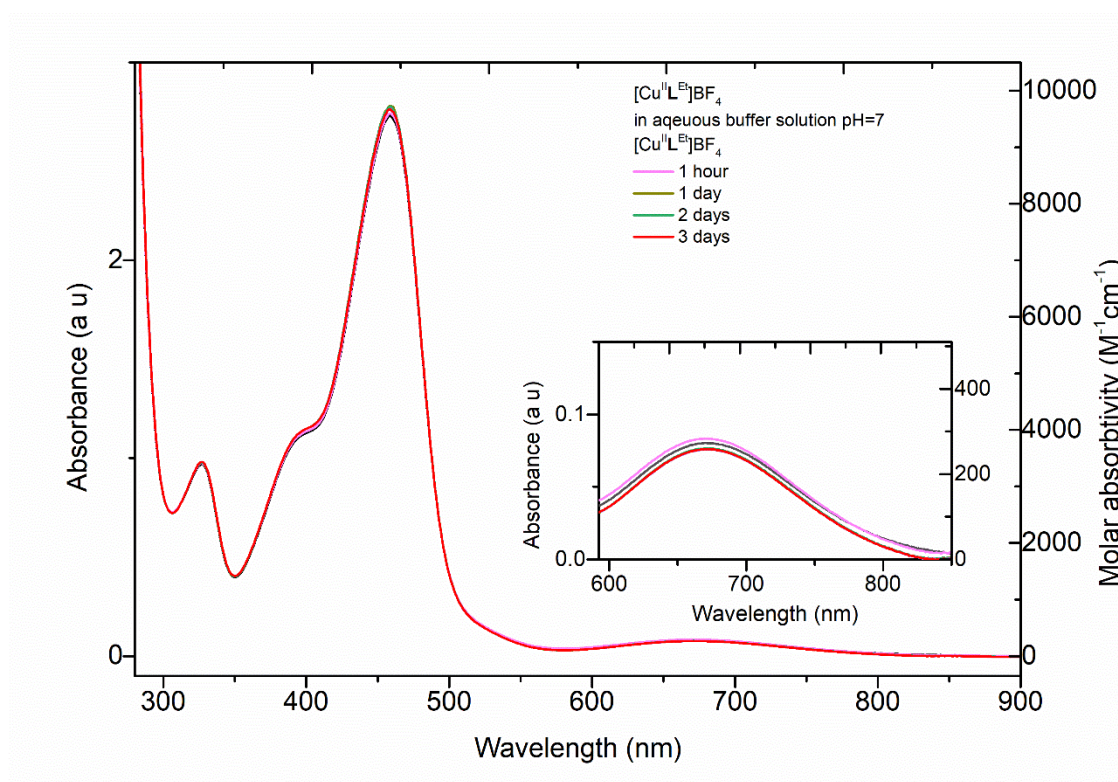


Figure S1. UV-vis spectra of 0.30 mM  $[\text{Cu}^{\text{II}}\text{L}^{\text{Et}}]\text{BF}_4$  (**1**) in 1 M aqueous phosphate buffer (pH = 7) recorded at the times noted, starting at the moment of dissolving, through to 3 days (note: no potential is being applied).

## S2. Electrochemical studies in the small “H-cell”

### S2.1 General electrochemistry information for small H-cell studies



Figure S2. Example setup of small electrochemical “H-cell” used for cyclic voltammetry and some of the controlled potential electrolysis (CPE) experiments; other CPE experiments were carried out in a larger cell (see section S3 below). The right is the working chamber with  $[\text{Cu}^{\text{II}}\text{L}^{\text{Et}}]\text{BF}_4$  (0.3 – 1 mM, usually 0.3 mM unless otherwise stated) present, the black rod is a small 3 mm diameter ( $A = 0.071 \text{ cm}^2$ ) glassy carbon working electrode (GCWE), and next to that is the reference electrode. The reference electrode is either 0.01 M  $\text{AgNO}_3|\text{Ag}$  or  $\text{Ag}|\text{AgCl}$ , used for the MeCN and aqueous experiments, respectively. The left side is the platinum counter electrode, either mesh (shown) or plate.

The small three neck “H-cell” electrochemical cell (Figure S2) and Pt counter electrode were carefully cleaned and dried between studies as follows: cleaned with acetone, rinsed thoroughly with copious water, filled and soaked in nitric acid (1 hour), rinsed thoroughly with copious water, filled and soaked in water (2 hours), rinsed with water, acetonitrile and acetone, soaked in dry MeCN for 24 hours, emptied and dried in an oven overnight before use.

The small glassy carbon working electrode (GCWE) was cleaned before each measurement by: rinsing with water, ethanol, and acetonitrile, then polishing with an alumina (13 nm, Sigma

718475, 99.8%) slurry on a MicroCloth/Spec-Cloth (EMS 50320-05), and finally rinsing with dry acetonitrile and drying in air with a hair drier.

Bu<sub>4</sub>NPF<sub>6</sub> (99 %, for electrochemical analysis) used in the MeCN studies in the small cell was purchased from Sigma Aldrich and used without further purification.

## S2.2 Small H-cell comparison of reference electrodes in MeCN

In our previous report,<sup>1</sup> the electrochemistry and electrocatalysis study on **1** was conducted in dry MeCN with a 0.01 M AgNO<sub>3</sub>|Ag reference electrode in the small H-cell. Shifting to conducting the studies in aqueous solution, as reported herein, meant also changing the reference electrode used to Ag|AgCl. To provide a comparison between these two electrodes, a CV of copper(II) complex **1** with added ferrocene was recorded in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> dry acetonitrile solution, in the small H-cell (Figure S3), first using 0.01 M AgNO<sub>3</sub>|Ag as the reference electrode,<sup>1</sup> and then using Ag|AgCl as the reference electrode (Figure S3). This gave:

$$E_{1/2}(\mathbf{1}) = -1.39 \text{ V plus } E_{1/2}(\text{Fc}^+/\text{Fc}) = +0.09 \text{ V vs } 0.01 \text{ M AgNO}_3|\text{Ag and}$$

$$E_{1/2}(\mathbf{1}) = -1.01 \text{ V plus } E_{1/2}(\text{Fc}^+/\text{Fc}) = +0.46 \text{ V vs Ag|AgCl.}$$

Therefore, the  $E_{1/2}$  of these two processes in MeCN increased by 0.38 or 0.37 V, respectively, on switching the reference electrode from 0.01 M AgNO<sub>3</sub>|Ag to vs Ag|AgCl.

It is useful to note the comments from Chang, Long and co-workers, who compared data obtained on various HER electrocatalysts using different solvent, reference and/or working electrode,<sup>2</sup> noting the limitations of the approach they took in order to do so, and we also acknowledge these limitations. The following is a quote from that work<sup>2</sup>:

“the reference potential can differ greatly depending on the solvent conditions. Although we acknowledge that such corrections have inherent limitations, for the sake of simplicity, we have adopted a standardized conversion between Ag/AgCl, SCE, or Fc/Fc+ to SHE for evaluating the range of catalysts reported to date. These corrections are as follows: Ag/AgCl (water), +0.210 V; SCE (water), +0.240 V; Fc/Fc+ (acetonitrile, water–acetonitrile), +0.640 V.”

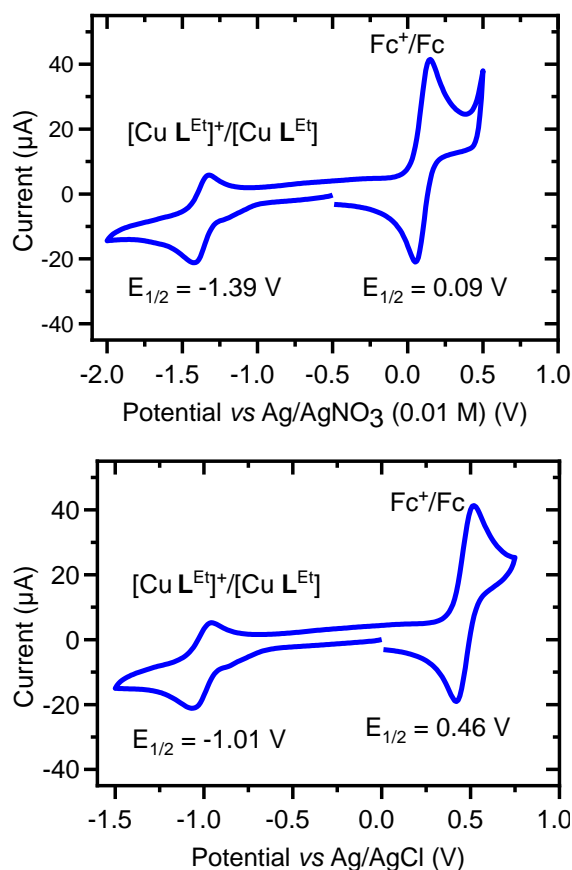


Figure S3. Cyclic voltammograms for a 1 mM of **1** in 0.1 M (NBu<sub>4</sub>)PF<sub>6</sub> **acetonitrile solution** in the presence of 1 mM **ferrocene (Fc) as an internal standard**, (top) 0 → -2.0 → 0.5 → 0 V vs **0.01 M AgNO<sub>3</sub>|Ag reference electrode**; (bottom) 0 → -1.5 → 0.75 → 0 V vs **Ag|AgCl reference electrode**. Conditions: 0.1 M (NBu<sub>4</sub>)PF<sub>6</sub>, glassy carbon working electrode (d = 3 mm, A = 0.071 cm<sup>2</sup>), scan rate 100 mV s<sup>-1</sup>. Note: **no acetic acid is present**. The top CV (obtained in MeCN) image was generated using data collected for our previous paper.<sup>1</sup>

### S2.3 Small H-cell initial cyclic voltammetry (CV) studies in water

The initial aqueous CVs were carried out in the small H-cell (Figure S2). The working compartment was filled with 8 mL 1 M pH 7 phosphate buffer solution (see section S1.1) and 0.30 mM copper complex or Cu<sup>II</sup>(BF<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O salt. The remainder of the ‘H’ was filled with ca. 10 mL of 1 M pH 7 phosphate buffer solution. The small glassy carbon electrode (D = 3 mm, A = 0.071 cm<sup>2</sup>) and the Ag|AgCl reference electrode were placed into the working compartment, and the Pt sheet counter electrode was placed in the auxiliary compartment.

The purity of the electrolyte and solvent and the cleanliness of the small H-cell setup was first checked by recording the CV from 0 to 1.0 to -1.4 to 0 V versus Ag|AgCl to confirm negligible

background current was observed, before adding the copper complex or salt and commencing the CV study (Figure S4 and further figures in the body of the paper, Table S1).

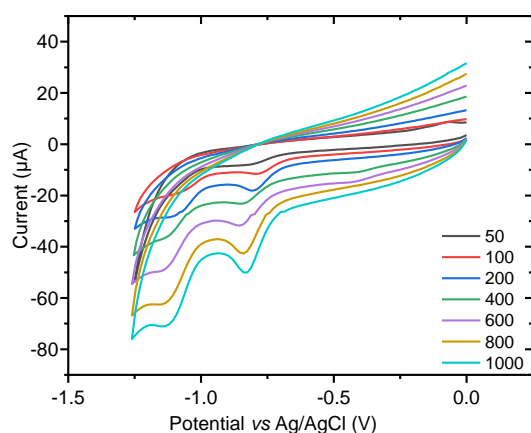


Figure S4. Cyclic voltammetry,  $0 \rightarrow -1.25 \rightarrow 0$  V vs Ag|AgCl, for a 0.30 mM  $[\text{Cu}^{\text{II}}\text{L}^{\text{Et}}]\text{BF}_4$  (**1**) in 1 M pH 7 phosphate buffer solution at different scan rates (mV/s). Conditions: 1 M pH 7 phosphate buffer solution buffer, pH = 7, glassy carbon working electrode ( $d = 3$  mm,  $A = 0.071$  cm<sup>2</sup>).

Table S1 Summary of cathodic peak ( $E_{\text{pc}}$ ) currents of the two redox events that occur, in the ranges -0.79 to -0.85 V and -1.08 to -1.13 V, in the CVs of **1** in 1 M pH 7 phosphate buffer solution (Figure S4). <sup>a</sup>No obvious peak at this scan rate, so best estimate given.

Scan Rate (mV/s)	Square Root of Scan Rate (V/s) <sup>1/2</sup>	Event at -0.79 to -0.84 V		Event at -1.08 to -1.134 V	
		$E_{\text{pc}}$ (V)	Current ( $\mu\text{A}$ )	$E_{\text{pc}}$ (V)	Current ( $\mu\text{A}$ )
50	0.2236	-0.80	-7.64	-1.08 <sup>a</sup>	-15.53 <sup>a</sup>
100	0.3162	-0.79	-11.55	-1.08	-18.81
200	0.4472	-0.81	-18.12	-1.12	-28.53
400	0.6325	-0.85	-23.23	-1.13	-36.47
600	0.7746	-0.84	-31.21	-1.13	-48.71
800	0.8944	-0.84	-42.62	-1.13	-61.96
1000	1	-0.84	-50.02	-1.13	-70.99



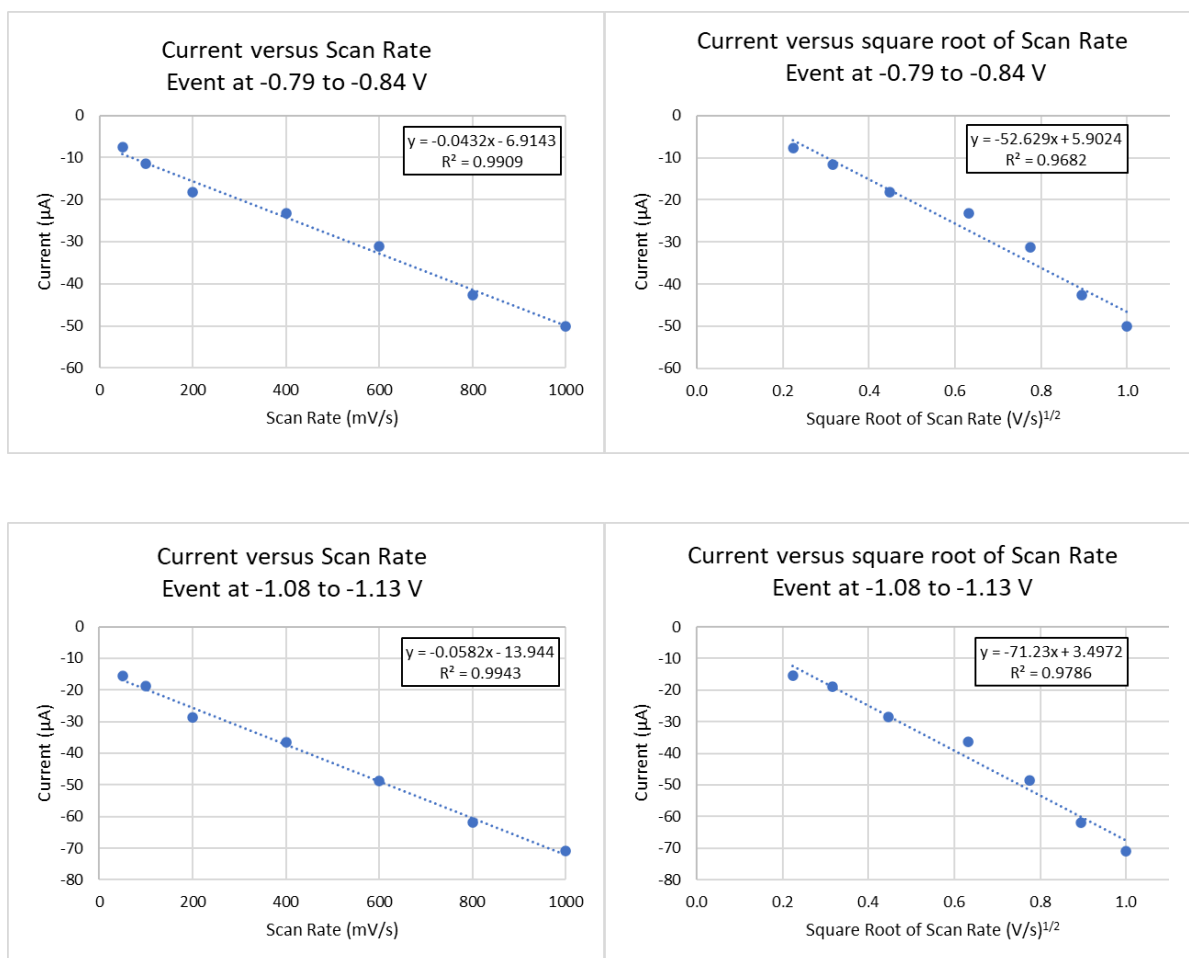


Figure S5. Plots of the current versus scan rate or square root of scan rate for the two reduction events observed at approximately -0.8 V (top) and -1.1 V (bottom) in the CVs (Figure S4, Table S1).

## S2.4 Small H-cell controlled potential electrolysis (CPE) studies in water

The initial aqueous CPE measurements were conducted using the small H-cell under the same conditions as described for the CVs above.



Figure S6. Visible evolution of bubbles on 3 mm glassy carbon working electrode ( $A = 0.071 \text{ cm}^2$ ) during recording the CPE of complex **1** in neutral aq. phosphate buffer. Conditions: 1 M pH 7 phosphate buffer solution, 3 mm glassy carbon working ( $A = 0.071 \text{ cm}^2$ ) and Pt counter electrode, Ag|AgCl reference, 100 mV/s.

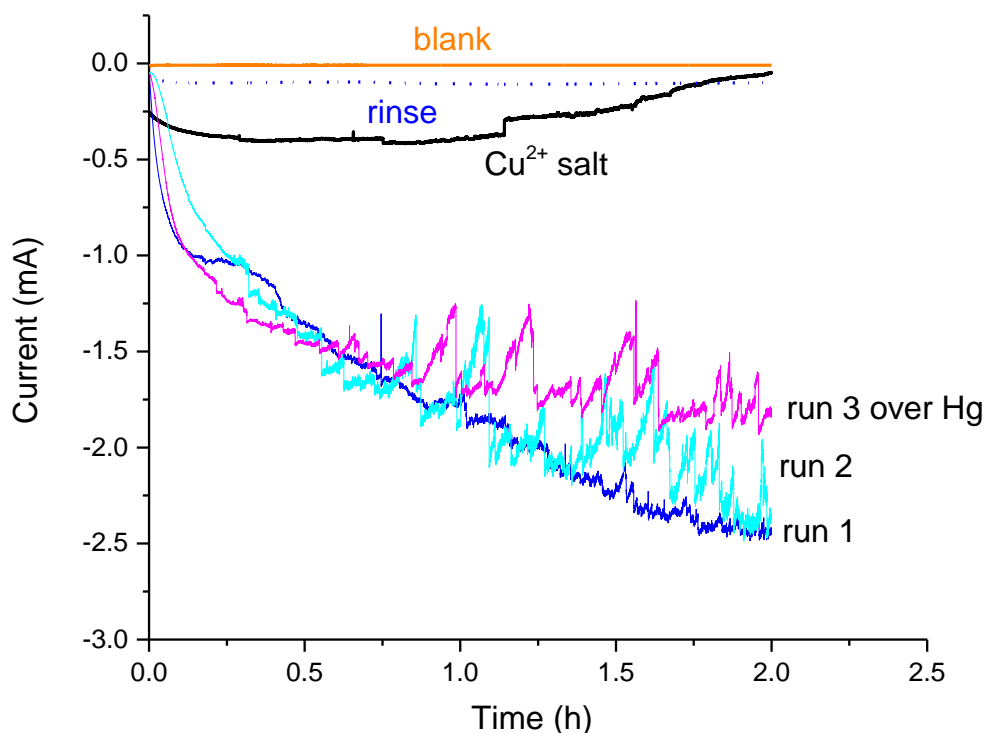


Figure S7. Current vs time during CPE for 2 hours at  $E_{\text{applied}} = -1.10$  V vs Ag|AgCl of an 8 mL solution of 1 M pH 7 phosphate buffer solution in the presence of 0.30 mM: **1** (blue),  $\text{Cu}^{\text{II}}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (black), or in the absence of a catalyst (blank, orange). After electrolysis with **1** the glassy carbon working electrode ( $d = 3$  mm,  $A = 0.071$  cm<sup>2</sup>) was rinsed with water by dipping a couple of times in fresh electrolyte and the electrolysis repeated in freshly made electrolyte of 1 M pH 7 phosphate buffer solution but without adding catalyst (blue dots; rinse and repeat test). Duplication run of **1** is shown in presence of (100  $\mu\text{L}$ ) of mercury drop (magenta) and in absence of mercury (cyan). Conditions: 1 M phosphate buffer, pH = 7, glassy carbon working electrode ( $d = 3$  mm,  $A = 0.071$  cm<sup>2</sup>), Pt counter electrode, small H-cell. These control tests are a good example of a negative result not disproving the positive, i.e. just because the Hg test and rinse test performed in this instance, on the small GCWE in the smaller cell, didn't show the presence of a heterogeneous deposit, doesn't mean that there wasn't one.

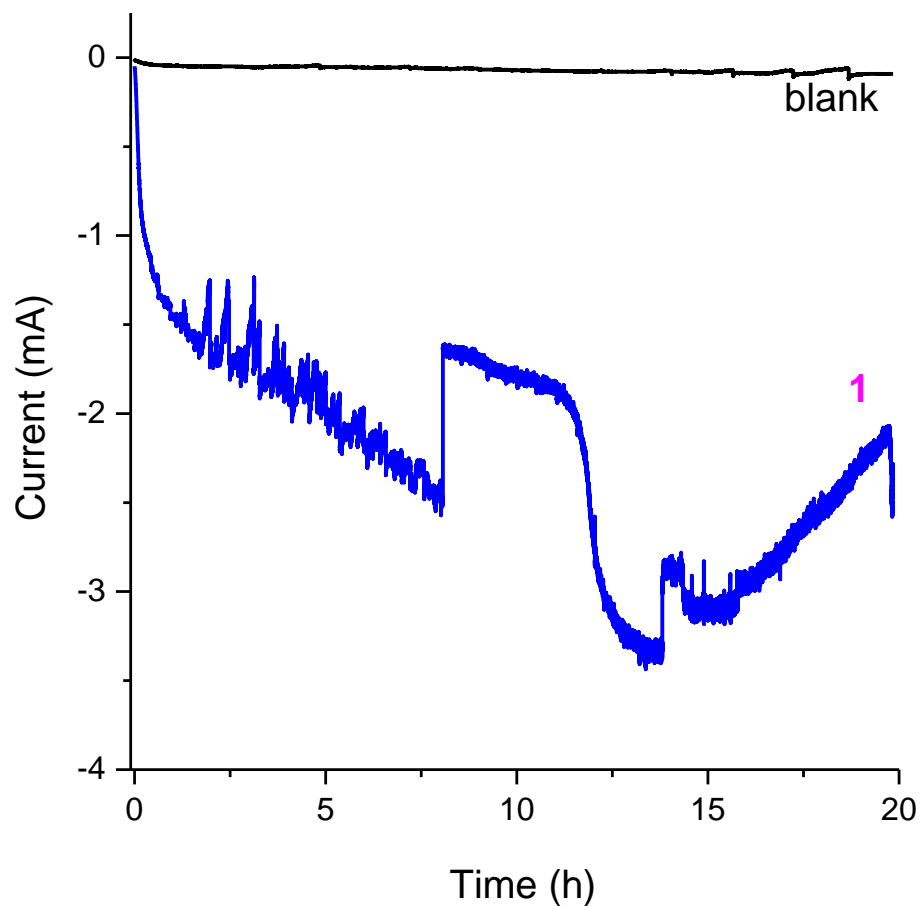


Figure S8. Current during CPE for 20 hours at  $E_{\text{applied}} = -1.10$  V vs Ag|AgCl of an 8 mL solution of 1 M pH 7 phosphate buffer solution in the presence of 0.30 mM: **1** (blue); small glassy carbon working electrode ( $d = 3$  mm,  $A = 0.071$  cm<sup>2</sup>), Pt counter electrode, small H-cell.

## S3 Electrochemical studies in the larger cell

### S3.1 General electrochemistry information for larger cell studies

The larger electrochemical cell (Figure S10) consists of a larger glass cell with a side opening to attach the large plate glassy carbon working electrode (GCWE), and a screw fitted top with a PTFE-lined silicone seal to allow for a gas outlet, gas inlet/bubbler, reference electrode, and counter electrode tube. The counter electrode tube consists of a ~22 cm long thin (4mm ID) tube with a larger bulb at the bottom with a glass frit base, into which is then inserted a Pt wire counter electrode, consisting of a ball of Pt wire connected to a long thin wire of Pt. The long thin counter tube means very minimal diffusion of air, which should ensure the working solution remains oxygen free.

The large glassy carbon plate working electrodes are SPI Glas 11 25x25mm, usually 5 mm thick, from SPI Supplies (2spi.com, 4385GCP-AB). The glassy carbon plates were typically aggressively cleaned with soapy water and paper towels then thoroughly rinsed with milli-Q water before being sanded with 1500 or 2000 grit sandpaper to remove any deposited materials, then polished with sequentially 9, 3, and 1  $\mu\text{m}$  diamond polish. Between grades the plates were washed with soapy water then thoroughly rinsed with DI water. After polishing the plates they were sonicated in acetone for  $\geq 10$  min, then milli-Q water, replacing the milli-Q water several times over  $>20$ min, before drying the plates with compressed air.

The large plate glassy carbon working electrodes (GCWE) were attached to the cell using a modified spherical joint clamp and an 18.7 mm ID O-ring to seal them on to the glass O-ring joint of the cell. The ID 18.7 mm O-ring results in a working surface area of approx. 2.7  $\text{cm}^2$ .

To confirm the gas tightness, the large cell can be pressurised with argon gas prior to starting an experiment by sealing the gas outlet, which causes the electrolyte in the counter chamber to rise. If the gas inlet is then sealed, the height of the electrolyte within the counter tube can be monitored to ensure there is no drop, and thus minimal gas escaping the pressurised cell.

Between experiments the large cell glassware and Pt counter electrode were cleaned with water, acetone, then thoroughly rinsed with milli-Q water before being cleaned with

concentrated nitric acid. The acid-cleaned glassware and Pt electrode were then rinsed again with milli-Q water before being oven dried (105 °C). The seals were typically used for several experiments before being replaced, either due to visible damage to the PTFE layer or losing the gas tightness. In between experiments the seals were thoroughly cleaned with water and paper towels, then the PTFE side carefully cleaned with acetone and paper towels (the silicone is not compatible with acetone), then the whole seal thoroughly rinsed with milli-Q H<sub>2</sub>O before drying with paper towels and compressed air.

The Ag|AgCl reference electrode used was stored in sat. KCl between experiments. See section S1.2 above for more information.

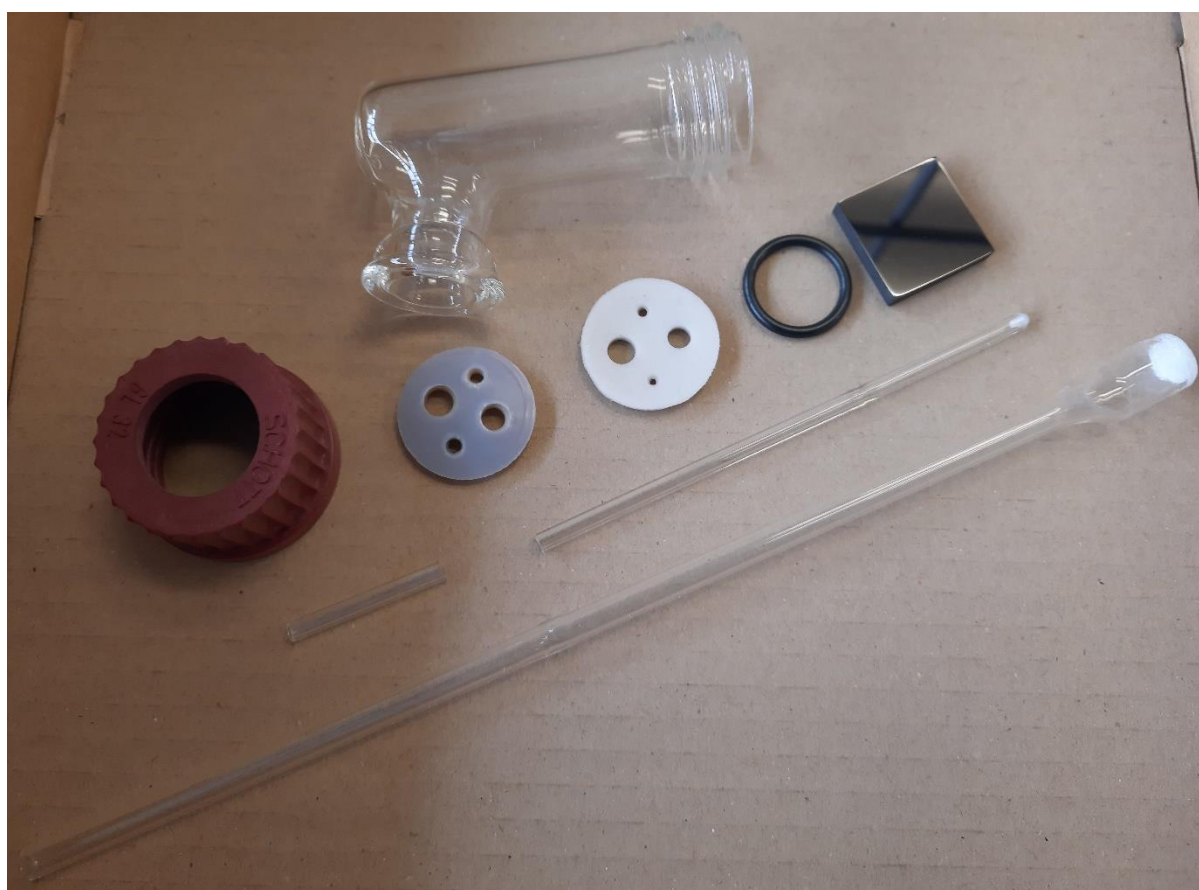


Figure S9. Some of the components of the large cell. Top is one of the glass cells; middle from left to right is the cap with central hole, a cap seal showing the PTFE side, a cap seal showing the silicone side, one of the O-rings, and one of the glassy carbon plates (25x25 mm Glas11); below that are the gas outlet tube on the left and the gas inlet/bubbler tube on the right; bottom is the counter electrode tube.

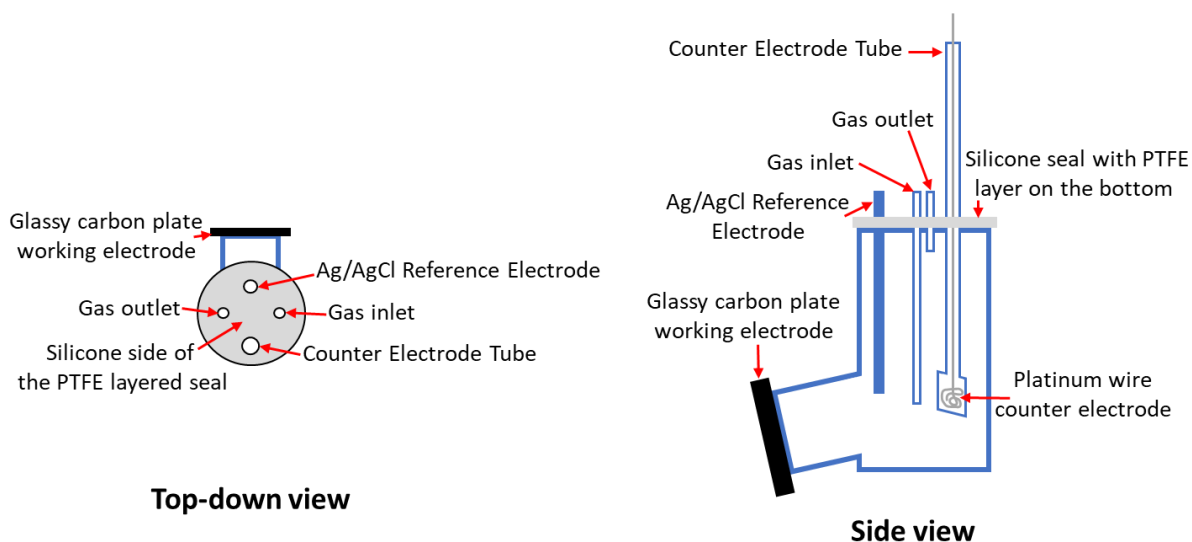
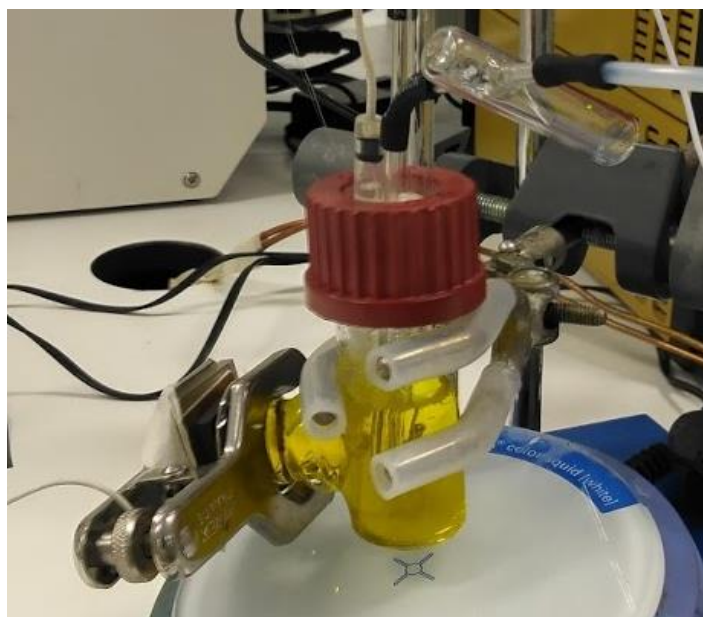


Figure S10. Top: Example setup of the large electrochemical cell, with 25 mL of 0.30 mM catalyst **1** in 1 M pH 7 phosphate buffer solution, deoxygenated with argon for >30 min before carrying out electrochemical experiments. Glassy carbon plates used as working electrodes were 25 x 25 mm Glas11 grade with an ID 18.7 mm O-ring limiting the working area to 2.7 cm<sup>2</sup>, Pt wire was used as counter electrode and Ag|AgCl as reference electrode. The ~3 mL overflow trap can be seen top right between the cell's gas outlet and the gas chromatograph. Bottom: Basic schematics of the large electrochemical cell, showing a top-down view (left) and a side view (right).

### S3.2 Instrument Information

The gas chromatographs (GC) used were SRI 8610C, either MG#3 or MG#5 configuration, Hayesep-D column, TCD and methanizer-FID detectors, argon carrier gas (99.99%, BOC Ltd), and with 1 mL sample loops set up for automatic sample injections. Powder XRD was measured using Cu  $K_{\alpha}$  radiation on a Rigaku Smartlab diffractometer. Electrochemical experiments with the large electrochemical cell were carried out using a Gamry Reference 600+ potentiostat. SEM and EDS/EDX measurements were done on either a JEOL JSM 7000F field emission SEM with JEOL EDX system or a JEOL JSM IT-300 with an Oxford Aztec SDD EDX system.

### S3.3 Large electrochemical cell studies and product quantification

All experiments using the large cell were carried out using 1 M pH 7 phosphate buffer solution (see section S1.1 Phosphate buffer preparation, above), Ag|AgCl as the reference electrode, large plate GCWE, Pt wire counter electrode, and were carried out at room temperature. The large GCWE electrodes and electrolyte were periodically checked prior to CPE experiments by running a brief (eg 15-30 min) CPE to ensure the current was dropping down to  $<1$  mA at  $E_{\text{setpoint}} = -1.1$  V vs Ag|AgCl.

The cell impedance was measured using potentiostatic electrochemical impedance spectroscopy (PSEIS) (1 MHz to 10 Hz) and taking a lower value from the high-frequency range. A value of approximately 90% of the measured value was then used to partially compensate for iR drop using positive feedback (PF) correction.<sup>3, 4</sup> The working solution was stirred with 20x6 mm magnetic flea, fast enough for vigorous stirring but with no risk of the flea jumping around (up to 850 rpm but usually set to 600 rpm). During experiments, after the solution has been thoroughly purged with argon, the argon flow rate is lowered to 5 SCCM, controlled with mass flow controller (Alicat). The gas outlet from the large cell headspace is connected to a ~3 mL overflow trap (top right, Figure S10) before going to the gas chromatograph.

Hydrogen is quantified using the gas chromatograph's TCD detector by comparing the measured peak areas to a calibration curve, which was calculated using the peak areas of



known hydrogen concentrations obtained by diluting a calibration gas with argon using mass flow controllers.

Where the electrolyte of an experiment was collected and then used as the electrolyte in another CPE experiment, the volume was topped up with fresh electrolyte if required to ensure 25 mL total of electrolyte in the cell.

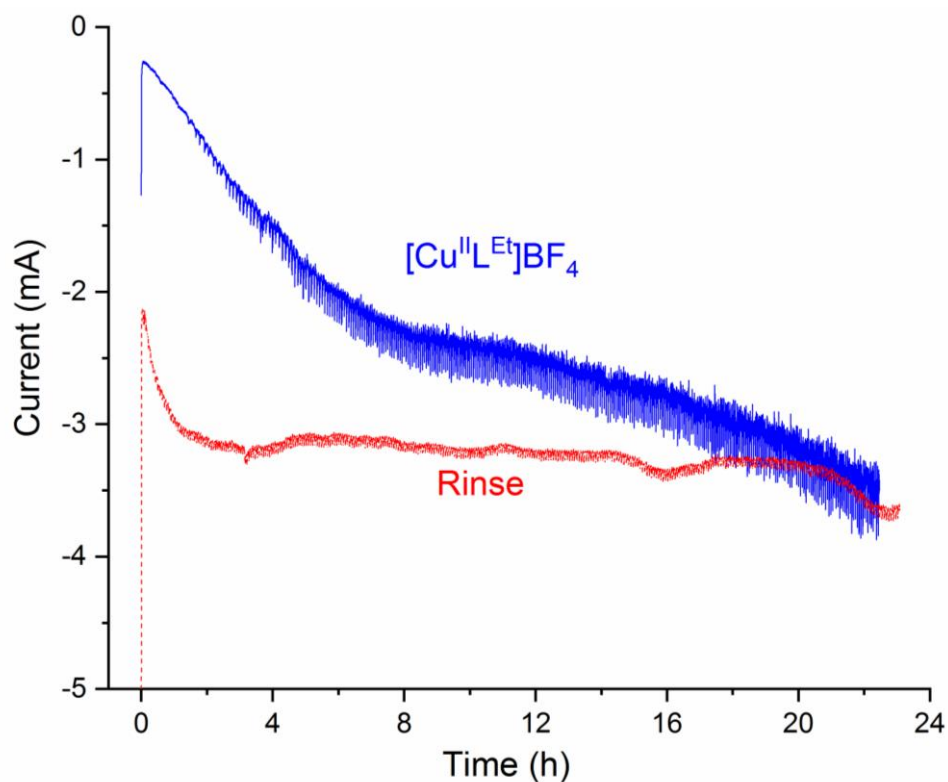


Figure S11. CPE at  $E_{\text{setpoint}} = -1.1$  V for 22 hours at  $-1.10$  V (vs Ag|AgCl) of 25 mL solution of 1M aq. phosphate buffer (pH = 7) in the presence of 0.30 mM: **1** (blue line), rinse (red line); larger cell with GCWE area  $2.7$  cm<sup>2</sup>.

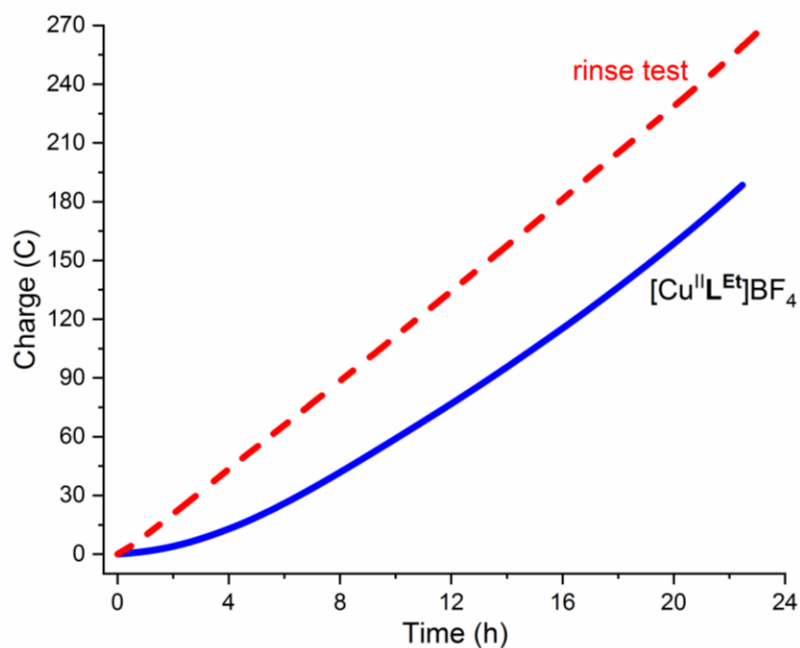


Figure S12. Charge transferred during CPE for 22 hours at  $-1.10$  V vs Ag|AgCl|sat. KCl of 25 mL solution of 1 M aq. pH 7 phosphate buffer in the presence of 0.3 mM catalyst **1**: **1** (blue), rinse (red dashes); larger cell with GCWE area  $2.7$  cm<sup>2</sup>.

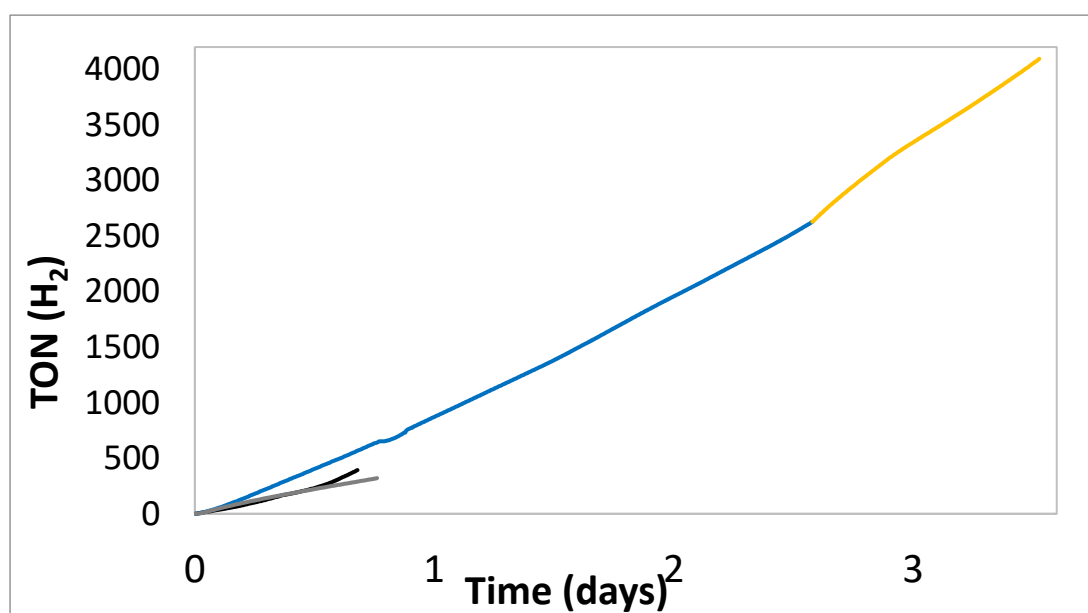


Figure S13. Hydrogen production of 0.3 mM **1** in 25 mL solution of 1 M pH 7 phosphate buffer solution, in larger cell with large plate GCWE (working A =  $2.7$  cm<sup>2</sup>), held at  $E_{\text{setpoint}} = -1.1$  V vs Ag|AgCl, shown as turnover number (TON) over time measured using gas chromatography. Blue: initial CPE runs, four consecutive experiments with no changes made in between them; Gold: heterogeneous (after rinsing the GCWE and cell and replacing the electrolyte with fresh electrolyte containing no additional **1**; i.e. rinse and repeat test); Grey: control,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ; Black: control,  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ .

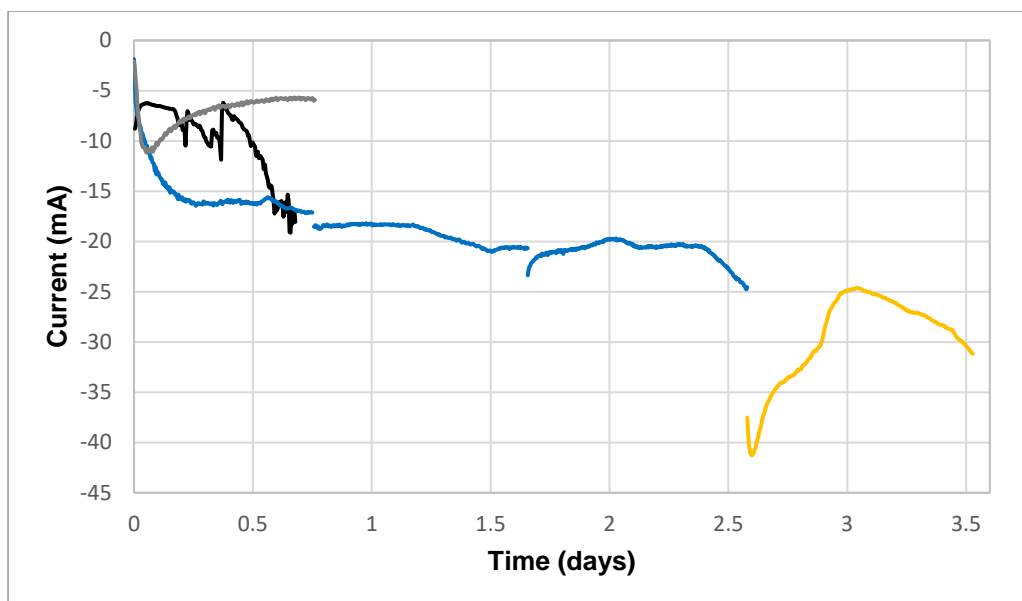


Figure S14. Current over time of 0.3 mM **1** (blue then gold),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  control (grey), or  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  control (black), in 25 mL solution of 1 M pH 7 phosphate buffer solution, with a large plate GCWE (working A = 2.7 cm<sup>2</sup>), during various CPE experiments at  $E_{\text{setpoint}} = -1.1$  V vs Ag|AgCl. Blue: initial CPE runs with **1**, then in Gold: rinse and repeat test = further CPE to test the activity of the deposit that had formed on the GCWE - after first removing the electrolyte working solution from the initial CPE run, rinsing the GCWE and cell with milli-Q H<sub>2</sub>O, and then replacing the electrolyte with fresh electrolyte containing no additional **1**.

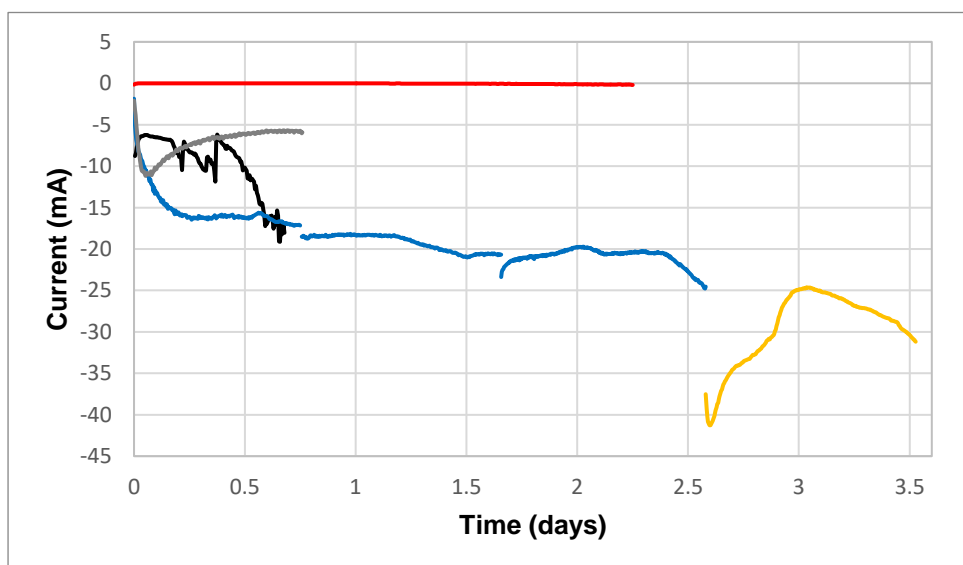


Figure S15. Current over time of 0.3 mM **1** (blue then gold),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  control (black), or  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  control (grey), in 25 mL solution of 1 M pH 7 phosphate buffer solution, with a large plate GCWE (working A = 2.7 cm<sup>2</sup>), during various CPE experiments at  $E_{\text{setpoint}} -1.1$  V vs Ag|AgCl. Blue: initial CPE runs with **1**, then in Gold: rinse and repeat test = further CPE to test the activity of the deposit that had formed on the GCWE - after first removing the electrolyte working solution from the initial CPE run, rinsing the GCWE and cell with milli-Q H<sub>2</sub>O, and then replacing the electrolyte with fresh electrolyte containing no additional **1**. Red: Blank, no catalyst added.

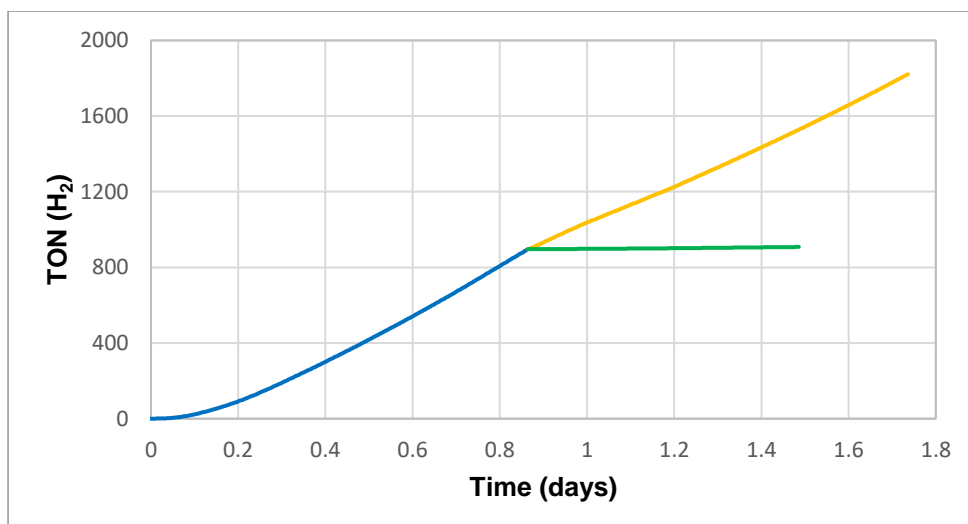


Figure S16. Hydrogen production of 0.3 mM **1** in 25 mL solution of 1 M pH 7 phosphate buffer solution, with a large plate GCWE (working A = 2.7 cm<sup>2</sup>), held at  $E_{\text{setpoint}} = -1.1$  V vs Ag|AgCl, shown as turnover number (TON) over time measured using gas chromatography. Blue: initial CPE run on **1**; Gold: rinse and repeat test = further CPE to test the activity of the deposit that had formed on the GCWE - after first removing the electrolyte working solution from the initial CPE run, rinsing the GCWE and cell with milli-Q H<sub>2</sub>O, and then replacing the electrolyte with fresh electrolyte containing no additional **1**. Green: further CPE on the electrolyte from the initial CPE, run with a fresh large GCWE.

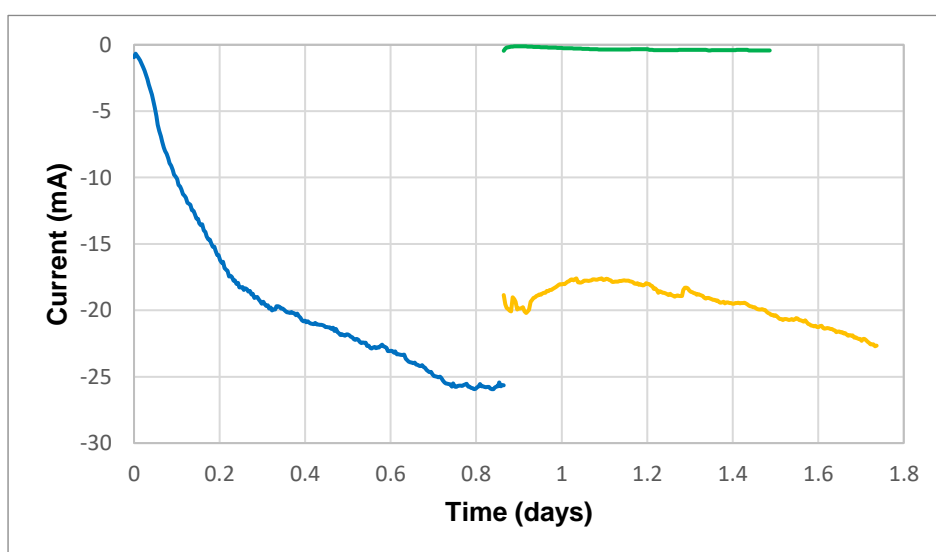


Figure S17. Current over time of 0.3 mM **1** in 25 mL solution of 1 M pH 7 phosphate buffer solution, with a large plate GCWE (working A = 2.7 cm<sup>2</sup>), during various CPE experiments at -1.1 V vs Ag|AgCl. Blue: initial CPE runs with **1**, then in Gold: rinse and repeat test = further CPE to test the activity of the deposit that had formed on the GCWE - after first removing the electrolyte working solution from the initial CPE run, rinsing the GCWE and cell with milli-Q H<sub>2</sub>O, and then replacing the electrolyte with fresh electrolyte containing no additional **1**; Green: further CPE on the electrolyte from an initial CPE run with a fresh large GCWE.

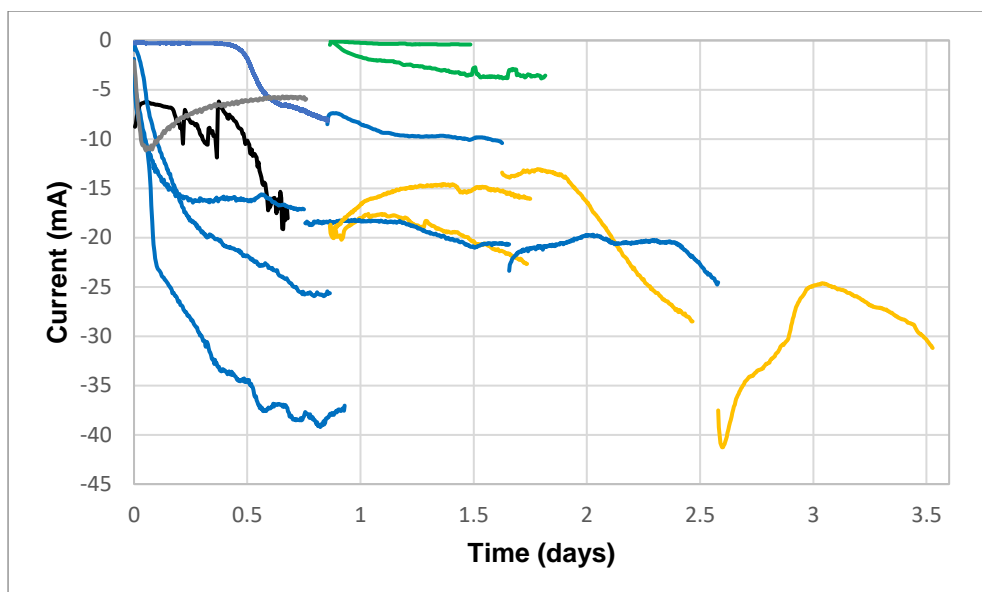


Figure S18. Current over time of 0.3 mM **1** in 25 mL solution of 1 M pH 7 phosphate buffer solution, with a large plate GCWE (working A = 2.7 cm<sup>2</sup>), during various CPE experiments at -1.1 V vs Ag|AgCl. Blue: initial CPE runs with **1**, then in Gold: rinse and repeat test = further CPE to test the activity of the deposit that had formed on the GCWE - after first removing the electrolyte working solution from the initial CPE run, rinsing the GCWE and cell with milli-Q H<sub>2</sub>O, and then replacing the electrolyte with fresh electrolyte containing no additional **1**. Green: further CPE on the electrolyte from the initial CPE, but run with a fresh large GCWE. Grey: control, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O; Black: control, Cu(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.

### S3.4 Analysis of the deposits on the larger glassy carbon working electrodes



Figure S19. Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (left), [CuL<sup>Et</sup>](BF<sub>4</sub>) (**1**) (middle), and Cu(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (right) deposits formed on the glassy carbon plate working electrodes after CPE at -1.1 V applied versus Ag|AgCl|sat. KCl, in 1M aq. phosphate buffer at pH 7.

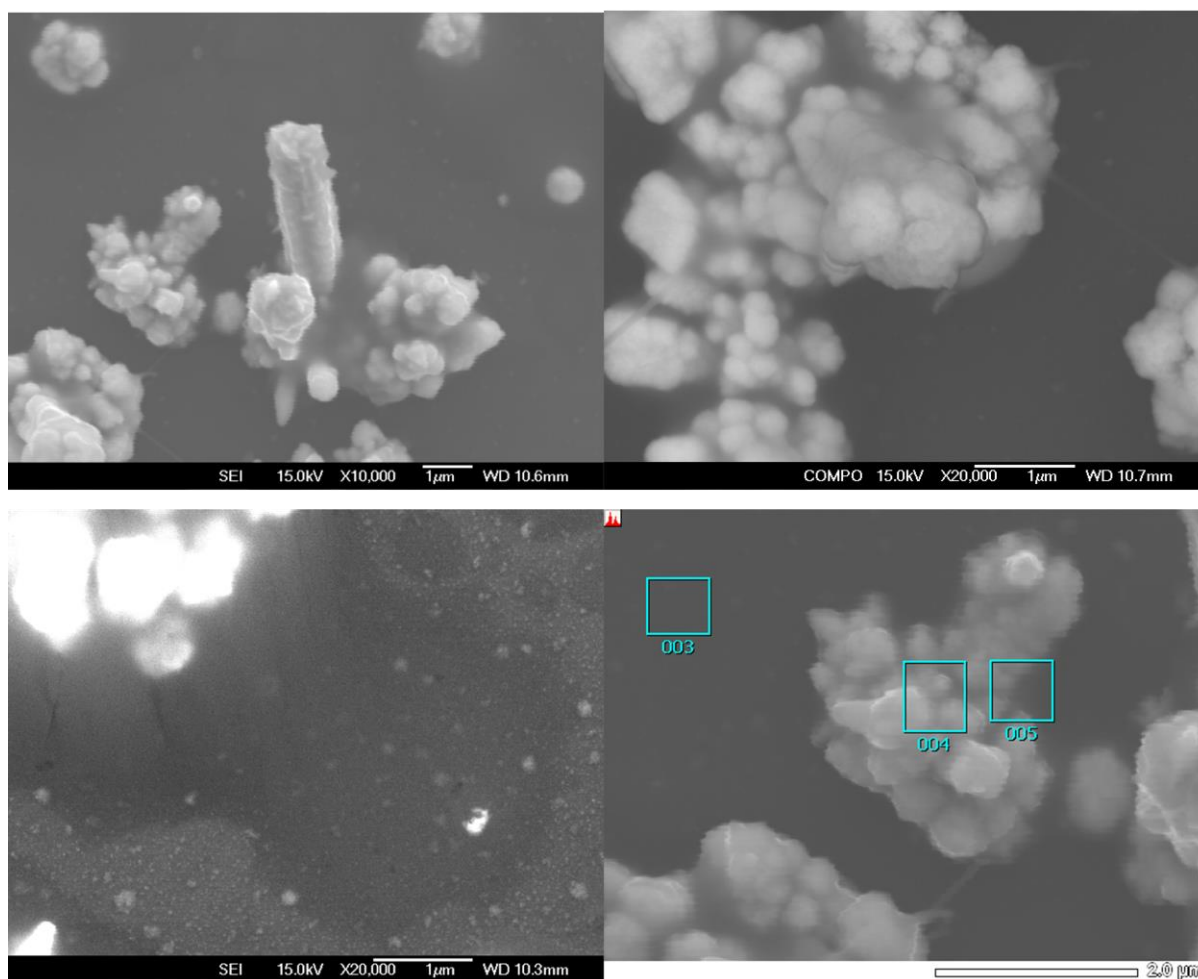


Figure S20. SEM Images of the deposited copper-based catalyst on the GCE. Top left shows one of the larger structures spread out over the GCE using secondary electron scattering; Top right shows the relatively elementally-homogeneous nature of the structures using back-scattered composition analysis; bottom left shows one of the many relatively bare spots of glassy carbon; bottom right shows the image of the analysis area used for EDS analysis, with the box analysis regions indicated.

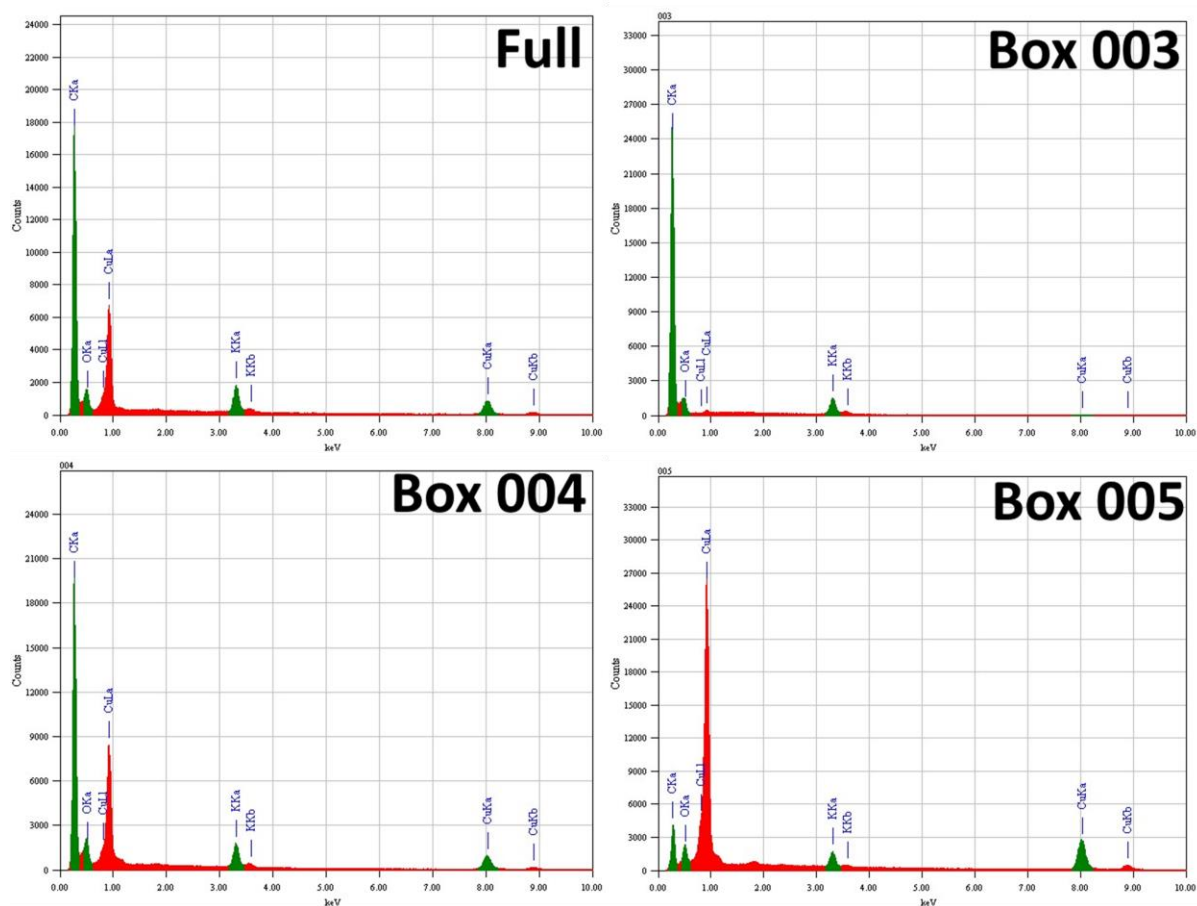


Figure S21. EDS analysis of the deposit on the GCE from the bottom right image in Figure S20. Top left is the whole area; top right is box003; bottom left is box004; bottom right is box005. The actual analysis box regions drifted to the left of where they're shown in the image in Figure S20, hence the relative compositions of 004 and 005 (ie 004 is actually partially over the GCE background, and 005 almost fully over the copper-based structure).

Table S2. Table of results from the EDS elemental analysis shown in Figure S21 of the GCWE deposit from the bottom right image in Figure S20.

Element (keV)	Relative mass % (Error %)			
	C K (0.277)	O K (0.525)	K K (3.312)	Cu K (8.040)
Full Area	65.68 (0.08)	5.00 (0.40)	4.37 (0.30)	24.94 (2.70)
Box 003	84.35 (0.07)	8.00 (0.93)	6.64 (0.53)	1.01 (5.14)
Box 004	66.16 (0.07)	5.72 (0.39)	3.87 (0.29)	24.25 (2.67)
Box 005	19.56 (0.20)	4.25 (0.30)	3.62 (0.41)	72.57 (3.39)

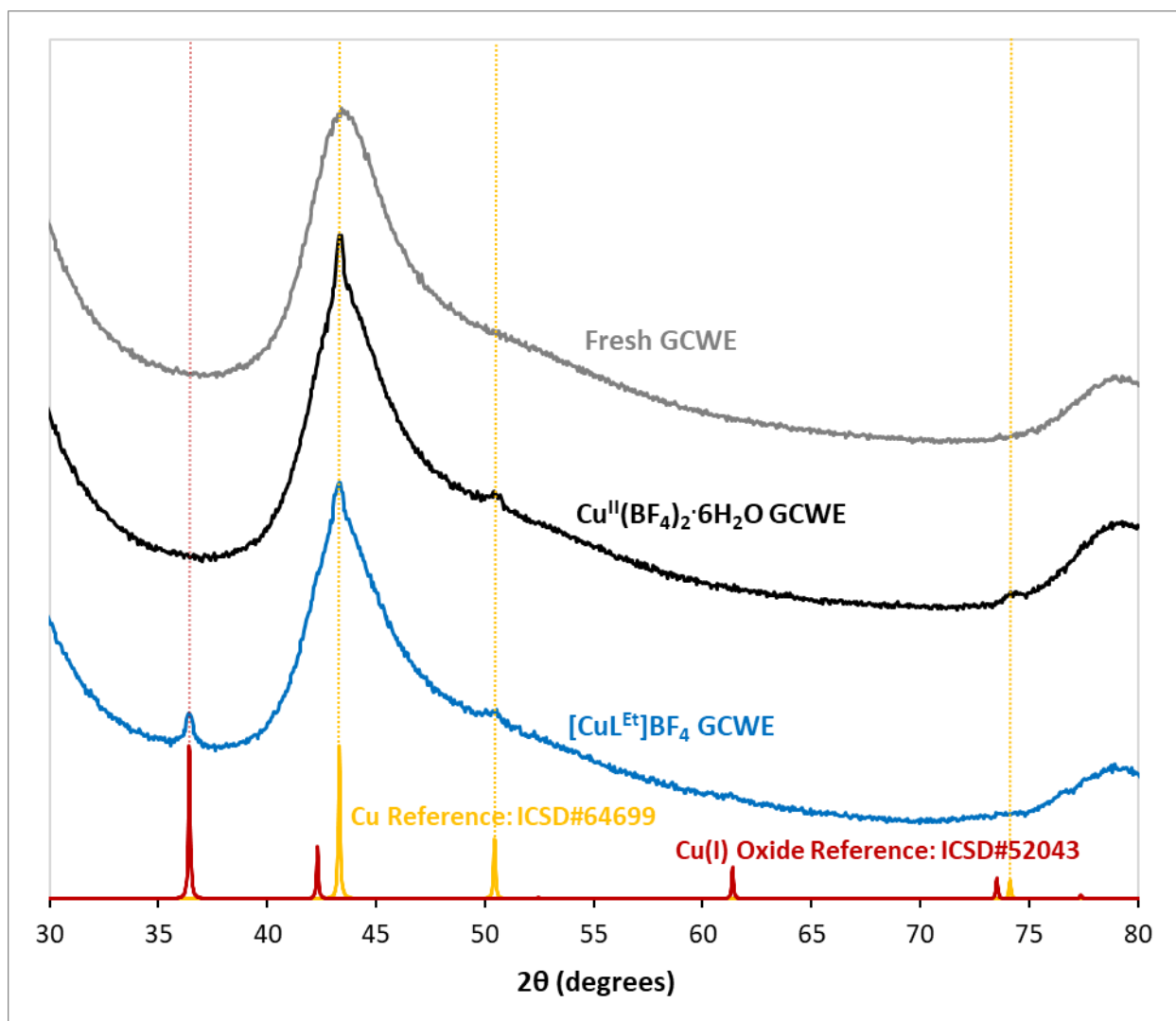


Figure S22. PXRD spectra of a freshly polished GCWE (top, grey), and of GCWEs with deposits after CPE with  $\text{Cu}^{\text{II}}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (middle, black) or  $[\text{CuL}^{\text{Et}}]\text{BF}_4$  (**1**) (bottom, blue) in 1 M aq. phosphate buffer. At the bottom are spectra calculated from ICSD database structures: Cu reference ICSD#64699 in yellow,<sup>5</sup> and Cu(I) Oxide reference ICSD#52043 in red.<sup>6</sup> The electrodes were very gently rinsed with Milli-Q water after electrolysis to remove electrolyte, so it's possible water soluble compounds were washed off.



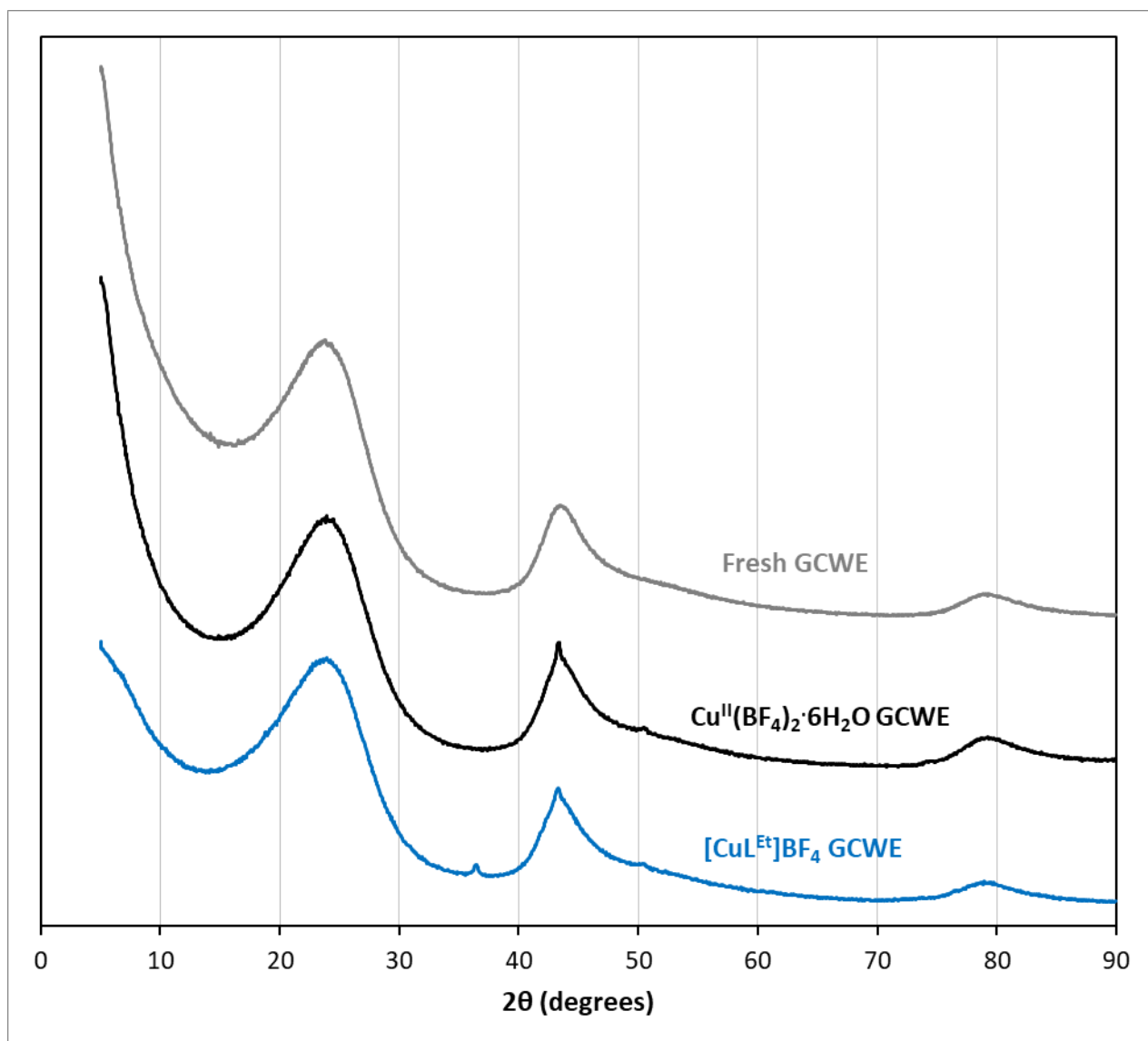


Figure S23. PXRD spectra of a freshly polished GCWE (top, grey), and of GCWEs with deposits after CPE with Cu<sup>II</sup>(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (middle, black) or [CuL<sup>Et</sup>]BF<sub>4</sub> (**1**) (bottom, blue) in 1 M aq. phosphate buffer. The electrodes were very gently rinsed with Milli-Q water after electrolysis to remove electrolyte, so it's possible water soluble compounds were washed off.

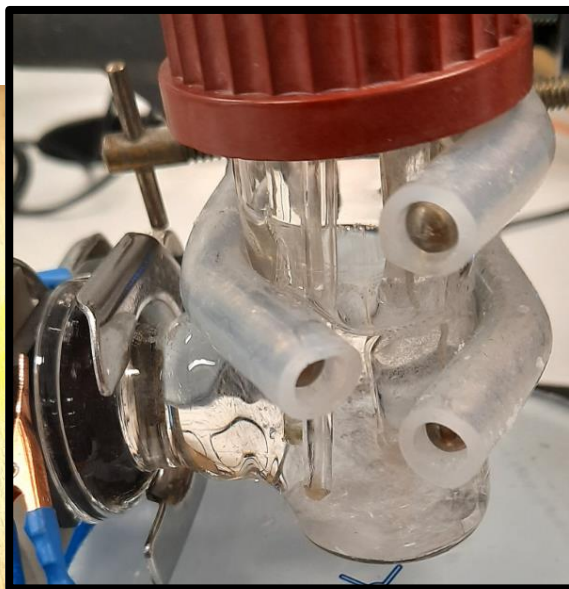
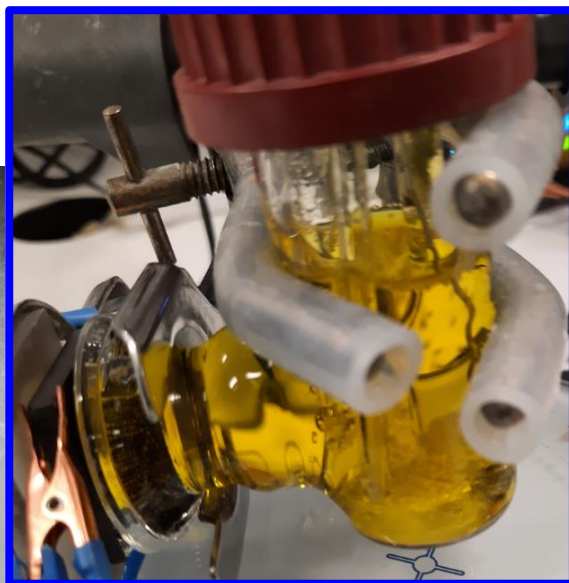


Figure S24. The larger GCWE ( $A = 2.7 \text{ cm}^2$ ) and cell setup at the start of the CPE (top) and after the CPE (bottom) using the large plate glassy carbon working electrode).

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