# Supporting Information

Mechanisms of Furfural Reduction on Metal Electrodes: Distinguishing Pathways for Selective Hydrogenation of Bioderived Oxygenates

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**I. Nafion 212 Membrane Pretreatment.**

Nafion 212 membranes were placed in a bath of 3% $H_2O_2$ solution heated to 80 °C for 1 h under magnetic stirring to remove organic impurities. Then, the membranes were rinsed in DI water and placed in a DI water bath at 100 °C for 2 h under magnetic stirring. Next, the membranes were placed in bath of 0.5 M $H_2SO_4$ at 80 °C for 1 h under magnetic stirring. Finally, the membranes were rinsed in DI water at 80 °C and stored in DI water.

## II. Product Separation, Identification, and Quantification.

Liquid aliquots were taken from the cathode electrolyte and gas trap and diluted in water or $CH_3CN$ for product analysis with an HPLC (Agilent Technologies 1260) equipped with a variable wavelength detector (VWD, G1314B) at 210 nm. Additionally, the reactor and components were rinsed in deionized water after completion of the reaction to collect residual species. The column (Phenomenex Inc., Gemini C18, 3 μm 110 Å) was operated at 45 °C with a binary gradient method containing water and $CH_3CN$ at 0.6 ml min$^{-1}$ flow rate. The $CH_3CN$ fraction was increased from an initial 15% (v/v) to 60% during 5–15 min, and then was decreased to 15% from 17–24 min. Peaks for FA, furfural and MF eluded at 10.8, 12.7, and 22.7 min, respectively. Hydrofuroin (1,2-di(furan-2-yl)ethane-1,2-diol) eluded at two different retention times (14.0 and 16.3 min). Products were identified by comparison with authentic samples prepared in 25% or 100% $CH_3CN$ solutions, except for hydrofuroin which was identified by fraction collection combined with $^1H$ NMR and MS analysis (see pages **S8-S10**).

A gas chromatograph (SRI Instrument 8610C MG#3) equipped with HaySep D column and MolSieve 5 Å columns was used for analyzing $H_2$ gas. A schematic of the gas flow path for preparative electrolysis experiments is shown in Figure S1. A thermal conductivity detector (TCD) was used to detect $H_2$ with Ar (Airgas, 99.999%) as the carrier gas. $H_2$ was calibrated with a commercial gas mixture (Matheson Tri Gas MicroMAT 14) under operating conditions. Gas aliquots were sampled every 12 minutes with the first injection starting approximately four minutes after the reaction initialized. The amount of gas evolved from D-electrolytes was approximated by assuming 100% $D_2$ product, and quantified using a calibration constant derived from the $H_2$ calibration after being adjusted for the different thermal conductivities of $H_2$ (1828 W cm$^{-1}$ K$^{-1}$) and $D_2$ (1372 W cm$^{-1}$ K$^{-1}$) at 293 K.[1]

Reference:

(1) Dean, J. A., *Lange's Handbook of Chemistry*. 15$^{th}$ ed.; McGraw-Hill, Inc.: New York, 1999.

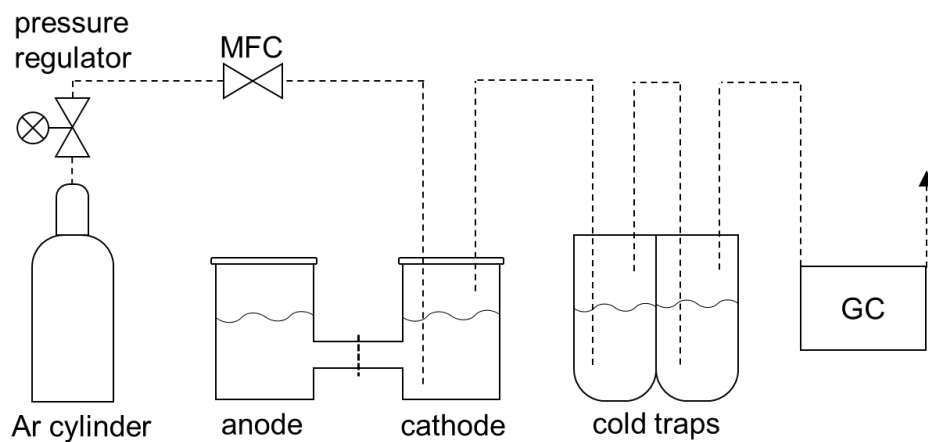## II. Product Separation, Identification, and Quantification (cont.)



**Figure S1.** Schematic of gas flow path for preparative electrolysis experiments. MFC = mass flow controller, GC = gas chromatograph.

### III. Calculations of Selectivity and Faradaic Efficiency.

Faradaic efficiency (FE) to liquid product $i$ ($i$ = MF, FA, hydrofuroin) was calculated by:

$$FE_i = \frac{N_i z_i F}{Q} \cdot 100\% \qquad (S1)$$

where $N_i$ is the number of moles of product $i$, $z_i$ is the number of electrons transferred per molecule of product ($z$ = 4 for MF and 2 for FA and hydrofuroin), $F$ is the Faraday constant (96,485.3 C mol$^{-1}$), and $Q$ is the total charge in coulombs transferred in the external circuit as measured by the electrochemical workstation. Product selectivity ($S_i$) was calculated using eqs S2–S4:

$$S_{FA} = \frac{N_{FA}}{N_{f,0}-N_{f,t}} \cdot 100\% \qquad (S2)$$

$$S_{MF} = \frac{N_{MF}}{N_{f,0}-N_{f,t}} \cdot 100\% \qquad (S3)$$

$$S_{hydrofuroin} = \frac{2N_{hydrofuroin}}{N_{f,0}-N_{f,t}} \cdot 100\% \qquad (S4)$$

where $n_{f,0}$ and $n_{f,t}$ are the initial and final amounts of furfural (moles).

The incremental amount of evolved H$_2$ ($n_{H_2}$, moles) was calculated by eq S5:

$$n_{H_2} = C_{H_2} \cdot 10^{-6} \cdot \frac{PV}{RT} \qquad (S5)$$

where $C_{H_2}$ is the concentration (ppm) of H$_2$ measured by GC, $P$ is atmospheric pressure ($P$ = 1.013×10$^5$ Pa), $V$ is the volume of GC sampling loop ($V$ = 1 cm$^3$), $R$ is the gas constant ($R$ = 8.314 J mol$^{-1}$ K$^{-1}$), $T$ is absolute temperature ($T$ = 293 K). The instantaneous faradaic efficiency of H$_2$ ($fe_{H_2}$) was calculated by eq S6:

$$fe_{H_2} = \frac{n_{H_2} z_{H_2} F}{\Delta Q} \cdot 100\% \qquad (S6)$$

where $z_{H_2}$ is the number of electrons transferred per molecule of H$_2$ ($z_{H_2}$ = 2), $\Delta Q$ is the incremental charge transferred during the time ($t$) required to fill the sampling loop. The time to fill the sample loop ($t$) was determined as: $t = \frac{V}{flow\ rate} = \frac{1\ cm^3}{208\ cm^3/min} \cdot \frac{60\ s}{1\ min} =$ 0.288 $s$. Overall faradaic efficiency to H$_2$ ($FE_{H_2}$) was determined as the average of $fe_{H_2}$ values measured throughout the reaction.

**III. Calculations of Selectivity and Faradaic Efficiency (cont.)**

The total amount of $H_2$ evolved ($N_{H2}$) during a reaction was estimated according to eq S7:

$$N_{H2} = \frac{FE_{H_2}Q}{z_{H_2}F} \tag{S7}$$

**IV. Additional Details of Hydrofuroin Identification and Quantification.**

A fraction of hydrofuroin was collected using an HPLC (Waters Alliance) equipped with an automatic fraction collector (Waters Fraction Collector III). The same column conditions and pumping method were used as described in Section II, except that 0.1% formic acid (Optima LC/MS grade, Fisher) was added to the mobile phases. The collected fractions were dried in a vacuum oven and then dissolved in water and $CH_3CN$ and analyzed with a Waters Acquity H-Class ultra-performance liquid chromatography (UPLC) instrument equipped with a mass detector (Waters ACQUITY QDa) and operated in positive ion mode. Both fractions were also dried in a vacuum oven and reconstituted in acetonitrile-$d_3$ (99.8 atom%, Cambridge Isotope Laboratories, Inc.) for ^{1}H NMR analysis with a Bruker 600 MHz NMR spectrometer (AVIII-600). Dimethyl sulfoxide (DMSO, 99.9%, Fisher Scientific) was added as an internal standard to determine the concentration of hydrofuroin. The same samples were analyzed by HPLC (as described in Section II) to acquire quantitative calibration curves at 210 nm on the basis of the concentrations determined by ^{1}H NMR. Those calibrations curves were used for quantitation of hydrofuroin used throughout the main text.

**1,2-di(furan-2-yl)ethane-1,2-diol (Hydrofuroin-1)**
^{1}H NMR (600 MHz, CD$_3$CN) δ 7.48 (dd, *J* = 1.9, 0.8 Hz, 2H), 6.41 (dd, *J* = 3.2, 1.8 Hz, 2H), 6.34 (dd, *J* = 3.2, 0.8 Hz, 2H), 4.87 (d, *J* = 3.2 Hz, 2H), 3.56 (s, 2H).
ESI-MS: $[M + H - H_2O]^+$ calculated m/z 177, found m/z 177.

**1,2-di(furan-2-yl)ethane-1,2-diol (Hydrofuroin-2)**
^{1}H NMR (600 MHz, CD$_3$CN) δ 7.41 (dd, *J* = 1.8, 0.9 Hz, 2H), 6.33 (dd, *J* = 3.2, 1.8 Hz, 2H), 6.25 (dd, *J* = 3.2, 0.9 Hz, 2H), 4.88 (d, *J* = 2.5 Hz, 2H), 3.81 (s, 2H)
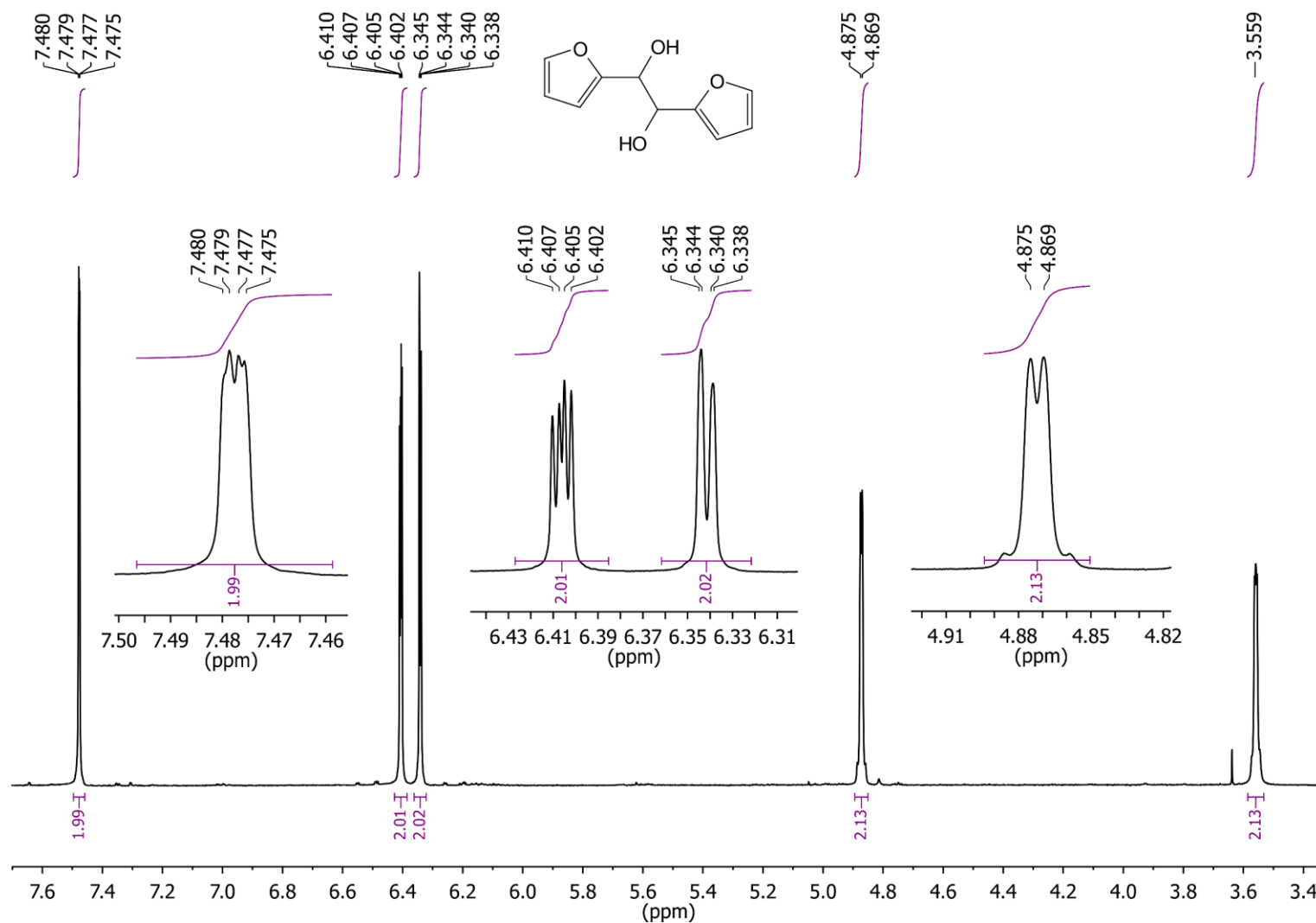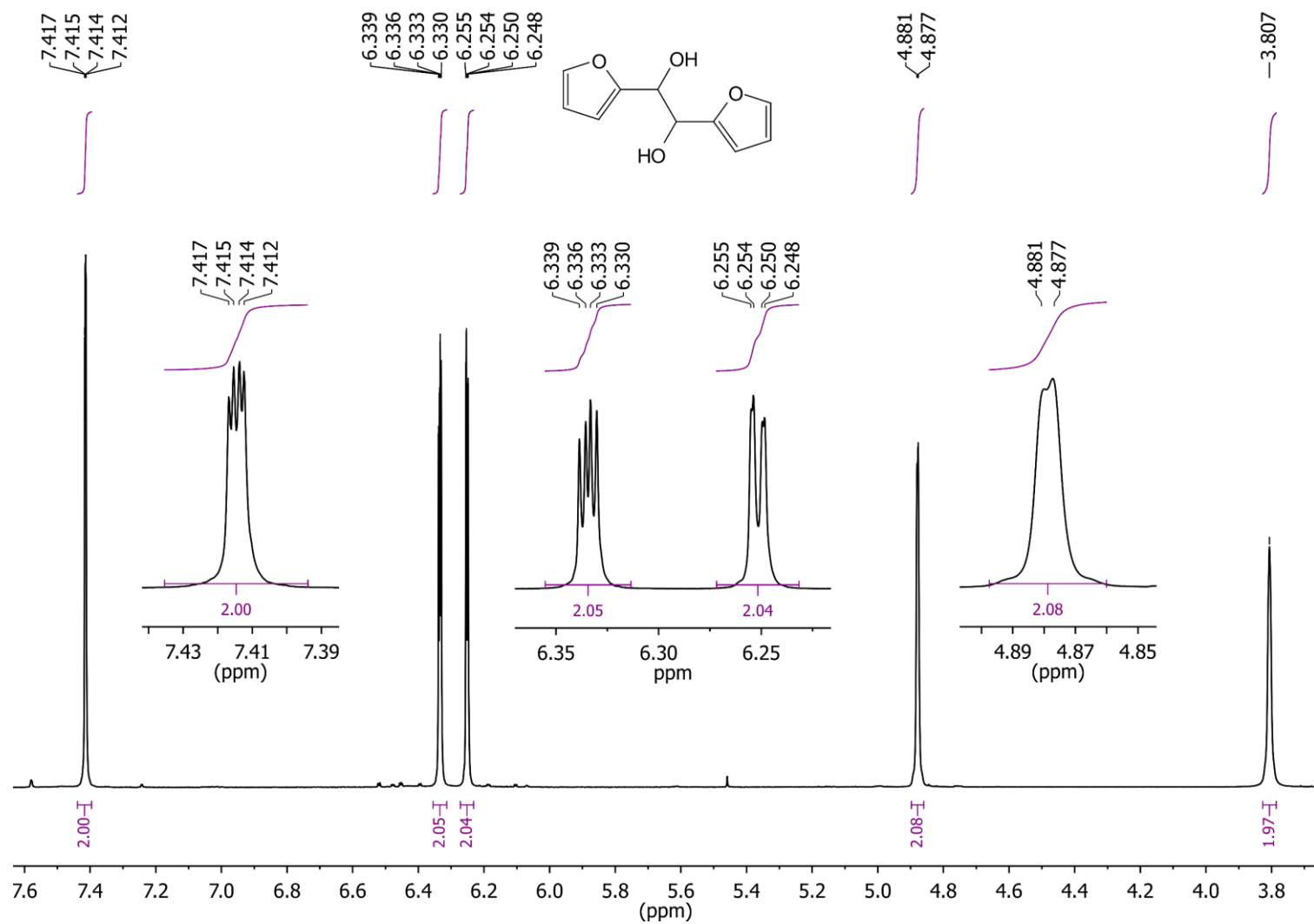ESI-MS: $[M + H - H_2O]^+$ calculated m/z 177, found m/z 177.

# $^1$H-NMR Spectra of Hydrofuroin-1



S9

# $^1$H-NMR Spectra of Hydrofuroin-2

## V. Additional Preparative Electrolysis Data.

**Table S1. Preparative electrolysis of 0.01 M furfuryl alcohol.[a]**

| entry | electrode | $E$ (V) | pH | $j_{avg}$ (mA cm$^{-2}$) | FA loss (mol%) | MF detected (μmol h$^{-1}$) | $FE_{H2}$ (%) | $FE_{MF}$ (%) |
|-------|-----------|---------|-----|--------------------------|-----------------|------------------------------|----------------|----------------|
| 1 | Cu | −0.55 | 0.5 | −6.7 | 9.6 | 1.28 | 100.2 | 0.26 |
| 2 | Cu[b] | OCP | 0.5 | 0 | 10.5 | 0.02 | - | - |
| 3 | none[c] | n/a | 0.5 | 0 | 11.7 | 0.03 | - | - |
| 4 | Cu | −0.55 | 3.0 | −1.7 | 1.8 | 0.09 | 101.4 | 0.06 |

[a] Conditions: reaction duration: 1 h. [b] control test with identical conditions to entry 1 except at open circuit potential conditions (OCP). [c] control test with no working electrode present.

**Table S2. Preparative electrolysis of 0.05 M furfural at various applied potentials at pH 0.5.[a]**

| $E$ (V) | electrode area (cm$^2$) | duration (min) | $S_{MF}$ (%) | $S_{FA}$ (%) | $S_{hydrofuroin}$ (%) | conversion (%) |
|---------|--------------------------|-----------------|---------------|---------------|------------------------|-----------------|
| −0.45 | 5 | 164 | 52.8 | 13.0 | 2.2 | 49.6 |
| −0.50 | 5 | 63 | 67.8 | 16.3 | 1.6 | 34.8 |
| −0.55 | 5 | 23 | 66.4 | 9.6 | 2.4 | 33.9 |
| −0.60 | 2.5 | 28 | 71.2 | 9.0 | 2.5 | 28.6 |
| −0.65 | 2.5 | 7 | 70.1 | 5.0 | 1.9 | 16.6 |

[a] Charge transferred 144 C.

## V. Additional Preparative Electrolysis Data (cont.)

**Table S3. Preparative electrolysis of furfural at various initial furfural concentrations at pH 0.5.**[a]

| initial concentration (M) | $Q$ (C) | $S_{MF}$ (%) | $S_{FA}$ (%) | $S_{hydrofuroin}$ (%) | conversion (%) |
|---|---|---|---|---|---|
| 0.01 | 89.2 | 70.1 | 11.3 | 0.8 | 36.9 |
| 0.05 | 181.8 | 68.6 | 10.4 | 1.6 | 37.9 |
| 0.1 | 189.7 | 55.2 | 12.1 | 5.3 | 27.4 |
| 0.2 | 142.3 | 32.7 | 13.4 | 13.6 | 14.6 |

[a] Conditions: $E = -0.55$ V, reaction duration: 30 min.

**Table S4. Preparative Electrolysis of 0.05 M furfural with various electrolyte pH.**[a]

| pH | $Q$ (C) | $S_{MF}$ (%) | $S_{FA}$ (%) | $S_{hydrofuroin}$ (%) | conversion (%) |
|---|---|---|---|---|---|
| 0.5[b] | 283.2 | 66.8 | 11.0 | 1.8 | 57.9 |
| 1.4 | 215.0 | 53.2 | 18.6 | 3.9 | 52.1 |
| 2 | 98.6 | 31.4 | 26.0 | 5.5 | 36.9 |
| 3[b] | 31.1 | 15.4 | 39.6 | 6.2 | 16.4 |

[a] Conditions: $E = -0.55$ V, reaction duration: 1 h. [b] values for pH 0.5 and 3.0 are averages of three experiments (see Table S6).

## V. Additional Preparative Electrolysis Data (cont.)

**Table S5. Preparative electrolysis of 0.05 M furfural on Cu-MPA, Cu-MBT, and Cu-MDA electrodes.**[a]

| pH | thiol | Exp. | $Q$ (C) | $N_{MF}$ (µmol) | $N_{FA}$ (µmol) | $N_{hydrofuroin}$ (µmol) | $N_{H2}$ (µmol) |
|---|---|---|---|---|---|---|---|
| | | 1 | 30.4 | 1.82 | 22.7 | 4.24 | 119 |
| | | 2 | 29.6 | 1.77 | 23.1 | 4.16 | 114 |
| 0.5 | MPA | 3 | 26.4 | 1.68 | 21.4 | 3.85 | 104 |
| | | average | 28.8 | 1.76 | 22.4 | 4.08 | 112 |
| | | σ | 2.1 | 0.07 | 0.9 | 0.21 | 7.7 |
| | | 1 | 10.1 | 0.088 | 2.81 | 6.35 | 33.5 |
| | | 2 | 6.7 | 0.028 | 2.02 | 4.13 | 20.1 |
| 0.5 | MBT | 3 | 11.0 | 0.086 | 3.17 | 6.61 | 35.9 |
| | | average | 9.3 | 0.067 | 2.66 | 5.70 | 29.9 |
| | | σ | 2.3 | 0.034 | 0.59 | 1.36 | 8.5 |
| 0.5 | MDA | 1 | 1.57 | 0.21 | 0.26 | 0.12 | 4.56 |
| | | 1 | 22.2 | 4.80 | 12.4 | 3.75 | 86.4 |
| | | 2 | 22.0 | 5.28 | 11.3 | 4.05 | 85.7 |
| 3.0 | MPA | 3 | 28.2 | 9.98 | 16.7 | 5.96 | 96.1 |
| | | average | 24.2 | 6.69 | 13.5 | 4.59 | 89.4 |
| | | σ | 3.5 | 2.86 | 2.9 | 1.20 | 5.8 |
| | | 1 | 4.1 | 0.033 | 2.05 | 3.30 | 9.96 |
| | | 2 | 6.0 | 0.035 | 2.22 | 2.91 | 19.5 |
| 3.0 | MBT | 3 | 5.1 | 0.029 | 2.19 | 3.49 | 14.5 |
| | | average | 5.1 | 0.032 | 2.15 | 3.24 | 14.7 |
| | | σ | 0.9 | 0.003 | 0.09 | 0.30 | 4.8 |
| 3.0 | MDA | 1 | 0.97 | 0.106 | 0.292 | 1.250 | 0.080 |

[a] Conditions: $E = -0.55$ V, thiol concentration: 0.25 mM, reaction duration: 1 h.

## V. Additional Preparative Electrolysis Data (cont.)

**Table S6. Preparative electrolysis of 0.05 M furfural on Cu.**[a]

| pH | Exp. | Q (C) | $N_{MF}$ (μmol) | $N_{FA}$ (μmol) | $N_{hydrofuroin}$ (μmol) | $N_{H2}$ (μmol) | $FE_{MF}$ (%) | $FE_{FA}$ (%) | $FE_{hydrofuroin}$ (%) | $FE_{H2}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 271.5 | 399 | 65.9 | 5.05 | 436 | 56.7 | 4.7 | 0.4 | 31.0 |
| | 2 | 310.0 | 395 | 66.8 | 5.59 | 606 | 49.2 | 4.2 | 0.3 | 37.7 |
| 0.5 | 3 | 268.1 | 379 | 60.9 | 5.46 | 438 | 54.6 | 4.4 | 0.4 | 31.5 |
| | average | 283.2 | 391 | 64.5 | 5.37 | 493 | 53.5 | 4.4 | 0.4 | 33.4 |
| | σ | 23.3 | 11 | 3.2 | 0.29 | 97.4 | 3.9 | 0.3 | 0.0 | 3.7 |
| | 1 | 32.0 | 28.5 | 62.9 | 5.18 | 22.1 | 34.4 | 37.9 | 3.1 | 13.3 |
| | 2 | 29.6 | 25.1 | 64.1 | 5.45 | 22.1 | 32.7 | 41.7 | 3.5 | 14.4 |
| 3.0 | 3 | 31.7 | 21.8 | 66.2 | 4.61 | 35.7 | 26.5 | 40.3 | 2.8 | 21.7 |
| | average | 31.1 | 25.2 | 64.4 | 5.08 | 26.6 | 31.2 | 40.0 | 3.2 | 16.5 |
| | σ | 1.3 | 3.4 | 1.7 | 0.42 | 7.9 | 4.1 | 1.9 | 0.4 | 4.6 |

[a] Conditions: $E$ = –0.55 V, thiol concentration: 0.25 mM, reaction duration: 1 h.

**V. Additional Preparative Electrolysis Data (cont.)**
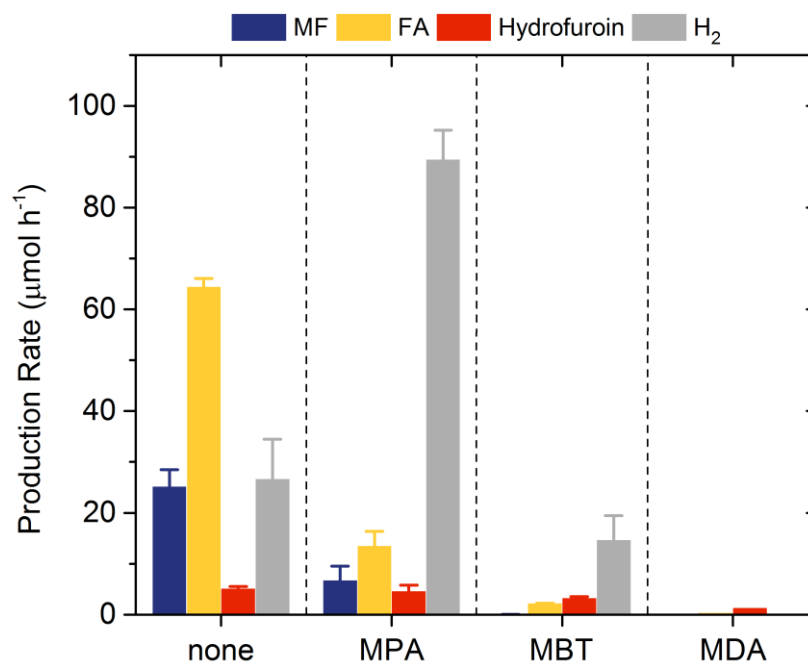


**Figure S2.** Observed production rates during preparative electrolysis of furfural on Cu, Cu-MPA, Cu-MBT, and Cu-MDA electrodes. Conditions: 0.05 M furfural and 0.25 mM of the indicated organothiol, pH 3.0 electrolyte, 1 h; $E = -0.55$ V.
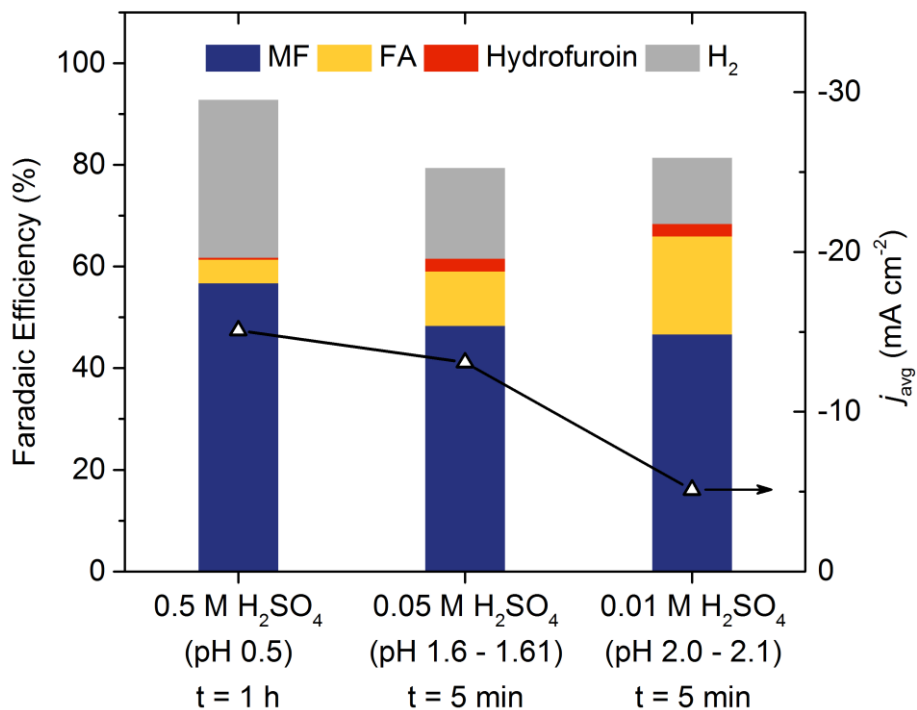
**V. Additional Preparative Electrolysis Data (cont.)**



**Figure S3**. Preparative electrolysis of furfural with electrolytes of various sulfuric acid ($H_2SO_4$) concentrations. The reaction duration was kept short for the 0.05 M and 0.01 M conditions to minimize changes in bulk electrolyte pH during electrolysis. Conditions: 0.05 M furfural, $E = -0.55$ V.
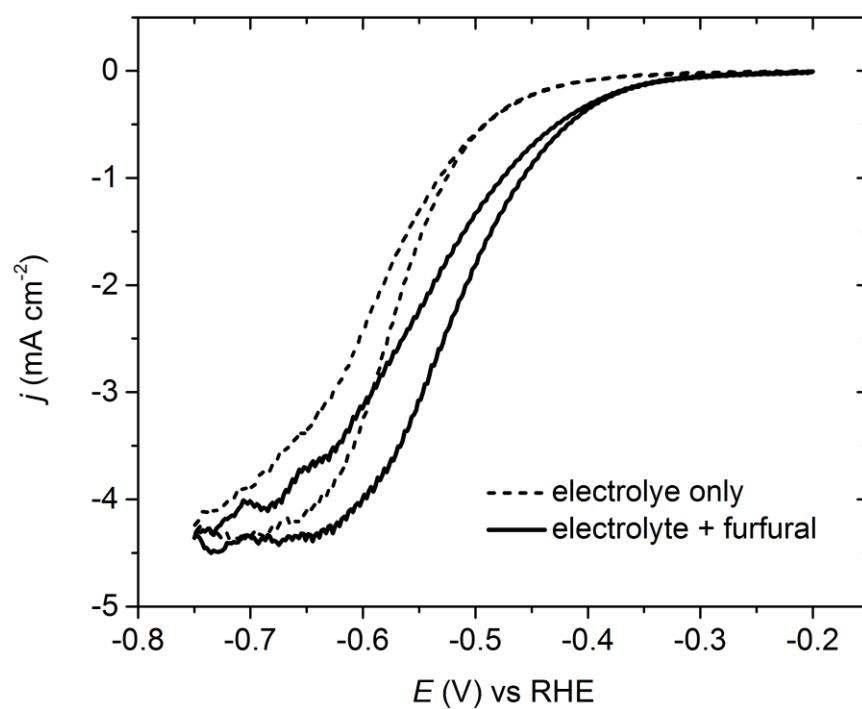
## VI. Additional RDE Voltammetry



**Figure S4.** Cyclic voltammograms on a 5.0 cm$^2$ Cu foil electrode under actual electrolysis conditions: sweep rate 50 mV s$^{-1}$, magnetic stirring at 1000 rpm setting, pH 3.0 electrolyte with or without addition of 0.05 M furfural.
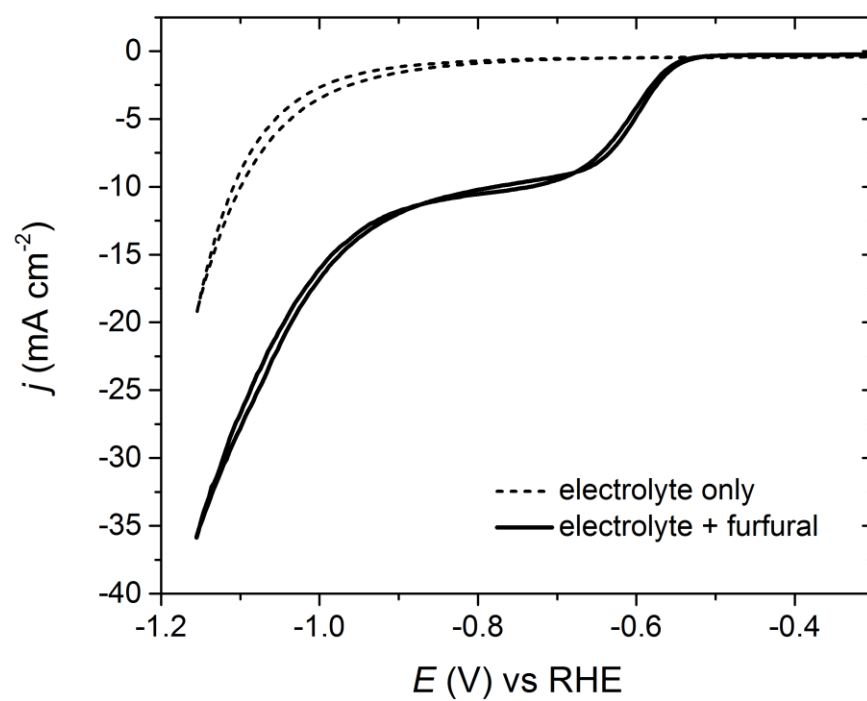
**Figure S5.** Cyclic voltammograms on a Pb RDE (5.0 mm diameter, Pine Research Instrumentation) in pH 0.5 electrolyte with or without addition of 0.05 M furfural.