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Electrocatalytic Hydrogenation of Furfural with Improved Activity and Selectivity at the Surface of Structured Copper Electrodes

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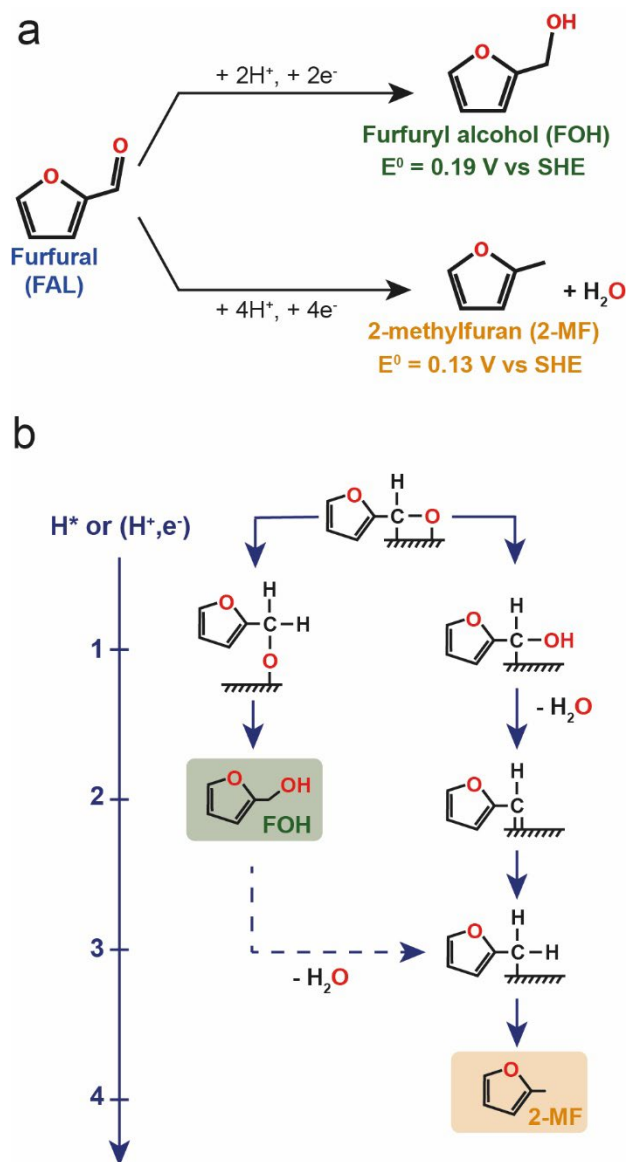
1 **ABSTRACT**

2 Furfural is a pivotal renewable platform molecule obtained from the chemical breakdown of
3 hemicellulose. While it has traditionally been valorized to value-added chemicals through catalytic
4 hydrogenation in biorefineries, its direct electrocatalytic hydrogenation presents attractive
5 advantages. This article describes the significant improvements brought by the structuring of
6 copper cathodes applied to this process, in terms of activity and selectivity. We show that
7 structured electrodes are capable of converting furfural to furfuryl alcohol with 100% selectivity
8 at potentials as high as - 0.2 V vs. the reversible hydrogen electrode (RHE) in neutral conditions
9 (pH 7.0). Moreover, the same electrode can selectively generate either furfuryl alcohol or 2-
10 methylfuran in acidic conditions (pH 1.0), depending on applied potential and temperature. We
11 further show the existence of optimal voltage-temperature conditions for the efficient conversion
12 of furfural to furfuryl alcohol or 2-methylfuran, highlighting the delicate influence of operating
13 conditions on the selectivity of furfural reduction, in competition with the hydrogen evolution
14 reaction in aqueous electrolytes. These performances are attributed to the resilience of Cu (I)
15 species under operating conditions and their likely contribution to the electrocatalytic active site,
16 as revealed by quasi-in-situ photoelectron spectroscopy.

17 **INTRODUCTION**

18 The defossilization of the chemical industry requires both to transition away from fossil fuels as a
19 source of energy and to replace petrochemical processes with alternatives based on renewable
20 carbon resources. In this context, the valorization of lignocellulose, the most abundant organic
21 substance on the planet, is of high interest. To achieve its efficient chemical valorization, most

22 common biorefinery models are built around a multi-stage scheme involving the separation of
23 lignin, cellulose, and hemicellulose (primary refining), followed by the breakdown of these
24 polymeric compounds into small platform molecules (secondary refining) and finally the chemical
25 upgrading of these platform compounds into value-added chemical feedstock or fuel.¹ Among
26 these platform molecules, furfural (FAL) has been identified as a promising substrate for the
27 production of strategic targets in the value chains of the chemical industry.² One attractive way to
28 renewably perform FAL valorization is to use decarbonized electricity to directly power its
29 electrocatalytic reduction, with the advantages of (i) mild temperature and pressure conditions, (ii)
30 the use of water as a source of hydrogen rather than H₂, (iii) a potentially more efficient use of
31 renewable electricity compared to electrically heated reactors, and (iv) the possibility of combining
32 FAL reduction with an oxidation process of interest in a single reactor. These concepts can in fact
33 be generalized for the development of electrochemical biorefineries for the sustainable production
34 of fuels and chemicals.^{3,4} Regarding FAL electroreduction, two main products are usually
35 identified (see **Figure 1**): furfuryl alcohol (FOH), produced by the reaction of FAL with two
36 protons and two electrons, and 2-methylfuran (2-MF), generated from the reaction of FAL with
37 four electrons and four protons accompanied by the elimination of a water molecule. Finally, a
38 third product is observed for higher concentrations of FAL: the hydrofuroin generated by the
39 reductive coupling of two FAL molecules involving two electrons and two protons (not shown
40 here). This latter product has traditionally been considered as less desirable, although it was
41 recently proposed as a valuable precursor for the development of jet and rocket fuel.^{5,6} **Figure 1b**
42 describes the commonly accepted elementary steps involved in the reaction mechanism for the
43 electrocatalytic reduction of FAL.⁷ There remains a debate whether these steps occur through an



44 **Figure 1.** a) Electrochemical reduction pathways of furfural into furfuryl alcohol or 2-methylfuran.
 45 For each product the corresponding standard reduction potential is reported vs. the standard
 46 hydrogen electrode (SHE) from reference 8 where it was calculated from the corresponding Gibbs
 47 free energy of formation. b) Corresponding proposed mechanisms involving either the chemical
 48 transfer of an adsorbed H (H^*) generated by a Volmer step (ECH mechanism) or a proton-coupled
 49 electron transfer (H^+ , e^-), or PCET, mechanism. The step corresponding to the dotted arrow,
 50 leading to the conversion of FOH to 2-MF is not observed under typical electrocatalytic conditions.
 51
 52 electrochemical hydrogenation (ECH) pathway⁹ or through a proton-coupled electron transfer
 53 (PCET) pathway.⁷ While the first report on the electrocatalytic reduction of FAL dates back to

54 1939,¹⁰ it has gained a renewed and rapidly growing interest over the last decade and has been the
55 object of several recent perspective and review articles.¹¹⁻¹⁴ Early studies described the
56 electrochemical reduction of FAL in aqueous media (sometimes containing methanol) inside H-
57 cell setups, on a range of metal electrodes – Pt, Ni, Cu, Al, and stainless steel.¹⁵⁻¹⁸ In more recent
58 studies, Cu has been mostly favored due to its superior activity and selectivity.^{9,19-27} These works
59 collectively show that, on bare copper, FAL is selectively converted to FOH under neutral
60 conditions, at applied potentials more negative than - 0.5 V vs. RHE, while 2-MF is the main
61 product under highly acidic conditions at potentials more negative than – 0.45 V vs. RHE (see
62 **Table S3** for a collection of recent data from the literature). In these studies, the concentration of
63 FAL was in the 0.01 – 0.1 M range, with the appearance of hydrofuroin as a secondary product at
64 higher concentrations. Moreover, modifying the copper active site has shown promising
65 improvement in performance. Indeed, employing single-atom copper sites allowed switching from
66 selectively producing FOH at - 0.75 V vs. RHE to selectively producing 2-MF at - 0.9 V vs. RHE
67 in a pH 5 acetate buffer.²⁴ Moreover, using bimetallic CuPd nanoparticles produced a faradaic
68 efficiency (FE) of 75% for 2-MF in the presence of 0.04 M FAL in 0.1 M acetic acid (pH 2.9) at
69 - 0.58 V vs. RHE, with a 100% selectivity (the remaining FE corresponding to H₂ evolution).²⁵
70 Similarly, Ni was employed to modulate the electrocatalytic properties of Cu.²⁷ Finally, a recent
71 study showed the ability of CuO nanowires grown on Cu to reduce FAL to FOH with a much
72 lower overpotential than Cu in 1M phosphate buffer (pH not reported) + 0.05 M FAL.²⁶ The
73 authors report the selective conversion of FAL to FOH at potentials as high as – 0.2 V vs. RHE,
74 and they attribute this performance to the resilience of some Cu(I) centers to the reductive
75 operating conditions. Finally, it is worth mentioning that some research has been done to
76 successfully implement electrocatalytic reduction of FAL to FOH in flow devices using Pd⁸ and

77 Cu²⁸ as cathode materials. Overall, despite significant progress achieved on Cu cathodes for FAL
78 reduction, control over the selectivity of the process remains complicated, as 100% selectivity
79 towards FOH or 2-MF is rarely achieved with the same material, and the potential applied in most
80 studies (- 0.5 to - 0.9 V vs. RHE) indicates the presence of a high overpotential for this
81 electrochemical process. Here, we address these shortcomings and we report the beneficial effects
82 of structuring copper electrodes by a self-templating electrochemical deposition on their
83 performance towards electrocatalytic FAL reduction. We find that, in neutral phosphate buffer (pH
84 7.0), FAL can be reduced towards FOH with a 100% selectivity at potentials as high as - 0.2 V vs.
85 RHE, representing a significant improvement over the typical potential of - 0.5 V vs. RHE required
86 on Cu electrodes. We further show that, in acidic conditions (pH 1.0) we can direct FAL reduction
87 with 100% selectivity towards either FOH or 2-MF at the surface of the same electrode, depending
88 on the applied potential and the temperature of the electrolyzer. Under all conditions structured
89 electrodes show improved current densities and comparable or better selectivity than
90 polycrystalline copper foil. Surface characterization by UV and X-ray photoelectron spectroscopy,
91 including in-situ measurements performed at the synchrotron, revealed the involvement of Cu(I)
92 species in the electrocatalytic active site, even under reductive operating conditions. Overall, we
93 present an easy and scalable strategy to produce active and selective copper electrodes for the
94 electrocatalytic reduction of FAL towards 2-MF or FOH in aqueous media.

95

96 **METHODS**

97
98 **Materials.** Furfural (99%, Sigma-Aldrich), furfuryl alcohol (98%, Sigma-aldrich), 2-methylfuran
99 (99% , contains 200-400 BHT as stabilizer), acetonitrile (HPLC-GOLD-Ultragradient grade, Carlo
100 Erba), phosphoric acid (ACS Reagent \geq 85%, Honeywell), potassium phosphate monobasic (\geq
101 99.0%, Sigma-Aldrich), potassium phosphate dibasic (ACS Reagent, \geq 98%, Sigma-Aldrich),
102 copper(II) sulfate pentahydrate (ACS Reagent, \geq 98%, Sigma Aldrich), and sulfuric acid (ACS
103 Reagent, 95.0-97.0%, Sigma Aldrich) were used without additional purification. An Elga
104 PURELAB Option DV 25 provided the deionised (DI) water ($\rho > 18.2 \text{ M}\Omega\cdot\text{cm}$). A commercial
105 Cu foil (0.25 mm thickness, 99.98% trace metal basis, Sigma-Aldrich) was used as the electrode
106 substrate.

107 **Cu electrodes preparation.** Cu foil pieces cut to $3 \times 1 \text{ cm}^2$ were cleaned thoroughly to remove
108 surface contaminants before testing or electrodeposition. The Cu electrodes were first rinsed with
109 DI water and acetone followed by a 10-min sonication step in acetone and an additional 10 min of
110 sonication in DI water. The Cu foil pieces were dried at room temperature and ready for further
111 electrochemical treatment. Self-templated structured Cu electrodes were produced according to a
112 previously reported methodology.^{29,30} Briefly, a current of $1 \text{ A}\cdot\text{cm}^{-2}$ was applied between two
113 pieces of copper foil immersed in an aqueous solution of $0.4 \text{ M CuSO}_4 + 0.1 \text{ M H}_2\text{SO}_4$ for different
114 durations using a 2-electrode setup powered by a RS-3005D (RadioSpare) power supply. The
115 deposition time was varied between 10 and 60 seconds. An optimum was found for a deposition
116 time of 40 seconds, corresponding to the maximal development of the porosity of the film, as
117 additional deposited Cu tended to block the pores at longer deposition times (see **Figure S1**). After
118 electrodeposition, the structured Cu electrodes were carefully rinsed using DI water and soaked
119 for 2 h in DI water to remove unreacted CuSO_4 . Drying was performed on a hot plate at 60°C for

120 18 hours. Epoxy resin was then used to coat the electrode and roughly delimit a 1x1 cm² active
121 surface area. A small area of pristine copper was left untouched to allow electrical contact with the
122 circuit, but was not exposed to the electrolyte during electrochemical testing. The precise surface
123 area of the electrode was measured each time using the software imageJ.

124 **Electrochemical setup and experiments.** A commercial air-tight jacketed H-type
125 electrochemical cell (from DekResearch) was used throughout the study. The cell was double-
126 jacketed and a Fisherbrand Polystat was used to control the temperature of the electrolyte. Both
127 compartments of the cell were separated by a proton exchange membrane (Nafion® 117). The
128 anode compartment was filled with 0.1 M potassium phosphate (KPi) buffer or 1 M H₃PO₄ for the
129 experiments performed at pH 7.0 and pH 1.0 respectively. FAL was only added to the cathode
130 chamber at a concentration of 0.01 M. All electrochemical experiments were performed with a
131 conventional three-electrode setup connected to a potentiostat (BioLogic SP-300). The Cu working
132 electrodes and the Ag/AgCl reference electrode (3.5 M KCl) were located in the cathode chamber
133 whereas the Pt coil counter electrode was placed into the anode chamber. The potential of the
134 reference electrode is expected to vary by ca. – 20 mV between 20°C and 50°C. When potentials
135 are referenced to the RHE, this shift is partially compensated by the temperature term of the Nernst
136 equation. Overall, the temperature is expected to affect the value of the potential by less than 15
137 mV in the range of this study. The catholyte was continuously sparged with a 25 mL.min⁻¹ N₂
138 flow. This vector gas flowed any volatile and gaseous products through the outlet of the
139 electrochemical cell into a cold trap (-10°C) filled with 15 mL of acetonitrile and cooled by a
140 custom thermostated Peltier device, and sealed with a septum allowing for sampling. Thus, 2-
141 methylfuran was collected in this acetonitrile cold trap, while H₂ and N₂ were analyzed in real time
142 in a micro-gas chromatograph (INFICON Micro GC Fusion™). During kinetic measurement, the

143 gas outlet was detached for less than a minute to collect samples using a syringe. Samples from
144 the cold trap were directly taken through the septum without removing the cap. A scheme and
145 photograph of the setup are provided in **Figure S2**.

146 **Analysis of products.** NMR experiments were performed by collecting 0.1 mL of electrolyte
147 which was mixed with 0.4 mL D₂O in an NMR tube. Samples were then analyzed in a Bruker 400
148 MHz NMR spectrometer and data processed in TopSpin 3.6.5. A water peak suppression
149 procedure was applied to each sample (see **Figure S13** for a representative spectrum). HPLC
150 analysis was also performed to analyze liquid products. A Shimadzu High-Performance Liquid
151 Chromatography (HPLC) system equipped with Phenomenex Synergi Hydro-RP column (150 ×
152 4.6 mm) and a Photodiode Array UV-Vis Detector (SPD-M20A) was used. The HPLC analytical
153 condition was set to a column temperature of 30 °C and 1 mL min⁻¹ of mobile phase flow rate.
154 Water acquired from an ELGA purelab option-Q purification system in which 0.5 v% H₃PO₄ was
155 dissolved (solvent A) and HPLC grade acetonitrile (solvent B) were used as mobile phase solvents.
156 The nonlinear gradient of the two solvents was set to 100% A and 0% B at the start of the
157 experiment and sequentially changed to 99% A and 1% B at 5 min, 80% A and 20% B at 6 min,
158 10% A and 90% B at 11 min and 100% A and 0% B at 14 min after injection. The total detection
159 duration was 16 min. For a typical measurement, 500 μL of analyte was collected inside in a 2 mL
160 HPLC vial. The results were taken at different wavelengths (210 nm for FAL; 230 nm for 2MF
161 and 232 nm for FOH) by the diode array detector. Identification of analytes was based on the
162 retention time of the HPLC chromatogram while the quantification was done according to
163 calibration curves (see **Figures S11 and S12**) and the ratio of peak areas between analyte and
164 internal standard. HPLC measurement error calculation based on the calibration procedure is
165 detailed in the SI. The H₂ production during the tests was quantified using the thermal conductivity

166 detector of an INFINICON Micro GC Fusion™. N₂ was used as a carrier gas to transport H₂ into
167 the micro GC for in-line analysis. The calibration of the system was performed using an
168 electrochemical method: H₂ was produced at different current densities on a Pt foil and the quantity
169 of produced H₂ was estimated using a 100% FE assumption. The associated measurement error
170 was estimated by averaging three measurements for each current density, and was passed onto FE
171 measurements for H₂.

172 **X-Ray diffraction.** The diffractograms of the electrodes were acquired with a Bruker D8 Advance
173 A25 diffractometer using Cu K α radiation ($\lambda=0.154184$ nm). Diffraction angles were scanned
174 between 10 and 80°, and the signal was collected with a one-dimensional multistrip detector
175 (Lynxeye, 192 channels on 2.95°)

176 **Scanning electron microscopy (SEM).** SEM images were recorded on a Zeiss Merlin Compact,
177 using the secondary electron detector and an acceleration voltage of 5 kV, to document the surface
178 morphology of the prepared electrodes.

179 **X-Ray Photoelectron Spectroscopy (XPS).** XPS analyses were conducted in an integrated
180 ultrahigh vacuum system, connected to an Axis Ultra DLD spectrometer (Kratos Analytical).
181 Spectra were recorded with a monochromatic Al K α source ($h\nu=1486.6$ eV) operated at a nominal
182 power of 150 W (10 mA x 15 kV). The pass energy was set to 160 eV for wide scans and 40 eV
183 for core levels and Auger lines. The binding energy scale was calibrated with the C 1s of
184 adventitious carbon (284.6 eV). The data were treated using IGOR Pro Software (Wavemetrics
185 Inc.). Peaks were fitted with Voigt functions and a Shirley background. The resolution of the
186 instrument is 0.6 eV.³¹ For quasi-in-situ experiments, a portable glove box filled with N₂ was used
187 to conduct the electrochemical experiment. The electrochemical cell was installed inside the glove

188 box while cables from the potentiostat were introduced through a tight aperture, properly sealed to
189 prevent air leaks inside the glove box. The glove box was under constant N₂ flow during the
190 experiment. When the electrochemical test was over, the working electrode was removed from the
191 cell, quickly rinsed and dried on a Kimtech wipe and transferred through an airlock directly from
192 the glove box to the XPS sample chamber, before being put under vacuum and tested. Photographs
193 of the glove-box setup are provided in **Figure S3**.

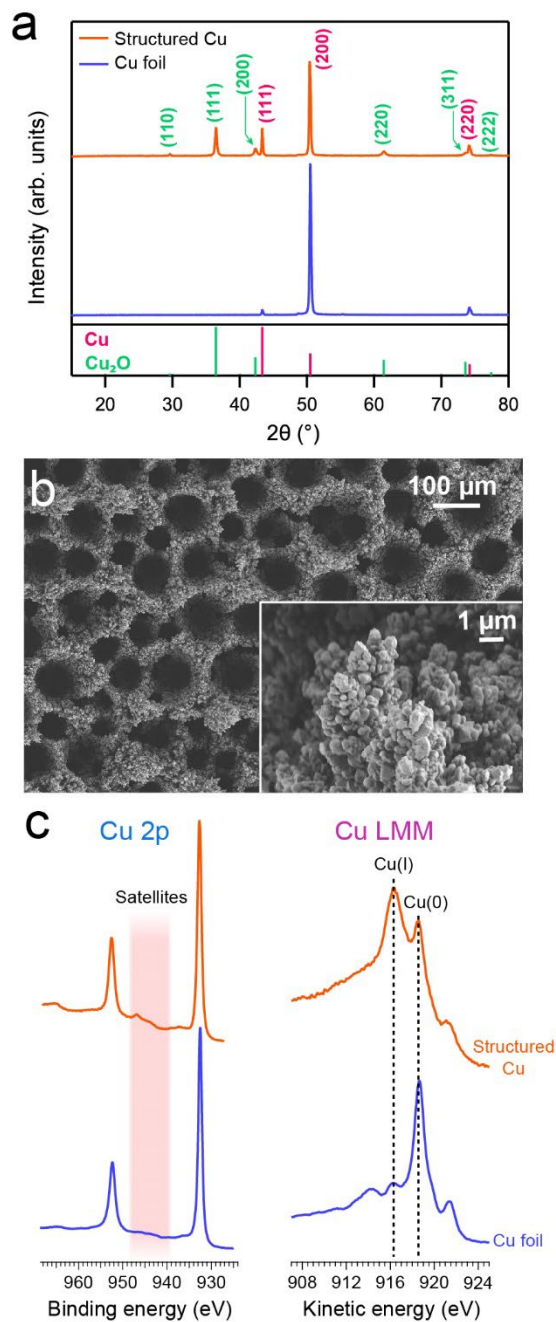
194 **In-situ XPS experiment at MAX IV facilities (HIPPIE beamline).** These experiments were
195 carried out at the HIPPIE beamline of the MAX IV Laboratory. Electrochemical experiments were
196 performed using the electrochemical cell available at the beamline, equipped with a three-electrode
197 setup connected to a Bio-Logic SP-200 potentiostat located outside of the instrument. The
198 beamline is equipped with a Scienta HIPP-3 analyzer, with an entrance cone of diameter ~0.15
199 mm, positioned in the horizontal plane at a 55° angle of the X-ray beam (set to linear-horizontal
200 polarization). An incident photon energy of 1600 eV was used to collect Cu 2p and C 1s spectra
201 and the projected spot size on the sample was ~100x25 μm². The overall photoelectron kinetic
202 energy resolution is estimated to be ~0.5 eV. The working electrode was a 2x1 cm² piece of copper
203 foil, the counter electrode was a Pt wire (diameter 0.3 mm) and the reference electrode was
204 Ag/AgCl/KCl (eDAQ ET072). All three electrodes were held by a manipulator set at the top of
205 the XPS chamber. A beaker containing 1M H₃PO₄ (degassed in a separate vacuum chamber prior
206 to use in the XPS instrument) and 0.01 M of furfural when needed, was supported on another
207 manipulator located at the bottom of the chamber. Under operation the equalized chamber pressure
208 was in the 12-15 mbar range after pumping down. For each measurement, a chronoamperometry
209 was performed with all three electrodes immersed in the electrolyte at a given applied potential for
210 30 min. At the end of the experiment, the electrodes were pulled out of the electrolyte, leaving a

211 thin layer of liquid at the surface of the working electrode. This working electrode was then
212 approached to a distance of ~ 0.3 mm of the analyzer to acquire the XPS data. The electrodes were
213 then immersed again in the electrolyte before proceeding to the next chronoamperometry.

214 **RESULTS AND DISCUSSION**

215 **Standard characterization**

216 The composition and morphology of the templated electrode was investigated by XRD, XPS and
217 SEM. The XRD data acquired for the electrodeposited copper and for the Cu foil substrate are
218 displayed in **Figure 2a**. The diffractogram of the Cu foil only showed crystalline face-centered
219 cubic Cu(0) with preferential orientation along the $\{200\}$ range of planes. Conversely, the
220 diffractogram of the structured electrode showed reduced texturing of the Cu(0) phase compared
221 to the pristine foil, and the presence of a Cu₂O phase that did not exhibit strong preferential
222 orientation along any diffraction plane. This indicated that the electrodeposited layer contained
223 randomly oriented Cu(0) and Cu₂O crystals. The morphology of these crystals was then monitored
224 by SEM. **Figure 2b** shows a picture of the typical surface observed for a structured electrode
225 obtained after a deposition time of 40 seconds. A hierarchical architecture was observed: the
226 electrodeposited layer contained microcrystals (in the 100 nm – 1 μ m size range) grown around
227 micropores of 10 – 100 μ m in diameter. These pores were generated by the concurrent evolution
228 of H₂ bubbles during the electrodeposition process. Finally, the chemical compositions of the
229 surface of both the foil and the structured electrode were probed by means of ex-situ XPS. The Cu
230 2p and Cu LMM signals are displayed in **Figure 2c**. They show that the surface of the copper foil
231 was expectedly mostly composed of Cu(0). This was evidenced by the main Cu 2p peak at 931 eV
232 and the secondary peak at 951 eV in binding energy (BE), stemming from spin-orbit splitting, as



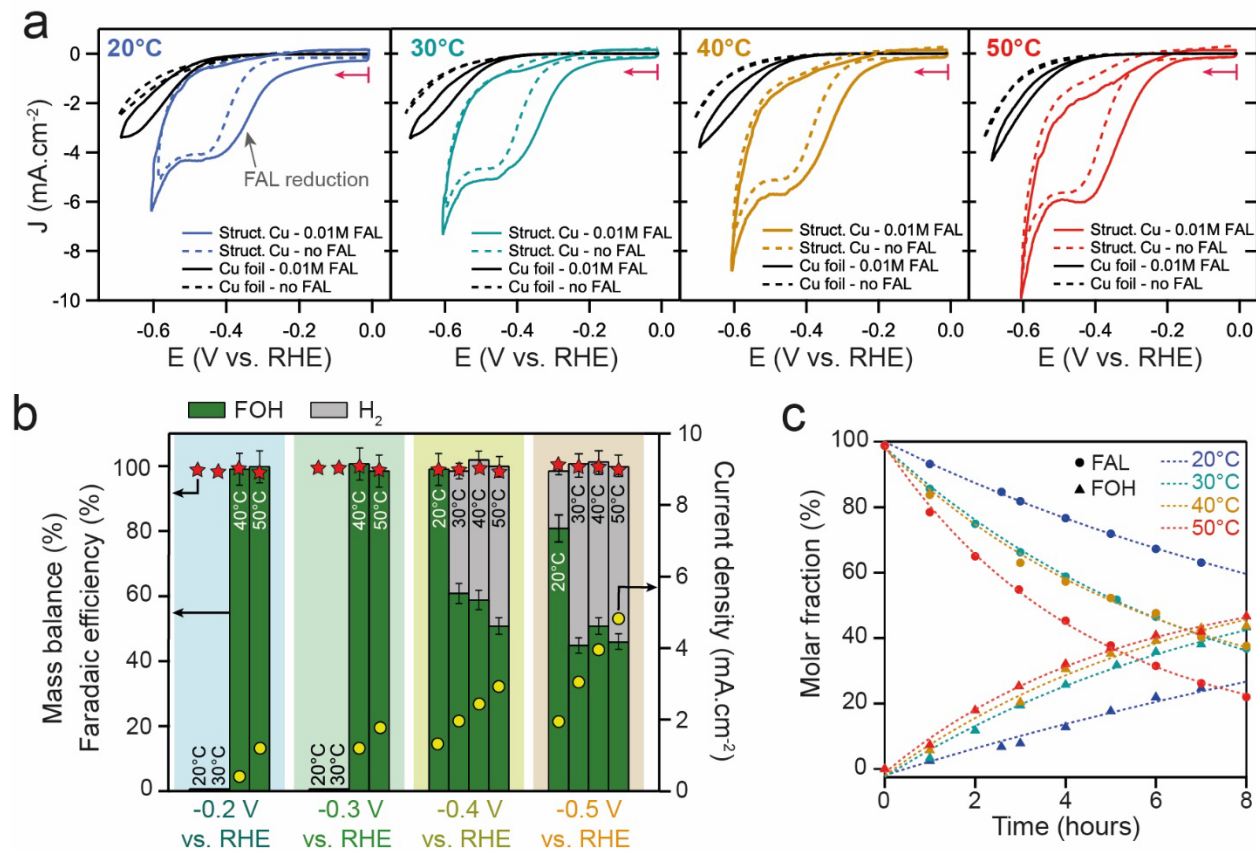
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235 **Figure 2** a) XRD data obtained on the electrodeposited Cu electrode and on the Cu foil substrate.
 236 b) Low-magnification SEM picture of the self-templated porous copper electrode Inset: higher
 237 magnification SEM picture showing the morphology of electrodeposited Cu microcrystals. c) Cu
 238 2p and Cu LMM XPS spectra measured on bare copper foil and on a structured electrode obtained
 239 after 40 seconds of electrodeposition.

240 well as by the Auger peak at 918.5 eV in kinetic energy (KE). The presence of faint satellite peaks
241 between 940 and 950 eV in BE in the Cu 2p spectrum and a small Auger peak at 916.5 eV in KE
242 indicated the presence of a small amount of Cu(I) at the surface of the copper foil. In contrast, the
243 XPS spectra of the electrodeposited structured layer show a more pronounced signal for Cu(I)
244 species – satellite peaks in the Cu 2p spectrum and an intense Auger peak at 916.5 eV in KE –
245 revealing that the Cu₂O phase identified by XRD was present at the surface of the freshly structured
246 electrode. Finally, an increase in electrochemical surface area (ECSA) of a factor 15 was found
247 between the bare Cu electrode and the structured one (see **Figure S4** and **S5**).

248 **Electrochemical conversion of furfural in neutral pH**

249 The structured copper film was tested as cathode for the reduction of FAL in a three-electrode
250 electrochemical cell (see **Figure S2**). First, cyclic voltammetry (CV) experiments were performed
251 at different temperatures. For each temperature, an iR-corrected CV was acquired on the Cu foil
252 and on the electrodeposited structured Cu electrode. The experiment was first conducted with both
253 the anode and cathode compartments filled with 0.1 M KPi buffer at pH 7.0, and then with the
254 cathode compartment filled with the same 0.1 M KPi buffer to which was added 0.01 M of FAL.
255 This FAL concentration was chosen to prevent the formation of hydrofuroin byproducts, observed
256 at higher concentrations and complicating the study at hand, while providing limited added value
257 to it. In the absence of FAL, the CV of the Cu foil appeared essentially featureless at all
258 temperatures, with a reduction current onset occurring at - 0.5 V vs. RHE, attributed to the HER.
259 On the contrary, the CV of the structured electrode showed an additional reduction wave at all
260 temperatures. This wave was located at - 0.45 V vs. RHE and was attributed to the reduction of
261 Cu(I), coexisting with and prolonged by the HER wave at more negative potentials.³² The CV
262 scans displayed in **Figure 3a** correspond to a stable measurement over multiple cycles, typically



263

264 **Figure 3** a) iR-corrected cyclic voltammograms obtained for Cu foil and a structured Cu electrode
 265 in the absence (dotted trace) and presence (solid trace) of 0.01 M FAL between 20°C and 50°C.
 266 Electrolyte: 0.1 M KPi buffer (pH 7.0). Scan rate: 20 mV.s⁻¹ (pink arrow: origin and direction of
 267 the scan). b) Values of faradaic efficiencies for H₂ and FOH production (bars, left axis) and mass
 268 balance (red stars, left axis) measured after 1 hour using structured Cu as working electrode in a
 269 0.1 M KPi + 0.01 M FAL (pH 7.0) between 20°C and 50°C and for applied potentials varying
 270 from - 0.2 to - 0.5 V vs. RHE. Yellow markers (right axis) indicate the average current density
 271 over the course of the experiment. c) Measured molar fraction of organic compounds collected
 272 over time, for an applied potential of - 0.5 V vs. RHE in 0.1M KPi + 0.01 M FAL (pH 7.0) between
 273 20°C and 50°C. The markers represent experimental data, while dotted lines correspond to their
 274 fitting with a first-order kinetic model. All measurements performed in under N₂ sparging.

275 obtained after two initial CV scans in which a large quantity of surface oxidized copper is reduced
 276 (see **Figure S6**). The fact that the reduction wave at - 0.44 V vs. RHE was part of the stable CV
 277 signal indicated that some Cu(I) remained steadily electrochemically accessible in the range of

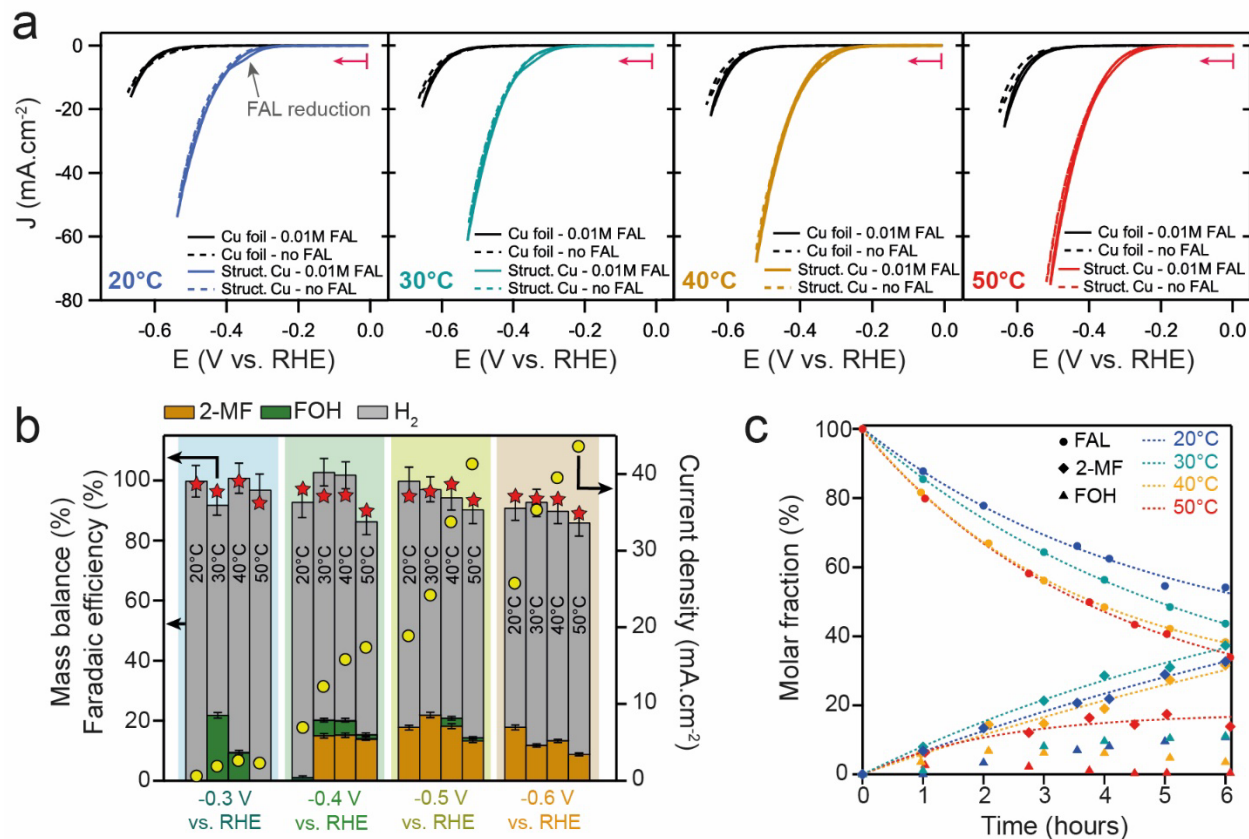
278 monitored potentials. Once FAL was added to the electrolyte, an increase in reduction current was
279 observed both for the Cu foil and the structured Cu. On Cu foil, the reduction current onset was
280 shifted positively by about 50 mV (thus occurring at -0.45 V vs. RHE) at all temperatures,
281 indicating the kinetically easier reduction of FAL on Cu compared to the HER. This additional
282 reduction current ranging from about -0.5 to -1.5 mA.cm⁻² at -0.6 V vs. RHE between 20°C and
283 50°C was associated with FAL reduction on bare Cu foil. On the structured electrode, a slightly
284 larger positive shift in the onset of reductive currents was observed upon FAL addition,
285 accompanied by an increase in current density forming an additional reduction wave. At all
286 temperatures, the onset of this reduction wave was about 0.1 V more positive than the Cu (I)
287 reduction wave onset and merged with it at lower potentials. Because this increase in reduction
288 current was directly linked to the presence of FAL in the electrolyte, it was attributed to the
289 reduction of FAL (indicated by an arrow in **Figure 3a**). Moreover, according to these CV
290 measurements and their proposed interpretation, the onset of FAL reduction on structured Cu
291 electrodes was measured at ca. -0.15 V vs. RHE. To confirm the ability of structured Cu to reduce
292 FAL at such low overpotentials and to study the selectivity of the process, chronoamperometry
293 (CA) measurements coupled with product identification and quantification were performed at
294 several potentials (-0.2 , -0.3 , -0.4 and -0.5 V vs. RHE) and temperatures (20°C, 30°C, 40°C and
295 50°C). The results obtained after 1 hour of CA under each condition are presented in **Figure 3b**.
296 No product was detected after one hour at -0.2 and -0.3 V vs. RHE at 20°C and 30°C. On the
297 contrary, when the temperature was raised to 40°C and above, FOH was generated with an FE of
298 100%. Furthermore, FOH could also be generated with a 100% FE at -0.4 V vs. RHE at 20°C.
299 Higher temperatures and more negative potentials resulted in the apparition of H₂ as a competing
300 reduction product from HER. Under all conditions, FOH was selectively produced from the

301 reduction of FAL as no other product was detected by NMR, HPLC or micro-GC, and a mass
302 balance above 95% was consistently measured. Interestingly, when the same experiment was
303 performed on Cu foil, negligible current densities and no FAL conversion were measured after 1
304 hour of polarization at - 0.5 V vs. RHE (see **Table S1**), highlighting the significantly improved
305 electrocatalytic properties of structured Cu electrodes compared to the performance of Cu foil: we
306 show that our structured Cu electrodes can selectively convert FAL to FOH with a 100% FE at
307 minimal overpotential. Furthermore, SEM analysis of our structured Cu electrode after 2 hours of
308 operation at - 0.5 V vs. RHE showed no evident alteration of the morphology compared to its
309 initial state (see **Figure S8**). While little data on FAL reduction on Cu at pH 7 is available in the
310 literature, this result represents an improvement over a 98% FE for FOH reported on Cu single
311 atoms at - 0.75 V vs. RHE in acetate buffer (pH 5.0),²⁴ or to a 70 - 85 % FE for FOH reported on
312 CuO nanowires for potentials between - 0.2 and - 0.3 V vs. RHE in phosphate buffer (unspecified
313 pH).²⁶ To investigate the kinetics of the process, FAL reduction was conducted on structured Cu
314 electrodes at - 0.5 V vs. RHE and at 20°C, 30°C, 40°C and 50°C. The results of this experiment
315 are shown in **Figure 3c**. Over the course of the experiment, no other FAL reduction product than
316 FOH was detected. The conversion of FAL to FOH was found to follow an apparent first-order
317 kinetic law at all temperatures, with a typical increase in the rate of reaction with the temperature.
318 However, as the temperature was increased, increasingly noticeable amounts of FAL evaporated
319 from the electrolyte over time, carried away by the sparging N₂ flow and was captured in the cold
320 trap. After 8 hours of experiment, 9% of unreacted FAL escaped the reactor at 20°C, while up to
321 25% of it escaped the reactor at 50°C. This explains the difference in apparent rate between FAL
322 disappearance from the electrolyte and FOH production at 50°C in **Figure 3f**. When fitted with
323 the Arrhenius equation, the kinetic data obtained for FOH production afforded an apparent

324 activation energy of 23 kJ.mol⁻¹ (see **Figure S7**). This value was found comparable to what others
325 measured for catalytic aldehyde hydrogenation towards alcohol in thermochemical or
326 electrochemical setups.³³⁻³⁷ However, considering the experimental setup employed in this study
327 (unstirred batch H-cell and low FAL concentration), we posit that diffusion kinetics are limiting.
328 This was supported by the fact that stirring the electrolyte resulted in an increase in current density
329 (see **Figure S7**) both in the presence and absence of FAL due to the poor ionic conductivity of the
330 0.1 M KPi electrolyte. Still, the increase in current was observed to be larger in the presence of
331 FAL, suggesting mass transport limitations. Overall, these experimental results prove that FAL
332 can be selectively converted to FOH at much improved overpotential on the surface of structured
333 Cu electrodes under neutral conditions and at temperatures below 50°C.

334 **Electrochemical conversion of furfural in acidic pH**

335 It is well known that pH has a strong influence on FAL reduction selectivity at the surface of
336 copper, with an increased selectivity towards 2-MF over FAL at low pH.¹⁰ While most studies
337 have been conducted in H₂SO₄ electrolytes (see **Table S3**), we chose to employ H₃PO₄ as a source
338 of protons, so as to keep the same counter anion (PO₄³⁻) as in our study in neutral conditions (in
339 which the electrolyte was buffered with potassium phosphate salts). Thus, the following
340 experiments were conducted in a 1M H₃PO₄ solution exhibiting a pH of 1.0. First, iR-corrected
341 CV were collected for Cu foil and structured Cu electrodes at 20°C, 30°C, 40°C and 50°C in the
342 absence and presence of 0.01M FAL. The resulting curves are shown in **Figure 4a**. They revealed
343 that, in acidic conditions, both Cu foil and structured Cu generated much higher current densities



344
 345 **Figure 4** a) iR-corrected cyclic voltammograms obtained for Cu foil and a structured Cu electrode
 346 in the absence (dotted trace) and presence (solid trace) of 0.01 M FAL between 20°C and 50°C.
 347 Electrolyte: 1 M H₃PO₄ (pH 1.0). Scan rate: 20 mV.s⁻¹ (pink arrow: origin and direction of the
 348 scan). b) Values of faradaic efficiencies for H₂, FOH, and 2-MF production (bars, left axis) and
 349 mass balance (red stars, left axis) measured after 1 hour using structured Cu as working electrode
 350 in a 1 M H₃PO₄ + 0.01 M FAL (pH 1.0) between 20°C and 50°C and for applied potentials varying
 351 from - 0.2 to - 0.5 V vs. RHE. Yellow markers (right axis) indicate the average current density
 352 over the course of the experiment. c) Measured molar fraction of dissolved organic compounds in
 353 the electrolyte and in the cold trap over time, for an applied potential of - 0.5 V vs. RHE in 1M
 354 H₃PO₄ + 0.01 M FAL (pH 1.0) between 20°C and 50°C. The markers represent experimental data,
 355 while dotted lines correspond to their fitting with a first-order kinetic model (only for FAL and 2-
 356 MF). All measurement performed under N₂ sparging

357 that in neutral pH, indicating a drastic promotion of HER on Cu electrodes at low pH. Interestingly,
 358 while the onset of HER was observed at - 0.50 V vs. RHE on Cu foil, it shifted to - 0.30 V vs.

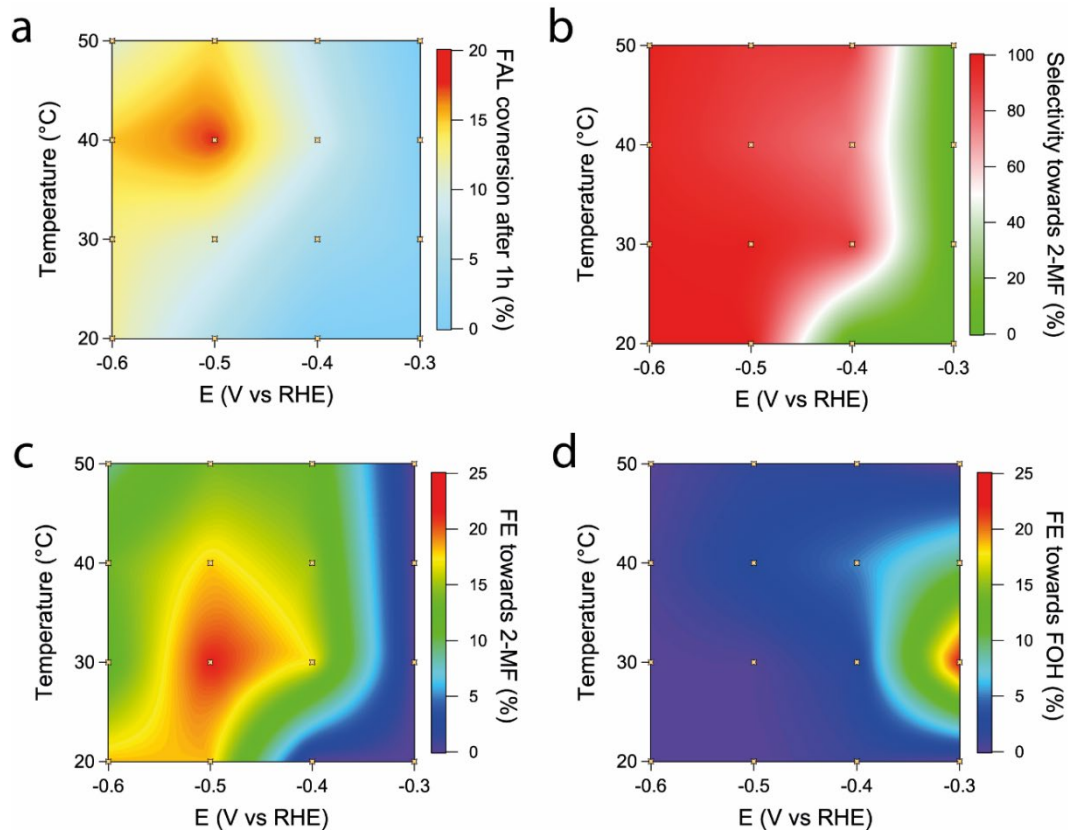
359 RHE on the structured electrode, showing significantly enhanced electrocatalytic HER activity.
360 Moreover, contrary to what was observed in neutral conditions, no defined feature was observed
361 in the CV of either the Cu foil or the structured Cu. This suggested that once reduced over the first
362 CV scan (see **Figure S6**), the surface oxide layer was not electro-active in this range of potentials.
363 When FAL was introduced in the electrolyte, a slight positive shift of a few tens of mV in onset
364 potential was observed on Cu foil at all temperatures. On the structured electrodes, the introduction
365 of FAL also resulted in a minor shift in onset potential, accompanied by the appearance of a
366 reduction wave located at the foot of the HER wave. This reduction wave, located roughly between
367 - 0.30 and - 0.35 V vs. RHE at all temperatures was thus attributed to FAL reduction (indicated by
368 an arrow in **Figure 4a**). Moreover, as the temperature increased, this FAL reduction wave was
369 increasingly merged with the HER wave, suggesting a different influence of temperature on the
370 reduction kinetics of water and FAL in 1M H₃PO₄. Contrary to what was observed under neutral
371 conditions, and similarly to what occurred on the Cu foil, there was little change in electrochemical
372 activity upon addition of FAL, indicating a stronger competition between the HER and FAL
373 reduction. Again, 1-hour CA experiments were performed at - 0.3, - 0.4, - 0.5 and - 0.6 V vs. RHE,
374 each at 20°C, 30°C, 40°C and 50°C in 1M H₃PO₄ + 0.01 M FAL on the Cu foil and on the
375 structured electrode. Importantly, 2-MF, because of its low solubility in water and relatively high
376 volatility, rapidly exited the electrochemical cell, carried away by the N₂ stream (something that
377 was not observed with FOH), justifying the use of a cold trap. 2-MF was recovered in this trap and
378 quantified by HPLC measurements, whereas FOH was collected and measured inside the working
379 electrode compartment (similar to under neutral conditions). Finally, H₂ evolution was quantified
380 by a micro-GC connected in-line with the outlet of the cold trap (see **Figure S2**). For all
381 measurements, a total FE in the 87 - 106 % range was obtained. Lower FE values were typically

382 obtained at high temperature, and were correlated to lower mass balance values (see **Figure 3b**).
383 Besides failure of trapping all products in the cold trap, a possible reason for these lower values
384 can be the existence of homogeneous side-reactions leading to the degradation of furanic
385 compounds in acidic conditions. These side reactions have been well documented by others,
386 especially at higher FAL concentration and have resulted in low mass balance values in the
387 past.^{13,20,21} The FE measured on the structured Cu after each CA are displayed in **Figure 4b**. At -
388 0.2 V vs. RHE, at all temperatures, very low current densities (below $0.1 \text{ mA}\cdot\text{cm}^{-2}$, not shown in
389 **Figure 4b**) were measured and only traces amount of H_2 were detected, in contrast with what was
390 observed in neutral conditions. When the potential of the working electrode was shifted to - 0.3 V
391 vs. RHE at 20°C , similarly low current densities were measured and only H_2 was detected as a
392 product. However, FAL conversion was observed to be selective towards FOH at 30°C and 40°C .
393 Further increasing the temperature from 30°C to 40°C at this potential led to an increase in H_2
394 production, but did not affect the selectivity of FAL reduction, which remained 100% directed
395 towards FOH. Interestingly, increasing the temperature to 50°C further favored the HER to the
396 point of preventing FAL reduction altogether. This indicated that, at - 0.3 V vs. RHE, increasing
397 the temperature improved the kinetics of both FAL reduction and HER, but that the HER was
398 kinetically more favored at high temperature. This resulted in an optimum for FAL reduction at
399 around 30°C . When subjected to - 0.4 V vs. RHE, the structured Cu was once again capable of
400 reducing FAL only at temperatures above 30°C , despite significant current densities drawn at
401 20°C , showing that HER proceeded more easily than FAL reduction at this temperature. However,
402 at this potential and above 30°C , the selectivity of FAL reduction was preferentially directed
403 towards 2-MF, although a significant amount of FOH was also detected as secondary product.
404 Once again, when the temperature was raised from 30 to 40 and finally 50°C , FAL reduction was

405 increasingly more disfavored compared to HER. However, the FE towards 2-MF was not affected
406 and remained quasi-constant at around 15%, indicating that temperature affected both reduction
407 pathways differently. Indeed, at - 0.4 V vs. RHE, the increase in H₂ production was exclusively
408 achieved to the detriment of FOH production (similarly to what was observed at - 0.3 V vs. RHE).
409 Finally, at - 0.5 V vs. RHE, a much better selectivity for 2-MF was achieved, since a conversion
410 of FAL with a 100% selectivity towards 2-MF was observed at 20°C and 30°C, while only a few
411 percent of FOH were detected at higher temperature. At this potential, an optimal activity for 2-
412 MF production was measured at 30°C, where a FE of 22% was obtained for 2-MF and no FOH
413 was detected. When subjected to the same conditions, Cu foil only produced very small current
414 densities, making the accurate quantification of products and the calculations of FE difficult with
415 our experimental setup, although we can report that only 2-MF and H₂ were detected as products
416 (see **Table S2**). Previous studies similarly showed that, on Cu foil and in acidic conditions, at low
417 FAL concentration (0.01 – 0.02 M), H₂ was the major product in the reduction range of FAL.^{9,21}
418 In these studies, the selectivity towards 2-MF could be improved by increasing FAL concentration,
419 but to the detriment of the overall mass balance, suffering from aforementioned homogeneous
420 degradation reactions. We show here that structuring Cu by our approach does not provide a
421 satisfying answer to the competition of HER, as both FAL reduction and HER were enhanced by
422 the structuration of the electrocatalyst. Kinetics measurements were then performed at - 0.5 V vs.
423 RHE for temperatures of 20°C, 30°C and 40°C and the results are presented in **Figure 4c**. As
424 expected, an increased rate of FAL reduction was measured with increasing temperature. Once
425 again 15 to 30% (at 20°C and 50°C respectively) of initial FAL was measured to evaporate and
426 leave the reactor over the course of the experiment. Furthermore, it appeared that, contrary to what
427 the data presented in **Figure 4b** and collected after only one hour may suggest, FOH was ultimately

428 produced at all temperatures, but with a temporal delay compared to 2-MF. This indicated a change
429 in the environment of the electrocatalytic site over time. We rationalize this behavior by suggesting
430 that as HER and FAL proceed at the surface of the electrode, the consumption of protons shifts the
431 local pH towards higher values, in turn shifting the selectivity of FAL reduction towards FOH
432 production. This is consistent with the observation that FOH production occurs sooner at higher
433 temperatures, at which higher current densities indicate faster proton consumption and therefore
434 faster increase in the local pH. Finally, we observe that the concentration of generated FOH
435 decreases over time, indicating chemical degradation of this compound in acidic media. This was
436 confirmed by NMR analysis, revealing that the furanic ring underwent an opening, leading to the
437 formation of a non-identified non-aromatic degradation product (see **Figure S12**). Furthermore,
438 attempts at calculating the apparent activation energy of the process based on the kinetics of 2-MF
439 production resulted in a non-Arrhenius behavior (see **Figure S10**). This uncharacteristic
440 dependence on temperature can be linked to an array of experimental hurdles with our setup: the
441 need to collect 2-MF in a separated cold trap with unclear transfer kinetics (e.g. condensation in
442 the transfer line), the aforementioned existence of homogeneous degradation of furanic
443 compounds in acidic conditions, and the existence of mass transport limitations. Indeed, similar to
444 what was observed under neutral conditions, increase in current upon stirring suggested that mass
445 transport was also limiting in our experiment (see **Figure S7b**) in acidic conditions. It is however
446 worth noting that others have successfully estimated an apparent activation energy for 2-MF
447 production in acidic conditions based on initial rate analysis, rather than fitting of data over the
448 course of several hours.³⁷ Finally, SEM analysis showed no significant change in the surface
449 morphology of structured copper after operating in acidic conditions (see **Figure S8**). Overall, the
450 results presented in **Figure 4** demonstrate the possibility to tune the selectivity of FAL reduction

451 as a function of applied potential and temperature, and show that the selectivity of the process is
452 highly sensitive to the local environment of the active site. We believe in particular that the local
453 pH can quickly change under operating conditions, resulting in shifts in selectivity over time.
454 Despite the preponderance of the HER under the conditions of this study, we demonstrated that
455 FAL could be converted in 1M H₃PO₄ at potentials as high as - 0.3 V vs. RHE and achieve
456 complete initial selectivity towards FOH at -0.3 V vs. RHE (although the product quickly
457 degrades) and towards 2-MF at - 0.4 V vs. RHE and below. To better illustrates the latter, **Figure**
458 **5** represents the evolution of different metrics as a function of applied potential and temperature
459 measured after 1 hour of FAL reduction in 1 M H₃PO₄. The contour plots represented in this figure
460 were obtained by interpolating experimental values measured on the location of each marker (16
461 data points for each plot). **Figure 5a** shows that there is an optimal combination of temperature
462 and applied potential to promote the conversion of FAL in our setup, namely 40°C and - 0.5 V vs.
463 RHE. Indeed, at more positive voltages and lower temperature, lower current densities resulted in
464 lower conversion rate, while at more negative voltage and higher temperature, HER was
465 increasingly favored over FAL reduction. Moreover, **Figure 5b** shows the existence of two
466 regimes of selectivity, mostly determined by the applied voltage: at potentials more positive than
467 - 0.35 V vs. RHE, FOH was the main product of FAL, while at potentials more negative to this
468 value, 2-MF was the major product. Importantly, it was found that both products could be
469 selectively obtained in appropriately chosen temperature/voltage domains, although FOH was
470 found to degrade over time in acidic conditions. This was confirmed with the measurement of FE
471 for both products, pictured in **Figure 5c-d**. These plots further show that a temperature-voltage
472 optimum exists for 2-MF production, as a result of the optimum in conversion rate and selectivity
473 discussed previously.



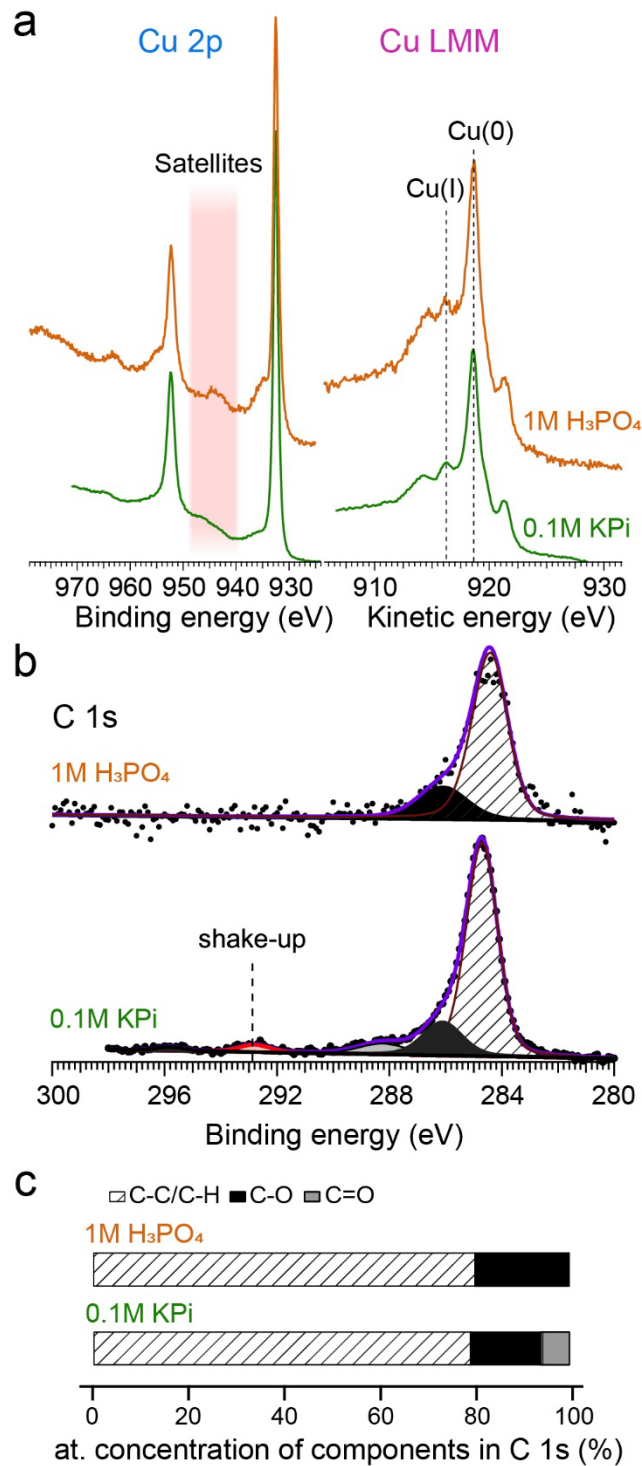
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475 **Figure 5** Contour plots of (a) the conversion of FAL, (b) the selectivity of FAL reduction towards
 476 2-MF, the only other conversion product being FOH, (c) the Faradaic efficiency towards FOH
 477 production and (d) the Faradaic efficiency towards 2-MF production, as a function of temperature
 478 and applied voltage after 1 hour of electrolysis at the surface of a structured Cu electrode in 1 M
 479 H₃PO₄ in our electrochemical cell. Markers indicate the experimental data used to plot the figures.

480 **Photoelectron spectroscopy analysis**

481 To understand the difference in activity and selectivity between our structured electrodeposited
 482 copper electrode and the copper foil, we relied on photoelectron spectroscopy. First, quasi-in- situ
 483 XPS experiments were performed in our laboratory. A structured electrode was subjected to
 484 electrolysis conditions (in neutral or acidic electrolyte) in the presence of FAL for 30 min at - 0.5
 485 V vs. RHE, and quickly transferred under inert atmosphere to the XPS chamber for analysis (see
 486 Methods section). The acquired Cu 2p and Cu LMM spectra are shown in **Figure 6a**. The spectral

487 signature of Cu(I) – satellites peaks and shoulder at 934 eV in the Cu 2p spectrum and the peak at
488 916.5 eV in KE in the Cu LMM spectrum – revealed that surface Cu(I) existed under operating
489 conditions at both pH. The corresponding C 1s spectra are displayed in **Figure 6b**, exhibiting
490 several peaks indicating the presence of different carbon species at the surface of the electrode.
491 Under acidic conditions, the main peak at 284.6 eV was attributed to C-C and C-H bonds, while
492 the smaller peak at 286.1 eV was attributed to C-O bonds. In neutral conditions, the same two
493 signals were observed, plus one small peak at 288.5 eV, attributed to C=O bonds, and finally a
494 shake-up peak at 292.9 eV, attributed to aromatic carbons.³⁸ These signals are thus generally
495 consistent with the spectral signatures of FAL and its reduction products adsorbed at the surface
496 of the electrode. We note that because of the lower signal-to-noise ratio obtained in acidic
497 conditions, it is probable that the small C=O and aromatic shake-up signals exist but are within the
498 noise of the measurement. To gain insight into the nature of the adsorbed chemicals, the atomic
499 contribution of each of the aforementioned XPS peaks to the entire spectrum have been measured
500 and are displayed in **Figure 6c**. In acidic conditions, we calculated an 80/20 ratio for the C-C/C-
501 H over C-O bond signals. This composition is close to the theoretical composition of 2-MF (83/17)
502 and suggests that the surface of the electrode is mostly covered in reduction products. On the other
503 hand, in neutral conditions, a 79/15/6 distribution for C-C/C-H, C-O and C=O bonds respectively
504 rather suggests a significant coverage of FAL (theoretical distribution of 72/18/9) molecules on
505 the surface of the electrode at the end of the electrolysis. This led us to conclude that FAL is rapidly

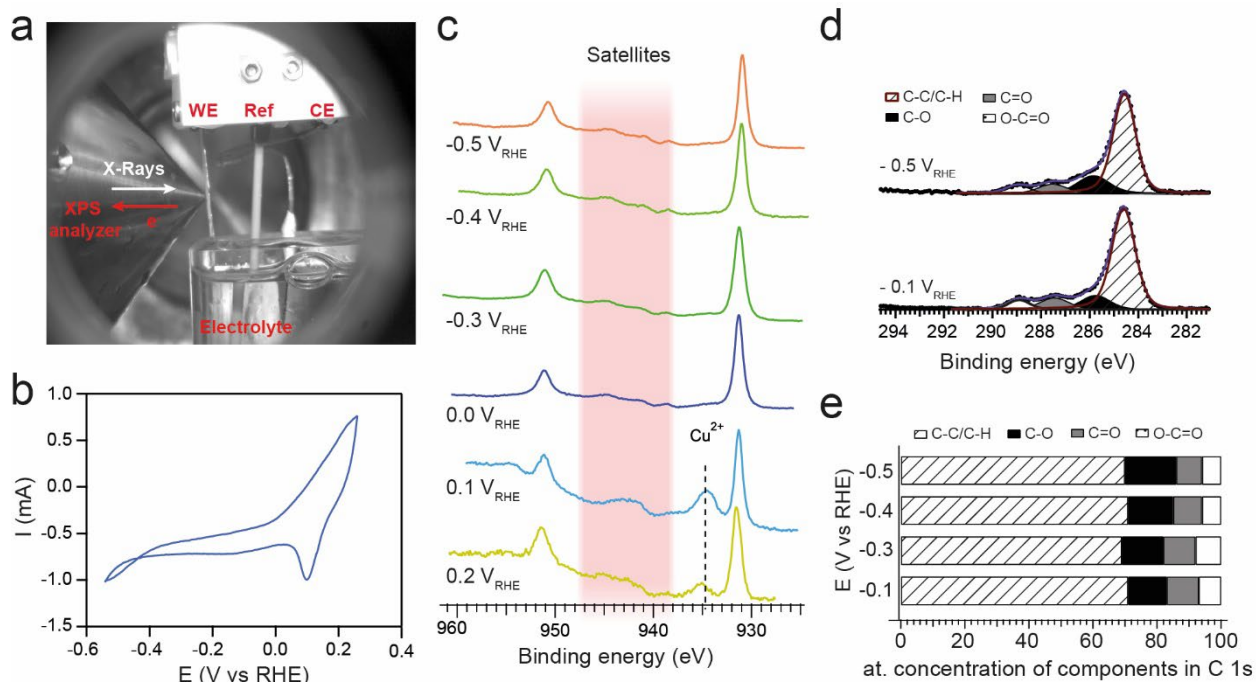


506

507 **Figure 6** a) Cu 2p and Cu LMM XPS spectra measured on structured electrodes under quasi in-
 508 situ conditions after 30 min of electrolysis at -0.5 V vs. RHE in 1M H₃PO₄ (orange trace) or 0.1M
 509 KPi (green trace) containing 0.01M FAL. b) C 1s spectra measured after 30 min of electrolysis at

510 – 0.5 V vs. RHE in 1M H₃PO₄ (top graph) or 0.1M KPi (bottom graph) containing 0.01M FAL. c)
511 Atomic percent of C 1s components extracted from spectra displayed in b.

512 reduced once adsorbed on the surface of the electrode in acidic conditions, making the
513 electrochemical process limited by the desorption of reaction products. On the contrary, FAL is
514 converted more slowly in neutral conditions and tends to accumulate on the surface of the
515 electrode, suggesting the electrochemical process is limited by its conversion. To further approach
516 operating conditions with our spectroscopy measurements, we set out to perform proper in-situ
517 atmospheric pressure XPS (AP-XPS) experiments at the HIPPIE beamline of the MAX IV
518 synchrotron light source in Lund, Sweden.³⁹ Briefly, it consisted in performing XPS measurements
519 directly at the surface of a working electrode connected to a three-electrode setup immersed in a
520 liquid electrolyte inside an analysis chamber pressurized at 12-15 mbar (see Methods section for
521 more details). Unfortunately, because the structured electrodes were rapidly soaked by the
522 electrolyte, the signals of interest (Cu 2p and C 1s) were masked by the water signal and they could
523 not be analyzed under this configuration. Still, in-situ XPS measurements were performed on
524 copper foil that presented suitable wettability. Moreover, 1M H₃PO₄ was chosen as the electrolyte,
525 because of the rapid precipitation of KPi at the surface of the electrode during the acquisition of
526 in-situ XPS data. The CV obtained on the copper electrode inside the XPS chamber is displayed
527 in **Figure 7**. A first series of measurements was conducted in pure 1 M H₃PO₄ electrolyte. The Cu
528 2p XPS spectrum of the electrode surface was measured at several potentials from + 0.2 V to - 0.5
529 V vs. RHE. The results are shown in **Figure 7c**. They revealed that, while Cu(II) species existed
530 at potentials higher than + 0.1 V vs. RHE, they were progressively reduced to Cu(0) and Cu(I)
531 species when scanning to more negative potentials. The presence of Cu(I) was also confirmed by
532 analysis of the Cu LMM Auger signal (see **Figure S15**). After adding 0.01 M FAL to the
533 electrolyte, the same experiment was conducted, only this time focusing on analyzing the C 1s



534

535 **Figure 7** a) Photograph picture of the experimental three-electrode setup inserted inside the XPS
 536 chamber on the HIPPIE beamline at the MAX IV light source facility. b) Cyclic voltammetry
 537 acquired with the setup pictured in a, on a copper foil immersed in a 1 M H₃PO₄ electrolyte
 538 containing 0.01 M of FAL. c) In-situ Cu 2p spectra acquired at different potentials for a copper
 539 foil immersed in 1 M H₃PO₄. d) In-situ C 1s spectra acquired at – 0.1 V and – 0.5 V vs. RHE at
 540 the surface of a copper foil immersed in a 1 M H₃PO₄ + 0.01 M FAL electrolyte. e) Atomic percent
 541 of C 1s components extracted from in-situ C 1s spectra acquired on copper foil at different
 542 potentials in 1 M H₃PO₄ + 0.01 M FAL electrolyte.

543 signal (because the organic layer deposited on the surface of the electrode was masking the Cu 2p
 544 signal of the substrate, it was not possible to monitor both elements at the same time). Quantitative
 545 analysis of the C 1s spectra (**Figure 7d-e**) revealed that as the potential was shifted more
 546 negatively, the ratio of C-O/C=O increased noticeably between – 0.4 V and – 0.5 V vs. RHE,
 547 confirming the reduction of FAL at the surface of the electrode. Interestingly, a peak attributed to
 548 O-C=O moieties, absent from the quasi in-situ experiment performed in the lab and reported in
 549 **Figure 7**, was identified at all potentials. This was attributed to the oxidation of FAL at the counter-

550 electrode and migration to the working electrode inside the undivided electrochemical cell. Indeed,
551 the electrochemical cell employed at the HIPPIE beamline was unseparated, as opposed to the one
552 employed in the experiment described in **Figure 6**. While the existence of this crossover affected
553 the analysis of the organic layer, it still supported the observations made with the quasi in-situ
554 experiment performed in the laboratory on the state of Cu and C under operating conditions. This
555 demonstrated the ability of using AP-XPS for analyzing both the oxidation state of the electrode
556 and the composition of the adsorbed organic layer at its surface under quasi-operating conditions,
557 providing insight into the catalytic process at the molecular level.

558 **Conclusion**

559 The self-templated copper electrocatalyst presented in this work exhibited improved activity and
560 selectivity compared to unstructured copper foil. More specifically, studying the influence of
561 temperature and applied potential on the outcome of the electrocatalytic process allowed to identify
562 experimental conditions in which (i) FOH could be selectively produced from FAL in a neutral
563 electrolyte with a 100% FE at unprecedentedly low overpotential and (ii) either FOH or 2-MF could
564 be selectively produced from FAL in acidic condition, at similarly low overpotentials, albeit with
565 strong HER competition. The existence of this optimum for FAL illustrates the importance of the
566 combined influence of these two driving forces (voltage and temperature) on the selectivity of
567 complex electrocatalytic processes. Quasi in-situ and in-situ photoelectron spectroscopy was
568 further found to be an insightful tool to shed light on the mechanism of this process, as the analysis
569 of Cu 2p and C 1s signal revealed the resilience of Cu (I) species under operating conditions, as
570 well as a difference in the oxidation state of the organic layer adsorbed at the surface of the
571 electrode, pointing towards differences in the limiting step of electrocatalytic mechanisms between
572 neutral and acidic conditions. While this work demonstrates the benefits of structured Cu

573 electrodes over Cu foil in terms of activity and selectivity, important competition from the HER
574 remained in acidic conditions. Experimental and theoretical investigations as well as cell design
575 optimization are under way to understand how to further improve the performance of this system.

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579 Author Contributions

580 The manuscript was written through contributions of all authors. All authors have given approval
581 to the final version of the manuscript.

582 Notes

583 The authors declare no competing financial interest.

584

585 **ASSOCIATED CONTENT**

586 **Supporting Information.** The following files are available free of charge.
587 A PDF containing illustrations of the methods employed in the study, additional SEM data,
588 additional cyclic voltammetry and chronoamperometry data, complementary activity and
589 selectivity data obtained on structured Cu and Cu foil, activation energy measurements, details on
590 the detection and quantification of dissolved products by HPLC and NMR, additional XPS data
591 and a literature survey of state-of-the-art electrocatalysts for the reduction of furfural.

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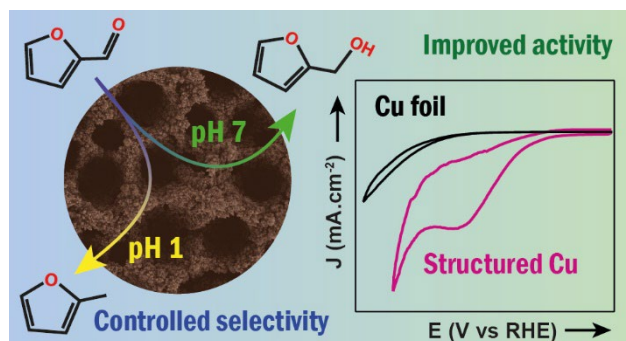
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742 **Graphical abstract:**



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