

Supporting Information

One-Pot Redox Cascade Paired Electrosynthesis of Gamma-Butyrolactone from Furoic Acid

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Redox chemical equations

During the reduction of 2-FO (Eq. 1), the hydrogen evolution reaction (Eq. 2) occurred in parallel on the cathode as well. As for the anodic processes, water splitting (Eq. 3) was the sole reaction since 2-FO could not be oxidized as control experiments verified. The electrochemical equations are as follows:

Cathode

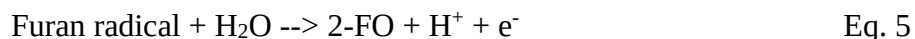


Anode



During the FA oxidation study in unpaired mode, furan-2-carboxylate anion (FA anion) underwent a single-electron oxidation to induce decarboxylation (Eq. 4) to become a furan radical, which reacts with water to yield 2-FO. (Eq. 5) The cathodic reaction would be a hydrogen evolution reaction. (Eq. 2) The electrochemical equations are as follows:

Anode



Cathode



Table S1. Electrocatalytic oxidation of FA at different anode and pH

Entry	WE	pH	Conversion (%)	Yield of products (%)			Sel of 2-FO (%)	CB (%)
				HFO	MA	2-FO		
1	Pt	1	100 ± 0.0	14.7 ± 2.6	3.2 ± 1.3	28.3 ± 1.8	28.3 ± 1.8	46.1 ± 3.1
2	Pt	5.5	88.9 ± 3.0	1.3 ± 0.5	3.0 ± 0.5	74.8 ± 4.4	84.2 ± 2.4	89.0 ± 1.6
3	Au	5.5	8.4 ± 3.6	0.8 ± 0.6	0.4 ± 0.2	6.5 ± 2.7	77.3 ± 4.0	92.2 ± 4.1

Reaction conditions: 10 mM FA in 10 mL of 0.5 M buffer at +1.8 V_{Ag/AgCl} referenced to working anode (WE) paired with a Pt counter electrode at 80 °C.

Table S2. Electrocatalytic oxidation of FA at different temperatures

Entry	Tem. (°C)	Conver. (%)	Yield of products (%)			Sel. (%)	CB (%)
			HFO	MA	2-FO		
1	20	100 ± 0.0	0.7 ± 0.6	5.0 ± 4.2	37.5 ± 3.5	37.5 ± 3.5	43.2 ± 0.7
2	40	100 ± 0.0	0.7 ± 0.6	1.4 ± 0.3	68.4 ± 3.3	68.4 ± 3.3	70.6 ± 2.8
3	60	98.0 ± 1.6	1.1 ± 0.3	2.0 ± 0.5	79.0 ± 6.8	80.5 ± 5.6	83.7 ± 4.9
4	80	88.9 ± 3.0	1.3 ± 0.5	3.0 ± 0.5	74.8 ± 4.4	84.2 ± 2.4	89.0 ± 1.6

Reaction conditions: 10 mM FA in 10 mL of 0.5 M pH 5.5 buffer at +1.8 V_{Ag/AgCl} referenced to the Pt working anode paired with a Pt counter electrode at 80 °C.

Table S3. Comparison of different systems for oxidation of furfural to produce furoic acid.

Entry	Catalyst	Reaction conditions	Performance	Ref.
1	SiO ₂ -Co(acac) ₂	Solvent-free, 50 °C, air, 5 h	85% isolated FA yield, 170 µmol/h	1
2	BTIC	125 mM FAL, DMSO with DBU, 40 °C, 0.1 MPa O ₂ , 4 h	> 99% FA yield, 62.5 µmol/h	2
3	MnO ₂ @CeO ₂	300 mM FAL, H ₂ O, 130 °C, 8 bar O ₂ , 4 h	96% FA yield, 750 µmol/h	3
4	Fe ^{III} Mo ₆	750 mM FAL, 0.75 M NaCO ₃ , 50 °C, 1 atm O ₂ , 8 h	97% isolated FA yield, 182 µmol/h	4
5	NiFe-1	100 mM FAL, 1.478 V vs. RHE, 1 M KOH	97% FA yield, 96% FE, 756 mA cm ⁻²	5
6	NiMoP/NF	100 mM FAL, 1.46 V vs. RHE, 1 M NaOH	99.2% FA yield, 96.7% FE, 500 mA cm ⁻²	6
7	Ni _x Se _y -NiFe LDH@NF	20 mM FAL, 1.423 V vs. RHE, 1 M KOH	99.7% FA yield, 99.5% FE, ~ 100 mA cm ⁻²	7
8	Ag ₂ O@Ni foam	530 mM FAL, 1.95 V OCV, 1 M KOH	90% FA yield, 94% FE, 400 mA cm ⁻²	8
9	<i>Comamonas testosteroni</i> SC1588	50 mM FAL, 30 °C, pH 7 buffer, 10 h	96% FA yield, 20 µmol/h	9
10	<i>P. putida</i> KT2440	204 mM FAL, 30 °C, pH 6 buffer, 3 h	>97% FA yield, 2425 µmol/h	10

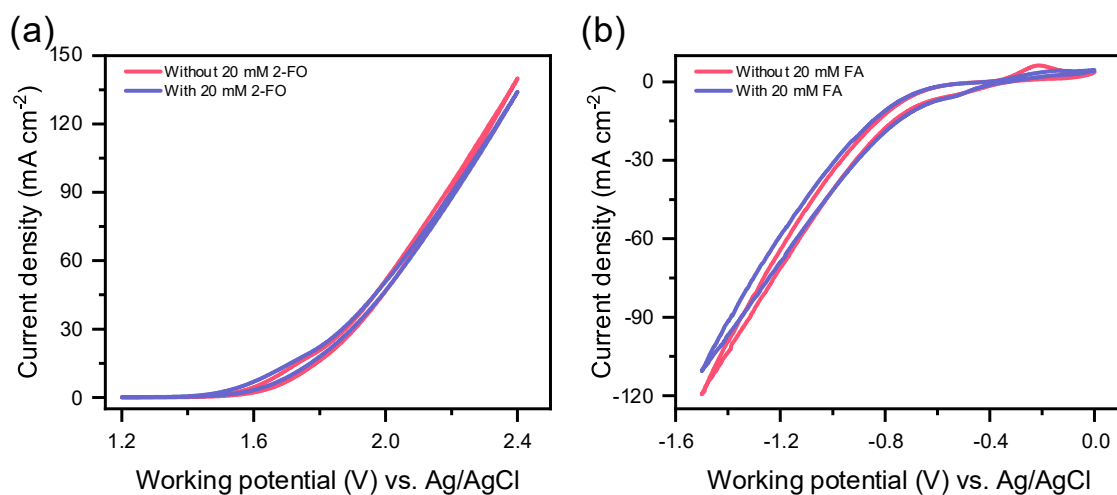


Fig. S1. Cyclic voltammograms (CVs) on Pt and Ni: **(a)** Positive scan using Pt as working electrode with and without 20 mM 2-FO and **(b)** Negative scan using Ni as working electrode with and without 20 mM FA in 20 mL pH 5.5 electrolyte at 80 °C respectively.

Preliminary Experiment: Product Identification

The time-resolved electrochemical oxidation (ECO) of 2-furoic acid (FA) galvanometric electrolysis was conducted using the Pt anode paired with a Pt cathode operating in pH 2 at 1 mA to investigate the change in Faradaic Efficiency (FE) and product distribution (Fig. S2). The Pt cathode was selected because the control experiment revealed it performed H^+ reduction to H_2 , aka. hydrogen evolution reaction (HER), almost exclusively instead of 2-FO in pH 2, which allowed us to analyze the 2-FO product more accurately. As the passed charge increased from 0 to 43.2 C (2.24 equivalence oxidizing charge), the FA conversion reached $89.6 \pm 0.8 \%$ and $73.7 \pm 2.0 \%$ 2-FO was produced. The reaction also produced $12.1 \pm 1.1 \%$ HFO and $2.6 \pm 0.2 \%$ MA. As the charge delivery increased to 86.4 C (4.5 oxidizing equivalent charge), all FA was consumed and yielded $83.6 \pm 1.0 \%$ of 2-FO, accompanied by a small amount of HFO and MA. This result suggested the side-reaction includes the over-oxidation of 2-FO to HFO and MA in this low current density (1 mA cm^{-2}) and acidic pH. The FE decreased as the FA diminished, which shifted the electrochemical reaction from oxidizing FA to water.

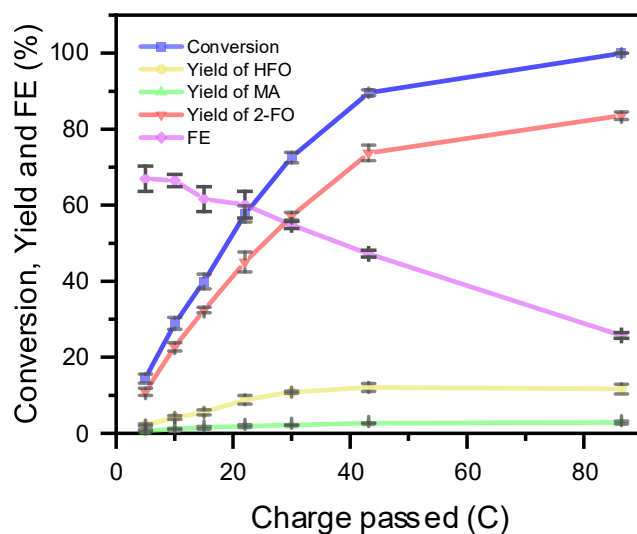


Fig. S2. The electrochemical oxidation of FA in pH 2. 10 mM FA at 1 mA constant current in pH 2 buffer at 80 °C with 0 – 86.4 C charge passed (24 h). WE: Pt, CE: Pt. Experiments were performed in triplicate and error bars correspond to the standard deviation of three independent measurements.

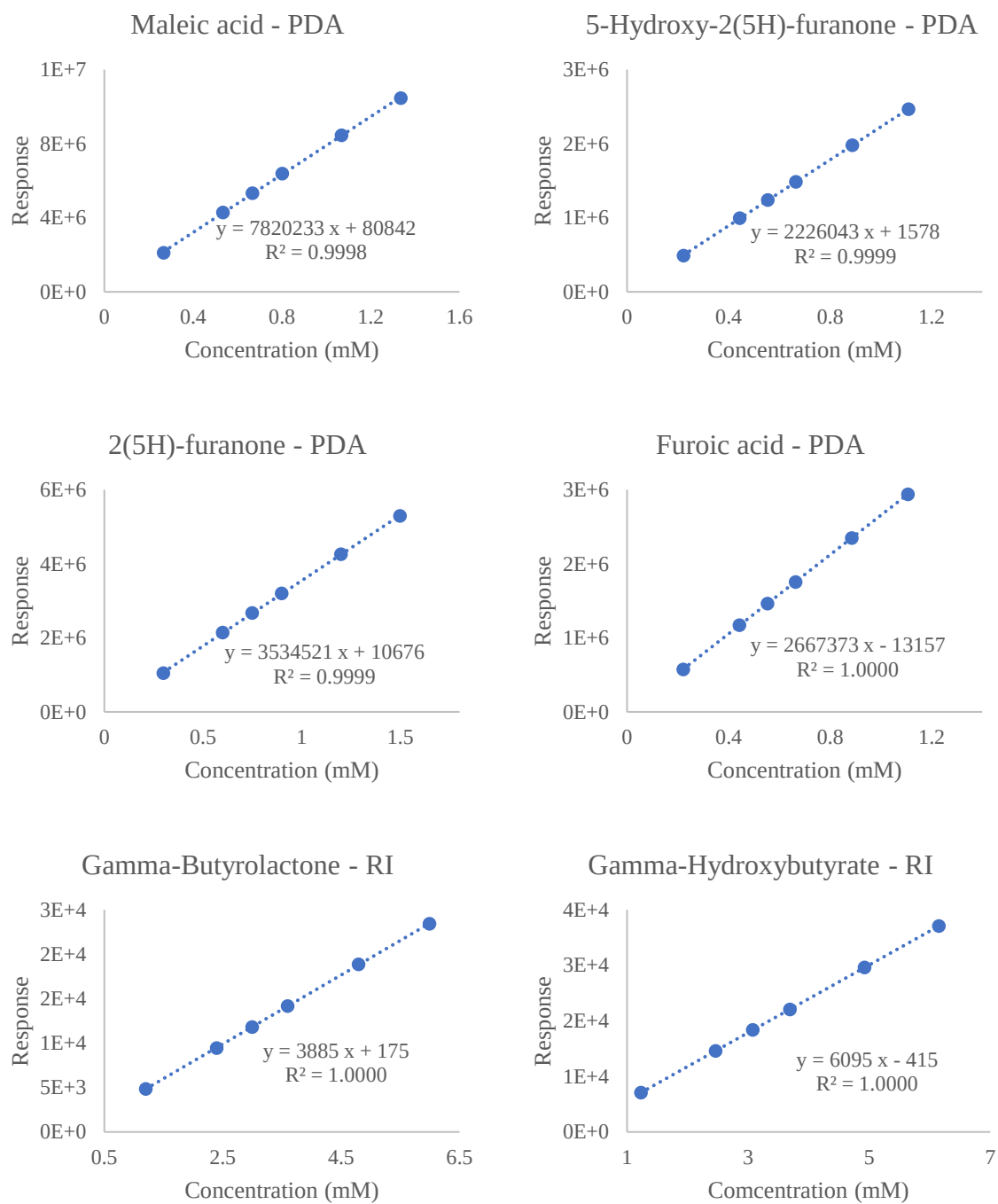


Fig. S3. HPLC calibration curves of different products. Obtained from the photodiode array (PDA) and refractive index (RI) detectors.

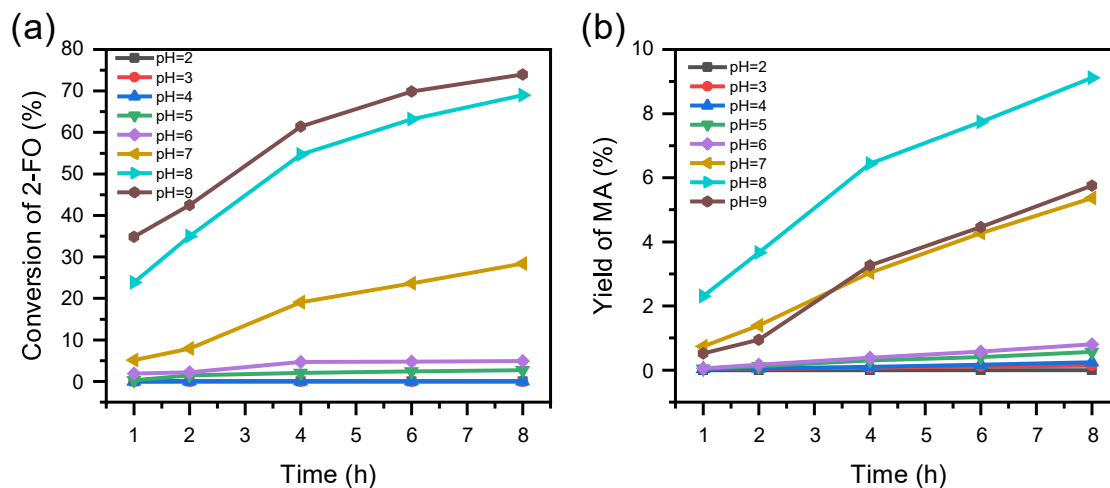


Fig. S4. pH stability examination of 2-FO in pH 2 to 9. **(a)** conversion of 2-FO and **(b)** yield of MA. Reaction conditions: 10 mM 2-FO in 10 mL different pH of 0.5 M potassium phosphate buffer at 80 °C.

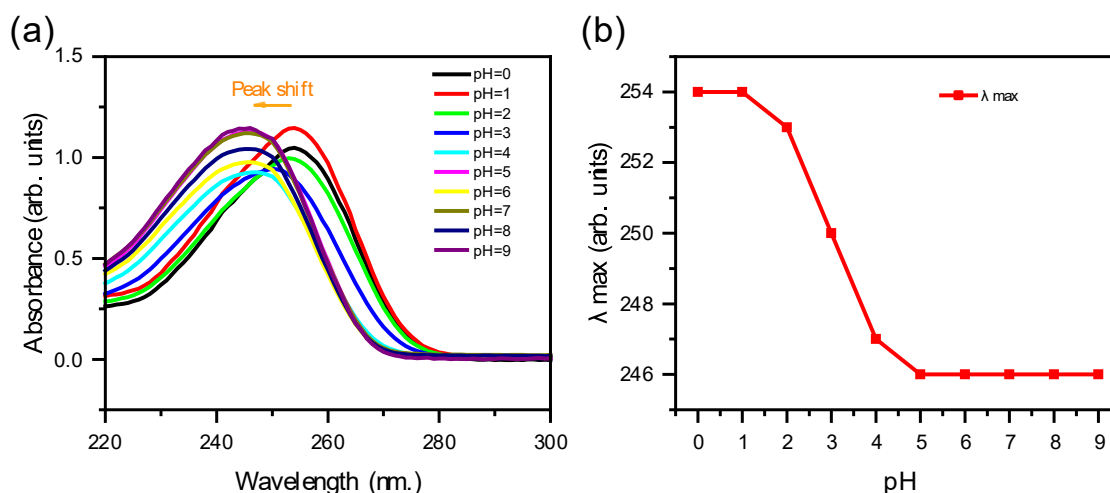


Fig. S5. (a) The UV-Vis absorbance of FA (0.1 mM) **(b)** The maximum UV-Vis absorbance ($\lambda_{\max}$) of FA from pH 2 to 9. The FA $\lambda_{\max}$ underwent a blue shift as the carboxyl group gradually deprotonated between pH 1 – 5, shifting the $\lambda_{\max}$ from 254 to 246 nm. A comparable $\lambda_{\max}$ shift could be seen with other aromatic acids.¹¹ The stable $\lambda_{\max}$ at pH before 1 and after pH 5 indicated that FA existed in FA molecular form and its anion form, respectively.

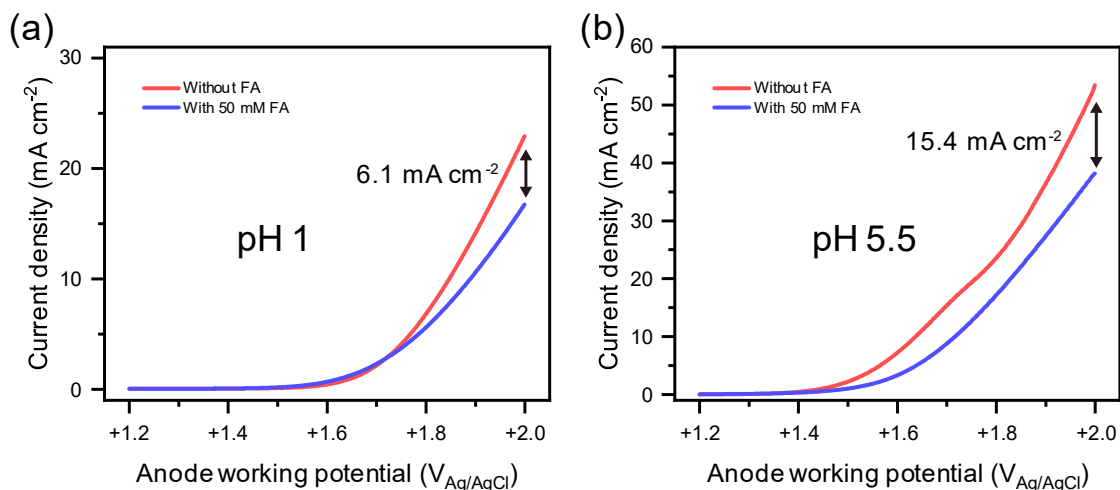


Fig. S6. LSV study at (a) pH 1 and (b) pH 5.5 with or without 50 mM FA. Reaction conditions: Scan rate 50 mV/s; 80 °C; WE: Pt; CE: Pt.

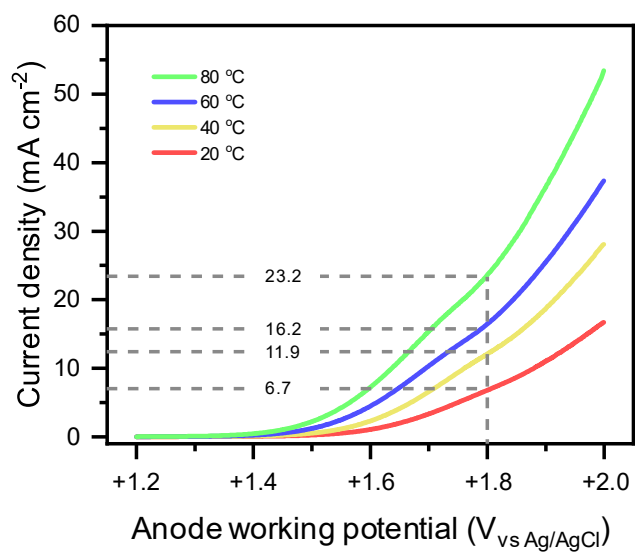


Fig. S7. Linear sweep voltammograms (LSVs) at 20 to 80 °C temperature range. Conditions: pH 5.5; without FA; WE: Pt; CE: Pt.

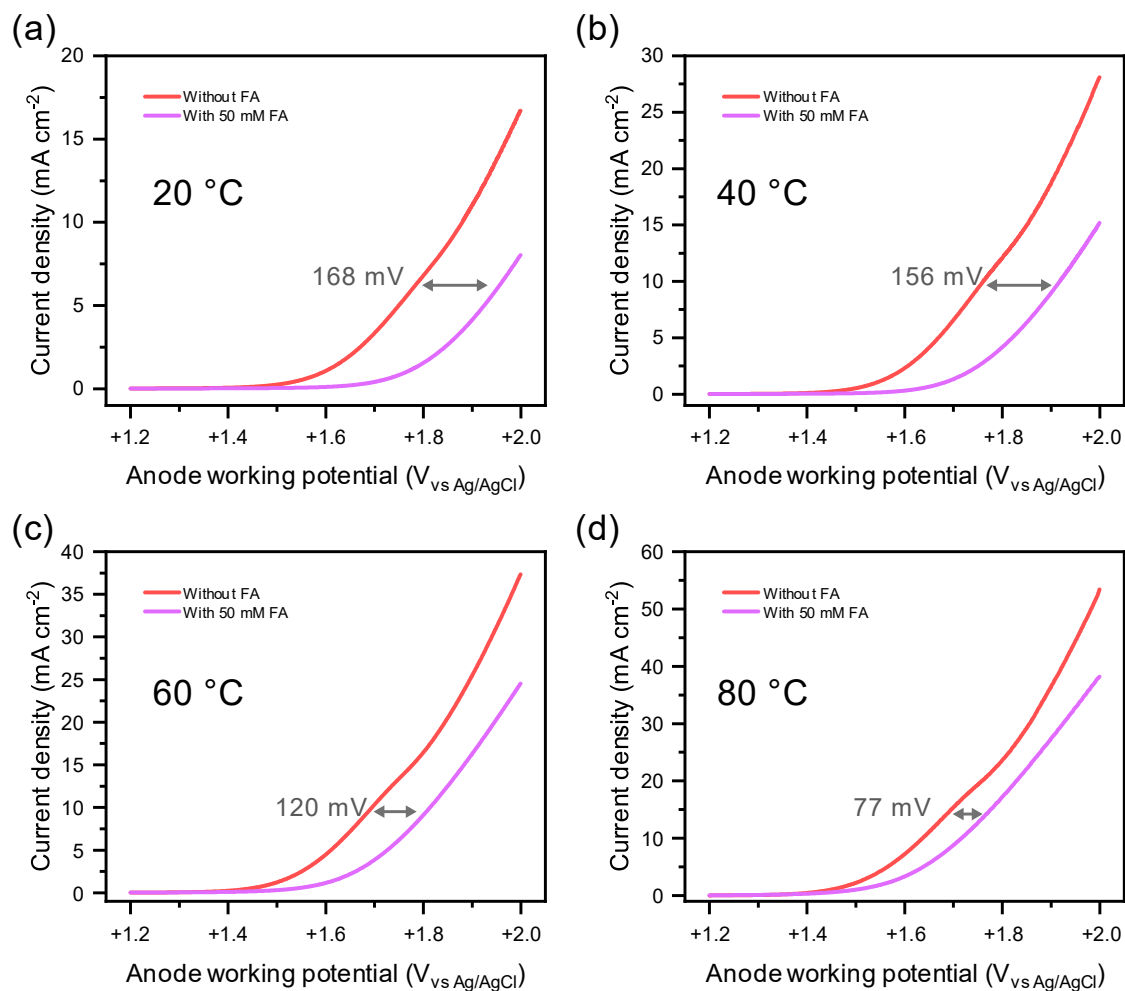


Fig. S8. Linear sweep voltammograms (LSVs) curve of the electrode in pH 5.5 buffer with and without 50 mM of FA at (a) 20 (b) 40 (c) 60 and (d) 80 °C, respectively. The potential differences were measured at $j = 7.5\ mA\ cm^{-2}$. WE: Pt; CE: Pt.

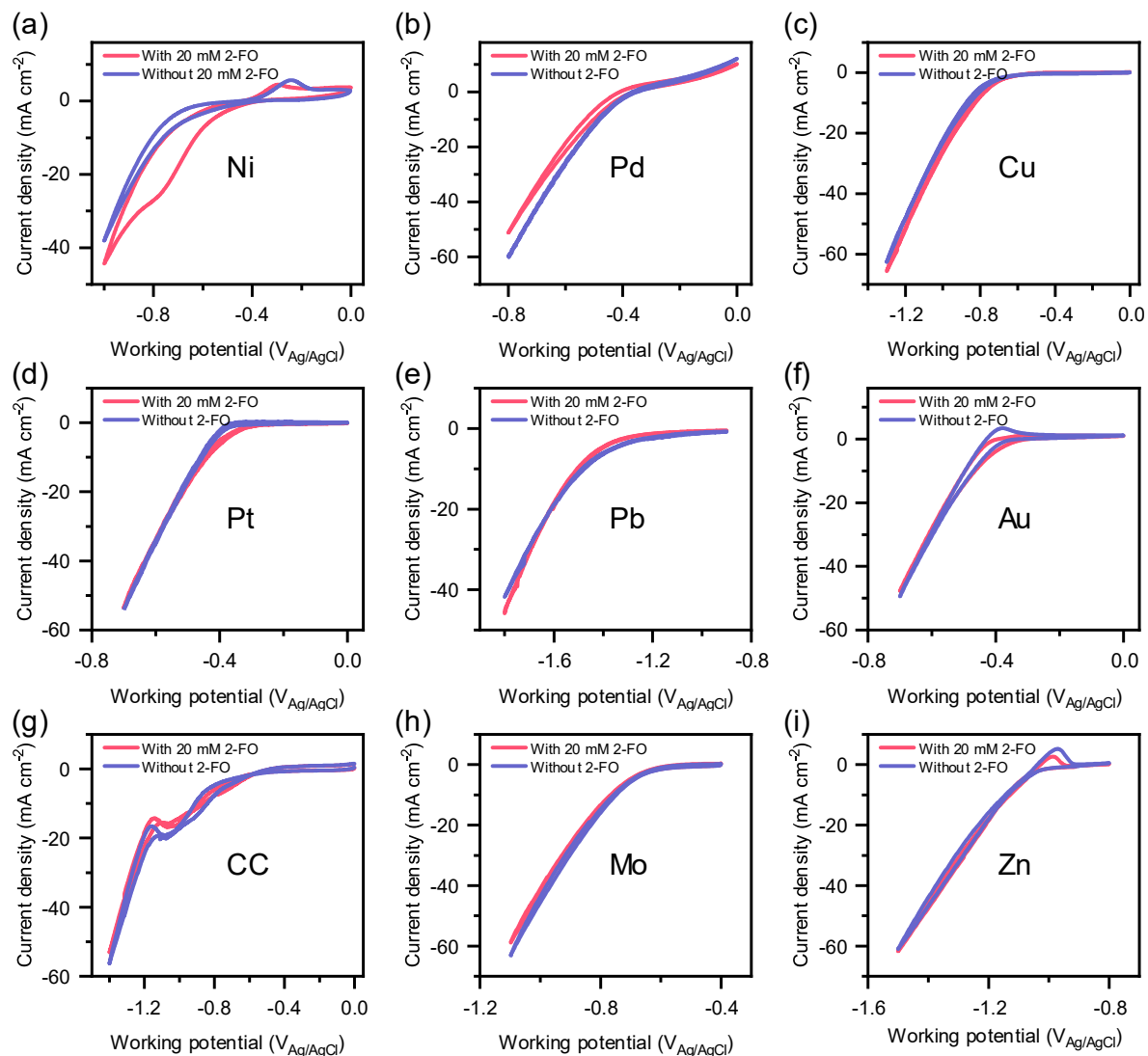


Fig. S9. Cyclic voltammograms (CVs) in the presence and absence of 20 mM of 2-FO in 20 mL pH 5.5 electrolyte at 80 °C using different working electrodes (a) Ni; (b) Pd; (c) Cu; (d) Pt; (e) Pb; (f) Au; (g) CC; (h) Mo; (i) Zn as WE, respectively.

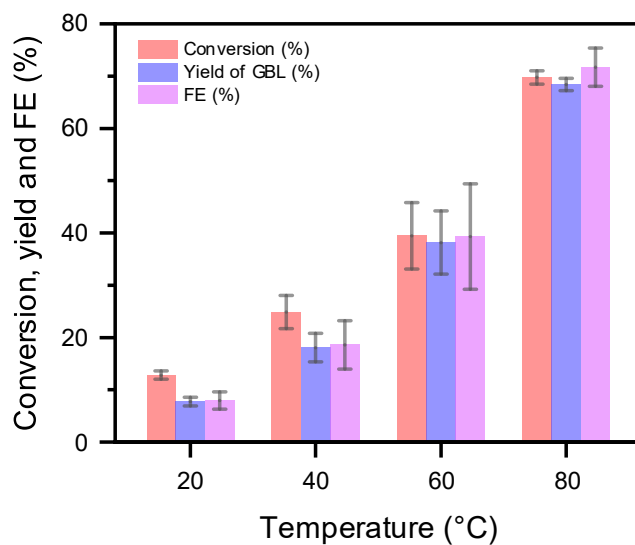


Fig. S10. The electrochemical reduction (ECH) of 2-FO at 20 – 80 °C. Experiments were performed in triplicate and error bars correspond to the standard deviation of three independent measurements. Reaction conditions: 20 mM 2-FO in 20 mL pH 5.5 buffer; 2.0 $V_{Ag/AgCl}$; WE: Pt, CE: Ni.

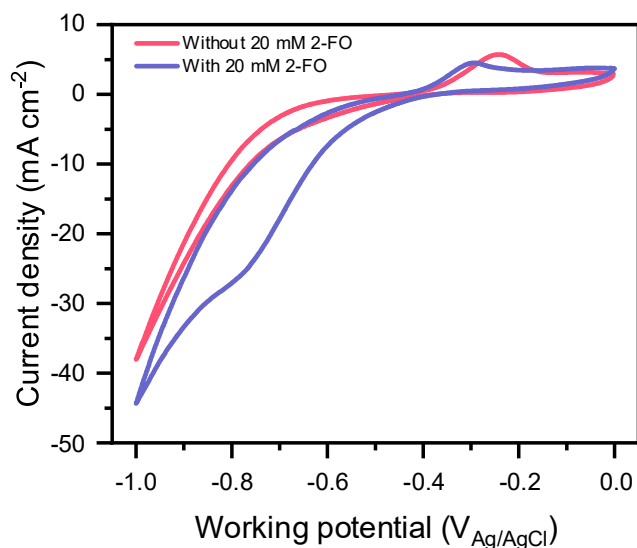


Fig. S11. Cyclic voltammograms (CVs): With and without 20 mM 2-FO in pH 5.5 electrolyte at 80 °C. WE: Ni; CE: Pt.

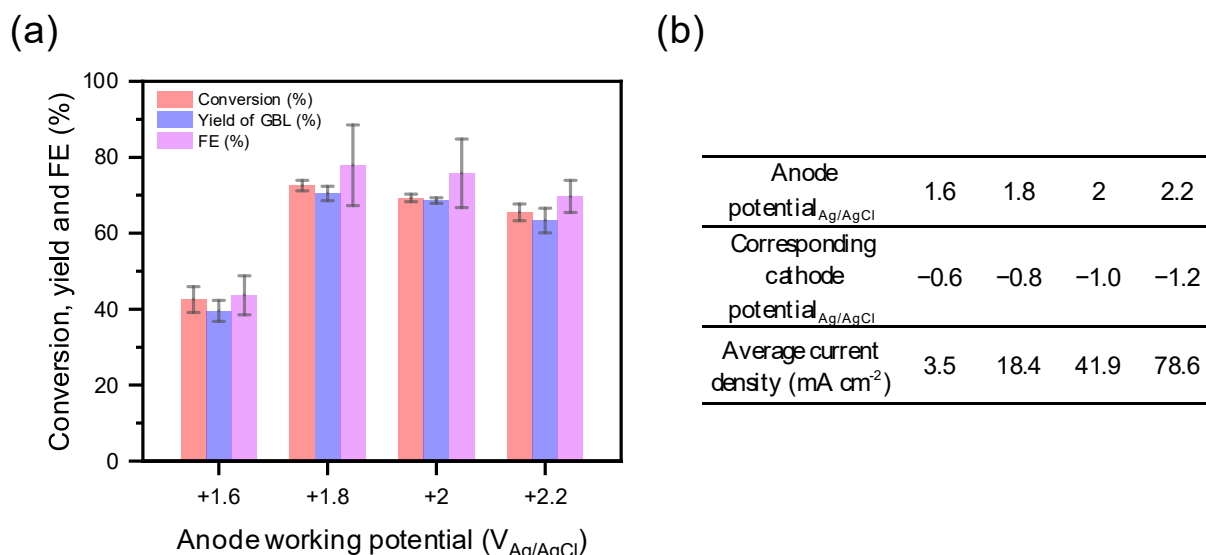


Fig. S12. (a) The electrochemical reduction (ECH) of 2-FO at an applied anodic potential of 1.6 to 2.2 V_{Ag/AgCl} and (b) the corresponding cathode potential. Experiments were performed in triplicate and error bars correspond to the standard deviation of three independent measurements. Reaction conditions: 20 mM 2-FO in 20 mL pH 5.5 buffer at 80 °C; WE: Pt, CE: Ni.

Note: The objective was to examine whether the ECO and ECH reactions would operate in a comparable potential range suitable for their integration. We recorded the cathode potentials using a multimeter (measured between the cathode and reference electrode) while the electrochemical workstation monitored the working potentials for the anode (Fig. S12). The investigation began with the Pt operated at +1.6 V_{Ag/AgCl}, which was the lowest potential that generated a reasonable current flow at an average of ~3.5 mA cm⁻². The CV analysis revealed that +1.6 V_{Ag/AgCl} was close to the onset potential of HER (Fig. S11). While the Pt operated at +1.6 V_{Ag/AgCl}, the Ni cathode working potential reached -0.6 V_{Ag/AgCl} and yielded 38.3% GBL. As the Pt working potential increased to +1.8 and +2.0 V_{Ag/AgCl}, the Ni reduction potential raised to -0.8 and -1.0 V_{Ag/AgCl}, respectively, and the GBL respective yield were 70.5 ± 1.9 % and 68.6 ± 0.7 %. After that, at +2.2 V, the corresponding cathodic working potential became too high that favoured HER instead of ECH of 2-FO to GBL, and thus the GBL yield, and FE began to decline.

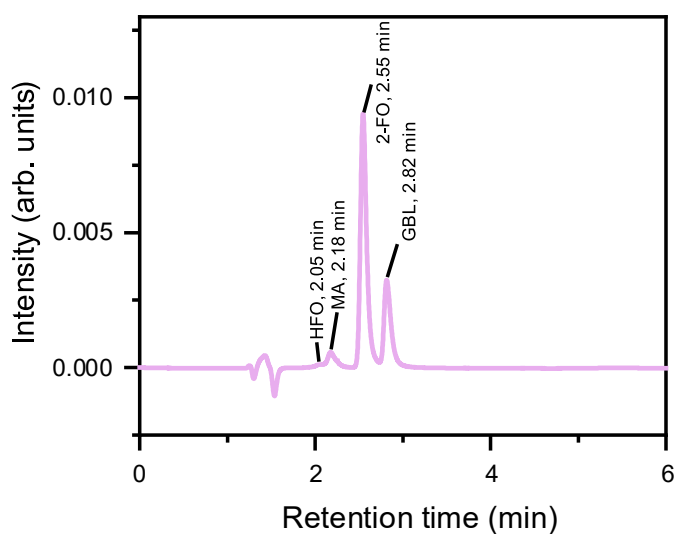


Fig. S13. HPLC chromatograms of PDA @ 210 nm sample analyses from the ECH of 20 mM 2-FO in 20 mL of 0.5 M pH 5.5 buffer at +2.0 V_{Ag/AgCl}, after 300-coulomb charge passed, referenced to the Pt anode paired with a Ni counter electrode at 80 °C. Note: MA: Maleic acid; HFO: 5-Hydroxy-2(5H)-furanone; 2-FO: 2(5H)-Furanone; GBL: Gamma-butyrolactone.

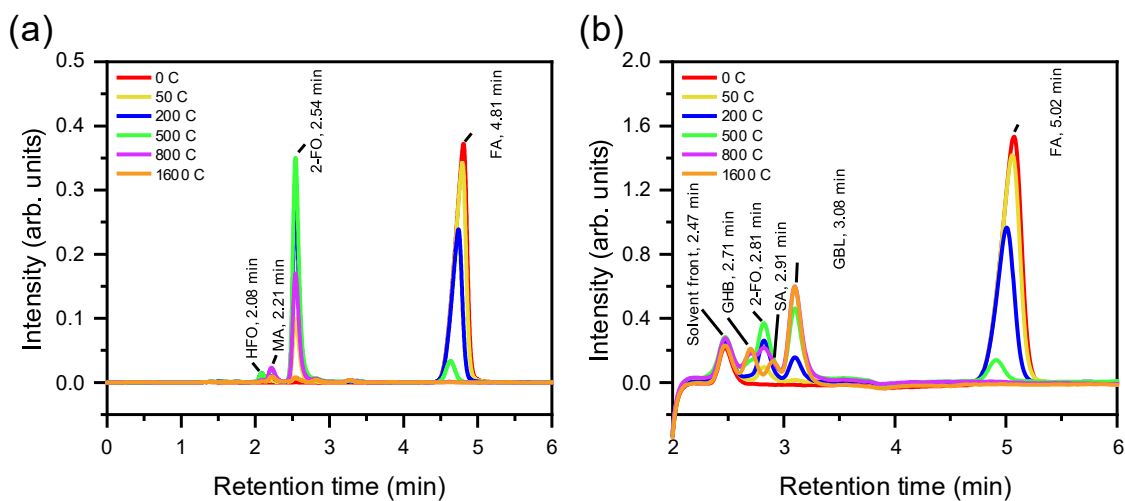


Fig. S14. HPLC chromatograms of (a) -PDA @ 210 nm and (b) -RI sample analyses collected periodically from a time-resolved electrolysis of 100 mM FA in 20 mL of 0.5 M pH 5.5 buffer at +2.0 V_{Ag/AgCl} referenced to the Pt anode paired with a Ni counter electrode at 80 °C. Note: MA: Maleic acid; HFO: 5-Hydroxy-2(5H)-furanone; 2-FO: 2(5H)-Furanone; FA: Furoic acid; GBL: Gamma-Butyrolactone; GHB: Gamma-Hydroxybutyrate; SA: Succinic acid.

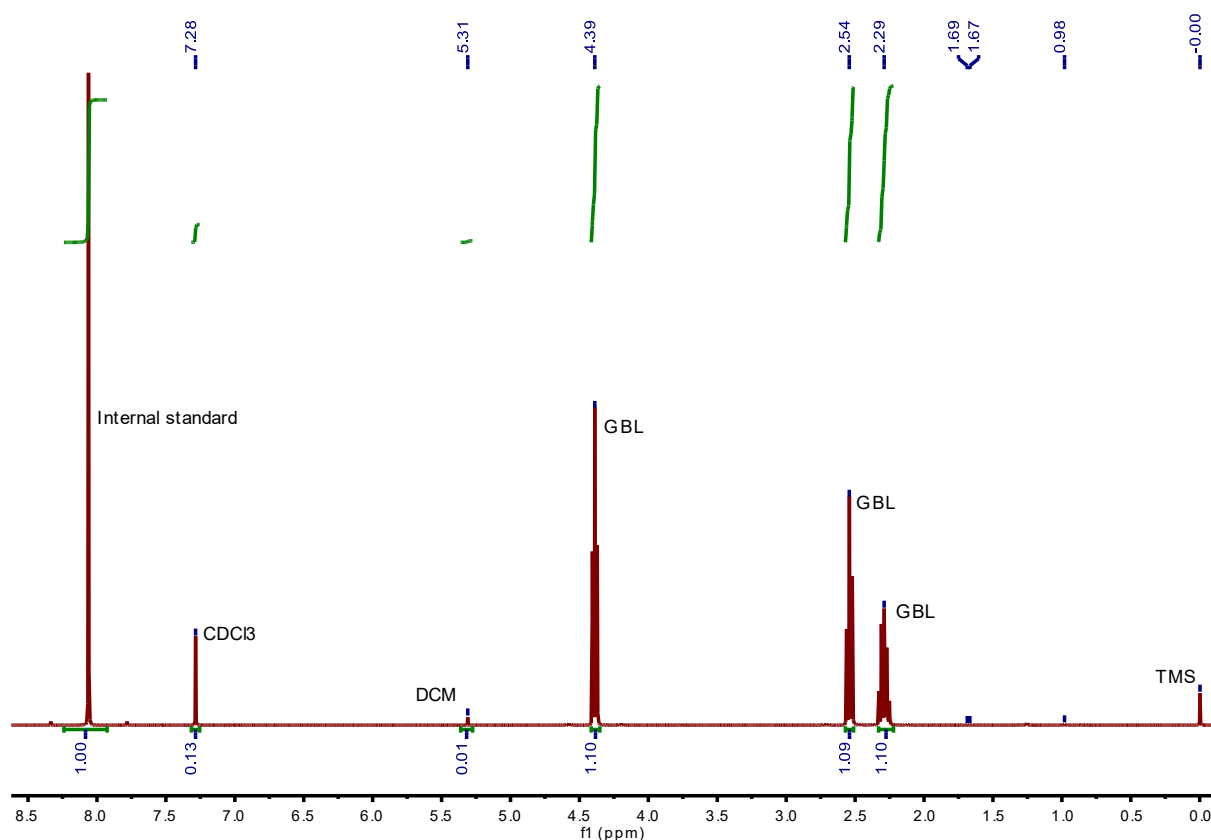


Fig. S15. The purity of GBL was examined by ¹H NMR. Reaction conditions: 50 mA cm⁻², 24 h, 5.6 g FA in 500 mL (100 mM) pH 5.5 buffer, 3*3 cm Pt as anode paired with 3*3 cm Ni as cathode, 80 °C. The solution was extracted by 500*2 mL of DCM. Then, the organic solution was rotary evaporated to obtain the high-purity GBL. Formic acid was used as an internal standard for quantitation.

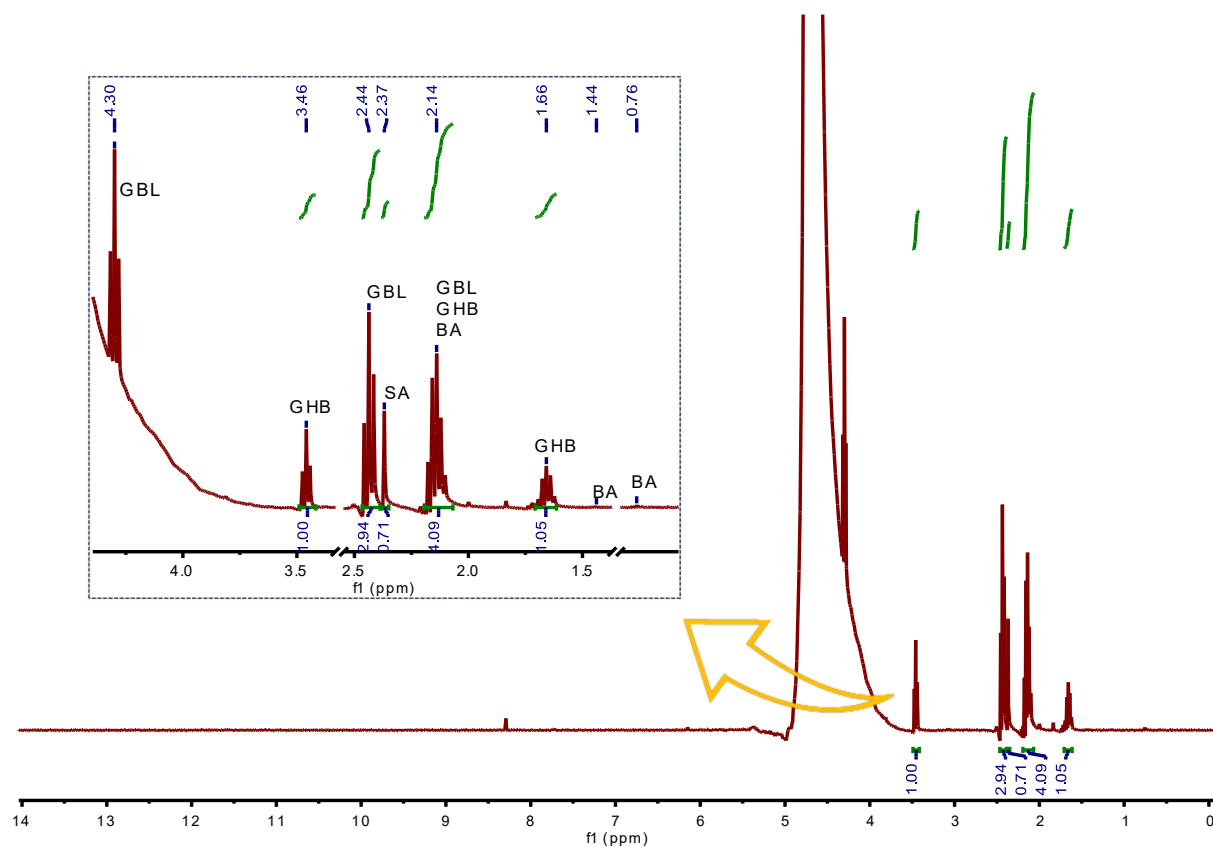


Fig. S16. ¹H NMR analysis of pre-extracted electrolyte in D₂O. Reaction conditions: 50 mA cm⁻², 24 h, 5.6 g FA in 500 mL (100 mM) pH 5.5 buffer, 3*3 cm Pt as anode paired with 3*3 cm Ni as cathode, 80 °C. Note: GBL: Gamma-Butyrolactone; GHB: Gamma-Hydroxybutyrate; SA: Succinic acid; BA: Butyric acid.

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