

Supplementary Information

Electrochemical production of methyltetrahydrofuran, a biofuel for diesel engines

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Background Information

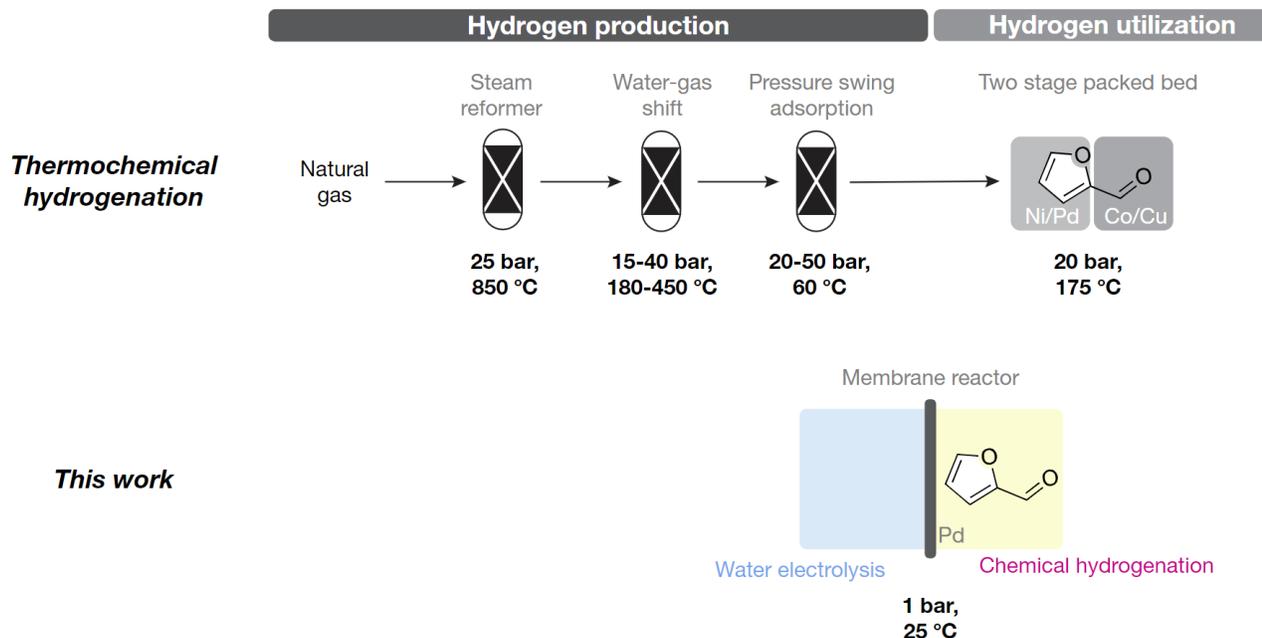


Fig. S1: Thermochemical hydrogenation of furfural compared to membrane reactor hydrogenation. Thermochemical hydrogenation sources hydrogen from natural gas, through a process called steam methane reforming. The resulting hydrogen gas is transported to a hydrogenation facility where it is fed into a two-stage packed bed reactor with furfural at 175 °C at 20 bar. The catalysts used in the first bed are typically Ni- or Pd-based, and the catalysts used in the second bed are typically Co- or Cu-based. Membrane reactor hydrogenation sources hydrogen from water electrolysis. The hydrogen permeates through a Pd membrane into a secondary compartment containing furfural and reacts on the Pd surface to form hydrogenated products. This reactor combines hydrogen production and utilization into a single system, and therefore bypasses the need for H₂ gas to be formed and/or transported.

Reduction potentials of water splitting, furfural, and its derivatives:^{1,2}





All potentials reported are vs. RHE.

Materials

Wafer bars (1-oz) of Pd (99.95%) were obtained from Silver Gold Bull. PdCl₂ (99.9%) was purchased from Strem Chemicals. DCM ($\geq 99.8\%$), H₂SO₄, HNO₃, H₂O₂ solution (30 wt. % in H₂O), *i*-PrOH (99.5%), *t*-BuOH ($\geq 99.7\%$), 2-methylfuran (MF; 99%), and 2-methyltetrahydrofuran (MTHF; $\geq 99\%$) were purchased from Sigma Aldrich. Furfural (98%), furfuryl alcohol (FA; 98%), tetrahydrofurfuryl alcohol (THFA; 99%), Pt gauze (52 mesh, 99.9%), and Pt wire (0.5 mm, 99.95%) were obtained from Alfa Aesar. Ag/AgCl reference electrodes (RE5B) were purchased from BASi. Viton o-rings, M3 and M4 socket head 10-24 stainless steel bolts, Aluminum sheet (1/4" thick) and acrylic sheet (1/8" thick) were purchased from McMaster Carr. Copper tape (1/4" wide) manufactured by 3M was purchased from Digikey.

Supplementary Experimental Methods

Membrane reactor design and assembly

The reactor was designed in-house using SolidWorks computer aided design (CAD) software (Fig. S2). The electrochemical compartment was machined from a block of polyetheretherketone (PEEK) and the hydrogenation compartment was 3D printed out of a clear resin (Form 3 stereolithography 3D printer, Formlabs). The catalyst-coated Pd membrane was sandwiched between the electrochemical and hydrogenation compartments. All interfaces were sealed together using viton o-rings. The compartments were clamped together using four 10-24 stainless steel screws secured to a ¼" thick aluminum backing plate. A ⅛" thick acrylic slide was sandwiched under a separate ¼" thick aluminum plate to provide a viewing window into the anode compartment. This window enables visual monitoring of H₂ bubble dispersion across the Pd membrane during operation. Both the anode and cathode compartments have a hole on the top face for the counter and reference electrodes to be placed in the electrolyte for use during electrodeposition.

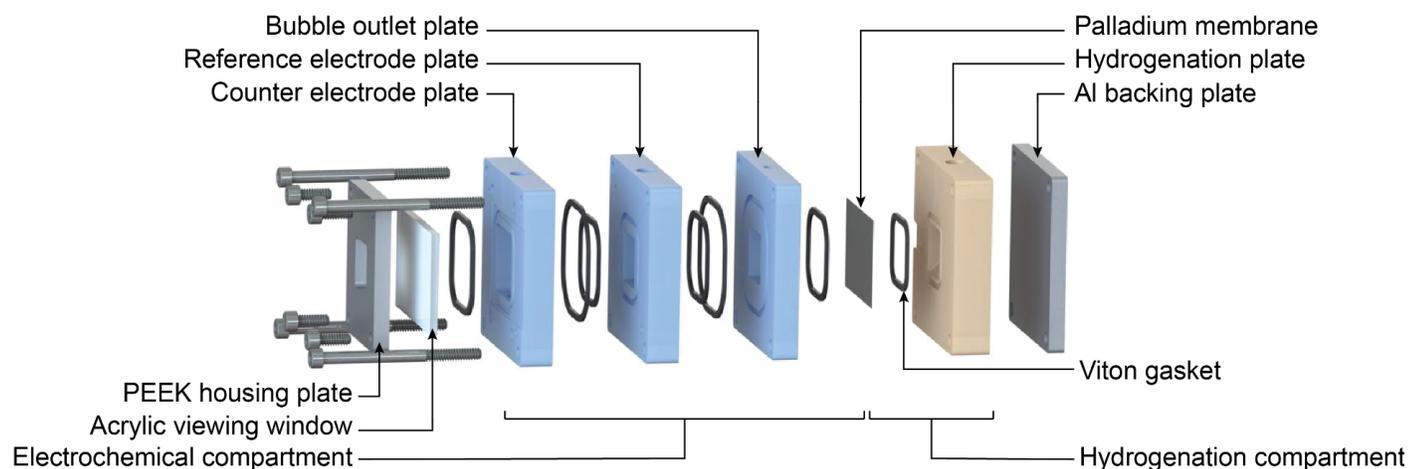


Fig. S2: Membrane reactor design and assembly. The electrochemical compartment (left, blue) consists of three plates, with openings for a counter electrode, reference electrode, and bubble escape,

respectively. A palladium membrane separates the electrochemical compartment (8 mL) from the hydrogenation compartment (2.5 mL) (right, orange). An acrylic viewing window enables visual inspection of the electrochemical compartment during reaction. The reactor is sandwiched together using a PEEK housing plate and an Al backing plate. Viton gaskets are used to seal the reactor upon assembly.

Pd membrane preparation

Pd foils were rolled from a 1-oz Pd wafer bar using an MTI MR-100A electric rolling mill. The bar was rolled to a thickness of 30 μm determined by a Mitutoyo digital micrometer. The resulting Pd foil was cut into $\sim 3 \times 3 \text{ cm}^2$ squares and annealed at 850 $^\circ\text{C}$ for 1.5 h under N_2 gas. The foils were then cleaned using 1:2:1 concentration $\text{HNO}_3:\text{H}_2\text{O}:\text{H}_2\text{O}_2$ v/v solution until vigorous bubbling subsided (~ 40 min), rinsed with Milli-Q water, then *i*-PrOH, then dried with N_2 gas.

Pd catalyst (Pd black) electrodeposition

Pd catalyst (Pd black) was electrodeposited on Pd foils using a one-compartment electrochemical cell. A Pd foil was clamped into the cell with an exposed geometric surface area of $2 \times 2 \text{ cm}^2$. The Pd foil served as a working electrode in reference to an Ag/AgCl reference electrode and Pt mesh counter electrode. The compartment was filled with 15 mL of 15.9 mM PdCl_2 in 1 M HCl electrolyte. A voltage of -0.2 V vs. Ag/AgCl was applied to the Pd foil working electrode to reduce Pd ions in solution. The electrodeposition ended when a charge of 30 C had been passed, corresponding to a catalyst loading of approximately 7.5 C cm^{-2} , similar to a previously reported procedure.^{3 4}

Pd membrane cycling

Used Pd membranes were recycled by electrochemically “deloading” the hydrogen from them upon completion of an experiment. An amperometric potential was applied across the membrane and

anode until no current flowed through the cell. The Pd black was etched away using concentrated nitric acid. The etched membranes were submerged into a 1:2:1 concentration $\text{HNO}_3:\text{H}_2\text{O}:\text{H}_2\text{O}_2$ v/v solution until bubbling subsided (~40 min), rinsed with Milli-Q water, then *i*-PrOH, then dried with N_2 gas. Pd black was redeposited onto the membrane prior to use. Our typical mode of failure is mechanical (pinhole formation, tearing around the gasket) and we found that a single membrane could be used around 7-8 times before reaching mechanical failure when handled according to the described procedure. Figure S3 demonstrates no deterioration in chemical activity for a Pd membrane that was used 8 times.

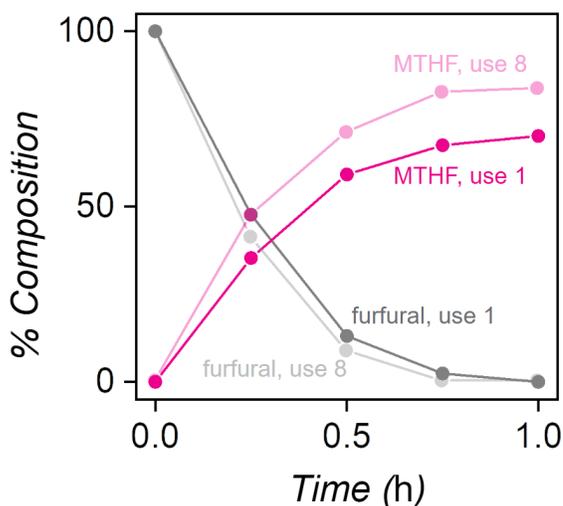


Fig. S3: Reaction profile for furfural hydrogenation to MTHF at 200 mA/cm^2 for a new membrane (first use) and a re-used membrane (8th use). The difference in reactivity falls within error for furfural hydrogenation at 200 mA/cm^2 .

Electrochemical surface area (ECSA) measurements⁵

ECSA measurements of a bare Pd membrane and a Pd black-deposited membrane (geometric surface area of 4 cm^2) were performed in the electrochemical compartment of the membrane reactor. The compartment was filled with 18 mL of 0.15 M potassium hexafluorophosphate (KPF_6) in dry

acetonitrile. An Ag/AgCl reference electrode was used for ECSA measurements. The electrode was rinsed with deionized water prior to use and referenced vs. 4.0 M KCl glass-body Ag/AgCl master reference electrode (Fisher Scientific 13-620-53) by measuring the open circuit potential between both electrodes in a saturated KCl solution. The reference electrode was then rinsed several times with the dry KPF₆ ECSA solution to remove any residual H₂O from the calibration. A 1-cm² Pt mesh counter electrode was used and cyclic voltammograms were performed at various scan rates (50 to 500 mV s⁻¹) with a potential range of ± 0.015 V from the open circuit potential. Current versus scan rates were plotted at 0.410 and 0.459 V vs. Ag/AgCl (the open circuit potential for the bare and Pd black-coated foil, respectively) and the slope of the plot was used to measure double-layer capacitance (Fig. S4). The ECSA for the bare Pd and Pd black-coated membranes were calculated, and the surface area of the Pd black-coated membrane was normalized against the bare Pd membrane. We determined that the addition of the Pd black catalyst to the bare Pd membrane increased the active surface area by 8-fold.

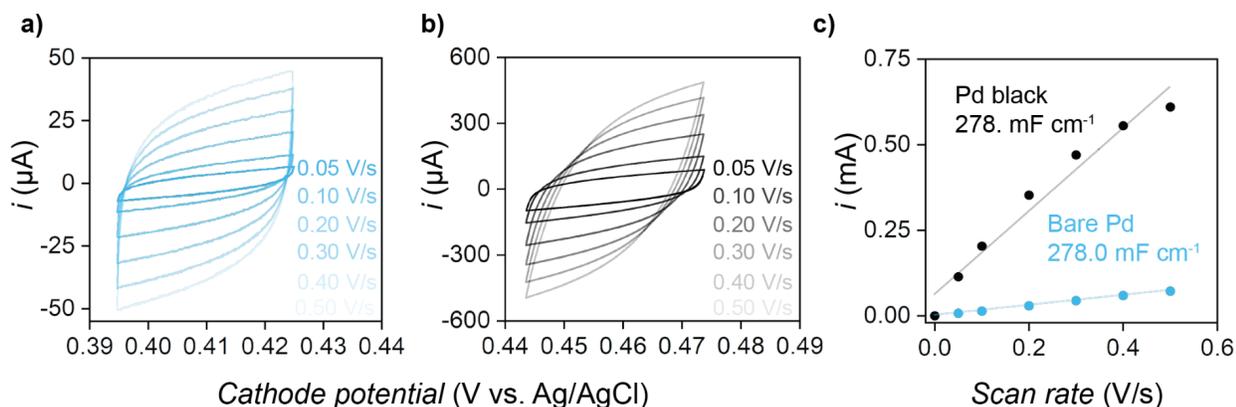


Fig. S4: Electrochemical surface area measurements on a bare and Pd black-coated Pd membrane. a) Cyclic voltammograms of a bare Pd membrane at different scan rates near the open circuit potential (0.410 V vs. Ag/AgCl). b) Cyclic voltammograms of a Pd black-coated membrane at different scan rates around the open circuit potential (0.459 V vs. Ag/AgCl). c) Double layer capacitance for a bare Pd membrane and a Pd black-coated membrane. Lines represent the lines-of-best-fit for each of the 7 data points. Double layer capacitance was calculated using measured data. The geometric surface area was 4 cm².

Gas chromatography mass spectroscopy (GC-MS)

Gas chromatography mass spectrometry (GC-MS) was used to quantify products for the hydrogenation of furfural. GC-MS measurements were conducted on an Agilent GC-MS using a HP-5ms column and electron ionization. For all membrane reactor experiments, aliquots of 30 μL diluted in 1 mL of pentane were taken at time intervals for up to 2 h of reaction. For all single cell (electrochemical hydrogenation) experiments, 100- μL aliquots were taken at time intervals of up to 1 h, and extracted with 1 mL of dichloromethane. The prepared samples were run on an autosampler with a 1- μL injection volume and a split ratio of 20:1. The oven temperature began at 40 $^{\circ}\text{C}$ for 1 min and ramped to 80 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ then to 200 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$. A solvent delay of 2.5 min was employed and the sequence ended after 14 minutes had passed to detect high mass products. For reaction pathway experiments, a solvent delay of 2 min was employed and the sequence was ended after 10.5 minutes. Product peaks were identified by searching the National Institute of Standards and Technology (NIST) database for matching mass spectra and confirmed with standards of each of the compounds (Fig. S5, S6).

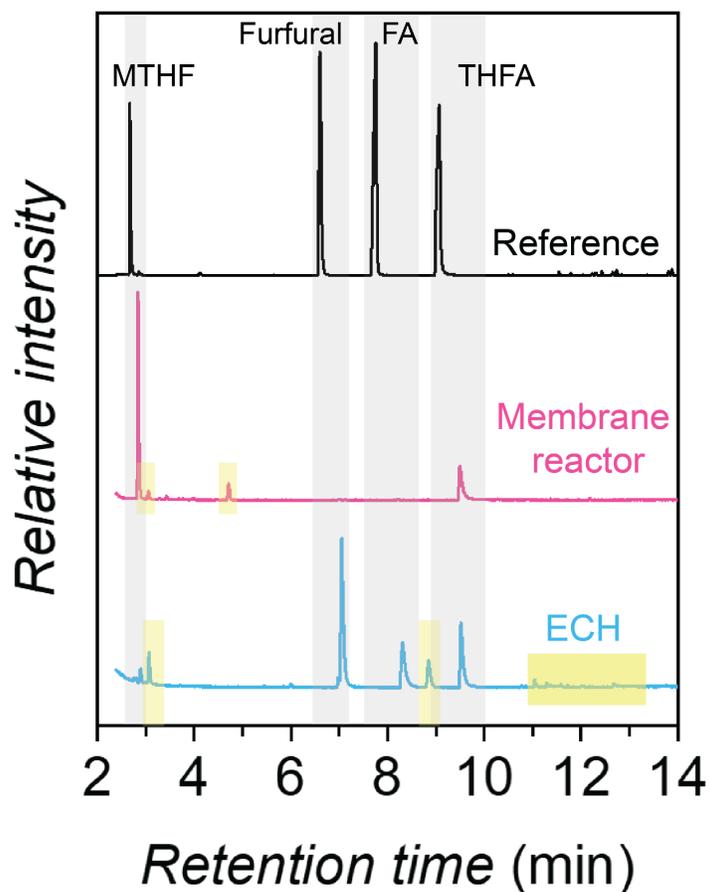


Fig. S5: GC chromatogram of a standard solution containing 2-methyltetrahydrofuran (MTHF), furfural, furfuryl alcohol (FA), and tetrahydrofurfuryl alcohol (THFA), overlaid with furfural hydrogenation at 200 mA/cm² in a membrane reactor, and furfural hydrogenation at 200 mA/cm² in a single electrochemical cell. The membrane reactor displays MTHF as the major product, while the single electrochemical cell displays multiple product peaks. Peaks highlighted in yellow represent “other” products (i.e. products that are not furfural, FA, THFA, or MTHF).

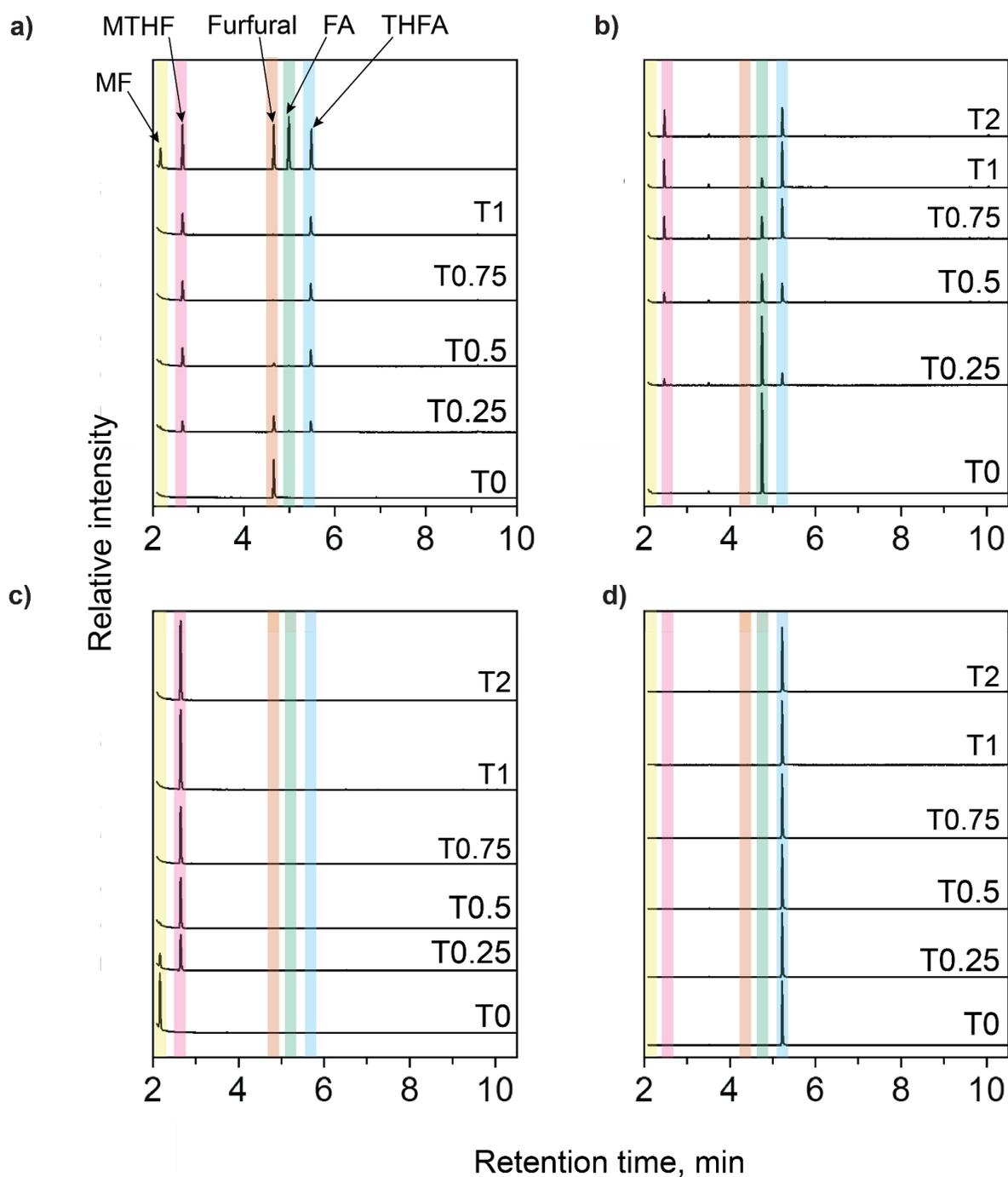


Fig. S6: a) GC chromatogram (signal intensity vs. time) of a standard solution containing 2-methylfuran (MF), 2-methyltetrahydrofuran (MTHF), furfural, furfuryl alcohol (FA), and tetrahydrofurfuryl alcohol (THFA), overlaid with furfural hydrogenation at 200 mA/cm². b) GC chromatogram of FA hydrogenation at 200 mA/cm². c) GC chromatogram of MF hydrogenation at 200 mA/cm². d) GC chromatogram of THFA hydrogenation at 200 mA/cm².

Faradaic Efficiency (FE%) Determination

The faradaic efficiencies towards MTHF production were calculated using the following equations:

$$FE\% = \frac{H_{MTHF}}{H_{Total}} \times 100\% \quad (S9)$$

$$H_{MTHF} = n_{MTHF} \times 8 \quad (S10)$$

$$H_{Total} = \frac{j \times A \times t}{F} \quad (S11)$$

Where H_{MTHF} is the number of moles of hydrogen reacted to form MTHF; H_{Total} is the total moles of hydrogen produced during electrolysis; n_{MTHF} is the number of moles of MTHF produced; j is the current density; A is the geometric area of the membrane/cathode; t is time; and F is Faraday's constant. We report the average faradaic efficiencies to MTHF for current densities where a significant change in selectivity occurred (50, 200, and 300 mA/cm²).

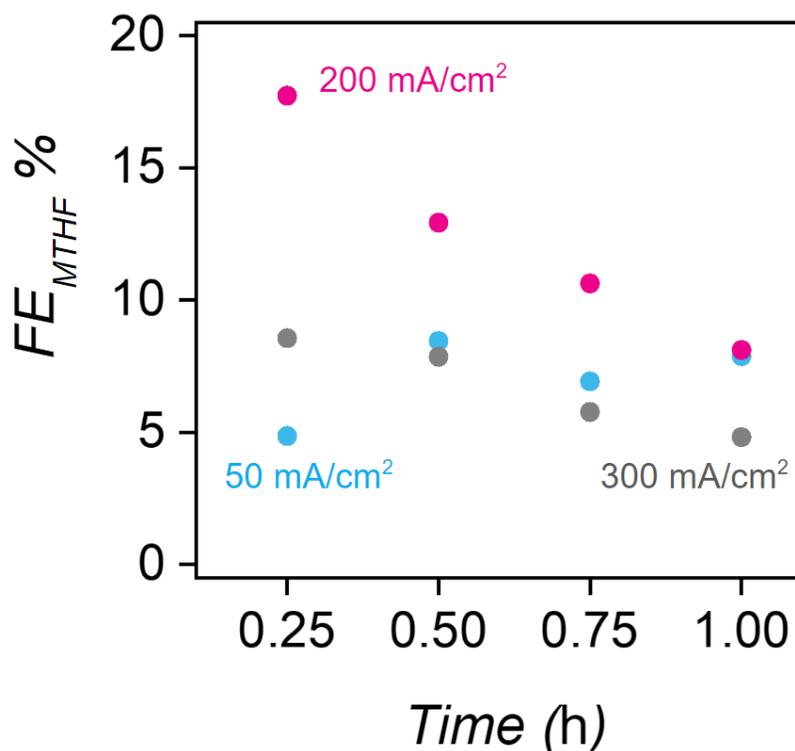


Figure S7: Faradaic efficiency (FE) of MTHF formation at 50, 200, and 300 mA/cm² in the membrane reactor. The FE at 200 and 300 mA/cm² declines over time. The FE at 50 mA/cm² increases over time because of the slower Pd-H loading at low current densities.

Electrochemical Hydrogenation Experiments

Electrochemical hydrogenation with a t-BuOH saturated electrolyte

A glass H-cell was assembled with Nafion separating the anode and cathode compartments. The anode compartment was filled with 1 M aqueous H₂SO₄ and the cathode compartment was filled with 1 M H₂SO₄ prepared using a 1:1 v/v H₂O to t-BuOH solution. The current was set to 0.80 A (200 mA/cm²) and the maximum voltage was set to 20 V. Before switching on the current, furfural was added to the cathode compartment to reach a concentration of 0.1 M. Electrolysis was run for 1 h and the product distribution was quantified using GC-MS.

Table S1. Comparison of electrochemical furfural hydrogenation using 1 M H₂SO₄ and a 1:1 *t*-BuOH: 1 M H₂SO₄ electrolyte. Percent compositions are reported for 1 h of electrolysis.

<i>Compound</i>	<i>%Composition 1 M H₂SO₄</i>	<i>%Composition 1:1 t-BuOH: 1 M H₂SO₄</i>
furfural	42.42	26.51
furfuryl alcohol (FA)	12.74	6.36
tetrahydrofurfuryl alcohol (THFA)	18.33	1.32
methyltetrahydrofuran (MTHF)	3.98	4.96
Other	22.52	60.86

Kinetic Analysis

The code used to generate the kinetic analysis plots in Figure 6 is available at https://github.com/berlinguette/ada/blob/master/2022_MTHF_Kinetic_analysis.ipynb. All code used in this study was based on the open-source Python packages numpy, matplotlib, scipy, and sklearn. Experimental data was plotted according to simple zero, first, and second order kinetic laws (Fig. S8, S9, S10). The resulting correlations were tabulated (Tables S2, 3, 4) and the laws that showed the best agreement were used to develop the code. We found that furfural reacts through zero order kinetics at 50 mA/cm², and first order kinetics at 200 mA/cm². FA reacts through zero order kinetics at both 50 and 200 mA/cm², while MF reacts through first order kinetics at both 50 and 200 mA/cm².

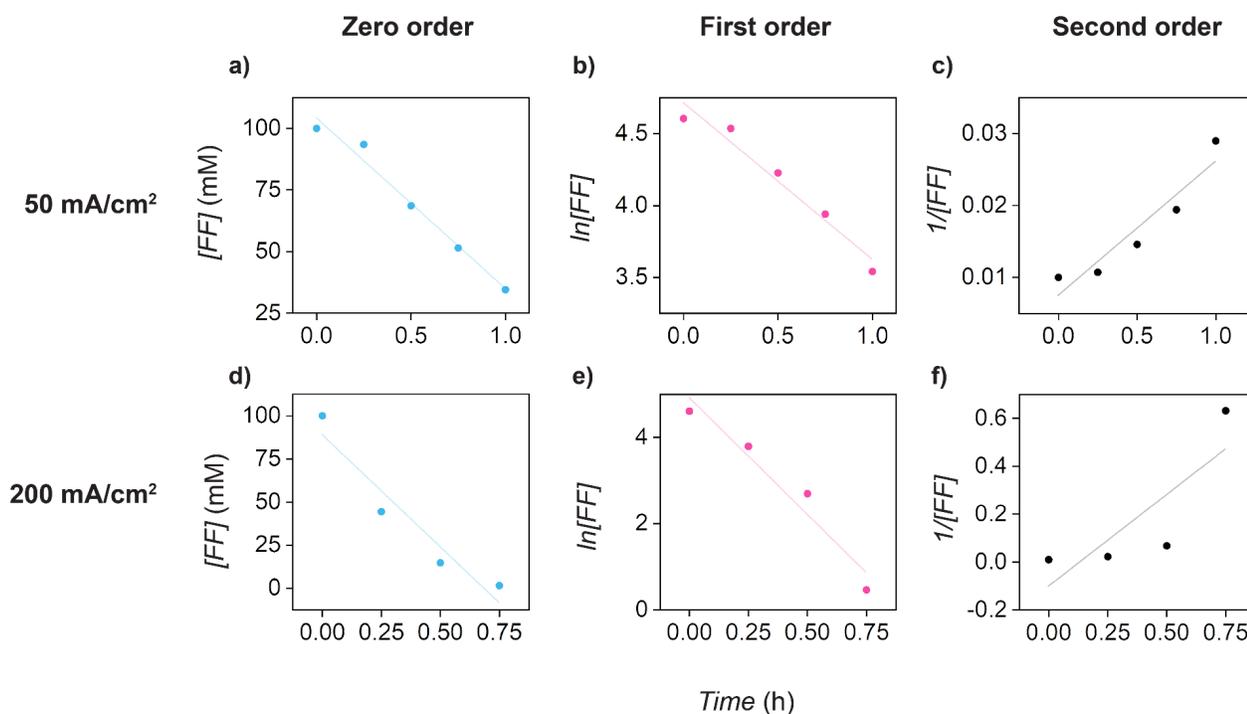


Fig. S8: [FF] denotes furfural concentration. a) Zero order kinetic plot of furfural concentration over time at 50 mA/cm². b) First order kinetic plot of the natural logarithm of furfural concentration over time at 50 mA/cm². c) Second order kinetic plot of the inverse of furfural concentration over time at 50 mA/cm². d) Zero order kinetic plot of furfural concentration over time at 200 mA/cm². e) First order kinetic plot of the natural logarithm of furfural concentration over time at 200 mA/cm². f) Second order kinetic plot of the inverse of furfural concentration over time at 200 mA/cm².

Table S2. R² values for zero, first, and second order fits for furfural hydrogenation at 50 and 200 mA/cm². Highest values are written in bold font.

Current density (mA/cm ²)	R ² zero order	R ² first order	R ² second order
50	0.980	0.957	0.894
200	0.840	0.994	0.675

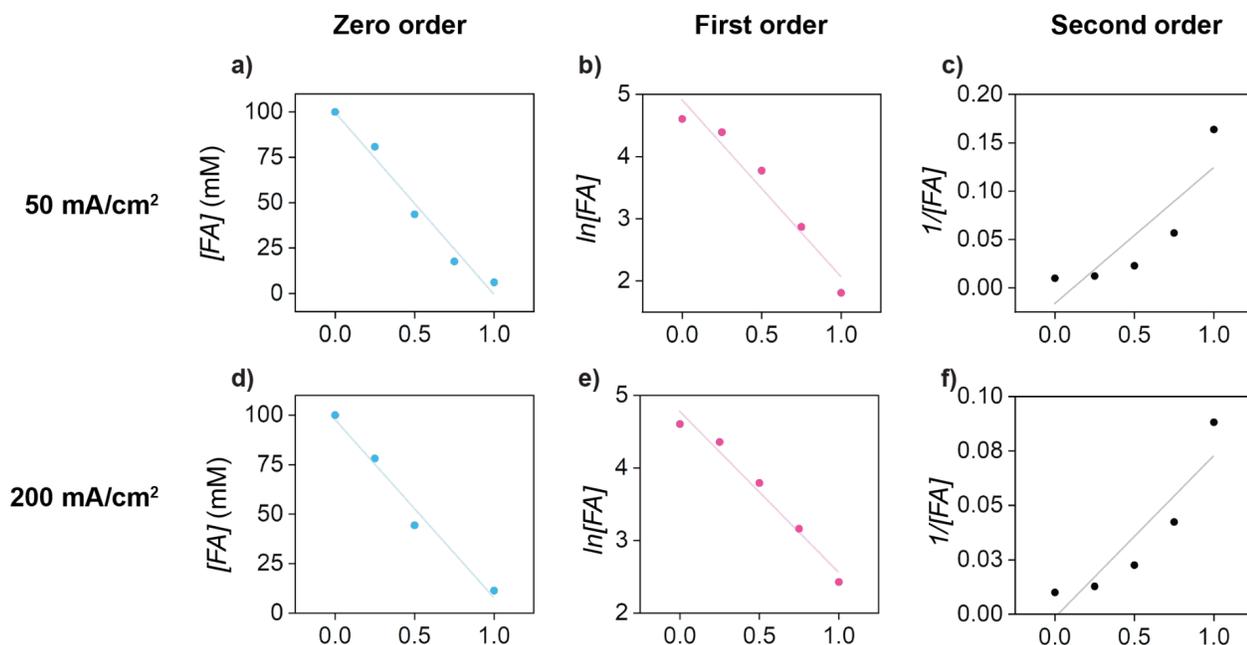


Fig. S9: [FA] denotes concentration of furfuryl alcohol. a) Zero order kinetic plot of FA concentration over time at 50 mA/cm². b) First order kinetic plot of the natural logarithm of FA concentration over time at 50 mA/cm². c) Second order kinetic plot of the inverse of FA concentration over time at 50 mA/cm². d) Zero order kinetic plot of FA concentration over time at 200 mA/cm². e) First order kinetic plot of the natural logarithm of FA concentration over time at 200 mA/cm². f) Second order kinetic plot of the inverse of FA concentration over time at 200 mA/cm².

Table S3. R² values for zero, first, and second order fits for FA hydrogenation at 50 and 200 mA/cm². Highest values are written in bold font.

Current density (mA/cm ²)	R ² zero order	R ² first order	R ² second order
50	0.974	0.946	0.742
200	0.980	0.974	0.831

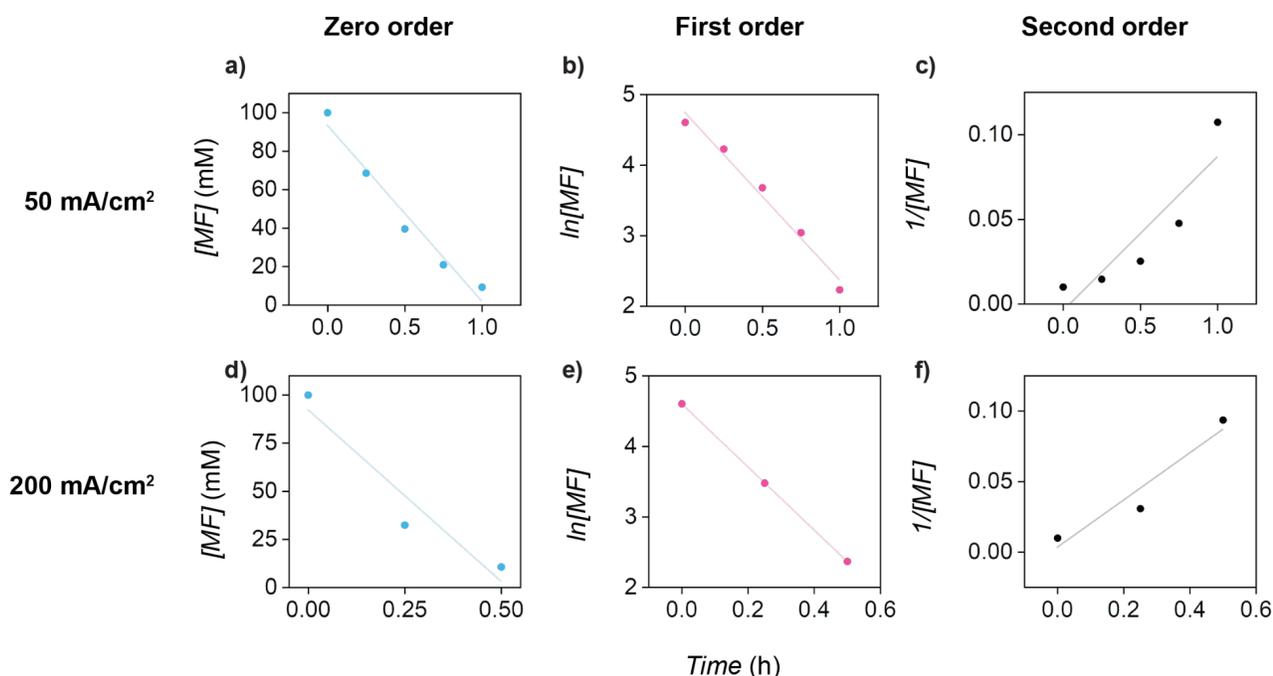


Fig. S10: [MF] denotes the concentration of methylfuran. a) Zero order kinetic plot of MF concentration over time at 50 mA/cm². b) First order kinetic plot of the natural logarithm of MF concentration over time at 50 mA/cm². c) Second order kinetic plot of the inverse of MF concentration over time at 50 mA/cm². d) Zero order kinetic plot of MF concentration over time at 200 mA/cm². e) First order kinetic plot of the natural logarithm of MF concentration over time at 200 mA/cm². f) Second order kinetic plot of the inverse of MF concentration over time at 200 mA/cm².

Table S4. R² values for zero, first, and second order fits for MF hydrogenation at 50 and 200 mA/cm². Highest values are written in bold font.

Current density (mA/cm ²)	R ² zero order	R ² first order	R ² second order
50	0.967	0.981	0.817
200	0.919	1.00	0.922

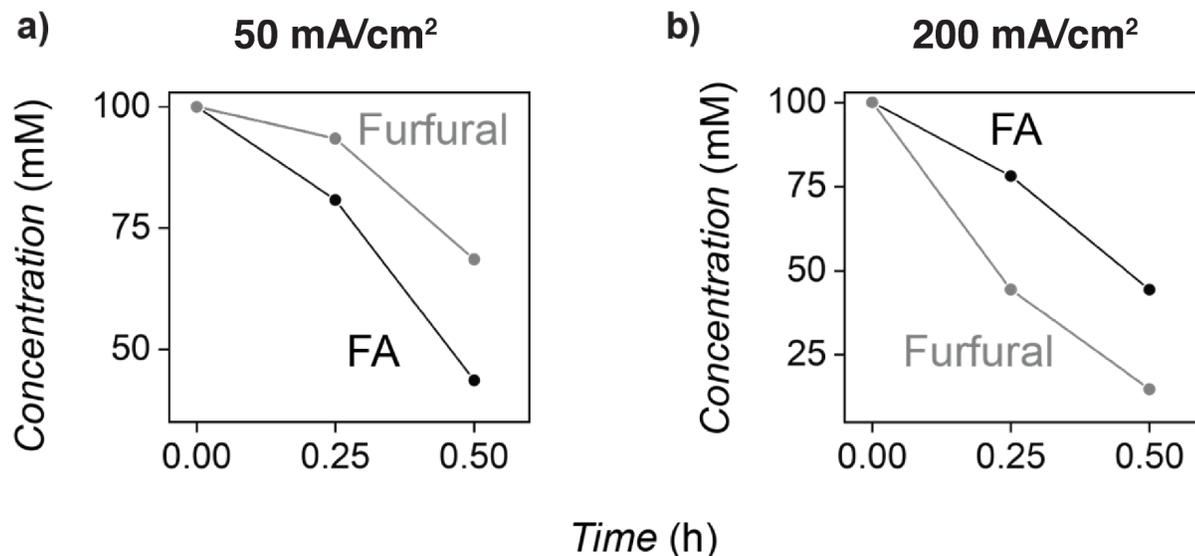


Fig. S11: a) Consumption rates of furfural and FA at 50 mA/cm². FA is consumed faster than furfural. b) Consumption rates of furfural and FA at 200 mA/cm². Furfural is consumed faster than FA.

Supplementary References

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- (3) Sherbo, R. S.; Delima, R. S.; Chiykowski, V. A.; MacLeod, B. P.; Berlinguette, C. P. Complete Electron Economy by Pairing Electrolysis with Hydrogenation. *Nature Catalysis* **2018**, *1* (7), 501–507.
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