Supporting Information

Efficient Electrocatalytic Reduction of Furfural to Furfuryl Alcohol in a Microchannel Flow Reactor

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1. Electrochemical devices

1.1 Flow reactor

The flow electrochemical reactor was manufactured by Equipment and Prototyping Center in Eindhoven University of Technology. The reinforcement part (grey plate in Figure S1) was made of stainless steel (SAE international type 316L), which offered great axial stress with the help of eight pairs of bolted joints (bolts with lock washers) distributed on the four edges and fastened by super flangeless fittings (Figure S2). The bolted joints guaranteed the packed structure and the gas tightness of the reactive part in the cell (Figure S3). The container part was made of polytetrafluoroethylene (PTFE) which provided chemical resistance and appropriate elastic modulus (proper stiffness for mechanical strength, suitable elastic deformation to prevent leakages). The spacer part was made of PTFE that was treated as insulator to partition the channels in the reactive chamber (Figure S4). The quasi-zero polar distance (0.25 mm) directly enabled the high Faraday efficiency in the system.

The electrodes were made of stainless steel (316L), copper (Cu-DHP) and super fine graphite plates (Figure S5). The entire design philosophy of the electrode aimed at a centrosymmetric plane (Figure S6). In every other reaction, the electrode plate would be set with 180 degree rotation to make the initial four channels behave as the last four instead, meanwhile nothing would be rearranged therewith. Otherwise, the last four channels would be corroded severely while the initial four were merely consumed slightly.
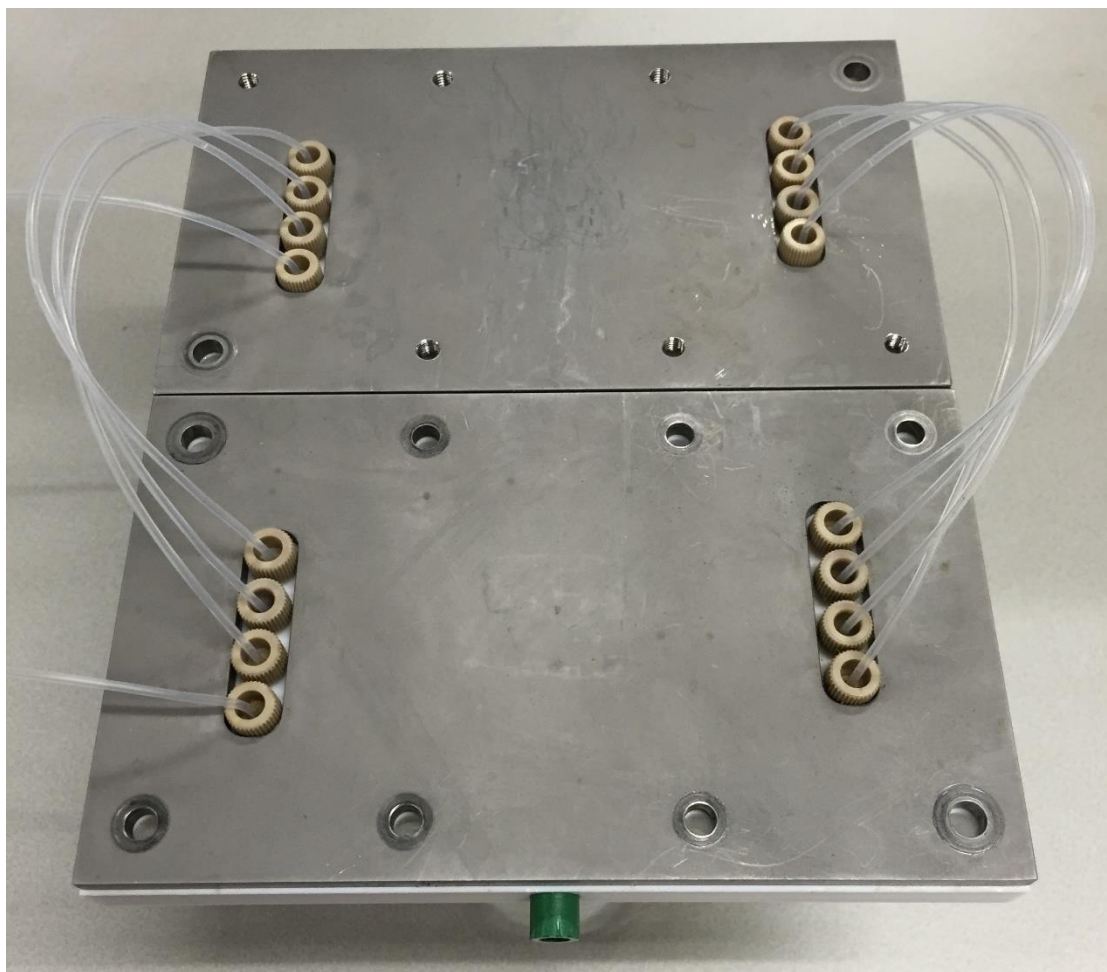
Figure S1. Top view of the unfolding electrochemical micro-channel flow reactor.
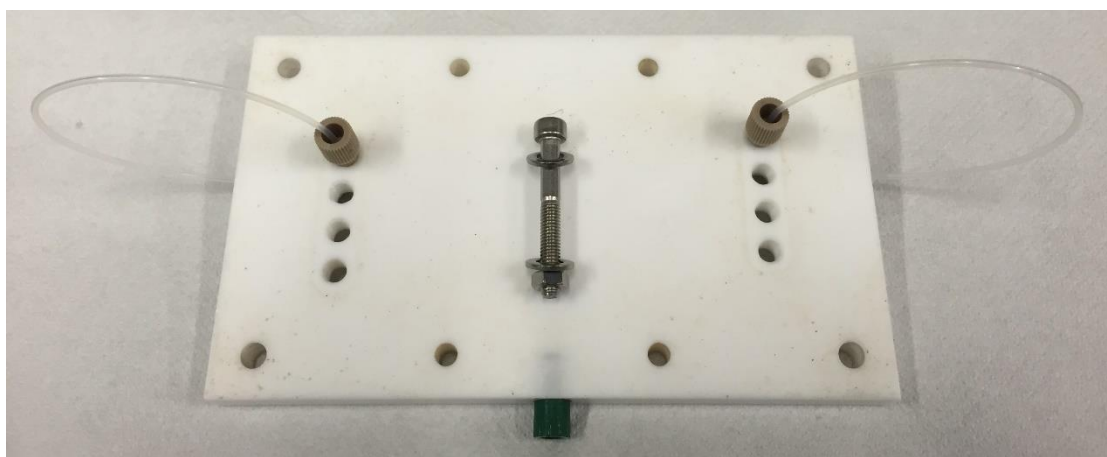

Figure S2. PTFE container, bolt joints and super flangeless fittings with tubings.
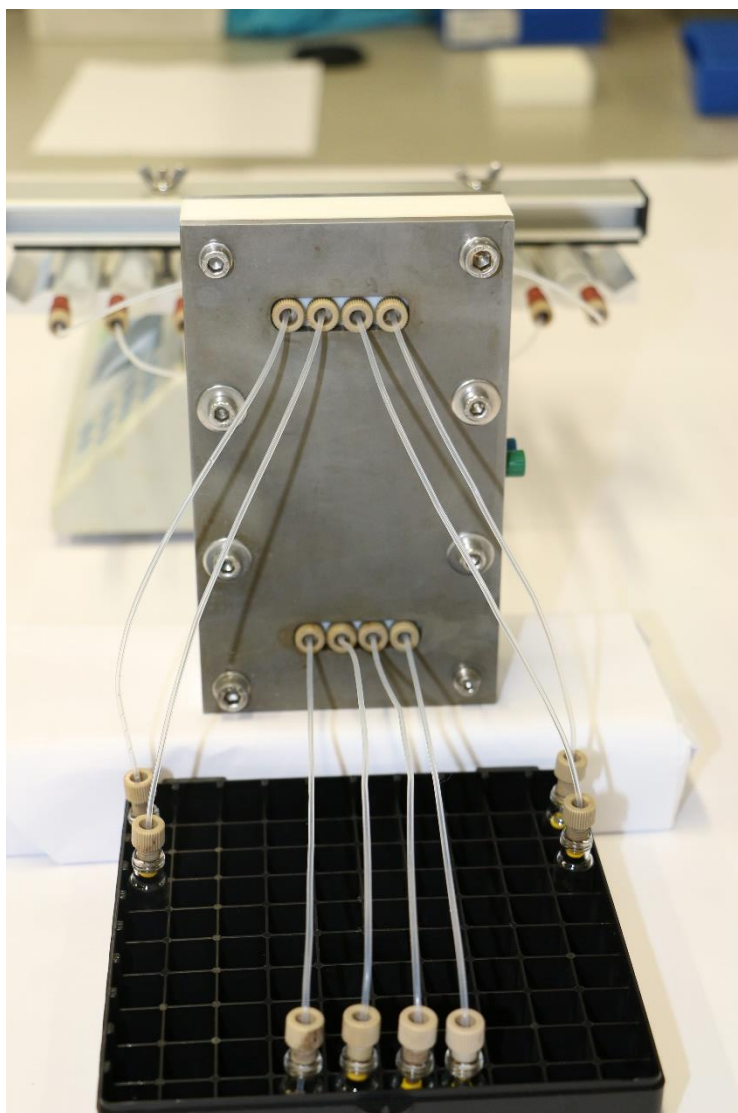
Figure S3. Running view of the electrochemical micro-channel flow reactor when operated in the parallel mode to collect 8 different samples.
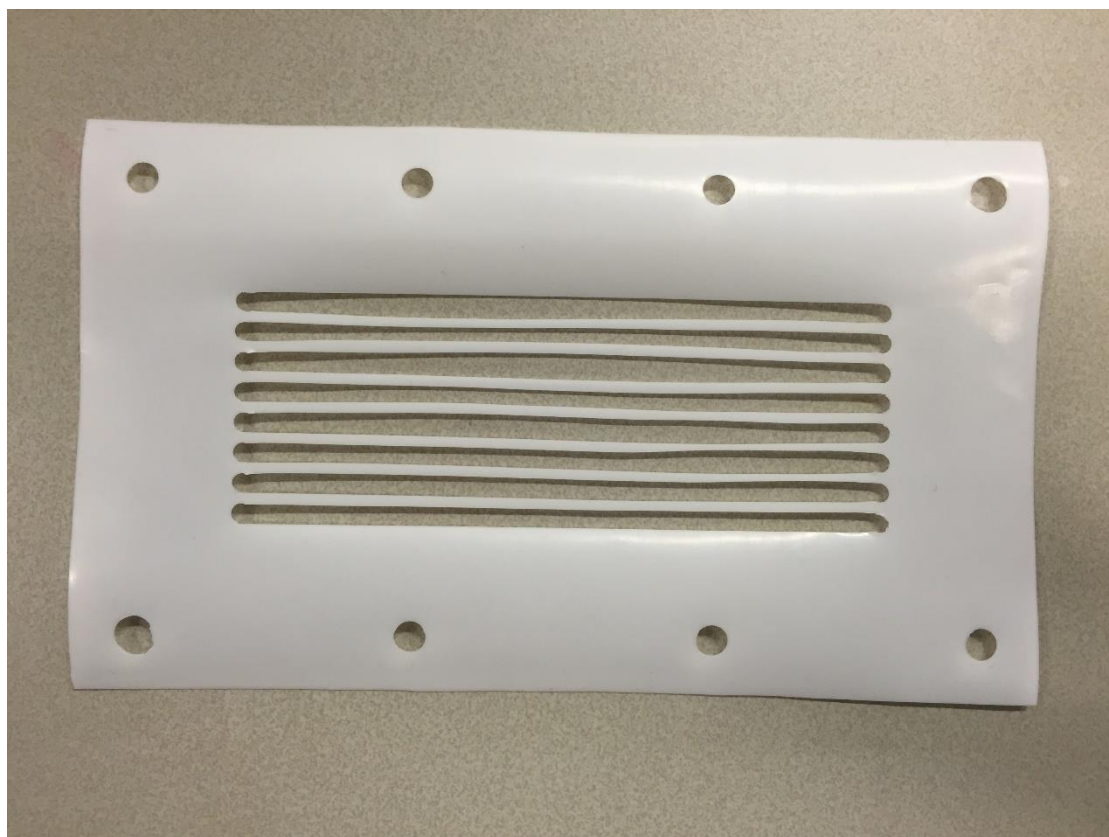
Figure S4. PTFE spacer for channel partition: this specific gasket splits the reactor in eight parallel channels.

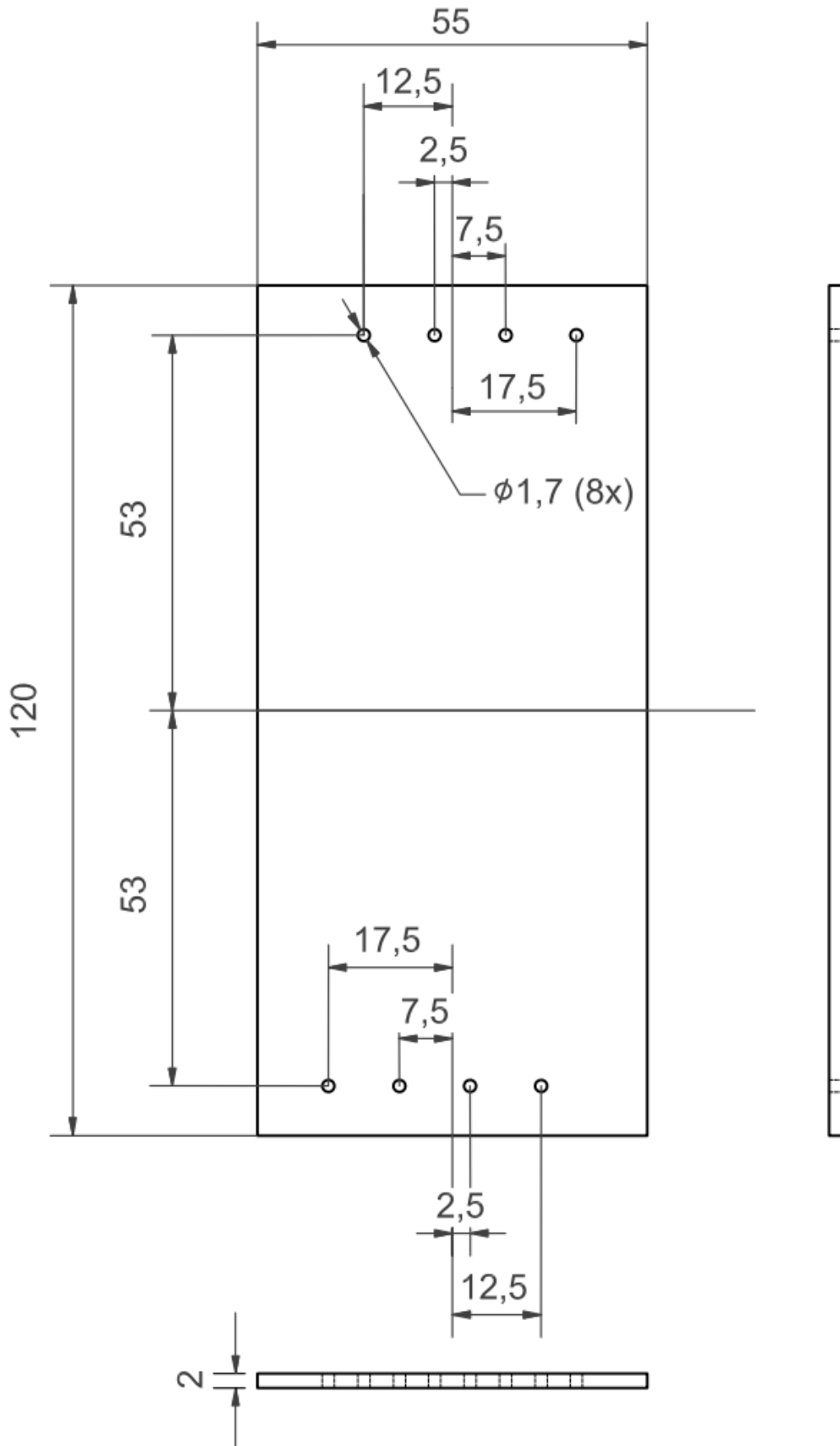*Figure S5. Copper (left), stainless steel (middle) and graphite (right) electrode plate.*

Figure S6. Electrode plate blueprint on three orthographic views (Software: AutoCAD. Unit: mm)

1.2   Batch reactor

The batch electrochemical reactor was manufactured by Equipment and Prototyping Center in Eindhoven University of Technology. The reactor body was made of glass with round bottom, which offered adequate space for a magnetic stir bar to ensure sufficient and fast mixing. The two electrode plates were fastened by two stainless steel wires with the assistant of joint bolts. The two wires were treated as conductor between electrode and power supply. Normally the stock solution for batch electrolysis was 50 mL, where the electrode plate would be half immersed into the liquid for electrochemical reactions. (Figure S7)

The basic and acidic reaction conditions are nearly the same as in flow: 0.1 M furfural, 0.05 M supporting electrolyte in 2.20 V (basic)/ 2.90 V (acidic) for 5 hours to get maximum yield. The stirring speed was 1000 rpm.
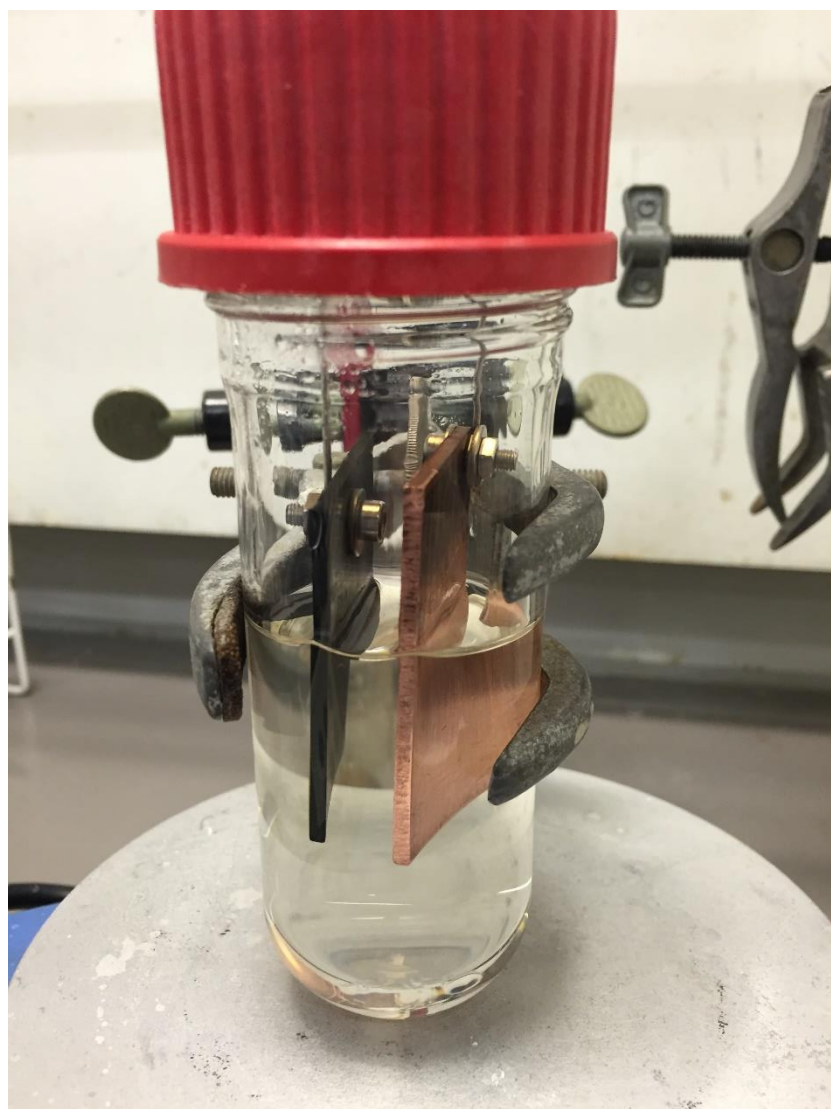

Figure S7. Undivided batch cell reactor with graphite and copper electrode.

2. Calculation of the Faradaic Efficiency

2.1 In flow

For the hydrogenation of furfural to furfuryl alcohol, it is a two-electron transfer reaction

$V_{reactor,flow} = 702 \ \mu L$

$C_{substrate} = 0.1 \ M$

$\tau_{flow} = 600 \ s$

$I_{basic,flow} = 24 \ mA$

$I_{acidic,flow} = 70 \ mA$

$F_{flow} = 0.075 \ mL * min^{-1}$

$Y_{basic,flow} = 90 \ \%$

$Y_{acidic,flow} = 55 \ \%$

$$\eta_{basic} = \frac{n_{exp,b}}{n_{theo,b}} * 100\% = \frac{0.067 \ mmol}{0.074 \ mmol} * 100\% = \ 90 \ \%$$

$$\eta_{acidic} = \frac{n_{exp,a}}{n_{theo,a}} * 100\% = \frac{0.041 \ mmol}{0.218 \ mmol} * 100\% = \ 19 \ \%$$

For the hydrogenation of 3-furfural to furan-3-methanol, it is also a two-electron transfer reaction:

$V_{reactor} = 702 \ \mu L$

$C_{substrate} = 0.1 \ M$

$\tau_r = 600 \ s$

$I_{basic} = 20 \ mA$

$I_{acidic} = 54 \ mA$

$F_v = 0.075 \ mL * min^{-1}$

$Y_{basic} = 78 \ \%$

$Y_{acidic} = 40 \ \%$

$$\eta_{basic} = \frac{n_{exp,b}}{n_{theo,b}} * 100\% = \frac{0.057 \ mmol}{0.062 \ mmol} * 100\% = \ 92 \ \%$$

$$\eta_{acidic} = \frac{n_{exp,a}}{n_{theo,a}} * 100\% = \frac{0.03 \ mmol}{0.17 \ mmol} * 100\% = \ 18 \ \%$$

2.2   In batch

$V_{reactor,batch} = 50\ mL$

$C_{substrate} = 0.1\ M$

$\tau_{batch} = 5\ h$

$I_{basic,batch} = 8\ mA$

$I_{acidic,batch} = 25\ mA$

$Y_{basic,batch} = 31\ \%$

$Y_{acidic,batch} = 18\ \%$

$$\eta_{basic,batch} = \frac{n_{exp,babatch}}{n_{theo,babatch}} * 100\% = \frac{0.45\ mmol}{0.74\ mmol} * 100\% = \ 60\%$$

$$\eta_{acidic,batch} = \frac{n_{exp,acbatch}}{n_{theo,acbatch}} * 100\% = \frac{0.27\ mmol}{2.33\ mmol} * 100\% = \ 11\ \%$$
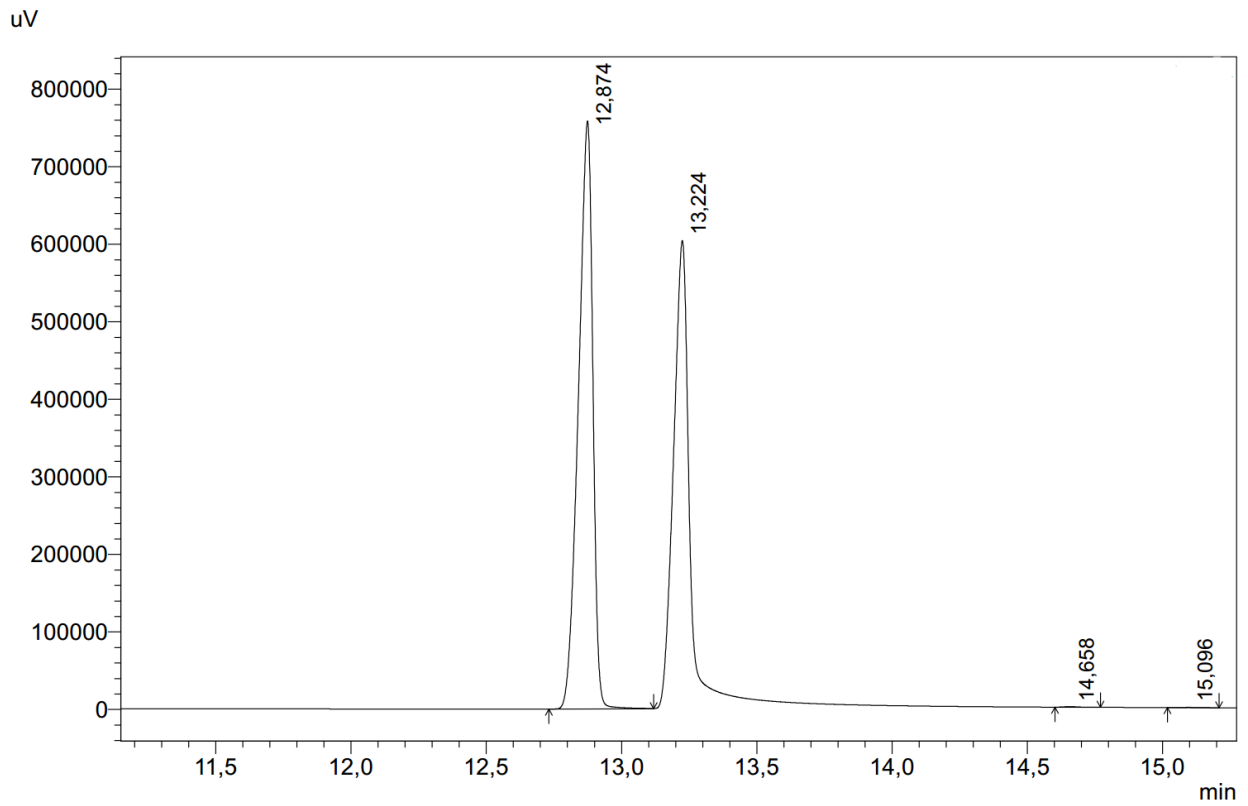
3. Gas Chromatograms

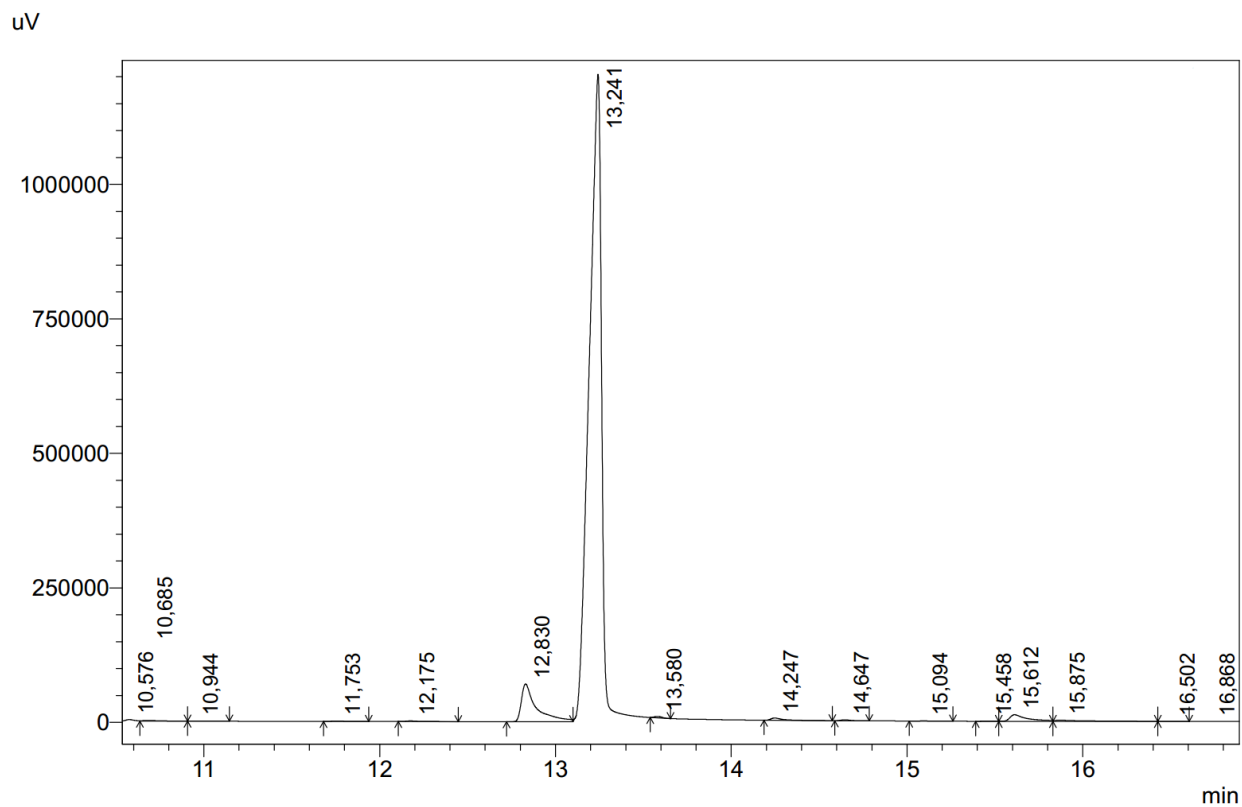*Figure S8: GC-FID graph of furfural and furfuryl alcohol standard sample*

Figure S9: GC-FID graph for the product sample of furfuryl alcohol (90% GC yield). Reaction conditions: 0.1 M furfural, 2.20 V, 0.05 M C_2H_5OK, ethanol solvent, flow rate 0.075 mL/min, residence time 10 min.
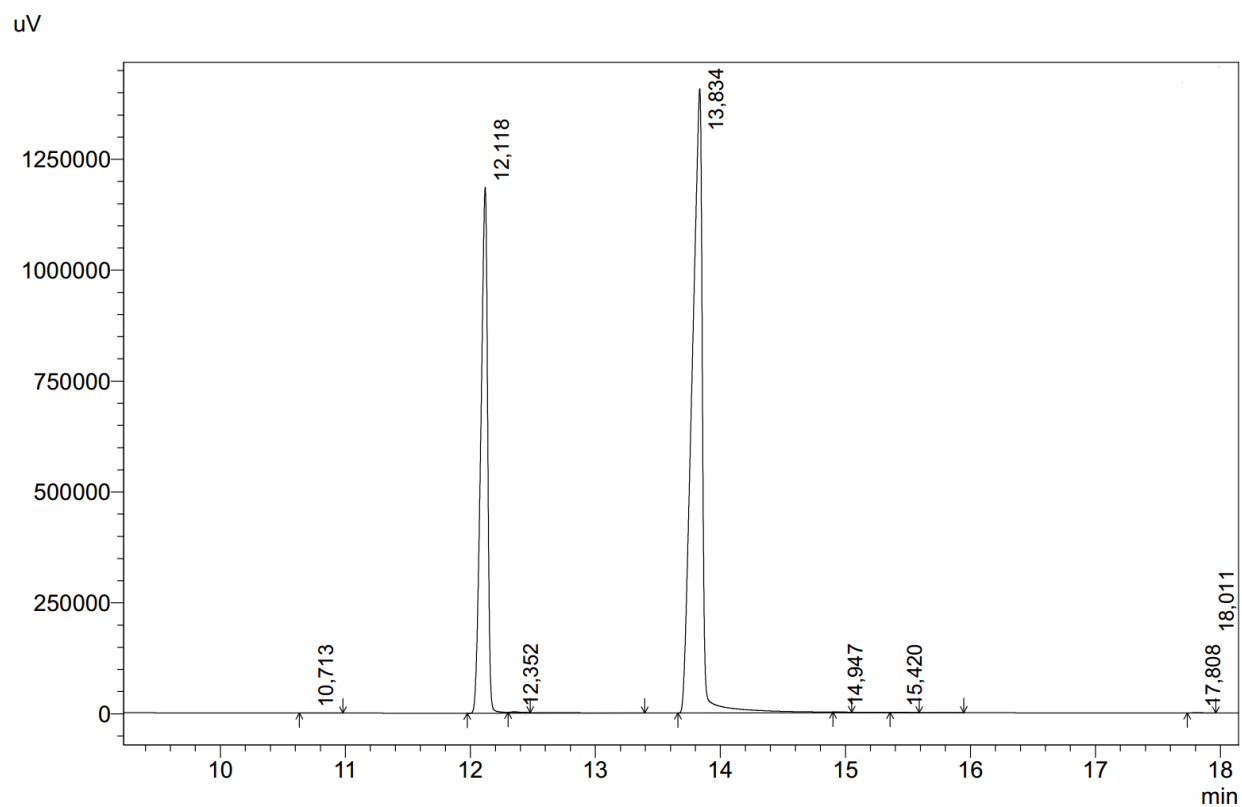
Figure S10: GC-FID graph for standard sample of 3-furfural and furan-3-methanol.
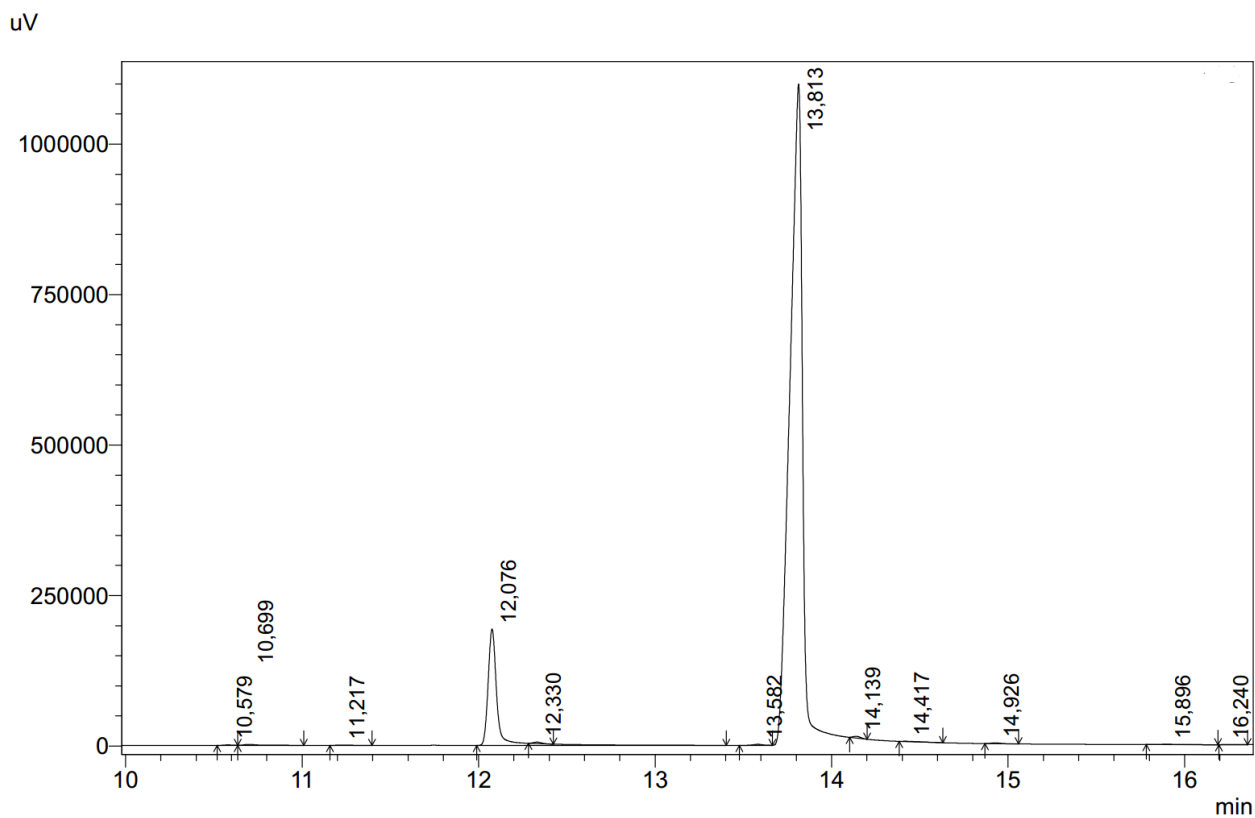
Figure S11: GC-FID graph for the product sample of furan-3-methanol (78% GC yield). Reaction conditions: 0.1 M 3-furfural, 2.20 V, 0.05 M C_2H_5OK, ethanol solvent, flow rate 0.075 mL/min, residence time 10 min.

4. Electrodes cleaning

4.1 Graphite electrode cleaning:[1]

1. Wipe off the residual substances successively using 18.2 MΩ H_2O and ethanol.

2. Scrub and polish the surface with fine emery paper.

3. Soak the graphite plate into ethanol for 1 hour to thoroughly remove residuals.

4. Let the clean graphite plate dry in the fume hood for 6 hours.

4.2 Stainless steel/copper electrode cleaning:[2]

1. Wipe off the residual substances successively using 1 M HCl and ethanol to get rid of inorganic

and organic residuals.

2. Scrub and polish the surface with fine emery paper.

3. Rinse the electrodes using 18.2 MΩ H_2O
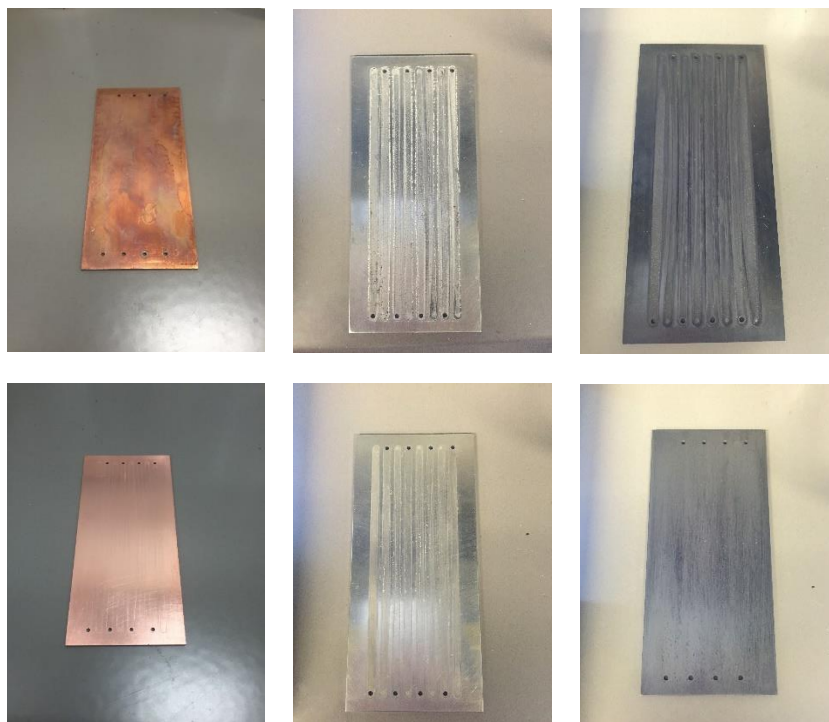
4. Dry the surface of electrodes.

Figure S12: Copper (left), stainless steel (middle), graphite (right) electrode before (upper row) and after (lower row) cleaning.

5. References

(1)   Somerville, L.; Bareño, J.; Jennings, P.; McGordon, A.; Lyness, C.; Bloom, I. The Effect of Pre-Analysis Washing on the Surface Film of Graphite Electrodes. *Electrochim. Acta*.**2016**, *206*, 70–76.

(2)   Hall, L. C. Cyclic Voltammetric Study of Copper Electrode Pretreatment for Metal Migration and Corrosion Rates. *J. Electrochem. Soc.* **1987**, *134* (8), 1902.