Supporting Information

to

Stabilization of 5-HMF in highly alkaline electrolytes through acetalization for the selective electrooxidation to FFCA

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Table of Contents

1 Materials

All chemicals were used without further purification if not stated otherwise.

1,3-propandiol (Sigma-Aldrich, 98%), AcOMF (Thermo Scientific, 97%), Amberlyst 15 (wet) (ROHM and HAAS France), cation exchange membrane/FM-FKL-PK-130 (Quintech), DCM (Fischer Chemicals, 99%), ethylene glycol (VWR chemicals, 99.9%), iron(III) chloride hexahydrate (Sigma Aldrich, 97%), hydrogen peroxide (Thermo Scientific, 35 wt%), HCl (J.T. Baker, 37%-38%), HMF (ava biochem, 99%), $In(OTf)_3$ (Thermo Scientific 98%), KOH pellets (VRW chemicals, 85.7%), Na_2CO_3 (acros organics, 99.6%), Na_2SO_4 (Fischer Scientific), neutral Aluminium oxide 40-300 mikrometer 60A (Thermo Scientific), Ni foam (recemat BV), Trimethyl orthoformate (Sigma Aldrich, 99.8%)

DI water was used for the synthesis of the HMF acetals and Milli-Q water (18.2 MΩ) was used for the modification of the nickel foam and all electrochemical experiments.

2 Stability of HMF acetals at elevated electrolyte concentration and temperature

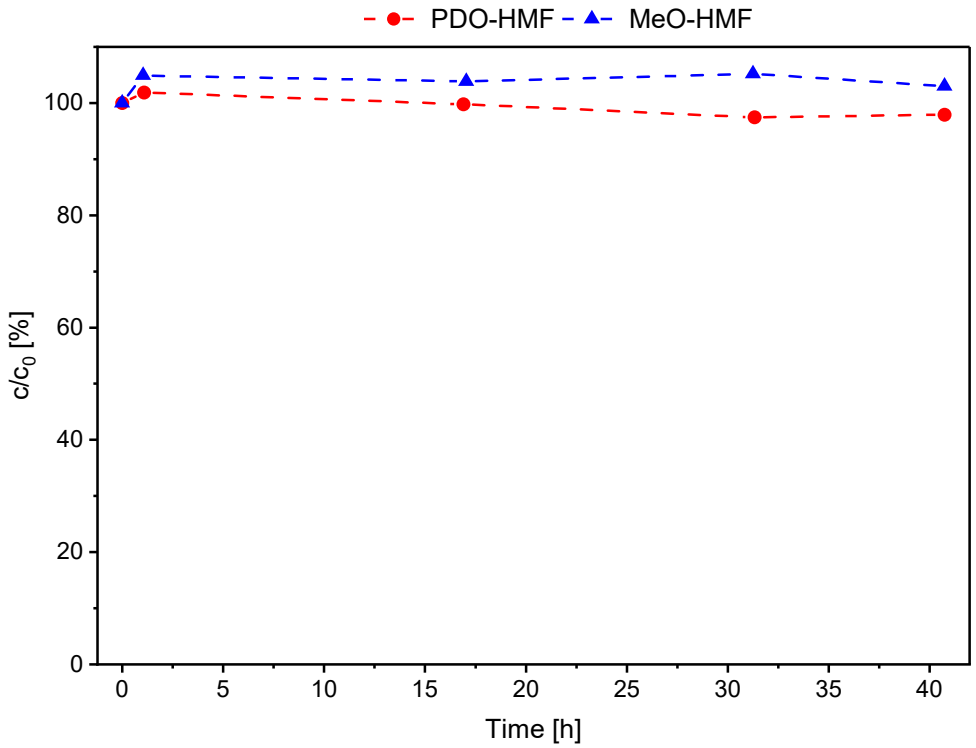

Fig. S 1: Stability of the HMF acetals (50 mM) in 5 M KOH at 80 °C. The stability was followed by qNMR and the initial measured concentration was taken as starting concentration.

3 Analytical methods

3.1 NMR

All ^{1}H and $^{13}C\{^{1}H\}$ spectra were measured with the Bruker 300 MHz AVIIIHD nanobay NMR spectrometer at 300 K.

A NMR water suppression as reported before from our group[1] was used for all NMR measurements involving water or KOH as solvent. The quantitative NMR measurements were conducted using a D_2O capillary and DMSO as internal standard. The signals from the furan and DMSO protons were used for the quantification.

3.2 HPLC

The HPLC analysis was conducted using a Shimadzu LC-2030 chromatograph, equipped with a 40 mm and 100 mm organic acid resin column with an 8.0 mm inner diameter. An aqueous solution with 2 mM trifluoroacetic acid was used for the mobile phase. The mobile phase was pumped at a rate of 1 $mLmin^{-1}$ at 40 °C through the system. A UV detector (270 nm) and an RI detector was used to identify the products. The products were then quantified via a one-point calibration.

4 HMF acetal synthesis

The synthesis of the HMF acetals has been adapted for each HMF acetal in order to minimize residues of unprotected HMF or the formation of the methyl ether HMF acetal. Therefore, the reaction time was extended for the EG-HMF acetal and a new protocol was chosen for the MeO-HMF.

4.1 Synthesis of MeO-HMF

HMF (2 g, 15.9 mmol) was dissolved in 100 ml methanol and $In(OTf)_3$ (120 mg, 0.013 eq.) was added to the solution. The reaction solution was stirred overnight at room temperature and the catalyst was removed via an Alox plug with DCM. The solution was then concentrated by vacuum distillation and 75 ml water were added, followed by extraction with 3 x 25 ml DCM. The combined organic layers were dried over Na_2SO_4 and the final product was obtained after the solvent was removed in vacuo (2.23 g, 13 mmol, 82%).

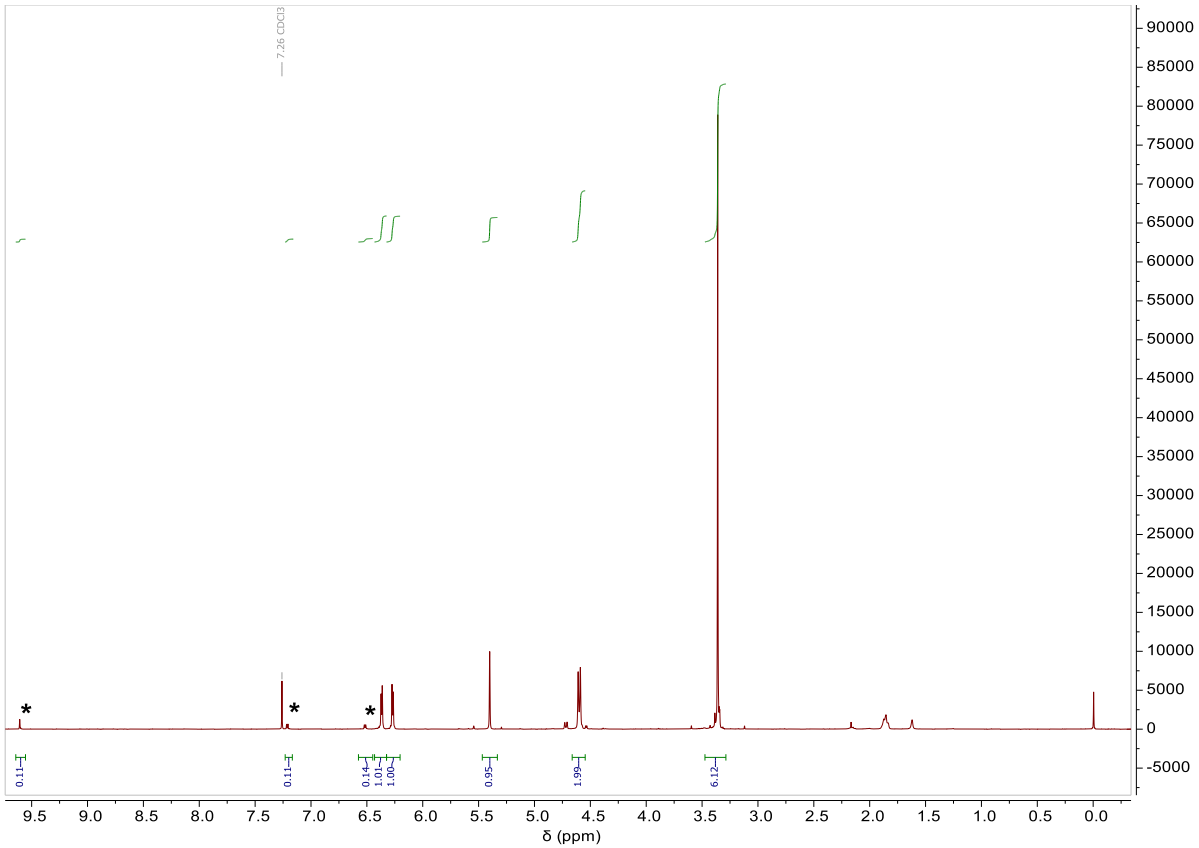

Fig. S 2: ^{1}H-NMR spectra of methanol protected HMF in $CDCl_3$. This first batch was used for the stability and electrochemical experiments except for elevated concentrations and charge resolved measurements. *Traces of HMF from the synthesis.

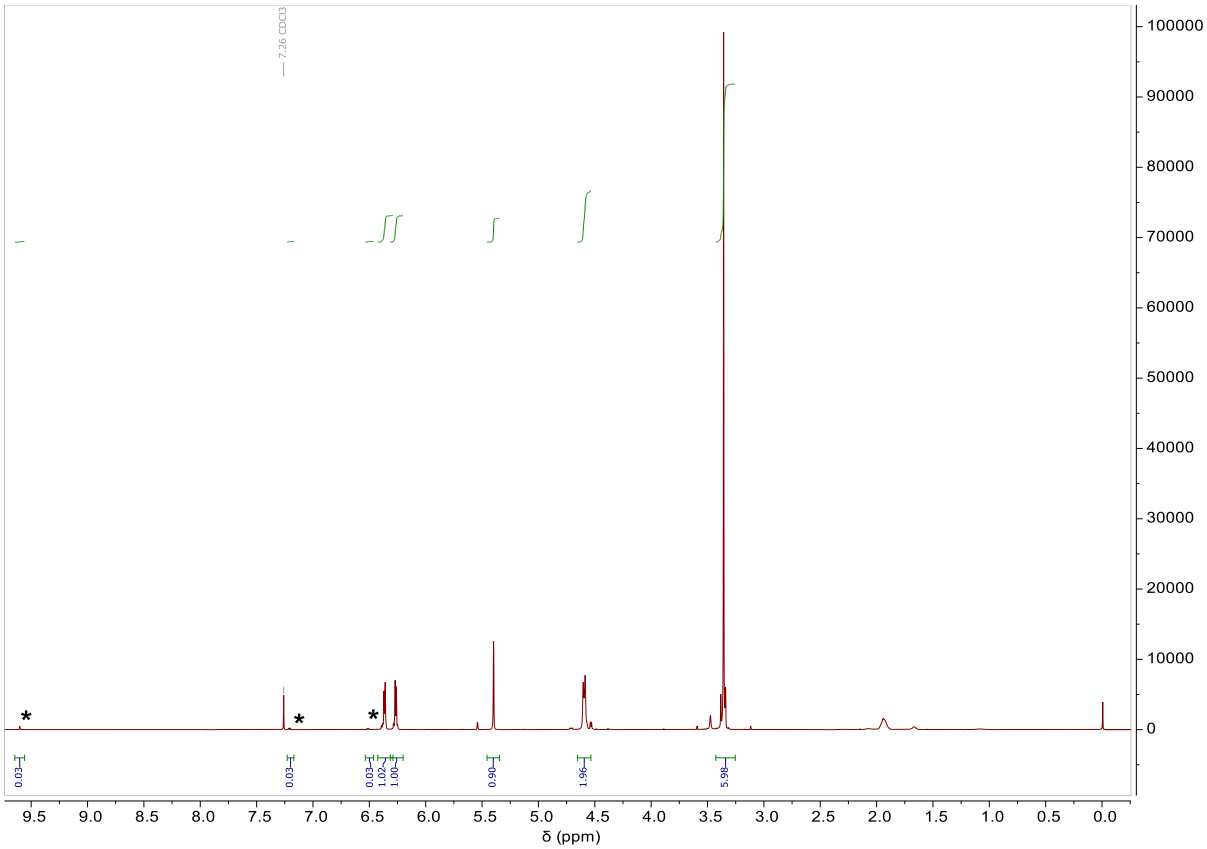

Fig. S 3: ^{1}H-NMR spectra of methanol protected HMF in $CDCl_3$. This second batch was used for the experiments at elevated concentrations and the charge resolved measurements. *Traces of HMF from the synthesis.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 (s, 1H), 6.27 (d, 1H), 5.40 (s, 1H), 4.59 (d, 2H), 3.36 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 150.9, 109.4, 108.3, 98.1, 57.6, 53.1.

4.2 Synthesis of PDO-HMF

AcOMF (2 g, 11.9 mmol) was dissolved in 40 ml DCM and 1,3-propandiol (2.6 ml, 36 mmol, 3 eq.) was added, followed by Amberlyst 15 (400 mg). Lastly, TMOF (1.56 ml, 14 mmol, 1.2 eq) was added and the reaction solution was stirred for 24 h at room temperature. Amberlyst 15 was removed by filtration and the reaction solution was reduced to 10 ml by removing the solvent in vacuo. The remaining solution was extracted with 25 ml sodium carbonate solution (1.33 g Na_2CO_3 in 25 ml H_2O).

The obtained product was dissolved in 24 ml ethanol and an aqueous sodium carbonate solution (4.76 g Na_2CO_3 in 71.6 ml water) was added. The reaction mixture was stirred overnight at room temperature and ethanol was removed under reduced pressure. The remaining solution was extracted with 3 x 20 ml ethyl acetate. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure, yielding the title compound (1.775 g, 9.6 mmol, 81%).

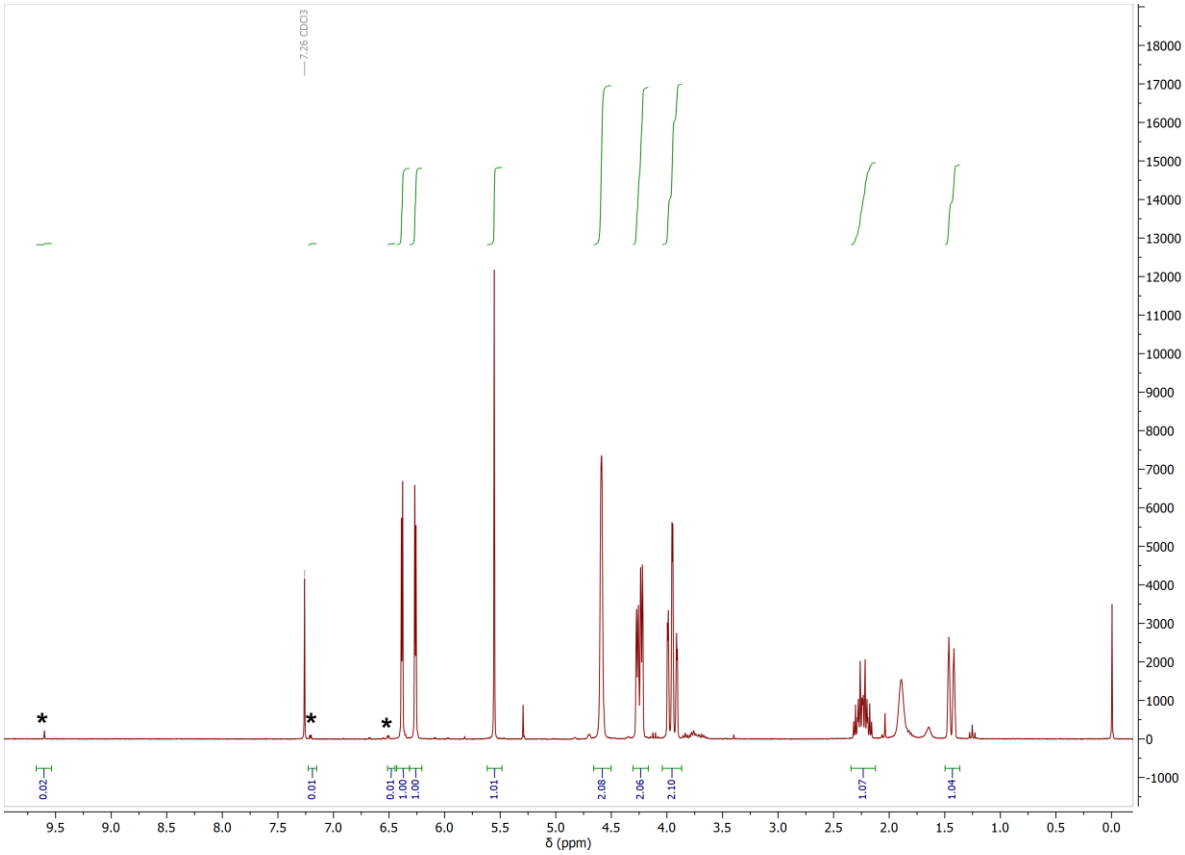

Fig. S 4: ^{1}H-NMR spectra of PDO protected HMF in $CDCl_3$. *Traces of HMF from the synthesis.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (d, 1H), 6.26 (d, 1H), 5.55 (s, 1H), 4.59 (s, 2H), 4.31 – 4.19 (m, 2H), 4.03 – 3.88 (m, 2H), 2.35 – 2.13 (m, 1H), 1.51 – 1.38 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 151.0, 108.4, 108.3, 96.2, 67.4, 57.5, 25.7.

4.3 Synthesis of EG-HMF

AcOMF (1.42 g, 8.4 mmol) was dissolved in 28 ml DCM and ethylene glycol (1.2 ml, 17.4 mmol, 2.1 eq) was added to the solution, followed by Amberlyst 15 (400 mg). Lastly, TMOF (0.6 ml, 5.8 mmol, 0.69 eq) was added and the reaction solution was stirred for 48 h at room temperature. After 24 h a second batch TMOF (0.6 ml, 5.8 mmol, 0.69 eq) was added. Amberlyst 15 was removed by filtration and the reaction solution was reduced to 10 ml by removing the solvent in vacuo. The remaining solution was extracted with 25 ml sodium carbonate solution (1.33 g Na_2CO_3 in 25 ml H_2O).

The obtained product was dissolved in ethanol and an aqueous sodium carbonate solution was added. The reaction mixture was stirred overnight at room temperature and ethanol was removed under reduced pressure. The remaining solution was extracted 3 x with ethyl acetate. The combined organic layers were dried over Na_2SO_4. Removing the solvent under reduced pressure yielded the title compound (0.92 g, 5.4 mmol, 64 %).

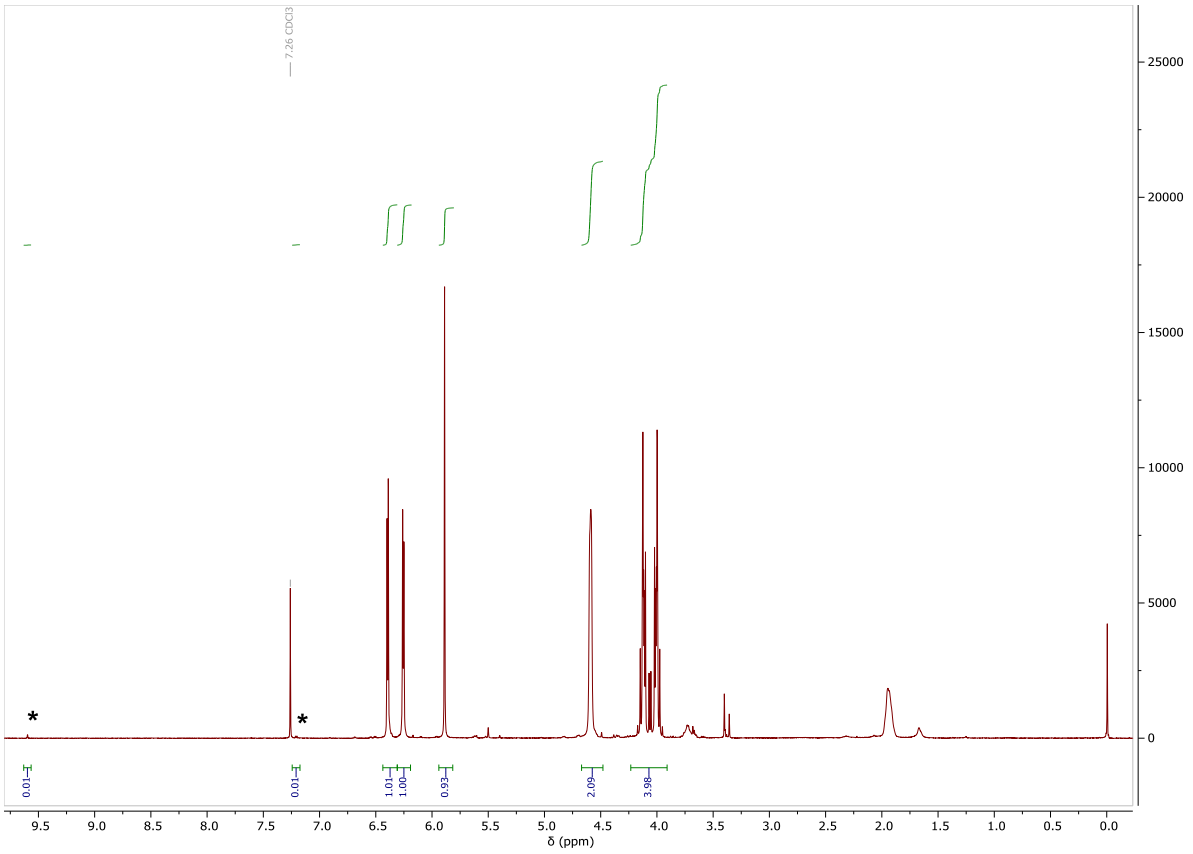

Fig. S 5: ^{1}H-NMR spectra of EG protected HMF in $CDCl_3$. *Traces of HMF from the synthesis.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (d, 1H), 6.26 (d, 1H), 5.89 (s, 1H), 4.60 (s, 2H), 4.21 – 3.93 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 151.0, 109.7, 108.4, 97.9, 65.3, 57.7.

4.4 Methyl ether

HMF (500 mg, 3.96 mmol) was dissolved in 10 ml DCM and methanol (0.4 ml, 9.87 mmol, 2.5 eq) followed by TMOF (0.95, 8.68 mmol, 2.2 eq) was added to the solution. The reaction mixture was stirred overnight at room temperature and Amberlyst 15 was removed via filtration. The reaction mixture was then extracted with 25 ml sodium carbonate solution (1.33 g Na_2CO_3 in 25 ml H_2O). The organic phase was dried over Na_2SO_4 and the title compound was obtained after removing the solvent under reduced pressure (0.615 g, 3.3 mmol, 83%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (d, 1H), 6.30 (d, 1H), 5.42 (s, 1H), 4.39 (s, 2H), 3.36 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 151.2, 109.9, 109.3, 98.2, 66.5, 58.0, 53.1.

4.5 Nickel foam modification

The nickel foam (1 x 3 cm) was ultrasonicated in 3 M HCl, acetone, ethanol, and water for 15 minutes. A $FeCl_3$ solution was prepared by dissolving 690 mg $FeCl_3 \cdot 6\ H_2O$ in 10 ml ultrapure water and 15 ml of a H_2O_2 solution (16.16 g H_2O_2 in 45.71 ml ultrapure water) was added to the $FeCl_3$ solution. The nickel foam was added to the solution after the solution had reacted for 5 min and was taken out of the solution after 1 min.

The nickel foam was washed by immersing the foam in ultrapure water. Subsequently, the washed nickel foam was dried at 60 °C for 24 hours.

The unmodified nickel foam was prepared in a similar manner without the treatment with the hydrogen peroxide iron(III)chloride solution.

For a detailed characterization of the electrode see.[2]

5 Electrochemical experiments

All electrochemical measurements were performed in a H-type cell using a three electrode setup with a platinum wire coil as counter electrode (CE), a Hg/HgO electrode with 1 M KOH as inner electrolyte as reference electrode (RE) and the nickel foam as working electrode (WE). The chambers were separated by a cation exchange membrane (thickness 130 µm). The WE and CE were positioned at a distance of 6 cm, while the WE and RE were positioned at a distance of 0.3 cm within the H-cell. The data was collected using the Gamry Interface 1010 B electrochemical workstation. The anode chamber was filled with 6.5 ml electrolyte and the cathode chamber was filled with 8.6 ml electrolyte. Before the electrooxidation 0.45 ml were sampled from the anode chamber and submitted to HPLC analysis. The nickel foam was activated prior to all measurements by running cyclic voltammetry with 20 cycles between 0 V and 0.7 V vs. Hg/HgO with a scan rate of 100 mV. The uncompensated resistance between WE and RE was determined by electrochemical impedance spectroscopy at 0 V. Linear sweep voltammetry was performed with and without the substrate before each electrooxidation between 0.2 V and 0.7 V with a scan rate of 5 mV/s (except for the charge resolved measurements). The electrolyte solution was stirred at 500 rpm in both chambers for all measurements.

The potentials against the Hg/HgO electrode were converted against RHE by using the Nernst equation:

$$E_RHE = E_{(Hg/HgO)} + 0.0592 \cdot pH + E^{\circ}_{(Hg/HgO(1MKOH))}$$

The standard potential of Hg/HgO in 1 M KOH with 105 mV was used, as 1 M KOH has been used as inner electrolyte of the electrode.[3] A pH of 15.11 was assumed for experiments using 5 M KOH using the excel tool provided by Hausmann et al.[4] The assumed pH and the reported potentials might be affected by the organic molecules present in the electrolyte solution.

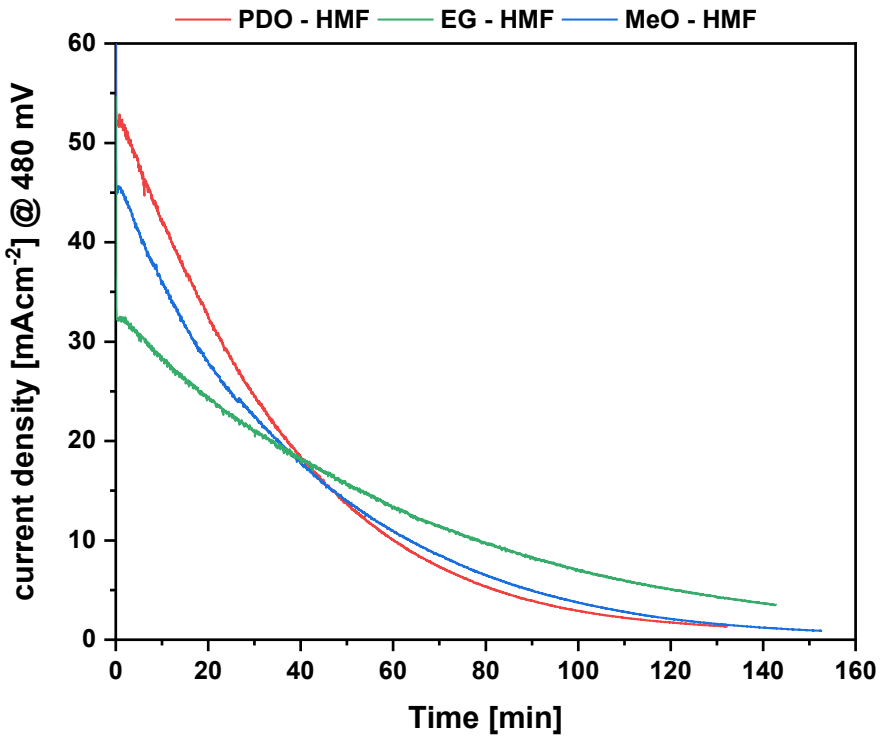

Fig. S 6: Electrooxidation of HMF acetals (50 mM) at 480 mV vs. Hg/HgO in 1 M KOH.

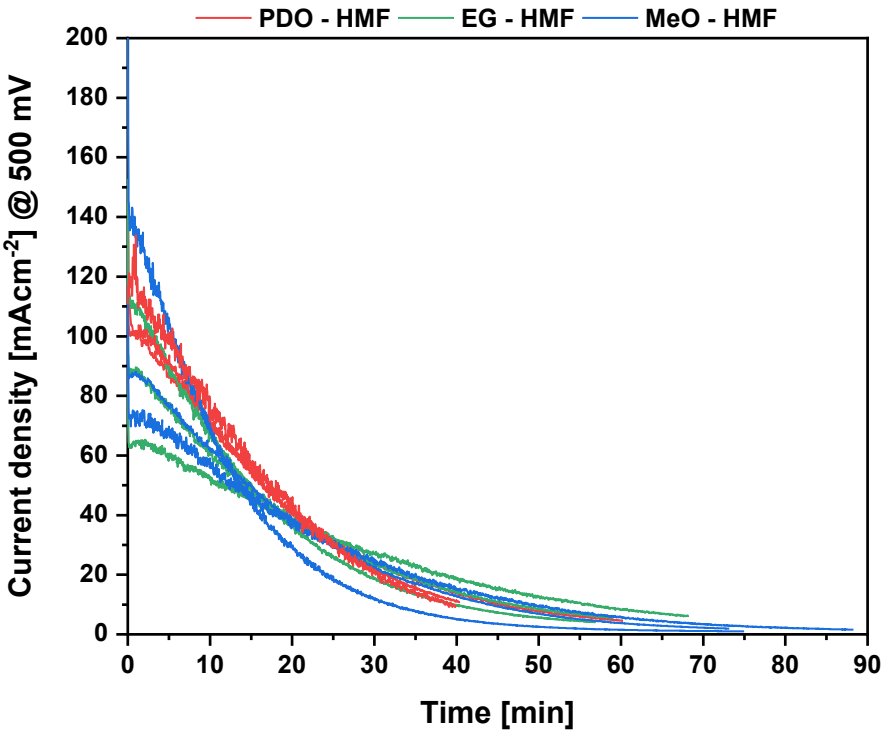

Fig. S 7: Electrooxidation of HMF acetals (50 mM) at 500 mV vs. Hg/HgO in 1 M KOH.

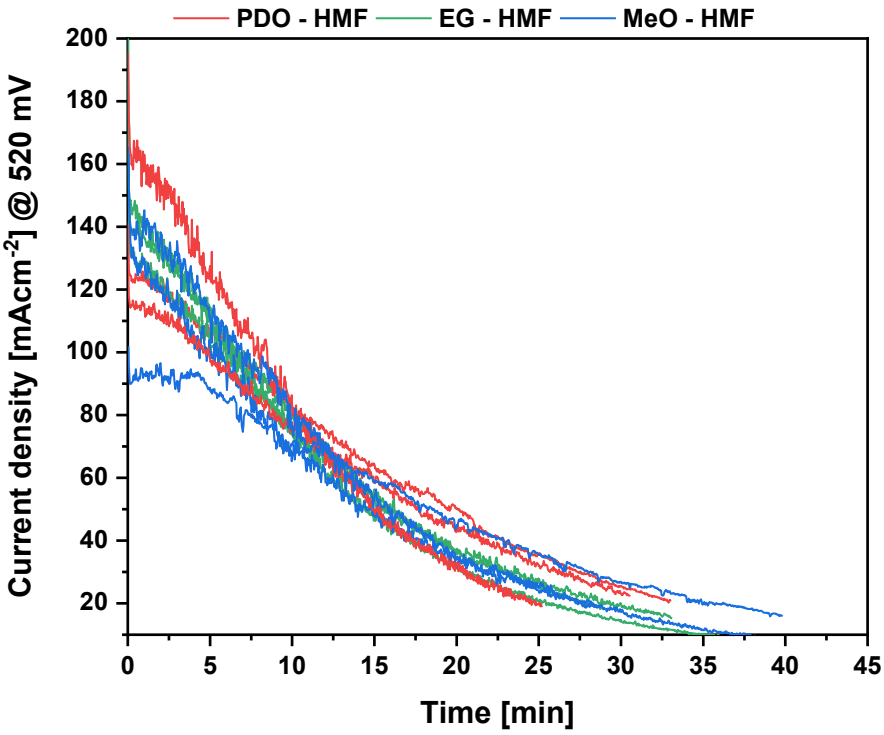

Fig. S 8: Electrooxidation of HMF acetals (50 mM) at 520 mV vs. Hg/HgO in 1 M KOH.

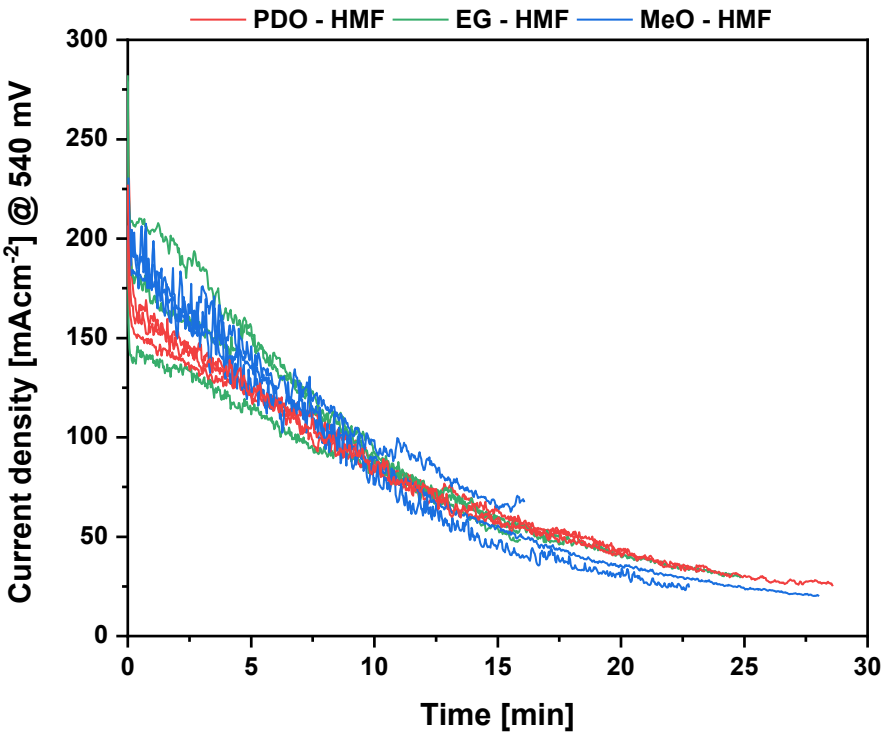

Fig. S 9: Electrooxidation of HMF acetals (50 mM) at 540 mV vs. Hg/HgO in 1 M KOH.

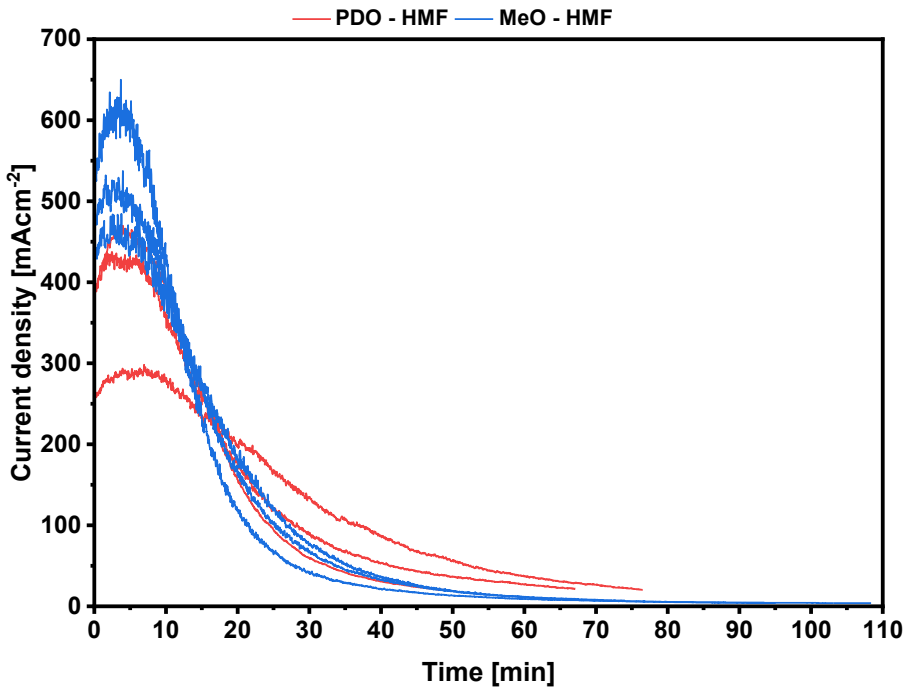

Fig. S 10: Electrooxidation of HMF acetals (250 mM) at 475 mV vs. Hg/HgO in 5 M KOH.

6 Methyl ether formation and influence on the electrooxidation

During the initial electrooxidation of MeO-HMF, we were unable to transfer the full charge equivalent to complete conversion of the substrate within a reasonable time frame. The HPLC analysis revealed an unidentified peak that could be attributed to the methyl ether of MeO-HMF. By switching to the synthesis method reported here for MeO-HMF, we were able to substantially reduce the intensity of the methyl ether peak in the HPLC analysis. Furthermore, the electrooxidation of the methyl ether free MeO-HMF proceeded at a rate comparable to the other two HMF acetals. As expected, the methyl ether is not electrochemically active on its own, as the two oxidizable functional groups are blocked. It is important to note that the HMF acetals should be free from the methyl ether, as it appears to inhibit the reaction, potentially by blocking the active sites of the catalyst.

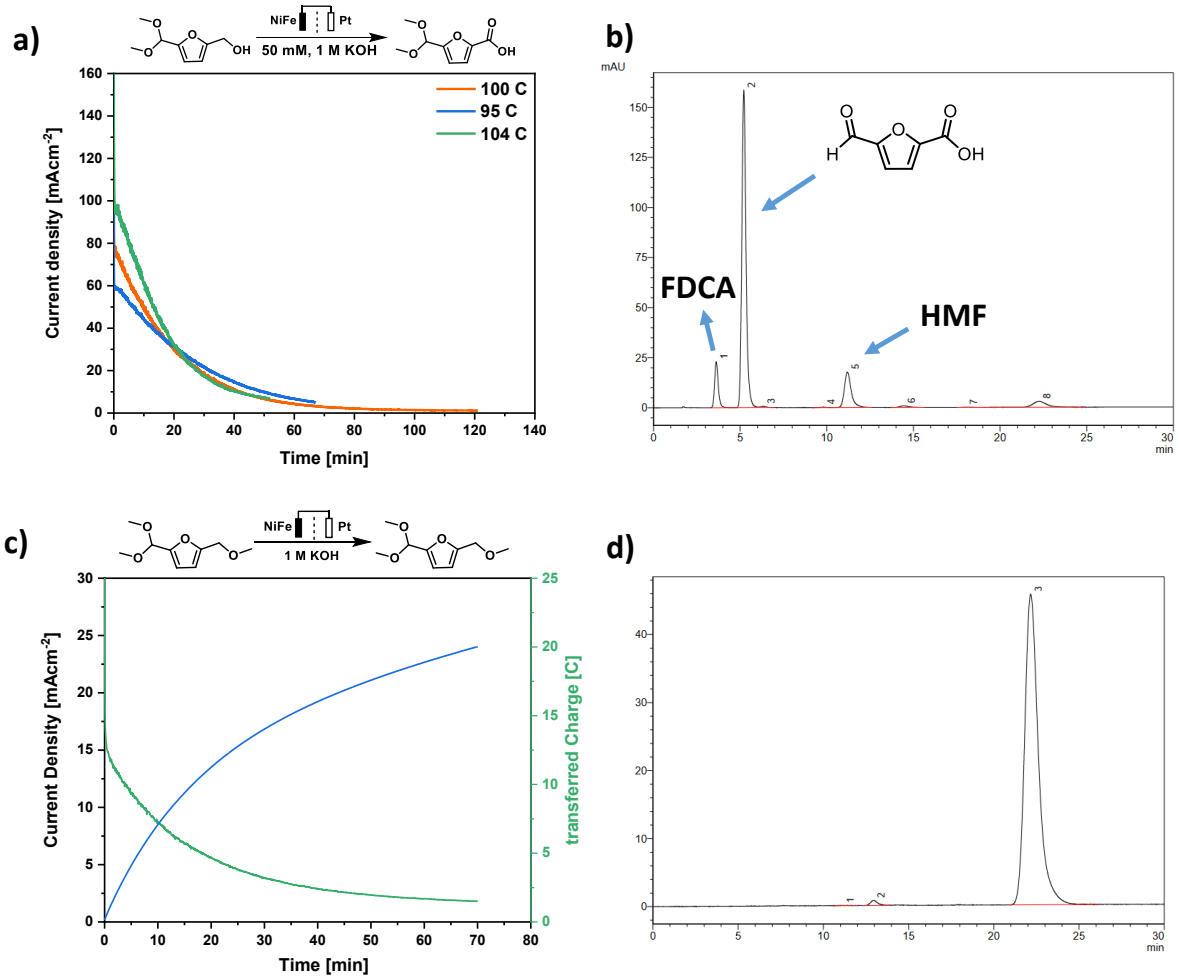

Fig. S 11: a) First electrooxidation of MeO-HMF b) HPLC results for the first electrooxidation of MeO-HMF, showing the residues of the methyl ether (peak at about 22 min retention time). c) Electrooxidation of the methyl ether. d) HPLC of the methyl ether.

7 Comparison of unprotected HMF with the HMF acetals

Table S 1: Comparison of unprotected HMF and HMF during the electrooxidation. The HMF acetal with the lowest yield was used for the comparison.

Electrolyte	Potential vs. RHE	Yield	Selectivity for FFCA	FE	Carbon balance
1 M KOH 50 mM HMF	1.42 V	98% FDCA	0%	98%	96%
1 M KOH 50 mM HMF acetal (MeOH)	1.42 V	89% FFCA	91%	89%	99%
5 M KOH 250 mM HMF	0.475 V vs. Hg/HgO	85% FDCA	<1%	86%	85%
5 M KOH 250 mM HMF acetal (PDO)	0.475 V vs. Hg/HgO	95% FFCA	94%	92%	>99%

8 Literature survey for the selective electrooxidation of HMF to FFCA

Table S 2: Overview of the conditions used for the electrooxidation of HMF to FFCA in literature. The HMF acetal with the highest yield was used for the comparison.

Catalyst	Electrolyte	Potential vs RHE	Yield	Selectivity	Ref
NiFe foam	1 M KOH 50 mM HMF acetal	1.42 V	92%	96%	**This work**
V-Ni$(OH)_2$	0.1 M $Na_2B_4O_7$ 10 mM HMF	1.63 V	-	72%	[5]
V-NiO-Rh/CF	0.2 M PBS 10 mM HMF	1.73 V	51%	71%	[6]
NiO_x-PtO_x/CF	0.2 M PBS 10 mM HMF	1.78 V	77%	84%	[7]
PANI/CP	0.1 M KOH 10 mM HMF	1.96 V	-	76%	[8]

9 References

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