Supporting information

Design of the 3E-flow cell

The design of the three-electrode flow cell (MicroFlowCell, ELECTROCELL, Denmark) is schematically shown in Figure S1. The cell consisted of two PTFE end plates (120 x 70 x 12 mm), two titanium sheets (95 x 45 x 1 mm, Eisenhuth GmbH, Germany) that served as working and counter electrodes and two PTFE flow frames (95 x 45 x 2.1 mm, ELECTROCELL, Denmark). The electrode compartments were separated by a fumasep FTAM-E anion exchange membrane (FumaTech, Germany). Viton gaskets, cut from a 2000 x 1200 x 1 mm piece (Technikplaza GmbH, Germany), were installed between each component (membrane, electrodes, flow frames and end plates). The surface area of the electrodes was defined by rectangular windows cut into the gaskets between the electrodes, flow frames and the membrane. Thus, 30 x 33 mm windows gave an electrode surface of ca. 10.0 cm^2 and a filling volume of 4.1 mL (defined by the electrode surface and the distance between electrode and membrane). Potentials were measured against a leak free Ag/AgCl 3.4 M KCl capillary reference electrode (Innovative Instruments, USA), which was inserted into the WE compartment through a hole in the respective flow frame. The flow was established by a Masterflex Reglo peristaltic pump (Cole-Parmer, USA) equipped with 2.06 mm ID Viton tubes (Cole-Parmer, USA).

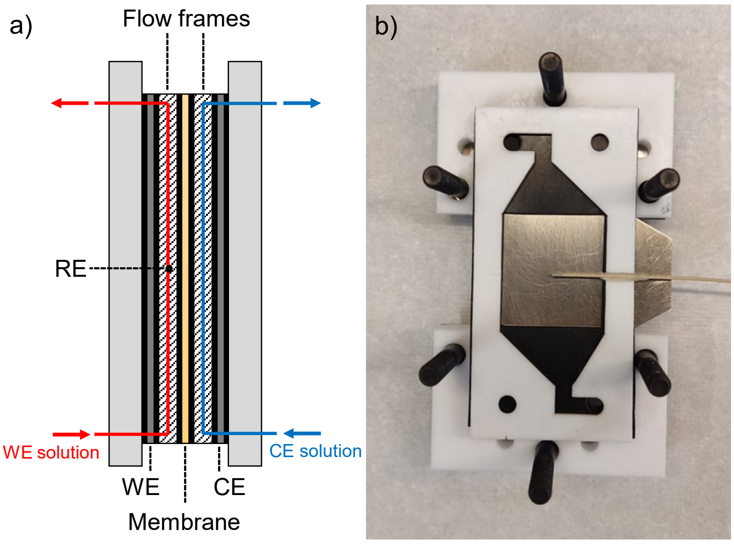

Figure S1: a) Schematic illustration of the used 3E-flow cell (not to scale) and b) photography of the open working electrode compartment with PTFE flow frame.

Design of the 2E-flow cell

The two-electrode flow cell was a custom-made cell from Eisenhuth GmbH (Germany). The cell design is schematically shown in Figure S2. The cell consisted of two stainless steel end plates (125 x 125 x 18 mm), two circular stainless steel contacting plates and two circular titanium electrodes (each 90 mm in diameter). A Viton layer, cut from a 2000 x 1200 x 1 mm piece (Technikplaza GmbH, Germany) was installed between the contacting plates and the end plates for electrical insulation. The flow design was based on two spiral-shaped channels (580 x 1.5 x 1.5 mm). This gave an electrode surface of 52.2 cm^2 and a filling volume of 2.6 mL in both compartments. The electrode compartments were separated with a fumasep FTAM-E anion exchange membrane (FumaTech, Germany) for the CoOOH coating experiments and with a fumasep FM-FKM cation exchange membrane (FumaTech, Germany) for the HMF oxidation experiments. The flow was established by a Masterflex Reglo peristaltic pump (Cole-Parmer, USA) equipped with 2.06 mm ID Viton tubes (Cole-Parmer, USA). The temperature was controlled by pipes embedded into the end plates, which were connected to a thermostat (Ecoline E103, Lauda, Germany). A water / ethylene glycol mixture (50 / 50 $\%_{\mathrm{Vol}}$) was used as heat transfer medium.

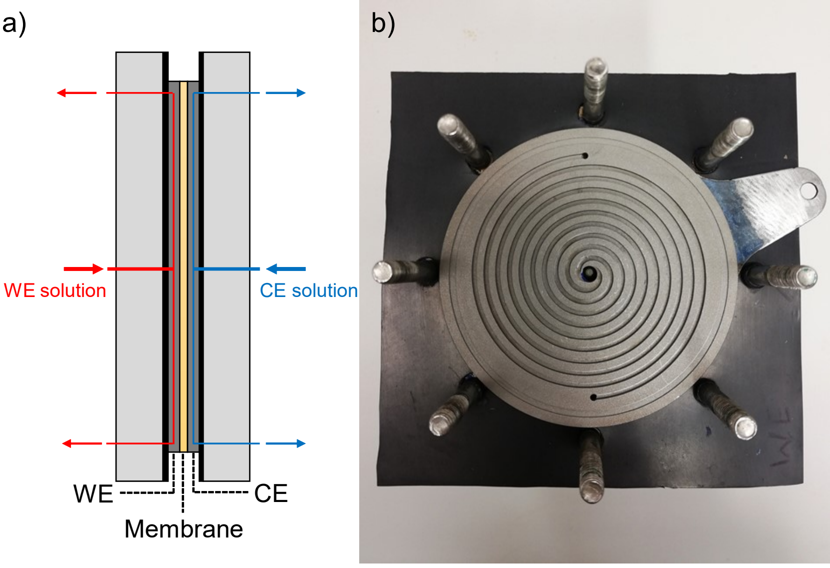

Figure S2: a) Schematic illustration of the used 2E-flow cell (not to scale) and b) photography of the open working electrode compartment.

Definition of performance parameters

Eqs. (S1) – (S3) were used to calculate the HMF conversion *X*, the product yield *Y* and the Coulomb efficiencies *CE*. The total Coulomb efficiency CE_{tot} was calculated from the *CE* values of the single products according to eq. S4. For all equations, a stochiometric coefficient of $\nu = 1$ is assumed.

$$X = \frac{n_{\mathrm{educt,\,0}} - n_{\mathrm{educt,\,t}}}{n_{\mathrm{educt,\,0}}} \cdot 100\ \% \tag{S1}$$

$$Y = \frac{n_{\mathrm{product,\,t}}}{n_{\mathrm{educt,\,0}}} \cdot 100\ \% \tag{S2}$$

$$CE = \frac{Q_{\mathrm{ideal}}}{Q_{\mathrm{experiment}}} \cdot 100\ \% = \frac{n_{\mathrm{product,\,t}} \cdot z \cdot F}{Q_{\mathrm{experiment}}} \cdot 100\ \% \tag{S3}$$

$$CE_{\mathrm{tot}} = CE_{\mathrm{DFF}} + CE_{\mathrm{HMFCA}} + CE_{\mathrm{FFCA}} + CE_{\mathrm{FDCA}} \tag{S4}$$

$$MB = \frac{n_{\mathrm{educt,\,t}} + \Sigma n_{\mathrm{product,\,t}}}{n_{\mathrm{educt,\,0}}} \cdot 100\ \% \tag{S5}$$

$n_{educt,0}$: amount of educt at the start of the reaction
$n_{educt,t}$: amount of educt at the end of the reaction
$n_{product,t}$: amount of product at the end of the reaction
Q_{ideal}: charge necessary for full conversion to product
$Q_{\mathrm{experiment}}$: total charge transferred during the experiment
z: number of electrons
F: Faraday’s constant

Calculation of Reynolds numbers

The Reynolds numbers of the 2E-flow cell is calculated according to eq. (S6).

$$\mathrm{Re} = \frac{V_{\mathrm{lin}} \cdot d}{v} \tag{S6}$$

V_{lin}: linear velocity of the medium
d: characteristic diameter (since flow channel has a quadratic profile: channel width)
v: kinematic viscosity of the medium

Since the flow channel has a quadratic profile, *d* is equal to the channel width (1.5 mm). The kinematic viscosity of water at RT – 80 °C was used.

Additional Figures

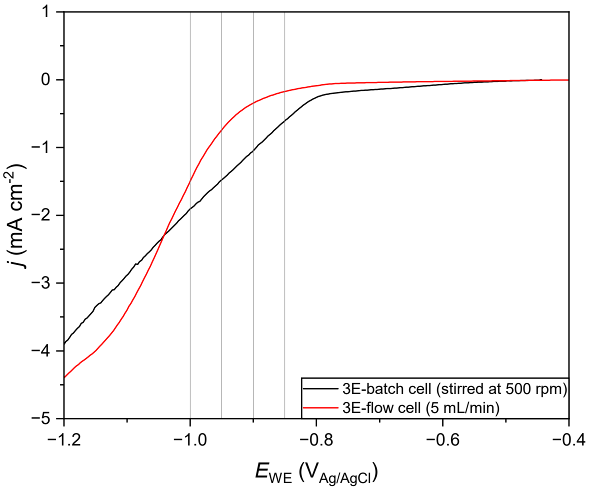

Figure S3: LSVs of Ti electrodes in 50 mM $Co(NO_3)_2$ solution in the unseparated 3E-batch cell and the separated 3E-flow cell (scan rate: 10 mV s^{-1}). Potentials used for $Co(OH)_2$ deposition are indicated.

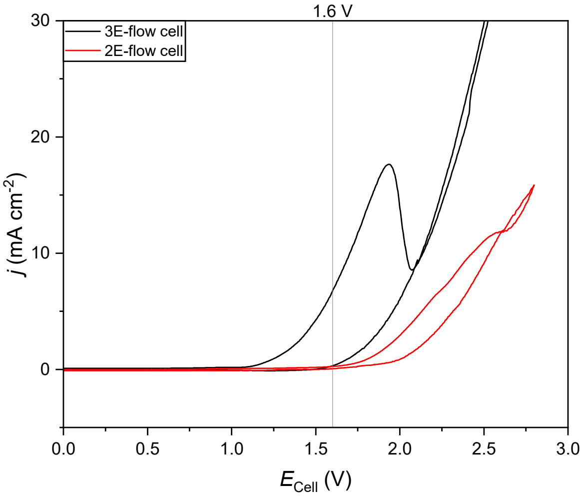

Figure S4: Cell voltage ramps of $Ti/Co(OH)_2$ electrodes of the 3E-flow cell and the 2E-flow cell in 1.0 M NaOH solution (scan rate: 10 mV s^{-1}). The films were deposited at a constant voltage of −2.75 V with a charge density σ_{Red} of 0.4 C cm^{-2}.

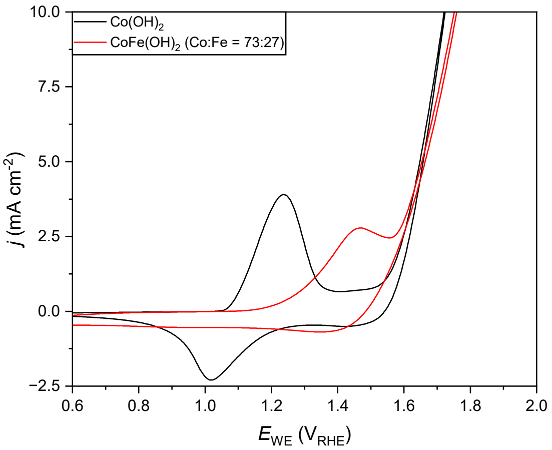

Figure S5: Exemplary cyclic voltammograms of Ti/$Co(OH)_2$ and Ti/$CoFe(OH)_2$ batch cell electrodes in 1.0 M NaOH (scan rate: 10 mV s^{-1}). Both films were deposited with σ_{Red} = 0.8 C cm^{-2} according to the standard procedure for batch cells given in the experimental section. For the $CoFe(OH)_2$ coating, a mixture of $Co(NO_3)_2$ and $Fe(NO_3)_2$ with a total cation concentration of 50 mM was used. The Co:Fe ratio was determined after the measurement by dissolving the film in 10 mL HCl (20 %) and analyzing the solution via ICP-OES.

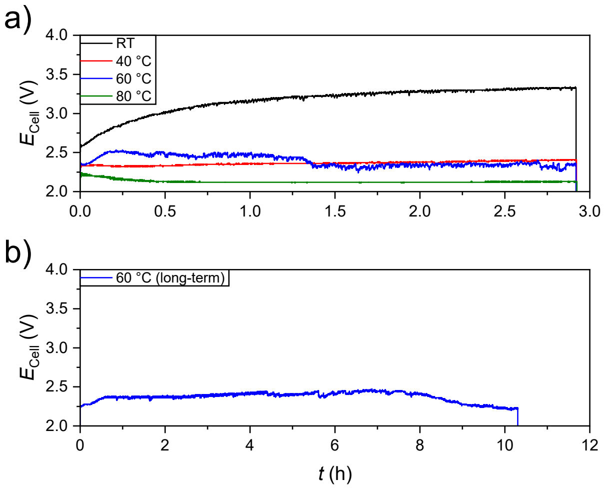

Figure S6: Exemplary cell voltage curves of the HMF oxidation experiments.

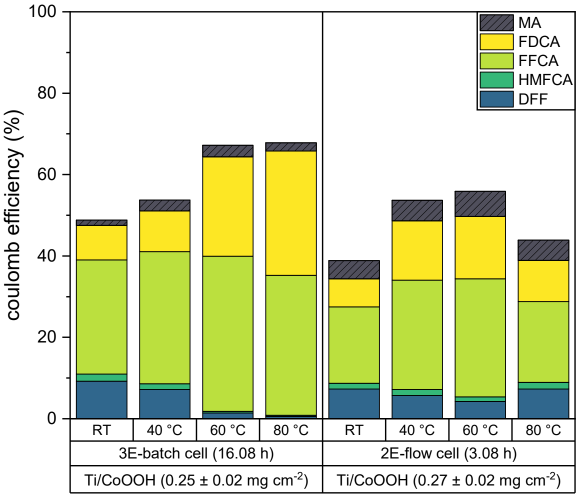

Figure S7: Coulomb efficiencies (*CE*) of the HMF oxidation in the 3E-batch cell and the 2E-flow cell at different temperatures. The *CE* values of DFF, HMFCA, FFCA and FDCA were summed up to form the total Coulomb efficiency (CE_{tot}). To calculate the *CE* of MA, full oxidation of the two C_1 products to CO_2 was assumed, resulting in a transport of 12 e^- per molecule.

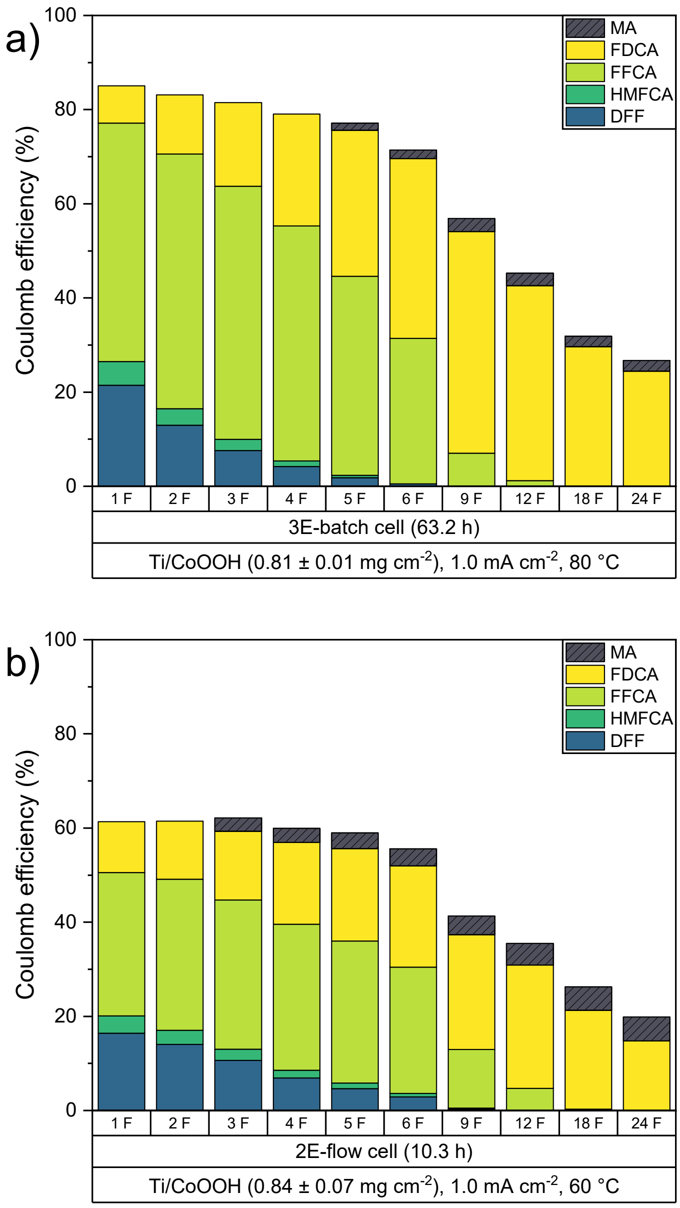

Figure S8: Coulomb efficiencies (*CE*) of the optimized HMF oxidations in the 3E-batch cell and the 2E-flow cell. The *CE* values of DFF, HMFCA, FFCA and FDCA were summed up to form the total Coulomb efficiency (CE_{tot}). To calculate the *CE* of MA, full oxidation of the two C_1 products to CO_2 was assumed, resulting in a transport of 12 e^- per molecule.

Additional Tables

Table S1: Performance parameters of the oxidation of 20 mM HMF solutions in acetate buffer (pH 5) in the 3E-batch cell and the 2E-flow cell (j = 1.0 mA cm^{-2}, m_{CoOOH} = 0.26 ± 0.03 mg cm^{-2}, 6 F transported). Mean values and standard deviations of duplicate reactions are given.*

	T **(°C)**	***X*** **(%)**	***MB*** **(%)**	**Product**	***Y*** **(%)**	***CE*** **(%)**
3E-batch cell	RT	89.9 ± 1.6	92.1 ± 1.7	**DFF**	27.0 ± 4.3	9.2 ± 1.5
				HMFCA	5.2 ± 0.4	1.8 ± 0.1
				FFCA	41.0 ± 2.8	28.1 ± 1.9
				FDCA	8.3 ± 1.7	8.5 ± 1.8
				MA**	0.6 ± 0.1	1.3 ± 0.3
	40	93.3 ± 2.8	90.2 ± 0.8	**DFF**	20.9 ± 6.7	7.2 ± 2.3
				HMFCA	4.2 ± 0.8	1.4 ± 0.3
				FFCA	47.4 ± 5.9	32.5 ± 4.0
				FDCA	9.7 ± 4.0	10.0 ± 4.1
				MA**	1.3 ± 0.4	2.7 ± 0.7
	60	98.9 ± 0.4	86.8 ± 1.6	**DFF**	4.1 ± 1.9	1.4 ± 0.6
				HMFCA	1.1 ± 0.3	0.4 ± 0.1
				FFCA	55.5 ± 2.0	38.2 ± 1.3
				FDCA	23.6 ± 2.9	24.4 ± 3.0
				MA**	1.4 ± 0.1	2.8 ± 0.3
	80	99.2 ± 0.1	84.9 ± 0.5	**DFF**	1.7 ± 0.2	0.6 ± 0.1
				HMFCA	0.7 ± 0.0	0.3 ± 0.0
				FFCA	50.7 ± 0.3	34.4 ± 0.0
				FDCA	29.7 ± 0.7	30.5 ± 0.8
				MA**	1.0 ± 0.1	2.0 ± 0.1
2E-flow cell	RT	74.7 ± 2.7	88.1 ± 1.1	**DFF**	21.6 ± 1.3	7.3 ± 0.5
				HMFCA	4.2 ± 0.0	1.4 ± 0.0
				FFCA	27.9 ± 3.4	18.8 ± 2.2
				FDCA	6.9 ± 1.7	6.9 ± 1.7
				MA**	2.2 ± 0.1	4.5 ± 0.3
	40	87.1 ± 0.5	91.2 ± 1.0	**DFF**	16.9 ± 1.4	5.7 ± 0.5
				HMFCA	4.5 ± 0.3	1.5 ± 0.1
				FFCA	39.9 ± 1.1	26.8 ± 0.7
				FDCA	14.5 ± 2.0	14.6 ± 2.0
				MA**	2.5 ± 0.0	5.0 ± 0.0
	60	86.3 ± 1.7	90.1 ± 1.8	**DFF**	12.5 ± 0.4	4.3 ± 0.1
				HMFCA	3.3 ± 0.3	1.1 ± 0.1
				FFCA	42.6 ± 0.8	29.0 ± 0.2
				FDCA	15.0 ± 0.1	15.3 ± 0.3
				MA**	3.0 ± 0.8	6.2 ± 1.6
	80	78.5 ± 4.1	90.5 ± 0.7	**DFF**	21.8 ± 3.1	7.3 ± 1.0
				HMFCA	4.9 ± 1.0	1.6 ± 0.3
				FFCA	29.8 ± 1.9	19.9 ± 1.2
				FDCA	10.0 ± 1.7	10.1 ± 1.7
				MA**	2.5 ± 0.5	5.0 ± 0.9

* Although standard deviations should generally only be used for at least three replicates, we chose these values for a better comparability with the respective reaction performance data.

** To calculate the *CE* of MA, full oxidation of the two C_1 products to CO_2 was assumed, resulting in a transport of 12 e^{-} per molecule.

Table S2: Performance parameters of the oxidation of 20 mM HMF solutions in acetate buffer (pH 5) under optimized conditions in the 3E-batch cell (j = 1.0 mA cm^{-2}, 80 °C, m_{CoOOH} = 0.81 ± 0.01 mg cm^{-2}). Mean values and standard deviations of duplicate reactions are given.*

	X (%)	*MB* (%)	Product	*Y* (%)	*CE* (%)
1 F	28.8 ± 0.5	98.5 ± 0.7	**DFF**	10.8 ± 0.2	21.5 ± 0.3
			HMFCA	2.5 ± 0.2	5.0 ± 0.4
			FFCA	12.7 ± 0.0	50.7 ± 0.1
			FDCA	1.3 ± 0.2	7.9 ± 1.0
			MA**	n.q.	n.q.
2 F	52.2 ± 0.1	95.6 ± 0.8	**DFF**	13.0 ± 0.5	13.0 ± 0.5
			HMFCA	3.5 ± 0.2	3.5 ± 0.2
			FFCA	27.1 ± 0.1	54.1 ± 0.1
			FDCA	4.2 ± 0.2	12.6 ± 0.5
			MA**	n.q.	n.q.
3 F	71.4 ± 0.1	92.5 ± 0.5	**DFF**	11.4 ± 0.5	7.6 ± 0.3
			HMFCA	3.4 ± 0.2	2.3 ± 0.1
			FFCA	40.2 ± 0.0	53.8 ± 0.1
			FDCA	8.9 ± 0.3	17.8 ± 0.6
			MA**	n.q.	n.q.
4 F	86.2 ± 0.0	89.6 ± 0.6	**DFF**	8.3 ± 0.3	4.2 ± 0.2
			HMFCA	2.4 ± 0.3	1.2 ± 0.1
			FFCA	49.5 ± 0.1	49.9 ± 0.2
			FDCA	15.7 ± 0.4	23.7 ± 0.6
			MA**	n.q.	n.q.
5 F	95.5 ± 0.1	88.7 ± 1.0	**DFF**	4.4 ± 0.2	1.8 ± 0.1
			HMFCA	1.3 ± 0.2	0.5 ± 0.1
			FFCA	52.2 ± 0.1	42.3 ± 0.1
			FDCA	25.5 ± 0.4	31.0 ± 0.6
			MA**	0.6 ± 0.0	1.5 ± 0.1
6 F	99.0 ± 0.1	86.5 ± 1.2	**DFF**	1.4 ± 0.3	0.5 ± 0.1
			HMFCA	n.q.	n.q.
			FFCA	45.7 ± 0.5	31.0 ± 0.4
			FDCA	37.6 ± 0.3	38.2 ± 0.3
			MA**	0.9 ± 0.1	1.9 ± 0.3
9 F	100.0	86.8 ± 1.6	**DFF**	n.q.	n.q.
			HMFCA	0.0	0.0
			FFCA	15.3 ± 1.5	7.0 ± 0.7
			FDCA	69.2 ± 0.3	47.1 ± 0.1
			MA**	2.0 ± 0.4	2.8 ± 0.5
12 F	100.0	86.9 ± 1.7	**DFF**	0.0	0.0
			HMFCA	0.0	0.0
			FFCA	3.4 ± 0.5	1.2 ± 0.2
			FDCA	80.9 ± 0.7	41.4 ± 0.4
			MA**	2.6 ± 0.4	2.7 ± 0.5
18 F	100.0	89.7 ± 1.9	**DFF**	0.0	0.0
			HMFCA	0.0	0.0
			FFCA	0.0	0.0
			FDCA	86.6 ± 1.3	29.7 ± 0.5
			MA**	3.2 ± 0.7	2.2 ± 0.5
24 F	100.0	99.1 ± 2.5	**DFF**	0.0	0.0
			HMFCA	0.0	0.0
			FFCA	0.0	0.0
			FDCA	94.7 ± 1.4	24.5 ± 0.4
			MA**	4.4 ± 1.1	2.2 ± 0.6

n.q. = not quantifiable

Table S3: Performance parameters of the oxidation of 20 mM HMF solutions in acetate buffer (pH 5) under optimized conditions in the 2E-flow cell (j = 1.0 mA cm^{-2}, 60 °C, m_{CoOOH} = 0.84 ± 0.07 mg cm^{-2}). Mean values and standard deviations of duplicate reactions are given.*

	X (%)	*MB* (%)	Product	*Y* (%)	*CE* (%)
1 F	20.1 ± 1.2	99.7 ± 0.3	DFF	8.3 ± 1.1	16.4 ± 2.2
			HMFCA	1.8 ± 0.2	3.6 ± 0.4
			FFCA	7.7 ± 1.5	30.5 ± 5.9
			FDCA	1.8 ± 0.6	10.8 ± 3.8
			MA**	n.q.	n.q.
2 F	39.6 ± 1.5	98.8 ± 0.1	DFF	14.4 ± 2.8	14.0 ± 2.8
			HMFCA	3.1 ± 0.6	3.0 ± 0.6
			FFCA	16.5 ± 3.4	32.1 ± 6.6
			FDCA	4.2 ± 1.7	12.3 ± 4.9
			MA**	n.q.	n.q.
3 F	54.6 ± 3.3	98.6 ± 0.2	DFF	16.5 ± 3.4	10.6 ± 2.2
			HMFCA	3.7 ± 0.7	2.4 ± 0.5
			FFCA	24.6 ± 5.0	31.7 ± 6.4
			FDCA	7.6 ± 2.3	14.6 ± 4.3
			MA**	0.7 ± 0.1	2.8 ± 0.3
4 F	66.6 ± 5.0	97.0 ± 0.4	DFF	14.5 ± 2.0	6.9 ± 1.0
			HMFCA	3.4 ± 0.4	1.6 ± 0.2
			FFCA	32.5 ± 5.4	31.0 ± 5.1
			FDCA	12.1 ± 2.6	17.4 ± 3.6
			MA**	1.0 ± 0.1	3.0 ± 0.4
5 F	78.2 ± 4.1	96.1 ± 0.9	DFF	12.3 ± 1.6	4.6 ± 0.6
			HMFCA	3.1 ± 0.3	1.2 ± 0.1
			FFCA	40.0 ± 3.5	30.2 ± 2.6
			FDCA	17.3 ± 3.5	19.6 ± 3.9
			MA**	1.5 ± 0.1	3.3 ± 0.1
6 F	87.3 ± 3.2	94.7 ± 0.2	DFF	9.5 ± 1.5	2.9 ± 0.5
			HMFCA	2.7 ± 0.4	0.8 ± 0.1
			FFCA	44.2 ± 0.8	26.8 ± 0.4
			FDCA	23.7 ± 4.1	21.5 ± 3.7
			MA**	2.0 ± 0.0	3.6 ± 0.1
9 F	98.8 ± 0.5	92.2 ± 0.3	DFF	2.1 ± 0.6	0.4 ± 0.1
			HMFCA	0.8 ± 0.2	0.1 ± 0.0
			FFCA	36.5 ± 3.9	12.5 ± 1.4
			FDCA	47.6 ± 5.4	24.4 ± 2.7
			MA**	3.9 ± 0.1	4.0 ± 0.1
12 F	100.0	90.2 ± 0.0	DFF	n.q.	n.q.
			HMFCA	n.q.	n.q.
			FFCA	17.9 ± 3.7	4.7 ± 1.0
			FDCA	66.4 ± 3.5	26.2 ± 1.3
			MA**	5.8 ± 0.1	4.6 ± 0.1
18 F	100.0	87.7 ± 0.8	DFF	0.0	0.0
			HMFCA	0.0	0.0
			FFCA	1.4 ± 0.5	0.3 ± 0.1
			FDCA	77.1 ± 1.3	21.0 ± 0.3
			MA**	9.2 ± 0.0	5.0 ± 0.0
24 F	100.0	83.8 ± 1.6	DFF	0.0	0.0
			HMFCA	0.0	0.0
			FFCA	0.0	0.0
			FDCA	71.5 ± 1.8	14.8 ± 0.3
			MA**	12.3 ± 0.2	5.1 ± 0.1

n.q. = not quantifiable