Supporting Information

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.

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

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

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

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

$n_{educt,0}$: 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
$Q_{experiment}$: total charge transferred during the experiment
z: number of electrons
F: Faraday's constant

Additional Figures

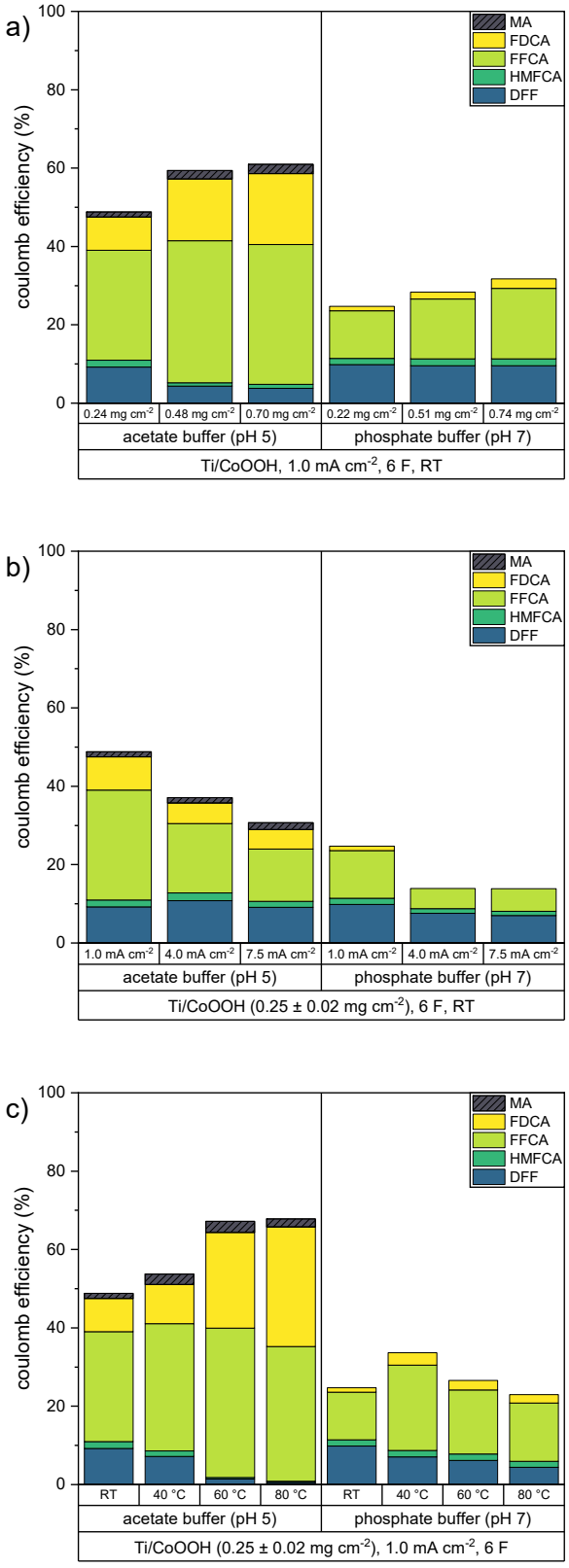

Figure S1: Coulomb efficiencies (*CE*) of the single products obtained during the galvanostatic reactions with a) different CoOOH loadings, b) different current densities and c) different electrolyte temperatures. The *CE* values of DFF, HMFCA, FFCA and FDCA were summed up to form the total Coulomb efficiency (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.

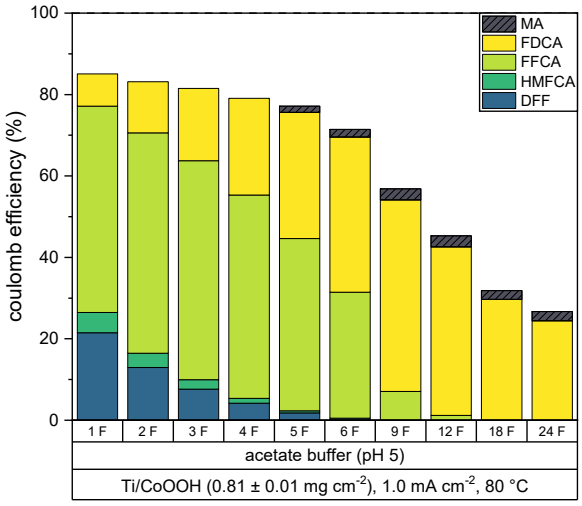

Figure S2: Coulomb efficiencies (CE) of the reaction under optimized conditions. The *CE* values of DFF, HMFCA, FFCA and FDCA were summed up to form the total Coulomb efficiency (CE_{tot}). To calculate the *CE* of MA, full oxidation of the two C_1 products to CO_2 was assumed, resulting in a transport of 12 e^- per molecule.

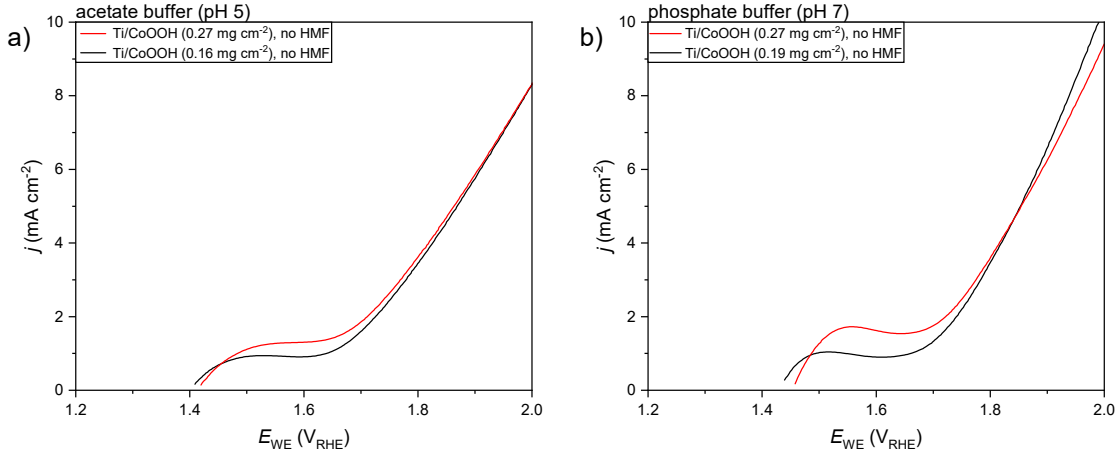

Figure S3: Linear sweep voltammograms of Ti/CoOOH of different catalyst loadings in a) acetate buffer (pH 5) and b) phosphate buffer (pH 7).

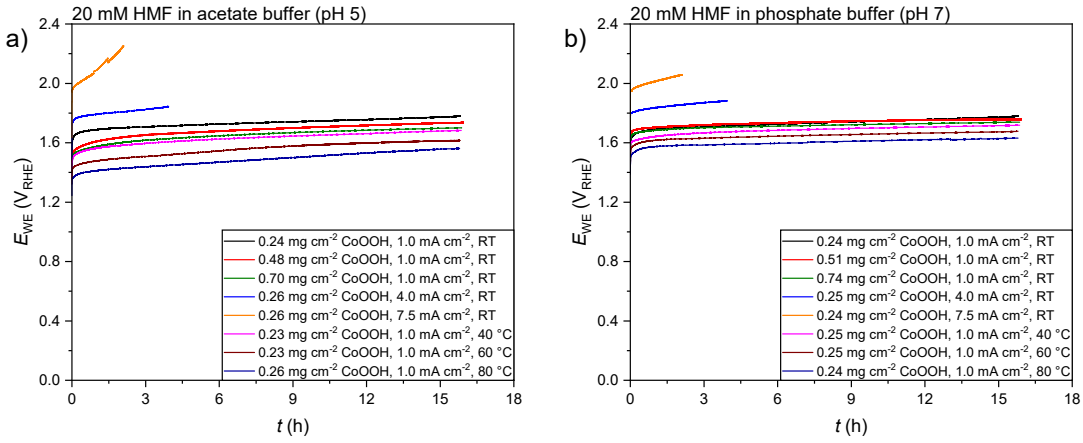

Figure S4: Exemplary potential curves of the HMF oxidation experiments with different parameters in a) the acetate buffer (pH 5) and b) in the phosphate buffer (pH 7).

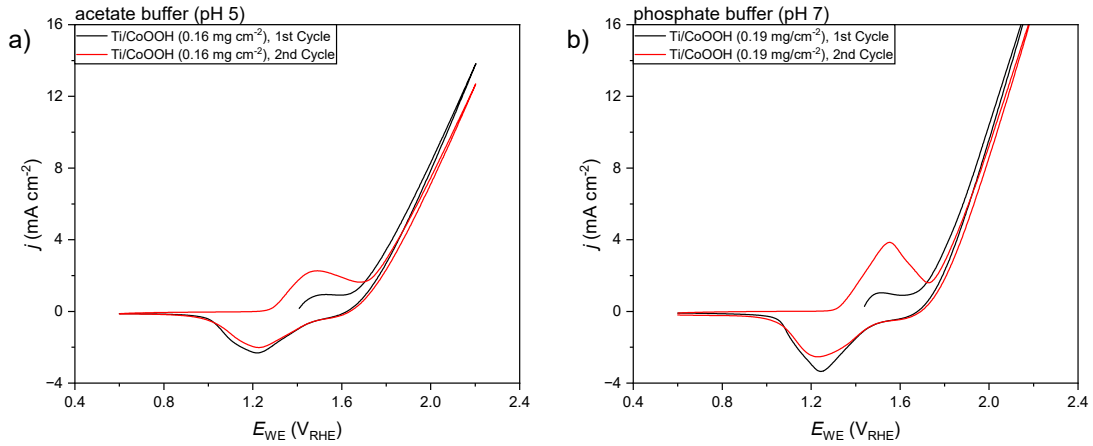

Figure S5: Cyclic voltammograms of Ti/CoOOH in a) acetate buffer (pH 5) and b) phosphate buffer (pH 7). Measurements were recorded starting from the open circuit potential (scan rate: 10 mV s^{-1}).

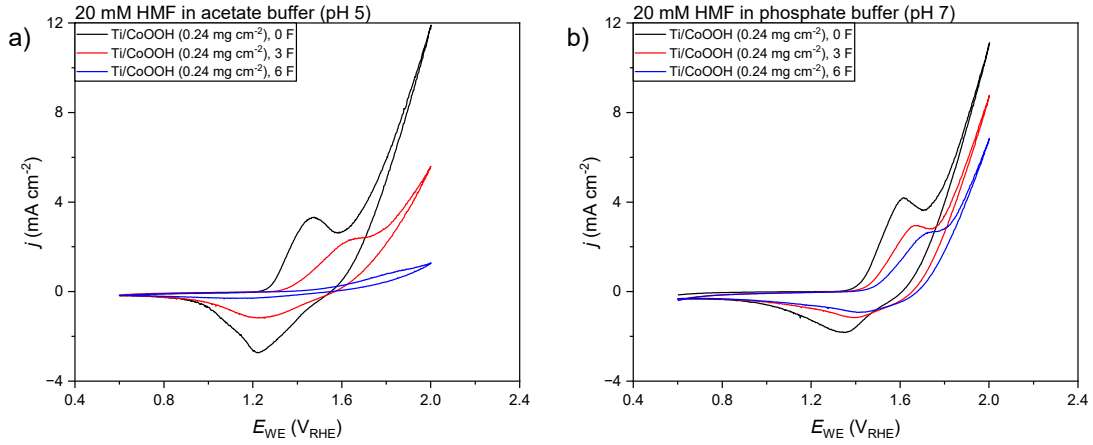

Figure S6: Cyclic voltammograms of Ti/CoOOH in 20 mM HMF solutions of a) acetate buffer (pH 5) and b) phosphate buffer (pH 7) obtained before (0 F), in the middle (3 F) and at the end (6 F) of a galvanostatic experiment at 1.0 mA cm^{-2}. Measurements were recorded starting from the respective open circuit potentials for two cycles (scan rate: 10 mV s^{-1}). The second cycles are depicted here.

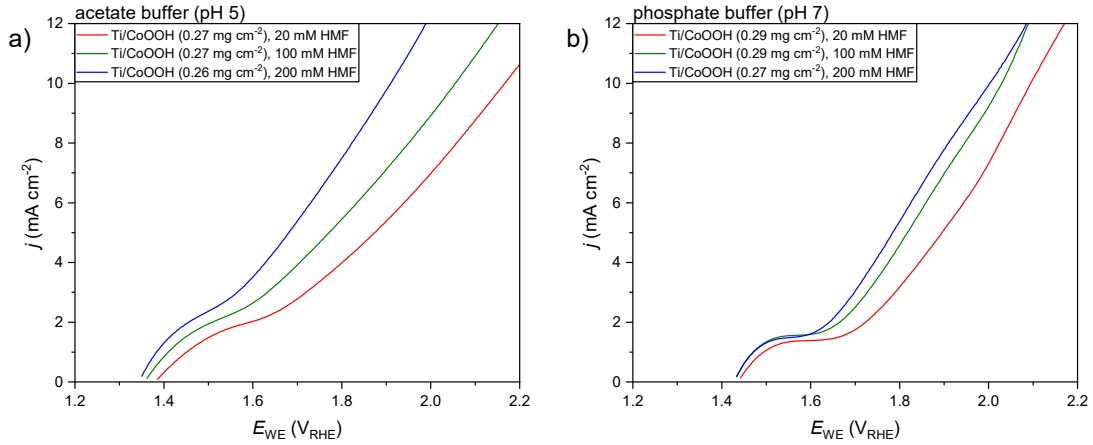

Figure S7: Linear sweep voltammograms of Ti/CoOOH in HMF solutions of a) acetate buffer (pH 5) and b) phosphate buffer (pH 7) at different HMF concentrations.

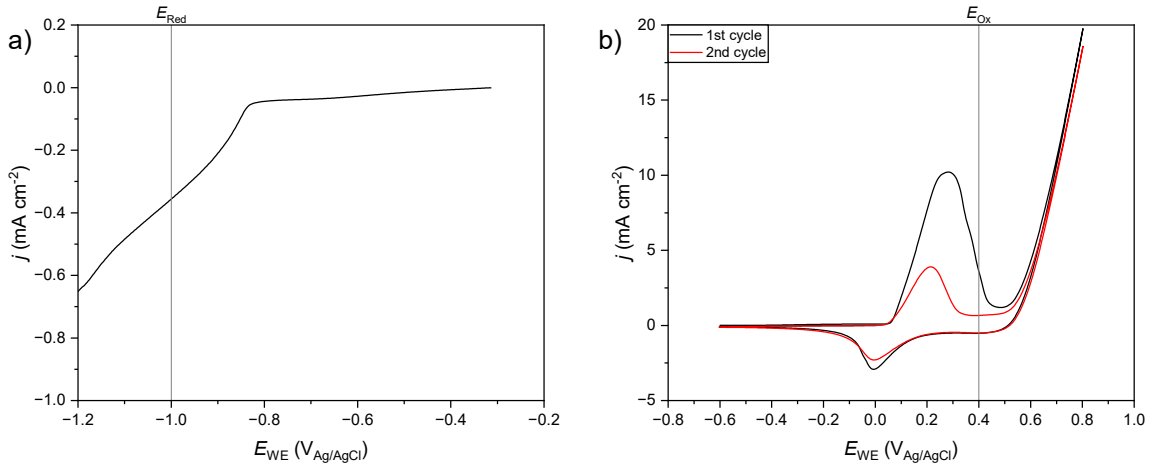

Figure S8: a) Linear sweep voltammogram of Ti in 0.05 M $Co(NO_3)_2$ solution, b) cyclic voltammogram of Ti/$Co(OH)_2$ in 1.0 M NaOH. Constant potentials used for $Co(OH)_2$ deposition and oxidation are indicated (scan rate: 10 mV s^{-1}).

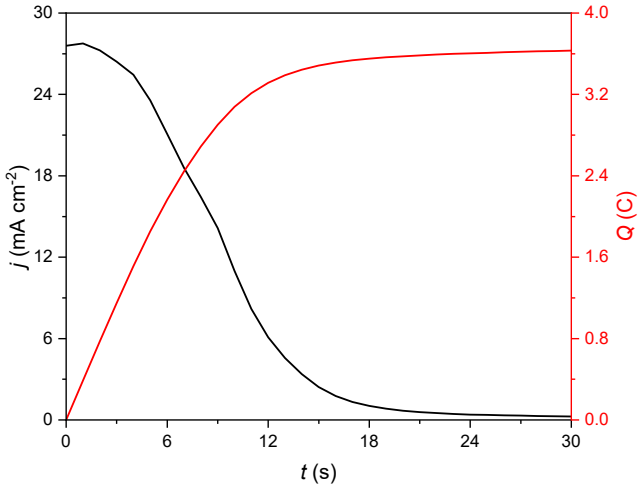

Figure S9: Exemplary current density and charge curves of a Ti/$Co(OH)_2$ oxidation in 1.0 M NaOH by application of 0.4 $V_{Ag/AgCl}$. The $Co(OH)_2$ film was deposited via reduction of a 0.05 M $Co(NO_3)_2$ solution at −1.0 $V_{Ag/AgCl}$ with a transported charge density of 0.8 C cm^{-2}.

Additional Tables

Table S1: Performance parameters of the HMF oxidation reactions under variation of the CoOOH loading m_{CoOOH} (j = 1.0 mA cm^{-2}, RT, 6 F transported). Mean values and standard deviations of duplicate reactions are given.*

	m_{CoOOH} (mg cm^{-2})	X (%)	MB (%)	a_{CoOOH} (%)	Product	Y (%)	CE (%)
Acetate buffer (pH 5)	0.24 ± 0.00	89.9 ± 1.6	92.1 ± 1.7	90.1 ± 2.2	**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
	0.48 ± 0.01	95.6 ± 0.2	89.5 ± 0.3	83.5 ± 1.8	**DFF**	12.8 ± 0.1	4.4 ± 0.0
					HMFCA	2.4 ± 0.0	0.8 ± 0.0
					FFCA	53.3 ± 0.4	36.3 ± 0.3
					FDCA	15.5 ± 0.0	15.8 ± 0.0
					MA**	1.0 ± 0.0	2.1 ± 0.1
	0.70 ± 0.01	95.8 ± 0.6	89.8 ± 0.3	87.5 ± 0.5	**DFF**	11.2 ± 1.1	3.8 ± 0.4
					HMFCA	2.9 ± 0.1	1.0 ± 0.0
					FFCA	52.3 ± 1.0	35.7 ± 0.8
					FDCA	17.8 ± 1.1	18.1 ± 1.2
					MA**	1.1 ± 0.0	2.3 ± 0.0
Phosphate buffer (pH 7)	0.22 ± 0.01	58.4 ± 3.1	93.9 ± 0.1	99.0 ± 0.2	**DFF**	28.7 ± 1.0	9.8 ± 0.3
					HMFCA	4.7 ± 0.3	1.6 ± 0.1
					FFCA	17.8 ± 1.8	12.2 ± 1.2
					FDCA	1.1 ± 0.2	1.1 ± 0.2
					MA**	0.0	0.0
	0.51 ± 0.00	64.3 ± 5.6	93.0 ± 1.4	99.3 ± 0.2	**DFF**	28.1 ± 0.7	9.6 ± 0.3
					HMFCA	5.1 ± 0.1	1.7 ± 0.0
					FFCA	22.4 ± 4.3	15.3 ± 2.9
					FDCA	1.7 ± 0.5	1.7 ± 0.6
					MA**	0.0	0.0
	0.74 ± 0.00	67.2 ± 3.1	94.3 ± 1.1	98.5 ± 0.2	**DFF**	27.8 ± 1.0	9.5 ± 0.4
					HMFCA	5.2 ± 0.0	1.8 ± 0.0
					FFCA	26.2 ± 2.4	18.0 ± 1.6
					FDCA	2.4 ± 0.5	2.5 ± 0.5
					MA**	0.0	0.0

Table S2: Performance parameters of the HMF oxidation reactions under variation of the current density *j* (m_{CoOOH} = 0.25 ± 0.02 mg cm^{-2}, RT, 6 F transported). Mean values and standard deviations of duplicate reactions are given.*

	j (mA cm^{-2})	*X* (%)	*MB* (%)	α_{CoOOH} (%)	Product	*Y* (%)	*CE* (%)
Acetate buffer (pH 5)	4.0	73.7 ± 2.8	94.9 ± 1.7	90.0 ± 2.6	**DFF**	31.4 ± 2.0	10.8 ± 0.7
					HMFCA	5.7 ± 0.4	2.0 ± 0.1
					FFCA	25.7 ± 2.1	17.7 ± 1.5
					FDCA	5.0 ± 1.2	5.2 ± 1.3
					MA**	0.7 ± 0.2	1.4 ± 0.3
	7.5	59.4 ± 3.5	94.6 ± 0.6	89.0 ± 0.8	**DFF**	25.6 ± 1.0	9.1 ± 0.4
					HMFCA	4.2 ± 0.2	1.5 ± 0.1
					FFCA	18.8 ± 1.5	13.4 ± 1.2
					FDCA	4.6 ± 0.3	5.0 ± 0.3
					MA**	0.8 ± 0.1	1.8 ± 0.2
Phosphate buffer (pH 7)	4.0	36.6 ± 1.8	96.7 ± 0.4	98.5 ± 0.5	**DFF**	22.3 ± 0.3	7.6 ± 0.1
					HMFCA	3.5 ± 0.1	1.2 ± 0.0
					FFCA	7.5 ± 0.9	5.1 ± 0.7
					FDCA	n.q.	n.q.
					MA**	0.0	0.0
	7.5	36.7 ± 4.7	95.7 ± 1.1	98.7 ± 0.2	**DFF**	20.8 ± 1.0	7.0 ± 0.3
					HMFCA	3.1 ± 0.1	1.1 ± 0.0
					FFCA	8.5 ± 2.5	5.8 ± 1.6
					FDCA	n.q.	n.q.
					MA**	0.0	0.0

n.q. = not quantifiable

Table S3: Performance parameters of the HMF oxidation reactions under variation of the temperature T (j = 1.0 mA cm^{-2}, m_{CoOOH} = 0.25 ± 0.02 mg cm^{-2}, 6 F transported). Mean values and standard deviations of duplicate reactions are given.*

	T (°C)	*X* (%)	*MB* (%)	α_{CoOOH} (%)	Product	*Y* (%)	*CE* (%)
Acetate buffer (pH 5)	40	93.3 ± 2.8	90.2 ± 0.8	87.5 ± 3.8	**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	84.3 ± 2.8	**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	77.2 ± 4.0	**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
Phosphate buffer (pH 7)	40	76.7 ± 3.2	83.8 ± 1.3	96.8 ± 1.0	**DFF**	20.7 ± 1.9	7.1 ± 0.7
					HMFCA	4.9 ± 0.1	1.7 ± 0.0
					FFCA	31.9 ± 2.9	21.8 ± 1.9
					FDCA	3.1 ± 0.9	3.2 ± 0.9
					MA**	0.0	0.0
	60	68.9 ± 7.9	80.3 ± 2.1	97.3 ± 1.6	**DFF**	18.2 ± 2.6	6.2 ± 0.9
					HMFCA	4.8 ± 0.2	1.6 ± 0.1
					FFCA	23.9 ± 7.1	16.3 ± 4.9
					FDCA	2.4 ± 1.4	2.4 ± 1.5
					MA**	0.0	0.0
	80	69.4 ± 3.4	72.9 ± 1.8	99.6 ± 0.1	**DFF**	13.2 ± 1.6	4.4 ± 0.5
					HMFCA	4.7 ± 0.1	1.6 ± 0.0
					FFCA	22.3 ± 2.7	14.9 ± 1.9
					FDCA	2.1 ± 0.5	2.1 ± 0.6
					MA**	0.0	0.0

* 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 S4: Performance parameters of a HMF oxidation under optimized conditions (20 mM HMF in acetate buffer (pH 5), 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* (%)**	**a_{CoOOH} (%)**	**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	83.9 ± 2.8	**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