Supporting Information

Boosting the valorization of biomass and green electrons to chemical building blocks: A study on the kinetics and mass transfer during the electrochemical conversion of HMF to FDCA in a microreactor

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1. Voltammetry

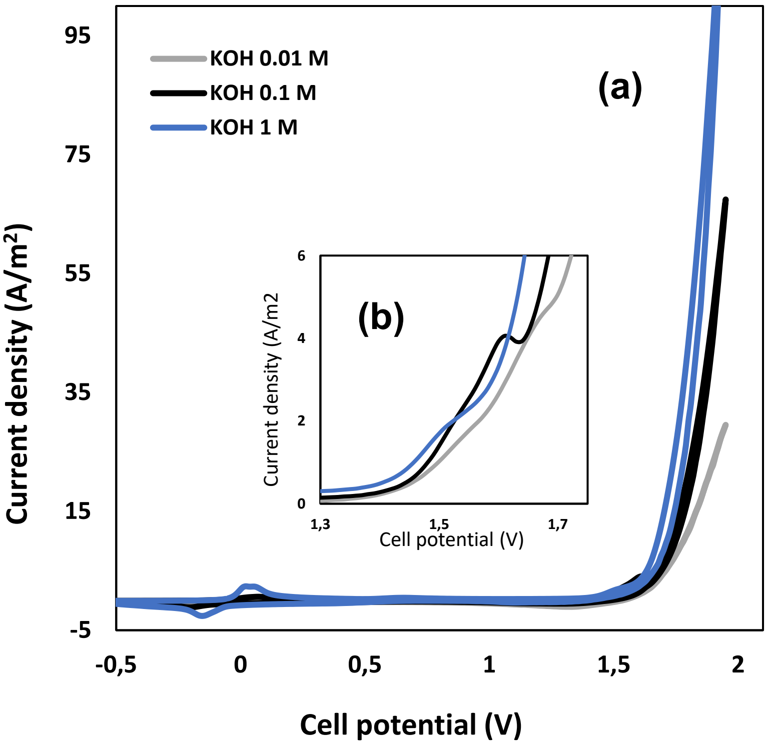

Figure S1. (a) CV measurement at different KOH concentrations in the absence of HMF, (b) forward scans from 1.3 to 1.7 V. Liquid flow rate of 0.5 mL/min, and scan rate of 10 mV/s.

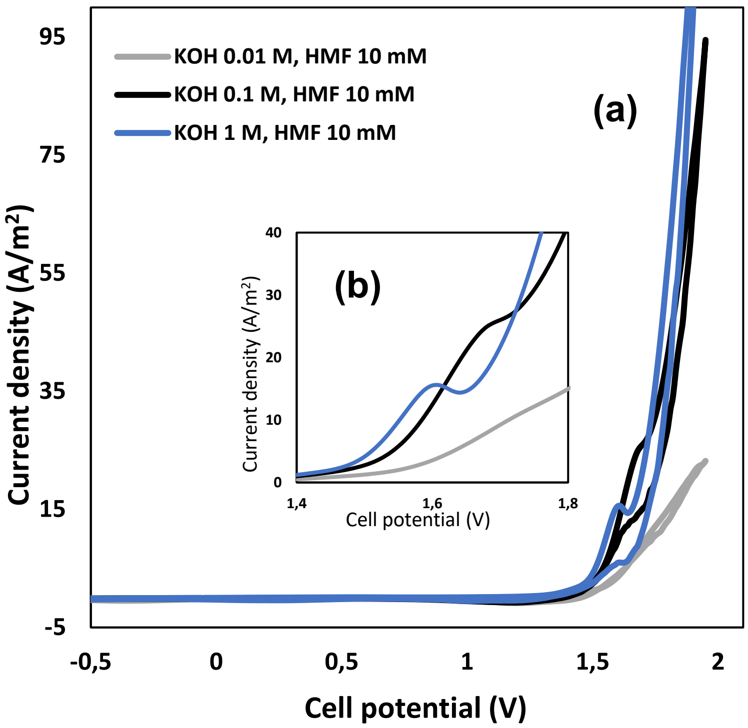

Figure S2. (a) CV measurement at different KOH concentrations in the presence of HMF, (b) forward scans from 1.4 to 1.8 V. Liquid flow rate of 0.5 mL/min, and scan rate of 10 mV/s.

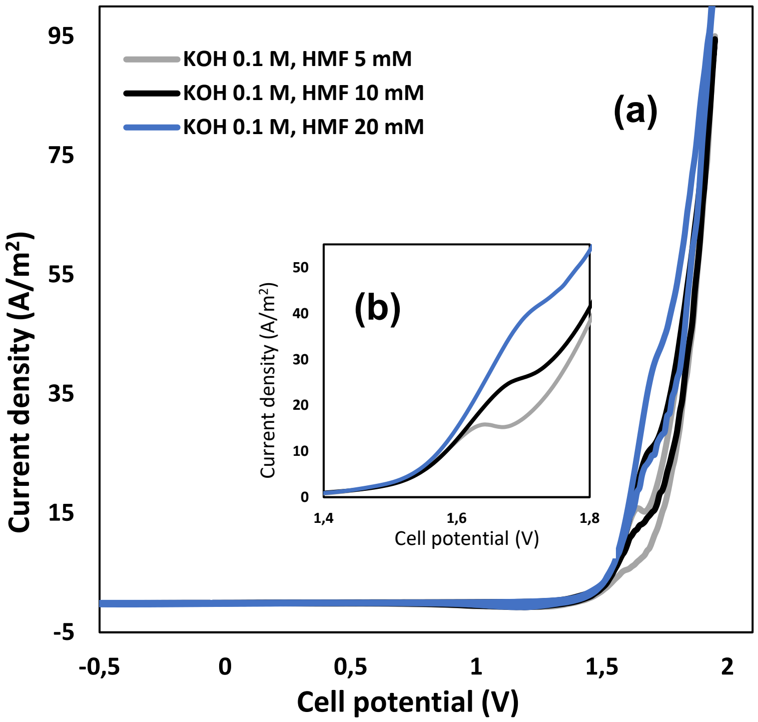

Figure S3. (a) CV measurement at 0.1 M KOH concentrations and different HMF concentrations, (b) forward scans from 1.4 to 1.8 V. Liquid flow rate of 0.5 mL/min, and scan rate of 10 mV/s.

2. Experimental results

Table S1. Product distribution at 1.8 V, various flow rates, pH 13, and 10 mM HMF.

Flowrate (mL/min)	Conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	97	2	10	87	26
0.2	85	3	19	58	31
0.3	74	4	20	44	35
0.4	66	4	20	35	39
0.5	61	4	20	30	43
0.7	53	4	19	23	48
0.85	48	3	18	19	50
1.0	45	3	18	16	52
1.5	35	3	14	10	50
2.0	29	2	11	7	50
3.0	21	2	8	4	53
4.0	17	2	6	3	51

Tables S2. Product distribution at 1.7 V, various flow rates, pH 13, and 10 mM HMF.

Flowrate (mL/min)	Conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	97	2	10	87	107
0.2	91	1	23	62	94
0.3	84	2	28	52	100
0.4	78	2	30	45	100
0.5	72	2	29	37	98
0.7	51	3	34	36	105
0.85	49	3	29	25	111
1.0	48	2	24	17	97
1.5	23	2	20	12	106
2.0	10	2	19	9	104
3.0	7	1	10	4	92
4.0	2	1	8	3	94

Table S3. Product distribution at 1.6 V, various flow rates, pH 13, and 10 mM HMF.

Flowrate (mL/min)	Conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	74	5	22	52	93
0.2	48	4	19	23	90
0.3	37	4	13	13	84
0.4	24	3	11	10	89
0.5	24	2	8	6	76
0.7	18	2	5	4	76
1.0	4	1	4	3	76
2.0	7	1	2	2	71
3.0	4	1	2	1	67

Table S4. Product distribution at pH 12, various flow rates, 1.7 V, and 10 mM HMF.

Flowrate (mL/min)	Conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	55	2	37	8	78
0.2	47	1	36	6	90
0.3	45	1	31	5	85
0.5	36	1	23	3	81
0.7	28	1	17	2	80
1.0	19	0	5	1	32
2.0	14	0	6	1	68
4.0	-1	0	3	0	71

Table S5. Product distribution at pH 14, various flow rates, 1.7 V, and 10 mM HMF.

Flowrate (mL/min)	Conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	90	5	3	77	57
0.2	69	9	7	56	74
0.3	60	8	7	40	74
0.5	43	7	7	23	67
0.7	37	6	6	16	70
1.0	28	6	5	11	66
2.0	14	4	3	4	63
3.0	11	3	2	3	65
4.0	7	3	1	2	52

Tables S6. Product distribution with inlet HMF concentration of 20 mM, at various flow rates, 1.7 V, and pH 13.

Flowrate (mL/min)	Conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	97	1	13	82	95
0.2	86	2	30	51	93
0.3	73	2	30	34	105
0.5	61	2	28	21	115
0.7	53	2	23	16	104
1	41	2	18	10	103
2.0	32	2	13	6	104
3.0	19	1	6	2	110
4.0	13	1	4	1	89

Table S7. Product distribution with inlet HMF concentration of 5 mM, at various flow rates, 1.7 V, and pH 13.

Flowrate (mL/min)	Conversion (%)	HMFCA yield (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	98	1	6	97	55
0.2	89	2	17	77	74
0.3	82	2	22	63	86
0.4	70	3	22	38	79
0.5	62	2	21	29	82
0.7	48	3	20	22	89
1	25	2	14	10	82
2.0	26	1	9	6	71
3.0	20	1	7	4	68

Table S8. Product distribution with inlet HMFCA concentration of 10 mM, at various flow rates, 1.7 V, and pH 13.

Flowrate (mL/min)	Conversion (%)	FFCA yield (%)	FDCA yield (%)	Current efficiency (%)
0.1	97	4	89	76
0.15	95	8	82	57
0.2	92	10	77	69
0.3	84	16	64	64
0.4	74	19	48	71
0.5	67	18	41	76
0.8	61	20	35	61
1.0	50	18	26	77
1.5	39	16	16	63

3. Kinetic derivation

3.1. HMF conversion to FFCA

HMF conversion to FFCA kinetic expression is derived based on the following mechanism:

$$\mathrm{Ni(OH)_2 + OH^- \underset{k_{-1}}{\overset{k_1}{\leftrightharpoons}} NiOOH + H_2O + e^-} \tag{1}$$

$$\mathrm{NiOOH + HMF \underset{k_{-2}}{\overset{k_2}{\leftrightharpoons}} HMF_s} \tag{2}$$

$$\mathrm{HMF_s \overset{k_3}{\rightarrow} I_s} \tag{3}$$

$$\mathrm{I_s + 3OH^- \overset{k_4}{\rightarrow} FFCA_s + 2H_2O + 3e^-} \tag{4}$$

$$\mathrm{FFCA_s \underset{k_{-5}}{\overset{k_5}{\leftrightharpoons}} FFCA + Ni(OH)_2} \tag{5}$$

Kinetic rate expression of HMF oxidation to FFCA was derived based on the above mechanism. The rate equations of reactions 1 to 5 are:

$$r_1 = (k_1\theta_1 C_{OH^-} - k_{-1}\theta_2)\phi_s \tag{6}$$

$$r_2 = (k_2\theta_2 C_{HMF} - k_{-2}\theta_3)\phi_s \tag{7}$$

$$r_3 = (k_3\theta_3)\phi_s \tag{8}$$

$$r_4 = (k_4\theta_4 C_{OH^-}^3)\phi_s \tag{9}$$

$$r_5 = (k_5\theta_5)\phi_s \tag{10}$$

where θ_1 to θ_5 are the surface coverage by Ni(OH)$_2$, NiOOH, HMF$_s$, I$_s$ and FFCA$_s$, respectively, and ϕ_s is the electrocatalyst saturated surface concentration. The site- and material- balance equations are:

$$\sum_{i=1}^{5} \theta_i = 1 \tag{11}$$

$$\phi_s \frac{d\theta_1}{dt} = -r_2 + r_6 \tag{12}$$

$$\phi_s \frac{d\theta_i}{dt} = -r_i + r_{i-1} \quad (\text{for } i = 3 \text{ to } 6) \tag{13}$$

With a quasi-steady-state approximation ($d\theta_i/dt = 0$) and from equations 6 to 13, the expressions of θ_1 to θ_5, and therefore the reaction rate expression can be derived:

$$r_{HMF} = \frac{I}{FA} = r_1 = \cdots = r_5 = \tag{14}$$

$$\frac{\phi_s C_{HMF}}{\left(\frac{1}{k_2} + \frac{1}{k_2 K_1 C_{OH^-}} + \frac{1}{k_3 K_2} + \frac{1}{k_3 K_1 K_2 C_{OH^-}}\right) + \left(\frac{1}{k_1 C_{OH^-}} + \frac{1}{k_3} + \frac{1}{k_4 C_{OH^-}^3} + \frac{1}{k_5}\right) C_{HMF}}$$

By lumping the kinetic parameters, equation 14 can be simplified to:

$$r_{HMF} = I/FA = \frac{k_1^{HMF} C_{HMF}}{1 + k_2^{HMF} C_{HMF}} \tag{15}$$

3.2. FFCA conversion to FDCA

Taking the same approach, FFCA to FDCA rate expression can be obtained:

$$NiOOH + FFCA \underset{k_{-2}}{\overset{k_2}{\leftrightharpoons}} FFCA_s \tag{16}$$

$$FFCA_s \overset{k_3}{\rightarrow} I_{s1} \tag{17}$$

$$I_{s1} + OH^- \overset{k_4}{\rightarrow} FDCA_s + e^- \tag{18}$$

$$FFCA_s \underset{k_{-5}}{\overset{k_5}{\leftrightharpoons}} FDCA + Ni(OH)_2 \tag{19}$$

Kinetic rate expression of FFCA oxidation to FDCA was derived based on the above mechanism. The rate equations of reactions 1 and 16 to 19 are:

$$r_1 = (k_1\theta_1 C_{OH^-} - k_{-1}\theta_2)\phi_s \tag{20}$$

$$r_2 = (k_2\theta_2 C_{FFCA} - k_{-2}\theta_3)\phi_s \tag{21}$$

$$r_3 = (k_3\theta_3)\phi_s \tag{22}$$

$$r_4 = (k_4\theta_4 C_{OH^-})\phi_s \tag{23}$$

$$r_5 = (k_5\theta_5)\phi_s \tag{24}$$

where θ_1 to θ_5 are the surface coverage by $Ni(OH)_2$, NiOOH, $FFCA_s$, I_{s1} and $FDCA_s$, respectively, and ϕ_s is the electrocatalyst saturated surface concentration. The site- and material- balance equations are:

$$\sum_{i=1}^{5} \theta_i = 1 \tag{25}$$

$$\phi_s \frac{d\theta_1}{dt} = -r_2 + r_6 \tag{26}$$

$$\phi_s \frac{d\theta_i}{dt} = -r_i + r_{i-1} \quad (\text{for } i = 3 \text{ to } 6) \tag{27}$$

With a quasi-steady-state approximation ($d\theta_i/dt = 0$) and from equations 20 to 27, the expressions of θ_1 to θ_5, and therefore the reaction rate expression can be derived:

$$r_{FF\,CA} = \frac{I}{FA} = r_1 = \cdots = r_5 = \tag{28}$$

$$\frac{\phi_s C_{FFCA}}{\left(\frac{1}{k_2} + \frac{1}{k_2 K_1 C_{OH^-}} + \frac{1}{k_3 K_2} + \frac{1}{k_3 K_1 K_2 C_{OH^-}}\right) + \left(\frac{1}{k_1 C_{OH^-}} + \frac{1}{k_3} + \frac{1}{k_4 C_{OH^-}} + \frac{1}{k_5}\right) C_{FFCA}}$$

By lumping the kinetic parameters, equation 28 can be simplified to:

$$r_{FFCA} = I/FA = \frac{k_1^{FFCA} C_{FFCA}}{1 + k_2^{FFCA} C_{FFCA}} \tag{29}$$