

Table S1. When assuming that the coulombic efficiency of the carboxylic acid is 100%, the amount of charge that needs to be transferred over time (Q_t) for the reactions of *n*-caproic acid at different concentrations using eqn (4-6). The FE was set with the range of 0.25 to 1.00.

Concentration (mM)	Q_t (C)			
	0.25 FE	0.50 FE	0.75 FE	1.00 FE
50	120.6	241.2	361.8	482.4
100	241.2	482.5	723.6	964.9
200	482.4	964.9	1447.3	1929.7
300	723.7	1447.3	2171.1	2894.6
400	964.9	1929.7	2894.6	3859.4
500	1206.1	2412.2	3618.3	4824.3
600	1447.3	2894.6	4331.9	5789.1
700	1688.5	3377.0	5065.5	6754.0
800	1929.7	3859.4	5789.1	7718.8
1000	2412.1	4824.3	7236.4	9648.5
1500	3618.2	7236.4	10854.6	14472.8

Table S2. Coulombic efficiency (CE) on different faraday equivalent (FE) and various concentrations of *n*-caproic acid for the Kolbe electrolysis reaction.

Parameters	Concentrations (mM)								
	50	100	200	300	400	500	600	700	800
0.25 FE	61.95%	72.17%	71.70%	81.61%	88.54%	73.92%	84.65%	96.82%	66.70%
0.50 FE	46.74%	52.88%	58.81%	63.43%	63.44%	61.83%	65.46%	64.41%	70.89%
0.75 FE	44.82%	48.87%	50.92%	46.43%	50.75%	44.71%	49.51%	60.55%	58.56%
1.00 FE	41.92%	36.87%	30.21%	45.12%	38.94%	25.62%	35.26%	45.95%	30.83%
Average FE	51.14%	52.70%	52.91%	59.15%	60.42%	50.51%	58.72%	66.93%	56.75%

Table S3. Experimental data of 800 mM *n*-caproic acid at different pH values after 1.00 FE electrolysis (n ≥ 3).

Parameters	pH values		
	5.86	6.92	9.60
Input charge number (cc)	7718.8		
Electrolysis time (s)	36376	28825	27506
Electric energy consumption (Wh)	7.51		
<i>iR</i> (V)	0.65	0.73	0.74
<i>n</i> -Decane production (mg)	2948.76	2905.02	2381.25
The amount of <i>n</i> -decane produced per unit of electric energy (g kWh ⁻¹)	392.64	386.82	317.01
<i>S</i> _{decane} (%)	45.85	45.85	38.31
FEff (%)	51.9	51.2	41.9
CE (%)	69.30	68.20	66.85
Total amount of generated gas (mL)	1646.63	1737.11	1074.35
H ₂ (mL, %)	932.8 (56.65%)	1081.52 (62.24%)	746.6 (69.48%)
O ₂ (mL, %)	16.50 (1.05%)	15.88 (0.91%)	27.19 (2.53%)
CO ₂ (mL, %)	374.98 (22.77%)	272.10 (15.66%)	96.83 (12.97%)