Supplementary Information (SI) for Catalysis Science & Technology.

Supporting Information

OH^- dependence for the electrocatalytic decarboxylation of medium-chain fatty acid into hydrocarbons on Pt and carbon electrode

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S1. Supporting Graphs

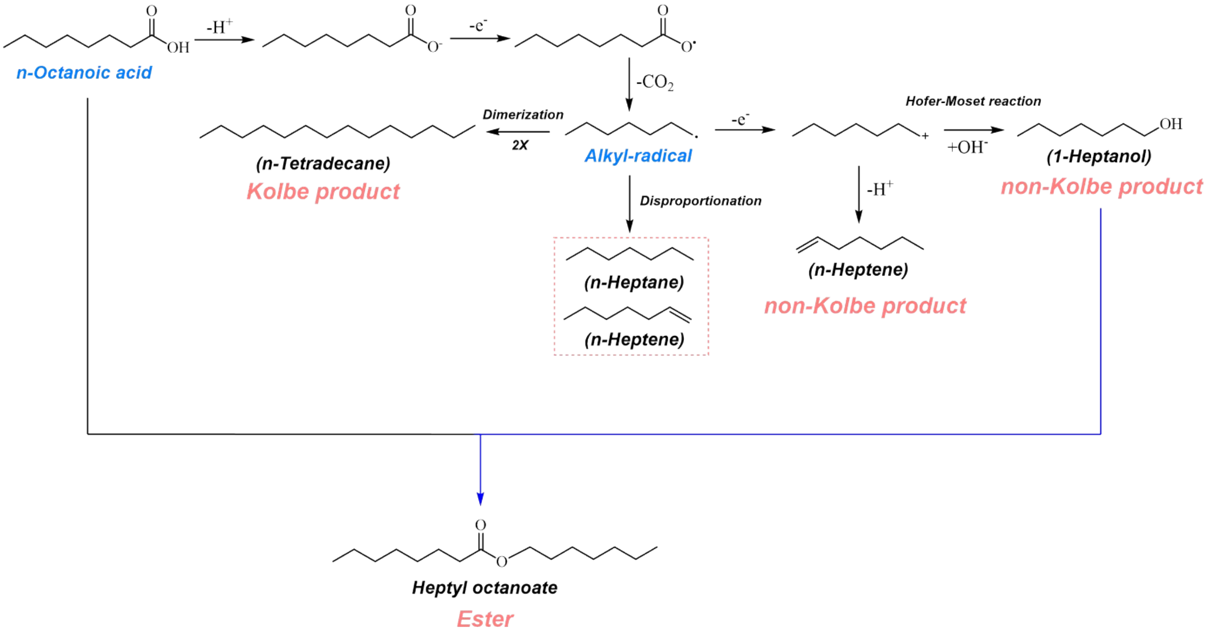

Fig. S1. Reaction mechanism for the formation of Kolbe products, non-Kolbe products and esters of electrochemical decarboxylation of n-Octanoic acid.

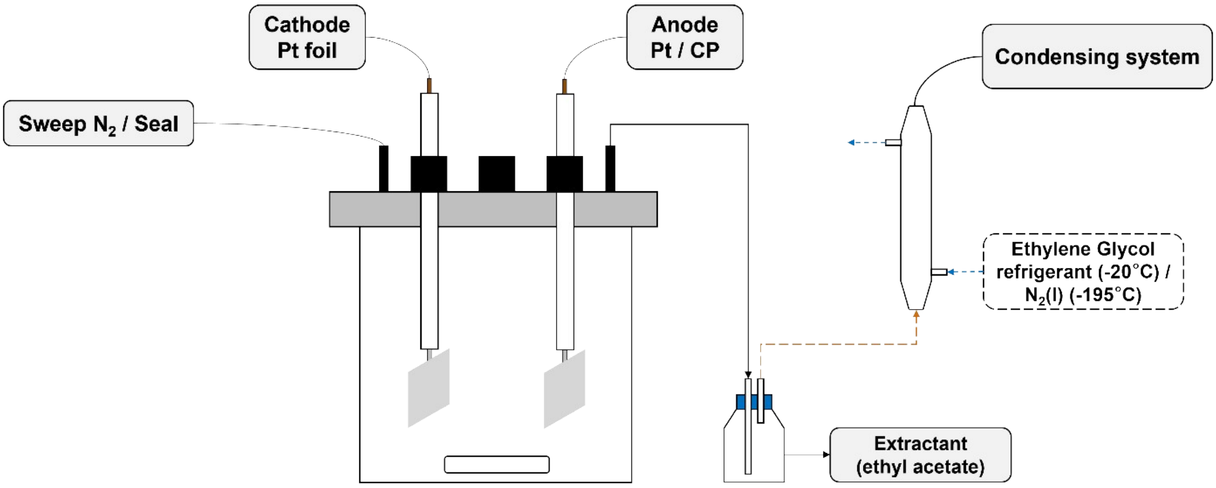

Fig. S2. Schematic diagram of electrocatalytic conversion and condensation reflux of n-Octanoic acid on anode in aqueous solution.

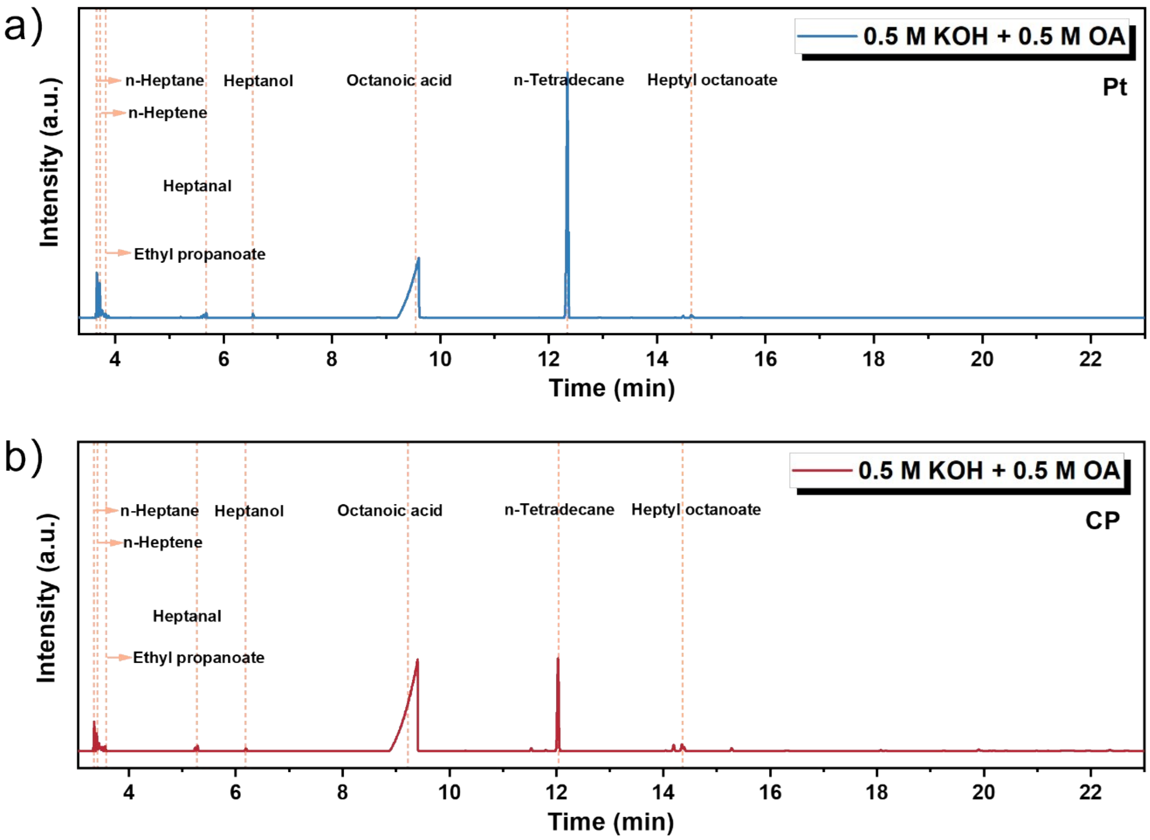

Fig. S3. GC chromatograms of the products of OA ECDX on a) Pt, and b) CP electrodes (Reactions were performed at constant-voltage 10 V for 1 h in the 0.5 M KOH + 0.5 M OA).

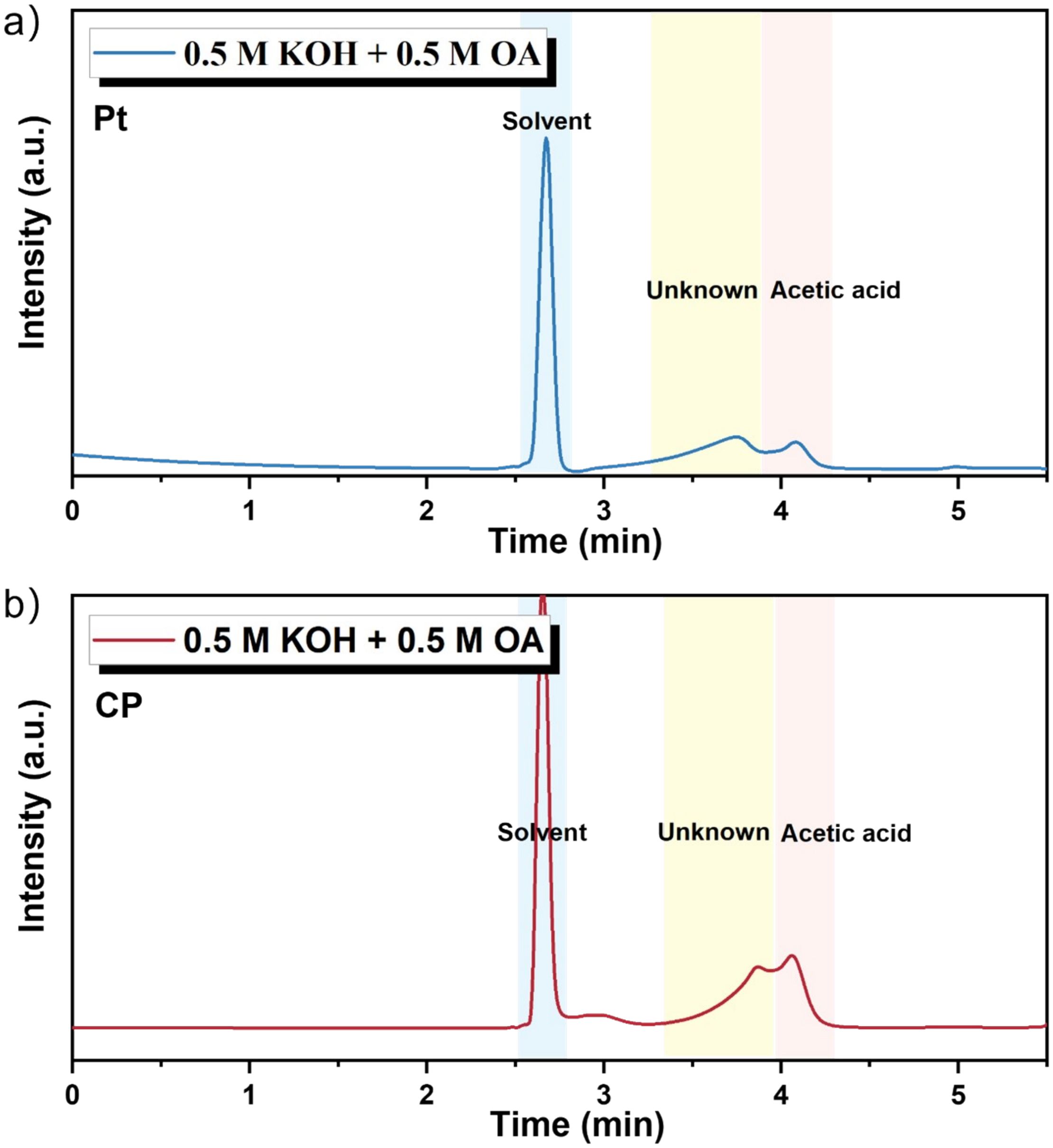

Fig. S4. HPLC chromatograms of OA ECDX on a) Pt, and b) CP electrodes (Reactions were performed at constant-voltage 10 V for 1 h in the 0.5 M KOH + 0.5 M OA).

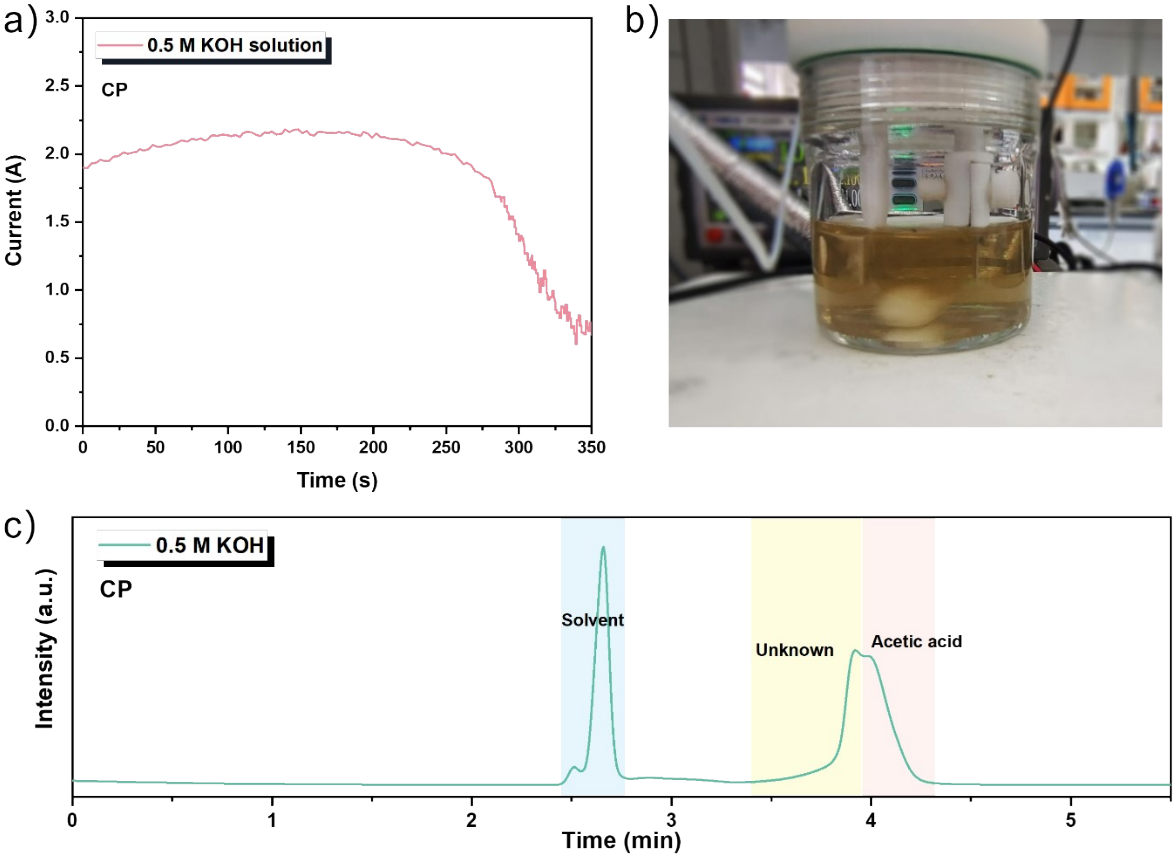

Fig. S5. a) The current – time curve of electrolysis on CP electrode in 0.5 M KOH solution at a voltage of 10 V, b) the color of electrolyte, and b) HPLC chromatogram after electrolysis on the CP electrode in 0.5 M KOH solution at a voltage of 10 V.

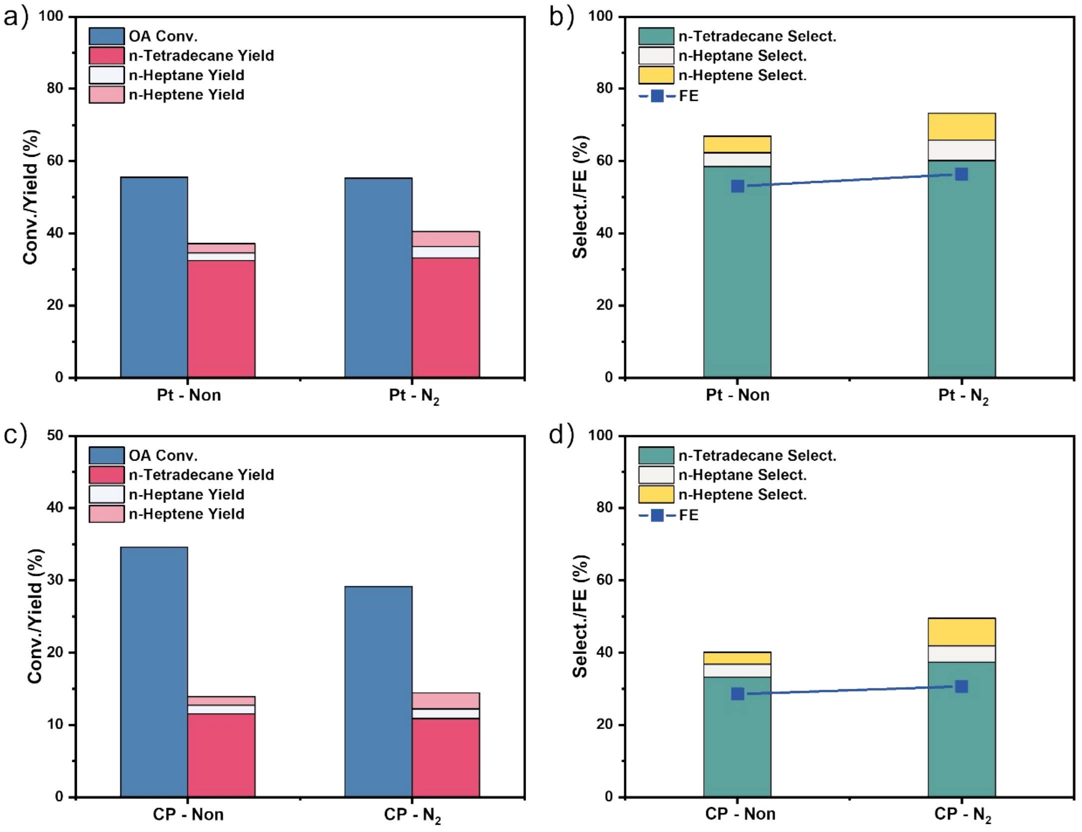

Fig. S6. a, c) Conversion of OA and yield of hydrocarbons; and b, d) selectivity and FE of hydrocarbons produced by OA ECDX for 60 min over Pt electrode and CP electrode at a voltage of 10 V with and without nitrogen purging. Reaction conditions: 30 mL of 0.5 M KOH + 0.5 M OA (pH 13.1) at room temperature.

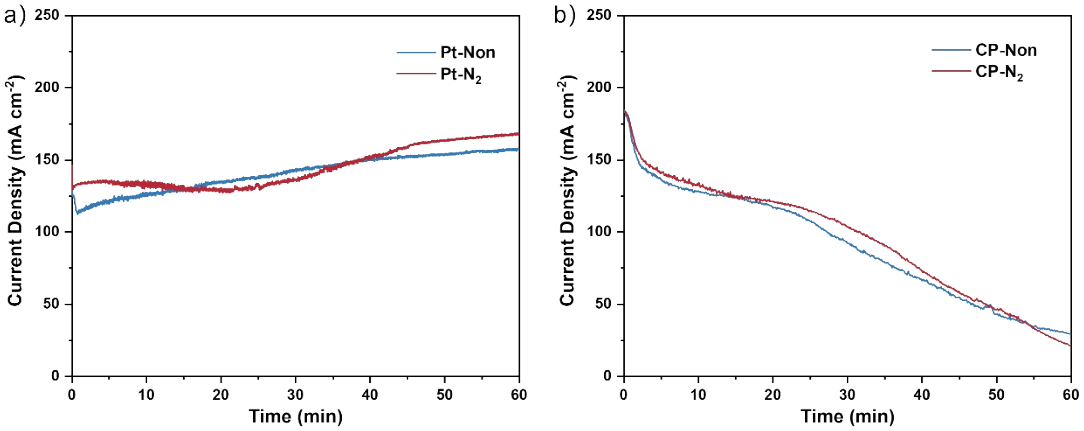

Fig. S7. a, b) The current density – time curves of OA ECDX for 60 min over Pt electrode and CP electrode at a voltage of 10 V with and without nitrogen purging. Reaction conditions: 30 mL of 0.5 M KOH + 0.5 M OA (pH 13.1) at room temperature.

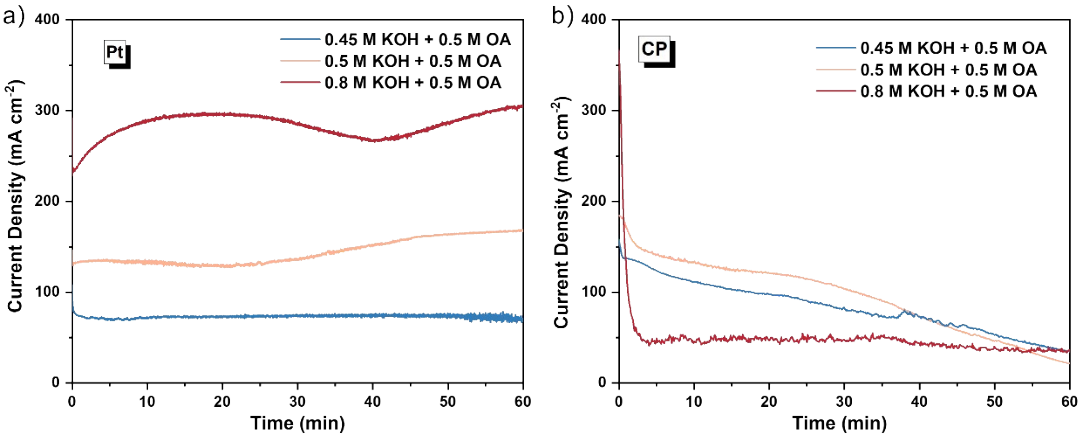

Fig. S8. a, b) The current density – time curves of OA ECDX for 60 min over Pt electrode and CP electrode at a voltage of 10 V in various concentrations of KOH (0.45 M, 0.5 M, and 0.8 M, respectively) + 0.5 M OA with nitrogen purging. Reaction conditions: 30 mL of 0.45 M KOH + 0.5 M OA, 0.5 M KOH + 0.5 M OA, and 0.8 M KOH + 0.5 M OA, respectively (pH 8, 13.1, and 13.9, respectively) at room temperature.

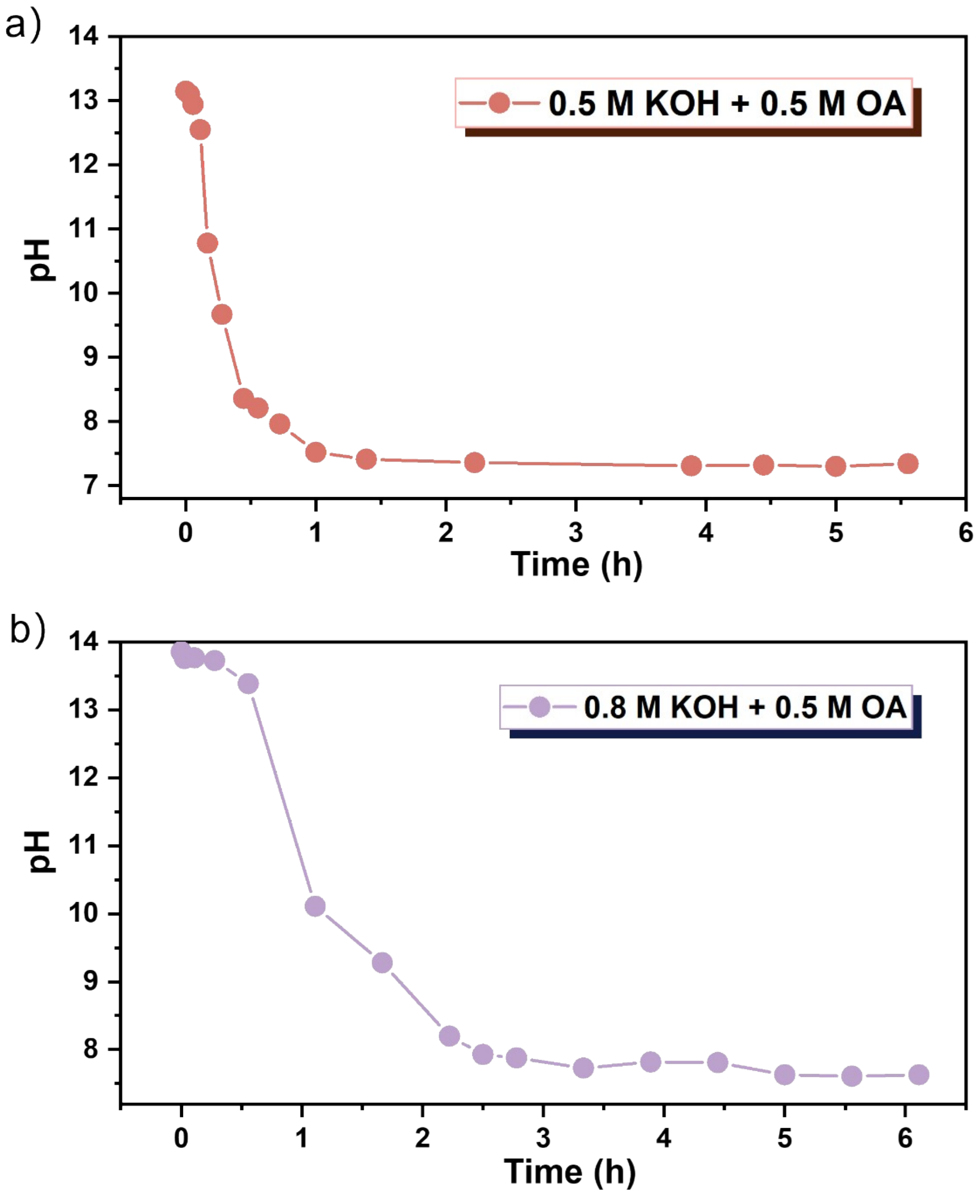

Fig. S9. The CO_2 saturation experiments of the curves of pH value - time in two kinds of electrolytes: a) 0.5 M KOH + 0.5 M OA, b) 0.8 M KOH + 0.5 M OA. Condition: CO_2 flow rate is 3 mL/min (Determine the amount of flowing CO_2 by assuming that all CO_2 is produced by decarboxylation or oxidation of the transformed-OA, the detailed calculation formulas can be found in paper).

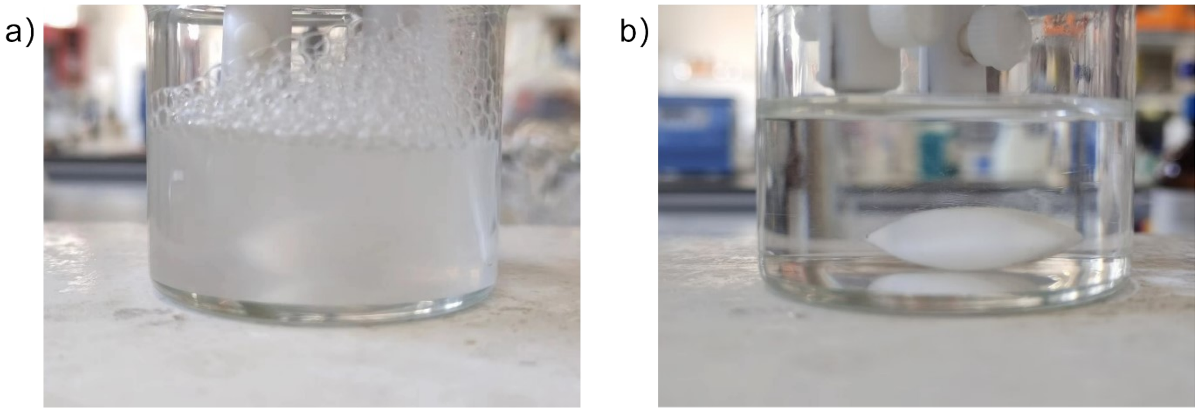

Fig. S10. a) The phenomenon of potassium octanoate precipitated was observed from the CO_2 saturation experiment, b) the clearing of the electrolyte when ceasing the CO_2 flow. Condition: CO_2 flow rate is 3 mL/min.

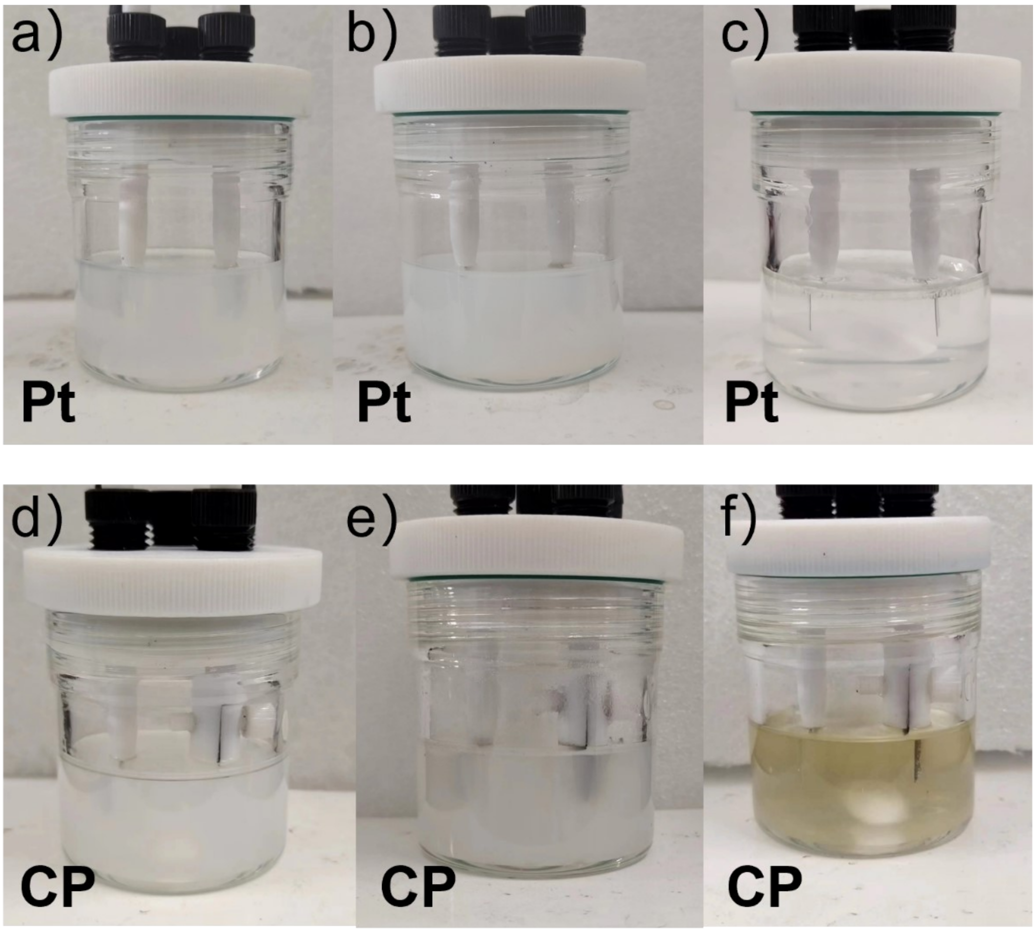

Fig. S11. The states of different electrolytes when the reaction stops: a, d) 0.45 M KOH + 0.5 M OA; b, e) 0.5 M KOH + 0.5 M OA; c, f) 0.8 M KOH + 0.5 M OA. Condition: 30 mL electrolyte reacts for 60 min at constant-voltage 10 V.

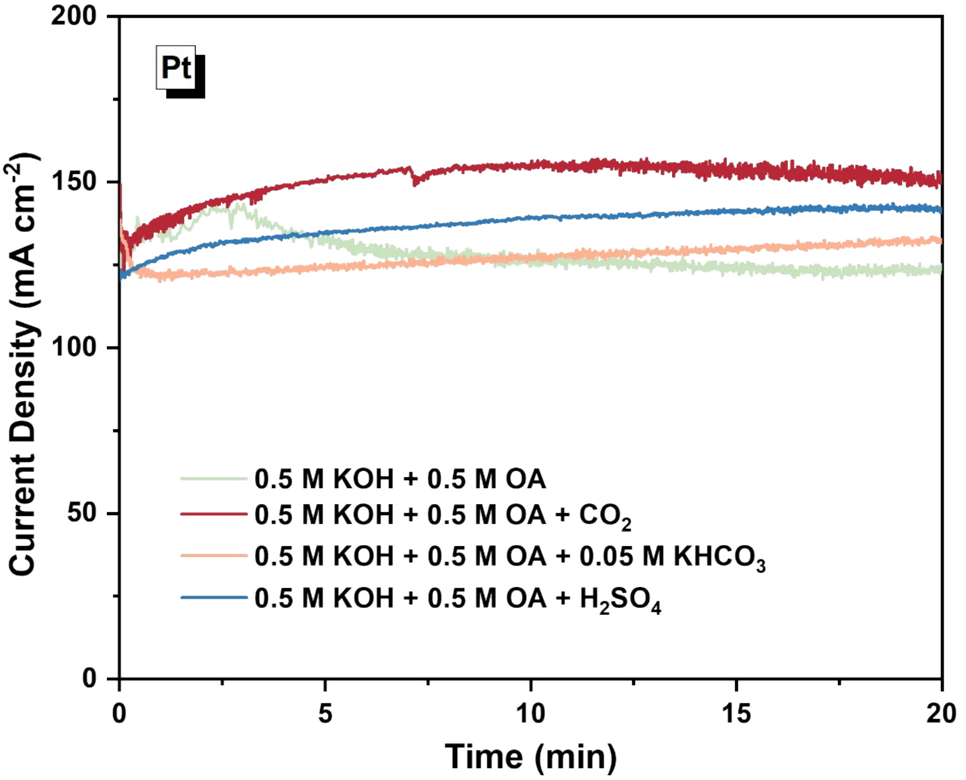

Fig. S12. Current density – time curves of OA ECDX for 20 min over Pt electrode at a voltage of 10 V with nitrogen purging.

S2. Supporting Tables

Table S1. Comparison of the effects of two condensation methods on the collection of volatile organic compounds from OA ECDX on carbon paper at a voltage of 8 V for 20 min. Reaction conditions: 30 mL of 0.5 M KOH + 0.5M OA (pH 13.1) at room temperature.

Method	**Conv. %**	**Yield %**			**Select. %**		
		n-Tetradecane	n-Heptane	1-Heptene	n-Tetradecane	n-Heptane	1-Heptene
Ethylene Glycol refrigerant(l)	25.29	5.10	0.71	1.13	20.18	2.82	4.48
N_2(l)	24.87	5.28	0.72	1.23	21.24	2.90	4.96

Table S2. The final pH of OA ECDX were measured at 20 min, 40 min, 60 min and 90 min over Pt and CP, and the initial pH of the electrolyte was measured at 13.1 (0.5 M OA + 0.5 M KOH).

Final pH	**20 min**	**40 min**	**60 min**	**90 min**
Pt	10.52	10.28	10.24	9.84
CP	10.16	9.93	9.86	9.71

Table S3. The quantity of electric charge of OA ECDX for 20 min, 40 min, 60 min and 90 min over Pt and CP.

Q (C) / Anodes	**20 min**	**40 min**	**60 min**	**90 min**
Pt	307.88	742.87	1039.02	1768.05
CP	341.10	564.66	681.80	569.36

Table S4. Onset potential, Tafel slope, and overpotential at 1 mA cm^{-2} obtained from linear sweep voltammetry tests conducted in different concentrations of KOH (0.45 M, 0.5 M, 0.8 M) solution with and without 0.5 M of n-Octanoic acid.

	C_{KOH}	OER E_{onset} [V vs. RHE]	OER Tafel slope [mV dec^{-1}]	Mixed reaction Tafel slope [mV dec^{-1}]	OER Eapplied @10 mA cm^{-2} [V vs. RHE]	Mixed reaction $E_{applied}$ @1mA cm^{-2} [V vs. RHE]
	0.45 M	1.505	47	367	1.670	2.928
Pt	0.5 M	1.516	48	168	1.672	2.708
	0.8 M	1.593	46	51	1.689	1.755
	0.45 M	1.536	173	130	2.047	2.145
CP	0.5 M	1.551	151	306	1.902	2.468
	0.8 M	1.559	95	246	1.740	1.998

Table S5. The initial pH four different electrolytes were measured at the beginning and the final pH of electrolytes were measured after reaction on Pt for 20 min at a voltage of 10 V.

pH	**0.5 M KOH + 0.5 M OA**	**0.5 M KOH + 0.5 M OA + CO_2**	**0.5 M KOH + 0.5 M OA + 0.05 M $KHCO_3$**	**0.5 M KOH + 0.5 M OA + H_2SO_4**
Initial	13.1	10.4	10.3	10.3
Final	10.5	10.1	10.1	10.2

Video S1. Video for monitoring the electrocatalytic decarboxylation reaction process of OA. Reaction conditions： 30 mL of 0.5 M OA + 0.5 M KOH (pH 13.1) at a voltage of 10 V.