

ChemElectroChem

Supporting Information

Paired and Tandem Electrochemical Conversion of 5-(Hydroxymethyl)furfural Using Membrane-Electrode Assembly-Based Electrolytic Systems

Hengzhou Liu, Ting-Han Lee, Yifu Chen, Eric W. Cochran,* and Wenzhen Li*

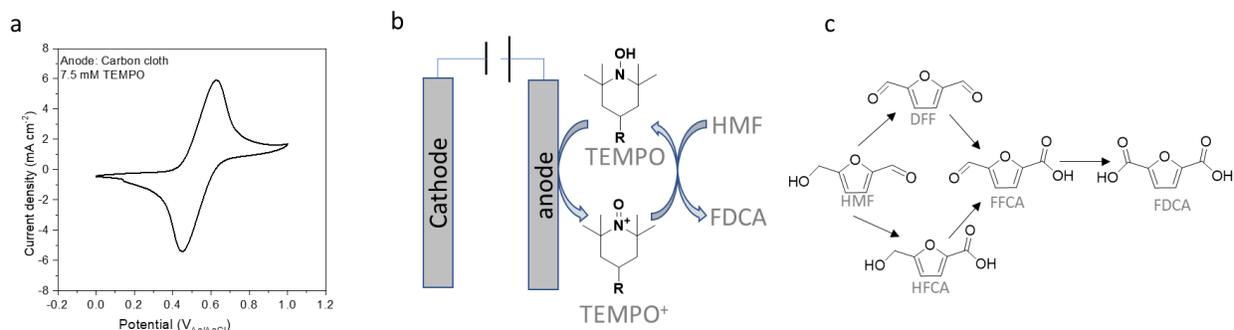


Figure S1. (a) Cyclic voltammograms of redox behavior of TEMPO in the H-type cell with three-electrode configuration. The scan rate was 20 mV s^{-1} . The working electrode, reference electrode, and counter electrode are hydrophilic carbon cloth, Ag/AgCl electrode, and Pt foil, respectively. The concentration of TEMPO is 7.5 mM. (b) Schematic illustration of TEMPO-mediated HMF oxidation. (c) Reaction pathways for HMF-to-FDCA reaction.

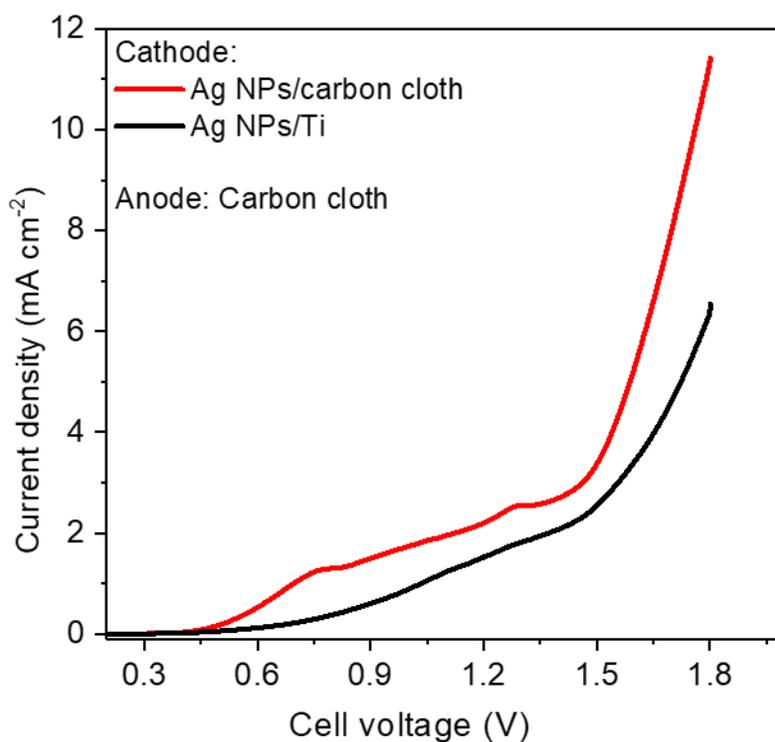


Figure S2. Linear sweep voltammograms of ECH-ECO paired electrolysis on different cathode substrates (carbon cloth and Ti felt) with a scan rate of 5 mV s^{-1} . The loading of Ag NPs was $\sim 1.0 \text{ mg}_{\text{Ag}} \text{ cm}^{-2}$, and hydrophilic carbon cloth was used as the anode. The catholyte was 20 ml of 0.5 M borate buffer (pH 9.2) with 20 mM HMF, and the anolyte was 20 ml of 0.5 M borate buffer (pH 9.2) with 10 mM HMF and 7.5 mM TEMPO.

a



b

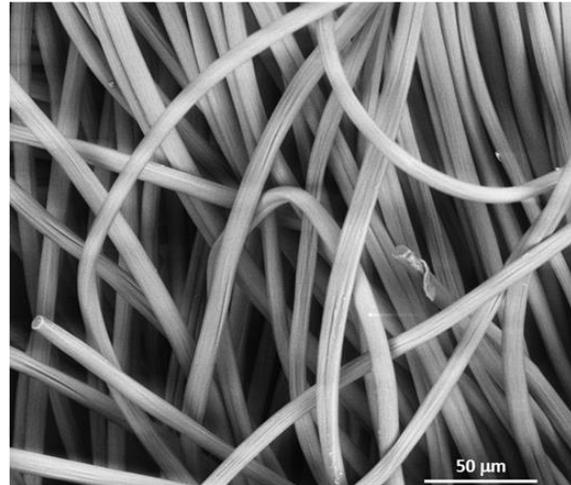


Figure S3. SEM images of (a) Ti felt and (b) plain carbon cloth.

Table S1. Results of ECH-ECO paired electrolysis for 24 hours with different membranes. ^a

Configuration	Resistance (Ω)	Energy efficiency (%)	Selectivity of ECH products in anolyte (%) ^b	Selectivity of ECO products in catholyte (%) ^b
AEM	1.4	19.0	2% BHH, 0.5% BHMF	2.6% FDCA, 5.5% HFCA, 5.6% FFCA
CEM	0.8	19.2	0	0
BPM	3.9	16.5	0	0

a. The catholyte was 100 ml of 0.5 M borate buffer (pH 9.2) with 50 mM HMF, and the anolyte was 100 ml of 0.5 M borate buffer (pH 9.2) with 13 mM HMF and 7.5 mM TEMPO. The cathode was Ag NPs/CC ($\sim 1.0 \text{ mg}_{\text{Ag}} \text{ cm}^{-2}$), and the anode was hydrophilic carbon cloth.

b. The detection of ECH products in anolyte and ECO products in catholyte for the AEM-based system was due to the crossover of species through the membrane.

Table S2. ECH results of the 24-hour paired electrolysis.

Configuration	Conversion (%)	BHMF selectivity (%)	BHMF FE (%)	BHH selectivity (%)	BHH FE (%)
AEM	61.3	73.8	50.2	17.9	6.1
CEM	64.1	75.5	54.3	12.2	4.3
BPM	63.3	70.4	47.5	18.4	6.4

Table S3. ECO results of the 24-hour paired electrolysis.

Configuration	Conversion (%)	FDCA selectivity (%)	FDCA FE (%)
AEM	100	83.0	72.5
CEM	100	98.3	86.3
BPM	100	96.5	83.3

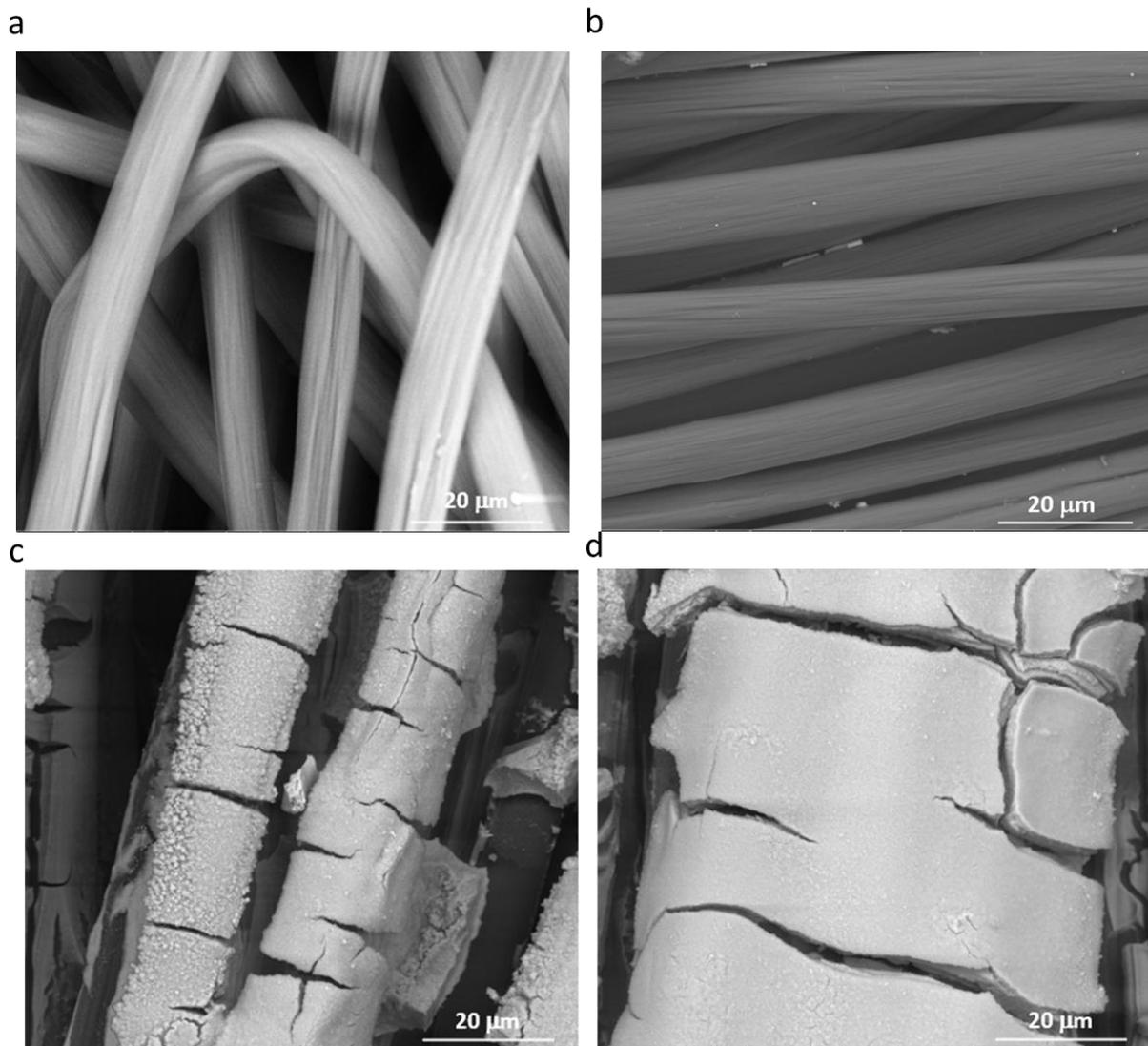


Figure S4. SEM images of (a) plain carbon cloth, (b) HNO₃-pretreated carbon cloth, and (c)–(d) electrodeposited NiFe oxide on HNO₃-treated carbon cloth.

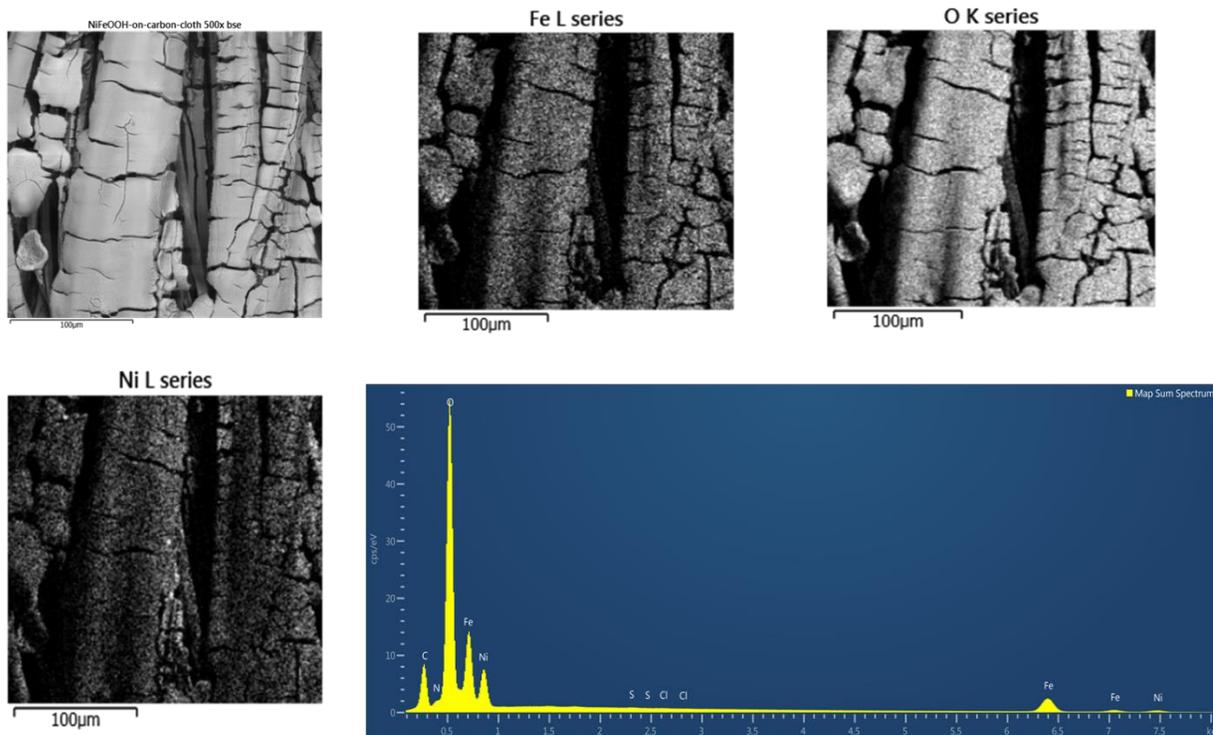


Figure S5. SEM image and the elemental mapping of Fe, Ni, and O with EDS analysis for the as-prepared NiFe/CC.

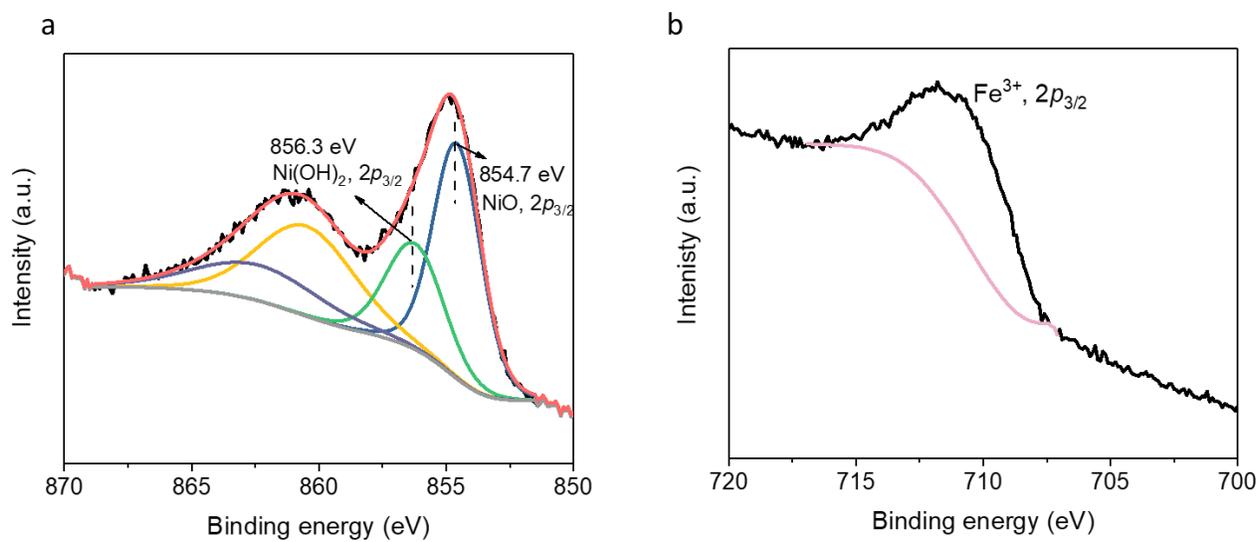


Figure S6. XPS (a) Ni $2p_{3/2}$ and (b) Fe $2p_{3/2}$ spectra of NiFe/CC.

Table S4. ECO results of HMF on NiFe/CC in the H-type cell.^a

Conversion (%)	FDCA selectivity (%)	FDCA FE (%)	HFCA selectivity (%)	HFCA FE (%)	FFCA selectivity (%)	FFCA FE (%)
97.0	95.1	81.5	1.6	0.5	4.1	2.3

- a. ECO of HMF was performed in 20 ml of 0.1 M KOH with 10 mM HMF at 10 mA. The geometric area of NiFe/CC was 2 cm², and the applied charge was 136 C. The theoretical charge required for 100% conversion of HMF to FDCA was 116 C ($0.01 \text{ M} \times 0.02 \text{ L} \times 6 \times 96485 \text{ C mol}^{-1} = 116 \text{ C}$).

Table S5. Results of ECH-ECO paired electrolysis in the pH-asymmetric configurations.^a

Configuration	Resistance (Ω)	Selectivity of ECH products in anolyte (%)	Selectivity of ECO products in catholyte (%)
CEM	0.57	0 ^b	0 ^b
BPM	1.30	0	0

- a. The catholyte was 50 ml of 0.5 M borate buffer (pH 9.2) with 50 mM HMF, and the anolyte was 20 ml of 0.1 M KOH with 10 mM HMF. The cathode was Ag NPs/CC ($\sim 1.0 \text{ mg}_{\text{Ag}} \text{ cm}^{-2}$), and the anode was NiFe/CC. The electrolysis was performed at 2 mA cm^{-2} for 4 h.
- b. No crossover of products was detected for the CEM and BPM-based systems.

Table S6. ECH results of the pH-asymmetric paired electrolysis for 4 h.

Membrane	Conversion (%)	BHMF selectivity (%)	BHMF FE (%)	BHH selectivity (%)	BHH FE (%)
CEM	19.2	75.5	46.1	23.4	7.6
BPM	17.7	71.5	42.4	20.2	6.0

Table S7. ECO results of the pH-asymmetric paired electrolysis for 4 h.

Membrane	Conversion (%)	FDCA selectivity (%)	FDCA FE (%)
CEM	100	96.8	80.1
BPM	100	96.1	77.3

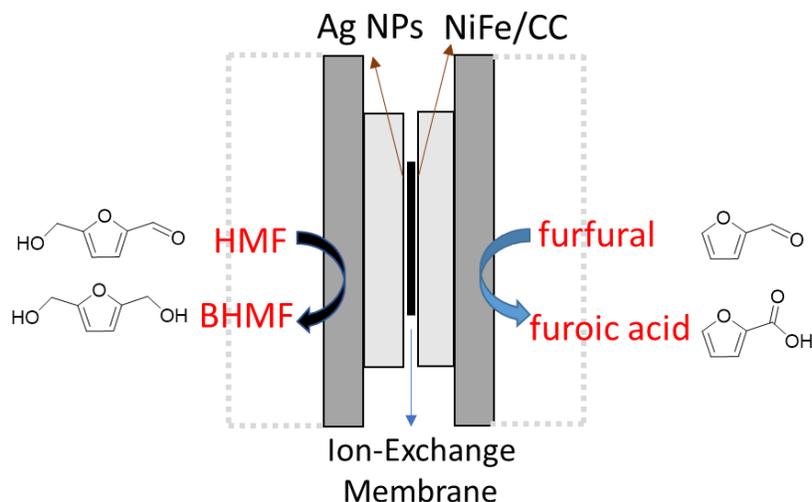


Figure S7. Schematic illustration of the HMF-furfural paired electrolysis in a BPM-based flow electrolyzer. The catholyte was 30 ml of 0.5 M borate buffer (pH 9.2) with 50 mM HMF, and the anolyte was 40 ml of 0.1 M KOH with 10 mM furfural. The cathode was Ag NPs/CC ($\sim 1.0 \text{ mg}_{\text{Ag}} \text{ cm}^{-2}$), and the anode was NiFe/CC. The electrolysis was performed 2 mA cm^{-2} for 3 h (corresponding to 108 C of applied charge). The theoretical charge required for 100% conversion of furfural to 2-furoic acid was 77.2 C ($0.01 \text{ M} \times 0.04 \text{ L} \times 2 \times 96485 \text{ C mol}^{-1} = 77.2 \text{ C}$).

Table S8. ECH results of HMF-furfural paired electrolysis in the pH-asymmetric configuration.

Conversion (%)	BHMF selectivity (%)	BHMF FE (%)	BHH selectivity (%)	BHH FE (%)
29.4	68.2	54.0	12.2	8.0

Table S9. ECO results of HMF-furfural paired electrolysis in the pH-asymmetric configuration.

Conversion (%)	2-furoic acid selectivity (%)	2-furoic acid FE (%)
99.3	95.0	70.5

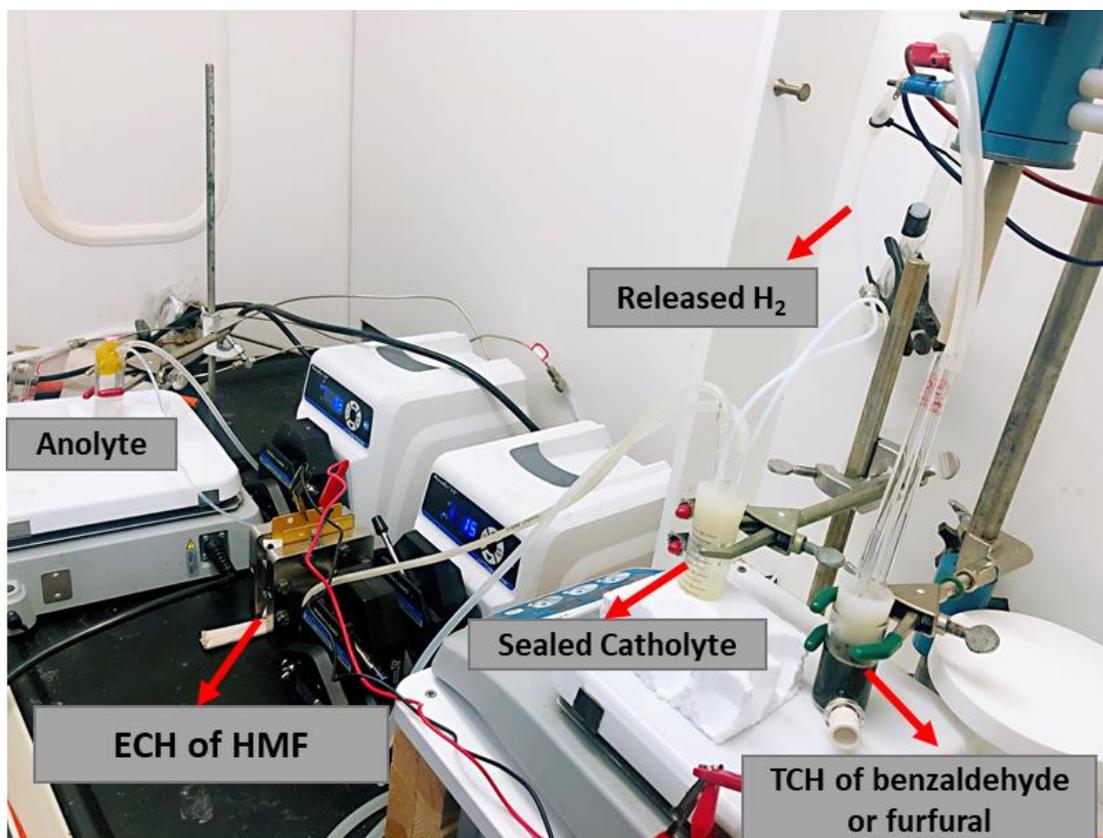


Figure S8. Photograph of the tandem electrocatalytic-catalytic system, including an MEA-based flow electrolyzer, the catholyte and anolyte vessels, and a batch reactor for thermocatalytic hydrogenation (TCH) of benzaldehyde or furfural. Electrocatalytic hydrogenation (ECH) of HMF was performed in the MEA-based electrolyzer.