

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

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Pairing the electrocatalytic hydrogenation (ECH) reaction with different anodic reactions holds great promise for producing value-added chemicals driven by renewable energy sources. Replacing the sluggish water oxidation with a bio-based upgrading reaction can reduce the overall energy cost and allows for the simultaneous generation of high-value products at both electrodes. Herein, we developed a membrane-electrode assembly (MEA)-based electrolysis system for the conversion of 5-(hydroxymethyl)furfural (HMF) to bis(hydroxymethyl)furan (BHMF) and 2,5-furandicarboxylic acid (FDCA). With (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)-mediated electrochemical oxidation (ECO) of HMF at the anode, the unique zero-gap configuration enabled a minimal cell voltage of 1.5 V at 10 mA, which was stable during a 24-hour period of continuous electrolysis, resulting in a combined

faradaic efficiency (FE) as high as 139% to BHMF and FDCA. High FE was also obtained in a pH-asymmetric mediator-free configuration, in which the ECO was carried out in 0.1 M KOH with an electrodeposited NiFe oxide catalyst and a bipolar membrane. Taking advantage of the low cell resistance of the MEA-based system, we also explored ECH of HMF at high current density (280 mA cm<sup>-2</sup>), in which a FE of 24% towards BHMF was achieved. The co-generated H<sub>2</sub> was supplied into a batch reactor in tandem for the catalytic hydrogenation of furfural or benzaldehyde under ambient conditions, resulting in an additional 7.3% of indirect FE in a single-pass operation. The co-electrolysis of bio-derived molecules and the tandem electrocatalytic-catalytic process provide sustainable avenues towards distributed, flexible, and energy-efficient routes for the synthesis of valuable chemicals.

## 1. Introduction

Electrocatalytic refinery of bio-derived feedstocks is emerging as a sustainable and environmentally-friendly method for producing high-value chemicals.<sup>[1]</sup> Compared to thermocatalytic processes in which energy is typically harvested from oxidants and reductants at elevated temperature and pressure, electrochemical reactions driven by the applied potential can be performed under significantly milder conditions. In many circumstances, such as the electrocatalytic hydrogenation (ECH), the half-reaction of interest is paired with the oxygen evolution reaction (OER,  $E^0 = 1.229$  V), which turns out to consume a large portion of electrical energy due to its sluggishness.<sup>[2]</sup> Coupling ECH with the electrochemical oxidation (ECO) of bio-derived molecules enables the simultaneous generation of valuable chemicals at both electrodes while enhancing the overall energy efficiency.<sup>[3]</sup>


Some intriguing paired electrolytic systems have been demonstrated in recent years, including CO<sub>2</sub> reduction-based<sup>[3b,4]</sup> and organic transformation-based<sup>[5]</sup> reactions. In theory, a 200% maximum faradaic efficiency (FE) to desired

products can be obtained. Of particular research interest is the paired electrolysis of 5-hydroxymethylfurfural (HMF), a bio-derived C<sub>6</sub> platform molecule, to produce 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-furandicarboxylic acid (FDCA) with high added value (*e.g.*, in foundry and polymer industries).<sup>[6]</sup>

In the past few years, research efforts have been devoted to exploring different electrocatalysts and/or processes, which have led to fundamental mechanistic understandings of ECH and ECO.<sup>[7]</sup> The typically-used H-type cell for performance evaluation, however, suffers from the high resistance and limited transport of reactants and products.<sup>[8]</sup> In this regard, continuous operation in a flow reactor with a compact membrane-electrode assembly (MEA) structure can greatly reduce the ohmic loss and thus improve the energy efficiency.<sup>[9]</sup> Moreover, the enhanced mass transport in the MEA-based flow electrolyzer allows for electrochemical transformations at much higher current density (*i.e.*, hundreds of mA cm<sup>-2</sup>) as compared to the H-type cell, which would be highly desirable for scale-up studies under commercially-relevant conditions.<sup>[4b,5a, c, 10]</sup>

In this work, we developed an MEA-based flow electrolyzer for paired electrolysis of HMF with Ag-catalyzed ECH at the cathode and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)-mediated ECO at the anode. The ECH-ECO configuration features a minimal cell voltage (1.5 V at 10 mA), which was stable for 24 hours of electrolysis. A combined FE as high as 139% towards BHMF and FDCA was achieved. Furthermore, similarly high FE was obtained in a pH-asymmetric mediator-free configuration, in which the ECO was catalyzed by an

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electrodeposited NiFe oxide in 0.1 M KOH. Finally, ECH at high current density ( $280 \text{ mA cm}^{-2}$ ) was performed in the MEA-based electrolyzer. Besides the 24% FE of the direct ECH product (BHMF) at the electrode, the co-generated  $\text{H}_2$  was supplied to a batch reactor for the catalytic hydrogenation of furfural or benzaldehyde under ambient conditions, resulting in an additional 7.3% of indirect FE in a single-pass operation. These results illustrate promising reactor configurations for the continuous and energy-efficient conversion of biomass-derived compounds to multiple valuable chemicals with enhanced energy harvesting from counter-reactions and by-products.

## 2. Results and Discussion

### 2.1. ECH-ECO Paired Electrolysis in the MEA-based Flow Electrolyzer

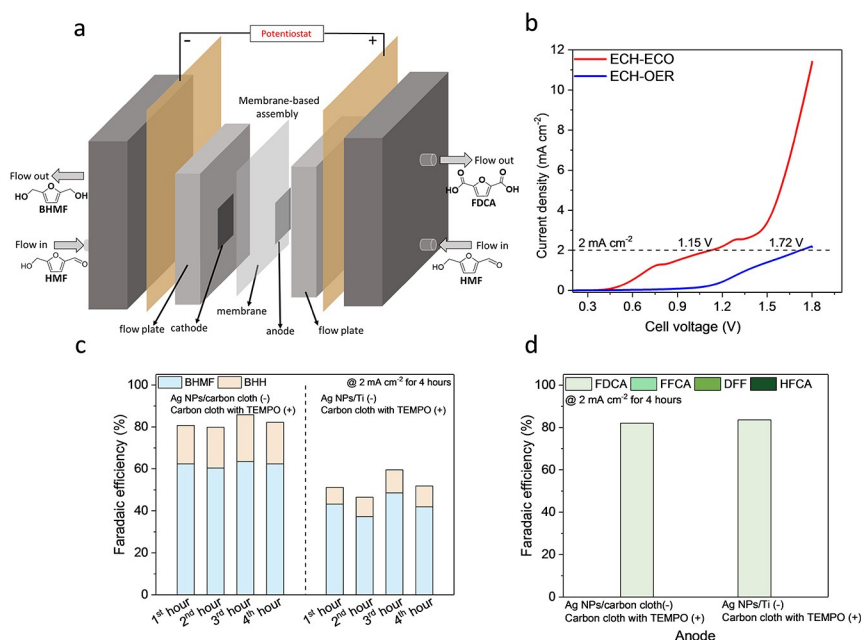
The four-electron OER process is known to consume a large fraction of cell voltage (the potential between the anode and

cathode) in typical ECH electrolyzers.<sup>[3b]</sup> In order to examine the feasibility of pairing ECO with ECH in one cell for HMF conversion, we first calculated the thermodynamic cell potentials ( $|E^0|$ ) of the ECH-OER and ECH-ECO systems. As shown in Table 1, replacing OER with the ECO of HMF to FDCA significantly reduces  $|E^0|$  from 1.11 V to 0.33 V. Noted that the thermodynamic calculation of ECO of HMF is assumed to be the same no matter it was catalyzed by homogeneous catalysts (e.g., TEMPO)<sup>[12]</sup> or heterogeneous catalysts (e.g., NiFe) in this work.

Experimentally, we carried out the ECH-OER and ECH-ECO paired electrolysis in an MEA-based flow electrolyzer (Figure 1a), in which the anion exchange membrane was sandwiched between the cathode and anode in a zero-gap configuration, which is similar to the one used for polymer electrolyte fuel cells, while is much different from a conventional flow cell with a spacer for electrolyte flow. ECH of HMF was catalyzed by Ag NPs and ECO of HMF was mediated by TEMPO (Figure S1).<sup>[7b,8a]</sup> Carbon cloths were used as the electrode substrates, which were treated in  $\text{HNO}_3$  to functionalize the surface with hydro-

Cathodic reaction	Anodic reaction	Overall reaction	$ E^0 $ [V]
$\text{HMF} + 2\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{BHMF} + 2\text{OH}^-$	(Water oxidation) $2\text{OH}^- \rightarrow \text{H}_2\text{O} + 0.5\text{O}_2 + 2\text{e}^-$	$\text{HMF} + \text{H}_2\text{O} \rightarrow \text{BHMF} + 0.5\text{O}_2$	1.11
	(HMF oxidation) $\text{HMF} + 6\text{OH}^- \rightarrow \text{FDCA} + 6\text{e}^- + 4\text{H}_2\text{O}$	$4\text{HMF} + 2\text{H}_2\text{O} \rightarrow 3\text{BHMF} + \text{FDCA}$	0.33

[a] The thermodynamic data are obtained from the literature.<sup>[11]</sup>



**Figure 1.** ECH-ECO paired electrolysis in the MEA-based flow electrolyzer. (a) Schematic illustration of the MEA-based flow electrolyzer. (b) Linear sweep voltammograms of ECH-OER and ECH-ECO systems. The scan rate was  $5 \text{ mV s}^{-1}$ . The cathode was Ag NPs/CC, and the anode was hydrophilic carbon cloth. (c) FE of cathodic products during four consecutive 1 hour measurements on Ag NPs/CC and AgNPs/Ti at 10 mA. (d) FE of anodic products in 4 hour measurements at 10 mA. 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. The TEMPO concentration of 7.5 mM was selected based on the previous works<sup>[7b]</sup> and its high concentration enhanced mass transport for HMF oxidation, especially for long-term electrolysis. The applied charge was 144 C, corresponding to 4 hour electrolysis. Fresh catholyte was replaced every hour during tests.

philic groups. Benefiting from the zero-gap structure of the MEA, the cell resistance was as low as 0.8  $\Omega$  (Table S1).

Results of LSV measurements in the MEA-based flow cell are in good agreement with the thermodynamic analysis. As can be seen in Figure 1b, the ECH-ECO system shows significantly lower cell voltage than the ECH-OER system at the same current density (1.15 vs. 1.72 V at 2.0 mA cm<sup>-2</sup>).

Bulk electrolysis was performed in the ECH-ECO paired system with a constant current density of 2.0 mA cm<sup>-2</sup> (10 mA). The total applied charge was 144 C (equals to 4 hour electrolysis), which is 24% more than the theoretical value (116 C) in order to fully oxidize HMF to FDCA. Fresh catholyte was replaced every hour, giving four consecutive 1-hour measurement results. As shown in Figure 1c and 1d, both cathodic FE of BHMF (60.4–63.5%) and anodic FE of FDCA (~83.5%) were stable throughout the electrolysis, leading to a combined FE of ~145% to the two desirable high-value products.

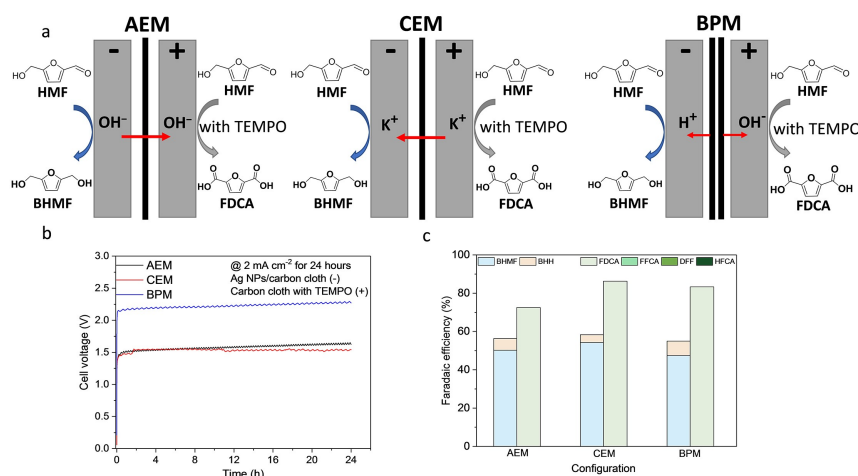
With the same loading of Ag NPs (1.0 mg cm<sup>-2</sup>), we compared the paired electrolysis with HNO<sub>3</sub>-treated carbon cloth (CC) and Ti felt as the cathode substrate. LSV curves show that Ag NPs/CC outperformed Ag NPs/Ti as a lower cell voltage was obtained at 2.0 mA cm<sup>-2</sup>: 1.15 V vs. 1.39 V (Figure S2). Besides the lower cell voltage, the FE of BHMF was also found to be higher on Ag NPs/CC (60.4–63.5%) than on Ag NPs/Ti (37.3–48.6%) in the 4-hour electrolysis (Figure 1c). As both substrates are hydrophilic, the superior performance with the carbon cloth substrate could be attributed to its favorable binding sites for Ag NPs and improves its dispersion. In addition, higher roughness and reinforced bonding strengths of the carbon cloth fibers due to the hydrophilic treatment may alter the transport properties of the electrolyte and thereby facilitate the ECH process.<sup>[13]</sup>

## 2.2. Long-term Performance of ECH-ECO Paired Electrolysis

The long-term performance of the ECH-ECO system was evaluated with three types of membranes (Figure 2a), including anion exchange membrane (AEM, Tokuyama A201), cation exchange membrane (CEM, Nafion 115, K<sup>+</sup> form), and bipolar membrane (BPM), in which anion and cation exchange layers are sandwiched together to dissociate water into H<sup>+</sup> and OH<sup>-</sup> when the potential difference exceeds 0.8 V under the reverse biased mode.<sup>[14]</sup>

24 hour electrolysis was carried out with excess amounts of HMF in catholyte and anolyte at 2 mA cm<sup>-2</sup> to examine the stability. The cell voltage profiles in Figure 2b show that all three systems remain stable within the period of test. The steady-state cell voltages of the systems with AEM and CEM were both ~1.5 V, while the system with BPM showed a higher cell voltage of ~2.2 V due to the higher membrane resistance and the additional voltage needed for water dissociation.<sup>[15]</sup> No apparent change in pH was observed for both catholyte and anolyte after the electrolysis.

For all three configurations, the cathodic FE of BHMF was ~50% with the dimeric side product [5,5'-bis(hydroxymethyl)hydrofuroin, BHH] minimized (FE < 8%); the anodic FE of FDCA was over 80% for the systems with CEM and BPM and slightly lower (73%) for the system with AEM (Figure 2c). This is because of the crossover of anionic intermediates and products from the catholyte to the anolyte during long-term operation, as confirmed by the composition of the catholyte and anolyte after electrolysis: the desired ECO product (FDCA) and intermediate species (HFCA and FFCA) were detected in the catholyte, with selectivity ranging from 2% to 6%; the ECH-related species (*i.e.*, BHMF and BHH) were also found in the anolyte (Table S1–S3). In contrast, no detectable crossover was found in the systems with CEM and BPM. For both systems, a



**Figure 2. Long-term performance of ECH-ECO paired electrolysis with different membranes.** (a) Schematic illustration of the MEA configurations with different ion-selective membranes, including AEM, CEM, and BPM. Red arrows indicate the possible charge-carrying ionic species that transport across the membranes. (b) Cell voltage profiles for continuous 24 hour electrolysis in the systems with AEM, CEM, and BPM at 2 mA cm<sup>-2</sup> (10 mA). (c) FE of ECH (left columns) and ECO (right columns) in different configurations. 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 and the anode was hydrophilic carbon cloth. Detailed results are listed in Table S1–S3.

total FE of ~130% towards BHMf and FDCA was obtained after 24 hours of electrolysis. Considering the cell voltage and FE, the highest energy efficiency of 19.2% was obtained in the CEM-based system.

### 2.3. Paired Electrolysis in pH-asymmetric Configurations without Homogeneous Mediator

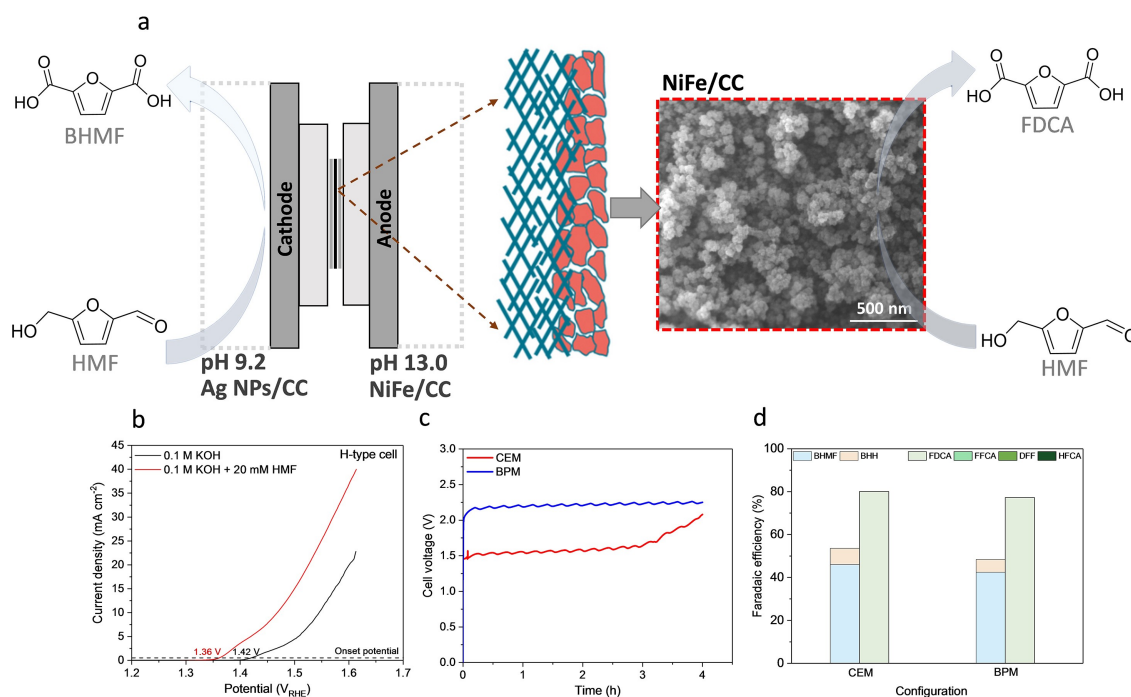
HMF oxidation in the above systems was performed with a homogeneous mediator TEMPO, posing additional cost in product/mediator separation and recycling. Alternatively, ECO of HMF can be catalyzed by Ni-based electrocatalysts in alkaline media without a redox mediator.<sup>[7c,16]</sup> Herein, a NiFe oxide<sup>[17]</sup> catalyst on hydrophilic carbon cloth (NiFe/CC) was prepared by electrodeposition for the HMF-to-FDCA reaction.

SEM imaging shows that NiFe particles of ~50 nm were successfully deposited on carbon cloth as a homogeneous layer (Figure 3a and S4). EDS elemental analysis confirmed that Ni, Fe, and O atoms are uniformly distributed (Figure S5). XPS Ni 2p and Fe 3p spectra (Figure S6) indicated their chemical states are Ni<sup>2+</sup> and Fe<sup>3+</sup>, corresponding to the composition of Ni-Fe mixed oxide.

It should be noted that although ECO of HMF is favorable in alkaline media, HMF itself may become unstable and degrade as pH increases (e.g., at pH 14).<sup>[18]</sup> Therefore, a diluted alkaline electrolyte (0.1 M KOH) was used in the present work. Through

LSV analysis on NiFe/CC in the H-type cell, the onset potentials (defined as the half-cell potential versus RHE at 0.5 mA cm<sup>-2</sup>) with and without added HMF were found to be 1.36 and 1.42 V<sub>RHE</sub>, respectively (Figure 3b), suggesting that ECO is more favorable than OER in 0.1 M KOH. In the constant-current electrolysis at 5 mA cm<sup>-2</sup>, 97% of HMF was converted with 95.1% selectivity to FDCA; the overall FE of FDCA was as high as 81.5% (Table S4).

A pH-asymmetric configuration was then adopted in the MEA-based flow electrolyzer for the co-electrolysis of HMF, employing its ECH at pH 9.2 on Ag NPs/CC cathode and its ECO at pH 13.0 on NiFe/CC anode (Figure 3a). To fully convert HMF to FDCA, 4 hour measurements were conducted at 2 mA cm<sup>-2</sup> (10 mA). In two individual measurements, CEM and BPM were used as the membrane. Similar to the results in the pH-symmetric configuration, the system with CEM showed a considerably lower cell voltage than the system with BPM in the 3 hours (1.5 vs. 2.2 V). However, a pronounced increase in cell voltage was observed in the 4<sup>th</sup> hour for the electrolysis with CEM (Figure 3c). This could be attributed to the consumption of OH<sup>-</sup> in the anolyte during the ECO of HMF, which increases the resistance of the anolyte and lowers the catalytic performance of NiFe. A similar observation has been reported for the CO<sub>2</sub> reduction-OER system.<sup>[15]</sup> In comparison, BPM offered a stable profile of cell voltage throughout the entire period of electrolysis, because the consumption of OH<sup>-</sup> was



**Figure 3.** ECH-ECO paired electrolysis in pH-asymmetric configurations without homogeneous mediator. (a) Schematic illustration of the MEA-based flow electrolyzer with NiFe oxide electrocatalysts for ECO. The inset image shows the SEM image of NiFe/CC. (b) Linear sweep voltammograms of the ECH-ECO system with NiFe/CC as the anode in 0.1 M KOH in an H-type cell, with or without added HMF. The onset potential is defined as the potential at 0.5 mA cm<sup>-2</sup>. (c) Cell voltage profiles for ECH-ECO paired electrolysis in pH-asymmetric MEA-based configurations with CEM or BPM at 2 mA cm<sup>-2</sup>. (d) Faradaic efficiency of ECH and ECO in different configurations. For (c) and (d), 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. Detailed results are shown in Table S5–S7.

compensated by the water dissociation at BPM under reverse bias.

The product distribution in the pH-asymmetric systems did not exhibit significant differences from the pH-symmetric systems: for the systems with CEM and BPM, a total FE of ~125% (including ~45% towards BHMF and ~80% towards FDCA) was attained, without any identified crossover of products or intermediate species (Figure 3d). In addition, HMF-furfural hybrid electrolysis was carried out in a similar BPM-based pH-asymmetric cell, resulting in a total FE of 124% towards BHMF and furoic acid (Figure S7 and Table S8–S9), demonstrating the versatility of the pH-asymmetric electrolyzer in upgrading a wide spectrum of bio-derived chemicals with aldehyde groups.

## 2.4. ECH at High Current Density in a Tandem Electrochemical-Catalytic System

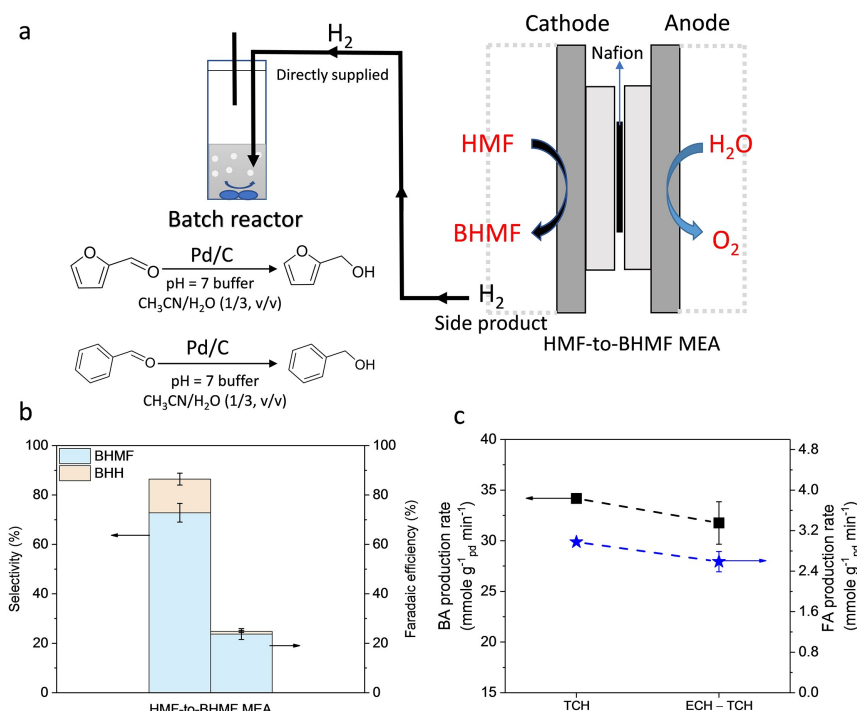
To date, most research works on the ECH of organic feedstocks suffer low current density (*i.e.*, < 10 mA cm<sup>-2</sup>) for high FE. At higher current density, the competitive hydrogen evolution reaction (HER) usually prevails over ECH, as both processes compete for the adsorbed hydrogen (H<sub>ads</sub>) as the crucial intermediate species, while the organic species in ECH are

subjected to limited mass transport both externally and internally.<sup>[7a]</sup> Alternatively, on-site utilization of the co-generated

H<sub>2</sub> can substantially improve the atom and energy efficiency of the whole process at high current density.<sup>[19]</sup> For instance, a tandem TCH reactor coupled with the ECH process allows for small-scale and distributed chemical production without using gaseous H<sub>2</sub> in pressurized containers, thus avoiding its transportation and storage issues.

Taking advantage of the ultralow overall resistance of the zero-gap MEA configuration, a tandem electrocatalytic-catalytic system was developed (Figure 4a and Figure S8): ECH of HMF was conducted in the ECH-OER system, and the side product H<sub>2</sub> was directly supplied into a batch reactor for the hydrogenation of benzaldehyde or furfural to produce alcohols at room temperature.<sup>[20]</sup> Constant-current electrolysis at 280 mA cm<sup>-2</sup> (1.4 A) was carried out with Ag NPs/CC as the cathode for ECH. As shown in Figure 4b, 95.0% of HMF was converted with a FE of 23.7% towards BHMF. In the batch reactor with 5 wt.% Pd/C as the TCH catalyst, benzyl alcohol or furfural alcohol were generated at a rate of 31.8 and 2.6 (mmol g<sup>-1</sup><sub>Pd</sub> min<sup>-1</sup>), respectively, using 50 mM of the corresponding aldehyde as the reactant (Figure 4c). This leads to an additional 7.3% of “indirect FE” due to the single-pass operation in the TCH reactor for hydrogenation of benzaldehyde via using the co-produced H<sub>2</sub>. Control experiments with H<sub>2</sub> from the cylinder suggested no considerable difference in the production rate with different sources of H<sub>2</sub>.

The tandem electrocatalytic-catalytic system uses water as the sole source of hydrogen and electricity as the only form of



**Figure 4. A tandem electrocatalytic-catalytic system.** (a) Schematic illustration of the tandem system, in which the H<sub>2</sub> produced from the electrolyzer is supplied to a batch reactor for TCH reactions. (b) Product selectivity and FE of ECH in the electrolyzer at 280 mA cm<sup>-2</sup> for 65 min electrolysis. (c) Production rates of benzyl alcohol (BA) and furfural alcohol (FA) in the TCH reactor, using electrochemically-produced H<sub>2</sub> from the ECH electrolyzer, or H<sub>2</sub> from the cylinder (10 ml min<sup>-1</sup>), in a 30 min period of operation. For the ECH electrolyzer, the catholyte was 25 ml of 0.5 M borate buffer (pH 9.2) with 100 mM HMF, and the anolyte was 25 ml of 0.5 M borate buffer (pH 9.2). TCH was performed with 50 mM benzaldehyde or furfural in phosphate buffer solution (pH 7) with 1:3 (v/v) CH<sub>3</sub>CN/H<sub>2</sub>O as co-solvent (20 ml), and 20 mg of 5 wt.% Pd/C as the catalyst.

energy input, which is not only robust but also flexible. Depending on the scale of the TCH reactor, the production rate of H<sub>2</sub> can be conveniently controlled by changing the applied current density. Moreover, by circulating the electrochemically-produced H<sub>2</sub> in the TCH reactor, higher “indirect FE” (and thus energy efficiency) can be achieved. A broader range of TCH reactions, and high-current density operations of the anodic reactions, could be explored and investigated in future studies.

### 3. Conclusion

In summary, we developed a versatile and flexible MEA-based flow electrolyzer for electrochemical upgrading of various bio-derived molecules (e.g., HMF, furfural) into value-added products. By pairing the ECH on Ag NPs/CC cathode with TEMPO-mediated ECO at the anode, continuous and stable production of BHMF and FDCA was achieved with a combined FE of > 120% at a minimum cell voltage of ~1.5 V. Similar high FE was also obtained in a mediator-free electrolyzer, in which the ECO was performed on an electrodeposited NiFe/CC in 0.1 M KOH in a pH-asymmetric configuration. Furthermore, the compact low-resistance design of the MEA-based electrolyzer allowed for ECH performance evaluation at high current density (280 mA cm<sup>-2</sup>). In light of the co-generation of H<sub>2</sub> alongside BHMF at high current density, a tandem electrocatalytic-catalytic system was developed to “fix” the on-site generated H<sub>2</sub> into bio-derived aldehydes by a Pd-catalyzed TCH process, resulting in an additional 7.3% indirect FE towards alcohol in a single-pass operation, besides the direct FE of BHMF (23.7%). Our present work highlights the application of zero-gap MEA configuration in advanced electrochemical system design for paired and tandem conversion of biomass-derived feedstocks, which offers promising approaches for sustainable and energy-efficient manufacturing of high-value chemicals in the future chemical industry.

## Experimental Section

### Chemicals and Materials

Sodium hydroxide (97%), potassium hydroxide (85%), sodium sulfate (99%), 5-(hydroxymethyl)furfural (HMF, 99%), furfural (99%), furfural alcohol (FA, 98%), TEMPO[(2,2,6,6-tetramethylpiperidin-1-yl)oxy] (98%), 2-furoic acid (98%), 5-hydroxymethyl-2-furancarboxylic acid (HFCA, 99%), 2,5-diformylfuran (DFF, 97%), 2,5-furandicarboxylic acid (FDCA, 97%), Nickel(II) nitrate hexahydrate (≥ 97%), benzyl alcohol (BA, 99.8%), benzaldehyde (≥ 99.5%), and palladium on active carbon (Pd/C, 5 wt.% Pd loading) were purchased from Sigma-Aldrich. Acetonitrile (CH<sub>3</sub>CN, HPLC grade), iron(III) nitrate nonahydrate (98.7%), platinum foil (0.025 mm thick, 99.9%), 2-propanol (99.9%), nitric acid (67–70%), sulfuric acid (98%), and boric acid (≥ 99%) were purchased from Fisher Scientific. 5-Formyl-2-furoic acid (FFCA, 99%) was purchased from TCI. 2,5-Bis(hydroxymethyl)furan (BHMF, 98%) was purchased from Ark Pharm, Inc. Silver nanopowder (20–40 nm, 99.9%) was purchased from Alfa Aesar. Teflon (0.002-inch thickness) and silicon (0.01 inch thickness) gaskets, Nafion and Bipolar membranes, and plain carbon cloth were purchased from Fuel Cell Store. A201 anion exchange

membrane was purchased from Tokuyama Corp. Deionized (DI) water (18.2 MΩ cm, Barnstead™ E-Pure™) was used for all experiments in this work.

### Preparation of the Working Electrodes

NiFe oxide on carbon cloth (NiFe/CC) was prepared by a modified electrodeposition method.<sup>117</sup> A piece of carbon cloth was first treated in 67–70 wt.% HNO<sub>3</sub> at 110 °C for 1 h 45 min to improve its hydrophilicity. The treated carbon cloth was rinsed with DI water, then immersed in an electrolyte containing 6 mM Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 4 mM Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. Platinum foil and Ag/AgCl (saturated KCl, Pine Research) were used as the counter electrode and reference electrode, respectively. A constant potential (−1.0 V<sub>Ag/AgCl</sub>) was applied to deposit NiFe. The deposition time was 5 and 25 min for 1 and 5 cm<sup>2</sup> carbon cloth, respectively. Finally, the prepared NiFe/CC was washed with DI water and dried in the air.

Ag nanoparticles (NPs) were deposited on the electrode substrate (CC or Ti felt) by airbrushing. The catalyst ink was prepared by dispersing Ag NPs in a mixture of DI water and 2-propanol (10 mg<sub>Ag</sub> mL<sup>-1</sup>) with added ionomer by ultrasonication. AS-4 and Nafion ionomers were used depending on the choice of the membrane: AS-4 for the anion exchange membrane (AEM); Nafion for the cation exchange membrane (CEM) and bipolar membrane (BPM). The mass ratio of Ag NPs and dry ionomer was 4:1. The ink was then airbrushed onto the substrate to a final loading of ~1.0 mg<sub>Ag</sub> cm<sup>-2</sup>.

### Electrochemical Measurements in the MEA-based Flow Electrolyzer

The flow electrolyzer contains gold current collectors, two graphite flow-field plates with serpentine channels (5 cm<sup>2</sup> active surface area), PTFE and silicone gaskets, and the MEA, which contains two catalyst-coated electrodes and a membrane, and was formed after assembling the cell hardware. The catholyte and anolyte were circulated by a peristaltic pump (Masterflex® L/S®) at 10 mL min<sup>-1</sup>. The applied potential or current was controlled by a Biologic SP-300 potentiostat/galvanostat.

### Electrochemical Measurements in the H-type Cell

To perform ECO of HMF in an H-type cell, a three-electrode configuration was set-up with Ag/AgCl as the reference electrode and Pt foil as the counter electrode. Anode and cathode compartments were separated by an A201 anion-exchange membrane. The resistance between the working and reference electrodes was determined by potentiostatic electrochemical impedance spectroscopy (PEIS), and 90% *iR*-compensation was applied for all measurements. LSV was carried out at a scan rate of 5 mV s<sup>-1</sup> without stirring. Chronopotentiometry (CP) was conducted at 10 mA with a stirring rate of 350 rpm by PTFE-coated magnetic bars (20×6 mm, Chemglass Life Sciences). Potentials (*E*) versus RHE relative to those versus Ag/AgCl was calculated by Eq. (1):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ V} \times \text{pH} \quad (1)$$

### Tandem Electrocatalytic–Catalytic Reactor

The combined electrocatalytic-catalytic process was operated in two reactors in tandem, including an ECH-OER flow electrolyzer and a batch reactor for the thermocatalytic hydrogenation (TCH)

reaction at room temperature (Figure S8). The electrolyzer contained an MEA, which consisted of an Ag NPs cathode ( $\sim 1.0 \text{ mg}_{\text{Ag}} \text{ cm}^{-2}$ ), hydrophilic carbon cloth anode, and a Nafion 115 membrane ( $\text{K}^+$  form). The catholyte was 25 ml of 100 mM HMF in 0.5 M borate buffer (pH 9.2), and the anolyte was 0.5 M borate buffer. The electrolyzer was operated at  $280 \text{ mA cm}^{-2}$  and its outlet gas was supplied to the batch reactor via a gas dispersion tube (Ace Glass, 7 mm O.D., 25–50 micron porosity). The TCH reactor contained 50 mM benzaldehyde or furfural in 20 ml of 0.1 M phosphate buffer solution (pH 7) with 1:3 (v/v)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  as co-solvent. 20 mg of 5 wt.% Pd/C was dispersed in the solution as the catalyst. The duration for each TCH test was 30 min. In a control experiment, ultra-high purity  $\text{H}_2$  from the cylinder was fed into the TCH reactor at  $10 \text{ ml min}^{-1}$ , instead of the electrochemically-produced  $\text{H}_2$ .

### Quantification of Reactants and Products

The electrolyte was analyzed by High-Performance Liquid Chromatography (HPLC, Agilent Technologies, 1260 Infinity II LC System) equipped with a variable wavelength detector (Agilent 1260 Infinity Variable Wavelength Detector VL). The wavelength of 225 nm and 260 nm was applied to quantify cathodic species (including HMF, BHMF, furfural, FA, and dimers) and anodic species (including HMF, FDCA, HFCA, FFCA, and DFF), respectively. Two isomers of the dimer product [5,5'-bis(hydroxymethyl)hydrofuroin, BHH] are reported together for simplicity. Detailed HPLC conditions were reported in our previous works.<sup>[7a,8a]</sup> For the quantification of furfural and 2-furoic acid, the same conditions for the analysis of HMF oxidation products were used except that the flow rate of the mobile phase was increased to  $1.1 \text{ ml min}^{-1}$ , and the retention time was around 28.7 min and 18.6 min for furfural and 2-furoic acid, respectively. For the quantification of benzaldehyde and benzyl alcohol, the retention time was around 16.5 min and 19.9 min, respectively. Conversion ( $C$ ), product selectivity ( $S_i$ ), and Faradaic efficiency ( $\text{FE}_i$ ) can be calculated by Eqs. (2)–(4).

$$C = \frac{n_0 - n}{n_0} \times 100\% \quad (2)$$

$$S_i = \frac{n_i}{n_0 - n} \times 100\% \quad (3)$$

$$\text{FE}_i = \frac{n_i z_i F}{Q} \times 100\% \quad (4)$$

Where  $n_0$  is initial moles of reactant;  $n$  is the moles of reactant after electrolysis;  $n_i$  is the moles of product  $i$ ;  $z_i$  is the number of electrons transferred for one product molecule;  $F$  is the Faraday constant ( $96,485 \text{ C mol}^{-1}$ );  $Q$  is the total charge passed through the electrolytic cell.

Energy efficiency ( $\epsilon$ ) as a function of cell voltage ( $V_{\text{cell}}$ ) was calculated by Eq. (5):

$$\epsilon = \frac{|E_{\text{cell}}|}{V_{\text{cell}}} = \frac{|\text{FE}_{\text{BHMF}} \cdot E_{\text{HMF/BHMF}} - \text{FE}_{\text{FDCA}} \cdot E_{\text{HMF/FDCA}}|}{V_{\text{cell}}} \times 200\% \quad (5)$$

Where  $E_{\text{HMF/BHMF}}$  and  $E_{\text{HMF/FDCA}}$  denote the thermodynamic reduction potentials for HMF-to-BHMF and FDCA-to-HMF reactions, respectively, under the testing conditions. It is worth noting that the electrons are transferred from the HMF at the anode directly to the HMF at the cathode, ideally there are no paired hydrogen and oxygen evolving from the paired electrolyzer, which does not need

two HMF electrolyzers for separate preparation of BHMF and FDCA, therefore, the maximum combined FE is 200%.<sup>[4b,5b]</sup>

### Physical Characterization

X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Amicus/ESCA 3400 X-ray photoelectron spectrometer with Mg K $\alpha$  X-ray (1,253.7 eV). All XPS spectra were calibrated with the C 1s peak at 284.8 eV. Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) was performed on a field-emission scanning electron microscope (FEI Quanta-250) equipped with a light-element X-ray detector and an Oxford Aztec energy-dispersive X-ray analysis system.

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### Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** electrocatalytic hydrogenation · membrane-electrode assembly · paired electrolysis · electrolyzer · biomass conversion

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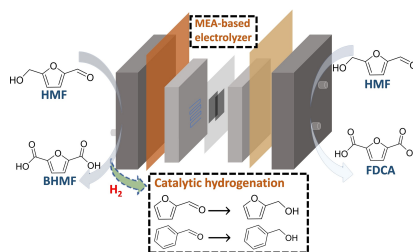
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## ARTICLES

**Paired electrolysis:** Pairing the electrocatalytic hydrogenation reaction with different anodic reactions in membrane-electrode assembly (MEA)-based electrolytic systems holds great promise for producing value-added chemicals with minimal energy input. Additionally, tandem electrocatalytic-catalytic systems enable electrolysis at high current density and simultaneously circulates the electrochemically produced  $H_2$  for energy-efficient chemical transformations with enhanced energy harvesting from by-product  $H_2$ .



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



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