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

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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 \(~1.0\ \text{mg}_{\text{Ag}}\ \text{cm}^{-2}\), 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.
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.\(^a\)

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

\(a\). 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 (~1.0 mg\(\text{Ag}\) 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.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Conversion (%)</th>
<th>BHMF selectivity (%)</th>
<th>BHMF FE (%)</th>
<th>BHH selectivity (%)</th>
<th>BHH FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM</td>
<td>61.3</td>
<td>73.8</td>
<td>50.2</td>
<td>17.9</td>
<td>6.1</td>
</tr>
<tr>
<td>CEM</td>
<td>64.1</td>
<td>75.5</td>
<td>54.3</td>
<td>12.2</td>
<td>4.3</td>
</tr>
<tr>
<td>BPM</td>
<td>63.3</td>
<td>70.4</td>
<td>47.5</td>
<td>18.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Conversion (%)</th>
<th>FDCA selectivity (%)</th>
<th>FDCA FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM</td>
<td>100</td>
<td>83.0</td>
<td>72.5</td>
</tr>
<tr>
<td>CEM</td>
<td>100</td>
<td>98.3</td>
<td>86.3</td>
</tr>
<tr>
<td>BPM</td>
<td>100</td>
<td>96.5</td>
<td>83.3</td>
</tr>
</tbody>
</table>
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.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>FDCA selectivity (%)</th>
<th>FDCA FE (%)</th>
<th>HFCA selectivity (%)</th>
<th>HFCA FE (%)</th>
<th>FFCA selectivity (%)</th>
<th>FFCA FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.0</td>
<td>95.1</td>
<td>81.5</td>
<td>1.6</td>
<td>0.5</td>
<td>4.1</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\textsuperscript{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 cm\textsuperscript{2}, and the applied charge was 136 C. The theoretical charge required for 100% conversion of HMF to FDCA was 116 C (0.01 M \times 0.02 L \times 6 \times 96485 C \text{ mol}^{-1} = 116 C).
Table S5. Results of ECH-ECO paired electrolysis in the pH-asymmetric configurations,a

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Resistance (Ω)</th>
<th>Selectivity of ECH products in anolyte (%)</th>
<th>Selectivity of ECO products in catholyte (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM</td>
<td>0.57</td>
<td>0⁵</td>
<td>0⁵</td>
</tr>
<tr>
<td>BPM</td>
<td>1.30</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

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 (~1.0 mg\textsubscript{Ag} cm\textsuperscript{-2}), and the anode was NiFe/CC. The electrolysis was performed at 2 mA cm\textsuperscript{-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.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Conversion (%)</th>
<th>BHMF selectivity (%)</th>
<th>BHMF FE (%)</th>
<th>BHH selectivity (%)</th>
<th>BHH FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM</td>
<td>19.2</td>
<td>75.5</td>
<td>46.1</td>
<td>23.4</td>
<td>7.6</td>
</tr>
<tr>
<td>BPM</td>
<td>17.7</td>
<td>71.5</td>
<td>42.4</td>
<td>20.2</td>
<td>6.0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Conversion (%)</th>
<th>FDCA selectivity (%)</th>
<th>FDCA FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM</td>
<td>100</td>
<td>96.8</td>
<td>80.1</td>
</tr>
<tr>
<td>BPM</td>
<td>100</td>
<td>96.1</td>
<td>77.3</td>
</tr>
</tbody>
</table>
**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 (~1.0 mg Ag 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 M × 0.04 L × 2 × 96485 C mol\(^{-1}\) = 77.2 C).

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

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>BHMF selectivity (%)</th>
<th>BHMF FE (%)</th>
<th>BHH selectivity (%)</th>
<th>BHH FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.4</td>
<td>68.2</td>
<td>54.0</td>
<td>12.2</td>
<td>8.0</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>2-furoic acid selectivity (%)</th>
<th>2-furoic acid FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.3</td>
<td>95.0</td>
<td>70.5</td>
</tr>
</tbody>
</table>
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.