

Paired Electrolysis of 5-(Hydroxymethyl)furfural (HMF) for Production of Higher-Valued Chemicals in Electrochemical Flow Cells

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Electrocatalytic upgrading of biomass-derived feedstocks driven by renewable electricity offers a greener way to reduce the global carbon footprint associated with the production of value-added chemicals. Paired electrolysis is an emerging platform for cogenerating high-valued chemicals from both the cathode and anode, potentially powered by renewable electricity from wind or solar sources. By pairing with an anodic biomass oxidation upgrading reaction, the elimination of the sluggish and less valuable water oxidation increases flow cell productivity and efficiency. In this presentation, we report our research progress on paired electrolysis of HMF to production of higher valued chemicals in electrochemical flow cells. We first prepared an oxide-derived Ag (OD-Ag) electrode with high activity and up to 98.2% selectivity for the ECH of 5-(hydroxymethyl)furfural (HMF) to 2,5-bis(hydroxymethyl)furan (BHMF), and such efficient conversion was achieved in a three-electrode flow cell. The excellent BHMF selectivity was maintained over a broad potential range with long-term operational stability. In HMF-to-BHMF paired with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-mediated HMF-to-FDCA conversion, a markedly reduced cell voltage from ~7.5 V to ~2.0 V was observed by transferring the electrolysis from the H-type cell to the flow cell, corresponding to more than four-fold increase in energy efficiency in operation at 10 mA. A combined faradaic efficiency of 163% was obtained to BHMF and FDCA. Alternatively, the anodic hydrogen oxidation reaction on platinum further reduced the cell voltage to only ~0.85 V at 10 mA. Next, we have demonstrated membrane electrode assembly (MEA)-based flow cells for the paired electrolysis of 5-(hydroxymethyl)furfural (HMF) paired electrolysis to bis(hydroxymethyl)furan (BHMF) and 2,5-furandicarboxylic acid (FDCA). In this work, the oxygen evolution reaction (OER) was substituted by TEMPO-mediated HMF oxidation, dropping the cell voltage was from 1.4 V to 0.7 V at a current density of  $1.0 \text{ mA cm}^{-2}$ . A minimized cell voltage of ~1.5 V for a continuous 24 h co-electrolysis of HMF was then achieved at the current density of  $2 \text{ mA cm}^{-2}$  (constant current of 10 mA), leading to the highest combined faradaic efficiency (FE) of 139% for HMF-to-BHMF and HMF-to-FDCA. A NiFe oxide catalyst on carbon cloth further replaced the anodic TEMPO mediator for HMF paired electrolysis in a pH-asymmetric flow cell. We envision renewable electrical energy can potentially drive the whole process, thus providing a sustainable avenue towards distributed, scalable, and energy-efficient electrosynthesis.