

Electrocatalytic Conversion of Furanic Compounds for Production of Valuable Chemicals

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Biomass is abundant, inexpensive and renewable, therefore, it is highly expected to play a significant role in our future energy and chemical landscapes. The US DOE has identified furanic compounds (furfural and 5-(hydroxymethyl)furfural (HMF)) as the top platform building-block chemicals that can be readily derived from biomass sources [1]. Electrocatalytic conversion of these furanic compounds is an emerging route for the sustainable production of valuable chemicals [2, 3].

In my presentation, I will first present our recent mechanistic study of electrochemical reduction of furfural through a combination of voltammetry, preparative electrolysis, thiol-electrode modifications, and kinetic isotope studies [4]. It is demonstrated that two distinct mechanisms are operable on metallic Cu electrodes in acidic electrolytes: (i) electrocatalytic hydrogenation (ECH) and (ii) direct electroreduction. The contributions of each mechanism to the observed product distribution are clarified by evaluating the requirement for direct chemical interactions with the electrode surface and the role of adsorbed hydrogen. Further analysis reveals that hydrogenation and hydrogenolysis products are generated by parallel ECH pathways. Understanding the underlying mechanisms enables the manipulation of furfural reduction by rationally tuning the electrode potential, electrolyte pH, and furfural concentration to promote selective formation of important bio-based polymer precursors and fuels.

Next, I will present electrocatalytic conversion of HMF to two biobased monomers in an H-type electrochemical cell [5]. HMF reduction (hydrogenation) to 2,5-bis(hydroxymethyl)furan (BHMF) was achieved under mild electrolyte conditions and ambient temperature using a Ag/C cathode. Meanwhile, HMF oxidation to 2,5-furandicarboxylic acid (FDCA) with ~100% efficiency was facilitated under the same conditions by a homogeneous nitroxyl radical redox mediator, together with an inexpensive carbon felt anode. The selectivity and efficiency for Ag-catalyzed BHMF formation were sensitive to cathode potential, owing to competition from HMF hydrodimerization reactions and water reduction (hydrogen evolution). Moreover, the carbon support of Ag/C was active for HMF reduction and contributed to undesired dimer/oligomer formation at strongly cathodic potentials. As a result, high BHMF selectivity and efficiency were only achieved within a narrow potential range near -1.3 V. Fortunately, the selectivity of redox-mediated HMF oxidation was insensitive to anode potential, thus allowing HMF hydrogenation and oxidation half reactions to be performed together in a single cathode-potential-controlled cell. Electrocatalytic HMF conversion in a paired cell achieved high molar yields of BHMF and FDCA, and nearly doubled electron efficiency compared to the unpaired cell.

Finally, I will briefly introduce our recent work on the development of a three-electrode flow cell with an oxide-derived Ag (OD-Ag) cathode and carbon felt anode for pairing electrocatalytic oxidation and reduction of HMF. The flow cell has a remarkable cell voltage reduction from ~7.5 V to ~2.0 V by transferring the electrolysis from the H-type cell to the flow cell [6]. This represents a more than fourfold increase in the energy efficiency at the 10 mA operation. 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 operation. These paired processes have shown potential for integrating renewable electricity and carbon for distributed chemical manufacturing in the future.

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