

## Abstract

The biomass-derived furfural (FF) transforms into platform chemicals such as furfuryl alcohol (FA), hydrofuroin (HF), furoic acid (FU), and 2(5H)-furanone (FN) for their use in polymer, pharmaceuticals, and bio-fuel industries. Electrocatalytic hydrogenation (ECH) of FF is an appealing process because of the in-situ generation of adsorbed hydrogen, ambient temperature-pressure conditions, and the use of electrical energy generated from renewables.

Herein, FF ECH in alkaline medium produced FA and HF, and their selectivity on Cu, Pt, and Ni-foam (NF, 10 cm<sup>2</sup>) electrocatalysts showed that their generation was dependent upon the availability of adsorbed hydrogen, which in turn varied with the choice of electrocatalyst and with applied potentials. The etching of Cu from a co-electrodeposited Ni-Cu electrode, followed by a re-electrodeposition of Cu led to the formation of Cu nanoplate, termed as Cu-NPNi/NF. The formation of Cu-nanoplates and bimetallic Ni-Cu for Cu-NPNi/NF resulted an increase in FA and HF formation rates as compared to Cu, Pt, and NF. As alkaline medium widened the scope for the type of materials, FF ECH using metal-oxide (In<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-x</sub>) electrocatalysts was studied. Through experimental and theoretical studies, we demonstrated that the binding energy and coverage of competing furfural and hydrogen adsorption processes determined the selectivity of FA over HF ( $S_{FA/HF}$ ). The Langmuir-Hinshelwood mechanism was found to be involved during FF ECH with pristine Pb<sub>2</sub>Ru<sub>2</sub>O<sub>7-x</sub> electrocatalyst, which resulted in the high surface coverage of FF and hydrogen leading to selective FA formation.

For scaling up of the electrode to enhance FA and HF formation rates, a batch electrochemical reactor was fabricated in which thermally treated large surface area (100 cm<sup>2</sup>) 3D-graphite felt cathode yielded the HF formation rate and HF selectivity as  $5.2 \pm 0.16$  mmol h<sup>-1</sup>, and  $65.7 \pm 1.9\%$  HF, respectively with a 97.8% conversion in 3 h of ECH. A silver deposited Ni-foam cathode (100 cm<sup>2</sup>) was employed in a fabricated continuous flow (flow rate = 10 mL min<sup>-1</sup>) electrochemical reactor to obtain  $10.5 \pm 0.5$  mmol h<sup>-1</sup> FA formation rate and  $78.2 \pm 2.1\%$  FA selectivity. Furthermore, the solar illumination reduced the electrical energy requirement as a photoelectrochemical cell (Cu-NPNi/NF|TiO<sub>2</sub>) depicted a lower applied bias to attain a FA formation rate comparable to that achieved from an electrochemical cell (Cu-NPNi/NF|Pt). The FF ECH was paired with photoelectrochemical oxidation of FF to coproduce FA at cathode and FU, FN at photoanode validating the feasibility of solar illumination utilization in biomass conversion. Overall, FA and HF produced from FF ECH had high formation rates and a competitive market pricing, which could be scaled-up and commercialized by the industries.