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# Electrocatalytic valorization of biomass-derived furfural on structured Cu electrodes

Mathieu S. Prévot, Maxime Nouaille-Degorce, Loïc Pendu, Luis Cardenas  
Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France  
[mathieu.prevot@ircelyon.univ-lyon1.fr](mailto:mathieu.prevot@ircelyon.univ-lyon1.fr)

The complete decarbonation of the chemical industry is ultimately contingent on the replacement of the current fossil-based petrochemical pathways by renewable alternatives. In particular the large-scale production of organic molecular building blocks must be rethought. As such, biomass, the largest reservoir of contemporary carbon, appears to be a prime renewable feedstock for the production of these compounds. Indeed, lignocellulosic biomass can be treated to provide a number of platform compounds that have been identified as molecular bricks that can be upgraded to high-value chemicals through redox chemistry. To operate this upgrade, electrocatalysis appears as an attractive tool, as it can be integrated with renewable sources of electricity, it can operate under ambient conditions, its selectivity can be fine-tuned by voltage monitoring, and it can use water as a source of protons and oxygen.<sup>1</sup> Here we present an application of these concepts where the aromatic platform compound furfural (obtained from the hydrolysis of hemicellulose) is electrocatalytically valorized on high surface area Cu electrodes.

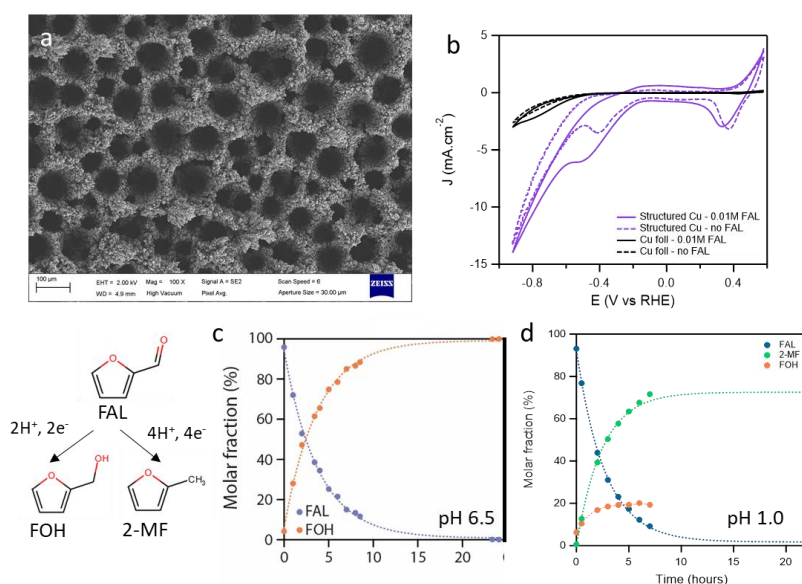


Figure 1 a) SEM image of a structured Cu electrode. b) Cyclic voltammograms of the same electrode and of Cu foil at pH 6.5 in the presence and absence of furfural. Furfural conversion in pH 6.5 (c) and pH 1.0 (d) electrolytes.

High surface area mesoporous copper films were electrodeposited on copper foil to generate the working electrodes. Then, electrocatalytic furfural reduction was studied at the surface of these electrodes as a function of several reaction parameters. We found that furfural can be selectively converted to furfuryl alcohol in neutral conditions (phosphate buffer), and with a 75%-25% selectivity towards 2-methylfuran-furfuryl alcohol under acidic conditions (phosphoric acid). The influence of temperature and concentration was also studied. While increasing the temperature improved conversion kinetics, it did not affect selectivity. Conversely, increasing furfural concentration above 0.05 M led to the formation of undesirable hydrofuroin byproducts. Importantly, we found that electrode structuring led to a significant reduction of overpotential ( $\sim 0.3$ V) for furfural reduction (compared to the reference copper foil) without compromising selectivity, and no sign of deactivation was observed after 24 hours of operation. Operando Raman spectroscopy experiments and in-situ near ambient pressure (NAP) XPS experiments (under 15 mbar of water vapor pressure) were conducted to identify the nature of the active sites under applied potential, primarily involving Cu(I) centers, and following furfural conversion on the surface of the metal.

- (1) Lucas, F. W. S.; Grim, R. G.; Tacey, S. A.; Downes, C. A.; Hasse, J.; Roman, A. M.; Farberow, C. A.; Schaidle, J. A.; Holeywinski, *ACS Energy Lett.* **2021**, 6 (4), 1205–1270.