Tuning Multifunctionality for the Co-production of H_2, Carboxylic Acids and Electricity in a Multi-purpose Biomass-Fuel Cell

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Significance and Relevance

The simultaneous production of both carboxylic acids and H_2 gas at the anode via an ultra-low voltage aldehyde oxidation was realized over a bimetallic CuNi alloy. The synergistic interaction between metallic Cu and Ni sites is found to be the dominant factor in controlling the production of H_2 and the cyclability of the electrodes with considerable carboxylic acid and H_2 production during consecutive cycles. Moreover, the importance of metallic sites in the activation of H* was confirmed thorough H_2 TPD analysis wherein, the absence of metallic sites resulted in weak to no interaction with H*.

Preferred and 2nd choice for the topic: *Sustainable and clean energy production and transport/* ***2nd choice****: Catalysis to electrify the chemical production*
Preferred presentation**:** *Oral preferred or short oral*

Introduction and Motivations

The development of economical and energy-efficient processes for the sustainable production of energy and green chemicals is fueled by the increasing concerns over exhausted petroleum resources, high oil prices, energy security and environmental concerns.[1] Hydrogen is a prospective clean fuel and a vital feedstock in industrial chemical processes. Despite the promise of water electrolysis as an alternative technology for producing high-purity H_2, the commercial scalability is limited by its high cost, due to the required high voltage input. While electrochemical biomass oxidation has been explored as an alternative anodic reaction for water electrolysis to produce cheap H_2, these conventional organic electrolyzer systems still require high voltage input (> 1V) resulting in high electricity consumption. Hence, the transformation of these energy input systems into an energy output system is of great significance. Unlike the conventional aldehyde electrooxidation, in which the hydrogen atom of the aldehyde group is oxidized into H_2O at high potentials, the ultralow-potential aldehyde oxidation enables the hydrogen atom to recombine into H_2 gas. [2] This H_2 generation from bio-based aldehydes can also be accompanied by the production of valuable by-products, such as carboxylic acids in the same anodic compartment. Cu is known to optimally balance the ability to activate the C-H bond, avoid CO poisoning and be stable in a metallic form at desired operating potentials.[3] Accordingly, in this work a CuNi alloy was constructed aiming to lower the barrier for C-H dissociation of the aldehyde group through the formation of diol-intermediates, while facilitating the adsorption of OH^- for the oxidation of furfural to furoic acid.

Materials and Methods

The self-supported Cubic CuNi alloys were synthesized via an electrodeposition method and directly used as anodes. The ultra-low potential aldehyde oxidation was performed by using furfural as a model aldehyde substrate in an H-type electrochemical cell separated by an AEM with a 1M KOH catholyte and 1M KOH + 400mM furfural anolyte. The simultaneous production of Furoic acid and H_2 at the anode was confirmed by high performance liquid chromatography (HPLC) and gas chromatography (GC) analysis.

Results and Discussion

The co-production of Furoic acid and H_2 gas at the anode was confirmed for the bimetallic CuNi alloys with the highest FA and H_2 production observed for 80%Cu and 20%Ni. Production of 0.7 mol FA and 0.16 mol H_2 was achieved per mole of furfural in just 30 mins of electrolysis at an applied voltage of 0.3V vs. RHE. The synergistic effect of metallic Ni and Cu was verified by the lack of H_2 production in the 1st cycle for electrodes with lower Ni% (<20%) content (**Figure 1**). For all the electrodes, an increased FA and H_2 production was observed after the 1st cycle which was accompanied by a decrease in (oxy)hydroxide peaks and an increase in the metallic Cu and Ni peaks which implies the in-situ reduction of (oxy)hydroxides to metallic active sites during the 1st cycle. These results suggest that metallic Cu/Ni sites to be the active sites for furfural activation/H_2 production which was confirmed by controlling the metallic composition by adjusting the synthesis parameters which increased H_2 production rate in the 1st cycle, followed by stable production of both H_2 and FA during successive cycles.

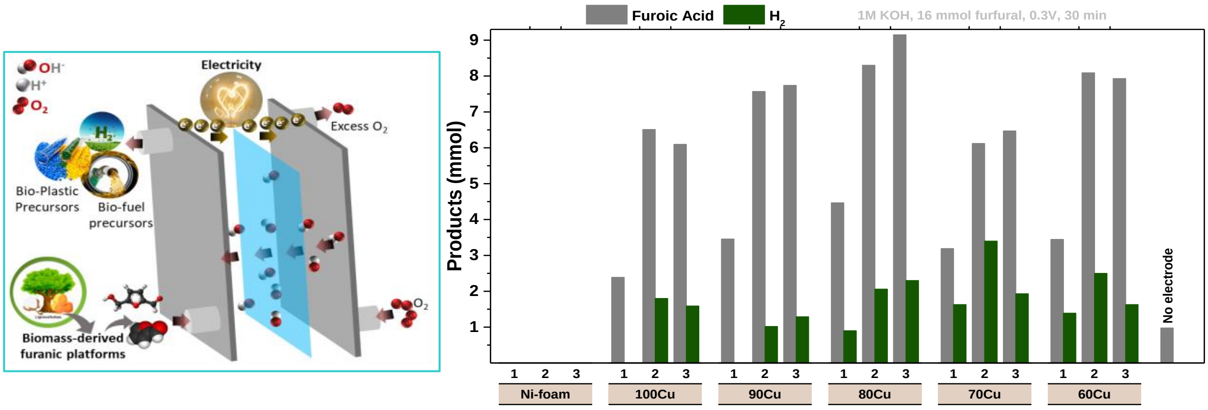

Figure 1. Schematic illustration of the proposed multipurpose biomass fuel cell (Left) and Effect of metal combination on the co-production of FA and H_2.

Accordingly, it is anticipated that due to the ultra-low applied voltage, the anodic furfural oxidation can be paired with cathodic ORR in a multi-purpose fuel cell to simultaneously produce H_2, FA and electricity advancing multifunctionality.

References

1. R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba and M. López Granados, *Energy Environ. Sci.*, **2016**, **9**, 1144–1189.
2. T. Wang, L. Tao, X. Zhu, C. Chen, W. Chen, S. Du, Y. Zhou, B. Zhou, D. Wang, C. Xie, P. Long, W. Li, Y. Wang, R. Chen, Y. Zou, X. Z. Fu, Y. Li, X. Duan and S. Wang, *Nat. Catal.*, **2022**, **5**, 66–73.
3. H. Liu, N. Agrawal, A. Ganguly, Y. Chen, J. Lee, J. Yu, W. Huang, M. Mba Wright, M. J. Janik and W. Li, *Energy Environ. Sci.*, **2022**, **15**, 4175–4189.

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