Sequential deposition of FeNC–Cu tandem CO_2 reduction electrocatalysts towards the low overpotential production of C_{2+} alcohols

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Highlights

- Sequential spray coating of FeNC-Cu to synthesize tandem electrocatalysts for C_{2+} products.
- The production of alcohols via favored CH_X–CO coupling from CO-making catalyst
- CO spillover effect on Cu nanoparticles toward C–C coupling for the formation of alcohol
- Higher CO coverage surface from different electrode configurations of tandem electrocatalyst

1. Introduction

The effective utilization of CO_2 by electrochemical reduction has become an attractive strategy for mitigating greenhouse gas emissions while simultaneously producing valuable chemicals. This technology aims to convert CO_2 into a variety of high value carbon-based products, such as hydrocarbons and alcohols, which can be used as fuels and feedstocks in various industrial processes. To achieve this aim, a significant amount of research has focused on creating efficient catalysts that are able to activate the CO_2 molecule (where the electrolyte cation plays a crucial role), convert it via proton-coupled electron transfer and release the desired products.

A tandem system where CO_2 is reduced to CO, and CO employed as feedstock for electrochemical C–C coupling reactions can increase the efficiency towards the formation of multi-carbon products by facilitating CO transfer and spillover. Spillover plays a crucial role in enhancing the catalytic activity and selectivity in the electrochemical reduction of CO_2 by transferring intermediates or reaction products from one catalyst surface to another. Spillover occurs when the adsorption energies of the intermediates on one catalyst surface are significantly different from those on the other catalyst surface. Heterogeneous tandem systems with single atom catalysts, such as atomic metal in nitrogen-doped carbons, or macrocycles (porphyrins or phthalocyanines), allow an easier tuning of the spatial distribution of the catalyst that produce the CO compared to alloyed nanoparticles, facilitating the spillover mechanism.

To address this issues and facilitate effective spillover, we show a sequential spray coating method to synthesize tandem electrocatalysts where we employed our recently reported porous FeNC as the CO-producing electrocatalyst. To target the production of alcohols, we employed commercial shape-selected Cu nanoparticles with exposed Cu (111) facets, which have been shown to form ethanol rather than ethylene due to the favored CH_X–CO coupling.

2. Methods

A high surface area nitrogen-doped carbon material (FeNC) was prepared as recently reported by our group by pyrolysis at 900 ◦C of a mixture comprised of 2,4,6 triaminopyrimidine (TAP) and magnesium chloride hexahydrate [1]. FeNC and Cu nanopowder were deposited onto hydrophobic carbon paper by means of spray-coating. Electrochemical reduction of CO_2 (CO_2RR) was carried out using a cell with

3-electrode configuration consisting of working, counter, and reference electrodes in a homemade gas diffusion cell.

3. Results and discussion

The different configuration within the tandem electrodes which will strongly impact the selectivity for the CO_2RR. The tandem electrocatalyst are prepared through sequential deposition of a CO-making catalyst and commercial copper nanoparticles in a gas diffusion electrode; where CO_2 flows through the gas diffusion layer, is reduced initially to CO in the surface of FeNC and the efficient CO spillover to the Cu nanoparticles results in C–C coupling towards the formation of ethanol and propanol. By screening different electrode configurations, we observed that the higher FE towards C_{2+} alcohols is achieved by the structure that provides a higher CO coverage in the Cu nanoparticle. This process requires fewer product selectivity probably arises due to the increased transfer of COand H species at higher applied intermediate steps and electron/proton transfers in comparison to the complex mechanisms involved in C_{2+} chemicals production. We hypothesize that in the case of FeNC+Cu, the CO spillover is unoptimized and owing to its low residence time, combined with the hydrophobicity of the electrode the production of C_{2+} products is hindered.

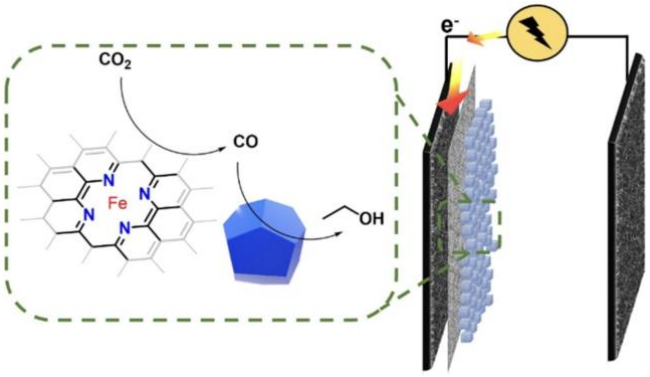

Figure 1. Representation of the tandem electrocatalyst with a FeNc–Cu configuration.

4. Conclusions

In this study, we have prepared tandem catalysts comprising a FeNC material as the CO-making catalysts and commercial Cu nanopowder with exposed Cu (111) facets for C_{2+} production. The electrodes are synthesized following a sequential spray-coating deposition that leads to different conformations and electrochemical activities. The tandem catalyst that consists of Cu spray coated on FeNC displays a much lower HER than that of commercial Cu nanopowder and allowed the formation of C2+ products at a much lower overpotential. This is attributed to the spillover mechanism of CO from FeNC to Cu, which promotes the formation of C_{2+} products. Moving forward, the approaches currently being studied to improve the efficiency and FE_{C2+} of single atom-Cu tandem electrocatalysts entail (a) modulating the CO_2 flow to screen the impact of CO residence time in the surface of Cu, (b) analyzing the effect of Cu content in the surface of a CO-making catalyst and (c) modulate the hydrophobicity of the Cu layer by tuning the amount of PTFE employed in the electrode.

References

[1] Barrio J et al, 2023 FeNC oxygen reduction electrocatalyst with high utilization penta-coordinated sites Adv. Mater. 35 e2211022

Keywords
single atom catalysts, electrochemical CO_2 reduction, electrode fabrication, copper