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Towards the electrochemical conversion of CO2 into formate optimization: flow cell parameters and bismuth-based catalyst stability

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PURPOSE OF THE ABSTRACT

The electrochemical conversion of CO2 to valuable products is a particularly appealing technology for the mitigation of anthropogenic CO2 emissions. Among the obtainable CO2 electrochemical conversion products, formate is a relevant target, owing its high accessibility (2 e- process) and its broad range of applications. [1] Among the studied electrocatalysts for the electrochemical CO2-to-formate conversion (e.g. based on Bi, Sn, In), Bi-based catalysts are the most promising option with respect to Faradaic efficiency (FE) and current density (j), particularly in comparison to the Sn-based ones, which show lower stability and activity. [2]

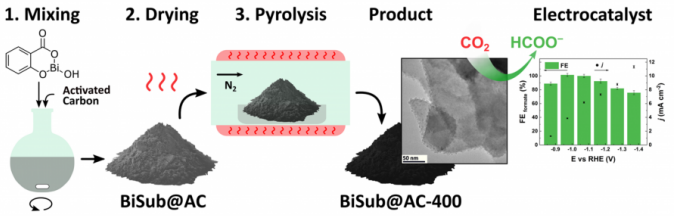
In order to achieve industrial relevant production rates ad selectivity (j > 200 mA cm-2, FE > 90 %), [2] it is not only important to develop new catalytic materials, seeking for lower overpotentials, but also to implement their use in electrochemical cells with similar features to large-scale, industrial electrolyzers.

In this context, the cell configuration, the electrocatalyst loading, the electrode preparation methods, the nature of the membrane and its arrangement, the electrolyte solutions and their pH have great impact on the final catalyst performance. [3-9] Another crucial parameter to enable the large-scale application of Bi electrocatalysts is their stability under operating conditions. Although multi hour stability tests (t > 10 h) are currently included in most studies, only few reports investigate the stability of Bi electrocatalysts in prolonged tests (t > 50 h), and with low emphasis on the optimization of the cell parameters, and how the cell configuration affects the catalyst stability. [4, 5, 7] In this work, we used a bismuth-based material we developed with a straightforward and scalable method. [1] The obtained BiSub@AC-400 material consists of small and highly dispersed Bi NPs (Ø ~ 6 nm) supported on activated carbon (AC). In a H-cell configuration, the electrocatalyst shows complete selectivty (FE > 99%) at E = -1.07 V vs RHE in CO2-saturated 0.5 M NaHCO3 electrolyte and high stability, mantaining j ~ 4 mA cm-2 at E = -0.97 V vs RHE for 48 h, therefore promising for scale up applications. [1]

Seeking for the implementation of the BiSub@AC-400 electrocatalyst use, we present a systematic study of the cell parameters for the prolonged application (t = 65 h) at industrially relevant current densities in a GDE in a two-compartment flow cell.

While the investigation and improvement of the cell parameters are often neglected in flow cell system studies, we demonstrated that these are critical factors to achieve the optimal exploitation of an electrocatalyst at high current densities. For example, we investigated how the CO2 and electrolyte flow, the membrane and electrolyte combination, the pH, and gas feed contaminants can influence the output performance and the catalyst stability. We proved that the tuning of the cell parameter combinations is essential to ensure high selectivity, activity and stability for the CO2-to-formate electrochemical conversion. Upon optimization, we obtained a final set up able to maintain FE > 70 % for 65 h at j = 100 mA cm-2.

FIGURES



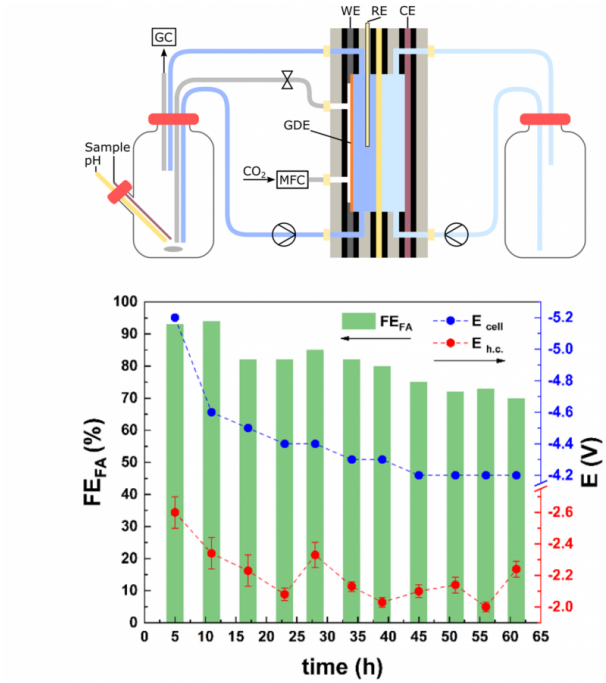


FIGURE 1

Bismuth-based electrocatalyst synthesis

representation of the BiSub@AC-400 catalyst synthesis [1].

FIGURE 2

Flow CO2-to-formate electrochemical conversion

Top) Flow cell representation and bottom) chronopotentiometry at 100 mA cm-2 in 0.5 M KHCO3 catholyte (pH= 7.5 control) and 0.5 M H2SO4 anolyte. FE formate (green bars), E cell (blue dots) and E h.c. (red dots).

KEYWORDS

CO2 | flow cell | electrocatalysis | formate

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