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Production of formate from CO₂ gas: towards flow through enzymatic reactors

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PURPOSE OF THE ABSTRACT

As mentioned in the last IPCC report, a drastic reduction of anthropogenic CO₂ emissions is mandatory to follow pathways that limit global warming to 1.5°C above pre-industrial levels in 2100.[1] To achieve this objective, global CO₂ emission must reach net zero in the foreseeable future (2040 to 2055). In this context, the carbon capture, utilization and recycling appears as a key challenge. CO₂ should not be seen anymore as a waste but as an alternative carbon feedstock to produce platform chemicals and energy carriers.[2, 3] However, the production of platform molecules from CO₂, such as methanol or formate, presents some drawbacks. CO₂ is thermodynamically stable and its difficult chemical activation has incited the scientific community to develop new heterogeneous catalysts. A promising alternative lies in biocatalytic processes, as they run on relatively mild conditions, are ecologically-friendly and highly selective.[4, 5]

Few biocatalysts including enzymes and bacteria have been studied for the conversion of CO₂. Amongst them, formate dehydrogenases (FDHs) have been widely used, especially the commercial one from *Candida Boidinii* (CbFDH). However, besides the low solubility of CO₂ in aqueous solutions, the use of FDHs presents two major limitations. The first limitation lies in the fact that most FDHs, including CbFDH, exhibit low CO₂-reducing activities. Few oxygen-stable FDHs have demonstrated superior CO₂-reducing properties including FDH from *Methylobacterium extorquens* AM1 (MeFDH).[6] The second limitation lies in the fact that FDHs require the loosely bound cofactor nicotinamide adenine dinucleotide (NAD) in its active reduced form, 1,4-NADH. As NAD is relatively unstable and expensive, it has to be regenerated in situ. In the last years, various strategies have been developed to selectively reduce NAD⁺ to 1,4-NADH.[7] However, most of those strategies are nonselective, inefficient, complex (by-products generation) and/or expensive. Amongst them, the enzymatic regeneration using phosphite dehydrogenases (PtDH) is highly selective and rather clean (no additional by-products).[5]

Recently, we could produce formate from CO₂ gas in a flow through biocatalytic reactor via the co-immobilization of these two enzymes (PtDH and MeFDH) together with the cofactor NAD⁺ within porous carbon monoliths (Figure 1).[8, 9] Polyethylene glycol-based cross-linkers were employed to overcome the low solubility of CO₂ and immobilize both enzymes and cofactors. We could produce 4 mmol formate per mg of MeFDH during 3 days, which is the highest formate productivity reported to date regarding biocatalytic processes. In this communication, we will present and discuss our latest results regarding the enzymatic production of formate from CO₂ gas.

FIGURES

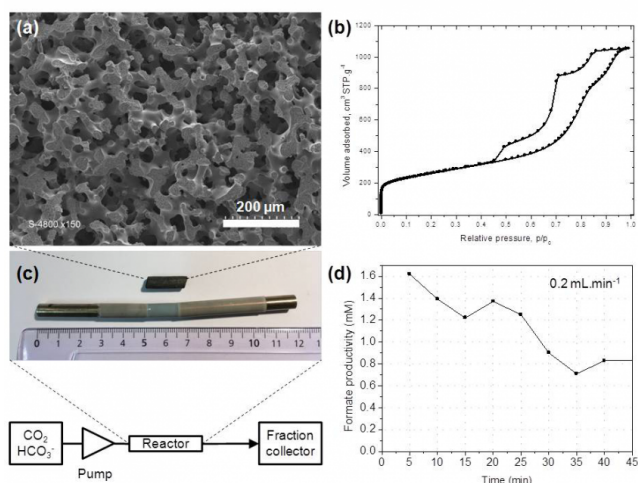


FIGURE 1

Flow through bioreactor

(a) SEM micrograph and (b) N₂ sorption isotherm at 77K of the carbon monolith employed for the preparation of the bioreactor. (c) Schematic representation of the flow through reactor. (d) Formate productivity over time.

FIGURE 2

KEYWORDS

CO₂ conversion | Biocatalysis | Flow-through reactor | Porous monolith

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