

# Improving trade-offs in the figures of merit by coupling the single-pass glycerol oxidation using Ni-Co foams with the continuous gas-phase electroreduction of CO<sub>2</sub> to formate

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## Highlights

- Continuous gas-phase operation at the cathode.
- Coupling a more relevant oxidation reaction than conventional oxidation reactions.
- High formate concentrations of up to 359 g L<sup>-1</sup> with high Faradaic efficiencies of 95 %.
- DHA productions of 0.434 mmol m<sup>-2</sup> s<sup>-1</sup> with the implementation of Ni-Co foam-based anodes.

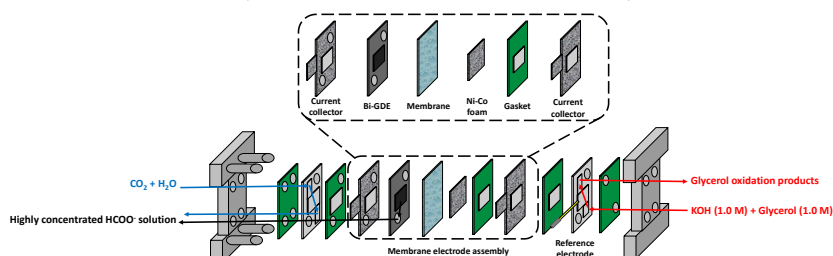
## 1. Introduction

The electrocatalytic reduction of CO<sub>2</sub> holds promise as an alternative for energy storage and valuable product generation, such as formic acid (HCOOH) or formate (HCOO<sup>-</sup>) [1]. Continuous gas-phase CO<sub>2</sub> electroreduction has demonstrated significant potential in producing high concentrations of HCOOH or HCOO<sup>-</sup> at the cathode, while allowing for oxygen evolution (OER) or hydrogen oxidation (HOR) reactions to occur at the anode. Utilizing a more relevant oxidation reaction, such as glycerol oxidation (GOR), which is a plentiful by-product of current biodiesel production processes [2], proves advantageous. This work successfully couples GOR with continuous gas-phase CO<sub>2</sub> electroreduction to obtain formate, employing Nickel-Cobalt foam-based anodes (Ni-Co foam) [3].

## 2. Methods

In this investigation, we utilized carbon-supported bismuth nanoparticles (Bi/C NPs) as electrocatalysts for the cathode, configuring them into a Gas Diffusion Electrode (Bi/C-GDE). The Bi/C-GDE comprises three layers: a carbonaceous support (Toray carbon paper, TGP-H-60), a microporous layer (MPL), and a catalytic layer (CL), which were deposited using the airbrushing technique. The anode, composed of Ni-Co foam, was fabricated by cathodic electrodeposition of nickel-cobalt electrocatalysts with atomic ratios of 1:2 on commercially available nickel foam substrates (Recemat Ni-4753, 1.6 mm thick) [4].

Both electrodes were assembled with a cation exchange membrane (Nafion 117), conforming the membrane electrode assembly (MEA) as depicted in Figure 1. A Vapour Delivery Module (VDM) was employed to set and feed the CO<sub>2</sub>/water steam mixture (V<sub>c</sub>/A) to 0.02 molH<sub>2</sub>O [molCO<sub>2</sub> cm<sup>2</sup>]<sup>-1</sup> to the cathode side of the filter-press reactor (Figure 1). All experiments were conducted under galvanostatic conditions by supplying a constant current density (j) of 45 mA cm<sup>-2</sup>. A peristaltic pump drove the anolyte

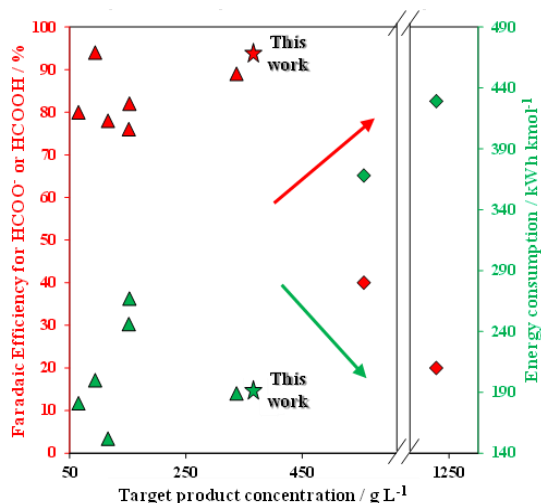


**Figure 1.** Schematic illustration of the CO<sub>2</sub> filter press reactor with its different stacked components, working with (from left to right) a Bi/C-GDE (cathode); a cationic exchange membrane (Nafion 117) and Ni-Co foam electrode (anode) assembled in a MEA-system fed with a humidified CO<sub>2</sub> stream at the cathode side, and an aqueous anolyte (1.0 M KOH + 1.0 M Glycerol) at the anode side, respectively [3].

( $Q_a/A$ ) to the filter press react at a flow rate per geometric electrode surface area of 0.57 and 2.28 mL  $\text{min}^{-1} \text{cm}^{-2}$ , respectively [3].

### 3. Results and discussion

Initial experiments were conducted at  $V_c/A$ ,  $j$  and  $Q_a/A$  of 0.02 molH<sub>2</sub>O [molCO<sub>2</sub> cm<sup>2</sup>]<sup>-1</sup>, 45 mA cm<sup>-2</sup> and 0.57 mL  $\text{min}^{-1} \text{cm}^{-2}$ , respectively, to compare results with previous studies under identical operating conditions, where the OER was catalyzed by a commercial DSA/O<sub>2</sub>-based anode [5]. High HCOO<sup>-</sup> concentrations and Faradaic efficiencies towards this product of 172.5 g L<sup>-1</sup> and 80 % were obtained, respectively, combined with excellent energy consumptions of 221 kWh kmol<sup>-1</sup> under these conditions.



**Figure 2.** Current state of the art for the continuous gas-phase CO<sub>2</sub> electrocatalytic reduction to HCOOH or HCOO<sup>-</sup> [3].

concentrations and Faradaic efficiencies for the target product (Figure 2). Additionally, DHA, the desired product of the Ni-Co-foam anode, was generated with a single-pass production rate of 0.434 mmol m<sup>-2</sup> s<sup>-1</sup>, accompanied by intriguing Faradaic efficiencies nearing 19% [3]. This advancement represents a notable improvement over our prior methodologies involving noble materials like Pt [2].

### 4. Conclusions

A pioneering MEA-reactor was created to enhance the co-valorization of CO<sub>2</sub> and glycerol, demonstrating notable performances at the cathode. This development contributes to an improved balance among the key performance indicators outlined in recent literature. Concurrently, on the Ni-Co foam surface, the GOR facilitates a compelling DHA production, reaching up to 0.434 mmol m<sup>-2</sup> s<sup>-1</sup>.

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### Keywords

“Continuous CO<sub>2</sub> electroreduction”, “Membrane electrode assembly”, “Single-pass glycerol oxidation reaction”, “Ni-Co foam-based anodes”

Nevertheless, the results in terms of target product concentrations fall short compared to those obtained with the DSA/O<sub>2</sub> for OER (337 g L<sup>-1</sup>) [5]. To alter the selectivity of GOR towards higher value-added C<sub>3</sub>-products such as dihydroxyacetone, the  $Q_a/A$  was modified from 0.57 to 2.28 mL  $\text{min}^{-1} \text{cm}^{-2}$ . Under these conditions, HCOO<sup>-</sup> concentrations increased to 359 g L<sup>-1</sup>, improving Faradaic efficiency and energy consumption to 95 % and 192 kWh kmol<sup>-1</sup>, respectively [3]. The improved performance of the cathode may be attributed to an optimized balance between membrane hydration and higher K<sup>+</sup> availability near the catalyst layer of Bi/C-GDE (vital for CO<sub>2</sub> reduction products and to reduce the hydrogen evolution reaction) [3].

Considering these results, the best trade-off between the main figures of merit was achieved, surpassing our previous work paired with the OER in terms of