

Single-Pass Electrooxidation of Glycerol on Bismuth-Modified Platinum Electrodes as an Anodic Process Coupled to the Continuous CO₂ Electroreduction toward Formate

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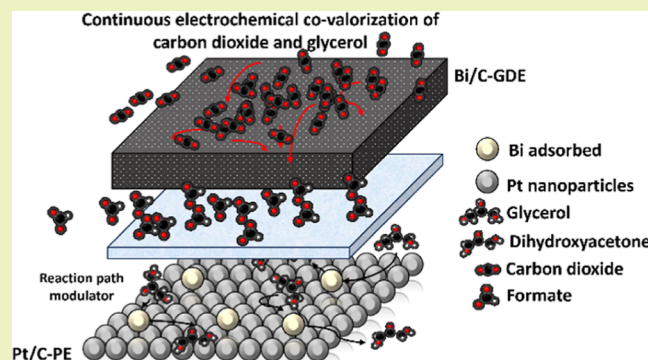
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ABSTRACT: CO₂ electroreduction has emerged as a promising strategy for reducing emissions while simultaneously generating valuable products, particularly formic acid/formate. To further enhance the sustainability of this process, the traditional oxygen evolution reaction at the anode can be replaced by a more interesting reaction like glycerol oxidation to high value-added products, in a covalorization approach. In this study, the effect of the presence of a bismuth (Bi) atom supplier (Bi₂O₃ particles) in the anolyte solution during the glycerol electrooxidation process on platinum (Pt) electrodes coupled with the electroreduction of CO₂ to formate is investigated for the first time, operating in a continuous mode with a single pass through the reactor. The results reveal that in the cathode, significant HCOO[−] production, with Faradaic efficiencies reaching 93%, and modest energy consumption of 208 kW h·kmol^{−1} were obtained in the continuous CO₂ electroreduction to formate using Bi gas diffusion electrodes. On the other hand, in the anode, the presence of Bi₂O₃ particles leads to a significant alteration in the distribution of high-value-added oxidation products obtained. For instance, the anode demonstrates remarkable dihydroxyacetone (DHA) production of 283 μmol·m^{−2}·s^{−1}, surpassing the results obtained with the nonmodified Pt electrodes. The performance of this system offers a promising pathway for the simultaneous coproduction of high-value-added products from both CO₂ and glycerol.

KEYWORDS: single-pass glycerol oxidation reaction, bismuth-modified platinum electrodes, high-value-added product, continuous CO₂ electroreduction, formate, Bi gas diffusion electrodes



1. INTRODUCTION

The electrochemical reduction of CO₂ (CO₂RR) is the subject of countless contributions. This is because this process is a very promising and attractive technology to convert CO₂ into valuable chemicals and fuels using renewable electricity. In this sense, in 2022, some of the most relevant researchers on the topic reported a roadmap in which they analyzed and discussed some relevant and recent advances in different aspects, including progress not only on the fundamental understanding of the reaction and the development and properties of new electrocatalysts but also on the issues and challenges related to the engineering and scaling-up of the process that can remarkably contribute toward the future commercialization of the CO₂RR technology.¹ During this last year, the increasing interest in this process has continued and, as proof of this, numerous and relevant reviews and articles dealing with the

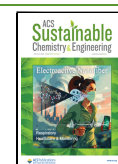
CO₂RR have been published.^{2–23} In addition, due to their interesting and practical applications, the electrochemical reduction of CO₂ to formic acid/formate has been extensively studied.^{5,24–30} It is also widely accepted that for future practical and industrial implementation of the CO₂RR technology, the use of electrochemical reactors working in continuous operation mode is more convenient.^{5,31,32} Besides, the employment of continuous flow conditions for electrochemical reactions has shown to provide relevant benefits over

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batch conditions, including not only better Faradaic efficiencies (FEs), higher selectivities, lower electrolyte loadings, and reduced energy consumption (EC) but also an improved control of the process and less difficulties for a subsequent scale-up.³³ Particularly for CO₂ electroreduction, working in continuous operation mode also significantly contributes to minimize the limitations attributed to mass transport, which allows reaching higher CO₂ conversion rates.³¹ In consequence, in recent years, relevant contributions have been reported dealing with the continuous CO₂ electroreduction to high-added-value products.^{5,34–36} For instance, Fernández-Caso et al.⁵ reviewed the electroreduction of CO₂ to HCOO[−] or HCOOH operating in continuous mode and quantitatively compared the performance of the different approaches in terms of the relevant figures of merit used (current density, HCOOH/HCOO[−] concentration, FE, production rate, and EC).

On the other hand, the oxygen evolution reaction (OER) has been typically the anodic half-cell reaction used in the CO₂RR. However, the sluggish kinetics of the OER and the low industrial value of the O₂ produced at the anode significantly reduce the competitiveness and economic feasibility of this process. In this way, coupling more valuable anodic reactions with CO₂ electroreduction has been the subject of recent and valuable contributions^{37–52} and has emerged as a promising approach to lower the overall cell voltage, and consequently the energy efficiency of the system, and also to simultaneously produce high-added-value products both at the cathode and anode. Among the different anodic processes used as paired reactions with CO₂RR, the electrooxidation of glycerol (GOR, glycerol oxidation reaction) to high-added-value products is one of the most interesting alternatives.^{38,41,43,46,51–53} Glycerol is the major waste product from biodiesel production and can be electrochemically oxidized into a variety of valuable chemicals.^{54–57} In this sense, Verma et al.³⁸ demonstrated that coupling CO₂RR with the electrooxidation of glycerol reduced the power consumption of the system by 53% compared to use of the OER as anodic process. More recently, Junqueira et al.⁴³ reported the simultaneous production of formate both at the anode and cathode from the paired CO₂RR and glycerol electrooxidation at high currents (200 mA cm^{−2}) with FEs of about 96 and 45% at the anode and cathode, respectively. Interestingly, Rumayor et al.⁵⁸ showed that the coproduction of HCOO[−] and dihydroxyacetone (DHA) from the CO₂RR and glycerol electrooxidation, respectively, can be economically feasible for DHA concentrations higher than 1.5 wt % in the anode.

Regarding the electrooxidation of glycerol, noble metal electrocatalysts are the most explored ones.^{57,59–62} In particular, Pt and Pt-based electrocatalysts have been widely used in the literature due to their high activity at different pH conditions. However, its high bond-breaking ability is inconvenient for the obtention of C2 and C3 oxidation products and is also easily poisoned by the CO and other intermediates generated during the glycerol electrooxidation. Among other strategies to overcome these limitations, the use of certain adatoms to decorate the surface of the Pt electrodes and consequently modifying their electrocatalytic properties have been reported to be an interesting approach.^{63–68} For instance, Bi-modified Pt electrodes, including polyoriented and single crystal electrodes, and Pt nanoparticles, displayed interesting properties toward glycerol electrooxidation in an alkaline solution both in fundamental electrochemical experi-

ments^{66,67} and in 3D-printed microfluidic fuel cell devices.⁶⁹ In this context, in this work, we explore the single-pass and continuous electrooxidation of glycerol on bismuth-modified platinum electrodes as an anodic process coupled to the continuous CO₂ electroreduction toward formate. As previously discussed by De Souza et al.,⁶⁶ it is more convenient to directly add a Bi atom supplier (in this case, Bi₂O₃ particles) into the anodic solution to avoid the clear deactivation of the Bi decoration that it is observed when the Pt surface is modified by irreversible adsorption of Bi. In addition, the results obtained will be analyzed and compared with some of our previous findings in which the OER and the glycerol electrooxidation (in absence of Bi) were employed as anodic reactions, while the continuous CO₂ electroreduction toward formate remained unmodified.^{35,36}

2. EXPERIMENTAL SECTION

2.1. Preparation and Characterization of the Electrodes.

Details regarding the synthesis and characterization of the carbon-supported Bi nanoparticles (Bi/C NPs) used as cathode electrocatalysts, as well as the subsequent fabrication and characterization of the gas diffusion electrodes incorporating these Bi nanoparticles (Bi/C-GDE), can be found in some of our previous publications.^{70,71} In brief, Bi/C-GDE is composed of a carbonaceous support (Teflonated Toray carbon paper TGP-H-60), a microporous layer (MPL), and a catalytic layer (CL). The MPL ink was prepared by combining Vulcan XC-72R and poly(tetrafluoroethylene) (PTFE preparation, 60 wt % dispersion on H₂O, Sigma-Aldrich) in a mass ratio of 40/60, and then diluted in isopropanol to achieve a final slurry of 3 wt %. The ink was sonicated for 30 min before it was sprayed with an airbrusher over the carbonaceous support. When the MPL reached a Vulcan XC-72R loading of 2 mg·cm^{−2}, both layers were sintered at 350 °C for 30 min. Subsequently, the CL was sprayed over the MPL using the same technique. The catalytic ink consisted of Bi/C NPs in Nafion (Nafion D-521 dispersion, 5 w/w % in water and 1-propanol, 0.92 mequiv·g^{−1} exchange capacity) with a mass ratio of 70/30, which was then diluted in isopropanol and sonicated in the same conditions as described previously for the MPL. The Bi/C NPs' loading was 0.75 mg·cm^{−2}, as in previous studies for the purpose of comparison.

The Pt particulate electrodes (Pt/C-PE) used as anode were prepared by direct deposition of the carbon-supported Pt nanoparticles (Pt/C) (20 wt %, particle size ≤ 5 nm, Sigma-Aldrich) onto a carbonaceous support (Teflonated Toray carbon paper TGP-H-60) using a similar methodology to that employed for the catalytic layer of the Bi/C-GDEs. The Pt loading deposited over the carbonaceous support was 1.00 mg·cm^{−2}. The physicochemical characterization of the Bi/C-GDE and Pt/C-PE was reported in some of our previous contributions.^{41,71}

2.2. Experimental Setup for Flow Cell Tests. The Bi/C-GDE and Pt/C-PE were used as cathode and anode, respectively, in a continuous filter press electrochemical reactor. Each electrode had a geometric surface area of 10 cm². The experimental setup consisted of a filter press reactor as the core component, along with peristaltic pumps (Watson Marlow 320, Watson Marlow Pumps Group), tanks, and a potentiostat–galvanostat (Arbin Instruments, MSTAT4). The cathodic compartment of the electrochemical reactor was fed with a solution composed of 0.5 M KCl (potassium chloride, pharma grade, PanReac AppliChem) + 0.45 M KHCO₃ (potassium hydrogen carbonate, pharma grade, PanReac AppliChem). Moreover, pure CO₂ was continuously supplied to the cathodic compartment at a flow rate of 200 mL·min^{−1}, similar as previous studies conducted by the group.^{41,70–74}

On the other hand, the anolyte consisted of an aqueous solution of 1.0 M KOH (potassium hydroxide, 85% purity, pharma grade, PanReac AppliChem) + 1.0 M GLY (glycerol, 99% purity, ReagentPlus, Sigma-Aldrich). About 150 mg of Bi₂O₃ particles (Bi₂O₃ powder, 99.999% trace metals basic) per liter (L) of anolyte was added into the anolyte feed tank, and the mixture was

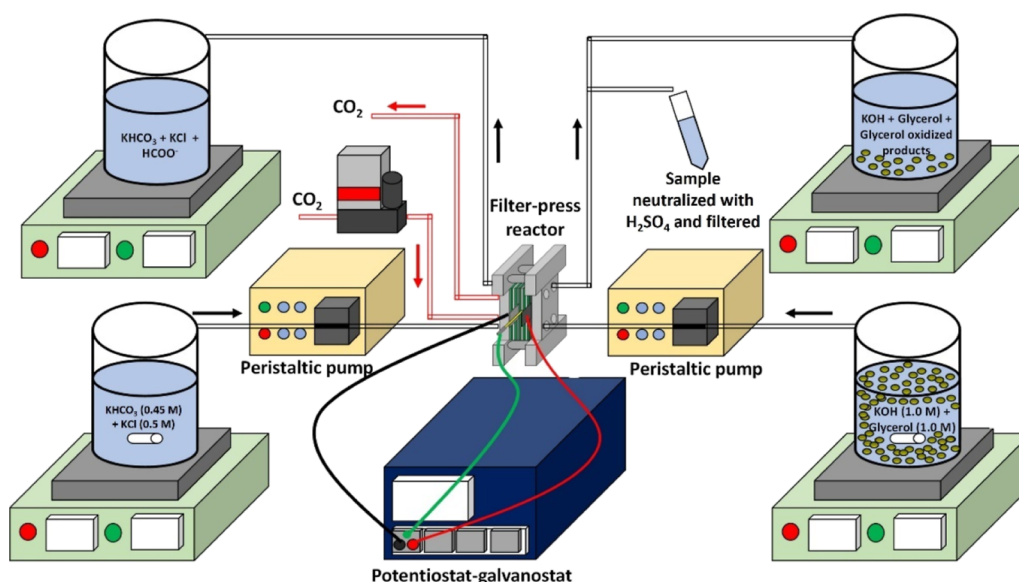


Figure 1. Experimental setup scheme employed for coupling the single-pass GOR to the continuous CO_2RR process to give HCOO^- .

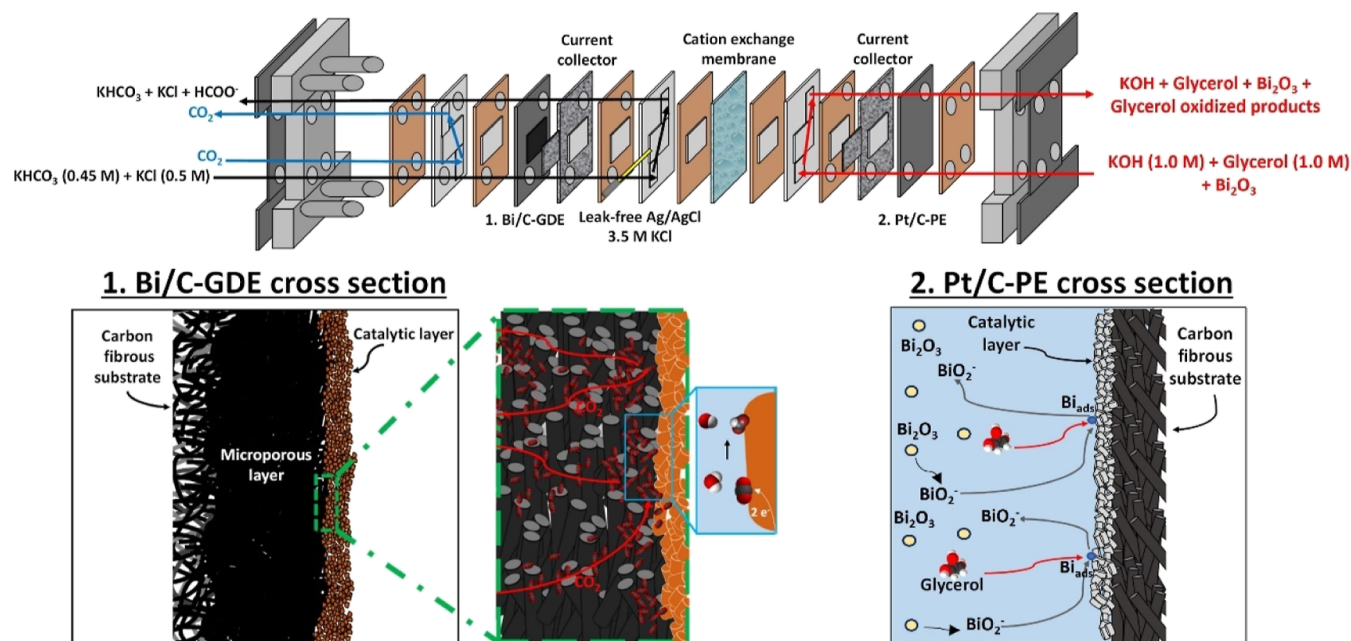


Figure 2. Schematic illustration of the filter press reactor with stacked components, indicating that the continuous CO_2 reaction to HCOO^- takes place on the Bi/C-GDE surface (1) and the single-pass GOR on the catalytic layer of Pt/C-PE (2) in the presence of Bi_2O_3 particles as the Bi atom supplier.

magnetically stirred for 10–15 min before being directly pumped into the electrochemical reactor. These Bi_2O_3 particles in the solution act as a Bi atom supplier. About 2 L of anolyte was prepared per experiment. Figure 1 schematically represents the experimental setup employed in the flow cell experiments.

Figure 2 illustrates the internal structure of the filter press reactor configuration with stacked components (Micro Flow Cell, Electro-Cell, A/s). The cathodic and anodic compartments of the CO_2 electrolyzer are separated by a Nafion 117 cationic exchange membrane (Alfa Aesar). A leak-free Ag/AgCl 3.5 M KCl reference electrode was placed close to the working electrode in the cathodic compartment. All the experiments were performed in duplicate with a duration of 60 min, in continuous mode with a single pass of reactants through the electrochemical reactor in both the cathodic and the anodic compartments. Moreover, all the tests were carried out at ambient conditions of pressure and temperature. At every 15 min, the

samples of the catholyte and anolyte were collected to measure the concentration of HCOO^- and glycerol, respectively. Samples of the anolyte were neutralized using a 1.0 M H_2SO_4 solution (sulfuric acid, 98% purity, pharma grade, PanReac AppliChem) to immediately reduce the pH of the sample to about 2 and stop the Cannizzaro reaction between aldehydes and alcohols. This particularly facilitates the determination of the dihydroxyacetone (DHA) and glyceraldehyde (GLAD) concentrations in alkaline media. The sample was also filtered (nylon syringe filters, 0.22 μm) before being analyzed. The different analytical techniques employed for the quantification of the concentration of HCOO^- , glycerol, and the different oxidized products from GOR are summarized in the Supporting Information. The figures of merit calculated through the eqs S1–S10 were used for the performance assessment of the coupled electrochemical device implemented in this work.

3. RESULTS AND DISCUSSION

3.1. Effects on the CO₂ Electroreduction to Formate.

In this section, we evaluate the effects of the presence of Bi₂O₃ particles in the anolyte during GOR on the performance of the continuous CO₂RR process to HCOO[−] in the cathode. To properly assess the effects of the presence of the Bi₂O₃ particles in the anolyte, the results obtained here have been compared with those obtained under the same experimental and operating conditions but in the absence of Bi₂O₃ particles in the anolyte and reported in some of our previous investigations.⁴¹ Also, previous results obtained in comparable experimental and operating conditions but using the OER at commercial dimensionally stable anodes (DSA/O₂) (Ir- MMO (mixed metal oxide) on platinum) as anodic process have been included in this comparative analysis.⁷⁰ This comparative analysis is displayed in Figure 3 in which the performance of

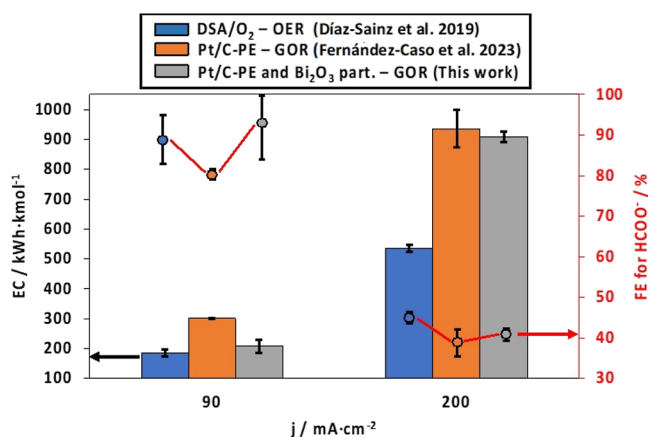


Figure 3. ECs per kmol of HCOO[−] [EC] and FEs for HCOO[−] [FE for HCOO[−]] as a function of the current density supplied [j] obtained for the different works with the same experimental setup but different anode systems; Diaz-Sainz et al. 2019 (ref 70) with a commercial DSA/O₂ for the OER (in blue); Fernández-Caso et al. 2023 (ref 41) with a Pt/C-PE for the GOR (in orange); and Bi-modified Pt/C-PE for the GOR (this work, in gray).

the CO₂RR to HCOO[−] in terms of the EC per kmol of HCOO[−] [EC] and FE of HCOO[−] [FE for HCOO[−]] attained in the cathode are compared. In addition, detailed results of the figures of merit, including the concentration ([HCOO[−]]) and production rate (rHCOO[−]) for this product, are summarized in Table S1.

The results shown in Table S1 indicate that, in the presence of Bi₂O₃ particles and working with a catholyte flow per geometric surface area of 0.15 mL·min^{−1}·cm^{−2} and a current density of −90 mA·cm^{−2}, high concentrations and production rates for HCOO[−] of about 7.9 g·L^{−1} and 4.37 mmol·m^{−2}·s^{−1}, respectively, were obtained in the cathode. These values are clearly better than those obtained in the absence of Bi₂O₃ particles (6.8 g·L^{−1} and 3.76 mmol·m^{−2}·s^{−1}, respectively) and also better than those using the OER as an anodic reaction (7.5 g·L^{−1} and 4.18 mmol·m^{−2}·s^{−1}). These results represent an increase of approximately 16% in comparison with those obtained in the absence of Bi₂O₃ particles, and about 4.5% in comparison with those obtained using the OER on a DSA/O₂ electrode. It is also worth noting that, in the presence of Bi₂O₃ particles, FEs toward HCOO[−] of up to 93% were also obtained. These FEs are higher than the FE values of 80 and 89% obtained in the absence of Bi₂O₃ particles and using the

OER, respectively. It is also interesting to mention that, working at −90 mA·cm^{−2}, the high HCOO[−] production obtained at the cathode, together with a relatively low cell voltage of −3.62 V, allows achieving ECs of only 208 kW h·kmol^{−1}. This value represents a remarkable drop of about 30% compared to the EC obtained when Bi₂O₃ particles were not added to the anolyte (Figure 3).⁴¹ This EC is similar to the value of 186 kW h·kmol^{−1} obtained when the OER on a DSA/O₂ electrode was used as a coupled anodic reaction.

As also shown in Table S1, for experiments performed at lower catholyte flow per geometric surface area (0.07 mL·min^{−1}·cm^{−2}) and more commercially relevant^{5,75} current densities of −200 mA·cm^{−2}, the HCOO[−] concentrations obtained in the presence and in the absence of Bi₂O₃ particles on the anolyte were very similar, 16.40 vs 15.60 g·L^{−1}, respectively. In terms of FE toward HCOO[−], a value of 41% was obtained, which is also similar to that obtained in the absence of Bi₂O₃ particles (39%) and that obtained when the OER is used as the anodic reaction (45%), Figure 3. Under these high current density conditions, similar cell voltages were found in the absence (−6.94 V)⁴¹ and in the presence (−6.91 V) of Bi₂O₃ particles in the anolyte (Table S1 of the Supporting Information). Consequently, similar ECs of 936 and 909 kW h·kmol^{−1} were obtained. However, as shown in Figure 3 and in Table S1 of the Supporting Information, these ECs are much higher than that obtained using the OER as an anodic reaction, which is only about 535 kW h·kmol^{−1} (−4.67 V).

These results indicate that, at a current density of −90 mA·cm^{−2}, when Bi₂O₃ is added in the anolyte, the figures of merit reported for the CO₂ electroreduction showed an interesting improvement in comparison with previous findings when the GOR in the absence of Bi₂O₃ or the OER was used as coupled anodic reactions. Nevertheless, this improvement is not observed at the higher current densities of 200 mA·cm^{−2}. At these high current densities and despite the results in terms of HCOO[−] production, FE, and ECs being similar in the absence and presence of Bi₂O₃ for the GOR, these are clearly worse than those observed when the OER is the coupled anodic reaction.

3.2. Effect of Addition of Bi₂O₃ Particles in the Anolyte in the Continuous Electrooxidation of Glycerol.

This section will be mainly focused on the effect of the incorporation of Bi₂O₃ particles in the anolyte on the distribution of products obtained in the continuous electrooxidation of glycerol in alkaline solution coupled to the electroreduction of CO₂ to formate. As in the previous section, the results obtained will be compared with those previously reported in comparable experimental and operating conditions but in the absence of the Bi₂O₃ particles in the anolyte.⁴¹ All experiments were performed at an anolyte flow rate per geometric anode surface area (Q_a/A) of 1.71 mL·min^{−1}·cm^{−2}. As reported in this previous contribution,⁴¹ the relatively high anolyte flow rate values of up to 1.71 mL·min^{−1}·cm^{−2} allowed us to maximize the formation of DHA in the output anolyte stream, since this compound can suffer a degradation reaction in highly concentrated alkaline environments, and therefore, it is important to reduce the DHA residence time in the alkaline anolyte before its neutralization with the acidic solution.^{41,66}

Before describing the main results obtained during the flow electrochemical experiments and to better understand the effect of the presence of Bi₂O₃ on the electrooxidation of glycerol in an alkaline solution on Pt electrodes, some

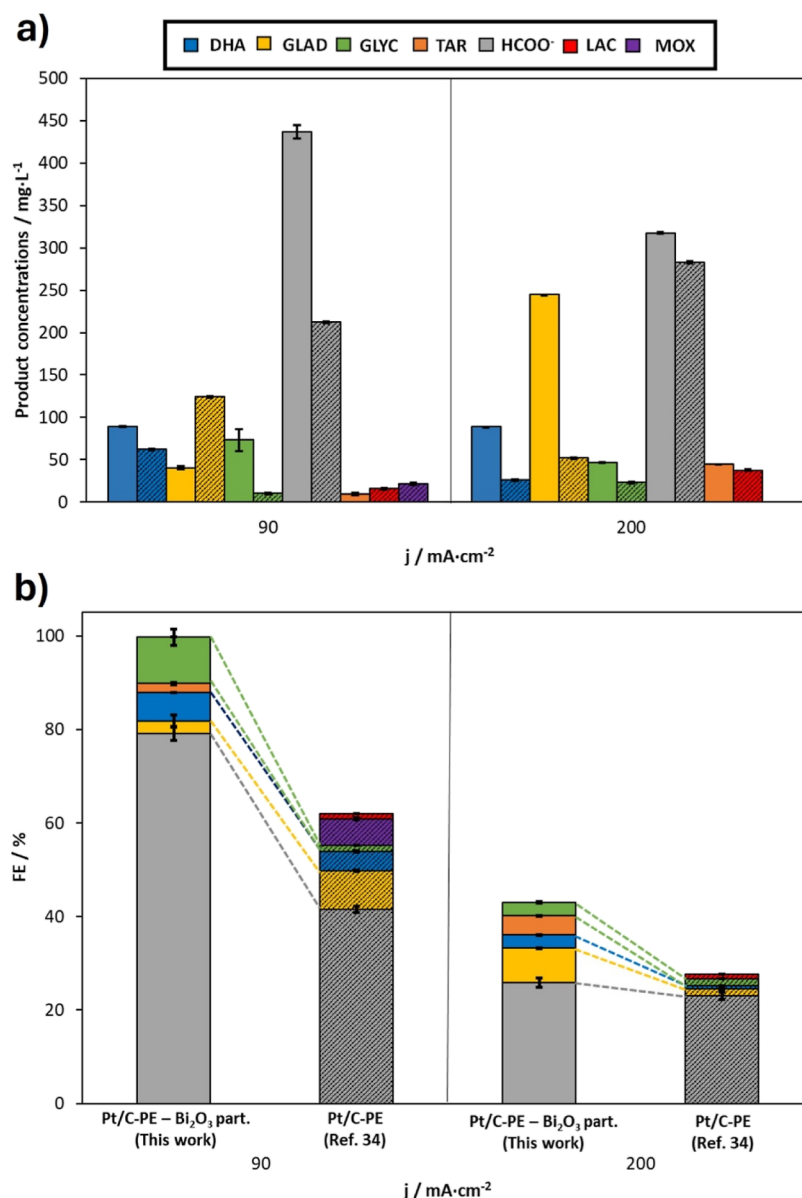


Figure 4. (a) Concentrations and (b) FEs of the different oxidized products from GOR in output anolyte stream when the Pt/C-PE was employed in the presence of Bi₂O₃ particles (this work as nonstriped bars) and previous approach with the Pt/C-PE (ref 34 as striped bars) as a function of the current density (j) supplied to the filter-press reactor.

preliminary voltammetric experiments were performed. Figure S1 shows the results obtained. Figure S1a displays the voltammetric response of a portion (geometric area of about 1 cm²) of the Pt/C-PE electrode in 0.5 M H₂SO₄ solution. As expected, the voltammetric features observed are characteristic of a clean and polyoriented Pt surface.^{76,77} The electroactive surface area (ECSA) of the Pt/C-PE electrode was estimated from the charge involved in the so-called hydrogen region, assuming a value of 0.21 mC cm⁻² for the total charge after the subtraction of the double-layer charging contribution.^{76,77} For a portion of the electrode of about 0.25 cm² (geometric area), a value of about 27 cm² of the ECSA was obtained, that is, about 108 cm² (ECSA) per cm² (geometric area). Figure S1b shows the voltammetric responses for the electrooxidation of glycerol in the presence and in the absence of Bi₂O₃ as the Bi atom supplier. In these voltammetric experiments and similar to the flow cell experiments (see the Experimental Section), before the electrochemical experiments, a certain amount of

Bi₂O₃ particles was added into the solution and magnetically stirred for 10 min before being used. Inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer, Optima 4300 D) measurements indicated that the concentration of Bi dissolved in solution from the Bi₂O₃ particles is about 30 ppm during the experiments. It is also worth noting that, as previously reported by Vivier et al.,⁷⁸ the Bi₂O₃ particles are partially dissolved into ionic BiO₂⁻ species in the alkaline solution, which are subsequently adsorbed and converted into Bi adsorbed species. Figure S1b shows that the addition of Bi₂O₃ particles shifts the onset potential of the oxidation of glycerol by about 200 mV to lower potentials. Similar observations have been reported in previous contributions.^{65–67,69,79} This is due to the irreversible adsorption of Bi adatoms at the surface of the Pt nanoparticles, which is well-known to enhance the electrocatalytic properties of Pt for many different processes including glycerol electrooxidation.^{64–67,69}

For the experiments performed in continuous operation of the filter press reactor at a current density of $90 \text{ mA}\cdot\text{cm}^{-2}$, Figure 4a, the addition of Bi_2O_3 particles allowed increasing of the DHA concentration from 62 (in the absence of Bi_2O_3 particles) to $89 \text{ mg}\cdot\text{L}^{-1}$, which represents an increase of up to 43%. This increase represents an interesting FE of about 6% (Table S2 of the Supporting Information). Working at these operating conditions of $90 \text{ mA}\cdot\text{cm}^{-2}$, GLAD, as the other intermediate of the GOR, was obtained with low concentrations of only $40 \text{ mg}\cdot\text{L}^{-1}$ in the output anolyte stream compared with the value of $124 \text{ mg}\cdot\text{L}^{-1}$ obtained in the absence of Bi_2O_3 particles (Figure 4a). Both intermediates are in equilibrium (isomerization reaction),⁸⁰ and the presence of higher amount of DHA justifies the minor GLAD formation.^{41,65,66} Thus, the FE for GLAD is 2.75%, almost 66% lower than that obtained in the absence of Bi_2O_3 particles in the anolyte (Table S3). It is worth noting that tartrate (TAR), a three-carbon GOR product, was detected under these operating conditions of $90 \text{ mA}\cdot\text{cm}^{-2}$. This finding contrasts with our previous results without Bi_2O_3 .⁴¹ TAR formation comes from the subsequent oxidation of the glycerate (GLCA) anion, which in turn comes from GLAD oxidation. This chemical route justifies the low GLAD concentrations detected.^{81–83} The low TAR concentrations of about $10 \text{ mg}\cdot\text{L}^{-1}$ (Figure 4a) and the eight electrons involved in the corresponding oxidation reaction give rise to FE toward this product of about 2% (Table S4). Another chemical route for further oxidation of the GLAD intermediate involves the production of glycolate (GLYC) from the GLCA anion. This two-carbon compound (GLYC) can be formed with concentrations and FE of $73 \text{ mg}\cdot\text{L}^{-1}$ and 9.9%, respectively (Table S5 of the Supporting Information). These results again contrast with those obtained in the absence of Bi_2O_3 particles and point out the improvement in the formation of the GLYC anion instead of the formation of the GLAD intermediate. In addition, another interesting compound formed through this chemical route involves the HCOO^- production, which is found to be the main oxidized product quantified from the GOR with a concentration and FE of up to $437 \text{ mg}\cdot\text{L}^{-1}$ and 80%, respectively (Figure 4a,b). At current densities of $90 \text{ mA}\cdot\text{cm}^{-2}$, the HCOO^- production was increased in the presence of Bi_2O_3 particles by up to 106% (Table S6 of the Supporting Information). The analytical quantification of all these oxidized products from GOR as well as the calculation of their corresponding FEs, allowed us to estimate a carbon balance of 6.94% and an overall FE of 99.80%, working at $90 \text{ mA}\cdot\text{cm}^{-2}$. These findings indicate that most of the carbon products have been successfully identified (Table S7).

Similar experiments were conducted at a more commercially relevant current density of $200 \text{ mA}\cdot\text{cm}^{-2}$. Similar to the experiments performed at $90 \text{ mA}\cdot\text{cm}^{-2}$, HCOO^- was again found to be the main oxidized product from GOR, although lower amounts of other oxidized products such as DHA, GLAD, and GLYC were also detected (Figure 4a). At these high current densities, the addition of Bi_2O_3 particles into the anolyte solution did not lead to a significant drop of the anode potential (Table S1 of the Supporting Information), in comparison to that in the previous experiments at $90 \text{ mA}\cdot\text{cm}^{-2}$, and a similar high cell voltage of up to -6.91 V was found, which is mainly attributed to the high anode potential (4.99 V vs Ag/AgCl). In terms of product distribution, at $200 \text{ mA}\cdot\text{cm}^{-2}$, the DHA concentration obtained drastically

increased from 26 to $88 \text{ mg}\cdot\text{L}^{-1}$ (Figure 4a) in the presence of Bi_2O_3 particles, thus leading to an FE of about 2.7% (Figure 4b). Although DHA can be formed in higher amounts at these current densities, the reoxidation of this compound into other more oxidized ones can also occur. Interestingly, as shown in Figure 4a,b and in Table S3, the results also indicate a remarkable increase in the formation of the GLAD in the presence of Bi_2O_3 particles. The GLAD concentration and FE increase from 52 to $245 \text{ mg}\cdot\text{L}^{-1}$ and from 1.5 to 7.5%, respectively. Regarding the production of TAR, a significant improvement is observed. The results obtained show that the TAR concentration and FE also increase from 9.6 to $44 \text{ mg}\cdot\text{L}^{-1}$ and from 2 to 4%, respectively, when the current density is increased from 90 to $200 \text{ mA}\cdot\text{cm}^{-2}$. A similar enhancement is again detected for GLYC concentrations and its FE, which increase up to $46 \text{ mg}\cdot\text{L}^{-1}$ and 2.8%, respectively, in the presence of Bi_2O_3 particles in comparison with the $23 \text{ mg}\cdot\text{L}^{-1}$ and 1.4%, respectively, reported in the absence of Bi_2O_3 particles under similar experimental and operating conditions. Finally, the results obtained at $200 \text{ mA}\cdot\text{cm}^{-2}$ evidence that although HCOO^- still is the main oxidized product, both the HCOO^- concentration and FE significantly decrease in comparison with the results obtained at $90 \text{ mA}\cdot\text{cm}^{-2}$. The results show a HCOO^- concentration and FE of about $317 \text{ mg}\cdot\text{L}^{-1}$ and 25%, respectively. These values are rather similar to those observed at the same current density ($200 \text{ mA}\cdot\text{cm}^{-2}$) but in the absence of the Bi_2O_3 particle in which values of about $283 \text{ mg}\cdot\text{L}^{-1}$ and 23%, were obtained, respectively. However, as shown in Figure 4b and Table S6, the FE toward HCOO^- decreases from 79 to 25% when the current density is increased from 90 to $200 \text{ mA}\cdot\text{cm}^{-2}$. In this sense, it is also worth noting that, as shown in Table S7, the glycerol conversion decreased from 7.47 (at $90 \text{ mA}\cdot\text{cm}^{-2}$) to 5.14% (at $200 \text{ mA}\cdot\text{cm}^{-2}$). This finding suggests that the parasitic OER seems to be enhanced at a major degree instead of GOR (which is thermodynamically more favorable) at these more positive anode potentials of up to 4.99 V vs Ag/AgCl , which justifies obtaining higher glycerol concentrations at $200 \text{ mA}\cdot\text{cm}^{-2}$ than at $90 \text{ mA}\cdot\text{cm}^{-2}$ in the output anolyte stream, as illustrated in Figures S2 and S3 of the Supporting Information. Also, considering this finding, the carbon balance and overall FE estimated for the experiments at relevant current densities of $200 \text{ mA}\cdot\text{cm}^{-2}$ were 4.46 and 43.0%, respectively (Figure S4 and Table S7).

In this work, the effects of the presence of Bi_2O_3 (acting as Bi atoms supplier during the experiments) in the anolyte in the single-pass electrooxidation of glycerol on platinum electrodes coupled to the continuous CO_2 electroreduction toward formate have been shown. The results obtained indicate that the continuous CO_2 electroreduction toward formate displays a slight improvement in terms of EC, FE, and HCOO^- concentration in comparison with the results obtained in the absence of Bi_2O_3 . However, in comparison with the use of the OER as coupled anodic reaction, the GOR is still non-competitive at high current densities of $-200 \text{ mA}\cdot\text{cm}^{-2}$, although interesting results were observed at $-90 \text{ mA}\cdot\text{cm}^{-2}$. Regarding the single-pass electrooxidation of glycerol on platinum electrodes in alkaline solution, the results clearly show that the presence of Bi_2O_3 significantly modifies the distribution of products obtained also including the detection of products (TAR), which are not observed in the absence of Bi_2O_3 . Also, interesting findings were obtained at $90 \text{ mA}\cdot\text{cm}^{-2}$ in terms of accumulated FE (almost 100%) although this

significantly decreases to about 43% at higher current densities (200 mA·cm⁻²).

4. CONCLUDING REMARKS

The innovative continuous system developed in this work has led to a more relevant modification of the distribution of glycerol oxidation products compared to that in our previous work.⁴¹ The presence of Bi₂O₃ (acting as a Bi atom supplier during the experiments) in the anolyte has resulted in the higher production of three carbon products, such as DHA or TAR, in the output anolyte stream. In addition, this enhancement is observed even at high and commercially relevant current densities of 200 mA cm⁻². This can be attributed not only to the shorter residence time in the alkaline anolyte prior to neutralization with H₂SO₄ but also to a change in the reaction mechanism due to the presence of adsorbed Bi species during the electrochemical experiments. Interestingly, at a current density of -90 mA·cm⁻², the presence of Bi₂O₃ in the anolyte also induces a slight improvement of the EC, FE, and HCOO⁻ concentration during the continuous CO₂ electroreduction toward formate. Despite obtaining these promising results in the continuous coelectrovalorization of CO₂ and glycerol, more work specifically oriented to the use of humidified CO₂ streams at the cathode in order to obtain higher HCOO⁻ concentrations is still required.⁶⁴ This continuous CO₂ electroreduction using humidified CO₂ streams should be also coupled with improvements in the GOR to produce higher-value three-carbon products.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c07131>.

Experimental details for voltammetric studies, description of the analytical techniques used for the quantification of products, details of the main figures of merit used, oxidation reactions of glycerol to the different products, ERCO₂ and comparison with previous papers, voltammetric response of the Pt/C-PE in 0.5 M H₂SO₄ and in 1 M KOH with and without GLY, different glycerol oxidation products, infrared spectra, and calibration plot for the quantification of glycerol in the anolyte output stream, and carbon balance for the anolyte stream in the presence of Bi₂O₃ at different current densities (PDF)

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Notes

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