CO_2 electroreduction to formate: continuous single-pass operation in a filter-press reactor at high current densities using Bi Gas Diffusion Electrodes

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Abstract

Electrocatalytic reduction of CO_2 has been taken into consideration as a fascinating option to store energy from intermittent renewable sources in the form of chemical value-added products. Among the different value-added products, formic acid or formate is particularly attractive since it can be used as a fuel for low-temperature fuel-cells and as a renewable hydrogen carrier. Very recently, a rapidly increasing number of studies have revealed Bi as a promising electrocatalytic material for the CO_2 electroreduction to formate, but the performance of Bi electrodes operating in a continuous mode and high current density (j) has been hardly investigated yet. Thus, this work aims at studying the CO_2 electroreduction to formate working in a continuous mode in a filter-press-reactor at a j up to 300 $mA \cdot cm^{-2}$ using Bi electrodes. Bismuth Gas Diffusion Electrodes (Bi-GDEs) were fabricated from carbon-supported Bismuth-nanoparticles. The influence of j and the electrolyte flow/area ratio in the performance of the Bi-GDEs towards formate were

evaluated. Working at j of 300 mA·cm^{-2}, a concentration of 5.2 g formate·L^{-1} with a faradaic efficiency (FE) and rate of 70% and 11 mmol·m^{-2}·s^{-1}, respectively were achieved. Lowering the j to 90 mA·cm^{-2}, formate concentrations of up to 7.5 g·L^{-1} could be obtained with an excellent FE of 90%. Interestingly, the highest concentration of formate obtained was 18 g·L^{-1}, but at expenses of an important decrease in FE. Although the results of this study are interesting and promising, further research is required to increase formate concentration for a future implementation at industrial scale.

Keywords

- CO_2 electroreduction
- Bismuth nanoparticles
- Formate
- GDEs (Gas diffusion electrodes)
- Continuous filter-press cell

1. Introduction

The concentration of carbon dioxide (CO_2) in the atmosphere has exceed the limit of 400 ppm [1]. It is critical to reduce emissions of CO_2 in order to mitigate climate change [2–4]. CO_2 emissions to atmosphere can be reduced by different strategies, such as improving efficiency in energy use, reducing reliance on carbon-based fuels or strategies based on capture and sequestration of CO_2 (CCS) and capture and utilization of CO_2 (CCU) [5]. In the last years, CO_2 valorisation into products of interest has been considered as an attractive option [6,7], because it allows tackling the problem of reducing CO_2 emissions, and at the same time, the CO_2 conversion into useful products [8,9].

CO_2 electroreduction is particularly interesting for CCU, since it is an attractive option for storing the excess of renewable sources of energy (e.g. solar or wind energy) in the form of chemical value-added products [10–15]. One of the main issues for a wider implementation of renewable energy is its intermittence. In this sense, the value-added products obtained by CO_2 electrochemical reduction could be used as fuels, adjusting the production with the consumption and making it possible to store energy for its use when needed (i.e. when these is lack of renewable supply) [16]. Among these value-added products, carbon monoxide (CO) [17,18], hydrocarbons (CH_4 or C_2H_4) [19,20], alcohols (CH_3OH or C_2H_6O) [21,22] or formic acid (HCOOH) [23,24] can be obtained.

One of the most engaging products of CO_2 electrocatalytic reduction is formic acid or formate (depending on pH), which is used in a wide variety of industries. Moreover, in the last years, formate is receiving increasing attention due to its use as a renewable hydrogen carrier molecule [25,26] and also as a fuel for fuel-cells [27,28].

In previous studies, different materials have been used as electrocatalysts in the electroconversion of CO_2 to give formate, for instance lead [29], indium [30], zinc [17],

cobalt [31], palladium [32] and especially tin [33–41]. Very recently, bismuth has started to be considered as a promising electrocatalytic material for the CO_2 electrocatalytic reduction to obtain formate at lower potentials than other metals, with a rapidly growing number studies using Bi in different forms [42-66]. Firstly, Zhang et al. [42] described the use of BiOCl nanosheets under ambient conditions in the electrochemical conversion of CO_2 to give formate with a maximum faradaic efficiency (FE) of 92% and a current density (j) of 3.7 $mA \cdot mg^{-1}$ at -1.5 V. Additionally, Zhong et al. [43] studied the electrochemical performance for CO_2 towards formate using bismuth dendrites on treated carbon paper as electrocatalyst in the working electrode, achieving a FE of 96.4% with a j of 15.2 $mA \cdot cm^{-2}$ at -1.8 V. More recently, the latest studies have performed CO_2 electrochemical conversion to formate working with different electrode configurations: electrodes based on bismuth nanoparticles synthesized on cupper surface [44,45,65,66]; bismuth nanoparticles synthesized on titanium substrate [46] and cupper substrate [47]; oxide-derived Bi films [48–52,63]; Bi nanosheets [53,54,64] or carbon-supported Bi nanoparticles [55]. All these studies above mentioned have been carried out in an aqueous bicarbonate medium with the exception of Zhang et al. [56] and Atifi et al. [57], which were done in a non-aqueous medium such as MeCN. The studies mentioned previously show promising results, which explains the growing attention to the study of the electrochemical valorisation of CO_2 to obtain formate using Bi as electrocatalyst. However, it is important to note that all these references have studied the CO_2 electrocatalytic reduction to give formate in a H-type electrochemical cell with two compartments. In the H-type configuration, both compartments are separated by a piece of membrane (e.g. Nafion 115 [42,43,58] , Nafion 117 [44,46,49,53,55,59] or Nafion 212 [51,56,57,60,65]), but the catholyte and the anolyte are not pumped to their respective compartments of the electrochemical cell during the CO_2 electroreduction to give

formate. High values of FE have been obtained, around 90 % (see Table S1 in the Supporting Information). Although some studies reported formate rate values, neither formate concentration or consumption of energy were provided. As can be seen in Table S1, the maximum j supplied to the electrochemical cell was 60 mA·cm^{-2} [58], with the exception of the study by García de Arquer et al. [50]. As a part of a comprehensive work on the characterization of 2D bismuth-based catalyst and the assessment of their performance for CO_2 electroreduction to formate in a three-electrode system and in H-cell setup, Garcia de Arquer et al [50] also mention the use of a flow-cell configuration supplying 200 mA·cm^{-2} and giving FE of 90%, but no more details about the flow-cell experiments are reported. As shown in Table S1, previous literature has not worked in a continuous mode with high values of current density supplied. These conditions will be necessary for an application at commercial scale in the future. Moreover, all the literature published using Bi have not reported formate concentration and energy consumption values, essential variables to assess the relevance of the electrochemical process. A study of the influence of variables has not been done either in order to optimise the electrochemical process of CO_2 to formate. In order to develop and improve the use of Bi as catalyst in the CO_2 electroreduction to obtain formate, studies in flow-cell operating in a continuous mode with a higher j than that reported previously are definitely needed. Alike, an assessment of the formate concentration and consumption of energy must also be carried out, since achieving high product concentration with an energy consumption as low as possible will be necessary for the application at commercial scale in the future.

In this context, here we study the CO_2 electrocatalytic reduction to obtain formate working in a continuous mode using carbon-supported Bi nanoparticles (Bi/C-NPs) as electrocatalytic material, operating at j of up to 300 mA·cm^{-2} in an innovative system with a filter-press electrochemical cell to allow high efficiencies with a single pass of the

catholyte through the cell. The performance of Gas Diffusion Electrodes (Bi-GDEs), prepared using the previous synthesized and characterized Bi/C-NPs, was assessed in a continuous flow-cell electrochemical reactor, with only a single pass of the electrolyte. Moreover, the influence of some important variables such as j and electrolyte flow per geometric surface area (Q/A) on the performance of the process was studied.

2. Methodology

2.1 Synthesis and characterisation of Bi NPs

Carbon-supported Bi nanoparticles (Bi/C-NPs) were prepared as described in detail in another contribution [67]. Very briefly, 0.316 g of $BiCl_3$ (99.99%, Aldrich) and 0.112 g of polyvinylpyrrolidone (PVP, K30, Mw ~55.000, Aldrich) were added into 37.92 g of N,N-Dimethylformamide (DMF, 99.8%, Sigma Aldrich) and sonicated until complete solubilisation. Then, 0.116 g of $NaBH_4$ (99%, Aldrich) were added to the solution at room temperature (20ºC) and under continuous magnetic stirring. The solution was magnetically stirred and sonicated (Selecta ultrasonic bath operating at 50/60 kHz, 360 power output) for at least 15 min. Subsequently, 0.836 g of carbon Vulcan XC-72R were added to the mixture to obtain a Bi loading of ca. 20 wt.%. The sample is then continuously sonicated during 60 min to properly dispersed the Bi nanoparticle on the carbon substrate. The sample is precipitated by adding acetone, and filtered and washed also with acetone, and finally dried overnight under vacuum conditions at 45 $^{\circ}$C.

Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 microscope, working at 200 kV and with a JEOL JEM-1400 Plus working at 120 kV to evaluate the size of the particle and dispersion of the Bi nanoparticles. The metal (Bi) loading was experimentally measured by atomic absorption spectroscopy (AAS) using a

SpectrAA-220 FS. A known amount of the Bi/C-NPs was treated in nitric acid and then filtered. The sample was then conveniently diluted using a 2 wt% HNO_3 water solution.

2.2 Bi-GDE fabrication and characterization

In the electrochemical reactor, Bi-GDE was used as working electrode. Bi/C NPs, previously synthesized and characterized as explained in Section 2.1, have been used as catalyst in Bi-GDE. A carbonaceous support (TGP-H-60), a microporous layer (MPL) and the catalytic layer (CL) shaped the Bi-GDE configuration, as shown in Fig. 1. The geometric surface area of the Bi-GDE was 10 cm^2.

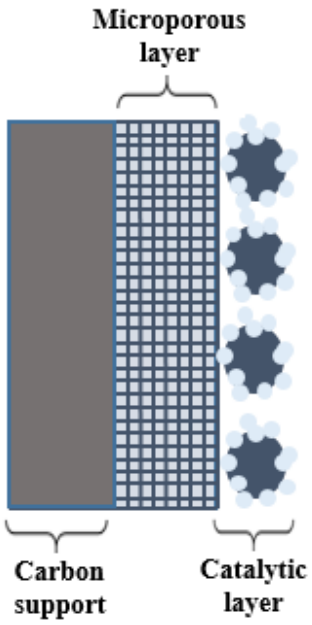

Fig 1. Scheme of the Bi-GDE configuration.

A Toray carbon paper was used as TGP-H-60 (Teflonated Paper, TGP-H-60). Firstly, a MPL was air-brushed over the carbonaceous support. An ink was prepared with Vulcan XC-72R and PTFE (Polytetrafluoroethylene preparation, 60 wt.% dispersion in H_2O, Sigma-Aldrich) in a ratio of 40/60, and then diluted in isopropanol in a final slurry of 3 wt.%. The ink was sonicated during 30 minutes before it was sprayed with the air-brusher.

When the microporous layer reached a Vulcan XC-72R loading of 2 mg·cm^{-2}, both layers were sintered at 350 ºC during 1800 seconds.

Subsequently, a CL was sprayed over the microporous layer by an air-brushing 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 meq/g exchange capacity) with ratio of 70/30, which were then diluted in isopropanol and sonicated in the same conditions as described previously for the microporous layer. The Bi/C NPs loading was 0.75 mg·cm^{-2}.

Scanning electron microscopy (SEM, HITACHI S-3000 N micro-scope working at 20 kV with X-ray detector Bruker Xflash 3001 for microanalysis) was employed to characterise the Bi-GDEs.

2.3 Filter press tests

The Bi-GDEs prepared and characterized were then used as working electrodes in an innovative continuous system with a filter press electrochemical cell. Apart from the filter press cell (Micro Flow Cell, ElectroCell A/s), the experimental set-up included peristaltic pumps (Watson Marlow 320, Watson Marlow Pumps Group), tanks and a potentiostat-galvanostat (Arbin Instruments, MSTAT4), as shown in Fig. 2.

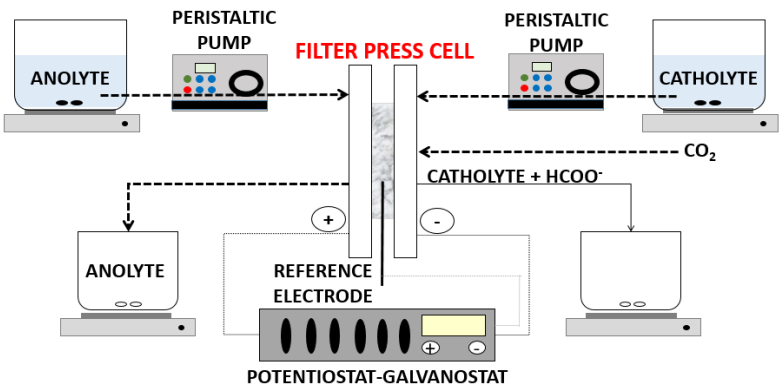

Fig. 2. Experimental set up used for the tests of Bi-GDEs for the continuous CO_2 electrocatalytic reduction to give formate.

Figure 3 represents a scheme of the cell. The internal structure of the filter press cell can be seen in figure S1 of the Supporting Information to improve the understanding of this electrochemical reactor. In this configuration, both compartments are separated by a cation exchange membrane, Nafion 117, which allows cations to cross from the anodic compartment to the cathodic compartment. The electrocatalytic reduction of CO_2 takes place in the cathode. Moreover, the electrolyte used in this compartment was a solution of 0.5 M KCl + 0.45 M $KHCO_3$. In addition, pure carbon dioxide was fed to the cathodic compartment at a flow rate of 200 $mL \cdot min^{-1}$.

The anolyte used in the anodic compartment, was a 1M KOH solution with a Q/A of 0.57 $mL \cdot min^{-1} \cdot cm^{-2}$. Moreover, a dimensionally stable anode, [DSA/O_2(Ir-MMO (mixed metal oxide) on platinum)]) was used as counter electrode.

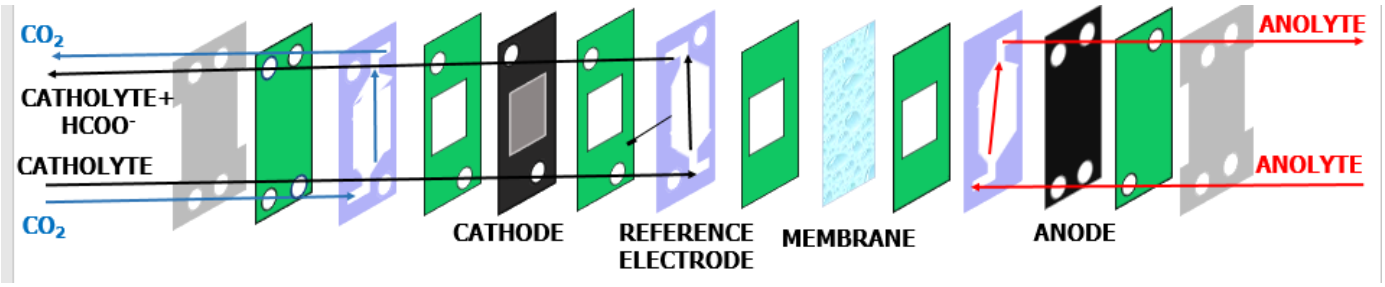

Fig 3. Filter press cell configuration used for the continuous CO_2 electrocatalytic reduction to give formate using Bi-GDEs.

As reference electrode, a leak-free Ag/AgCl 3.4 M KCl was also placed near the working electrode, in the cathodic compartment.

Experiments were performed in a continuous mode with a single pass of the catholyte and anolyte across the cell. Moreover, during 5400 seconds experiments were executed at ambient pressure (101325 Pa) and temperature (20ºC). The main variables studied were Q/A and j, which was supplied by the potentiostat-galvanostat. Each 30 minutes, samples were taken by duplicate. Concentration of formate was analysed by ion chromatograph (Dionex ICS 1100 equipped with an AS9-HC column, using Na_2CO_3 as the eluent with a

concentration, flow-rate, conductivity and pressure of 4.5 mM, 1 mL·min^{-1}, 15 µS and 1800 psi, respectively).

A mean value of formate concentration was obtained for each experiment in order to determine the FE, rate and consumption of energy (CE). The FE is described as the total charge supplied by the potentiostat that is applied to obtain the desired product, formate in this case [68]. The FE can be calculated by equation (1):

$$\mathrm{FE}(\%) = \frac{z \cdot F \cdot C_{HCOO^-}}{Q} \cdot 100 \qquad (1)$$

where z is the number of electrons exchanged in the electrochemical process, F is the Faraday constant (96485·mol^{-1}), C_{HCOO-} is the molar flow rate of formate (mol·s^{-1}) and Q is defined as the total charge supplied by potentiostat-galvanostat (A).

The rate of formate production expressed the total amount of formate per unit of working electrode area and unit of time, defined by equation (2):

$$\mathrm{Rate}\left(\frac{\mathrm{mol}}{\mathrm{m^2\ s}}\right) = \frac{C_{HCOO^-}}{A} \qquad (2)$$

where C_{HCOO-} is also the molar flow of formate obtained in each experiment (mol·s^{-1}) and A is the geometric surface area of the working electrode (m^2).

The CE was expressed as the amount of energy used in the electrochemical reactor to produce a certain amount of formate. (i.e. kWh per kmol). The CE can be calculated by equation (3):

$$\mathrm{CE}\left(\frac{\mathrm{kWh}}{\mathrm{kmol}}\right) = \frac{Q \cdot V}{C_{HCOO^-}} \qquad (3)$$

where Q and C_{HCOO-} have the same meaning as in equation (1) and (2) and V is the absolute potential in the filter-press cell (V).

3. Results

3.1 Bi/C NPs characterization

Figures 4a and 4b show some representative TEM images of the Bi/C NPs. As shown by the corresponding histogram (figure 4c), the particle size is 9.3 ± 1.6 nm. As expected, the Bi NPs display a quasi-spherical shape and a good distribution on the carbon substrate. The metal loading was found to be about 15 ± 1 wt. %, slightly lower than the nominal one.

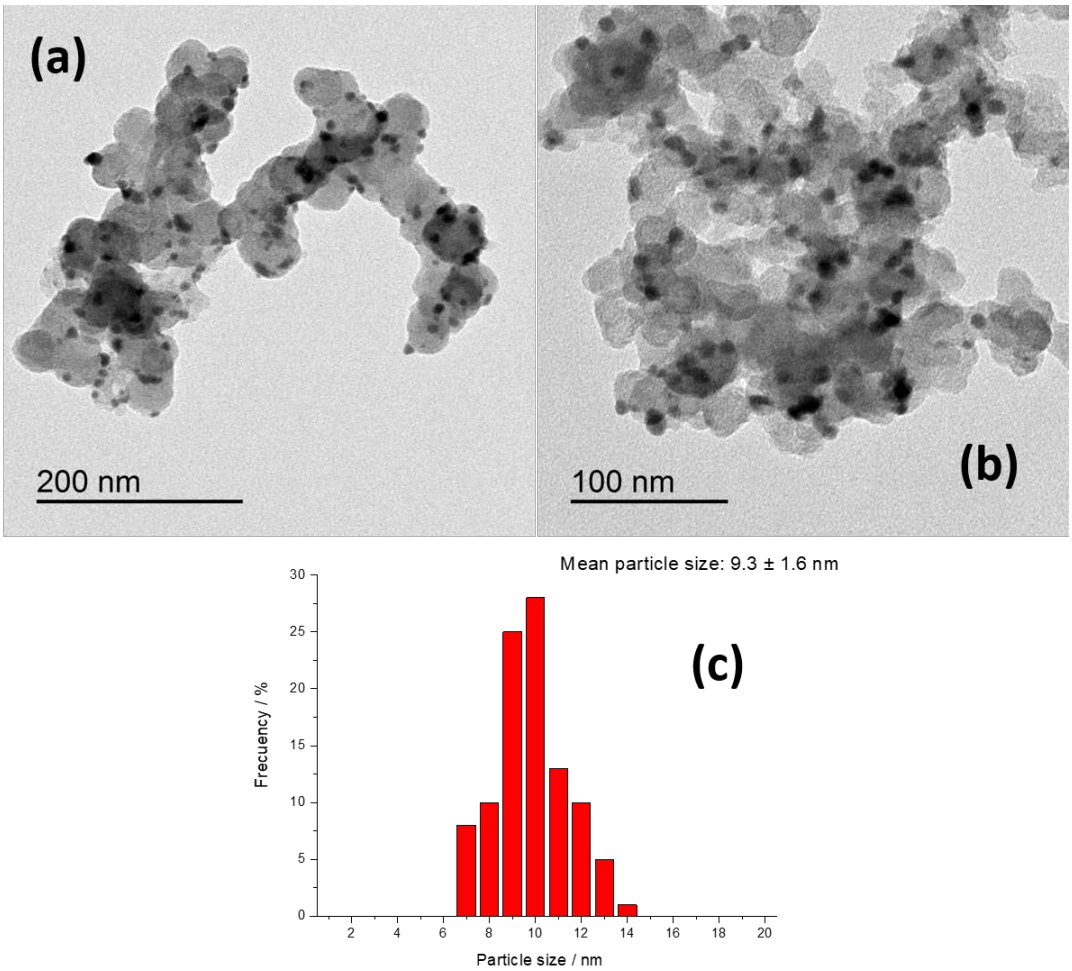

Fig 4. (a-b) TEM images and (c) particle size histogram corresponding to the Bi/C NPs.

3.2 Bi-GDE characterization

The Bi GDEs were also characterized (surface and cross section) by SEM/EDX. Figure 5 reports some representative SEM images obtained using backscattered electrons. Figure 5a shows a low magnification SEM image of the surface of the Bi GDE. The deposit seems uniform although some fractures are clearly visible. At much higher magnification (figure 5b), it is even possible to visualize the good dispersion of the Bi nanoparticles. On the other hand, from the analysis of the cross-section SEM images (figures 5b and 5c), the thickness of the MPL and the CL can be analysed. The thickness of the MPL and CL are estimated to be about 100-125 µm and 15-20 µm, respectively.

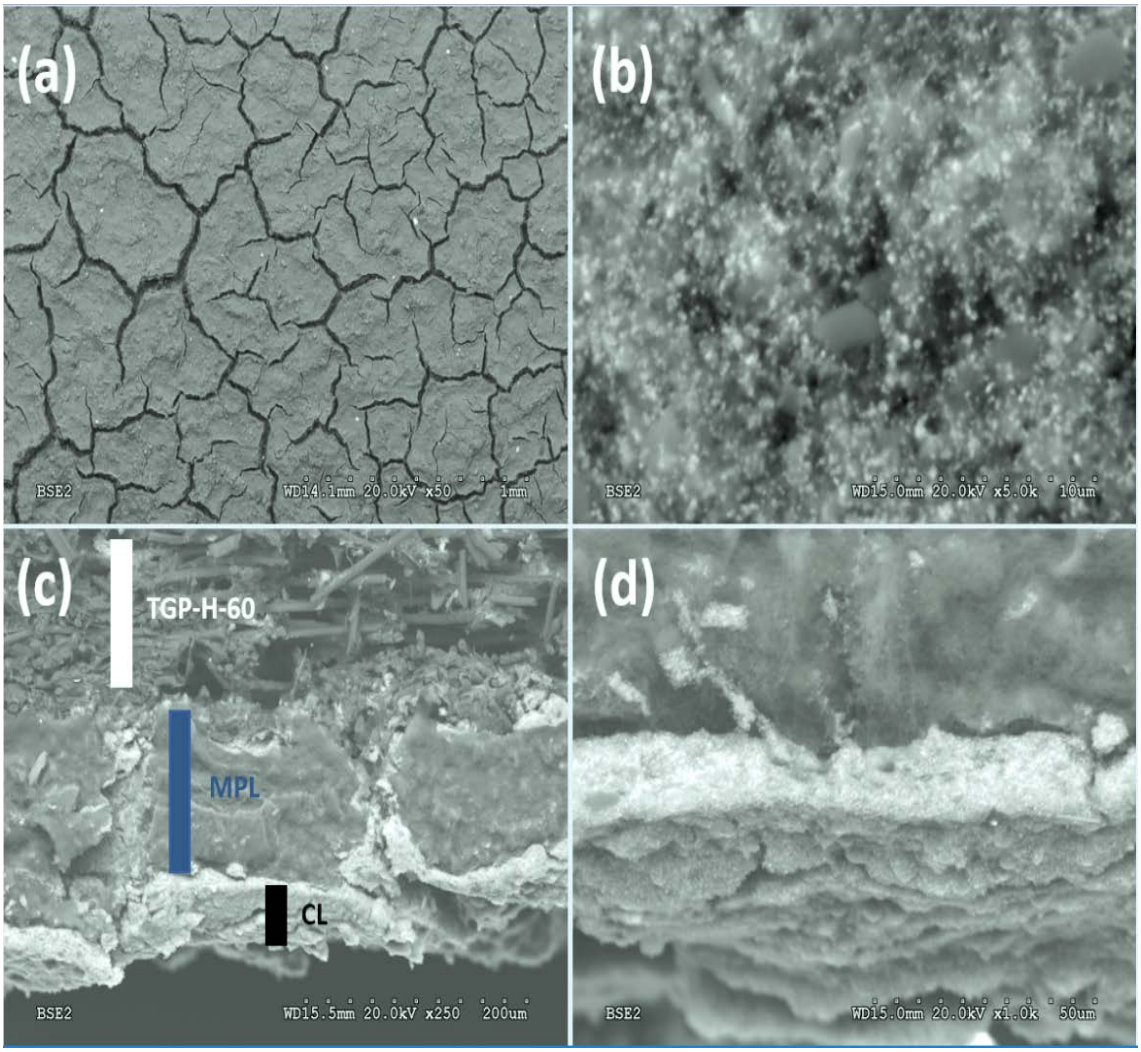

Fig 5. SEM images of the Bi-GDEs, (a, b) surface and (c, d) cross section.

To complete this analysis, figure 6 displays some SEM/EDX images of the Bi-GDEs. In both cases (surface and cross section), the EDX mapping shows a homogeneous distribution of the Bi nanoparticles.

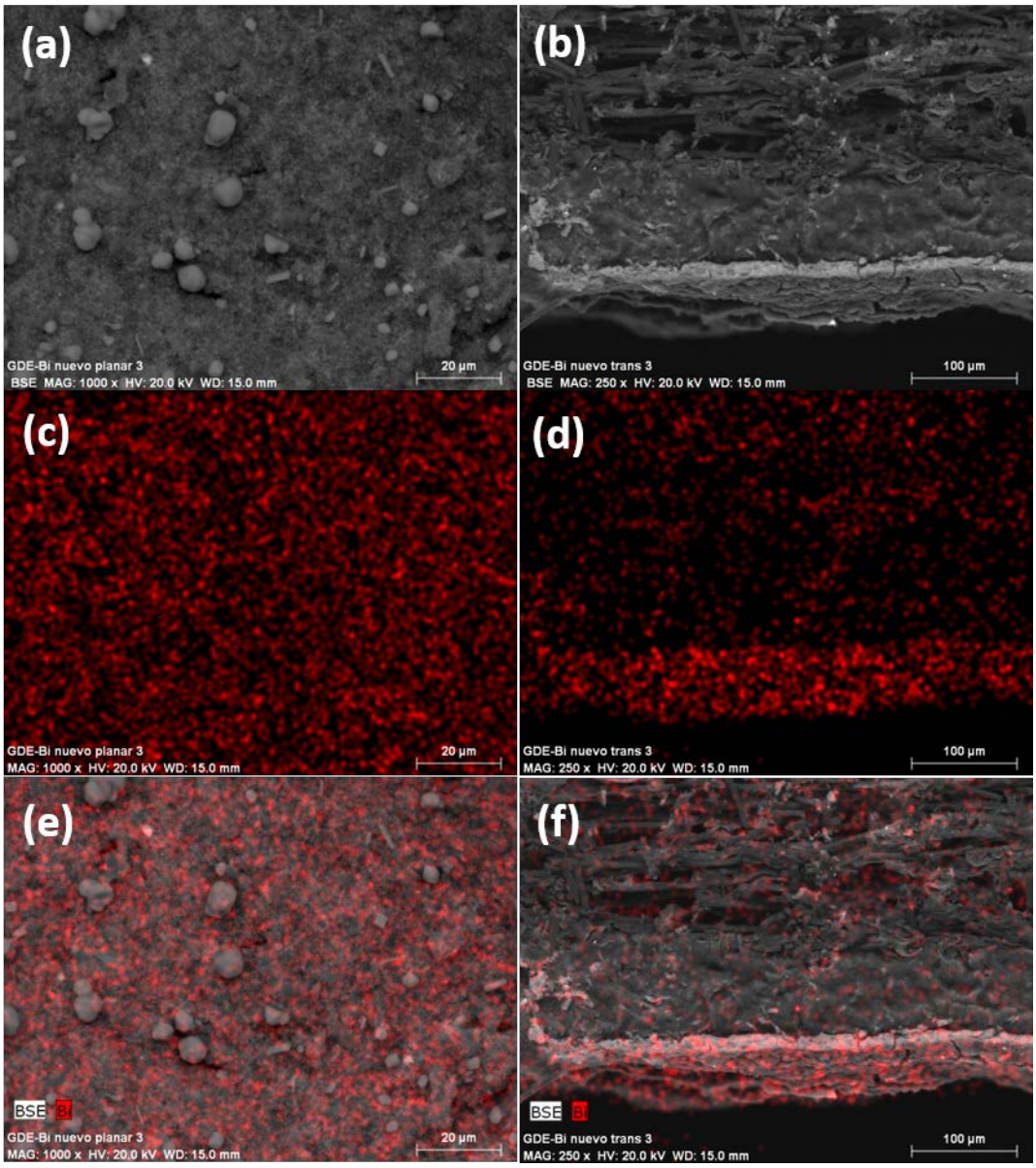

Fig 6. SEM/EDX images of the Bi-GDEs, (a, c, d) surface and (b, d, f) cross section.

3.3 Filter press reactor tests

In table 1, the main results obtained in this study are summarized with the conditions explained in last subsections.

Table 1. Results of Bi-GDE obtained operating in continuous reactor with only a single pass of the electrolyte. Electrode catalyst loading: 0.75 mg·cm^{-2} of Bi carbon supported nanoparticles.

Point	Current density, j (mA cm^{-2})	Electrolyte flow/area, Q/A (mL·min^{-1}·cm^{-2})	Average $HCOO^-$ concentration, (g·L^{-1})	Average faradaic efficiency, FE (%)	Average $HCOO^-$ rate, r (mmol·m^{-2}·s^{-1})	Average energy consumption, CE (kWh·kmol^{-1})	Standard deviation (%)	Cathode potential (V)	Absolute cell potential (V)
1	90	0.57	2.04	92.4	4.31	177	7.27	-1.3	3.1
2	150	0.57	3.06	83.1	6.46	240	9.86	-1.5	3.7
3	200	0.57	3.95	80.4	8.33	277	1.80	-1.6	4.2
4	300	0.57	5.20	70.6	10.97	410	2.63	-2.5	5.4
5	90	0.15	7.51	89.5	4.18	186	6.49	-1.3	3.1
6	200	0.15	11.70	62.7	6.5	364	3.79	-1.6	4.3
7	200	0.07	18.02	45.1	4.67	535	2.15	-1.9	4.5

Different filter press experiments were carried out in order to study the influence of the j and the Q/A. First, tests at an Q/A of 0.57 mL·min^{-1}·cm^{-2} and different j were carried out. Working at 90 mA cm^{-2} and 0.57 mL·min^{-1}·cm^{-2}, an excellent value of FE of 92.4 % was achieved, with a rate of 4.31 mmol·m^{-2}·s^{-1} (point 1). As shown in Table 1, concentration of formate increased, when j was increased from 90 to 300 mA·cm^{-2} (Table 1, point 4), from 2.04 to 5.20 g formate·L^{-1}, which represents an increase of 155%.

Although concentration of formate was increased, FE lowered approximately 20 points in percentage (from 92.4 to 70.6%) when j was raised from 90 to 300 mA·cm^{-2}. As middle points, tests were carried out at 150 and 200 mA·cm^{-2} (point 2 – 3), giving FEs around 80 %.

Even though increasing j resulted in less FE, there was an important rise in the value of formate rate obtained. If at 90 mA·cm^{-2} the formate rate achieved was 4.31 mmol·m^{-2}·s^{-}

^{1}, increasing the j to 150 mA·cm^{-2} was beneficial to the process, giving a rate more than 50% higher than the value of rate obtained working at 90 mA·cm^{-2}. This rising in formate rate was also observed when j was increased to 200 and 300 mA·cm^{-2}, resulting in a rate value of 8.33 and 10.97 mmol·m^{-2}·s^{-1}, respectively.

In terms of CE, the results obtained show that j and absolute potential in the electrochemical reactor affect CE in a proportional way (see values in Table 1). The CE per kmol of formate of 177 kWh kmol^{-1} was achieved with a j of 90 mA·cm^{-2}., which corresponds to an energy efficiency towards formate of 30%. However, working with a higher j of 150, 200 or 300 mA·cm^{-2}, the CE per kmol of formate increased proportionally in more than 35%, 55% and 125% with respect to the value of j of 90 mA·cm^{-2}.

Operating in a continuous mode with a j as high as possible, and keeping high efficiencies, have been suggested as requirements for the industrial implementation of this type of CO_2 electroconversion process. Moreover, concentration of formate must also be as high as possible, since studies have shown that the energy needed to concentrate the formate solution obtained from the CO_2 electrochemical conversion process until levels of commercial interest will definitely play an important function in the feasibility of this electrochemical process at industrial scale [69,70]. Consequently, the influence of Q/A was further analysed in order to obtain a formate product as concentrated as possible. Graphs have been included in Fig. 7 and 8 to allow for a clearer visualization of the results of formate concentration and FE achieved.

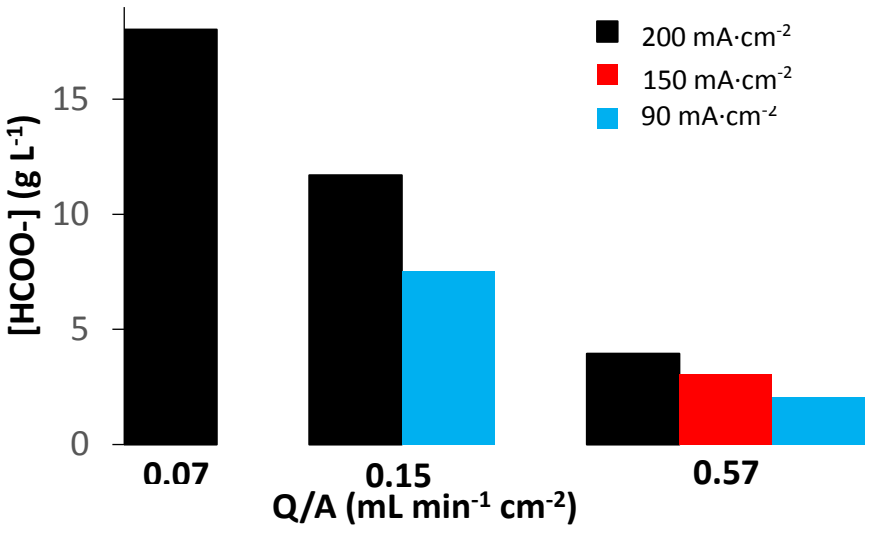

Fig. 7. Concentration of formate as a function of the j and Q/A.

As illustrated in Fig. 7, concentration of formate obtained raised approximately 4 times (from 2.04 to 7.51 g formate·L^{-1}) when the Q/A decreased from 0.57 to 0.15 mL·min^{-1}·cm^{-2}, working at 90 mA·cm^{-2}. Even though reducing the Q/A provides higher concentration of formate, FE and formate rate keep similar values, around 90% and 4.25 mmol·m^{-2}·s^{-1}, respectively.

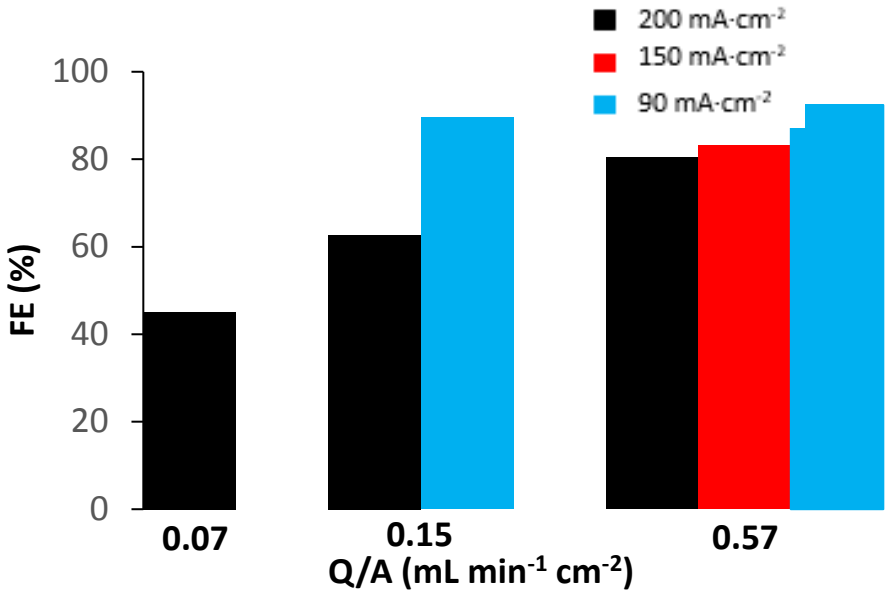

Fig. 8. FE as a function of the j and Q/A.

The same analysis was carried out working with a j of 200 mA·cm^{-2}. The formate concentration increased from 3.95 to 11.70 g formate·L^{-1}, when the electrolyte Q/A was reduced from 0.57 to 0.15 mL·min^{-1}·cm^{-2}. By decreasing Q/A, a decline of FE (as shown in Fig. 8) and formate rate values happened, from 80% and 8.33 mmol·m^{-2}·s^{-1} to 63% and 6.50 mmol·m^{-2}·s^{-1} respectively. A maximum concentration of 18.02 g formate·L^{-1} was achieved with an additional drop of Q/A to 0.07 mL·min^{-1}·cm^{-2}. Although working with this value of Q/A provides the highest formate concentration, FE and rate of production had an important drop of 50% with respect to the scenario of working with an Q/A of 0.57 mL·min^{-1}·cm^{-2}, from 80% and 8.33 mmol·m^{-2}·s^{-1} to 45% and 4.67 mmol·m^{-2} ·s^{-1}.

Finally, Table 2 summarizes the results of this study and the best results reported in literature for the electrocatalytic reduction of CO_2 to give formate or formic acid, including the product concentration or the FE obtained and the j employed in the electrochemical process. It is important to remark that different operating conditions and cell configurations are applied in each study.

Table 2. Summary of best results reported in literature for the electrocatalytic reduction of CO_2 to obtain formate or formic acid: concentration, FE and rate

Electrocatalyst	**Electrode**	**Average $HCOO^-$ concentration, (g·L^{-1})**	**Average faradaic efficiency, FE (%)**	**Average $HCOO^-$ rate, r (mmol·m^{-2}·s^{-1})**	**Current density, j (mA·cm^{-2})**	**Absolute cell potential (V)**	**Reference**
Bi/C - NPs	GDE	7.51	89.5	4.18	90	3.1	This work
Sn/C NPs	GDE	5.05	60.2	2.81	90	3.0	[36]
Sn	GDE	205	32	4.63	140	3.3	[38][a]
Sn	Metal plate	17.2	55		50		[40][b]
Sn	Metal plate	20	65		100	4	[71][b]
Sn	CCME	19.2	49.4.	1.15	45	2.2	[72][c]
Sn	CCME	41.5	93.3		51.7	2.2	[41][c]

[a]The electrochemical reactor utilises a Dioxide Materials Sustainion™ anion exchange membrane

[b]A high pressure electrochemical reactor is used.

[c]Electrocatalytic reduction of CO_2 to give formate is done operating in a gaseous phase.

As can be noted in Table 2, the best results reported previously in the literature have been obtained using Sn as electrocatalyst. This catalyst has been greatly investigated for this application, and these research efforts have led to reactor designs and operational conditions optimized for Sn-based catalysts. The results achieved with the Bi/C NPs studied in this work, although still lower than the best results with Sn, are promising, particularly considering that the reactor design and the operational conditions are yet to be optimized for Bi-based electrocatalysts.

Moreover, as can be noted looking at Table S1, the results reported in this paper are especially noteworthy when compared with previous studies using Bi, which had not worked in a continuous mode with high values of current density supplied.

Recent studies on electrochemical valorisation of CO_2 to formate using Bi as catalyst have been carried out in a discontinuous mode in a two-compartment electrochemical reactor. It is important to remark that the results of this study have been obtained in an innovative continuous system with a filter press cell working with j up to 300 $mA \cdot cm^{-2}$, greater than j reported in literature. The results obtained in this work confirm that the Bi-GDEs allow working in a continuous electrochemical cell with higher j values compared with recent contributions, compulsory for the technical viability of CO_2 electrocatalytic reduction, keeping reasonable values of formate concentration, FE, rate and CE per kmol of product. Moreover, on the one hand concentration of formate can be even increased at the expense of decreasing FE and rate or increasing CE per kmol of formate, as shown in Fig. 7. On the other hand, as illustrated in Table 2, the performance of the electrochemical process could be enhanced optimizing the reactor design and the operating conditions.

4. Conclusions

This work presents novel results on CO_2 electrovalorisation towards formate working in a continuous mode in a filter press cell using Bi-GDEs. Bi-GDEs were fabricated using Bi/C-NPs, which were synthesized and characterized. Bi-GDEs were able to work at a j up to 300 mA·cm^{-2}, obtaining 5.2 g formate·L^{-1} with FE of 70 % and rate of 11 mmol·m^{-2}·s^{-1}. Decreasing j to 90 mA·cm^{-2}, the concentration obtained was 7.5 g formate·L^{-1} with an increase of FE up to 90% and CE of only 186 kWh kmol^{-1}. Moreover, the highest concentration of formate obtained is 18 g L^{-1}, but with an important decrease in FE compared with other points. It is important to emphasise that these results were obtained working at higher j than previous studies in the literature, and they also were obtained working in a continuous mode with only a single pass of the catholyte across the filter press cell. These conditions are compulsory to remark the feasibility of the process using Bi/C-NPs in Bi-GDEs.

Finally, results from this work are promising but more research is needed. A future step to further improve this process of electrocatalytic conversion of CO_2 to formate would be to work in gas phase using the electrode configuration so called "Catalyst Coated Membrane Electrode", in which the promising Bi/C-NPs, described in this paper could be deposited directly over membrane. With this configuration, formate concentration should be increased, while at the same time, CE per kmol of formate shall be lower.

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