



Gas–liquid–solid reaction system for CO₂ electroreduction to formate without using supporting electrolyte

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Abstract

The use of bismuth-based catalysts is promising for formate production by the electroreduction of CO₂ captured from waste streams. However, compared to the extensive research on catalysts, only a few studies have focused on electrochemical reactor performance. Hence, this work studied a continuous-mode gas–liquid–solid reaction system for investigating CO₂ electroreduction to formate using Bi-catalyst-coated membrane electrodes as cathodes. The experimental setup was designed to analyze products obtained in both liquid and gas phases. The influence of relevant variables (e.g.,

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temperature and input water flow) was analyzed, with the thickness of the liquid film formed over the cathode surface being a key parameter affecting system performance. Promising results, including a high formate concentration of $34 \text{ g}\cdot\text{L}^{-1}$ with Faradaic efficiency for formate of 72%, were achieved.

Keywords: CO₂ electroreduction, Bismuth, Formate, CCMEs (catalyst-coated membrane electrodes), G–L–S reaction system

Introduction

One of the most important challenges we are faced with as a global community is climate change mitigation. According to the Paris Climate Conference (COP21), limiting the temperature increase to below 2.0 °C and pursuing efforts to limit it to 1.5 °C will be crucial to diminish the risks and the consequences of climate change ¹. Moreover, the primary contributors to global climate change are greenhouse gases such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide, and fluorinated gases (chlorofluorocarbons, hydrochlorofluorocarbons, and halons) ². CO₂ is the main greenhouse gas released through anthropogenic activities, so reducing anthropogenic CO₂ emissions into the atmosphere should be a priority in order to mitigate climate change ³.

Different approaches have been considered to lower CO₂ emissions ⁴. Improving energy efficiency or fuel switching to renewable sources of energy is one of the most common alternatives to reduce CO₂ emissions ⁵. However, recent studies based on carbon capture and sequestration (CCS) and carbon capture and utilization (CCU) show the promise of

these technologies in reducing CO₂ emissions⁶. In particular, the valorization of CO₂ into useful products has been highlighted as a promising strategy, because it mitigates CO₂ emissions and, concurrently, converts CO₂ into value-added chemicals⁷⁻⁹.

In fact, CO₂ can be converted into useful products through various routes, such as thermochemical or mineralization processes¹⁰, photochemical reduction¹¹ or electrochemical reduction¹². Among these options, the electrocatalytic reduction of CO₂ into useful chemicals has been considered as a promising strategy for CCU because it would allow the storage of excess renewable and intermittent sources of energy into value-added chemical products, which could be utilized to produce fuels¹³⁻¹⁵.

In this context, different chemical products can be obtained by the electrochemical reduction of CO₂ depending on different aspects, for example, the catalytic material used, the reaction medium used, or the voltage applied in the electrochemical process, among others¹⁶. The possible products that can be obtained by CO₂ electroreduction include formic acid (HCOOH)¹⁷, carbon monoxide (CO)¹⁸, and hydrocarbons or alcohols¹⁹.

Formic acid or formate (HCOO⁻), depending on pH, can be used in various industries¹⁷. Moreover, this chemical has been proposed as a fuel for low-temperature fuel cells²⁰ and as a hydrogen carrier²¹. According to previous studies, different electrocatalysts and systems with a filter-press electrochemical cell have been used in the electroconversion of CO₂ to obtain HCOO⁻. Sn has been widely studied as a catalyst in CO₂ electroreduction to HCOO⁻²²⁻²⁹. However, other electrocatalysts have also been tested for CO₂ conversion to obtain HCOO⁻, such as Pb³⁰⁻³², In^{33,34}, Pd^{35,36}, and Bi³⁷⁻⁴³, which are less common.

Bi could be an effective alternative to Sn owing to the lower potentials required in the electrochemical reactor with respect to other electrocatalysts^{44–46}.

Compared to the vast amount of research on catalysts, few studies have focused on the electrochemical reactor, as has recently been highlighted by Vennekoetter et al. 2019⁴⁷.

The previous work of our research group studied the use of Pb, Sn, and Bi in the CO₂ electroconversion to HCOO⁻ in various systems with a filter-press electrochemical reactor. Metal plates were initially used as working electrodes in the electrochemical conversion of CO₂ to obtain HCOO⁻^{32,48}. Gas diffusion electrodes (GDEs) have also been developed, in which the electrocatalyst is deposited over a carbonaceous support^{49–51}. In fact, in both configurations of working electrodes (i.e., metal plates and GDEs), the CO₂-saturated catholyte stream is fed to the electrochemical reactor for CO₂ electroreduction to HCOO⁻. In the GDE configuration, the additional supply of CO₂ in an input gaseous stream allows the reaction to occur in a three-phase boundary gas–liquid–solid (G–L–S). The system is limited because of the low CO₂ concentration in the liquid electrolyte, the effects of diluting the products in the liquid electrolyte and the costs associated with the subsequent separation process of the liquid product from the electrolyte.

Accordingly, some recent studies from our research group⁵² have focused on the development of CO₂ gas-phase electroconversion to produce formate through the use of Sn-catalyst-coated membrane electrodes (Sn-CCMEs), avoiding the use of a liquid electrolyte in order to improve the CO₂ solubility and the cost attributed to the separation process. First, a humidified CO₂ stream is fed to the electrochemical reactor instead of introducing the CO₂-saturated liquid electrolyte stream. Moreover, the fabrication

methodology of the working electrode is different from that of GDEs, with the electrocatalyst deposited directly over the Nafion 117 membrane instead of depositing it over the carbonaceous support. Hence, a humidified CO₂ gas stream improves the delivery of gaseous CO₂ to the G–L–S interface, avoiding the use of a liquid electrolyte and therefore, the CO₂ solubility limitation in the electrolyte. The Nafion 117 membrane acts as a solid polymer electrolyte and as a support for the catalytic material. Nevertheless, the performance of this type of reaction system has rarely been studied in the CO₂ electroconversion to give formate using Bi as the catalyst, while working in a continuous mode with a single pass of the saturated CO₂ stream with H₂O in a filter-press electrochemical reactor.

This work studies the electrochemical reduction of CO₂ to produce formate using Bi carbon-supported nanoparticles (Bi/C NPs) as catalysts in the form of CCMEs (Bi/C-CCMEs) within a G–L–S electrochemical reaction system, operating in a continuous mode with a single pass of CO₂ humidified stream through the reactor. Moreover, some important key variables have been studied, such as temperature, water flow in the CO₂ stream, current density (J), and Bi catalyst loading (CL), in order to assess the performance of the electrochemical G–L–S reaction, which has only been reported in a few previous studies^{23,52} on CO₂ electrovalorization to obtain formate. Although this study focuses on obtaining formate as the main product, both liquid and gas phases were analyzed in order to detect and quantify other byproducts that could be obtained in the CO₂ electroreduction process using Bi/C-CCMEs.

Methodology

Fabrication of Bi/C-CCMEs

To prepare Bi/C-CCMEs, carbon-supported Bi nanoparticles (9–10 nm) (Bi/C NPs) were prepared using a methodology described in previous studies⁵³. An airbrushing technique was used to fabricate Bi/C-CCMEs, as shown in Figure 1. First, the catalytic ink was prepared by mixing Bi/C NPs and a certain amount of Nafion (Nafion D-521 dispersion, 5% w/w in water and 1-propanol, ≥ 0.92 meq/g exchange capacity, Alfa Aesar) in a ratio of 70:30 and diluted in isopropanol (isopropanol, 99.5%, Extra Dry over Molecular Sieve, AcroSeal®) in a final solution of 3 wt.% of catalyst/Nafion in isopropanol.

Figure 1. Schematic of the airbrushing technique used to fabricate Bi/C-CCMEs.

Consequently, the catalytic ink was sonicated for 30 min and then sprayed over the Nafion 117 membrane, which had a geometric surface area of 10 cm². The Nafion 117 membrane was placed over a hot metallic plate set to a temperature of 60–70 °C in order to improve isopropanol evaporation. Different Bi *CLs*—0.75 and 1.5 mg·cm⁻²—were used.

Characterization of Bi/C-CCMEs

Field emission scanning electron microscopy (FESEM, ZEISS Merlin VP Compact microscope with an X-ray detector BRUKER Quantax 400 for EDX microanalysis and mapping) was employed to analyze the morphology and Bi distribution of the CCMEs.

Filter-press cells and experimental conditions

Figure 2 depicts the experimental setup for the electrocatalytic reduction of CO₂ to obtain HCOO⁻ in a filter-press electrochemical reactor (Micro Flow Cell, ElectroCell A/S) using Bi/C-CCME as the working electrode.

Figure 2. Experimental setup used for the tests of Bi/C-CCMEs for the study of CO₂ electrochemical reduction to obtain HCOO⁻: 1 (Peristaltic pump); 2 (Filter press reactor); 3 (Vapor Delivery Module); 4 (Potentiostat-galvanostat); 5 (G/L Separator); 6 (Filters); 7 (Trap); 8 (Ion chromatography); 9 (Gas chromatography).

As illustrated in Figure 3, the Bi/C-CCME acts as a cathode and simultaneously acts as a separator between the anode and cathode compartments. At the cathode side, a humidified CO₂ stream was fed to the working electrode compartment of the electrochemical reactor, and a tinned steel mesh was used as the current collector. Moreover, the water flow in the CO₂ stream and the temperature were controlled by a vapor delivery module. These variables were also measured in the output stream of the electrochemical reactor using a HygroFlex HF5 humidity temperature transmitter. At the anode side, a commercial dimensionally stable anode [DSA/O₂ (Ir-MMO (mixed metal oxide) on platinum), Electrocell] was used in the electrochemical filter-press reactor. On the one hand, the metal mix of the counter electrode is composed by both Ti and Ir oxides. In contrast, the Ir loading in the mix was 16 g·m⁻². In addition, a 1 M KOH (potassium hydroxide, 85%

purity, pharma grade, PanReac AppliChem) aqueous solution was used as the analyte with a flow of 5.7 mL·min⁻¹.

Figure 3. Electrochemical filter-press reactor configuration for the tests of Bi/C-CCMEs used for the continuous electroreduction of CO₂ to obtain HCOO⁻.

The experimental setup was developed to allow the analysis of both liquid and gas phases, instead of only analyzing the liquid phase, as in our previous studies⁵². The gas phase was analyzed using a 4-channel micro gas chromatograph (490, Micro GC, Agilent Technologies) equipped with a thermal conductivity detector (Micro-TCD). Helium and argon (99.99% purity) were employed as the carrier gases. Hydrogen (H₂), nitrogen (N₂), oxygen (O₂), CO, CH₄ and noble gases were separated in a molecular sieve 5 Å column (10 m MS5A Hi-BF SP1 pre-column), whereas CO₂ and long-chain hydrocarbons were separated in a PoraPLOT U PLO mm ID column (10 m PPU HI-BF). Volatile solvents and polar compounds were also measured using a CP-Sil 5 CB, 015 mm ID (8 m, 5CB HI-Str) and an SP1 column (10 m, 52 CB HI-Str), respectively. Moreover, the liquid phase was analyzed using an ion chromatograph (Dionex ICS 1100) equipped with an AS9-HC column and a headspace gas chromatograph (GCMSQP2010 Ultra Shimadzu) equipped with a flame ionization detector. The experiments had a duration of 90 min. Samples were taken every 30 min to analyze both the liquid and gas phases, and the average value of the concentrations of each detected product was obtained for each experiment. Moreover, all experiments were performed in duplicate under the same operating conditions, ensuring the maximum standard deviations for the replicates of each experimental point were lower than 10% of the average concentration of each product.

The performance of the electrochemical process is assessed by the Faradaic efficiency and the concentration of each product as well as the rate and consumption of energy of HCOO^- . The different equations used to calculate these performance criteria can be found in literature ⁵².

Results and Discussion

Characterization of Bi/C-CCMEs

Figure S1 of the Supporting Information shows the representative SEM images (surface and cross section) of the Bi/C-CCMEs, including some EDX Bi mapping profiles. The SEM-EDX results show that the Bi electrocatalyst is well-dispersed and homogeneously distributed over the surface of the electrode. The thickness of the catalytic layer is approximately 15–20 μm .

Performance of the G–L–S continuous reaction system

Temperature

Various tests were carried out to analyze the influence of temperature on the performance of the reaction system. All experiments were carried out in a continuous mode with only one pass of the input stream through the electrochemical reactor. In this subsection, all tests were performed at a current density (J) of $45 \text{ mA}\cdot\text{cm}^{-2}$ with a Bi CL of $0.75 \text{ mg}\cdot\text{cm}^{-2}$.

For each experiment, both the liquid and gas phases were analyzed in duplicate to determine the Faradaic efficiency (FE) and rate (r) for each product. Formate is the main product detected in the liquid phase using ion chromatography, with traces of methanol (CH_3OH) and ethanol (C_2H_5OH) determined by headspace gas chromatography. Thus, the formate concentration ($[HCOO^-]$) and the consumption of energy per kilogram of formate (EC) are calculated.

Experiments were performed between 293 K and 323 K, with intermediate temperature values of 298 K and 310.5 K. The experiments were performed with a constant relative humidity in the CO_2 stream of 100%. Figure 4 summarizes the results regarding formate production in the liquid phase. On the one hand, Figure 4a represents the variation of formate rate (r_F) and the Faradaic efficiency for formate (FE_F) for different values of temperature tested. In contrast, Figure 4b shows the influence of temperature on $[HCOO^-]$ and the EC needed to produce formate.

Figure 4. Influence of temperature on (a) formate rate ($mmol \cdot m^{-2} \cdot s^{-1}$) and Faradaic efficiency for formate (%) and (b) the consumption of energy per kmol of formate ($MJ \cdot kmol^{-1}$) and Formate concentration ($g \cdot L^{-1}$) in the temperature range of 293–323 K applied at constant current density = $45 \text{ mA} \cdot \text{cm}^{-2}$, Bi CL = $0.75 \text{ mg} \cdot \text{cm}^{-2}$, and relative humidity = 100%.

As can be seen in Figure 4a, at a temperature of 293 K, r_F of $1.10 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ is obtained. However, increasing the temperature of the saturated CO_2 stream in the input of the electrochemical reactor from 293 K to 298 K, the r_F drops to $1.08 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. This variation in r_F can be attributed to the standard deviation (SD) of the experiments (SD values are reported in Table S1 of the Supporting Information). Nevertheless, after

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increasing the temperature to 323 K, r_F and FE_F decrease by approximately 14.5% compared to room temperature. Although Lee et al. 2018²³ reported a different trend in the influence of temperature, these results are in agreement with those previously reported in literature, where working at 293 K represents the optimal operating temperature⁵⁴, which could be attributed to the fact that the solubility of CO₂ in the liquid layer of water formed in the G–L–S reaction system decreases with increasing temperature.

Figure 4b shows that the highest $[HCOO^-]$ obtained was at a temperature of 293 K (22.3 g·L⁻¹). Moreover, by performing the electrochemical process at 293 K, the lowest value of EC per kmol of formate is also reached, which is approximately 1123.2 MJ·kmol⁻¹. On the one hand, increasing the temperature of the input CO₂ stream to 313 K, the $[HCOO^-]$ decreases by approximately 21%, from 22.3 to 17.6 g·L⁻¹. The CO₂ stream in the electrochemical filter-press reactor was fed as a saturated stream with H₂O; therefore, the higher temperature led to an increase in the amount of water in the CO₂ stream in order to achieve saturation in the CO₂ stream. Increasing the water flow in the CO₂ stream may be directly related to the performance in the filter-press reactor, which is closer to that corresponding to a liquid electrolyte instead of a solid polymer electrolyte. In contrast, operating at a temperature of 313 K increases the EC to give formate by approximately 30%, from 1123.2 to 1465.2 MJ·kmol⁻¹, which is higher than operating at room temperature.

Both the liquid and gas phases were analyzed in order to determine the product distribution over the temperature range of 293–323 K. The results are summarized in Figure 5 (values are described in Table S2 in the Supporting Information). In addition to

HCOO⁻ in the liquid phase, H₂, CO, CH₄, and ethylene (C₂H₄) were detected as gaseous products. It should be noted that the accumulated FE_F, the Faradaic efficiency for H₂ (FE_H), the Faradaic efficiency for CO (FE_C), the Faradaic efficiency for CH₄ (FE_C) and the Faradaic efficiency for C₂H₄ (FE_C) values of these products were close to 100%. As shown in Figure 5, increasing the temperature from 293 K to 323 K results in a lower FE_F. This decrease is mostly due to the hydrogen evolution reaction, which is favored as the temperature increases⁵⁵. The highest FE_H value (50.9%) was obtained at an operating temperature of 323 K, which is 26% higher than that obtained at room temperature (40.2%). However, FE_C and FE_M were almost constant at 10 and 2.5% at 293–313 K, respectively. Furthermore, small traces of C₂H₄ appeared at operating temperatures of 310.5 and 323 K in the CO₂ saturated stream with H₂O.

Figure 5. Influence of temperature on the FE of formate (FE_F), hydrogen (FE_H), carbon monoxide (FE_C), methane (FE_M), and ethylene (FE_E) in the temperature range of 293 to 323 K applied at constant current density = 45 mA·cm⁻², Bi CL = 0.75 mg·cm⁻², and relative humidity of 100%.

From the results obtained, the optimal operating condition for the electrocatalytic conversion of CO₂ to obtain formate using Bi/C-CCMEs is considered to be a temperature of 293 K. Similarly, when CO₂ electrovalorization to produce formate was carried out using Sn as the electrocatalyst in configuration CCMEs⁵², this temperature was considered to be the optimal operating condition.

Amount of water in the CO₂ stream

Further experiments were carried out with the aim of analyzing the influence of the water flow in the input stream on the CO₂ electrocatalytic reduction to formate using this new

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configuration of the G–L–S reaction system employing Bi/C-CCMEs as the working electrode. Before conducting these experiments, we hypothesized that the highest performance of this G–L–S system would be achieved when the amount of liquid in the system would be adequate for the progress of the reaction, but not so low as to hinder the reduction reaction or as high as to nullify the benefits arising from the use of a solid electrolyte. Under this operating condition, the performance higher than that of a conventional system with a liquid electrolyte could be achieved. Therefore, the analysis of the influence of the water input flow is essential for understanding reactor performance.

According to the results presented in the previous subsection on the influence of temperature, in these experiments, the temperature was fixed at 293 K. In addition, all the tests were performed using CCMEs with a CL of $0.75 \text{ mg}\cdot\text{cm}^{-2}$ for carbon-supported Bi nanoparticles, and the current density supplied by a potentiostat-galvanostat was $45 \text{ mA}\cdot\text{cm}^{-2}$. For each test, both phases were analyzed in order to determine the influence of the water flow in the CO_2 stream on r_F , FE of all products, EC , and $[\text{HCOO}^-]$. Figure 6 and 8 summarize the results obtained, while the detailed values are reported in Table S3 of the Supporting Information.

Figure 6. Influence of water flow in the CO_2 stream on (a) formate rate ($\text{mmol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) and Faradaic efficiency for formate (%) and (b) the consumption of energy per kmol of formate ($\text{MJ}\cdot\text{kmol}^{-1}$) and formate concentration ($\text{g}\cdot\text{L}^{-1}$) in the water flow range of $0.15\text{--}1 \text{ g}\cdot\text{h}^{-1}$ applied at constant current density = $45 \text{ mA}\cdot\text{cm}^{-2}$, Bi $CL = 0.75 \text{ mg}\cdot\text{cm}^{-2}$, as measured at room temperature.

The lowest performance in terms of r_F and FE_F was observed when the CO_2 input stream introduced to the electrochemical reactor was not saturated ($0.15 \text{ g}\cdot\text{h}^{-1}$). These data points

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correspond to a relative humidity of 66%. As illustrated in Figure 6a, increasing the water flow in the CO₂ stream from 0.15 to 0.227 g·h⁻¹, which corresponds to the saturated conditions of the CO₂ stream introduced to the filter-press reactor, enhances the electrochemical process to give formate. On the one hand, r_F and FE_F increase by more than 19% with respect to the values of r_F and FE_F working with a non-saturated CO₂ stream, with values of 1.10 mmol·m⁻²·s⁻¹ and 47.2%, respectively. In contrast, when the electrochemical reactor was fed with a saturated CO₂ stream, the EC decreased from 1224 to 1123.2 MJ·kmol⁻¹, while $[HCOO^-]$ increased from 18.6 to 22.3 g·L⁻¹, thus achieving an increase of approximately 8.2% and 20%, respectively (Figure 6b).

A possible explanation for these results may be related to the influence of the amount of water supplied to the liquid layer formed in the G–L–S reaction system, as schematically illustrated in Figure 7. The vapor supplied in the CO₂ stream introduced to the electrochemical reactor condenses over the CCME surface, forming a liquid film. In this way, the thickness of this liquid film depends on the amount of vapor condensed, and it also affects the ohmic resistance of the system. Therefore, the control of the water flow in the CO₂ stream is important in order to improve the performance of the G–L–S reaction system. These ideas are in accordance with Vennekoetter et al., who also points to the importance of controlling the thickness of the liquid layer and the hydrodynamics in the reactor for effective CO₂ conversion⁴⁷.

When the amount of water in the CO₂ input stream to the reactor was low (i.e., less than 0.5 g·h⁻¹), the results suggest that the G–L–S reaction system was not operating under the optimal hydrodynamic conditions because the amount of water vapor condensed on the

CCME surface was not sufficient to form a liquid film of appropriate thickness (Figure 7a).

Figure 7. Schematic of liquid film formation over the CCME surface depending on the amount of water in the CO₂ stream: (a) scarce amount of water in the CO₂ input stream, (b) optimal amount of water in the CO₂ input stream (solid polymer electrolyte), and (c) excess amount of water in the CO₂ stream (liquid electrolyte).

Interestingly, as shown in Figure 6a, increasing the water flow in the CO₂ stream from 0.227 (which corresponds to a relative humidity of 100%) to 0.5 g·h⁻¹ results in an important increase in r_F and FE_F , from 1.10 mmol·m⁻²·s⁻¹ and 47.2% to 1.28 mmol·m⁻²·s⁻¹ and 54.8%, respectively. In contrast to the previous tests conducted at different water flow rates in the CO₂ stream, operating with 0.5 g·h⁻¹ of water resulted in the optimal conditions for CO₂ electroconversion to formate using Bi/C-CCMEs. Consequently, under these operating conditions, it may be concluded that enough water is condensed on the electrode surface, resulting in the optimal hydrodynamic conditions in the G–L–S system for the CO₂ electroconversion process (Figure 7b).

However, a further increase in the water flow in the CO₂ stream to 1 g·h⁻¹ lowered r_F and FE_F . In terms of EC and $[HCOO^-]$, the optimum water flow in the CO₂ stream was also 0.5 g·h⁻¹, achieving a value of 956.88 MJ·kmol⁻¹ and 25.9 g·L⁻¹, respectively (Figure 6). However, increasing the amount of water in the CO₂ stream from 0.5 to 1 g·h⁻¹ decreased $[HCOO^-]$ from 25.9 to 22.6 g·L⁻¹. At this water flow rate in the input CO₂ stream the electrochemical process was disturbed, increasing the liquid film over the CCMEs and inhibiting the input of the CO₂ stream to the catalytic layer of the working electrode. In

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this way, the thickness of the liquid film provides a larger distance between the catalytic surface of the working electrode and the surface of the liquid film formed (Figure 7c). Therefore, the electrochemical cell potential increased (see values in Table S3 of the Supporting Information) as water flow in the CO₂ stream increased. Moreover, this excess water flow in the CO₂ stream also affected the behavior of the filter-press reactor, approximating the performance of a conventional system in which the catholyte acts as a liquid electrolyte and dilutes the reaction products in the output stream of the reactor.

In addition to reporting liquid phase analysis, the gas phase was also analyzed in order to gain additional understanding of the CO₂ electrochemical process. Figure 8 summarizes the influence of water flow in the CO₂ stream on the *FE* of the products detected in both phases (values are described in Table S4 of the Supporting Information). It should be noted that the same gaseous products as in the experiments reported in the previous subsection at different temperatures (Figure 5) are detected (H₂, CO, CH₄, and C₂H₄).

Figure 8. Influence of water input flow in the CO₂ stream on *FE* to formate (*FE_F*), hydrogen (*FE_H*), carbon monoxide (*FE_C*), methane (*FE_M*), and ethylene (*FE_E*) in the water flow range of 0.15–1 g·h⁻¹ applied at constant current density = 45 mA·cm⁻², Bi *CL* = 0.75 mg·cm⁻², as measured at room temperature.

Working with a CO₂ stream non-saturated with H₂O (which corresponds to a water flow in the CO₂ stream of 0.15 g·h⁻¹), the main product detected was H₂, with an *FE_H* of 46.1%, with formate detected with an *FE_F* of 39.4%. Note that, as depicted in Figure 8, when the CO₂ electroreduction process to formate proceeds with a water flow of 0.15 g·h⁻¹ or a non-saturated stream of CO₂, formate is not the main product detected in both phases. As shown in Figure 6a, increasing the water flow in the CO₂ stream to 0.5 g·h⁻¹, the optimal

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performance of the electrochemical process is achieved, yielding an FE_F of 54.8%. Operating under these conditions, an FE_H of 40.9% is obtained, approximately 12.5% lower than that when operating with a water flow of $0.15 \text{ g}\cdot\text{h}^{-1}$. However, increasing the water flow from $0.52 \text{ g}\cdot\text{h}^{-1}$ (see values in Table S4 of the Supporting Information), FE_F decreased to 41.1% (approximately 25% lower). Thus, this decrease in FE_F leads to an increase in FE_H , from 40.9% to 46.1% (corresponding to a water flow of $2 \text{ g}\cdot\text{h}^{-1}$), which may be attributed to the fact that the excess water condensed over the surface could improve the hydrogen evolution reaction. As seen in Figure 8, FE_C and FE_M are similar for the range of the water flow studied, approximately 10% and 2%, respectively. In addition, C_2H_4 was detected using a non-saturated CO_2 stream ($0.15 \text{ g}\cdot\text{h}^{-1}$ of water flow) or with a CO_2 stream with a flow of $2 \text{ g}\cdot\text{h}^{-1}$. It should be noted that the accumulated FE for these products detected in both phases was approximately 100% in all tests.

Further improvements in G–L–S reaction system performance

Additional tests were carried out in an attempt to improve the performance of the G–L–S system for the electrochemical conversion of CO_2 to formate using Bi/C-CCMEs. According to the results reported in the previous section, these tests were conducted at room temperature (293 K) to achieve the highest performance of the reaction system. These additional experiments focus on further analyzing the influence of i) increasing the CL in the CCME, and ii) increasing the current density (J) at which the process is performed.

Increasing the catalyst loading CL

First, the CL , is increased to $1.5 \text{ mg}\cdot\text{cm}^{-2}$, instead of $0.75 \text{ mg}\cdot\text{cm}^{-2}$. As in previous section, these experiments were conducted to investigate the influence of the vapor supplied in the CO_2 stream and introduced to the electrochemical reactor, analyzing both the liquid and gas phases, and operating with a constant $J = 45 \text{ mA}\cdot\text{cm}^{-2}$.

The effects of vapor supplied in the CO_2 stream on FE_F (Figure 9a), $[\text{HCOO}^-]$ (Figure 9b), r_F (Figure S2a), and EC (Figure S2b) and the comparison with electrodes with a CL of $0.75 \text{ mg}\cdot\text{cm}^{-2}$ were studied (values are described in Table S5 in the Supporting Information). The range of water flow in the analyzed CO_2 stream is between $0.5 \text{ g}\cdot\text{h}^{-1}$ (which corresponds to the optimal behavior at CL of $0.75 \text{ mg}\cdot\text{cm}^{-2}$) and $5 \text{ g}\cdot\text{h}^{-1}$. Although at a water flow in the CO_2 stream of $0.5 \text{ g}\cdot\text{h}^{-1}$ the resulting r_F and FE_F are similar for both CL s of $1.3 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and 55% , respectively, the highest performance of the working electrode with a CL of $1.5 \text{ mg}\cdot\text{cm}^{-2}$ is achieved when the amount of vapor supplied in the CO_2 stream increases. The highest performance is obtained with a flow of vapor in a CO_2 stream of $3 \text{ g}\cdot\text{h}^{-1}$, instead of introducing $0.5 \text{ g}\cdot\text{h}^{-1}$ with a CL of $0.75 \text{ mg}\cdot\text{cm}^{-2}$. However, increasing the water flow in the CO_2 stream from 3 to $5 \text{ g}\cdot\text{h}^{-1}$, both r_F and FE_F decrease to $1.31 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and 56% , respectively, 21% lower than those under the optimal conditions.

Figure 9. Influence of water flow in the CO_2 stream on (a) Faradaic efficiency for formate (%) and (b) formate concentration ($\text{g}\cdot\text{L}^{-1}$) working with Bi/C-CCMEs with a Bi $CL = 0.75 \text{ mg}\cdot\text{cm}^{-2}$ and $1.5 \text{ mg}\cdot\text{cm}^{-2}$ in the water flow range of $0.5\text{--}5 \text{ g}\cdot\text{h}^{-1}$ at a constant current density of $45 \text{ mA}\cdot\text{cm}^{-2}$ as measured at room temperature.

In terms of $[HCOO^-]$ (Figure 9b) and EC (Figure S2b), the performance of the electrochemical reactor is similar to that discussed in Figure 9. On the one hand, the optimal result was obtained when the filter-press cell is fed with a water flow of $3 \text{ g}\cdot\text{h}^{-1}$. In contrast, increasing the vapor supplied in the CO_2 stream yields unsatisfactory results for $[HCOO^-]$ and EC , decreasing $[HCOO^-]$ from 34 to $27 \text{ g}\cdot\text{L}^{-1}$ and increasing EC from 835.2 to $1080 \text{ MJ}\cdot\text{kmol}^{-1}$.

Therefore, using a working electrode with a CL of $1.5 \text{ g}\cdot\text{cm}^{-2}$ leads to higher performance than that at a CL of $0.75 \text{ mg}\cdot\text{cm}^{-2}$, considering the criteria analyzed: r_F , FE_F , $[HCOO^-]$, and EC . The performance of the electrochemical process was similar under both conditions. Similarly, the amount of water that condenses over the CCME surface must be optimized in order to achieve optimal hydrodynamic conditions in the electrochemical reactor. Increasing the CL of Bi deposited over the electrode from 7.5 to 15 mg resulted in the optimal conditions, under which the water flow rate introduced in the CO_2 stream could be increased from 0.5 to $3 \text{ g}\cdot\text{h}^{-1}$. As discussed in the previous section, the water condensing over the electrode is responsible for the thickness of the liquid film over the electrode surface, this thickness directly affects the ohmic resistance of the electrochemical reactor. Thus, when operating at a water flow in the CO_2 input stream of $3 \text{ g}\cdot\text{h}^{-1}$, it may be argued that the distance between the liquid film and the catalyst affects the input of CO_2 to the electrode surface. However, when the water flow increases to $5 \text{ g}\cdot\text{h}^{-1}$, the thickness of the liquid film increases, resulting in poor hydrodynamic conditions and interaction between the G–L–S phases, CO_2 , and electrode surface.

Apart from the production of formate in the liquid phase, other products were detected in the gas phase, such as H₂, CO, and CH₄, when working with a *CL* of 1.5 mg·cm⁻². As illustrated in Figure 10 (values are reported in Table S6 of the Supporting Information), the influence of the vapor supplied to the electrochemical reactor was studied in terms of *FE_F*, *FE_H*, *FE_C*, and *FE_M*. As explained previously, *FE_F* has its optimal value operating at a water flow of 3 g·h⁻¹ under the operating condition of *FE_H* of 22.3%, *FE_C* of 7.5%, and *FE_M* of 3.7%. At 0.5–5 g·h⁻¹, the *FE_C* and *FE_M* values were similar. However, *FE_H* has an important fluctuation operating at different water flows in the CO₂ stream fed to the electrochemical filter-press. Increasing the water flow from the optimal value to 5 g·h⁻¹ results in an increase in *FE_H*, increasing approximately 54% than when operating at 3 g·h⁻¹. As explained in the last section (*CL* of 0.75 mg·cm⁻²), increasing the water flow favors the hydrogen evolution reaction, which explains the higher production of hydrogen observed. Furthermore, it is important to consider that the *FE* accumulated for all the products detected in both the liquid and gas phases ranged between 98% and 105%.

Figure 10. Influence of water input flow in the CO₂ stream on FE to formate (*FE_F*), hydrogen (*FE_H*), carbon monoxide (*FE_C*), and methane (*FE_M*) working with Bi/C-CCMEs with a Bi *CL* = 1.5 mg·cm⁻² in the water flow range of 0.5–5 g·h⁻¹ applied at a constant current density of 45 mA·cm⁻², as measured at room temperature.

Increasing the current density *J*

According to previous results, additional experiments were carried out in order to study the influence of *J* on CO₂ electroconversion to formate using working electrodes with different *CL* operating under the optimal conditions of water flow in the CO₂ stream. As

discussed in the previous subsection, the electroreduction of CO₂ to formate at a *CL* of 1.5 mg·cm⁻² gives better results than that at a *CL* of 0.75 mg·cm⁻². For this reason, the figures showing the influence of *J* on *r_F*, *FE_F*, [*HCOO*⁻], and *EC* with *J* at *CL* of 0.75 mg·cm⁻² are included in the Supporting Information (Figure S3). In addition, the values are reported in Table S7 of the Supporting Information.

The electrochemical conversion of CO₂ was studied for a *CL* of 1.5 mg·cm⁻² with an optimal water flow of 3 g·h⁻¹, as studied in the previous subsection. Figure 11a shows the influence of *J* on *r_F* and *FE_F*, whereas Figure 11b also displays the effect of *J* on *EC* and [*HCOO*⁻] (values are described in Table S8 in the Supporting Information). When increasing *CL*, the behavior of the electrochemical reactor is similar to when *J* is increased. An *r_F* of 3.06 mmol·m⁻²·s⁻¹ and a noteworthy [*HCOO*⁻] of 46.5 g·L⁻¹ is obtained when *J* increases from 45 to 200 mA·cm⁻². Nevertheless, *FE_F* and *EC* decrease when *J* is increased, achieving values of 46.1% and 1452.24 MJ·kmol⁻¹, respectively.

Figure 11. Influence of current density on (a) formate rate (mmol·m⁻²·s⁻¹) and Faradaic efficiency for formate (%) and (b) consumption of energy per kmol of formate (MJ·kmol⁻¹) and formate concentration (g·L⁻¹) in the current density range of 45–200 mA·cm⁻² operating at 293 K, Bi *CL* = 1.5 mg·cm⁻², and water flow in the CO₂ stream = 3 g·h⁻¹.

Conclusions

In this study, continuous CO₂ electroreduction to formate in a G–L–S reaction system was developed with a single pass of the CO₂ humidified stream through the electrochemical reactor. The cathodes were prepared by airbrushing the Bi/C NPs directly over the Nafion 117 membrane. Both the liquid and gas phases were analyzed. In the

liquid phase, only formate was detected in all experiments with traces of alcohols. The influence of temperature and the amount of water in the CO₂ input stream were studied. The results show that it is possible to improve the performance of a G–L–S reaction system operating at room temperature by varying the water content of the input stream, instead of operating with a saturated stream and increasing the water content by increasing the temperature of the input stream, resulting in a system with the advantage of operating at room temperature. Concentrations of HCOO⁻ of up to 25.9 g·L⁻¹ were achieved operating at a temperature of 293 K and with a water flow in the CO₂ stream of 0.5 g·h⁻¹. This could be attributed to the fact that under these operating conditions the thickness of the liquid film that coats the Bi/C-CCME surface is optimal for performance. Increasing the water flow in the CO₂ input stream hinders the performance of the electrochemical reactor, with performance approaching that of a corresponding liquid electrolyte reactor. This is because of the hydrodynamic conditions, which lead to an increase in the ohmic resistance of the electrochemical reactor. For this reason, when the water flow in the CO₂ stream was increased, the performance of the electrochemical conversion of CO₂ to formate decreased in terms of the r_F , FE_F , $[HCOO^-]$, and EC . More work is in progress to properly understand the fundamental aspects involved in these findings in terms of CO₂ reaction mechanisms, pathways, and intermediates. This fundamental understanding will help to fully explain the experimental results reported in this paper, and also to improve them.

Further experiments were developed with the aim of improving the performance of the G–L–S reaction system. When the Bi CL was increased from 0.75 mg·cm⁻² to 1.5 mg·cm⁻²

², a larger amount of water in the CO₂ input stream was required (3 g·h⁻¹) in order to achieve the optimal hydrodynamic conditions for the electrochemical reactor. The optimal result was obtained when the electrochemical reactor was fed with a water flow in the CO₂ stream of 3 g·h⁻¹, achieving a [HCOO⁻] and FE_F value of 34 g·L⁻¹ and 72%, respectively. Moreover, [HCOO⁻] could be increased (46.5 g·L⁻¹) when *J* was increased from 45 mA·cm⁻² to 200 mA·cm⁻², but at the expense of a decrease in FE_F. It is important to note that the results of this study have been obtained in a continuous G–L–S reaction system, working with a single pass of the CO₂ humidified stream through the electrochemical reactor. However, further research is still required to improve the performance of the G–L–S reaction system for the electrocatalytic conversion of CO₂ to formate using Bi/C-CCMEs for the future implementation of the electrochemical process at the industrial scale.

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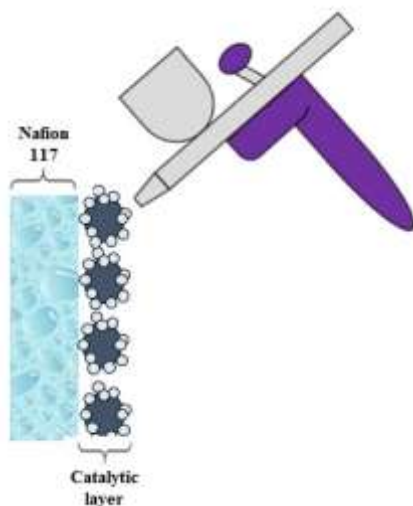


Fig. 1. Schematic of the airbrushing technique used to fabricate Bi/C-CCMEs.

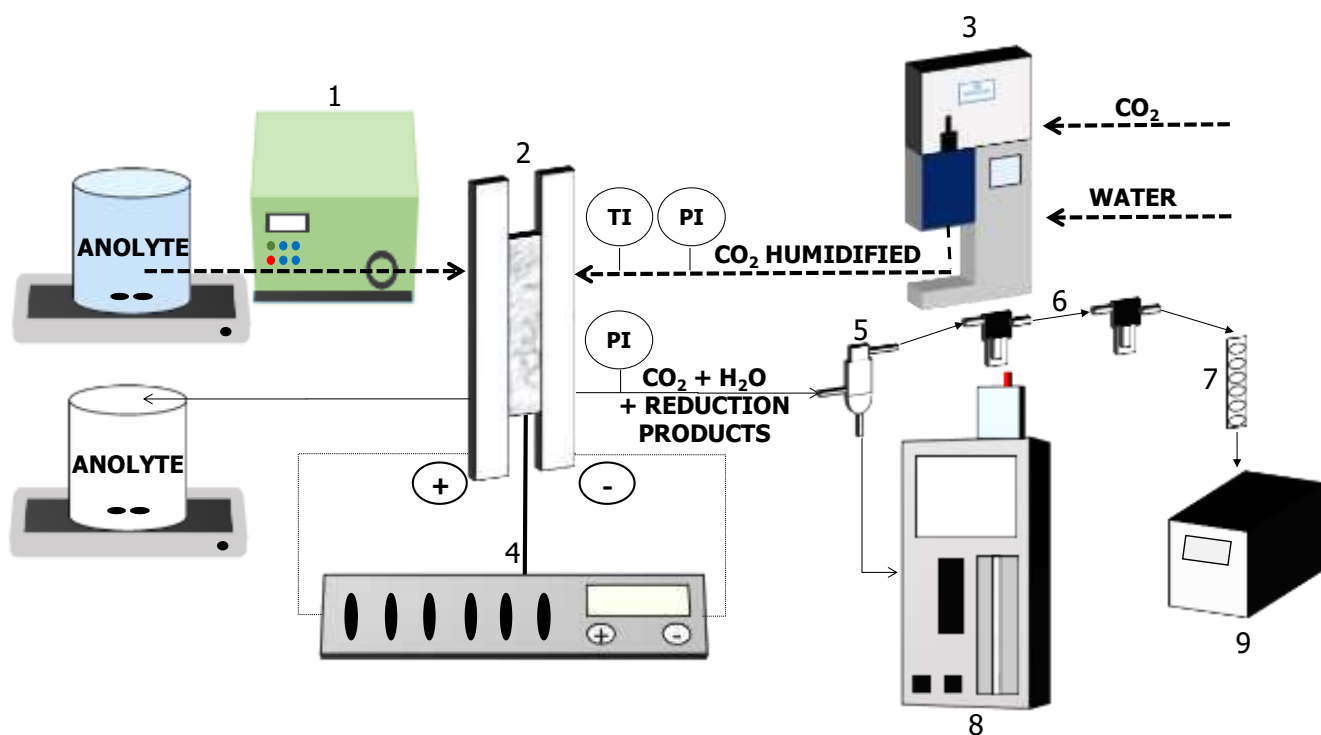


Fig. 2. Experimental setup used for the tests of Bi/C-CCMEs for the study of CO₂ electrochemical reduction to obtain HCOO⁻: 1 (Peristaltic pump); 2 (Filter press reactor); 3 (Vapor Delivery Module); 4 (Potentiostat-galvanostat); 5 (G/L Separator); 6 (Filters); 7 (Trap); 8 (Ion chromatography); 9 (Gas chromatography).

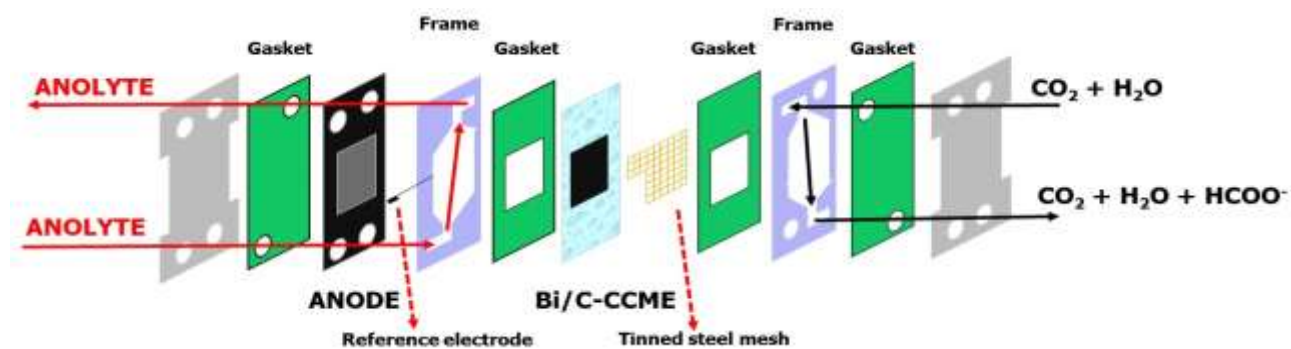


Fig. 3. Electrochemical filter-press reactor configuration for the tests of Bi/C-CCMEs used for the continuous electroreduction of CO_2 to obtain HCOO^- .

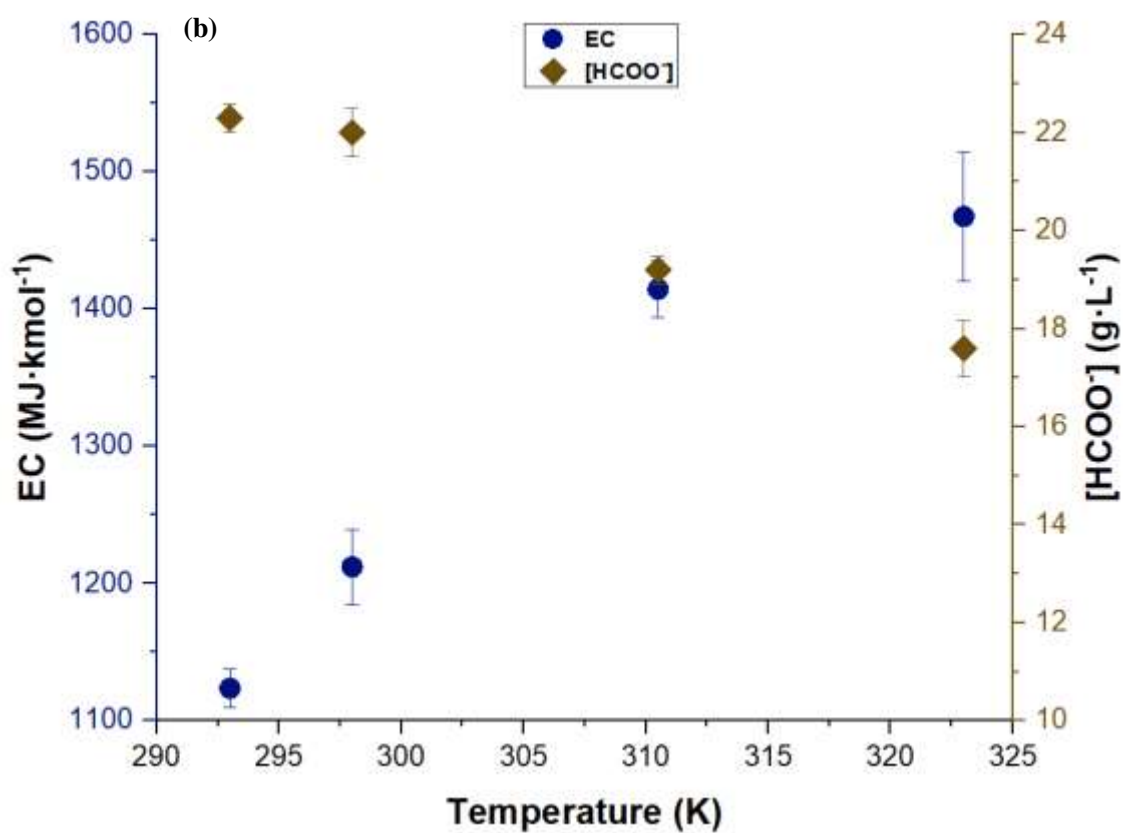
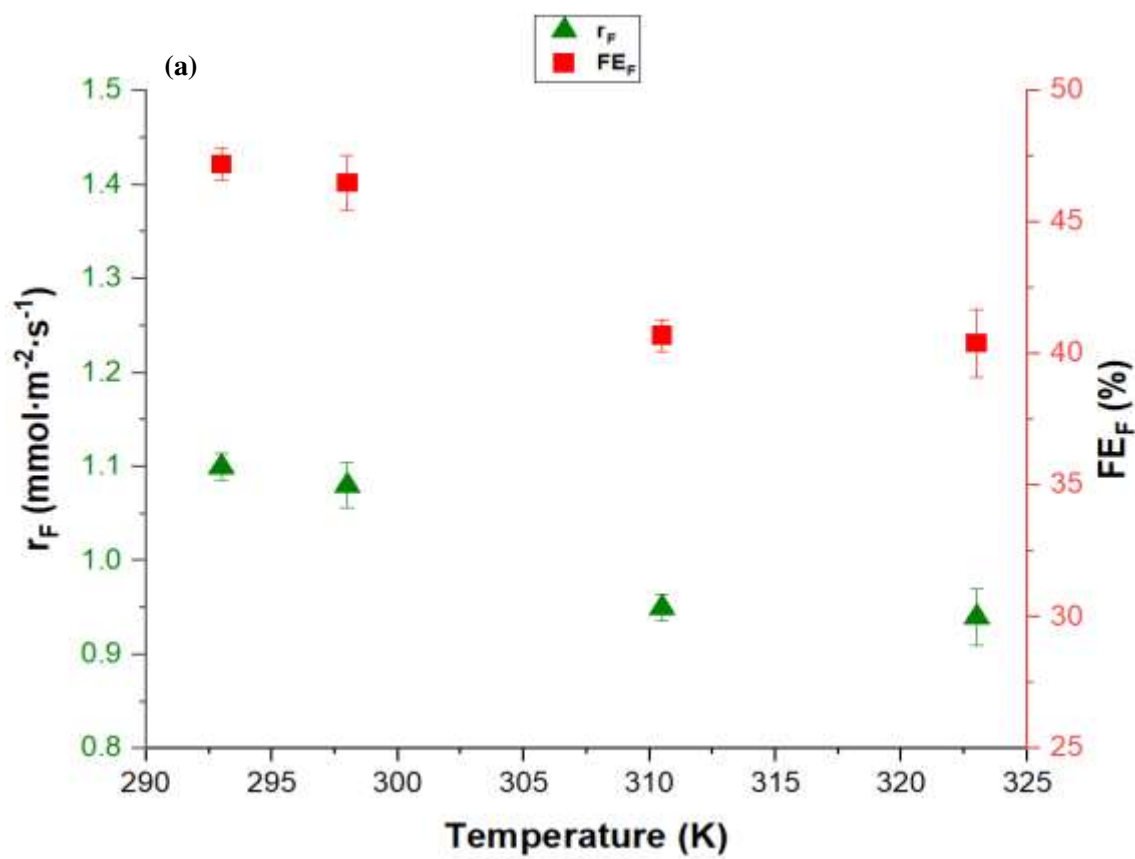


Fig. 4. Influence of temperature on (a) formate rate ($\text{mmol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) and Faradaic efficiency for formate (%) and (b) the consumption of energy per kmol of formate ($\text{MJ}\cdot\text{kmol}^{-1}$) and Formate concentration ($\text{g}\cdot\text{L}^{-1}$) in the temperature range of 293–323 K applied at constant current density = $45 \text{ mA}\cdot\text{cm}^{-2}$, Bi CL = $0.75 \text{ mg}\cdot\text{cm}^{-2}$, and relative humidity = 100%.

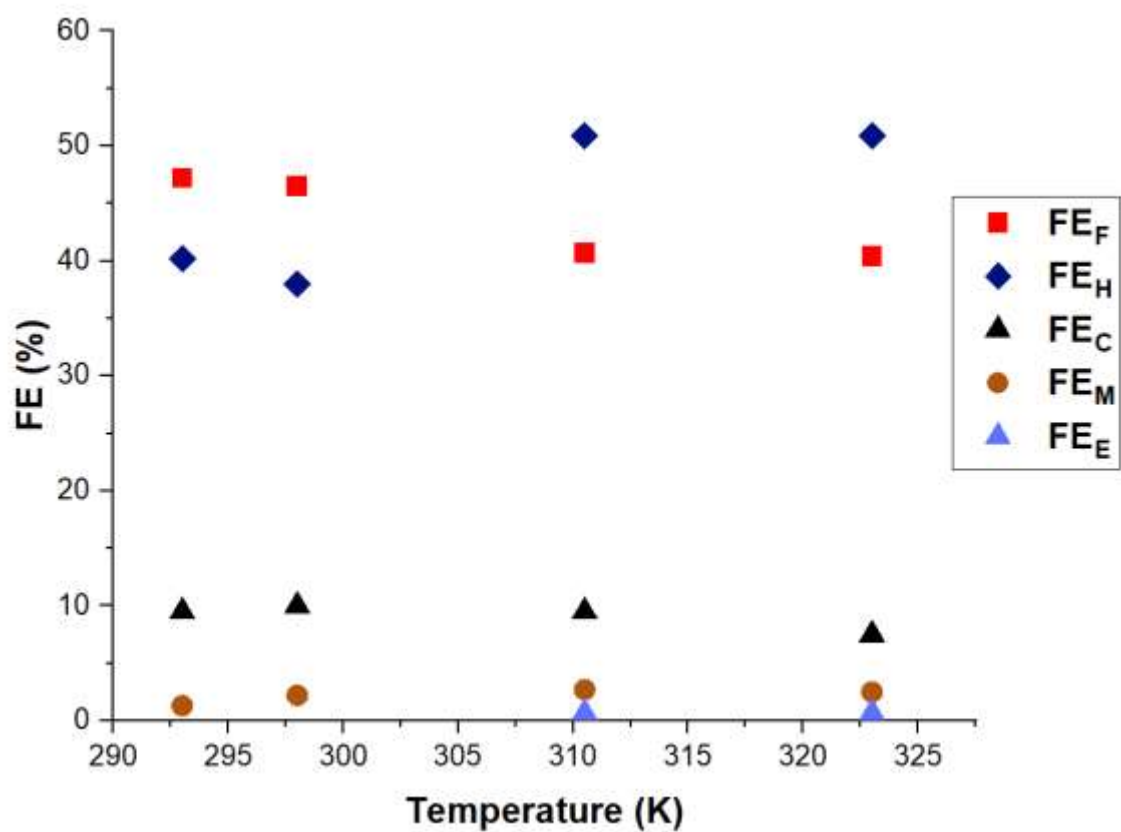


Fig. 5. Influence of temperature on the FE of formate (FE_F), hydrogen (FE_H), carbon monoxide (FE_C), methane (FE_M), and ethylene (FE_E) in the temperature range of 293 to 323 K applied at constant current density = $45 \text{ mA}\cdot\text{cm}^{-2}$, Bi $CL = 0.75 \text{ mg}\cdot\text{cm}^{-2}$, and relative humidity of 100%.

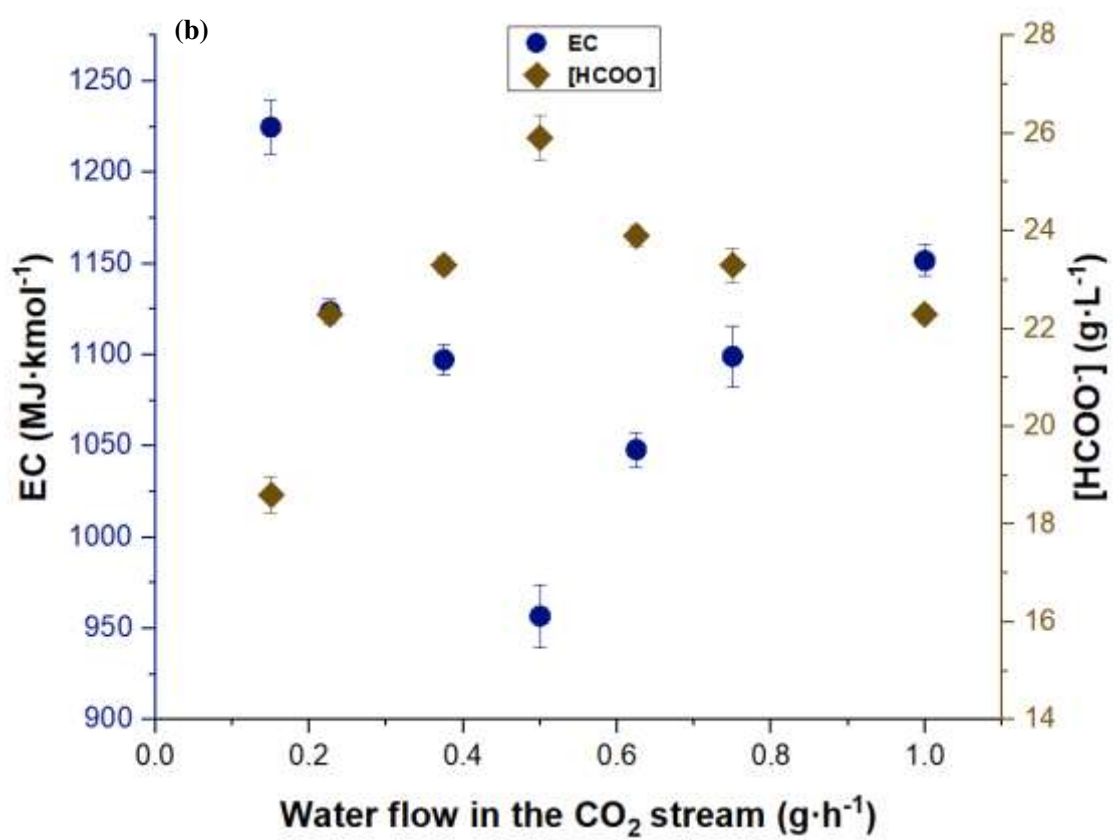
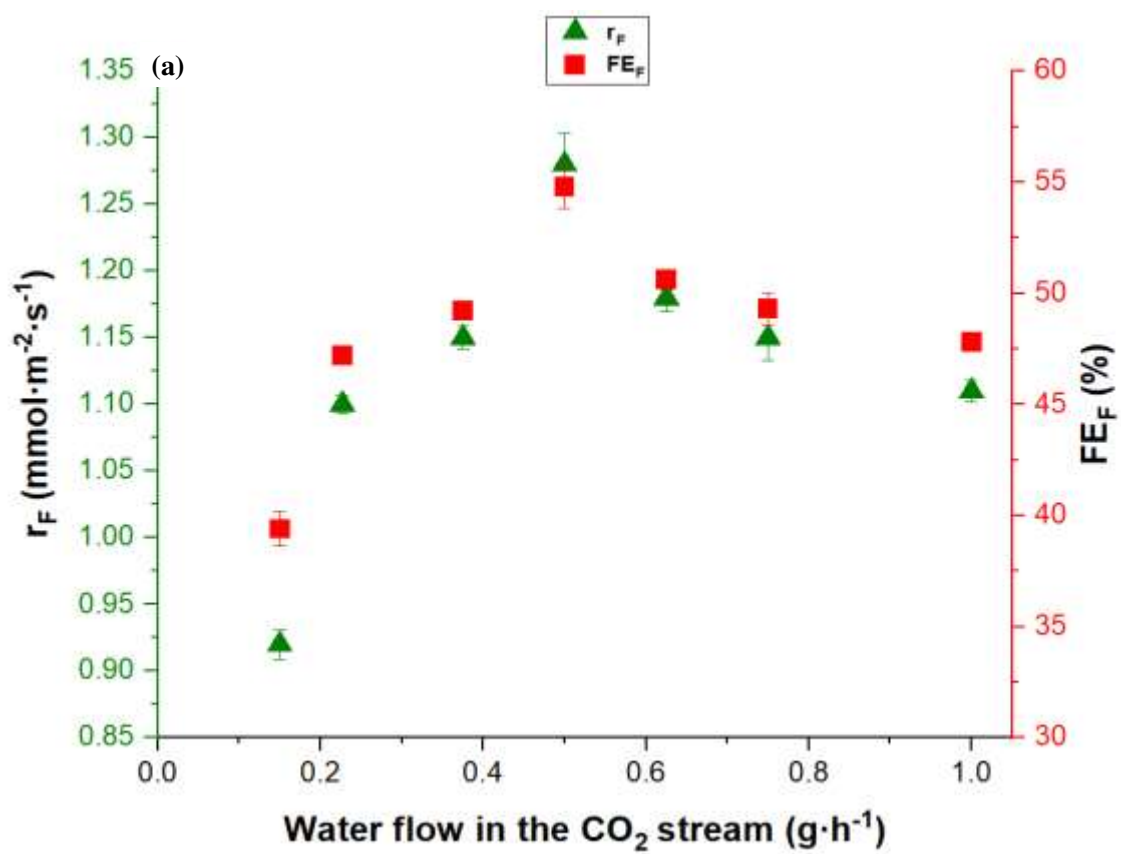


Fig. 6. Influence of water flow in the CO₂ stream on (a) formate rate (mmol·m⁻²·s⁻¹) and Faradaic efficiency for formate (%) and (b) the consumption of energy per kmol of formate (MJ·kmol⁻¹) and formate concentration (g·L⁻¹) in the water flow range of 0.15–1 g·h⁻¹ applied at constant current density = 45 mA·cm⁻², Bi CL = 0.75 mg·cm⁻², as measured at room temperature.

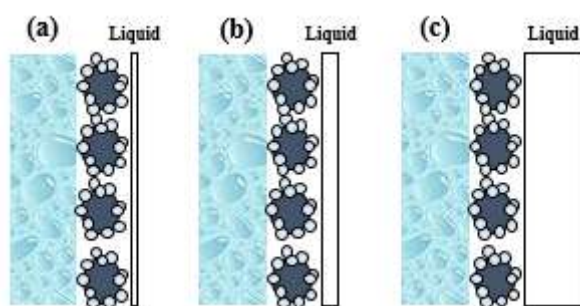


Fig. 7. Schematic of liquid film formation over the CCME surface depending on the amount of water in the CO₂ stream: (a) scarce amount of water in the CO₂ input stream, (b) optimal amount of water in the CO₂ input stream (solid polymer electrolyte), and (c) excess amount of water in the CO₂ stream (liquid electrolyte).

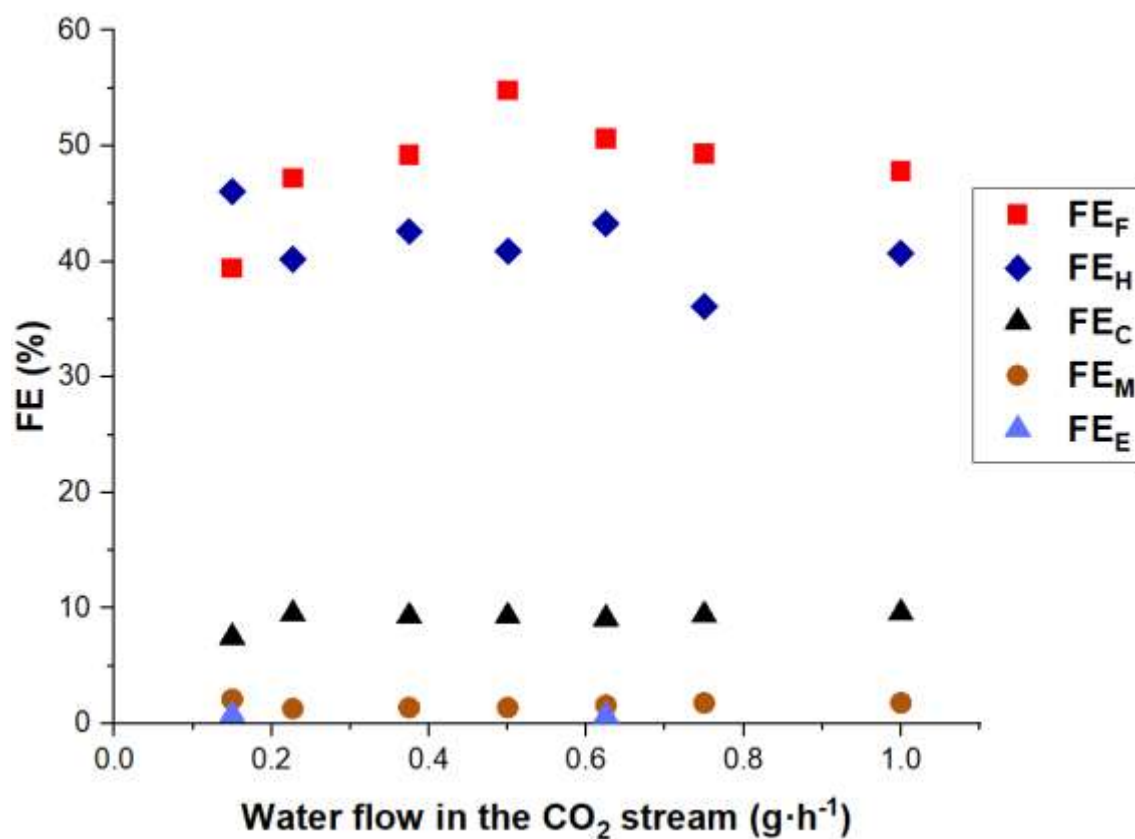


Fig. 8. Influence of water input flow in the CO₂ stream on FE to formate (FE_F), hydrogen (FE_H), carbon monoxide (FE_C), methane (FE_M), and ethylene (FE_E) in the water flow range of 0.15–1 g·h⁻¹ applied at constant current density = 45 mA·cm⁻², Bi $CL = 0.75$ mg·cm⁻², as measured at room temperature.

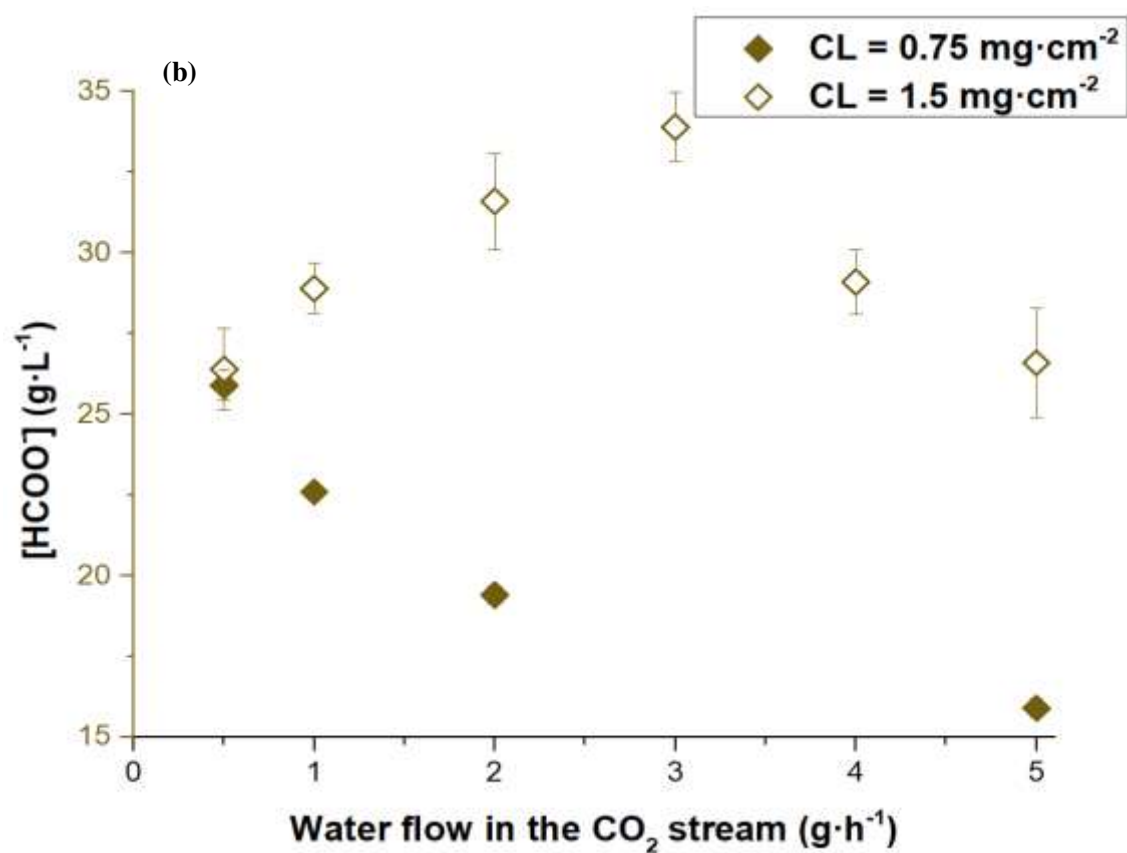
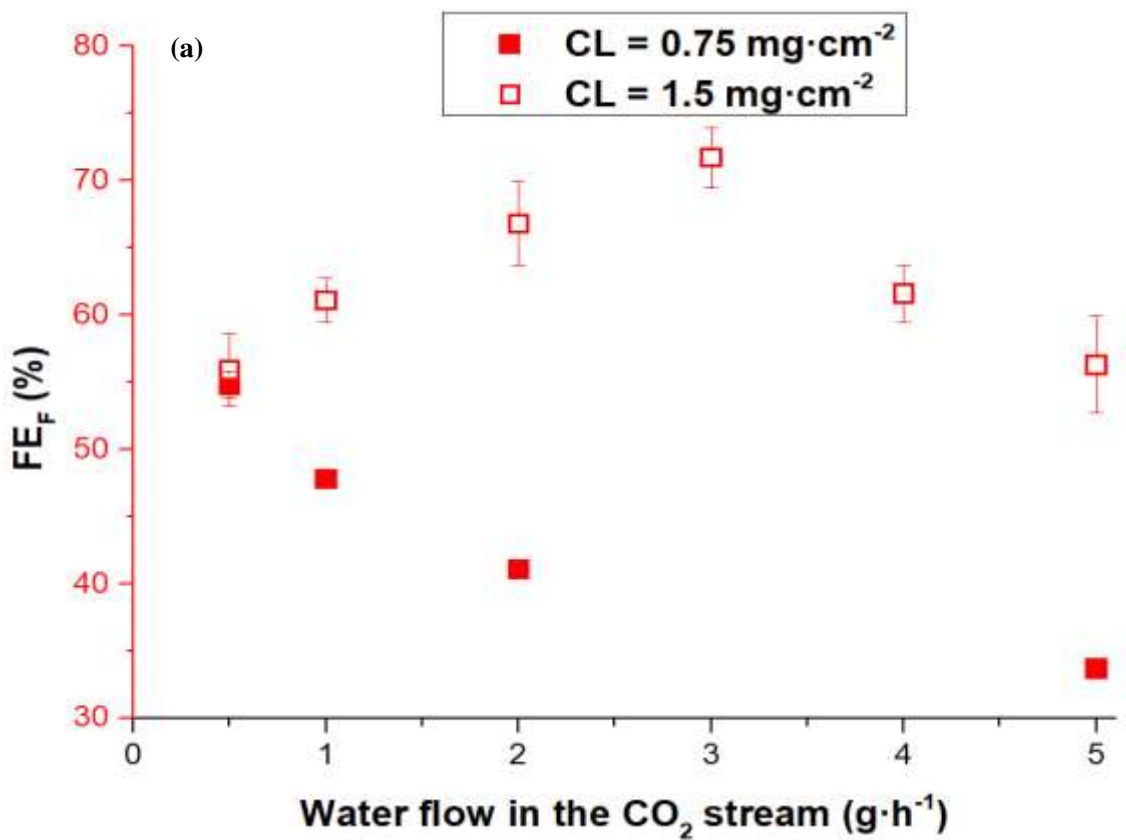


Fig. 9. Influence of water flow in the CO₂ stream on (a) Faradaic efficiency for formate (%) and (b) formate concentration (g·L⁻¹) working with Bi/C-CCMEs with a Bi CL = 0.75 mg·cm⁻² and 1.5 mg·cm⁻² in the water flow range of 0.5–5 g·h⁻¹ at a constant current density of 45 mA·cm⁻² as measured at room temperature.

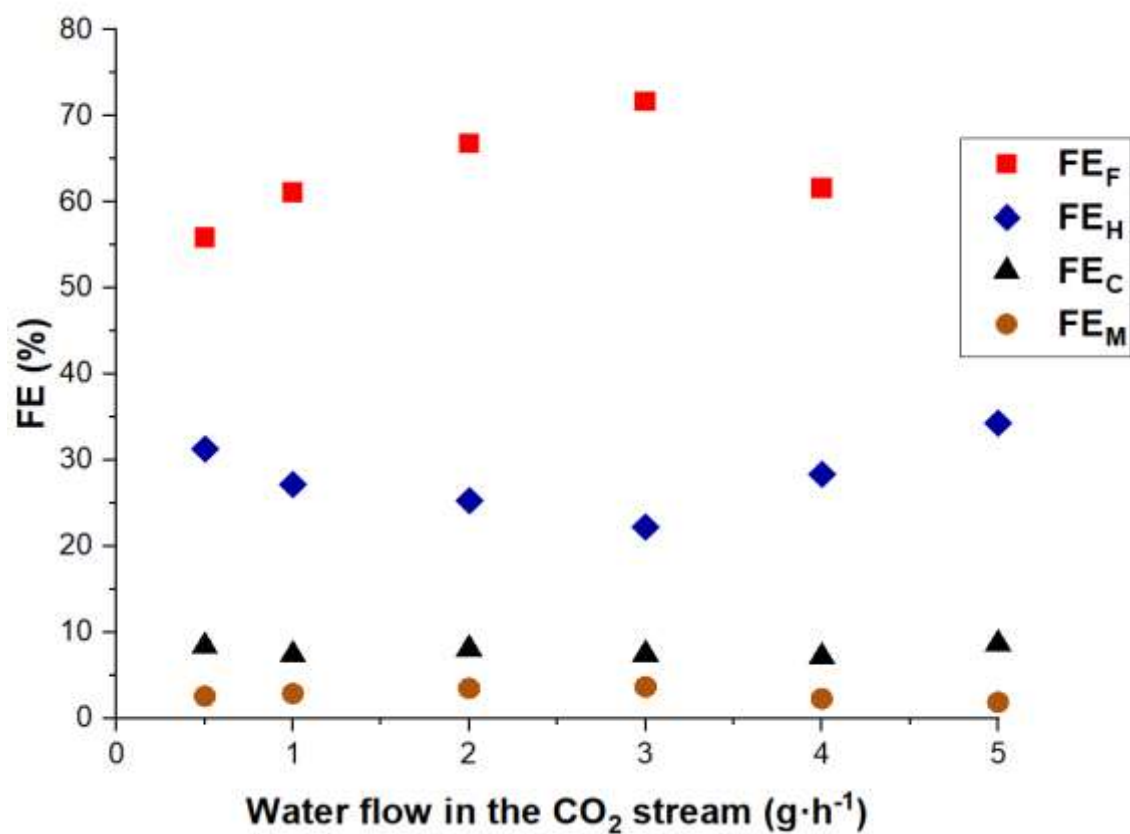


Fig. 10. Influence of water input flow in the CO₂ stream on FE to formate (FE_F), hydrogen (FE_H), carbon monoxide (FE_C), and methane (FE_M) working with Bi/C-CCMEs with a Bi $CL = 1.5 \text{ mg}\cdot\text{cm}^{-2}$ in the water flow range of 0.5–5 g·h⁻¹ applied at a constant current density of 45 mA·cm⁻², as measured at room temperature.

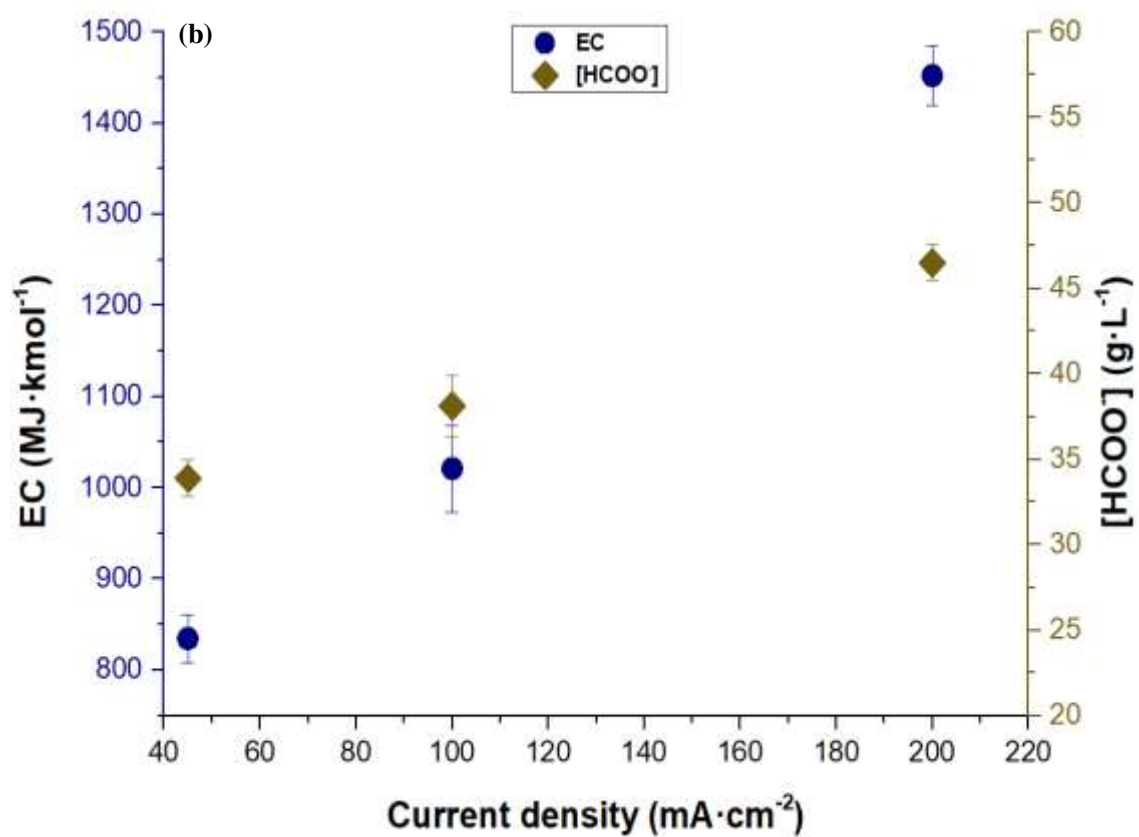
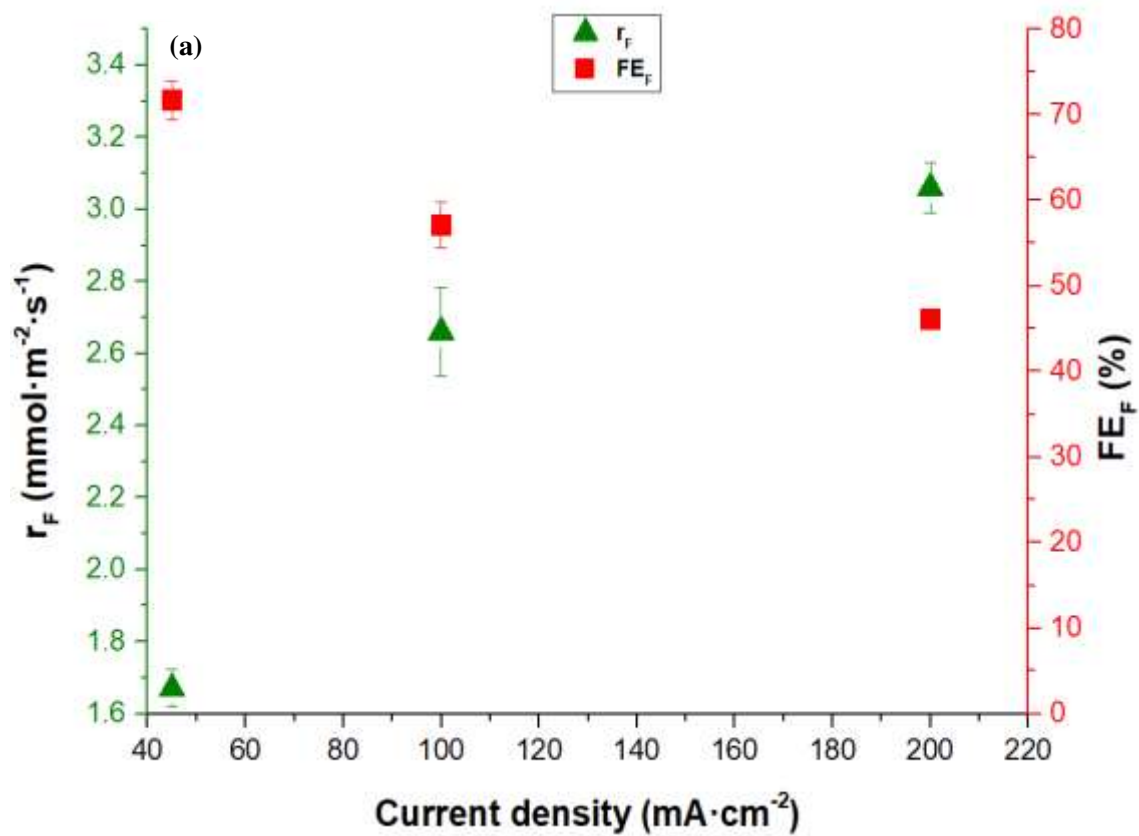


Fig. 11. Influence of current density on (a) formate rate ($\text{mmol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) and Faradaic efficiency for formate (%) and (b) consumption of energy per kmol of formate ($\text{MJ}\cdot\text{kmol}^{-1}$) and formate concentration ($\text{g}\cdot\text{L}^{-1}$) in the current density range of 45–200 $\text{mA}\cdot\text{cm}^{-2}$ operating at 293 K, Bi $CL = 1.5 \text{ mg}\cdot\text{cm}^{-2}$, and water flow in the CO_2 stream = $3 \text{ g}\cdot\text{h}^{-1}$.