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Catalyst Coated Membrane Electrodes for the gas phase CO_2 electroreduction to formate

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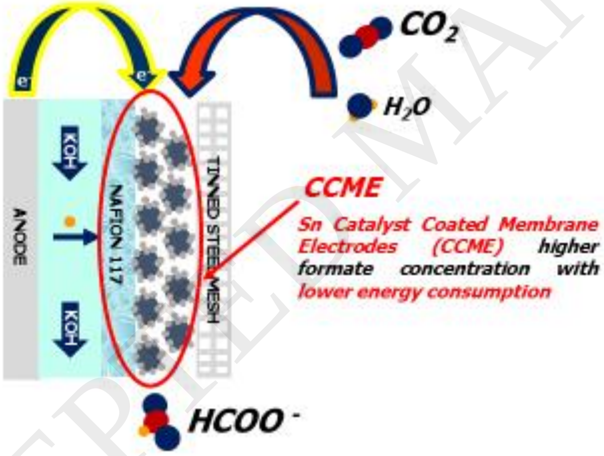
Graphical abstract



Highlights:

- Catalyst Coated Membrane Electrodes (CCMEs) were developed.
- CCMEs allowed obtaining formate in a continuous mode without a liquid catholyte.
- CCMEs was compared with GDEs using the same catalyst and operating conditions.

- CCMEs gave higher concentration than GDEs with an important saving of energy.
- The influence of temperature and the amount of water in CO_2 stream was analysed.

ABSTRACT

The electrochemical valorisation of captured CO_2 is an attractive option to obtain value-added products, and at the same time, to chemically store energy from intermittent renewable sources. Among the different products, formic acid/formate is particularly interesting since it is one of the most promising materials for hydrogen storage and candidate fuel for low-temperature fuel cells. In this work, a process for CO_2 electroreduction to formate is studied on a continuous filter-press cell using an innovative electrode: Sn Catalyst Coated Membrane Electrodes (Sn-CCMEs) - comparing with previous approaches based on Sn Gas Diffusion Electrodes (Sn-GDEs), using the same synthesised tin nanoparticles (Sn NPs) and operating conditions. The Sn-CCME is prepared by depositing Sn NPs directly over a Nafion 117 membrane, and it allows working with a gaseous CO_2 flow humidified with water as the input of the electrochemical cell, avoiding the use of the liquid catholyte. Sn-CCME operates at lower current densities (45 mA cm^{-2}) than previous Sn-GDEs (200 mA cm^{-2}), which resulted in lower rates of formate production. However, the proposed Sn-CCME, allowed achieving even higher formate concentrations with an energy consumption 50% lower than with the Sn-GDEs. The influence of key variables such as temperature and water input flow on the performance of the process using Sn-CCMEs was also analysed in a controlled experimental set-up specifically designed and built for this goal. Increasing the temperature of the gaseous stream did not improve the performance. The best results were obtained at ambient conditions of temperature (20ºC) and with the amount of water in the CO_2 stream at 0.5 g h^{-1}, giving the highest formate concentration (19.2 g L^{-1}) with a Faradaic efficiency close to 50% and an energy consumption of 244 kWh $kmol^{-1}$. More research is still required to further improve CCME configuration in order to increase formate rate and efficiency without increasing energy consumption.

Keywords:

- CO_2 electroreduction
- Formate
- Sn nanoparticles
- Catalyst Coated Membrane Electrode
- Gas phase

1. Introduction

Carbon dioxide (CO_2) concentration in the atmosphere is currently upon 410 ppm [1] so there is an urgent need for developing strategies for reducing CO_2 emissions and mitigate climate change [2-5]. One of the most promising options to achieve this challenge is the capture and valorisation of CO_2 [6-9]. In this context, CO_2 can be converted by chemical, photochemical and electrochemical techniques [10-12].

Particularly, the electrocatalytic conversion of CO_2 into value-added products is receiving increasing attention in the last years [13-15]. Apart from such beneficial use from CO_2 capture, the electrochemical utilisation of CO_2 is thought to constitute an attractive future option for storing energy from renewable sources like wind or solar energy [16,17]. Renewable energy sources are intermittent and difficult to predict accurately, so electrochemical CO_2 conversion processes could allow the use of excess renewable electricity for the valorisation of captured CO_2 obtaining products with value-added, making simultaneously possible the electrical energy storage in chemical form.

A wide variety of interesting products can be obtained from the electroreduction of CO_2 such as formic acid (HCOOH) or formate ($HCOO^-$) (depending on the pH value) [18,19], carbon monoxide (CO) [20,21], hydrocarbons (CH_4 or C_2H_4) [22,23] or alcohols (CH_3OH or C_2H_6O) [24,25].

In this sense, among all these different products, formic acid or formate are commonly used at several industries such as leather, manufacturing of rubber, pharmaceuticals and crop protection agents and silage/animal food [26]. It is also a promising candidate fuel for low-temperature fuel-cells [27,28] as well as a promising hydrogen storage material [29,30].

In the process of CO_2 electroreduction to formate, different electrocatalytic material can be used, being stand out lead [31,32], indium [33,34], zinc [35,36], bismuth [37], cobalt [38], palladium [39] or particularly tin [40-48]. The electrocatalytic material is usually deposited in form of nanoparticles in order to maximize the surface area with the minimum amount of catalyst.

Our previous studies using Gas Diffusion Electrodes (GDEs) containing low metallic electrocatalyst loading achieved formate concentrations of up to 16 g L^{-1} on a continuous mode with only one pass of the catholyte through the electrochemical reactor [42], with an energy consumption over 500 kWh per kmol of formate. These results together with other recent studies [49-51] can be considered as promising advances on continuous CO_2 electroreduction processes to obtain formate. However, improvements are still needed in these technologies to approach practical application and enable feasible production of formic acid or formate. For example, formate concentration must be high (and as close as possible to 85% wt., the most common concentration in the market [52]) at the output stream of the electrochemical reactor because the purification step consumes a lot of energy and it is a critical step for the industrial implementation of this process [53,54].

One way of improvement, scarcely explored yet, may be related to the development of electrodes and electrochemical reactor configurations that allow reducing, or even avoiding, the use of liquid catholyte, working accordingly in gaseous phase in the cathode. Few attempts of studying the electroreduction of CO_2 to formate in gas-phase with no liquid catholyte have been reported. Lee et al. [55] and Lee et al. [56] carried out studies supplying CO_2 directly in gas phase using a zero gap electrolytic cell configuration, while Genovese et al. [57] developed the CO_2 electroreduction to formate using an electrochemical reactor, working in gas phase. We reported preliminary studies with a new design of zero-gap electrochemical reactor for direct and continuous conversion of humidified gaseous CO_2 toward formate avoiding the use of liquid catholyte [58,59]. Despite a home-made system was difficult to control, the results obtained were promising and revealed an influence of temperature and of the amount of water in the CO_2 stream, pointing to the need of further studies with an accurately controlled system specifically designed to allow a systematic analysis of the influence of these key variables. These works correspond to our first membrane electrode assembly (MEA) configuration experience in which the nanoparticulated electrocatalyst is directly sprayed over a Nafion Membrane. This MEA configuration is named Catalysts Coated Membrane Electrode (CCME). Accordingly, Nafion membrane acts as electrolyte in addition to separator of both cathodic and anodic compartments. The use of ion-exchange membrane as electrolyte (solid polymer electrolyte, SPE) leads to solve the problem of low solubility of CO_2 that limits reaction rate, and other significant disadvantages related to the possibility of secondary reactions and complicated separation and purification processes of reaction final products. Very recent results on catholyte-free electrochemical CO_2 reduction to formate using commercial tin nanoparticles (NPs) [60] also reinforce the interest in the study of approaches avoiding the use of liquid catholyte.

In this context, the main aim of this work is to study the continuous and direct electrochemical reduction of CO_2 to formate with Sn-CCME to achieve the optimal configuration in order to increase the performance at low energy consumption. For that, the present study focuses on the comparative analysis in terms of the energy consumption, faradaic efficiency and formate formation between two types of configurations within the same electrochemical membrane reactor: i) Sn-CCME configuration which does not require of liquid electrolyte, and ii) GDEs configuration, using the same Sn/C-NPs [42]. Moreover, the influence of key variables such as temperature and water input flow on the electrochemical performance of the process using Sn-CCMEs is also systematically analysed in a controlled experimental set-up specifically designed and built for this goal.

2. Methods

2.1 Sn-CCME fabrication

For the fabrication of homemade Sn-CCMEs, the Sn/C NPs were the same as those used in previous work [42] whose mean size is about 10-15 nm. A detailed electrochemical characterization of these NPs can also be found in a previous publication [42].

Sn-CCMEs were prepared by airbrushing technique. For that, the catalytic ink based on Sn/C NPs was prepared by mixing catalytic material with isopropyl alcohol (Isopropanol, 99.5%, Extra Dry over Molecular Sieve, AcroSeal®) and a certain amount of Nafion (from Nafion D-521 dispersion, 5% w/w in water and 1-propanol, ≥0.92 meq/g exchange capacity, Alfa Aesar) followed by sonication for 30 min. The catalytic ink consisted then of Sn/C NPs to Nafion ratio of 70/30 w/w with a wt.% total solid in final alcoholic dispersion of 3 wt.%. Thereafter, the catalyst slurry was directly sprayed over a Nafion 117 membrane with a geometric surface area of 10 cm^2 placed on a hot metallic plate in a range of temperature at 65±5 ºC to facilitate solvent evaporation. The final Sn loading was 0.75 mg cm^{-2}.

2.2. Sn-CCME characterisation

Scanning electron microscopy (SEM, HITACHI S-3000 N micro-scope working at 20 kV with a X-ray detector XFlash 3001 (Bruker) for EDX microanalysis and mapping) was employed to analyse the morphology and atomic composition of the Sn-CCME.

2.3 Gas-phase operation in the cathode

2.3.1 Preliminary set-up

In our previous and preliminary tests for assessing the feasibility of CCMEs [58,59] a home-made bubble-type humidifier was initially used to prepare a humidified gaseous CO_2 stream that was the input to the electrochemical reactor (see Figure S1 in the Supporting Information). The results of these preliminary tests suggested the feasibility of the new CCME configuration, but also showed that this home-made system lacked of the accurate control of crucial operating variables like the temperature of the streams and the ratio between gaseous CO_2 and water vapour. Since one of the aims of the present study was to carry out a rigorous assessment of the influence of these operating variables, a new system was designed and built as described in the next subsection.

2.3.2 Experimental setup

Sn-CCMEs were tested on an experimental setup that included three tanks, a peristaltic pump, a potentiostat, an electrochemical cell, a cooler and a vapour delivery module (VDM), as shown in Fig. 1.

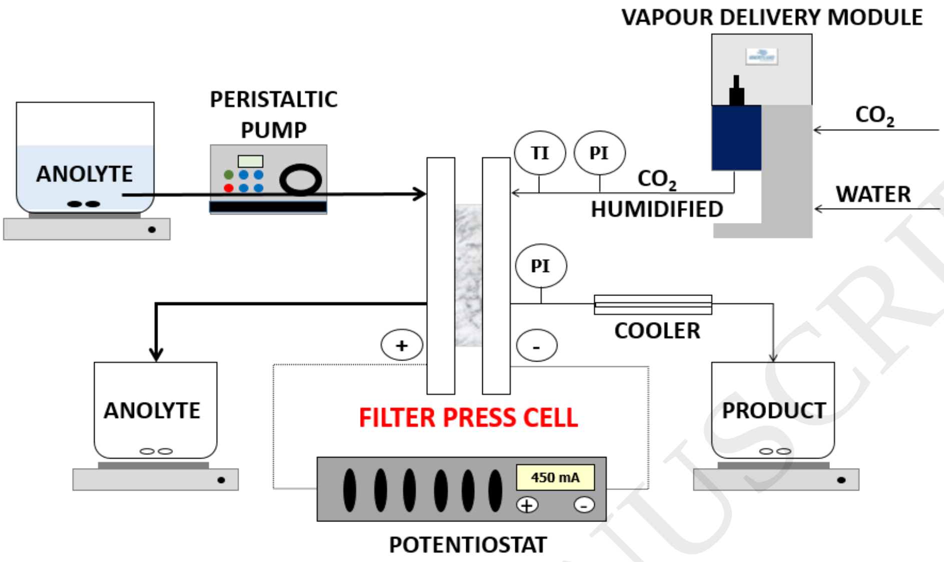


Fig 1. Experimental plant scheme.

The electrochemical reduction of CO_2 to formate occurred in the cathodic compartment of the electrochemical membrane reactor (Micro Flow Cell, ElectroCell A/s) on a continuous mode with a single pass of the catholyte through the electrochemical reactor with the current supplied by the potentiostat (Arbin Instruments, MSTAT4). The main advantage of using Sn-CCMEs is avoiding the use of aqueous electrolyte where the solubility of CO_2 is significantly low and therefore the rate reaction is limited. For this configuration, the CO_2 stream must be humidified and directly fed in gaseous phase to the reactor so the electrochemical cell is coupled to a Vapour Delivery Module (VDM) (Bronkhorst, SW-200). The VDM allows accurately controlling and adjusting the feed gas temperature and the ratio between CO_2 flow and H_2O in the input stream. As required, the experimental setup designed was also able to measure relative humidity and the temperature of the input stream of the electrochemical by HygroFlex HF5 Humidity

Temperature Transmitters (TI). Pressure was also measured in the input and the output of the electrochemical cell by pressure transmitters (PI). As in previous studies [42], pure gaseous CO_2 was fed to the electrochemical cell at a constant flow rate of 200 mL min^{-1}.

2.4 Experimental tests

The Sn-CCME was used as cathode, which was manufactured as previously described by depositing Sn/C NPs directly over a Nafion 117 membrane. Therefore, the Nafion 117 membrane is used both as cell divider and as support for the electrocatalytic material.

As in previous studies using Sn-GDEs [42], a 1 mol L^{-1} KOH solution was used as the anolyte with an anolyte flow per electrode area of 0.57 mL min^{-1} cm^{-2} and it was circulated to the anodic compartment of the electrochemical cell by a peristaltic pump (Watson Marlow 320, Watson Marlow Pumps Group). A tinned steel mesh was used as current collector and a Dimensionally Stable Anode [DSA/O_2 (Ir-MMO (Mixed Metal Oxide) on Platinum) was used as the counter electrode in the electrochemical membrane reactor. In the anodic compartment, the oxygen evolution reaction takes place, according to the next reaction:

$$4\mathrm{OH}^- \rightarrow \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^- \qquad (1)$$

whereas in the cathodic compartment the electrochemical reduction of CO_2 to formate occurs, following the next reaction:

$$\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} + 2\mathrm{e}^- \rightarrow \mathrm{HCOO}^- + \mathrm{OH}^- \qquad (2)$$

Fig. 2 represents a scheme of the electrochemical membrane reactor and electrode configuration.

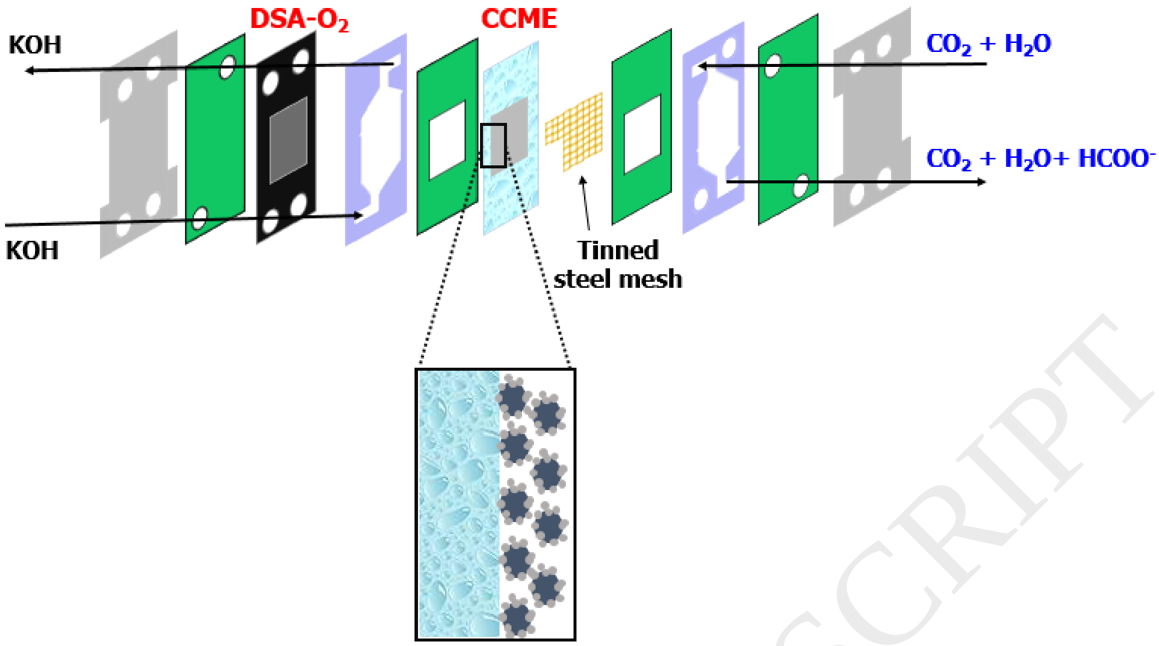


Fig 2. Electrochemical membrane reactor and electrode configuration.

Different experiments were carried out at ambient conditions of pressure and modifying the conditions of temperature and water input flow of the input stream of the electrochemical cell. Experiments had a duration of 90 min. Output stream of the electrochemical cell is cooled and then collected in a tank.

Samples were taken every 30 min and then analysed by ion chromatograph in order to obtain the formate concentration. The analysis was carried out with a Dionex ICS 1100 equipped with and AS9-HC column, using a solution of 4.5 mmol L^{-1} of Na_2CO_3 as the eluent at a flow rate of 1 mL min^{-1}, and a pressure and conductivity of approximately 15.18 MPa and 17.88 mS respectively.

For each experiment, an average formate concentration was obtained in order to determine the Faradaic efficiency, the formate rate and the energy consumption. The Faradaic efficiency (FE) represents the percentage of the total charge supplied that is used to obtain formate [14]. The FE can be obtained by equation (3):

$$\mathrm{FE}(\%) = \frac{z \cdot n \cdot F}{Q} \qquad (3)$$

where z is the number of electrons exchanged (e.g., z = 2 for reduction of CO_2 to formate), n is the number of moles of formate produced, F is the Faraday constant (96485 C mol^{-1}), and Q represents the total charge passed.

Besides the formate rate is defined as the amount of formate produced per unit of cathode area and unit of time. The rate can be calculated by equation (4):

$$\mathrm{Rate}\left(\frac{\mathrm{mol}}{\mathrm{m^2\ s}}\right) = \frac{n}{A \cdot t} \qquad (4)$$

where n is also the number of moles of formate produced in each experiment, A is the geometric surface area of the cathode and t is the duration of each experiment.

Finally, the energy consumption is defined as the amount of energy used to produce formate. The energy consumption can be defined by equation (5):

$$\text{Energy consumption}\left(\frac{\mathrm{kWh}}{\mathrm{kmol}}\right) = \frac{Q \cdot V}{n} \qquad (5)$$

where Q and n have the same meaning as in equation (3), and V is the absolute cell potential in the electrochemical membrane reactor.

3. Results

3.1. Sn-CCMEs characterisation

Fig. 3 show SEM images of the surface (Fig. 3A) and cross section morphology of the Sn-CCME (Fig. 3B) also including their corresponding EDX mapping (Figs 3C and D). In Fig. 3A, metal catalyst seems to be homogeneously distributed over the entire electrode surface as clearly verified by its corresponding EDX mapping (Fig. 3C). On the other hand, the thickness of the catalytic layer is about 15 µm (Fig. 3B) from its corresponding EDX mapping, it is clearly observed that the catalytic layer exclusively covers upper side of the Nafion membrane without obvious percolation (Fig. 3D).

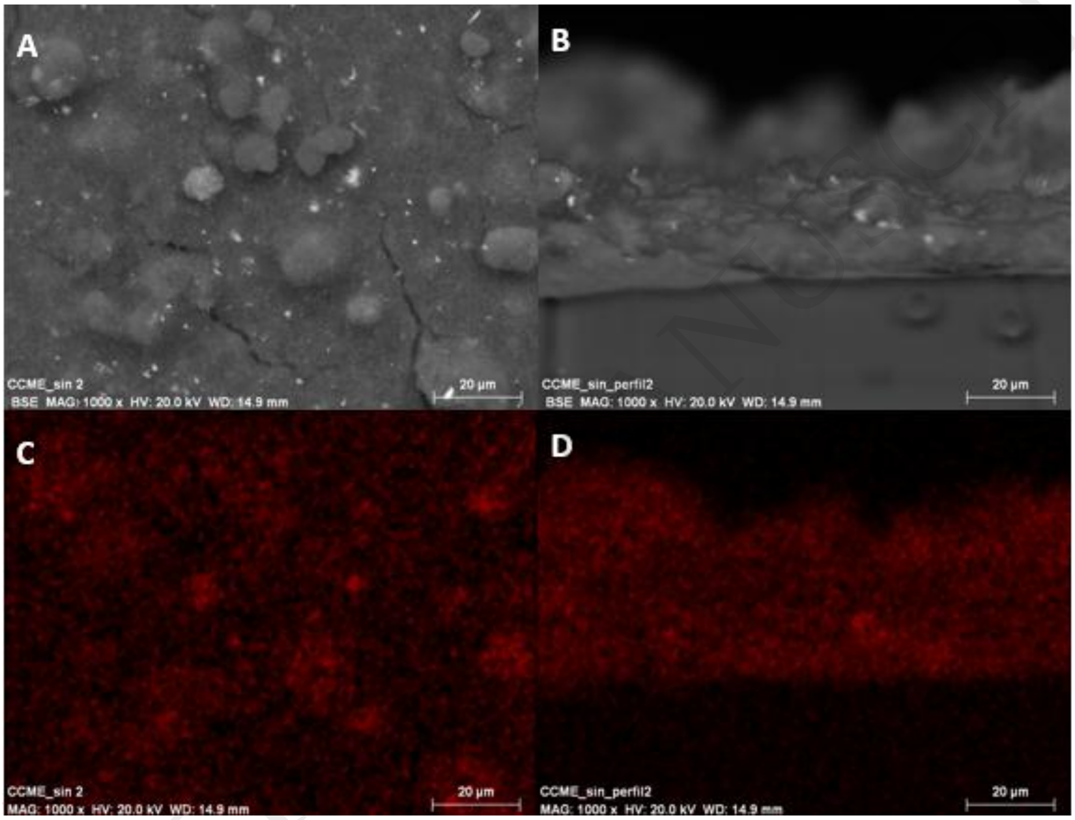


Fig 3. SEM images (A) surface and (B) cross section, and EDX mapping (C) surface and (D) cross section of the Sn-CCMEs.

3.2 Preliminary assessment of Sn-CCMEs

Initial tests were carried out to assess the feasibility of working with Sn-CCMEs in our experimental set-up. Different current densities were initially evaluated and 45 mA cm^{-2} was fixed as optimal value for carrying out the electrochemical tests at constant current density. The possibility of working at higher values of current densities was explored but the cell potentials obtained were even higher than those obtained using Sn-GDEs with the same catalysts operating at the same values of current densities. In addition, no improvement in the performance in terms of formate concentration and energy consumption were observed.

3.3 Influence of temperature

Different experiments were carried out in order to analyse the influence of temperature for continuous electroreduction of CO_2 to formate using Sn-CCMEs. The values of temperature tested were 20, 25, 37.5 and 50 °C, and all experiments were carried out on a continuous mode with single pass of the catholyte through the electrochemical reactor at a current density of 45 mA cm^{-2} with a stream of CO_2 saturated with the water at the corresponding temperature.

Results of rate of formate production and Faradaic efficiency (FE), together with the results of energy consumption and formate concentration as a function of temperature are summarised in Fig. 4 and Fig. 5, respectively. The detailed results are reported in Table S1 as Supporting Information.

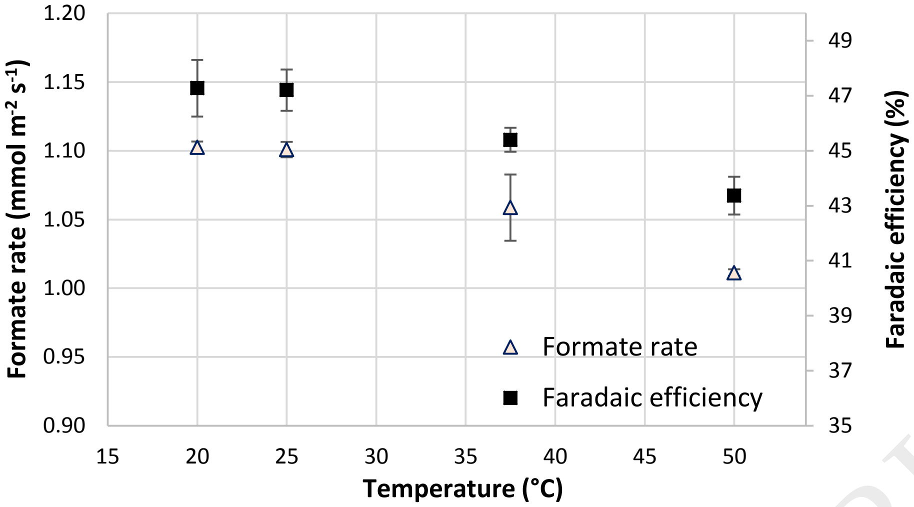


Fig 4. Formate rate and faradaic efficiency as a function of temperature obtained with a relative humidity of 100% on a continuous mode with a single pass of the catholyte through the electrochemical reactor at a current density of 45 mA cm^{-2}.

As shown in Fig. 4, the formate rate and FE values were practically equal for 20 and 25 ºC. However, a slightly decrease of formate rate and FE was observed as temperature increased. The best result was obtained when the electrochemical cell is fed with input stream at room temperature (20 °C), achieving a value of formate rate of 1.1 mmol m^{-2} s^{-1} with a FE of 47%. However, when the temperature of the CO_2 stream saturated with H_2O is increased to 50 ºC, the production rate decreased to 1 mmol m^{-2} s^{-1} and FE lowered to 43%.

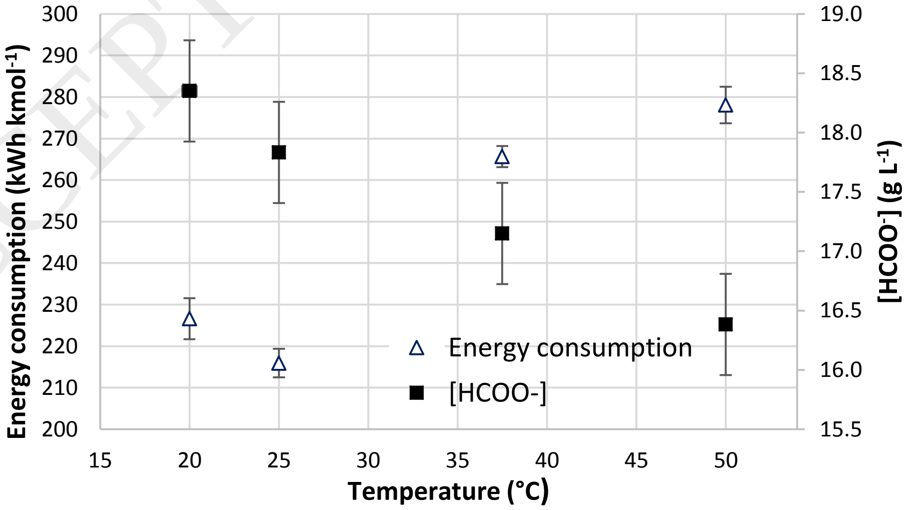


Fig 5. Energy consumption and formate concentration as a function of temperature obtained with a relative humidity of 100% on a continuous mode with a single pass of the catholyte through the electrochemical reactor at a current density of 45 mA cm^{-2}.

The effect of the temperature on the concentration of the product and on the energy consumption is shown in Fig. 5. As can be noted, the formate concentration also followed a linear decreasing trend with temperature. If at 20 ºC the formate concentration achieved was 18.4 g L^{-1}, increasing the working temperature to 50 ºC was detrimental, giving a lower concentration of 16.4 g L^{-1}. The results shown in Fig. 5 also clearly indicate that lowering temperature, an important saving in energy consumption is obtained. Energy consumption per kmol of product obtained resulted to be very similar at 20 and 25 ºC (with less than 5% of difference), but it noticeably increases at higher temperatures. In this way, when the CO_2 electroreduction was carried out at 50 °C, there was an increase in the energy consumption of more than 22% with respect to the value of energy consumption obtained working at 20 ºC. In conclusion, these results clearly show that all the figures of merit used for assessing the performance of the process worsened when temperature was increased.

3.4 Influence of water input flow

According to the results presented and discussed in the previous subsection, CO_2 electroreduction to formate using CCMEs working at room temperature gives better results in terms of formate rate, FE, energy consumption and formate concentration than working at higher temperatures. Therefore, further tests were carried out at 20 ºC, which provided the best results.

Accordingly, it is feasible to think that electrochemical behaviour of CO_2 reduction can also be controlled by varying other parameters such as degree of humidity of CO_2. In this sense, in order to evaluate the influence of the amount of water introduced with the CO_2, several tests were carried out at 20 ºC and different water input flows on a continuous mode with only one pass through the electrochemical reactor at a current density of 45 mA cm^{-2}. Results of formate rate and FE, and energy consumption and formate concentration obtained at different water input flow points are depicted in Fig. 6 and Fig. 7 respectively. The detailed results are reported in Table S2 as Supporting Information.

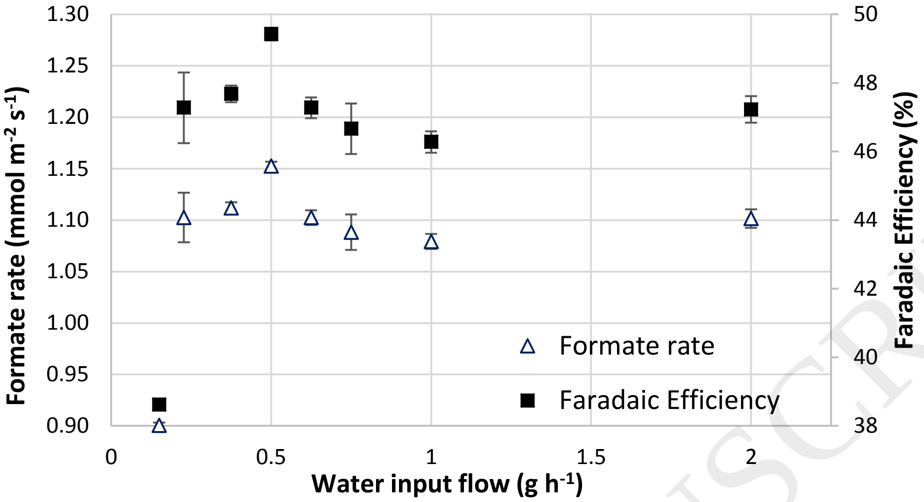


Fig 6. Formate rate and Faradaic efficiency as a function of water input flow working at 20°C on a continuous mode with a single pass of the catholyte through the electrochemical reactor at a current density of 45 mA cm^{-2}.

First, it should be noted that the electrochemical performance of the process got worse when a water input flow lower than the corresponding to a saturated stream was used. In this way, as shown in Fig. 6, a significant decline of FE and rate of production values (approximately 20% lower) happened by decreasing the water input flow from 0.227 g h^{-1} (which corresponds to 100% relative humidity at 20 ºC) to 0.15 g h^{-1}. This fact can be attributed to mass transfer caused by an insufficient supply of CO_2 along with water vapour. Similar results have been reported in [60]. However, Fig. 6 also reveals than when working with vapour flows higher than 0.227 g h^{-1}, the influence of the amount of water supplied on the FE and rate resulted to be more limited, with differences in the range of ± 5%. The best result was obtained when the electrochemical reactor was fed with a water input flow of 0.5 g h^{-1}, achieving a value of formate rate of 1.15 mmol m^{-2} s^{-1}, with a FE of 49%. Increasing the amount of water in the CO_2 stream, the results obtained were very similar, with a decrease in formate rate and FE of less than 5% (Fig. 6).

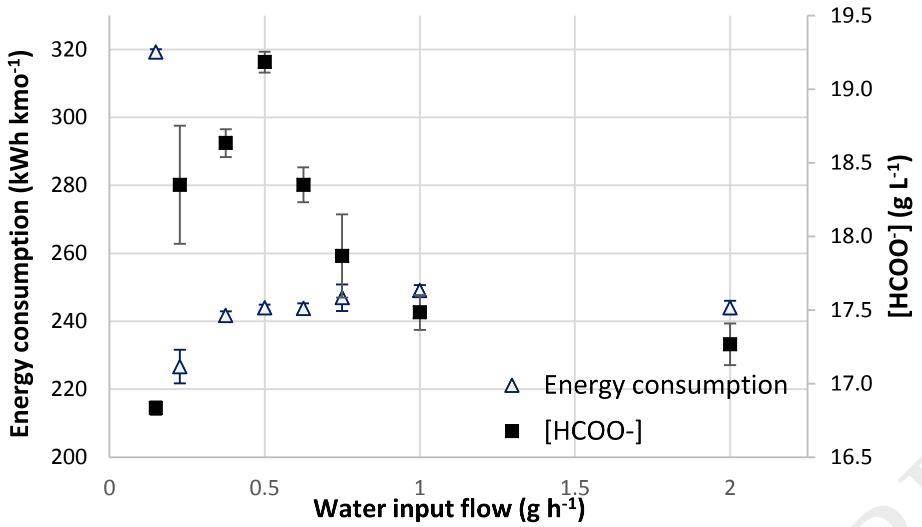


Fig 7. Energy consumption and formate concentration as a function of water input flow working at 20 °C on a continuous mode with a single pass of the catholyte through the electrochemical reactor at a current density of 45 mA cm^{-2}.

The influence of the water input flow on the concentration of formate and on the energy consumption can be seen in Fig. 7. As can be noted, the formate concentration and the energy consumption had a similar behaviour as described in Fig. 6 for formate rate and FE, but in general with slightly greater effect on the values obtained. The highest formate concentration value was achieved when the electrochemical cell is fed with a water input flow of 0.5 g h^{-1}, giving a value of formate concentration of 19.2 g L^{-1}. Increasing the amount of water in the CO_2 stream (2 g h^{-1}) was not beneficial to the process since less dissolved CO_2 can achieve surface area, giving a 10 % lower formate concentration (17.3 g L^{-1}) as the consequence of the dilution with the amount of water in the CO_2 stream. The results shown in Fig. 7 also clearly indicate that the lowest energy consumption per kmol of product (226 kWh kmol^{-1}) was obtained working with a water input flow of 0.227 g h^{-1}. Increasing the amount of water in the CO_2 stream in a range from 0.375 g h^{-1} to 2 g h^{-1} did not result in a significant difference in terms of energy consumption per kmol of product (with less than 5% of difference). However, working with a water input flow of 0.15 g h^{-1}, energy consumption per kmol of product noticeably increased in more than

40% with respect to the value of energy consumption working with the saturated CO_2 stream of 0.227 g h^{-1}.

3.5 Comparative with CCMEs-GDEs with the same Sn NPs

The performance of the process with the proposed CCME configuration is compared with the GDE approach used in our previous studies [42]. In both configurations, the same Sn-NPs were used as electrocatalysts. Consequently, the main difference between both configurations was the laying of catalytic material in cathodic compartment. While in the Sn-CCME configuration, the Sn-NPs are deposited directly over the membrane, in the Sn-GDE one, the Sn-NPs are deposited over a carbon paper used as carbonaceous support containing a carbon microporous layer (MPL). In the latter configuration, the membrane is used only as separator between the cathodic and anodic compartment since 0.45 mol L^{-1} $KHCO_3$ + 0.5 mol L^{-1} KCl and 1 M KOH were used as catholyte and anolyte, respectively. Unlike it, no supply of catholyte was required for the Sn-CCMEs configuration. Accordingly, in that case, Nafion membrane not only acts as separator between both cathodic and anodic compartments, but also the polymeric electrolyte. It is worth recall that in both configurations, all the variables were fixed to the same values (anolyte flow per electrode area, CO_2 flow, geometric surface area and catalyst loading) except the current density, as explained in subsection 3.2. Both configurations were tested on an electrochemical membrane reactor, working on a continuous mode with a single pass of the catholyte through the electrochemical reactor and the same catalytic material was used in both configurations. Table 1 summarizes a comparative of the results obtained from both Sn-GDE and Sn-CCME configurations using the same electrochemical reactor.

Table 1. Results of rate, FE, formate concentration and energy consumption obtained with the Sn-CCME and Sn-GDE configurations.

Configuration	**Sn-GDEs [42]**		**Sn-CCMEs (this work)**
Max. formate rate (mmol m^{-2} s^{-1})	5.45	4.38	1.15
Max. Faradaic efficiency (%)	70%	45%	49.4%
Max. current density (mA cm^{-2})	150	200	45
Max. $HCOO^-$ concentration (g L^{-1})	2.5	16.9	19.2
Energy consumption (kWh $kmol^{-1}$)	284	513	244

As shown in Table 1, it should be remarked that, under similar experimental conditions, higher formate concentration were obtained working with the Sn-CCMEs configuration also including an important saving in the energy consumption per kmol of product. Thus, Sn-CCME configuration provided the highest formate concentration of 19.2 g L^{-1} working at a current density of 45 mA cm^{-2}. However, working with the Sn-GDE configuration, the highest formate concentration achieved was 16.9 g L^{-1}, but using a much higher current density of 200 mA cm^{-2} and an electrolyte flow per electrode area of 0.07 mL min^{-1} cm^{-2}. Higher cell potential in Sn-GDE configuration is attained with current density and, consequently, a major energy consumption per kmol of product is required, more than 100% higher with respect to the energy consumption working with Sn-CCMEs. Our previous results obtained with Sn-GDEs showed that it could be possible to lower the energy consumption per kmol of product by operating at lower current density (see Table 1) [42]. But in Sn-GDEs, this saving in the energy consumption is associated with much lower formate concentration. For example, working at 150 mA cm^{-2}, the formate concentration obtained was almost one order of magnitude lower (2.5 g L^{-1}) with respect to the concentration obtained working at 200 mA cm^{-2} (16.9 g L^{-1}).

Even though working with the proposed Sn-CCMEs provides higher formate concentration with an important energy saving, there were no significant improvement in the formate rate and the FE with respect to Sn-GDEs. The CCME configurations seem to decrease the ohmic resistance (the cell voltage is clearly lower) also improving the mass transport of the species involved in the electrochemical reactor. In both configurations, the highest concentration was achieved with Faradaic efficiencies of similar values (in the range 45-50%). However, formate rate in the proposed Sn-CCMEs was more than 75% lower with respect to the Sn-GDEs. The lower rate is a consequence of the already discussed need of operating at lower current density with Sn-CCMEs. However, despite this lower operating current density, which results in lower rates of formate production, the main advantage of the proposed Sn-CCMEs is the possibility of achieving higher formate concentrations than with the Sn-GDEs with an energy consumption significantly lower.

4. Conclusions

This study presents the results of the CO_2 electroreduction to formate in a continuous electrochemical membrane reactor with a single pass of catholyte through the electrochemical reactor using Sn-CCMEs configuration that involves working in gaseous phase. In this way, there is no feed of liquid catholyte and Sn-NPs are directly deposited over Nafion 117 membrane, which worked as solid electrolyte. An experimental set-up using Sn-CCMEs was designed and built for this goal, working with the same CO_2 flow, anolyte flow per electrode area, geometric surface area, catalyst loading and Sn-NPs used in our previous studies [42]. In this contribution, some key variables such as temperature and water input flow were analysed. The results obtained suggest that, feeding the electrochemical cell with a saturated stream of CO_2 at ambient temperature (20ºC) is beneficial for the performance of the process, giving a formate concentration of 18.4 g L^{-1} with an energy consumption per kmol of product of 226.6 kWh $kmol^{-1}$. Further experiments at ambient temperature but with different amount of water in the CO_2 stream, a high formate concentration of about 19 g L^{-1} was obtained by using a water input flow of 0.5 g h^{-1}. Even though, working with a saturated stream of CO_2 (0.227 g h^{-1}) gives lower rate and Faradaic Efficiency but also a decrease in energy consumption per kmol of product. A comparison between the Sn-CCME and the Sn-GDE configurations has been established. Using the Sn-CCME approach allows achieving higher formate concentration with an important saving of energy per kmol of product with respect to the Sn-GDEs. It is worth recall that both configurations work in a continuous electrochemical membrane reactor with a single pass of the catholyte through the electrochemical reactor and with the same Sn-NPs. Further research is still needed to increase the values of rate and Faradaic efficiency with the Sn-CCME configuration without increasing the energy consumption of this CO_2 electroreduction process.

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