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Conversion of CO₂ to formic acid in a microfluidic electrochemical cell with and without supporting electrolyte

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ABSTRACT

Electrochemical reduction of carbon dioxide to formic acid or formate (FA) is considered an interesting route to valorize CO₂ effluents. Here, we have performed the conversion of CO₂ to FA in an undivided microchannel electrochemical reactor characterized by very small inter-electrode distances (75–250 μm) using Na₂SO₄ as supporting electrolyte (SE). It was found that the use of the microfluidic cell allows to work both in the presence and in the absence of SE with lower cell potentials with respect to conventional cells and to obtain significant conversions per pass of CO₂ to FA. The effect of many parameters, such as distance between electrodes, flow rate, current density, concentration of Na₂SO₄ and pH, was studied. In particular, it was shown that the production of FA increases by reducing the concentrations of Na₂SO₄ and it presents the maximum value in the absence of it.

1. Introduction

Many companies, research centres and universities are currently trying to develop effective routes for the conversion of CO₂ into various chemicals. Up to now, a promising approach to valorise waste-CO₂ is its cathodic reduction (CO₂CR) to various chemicals, including formic acid or formate (FA), carbon monoxide and synthesis gas [1–6]. CO₂CR presents various advantages such as the involvement of mild operative conditions (such as pressures lower than 30 bar and room temperatures) in the absence of reductants and to obtain different interesting products by a proper choice of the cathode. In addition, CO₂ can be used for the synthesis of carboxylic acids in aprotic solvents by addition of aromatic ketones or benzylic halides [7]. The CO₂CR to CO and FA is particularly appealing because of the low number of electrons involved ($n = 2$), the high faradic efficiencies (FE), current densities (j) and selectivity reported in literature [1–5] and the promising economic data [8–10]. In addition, this innovative route is expected to give a less negative environmental impact with respect to traditional processes [4]. It was recently highlighted that the economic figures of CO₂CR can be strongly improved using a proper anodic process that can add economic value to the overall system (such as the Cl₂ production or the treatment of wastewater [11,12]) or both a salinity gradient and an Assisted Reverse Electrodialysis stack to reduce the energy consumption [13]. However, to develop CO₂CR on an applicative scale some aspects of the process should be significantly improved. It would be necessary to:

- (i) obtain high FEs (> 70–80%) and productivities (current densities > 0.1 A m⁻²);
- (ii) guarantee stable performances for long times;
- (iii) reduce the cell potentials (ΔV);
- (iv) decrease the capital and operative costs including that of the electrolyte solution.

High FEs and productivities were obtained for the synthesis of various products using suitable electrodes such as proper gas diffusion ones or high-performances cells like pressurized ones [1–4,14–16]. Moreover, the results obtained by CO₂CR processes depend on the nature and concentration of the supporting electrolyte (SE) [17–24]. The addition of SE allows to increase the conductivity of the solution and consequently to reduce the ΔV . However, the use of SE gives rise to an increase of the operative costs and to a more difficult separation of the products. Moreover, the SE can affect the cathodic conversion of CO₂ to various products [21,22] and it is not completely clear if the presence of SE has or not a beneficial effect on the selectivity of the process. As an example, according to Wu and co-authors [15], the CO₂CR to formate gave higher FEs at lower concentrations of Na₂SO₄. Conversely, Monteiro et al. [49] reported, in the case of Au, Ag and Cu, that CO is only produced if a metal cation is added to the electrolyte.

To avoid the use of liquid SE, two main strategies can be considered: the use of solid electrolyte [48], which avoids the use of a liquid electrolyte, or the adoption of microfluidic channels with very small

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interelectrode distances, thus allowing to reduce drastically the ohmic drops that depend on the conductivity of the solution and on the distance between the electrodes. In the last years, it was highlighted that the performances of various electrochemical processes, including both the treatment of wastewaters [25,26] and the synthesis of various kinds of chemicals [27–34], can benefit from the adoption of microfluidic electrochemical cells characterized by an inter-electrode distance $h < 1000 \mu\text{m}$. The adoption of very small h can give many advantages, including the possibility to: (i) carry out the electrolyses under a continuous mode with a high conversion of the reagent for a single passage of the electrolytic solution inside the cell; (ii); accelerate the mass transport of reagents towards the electrodes; (iii) operate with low concentrations of the supporting electrolytes at low ΔV due to the small distances between the electrodes; (iv) easily control the temperature; (v) achieve, in a relatively easy way, the scale-up through parallelization of many microcells; and (vi) avoid the use of separators using laminar streams in order to separate cathodic and anodic solutions [30–34].

Microfluidic cells were adopted in the recent years also in the frame of CO_2CR processes for the synthesis of various products including FA [35–38], CO [39] and C_2H_4 [40]. However, many studies used a relatively large distance between the electrodes ($h \geq 200 \mu\text{m}$), thus not allowing to fully exploit some of the potential advantages of microfluidic cells and requiring the use of significant concentrations of SE similar to that used in conventional systems. Some microfluidic cells were equipped with a separator to divide the cathodic and the anodic compartments [35], thus increasing the ΔV and the overall cost of the cell, and/or with a gas diffusion electrode. However, some authors have shown that the adoption of microfluidic cells can allow to avoid the utilization of the separator using two solutions under a laminar flow which form a limited mixed zone [37]. Microcells were also used in the presence of ionic liquids [41].

In this work, we have studied the possibility to operate the CO_2CR processes in an undivided micro electrochemical reactor equipped with a small h in the range of 75–250 μm . To focus only on the potential advantages given by the utilization of the microfluidic cell, we decided to use very cheap and simple tin plates as cathodes at room temperature. For the same purpose, we decided not to use a gas diffusion electrode and experiments were performed at 1 bar. Na_2SO_4 was used as the supporting electrolyte (SE). The effect of many parameters, such as distance between electrodes, flow rate, current density, concentration of Na_2SO_4 and pH, was studied. In particular, it was found that the use of the microfluidic cell allows to work both in the presence and in the absence of SE with low cell potentials and that the production of FA increases by reducing the concentrations of Na_2SO_4 .

2. Materials and methods

2.1. Electrochemical apparatus

Electrolyses were carried out both in a conventional lab cell and in microdevices. The microdevice was a undivided filter press flow cell from ElectroCell AB with proper modifications equipped with one or

more polytetrafluoroethylene (PTFE) spacers with an overall nominal thickness h of 250, 120 and 75 μm (Bohlender GmbH, Germany) (Fig. 1). Two plate electrodes (working area of 4.15 cm^2) of Sn and $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$, were used as anode and cathode, respectively (see reference [25, 27] for details). A GILSON 307 pump was used to feed solutions in the cell system. The conventional lab cell consisted of an undivided tank glass cell equipped with the same electrodes used in the microfluidic cell and with magnetic stirring at 500 rpm.

2.2. Electrolysis and analyses

A potentiostat/galvanostat Amel instruments model 2053 was used to carry out the experiments under galvanostatic condition (j from -4 mA cm^{-2} to -16 mA cm^{-2}). Electrolyses were performed with water previously put in contact with CO_2 (99.999% purity from Rivoira) at 1 bar and at room temperature. When used, the SE was Na_2SO_4 (Sigma-Aldrich); H_2SO_4 (Sigma-Aldrich) or NaOH (Sigma-Aldrich) were used to achieve the target initial pH. To work at pH 4, a solution of 0.2 mM of H_2SO_4 was used (to reach pH 4, $10 \mu\text{L}$ of H_2SO_4 was added to 1 L of water or electrolyte solution). Before each electrolysis, the Sn plate cathode was treated by mechanically smoothing by lapping machine equipped with different abrasive sanding disc (180-grit, 500-grit, 800-grit) to obtain a smooth surface. [FA] was evaluated by Agilent HP 1100 HPLC fitted out with Rezex ROA-Organic Acid H+ (8%). The temperature column was fixed at 20°C . the analyses were carried out with an UV detector at 210 nm using a 0.005 N H_2SO_4 water solution at pH 2.5 as mobile phase eluted at 0.5 mL min^{-1} . Under the adopted operative condition, the retention time of FA was 18 minutes. The gas products were analyzed by gas chromatography using an Agilent 7890B GC fitted out with a Supelco Carboxen® 60/80 column and a thermal conductivity detector (TCD), working at 230°C . Helium (99.999%, Air Liquide) at 1 bar was used as carrier gas. The column temperature was i) at 35°C for 5 min ii) followed by a $20^\circ\text{C min}^{-1}$ ramp up to 225°C and iii) by an isothermal step at 225°C for 40 min.

The following figures of merit were considered:

- Faradic Efficiency of FA (FE_{FA}) defined by Eq. 1:

$$\text{FE}_{\text{FA}} = n * F * V * [\text{FA}] / (I * t) * 100 = n * F * [\text{FA}] * Q / (I) * 100 \quad (1)$$

where n is the number of electrons exchanged ($n = 2$ in the case of FA), F the Faraday constant (96485 C mol^{-1}), $[\text{FA}]$ the concentration at the outlet of the electrochemical reactor (mol L^{-1}) at the time τ (s) (the average residence time of the solution in the cell), V (L) the volume of the solution, Q the volumetric flow rate and A the working electrode area (cm^2).

- The yield defined by Eq. 2:

$$X = [\text{FA}] / c_{\text{CO}_2}^b \quad (2)$$

where $c_{\text{CO}_2}^b$ is the initial concentration of CO_2 dissolved in water (at 25°C and 1.3 bar it was estimated to be close to 34 mM) [15].

- Energy consumption (EC) (Eq. 3):

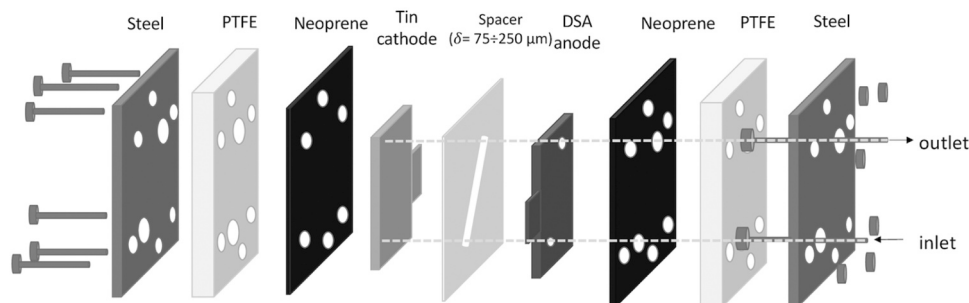


Fig. 1. Schematic view of the microelectrochemical cell.

$$EC = \Delta V * I * t / \text{mol}_{\text{FA}} \quad (3)$$

where ΔV is the cell potential, and mol_{FA} the amount of FA obtained (mol).

- The residence time (τ) was computed by Eq. 4:

$$\tau = \text{Vol} / Q * 3600 [=] \text{ s} \quad (4)$$

where Vol is the reactor volume (mL).

For each experiment, at least 5 data were achieved each 5 minutes after 10 minutes; indeed, a set of preliminary electrolyses have shown that steady state conditions were reached (e.g. constant concentration of FA) before 10 minutes. In most of cases data were reproducible with an error lower than 10% in most of cases. Moreover, each experiment was replicated three times. Average data were provided in the manuscript.

3. Results and discussion

3.1. Effect of the concentration of Na_2SO_4 in conventional and microfluidic cells

Some authors have previously shown that CO_2CR to FA depends significantly on the nature of SE and on the pH value. According to Wu et al. [17], the use of Na_2SO_4 gives larger FE_{FA} with respect to KCl, KHCO_3 , K_2SO_4 and Cs_2SO_4 . Moreover, according to Scialdone and co-authors [22], higher concentrations of FA are achieved at pH values close to 3–4. In addition, Wu and coauthors reported that the CO_2CR to formate under potentiostatic conditions at -1.7 V vs. SCE gave higher FEs at lower concentrations of Na_2SO_4 ; however, a lower productivity in formate was recorded at the lowest adopted concentrations of Na_2SO_4 because of the decrease of j [15], probably due to the larger ohmic drops achieved at low concentrations of the SE. Here, numerous experiments were carried-out using a water solution of Na_2SO_4 , at various concentrations and an initial pH of 4 at j of -8 mA cm^{-2} using both (i) a conventional laboratory macro cell under batch conditions and (ii) a microfluidic cell under continuous conditions with an inter-electrode distance h of $75 \mu\text{m}$ fed with the electrolyte ($Q = 0.4 \text{ mL min}^{-1}$). An initial pH of 4 was used by addition of a proper amount of H_2SO_4 ; after the CO_2 saturation time the starting pH decreased to 3.8

According to the literature [4], the CO_2CR at tin cathodes under all adopted operative conditions gave rise to the formation of formic acid (eq.ns (5)-(8)):



Only a very small amount of CO was obtained. A relevant generation of H_2 was observed, since at tin cathodes the production of FA competes prevalently with the hydrogen evolution (Eq. (9)) [4]:



In particular, a faradic efficiency in H_2 higher than 50% was obtained. As shown in Fig. 2a, in the conventional reactor, the concentration of Na_2SO_4 strongly affected both the final concentration of FA and the ΔV . When the electrolyses were carried out with a concentration of SE of 0.50 M, FA was synthesized with a final concentration of 2.1 mM after 60 C and with a ΔV of 2.1 V. When the electrolysis was repeated with a lower concentration of the SE, an increase of both the concentration of FA and of the ΔV was observed. As an example, the reduction of the concentration of Na_2SO_4 from 0.50 to 0.03 M allowed to increase the production of FA from 2.1 to 3.9 mM but resulted in a significant increase of the ΔV from 3.1 to 4.8 V as a result of the lower conductivity of the solution. A second set of experiments was performed in the microfluidic reactor under a continuous mode with different concentrations of Na_2SO_4 (0.03, 0.06, 0.10 and 0.50 M). It is worth to mention that at 0.4 mL min^{-1} a residence time (τ) close to 7.5 sec took place. Despite the very low τ , an appreciable amount of FA was produced (Fig. 2b) as a result of the very high ratio surface/volume (A/V). Indeed, a ratio A/V close to 130 cm^{-1} is presented by the microfluidic cell against the conventional ratio close to $0.1\text{--}0.4 \text{ cm}^{-1}$ achieved in the conventional laboratory macro cells. As shown in Fig. 2b, a remarkable effect of the concentration of Na_2SO_4 on the production of FA was observed: the lower the concentration of Na_2SO_4 , the higher the production of FA. As an example, the reduction of Na_2SO_4 concentration from 0.50 to 0.03 M gave a drastic increase of the concentration of FA from 2.0 to 7.7 mM, of FE_{FA} from 6% to 30% and of the conversion per pass X from approximately 6 to 23%. In the case of the experiments performed in the microreactor, this strong reduction of the concentration of the SE gave a not appreciable increase of the ΔV , due to the very small h value (ΔV of approximately 3.2 and 3.4 V at a Na_2SO_4 concentration of 0.50 and 0.03 M, respectively). Hence, on overall the reduction of Na_2SO_4 concentration from 0.50 to 0.03 M gave a significant decrease of the EC for number of moles of FA produced (EC was reduced from 2.7 to 0.6 $\text{kWh/mol}_{\text{FA}}$). Prompt by these promising results, some electrolyses were carried in the absence of Na_2SO_4 with an initial value of pH of 4 by addition of a proper amount of H_2SO_4 (0.2 mM). The absence of Na_2SO_4 did not present an adverse effect on the generation of

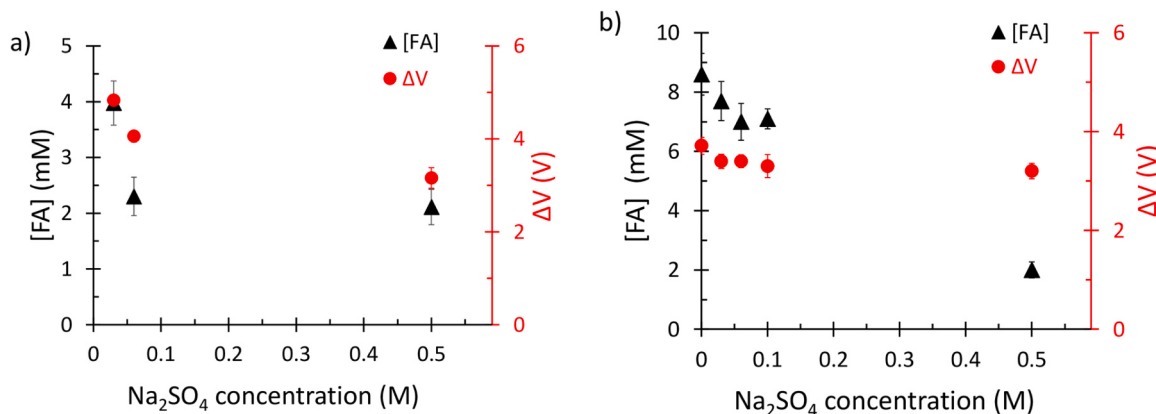


Fig. 2. Effect of the concentration of SE on the conversion of CO_2 to FA and on the cell potential in a conventional laboratory macro cell under batch conditions (Fig. 2a) and in a microfluidic cell equipped with a h of $75 \mu\text{m}$ (Fig. 2b). A water solution of Na_2SO_4 and H_2SO_4 (initial pH 3.8) saturated with CO_2 was fed for a single passage to the microfluidic electrochemical cell using a tin cathode, a $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode at -8 mA cm^{-2} . The micro cell was fed with Q of 0.4 mL min^{-1} . The macro cell was fed with 50 mL of the electrolyte solution for 0.5 h and mixed by magnetic stirrer. A tin cathode and a $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode were used.

FA; conversely, a concentration of FA of 8.6 mM (Fig. 2B) was produced coupled with a small increase of the ΔV (from 3.2 V at 0.50 M of Na_2SO_4 to 3.7 V in the absence of Na_2SO_4) and a limited EC ($\text{EC} = 0.6 \text{ kWh/mol}_{\text{FA}}$). It is worth to mention that the ΔV recorded in the microreactor in the absence of Na_2SO_4 was very close to that observed in the conventional cell with 0.1 M Na_2SO_4 as a result of the very small inter-electrode distance used in the microcell. Hence, it can be concluded that this set of experiments shows that Na_2SO_4 has an adverse effect on the electrochemical reduction of CO_2 to FA. The positive results obtained in the absence of Na_2SO_4 can be due to numerous factors. Indeed, the presence of the SE is expected to affect the process in different ways:

- a larger salinity gives a slightly decrease of the CO_2 solubility [20], thus resulting in slower rates of CO_2 reduction;

- the adsorption of cations at the cathode is expected to result in less negative potentials at the outer Helmholtz Plane (OHP) [17]; hence, a decrease of SE concentration and, as a consequence, of the cations concentrations is expected to lead to more negative potentials at OHP, thus favoring (i) the CO_2 reduction and (ii) increasing the local concentration of protons, which favor both the hydrogen evolution and the production of FA [42]. However, Na^+ is expected to affect in a very small way the process: the high hydration number of this small cation restricts its specific adsorption; moreover it is expected not to be involved in a significant way in hydrolysis [19];

- according to some authors, anions can be adsorbed at the electrocatalytic surface, thus potentially affecting the adsorption of CO_2 and its reduction path [45].

It is worth to mention that in the case of Au, Ag and Cu, a more complex effect of SE was observed. In particular, for these cathodes, CO was produced only if a metal cation was added to the electrolyte [49]. Our results show that a quite different picture is found for the CO_2CR to FA at tin cathodes.

3.2. Effect of flow rate and current density

To evaluate the effect of j and of Q , numerous electrolyses were operated in the absence of Na_2SO_4 with an initial pH of 4 at various j and Q . First, the effect of j was investigated at 0.4 mL min^{-1} imposing j of -4 , -8 , -12 and -16 mA cm^{-2} with a h of $75 \mu\text{m}$. As shown in Fig. 3a, the plot $[\text{FA}]$ vs. j resulted in a curve with a maximum for a j of -8 mA cm^{-2} . This trend is in line with results obtained for conventional cells; indeed, it was shown several times that FE_{FA} presents a maximum with both the working potential and j [4,15]. Moreover, the increase of j resulted in higher ΔV (Fig. 3a) and, as a consequence, in higher EC (from 0.6 to $1.7 \text{ kWh/mol}_{\text{FA}}$ enhancing j from -8 to -16 mA cm^{-2}). The effect of Q was studied by performing a series of experiments at -8 mA cm^{-2} and 0.1, 0.2, 0.4 and 0.6 mL min^{-1} . A lower Q resulted in a higher production of FA (Fig. 3b) because of the higher τ . In particular, at 0.1 mL min^{-1} a

concentration of FA close to 17 mM was achieved corresponding to a X close to 50%. A relatively low FE_{FA} of 16% was achieved due to high conversions achieved under these conditions that give rise to low concentrations of CO_2 in the final part of the reactor, thus favoring the hydrogen evolution. When Q was increased, a lower τ was achieved, thus resulting in lower final concentrations of FA, in lower conversions of CO_2 but in higher FE_{FA} . At 0.6 mL min^{-1} , a $[\text{FA}]$ close to 7 mM and a FE_{FA} close to 40% were obtained because of the very low τ close to 3 sec.

The values of the X per pass of CO_2 to FA achieved in these experiments (up to 50%) seem particularly interesting if compared with that reported in the literature. Indeed, most of the works do not report the CO_2 conversion per pass and were carried out under large excess of CO_2 . According to the recent review of Irabien and co-authors [43], for the continuous CO_2CR to HCOOH or HCOO^- very small conversions per pass were obtained ranging in most of the cases between 1.5% and 44% [46]. Up to our knowledge, only Li and Oleman reported a X higher than that obtained in this work using a “trickle-bed” reactor equipped with granulated tin cathodes for the cathodic conversion of CO_2 to potassium formate [47]. However, in this work, the FEs were quite small due to the use of very simple cathode plates and not pressurized CO_2 [42].

3.3. Effect of the pH

Some authors have reported that the performances of CO_2CR to FA/formate in macro cells depend on the solution pH [15,22]. Hence, some electrolyses were performed using different values of the initial pH (from 2 to 8) by addition of proper amounts of H_2SO_4 or NaOH .

As shown in Table 1, the experiments performed with an initial pH of 2 gave rise to a very low concentration of FA (entry 1). Indeed, according to the literature, at very low pH, the evolution of hydrogen is strongly favored and prevails on the reduction of CO_2 . When the initial pH was increased to 4, a significant increase of $[\text{FA}]$ to 8.6 mM was observed (Table 1, entry 2). Indeed, according to the literature, the CO_2CR in conventional macro cells gives the highest production of FA/formate at

Table 1
Effect of the initial pH on the CO_2CR to FA^a.

Entry	Initial pH	Final pH	$[\text{FA}]$ (mM)	ΔV (V)	FE_{FA} (%)
1	2	2	< 0.01	$2.7 \pm$	n.d.
2	4	3	8.6 ± 0.90	3.3 ± 0.13	34
3	6	5	6.6 ± 0.18	3.3 ± 0.15	25
4	8	7	5.5 ± 0.35	3.4 ± 0.06	21

[a] Effect of the pH on the final concentration of FA in a microfluidic cell with $h = 75 \mu\text{m}$. An aqueous solution of H_2SO_4 or NaOH (saturated with CO_2) with $Q = 0.4 \text{ mL min}^{-1}$ and a constant $j = -8 \text{ mA cm}^{-2}$ were used. A tin cathode and a $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$ anode were used.

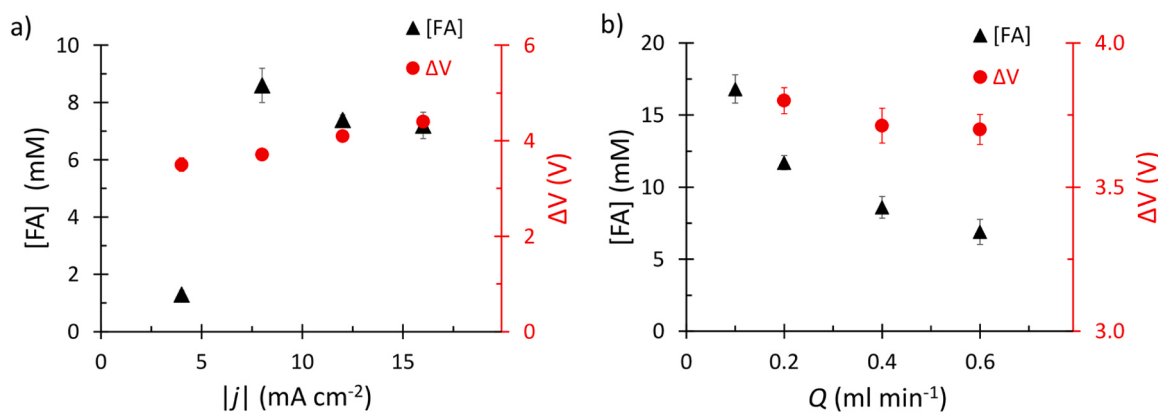


Fig. 3. Effect of j at 0.4 mL min^{-1} (Fig. 3a) and of Q at -8 mA cm^{-2} (Fig. 3b) on the reduction of CO_2 to FA. An aqueous solution of H_2SO_4 (initial pH 4) saturated with CO_2 was fed for a single passage to the electrochemical cell using a tin cathode, a $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$ anode and a h of $75 \mu\text{m}$.

pH close to 4 [22]. A further increase of the initial pH (to 6 and 8) (Table 1, entry 3) gave rise to a small decrease of FA (formic acid/formate) concentration and of FE_{FA} , because of the lower amount of protons available for the reaction. Indeed, as shown in eqn.s (7) and (8) the presence of protons is necessary to generate FA. Moreover at high pH a lower concentration of CO_2 is expected because a part of it is present under the form of HCO_3^- .

It is interesting to observe that the final pH for pH higher than 2 was always lower than the initial value because of the very effective acidification, given by both (i) the protons generated at the anode and (ii) FA generated at the cathode, favored by the very small ratio V/A.

3.4. Electrolyses performed without Na_2SO_4 and H_2SO_4

The experiments described in the previous paragraphs in the absence of Na_2SO_4 presented in most of cases a very small concentration of electrolyte given by the H_2SO_4 added to acidify the system. Hence, to reduce the process costs and to work in complete absence of electrolyte, it would be interesting to avoid the use of both Na_2SO_4 and of the acid used to decrease the pH. Thus, a large set of electrolyses was carried out using only water saturated with CO_2 with different distances between the electrodes (75, 120 and 250 μm) and current densities (-4 , -8 , -12 and -16 $mA\ cm^{-2}$).

In the first experiments, performed with $Q = 0.4\ mL\ min^{-1}$ and $j = -12\ mA\ cm^{-2}$ with different values of h (75, 120 and 250 μm), the initial pH was close to 4.4 because of the acidification produced by CO_2 . A production of FA of 3.6–4.4 mM was achieved (Table 2, entries 1–3), thus showing that it is possible to work without both supporting electrolyte and acid. The highest concentrations of FA were achieved at 120 μm , while the lowest ΔV were recorded with the smallest h . The following experiments were conducted at -4 , -8 and $-16\ mA\ cm^{-2}$ with different values of h (75, 120 and 250 μm). As shown in Table 2, at both -8 (Table 2, entries 4–6) and $16\ mA\ cm^{-2}$ (Table 2, entries 7–9), the highest concentrations of the target product were obtained at 120 μm . However, at $-4\ mA\ cm^{-2}$, a very small effect of h was observed and the highest production of FA was achieved at 240 μm (Table 2, entries 10–12). Moreover, at all adopted j , the lowest ΔV were recorded with $h = 75\ \mu m$. In order to explain the effect of h , it is necessary to remember that the inter-electrode distance is expected to affect the process in different ways. First, the lower is h the faster is the mass transport of both CO_2 to the cathode surface and of FA to the anodic one. In particular, when the process is under the kinetic control of the mass transfer of CO_2 to the cathode, by neglecting the contribution to mass transfer of gas evolution, the kinetic of this stage is approximatively given by Eq. (11) [27,43,44]:

$$j_{CO_2} = -4.86D \ (c_{CO_2}^b)_x / 2h \quad (11)$$

which becomes faster for smaller values of h . In particular, the value of the limiting current densities ($j_{lim,CO_2} = 2 * F * J$) at the inlet of the cell computed on the bases of Eq. (11) are expected to be close to -10 , -22 and $-36\ mA\ cm^{-2}$ for h of 250, 120 and 75 μm , respectively, while slightly lower values are expected in the final part of the cell due to the consumption of CO_2 . Hence, at $j = -8$ – $-16\ mA\ cm^{-2}$, the cathodic reduction of CO_2 is limited in a significant way by the mass transfer stage only for h of 250 μm , thus explaining the worse results obtained for this inter-electrode distance. Conversely, since FA presents lower concentrations than CO_2 (its average value in the cell is close to 1.5–3.5 mM), the j_{lim} for its mass transfer to the anodic surface is expected to be significantly lower ($< -4\ mA\ cm^{-2}$) under all the operative conditions reported in Table 2. Hence, the lowest value of h of 75 μm favors the mass transfer of FA to the anode surface, thus favoring its anodic oxidation. Moreover, the lower the h , the more probable the partial occlusion of the cell from gas bubbles generated at the electrodes. It is interesting to observe that these considerations are in line with the results observed at $-4\ mA\ cm^{-2}$. Indeed, under these conditions the cathodic reduction of CO_2 is not expected to be affected by mass transfer also at 250 μm , thus explaining the fact that highest concentrations of FA at this value of j were achieved with the highest adopted h (entries 10–12).

As shown in Table 2, a significant effect of j is observed at all adopted h : in particular, in all cases the plot [FA] vs. j gave a curve with a maximum for $-8\ mA\ cm^{-2}$, as observed for the experiments recorded in the presence of H_2SO_4 (Fig. 3A). Hence, on overall, under the conditions reported in Table 2 (entries 1–6), a maximum [FA] was achieved for $h = 120\ \mu m$ and $j = -8\ mA\ cm^{-2}$, close to 7 mM, lower with respect to that recorded in the presence of H_2SO_4 ([FA] = 8.6 mM) under the same operative conditions, probably due to the fact that the first part of the reactor works under less acidic pH when H_2SO_4 is not added.

In conclusion, the use of the microfluidic cell allowed to operate without SE with relatively low ΔV and higher [FA]. As an example, when the experiments were performed under the operative conditions often adopted in the conventional industrial cells in order to reduce the cell potentials (presence of H_2SO_4 and concentration of Na_2SO_4 of 0.5 M) or without any electrolyte, under the same operative conditions ($h = 75\ \mu m$, $j = -8\ mA\ cm^{-2}$, $Q = 0.4\ mL\ min^{-1}$), a concentration of FA, respectively, lower than 2 and close to 5 mM was achieved. However, this interesting result was coupled with quite low [FA] (7 mM) and FE_{FA} ($< 45\%$) with respect to the state-of-the-art technologies for the conversion of CO_2 to FA which use GDEs or pressurized CO_2 (FE_{FA} 60–90%; [FA] $> 0.1\ M$) [4].

4. Conclusions and next steps

In this work, the CO_2 CR into FA in water was investigated utilizing a microfluidic undivided cell, with very low inter-electrode distances (h 75–250 μm), different j and Q . It was demonstrated for the first time, up to the best of our knowledge, that the utilization of microfluidic cells equipped with small distances between the electrodes ($h < 150\ \mu m$) can allow:

- to perform the electrolysis of CO_2 in water in the absence of any added chemical with relatively low ΔV and appreciable generation of FA;
- to achieve higher concentrations of FA and lower EC decreasing the concentration of SE and even working in the absence of it.

It was also shown that the final concentration of FA increases using:

- intermediate inter-electrode distances of 120 μm ;

Table 2

Electrolyses carried out without SE (e.g. without both Na_2SO_4 and H_2SO_4).

Entry	h (μm)	j ($mA\ cm^{-2}$)	[FA] (mM)	ΔV (V)
1	75	12	3.9 ± 0.50	3.7 ± 0.15
2	120	12	4.4 ± 0.38	4.3 ± 0.13
3	250	12	3.6 ± 0.21	5.0 ± 0.14
4	75	8	5.0 ± 0.48	3.5 ± 0.15
5	120	8	7.0 ± 0.40	3.7 ± 0.20
6	250	8	5.5 ± 0.25	5.0 ± 0.20
7	75	16	2.9 ± 0.20	4.8 ± 0.30
8	120	16	6.0 ± 0.50	5.0 ± 0.20
9	250	16	5.4 ± 0.20	6.9 ± 0.16
10	75	4	3.0 ± 0.10	3.3 ± 0.10
11	120	4	3.2 ± 0.55	3.5 ± 0.20
12	250	4	3.6 ± 0.30	3.8 ± 0.20

[a] Effect of various operative parameters on the final concentration of FA in the microfluidic cell equipped with a tin cathode and a Ti/IrO₂-Ta₂O₅ anode. An aqueous solution saturated with CO_2 with $Q = 0.4\ mL\ min^{-1}$ was used. Experiments 1–6 were performed in the microcell with a single passage of the solution inside the cell. Initial pH after CO_2 saturation: 4.4.

- intermediate values of j , since low values result in low productivity while high ones favour the hydrogen evolution;
- low Q ;
- values of initial pH close to 3–4.

These results probably will promote new investigations aimed to explore the large potentialities of microfluidic cells, characterized by very low inter-electrode distances, for the CO₂CR process. Indeed, in this work a very simple set-up was used to highlight the role of the microfluidic apparatus. In particular, the use of very simple plates electrodes coupled with water saturated with CO₂ at 1 bar resulted in limited final concentrations of FA and FE_{FA}. Moreover, the use of continuous operations with a single passage of the solution inside the cell determined a low average concentration of CO₂ and low [FA]. Hence, in the next future in order to increase the FE_{FA}, the current density and the final concentration of FA, it will be necessary to use such devices with more performing cathodes and using more suitable operative conditions such as pressurized CO₂ and low temperatures, as well as to exploit other potential advantages of microfluidic systems such as the use of segmented flows with very low inter-electrode distances and/or of “segmented” reactors which should intensify the mass transfer stages or to use more microfluidic cells in series or a continuous recirculation system. Moreover, it will be also necessary to study the effect of the concentration of SE using other salts in order to understand if the negative effect given by Na₂SO₄ can be avoided using other SEs.

CRediT authorship contribution statement

Paola Meli: Investigation. **Chiara Miceli:** Investigation. **Alessandro Galia:** Writing – review & editing. **Federica Proietto:** Writing – review & editing, Methodology, Conceptualization. **Onofrio Scialdone:** Writing – original draft, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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