

Electrochemical conversion of CO₂ to formic acid using a Sn based cathode: Combined effect of temperature and pressure

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ABSTRACT

Electrochemical conversion of CO₂ in the aqueous electrolyte into value-added chemicals is considered one of the most promising strategies to valorize waste-CO₂. In the last decade, high attention was focused on the electrochemical synthesis of formic acid (FA) via CO₂ reduction using Sn cathodes. To improve the final concentration of FA in aqueous electrolytes, several approaches, including the utilization of different technologies (i.e. pressurized CO₂ reactor, a gas diffusion electrode, divided cell etc...) and different operative conditions (i.e. pH, current densities, temperature, mixing rate, etc...) were investigated in detail. To date, the effect of temperature (*T*) on the electrochemical conversion of CO₂ into FA under pressurized undivided cells is still unexplored. Hence, in this work, the simultaneous effect of CO₂ pressure (*P*_{CO₂}) (1 ÷ 3 bar) and *T* (3 ÷ 60 °C) on the electrochemical synthesis of FA in an aqueous electrolyte using a Sn cathode was studied in detail. It was found that the adoption of low *T* and high *P*_{CO₂} values allows to work at high current densities (*j*) by achieving high final concentrations of FA ([FA]) and good relative faradaic efficiency (FE_{FA}). As an example, a quite high final [FA] of approximately 360 mM coupled with a FE_{FA} higher than 50% was reached in an aqueous electrolyte by working at *T* of 10 °C, *j* of −75 mA cm^{−2} and *P*_{CO₂} of 30 bar.

1. Introduction

In the last decade, to curb the climate global changes and valorise the waste CO₂, the electrochemical conversion of CO₂ (CO₂EC) to value-added chemicals was considered a topic of intense interest from both industrial and academic communities [1–5]. CO₂ can be electrochemically converted into various chemicals, such as formic acid (FA), carbon monoxide, methanol, methane, ethylene, etc., by choosing specific operative conditions (such as cathode nature, working potential, nature of the solvent, pH, supporting electrolyte, etc.) [4,6]. Generally, CO₂EC processes require mild conditions and its scale up stages are relatively easy. Moreover, CO₂EC processes could store the excess electric energy from intermittent renewable sources, available at a low price, as chemical energy, without any additional fossil fuel-based electricity, thus reducing the process' costs [7]. According to several techno-economic analyses, the synthesis of FA, as well as the production of syngas (mixture CO and H₂), via CO₂EC seem the most suitable processes at an industrial level [7]. FA is extensively utilized in agriculture, pharmaceutical and chemical industries, food technology and natural rubber, fibres and leathers productions. In addition, at ambient

temperature, FA is a liquid product that could be stored and handled more easily compared to gaseous products that can be used as a H₂ storage medium [4,5]. The production of FA via the CO₂EC process is expected to have a smaller environmental impact than current industrial processes [7]. Moreover, the economics of the process can be significantly improved by coupling the CO₂EC cathodic process with a suitable anodic one (such as the wastewater treatment or the synthesis of Cl₂ [8, 9]) or with an Assisted Reverse Electrodialysis process (A-RED) [10]. A-RED allows to reduce the energetic consumption, by using the energy provided by salinity gradients of two water streams with different salt content [10].

FA can be selectively produced in aqueous electrolyte via CO₂EC using Sn-based cathodes, even if, according to the literature, it is difficult to reach simultaneously the main targets needed for the implementation on a large scale: i.e., high current density (*j*) (*|j|* > 100 mA cm^{−2}), high faradaic efficiency towards FA (FE_{FA}), high FA concentration ([FA]) as well as long-term stability and low cell potential [7]. One of the major limitations of this process is the relatively slow mass transfer of CO₂ to the catalytic surface due to its low solubility at atmospheric pressure and ambient temperature (~ 33 mM at 1 atm and 25 °C), thus limiting the

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productivity of the process. To overcome this obstacle, many researchers have attempted to increase the availability of CO₂ on the cathode surface enhancing its solubility in water by either (1) increasing the pressure (P_{CO_2}) or (2) lowering the temperature (T) or, alternatively, using the well-known Gas Diffusion Electrodes (GDEs), as described below.

An increase of P_{CO_2} gives rise to (i) higher CO₂ concentrations in solution, according to Henry's law [11], (ii) the possibility to work at higher T (as an increase in T leads to lower CO₂ solubility) that could favour the kinetics, (iii) drive the reaction towards different target products by affecting the selectivity, and (iv) the chance to reduce CO₂ at lower negative potentials. Recently, the effect of P_{CO_2} on the performances of the CO₂EC into FA was investigated in detail by a few authors [12–20]. Scialdone [17], Proietto [18,19] and co-workers showed a significant improvement in the performances of the CO₂EC to FA using Sn cathodes in aqueous electrolytes by coupling an enhancement of j (up to -90 mA cm^{-2}) and P_{CO_2} (up to 30 bar). According to these works, it is possible to scale up the pressurized CO₂EC process into FA while maintaining good performance. In line with this research, Ramdin et al. [20] showed that an increase of P_{CO_2} up to 50 bar allows to drive the CO₂EC at -30 mA cm^{-2} in aqueous electrolyte with $FE_{\text{Formate}} \sim 80\%$ and a formate concentration of 200 mM. Even if long-term stability was not investigated, the remarkable discovery of this research was that a bipolar membrane is able to maintain a different pH between the anodic and the cathodic compartments at high P_{CO_2} .

An increase of T is expected to enhance the CO₂ reduction kinetics, to increase the CO₂ diffusivity but, simultaneously, to decrease the CO₂ solubility. To date, the effect of T on the performances of the CO₂EC process to FA in an aqueous electrolyte was poorly investigated [21–23]. The common finding is that T in the range of 20–35 °C results in the highest values of FE_{FA} . At fixed values of P_{CO_2} , low T values decrease the kinetics of the process, while high T values allow to drive the CO₂EC process at higher j values but result in an increase of the H₂ generation rate (which is the primary competitive cathodic process with respect to CO₂ reduction) and in slower mass transports of CO₂ due its lower solubility. In 1994, Mizuno et al. [21] reported that FE_{FA} up to 99% were achieved at 20 °C using Sn cathode. Recently, Löwe et al. [23] studied the effect of T (20 – 70 °C) on the performances of the CO₂EC process into formate using SnO₂-GDE technologies. In contrast with previous studies, these authors reported that the optimal T to perform the CO₂EC process was of ~ 50 °C by maintaining faradaic selectivity above 80% for 45 min at -1000 mA cm^{-2} . In this context, several works on the CO₂EC process using different cathodes have shown that in general the T affects the C-based product distribution [24–29] and that the higher the T , the higher the H₂ generation.

Alternatively, at ambient P_{CO_2} and T , the utilisation of the GDEs-based technologies has shown interesting results in terms of CO₂ reduction rates and selectivity towards the target products [30–32]. Del Castillo et al. [30] reported a high j of -200 mA cm^{-2} coupled with a quite high concentration of formate of 0.35 M and a lower FE of 43% by using a filter press divided cell equipped with Sn-GDE in an aqueous electrolyte. Recently, Kaczur and co-workers [32] reported that it is possible to perform the CO₂EC process at a high reduction rate ($j \sim -140 \text{ mA cm}^{-2}$) coupled with high selectivity towards FA ($FE_{\text{av}} \sim 85\%$) in aqueous electrolyte for long-term electrolysis (140 h) using a Sn-based GDE electrochemical cell, showing that the process could be suitable for the applicative scale. However, further studies on the stability of these technologies are necessary to use them for long-term electrolysis and larger system [4,5].

Another key factor of the implementation on a large scale of the CO₂EC is the separator membrane. The presence of membranes avoids the crossover of the CO₂ reduction products from the cathode to the anode compartments, which can cause the anodic oxidation of the C-based product at the anode side, and it is considered a useful safety feature. However, their presences have a significant impact on the overall cell resistance [4], due to their low conductivity relatively to that of the aqueous electrolyte, and their irreversible degradation at high T .

In this framework, the implementation of undivided electrolysis cells becomes a topic of interest from the applicative standpoint as it results in a reduction of both cell potential and capital cost, while some safety issues for the implementation large scale should be addressed, i.e., avoiding the production of gaseous streams of H₂ and O₂, as discussed in detail in ref. [7].

To date, the effect of T on the CO₂EC process into FA at a higher pressure than the atmospheric one is still unexplored. Moreover, up to our knowledge, the simultaneous effect of P_{CO_2} and T on the performances of the CO₂EC process into FA in an aqueous electrolyte using undivided cells equipped with Sn-based cathodes was not investigated at all. Hence, in this work, the CO₂EC using a Sn cathode in an undivided cell able to work at high pressure was studied by changing the values of both P_{CO_2} and T . It was found that the effect of the T on the process is very complex, but using low T coupled with high P_{CO_2} values allowed to work at high $|j|$ and achieve high final [FA] and quite good relative FE_{FA} .

2. Materials and methods

2.1. Electrochemical apparatus

Pseudo-polarizations and electrolyses were performed by using an AISI316 stainless steel cell with a cylindrical geometry, described in detail in ref. [17], equipped with a Sn sheet cathode (metallic tin foil RPE, assay > 99%, supplied by Carlo Erba) as the working electrode and a Ti/IrO₂-Ta₂O₅ sheet anode (commercial DSA® from ElectroCell AB) as the counter electrode. The T was controlled through different systems. To investigate the effect of the T at values above 20 °C, heating was obtained using a heating band wrapped around the reactor and connected to a temperature controller Eurotherm. On the other hand, to investigate the effect of the T at values below 20 °C, cooling was obtained using a tube wrapped around the reactor and connected to a chiller K20. The pump of the chiller allowed the circulation of the refrigerant liquid which was a water solution of 33% v/v ethylene glycol. The thermal insulation was obtained by covering the body of the reactor with a glass wool layer. A two-electrodes configuration was used in this system, with the reference set on the counter. The interelectrode gap was fixed at 1 cm.

2.2. Pseudo-polarizations

Pseudo-polarization curves were recorded by changing the overall cell potential ($|\Delta V|$) from 0.9 V to 4.5 V. The working electrode was a Sn foil ($A_{\text{W}} = 0.1 \text{ cm}^2$); before each characterization, it was subjected to mechanically smoothing treatment, chemically pretreated with 11%v/v HNO₃ (VWR Chemicals) water solution for 2 min and washed with an ultrasound bath in bi-distillate water for 5 min. DSA® with a wet surface area of 1 cm² was used as the counter electrode. The electrolyte solution was a 0.1 M Na₂SO₄ (Sigma-Aldrich) aqueous solution ($V = 0.05 \text{ L}$); H₂SO₄ (Sigma Aldrich) was used to set the initial pH at 4. The characterizations were performed at several values of P_{CO_2} (1–30 bars) and at several T (10–60 °C). Prior to all characterization, the solution was purged for 25 min by either N₂ (99.999% purity; supplied by Air Liquide) or CO₂ (99.999% purity; supplied by Rivoira). j_{N_2} and j_{tot} are the current densities recorded under N₂ and CO₂ atmosphere, respectively. The apparent current density of CO₂ reduction (j_{CO_2}) was computed under the assumption that the current of the H₂ evolution and of the CO₂ reduction can add up and the only competitive route to the CO₂ cathodic reaction is the H₂ evolution. Pseudo-polarizations were acquired with a scan rate of 5 mV s^{-1} and using an AutoLab PG-STAT12.

2.3. Electrolysis and analyses

Electrolyses were performed by using a potentiostat/galvanostat Amel instruments model 2053. The experiments were conducted at constant $|\Delta V|$ in a range from 2.7 V to 3.7 V, and under the galvano-

static conditions in a range of j from -11.6 mA cm^{-2} to -75 mA cm^{-2} . CO₂ (99.999% purity; supplied by Rivoira) was used for the electrolysis. P_{CO_2} varied from 1 to 30 bar and T from 3° to 60°C. The electrolyte solution was a 0.1 M Na₂SO₄ (Sigma-Aldrich) aqueous solution ($V=0.05 \text{ L}$); H₂SO₄ (Sigma Aldrich) was used to set the initial pH at 4. Prior to all the electrolyses, the solution was purged for 30 min by CO₂ and the cathode was subjected to mechanically smoothing treatment, chemically pretreated with 11%v/v HNO₃ (VWR Chemicals) water solution for 2 min and washed with an ultrasound bath in bi-distillate water for 5 min.

To investigate the effect of the T on the oxidation of FA at the anode surface, an aqueous solution of 0.05 or 0.12 M FA (puriss. p.a. ACS reagent, Ph. Eur. $\geq 98\%$ purchased from Sigma Aldrich) and 0.1 M Na₂SO₄ was used. Ti/IrO₂-Ta₂O₅ (commercial DSA® supplied by De Nora) and Ni or Sn foil were used as anode and cathode electrodes, respectively.

The performances of the process were discussed in terms of two main figures of merit:

- Current density (j ; mA cm^{-2}) is a measure of the velocity of the reaction and is defined as

$$j = I/A$$

where I is the current intensity (A) and A is the cathodic wet surface area (cm^2);

- Faradic efficiency (FE , %) measures the process' selectivity towards the desired product and, in the case of FA is defined as

$$FE_{\text{FA}} = z F [FA]_t / I t * 100$$

where z is the number of electrons exchanged in the main reaction ($z = 2$ in the case of FA), F is the Faraday constant (96485 C mol^{-1}), $[FA]_t$ is the FA concentration (mol L^{-1}) at the time t (s), V (L) is the volume of the solution.

Limiting current density, j_{lim} was computed as

$$j_{\text{lim}}(T) = z F (\mathcal{D}_{\text{CO}_2}(T) / \delta) c_{\text{CO}_2}^b(T)$$

where $\mathcal{D}_{\text{CO}_2}(T)$ is the CO₂ diffusion coefficient estimated at different T values ($\text{m}^2 \text{ s}^{-1}$), δ is the thickness of the stagnant layer assumed of 100 μm , and, at fixed P_{CO_2} , $c_{\text{CO}_2}^b(T)$ is the bulk CO₂ concentration.

To evaluate the formic acid concentration ([FA]), Agilent HP 1100 HPLC fitted out with Rezex ROA-Organic Acid H+ (8%) column at 55 °C and coupled with a UV detector (210 nm) was used; 0.005 N H₂SO₄ water solution at pH 2.5 was eluted at 0.5 mL min⁻¹ as mobile phase. 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 temperature of the column was programmed, that is an isotherm at 35 °C for 5 min followed by a 20 °C min⁻¹ ramp up to 225 °C and by an isothermal step for 40 min. The presence of formaldehyde is controlled at Agilent technologies Cary 60 UV-Vis using the Formaldehyde Cell Test Spectroquant® (Merck).

3. Results and discussion

3.1. Pseudo-polarizations

Polarization curves were largely used in the literature to obtain information on the cathodic reduction of CO₂ at various electrode materials. For pressurized systems that do not contain reference electrodes, also pseudo-polarization curves were used to gain data on such processes changing the overall cell potential imposed on the cell. Here, to achieve preliminary information on the combined effect of the P_{CO_2} and T on the electrochemical reduction of CO₂ to FA using a Sn cathode, a series of

pseudo-polarization curves was recorded in a Na₂SO₄ aqueous electrolyte by changing both P and T in a range from 1 to 30 bar and from 10° to 60°C, respectively, under N₂ or CO₂ atmosphere. All the pseudo-polarizations were recorded by changing the absolute value of the cell potential ($|\Delta V|$) in the range 0.90–4.50 V. Fig. 1 reports the pseudo-polarization curves recorded at 1 bar and 10 and 60 °C, respectively, while Fig. S1 reports the curves obtained at 1 bar and 20 and 40 °C (see Supporting Information). Under N₂ atmosphere at 1 bar and 10 °C (Fig. 1a), the current density (j) starts to increase at a $|\Delta V|$ of about 2.00 V and the dependence of j from the $|\Delta V|$ becomes more relevant at $|\Delta V|$ higher than 3.20 V. Under these conditions, the increase of j is due to the hydrogen evolution reaction (HER), which is expected to take place by the following reactions [33]: (i) cathodic reduction of protons to adsorbed hydrogen ($H^+ + e^- = H_{\text{(ads)}}$) and (ii) evolution of hydrogen by the Heyrovsky step ($H_{\text{(ads)}} + H^+ + e^- = H_2$). According to the literature [33], at Sn cathode in acidic conditions and low negative potentials, the Heyrovsky step is the r.d.s. and the superficial coverage by adsorbed hydrogen is negligible. Conversely, at high negative potentials, the surface coverage of the electrode by adsorbed hydrogen reaches a higher value. At 1 bar and under N₂ atmosphere, an increase of T from 10 to 20, 40 and 60 °C determines a progressive enhancement of the j for all the $|\Delta V|$ values under investigation. In addition, the higher the T , the lower the $|\Delta V|$ value where the HER starts (Fig. S2, see Supporting Information).

When CO₂ is added to the system, an increase of the j is observed for $|\Delta V|$ values between 2.10 and 3.50 V. Conversely, for $|\Delta V| > 3.50 \text{ V}$ the j recorded in the presence of CO₂ is lower than that observed with N₂ thus probably indicating, according to the literature, that CO₂ or, more probably, its reduction products are adsorbed at the Sn surface, thus limiting the H₂O reduction [19]. In particular, the difference between the overall current (j_{tot}) and the current recorded in the absence of CO₂ (j_{N_2}), called j_{CO_2} , increases up to about 3.15 V (Fig. 1a) and decreases for more negative potentials (Fig. 1a).

According to the literature [17,19,34–36], the CO₂EC to FA using Sn cathodes in the aqueous electrolyte is likely to involve the following stages: (i) mass transfer of dissolved CO₂ to the cathode surface; (ii) adsorption of CO_{2(aq)}} (Eq. (1)); (iii) cathodic reduction of CO_{2(ads)}} to adsorbed CO_{2(ads)-} (Eq. (2)); (iv) cathodic reduction of CO_{2(ads)-} to FA (Eqs. (3) and (4)).



Moreover, according to Proietto et al. [19] the experimental data reported in Fig. 1a for CO₂ reduction, can be rationalized as follows:

- 1) For low $|\Delta V|$ values, CO₂ reduction does not take place in a significant way for kinetic reasons. Under these conditions [37], the r.d.s. is likely to be the second electron transfer (Eq. (4));
- 2) For intermediate values of $|\Delta V|$, the CO₂ reduction is under the mixed kinetic control of the mass transfer of CO₂ to the cathode surface and of the reduction of adsorbed CO₂; in particular, the reduction rate is expected to reach a plateau value for the highest $|\Delta V|$ values of this interval since the process becomes limited by mass transfer (for low concentration of CO₂) or by high coverages of the surface by adsorbed CO₂ (for a high concentration of CO₂);
- 3) For high values of $|\Delta V|$, the cathodic reduction of water is expected to be very fast, thus limiting the formation of FA. However, also under these conditions CO₂ and/or, more probably, its reduction products cover part of the cathode surface, thus reducing the H₂ evolution.

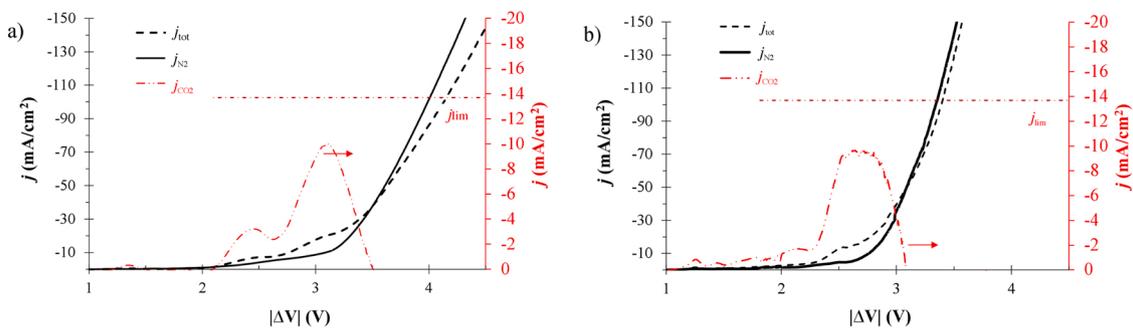


Fig. 1. Pseudo-polarization curves recorded in a $|\Delta V|$ values range between 0.90 and 4.50 V at 1 bar and (a) 10 °C and (b) 60 °C under CO₂ (j_{tot}) and N₂ (j_{N_2}) atmosphere. j_{CO_2} : difference between j_{tot} and j_{N_2} . j_{lim} : limiting current density evaluated in absence of mixing. Working electrode: Sn; $A_{\text{working}} = 0.1 \text{ cm}^2$. Counter electrode: DSA®; $A_{\text{counter}} = 1 \text{ cm}^2$. Electrolyte: aqueous solution of 0.1 M Na₂SO₄ (50 mL). Scan rate: 5 mV s⁻¹.

As shown in Fig. 1b and S1, at higher T a similar plot is observed. However, the total j strongly increases and j_{CO_2} reaches its maximum value and starts to decrease at lower values of $|\Delta V|$. This is probably due to the fact that higher T accelerates the kinetics of reaction stages involved in both CO₂ reduction and H₂ evolution, thus shifting at lower values of $|\Delta V|$ all the steps observed at 10 °C. Hence, on the one hand, CO₂ reduction reaches its maximum rate at lower $|\Delta V|$, but, on the other hand, H₂ evolution starts to annihilate the CO₂ reduction at less negative potentials. In both cases (Figs. 1a and 1b), the limiting current density (j_{lim}) estimated for a process under the kinetic control of the mass transfer in the absence of mixing is higher than the j_{CO_2} values. This shows that, under the adopted conditions, the process is not limited by the mass transfer of CO₂ to the cathode surface.

Figs. 2 and 3 report the data achieved under the same operative conditions but at higher P_{CO_2} (10 and 30 bars). It is worth mentioning that the increase of P_{CO_2} enhances remarkably both the j_{tot} and the j_{CO_2} . Moreover, at higher P_{CO_2} , the decrease of j_{CO_2} shifts to higher values of $|\Delta V|$, thus potentially allowing to reduce CO₂ at high currents and achieving higher productivities of the cell. These positive effects are due to the drastic increase of the CO₂ solubility with the P_{CO_2} that accelerates the mass transfer of CO₂, increases the adsorption of CO_{2(aq)} (Eq. (1)) and consequently accelerates the cathodic reduction of CO_{2(ads)} to adsorbed CO_{2(ads)}⁻ (Eq. (2)). The effect of the T is more complex. Indeed, high T values cause an increase of the j_{tot} and of j_{CO_2} (the last for P_{CO_2} of 10 and 30 bars), but they reduce the minimum value of $|\Delta V|$ where j_{CO_2} starts to decrease, thus limiting the operative j .

Fig. 4 reports the ratio between j_{CO_2} and the j_{tot} . It can be observed that it presents a maximum value close to 85% and 50% at 30 and 1 bar, respectively. Moreover, this ratio strongly decreases for high $|\Delta V|$. It can be observed that this ratio starts to decrease for lower values of $|\Delta V|$ when the T is increased or the P_{CO_2} is decreased. Hence, overall, pseudo-polarization curves suggest that low T and high P_{CO_2} seem particularly promising to achieve high productivity and faradaic

efficiency. Of course, the ratio between j_{CO_2} and the j_{tot} cannot be considered an accurate way to evaluate the competition between the CO₂ reduction and the H₂ evolutions since the j_{tot} is not expected to be the simple addition of that achieved by the two separated process, but only an interesting signal that needs to be verified by means of suitable electrolyses, as described in the following section.

3.2. Electrolysis at fixed cell potential

3.2.1. Effect of cell potential, temperature, and pressure

First electrolyses were performed using a Sn cathode with a water solution of 0.1 M Na₂SO₄ at pH 4, 40 °C and 10 bars imposing a constant $|\Delta V|$. Four different $|\Delta V|$ were used: 2.7, 3.0, 3.5 and 3.7 V. As shown in Fig. 5, the performance of the process strongly depends on the $|\Delta V|$ value. At 2.7 V, the electrolysis gave relatively low j (close to -14 mA cm⁻², Fig. 5a) and productions of FA (about 1.48 mM) with a FE_{FA} close to 59% (Fig. 5b). When the $|\Delta V|$ was increased to 3.0 V, the processes benefited of higher j (up to -65 mA cm⁻², Fig. 5a) and higher productions of FA (of 2.2 mM, Fig. 5b). Moreover, at this $|\Delta V|$ the CO₂ reduction was significantly favored with respect to the H₂ evolution and the FE_{FA} increased to approximately 82% (Fig. 5b). Conversely, further increases of the $|\Delta V|$ to 3.5 and 3.7 V resulted in lower productions of FA despite the higher j as a result of the decrease of the FE_{FA} (Fig. 5). These results can be rationalized, according to the pseudo-polarization curves reported in previous paragraph and with previous literature, considering that the electrolysis of pressurized CO₂ is limited at low $|\Delta V|$ by slow kinetics of CO₂ reduction (probably of the second electron transfer) and at high $|\Delta V|$ by the massive H₂ evolution that partially inhibits the CO₂ reduction.

To investigate the effect of the T under relatively high P_{CO_2} , this series of electrolyses was repeated at 10 and 60 °C (Fig. 6). According to the pseudo-polarization curves reported in the previous section, at fixed $|\Delta V|$, an increase of the T gave rise to an enhancement of j , i.e. of the

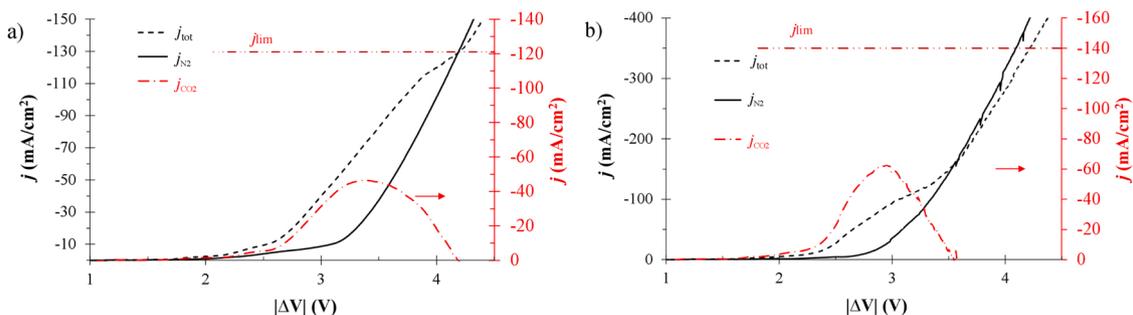


Fig. 2. Pseudo-polarization curves recorded in a $|\Delta V|$ values range between 0.90 and 4.50 V at 10 bar and (a) 10 °C and (b) 60 °C under CO₂ (j_{tot}) and N₂ (j_{N_2}) atmosphere. j_{CO_2} : difference between j_{tot} and j_{N_2} . j_{lim} : limiting current density evaluated in absence of mixing. Working electrode: Sn; $A_{\text{working}} = 0.1 \text{ cm}^2$. Counter electrode: DSA®; $A_{\text{counter}} = 1 \text{ cm}^2$. Electrolyte: aqueous solution of 0.1 M Na₂SO₄ (50 mL). Scan rate: 5 mV s⁻¹.

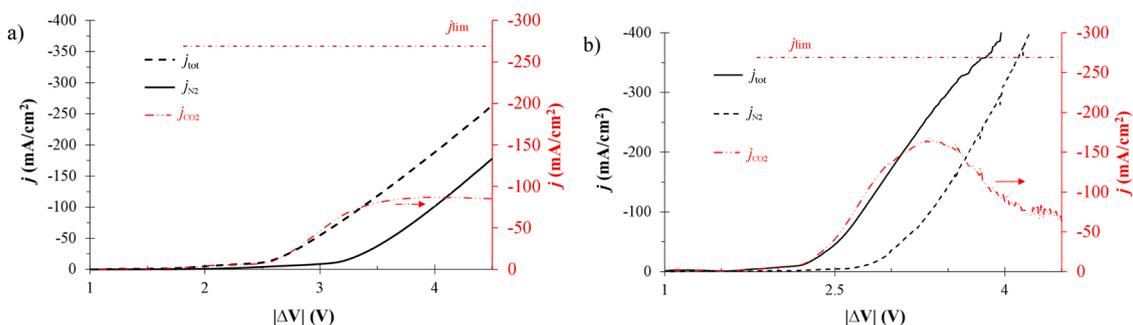


Fig. 3. Pseudo-polarization curves recorded in a $|\Delta V|$ values range between 0.90 and 4.50 V at 30 bar and (a) 10 °C and (b) 60 °C under CO₂ (j_{tot}) and N₂ (j_{N_2}) atmosphere. j_{CO_2} : difference between j_{tot} and j_{N_2} . j_{lim} : limiting current density evaluated in absence of mixing. Working electrode: Sn; $A_{\text{working}} = 0.1 \text{ cm}^2$. Counter electrode: DSA®; $A_{\text{counter}} = 1 \text{ cm}^2$. Electrolyte: aqueous solution of 0.1 M Na₂SO₄ (50 mL). Scan rate: 5 mV s⁻¹.

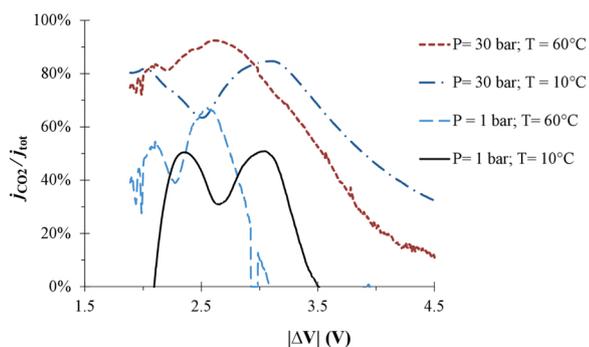


Fig. 4. Plot of the ratio between j_{CO_2} and j_{tot} as a function of the $|\Delta V|$ under different values of P_{CO_2} (1 and 30 bar) and T (10 and 60 °C) of the data reported in Figs. 1 and 3.

reaction rates. An increase of the T from 10 to 40 or 60 °C allows to increase the j from -33 to -65 or -100 mA cm^{-2} at 3.0 V and from -100 to -170 or -235 mA cm^{-2} at 3.7 V (Fig. 6a). The effect of T on the production of FA even if more complex (see Figs. 6b and 6c) agrees with the pseudo-polarization curves, as described below.

For all the adopted T , the plot of the final [FA] and FE_{FA} vs. $|\Delta V|$ presents a trend with a maximum which moves to lower $|\Delta V|$ values by increasing the T (Figs. 6b and 6c). As an example, the maximum FE_{FA} values were 88.5% at 10 °C and 3.5 V and 75.5% at 60 °C and 3.0 V.

At the lowest values of $|\Delta V|$ of 2.7 V, similar results in terms of final [FA] and FE_{FA} were obtained at all adopted T .

Conversely, at high $|\Delta V|$ values, an increase of [FA] and FE_{FA} was achieved by lowering the T . As an example, at 3.7 V, an enhancement of the final [FA] from 1.10 to 2.00 mM and of FE_{FA} from 42.0% to 77.5 was observed by lowering the T from 60° to 10°C, respectively. As above mentioned, this effect is probably because higher T accelerates the

kinetic constants of the reaction stages of both CO₂ reduction and H₂ evolution, thus shifting to lower $|\Delta V|$ the region where the H₂ evolution annihilates the CO₂ reduction. Moreover, high T leads to a decrease in CO₂ solubility, thus partially contrasting the positive effect of the T on the kinetic constants of reactions involved in CO₂ reduction.

The highest [FA] and FE_{FA} up to 2.35 mM and 88.5%, respectively, were reached at 10 °C and 3.5 V.

The strong reduction of FE_{FA} with the $|\Delta V|$ was observed several times in the literature. As previously mentioned, it is probably due mainly to the predominance of H₂ evolution that annihilates CO₂ reduction. In particular, according to Proietto et al. [19], the following phenomena are likely to take place at the more negative working potentials: (i) the H coverage is expected to increase, thus limiting the rate of CO₂ adsorption; (ii) the concentration of protons at the tin surface is expected to decrease, thus reducing the rate of both Eqs. (3) and (4); (iii) the high H₂ evolution can cause a partial covering of the electrode surface by the gas bubbles, thus decreasing the rate of the mass transfer of CO₂ to the cathode.

In all the electrolyses, only a small amount of CO was obtained with a FE_{CO} of approximately 4%.

To investigate the impact of the P_{CO_2} , electrolyses were performed at 10 °C at a fixed $|\Delta V|$ value of 3.5 V using a Sn cathode in a wide range of P_{CO_2} (1, 10 and 30 bar). As shown in Fig. 7, according to the pseudo-polarization curves, an increase of the P_{CO_2} allows to reach higher j values, due to the higher bulk CO₂ concentration which aids to speed up the CO₂ reduction stages. According to the literature, at ambient T , the CO₂EC into FA using Sn cathode is likely to be kinetically controlled by the mass transfer or the first reduction stage, depending on the value of the P_{CO_2} [19]. The rise of the P_{CO_2} from 1 to 10 and 30, step by step, determines an increase of the j from -48 to -84 and -98 mA cm^{-2} , respectively (Fig. 7a). Furthermore, the effect of the P_{CO_2} gave rise to an enhancement of the overall performances of the process by increasing the P_{CO_2} from 1 to 10 bar: [FA] and FE_{FA} were significantly increased

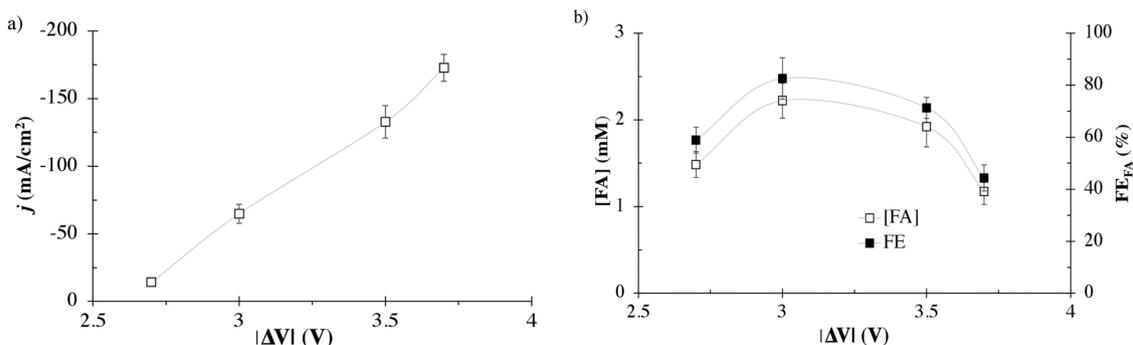


Fig. 5. Plot of the (a) j , (b) [FA] and FE_{FA} vs. $|\Delta V|$ of electrolyses performed at fixed $|\Delta V|$ values of 2.7, 3.0, 3.5, 3.7 V at 10 bar and 40 °C. $V = 50 \text{ mL}$ of a water solution 0.1 M Na₂SO₄ at pH 4. Working electrode: Sn; $A_{\text{working}} = 0.1 \text{ cm}^2$. Counter electrode: DSA®; $A_{\text{counter}} = 1 \text{ cm}^2$. $Q = 27 \text{ C}$.

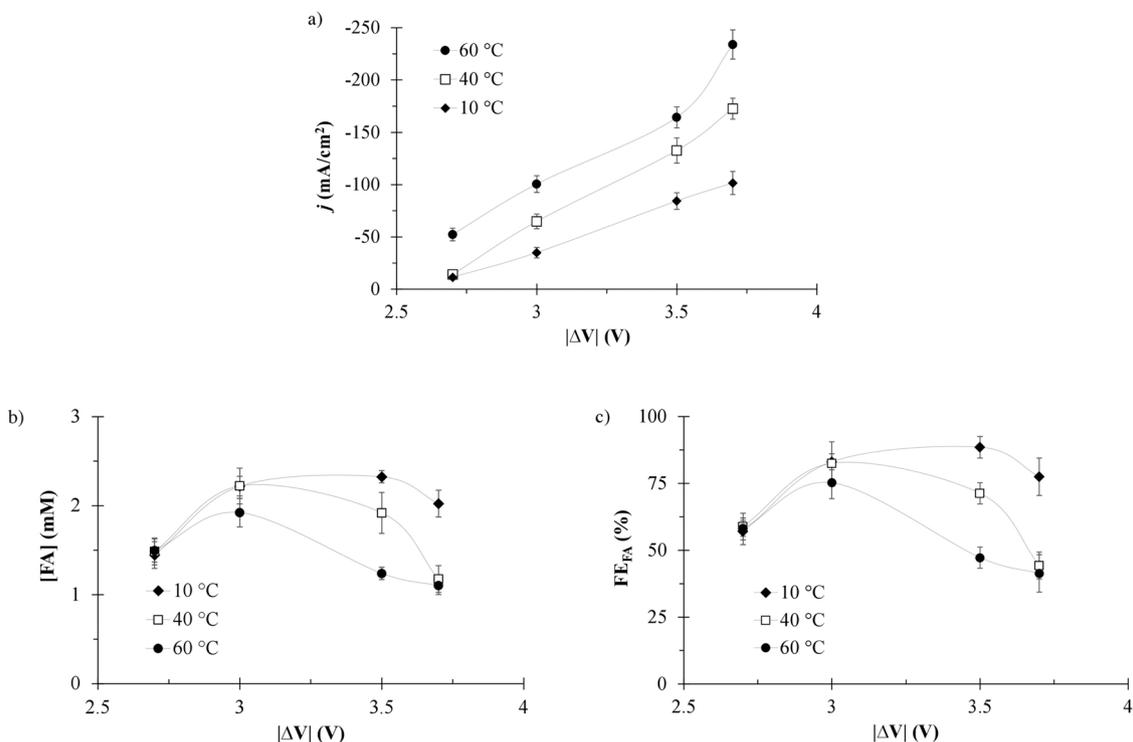


Fig. 6. Effect of the T (10, 40 and 60 °C) on the CO₂EC into FA at 10 bar. Plot of the (a) j , (b) [FA] and (c) FE_{FA} vs. $|\Delta V|$. Electrolyses were performed at fixed $|\Delta V|$ value (2.7, 3.0, 3.5, 3.7 V), 10 bar and 10, 40 or 60 °C. $V = 50 \text{ mL}$ of a water solution 0.1 M Na₂SO₄ at pH 4. Working electrode: Sn; $A_{\text{working}} = 0.1 \text{ cm}^2$. Counter electrode: DSA®; $A_{\text{counter}} = 1 \text{ cm}^2$. $Q = 27 \text{ C}$.

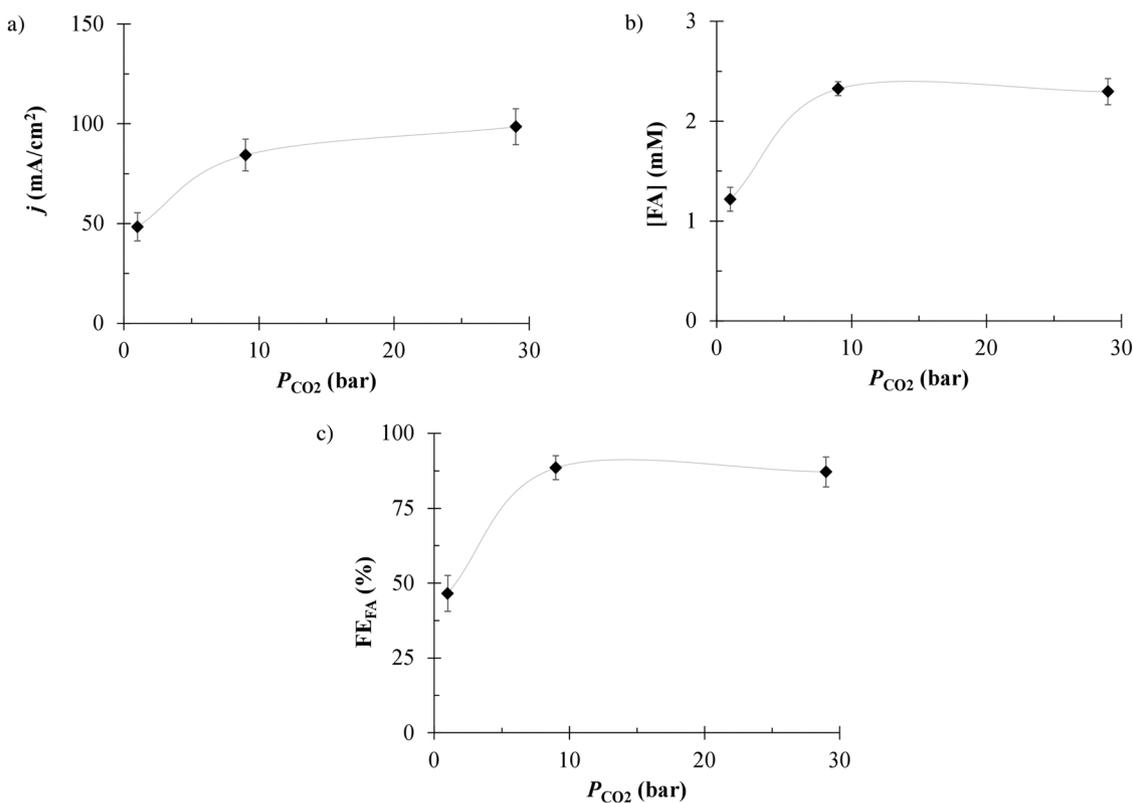


Fig. 7. Effect of the CO₂ pressure on the (a) j , (b) [FA] and (c) FE_{FA}. Electrolyses were carried out at fixed $|\Delta V|$ value of 3.5 V, at 10 °C and at 1, 10 or 30 bar. $V = 50 \text{ mL}$ of a water solution 0.1 M Na₂SO₄ at pH 4. Working electrode: Sn; $A_{\text{working}} = 0.1 \text{ cm}^2$. Counter electrode: DSA®; $A_{\text{counter}} = 1 \text{ cm}^2$. $Q = 27 \text{ C}$.

from 1.20 mM and 46.6% to 2.35 mM and 88.5%, due to the high CO₂ concentration in solution which allows to increase the coverage of the surface by CO₂. Conversely, a further increase of the P_{CO_2} to 30 bar did not give an appreciable effect on the [FA] and FE_{FA} of the process (Figs. 7b and 7c), probably because, at these high pressures, the process becomes kinetically limited by the high coverage of the cathode surface by the adsorption of CO₂ and/or its reduction products.

3.3. Electrolysis under amperostatic mode

3.3.1. Effect of cathode surface and time passed

Often, electrolyses on an applicative scale are performed under amperostatic mode. Hence, some electrolyses were repeated at 10 °C and 10 bar using a water solution of Na₂SO₄ at pH 4. A j of -30 mA cm^{-2} was adopted which corresponds to a $|\Delta V|$ close to 3.0 V. As shown in Table 1, results obtained with a fixed $|\Delta V|$ of 3.0 V (entry 1) and under amperostatic mode with -30 mA cm^{-2} (entry 2) gave very similar results in terms of final [FA] and FE_{FA} . To achieve other information useful for scale up procedures, the effect of the surface electrode was also investigated. Hence, a series of electrolysis was performed at -30 mA cm^{-2} , 10 bar and 10 °C for 2.5 h by changing the dimension of the cathodic surface area (A_w) (Table 1). An increase of A_w gave rise to a proportional enhancement of the [FA] in solution; by enlarging the A_w approximately 20 or 40 times, the [FA] increases from 2 to 44 and 80 mM, respectively, due to the higher passed charge, coupled with a little decrease of the FE_{FA} (Table 1, entries 2–4). The increase of the A_w was also associated with an increase of the $|\Delta V|$ value (Table 1, entries 2–4) due to the higher ohmic drops caused by the higher j .

To increase the [FA], the reaction time of the CO₂EC using a Sn cathode with an A_w of 4.3 cm² was extended from 2.5 h to 6 h. It was shown that an increase in the time gave rise to an enhancement of the [FA] up to approximately 170 mM. However, a slight decrease in the FE_{FA} was observed (Table 1, entry 5).

3.3.2. Effect of temperature, pressure and current density

To evaluate the effect of T and P_{CO_2} on the CO₂EC to FA under amperostatic conditions, which are more appealing from the applicative point of view, a large series of electrolyses was performed using a Sn cathode ($A_w = 4.3 \text{ cm}^2$) at 1 bar and 10 bars, by adopting many different T in the range between 3 and 60 °C. Most of the electrolysis was carried out at two different j (-11.6 and -30 mA cm^{-2}) and for 6 h.

Fig. 8 reports the final [FA] achieved after 6 h in the various electrolyses performed at 1 bar and -11.6 mA cm^{-2} and the corresponding FE_{FA} . According to the results obtained with a fixed $|\Delta V|$, the highest production of FA and the highest FE_{FA} were achieved at the lowest T . In particular, the reduction of the T from 60° to 20°C allows to increase the final [FA] from about 17 to 27 mM. A further decrease of T to 3 °C allows to achieve a final [FA] close to 40 mM with a corresponding FE_{FA} of 35.4% after 6 h, as a consequence of the fact that at 3 °C the solubility of CO₂ can be estimated to be approximately 2.6 times higher than that at

Table 1

Effect of the cathodic surface area (A_w) on the performances of the CO₂EC under pressurized conditions.^a

Entry	A_w (cm ²)	j (mA cm ⁻²)	Q (C)	t (h)	$ \Delta V $ (V)	[FA] (mM)	FE_{FA} (%)
1	0.1	-26.8 ÷ -33.2	27	2.5	3.0	2.2	83
2	0.1	-30.0	26	2.5	3.0	2.0	79
3	2.0	-30.0	513	2.5	4.6	44	82
4	4.3	-30.0	1107	2.5	5.6	80	70
5	4.3	-30.0	2657	6.0	5.6	169	61

^a Electrolyses were performed at 10 °C and 10 bar using a water solution 0.1 M Na₂SO₄ at pH 4. Experiment performed with constant $|\Delta V|$ (entry 1) or under amperostatic mode at -30 mA cm^{-2} (entries 2–5)). V: 50 mL. Working electrode: Sn. Counter electrode: DSA®; $A_{\text{counter}} = 1 \text{ cm}^2$.

20 °C (solubility of approximately 72 and 38 mM at 3 and 20 °C, respectively). It is interesting to observe that these results seem in contrast with the work of Kim et al. [22] which reports no formation of FA at 3 °C. An improvement in the performance of the CO₂ reduction to FA is observed by increasing the P_{CO_2} . As shown in Fig. 8, when the P_{CO_2} is increased to 10 bar, an increase of final [FA] is observed at all the T under investigation due to the higher concentration of dissolved CO₂ in solution. At 3 °C, an increase of P_{CO_2} from 1 to 10 bar allows to enhance the final [FA] from 40 to 70 mM (Fig. 8a) coupled with an increase of the FE_{FA} from 35% to 64% (Fig. 8b). Moreover, also under pressurized conditions, the higher the T , the lower the final [FA]. As an example, the [FA] achieved after 6 h was lower than 30 and close to 70 mM at 60 and 3 °C, respectively. It is worth to mention that under pressurized conditions the working j is significantly lower than the j_{lim} (of approximately -125 mA cm^{-2}), thus showing that the process is not under the kinetic control of the mass transport of CO₂.

Furthermore, under atmospheric P_{CO_2} , only H₂ was detected as a by-product of the cathodic process, while, under pressurized conditions, it was also observed CO with a small FE of approximately 4%.

To investigate the effect of T at high values of j , electrolyses were performed also at -30 mA cm^{-2} under pressurized condition of 10 bar by changing the T . As shown in Fig. 8, the increase of the j from -11.6 to -30 mA cm^{-2} did not result in a significant change of the FE_{FA} probably because, at both these j , the $|\Delta V|$ are in the region of pseudo-polarization curves where both j_{CO_2} and j_{CO_2}/j_{tot} reach their highest values (see Section 3.1). However, the increase of j , at all the adopted T , allows to double up the [FA] in solution due to the higher passed charge, by maintaining the similar values of FE_{FA} . Quite interesting results were achieved at 3 °C, in which the [FA] rise up to 148 mM coupled with a FE_{FA} of approximately 65% by working at -30 mA cm^{-2} (Fig. 8). Similarly, at 10 °C the final [FA] reached values close to 130 mM (Fig. 8).

These results confirm that, under pressurized conditions and also at higher j values, high [FA] can be obtained at lower T , plausibly due to the higher CO₂ coverage of the cathodic surface as a consequence of the higher CO₂ dissolved in solution and the partial suppression of the HER (as showed in the pseudo-polarization curves) due to its low water reduction rate under these conditions.

3.3.3. Experiments performed at high pressures (30 bars) and current densities

It has been shown that the economics of the electrochemical conversion of CO₂ to FA strongly depends on the productivity of the cell and on the final [FA]. Hence, to improve the productivity in FA of the cell and the final [FA], a further series of amperostatic electrolysis was performed at higher values of j (-75 mA cm^{-2}) and P_{CO_2} (30 bar), by changing the T in the range between 10 and 60 °C. As shown in Fig. 8, the coupled utilization of high P_{CO_2} and j allows to maintain good FE_{FA} and increase drastically the final [FA] in the same amount of time passed. Also, in this case, highest performances were achieved by working at the lowest T values; in particular, at 10 °C, a quite high [FA] of 360 mM coupled with a FE_{FA} of 50% was achieved after 6 h (Fig. 8). Similarly, a final [FA] of approximately 180 mM and a FE_{FA} of 27% were reached working at 20 °C (Fig. 8).

3.3.4. Stability of the process

As shown in previous paragraphs, the FE_{FA} in some cases has shown a slight decrease with the time passed. This phenomenon can be attributed to different causes. As an example, the FE_{FA} may decrease due to the anodic oxidation of FA which is expected to enhance with charge passed due to the accumulation of FA in the solution. To verify this hypothesis, a series of electrolysis was performed using an aqueous electrolyte of 0.1 M Na₂SO₄ and different initial [FA] (120 or 50 mM) using Sn or Ni as cathode and DSA as anode, respectively, at -11.6 or -75 mA cm^{-2} , atmospheric pressure in absence of CO₂ and different T . Ni cathode was chosen to avoid a further reduction of the FA to other C-based products

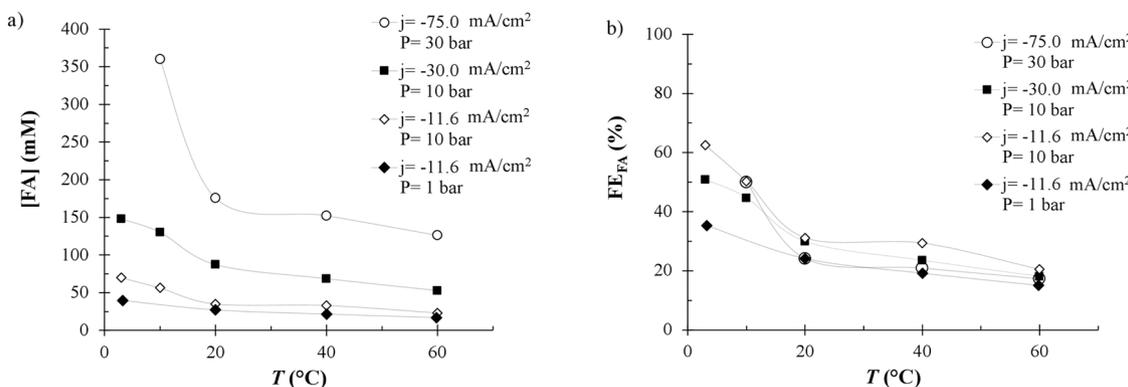


Fig. 8. Plot of the (a) final [FA] and the (b) corresponding FE_{FA} vs. the T ($3 \div 60$ °C) under different values of P_{CO_2} ($1 \div 30$ bar) and j ($-11.6 \div -75$ mA cm^{-2}). Galvanostatic mode. $V = 50$ mL of a water solution 0.1 M Na_2SO_4 at pH 4. Working electrode: Sn; $A_{working} = 4.3$ cm^2 . Counter electrode: DSA®; $A_{counter} = 1$ cm^2 . Time: 6 h.

Table 2

Anodic oxidation of FA at different T and j^a .

Entry	Cathode	j (mA cm^{-2})	Q (C)	[FA]/[FA] ^{°b}
1	Ni	-11.6	288	0.99 ^c – 0.99 ^d
			280	0.99 ^c – 0.99 ^d
2	Sn	-11.6	540	0.97 ^c – 0.94 ^d
			1080	0.94 ^c – 0.95 ^d
			580	0.91 ^c
3	Sn	-75.0	1161	0.85 ^c
			2903	0.62 ^c

^a Electrolyses were carried out using an undivided glass cell equipped with DSA as anode. $V = 50$ mL. Supporting electrolyte: 0.1 M Na_2SO_4 water solution. No mixing

^b Initial concentration of formic acid [FA][°] was 0.05 M or 0.12 M using Ni or Sn as cathode respectively.

^c Electrolysis was performed at T of 20 °C.

^d Electrolysis was performed at T of 60 °C.

at the cathode surface and favor the H_2 evolution reaction at the cathode surface. Table 2 reports the normalized $[FA]/[FA]^\circ$ as a function of the charge passed under the adopted conditions. At 20 and 60 °C, slightly decrease of the $[FA]/[FA]^\circ$ of 1% were observed after approximately 288 or 280 C by using both Ni or Sn as cathode, respectively, (Table 2, entries 1 and 2). A further reduction of the $[FA]/[FA]^\circ$ of approximately 5–6% was achieved by increasing the charge passed up to 1080 C (Table 2, entry 2) using Sn cathodes at -11 mA cm^{-2} . Similar results were achieved by working at higher j ; indeed, $[FA]/[FA]^\circ$ value decrease with the charge passed also at -75 mA cm^{-2} reaching 0.62 after approximately 2900 C (Table 2, entry 3). These results allow to show that the decrease in faradaic selectivity of the process can be due to the consumption of FA by the anodic oxidation process: the higher the charge passed, the higher the consumption of FA.

A second hypothesis is that the performances of the cathode change with the time. In order to test this possibility, the electrolysis carried out at 10 bar and 10 °C was prolonged for 10 h. At the end of the electrolysis, a [FA] slightly higher than 200 mM was obtained with a FE_{FA} close to 50%, just slightly lower than that achieved after 6 h. Hence, the experiment was repeated by using the same cathode adopted in the first test without any treatment. It is worth to mention that also in this case a final concentration of FA close to 200 mM was obtained. Moreover, in this case, the FE_{FA} was constant for all the process. Hence, it seems reasonable to suppose that the cathode shows quite constant performances after an initial transitory phase.

4. Conclusions

In this work, the simultaneous effect of P_{CO_2} and T on the

performances of CO₂EC process into FA in an aqueous electrolyte using an undivided cell equipped with a Sn cathode was investigated under different operative conditions by electrochemical characterizations and electrolyses. It was found that the effect of the T on the production of FA is very complex, overall, the adoption of low T values and/or high P_{CO_2} values allow to significantly improve performances of the process under all the adopted operative conditions.

In detail, the main findings of this work are summarized below.

According to the pseudo-polarization curves recorded in a wide range of T (up to 60 °C), P_{CO_2} (up to 30 bar) and $|\Delta V|$ (0.9–4.5 V) values and the assumed mechanism reaction, high T values, from one hand, can accelerate the kinetic constants of the reaction stages involved on both the CO₂ reduction and H_2 evolution, thus shifting to lower $|\Delta V|$ values the region where the H_2 evolution annihilates the CO₂ reduction; from the other hand, high T leads to a decrease of the CO₂ solubility, thus partially contrasting the positive effect of the T on the kinetic constants of reactions involved in CO₂ reduction.

The performance of the process strongly depends on the applied $|\Delta V|$ value. At low values of $|\Delta V|$, similar results in terms of final [FA] and FE_{FA} were obtained at all adopted T ; while at high $|\Delta V|$ values, an increase of the [FA] and of FE_{FA} was achieved by lowering the T . As an example, at 3.7 V, an enhancement of the final [FA] from 1.10 to 2.00 mM and of FE_{FA} from 42.0% to 77.5% was observed by lowering the T from 60° to 10° C, respectively.

For all the adopted T and j , the increase of the P_{CO_2} value allows to significantly increase the reaction rate and the production of FA, due to the high CO₂ dissolved in the solution.

An increase of cathodic area (A_w) and/or the time of electrolysis gave rise to an almost proportionally enhancement of the [FA] in solution. At 10 °C, by enlarging the A_w approximately 20 or 40 times, the [FA] increases from 2 to 44 and 80 mM, respectively, and an increase of the time from 2.5 to 6 h gave rise to an enhancement of the [FA] from 80 to 170 mM, respectively, due to the higher passed charge.

For all the adopted T and j values, high [FA] are achieved by lowering T , plausibly due to the higher CO₂ coverage of the cathodic surface because of the higher concentration of CO₂ dissolved in the solution and the partial suppression of the HER due to its low water reduction rate. As an example, quite interesting results were achieved at 3 °C and 10 °C, in which the [FA] rise up to 148 and 130 mM, respectively, coupled with a FE_{FA} of approximately 65% by working at -30 mA cm^{-2} .

A relevant improvement of the performances of the CO₂EC into FA was observed by a coupled enhancement of the P_{CO_2} and j values and a decrease of the T . In particular, a quite high final [FA] of approximately 360 mM was reached in an aqueous electrolyte by working at T of 10 °C, j of -75 mA cm^{-2} and P_{CO_2} of 30 bar.

CRedit authorship contribution statement

Federica Proietto: Investigation, Methodology, Data curation, Writing - review & editing. **Riccardo Rinicella:** Investigation, Data curation. **Alessandro Galia:** Writing - review & editing, Funding acquisition. **Onofrio Scialdone:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition.

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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2022.102338.

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