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Towards the Electrochemical Conversion of CO₂ to Formic Acid at an Applicative Scale: Technical and Economic Analysis of Most Promising Routes

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In the last decade, the electrochemical conversion of CO₂ to formic acid, FA, using Sn-based cathodes, was widely investigated. In this work, the technical feasibility and economic viability of this process were evaluated considering the most promising electrochemical routes reported in the literature. Five case studies, based on the utilisation of gas diffusion electrode (GDE) technologies or high CO₂ pressures, were analysed. The cost for producing FA by the electrochemical route was compared with that of the conventional chemical route. Several scenarios were envisioned finding the target figures of merit, the potential bottlenecks (including low FA concentration, GDE

cost and high energy consumption) of each technology and the challenges that need to be faced. It was shown that the performances of these processes are not still adequate from an economic point of view and the improvements that should be achieved were identified. To be suitable for the commercialisation, the process should reach simultaneously high current density, faradaic efficiency and actual FA concentration as well as good stability with time and a limited cost of electrodes. In addition, it was shown that the utilisation of the excess electric energy generated from renewable sources could significantly reduce the costs of the process.

1. Introduction

The electrochemical reduction of CO₂ (ERCO₂) is considered one of the most promising strategies to valorise waste-CO₂ as a feedstock to produce value-added chemicals, such as carbon monoxide, formic acid (FA), methanol, methane and ethene.^[1–5] From the industrial standpoint, the electrochemical production of chemicals from CO₂ could be an appealing strategy to cope with the stringent environmental regulations on greenhouse gas (GHG) emissions. To encourage companies to reduce GHG emissions, several initiatives were implemented in the last decade, including the Emissions Trading System (ETS) and the Carbon Tax (CT).^[6] Industrial companies could find more economically convenient to capture and convert their own produced CO₂ rather than to emit it into the atmosphere since they would benefit from lower CTs and revenues by selling the value-added chemicals. To date, CTs significantly depend on countries' legislation (Table 1).^[6] Furthermore, ERCO₂ could potentially store the excess electric energy from intermittent renewable sources as chemical energy, which is one of the key advantages of this technology. Indeed, due to their unforeseeable nature, electricity supplied from these sources may not


Table 1. Carbon taxes of several countries.^{[6][a]}


Countries	CT [€/t _{CO2}]
Sweden	108.8
Switzerland, Liechtenstein	90.5
Finland	62.2
Norway	48.4
France	44.8
Iceland	27.4
Ireland, Germany, ^[b] Denmark, Portugal, Spain, Northwest Territories, Labrador, Latvia, South Africa, Argentina, Chile, Colombia, Singapore, Japan, Estonia, Ukraine, Poland	< 25.6

[a] Nominal prices on April 1, 2020. [b] Nominal price of 25 €/t_{CO2} on January 1, 2021.

match the demand throughout the day, and often, this mismatch results in a surplus of electrical energy that is available at low prices. Among the ERCO₂ products, FA is a valuable building block with a mature market and a relatively high value. Traditionally, FA is used in food technologies, agriculture, pharmaceutical industry and in the production of leather and textiles.^[7,8] Currently, the synthesis of FA is a fossil fuels-based process, which is not straightforward neither environmentally friendly, and, according to some estimations, the electrochemical production of FA may become cheaper than commercial routes.^[4] Extensive studies have shown that ERCO₂ using Sn-based cathodes [9–20] can lead to the production of FA/formate with high selectivity. Appealing results were reported by using both Sn gas diffusion electrodes (GDEs)^[12,15,16,20,21] and high CO₂ pressures (HPs).^[13,18,19,22] However, to date, the real potential of ERCO₂ on an industrial scale is still uncertain.^[8,19,23–27] Hence, this work reports a technical-economic analysis of ERCO₂ to FA/formate using Sn-based cathode in

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 An invited contribution to a joint Special Collection in memory of Prof. Jean-Michel Savéant

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aqueous electrolyte considering the most promising electrochemical routes reported in the literature.

Five case studies (CSs) were investigated in detail. The utilisation of GDE-based technologies at atmospheric pressure and of pressurised systems equipped with simple Sn plate cathodes was analysed and compared. A simplified supply chain was envisioned, which includes the stage of *i*) CO₂ capture and recycling (C&R), *ii*) ERCO₂ and, *iii*) FA concentration and separation (C&S). Furthermore, several scenarios were envisioned aiming to find the bottlenecks of each technology and to highlight the challenges that need to be faced for the implementation on a large-scale. Eventually, the possibility to use the excess electric energy was analysed. It was shown that the performances of these processes are not still adequate from an economic point of view and the improvements that should be achieved were identified. In particular, to be suitable for the commercialisation, the ERCO₂ to FA using Sn-based electrodes should reach simultaneously high current density, j , ($\geq 120 \text{ mA cm}^{-2}$), faradaic efficiency, FE, ($\geq 95\%$) and high actual FA concentration, [FA], ($\geq 30 \text{ wt.}\%$) as well as limited cost and good stability with time of cathodes.

2. Results and Discussion

The flowchart of the process shown in Figure 1 was envisioned. According to this process scheme, CO₂ is captured from industrial point's source and used as a feedstock for the electrochemical unit. This is supported by a scenario reported by the CRI company.^[28] In Iceland, this company commissioned a first facility CO₂-to-CH₃OH (branded Vulcanol™) via catalytic hydrogenation with a capacity of 4000 t_{CH₃OH}/y. The plant converts 5500 t_{CO₂}/y captured from a flue gas released by a geothermal power plant located close to the CRI facility. Vulcanol™ is already sold in the Iceland market.^[29] For the electrolysis, five different CSs, characterized according to the literature by particularly good performances and cost-effective technologies, were considered (section 2.1). Then, the FA

diluted solution obtained by the electrochemical stage is concentrated and separated to reach the target concentration of FA required by the market (85 wt.%), considering conventional methods. Hence, the technical-economic analysis includes the main costs related to C&R, CO₂ER and C&S stages: $C_{EP} = C_{C\&R} + C_E + C_{C\&S}$ (where C_{EP} is the total cost for the conversion of CO₂ into FA at 85 wt.%; $C_{C\&R}$ are the costs due to the carbon capture and recycling; C_E are the total costs of the electrolysis, including the capital investment (C_{E-I}), and energetic costs (C_{E-O}), and $C_{C\&S}$ are the costs related to the C&S of the FA solution up to 85 wt.%), as described in detail in the methodology section.

2.1. Description of the Case Studies

Five CSs, all based on ERCO₂ to FA/formate using Sn-based electrodes in aqueous electrolyte, reported in the literature and characterised by particularly good performances and by usage of relatively cheap materials and simple cell designs were selected.^[15,17,18,20,30] Indeed, most of the investigated technologies in the literature were based on the usage of more expensive cathodes (including core-shell structured Cu₂O/Cu@C immobilized on nitrogen-doped graphene sheets (Cu₂O/Cu@C/NG),^[31] Bi₂O₂CO₃ nanosheets,^[32] Sn(S)/Au nanoparticles,^[33] Bi–SnO/Cu foam,^[34] SnCu alloys,^[35] Ag_xSn_y alloys,^[36–37] In_xSn_y alloys,^[38,39] Sn_xPb_y alloys,^[40] Sn_xPb_yBi_z alloys,^[41] Cu_xIn_y alloys,^[42–45] Pd-,^[46] PdPt-^[47] or Bi- based catalyst,^[48–50] etc.) or more complex reactor designs, which are more difficult to scale-up. As an example, Diaz-Sainz et al.^[48,49] achieved higher [FA] and FE than that obtained with Sn-based cathodes using Bi-based catalysts fitted in coated membrane electrodes complex reactors, but drastically increasing the energy consumption and, consequently, the energetic costs, and reducing the economic viability.

Table 2 reports the technological details and figures of merit of each CS. CS I, CS II and CS III were based on Sn–GDE technology at atmospheric pressure. At 1 bar, the CO₂ solubility

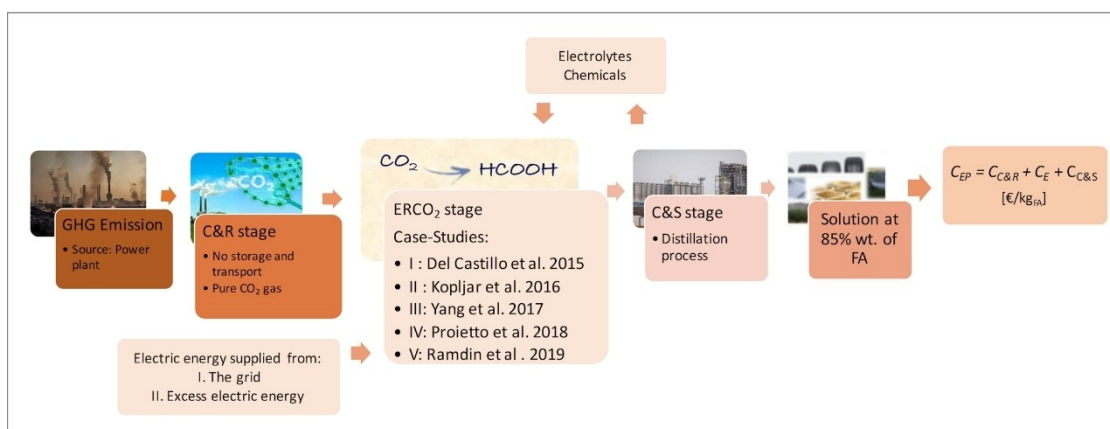


Figure 1. Flowchart of the process structure. C&R stage: Capture and recycling stage. C&S stage: Concentration and separation stage. $C_{EP} = C_{C\&R} + C_E + C_{C\&S}$, where C_{EP} is the total cost for the conversion of CO₂ into FA at 85 wt.%; $C_{C\&R}$ are the costs due to the carbon capture and recycling; C_E are the total costs of the electrolysis, and $C_{C\&S}$ are the costs related to the C&S of the FA solution up to 85 wt.%.

Table 2. Electrochemical conversion of CO₂ using Sn-based electrodes: Figures of merit and description of CSs.^[a]

Conditions ↓	Case studies I	II	III	IV	V
Electrochemical set-up	Divided filter press cell – single pass	Micro structured divided flow cell – single pass	Three-compartment divided cell – single pass	Undivided pressurized filter press cell with a continuous recirculation of the solution	Divided pressurized cell with a continuous recirculation of the solution
Cathode	Sn/C–GDE	SnO ₂ /C–GDE	Sn/C–GDE	Sn plate	Sn plate
Anode	DSA–O ₂	Pt–C CCM	MMO–IrO ₂	DSA–O ₂	MMO–Ir
Membrane	Nafion® 117	Nafion® 117	Sustanion™ AEM ^[c] on the cathode side; Nafion 324 CEM ^[c] on the anode side	No membrane	Bipolar Membrane, BPM
Electrolyte ^[b]	A: 1 M KOH C: 0.45 M KHCO ₃ + 0.5 M KCl	A: 1 M KOH C: 1 M KOH	Water through a cation exchange resin media	0.5 M Na ₂ SO ₄	A: 1 M KOH C: 0.25 M K ₂ SO ₄
Geometrical area cathode [cm ²]	10	2.7	5.0	9.0	80
Current density [mA cm ⁻²]	150	196	140	50	30
Cell Voltage [V]	3.70	3.08	3.60	5.00 ^[d]	3.50
Pressure [bar]	1	1	1	23	50
Faradaic efficiency [%]	70.2	83.0	87.0	82.5	80.0
Concentration [%wt.]	0.25	0.69	9.40	1.26	0.60
Production rate [kg h ⁻¹ m ⁻²]	0.90	1.39	1.12	0.34	0.19
Electrolyte flow rate [mL min ⁻¹ cm ⁻²]	0.57	0.37	0.02	3.30	0.12
Product	Formate	Formate	Formic acid	Formic acid	Formic acid
References	Del Castillo et al. ^[15]	Kopljär et al. ^[20]	Yang et al. ^[17]	Proietto et al. ^[18]	Ramdin et al. ^[30]

[a] All these electrolyses were performed in aqueous electrolyte at ambient temperature. [b] A: Anolyte; C: Catholyte. [c] AEM: Anion exchange membrane; CEM: Cation exchange membrane. [d] Value based on the utilisation of 0.5 M Na₂SO₄.

is relatively low in aqueous electrolyte (~33 mM) which results in low limiting current density values, j_{lim} (i.e., the current densities achieved under the kinetic control of the mass transport of CO₂ to the cathode surface). j_{lim} of CO₂ on plate electrodes is ~30 mA cm⁻².^[22,51,52] At $j > j_{lim}$, the mass transfer of CO₂ to the electrode surface becomes the rate-determining step and H₂ generation becomes the predominant cathodic process, negatively affecting the FE.

The utilisation of GDE technologies allows to overcome the mass transport limitation. GDEs take advantage of the three-phase boundary area among solid catalyst, liquid electrolyte and gaseous CO₂ reagent, where the reaction takes place, significantly enhancing the productivity. Del Castillo et al.^[15] showed that it is possible to convert CO₂ into formate using Sn–GDEs at ambient temperature and pressure in a continuous and single pass divided filter-press cell with a high j ($j = 150$ mA cm⁻², production rate: 0.9 kg h⁻¹ m⁻²) and FE (close to 70%) and an actual formate concentration of 0.25%wt. (CS I, Table 2). In the same line, Kopljär et al.^[20] showed that higher j (close to 200 mA cm⁻²) coupled with FE of 83% can be achieved in a similarly divided flow-cell using SnO_x–GDEs (CS II). This work reports the highest formate production rate (1.39 kg h⁻¹ m⁻²) and the lowest cell potentials, ΔV , (Table 2). Despite these promising results, it is necessary to highlight that a high stability of any tin-oxide phase electrode under cathodic

conditions has to be still addressed.^[53,54] Furthermore, a quite low formate concentration was obtained (0.69%wt.). Yang et al.^[17] proposed for the first time the utilisation of a three-compartment cell design, which consists of an anode compartment, a middle flow chamber containing a cation ion exchange resin media (Amberlite) and a cathode compartment where the ERCO₂ to formate ions occurs using a Sn–GDE. A cation exchange membrane and a new imidazolium-based anion exchange membrane, called “Sustanion®”, are placed adjoining to the anode and cathode compartments, respectively. This cell operated at 140 mA cm⁻² with FE of ~87% for more than 140 h (CS III). In addition, the highest final [FA] (up to 9.4 wt.%) reported in literature according to the available data was obtained. However, the overall system is still under development stages.

CS IV and CS V refer both to the utilisation of pressurized CO₂ and cheap Sn plate cathodes. An increase of the CO₂ pressure, P_{CO_2} , gives rise to a higher concentration of CO₂ in the aqueous solution, enhancing the kinetics. Indeed, it was shown that the utilisation of pressurized CO₂ significantly improved the process performances.^[13,18,19,22,30,55] In particular, Proietto et al.^[18] carried out ERCO₂ using a cheap Sn plate cathode in an undivided filter press cell with a continuous recirculation of the electrolyte; the total volume was ca. 20-fold greater than that of typical cells used in laboratory-scale studies (~1L), showing that

it is possible to scale up the pressurized process by maintaining good results. These authors achieved a quite high [FA] (~1.26% wt.) coupled with a FE of 82% using relatively high P_{CO_2} (~23 bar) and j (~50 mA cm⁻²) (CS IV). Furthermore, it was demonstrated that operating pressures up to 20 bar could be economically viable.^[42] Also, Ramdin et al.^[30] have performed the ER_{CO}₂ using a Sn plate cathode and HP system; however, they used a divided semi-continuous batch cell equipped with bipolar membranes (BPMs) driving the reaction at 30 mA cm⁻² with a FE of approximately 80% (CS V). The remarkably discover of these researchers was a cheaper BMP that can maintain a different compartment pH between anodic and cathodic compartment at high P_{CO_2} . This limits the crossover of the liquid product, which is crucial for the economics of a large-scale CO₂ electrolysis process.

Among these CSs, the works of Yang,^[17] Proietto^[18] and Ramdin^[30] et al. directly produced FA (CS III–V). In the other CSs, the main product on the cathode side was formate.

2.2. Economic Evaluation of the Five Case Studies

Figure 2A compares the costs (capital and energetic ones and their sum C_E , computed in terms of €/kg_{FA}) due to the electrolysis stage for the five CSs presented in section 2.1. The three CSs characterized by the use of GDE (CSs I–III) present lower C_E . In particular, CS II, which uses SnO_x-GDEs, presents both the lowest capital and energetic costs as described below in detail.

1) *Capital costs, C_{E-I} , for the electrolysis stage.* CSs I–III present higher C_{E-I} for the unit of electrode surface (Figure 2B), due to the use of expensive GDEs, with respect to CSs IV–V, which use pressurised CO₂ and cheap Sn cathodes. In particular, the highest C_{E-I} are related to CS III, that couples the utilisation of GDE and two membranes due to the adoption of a 3-compartment cell, and the lowest ones to CS IV, that uses an undivided cell and relatively low pressures (close to 20 bars). However, for the CSs performed with GDE, it was possible to achieve high FEs working at high j (Table 2), thus allowing quite high productivity of the electrochemical cell. Indeed, CSs I, II and III present a productivity of 0.9, 1.39 and 1.12 kg h⁻¹ m⁻², respectively, while CSs IV and V 0.34 and 0.19 kg h⁻¹ m⁻², respectively (Table 2). Hence, overall, CSs II–III presented the lowest C_{E-I} for kg of FA produced and CS V the highest (Figure 2B).

2) *Energetic costs, C_{E-O} .* As shown in Figure 2A, CS II presents the lowest C_{E-O} for the electrolysis stage, because of the low overpotentials presented by SnO_x-GDEs.

Figure 2C reports an estimation of the overall costs for the electrochemical conversion of CO₂ to FA at 85%wt., C_{EP} , for each CSs, including capture, recycling, electrolysis, concentration and purification costs. CS I presents the highest C_{EP} , followed by CS V, CS II, CS IV and CS III.

To show their market competitiveness, C_{EP} was compared with the sum of the costs for producing FA by the conventional chemical route, C_{CP} , (0.475 €/kg_{FA})^[56] and the CT value, that would be saved converting CO₂ into FA, $C_{CP} + CT$, and the FA

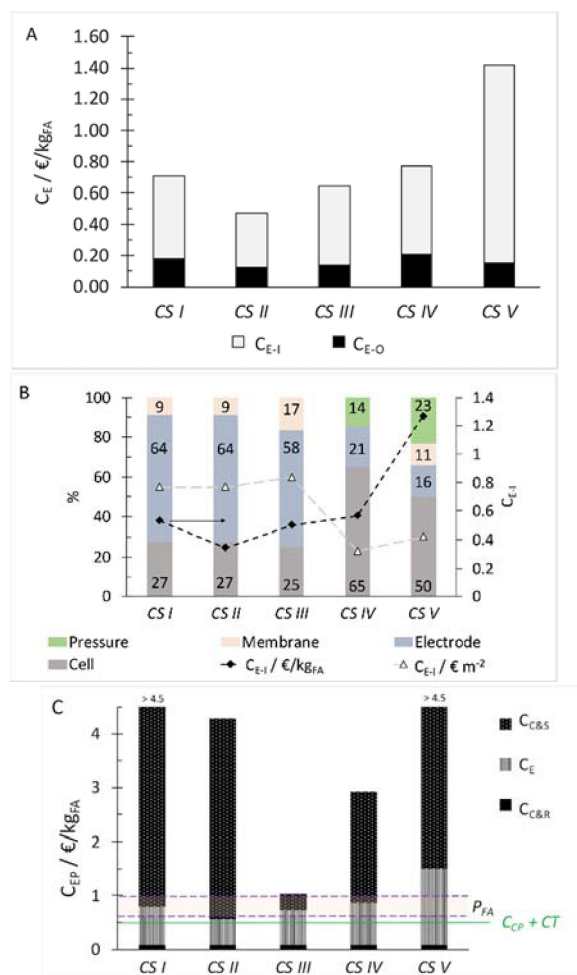


Figure 2. A) Comparison of electrolysis costs, $C_E = C_{E-I} + C_{E-O}$, for each CS. B) Comparison of C_{E-I} for kg of FA produced, €/kg_{FA} (◆) and for the unit of electrode surface, €/m², (-△-). Percentage shares of the main components on the C_{E-I} : Cell; Electrode, Membrane, Pressure. C) Comparison of the C_{EP} for each CS based on the figures of merit reported in Table 2 with the FA market price, $P_{FA} = 0.6 \pm 1$ €/kg_{FA}, and the sum of conventional production process cost and the Carbon tax, $C_{CP} + CT = 0.500$ €/kg_{FA}. Estimation costs were evaluated considering a plant lifetime of 20 years, 8000 h/years of operation and a plant with characteristics similar to that of the chlor-alkali process: 2 stacks of electrolyzers, both equipped with 75-single cells, with an electrode area, A, of 2.8 m² for each cell. Electricity price (P_E), of 0,03 €/kWh. In a first approximation approach, labours, overheads, maintenance, depreciation, inflation, interest rates and taxes were not considered.

market price (P_{FA}), (0.6–1 €/kg_{FA})^[57] (Figure 2C). CT depends on the country as shown in Table 1 and it was assumed here to be 0.025 €/kg_{FA}.

It is worth to mention that C_{EP} resulted higher than both the $C_{CP} + CT$ and P_{FA} range values for all the five CSs under investigation (Figure 2C), thus showing that, to date, the electrochemical route is not more cost-effective than the commercial chemical one. The C&S stage presents the highest costs (Figure 2C) and the C&R stage the lowest. Indeed, $C_{C\&S}$ constitutes more than 70% of C_{EP} for CSs I, II, IV and V due to the low final concentrations of FA obtained in the electrolysis stage (<10%wt., see Table 2). Conversely, for CS III, where a final concentration of FA close to 10%wt. was obtained, $C_{C\&S}$ are

about 28% of the total C_{EP} , which is close to P_{FA} . Previously, other studies showed the considerable influence of the C&S stages on the overall economy of the process.^[23,30] In particular, Ramdin et al.^[30] highlighted that, for a [FA] lower than 10 wt.%, the C&S stages based on distillation units create excessive costs since the process requires an excessive amount of energy for water removal. Hence, according to these findings, future research should aim to rise up the final [FA] from the electrolyser unit. In parallel, to reduce the $C_{C&S}$, new cost-effective strategies and low-energy downstream processes to purify and concentrate FA solution for commercial application should be implemented. Since the separation of small carboxylic acid from aqueous solutions is rather expensive,^[30] the discovery of lower energy demand technologies or the integration of new stages with the conventional process would be very useful to improve the economic viability of the process on a large scale. Several authors reported the possibility to concentrate a FA solution by electrodialysis process.^[58–60] These technologies could run on renewable excess electric energy during off-peak hours when the electricity is available at lower price. This strategy would be suitable to feed the electrolysis unit as well (as envisioned in section 2.4). Kaczur et al.^[61] proposed to incorporate pervaporation into FA azeotropic distillation system maximizing steam utilization and lowering the overall energy cost for FA purification. Hence, future work should also focus on the implementation of new technologies/systems to purify FA at low energy consumption. In the following sections, our cost estimations were based on the purification of FA from water by conventional processes since they are the current practicable technologies at the industrial scale.

Overall, CS III and IV presented the lowest C_{EP} since these processes presented the highest final [FA] (see Table 2). Also, it is relevant to mention that CS III is likely to be characterised by the lowest cost of the electrolyte/media with respect to the other CSs. Indeed, this technology is characterized by a three-compartment cell design in which pure water flows in the middle compartment through an ion exchange resin without the addition of a supporting electrolyte, avoiding the related costs. Conversely, CS II, which presented the lowest electrolysis costs, is among the most expensive due to the quite low final [FA]. Overall, as shown in Figure 2C, in all the investigated cases, ERCO₂ presents too high costs.

To improve the potentials of ERCO₂ technologies on a large scale, several efforts have to be implemented to reduce C_{EP} . Previously, also Spurgeon et al.^[25] found that the production of FA is not economically viable. These authors estimated a FA production cost 1.8 times higher than the commercial price (i.e. 1.16 $\$/kg_{FA}$ with respect to the commercial price of 0.65 $\$/kg_{FA}$). In the next sections, the technological improvements necessary to achieve a process sustainable from an economic point of view will be identified and discussed in detail.

2.3. Optimisation of Each Case Study

Following the economic estimations provided in section 2.2, each CS will be investigated in detail in the following. To depict

future steps of research, several scenarios will be envisioned aiming to reduce the C_{EP} . The sum of C_{CP} and CT is used here as a target cost for the FA production by ERCO₂ ($C_{CP} + CT = 0.500 \text{ €/kg}_{FA}$), which reflects the cost for producing FA via conventional chemical route and the CT saved from companies for the avoided emissions of CO₂. Hence, the data considered in the previous paragraph (Scenario 1, S1) will be compared with various scenarios (Sx) characterized by some potential target technological improvements. In particular, in the next sections, target [FA], GDE lifetime and its cost, membrane lifetime and its cost, j , FE and ΔV were supposed and used as figures of merit to identify the target performances for the individual economic viability of each technology at industrial scale.

2.3.1. Optimisation of GDE-Based Technologies (CS I and III)

For GDE technologies, the analysis was focused on the potential optimisation of CS I and CS III, but similar considerations can be done for CS II. According to the estimations presented in section 2.2, CS I presents the highest C_{EP} . In this case, the main factor that significantly limits the economic viability of the process is the low [FA] value. Indeed, an actual [FA] of 0.25 wt. was achieved, which results in very high $C_{C&S}$ (S1, Figure 3). In this frame, it is useful to recall that, in the industrial synthesis of FA, the concentration step is often performed by distillation of a water solution containing 20 to 50 wt. of FA.^[62] Hence, to achieve costs comparable to that of conventional processes, it would be mandatory to achieve in the electrolysis stage a quite high [FA] maintaining high values of j , FE and low ΔV by, as an example, increasing the A/V (area/volume, m^2/m^3) ratio of the system and recirculating the solution to accumulate FA in the solution. In Figure 3, S2 and S3 show the value of C_{EP} that could be obtained if the electrochemical step could reach a final [FA] value of 10 and 30 wt., respectively, by working at the same figures of merit, j , FE and ΔV , reported in Table 2. Under these hypotheses, the $C_{C&S}$ would be significantly reduced resulting in C_{EP} close to 1.1 and 0.9 $\$/kg_{FA}$ for S2 and S3, respectively, but still higher than $C_{CP} + CT$. Hence, further improvements would

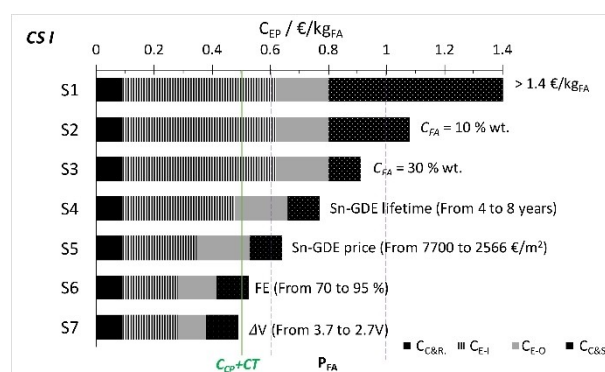


Figure 3. Optimisation of CS I. Estimation costs of S1 were based on the figures of merit reported in Table 2 and shown in Figure 2. $C_{CP} + CT = 0.5 \text{ €/kg}_{FA}$. $P_{FA} = 0.6\text{--}1 \text{ €/kg}_{FA}$. S1–7: Scenario 1–7. S4 includes $C_{FA} = 30 \text{ wt.}$; S5 includes $C_{FA} = 30 \text{ wt.}$ and Sn–GDE lifetime of 8 years; S6 and S7 include all the assumptions of S5 and S6, respectively.

be required to make this process competitive. In particular, since the C_{E-I} of the process is strongly affected by that of the GDEs, *S4* shows the potential impact on C_{EP} of a longer lifetime (from 4 to 8 years, as for conventional cathodes) while *S5* shows the effect of both a longer lifetime and of a reduction of the manufacturing cost (Figure 3) (in both cases a [FA] value of 30%wt. was considered). To reduce the C_{E-O} of the electrolysis, it would be necessary to increase the FE and/or to reduce the ΔV of the process. Indeed, an increase of the FE up to 95% and a reduction of the ΔV to 2.7 V would result in a reduction of C_{E-O} of 27%. Under all these hypotheses ($C_{FA} = 30\%$ wt., Sn-GDE with lifetime 8 years and cost of 2566 €/m², FE = 95%, $\Delta V = 2.7$ V), the C_{EP} would drop to approximately 0.488 €/kg_{FA}, which is less than $C_{CP} + CT$ as shown in Figure 3 by scenario *S7*.

Following the analysis provided in section 2.2, the electrochemical technology implemented by Yang et al. was the most economically competitive technology with respect to the other CS' ones (Figure 2). This is due to the high [FA] values close to 10%wt. reported by this study.

However, also in this case to have a process competitive with traditional ones, some improvements of the technology should be achieved, such as a further increase of the final [FA] (*S2*, Figure 4) and an enhancement of the lifetime and a reduction of the cost of GDE (*S3–S4*, Figure 4). Under these hypotheses, C_{EP} would be reduced to about 0.6 €/kg_{FA} (from *S1* to *S4*, Figure 4). Also, by working on the FE and ΔV , a further minimisation of the C_{EP} of 20% may be achieved (from *S4* to *S6*, Figure 4). In particular, according to our assumptions, it was seen that the cost of the membrane and its lifetime does not strongly impact the overall economy of the process (data not reported) due to the lowest weight percentage of the membrane on the overall C_{E-I} (Figure 2B). In this context, it is relevant to mention that membranes used in the chlor-alkali process, here considered as an electrochemical industrial model process, are characterized by a high chemical and mechanical stability in different media electrolytes and a longer operative lifetime.

In conclusion, these results allow us to identify different target performance metrics that must be reached to improve

the potential implementation of the GDE technologies on a large scale. In particular, for these technologies both an increase of the final [FA] from the electrolysis stage to 30%wt. and a strong improvement of GDE, in term of stability and manufacture cost, should be achieved. Additionally, an improvement of the FE to 95% and ΔV less than 3 V allows to slight positively affect the overall economy of the process.

On overall, increasing the A/V ratio of the system and recirculating the solution to accumulate FA could be a possible strategy to reach the target [FA] of 30%wt. from the electrolysis stage. Furthermore, researchers must focus on a strong optimisation of Sn-GDEs, that currently at laboratory scale can suffer from *i)* loss of catalyst, *ii)* low stability with time, *iii)* time-consuming manufacturing procedure and *vi)* salt deposition on the gas diffusion layer (GDL) determining a blockage of CO₂ access in the GDE.^[63,64] In addition, from a purely technological viewpoint, GDEs should meet strictly several requirements for successful operations on a large scale, including: *i)* high chemical and mechanical stability in electrolyser with large areas; *ii)* high electrical conductivity and low thickness; *iii)* appropriate hydrophobic/hydrophilic pore structure to favour the access of gases and liquids avoiding, on one hand, the passage of the gaseous CO₂ through the GDL and, on the other hand, the flooding of the gas side by liquid electrolyte. All these conditions should be available at affordable costs. In addition, considering the chlor-alkali process as an electrochemical industrial model process, industrial electrodes for ERCO₂ should be placed in a vertical position and be higher than 1 meter. This outcome in hydraulic pressure differences between the top and the bottom which can limit the active height to only 1/4 of the total.^[65] To overcome this issue on a large-scale application, it should be considered for the ERCO₂ process the usage of a "falling film electrolyses cell" used in the OCD technologies or to investigate the possibility to place the cell horizontally. The first strategy could allow to operate with a very small gap between electrodes and membrane (< 1 mm), thus assuring a high A/V ratio, which, as above mentioned, could be a viable way to increase the [FA].

2.3.2. Optimisation of HP-Based Technologies (CSs IV and V)

The technology of CS *IV* was based on the utilisation of an undivided and pressurised filter-press cell, with a continuous recirculation of the electrolyte, equipped with a cheap and stable Sn cathode. The key parameter to optimise the electrochemical synthesis of FA was the utilisation of pressurised CO₂ which allows to reach relatively high [FA] values while maintaining a stable FE. Figure 5 shows the estimated costs for the optimised scenarios. Overall, for this CS, the minimum gross profit of 0.100 €/kg_{FA} for FA production by ERCO₂ process may be obtained by increasing the [FA] value (up to 30%wt.), the CO₂ reduction rate (up to 120 mA cm⁻²) as well as the FE (to 100%) and reducing the ΔV of the electrolysis unit (from *S1* to *S6*, Figure 5). Under these assumptions, the C_{EP} would be reduced by 83% with respect to the original scenario (i.e., 2.9 and 0.5 €/kg_{FA} for *S1* and *S6*). It is worth to mention that the

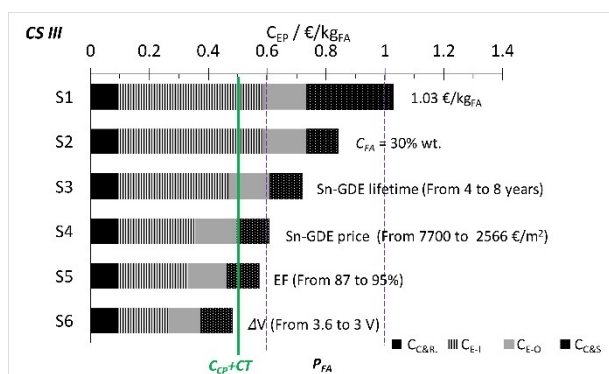


Figure 4. Optimisation of CS *III*. Estimation costs of *S1* were based on the figures of merit reported in Table 2 and shown in Figure 2. $C_{CP} + CT = 0.5$ €/kg_{FA}. $P_{FA} = 0.6–1$ €/kg_{FA}. *S1–6*: Scenario 1–6. *S3* includes $C_{FA} = 30\%$ wt.; *S4* includes $C_{FA} = 30\%$ wt. and Sn-GDE lifetime of 8 years; *S5* and *S6* include all the assumptions of *S4* and *S5*, respectively.

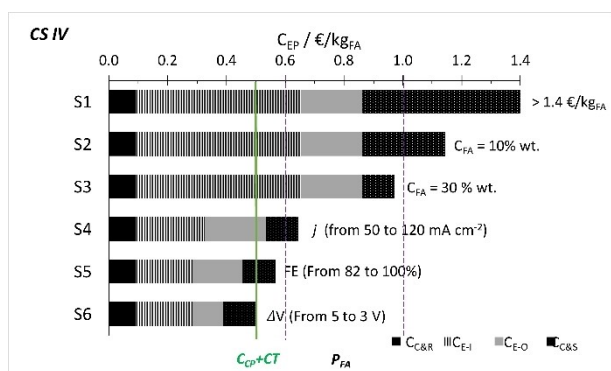


Figure 5. Optimisation of CS IV. Estimation costs of S1 were based on the figures of merit reported in Table 2 and shown in Figure 2. $C_{CP+CT} = 0.5 \text{ € / kg}_{FA}$. $P_{FA} = 0.6\text{--}1 \text{ € / kg}_{FA}$. S1–6: Scenario 1–6. S4 includes $C_{FA} = 30\% \text{ wt.}$; S5 and S6 include all the assumptions of S4 and S6, respectively.

increase of the j to about 120 mA cm^{-2} seems not to be particularly difficult since some results in literature were obtained at 90 mA cm^{-2} .^[13] However, the use of an undivided cell makes quite difficult to achieve a high actual [FA] with a high FE, since FA generated at the cathode side could be oxidized at the anode and the higher is the [FA], the higher is the FA oxidation rate. Hence, to reach the target outcomes of 30%wt. of FA, further investigations could be focused on the implementation and development of new anodes which limits selectively the FA degradation and on the development of a new cell design to increase the ratio A/V . From the electrochemical viewpoint, pressurised conditions increase the CO_2 concentration and allow to convert the CO_2 at less negative potential.

This CS reported a ΔV of 5 V, resulting in considerable energy consumption (EC). In our analysis, the reduction of ΔV to 3 V results in a lower EC and, consequently, reduces the C_{E-O} by 40% (S5–S6, Figure 5). ΔV are associated with overpotentials for *i*) the kinetic activation of redox reactions, *ii*) the presence of ohmic resistances and *iii*) the mass transport to the cathode and anode surfaces. At the applicative scale, the minimisation of the gap between anode and cathode and the use of low-overpotentials electrodes would lead to reduced power consumption. In addition, the choice of a proper supporting electrolyte with a high concentration could reduce the ohmic resistance and, consequently, the EC.

However, this process may undergo the potential formation of an explosive mixture of H_2 and O_2 . Hence, to improve the scalability on a large scale of this technology, further studies will be necessary including *i*) the use of sacrificial anodes to avoid O_2 generation; *ii*) the application of higher-selective FA 3D-cathodes to suppress the H_2 production and increase the FA productivity at high pressure; and *iii*) the development of innovative reactor configurations to inhibit the mixing of H_2 with O_2 and to enhance the CO_2 conversion rate.

The electrochemical technology proposed in CS V was a divided and pressurised semi-continuous batch cell equipped with a stable Sn plate cathode. This cell used a bipolar membrane, which can maintain a different pH between the

anodic and cathodic compartments at high P_{CO_2} up to 50 bar. The driving forces for the implementation of this HP technology on large scale are subjected to all the considerations reported for CS IV, including the need to achieve higher [FA] values, production rate and FE and lower overpotentials (from S1 to S6, Figure 6). Sn plate cathodes are cheap and stable; however, their utilisation resulted in a low j , which are not economically and technologically suitable for the applicative scale, and, consequently, in very high C_{E-I} (i.e., $\sim 1.26 \text{ € / kg}_{FA}$). A considerable reduction of the C_{E-I} of approximately 80% would be observed increasing the j up to 140 mA cm^{-2} (S3–S4, Figure 6).

In this case, it should be considered that, in spite of some disadvantages given by the utilisation of the membrane (i.e. higher cell potentials and costs, pH imbalance, etc.),^[19] its implementation on HP technology on a large scale would *i*) significantly enhance the [FA] values in the cathodic compartment, limiting its anodic oxidation, *ii*) prevent the formation of the explosive mixture H_2 and O_2 and *iii*) optimistically open the pathway to the possibility of coupling CO_2 reduction at high P_{CO_2} with a suitable anodic process, such as the treatment of wastewater and synthesis of chlorine,^[66–68] which was demonstrated to increase the overall economics of the process.

Technologically, a specific challenge for implementing this electrolyser on large scale will include maintaining a pressure balance close to the membrane, placed between the anodic and cathodic compartment, in electrolyser with large areas, avoiding its damage.

In summary, for the HP technologies, high [FA] to 30% from the electrolysis stages and high $j \geq 120 \text{ mA cm}^{-2}$ coupled with $\Delta V < 3 \text{ V}$ as well FE up to 100% were here identified as the target performances for the economic viability of these technologies at industrial scale.

2.4. Effect of Electricity Price due to the Excess Electric Energy Generated by Renewable Sources

According to the literature, one of the main advantages of ER CO_2 processes is the possibility to use and store the excess electric energy from intermittent renewable sources. In the last

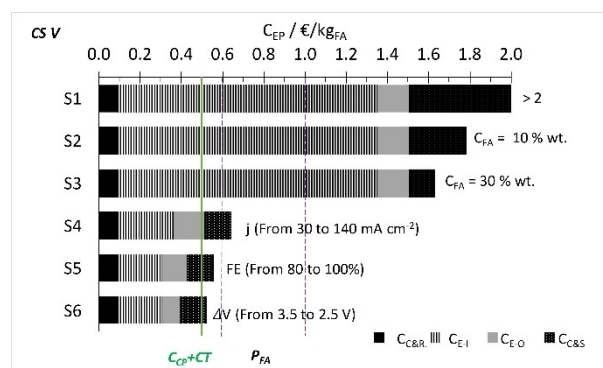


Figure 6. Optimisation of CS V. Estimation costs of S1 were based on the figures of merit reported in Table 2 and shown in Figure 2. $C_{CP+CT} = 0.5 \text{ € / kg}_{FA}$. $P_{FA} = 0.6\text{--}1 \text{ € / kg}_{FA}$. S1–6: Scenario 1–6. S4 includes $C_{FA} = 30\% \text{ wt.}$; S5 and S6 include all the assumptions of S4 and S6, respectively.

years, the imperative of moving towards low-carbon power generation had a significant impact on the electricity price, P_E . The rising share of renewable power sources made the P_E volatile. Negative P_E is becoming a common phenomenon, which occurs when a high and inflexible power generation appears simultaneously with low electricity demand. It became more profitable for the electricity producers paid customers to use their produced energy than turning off plants because it was less costly. Negative P_E could be a positive thing that offers companies new business opportunities by adapting to demand.

In this framework, we envisioned a scenario in which the electrochemical facility could operate when there is an oversupply of electricity and its price decreases. Following these considerations, a further investigation was performed by assuming that the ERCO₂ process was in production mode only for the hours in which the P_E was lower than the annual average P_E of 0.03 €/kWh and that electrolyser components were not suggested to degradation (i.e., their lifetime depends only on the operation time). Figure 7A displays the average P_E in three different cases: *i*) 100% h/y, which means that the ERCO₂ process runs for 8000 h/y; *ii*) 38% h/y and *iii*) for the 23% h/y, estimated according to the data reported in Ref. [69].

Among the other CSs, CS III (S1) was chosen for this investigation because it is likely to be up to now among the most competitive ones (Figure 2C). As shown in Figure 7B, the use of excess electric energy available at low-price could strongly reduce the energetic cost of the electrolyser unit. A reduction of the C_{E-O} of 38% for the 38% h/y of operation time and 62% for the 23% h/y of operation time would be observed. The C_E would be decreased in both cases by approximately 10% with respect to the original scenario (S1, CS III). In this frame, it should be considered that an electrochemical process could fit with these scenarios due to its versatility to respond to the supply of electricity.

Alternatively, the production of FA directly using energy renewable sources, such as salinity gradient power, was investigated on a laboratory-scale by several authors,^[68,70] aiming to improve the economic data of the process. A further investigation on this topic may be quite important for developing this process on a large scale.

3. Conclusions

In this work, a technical-economic analysis of ERCO₂ to FA/formate in aqueous electrolyte using Sn-based cathodes was performed considering the most promising routes reported in the literature. Five CSs based on the utilisation of GDE- (CS I–III) and HP- (CS IV–V) technologies were analysed. A simplified supply chain was envisioned including the stage of *i*) CO₂ C&R, *ii*) ERCO₂, and *iii*) FA C&S.

Under the hypotheses of this study, it was found that the FA electrochemical production process based on both GDE- and HP- technologies is not able yet to compete with the conventional FA production process. Economic viability is significantly limited by the low [FA] obtained in the electrolysis stage, due to the expensive costs for the C&S for FA diluted solution. CS I presented the highest C_{EP} , CS III and IV the lowest C_{EP} , since these processes presented the highest final [FA], even if not competitive with the conventional process.

It was shown that the successful implementation of different technological improvements would make the ERCO₂ process economically suitable. Indeed, to be suitable for the commercialization, the ERCO₂ to FA using Sn-based electrodes should reach simultaneously high j , FE, [FA], low EC as well as long term stability. To reach these outcomes, several technological improvements must be implemented, as summarised below.

- For both GDE- and HP- based technologies, it would be mandatory to achieve in the electrolysis a quite high [FA] of 30%wt. maintaining high values of $j \geq 120 \text{ mA cm}^{-2}$, $FE \geq 95\%$, and low $\Delta V \sim 2.5\text{--}3 \text{ V}$, by for example focusing on the optimisation of the cell design, operation mode and, in the case of the undivided cell, electrocatalyst engineering of new anodes which limits selectively the FA degradation. Moreover, at an applicative scale, the minimisation of the inter-electrodes gap, the use of low-overpotentials electrodes and proper supporting electrolyte would lead to reduced power consumption.

- For GDE-based technologies, several efforts must focus on the GDE optimisation decreasing its cost and enhancing the long-term stability.

- For HP-based technologies, the main technological challenge is to strongly improve the productivity of the process. This could be achieved by developing higher-selective FA

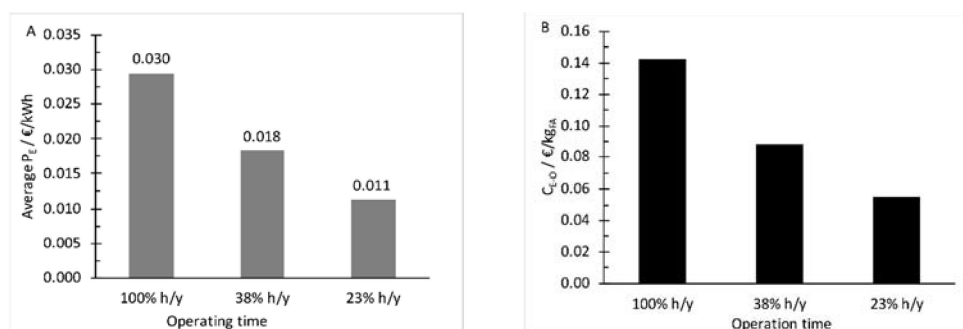


Figure 7. A) Average electricity price, P_E , for different operating time (% h/y) (Average values from 01/01/2020 to 31/12/2020 Germany).^[69] B) Effect of P_E on the C_{E-O} for different operation time (% h/y).

cathodes with a high active surface, which could allow to suppress the H₂ evolution and increase the CO₂ reduction rate.

Furthermore, it was shown that the potential use of excess electric energy generated by renewables sources to feed the electrolyser could significantly reduce the cost of energy.

Methodology Section

Analysis of the main costs

The technical-economic analysis reported in this work includes the main costs related to C&R, CO₂ER and C&S stages and $C_{EP} = C_{C\&R} + C_E + C_{C\&S}$, where C_{EP} is the total cost for the conversion of CO₂ into FA at 85%wt.; $C_{C\&R}$ are the costs due to the carbon capture and recycling; C_E are the total costs of the electrolysis, including the capital investment (C_{E-I}) and energetic costs (C_{E-O}) and $C_{C\&S}$ are the costs related to the C&S of the FA solution up to 85%wt. Table 3–4 report the main figures used for the estimation of the costs as described in detail in the following paragraphs.

CO₂ capture and recycling

The economy of the C&R process is considerably affected by the adopted technology, CO₂ concentration and its sources. CO₂ can be captured from a point source (power plant or chemical industry) or from the atmosphere (direct air capture – DAC). However, DAC technologies are still under development stages and they are characterized by a high cost which was estimated to be between 100 and 1000 \$/t_{CO₂}.^[71–74] Hence, we have considered the option to capture CO₂ from point sources that present significantly lower costs (i.e., i) 36–53 \$/t_{CO₂} for supercritical pulverized coal power plants; ii) 48–104 \$/t_{CO₂} for natural gas combined cycle power plants; iii) 28–41 \$/t_{CO₂} for pre-combustion capture at coal-based integrated gasification combined cycle (IGCC) power).^[75] One of the main disadvantages of this technology is the purity of the stream obtained from combustion due to the presence of other combustion products, such as SO_x or NO_x, that could affect the performances of the electrolysis. However, in the literature, this aspect was not investigated in detail yet. Hence, in a first approximation approach, we assumed to feed pure CO₂ at CO₂ capture cost of 40 \$/t_{CO₂} (34 €/t_{CO₂}, 1 € = 1.18\$) according to Refs. [75], [76]. According to the literature, the CO₂ conversion per pass for the current electrochemical technologies is drastically lower than 100%. Hence, unreacted CO₂ needs to be recirculated; the lower is the CO₂ conversion, the higher are the separation costs of by-products in the CO₂ recycled stream. Table 3 reports the main parameters and costs for the C&R stage.

Electrolysis stage

To date, the current electrochemical technologies for CO₂ conversion are not ready for the commercialization since they are still under development at laboratory scale (Technology Readiness Level, TRL = 3–5) and there are no long-term stability investigations. Hence, the estimation of the cost of electrolyser unit involves some degree of uncertainty. Capital investments, C_{E-I} , were estimated considering a plant lifetime of 20 years, 8000 h/years of operation and a plant with characteristics similar to that of the chlor-alkali process (2 stacks of electrolysers, both equipped with 75-single cells, with a working area of 2.8 m² for each cell)^[65] as reported in Table 4.

Table 3. CO₂ capture and recycling costs, $C_{C\&R}$.

Case	#
CO ₂ capture cost (€/kg _{CO₂})	0.034 ^[a]
CO ₂ required (kg _{CO₂} /kg _{FA})	1.910 ^[b]
CO ₂ recycling cost (€/kg _{CO₂})	0.027 ^[c]
CO ₂ recycling (kg _{CO₂} /kg _{FA})	0.960 ^[b]
CO ₂ capture cost (€/kg _{FA})	0.065
CO ₂ recycling cost (€/kg _{FA})	0.026
$C_{C\&R}$ (€/kg _{FA})	0.091

[a] Exchange value 1 € = 1.18 \$ on October 20th, 2020. [b] These values were computed considering that 1 mol of FA requires 1 mol of CO₂, for a conversion of 50%, the amount of CO₂ required is twice the stoichiometric amount, hence $m_{CO_2}/m_{FA} = 2 MW_{CO_2}/MW_{FA}$ and the 50% of this needs to be recycled. $MW_{CO_2} = 0.044$ kg/mol. $MW_{FA} = 0.046$ kg/mol. [c] CO₂ recycling cost were evaluated as the 80% of the CO₂ capture cost according to Ref. [30].

For practical application, one of the main bottlenecks in the development of the CO₂ electrochemical conversion is the long-term stability which makes the scaling up of the process highly challenging. Indeed, to date, the long-term stability was scarcely investigated in the literature; a few examples of electrolysers carried out for more than 10 h were reported. For C_{E-I} estimations, the utilisation of a replacement factor, RF, based on the actual hour reported for the different CSs (Table 2) is not realistic from an industrial point of view, because it would lead to senseless results. Hence, it was assumed that the replacement factors were similar to that of commercialized chlor-alkali technologies, as reported in detail in Table 4.

Operative costs are dominated by energetic ones. Hence, other operative costs were neglected. In particular, in a first approximation approach, the cost of water and supporting electrolyte was neglected because, according to several authors, they could be recycled to the electrolyser unit.^[30,77] Energetic costs, C_{E-O} , were estimated considering the energy consumption, EC, of the

Table 4. Main cost parameters of electrolysis unit.^[a]

Case	Price [€/m ²]	RF
Sn–GDE	7700 ^[b]	5.3 ^[c]
Sn Plate	2700 ^[d]	2.4 ^[e]
Membrane	1100 ^[f] –847 ^[g]	5.3 ^[h]
Pressure factor	22% of P_{EC} ^[i] at 23 bar 47% of P_{EC} ^[i] at 50 bar	

[a] Equipment prices were assumed to be linear scaling with A , resulting in an overestimation of the overall C_{E-I} . Exchange value 1 € = 1.18 \$ on October 20th, 2020. [b] According to Ref. [23]. [c, e] RF was evaluated as the ratio Plant lifetime/electrode lifetime. [c] Sn–GDEs operation time was assumed of 30000 hours based on the oxygen depolarized cathode lifetime used in the chlor-alkali process (of approximately 4 years).^[78] [e] Sn plate operation time was assumed of 65000 hours based on the conventional cathode service life of chloro-alkali process (of approximately 8 years).^[65] [d] According to the market value of a Sn foil (thickness 0.5 mm, 99.998% trace metals basis supplied by Sigma-Aldrich). [f] This price refers to the fluorinated membrane price according to Ref. [66]. [g] This price refers to the BPM price according to Ref. [30]. [h] RF was evaluated as the ratio plant lifetime/membrane lifetime; the membrane lifetime was assumed of 30000 hours which reflects the operative membrane lifetime used in chlor-alkali process.^[65] [i] P_{EC} is the price of the main equipment of an undivided electrochemical cell according to the relationship reported by Cañizares et al.^[79] Pressure factor for process equipment was estimated according to Ref. [80] P_{CO_2} up to 20 bars does not affect the cell manufacturing cost and piping cost, but only auxiliary equipment price (i.e., pumps). This because commercial filter press cell and tube thickness are usually made to resist pressures of up to 20 bar.

electrolysis unit, i.e. the power consumption for a given capacity (kWh/kg_{FA}) [Eq. (1)]:

$$EC = \Delta V n F / t MW_{FA} FE \quad (1)$$

where ΔV is the cell potential, n is the number of electrons ($n=2$ for FA), F is the Faraday constant (96485 C/mol), t is the time (s), MW_{FA} molecular weight of FA (kg/mol) and FE the faradic efficiency of the product. The electricity price strongly depends on the country. In this work, the annual average electricity price, P_E , in Germany in 2020 of 0.03 €/kWh was considered.^[69]

Downstream stage

The C&S stage of the FA solution from the electrolyser unit has a relevant impact on the economy of the overall process. Commercial FA is available at a concentration higher than 85 % wt. in water and an aqueous solution of FA forms an azeotropic mixture at 77.6 % wt.. The concentration steps of the main industrial companies, such as BASF, involve an azeotropic distillation step followed by a vacuum one. According to the literature, purification costs of FA from 30 to 85%wt. were estimated to be 97 €/t_{FA} for the BASF process and 122 €/t_{FA} for the Kemira-Leonard process. For our analysis 110 €/t_{FA} was assumed as the average value cost for the concentration of FA from 30 to 85%wt. The costs related to the concentration of more dilute solutions were computed according to data reported by Ramdin et al.^[30] and assuming that $C_{C&S}$ depends on the energy required for removal of water.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: reduction · CO₂ · formic acid · tin · technical-economic analysis

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