

1 **Environmental and economic assessment of the formic acid electrochemical manufacture**
2 **using carbon dioxide: influence of the electrode lifetime**

3 M. Rumayor, A. Dominguez-Ramos, A. Irabien*

4 University of Cantabria, Department of Chemical and Biomolecular Engineering, Av. Los
5 Castros s/n, Santander, Spain

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8 * **Corresponding author:** Angel Irabien

9 University of Cantabria, Department of Chemical and Biomolecular Engineering

10 Av. Los Castros s/n, 39005 Santander, Spain;

11 E-mail: angel.irabien@unican.es;

12 Tlf: (+34) 942 20 67 49

13

14 **Abstract**

15 This paper focuses on the study of the environmental and economic feasibility of the formic acid
16 (FA) synthesis by means of electrochemical reduction (ER) of carbon dioxide (CO₂) with special
17 emphasis on the cathode lifetime. The study has used a Life Cycle Assessment (LCA) approach
18 in order to obtain the environmental indicators as Global Warming Potential (GWP) and Abiotic
19 Depletion (ADP) (both elements and fossil resources ADPs). The values of the indicators obtained
20 in the assessment were representative of the Carbon Footprint (CF) and resource savings of this
21 fabrication process. The commercial/conventional process for FA production was used as
22 benchmark. The novelty of the study is the incorporation into the Life Cycle Inventory (LCI) of
23 those materials and chemicals that are used in the fabrication of an ER cell, and in particular in
24 the cathode. Hence, the lifetime of the cathode was used as a main parameter. The results obtained

25 for a baseline case demonstrated that cathode lifetimes over 210 hours would be enough to neglect
26 the influence of the cathode fabrication from an environmental perspective. A first approach to
27 the utility costs of CO₂ ER process was also proposed in the study. Cost of utilities ranged
28 between 0.16 €kg⁻¹ and 1.40 €kg⁻¹ of FA in an ER process compared with 0.21 €kg⁻¹ and 0.43
29 €kg⁻¹ of FA in the conventional process depending on the market prices. This study demonstrated
30 that the ER-based process could be competitive under future conditions if a reasonable
31 electrocatalytic performance (in terms of cell voltage, current density, and faradaic efficiency) is
32 achieved within a reasonable medium or long-term horizon. The results obtained aim to provide
33 useful insights for decision-makers on the future developments within a decarbonised chemical
34 industry.

35

36 **1. Introduction**

37 Almost without exception, the manufacture of commodity chemicals is still based on primary
38 building blocks or platform chemicals extracted from fossil resources (Zero Emissions Platform,
39 2015). However, in the recent years, the concept of “Green Chemistry” has gained momentum
40 and industrial sectors are making substantial investments on eco-friendly technologies
41 considering a decarbonised industrial sector under a reasonable medium or long-term horizon
42 industry (Peters et al., 2011). An interesting novel approach capable of turning captured CO₂, as
43 a carbon feedstock, into value-added products, can contribute to shortening these greenhouse gas
44 emissions representing important steps towards a less carbon-intensive industry (Plasseraud,
45 2010). Of course, there is not a single and universal pathway for turning carbon dioxide (CO₂)
46 into value-added products. The available options have a wide variance in terms of technological
47 maturity expressed as Technology readiness levels (TRLs) (European Commission, 2015; Jarvis
48 and Samsatli, 2018). At the current stage, it is necessary to further explore their technological
49 feasibility to provide them economic and technical coherence (Centi and Perathoner, 2009).
50 Among all alternatives, the electrochemical reduction (ER) of CO₂ presents several advantages:
51 (i) it can be fully developed at atmospheric temperature and pressure; (ii) it can utilize excess of

52 energy from intermittent renewable sources to drive the ER process (Ganesh, 2016; Jhong et al.,
53 2013); (iii) generally, the electrochemical system is modular so it can be scale-up relatively easy;
54 (iv) the ER systems have a compact design. Several chemicals can be synthesised by ER of CO₂
55 such as carbon monoxide (CO), formic acid (HCOOH), methanol (CH₃OH), ethylene (C₂H₄) and
56 methane (CH₄) using suitable electrode and cathode materials (Alper and Yuksel Orhan, 2017).

57 In this study, it was carried out a sustainability assessment of a small-scale production process
58 based on the ER of CO₂ into formic acid (FA). The chemical FA was chosen as it has been
59 predicted as one of the most current profitable products of CO₂ ER, according to the series
60 CO>HCOOH>CH₃OH>>C₂H₄>CH₄ (Agarwal et al., 2011). FA is a valuable building block
61 chemical with a production capacity rate of 950,000 tons per year in 2014 and is traditionally used
62 in food technology, agriculture, and the industries of leather and rubber (Hietala et al., 2000). In
63 addition, it has recently been considered as a promising candidate material for hydrogen storage
64 (Grasemann and Laurency, 2012) which have caused that more and more attention is pointed to
65 this chemical. During the past two centuries, the conventional production of FA has been
66 exclusively based on the utilization of fossil fuels, such as oil and natural gas being the hydrolysis
67 of methyl formate the main synthesis route (Hietala et al., 2000). Over the last decade, it was
68 demonstrated that FA can be synthesized at lab-scale through ER of CO₂ with a relatively low
69 energy consumption and a high faradaic efficiency (Del Castillo et al., 2017; Scialdone et al.,
70 2016; Yang et al., 2017). However, environmental benefits from this CO₂ conversion route cannot
71 be still taken for granted. Despite this process appears to be promising, several factors must be
72 still addressed to ensure its commercial viability: (i) the reduction of the specific energy
73 consumption due to the reduction and the separation processes; (ii) the cathode durability; and
74 (iii) the reduction of the consumption of chemicals (Agarwal et al., 2011). The transformation of
75 the CO₂ molecule requires some form of energy. In fact, energy is one of the key environmental
76 indicators as its generation will in turn also be associated with CO₂ emissions and resource
77 depletion. Energy will be determined by the number of electrons involved in the reaction, the
78 faraday efficiency and the total cell voltage (Jhong et al., 2013).

79 The maturity of the technique based on the electrochemical conversion of CO₂ is currently
80 limited. It was assigned at a TRL range of 3–5 (Pérez-Fortes and Tzimas, 2016) which in fact,
81 reflects the progress of its commercialisation. Until now many efforts have been focussed on the
82 development at laboratory scale of different electrocatalysts (Endrödi et al., 2017) in order to
83 reduce the high overpotentials associated. At the current stage, it has been suggested to start
84 exploring their environmental and technological feasibility for improving the associated TRL
85 (Centi and Perathoner, 2009). For example, several techno-economical assessments related to
86 another possible utilization option as direct hydrogenation of CO₂ to FA may already be found
87 (Pérez-Fortes et al., 2016; Saavalainen et al., 2017; Sternberg et al., 2017). These studies analysed
88 mainly the competitiveness of the developments compared to current market conditions. Only a
89 few techno-economic studies can already be found concerning to the synthesis of FA by means
90 of ER of CO₂, (Agarwal et al., 2011; Jarvis and Samsatli, 2018; Shemfe et al., 2018).

91 A recent study carried out by the authors has evaluated the main technological challenges of the
92 technology demonstrating that the carbon footprint (CF) of the ER-based alternative route for
93 manufacturing FA could potentially even the CF of the conventional route under proper
94 technology developments (Rumayor et al., 2018). Briefly, in that study it was assessed the
95 relevance of (i) the reaction, by means of the concentration of FA at the outlet stream of the ER
96 cell, the total cell voltage, the faradic efficiency, and the mode of operation (i.e., recirculation);
97 and (ii) the separation step, by means of azeotropic distillation. It was concluded that an increment
98 of FA concentration in the outlet stream of ER reactor up to 21% wt. can reduce the steam
99 consumption and then the overall CF up to the value of the CF corresponding to the conventional
100 process of FA production. These statements were in line with previous studies pointing out the
101 relevance of the energy requirements of purification and utilizing renewable electricity as
102 Photovoltaic solar energy in order to ensure the environmental sustainability of the ER of CO₂
103 (Dominguez-Ramos et al., 2015).

104 However, one of the hypotheses of our previous study is that the infrastructure is neglected due
105 to the assumption of decades of operation without replacement. However, when catalysts,

106 batteries or electrodes are involved such in electrochemistry based processes, its infrastructure
107 may potentially have an impact. This can be an issue as the life cycle inventories may be presented
108 at a high level of aggregation thus making hot spots difficult to be analysed. Under the hypothesis
109 of a reduced lifetime use, this does lead to a relatively high frequency of replacement. Overall, a
110 better stability will reduce maintenance and replacement costs. The figures of merits have
111 suggested lifetimes in the range of thousands of hours under typical cycling loads from renewable
112 energy sources considering 5,000 h as a first approach (Martín et al., 2016). In general, lifetimes
113 of electrode materials and catalysts in the techno-economical assessments are assumed to be long-
114 lasting to neglect their CFs (Pérez-Fortes et al., 2016; Rumayor et al., 2018; Shemfe et al., 2018).
115 Nevertheless, the performance of current electrochemical cell developments is known to be
116 strongly limited by different factors such as the mass transport limitations or the degradation of
117 the electrodes (Klans, 2007). Therefore, the lifetime of the electrodes can arise as a fundamental
118 key point in the discussion of the environmental performance of the process under short durations
119 (Martín et al., 2016).

120 Another key element, which is not typically discussed, is the potential savings in terms of natural
121 resources that go together with the production of FA by ER. Fossil fuels such as natural gas that
122 is consumed in the production of the commodities for the industrial FA manufacture are no longer
123 required. This issue must be also included to support the potential environmental benefits of the
124 ER of CO₂ to FA. As in this work is expected to consider the use of metals like Sn for the cathode,
125 the consumption of these natural resources will be also quantified into a much more broad picture
126 that the one which is usually considered in the related literature.

127 Therefore, the aim of the case of study presented is to analyse the environmental and economic
128 sustainability of the ER of CO₂ to FA including as the main variable the influence of the lifetime
129 of the cathode. The environmental sustainability analysis has been completed in terms of
130 environmental burdens and natural resource savings. For this reason, a Life Cycle Assessment
131 (LCA) framework was used to determine two of the most relevant environmental indicators: (i)
132 the abiotic resource depletion potential (ADP), including fossil fuels (MJ-eq.) and elements (kg

133 Sb-eq.), and (ii) the global warming potential (GWP) as representative of the Carbon Footprint
134 (CF) (kg CO₂-eq.). The process operation and the ER cell fabrication were included in the
135 resource utilization. For economic sustainability, a preliminary study of the utility costs was
136 carried out. Both environmental and economic figures were benchmarked against the
137 conventional process, supporting the idea of a future industrial competitiveness.

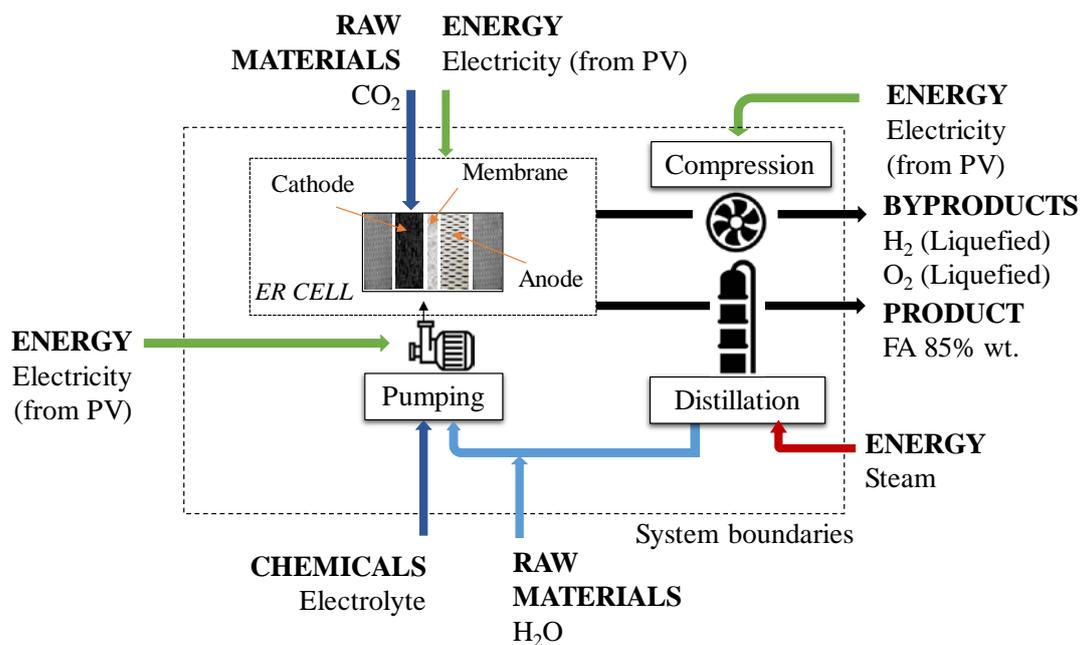
138 The results provided can supplement those results obtained in the mentioned previous study
139 carried out by the authors. The main novelty of the current study is the consideration of the
140 influence of the ER cell components lifetimes (i.e. cathode, anode and separator membrane) on
141 the two chosen environmental indicators. The comparison will demonstrate the potential
142 sustainability advantages and the feasibility of the ER approach. The outcome is expected to
143 complement the existing studies giving a better understanding of the environmental and economic
144 impacts and to provide useful insights for decision-makers on the future sustainable developments
145 within a decarbonised FA industry.

146

147 **2. Methodology**

148 *2.1. Model description*

149 The overall process based on the ER of CO₂ for producing FA at 85% wt. involves three main
150 steps: (i) the ER of CO₂ in the ER cell; (ii) the distillation of the azeotropic mixture FA/water to
151 the desired purity (85% wt.); and (iii) the compression of by-products H₂ and O₂ to the liquid
152 forms that are ready to transport. Figure 1 displays the process diagram of the proposed process
153 for the production of FA at 85% wt.



154

155 **Figure 1.** Process diagram of electrochemical reduction of CO₂ to FA

156 The electrochemical cell (ER cell) was modelled as a black box unit using two set of parameters:
 157 i) experimental data obtained within the research group of the authors (Del Castillo et al., 2017);
 158 and ii) a set of optimistic parameters that may be achieved in the future under proper
 159 developments. These consists of (i) current density; (ii) cell potential; (iii) FE; (iv) concentration
 160 of FA at the outlet stream of the ER cell; and (v) lifetimes of the cathode, anode, and membrane.
 161 The values of these parameters in each set can be found in the Supporting Information. The
 162 concentration of FA at the outlet stream of the ER cell is assumed to be as high as 21% wt.
 163 corresponding to the benchmark established in our previous study (Rumayor et al., 2018). As a
 164 requisite, the energy consumption is considered as PV solar electricity for the reduction step and
 165 heat (steam) for the separation step according to the nature of each individual process. Mass
 166 balances are based on the reaction of the CO₂ ER shown in Table 1, assuming neutral to alkaline
 167 conditions (Li and Oloman, 2006; Oloman and Li, 2008). CO₂ and water are injected in the
 168 cathode. The black-box model does not include a transfer model so solubility of CO₂ is assumed
 169 very high. The soluble CO₂ that reaches the cathode surface is reduced to formate (HCOO⁻) and
 170 H₂O to hydroxide ions (OH⁻) liberating the stoichiometric amount of H₂, in the presence of the
 171 correspondent electrolyte in the cathodic compartment of the ER cell. Simultaneously, the

172 formation of oxygen (O₂) and protons (H⁺) is considered as the only reaction taking place in the
 173 anodic compartment. Both the HCOO⁻ ions and OH⁻ ions are balanced by the H⁺ produced in the
 174 anode and transported through the membrane. This way, it is formed FA (HCOOH) and water
 175 (H₂O). In an ideal ER reactor, an excellent electrode would lead to a value of 100% for the
 176 faradaic current efficiency (FE). This would correspond with the formation of pure HCOOH in
 177 the cathode and pure O₂ in the anode. The applied current density is partly deviated to other
 178 parallel/parasitic reactions (Oloman and Li, 2008), reducing the FE to FA production. In this
 179 study, H₂ evolution reaction (HER) is assumed as the unique parallel/parasitic reaction. It is
 180 considered that H₂O is the chemical compound that is consumed regardless of the pH in the half-
 181 cell being acid or basic. The O₂ evolution reaction (OER) is the only reaction taking place in the
 182 anode.

183 **Table 1.** Main and side reactions

Cathodic reaction	Anodic reaction
$\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HCOO}^- + \text{OH}^-$	$\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^- + 1/2 \text{O}_2$
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$	
Overall reaction	
$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{O}_2 + \text{H}_2$	

184

185 In order to increase the FA concentration up to 85% wt. (commercial concentration value) at the
 186 outlet stream of the ER cell, it is necessary to consider a purification process in the form of a
 187 distillation. Then, cooling and heating are needed. The distillation process was simulated in a
 188 previous study carried out by the authors (Dominguez-Ramos et al., 2015). The simulation
 189 considers only the presence of water (obtained as a head product) and FA (obtained as the bottom
 190 product) at the required concentration. Distilled water is recirculated and reinjected to the inlet
 191 freshwater stream to the cathode. The net water consumption is the difference between water in
 192 the inlet stream and water that is recirculated. The pure O₂ produced as a secondary product,

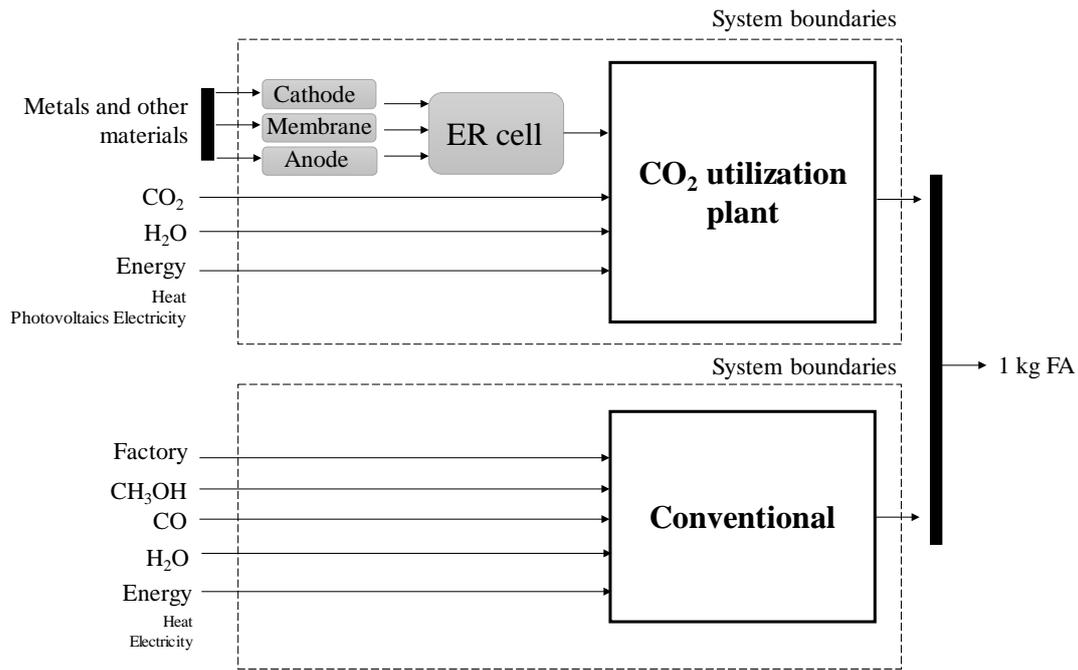
193 mainly by the anodic reaction is separated, liquefied and recovered, as well as, H₂, which is
194 produced by the competing reaction and it is assumed to be pure.

195 The hypothesis made to build the model are similar to those described in the mentioned previous
196 study (Rumayor et al., 2018). Briefly, authors considered that the CO₂ valorisation plant was in
197 the same site of the CO₂ source and hence no transport was required. CO₂ was feed to the plant
198 as a pure component and with a suitable pressure for the ER process. In addition, the CO₂ feed
199 was assumed to have no cost or environmental burdens as they are allocated to the product that
200 directly releases the CO₂, e.g., electricity from a coal-fired power plant. In any case, the results
201 would depend on the specific allocation criteria of the study according to von der Assen et al.,
202 2014. Additionally, it was assumed that i) the vapour steam needed for FA purification is at dry
203 saturated conditions, and ii) electrolytes used in the ER process are assumed to be perfectly
204 separated.

205 *2.2. Environmental assessment of formic acid production*

206 The case of study presented aimed to supplement the existing knowledge by covering the
207 importance of the cathode lifetime. Two environmental indicators were employed to carry out
208 this environmental assessment: abiotic resource depletion potential (ADP) and global warming
209 potential (GWP) as the basis for the corresponding CF. In order to obtain both indicators a Life
210 cycle assessment (LCA) framework was applied in the study according to the standards published
211 by the International Organization for Standardization (ISO) (International Organization for
212 Standardization, 2006a, 2006b). The analysis employed the described four steps: goal and scope
213 definition, life cycle inventory (LCI) analysis, life cycle impact assessment and interpretation. In
214 this study a “cradle to gate” analysis of the production of FA at a commercial concentration (85%
215 wt.) by CO₂-ER route has been managed. This means that transportation to the site in which is
216 used is not considered. The conventional/commercial FA process has also been environmentally
217 assessed and used as a benchmark. The environmental burdens do include the impacts on the
218 environment such as the depletion of natural resources, the energy consumption, and the on-site
219 emissions. The functional unit of the system was defined as 1 kg of FA produced at 85% wt.

220 purity. The system boundaries of the FA manufacture were defined as “cradle-to-gate”. Main raw
 221 materials, energy, utilities (e.g., electricity, steam and water), auxiliary chemicals and emissions
 222 involved in each stage were taken into account. The avoided emissions from the commercial
 223 manufacture of the by-products O₂ and H₂ were not taken into consideration in this study. The
 224 system boundaries of the manufacture of 1 kg of FA based on CO₂-ER and the conventional
 225 process (benchmark) are shown in Figure 2.



226
 227 **Figure 2.** System boundaries of: (a) FA manufacture based on ER of CO₂; and (b)
 228 conventional/commercial FA process

229
 230 The Life Cycle Inventory (LCI) of the ER route was performed on the basis of the above
 231 mentioned system model. Briefly, the first scenario (labelled as the baseline) used the
 232 experimental conditions obtained in the research group of the authors (Del Castillo et al., 2017)
 233 and the second scenario (labelled as the optimistic) was created using optimistic ER parameters
 234 derived from the literature (Jouny et al., 2018). Those parameters (i.e. current density, cell
 235 potential, FE, concentration of FA at the outlet stream of the ER cell and lifetimes) are displayed
 236 in the Supporting information. The LCI was created including the EC cell fabrication in order to

237 identify the system “hot spots” that will result in suggestions and target values for a competitive
238 development. Ecoinvent v3.2 was used to obtain the background data. LCI data in the European
239 Union (nominated here as RER) was used when available; otherwise, a global average was used
240 (named here as GLO). For the production of electricity either from the grid mix or renewable (i.e.
241 photovoltaic and wind), Spain (nominated as ES) was used as reference. LCA was carried out by
242 means of GaBi Professional software (Thinkstep AG., 1991) using the a mid-point method CML
243 2001, which restricts quantitative modelling to early stages in the cause-effect chain to limit
244 uncertainties (Guinée et al., 2002). This method allows the assessment grouped in midpoint
245 categories according to common mechanisms (e.g. climate change, abiotic depletion, etc.) or
246 commonly accepted groupings (e.g. ecotoxicity). As previously mentioned, the CF and the
247 indicators ADP-elements and ADP-fossils were calculated and compared with the indicator
248 results from the conventional process giving an idea of the emissions as unit of mass of CO₂-eq.
249 and the potential natural resource savings as unit of mass of kg Sb-eq. and MJ eq. respectively.

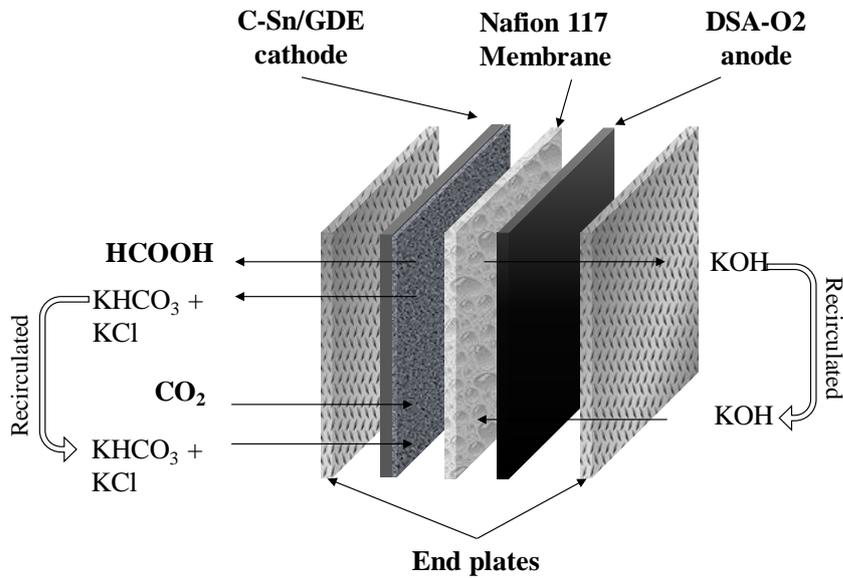
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251 *2.2.1. The electrochemical cell*

252 The ER cell considered in our model consists of a filter-press cell (Figure 3) with a geometric
253 surface area of 10 cm². The main components of this cell are: i) a cathode: a Gas Diffusion
254 Electrode with carbon supported Sn nanoparticles (Sn/C-GDE), ii) an anode: a commercially
255 available Dimensionally Stable Anode (DSA-O₂ on Platinum), and iii) a separation membrane: a
256 commercial Nafion 117. Both the anolyte (KOH) and the catholyte (KHCO₃ and KCl) are
257 supposed to be recirculated and they were not taken into consideration. The main components of
258 the cell are clamped by two end plates made from aluminum (1·10⁻³ m as thickness). Steel tie rods
259 are used as well in the assembly process. From the perspective of environmental impact and
260 economics, anode, cathode and membrane are made from components that are expected to have
261 much higher impact than simple steel tie rods or aluminum endplates (i.e. platinum, titanium,
262 carbon fiber, tin, etc). Because of this reason, those secondary components (steel tie rods or
263 aluminum endplates) can be neglected from the assessment. The durability of these components

264 is of course finite. Thus, as we are neglecting the impact that will be equivalent to have an infinite
 265 lifetime. No doubt, when the technique is close to be industrially viable, a refined study should
 266 consider those components.

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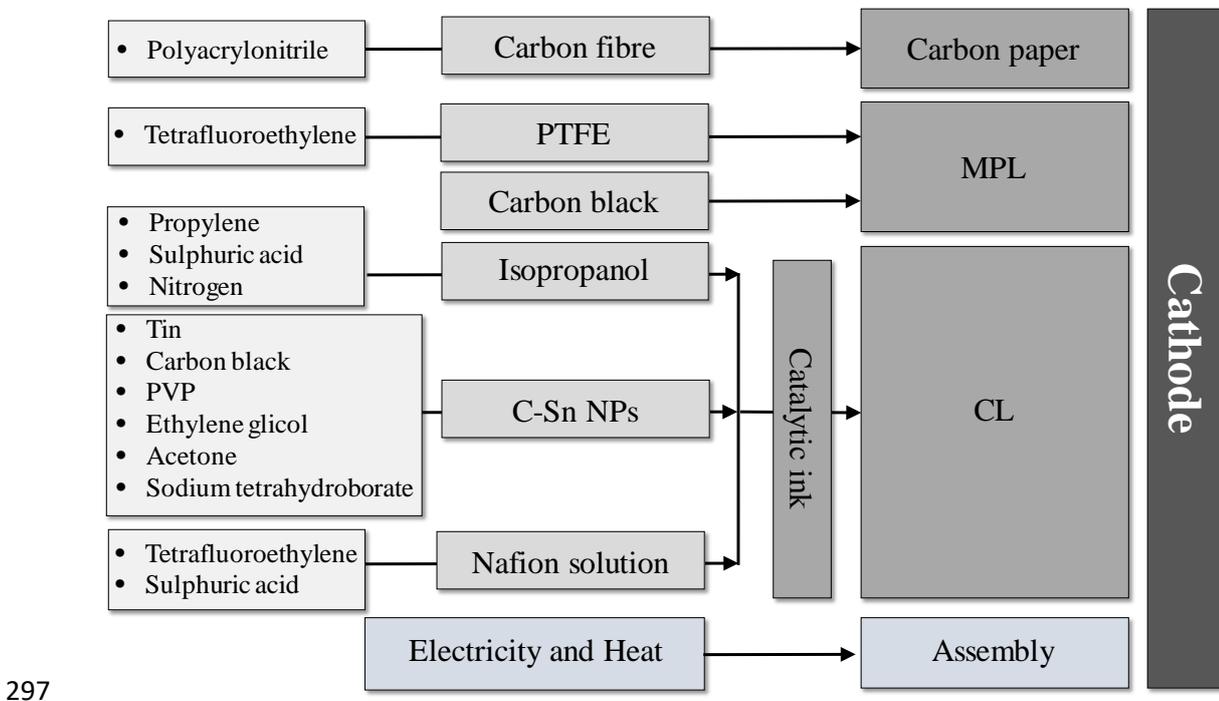
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269 **Figure 3.** Electrochemical cell (ER cell) based on a filter-press cell

270

271 The Nafion membrane is made from perfluorosulfonic acid (PFSA). The anode, a commercially-
 272 available DSA-O₂ on platinum (Pt), consists of a titanium-based material in the form of expanded
 273 metal (weight geometrical area of 23.76 g·dm⁻²) with a standard Pt layer thickness around 3.5·10⁻⁶
 274 m (normal range between 2·10⁻⁶ m and 5·10⁻⁶ m) and a Pt loading around 7 mg·cm⁻². The lifetime
 275 of the platinised Ti anodes is in particular dependent on the medium (electrolyte) and the anodic
 276 current (specific current density). According to that established in commercial websites (e.g.
 277 (“PolyTechs Technology,” 2018)), the durability of DSA-O₂ anodes can be 10 years. In this study,
 278 the lifetime corresponding with the anode was hypothesized to be 10 years and the corresponding
 279 with the membrane at 60,000 h (Rozière and Jones, 2003). Considering that both components are
 280 long-lasting, composition proxies can be used as it was done in other LCA studies found in
 281 literature (Evangelisti et al., 2017; Shemfe et al., 2018). The proxy used for PFSA consist of

282 57.4% wt., TFE and 42.6% wt. sulphuric acid (Simons and Bauer, 2015). The thickness of the
 283 membrane is 0.007 in and its basis weight 360 g·m⁻². A basic extrusion plastic film process was
 284 used to represent the energy consumed for the membrane casting. On the contrary, the cathode
 285 lifetime is much shorter and the influence was considered as a parameter by the inclusion of a
 286 sensitivity analysis to assess its influence. Lifetime was evaluated in the range between 1 h to
 287 several hours. The LCI data of the cathode was obtained following the hierarchy shown in Figure
 288 4. Briefly, it includes the preparation of a catalytic layer (CL) and a microporous layer (MPL) on
 289 a carbon paper. The CL and the MPL are then hot pressed to guarantee an intimate contact
 290 between layers. The detailed description of the cathode and the amounts used per 10 cm² of
 291 cathode can be found in the Supporting information and it is based in the methodology found in
 292 the literature (Del Castillo et al., 2017). In order to take into account the heat and the electricity
 293 consumption, proxies of the processes thermoforming and coating and curing have been
 294 accordingly. Briefly, thermoforming was used for the application of PTFE on carbon black and a
 295 general coating and curing to account the consumption for mixing catalytic ink, painting onto the
 296 carbon paper and baking to dry (Simons and Bauer, 2015).



297
 298 **Figure 4.** Components, chemicals and raw materials within the cathode LCA system

299 2.2.2. *The conventional manufacture of formic acid (FA)*

300 Conventional FA manufacture, labelled as CONV, was considered as hydrolysis of methyl
301 formate. This route consists on a two-stage process: in the first stage, methanol is carbonylated
302 with carbon monoxide ($\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{HCOOCH}_3$) and in a second stage, methyl formate is
303 hydrolysed to FA and methanol ($\text{CH}_3\text{OOCH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH}$). Then, methanol and
304 the dissolved catalyst are returned to the reactor (Hietala et al., 2000). The stages with main energy
305 consumptions in FA synthesis are syngas production and steam needs. Limitations of the FA
306 conventional process can include slow reaction rate, undesirable by-products, high cost of
307 investment, and issues related to the environment such as the high energy requirements (in the
308 separation stage) and a noticeable dependence on fossil fuel (heavy fuel oil is used in the synthesis
309 of CO) (Sharma et al., 2018).

310 In order to compare the consumptions of energy and raw materials with the ER alternative, the
311 LCI of the conventional process was created. The corresponding LCI data was obtained from
312 Ecoinvent database v3.2 (Swiss Centre for Life Cycle Inventories, 2016). Heat for the separation
313 step was assumed to come 100% from natural gas (the same assumption was taken in the case of
314 the alternative ER of CO₂). It should be noted that accordingly to Ecoinvent database, there are
315 two sources for heat in a conventional plant of FA: natural gas (14.6 MJ) and other sources than
316 natural gas (i.e. waste incineration, coal, oil, diesel, wood, etc.) (8.17 MJ). The calculated value
317 for the GWP indicator as representative of the CF in this study is 3.00 kg·kg⁻¹ (expressed as unit
318 of mass of CO₂-eq. per unit of mass of FA produced). This value could decrease up to 2.88 kg·kg⁻¹
319 whether PV solar was supplied to a FA conventional plant instead of electricity from the
320 production mix. Using the distribution of heat sources established in Ecoinvent databased, the CF
321 value could be as low as 2.2 kg·kg⁻¹.

322 2.3. *Assessment of the utility costs*

323 Taken into account that ER is still found at low TRL and still far away from its practical
324 exploitation, authors considered that the only possible fair comparison with the conventional

325 process could be done in terms of the cost of utilities and not in terms of the capital cost. It should
326 be highlighted that the cost of consumables, which are related to the lifetime of the ER cell
327 components have to be considered in a more detailed study of the operating cost. The authors
328 consider that the mentioned study is currently out of the scope of the present one. The utility costs
329 include the costs of raw materials, electricity, steam, and water. Table 2 shows the range of prices
330 considered for the utilities. A sensitivity analysis was carried out considering an optimistic (using
331 the LCI from the optimistic scenario and the lowest range prices) and a conservative (using the
332 baseline LCI and the highest range prices) scenario. The displayed values correspond to the latest
333 statistics found in the literature and the currency exchange rate used is €2017, which was based
334 on Eurostat data (European Commission, 2018). Steam was assumed to come exclusively from
335 natural gas. The prices of natural gas during the second half of 2017 varied widely among the EU
336 Member States being the highest in Finland (0.053 €kWh^{-1}), Sweden (0.047 €kWh^{-1}) and in
337 France (0.035 €kWh^{-1}); they were the lowest in the United Kingdom (0.022 €kWh^{-1}) (Eurostat,
338 2017). Please note that the price of electricity from Photovoltaic solar (PV) has decreased
339 dramatically over the past years. The range of prices showed in Table 2 corresponds with the
340 Levelised Cost of Electricity (LCOE) that is widely used to make fair comparisons with electricity
341 prices and the cost of other power generation technologies. LCOE is defined to be the average
342 generation cost, i.e., including all the costs involved in supplying PV at the point of connection
343 to the grid. PV LCOE for a ground-mounted 1 MWp system varies currently from about $55 \cdot 10^{-3}$
344 €kWh^{-1} in Spain to about $95 \cdot 10^{-3} \text{ €kWh}^{-1}$ in the UK (Vartiainen et al., 2015). Additionally, recent
345 estimations carried out in multiple countries have determined that the price of renewable
346 electricity (PV solar) could be as low as 0.02 €kWh^{-1} in 2030 (Haegel et al., 2017). The tariff of
347 water also differs from country to country from 1.5 €m^{-3} (in Italy) to 9.0 €m^{-3} (in Denmark)
348 (EurEau The European Federation of National Associations of Water Services, 2017). While the
349 spatial reference for the CF of the electricity was Spain, in the economic assessment authors
350 considered more appropriate a range of prices from the European Union.

351

352 **Table 2.** Prices of utilities for the European Union

Item	Scenarios		Unit	Reference
	Optimistic	Conservative		
PV electricity	20*	95	€MWh ⁻¹	(Vartiainen et al., 2015)
Steam	20	45	€ton ⁻¹	(Eurostat, 2017)
Carbon monoxide	70	70	€ton ⁻¹	(Jouny et al., 2018)
Methanol	380	380	€ton ⁻¹	(“Methanex Corporation,” 2015)
Water	1.5	9.0	€m ⁻³	(EurEau The European Federation of National Associations of Water Services, 2017)

353 * Optimistic price of renewable PV solar based on estimations to the year 2030 (Haegel et al.,
 354 2017)

355

356 **3. Results and discussion**

357 *3.1. Environmental assessment*

358 *3.1.1. Life cycle inventory (LCI)*

359 Table 3 displays the comparison of the operating LCIs results obtained for the production of 1 kg
 360 of FA (at 85% wt. commercial concentration) using the alternatives: i) ER of CO₂ and ii)
 361 commercial (CONV). The alternative CONV was used as benchmark for comparing the operating
 362 LCIs that includes the values for utilities (heat and electricity) as well as the raw materials used
 363 in the processes. The results related to the optimistic scenario are also displayed. The results
 364 obtained have indicated that the main advantage of ER of CO₂ alternative is its savings in fossil-
 365 based chemicals. These fossil-based chemicals are used as raw materials in CONV such as carbon
 366 monoxide (CO) and methanol (CH₃OH). However, it should be remarked that the total electricity
 367 consumption in the baseline CO₂ ER scenario (12 kWh·kg⁻¹ of FA) is much higher than the
 368 consumption in CONV (0.290 kWh·kg⁻¹ of FA). This high consumption is related especially with
 369 the ER of CO₂ as well as compression and pumping. Water is used as raw material in both

370 alternatives with consumptions around 1.10 kg·kg⁻¹, 0.611 kg·kg⁻¹ and 0.60 kg·kg⁻¹ of FA for both
 371 ER-based and the commercial routes, respectively. Steam needs per unit of mass of FA is slightly
 372 lower in CO₂ ER alternatives. This fact highlighted the significance of the purification step in
 373 both cases. Only if PV solar electricity is considered, the CO₂ ER alternative would be
 374 environmentally positive compared with CONV. Otherwise, the ER alternative would release
 375 more CO₂ than the one utilized to produce FA. As it was mentioned previously, the current work
 376 assumed the surpluses of renewable energy from PV solar energy to be used for supplying
 377 electricity to ER, pumping, and compression. The optimistic case of ER of CO₂ has demonstrated
 378 a notable drop in electricity consumption respect the baseline, concretely, from 12 kWh·kg⁻¹ to
 379 2.59 kWh·kg⁻¹ of FA produced due to the great improvement of the ER performance (in terms of
 380 cell voltage, current density, and faradaic efficiency). The amounts of H₂ and O₂ that are co-
 381 produced are 0.005 kg·kg⁻¹ and 0.386 kg·kg⁻¹, respectively, in baseline scenario. In the case of
 382 optimistic scenario only an amount of O₂ of 0.386 kg·kg⁻¹ is co-produced.

383

384 **Table 3.** Operating LCI of the CO₂ ER-based process and conventional/commercial process
 385 (CONV) for FA manufacturing (Functional unit: 1 kg of FA)

		FA manufacturing alternatives		
		ER of CO ₂		CONV
UNITS		Baseline	Optimistic	
Raw materials				
CO ₂	kg	0.957	0.957	-
H ₂ O	kg	1.100	0.611	0.600
CO	kg	-	-	0.610
CH ₃ OH	kg	-	-	0.040
Energy				
<i>Electricity</i>				
ER	kWh	11.80	2.59	
Pump	kWh	<0.01	<0.01	
Compression	kWh	<0.01	<0.01	

TOTAL	kWh	12.00	2.63	0.290
<i>Heat demand</i>				
Steam	MJ	17.08	17.08	22.77

386

387 Besides the operating LCI, this study aims to include and to analyse the ER cell components.

388 Table 4 displays the corresponding LCI database for the production of the main components of a

389 typical ER cell: anode, cathode and membrane. It is shown the requested amounts of raw materials

390 and chemicals, as well as the electricity and steam for the fabrication and assembly of these

391 components.

392 **Table 4.** LCI of the main ER cell components: anode, cathode and membrane

Component	Area	Unit	Process name (Swiss Centre for Life Cycle Inventories, 2016)
Anode	0.001	m ²	Market for Pt [$7 \cdot 10^{-5}$ kg]; Ti production: [0.0023 kg]
Membrane	0.001	m ²	Tetrafluoroethylene: [0.0002 kg]; Sulphuric acid production: [0.00015 kg]; market for electricity, medium voltage: [0.000855 MJ]; market for heat in chemical industry: [0.000216 MJ]; steam production in chemical industry: [$2.08 \cdot 10^{-5}$ kg]
Cathode	0.001	m ²	<p>CL: [0.00132 kg]; Carbon paper: [0.000123 kg]; MPL: [0.000143 kg]</p> <p><u>Inputs for CL</u> [0.00132 kg]: C-Sn NPS [$2.5 \cdot 10^{-5}$ kg]; Nafion solution [0.000175 kg]; Isopropanol [0.0012 kg]; heat in chemical industry [0.0344 MJ]; electricity, medium voltage [0.00468MJ]</p> <ul style="list-style-type: none"> ➤ Inputs for C-Sn NPS [$2.5 \cdot 10^{-5}$ kg]: Tin production [$8.92 \cdot 10^{-6}$ kg]; Hydrochloric acid (Mannheim process) [$5.49 \cdot 10^{-6}$ kg]; carbon black production [$1.75 \cdot 10^{-5}$ kg]; Sodium tetrahydridoborate (Brown-Schlesinger process) [$1.43 \cdot 10^{-5}$ kg]; Ethylene glycol production [0.00316 kg]; Acetone production [0.00223 kg]; PVP production [$4.28 \cdot 10^{-6}$ kg] <p><u>Inputs for MPL</u> [0.000143 kg]: Carbon black production [$7.13 \cdot 10^{-5}$]; PTFE [$8.55 \cdot 10^{-5}$ kg]; market for heat in chemical industry [0.000116 MJ]; Market group for electricity, medium voltage [0.000514 MJ]; Steam production in chemical industry [$8.29 \cdot 10^{-5}$ kg]</p> <ul style="list-style-type: none"> ➤ Inputs for PTFE [$8.55 \cdot 10^{-5}$ kg]: Ammonium sulphate production [$4.87 \cdot 10^{-6}$ kg]; water, deionised from tap water at user [2.57310^{-6} kg]; Tetrafluoroethylene production [$8.29 \cdot 10^{-5}$]; Borax production [$3.64 \cdot 10^{-8}$ kg] <p><u>Inputs for Carbon paper</u> [0.000123 kg]: Carbon fibre [0.000123 kg]; CO₂ emissions [0.0246 kg]</p>

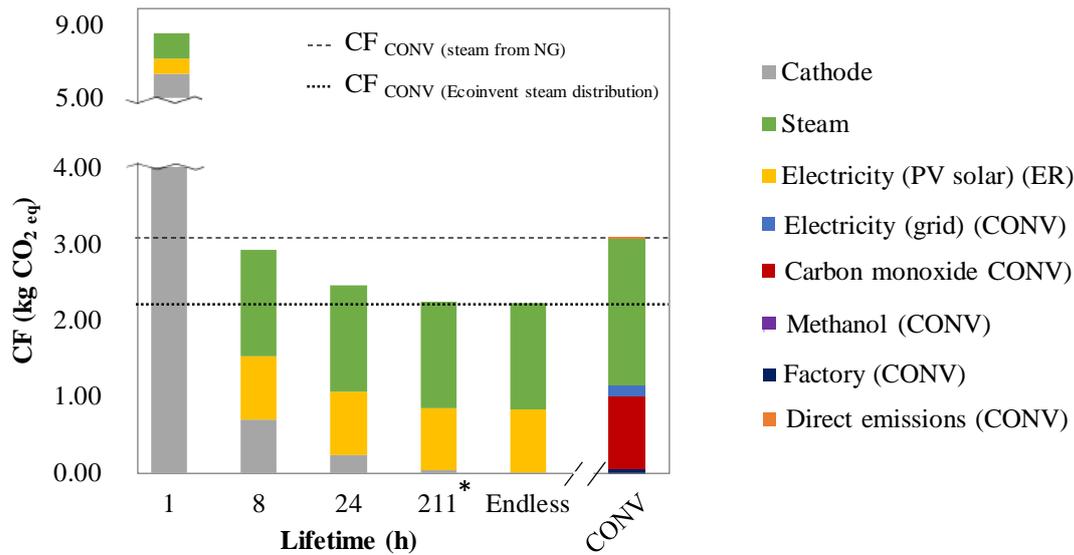
394 Accordingly, with the proposed lifetimes for the anode (10 years) and the membrane (60,000 h),
395 their overall areas needed for producing FA were calculated as $1.23 \cdot 10^{-6} \text{ m}^2 \cdot \text{kg}^{-1}$ and $8.42 \cdot 10^{-7}$
396 $\text{m}^2 \cdot \text{kg}^{-1}$, respectively. A sensitivity analysis of the influence of cathode lifetime was carried out.
397 The lifetime of the cathode was varied between 1 h to 5,000 hours. The midpoint categories of
398 GWP (climate change) as Carbon Footprint (CF), ADP-elements and ADP-fossil fuels (abiotic
399 depletion) of the ER cell components, the operating inventory and the conventional route were
400 determined by means of GaBi software. Other midpoint categories are also included in the
401 Supplementary material.

402

403 *3.1.2. Carbon footprint assessment*

404 Figure 5 shows the impact of the cathode durability in the CF, expressed as mass of CO₂ per unit
405 of mass of FA $\text{kg} \cdot \text{kg}^{-1}$ manufactured by means of the alternative of ER of CO₂ (only the results
406 from the baseline case were presented as it is the worst-case scenario). In order to compare with
407 the CONV route, the CF distribution was also displayed. The reference CONV used in this study
408 presents an overall CF value of $3.00 \text{ kg} \cdot \text{kg}^{-1}$ considering that all the heat requirement comes from
409 natural gas (NG). In the case of using the Ecoinvent distribution for steam, a value of $2.20 \text{ kg} \cdot \text{kg}^{-1}$
410 would be representative of the CF of FA production (RER process). Both reference values for
411 the CF (CONV and Ecoinvent) are represented in Figure 5 as a discontinuous line (CF of 3.00
412 $\text{kg} \cdot \text{kg}^{-1}$) and a dotted line (CF of $2.20 \text{ kg} \cdot \text{kg}^{-1}$). Note that the reference value for CONV does not
413 take into account renewable sources (it was kept as reported by the LCA software GaBi for the
414 reference process). Electricity is withdrawn from the mix grid so the Spanish average (nominated
415 as ES) was used with a CF contribution value of $0.431 \text{ kg} \cdot \text{kWh}^{-1}$. The CF value of CONV could
416 decrease to $2.88 \text{ kg} \cdot \text{kg}^{-1}$ whether PV solar was supplied to a FA conventional plant instead of
417 electricity from the production mix. Note that PV solar (ES) presents a contribution to the CF as
418 low as $0.068 \text{ kg} \cdot \text{kWh}^{-1}$. As it can be expected, the results from Figure 5 demonstrated that the
419 shorter the cathode lifetime, the higher the cathode influence in the CF. From an environmental
420 point of view, the results obtained demonstrated that lifetimes above 211 hours would be enough

421 to neglect the influence of the ER cell in the CF (contribution below 1.00%). It should be remarked
422 that other midpoint categories, as well as economic aspects, should be analysed for a final decision
423 for competitive designs. It must be also kept in mind that a recent study has proposed 5,000 h as
424 a first cornerstone for the ER cell lifetime (Martín et al., 2016) but it was determined from an
425 economic and competitive perspective. As can be seen in Figure 5, cathode lifetimes longer than
426 211 hours shift to other operating factors (as electricity and steam supply) the main contribution
427 to the CF. Cell components contributed lesser than 1.00 % (for lifetimes over 211 hours) to the
428 total CF. In particular, the CF of the cathode, anode and membrane, expressed as $\text{kg}\cdot\text{kg}^{-1}$ of FA,
429 were $2.62\cdot 10^{-2} \text{ kg}\cdot\text{kg}^{-1}$, $1.74\cdot 10^{-3} \text{ kg}\cdot\text{kg}^{-1}$ and $7.44\cdot 10^{-5} \text{ kg}\cdot\text{kg}^{-1}$, respectively. The finding is in
430 agreement with similar studies where the impact into the CF of some different electrolyser
431 systems constructions were minimal in comparison with other operating categories of the
432 processes such energy demand (Jung et al., 2014; Sadhukhan et al., 2017; Shemfe et al., 2018).
433 Water supply is negligible: the CF score of water supply was about $1.33\cdot 10^{-3} \text{ kg}\cdot\text{kg}^{-1}$ (a value of
434 $1\cdot 10^{-3} \text{ kg}\cdot\text{kg}^{-1}$ was the water contribution obtained in CONV route). In the case of the commercial
435 alternative CONV, CO feed (raw material) represents the most significant score in the CF,
436 specifically, a value of $0.937 \text{ kg}\cdot\text{kg}^{-1}$, which is related with the fabrication of the required amount
437 of CO. In the case of methanol feed (CONV), the contribution is negligible ($0.001 \text{ kg}\cdot\text{kg}^{-1}$) as this
438 chemical is recirculated in CONV process. Therefore, the CO_2 ER alternative was considered
439 beneficial from a CF point of view. Regarding steam and electricity scores, both alternatives have
440 relatively high steam consumption and as it was expected, the CF contribution of the electricity
441 was higher in the alternative ER than in the commercial CONV route. In fact, it is known that the
442 success of this kind of CO_2 valorisation alternatives, like the present CO_2 ER process among
443 others, will be always depending on other technologies and/or developments, being the
444 availability of renewable electricity and steam the most important issue (Dominguez-Ramos et
445 al., 2015; Pérez-Fortes et al., 2016). The CO_2 used as feedstock was assumed not to contribute to
446 the CF. The mass of CO_2 used in ER per unit of mass of FA was excluded from the use of
447 resources, but anyway it would represent a value of $-0.957 \text{ kg}\cdot\text{kg}^{-1}$ (stoichiometric ratio).



448

449 *Cathode lifetime needed to neglect the cathode influence in CF (influence $\leq 1\%$)

450 **Figure 5.** Influence of the cathode lifetime in the CF (kg CO₂-eq·kg⁻¹) distribution and
 451 comparison with the conventional process (CONV) (Functional unit: 1 kg of FA)

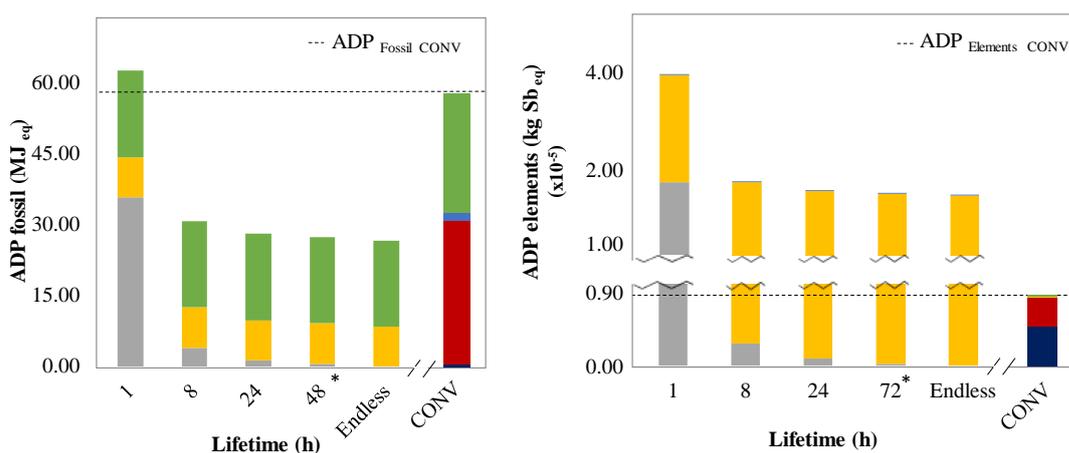
452 The overall CF indicator corresponding with the optimistic scenario presented a value of 1.58
 453 kg·kg⁻¹ of FA produced due to its low electrical consumption comparing to that from the baseline
 454 case (2.63 kWh·kg⁻¹ of FA compared with 12 kWh·kg⁻¹ of FA, respectively).

455

456 3.1.3. Resource depletion assessment: Abiotic depletion potential (ADP)

457 The environmental impact category Abiotic depletion potential (ADP) includes depletion of non-
 458 renewable resources, both fossil fuels and metals plus minerals. Note that ADP involves not only
 459 an environmental but also an economic problem. The fossil fuels and elements resource depletions
 460 were determined by the midpoint categories of ADP fossil (expressed as unit of MJ equivalent
 461 per unit of mass of FA) and ADP elements (expressed as the unit of mass of Sb equivalent per
 462 unit of mass of FA), respectively (Figure 6 (a-b)). ADP fossil and ADP elements of the CONV
 463 process were used as benchmark and they represent overall values of 55 MJ·kg⁻¹ and 7.96·10⁻⁶
 464 kg·kg⁻¹ of FA, respectively (Swiss Centre for Life Cycle Inventories, 2016). As in the previous
 465 section, those distributions related with commercial route CONV, were also shown in the figure

466 to facilitate the comparison. The fossil resource savings of CO₂ ER alternative in comparison
 467 with the commercial route CONV were indubitable (Figure 6a). On one hand, according to the
 468 trend of the influence of cathode lifetime on fossil resource depletion, it can be concluded that
 469 lifetimes over 100 hours were acceptable from this perspective. On the other hand, it was
 470 demonstrated that the steam consumption (for purification) is the hot spot in this case but the
 471 scores are similar in both alternatives ER CO₂ and CONV. The contributions of the steam
 472 consumption to the ADP-fossil values obtained, expressed as the net calorific value per unit of
 473 mass of FA, were 24 MJ·kg⁻¹ in CONV (from an overall value of 55 MJ·kg⁻¹) and around 18
 474 MJ·kg⁻¹ in ER CO₂ (from an overall value of 26.8 MJ·kg⁻¹). As it was expected, the main
 475 advantage of the route ER of CO₂ is the no utilization of any chemicals from the fossil-based
 476 industry, especially CO. This raw material is the main reactant in the CONV route together with
 477 CH₃OH. CO represents the highest score in the ADP fossil indicator of this manufacturing option
 478 (29 MJ·kg⁻¹ from an overall ADP fossil value of 55 MJ·kg⁻¹). CO is produced in the industry from
 479 a partial combustion of heavy oil (Swiss Centre for Life Cycle Inventories, 2016). Other
 480 contributions to the ADP fossil are negligible such as the anode (1.90·10⁻² kg·kg⁻¹), membrane
 481 (4.15·10⁻⁵ kg·kg⁻¹) and water (either 1.23·10⁻² kg·kg⁻¹ in ER or 7.00·10⁻³ kg·kg⁻¹ in CONV).



482

483 *Cathode lifetime needed to neglect the cathode influence in ADP fossil and ADP elements (influence
 484 ≤1%)

485 **Figure 6.** Influence of the cathode lifetime of the ER of CO₂ process (baseline) in the resource
486 depletion (ADP): (a) fossil (MJ-eq.) and (b) elements (kg Sb-eq.) and comparison with the
487 conventional process (CONV) (Functional unit: 1 kg of FA)

488

489 Regarding metals and minerals depletion (Figure 6b), the trend obtained for the influence of
490 cathode lifetime is similar to that obtained in the CF assessment. Cathode lifetimes about 48 hours
491 and 72 hours or more would be enough from a perspective of resource depletion both fossil and
492 elements, respectively. On the contrary, cathode lifetimes below those times values can make the
493 contribution of the cathode fabrication the main contributor, even more than the PV solar. This
494 fact is mainly related to the production of metals like Tin, which is used in the cathode fabrication.
495 It can be observed that the indicator ADP elements is also highly related with the PV solar
496 electricity, which represent a clear hot spot in this case. The high consumption of electricity in
497 the alternative CO₂ ER together with the fact that current developments of PV solar systems used
498 considerable amounts of metals and other materials, the resource depletion tend to dominate the
499 impact results of all those systems that use PV solar instead electricity from fossil fuels. Taken
500 into account the electrical consumption of our CO₂ ER system (12 kWh·kg⁻¹ of FA) the overall
501 ADP elements indicator of that system ($2.26 \cdot 10^{-5}$ kg·kg⁻¹ of FA) cannot be reduced below the
502 ADP elements value of CONV ($7.96 \cdot 10^{-6}$ kg·kg⁻¹ of FA). However, it is obvious that electricity
503 production through PV solar module is cleaner in terms of CF in comparison to coal and fossil
504 fuel in other impact categories. The use of PV solar reduces the CO₂ emissions but it can release
505 other hazardous substances during the manufacture still (Chatzisideris et al., 2016). In this
506 context, many efforts are being currently focussed on recycling the PV materials in order to
507 minimize the environmental effect of PV technology during the entire period of life (Tyagi et al.,
508 2013). Other contributions to the ADP elements are negligible such as the anode ($1.32 \cdot 10^{-7}$ kg·kg⁻¹
509 ¹), membrane ($6.31 \cdot 10^{-11}$ kg·kg⁻¹) and water (either $8.38 \cdot 10^{-9}$ kg·kg⁻¹ in ER or $4.56 \cdot 10^{-9}$ kg·kg⁻¹ in
510 CONV).

511 Considering that the ER process involves a high energy consumption from renewables, future
 512 research should consider other impact categories such as health impact, photochemical oxidant
 513 creation, terrestrial eco-toxicity, and ozone layer depletion, among others (Kouloumpis et al.,
 514 2015). In the present study, a sensitivity analysis of the influence of three sources of electricity in
 515 the three indicators studied was carried out. In this analysis, the electricity source was considered
 516 the same for both manufacturing alternatives for a fair comparison. Table 5 displays the total
 517 value of CF, ADP elements and ADP fossil obtained for the alternatives CONV and CO₂ ER.
 518 Cathode lifetime was considered endless in the case of CO₂ ER. The sources of the electricity
 519 supply analysed were: (i) electricity from wind (1 MW – 3 MW turbine, onshore); ii) electricity
 520 from photovoltaic (570 kWp open ground installation, multi-Si); and iii) fossil-based electricity.
 521 The process used come from the Spanish (ES) market (Swiss Centre for Life Cycle Inventories,
 522 2016).

523

524 **Table 5.** Environmental indicators per functional unit for the alternatives CONV and CO₂ ER
 525 using different sources of electricity (Spanish (ES) proxies) (Swiss Centre for Life Cycle
 526 Inventories, 2016) (Functional unit: 1 kg of FA produced)

Electricity source	CONVENTIONAL			ER of CO ₂ (<i>baseline scenario</i>)		
	CF	ADP elements	ADP fossil	CF	ADP elements	ADP fossil
	(kg CO ₂ - eq.)	(kg Sb-eq.) (x 10 ⁻⁶)	(MJ-eq.)	(kg CO ₂ - eq.)	(kg Sb-eq.) (x 10 ⁻⁶)	(MJ-eq.)
<i>Wind (ES)</i>	2.87	8.02	54.07	1.57	3.86	20.20
<i>Photovoltaic (ES)</i>	2.88	8.47	54.22	2.22	22.6	26.8
<i>Market group (ES)</i>	3.00	7.98	55.54	7.37	2.55	81.43

527

528 The sensitivity analysis confirms that the CO₂ ER process will have a lower CF than the CONV
 529 process providing that the electricity supply is based on renewables (either PV solar or wind)
 530 instead of fossil fuels. No doubt that the commercial CONV is involved into a clear fossil fuels

531 depletion even if renewable energy was supplied to a conventional plant. In fact, the total ADP
 532 fossil impact of CONV ranged between 54 MJ·kg⁻¹ and 55.5 MJ·kg⁻¹ of FA, no matter the applied
 533 energy source. It should be kept in mind that CONV presents a low electricity consumption (0.29
 534 kWh·kg⁻¹ of FA) and that ADP fossil indicator is almost dominated by CO (as raw material). As
 535 it was expected, only in the case that the CO₂ ER plant was supplied by electricity from the market
 536 group, both CF and ADP fossil values of this alternative would sharply increase (7.37 kg·kg⁻¹ and
 537 81.43 MJ·kg⁻¹ of FA, respectively) turning the alternative into non-environmental friendly.

538 3.2. Utility costs assessment

539 The prospect of producing FA by the ER of CO₂ at industrial scale depends not only from the
 540 operational and environmental perspectives but also from an economic framework. A preliminary
 541 economic feasibility analysis was performed in this section (Table 6). The analysis has considered
 542 only the cost of operation due to the current limited TRL level of the alternative CO₂ ER
 543 compared with the commercial route. It is worthy to note that the current CO₂ ER cells exist only
 544 at the bench scale with no standard design (Jouny et al., 2018). Until now, only lab-scale systems
 545 have been demonstrated (Del Castillo et al., 2017; Yang et al., 2017). Utility costs considered
 546 here includes raw materials and external energy (both electricity and heat as steam) and those
 547 were estimated from the current market prices. Both optimistic and conservative case-scenarios
 548 were created using the range of prices found in the literature (Table 2). The maintenance cost and
 549 consumables were excluded from this preliminary approach assessment as it depends basically
 550 on the industrial equipment (omitted from this study). Energy sources were considered the same
 551 for both ER and CONV processes to obtain a fair comparison between these alternatives. In
 552 particular, heat was assumed to come from steam as natural gas and electricity was considered as
 553 renewable (PV solar).

554 **Table 6.** Utility costs €per 1 kg of FA produced

	ER of CO ₂		CONV	
	<i>Optimistic</i>	<i>Conservative</i>	<i>Optimistic</i>	<i>Conservative</i>
<i>Raw materials</i>				
CO ₂	<i>free</i>	<i>free</i>	-	-

H ₂ O	<0.01	0.01	<0.01	<0.01
CO	-	-	0.04	0.04
CH ₃ OH	-	-	0.02	0.02
<i>Utilities</i>				
Electricity	0.05	1.14	0.01	0.03
Heat demand (Steam)	0.11	0.25	0.15	0.33
<hr/>				
Utility costs (€)	0.16	1.40	0.21	0.43
<hr/>				

555

556 The total cost of utilities of the alternative based on ER of CO₂ ranges from 0.16 €kg⁻¹ to 1.40
557 €kg⁻¹ of FA produced while that corresponding to the conventional route ranges between 0.21
558 €kg⁻¹ and 0.43 €kg⁻¹ of FA produced. A recent techno-economic study of the manufacture of FA
559 by another CO₂ valorisation option, direct hydrogenation of CO₂, has determined an overall
560 operating cost value around 0.58 €kg⁻¹ of FA (according to the market prices established in the
561 study and excluding maintenance, consumables, interest and salaries) (Pérez-Fortes et al., 2016).
562 In order to compare in a fair way, the utility costs obtained in our study, the cost of utilities of the
563 mentioned alternative was re-calculated using the LCI data showed in the reference but employing
564 the market prices established in our study. The range of the utility costs calculated was from 0.36
565 €kg⁻¹ and 0.54 €kg⁻¹ using both optimistic and conservative market prices. It should be noted
566 that the alternative showed in the reference presents a low consumption of utilities due to the fact
567 that the plant integrates part of the heating needs. In the case of the present study, most of the cost
568 of utilities was associated with the high electricity consumption by the ER cell. It should be noted
569 that the baseline case for modelling exhibited a moderate faraday efficiency (42%); however,
570 recent studies have suggested faradaic efficiencies up to 90% for the chemical FA (Jouny et al.,
571 2018). The fulfillment of this fact would finally represent a great drop in the utility costs (from
572 1.40 €kg⁻¹ to just 0.16 €kg⁻¹ of FA). On the other hand, the challenging distillation process as
573 demonstrated by the heat cost is similar in both processes. Of course, other cost-effective
574 processes than distillation could be explored for further improving the profitability of FA. As
575 stated earlier, there are industrial processes that may be more cost-effective than distillation,

576 which could further improve the profitability of formic acid. The economic results obtained have
577 demonstrated that FA could be a promising and profitable CO₂ reduction product under an utility
578 costs perspective. Note that an overall economic assessment must take into account the state-of-
579 the-art technology, such as catalyst, ER cell design, separation technology, and storage.

580

581 **4. Conclusions**

582 This study has demonstrated that the electrochemical reduction (ER) of CO₂ into formic acid (FA)
583 can be potentially a sustainable option under proper technological developments promoting a
584 decarbonised chemical industry. We have developed a model based on mass and energy balances
585 that used current lab-scale data and can take into account the influence of the lifetime of the
586 cathode. This model was employed to calculate the reduction of the CF of FA produced by means
587 of the ER of CO₂ compared to the CF of FA from typical industrial plants based on the
588 carbonylation of methanol. According to our estimations, cathode lifetimes over c.a. 210 hours
589 were enough to neglect the influence of the cathode (and hence the ER cell) from an
590 environmental perspective. The environmental assessment results obtained in the present study
591 have demonstrated that this technology could play a significant role in the natural resources
592 savings, especially fossil fuels (in terms of ADP-fossil) in the comparison against industrial plants
593 based on the carbonylation of methanol. The ER of CO₂ option represents a prominent fossil fuel
594 savings related with CO used as raw material in the commercial/conventional process. However,
595 the indicator results of ADP elements were highly influenced by PV solar electricity used in the
596 ER alternative. In fact, electricity consumption has represented one of the hot spots of the ER
597 alternative. Dismissing the cathode influence (in general, for a cathode lifetime over 210 h), the
598 main contribution to the indicator ADP elements was the electricity consumption (due to PV solar
599 modules manufacture) while the consumption of steam was the main contribution to the indicators
600 GWP for CF and ADP fossil. A percentage of 97% of the score ADP elements obtained
601 corresponded with the PV solar electricity while the share of steam consumption in CF and ADP
602 fossil scores were 62% and 67%, respectively. The high consumption of electricity together with

603 the fact that current developments of PV solar systems used considerable amounts of metals and
604 other materials have turned out that PV solar electricity presented the highest score in the ADP-
605 elements indicator. Overall, further efforts are still needed to develop catalysts for CO₂ reduction
606 achieving high current densities, and better efficiencies both energetic and faradaic. An optimistic
607 ER scenario has demonstrated that the electricity consumption could be reduced almost to the
608 value of a conventional plant. The separation step is another hot spot of the synthesis of FA.
609 However, this was found in both alternatives (conventional and ER of CO₂) and this could be
610 overcome by using other cost-effective processes than distillation or even by using renewable
611 steam. The economic results obtained have demonstrated that FA could be a promising and
612 profitable CO₂ reduction product under a utility costs perspective. A remarkable drop in the
613 operational cost (from 1.40 €kg⁻¹ to 0.16 €kg⁻¹ of FA) could be reached when the recently
614 proposed target of faradaic efficiency (90% for the chemical FA) can be achieved, which is
615 expected for the future ER of CO₂ developments.

616 **Acknowledgments** Authors thank to Spanish Ministry of Economy and Competitiveness
617 (MINECO) for the financial support through the project CTQ2016-76231-C2-1-R. We would like
618 also to thank MINECO for providing Marta Rumayor with a Juan de la Cierva postdoctoral
619 contract (FJCI-2015-23658).

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