**Technical and economic analysis of most promising electrochemical routes**

**for the conversion of CO2 to formic acid**

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**1.Introduction**

In the last decade, the electrochemical conversion of CO2 (ERCO2) to formic acid (FA) using Sn-based cathodes, was widely investigated *i*) to valorise waste-CO2 as a feedstock to produce value-added chemicals, ii) from the industrial standpoint, to cope with the stringent environmental regulations on greenhouse gas (GHG) emissions and *iii*) to potentially store the excess electric energy from intermittent renewable sources as chemical energy. Among the ERCO2 products, FA is a valuable building block with a mature market and a relatively high value, which is used in food technologies, agriculture and pharmaceutical industry [1]. Currently, the synthesis of FA is a fossil fuels-based process, which is not straightforward neither environmentally friendly [2]. Extensive studies have shown that ERCO2 using Sn-based cathodes can lead to the production of FA/formate with high selectivity. Appealing results were reported by using both Sn gas diffusion electrodes (GDEs) and high CO2 pressures (HPs); however, to date, the real potential of ERCO2 on an industrial scale is still uncertain [3] 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 were examined. 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.

**2. Methods**

*Analysis of the main costs.* The technical-economic analysis reported in this work includes the main costs related to the stages of *i*) CO2 capture and recycling (C&R), *ii*) ERCO2 and, *iii*) FA concentration and separation (C&S). The total cost for the conversion of CO2 into FA at 85%wt. was estimates by eq. (1).

CEP =CC&R +CE+CC&S (1)

where CC&R are the costs due to the carbon capture and recycling; CE are the total costs of the electrolysis, including the capital investment (CE–I) and energetic costs (CE–O) and CC&S are the costs related to the C&S of the FA solution up to 85%wt. The main figures used for the estimation of the costs as described in detail in Proietto et al. [3].

**3. Results and discussion**

A simplified supply chain was envisioned, which includes the stage of i) CO2 C&R, ii) ERCO2 and, iii) FA C&S. For the ERCO2 stage, five case studies (CSs) including the utilisation of GDE-based technologies at atmospheric pressure (CS I [4], CS II [5], CS III [6]) and of pressurised systems equipped with simple Sn plate cathodes (CS IV[7], CS V [8]), were investigated in detail.

Figure 1 reports an estimation of the overall costs for the electrochemical conversion of CO2 to FA at 85%wt., CEP, for each CSs. CS I presents the highest CEP followed by CS V, CS II, CS IV and CS III. To show their market competitiveness, CEP was compared with the sum of the costs for producing FA by the conventional chemical route (CCP) and the Carbon Tax (CT) value, that would be saved by converting CO2 into FA, CCP+CT, and the FA market price (PFA) (Fig.1). It was shown that, to date, the electrochemical route is not more cost-effective than the commercial chemical one. The C&S stage presents the highest costs (Fig.1) due to the low final concentrations of FA obtained in the electrolysis stage (<10%wt.). Overall, CS III and IV presented the lowest CEP since these processes presented the highest final [FA]. In addition, the technological improvements necessary to achieve a process sustainable from an economic point of view were identified and discussed for the future steps of research. Hence, several scenarios, characterized by some potential target technological improvements, were envisioned aiming to find the bottlenecks of each technology, to reduce the CEP and to highlight the challenges that need to be faced for the implementation on a large-scale.



**Figure 1.** Comparison of the CEP for each CS with the FA market price, PFA (0.6–1 €/kgFA), and the sum of conventional production process cost and the Carbon tax (CCP = 0.475 €/kgFA and CT = 0.025 €/kgFA) [3].

**4. 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. 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. In addition, it was shown that the successful implementation of different technological improvements for both electrochemical routes 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 ~120 mA cm-2, FE ~ 95%, [FA] > 30% wt., and low EC as well as long term stability. For GDE-based technologies, several efforts must focus on 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. Furthermore, it was shown that the potential use of excess electric energy generated by renewable sources to feed the electrolyser could significantly reduce the cost of energy.

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