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Sustainable Electrochemical Production of Tartaric Acid

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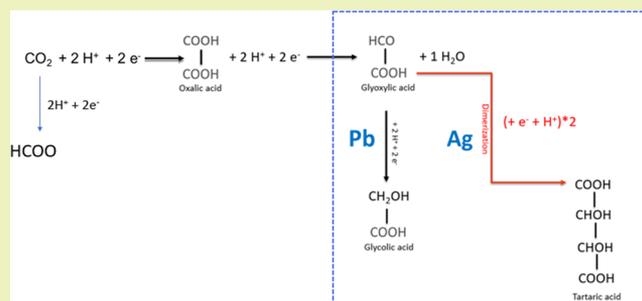
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Supporting Information

ABSTRACT: Herein, we describe a study of the electrochemical reduction of oxalic and glyoxylic acids toward a feasible green and sustainable production of tartaric acid in aqueous and/or acetonitrile solvent using silver and lead electrodes. Our results show that on the silver electrode, for both oxalic acid and glyoxylic acid, the reduction reaction is more favorable toward the dimerization step, leading to tartaric acid, due to the increase in the local pH, while on the lead electrode, the step involving the protonation of the intermediate is more favorable, leading to the formation of glycolate. Techno-economic analysis shows that tartaric acid production from glyoxylic acid and from oxalic acid via electrochemical synthesis can be a potential process at the industrial scale. In the present case, the oxygen evolution reaction was chosen as the reaction at the other electrode for practical reasons, but oxygen is a low-value product. Another anodic reaction with a more valuable oxidation product can be selected to increase the profitability of the overall electrochemical process and thereby decrease the total production costs of tartaric acid.

KEYWORDS: *electro-organic synthesis, green synthesis, sustainable chemistry, electro-dimerization reaction, tartaric acid production, techno-economic analysis*



1. INTRODUCTION

The development of green industrial processes has been attracting more attention in the last years, and it requires renewable energy sources. Large-scale electrification of the energy and chemistry sectors is a crucial condition for the transition from a society based on fossil resources to a sustainable society based on renewable building blocks.

Electricity or electrons hold the key for transferring the renewable energy generated by sunlight or wind, ultimately enabling greener industrial processes. In parallel, the use of electrochemical methods for the synthesis of organic molecules has undergone a revival in last few decades^{1,2} because it enables the direct use of electricity to generate valuable compounds.

Transformation of CO₂ into chemicals has been intensively studied over the past decades because this molecule can be used as C₁ feedstock in electro-organic synthesis due to its abundant, cheap, renewable, and non-toxic nature.^{3–5} Of particular interest of this molecule is the synthesis of two- to four-carbon atom products (C₂–C₄), which, besides adding value, are key chemical feedstocks to synthesize a wide range of products such as polymers, solvents, drugs, central metabolites, etc.^{5–9} Electrosynthesis has also been shown to be efficient for the synthesis of azoxy-, azo- and amino-aromatics using a CoP nanosheet catalyst,¹⁰ which are important building blocks in materials science pharmaceuticals, and synthetic chemistry.

Concerning the synthesis of C₂–C₄ products, tartaric acid (TTA) attracts attention because it is an important product

used in the textile printing, dyeing, pharmaceutical, and food industries.¹¹ It is found in the juice of grapes and is a byproduct in the wine industry, and commercially, it is produced by oxidation of carbohydrates and maleic acid.^{11–13}

In the past years, the price of TTA and its salts has varied as much as 50%, as might be expected when the source of the raw material is a by-product of another industry. The global market value of TTA reached a value of USD 215.7 million in 2017 and is expected to grow at a compound annual growth rate (CAGR) of 5.77%.¹⁴ In this sense, finding new pathways for the synthesis of TTA that could be more selective and profitable can represent a big business opportunity.

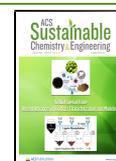
Electrochemical synthesis is a potential candidate since TTA can be easily produced from the electrochemical reduction of glyoxylic acid (GLYA)^{11,15} following the mechanism shown in Figure 1. GLYA is also a product from the electrochemical reduction of oxalic acid (OxA), a C₂ product from CO₂ reduction,¹⁵ which makes its production a sustainable process.

Despite innumerable papers on building blocks from CO₂ electrochemical reduction, still little is known about the reaction pathway that leads to the formation of TTA.

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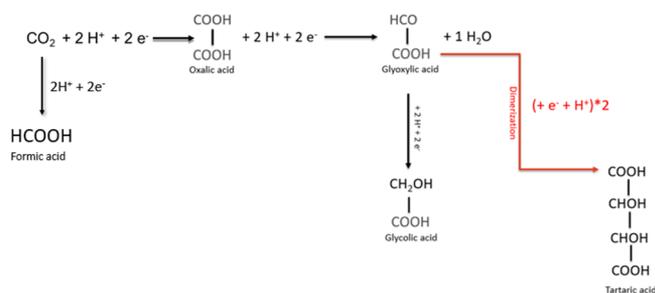


Figure 1. Reaction pathway for the electrochemical reduction of carbon dioxide toward C₂–C₄ products.

According to Egghins et al.,¹² glyoxylic acid can be formed directly from the electrochemical reduction of CO₂ at pH 9–10 on mercury and glassy carbon electrodes, while on lead electrode, only glycolic acid was detected as the main product. The authors showed that the electrochemical reduction of glyoxylic acid goes via two-electron transfer to give glycolic acid, but it can also be reduced to a pinacol dimer by one-electron transfer, which results in the formation of tartaric acid (red pathway, Figure 1).

In order to understand the conditions (solvent and reactant) that favor the mechanism of the reaction through one- or two-electron transfer, we investigated the electrochemical reduction of oxalic and glyoxylic acids using (Ag) and lead (Pb) electrodes.

Our results showed that the reduction of OxA and GLYA in acetonitrile (ACN) and aqueous solvent, respectively, are more selective to TTA on Ag electrode, while on Pb electrode, the reactions are more selective to the production of glycolic acid (GA), meaning that on Ag electrode, the dimerization step is more favorable, while on Pb electrode, the reduction step to GA involving two electrons is dominant.

In order to evaluate the commercial feasibility of an industrially relevant process for the production of TTA from GLYA or OxA, a techno-economic analysis (TEA) has been performed. The results point out that the synthesis of TTA from both OxA and GLYA is a potential industrial electrochemical process.

2. EXPERIMENTAL DETAILS

The electrochemical measurements were performed in a two compartment electrochemistry cell configuration (H-type cell) at room temperature using platinum (Pt) wire and an Ag/Ag⁺ as counter and reference electrodes, respectively. The reference electrode was prepared with an Ag wire in a solution of 0.1 M AgClO₄ (97% from Sigma-Aldrich) or a solution of 0.1 M AgClO₄ in ACN (99.8% anhydrous from Sigma-Aldrich) as described previously.⁸ Prior to the measurements, the working electrodes Ag and Pb wires (10 cm²) were cleaned by polishing with alumina suspension, rinsed with Milli-Q water (18.4 MΩ), and sonicated for 5 min in acetone/water solution (1:1) in the case of Ag, and electropolished in 0.1 M H₂SO₄ (98% from Sigma-Aldrich) by applying –2.5 V during 500 s, in the case of Pb.

The electrochemistry measurements were carried out in aqueous solution using buffer phosphate (pH 7.5) as a supporting electrolyte and in ACN solution containing 0.1 M of supporting electrolyte tetraethylammonium chloride (TEACl) (99.0% from Sigma-Aldrich). Prior to the measurements, nitrogen gas (Linde) was purged into the electrolyte for 10 min to remove oxygen. Cyclic voltammograms (CV) were recorded to test the profiles of each metal in the different supporting electrolytes. Next, appropriate amounts of OxA or GLYA (both, 98% from Sigma-Aldrich) were added into the cell in order to study the electrochemical reduction of the corresponding reactant to TTA.

Afterward, electrolyses were performed at different potentials for 5–6 h. All electrochemical measurements were controlled with a potentiostat/galvanostat (μ Autolab Type III). All the potentials described in this work are related to the Ag/AgCl. It is important to mention that IR-correction was controlled in all experiments.

During electrolyses, samples were collected every 1 h. The liquid products of the reaction were analyzed by high-performance liquid chromatography (Agilent – 1260-Infinity, HPLC). A total of 30 μ L of the sample was injected into the column configuration of an Aminex HPX-87H and diluted sulfuric acid (0.5 mM) was used as the eluent. The temperature of the column was maintained at 45 °C, and the separated products were detected with a refractive index detector (RID-10A). The expected products were analyzed separately to produce standard calibration curves.

With respect to the TEA, capital expenditure (CAPEX) and operational expenditure (OPEX) of the processes were estimated for case 1, GLYA→TTA, and case 2, OxA → TTA, for a continuous production using an electrochemical flow cell (see Figure S5 in the Supporting Information). The CAPEX corresponds to the capital investment referred to the electrochemical cell and the supporting equipment around it, and the OPEX refers to the energy costs

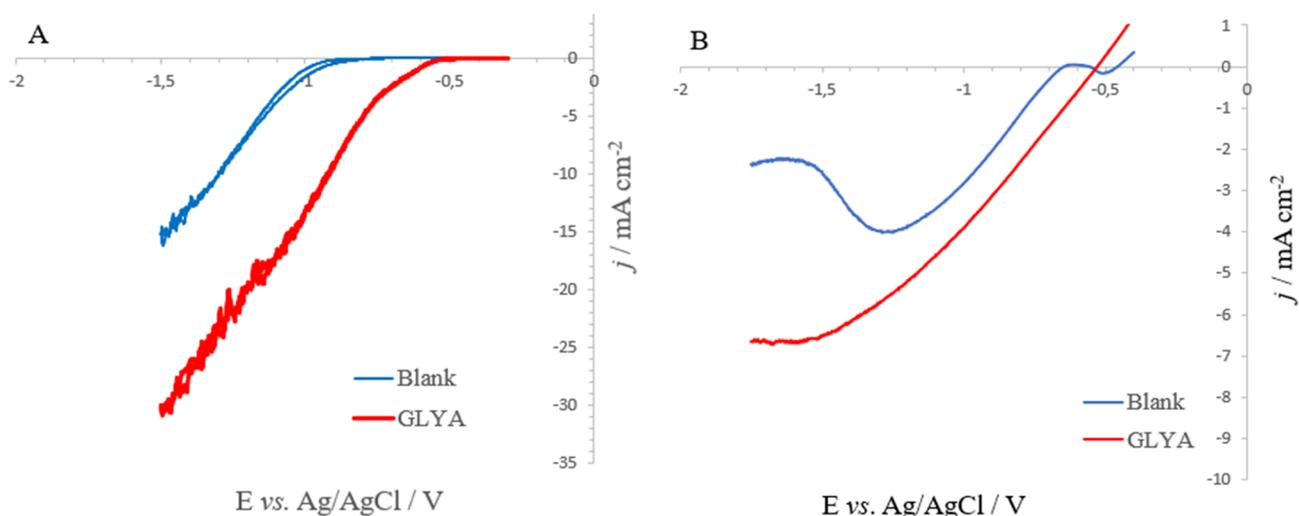


Figure 2. Cyclic voltammograms of (A) Ag and (B) Pb electrodes obtained in phosphate buffer solution (pH 7.5) + 0.1 M GLYA at 10 mV s⁻¹.

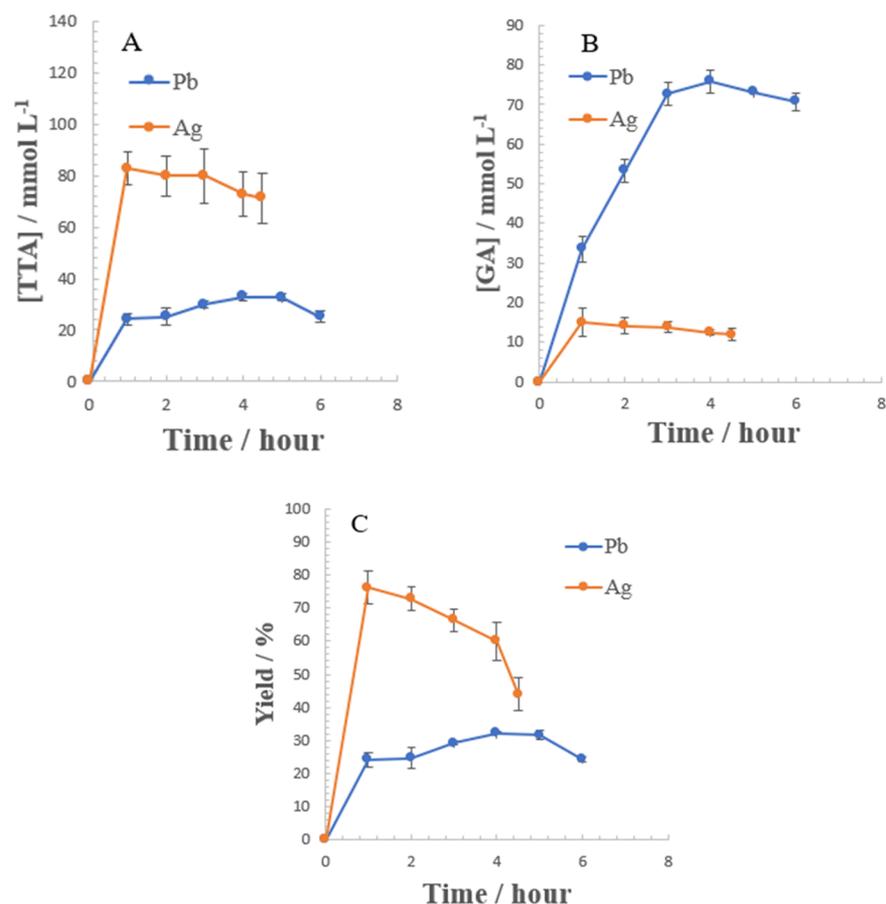


Figure 3. Concentration of (A) TTA and (B) GA and (C) yield (%) toward TTA using Ag and Pb electrodes in pH 7.5 buffer phosphate solution containing 0.1 M of GLYA. $E = -1.0$ V versus Ag/AgCl.

(electricity) and the purchase of the reactant. CAPEX and OPEX lead to the total production costs of TTA, in $\left[\frac{\text{€}}{\text{kg TTA}}\right]$, which are compared to the current market price of TTA as a reference for the economic feasibility for both case 1 and case 2. More information about the calculation procedure and assumptions taken in the TEA can be found in the [Supporting Information](#), Section Techno-Economic Analysis.

3. RESULTS AND DISCUSSION

3.1. Electroreduction of Glyoxylic Acid in pH 7.5 Buffer Phosphate Solution. The voltammetric profiles for the electrochemical reduction of GLYA on Ag and Pb electrodes in 0.1 M phosphate buffer solution are depicted in [Figure 2](#). The blank CVs (blue line) show that the onset potential for the hydrogen evolution reaction (HER) on Ag electrode ([Figure 2A](#)) is close to -0.9 V, while on Pb electrode ([Figure 2B](#)) a broad cathodic peak is observed at -1.3 V. According to the literature,¹⁶ this peak is related to the reduction of PbHPO_4 , since in the presence of phosphate solution, lead is oxidized to hydrophosphates at around -0.58 V and is further reduced to lead metal at around -1.1 V. In the particular case of the Pb electrode, the positive current observed at the beginning of the curve is due to the fact that Pb can be oxidized at a negative potential, giving rise the positive peak; however, as we scanned up to -1.8 V, the oxide is reduced and this does not change the properties of our catalyst.

The addition of the corresponding amount of GLYA into the solution shifted the curve to more positive potential (approximately -0.5 V) on Ag, indicating a competition between the electrochemical reduction of GLYA and the hydrogen evolution reaction (HER).¹⁷ On the Pb electrode, the same shift was observed (approximately -0.55 V) and the cathodic peak, previously observed in the blank solution, is no longer well defined, suggesting that, on the Pb electrode, GLYA inhibits the formation of PbHPO_4 and the observed currents result from the HER and GLYA reduction reactions. A comparison between both electrodes shows that the current density obtained from the GLYA reduction is four times higher on Ag than on the Pb electrode, suggesting that the Ag electrode is more active toward electrochemical reduction of GLYA and HER than Pb.

To investigate the electrochemical conversion of GLYA to TTA, electrolyses were performed at -1.0 V for 5 and 6 h on Ag and Pb electrodes, respectively.

Comparison of the concentration of TTA and GA, which are the main liquid products detected by HPLC, versus time are displayed in [Figure 3](#) for both electrodes. According to the results, the Ag electrode is more active for the reduction of GLYA to TTA ([Figure 3A](#)) with a maximum concentration of TTA of 80 mmol/L obtained after 1 h of electrolysis versus 30 mmol/L obtained for the Pb electrode, which was revealed to be more active toward the formation of GA ([Figure 3B](#)). These results also shown that in the first hour, the reduction of GLYA to TTA is faster; afterward, tartaric acid is likely reduced to other products due to the high enough applied potential.

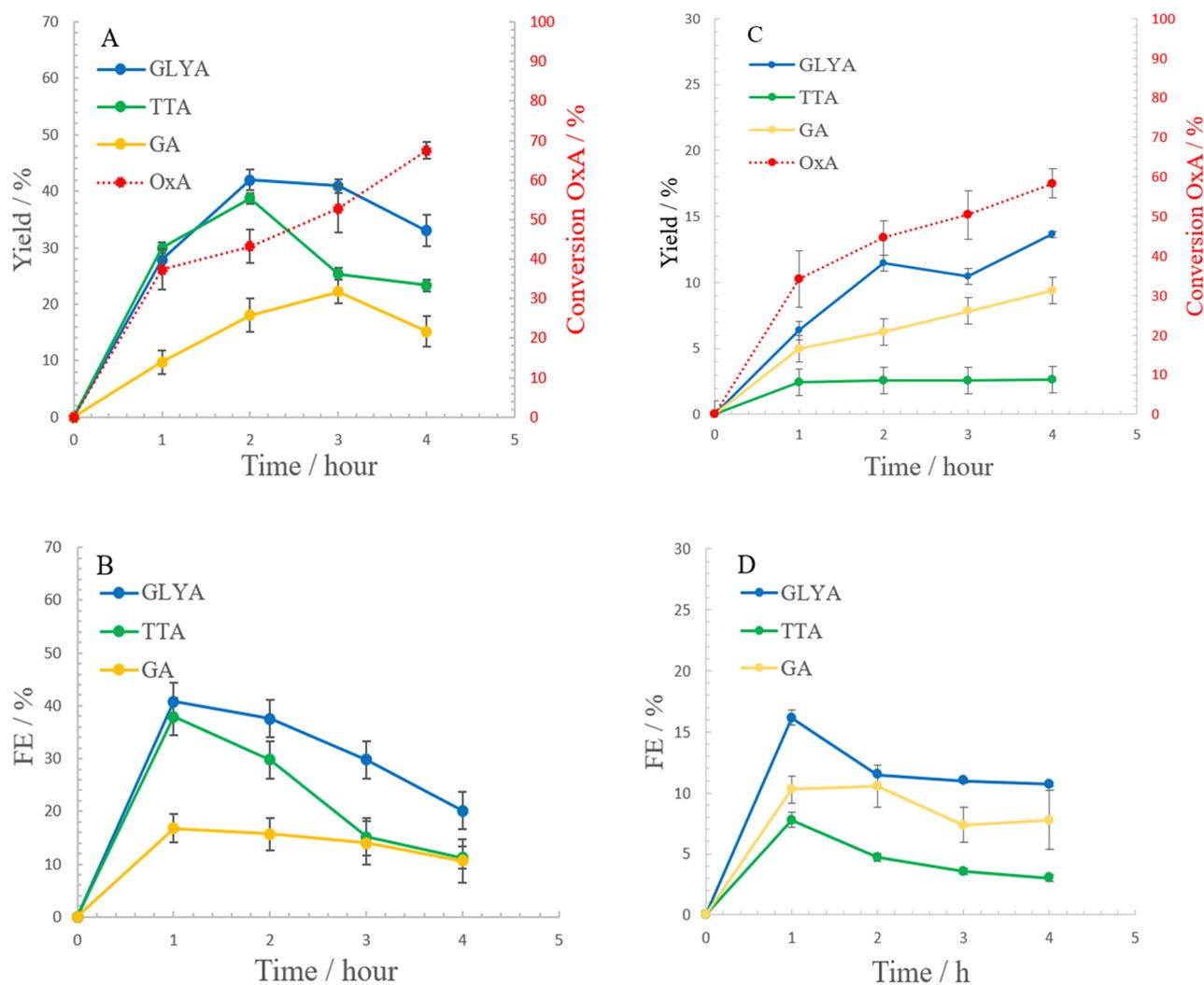


Figure 4. Calculated yield, conversion, and faraday efficiency of the main liquid products detected by HPLC on (A, B) Ag and (C, D) Pb electrodes in ACN solution +0.1 M TEACl +0.1 M OxA.

The yield toward the production of TTA (Figure 3C) also shows higher values for Ag electrode, ~80 versus 30% for the Pb electrode. The conversion of GLYA and the Faraday efficiency (FE%) toward TTA and GA are presented in the Supporting Information, Figure S1.

The results show that the conversion on both Ag and Pb electrodes are very similar; however, the FE obtained for the production of TTA on the Ag electrode was 70% in the first hour, dropping to 50% in the next hours, and around 25% on the Pb electrode, while the overall FE% toward GA was 10 and 50% obtained on Ag and Pb electrodes, respectively. These results suggest the formation of other products than TTA and GA from the reduction of GLYA. Indeed, the chromatograms obtained from the HPLC analysis indicated other peaks; however, we could not identify them. Moreover, it is likely that hydrogen is a product from the electrochemical reduction of GLYA on both Ag and Pb electrodes in aqueous buffer phosphate solution.

3.2. Electrochemical Reduction of Oxalic Acid in ACN.

In order to investigate the effect of the solvent and to minimize the competition with the HER, the synthesis of TTA was also investigated from the electrochemical reduction of OxA in ACN solvent containing 0.1 M TEACl. Voltammetric studies were carried out using Ag and Pb electrodes to determine the

appropriate potential for controlled electrolyses. According to the voltammograms showed in Figure 2, the current density obtained for the Ag electrode in ACN solution containing OxA is slightly lower than the currents obtained on the Pb electrode. A cathodic peak, which corresponds to the reduction of ACN is observed at around -0.5 and -0.8 V on Ag and Pb electrodes, respectively. A reduction wave is observed at -0.8 V on the Ag electrode and at -1.0 V on the Pb electrode, suggesting that this is the onset potential for the electrochemical reduction of oxalic acid. The lower current densities obtained in acetonitrile solution in comparison with the results obtained in aqueous solvent (Figure 2) is due to the lower activity of oxalic acid reduction in the organic medium and also lower competition with the hydrogen evolution in organic solvents.^{18,19}

Chronoamperometry measurements were carried out at -1.0 and -1.3 V using Ag and Pb electrodes, respectively, because at more negative potential TTA can be electrochemically reduced to malic acid.¹⁵ The yield % and FE % related to the main liquid products detected by HPLC are shown in Figure 4.

On both Ag and Pb electrodes, GLYA, GA and TTA are products from the electrochemical reduction of OxA in ACN. On the Ag electrode (Figure 4A), GLYA was found to be the

main product with a maximum of 45% yield after 2 h of electrolysis, and TTA is the major product from its over-reduction, with 40% yield after 2 h compared to 20% yield toward GA. The corresponding overall FE values (Figure 4B) for GLYA, TTA, and GA are 40, 35, and 15%, respectively, suggesting that hydrogen is also formed during the reduction of OxA in acetonitrile solution. Afterward, these values drop, likely because of the over-reduction of these products and mainly because of the concentration of reactant (OxA) decreasing due to the high conversion, as seen in Figure 4A (red line).

A different trend was observed on the Pb electrode (Figure 4C). The reduction of OxA also led to GLYA, GA, and TTA; however, in this case, the yield and FE toward GA were higher than the values obtained for TTA. This fact suggests that on the Pb electrode, the electrochemical reduction of OxA leads to GLYA, with the latter being more favorably reduced to GA than to TTA. Another important observation is that the corresponding FE (Figure 4D) is relatively low, 15, 10, and 5% for GLYA, TTA, and GA, respectively, meaning unidentified products were formed.

The results also show that the conversion rate of OxA is higher on Ag than on the Pb electrode, in agreement with the higher values of yield and concentration (Figure 3) of products obtained for the Ag electrode.

Comparing the values of yield obtained in aqueous (Figure 3C) and acetonitrile (Figure 4A and C) solutions, Ag electrode showed to be more selective toward the production of TTA than the Pb electrode, in both solvent conditions. Our results show that the product distribution depends on the solvent and nature of the metal quantitatively, since TTA and GA were observed in both Ag and Pb metal electrodes.

In a previous paper, Parker et al.²⁰ showed using carbon, lead, and mercury electrodes that during the electrochemical reduction of carboxylic acids in basic solution, the predominant mechanism involves the dimerization of the anion radical, whereas in neutral and acid solutions, protonation of the radical anion precedes dimerization.¹²

In aqueous solvent (pH 7.5), the electrochemical reduction of GLYA competes with the HER (eq. 01), and as a consequence, the pH of the solution close to the electrode tends to become more alkaline due to the generation of OH⁻ (hydroxyl ions).



Although the concentration of water in ACN solution is low, still HER can take place, showed by Ledezma-Yanez and Koper,¹⁸ leading to the generation of OH⁻ as well; however, comparing the blank cyclic voltammograms (blue line) obtained for each metal in the different solvent conditions (Figure 2 and Figure S2), the current densities are much higher in buffer solution (pH 7.5) than in acetonitrile solution, meaning more OH⁻ is generated in aqueous solution, as expected.¹⁹ As a consequence, the local pH effect is higher in water solution than in acetonitrile. This observation explains the higher yield toward TTA (dimerization step) obtained in aqueous solvent than in ACN solution, in agreement with the observation of Parker and Lerflaten.²⁰

According to our results, there is a local pH effect of the solvent on the mechanism of the reaction, but clearly, there is also a dependence on the metal electrode, since in both solvent conditions, we showed that Ag electrode is more selective to the production of TTA, while Pb is more selective toward GA.

On the one hand, in aqueous solution, Ag is more active for the HER than Pb, as observed by the higher current densities (Figure 2A and B). Consequently more OH⁻ is produced, turning the pH more alkaline, which favors the dimerization of glyoxylate radical to TTA, but in ACN solution, the current densities are similar. The difference in trend related to the predominant mechanism of the reaction toward TTA or GA can be explained by the fact that Pb electrode is considered an inert electrode due to the weak interaction between the electrode and reactants and intermediates.²¹ We therefore postulate that for the dimerization step to proceed, the intermediate glyoxylate should interact with the electrode surface so the electron transfer can take place, if this interaction is weak the intermediate will be easily protonated, giving rise to GA.

Based on this discussion, we propose a general mechanism (Figure 5) for the electrochemical reduction of OxA and/or

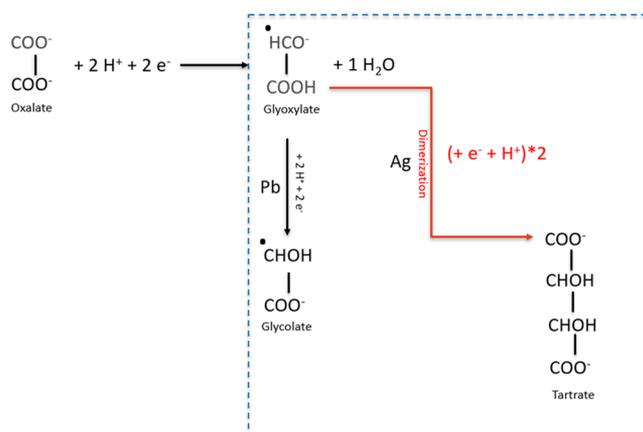


Figure 5. OxA and GLYA reduction mechanism for acetonitrile and aqueous solutions, respectively, on Ag and Pb electrodes.

GLYA, in ACN/organic and aqueous solvents, respectively, which explains the different results observed on Ag and Pb electrodes. First, oxalate anion is reduced via a two-electron step to the glyoxylate anion radical. Glyoxylate can be reduced via two different pathways, and we showed that this step depends on the local pH: in more alkaline local pH, the formation of tartrate by a one-electron reduction of glyoxylate is followed by a dimerization (pinacol formation), and another pathway, less alkaline local pH, via the two-electron step that gives glycolate, similar to what is observed in photochemistry, which during the irradiation, glyoxylic acid can undergo α cleavage or participate in hydrogen abstractions leading to the production of glyoxal.²² Similar to the electrochemistry, in photochemistry, tartaric acid was also identified as a photo-product from the glyoxylic acid.

Our results pointed out that on the Ag electrode, the predominant mechanism is the one involving dimerization of the glyoxylate anion radical, while on Pb, the protonation of the radical anion precedes dimerization.¹²

3.3. Results from Techno-Economic Analysis. To evaluate the economic feasibility of the studied reactions for TTA synthesis, a techno-economic analysis (TEA) for the TTA industrial production is performed for two cases with different starting materials: case 1, GLYA \rightarrow TTA, and case 2, OxA \rightarrow TTA.

The chosen process conditions of the electrochemical reaction to perform the TEA must match those of an

optimized industrial process. Thus, best case scenario values for Faradaic efficiency, product yield, and current density are selected to make the production of TTA economically feasible in terms of the electrochemical process. The only experimental value used in the TEA is the cathode potential for the electroreduction on both cases, as it is understood that it will remain the same for a scaled-up electrochemical process.

The oxidation reaction on the anode is chosen to be the oxygen evolution reaction, as it is a non-limiting reaction for the GLYA or OxA reduction reactions to TTA. It is assumed that the OER has no influence on the TTA production at the cathode, but it does have an effect in the economics of the process, as it determines the anode potential and, subsequently, the total cell voltage. The produced oxygen in the anode is not accounted for in the economic analysis, as it is a low-value product compared to TTA.

In this analysis, the downstream processing strategy for the purification of the TTA and its cost estimation are out of the scope of the present work. The performed TEA is intended to give a preliminary order of magnitude estimation of the production costs of TTA, and assess the feasibility of such an industrial process.

In Figure 6a, a comparison between the total production costs of cases 1 and 2 for an industrial scale electrochemical

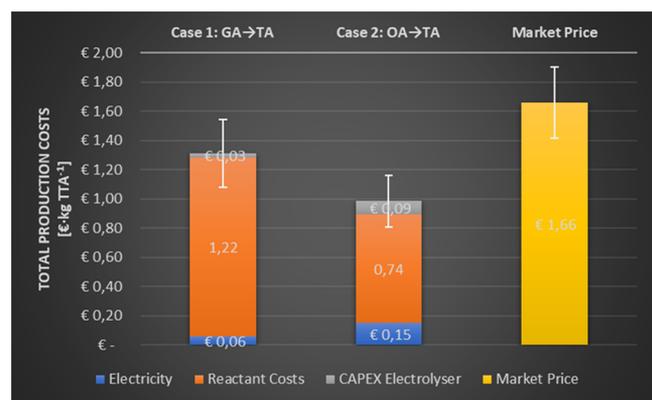


Figure 6. OPEX, CAPEX, and total production costs for TTA for case 1 (from GLYA) and case 2 (from OxA) and market price for TTA from vendors. More information about the TTA market price can be found in the Supporting information, Section Techno-Economic Analysis.

process, and the current market price for TTA, is shown. The most remarkable cost for both cases is the reactant cost, representing 93 and 75% of the total production costs for cases 1 and 2, respectively. In both cases, the process economics are dominated by the price of the starting materials, indicating that the selected process conditions to run the reaction minimize the CAPEX and electricity consumption. This fact renders the present process tremendously dependent on the raw material costs. The uncertainty on the reactant costs ranges is represented by the error bars, being ~20% for both cases and around 15% for the TTA market price.

4. CONCLUSIONS

We showed a green and sustainable method to produce tartaric acid efficiently using electrosynthesis as the approach.

The elucidation of the mechanism of the electrochemical reduction of OxA and GLYA toward the formation of TTA is

complex, since it involves the formation of intermediates and reaction steps including protonation and dimerization.

We showed by a combination of basic electrochemical measurements and analytical techniques that the formation of pinacol, which is the main intermediate for the formation of the dimer, is dependent on the local pH and on the electrode material. On the Ag electrode, either OxA and GLYA, in ACN and aqueous solution, respectively, the reduction reaction is more favorable following the dimerization step, leading to TTA, as a consequence of the increase in the local pH due to the higher concentration of OH⁻, that are produced by the HER. On the Pb electrode, the generation of OH⁻ is lower due to the lower activity of this metal to HER. Moreover, the Pb electrode displays a weak interaction between reactant and intermediates, and as a consequence, the protonation of the intermediate is favorable, leading the reaction to the formation of glycolate.

Our experimental results have provided information that helps to develop an efficient and continuous process for the production of TTA.

The performed TEA showed that TTA production via electrochemical synthesis has the potential to be industrially scaled up for both cases, from GLYA and from OxA. A more detailed study including the downstream processing for the purification of TTA is necessary to have a more realistic cost estimate. One way to increase the profitability of the TTA production process is to valorize the anodic product. In the present case, OER was chosen due to practical reasons—well-understood reaction, non-limiting with respect to TTA production in cathode—but oxygen is a low-value product. Another anodic reaction with a more valuable oxidation product can be selected to increase the profitability of the overall electrochemical process, and so, decrease the total production costs of TTA.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c02493>.

Cyclic voltammograms in organic solvent, analytical results obtained from electrolysis measurements, and detailed Techno-economic analysis (TEA) for the TTA industrial production (PDF)

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Notes

The authors declare no competing financial interest.

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