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Two-steps synthesis of D-glucaric acid via D-gluconic acid by electrocatalytic oxidation of D-glucose on gold electrode: influence of operational parameters.

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ABSTRACT

Glucose electrooxidation to glucaric acid, a highly valuable platform chemical, has been conducted, for the first time, in two consecutive steps employing a bare gold electrode in a batch reactor. The first step, at low potential, enabled the effective formation of the intermediate, gluconic acid, promoted by the oxidation of the aldehyde group on C1. For this reaction step, except for the reaction time, all the operational parameters had a strong impact on the selectivity. At the optimal conditions of pH 11.3, 5 °C and 0.04 M initial glucose, a maximum selectivity of 97.6% was obtained, the highest reported to date for the electrochemical process, with a conversion of 25%. At higher potential, gluconic acid was further converted to glucaric acid by the oxidation of the hydroxymethyl group on C6. For this oxidation step, the variation of the operational parameters (pH, gluconic acid initial concentration, reaction temperature and time) had no conspicuous effect on the selectivity, while the applied potential had a major role: at 1.1 V_{RHE}, a maximum selectivity of 89.5% to glucaric acid was obtained, which is one of the highest values reported in literature so far. In all experiments, irrespective of conditions and reaction time, a maximum concentration of ca 1.2 mM of glucaric acid was achieved, and a drastic decrease of the current density was observed in the first hours of electrolysis. Additional control experiments revealed a poisoning process caused by glucaric acid that, once formed, remains strongly bonded to the catalyst's active sites, thus deactivating it.

Introduction

The transition from a fossil-fuel economy to a carbon neutral economy has become an essential target in the ambition to stop global warming. This will inevitably pass through the use of renewable energy, such as wind, water and solar [1]. In the same way, also the production of chemicals has to reduce its dependence on petroleum-based feedstocks, and encourage, instead, the use of waste biomass (estimated at up to 138 million tons per year in the European Union alone [2]), fitting with the concept of circular economy. The production of value added chemicals from biomass represents a key opportunity for the chemical industry [3]. The selective oxidation of glucose to glucaric acid, via gluconic acid, is a perfect example of the biomass-to-chemicals value chain [4]. Gluconic acid and its salts are valuable compounds with numerous applications in the food and beverages, pharmaceuticals, textile and paper industries [5–7]. In

2004, the US Department of Energy (DOE) identified 12 top value added chemicals, derived from the conversion of biomass, which could be used as building block chemicals in a bio-based economy [8]. One of these products is glucaric acid, whose immense market value (at USD 550.4 million in 2016 [9]) is due to its high functionalization, which makes it a potential building block for the production of a variety of commodity products: i.e. detergents [10], polymers [11–15], new nylons (sustainable precursor for adipic acid production [13]), hyperbranched polyesters and food [16], cement and concrete additives [17]. In particular, the interest in the use of glucaric acid for the manufacture of detergents originates from recent economic policies adopted in the EU and US against the use of phosphates, as they are responsible for a decrease in water quality [18–21]. Glucaric acid represents the ideal candidate to replace phosphates due to its chelating properties in sequestering metal ions [22]. However, the current very limited supply of glucaric acid is not sufficient to satisfy the demand of such a large market. New large scale and price competitive production technologies are needed in order to make bio-derived glucaric acid available to this huge market.

As for the production of glucaric acid, the main focus of our study, the oxidation of glucose with nitric acid (a toxic oxidant) still remains the most economic route [23], despite it being poorly selective and unsustainable, as it leads to the formation of 85 kg of waste nitric acid per 100 kg of glucaric acid produced [24]. In an attempt to lower the consumption of nitric acid, Rivertop Renewables has modified this technology by conducting the reaction under an atmosphere of oxygen in a closed reaction flask in order to effect a catalytic oxidation process using oxygen as the terminal oxidant, fostering regeneration of spent nitric acid and lowering the required amount. Despite the better control over the highly exothermic reaction, allowing the oxidation at relatively low temperatures (25-30 °C), the modification does not increase the selectivity of the process, which remains very low, leading to modest yields of glucaric acid (ca. 40-45 %). Besides expensive separation units are still required for the removal of nitric acid from the product solution [24]. All the above-mentioned drawbacks make this technology extremely unsustainable, nevertheless its relative simplicity makes it still attractive for commercialization [17].

Other smaller scale, alternative oxidation methods have been reported in literature like aerobic oxidation using platinum and gold as catalysts and microbial fermentation [25–36]. However, both methods suffer from several drawbacks, so more sustainable and green methods are still envisaged. Therefore, it is evident that the role of research is now to go beyond the limits of these old methods and propose new, more environmentally friendly techniques [37].
In this context, electrochemical oxidation, involving the transfer of electrons in the reaction, is a promising alternative for the conventional oxidation, given the possibility to make use of electricity from renewable energy sources to drive the process. Moreover, it eliminates the use of high O_2 partial pressure or of hazardous oxidants, can be operated in mild conditions and allows controlling the selectivity by tuning the electrode potential.
For these reasons, in the last few years, there has been a growing interest in the electrochemical oxidation of glucose to glucaric acid, as demonstrated by the recently published literature in this field [28,38–41].

For example, there are a few studies in which 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) has been effectively employed as electrocatalytic mediator in the electrolysis of glucose to glucaric acid resulting in a yield of 85% [38,39]. However, the high cost and difficulty of the downstream processing (TEMPO separation and recycling) make this technology inconvenient for industrial applications. Electrochemical oxidation using heterogeneous catalysts represents the answer to the need for a more sustainable and cost-effective process. Indeed, successfully converting glucose into glucaric acid on metal or metal oxide electrodes (heterogeneous catalysts) would be favourable as it does not require harmful or expensive reagents (only glucose, salt and water are required) nor separation of the catalyst from the products. In literature, a series of transition metal-based catalysts have been developed and successfully tested for glucose electrooxidation in alkaline media [42,43] such as platinum [44], palladium [45], silver [46], copper [47] and nickel [28,48]. Nevertheless, the highest activities at low electrode potentials were obtained on noble metals, such as platinum, palladium and gold [49–56]. Of these three metals, the highest electrocatalytic activity is obtained with gold [49].

High values of glucaric acid yield and selectivity have been recently reported by two studies where more complex catalytic systems have been employed directly on a big scale (at current densities of 100 mA cm^{-2} [28,41]). The first, by Liu *et al.,* reports a glucaric acid yield of 83% obtained from glucose electrolysis on complex $NiFeO_x$ and $NiFeN_x$ catalytic systems [28]. The second publication, by Zhao *et al.*, reports a glucaric acid selectivity of 97.9 % obtained by electrooxidation of sodium gluconate (the sodium salt of gluconic acid) over a $Ni_3(BTC)_2$/NiF bifunctional catalyst [41]. In both cases, highly concentrated solutions of NaOH have been used as electrolyte, respectively, 1[28] and 8[41] M. Indeed, a major downside of these methods is the use of such large amounts of hydroxide salt (370 tons per 1000 tons of glucaric acid [57]) that requires specific equipment. From these studies, we can deduce that the production of glucaric acid by electrochemical oxidation of glucose using heterogeneous catalysts, without addition of any mediator or oxidative agent, is not only feasible but can be economically advantageous. What is also clear, is the major role of the catalytic system used in determining the overall process performance in terms of selectivity and yield. In this context, there is still room for improvement. Indeed, further efforts should focus on developing new catalytic systems (or improving old ones), which are long lasting and stable, using simpler materials and synthesis methods. Importantly, an analysis of the reaction parameters to understand the mechanism and optimize the operating conditions is still missing.

It is well known that Au is the most efficient electrocatalyst for glucose oxidation in alkaline media because of its high activity and tolerance to poisoning [58]. Moreover, in our previous work, we showed the correlation between oxidation potential and reactivity of the functional groups of the glucose molecule and highlighted its role in the determination of the selectivity to gluconic and glucaric acid [40]. It was found that, in all cases, the predominant product is gluconic acid, in agreement with previous literature, which indicated the formation of gluconic acid as the rate-determining step [59–66]. However, we found that, while at low oxidation potential (~0.6 V_{RHE}) the formation of D-gluconic acid is promoted by the oxidation of the aldehyde group on C1, at higher potential (~1.3 V_{RHE}) the oxidation of the hydroxymethyl group on C6 also takes place, allowing the further oxidation to D-glucaric acid [40].

Based on these results, Au appears to be able to oxidize glucose to glucaric acid in two consecutive oxidation steps, each characterized by an oxidation potential: the first step allowing the oxidation of D-glucose to the intermediate D-gluconic acid and the second step completing the oxidation to D-glucaric acid.

Besides the type of metal, the reaction conditions also play an important role in determining the sustainability of this process. First of all, because glucose, in alkaline media, is consumed by two chemical reactions: the isomerization of D-glucose into D-fructose and its subsequent thermal oxidative degradation [67], whose kinetics are controlled by thermodynamic parameters and, for which, bases are common heterogeneous catalysts [67]. The presence of these chemical side-reactions, competing with the electrochemical one, has a dramatic impact on the selectivity of the process. Secondly, it has been pointed out recently that the kinetic of glucose oxidation is strongly affected by the experimental conditions (temperature, concentration etc.) [68]. Therefore, in this work, to gain a better understanding of the reaction mechanism, we systematically investigated the influence of different operational parameters, i.e., pH, initial substrate concentration, applied potential, reaction temperature and time, on both oxidation steps. Then, a set of operational parameters is selected to carry out the two steps in cascade, proving, for the first time, the ability of Au to not only enable the oxidation of glucose to gluconic acid but also promote its further oxidation to glucaric acid. Finally, since to be effective a catalyst needs to be stable as well as productive, this aspect, often overlooked, was also investigated by measuring the quantity of Au leaching in the reaction solution and eventual loss of electrocatalytic activity during the long-term electrolysis.

Experimental

Materials

The supporting electrolytes were prepared with ultrapure water (Synergy UV system), sodium carbonate (Sigma-Aldrich, 98%) and sodium hydroxide (Sigma-Aldrich, 98%). Anhydrous D-glucose was purchased from VWR (99.5%), D-gluconic acid potassium salt (98%) and D-saccharic acid potassium salt (98%) from Sigma Aldrich and D-gluconic acid sodium salt (99%) from Acros Organics. All chemicals were used without further modifications.

Electrochemical setup

Electrolysis measurements were conducted in an in-house designed and developed two-compartment thermostated batch cell with a volume of 50 mL at the cathode side and 3.5 mL at the anode, separated by a Nafion 117 cation-exchange membrane (Fig. 1). Unless otherwise stated, the temperature was set at 20°C.

Figure 1. Electrochemical set-up designed for the long-term electrolysis: (1) Pt counter electrode (CE), in the cathodic compartment; (2) Nafion membrane; (3) reference electrode (RE) and (4) working electrode (WE), both in the anodic compartment.

A silver-silver chloride electrode (Ag/AgCl) and a platinum plate were used as reference and counter electrode, respectively. A gold (0.08 cm^2) RDE purchased from AISI 304, Goodfellow was used as working electrode. The electrochemical instrumentation consisted of a Bio-Logic VSP-300 Potentiostat. All the electrode activities reported are represented with current densities (measured at the beginning of every electrolysis), utilizing the geometric area as active area and with respect to the reversible hydrogen electrode (RHE). The tested potential vs. Ag/AgCl was converted into potential vs. RHE using the Nernst equation (Eq. 1):

$$E_{RHE} = E_{Ag/AgCl} + \ln(10) \cdot \frac{RT}{F} \cdot pH + 0.197 \quad (1)$$

With R being the universal gas constant (8.314472 J K^{-1} mol^{-1}), F the Faraday constant (96485.332 C mol^{-1}) and T the temperature.
Before every electrochemical measurement, the working electrode surface was carefully polished with aluminium (Φ 1 µm) slurry on a polishing cloth and then sonicated in MilliQ water for 5 min. Finally, the electrode was dried with high purity N_2 (99.999%).

Reaction procedure

The long-term experiments (24 h) were carried out using a technique of potential-programmed electrolysis first developed by the authors Belgsir *et al.* and intended to keep the activity of the Au electrode high for long periods, by avoiding the blockage of the active sites by poisoning species [60]. The optimized potential program included three potential plateaus, in order to ensure an optimal electrocatalytic activity throughout the course of the experiment [40,61,62].

The oxidation plateau (30 s) was followed by a reactivation procedure consisting of two short potential pulses (1 s): one at 2.40 V_{RHE}, that allowed to reactivate the electrode by clearing out the poisoning species, and the second at 0 V_{RHE} that served to reduce the metal surface and allowed the adsorption of the organic molecule (Fig. 2). These steps were repeated over the whole course of the experiments. The identification of reaction products was carried out by gas chromatography coupled with mass spectrometry (GC-MS) using a RXI-1ms (Restek) capillary (30 m, 0.32 mm i.d. and 0.25 µm film thickness). The electrolytic solutions were treated before analysis according to the following procedure: (1) the water was removed by lyophilization to leave dry samples of electrolyzed material. (2) This material was then trimethylsilylated using Supelco HMDS+TMCS+pyridine, 3:1:9 (Sylon HTP) Kit, as described in [69]. (3) The resulting materials were then analysed by GC-MS. Authentic samples of the expected reaction products were also trimethylsilylated and their chromatographic data were used for the product identification. Moreover, to have an additional confirmation of the formation of gluconic and glucaric acid, we performed liquid chromatography mass spectrometry (LC-MS) analysis using an Acquity Arc UHPLC (Waters) fitted with a KC811 Ion-exclusion column (Shodex) and coupled to a QDa single quad mass spectrometer (Waters). Detailed procedure and results of this analysis are reported in the SI, from which it can be concluded that gluconic and glucaric acid are indeed produced.

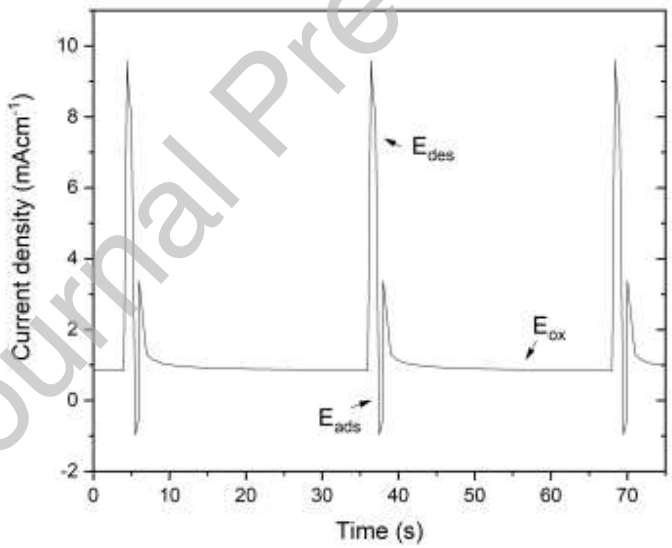


Figure 2. The optimized potential program used for the long-term electrolysis (adapted from [60]).

The quantification of the reaction products was performed by HPLC (Alliance 2695, Waters, USA) fitted with a Waters IC-Pak Ion Exclusion column (IC-Pak, Waters, USA) and equipped with a UV detector set at λ=210 nm and a refractive index (RI) detector. A solution with 0.1% v/v perchloric acid was used as the mobile phase at 1 mL min^{-1} flow rate. The instrument was calibrated with high purity standards purchased from Sigma Aldrich prior to product analysis. Authentic samples

of D-glucose and of the expected reaction products were analysed and their chromatographic data were used for the identification of the products present after reaction. The aqueous solutions of HPLC references were prepared from standard products >99% pure for gluconic, glucaric, glycolic, tartaric, formic and oxalic acids. The conversion (X_G), productivity (P_i) and selectivity (S_i) were calculated using the following equations (Eqs. 2-4):

$$X_G(\%) = \frac{n_{reagent\ initial} - n_{reagent\ final}}{n_{reagent\ initial}} \cdot 100$$

(2)

$$P_i(\%) = \frac{n_{product\ i}}{S_{catalyst} \cdot t_{electrolysis}} \cdot 100$$

(3)

$$S_i(\%) = \frac{n_{product\ i}}{n_{reagent\ consumed}} \cdot \frac{\mu}{\vartheta} \cdot 100$$

(4)

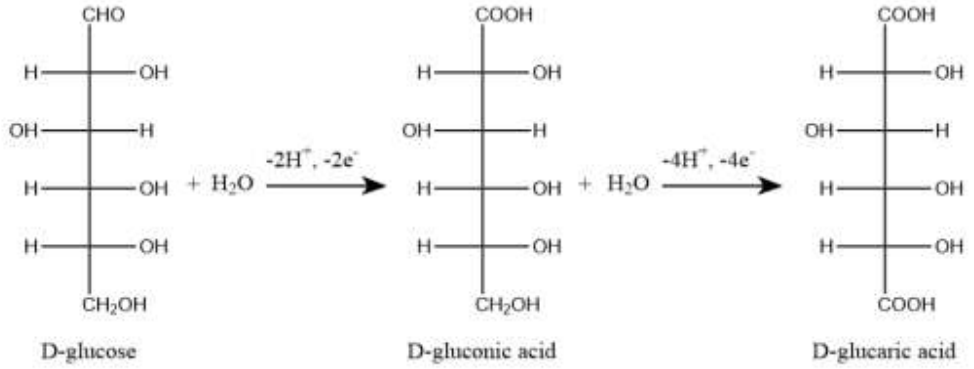
Where $S_{catalyst}$ and $t_{electrolysis}$ are, respectively, the geometrical area of the catalyst (in cm^2) and the electrolysis time (in h). The symbols μ and δ in Eq. 4 represent the stoichiometric coefficients of the reaction. All the measurements were performed three times and the errors measured on the values of conversion, selectivity and productivity were, in all cases, lower than 3%. The analysis of the gas phase was performed by Gas Chromatography (GC): no gaseous product was formed during the electrolysis. The pH was measured at the end of each electrolysis to check its possible development: in all experiments, no evident pH change was detected.

Catalyst stability

For the study of the catalyst stability, two deactivation parameters were analysed in this work: dissolution and loss in current response. To determine the quantity of catalyst leaching, samples of the reaction solution, taken after prolonged electrolysis time (24h) were analysed using an Agilent 7500 series inductively coupled plasma mass spectrometry (ICP-MS). The samples were diluted to a 1:20 ratio in a 2% HCl matrix and a calibration curve was fitted from 1 to 1000 ppb to determine the sample Au contents. Standards for gold were purchased from Alfa Aesar. The current density was monitored during the course of all the chronoamperometry experiments. The results of cyclic voltammetry performed in a fresh solution before and after the prolonged electrolysis were compared to detect possible losses in catalyst activity.

Results and discussion

The anodic reactions taking place at the Au working electrode, leading to the formation of D-gluconic acid (first reaction) and D-glucaric acid (second reaction) are illustrated in Scheme 1. In the cathodic compartment, at the Pt counter electrode, the hydrogen evolution reaction (HER) takes place (S1) [70].



Scheme 1: The oxidation of D-glucose to D-glucaric acid in two-steps (for simplicity D-glucose is represented in the open-chain form).

In the following paragraphs, we analyse the influence of pH, substrate concentration, applied potential, temperature and reaction time on the selectivity to D-gluconic acid (first process) and to D-glucaric acid (second process) by measuring the products of long-term electrolysis. To do so, long-term electrolysis measurements were carried out under different operating conditions (i.e. pH, substrate concentration, cell voltage, temperature and reaction time) in the 3.5 mL anodic compartment.

The oxidation of glucose to gluconic acid: impact of the operational parameters

pH

The D-glucose oxidation was studied under alkaline conditions, in a pH range between 11 and 13. In fact, it is well established that alkaline conditions are required for glucose electrooxidation since, at high pH, D-glucose is transformed into β-D-glucopyranose, its most active anomeric form [61,62]. For this reason, only alkaline pH conditions were considered in this work. However, strong bases (like alkali bases, such as NaOH) also initiate glucose isomerization (production of D-fructose) and oxidative degradation reactions (production of low molar mass carboxylic acids i.e. formic and oxalic acid), which would result in a reduced glucose availability for the electrochemical oxidation [67]. For this reason, a weaker base, Na_2CO_3, was also used in the pH range between 11 and 12 and the results were compared with those obtained at higher pH using NaOH as electrolyte.

The influence of the pH (11-13) on the 2-electron oxidation of glucose is represented in Fig. 3 (selectivity) and Table 1 (conversion and productivity). The results confirm our initial idea that the pH has a strong impact on the products' distribution: electrochemical product (gluconic acid) vs. chemical degradation products (fructose and small molar mass carboxylic acids). When a strong alkaline solution (high pH) is used as electrolyte, the selectivity to gluconic acid remains below 50%, while the selectivity to fructose goes up to 50% (Fig. 3). On the contrary, when a less

strong base as Na_2CO_3 is used as electrolyte (lower pH), D-gluconic acid becomes the main product, reaching a selectivity up to 90% for pH 11.3 (Fig. 3). At the lowest concentration of Na_2CO_3 (0.01 M, pH 11.0), glucose conversion is very low due to both the poor conductivity of the solution and the small amount of glucose that is converted into active β-D-glucopyranose at this "low" pH (Table 1). Increasing the concentration of the base, Na_2CO_3, from 0.01 M (pH 11.0) to 0.1 M (pH 11.3), results in a higher amount of D-glucose that is converted into D-gluconic acid, as evidenced by the increase of glucose conversion and gluconic acid productivity (Table 1). However, a further increase to 1.0 M Na_2CO_3 (pH 11.4) causes a decrease of the selectivity to D-gluconic acid until a value of 53.6%, indicating that isomerization and degradation reactions are taking over due to the high concentration of the base, which is a catalyst for these reactions. Furthermore, it is interesting to note that, while initially D-glucose conversion and D-gluconic acid productivity increase with the concentration of Na_2CO_3 (from, respectively, 5.7% and 1.1 mmol cm^{-2} h^{-1} at 0.01 M, to 23.3% and 4.7 mmol cm^{-2} h^{-1} at 0.1 M), for concentrations >0.5 M, both parameters drop to lower values (Table 1). The same trend is followed by the current density (S2). One possible explanation is that higher concentrations of electrolyte (Na_2CO_3 or NaOH) provide more reacting hydroxyl (OH^-) species, which are essential for glucose oxidation [68,71–74], thus enhancing the reaction kinetic. But, as pointed out by the authors Holade *et al.*, a too high concentration of electrolyte might decrease the number of active sites available for glucose adsorption, thus diminishing the cell performance [68]. This behaviour of the current density with the electrolyte concentration (pH) had been also observed by the authors Tung et al. who attributed it to the passivation of the electrode by gold oxides [52]. From this analysis, we could conclude that, for this reaction step, Na_2CO_3 in concentrations of ca. 0.1 M, corresponding to a pH of ca 11.3, yields the best results in terms of both selectivity and productivity (Table 1). All further experiments starting from glucose have been, therefore, conducted using 0.1 M Na_2CO_3 as electrolyte.

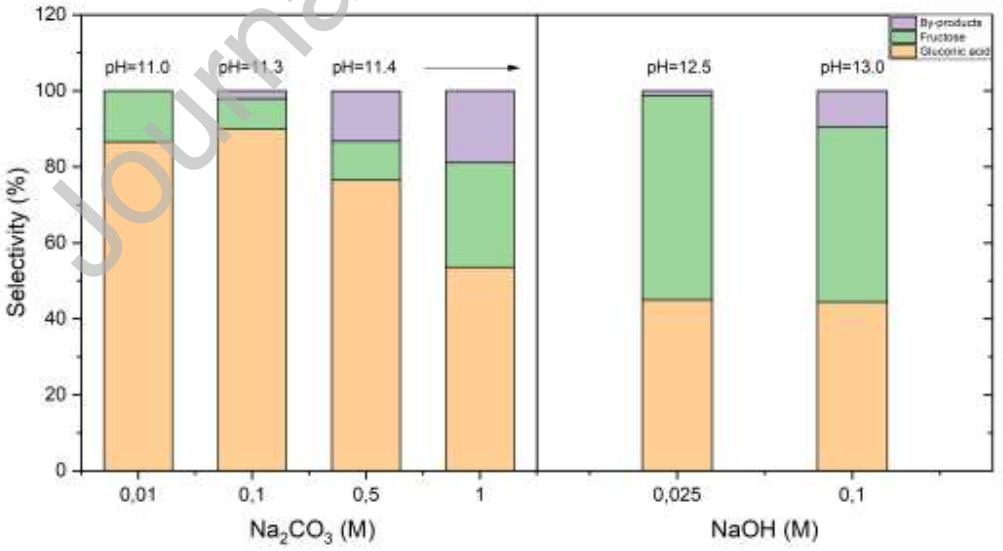


Figure 3. Influence of pH on the selectivity to D-gluconic acid (orange), D-fructose (green) and by-products (violet) for the oxidation of 0.04 M D-glucose on Au at 20°C after 24 h.

Table 1
Summary of the results obtained in the glucose electrooxidation to gluconic acid in function of the pH.

Operating conditions					Catalytic results		
t^a (h)	$C_G{}^b$ (M)	$C_E{}^c$ (M)	pH	T^d (°C)	$X_G{}^e$ (%)	$S_{GO}{}^f$ (%)	$P_{GO}{}^g$ (mmol cm^{-2} h^{-1})
24	0.04	Na_2CO_3 0.01	11.0	20	5.7	86.6	1.1
24	0.04	Na_2CO_3 0.1	11.3	20	23.3	90.8	4.7
24	0.04	Na_2CO_3 0.5	11.4	20	22.0	76.5	3.6
24	0.04	Na_2CO_3 1.0	11.4	20	17.2	53.6	1.9
24	0.04	NaOH 0.025	12.5	20	16.7	45.0	1.6
24	0.04	NaOH 0.1	13.0	20	45.6	44.4	4.5

[a] Reaction time, h; [b] Substrate (glucose) initial concentration, M; [c] Electrolyte concentration, M; [d] Reaction temperature, °C; [e] Glucose conversion, %; [f] Selectivity to gluconic acid, %; [g] Productivity of gluconic acid, mmol cm^{-2} h^{-1}.

D-glucose initial concentration

The initial D-glucose concentration was varied in the range 0.01-0.16 M. Fig. 4 shows the current density response to the variation of glucose concentration from 0.01 M to 0.16 M as derived from the peak potentials in the respective CV curves. The electrocatalytic activity values strongly increased with the initial D-glucose concentration up to 0.1 M, where the further increments get smaller and smaller, until a plateau is reached for concentrations >0.1 M (Fig. 4). The initial activity enhancement can simply be attributed to the presence of an increased reactant availability at the active surface and thus a decrease in the mass transfer limitations [52]. After the maximum performance is reached, further increase of the reactant concentration becomes ineffective. This saturation effect has been previously observed by the authors Kokoh *et al.* who studied the influence of the concentration of glucose (from 1 mM to 50 mM) on the reaction mechanism and kinetic on a pure gold anode by cyclic voltammetry [61]. Indeed, they found that, at low initial concentration of glucose, the reaction had order 1, while, at higher concentration, a saturation mechanism takes place, dropping the order to 0 [61]. There are simply not enough Au sites available to accommodate the growing number of glucose molecules, explaining this stagnation.

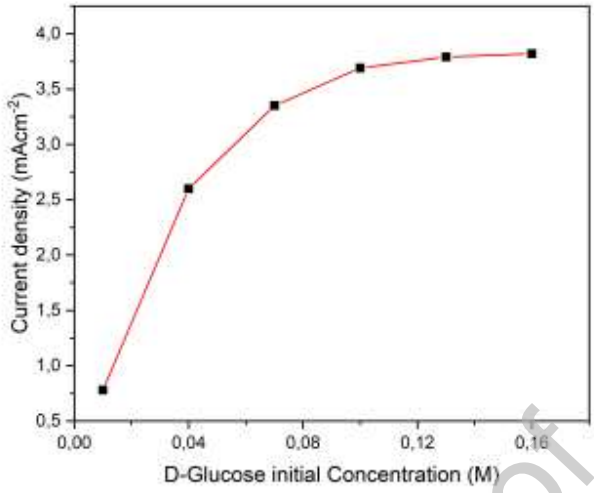


Figure 2. Current density response to the variation of initial glucose concentration derived from the respective cyclic voltammogram at 10 mVs^{-1}(Na_2CO_3 0.1 M).

The results of 24 h electrolysis experiments at various D-glucose initial concentrations are shown in Fig. 5 (selectivity) and Table 2 (conversion and productivity). It is observed that, at low initial concentration of glucose (0.01 M), the productivity of the electrochemical product, D-gluconic acid, is low due to the mass transfer limitation (Table 2) and so is its selectivity. Due to the presence, in this system, of homogeneous side-reactions that compete with the electrochemical (heterogeneous) process, when increasing the initial concentration of glucose, a greater amount of reactant reaches the electrode surface, thus increasing the selectivity towards gluconic acid (Fig. 5). Nevertheless, as for the current density, after a maximum value of 92.0% is reached at 0.07 M initial D-glucose, a decrease in cell performance is observed for concentrations >0.1 M, until a selectivity as low as 60.7% is obtained at 0.16 M (Fig. 5). At the same time, glucose conversion and gluconic acid productivity also decrease, while the amount of fructose formed keeps increasing with the available amount of glucose in the solution (Table 2). Three possible explanations have been given for this behaviour: 1) at high concentration of glucose, the coverage rate of the electrode surface is so high that the catalyst surface rapidly becomes saturated. In these conditions, the hydroxyl species cannot adsorb on the active sites, which diminishes the kinetic of the electrochemical reaction [68]; 2) the second explanation is based on the fact that an increase of glucose concentration increases the viscosity of the solution, which hinders the mass transfer towards the Au active sites, required for the heterogeneous, electrochemical reaction. It must be pointed out that a decrease in cell performance at high concentrations has been observed for a wide range of systems of other organic molecules even when a flow cell is used [75–78]. Glucose, in particular, has a rather low diffusivity ($D=6.9x10^{-10}$ m^2 s^{-1}) compared to other, smaller, organic molecules like, for example, formic acid, which has a diffusion coefficient of ca $14.7x10^{-10}$ m^2 s^{-1}) [79–81]. So, especially in batch, it becomes clear why the system is subjected to such mass transfer limitations; 3) the third, and last, explanation is

based on the fact that more fructose is also formed at higher glucose concentrations, which may occupy the Au active sites as such impeding adsorption of glucose [54].

From this section we could conclude that the initial glucose concentration is best taken in between 0.04-0.1 M, as this yields the best performance in terms of selectivity (>90%) and productivity (>4.7 mmol cm^{-2} h^{-1}) (Table 2). For this reason, we chose an initial concentration of glucose of 0.04 M for all remaining experiments.

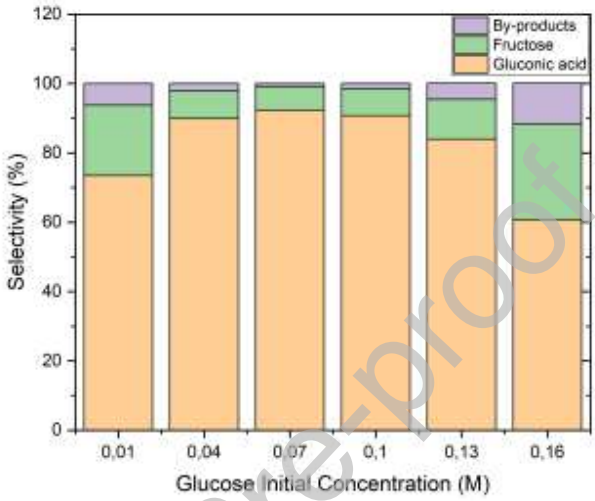


Figure 5. Selectivity to D-gluconic acid (orange), D-fructose (green) and by-products (violet) in dependence of initial amount of glucose. Reaction conditions: 0.1 M Na_2CO_3, 20°C, pH 11.3, 24h.

Table 2

Summary of the results obtained in the glucose electrooxidation to gluconic acid in function of the initial concentration of glucose.

Operating conditions					Catalytic results		
t[a] (h)	C_G[b] (M)	C_E[c] (M)	pH	T[d] (°C)	X_G[e] (%)	S_{GO}[f] (%)	P_{GO}[g] (mmol cm^{-2} h^{-1})
24	**0.01**	Na_2CO_3 0.1	11.3	20	43.3	73.5	1.8
24	**0.04**	Na_2CO_3 0.1	11.3	20	23.3	90.8	4.7
24	**0.07**	Na_2CO_3 0.1	11.3	20	17.6	92.0	6.2
24	**0.1**	Na_2CO_3 0.1	11.3	20	15.5	90.8	7.6
24	**0.13**	Na_2CO_3 0.1	11.3	20	10.8	84.0	6.4
24	**0.16**	Na_2CO_3 0.1	11.3	20	4.7	60.7	2.4

[a] Reaction time, h. [b] Substrate (glucose) initial concentration, M. [c] Electrolyte concentration, M. [d] Reaction temperature, °C. [e] Glucose conversion, %. [f] Selectivity to gluconic acid, %. [g] Productivity of gluconic acid, mmol cm^{-2} h^{-1}.

Reaction temperature

The influence of the reaction temperature on D-glucose oxidation to D-gluconic acid was studied in the range 5-50°C. Based on the electrocatalytic activity values derived from the voltammograms recorded at different temperatures, an Arrhenius plot was established for T>20°C (S3). The apparent activation energy was calculated to be 19.1 kJ mol^{-1} (using eq. in S3), confirming that the electrochemical process is dominated by the diffusion of the reactants and/or products, with a substantial contribution from adsorption [55,68,82].

The obtained values of selectivity are shown in Fig. 6, while the values of conversion and productivity are given in Table 3. As expected, the selectivity to D-gluconic acid decreases with the reaction temperature, with the maximum of 97.6% reached at 5°C. In fact, higher temperatures promote the isomerization to fructose and the oxidative degradation reactions leading to low molar mass carboxylic acids (glycolic, oxalic, formic and tartaric acid), thus decreasing the selectivity to the electrochemical process. Moreover, while below 40°C the selectivity decreases only slightly with the temperature, remaining over 80%, at 50°C, in agreement with literature, the solution degrades rapidly assuming a yellowish color [54,83] and the selectivity to gluconic acid drops to a value of ca 60% (Fig. 6).

As for conversion, productivity (Table 3) and current density (results not shown) we observe slightly higher values at 5 and 10 °C compared to those at 20°C, and then again an increase for T>20 °C, due to the increased reaction kinetics. A maximum conversion of 48.5% is reached at 50°C, with as unfortunate downside that gluconic acid selectivity and productivity drop dramatically due to the above-mentioned rapid degradation of the solution. In fact, it seems that, from a certain point, by increasing the temperature, the rate of conversion of glucose into fructose increases so rapidly that it overtakes the electrochemical reaction (Table 3). This fluctuating behaviour of the current density had been already observed in a previous study by the authors Yei *et al.*, who interpreted it assuming an inhibiting effect on the electrocatalytic activity caused by the formation of fructose, that starts being pronounced above 20 °C [54]. They concluded that the real reactivity of glucose can only be observed at low temperatures (below 10 °C), where the rate of isomerization to fructose is negligible [54]. Then, above 20°C, the temperature raise affects the kinetics of the electrocatalytic reaction more strongly, resulting in an activity enhancement (S3) and increase of the conversion rate (Table 3). Our results seem to confirm these assumptions: at 5 °C, glucose conversion is 25 % but fructose has not formed, so the selectivity to gluconic acid is maximum (97.6 %). Instead, at 20 °C, despite the quantity of glucose converted is similar (23.3%), a greater amount of it is transformed to fructose which inhibits the productivity of gluconic acid (Table 3). Then, above 20 °C, both conversion and productivity increase again because of the improved reaction kinetics.

From this analysis, we concluded that, if the aim is to obtain the maximum selectivity, the best temperature to work at is 5 °C, but to have the highest conversion rate and the highest productivity of gluconic acid, albeit losing a bit of selectivity, then 40 °C is the optimum. For our next experiments, we decided to work at ambient temperature, 20 °C.

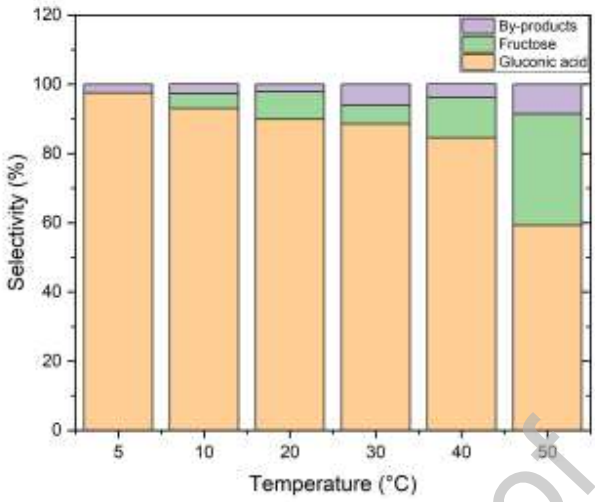


Figure 6. Dependence of the selectivity to D-gluconic acid (orange), D-fructose (green) and by-products (violet) with the reaction temperature for the oxidation of 0.04 M D-glucose in 0.1 M Na_2CO_3 for 24 h.

Table 3
Summary of the results obtained in the glucose electrooxidation to gluconic acid in function of the reaction temperature.

Operating conditions					Catalytic results		
t^a (h)	$C_G{}^b$ (M)	$C_E{}^c$ (M)	pH	T^d (°C)	$X_G{}^e$ (%)	$S_{GO}{}^f$ (%)	$P_{GO}{}^g$ (mmol cm^{-2} h^{-1})
24	0.04	Na_2CO_3 0.1	11.3	**5**	25.0	97.6	5.4
24	0.04	Na_2CO_3 0.1	11.3	**10**	27.0	93.1	5.3
24	0.04	Na_2CO_3 0.1	11.3	**20**	23.3	90.8	4.7
24	0.04	Na_2CO_3 0.1	11.3	**30**	34.5	88.6	6.5
24	0.04	Na_2CO_3 0.1	11.3	**40**	41.9	84.6	7.6
24	0.04	Na_2CO_3 0.1	11.3	**50**	48.5	59.3	6.1

[a] Reaction time, h. [b] Substrate (glucose) initial concentration, M. [c] Electrolyte concentration, M. [d] Reaction temperature, °C. [e] Glucose conversion, %. [f] Selectivity to gluconic acid, %. [g] Productivity of gluconic acid, mmol cm^{-2} h^{-1}.

Oxidation potential and reaction time

Next, the analysis of the impact of the applied potential on the selectivity of the reaction was conducted. The results (shown in S4) highlight that, whatever potential is chosen, as long as it

stays within the oxidation peak, the selectivity remains about the same. It was thus concluded that this parameter does not have a significant impact on the outcome of the first reaction step.

Finally, the impact of the reaction time was investigated and for this, the Au catalyst was tested for prolonged reaction times to evaluate the evolution of the products over time and to assess the deactivation behaviour. Conversion and selectivity to gluconic acid as a function of time are shown in Fig. 7 while the productivity values are reported in Table 4. The maximum selectivity to gluconic acid (ca. 98%) was obtained for low reaction times (6 h). After 12 h, the selectivity decreases to ca. 90%, where it remains constant for the remainder of the electrolysis experiment. The cause for this higher selectivity at short reaction times could either be attributed to the fact that fructose and by-products are not formed yet at this point due to the slower kinetics of the catalytic reactions or simply because their presence cannot be detected by the analytical instrumentation as these compounds have a higher detection limit (~10 ppm).
Glucose conversion increases continuously with time (Fig. 7), although, a slight reduction of the conversion rate discovered after 24 h of electrolysis was attributed to the limited mass transfer in the batch cell due to the reduced concentration of glucose in the solution at this point. A logarithmic fit was calculated for the values of glucose conversion: the resulting curve is shown in Fig. 7. In an optimal process, the electrolysis should be stopped after 18-24 h because, in this range, a good value of conversion is reached (~20 %) and the conversion rate is still high.

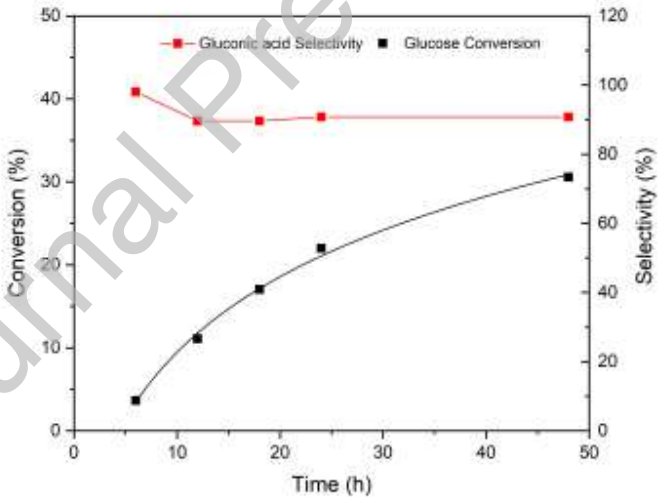


Figure 7. Variation with the reaction time of glucose conversion (black line) and gluconic acid selectivity (red line).

Table 4
Summary of the results obtained in the glucose electrooxidation to gluconic acid in function of the reaction time.

Operating conditions	Catalytic results

t[a] (h)	C_G[b] (M)	C_E[c] (M)	pH	T[d] (°C)	X_G[e] (%)	S_{GO}[f] (%)	P_{GO}[g] (mmol cm^{-2} h^{-1})
6	0.04	Na_2CO_3 0.1	11.3	20	3.6	98.1	0.8
12	0.04	Na_2CO_3 0.1	11.3	20	11.1	89.6	2.1
18	0.04	Na_2CO_3 0.1	11.3	20	17.0	89.6	3.1
24	0.04	Na_2CO_3 0.1	11.3	20	23.3	90.8	4.7
48	0.04	Na_2CO_3 0.1	11.3	20	30.6	90.0	6.1

[a] Reaction time, h. [b] Substrate (glucose) initial concentration, M. [c] Electrolyte concentration, M. [d] Reaction temperature, °C. [e] Glucose conversion, %. [f] Selectivity to gluconic acid, %. [g] Productivity of gluconic acid, mmol cm^{-2} h^{-1}.

The oxidation of gluconic acid to glucaric acid: impact of the operational parameters

As done for the first oxidation step, we also investigated the impact of the operational parameters (pH, gluconic acid initial concentration, reaction temperature and time) on the performance of the second oxidation reaction (results shown in Table 5). In this case, contrary to the oxidation of glucose, gluconic acid is stable in alkaline solution, so, it does not undergo degradation.

It was found that none of the operational parameters examined had an appreciable impact on the selectivity of this process. The only observable trend is a slight increase of gluconic acid conversion with the pH and with the reaction temperature (Table 5). It is possible that, as for the oxidation of glucose to gluconic acid, the presence of more reacting hydroxyl (OH^-) species and higher temperatures enhance the reaction kinetics, thus increasing the conversion rate.

Table 5

Summary of the results obtained in the gluconic acid electrooxidation to glucaric acid, at 1.3 V_{RHE}, in function of pH, gluconic acid initial concentration, reaction temperature and time.

Operating conditions					Catalytic results		
t[a] (h)	C_{GO}[b] (M)	C_E[c] (M)	pH	T[d] (°C)	X_{GO}[e] (%)	S_{GA}[f] (%)	P_{GA}[g] (mmol cm^{-2} h^{-1})
24	0.04	**Na_2CO_3 0.1**	**11.5**	20	2.6	66.3	0.4
24	**0.04**	**NaOH 0.025**	**12.5**	**20**	4.1	72.3	0.6
24	0.04	**NaOH 0.1**	**13.0**	20	7.4	60.4	0.9
24	0.04	**NaOH 0.8**	**13.5**	20	15.6	60.6	1.9
24	**0.01**	NaOH 0.025	12.5	20	21.0	75.2	0.8
24	**0.07**	NaOH 0.025	12.5	20	1.9	72.3	0.5
24	0.04	NaOH 0.025	12.5	**10**	4.5	76.1	0.7
24	0.04	NaOH 0.025	12.5	**40**	6.4	72.7	0.9

6	0.04	NaOH 0.025	12.5	20	0.8	64.1	0.1
18	0.04	NaOH 0.025	12.5	20	3.0	73.0	0.4

[a] Reaction time, h. [b] Substrate (gluconic acid) initial concentration, M. [c] Electrolyte concentration, M. [d] Reaction temperature, °C. [e] Gluconic acid conversion, %. [f] Selectivity to glucaric acid, %. [g] Productivity of glucaric acid, mmol cm^{-2} h^{-1}.

However, while, on one hand, pH, substrate initial concentration, reaction temperature and time had no substantial effect (Table 5), the applied potential seems to play an important role in the determination of the products' distribution, and thus on the selectivity (Table 6). In fact, the selectivity to glucaric acid varies from a minimum of 64.9% obtained at 1.4 V_{RHE}, to a maximum of 89.5% reached at 1.1 V_{RHE}. It has been reported in literature that, depending on the applied potential, three species of Au are involved in the oxidation of glucose in alkaline media [68,71–74]: Au metal, around 0.6 V_{RHE} (peak 1 in the CV reported in S5), that, in our work, is responsible for the oxidation of glucose to gluconic acid; Au(OH)x, around 1.1 V_{RHE} (left shoulder of peak 2 in S5); and AuOx, around 1.3 V_{RHE} (peak 2 in S5). The authors Holade *et al.* performed chronoamperometry experiments coupled with FTIR spectroscopy and chromatographic analysis of the products to monitor glucose electrooxidation reaction at various electrode potentials, from 0.2 to 1.4 V_{RHE} [68]. Surprisingly, although the CA results changed from one potential to another, they did not report any appreciable difference in the distribution of the products [68]. In our case, for the oxidation of gluconic acid, the applied potential for the electrolysis does have an impact on the products' distribution. We believe that this variation is ascribed to distinct reaction mechanisms taking place at the different Au oxide species. Similarly, also Belgsir *et al*. reported a variation of the product distribution (selectivity) with the potential at which the glucose oxidation reaction was conducted (0.5, 0.6, and 0.9 V_{RHE}) for a system consisting of Au modified with Pb adatoms [60].

Table 6

Summary of the results obtained in the gluconic acid electrooxidation to glucaric acid in function of the applied potential.

Operating conditions						Catalytic results		
t^a (h)	$C_{GO}{}^b$ (M)	$C_E{}^c$ (M)	pH	T^d (°C)	E^e (V_{RHE})	$X_{GO}{}^f$ (%)	$S_{GA}{}^g$ (%)	$P_{GA}{}^h$ (mmol cm^{-2} h^{-1})
24	0.04	NaOH 0.025	12.5	20	**1.0**	3.2	84.6	0.6
24	0.04	NaOH 0.025	12.5	20	**1.1**	4.6	89.5	0.8
24	0.04	NaOH 0.025	12.5	20	**1.2**	4.9	82.0	0.8
24	0.04	NaOH 0.025	12.5	20	**1.3**	4.1	72.3	0.6
24	0.04	NaOH 0.025	12.5	20	**1.4**	3.2	64.9	0.4

[a] Reaction time, h. [b] Substrate (gluconic acid) initial concentration, M. [c] Electrolyte concentration, M. [d] Reaction temperature, °C. [e] Oxidation potential, V_{RHE}. [f] Gluconic acid conversion, %. [f] Selectivity to glucaric acid, %. [g] Productivity of glucaric acid, mmol cm^{-2} h^{-1}.

However, as it is evidenced by the very low values of conversion obtained in all experiments, independent on the reaction conditions/time (Table 6), for this reaction step there was a limit on the maximum achievable concentration of glucaric acid, which was rather low (~ 1.2 mM). In addition to this, we noticed that the current density decreased drastically already in the first hours of electrolysis (S6), where the reaction, in fact, stopped, which explains also the very low productivity values. This behaviour indicates a deactivation process, involving the Au catalyst, which will be further discussed in the paragraph "Catalyst stability".

The two steps in cascade

Despite the limit in the achievable concentration of glucaric acid due to the deactivation phenomena, we did attempt the two electrolysis steps in cascade as proof of concept. A set of optimal operating parameters was selected to first convert D-glucose to D-gluconic acid at 0.6 V_{RHE}, the potential corresponding to this oxidation step, and then to convert the latter to glucaric acid, at 1.1 V_{RHE}. A concentration of 0.1 M Na_2CO_3 (corresponding to pH 11.3) was chosen for the electrolyte because it gave the best selectivity to gluconic acid (Table 1). The quantity of glucose converted to gluconic acid in the first step had to be high enough to guarantee a sufficient concentration of gluconic acid in solution to initiate the second oxidation step. For this reason, the first electrolysis step was conducted at 40°C for 48h, starting from a solution of 0.1 M glucose (all values corresponding to the maximum productivity, see Table 2-3-4). Therefore, after 48h, the second electrolysis was immediately started by switching the oxidation potential from 0.6 V_{RHE} (used for the first step) to 1.1 V_{RHE}, which was kept for additional 18 h of electrolysis, without modification of any of the other reaction parameters. In fact, after 18 h the catalyst was completely deactivated, as the current density dropped to zero, so the electrolysis was stopped.
The results, reported in Table 7, show that only 2.4% of the gluconic acid formed in the first reaction step is converted to glucaric acid in the second oxidation step, with a selectivity of 89.0%.

Table 7

Summary of the results of the cascade process.

Oxidation step	Catalytic results					
Nr	X_G [a] (%)	S_{GO} [b] (%)	X_{GO} [c] (%)	S_{GA} [d] (%)	P_{GO} [e] (mmol cm^{-2} h^{-1})	P_{GA} [f] (mmol cm^{-2} h^{-1})
1	17.5	83.9	-	-	3.8	-
2	25.0	87.4	2.4*	89.0*	4.1	0.2

[a] Glucose conversion, %. [b] Selectivity to gluconic acid, %. [c] Gluconic acid conversion, %. [d] Selectivity to glucaric acid, %. [e] Productivity of gluconic acid, mmol cm^{-2} h^{-1}. [f] Productivity of glucaric acid, mmol cm^{-2} h^{-1}. *These results refer to the sole oxidation of gluconic acid.

In fact, while the first oxidation proceeds rather effectively, with 17.5% of the initial glucose converted mainly to gluconic acid (83.9% of selectivity), the second reaction step is characterized by a very limited productivity (only 0.2 mmol cm^{-2} h^{-1}), which is justified considering that the reaction actually stops after a few hours of electrolysis due to deactivation of the catalyst.

It is important to point out that, during the second oxidation step, at the constant potential of 1.1 V_{RHE}, gluconic acid is still produced by the much easier oxidation of the aldehyde group on C1. In fact, as we showed in our previous work, at this potential, gold is able to oxidize both, the aldehyde group on C1 and the hydroxymethyl group on C6 [40]. The final conversion of glucose, obtained with the two electrolysis in cascade, is 25%, with a total selectivity to gluconic acid of 87.4%, which remains, for the major part, unreacted.

In the next paragraph we investigate the catalyst stability and try to address the cause of the rapid deactivation of the catalyst during the second oxidation step.

Catalyst stability

The stability of the Au catalyst was studied in two ways: firstly, by comparing the activity of the electrocatalyst before and after electrolysis, secondly by measuring the dissolution of the active phase in the reaction solution after long electrolysis time. The comparison of the CVs of Au in a fresh solution of 0.04 M glucose and 0.1 M Na_2CO_3 recorded before and after 48h electrolysis at 0.6 V_{RHE} (S5(a)), evidences no loss of electrocatalytic activity during the oxidation of glucose to gluconic acid, mainly thanks to the use of the potential-program that assures the cleaning of the electrode surface after each electrolysis sequence (see in "Experimental" section). On the other hand, the CVs of Au in a fresh solution of 0.04 M gluconic acid and 0.025 M NaOH recorded before and after 18h electrolysis at 1.1 V_{RHE} (S5(b)) appear different, with a larger left shoulder and a surprisingly higher current density in the CV of the recovered catalyst (which was thoroughly rinsed with MilliQ water before the CV). This might be explained assuming that, after one cycle of electrolysis, a greater amount of hydroxyl (OH^-) species adsorbed onto the catalyst's surface to form active Au(OH)x species, thus increasing its activity.
Next, in order to exclude possible losses of gold active phase due to dissolution, the reaction solution was analysed after electrolysis with ICP-MS to determine the quantity of metal leaching. The results, shown in S7, indicate no significant loss of metal during both oxidations, confirming the inherent stability of the catalyst itself.

A recent review article from the authors Iglesias *et al.,* reports that, due to the blockage of the catalyst active sites by strongly adsorbed glucaric acid, the oxidation of gluconic acid requires more drastic conditions than that of glucose [57]. The results to which they refer, are those from the authors Lee *et al.*, who estimated the free energy of adsorption of various compounds on a Pt catalyst in the aerobic oxidation of glucose to glucaric acid, in order to rationalize an observed difference in reactivity of the aldehyde group of glucose and of the $-CH_2OH$ of gluconic acid [30]. They found out that the C=O group interacts more strongly with the catalyst compared to the alcoholic group thus, while glucose and gluconic acid adsorb with similar strengths, glucaric acid adsorbs more strongly [30]. As a consequence, glucaric acid blocks the active sites and slows down the reaction [30]. Moreover, they also ascribe the lower oxidation rate of gluconic acid,

compared to that of glucose, to the slow kinetics of the dehydrogenation of $–CH_2OH$ to –CHO, which is an important step for activating the molecule and is unnecessary in the oxidation of glucose to gluconic acid [30]. In light of their results, we suspected that the same phenomena as observed for Pt are also at play here for Au and were responsible for the deactivation encountered during our experiments. To verify this hypothesis, we conducted some additional tests.

First, a sample of water, brought in contact with the catalyst right after the electrolysis, was analysed with HPLC to trace the presence of glucaric acid coming off the catalyst. Glucaric acid was found in the sample at concentrations comparable to those measured in the bulk after the electrolysis, thus providing a first proof for our hypothesis. Secondly, an electrolysis experiment was performed starting from a solution of gluconic acid containing already a small amount of glucaric acid, to see if the presence of glucaric acid at the beginning of the electrolysis inhibited the reaction already from the start of the experiment. Indeed, we observed that in the cyclic voltammetry study (S8) in presence of glucaric acid, the current density corresponding to the oxidation peak is much lower than in its absence, meaning that the glucaric acid introduced in the solution adsorbs onto the catalyst surface, thereby deactivating it. The subsequent electrolysis showed a very low starting current (as compared to that in the glucaric acid free solution) which further decreased during the experiment. The products analysis confirmed our conclusion: at the end of the electrolysis, we measured a lower concentration of glucaric acid compared to that introduced at the start, thus indicating that part of it remained adsorbed onto the Au surface, as such deactivating it. This further confirmed our original hypothesis that glucaric acid acts as an inhibitor through adsorption on the Au surface.
However, whether this adsorption was reversible or not (physical vs. chemical adsorption) remained to be determined. In case of physical adsorption, an easy solution would be working in a flow configuration, as this might shift the equilibrium towards desorption as a consequence of the constant product removal and/or enhanced mass transport (away from the surface). To verify if an increased mass transfer could facilitate the glucaric acid desorption, we conducted an electrolysis (24h, 20°C, starting solution: 0.04 M gluconic acid in 0.025 M NaOH) with a rotating disk electrode. The results showed, again, the occurrence of Au deactivation as similar glucaric acid productivity and concentration were achieved.
So, in conclusion, the deactivation of the catalyst during the oxidation of gluconic acid to glucaric acid was finally ascribed to poisoning by the product, glucaric acid, which, once formed, remains chemically adsorbed onto the catalyst surface, as such poisoning it.

This work was intended to gain an understanding on the electrooxidation of glucose to glucaric acid on gold using a 2-steps process, thus, the use of a simple Au flat electrode in a batch reactor was suitable for such small-scale application. Although, to increase the productivity and assess the performance of this catalytic technology, we intend to 1) synthesize an Au-based catalyst characterized by higher electrocatalytic activity and tolerance to poisoning and 2) scale the process to an industrial-like level by applying flow conditions. To improve the catalyst's activity and tolerance to poisoning, we will modify the catalyst's morphology, increasing its active surface area, and composition, altering the bonds' strength to promote desorption of glucaric acid, and avoid deactivation.

One method to avoid the poisoning effect of the strongly adsorbed glucaric acid is to alloy gold with a second metal. For example, Rafaïdeen *et al.* demonstrated that alloyed PdAu bimetallic nanocatalysts have a much higher tolerance to poisoning and higher selectivity compared to the corresponding monometallic systems proposed in literature under similar experimental conditions [51]. Another way, often reported in literature, to minimise deactivation and improve the selectivity is adding to the catalytic system a promoter, such as Bi or Pb [60,84–89].

Conclusions

In conclusion, we report a novel, two-steps synthesis method for the oxidation of D-glucose to D-glucaric acid using a bare Au electrode in a batch cell, evidencing the limits of such electrode configuration for efficient synthesis of glucaric acid, for which improved activity and poisoning resistance are required and that will be part of our future work. The impact of the operating parameters has been investigated for both oxidation steps to understand the reaction mechanisms and identify the conditions that maximise the selectivity. In the glucose electrooxidation to gluconic acid, pH, glucose initial concentration, reaction temperature and time had a major impact on the reaction mechanism and on the kinetics, thus affecting selectivity and conversion. A maximum 97.6% selectivity at pH 11.3, 0.04 M initial glucose and 5°C was achieved, which, to the best of our knowledge, is the highest value ever obtained in literature for electrochemical process. Higher temperatures increase the conversion rate but cause also the rapid degradation of glucose due to the increased kinetics of the chemical side-reactions (48.5% conversion is achieved at 50°C after 24h but the selectivity drops to 59.3%). Similarly, by increasing the pH, glucose conversion also increases (up to 45.6% at pH 13.0), but the selectivity to gluconic acid drops to 44.4% due to an excessive adsorption of the hydroxyl ions (OH^-) onto the Au surface which decreases the number of active sites available for glucose, thus diminishing the cell performance. The electrolysis of more concentrated solutions of glucose resulted in a lower selectivity to gluconic acid because of the rapid saturation of the catalyst surface and increased viscosity of the solution, which hinders the mass transfer towards the Au active sites, thus limiting the (heterogeneous) electrochemical reaction. Finally, it was found that, while the selectivity remains constant even for prolonged reaction time (up to 48 h), glucose conversion continuously increases, with just a slight reduction of the conversion rate due to mass transfer limitations. As for the oxidation of gluconic acid to glucaric acid, a variation of the products' distribution was observed when changing the potential at which the gluconic acid oxidation reaction was conducted. A maximum selectivity of 89.5%, one of the highest reported in literature, was obtained at 1.1 V_{RHE}, where $Au(OH)_x$ is the main species of gold involved in the catalytic process. In this case, no chemical side-reaction competed with the electrochemical process, because gluconic acid is stable in alkaline media. Therefore, none of the operational parameters examined (pH, gluconic acid initial concentration, reaction temperature and time) had a significant impact on the products' distribution. Nevertheless, higher pH and temperature slightly affected the reaction kinetic, thus increasing the conversion rate. In all cases, a very limited concentration of glucaric acid was obtained due to an early deactivation of the Au electrode, which was found to be caused by poisoning by glucaric acid itself. We are currently trying to address this issue with appropriate catalyst's modification (i.e. morphology and

composition). Importantly, no Au leaching was detected during both oxidation reactions and the catalyst remained stable even after long electrolysis time.

Conflicts of interest

The authors declare no conflict of interests.

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Credit author statement

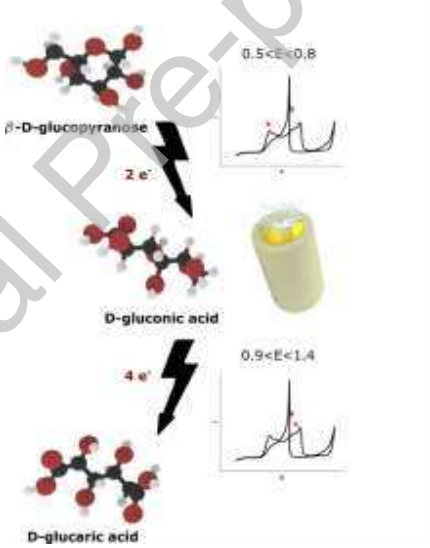
Giulia Moggia devised the concept, carried out the experiments, wrote and revised the manuscript, Jonathan Schalck designed and assembled the electrochemical cell, Nick Daems supervised the project and assisted with the writing and revision of the manuscript, Tom Breugelmans conceived and designed the project.

Declaration of Interest Statement

The authors declare no conflict of interests.

Table of Contents

A two-steps electrosynthetic process was here developed for the transformation of abundant, biomass-derived glucose into a highly valuable platform chemical, glucaric acid, employing a bare gold electrode in a batch reactor. A strong dependence of the selectivity on the operational parameters was found for the first oxidation step, while, the applied potential demonstrated to be key for the control of the selectivity of the second step. We successfully performed the two electrolysis in cascade and discovered a poisoning process caused by glucaric acid that, once formed, blocks the catalyst's active sites, thus deactivating it.



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Two-steps synthesis of D-glucaric acid via D-gluconic acid by electrocatalytic oxidation of D-glucose on gold electrode: influence of operational parameters

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