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Electrosynthesis of glyoxylic acid using a continuously electrogenerated lead cathode

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Glyoxylic acid is an important intermediate in organic synthesis. Its production by electroreduction of oxalic acid is very well known. However, attempts to scale up the process have failed due to rapid deactivation of the cathode. In this paper a process for overcoming this problem is described. The cathode activity can be continuously restored by adding small amounts of a Pb(II) salt in both anolyte and catholyte. In this way, the process has been continuously run for more than 300 h with a current efficiency of 92% and a selectivity higher than 95%.

1. Introduction

Electrosynthesis of glyoxylic acid by electroreduction of oxalic acid using cathodes of high hydrogen overvoltage has been known since 1903 [1]. To avoid electrooxidation of both oxalic acid and glyoxylic acid, the process is carried out in a divided cell using as catholyte a solution of oxalic acid in aqueous sulphuric acid [1, 2] or simply an aqueous solution of the substrate [3–6]. Practically, all the procedures described use carbon, lead dioxide, platinum and DSA® as anodes and mercury and lead as cathodes. Up to now, attempts to carry out the reaction in an undivided cell [7, 8] have been unsuccessful from an economic point of view due to the low material and faradaic yields obtained.

The main problem for scaling up the process is that the performance of the cathode is strongly affected by the presence of low hydrogen overvoltage metals [9, 10]. Consequently, the faradaic yield decreases dramatically throughout the operation time. To overcome this problem several alternatives have been proposed, such as addition of quaternary ammonium salts to the catholyte in small amounts [11] and chemical cleaning of the cathode surface with an aqueous solution of NaOH [12].

In this paper, an alternative and elegant way of preventing the loss of lead cathode activity is reported. Basically, it consists in adding small amounts of a Pb(II) salt to the electrolytes so that fresh cathode surface is continuously created by electrodeposition. The process is under patent [13, 14].

2. Experimental details

2.1. *Cell design and synthetic procedures*

The preparative electrolyses were carried out at constant current using a Promax FAC-365, 5 A, 30 V rectifier. A parallel-plate filter press assembly was used as flow cell. Experiments were made in a divided cell. The electrode area was 20 cm^2. The membrane to electrode gap (4.5 mm) was defined by a Teflon frame and two Viton rubber gaskets. A polypropylene mesh between the membrane and electrode was used as turbulence promoter. Both electrolytes were contained in two 250 cm^3 jacketed glass reservoirs and were pumped through their respective compartments by means of two magnetic pumps (Iwaki MD-20-R) to provide flow rates ranging from 1.5 to 2 $dm^3\,min^{-1}$. Temperature was controlled by recirculating water through the jackets of the reservoirs from a cryostat.

Experimental conditions were always the same for all the electrolyses: cathode: Pb (purity higher than 99.7%) supplied by Figueroa S.A.; separator: Nafion® 324 cation exchange membrane; current density 2000 $A\,m^{-2}$; catholyte: saturated aqueous solution of oxalic acid (purity 99.5%, supplied by VIMBODI S.A.) throughout the operation time; anolyte: 10% w/w aqueous sulphuric acid; temperature 12–14 °C; anode: Pt/Ti and DSA® (IrO_x/Ti) both supplied by Electrocell AB; electrolyses time: each experiment consisted in several electrolyses, each of which was run in such a way that the final glyoxylic acid concentration were less than 90 $g\,dm^{-3}$ to prevent its electroreduction to glycolic acid; charge: between 75% and 86% of theoretical to electroreduce the oxalic acid involved in the reaction. These experimental conditions were chosen as optimum in a preliminary study carried out in Ercros I&D [7].

2.2. *Analysis*

Oxalic acid concentration was quantified photometrically at 440 nm by means of a Perkin–Elmer spectrophotometer Coleman 570 according to a method

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developed by Szetey *et al.* [15] on the basis of the light absorption properties of its Fe(III) complex in a strongly acid medium of sulphuric acid (1 M). Glyoxylic acid concentration was quantified by two methods: (i) by differential pulse polarography with a dropping mercury electrode, in NaOH 0.25 M by means of both a Metrohm polarograph 646 VA processor and a Tacussel polaroprocesseur. The peak potential was −1350 mV with respect to the Ag/AgCl/Cl$^-$ reference electrode [16], and (ii) by HPLC with a Perkin–Elmer chromatograph 410 and a Perkin–Elmer u.v. detector 235. The column was an ION-300 (length 30 cm, internal diameter 0.78 cm). Analyses conditions were: λ 200 nm, flow rate 0.4 dm^3 min^{-1}. The eluent was aqueous sulphuric acid 0.005 N.

Glycolic acid determinations were carried out by HPLC at the same conditions as glyoxylic acid.

3. Results

3.1. *Influence of cation exchange membrane*

Initial runs were carried out on a number of cation exchange membranes to determine their suitability for use in the process. Prerequisites for successful use were good electrical conductivity, low permeability to water and glyoxylic acid, and good mechanical stability. The results obtained are given in Table 1. The selectivity is clearly affected by the type of membrane. It ranges from 90 to 95% in almost all cases but it decreases sharply when Nafion® 417 and Nafion® 423 were used. It was obvious that glyoxylic acid migrated from catholyte to anolyte through these membranes due, probably, to their high pore size. The migration is favoured because at the catholyte pH (0.8–1.4) glyoxylic acid is found in its nondissociated form. Migration was only observed when the electric field was applied. Runs were carried out for 24 h without applying electricity starting with a solution of oxalic acid (60 g dm^{-3}) and glyoxylic acid (90 g dm^{-3}) as catholyte and migration was negligible. Finally, taking into account the selectivity of the process and the mechanical stability of the membranes, Nafion® 324 was chosen. Its water permeability was 45 cm^3 per faraday.

Table 1. Influence of the cation exchange membrane on the selectivity (S)

Membrane	*S/%*
Nafion® 417	74
Nafion® 417	71.3
Nafion® 423	66
Nafion® 324	93.5
Selemion CMV	93.5
Selemion CMV	95
Neosepta CL 25 T	94
Neosepta CL 25 T	89
Neosepta CM 1	94
Neosepta C6610F	91
Neosepta CMH	91

Anode: DSA® (IrO$_x$/Ti). Cathode: Pb. Anolyte: sulphuric acid 10% w/w. Catholyte: saturated oxalic acid aqueous solution throughout all the electrolyses. Temperature: 12–14 °C. Flow rate: 2 dm^3 min^{-1}. Interelectrode gap: 9 mm. Electrode area: 20 cm^2. Current density 2000 A m^{-2}.

3.2. *Electrode material and water quality influence*

The influence of these parameters can be seen in Fig. 1 where the current efficiency with respect to oxalic acid against the number of faradays is plotted. Each faraday corresponds to 6.7 operating hours. As can be seen, using a DSA® oxygen anode and demineralized water it is possible to maintain the cathode activity for at least 80 h. However, with both a Pt/Ti anode and a deteriorated DSA® oxygen anode (damaging its stability by changing the cell polarity for 1 h) the current efficiency falls dramatically after a few hours. Likewise, use of tap water speeds up the cathode deactivation. It seems obvious that loss of cathode activity is related to electrodeposition of low hydrogen overvoltage metals on the cathode surface, originating from tap water or from slight anode corrosion (Pt, Ir).

Therefore, for the rest of the study demineralized water was always used. In contrast, deteriorated DSA® oxygen was chosen as one of the anode materials to clearly demonstrate the feasibility of the proposed method to regenerate and maintain the cathode activity.

3.3. *Continuous electrogenerated cathode. Pt-anode*

The first attempt to regenerate the cathode activity was by reversing its polarity (*a*: for 30 s at 2000 A m^{-2}; *b*: for 10 min at 100 A m^{-2}), but this

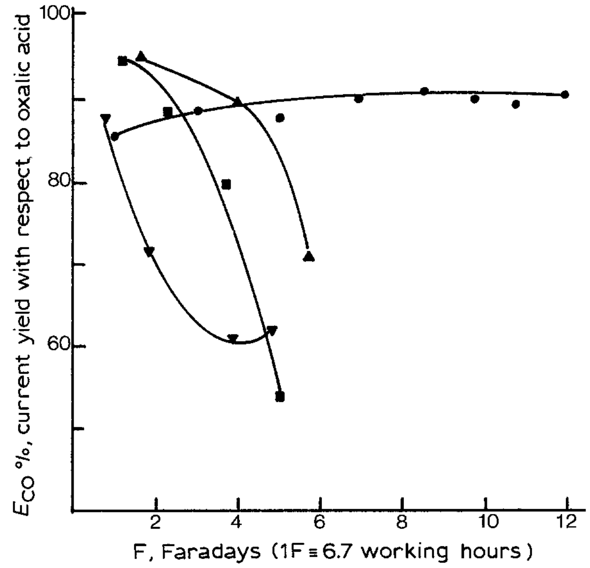

Fig. 1. Electrode material and water quality influence. Electrode area: 20 cm^2. Flow rate: 2 dm^3 min^{-1}. Anolyte: sulphuric acid 10% w/w. Interelectrode gap: 9 mm. Charge: 85% of theoretical. Temperature: 12–14 °C. Current density: 2000 A m^{-2}. (●) DSA® O$_2$ anode, demineralized water. (▼) Pt/Ti anode, demineralized water. (▲) Deteriorated DSA® O$_2$ anode, demineralized water. (■) Deteriorated DSA® O$_2$ anode, tap water (31 p.p.m. as CaCO$_3$).

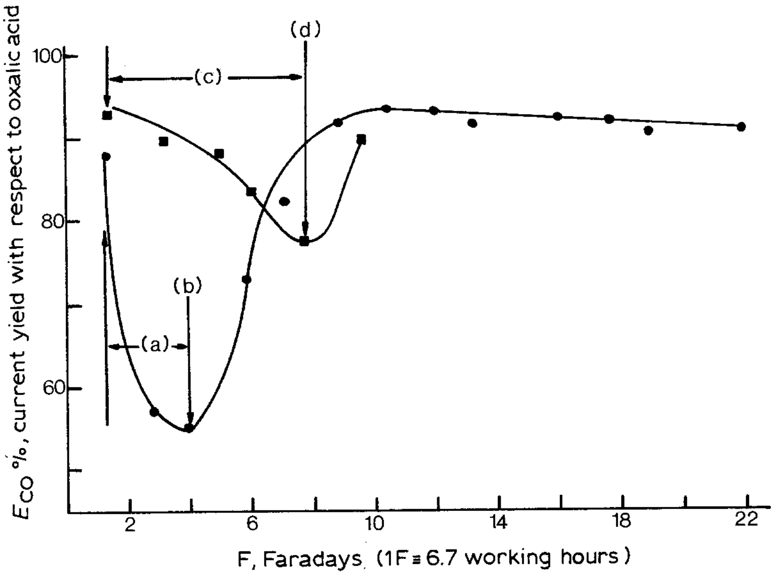

Fig. 2. Cathode electroregeneration. Pt/Ti anode. Experimental conditions as in Fig. 1 Demineralized water. (●) Without Pb(II) addition (a). Pb(II) sulphate addition to the anolyte in (b). (■) Pb(II) sulphate (38 mg F^{-1}) to the catholyte (c). Cathode washing with 10% w/w aqueous nitric acid in (d) for 5 min.

procedure was ineffective. Consequently, the possibility was considered of solving the problem by adding, throughout the electrolyses, small amounts of Pb(II) salts in such a way that its electrodeposition on the lead cathode surface would create a fresh cathode surface and therefore the cathode activity would be continuously restored. The presence of a low concentration of a metal in the electrolyte has been shown to be very effective in other electrosynthesis [17–20].

At first, two experiments were run. In the first, Pb(II) sulphate was added to the anolyte in sufficient amount for saturation to occur. In the second, 38 mg of Pb(II) sulphate per faraday were added to the catholyte. The results can be seen in Fig. 2 where the current efficiency with respect to the oxalic acid consumption (Eco) against the number of faradays ($1\,F \equiv 6.7$ working hours) is plotted. When no Pb(II) sulphate is added the current efficiency decreases dramatically after a few hours. When Pb(II) sulphate is added to the anolyte the cathode activity is spectacularly restored in 25 h, the faradaic yields being even higher than those obtained at the beginning of the experiment.

After 94 working hours the average current efficiency was 91%, the selectivity 96%, and the mean voltage 5.7 V (power consumption 4.7 kWh kg^{-1}). By contrast, when Pb(II) sulphate was added to the catholyte from the beginning of the experiment, the current efficiency decreased slowly from 92.5 to 77.5% in 52 h. The cathode activity was restored by washing it with 10% w/w aqueous nitric acid solution for 5 min. The results clearly indicate that Pb(II) sulphate addition to the anolyte is more effective than addition to the catholyte, although comparing the results obtained without Pb(II) sulphate (see Fig. 1) and with Pb(II) sulphate in the catholyte, the positive influence of Pb(II) on the cathode performance is obvious. However, when Pb(II) sulphate is added to the catholyte, lead electrodeposition slows the loss of cathode activity but it does not avoid it. Lead electrodeposition can not compete with platinum electrodeposition. Probably Pb(II) addition to the anolyte is more effective because during electrolyses lead is deposited on the anode surface forming a lead dioxide layer which prevents, or minimizes, its corrosion. In fact, after dismantling the cell, a brown layer of lead dioxide was observed on the Pt/Ti anode surface.

In spite of the good results obtained adding Pb(II) sulphate to the anolyte, this procedure was abandoned because in some of the additional experiments carried out to confirm these results, a sudden increase in the cell voltage, along with a dramatic increase in hydrogen evolution, was observed. A white precipitate of Pb(II) sulphate arose on the anode face of the membrane causing damage.

3.4. Continuous electrogenerated cathode. DSA® O_2 anode

3.4.1. 20 cm^2 electrode area cell: To show the beneficial effect of the Pb(II) salt addition, a deteriorated DSA® oxygen anode was used. An experiment was run to study the effect of lead addition in both anolyte and catholyte. The results obtained are shown in Fig. 3 where the current efficiency with respect to the oxalic acid consumption against the number of faradays ($1\,F \equiv 6.7$ working hours) is plotted. At the beginning of the experiment Pb(II) sulphate was added to the anolyte without any positive effect. The cell voltage increased by 2 V just after adding Pb(II). The faradaic yield decreased from 83 to 67% in 50 h. Then, Pb(II) sulphate addition to the anolyte was stopped and a 30 mg per faraday Pb(II) carbonate addition to the catholyte was initiated. In 20 h, the current yield suddenly increased from 67 to

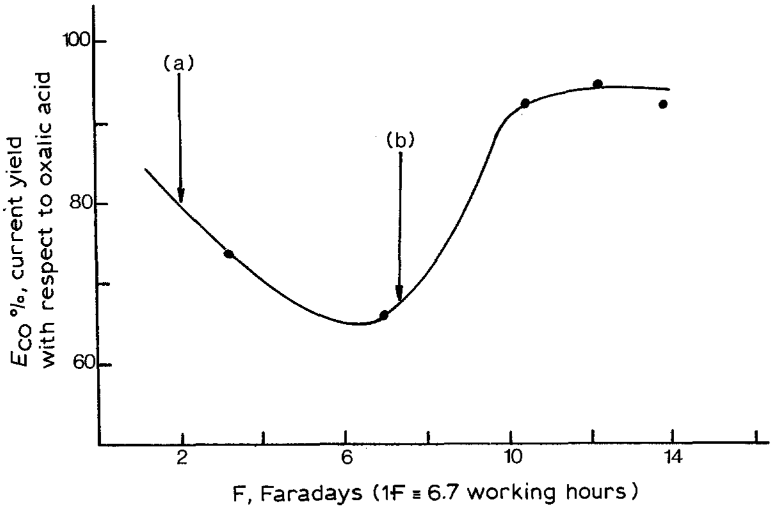

Fig. 3. Cathode electroregeneration. Deteriorated DSA® O_2 anode. Experimental conditions as in Fig. 1. Demineralized water (a) Pb(II) sulphate addition to the anolyte; (b) $PbCO_3$ addition ($30\,mg\,F^{-1}$) to the catholyte.

92% and remained constant to the end of the experiment. Selectivity was higher than 95% and the mean cell voltage was 7.5 V. The results obtained by adding Pb(II) carbonate to the catholyte when a deteriorated DSA® oxygen anode is used are as good as those obtained with a stable DSA® oxygen anode (see Fig. 1).

Subsequently, an experiment was run in order to determine how long the cathode activity could be maintained by adding Pb(II) oxalate to the catholyte without dismantling the cell for mechanical cleaning of the cathode. The results are plotted in the upper part of Fig. 4 and are compared with those obtained without Pb(II) addition. As can be seen, the effect of Pb(II) addition is spectacular. After 63.5 working hours the current efficiency was higher than 90%. By contrast, without addition of Pb(II) the current efficiency fell in 39 h from 97 to 70%. However, in the course of time the faradaic yield decreased slowly in such a way that to restore the cathode activity it was necessary to wash the cathode surface with an aqueous solution of nitric acid 10% w/w for 5 min. After this operation, current efficiency was restored to its original value (97%). Likewise, it is evident from Fig. 4 that the lower the amount of Pb(II) oxalate added to the catholyte, the greater the time between each cathode washing with 10% w/w nitric acid. Thus, adding 33.5 mg per faraday, a washing every 67 h is necessary. Adding 1.67 mg per faraday the time between washings is 87 h, and adding 0.75 mg per faraday the time increases to 134 h.

Apparently, the loss of the cathode activity in the course of electrolysis is related to the presence of a lead precipitate on the cathode surface which prevents transport of oxalic acid from the solution to the cathode surface, thus favouring hydrogen evolution. Washing with dilute nitric acid dissolves the lead precipitate and restores the cathode activity. This chemical cleaning procedure avoids the necessity for cell dismantling but, unfortunately, if carried out frequently, the cathode life can be seriously shortened. Thus, the economic penalty is obvious. To overcome this problem, attention was focused on the previously mentioned observation that there is a relationship between the amount of Pb(II) added and the need for washing the cathode surface with dilute

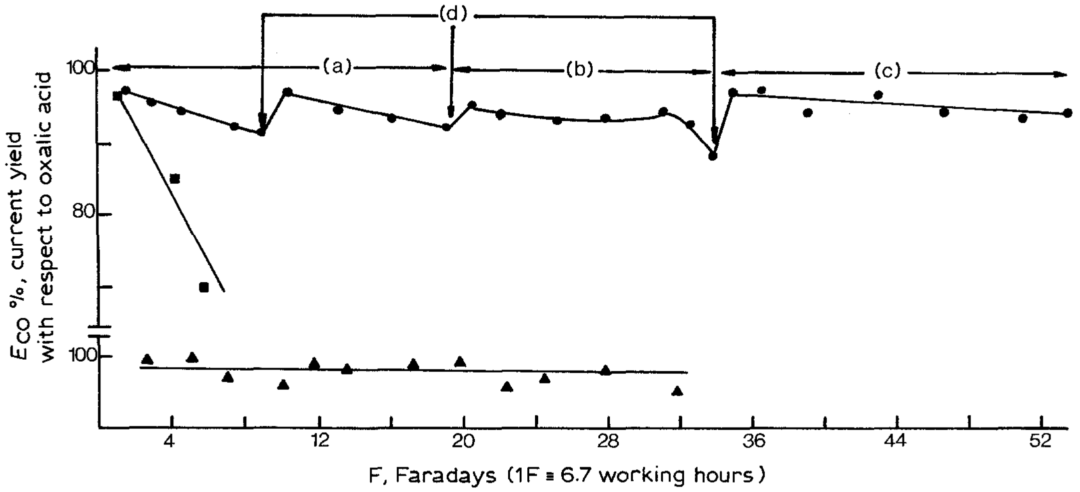

Fig. 4. Cathode electroregeneration. Deteriorated DSA® O_2 anode. Experimental conditions as in Fig. 1. (●) Pb(II) oxalate addition to the catholyte: (a) $33.5\,mg\,F^{-1}$; (b) $1.67\,mg\,F^{-1}$; (c) $0.75\,mg\,F^{-1}$; (d) cathode washing with 10% aqueous nitric acid for 5 min. (■) Without adding Pb(II) oxalate. (▲) Pb(II) oxalate addition to the catholyte: $9.8\,\mu g\,F^{-1}$ ($6.7\,\mu g$ as Pb(II)). Charge: 75% of theoretical.

nitric acid. By decreasing the amount of Pb(II) it should be possible to space the time between each washing. An amount of Pb(II) to regenerate a cathode layer with volume corresponding to one monolayer of lead atoms per faraday is necessary. The thickness of this monolayer would be equivalent to the covalent diameter of lead; 0.294 nm. Therefore, taking into account the electrode area and the density of lead, 6.7 μg of Pb(II) per faraday was calculated as sufficient. An experiment was run adding this amount to the catholyte and stopping each batch when 75% of theoretical charge had been passed. The results are plotted at the bottom of Fig. 4. As can be seen, after 32 faradays (214.4 working hours) the current efficiency for oxalic acid consumption was almost constant and equal to 97%. No nitric acid washing was necessary. Selectivity ranged between 96 and 99%.

Glycolic acid concentration in the electrolysed liquor was less than 0.1% when detected. The mean cell voltage was 7 V. The mean power consumption was 5.4 kWh kg^{-1}.

The results clearly show that addition of Pb(II) traces to the catholyte permits both a continuous regeneration of the cathode activity and an increase in the yield.

4. Conclusions

The results obtained are, to the best of our knowledge, the best so far reported for the electrosynthesis of glyoxylic acid from oxalic acid and show both the industrial feasibility of the process and the utility of continuously deposited cathodes for improving the performance of the electrochemical processes. This type of cathode may play an important role in electrosynthesis.

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