ELECTROSYNTHESIS OF GLYOXYLIC ACID

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Summary

Based on laboratory scale experiments to produce glyoxylic acid by electochemical reduction of oxalic acid in a continuously operated cell similar to a filter press, we designed and constructed pilot-scale electrosynthesis equipment with an output of 20 t/yr. The catholyte is a saturated aqueous solution of oxalic acid, the anolyte is a 10% sulfuric acid solution. The material of the electrodes is lead, that of the cell frames is PVC. The diaphragm applied is a cation-exchange membrane (Nafion 425). At current density of 20 A/dm^2 and current efficiency of 60–65%, the yield obtained is 94–96%.

Introduction

Several processes to produce glyoxylic acid electrochemically are known. However, organic electrosynthesis is still novel in Hungary, and for this reason it appeared preferable to develop a process based on own experiments, in order to study the applicability of electrosynthesis processes under domestic conditions.

The purpose of our work was on the one hand to interpret the chemical and electrochemical parameters of electrosynthesis by own experiments, and on the other hand to find a suitable method for economic recovery of glyoxylic acid from the electrolyte. A further objective was to put into practice—on a pilot scale—an organic electrosynthesis process which might serve as a reference plant for the implementation of further similar processes.

To produce glyoxylic acid by electrolysis, two paths exist: one starting from the aqueous solution of oxalic acid containing mineral acid [1, 2], the other using oxalic acid free of mineral acid [3] in a cell fitted with a cation-exchange membrane [4, 5]. The latter path has the advantage that the electrolyte contains no impurities and is hence easier processes to glyoxylic acid. The reduction of oxalic acid on the cathode proceeds by the following equation:

$$\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} + 2\,\text{H}^+ + 2\,\text{e}^- \longrightarrow \begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array} + \text{H}_2\text{O}$$
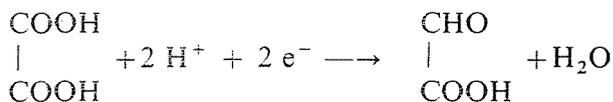
On the indifferent anode, oxygen evolution takes place from the sulfuric acid anolyte:

$$2\,H_2O \rightarrow 4\,H^+ + O_2 + 4\,e^-.$$
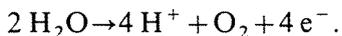
The hydrogen ions formed on the anode pass through the ion-exchange membrane into the catholyte and supply the hydrogen ion concentration required for the reduction process.

In addition to the formation of glyoxylic acid, hydrogen evolution is also observed on the cathode. The rate of hydrogen evolution is largely influenced by conditions: above all by the nature of the cathode material, by the presence of metal impurities, by the concentrations of oxalic acid and glyoxylic acid in the catholyte, by purity and temperature of the catholyte and by current density. All these parameters affect current efficiency and product yield.

Experimental

We used the electrosynthesis equipment resembling a filter press in the experiments. This equipment was constructed by us and has been described in detail in our earlier papers [6, 7]. The catholyte was a 70 g/dm³ oxalic acid solution made of technical grade oxalic acid dihydrate. The anolyte was 10% sulfuric acid solution. Tap water was used to make the solutions. The ion-exchange membrane separating the cathode and anode compartments was Nafion 425. The section of a cell unit is represented by Fig. 1.

The cathode materials were 99.5% lead, 99.99% lead and amalgamated lead; lead plates of the above grades, titanium and DSA electrodes (titanium coated with noble metal) were used for anodes.
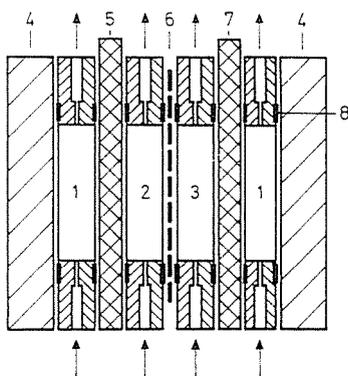
Fig. 1. Section of electrolytic cell of the filter-press type with ion-exchange membrane
1 — Cooling compartment; 2 — Anode compartment; 3 — Cathode compartment; 4 — Cover plate; 5 — Anode; 6 — Ion-exchange membrane; 7 — Cathode; 8 — Sealing ring

Experiments with the batchwise-operated laboratory cell

Experiments performed with electrodes made of different materials demonstrated that for the cathode, the purer-grade lead is preferable from the view of current efficiency, since impurities in the cathode material promote hydrogen as by-product formation. Amalgamation of the lead cathode improved current efficiency at the start of the electrolysis; its practical advantage, however, is little, since the amalgamated layer disappears from the surface after one day of electrolysis, at the rate of about 10 Faraday/dm^2 amount of current having passed through the cell.

Using lead anodes, ozone and lead dioxide are generated in addition to oxygen evolution the oxide partly adheres to the surface of the anode, and partly flows in form of a finely dispersed precipitate with the anolyte. The applicability of titanium anodes was also investigated; however, the passive layer developing on the surface largely increases the cell voltage required for electrolysis and is hence economically unfavourable. Various lead alloys look promising anode materials, since the alloying materials suppress lead
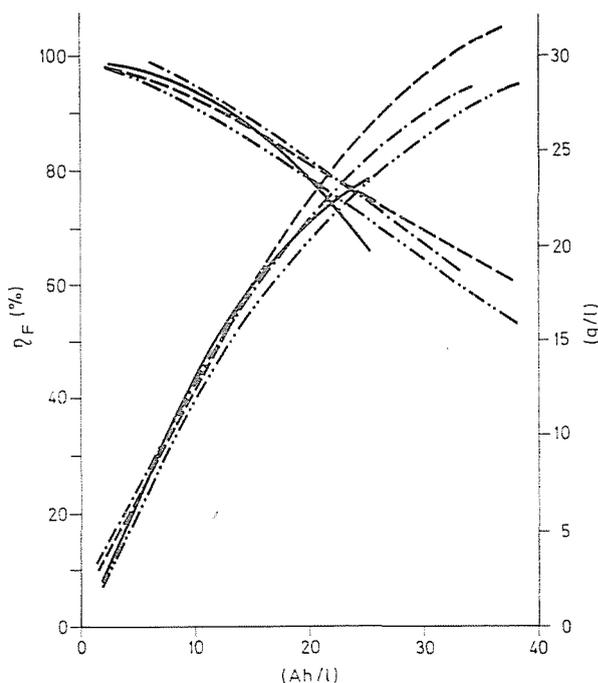
Fig. 2. Current efficiency and glyoxylic acid concentration *vs.* amount of charge per dm^3 catholyte.
———— amalgamated lead cathode; — · · — 99.5% lead cathode; — · — 99.99% lead cathode; — — — DSA anode, 99.99% lead cathode

dissolution, and so do DSA electrodes which can be applied in sulfuric acid media.

In batchwise electrolysis, decrease of the current efficiency was observed. It may be caused both by changes in the cathode surface during electrolysis and by changes in the composition of the catholyte. Experiments showed that change in the cathode surface area has minor importance than keeping constant of oxalic acid concentration on a slight increase in glyoxylic acid concentration. From the view of current efficiency and yield it is preferable to keep oxalic acid concentration constant, corresponding its saturation value, and not to let glyoxylic acid concentration exceed 30–40 g/dm³ .

Some characteristic examples are shown in Fig. 2. They refer to batchwise experiments; at the start of the measurements the catholyte contained oxalic acid only. No essential differences between the processes using different electrode materials exist between the curves representing glyoxylic acid concentration *versus* amount of charge per 1 dm³ catholyte. Current efficiency
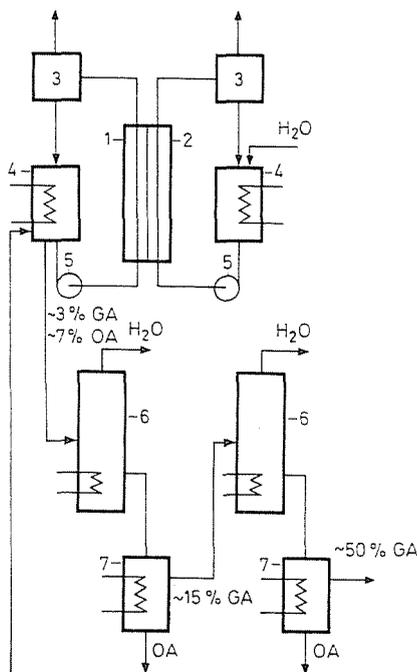
Fig. 3. Schematic representation of the electrosynthesis of glyoxylic acid and of the processing technology of the catholyte

1 — Cathode compartment; 2 — Anode compartment; 3 — Degasser; 4 — Cooler of electrolyte; 5 — Pump; 6 — Vacuum evaporator; 7 — Cooling and filtering; GA — Glyoxylic acid; OA — Oxalic acid

declines in all cases with increasing concentration of glyoxylic acid. For continuous operation one must therefore find a work point with a glyoxylic acid concentration where losses in current efficiency will not render the process uneconomical.

In the batchwise experiments the yield relative to oxalic acid consumption was 94–96%.

Processing of the catholyte

If favourable parameters of electrolysis are to be established, the problem how to process the catholyte leaving the cell cannot be disregarded. The end-product of the ion-exchange membrane process has the advantage that it can be processed by vacuum evaporation. The solution containing oxalic acid and glyoxylic acid is evaporated at 30–40 °C until oxalic acid crystallizes. The solution is then cooled to 0 °C and the oxalic acid crystals are filtered off; the filtrate is again subjected to vacuum evaporation until the required glyoxylic acid concentration is reached. The oxalic acid crystals will always contain a certain amount of glyoxylic acid; this does not, however, represent any loss, since the oxalic acid is recycled into the catholyte. With this method of processing a 40–50% concentration of glyoxylic acid is attained in two steps. Figure 3 is a diagrammatic representation of electrolysis and vacuum evaporation processing of the catholyte.

Continuous laboratory-scale electrosynthesis

In the batchwise experiments we worked with a defined catholyte volume and stopped electrolysis when a concentration of 3–4% glyoxylic acid was reached, since this was found satisfactory from the view of both current efficiency and yield. To change over to continuous operation, part of the catholyte, after having attained the required concentration, is led to processing, and the corresponding volume of saturated oxalic acid solution is introduced into the system. This way, following initial start-up period glyoxylic acid production becomes continuous. Measurements made in our laboratory equipment with a cathode surface area of $0.5\ dm^2$ confirmed that continuous glyoxylic acid production is achieved at current efficiencies of 60–65% by continuously drawing off catholyte at a flow rate of $0.5\ dm^3/hr$ per dm^2 of cathode surface area.

Using this equipment we studied changes in yield and current efficiency *versus* temperature, flow rate and current density. Temperature was varied between 15 and 35 °C, flow rate from 10 to 50 dm^3/hr, current density from 20 to 30 A/dm^2. Our measurements indicated that at higher current densities yield depends to a greater extent on temperature. At identical current densities, it

was preferable to increase flow rate, since in this manner slighter temperature increase will manifest itself in the individual cells. Lower current densities also favours establishment of better temperature distribution conditions.

Pilot-scale electrosynthesis

Based on the results with the laboratory apparatus, the following data were used to design and construct a pilot-scale cell assembly for an output of 20 t glyoxylic acid per year:

Current density : 20 A/dm^2
Flow rate of catholyte: 50 dm^3/dm^{2}hr
Glyoxylic acid content of catholyte: 30–40 g/dm^3
Total-required cathode surface: 200 dm^2
Total current: 4000 A.
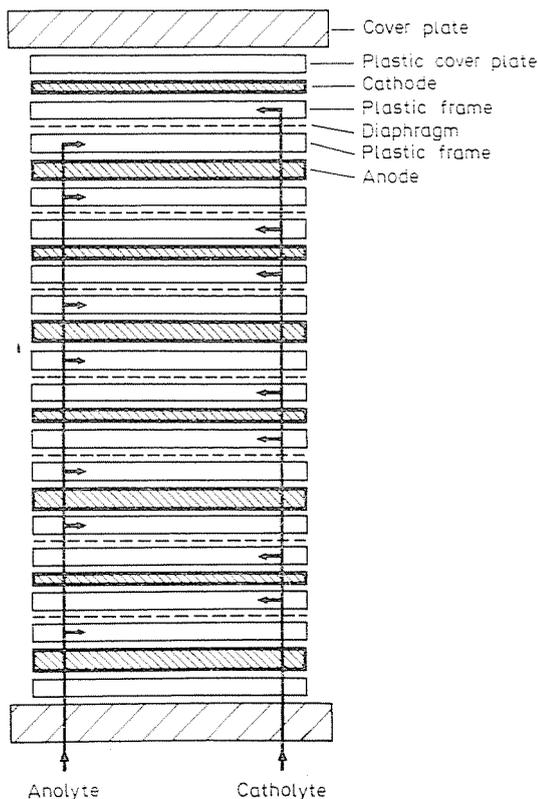
Fig. 4. Top view of the pilot-scale electrosynthesis assembly

To attain the output required, a cell assembly consisting of several cells is necessary. Its electrolyte and electric system may be connected in series or parallelly. In parallel electrolyte flow, pressure conditions are identical in each cell unit, and cooling of the electrolyte is feasible using external cooling by heat exchangers. From the view of electric danger to life, parallel connection is again preferable, since higher currents and lower voltages can be applied.

The external dimensions of the equipment constructed by us are 610 $\times$ 812 mm. The free surface area of one electrode is 28 dm^2. To have 200 dm^2 surface area required for the design output, seven cathodes and seven anodes are needed. Since only one surface of the electrode plates at the ends of cell assembly is in operation, four cathode plates and four anode plates are wanted.

Cathodes and anodes were both made of 99.95% grade lead plate. Their thickness was 5 and 10 mm, resp. The construction would have allowed to use DSA anodes which proved superior in the preliminary experiments, but we had none at disposal in the required size.

The equipment is assembled by fitting the anode and cathode plates, the PVC frames forming the electrode compartments, the rubber seals and the ion-exchange membranes in the appropriate order (Fig. 4). Total width of the assembly is 370 mm. Total mass is around 700 kg. When fixed with bolts, it can be mounted on a support.

In test runs we stated that at current density of 20 A/dm^2 the cell voltage measured on a single cell unit was 8.5 V. The losses by voltage drops over electric connections were less than 0.1 V and can hence be neglected. The temperature increase of the electrolyte when passing through the cell operated at 25 °C was 1–1.5 °C. The glyoxylic acid concentration in the catholyte led off to processing was 35 g/dm^3. For a 20 t/yr output, 32 kW d.c. power is required.

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