Scale-up of electrocarboxylation reactions with a consumable anode

J. CHAUSSARD, M. TROUPEL, Y. ROBIN, G. JACOB, J. P. JUHASZ

S.N.P.E. Research Centre Le Bouchet, B.P. 2, Le Bouchet, 91710 Vert le Petit, France

Efficient carboxylation of various organic halides can be achieved by electroreduction in aprotic solvents under an atmosphere of carbon dioxide when the selected anodic reaction is the electro-dissolution of a magnesium electrode. Successful scale-up from 30 ml atmospheric pressure laboratory cells to a 400 l pressurized pilot unit clearly demonstrates the technical feasibility of this new process for large-scale production of valuable carboxylic acids.

1. Introduction

The electrochemical reduction of organic compounds in aprotic solvents is a very suitable way of preparing reactive anionic intermediates of great synthetic value. For instance, carbanions generated from organic halides [1–3], carbonyl compounds [4, 5], olefinic compounds [1, 6, 7] and Schiff bases [8] readily react with carbon dioxide to yield carboxylic acids.

Unfortunately, in spite of their obvious synthetic interest, these reactions could not, up to now, be used for large-scale production because of the lack of a convenient anodic counter reaction. The required anodic reaction, while avoiding the need of a divided cell, should preferably consume a cheap material, yield no acidic, electrophilic, or easily reducible by-product, and should involve neither the starting material nor the product of the cathodic process. The anodic oxidation of tetraalkylammonium oxalate [8] or lithium oxalate [3] is of special interest, as its only by-product is carbon dioxide. Its major drawback is the consumption of large amounts of very expensive salts.

Recent laboratory studies have clearly demonstrated the numerous advantages (yields, selectivity, easy use) of metallic anode (magnesium, aluminium, etc.) electrodissolution, not only for these electro-carboxylations [9–13] but also for the coupling of electrogenerated carbanions with various electrophiles to yield ketones [14, 15], alcohols [16, 17] and phosphines [18, 19]. However, for larger scale production, it was necessary to devise special electrolytic cells, fulfilling the following requirements:

narrow and constant interelectrode gap in time and space;

good agitation between the electrodes;

efficient heat removal from the cell;

easy replacing of consumed anodes;

use of consumable anodes in a readily available form (for example, ingots);

pressure resistant apparatus so as to make gas handling easier.

In this paper, we present a review of our work on the electrocarboxylation of organic halides using a sacrificial magnesium anode, from small laboratory glass electrolytic cells to large-scale stainless steel pressurized production cells. These new electrolytic cells were successfully used for the synthesis of various carboxylic acids such as naphthylacetic acid, diphenyl-acetic acid, trifluoromethylbenzoic acid and isobutyl-hydratropic acid, these being valuable intermediates for a plant growth regulator, a herbicide, a fungicide and a non-steroidal anti-inflammatory agent.

2. Experimental details

2.1. Glass laboratory cells

The first electrolytic cell used by Perichon *et al.* for the electrocarboxylation of organic halides was an improved 'beaker cell' already described elsewhere [13] (see Fig. 1). A vertical magnesium rod is used as the anode, surrounded by a concentric stainless steel grid cylinder used as the cathode. Carbon dioxide is bubbled into the solution which is agitated by a magnetic stirrer. This cell is very suitable for test preparations of gram scale samples of carboxylic acids. Unfortunately it cannot be scaled up, as stirring problems occur as soon as the size of the anode is increased.

2.2. Flow-through tubular cells

In larger cells (1 dm^2), good agitation is achieved by pumping the electrolytic solution between the electrodes. The cell is made of an outer cylindrical stainless steel wall (2 cm in diameter) used as the cathode, and a central cylindrical magnesium rod (1 cm in diameter) used as the anode (see Fig. 2). The electrolytic solution is cooled and saturated with carbon dioxide in a separate tank (0.1–1 l). The agitation caused by the circulation of the solution between the electrodes is sufficiently homogeneous to ensure a regular consumption of the anode during electrolyses.
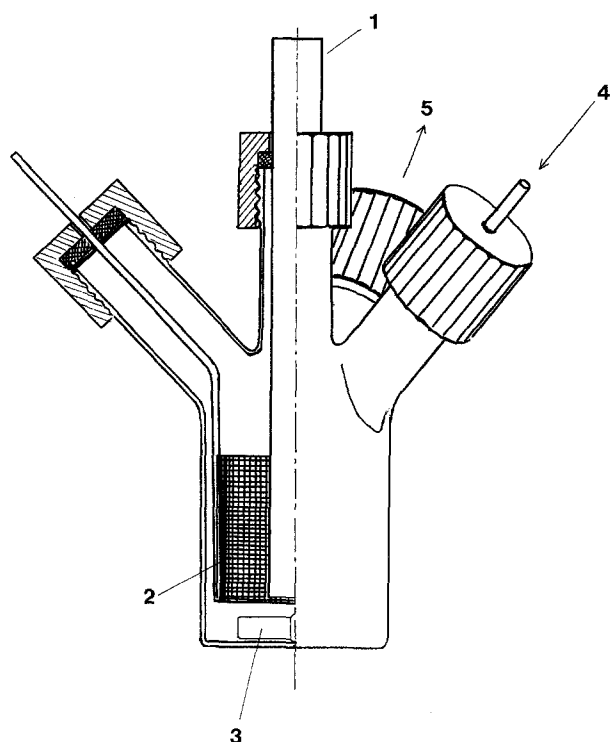
Fig. 1. Glass laboratory cell. (1) Magnesium rod (anode); (2) stainless steel grid (cathode); (3) magnetic stirrer; (4) carbon dioxide inlet; (5) gas outlet.

The magnesium consumable anode is replaced every 20 h, when its diameter has been reduced from 10 mm to about 2 mm. At this stage, the interelectrode gap has increased (about 10 mm), producing a significant ohmic drop when poorly conducting organic solvents are used.

This is the major drawback of these tubular cells which cannot be scaled up with large diameter consumable electrodes. On the other hand, if the diameter is limited, the electrode needs to be replaced very frequently, which is hardly feasible for industrial production. Nevertheless, this apparatus is very suitable for the preparation of 10 to 100 g of carboxylic acids. Results are presented in Table 1.

2.3. V-Shaped 'ingot-eating' electrolytic cells [20]

Obviously, the problem of introducing new anode material as soon as it is consumed can be solved only by continuous movement of the anode towards the cathode. Complicated mechanical devices have previously been used for this purpose [21]. Much more interesting is the electrolytic cell developed by Nalco for tetraalkyl lead electrosynthesis [22]. The consumable lead anode is a bed of lead pellets which is enclosed in a cylindrical porous bag. The geometry of the cell is constant during the electrolysis and the anode material is readily replaced by refilling the bag. Unfortunately, the use of such a cell for electrocarboxylation proved unsatisfactory because of the bad electrical contact between the magnesium particles which are always more or less covered by an insulating oxide layer [23]. Only the use of a massive consumable
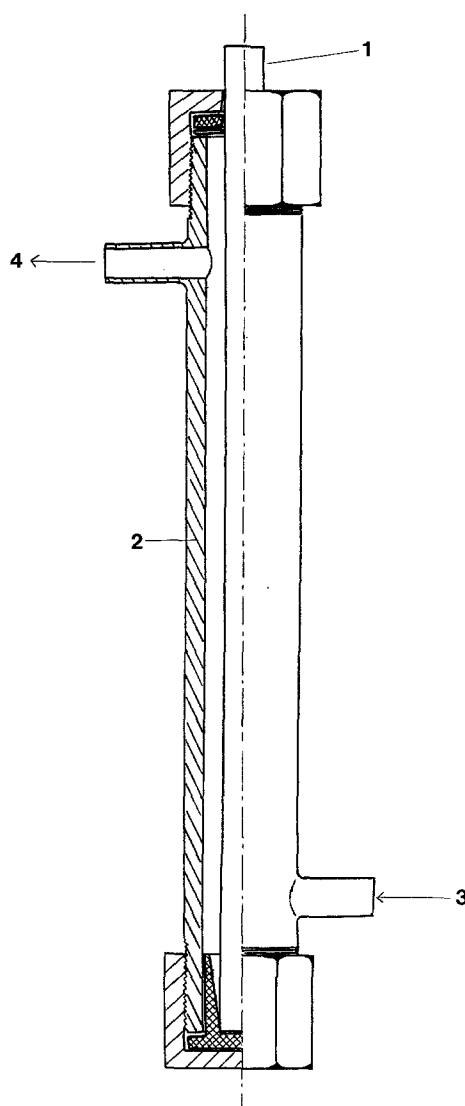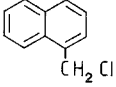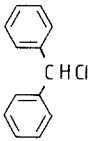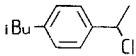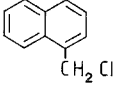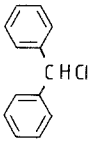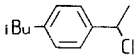

Fig. 2. Flow-through tubular cell. (1) Magnesium rod (anode); (2) stainless steel cathode; (3) electrolyte inlet; (4) electrolyte outlet.

anode moving toward the cathode during the electrolysis was satisfactory.

In the cell presented below (see Fig. 3), the anode is separated from the cathode only by a 3-mm polyethylene grid. The anode, resting on the polyethylene spacer, is pressed down on the cathode by its own weight. In this way, it is evenly consumed and descends towards the cathode throughout the electrolysis, thus ensuring a constant interelectrode gap. It is noteworthy to add that in such a device the local current density and, consequently, the anode 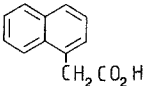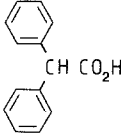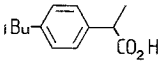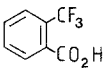electro-erosion rate, will be higher in places where the spacing between electrodes is smaller (because of reduced ohmic drop); the anode will thus have a tendency to fit closely to the cathode shape during the electrolysis. The best results obtained in our laboratory were with a dihedron-shaped 20-dm^2 cathode as shown in Fig. 3. The anode consists of magnesium ingots (35 cm long, 13 cm wide and 5 cm high) that are piled on the cathode. During the electrolysis, they are electro-eroded to a V-shaped anode fitting closely the cathodic dihedron. Good agitation is ensured by pumping the electrolytic solution upwards between the electrodes

Table 1. Electrocarboxylation in a 1 dm² flow-through tubular cell (FTC) and in a 20 dm² V-shaped pressurized cell (VSPC)

Starting material		naphthalene-CH₂Cl	(C₆H₅)₂CHCl	iBu-C₆H₄-CHCl-CH₃	C₆H₄(CF₃)(Cl)
Product		naphthalene-CH₂CO₂H	(C₆H₅)₂CH CO₂H	iBu-C₆H₄-CH(CO₂H)-CH₃	C₆H₄(CF₃)(CO₂H)
Amount of starting material (g)	FTC	10	100	10	10
	VSPC	2570	5250	2550	6000
Starting material concentration	FTC	8.3	11	7	8.2
(% w/w)	VSPC	10	21	10	32
Electrolyte concentration	FTC	1.6	1	1.4	1.6
(% w/w)	VSPC	0.16	0.02	0.23	1
Temperature (°C)	FTC	2	2	2	2
	VSPC	45	35	38	35
Pressure (bar)	FTC	1	1	1	1
	VSPC	4	4	4	4
Current (A)	FTC	2	2	2	2
	VSPC	75	120	100	100
Cell voltage, mean value (V)	FTC	13	12	15	15
	VSPC	17	22	12	17
Conversion (%)	FTC	80	100	100	100
	VSPC	100	96	96	49
Faradaic yield (%)	FTC	72	79	80	61
	VSPC	70	99	68	63
Chemical yield (%)	FTC	79	73	95	67
(vs consumed start. mat.)	VSPC	82	75	89	64

and across the polyethylene spacer which is used as an efficient turbulence promoter. The bulk of the electrolytic solution is contained in a 30-l stainless steel tank cooled by means of an outer jacket and an inner coil. It is pumped from this tank through the electrolytic cell and back to the tank by means of a centrifugal pump ($2500\,l\,h^{-1}$). The whole apparatus can be pressurized up to 5 bar with carbon dioxide. The electrodes are connected to a constant current generator supplying up to 150 A and 40 V.

2.4. Electrocarboxylation of organic halides

The experimental procedure was described elsewhere [10, 11]. It is the same for small- and large-scale syntheses. A solution of the organic halide to be carboxylated (10–20% w/w, i.e. 0.8–1.6 M on average) and tetrabutylammonium bromide (0.1–1.5% w/w, i.e. 3×10^{-3} to 5×10^{-2} M) in dimethylformamide is electrolyzed in the presence of carbon dioxide with current densities ranging from 2 to $7\,A\,dm^{-2}$. When the electrolysis is carried out at atmospheric pressure, the temperature must be lowered to about 10° C to increase the solubility of carbon dioxide which is close to 0.2 M in DMF at 25° C. When it is carried out at 5 bar carbon dioxide, the yields are not affected by raising the temperature up to 40° C. Unless otherwise stated (see Table 1), the electrolysis is stopped when the starting material conversion (determined by gas chromatography) is higher than 95%. The solvent is removed by vacuum distillation, the residue is treated with concentrated hydrochloric acid and the product is extracted in a suitable organic solvent.

3. Results and discussion

The purpose of the present study of a new electrochemical cell with a sacrificial anode was to answer two questions:

is the V-shaped electrolytic cell a feasible technical solution for large-scale electrolysis with sacrificial anodes?

is the course of the electrochemical carboxylation affected by the special geometry and operating conditions of the new cell?

Concerning the first question (the technical feasibility), the main point was to know whether the flow and current distributions would be sufficiently even over the electrode surface to ensure a regular electro-erosion of the anode. Indeed, an uneven consumption of the anode could prevent the ingot piling from progressing downwards, induce short circuits by direct contact of irregularities of the anode to the cathode, or favor an accumulation of magnesium lumps at the bottom of the cell.

In practice, after a couple of days of satisfactory operation, the cell was opened and the magnesium blocks were removed for examination. The anode surface was perfectly clean and glossy, bearing a printed image of the polethylene spacer. Its electro-erosion
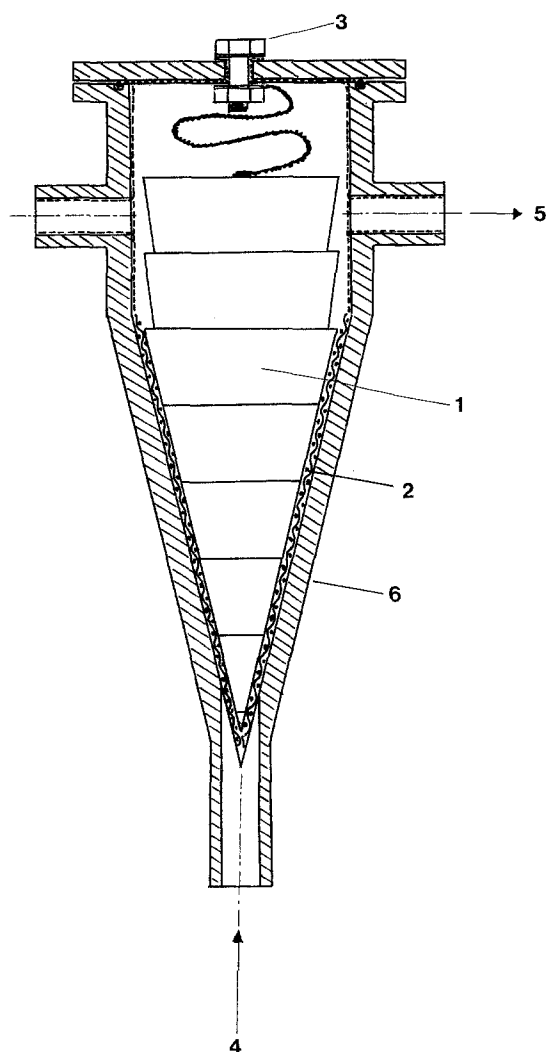
Fig. 3. V-shaped electrolytic cell. (1) Magnesium ingot (anode); (2) polyethylene spacer; (3) anodic connection; (4) electrolyte inlet; (5) electrolyte outlet; (6) stainless steel wall (cathode).

was quite regular, without any dendrites, sharp edges or lumps. Only the inlet and outlet areas, where the flow velocity was much higher, were eroded more deeply. In these places, the current densities must have been very high in spite of a rather large electrode gap and a consequently large ohmic drop. The relatively limited sunken areas did not prevent the magnesium anode from descending very regularly as it was consumed by the electrochemical reaction. No magnesium fragments were found lying on the bottom of the cell.

The second question was to know whether the change of scale (1 l to 30 l, 2 A to 100 A), the change of cell geometry (different flow rate, increased residence time in the cell, turbulence promoters) and the change in operating conditions (mainly higher temperature and pressure, higher current densities, higher concentration), would affect the yield of the electrochemical reaction.

Table 1 presents comparative results for electrocarboxylation of several organic halides in a tubular 1 dm^2 laboratory cell and in the 20 dm^2 V-shaped

pressurized cell. It can be noted that in the pressurized cell, the temperature, starting material concentration, and current densities were significantly increased without a dramatic drop in the faradic and chemical yields which is of special interest from the economic point of view.

4. Conclusion

The present study has clearly demonstrated the technical feasibility of the V-shaped cell for preparative electrocarboxylations with sacrificial anodes. The 20 dm^2 cell proved convenient for the preparation of a few kg of several valuable carboxylic acids.

On the basis of these results, we were able to proceed further in the development of this process. An industrial pilot unit (1000 A) has been successfully operated for about 1 year at SNPE and has already produced four different carboxylic acids, corresponding to an overall production of several metric tons. The detailed characteristics of this larger electrolytic cell will be published later.

The use of these electrolytic cells with a consumable electrode is by no means limited to electrocarboxylation reactions. Other electroreductions in aprotic solvents such as electroacylation reactions [14, 15] or synthesis of organometallics are currently under investigation.

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