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THE ELECTROCHEMICAL FLUORINATION OF OCTANOYL FLUORIDE WITH ELECTROLYTE CIRCULATION

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SUMMARY

A modification to the standard method of electrochemical fluorination is described which embodies a forced flow of electrolyte through the electrode pack. A preliminary study of flow characteristics through an electrode pack was carried out.

Good yields of perfluorooctanoyl fluoride and associated perfluorinated products are reported. The nature of the anode surface was studied before and after fluorination by scanning electron microscopy.

INTRODUCTION

The electrochemical method of fluorination was discovered by J.H. Simons and co-workers in 1941 although publication of this work had to be deferred until 1949 [1, 2]. This basic design has not changed to any extent during the ensuing 40 years. Several reviews have appeared and the reader is referred to those for a more detailed account of previous work [3,4,5,6,7,8].

In essence, the apparatus may be divided into three sections. The electrochemical cell, containing a pack of alternating anodes and cathodes. A refrigeration facility for cooling both the cell and the exit gases. An exit gas treatment unit where fluorinated material can be abstracted from the exit gas stream. For laboratory work the volume of the cell varies from a few c.c. s to ∿10 litres whereas industrial production units are of the order of 5,000 litres. Operation of such cells follows a similar pattern. The cell is charged with anhydrous hydrogen fluoride which is dried further by electrolysis, the substrate to be fluorinated is added and electrolysis is carried out usually at a potential in the range 5-7 v. and a current density of 0.08 - 2.0 Amps dm^{-2}. Operating potentials are selected so as to avoid the liberation of elemental fluorine. Potentials as high as 6-13 volts have been used with no significant evolution of elemental fluorine [9].

In most of the work described in the literature the transport of substrate to the electrodes relies on diffusion and the agitation produced by gas evolution.

Some reports have appeared of attempts to agitate the electrolyte by stirring or bubbling an inert gas through the electrode pack and improved yields of perfluorinated products have resulted [10,11,12,13]. In addition examples of forced flow of electrolyte through the electrode pack have been reported with concommitant improvements in heat dissipation product yields, and current efficiencies [14 - 19]. In none of this work has a systematic study of flow patterns through an electrode pack been reported.

In the present work the design and operation of a forced flow electrochemical fluorination apparatus is described, an essential preliminary to which is the study of electrolyte flow through an electrode pack with various inlet and outlet geometries.

EXPERIMENTAL

A Study of Flow Patterns through the Electrode Pack

A perspex cell of the same dimensions as the electrochemical cell was constructed, and equipped with various inlet positions and outlet points. This cell was equipped with a perspex lid from which the electrode pack was suspended. A circulating pump (Iwaki MD 15, flow rate 750 cc min^{-1} against a 0.5 m head of liquid), and a reservoir were provided which could be readily connected to any of the inlet positions, the liquid outlet was run to waste. Between the circulating pump and and inlet point provision was made for the injection of a suitable dye. Water was used as the circulating liquid even though its physical properties at ambient are not the same as those of hydrogen fluoride at $0^{o}C$. The densities of the two compounds are similar (ca 1000 kg m^{-3}) but their viscosities are not (HF at $0^{o}C = 0.26$ cP; water at $20^{o}C = 1$ cp), however it was not expected that flow patterns would differ greatly for the two fluids. In order to facilitate observations the electrode pack was illuminated from behind and from below by 500 watt Philips Photolita No. 2 bulbs. Such high orders of illumination were used since in some cases it was necessary to record flow patterns photographically. Preliminary experiments showed that it was essential to insert baffles between the electrode pack and the walls of the containing vessel. A diagram of the apparatus is shown in Figure 1.

In operation an inlet and outlet point were selected for study, all other inlet and outlet points were blocked, flow was established, and a small amount of a concentrated solution of dye injected into the inlet line. Approximately 10 sec after the injection the distribution of the dye in the electrode pack was observed through the electrode pack at right angles to the direction of flow. Most of the observations were made visually but some were recorded photographically.

Twenty seven such experiments were carried out using different combinations of the inlet and outlet points. The results of a selection of these experiments are given in Table 1. The position of inlet and outlet points is illustrated in Figure 2. After assessing the results of these experiments the inlet position was modified by extending it into the body of the cell. Several different inlet extensions were studied, these are illustrated in Figure 3. The vertical broken line in Figure 3 indicates the centre of the cell and shows the relative positions of the inlet extensions. A further series of 56 experiments was carried out with the modified inlet system; again, the results from some of these experiments are given in Table 1. Some of these observations were made whilst electrolysis was taking place, under these conditions direct visual observation was very difficult and a photographic record was made instead.

Examination of the results in Table 1 shows that experiments 32, 33, 35 and 36 gave the most even distribution of electrolyte through the electrode pack. Accordingly the electrochemical fluorination cell was equipped with an inlet exactly equivalent to I1 and an outlet point between O2 and O4.

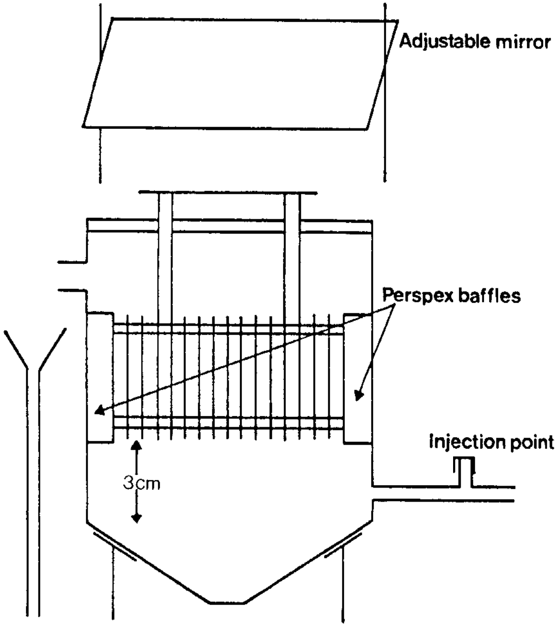


Fig.1 Apparatus used to study flow patterns through an electrode pack

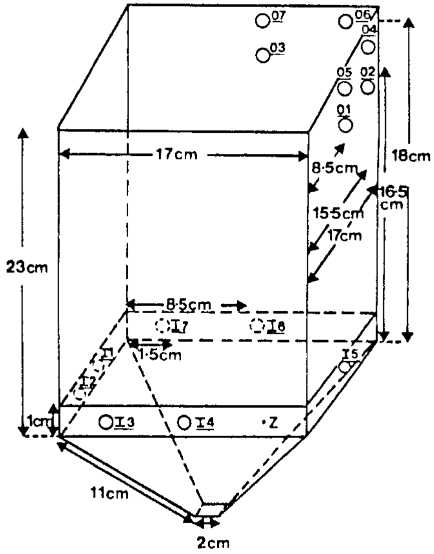
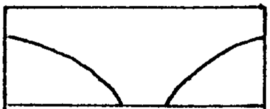
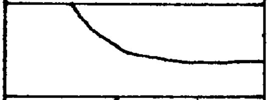
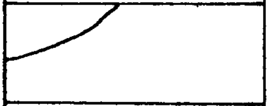
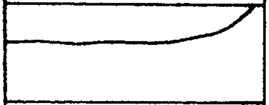
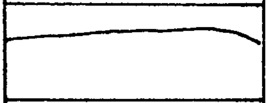
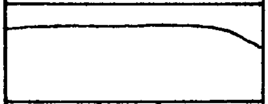
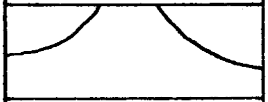
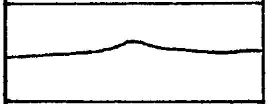
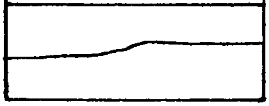


Fig.2 Perspex cell showing inlet and outlet positions

TABLE 1.
Selected data illustrating electrolyte flow through an electrode pack

Exp. No	Inlet position	Outlet position	Inlet extension	Diagramatic representation of flow pattern
1	I1	01	None	
2	I1	01	None	
7	I2	01	None	
15	I3	03	None	
17	I3	06	None	
24	I5	03	None	
28	I1	01	a, directed to I3	
31	I1	01	a, directed to I4	
32	I1	02	a, directed to I4	
33	I1	02	a, directed to I4	
34	I1	03	a, directed to I4	
35	I1	04	a, directed to I4	
36	I1	04	a, directed to I4	

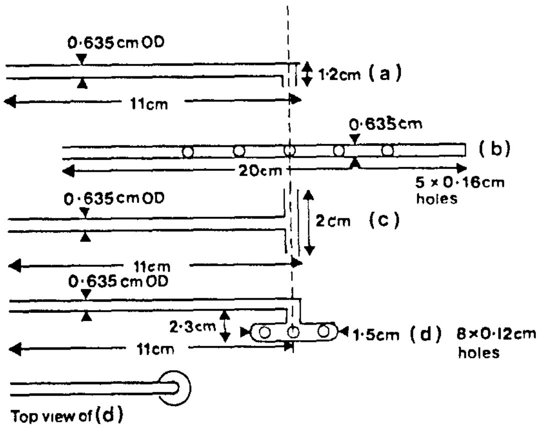


Fig.3 Inlet extensions used for flow studies

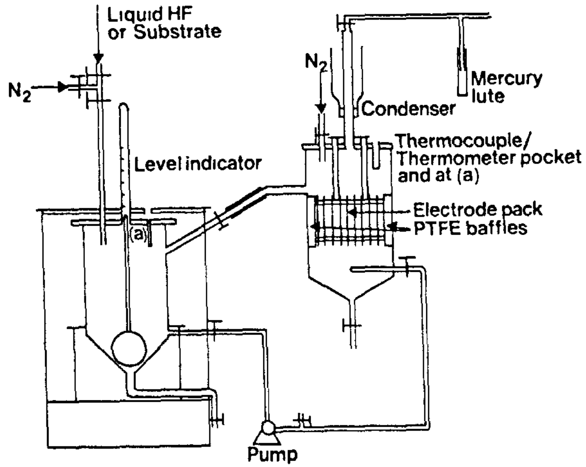


Fig.4 Electrochemical Fluorination Apparatus (not to scale)

Design and Construction of the E.C.F. Apparatus

A diagram of the apparatus is shown in Figure 4. The E.C.F. cell and the reservoir were constructed from 3.25 mm mild steel sheet, flanged and equipped with lids which could be bolted into place. A gas tight seal was ensured by using a P.T.F.E. gasket. The lid of each vessel was equipped, as appropriate with: a condenser to return AHF to the E.C.F. cell, electrode connecting bars, AHF or substrate filling point and nitrogen purge line, thermocouple pockets, and an AHF level indicator. An overflow pipe incorporating a short sight tube of polypropylene connected the E.C.F. cell with the reservoir. This sight tube enabled direct observation to be made of the flow of electrolyte and provided immediate warning of pump failure and/or blockage. The remaining pipework consisted of 6.35 mm O.D., 4.75 mm I.D copper tubing connected as appropriate with compression fittings. Valves were incorporated into the apparatus as shown in Figure 4 to facilitate safe shutdown during non-operational periods and to allow products to be drained from both reservoir and E.C.F. cell.

The electrode pack consisted of 16 cathodes and 15 anodes each of 1.5 dm wide x 1.2 dm high x 1.22 mm thick sheet nickel. The whole was assembled using nickel rod and nickel spacers together with insulating PTFE spacers and rods to ensure rigidity, the inter-electrode gap being 3.4 mm. Nickel plated brass bars connected the electrode pack to a busbar just above the cell lid and hence to a source of power. Where the connecting bars pass through the cell lid a gas-tight and electrically insulating seal was obtained using P.T.F.E. bushes. Each electrode was numbered to facilitate monitoring weight changes at various stages of the work. The gaps between the electrode pack and the sides of the containing vessel were filled with tightly fitting pieces of P.T.F.E. thus ensuring that all the electrolyte had to pass through the electrode pack.

Refrigeration of the electrolyte was effected by keeping the storage vessel in a conventional deep freeze unit with appropriate modifications to accommodate inlet and outlet pipes. In addition the exit gas line from the E.C.F. cell was fitted with a condenser which was cooled with a mixture of 'Dricold' and isopropanol when the cell was in operation. This condenser returned the bulk of the evaporated HF to the cell, any residual HF in the gas stream was removed by a sodium fluoride scrubber. Other ancillary equipment is shown in figure 4.

Operation of the E.C.F. Cell.

The reservoir and E.C.F. cell were charged with liquid anhydrous hydrogen fluoride. The AHF had a moisture content of ca. 0.08% which was removed by electrolysis while the electrolyte was circulated through the electrode pack. A small and constant current reading was taken as indicative that all the moisture had been removed. A current reversal procedure was not used. During the course of this drying procedure a nitrogen flow rate of 40-50 cc. min^{-1} was maintained to dilute the exit gas and avoid the build up of oxygen difluoride which can give rise to explosions.

Octanoyl chloride (150 g) was added, in 10 cc portions, to the circulating dry AHF via the filling line. After each addition the liberated hydrogen chloride was allowed to escape from the top of the condenser before adding the next portion. This procedure gave an ∿ 2% w.w. solution of octanoyl fluoride. Circulation of the solution was continued for several hours and samples of the solution analysed periodically for octanoic acid equivalent. See below for analytical methods used. This enabled a check to be made on the homogeneity of the solution. A value of 1.88% w.w. octanoic acid was finally obtained, equivalent to 135 g (0.925 m) octanoyl fluoride in solution.

Electrolysis of this solution was started at a potential of 6 volts and a current density of 0.37 A dm^{-2}. This current was held constant as long as possible after which a new value of current and current density was selected, this procedure was repeated until a total of 927 Ah had been passed. The temperature of the electrolyte rose to approximately $10^{o}C$ during the first two hours of electrolysis but thereafter remained constant. During the course of the electrolysis samples of electrolyte were removed at regular intervals for analysis. Products which collected at the base of the electrolysis cell and the reservoir tank were drained out from time to time, during the course of the electtrolysis, for analysis. No attempt was made to collect gaseous products.

All the samples taken up to 500 Ah were red solutions. After approximately 590 Ah had passed the solutions were a yellow colour or colourless. Red solutions were also observed in the overflow pipe from the ECF cell.

During the course of the electrolysis further additions of AHF were made, which was not pre-dried. Some 200 Ah after such additions one or two minor explosions occurred. At the end of an electrolysis a current density of ∿ 0.09 A dm^2 at a potential of 9 volts pertained.

During the course of a fluorination it was necessary to switch off the current after five hours. At this stage a residual potential of + 2.65 volts was noted which by the following morning had fallen to a value of + 1.0 volt. After a further seven hours fluorination a residual potential of + 2.8 volts was observed.

Analytical methods

A method for the analysis of hydrofluoric acid solutions of octanoyl fluoride was developed in order that the rate of use of octanoyl fluoride could be followed during the course of the reaction. Likewise the formation of products was followed by removing them from the base of the two vessels from time-to-time for analysis.

Octanoyl Fluoride

Samples (ca. 15 g of solution) were run onto crushed ice (ca. 30 g) contained in polypropylene bottles, thus resulting in an octanoic acid solution in ca. 30% hydrogen fluoride.

Each sample was transferred to a 500 cc polythene wash bottle and extracted with 2 x 20 cc portions of chloroform, the first portion also being used to rinse the sample bottle. The lower chloroform layer was easily removed by carefully squeezing the wash bottle. The combined extracts were dried over magnesium sulphate, allowed to evaporate to just less than 5 cc, made up to 5 cc in a previously weighed graduated flask; and finally reweighed. For low concentration samples the method was modified by reducing the volume of chloroform solution from 5 cc to 0.5 cc.

The chloroform solution was analysed for octanoic acid by G.L.C. using a 0.5 m x 4.75 mm column of 10% fluorolube oil on Teflon 6 (30-60 mesh), a nitrogen flow rate of 30 cc min^{-1}, $154^{o}C$, and a flame ionisation detector. The column was calibrated by preparing solutions of octanoic acid directly in chloroform and the complete technique was checked by preparing synthetic mixtures of octanoic acid in 40% hydrogen fluoride. Reproducibility was ± 2%.

The results for a typical electrochemical fluorination of octanoyl fluoride are shown in Table 2.

Products

Fluorinated products drained from the base of the two vessels were analysed in diethyl ether solution by G.L.C. A 0.5 m x 4.75 mm fluorolube oil 2000 (10%) on Teflon 6 (30-60 mesh) was used at 135^{o}C, a carrier gas flow rate of 20 cc min^{-1} nitrogen and a flame ionisation detector. A preliminary chloroform extraction of a sample of these products and analysis as described above demonstrated that no octanoyl fluoride was present (limit of detection 0.01%).

The products were analysed quantitatively for perfluorooctanoic acid, the mixed cyclic ethers $C_8F_{16}O$ and perfluoroheptane. Since perfluoroheptance and diethyl ether have a similar retention time under the conditions used the perfluoroheptane analysis was carried out on the undiluted cell products. Other peaks were observed on the G.L.C. traces but were not identified. The results for a typical electrolysis, taken at intervals are given in Table 2.

TABLE 2

Product analyses after fluorination of actanoyl fluoride

Ampere hours	Sample weight after hydrolysis	source	$C_7F_{15}COOH$ g (%)	$C_8F_{16}O$ g(%)	C_7F_{16} g (%)	Residual $C_7H_{15}COF$ (%)
174	11.17	ECF cell	5.35 (48.0)	5.38 (48.2)	0.17 (1.5)	36.3
320	16.10	res. tank	6.62 (41.1)	9.10 (56.5)	0.18 (1.1)	16.3
725	11.60	ECF cell	5.22 (45.0)	6.10 (52.6)	0.18 (1.6)	1.7
927	138.80	ECF cell	47.0 (33.9)	68.4 (49.3)	16.4 (11.8)	trace
	83.3	res. tank	28.2 (33.9)	40.0 (48.0)	9.9 (11.9)	trace

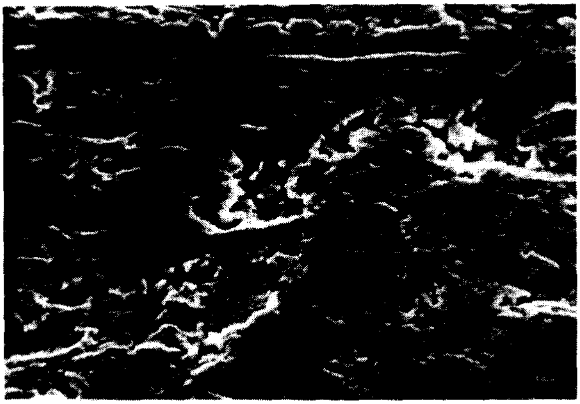
Investigation of the elelectrodes

All the electrodes were dried ana weighed before assembly, and also after drying hydrogen fluoride and electrolysing octanoyl fluoride. In addition one anode was prepared, by drilling a series of 6 mm holes down the centre of the plate. This facilitated the subsequent removal of samples of the anode from between these holes for examination of the surface by electron microscopy. Electron micrographs were taken with a Cambridge Stereoscan Mark 2A Scanning Electron Microscope using gold sputtering as necessary to increase the electrical conductance of the surface. Samples of the anode were examined at x 1000 and x 10,000 at the following stages: a; prior to use, b; after drying hydrogen fluoride and c; after electrochemical fluorination of octanoyl fluoride. Only in the latter case was it necessary to use gold sputtering. The results are shown in Figure 5 a - f.

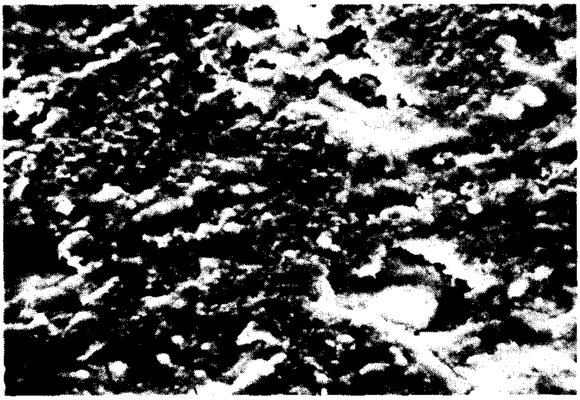
When removed from the cell, after fluorination of octanoyl fluoride, there was no sign whatsoever of any tarry material. Both anodes and cathodes were covered with a yellow flaky material. When this was removed from the anodes further yellow material was revealed which on standing overnight became mottled with brown and grey. The texture of the surface remained tacky and spongy. This mottled layer was firmly adhered to the anodes and was very difficult to remove even with a coarse abrasive paper. Selected anodes were baked at 110°C for 3 hours to facilitate removal of this layer. After removal of this layer the anodes showed a weight loss of *ca.* 1.35% of their original weight (see Table 3). After removing the yellow flakes from the cathodes a grey colour was evident. The data in Table 3 show that the cathodes suffer little weight loss during fluorination.

TABLE 3
Weights of Electrodes before and after Fluorination

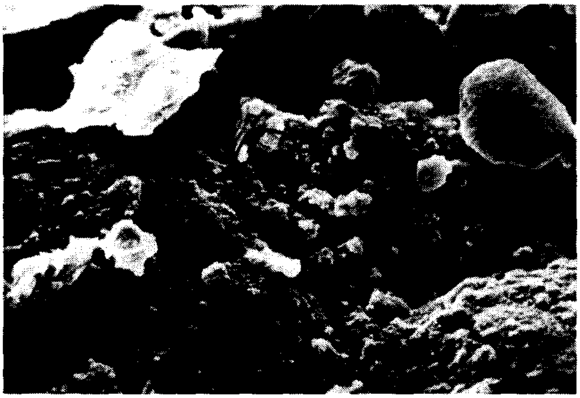
Number	Weight before fluorination	Weight after fluorination	Weight after removing coating	Weight loss
Anodes				
14	198.1	198.2	195.2	2.9
16	197.3	198.1	194.7	2.6
18	196.0	197.1	193.2	2.8
20	199.1	200.1	196.5	2.6
22	198.8	200.3	196.1	2.7
24	196.6	198.5	194.2	2.4
26	197.6	199.5	195.0	2.6
28	198.3	200.4		
Cathodes				
1	197.1	196.7		0.4
3	198.2	197.9		0.3
5	195.5	195.0		0.5
7	195.7	195.3		0.4
9	195.9	195.4		0.5



(a)
Nickel anode
prior to use
x 1000



(b)
Nickel anode
after drying
hydrogen
fluoride x 1000

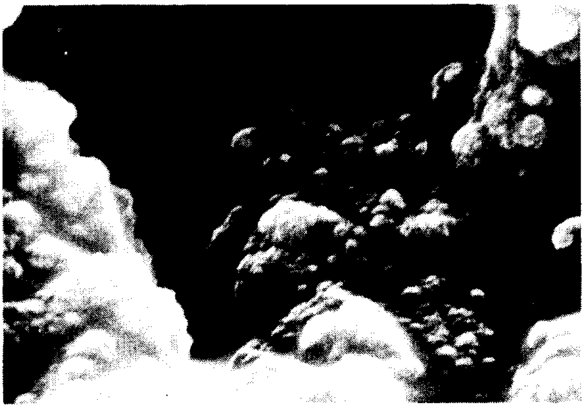


(c)
Nickel anode
after electrochemical
fluorination of
octanoyl fluoride
x 1000

Fig. 5. Scanning electron photomicrographs of nickel anode.

(d)
as at (a)
x 10,000

(e)
as at (b)
x 10,000



(f)
as at (c)
x 10,000

Examination of the electron micrographs shows the anodes to have a smoother surface after drying the hydrogen fluoride than before, but after ECF a distinct roughness is perceived. This roughness is attributed to the existence of many, variously sized pores, in the anode surface coating.

DISCUSSION

Study of Electrolyte Flow

The adoption of a flow system for E.C.F. may be expected to confer the following advantages vis a vis a static system:

1. An even distribution of substrate throughout the reaction zone and hence a better current efficiency.
2. Rapid removal of products from the reaction zone should reduce breakdown and the formation of tarry deposits on the electrode surface.
3. More efficient dissipation of the heat of reaction and hence a better control of reaction temperature.
4. Control of contact time of the substrate in the reaction zone will give an opportunity to study the formation of partially fluorinated products, and hence give an understanding of the mechanism of the fluorination process.
5. Enable a truly continuous process to be developed.
6. Ensure that effective use is made of the whole of the anode surface, with certain reservations to be discussed below.

In order to make effective use of all the anode surface substrate must be freely available at the anode surface at all times. So little data is available that one can only speculate as to the proportion of active anode surface available in a static cell. It is self-evident, that, for efficient use of the anode surface in a flow system, the electrolyte must pass evenly through the electrode pack without any streaming effects. It was with the aim of ensuring this condition that the flow study was carried out.

The results of some of the 86 experiments carried out during this study are given in Table 1. In general all the inlet positions gave rise to a streaming effect below the electrode pack followed by an irregular movement through the electrode gaps. This streaming effect was eventually overcome using an inlet extension.

Throughout this study the basic concept of a single inlet/single outlet system was maintained since this simplified construction of the E.C.F. cell. The use of multi-inlet/outlet systems may possibly be more effective especially with larger installations.

The Electrochemical Fluorination of Octanoyl Fluoride with Circulation of Electrolyte

Octanoyl fluoride was prepared in situ by adding octanoyl chloride to the circulating, previously dried electrolyte in small batches and venting the hydrogen chloride so produced. In this way a 2% solution by weight was prepared. Fluorination was carried out at 6-10 volts, 0.37-0.09 A dm^{-2}, 0-10°C and a flow rate 750 cc min^{-1}. Such a flow rate ensures turbulent flow conditions in the interelectrode gap. The rest of the reaction conditions are typical of those used for analogous fluorinations carried out without electrolyte flow. In a typical experiment such reaction conditions gave a 24% molar yield of perfluorooctanoic acid. This result compares favourably with those of other workers [20, 21, 22] using static systems and is second only to results reported by Swiss workers operating at unconventionally high potentials (8-13 volts) [9, 23].

These results demonstrate the effectiveness of a flow system for electrochemical fluorination although further work will be necessary to determine optimum conditions. The clean condition of the electrodes after fluorination suggests that such a system could be readily adapted to continuous operation by maintaining the concentration of octanoyl fluoride.

The observation of a back potential of ca 2.7 volts when the electtrolysing current is switched off is interesting and in agreement with a similar observation made by Donahue *et al* [24]. This potential is probably that of a Ni^{4+} and/or a Ni^{3+} species at the anode. The decay of the potential with time may be attributed to the reduction of Ni^{4+} and/or Ni^{3+} species to a lower oxidation state of nickel. This would be in keeping with the mechanism previously advanced [25] where it is suggested that an anodic nickel(IV) species oxidises a hydrogen atom of a bound organic group, being itself reduced to a nickel(III) species and creating a radical centre on a carbon atom. Under the normal conditions of electrolysis this is then followed by fluorine atom transfer from the anode layer to the carbon free radical and anodic oxidation of the nickel(III) species to a nickel(IV) species. When the current is off some oxidation and fluorination will continue but the nickel(III) species cannot be reoxidised to nickel(IV) species, hence the back potential decays. It is expected that the nickel(III) species will disproportionate to nickel(II) and nickel(IV) until eventually only nickel(II) remains [26].

The Electrode Surface

The photomicrographs in Figure 5 clearly show that some change takes place at the anode surface. After electrofluorination of octanoyl fluoride an even greater change can be seen. In particular the nodular nature of the surface is apparent, bottom left of 5c and bottom right of 5f. This nodular structure is not seen in 5b and 5e. Furthermore, after electrofluorination a more open and irregular structure can be seen and the presence of many cavities of various sizes is evident. This evidence thus suggests that the anode surface takes an active part in the fluorination process. The change in the nature of the surface before and after electrofluorination may be attributed to irregular build-up and errosion as fluorination proceeds.

REFERENCES

1 J.H. Simons et al, J. Electrochem. Soc., 95 (1949) 47, 53, 55, 59, 64.

2 J.H. Simons, U.S. Patent, 2, 519, 983, (1950).
Japan Patent 224, 948, (1956).

3 J. Burdon and J.C. Tatlow, Advan. Fluorine Chem., 1, (1960), 129.

4 E. Forche, Methoden der Organischen Chemie 5/3 (1962), 38.

5 M. Schmisser and P. Sartori, Chem. Ingr. Tech., 36, (1964) 9.

6 F. Dvorak, Chem. Listy 59, (1965), 698.

7 S. Nagase, Fluorine Chem. Rev., 1 (1967), 77.

8 N.L. Weinberg, Technique of Electroorganic Synthesis, 5 (1975), 1.

9 Ch. Comminellis, Ph. Javet and E. Plattner, J. Appl. Electrochem., 4 (1974) 289.

10 V.J. Davis, R.N, Haszeldine and A.E. Tipping, J. Chem. Soc. Perk. Trans I, (1975), 1263.

11 H. Kizaki, S. Mabuchi and T, Sakomura, Denki Kagaku 34 (1966) 24.

12 General Electric Co. British Patent, 758, 492 (1956).

13 M. Haruta and N. Watanabe, J. Fluorine Chem., 7 (1976) 159.

14 Farbenfabriken Bayer A-G, Brit. Patent 740, 723 (1955).

15 G.P. Gamboretto, G. Troilo, and M. Napoli, La Chimica and L'Industria, 52 (1970) 1097.

16 S. Benninger, German Patent 2, 302, 132 (1974).

17 S. Benninger and S. Rebsdat, U.S. Patent 3, 891, 625 (1975).

18 V. Ya. Kazkov, L.A. Savel'ev, R.A. Dzerzhinskaya, E.A. Shishkin and N. Gudimov, Russ. J. App. Chem., 41, (1968) 2089.

19 F.G. Drakesmith and D.A. Hughes, J, Appl. Electrochem., 6 (1976), 23.

20 A.J. Rudge, Industrial Electrochemical Processes, (1971) Elsevier, Ed. A.T. Kuhn.

21 H.M. Scholberg and H.G. Brice, U.S. Patent 2, 717, 871 (1955).

22 G. Zuliami and G. Pizzolotto,, Nuovo Chim., 2 (1972) 1.

23 Ciba-Geigy A.G., German Patent, 2442, 106 (1975).

24 J.A. Donohue, A. Zletz and R.T. Flannery, J. Electrochem. Soc., 115, (1968) 1042.

25 H. Sutcliffe, J. Fluorine Chem., in the press.

26 L. Stein, J.M. Neil, and G.R. Alms, Inorg. Chem., 8 (1969) 2472.