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PROCESS IMPROVEMENTS IN THE ELECTROCHEMICAL FLUORINATION OF OCTANOYL CHLORIDE

H.W. PROKOP, H-J ZHOU, S-Q XU, C-H WU, S.R. CHUEY and C.C. LIU*

Chemical Engineering Department, Case Western Reserve
University, Cleveland, Ohio 44106 (U.S.A.)

SUMMARY

The electrochemical fluorination of octanoyl chloride to produce perfluorooctanoyl fluoride in anhydrous hydrogen fluoride was investigated. The study was carried out in a microprocessor-aided modified Simons reactor system using a Cu/CuF_2 reference electrode. The formation of polymeric tar at the anode surface was limited by the addition of a mercaptan compound and by constant current density operation. Continuous operation was achieved through frequent additions of a solution of hydrogen fluoride and reactant. Conversion of reactant to perfluorinated products was improved to 80 % with good selectivity.

Experimental results of this investigation are presented and discussed.

INTRODUCTION

Perfluorinated carboxylic acids can be conveniently synthesized by the electrochemical fluorination (ECF) method. The Simons ECF process, which is characterized by an anhydrous hydrogen fluoride (AHF) electrolyte and nickel anodes, is

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* To whom correspondence should be addressed

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attractive for carboxylic acid derivatives as substrates. Expected yields for ECF decrease with longer carbon chains. However, octanoyl chloride has good solubility in AHF and forms a conductive solution.

Perfluorooctanoyl fluoride (POF), the desired product of this investigation, is a commodity chemical in the acid form. This material has application mainly as a high performance surfactant. A patent for its manufacture was issued in 1955 [1]. Since then, several researchers have studied the ECF of octanoyl chloride. Comninellis, et al [2] studied the effect of high cell potentials. Lines and Sutcliffe [3] improved the process with forced electrolyte flow. More recently, Drakesmith and Hughes [4,5] performed a detailed study including preparation of the anode, reactant concentration, and selectivity of the fluorination. Recently, perfluorocaprylyl fluoride by electrochemical fluorination has also been reported [6]. Many ECF studies focus on the weaknesses of ECF, namely, poor reproducibility, low chemical yield, poor selectivity, and low current densities. This study seeks to complement the existing knowledge for the process and make improvements in these weak areas.

A microprocessor-aided Simons reactor system [7-10] was modified for this study. The reactor design is focused on enhanced mass transfer characteristics based on batch mixing and on uniform anodic current density distribution. A computer-based data acquisition system monitors and controls the process [7-10]. The results from modifications to the ECF system and its operating parameters will be discussed.

EXPERIMENTAL

The modified Simons reactor and the experimental system are described in detail elsewhere [7-10] and will not be repeated here Several new features were added to the system, as shown in Fig. 1. There was a special tube for the addition of a surface additive, 1-methyl-1-propanethiol (hereafter referred to as mercaptan). Mercaptan compounds are known to reduce the extent of polymer tar formation in ECF [11]. A solenoid valve was installed to allow the mercaptan addition to be controlled automatically from the software of the personal computer used. The reactant container was a monel vessel identical to the ECF reactor that served as a reservoir holding a solution of AHF and reactant; this was used to simulate continuous operation. The reactant container was jacketed for methanol coolant, and it was kept somewhat cooler than the ECF reactor. Special tubing and connections were added so that nitrogen pressure could be used to transfer AHF to the reactant container. Also, tubing was added to allow volumetric additions from the reactant container.

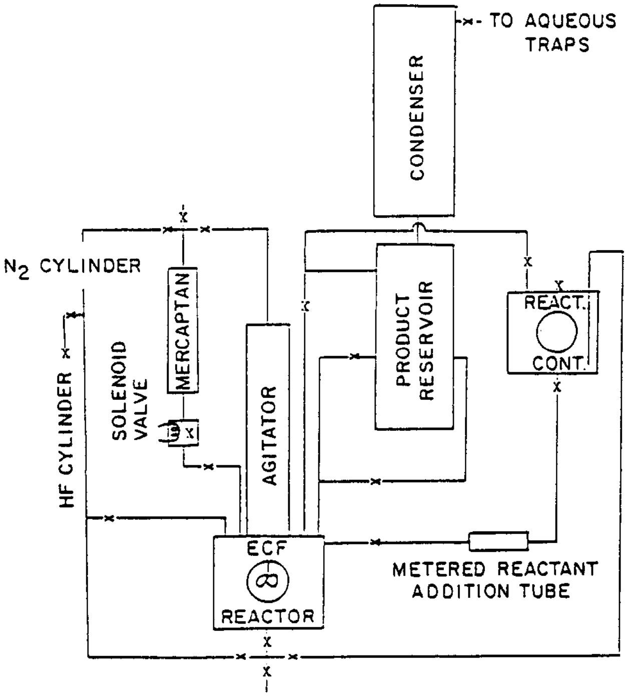

Fig. 1. Schematic of the Electrochemical Fluorination System Used in this Study.

There were two types of electrode configurations used in this study. First, four sets of packed, alternating anodes and cathodes as previously described elsewhere [9] were used for the initial part of the investigation. Secondly, for the runs simulating continuous operation special high surface area electrodes were constructed. The assembly, shown in Fig. 2, is similar to the rectangular electrode assembly. Five rectangular pieces of 1/32 inch thick nickel 200 sheet (99.67 % nickel) were rolled into hollow cylinders and spark welded. Holes were drilled to allow for the teflon spacers and nickel rings. Tiny holes were drilled over the surface to enhance mass transfer. All the cylinders are 9.0 cm high. The cylinder diameters are as follows:

Number	Anode/Cathode	Diameter (cm)
1 (innermost)	cathode	5.1
2	anode	6.0
3	cathode	6.9
4	anode	7.8
5 (outermost)	cathode	8.7

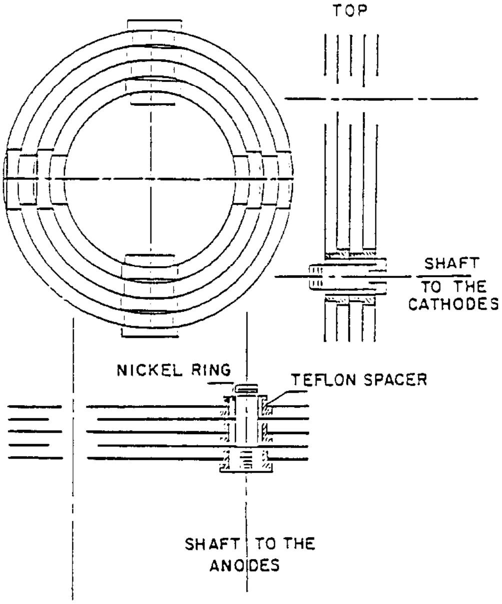

Fig. 2. Configuration of the Hollow Cylinder Nickel Electrode Used in the Constant Current Density, Continuous Operation.

The total geometric anodic area is 775 cm^2 and the cathodic area is 1070 cm^2. The electrodes were connected in a monopolar fashion.

Before an experiment, the anodes and cathodes were cleaned in a liquid sandblaster and rinsed. Two copper rods (6 mm in diameter) were placed at opposing positions in the reactor to serve as Cu/CuF_2 reference electrodes. The reference electrodes were refreshed with nitric acid and placed in the reactor under a nitrogen purge of 20-30 ml/min. The nitrogen purge prevents the build-up of oxygen difluoride, which is explosive in contact with organics.

Hydrogen fluoride (99.9%, Matheson) was added to the reactor by heating the cylinder and then the hydrogen fluoride was condensed in the cooled reactor. The reactor was filled to its volume of 750 ml, and the mechanical agitator was started. Trace moisture from the hydrogen fluoride was removed by a pre-electrolysis at a constant cell voltage of 5.5 volts and a reactor temperature of 0°C. After about 20 A-hr the current reached a low, steady value.

The cell potential was then turned off. About 50 grams of octanoyl chloride (99%, Aldrich) was added to the reactor. The halogen exchange reaction,

$$C_7H_{15}COCl + HF = C_7H_{15}COF + HCl$$

is slow and endothermic. Octanoyl chloride is insoluble in AHF, so the progress of the reaction was monitored by the reactor temperature and the amount of the chloride present. An initial charge of the mercaptan was added. Once these steps were complete ECF could be initiated.

For the continuous operation experiments, the procedure was modified. After the pre-electrolysis was complete, reactant was then added to the reactant container. Nitrogen pressure was used to force the AHF up into the reactant container to mix with the reactant. Nitrogen was bubbled through the mixture for 15 minutes to provide agitation. The valve between the reactant container and the product reservoir was then open to vent the evolved HCl.

A second batch of hydrogen fluoride was added to the reactor, and a second pre-electrolysis was then performed.

Some of the electrical charge passed during the pre-electrolysis actually goes toward the conditioning of the anode surface. Although the actual mechanism is not well known, it is probable that a film of nickel fluorides, possibly of high valence, forms on the anode surface. This nickel fluoride complex is the actual fluorinating agent. During the time while the anode conditioning takes place, known as the induction period, elemental fluorine is evolved.

Under continuous operation, the current was interrupted for less than 10 minutes as reactant solution was added from the container and the potentiostat was switched to constant current operation. The nickel fluoride film was therefore maintained intact after the induction period. During the batch operation experiments, the current was interrupted for 2 to 3 hours as the halogen exchange took place in the reactor. The anode film dissipated, so another induction period took place when current was restored. During constant anode potential operation, this was characterized by a rapid rise in current up to a maximum value. During the induction period, no perfluorinated products were obtained.

Immediately after the induction period, ECF was performed. The desired anodic and cathodic reactions are:

anode: $C_7H_{15}COF + 30F^- - C_7F_{15}COF + 15HF + 30e^-$

cathode: $30HF + 30e^- - 30F^- + 15H_2$

In this study, three modes of fluorination were performed: batchwise at constant anode potential, batchwise at constant current density, and continuously at constant current density. Reactor temperatures were always maintained between 4 and 6°C. Nitrogen pressure was near 7 psig. Other conditions for these modes of operation were as follows:

Constant anode potential, batchwise

Anode potential: 5 volts vs. Cu/CuF_2
Agitation speed: 450-550 RPM
Initial Reactant Concentration: ~ 7 weight %
Mercaptan Addition Rate: 1.5 ml/day

Constant current density, batchwise

Current Density: 6 to 7 mA/cm^2
Agitation speed: 450-550 RPM
Initial Reactant Concentration: ~ 7 weight %
Mercaptan Addition Rate: 1.5 ml/day or 0.2 ml every 2 hrs

Constant current density, continuous operation

Current Density: 5.5 mA/cm^2
Agitation speed: 250-350 RPM
Initial Reactant Concentration: 2.5, 4, 10 weight %
Mercaptan Addition Rate: 0.25-0.3 ml every hr

Product samples were removed from the bottom of the reactor once or twice daily. The fluorinated products are insoluble in AHF, and they form a clear, dense layer at the bottom of the reactor. The products are, however, soluble in the organic phase in the electrolyte.

Under continuous operation, solution was added from the container once or twice daily to replenish the consumed reactant. Once all of the reactant had been consumed, the electrolyte rapidly darkened due to the rapid formation of tar. At some point during the run, the electrolyte turned clear as the tar was decomposed from the anode surface. Once the tar was totally decomposed, the experiment was terminated. The electrolyte and any materials remaining in the product reservoir were poured over crushed ice.

The products were analyzed by capillary gas chromatography. Details of this analysis are given elsewhere [12]. Besides the desired product, ring closure products that are perfluorinated five- or six- membered cyclic ethers are obtained. These cyclic ethers are a less desirable by-product, but they are often the majority product. A product from the degradation of POF is perfluoroheptane. This is mainly observed late in the process.

RESULTS AND DISCUSSION

The current profile for a batchwise, constant anode potential run is shown in Fig. 3. During this experiment, two extra reactant additions were made. The current was interrupted for about 45 minutes to allow the halogen exchange to take place (points A1 and A2 in Figure 3). The reactant additions were attempts at maintaining a high level of reactant concentration. Initially, the electrolyte was clear, and the induction period began. The first products were obtained 45 hours after fluorination had begun (point B). The electrolyte continued to darken from yellow to brown at point C. From 70 hours (point C) to 145 hours (point D) the electrolyte remained brown as the current was steady near 1.5 amps (7 mA/cm^2). A short time later the reactant was exhausted, and fluctuations in the current were observed. The electrolyte darkened very quickly to become opaque. A characteristic of constant anode potential operation is a second current maximum when the electrolyte is darkest (point E). In less than 24 hours the electrolyte cleared, and the anode was no longer active. The corresponding yield rate of rough fluorinated products is shown in Fig. 4. Rough fluorinated products are defined as the total fluorinated products produced. During the induction period, there are no products. The appearance of product may be delayed by solubility in the organics in the electrolyte. The rate of obtaining products is fairly stable and at a maximum when the current is in the stable period between points C and D. Late in the run the product rate is very low, and analysis shows that the products are largely degradation products (very little POF and cyclic ethers are found). Another experiment under the same conditions was run with more frequent reactant additions, so the reactant concentration was higher than that of a previous

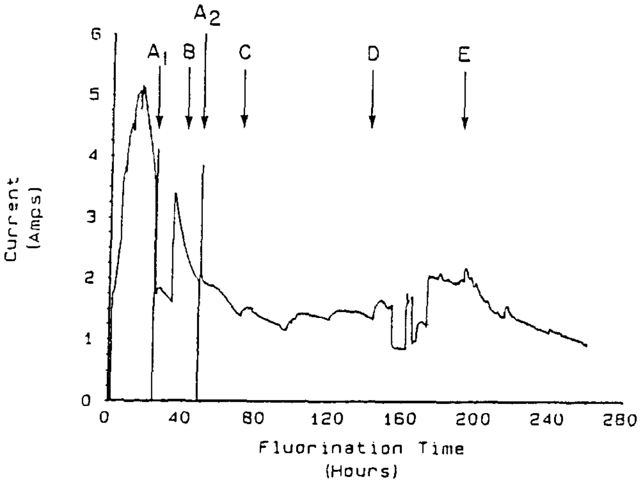

Fig. 3. Time-Dependent Current Profile for the Constant Anode Potential, Batchwise Operation.

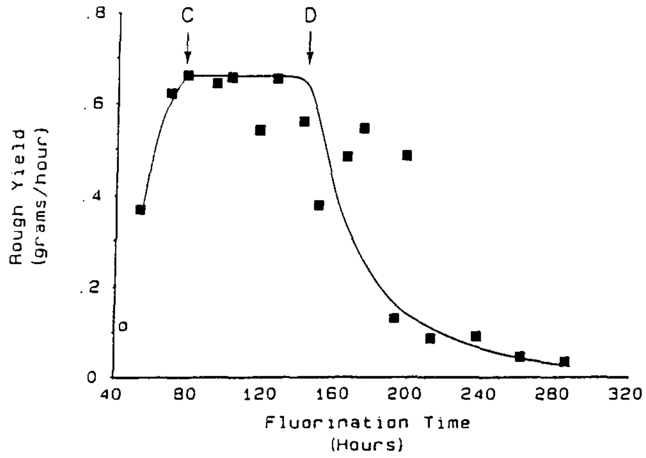

Fig. 4. Production Rate of Fluorinated Products for the Constant Anode Potential, Batchwise Operation.

constant anode potential run.. The production rate was higher and less smoothly behaved. Frequent reactant additions disturb the current and production rate profiles, but they increase the yield. The conversion of reactant to rough fluorinated products was 50% for the run at constant anode potential, batchwise operation and 63% for the run at the same operating condition with more frequent reactant additions.

When the process is operated at constant anode potential, the current decays over time, as does the production rate of the fluorinated products. The main reason for the degradation of the process is tar formation. When tar covers up the anodic surface, the activity of the anode is reduced. Electrolyte color can be used as an indicator of the extent of tar formation. When the process is well operated, the electrolyte color is brown or lighter. Once the reactant is consumed, tar formation becomes the dominant process, and rapid darkening of the electrolyte is observed. At some point the tar begins to decompose, and the electrolyte turns clear. Since less than half of the products can be accounted for as POF or cyclic ethers at the end of the run, tar decomposition may be the source of the degradation products. Thus, tar formation and destruction can be treated as an equilibrium process. This formation and destruction are balanced when the current is steady.

Taking advantage of this information, a run was performed at constant current density near the desirable 7 mA/cm^2 value and batchwise operation. A typical anode potential for a constant current density experiment is given in Fig. 5. The anode potential is very stable, except for an initial decay and fluctuations late in the run. These later fluctuations appear when the reactant is consumed and the electrolyte conductivity is low. Also, the addition of mercaptan or sample removal somewhat disturb the anode potential. The production rate of this constant current density batchwise run is shown in Fig. 6. Since the current density is lower than that for the constant anode potential run (Figure 3), the product rate is also lower. The yield obtainable at 100% current efficiency is calculated and shown in Figure 6. The rough product yield for this constant current density batch-

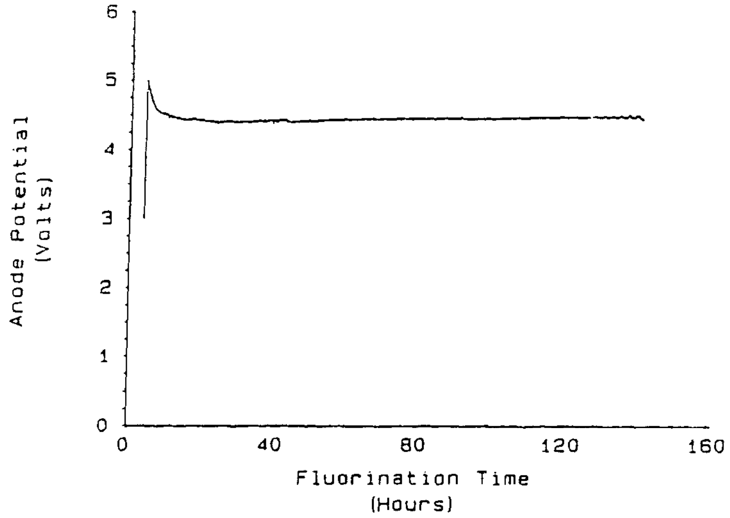

Fig. 5. Typical Time-Dependent Anode Potential Profile for a Constant Current Operation.

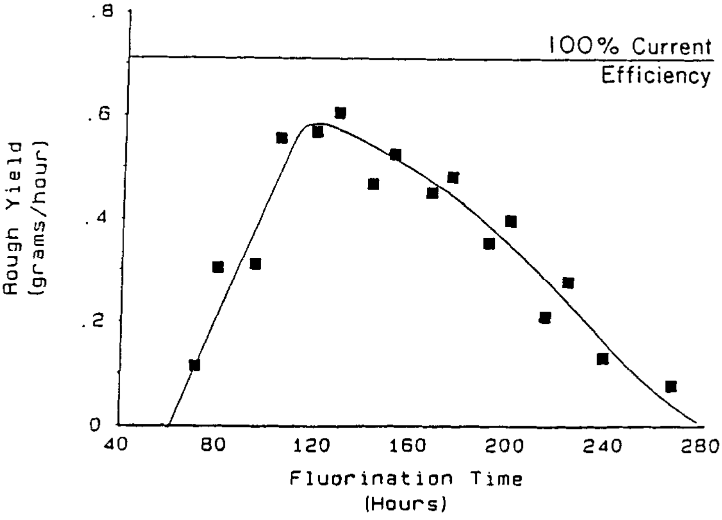

Fig. 6. Production Rate of Fluorinated Products for the Constant Current, Batchwise Operation.

wise run was 57%. Tar formation was maintained at a low level until the reactant was consumed. For the first 150 hours of fluorination the electrolyte was yellow. After this the electrolyte rapidly darkened.

A phenomemon was observed during this constant current density, batchwise run. Although the overall behavior of the production rate curve is smooth, alternating samples show first a higher, then a lower production rate. Alternating samples were taken at 8 and 16 hour intervals. The lower production rates correspond to the longer sampling intervals. It is possible that the product may be consumed while remaining inside the reactor due to chemical or electrochemical mechanisms, or due to the consumption of the mercaptan. In order to test the last mechanism, a solenoid valve was installed for continuous mercaptan addition every hour.

Operating conditions for this particular run were nearly identical to those of the constant current density, batchwise run, except for the continuous mercaptan additions. The higher rate of mercaptan addition did not decrease tar formation during the process, nor did the product degradation phenomenon cease. In fact, the production rate, shown in Fig. 7, was initially very low until it rose to a maximum later. The electrolyte was still yellow up to the point of total reactant consumption. This result suggests that a low concentration of mercaptan is sufficient to inhibit tar formation without consuming excessive current, and thus reducing the production rate of the fluorinated products.

In these experiments, it is possible that tars may be fluorinated to produce perfluorinated volatiles. Because of the safety involved in entrapping the volatiles, no attempt was made to verify the substances of these low molecular weight fluorinated volatiles.

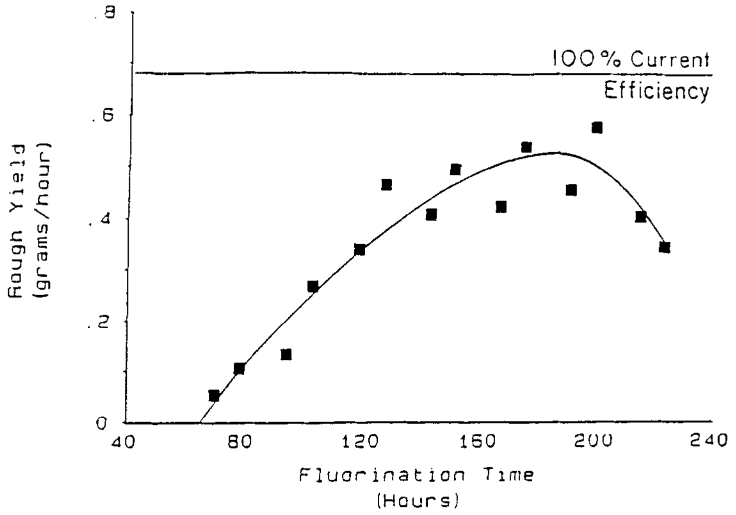

Fig. 7. Production Rate of Fluorinated Products for the Constant Current, Batchwise Operation with Continuous Additions of Mercaptan During the Run.

Constant current density operation near 7 mA/cm^2 allows the tar formation to be arrested until the reactant is consumed. Furthermore, the input power is stable throughout the process, unlike constant anode potential operation. This current density may be an optimum value, since smaller values may extend the time period of the process. Higher values might not control tar formation.

To further understand the role of mercaptan in the process, a run was performed adding only mercaptan as the reactant. The solution was very conductive, and the current stabilized at a low value after 6 A-hr were consumed. If the mercaptan were perfluorinated, 30 A-hr would be required. The mercaptan is probably decomposed by a chemical process, rather than an electrochemical one. These compounds are known to be unstable during ECF [13]. However, their effectiveness in controlling tar remains with daily additions.

A possible mechanism for tar reduction might be that the mercaptan decomposes to elemental sulfur, which absorbs strongly on the anode. The mechanism for ECF is considered to involve free radical species [14], so the formation of polymers can result from the association of reactants as radical species. The presence of sulfur on the anode surface should reduce the extent of radical association, thereby reducing tar formation. This mechanism supports the empirical observation that low mercaptan concentrations are preferred in this process On the other hand, insufficient mercaptan may not be able to limit the tar formation. Indeed, attempted experiments without the addition of mercaptan resulted in little or no perfluorinated product and large quantities of tar.

In order to perform experiments under constant current density continuous operation, a reactant container was installed. Due to the low current density, high anodic area electrodes were designed to reduce the length of time required for the experiment. Three experiments were run in the continuous constant current density mode under the conditions mentioned previously. The behavior of the anode potential for these runs was almost identical to that shown in Figure 5. The steady-state anode potentials were always consistently between 4.3 and 4.5 volts. Minute disturbances in the potential were caused by reactant additions. The anode potential remained stable until after the last reactant solution was added. The production rate for this constant current, continuous run which employed an initial reactant concentration of 2.5 wt% is shown in Fig. 8. It appears that the production rate is also stable until shortly after the last reactant addition (point L in Figure 8). During this period when the process variables were stabilized, the electrolyte color was consistently brown. At higher reactant concentrations, the solubility of the products in the organic materials was apparent. After the last reactant was added, there was a brief time period during which the production rate increased. As the organic content of the electrolyte diminished, the dissolved products were released and the production rate rapidly dropped. Conversions of reactant to rough products were consistent at 80%. The product distribution for this constant current, continuous run is given in Fig. 9. It is interesting to note that the product distribution remains relatively constant until approximately thirty hours after the last reactant addition. At the end of the run, the degradation products become the predominant ones.

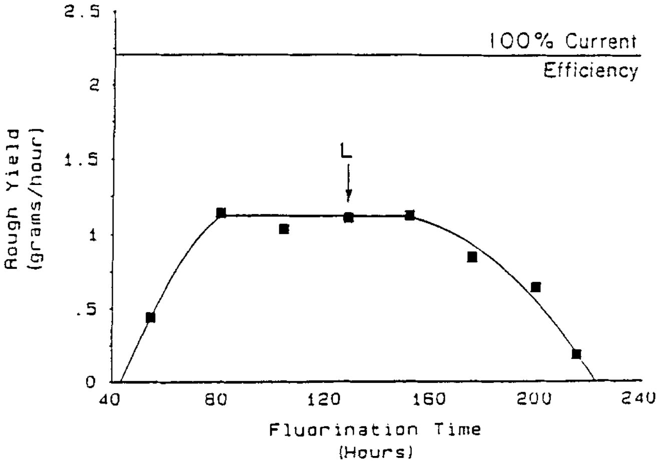

Fig. 8. Production Rate of Fluorinated Products for the Constant Current, Continuous Operation.

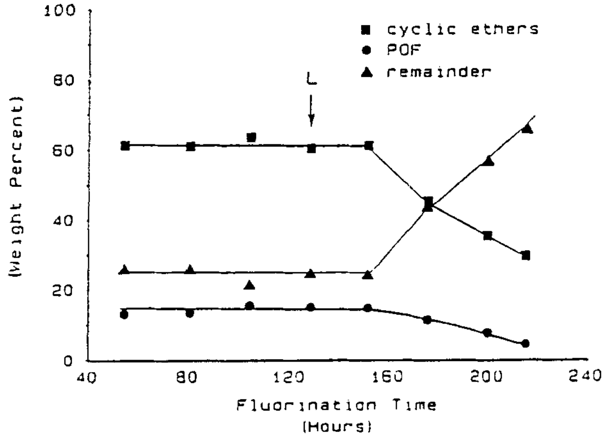

Fig. 9. Product Distribution of the Fluorinated Products from the Constant Current, Continuous Operation.

A parameter, the product ratio, which is defined as the ratio between weight percent of perfluorooctanoyl fluoride (POF) and weight percent of combined cyclic ethers was introduced by Drakesmith and Hughes [4,5]. This product ratio for our constant current density, continuous operation with an initial reactant concentration of 2.5 wt% is shown in Fig. 10. By comparison, typical results from Drakesmith and Hughes show the product ratio reaching a maximum of 18% over a short period of time, then declining to a steady value of 8%. The results of our constant current, continuous run show a product ratio of 22-24% which is maintained throughout the process until near the end of the run.

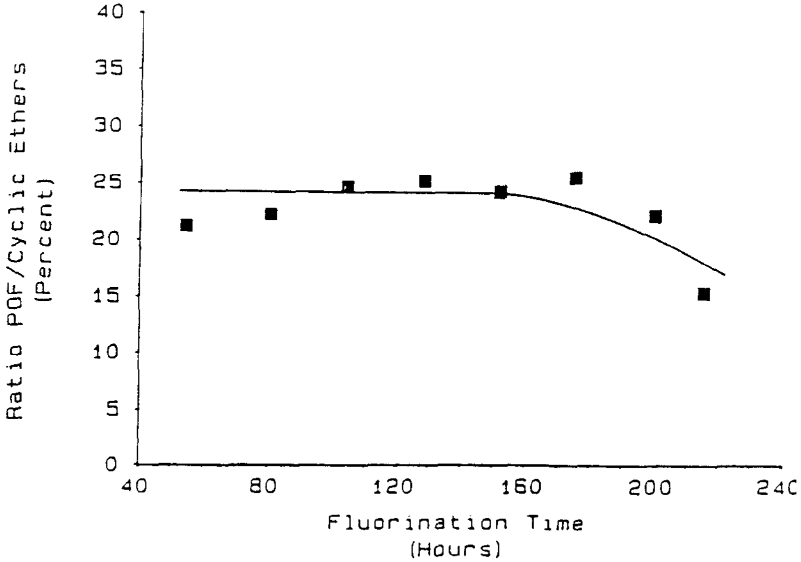

Fig. 10. Product Ratio of Perfluorooctanoyl Fluoride to Cyclic Ethers from the Constant Current, Continuous Operation.

In another constant current density, continuous operation run, we employ a higher initial reactant concentration, i.e. 4.0 wt% compared to the previous run using 2.5 wt%. The product distribution improved, with the level of the desired product (POF) reaching 20% of the total fluorinated products over a stable 200 hours of fluorination time. The product ratio for this higher initial reactant concentration run is also better -- reaching 35% during the stable 200 hours of fluorination time. For the run using an initial reactant concentration of 10 wt%, current efficiency and product ratio are reasonably similar to the run with 4.0 wt% of initial reactant concentration with approximately 28% of the product ratio at the 10 wt% run. However, this difference could not be viewed significant in view of the uncertainty in experiments.

Operation under constant current conditions with frequent additions to maintain reactant concentration provides several advantages over batchwise, constant anode potential operation. (1) Higher yields of rough fluorinated products can be achieved. (2) The extent of tar formation can be controlled at some constant level. (3) The halogen exchange reaction can be isolated from the reactor so that the anodic film can be maintained. (4) The process variables behave in a consistent and reproducible manner. Lack of reproducibility is a perennial bane to ECF. (5) Good selectivity and yield can be maintained continuously, as long as the reactant concentration is maintained.

Some disadvantages are incurred by this mode of operation. Low current densities imply long processing times. This can be counteracted using electrodes with higher specific surface areas. The cylindrical electrodes represent a factor of 3.6 increase in specific anodic area over the rectangular packs without introducing mass transfer limitations. The additional apparatus required for the reactant reservoir is another complication that requires more attention to the engineering of a safe and efficient ECF system.

CONCLUSIONS

Under constant anode potential operation, the effectiveness of the process decays over time due to polymeric tar deactivating the anodic surface. The extent of tar formation can be limited by the addition of small quantities of 1-methyl-1-propanethiol. Larger quantities of mercaptan result in decreasing yields. Tar formation/destruction is an equilibrium process that can be arrested by constant current density operation at 7 mA/cm^2.

Continuous operation can be achieved with stable process variables if reactant is added periodically to maintain reactant concentration. This is conveniently achieved by mixing the reactant with AHF before addition.

These procedures are recommended for other ECF syntheses that are presently limited or prevented by tar formation.

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