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ELECTROCHEMICAL FLUORINATION OF METHANEDISULFONYL FLUORIDE

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SUMMARY

The electrochemical fluorination of methanedisulfonyl fluoride in anhydrous hydrogen fluoride to produce difluoromethanedisulfonyl fluoride, a precursor of difluoromethane disulfonic acid, was investigated. This study was carried out in a microprocessor-aided modified Simons' reactor system at constant anodic potential using a Cu/CuF$_2$ reference electrode. Product yields of 75-82%, current efficiencies in excess of 66%, and electrical energy efficiencies of at least 33% were obtained for the electrochemical fluorination step.

Experimental results of this investigation are presented and discussed.

INTRODUCTION

Perfluorinated difunctional organic acids are a class of fluorocarbons possessing no carbon-bound hydrogen and characterized by great acidic strength. These strong acids are potentially interesting candidates as fuel cell electrolytes or electrolytic additives [1,2].

Synthetic routes based on electrochemical fluorination (ECF) in an anhydrous hydrogen fluoride (AHF) electrolyte are attractive for the preparation of perfluoroalkane sulfonic acids. Although fluorination of the alkane sulfonic acids cannot be carried out directly by ECF [3-5], the alkane sulfonyl fluorides can be successfully fluorinated by electrochemical means with fairly high yields. The perfluorinated sulfonyl fluoride produced then may be converted to the corresponding acid salt by alkaline hydrolysis. The free acid can then be obtained either by dis-

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tillation from a solution of concentrated sulfuric acid and sulfonic acid salt or by ion exchanging solutions of the salt [6]. Hence, the electrochemical fluorination of methanedisulfonyl flouride, $H_2C(SO_2F)_2$, to difluoromethane disulfonyl fluoride, $F_2C(SO_2F)_2$, a valuable intermediate in the synthesis of difluoromethane disulfonic acid is investigated in this study. The formation of $F_2C(SO_2F)_2$ from $H_2C(SO_2F)_2$ via ECF has been reported previously [7,8]. It is, however, believed that an investigation of electrochemical fluorination in general, and of this process in particular, under careful control of the experimental parameters and in a well-designed electrochemical reactor may clarify the reaction mechanisms and enhance the yield of the product.

A microprocessor-aided modified Simons' reactor [9,10] was constructed and used in this study. The modified Simons' reactor employed batch mixer design criteria enhancing the mass transfer characteristics of the reactor. The configuration in the reactor was arranged in a manner so that a more uniform anodic current density distribution was achieved and the electrode packs were orientated to serve as baffles in the mixer flow field. This reactor system was incorporated with a microprocessor system for data acquisition, monitoring and control of the process [9,10]. The results of the electrochemical fluorination of methanedisulfonyl fluoride in this reactor system will be discussed in this paper.

EXPERIMENTAL

As mentioned, the modified Simons' reactor and the complete experimental system are described in detail elsewhere [9,10] and will not be repeated here. The electrochemical fluorination process of this study was operated in a controlled anodic potential mode. The Cu/CuF_2 couple was used as a reference electrode. Typically, three reference electrodes were placed in various positions inside the reactor. The copper rods (6 mm in diameter) were etched in concentrated nitric acid and immediately placed in the reactor. To prevent any reoxidation of the fresh surface, a nitrogen purge of 20-30 ml/min was established throughout the reactor.

The nickel anodes and cathodes were rinsed with hot water and soaked for several hours in a mild solution of acetic acid between experiments.

Following this, the electrodes were thoroughly cleaned in a liquid sandblaster, rinsed, dried and weighed. This was sufficient to remove any nickel salts formed in the preceding experimental runs.

The anhydrous hydrogen fluoride (AHF) electrolyte (99% pure, Matheson) was added to the reactor by heating the cylinder and condensing the vaporized AHF in the cooled reactor. Approximately 1.5 liters of electrolyte was charged to the reactor in this manner and the agitation was initiated. Pre-electrolysis was carried out at a constant cell voltage of 5.0 V in order to remove any water in the AHF and to condition the anodes. When the current decreased to a constant value of ~2 mA/cm^2 the first phase of the pre-electrolysis was considered to be completed. Typically this required 20 to 30 A-hr over a 12 - 18 hour period. The anode potential with respect to the reference electrode was monitored but not employed for potentiostatic operation during this phase of the pre-electrolysis.

The second phase of the pre-electrolysis involved the growth of the anodic film at the potential which would be employed during the ECF step. This phase of the experiment was carried out under constant anodic potential (3.75 - 6.0 volts versus Cu/CuF$_2$) but no organic reactant was added. The current decreased as the thickness of the anodic film increased. When the current value reached a baseline value of 2 mA/cm^2 the second phase of pre-electrolysis was considered accomplished. The charge passed and the amount of time elapsed during this phase varied depending on the potential applied. However, it seldom exceeded 10 A-hrs over a 4 hour period of time.

The synthesis was carried out in a batch mode and the following experimental conditions were generally employed:

Anodic Potential	3.75 - 6.00 V vs Cu/CuF$_2$
Reactor Temperature	0 - 15 °C
Reactor Operating Pressure	~10 kPa above ambient
Reactor Agitation	600 RPM
Initial Reactant Concentration	0.5 - 3.0 M.

The agitation rate of 600 RPM corresponded to an agitation Reynolds number of 87,000. At this Reynolds number the flow region was turbulent both in the bulk of the electrolyte and between the electrodes [10]. Upon completion of the pre-electrolysis of the electrolyte, the reactant was added and the electrochemical fluorination began. Periodically, well-stirred electrolyte samples were removed from the bottom of the reactor for analysis. Samples of the solutions in the aqueous traps of the reactor system were also periodically removed for analysis.

The ECF process would continue until the current decayed to the baseline value of ~2 mA/cm^2 and the analysis of the electrolyte samples showed that the reactant was consumed. The process was then terminated. In the product recovery step, the reactor contents were vaporized by heating the reactor to $40^{o}C$ and were then collected in the cooled product reservoir. The condensed contents were drained into an ice water trap where the majority of the reaction product formed a heavy fluorocarbon phase and the HF dissolved in the aqueous phase. The product phase was separated from the aqueous phase using a separating funnel and washed several times with distilled water. The weight and volume of the product were then determined.

The analysis of the electrolyte samples were accomplished using capillary gas chromatography. Because of the large quantity of HF presented in the sample, an excess of acetic anhydride was used to neutralize the HF. The neutralized samples containing the organic feed and the fluorocarbon product dissolved in a solution of acetic acid and acetyl fluoride were then analyzed.

Another analytical technique used in our study was iodimetric titration of the samples in the aqueous traps. This was to determine the amount of F_2 produced in the electrochemical fluorination process. The details of both analytical methods are given elsewhere [10].

RESULTS AND DISCUSSION

The feasibility of electrochemical fluorination of the $H_2C(SO_2F)_2$ to $F_2C(SO_2F)_2$ was first evaluated in a traditional Simons' cell [11]. Confirmation of the structure of the $F_2C(SO_2F)_2$ product was made using both proton and fluorine NMR. Evidence of the high purity of the product as recovered was provided by fractional distillation. Briefly stated, conversion efficiencies averaged 70% and current efficiencies from 34 to 55% were obtained.

The experimental results of the studies using the modified Simons' reactor are summarized in Table 1. The only fluorinated organic product recovered was $F_2C(SO_2F)_2$. It is of interest that no monofluorinated product was recovered or revealed by G.C. analysis of the electrolyte. Conversion efficiencies ranged from 57 to 82 %. Current efficiencies based on four electrons transferred per molecule of $F_2C(SO_2F)_2$ produced (two electrons per fluorine atoms substituted) ranged from 33 to 66%. Electrical energy efficiencies varied from 18 to 33%.

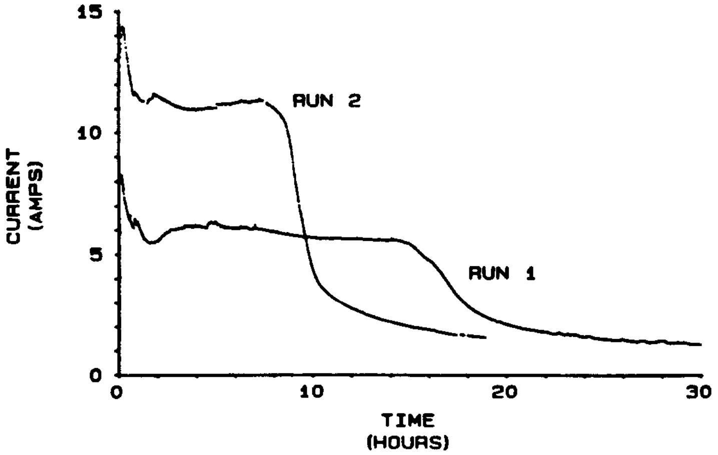

Fig. 1. Typical Current Profile for Experimental Runs.

Figure 1 displays typical current traces for the experimental runs. Immediately upon the addition of the reactant the current increased, passed through a maximum and within ~1 hour stabilized at a plateau value. This current value at the plateau was much higher than the pre-electrolysis current value at the same anodic potential prior to the addition of the reactant. As the last of the reactant was consummed, the current decreased significantly to a baseline value lower than the pre-electrolysis current value. Run 1 was conducted with an anodic potential vs Cu/CuF_2 of 5.3 V whereas Run 2 was with an anodic potential of 6.0 V. All other controlled parameters, i.e. initial reactant concentration, temperature, agitation were idential for the two experiments. The cell voltage for Run 2 was approximately 7.1 V, 1 V more than in Run 1. Thus the cell polarizations were 3.2 and 4.2 V for Runs 1 and 2, respectively,

TABLE 1

Summary of the experimental results for the electrochemical fluorination of $H_2C(SO_2F)_2$

Run	Anode Potential (V vs Cu/CuF_2)	Cell Temperature (°C)	Initial Reactant Concentration (M)	Conversion Efficiency* (%)	Current Efficiency† (%)	Electrical Energy Efficiency† (%)
1	5.3	15	0.5	64	47	22
2	6.0	15	0.5	66	48	18
3	4.5	0	0.5	68	42	22
4	3.7	0	0.5	57	33	21
5	5.3	15	1.5	81	60	31
6	4.5	15	3.0	82	66	33

*Based on the product recovered

†Based on the product recovered and the completion point determined from the G.C. analysis of the electrolyte samples

assuming an equilibrium potential of 2.85 V. If the ohmic polarization of the electrolyte was the controlling resistance for the reaction, a 30% increase in the cell polarization, as observed between the two runs, should produce a ~30% increase in the reactor current. However, as displayed in Fig. 1, the current increased by nearly 100% between the two runs. Hence the ohmic resistance of the electrolyte is not the controlling resistance to this reaction.

The agreement among the three Cu/CuF_2 reference electrodes was quite satisfactory with very little dependence on the reference electrode location, another indication that the ohmic drop in the electrolyte was not large.

The plateau regions of the current traces suggest that the reaction rate is effectively zero order during that time period. This observation was confirmed by the gas chromatographic analysis of samples of the electrolyte. Figure 2 shows the conversion with respect to the normalized charge, which is defined as the charge passed since the addition of reactant divided by the theoretical charge required for the complete conversion of the reactant.

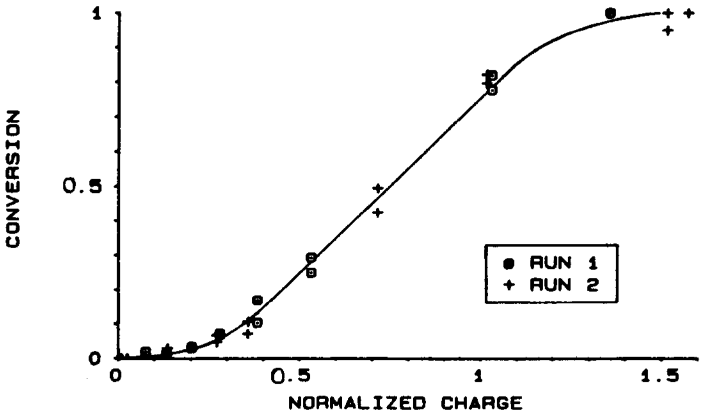

Fig. 2. Conversion Plot Showing the Induction Period Following the Addition of $H_2C\ (SO_2F)_2$.

Figure 2 also reveals an induction period following the addition of the reactant. During the induction period, little fluorination of the reactant, $H_2C(SO_2F)_2$, occurred although a disproportionately large quantity of charge was passed. The charge passed during this induction period was typically 20 to 30% of the total theoretical charge needed for the complete conversion of the $H_2C(SO_2F)_2$ to $F_2C(SO_2F)_2$.

An induction period was often reported for ECF with new nickel electrodes [12]. Since the nickel electrodes were thoroughly cleaned before each run, the electrodes should behave like new nickel electrodes in each experiment. In their work at cell voltage of 4 - 8 V, Comninellis et al. observed an induction period in the ECF of alkylsulfonyl fluorides during which 30% of the theoretical charge passed and no fluorinated products were formed [13]. This observation agrees reasonably well with ours.

Corrosion of the nickel anodes to form nickel fluorides during the induction period could account for a portion of the charge passed during the induction period. Pitting of the anodes could be observed after a few experiments, whereas the cathodes remained relatively smooth. Green deposits of nickel fluoride salts were observed coating the anodes and at the bottom of the reactor at the end of the experiment. Elemental analysis of the green deposit in powdered form showed that it was comprised principally of fluorine and nickel in a 2:1 ratio, probably NiF_2. However, the nickel could have been at a higher valence state during the experiment; the samples were exposed to air for a period of time following the completion of the experiment. In this investigation, the cathode weight losses were typically 40 times less than those observed for the anode. Table 2 summarizes the corrosion data for the nickel electrodes in these experiments.

A portion of the anodic corrosion might occur prior to the addition of the $H_2C(SO_2F)_2$ during the pre-electrolysis period. Hackerman et al. observed that nickel electrodes would corrode at a high rate in pure AHF to form NiF_2 [14]. In Table 2, the total anodic corrosion is estimated as a percentage of the theoretical charge for the fluorination reaction. However, the estimated charge for anodic corrosion cannot account for the total charge in the induction period. This indicates that anodic corrosion is the major cause of the induction charge. It appears that fluorine is the principle anodic product during the induction period [10].

TABLE 2

Nickel electrode corrosion results

Run	Avg. Anode Weight Loss[†] (g/cm^2)	Standard Deviation (g/cm^2)	Avg. Cathode Weight Loss[†] (g/cm^2)	Standard Deviation (g/cm^2)	% Theoretical Charge[*]
1	0.02348	9.26×10^{-4}	5.55×10^{-4}	7.95×10^{-5}	16.5
2	0.02581	3.51×10^{-4}	3.93×10^{-4}	2.68×10^{-4}	18.0
3	0.01174	4.27×10^{-4}	2.96×10^{-4}	1.98×10^{-4}	8.3
4	0.00774	2.12×10^{-4}	2.43×10^{-4}	5.51×10^{-5}	5.5
5	0.01703	6.17×10^{-4}	5.30×10^{-5}	9.65×10^{-5}	3.9
6	0.01497	4.68×10^{-4}	1.01×10^{-3}	2.22×10^{-4}	1.7

[†] Apparent area, 77.5 cm^2 per electrode.

[*] Based on the total amount of $H_2C(SO_2F)_2$ added and assuming all of the anodic corrosion occurs during the induction period with the formation of NiF_2.

The total amount of anodic corrosion during ECF depends on the operating potential. Figure 3 shows the average mass loss of the nickel anode with respect to the anodic potential for the experimental run. Other factors contributing to this anodic corrosion, such as the operating temperature and the initial degree of roughness of the anode, are not accounted for in this figure. However, from the results of this study and other investigation of the ECF process in our laboratory, it is obvious that the anodic corrosion is effected strongly by the applied anodic potential.

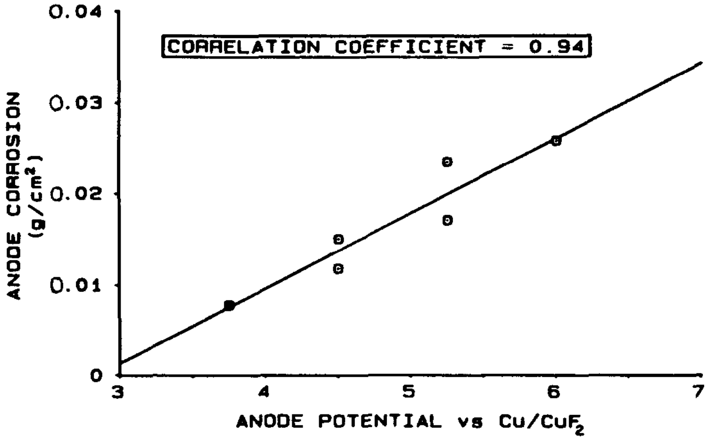

Fig. 3. Potential Dependence of the Total Anodic Corrosion During the Experimental Runs

The completion of the conversion in Figure 1 confirms that the reaction to form $F_2C(SO_2F)_2$ is not reversible at the experimental conditions and the fluorcarbon does not degrade. For this ECF reaction a high conversion, i.e. greater than 90%, of $H_2C(SO_2F)_2$ to $F_2C(SO_2F)_2$ would not be surprising based on the other reports on ECF of similar species. For instance, Gramstad and Haszeldine reported conversion efficiency of as high as 96% for the production of F_3CSO_2F from H_3CSO_2F [15]. The conversion values given in Table 1 are based on the $F_2C(SO_2F)_2$ recovered from contacting the electrolyte with ice-water at the end of the experiment. Even a small solubility of $F_2C(SO_2F)_2$ in cold water, e.g. at 15 g/liter, would contribute significantly to the lower conversion values reported in

Table 1. The slope of the linear portion of the curve in Fig. 1 approaches unity indicating the reaction is virtually 100 percent current efficient during this portion of the reaction. Based on these results and the gas chromotographic analysis of the complete electrolyte we feel that the conversion of this ECF process approaches 100%.

For practical reasons the electrical energy usage of the electrochemical process provides valuable information. The assessment of the electrical energy consumption in these experiments may be obtained in Fig. 4, which relates the normalized energy with respect to the normalized time.

The electrical energy is the product of the voltage and current integrated over time, and the normalized energy is defined as the energy consumed divided by the theoretical energy value required for the complete conversion of the reactant. The theoretical energy is defined as the product of the equilibrium voltage for the reaction, assumed to be 2.85 V for ECF, and the theoretical charge required for the conversion of all of the reactant.

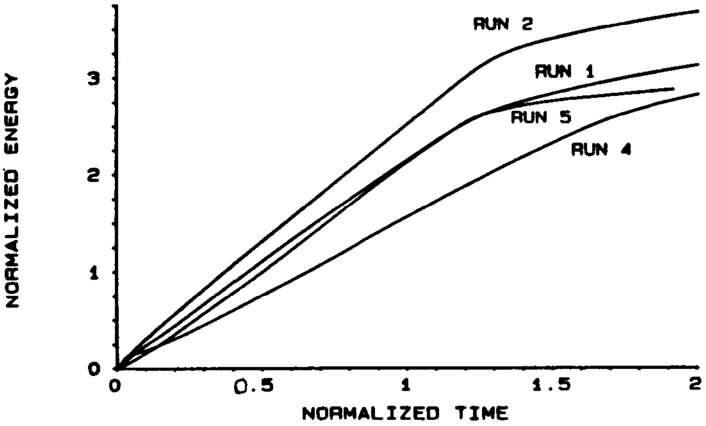

Fig. 4. Dimensionless Energy Profiles for the Experimental Runs

Figure 4 provides useful information for the process. First, an upper limit of the overall energy efficiency may be obtained from the reciprocal of the ordinate value at the point where the slope changes as the last of the reactant is consumed. Second, an upper limit estimate of the current efficiency may be obtained from the reciprocal of the abscissa value at the point where the slope changes. Also, since the cell voltage parallels the anode potential and is quite constant until the last of the reactant is consumed, the reciprocal of the slope of the linear portion of the plot is equivalent to the voltaic efficiency for the ECF process. Hence, voltaic, faradaic and energy efficiency information for each experiment can be obtained from Fig. 4.

Experimental conditions for Run 1 and Run 5 were identical, except for the initial reactant concentrations as shown in Table 1. The characteristics of both runs in Fig. 4 indicate that the reproducibility of the experiments was very good.

The presence of the constant current plateau and the requirement of an induction period after the reactant was added suggest that the organic (reactant) may play a role in the mechanisms of the ECF process. The potential dependent organic adsorption mechanisms suggested by Comninellis et al. [13] in which reaction between an adsorbed organic and adsorbed fluorine occurs, appeared to be consistent with the observed zero-order behavior and the presence of the induction period. Comninellis et al. [13] also observed higher conversions and current efficiencies at higher cell voltages and suggested the surface coverage by the organic was higher in this case. This appears to be supported by our experimental data, which showed the lowest current efficiency was obtained when the anodic potential was the lowest.

CONCLUSIONS

The utilization of a microprocessor-aided modified Simons reactor for the electrochemical fluorination process appears to be very effective. The electrochemical fluorination of methanedisulfonyl fluoride to produce difluoromethanedisulfonyl fluoride in this reactor is successful. Product recovered based yields of 75-82%, current efficiencies in excess of 66%, and electrical energy efficiencies of 33% are obtained.

Mechanistically, the electrochemical fluorination of $H_2C(SO_2F)_2$ exhibited a zero-order dependence on reactant concentration at concentrations above 0.002 moles/liter. After the reactant was added, an induction period, typically accounting for 30% of the theoretical total charge, was observed suggesting that organic (reactant) interaction with the anodic film nickel fluoride was necessary for the process.

The corrosion of the anodes was approximately 40 times greater than the corrosion of the cathodes. The amount of this corrosion is directly related to the anodic potential applied; the higher the anodic potential, the larger the anodic corrosion.

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