

# Production of fluorine with pulsed currents

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During the d.c. electrolysis of KF-*n*HF melts, a passivating film of graphite fluoride (CF<sub>x</sub>) is formed on the carbon electrodes, leading to high anodic overvoltage. Pulsed electrolysis enables fluorine production with significant improvements if, during the lowest potential of the pulse, a small reduction current is applied to the carbon electrode, leading to the partial reduction of CF<sub>x</sub>. Rectangular or sinusoidal waves have been studied. Very high peak values of the current density (150 A dm<sup>-2</sup>, *i.e.* 10 times more than the values usually reached with d.c.) were obtained in some particular cases.

## 1. Introduction

Fluorine production takes place by electrolysis of molten KF-2HF at 85-100 °C. Industrial cells are described in recent review articles [1, 2]. Although the thermodynamic potential of HF decomposition was demonstrated to be  $E_{\text{HF}} = 2.9 \text{ V}$  [3], a voltage of 8-12 V must be applied.

The mechanism of fluorine evolution is described in the literature [4-6]. The high anodic overvoltage is mainly attributed to the inhibition of electron transfer by a graphite fluoride film, characterized by a high resistivity and a very low surface energy [7]. This results in unusually low values of the transfer coefficient, compatible with a mechanism involving electron tunnelling through a passivating film [6, 8]. The interface constitutes the so-called "M.I.E." structure; in the present case, the electronic conductor "M" is the carbon anode, the insulating layer "I" is graphite fluoride (CF<sub>x</sub>) and the electrolyte "E" is molten KF-2HF.

The general aspects of electron transfer by the tunnel effect at these interfaces have been reviewed in the literature [9, 10]. The intensity of the anodic current depends on  $\exp(-kdE^{1/2})$ , where  $d$  is the thickness of the potential barrier,  $E$  its average height and  $k$  a constant.

Insulating graphite fluoride films are formed on carbon anodes when potentials greater than 3.5 V are applied to the electrode. In recent work, Brown *et al.* [11] concluded from electron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) that although the film thickness does not increase greatly with electrode potential, the degree of fluorination does.

Estimates of the thickness of the layer of graphite fluoride have been proposed in the literature [12]. However, the chemical composition of the film is not uniform; the degree of fluorination increases progressively from the carbon towards the melt [10, 11, 13]. Thus, outer perfluorinated layers constitute the very thin dielectric film (a few angstroms thick) through which the tunnel effect occurs; the inner region (thick-

ness greater than one micrometer) has a much higher conductivity [6].

In 6000 A-industrial cells, the current density is 12 A dm<sup>-2</sup>; as the ohmic drop in the electrolyte is about 3 V, the thermodynamic potential for HF decomposition 2.9 V and the total voltage 9 V, the anodic overvoltage is about 3 V. Sometimes, the latter increases drastically. New electrolytes have been proposed in the literature: NH<sub>4</sub>F-*n*HF [14] or CaF<sub>2</sub>-LiBF<sub>4</sub> [15] melts, in order to overcome the anodic polarization. However, these attempts have not yet given rise to industrial production of fluorine.

Many improvements deal with KF-2HF melts: addition of LiF or AlF<sub>3</sub> [1, 16, 17], choice of polished [18-20] or impregnated [21, 22] electrodes and, lastly, the use of pulsed currents [23]. This last technique is also reported to improve the behaviour of polarized anodes. Triangular or rectangular waves are applied to the carbon electrode, which is always used as an anode. Very high values of the pulse peak voltage (> 80 V) lead to the destruction of the anodic material. The authors claim that this technique is better than imposing a high d.c. voltage (30-48 V) on the electrode for a few minutes, as reported previously [24], because the anode effect can take place again after such d.c. treatments.

In both methods, the very high voltage treatment causes the increase of the bath and interface temperature, favouring the decomposition of the passivating compounds at the interface. In fact, in previous work [25], it has been demonstrated that when the temperature increases, gaseous fluorocarbons are evolved, due to the thermal decomposition of CF<sub>x</sub>.

## 2. Experimental details

The experiments were performed at 85 °C, in a PVDF cell [3] or in a Monel cell, containing, respectively, 0.8 kg and 5 kg of molten KF-*n*HF. The acidity of the KF-*n*HF melts is generally expressed as C (HF weight percent), with  $C = 2000n/(58.1 + 20n)$ . The usual value,  $C = 40.8$ , was used, corresponding to  $n = 2$ .

A long low voltage pre-electrolysis was made in order to eliminate trace amounts of water.

For the experiments reported in paragraph 3.1, a two-electrode setup was used. The cell was connected to a power amplifier built in our laboratory, fitted with a Hewlett-Packard 200 AB oscillator. With this apparatus, the maximal peak-to-peak voltage may be 25 V, and the maximal peak-to-peak intensity 6 A.

For the small scale electrolytic cell, the working electrode was a rod of "P2J" industrial non-graphitized carbon for fluorine production manufactured by S.E.R.S. (France) or a rod of "C205" non-graphitized carbon from Le Carbone Lorraine (France). In the Monel cell, large "P2J" electrodes were used ( $S = 25$  to  $120 \text{ cm}^2$ ). Instead of a metallic auxiliary electrode, graphite ("Ellor 10" Le Carbone Lorraine) was chosen to prevent any pollution of the melt by metal cations, resulting from corrosion.

For fluorine production experiments, a three-electrode setup was preferred. In this case, the electrode potentials were measured with respect to a Pt- $\text{H}_2$  reference electrode which is suitable in constant acidity KF-2HF melts [3, 26]. The potentiostat (Tacussel PRT 20\*10) was driven by a function generator (Amel 565 for square waves and Hewlett-Packard 200 AB for sinusoidal waves). A potential adder-amplifier built in our laboratory was also used.

All the curves were stored on a Tektronix 7313 oscilloscope with the following plug-in units:  $Y_0$ : 7B50 time base,  $Y_1$ : 7A18N dual trace amplifier (Channel 1 and Channel 2),  $Y_2$ : 7A22 differential amplifier.

### 3. Results and discussion

#### 3.1. Electrode depassivation by sinusoidal currents

In this paper, the behaviour of a carbon electrode covered with a passivating layer of  $\text{CF}_x$  is studied. After fluorine production with d.c. a sinusoidal wave was applied. The current may be attributed to two contributions: the capacitive term and the faradaic term.

The amplitude  $E_{ac}$  of the sinusoidal signal is not sufficient ( $< 7 \text{ V}$  peak-to-peak) for fluorine evolution. Thus, the possible anodic reactions are: formation of graphite fluoride or evolution of oxygenated gases such as  $\text{F}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{COF}_2$  due to the discharge of water, if the pre-electrolysis is not correctly performed. The cathodic reaction may be hydrogen evolution or reduction of  $\text{CF}_x$ .

The faradaic current may be limited by several factors: mass transfer, kinetics of electron transfer and ohmic drop. The diffusion of fluoride ions is not a limiting factor in our melt. Previous studies have proved that the kinetics of formation of a low-conducting film of  $\text{CF}_x$  on carbon electrodes is controlled by the "ohmic drop", including the resistance of the melt and the contribution of the passivating layer [12].

For low frequencies of the sinusoidal potential pulse ( $f < 1 \text{ kHz}$ ), the  $I-t$  curve was not sinusoidal.

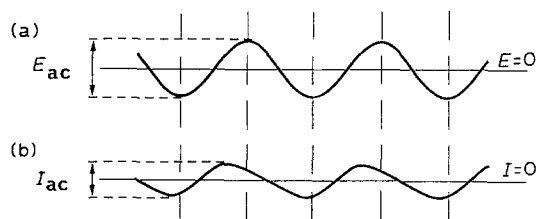


Fig. 1. E-t and I-t curves: depassivation experiment. Working electrode: "P2J" carbon;  $S = 4.5 \text{ cm}^2$ . (a) sinusoidal potential signal:  $E_{ac} = 7 \text{ V}$ ;  $f = 500 \text{ Hz}$ , (b) response of the system:  $I_{ac} = 750 \text{ mA}$ .

For higher values of  $f$ , a sinusoidal response was observed. Figure 1 presents the curve obtained for  $f = 500 \text{ Hz}$  and  $E_{ac} = 7 \text{ V}$ . The amplitude of the response  $I_{ac}$  (peak-to-peak) increases with time, attesting the progressive depassivation of the electrode.

Passivation and depassivation of the carbon electrodes in KF-2HF melts may be investigated by cyclic voltammetry experiments, performed over a large potential range (0.5 to 9.5 V against Pt/ $\text{H}_2$ ). As is reported in a recent publication [17], the current intensity at 9.5 V decreases for consecutive scans, due to the progressive passivation of the electrode under d.c. polarization. The ratio of the intensity at 9.5 V for the considered scan ( $n$ ) and the intensity,  $I_1$ , observed in the first scan performed with a new electrode rapidly tends to a roughly constant value for non-graphitized carbon anodes ( $n = 20$ ). A value of  $I_{20}/I_1 = 0.06$  was obtained with a P 2J carbon anode. If that electrode was left in the melt for three hours before performing the 21st voltammogram, a value of 0.06 was obtained for the ratio  $I_{21}/I_1$ .

However, if a sinusoidal potential ( $f = 500 \text{ Hz}$ ;  $E_{ac} = 7 \text{ V}$ ) was applied for three hours, the value of the ratio  $I_{21}'/I_1$  reached 0.70, indicating a very efficient depassivation of the electrode. For all cyclic voltammetry experiments, the scan rate was  $0.4 \text{ V s}^{-1}$ .

In addition, it was observed that  $I_{ac}$  increases with the frequency of the alternating potential signal, as shown in Table 1. This result is in agreement with the theoretical predictions obtained with a model based on the behaviour of low-conducting films under ohmic resistance control [12, 27, 28].

It was necessary to verify that the carbon electrodes were not corroded due to the dissipation of increasing electric power. The gases of the two compartments of the largest electrolytic cell were analysed by infrared spectroscopy, in a cell fitted with AgCl windows. HF,  $\text{F}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{COF}_2$  and gaseous fluorocarbons such as  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_x\text{F}_y\text{H}_z$  . . . are easily detectable by this technique [25]. Small amounts of gaseous fluorocarbons were detected, resulting from the expected

Table 1. Influence of the frequency of the potential pulse on the amplitude of the response. Working electrode: "C205";  $S = 2.6 \text{ cm}^2$ ;  $C = 41.2 \text{ wt} \% \text{ HF}$ ;  $E_{ac} = 3 \text{ V}$ .

$f/\text{Hz}$	20	50	500	5000	10000
$I_{ac}/\text{mA}$	530	640	800	880	880

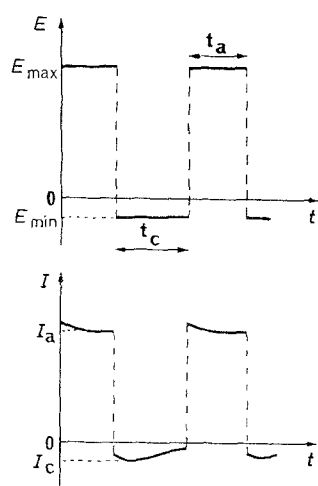


Fig. 2. Schematic E-t and I-t curves: fluorine production with rectangular potential pulses.

It is clear that the anodic faradaic current mainly contributes to the formation of  $\text{CF}_x$  compounds which are reduced during the following cathodic wave. When large amplitude sinusoidal potentials are applied to passivated carbon electrodes, the temperature of the interface increases. Thus, the thermal decomposition of the passivating  $\text{CF}_x$  layers may also contribute to depassivation, although the present aim was to recover the electrode reactivity only by electroreduction of the insulating layer.

### 3.2. Production of fluorine with pulsed currents

Significant improvements may be obtained if, during the lowest potential of the pulse, a small reduction current is applied to the carbon electrode, leading to the partial reduction of  $\text{CF}_x$ . The value of the lowest potential of the carbon working electrode during the pulse is carefully controlled for avoiding hydrogen production, which would result in a drastic fall of the faradaic yield due to the recombination reaction. It follows that, during the reduction of the  $\text{CF}_x$  layers on the carbon working electrode, the potential of the

Table 2. Fluorine production with rectangular pulses. Working electrode: "C205";  $C = 41.2 \text{ wt } \% \text{ HF}$

(a) $E_{\text{max}} = 7 \text{ V}$ ; $E_{\text{min}} = 0 \text{ V}$ ; $t_a = t_c = 20 \text{ ms}$				
$t/\text{min}$	0	4	10	30
$j_a/\text{A dm}^{-2}$	64	31	5.4	2.7
$j_c/\text{A dm}^{-2}$	$\sim 0$	$\sim 0$	$\sim 0$	$\sim 0$
(b) $E_{\text{max}} = 7 \text{ V}$ ; $E_{\text{min}} = -0.72 \text{ V}$ ; $t_a = t_c = 50 \text{ ms}$				
$t/\text{min}$	0	5	10	
$j_a/\text{A dm}^{-2}$	99	97	100	
$j_c/\text{A dm}^{-2}$	3.6	3.4	3.7	

counter electrode is never sufficiently high for fluorine generation.

**3.2.1. Rectangular pulses.** The potential,  $E_{\text{max}}$ , of the anodic pulse is applied during  $t_a$  and is followed by a cathodic pulse ( $E_{\text{min}}$ , duration:  $t_c$ ) as shown in Fig. 2. After a rapid decrease, the anodic current tends to a constant value  $I_a$ . The maximum value of the reduction current is denoted  $I_c$ .

Table 2(a) clearly shows that if  $E_{\text{min}}$  is not sufficiently low to allow the reduction of the  $\text{CF}_x$  compounds ( $E_{\text{min}} > -0.2 \text{ V}$  against  $\text{Pt-H}_2$ ), the mean current  $I_a$  decreases drastically for consecutive pulses. However, when the reduction is possible (Table 2(b),  $E_{\text{min}} = -0.72 \text{ V}$ ), the anodic current is very high and remains constant. It was possible to obtain current densities,  $j_a$ , of approximately  $100 \text{ A dm}^{-2}$ . Taking into account that fluorine production occurs only during half the total pulse and that the contribution of the oxidation-reduction of  $\text{CF}_x$  must be subtracted, average values  $\sim 45 \text{ A dm}^{-2}$  are obtained, *i.e.* 4 times more than for d.c. electrolysis.

The largest current densities were obtained when  $t_a = t_c = \tau$  and were quite similar for  $20 \text{ ms} \leq \tau \leq 200 \text{ ms}$ .

In addition, the response of the electrodes was

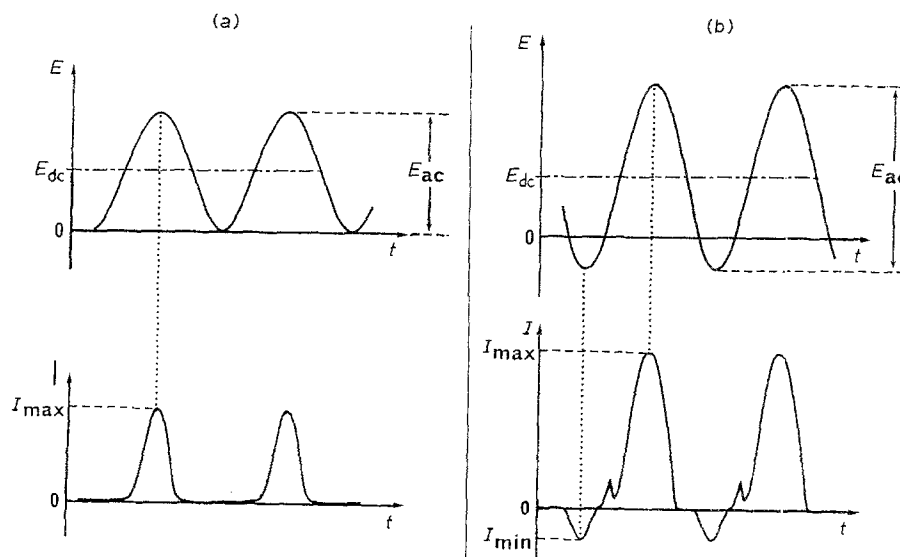


Fig. 3. E-t and I-t curves: fluorine production with superimposed sinusoidal signals ( $f = 50 \text{ Hz}$ ). Working electrode: "C205";  $S = 1 \text{ cm}^2$ ;  $C = 41.2 \text{ wt } \% \text{ HF}$ . (a)  $E_{\text{dc}} = 4 \text{ V}$ ;  $E_{\text{ac}} = 8 \text{ V}$ , (b)  $E_{\text{dc}} = 4 \text{ V}$ ;  $E_{\text{ac}} = 12 \text{ V}$ .

Table 3. Yield of fluorine production by pulsed currents (sinusoidal waves)

Experimental conditions reported in:	Yield/%
Fig. 3a and Table 4a	100
Fig. 3b and Table 4a	91
Fig. 4a	72
Fig. 4b	36

studied, when sinusoidal signals were applied, using the mains frequency (50 Hz).

**3.2.2. Sinusoidal signals superimposed on d.c.** Figure 3 presents schematic E-t curves and the resulting I-t responses. If the values of the peak-to-peak potential,  $E_{ac}$ , and the superimposed d.c. potential,  $E_{dc}$ , do not allow the reduction of the  $CF_x$  layers, the yield of fluorine production is quite good (see Table 3), but the maximum anodic current  $I_{max}$  decreases drastically with time, the steady value being  $1.8 \text{ A dm}^{-2}$  (see Table 4a:  $E_{ac} = 8 \text{ V}$  and  $E_{dc} = 4 \text{ V}$ ). This result shows the progressive formation of a  $CF_x$  insulating film.

By contrast, when the reduction of  $CF_x$  is possible ( $E_{ac} = 12 \text{ V}$  and  $E_{dc} = 4 \text{ V}$  were applied to that passivated electrode), high  $I_{max}$  values are observed (see Table 4b). With the same electrode, it was even possible, for  $E_{ac} = 14 \text{ V}$  and  $E_{dc} = 5 \text{ V}$ , to obtain  $I_{max} = 1.5 \text{ A}$  (i.e.  $150 \text{ A dm}^{-2}$ ).

Long duration experiments were performed in the Monel electrolytic cell, using large industrial "P2J" working electrodes with the following conditions:  $E_{ac} = 11 \text{ V}$ ;  $E_{dc} = 3 \text{ V}$ ;  $S = 38 \text{ cm}^2$ ;  $I_{max} = 12 \text{ A}$ ;  $I_{min} = 3 \text{ A}$ . The gas flow was measured ( $1.0 \pm 0.1 \text{ dm}^3 \text{ h}^{-1}$ ); the value was in good agreement with the value calculated from the integration of the I-t curves, assuming that the area of the cathodic peak, corresponding to the reduction of  $CF_x$ , must be subtracted from the area of the anodic peak. The value of the d.c. current density that would give the same production is  $8 \text{ A dm}^{-2}$ . The energy required for the fluorine production in the large laboratory cell was calculated for our experiments:  $W_1 = 16 \text{ kWh (kgF}_2\text{)}^{-1}$ . It is comparable to the values obtained with d.c. industrial cells:  $W_2 = 15.2 \text{ kWh (kgF}_2\text{)}^{-1}$ , for  $I = 6000 \text{ A}$  ( $j = 12 \text{ A dm}^{-2}$ ) and  $\Delta V = 9.6 \text{ V}$ .

The purity of the fluorine evolved during the experiments reported above was estimated by i.r. analysis. It

Table 4. Fluorine production with sinusoidal pulses. Working electrode: "C205";  $S = 2.6 \text{ cm}^2$ ;  $C = 41.2 \text{ wt \% HF}$ ;  $f = 50 \text{ Hz}$

(a)  $E_{dc} = 4 \text{ V}$ ;  $E_{ac} = 8 \text{ V}$

t/min	0	20	30	40	50	140
$j_{max}/\text{mA cm}^{-2}$	380	280	180	120	55	18

(b)  $E_{dc} = 4 \text{ V}$ ;  $E_{ac} = 12 \text{ V}$

t/min	0	1	3	7	20*
$j_{max}/\text{mA cm}^{-2}$	18	250	360	550	710

\*and later

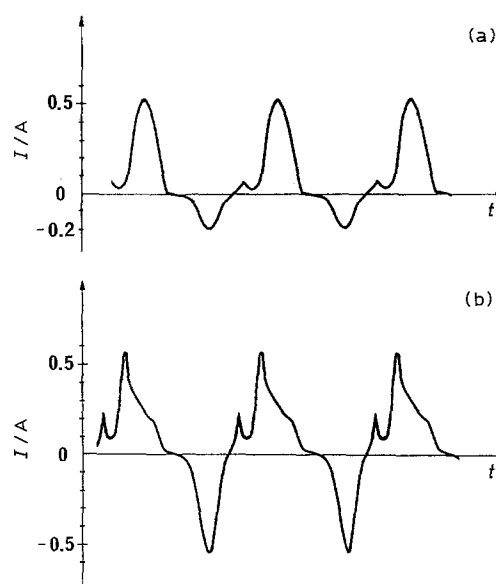


Fig. 4. I-t curves ( $f = 50 \text{ Hz}$ ) in acidic melts ( $C = 46.9 \text{ w \% HF}$ ). Working electrode: "P2J" carbon;  $S = 66 \text{ cm}^2$ . (a)  $E'_{dc} = 3 \text{ V}$ ;  $E'_{ac} = 8 \text{ V}$ , (b)  $E'_{dc} = 3.25 \text{ V}$ ;  $E'_{ac} = 10 \text{ V}$ .

was found comparable to that observed during d.c. electrolysis. Larger quantities of  $CF_4$  and gaseous fluorocarbons may be detected when higher current densities are applied. So, when very pure fluorine is needed, the values of  $E_{ac}$  and  $E_{dc}$  must be optimized.

**3.2.3. Influence of electrolyte composition.** The response of the system under ac superimposed on d.c. is a very useful tool for a fundamental study of the electrochemical behaviour of carbon electrodes in  $KF-2HF$  or for on-line control. For example, the determining influence of the acidity of the melt was easily observed: when anhydrous HF was added during fluorine production,  $I_{max}$  decreased sharply. Thus, the values of  $E_{ac}$  and  $E_{dc}$  had to be modified for restoring the same intensity, but the faradaic yield of fluorine production fell.

The experiments presented in Fig. 4 confirm previous results obtained by cyclic voltammetry [12]. They were performed in a two-electrode setup.  $E'_{ac}$  and  $E'_{dc}$  are referred to the counter electrode. The Pt- $H_2$  reference electrode was not useful because its potential depends on the acidity of the melt.

When the acidity of the melt is too high, the ratio  $Q_a/Q_c$ , calculated from the area of the anodic and cathodic peaks, decreases drastically (Fig. 4a) and the yield of fluorine is poor, as shown in Table 3. If higher values of  $E'_{ac}$  and  $E'_{dc}$  are applied, (Fig. 4b), the I-t curves may be completely distorted and the fluorine production is non-existent. The faradaic current mainly contributes to the  $CF_x$  oxido-reduction process.

## 4. Conclusion

Although the pulsed current technique is not readily applicable to industrial fluorine cells, the results reported above show that the technique achieved better improvements than those proposed in the patent literature [23]. It was possible to apply unusually high current densities, such as  $150 \text{ A dm}^{-2}$  (peak values),

without any polarization or deterioration of the carbon electrode.

Metallic cathodes (copper, Monel, steel) are used in d.c. fluorine production cells. All the experiments reported above were performed with a graphite counter electrode because metallic electrodes could be corroded with the pulsed current treatment. Of course, the cathode (material, purity, structure) should be chosen so as to minimize the corrosion process.

The results concerning the influence of the electrolysis parameters obtained in this work are in full agreement with the fundamental predictions concerning the fluorine evolution reaction, *i.e.* electron transfer through a passivating layer of graphite fluoride.

5000 A generators, working with 40–60 peak-to-peak voltages and frequencies lower than  $10^4$  Hz, are now available. In the near future, pulsed currents will perhaps be applied not only in the field of electrodeposition. This work has proved that, in the particular case where electrodes are passivated, sinusoidal a.c. superimposed on d.c. may bring significant improvements.

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#### References

- [1] M. Jaccaud, R. Faron, D. Devilliers and R. Romano, in 'Ullmann's Encyclopedia of Industrial Chemistry', Vol. A11, VCH, Weinheim (1988) p. 293.
- [2] J. F. Ellis and G. F. May, *J. Fluorine Chem.* **33** (1986) 133.
- [3] D. Devilliers, F. Lantelme and M. Chemla, *J. Chim. Phys.* **76** (1979) 428.
- [4] A. J. Rudge, in 'Industrial Electrochemical Processes', (edited by A. T. Kuhn), Elsevier, Amsterdam (1971) Chapter 1.
- [5] L. Bai and B. E. Conway, *J. Appl. Electrochem.* **18** (1988) 839.
- [6] M. Chemla and D. Devilliers, *J. Electrochem. Soc.* **136** (1989) 87.
- [7] H. Imoto, T. Nakajima and N. Watanabe, *Bull. Chem. Soc. Jpn.* **48** (1975) 1633.
- [8] D. Devilliers, F. Lantelme and M. Chemla, in 'Centenary of the Discovery of Fluorine', International Symposium, Paris (1986) abstract p. 216.
- [9] H. Gerischer, *Z. Phys. Chem. Neue Folge* **26** (1960) 223.
- [10] *Idem*, in 'Physical Chemistry', (edited by H. Eyring), Vol. IX A, Academic Press, New York (1970) Chapter 5.
- [11] O. R. Brown, B. M. Ikeda and M. J. Wilmott, *Electrochimica Acta* **32** (1987) 1163.
- [12] D. Devilliers, F. Lantelme and M. Chemla, *ibid.* **31** (1986) 1235.
- [13] O. R. Brown and M. J. Wilmott, in 'Centenary of the Discovery of Fluorine', International Symposium, Paris (1986) abstract p. 218.
- [14] M. Caron, P. Coste, C. Coquet and M. Rey, *French Patent* 2082 366 (1971), (Société des Usines Chimiques de Pierrelatte).
- [15] G. Mamantov and T. M. Laher, *J. Electrochem. Soc.* **136** (1989) 673.
- [16] T. Nakajima, T. Ogawa and N. Watanabe, *ibid.* **134** (1987) 8.
- [17] D. Devilliers, B. Teisseyre and M. Chemla, *Electrochimica Acta* **35** (1990) 153.
- [18] P. T. Hough and D. M. Novak-Antoniou, *US Patent* 4 602 985 (1986), (Eldorado Resources Ltd).
- [19] P. T. Hough and D. M. Novak-Antoniou, in 'Centenary of the Discovery of Fluorine', International Symposium, Paris, (1986) abstract p. 211.
- [20] D. Devilliers, B. Teisseyre, M. Vogler and M. Chemla, *J. Appl. Electrochem.* **20** (1990) 91.
- [21] T. Tojo, J. Hiraiwa, Y. Chong and N. Watanabe, in 'Molten Salt Chemistry and Technology', (edited by M. Chemla and D. Devilliers), Trans Tech Publications, Zürich (1991) p. 609.
- [22] O. R. Brown and M. J. Wilmott, *European Patent* 255 225 (1988), (British Nuclear Fuels PLC).
- [23] M. Aramaki, Y. Kobayashi and T. Nakamura, *Japanese Patent JP-Kokai* 57 54 286 (1982), (Central Glass Co. Ltd).
- [24] J. Dykstra, S. Katz, C. B. Clifford, E. W. Powell and G. H. Montillon, *Ind. Eng. Chem.* **47** (1955) 883.
- [25] D. Devilliers, M. Vogler, F. Lantelme and M. Chemla, *Anal. Chim. Acta* **153** (1983) 69.
- [26] D. Devilliers, B. Teisseyre and M. Chemla, *J. Chim. Phys.* **85** (1988) 789.
- [27] B. Teisseyre, Thesis, Pierre et Marie Curie University, Paris (1988).
- [28] D. Devilliers, B. Teisseyre, H. Groult and M. Chemla, in 'Molten Salt Chemistry and Technology', (edited by M. Chemla and D. Devilliers) Trans Tech Publications, Zürich (1991) p. 381.