

Polished carbon electrodes for improving the fluorine production process

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Improvements in the fluorine production process may be obtained by forming a ternary conducting layer CF_xM_y at the surface of the carbon anodes (M is a metal: Li, Mg, Al, . . .). Electron transfer at the interface is thus enhanced and the wettability of the electrode by the KF-2HF melt is improved. In this paper, we show that polishing the carbon electrodes with alumina or magnesia actually dopes the carbon by mechanical insertion of the latter compound. Scanning electron microscopy experiments show that particles of aluminium oxide or magnesium oxide are inserted during the polishing process; they give the corresponding fluorides during electrolysis in the KF-2HF melt. A surfacic ternary conducting compound is formed, as in the case of electrodes doped by additions of LiF or AlF_3 into the melt. The electrochemical behaviour of the polished electrodes has been studied by cyclic voltammetry experiments and impedance measurements.

1. Introduction

In all modern fluorine production units, 'medium temperature cells' are used. During electrolysis of KF-2HF melts, hydrogen is liberated at the cathode and fluoride ions are oxidized to fluorine at the anode. The cell operating voltage always lies in the range 10-12 V because a large anodic overvoltage takes place, inducing a considerable energy loss [1, 2].

The anodic overvoltage is a consequence of the presence of a passivating layer of graphite fluoride at the surface of the carbon electrodes. The electron transfer is thus inhibited, and very low values of the transfer coefficient are observed for the electrochemical reaction of discharge of fluoride ions at the interface [3].

In a recent paper [4], we recalled the kinetics of the electron transfer during this reaction and the numerous attempts which have been made to improve the efficiency of the overall electrochemical process. In that paper, after presenting a rapid voltammetric test useful for comparing the electrochemical behaviour of several carbonaceous anodic materials, we showed that the addition of lithium or aluminium fluoride in the melt is effective for improving the performances of the carbon materials. Our investigations clarify the effect of several additives that had been proposed in the literature: the formation of a conducting ternary compound CF_xM_y , where M is a metal such as Al or Mg, is supposed to be formed at the interface. These compounds would be similar to those chemically prepared by Nakajima [5]. The electron transfer is thus enhanced, as is the wettability of the anode by the electrolyte.

In the present paper, we demonstrate that the same goal may be reached by introducing the metal M into the carbon sample before electrolysis. The insertion of

the doping agent in the carbon anode may be performed by polishing it.

Before giving our experimental results, we report from the literature some empirical improvements based on preliminary treatments of the anodes before electrolysis. Following this, we describe the electrochemical technique used for comparing the various anodic material. This is based on cyclic voltammetric experiments coupled with impedance measurements.

2. Improving the anodic material

It is now well known that, in the fluorine production process, the anodic overvoltage is mainly due to the presence of a passivating layer of graphite fluoride at the interface, inhibiting the electron transfer. The electric properties of the insulating layer strongly depend on the nature of the carbonaceous material. Graphite electrodes give rise to the formation of large amounts of insulating compound at the interface and therefore must not be chosen for the industrial preparation of fluorine. The characteristics of the anodes, recommended for electrolysis in 'medium temperature cells', are discussed in the literature [6]. For example, the manufacturing process must be controlled to avoid the formation of graphite phases; in addition, the material is often porous, in order to allow the possibility of removing fluorine internally, via internal pathways provided by the porosity.

Indirect improvement of the anodic behaviour is obtained by adding lithium fluoride (1 to 2 wt %) to the melt. The anodic polarization problems are reported to be less intense, due to the formation of a graphite intercalation compound (GIC) at the interface: this compound is much more conducting than graphite fluoride [7].

The presence of nickel salts in the electrolyte,

resulting from the corrosion of the Monel parts of the cell, is also reported to have the same beneficial effect on the electrolytic process [1, 6]. The addition of NiF_2 , MgF_2 or AlF_3 prevents the anode effect by reducing the anode–electrolyte contact angle [8]. The electrodes are covered by a layer (containing metallic ions) which is wetted by the melt, thus reducing anode polarization.

Several attempts at improving the behaviour of the carbon electrodes by means of a preliminary treatment *before* electrolysis are reported below.

2.1. Polished carbon electrodes

It is reported in the patent literature [9] that the efficiency of the process may be markedly improved (i.e. the amount of electricity consumed in a given cell to produce a specified amount of fluorine may be lowered) when ‘modifying the surface texture’ of the carbon anodes by polishing.

Smooth surfaces are obtained by using a sequence of abrading materials, in the presence of a liquid which can be water or a polar organic water-soluble solvent. It is claimed that the nature of this liquid is of considerable importance because it affects the efficiency of the polished electrodes. This effect is not understood, nor are the anodic properties of polished anodes fully understood [10].

After polishing, the samples are cleaned in water and dried before testing. Comparison between polished and unpolished electrodes cut from the same carbon sample have been made. For small scale anodes, rapid cyclic voltammetry tests have been performed; the results are in good agreement with long time tests performed with an industrial cell.

2.2. Impregnation

This technique is useful for introducing a ‘doping agent’ into the carbon electrodes. For example, impregnation of the anodes by immersing them into molten lithium fluoride under pressure was first proposed by Watanabe several years ago [11]. This work has been resumed recently [12, 13]. This technique was reported to be much more effective than the addition of LiF into the melt. After this operation, the porosity of the material tends to zero. With these impregnated electrodes, the potential for a given current density is lowered and it is possible to operate at higher current density without the onset of anode effect.

In the patent literature, Brown and Wilmott claim that the anodic overvoltage is lowered by the presence of dispersed transition metals in the electrodes [14]. These dopants, preferably selected from nickel, vanadium and cobalt, are derived from thermally decomposed organic complexes. The manufacture of the ‘modified’ electrodes consists of three steps. First, the transition metal is dispersed, as an organic complex, in a ‘precursor’ in the liquid phase. This precursor is petroleum or coal-tar. Secondly, the impregnated precursor is carbonized and pulverized. Then, com-

bined with a suitable binder, it is heat-treated to produce the doped electrode.

In our study, our goal is to understand the effect of polishing the carbon sample and to demonstrate that this technique is an indirect way of doping the carbon. The behaviour of raw on modified anodes is compared using rapid electrochemical tests.

3. Experimental

Cyclic voltammetry experiments and impedance measurements have been performed in order to demonstrate the effect of polishing on the electrochemical behaviour of the carbon electrodes. Scanning electron microscopy has also been used to study the surface texture of the samples, especially the polished ones.

3.1. Experimental procedure

3.1.1. Electrolytic cell, anodic material. Our laboratory cell is described elsewhere [15]. It contained approximately 1.5 kg of molten KF-2HF . For all the experiments, the acidity was maintained constant as well as the temperature (85°C), because these two parameters have a considerable influence on the behaviour of anodic materials [16, 17]. A careful pre-electrolysis was made in order to avoid the presence of water.

For the cyclic voltammetry experiments, an Amel 555 potentiostat was driven by a function generator (Amel 565) and a potential adder-amplifier built in our laboratory. Scans were done over a very large potential range: -10 to $+10$ V against a Pt-H_2 reference electrode. For all our investigations presented here, the potential sweep rate was: $v = 0.4 \text{ V s}^{-1}$.

Impedance measurements were performed with a Hewlett Packard 4192A LF Impedance Analyser, driven by a Hewlett Packard 9816S computer. The frequency range lay between 5 Hz and 13 MHz; the amplitude of the AC signal was equal to 30 mV.

This configuration is useful for determining the electric characteristics of passivating layers, when the faradic current is very low. The elements of the equivalent circuit are deduced by exploitation of impedance or admittance plots in the complex plane.

A graphite auxiliary electrode was chosen to prevent any pollution of the melt by metallic cations. The anodic material of the working electrode was P2J industrial non-graphitized carbon for fluorine production manufactured by SERS, France. The anodes were Teflon-shielded cylinders (diameter: 12 mm). The area exposed to the melt was a vertical disc ($S = 1.13 \text{ cm}^2$).

3.1.2. Preparation of modified electrodes by ‘mechanical insertion’. Four kinds of samples were prepared from industrial P2J non-graphitized carbon, with a JPS 150 polisher using different polishing agents:

- sample 1: silicon carbide abrasive papers (Grit 360 and 1200) only
- sample 2: pre-polishing with SiC abrasive papers,

followed by final polishing with aluminium oxide suspensions Durmax JPS (1 and 0.1 μm) on a suitable polishing cloth

- sample 3: pre-polishing with SiC abrasive papers, followed by final polishing with a magnesium oxide suspension Magomet Buehler on a polishing cloth
- sample 4: Buehler diamond grinding disc (6 μm , resin-bonded). Each sample preparation with this disc needed several hours. It was possible to reduce this time by using several diamond discs: the first for coarse grinding and the final one for fine grinding.

After polishing, the samples were ultrasonically cleaned in distilled water, dried, and heat-treated at 545 or 1000°C for several hours. A quartz tube, containing the samples, was introduced into the furnace; the temperature was progressively raised under vacuum; after the heat-treatment, i.e. 15 h at the suitable temperature, the tube was progressively cooled at room temperature, the samples being under controlled atmosphere (argon) to avoid oxidation of the carbon.

Another attempt to insert doping particles was to brush on the carbon electrodes suspensions of the polishing agents reported above:

- sample 5, prepared with a suspension of aluminium oxide (Durmax, 0.1 μm)
- sample 6, prepared with a suspension of magnesium oxide (Magomet Buehler)

3.1.3. Scanning electron microscopy. Scanning electron micrographs of the polished samples were made with a Jeol JEM 100 CX II transmission electron microscope equipped with a Jeol high resolution scanning attachment (STEM-SEM ASID 4D) and an energy dispersive X-ray detector (Li-doped Si, $S = 30 \text{ mm}^2$, with ultra-thin window), Link AN 10000. The X-ray spectra give the elemental composition of the samples.

3.2. Electrochemical tests on carbon electrodes

A new electrode was introduced into the cell. The admittance diagram was determined before and after performing the cyclic voltammetry test described below.

3.2.1. Cyclic voltammetry. In a previous paper [4], we emphasized that cyclic voltammetry experiments were useful for comparing the electrochemical behaviour of several anodic materials in the KF-2HF melt. It was established that the anodic passivation peak near 2.5 V, observed in the first scan performed with a new carbon electrode, corresponds to the formation of intercalation compounds. The intensity of this peak (denoted I_p) and the charge Q_a are related to the quantity of these compounds.

On the one hand, scans over a small potential range (-0.5 to 3 V) gave information on the ability of the intercalation compounds to be formed and reduced. On the other hand, scans over a wide potential range (+0.5 to 9.5 V) gave information on the behaviour of

an anodic material during the evolution of fluorine. These latter experiments were particularly useful for comparing carbon electrode materials subject to severe conditions (high current density). For the scan number n , the intensity at 9.5 V is denoted I_n . I_n is generally lower than I_1 . For graphite electrodes I_1 is large (80 A dm^{-2}), but the ratio I_n/I_1 rapidly tends to zero. On the contrary, for carbon electrodes, I_1 (40–50 A dm^{-2}) is lower than the value obtained with graphite, but I_n does not decrease so quickly. The I_{20} value may often be considered as a 'stationary' value. It has been observed that there is a good correlation between the results of this kind of test and those of long potentiostatic experiments performed in a full scale cell with the same anodic material [9]. We have observed that the samples which exhibit the highest values of I_1 and I_{20}/I_1 and the lowest values of I_p generally present the lowest anodic overvoltage.

Thus, twenty scans were performed with each carbon sample, and the values of I_1 and I_{20}/I_1 were compared. The current intensity depended on the potential sweep rate, the latter being arbitrarily chosen for all the experiments at $v = 0.4 \text{ V s}^{-1}$.

3.2.2. Impedance measurements. The electric properties of the passivating layer formed at high potential on a carbon anode in molten KF-2HF may be deduced from the impedance (or admittance) diagram of the system comprising the passivated electrode and the auxiliary electrode both immersed in the cell. This system may be simulated by a very simple equivalent circuit: a resistor R_p in parallel with a capacitor C , this loop being in series with a resistor R_s [18]. This model is correct if the following conditions are satisfied:

- use of a large auxiliary electrode; the best configuration is a platinum basket surrounding the working electrode. The contribution of the auxiliary electrode in the total impedance is thus negligible.

- if a ddp is applied between the two electrodes, it must be sufficiently low to avoid a perceptible faradic current to flow. Thus, the thickness of the film remains roughly constant, fluorine evolution does not occur, and it is actually possible to measure the electric properties of the passivating layer.

It is possible to plot impedance data in the complex plane. In Nyquist diagrams, the imaginary part X (reactance) of Z (impedance) is shown against its real part R (resistance), the pulsation w of the AC signal being the parameter. The diagram corresponding to the equivalent model described above is a semicircle. We prefer to plot the imaginary part B (susceptance) of Y (admittance) against its real part G (conductance). For our equivalent circuit, the admittance diagram is also a semicircle. When w tends to infinity, B tends to zero and G to $1/R_s$; when w tends to zero, B tends to zero and G to $1/(R_p + R_s)$. B passes through a maximum for a given value of w which will be denoted w_M . The capacity C is deduced from the equation:

$$C = (R_p + R_s)/R_p R_s w_M \quad (1)$$

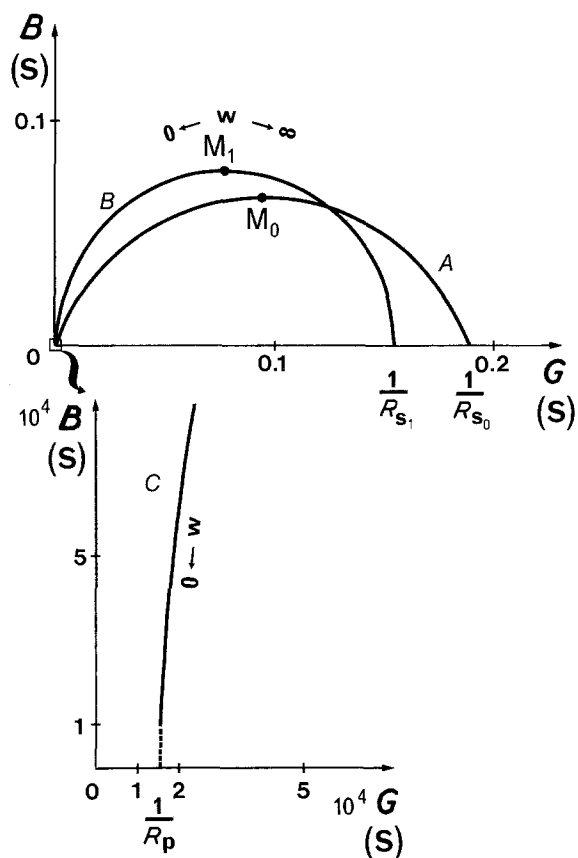


Fig. 1. Schematic admittance diagrams for carbon electrodes in KF-2HF melts. Curve A, new electrode; curve B, passivated electrode; curve C, enlargement of curve (B) for low frequencies.

In the case of passivating layers, $R_p \gg R_s$. Thus, the equation may be simplified as follows:

$$C = 1/R_s w_M \quad (2)$$

The results obtained with a new electrode immersed in the electrolyte do not meet the above conditions since the passivating layer is not yet formed. The admittance diagram is a flattened semicircle. The extrapolation of G at high frequency gives the value $1/R_{s0}$. The maximum value of the imaginary part gives a rough estimation of the capacitive term C_0 before passivation, i.e. $10\text{--}30 \mu\text{F cm}^{-2}$ (point M_0 on Fig. 1, curve A).

After the voltammetric test, the electrode is covered by a passivating film and the equivalent circuit proposed above fits the system correctly.

The admittance diagram is plotted, for a DC polarization of 3.5 V. The extrapolation of G at high frequency leads to the value R_{s1} , which is always greater than R_{s0} . The extrapolation at zero frequency leads to the value of R_p . The capacity C is deduced from Equation (2). Several remarkable results must be noted:

- The maximum value of B (point M_1 on Fig. 1, curve B) occurs for large values of the pulsation $w_{M1} \gg w_{M0}$; this means that the passivation of the electrode leads to a considerable decrease of the capacitive term [18-20]; C/C_0 is often lower than 0.01. It is considered that the lowest value of this ratio is related to the most passivated electrode [20, 21].

- The ratio R_{s1}/R_{s0} is always slightly greater than 1 [21], indicating that the R_s term of the equivalent circuit contains a contribution from the passivating layer and not only the contribution from the electrolyte, as is often considered. Highly passivated electrodes are characterized by the greatest values of this ratio.

- The value of R_p is always much greater than R_s . High values of R_p are related to highly passivated electrodes, for which the rate of electron tunnelling across the graphite fluoride film will be strongly inhibited.

The determination of the electric characteristics of the passivating layers formed at various potentials on vitreous carbon have been made by Brown *et al.* However, their experimental procedure is quite different: these authors fluorinated the carbon sample by constant potential polarization and removed the electrode from the melt. Then, the impedance diagram was plotted, corresponding to the behaviour of the fluorinated electrode in acetonitrile containing the ferrocene/ferrocinium redox couple [22]. The results globally agreed with our conclusions concerning the decrease of the interfacial capacitance.

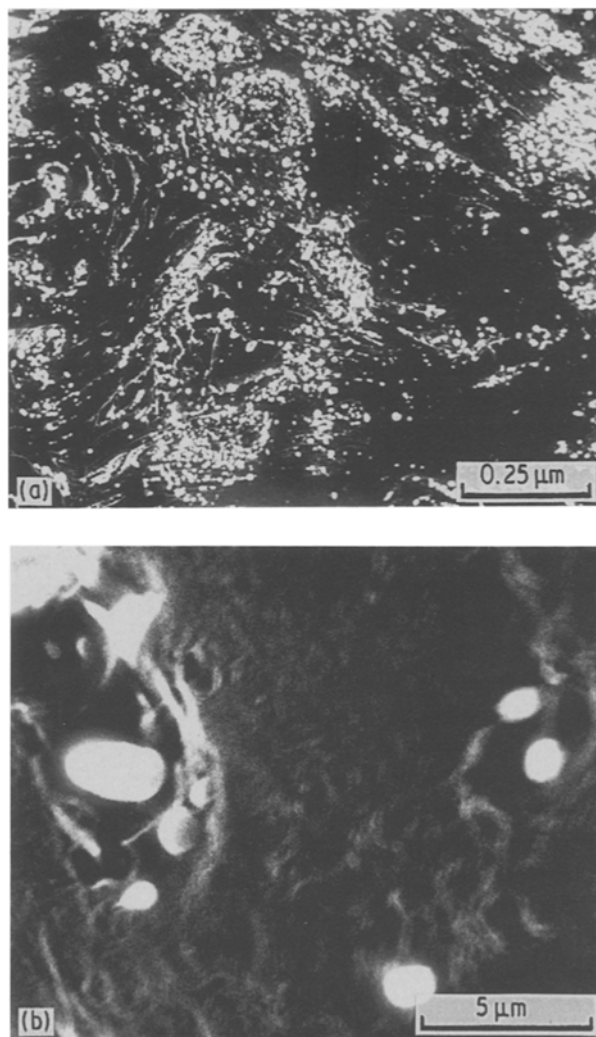


Fig. 2. Scanning electron micrographs showing the distribution of inserted particles on the surface of a P2J carbon electrode polished with MgO and heat-treated at 1000°C .

4. Results and discussion

In this section, we show that it is possible to dope carbon electrodes by mechanical insertion of a suitable agent. The first method is by polishing the material; a second possible method is by brushing the electrodes with a suspension of the doping agent.

4.1. Characterization of the surface of polished samples

We have observed by scanning electron microscopy that the surface of the polished samples which have been heat-treated at 545°C do not present apparent inclusions of the polishing oxide. However, for the samples heat-treated at 1000°C, these inclusions are clearly visible. We believe that the high temperature facilitates the diffusion of the inserted particles from the matrix of the sample to the interface.

In Fig. 2 we present micrographs of an electrode polished with MgO and heat-treated at 1000°C. Inserted particles are clearly visible; the chemical compositions of these inclusions is determined from the X-ray spectrum of the sample, which is compared with the spectrum obtained with a raw carbon sample. Two peaks corresponding to the elements Mg and Si are noticed for the electrode polished with MgO.

Our conclusion is that polishing electrodes introduces very small particles of the polishing agent into the electrode; ultrasonic cleaning is not sufficient to remove all these particles which can act as doping agents and improve the electron transfer during the discharge of fluoride ions.

4.2. Electrochemical tests

The results of the voltammetric test performed with the modified electrodes are presented in Table 1. These are compared with those obtained with raw carbon anodes. Modified electrodes generally give rise to higher values of I_p than the reference sample because, in the same range of potential, the fluorination of the inserted particles occurs in addition to the intercalation compound formation. So, the most suitable modified carbon electrodes for fluorine production are only characterized by the higher values of I_1 and I_{20}/I_1 .

In Table 2 we report the results of impedance measurements. For all the polished samples, R_p is

Table 2. Results of impedance measurements with polished P2J carbon electrodes

Sample	R_{s0} (0 V) (Ω)	R_{s1} (3.5 V) (Ω)	R_p (Ω)	C (μF)	R_{s1}/R_{s0}
0	6.7	7.2	6700	0.062	1.07
1	6.5	6.9	4200	0.13	1.06
2	6.1	6.5	5000	0.22	1.06
3	6.1	6.4	2600	0.22	1.05
4	8.1	7.7	4800	0.065	0.95
5	8.0	5.6	700	0.029	0.70
6	6.5	8.3	2600	0.034	1.28

lower than that of the reference sample. These results clarify the effect of polishing on the performance of the electrodes during fluorine production.

Samples 1 to 3 present better characteristics than raw carbon (Sample 0) because they exhibit lower values of R_p , and higher values of I_{20}/I_1 and C . We attribute this phenomenon to the presence of inserted particles at the interface. The particles of aluminium oxide or magnesium oxide give the corresponding fluorides during electrolysis and the surface layer is then composed of a ternary conducting compound, as in the case of electrodes doped by additions of LiF or AlF₃ in the melt. Doping the carbon with Si may not be interpreted in the same way. In this last case (sample 1), the wettability of the electrode by the melt may be improved by the presence of silicon at the interface. However, we think that these Si-doped electrodes would not maintain this property during long-time electrolysis, because Si would progressively be removed, leading to the evolution of SiF₄.

Sample 4, which was polished only, without any insertion (diamond disc), does not present good characteristics because the ratio I_{20}/I_1 is lower than that of the reference sample. This result clearly shows that polishing itself is not effective for improving the performances of the electrodes.

Brushing the electrodes is a convenient technique for doping them with aluminium or magnesium. However, Samples 5 and 6 do not exhibit significantly improved performance. We think that the conducting ternary compounds CF_xM_y are hardly formed at the interface because the oxide particles, which are not sufficiently anchored to the carbon, are progressively carried to the bottom of the cell.

5. Conclusion

Our experiments show that significant improvements of the fluorine production process may be obtained by forming a ternary conducting layer CF_xM_y at the interface. This compound is thought to enhance electron transfer at the interface and to improve the wettability of the electrode by the melt. The layer may be formed either by adding a fluoride in the melt or by polishing the carbon electrodes, because this later process actually dopes the carbon by mechanical insertion of a polishing agent which may be considered as a promotor in the catalytic doping process.

Table 1. Results of cyclic voltammetry experiments with polished P2J carbon electrodes

Sample	I_p ($mA\ cm^{-2}$)	I_1 ($mA\ cm^{-2}$)	I_{20} ($mA\ cm^{-2}$)	I_{20}/I_1 (%)
0	10.6	663	531	80
1	18.6	813	778	96
2	19.5	752	707	94
3	49.5	707	707	100
4	16.4	486	296	61
5	17	707	353	50
6	67	707	619	88

In this paper, we have shown that the insertion of alumina or magnesia into the electrodes improves their performance. The particles of aluminium oxide or magnesium oxide are thought to give the corresponding fluorides during electrolysis; the surface layer is then composed of a ternary conducting compound, as in the case of electrodes doped by additions of LiF or AlF_3 in the melt. We have proposed another method of mechanical insertion, i.e. brushing the electrodes with a suspension of a suitable doping agent. However, we think that polishing may give rise to a better insertion and to better performance in long-time electrolysis.

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