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Modification of carbon electrodes by a nitrate-based treatment

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The modification of raw carbon electrodes by a nitrate-based treatment improves the fluorine evolution process on carbon anodes. In the case of $Al(NO_3)_3$-impregnated electrodes, these improvements are attributed to the formation, at the electrode/KF-2HF interface, of a ternary conducting compound $C_x(AlF_3)_yF$, i.e. a GIC, instead of insulating graphite fluorides, CF_x. In addition, the effect of the NO_3^- anions of the impregnation solution is demonstrated by impedance spectroscopy, scanning electron microscopy and mercury porosimetry. Impregnation of crude carbon electrodes by nitrate salts, followed by heat treatment, induces smoothing of the electrode surfaces and an increase in the diameter of the pores. This treatment also improves the electronic transfer at the interface and enhances the wettability of the electrode by the melt.

1. Introduction

The production of fluorine from the electrolysis of molten KF–2HF at 85–100° C is characterized by a high anodic overvoltage (~3 V) [1, 2] which is commonly assigned to the formation of a low-conducting film of solid carbon-fluorine compounds, CF_x, at the surface of the carbon anode [3–5]. This film has a very low surface energy and gives rise to inhibition of the electronic transfer [6, 7]. This low surface energy induces a decrease in the electroactive area of the electrode [8] since bubbles are large, lenticular and adherent to the anode surface.

In previous work [9–11], it was reported that the charge transfer kinetic at the carbon electrode/insulating CF_x film/KF–2HF electrolyte interface may be significantly improved by doping the insulator. The impregnation technique is useful for introducing a doping agent into carbon electrodes [11]. It consists in inserting a precursor agent into the carbon lattice. The samples are then heated at high temperature in a controlled atmosphere to give a second precursor compound. The latter is fluorinated *in situ* during the electrolysis of the melt, leading to the formation of a ternary conducting compound $C_x(MF_z)_yF$, i.e. a GIC instead of CF_x. It is reported [11] that it is possible to significantly reduce the anodic overvoltage if the impregnation of the carbon electrode is performed with an $Al(NO_3)_3$ solution.

In this paper several experiments are reported. They were performed in order to optimize the choice of the impregnation solution: solvent, concentration of the Al^{3+}-doping cation and choice of the anion of the aluminium salt.

The electrochemical behaviour of several kinds of aluminium-doped carbon electrodes, prepared from different impregnation solutions, was studied. As the best results were obtained with $Al(NO_3)_3$ solutions, it was thought that the anion NO_3^- had an influence on the properties of the modified electrodes. This hypothesis was confirmed by the study of carbon samples impregnated with KNO_3 solutions. This salt only allows study of the influence of the anion of the impregnation solution: potassium is not a doping element since it is one of the components of the KF–2HF electrolyte used for the electrolytic preparation of fluorine.

The electrochemical experiments were coupled with surface analysis techniques such as scanning electron microscopy and mercury porosimetry in order to establish correlations between the electrochemical behaviour and the surface texture of the samples.

2. Experimental details

The electrochemical cell was described previously [12]. Anhydrous molten KF–2HF at 85° C was used as the electrolyte for the fluorine evolution reaction. The presence of water in the melt gives rise to the evolution of O_2, CO, CO_2, COF_2 and F_2O in the anodic compartment [4, 13] and contributes to the electrogeneration of CF_x at the interface [14, 15]. Therefore, it is necessary to perform a careful pre-electrolysis before the first experiments, for removing moisture traces and other impurities such as metallic cations.

Potentials are referred to $Pt–H_2$ although a Cu/CuF_2 reference electrode, as described in reference [16], was actually used for all the experiments.

A graphite counter-electrode was used. The preparation of the 'modified' carbon anodes used as working electrodes is described later.

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2.1. *Chemicals*

The industrial electrolyte KF–2HF was provided by Comurhex, Pierrelatte (France) and was carefully purified as described previously. The other chemicals were: ethanol, absolute (R.P. Normapur^{TM}, Prolabo); aluminium nitrate $Al(NO_3)_3 . 9H_2O$ (Rectapur®, Prolabo); potassium nitrate KNO_3 (Rectapur®, Prolabo); trispentanedionato-2,4 aluminium (aluminium acetylacetonate) $Al(C_5H_7O_2)_3$ (Fluka, purum).

2.2. *Working electrode material*

The anodic material was P2J (samples A) or P2JA (samples B) industrial nongraphitized carbon for fluorine production, manufactured by SERS–France. The P2J carbon electrodes were prepared using one-step baking and the P2JA using a three-step baking.

Deep impregnation of carbon was made using nitrate salts, KNO_3, $Al(NO_3)_3$, or an Al-organic complex, $Al(C_5H_7O_2)_3$, as precursor compounds. The impregnation of carbon electrodes with alcoholic solutions is easier than with aqueous solutions. Therefore, ethanol was chosen as the solvent. However, as the solubility of potassium nitrate in CH_3CH_2OH is lower than that of aluminium nitrate, concentrated KNO_3 solutions were prepared in a mixed-solvent H_2O/CH_3CH_2OH 50/50 vol % by dissolving the salt in water and adding ethanol.

Hereafter the different samples are numbered as follows, depending on their modification procedure:

Samples 1: crude carbon
Samples 2: carbon electrodes impregnated with an $Al(NO_3)_3$ solution in ethanol
Samples 3: carbon electrodes impregnated with a 0.1 M aluminium acetylacetonate solution in ethanol
Samples 4: carbon electrodes impregnated with a KNO_3 solution in water/ethanol.

Each sample was heat treated at 1000° C in a controlled atmosphere after impregnation as described in [10]. 'Reference' crude carbon samples (samples 1A and 1B), which were not impregnated, were also heat treated under the same conditions.

The concentration of the impregnation solutions was 0.01 M, 0.1 M or 0.25 M for the $Al(NO_3)_3$–P2J impregnated samples, respectively denoted samples 2Aa, 2Ab and 2Ac, and 0.03 M, 0.3 M and 0.75 M for the KNO_3–P2J impregnated samples, respectively denoted samples 4Aa, 4Ab and 4Ac. With such conditions, the effective concentrations of nitrate anions were the same for both sets of solutions.

2.3. *Apparatus*

Impedance measurements were performed in the frequency range 10^5–10^{-2} Hz with a 'Z-Computer' Tacussel impedance analyser driven by a HP9816 Hewlett-Packard microcomputer.

A Jeol JEM 100 CX II transmission electron microscope equipped with a Jeol high resolution scanning attachment was used to obtain scanning electron micrographs.

Mercury porosimetry experiments were made with a 'Poresizer 9310' Coulter (RS232C interface) driven by an IBM microcomputer.

3. Results and discussion

3.1. *Impedance measurements*

Electrochemical impedance spectroscopy is considered as a powerful tool to investigate electrode processes. For example, this technique provides rapid information about the electrical properties of the passivating layer formed on a carbon anode in KF–2HF melts [17]. In contrast, Tafel plots [8, 18] only give global information on the kinetics and a long time is needed to obtain the steady state I–V curves. Moreover, it was shown [11] that the behaviour of carbon anodes subject to fluorine evolution at high potentials (8–10 V) can be predicted from impedance diagrams made at low potentials (~4 V).

The classical system composed of an inert metallic electrode in the presence of a redox couple in solution is correctly represented by the Randles equivalent circuit. However, the problem is more complicated when considering heterogeneous electrodes because the microscopic properties of the material are distributed. The charge transfer resistance and the capacitance vary, depending on the local properties of the interface. Only average effects over the entire electrode surface can be observed. Because of these surface heterogeneities, one can observe a dispersion of the capacitance term with frequency. The electrode behaves like a transmission line which is a particular constant phase element (CPE). Its impedance is described by the empirical equation:

$$Z_{\mathrm{CPE}} = \frac{1}{T(\mathrm{j}\omega)^p} = \frac{1}{T\omega^p[\cos(p\pi/2) + \mathrm{j}\sin(p\pi/2)]} \quad (1)$$

where ω is the pulsation of the signal [19–21].

The CPE is characterized by two parameters: (i) the 'pseudo-capacitance' T, expressed in $\mu F\,\mathrm{cm}^{-2}\,\mathrm{s}^{p-1}$, and (ii) the exponent $p (0 \le p \le 1)$, related to the constant phase angle, Θ, of the CPE in the complex plane: $\Theta = (1 - p)\pi/2$ (Θ is expressed in radians). If Θ values are different from 0, surface heterogeneities are expected to be present.

3.1.1. Choice of the equivalent circuit. For the determination of the suitable equivalent circuit to describe impedance diagrams obtained with carbon/KF–2HF interfaces, two different cases must be taken into account as follows.

(a) *Crude carbon electrodes*
An insulating film of graphite fluorides (CF_x) is generated at the electrode surface during the electrolysis of the melt. The electronic transfer involves

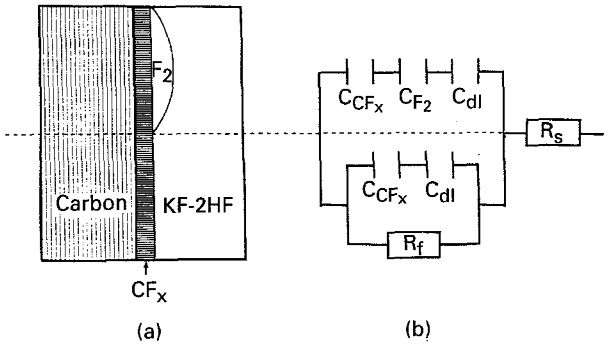

Fig. 1. Passivated crude carbon electrodes. (a) Schematic representation of the electrode/electrolyte interface and (b) corresponding equivalent circuit.

only the outer layers of the CF_x film [17]. A schematic representation of the interface is given in Fig. 1(a). The surface energy of the CF_x film is very low and therefore bubbles of fluorine are locally adherent. In that part of the anode, the electronic transfer is completely blocked and the capacitance term is composed of three contributions in series: C_{CF_x}, C_{F_2} and C_{dl}, which are the capacitances due to the CF_x layer, to the fluorine bubbles and to the double layer, respectively.

As bubbles of fluorine are flat and lenticular, the gas film is thick and $C_{F_2} \ll C_{CF_x} \ll C_{dl}$. As the values of C_{F_2} are very low, the corresponding impedance of this term is infinite and its contribution to the total impedance is neglected.

In contrast, on the part of the electrode not covered by fluorine gas, electrochemical reaction occurs. The capacitance term is described by two terms in series: C_{CF_x}, C_{dl}, in which the C_{CF_x} values are usually very low ($<1\,\mu F\,cm^{-2}$); therefore, the capacitance of this part is $\approx C_{CF_x}$. A faradaic resistance, R_f, in parallel with C_{CF_x}, must also be considered in the impedance of this part.

The equivalent circuit representing the whole interface is constituted by a resistance R_s in series with a loop which contains two terms in parallel (Fig. 1(b)). In this circuit, R_s is mainly attributed to the electrolyte resistance, R_f is the faradaic resistance corresponding to charge transfer during the fluorine evolution reaction, occurring at the surface of the passivated carbon electrode:

$$HF_2^- \rightarrow HF + \tfrac{1}{2}F_2 + e^- \qquad (2)$$

As it is supposed that the stoichiometry of the surface film is uniform, no dispersion of the capacitance with frequency is expected. A simplified equivalent circuit may be proposed (Fig. 2), comprising R_s in series with a loop (R_f, C_{CF_x}).

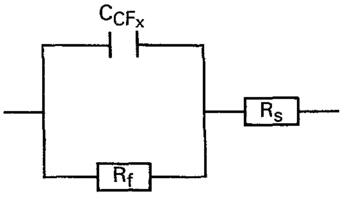

Fig. 2. Simplified equivalent circuit for the passivated crude carbon/KF–2HF interface.

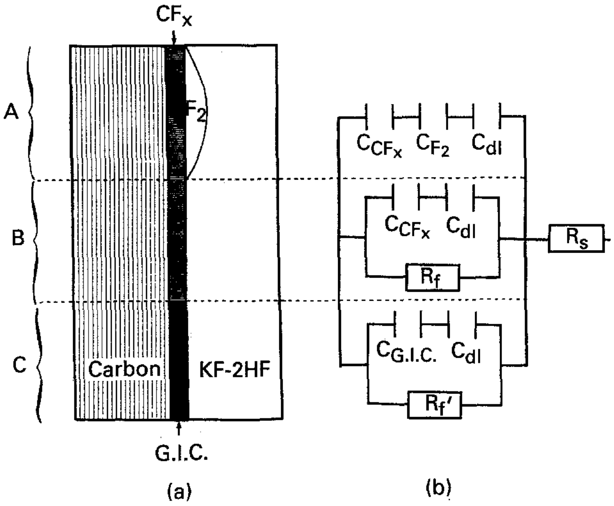

Fig. 3. Passivated aluminium-modified carbon electrodes. (a) Schematic representation of the electrode/electrolyte interface and (b) corresponding equivalent circuit.

(b) *Modified carbon electrodes*

The modification of the carbon electrodes involves doping the carbon with a metallic agent. During the electrolysis, a $C_x(MF_z)_yF$ compound (where M is a metal and z its oxidation state), i.e. a GIC, is randomly generated at the surface. This type of compound is known to be conducting and wetted by KF–2HF; it also improves the detachment of fluorine bubbles and the electroactive area is increased. The interface is composed of three different parts: $C/CF_x/F_2$/KF–2HF (part A, on which the electronic transfer is completely blocked), C/CF_x/KF–2HF (part B) and C/GIC/KF–2HF (part C). A schematic representation of the interface and the corresponding equivalent circuit are given in Fig. 3(a) and (b).

As mentioned previously, the impedance of part A is infinite and the capacitance of part B is $\approx C_{CF_x}$. Moreover, the C_{GIC} values are assumed to be higher than C_{CF_x} values since the GIC is not an insulating compound; for part C, the C_{dl} contribution cannot be neglected. Because of the local variation of the stoichiometry at the surface of the electroactive area, a dispersion of the total capacitance term with frequency is expected [21]. The total equivalent circuit may be described by a loop (R_f, CPE) in series with R_s as shown in Fig. 4. High values of the pseudocapacitance term T are expected as well as large values of Θ.

The impedance of the loop is:

$$Z_{loop} = \frac{R_f}{1 + R_f(Z_{CPE})^{-1}} \qquad (3)$$

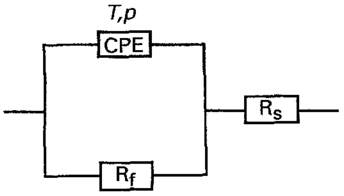

Fig. 4. Simplified equivalent circuit of the passivated aluminium-modified carbon/KF–2HF interface.

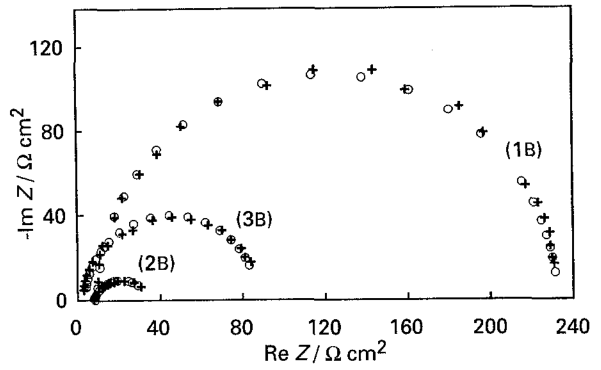

Fig. 5. Nyquist plots with crude carbon (sample 1B) and aluminium-modified carbons (samples 3B and 2B); $E = 4.4$ V vs Pt–H_2. (+) Experimental curves; (○) simulated curves.

and the total impedance of the modified carbon/KF–2HF interface may be expressed as [11]

$$Z = R_s + R_f \times \frac{1 + TR_f\omega^p\cos(p\pi/2) - jTR_f\omega^p\sin(p\pi/2)}{[1 + TR_f\omega^p\cos(p\pi/2)]^2 + [TR_f\omega^p\sin(p\pi/2)]^2} \qquad (4)$$

For modified carbon, it is possible to establish a correlation between the wettability of the electrode by KF–2HF and the values of T and p. Indeed, when the percentage of GIC compound at the surface is high, (i) the capacitance is more distributed, (ii) the T and p values are larger and (iii) the electroactive area of the electrode is increased.

The same model can be chosen for both modified and crude passivated carbon electrodes. In the latter case, a pure capacitor C_{CF_x} will be observed instead of a CPE. Indeed, a pure capacitance is a particular CPE in which $T \equiv C$ and $p = 1$.

Diffusion of electroactive species is not a limiting factor since HF_2^- ions are the main component of the melt [17]. In addition, the experiments at very low frequencies do not give accurate results because the evolution of gas bubbles leads to irreproducibility. So, the equivalent circuit does not contain any term attributed to diffusion.

3.1.2. Results. Experimental data were analysed with the LEVM fitting program (J. R. Macdonald, University of North Carolina) to estimate the parameters (R_s, R_f, T, p) of the equivalent circuit. All the impedance spectra were obtained at potentials greater than 3 V in order to observe actual fluorine evolution [11]. The potential was applied to each sample, prior to impedance measurements, for a sufficiently long time in order to obtain a steady passivating layer with reproducible stoichiometry and constant thickness. The aim of the experiments was to study the influence of the impregnation solution on the electrochemical behaviour of the 'modified' carbon anodes.

Table 1. Parameters of the equivalent circuit deduced from impedance data with the LEVM fitting program. Applied potential: E = 4.4 *V vs Pt–H_2. Comparison of a crude carbon electrode (sample 1B) with aluminium-modified electrodes (samples 3B and 2B)*

Samples	$R_s/\Omega\ cm^2$	$R_f/\Omega\ cm^2$	$T/\mu F\ cm^{-2}\ s^{p-1}$	p	Θ/*degree*
1B	8.0	233	0.20	0.99	0.9
3B	3.4	84	0.36	0.98	1.8
2B	7.8	26	50.00	0.80	18.0

(a) *Influence of aluminium particles*

The presence of aluminium in the impregnation solution is necessary since the aim is to prepare a C–Al–F GIC at the interface. Several methods for introducing aluminium particles were used. The impedance diagrams obtained at $E = 4.4$ V with 0.1 M aluminium nitrate or 0.1 M aluminium acetylacetonate impregnation solutions are shown in Fig. 5. It was observed that with the latter solutions, the doping effect of aluminium was not so clearly visible as that with nitrate solutions of the same Al^{3+} concentration: the analysis of impedance data (Table 1) showed that with sample 3B the electronic transfer is scarcely enhanced (high values of R_f). Moreover, the values of p obtained for the sample 1B are close to 1 as expected.

As the best results were obtained with $Al(NO_3)_3$ impregnation solutions, the influence of Al^{3+} concentration on impedance spectra was studied only with those solutions.

For the impedance measurements, the potential applied to the working electrode was $E = 4.1$ V. The results are presented in Table 2.

The decrease of the R_f values is accompanied by an increase of T and Θ. This decrease of R_f indicates that the electronic transfer is enhanced for aluminium-modified electrodes; when concentrated impregnation solutions are used for modifying the carbon electrodes, the abnormally high values of T and Θ, obtained from the analysis of data with the LEVM program, prove the presence of local variations of the stoichiometry of the film. The T and Θ values increase with the $Al(NO_3)_3$ concentration. The higher percentage of $C_x(AlF_3)_yF$ sites is responsible for the greater dispersion of the capacitance term.

Table 2. Parameters of the equivalent circuit deduced from impedance data with the LEVM fitting program. Applied potential: E = 4.1 *V vs Pt–H_2. Influence of the concentration* C *of the $Al(NO_3)_3$ impregnation solution*

Samples	$C/mol\ dm^{-3}$	$R_s/\Omega\ cm^2$	$R_f/\Omega\ cm^2$	$T/\mu F\ cm^{-2}\ s^{p-1}$	p	Θ/*degree*
1A	0.00	5.0	95	0.21	1.000	0.00
2Aa	0.01	5.8	61	0.38	0.997	0.30
2Ab	0.10	8.0	34	2.89	0.898	9.17
2Ac	0.25	7.5	26	8.57	0.869	11.77

Table 3. Parameters of the equivalent circuit deduced from impedance data with the LEVM fitting program. Applied potential: E = 4.1 *V vs Pt–H_2. Influence of the concentration* C *of the KNO_3 impregnation solution*

Samples	C/*mol dm*$^{-3}$	$R_s/\Omega\,cm^2$	$R_f/\Omega\,cm^2$	$T/\mu F\,cm^{-2}\,s^{p-1}$	p	Θ/*degree*
1A	0.00	5.0	95	0.21	1.00	0.0
4Aa	0.03	4.4	88	0.28	0.98	1.8
4Ab	0.30	3.7	50	0.30	0.99	0.9
4Ac	0.75	4.0	40	0.35	0.98	1.8

The wettability of the electrode by the melt is higher than that for a crude carbon because of the formation of a $C_x(AlF_3)_yF$ compound at the interface. The electrolyte penetrates easily into the inner porosity as suggested previously [9–11]. When such modified anodes were removed from the electrochemical cell, it was observed that they were perfectly wetted by the melt. Therefore, the gaseous film of elemental fluorine was removed more easily, leading to a decrease in the bubble overvoltage.

(b) *Influence of nitrate ions in the impregnation process* As the nature of the aluminium-containing solutions seemed to be an important parameter, experiments were made with nitrate solutions without Al^{3+} cations, in order to study the influence of the NO_3^--based treatment.

A further set of experiments was carried out with modified anodes prepared by impregnation of carbon electrodes with a KNO_3 solution in a water/ethanol mixed solvent.

As for the samples 2Aa, 2Ab and 2Ac, the potential applied to the working electrodes was $E = 4.1$ V. The results of impedance spectroscopy experiments are reported in Table 3. The electronic transfer is enhanced when high concentration solutions are used but the effect is always less important than with samples 2. For example, for $[NO_3^-] = 0.75$ M (Fig. 6), the R_f values, deduced from impedance data with the LEVM fitting program, are: 95 Ω cm^2 (sample 1A), 40 Ω cm^2 (sample 4Ac) and 26 Ω cm^2 (sample 2Ac).

The capacitance term scarcely increases when the concentration increases as the smoothing of the surface is higher with higher nitrate concentration.

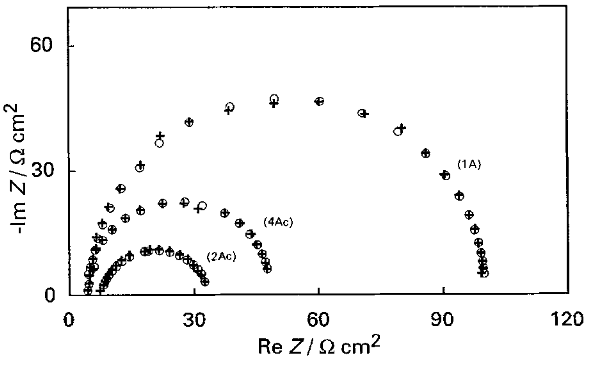

Fig. 6. Nyquist plots with crude carbon (sample 1A) and nitrate-modified carbons (samples 4Ac and 2Ac); $E = 4.1$ V vs Pt–H_2. (+) Experimental curves; (○) simulated curves.

At the same time, the value of Θ is almost constant and approximately equal to zero as for a crude carbon electrode. In that case, as potassium is one of the components of the KF–2HF electrolyte, it is not considered as a doping element. Thus, no composition heterogeneities of the surface film are present and low values of Θ are obtained.

3.2. *Surface analysis*

The impregnation of carbon electrodes with solutions containing nitrate ions and the subsequent heat treatment lead to important modifications of their electrochemical behaviour. For the understanding of these modifications, surface analysis was performed both on crude and modified carbon samples, before their use as anodes in the KF–2HF electrolyte.

3.2.1. Scanning electron microscopy. Scanning electron micrographs of crude and modified electrodes are presented in Fig. 7 and Fig. 8, respectively, to study the texture of these samples.

It was observed that the surface of modified electrodes (Fig. 8(a) and (b)) was smoothed and 'cleaned' by the nitrate-based treatment. Therefore, such a treatment removes many preferential fluorination sites which usually induce the formation of perfluorinated insulating zones. In addition, the detachment of fluorine bubbles may occur more easily on these modified electrodes.

The oxidizing power of the nitrate ions may account for the behaviour modifications observed before. According to Zawadzki [22], it is thought that the oxidation of the carbonaceous material by nitrate ions can break the micropore walls and change the pore size distribution of nitrate-treated samples. The oxidation products depend strongly on the conditions of the reaction such as temperature and concentration of the impregnation solution, and on the structure of the host material.

To verify these assumptions, the porosimetry of the samples was measured.

3.2.2. Mercury porosimetry. The analysis was performed with crude carbon (sample 1A) and modified carbon impregnated with KNO_3 (sample 4Ac) or $Al(NO_3)_3$ (sample 2Ab) solutions.

The technique consists in measuring the quantity of mercury which penetrates into the carbon in

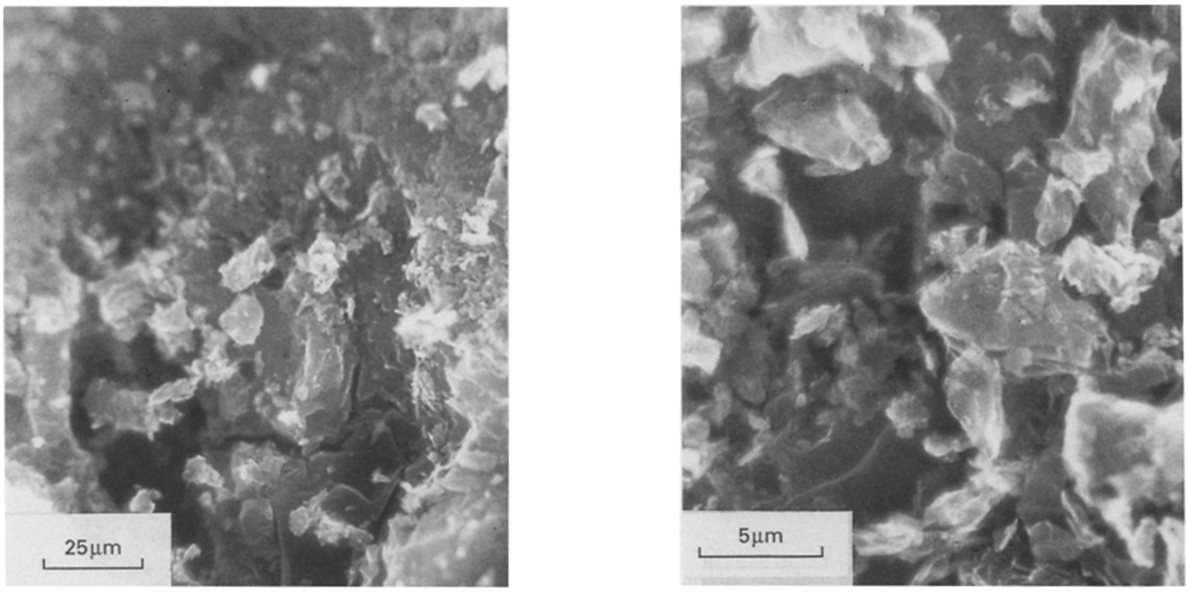

Fig. 7. Scanning electron micrographs of a nonpassivated crude carbon electrode.

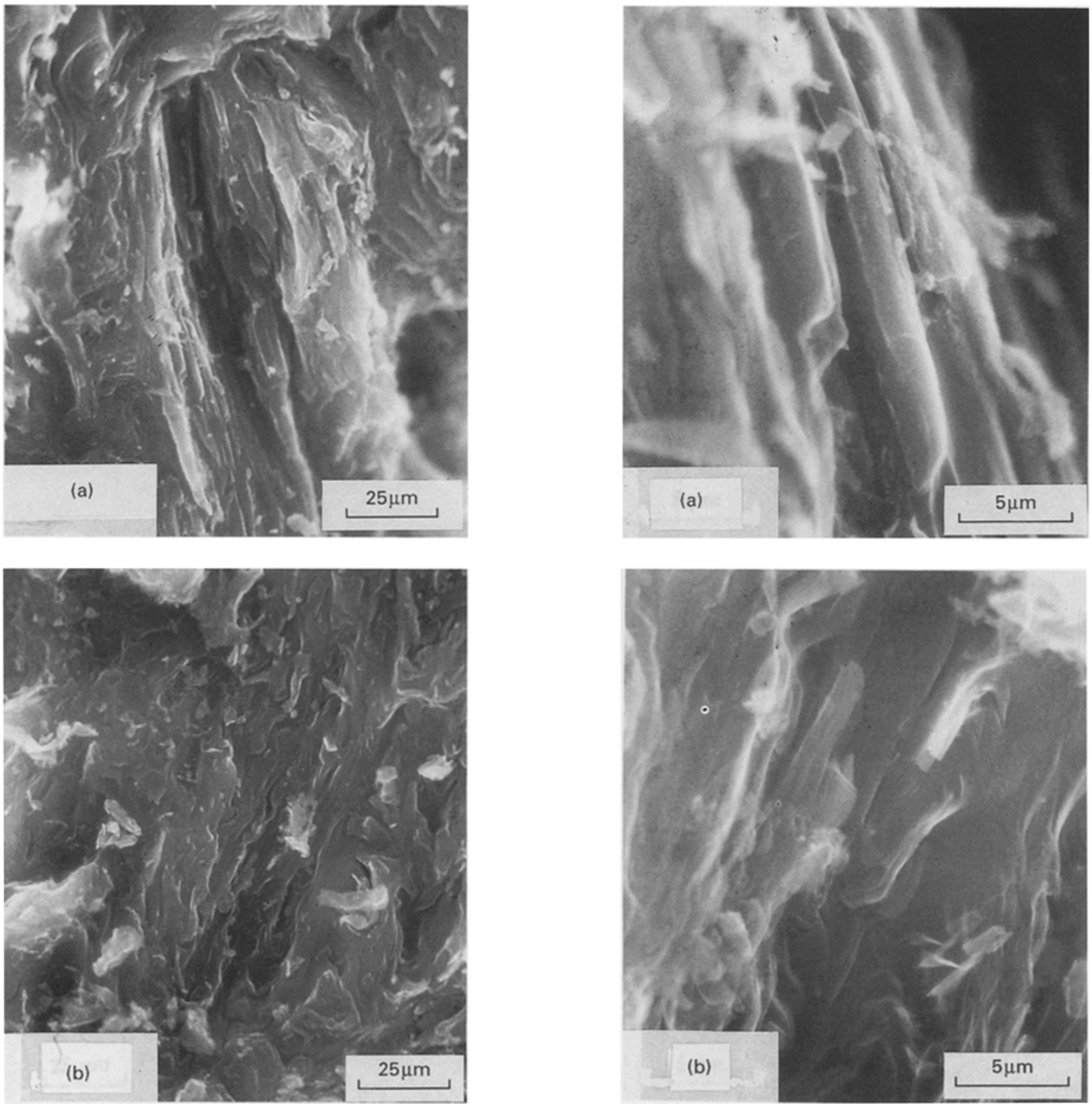

Fig. 8. Scanning electron micrographs of a nonpassivated modified electrodes. (a) Sample 2Ab; (b) sample 4Ac

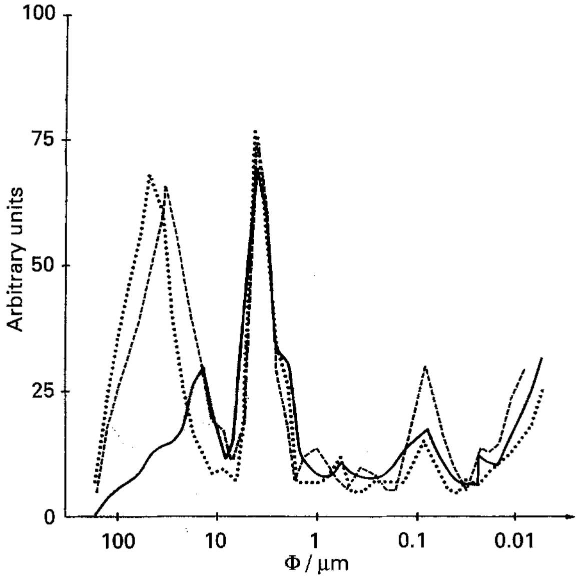

Fig. 9. Pore distribution for three kinds of carbon samples. Key: (——) sample 1A; (- - - -) sample 4Ac; (· · · ·) sample 2Ab.

accordance with the applied hydrostatic pressure. This gives access to the pore distribution and to the total volume of the pores.

The bulk distribution of the pores (arbitrary units) versus their diameter, Φ, is presented in Fig. 9. For all the modified electrodes, an increase of the number of pores with diameter between 20 and 183 μm is observed, in agreement with the results of Zawadzki [22].

Thus, surface analysis proves that the use of NO_3^--based impregnation solutions for the preparation of modified carbon electrodes smoothes their surface and facilitates the detachment of fluorine bubbles. This explains the decrease of the faradaic resistance R_f and the increase of the pseudo-capacitance T with nitrate concentration (see Tables 2 and 3). However, the effect of nitrate alone is not sufficient: the values of T do not increase so much. It may be considered that, for samples 4, the smoothing is also realized but wettability of the electrode by the melt is not achieved, since this effect is only attributed to the presence of a $C_x(AlF_3)_yF$ compound at the surface of the electrodes (samples 2) [11].

The macroporosity has little influence and the constant phase angle of the CPE in the impedance diagrams is small for samples 4.

4. Conclusions

Significant improvements in the fluorine production process may be obtained by impregnation of raw carbon electrodes by a solution containing an aluminium salt, followed by heat treatment. The best results are obtained with concentrated aluminium nitrate solutions.

The modification of the carbon electrodes by this technique induces: (i) smoothing of the electrode surface and increase of the pore size in the host material, and (ii) increased wettability of the electrode by the melt due to the formation of a $C_x(AlF_3)_yF$ compound at the interface during the electrolysis of KF–2HF. Therefore, the electroactive area is larger for these electrodes. This results in improvement of the electronic transfer rate at the interface for the discharge of HF_2^- ions (decrease of the faradaic resistance R_f).

The oxidizing character of the impregnation solutions containing aluminium nitrate ($pH \approx 1$) and the high temperature treatment explains the structural modifications of the anode surface. For samples 2, the improvement of the wettability of the electrodes by KF–2HF and the decrease of R_f is attributed to the formation, during electrolysis, of a surface conducting compound $C_x(AlF_3)_yF$, i.e. a GIC, instead of insulating graphite fluorides, CF_x, usually electrogenerated at the surface. This new compound improves the electronic transfer at the interface and the fluorine evolution process.

Important structural modifications are observed on the surface of carbon electrodes impregnated by a nitrate solution and heat treated. The bubbles of fluorine evolve more easily on these smoothed electrodes. Smooth carbon electrodes can also be obtained by polishing and have been proposed in the patent literature with the aim of facilitating fluorine evolution [23]. However, the wettability of such electrodes by the melt is not so high if the polishing agent is not chosen carefully.

In this paper it is shown that a real doping of the carbon electrodes suitable for fluorine production, is only obtained when aluminium nitrate is used because of the dual action of nitrate (smoothing) and aluminium (enhancement of wettability). Similar results were previously obtained by polishing carbon anodes with Al_2O_3, leading to insertion of aluminium-containing particles and smoothing of the electrodes by a mechanical action [10].

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