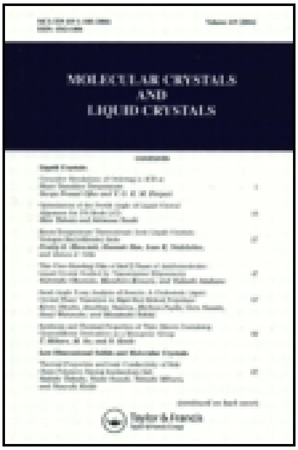

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ELECTROCHEMICAL EXFOLIATION OF GRAPHITE IN TRIFLUOROACETIC MEDIA.

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Abstract Electrochemical anodization of graphite in trifluoroacetic media, when performed with a sufficiently high current density, leads to exfoliation of graphite. This reaction has been studied using X-ray diffractometry, A.C Impedance Spectroscopy and gas analysis in various experimental conditions. A mechanism is proposed based on a Kolbe reaction occuring in the interlayer spacings.

INTRODUCTION

Although used for decades in the industrial production of graphite foils (Grafoil of Union Carbide, Papyex of Le Carbone Lorraine and Sigraflex of Sigri ...) the exfoliation processes of graphite are fundamentally badly understood[1-5]. Exfoliation is usually obtained by thermal treatment of graphite intercalation compounds. Cases of chemical exfoliation, at room temperature, have been scarcely reported[6]. Some cases of exfoliation have also been reported during anodic oxidation of graphite, for instance in halogenated sulfonic acids by H.P. BOEHM[7] and more recently in CF_3COOH solutions by P. SCHARFF[8].

Electrochemical exfoliation needs at first the occurence of an intercalation process and afterwards of electrochemical decomposition of the intercalated layers. This mechanism is thus rather striking, showing an example of electrochemical reactivity at the internal graphene - intercalant interfaces (electrochemical reduction of graphite intercalated with halogenides of transition metals is another example of this behaviour[9]).

We have studied exfoliation in CF_3COO^- media where intercalation and exfoliation seem to occur simultaneously, exploring various experimental conditions including different varieties of graphite.

EXPERIMENTAL

Four graphite varieties have been examinated :

* HOPG samples (typically 4*4*0.1mm^3 ,3.5 mg), natural graphite flakes from China (1-2 mm), industrial graphite blocks (agglomerated) and Papyex (graphite foil).

* in three trifluoroacetic media : CF_3COOH/CH_3CN (6 mol/l) , CF_3COONa/H_2O(6 mol/l) and CF_3COOH/H_2O(6 mol/l).

Galvanostatic anodization was performed :

* in a cell I adapted for in situ X ray diffractometry (Figure 1), when studying HOPG, Papyex or industrial graphite. The cell was positionned on the axis of an INEL Diffractometer (Mo Kα = 70.93 pm) in order to record the 001 lines.

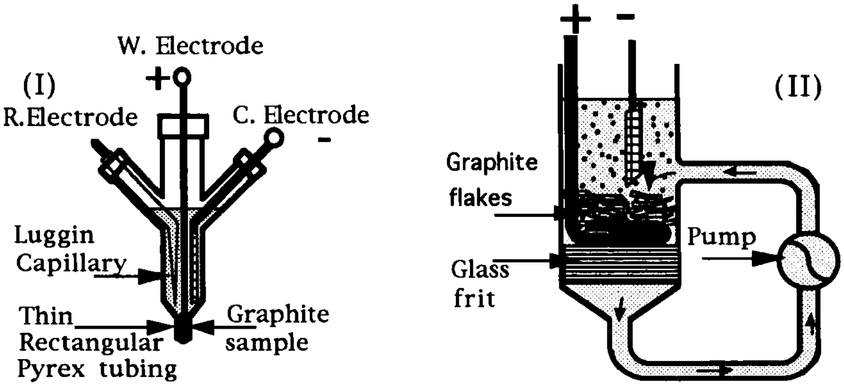

FIGURE 1 : Electrochemical cells (I) and (II)

* Or in a cell II adapted for the measurement of the expansion of graphite flakes. In this cell the circulation of the electrolyte maintained the flakes on a glass frit, in electric contact with a platinum current collector.

AC Impedance spectra were recorded at rest potential using the cell I connected to a Frequency Response Analyser SOLARTRON 1250 or 1253 and a Potentiostat 1286.

The gases emitted during the exfoliation process were analysed by means of a Gas Phase Chromatograph (DELSI - DI-700 DCI) coupled with a Quadrupolar Mass Spectrometer (NERMAG - R10 - 10 H).

RESULTS AND DISCUSSION

Elementary process analysis

For this purpose HOPG samples have been anodized at various current densities. Figure 2 reports a potential-time curve obtained at low current density (i=9 μA, m=2.2 mg) in CF3COOH - CH3CN (6 mol/l).

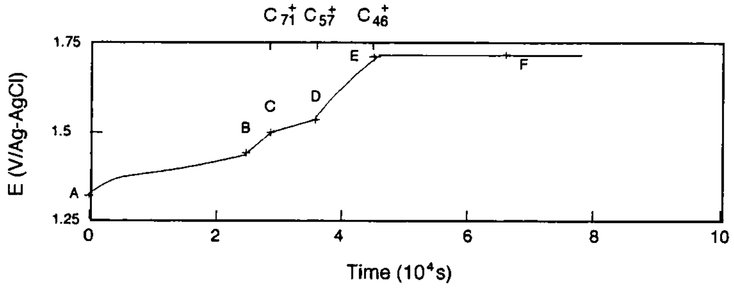

FIGURE 2 : Potential-time curve plotted during electrochemical intercalation of CF3COOH-CH3CN into HOPG (m = 2.2 mg, i = 9 μA).

Between C_{57}^+ and C_{46}^+, the X ray diffractogram (Figure 3) shows a second stage compound with c = 1148 pm and an intercalate spacing of 478 pm in good agrement with RUEDORFF's results[10] : c = 1152 pm.

During the potential plateau EF the position of the second stage 001 lines on the diffractogram did not change but their intensities decreased, without apparition of new lines. Therefore, the first stage did not appear, probably due to a parasitic reaction. Some small gas bubbles were observed without exfoliation.

With higher current densities (a few tens of μA/mg) exfoliation occured, whereas X ray diffraction showed a mixture of graphite intercalation compounds of the second and higher stages.

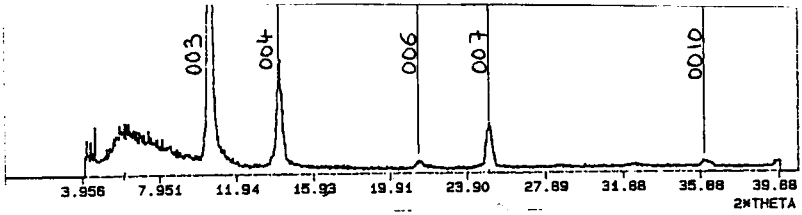

FIGURE 3 Xray diffractogram of a second stage CF_3COOH-HOPG Compound(Mo Kα).

Analysis of the evolved gases showed the presence of C_2F_6 and CO_2 together with O_2 and N_2 (air).

Those gases clearly demonstrate the KOLBE reaction i.e. electrochemical oxidation of the trifluoroacetic ion according to:

$$CF_3COO^- \longrightarrow {}^\bullet CF_3 + CO_2 + e^-$$

$$2\ {}^\bullet CF_3 \longrightarrow C_2F_6$$

This mechanism has already been suggested but not verified by SCHARFF[8].

HOPG has also been anodized in CF_3COOH-H_2O solutions under various current densities i, and the limit values of the swelling t/t_0 have been noticed (t_0 and t are the pristine and limit thicknesses of the sample).

A quasi linear relation between t/t_0 and i is observed (Figure 4), that can been explained if considering the competition of three electrochemical reactions which consume the total intensity i (Figure 5):

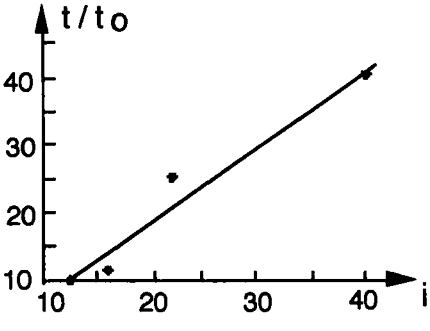

FIGURE 4 Limit value of the swelling ratio t/to as a function of the exfoliating current i (μA/mg)

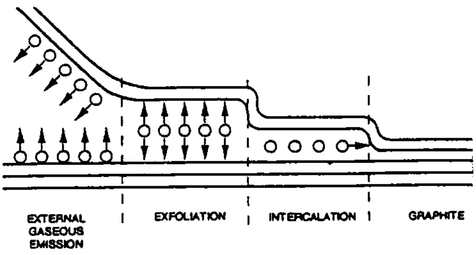

FIGURE 5 Proposed mechanism for electrochemical exfoliation

a) an intercalation current,

b) an exfoliation current corresponding to the internal Kolbe reaction,

c) a current for the external Kolbe reaction on the area developped by the previous exfoliation.

When the exfoliated external area is large enough, the total current is used by the external reaction c) preventing further exfoliation ($i=i_c$).

AC Impedance results

AC Impedance Spectroscopy has been performed in order to evaluate the extended area as a criterium of exfoliation. For example on figure 6, the low frequency capacitance can be calculated as 10 mF i.e. 0.59 F/g. Assuming a surface capacity around 10 μF/cm^2 for graphite[11], this value corresponds to a specific area of 6 m^2/g (similar to a BET area). As the total area of graphene layer is 2600 m^2/g, it corresponds to paquets of 450 layers with a mean thickness 0.15 μm.

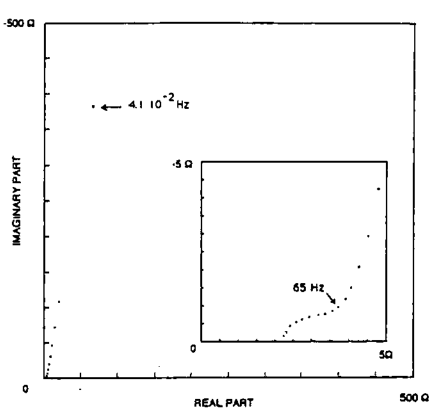

FIGURE 6 A.C Impedance diagram of an exfoliated HOPG sample (m = 17 mg, $CF_3COONa-H_2O$, 6 mol/l)

Experiment on other graphite types

TABLE I Mechanical effect of anodization in $CF_3COONa-H_2O$ for various graphites (m : mass , i : intensity , t : thickness)

graphite	HOPG	natural	Papyex	agglomerated
m (mg)	8.7	400	20.5	70
i (μA/mg)	45	30	40	35
t/to (swelling ratio)	125 *	50 (bed)	no exfoliation	disagregation

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* This value is larger than on figure 4, due to the substitution of CF_3COOH by CF_3COONa.

Some experiments have been performed other types of graphite in CF_3COONa/H_2O solutions. Typical results are reported in table I. It appears that only well organized graphites allow a good exfoliation : only cristallites large enough can be expanded by the internal gas evolution[5].

CONCLUSION :

This study of electrochemical exfoliation has showed the complexity of the problem, as many factors and parameters are involved.Furthermore compromise between intercalation and gas production, by decomposition of the intercalate, seems necessary.

The current density seems crucious and it appears that a continous increase of the current would be necessary in order to follow the expanding surface area and so to obtain the best results. The crystallite sizes of the carbon is also very important.

Undoubtly electrochemical exfoliation is practically less convenient than the thermal process. Nevertheless a possible advantage may be *in situ* exfoliation of graphite in organic media in order to obtain dispersions for the preparation of composite materials.

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