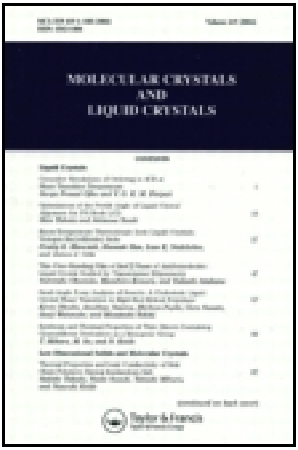

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INTERCALATION OF TRIFLUOROACETIC ACID IN GRAPHITE

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Abstract Electrochemical synthesis of pure second stage graphite-trifluoroacetic acid is discussed as a function of the nature of the electrolytic salt as well as the cristallographic structure and electrical conductivity.

INTRODUCTION

The first report of first and second stages graphite-CF_3COOH intercalation compounds is due to Rüdorff and Siecke[1] using $KMnO_4$ as oxidant. For stage 1, the identity period along the graphite c axis and the interlayer distance are equal to 818 pm as the graphite layers adjacent to the intercalant are superimposed.

Scharff [2] has reported the electrochemical formation of a mixture of stages (1+2) with a huge charge transfer $C_1^+ X^-$ and decomposition of trifluoroacetic acid according to a Kolbe reaction:

$$2\ CF_3COOH - 2\ e^- \text{---------->}\ 2\ CO_2 + C_2F_6 + 2\ H^+$$

In this case, the charge transfer involves both the GIC and the solvent.

More recently, Metrot and Douglade[3] were able to prepare a second stage compound using smooth electrochemical intercalation in an acetonitrile solution, the identity period of 114.8 pm was closed to that presented by Rüdorff : 115.2 pm. When using high current densities, exfoliation of the HOPG samples appeares as well as formation of a mixture of second and higher stages. Analysis of the gas evolved during this reaction confirms the Kolbe reaction suggested by Scharff.

EXPERIMENTAL

Trifluoroacetic acid is a molecular solvent and electrochemical reactions in this medium require the introduction of inorganic salts to improve its conductivity.

The potential values related to the trifluoroacetic medium or to the graphite intercalation compounds are presented versus the potential of the hydrogen reference electrode (ENH).

The experimental electrode potentials are determined by polarography using the mercurous acetate reference electrode and itself in relation to the ferrocene/ferricinium reference system according to the Strehlow hypothesis.

The electrochemical intercalation reaction is realized in a three electrodes cell described elsewhere [4] connected to a galvanostat-potentiostat PJT-1 Taccussel. At the bottom of the apparatus is a rectangular glass tube containing the highly oriented pyrolytic graphite (HOPG) sample which can be studied, in situ, by X ray diffraction: (001) lines or contactless electrical conductivity.

Intercalation in CF_3COOH + (CH_3COONa 3 H_2O) solutions

In this case, the electrochemical oxidation of HOPG samples produces mainly a mixture of carbon fluoride compounds and a small amount of graphite-CF_3COOH compounds (stages = 1+2) as deduced from (001) X ray diffraction lines. This mixture corresponds mainly to two kinds of carbon fluoride compounds A and B :

A : 1st stage : d_i = 625 pm and 2nd stage : I_c = 960 pm
B : 2nd stage : d_i = 710 pm

Similar fluoride compounds were synthetised by Nakajima [5] by reaction of fluorides (AgF, WF_6 and SbF_5) on HOPG samples.The synthesis of carbon fluoride compounds is supported by the Raman spectrum of Figure 1(a) very closed to that of the C_4F compound of Figure 1(b).

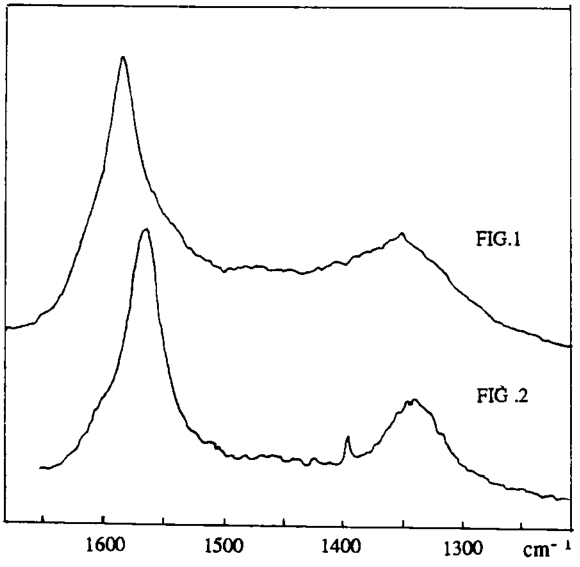


FIGURE 1 Raman spectra of fluorinated CF_3COOH GIC (a) and of C_4F compound (b)

Intercalation in $CF_3COOH + LiClO_4$ solutions

Synthesis of G.I.C in anhydrous conditions can be realized by using $LiClO_4$ salt as electrolyte. Electrochemical intercalation is performed with a small electrical current intensity (17 µA), to avoid mechanical defects in the graphite layers.

The by-product is a mixture of stages (1+2) and the current efficiency is low, only 20% but no exfoliation can be observed. During the intercalation process, the electrical resistivity decreases progressively from 45 µΩcm for HOPG to 5.2 µΩcm for the mixture of stages. A pure stage 2 compound (I_c = 114.6 pm) can be obtained and its diffractogram is presented in Figure 2. In air, hydrolysis of this compound occurs rapidly to give a mixture of stages (2+3) and then stage 4.

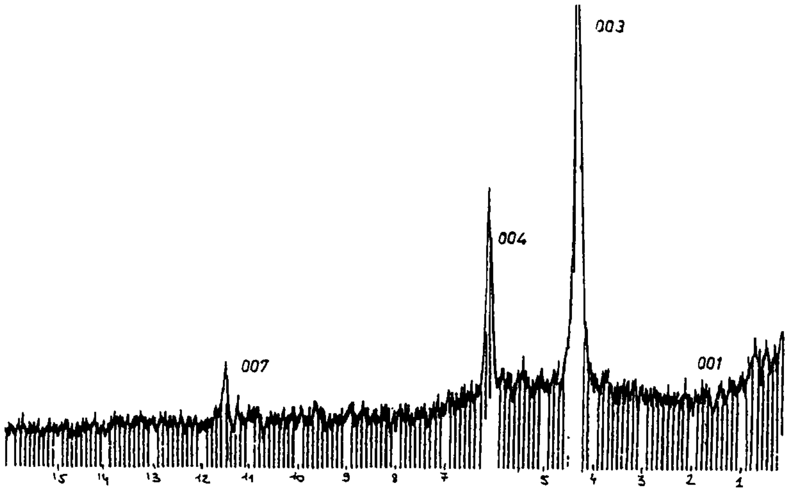


FIGURE 2 X ray diffractogram of stage 2 graphite-CF3COOH : (00l) lines.

Intercalation in $CF_3COOH + CH_3COOK$ solutions

With CH_3COOK salt, intercalation of trifluoroacetic acid is more easily performed, with a 100% coulometric efficiency, up to the second stage compound with I_c = 114.2 pm. In controlled conditions, the charge transfer can be easily determined by coulometry:: $C^+_{60,6}$ CF_3COO^-, x CF_3COOH. (This value is in the range observed for the sulfate G.I.C : C_{48}^+ to C_{58}^+ HSO_4^-, x H_2SO_4.) From X ray diffractogram, the I_c value (113.6 pm) is slightly smaller than above, this is probably due to the overcharge effect which was also observed with the graphite-sulfate compounds[6]. The electrochemical potential 1.915 V of this second stage compound must be compared to the 1.700 V value observed in $LiClO_4$ solution. During the intercalation process from graphite up to stage 2 the electrical resistivity along the graphite layers ρ_a (T=20°C) decreases steadily without a plateau or a minimum as in the other graphite-acceptor compounds. Pure stage 2 compounds exhibit I_c values in the range : 113.6 to 114.2 pm and electrical resistivity about 3.9 to 4.2 μΩcm, but in one case a low value of 2.8 μΩcm was observed. During the formation of the stage 1 compound, the resistivity value increases with the oxidation time. This variation can be explained by the overoxidation process[6].

Discussion

In these conditions, the limit value of the oxidation potential of trifluoroacetic acid is displaced towards more or less high values according to the nature of the electrolytic salt : 1.7 V / ENH with $LiClO_4$ and 3.6 V / ENH with CH_3COOK (Figure 3.).

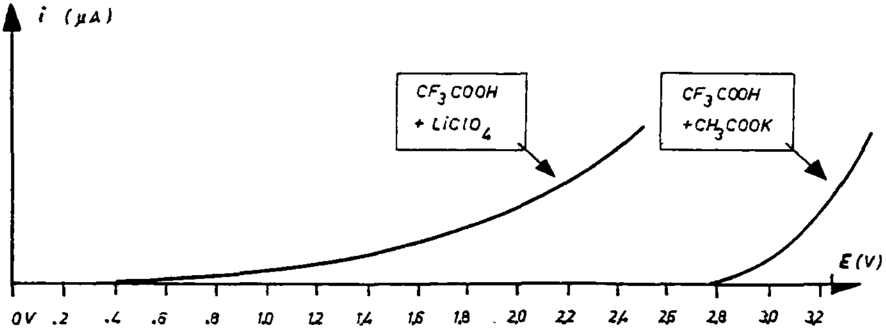
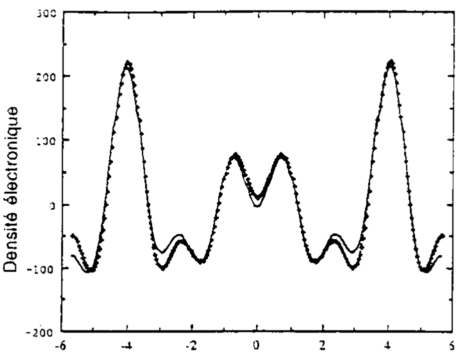


FIGURE 3 Oxidation domain (i = f(E)) of trifluoroacetic acid with "indifferent" electrolytes (reference electrode HgAcO/AcOH)

We must take into account that the intercalation potential usually presents high values:: 1.735 to 2.020 V / ENHfor the stage 1 graphite-sulfate compounds: . In sulfuric acid solutions, the coulometric efficiency of intercalation is very good for concentrated solutions and becomes low when the solvent is partially oxidised. Furthermore, the coulometric efficiency decreases with the stage as the potential increases during the intercalation process towards and even beyond the oxidation "wall "of the solution. At this "wall" value and already before, oxidation of the free and intercalated reagent appears during the intercalation process.

CRISTALLOGRAPHIC STRUCTURE

Experimental and calculated Fourrier transforms of the (001) X ray lines for a stage 2 compound with I_c = 114 pm are in good agreement (Figure 4.) and allow us to represent the structure of the intercalated species along the c axis (Figure 6.).



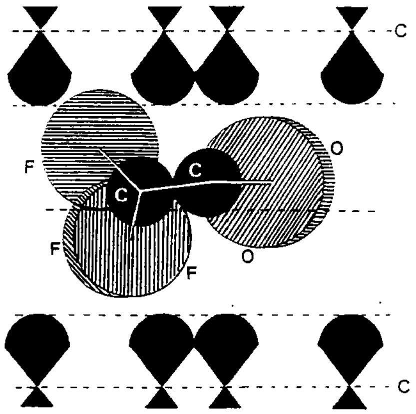


FIGURE 4 (left) Electronic distribution pattern along the graphite c axis for a stage 2 graphite-CF_3COOH compound (dashed line : calculated, dotted line :experimental)
FIGURE 5 (right) Structure along graphite c axis of graphite- CF_3COOH compounds.

The composition of the lamellar compound cannot be measured as there is always an excess of liquid acid on the sample and heating or washing will partially decompose the sample. The chemical composition has been evaluated, in the same way as for the other oxide or acids GICs. using the density d = 1.535 of trifluoroacetic acid and the measured interlayer distance, the compound formula was roughly C_{10s} CF_3COOH for stage s compounds . The best agreement for the structure factors was obtained with C_{16} CF_3COOH for a stage 2; obviously, intercalation increases the compounds density as the lamellar compound is more stable than its constituents. No Debye-Waller factor has been used to improve the reliability factor : 13.6% in good agreement for this preliminary model. By this way, the formula of the graphite-trifluoroacetate compounds corresponds to :

C_{30s}^{+} CF_3COO^{-} 2.75 CF_3COOH for stage s.

Intercalation of trifluoroacetic acid can be realized without any side oxidation reaction up to a stage 2 compound of composition : C_{60}^{+} CF_3COO^- 2.75 CF_3COOH and interlayer distance : d_i = 805 pm.

The change of the electrolytic salt ($LiClO_4$ to CH_3COOK), which was done to verify the abscence of ClO_4^- intercalation, revealed a large effect of the "indifferent" salt. The oxidation "wall" can be displaced of nearly 2 V towards high potentials, which allows intercalation without sides reactions up to the stage 2 compound as its electrochemical potential is only : 1.915 V/ ENH.

The calculated cristallographic structure along the c axis is in good agreement with the experimental structure factors of the (001) diffraction lines which permits to represent the intercalated molecules.

During the intercalation process, the electrical resistivity along the graphite layers decreases regularly down to ρ = 3.8 - 4.2 µΩcm for the stage 2 GIC and, in one case, to aluminium level.

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