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Highly fluorinated graphite prepared from graphite fluoride formed using BF_3 catalyst

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Abstract

Fluorinated graphites ($CF_{0.47}$) were obtained by reaction at room temperature of fluorine gas with graphite in the presence of boron trifluoride and hydrogen fluoride as catalysts. Their thermal treatments under fluorine at temperatures up to 600 °C lead to a progressive increase of the fluorine level resulting in an highly fluorinated graphite ($CF_{1.02}$). Whatever the fluorination level, a stage one fluorine–graphite intercalation compound is obtained. The sp^2 carbon hybridization is maintained for treatment temperature below 300 °C and two types of structure coexist for T_T in the range 350–550 °C. Finally, above 550 °C, carbon hybridization is sp^3.

The resulting materials were studied by ^{11}B, ^{1}H, and ^{19}F NMR and EPR at different experimental temperatures giving informations about the intercalated fluoride species, the temperature of their removal from the host fluorocarbon matrix, as well as their mobility.

Keywords: Fluorination; Graphite fluoride; Boron trifluoride; Graphite intercalation compounds; Electron paramagnetic resonance; Nuclear magnetic resonance; Thermal treatment

1. Introduction

Conventional solid state carbon fluorides CF_x were prepared by direct reaction of pure fluorine with carbon materials. A reaction temperature above 350 °C was necessary if graphite was used as starting material. The higher the reaction temperature T up to 600 °C, the higher the fluorination level $x = F/C$ ($0.5 < x < 1$ when $350 < T < 600$ °C). Two kinds of graphite fluoride have been particularly studied [1,2]: $CF_{0.5}$ (noted $(C_2F)_n$) and CF_1 (noted $(CF)_n$), where the carbon atoms assume the sp^3 hybridization. The reaction temperature cannot exceed 600 °C because of compound decomposition, where x is slightly greater than one or equal to one depending both on particle size and graphite nature [1].

To enhance fluorine reactivity and therefore to apply lower reaction temperatures, minute amounts of a volatile fluoride such as HF, AsF_5, IF_5, OsF_6, WF_6 or SbF_5 [3,4] were introduced into the fluorine atmosphere and fluorinated graphite compounds were thereby obtained from room temperature up to 100 °C. All these compounds exhibit a fluorination level, x, below 0.5, with C–F bonding either ionic (weak bonding energies for $x < 0.25$) or semi-ionic (or semi-covalent) involving greater binding energies (for $0.25 < x < 0.5$) but less than that corresponding to covalent bonding. Moreover, it has been shown that whatever the stage number, sp^2 carbon hybridization and then the planarity of graphene layers is maintained despite higher fluorine content [4,5]. The nature of C–F bonding in such compounds changes from ionic to semi-ionic with increasing fluorine content, as characterized by X-ray photoelectron spectroscopy [6], optical reflectivity measurement [7], and infrared spectroscopy [4,8].

At room temperature, the reactivity of fluorine with graphite is greatly improved by the presence of a volatile fluoride together with gaseous anhydrous HF [8]. The volatile fluorides MF_n used were: ClF_3, BF_3, IF_5, BrF_5,

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ReF_6, WF_6 or MoF_6. First stage highly fluorinated graphite compounds of formula $CF_x(M_y)$, with $0.5 < x < 0.9$ and $0.02 < y < 0.06$, were obtained. The interlayer distance I_c varies from 0.57 to 0.61 nm. It has been suggested that the planarity of the graphene layers is preserved and that the C–F bonds have a semi-ionic character. The x value also depended on the fluoride MF_n used. The fluorination level is related to the Lewis acidity of the volatile fluoride and its interaction with HF. The higher values of x seem to correspond to Lewis acidity of fluoride less than that of HF [9]. The highest degree of fluorination was achieved using IF_5 which is a slightly weaker Lewis acid than HF. The semi-ionic character of the bonding, which is considered intermediate between ionic and covalent character, has been evidenced by many physicochemical measurements: X-ray diffraction (XRD), Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), electronic paramagnetic resonance (EPR), ... [9–11].

Recently, graphite fluorides obtained at room temperature by the reaction of IF_5, HF, and F_2 with graphite have been treated under fluorine at temperatures between 100 and 600 °C [12,13]. High fluorination yield together with the coexistence of sp^2 and sp^3 carbons in these materials confers on these compounds very interesting electrochemical properties in primary lithium batteries [14]. This includes a tuneable discharge voltage between 2.3 and 3.0 V versus Li^+/ Li, a high discharge capacity up to 900 Ah kg^{-1} and a high energy density above 2200 Wh kg^{-1}. However, CF_x–IF_5 suffers from electrode pitting initiated by transformation of IF_5 into iodine during ageing tests.

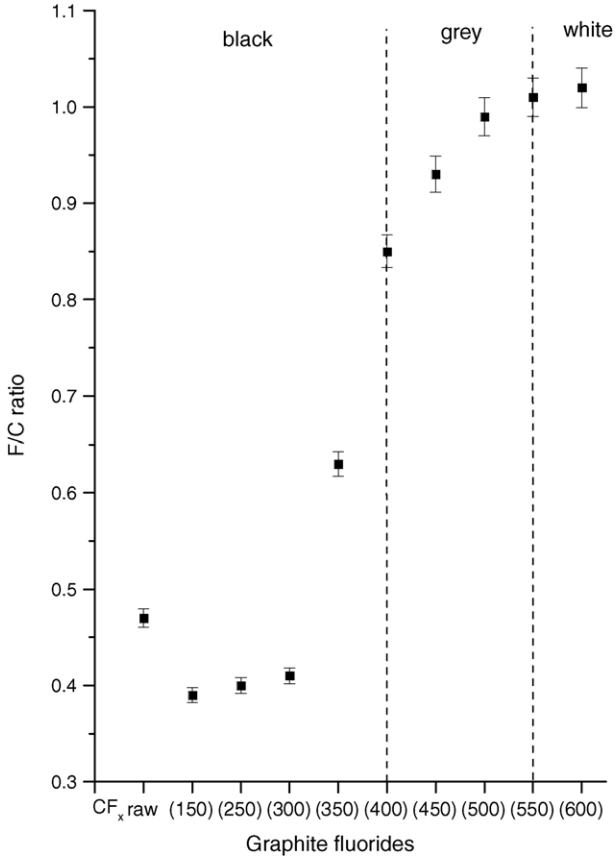
In order to prevent such electrochemical failures, graphite fluorides obtained at room temperature in the presence of another volatile fluoride, whose chemical nature is close to that of $LiBF_4$ electrolyte salt, were prepared. So, we will focus this study on a new family of compounds obtained from a thermal treatment (T_T) under fluorine of graphite fluoride prepared at room temperature using a mixture of HF, F_2, and BF_3. The raw compound will be named CF_x-raw and its formula is $CF_{0.47 \pm 0.02}$. The treated samples will be named $CF_x(T_T)$. For comparison, conventional graphite fluorides, $(CF)_n$, and $(C_2F)_n$, were also prepared under pure fluorine. Their chemical compositions are $CF_{1.10}$(HT) and $CF_{0.60}$(HT), respectively. The physicochemical characterizations by a combination of techniques (NMR, XRD, FTIR, EPR) will be discussed, in particular the evolution of the C–F bonding as a function of the treatment temperature (T_T). Some preliminary electrochemical experiments will also be presented.

2. Results and discussion

2.1. Chemical composition of graphite fluorides obtained

As expected [8], graphite fluorides, CF_x-raw, were obtained at room temperature by reaction of F_2–HF–BF_3 mixture with graphite. Then, more highly fluorinated materials, $CF_x(T_T)$, were prepared by the reaction of CF_x-raw with fluorine at temperatures up to 600 °C (Scheme 1). The F/C ratio decreases from 0.47 to 0.39 for $CF_x(150)$ suggesting a de-intercalation of fluorinated species. Then, the F/C ratio x increases continuously with treatment temperature under fluorine from 0.39 for $CF_x(150)$ to 0.63 for $CF_x(350)$ and to 1.02 for $CF_x(600)$ showing that the fluorine content is significantly improved even above 300 °C. Rüdorff and Rüdorff [15] have shown that direct fluorination of graphite in a pure fluorine atmosphere starts at 300 °C and, at 350 °C, it leads to the formation of C_2F ($CF_{0.5}$). The compounds with F/C lower than 0.63 are still black and the colour lightens with increasing fluorine content. The compound with highest fluorine content is a uniformly white powder exhibiting a chemical composition $CF_{1.02}$. The thermal treatments at 550 and 600 °C result in F/C ratios equal to 1.01 and 1.02, respectively. For this latter temperature (600 °C), direct fluorination of graphite (in pure F_2) leads to the formation of $CF_{1.10–1.20}$ [16].

CF_x ($T_T > 350$ °C) compounds are stable in ambient air, whereas for the other compounds a weight uptake of about 2% was noted after exposure to air. In addition, the thermal stability of CF_x is enhanced significantly with increasing temperature.



Scheme 1. F/C ratio and colour of graphite fluorides obtained.