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Synthesis and Characterization of Highly Fluorinated Graphite Containing sp^2 and sp^3 Carbon

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Highly fluorinated graphites were obtained by reaction of fluorine with graphite, at room temperature, in the presence of iodine pentafluoride and hydrogen fluoride. The re-fluorination between 100 and 600 °C yielded a series of fluorinated graphites with semi-ionic and covalent C−F bonds with varying amounts of sp^2- and sp^3-type carbon hybridization. Three types of materials have been generated: for re-fluorination lower than 400 °C, the C−F bond is still mainly semi-ionic and the carbon atoms are sp^2 coplanar; for re-fluorination temperatures between 400 and 550 °C, "hybrid" graphite fluorides characterized by two types of C−F bonds, semi-ionic and covalent, with sp^2 and sp^3 carbon hybridization were found. For higher re-fluorination temperatures (between 550 and 600 °C), despite a similar fluorination amount and a covalent C−F bond, the sp^2 character never completely vanished even at a high re-fluorination temperature of 600 °C. At such a temperature, a directly fluorinated graphite would be of the pure sp^3 type.

Introduction

Graphite fluorides are known for their application as lubricants or as cathode materials in primary lithium batteries.[1−2] Whereas the first application is based on both weak surface interactions and on the presence of C−F hydrophobic groups, the second one results not only from the easy lithium ion intercalation into the materials during the battery discharge process but also from the high affinity of the graphite fluoride to lithium. In addition, the low equivalent weight of the carbon and fluorine elements allows a high specific energy density to be achieved.

Different processes are known to yield graphite fluorides with variable properties. Commonly, commercial graphite fluorides are prepared by direct reaction of fluorine gas over graphite at temperatures between 300 and 600 °C. Indeed, pure fluorine gas reacts with graphite only at high temperature (HT) to give a compound of general composition $(CF_x)_n$ (called CF(HT)). The F/C ratio "x" varies from 0.6 to 1 when the temperature increases from 300 to 600 °C.[3,4] These materials are characterized by a strong covalent C−F bond where the carbon atoms assume the sp^3 hybridization. When used as a cathode material in primary lithium batteries, the power density ($W{\cdot}kg^{-1}$) of these $(CF_x)_n$ compounds is rather low because of their low electrical conductivity.

Therefore, lowering the synthesis temperature and adding volatile fluorides as catalysts in the fluorine gas atmosphere makes it possible for fluorine−graphite intercalation compounds (GIC) to be prepared. Such compounds are usually denoted as C_xF with the C−F bonds either ionic or semi-covalent.[5−7] The synthesis of fluorine−GIC C_xF (ionic structure) was first reported by Rüdorff et al. who synthesized stage 1 by flowing fluorine gas and hydrogen fluoride above graphite. Since 1980, many researchers have been working on the synthesis of low-temperature graphite fluoride using various volatile fluorides as catalysts. Nakajima et al. reported stages 1 to 4 obtained in a fluorine atmosphere with HF, WF_6, SbF_5, and LiF.[9] Selig et al. synthesized similar compounds prepared in a fluorine atmosphere containing a small amount of HF, AsF_5, IF_5, or OsF_6 at ambient temperature.[7] All these compounds have a F/C ratio lower than 0.5. In our laboratory, we have been

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working on low-temperature graphite fluorination with high F/C ratio ($x > 0.8$). This was achieved when the graphite fluoride synthesis was performed at room temperature, in the presence of a gaseous mixture composed of a volatile fluoride, such as IF_5, HF, and F_2.[10] Highly fluorinated first stage compounds (called CF(LT)) of average formula $CF_{0.9}I_{0.02}$ were formed.

Physicochemical characterizations studies of C_xF have focused on the evolution of the structure and the C−F bonding nature with fluorine content and stage number in C_xF. For synthesis temperature below 100 °C, it has been shown that whatever the stage number, sp^2 carbon hybridization (i.e., planarity of graphene layers) is maintained despite the fluorine intercalation reaction into graphite.[8−10] In the composition domain where C−F bonding is ionic ($x > 20$ in C_xF) or almost ionic ($4 < x < 10$), X-ray diffraction data indicate that the C−F bond length is approximately 0.3 nm. When semi-covalent C−F bonding occurs in the stage 1 phase, the C−F bond length is reduced significantly to 0.17 nm but it is still larger than the typical C−F covalent bond length of 0.141 nm. The nature of C−F bonding changes from ionic to semi-ionic or semi-covalent with increasing fluorine content and decreasing stage number in C_xF and it has been well characterized by X-ray photoelectron spectroscopy,[9] optical reflectivity measurement,[11] and infrared spectroscopy. The formation of a C−F bond is demonstrated by XPS data;[12] indeed, for low fluorine content $x > 20$, the binding energy value of the F_{1s} electron is in the same order as in metal fluoride with an ionic bond. When x decreases below 10, localization of the electrons takes place due to the formation of a stronger C−F bond. This gives rise to a shift in the binding energy toward semi-covalent C−F bonding between fluorine and sp^2 hybridized carbon atoms. In accordance with the change of C−F bonding with composition and stage number, C_xF varies from a metallic conductor to a semiconductor. Moreover, the electrochemical properties were also investigated in an organic solvent or in polymer electrolytes.

The aim of this study was to investigate the effects of the re-fluorination temperature on the physicochemical characteristics of CF(LT). An emphasis is placed on the temperature dependence of both the C−F bond nature and the sp^2/sp^3 carbon atom ratio, which we believe controls the properties of these materials, including their behavior as cathode materials in lithium batteries.

Experimental Section

Synthesis of Graphite Fluorides. *a. First Fluorination.* The starting material is a natural graphite from Madagascar with average particle size of about 4 μm. Graphite fluoride compounds are obtained by room-temperature reaction of graphite with a gaseous mixture of HF, F_2, and IF_5, as volatile fluoride.[13] The operating conditions have been described elsewhere.[10] First, 12 g of carbon (1 mol) was treated under vacuum at 300 °C during 5 h and introduced into the reactor. Then, 27 g of IF_5 (0.12 mol) was added with 30 g of F_2 (0.8 mol) and 12 g of HF (0.6 mol). After 10 h of reaction at room temperature, the reacting medium was evacuated under N_2 flow. The product (32 g) has been analyzed and characterized by different techniques. The chemical composition for this product (abbreviated as CF(LT)-RAW) is $CF_{0.89}I_{0.02}H_{0.06}$.

b. Second Fluorination. CF(LT)-RAW (2 g) was introduced into the reactor, and dried under vacuum at room temperature during 4 h and then under dry N_2 during 4 h (1 atm). Then 0.03 mol of F_2 was flowed into the reactor. Afterward, the temperature was regularly increased (1 °C·min^{-1}) to the final temperature T (°C) and was maintained during 3 h. The temperature chosen for each experiment was included between 100 and 600 °C with steps of 50 °C. At the end of the reaction, the furnace was cooled to room temperature. Next, the excess of fluorine was evacuated under dry N_2 flow during 3 h. The so-obtained samples will be referred to as CF(LT)-T. Thermogravimetric analysis, X-ray diffraction, infrared spectroscopy, nuclear magnetic resonance, and electron spin resonance were performed to characterize the products and compare them to the CF(HT) physicochemical characteristics. The covalent carbon fluoride CF(HT) ($CF_{1.1}$) was synthesized using the conventional method: a monel boat containing Madagascar graphite (1 g) was placed in a nickel reactor and it was then heated at 600 °C under pure fluorine gas flow (8 mL·min^{-1}) during 5 h.

Physicochemical Characterizations. Thermogravimetric analysis (TGA) and chemical analysis were performed after re-fluorination. TGA was carried out with about 20 mg of product under a dry nitrogen atmosphere. A heating rate of 2 °C·min^{-1} was used.

Powder X-ray diffraction (XRD) measurements were performed using a PHILIPS XPERT diffractometer with a Cu Kα radiation. Fourier transform infrared spectroscopy (FTIR) was performed with a SHIMADZU FTIR-8300 spectrometer. Spectra were recorded under the transmission mode in a dry air atmosphere between 400 and 4000 cm^{-1}. Spectra accumulation (20) was performed through a pellet made of 2−3 mg of the sample material diluted in KBr (200 mg). No absorption bands were recorded between 2000 and 4000 cm^{-1}, therefore FTIR results will be presented only between 400 and 2000 cm^{-1}.

Static ^{19}F NMR spectra were recorded at room temperature on a Bruker AVANCE DSX 300 spectrometer at 282.36 MHz. The external reference was CF_3COOH. The NMR techniques have already been described in detail.[14] The ^{13}C NMR measurements were performed by means of a Bruker MSL 300 spectrometer and a superconducting coil delivering a 7.05 T magnetic field (working frequency for ^{13}C: 75.47 MHz). All chemical shifts are given with respect to ^{13}C resonance of tetramethylsilane (TMS).

ESR spectra were recorded using a X Band Bruker EMX spectrometer operating at 9.653 GHz. Diphenylpicrylhydrazyl (DPPH) was used as reference of calibration to determine the resonance frequency ($g = 2.0036 \pm 0.0002$) and the densities of spin carriers. Spectra were recorded at 6.35 mW microwave power with 5 G modulation amplitude and 100 kHz frequency modulation to avoid saturation and line shape distortions. Spectra processing and simulations were performed using Bruker WIN-EPR and SimFonia software packages.

Results and Discussion

Chemical Composition and Stability of CF(LT)-T. The CF(LT)-T products color, weight variation, and composition are summarized in Figure 1. The color evolves from green to white through yellow as the re-fluorination temperature increases and iodine fluoride content decreases. All these compounds are very stable in air and no attack on the glass flask is noticed.

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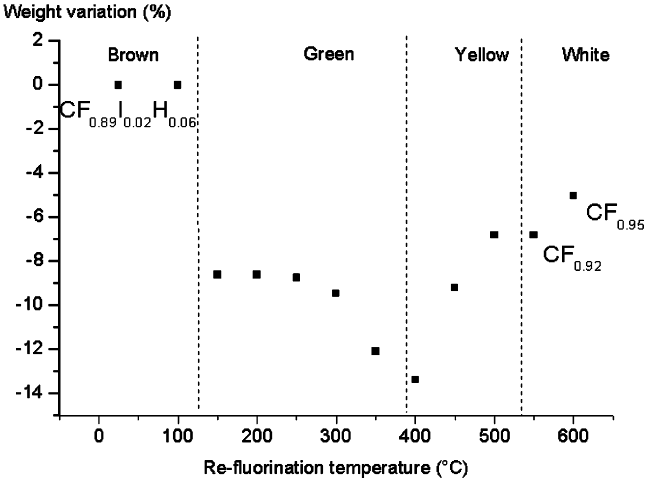

Figure 1. Color and weight variation as a function of re-fluorination temperature.

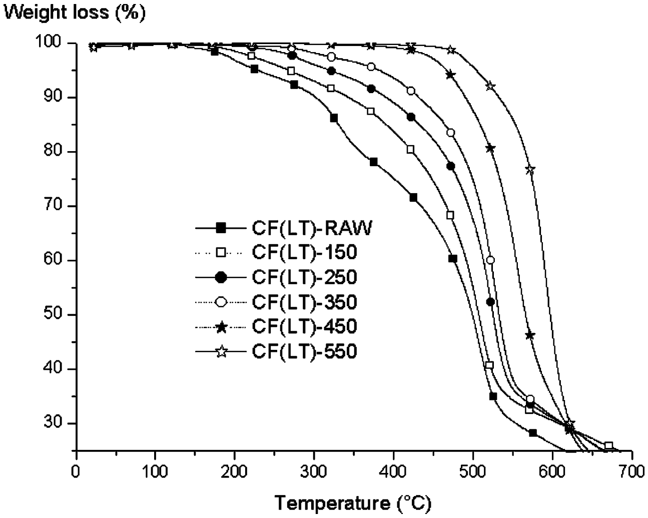

Figure 2. TGA curves of CF(LT) posttreated at various fluorination temperatures.

Surprisingly enough, no significant weight uptake was recorded during the compounds re-fluorination, even though the F/C molar ratio increased for re-fluorination temperatures higher than 400 °C. This confirms the deintercalation of the IF_y species (IF_5, IF_6^-, and IF_7), as will be shown by ^{19}F NMR investigation, and their substitution by fluorine atoms in the fluorographite matrix. The weight variation is weak except for the compound re-fluorinated at 150 °C (CF(LT)-150). Indeed, for this last compound, a high 8% weight loss is observed and should be due to the departure of HF residues which have been trapped in the graphite−fluoride matrix in the form of the fluoride−HF complex.[15]

However, with increasing temperatures, the thermal stability of CF(LT)-T is significantly enhanced as shown in Figure 2 which presents the TGA curves. Only for the raw material two weight loss steps below 400 °C are present which may correspond to the departure of HF residues and also to the departure of the iodine fluoride species with some fluorine. HF residues should be released at about 150 °C; on the contrary, the iodine fluoride species with some fluorine can be removed between 200 and 500 °C from the graphite−fluorine matrix. This could be explained by the formation mechanism of the low-temperature fluorinated graphite which involves different interactions of HF with IF_y in the host lattice (complex formation).[15]

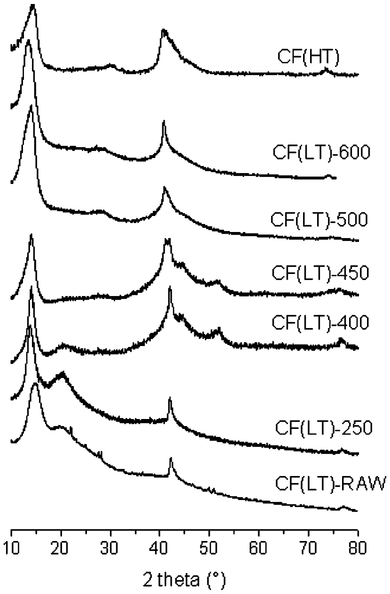

Figure 3. X-ray diffractogramms of CF(LT) re-fluorinated at different temperatures and of CF(HT).

Structural Evolution of CF(LT)-T. Figure 3 shows the XRD patterns of CF(LT)-T and conventional CF(HT) samples. Four main reflections can be observed. The first one at 2θ around 14° could be indexed in a hexagonal system either as the 001 reflection[15] particularly for compounds exhibiting very high fluorine levels $F/C \approx 1$ (i.e., for CF(HT) or CF(LT)-T with $T > 400$ °C) or as a 002 reflection as suggested elsewhere.[2,15] This reflection corresponds to an average interlayer spacing of about 0.631 nm, typical of stage 1 CF_x intercalation compounds. The second one at around 21° ($d = 0.423$ nm) is related to the 002 reflection of a residual stage 1 of the IF_y−graphite intercalation compound ($IF_y = IF_5$, IF_6^-, and IF_7) which is formed at the beginning of the fluorination reaction process at room temperature[15] ($d_1 = 0.844$ nm).[16] The third one at around 41−42° could be indexed simply as a 100 reflection with corresponding reticular distances between 0.214 and 0.221 nm. Such distances are associated with the C−C in-plane length. In the same manner, the C−C length values were also deduced from the 110 reflection at 2θ around 77−78°. With increasing temperature, the hexagonal unit cell parameters change from 0.247 to 0.254 nm for a and from 0.597 to 0.657 nm for c. The evolution of the corresponding interlayer spacing as a function of the re-fluorination temperature is shown in Figure 4.

Up to 400 °C, the C−C length is close to 0.142 nm, a value close to that of the pristine graphite. Such a result suggests that the planarity of the graphene layers is preserved for a re-fluorination temperature as high as 400 °C. Moreover, the broad peak at 21° is still present; clearly indicating the persistence of the catalyst species most likely trapped between the graphene layers.

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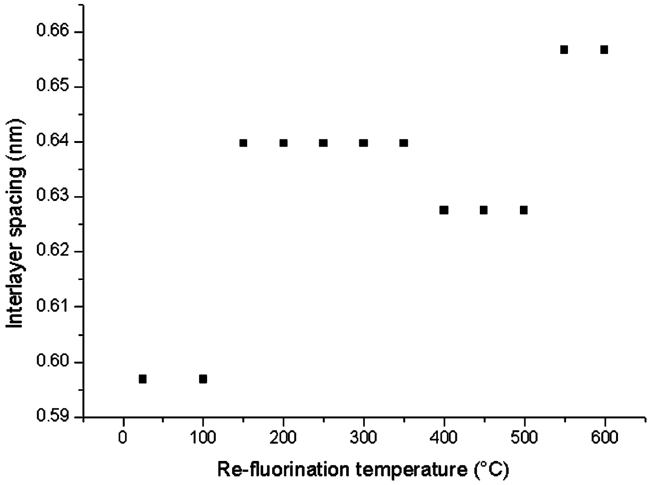

Figure 4. Interlayer spacing of CF(LT)-T as a function of the re-fluorination temperature.

For re-treatment temperatures between 400 and 500 °C, a 001 line dissymmetry appears in the XRD diagrams along with two neighbor peaks centered at around 41.0 and 42.3° corresponding to the 100 reflection. Such a doublet indicates a new structure is formed with a larger d_{100} of 0.221 nm, characteristic of covalent C−F with, consequently, carbon sp^3 hybridization. Moreover, the total disappearance of the reflection at around 21° indicates that no more residual catalyst is trapped into the graphene interlayer spacing.

For temperatures higher than 500 °C, only one single structure remains, which is quite different from the CF(HT) structure: even if the C−C bond length is similar for CF(LT)-600 and CF(HT) (d_{110} = 0.128 nm), the interlayer spacing is higher for the first one (0.657 nm) compared to the second (0.616 nm). This confirms that the planarity is broken and an armchair structure is formed.

Finally, our compounds exhibit a higher degree of crystallinity in comparison with the CF(HT) as revealed by the XRD peaks broadening. The coherence length along the c-axis, L_c, derived from the Scherrer equation yields 3.70 nm for CF(LT)-600 and 2.70 nm for CF(HT).

C−F Bond Nature Evolution with the Posttreatment. Figure 5 shows the FTIR spectra recorded between 400 and 2000 cm^{-1}. The absorption bands observed at frequencies lower than 800 cm^{-1} are attributed to residual catalysts (i.e., iodine fluoride species). The band at 640 cm^{-1} is attributed to IF_5;[17] its intensity diminishes progressively with temperature and vanishes for re-fluorination temperature higher than 450 °C. IF_6^- and IF_7 should give bands at 624[18] and 670 cm^{-1},[19] respectively, but in our spectra these bands are hardly visible because of their low content in the fluorocarbon matrix.

When the re-fluorination temperature is increased to 450 °C, a shift from 1127 to 1148 cm^{-1} in the strong band takes place; the latter is related to vibration of the semi-ionic C−F bonds.[10]

For re-treatment temperatures below 400 °C, the C−F bond is mostly semi-ionic in character. An additional band at 1216 cm^{-1}, attributed to covalent C−F bonding,[10] appears for T equal to 350 °C. Its intensity increases continuously with temperature. For temperatures between 400 and 550 °C, the C−F bonding is of two natures: semi-ionic and covalent. With regard to the evolution of the vibration frequencies ν(C−F) for the semi-ionic and covalent bonds as a function of the re-fluorination temperature, the ν(C−F) for covalent bonds is constant at 1216 cm^{-1} for re-fluorination temperature higher than 350 °C. In contrast, the frequency of the semi-ionic C−F shifts to higher frequencies (i.e., to a more covalent position) with increasing temperature going from 1127 cm^{-1} for CF(LT)-RAW to 1148 cm^{-1} for CF(LT)-450. Moreover, the intensity of the 1148 cm^{-1} band continuously decreases with the re-fluorination temperature increase and disappears above 500 °C. Noteworthy is the fact that two bands at 1256 and 1530 cm^{-1} disappear concomitantly with the former band. The 1256 cm^{-1} band may be correlated to semi-ionic C−F interactions and the 1530 cm^{-1} band corresponds to in-plane C=C bonds which are progressively broken at temperatures higher than 400 °C in agreement with the XRD measurements.

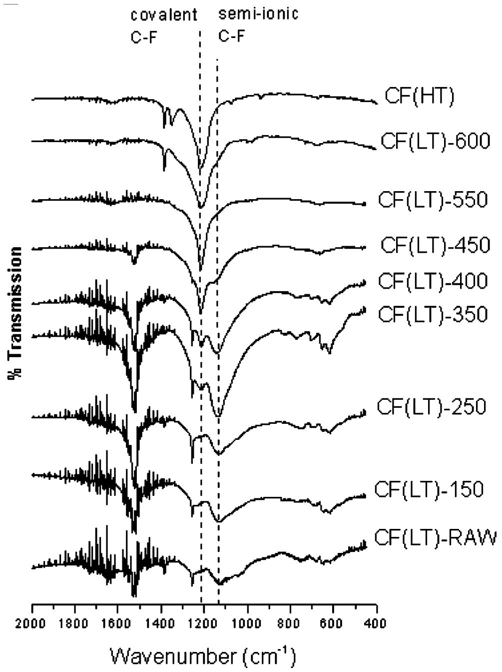

Figure 5. FTIR spectra of CF(LT) re-fluorinated at different temperatures and of CF(HT).

For a re-fluorination temperature equal to 600 °C, the C−F bond is basically covalent in nature. However, its spectrum differs from the one of CF(HT) by the bands at 1342 and 1072 cm^{-1}, which have been assigned to the asymmetric and symmetric stretching vibration of $>CF_2$ groups at the edge of the graphite layers.[4]

Figure 6 shows typical MAS/^{13}C NMR spectra of CF(LT)-400 and CF(HT) samples. The spectrum corresponding to the CF(LT)-400 compound is typical of all the CF(LT)-T series. It exhibits two lines at 82 and 137 ppm/TMS, which indicate two types of C−F interactions. The CF(HT) sample exhibits only one line at around 82 ppm, usually called η, characteristic of covalent C−F

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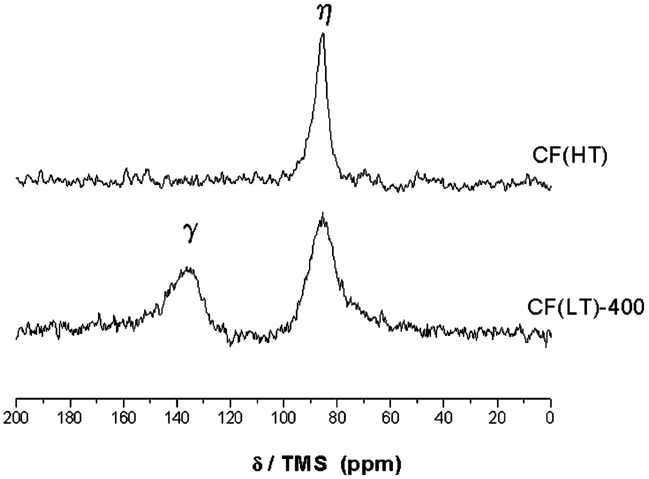

Figure 6. MAS/^{13}C NMR spectra at room temperature of CF(LT) re-fluorinated at 400 °C and of CF(HT).

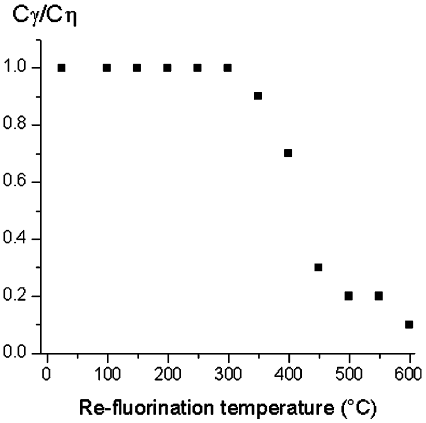

Figure 7. ^{13}C NMR $C\gamma/C\eta$ ratio as a function of the re-fluorination temperature.

bonding in which carbon is in the sp^3 hybridization form (carbon in diamond $\delta = 35$ ppm).

The line at 137 ppm, usually called γ, corresponds to carbons which interact weakly with fluorine atoms and whose hybridization is near sp^2 (carbon in graphite $\delta = 118$ ppm).[20] The evolution of the ratio of integrated intensity from the γ and η lines, C_γ/C_η, with re-fluorination temperature is shown in Figure 7. C_γ/C_η remains almost unchanged for temperatures up to 300 °C, then it sharply decreases to reach 0.1 at 600 °C. This indicates a drastic change of the C$-$F bonds from semi-ionic to covalent when the samples are treated in the range 400$-$550 °C.

The ^{19}F NMR spectra shown in Figure 8 exhibit two narrow lines. Furthermore, a broad asymmetric line was observed in the -320 and $+80$ ppm range, centered near -100 ppm/CF$_3$COOH.

The narrow lines at $+83$ and $+134$ ppm are attributed to IF$_5$ species.[10,21] An additional narrow line is observed at $+93$ ppm; this chemical shift is characteristic of IF_6^- ions.[10] According to ^{19}F NMR data recorded at various temperature (from -70 to 90 °C) and ESR measurements (performed in the range -160 to 25 °C), which both allow evaluation of the mobility of the intercalated species,[22] we propose that, because of their low translation mobility in the fluorocarbon interlayer space, the iodine fluoride species hinder the diffusion of the F$_2$ molecules and shield the dangling bonds. In other words, they strengthen the planar configuration of the carbon sheets for re-fluorination temperatures lower than 400 °C. For temperatures higher than 400 °C, iodine fluoride species keep on being deintercalated or transformed into IF$_7$ (which exhibits a chemical shift equal to $+240$ ppm) until a temperature of 500 °C and can no more maintain the planar configuration.

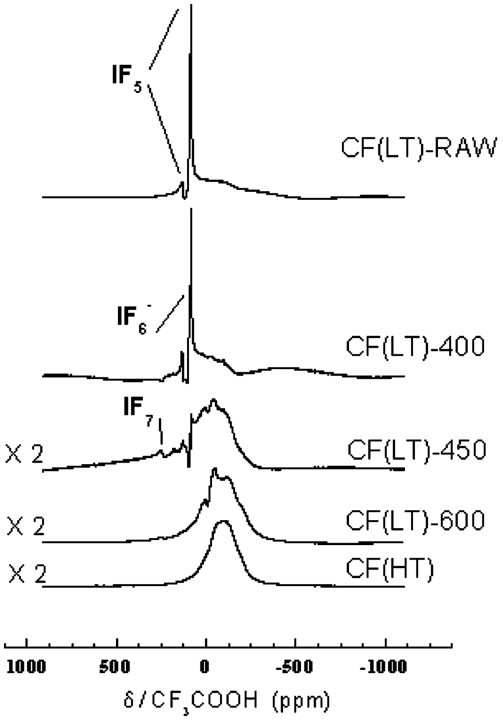

Figure 8. ^{19}F NMR spectra at room temperature of CF(LT) posttreated at different re-fluorination temperatures and of CF(HT).

Moreover, the broad line centered near -100 ppm is typical of C$-$F bonds in fluorinated graphite compounds.[10,20-22] Its center of gravity shifts from -80 ± 10 ppm to -110 ± 10 ppm when the temperature of the posttreatment increases. This shift corresponds to the change to the covalent character of the C$-$F bonds in the fluorographite bulk in accordance with the FTIR and ^{13}C NMR measurements. The CF(LT)-600 spectrum displays at least four distinct lines at $+10$, -50, -110, and -200 ppm. This demonstrates the complexity of the different carbon$-$fluorine environment for re-fluorinated low-temperature graphite fluorides. In the case of CF(HT), the broad ^{19}F NMR line could result from the superposition of several contributions due to C$-$F bonds in the fluorographite layers and also to CF$_2$ groups at the edge of sheets.[20]

Figure 9 displays the ESR spectra of low-temperature fluorinated graphite (raw and re-fluorinated at 600 °C) and of high-temperature fluorinated graphite CF$_x$ (CF(HT)) samples. The origin of the main broad line was identified as carbon dangling bonds having a localized spin. Such spin carriers had been proposed for other fluorinated carbons obtained in a F$_2$ atmosphere.[23-25]

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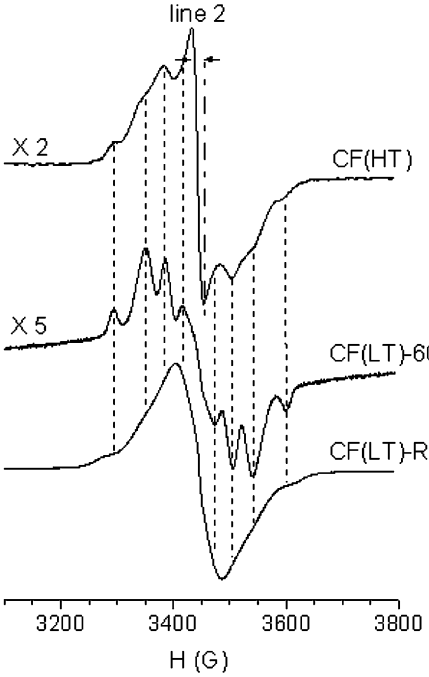

Figure 9. ESR spectra at room temperature of CF(LT), CF(LT) re-fluorinated at 600 °C, and CF(HT).

Whatever the sample, the g-factor, which is typical for free radicals and localized structural defects, is close to 2.003 ± 0.002. A hyperfine structure appears clearly for CF(HT) and CF(LT)-600: seven lines are present. This phenomenon is due to the hyperfine interaction between the dangling bond electron and six neighboring fluorine nuclei (nuclear spin $I = {}^1/_2$) yielding $(2nI + 1) = 7$ lines. The simulation of the signal in the case of the sample retreated at 600 °C and CF(HT) leads to the hyperfine parameter $A = 45 \pm 2$ G, a line width $\Delta H_{PP} = 36$ G $\pm$ 2 G, and a g-factor of 2.003 ± 0.001. These ESR parameters are close to the ones proposed by Panich et al.[23] who have studied fluorinated petroleum cokes; in this case the hyperfine structure was less well resolved. These authors have interpreted the large line width by the joint effect of dipole−dipole and exchange interactions between paramagnetic centers.

The broad ESR spectrum of the raw CF_x obtained at room temperature results from the nonresolved hyperfine structure of the dangling bond electrons interacting with the neighboring fluorine nuclei; only the wings of this one can be observed.

Because of the interaction of the dangling bonds with F_2 during the posttreatment, the spin density (D_s) decreases drastically after the posttreatment in a F_2 atmosphere at 600°C; it decreases from $120 \times 10^{18} \pm 20 \times 10^{18}$ spin·g^{-1} to $1 \times 10^{18} \pm 0.2 \times 10^{18}$ spin·g^{-1} for CF(LT)-RAW and CF(LT)-600, respectively.

The spin−spin interaction is due to the high density of spin carriers and could lead to the unsolved hyperfine structure in the raw material. It decreases as the re-fluorination temperature is increased to 600 °C. Moreover, in the case of the raw material, dangling bond centers could also adopt different configurations of the surrounding fluorine atoms; this disorder could also lead to the unresolved hyperfine structure. During the re-fluorination treatment, this disorder is significantly lowered because the fluorine content increases and the degree of crystallinity is still high, as discussed before on the basis of the XRD data.

In comparison with CF(LT)-600, an additional line is present in the ESR spectrum (denoted line 2, $\Delta H_{PP} = 20 \pm 1$ G) in the case of CF(HT): another type of defect with a different environment is present in this material, contrary to the sample re-treated at 600 °C in F_2 gas. Moreover, the spin density of CF(HT) is higher than the one of CF(LT)-600: it is equal to $12 \times 10^{18} \pm 2 \times 10^{18}$ spin·g^{-1}.

Three Types of Graphite Fluoride Materials. Re-fluorinating low-temperature fluorinated graphite gives three types of materials whose properties differ from those of classical low-temperature or high-temperature fluorinated graphite.

The materials can be characterized as follows. (i) When the re-fluorination temperature is between 150 and 400 °C, the material contains no more intercalated hydrogen fluoride, but iodine fluoride species (IF_5, IF_6^-) are still intercalated. The graphene layers are planar and the C−F bonds are mainly semi-ionic. (ii) For re-fluorination temperatures ranging between 400 and 550 °C, the iodine fluoride species content decreased progressively by their elimination from the graphitic matrix and by conversion into IF_7. Here the C−F bonds are of two natures owing to the coexistence of both semi-ionic and covalent bonds. Moreover, two structures are identified by XRD. In one the planarity of the graphene layers (carbon close to sp^2 hybridization) is preserved and in the other the carbon hexagons are buckled due to the carbon sp^3 hybridization. (iii) When the re-fluorination temperature is higher than 550 °C, no more iodine fluoride species are trapped in the graphite fluoride matrix, the C−F bonds are mainly covalent, and only one structure is observed by XRD which results from a hybridization of carbon near to sp^3 as shown by ^{13}C NMR.

In contrast to hydrogen fluoride trapped in the fluorinated graphite matrix, iodine fluoride species play a key role in the physicochemical characteristics of these three types of materials. Indeed, when iodine fluoride species are eliminated, both the C−F bond character and carbon hybridization change drastically.

For re-fluorination temperatures between 150 and 400 °C under fluorine gas, the iodine fluoride species maintain the graphene layers' planarity and favor a semi-ionic bond. No significant weight uptake could be recorded during the treatment. Nevertheless, because of the increase of the thermal stability after a re-fluorination treatment, some fluorine atoms should have compensated for the decrease in IF_y content.

For temperatures included between 400 and 550 °C, as iodine fluoride species are progressively removed from the structure, the planarity of the graphene sheets becomes harder to maintain: fluorination of old iodine fluoride fixation sites leads to carbon−fluorine bond formation and extra-fluorination is allowed. These newly created bonds have a covalent character. Moreover, semi-ionic carbon fluorine bonds shift to a more

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covalent position as shown by ^{19}F NMR measurements. So, the semi-ionic graphite fluoride may still intercalate fluoride species due to the persistence of π-type electrons, which stabilizes the structure through charge transfer. In covalent C−F, the π electrons are no longer present and the iodine fluoride species can no longer be intercalated. Therefore the deintercalation of iodine fluorides goes together with the change of the carbon hybridization from sp^2 to sp^3. In our re-fluorinated materials, both hybridizations are present even at a temperature of 550 °C as shown by ^{13}C NMR. These graphite fluoride materials, characterized by two types of C−F bonds, semi-ionic and covalent, with sp^2 and sp^3 carbon hybridization could be designed as “hybrid” graphite fluorides. Moreover, the stage 1 IF$_y$-GICs phase is unstable at temperatures higher than 100 °C and must be decomposed from this temperature to form higher stages.[16] The 002 reflection related to the residual stage 1 of the IF$_y$-GICs, shown by the XRD measurements, may be explained by two types of iodine fluoride trapping mechanisms. The first one is related to propagation of the re-fluorination process starting from the graphene edges and progressing toward the crystallite core. Such a mechanism traps the iodine species into the crystallite core as the fluorine atoms linked to the sp^3 carbon atoms are oriented over and under the armchair carbon sheets and reduce the mobility of the iodine fluoride species within the fluorographite layers by steric hindrance. A residual stage 1 GIC can also be maintained even at high re-fluorination temperature because of its nonaccessibility to fluorine gas. As a matter of fact, these crystallites could be trapped into the bulk of fluorographite. These two types of iodine trapping mechanisms can be mentioned to explain the coexistence of sp^2 and sp^3 carbon atoms. Indeed, electrochemical data of these compounds used as cathode materials in primary lithium batteries exclude the presence of two separate phases in the “hybrid” compound for which sp^2 and sp^3 carbon atoms coexist.[26] The electroreductions of semi-ionic and covalent fluorographites, CF(LT) and CF(HT), occur at around 3.2 and 2.2 V vs Li$^+$/Li, respectively.[27] As the gap between the discharge potential of CF(LT) and CF(HT) is high (~1.0 V), the presence of two separate phases should lead to two discharge plateaus: a high discharge plateau related to the reduction of sp^2 hybridized C(−F) and a low voltage plateau related to sp^3 hybridized ones. The electrochemical discharge curves of CF(LT)-T exhibit a unique plateau whatever the re-fluorination temperature: the discharge potential depends on the re-fluorination temperature and evolves from 3.01 to 2.31 V for CF(LT)-100 and CF(LT)-600, respectively. The hypothesis of the presence of two separate phases can then not be retained on the basis of the electrochemical characterization. This result is in agreement with TGA analysis which indicate a single decomposition step for re-fluorinated samples. The compounds obtained with re-fluorination temperature higher than 400 °C contain both covalent and semi-ionic C−F bonds with proportions varying with the re-fluorination temperature and could be described as “hybrid” carbon fluorides. Nevertheless, more complete structural and electrochemical studies are needed for advanced structural determination of these materials.

Despite the fact that the same synthesis final temperature of 600 °C was used, the physicochemical characteristics of the CF(LT)-600 are different from those of graphite fluoride prepared by direct fluorination of graphite CF(HT). Differences include the results obtained from XRD, ESR, and ^{19}F NMR measurements. For this high re-fluorination temperature, the fluorination treatment consisted of the elimination of the residual dangling bonds.

Conclusion

Graphite fluorides obtained at room temperature by the reaction of IF$_5$, HF, and F$_2$ with graphite have been re-fluorinated at temperatures between 100 and 600 °C. When the re-fluorination temperature increases, highly fluorinated graphite with physicochemical characteristics strongly related to both the C−F bond nature and the sp^2/sp^3 carbon atom ratio are obtained. In the 400−550 °C temperature range, “hybrid” graphite fluorides have been prepared; these compounds contain minor catalyst residues and exhibit double crystalline structures and double C−F bonds, semi-ionic and covalent. A structural simulation is in progress. High yield of fluorination and the coexistence of sp^2 and sp^3 carbons in these materials confer to these compounds unique physicochemical characteristics together with very interesting electrochemical properties in lithium primary batteries.

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