

Solid-state ^{19}F and ^{13}C NMR of room temperature fluorinated graphite and samples thermally treated under fluorine: Low-field and high-resolution studies

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Abstract

Room temperature graphite fluorides consisting of raw material and samples post-treated in pure fluorine atmosphere in the temperature range 100–500 °C have been studied by solid-state NMR. Several NMR approaches have been used, both high and low-field ^{19}F , ^{19}F MAS and ^{13}C MAS with ^{19}F to ^{13}C cross polarization. The modifications, in the graphitic lattice, of the catalytic iodine fluorides products have been examined. A transformation of the C–F bond character from semi-ionic to covalent has been found to occur at a post-treatment temperature close to 400 °C. It is shown that covalency increases with temperature.

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1. Introduction

Reaction of graphite with fluorine gas results in a wide range of compounds [1]. These materials can be classified into two categories with different properties. First, graphite fluorides $(\text{C}_2\text{F})_n$ and $(\text{CF})_n$ prepared at, respectively, 350 and 600 °C are electronic insulators. Their carbon skeleton is formed either of *trans*-linked cyclohexane chairs [2,3] or *cis*-*trans*-linked cyclohexane boats [3,4] with sp^3 bonding. The C–F bond is then completely covalent [1]. The materials of the second group are conductors [1] composed of fluorine–graphite intercalation compounds (fluorine-GIC, C_xF) obtained at temperatures below 100 °C. In this case, the planar configuration of the graphite sheets is preserved. The nature of the C–F bond goes from ionic for low fluorine

content to semi-ionic at high fluorine content [1,5,6]. Moreover, the carbons atoms are mainly in sp^2 hybridization.

More recently, fluorinated graphite has been obtained at room temperature by Hamwi et al. [7,8] by using a gaseous mixture of fluorine, HF and volatile fluorides (BF_3 , IF_5 , IF_7 , WF_6 , etc.). In this case, the graphitic character of the sheets is preserved. For material electrode applications, the use of IF_5 provides the most interesting compounds. Their general chemical formula is $\text{CF}_x(\text{IF}_z)_y$ ($0.5 \leq x \leq 0.9$; $0.06 \geq y \geq 0.02$ and $z \approx 5$). Iodine fluoride species (IF_z) consist of a blend of IF_5 , IF_6^- and IF_7 groups with IF_5 as main species [9,10]. Electrochemical properties are increased by a post-synthesis thermal treatment under pure fluorine gas [11]. The effect of this thermal post-treatment (TPT) is to progressively modify the carbon hybridization which evolves from the initial raw material sp^2 to sp^3 characteristic of covalent fluorinated compounds.

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For these inorganic compounds, the use of Nuclear Magnetic Resonance (NMR) is very informative. Previous data show that the ^{19}F NMR spectra of high-temperature graphite fluorides $(\text{CF})_n$ and $(\text{C}_2\text{F})_n$ exhibit a broad dipolar coupled peak centred near -200 ppm (relative to CFCl_3). For $(\text{C}_2\text{F})_n$ a weak narrow line, attributed to weakly bound fluorine atoms, is also observed [12]. A study using ^{19}F MAS and ^{13}C MAS associated to ^{19}F to ^{13}C cross polarization shows the presence of CF and CF_2 groups [13]. A typical ^{19}F spectrum of fluorine-GIC, C_xF , prepared at temperature lower than 100°C consists of two resonance lines: a narrow one due to mobile fluorine and a broad one for fluorine involved in C–F bonds (as in the case of $(\text{CF})_n$ and $(\text{C}_2\text{F})_n$ the line-width broadening is due to dipolar interactions) [14–16]. For dilute compounds ($x > 8$), only the narrow line appears; the intensity of the broad peak increases with the fluorine content [15,16].

When studied by ^{19}F static NMR, room temperature fluorinated graphite $(\text{CF}_x(\text{IF}_z)_y)$ (prepared as described elsewhere [7,8]) exhibits a different NMR behaviour. The spectra consist of a broad peak, attributed to C–F groups plus narrow lines attributed to IF_z groups [17]. Thermally post-treated compounds have also been studied by low-resolution NMR [18] which confirms the carbon hybridization evolution.

In this paper and for the first time, these $(\text{CF}_x(\text{IF}_z)_y)$ samples together with the post-treated compounds are studied both at low-field and high-resolution NMR. High resolution involves both ^{19}F MAS NMR and ^{13}C MAS NMR with ^{19}F to ^{13}C cross polarization. This new approach leads to a better and more complete characterization of both the compounds and effect of TPT.

2. Experimental

2.1. Graphite fluoride preparation

As described in detail elsewhere [7,8], graphite fluoride was synthesized using a room temperature procedure with a gaseous mixture of F_2 , HF and IF_5 . The chemical composition of the obtained compound is $\text{CF}_{0.73}(\text{IF}_z)_{0.03}$ ($z \approx 5$). The TPT is performed under a fluorine gas flow in the temperature (TPT) range 100 – 500°C . The starting material, without TPT, is called CF-0; the other materials are named CF- T where T is the post-treatment temperature [19].

2.2. NMR characterization

Low-frequency ^{19}F experiments were recorded on a Maran Ultra spectrometer (Resonance Instruments) working at 18.9 MHz. The magnetic field was obtained with a permanent magnet of 0.5 T. A static $^1\text{H}/^{19}\text{F}$ NMR probe from Resonance Instruments was used. All

experiments were recorded at 30°C using a solid echo sequence (two $3.75\ \mu\text{s}$ $\pi/2$ pulses separated by $15\ \mu\text{s}$), which allows a quantitative determination of the different contributions. The dwell time and the number of data points were $0.1\ \mu\text{s}$ and 16 K, respectively. The number of accumulations varies from 8200 to 57088 . The recycle delay was set to 5 s.

Other NMR experiments were performed on a Bruker MSL 300 spectrometer associated to a superconducting coil giving a magnetic field of 7.049 T (working frequency for ^{13}C and ^{19}F : 73.4 and 282.2 MHz, respectively). A Bruker special preparation (without fluoropolymer) 4 mm rotor cross polarization/magic angle spinning NMR probe (with fluorine decoupling) was used. The spinning speed was set to 12 kHz.

For ^{19}F MAS spectra, a total of 16 K data were acquired, with a dwell time of $0.4\ \mu\text{s}$, after a $4\ \mu\text{s}$ $\pi/2$ pulse and an electronic dead time of $10\ \mu\text{s}$. Sixty-four scans were recorded at a repetition rate of 10 s.

The ^{19}F – ^{13}C match was optimized with polytetrafluoroethylene (PTFE) by adjusting the ^{13}C power level to coincide with the previously determined ^{19}F $\pi/2$ pulse width ($4\ \mu\text{s}$). A contact time of 1.5 ms was used. 16 K data points were collected with a number of scans varying from 2032 to 29960 . The electronic dead time, dwell time and repetition time were, respectively, $20\ \mu\text{s}$, $2\ \mu\text{s}$ and 5 s. A 50 ms fluorine decoupling field is applied during acquisition.

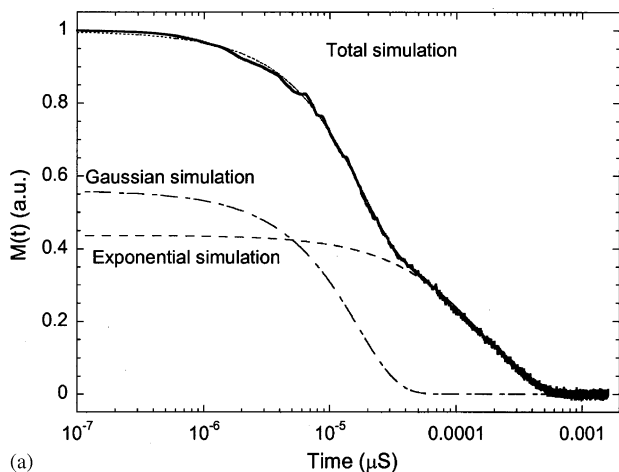
^{13}C and ^{19}F chemical shifts were externally referenced to tetramethylsilane (TMS) and CF_3COOH , respectively. ^{19}F chemical shift were referenced with respect to CFCl_3 ($\delta_{\text{CF}_3\text{COOH}} = -78.5$ ppm vs. δ_{CFCl_3}). The ^{19}F T_1 relaxation time at 282.2 MHz was found to be about 400 ms [17].

3. Results and discussion

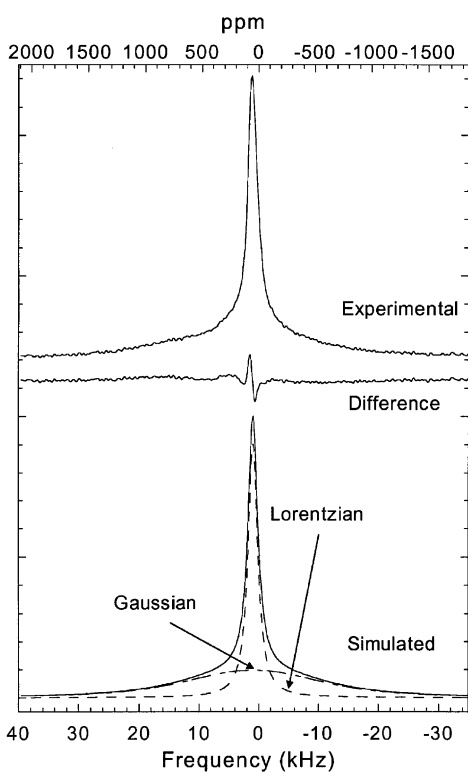
3.1. ^{19}F low-frequency study

Because the chemical shift depends on the working frequency (i.e. Larmor frequency), the wide-line NMR spectrum of graphite fluoride is easier to characterize by working at low field. For the CF-0 sample, the Free Induction Decay (FID) recorded at 30°C after a solid echo sequence, shows (Fig. 1a) two contributions: one Gaussian (characteristic time $\tau_1 = 3.2731 \times 10^{-5}$ μs) and the other exponential ($\tau_2 = 1.643 \times 10^{-4}$ μs), attributed, respectively, to CF and IF_z groups [17,20,21].

A simulation of the corresponding Gaussian and Lorentzian Fourier Transform (FT) is then carried out (see Fig. 1b). The broad Gaussian peak (FWHM ≈ 31 kHz) is typical of dipole–dipole homonuclear fluorine coupling while the narrow Lorentzian line (FWHM ≈ 2 kHz) is due to the mobility of the intercalated fluorinated species. As shown, the



(a)



(b)

Fig. 1. (a) ^{19}F free induction decay (FID) of CF-0 at 18.9 MHz. Fit contributions are indicated on the figure. (b) ^{19}F experimental spectrum (top), simulation spectrum (bottom) of CF-0 at 18.9 MHz. The difference is represented between the two spectra. Fit contributions are indicated on the figure.

difference between experimental and simulation curves is small, thus making the latter good enough for quantitative use. The extracted Lorentzian/Gaussian ratio is equal to 0.78. The corresponding fluorine contents for the CF and IF_z groups are then, respectively, 56% and 44%, which leads to a chemical formula as deduced by NMR of the form $\text{CF}_{0.73n}(\text{IF}_z)_{0.11n}$, with n real. A more accurate chemical formula, obtained by chemical analysis, being $\text{CF}_{0.73}(\text{IF}_z)_{0.03}$, one of the two components is over or underestimated by NMR. More

precisely, the chemical formula could be written $\text{CF}_{0.73m}(\text{IF}_z)_{0.03m}$, with $m = \alpha n$ where $\alpha \approx 3.7$ (α is an NMR correction term). We can assume that this correction remains constant for all samples because it only depends on the kind of chemical groups present and not on their ratio.

The NMR second moment directly determined (after a solid echo) from the ^{19}F measurement of the Gaussian resonance (CF groups), is $181.1 \cdot 10^6 \text{ Hz}^2$ (Fig. 1b). This gives according to Van Vleck's equation [22] an average F–F distance of $r = 0.298 \text{ nm}$. This value is compatible with the F–F distances extracted from the structural model proposed by Hamwi et al. [23] whose range for the shortest distances is between 0.284 and 0.575 nm (for an interlayer distance I_c equal to 0.62 nm).

TPT temperature variation of the ^{19}F NMR spectrum is shown in Fig. 2a. The two characteristic broad and narrow peaks of CF-0 are present whatever the compound but their relative ratio varies with post-treatment temperature. In order to follow this ratio, the area of each peak is determined by a fit carried out on all the experimental ^{19}F spectra. The contribution to the resonance of the broad component slightly decreases from 0 to 250°C (Fig. 2b), then strongly increases at higher temperatures. At a post-treatment temperature close to 450°C the NMR signal is essentially Gaussian, indicating that the IF_z groups have almost entirely disappeared. As shown by the signal/noise ratio, this increase of the Gaussian contribution, at post-treatment temperatures higher than 250°C , is caused by both an increase in CF content and a decrease in IF_z groups.

Accordingly, it seems that this temperature evolution involves several different phenomena. First, below 250°C , the low decrease (around 4%) of the Gaussian CF contribution probably involves a progressive deintercalation of weakly bounded fluorine molecules from the fluorocarbon surface. A weak removal of iodine species IF_z also occurs in this region. Additionally, a reaction leading to the formation in the carbon interlayer of IF_6^- , $\text{C}_n\text{F} + \text{IF}_5 \rightarrow \text{C}_n^+ + \text{IF}_6^-$, leads to a decrease of CF fluorine and therefore of the Gaussian contribution. For TPT higher than 300°C , a drastic increase of the Gaussian percentage is observed. This is caused both by the formation of strong C–F bonds and a noticeable but partial deintercalation of IF_z species (indeed, the presence of an IF_z NMR signal is still observed at 450°C).

The complete deintercalation occurs at TPT equal to $500\text{--}550^\circ\text{C}$ [18]. IF_y -GICs phases are unstable and decompose at temperatures higher than 100°C [24]. The presence of iodine species even at refluorination temperatures higher than 300°C suggests that these species are trapped within the fluorocarbon matrix. Refluorination first begins at the graphene edges; it then progresses towards the crystalline core changing the carbon hybridization from sp^2 to sp^3 [18]. Such a

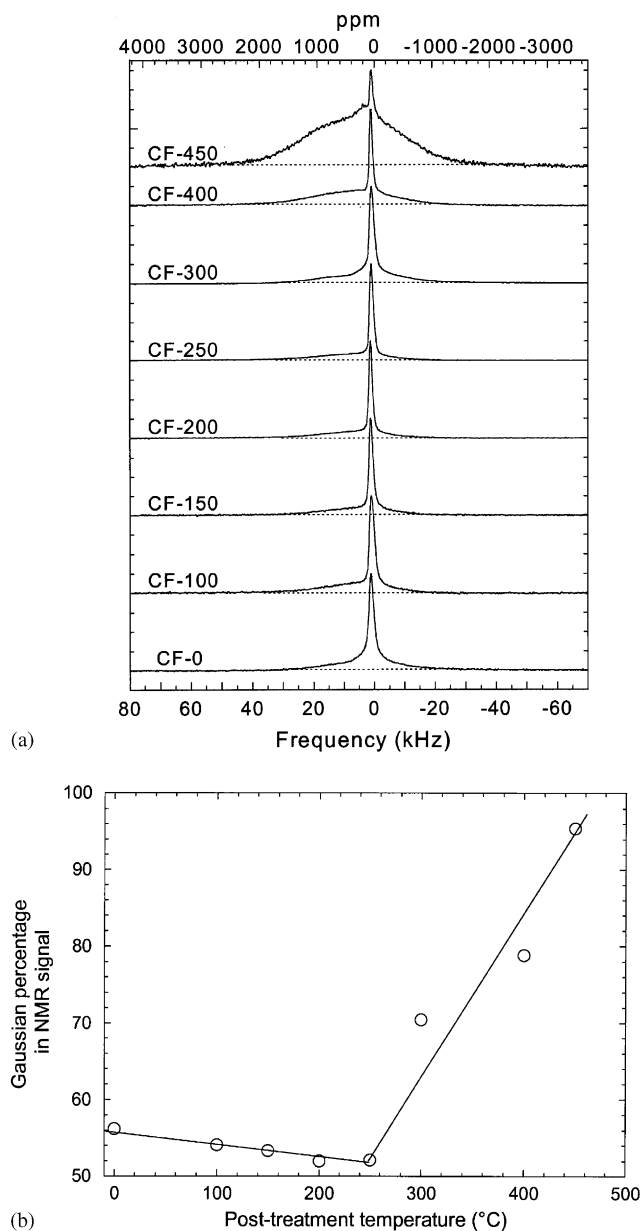


Fig. 2. (a) ^{19}F spectra at 18.9 MHz of CF-0 and post-treated compounds. (b) Evolution of the Gaussian percentage present in the NMR signal with the post-treatment temperature.

mechanism traps the iodine species in the crystalline core since the fluorine atoms, linked to sp^3 carbon atoms, are orientated over and under the deformed carbon sheets. The mobility of the iodine fluoride species within the fluorographite layers is therefore reduced by steric hindrance.

3.2. ^{19}F MAS and ^{13}C CP-MAS studies

The room temperature ^{19}F MAS NMR (at 12 kHz) spectrum of CF-0 exhibits several peaks (Figs. 3a and b):

three narrow peaks and a broad one. The latter, denoted S1 centred at -160 ppm and covering the range $-80/-280$ ppm, is characteristic of the rigid fluorinated carbon lattice. This peak is attributed to C–F groups, its width is caused by a large homonuclear dipolar coupling of fluorine nuclei. On the contrary, the narrowness of the three other lines is typical of mobile fluorinated species. These lines, denoted S2, S3 and S4 at 2, 10 and 50 ppm, respectively, are attributed to IF_5 (S2 and S4) [17,20,21] and IF_6^- species (S3) [17,25]. The S2–S4 doublet observed for IF_5 is due to their group molecular structure (square based pyramid with 2 non-equivalent fluorine sites i.e. 4 and 1 atoms). The S2/S4 area ratio of ≈ 4 is found to be constant whatever the treatment temperature. The effect of MAS on the CF-0 peaks is shown in Fig. 3b: the peaks are narrowed by dipolar interaction averaging. When run under static conditions, the resolution between lines S2 and S3 is poor; under MAS, however, this resolution is much improved.

As shown in Fig. 3, TPT in pure fluorine atmosphere induces significant modifications of the ^{19}F NMR spectra. For each species (CF and iodine fluorides), the observed effects are different. The position of S1 remains unchanged (-160 ppm) for post-treatment temperatures lower than 400°C but shifts to -193 ppm for higher TPT values. According to Panich and Nakajima [26], the decrease of chemical shift with increasing post-treatment temperature is due to an evolution of the C–F bond from semi-ionic to covalent. This fact is confirmed by FT-IR and XRD measurements [18].

Moreover, for post-treatment temperatures above 400°C , the peak definitely narrows and now resembles the one found for $(\text{CF})_n$ [13] which is a well-organized material with only covalent C–F bonds. Post-treatment in fluorine gas at temperatures higher than 400°C therefore leads to the formation of covalent C–F bonds and an enhancement in structural order. This agrees with results obtained previously by Electron Paramagnetic Resonance (EPR) [18]. It was indeed shown that the structure becomes more regular as the post-treatment temperature increases. Moreover, the detected residual dangling bonds behave as isolated spins within a regular environment (six neighbouring fluorine atoms). This leads in the EPR spectra to the formation of a well-defined superhyperfine structure. Contrary to the $(\text{CF})_n$ sample [13], no CF_2 groups are observed even for the highest temperature sample.

Fig. 3b shows the TPT evolution of the IF_5 and IF_6^- groups. It is observed that the separation between S2 and S3 lines increases. Fig. 3c represents the S2/S3 ($\text{IF}_5/\text{IF}_6^-$) area ratio as a function of post-treatment temperature. This ratio decreases linearly with temperature. This evolution can be explained by a thermal conversion of IF_5 into IF_6^- according to the following

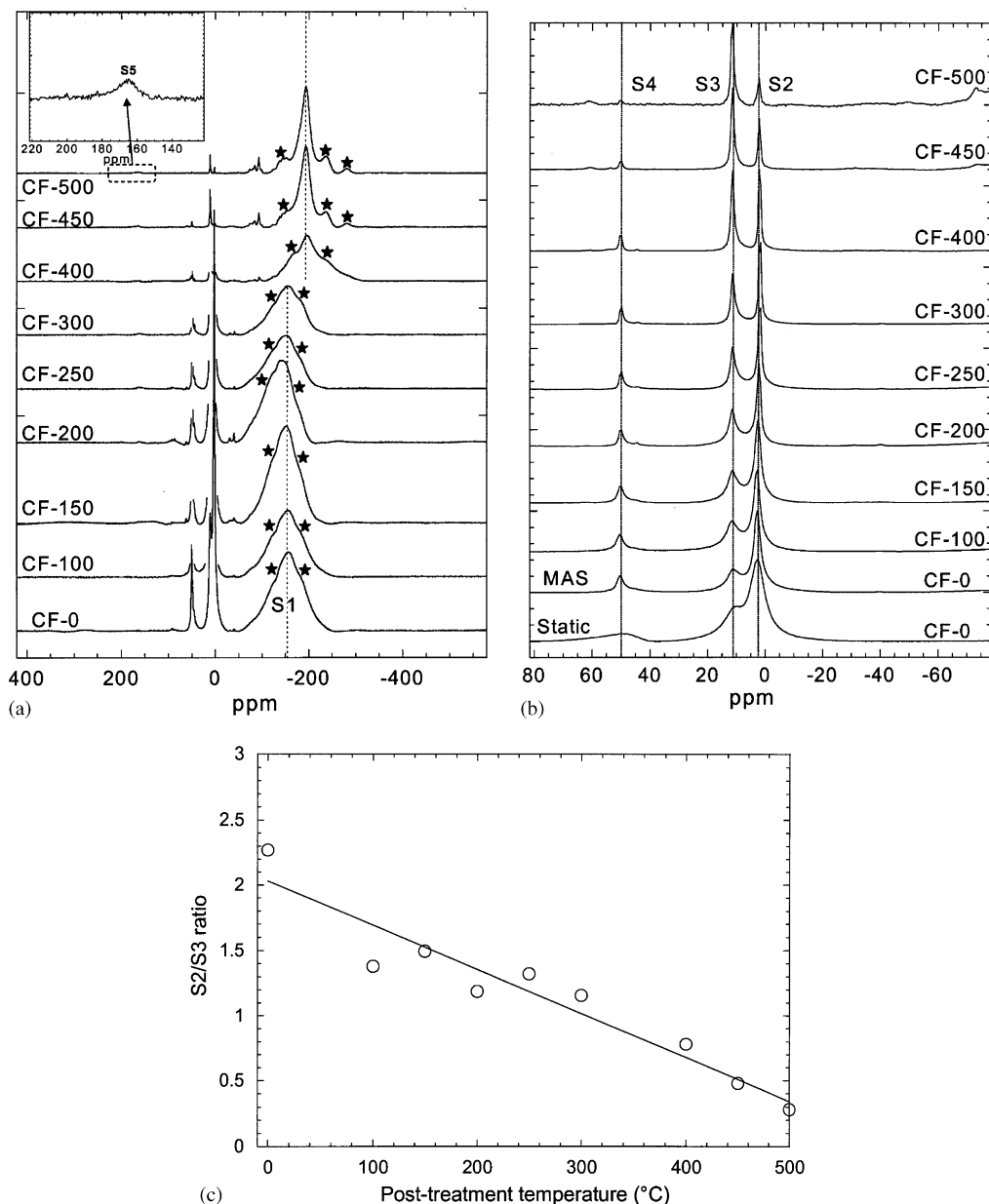
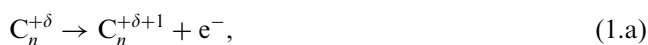


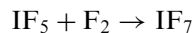
Fig. 3. (a) ^{19}F MAS spectra, at 12 kHz, of fluorinated samples with different post-treatment temperatures. Stars denote spinning sidebands. For low temperature, post acquisition correction baseline could overestimate the S1 surface and slightly distort the line shape. In the $-80/80$ ppm range, only peaks of CF-0 compounds are integrally shown, for the other compounds peaks are partially masked. (b) ^{19}F MAS spectra of (a) in the range $-80/80$ ppm. For comparison, a static ^{19}F spectrum of CF-0 is added. (c) Evolution of the S2/S3 ratio as a function of the fluorination post-treatment temperature.

equations:

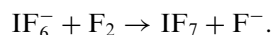


Eq. (1.a) describes the oxidation of the graphitic layers, the efficiency of which increases with temperature. This parameter also governs the IF_6^- content as described by Eq. (3) with fluorine ions F^- being provided through either Eq. (1.b) or Eq. (2). As shown by the decrease in signal/noise of the NMR spectra at higher temperatures, an equal loss of IF_5 and IF_6^- species occurs. For TPT equal to 500°C iodine products are almost totally removed. This fact is in good

agreement with low-field and static results. For TPT higher than 200 °C, an additional low-intensity resonance S5 is present at 164 ppm (Fig. 3a) and is attributed to IF₇. The latter is formed by oxidation of IF₅ and/or IF₆⁻ with gaseous fluorine:



and/or



Spectra acquired via a ¹⁹F to ¹³C CP-MAS sequence, at a spinning speed of 12 kHz, exhibit two peaks P1 and P2 located in the 84–88 ppm and 135–137 ppm ranges, respectively (Fig. 4a). According to Refs. [16,26–28], the

P2 peak can be attributed to graphitic carbons. As a matter of comparison, a chemical shift of 119 ppm has been measured for graphite [29]. P1 resonance is characteristic of fluorinated carbons [16,26–28]. Whatever the temperature, the position of P2 line remains unchanged. On the other hand, the chemical shift of P1 increases appreciably for TPT higher than 300 °C (Fig. 4b). Up to 300 °C, the semi-ionic character of the C–F bond is unchanged and the chemical shift is close to 84 ppm. At higher temperatures, the chemical shift reaches the value 88.5 ppm which corresponds to an essentially covalent C–F bond in (CF)_n compounds [13,30]. The covalent character is progressively and linearly increased with the post-treatment temperature. This agrees with our recent study using ¹³C MAS NMR [18] which clearly shows that the evolution of the amount of P1 coincides with the appearance of a new covalent C–F bond in the range 300–400 °C.

For CF-400 and CF-500, a shoulder near 110 ppm indicates the presence of some CF₂ groups [13,30], certainly located on the fluorographite edges.

4. Conclusion

Post-synthesis thermal treatment of room temperature graphite fluoride up to 500 °C results in important modifications of the physical properties of the resulting graphite fluorides. This evolution was studied by a combination of ¹⁹F low-field (18.9 MHz) and high-resolution ¹⁹F MAS and ¹³C MAS with ¹⁹F to ¹³C cross polarization. For post-treatment temperatures between 300 and 400 °C, the nature of the C–F bonds changes. The bonds become more and more covalent with increasing post-treatment temperature. This is clearly shown by the position of the ¹⁹F and ¹³C lines which shift towards the typical values found for covalent (CF)_n. This C–F bond formation is accompanied by an increase in internal structural order. Since fluorination evolves progressively from a semi-ionic graphite fluoride to a covalent compound, the TPT in F₂ gas prevents the formation of structural defects.

Residual iodine fluorides present in the raw materials are progressively eliminated by a deinsertion mechanism. Concurrently, a thermal conversion of IF₅ into IF₆⁻ and/or into IF₇ occurs as a function of the temperature. The iodine species disappear almost totally at post-treatment temperature higher than 450 °C. As recently proposed [18], the iodine fluoride species play an important role in the post-fluorination mechanisms because they could strengthen the planar configuration of the carbon sheets. As a matter of fact, because of their low mobility in the fluorocarbon interlayer space, the iodine fluoride species could hinder the diffusion of the F₂ molecules and shield the dangling bonds. This allows a progressive fluorination process.

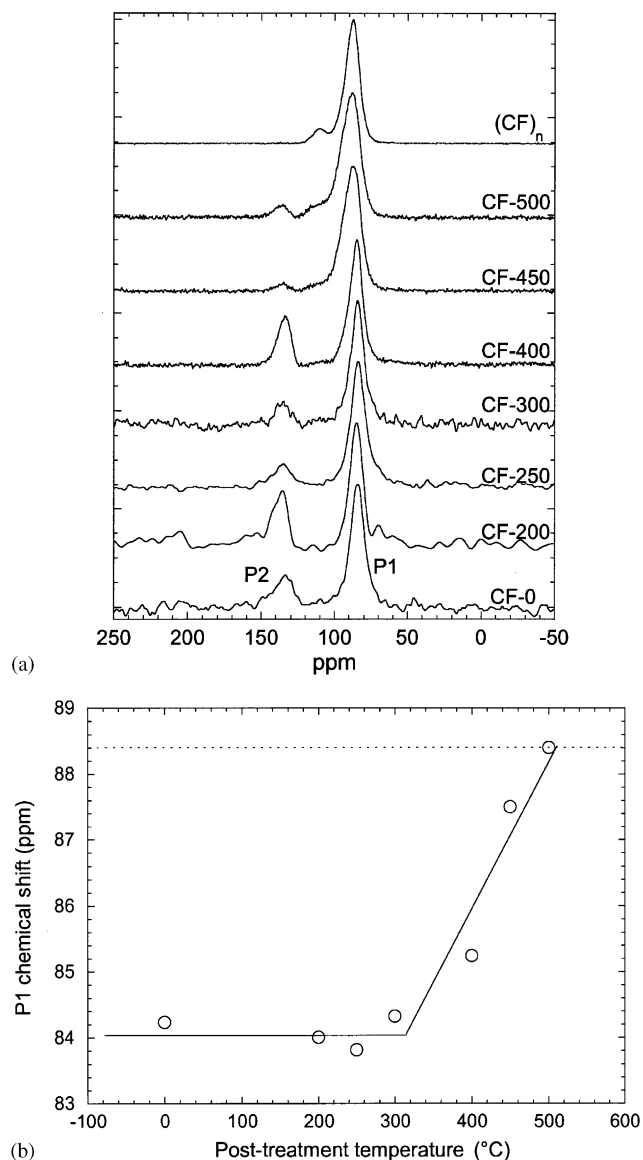


Fig. 4. (a) ¹³C MAS spectra with ¹⁹F to ¹³C cross polarization, at 12 kHz, of fluorinated samples at different post-treatment temperatures. The (CF)_n spectra is acquired with a spinning speed of 15 kHz. (b) Evolution with the post-treatment temperature of the ¹³C chemical shift of the P1 line.

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