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Intercalation chemistry of graphite fluorides

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Abstract

Graphite fluorides of the general composition CF_n, with $n = 0.25–1.0$, are found, according to X-ray diffraction and X-ray photoelectron studies, to contain graphitic zones which allow oxidative intercalation by bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, as well as intercalation by fluorosulfuric acid HSO_3F and trifluoromethylsulfuric acid HSO_3CF_3. The reactions produce materials of the general composition $CF_n(SO_3F)_m$ or $CF_n(HSO_3X)_m$, with $X = F$ or CF_3. While intercalation of $S_2O_6F_2$ into the graphitic zones results in the formation of first-stage intercalation products in all instances, higher-stage materials form with HSO_3F and to an increased degree with HSO_3CF_3, particularly when graphite fluorides with low fluorine contents are used. Interestingly, according to their X-ray photoelectron spectra, intercalation of all three reagents causes an increase in the polarity of the C–F bond; the oxidized graphitic zones appear to increase while the fluorine 1s binding energies suggest an increased ionic character.

Introduction

Graphite fluorides are frequently non-stoichiometric solid materials of the general composition CF_n, with n ranging from 0.25 to ~1.3 [1]. The general synthetic route to these compounds is the high temperature fluorination of graphite or graphitic materials by elemental fluorine. The composition of the final product depends on the fluorination temperature and the structural properties of the starting material.

Among the resulting materials, two distinct compounds with different structures and properties have been identified: poly(carbon monofluoride), $(CF)_n$ [2–5] and poly(dicarbon monofluoride) $(C_2F)_n$ [5]. A third reasonably well-defined compound, poly(tetracarbon monofluoride) $(C_4F)_n$, first reported by Rüdorff and Rüdorff [3], exhibits limited thermal stability [6] and may contain relatively large amounts of anhydrous HF, so that formulation as a binary graphite fluoride may not be appropriate [1b].

The remaining graphite fluorides, with compositions differing from these three compounds [2–6], are best viewed as incompletely fluorinated graphite. The presence of graphitic zones in these materials has recently

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been verified by X-ray powder diffraction [7] and X-ray photoelectron spectroscopy, X-PES [8]. Hence it should be possible to involve these non-stoichiometric graphite fluorides in the intercalation of suitable reagents.

Previous reports on the intercalation reactions of graphite fluorides are limited to the study of their interaction with antimony pentafluoride, SbF_5. In an earlier report Ebert *et al.* [9] had studied its reaction with poly(carbon monofluoride) of the stated composition $CF_{1.06}$ and had claimed the formation of materials of the stoichiometry $(CF_{1.06})_{11}SbF_5$. The authors had suggested partial formation of $\cdot\cdot F{-}SbF_5^-$ groups. A subsequent more detailed study of the interaction of SbF_5 with $CF_{0.8}$, $CF_{1.0}$ and $CF_{1.1}$ has shown that only the former two materials will intercalate SbF_5 and that the graphitic zones in these compounds are active in the intercalation process [10], while fully fluorinated graphite remains inactive.

In this study, the interaction of bis(fluorosulfuryl)peroxide), $S_2O_6F_2$, with various graphite fluorides is investigated. The intercalant, $S_2O_6F_2$ offers a number of advantages over the use of SbF_5. Fluoride ion abstraction as postulated by Ebert *et al.* [9] is in the case of $S_2O_6F_2$ or the SO_3F radical unlikely. Their direct and unassisted oxidative intercalation into graphite has been studied extensively previously [11–14]. According to these studies, bis(fluorosulfuryl)peroxide) acts as a two-electron oxidizer:

$$S_2O_6F_2 + 2e^- \rightarrow 2SO_3F^- \qquad (1)$$

The composition of the well-defined first stage material has been found to be approximately C_7SO_3F, and its structural characterization has involved X-ray powder diffraction, Raman and ^{19}F NMR spectroscopy [14] as well as electrical conductivity studies [15] and more recently X-ray photoelectron spectroscopy, X-PES [8]. The relatively high volatility of $S_2O_6F_2$ [16] allows the facile removal of excess reagent from the product.

Extension of the study to the related protonic acids fluorosulfuric acid, HSO_3F, and trifluoromethylsulfuric acid, HSO_3CF_3, provides a useful test of the possibility to observe non-oxidative intercalation into partly fluorinated graphite. It has previously been observed that pure HSO_3F will intercalate readily into higher-stage graphite fluorosulfates [17] but not into graphite [17, 18], whereas assisted intercalation, *e.g.* via anodic oxidation [19, 20] is reported to give acid fluorosulfates of variable composition. Likewise for HSO_3CF_3, only assisted intercalation by anodic oxidation of graphite is reported [21].

The ultimate objective of this study is the enhancement of the electrical conductivity of graphite fluorides by oxidative intercalation. We now wish to report on the synthetic aspects of the work and on the subsequent structural characterization of the resulting products by X-ray powder diffraction and by X-ray photoelectron spectroscopy.

Experimental

Chemicals

Bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, was prepared by the catalytic (AgF_2) fluorination of sulfur trioxide at ~180 °C [22, 23]. Technical grade fluorosulfuric acid (Orange County Chemicals) was purified by double distillation at atmospheric pressure [24]. HSO_3CF_3 was obtained from the 3M Co. and purified by trap-to-trap distillation before use. Various samples of graphite fluorides were obtained from Ozark Mahoning-Pennwalt (now Atochem North America). The samples were of the general composition CF_n with n ranging from 0.25 to 1.00. They were dark to light grey in colour.

Instrumentation

X-ray powder diffraction patterns were recorded on a high briliancy, Ru 200B series Rigaku rotating anode X-ray powder diffractometer operating in line focus with 12 kW maximum operating power. The diffractometer detected Cu K_α target radiation though a 20 μm Ni filter with a horizontal-type NaI scintillator probe (SC-30). The parameters were: $2\theta = 0.002$, $\theta = 0.60$. A horizontal goniometer was used for the rotating anode. The diffractometer was interfaced with DMax/B computer system driven by an IBM PS/2. The peak-finding program was provided by Rigaku. Powdered samples were put on glass plates with double-sided scotch tape and a plastic film was employed to seal samples from moisture. All manipulations were carried out in the dry box and samples were analyzed as soon as possible after they were removed from the dry box.

X-ray photoelectron spectra were recorded with a Varian IEE-15 XPS spectrometer using Al K_α X-rays of 1486.6 eV energy. Samples were carefully dusted as a thin film onto a 2 cm long piece of 3M Scotch tape, wrapped around the sample slug [25] in the dry box. The carbon 1s binding energy at 284.0 eV obtained with SP-1 graphite was used as a reference for our measurements [8]. Peak heights were used to estimate approximate relative abundances. All XPS values are reported here with an accuracy limit of ± 0.1 eV.

Chemical purity and identity were verified by microanalysis. Carbon, hydrogen and sulfur elemental analyses were carried out by P. Borda of the Chemistry Department of the University of British Columbia. A Carlo Erba Model 1106 analyzer employing a flash oxidation technique was used. The samples were treated with powdered CuO to avoid formation of CF_4 during combustion. Details of this method have been published [25].

A Spex-Ramalog 5 spectrometer equipped with an Ar^+ ion laser operating at 514.5 nm was employed. A Perkin Elmer 598 grating spectrometer was used. Solid samples were pressed as thin films between KBr or AgBr windows.

Synthetic procedures

The general procedure used was adopted from the methods for the intercalation of $S_2O_6F_2$ into graphite [13, 14] or of HSO_3F into higher-stage graphite fluorosulfates [17]. All reactions were carried out at room temperature and involved an excess of the respective intercalant. Vacuum line techniques were employed for the transport of $S_2O_6F_2$ or the protonic acids from the storage vessel to the reactor. One-part Pyrex reactors (fitted with Teflon-coated stirring bars and Kontes Teflon stem valves) of ~50 to 100 ml volume were used and approximately 200 mg of graphite fluoride was stirred magnetically for 48 to 96 h in ~10 ml of the liquid intercalant. Removal of excess reagent was continued until constant weight was reached, with the sample in a dynamic vacuum and the reactor at room temperature. All reactions were followed by weighing.

Solid materials were manipulated inside a Vacuum Corporation Inert Atmosphere box type 'Dri-Lab' HE-493 filled with dry nitrogen and equipped with a HE-493 'Dri Train'.

The composition of the final product was obtained both from the weight increase and elemental analysis for C, S and, where applicable, H content. In the case of the products obtained by the intercalation of HSO_3F into graphite fluorides, de-intercalation at 200 °C was used to confirm the composition. A one-part reactor fitted with a side arm was employed for the de-intercalation experiment. The side arm was cooled with liquid nitrogen and the trapped volatile material was studied by Raman spectroscopy and identified as HSO_3F by comparison with the previously published Raman spectrum [27].

Results and discussion

Intercalation reactions

In all instances intercalation of either bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, or the two strong protonic acids HSO_3F and HSO_3CF_3 occurs readily at room temperature. There is a perceptible change in colour as the solid reactants turn light blue during the reaction. The weight increase observed after all excess intercalant is removed *in vacuo*, is consistent with chemical analysis for C, S or H content. The results are given in Table 1 for representative reactions The ratio $\Delta W/W$, the weight increase on intercalation over the weight of the graphite fluoride in percent is plotted *vs* the fluorine content n in the CF_n starting materials as shown in Fig. 1 for the intercalations of $S_2O_6F_2$ and HSO_3F. The fairly linear curve for the $S_2O_6F_2$ intercalation and the inverted V-shaped plot obtained for HSO_3F reveal an interesting discrepancy between the oxidative intercalation by $S_2O_6F_2$ and the non-oxidative intercalation by HSO_3F. While there appears to be only a slight difference for graphite fluoride samples with a high fluorine content $CF_{1.0}$ and also $CF_{0.83}$, for samples with a low fluorine content a noticeable difference emerges:

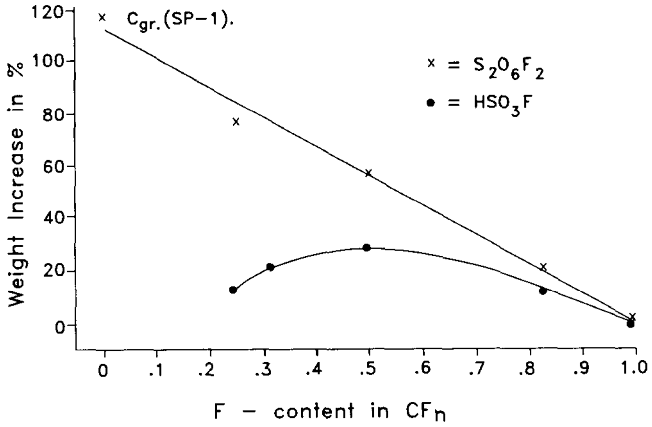

Fig. 1. The intercalation of graphite fluorides, CF_n, by bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, and fluorosulfuric acid, HSO_3F, as a function of fluorine content in CF_n.

extensive intercalation is observed only for $S_2O_6F_2$, resulting in all instances in the conversion of graphite to stage I materials. Only small amounts of HSO_3F and HSO_3CF_3, as seen in Table 1, are intercalated. The implication is that oxidative intercalation makes use of all graphitic zones present in graphite fluoride samples, while intercalation by HSO_3F or HSO_3CF_3 affects only some of these graphitic zones, presumably those

TABLE 1

The intercalation of $S_2O_6F_2$, HSO_3F and HSO_3CF_3 into various graphite fluorides

Intercalant	CF_x composition[a]	Weight CF_x (g)	ΔW (g)	$\Delta W/W_{CF_x}$	Suggested composition
$S_2O_6F_{2(e)}$	C	0.1765	0.2045	1.160	C_7SO_3F
	$CF_{0.25}$	0.1930	0.1496	0.775	$(CF_{0.25})_{7.6}SO_3F$
	$CF_{0.50}$	0.1259	0.0783	0.586	$(CF_{0.5})_{7.9}SO_3F$
	$CF_{0.83}$	0.1998	0.0443	0.222	$(CF_{0.83})_{16.1}SO_3F$
	$CF_{1.00}$	0.2532	0.0070	0.028	$(CF_{1.00})_{115.5}SO_3F$
HSO_3F	$CF_{0.25}$	0.2154	0.0280	0.130	$(CF_{0.25})_{45.9}HSO_3F$
	$CF_{0.33}$	0.1709	0.0366	0.2142	$(CF_{0.33})_{25.6}HSO_3F$
	$CF_{0.50}$	0.1527	0.0459	0.3005	$(CF_{0.5})_{15.5}HSO_3F$
	$CF_{0.83}$	0.1857	0.0289	0.1556	$(CF_{0.83})_{23.1}HSO_3F$
	$CF_{1.0}$	0.2927	0.0082	0.0280	$(CF_{1.0)_{117HSO_3F}}$
HSO_3CF_3	$CF_{0.25}$	0.2008	0.0520	0.2621	$(CF_{0.25})_{34.6}HSO_3CF_3$
	$CF_{0.33}$	0.1663	0.0484	0.2949	$(CF_{0.33})_{28.2}HSO_3CF_3$
	$CF_{0.5}$	0.1763	0.0693	0.393F	$(CF_{0.5})_{17.8}HSO_3CF_3$
	$CF_{0.83}$	0.1839	0.0456	0.249	$(CF_{0.83})_{21.8}HSO_3CF_3$

[a] As stated by the supplier.

already weakened by partial fluorination, as suggested by the collected data.

The intercalation of HSO_3F and HSO_3CF_3 into graphite fluorides thus becomes comparable to the intercalation of HSO_3F into higher-stage graphite fluorosulfates reported earlier by our group [17], and first-stage materials result only where a high fluorine content suggests the presence of limited graphitic areas as *e.g.* in $CF_{1.0}$ and $CF_{0.83}$.

The intercalation of the two protonic acids into graphite fluoride is supported by two additional observations. The product of the composition $(CF_{0.5})_{17.8}HSO_3CF_3$ gives a reasonably well-resolved IR spectrum, just like the binary intercalation compound $C_{12}SO_3CF_3$ [13], for which also a Raman spectrum is reported. An intense broad band at ~ 3550 cm^{-1} and a shoulder at ~ 970 cm^{-1} are attributed to νOH and δOH respectively, with the remaining bands also consistent with the presence of trifluoromethyl sulfuric acid as intercalate by comparison with the reported spectrum [28].

For the ternary compound $(CF_{0.83})_{23.1}HSO_3F$, an IR spectrum was not obtained but de-intercalation at ~ 200 C *in vacuo* leads to a solid residue of the approximate composition $CF_{0.8}$ and a liquid, which is identified by its Raman spectrum as HSO_3F by comparison with the published spectrum [27].

While all these observations are consistent with the formation of novel ternary graphite fluoride intercalation compounds, conclusive evidence that intercalation has occurred will have to come from X-ray powder diffraction patterns and from X-PES measurements, which will be discussed next.

X-ray powder diffraction

All samples of graphite fluoride used in this study except for $CF_{1.0}$ had given X-ray powder diffraction patterns with a sharp line at $2\theta = 26.58$, which was attributed to the 002 line of graphite by comparison to samples of pristine graphite. On intercalation by $S_2O_6F_2$ this line shifts to $2\theta = 22.5$ for the products formed from $CF_{0.25}$, $CF_{0.50}$ and $CF_{0.83}$. This suggests an interlayer separation of $I_c = 8.4$ Å, while for C_7SO_3F an I_c value of 7.81 Å is reported [13, 14]. The difference may be explained by stronger electrostatic interaction in C_7SO_3F between the more extensively oxidized graphite layers and the higher abundance of intercalate anions in the galleries. For all three products, graphite fluoride fluorosulfate intercalation compounds of stage I composition are suggested. The same conclusion applies to $(CF_{1.0})_{115.3}SO_3F$, however here diffraction lines of both the starting material and the intercalation product are rather broad and only an approximate I_c value of ~ 8 Å is obtainable.

Analysis of the X-ray diffraction pattern obtained for the intercalation products of HSO_3F suggests primarily stage II composition for the products of $CF_{0.25}$ and $CF_{0.83}$ with $I_c = 11.30$ Å, while $CF_{0.5}$ and $CF_{0.33}$ form with HSO_3F materials of an intermediate composition between stages I and II.

Judging by the X-ray diffraction pattern, HSO_3CF_3 does not appear to intercalate very well because in the products formed with $CF_{0.25}$ and $CF_{0.33}$ a strong peak of $2\theta = 26.5$ Å remains, which suggests that graphitic zones are still present. In addition $(CF_{0.5})_{17.8}HSO_3CF_3$ shows diffraction lines which suggest stage III or even stage IV materials, even though the diffraction line due to graphite is missing. Finally the rather broad diffraction lines found for $(C_{0.83})_{21.8}HSO_3CF_3$ allow no clear assignment.

An apparent contradiction deserves comment. According to the X-ray powder diffraction pattern discussed above, less HSO_3CF than HSO_3F appears to be intercalated, giving rise to higher-stage materials. On the other hand the weight changes listed in Table 1 suggest that comparable or even larger amounts of trifluoromethyl sulfuric acids are retained by the graphite fluorides and its must be concluded that not all HSO_3CF_3 is intercalated, and some may possibly be trapped in the solid in some form. The reason for this difference in behavior, shown by two sulfonic acids of comparable volatility [32, 33], is not obvious and the nature of the interaction is unclear. It may be surmised however, that fluorine $\cdots$ fluorine repulsion between the CF_3 group and the C–F groups in the graphitic fluorides may hinder intercalation to some extent.

In summary, some supporting information for the suggested intercalation of either $S_2O_6F_2$ or the two sulfonic acids is obtained from shifts of the 002 lines of graphite. The higher fluorinated materials such as $CF_{0.83}$ and $CF_{1.00}$ given rather broad diffraction lines before and after intercalation and provide less useful information.

All observations made during this part of the study support the claim in respect to intercalation by SbF_5 [10] that fully fluorinated graphites will not be intercalated, and that $S_2O_6F_2$ or the protonic acids HSO_3F and HSO_3CF_3 do not react differently from SbF_5, and only graphitic zones in incompletely fluorinated graphites will allow both oxidizing and to a lesser degree nonoxidizing intercalation. The disappearance of the graphite 002 lines on oxidative intercalation provides the clearest evidence in this respect.

X-ray photoelectron spectra

Binding energies of both the C 1s and the F 1s level are listed in Table 2 for the graphite fluorides, their intercalation compounds, various forms of graphite and some related compounds.

A previous X-PES study of binary graphite fluorides and fluorosulfates by us [8] concluded that in graphite fluorosulfates, as well as in other acceptor intercalation compounds, the C 1s binding energies are shifted to slightly lower energies by ~0.3 to ~1.0 eV relative to graphite. In graphite fluorides, two well-resolved peaks due to the C $1s_{1/2}$ transition are observed. One peak at ~284 eV is attributed to graphitic sp^2-hybridized carbon, while the second peak at ~290 eV appears to be caused by fluorinated sp^3-hybridized carbon. The assignment is supported by observation by comparable, slightly higher binding energies of 291.8 eV

TABLE 2

Binding energies[a] in eV of the C 1s and F 1s core levels

Compounds	C 1s (sp^2)	C 1s (sp^3)	F 1s	Reference
graphites SP1	284.0			[8]
graphite	284.2			[29]
graphite HOPG	284.4			[30]
$CF_{1.0}$	284.6	289.8	688.3	[8]
$CF_{0.83}$	284.7	290.1	688.3	[b]
$CF_{0.83} + S_2O_6F_2$	284.3	289.7	688.8	[b]
$CF_{0.83} + HSO_3CF_3$	283.6	288.3	687.5	[b]
$CF_{0.5}$	284.0	289.2	687.3	[8]
$CF_{0.33}$	283.5	289.7		[b]
$CF_{0.33} + S_2O_6F_2$	283.8	289.0		[b]
C_7SO_3F	283.1		686.6	[8]
$(CF_2)_x$		291.8	689.1	[31]
$C_{2.5}F_{1-\delta}(HF)_\delta$	284.6	-	686.6	[1b]
LiF	--	-	684.9	[29]

[a] Binding energy values quoted from the literature are within ±0.2 eV in most instances

[b] This work

for perfluoropolyethylene [31]. The relative intensity of both peaks observed in graphitic fluorides reflects approximately the composition CF_n of these materials (see *e.g.* the upper tracing in Fig. 2).

For these graphitic fluorides, the F 1s binding energies range from 688 to ~689 eV and are consistent with the presence of covalently bonded fluorine [29, 31], while ionic fluorides such as LiF show lower binding energies of ~685 eV [29].

On intercalation of either $S_2O_6F_2$ or the two sulfonic acids, three interesting changes in the X-PES spectra were noted and discussed for $CF_{0.83}$ and its intercalation compounds:

(i) In the C 1s region two peaks are again observed. The transition due to sp^2-hybridized carbon is shifted to slightly lower binding energies, consistent with findings for acceptor intercalation compounds [8], while the second peak is also very slightly shifted to lower binding energies by 0.4–0.8 eV.

(ii) As is best illustrated in Fig. 2, the relative intensities of the two peaks have noticeably changed and the peak at lower binding energy is now of considerably higher intensity than the peak due to sp^3-hybridized carbon.

(iii) Fluorine 1s binding energies are shifted to lower values, indicating increased ionic character of F in the intercalated product. This shift of ~1.5 eV is most noticeable for the product of the intercalation by $S_2O_6F_2$ into $CF_{0.83}$, which has the composition $(CF_{0.83})_{16.1}SO_3F$. For fluorine attached to sulfur, a peak at 686.6 eV is expected, judging by its position in C_7SO_3F [8]. This peak, which should be of low intensity in the case of $(CF_{0.83})_{16.1}HSO_3F$, is seemingly not resolved.

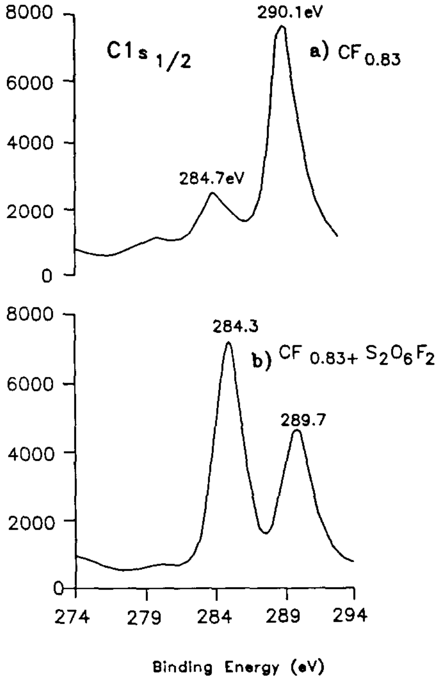

Fig. 2. X-ray photoelectron spectra of $CF_{0.83}$ before and after intercalation by $S_2O_6F_2$.

It appears that on intercalation the C–F bond has in some areas become more polarized towards $C_n^+ \cdots F^-$ and interestingly the binding energies for $(CF_{0.83})_{16.1}SO_3F$ for the sp^2-carbon peak and the fluorine $1s_{1/2}$ transition are within error limits identical to binding energies of 284.6 ± 0.2 and 686.6 ± 0.2 eV respectively, reported for $C_{2.5}F_{1-\delta}(HF)_\delta$ [1(b), 34], where intercalated fluoride is claimed.

The similarity in the X-PES spectra is even more surprising when the difference genesis of the materials is considered. First-stage intercalation compounds of the general composition $C_xF_{1-\delta}(HF)_\delta$ with $x/\delta \approx 12$ and $2 < x < 5$–6 [1(b), 34] are obtained in the reaction of graphite powder with F_2 in the presence of gaseous of liquid HF, usually at room temperature, whle our approach involves the intercalation of graphitic zones in partly fluorinated graphite fluorides by either $S_2O_6F_2$ or HSO_3X, X = F or CF_3. The latter approach will ultimately lead to more complex, ternary systems, with different interlayer separation. Reported I_c values for $C_xF_{1-\delta}(HF)_\delta$ usually fall between 5.2 and 6.4 [1(b)]. The dramatic intensity reversal seen in Fig. 2 and the similarity in the binding energy spectra between the two groups of compounds is highly unexpected and surprising, and it is interesting to note that the relatively small amount of $S_2O_6F_2$ intercalated causes such a major change in the electronic structure of the material.

Similar observations apply also to the intercalation products of $CF_{0.83}$ with HSO_3F and HSO_3CF_3 and for $CF_{0.33}$ intercalated by $S_2O_6F_2$, but are not as pronounced in these cases. Again, the change in relative intensity of the two binding energy peaks in the C 1s region is most noticeable in all instances. The observation of two binding energy peaks in all intercalated graphite fluorides indicates however, that, some sp^3-hybridized carbon remains, and that inhomogeneous products are obtained by intercalation.

Conclusions

The results reported here suggest that incompletely fluorinated graphite materials of the composition CF_n possess graphitic zones, which allow oxidative intercalation by $S_2O_6F_2$, which is an excellent oxidizing intercalant, and also by HSO_3F and HSO_3CF_3, neither of which intercalate well into graphite, but form second or third stage compounds, and in the case of HSO_3F even first stage compounds. While it is not surprising that $S_2O_6F_2$ produces first-stage intercalation compounds only, it is surprising that the X-ray photoelectron spectra of the intercalation products suggest changes in the electronic structure of the graphite fluorides towards more strongly polarized $\overset{\delta+}{C}-\overset{\delta-}{F}$ bonds and the formation of partly oxidized graphitic zones

^{19}F NMR and electric conductance measurements are currently planned to hopefully support the findings made in this study.

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