EFFECT OF CURVATURE ON C-F BONDING IN FLUORINATED CARBONS : FROM FULLERENES AND DERIVATES TO GRAPHITE

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Introduction

Due to the polymorphism of carbonaceous materials and the versatility of the C-F bonding, the carbon/fluorine combination in fluorinated carbons is an unique association in chemistry. This results in interesting materials for many technological applications such as electrode materials for lithium batteries and solid lubricants. The resulting C-F bonding in fluorinated carbons could be classified into two categories with different application properties: covalent and ionic. For the first category i.e. covalent compounds, the graphite fluorides $(C_2F)_n$ and $(CF)_n$, prepared at 350 °C and 600 °C, respectively, are electronic insulators, the carbon skeleton consists of trans-linked cyclohexane chairs or cis-trans linked cyclohexane boats with sp^3 bonding. The second category is composed of fluorine-graphite intercalation compounds (C_xF), obtained at temperature lower than 100 °C, which have higher electronic conductivity. In this case the planar configuration of graphite is partially preserved. The nature of the C-F bond evolves from ionic for low fluorine content to "semi-covalent" for higher fluorine content. The carbon atoms are in almost sp^2 hybridization.

When these fluorinated carbons are used as electrode material in primary lithium battery, the modulation of both the C-F bonding and the fluorine content allows either high capacities, high discharge potentials or high power densities to be obtained as a function of the required application [1-3].

The present work investigates the effect of the curvature of the carbon lattice on the C-F bonding. With such aim various fluorinated carbons were synthesized:

i) using a heat-treatment under fluorine F_2 gas or a two-step process which consists in a catalytic fluorination at room temperature by the use of a mixture of F_2, HF and a volatile fluoride (BF_3, IF_5, ClF_3) followed by a post-treatment under fluorine gas for temperatures up to 680°C. The temperature increase leads to C-F covalence increase [4].

ii) by changing the curvature of the carbon lattice for various nanotubes.

In order to investigate the C-F bonding, five parameters were defined: the ^{13}C and ^{19}F NMR chemical shifts of the C-F bonds, the C-F bond length as seen by NMR, the wavenumber of the C-F vibration determined by infrared spectroscopy and the average discharge potential of fluorinated carbons in primary lithium battery. As a matter of fact, the discharge results in the irreversible breaking of the C-F bonds to form LiF and C. The change of the covalence leads to different discharge potentials.

Experimental

Fluorinated graphites were prepared using Madagascar natural graphite powder (particle size of 7.5 lm) at room temperature using synthesis methods already described elsewhere [2,4] which utilize a gaseous mixture of fluorine (F_2), hydrogen fluoride (HF) and an inorganic fluoride (MF_n).

Table 1 summarizes the synthesis and fluorination methods (by treatment with gaseous F_2) for various nanocarbons. Fluorine level F/C is obtained by weight uptake.

Table 1. Synthesis methods of the nanocarbons and fluorination conditions using F_2 gas

	Producer	Synthesis method	Purity	$<\Phi>$** (nm)	t (h)	T_F (°C)	F/C
SWCNTs	HiPCO	CVD	> 95%	1.1	3	200	0.37
	EA	Electro-arc	> 95%	1.5	5	190	0.32
DWCNTs	Helix	CVD	90%	~ 4	3	300	0.42
MWCNTs	Helix	CVD	95%	50 +/- 50	3	380	0.43
					3	400	0.73
CNFs	MER	CVD	> 90%	140 +/-30	16	420	0.39
C60	MER		99.9%		3	300	0.80
C60	MER		99.9%		48	133	0.80

* chemical vapour deposition ** average diameter (producer data)

NMR experiments were performed at room temperature using a Tecmag spectrometer (working frequencies for ^{13}C and ^{19}F were equal to 73.4 and 282.2 MHz respectively). The ^{13}C spectra were recorded using a solid echo sequence (two 5.5 µs $\pi/2$ pulses separated by 25 µs); this sequence allows the acquisition of the whole signal without loss due to the electronic dead time followed by a quantitative determination of the different contributions.

C-F bond length could be obtained by NMR measurements, since the C-F bond length correlates with the intensity of the dipolar interaction revealed by the Inverse Cross Polarization (ICP) sequence. This method was successfully applied to $(CF)_n$ and $(C_2F)_n$ covalent graphite fluorides [6]. ^{19}F and ^{13}C chemical shifts were referenced to $CFCl_3$ and tetramethylsilane (TMS), respectively. The recycle times were equal to 5 s for ^{19}F and CP spectra and 100 s for ^{13}C spectra.

The electrochemical procedure for the investigation of the discharge potential of CFx electrode in primary lithium battery is described elsewhere [1,3].

Results and Discussion

Single wall carbon nanotubes can be considered as intermediate between planar graphite and spherical fullerene, its ^{19}F chemical shift should be included between ones of $(CF)_n$ (-190 ppm) and fluorinated C_{60} (-151 ppm). The δ value for fluorinated SWCNTs (produced by electro-arc method) of $CF_{0.35}$ composition was equal to -168 ppm. This preliminary comparison underlines that the curvature could play a key role. To quantify the effect of curvature, various SWCNTs produced by different methods were fluorinated. The fluorine levels are given in Table 1. The MAS ^{19}F spectra lines of fluorine atoms involved in the C-F bond exhibit chemical shifts of -163 and -168 ppm for fluorinated HiPCO (of initial diameter 1.1 nm), and EA (of initial diameter 1.5 nm). The value for DWCNTs and MWCNTs fluorinated at 300°C (initial diameters of about 4 and 50 nm, respectively) are equal to – 178 and -184 ppm. For all the studied samples the following dependence exists: decrease of curvature (or increase of the nanotube diameter) leads to decrease of a chemical shift and increase of the covalence (Fig. 1). Moreover, the wavenumber values of the fluorinated CNTs (SWCNTs, DWCNTs and MWCNTs) are placed in between the two limits corresponding to the spherical fullerene and planar graphite fluorides. Another indicator of the C-F covalence is the wavenumber of the IR C-F vibration. Its strong correlation with ^{19}F chemical shift was visualized in the Figure 1. The increase of the covalence results in a shift of the wavenumber to 1220 cm^{-1}. For highly fluorinated fullerenes with $C_{60}F_{48}$ composition different C-F bonds coexist. Both NMR and IR studies unambiguously indicate the strong effect of the curvature on both the C-F bonding covalence and the bond length. Those two parameters are definitely correlated. A series of ^{19}F and ^{13}C chemical shifts for various graphite fluorides, $(CF)_n$ and $(C_2F)_n$, fluorine-GIC $(C_{2.5}F)_n$, and room temperature graphite fluorides post-treated under fluorine gas $(CF(IF_5)-350$ and $CF(IF_5)-530$, 350 and 530 are the post-treatment temperatures) was also plotted. The samples can be classified into three types : i) compounds exhibiting weakened covalence due to the hyperconjugaison (fluorine-GIC) ii) covalent graphite fluorides, fluorinated nanofibres, room temperature graphite fluoride post-treated under F_2 gas iii) fluorinated nanotubes, where covalence depends on the fluorinated tube diameter. A quasi linear dependence between ^{13}C and ^{19}F chemical shifts is found as a function of the diameter. Such a behavior is confirmed by the other indicators. The increase of the C-F covalence results in the decrease of the C-F bond length from 0.144 to 0.138 ± 0.002 nm [6]. Moreover, the average discharge potentials decrease from 3.6 to 2.1 V vs Li$^+$/Li when the C-F bonds become more and more covalent.
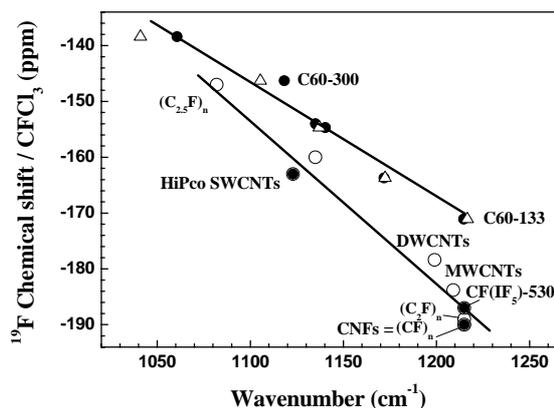

Fig. 1 ^{19}F chemical shifts vs. the wavenumber of the IR C-F vibration in fluorinated carbons

Conclusions

The curvature prevents the formation of a pure sp^3 hybridization for the carbon atom, since it requires an important local strain. The residual sp^2 hybridized orbitals imply a weakening of the overlapping of the hybridized lobes of carbon and of the fluorine atomic orbitals. In other terms, this results in a weakening of the C-F bonding covalence. This covalence weakening affects the C-F bond strength and leads to a lack of robustness of the C-F interaction within fluorofullerene clusters. Such an effect can be experimentally observed by their thermally activated decomposition. Whereas a perfluorinated graphite plane remains unaffected, fluorofullerenes readily loose bonded fluorine above 350°C in the absence of a fluorine atmosphere. A quasi linear relationship of δ_{19F} with the wavenumber is observed for graphite fluorides, fluorine-GIC and fluorinated CNTs (see Fig. 1) in accordance with either the hyperconjugaison or the curvature effect. But the data set for C_{60} cannot be included in this relationship. The same remark can be done from chemical shifts dependence (^{13}C and ^{19}F). It could indicate that the curvature is not the only parameter which affects the C-F bonding in fluorinated C_{60} and the steric hindrance between fluorine atoms should be also taken into account.

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