



Tuning the discharge potential of fluorinated carbon used as electrode in primary lithium battery

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ABSTRACT

When the carbon lattice of the starting material exhibits a curvature as in the case of fullerenes and derivatives, the C–F bonding in the compounds resulting from the fluorination using molecular fluorine is strongly affected and the covalence is significantly weakened. ¹⁹F solid state NMR underlines that the higher the curvature the lower the C–F bonding covalence is. The electrochemical discharge potentials of these materials used as electrode in primary lithium batteries can be then tuned according to the curvature, i.e. the diameter of the outer tubes. The potential decreases from 2.9 to 2.3 V versus Li⁺/Li⁰ according to the following classification: SWCNTs, MWCNTs and carbon nanofibres, which can be described as MWCNTs with large diameter due to the high number of walls. The case of highly fluorinated fullerenes is different because several types of bonding coexist and are progressively broken during the electrochemical process at potentials ranged in between 2.0 and 3.6 V. The behaviour of fluorinated nanocarbons is also compared to conventional graphite fluorides.

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1. Introduction

Because of, on one hand, the exceptional reactivity of molecular or atomic fluorine, its ionic radius, the electronegativity of the element, the highest of the periodic classification, and, on the other hand, the number of the allotropic varieties of carbon, the association of fluorine and carbon atoms is quite unique in chemistry. Contrary to the hydrides where the C–H bonding is purely covalent, the C–F bonding is highly versatile in fluorinated carbons. The nature of the interactions between the fluorine and carbon atoms can considerably vary: in the case of the fluorine adsorption on the surface of carbonaceous material, these interactions are very weak. On the other hand, a covalent, semi-ionic or ionic character can be obtained [1]. In particular, intermediate states are observed in compounds where fluorinated carbon atoms, with sp³ hybridization, and non-fluorinated sp² ones coexist in the layers (hyperconjugation) [2]. The bonding depends on the synthesis conditions; for covalent compounds, namely graphite fluorides (C₂F)_n and (CF)_n, prepared with molecular fluorine at 350 °C and 600 °C [3,4], respectively, the carbon skeleton consists of *trans*-linked cyclohexane chairs or *cis*-*trans* linked cyclohexane boats

with sp³ bonding. In the case of fluorine–graphite intercalation compounds (C_xF), obtained at temperature lower than 100 °C, the planar configuration of graphite is partially preserved; the nature of the C–F bond evolves from ionic for low fluorine content to weakly covalent for higher fluorine content. The carbon atoms are mainly in sp² hybridization state. More recently, fluorinated graphites (denoted RT-GF) were prepared using a room temperature synthesis in presence of gaseous mixture of fluorine, HF and volatile fluorides (BF₃, IF₅, ClF_x, etc.) [5]. Firstly applied to graphite, fluorination was also applied to nanocarbons such as nanotubes [6,7], nanohorns [8], nanofibres [9] or nanodiscs [10]. The curvature of the carbon lattice also acts on the C–F bonding: In the raw fullerenes or derivatives, the carbon hybridization is not only sp² because of the curvature; the higher the curvature, the higher the percentage of sp³ hybridization is. After fluorination and the conversion of the carbon hybridization from sp² into sp³, the case is opposite. sp³ is in majority whereas a few sp² hybridization is still maintained because of the curvature. The small percentage of sp² hybridization hinders the overlapping between the atomic orbitals of carbon and fluorine, that weakens the covalence of the C–F bond [11]. For a spherical molecule, then with maximal curvature, such as highly fluorinated fullerene with composition C₆₀F₄₈, this covalence weakening affects the C–F bond strength and leads to a lack of robustness of the C–F interaction within fluorofullerene clusters.

Since several decades, fluorinated carbons and in particular graphite fluorides are well known for application as electrode

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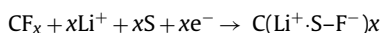
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material for primary lithium battery [12–20]. The higher the covalence, i.e. the higher the strength of the bonding, the lower the discharge potential is.

This work focuses on different nanotubes and fullerenes in order to change the curvature and to underline its effect on electrochemical discharge potential. The starting materials were then C₆₀, C₇₀ fullerenes, single, double and multiwall carbon nanotubes (SWCNTs, DWCNTs and MWCNTs), including nanofibres with large diameter because of the number of walls (about 35). According to the producer (MER corporation) the called nanofibres are MWCNTs, with no well defined internal core, produced by catalytic chemical vapor deposition (CVD) with 140 ± 30 nm diameter and 7 ± 2 μm length. Molecular fluorine has been chosen as reactive species and the reaction temperatures were optimized in order to obtain nearly similar fluorine content *x* in CF_{*x*}, i.e. the atomic F/C ratio. In such conditions, only the curvature changes because hyperconjugation is equivalent. For comparison, graphite has been fluorinated using two ways: the conventional method with F₂ and the catalytic route to complete this study.

The covalence of the C–F bonding was investigated using two parameters: (i) the chemical shifts for ¹⁹F nuclei in nuclear magnetic resonance (NMR) measurements because the values of weakened and pure covalent bonds significantly change in the –150/–190 ppm range versus CFCl₃, the lower value being related to covalent C–F; (ii) the wavenumber of the C–F vibration in infrared spectroscopy, the values being equal to 1100 and 1220 cm^{–1} for weakened and covalent bonding, respectively. These two values will be correlated with the discharge potentials in lithium batteries. Moreover, C–F bond length can be estimated using NMR [21], the increase of the covalence results in the shortening of the C–F bond length, which can also be used as an indication of the covalence.

Taking into account the strong effect of solvents on the cell open circuit voltage OCV and discharge voltage, the following discharge mechanism in Li/CF_{*x*} battery has been recently proposed [22]



where *S* represents one or more solvent molecules coordinated with each Li⁺ ion. Upon formation, the intermediate graphite intercalation compounds (GIC) subsequently decomposes into the final discharge products, carbon and lithium fluoride, as



The solvated Li⁺ ions are intercalated into graphite fluoride layers and the discharge voltage of a Li/CF_{*x*} cell is related to the solvation energy of Li⁺ ions.

Li-intercalated carbon nanotube ropes have been investigated by first-principles methods [23]. Results underline that Li⁺ intercalation potential of a single-walled nanotube rope is comparable to that of graphite. The intercalation energy is then supposed to be close whatever the CF_{*x*} materials. In our study, only the C–F bonding significantly changes since solvation energy of Li⁺ ion is equal. The comparison of the discharge potentials is then possible. Diffusion/migration resistance of Li⁺ ion in the discharged products, i.e. in graphene layers of CNFs and MWCNTs, among SWCNT bundles and among C₆₀ and C₇₀ molecules, may also act. The intercalation and diffusion of lithium ions in a bundle of carbon nanotubes (CNTs) were investigated *via* an *ab initio* molecular dynamics simulation method based on the density functional theory. The authors found that lithium ions quickly penetrate into the CNTs and the space between neighbouring CNTs [24]. The rapid diffusion of lithium into the bulk has been experimentally confirmed regarding the electronic properties of lithium intercalated single walled carbon nanotubes in a bucky paper sample, investigated by electron energy loss spectroscopy and photoemission spectroscopy [25]. The diffusion/migration resistance of Li⁺ is favoured into nanotubes and its

effect could be decreased, especially for very low applied current density.

Finally, it is important to note that the discussed properties are not thermodynamic ones but obtained by kinetic measurements. Nevertheless, the main goal of our work is to select the best fluorinated carbon materials to be used in useable primary lithium battery.

2. Strategies of fluorination and materials

2.1. Fluorination and materials

Table 1 summarizes the synthesis method of the starting materials and applied fluorination conditions (by treatment with 1 atm of pure gaseous F₂ under dynamic condition) for various nanocarbons. The complete physicochemical characterization is described in the corresponding papers.

An alternative to fluorination at high temperature (between 300 and 600 °C), generating two types of covalent fluorinated graphites (C₂F)_{*n*} and (CF)_{*n*}, consists in the use of a catalytic gaseous mixture F₂/MF_{*n*}/anhydrous HF in order to increase the reactivity of fluorine with graphite at room temperature (MF_{*n*} = IF₅, IF₇, BrF₅, ClF₃, WF₆, MoF₆, BF₃) [5]. The obtained fluorinated graphites, noted IF₅ and (C_{2.5}F)_{*n*} when IF₅ and ClF_{*x*} were used as catalyst, respectively, exhibit a semi-covalent character, i.e. weakened covalence, and similarities with graphite intercalation compounds (GICs) because few residual catalysts are still intercalated [26–28]. With the aim to both progressively convert the C–F bonding to a covalent character and to increase the fluorine content, RT-GF have been post-treated in pure F₂ gas at temperatures *T*_{PF} ranged in between 100 and 600 °C [26,29,30]; the resulting samples, denoted IF₅-*T*_{PF} (*T*_{PF} = 250, 350 and 550 °C) and (C_{2.5}F)_{*n*}-*T*_{PF} (*T*_{PF} = 250 and 350 °C), are our references. The two-step process is called bi-fluorination.

2.2. Physico-chemical characterization

Fourier Transform Infrared spectroscopy (FT-IR) was carried out using a Thermo Nicolet 5700 in Attenuated Total Reflectance (ATR) configuration. NMR experiments were performed at room temperature using a Tecmag spectrometer (working frequencies for ¹³C and ¹⁹F: 73.4 and 282.2 MHz, respectively). For ¹⁹F MAS spectra, a simple sequence was used with a single π/2 pulse duration of 5.5 μs. The ¹³C spectra were recorded using a solid echo sequence (two 5.5 μs π/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. ¹³C and ¹⁹F chemical shifts refer to tetramethylsilane (TMS) and CFCl₃, respectively.

2.3. Electrochemical study

The electrochemical tests were performed for fluorinated materials with similar fluorine content using galvanostatic discharges. The electrodes were composed of fluorinated carbon (about 80% by weight, w/w), graphite powder (synthetic graphite UF₄ from Mersen 10%, w/w) to insure electronic conductivity and polyvinylidene difluoride (PVDF 10%, w/w) as binder. After stirring in propylene carbonate (PC), the mixture was spread uniformly onto a stainless steel current collector disk of 10 mm in diameter. Finally, after the PC evaporation the disk was heated under vacuum at 150 °C for 1 h, to remove traces of water and solvent. A two electrode cell was used (Swagelok cell type), where lithium was both reference and counter electrodes. A PVDF microporous film wet with electrolyte composed of a lithium salt (LiClO₄) dissolved as 1 mol L^{–1} in PC (doubly distilled), was sandwiched between the

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