Fluorine-carbon materials

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Résumé   **Matériaux carbonés fluorés**
Les carbonés fluorés constituent d'excellents matériaux pour batteries primaires à ion Li et de possibles candidats pour anodes de batteries secondaires à ion Li utilisant des solvants organiques. Les nanocarbones fluorés tels que les fullerènes et nanotubes fluorés présentent des propriétés uniques. Cet article fait le point sur les résultats les plus récents obtenus sur les batteries lithium/fluorure de graphite, [Li/(CF)$_n$], les nouvelles techniques de fluoration de matériaux anodiques et les voies de synthèses, propriétés structurales et liaisons chimiques dans les nanocarbones fluorés.

Mots-clés   **Matériaux carbonés fluorés, fluoration, batteries lithium, nanocarbones, fullerènes fluorés, nanotubes fluorés.**

Abstract   Historical aspect on the synthesis, structures and properties of fluorinated carbon materials has been summarized. Fluorinated carbon materials are excellent cathodes of primary lithium battery and new candidates of anode for secondary lithium battery. The fluorinated nanocarbons such as fluorinated fullerenes and carbon nanotubes show unique structures and properties. The present review surveys the history of fluorinated carbon materials and recent topics on primary lithium/graphite fluoride (Li/(CF)$_n$) battery, new approach employing fluorination techniques to anode material of secondary lithium battery, and synthesis, structures and chemical bonds of fluorinated nanocarbons.

Keywords   **Fluorinated carbon materials, fluorination, lithium battery, nanocarbon, fluorinated fullerene, fluorinated carbon nanotube.**

It was reported by Ruff and Bretschneider in 1934 that the reaction of elemental fluorine with graphite at 420°C yielded gray graphite fluoride, $CF_{0.92}$ with hydrophobic and electrically insulating properties [1]. In 1947, a paper was published by Rüdorff and Rüdorff on the preparation of $CF_{0.676}$-$CF_{0.988}$ at 410-550°C and a structure model of (CF)$_n$ with sp^3 bonds was proposed [2]. The covalent nature of C-F bond [3-4] and IR spectrum of graphite fluoride [5] were also reported. Watanabe and his coworkers published several papers on the carbon anode reaction (anode effect) in electrolytic production of elemental fluorine [6-7]. Margrave and his coworkers reported the synthesis, structure and thermodynamic properties of graphite fluoride [8-10]. Lubricative properties of graphite fluoride were also examined at this time; the results were summarized in the monographs [11-12]. Fluorine reacts with graphite in the presence of an acidic fluoride at room temperature, yielding fluorine-intercalated graphite, C_xF with ionic ~ covalent C-F bond. Rüdorff and Rüdorff first reported the synthesis of stage-1 C_xF with composition of $C_{3.6}F$-$C_{4.0}F$ and structure model of C_4F [13]. Lagow *et al.* also prepared C_4F using a mixture of elemental fluorine and HF [14]. From the beginning of 1980s, several groups (Nakajima, Bartlett, Selig and their coworkers) studied the synthesis, structures and physical and chemical properties of C_xF. Hamwi, Touhara, Tressaud and their coworkers also reported the synthesis and properties on fluorinated graphite. The results are summarized in the monographs [11, 15-16]. Cardinaud and Tressaud published a review on the surface modification of carbon materials by plasma treatment using CF_4 [17]. Recently, Hagiwara *et al.* reported new data on the structures of graphite fluoride and C_xF [18].

Fluorinated carbons as cathode of primary lithium battery

Many efforts were made to manufacture primary lithium batteries using lithium anode and organic solvents. Metal fluorides (CuF_2, NiF_2, CdF_2 etc.), chlorides ($CuCl_2$, AgCl, $SOCl_2$, $POCl_3$ etc.), sulfides (Ni_3S_2, CuS etc.) and oxides (MoO_3, SO_2, Ag_2CrO_4 etc.) were investigated as cathodes of primary lithium batteries [19]. These materials were not suitable for the practical use as cathodes. It was found that the best cathode material was graphite fluoride, (CF)$_n$ [11, 20-22]. It was about 30 years ago that primary Li/(CF)$_n$ battery was commercialized by Matsushita Industries Ltd in Japan. The Li/(CF)$_n$ battery was the first widely usable battery using lithium anode and organic solvents. *Figure 1* shows the practical Li/(CF)$_n$ batteries.

Graphite fluoride is prepared by the fluorination of carbon materials using fluorine gas in the temperature range of 350 to 600°C. Two crystal forms, (CF)$_n$ and (C_2F)$_n$ are known [11, 18, 20]. In the case of a high crystalline graphite such as natural graphite, (CF)$_n$ is obtained at high temperatures close to 600°C while (C_2F)$_n$ is formed in a limited temperature range of 350 to 400°C. Between these temperatures, a mixture of (CF)$_n$ and (C_2F)$_n$ is prepared. Only (CF)$_n$ is obtained from a low crystalline carbon such as petroleum coke.

(CF)$_n$ gives a flat discharge potential between 2 and 3 V relative to Li reference electrode and high discharge capacity of ~ 800 mAh/g [11, 20-21]. (C_2F)$_n$ has the higher discharge potential than (CF)$_n$ because (C_2F)$_n$ contains active fluorine atoms bonded to sp^2 carbons. The discharge capacity of (C_2F)$_n$ is, however, lower than that of (CF)$_n$ due to its lower

Figure 1 - Li/(CF)$_n$ batteries (*National Lithium Batteries Technical Handbook*, **1985**).

Figure 2 - Graphitized petroleum coke (PC2800) (a) and that fluorinated by F$_2$ (3×10^4 Pa) at 400°C for 2 min (b).

fluorine content. Practical batteries use (CF)$_n$ prepared from petroleum coke.

Recently, new fluorinated carbon materials with high cathode performance are requested for the medical application. New candidates of the cathode are (CF)$_n$ synthesized from the carbon obtained by the decomposition of graphite oxide [11, 20-21], (C$_2$F)$_n$ prepared from graphite between 350 and 400°C [11, 20], fluorine-graphite intercalation compound, C$_x$F prepared at room temperature [11, 15, 22], and graphite fluoride prepared by refluorination of C$_x$F at high temperatures [23]. The (CF)$_n$ prepared from the residual carbon has large discharge capacities of ~ 850 mAh/g and high energy densities of ~ 1930 Wh/kg. C$_x$F prepared at room temperature has the higher discharge potential than (CF)$_n$ prepared at high temperatures. Graphite fluorides obtained by high temperature refluorination of C$_x$F samples which are prepared at room temperature also have high discharge capacities and energy densities [23].

Application of fluorination techniques to anode of secondary lithium battery

It was in 1990 that lithium ion secondary battery was first proposed by Sony Co. Ltd. For the development of secondary (rechargeable) lithium battery with high performance, the importance of fluorine chemistry is rapidly increasing. High crystalline graphite is mainly used as anode material of lithium ion battery. Several methods of surface modification such as surface oxidation, surface fluorination and carbon coating have been applied to improve the anode characteristics of carbon materials [22]. High temperature fluorination of carbon materials by elemental fluorine easily proceeds with formation of C-F covalent bonds accompanying carbon-carbon bond breaking. In the case of natural graphite samples ($\approx$ 7, $\approx$ 25 and $\approx$ 40 μm, BET surface area: 4.8, 3.7 and 2.9 m^2/g, respectively), light fluorination (F$_2$: 3×10^4 Pa, 200°C~350°C, 2 min) increased specific surface areas by 39-78% and small mesopores with
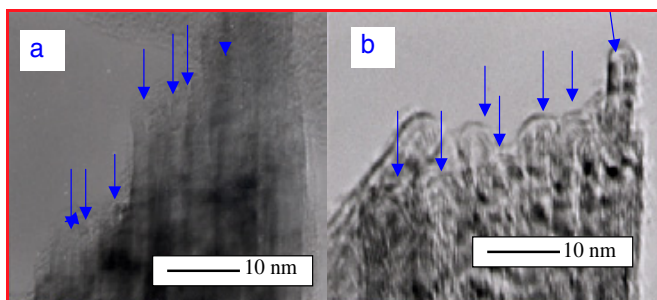
diameters of 1.5-2 nm and 2-3 nm [22, 24-25]. Plasma-fluorination using CF$_4$ effectively fluorinates only thin surface layers of graphite to change the surface structure [26]. Charge/discharge cycling experiments showed that surface fluorination of these natural graphite samples by elemental fluorine and plasma treatment increased their discharge capacities to 380~390 mAh/g, which are higher than the theoretical capacity of graphite, 372 mAh/g, corresponding to fully lithium-intercalated graphite, LiC$_6$ [22, 24-26].

On the other hand, petroleum cokes graphitized by heat-treatment at 2300, 2600 and 2800°C (PC2300, PC2600 and PC2800) have different surface structure from natural graphite. During the graphitization at 2300-2800°C, surface oxygen is removed as CO, accompanying carbon-carbon bond breaking. Resulting dangling bonds are combined with each other during the graphitization process, giving closed edge plane as shown in *figure 2a* [27]. Coulombic efficiencies (= discharge capacity/charge capacity) at 1st cycle were 71.9%, 67.0% and 65.4% for PC2300, PC2600 and PC2800 at 60 mA/g, respectively, while those of petroleum coke samples heat-treated at 1860 and 2100°C were 90.2% and 90.5%, respectively [22, 27-28]. Light fluorination opened the closed edge surface of graphitized petroleum coke as shown in *figure 2b*, highly increasing the first coulombic efficiencies of PC2300, PC2600 and PC2800 to 84.1%, 79.1% and 83.6%, respectively, i.e. reducing their irreversible capacities (*table I*) [22, 27-28]. Plasma-fluorination using CF$_4$ is also effective for opening the closed edge surface of graphitized petroleum cokes, increasing their first coulombic efficiencies.

Table I - First coulombic efficiencies (%) for petroleum coke samples at a current density of 60 mA/g.

Fluorination temperature (°C)	Petroleum coke					
	PC	PC1860	PC2100	PC2300	PC2600	PC2800
Non-fluorinated	72.3	90.2	90.5	71.9	67.0	65.4
300°C	47.4	83.3	87.1	84.1	79.1	83.6

Syntheses, structures and chemical bonds of fluorinated nanocarbons

Fluorination is one of the most effective chemical methods to modify and control physicochemical properties of carbon materials [29-31]. Some visual demonstrations are made to show how effectively fluorination can modify nanocarbon materials. *Figure 3a* shows activated carbon
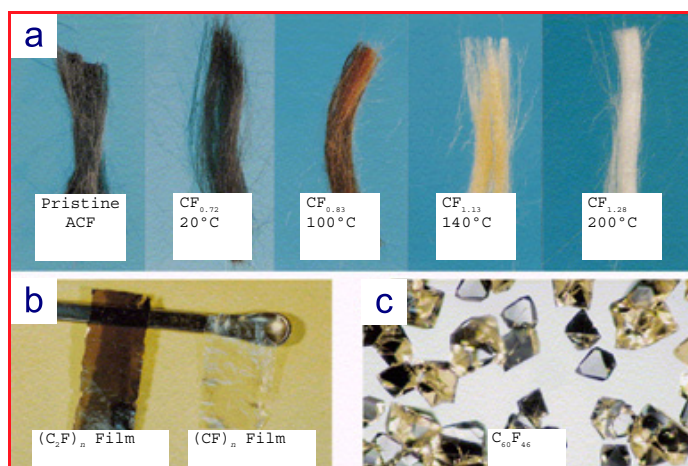
Figure 3 - (a): activated carbon fibers before fluorination, and fluorinated under F_2 (1×10^5 Pa) for seven days at 20, 100, 140 and 200ºC; (b): fluorinated carbon films, dark transparent $(C_2F)_n$ and transparent $(CF)_n$; (c): single crystals of fluorinated fullerene $C_{60}F_{46}$.
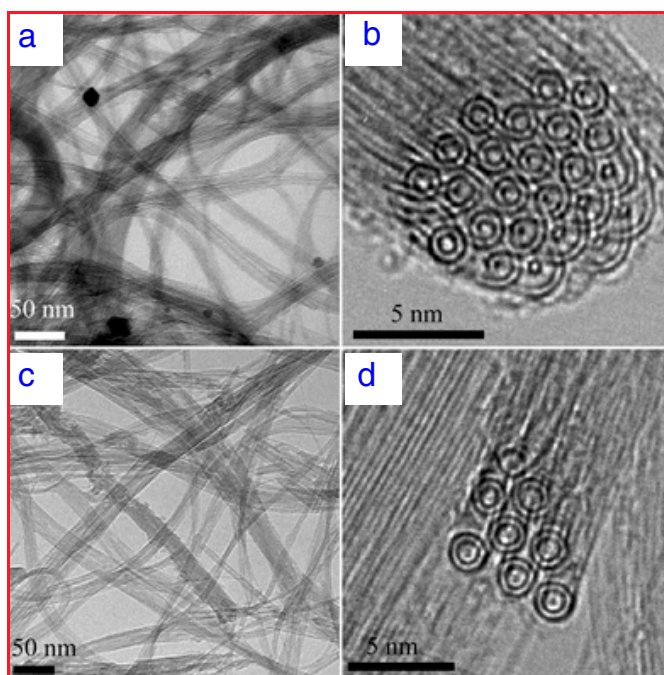

Figure 4 - (a): low-resolution and (b): high-resolution cross-sectional TEM images of the pristine DWNTs; (c): low-resolution and (d): high-resolution cross-sectional TEM images of the fluorinated DWNTs.

fibers (ACFs) fluorinated at different temperatures [32]. ACF consists of fibrous aggregates of nano-sized graphite. The colors of fluorinated ACFs (F-ACFs) vary from black, through brown and yellow, to white. The F/C atomic ratio ($CF_{0.72}$ - $CF_{1.28}$) and color are strongly dependent on the fluorination conditions. The characteristic variation in the color of the F-ACFs indicates the progressive change of C-F bonding nature from ionic to covalent bond, hence the electronic structure of F-ACFs. *Figure 3b* shows fluorinated HOPG (highly-oriented pyrolytic graphite) films as comparison materials towards nanocarbons. The transparent film is graphite fluoride $(CF)_n$ and the dark and transparent film is $(C_2F)_n$. The former is a stage-1-type fluorine-graphite intercalation compound made by the direct fluorination of graphite at 600ºC and the latter a stage-2-type compound at 400ºC. *Figure 3c* shows single crystals of fluorinated fullerene $C_{60}F_{46}$. The $C_{60}F_{46}$ powder was made by the direct fluorination of fullerene C_{60} at 225ºC under F_2 (1×10^5 Pa) for two days [33]. The single crystals were grown by subliming $C_{60}F_{46}$ powder. $C_{60}F_{46}$ powder before crystal growth looks white. It is amazing that brown/black C_{60} is transformed into transparent single crystals, which resemble diamond in appearance. This resemblance is explained by the electrical insulating nature of both diamond and $C_{60}F_{46}$. However, $C_{60}F_{46}$ crystal is very fragile while diamond is very hard. This is explained by the differences in structure and chemical bonding of the two materials. $C_{60}F_{46}$ is a molecular solid with inter-molecular van der Waals interactions and intra-molecular C-F and C-C covalent bonds, while diamond has an infinite network of covalent C-C bonds. The difference in colors of C_{60} and $C_{60}F_{46}$ resembles that of graphite and graphite fluoride $(CF)_n$. As demonstrated above, fluorination of nanocarbons can change their structural and electronic properties in a very wide range.

A series of investigations have been carried out on fluorination of nanocarbons such as fullerenes [34-35], single-walled carbon nanotubes (SWNTs) [36], double-walled carbon nanotubes (DWNTs) [37], multi-walled carbon nanotubes (MWNT) [31], cup-stacked carbon nanotubes [38] and carbon nanohorns [39]. The behavior of DWNTs towards fluorination is particularly interesting [37]. DWNTs were fluorinated with F_2 (1×10^5 Pa) at 200ºC for 5 h. The stoichiometry of the fluorinated DWNTs determined by XPS

was $CF_{0.30}$ with C-F covalent bonds. TEM images of the pristine and fluorinated DWNTs (F-DWNTs) are shown in *figure 4*. The low-resolution images show that DWNTs exist mainly in bundles both before and after fluorination. The high-resolution (HR) images show that DWNTs are hexagonally packed. It is noteworthy that double-walled cylindrical shells are clearly observed for the F-DWNTs. The hexagonal packing structure is disturbed probably due to the fluorine atoms bound to the outer shells of DWNTs. By tuning the electronic property of only the outer shell and by controlling the dispersability of DWNTs without disrupting the double-layered concentric shell morphology through fluorination, we envisage these chemically modified DWNTs to be useful in the fabrication of novel sensors, nanocomposites and electronic devices, *e.g.* a nano-sealed-wire with an inner conducting "SWNT" sealed coaxially by an outer insulating "F-SWNT" can be prepared by fluorination of DWNTs. The fluorination chemistry of nanocarbons is extensive and diverse, and is expected to bring about further development in energy-related applications such as lithium cells, electric double layer capacitors, fuel cells [40], gas storage, and synthons for the preparation of new forms of nanocarbons.

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