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# $C_{60}$-Inorganic fluorides intercalation compounds: some formation condition data and their electrochemical behavior in lithium cell systems

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**Abstract**

An overview of our contribution to the worldwide work on fluorinated carbons and inorganic fluorides-based intercalation compounds is presented. Recent results concerning the intercalation of $NbF_5$, $TaF_5$ and $TiF_4$ into the $C_{60}$ lattice and the behavior of a wide series of $C_{60}(MF_n)_x$ phases used as cathode materials in lithium batteries are described. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Fluorinated graphite; Fluorinated fullerenes; Inorganic fluorides; Intercalation compounds; Lithium batteries

## 1. Introduction

In our laboratory, we have been working for several years in fluorine chemistry, inorganic fluorides synthesis and their intercalation compounds with graphite. We have investigated the intercalation reaction of metallic or non-metallic fluorides $MF_n$ ($BF_3$, $IF_5$, $NbF_5$, $TaF_5$, $MoF_6$, $WF_6$, ...) with graphite in a fluorine atmosphere and, generally, first stage compounds were formed [1]. Because of their excellent performances as cathode materials for lithium batteries, graphite fluorides have been intensively studied all over the world [2,3]. Still recently, we succeeded in obtaining improved electrochemical performances [4] when the graphite fluoride synthesis was performed at room temperature, in the presence of a gaseous mixture composed of a volatile fluoride (like $IF_5$)-anhydrous HF–$F_2$ [5]. In such conditions, the formed compounds present a semi-ionic character of the C–F bond and planarity or quasi-planarity of the graphene layers [6]. Note that graphite is completely inert towards a pure fluorine atmosphere at room temperature and up to 300°C, for which weakly fluorinated graphite compounds $CF_x$ are obtained. The $x$ value varies from 0.5 to 1 as the temperature is increased from about 350 to 600°C, the C–F bond being considered to be highly covalent since the planarity of the carbon layers is lost.

Although, the research in chemistry of graphite lasts since several decades, it directly contributed to the emergence of very interesting results for fullerenes and their inorganic derivatives since only few years. Thus, by analogy with graphite, fullerenes intercalation compounds with alkali metals (A) were prepared and were later characterized as high temperature superconductors, for the composition $A_3C_{60}$. The study of the last born allotropic forms of carbon happened therefore, as a natural continuity in our work. Unlike graphite, fullerenes $C_{60}$ and $C_{70}$ readily react with gaseous elemental fluorine at room temperature, yielding a broad range of poorly crystallized fluorinated fullerenes with average formulae $C_{60}F_{46}$ and $C_{70}F_{52}$ [6]. Increasing the reaction temperature up to 300°C allowed us to restrict the composition range and highly crystallized compounds of formulae $C_{60}F_{54}$ [7] and $C_{70}F_{56}$ [8] were obtained in much shorter reaction times. Globally, the electrochemical behavior of fluorinated fullerenes strongly depends on the composition as well as on their reactivity with the electrolyte [6]. Fluorination of carbon nanotubes was also studied using the same conditions as graphite, at room or at high temperature (500°C) [9]. At present, it seems that the electrochemical properties of fluorinated carbon nanotubes are quite different from those of graphite fluorides [10].

Concerning fullerene $C_{60}$ intercalation compounds, we have also shown that $C_{60}$ is very reactive towards some inorganic fluorides. We have reported the solid–gas reaction of $C_{60}$ with $MoF_6$ and $IrF_6$ and compounds having up to nine $MoF_6$ and 19 $IrF_6$ per $C_{60}$ were obtained [11]. Some other

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fluorides also react with $C_{60}$ but the final $MF_n/C_{60}$ ratios never reached the one observed for $MoF_6$ [12]. $WF_6$ and $TiF_4$ showed a low reactivity whatever the reaction time, giving compounds with low ratios, whereas gaseous $BF_3$ and $MoF_5$, for instance, do not react with $C_{60}$. Consequently, it turns out that Lewis acidity is not the only criterion governing the intercalation process and a strong oxidizing power is required as well. In previous papers [11,12], we reported on the reactivity of fullerenes towards inorganic fluorides $NbF_5$, $TaF_5$ and $TiF_4$. However, under reaction conditions (time, temperature) similar to the ones generally used for the intercalation of fluorides into graphite, the $x = MF_n/C_{60}$ ratios, measured by mass uptake, never exceeded two and the formation of reduced fluorides was observed. By varying the experimental conditions, we recently succeeded to synthesize compounds with higher $x$ values with these fluorides. In this paper, we will therefore report some additional results explaining the conditions allowing to obtain different novel phases with $NbF_5$, $TaF_5$ and $TiF_4$, which exhibit a good crystallinity and appreciable $MF_n/C_{60}$ ratios. As already observed [12], anionic $MF_x^{y-}$ species have been identified. Their presence may suggest a fullerene oxidation process. As part of an exploratory research program on materials suitable for use as electrodes in lithium cells, we will also present some results on the behavior of several $C_{60}(MF_n)_x$ compounds.

## 2. Intercalation of metallic fluorides into the $C_{60}$ lattice

### 2.1. Synthesis and characterization

The starting mixture was composed of about 40 mg $C_{60}$ and metal fluoride in excess. Table 1 gives suitable temperatures at which high ratios could be obtained for many fluorides and Fig. 1 illustrates, from an example with $TaF_5$, the role of the reaction temperature, for a constant reaction time. The influence of the reaction time, for a given temperature, also appears as a determining parameter. While the weight uptake increased as a function of time and reached maximum values in the cases of $MoF_6$ and $WF_6$, the behavior is very different for $NbF_5$, $TaF_5$ and $TiF_4$. In these latter cases, the maximum ratio $x$ was reached relatively quickly and decreased for longer reaction times. Fig. 2 shows an example for the reaction with $NbF_5$ at 150°C.

Thus, after a short reaction time, X-ray diffraction patterns showed new isostructural $MF_n$-rich intercalated phases

Table 1
Experimental conditions giving the highest $MF_n/C_{60}$ ratios for different metal fluorides

| Fluorides $MF_n$ | $MoF_6$ | $WF_6$ | $NbF_5$ | $TaF_5$ | $TiF_4$ |
|---|---|---|---|---|---|
| Reaction temperature (°C) | 60 | 40 | 150 | 210 | 400 |
| Reaction time (day) | 7 | 4 | 0.6 | 1 | 1 |
| $MF_n/C_{60}$ ratio | 9.2 | 1.27 | 10 | 6 | 0.58 |

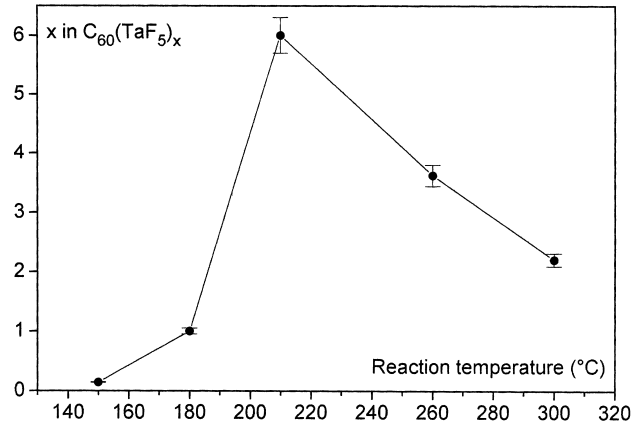


Fig. 1. Evolution of the $TaF_5/C_{60}$ ratio as a function of the reaction temperature, for a 24 h reaction time (line is a guide to the eye and error bars denote the accuracy in the determination of $x$).

for both $NbF_5$ and $TaF_5$ fluorides. After longer reaction times, Bragg reflections characteristic of $C_{60}$ and $MF_3$ predominate. The observed weight loss should therefore be due to the decomposition, at the moderately high temperature used, of the initial $MF_n$-rich phases. Infra-red spectra showed intense bands in the 400–700 $cm^{-1}$ region, assigned to reduced and anionic fluorinated species such as $MF_3$, $MF_6^-$, $MF_7^{2-}$ according to $x$. As observed earlier [11], the intensities of the $C_{60}$ characteristic bands decreased as the $x$ value increased and completely disappeared for the highest $x$ values. $^{19}F$ NMR measurements also confirmed the presence of $MF_6^-$, $MF_7^{2-}$ and neutral $MF_n$ species. Fig. 3 shows typical NMR spectra obtained from samples of different $C_{60}(NbF_5)_x$ compositions. A main narrow line was observed at about 221 ppm/$CF_3COOH$ and another one clearly appeared at about +180 ppm for the highest $x$ values (the chemical shifts values reported in the literature are $\delta = +193$ and +152 ppm for $NbF_6^-$ and $NbF_7^{2-}$, respectively, and +220 ppm for $NbF_5^-$ in graphite intercalation compounds [13]).

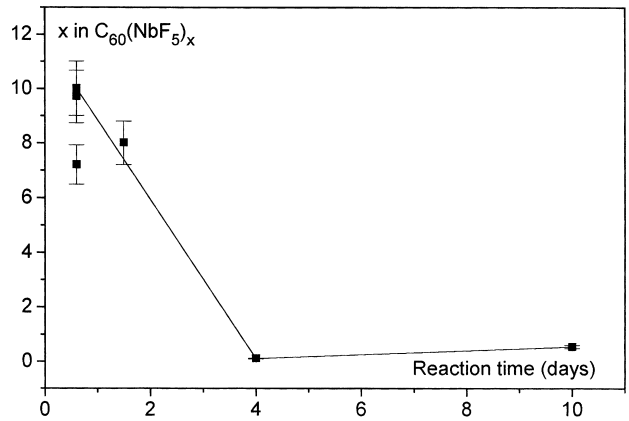


Fig. 2. Evolution of the $NbF_5/C_{60}$ ratio as a function of the reaction time, at 150°C (line is a guide to the eye and error bars denote the accuracy in the determination of $x$).

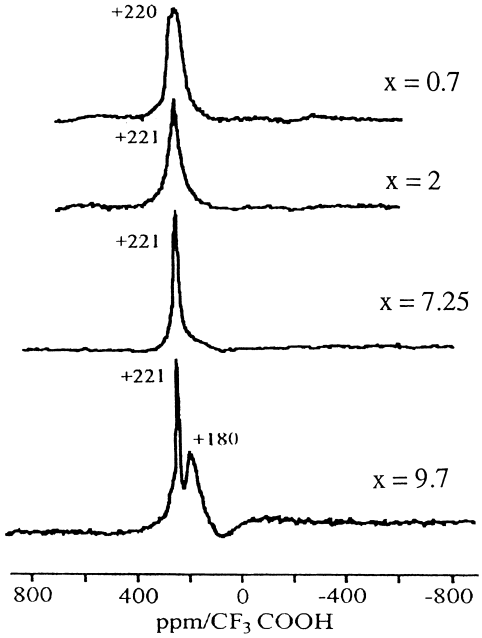


Fig. 3. Room temperature $^{19}F$ NMR spectra of different $C_{60}(NbF_5)_x$ compounds.

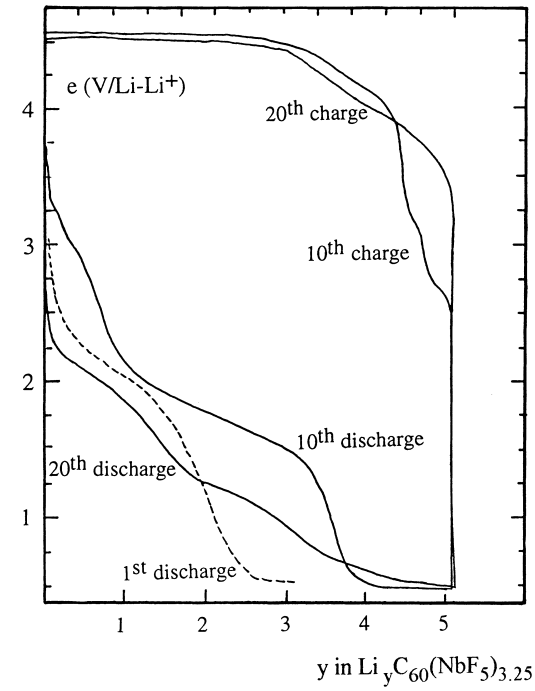


Fig. 5. Galvanostatic charge-discharge curves of $C_{60}(NbF_5)_{3.25}$ ($i = 50$ μA).

### 2.2. Electrochemical studies

The electrochemical study was carried out using Li/$LiClO_4$− 1 M, PC/$C_{60}(MF_n)_x$ (PC = propylene carbonate) lithium cells, operated at room temperature. The $C_{60}(MF_n)_x$ mass used was between 10 and 15 mg each time. The intensiostatic discharge curves for a current intensity of 50 μA are presented in Figs. 4–6 for $MF_n = WF_6$ and $TiF_4$, $NbF_5$, and $TaF_5$, respectively. They generally show a plateau at about 2 V versus $Li^+/Li$. The number of lithium corresponding to the complete discharge of each system is in the range 2–5 Li per $C_{60}$. As already reported in the case of

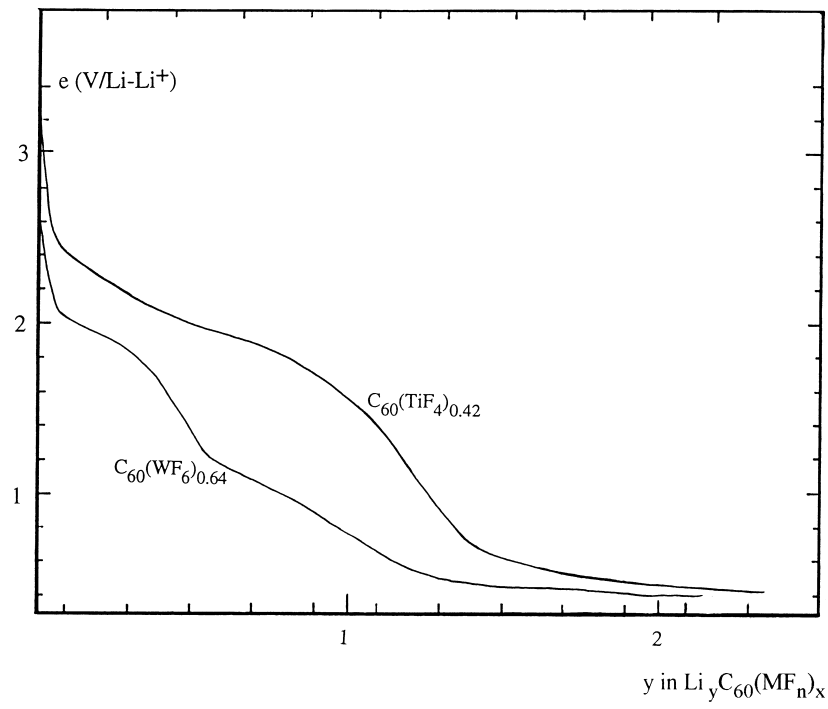


Fig. 4. Galvanostatic discharge curves of $C_{60}(TiF_4)_{0.42}$ and $C_{60}(WF_6)_{0.64}$ ($i = 50$ μA).

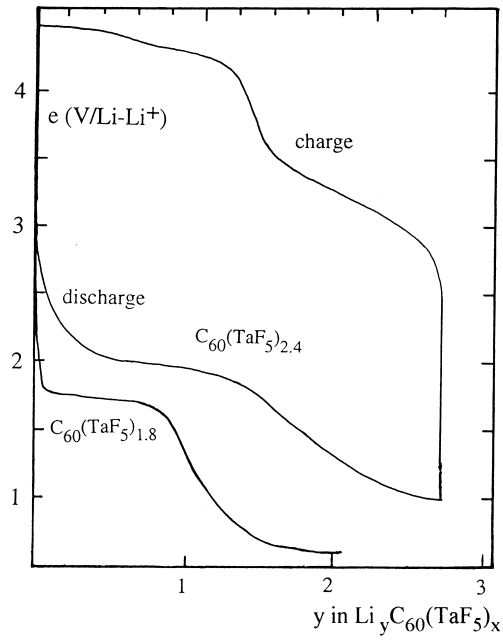


Fig. 6. Galvanostatic charge-discharge curves of $C_{60}(TaF_5)_x$ ($i = 50$ μA).

$MF_n$-graphite intercalation compounds [14], we suggest that during the discharge process $Li^+$ cations intercalate into the lattice and form a complex with the metallic anions. The global reduction scheme should be written:

$$C_{60}{}^{\delta+} + p\,MF_{n+y}{}^{y-} + yp\,Li^+ + yp\,e^- \rightarrow C_{60}{}^{(\delta-yp)-} + p\,Li_yMF_{n+y}$$

and corresponds to a reduction of the carbon molecules. Somehow, the strong evolution of the curves shape on cycling (see Fig. 5) seems to indicate that the above reaction is very partially reversible and that other electrochemical processes have to be considered after few discharges.

Some cyclic voltammetry curves are presented in Figs. 7 and 8. As shown in these figures and in previous Fig. 5, most systems exhibit a good reversibility of the charge–discharge process after several cycles. A strong hysteresis of at least 2 V is observed during the reoxidation step, which may be due to a variation in the conductivity of the compounds upon lithium doping and/or to the presence of some local disorder.

Much work would remain to be done in order to characterize these materials during discharge.

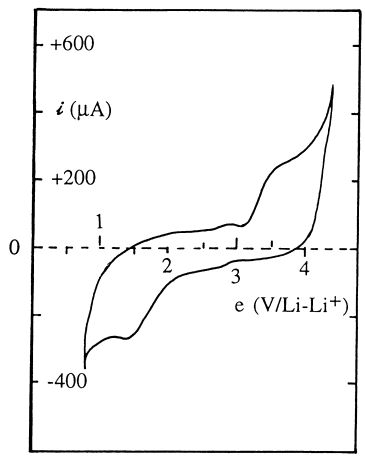


Fig. 7. Cyclic voltammetry curve (15th cycle) of $C_{60}(TaF_5)_{2.4}$ (15 mV $min^{-1}$).

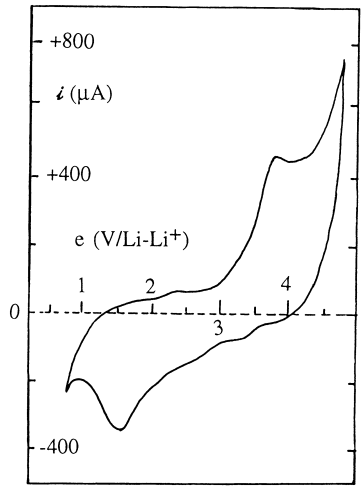


Fig. 8. Cyclic voltammetry curve (20th cycle) of $C_{60}(NbF_5)_{2.5}$ (15 mV $min^{-1}$).

## 3. Conclusions

Up to date, graphite fluoride prepared at room temperature remains the last practically useful cathode material for primary lithium batteries. So far, fullerene–metal fluorides intercalation compounds, fullerene fluorides and fluorinated carbon nanotubes cannot be considered for such an application because of their low efficiency and actual high cost.

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