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C₆₀-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 NbF₅, TaF₅ and TiF₄ into the C₆₀ lattice and the behavior of a wide series of C₆₀ (MF_n)_x phases used as cathode materials in lithium batteries are described.

Keywords: fluorinated graphite; fluorinated fullerenes; inorganic fluorides; intercalation compounds; lithium batteries

1. Introduction

In our laboratory, we've 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 (BF₃, IF₅, NbF₅, TaF₅, MoF₆, WF₆,...) 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 IF₅)-anhydrous HF-F₂ [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 latter 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 9 MoF_6 and 19 IrF_6 per C_{60} were obtained [11]. Some other 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 criteria 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 2 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 NbF₅, TaF₅ and TiF₄, which exhibit a good crystallinity and appreciable MF_n/C₆₀ 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 C₆₀(MF_n)_x compounds.

2. Intercalation of metallic fluorides into the C₆₀ lattice

2.1. Synthesis and characterization

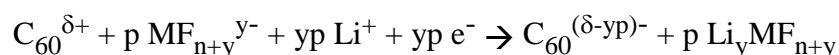
The starting mixture was composed of about 40 mg C₆₀ and metal fluoride in excess. Table 1 gives suitable temperatures at which high ratios could be obtained for many fluorides and figure 1 illustrates, from an example with TaF₅, the role of the reaction temperature, for a constant reaction time. The 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 MoF₆ and WF₆, the behavior is very different for NbF₅, TaF₅ and TiF₄. In these latter cases, the maximum ratio *x* was reached relatively quickly and decreased for longer reaction times. Figure 2 shows an example for the reaction with NbF₅ at 150°C.

Thus, after a short reaction time, X-ray diffraction patterns evidenced new isostructural MF_n-rich intercalated phases for both NbF₅ and TaF₅ fluorides. After longer reaction times, Bragg reflections characteristic of C₆₀ and MF₃ 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 MF₃, MF₆⁻, MF₇²⁻ according to *x*. As observed earlier [11], the intensities of the C₆₀ characteristic bands decreased as the *x* value increased and completely disappeared for the highest *x* values. ¹⁹F NMR measurements also confirmed the presence of MF₆⁻, MF₇²⁻ and neutral MF_n species. Figure 3 shows typical NMR spectra obtained from samples of different C₆₀(NbF₅)_x compositions. A main narrow line was observed at about 221 ppm/CF₃COOH 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]).

2.2. Electrochemical studies

The electrochemical study was carried out using Li/ LiClO_4 -1M, PC / $\text{C}_{60}(\text{MF}_n)_x$ (PC = propylene carbonate) lithium cells, operated at room temperature. The $\text{C}_{60}(\text{MF}_n)_x$ mass used was between 10 and 15 mg each time. The intensiostatic discharge curves for a current intensity of 50 μA are presented in figures 4, 5, 6 for $\text{MF}_n = \text{WF}_6$ and TiF_4 , NbF_5 , and TaF_5 , respectively. They generally show a plateau at about 2 V vs 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 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:



and corresponds to a reduction of the carbon molecules. Somehow, the strong evolution of the curves shape on cycling (see figure 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 figures 7 and 8. As shown on these figures and on previous figure 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.

3. Conclusion

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 can not be considered for such an application because of their low efficiency and actual high cost.

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Tables and figures captions

Table 1: Experimental conditions allowing to obtain the highest $\text{MF}_n/\text{C}_{60}$ ratios for different metal fluorides.

Figure 1: Evolution of the $\text{TaF}_5/\text{C}_{60}$ 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).

Figure 2: Evolution of the $\text{NbF}_5/\text{C}_{60}$ 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).

Figure 3: Room temperature ^{19}F NMR spectra of different $\text{C}_{60}(\text{NbF}_5)_x$ compounds.

Figure 4: Galvanostatic discharge curves of $\text{C}_{60}(\text{TiF}_4)_{0.42}$ and $\text{C}_{60}(\text{WF}_6)_{0.64}$ ($i=50 \mu\text{A}$).

Figure 5: Galvanostatic charge-discharge curves of $\text{C}_{60}(\text{NbF}_5)_{3.25}$ ($i=50 \mu\text{A}$).

Figure 6: Galvanostatic charge-discharge curves of $\text{C}_{60}(\text{TaF}_5)_x$ ($i=50 \mu\text{A}$).

Figure 7: Cyclic voltammetry curve (15th cycle) of $\text{C}_{60}(\text{TaF}_5)_{2.4}$ ($15 \text{ mV}\cdot\text{min}^{-1}$).

Figure 8: Cyclic voltammetry curve (20th cycle) of $\text{C}_{60}(\text{NbF}_5)_{2.5}$ ($15 \text{ mV}\cdot\text{min}^{-1}$).

Table 1

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