

NOVEL GRAPHITE INTERCALATION COMPOUNDS WITH FLUORINE,
AND FLUORIDES: SYNTHETIC PATHWAYS, PROPERTIES AND
MANIFESTATION MECHANISM OF FUNCTIONALITY

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ABSTRACT

Attempts have been made to prepare a series of fluorine- and fluoride-graphite intercalation compounds (GICs), physical and chemical properties of which are well controlled in a wide range. Because of the interactions characteristic of fluorine with graphite, controlled reactions of elemental fluorine have been applied to a very broad array of carbon materials ranging from a precursor of graphite, mesophase pitch to HOPG. In addition to the direct fluorination method, a new synthetic pathway to involatile fluoride-GICs has been developed in anhydrous hydrogen fluoride (AHF) solutions which are saturated with F_2 and fluoro-metallates. The intercalation reactions in these systems have been investigated by means of X-ray diffraction, and *ab initio* MO calculations for species which are concerned with the intercalation reactions.

The diverse properties of these GICs suggest a number of potential applications such as high electrical conductors, battery, electrode materials, precursors for two-dimensional metal clusters and so on.

INTRODUCTION

We have seen a great number of graphite intercalation compounds prepared, and their chemical and physical properties investigated. The preparations, however, have been made more or less haphazardly owing to the limited amount of data available on the graphite intercalation compounds. Furthermore a little attention has been paid to the systematic property change within a single system; some system, for example, exhibits a wide range of property differences in conductivity and color according to the

composition change. Once the relationships between reaction conditions, compositions and properties become clear, it will be possible to control the intercalation reactions to obtain a desired property in a given system. With the use of MO calculations a new compound with new properties may be able to be synthesized as designed. Based on these considerations we have carried out the following investigations.

EXPERIMENTAL

The importance of fluorine gas purity in fluorine-graphite reaction cannot be stressed enough. Particularly, HF has a strong influence on the intercalation reactions and on the resulting compounds. The fluorine gas used in this work was supplied by Daikin Industries, Ltd.. Its purity is higher than 99.7% with most of the impurities being nitrogen. This level of purity was attained by charging fluorine into the cylinder through the vaporization of liquid fluorine. Before being used, trace amounts of HF were further removed by passing the gas through NaF columns heated at 100 °C. The HF content was estimated to be less than 0.01 mol% by infrared spectroscopy [1]. Mesophase pitch, activated carbon fibers and HOPG chips (5x5 mm, ca. 0.5 mm thick) were heat-treated at 600 °C in vacuo prior to use. The nickel reaction tube equipped with the stainless steel vacuum system was passivated before each reaction by combination of repeated evacuation and introduction of fluorine. Each carbon material contained in a nickel vessel in the reaction tube was then exposed to 1 atm fluorine at prescribed temperature. After a desired reaction time, the system was evacuated and filled with argon. Further experimental details have been given elsewhere [2,3].

As for the preparations of involatile fluoride-GICs, all of the fluorides used were treated by fluorine at appropriate temperatures. Hydrogen fluoride purified by repeated distillations was introduced in the Kel-F reaction tube containing HOPG chips and the fluoride. Fluorine gas was then admitted to flow intermittently at 15 °C for several hours, and the reaction system was allowed to stand for prescribed days. After the reaction, HF was removed by evaporation using a flow of pure argon.

RESULTS AND DISCUSSION

Carbon-Fluorine Compounds C_xF .

The structural properties of starting carbon materials have an important influence not only on fluorination or fluorine intercalation reaction, but also on physical and chemical properties of the resulting compounds. The results for mesophase pitch, activated carbon fibers and HOPG are shown with typical examples.

F₂-Mesophase Pitch System: Mesophase pitch and mesocarbon micro-beads react with elemental fluorine at extremely low temperatures ranging from 0°C to 250°C to produce CF_{0.84}-CF_{1.27}. The X-ray diffraction data indicate that the products are lamellar compounds with the repeat distance

I_C of 6.8-7.4 Å. The C-F bond is almost of covalent character, which is evidenced by C_{1s} and F_{1s} binding energies. An attractive feature of these compounds is that a transparent thin film (3000-5000 Å) can be formed on metal and silicon substrates by means of vacuum vapor deposition at around 400 °C. This film has a larger contact angle (113°) against water than PTFE (109°) indicating the lower surface energy.

E₂ -Activated Carbon Fiber System: Activated carbon fibers (ACFs) prepared from rayon-derived precursor material readily react with elemental fluorine at significantly low temperatures ranging from 20-200 °C under fluorine pressure of 100-760 torr to give fluorinated ACFs(F-ACF), $CF_{0.72}$ - $CF_{1.28}$. The colors of F-ACFs vary from black, through brown and yellow, to white. The F/C atomic ratio and color are strongly dependent on the fluorination temperature, pressure, and time. However, they approach a certain F/C and color under a fixed fluorination temperature after a prolonged reaction time. The characteristic variation in the color of the F-ACFs can be explained in terms of C-F bond nature, hence the electronic structure of F-ACFs. Spectroscopic studies by solid state ^{19}F -NMR, IR, XPS indicated that the nature of the C-F bond in F-ACFs varies from physical adsorption, through semi-ionic to completely covalent bonds, depending on the reaction temperatures, which are lower than 200 °C. The strong interaction of ACFs with fluorine arises from the characteristic structural properties such as the microcrystallinity with monodispersive micropores, and the defects where dangling bonds exist and unpaired electrons are trapped.

E₂ -HOPG System: No reaction occurs between HOPG and elemental fluorine at room temperature even with a high fluorine pressure of 5 kbar, and 19-day reaction time. This result still suggests that graphite and fluorine gas do not interact at ordinary temperature and pressure, when the vacuum line is well passivated by fluorine free from Lewis acid impurities. On the other hand, spontaneous intercalation of fluorine into graphite has recently been found in the presence of gaseous or liquid HF. Compositions, structural and physical properties of resulting compounds C_xF , C_xHF_2 , and $C_xF_{1-y}(HF)_y$ strongly depend on preparative methods and HF content in the reaction system.

In this context, the interaction between graphite and elemental fluorine with available highest purity (less than 0.01 mol% HF impurity) has been examined at 50 °C in an assembled line which is vacuum tight to the order of 10^{-9} torr. Under the conditions, the rate of reaction was unusually low, but fluorine-graphite intercalation compounds C_xF ($15 > x > 5.6$) have been obtained by longer reaction time exceeding 30 days. The values of identity period I_C and the intercalate thickness d_i of stage-2 $C_{6.3}F$ are 9.46 and 2.76 Å, respectively. The d_i value is almost the same as the size of fluoride ion.

Fig.1 shows the chemical shifts of C_{1s} and F_{1s} binding energies of fluorine-graphite compounds and reference materials. The C_{1s} binding energies of stage-2 C_6F , 284.2 eV, is the same as that of pristine HOPG, and F_{1s} binding energies, 686 eV, is close to that of LiF. These results suggest that C_6F reserves the planarity of carbon layers with SP^2

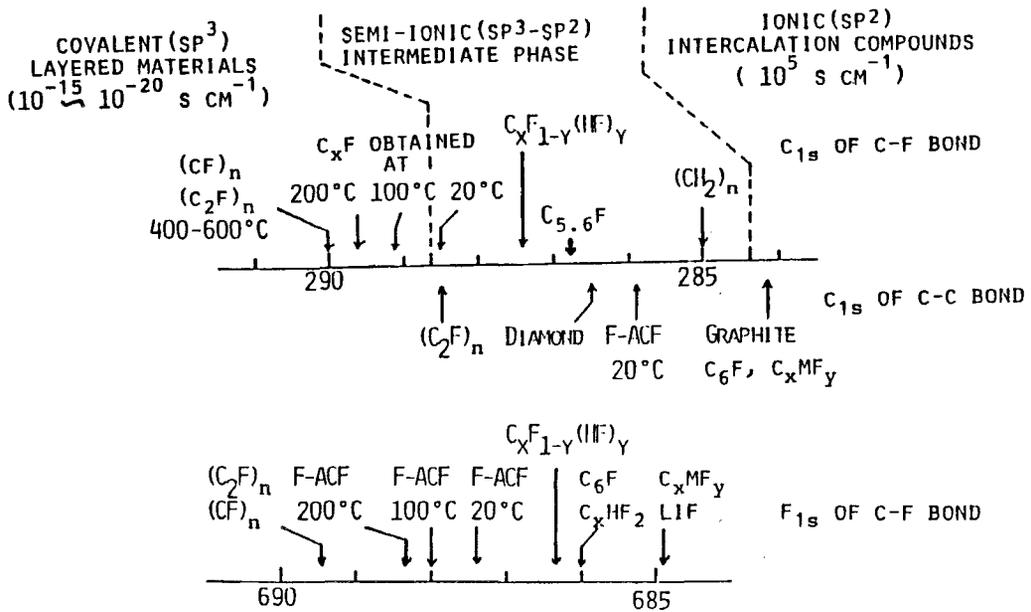


Figure 1. XPS binding energies(eV) of fluoride-graphite intercalation compounds

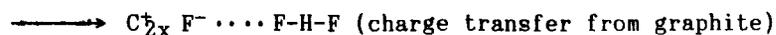
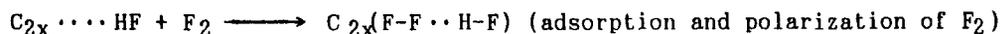
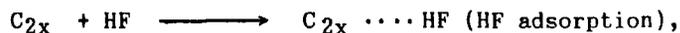
hybridization and that the C-F bond is completely ionic in character. The material shows high electrical conductivity with metallic behaviour. The stage-1 C_{5.6}F prepared from HOPG, C_xF-obtained at 20°C from ACF, and graphite hydrofluoride C_xF_{1-y}(HF)_y have semi-ionic C-F bonds, namely, intermediate hybridization between SP² and SP³; this is because their C_{1s} binding energies lie between those of graphite and graphite fluorides (CF)_n and (C₂F)_n, which are formed by the fluorination of graphite at temperature higher than 400°C. C_xF obtained from ACF at temperatures higher than 100 °C, (CF)_n and (C₂F)_n have C_{1s} binding energies near 290 eV and F_{1s} binding energies near 689 eV, indicating covalent compounds of graphite. These materials are electrical insulators.

Based on the experimental results and discussion so far, it is obvious that one can control physical and chemical properties of fluorine-graphite compounds by the choice of starting carbon materials with different structural properties and by the control of fluorination or fluorine intercalation conditions. Among simple binary systems, only with fluorine-graphite system is it possible to control physical properties of resulting compounds in a wide range from "synthetic metal" to electrical insulator.

Intercalation Reactions in Fluorine-HOPG System and Cl₂-HOPG System.

Since the impurity amount of HF has a strong influence on fluorine intercalation, *ab initio* MO calculations have been carried out by Gaussian 82 program with a 6-31 G** basis set. Geometrical optimization and

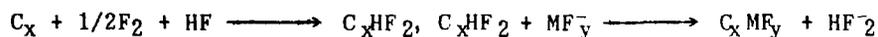
energies calculations were performed by Moller-Plesset perturbation method of second order (MP2) and forth order (MP4/SDTQ), respectively. The results show that charge transfer dose occur from fluorine to HF and the F₂-HF complex has a considerable stabilization energy (-10.5 kJ/mol). F₂ molecule consequently becomes a polarizable "soft Lewis acid". On the basis of these results and relevant experimental evidences, spontaneous fluorine intercalation reaction mechanism is deduced as follows;



The same calculations were extended to the Cl₂-HF system. Although the interaction in this system is slightly weaker than that of the F₂-HF, changes in molecular properties and charge distribution occur via Cl₂-HF complex formation. No reaction, however, has been observed between Cl₂-HF and F₂. Therefore, the interaction between chlorine and HOPG has been examined under the presence of HF or F₂. Chlorine intercalation dose occur after 14-day reaction in 2atm chlorine at 15 °C, but fluorine intercalation occurs simultaneously. The pure stage-2 compounds are C₁₁₋₁₂ClF with d_i values of 3.06-3.26 Å. These materials are very stable even in moist air. The other stage compounds other than stage-2 are obtained as admixtures.

Involatile Fluoride-GIC.

We have found a new synthetic pathway to involatile fluoride-based GICs in liquid AHF which is saturated with fluorine gas and the species to be intercalated. The intercalation reaction proceeds through the substitution of bifluoride by fluorometallate as follows;



An attractive feature of this method is that the stage can be controlled by changing the concentration of fluorometallate in AHF. This preparative method has been giving a series of new C_xMF_y based on involatile fluorides, SnF₄, PbF₄, CrF₄, SbF₃, RhF₃, and LiBF₄.

Properties and Potential Applications.

The fluorine-graphite system and intercalations in liquid AHF solutions provide a number of GICs containing fluorine and fluorometallate, respectively. The diverse properties of these materials, ranging from high electrical conductor through intermediate phase with semi-ionic C-F bonds to insulator, suggest potential applications. Here emphases are placed on battery applications, because all of these compounds could be good candidates for active materials in a primary or a secondary battery. Electrochemical characteristics have so far been investigated on the following cells: lithium cells with an electrolyte solution, Li/LiClO₄-PC/C_xF, C_xMF_y; all-solid-state lithium cells with a polymer electrolyte, Li/Li⁺-(PEO)₈/C_xF, C_xMF_y. Typical examples are shown in Fig.2. Among these, the lithium cells with an electrolyte solution are still more interesting and important from the viewpoint of battery

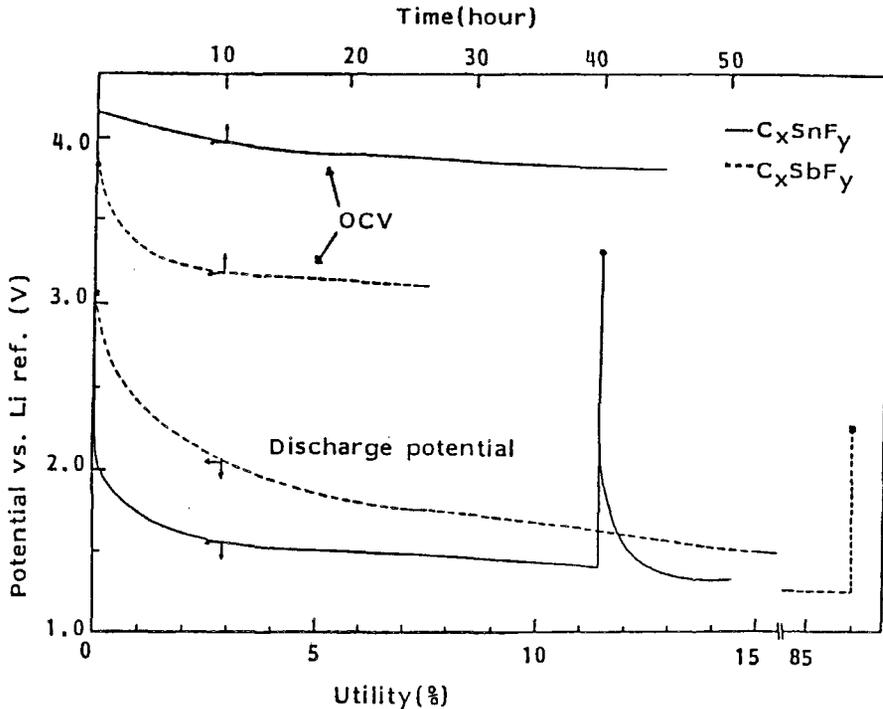


Figure 2. OCV stability and discharge curves of Li/1M LiClO₄-PC/C_xSnF_y, C_xSbF_y cells at 0.1mA/cm² current density.

performances: high open-circuit voltage(OCV), low overpotential, high cathode utilization and energy density. The important results obtained recently for the cells are summarized as follows. As shown in Figure 3, OCV values against the Li reference electrode varies as a function of the fluorination temperature, that is, a function of the nature of interaction between fluorine and carbon layers; the ionic compounds C_xF and C_xMF_y show very high OCVs, 4-4.2V, and the values decrease to ca. 3.2V with increase in the covalency of C-F bond. On the contrary, cathode overpotentials increase with increasing ionic property in the C-F bond. Structural properties of GICs have also important influences on overpotential, cathode utilization, and stability of discharge potential. Each GIC has an optimum size of crystallite along both the ab-axis and the c-axis so as to optimize the above three battery performances.

The required properties of electrode materials in batteries for GICs have almost become clear, and a turning point in GIC chemistry has come; now we should try to prepare "designed GIC", with controlled physical, chemical, and structural properties.

Another interesting property of the GICs is their high electrical conductivity. In-plane electrical conductivities(σ_a) of fluorine-HOPG intercalation compounds C_xF are given in Table 1. In the case of the

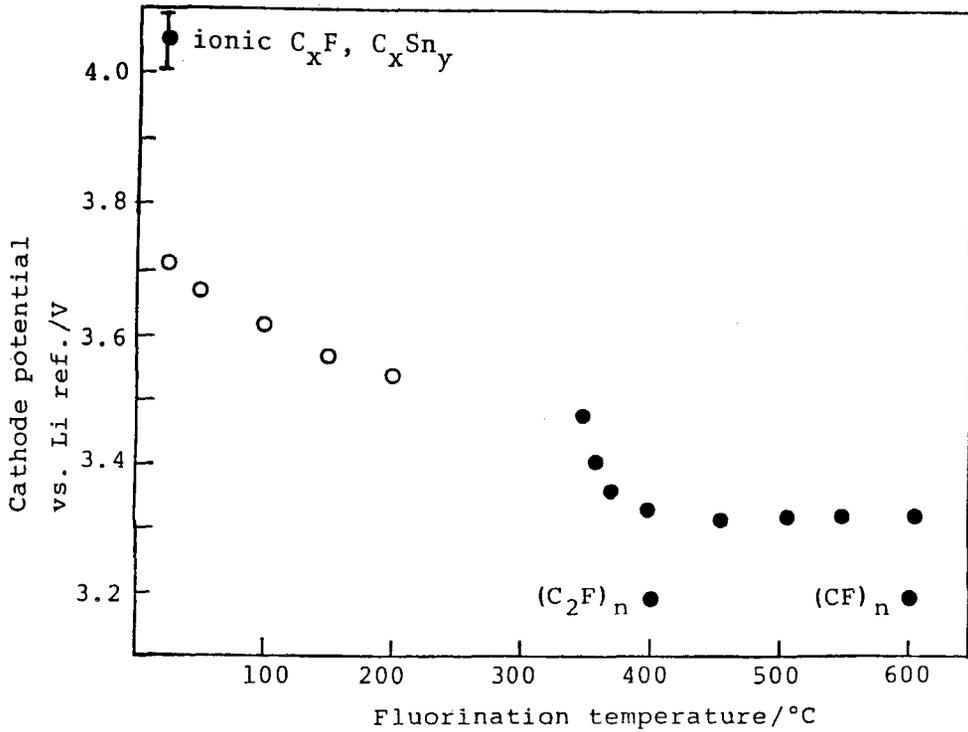


Figure 3. Dependence of OCV values on fluorination temperature.
 ○, fluorine intercalated ACFs;
 ●, fluorine intercalated VGCFs.

TABLE 1
 In-plane electrical conductivities (σ_a) of C_xF at 298.15 K

Sample	Stage	$\sigma_a / S \text{ cm}^{-1}$	$\sigma_a / \sigma_a^a \text{ HOPG}$
$C_{11.7}^F$	Mixture of 3 and 4	6.7×10^4	9.7
$C_{10.5}^F$		7.9×10^4	8.3
$C_{14.4}^F$	Mixed stage of 2 and 3	9.0×10^4	8.9
$C_{11.0}^F$		1.5×10^5	9.3
$C_{6.4}^F$	2	9.3×10^4	7.1
$C_{6.3}^F$		8.9×10^4	7.9
$C_{5.6}^F$	Mixture of 2 and 1	4.8×10^4	4.9

a: pristine HOPG's with different $\sigma_a \text{ HOPG}$ are used.

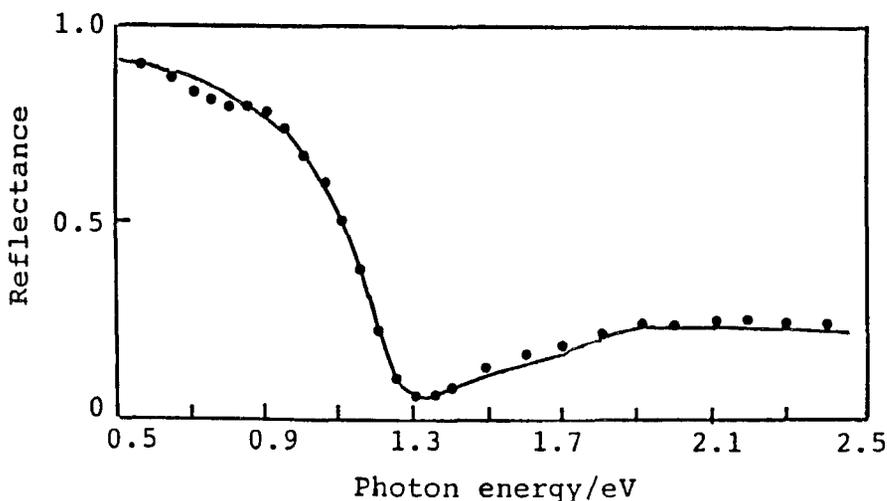


Figure 4. Reflectance spectrum of stage-2 C_6F . Closed circles, observed values; solid line, fitting curve based on Blinowski-Rigaux model.

mixed stage compound of stage 2 and stage 3, the in-plane conductivity is in the order of 10^5 S/cm. This value is about 10 times higher than that of pristine HOPG. In order to elucidate the high electrical conductivity, the reflectance spectra were measured as a function of photon energy. A typical example is given in Fig.4 for stage-2 C_6F . A metallic reflectance is observed in the low frequency region followed by the plasma edge with a well pronounced minimum in the 1.3 eV energy region. For the qualitative analysis of the reflectance data, we used 2D band structure to describe electronic states in the low stage GICs. The tight binding method is applied taking intra- and inter-layer nearest neighbour interactions into account. From the theoretical fitting of experimental spectrum, we have deduced the some physical properties as are given in Table 2. The most important and interesting results are on carrier density and hole mobility. The carrier density of stage-2 C_xF obtained at 50°C is 100 times higher than that of pristine HOPG, whereas the hole mobility of the GIC is 1/10 of the pristine HOPG. This results in high electrical conductivity of the GIC. The hole mobilities increase with decreasing temperature of intercalation. These results suggest that less defective crystal is formed at lower temperature.

TABLE 2
Physical properties of stage-2 C_xF

Intercalation temperature	Fermi	Relaxation	Charge	Optical	Carrier	Hole
	energy/eV	time/x10 ⁻¹⁴ s	transfer	conductivity	density	mobility
				x 10 ⁴ scm ⁻¹	10 ²¹ cm ⁻³	cm ² V ⁻¹ s ⁻¹
5 0 °C	0. 9 2	3. 0	0. 0 1 6	6. 6	1. 3	3 1 7
1 5 °C	0. 9 4	4. 4	0. 0 1 6	9. 9	-	4 7 5
- 2 0 °C	0. 9 3	7. 2	0. 0 1 6	1 6	-	7 6 8
- 8 0 °C	0. 9 7	1 1. 0	0. 0 1 7	2 6	1. 4 2	1 1 3 0

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