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Long-term stability of fluorine–graphite intercalation compound prepared under high pressure of fluorine

Hiroyuki Fujimoto [a,*], *Alain Tressaud* [b]

[a] *Energy Technology Laboratories, Osaka Gas Co., Ltd., 6-19-9 Torishima, Konohana-ku, Osaka 554-0051, Japan*

[b] *Institut de Chimie de la Matière Condensée de Bordeaux, CNRS, Université Bordeaux, 87 Avenue Dr. A. Schweitzer, 33608 Pessac, France*

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ABSTRACT

Fluorine–graphite intercalation compounds were prepared from highly oriented pyrolytic graphite (HOPG) and natural graphite under high pressure of fluorine (16 MPa) at room temperature and were analyzed by means of X-ray diffraction. The rate of intercalation under high pressure of fluorine was higher than that under ordinary pressure. The compositions of the compounds obtained from HOPG and natural graphite were estimated by the weight change before and after fluorination to be $C_{3.41}F$ and $C_{5.62}F$, respectively. They were blue–black compounds composed of two different phases. One phase is a conventional stage II C_xF with the repeat distance of ca. 0.93–0.96 nm which was the same compound as that obtained under ordinary pressure of fluorine, and the other was also a stage II with a different repeat distance of ca. 1.03–1.18 nm. The fluorine species intercalated between the graphene layers can easily move between both phases and the phase transition occurs periodically. The decomposition rate of fluorine-intercalated HOPG was extremely low and it shows a long-term stability in air for 26 years.

1. Introduction

Graphite fluorides, $(CF)_n$ and $(C_2F)_n$, are well-known as compounds obtained by direct fluorination of carbon materials [1–5], and the former has been already commercialized as cathode material of primary lithium batteries. These compounds are generally prepared from rather well crystallized graphite at temperatures considerably higher than 300 °C, that is at ca. 600 °C for $(CF)_n$, and 350 °C for $(C_2F)_n$. Between these temperatures, mixtures of $(CF)_n$ and $(C_2F)_n$ are obtained. Below 300 °C, it was initially believed that fluorine does not react with graphite. However, in 1980's, Nakajima et al. found that graphite does react with fluorine in the presence of some metal fluorides such as LiF, MgF_2 and CuF_2 to give C_xF graphite intercalation compounds (GIC) [6–8]. After that, Mallouk et al. found that fluorine intercalates into graphite in the presence of gaseous or liquid hydrogen fluoride even at room temperature [9,10]. Vaknin et al. prepared C_xF by exposing HOPG to fluorine gas for several days [11]. They found "pure" stage II within the composition range C_8F–C_4F. They concluded that completely filled stage II, III and IV compounds correspond to C_4F, C_6F, C_8F formulations, respectively. After these studies, a new type of C_xF GIC with a repeat distance, I_c of ca. 1.1 nm was independently found by Ohana and by Nakajima [12–14]. Concerning these GIC, Ohana proposed a new stage II model in which fluorine molecules were oriented perpendicularly

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[*] *Corresponding author*: Fax: +81 6 4801 9567.
E-mail address: hfuji@osakagas.co.jp (H. Fujimoto).

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to the graphene sheets, while Nakajima suggested a bi-intercalation structure in which two kinds of C–F bonds (ionic and semi-ionic), having different lengths are present in every other graphene layer. However, they did not calculate in detail the structure factors of their model, and the discussion about which structure is feasible remained inconclusive. In addition, the recent studies by Panich and Sato et al. have clarified that the so-called "semi-ionic bond" is rather "substantially-covalent" than "semi-ionic" [15–18].

The main object of the present study is to elucidate the detailed structure of C_xF GIC by the calculations of the structure factor, F_{00l} and electron density and to refine the structural parameters by the fitting of observed X-ray diffraction (XRD) profiles with using the structure factors. Though the other groups also have reported concerning the C_xF GIC [16,19,20], all the previous studies were carried out under an atmospheric F_2 pressure, and the behavior of graphite under a high pressure of fluorine had not been investigated. The second object in the present study is therefore to investigate C_xF GIC obtained under a high pressure of fluorine, in particular their long-term stability in air.

2. Experimental and results

2.1. *Preparation of the* C_xF **intercalation compounds**

Highly-oriented pyrolytic graphite (HOPG) (5 × 5 × 3 mm samples) and flaky natural graphite were used as starting materials for preparing C_xF. These graphite materials were placed in a nickel reaction tube and evacuated at 150 °C for 1 h. After that, fluorine gas was introduced up to 0.05 MPa into the reactor pre-cooled by liquefied nitrogen. Then, the pressure of F_2 in the reactor was increased by heating the tube up to room temperature. Finally, the graphite samples were reacted with 16 MPa of fluorine for 20 h. After the fluorination, residual fluorine was passed through a CaO tower to be removed in the form of CaF_2. Hereafter, fluorinated HOPG and natural graphite will be referred to as F-HOPG and F-NG, respectively.

The compositions of F-HOPG and F-NG estimated from the weight uptakes just after preparation were $C_{3.41}F$ and $C_{5.62}F$, respectively. It clearly indicates that the reactivity of carbon and fluorine and the structure of the resulting compound by the fluorination largely depend on the crystallinity of pristine graphite. The carbon with higher crystallinity requires longer reaction time. The degree of graphitization of natural graphite is higher than that of HOPG. Moreover, the interlayer spacing of the former (0.3354 nm) is slightly smaller than that of HOPG (0.336). That is why the stage number of the F-NG is higher than that of the F-HOPG.

Ohana et al. reported that it takes several days to prepare the C_xF under ordinary pressure of fluorine. They also reported that, using HOPG samples of 5 × 5 × 0.5 mm size, it is very hard to obtain C_xF GIC with x lower than 4, and that it is easy to obtain higher fluorine concentrations by choosing very thin pristine HOPG (less than 20 pm along the z-axis direction), then reaching $C_{2.3}F$ composition. With the experimental conditions given above, HOPG samples of 3 mm thickness react under high pressure fluorine for 20 h yielding ~$C_{3.4}F$ final compositions. The required reaction time to get the C_xF GIC is decreased because of the higher reactivity under higher F_2 pressures.

Speaking empirically, the graphite structure changes from sp^2 to sp^3 by the fluorination reaction and the planarity of graphene is lost depending on the degree of fluorination. At the same time, the gloss of the graphite is also gradually lost and changes to white via brown. The electrical conductivity is also lost. However, the F-HOPG is a metallic blue–black compound, and its electrical conductivity was 9.3×10^3 $S cm^{-1}$. It indicates that the sp^2 bonding nature of the pristine graphite is maintained after the fluorination.

2.2. *Stability of* C_xF *GIC in air*

In order to examine the stability of C_xF in air, the weight change of F-HOPG over time was investigated. When the C_xF-GIC is kept in the glass tube, the inside of the tube becomes cloudy gradually because of HF formed by the reaction of moisture and fluorine desorbed. Hence, the amount of de-intercalated and/or desorbed fluorine species can be simply estimated by the weight change before and after intercalation. We don't have to consider the effect of the reactions between the fluorine desorbed and other species. Fig. 1 shows the weight changes and the corresponding composition changes of F-HOPG as a function of elapsed days. During the first 5 days, the weight decreased abruptly by 4% and the corresponding composition changed from $C_{3.41}F$ to $C_{3.95}F$. During the following two weeks, the weight was almost constant. After that, the weight decreased again by 2% and the composition became $C_{4.16}F$ after 40 days. The first weight decrease would be mainly due to the desorption of adsorbed fluorine onto the surface of the F-GIC subsequent to the abrupt pressure release. Of course, some decomposition of F-GIC might somewhat occur. The second weight loss could be linked to the phase transition. The degree of decomposition will discussed later.

Such a stepwise weight decrease of F-HOPG was interpreted in relation to the modification of XRD profiles in air, as shown in Fig. 2. We observed 6 diffraction lines in the range

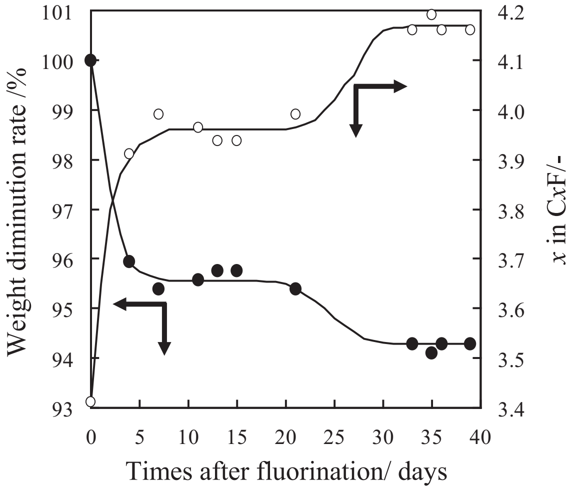

Fig. 1 – Changes in weight and subsequent composition of F-HOPG C_xF over time.