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The Preparation of Poly(dicarbon monofluoride) *via* the Graphite Intercalation Compound

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Poly(dicarbon monofluoride), $(C_2F)_n$ is prepared with a higher reaction rate *via* the graphite intercalation compound formed through a reaction with F_2 and AlF_3 than from exfoliated graphite itself. The former process also has the advantage of including the formation of exfoliated graphite by the decomposition of an intercalation compound and its fluorination. The graphite fluoride thus prepared contained $(C_2F)_n$ by 60—78%. The reaction time required for completing the reaction did not give a linear relationship, but a minimum point around 267×10^2 Pa against the fluorine pressure and there was almost no increase above 667×10^2 Pa of fluorine. However, the F/C ratios of graphite fluoride had, inversely, a maximum point against the fluorine pressure, indicating that the $(C_2F)_n$ content in graphite fluoride was approximately proportional to the reaction time.

There are two kinds of graphite fluorides, poly(carbon monofluoride), $(CF)_n$ and poly(dicarbon monofluoride), $(C_2F)_n$.[1] The former is now commercially available and is used as a cathode material of lithium batteries and as a solid lubricant. $(C_2F)_n$ also has great possibilities as a new active mass for lithium batteries because it shows a higher discharge potential than $(CF)_n$,[2] however, compared with $(CF)_n$, it takes a significantly longer time to prepare $(C_2F)_n$ due to the low formation temperature, 350—400 °C. In order to facilitate the reaction rate of carbon with fluorine, exfoliated graphite[3] has been employed as a starting material; the results indicate that $(C_2F)_n$ in prepared at lower temperatures, 335—374 °C, with a higher reaction rate than in the case of flaky natural graphite.[4] It has been found that metal fluorides, such as AlF_3 and MgF_2, with a high sublimation or boiling point are intercalated into graphite layers with fluorine and that $(C_2F)_n$ is formed through the decomposition and subsequent fluorination of the graphite intercalation compound.[5,6] In this paper, the preparation of $(C_2F)_n$ *via* the graphite intercalation compound is reported.

Experimental

The starting materials are Madagascar natural graphite (149—279 μm, purity 99.4%), petroleum coke heat-treated at 2700 °C, commercial aluminum fluoride (purity 98%), and high-purity fluorine gas (purity 99.7%) supplied by the Daikin Kogyo Company, Ltd. The fluorination reaction was carried out using an automatic thermobalance.[7] Aluminum fluoride (50 mg) and graphite (50 mg) were placed in a nickel vessel hung by a nickel spring. After fluorine gas had been introduced into the nickel reaction vessel, the reaction system was kept at room temperature for 1 or 2 h; the temperature was then increased to 357—393 °C at a rate of 16 °C/min, followed by a reaction at that temperature until no weight increase was observed. The graphite fluoride thus prepared was analyzed by means of X-ray diffractometry and elemental analysis. The reaction was stopped prior to the complete fluorination of graphite, and the reaction rate was compared with that in the fluorination of exfoliated graphite by analysing the intermediate products.

Results and Discussion

Formation Process of Graphite Fluoride via *Graphite Intercalation Compound.* A typical thermogravimetric curve is shown in Fig. 1. Almost no weight charge was detected in the AlF_3–F_2 system at temperatures between room temperature and 400 °C; however, in the ternary system of natural graphite, AlF_3, and F_2, a weight increase due to the formation of a graphite intercalation compound was observed. The increase in temperature to 350—400 °C caused the decomposition of the intercalation compound, with an accompanying weight decrease, when natural graphite was expanded along the c-axis by release of the intercalant. A large weight increase was observed due to the subsequent fluorination of exfoliated graphite at temperatures between 350 and 400 °C:

$$\text{Graphite} + AlF_3 + F_2 \xrightarrow[\text{Room temperature}]{} C_xF(AlF_3)_y$$

$$\xrightarrow[350\text{—}400\ ^\circ C]{F_2} \text{Formation of exfoliated graphite} \xrightarrow[350\text{—}400\ ^\circ C]{F_2}$$

$$\text{Graphite fluoride} + AlF_3$$

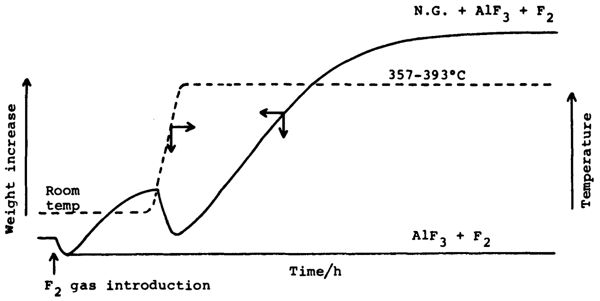

Fig. 1. Thermogravimetry for the reactions of AlF_3 with F_2 and of natural graphite (N.G.) + AlF_3 with F_2.

TABLE 1. COMPOSITION OF INTERMEDIATE PRODUCTS PREPARED FROM NATURAL GRAPHITE + AlF_3 AND FROM EXFOLIATED GRAPHITE AT 357 °C

Reaction time/h	Natural graphite + AlF_3 F/C ratio	Exfoliated graphite F/C ratio
0.3	0.06	0.03
1	0.17	0.05
2	0.15	0.07
4.5	0.40	0.16

TABLE 2. REACTION TIME AND STRUCTURAL PARAMETERS OF GRAPHITE FLUORIDE PREPARED FROM NATURAL GRAPHITE-AlF_3 SYSTEM (F_2: 267×10^2 Pa)

Reaction temp/°C	Reaction time at room temp	Reaction time at 357—393 °C	d_{001}/nm	β_{001}/°	F/C ratio
	h	h			
357	1	49	0.86	3.4	0.55
357	2	22	0.81	3.5	0.69
376	2	16	0.84	3.8	0.64
393	2	9	0.83	3.9	0.71
357[a]	—	32	0.89	2.9	0.57

a) Prepared from exfoliated graphite.

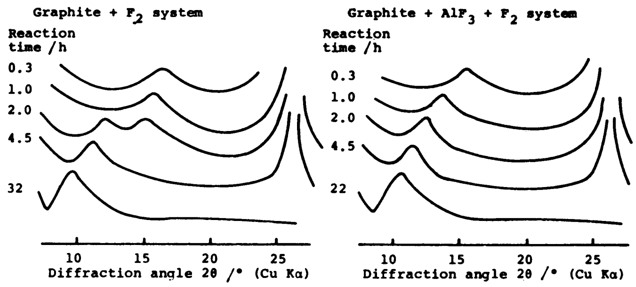

Fig. 2. Variation of (001) diffraction patterns of graphite fluoride prepared at 357 °C as a function of reaction time.

Comparison of Reaction Rates between Exfoliated Graphite and Graphite with AlF_3 Systems. In order to compare the reaction rate of exfoliated graphite with that of flaky natural graphite with an AlF_3 system, the fluorination was stopped at the initial stages of the reaction and the intermediate products were analysed. The reaction times for graphite with an AlF_3 system were those when the reaction system was above 335 °C, while for the reaction of exfoliated graphite, fluorine gas was introduced into the thermobalance maintained at a reaction temperature and the elapsed time after fluorine introduction was adopted as the reaction time. The results of elemental analyses of the products are shown in Table 1. The products obtained from graphite with an AlF_3 system contained more fluorine than those from exfoliated graphite, though the complete combustion of the products was difficult in analysis by the conventional oxygen-flask method.[8] Figure 2 shows the X-ray diffraction patterns of these products. The small peaks between 10° and 15° in 2θ (by Cu $K\alpha$) are due to graphite fluoride, while the strong ones around 26° are due to the unreacted graphite. Since much unreacted graphite remains at the initial stage of the reaction, the intensity of the X-ray diffraction peaks for graphite fluoride was much weaker than those of unreacted graphite, though they gradually increased with the progress in the fluorination reaction. With an increase in the reaction time, the diffraction peak shifted from a higher angle due to $(CF)_n$ to a lower one due to $(C_2F)_n$ for both exfoliated graphite and graphite with AlF_3 systems, which means that $(CF)_n$ is first formed around the surface with disordered structure, followed by the formation of $(C_2F)_n$. The movement of the diffraction peak to a lower angle is faster in graphite with an AlF_3 system than for exfoliated graphite. Table 2 gives the analytical data of the products as a function of the reaction time at room temperature and also the reaction temperatures after the temperature-increase to 350—400 °C. The time required for completing the reaction was 22 h for graphite with an AlF_3 system, while it was 32 h for exfoliated graphite at 357 °C. The fluorination of graphite proceeds faster *via* the graphite intercalation compound than that of exfoliated graphite. Another advantage is that the former process includes the formation of exfoliated graphite and its fluorination.

The amount of F_2 and AlF_3 intercalated into graphite depends on the reaction time at room temperature. When the reaction time is short, only a small amount of F_2 and AlF_3 is intercalated into graphite. As a result, graphite is not fully expanded in the temperature-increase process and it takes a longer time to finish the fluorination of graphite. However, the product contains larger amount of $(C_2F)_n$ because of the lower expansion of graphite. The reaction time decreased with an increase in the reaction temperature between 357—393 °C. Compared with graphite fluoride prepared from exfoliated graphite at 357 °C, the interlayer spacing, d_{001}, of that prepared from graphite with an AlF_3 system decreased by 0.05—0.08 nm, while the half-width and the F/C ratio increased by 0.6—1° and 0.07—0.14 respectively, which means that the latter graphite fluoride contains a smaller amount of $(C_2F)_n$ than the former. These results are attributed to the larger expansion of the graphite formed by the decomposition of the intercalation compound than that of the exfoliated graphite used for comparison; this attribution was confirmed by the analytical data (Table 2) of the expanded products.

Effect of Fluorine Pressure on the Reaction Rate. The time required for completing the reaction did not give a linear relationship, but a minimum point around 267×10^2 Pa against the fluorine pressure. The reaction times were almost the same above 667×10^2 Pa of fluorine, whereas under 133×10^2 Pa it was about twice that under 267×10^2 Pa (Fig. 3). On the contrary, the F/C ratio of the products had a maximum value under 267×10^2 Pa of fluorine (Fig. 4). As was reported in a previous paper,[3] the $(C_2F)_n$ contained in graphite fluoride can be related to the F/C ratio by representing the amounts of $(C_2F)_n$ and $(CF)_n$ as x and $1-x$ respectively: $F/C=1-1/2\times x$. The values calculated by the above equation are as follows: $(C_2F)_n$, 76—78% (F_2: 800×10^2—1013×10^2 Pa); $(C_2F)_n$, 70% (F_2: 133×10^2,

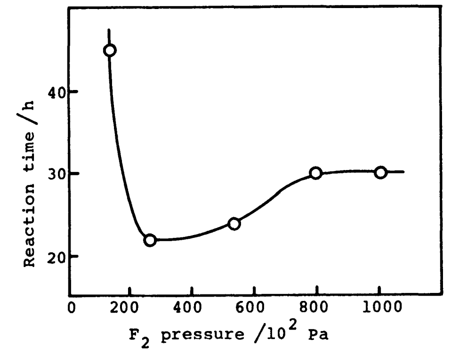

Fig. 3. Variation of reaction time of graphite fluoride as a function of F_2 pressure. Reaction temperature: 357 °C.

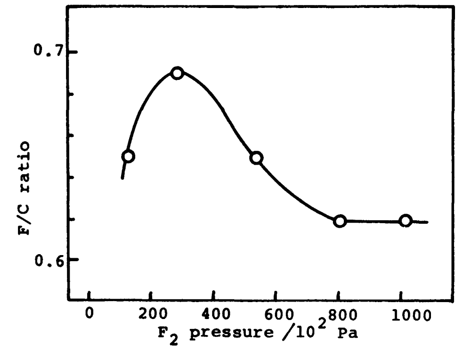

Fig. 4. Variation of F/C ratio of graphite fluuoride as a function of F_2 pressure. Reaction temperature: 357 °C.

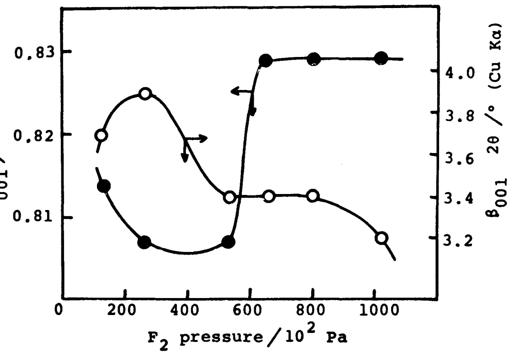

Fig. 5. Variation of d_{001} and β_{001} of graphite fluoride as a function of F_2 pressure. Reaction temperature: 357 °C.

533×10^2 Pa); $(C_2F)_n$, 62% (F_2: 267×10^2 Pa). With a decrease in the content of $(C_2F)_n$ in graphite fluoride, the interlayer spacing d_{001}, decreases, while the half-width, β_{001}, increases much as in graphite fluoride with a low crystallinity. These results show that the highest reaction rate observed under 267×10^2 Pa of fluorine is attributable to the rapid decomposition of the intercalation compound, accompanied by the large expansion of graphite. The fluorine uptake by graphite was almost the same at room temperature even under fluorine pressures of higher than 267×10^2 Pa; however, in the same range of fluorine pressure, a smaller expansion of graphite was observed, probably because the release of fluorine by the decomposition of the intercalation compound was restrained by the higher atmospheric pressure in the temperature-increase process. As a result, the reaction rate of graphite with fluorine is slower under fluorine pressure above 267×10^2 Pa. On the other hand, under a fluorine pressure of 133×10^2 Pa, the amount of fluorine absorbed by graphite at room temperature was much smaller than in other cases and the graphite was not largely expanded on the temperature-increase, which would lead to a slow reaction rate under a low fluorine pressure.

Table 3. Preparation of $(C_2F)_n$ from petroleum coke (PC)

Reaction system	Reaction temp/°C	Reaction time/h	F/C ratio	d_{001}/nm	β_{001}/°
PC–AlF_3	385	7	0.71	0.76	4.4
PC–MgF_2	383	9	0.73	0.81	4.4
PC	380	33	0.71	0.87	4.3
PC	380	13	0.67	0.86	4.3

F_2 pressure: 1013×10^2 Pa.

Preparation of $(C_2F)_n$ from Petroleum Coke (PC). Table 3 shows the data for graphite fluoride prepared from petroleum coke. As in the case of natural graphite, the reaction time decreased in the presence of AlF_3. The addition of MgF_2 also gave a similar result. The F/C ratios and half-widths of the (001) diffraction lines were slightly larger than those for graphite fluorides prepared by the direct fluorination of petroleum coke whereas the interlayer spacings, d_{001}, had an opposite relation.

As is shown in Fig. 4, graphite fluoride prepared under a fluorine pressure of 267×10^2 Pa contains the maximum amount of $(CF)_n$ in the case of natural graphite. A comparison of this graphite fluoride with that prepared from petroleum coke in the presence of AlF_3 or MgF_2 reveals that $(C_2F)_n$ is preferentially formed from natural graphite with larger crystallites. The $(C_2F)_n$ content is estimated to be 54—58% for PC with an AlF_3 or MgF_2 system and 59—66% for a PC system.

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