Properties and initial discharge behaviour of graphite fluorides decomposed under chlorine

RIKA HAGIWARA, TSUYOSHI NAKAJIMA, KAORU NOGAWA, NOBUATSU WATANABE

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Kyoto-shi, Sakyo-ku 606, Japan

Two types of graphite fluoride, $(CF)_n$ and $(C_2F)_n$, were partially decomposed under a chlorine atmosphere at several temperatures between 250 and 450° C. The main reaction was the C–F bond rupture to form graphite-like carbon around the particle surface. Graphite fluoride itself is an electrical insulator, but the formation of a carbon film around the surface of the graphite fluoride particles decreased the initial overpotential without a significant decrease in the capacity.

1. Introduction

Graphite fluorides have many excellent characteristics as cathode materials for primary lithium batteries in non-aqueous electrolyte systems, especially their flat and high discharge potentials and large capacities. Two types of graphite fluoride, $(CF)_n$ and $(C_2F)_n$, are prepared in the form of paracrystallite by careful choice of a carbon material and fluorination temperature [1]. $(CF)_n$ is regarded as a first stage graphite intercalation compound and $(C_2F)_n$ as a second stage. Both have layered structures in which fluorine atoms are covalently bonded to an array of translinked cyclohexane chains of carbon atoms [2], having lost the aromatic nature of the host graphite, an essential difference from general intercalation compounds with planar graphite layers. Therefore graphite fluorides are electrical insulators.

On discharge the lithium ion is intercalated between the graphite fluoride layers to form a thin layer of graphite intercalation compound composed of carbon, fluorine and lithium with solvent molecules, which decomposes to lithium fluoride, graphite-like carbon and solvent molecule as the discharge proceeds [3–5]. At the beginning of discharge, a considerable drop in discharge potential is observed because insufficient formation of the conductive phase around the surface area of the graphite fluoride particles has occurred, so potential recovery needs up to ∼ 10% of discharge. Such behaviour is undesirable from the viewpoint of the practical use of the battery; for example, the initial low potential is disadvantageous for determining the appropriate end point of the battery for instrument usage. To decrease the potential drop, the content of conductive additive must be increased in the cathode mixture in spite of the decrease in capacity of the cell. In this paper, partial decomposition of graphite fluoride was carried out in a chlorine atmosphere and improvement in initial discharge behaviour was investigated.

2. Experimental details

Graphite fluorides were prepared by direct fluorination of Madagascar natural graphite (61–74 μm) under a fluorine atmosphere (1 atm pressure). The reaction temperature and time were 600° C and 33 h for $(CF)_n$ and 350° C and 21 days for $(C_2F)_n$. Decomposition of the samples was performed under 1 atm of chlorine in a silica tube. Between 0.5 and 1 g of the sample was put into the reaction tube which was then evacuated, and the temperature was increased up to that at which the partial decomposition of graphite fluoride would take place. After reaching the required temperature, the system was
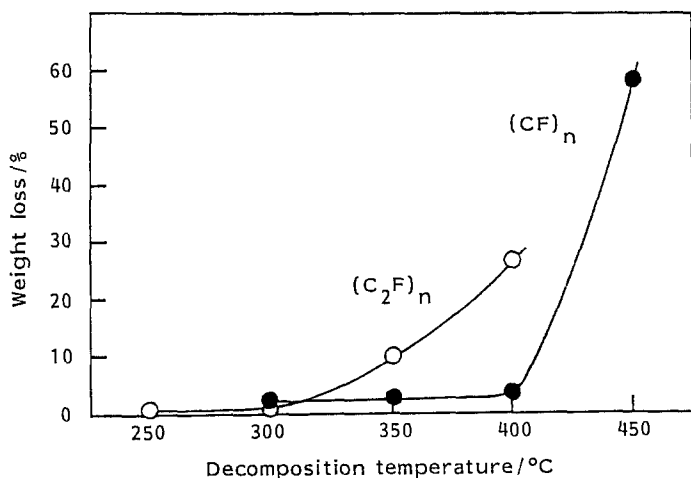
Fig. 1. Change in weight loss of graphite fluorides under chlorine atmosphere.

maintained for more than 10 h in vacuum to adjust the temperature and to dry the sample. Chlorine gas was then introduced into the reaction tube after passing through calcium chloride at a pressure up to 1 atm. After 5 h the reaction tube was cooled to the ambient temperature and residual chlorine gas was removed by argon flow. Elemental analysis, X-ray diffraction and ESCA measurements were performed on the samples.

Electrode preparation and cell assembly were the same as previously reported [3]. The electrolyte used was 1 M $LiClO_4$–propylene carbonate solution (water content was less than 100 p.p.m). The cell was galvanostatically discharged at an apparent current density of 0.5 mA cm^{-2} in a dry box filled with high purity argon.

3. Results and discussion

3.1. Decomposition of graphite fluorides under a chlorine atmosphere

Fig. 1 shows the relation between the decomposition temperature and weight loss of the samples. In the case of $(CF)_n$ the weight was almost unchanged below 400° C and a sudden weight decrease occurred at around 450° C. On the other hand, $(C_2F)_n$ gave little weight loss up to 300° C, but the sample weight gradually decreased with increasing temperature above 300° C. Fig. 2 shows the change in X-ray diffraction powder pattern of $(C_2F)_n$. No change was

observed for $(C_2F)_n$ decomposed under 300° C; however, the peak at around 26°, ascribed to the graphite (0 0 2) diffraction line, appeared on decomposition at 350° C. For $(CF)_n$, a large (0 0 2) graphite peak was first observed on decomposition at 450° C. Thus the residual carbon produced by this reaction possessed a graphite structure. The F/C ratios obtained from elemental analysis are shown as a function of weight decreases of graphite fluorides in Fig. 3. The solid lines in the figure indicate the F/C ratio calculated on the assumption that only the release of fluorine contributes to the weight loss of graphite fluoride. Hence the decrease of the F/C ratio is very large in comparison with other decomposition reactions of graphite fluoride in which fluorocarbons are formed [6–8]. The experimental values agreed well with the calculated lines. Deviation from the theoretical lines is considered to be caused by weight increase due to chlorine species adsorbed on to the surface of the graphite fluoride particles which can be detected by elemental analysis and Cl_{2p} ESCA spectra. The amount of adsorbed chlorine was about 0.5 wt % of the sample.

The F_{1s}, C_{1s} and Cl_{2p} ESCA spectra of partially decomposed $(C_2F)_n$ are shown in Fig. 4. With increasing temperature, the binding energy shifted to a lower position and the peak intensity decreased over 300° C in the F_{1s} spectra. This means that the covalent bond of fluorine around the surface of graphite fluoride changed to a weak bond such as is characteristic of chemical adsorption. The change of peak intensity coin-
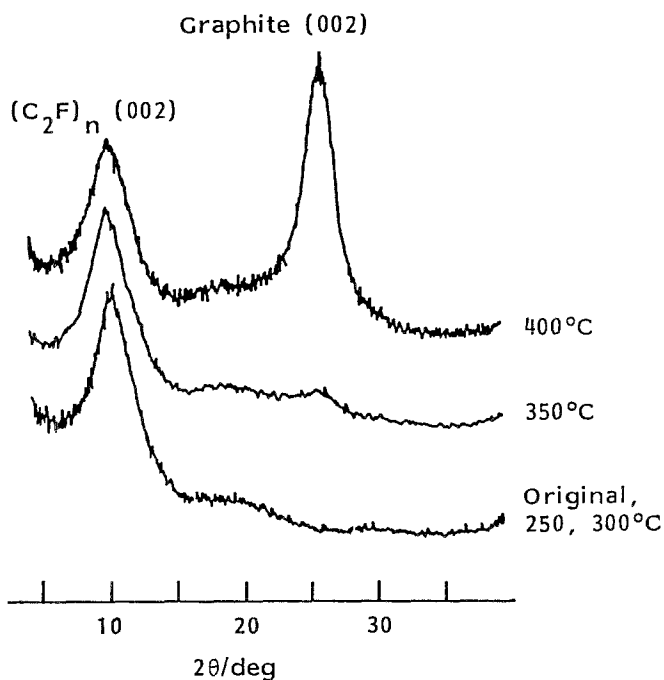
Graphite (002)

$(C_2F)_n$ (002)

400°C

350°C

Original,
250, 300°C

10   20   30

2θ/deg

Fig. 2. X-ray diffraction pattern of $(C_2F)_n$ partially decomposed under chlorine atmosphere.

cides with the weight decrease results. In the C_{1s} ESCA spectra, the peak at 291 eV, corresponding to a covalent bond with fluorine, shifted to a lower binding energy and the intensity decreased with increase of heat treatment temperature. On the other hand, a small peak at 284.3 eV corresponding to a C–C bond of graphite appeared for the sample decomposed at 300° C, but the carbon phase could not be detected by X-ray diffractometry. This peak increased greatly as the temperature increased. In Cl_{2p} spectra, three peaks were observed at and above 350° C. The Cl_{2p} spectrum includes two peaks, $Cl_{2p^{\frac{1}{2}}}$ (L_{II}) and $Cl_{2p^{\frac{3}{2}}}$ (L_{III}). The peaks at 202 and 200 eV correspond to a Cl–Cl covalent bond, and those at 200 and 198 eV are ascribed to a partially ionized chlorine species. The two peaks at 200 eV are overlapped. In the case of $(CF)_n$ the same

1.2

Original,
300°C, 350°C

1.0   ←400°C

0.8

Original,
250°C

0.6

300°C

(CF)$_n$

350°C

0.4

$(C_2F)_n$

0.2

400°C

450°C

0.0
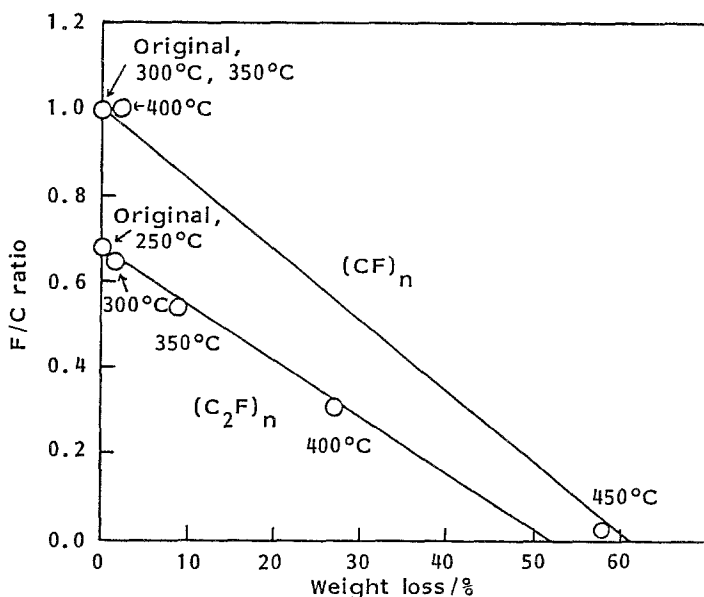0   10   20   30   40   50   60

Weight loss/%

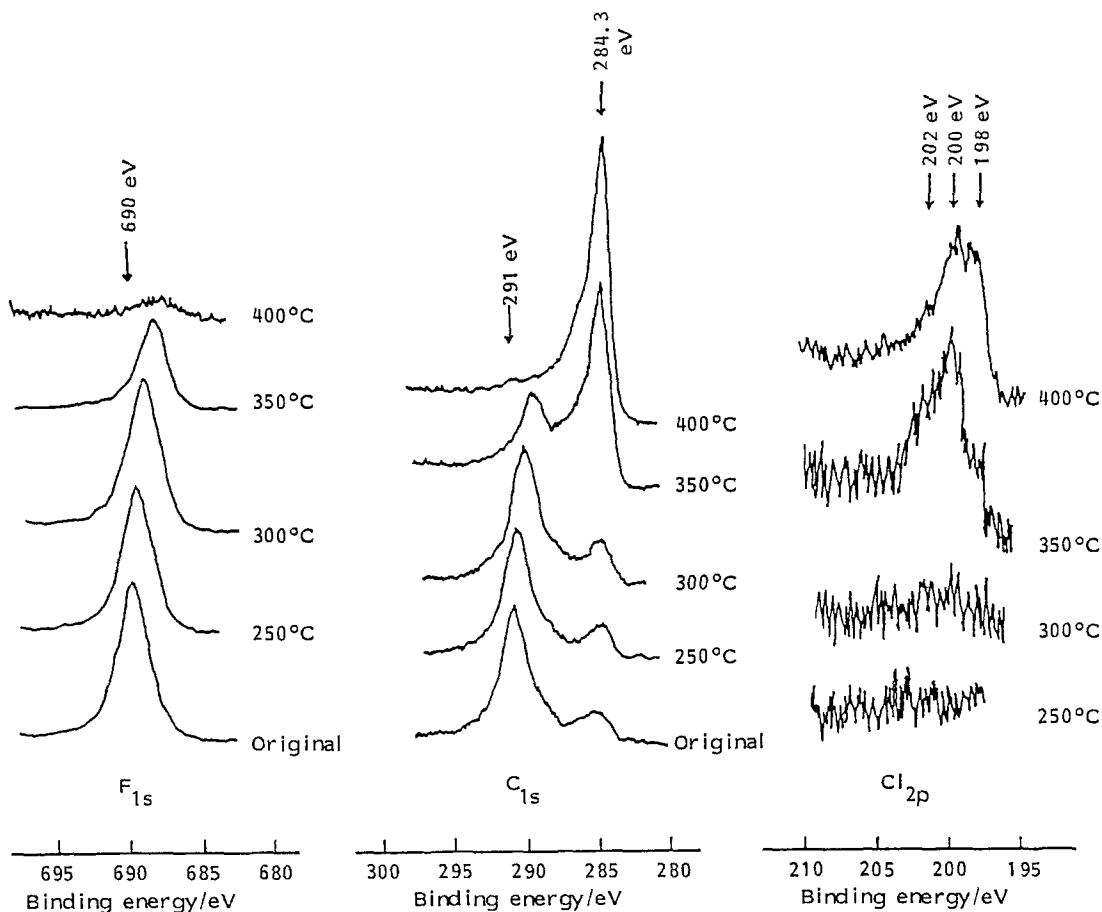Fig. 3. Change in F/C ratio of graphite fluorides partially decomposed under chlorine atmosphere.

Fig. 4. ESCA spectra of $(C_2F)_n$ partially decomposed under chlorine atmosphere.

phenomenon was found in ESCA spectra, but the change started at around 350° C.

Thus the decomposition of graphite fluorides in a chlorine atmosphere is essentially different from that in other atmospheres previously reported [6–8]. In Table 1, the decomposition of graphite fluorides in a chlorine atmosphere is

Table 1. Decomposition of graphite fluoride

	Atmosphere	F/C ratio of gas products	Decomposition temp. (° C)
$(CF)_n$	Vacuum [6, 8]	2:1	620
	N_2 [8]	2:1	560
	O_2 [7, 8]	1:1	< 560
	Cl_2	1:0	≃ 400
$(C_2F)_n$	Vacuum [8]	4:1	590
	Ar [8]	4:1	570
	Cl_2	1:0	≃ 300

compared with the decomposition in other atmospheres. The decomposition temperatures were much lower in chlorine and, moreover, no carbon consumption was found during the decomposition in this atmosphere. The results obtained suggests that graphite fluorides decompose to give inter-halogen compounds such as ClF and ClF_3 in a chlorine atmosphere:
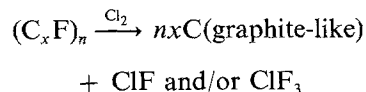
$$(C_xF)_n \xrightarrow{Cl_2} nxC(\text{graphite-like})$$

$$+ \text{ ClF and/or ClF}_3$$

3.2. *Effects of partial decomposition of graphite fluorides in a chlorine atmosphere on the discharge characteristics*

If the reaction temperature and time are carefully controlled, the partial decomposition is expected to produce an electrically conductive
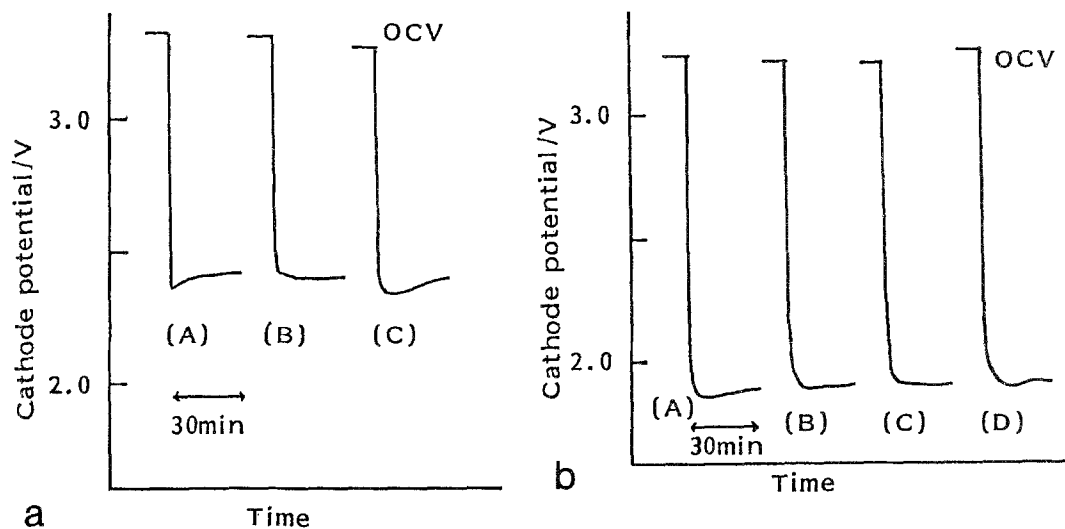
Fig. 5. (a) Initial discharge characteristics of $(C_2F)_n$ partially decomposed under chlorine atmosphere: (A) original; (B) at 300° C; (C) at 350° C. (b) Initial discharge characteristics of $(CF)_n$ partially decomposed under chlorine atmosphere: (A) original; (B) at 300° C; (C) at 350° C; (D) at 400° C.

carbon phase around the surface of the graphite fluoride particles without carbon loss. It has been reported that an increase in overpotential is observed when heat treatment of $(C_2F)_n$ is carried out at more than 450° C [4]. Low-temperature heat treatment in a chlorine atmosphere can avoid such a problem.

Since graphite fluoride is an electrical insulator as a whole and the surface is covered with many CF_2 and CF_3 groups, addition of some electroconductive material and activation energy are needed to initiate the electrochemical reaction. For this reason, significant potential drop is generally observed at the beginning of discharge. In the commercial battery, acetylene black (5–20 wt %) is added to graphite fluoride as the conductive additive. For batteries containing acetylene black (9 wt %) the initial potential drops range between 130 and 150 mV, and it takes up to 8 h to reach the flat discharge potential which corresponds to $\sim 10\%$ discharge [9]. Fig. 5 shows the effects of partial decomposition under a chlorine atmosphere on the initial discharge characteristics of graphite fluoride electrodes. In the present study the graphite fluoride electrode was prepared by moulding a 1 : 1 : 1 mixture in weight of graphite fluoride, acetylene black and polyethylene (binder) into a pellet; therefore, the initial potential drop was not so large as that of the commer-

cial battery due to increase of the conductive additive. It is, however, obvious that the initial potential drop of non-heat-treated $(C_2F)_n$ disappeared when the sample was treated at 300° C. This can be ascribed to the increase of electrical conductivity through the carbon phase formed around the particle surface. However, some potential drop appeared again for the sample decomposed at 350° C, and a flat discharge potential was no longer observed for that decomposed at 400° C. This was possibly due to the difficulty in lithium ion transfer caused by perfect covering with graphite-like carbon around the surface. Additionally, the decrease of the discharge capacity caused by fluorine loss was significant for the samples decomposed at a temperature higher than 350° C, being more than 10%. In the case of $(CF)_n$ the effects were not so marked as those with $(C_2F)_n$, but the optimum decomposition temperature found was 350° C.

References

[1]   Y. Kita, N. Watanabe and Y. Fujii, *J. Amer. Chem. Soc.* **101** (1979) 3832.
[2]   H. Touhara, K. Kadono and N. Watanabe, *Tanso* **117** (1984) 98.
[3]   N. Watanabe, R. Hagiwara, T. Nakajima, H. Touhara and K. Ueno, *Electrochim. Acta* **27** (1982) 1615.
[4]   N. Watanabe, R. Hagiwara and T. Nakajima, *J. Electrochem. Soc.* **131** (1984) 1980.

[5] H. Touhara, H. Fujimoto, N. Watanabe and A. Tressaud, *Solid State Ionics* **14** (1984) 163.

[6] N. Watanabe, S. Koyama and H. Imoto, *Bull. Chem. Soc. Jpn.* **53** (1980) 2731.

[7] N. Watanabe, T. Kawamura and S. Koyama, *ibid.* **53** (1980) 3100.

[8] S. Koyama, PhD Thesis, Kyoto University, Kyoto, Japan (1980).

[9] A. Morita, T. Iijima, T. Fujii and H. Ogawa, *J. Power Sources* **5** (1980) 111.