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Effect on discharge of the heat treatment of graphite fluoride under a hydrogen atmosphere

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Thermal decomposition of two types of graphite fluorides $(CF)_n$ and $(C_2F)_n$, has been carried out in a hydrogen atmosphere at several temperatures between 100 and 500 °C, with the object of improving the initial discharge behaviour of the Li/graphite flouride cell. The main reaction was the C–F bond rupture to form graphite-like carbon around the particle surface. The drop in cell voltage at the beginning of discharge could be minimized, and the polarization during discharge reduced by heat treatment under a hydrogen atmosphere. $(CF)_n$, heat treated at 400 °C for 1 h, yielded a discharge capacity of 730–800 mA h per g of active material, corresponding to the discharge efficiency of $83 \sim 90\%$ at 25 °C, and $(C_2F)_n$, heat treated at 350 °C, for 10 h, gave 670 mA h g^{-1}, corresponding to 91% at 25 °C.

1. Introduction

Graphite fluorides have some excellent characteristics as cathode materials for primary lithium cells in non-aqueous electrolyte systems, especially their flat and high discharge potentials and large capacities. Two types of graphite fluoride $(CF)_n$ and $(C_2F)_n$, were 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 and electrical insulators.

On discharging, the lithium ion is intercalated into the graphite fluoride layers to form a 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 the discharge reaction, a considerable drop in discharge potential is observed because of the existence of many CF_2 and CF_3 groups around the surface of the graphite fluoride particles. Such behaviour is not desirable from the viewpoint of battery use.

In a previous paper [6], graphite fluorides were partially decomposed under a chlorine atmosphere at several temperatures between 250 and 450 °C, and it was found that the voltage drop in the initial discharge reaction of the cell was recovered by the previous treatment. In this paper, the hydrogen treatment of two types of graphite fluoride, $(CF)_n$ and $(C_2F)_n$ was performed and the improvement in initial discharge behaviour of the primary lithium cell was investigated.

2. Experimental details

Two types of graphite fluoride, Central Glass Co., Cerbon-DM (fluorine content, 63 wt%) and Cerbon-CMC (fluorine content, 52 wt%) were used as $(CF)_n$ and $(C_2F)_n$, respectively. The treatment of the samples was carried out under 1 atm of hydrogen in a porcelain tube. About 1 g of the sample was put into the reaction tube, and hydrogen gas was introduced into the tube. The temperature was increased up to the desired value. After reaching the

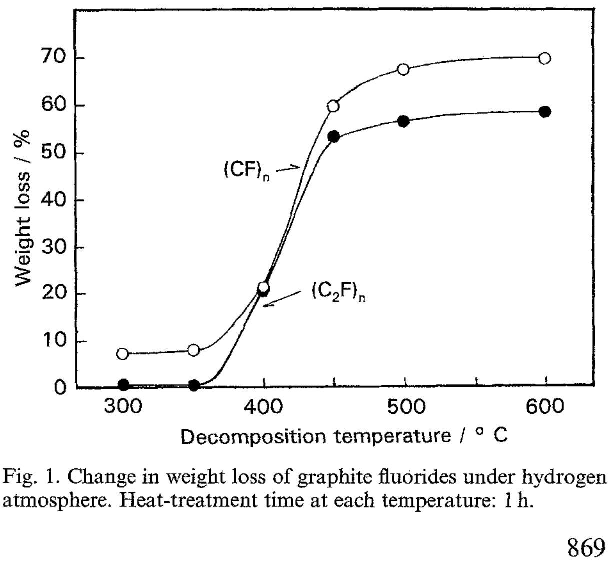

Fig. 1. Change in weight loss of graphite fluorides under hydrogen atmosphere. Heat-treatment time at each temperature: 1 h.

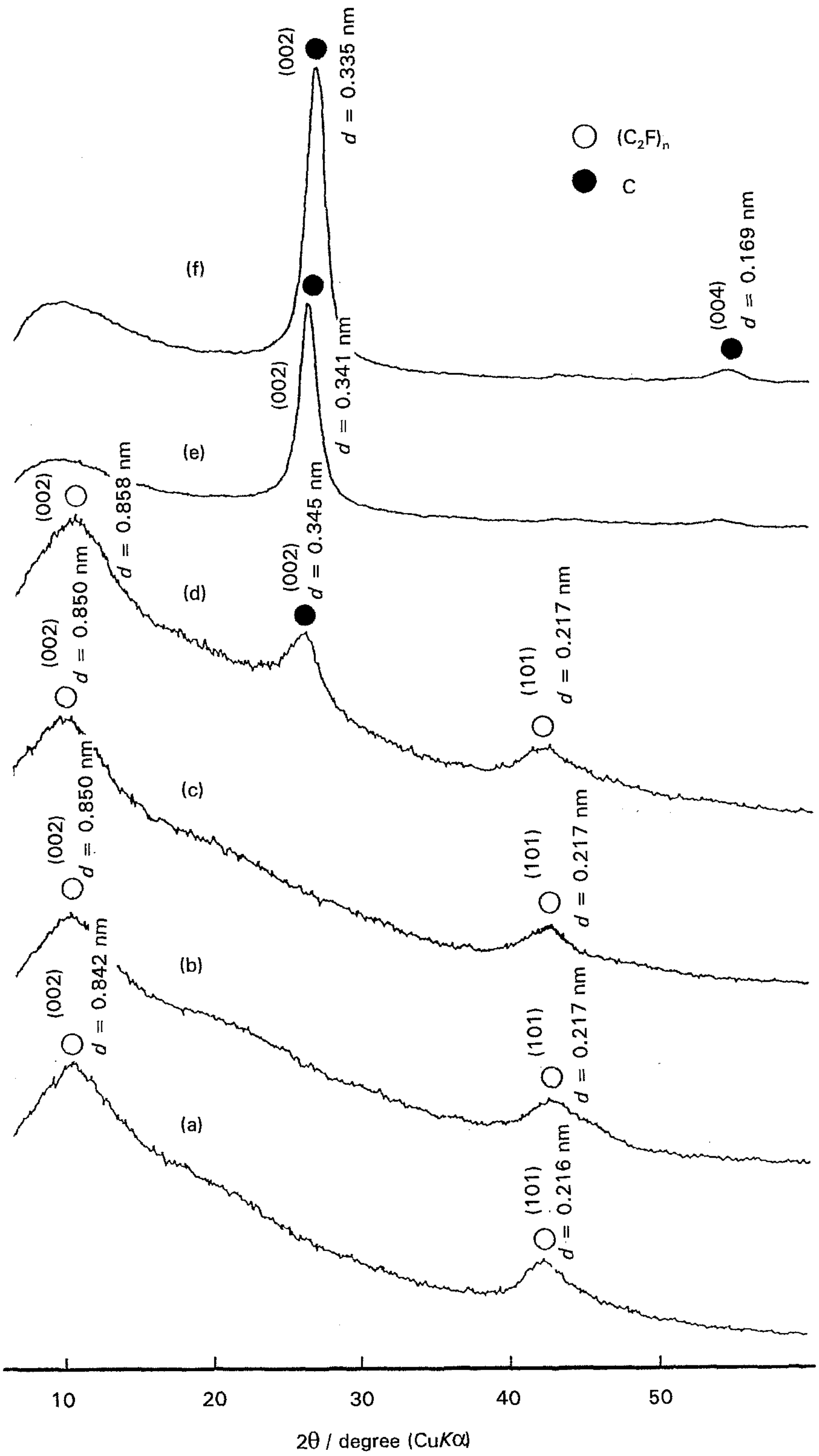

Fig. 2. X-ray diffraction patterns of $(C_2F)_n$ decomposed under hydrogen atmosphere. Key: (a) original; (b) 300 °C, 1 h; (c) 350 °C, 1 h; (d) 400 °C, 1 h; (e) 450 °C, 1 h; (f) 500 °C, 1 h.

temperature, the system was maintained for more than 1 h. Then the reaction tube was cooled to room temperature and residual hydrogen gas was removed by argon flow. Thermogravimetric analysis, X-ray diffraction and electrochemical measurements were performed on each sample.

The preparation of electrodes, design of the cell and method of conducting electrochemical measurements were the same as previously reported [7]. The sample of about 20 mg cm^{-2} was combined with graphite in a weight ratio of 1 : 1 and the mixture was compression-moulded on a nickel mesh under 50 MPa. Lithium pellets were used for both the negative and the reference electrodes. The electrolyte was 1 M $LiClO_4$-propylene carbonate (PC) (water content was less than 20 ppm). The cell was galvanostatically discharged at a nominal current density of 0.2–1.0 mA cm^{-2} (geometrical surface area of graphite fluoride electrode, 2.8 cm^2) in a dry box filled with high purity argon.

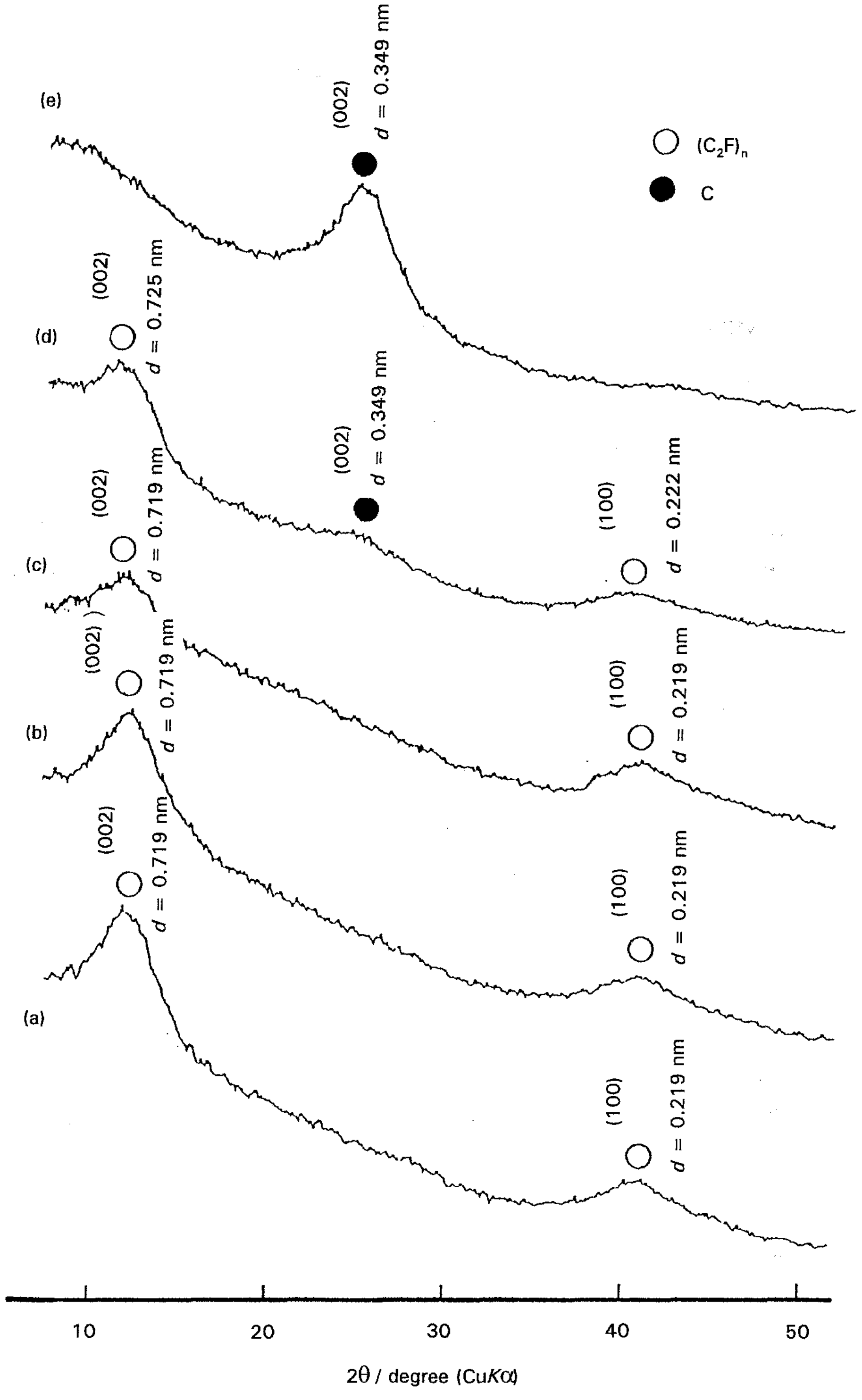

Fig. 3. X-ray diffraction patterns of $(CF)_n$ decomposed under hydrogen atmosphere. Key: (a) original; (b) 300 °C, 1 h; (c) 350 °C, 1 h; (d) 400 °C, 1 h; (e) 450 °C, 1 h.

3. Results and discussion

3.1. *Thermal decomposition of graphite fluorides under a hydrogen atmosphere*

Figure 1 shows the relation between the treatment temperature and weight loss of the samples. In the case of $(C_2F)_n$ the weight was almost unchanged below 350 °C and a weight decrease occurred at around 400 °C. On the other hand, $(CF)_n$ gave little weight change up to 350 °C, but the sample weight decreased markedly with increasing temperature above 400 °C. Figure 2 shows the change in X-ray diffraction powder pattern of $(C_2F)_n$. No change was observed for $(C_2F)_n$ treated below 350 °C; however, the peak at around 26°, ascribed to the graphite (0 0 2) diffraction line, appeared on decomposition of graphite fluoride above 400 °C. The *d*-values obtained from graphite (0 0 2) lines, which indicate the interlayer distance, decreased with increasing temperature in the range 400 to 500 °C (d)–(f). For $(CF)_n$ (Fig. 3), a (0 0 2) graphite peak was first observed on the treatment at 400 °C and the (0 0 2) peak increased with increasing temperature. The

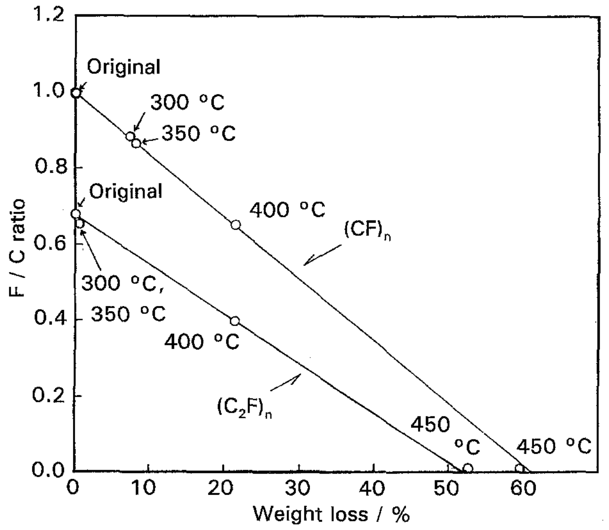

Fig. 4. Change in F/C ratios of graphite fluorides decomposed under hydrogen atmosphere. Heat-treatment time at each temperature: 1 h.

d-values obtained from graphite (0 0 2) lines remained almost unchanged in the temperature range 450 to 600 °C. Thus the formed residual carbon possessed a graphite structure.

The F/C ratios of graphite fluorides decomposed under hydrogen atmosphere decreased linearly with weight decrease of graphite fluorides, as shown in Fig. 4. The F/C ratios obtained from the weight losses at temperatures of 300–450 °C are found around the calculated lines. The variation in the F/C ratios during hydrogen treatment is similar to that observed during chlorine treatment [6], where no carbon consumption was found during decomposition at 250 to 400 °C. However, the F/C values of $(CF)_n$ treated in hydrogen at 300 to 400 °C are considerably lower than those in a chlorine atmosphere (F/C ratio = 1.0 at 300 to 400 °C) [6]. From the results obtained, graphite fluorides may decompose to give HF in a hydrogen atmosphere:

$$(C_xF)_n \longrightarrow nx\,\mathrm{C}\,(\text{graphite-like}) + n\,\mathrm{HF}$$

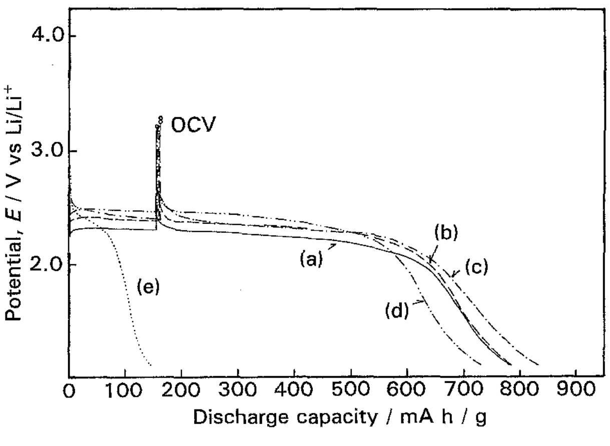

Fig. 5. Effect of heat-treatment temperature on discharge characteristics of $(CF)_n$ at a current density of 0.5 mA cm^{-2} in $LiClO_4$–PC at 25 °C. Discharge curves down to 1.1 V vs Li/Li$^+$. Key: (a) original; (b) 300 °C, 1 h; (c) 350 °C, 1 h; (d) 400 °C, 1 h; (e) 450 °C, 1 h.

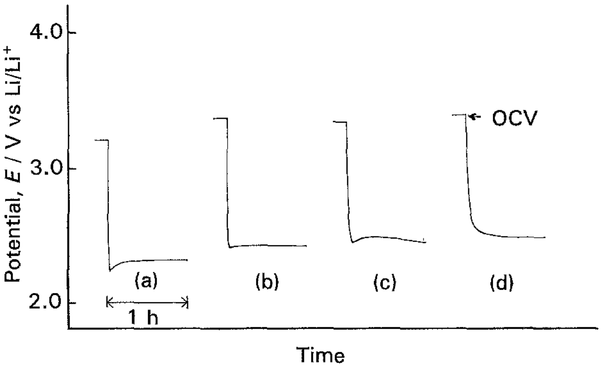

Fig. 6. Effect of heat-treatment temperature on discharge in $LiClO_4$–PC at 25 °C. Initial discharge curves. Key: (a) original; (b) 300 °C, 1 h; (c) 350 °C, 1 h; (d) 400 °C, 1 h.

3.2. *Effects of heat-treatment of graphite fluorides in a hydrogen atmosphere on the discharge characteristics*

If the reaction temperature and time are carefully controlled, the thermal decomposition is expected to produce an electrically conductive carbon phase around the surface of the graphite fluoride particles without carbon loss.

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 ~10% discharge [8].

Figures 5 to 10 show the effect of thermal decomposition under a hydrogen atmosphere on the initial discharge characteristics of graphite fluoride electrodes. In the present study the graphite fluoride electrodes were prepared by moulding a 1 : 1 mixture of graphite fluoride and graphite into a pellet; therefore, the initial potential drop was not so large as that for the

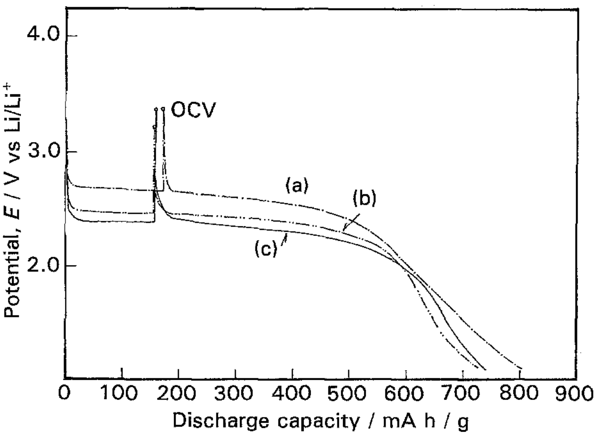

Fig. 7. Effect of current density on discharge characteristics of $(CF)_n$ heat-treated at 400 °C for 1 h in hydrogen atmosphere. Current density: (a) 0.2, (b) 0.5 and (c) 1.0 mA cm^{-2}.

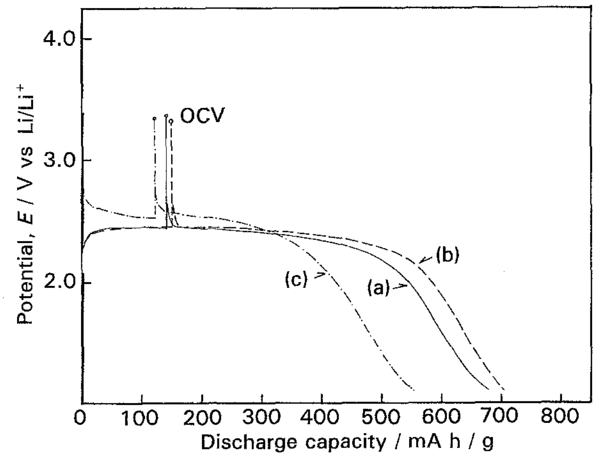

Fig. 8. Effect of heat-treatment temperature on discharge characteristics of $(C_2F)_n$ at a current density of 0.5 mA cm^{-2}. Key: (a) original; (b) 350 °C, 1 h; (C) 400 °C, 1 h.

commercial battery due to increase of the conductive additive. It is, however, obvious from Figs 5 and 6 that the initial potential drop of non-heat-treated $(CF)_n$ disappeared without a large loss in discharge capacity when the sample was heated at 400 °C for 1 h. Moreover, the $(CF)_n$ heat-treated at 300–400 °C show a higher potential, compared to non-heat-treated $(CF)_n$, leading to lower polarization during discharge. This can be ascribed to the increase in electrical conductivity through the carbon phase formed around the particle surface. However, when the $(CF)_n$ sample was heated above 450 °C, the discharge capacity decreased signficantly. When the $(CF)_n$ heat-treated at 400 °C for 1 h in hydrogen was discharged at several current densities between 0.2–1.0 mA cm^{-2}, no initial potential drop occurred and the discharge capacity of 730–800 mAh per g of active material corresponding to the discharge efficiency of 83–90% was obtained (Fig. 7).

On the other hand, the initial drop of non-heat-treated $(C_2F)_n$ disappeared when the sample was heated at 400 °C for 1 h (Fig. 8). At the heat-treatment condition, however, a large decrease in the discharge capacity occurred due to a large fluorine loss. Therefore, the $(C_2F)_n$ sample was heat-treated at a lower temperature of 350 °C for a longer period. The weight loss increased with increasing heat-treatment time, being 10.7% for 10 h at 350 °C. As seen in Figs 9 and 10, when the sample was heated at 350 °C for 10 h, the initial potential drop mostly disappeared without a large loss of discharge capacity, and the polarization during discharge decreased with increasing heat-treatment time.

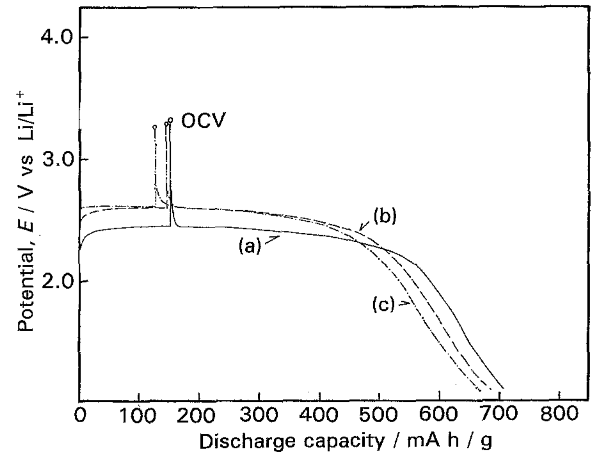

Fig. 9. Effect of heat-treatment time on discharge characteristics of $(C_2F)_n$ at a current density of 0.5 mA cm^{-2}. Discharge curves down to 1.1 V vs Li/Li$^+$. Key: (a) 350 °C, 1 h; (b) 350 °C, 5 h; (c) 350 °C, 10 h.

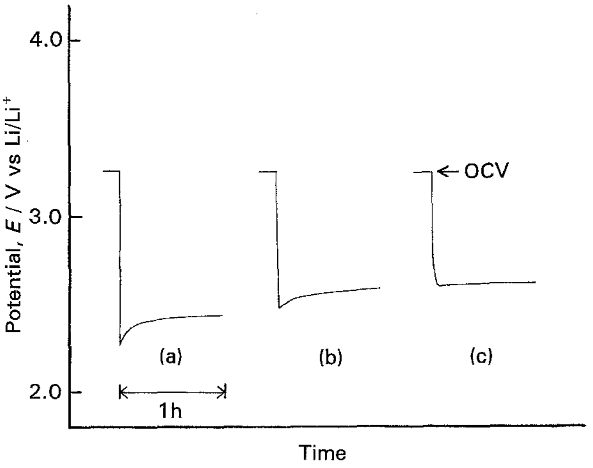

Fig. 10. Effect of heat-treatment time on discharge characteristics of $(C_2F)_n$ at a current density of 0.5 mA cm^{-2}. Initial discharge curves. Key: (a) 350 °C, 1 h: (b) 350 °C, 5 h; (c) 350 °C, 10 h.

When the graphite fluorides were partially decomposed under a chlorine atmosphere, the initial potential drops disappeared only at given heat-treatment temperatures of 300 °C for $(C_2F)_n$ and 350 °C for $(CF)_n$ [6], and the effects of the partial decomposition on the discharge characteristics were not so marked as those in a hydrogen atmosphere. The initial potential drop and the polarization during discharge decreased markedly with increasing heat-treatment temperature and time in the range 300 to 400 °C under a hydrogen atmosphere; the optimum decomposition temperatures and times were found to be 400 °C and 1 h for $(CF)_n$ and 350 °C and 10 h for $(C_2F)_n$.

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