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Carbon–fluorine compounds as battery materials

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Abstract

Historical aspects on the syntheses and structure models of carbon–fluorine compounds, discharge reaction and characteristics of Li/$(CF)_n$ batteries, and syntheses and electrochemical behavior of new alternating cathode materials have been reviewed.

Keywords: Fluorine; Graphite; Intercalation; Lithium battery

1. Pioneering works on carbon–fluorine compounds

Carbon and its compounds have such layered structures that are suitable for intercalation and deintercalation of foreign chemical species. This property prompts the application of carbon materials to new electrochemical devices.

Ruff and Bretschneider [1] prepared gray graphite fluoride, $CF_{0.92}$ by the action of elemental fluorine on graphite at 420°C. Their paper published in 1934 qualitatively clarified that graphite fluoride is a hydrophobic and high resistance material, yielding gaseous fluorocarbons by thermal decomposition. In 1947, a paper on the structure of graphite fluoride was published by Rüdorff and Rüdorff [2]. Th eir products were $CF_{0.676} - CF_{0.988}$ fluorinated at 410–550°C. From X-ray diffraction data, they proposed a structure model with an infinite array of cyclohexane chairs of carbons in which the chemical bonds was completely changed to sp^3 σ bonds. This is a basic structure model of $(CF)_n$ type graphite fluoride. In addition to these works, Bigelow [3], Palin and Wadsworth [4], and Rüdorff and Brodersen [5] reported the covalent nature of C–F bond [3,4] and IR spectrum of graphite fluoride [5]. In 1960s, Watanabe and his co-workers [6,7] published several papers on the carbon anode reaction in electrolytic production of elemental fluorine. They claimed that a low surface energy of thin C–F film formed on carbon anode caused the anode effect. In the same period, Margrave and his co-workers [8–12] were active in studying the synthesis, structure and thermodynamic properties of graphite fluoride. They determined thermodynamic functions of graphite fluoride from the measurements of heat capacity and heat of combustion. Mahajan et al. [10] and Takashima and Watanabe [13] both proposed the same chair type structure model of $(CF)_n$ as that of Rüdorff and Rüdorff by means of X-ray and electron diffraction data, and IR absorption spectra. On the other hand, Ebert et al. [14] proposed the boat type structure from ^{19}F NMR measurement.

Fluorine reacts with graphite in the presence of an acidic fluoride at a temperature less than 100°C, yielding fluorine–graphite intercalation compounds C_xF with ionic or semi-ionic C–F bonding. The C_xF has planar graphene layers and different properties from those of graphite fluoride having covalent bond. Rüdorff and Rüdorff [15] first reported that fluorine is intercalated into graphite with HF. They synthesized stage 1 compounds with compositions of $C_{3.6}F$ to $C_{4.0}F$ and proposed a structure model of C_4F based on X-ray powder diffraction data. Lagow et al. [16] also synthesized C_4F using a mixture of fluorine and HF gases.

2. Electrochemical application of graphite fluoride

Lithium is easily combined with fluorides, yielding LiF having a large Gibbs free energy change of formation. This persuaded us to make a new primary energy conversion device using lithium and a fluoride. Discharge characteristics of various fluorides were investigated in combination with lithium anode, however, many attempts to use metal and non-metal fluorides were unsuccessful except graphite fluoride $(CF)_n$ with covalent C–F bonds. Graphite fluoride is a stable compound under usual environment, however, very easily reduced when subjected to electrochemical reduction. It is an electric insulator because of the covalent nature of C–F bonds. An electroconductive additive such as carbon is

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therefore needed to initiate electrochemical reduction of graphite fluoride. Graphite fluoride is a very convenient material for a battery because the electrochemical reduction recovers an electroconductive carbon, through which electrons are effectively supplied. The large Gibbs free energy change for LiF formation and recovery of carbon enable the continuous discharge of graphite fluoride. Based on these findings, lithium–graphite fluoride battery was developed by Matsushita Battery Industrial Co. Ltd. in Japan [17]. It was a first battery using metallic lithium as anode and organic electrolyte solution. It is not possible to use an aqueous solution since lithium readily reacts with water, evolving hydrogen gas.

The Li/$(CF)_n$ battery is composed of Li anode and $(CF)_n$ cathode with aprotic solvents containing $LiBF_4$. Commercial batteries contain $LiBF_4$ as an electrolyte salt, however $LiClO_4$ is often used in laboratory cells. The aprotic solvents usually employed are propylene carbonate (PC), dimethyl sulfoxide (DMSO), γ-butyrolactone (BL), tetramethylene sulfone (sulfolane, TMS), dimethoxyethane (DME) and so on.

The total cell reaction is simply expressed as follows:

$$n\mathrm{Li} + (\mathrm{CF})_n \rightarrow n\mathrm{LiF} + n\mathrm{C}. \qquad (1)$$

However, the final reaction products, LiF and carbon are not readily formed. The open circuit voltage (OCV) for the reaction (1) is calculated to be 4.57 V from the thermodynamic functions of lithium and graphite fluoride [11,12], whereas the actually observed OCVs are in the range of 3.2–3.5 V depending on the Li^+ solvation energies of solvents and crystallinity of graphite fluoride. Tiedeman [18] ascribed the discrepaney between the calculated and observed OCVs to a mixed potential consisting of the reduction of graphite fluoride and oxidation of organic solvents. Whittingham [19] suggested that discharge products were not LiF and carbon but a ternary intercalation compound composed of C, Li and F. Analysis of partially discharged products by X-ray diffraction revealed that low crystalline carbon, LiF, Li_2CO_3 and unreacted graphite fluoride existed without an intercalated phase [20], however, X-ray photoelectron spectra of partially discharged products indicated the existence of an intermediate C–F bonding between the covalent and ionic ones [20]. ^{7}Li NMR spectra also suggested the existence of Li^+ ion having a weak chemical bond [20]. These results show that electrochemically reduced graphite fluoride does not yield such an intercalated phase that is detected by X-ray diffraction but a thin intermediate phase where a discharged fluoride ion still has a weak chemical bond with carbon. This intermediate phase would be responsible for the electrode potential of graphite fluoride cathode. The OCV measurements in different solvents provided another important information that OCV value increased with increasing solvation energy for Li^+ ion, which means that the discharge product determining the cathode potential involves solvent molecules, i.e. solvent molecules are not completely desolvated in the intermediate discharge product [21]. The discharge reaction of Li/$(CF)_n$ cell is then expressed as follows:

$$\mathrm{Li} + \mathrm{CF} + x\mathrm{S} \rightarrow \mathrm{CF}^- \cdot \mathrm{Li}^+ \cdot y\mathrm{S} + (x-y)\mathrm{S}, \qquad (2)$$

where S is a solvent molecule. The discharge product $CF^- \cdot Li^+ \cdot yS$ determines the OCV value, and exothermically decompose to LiF carbon and solvent as shown in Fig. 1 [22]:

$$\mathrm{CF}^- \cdot \mathrm{Li}^+ \cdot y\mathrm{S} \rightarrow \mathrm{LiF} + \mathrm{C} + y\mathrm{S}. \qquad (3)$$

The discharge characteristics of graphite fluoride are governed by several factors: crystallinity, surface area and C–F bond. These factors of graphite fluoride vary depending on raw carbon materials and fluorination temperature. For example, highly crystalline natural graphite yields well ordered graphite fluoride with a relatively smaller d-spacing along c-axis, however, low crystalline petroleum coke produces less ordered graphite fluoride. Because the discharge of graphite fluoride proceeds with Li^+ ion insertion into graphite fluoride layers, graphite fluoride prepared from petroleum coke gives a higher discharge potential than that obtained from natural graphite due to its larger d-spacing, but its smaller crystallite size somewhat decreases the discharge potential. On the other hand, graphite fluoride from natural graphite shows flat and lower discharge potential owing to its higher crystalilinity and smaller d-spacing. Commercial LiI$(CF)_n$ batteries employ graphite fluoride prepared from petroleum coke. Graphite fluoride having a large surface area gives a high discharge potential because its current density becomes low. Fluorination temperature is also one of the factors influencing the discharge characteristics. When a fluorination temperature is low, a small amount of chemically active fluorine is involved in graphite fluoride. It causes a slight increase in the cell and discharge potentials.

Matsushita Battery Industrial Co. Ltd. commercialized Li/$(CF)_n$ batteries used for various objectives. A cylindrical type battery was developed in 1973 for marker light, observation baloon and so on. A pin type battery with aluminum case is used for fishing floats and as indicator

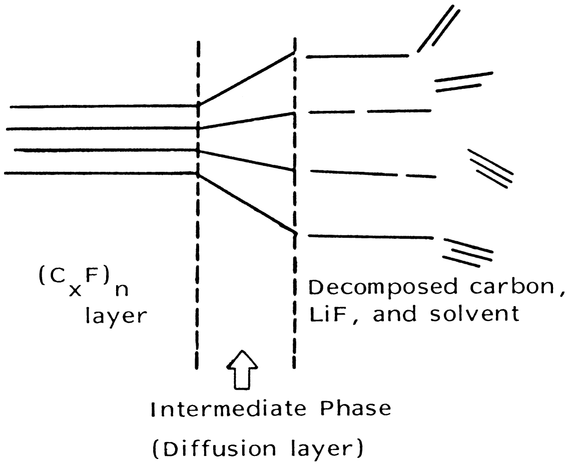

Fig. 1. Discharge reaction of Li/$(CF)_n$ batteries.

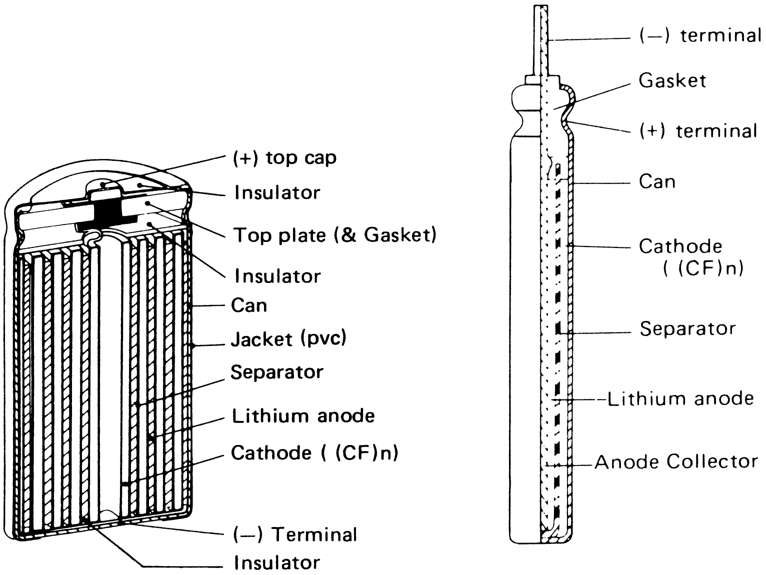

Fig. 2. Cross-sectional views of cylindrical and pin type Li/$(CF)_n$ batteries.

of the top of fishing rods. A coin type battery is used for electronic instrument such as watches and calculators or for memory back-up. Fig. 2 shows the constitutions of commercial batteries.

Various types of Li/$(CF)_n$ batteries have unique characteristics compared with conventional ones [23,24].

1. The discharge potentials are in the range of 2–3 V, depending on a current density. These values are much higher than those of conventional batteries using aqueous solutions.
2. The Li/$(CF)_n$ battery has much higher energy density than other conventional batteries.
3. Discharge characteristics are excellent at low temperatures below 0°C although not as good as the Li/MnO_2 system.
4. The Li/$(CF)_n$ batteries can be stored for many years without decrease in the capacity and leakage of the electrolyte solution.
5. $(CF)_n$ is a chemically and thermally stable compound as well as the discharge product LiF.

Fig. 3 shows the examples of pin type, cylindrical type and coin type batteries [24]. Fig. 4 is the comparison of discharge curves of Li/$(CF)_n$ battery with those of conventional manganese battery.

Recently coin type Li/$(CF)_n$ batteries were improved so as to possess higher thermal stability for the uses in electric vehicles [25]. The highest temperature for the practical use of conventional Li/$(CF)_n$ batteries is 85°C. Polypropylene used as gasket and separator have been altered to polyphenylenesulfide and polybutyleneterephthalate, respectively, and the organic solvent has been changed to γ-butyrolactone with a high boiling point (m.p. −43.5°C, b.p. 204°C). This alternation of battery materials has enabled the use of Li/$(CF)_n$ batteries up to 150°C.

Fig. 3. Commercial Li/$(CF)_n$ batteries.

3. New cathode materials for primary lithium batteries

New alternating cathode materials have been studied since Li/$(CF)_n$ battery was commercialized. The commercial Li/$(CF)_n$ batteries use graphite fluoride prepared from petroleum coke, which gives slightly higher discharge potential than $(CF)_n$ prepared from high crystalline graphite, but the discharge potential somewhat decrease with progress in the discharge, while the $(CF)_n$ prepared from highly crystallized graphite shows a flat discharge potential.

The successful replacement of $(CF)_n$ by manganese dioxide, MnO_2 was achieved by Sanyo Electric Co., Ltd. in Japan. Though Li/MnO_2 batteries show slightly different discharge behavior, it has now larger market than Li/$(CF)_n$ batteries due to several reasons such as the lower cost of MnO_2, well known technologies of MnO_2 and so on.

Other candidates are all fluorides or oxide fluorides of carbon materials because fluorine or oxygen gives a high potential of around 3 V against lithium anode and fluorides or oxide fluorides of carbon materials are stable under usual

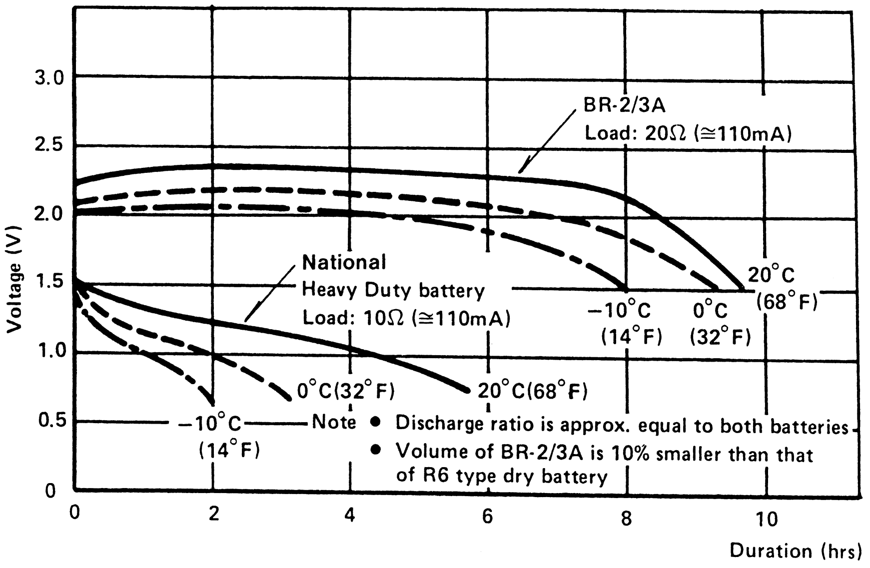

Fig. 4. Comparison of discharge curves of Li/$(CF)_n$ battery with those of conventional manganese battery.

environment. Fluorination of high crystalline graphite at 350–400°C yields $(C_2F)_n$ type graphite fluoride having C–F covalent bonds. $(C_2F)_n$ has a different crystal structure from $(CF)_n$ [26] and shows the higher discharge potential than $(CF)_n$ [27]. $(C_2F)_n$ is black, containing a small amount of active fluorine atoms. One problem of $(C_2F)_n$ is that the discharge capacity is smaller than that of $(CF)_n$ due to its lower fluorine content. $(CF)_n$ prepared from a new carbon which is obtained by thermal decomposition of graphite oxide shows an excellent discharge behavior: higher discharge potential and capacity than $(C_2F)_n$ and usual $(CF)_n$ samples (Fig. 5) [27]. The carbon obtained by thermal decomposition of graphite oxide has the larger *d*-spacing and surface area, and relatively longer crystallite size along graphene layer than usual carbon materials. Such new carbon yields $(CF)_n$ into which lithium ion is easily intercalated during discharge.

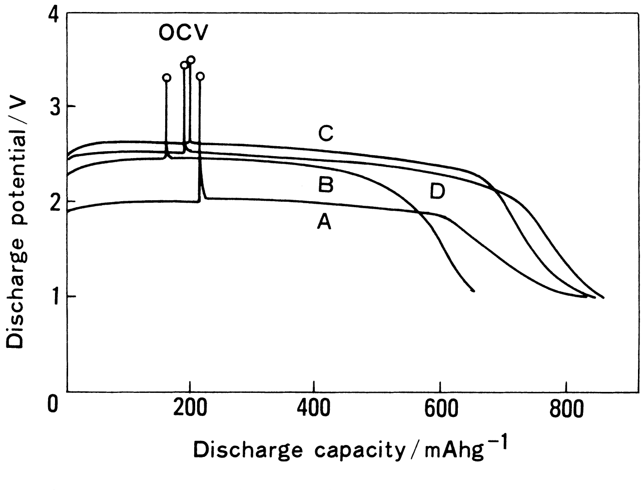

Fig. 5. Discharge curves of graphite fluoride cathodes in 1 M $LiClO_4$–PC at 25°C (current density: 0.05 Adm^{-2}). A: $(CF)_n$ prepared from natural graphite at 600°C, B: $(C_2F)_n$ prepared from natural graphite at 350°C, C: $(CF)_n$ prepared from residual carbon via $(C_2F)_n$ at 450°C, D: $(CF)_n$ prepared from residual carbon via graphite oxide at 400°C.

Fluorine is easily intercalated in graphite at room temperature in aHF [28,29] or in the presence of a Lewis acid. Highly fluorinated stage 1 C_xF is a stable compound due to semi-ionic C–F bonding. The highest fluorine content is usually $x = 2$ in C_xF C_2F gives the higher discharge potentials than $(CF)_n$ because of in-plane diffusion and higher activity of semi-ionic fluorine [30], however, the discharge capacity is inferior to that of $(CF)_n$ due to its lower fluorine content.

Fine graphite powder was highly fluorinated by combining fluorine gas with not only HF but also a Lewis acid such as IF_5 [31]. Though a product still contains a trace of iodine fluoride, it gives a high discharge potential and large capacity [32]. Recently the fluorination method was modified by employing two-step reactions [33]. Fine graphite powder was fluorinated by a gas mixture of F_2, HF and IF_5 at room temperature and further fluorinated by fluorine gas at an elevated temperature between 150°C and 350°C. C–F bond changed from nearly semi-ionic to almost covalent with increasing second fluorination temperature. These fluorinated materials enable the discharge at high current densities.

Graphite oxide is prepared by several methods using $KClO_3$, HNO_3, H_2SO_4 and so on. It is hygroscopic and thermally less stable than graphite fluoride, however, partial fluorination of graphite oxide at 90–200°C gives an oxide fluoride of graphite with hydrophobicity and higher thermal stability [34]. Though the discharge of graphite oxide itself does not proceed well, fluorinated graphite oxide is easily discharged without initial potential drop. Fig. 6 shows examples of the discharge curves.

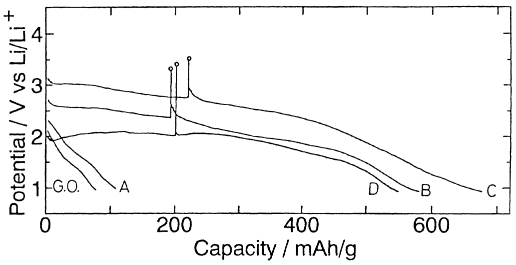

Fig. 6. Discharge curves of graphite oxide and those fluorinated at various temperatures in 1 M $LiClO_4$–PC at 25°C (current density: 0.05 Adm^{-2}). G.O.: graphite oxide, $C_8O_{2.99}H_{1.71}$; A: fluorinated at room temperature, $C_8O_{2.73}H_{2.08}F_{0.01}$; B: fluorinated at 100°C, $C_8O_{1.80}H_{0.84}F_{3.38}$; C: fluorinated at 110°C, $C_8O_{1.09}F_{5.47}$; D: fluorinated at 200°C, $C_8O_{0.71}F_{5.93}$.

4. Summary and future scope

Carbon materials are good electric conductors and commonly have the layered structures into and from which foreign species can be intercalated and deintercalated. These properties enable the applications of carbon materials and their compounds to battery materials. Li/$(CF)_n$ battery is a typical example using a fluorides of carbon. Development of a new cathode material is still one of research subjects in this field. The Li/$(CF)_n$ batteries and alternating cathode materials are precisely described in the previously published books [35,36]. In these years, research interest is focused on the development and improvement of lithium secondary batteries, in which fluorine chemistry also has an important role, i.e., fluoride salt and fluoropolymer are commonly employed in practical batteries and synthesis of new fluoride electrolytes, development of organofluorine compounds as solvents, improvement of anode and cathode performances by surface modification using fluorine and so on are now actively investigated.

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