DISCHARGE REACTION AND OVERPOTENTIAL OF THE GRAPHITE FLUORIDE CATHODE IN A NONAQUEOUS LITHIUM CELL

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Summary

Analyses of discharge products, and OCV measurements in different solvents indicate that the discharge reaction of an Li–$(C_x F)_n$ cell is the electrochemical formation, and subsequent chemical decomposition, of an intermediate phase composed of carbon, fluoride ion and solvated lithium ion. The overpotential of the graphite fluoride cathode decreases with decreasing thickness of the crystallite along the *c* axis, and with increasing space between the monolayers and the defect concentration of graphite fluoride. The capacity and utilization of fluorine increase with increasing crystallite size along the *a* axis.

Introduction

About 15 years ago, the lithium–graphite fluoride cell using organic solvents was proposed as a primary battery. Since then, several mechanisms have been advanced for the reaction of the graphite fluoride cathode. Margrave *et al.* [1] calculated the theoretical electromotive force of the Li–$(CF)_n$ cell, assuming that the cell reaction was the formation of lithium fluoride and carbon:

$$CF + Li \longrightarrow C + LiF \tag{1}$$

The calculated e.m.f. was 4.57 V. However, the OCV of an actual cell is 3.2 - 3.3 V in 1 M $LiClO_4$–PC solution at 25 °C. To explain this difference between the calculated and observed e.m.f. values, Whittingham [2] suggested that the discharge product responsible for the electrochemical reaction is not carbon and LiF, but rather a ternary graphite intercalation compound composed of C, Li and F:

$$CF + Li \longrightarrow CLi_x F \tag{2}$$

No experimental evidence was given for this reaction, however.

The discharge performance of the cell depends on the crystal form and the crystallinity of the graphite fluoride. These factors are controlled by

choosing a pristine carbon and the reaction conditions, but it is difficult to prepare a single crystal of graphite fluoride.

In this paper, the reaction mechanism of the graphite fluoride cathode, and several structural factors that determine the discharge characteristics, are reported.

Experimental

Graphite fluorides were synthesized by direct fluorination of natural graphite (purity 99.4%). The cathode was prepared by pressing a mixture of graphite fluoride (10 mg), acetylene black (10 mg, conductive additive), and polyethylene (10 mg, binder). The anode and the reference electrode were lithium metal pressed on a nickel screen. The electrolyte solutions were dimethyl sulfoxide (DMSO), γ-butyrolactone (BL), propylene carbonate (PC), and sulfolane (TMS) containing 1 M $LiClO_4$. The water content was less than 100 ppm. The cells were discharged at a constant current density of 0.5 mA cm^{-2} at 25 °C in a glove box with an argon atmosphere.

Results and discussion

Discharge reaction of graphite fluoride cathode

The discharge potential of graphite fluoride is almost flat to 70 - 80% discharge. As the open-circuit potential is a constant value over this range, the overpotential is also considered to be invariant. This phenomenon in the discharge of a layered material suggests that the activity of the species that determines the electrode potential is kept constant by decomposition of an intermediate discharge product which might form a so-called diffusion layer.

In a previous paper [3], ESCA spectra of a discharged cathode showed that the discharge product contained an intermediate substance composed of C, F^- and Li^+, which had a chemical bond intermediate between covalent and ionic types, together with LiF and carbon. Thermodynamic calculation and analysis of the discharge product also indicated that the propylene carbonate solvent participated in the cell reaction [4, 5]. The discharge product was recently analyzed more precisely [6]. In the C_{1s} ESCA spectra of the discharge product, the intensity of a peak at 290.4 eV originating from $(CF)_n$ decreased with increasing discharge, and a peak indicating carbon appeared strongly at 284.2 eV. Several new peaks were observed between 290 and 285 eV. New peaks also appeared in the F_{1s} spectra between those for $(CF)_n$ and LiF. A semi-ionic bond between carbon and fluorine, observed in C_{1s} and F_{1s} spectra, suggests that the discharge product which is responsible for the electrochemical reaction is not carbon and LiF but an intermediate substance containing carbon, lithium, and fluoride ions. This could be formed by intercalation of Li^+ ions into graphite fluoride.

The formation of the intermediate substance was further supported by studies of ^{19}F- and ^{7}Li-NMR spectra [6].

Lithium reference electrodes show a different potential in each solvent, due to a difference in the solvation energies of the lithium ions. The free energy of solvation for a single ion was estimated from the modified Born's equation:

$$\Delta G_{solv} = -\frac{Ne^2}{2}\left(1 - \frac{1}{\epsilon}\right)\left(\frac{z^2}{r + r'}\right) \tag{3}$$

where N is Avogadro's number, r is the ionic radius, Ze is the ion charge, ϵ is the dielectric constant of the solvent and r' is the correction factor. The solvation energies calculated from eqn. (3) were -5.00×10^5, -4.80×10^5, -4.56×10^5, -4.58×10^5 J mol^{-1}-Li$^+$ for DMSO, BL, PC and TMS, respectively. The differences in these solvation free energies correspond to the differences in lithium electrode potentials in the solvents; the potentials relative to that in 1 M LiClO$_4$–PC solution are -0.45 V in DMSO, -0.25 V in BL at 25 °C, and -0.02 V in TMS at 30 °C.

If complete desolvation of the solvent molecule from the Li$^+$ ion occurs on the cathode surface at an equilibrium state, the OCV of the cell will be the same in every solvent. Table 1 shows the OCV after 25% discharge. The OCVs of lithium–(CF)$_n$ and (C$_2$F)$_n$ batteries are equivalent in the same solvent. However, OCVs are different in different solvents. The value of the OCV increases with increasing solvation energy for the Li$^+$ ion. The difference in OCVs is 0.12 - 0.22 V. This result indicates that the solvent molecule participates in the cell reaction, namely, the discharge product determining the equilibrium potential is an intermediate phase composed of carbon, lithium ion, fluoride ion, and solvent molecule. From these results, the cell reaction of the Li–(CF)$_n$ or (C$_2$F)$_n$ battery is derived as follows. A solvated Li$^+$ ion is intercalated in the graphite fluoride layer to make an intermediate phase, namely, the diffusion layer, i.e.,

$$C_xF + Li + zS \longrightarrow C_x \cdot F^- \cdot Li^+ \cdot zS \text{ (Electrochemical reaction)} \tag{4}$$

where z is the solvation number and S is the solvent molecule. The intermediate discharge product gradually decomposes to carbon, LiF, and solvent molecule.

TABLE 1

OCV of lithium–graphite fluoride cells in different solvents (at 25% discharge) (V)

Graphite fluoride	Solvent			
	DMSO	BL	PC	TMS
(CF)$_n$	3.50	3.30	3.28	3.28
(C$_2$F)$_n$	3.47	3.39	3.26	3.27

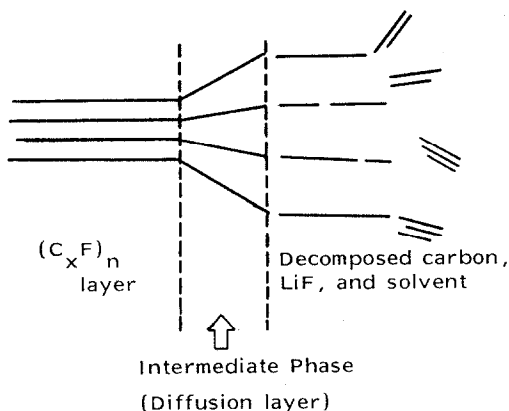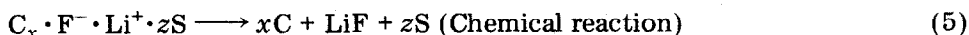Fig. 1. Schematic diagram of discharge reaction of Li–$(CF)_n$ or $(C_2F)_n$ battery.

$$C_x \cdot F^- \cdot Li^+ \cdot zS \longrightarrow xC + LiF + zS \text{ (Chemical reaction)} \tag{5}$$

The discharge reaction of an Li–$(CF)_n$ or $(C_2F)_n$ battery is illustrated schematically in Fig. 1.

Structural factors determining discharge characteristics

The cathode overpotential decreases with increasing $d(002)$ interlayer spacing and the half width $\beta(002)$ of the (002) X-ray diffraction line of $(CF)_n$ [7]. Since the thickness of the graphite fluoride monolayer is the same in every $(CF)_n$, the space between monolayers increases with increasing $d(002)$. The half width, $\beta(002)$, is inversely proportional to the thickness of graphite fluoride crystallite along the c axis. The large $\beta(002)$ means that $(CF)_n$ is composed of thin crystallites along the c axis. These factors make the Li^+ ion transfer easier in the diffusion layer formed by the discharge. On the other hand, it is difficult to prepare $(C_2F)_n$ with large differences in $d(002)$ and $\beta(002)$ because pristine carbon and the reaction temperature are limited. $(C_2F)_n$ is prepared only from a highly graphitized carbon material at 350 - 400 °C. The lower overpotential of $(C_2F)_n$ than that of $(CF)_n$ is mainly ascribed to another structural factor. ^{19}F-NMR and ESR spectra indicate that $(C_2F)_n$ contains a small amount of unreacted fluorine and carbon that are distributed so randomly that they cannot be detected by X-ray diffractometry or elemental analysis. This is regarded as a kind of lattice defect which facilitates the decomposition of the intermediate phase and therefore the Li^+ ion transfer in the diffusion layer [7]. The wide space between monolayers, the thinness of the graphite fluoride crystallite along the c axis, and the high defect concentration, all act to decrease the overpotential of the graphite fluoride cathode during the discharge process.

The crystallite size along the a axis, perpendicular to the c axis, also significantly affects the discharge performance of graphite fluoride. During discharge, solvated Li^+ ions are intercalated in the graphite fluoride, making a thin, intermediate phase, regarded as a diffusion layer, which decomposes
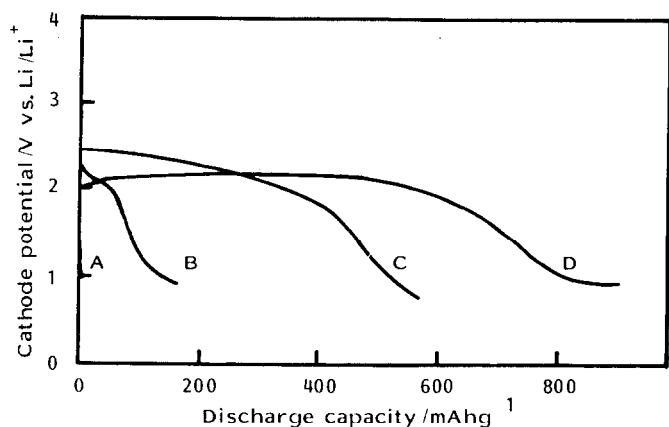
Fig. 2. Discharge characteristics of several fluorocarbons (1 M LiClO$_4$–PC solution, 0.5 mA cm^{-2}, 25 °C). A, Polytetrafluoroethylene; B, C$_{24}$F$_{36}$; C, (CF)$_n$ prepared from non-heat-treated petroleum coke; D, (CF)$_n$ prepared from Madagascar natural graphite.

TABLE 2

Physical and chemical properties of fluorocarbons

Fluorocarbons	Empirical formula	F/C	Carbon framework	Specific resistance (Ω cm)
Polytetrafluoroethylene	CF$_2$	2	straight chain	$> 10^{14}$
Coronene fluoride (C$_{24}$F$_{36}$)	C$_2$F$_3$	1.5		—
(CF)$_n$ prepared from non-heat-treated petroleum coke	CF	1	trans-linked cyclohexane chairs	$> 10^{20}$
(CF)$_n$ prepared from Madagascar natural graphite	CF	1		$> 10^{20}$

gradually to carbon, LiF, and solvent. This maintains the constant thickness of the diffusion layer to give a flat discharge potential. Figure 2 shows the discharge curves of several kinds of fluorocarbons. Their structural features and physical properties are listed in Table 2. The chemical bonds between carbon and fluorine in these fluorocarbons are essentially the same, namely, covalent. These compounds are all electrical insulators. The variation in the electrochemical activity between polytetrafluoroethylene and the other fluorocarbons is obvious, as shown in Fig. 2. It arises from a difference in their carbon frameworks: the former is composed of straight chains and the latter are composed of trans-linked cyclohexane chairs stacked along the c axis. The carbon framework of graphite fluoride can easily revert to the carbon structure in the cathode reduction process. With decreasing size of the arrays of cyclohexane chairs along the a axis in fluorocarbons, in other words, with decreasing crystallite size along the a axis, the discharge capacity and utility of the fluorine is decreased. This is due to the difficulty in the

recovery of the electroconductive carbon structure, namely, to the localization of electrons in benzene rings, which occurs when the number of benzene rings is small. Thus, the crystallite size of graphite fluoride along the a axis determines the cell capacity and the utility of the fluorine.

References

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