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THERMODYNAMIC STUDIES OF DISCHARGE REACTION OF GRAPHITE FLUORIDE-LITHIUM BATTERY

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SUMMARY

The changes in thermodynamic functions, ΔG, ΔS and ΔH were evaluated for (CF)n/Li and $(C_2F)n$/Li cell reactions. Thermodynamic data were obtained by measuring the cell electromotive forces and temperature coefficients. It was found for $CF_{0.93}$ that the observed free energy and enthalpy changes are smaller by ca. 100 kJ mol^{-1} than those calculated while the entropy change is larger than the calculated value by a·factor of more than 10. This difference is understandable from the model that the discharged product is not carbon and lithium fluoride but an intercalation compound having solvated lithium and fluoride ions in its layered lattice. The value of ΔS for the $(C_2F)n$/Li cell was about half of that for (CF)n.

INTRODUCTION

Graphite fluoride, (CF)n, is one of the excellent cathode materials for high energy density lithium battery [1-4]. The postulated cell reaction:

$$\frac{1}{n}(CF)n + Li \longrightarrow \frac{1}{n}(C)n + LiF \qquad (1)$$

requires an open-circuit voltage (OCV) of ca. 4.6 V based on the thermodynamic quantities of LiF and (CF)n[5], however, the reported OCV s are around 3.2 V. In order to explain this discrepancy, it has been proposed that Li^+ ions diffuse between the layers of the graphite lattice to react with fluorine and form a ternary intercalation compound CLi_xF $(x<1)$[6].

$$\frac{1}{n}(CF)n + xLi \longrightarrow CLi_xF \tag{2}$$

Recently we have found that the discharged product was a ternary intercalation compound having solvated Li^+ ions[7]. The discharge process may be a kind of topochemical reaction, followed by decomposition of the compound:

$$\begin{aligned} &CF_x + xLi + yPC \longrightarrow C(LiF)_x{\cdot}yPC \\ &\qquad\qquad\qquad\qquad\qquad \text{(electrochemical reaction)} \\ &C(LiF)_x{\cdot}yPC \longrightarrow C + xLiF + yPC \\ &\qquad\qquad\qquad\qquad\qquad \text{(chemical reaction)} \end{aligned} \tag{3}$$

where PC designates propylene carbonate, $\underbrace{OCH(CH_3)CH_2OCO}$.

EXPERIMENTAL

Synthetic conditions and some structual parameters of (CF)n and $(C_2F)n$ prepared from natural graphite are summarized in Table 1.

A graphite fluoride cathode was made up in the following manner. Graphite fluoride, acetylene black, and polyethylene powder(Merck, guaranteed grade) were mixed in a weight ratio ; 2:1:1. The mixture is dried under reduced pressure, and compression molded under 400 $kgcm^{-2}$, then sandwiched by two round nickel mesh(13 mm dia., 100 mesh). The cathode pellet thus obtained was wound by a graphite fiber at its peripheral edge for electric connection.

The anode was lithium metal pressed on a nickel mesh (15×15 mm) connected with a nickel wire.

The reference electrode was lithium metal bar(ca.2×2×15 mm) cut out from the metal block just before each experiment.

1M $LiClO_4$-propylene carbonate(PC) solution was used as an electrolyte. The purification method was described in

TABLE 1

Synthetic conditions and some structural parameters of (CF)n and $(C_2F)n$ samples

i) Synthetic conditions

	Starting Material	Temp./°C	F_2 Pressure/mmHg	Time/d	Method
(CF)n	Natural graphite (Madagascar,46-62μm)	600	760	0.9	Flow
$(C_2F)n$	"	380	760	7	Batch

ii) Composition and X-ray diffraction data

	F content/%	F/C molar ratio	d(001)/Å	d(100)/Å
(CF)n	59.6	0.93	5.86	2.23
$(C_2F)n$	49.5	0.62	8.86	2.16

previous paper[4]. The temperature of electrolyte was monitored with a mercury thermometer accurate to 0.01°C.

Potential measurements were carried out in the range of 18 to 32°C by using a digital potentiometer with voltage follower having high input-impedance($10^{14}\Omega$). The first 5% of the capacity was discharged as a preliminary electrolysis to avoid influence of surface functional groups(e.g., $>CF_2$, $-CF_3$). The stable potential was measured after opening the circuit for over 24 hours.

RESULTS AND DISCUSSION

ΔG, ΔS and ΔH for Li/CF)n cell

The change in Gibbs free energy ΔG for a cell reaction is related to the reversible electromotive force (EMF) of the cell:

$$\Delta G = -nFE, \tag{4}$$

where n and F are equivalent number of electrons for the reaction concerned and Faraday's constant, respectively. When eq.(4) is substituted into the Gibbs-helmholtz equation:

$$[\partial(\Delta G)/\partial T]_p = -\Delta S, \tag{5}$$

we obtain

$$nF(\partial E/\partial T)_p = \Delta S. \tag{6}$$

The entropy change ΔS is thus derived from the temperature coefficient of EMF, dE/dT. The enthalpy change ΔH is determined from the equation:

$$\Delta G = \Delta H - T\Delta S, \tag{7}$$

that is,

$$\Delta H = -nFE + nFT(dE/dT). \tag{8}$$

Figure 1 shows the variation of OCV(E) of the (CF)n-Li system with temperature(T). In the temperature range from 19 to 30°C there is a linear relationship between E and T, satisfying eq.(6).

Margrave et al. calculated the standard formation enthalpy for CF_n from the heat of combustion obtained by a fluorine bomb calorimeter[5].

$$\Delta H_f(CF_n) = (4.53 - 178.01n)\ \mathrm{kJ\ mol^{-1}} \tag{9}$$

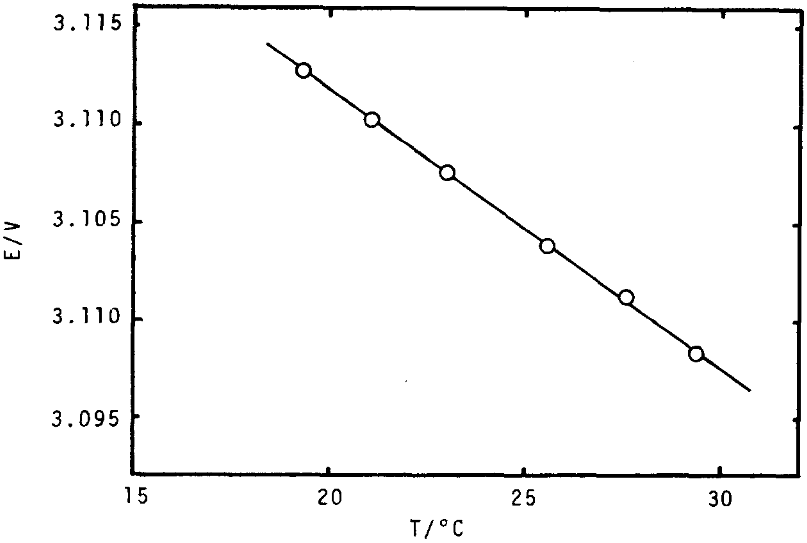

Fig. 1 Variation of OCV of (CF)n-Li cell with temperature.

The standard entropy of CF_n was also obtained from its heat capacity[5].

$$S(CF_n) = (4.62 + 16.91n)\ J\ mol^{-1}K^{-1} \qquad (10)$$

Using these results, they evaluated the thermodynamic quantities for the following reaction[5]:

$$CF_n(s) + nLi(s) \longrightarrow C(s) + nLiF(s). \qquad (11)$$

$$\Delta H = -(438.92n + 4.53)\quad kJ\ mol^{-1} \qquad (12)$$

$$\Delta S = (1.07 - 10.35n)\quad Jmol^{-1}K^{-1} \qquad (13)$$

$$\Delta G = -(435.83n + 4.85)\quad kJ\ mol^{-1} \qquad (14)$$

Table 2 shows thermodynamic data calculated on the basis of the experimental results, and those obtained from equations (12)∿(14) for $CF_{0.93}$ used in this experiment. There is a remarkable difference between them with respect to all the thermodynamic parameters. Margrave et al. regarded graphite and solid LiF as the discharged product, however, the actual discharged product is an intercalation compound containing some solvent molecules as described in eq.(3). The contribution of ion solvation and insertion of solvated ions into layered lattice to total changes in thermodynamic functions was evaluated by postulating the following reactions:

TABLE 2

Thermodynamic data for $CF_{0.93}$-Li system at 25°C.

	I	II	Ave.	Calculated*)
EMF, E/V	3.11	3.09	3.10	4.57
$(\partial E/\partial T)_p$/ mVK^{-1}	-1.41	-1.46	-1.44	-0.1
$-\Delta S/Jmol^{-1}K^{-1}$	127	131	129	8.6
$-T\Delta S/kJmol^{-1}$	37.8	39.0	38.4	2.6
$-\Delta G/kJmol^{-1}$	279	277	278	410
$-\Delta H/kJmol^{-1}$	317	316	317	413

* The values in this column were calculated based on the following discharge reaction:

$CF_{0.93}(s) + 0.93Li(s) \longrightarrow C(s) + 0.93LiF(s)$.

TABLE 3

Free energy, enthalpy and entropy changes for the solvation process of LiF in propylene carbonate.

	ΔG / $kJ\ mol^{-1}$	ΔH / $kJ\ mol^{-1}$	$-298\Delta S$ / $kJ\ mol^{-1}$	ΔS / $J\ mol^{-1}K^{-1}$
lattice formation				
$\Delta X_{lat}(LiF)^a$	-962.3	-1040.1	77.8	-261
hydration				
$\Delta X_{hyd}(Li^+)^b$	-516.7	-558.6	41.9	-141
$\Delta X_{hyd}(F^-)^b$	-434.3	-474.0	39.7	-133
transfer from H_2O to PC				
$\Delta X_{tr}(Li^+)^c$	23.8	3.7	20.1	-67.4
$\Delta X_{tr}(F^-)$	56.1[c]	58.7[d]	-2.6[e]	8.8[e]

a)M. Salomon, J. Phys. Chem., 74,2519(1970). b)H.L. Friedman, C.V. Krishnan, 'Water'(F. Frank, ed.), vol.3, p.55, Plenum Press, New York (1973). c)ref.8. d)calculated by other two functions. e)extrapolated from the data of Cl^-, Br^- and I^-.

$$CF_{0.93} + 0.93Li \longrightarrow C + 0.93LiF, \tag{15}$$

$$C + 0.93LiF \longrightarrow C + 0.93Li^{+}\cdot PC + 0.93F^{-}\cdot PC, \tag{16}$$

$$C + 0.93Li^{+}\cdot PC + 0.93F^{-}\cdot PC \longrightarrow C\cdot 0.93LiF\cdot PC, \tag{17}$$

where $Li^{+}\cdot PC$ and $F^{-}\cdot PC$ mean the ions solvated by PC. In addition to the results for eq.(15), if the thermodynamic functions for solvation process of LiF (eq.(16)) are obtained, those for the insertion of solvated Li^{+} and F^{-} into graphite (eq.(17)) can be estimated. Solvation energy ΔX_{solv} (X=G,H,S) is calculated from lattice energy ΔX_{lat} of LiF, hydration energy ΔX_{hyd} and intersolvent transfer energy from water to PC ΔX_{tr}:

$$\Delta X_{solv} = -\Delta X_{lat}(LiF)+\{\Delta X_{hyd}(Li^{+})+\Delta X_{hyd}(F^{-})\} +\{\Delta X_{tr}(Li^{+})+X_{tr}(F^{-})\}. \tag{18}$$

The values of ΔX_{lat}, ΔX_{hyd} and ΔX_{tr} are shown in Table 3. Since the $\Delta S_{tr}(F^{-})$ and $\Delta H_{tr}(F^{-})$ are not available, the ΔS_{tr} was estimated by the following method and $\Delta H_{tr}(F^{-})$ was calculated from $\Delta G_{tr}(F^{-})$ and the estimated $\Delta S_{tr}(F^{-})$. When halide ions (F^{-}, Cl^{-}, Br^{-} and I^{-}) are transfered to real solvent from ideal non-interacting solvent having the same density and molecular weight as the real solvent, their entropy changes give a straight line against the reciprocal ionic radius of halide ion in the case of methanol and formamide [8]. Then the ΔS_{tr} (F^{-}, ideal solv.→ PC) was obtained by the extrapolation of the plot of ΔS_{tr} (ideal solv.→ PC) for Cl^{-}, Br^{-} and I^{-} <u>vs</u>. $1/r_i$ of each ion. The $\Delta S_{tr}(F^{-})$ from water to propylene carbonate was calculated by using this value as follows:

$$\Delta S_{tr}(F^{-}) = \Delta S_{tr}(F^{-}, \text{ideal solv.} \rightarrow PC)-\Delta S_{tr}(F^{-}, \text{ideal solv.} \rightarrow H_2O)+\Delta S_{corr}. \tag{19}$$

LiF

where ΔS_{corr} is a correction value between ideal water and propylene carbonate [8]. Though the value of $\Delta S_{tr}(F^{-})$ depends on the method of estimation, the plus sign of $\Delta G_{tr}(LiF)$ and $\Delta H_{tr}(LiF)$ would not be changed. In Table 3, it is noted that the ΔG_{tr} s are both positive for Li^{+} and F^{-}

TABLE 4

Thermodynamic functions for each process of the discharge reaction of $CF_{0.93}$-Li cell.

	ΔG / kJ mol^{-1}	ΔH / kJ mol^{-1}	$-298\Delta S$ / kJ mol^{-1}	ΔS / $Jk^{-1}mol^{-1}$
Observed reaction				
ΔX_{obs}	-278.0	-316.4	38.4	-129
total reaction				
ΔX_{calcd}	-410.0	-412.6	2.6	-9
solvation of 0.93Li				
ΔX_{solv}	84.8	65.0	19.8	-66
insertion of 0.93Li F·PC				
ΔX_{ins}	47.2	30.6	16.6	-54

TABLE 5

Thermodynamic data for $CF_{0.62}$-Li system at 25°C.

	I	II	Ave.	$CF_{0.93}\times\frac{0.62}{0.93}$
EMF,E/V	3.31	3.38	3.35	
$(\partial E/\partial T)_p/mVK^{-1}$	-0.85	-0.89	-0.87	
$-\Delta S/Jmol^{-1}K^{-1}$	50.8	53.2	52.0	86.0
$-T\Delta S/kJmol^{-1}$	15.1	15.9	15.5	25.6
$-\Delta G/kJmol^{-1}$	198	202	200	185
$-\Delta H/kJmol^{-1}$	213	218	216	211

ions, and their interactions with PC are contrastive with each other as shown in ΔH_{tr} and ΔS_{tr} since PC has electronegative three oxygen atoms. By using the thermodynamic functions for eq.(15),(16)(ΔX_{cald}, ΔX_{solv}) and the values experimentally obtained(ΔX_{obs}), those for the insertion of the ions into graphite(ΔX_{ins}) are calculated:

$$\Delta X_{ins} = \Delta X_{obs} - (\Delta X_{calcd} + \Delta X_{solv}) \qquad (20)$$

The results are summarized in Table 4 with those for solvation of LiF and other two processes. Both ΔG and

ΔH give positive values for the solvation of LiF and insertion of solvated ions while the ΔS is negative in both cases, which would be a reasonable result. The increase in the free energy changes corresponds to the decrease of the cell voltage. About 1.3 V in the original EMF given by the total cell reaction is consumed to form the ternary intercalation compound with solvated ions. As the discharge reaction proceeds, the graphite intercalation compound $C(LiF)_x \cdot yPC$ formed by the electrochemical reaction gradually decomposes to graphite, LiF and propylene carbonate.

Thermodynamic quantities for Li/(C_2F)n cell

Thermodynamic data for $CF_{0.62}$ are shown in Table 5. From the comparison of these data with the hypothetical thermodynamic functions of (CF)n, calculated on the basis of the empirical formula of graphite fluoride used in this experiment(data for $CF_{0.93}$ ×0.62/0.93), it is found that the enthalpy change for(C_2F)n is comparable with that for (CF)n whereas entropy decrease is much smaller in (C_2F)n than in (CF)n. (C_2F)n-type graphite fluoride is a second stage intercalation compound different from (CF)n, having a diamond-like C-C covalent bond perpendicular to the carbon network[4]. When (C_2F)n is discharged, a second stage intercalation compound would be formed accompanying the break of C-C bond perpendicular to the carbon layers, which would yield some entropy increase and result in the smaller decrease in entropy in the cell reaction. For this reason, equations (11)∿(14) cannot be applied to the discharge reaction:

$$CF_{0.62} + 0.62Li \longrightarrow C + 0.62LiF,$$

and a large error would be produced if estimation of the entropy change for the insertion of solvated ions into graphite is made from the result obtained for Li/(CF)n cell reaction. In order to calculate the energy change for each process of the discharge reaction, the enthalpy change of formation and standard entropy for (C_2F)n have to be determined.

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