

DISCHARGE CHARACTERISTICS OF GRAPHITE FLUORIDE PREPARED VIA GRAPHITE OXIDE

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Summary

The discharge performance of graphite fluoride, prepared by fluorinating residual carbon from the thermal decomposition of graphite oxide, has been evaluated. In most cases, the graphite fluoride was $(CF)_n$. That prepared from flaky natural graphite gave a higher OCV and discharge potential than $(C_2F)_n$ prepared by direct fluorination; the overpotential was similar. The energy density increased by 20 - 30%. In the case of $(CF)_n$ prepared from graphitized petroleum coke, a large overpotential, which commonly appears at the beginning of discharge, was not observed, and the discharge potential gradually decreased with the progress of the discharge reaction.

Introduction

There are two crystal forms of $(CF)_n$ and $(C_2F)_n$ in graphite fluoride, in which intercalated fluorines are covalently bonded to sp^3 carbon atoms linked in a cyclohexane chair configuration. The discharge performances of $(CF)_n$ and $(C_2F)_n$ are strongly dependent on their crystallinity and composition [1]. The discharge capacity is higher in $(CF)_n$ than in $(C_2F)_n$, according to their fluorine contents, but the overpotential is smaller in the $(C_2F)_n$ compound due to faster Li^+ ion transfer in the diffusion layer. The latter arises from the thinness of the crystallites along the c axis and the high defect concentration in $(C_2F)_n$ which promotes decomposition of the diffusion layer [1].

Based on the relation between the discharge performance and the crystallinity and composition of graphite fluoride, attempts have been made to prepare graphite fluoride, mainly $(C_2F)_n$, by fluorinating expanded residual graphite that was obtained by thermal decomposition of a graphite intercalation compound (GIC) of fluorine having an ionic bond. The discharge performance of the $(C_2F)_n$ thus prepared has been evaluated previously [2]: the open-circuit potential was higher than that of a conventional graphite

fluoride, but the overpotential was almost the same. GICs having covalent bonds comprise only graphite fluoride and graphite oxide, which are expected to provide a residual carbon composed of smaller crystallites than a GIC with an ionic bond. In the present study, the discharge performance of $(CF)_n$ prepared from a residual carbon is reported.

Experimental

Preparation of residual carbon

The preparation of graphite oxide and the subsequent thermal decomposition was as follows. Flaky natural graphite or graphitized petroleum coke (10 g) and $NaNO_3$ (5 g) were placed in H_2SO_4 (230 ml) and then $KMnO_4$ (30 g) was gradually added with stirring. Water was then added in aliquots over a period of 10 min. During this procedure, the temperature of the solution increased to around 180 °C through the heat of hydration. These conditions resulted in the formation of graphite oxide, and its thermal decomposition, in successive steps. The residual carbon was filtered out and then washed with water for several tens of times. The carbon was dried under vacuum at 60 °C for 1 day, followed by heating under vacuum at 120 - 600 °C for 2 h.

Fluorination of residual carbon and electrochemical measurement

Fluorination of residual carbon was conducted between room temperature and 600 °C under a flow of F_2 gas. The electrochemical cell consisted of a lithium anode, a graphite fluoride cathode and a lithium reference electrode in 1 M $LiClO_4$ -propylene carbonate (PC) solution. The cathode was prepared by pressing a mixture of graphite fluoride (10 mg), acetylene black (10 mg, conductive additive) and polyethylene (10 mg binder). All measurements were conducted, at 25 °C, in a glove box filled with argon.

Results and discussion

Characteristics of residual carbon and graphite fluoride

Table 1 shows the oxygen content and X-ray diffraction data of residual carbon obtained via graphite oxide. The residual carbon prepared from natural graphite contained 20 wt.% oxygen, which decreased to between 12 and 6 wt.% after heat treatment between 400 and 600 °C, respectively. On the other hand, more oxygen was present in the residual carbon prepared from petroleum coke; this decreased by only 3 wt.% on heat treatment at 400 °C. The d spacing for the (002) diffraction line of residual carbon indicates the distance between two carbon layers stacked along the c axis. The d spacing was somewhat larger than that of pristine natural graphite, approaching 3.35 Å after heat treatment. The residual carbon from petroleum coke had a larger d spacing than that from natural graphite. The $\beta(002)$, half width of

TABLE 1

Oxygen content and XRD data of residual carbon obtained by thermal decomposition of graphite oxide

Sample	Oxygen (wt.%)	XRD data	
		$\beta(002)$ (deg)	$d(002)$ (Å)
<i>Original natural graphite</i>	0	0.48	3.35
NG-60	20	2.05	3.42
NG-400	12	0.83	3.35
NG-500 ^(a)	11	0.83	3.37
NG-600	6	0.84	3.37
<i>Original graphitized petroleum coke</i>	0	0.29	3.37
PC-60	28	5.4	3.66
PC-120 ^(b)	—	5.3	3.66
PC-400	25	—	3.4 (3.6 ^(c))

^(a)Residual carbon obtained from natural graphite (NG). Figure indicates heat-treatment temperature under vacuum.

^(b)Residual carbon obtained from petroleum coke (PC) graphitized at 2800 °C. Figure indicates heat-treatment temperature under vacuum.

^(c)Peak split occurred.

the (002) diffraction line, is inversely proportional to the crystallite size along the *c* axis. Although the crystallite size was increased by heat treatment due to the removal of oxygen as CO₂, it was smaller than that of pristine graphites.

The larger values of $\beta(002)$ and $d(002)$ for residual carbon from petroleum coke indicate that this carbon has a more disordered structure than that prepared from natural graphite. This is because natural graphite has a higher crystallinity and a smaller surface area than graphitized petroleum coke. Considering the values of the *d* spacing, the oxygen may exist in the grain boundaries of carbons. Pristine natural graphite and graphitized petroleum coke consist of large crystallites ($L_c > 1000$ Å, $L_a > 1000$ Å), while ungraphitized petroleum coke has very small crystallites ($L_c = 36$ Å, $L_a = 28$ Å). When the latter is graphitized at 2800 - 3000 °C, the crystallites grow in the direction of both the *a* and *c* axes. However, the residual carbon thus obtained is composed of very thin crystallites having a somewhat larger dimension along the *a* axis [3].

The residual carbons were fluorinated to graphite fluoride at a lower temperature and over a shorter time than the pristine graphites. The fluorination temperature and the analyses of the products are shown in Table 2. In most cases, the product was (CF)_{*n*} having 6 - 7 Å as the repeat distance and an F/C ratio of 0.94 - 1.2. The half width of the (002) line of (CF)_{*n*} prepared

TABLE 2

Composition and XRD data of $(CF)_n$ prepared from residual carbons

Starting carbon	Fluorination temp. (°C)	F/C	XRD data	
			$\beta(002)$ (deg)	$d(002)$ (Å)
NG-400	600	1.11	1.35	5.82
	500	0.94	3.20	6.26
	450	0.96	3.95	6.52
	400	0.95	4.58	6.99
	350	0.74 ^(a)	3.82	7.82
	300	0.52 ^(a)	4.5	7.8
PC-400	400	1.19	2.32	6.06
	300	1.19	3.55	6.29
	200	1.08	3.96	6.56
	100	1.03	4.00	6.83
	30	0.64 ^(b)	3.84	6.29

^(a)Product contains $(C_2F)_n$.^(b)Oxygen may still be present after fluorination.

from residual carbon was 3.20 - 4.00°, except for material prepared at a high temperature, while that of $(CF)_n$ obtained by direct fluorination was 1.4°. This means that $(CF)_n$ prepared from residual carbon consists of much smaller crystallites along the c axis than conventional $(CF)_n$. The d spacing of $(CF)_n$ has a value greater than 6 Å, except in material prepared at 600 °C, which shows that the space between two adjacent $(CF)_n$ layers is larger than that in $(CF)_n$ prepared by direct fluorination of graphite. These factors make the transfer of Li^+ ion in the diffusion layer easier when $(CF)_n$ is discharged.

The ^{19}F -NMR spectrum of $(CF)_n$ has wide and small absorption derivatives. The former indicate fluorines covalently bonded to carbons. The peak-to-peak width was 8 G, which is smaller than the 9 G of $(CF)_n$ prepared from natural graphite. This indicates that the fluorines are in a more active state in $(CF)_n$ prepared from residual carbon.

Discharge performance of $(CF)_n$ prepared from residual carbon

Figure 1 compares the discharge curve of $(CF)_n$ prepared from residual carbon with those for $(CF)_n$ and $(C_2F)_n$ prepared by direct fluorination of natural graphite. The discharge characteristics are summarized in Table 3. $(CF)_n$ (NG-F400) showed a slightly higher discharge potential than $(C_2F)_n$. This arises from the difference in OCVs. The overpotentials of $(CF)_n$ compounds made from residual carbon (NG-F500, 450, 400) were almost the same as that of $(C_2F)_n$, namely, ~ 0.9 V at a current density of 0.5 mA cm^{-2} . As the utilization of fluorine was almost 100%, the energy density increased by 20 - 30%, compared with that of conventional $(CF)_n$. The OCV increased with decrease in the fluorination temperature. However, the discharge

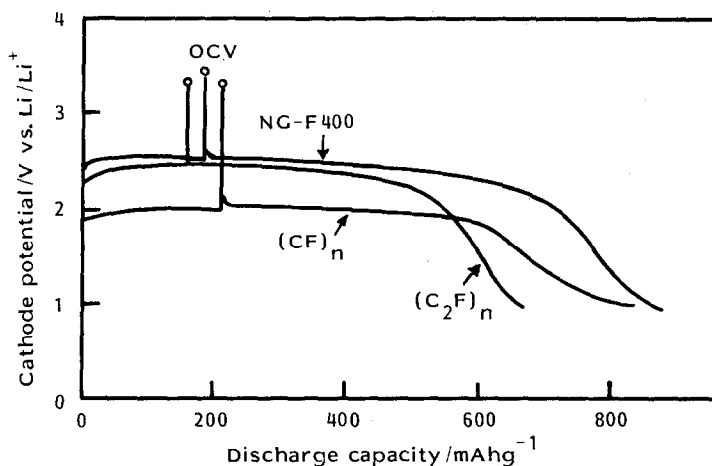


Fig. 1. Comparison of discharge curve of $(CF)_n$ prepared from residual carbon with those of conventional $(CF)_n$ and $(C_2F)_n$. NG-F400 = $(CF)_n$ prepared at 400 °C from residual carbon (pristine graphite: natural graphite); $(CF)_n$ = $(CF)_n$ prepared by direct fluorination of natural graphite at 610 °C; $(C_2F)_n$ = $(C_2F)_n$ prepared by direct fluorination of natural graphite at 350 °C.

TABLE 3

Discharge characteristics of graphite fluoride prepared from residual carbon (apparent current density: 0.5 mA cm^{-2})

Sample ^(a)	OCV ^(b) (V)	CCV ^(b) (V)	Overpoten- tial ^(b) (V)	Discharge capacity (mA h g^{-1})	Energy density (W h kg^{-1})	Utilization (%)
NG-F600	3.32	1.95	1.37	710	1280	80
NG-F500	3.32	2.35	0.97	840	1690	100
NG-F450	3.36	2.40	0.96	850	1770	100
NG-F400	3.45	2.51	0.94	850	1870	100
NG-F350	3.55	2.7	0.9	740	1700	95
NG-F300	3.62	2.9	0.7	600	1420	95
PC-F400	3.38	2.24	1.14	880	1720	95
PC-F300	3.42	2.29	1.13	870	1740	95
PC-F200	3.42	2.41	1.01	810	1680	90
PC-F100	3.55	2.8	0.8	870	1950	100
PC-F30	3.70	3.1	0.6	660	1660	90

(a) Samples prepared from NG-400 and PC-400. Figure after "F" indicates the fluorination temperature.

(b) At 25% discharge.

capacity and energy density were lowered due to the formation of $(C_2F)_n$. $(CF)_n$ prepared at 600 °C (NG-F600) gave a similar discharge performance to that of conventional $(CF)_n$, because the amorphous part of the residual carbon was lost as gaseous fluorocarbons, and $(CF)_n$ was therefore formed from carbon that had a high crystallinity.

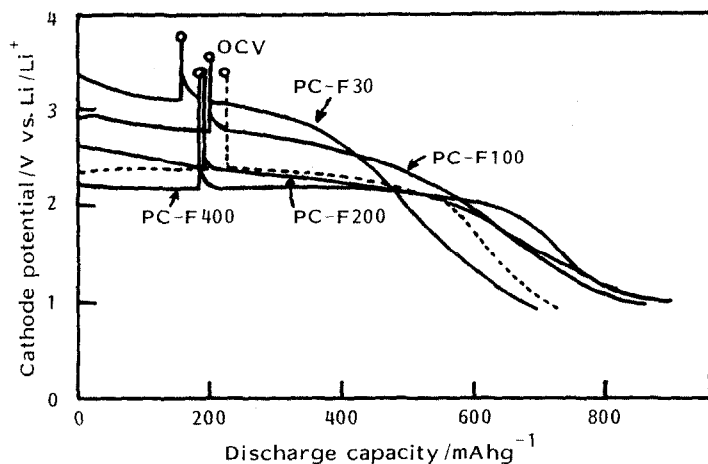


Fig. 2. Discharge curves of $(CF)_n$ prepared via graphite oxide (from graphitized petroleum coke). Fluorination of PC-F30 at room temperature; PC-F100 at 100 °C; PC-F200 at 200 °C; and PC-F400 at 400 °C. Dashed curve obtained for commercial $(CF)_n$ prepared from ungraphitized PC.

Figure 2 shows the discharge curves of $(CF)_n$ specimens obtained from graphitized petroleum coke via graphite oxide. Open-circuit potentials were higher and overpotentials were also larger than those of graphite fluoride obtained from natural graphite (NG-F series in Table 3). The most characteristic feature is that a large overpotential was not observed at the beginning of discharge, and the discharge potential gradually decreased as the discharge reaction proceeded. The discharge performance of $(CF)_n$ prepared at 100 - 200 °C was superior to that of commercial $(CF)_n$ prepared by direct fluorination of ungraphitized petroleum coke.

References

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