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INTRODUCTION

Covalent graphite fluoride (CF)_n is prepared by reaction of fluorine on graphite and the products can be co-intercalated by lithium atoms forming an excellent positive material for lithium primary battery [1-6].

The use of covalent-type fluoride carbon as cathode materials in non aqueous primary lithium batteries started at the beginning of the 70's [7]. The first lithium battery produced by Matsushita battery Co. in Japan was the Li/(CF)_n battery in 1973.

The use of these materials showed two main difficulties :

- a high temperature synthesis (> 400°C)
- a battery discharge potential lower than 2,6 V.

Hamwi et al. [8-9] showed that the graphite fluorination occurs at temperature as low as the ambient, and rich in fluorine stage-1 graphite intercalation compounds (GICs) can be obtained. This important finding opened the way for new investigations on the electrochemical properties of the low temperature carbon fluorides (LT-CF_x) in comparison with the conventional high temperature and strongly covalent ones (HT-CF_n).

The aim of this study is to show that LT-CF_x have better positive electrode kinetics in non aqueous primary lithium battery compared with HT-CF_n.

EXPERIMENTAL

Low temperature fluorocarbons (LT-CF_x) are obtained after a preliminary intercalation of a volatile fluoride of iodine in HF+F₂ atmosphere at ambient temperature [9,10].

The working composite electrode is prepared as follow :

Fluorographite powders (active materials) and acetylene black NA (as electrical conductor) are dispersed into acetonitrile solution of polyethylene oxide POE (as binder). The mixture is stirred for several hours and then, acetonitrile is removed at ambient temperature. The weight composition of this mixture is 10% POE, 10% NA and 80% CF_x.

A part of the mixture (about 30 mg) is pressed into a pellet (diameter 16 mm) under 2,5 T.

The negative electrode is lithium foil and the electrolyte is propylene carbonate PC/ethylene carbonate EC/ dimethoxyethane DME (1/1/2 in volume ratio) containing 1M LiClO₄.

The separator is a microporous polyethylene film (Celgard 2502).

For the evaluation of the fluorocarbon electrode, button type CR2430 cells are mounted in a dried argon filled box. Galvanostatic discharge are used in this study in the C/30 to C/5 range.

RESULTS AND DISCUSSION

Typical galvanostatic discharge curves at C/20 of Li/LT-CF_x cells (for different x values) and a Li/HT-CF_n cell are shown in figure 1.

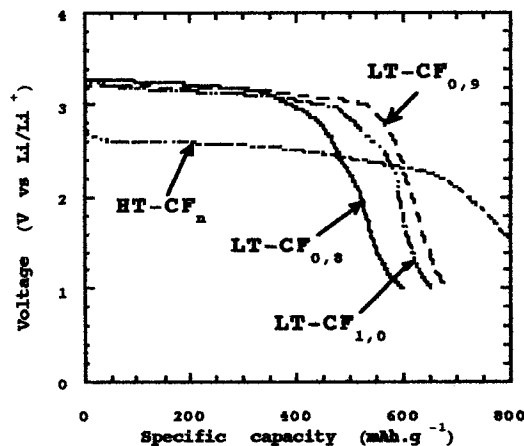


Figure 1 : Galvanostatic discharge curves (C/20 regime) of button type CR2430 cells Li/LiClO₄ 1M + EC/PC/DME/CF_x

Li/LT-CF_x cells have a high discharge voltage wich decreases from 3,26 to 3,15 V (vs Li/Li⁺) when x increases from 0,8 to 1. This observation was attributed to increased covalent character of carbon fluoride bond with the fluorine concentration [8].

The discharge potential was found about 27% lower with HT-CF_n compared with LT-CF_x under the same discharge conditions.

Table 1 summarizes the main characteristics of galvanostatic discharge curves of Li/LT-CF_x and Li/HT-CF_n systems for different regimes.

The specific capacity of Li/LT-CF_x batteries is about 600 mAh.g⁻¹ and varies with the F/C ratio. This capacity is practically constant for discharge regimes from C/30 to C/5 (figure 2). Li/HT-CF_n batteries show a very high discharge capacity under a C/30 galvanostatic regime (735 mAh.g⁻¹). This capacity falls down with fast discharge regimes.

Energy density of Li/LT-CF_x batteries is very important in comparison with Li/HT-CF_n batteries, especially for fast discharge regime. The electrode polarization is low for both materials.

The different electrochemical behaviour of the two types of carbon fluoride could be explained by the character of the chemical C-F bond and by chemical structure. The C-F bond in LT-CF_x is partially ionic (this characteristic increasing when F/C ratio is decreasing). The fluorination doesn't modify the planarity of the graphenes.

In the case of HT-CF_n, the C-F bond is covalent and the graphene planes are deformed [11,12].

compared with primary cells using a covalent fluoride graphite compounds (CF)_n prepared at high temperature. It appears that primary cells using LT-CF_x have a higher discharge potential and a better behaviour under heavy discharge regimes.

In conclusion, LT-CF_x are better positive electrode materials in non aqueous primary cells than HT-CF_n.

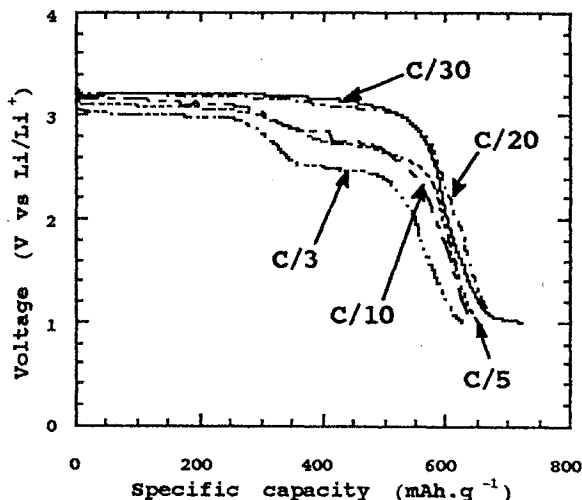


Figure 2 : Galvanostatic discharge curves of button type CR2430 cells Li/LiClO₄ 1M + EC/PC/DME/CF_{0,9} function of discharge regimes.

CONCLUSION

Semi-covalent type carbon fluorides have been tested as positive electrode materials in non aqueous primary lithium batteries. Their performances have been

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carbon fluoride type	discharge regime	OCV (V vs Li/Li ⁺)	medium discharge potential (V vs Li/Li ⁺)	Specific capacity (Ah.kg ⁻¹)	Energy density (Wh.kg ⁻¹)
HT-(CF) _n	C/30	3,18	2,54	735	1867
	C/20	3,19	2,52	726	1830
	C/10	3,20	2,52	632	1592
	C/5	3,20	2,46	640	1574
	C/3	3,03	2,15	246	529
LT-CF _{1,0}	C/30	3,70	3,15	619	1950
	C/20	3,77	3,10	599	1857
	C/10	3,62	2,97	602	1788
	C/5	3,78	3,00	582	1746
	C/3	3,80	2,50	433	1083
LT-CF _{0,9}	C/30	3,60	3,22	611	1967
	C/20	3,56	3,20	619	1981
	C/10	3,66	2,90	590	1711
	C/5	3,70	2,90	603	1749
	C/3	3,64	2,75	553	1521
LT-CF _{0,8}	C/30	3,58	3,26	530	1728
	C/20	3,70	3,26	528	1721
	C/10	3,73	3,10	530	1643
	C/5	3,71	2,91	523	1522

Table 1: Galvanostatic characteristics of Li/LT-CF_x and Li/HT-CF_n batteries