

Low-temperature carbon fluoride for high power density lithium primary batteries

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Abstract

Quantitative fluorination of graphite has been achieved at ambient temperature by the preliminary intercalation of iodine fluoride in HF + F₂ atmosphere. This fluorinated graphite LT-CF_x was used as the cathode material in liquid electrolyte lithium cells; rate capability tests were carried out. Results are presented in comparison with those obtained with conventional HT-CF_x. An outstanding behavior with LT-CF_x is found, especially at high rate. © 1997 Elsevier Science S.A.

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1. Introduction

Graphite fluorides with F/C ratios higher than 0.6 are prepared by two different methods:

1. Reaction with F₂ in the 400–600 °C temperature range. These compounds are characterized by a strong covalency of the C–F bonding as can be determined by X-ray photoelectron spectroscopy (XPS). The F(1s) binding energy is in the 689 eV range and the C(1s) lies in the 290 eV range [1].
2. Reaction with F₂ in HF + MF_n gaseous atmosphere at the ambient temperature, MF_n being a volatile fluoride such as IF₅, ClF₃, BF₃ ... [2].

In such compounds, the C–F binding energy is weaker than in the covalent-type ones. As consequence, their electrical conductivity is higher though they are considered as semi-conductors with high energy gap. The differences in the electrical conductivity and in the type of C–F bonding showed to affect considerably the electrode properties of the two types of graphitic fluorides when used as the cathode materials in lithium primary batteries [3]. As a matter of fact CF_x prepared at low-temperature LT-CF_x discharges at ~600 mV higher voltage than its counterpart prepared at high temperature HT-CF_x.

In this study we give further characterization of LT-CF_x by XPS and compare their rate capability with HT-CF_x in lithium/liquid electrolyte cells.

2. Experimental

We have used the same grade of natural graphite from Madagascar in fine powder (4 μm as average grain size) to prepare both LT- and HT-CF_x samples. We used IF₅ as the volatile fluoride because it yields the highest F/C ratio. Samples of different fluorine content were obtained by controlling the reaction time and the final homogenization heat-treatment temperature [2]. HT-CF_x was prepared at 600 °C under pure F₂ atmosphere for 2 h. The F/C ratio was close to 1. The samples were characterized by X-ray diffraction (XRD) and XPS. XPS data were obtained using an Ulvac Phi Model 5500 spectrometer.

Coin-type (2430) lithium cells were used for the electrochemical tests. The positive electrode consisted of a pellet with a diameter of 16 mm and was composed of 80 wt.% CF_x, 10 wt.% poly(ethylene oxide) (binder) and 10 wt.% carbon black. The electrolyte is 1 M solution of LiClO₄ in EC:PC:DME (1:1:2) mixture. Continuous galvanostatic discharge was performed at a C/30–C/3 current rate.

3. Results and discussion

3.1. XRD and XPS analysis

From XRD analysis, it was possible to determine the periodic interlayer spacing *I_c* and the in-plan parameter of LT-

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Table 1
XPS results obtained with LT- and HT-CF_x (numbers given between brackets give the relative intensity of the corresponding peak)

XPS binding energy	C(1S) (eV)	F(1S) (eV)	C-F bonding type
LT-CF _x	291.2 (2.0%)	688 (96.7%)	Semi-covalent
	289.4 (61.3%),	685.9 (3.3%)	
	287.0 (32.9%),		
	285.1 (3.8%)		
HT-CF _x	294.9 (3.4%)	691.4 (91.6%)	Covalent
	292.6 (85.6%)	688.5 (8.4%)	
	289.7 (11.0%)		

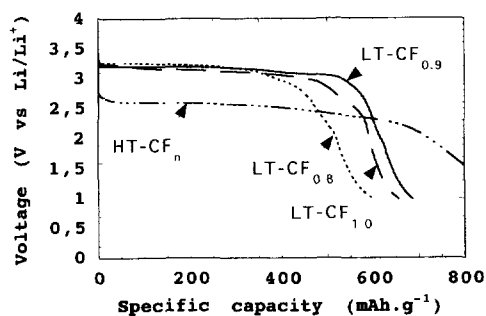


Fig. 1 Galvanostatic discharge curves (C/20 regime) of button-type CR2430 cells Li/1 M LiClO₄ + EC:PC:DME/LT-CF_x and HT-CF_x.

and HT-CF_x. In the former $I_c = 5.9 \text{ \AA}$ and $a = 2.46 \text{ \AA}$ and in the latter, $I_c = 6.02 \text{ \AA}$ and $a = 2.53 \text{ \AA}$. The differences in the a value come from the arrangement of the fluorine layer and from the change in the geometry of the carbon hexagons. In LT-CF_x, the hexagons remained planar as in the parent graphite with a very slight change in the in-plane C–C bonding

length, while in HT-CF_x, the hexagons adopt the chair-like geometry as in cyclohexane due to the sp^3 hybridization and the strong covalence of the C–F bonding.

The semi-ionic character of LT-CF_x was more clearly shown by XPS measurements. Table 1 gives typical values of the binding energy for C(1s) and F(1s). The binding energy correction relative to the binding energy of Au_{4f7/2} electrons was made for each sample.

The C(1s) peak at 289.4 eV for LT-CF_x and at 292.6 eV for HT-CF_x is assigned to a carbon bonded to a fluorine atom. The C(1s) peak at 287 eV for LT-CF_x and at 289.7 eV for HT-CF_x is assigned to a carbon bonded to a carbon atom.

3.2. Electrochemical studies

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

Li/LT-CF_x cells have a high discharge voltage which decreases from 3.26 to 3.15 V (versus Li/Li⁺) when x increases from 0.8 to 1. This result was attributed to an increased covalent character of carbon fluoride bond versus fluorine concentration [3]. The discharge potential was found about 27% lower with HT-CF_x compared with that of LT-CF_x under the same discharge conditions.

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. Note that Li/HT-CF_x batteries show a very high discharge capacity under a C/30 galvanostatic regime (735 mAh g⁻¹).

Table 2
Galvanostatic characteristics of Li/LT-CF_x and Li/HT-CF_x batteries

Carbon fluoride type	Discharge regime	OCV (V vs. Li/Li ⁺)	Medium discharge potential (V vs. Li/Li ⁺)	Specific capacity (Ah kg ⁻¹) (at 2 V)	Energy density (Wh kg ⁻¹)
HT-CF _x	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

The specific capacity for LT-CF_x is significantly higher than that for C_2F prepared by Hagiwara et al. [4] being close to 350 mAh g^{-1} . Table 2 summarizes the discharge characteristics for LT-CF_x samples under increasing rates.

The energy density based on the active electrode weight is higher for LT-CF_x with $x \geq 0.9$ than in HT-CF_x . The difference becomes more quantitative for discharge rates higher than $C/10$. At $C/3$, $\text{LT-CF}_{0.9}$ retains almost three times more energy than HT-CF_x . The electrochemical behavior of the two types of carbon fluoride could be explained by the nature of the chemical C–F bonding and by the chemical structure. The stronger covalency of HT-CF_x induces a higher electrode polarization due to its insulating character. In addition, the

reduction of HT-CF_x involves the breaking of more energetically stable C–F bonding as showed by XPS measurements. The activation energy is therefore higher than in LT-CF_x .

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