

## NEW GRAPHITE FLUORIDES AS ELECTRODE MATERIALS IN LITHIUM BATTERIES (EXTENDED ABSTRACT)

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It is well known that  $(C_2F)_n$  and  $(CF)_n$  prepared at high temperature (HT) have many good characteristics as cathode materials for lithium batteries in nonaqueous electrolyte systems [1].

Recently, we have shown that it is possible to prepare graphite fluorides of general formula  $CF_xM_y$  ( $0.5 \leq x \leq 0.80$ ,  $0.02 \leq y \leq 0.06$  and  $M = I, Br, Cl, B, \dots$ ) at room temperature (RT) [2]. The electrochemical performance exhibited by these new graphite fluorides is proving better than that of graphite fluorides (HT).

Several graphite fluoride (RT) samples have been tested as cathode materials in lithium batteries (typically, 30 mg, well mixed and pressed with 10 wt.% of an organic polymer,  $P(OE)_8LiClO_4$ , in acetonitrile as binder) in 1 M  $LiClO_4$ -propylene carbonate solution (Fig. 1).

In every case a high OCV value is obtained (3.71 V - 4 V). The discharge potential is very stable and lies between 3 and 3.2 V. It must also be

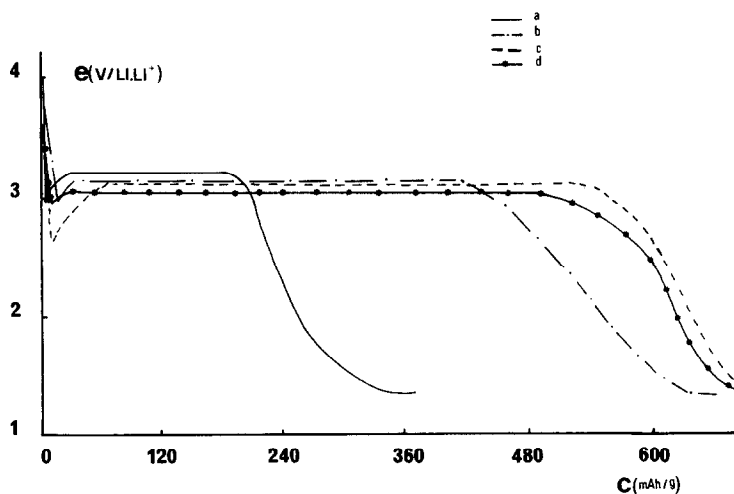


Fig. 1. Galvanostatic discharge curves of  $(CF_x)_n$  (RT) electrodes at 25 °C under  $i = 0.5$  mA  $cm^{-2}$ . (a)  $CF_{0.35}$  (RT) black; (b)  $CF_{0.65}$  (RT) green; (c)  $CF_{0.80}$  (RT) white; (d)  $CF_{0.75}$  (RT) yellow.

noted that the higher the value of  $x$ , the higher the corresponding electrode capacity.

For comparison, two electrodes have been tested under similar conditions. The first was made of CF (HT), the second of CF<sub>0.80</sub> (RT). The cells were discharged under  $i = 0.50 \text{ mA cm}^{-2}$  (Fig. 2(b), (c) and Table 1).

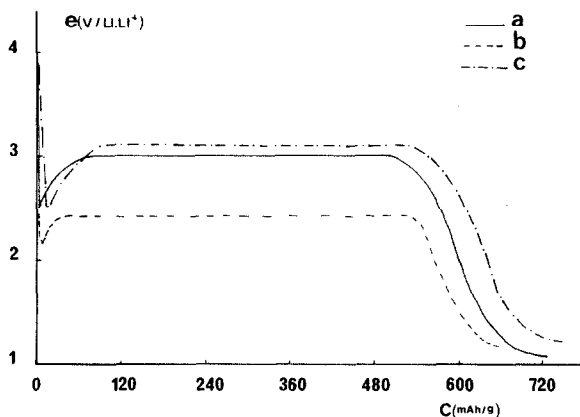


Fig. 2. Galvanostatic discharge curves of: (a) CF<sub>0.80</sub> (RT) electrode under  $i = 1 \text{ mA cm}^{-2}$ ; (b) CF (HT) electrode under  $i = 0.5 \text{ mA cm}^{-2}$ ; (c) CF<sub>0.80</sub> (RT) electrode under  $i = 0.5 \text{ mA cm}^{-2}$  in CF/1 M LiClO<sub>4</sub>-PC/Li cell at 25 °C.

TABLE 1

CF <sub>x</sub>	OCV (V)	Discharge po- tential $\langle e \rangle_i$	Capacity (mA h g <sup>-1</sup> )	Energy density (W h kg <sup>-1</sup> )
CF (HT)	3.30	2.42	600	1452
CF <sub>0.80</sub> (RT)	3.80	3.10	667	2068

These results show that the CF<sub>0.80</sub> (RT) electrode exhibits a discharge voltage of 3.1 V *vs.* the Li electrode, *i.e.*, 0.68 V above that obtained with the CF (HT) electrode. Moreover, the two electrodes have almost the same capacity. Figure 2(a) shows the discharge curve of the CF<sub>0.80</sub> (RT) electrode under  $i = 1 \text{ mA cm}^{-2}$ . Even under this condition, the electrode capacity remains superior to 600 mA h g<sup>-1</sup> (energy density = 2000 W h kg<sup>-1</sup>).

Both the excellent discharge performance and the high energy density exhibited by the CF<sub>0.80</sub> (RT) electrode constitute additional results to show that C-F bondings involved in CF<sub>x</sub> (RT) are predominantly ionic in character, and, on the other hand, that the Li<sup>+</sup> ions (or solvated Li<sup>+</sup> ions) diffuse more rapidly in this electrode than in CF (HT). These results corroborate those previously obtained by powder X-ray diffractometry and IR spectroscopy [2].

The cyclic voltammograms obtained with the Li/PC + LiClO<sub>4</sub> (1 M)/CF<sub>0.75</sub> I<sub>0.03</sub> (RT) system are displayed in Fig. 3. The first scan (Fig. 3(a))

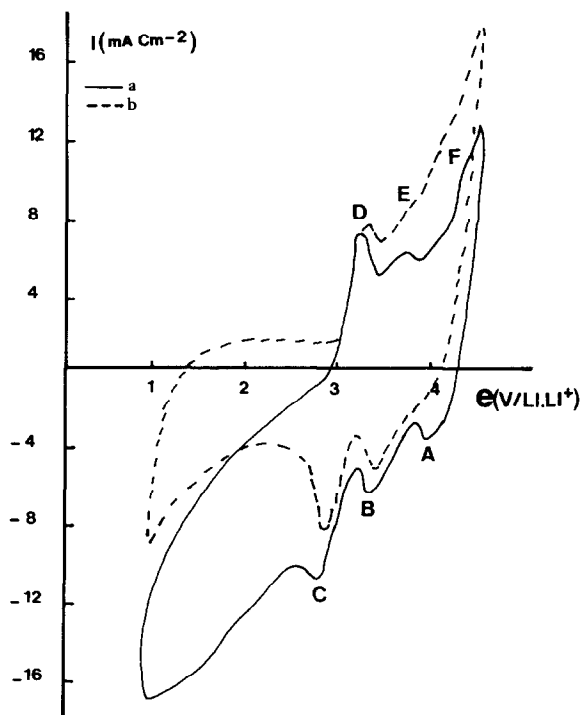


Fig. 3. Potential scanning curves at 150 mV/mn for  $\text{CF}_{0.75}\text{I}_{0.030}$  in 1 M  $\text{LiClO}_4$ -PC. (a) 1st scan; (b) 10th scan.

reveals three reduction peaks and three oxidation peaks which are, respectively, denoted A ( $e_A = 4.02$  V), B ( $e_B = 3.38$  V), C ( $e_C = 2.86$  V), D ( $e_D = 3.23$  V), E ( $e_E = 3.68$  V), F ( $e_F = 4.36$  V).

After 10 scans, the voltammogram obtained (Fig. 3(b)) exhibits only the B, C, D peaks, while all the others have progressively disappeared. From these results it is clear that peaks C and D can be attributed, respectively, to the reduction and oxidation of carbon. Considering the behaviour of the electrochemical system under cycling, it seems reasonable to assume that peaks A and B probably correspond to the reduction of the following species:



Finally, all the electrochemical properties of these new graphite fluorides prove that they are promising materials for such applications. It should be noted that these electrochemical cells can be used as accumulators if they are recharged before being completely discharged. Studies are in progress to clarify this point.

**References**

- 1 N. Watanabe and M. Fukuda, *U.S. Pat.* 3,536,532; 3,700,502 (1970).
- 2 M. Daoud, A. Hamwi and J. C. Cousseins, *Expermat.* 87, *Bordeaux, France*, 23  
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