

NEW GRAPHITE FLUORIDES AS ELECTRODE MATERIALS IN LITHIUM BATTERIES

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(Received September 30, 1988; in revised form March 27, 1989)

Summary

Graphite fluorination at room temperature can be achieved with the use of a volatile fluoride such as BF_3 , BrF_5 , ClF_3 and IF_5 in a $\text{F}_2 + \text{HF}$ atmosphere. The compounds obtained by this new method have a ternary composition and a layered structure in which the carbon hexagons remain planar and the C-F bonds are slightly ionic. This enhances their properties as cathode materials in lithium batteries utilizing liquid or solid polymer electrolytes. Energy densities higher than 2 kW h kg^{-1} have been achieved in both these media particularly with IF_5 derived compounds.

Introduction

A new method for the fluorination of natural graphite has been recently described by Hamwi *et al.* [1] who first succeeded in obtaining fluorine rich compounds at room temperature (RT), whereas the classical method commonly used until now involves maintaining the elements at high temperature (HT) in the $350 - 650 \text{ }^\circ\text{C}$ range [2, 3]. This was made possible with the introduction along with gaseous fluorine, of a mixture of a volatile fluoride MF_n ($M = \text{I, Br, Cl, W, Mo, B, Re, } \dots$) and HF which act as catalysts and lower the energy barrier for the formation of C-F bonds. It is now believed that an intermediate graphite salt of general formula $\text{C}_p^+ \text{MF}_{n+1}^-$ is formed in the first step of the fluorination and results in a preliminary oxidation of the carbon layers.

In contrast to graphite fluorides obtained at high temperature (HT- CF_x) in which the C-F bonding is strongly covalent in nature, an ionic contribu-

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tion in the bonding appears in RT-CF_x due to the persistence in these compounds of a small amount of intercalated MF_n, with the possible occurrence of an internal exchange of fluorine between MF_n and C-F [4]. Two main consequences to this partial ionicity in RT-CF_x compared with HT-CF_x are observed: (i) enhancement of the electronic conductivity of two or three orders of magnitude due to the remaining delocalized π -electron and the planar shape of the carbon hexagons [1, 4], (ii) higher discharge potential (by ~ 0.6 V) when RT-CF_x obtained with IF₅ is used as cathode material in lithium batteries under the same discharge conditions [5, 6].

In this paper we focus on the effects of both the chemical nature of the catalyst MF_n and the state of the electrolyte (organic liquid or solid polymer) on the lithium batteries performances. Although it was shown that IF₅-based RT-CF_x lead to the highest fluorine content [1], other fluorides such as BrF₅, BF₃ and ClF₃ show good catalytic activities and allow the synthesis of graphite fluorides having good cathode properties. In addition, the use of a solid state polymer should give relevant indications about the mechanism of the cathode reaction during the battery discharge.

Experimental

Sample preparation and characterization

Two hundred mg of a finely powdered (~ 10 μm of grain size) natural graphite from Madagascar are preliminarily dehydrated under a primary vacuum at 500 °C, then introduced into the monel reactor tube. IF₅, BrF₅, BF₃ and ClF₃ were freshly prepared *in situ* by a direct fluorination of the elements or their salts [1]. A permanent flow of F₂ and HF is maintained over the graphite powder for several hours at room temperature.

The composition of the final compounds was determined by elemental analysis. A very small amount of hydrogen was detected ($<0.01\%$) so HF behaves as a real catalyst during the fluorination process. Table 1 gives the rough formula of the corresponding compounds and it should be pointed out that in their general presentation CF_xM_y, the y value decreases with increasing x in the order BF₃ > BrF₅ \sim ClF₃ > IF₅. The structure was determined by means of XRD and IR spectrometry. Details of these analyses are given elsewhere [1].

Electrochemical cells

We used two types of cell designs adapted to the type of electrolyte: organic liquid (1 M LiClO₄ in propylene carbonate (PC)) [7] or a solid state polymer (polyethylene oxide: P(EO)₈-LiClO₄) [8]. The positive electrode (5 - 40 mg in weight for PC and 2 - 3 mg for PEO batteries) has a composite constitution with a mixture of CF_xM_y, graphite and P(EO)₈-LiClO₄ as ionically conducting binder, and was either pressed under 1 ton/cm² to form a pellet of 8 mm diameter for the liquid electrolyte batteries or sprayed on a stainless steel disc of 20 mm diameter for the polymer system [8]. The

TABLE 1

RT-CF_x formula and galvanostatic discharge characteristics of corresponding lithium batteries. The highest energy density is reached with the IF₅ derived compound in both liquid PC (Fig. 1d) or solid polymer electrolyte (Fig. 2) based batteries.

Figure	RT-CF _x formula	OCV (V)	Plateau voltage <i>e</i> (V)	Faradaic capacity (mA h g ⁻¹)	Energy density (W h kg ⁻¹)
1a	CF _{0.52} B _{0.06}	4	3.2	310	1000
1b	CF _{0.62} Br _{0.05}	3.96	3.15	600	1900
1c	CF _{0.65} Cl _{0.05}	3.93	3.14	628	1980
1d	CF _{0.80} I _{0.02}	3.83	3.10	667	2060
2	CF _{0.80} I _{0.02}	3.73	3.10	670	2000

discharge tests were carried out using continuous (in PC media) or intermittent (in PEO media) galvanostatic techniques (1 h of discharge, 3 h of relaxation) or by slow scan voltammetry with sweeping rates of 0.2 and 1 mV mn⁻¹ for PC- PEO-based cells respectively.

Results and discussion

Galvanostatic discharge

In Fig. 1 are plotted the continuous discharge curves under the same current intensity of 250 μA performed with 30 - 40 mg of RT-CF_x containing BF₃ (a), BrF₅ (b), ClF₃ (c) and IF₅ (d) in 1 M LiClO₄-PC solution. The

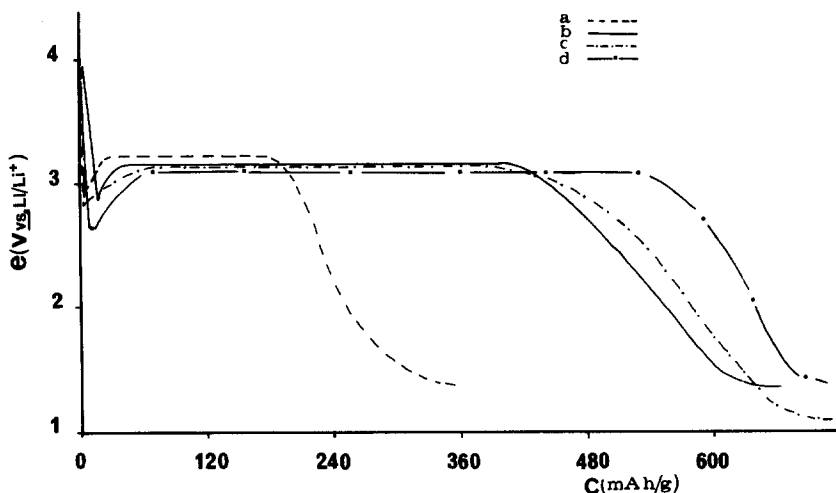


Fig. 1. Galvanostatic discharge curves ($i = 250 \mu\text{A}$) of Li/LiClO₄ 1 M in PC/RT-CF_x batteries. The active electrode weight was 5 - 10 mg. RT-CF_x = (a) CF_{0.52}B_{0.06}, (b) CF_{0.62}Br_{0.05}, (c) CF_{0.65}Cl_{0.05}, (d) CF_{0.80}I_{0.02}.

battery potential is related to the experimental active electrode capacity C (mA h g^{-1}). Curves show an abrupt drop of potential at the beginning of the discharge which is generally attributed to the poor conducting character of the active electrode, then the potential increases and stabilizes at plateau values between 3.2 and 3.1 V. The cathode reaction consists of an electrochemical intercalation of lithium and a reduction of C-F to conducting graphite and LiF, which induces an enhancement of the electrode/electrolyte interface transfer properties.

The main characteristics of the discharge curves are reported in Table 1 with the open circuit voltage (OCV) measured before the current was set up, the plateau mean voltage e , the actual electrode faradaic capacity C reached at 1.5 V as potential cut-off and the energy density deduced from e and C values.

It is worth noticing that the OCV and e decrease slightly with x in BF_3 , BrF_5 , ClF_3 and IF_5 based RT- CF_x respectively while concomitantly y increases. This should be in close relation with the degree of ionicity in the corresponding compounds. The fluorination proceeds through the formation of a strongly ionic graphite salt $\text{C}_p^+\text{MF}_{n+1}^-$ and the covalent character associated with the formation of the C-F bonding becomes more predominant as the reaction progresses [1, 4]. The amount of residual graphite salt is proportional to y in CF_xM_y , and should control the charge transfer on the carbon atoms and thus the electrode potential. However higher electrode capacities are reached with high fluorination amount x as particularly observed in IF_5 based RT- CF_x , leading to an excellent energy density superior to 2 kW h kg^{-1} ($\sim 1 \text{ kW h l}^{-1}$) counting the reactants only.

The intermittent discharge curve of the solid state battery with $\text{P}(\text{EO})_8\text{-LiClO}_4$ as electrolyte and $\text{CF}_{0.8}\text{I}_{0.02}$ as active electrode is shown in Fig. 2 with the OCV reached after 3 h of relaxation in curve a and the voltage after

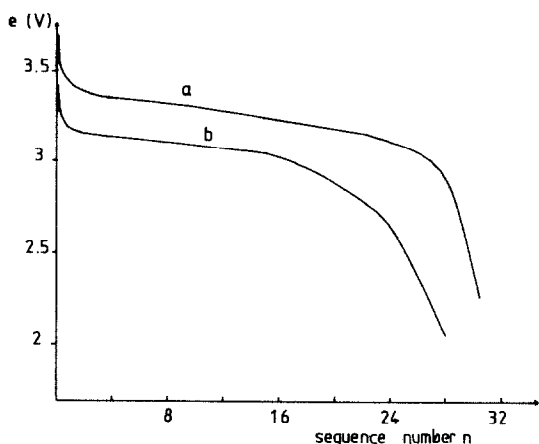


Fig. 2. Intermittent galvanostatic discharge curves ($C/30$) of the $\text{Li}/\text{P}(\text{EO})_8\text{LiClO}_4/\text{CF}_{0.8}\text{I}_{0.02}$ battery at 80°C , with $\sim 2 \text{ mg}$ of active electrode. (a) OCV reached after 3 h of relaxation, (b) voltage after 1 h of discharge.

1 h under a current flow of $C/30$ in curve b. The battery was operated at $80\text{ }^\circ\text{C}$, and the discharge curve is given as function of the sequence number n , $0 < n < 30$. The current intensity was chosen so that at each sequence the amount of intercalated lithium was increased by $1/30$ of the total theoretical cathode capacity. A remarkably high average potential is obtained for both curves (~ 3.23 and ~ 3.10 V for a and b respectively) with good discharge yield. The energy density deduced from curve a is also in the order of 2 kW h kg^{-1} and should be considered as the highest reached in PEO-based lithium batteries [9].

A noticeable difference appears in the shape of the discharge curves obtained in liquid and solid state electrolytes. Whereas in the first case, Fig. 1, curve d shows a voltage plateau characteristic of an electrode reaction involving the formation of a new phase, in the second case the voltage decreases uniformly which should indicate no change in the phase number during the lithium intercalation between the CF_x layers. The cointercalation of solvent molecules in the PC media should favor the internal displacement of fluorine from carbon to lithium and so LiF is precipitated and pristine graphite is formed. The partial ionicity found in RT-CF_x is probably responsible for the difference in the cathode reaction mechanism found with HT-CF_x in which an intermediate ternary product is formed involving solvated Li^+ intercalated between the CF_x layers [10 - 12]. In RT-CF_x , both LiF and graphite were identified by XRD performed on partially discharged active electrode [6]. In the solid state battery, lithium diffuses between the CF_x layers free from any solvation sphere and should acquire a higher mobility which delays the formation of LiF . This assumption will be verified by an *in situ* XRD study in a solid state battery.

Voltammetric discharge

Figure 3 shows voltammograms obtained in the PC media with 5 - 10 mg of cathode materials taken in the same order as in Fig. 1, whereas Fig. 4 corresponds to that in the PEO cell with IF_5 based RT-CF_x . A current peak associated with the reduction of the carbon fluoride is observed in each case whose intensity i_{peak} and voltage e_{peak} are shown in Table 2 and depend on the cathode composition and the electrolyte type. In PC media, i_{peak} increases with the electrode capacity C , even when the active electrode weights are in the same range. In addition, e_{peak} is higher for ClF_3 , IF_5 and BrF_5 than for BF_3 based RT-CF_x despite the larger corresponding i_{peak} values. As i_{peak} and e_{peak} are mainly associated with the lithium diffusion coefficient D_{Li^+} and the electrode reaction affinity, this seems to indicate a close dependence of D_{Li^+} on the type of catalyst.

In PEO media, a very sharp current peak at 2.5 V and a shoulder at 2.05 V are observed and should correspond to the lithium localization in the vicinity of C-F and I-F redox centers in the van der Waal's gap respectively. The diffusion coefficient of the unsolvated lithium calculated on the basis of both intermittent galvanostatic [13] and voltammetric discharge techniques [14] is as high as $10^{-9}\text{ cm}^2\text{ s}^{-1}$ at $80\text{ }^\circ\text{C}$.

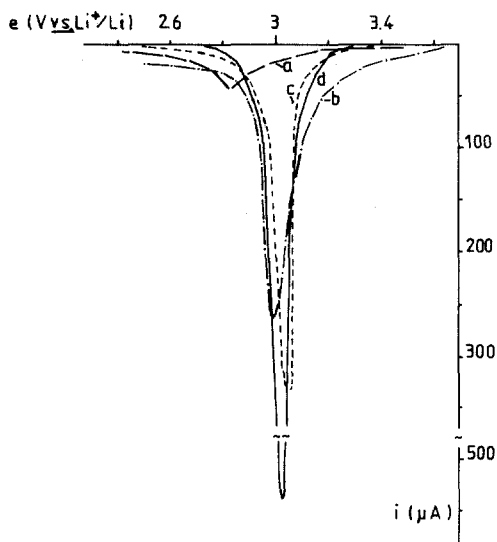


Fig. 3. Voltammetric discharge under a sweeping of $(-0.2) \text{ mV mn}^{-1}$ of Li/LiClO_4 1 M in $\text{PC}/\text{RT-CF}_x$ batteries. $\text{RT-CF}_x =$ (a) $\text{CF}_{0.52}\text{B}_{0.06}$, (b) $\text{CF}_{0.62}\text{Br}_{0.05}$, (c) $\text{CF}_{0.65}\text{Cl}_{0.05}$, (d) $\text{CF}_{0.80}\text{I}_{0.02}$, with 5 - 10 mg of active electrode weight.

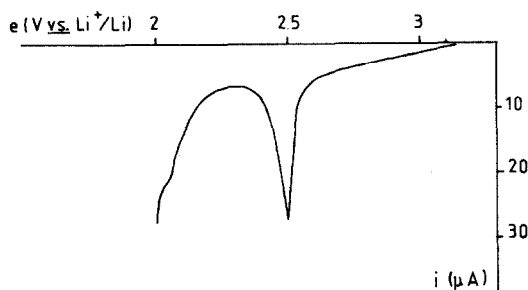


Fig. 4. Voltammetric discharge curve under a sweeping of $(-1) \text{ mV mn}^{-1}$ of the $\text{Li}/\text{P}(\text{EO})_8\text{LiClO}_4/\text{CF}_{0.80}\text{I}_{0.02}$ battery at 80°C , with ~ 3 mg of active electrode weight.

TABLE 2

Current peak characteristics during the voltammetric discharge (see Table 1 for RT-CF_x)

Figure	e_{peak} (V)	I_{peak} (μA)
3a	2.84	40
3b	3.02	270
3c	3.07	330
3d	3.04	550
4	2.5	27

Conclusion

Graphite fluorides obtained at room temperature using appropriate catalysts show excellent positive electrode behaviour in lithium batteries. We have emphasized the effect of the partial ionicity found in these compounds which allows a voltage plateau about 0.6 V higher than that found in covalent type HT-CF_x to be reached, under the same experimental conditions of discharge [5, 6]. In addition, the IF₅ based RT-CF_x has a faradaic capacity equivalent to that of the richest in fluorine HT-CF_x, and taking into account its lower preparative cost due to energy consideration, this compound constitutes an excellent candidate for high energy and high power densities lithium batteries. Further fundamental studies are still underway for a better knowledge of the cathode reaction mechanism and how this mechanism is affected by the nature of the catalyst and the electrolyte.

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