

Graphite oxyfluoride: behaviour as electrode material in lithium batteries

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(Received February 11, 1993; in revised form September 21, 1993; accepted September 24, 1993)

Abstract

On the basis of the recent preparation method of graphite oxyfluorides, discharge characteristic studies of these compounds as cathode materials in lithium-battery systems, using liquid or solid electrolytes, are reported. Their performances are compared with those of original graphite oxide and graphite fluoride compounds. Good electrochemical behaviour is exhibited by graphite oxyfluoride which depends on the O/F ratio, and on the origin of the starting material for its preparation.

Introduction

Although a large number of cathode materials have been investigated for electrochemical primary and secondary systems with lithium anode [1], graphite compounds (GCs) can still be considered as one of the most suitable cathode materials exhibiting good performances such as high faradaic capacity and high specific energy density [2]. The development of graphite fluoride (GF) as a new cathode material has resulted in a particularly viable lithium battery, now manufactured on a large scale [1, 3]. This cathode material $(CF_x)_n(\text{HT})$ (HT=high temperature) can be prepared by direct reaction of graphite powder with fluorine gas at elevated temperatures (generally between 500 and 600 °C, $x=1$). The corresponding lithium cell has a working voltage of 2.43 V and a practical energy density of 1458 Wh kg⁻¹ relative to the graphite fluoride cathode mass [4]. Similarly, there is some interest in graphite oxide (GO) (whose ideal formula is $C_n\text{OOH}$) positive electrode for organic electrolyte-lithium batteries [5, 6] although the working potential of Li/GO cells is less than that of Li/ $(CF_x)_n(\text{HT})$. The practical energy densities for the two systems are very close. However, the calculated theoretical energy density of Li/GO cells is twice as high (3000 Wh kg⁻¹ based on the open-cell voltage (OCV) of 3 V), because its faradaic capacity is higher. The main advantage of GO over $(CF_x)_n(\text{HT})$ is its low cost. Graphite oxides have been well known for many years and several methods of synthesis have been reported. They were based on graphite oxidation by strong oxidizing agents, as for example a mixture of fuming HNO_3 and KClO_3 [7].

Moreover, it has been reported, not long ago, that graphite fluoride $(CF_x)_n(\text{RT})$ could also be prepared at room temperature (RT) [8], leading consequently to electrochemical performances higher than those of $(CF_x)_n(\text{HT})$ [4]. Indeed, the lithium cell based on $(CF_x)_n(\text{RT})$ cathode material exhibits an energy density of about

TABLE 1

Some discharge characteristic data of CF(HT), GO, and CF(RT) cathode liquid electrolyte systems

Compound	Composition	Initial potential (V vs. Li/Li ⁺)	Current density (mA cm ⁻²)	Discharge potential (V vs. Li/Li ⁺)	Faradaic capacity (Ah kg ⁻¹)	Energy density (Wh kg ⁻¹)	Ref.
CF(HT)	CF	3.40	0.5 1	2.43 2.00	600 300	1458 600	4 4
GO	C ₈ O ₄ H ₃	3.30	0.10 0.63	2.50 2.30	790 790	1817 1817	10 6
CF(RT)	CF _{0.8} I _{0.02} *	3.83	0.5 1	3.10 3.00	667 630	2001 1890	4 4

*The presence of iodine is due to a small amount of intercalated IF₃ [12] (see Experimental).

2000 Wh kg⁻¹ and a working voltage of 3.1 V. These compounds were prepared by developing a specific method of synthesis which consists in reacting graphite at room temperature with a gas mixture of F₂, HF, and a volatile inorganic fluoride such as IF₅ [8]. It should be noted that (CF_x)_n(RT) also presents high performances as an electrode material in a solid polymer electrolyte based lithium secondary cell [9]. As a comparison, Table 1 collects the main discharge characteristics of three lithium systems with (CF_x)_n(HT), GO, and (CF_x)_n(RT).

Starting from GF(HT) or GO-like compounds, several attempts to prepare graphite oxyfluorides have been made. For example, the fluorination of graphite oxide at room temperature, under an atmosphere of fluorine, results in a compound whose mean chemical formula is C_{4.35}OF_{0.85} [11]. In a previous paper [12], we presented new method for the preparation of graphite oxyfluorides taking advantage of the specific method of fluorination of graphite at room temperature. This paper deals with the results we obtained from testing these compounds as cathode materials in lithium batteries. In particular, their characteristics are compared with those of (CF_x)_n(RT) and GO.

Experimental

The starting material is a natural Madagascar graphite powder (80 μm particle size). Two different ways for the preparation of graphite oxyfluoride have been used:

(i) oxygenation of a fluorine-unsaturated (CF_x)_n(RT) compound; the system obtained is then denoted by GFO.

(ii) fluorination of an oxygen-unsaturated GO giving a compound denoted by GOF.

The oxygenation step was carried out using a standard oxidant solution of KClO₃ in fuming HNO₃ at room temperature or at 70 °C. The fluorination step was accomplished with a gaseous F₂/HF/IF₅ mixture at room temperature. More details on the preparation and the characterization of these compounds can be found in a previous publication [13]. Following these procedures, many GFO and GOF compounds were obtained. The relative oxygen and fluorine rates they exhibited were dependent on the details of each preparation. Prior to use, hygroscopic compounds such as GO and GOF were dehydrated at 100 °C under vacuum.

So-called 'two-electrode' cells were built with either liquid or solid electrolyte (Fig. 1). The liquid electrolyte was a 1 M solution of LiClO₄ in propylene carbonate (PC), while the solid one was a well-known polymeric membrane made of a solid solution of LiClO₄ within poly(ethylene oxide) (P(EO)₈LiClO₄). In all cases, the negative electrode was made of a lithium disk, 0.2 mm thick and 10 mm in diameter. The positive electrode was formed from a composite mixture of the active material and 10 wt.% P(EO)₈LiClO₄, which acts as an ionically conductive binder, suspended beforehand in acetonitrile. It took the form of a thin film deposited on a stainless-steel disk-shaped current collector with a diameter of 20 mm. This thin film cathode (4–8 mg), formed after acetonitrile evaporation, is then used for electrolyte solid systems schematized in Fig. 1(b), working at 80 °C. When a liquid electrolyte was used, the composite working electrode was pressed as a pellet with a diameter of 6 to 8 mm (20–30 mg weight) and the cells were operated at room temperature. Figure 1(a) shows the main cell elements.

Electrochemical studies were performed by means of a galvanostatic discharge mode. The electrochemical behaviour of oxyfluoride compounds was compared with that of the starting materials graphite oxide and graphite fluoride.

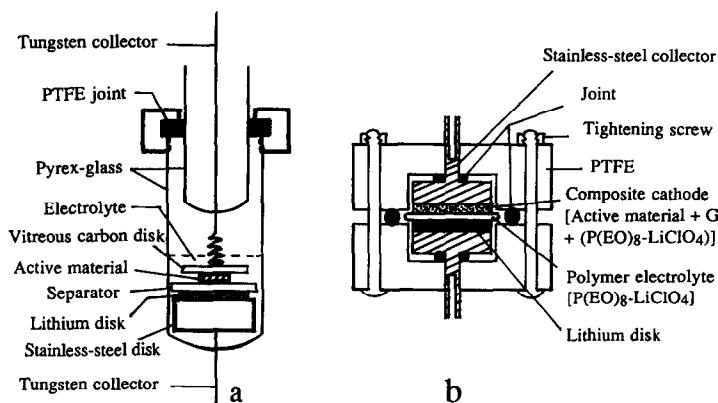


Fig. 1. Schematical representation of electrochemical cells: (a) 1 M LiClO_4 in propylene carbonate (PC) liquid electrolyte, and (b) solid electrolyte.

Results

In this study we have considered it necessary to present the electrochemical behaviour of graphite oxide (GO) and graphite fluoride (GF) compounds that were used as starting materials for the graphite oxyfluoride synthesis, even though these compounds (GO and GF) are well known for their highly oxygenated [14, 15] or fluorinated [8] compounds. There are two reasons to this: firstly, the weakly or moderately oxidized or fluorinated compounds have not been dealt with to any great extent, and secondly it is interesting to compare them with their fluorinated (GOF) and oxidized (GFO) derivatives presenting higher carbon oxidation numbers.

Liquid electrolyte cell

Galvanostatic discharge of GO

Galvanostatic discharge curves, performed with a dehydrated sample of $\text{C}_4\text{O}_x\text{H}_y$, (oxygen-saturated graphite oxide has an ideal formula of $\text{C}_4\text{O}_2\text{H}$) as the cathode material, are plotted in Fig. 2 for different compositions and under a current density of 0.2 mA cm^{-2} . They show an average discharge voltage $\langle e \rangle$ of about 1.92 V. In Table 2, we report some discharge characteristic data as a function of carbon oxidation number.

The specific capacity decreases as the O/C ratio decreases, whereas the discharge voltage practically does not change. Thus, the reduction of oxygen-unsaturated GOs is performed at nearly the same potential as for oxygen-saturated compounds. It seems that the electron injections and the lithium diffusion in the GO host structure should not be affected by the oxygenation ratio. Moreover, the practical faradaic capacity C_{pr} is about 50 to 60% of the theoretical one, C_{th} , calculated from CON. Figure 3 shows some discharge curves under different current densities of a sample with the formula $\text{C}_4\text{O}_{1.8}\text{H}_{1.04}$. The increase in current density results in an important polarization of the GO-positive electrode. The average discharge potential $\langle e \rangle$ decreases by about 0.3 V when the current density is increased from 0.025 to 0.5 mA cm^{-2} . The specific capacity decreases by about 20%. Indeed, in a high discharge current mode, all electrochemical active sites are not reached because of the slow diffusion of Li^+ .

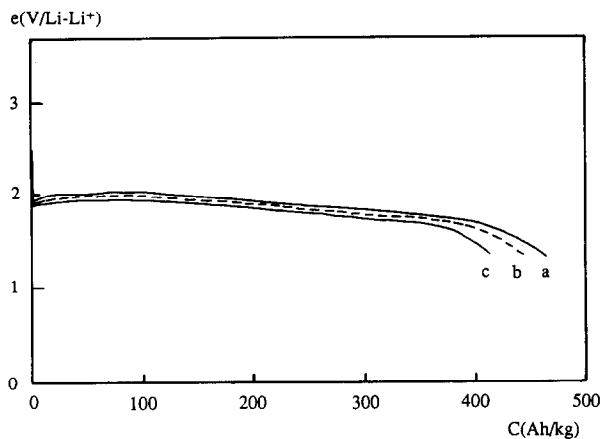


Fig. 2. Galvanostatic discharge of Li/1 M LiClO₄, PC/GO cells under 0.2 mA cm⁻²; (a) GO = C₄O_{1.80}H_{1.04}; (b) C₄O_{1.72}H_{1.40}, and (c) C₄O_{1.52}H_{0.84}.

TABLE 2

Galvanostatic discharge curve characteristics of Li/1 M LiClO₄, PC/GO cells, under current density of 0.2 mA cm⁻²

Curve (see Fig. 2)	Cathode composition	OCV (V vs. Li/Li ⁺)	Calculated capacity, C_{cal} (Ah kg ⁻¹)	Practical capacity, C_{pr} (Ah kg ⁻¹)	Practical energy density, D_{pr} (Wh kg ⁻¹)	Carbon oxidation number
a	C ₄ O _{1.80} H _{1.04}	2.61	881	464	891	0.64
b	C ₄ O _{1.72} H _{1.40}	2.65	711	440	845	0.51
c	C ₄ O _{1.52} H _{0.84}	2.67	806	411	785	0.55

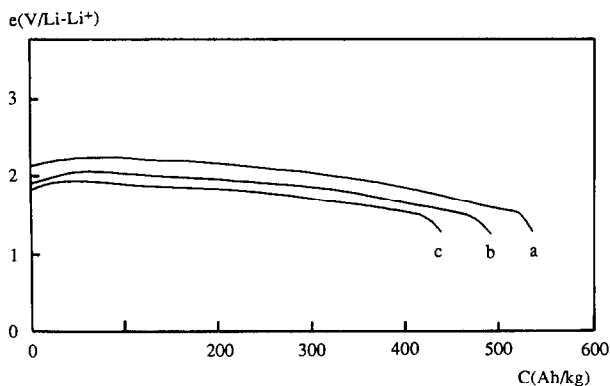


Fig. 3. Galvanostatic discharge of Li/1 M LiClO₄, PC/C₄O_{1.80}H_{1.04} cell under different current densities: (a) $i = 0.025$ mA cm⁻²; (b) $i = 0.2$ mA cm⁻², and (c) $i = 0.5$ mA cm⁻².

Galvanostatic discharge of GOF

We present here the results obtained from GOF that were prepared by fluorination of oxygen-unsaturated graphite oxide, studied beforehand. Figure 4 shows discharge curves of GOF with different compositions under a current density of 0.3 mA cm^{-2} . We may note the variation of the discharge potential as a function of the F/O ratio. Generally, it decreases as this ratio decreases. Experimental results are collected in Table 3. The C_{pr} is about 71% of C_{th} and the electrochemical behaviour of cells made from GOF is different from that of cells made from GO (starting material). The $\langle e \rangle$ of GOF is 0.15 V higher than that exhibited by GO. Figure 5 shows discharge curves of a $\text{C}_4\text{O}_{1.48}\text{F}_{1.32}\text{H}_{0.56}$ sample under different current densities. We notice that the galvanic efficiency decreases as the current density increases. It varies from 96 to 51% for $i = 0.025$ and 0.45 mA cm^{-2} , respectively.

Galvanostatic discharge of GF

In a previous study, the good behaviour of fluorine-saturated graphite compounds has been demonstrated in liquid [4] or solid-state [16] lithium cells. Generally, weakly fluorinated compounds are not attractive as cathode materials because of the low faradaic capacity they exhibit. However, it may be interesting to investigate their electrochemical behaviour in order to compare it with that of derivative GFO compounds.

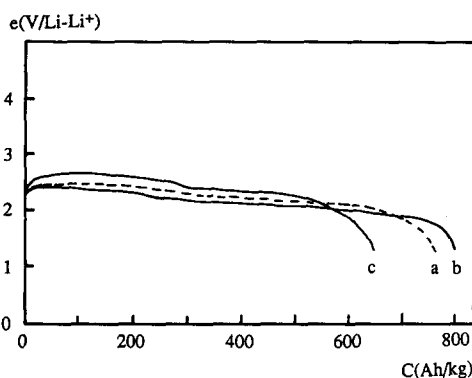


Fig. 4. Galvanostatic discharge of Li/1 M LiClO_4 , PC/GOF cells under 0.3 mA cm^{-2} ; (a) GOF = $\text{C}_4\text{O}_{1.48}\text{F}_{1.32}\text{H}_{0.56}$; (b) $\text{C}_4\text{O}_{1.80}\text{F}_{1.12}\text{H}_{0.88}$; and (c) $\text{C}_4\text{O}_{1.32}\text{F}_{1.32}\text{H}_{0.92}$.

TABLE 3

Galvanostatic discharge curve characteristics of Li/1 M LiClO_4 , PC/GOF cells, under $i = 0.3 \text{ mA cm}^{-2}$

Curve (see Fig. 4)	Cathode composition	OCV (V vs. Li/Li ⁺)	Calculated capacity, C_{cal} (Ah kg ⁻¹)	Practical capacity, C_{pr} (Ah kg ⁻¹)	Practical energy density, D_{pr} (Wh kg ⁻¹)	Carbon oxidation number
a	$\text{C}_4\text{O}_{1.48}\text{F}_{1.32}\text{H}_{0.56}$	3.35	1024	735	1543	0.93
b	$\text{C}_4\text{O}_{1.80}\text{F}_{1.12}\text{H}_{0.88}$	3.33	1040	746	1492	0.96
c	$\text{C}_4\text{O}_{1.32}\text{F}_{1.32}\text{H}_{0.92}$	3.40	856	609	1370	0.76

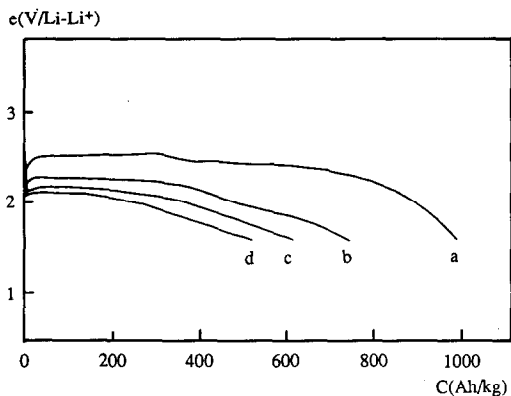


Fig. 5. Galvanostatic discharge of Li/1 M LiClO₄, PC/C₄O_{1.48}F_{1.32}H_{0.56} cell under different current densities: (a) $i=0.025 \text{ mA cm}^{-2}$; (b) $i=0.3 \text{ mA cm}^{-2}$; (c) $i=0.5 \text{ mA cm}^{-2}$, and (d) $i=0.75 \text{ mA cm}^{-2}$.

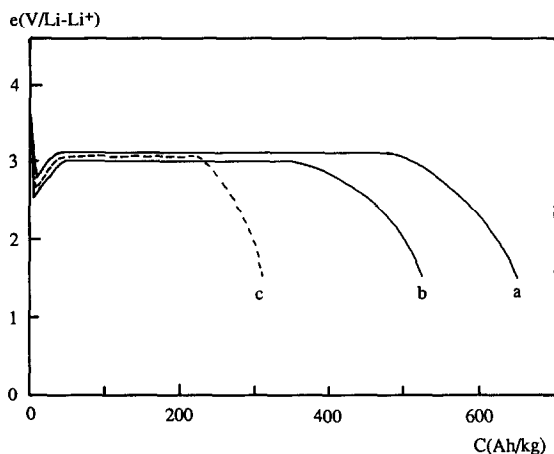


Fig. 6. Galvanostatic discharge of Li/1 M LiClO₄, PC/GF cells under 0.5 mA cm^{-2} : (a) GF=C₄F_{3.20}I_{0.08}; (b) C₄F_{1.97}H_{0.05}, and (c) C₄F_{1.48}H_{0.44}.

Most samples were prepared using a F₂/HF/IF₅ gas mixture, although in some cases the fluorination step of graphite was accomplished with only a F₂/HF mixture allowing lower fluorine content compounds [17].

The curves of Fig. 6 are related to a discharge made under 0.5 mA cm^{-2} for different sample compositions. The main characteristic of this Li/1 M LiClO₄, PC/GF system is the high stability of the discharge electrical potential. Table 4 summarizes some discharge characteristics. We note that the faradaic capacity increases as the F/C ratio increases, but the OCV values are different. They change from one cell to the other and their values lie between 3.3 and 4 V. We present in Fig. 7 three discharge curves of C₄F_{1.48}H_{0.44} carried out under different current densities. As anticipated, an increase in current only involves a weak polarization of the GF cathode, even under relatively high current densities. The discharge potential decreases with $\sim 0.18 \text{ V}$ as

TABLE 4

Galvanostatic discharge curve characteristics of Li/1 M LiClO₄, PC/GF cells, under $i = 0.5 \text{ mA cm}^{-2}$

Curve (see Fig. 6)	Cathode composition	OCV (V vs. Li/Li ⁺)	Calculated capacity, C_{cal} (Ah kg ⁻¹)	Practical capacity, C_{pr} (Ah kg ⁻¹)	Practical energy density, D_{pr} (Wh kg ⁻¹)	Carbon oxidation number
a	C ₄ F _{3.20} I _{0.08}	3.84	721	643	1993	0.70
b	C ₄ F _{1.97} H _{0.05}	3.81	575	530	1590	0.43
c	C ₄ F _{1.48} H _{0.44}	3.42	364	303	924	0.26

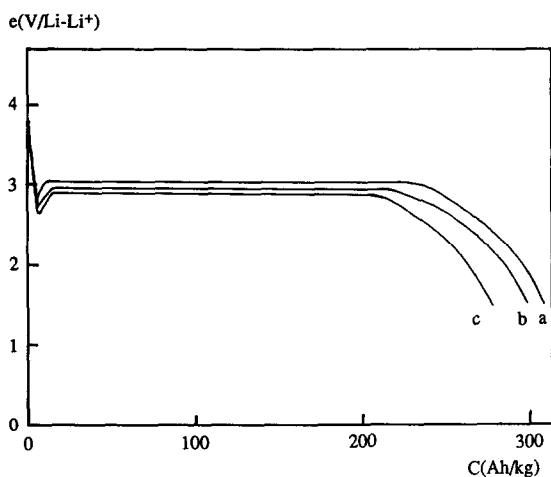


Fig. 7. Galvanostatic discharge of Li/1 M LiClO₄, PC/C₄F_{1.48}H_{0.44} cell under different current densities: (a) $i = 0.5 \text{ mA cm}^{-2}$; (b) $i = 0.75 \text{ mA cm}^{-2}$, and (c) 1.0 mA cm^{-2} .

the current density is increased from 0.5 to 1 mA cm^{-2} , whereas the faradaic capacity only decreases by $\sim 10\%$.

Galvanostatic discharge of GFO

Figure 8 shows three discharge curves for different compositions of GFO under 0.5 mA cm^{-1} . They seem similar to those of GF (starting material) presented above. We first notice an increase in the faradaic capacity, as a consequence of oxygenation, as well as a slight decrease in the discharge potential compared with those of GF. It decreases as the O/F ratio is increased. Table 5 summarizes some characteristic data.

Figure 9 shows discharge curves of C₄F_{2.6}O_{0.76}I_{0.12}H_{0.64} under different current densities. They indicate that the discharge potential decreases from 3.05 to 2.72 V as the current density is increased from 0.5 to 1 mA cm^{-2} .

Comparative galvanostatic discharge study of GO, GOF, GF and GFO

Figure 10 displays discharge curves recorded under the same experimental conditions for those different graphite compounds (GC). The electrochemical properties of GO

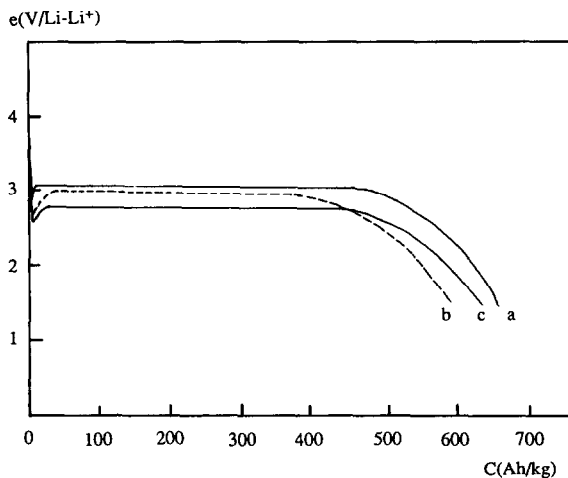


Fig. 8. Galvanostatic discharge of Li/1 M LiClO₄, PC/GFO cells under 0.5 mA cm⁻²: (a) GFO = C₄F_{2.60}O_{0.76}I_{0.12}H_{0.64}; (b) C₄F_{1.36}O_{0.60}H_{0.60}, and (c) C₄F_{1.44}O_{0.60}H_{0.44}.

TABLE 5

Galvanostatic discharge curve characteristics of Li/1 M LiClO₄, PC/GFO cells, under $i = 0.5 \text{ mA cm}^{-2}$

Curve (see Fig. 8)	Cathode composition	OCV (V vs. Li/Li ⁺)	Calculated capacity, C_{cal} (Ah kg ⁻¹)	Practical capacity, C_{pr} (Ah kg ⁻¹)	Practical energy density, D_{pr} (Wh kg ⁻¹)	Carbon oxidation number
a	C ₄ F _{2.6} O _{0.76} I _{0.12} H _{0.64}	3.87	743	653	1990	0.72
b	C ₄ F _{1.36} O _{0.60} H _{0.60}	3.80	600	596	1752	0.47
c	C ₄ F _{1.44} O _{0.60} H _{0.44}	3.38	690	636	1755	0.55

and GF were compared with those of derivative compounds GOF and GFO, respectively. The corresponding performances are listed in Table 6. It should be noted that the capacities obtained with GO and GF materials are somewhat weak. As previously mentioned, this is due to the fact that these compounds are not fully oxidized (oxygenated or fluorinated). Indeed, we must emphasize that this condition has to be fulfilled in order to be able to prepare a graphite oxyfluoride [13].

Figure 11 shows polarization curves of GO, GOF, GF and GFO with defined compositions. They indicate the variation in discharge potential as a function of current density. In all cases, an increase in the discharge current involved a decrease in the efficiency (or in the faradaic capacity), that seems to be very significant for a current density greater than 1 mA cm⁻² for GO and GOF, and greater than 2 mA cm⁻² for GF and GFO. Moreover, the discharge potential value increases with F/O ratio. It means that $\langle e \rangle$ increases when graphite oxide is fluorinated and decreases when graphite fluoride is oxygenated.

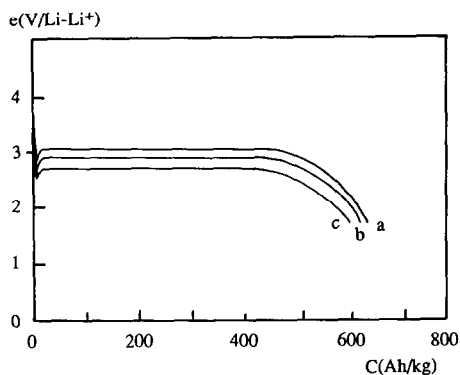


Fig. 9. Galvanostatic discharge of Li/1 M LiClO₄, PC/C₄F_{2.60}O_{0.76}I_{0.12}H_{0.64} cell under different current densities: (a) $i=0.5 \text{ mA cm}^{-2}$; (b) $i=0.7 \text{ mA cm}^{-2}$, and (c) 1.0 mA cm^{-2} .

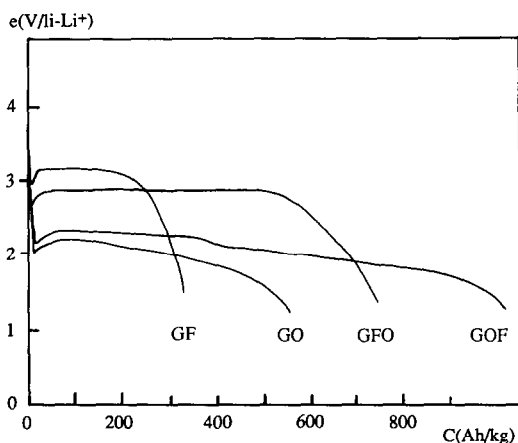


Fig. 10. Galvanostatic discharge of Li/1 M LiClO₄, PC/GC cells under 0.025 mA cm^{-2} : (GO) GC=C₄O_{1.80}H_{1.04}; (GOF) C₄O_{1.48}F_{1.32}H_{0.56}; (GF) C₄F_{1.48}H_{0.44}, and (GFO) C₄F_{1.44}O_{0.60}H_{0.44}.

Solid electrolyte cell

Galvanostatic discharges were performed at 80 °C under an argon atmosphere, because the ionic conductivity of the solid polymer electrolyte is improved at this temperature, graphite compound cathodes are still thermally stable. Discharge curves shown in Fig. 12 are similar to those obtained with liquid electrolyte cells. At the beginning of the discharge, the cell potential decreases rapidly and afterwards increases progressively until it reaches the corresponding discharge value. This phenomenon was interpreted before [4] as a resistance overvoltage of the cathode material, which becomes a good electronic conductor during the discharge process. In Table 7 we report the discharge curve characteristics. The discharge potential depends on the composition of the positive cathode compounds. Their behaviour is analogous to that of liquid electrolyte cells. However, the faradaic capacity is lower than that exhibited by liquid electrolyte systems.

TABLE 6

Galvanostatic discharge characteristics of liquid electrolyte system of the compounds GO and GF and their GOF and GFO derivatives, under $i = 0.025 \text{ mA cm}^{-2}$

Curve (see Fig. 10)	Cathode composition	OCV (V vs. Li/Li ⁺)	Average discharge potential, $\langle e \rangle$ (V vs. Li/Li ⁺)	Calculated capacity, C_{cal} (Ah kg ⁻¹)	Practical capacity, C_{pr} (Ah kg ⁻¹)	Practical energy density, D_{pr} (Wh kg ⁻¹)	Carbon oxidation number
GO	C ₄ O _{1.80} H _{1.04}	2.61	2.15	881	528	1135	0.64
GOF	C ₄ O _{1.48} F _{1.32} H _{0.56}	3.35	2.30	1024	985	2265	0.93
GF	C ₄ F _{1.48} H _{0.44}	3.40	3.15	364	316	995	0.21
GFO	C ₄ F _{1.44} O _{0.60} H _{0.44}	3.38	2.90	690	725	1983	0.55

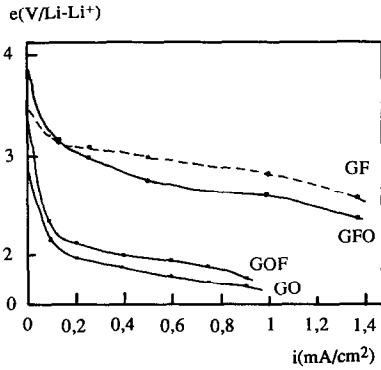


Fig. 11. Galvanostatic discharge potential as a function of discharge current density (polarization curve) of Li/1 M LiClO₄, PC/GC cells: (GO)GC = C₄O_{1.80}H_{1.04}; (GOF) C₄O_{1.48}F_{1.32}H_{0.56}; (GF) C₄F_{1.48}H_{0.44}, and (GFO) C₄F_{1.44}O_{0.60}H_{0.44}.

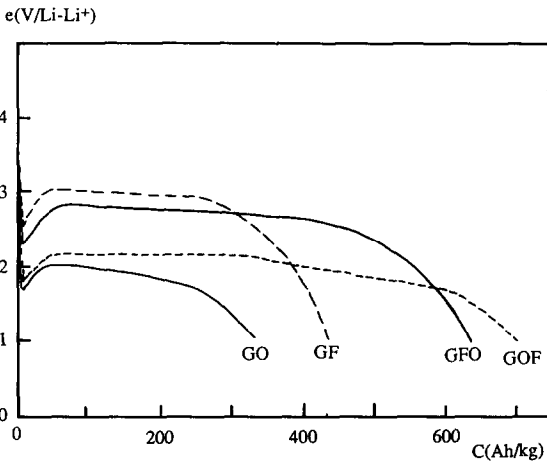


Fig. 12. Galvanostatic discharge of Li/P(EO)₈, LiClO₄/GC polymer solid electrolyte cells: (GO) GC = C₄O_{1.68}H_{0.96}; (GOF) C₄O_{1.52}F_{1.24}H_{0.48}; (GF) C₄F_{2.24}H_{0.40}, and (GFO) C₄F_{2.16}O_{0.64}H_{0.36}.

Discussion

All measurements collected in the preceding Tables clearly show that electrochemical properties of the cathode depend on the compound and its chemical composition. Graphite compounds containing only oxygen atoms (and hydroxyl groups) have the lowest discharge potential, whereas those containing only fluorine atoms have the highest. The discharge potential of cells using a graphite oxyfluoride cathode is evaluated as lying between these two values, the higher the F/O ratio the higher the cell potential. The reactivity of fluorine containing compounds is certainly due to the C-F bond character and so to the structure of the carbon layers.

The electrochemical reaction of the oxyfluoride cathode may be defined as the sum of the two Li/GO [6] and Li/GF [4] reaction cells as follows:

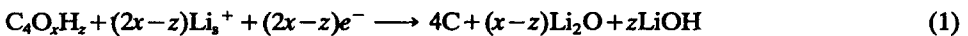
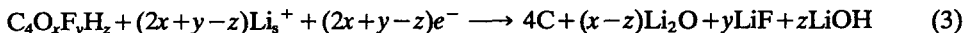


TABLE 7

Galvanostatic discharge characteristics of solid electrolyte system of the compounds GO and GF and their GOF and GFO derivatives, under $i = 0.025 \text{ mA cm}^{-2}$

Curve (see Fig. 12)	Cathode composition	OCV (V vs. Li/Li ⁺)	Average discharge potential, $\langle e \rangle$ (V vs. Li/Li ⁺)	Calculated capacity, C_{cal} (Ah kg ⁻¹)	Practical capacity, C_{pr} (Ah kg ⁻¹)	Practical energy density, D_{pr} (Wh kg ⁻¹)	Carbon oxidation number
GO	C ₄ O _{1.08} H _{0.96}	2.73	1.90	848	326	619	0.6
GOF	C ₄ O _{1.52} F _{1.24} H _{0.48}	3.36	2.17	1149	698	1514	0.95
GF	C ₄ F _{2.24} H _{0.40}	3.76	3.00	660	430	1290	0.46
GFO	C ₄ F _{2.16} O _{0.64} H _{0.36}	3.72	2.80	828	627	1755	0.77



As a matter of fact, under weak current densities, the discharge curves exhibit two plateaus (Fig. 5), the one of higher potential corresponding to the reduction of bound fluorine-carbon atoms, the one of lower potential corresponding to the reduction of bound oxygen-carbon atoms. This phenomenon depends on the current density and on the electroactive material mass. Moreover, the final cathode product, after discharge, was examined by means of X-ray diffraction. The diffractogram exhibits peaks corresponding to LiF, Li₂O, LiOH, and graphite. In a previous study [18], it was reported that the discharge process of (CF_x)_n(HT)/Li cell suggested the formation of an intermediate solvated Li⁺-graphite fluoride intercalation compound, which decomposed into carbon, LiF and Li₂CO₃. In the case of our compounds (fluorinated at room temperature), no evidence of the formation of this intercalation phase could be found. It seems that this phase is very unstable in our experimental conditions. Moreover, some experiments concerning the reactivity of graphite fluorides, prepared at high or room temperature, with n-butyllithium solution in hexane showed that white (CF_x)_n(HT) transformed progressively to black-coloured powder, which would prove the formation of an intermediate phase slowly decomposing into graphite and LiF. However, white (CF_x)_n(RT) transformed spontaneously into graphite, showing the instability of this intermediate phase, assuming its formation.

The structural study showed that C-F bonds in GF compounds prepared at room temperature have a semi-ionic character and that carbon layers are planar [8, 19–21]. It has been demonstrated that the C-F chemical bond is almost ionic in the low fluorine content region. With increasing fluorine concentration, the covalency increases and the C-F bond reaches a semi-ionic character in high fluorine content compounds. In a previous structural study [22], the persistence of C=C bond in GFO compounds was reported from ¹³C NMR measurements, whatever the composition, whereas in GOF the carbon bonds are completely saturated. The electrochemical properties of GFO are thus close to those exhibited by GF (starting product). The fluorine ratio is more important than that of oxygen, resulting in a predominant C-F nature. Whereas in GOF compounds, where the oxygen ratio is more important than that of fluorine, the C-F bonds rather have a covalent character and carbon layers are distorted, as in GO compounds. These characteristics may explain the lower discharge potential of GOF compounds compared with that of GFO and GF. Indeed, the ionic character of the C-F bond allows an increase in the compound's reactivity as well as a good Li⁺ diffusion, due to the planar nature of the layers.

Conclusions

The electrochemical behaviour of graphite oxyfluorides GFO and GOF is presented. Both show good performances in lithium battery systems having a high energy density. The discharge potential of the Li/GFO system is higher than that of the Li/GOF; it depends on the origin of the starting materials (GO or GF) used for their preparation. Consequently, their performance is directly related to the structure and the nature of C-F and C-O bonds. Finally, the increase of the carbon oxidation number increased the cell faradaic capacity. This may be realized without destruction of the carbon host structure. This study is now in progress.

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