

TEM characterization of the passivating layer formed during the reduction of graphite electrodes in selected electrolytes

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Abstract

The electrochemical intercalation of lithium ions into graphite was studied in various electrolytes. The first cycle is accompanied by the irreversible process attributed to the formation of a passivating layer. The reduction of Cl-EC and EC begins at potentials equal to 1.7 and 0.9 V vs. Li⁺/Li, respectively. The electrochemical behaviour is considerably affected by the nature of the salt. Contrary to LiBF₄, a good cycleability is obtained with LiClO₄ and LiAsF₆. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Many carbon varieties have been investigated as possible anode materials for rocking-chair secondary lithium-ion batteries. The amount of lithium inserted reversibly into a carbon matrix depends on the electrolyte system used in the battery as well as the nature of the carbon material.

It is generally accepted that certain solvents like propylene carbonate (PC) are not suitable for lithium intercalation in well-crystallized graphite electrodes [1,2]. In such a case, an irreversible graphite degradation (exfoliation) occurs due to the decomposition of PC and the subsequent propylene evolution between the graphene layers. The low coulombic efficiency observed for the first electrochemical intercalation of lithium ions into carbons has been attributed to the decomposition of the electrolyte on the electrode surface to form a passivating layer [3–5]. The detailed mechanisms of these phenomena have been studied in detail. The nature of the protective film and its characteristics have a dramatic influence on cycle life and safety. Electrolytic solutions containing ethylene carbonate as a solvent show high capability for carbon materials [6,7].

In this work, the electrochemical behaviour of a graphite electrode was investigated in several non-aqueous elec-

trolyte solutions. The surface film formed at the first cycle was observed by TEM spectroscopy.

2. Experimental

The composite working electrode is composed of graphite (96% w/w) as active material and PVDF (4% w/w) as binder. This graphite is mixed in a stirred solution of PVDF in propylene carbonate (water content < 50 ppm) at room temperature. This mixture is then deposited on a titanium electrode (0.5 cm²) and finally heated at 150°C to remove the solvent. The intercalation reactions are performed in a two-electrode cell with a lithium foil acting simultaneously as counter and reference electrodes. TEM studies were conducted on a CM 20 Philips microscope at 200 kV equipped with a parallel electron energy loss (EEL) spectrometer (Gatan 666). The samples were deposited on a copper grid covered with a holey amorphous carbon film. Electrochemical intercalation of lithium ions into graphite was carried out in various electrolytes composed of a lithium salt LiX (X⁻ = ClO₄⁻, BF₄⁻, AsF₆⁻) and a solvent EC, PC, Cl-EC and their mixtures. The purification of these chemicals were described elsewhere [5,8]. The active electrode material was a natural graphite powder UF4 manufactured by Le Carbone Lorraine (the average particle size is about 6 μm and the crystallographic parameters are $d_{002} = 0.335$ nm, $L_c = 37$ nm).

The cycleability of the electrodes was examined by galvanostatic charge and discharge cyclings (20 μA mg⁻¹,

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$60 \mu\text{A cm}^{-2}$) using a multichannel microprocessor-controlled Mac-Pile potentiostat/galvanostat. The potentials are referred to a Li^+/Li electrode.

3. Results and discussion

3.1. Graphite cycling in EC-based electrolyte

The reactivity of EC in the presence of LiClO_4 was described elsewhere [5]. A typical first charge/discharge galvanostatic curve carried at room temperature is shown in Fig. 1a. The plateau at 0.8 V, observed only at the first reduction cycle, is concerned with the formation of a film on the graphite surface. Such a film, the so-called passivation layer, is impervious to the solvent molecules but allows the diffusion of lithium ions through its bulk. The presence of such a film is necessary to avoid graphite exfoliation and to obtain a reversible lithium intercalation. The plateaux at 0.2, 0.11 and 0.08 V are related to lithium insertion which occurs with formation of successive intercalation stages as previously described [6,9,10]. These steps can be better illustrated by plotting the derivative capacity dX/dV vs. V as shown in Fig. 1b.

The surface of the graphite particles after one cycle was covered with a smooth film visible on the TEM micro-

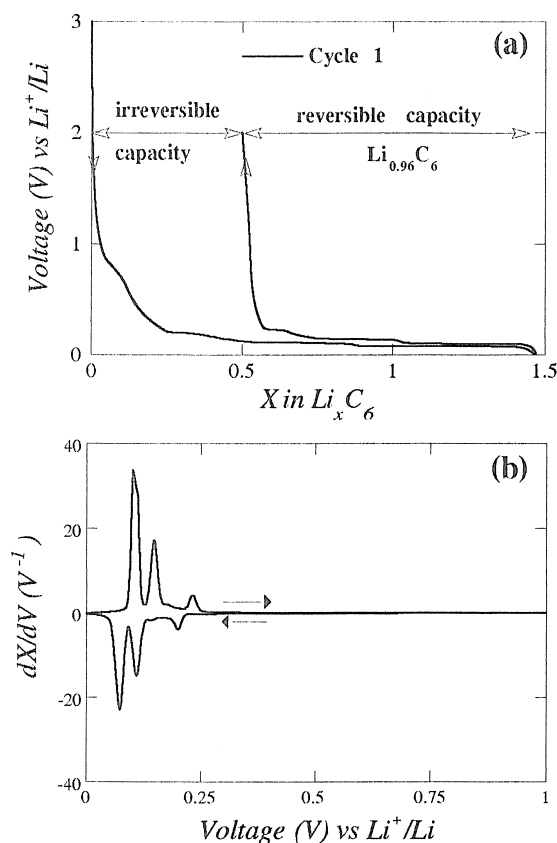


Fig. 1. Charge and discharge curves of the composite electrode UF4-PVDF (96:4) in EC/ LiClO_4 electrolyte.

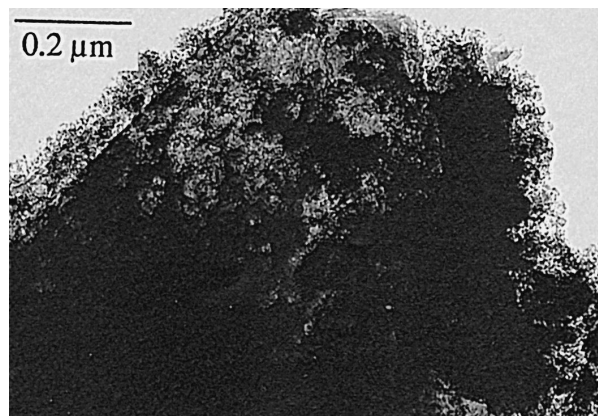


Fig. 2. TEM micrograph of the graphite after one cycle in EC/ LiClO_4 .

graph presented in Fig. 2. The identification of the film components was described elsewhere [5]. EELS and FT-IR spectroscopic measurements indicated that such a film is constituted of Li_2CO_3 , different alkylcarbonates and LiCl , the formation of which depending on the reduction potential value. Eventually, when the film thickness reaches a critical value, further ion transfer is prevented, which inhibits the intercalation reaction. At 60°C , similar results are obtained.

When graphite is reduced in EC- LiBF_4 (1 mol kg^{-1}), the shape of the galvanostatic curves depends on the temperature. At 60°C , a long plateau is observed at 2 V (Fig. 3). At 20°C , the 2 V plateau is absent and the curve is similar to that observed in Fig. 1 related to the EC- LiClO_4 electrolyte. At 40°C , two irreversible plateaux are marked respectively at 2 and 0.8 V. To shed more light on the mechanisms originating these plateaux, the electrode was examined by TEM.

Immediately after the reduction at 2 V, graphite is covered by hemispherical particles as shown in the micrograph presented in Fig. 4. Electron diffraction studies carried out on these particles allowed identification of LiF .

Fig. 5 presents the electron energy loss spectra of the products formed in EC/ LiBF_4 at 2 V. The EEL spectrum

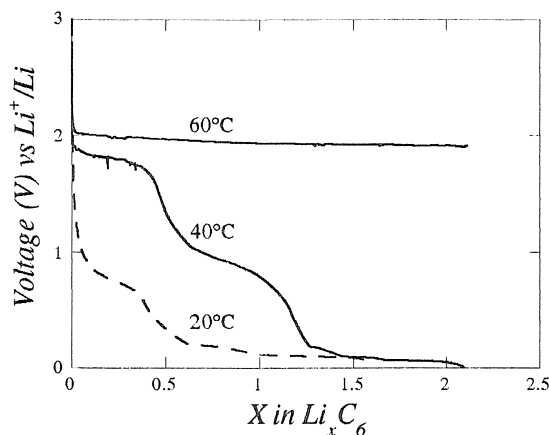


Fig. 3. First reduction of graphite in EC/ LiBF_4 at different temperatures.

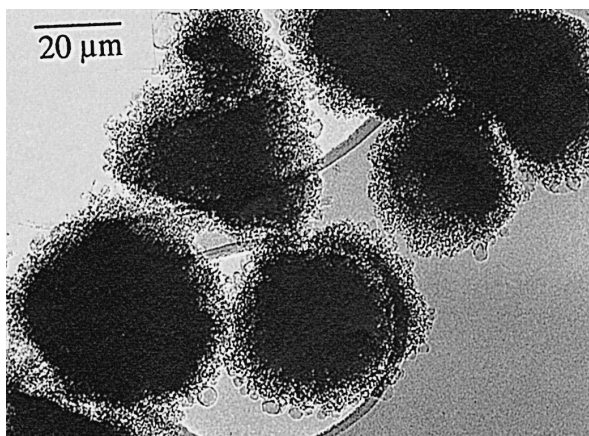


Fig. 4. TEM micrograph of LiF particles formed during graphite reduction in EC/LiBF₄ electrolyte at 60°C.

in Fig. 5a is typical for Li⁺ cations at 60 eV while that presented in Fig. 5b shows an energy loss peak at 690 eV characteristic of fluorine at the ionization K-edge. No other elements than Li and F are detected by these EELS measurements. Consequently, the plateau at 2 V can be attributed to the reduction of LiBF₄ as previously proposed by Kanamura et al. [11].

The second plateau at around 0.8 V corresponds to the formation of Li₂CO₃ as previously described for the

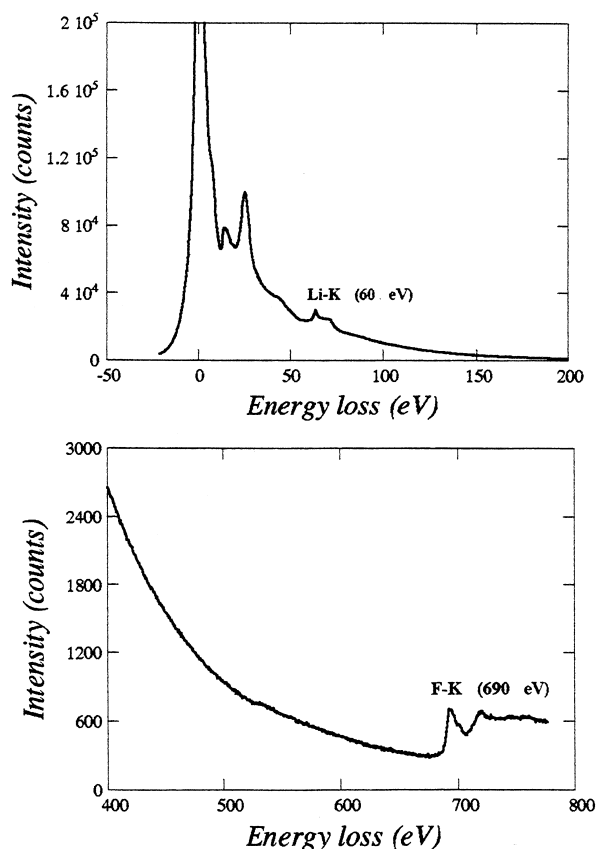


Fig. 5. EEL spectra of the reduction products of the EC/LiBF₄ electrolyte at 60°C.

Table 1
Variation of the electrochemical capacity with cycle number

Cycles	X in Li _x C ₆ (reduction)
1	2.07
2	0.8
3	0.6
4	0.28
5	0.11
6	0.08

EC/LiClO₄ system. Below 0.8 V, formation of lithium alkylcarbonates occurs while lithium ions are inserted below 0.2 V [5]. At 40°C, the reduction of LiBF₄ occurs prior to the formation of the passivating layer formed of Li₂CO₃ and lithium alkylcarbonates. That affects the characteristics of this passivating layer which appears less suitable for a good lithium ion diffusion, especially for prolong cyclings. The decrease of the total electrochemical capacity as a function of the cycle number is presented in Table 1. The capacity is almost equal to zero at the sixth cycle, indicating a variation in the properties of the surface layer probably due to the migration of LiF in the porosity of the carbonate based structure.

3.2. Graphite cycling in PC-ChloroEC based electrolyte

The high solubility of lithium salts in PC, together with its high dielectric constant, low volatility and lack of toxicity have prompted special attention to systems containing this solvent. However, poor cycling efficiency for the graphite electrode is obtained.

Fig. 6 displays the first charge/discharge curve of an UF₄ electrode in PC(95% v) + Cl-EC(5% v)/LiClO₄ (1 mol dm⁻³) electrolyte. This curve presents various potential plateaux. The one at 1.7 V can be attributed to the electrolyte reduction [12,13]. The other plateaux at poten-

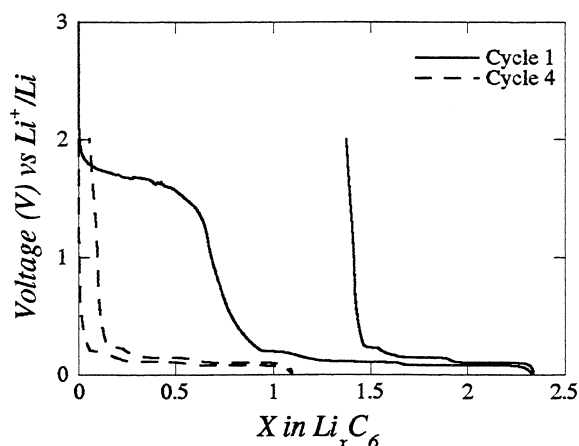


Fig. 6. Charge/discharge galvanostatic cycles of the composite electrode UF₄-PVDF (96:4 w/w) in PC(95% v) + Cl-EC(5% v)/LiClO₄.

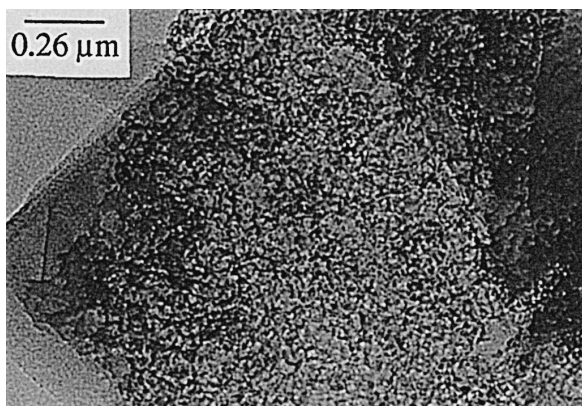


Fig. 7. TEM micrograph of graphite covered by the passivating layer formed in PC(95v)+Cl-EC(95% v)/LiClO₄.

tials lower than 0.25 V are typical of the formation of the different lithium-graphite intercalation compounds. An high irreversible capacity ($\Delta X = 1.3$) is observed for the first cycle. For the following cycles, a good reversibility is found and it must be pointed out that the reversible capacity is slightly higher ($X = 1.05$) than those obtained in pure EC based electrolytes.

After a first cycle, the sample electrode is analysed by TEM. Fig. 7 shows that the surface of graphite is covered with a thin spongy layer, which did not form after open-circuit immersion for several hours. Such a layer inhibits the PC decomposition which occurs at 0.9 V allowing lithium to be inserted reversibly.

Analysis by EELS spectroscopy indicates that the layer is composed of chlorine, carbon and oxygen (Fig. 8). Carbon analysis yields the presence of two peaks, one located at 288 eV (C=O) and the other one at 298 eV (C-O).

The nature of the salt influences the reversible capacity. Fig. 9 presents the variation of the reversible capacity against the cycle number. A drastic decline in capacity is

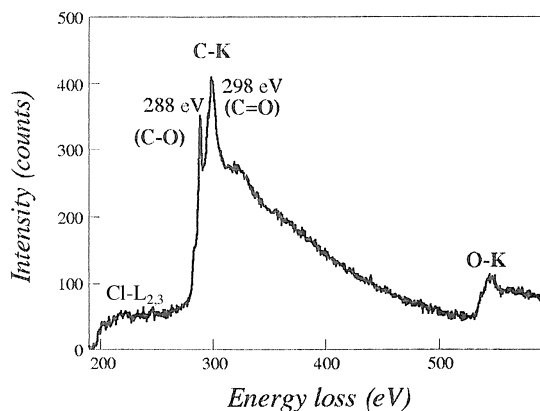


Fig. 8. EEL spectrum of the reduction products of the PC+Cl-EC/LiClO₄ electrolyte.

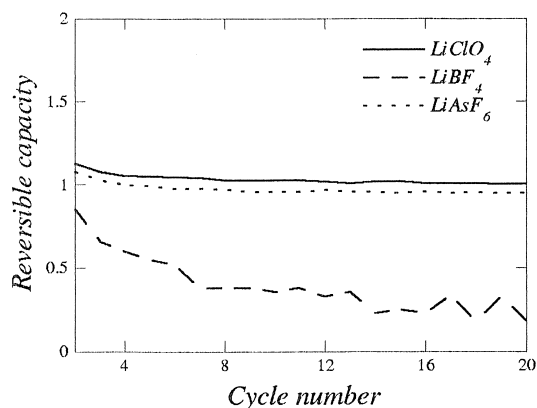


Fig. 9. Influence of the nature of the salt on the reversible capacity at 20°C (PC(90% v)+Cl-EC(10% v)).

observed when LiBF₄ is used contrary to LiClO₄ and LiAsF₆. Such a rapid decline in capacity can be explained either by the massive reduction of LiBF₄ or by chemical modifications occurring in the passivating layer due to the reaction of some components, presumably alkylcarbonates, with trace amount of impurities like water [11]. In this case, the resistance of this layer is important and inhibits rapid diffusion of Li⁺ ion into the graphite host.

4. Conclusion

Lithium electrochemical intercalation into graphite has been examined. In the first cycle, decomposition of the electrolyte occurs prior to lithium intercalation and results in the formation of a passivating layer. The side reactions, responsible for the irreversible capacity, are characterized by the plateaux at 0.8 V with EC and at 1.7 V with Cl-EC based electrolytes.

The electrochemical performances of lithium intercalated carbon are strongly dependent on the nature of the lithium salt. The electrochemical behaviour observed during the charge/discharge process in the electrolyte containing LiBF₄ is different from the ones containing LiClO₄ and LiAsF₆. The poor cycleability with LiBF₄ can be related to the massive formation of LiF.

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