On the choice of graphite for lithium ion batteries

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Abstract

Graphites as active materials for negative electrode in lithium batteries are particularly attractive because of their large capacity of lithium intercalation and their low average voltage. In some conditions, they are known to suffer from low reversibility of the initial intercalation process. This phenomenon is shown to be unambiguously related to an exfoliation of graphene layers, that can occur even in EC based electrolytes. Occurrence of a clear correlation between the extent of irreversible behaviour and rhombohedral phase content of graphites is discussed. Milling or thermal treatment of pristine graphites are also shown to influence electrochemical properties. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Carbon materials offer a large variety of host structure for the negative electrode of lithium ion batteries [1–3]. The choice among the numerous kind of carbons with different electrochemical behaviour is mainly directed by their capacity for lithium doping and undoping, the electrochemical potential of the process and its faradaic efficiency. The first two criteria determinate the potentiality of the active material to achieve high energy density electrodes. 'Graphites' appear to be particularly attractive in this purpose. Reversible capacity of crystalline carbon materials increase with their degree of graphitation [4,5] to reach a maximum for a monocrystal of graphite. For graphitic materials presenting a low degree of turbostatic disorder, generally designed as graphites, LiC_6 stoichiometry (372 (mAh)/g) can be actually approached within 0–300 mV vs. metallic Li [6,7]. The high crystallinity of these materials can be characterized by interlayer space distance < 0.336 nm, very close to that of a monocrystal of graphite.

The faradaic efficiency (charge to discharge ratio) is equally important for the complete battery that is assembled in the discharged state with pristine carbon and lithiated metal oxide. Any faradaic loss results in a decrease of the battery energy density. Irreversible side reactions do occur and are concentrated on the first charge of the negative carbon electrode. A common source of irreversibility consists of electrolyte reduction at low potential [6,8,9], that in the best cases leads to the formation of a lithium ion conducting layer on the carbon surface (passivation).

As a consequence, when passivation is the main contributor to irreversible losses, as it is the case for some cokes, a good correlation is generally found between the surface area of the carbon and the amount of irreversible losses [10,11]. Optimization of particle size and morphology can be helpful to increase efficiency, for example with spherically or cylindrically shaped materials.

However, highly crystalline materials have been reported to suffer additional faradaic losses originating from intercalation of solvated ions [6,8,9]. The solvent is believed to reduce eventually within the graphene layers with gaseous release and separation of the layers (exfoliation).

Graphites show very variable sensitivity to this phenomenon, although their crystalline characteristics are very close. However, rhombohedral content was a measurable source of differentiation. The usual structure of graphite is hexagonal with ABABAB... stacking of the graphene layers, but evidence of ABCABC... sequence of the rhombohedral structure can be found at a variable degree in commercial graphite powders. The rhombohedral content in itself has no marked influence on capacity or electrochemical potential [5] but has a remarkable impact on irreversible losses [4].

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In this study, the exfoliation of carbons crystalline enough to approach closely LiC_6 stoichiometry is investigated with further comparison in relation to their rhombohedral phase content.

2. Experimental

Natural or artificial graphite samples were supplied as powders by Timcal (A1, A2, A3, A5) CGW (A4, N1, N2, N3, N4) Kropfmühl (N5, N6, N7) Le Carbone Lorraine (N8) and Nipp. Kokk. (E1). They all possess high crystallinity attested by interlayer distance inferior to 0.336 nm. The amount of rhombohedral phase was evaluated from X-ray diffraction spectra by a graphical method. The peaks corresponding to reflections along the directions (012) (rhombohedral), (101) (hexagonal) (101) (rhombohedral) and (100) (hexagonal) were assigned to be symmetrical and their contribution subtracted in this order from the spectra. The amount of rhombohedral graphite (R) was found by comparing the integrated intensities for both structures, taking into account the differences in structure factor.

All the graphite powders tested here actually achieve 360–370 (mAh)/g capacity at low kinetics.

Electrodes were fabricated on a weight basis of 95% carbon, 5% teflon. Carbon black was added in some cases (5%) to improve electrode performance, and its contribution to surface area and irreversibility was taken into account. Due to its low surface energy, carbon particles remain uncoated in teflon based electrodes. This structure was found to allow exfoliation to proceed freely and was desirable to compare intrinsic resistance to exfoliation of carbon materials. The electrodes were obtained by mixing carbon powders, teflon aqueous dispersion (Algoflon D60VB) and ethanol. The paste was kneaded and rolled to a foil. Electrodes (1 cm^2) were cut from this foil, dried, applied on a nickel grid (2 t/cm^2 pressure) and dried at 120°C under vacuum before cell assembly.

The cell test consisted of a 2025 coin cell with metallic lithium as counter electrode, and microporous polypropylene sheet (Celgard) as separator.

The electrolytes were based on organic carbonates (PC propylene carbonate, EC ethylene carbonate, DMC dimethylcarbonate): EC/DMC $LiPF_6$ 1 M and PC/EC/3DMC $LiPF_6$ 1 M. Electrochemical experiments were performed with a MacPile potentiostat/galvanostat. The cells were cycled galvanostatically at 20 mA/g (carbon) current density in 0–2 V potential range.

Double layer capacity of pristine electrodes was measured by impedance spectroscopy measurements with a Solartron 1250 equipment in the same coin cell with an additional reference electrode [10]. The reference electrode consisted of a thin strip of insulated stainless steel foil plated with lithium, incorporated under the polypropylene gasket.

All capacities are expressed per gram of studied material.

3. Results and discussion

3.1. Evidence of graphite exfoliation

Whereas exfoliation is often mentioned as the cause of the large irreversible faradaic losses experienced with graphites in some conditions, little evidence has been presented, except by in situ X-ray [12] or by STM [13]. The latter result was however suspected by using an AFM technique [14]. A more direct technique was used as follows.

A sufficient number of button cells were assembled in order to evaluate the specific surface area of the carbon material after one charge discharge cycle. The irreversible capacity was reproducible. Pristine or cycled electrodes were thoroughly rinsed in DMC and in water, then their specific surface area were measured with an apparatus based on one point BET technique (Micromeritics Flowsorb 2300).

The results presented in Table 1 show clearly that large irreversible losses at the first cycle are associated with important increase of surface area, indicating particle fragmentation. This is confirmed by SEM, where electrodes experiencing large irreversible losses show a large number of particles that obviously suffered exfoliation (Fig. 1).

These results also confirm that graphites are not equally sensitive to exfoliation. One of them shows surface area increase even in EC based electrolyte, that is generally considered as 'safe' for graphites [6,7,15].

3.2. Effect of rhombohedral content in commercial graphites

A method to evaluate the extent of exfoliation was proposed in Ref. [10] and can be described as follows.

Table 1
Surface area measurement (BET) of graphite electrodes after one cycle

Graphite sample	Electrolyte	Losses at 1st cycle ((mAh)/g)	Surface area (m^2/g)
A.1.1	pristine		6.5
	EC/DMC	30–36	5.6
	PC/EC/3DMC	228–290	11.3
A.1.2	pristine		16.2
	PC/EC/3DMC	97–105	14.8
A.2.1	pristine		9.4
	EC/DMC	201–226	10.2
N8	pristine		1.9
	EC/DMC	254–272	6.8

A = artificial graphite, N = natural graphites.

Fig. 1. SEM micrograph of graphite A.1.1 after one cycle in PC/EC/3DMC LiPF$_6$ 1 M.
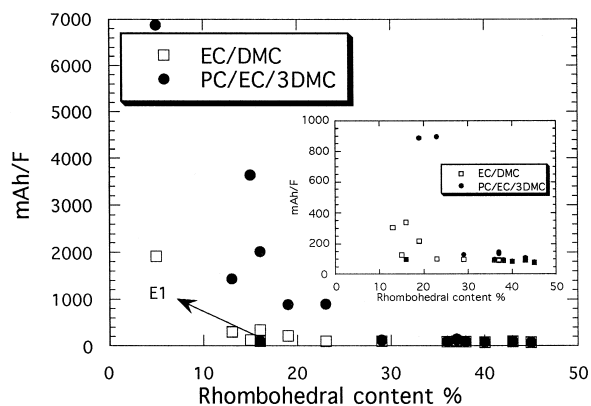

Fig. 2. Irreversible losses (expressed per unit of double layer capacity) after one cycle of teflon based electrodes in relation with rhombohedral phase content of graphite samples.

The first step is the evaluation of double layer capacity that is representative of the electrochemically active surface area of the graphite. If present, carbon black contribution was subtracted.

The total amount of irreversible capacity at the first cycle contains contribution of other sources of side reaction, e.g., passivation of carbon black and teflon reduction. These contributions have been estimated by varying the amount of binder and carbon black in the electrode [16] and were subtracted from the total losses.

When passivation occurs without exfoliation, the amount of irreversible losses closely follows the double layer capacity (it is the case for cokes or when no visible exfoliation have been detected by the BET technique). The irreversible losses by unit of double layer capacity (expressed as (mAh)/F) yields values in the range 80–120

(mAh)/F. Deviation from this base line can then be expected to represent other sources of irreversibility, and particularly the extent of exfoliation in the case of graphites.

From the results of Table 2, it can be seen that graphites show a large variability in sensitivity to exfoliation. The higher the rhombohedral content of the graphite, the higher its faradaic efficiency and its resistance to exfoliation (Fig. 2). Indeed, graphites with more than 35% rhombohedral content can withstand PC containing electrolyte, up to 90% PC [10]. However, no sample was able to cycle in full PC electrolyte.

Conversely, graphites with low rhombohedral content deviate largely from the amount of losses expected from a simple passivation process. This is particularly obvious in

Table 2
Relation between rhombohedral content of graphite samples and irreversible capacity at the first cycle in 1: EC/DMC electrolyte, 2: PC/EC/3DMC electrolyte

Graphite samples	Rhombohedral (%)	Cdl (mF/g)	Irreversible losses 1		Irreversible losses 2	
			((mAh)/g)	((mAh)/F)	((mAh)/g)	((mAh)/F)
A.1.1	23	310	31	100	278	897
A.1.2	43	1030	105	102	111	108
A.2.1	13	670	204	304	963	1437
A.2.2	43	1110	101	91	105	95
A.3	16	600	204	340	1210	2016
A.4	19	770	168	218	684	888
A.5	15	240	30	125	875	3646
N1	37	360	34	94	52	144
N2	37	370	33	89	50	135
N3	38	450	40	89	43	96
N4	45	760	58	76	61	80
N5	40	1020	85	83	87	85
N5 2400°C	21	660	723	1095	1307	1980
N5 1800°C	35	510	658	1290		
N6	36	380	35	92	37	97
N7	29	540	52	96	69	128
N8	5	140	268	1914	963	6878
N8 15 mn grinding	40	800	78	97	93	116
E1	16	1250	120	96	121	97

A = artificial graphite, N = natural graphites, E = exfoliated graphite.

PC containing electrolyte, but it is also apparent in the EC based electrolyte for the hexagonal phase rich samples.

One sample (E1) clearly departs from the general tendency, it is the graphite already exfoliated by chemical route. But the resulting high surface area yields large irreversibility due to passivation this time.

A precise physical mechanism able to explain the observed correlation remains to be determined as it can possibly be an indirect one.

As exfoliation implies penetration of large species far in the interlayer plane, the intercalation of solvated ion is favoured only if the solvation energy compensates for the work for layers opening.

High resistance to exfoliation is found in non-crystalline carbons as cokes, or in crystalline carbon containing significant amount of turbostatic disorder, where this work is high due to smaller crystallite sizes, interstitial carbons or other defects thus preventing exfoliation. But their capacity for intercalation at low potential is also reduced compared to graphite. It is possible that layer opening of high rhombohedral content graphite is harder than for pure hexagonal graphite because of the greater presence of phase boundary and dislocations that hinder solvent co-intercalation on a large scale.

It is recommended to select graphites with as high as possible rhombohedral phase [17], 40–50% seeming to be the upper limit. However, it must be remembered that other parameters like pressure on the electrode, temperature, binder nature also influence exfoliation occurrence [18] and are more favorable in battery environment. Thus graphites with less rhombohedral phase could all the same be suitable in actual batteries.

3.3. Modification of rhombohedral content

It is known that rhombohedral phase can be introduced in hexagonal graphites by grinding [19]. It is the case for commercial samples A1.2 and A2.2, that are obtained from
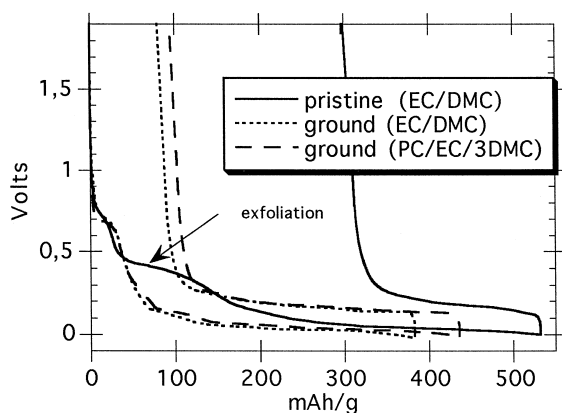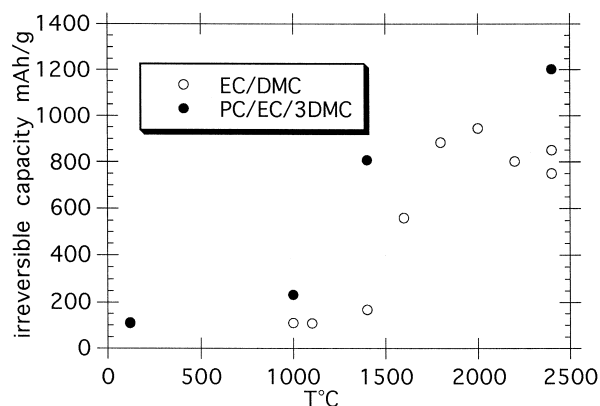

Fig. 4. Irreversible losses at the first cycle of teflon based electrodes with N5 graphite. Effect of graphite heat treatment 1 hour under argon atmosphere.

the same precursor than respectively A1.1 and A2.1 by further grinding. The crystallinity and the electrochemical capacity remain high, and the reversibility is improved by suppression of exfoliation. However, grinding also develops surface area and irreversible losses due to passivation, as it should increase self-discharge and reactivity.

Similar results were observed with natural graphite N8 that presents the poorest rhombohedral content. Fifteen minutes grinding with rotor blade grinder was sufficient to develop large rhombohedral content and markedly decrease exfoliation (Table 2, Fig. 3).

Thermal treatment at high temperature decreases the rhombohedral content as it is not the thermodynamically stable phase. As a consequence, it is expected to favor exfoliation of otherwise resistant graphite. N5 was selected as exfoliation resistant graphite and heat treated at different temperature for one hour under argon atmosphere. Heat treatment at high temperature clearly restores exfoliation (Fig. 4), as the surface area itself is not increased. The effect appears so drastic that it deserves further investigation.

From these results it appears that if purification or heat treatment is scheduled, it is more desirable that grinding until the desired particle size should be the last step of sample preparations rather than ending the process by heat treatment.

4. Conclusion

Exfoliation of graphene layers during the initial lithium ion doping in crystalline carbons is a major source of irreversibility of the process. Although not fully explained, resistance to this phenomenon can be related to rhombohedral phase content of the sample. Thus, graphites presenting large amount of rhombohedral phase content are particularly attractive for lithium ion battery application, but thermal treatment can restore exfoliation occurrence.

Fig. 3. First galvanostatic cycle of teflon based N8 graphite electrode, 20 mA/g. Effect of grinding 15 min with rotor blade grinder.

Conversely, hexagonal phase rich graphites can experience exfoliation even in EC based electrolytes that are generally presented to suit graphite materials. Their rhombohedral content and exfoliation resistance can be readily increased by grinding. The grinding technique has to be optimized to avoid development of large surface area.

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