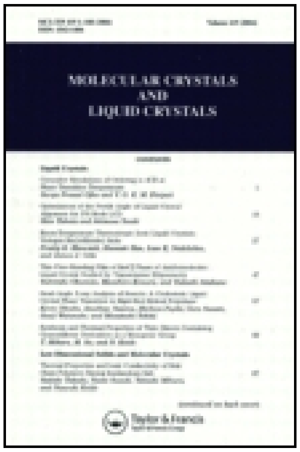

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Hexagonal vs Rhombohedral Graphite: the Effect of Crystal Structure on Electrochemical Intercalation of Lithium Ions

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Hexagonal vs Rhombohedral Graphite: The Effect of Crystal Structure on Electrochemical Intercalation of Lithium Ions

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Graphite samples with different crystalline characteristics were evaluated as negative materials for lithium ion batteries. Conversely to non crystalline coke materials, they were found to experience exfoliation problems to a variable extent during the first electrochemical reduction process. A clear correlation was found between their rhombohedral phase content and their resistance to exfoliation.

Keywords: graphite, lithium, intercalation, exfoliation

INTRODUCTION

Carbon materials as host structures for lithium ions at low potential have been extensively studied as alternatives to metallic lithium [1,2,3]. Their electrochemical performances are highly sensitive to their physical microstructure [4]. Among the various carbonaceous materials, graphites are particularly attractive because of availability, low cost, large capacity (372 mAh/g for LiC_6 stoichiometry can be actually achieved) and their low average voltage [5,6,7,8]. The faradaic efficiency of the process has to be considered carefully as the battery is assembled in the discharged state with pristine carbon and lithiated metal oxyde as $LiCoO_2$. Indeed, side reaction occur during the first charge of the carbon electrode, mainly electrolyte reduction at low potential [5,9,10]. In the best cases, this reduction leads to the formation of a lithium ion conducting layer on the carbon surface. As a consequence, a good correlation is generally found between the electrochemically active surface area of the carbon and the amount of irreversible losses [11,12,13].

However, graphites have been reported to suffer additional faradaic losses due to intercalation of solvated ions, especially in presence of propylene carbonate [5,9]. The solvent eventually reduces within the graphene layers with gazeous release and separation of the layers (exfoliation). However, graphites do not seem to be equally sensitive to this phenomenon, although their crystalline characteristics are very close. The usual structure of graphite is hexagonal with ABABAB... stacking of the graphene layers, but evidence of ABCABC.. sequence of the rhombohedral structure has been found in a variable amount in graphite powders, that can be increased by mechanical grinding. In the present study, this parameter was found to influence the reversibility of electrochemical intercalation of lithium.

EXPERIMENTAL

Natural or artificial graphite samples were supplied as powders from Carbone Lorraine, Chuetsu Graphite Werk, Timcal and Kropfmühl (Table 1). They all present high crystallinity attested by interlayer distance inferior to 0.336 nm. The amount of rhomboedral phase was evaluated from X-ray diffraction spectra by a graphical method. The shape of (012) rhomboedral (101) hexagonal (101) rhomboedral and (101) rhombohedral reflexions were assigned to be symmetrical and their contribution substracted in this order from the spectra. The ratio of rhombohedral graphite (R) was found by comparing the integrated intensities for both structures, taking into account the differences in structure factor. Various cokes materials (petroleum, anthracene) were supplied for comparison.

Electrodes were fabricated on a weight basis of 90% carbon, 5% teflon and 5% acetylene black (YS). Due to its linear structure, carbon black ensures a high electronic conductivity even in case of electrode swelling. Due to its low surface energy, carbon particles are not coated 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 malaxed and rolled to a foil. Electrodes (1cm2) were cut from this foil, dried, applied on a nickel grid (2t/cm2 pressure) and dried at 120°C under vacuum before cell assembly.

The cell test consists in a 2025 coin cell with metallic lithium as counter electrode, and microporous polypropylene sheet (Celgard) as separator. Electrochemical experiments were performed with a MacPile potentiostat galvanostat. The electrolytes were based on organic carbonates (PC propylene carbonate, EC ethylene carbonate, DMC dimethylcarbonate):EC/DMC LiPF6 1M and PC/EC/3DMC LiPF6 1M , the latter being selected by Saft for its optimum of ionic conductivity in a wide temperature range [16]. The cells were cycled galvanostatically at 20 mA/g (carbon) current density in 0-2V potential range. The evaluation of double layer capacity of pristine electrodes was conducted in the same coin cell with an additional reference electrode by impedance spectroscopy measurements with a Solartron 1250 equipment. The reference electrode consisted in 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.

RESULTS AND DISCUSSION

Double layer capacity measurements

Except in some cases such as activated carbons, the surface area measured by B.E.T method correlates well with double layer capacity, which can be considered as representative of the electrochemically active surface area for similar materials. The response of carbon electrodes at rest potential prior to cycling under periodic perturbation (25 mV) approached a purely capacitive one at low frequency.

The associated capacity was calculated from the imaginary part :

$$C = (\mathrm{Im}(Z) * 2\pi * f)^{-1}$$

The results yield nearly constant values under 0.1Hz (Figure 1) that can be assigned to the double layer capacity response.

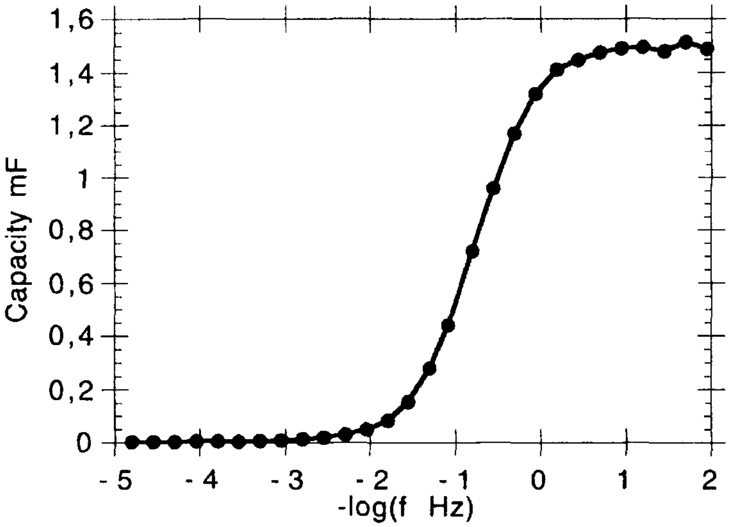

FIGURE 1 Capacitive contribution in the impedance of a graphite electrode

Irreversible faradaic losses at the first cycle

During the first galvanostatic charge-discharge cycle at ambient temperature, intercalation of lithium in the carbon electrodes proceeds with faradaic losses. However, the efficiency increases readily to nearly 100% at the second cycle.

For coke materials, no exfoliation occurs and the irreversible capacity can be considered as due to the passivation process only. As a consequence, a good correlation is observed between the losses and the double layer capacity representative of the surface area, irrespective of the electrolyte formulation (Figure 2).

The non zero intercept with the y axis is due to the constant contribution of other constituants to the irreversible losses (passivation of carbon black, reduction of teflon). This correlation is useful to predict the amount of irreversible losses at the first cycle that can be attributable to passivation phenomenon.

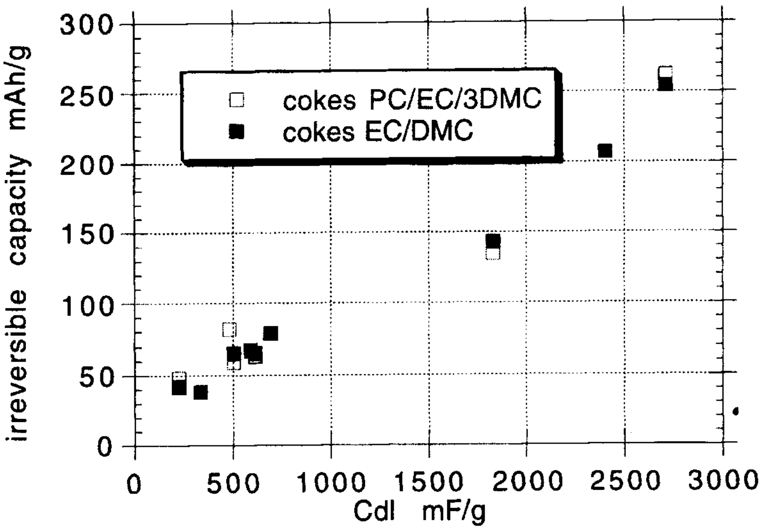

FIGURE 2 Faradaic losses at the first cycle of coke teflon electrodes

graphite	Rhombo. content %	Cdl mF/g	losses in EC/DMC mAh/g	losses in PC/EC/3DMC mAh/g
Natural A	1	255	501	983
Artificial A	12	865	198	
Natural B	19	572	58	130
Natural C	45	865	88	91
Natural D	30	458	57	82
Artificial B	13	765	206	960
Artificial C	16	820	200	1216
Artificial D	23	405	53	380
Natural E	40	1141	100	112
Natural F	36	490	57	65

TABLE 1 Characteristics of graphites and graphite electrodes

For graphite electrodes, the amount of irreversible losses is generally higher than expected from Cdl and dependent on solvent formulation (Table 1).

From these results, it is thus reasonable to consider that the additional losses are due to exfoliation that generates new surface to be passivated, and that exfoliation is less severe in absence of PC, but is however possible in EC based electrolyte. The extent of exfoliation seems very different from one graphite to another, and some graphites do not experience exfoliation even in PC based electrolyte as they present the expected losses for passivation .

A clear correlation with the rhombohedral content of the graphite was found. It appeared that the higher the rhombohedral content of the graphite, the higher its resistance to exfoliation. This result is featured on Figure 3, where the losses at the first cycle have been considered by unit of double layer capacity. If only passivation occured, the result should be constant and amount to 90-100 mAh/F (see Figure 2). Graphites with low rhombohedral content deviate largely from this base line, particularly in PC containing electrolyte. Graphites with large rhombohedral content do not experience exfoliation in the base electrolytes, and can withstand high PC content without faradaic losses increase (Figure 4).

CONCLUSION

Tested in the same conditions, graphite powders with a large amount of rhomboedral phase content are less prone to exfoliation during electrochemical intercalation of lithium ions, and appear particularly attractive for lithium ion battery application [17]. A low surface area is also desirable to reduce irreversible losses due to passivation phenomenon.

A precise physical mechanism able to explain this behaviour remains to be determinated, and the correlation observed 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. In non crystalline carbons such as cokes, this work is high due to small crystallite sizes and intersticial carbons, thus preventing exfoliation. It is possible that layer opening of high rhombohedral content graphite is harder than for pure hexagonal graphite because of the presence of phase boundary and dislocations in greater amount.

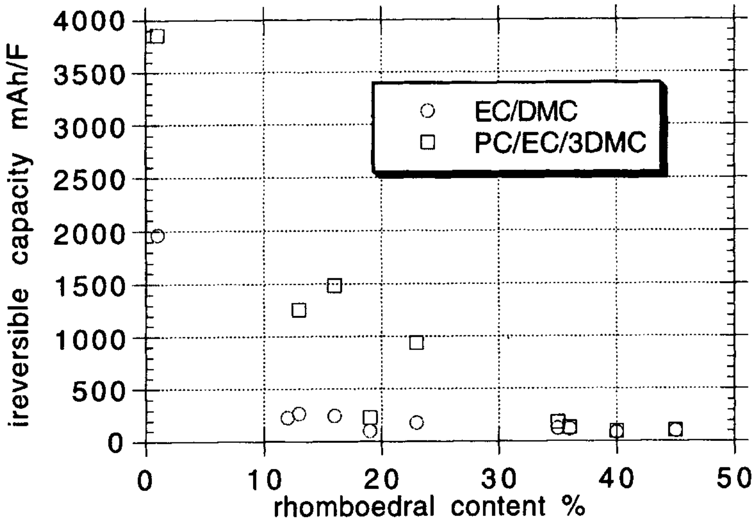

FIGURE 3 Faradaic losses at the first cycle for various graphites

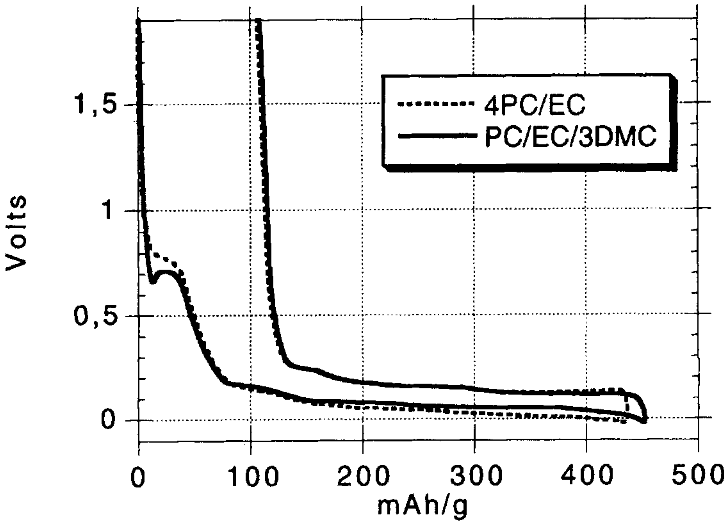

FIGURE 4 First cycle of natural graphite E electrode, 20 mA/g, LiPF6 1M

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