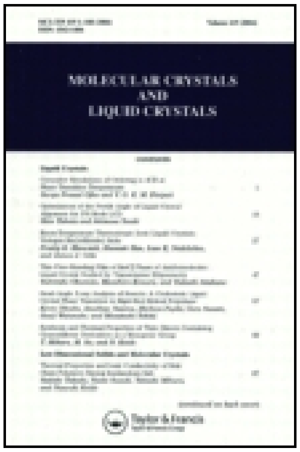


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

On the Electrochemical Intercalation of Lithium into Graphitizable Carbons

S. Flandrois [a] , A. Fevrier-bouvier [a] , K. Guerin [a] , B. Simon [b] & P. Biensan [b]

[a] Centre de Recherche Paul Pascal, Avenue A. Schweitzer, 33600, PESSAC, FRANCE

[b] Alcatel-Alsthom-Recherche, Route de Nozay, 91460, MARCOUSSIS, FRANCE

Version of record first published: 04 Oct 2006

To cite this article: S. Flandrois, A. Fevrier-bouvier, K. Guerin, B. Simon & P. Biensan (1998): On the Electrochemical Intercalation of Lithium into Graphitizable Carbons, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 389-396

To link to this article: http://dx.doi.org/10.1080/10587259808045367

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 389–396
Reprints available directly from the publisher
Photocopying permitted by license only

On the Electrochemical Intercalation of Lithium into Graphitizable Carbons

S. FLANDROIS, A. FEVRIER-BOUVIER, K. GUERIN, B. SIMON* and P. BIENSAN*
Centre de Recherche Paul Pascal, Avenue A. Schweitzer, 33600 PESSAC, FRANCE
* Alcatel-Alsthom-Recherche, Route de Nozay, 91460 MARCOUSSIS, FRANCE

Coke samples heat-treated between 1200 and 2800°C have been characterized by X-ray diffraction and their performance as electrodes for lithium batteries has been determined on coin cells with LiTFSI dissolved in EC/DMC as electrolyte. The data show that the electrochemical behaviour is strongly dependent on the structural characteristics of the carbon materials. It is shown that Mering's graphitization model can account for the values of reversible capacities measured for the different materials, as well as for the appearance of voltage plateaus for carbon heat-treated above 2000°C.

Keywords: lithium batteries, graphitizable cokes.

INTRODUCTION

The ability of lithium to be intercalated (or inserted) into carbon materials, whatever their crystallinity degree, has led to a large number of studies whose aim was to find materials with the best electrochemical performance. Indeed, carbon materials are particularly remarkable for the various shapes, textures and structures they may exhibit according to the nature of the organic precursor, the preparation method, the thermal or chemical treatment. Thus, there exist numerous different carbon materials which have different electrochemical performances when used as lithium reservoir in batteries.

In simple terms, the transformation by heat treatment of an organic material occurs in two steps: carbonization and graphitization [1]. The carbonization process, which involves the loss of the majority of the heteroatoms, gives rise to an almost "pure carbon" and ends approximately between 1100 and 1300°C. The structural evolution occurring during this step leads to more or less distorted columns made up of stacked BSU (Basic Structural Units) where 2 or 3 aromatic molecules (diameter ~ 10 Å) are piled up. At higher temperature, the graphitization process corresponds to the coalescence of columns with an increase in coherence length in both the parallel and perpendicular directions to the layers. For soft carbons, the final structure, obtained by heat-treatment at 2800-3000°C, can be close to graphite. However, for some carbons called hard carbons, only short-range ordering is observed.

Clearly, the mechanism, which allows lithium to be stored into the carbon material, differs depending on whether a soft or hard carbon is concerned and whether the heat-treatment corresponds to the carbonization or the graphitization step. The purpose of this paper is to investigate the graphitization step and its influence on the electrochemical behaviour of graphitizable cokes. In this case only, it is justifiable to talk about "lithium intercalation". In the other cases, it is rather "lithium insertion", involving unknown contributions of porosity and defects. We will show that Mering's graphitization model [2] can account for the values of the reversible capacities, as well as for the appearance of voltage plateaus for soft carbons heat-treated above 2000°C.

EXPERIMENTAL

Three types of carbons were used in our study. Petroleum cokes were obtained from Conoco Inc. They were heat-treated at temperatures from 1300°C to 2800°C. Anthracene cokes heat-treated at 1200 and 2000°C were reference carbons obtained from GFEC (Groupe Français d'Etude des Carbones). A sample of commercial UF2 graphite from Kropfmühl was also used for the purpose of comparison.

Powder X-ray diffraction measurements were made using an INEL curved-counter which collects data over 120° (2θ) simultaneously. Electrodes were fabricated on a weight basis of 90 % carbon powder, 5 % teflon and 5 % acetylene black (YS). Carbon black addition ensures a high electronic conductivity, even in the case of electrode swelling. Electrodes were obtained by mixing carbon powder, teflon aqueous dispersion

(Algoflon D60VB) and ethanol. The resultant paste was malaxed and rolled into a foil. Electrodes (1 cm^2) were cut from this foil, dried at 120°C under vacuum and then weighed and pressed onto a nickel grid under a pressure of about 200 MP.

Coin-type cells were made using these electrodes. The counter-electrode was a metallic lithium foil, the separator a microporous polypropylene sheet (Celgard). The electrolyte was a 1 M solution of lithium trifluoromethanesulfonimide salt (LiTFSI) dissolved in a 50:50 volume percent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC).

Electrochemical cycling was performed with a Mac Pile potentiostat-galvanostat. The coin cells were cycled galvano-statically at a current density of 20 mA/g of carbon in the voltage range of 2 V to - 0.02 V. The slightly negative voltage at the end of the reduction process compensates for the counter-electrode polarization. Li metal deposition on the electrode and internal surface of coin cells was observed in this configuration at voltages lower than - 30 mV. Low kinetic experiments were performed after a few cycles (fully passivated electrodes), in the following way. First, the electrodes were fully lithiated by imposing a zero Volt voltage over 48 hours. Then, intercalated Li was extracted from the carbon at a rate of 5 mA/g, with rest periods of 1 hour every 5 mAh/g. At the end of these relaxation periods the voltage was close to an equilibrium value. Finally, a third electrochemical characterization was made with the evaluation of the double layer capacity (DLC) of the carbons. These measurements were carried out on pristine electrodes in a three-electrode cell using the same electrolyte as above.

RESULTS

First cycle irreversible losses

In the first cycle, all of the carbon samples exhibited a low faradic efficiency, that gradually increased to reach 100 % at the fifth cycle. For pregraphitic carbons, the irreversible losses can be mainly attributed to electrolyte reduction, resulting in passivation of the electrochemical active surface area [3]. In addition, for graphite and highly graphitized materials, irreversible losses can be accounted for by the occurrence of some exfoliation.

The double layer capacity (DLC) is related to the active surface area: $DLC=\varepsilon S/e$, where ε is the dielectric constant of the electrolyte, S the active surface area and e the thickness of the double layer. A direct relationship can thus be expected between the DLC and the irreversible losses for pregraphitic carbons.

DLC values were obtained from Nyquist plots of impedance spectra for carbon electrodes prior to cycling. As expected for electrodes with limited redox activity, the behaviour at low frequency approached a purely capacitive one and can be attributed to the double layer response. We observed a 45° slope in the medium frequency range which is characteristic of alternative current penetration in a porous electrode. DLC values calculated from the imaginary part at low frequency yielded constant values under 0.1 Hz.

The DLC values are shown in Table 1 for the series of petroleum cokes under study. A decrease in DLC with increasing heat treatment temperature (HTT) is observed. Therefore one can assume a decrease of active surface area resulting from structural reorganization (elimination of microporosity). As expected, the effect is the greatest at the beginning of the graphitization process (from HTT=1300°C to 2000°C). A similar decrease is observed for the irreversible losses, with the exception of the 2800 sample where some exfoliation occurred. The quasi linear relationship found between DLC and irreversible losses shows that, in these pregraphitic carbons, the active surface area is the most pertinent parameter to monitor irreversible capacities.

Reversible capacities and voltage behaviour

The reversible capacities were obtained for fully passivated electrodes in the low kinetics experiments described above (quasi equilibrium conditions). The data are gathered in Table 1. It is clear that the capacity values are lower than that of regular graphite (372 mAh/g, corresponding to LiC_6 composition), with a minimum at the HTT-2000 sample.

TABLE 1: Electrochemical and X-ray data for petroleum cokes

HTT (°C)	DLC (mF/g)	Irreversible losses (mAh/g)	Reversible capacity (mAh/g)	g parameter
1300	1800	140	260	0
1700	1200	115	265	0.13
2000	600	60	182	0.29
2200	600	50	205	0.50
2400	550	50	280	0.75
2800	400	110	310	0.94

In fact, this HTT value delimits two domains with different voltage behaviours. For cokes heat-treated above this temperature, the cell voltage exhibits the progressive appearance of plateaus, characteristic of diphasic domains (Figure 1). On the other hand, for cokes heat-treated at 2000°C and below, the voltage varies continuously, as expected for monophasic systems.

The voltage plateaus occur at about the same values regardless of the heat-treatment temperature. They are particularly visible on the graphite curve and correspond to equilibrium between successive stages of intercalation.

DISCUSSION

The results point to the existence of two domains of electrochemical behaviour according to whether the heat-treatment temperature is higher or lower than 2000°C. In fact, since the Sixties, when the graphitization of soft carbon was thoroughly investigated, it has been known that this value of HTT is a critical value for the behaviour of numerous physical and structural properties. It corresponds to a sharp increase in three-dimensional ordering, which is evidenced by the appearance of modulations on the (hk) bands of the X-ray spectra. The increase of reversible capacities above HTT-2000 can therefore be understood as resulting from increased crystallinity. The capacity increase for low HTT's was unexpected. High capacities have been observed previously [4] for carbon materials obtained from organic precursors pyrolyzed at low temperatures (700-1000°C: carbonization step). Two main explanations have been proposed: surface binding of Li with heteroatoms (especially hydrogen) [5] or filling of internal microporosity [6]. Neither of these is valid for our samples: (i) the amount of heteroatoms is quite small in cokes treated at 1300°C and above; (ii) the internal porosity is negligible (He pycnometry gives density values close to those deduced from X-ray diffraction). As a matter of fact, the dependence of capacities and voltage behaviour on HTT can be understood within the framework of Mering's model of graphitization [2].

Mering and his coworkers have done extensive work on pregraphic carbon X-ray diffraction. Based on these studies and on others, such as bromine intercalation and oxidation kinetics, a model was proposed for the graphitization of soft carbons, which has never been refuted. Contrary to previous ideas (Franklin's model) where graphitization was thought to be simply the transformation of disordered stacks of graphitic atomic layers into an ordered arrangement, in Mering's model the structure of each layer is disordered, contains defects and the fundamental process of graphitization lies in the transformation of elementary layer states. The rearrangement of the layers then appears only as a consequence of this internal transformation.

From a quantitative analysis of X-ray data, Mering assumed that each face of an elementary layer can be in either an α state or a β state. The β state is that of the surface of a perfect graphite, whereas the α state results from the presence of interstitial carbon atoms grafted onto the face of the layer, with a corresponding extra thickness. Graphitization thus consists of a cleaning of the face of each layer, converting it from the α to the β state. As this cleaning must occur independently on each face, the ordered arrangement is possible only between two adjacent $\beta\beta$ faces. Thus, in a partially graphitized carbon, three types of elementary interlayer spaces are present: $\alpha\alpha$, $\alpha\beta$ and $\beta\beta$ (graphite layer). Given g as the fraction of layer faces in the β state, the relative proportion of each type is: $(1\text{-}g)^2$ for $\alpha\alpha$, $2g(1\text{-}g)$ for $\alpha\beta$ and g^2 for $\beta\beta$. The g parameter is given by the X-ray diagram. It has been found that, at the end of the carbonization process (HTT ~ 1100 - 1200°C), where only the presence of $\alpha\alpha$ spaces can be assumed, all soft carbons exhibit a mean interlayer distance d_m close to 3.44 Å, whereas it is 3.354 Å in graphite ($\beta\beta$ spaces). Thus, for a partially graphitized carbon, the mean interlayer distance can be expressed as:

$$d_m = 3.354\, g^2 + [(3.354 + 3.44)/2]\, 2g(1\text{-}g) + 3.44\, (1\text{-}g)^2$$

or, equivalently: $g = (3.44 - d_m)/(3.44 - 3.354)$

The composition corresponding to the reversible capacities of our samples is plotted in Figure 2 as a function of g (values given in Table 1). The dot at g = 1 corresponds to graphite with LiC_6 composition. The other dots are for the petroleum coke samples and the two triangles are for the anthracene coke samples (HTT - 1200 and 2000). For each carbon sample, the composition (or the stoichiometric coefficient x in Li_xC_6) must be the sum of the contributions of $\alpha\alpha$, $\alpha\beta$ and $\beta\beta$ spaces, with $x_{\beta\beta} = 1$ (graphite):

$$x = (1\text{-}g)^2\, x_{\alpha\alpha} + 2g(1\text{-}g)x_{\alpha\beta} + g^2$$

The solid line in Figure 2 is the fit with $x_{\alpha\alpha} = 0.75$ and $x_{\alpha\beta} = 0.20$. The agreement is remarkable. The lower value of $x_{\alpha\beta}$ can be qualitatively understood from STM observations [7] on pyrocarbon heat-treated at 2000°C. It has been shown that, in the $\alpha\beta$ state, interstitial atoms form clusters in which they are regularly arranged in a $(\sqrt{7}\times\sqrt{7})$ R 19°1 lattice,

Fig. 1 : low kinetics characteristics of cokes heat treated at high temperatures

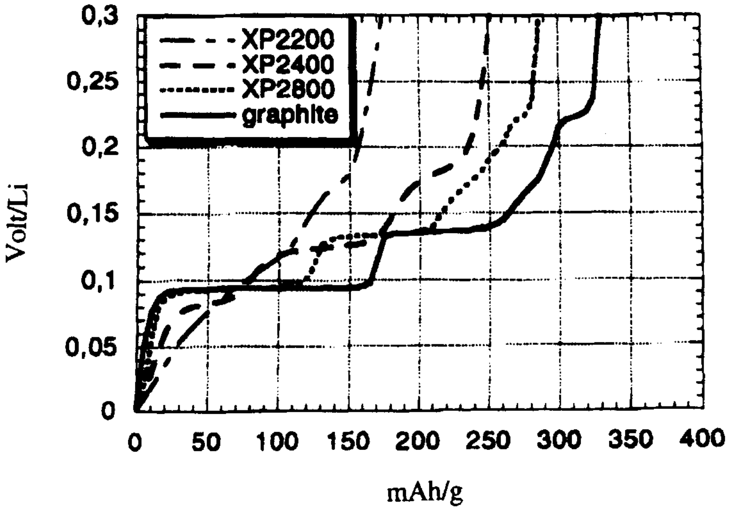
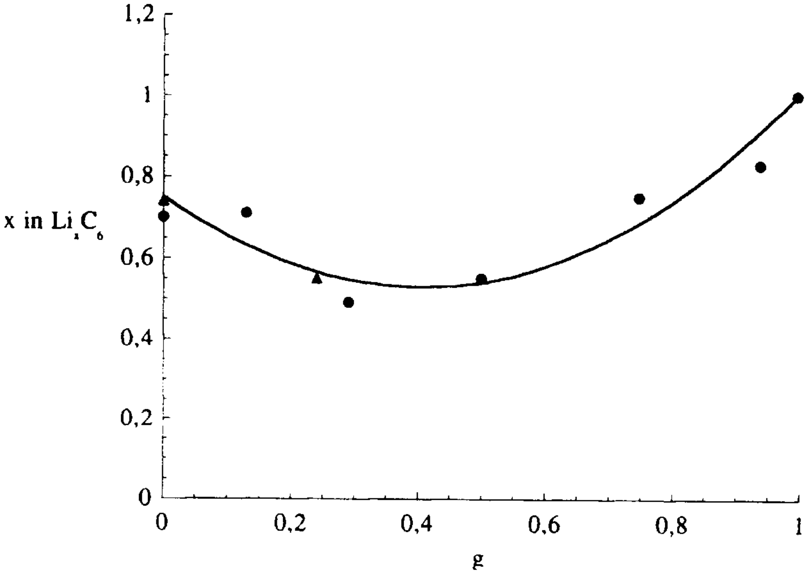


Fig. 2 : Reversible capacities of cokes as a function of g parameter



commensurate with the graphite lattice. Thus, the sites that lithium normally fills, are already occupied by interstitial carbon atoms. Since Li cannot penetrate these clusters, there is a resulting decrease in x with respect to a random distribution of interstitials. It remains to quantitatively understand the values of $x_{\alpha\alpha}$ and $x_{\alpha\beta}$.

Mering's model may also help us understand the appearance of voltage plateaus for HTT higher than 2000°C. For the HTT - 2200 sample, one plateau is visible for a voltage of about 0.18 V (Fig.1), a voltage which corresponds to the equilibrium between stage 4 and dilute stage 1 [8]. For this sample we can assume the formation of a stage 4 and richer compositions do not correspond to a defined stage. The g parameter of 0.5 for this sample gives g^2=0.25, which means that, on average, one interlayer space out of four is of ββ type and can be filled completely by lithium. In the same way, the plateaus observed on the curve for the HTT - 2400 sample lead to the formation of a stage 2; for this sample $g^2 \sim 0.5$, which means that, on average, one interlayer space out of two is ββ.

References

[1.] A. Oberlin, Carbon, **22**, 521 (1984)

[2.] J. Maire and J. Méring in Chemistry and Physics of Carbon, **6**, Edited by P.C. Walker, Marcel Dekker N.Y., 125 (1970)

[3.] R. Fong, U. Von Sacken and J.R. Dahn, J. Electrochem. Soc., **137**, 2009 (1990)

[4.] J.R. Dahn, T. Zheng, Y. Liu and J.S. Xue, Science, **270**, 590 (1995)

[5.] S. Yata, Synth. Met., **62**, 153 (1994)

[6.] A. Mabuchi, K. Tokumitsu, H. Fujimoto and T. Kasuh, Proceedings of the 7th Intern. Meeting on Li Batteries, Boston, p.207 (1994)

[7.] H. Saadaoui, J.C. Roux, S. Flandrois and B. Nysten, Carbon, **31**, 481 (1993)

[8.] D. Billaud, F.X. Henry, M. Lelaurain and P. Willman, J. Phys. Chem. Solids, **57**, 775 (1996)