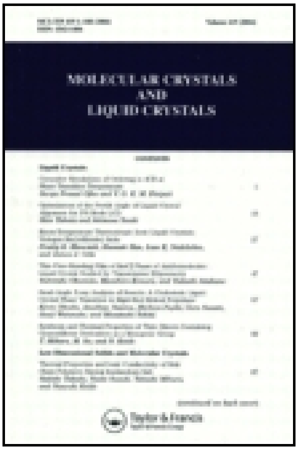

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Version of record first published: 24 Sep 2006

To cite this article: Maheshwar Sharon, Mukul Kumar, P. D. Kichambare, Neil R. Avery & Krista J. Black (2000): Lithium-Ion Intercalation into Carbons Derived from Pyrolysis of Camphor, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 523-528

To link to this article: http://dx.doi.org/10.1080/10587250008025519

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 523-528
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Lithium-Ion Intercalation into Carbons Derived from Pyrolysis of Camphor

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Carbon electrodes prepared from the pyrolysis of camphor at 1000°C in argon atmosphere have been found to facilitate Li-ion intercalation similar to that observed with carbons generally prepared at temperatures well above 2000°C. An irreversible intercalation capacity of these carbon/lithium half cells during the initial discharge was measured to be 0.34, after which fully reversible Li-ion intercalation takes place right from the 1st to the 20th charge-discharge cycle, with a constant intercalation capacity of 0.61. Camphor-pyrolyzed carbon thus appears as a promising candidate for investigation as a lithium battery electrode material.

Keywords: Camphor; Carbon; Li-battery; Li-ion intercalation capacity

INTRODUCTION

Success of the recently developed lithium-ion secondary battery technology is highly dependent on the introduction of suitable carbon materials as a replacement of metallic lithium to be used as anodes. This application exploited the well known property of graphitized carbon to intercalate ions in between the graphene layers. By virtue of the complexity of carbon structures[1], considerable variation and subtlety in the intercalation of lithium-ions into carbon prepared by different roots and different ways have been characterised[2]. This paper presents some preliminary results of intercalation of lithium ions into different carbon samples prepared by low-temperature (1000°C) pyrolysis of camphor. While some samples showed lithium-ion intercalation characteristics typical of disordered carbons, others were more characteristic of graphite, normally prepared at temperatures well above 2000°C.

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EXPERIMENTAL

Commercially available camphor ($C_{10}H_{16}O$; Camphor and Allied Products, India) was pyrolyzed at 1000°C for 2 h in argon atmosphere. As-obtained camphor-pyrolyzed carbon (CPC) samples (in flake and powder form) were ground to pass through a 200 mesh sieve. Weighed portions of the ground carbon were then blended with acetylene black (added as a conductivity aid) and ethylene-propylene-diene monomer (EPDM) binder dissolved in cyclohexane. This mixture was ball milled and cast onto standard 2 cm^2 copper disks to produce a film typically about 0.1 mm thick. The resulting electrode contained EPDM and acetylene black of 4% and 10% (by weight), respectively.

Custom made hermetically sealed electrochemical test cells were assembled in an argon atmosphere glove box. The test cells consisted of a freshly cleaned and etched lithium metal disk counter/reference electrode, celgard microporous separator and the copper-mounted carbon electrode. During assembling the cell, the separator was saturated with thoroughly dried 1 M $LiPF_6$ in 1:1 ethylene carbonate:dimethyl carbonate electrolyte. Finally, spring pressure of 400 kPa was applied to the electrodes as the cell was sealed.

Electrochemical cycling was done on an automated Arbin battery testing station. These half cells, incorporating a lithium metal counter electrode, were assembled in a charged state. During testing, the cell was first discharged as lithium-ions were incorporated into the carbon electrode. Subsequent charge–discharge cycles then follow the lithium-ion deintercalation–intercalation process, respectively. These tests were performed with a charge–discharge current of 0.15 mA cm^{-2} at 23°C. Voltages were relative to the lithium potential (–3.05 V vs standard hydrogen potential).

RESULTS AND DISCUSSION

Carbon Structure

Basically, two kinds of carbon materials were collected from the reaction tube after the pyrolysis was over: (i) metal-like shiny laminar deposit on the inner wall of the reaction tube, which was easily peeled off by simple scrapping; and (ii) wool-like black powder cluster grown in the center of the tube. These were structurally found to be nanobeads of diameter 250 nm and 500–750 nm, respectively, as characterised by scanning electron microscopy[3]. Transmission electron microscopy of the wool-like clusters revealed them to be amorphous (nongraphitic) nanobeads of diameter ~500 nm, covered with a graphitic shell of thickness 80–100 nm. These graphitic shells were further analysed by high resolution transmission electron microscopy and found to be consisted of broken graphitic layers[3]. This structure led us to explore the possibility of Li-ion intercalation through the broken graphitic layers. These specimens are hereafter referred to as graphitic-type (G-type) carbon. Metal-like laminar deposit, on the other hand, was observed to be purely amorphous nanobeads without any trace of graphitic shell. Average surface area of these nanobeads was, however, found to be 16 m^2g^{-1}, suitable for developing lithium battery[4]. These specimens are designated as disordered-type (D-type) carbon.

Lithium-ion Intercalation

Camphor-pyrolyzed carbon samples were electrochemically tested for Li-ion intercalation. Theoretically, graphite can intercalate up to one Li atom per six C atoms, in ambient conditions[5]. The intercalated carbon is, however, Li_xC_6; where the intercalated Li stoichiometry (x) is quantitatively determined as the ratio of the observed intercalation capacity (for Li_xC_6) to the ideal (fully reversible) intercalation capacity, 371 mA h g^{-1} for LiC_6 (x=1). Although both G-type and D-type carbon samples were produced simultaneously in the same reaction tube, Li-intercalation is favoured with G-type, as compared to D-type samples. Also, though the charge/discharge current is kept constant (0.15 mA cm^{-2}) for both the cells, the G-type electrode gets charged/discharged faster than the D-type electrode. Typical discharge-charge cycles for these two types of carbon are shown in Figures 1 and 2, respectively and the lithium stoichiometries are given in Table 1.

TABLE 1 Lithium uptakes by the two classes of carbon expressed as a fraction of full reversible intercalation in graphite (x=1)

Carbon sample	Initial Irreversible Capacity (x_1)	Reversible Capacity (x_2) 1st cycle	Reversible Capacity (x_2) 20th cycle
G-type	0.34	0.61	0.61
D-type	0.34	0.50	0.47

Lithium-ion Intercalation into G-type carbon electrode

Initial discharge with a G-type carbon electrode leads to consumption of lithium-ions as per the voltage-time profile shown in Figure 1. The plateau near 0.8 V is associated with irreversible consumption of lithium-ions in the formation of a passivating surface-electrolyte interface (SEI) layer[6]. Following this passivation, lithium-ions are intercalated into the carbon electrode, substantially in a region <0.2 V above the metallic lithium (Li^0) potential and with discernible fine structure. Subsequent charge and discharge cycles (the first is shown in Fig.1), corresponding to deintercalation and intercalation, respectively, occurs with a reversible capacity corresponding to x_2=0.61 (Table 1). The difference between this reversible capacity and that seen during the initial discharge (x=0.95), gives the irreversible consumption of lithium-ions in forming the SEI layer (x_1= 0.34) and also the residual compounds (about 20% in graphite). Further charge-discharge cycles, as

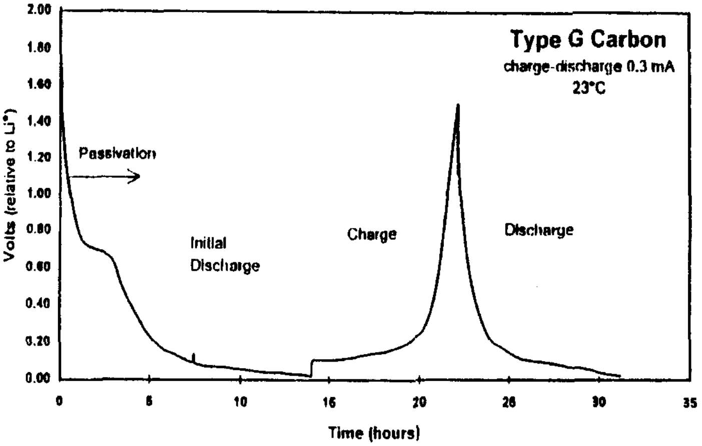

FIGURE 1. Voltage-Time profile for a G-type (graphite-like) sample in a C/Li half cell.

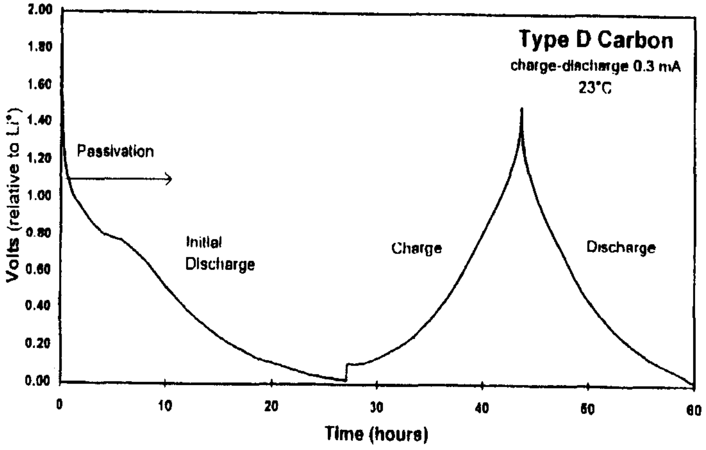

FIGURE 2. Voltage-Time profile for a D-type (disordered carbon-like) sample in a C/Li half cell.

measured up to 20 cycles, were fully reversible and occurred without any detectable decrease in intercalation capacity (Table 1). The features seen here in the intercalation voltage profiles are strikingly similar to those seen with graphite, in particular, the flat intercalation region near the Li potential and with discernible into well-ordered graphite[2,7,8]. These steps have been correlated with the well-known phenomenon of staging of intercalated layers in well-ordered graphite. For example, at full intercalation (the first stage), every graphite layer is fully occupied with lithium to a stoichiometry of LiC_6. At half the saturation, every second layer is fully occupied with LiC_6, leaving alternate layers unoccupied. Similarly, for the third stage, only every third layer is fully occupied. For the G-type carbon electrode, the reversible lithium-ion capacity was only 61% of that expected for graphite at equilibrium. This is believed to be due to kinetic factors limiting the rate of intercalation at the charge-discharge rates used here. Despite this limitation, the clear evidence of staging is a good indication that intercalation is occurring into well-ordered graphitic carbon. The inescapeable conclusion is that the CPC electrodes displaying G-type intercalation characteristics are essentially graphitic, in spite of their low temperature of preparation (1000°C).

Lithium-ion Intercalation into D-type carbon electrode

Initial discharge with D-type carbon electrode leads to consumption of lithium-ions as per the voltage profile shown in Figure 2. Again, the plateau near 0.8 V is associated with the irreversible formation of a SEI layer[6] and with increasing lithium-ion consumption, a voltage profile steeper than that seen with the G-type one. The irreversible and reversible capacities are given in Table 1. Though the consumption of lithium-ions in the formation of the SEI layer is comparable to that seen with the G-type carbon, the first cycle's reversible intercalation capacity is somewhat lower (x_2=0.5) and is further reduced by ~6% after 20 cycles.

It is worth mentioning that the lithium-ion intercalation into graphitic carbon is redox-like, whereas the corresponding intercalation into disordered carbon is more capacitor-like, showing almost a linear voltage-charge characteristic. This typically occurs with a reversible capacity of x_2=0.5–0.6, i.e., less than that of fully intercalated graphite. D-type carbons may therefore be identified with disordered carbons of general type.

Disorder in carbon may occur by rotational and/or shear between successive parallel graphene layers, breaking the periodic ABA crystallographic structure of graphite[1]. The resulting structure leads to a 'soft carbon' with essentially parallel but slightly dilated (compared with graphite) graphene layers. Such a carbon may be converted into graphite by annealing it to >2000°C. A higher degree of disorder occurs in 'hard carbon' where nanoscale graphene layers are intermeshed in a 'house of cards' structure[9] to the extent that they cannot be annealed to a graphitic structure. Both these forms of disorder, however, lead to a lithium-ion intercalation voltage profile similar to that seen for the D-type carbon identified in this study.

CONCLUSION

Although all samples investigated showed varying degrees of these two carbon-types, electrochemical lithium-ion intercalation showed voltage profiles which resemble either those of well-ordered graphite (G-type) or disordered carbon (D-type). The identification of graphitic intercalation behaviour from a carbon prepared at a temperature as low as 1000°C has no precedence known to the authors. Though not demonstrated in this study, it is expected that this graphitic intercalation behaviour arises from the dense material which developed an anisotropic mesophase during its thermal processing. The study is still in progress.

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