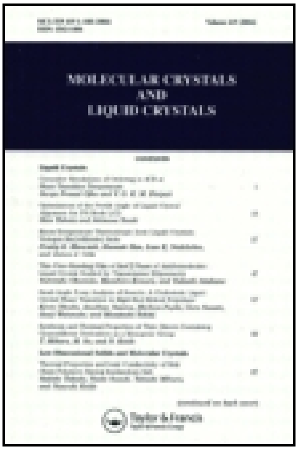

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Version of record first published: 23 Oct 2006.

To cite this article: Denis Billaud , Francois Henry & Patrick Wellmann (1994): Electrochemical Intercalation of Lithium into Carbon Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 159-164

To link to this article: http://dx.doi.org/10.1080/10587259408051682

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 159–164
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Printed in the United States of America

ELECTROCHEMICAL INTERCALATION OF LITHIUM INTO CARBON MATERIALS

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Abstract The electrochemical synthesis of unsolvated Li^+-graphite intercalation compounds (GIC's) has been carried out using oriented pyrographite and a liquid ethylene carbonate based electrolyte. Different pure intercalation stages have been isolated and characterized by in situ 00l X-ray diffraction (XRD) experiments performed during the electrochemical intercalation process. Determination of the in-plane organization of the intercalated species in selected phases has been carried out using hk0 XRD studies. The richest compound of golden colour is similar to the stage I LiC_6 compound obtained by direct reaction of lithium with graphite. Galvanostatic charge and discharge curves exhibiting voltage slopes and plateaus are discussed as regards to the phases identified by XRD analyses. Finally, the effects of the current density on the kinetics of the intercalation and deintercalation are discussed.

INTRODUCTION

Rechargeable lithium batteries offer high energy density and therefore appear very attractive candidates for applications where mass constraints are high. However, a strong limitation in the development of these batteries is caused by the poor reversibility of the lithium electrode due mainly to the reactivity of the metal with the electrolyte and also to the dendritic growth which occurs upon cycling.

Among the proposed replacement materials, some lithium alloys were tested[1].One of the most studied was the Li-Al system[2-4]. However, significant differences in the volume of this alloy appear during cycling and therefore generates mechanical stress and cracks which cause the electrode destruction[5].

To overcome these problems, lithium graphite intercalation compounds appear to be a promising solution[6]. Several recent publications have reported that some carbon based materials which offer high cycleability may be suitable as lithium host electrode[7-12].

As a matter of fact, it is known since years that lithium in gaseous, liquid or solid state can react with graphite to give Li-GIC's. These materials presenting various discrete compositions or intercalation stages can be characterized by their stage number i.e the number of carbon sheets separating two successive intercalated layers[13-17]. These direct reactions of lithium with graphite allow the obtention of the LiC_6 stage I GIC.

In spite of the numerous attempts to prepare LiC_6 compounds by electrochemical techniques, synthesis of such materials by electroreduction of graphite in liquid electrolytes was never reported[18,19]. Depending on the nature of the electrolyte, coinsertion of solvent molecules or cathodic reduction of the inserted solvent leading to graphite exfoliation may occur[20].

In contrast with these previous works, our recent investigations have shown that unsolvated Li^+ ion could be electrointercalated in liquid ethylene carbonate (EC) based electrolyte and that the LiC_6 composition could be reached[21]. In this paper, we will discuss the galvanostatic charge and discharge curves as regards to the phases (stages) identified by X-ray analyses. A special attention will be paid to the characterization of the different stage II compounds isolated in this study. Finally, the self discharge on storage and the influence of the current density which are important parameters for practical electrodes have been also investigated.

EXPERIMENTAL

Oriented pyrolytic graphite PGCCL from Le Carbone Lorraine was used after being cut and cleaved in parallelepipeds (12x1x0.15 mm^3) suitable for X-ray characterization. Lithium perchlorate (Aldrich products) was dried at 180°C under secondary dynamic pumping. Ethylene carbonate (EC), (Fluka product) was outgassed under secondary vacuum. Intercalation was carried out in a classical three electrode cell : the working electrode was a pyrographite sample connected to a titanium wire, the reference and counter electrodes were lithium foils. The cell was operated under argon atmosphere. The electrolyte used was a solution of $LiClO_4$ in EC (1 mole $LiClO_4$/kg EC).

X-ray diffraction studies were carried out using a $\theta/2\theta$ goniometer operating with the MoKα radiation and performed directly through the electrolysis cell in order to avoid any contamination or degradation of the samples studied. For kh0 reflections studies, the samples were transferred through a Lindemann glass in a pure argon glove box and analyzed by using a rotating anode associated with a curved detector.

Intercalation-deintercalation process was studied by intensiostatic potentiometry.

RESULTS AND DISCUSSION

Figure 1 shows an example of voltage time recording reported during the galvanostatic charge of a PGCCL electrode in the EC-$LiClO_4$ electrolyte at 51°C and for a current density of 8.7 μA/mg. The general shape of this curve which presents slopes (stoichiometry domains of pure phases) and plateaus (two-phase systems) is comparable with what is classically observed during the electrointercalation of anionic species such as HSO_4^- [20,22]. Our previous preliminary in situ XRD diffraction studies carried out during this charge[21,23] have allowed the identification of the different stages n based on their identity period along c-axis I_c and their interplanar spacing d_I according to the relation $I_c(Å) = d_I(Å) + (n-1)\ 3.35$.

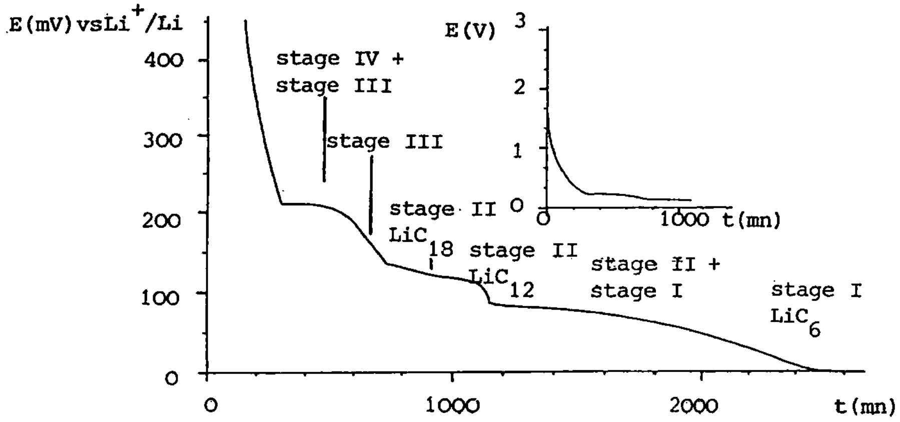

Figure 1.First constant current charge of the system Li/LiClO$_4$-EC/PGCCL at 8.7 µA/mgC

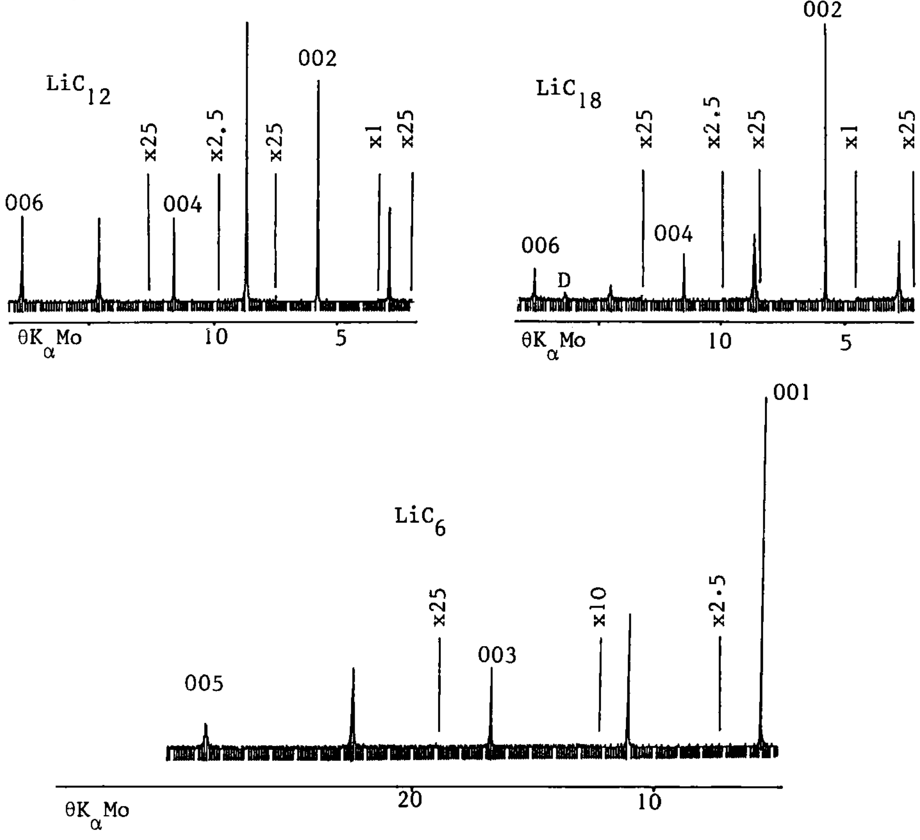

Figure 2. 001 X-ray diffraction diagrams of LiC$_6$ stage I, metal rich LiC$_{12}$ stage II and metal poor "LiC$_{18}$" stage II. D refers to a diamond reference

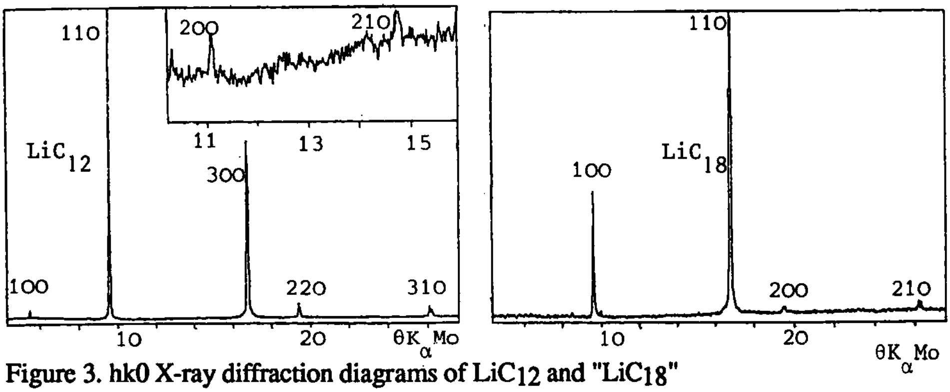

Figure 3. hk0 X-ray diffraction diagrams of LiC_{12} and "LiC_{18}"

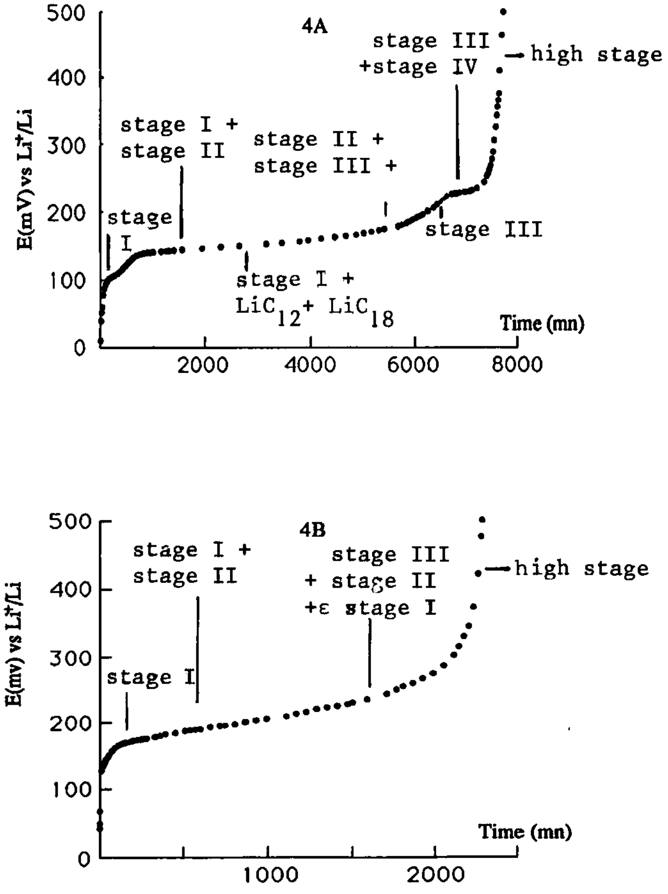

Figure 4. First constant current discharge of the system Li/$LiClO_4$-EC/PGCCL at 8 μA (4A) and 32.1 μA (4B).

The identity periods of stage I to IV compounds have been found comparable to those of materials prepared by direct reaction of lithium with graphite[14-17,25],in particular for the richest golden LiC_6 compound which was the most studied among the Li-GIC's. For stage II compounds, a new phenomenon was also reported : it involves two compounds of different formulae but of same stage. The metal rich copper-coloured stage II is characterized on the curve presented in figure 1 by a strong potential decrease centred around 100 mV while the blue-coloured metal poor stage II is only marked by a potential shoulder at around 125 mV. The 001 X-ray diffractogramms of these stage II compounds are presented in figure 2 : differences appear in the intensity values and in the interplanar distances which were found equal to 7.025 and 7.07 Å for the lithium rich and lithium poor compounds respectively. Moreover, the in-plane organization of both compounds can be obtained from the study of the hk0 reflections presented in figure 3.For the metal rich compound, the first hk0 lines appear at 3.70, 2.13, 1.85, 1.39 and 1.23 Å. They can be indexed respectively as the 100, 110, 200, 210, 300 reflections of the well known hexal structure, where the lithium sublattice is commensurate with that of graphite[14]. The a parameter of this hexal cell is equal to 4.26 Å and the corresponding GIC can be formulated LiC_{12}. In the case of the low metal content stage II, only the 100 and 110 peaks of the graphite sublattice are apparent. The reflections assigned to the metal sublattice are missing which would indicate both the absence of a 2D hexal structure and that of a well organized open structure corresponding to a "LiC_{18}" ideal phase. More refined structural determinations carried out especially at lower temperatures are now in progress with the aim to clarify the 3D organization of these stage II compounds.

In order to investigate the effects of the intensity of the electrolysis current on the intercalation phenomena, cyclings have been carried out at various current rates. It has been previously shown that a voltage plateau corresponding to the stage II to stage I transformation is apparent for low intensity currents such as 4 μA[24]. For higher intensity values, a continuous voltage decrease is observed instead of a plateau as seen in figure (1). In fact, tests performed at even higher currents have shown that the lithium plating and the intercalation reaction can occur simultaneously. Figures 4A and 4B present the first discharge curves obtained respectively at 8 and 32.1 μA. If a long plateau appears on each curve but however at different potentials, the short plateau observed in figure 4A at 225 mV is missing in figure 4B. XRD studies carried out during the discharge process have allowed the identification of the phases appearing at the points marked on the curves. It is obvious that simultaneous deintercalation of different stages occurs particularly when high electrolysis currents are passed through the cell.

In order to evaluate the stability of the Li-GIC's, we have stored the LiC_6 stage I in the electrolyte used for the electrosynthesis. After two months both the colour and the 001 diagram of the sample appear unmodified.

CONCLUSION

Electrointercalation of unsolvated lithium in liquid electrolyte has been performed. The richest phase obtained in our experimental conditions is the golden LiC_6 stage I. For the first time, two different stage II compounds have been clearly isolated and characterized. The richest one, copper-coloured is LiC_{12} which presents a well 3D organized structure in contrast with the other blue-coloured stage II compound, of ideal formula "LiC_{18}", in which a structural desorganization of the intercalated lithium species is obvious, at least at room temperature.

The differences observed in the shapes of the charge and discharge curves at constant electrolysis current underline various kinetic effects. This observation tends to indicate that the limiting kinetic factor is not the diffusion of lithium species inside the graphite layers but rather the desolvation of Li^+ just before the intercalation. It is clear that the possibility to intercalate unsolvated Li^+ is related to a balance between the cation solvation energy and the energy needed to obtain unsolvated intercalated cations. Studies are currently extended to other solvents in order to have a better understanding of the relations existing between intercalation and solvation.

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Acknowledgments. The work at the University of Nancy was supported in part by a CNES grant (896/92/1650/00).