Synthesis and characterization of a new lithium-rich graphite intercalation compound: $Li_2C_6O_y$ ($y \approx 0.5$)

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The electrochemical reduction of the blue, second-stage $NaC_6O_{0.5}$ graphite intercalation compound (GIC) in $LiClO_4$–ethylene carbonate electrolyte results in the formation of the new yellow quasi-stage 1 GIC, of biintercalation type and ideally formulated as $Li_2C_6O_{0.5}$. Such a high lithium concentration has never been observed in GICs synthesized in ambient conditions. The identity period along the *c* axis is equal to 1035 pm and results, as in biintercalation compounds, in the addition of two interplanar spacings of different values: one equal to 370 pm as in LiC_6 and the other equal to 665 pm, resulting from the intercalation of five alternating layers, three of lithium and two of oxygen. Sodium is present in this material in the form of regularly distributed metallic clusters.

The development of secondary 'lithium ion' batteries using carbonaceous materials as anodes able to intercalate lithium reversibly is strongly dependent on the increase of the electrochemical capacity and consequently on the C : Li ratio. When graphite reacts with lithium, either in the gaseous, the liquid or the solid state, the yellow, first-stage LiC_6 graphite intercalation compound (GIC) can be obtained.[1,2] Lithium electrointercalation in selected electrolytes can lead also to the formation of LiC_6.[3,4] Under high pressures, lithium-rich compounds LiC_2 and LiC_4 containing intercalated metal monolayers have been synthesized but they are metastable and decompose under standard conditions.[5]

The obtention of alkali-metal-rich GICs is also possible when electronegative or less electropositive elements are added to the metal prior to its reaction with graphite. For instance, in the presence of mixtures of nitrogen and hydrogen[6] or with barium,[7] two sodium layers, separated by an extra-element one, can be intercalated in the graphite Van der Waals (VdW) space. In this case, the atomic C : Na ratio, related to the filled VdW space, is close to 3.[8] More recently, the addition of oxygen to sodium has resulted in the formation of a second-stage GIC of theoretical composition $NaC_6O_{0.5}$.[9] Up to now, the obtention of similar compounds with lithium was never reported. In this communication, we will describe, for the first time, the synthesis of such a new lithium-rich compound, $Li_2C_6O_{0.5}$. This compound was obtained by simultaneous intercalation of lithium both in the empty VdW space of the $NaC_6O_{0.5}$ stage 2 compound and also in the intercalated sodium-oxygen multilayer through the exchange of sodium by lithium.

Experimental

The synthesis of the stage 2 $NaC_6O_{0.5}$ graphite intercalation compound was previously described by El Gadi *et al.*[10,11] In our study, we used the stainless steel reactor, presented in Fig. 1, to synthesize the $NaC_6O_{0.5}$ compound starting from a massive pyrographite sample (PGCCL from Le Carbone Lorraine). This reactor is composed of two parts separated by a stainless steel grid.[8] Sodium partly oxidized in air was placed in one compartment, while the pyrographite sample was placed in the second one. This operation was conducted under a pure argon atmosphere in a glove box. The two parts of the reactor were screwed together and a copper O-ring was used to insure the air-tightness of the reactor. The latter was heated and then maintained at 200 °C in a vertical oven. Then, the reactor was centrifugated for about 15 min at 5000 rpm in order to allow the molten sodium to be transferred to the compartment containing the graphite sample. The reactor was then heated in a furnace at 470 °C for 3 days in order to obtain the intercalation of oxidized sodium into the pyrographite sample. Finally, the blue intercalation compound was separated from the excess of sodium by a second centrifugation at 5000 rpm.

X-Ray diffraction studies were carried out using a classical θ/2θ diffractometer, composed of a molybdenum source (λ = 0.709 26 pm), a quartz monochromator and a scintillation counter. The 00*l* diffractograms were analyzed using the Diffrac AT software (Siemens).

Electrochemical intercalation of lithium in the $NaC_6O_{0.5}$ stage 2 compound was carried out in a two-electrode cell using a computer-controlled multichannel potentiostat-galvanostat Mac Pile. The working electrode was a $10 \times 2 \times 0.5$ mm^3 piece of $NaC_6O_{0.5}$ obtained from PGCCL pyrographite. A lithium ribbon was used both as counter and

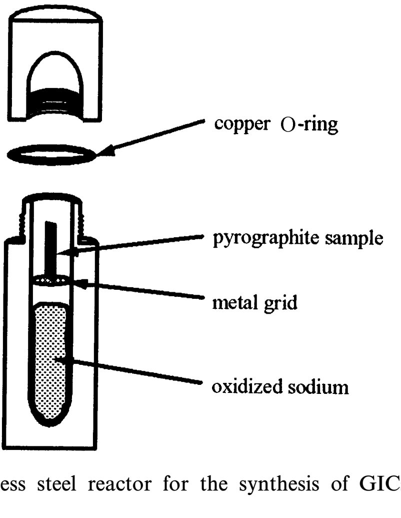

Fig. 1 Stainless steel reactor for the synthesis of GICs in molten metal

reference electrodes. The electrolyte was a lithium perchlorate (1.5 mol kg^{-1})–ethylene carbonate solution.

A 200 kV transmission electron microscope (Philips CM 20) coupled with an EDS (energy dispersive X-ray spectrometry) analyzer (EDAX) and a parallel electron energy loss (EELS) spectrometer (Gatan 666) allowed the identification of the elements present in the synthesized samples. For such an experiment, the samples were ground under argon atmosphere and placed on a copper observation grid covered with a holey amorphous carbon film.

Results and Discussion

The compound obtained after reaction of pyrographite with oxidized sodium is a blue material. The corresponding X-ray diffractogram presented in Fig. 2 displays a set of 001 reflections that allow one to calculate an identity period along the *c* axis equal to 1080 pm. Measurements of the sample thickness before and after intercalation give evidence for a relative dilatation of about 60%, in agreement with the formation of a stage 2 compound. The distance separating two adjacent graphene layers, that is the interplanar distance d_I, was found to be equal to 745 pm, a value in between those previously published for the α phase ($d_I = 742$ pm) and the β phase ($d_I = 747$ pm).[10] Our experimental conditions never allowed the obtention of different stage 2 compounds exhibiting various interplanar spacings, as quoted in ref. 10. According to the literature, there exists some discrepancies between the theoretical formula, $NaC_6O_{0.5}$, and that obtained from the elemental analysis $NaC_{4.75}O_{0.35}$. The excess of metallic sodium, evidenced by sodium NMR, could be present as inclusions of too small a size to show up on the X-ray diffraction diagram.[11] The structural model, along the *c* axis direction, previously proposed by El Gadi,[10] is presented in Fig. 3. In such a model, the three sodium layers are separated alternately by two oxygen layers.

Electrochemical intercalation of lithium was carried out by reducing this $NaC_6O_{0.5}$ compound in a $LiClO_4$–ethylene carbonate solution. For this purpose, the obtained working electrode was held at 80 °C at a constant potential equal to 1 mV *vs.* Li^+/Li. The 80 °C temperature was only chosen to increase the lithium diffusion into the $NaC_6O_{0.5}$ compound. During this process, the initial blue sample changed to a yellow compound. Fig. 4 presents the evolution of the electrolysis current as a function of the composition *x* (*x* refers to Li_xC_6) when the 1 mV potential is applied. The absolute value of the intensity increases strongly up to about 1.6 mA and then decreases regularly in accordance with the evolution of the intercalation reaction, which can be considered to be achieved when the intensity is as low as −10 μA. At this step, *x* is equal to 2. The yellow sample is then transferred under a pure argon atmosphere to a Lindeman tube in order to proceed with its X-ray characterization.

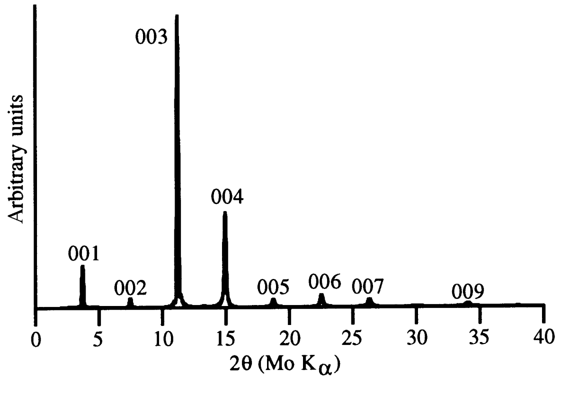

Fig. 2 X-Ray diffractogram (MoKα radiation) of the $NaC_6O_{0.5}$ compound showing the 00*l* reflections

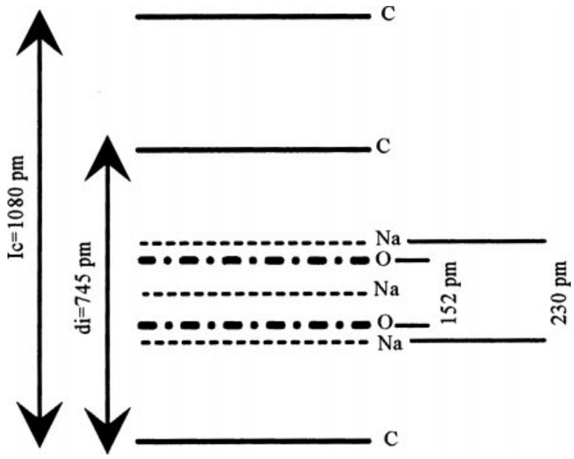

Fig. 3 Structural model along the *c* direction of the $NaC_6O_{0.5}$ compound

Fig. 5 shows the corresponding 00*l* diffractogram, which displays a set of broad reflections whose positions provide a value for the identity period along the *c* axis (I_c) equal to 1035 pm. The half-height width of these broad reflections is close to $\Delta 2\theta = 0.8°$, which corresponds to a coherence length along the *c* axis, L_c, of 5000 pm. Such a value is only about five times the value of I_c, indicating that this new compound is poorly organized along the *c* axis direction. The two extra thin lines present at $2\theta = 13.4°$ and 27° can be indexed as the 110 and 220 reflections of metallic sodium present in the bulk of the material in the form of clusters and characterized elsewhere.[12] The size of such crystalline sodium domains in the *c* axis direction is close to 50 nm, as determined by Scherrer's formula.

The analysis of the EDS spectrum of the yellow compound indicates the presence of the following elements: carbon,

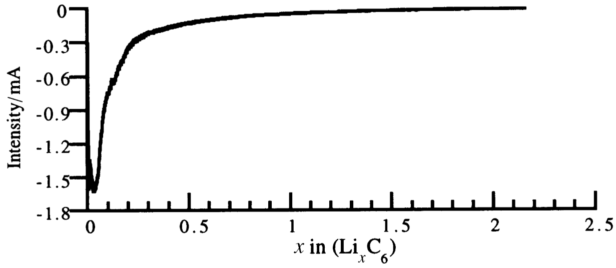

Fig. 4 Electrochemical intensity *vs.* composition curve when the $NaC_6O_{0.5}$ compound is maintained at 1 mV *vs.* Li^+/Li in $LiClO_4$–ethylene carbonate electrolyte

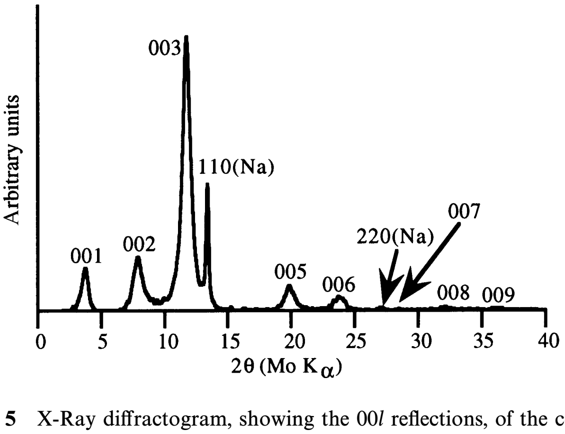

Fig. 5 X-Ray diffractogram, showing the 00*l* reflections, of the compound obtained after electrointercalation of lithium into $NaC_6O_{0.5}$

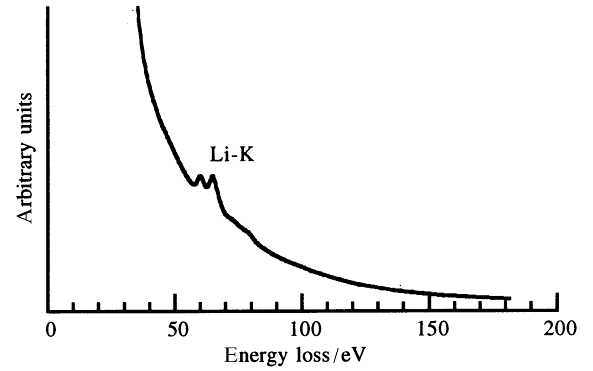

Fig. 6 Electron energy loss spectrum showing the characteristic K edge absorption double peak of lithium

oxygen and sodium. The presence of lithium, not visible in the EDS measurements, is clearly evidenced in the electron energy loss spectrum (EELS) by the peak at 60 eV, characteristic of ionization at the lithium K edge (Fig. 6).

The elemental analysis carried out on this yellow material gives the following relative mass composition: C (49.47 ± 0.40%); Li (10.10%) and Na (14.20%) that corresponds to the ideal composition Li_2NaC_6. The oxygen content was not determined directly by chemical analyses but EELS studies indicate that oxygen is present in the material in the peroxide state.[12]

DSC analysis gives evidence that all sodium contained in the material is in the form of metallic inclusions.[12] Therefore, only sodium substitution by lithium and lithium insertion are responsible for the formation of the ternary Li—O—C compound, and, if the oxygen content is comparable to its concentration in the starting Na—O—C compound, the formula of the new yellow ternary compound is written $Li_2C_6O_{0.5}$.

Lithium intercalation in the second-stage $NaC_6O_{0.5}$ compound does not result in any modification of its thickness, only a color change from blue to yellow is observed.

The *hk*0 X-ray diffractogram of this yellow material exhibits, besides the expected 100 and 110 reflections related to graphite, a low intensity reflection at $2\theta = 11.16°$ characteristic of a hexal organization of intercalated lithium, like the one observed in LiC_6 or LiC_{12}.[1,13]

Taking into account the value of the identity period along the *c* axis, the relative expansion after lithium intercalation, the elemental analysis, the in-plane structural organization of lithium and the peroxide nature of the intercalated oxygen, different hypotheses concerning the structure along the *c* direction of this lithium-rich compound can be formulated. The best fit between the experimental intensities of the first eleven 001 reflections and the corresponding calculated structure factors corresponds to the *c* direction structure presented in Fig. 7.

Table 1 shows that a good agreement exists between the values of the theoretical intensities and the experimental ones.

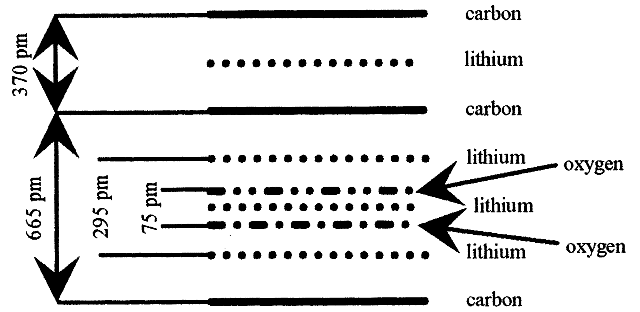

Fig. 7 Structural model along the *c* direction of the $Li_2C_6O_{0.5}$ compound

Table 1 Experimental and calculated structure factors (absolute values) for the 00*l* reflections of the $Li_2C_6O_y$ compound

Reflection	Abs. exptal. structure factor	Abs. theoret. structure factor
001	5.33	10.0
002	9.40	13.2
003	25.8	25.8
004	2.3	1.6
005	11.22	11.7
006	8.96	13.9
007	2.15	0.8
008	6.07	6.2
009	5.01	4.9
0010	0.8	1.4
0011	2.70	5.5

The relative variation of the intensities is respected and especially the higher intensity of the first three reflections and the extinction of the 004, 007 and 0010 reflections is reproduced.

The yellow $Li_2C_6O_{0.5}$ compound corresponds to a so-called biintercalation compound since two successive VdW spaces are filled alternately with layers of different compositions, one containing lithium only and the other one containing five layers, three lithium sheets alternating with two oxygen ones. Such a structure derives naturally from the one of the second-stage compound, $NaC_6O_{0.5}$. Intercalation of lithium occurs both in the empty VdW space of $NaC_6O_{0.5}$ and in the Na—O layers, where sodium species are exchanged by lithium ones. The exchanged sodium ions are cathodically reduced to form neutral sodium atoms, which are at the origin of the metallic sodium clusters dispersed regularly in the bulk of the material. The electrochemical capacity $x = 2$ agrees with the transformation of $NaC_6O_{0.5}$ into $Li_2C_6O_{0.5}$.

As for $NaC_6O_{0.5}$, the oxygen content in the new compound can vary around the theoretical value and, moreover, the oxygen vacancies are probably distributed at random, in accordance with the lack of specific diffraction peaks related to the peroxide stacking.

Conclusion

For the first time, a new lithium-rich graphite intercalation compound was synthesized under ambient conditions of pressure and temperature. The synthesis was carried out after electrointercalation of lithium in the empty VdW spaces of the $NaC_6O_{0.5}$ compound and exchange of sodium by lithium. Sodium is present only as metallic inclusions dispersed regularly in the material matrix. This new yellow compound, of biintercalation type, is in fact a quasi stage 1 material in which the lithium concentration is twice that of LiC_6.

Further characterizations of this compound, such as the structural characterization in the (*a*,*b*) directions by transmission electron microscopy, X-ray and neutron diffraction, EELS, electrical conductivity measurements and NMR studies are now in progress.

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