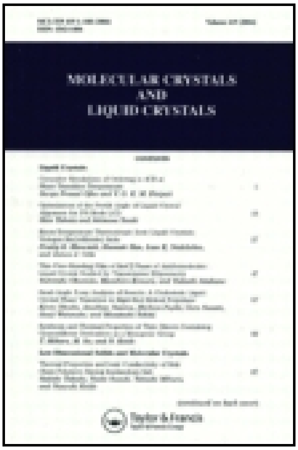

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New Lithium Rich Graphite Intercalation Compounds: $Li_2C_6O_{0.5}$ and Derived Products

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New Lithium Rich Graphite Intercalation Compounds : $Li_2C_6O_{0.5}$ and Derived Products

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Lithium intercalation and concomitant exchange of sodium by lithium in the second stage $NaC_6O_{0.5}$ graphite intercalation compound (GIC) result in the formation of new types of lithium-rich GICs. Each of them contains multilayered stackings composed of five intercalated layers, three of lithium alternating with two of oxygen. The corresponding interplanar distance d_I is equal to 665 pm. The highest lithium concentration was found in the yellow $Li_2C_6O_{0.5}$ compound which is a bi-intercalation compound since two successive Van der Waals (VdW) spaces are filled alternately with layers of different compositions, one containing lithium only and the other one containing the five oxygen and lithium layers. Other derived compounds have been isolated : a classical stage 3 compound composed of two empty VdW spaces and one containing the characteristic five layers stacking corresponding to an identity period along c-axis, I_c, equal to 1335 pm ; a bi-intercalation compound which results in the intercalation of lithium in the two VdW spaces of the previous stage 3 compound and exhibitis a I_c value of 1405 pm. All of these lithium-rich compounds contain sodium clusters trapped in their bulk.

Keywords: graphite intercalation compound; lithium; ethylene carbonate

INTRODUCTION

A large number of carbonaceous materials able to insert lithium reversibly are currently studied for their use as anodes of rechargeable lithium-ion batteries. With graphite, intercalation of lithium by chemical or electrochemical techniques, under standard conditions, leads to the formation of the yellow first-stage LiC_6 graphite intercalation compound (GIC)[1-4]. Under high pressure, superdense LiC_2 and LiC_4 GICs can be obtained but they are not stable under standard conditions[5]. Contrary to other alkali metals, lithium, associated with selected heteroelements, is not expected to be intercalated into graphite to give metal rich compounds composed of several metal sheets alternating with heteroelement layers. For instance, such sodium rich GICs were synthesized when sodium reacts with graphite in the presence of hydrogen-nitrogen mixtures[6] or oxygen[7]. In the last case, a second stage GIC of theoretical composition $NaC_6O_{0.5}$ was obtained, in which three sodium layers are separated alternately with two oxygen layers. Recently, we showed that a new lithium rich GIC of formula $Li_2C_6O_{0.5}$ could be obtained under mild conditions after electrochemical reduction of $NaC_6O_{0.5}$ in a $LiClO_4$-ethylene carbonate electrolyte[8,9]. In this communication, we will present some other lithium-rich GICs, the structures of which are derived from that of $NaC_6O_{0.5}$.

EXPERIMENTAL

The synthesis of the starting materials $NaC_6O_{0.5}$ was presented elsewhere[8]. Small pyrographite samples (10 x 2 x 0.5 mm^3) suitable for X-ray characterization were used in this study. The electrochemical reduction of $NaC_6O_{0.5}$ was carried out in a two-electrode cell connected to a computer-controlled multichannel potentiostat-galvanostat Mac Pile working in the potentiostatic mode. The working electrode was a piece of $NaC_6O_{0.5}$ while lithium acts both as counter and reference electrodes. The electrolyte was a solution of lithium perchlorate (1.5 mol kg^{-1}) in ethylene carbonate (EC). The electrochemical cell was immersed in a thermostatic controlled oil bath. X-ray diffraction (XRD) analyses were performed with a classical q/2q diffractometer working in the transmission mode (radiation MoKα).

RESULTS AND DISCUSSION

The experimental conditions for the obtention of the highest metal content GIC $Li_2C_6O_{0.5}$ were presented elsewhere[8]. To summarize, the starting blue stage II, of ideal formula $NaC_6O_{0.5}$, was reduced in $LiClO_4$ (1.5 mol kg^{-1})-EC at 80°C at a constant potential of 1 mV vs Li^+/Li. Fig. 1 shows the X-ray 00*l* diffractogram of the yellow $Li_2C_6O_{0.5}$ compound obtained after complete electroreduction of $NaC_6O_{0.5}$. The broadness of the 00*l* reflections are characteristic of a poorly organized material. Indeed, the coherence length along c-axis, L_c, is close to 5000 pm, about five times the value of the identity period along c-axis, I_c, equal to 1035 pm. Comparison of the experimental and the calculated intensities of the 00*l* reflections allowed to propose the structural model presented in Fig. 2[8]. Such a model is derived from that of the starting $NaC_6O_{0.5}$ compound, in which intercalation of lithium occurs both in the empty Van der Waals (VdW) gap and in the sodium-oxygen stacking in which sodium species are exchanged by lithium ones. As a result, sodium remains in the new material in the form of metallic clusters evidenced by their characteristic diffraction peaks present both on the 00*l* (Fig. 1) and on the hk0[9] diffraction diagram of $Li_2C_6O_{0.5}$. The multilayer lithium-oxygen stacking corresponds to an interplanar distance d_i of 665 pm. It is composed of five layers, three lithium sheets alternating with two oxygen layers. Oxygen is present in the peroxide state as evidenced by EELS studies. Contrary to oxygen which does not present any 2D-organization, lithium species are arranged according to the hexal structure also present in LiC_6 and LiC_{12}[1,9,10]. Therefore, the extended formula of this compound can be written $(Li_3C_6O_{0.5})$ (LiC_6). Surprisingly, even by using the same experimental conditions for the intercalation of lithium into $NaC_6O_{0.5}$, a new yellow compound, different of $Li_2C_6O_{0.5}$, can be obtained. The corresponding 00*l* X-ray diffractogram, shown in Fig. 3, displays a set of 00*l* broad lines allowing to calculate a I_c value of 1406 pm. The reflections of metallic sodium are also present and indicate that intercalated sodium species have been exchanged by lithium ones. The comparison between the experimental and the calculated intensities of the 00*l* reflections of this new compound agrees fairly with the model presented in Fig. 4[11]. It can be described as a biintercalation compound composed of a stacking of one 665 pm unit resulting in the five alternating lithium-oxygen layers and two 370 pm units corresponding to the intercalation of one lithium monolayer. The related detailed formula is $(Li_3C_6O_{0.5})(LiC_6)_2$ corresponding to the $Li_{1.67}C_6O_{0.5}$ composition. Hence, two different compounds $(Li_3C_6O_{0.5})(LiC_6)$ and $(Li_3C_6O_{0.5})(LiC_6)_2$ can be obtained after electroreduction of $NaC_6O_{0.5}$ in the same experimental conditions.

The obtention of one or the other compound is probably related to variations in the composition of the pristine material. As a matter of fact, according to El Gadi[12] there exists some discrepancies between the theoretical formula $NaC_6O_{0.5}$ and that resulting from the elemental analysis. Moreover, a part of sodium is present in the metal state[2]. Therefore, it can be tentatively concluded that these variations in the oxygen or sodium contents can govern the composition of the final lithium-rich compound.

When using different reduction procedures of $NaC_6O_{0.5}$, other compounds can be also obtained. For instance, when $NaC_6O_{0.5}$ is reduced in EC-$LiClO_4$ at room temperature at a constant potential of 0 V vs Li^+/Li, the total exchange of sodium by lithium is not completed, even after a month of reduction. The resulting compound is a mixture of the pristine material and of a new phase characterized by broad 00*l* lines and by a I_c value varying around 1370 pm. If this mixed compound is annealed at 110°C for three days in a vacuum sealed container, a new grey-bluish pure phase is obtained. Fig. 5 presents the related 00*l* diffractogram which displays a set of broad 00*l* reflections and the 110 reflection of metallic sodium.The I_c value is equal to 1350 pm.

Finally, the electroreduction at 50°C and at a constant potential of 1 mV for seven days of a sample containing $NaC_6O_{0.5}$ and its related third stage, leads also to a multiphase product containing the initial compounds and a new one characterized by a I_c value of 1370 pm. Annealing such a mixture at 110°C for three days in a vacuum sealed reactor leads to the formation of a pure phase the 00*l* diffractogram of which is shown in Fig. 6. The I_c value is equal to 1340 pm and metallic sodium is still present. The elemental analysis of this material agrees with the following formula $LiC_{5.8}Na_{0.46}$ in which oxygen was not titrated[13]. It must be pointed out that the annealing process has reduced by half the sodium content. Intensity calculations of the 00*l* reflections agree with the model presented in Fig. 7. The detailed ideal formula of the related compound is therefore $(Li_3C_6O_{0.5})(C_6)_2$ in agreement with the experimental formula. The compounds characterized by I_c values close to 1370 pm and appearing transiently when the reduction process is not achieved can be described by the model presented in Fig. 8 and corresponding to the formula $(Li_3C_6O_{0.5})(LiC_6)(C_6)$.

CONCLUSION

The electroreduction of the ideally formulated stage two $NaC_6O_{0.5}$ compounds, in $LiClO_4$-EC electrolytes, results in the obtention of a new series of lithium-rich GICs. Depending on the experimental reduction processes and on the annealing procedures, different compounds have been obtained. All of them are characterized by a Van der Waals space filled with five layers, three of lithium separated alternatively by two of oxygen. The corresponding interplanar distance is equal to 665 pm. The highest lithium content material obtained is $Li_2C_6O_{0.5}$ or $(Li_3C_6O_{0.5})(LiC_6)$. Other compounds of formulas $(Li_3C_6O_{0.5})(LiC_6)_2$, $(Li_3C_6O_{0.5})(LiC_6)(C_6)$ and $(Li_3C_6O_{0.5})(C_6)_2$ have been identified. The cohesion energy in these new compounds is probably related to strong lithium-carbon interactions as suggested by the hexal organization of lithium. To the contrary, there is no occurrence of a 2D-organization of the peroxide species. Finally, all these new materials contain metallic sodium clusters distributed in their bulk.

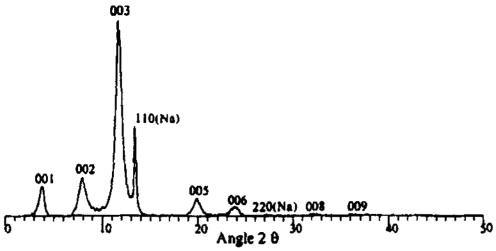

FIGURE 1 X-ray diffractogram of $Li_2C_6O_{0.5}$

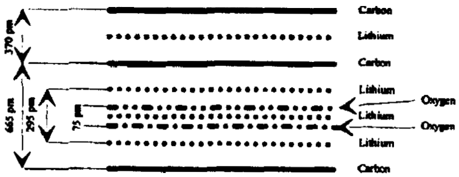

FIGURE 2 Structural model along the c direction of $Li_2C_6O_{0.5}$

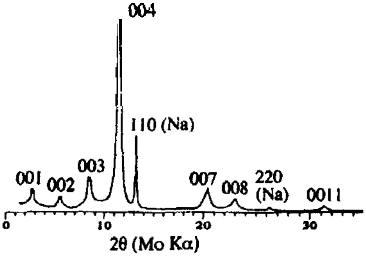

FIGURE 3 X-ray diffractogram of $(Li_3C_6O_{0.5})(LiC_6)_2$

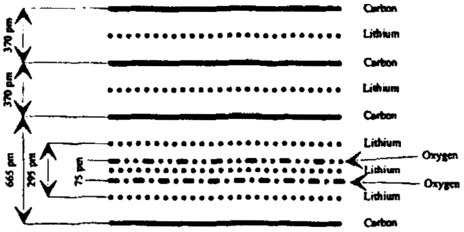

FIGURE 4 Structural model along the c direction of $(Li_3C_6O_{0.5})(LiC_6)_2$

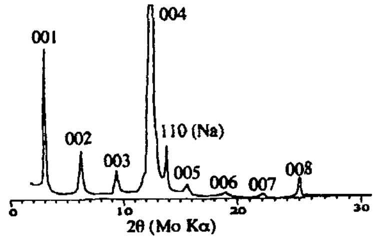

FIGURE 5 X-ray diffractogram of an intermediate compound with I_c = 1350 pm

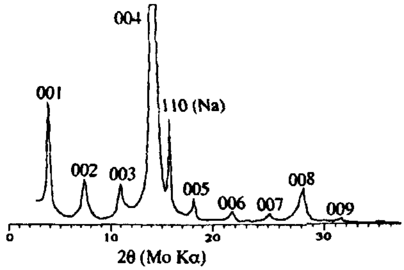

FIGURE 6 X-ray diffractogram of $(Li_3C_6O_{0.5})(C_6)_2$

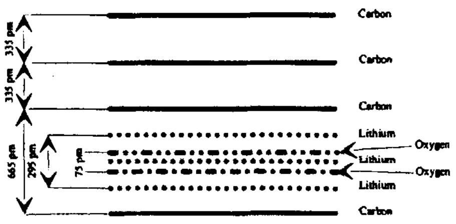

FIGURE 7 Structural model along the c direction of $(Li_3C_6O_{0.5})(C_6)_2$

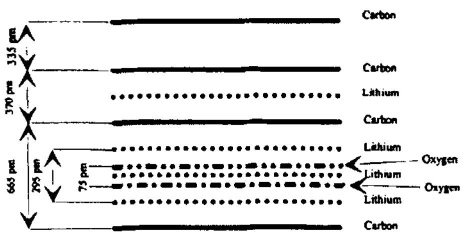

FIGURE 8 Structural model along the c direction of $(Li_3C_6O_{0.5})(LiC_6)(C_6)$

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