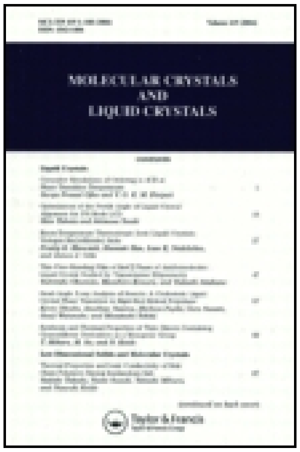

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High pressure lithium intercalation into catalytic carbon nanotubes

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The successful intercalation of lithium into catalytic carbon nanotubes under high pressure conditions is reported. The compounds obtained have Li contents as high as 1-2 Li/ 1C and repeat distances along the c-axis 3.69-4.11 Å, preserving the tubular structure of the nanotubes. XRD, Infrared spectroscopy and ^{7}Li NMR investigations are performed to characterize the compounds obtained.

Keywords: carbon nanotubes, lithium, intercalation, high pressure, infrared spectroscopy, NMR

INTRODUCTION

Great interest to the fullerene compounds on one hand and to the new carbon materials for lithium ion batteries on the other results in significant progress in the investigation of new forms of carbon. Among these new materials carbon nanotubes are of special interest as they combine structural features of graphite and fullerens and open different ways of interaction with other atoms or molecules: i.e. intercalation between the graphitic layers and/or insertion inside of the tube (capillary effects) [1]. Potassium and rubidium and K and $FeCl_3$ intercalation into multiwall carbon nanotubes were reported in refs. [2,3]. To our knowledge, up to now, there are no publications concerning Li intercalation into carbon nanotubes. Li intercalation into graphite was shown to be favored by high pressures leading to the production of the compounds with Li density nearly three times as high as in "normal" LiC_6 compound [4]. According to our estimation of volume effect of alkali metal intercalation into carbon nanotubes, we expected high pressure to promote the formation of the compounds with high Li content.

EXPERIMENTAL

For the synthesis we used multiwall carbon nanotubes produced by the catalytic decomposition of acetylene [5]. The dimensions of the nanotubes are: internal diameter ~ 40 Å, external diameter ~ 300 Å, the length reaches 10 μm. Carbon nanotubes synthesis was carried out in a vertical flow furnace. A catalyst precursor (cobalt nitrate on silica substrate) was reduced under a 10%/90% hydrogen/nitrogen flow at 500°C during 2 hours. Then a 10%/90% acetylene/nitrogen flow was passed over the catalyst at 900°C during 30 minutes for the production of nanotubes. After reaction, silica was dissolved into 73% hydrofluoric acid, whereas the residual catalyst was eliminated with 3N nitric acid. In some cases the purified nanotubes were heat treated at 2800°C to improve their structure. For high pressure synthesis we used nanotubes both: "as synthesized" and heat treated.

We have carried out both liquid phase and high pressure synthesis. The liquid phase synthesis was fulfilled in stainless steel ampoule under argon atmosphere at 400°C for 48 hours. The conditions applied are basically the same as for Li-GICs synthesis [6].

The high pressure synthesis was performed under quasihydrostatic conditions in an anvil apparatus with internal heating of the high pressure cell by graphite furnace. The high pressure apparatus used has primary double acting hydraulic cylinder with a capacity of 500 tons. The special lenticular assembly made of pyrophyllite was placed between the pressure plates with tungsten carbide anvils shaped to fit the assembly. Controlled high temperature was generated by applying a regulated voltage to the furnace and monitoring the temperature with a thermocouple. The selfsealing ampoule containing the sample - 5-8 mm in diameter and 6-7 mm high - was placed inside the furnace. In order to locate the sample at the vertical mid-point of the furnace it was supported from the bottom by the thermocouple block (Chromel - Alumel thermocouple press-fitted into NaCl pellet) and by NaCl plug from the top.

Carbon nanotubes and Li metal were loaded into the stainless steel ampoule in the glove box under dry argon atmosphere. The ampoule was pressure sealed and installed into the high pressure apparatus. Synthesis was performed at 45-60 kbar and 300°C for 1-3 hours, depending on the sample.

For the X-ray diffraction study we used powder diffractometer Siemens D500 with CuK_α radiation. IR spectra of Li-nanotubes compounds in the region 200-4000 cm^{-1} were registered using Specord-M-82 spectrophotometer.

^{7}Li NMR investigations were performed on a Bruker DSX broad-band spectrometer at 8.5 T (Larmor frequency: ν_0 = 140 MHz), using a spin-echo technique. The frequency shifts have been measured relatively to an aqueous solution of Li^+ ions, and the T_1 values have been only roughly estimated from the intensity dependence *vs* recycling time between successive scans.

RESULTS - DISCUSSION

XRD pattern of initial nanotubes is shown in Fig.1^a. The 001 reflection observed at 26 degree (in 2Θ), corresponds to d = 3.4245 Å, close to that in turbostratic graphite. The broad asymmetric line at around 42.3 degrees corresponds to 100 reflection of graphite honeycombs. "As synthesised" nanotubes show the same repeat distance along the c-axis as heat treated.

To check the stability of the nanotubes at synthesis conditions we first recorded the XRD spectrum and TEM picture of the nanotubes after applying the high pressure (up to 46 kbar at 300°C). The spectrum and TEM image appeared to be identical with the initial ones. The resistivity *vs.* pressure and temperature (at given P) and volume *vs.* pressure measurements also did not reveal any reversible changes under pressure and temperature in these limits.

The X-ray diffraction diagram of the sample, prepared from liquid metal phase under argon atmosphere represents nearly pure lithium carbide. The diagrams of the samples obtained under pressure are presented in Fig. $1^{b,c}$ and do not show any trace of lithium carbide. For "as synthesized" nanotubes samples we observe very good (much more intense and narrow than in pristine nanotubes!) line at 42.30 (2.13 Å), corresponding to 100 of graphitic plane, and 001 and 002 lines of the compound with I_c = 4.11 Å. The narrowing of the 100 line could be provoked by a change from tubular structure to planar graphitic structure. However, TEM observation after intercalation-deintercalation process on the nanotubes still show the perfect tubular morphology. The value 4.11 Å is 10% higher than that for LiC_6-LiC_2 compounds (3.70 Å.). The amount of Li intercalated seems to be very high - the initial Li/C ratio was about 2/1. After synthesis we did not observe any trace of metallic Li, XRD pattern also did not contain any reflections of Li metal. On the other hand, the new distance between graphitic planes is big enough to accommodate large amounts of intercalated lithium. From XPS experiments on these "as synthesized" nanotubes, we detected large oxygen amount attributed to C-O and C=O bonds. This oxygen is coming from mild oxidation by nitric acid used for cobalt catalyst elimination. We think that oxygen traces could favor the formation of a lithium double layer as it is the case for graphite intercalation compounds [7].

The XRD pattern for the intercalation compound of heat treated sample (fig. 1^c) corresponds to the same repeat distance as for GICs - I_c=3.69 Å. The hk0 reflections observed correspond to the hexagonal structure with a=4.296 Å. The striking decrease of I_c with respect to that in not heat treated samples can be explained by more perfect (and at the same time more rigid) structure of

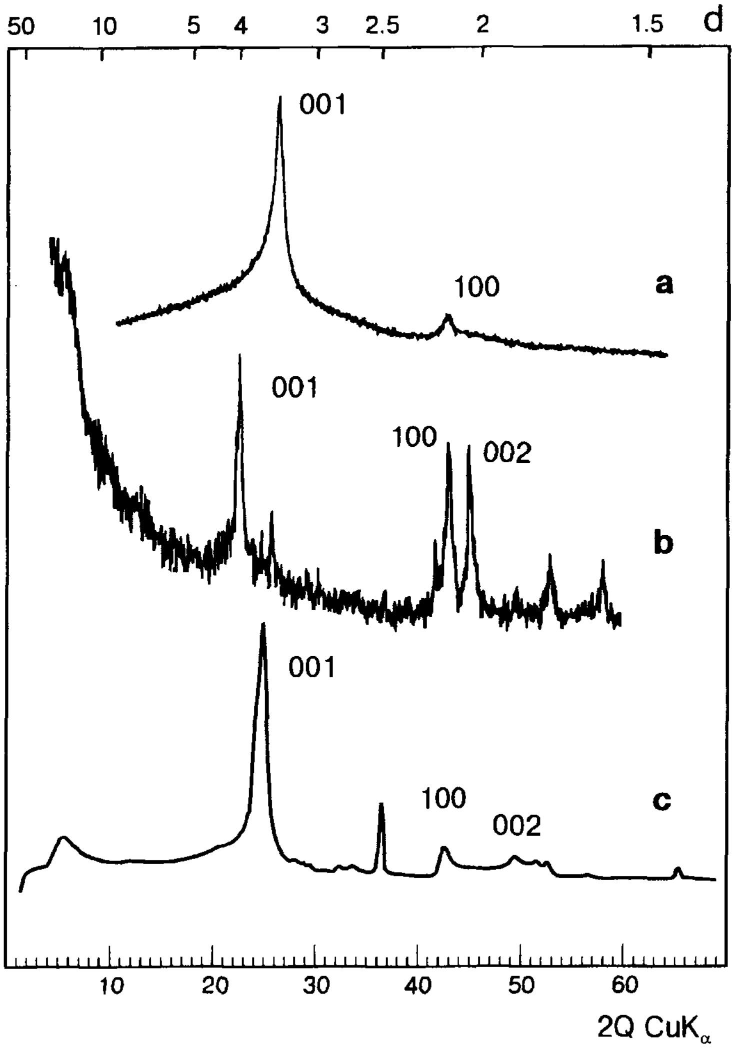

Figure 1. X-ray diffraction diagrams (CuK$_\alpha$ radiation): pristine nanotubes (a); Li compound with: "as synthesized" (b) and heat treated at 2800°C nanotubes (c)

heat treated nanotubes and/or by the fact that heating at 2800°C eliminates completely surface oxygen groups, as it was demonstrated by almost complete absence of oxygen in the XPS analysis of the tubes. Consequently there is no longer any reason for a lithium double layer, and maximum Li content in the compound with I_c=3.69 Å decreases and does not exceed 0.8 Li / 1 C.

To understand better Li state in carbon nanotubes we performed IR spectroscopy study. The number of absorption bands in IR spectrum of pristine nanotubes is much more than in IR spectra of C_{60} and C_{70} fullerenes probably due to the large number of edge planes. In IR spectra of Li - nanotubes compounds, the bands observed for 5 different samples are completely reproducible. Li-nanotubes spectra differ from those of pristine nanotubes, mostly in the region below 900 cm^{-1}. The bands at 690, 653, 474 cm^{-1} in IR spectra of Li-nanotubes are very close to those observed in Li GIC spectra [8] and should be attributed to the stretching of Li-C bonds in structural units with 6-fold symmetry. The variety of bands observed in Li-nanotubes spectrum at 871-730 cm^{-1} and can be assigned to Li-Li bonds stretching [8]. All the bands mentioned above (except those corresponding to C-C stretching and C-C-C angle deformations) are observed in IR spectra of Li-nanotubes under inert conditions only. At exposure of the sample to air they disappear from spectra in 1-2 minutes. It proves that they correspond to M-C and M-M bonds chemically unstable in the air.

^{7}Li NMR spectra were recorded for the intercalation compound prepared from the heat-treated sample, and showed 3 lines, with the following characteristics [9]:

	δ (ppm)	rel.int. (%)	T_1 (s)	T_2 (μs)
Line #1	+262±1	71±5	0.2	690
Line #2	+43±3	15±5	1	160
Line #3	+16±3	14±5	1	110

All these lines can be simulated by Lorentzian shapes. From their resonance frequencies, we have assigned them respectively to metallic Li or LiC_2 (line #1) [10], to LiC_{6s} (line#2), and to LiC_{9s} (line#3), where *s* is the stage [11]. Whereas the lines #2 and #3 give evidence of Li insertion between successive sheets of carbon, it cannot be easily concluded for line #1, since its position is compatible both with metallic lithium or a superdense intercalation compound. Since XRD and IR do not provide any evidence of a separate metallic Li phase, and since the internal channel of the tubes is quite large, we believe that this line could be assigned to disordered metallic Li, which can form nanowires inside the tubes.

CONCLUSION

High pressure synthesis of Li-multiwall carbon nanotubes yielded intercalation compounds with very high Li contents (upto 0.8-2Li/1C) and I_c=3.69-4.11 Å. Their structure and the amount of the intercalated Li depends on the quality of pristine nanotubes.

References

[1.] E. Dujardin, T.W. Ebbesen, H. Hiura, and K. Tanigaki, *Science*, **262**,1850 (1994).

[2.] O. Zhou, R.M. Fleming, D.M. Murphy, C.H. Chen, R.C. Haddon, A.P. Ramirez, and S.H. Glarum, *Science*, **263**,1744 (1994).

[3.] V.Z. Mordkovich, M. Baxendale, S.Yoshimura and R.P.H. Chang, *Carbon*, **34**, N10, 1301 (1996).

[4.] V.A.Nalimova, V.V. Avdeev, K.N. Semenenko, *Material Science Forum*, **91-93**, 11 (1992).

[5.] H Gaucher-Alvergnat, S. Bonnamy and F. Beguin, accepted in *Carbon*.

[6.] S.Bagi, C. Zeller, P.J. Franders, C.D. Fuerst, W.D. Johnson, J.E. Fischer, *Mater. Sci. Eng.*, **38**, 275 (1979).

[7.] M.El Gadi, A. Herold, C. Herold, P. Lagrange, M. Lelaurain, J.-F. Mareche *Mol. Cryst. Liq. Cryst.*, **244**, 29 (1994).

[8.] V.A. Nalimova, G.N. Bondarenko, V.L. Kofman, V.V. Avdeev, and K.N. Semenenko, 20th Biennial Conference on Carbon, Santa Barbara, June 23-28, (1991).

[9.] S. Menu, H. Gaucher, J. Conard, P. Lauginie, A. Nozhov, V.A. Nalimova, International Winterschool on Electronic Properties of Novel Materials, Kirchberg, Austria, March 1-8, (1997).

[10.] J. Conard, V.A. Nalimova and D.Guerard, *Mol. Cryst. Liq. Cryst.*, **245**, 25 (1994).

[11.] J. Conard, *Proceedings of First Scientific Workshop for electrochemical Materials - Material Chemistry for Batteries and Fuel Cells* - ed. T.Kodama and H. Ishikawa (Osaka National Research Institute, Japan, 1996) 17-25.