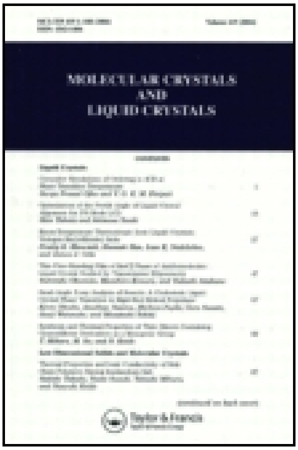

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# Lithium Insertion in Carbon Nanotubes

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Different types of multi-walled carbon nanotubes obtained by catalytic decomposition of acetylene or pyrolysis of propylene on an alumina template have been investigated for lithium storage in aprotic medium. The samples presented a high reversible storage capacity of lithium, ranging from 350 mAh/g to 780 mAh/g, depending on their physico-chemical characteristics. It has been found that the mesoporous character of the nanotubes is responsible for an important overvoltage between insertion and extraction of lithium. Especially swelling mesopores, created by the entanglement of flexible nanotubes, facilitate charging of an electrical double layer. This contributes to the important reversible capacity observed in the range from 1 V to 3 V *vs* Li (up to 580 mAh/g). On the other hand, solvated lithium cations easily penetrate the mesopores and the solvent molecules are decomposed at the carbon surface forming the solid electrolyte interphase (SEI). That is at the origin of the important irreversible capacity ranging from 570 mAh/g to 1080 mAh/g. Due to their pseudo-capacitance properties, these nanotubes are very promising as electrode materials of electrochemical capacitors.

*Keywords:* carbon nanotubes; lithium insertion; mesopores; capacitance character

## INTRODUCTION

Finding of new carbon materials as substrate for the negative electrode in lithium-ion batteries is a challenge for improving their performance. Presently, most of the commercially available systems are based on graphite which at saturation gives a capacity of 372 mAh/g, corresponding to the stoichiometric composition $LiC_6$. Except the fact that there is a requirement for increasing the storage capacity, the use of graphite can arise some problems due to the exfoliation provoked by solvent co-intercalation. There is presently a lot of research work on hard carbons formed close to 1000°C, which in some cases give more than twice the reversible capacity of graphite. However, their practical use is not yet possible due to a big irreversible capacity and an important overvoltage between insertion and de-insertion of lithium. Multi-walled carbon nanotubes (MWNT) are interesting to be tested due to possible insertion of lithium both in the mesoporous volumes and in the van der Waals space between the carbon layers [1].

In the present work, we compare the electrochemical storage in MWNT formed by catalytic decomposition of acetylene [2-3] or by thermal decomposition of propylene on an alumina template [4]. It will be shown that galvanostatic characteristics are strongly related to the kind of porous microtexture.

## EXPERIMENTAL

Preparation methods of carbon MWNT used for this work were:

1) Catalytic decomposition of acetylene:

- at 700°C (Si/Co700) and 900°C (Si/Co900) using cobalt (in the proportion of 10 wt%) supported on silica [2]. As-received samples were treated in 73 wt% aqueous HF solution and then refluxed in 3 $mol.l^{-1}$ nitric acid, to get rid of silica and cobalt, respectively. After preparation, some samples were also annealed for one hour at 2400°C under argon flow.
- at 600°C using 2.5 wt% of Co supported on zeolite NaY (NaY/Co600) [3]. Zeolite was fully removed by 40% hydrofluoric acid.

2) Thermal decomposition of propylene at 800°C within the pores of an alumina membrane (AlTempl800). The oxide template was dissolved in 46% HF solution [4].

The structural and textural properties were determined by Transmission Electron Microscopy (TEM, Philips CM20) and nitrogen adsorption at 77K (ASAP2010, Micromeritics). Prior to adsorption experiments, the samples were outgassed ($10^{-6}$ mbar) at 350°C during 12 hours.

Composite electrodes were pressed from a mixture of carbon MWNT as active material (85%), acetylene black (10%) and polyvinylidene fluoride (5%) as an organic binder.

Electrochemical insertion of lithium into MWNT was investigated by galvanostatic charge-discharge experiments (20mA/g) with a two electrode lithium/carbon cell, using a Mac Pile multichannel generator (Biologic) in the voltage range from 3.0V to -20mV *vs* $Li/Li^+$. The electrolyte was 1M $LiPF_6$ in 1/1 mixture of ethylene carbonate (EC)/diethylcarbonate (DEC).

## RESULTS - DISCUSSION

The materials used for this study contained almost exclusively nanotubes. The AlTemp800 sample consisted of stiff nanotubes, with a canal diameter ranging from 35 to 55 nm, and relatively thin walls. It differed from the other specimens for which the nanotubes were strongly entangled. Si/Co700 and NaY/Co600 had a very well-defined canal and the aromatic carbon layers were parallel to the tube axis, whereas Si/Co900 had a characteristic fishbone morphology. Si/Co700 and Si/Co900 had opened tips, while the canal of NaY/Co600 was not accessible. In all cases, annealing of catalytic nanotubes above 2000°C created more straight layers and could cause closure of the tubes.

These microtextural properties are well illustrated by gas adsorption data. The general shape of the nitrogen adsorption isotherms is relatively comparable for Si/Co700, Si/Co900 and NaY/Co600. An example is given for Si/Co700 in figure 1a which shows a type IV isotherm with a hysteresis between adsorption and desorption, typical of a mesoporous character. The absence of a plateau at $P/P_0 \approx 1$ demonstrates that this material swells at the high pressure of nitrogen. We interpret this phenomenon by the contribution of the mesopores formed by the entangled network of nanotubes, which are able to increase in size due to the flexibility of the tubes. This is supported by the isotherm plot of AlTempl800 which gives a saturation plateau at $P/P_0 \approx 1$ and for which, due to the stiffness of the tubes, the mesopores formed at the point of entanglement cannot grow at high nitrogen pressure (Figure 1b).

Figure 1 Nitrogen adsorption/desorption at 77 K in multi-walled nanotubes: (a) Si/Co700; (b) AlTempl800

The data computed from the isotherms are given in table I. All the samples are essentially mesoporous, and the contribution of micropores can be neglected. Quite high and comparable values of specific surface area were remarked for Si/Co700 and Si/Co900, even if these two samples are representative of different orientations of aromatic layers with respect to the tube axis, parallel and fishbone. On the other hand, NaY/Co600 which had a morphology comparable to Si/Co700 but with closed tips presented a rather small value of specific surface area. This is the best proof of the important role played by the accessibility of the canal in the adsorptive properties of the nanotubes. In addition, this is supported by the fact that annealing had a very little effect on the BET surface area of NaY/Co600 which only slightly decreased to 103 $m^2/g$. On the other hand the decrease is quite important for Si/Co900 annealed, because in this case thermal treatment provokes the closure of nanotubes tips (Table 1).

TABLE 1 BET specific surface area ($m^2/g$), micropore and mesopore volumes ($cm^3/g$) of the nanotubes

| Sample | Si/Co700 | Si/Co900 | Si/Co900 annealed | NaY/Co600 | AlTempl800 |
|---|---|---|---|---|---|
| $S_{BET}$ | 411 | 396 | 191 | 128 | 311 |
| $V_{micro}$ | 0.003 | 0 | 0 | 0.004 | 0.014 |
| $V_{meso}$ | 0.76 | 0.66 | 0.41 | 0.43 | 1.04 |

A typical galvanostatic curve of lithium insertion/de-insertion for nanotubes Si/Co700 is shown in figure 2. Irreversible capacity is very important for this sample (900 mAh/g). Indeed, solvated lithium cations can easily penetrate in the mesopores created by the central canal and the entanglement of nanotubes, and the solvent molecules are decomposed at the carbon surface forming the solid electrolyte interphase (SEI). Another effect of the presence of mesopores is the important overvoltage between 1 V and 3 V *vs* Li, that is never observed for essentially microporous hard carbons. This hysteresis is due to a capacitance and/or pseudo-capacitance effect accompanying the charge transfer processes. The presence of mesopores facilitates the charging of an electrical double layer. The high overvoltage, especially at the end of lithium de-insertion, contains also a contribution of ohmic polarization. The part of hysteresis observed below 1 V *vs* Li for Si/Co700 is rather due to the presence of oxygenated surface groups which to some extent hinder lithium de-intercalation due to its transient trapping through interactions with the surface, such as $-C-O^- Li^+$. It must be reminded that nanotubes are slightly oxidized during the purification step using 3 $mol.l^{-1}$ nitric acid. Elemental analysis on Si/Co700 gave in mass: 82 % C, 11 % O, 1 % H. On the other hand Si/Co700 annealed at 2400°C, which is pure carbon, without any surface oxygen, gave a quite good reversibility at low potential, that is characteristic of a true

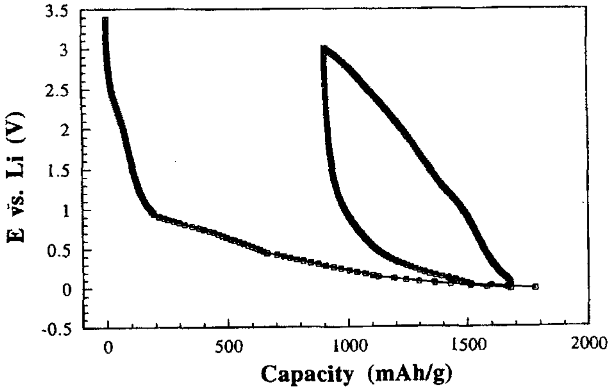

Figure 2 Galvanostatic lithium insertion/de-insertion in Si/Co700 multi-walled carbon nanotubes. Current load 20 mA/g

intercalation between the concentric layers of the nanotubes. In the potential range 1 V – 3 V *vs* Li, there is still a marked polarisation for annealed nanotubes, because of their important mesopore volume.

No important differences were remarked in the charge-discharge curves of the different samples examined in this work. In all cases, hysteresis and irreversible capacity were quite large (Table 2). By comparison with the value of mesopore volume (Table 1), it is easily seen that there is almost a proportional dependence between these two parameters.

TABLE 2 Reversible ($Q_{rev}$) and irreversible ($Q_{irr}$) capacities for lithium storage in multi-walled carbon nanotubes (mAh/g). Reversible capacity is given in two potential ranges *vs* Li.

| Sample | Si/Co700 | Si/Co900 | NaY/Co600 | AlTempl800 |
|---|---|---|---|---|
| $Q_{rev}$ (0 – 1 V) | 200 | 160 | 160 | 210 |
| $Q_{rev}$ (1 – 3 V) | 580 | 230 | 190 | 270 |
| $Q_{irr}$ | 900 | 570 | 630 | 1080 |

A noticeable reversible lithium storage capacity ranging from 350 mAh/g for sample NaY/Co600 to 780 mAh/g for sample Si/Co700 was found. Whatever the kind of nanotube, the reversible capacity due to true intercalation (between 0 and 1 V *vs* Li) is almost the same (of the order of 200 mAh/g). The main differences in the total capacity are coming from the contribution in the range of potential between 1 V and 3 V *vs* Li, where the quasi-linear response with charge capacity confirms the pseudo-faradaic properties of MWNT (Figure 2). The most interesting comparison is between Si/Co700 and AlTempl800 which have both a large mesopore volume, estimated from nitrogen adsorption (Table 1). The important value of Qrev (1 – 3 V) for Si/Co700 is due to a pseudo-capacitance contribution coming from the oxygen presence (11 wt%) and from an easy penetration of big solvated lithium cations in the swelling mesopores formed by the entanglement of these flexible nanotubes. Even if AlTempl800 has the highest mesopore volume among all the samples, the penetration of the lithium cations between the rigid, heavy tubes is not so easy. On the other hand, the biggest value of irreversible capacity (1080 mAh/g) is related with an access of ions into the central canal.

Cyclic voltammetry gave well-defined rectangular curves between 1 V and 3 V *vs* Li, demonstrating the capacitance effect for all multi-walled nanotubes. Capacitance has been measured in capacitors made of two MWNT electrodes, and as it could be expected from the above remarks, the highest value (70 F/g) was detected for Si/Co700 [5].

## CONCLUSION

Multi-walled carbon nanotubes obtained by decomposition of hydrocarbons at low temperature are strongly mesoporous materials. They are able to sorb reversibly large amounts of lithium, but with a high polarisation between insertion and de-insertion due to capacitance processes in the mesopores. The charging of an electrical double layer with a possibility of pseudo-faradaic phenomena is especially facilitated by swelling mesopores. On the other hand, mesopores enable an easy access of the solvated lithium cations and the decomposition of solvent during the first discharge, which are at the origin of an important irreversible capacity. For all these reasons, it looks that carbon nanotubes could not have any application in Li-ion batteries. On the contrary, they are very promising as electrode materials of electrochemical capacitors.

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