

Electrochemical insertion of lithium in catalytic multi-walled carbon nanotubes

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Abstract

Electrochemical lithium insertion was studied into purified and heat-treated catalytic multi-walled carbon nanotubes. It appears that the irreversible capacity for the MWNTs is relatively large, but decreasing with annealing temperature. This clearly shows that the intrinsic entanglement and the microtexture of the nanotubes must be responsible for this drawback of any potential application as an anode. The crucial role of the charge cut-off on the «traditional» intercalation was underlined and the reversible capacity was assigned to particular Li sites by high resolution NMR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since the discovery of single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs), there has been a great interest for their diverse promising applications. Recently, Tans et al. [1] have reported the use of a single carbon nanotube for a field effect transistor working at room temperature. For carbon MWNTs, many studies involve their potential applications for the electrochemical storage of energy [2]. Specific capacitances of ~ 35 to 50 F/g were reported by two different groups on catalytically grown carbon nanotubes [3,4]. The fascinating 1D-type host lattice, defined by the central canal and the concentric graphitic layers, is very attractive for intercalation processes. It has been already proved that ~ 2 Li per C atom can be stored in catalytic MWNTs under a high pressure of 6 GPa [5]. These promising results have then prompted us to study Li electrochemical insertion into MWNTs. Preliminary results show that the Li insertion process did occur but at a much less extent and associated with large irreversible capacities [6].

Here, we report the influence of chemical and heat treatments on the electrochemical response of carbon MWNTs, prepared by catalytic route. The large polarization observed for purified MWNTs was examined by relaxation experiments. The different Li sites were analyzed by solid state ⁷Li nuclear magnetic resonance (NMR) spectroscopy and correlated to the specific capacities.

2. Experimental

2.1. Preparation of MWNTs

MWNTs were prepared via the catalytic decomposition of acetylene. The catalyst was composed of metallic cobalt supported on silica in the proportion of 10 wt.%. Its preparation is reported in Ref. [6]. A gaseous mixture of acetylene and nitrogen (10/90, v/v) was passed over the catalyst at 900°C during 2 h in a vertical tubular oven. The as-prepared sample was purified with a solution of hydrofluoric acid (72%) in order to remove silica. After filtration, the recovered solid was refluxed in 3 N nitric acid. After these chemical cleanings, elemental analysis and TEM showed that a part of cobalt (~ 1.5 wt.%) remained trapped in few carbon shells. The microtextural characterization of the carbon nanotubes was realized by high resolution transmission electron microscopy (Philips

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CM20). The material was dispersed in anhydrous alcohol and a droplet was put on a copper grid covered by a holed carbon film.

2.2. Electrochemical measurements

Composite electrodes were prepared from the carbon nanotubes as active material, carbon black and polyvinylidene fluoride as an organic binder. The powders in the weight proportion 85, 10, and 5, respectively, were mixed in acetone and the slurry was spread onto a nickel disk. Before loading the electrode materials into the glove box, they were heated at 120°C for 2 h in order to remove free water from the composite electrode. A solution EC + DEC (1:1 in vol.) containing 1 M LiPF₆ was used as electrolyte. Swagelok cells were assembled in an argon filled glove box. Electrodes had a surface area of 1 cm² and contained 5 to 8 mg of active material. A multichannel galvanostatic/potentiostatic system (Mac-Pile) was used for the electrochemical study. In the galvanostatic mode, a discharge cut-off voltage of -20 mV vs. Li was selected in order to take into account the lithium metal passivation. No Li metal plating was observed at this potential, in agreement with Ref. [7] showing that it occurs below -40 mV for an interface carbon/electrolyte. The current density corresponded to the insertion of one Li per 20 h per six carbon atoms.

Open circuit voltage experiments were carried out for the purified MWNT (before any heat treatment), consisting of current pulses. The charge transfer was 0.1 F per six carbon atoms, followed by relaxation periods under open circuit condition (GITT: galvanostatic intermittent titration technique).

2.3. ⁷Li NMR

The fully Li reacted MWNTs were examined by solid state ⁷Li NMR. The electrode materials, obtained after relaxation at the end of the first discharge, were dried overnight in the glove box without air exposure. Experiments were carried out on a Bruker 360 spectrometer (⁷Li resonance frequency of 139.9 MHz) with a magic angle spinning condition of 4 kHz, using a $\pi/2$ -acquisition sequence. Line shifts were referred to LiCl as an external standard. In order to avoid any paramagnetic effect due to the catalytic Co particles, all the experiments were performed on carbon MWNTs after heat treatment at $T > 1600^\circ\text{C}$.

3. Results and discussion

3.1. Description of the carbon MWNTs

The TEM images show that the as-prepared catalytic MWNTs, up to 10 μm in length, are sinuous and entan-

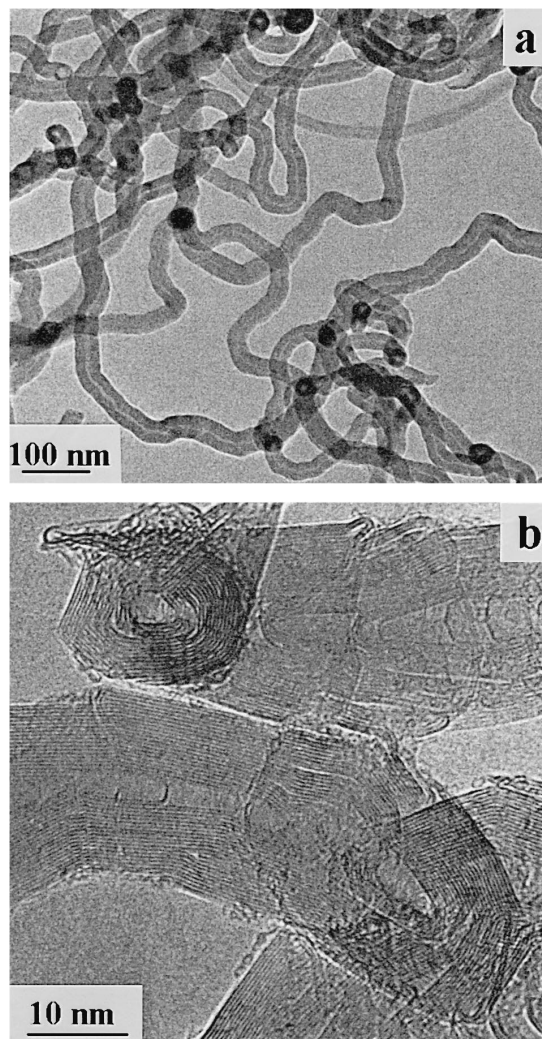


Fig. 1. TEM pictures of (a) as-prepared and (b) 2800°C carbon MWNTs.

gled (Fig. 1a). Their outer diameter ranges from 20 to 40 nm, and the hollow core from 4 to 6 nm. They are made of almost continuous aromatic layers, slightly wrinkled and tilted of about 30° with respect to the tube axis. Although the tips are opened, the core of the nanotubes is free of any cobalt particle. Heat treatment up to 2800°C closes most of the tubes and transforms the wrinkled carbon layers into stiff ones, however, with disinclinations due to the cumulation of defects at grain boundaries (Fig. 1b).

3.2. Electrochemical study

The electrochemical response of purified as received MWNTs and heat treated MWNTs (T-MWNTs) were studied in galvanostatic mode (Fig. 2). In all cases, the large irreversible capacities can be explained by the formation of the passivation layer on the tube surface and also in the cavities defined by the entangling situation of the tubes (Fig. 1). This irreversibility was partly cured by the heat

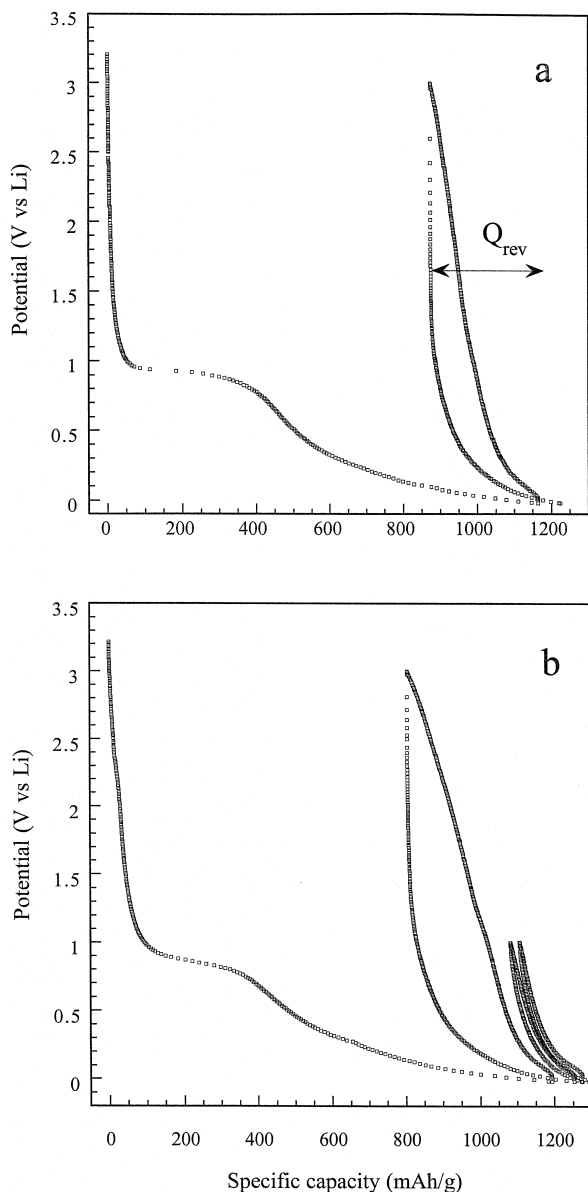


Fig. 2. Effect of the oxidative treatment on the electrochemical response of carbon MWNTs (a) after HF, (b) after HF + HNO₃. A current density of 30 mA/g was used. For (b) the charge cut-off voltage was changed from 3 V to 1 V vs. Li after the first charge.

treatment, as shown in Table 1. This is consistent with the decrease of surface area of the entangled MWNTs with the increase of heat treatment temperature [8]. This change in

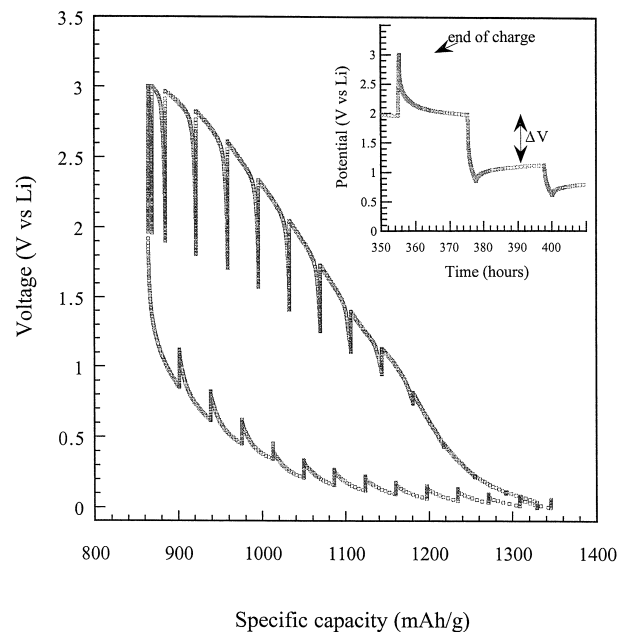


Fig. 3. GITT experiments on purified (by HF + HNO₃) as-received carbon MWNTs after the first discharge process. A charge transfer of 0.1 F per 6 C was used. The current density under constant current was of 15 mA/g. Relaxation time was 20 h. The inset shows the voltage drop vs. time at the end of the charge.

the irreversible capacity was also associated with a decrease of the reversible capacity, from 390 mA h/g for purified as-prepared MWNTs to 230 mA h/g for the 2800°C-MWNTs. By comparison to graphite, such values correspond to Li_{1.04}C₆ and Li_{0.62}C₆, respectively.

Besides the specific capacities considerations, the shape of the discharge–charge profile was found to be interesting to analyze. The effect of nitric acid treatment on the electrochemical response of MWNT was observed by comparing the voltage profiles (Fig. 2a and b). After HNO₃ treatment, the polarization (difference of potential between the first charge and the second discharge) was much higher than after HF treatment. This striking difference in hysteresis may be due to the surface oxygenated groups, generated by the oxidative chemical treatment, as already mentioned in Ref. [6]. For the totally purified (HF + HNO₃) carbon MWNTs, a quasi-linear potential response was obtained vs. the charge capacity in the 1–3 V vs. Li voltage domain. This effect cannot be attributed to a

Table 1

Evolution of the reversible and irreversible capacities for carbon MWNTs as a function of their chemical and heat treatment preparation

MWNT	HF	HF + HNO ₃	1800°C (10 h)	2000°C (15 h)	2400°C (15 h)	2800°C (15 h)
Q_{irr} (mA h/g)	870	800	515	580	460	370
Q_{rev} (mA h/g)	290	390	230	260	220	230

These capacities are obtained by galvanostatic studies with a current density of 30 mA/g in the voltage range 3.0 V to –20 mV vs. Li.

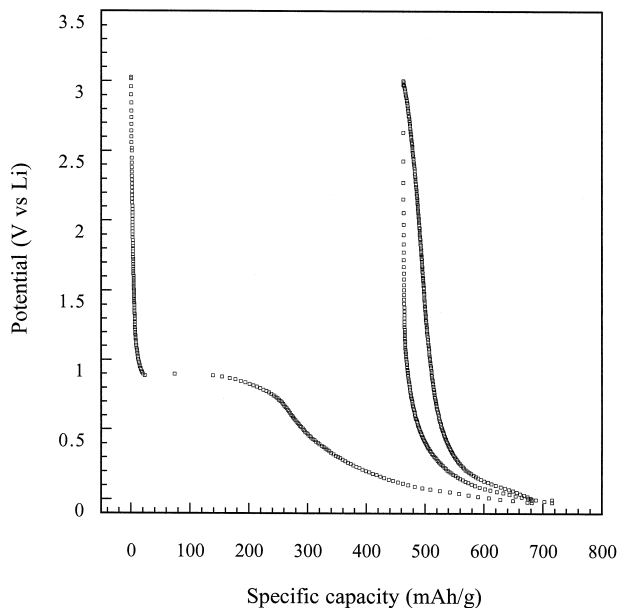


Fig. 4. Voltage profile for 2400°-MWNT. The same current density as in Fig. 2 was used.

capacitance type behavior, due to the lack of reversibility, and additionally, to the fact that the observed capacities

were different each other: the capacity in charge obtained between 1 and 3 V vs. Li corresponds to 228 mA h/g, whereas the capacitance behavior (~ 40 F/g) is 10 times less (< 20 mA h/g) [4].

With the change of the charge cut-off from 3 V to 1 V vs. Li, the hysteresis disappeared almost completely, showing that this faradic effect was due to surface-bonded lithium ions (Fig. 2b). A similar effect, observed for milled carbons was also explained by Li ions bonded to surface functional groups or to carbon radicals [9].

In order to emphasize the nature of trapped Li and to be more convinced of the presence of two different Li reaction mechanisms into the MWNTs, GITT experiments were carried out during the first charge and the second discharge (Fig. 3). Compared to the constant current experiments, this underlines the kinetic limitation of the Li ions extraction/insertion process, as exemplified on the inset for the end of the charge. The ΔV potential drop between the relaxation potentials revealed the resistive intrinsic nature of the electrode material and the highly irreversible Li extraction occurring at the end of the charge process. This suggests that the main part of the polarization is due to the microporous character of the carbon MWNTs, combined with the rich oxygen-containing surface functionality. At

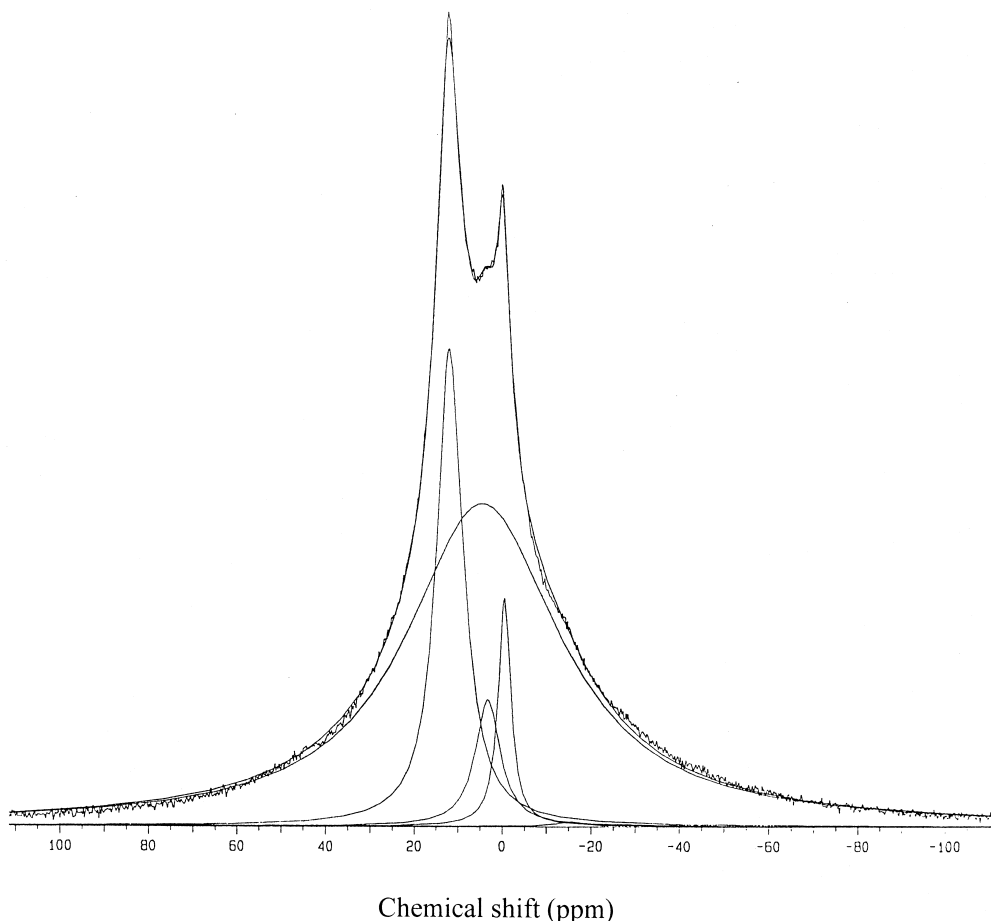


Fig. 5. High resolution ^7Li NMR spectra obtained on fully lithiated 2400°-MWNT (MAS at 4 kHz). The fitting by Lorentzian peaks is also presented. No quadrupolar splitting is observed.

Table 2

Comparison of the reversible capacity for some carbon-based materials with the downfield shift obtained in ^7Li NMR at room temperature

Samples and heat treatment	PAN 1000°C	PPP 700°C	MCMB 2400°C	MCF 550°C	Carbon MWNTs	
	Ref. [11]	Ref. [12]	Ref. [13]	Ref. [14]	2000°C	2400°C
δ Li (ppm)	14	9.2	30	20.9	13	12
Q_{rev} (mA h/g)	250	300	170	600	260	220

PAN = polyacrylonitrile.

PPP = polyparaphenylene.

MCMB = mesocarbon microbeads.

MCF = mesophase pitch-based carbon fibers.

2400°C surface functionality disappears as well as this polarization (Fig. 4).

3.3. Li NMR studies

High resolution ^7Li solid state NMR experiments were performed after full lithiation of high temperature treated MWNTs. The presence of metallic lithium was not observed. All the spectra were fitted with the same number of contributions (Fig. 5). The peak at ~ 0 ppm was associated to the presence of the lithium salt.

By reference with the well-known values for lithium graphite intercalation compounds [10], the peak at ~ 12 ppm was attributed to intercalated Li.

The proportion of this Li population ($\sim 20\%$ in the case of 2400°-MWNT) is quite consistent with the specific capacity obtained between -20 mV and 1 V vs. Li, allowing us to assume that the shift at ~ 12 ppm was due to the intercalated Li between the concentric carbon layers.

Li insertion into many different kinds of carbons has been studied by solid state NMR [11–14]. No general trend between the shift on Li NMR spectra (at room temperature) and the specific capacity can be obviously detected (Table 2). Large shifts, $\delta > 20$ ppm, are typically observed for fully inserted carbons, which present high specific capacity, but also for much smaller capacity as well. This suggests that the shifts are not directly related to the Li storage capacities, but have to be explained by the intrinsic organization of the carbon atoms in these materials. However, among the heat-treated MWNTs, a downfield shift was observed with the slight increase of the reversible capacity, as one may expect from the formation of a denser Li phase. From the fitting procedure, other Li sites were proved by a broad peak centered at ~ 4.5 ppm (width of 5.9 kHz) and another peak located at its gravity center (width of 950 Hz). These two contributions can be described by a «super-lorentzian» curve, which may be assigned to the presence of diffusive Li ions. At this point, the origin of this contribution is not well-understood. If one considers the total Li capacity, with the assumption that the reversible capacity is described by the shift at ~ 12 ppm, the other reactions have to be explained by the other Li population sites on the NMR spectra.

With an increase of the temperature, a change of the Li population was observed. The peak at $\delta = 12$ ppm was shifted to high field, and its proportion was decreasing to the profit of the «super-lorentzian» peak, indicating the diffusion of the inserted Li ions to another environment. The spin–lattice relaxation times T_1 vs. temperature were measured by inversion recovery pulses sequence. At a first glance, T_1 seems to follow the BPP (Bloembergen-Pound-Purcell) model. A detailed study will be presented elsewhere.

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