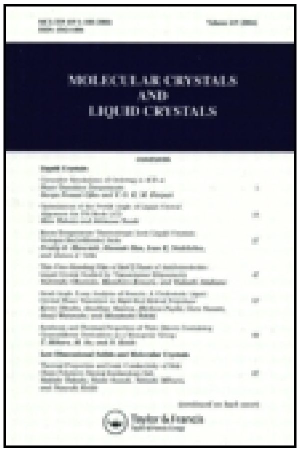

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Electrochemical Properties of Carbon Nanotube Fluorides in a Lithium Cell System

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Carbon nanotubes synthesized by decomposition of acetylene over silica-supported cobalt catalysts were fluorinated in different conditions : at room or high temperature, ca. 500 °C. The electrochemical behaviour of these carbon nanotube fluorides as electrode materials in a lithium cell was investigated using a liquid electrolyte. Results are compared to those obtained with graphite fluoride compounds which present a well known high electrochemical performance.

Keywords: nanotubes; fluorides; electrochemical properties; lithium batteries.

INTRODUCTION

Because of their interesting electrochemical properties, carbon fluorides have been intensively studied as cathode materials in high energy densities lithium batteries[1]. Their discharge performance was investigated using a large variety of carbons of different crystallinity such as natural and artificial graphite, petroleum coke, amorphous carbon black and active carbon[2]. The increase in the crystallinity decreases the discharge potentials but increases the capacity and energy density. Moreover, the higher the fluorine content x in $(CF_x)_n$ and the lower the preparation temperature, the higher the capacity and the discharge potentials are. Fluorination of new cristallographic variety of carbon such as fullerenes has also attracted much attention as a means of obtaining compounds with better electrochemical properties than graphite fluorides[1]. Unfortunately, electrochemical behaviour strongly depends on the composition of the fluorinated compounds and their reactivity with the electrolyte.

Firstly obtained as a by-product of fullerenes formation by an arc-discharge between two graphite rods, carbon nanotubes (CNT) have prompted considerable interest in their mechanical, electronic and magnetic properties[3]. In a previous work[4], we studied the optimization of the decomposition of acetylene over silica-supported cobalt catalyst for the production of CNT. The reactivity of these CNT towards fluorine at room and high temperatures yielding carbon-fluorine compounds was also investigated. This paper deals with the results we obtained from testing these compounds as cathode materials in lithium batteries.

EXPERIMENTAL

The starting materials were carbon nanotubes treated with concentrated hydrofluoric acid and diluted nitric acid in order to eliminate the silica substrate and most of the remaining cobalt catalyst, respectively. Some simple graphitization at 2800°C has also been performed. Fluorinated graphitized or none graphitized nanotube, FCNT, $(CF_x)_n$ prepared at room (RT) or high temperatures (HT) were used for electrochemical studies. High temperature fluorination was carried out under pure F_2 gas atmosphere, while a gasous mixture of F_2, HF, and IF_5 was used for room temperature fluorination[4].
The experimental electrochemical cell is represented as follows :

(-) Li / 1M $LiClO_4$ - P.C. liquid electrolyte / FCNT (+)

The negative electrode was made of a lithium disk, 0.5 mm thick and 10 mm in diameter. The liquid electrolyte was a 1M anhydrous solution of $LiClO_4$ in propylene carbonate (P.C.) and the cells were operated at room temperature. The positive electrode pellet was formed from a pressed composite mixture of active material and 10 wt.% $P(EO)_8LiClO_4$ acting as an ionically conductive binder (PEO = polyethylene oxide). Stainless-steel disks were used as current collectors. All the elements were set-up in tight pyrex-glass systems. Electrochemical studies were performed by means of a galvanostatic discharge and a slow scan cyclovoltammetry modes.

RESULTS AND DISCUSSION

Figure 1 shows the galvanostatic discharge curves of fluorinated samples FCNT prepared either at room temperature (Fig.1a and b) or at high temperature (Fig.1c and d). It appears that the discharge capacity and potential (≈ 3 V) are strongly related to the F/C ratio and to the high reactivity (RT) FCNT samples, respectively. This latter results from the semi-ionic C-F bond character[1,4].

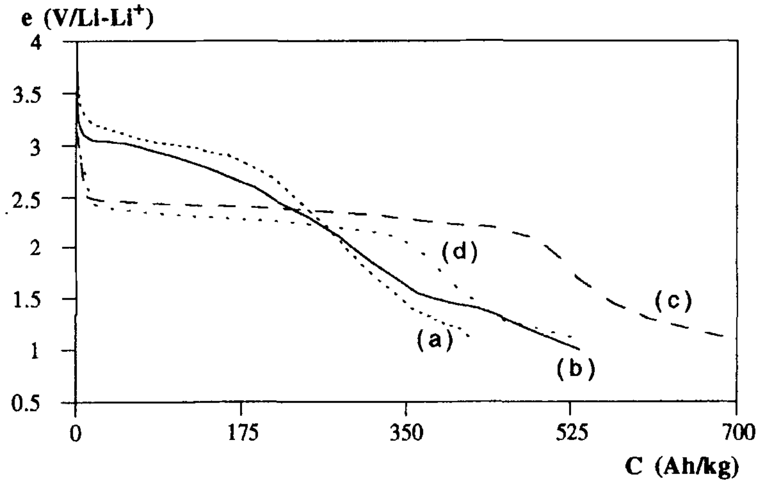

FIGURE. 1 : Galvanostatic discharge of Li / 1M $LiClO_4$-P.C. / FCNT cells under 0.1mA cm^{-2}. FCNT, fluorinated carbon nanotube, CF_x : (RT)$CF_{0.22}$ (a); (RT)$CF_{0.37}$ (b) ; (HT)CF_x prepared at 480 °C (c) and 508 °C (d).

It is important to note that graphitized CNT readily react with fluorine producing (RT)$CF_{0.37}$ with a higher fluorine content than the none graphitized one (RT)$CF_{0.22}$. The observed high electrochemical performance of (RT) $CF_{0.37}$ (500 $Ah.kg^{-1}$, Fig.1b) is probably due to the perfect arrangement of the layers in graphitized CNT which leads to better lithium ionic diffusion. Moreover, FCNT, (RT)CF$_x$ do not exhibit a constant discharge potential as graphite fluorides compounds do. This behaviour could be related to the concentric form of the sheets in CNT fluorides. In contrast, (HT) FCNT, in which the C-F bond has a covalent character, show discharge potential at ca. 2.4 V and a greater faradaic capacity of 620 Ah.kg^{-1} (fluorinated sample at 480°C, Fig.1c) owing to their higher fluorine content. However, sample fluorinated at 508°C gives a faradaic capacity of 520 Ah.kg^{-1} and discharge potential at 2.3 V (Fig.1d). This may be due to more disordered and distorted concentric layers under fluorination above 500°C.

Cyclic voltammetric experiments have also been performed. Figure 2 displays a typical voltammogram of a graphitized CNT.

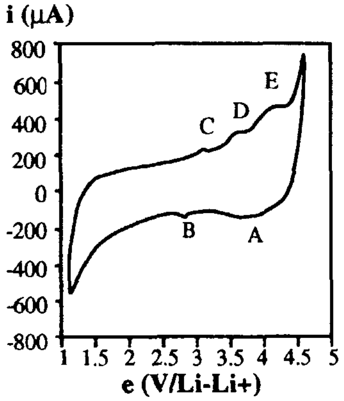

FIGURE 2 : Cyclic voltammogram of pure CNT (6 mV/min).

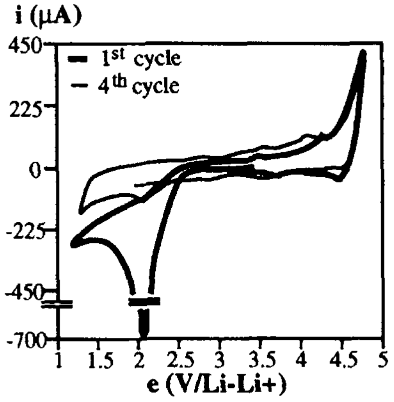

FIGURE 3 : Cyclic voltammogram of (508°C)(HT) FCNT (6 mV/min).

On an initial scan to reduce the material (not shown), one cathodic peak potential is observed at 2.86 V/Li-Li$^+$. In the oxidation process, three anodic peak potentials are detected at 3.12, 3.68 and 4.12 V/Li-Li$^+$. The second reduction presents two peaks at 3.7 and 2.86 V and no more changes are observed upon continuous cycling. These interesting results should be compared to those of C$_{60}$ in which some reduction-oxidation peaks were obtained between 1.5 and 2.5 V[5]. Although the intensity of the peaks is low, it could be assumed that lithium intercalation-deintercalation phenomena reversibly occur. Compared to this voltammogram, a complete reduction / oxidation cycle of (HT) FCNT is given on Fig.3. The intensity of the reduction peak at 2.12 V, decreases on cycling until most of the material is reduced (scan rate is too high in regards to the active material mass). Only two anodic peaks at 3.52 and 4.28 V are observed on first oxidation process. Then, two reduction peaks appear at 4.46 and 3.74 V. The peaks evolve until the voltammogram is composed of three reduction (4.46, 3.5 and 2.87 V) and three oxidation peaks (2.80, 3.57 and 4.08 V) on the 4th cycle. It is important to note that features observed on the last cycle are quite similar to those seen on the pure CNT voltammogram (Fig.2). The cyclic voltammogram of the (RT) FCNT is very similar to that exhibited by (HT) FCNT, except the main reduction peak which is situated at 2.90 V instead of 2.12 V. These results are in good agreement with previous intensiostatic discharge curves of Fig.1.

Starting from either fluorinated or pure CNT, IR spectra of the resulting materials after discharge-charge cycles, are nearly identical (Fig.4).

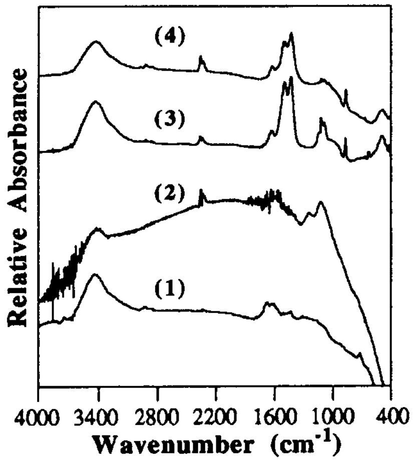

FIGURE 4 : I.R. spectra of : CNT (1); (RT)$CF_{0.22}$ (2); CNT and (RT) FCNT, $CF_{0.22}$, after charge-discharge (3) and (4), respectively.

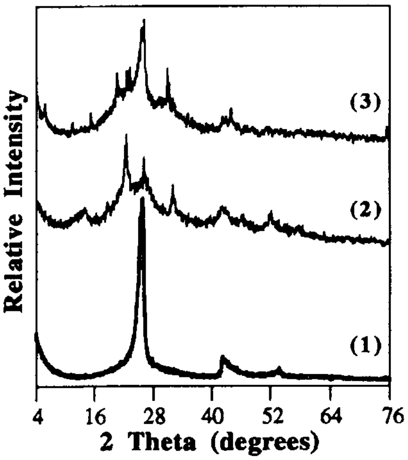

FIGURE 5 : XRD patterns of Graphitized CNT(1); (RT) FCNT, $CF_{0.22}$ (2); and resulting sample of the charge-discharge cycle (3).

These data confirm the electrochemical study, since we have observed high similarities between the last voltammetric cycle of (HT) FCNT and that of pure

CNT. The $\nu_{C\text{-}O}$ stretching vibrations are detected in the 1150 - 1050 cm^{-1} region. The electrolytic medium could be responsible of such an oxidation phenomenon. Consequently, the very intense band at 1441 cm^{-1} should correspond to C=C bond. A similar shift for C=C stretching vibration has also been reported for fullerenes materials[6]. The weaker band at 1636 cm^{-1}, which is generally attributed to aromatic C=C bond, as observed in graphite, remains unchanged. Therefore, the presence of a new phase is strongly suspected.

X-ray diffraction patterns of charge-discharge resulting samples are very similar whatever the starting materials (CNT or FCNT). Because of the broadeness of the peak, the 002 graphitic material reflection is not clearly observed (Fig.5). However, some additional reflections (001 sequence of $I_c = 15.20$ Å) appear which could correspond to an intercalation phase.

In conclusion, the electrochemical properties of fluorinated carbon nanotubes strongly depend on the nature of the carbon-fluorine interaction. Good discharge capacities and discharge potentials are obtained for fluorinated compounds prepared at room or high temperature. Indeed, fluorination at room temperature gives low fluorine content but the ordered concentric layers favour the lithium diffusion. At present this interesting behaviour has not been fully investigated but it seems that electrochemical properties of carbon nanotubes are quite different from those of graphite. Further works, including "in situ" DRX study and TEM images of the compounds obtained during the charge-discharge process, would be helpful to understand the complex cathodic reaction.

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