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Single walled carbon nanotubes for enhanced performance of Li-ion batteries

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ABSTRACT In the best of our knowledge, Li-ion batteries are still encountering some problems such as formation of dendrites due to the accumulation of the Li atoms in the graphite until forming a bridge between the anode and cathode then that causes short circuits .This situation has prompted us to think about finding alternatives to the anodic side of the battery, thus, this work is devoted to the use of single walled carbon nanotubes having a diameter of about 1.75 nm in the batteries of lithium ion in order to increase their performance. As the carbon nanotube was used as an anode to receive more lithium and the performance of this anode were compared to the graphite, it has been found that in fact the carbon nanotube allows a longer life cycle of the battery and avoids many problems during its use.

Keywords: Li-ion batteries; single walled carbon nanotubes; life cycle; anode.

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1. INTRODUCTION

Due to advances in technology and the rapid evolution of mobile systems, many habits are changing; this new trend is creating a strong demand for power supply that needs to be the most efficient in terms of reliability, charging time or discharge and especially occupied area. In accordance to all these stated points, the lithium battery appears as the most suitable solution. The lithium ion battery operates on the reversible exchange of the lithium ion between a positive electrode, usually and a graphite as a negative electrode, the use of an aprotic electrolyte is mandatory to avoid degrade the highly reactive electrodes [1-3].

A lithium-ion battery is a system consisting of two electrodes separated by an electrolyte. Its operating principle is based on the conversion of chemical energy into electrical energy [4, 5] through two oxidation-reduction reactions taking place at the negative and positive electrodes respectively [6]. The operation of a Li-ion battery is shown in Figure 1.

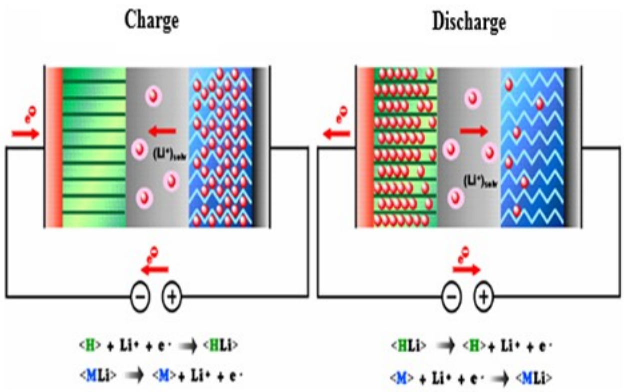

Fig. 1. Schematic representation of Li-ion battery.

The positive electrode material must meet a number of criteria [7], namely:

- Good ionic conductivity for good diffusion of Li+ ions from the surface to the material;
- Good electronic conductivity;
- A high volume capacity;
- A sufficiently high standard potential compared to that of the negative electrode to obtain a difference of potential suitable for the intended application;
-Good chemical stability with respect to the electrolyte;
-Good reversibility of the insertion reaction;

The negative electrode materials must meet also several criteria such as:
-A good ionic conductivity permitting the diffusion of Li+ ions from the surface towards the inside of the material,
-A good electronic conductivity,
-A high mass and volume capacity,
-A good chemical stability with respect to the electrolyte,
-A high standard potential compared to that of the Li / Li+ redox couple,
- Good reversibility (structural stability).

Graphite is one of the natural allotropic forms of carbon. It is used like positive electrode materials [8], whose applications are in lithium batteries [9, 10]. The crystalline structure consists of a stack of graphene layers [11, 12]. The material is anisotropic. Graphite is classified according to the production method either as natural graphite or artificial graphite. The inter-planar distance of the graphite is 0.335 nm and the reversible capacity is about 360 mAh/g. When intercalating lithium ion, the volume increase is about 10% [12].

Carbon nanotubes may have a structure close to graphite [13, 14], their intrinsic properties are very different and sometimes more interesting [15-18]. Their mechanical strength and electrical conductivity are generally emphasized but their chemical reactivity, their adsorption properties or their thermal conductivity are also interesting for several potential applications. The basis of the extraordinary mechanical properties of nanotubes comes from their structure composed only of covalent C-C bonds hybridized sp2 (one of the strongest and most stable of nature). These synthetic structures have Young's module (of the order of 1 TPa for the SWCNTs [19]. As for their tensile strength, it is also exceptional (between 30 and 150 GPa). Finally, they have the ability to deform elastically over a very wide range of pressures and stresses [20]. All these properties make these materials excellent candidates for the development of new batteries. Because of their many remarkable properties, research is conducted to develop and optimize nanotubes applications for carbon. We will briefly introduce some of them. The excellent mechanical properties of nanotubes as well as their low density make these materials SWCNTs of excellent performance [21]. The researchers verified that such an anode, much lighter than a graphite anode, can accommodate 10 times more lithium during recharging! And, the big surprise was to realize that carbon nanotubes prevent dendrites from forming when as much lithium is deposited on the anode. Short circuits occur in this type of batteries due to dendrodates growing between the electrodes. Moreover, the repetition of these micro short circuits contributes to a rapid discharge of the cell. Thus, the Li-ion cell will last forever.

Indeed, these dendrites are lithium growths that grow on the anode and eventually destroy the battery, bridging with the other electrode (the cathode), resulting in a short circuit. The battery can then catch fire or even explode, depending on the chemistry of its constituents.

Since the life of the batteries is an essential element for defining it performance, our concern is to protect the batteries of all potential damages which might extend their life. Thus, the purpose of our study is focused on utilizing single walled carbon nanotubes as anode of Li-ion battery to replace the usual conductive agents such as carbon black and graphite.

2. EXPERIMENTAL

2.1. Synthesis of SWCNT

There are many methods of synthesis of CNTs that can be classified into two major categories. They are distinguished from each other by the involved level of the temperatures. There are methods known as "high temperature" such as laser ablation and electric arc, also we can find methods related to “medium temperature" (CVD (or CCVD for "Catalytic Chemical Vapor Deposition). Nevertheless, in this section we will briefly introduce and insist on the specificities and the potentialities of the process used during this work namely laser ablation.

"High temperature" techniques are based on the condensation of carbon atoms generated by the evaporation of a carbon source in solid form (graphite). This reaction is carried out in a chamber in which there is a strong temperature gradient and a partial pressure of an inert gas such as helium or argon. The involved temperatures are of the order of 3000-4000 ° C or more and are close to the sublimation temperature of the graphite. The various techniques using this principle are distinguished by the process of vaporization of the graphite involved. Laser ablation technique consists of ablating a graphite target with pulsed or continuous laser radiation of high energy (of the order of MW / cm 2 and beyond, it is that is enough to ablate a target). This process, certainly more expensive than the previous one, produces CNTs with a very good yield because between 70 and 90% of the starting graphite mass is converted into nanotubes. Previous studies [22, 23] have shown that CNTs produced by these techniques have a high degree of crystallinity.

2.2. Scanning electron microscopy of SWCNT

The scanning electron microscope (FEI model JEOL JSM-7600TFE) is used in experiments for the analysis of the morphology of the obtained carbon nanotubes. The SEM allows the high-resolution magnification of images, from 10X to 300000X, with a typical resolution of about 5 nm. An acceleration voltage of 15 kV was used. The carbon nanotubes have been isolated to allow visualization of their size by SEM observations.

2.3. Capacity measurement

The capacity measurements were done via voltage cycling using a coin cell cycler (Arbin) with environment chamber

(CSZ). Each channel of cycler operates independently and runs Galvanostatic Cycling and Cyclic Voltammetry tests on batteries at the same time. In order to ensure the cells are cycled under a specified temperature, cells are put into the environment chamber in which the temperature can be controlled at 25 degrees. The capacity test is designed to measure the maximum capacity (or charge) that cell can supply between two predefined voltage limits, and the voltage limits are depending on the materials of anodes or cathodes.

The used SWCNTs within battery's anode can ensure the Li-ion battery having the best cycle performance. It's to be noted that the determination of the performance includes measuring the capacity. A battery test consists of measuring the charge-discharge cycling between fixed voltage limits with constant current I:

$$Q_c = I * t_c \quad (1)$$
$$Q_d = I * t_d \quad (2)$$
$$CE = Q_c/Q_d \quad (3)$$

Note that CE is expressed by the ratio of charge out and charge in, and CE=1 means that Li-ion battery will last forever.

3. RESULTS

3.1. SEM micrographs

Figure 2 shows an SEM of SWCNTs produced by laser vaporization of a graphite target.it is obvious that the diameters of the SWCNTs are different for the three analyzed samples, these carbon nanotubes have the same magnification (x50 000 times).the smaller diameter is about 0.4 nm , the second analyzed specimen is of average diameter of 0.9 nm, the greater one was found to be about 1.75 nm.

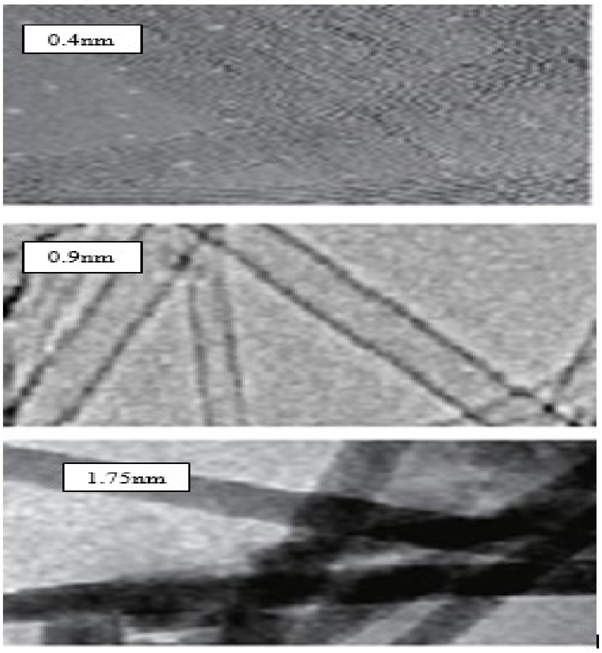

Fig. 2. Scanning electron microscopy of isolated single walled carbon nanotubes (magnified 50 000 times).

3.2. Cycling tests

Figure 3 is showing SWCNT anode capacity versus cycling number. The calculated capacity based on the charge and discharge times showed excellent reversibility after the initial cycle. SWCNT anodes had a Li capacity over 1200 mAh/g after 60 charge-discharge cycles for diameter of 1.75nm. However, for anodes based on SWCNT with diameter of 0.9nm the capacity is reduced to below 400 mAh/g for the same number of charge discharge cycles. Thus, the diameter size of the SWCNT is one of the main factors that optimize Li capacity.

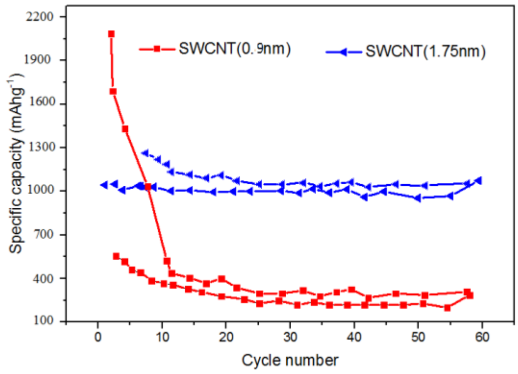

Fig. 3. capacity versus cycle number of CNT-based anode Li-ion battery.

4. CONCLUSION

As Lithium ion batteries are attracting much considerable attention in many applications , ranging from portable electronics to electric vehicles, due to their electrical and mechanical properties .Within this study we have used the SWCNTS as positive electrode of the Li-ion battery in order to improve the capacity and the cycle life .The measured reversible lithium ion capacities for CNT-based anode exceeded 1200 mAh with diameter of 1.75 only this means that for higher nanotubes diameters, the capacity will be more improved and can exceed the conventional graphite anodes .

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