



Short communication

Preparation and application of bamboo-like carbon nanotubes in lithium ion batteries

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ABSTRACT

CNTs with bamboo-like structure (B-CNTs) has been prepared via a CVD process with novel carbon precursor. The potential application of B-CNTs as electric conductive additive and anode materials for lithium ion batteries was explored. The EIS spectra prove that it is better electric conductive additive than multiwalled CNTs and traditional carbon black (CB). The electric resistance of the electrode is decreased around $20\ \Omega$ when B-CNTs is used instead of CB. The cycle stability is also enhanced. However, the test cell with B-CNTs as anode material shows low reversible capacity of $135\ \text{mAh g}^{-1}$ and very low initial cycle efficiency of 17.3%, which indicates that so-prepared B-CNTs is not suitable for anode material.

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1. Introduction

Carbon nanotubes (CNTs) has been suggested as a substitute for the graphite anode in lithium ion batteries for their unique one-dimensional structure, large surface area and high electric conductivity [1]. Compared with the theoretic capacity of graphite (LiC_6), experiments found much higher Li capacity ($\text{Li}_{1.6}\text{C}_6$) in single-walled CNTs (SWCNTs) [2], $640\ \text{mAh g}^{-1}$ in slightly graphitized multiwalled CNTs (MWCNTs) and $280\ \text{mAh g}^{-1}$ in graphitized MWCNTs [3]. First principle calculation was used to model the intercalation of lithium ion. Zhao et al. [4] indicated that the inside of the tube was as favorable as interstitial sites for intercalation. It was also considered [4] that the intercalation potential of Li/SWCNT was comparable to the formation energy of bulk Li and independent of Li density up to about $\text{Li}_{0.5}\text{C}$. Furthermore, MWCNTs as electric conductive additive of cathode electrode has been investigated [5,11]. Electric conductive properties of electrode can be greatly improved because of the formation of three-dimensional electric conductive network by MWCNTs.

Recently, bamboo-like CNTs (B-CNTs) has been synthesized and investigated. B-CNTs synthesized by microwave-plasma enhanced chemical vapor deposition [6] displayed high reversible Li-storage capacity of $460\ \text{mAh g}^{-1}$ and stable cyclic capability. B-CNTs synthesized by solid state method [7] showed a faster electron transfer rate

in KCl solution as compared with commercial MWCNTs and glassy carbon electrodes, by which we can presume that B-CNTs could be good electric conductive additive for lithium ion batteries.

Herein we prepared B-CNTs via a simple CVD method with a novel carbon precursor. The application of so-prepared B-CNTs as electric conductive additive and anode material in lithium ion batteries was investigated.

2. Experimental/Materials and methods

2.1. Material preparation

The experimental setup and procedure are similar to that described in our previous report about FeNi-filled CNTs [8], but we use cresol rather than $\text{C}_6\text{H}_{6-x}\text{Cl}_x$ ($x=0-3$) as carbon precursor. Ferrocene powders were dissolved in 10 ml cresol to form a solution with concentration of $0.06\ \text{g ml}^{-1}$, and fed into CVD furnace by a syringe pump at a constant rate of $0.12\ \text{ml min}^{-1}$ for 30 min. A mixture of Ar and H_2 was flowing through the system at 2000 sccm and 300 sccm, respectively. A quartz slide was placed in the middle of furnace to collect CNTs for characterization at a reaction temperature of $860\ ^\circ\text{C}$. The as-received sample was heated in air to remove the amorphous carbon coating on the catalyst metal particles, and then it was purified in dilute HCl solution to remove the catalyst. After that, it was dispersed in an aqueous solution of H_2O_2 (30 wt.%) for 1 h in an ultrasonic bath at room-temperature and then dried. MWCNTs was also used (Prof. F. Wei, Department of Chemistry, Tsinghua University, China) for comparison.

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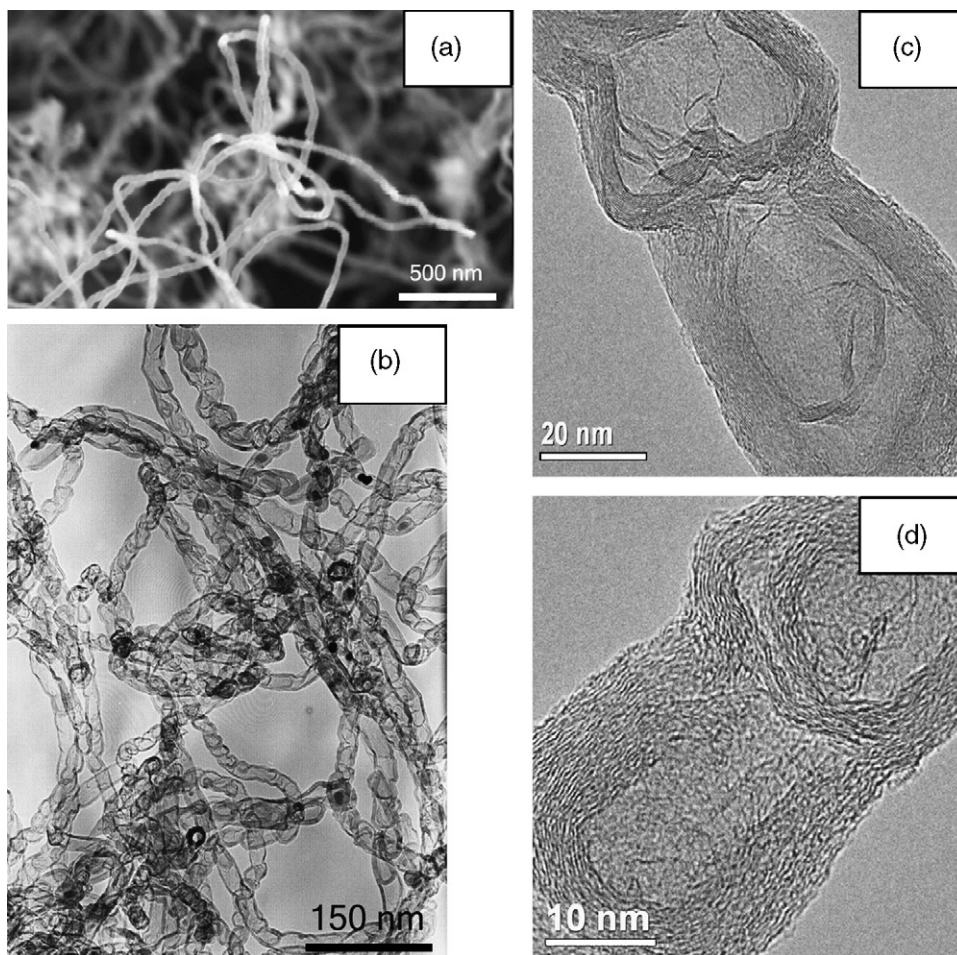


Fig. 1. (a) SEM image of B-CNTs; (b) TEM image of B-CNTs; (c) and (d) HRTEM images of B-CNTs.

2.2. Electrochemical testing

The working electrode was prepared by casting the following slurry dissolved in *N*-methylpyrrolidone (NMP) on a copper foil.

- (1) B-CNTs or MWCNTs or carbon black (CB) (5 wt.%), natural flake graphite (85 wt.%, Chenzhou, China) and polyvinylidene fluoride (PVDF) (10 wt.%).
- (2) B-CNTs or MWCNTs (90 wt.%) and PVDF (10 wt.%).

The foil was then dried at 80 °C for 8 h and later dried in vacuum at 120 °C for 12 h. Lithium foil was used as the counter electrode and 1 M LiPF₆ dissolved in a mixture of ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1 in volume) as the electrolyte. The working and the counter electrodes were separated with Celgard 2400 separator. The cell was galvanostatically cycled between 0 V and 2.00 V versus Li/Li⁺ at 0.2 C rate.

3. Results and discussion

3.1. Morphology and structure of B-CNTs

The morphology and microstructure of B-CNTs was determined by SEM, TEM and HRTEM. Fig. 1 shows the SEM, TEM and HRTEM images of B-CNTs. One can see the diameter of B-CNTs is about 20–30 nm. Unlike the common CNTs with an integrated hollow cylindrical structure, the inner of B-CNTs is divided by bending graphite-like sheets and form many separated cavities, very sim-

ilar with bamboo structure. It also can be considered as strings of short MWCNTs linked end by end.

3.2. B-CNTs as electric conductive additive

The electrode with electric conductive additive added was prepared as slurry 1. Fig. 2 shows the cycle performance of natural

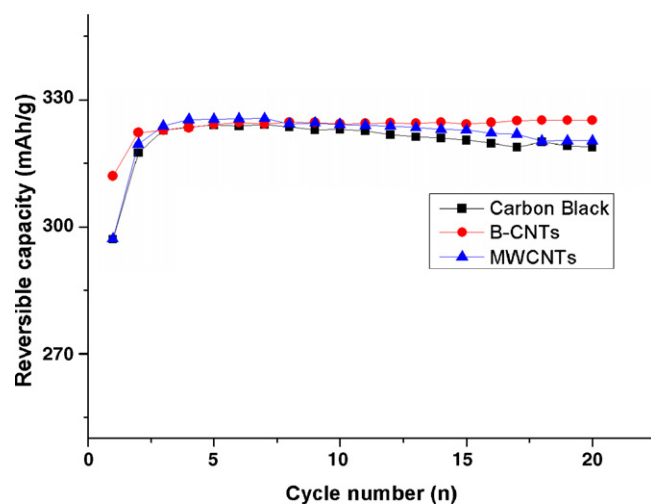


Fig. 2. Cycle performance of natural flake graphite as anode material with carbon black or B-CNTs added as electric conductive additive.

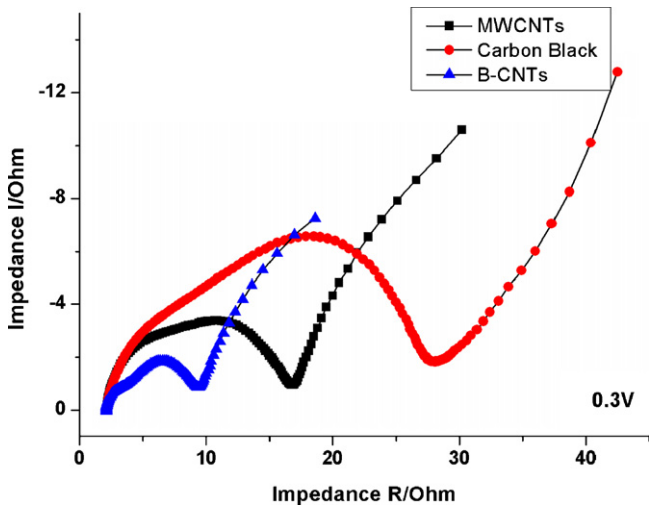


Fig. 3. ac impedance spectra of natural flake graphite anode with B-CNTs, MWCNTs or CB as electric conductive additive at 0.3 V.

flake graphite anode with CB, MWCNTs or B-CNTs added. Different additives did not lead to notable difference in first cycle efficiency or reversible capacity. The first cycle efficiency of these samples is around 85% and the reversible capacity is nearly the same before 8th cycle. However, anode with B-CNTs added exhibits better cycle sta-

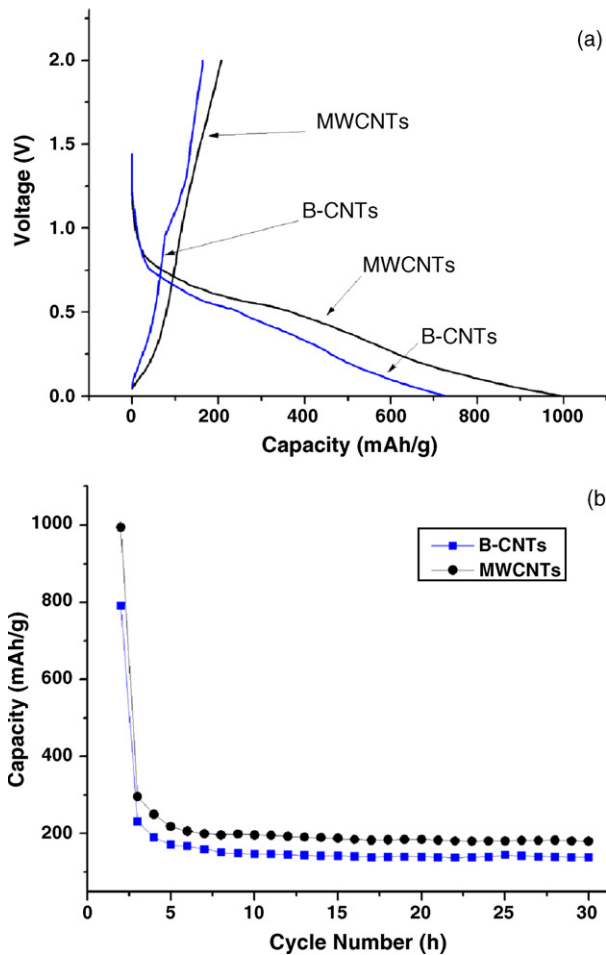


Fig. 4. (a) Initial cycle performance of MWCNTs and B-CNT as anode materials and (b) cycle performance of MWCNTs and B-CNTs.

bility than the others. The capacity of anode with CB added begins to decrease slightly from the 9th cycle. The other one with MWCNTs added shows similar properties. However, the third one with B-CNTs added keeps 100% capacity after 20 cycles.

Fig. 3 displays ac impedance spectra of natural flake graphite anode with CB, MWCNTs or B-CNTs added. According to previous work [9], the high frequency semicircle in the spectra is summarized to be the SEI film and contact resistance. The mid-frequency semicircle is considered as the charge-transfer impedance on electrode/electrolyte interface. The spectra show that the resistance is greatly decreased when CNTs is used instead of CB. The incline, which indicates the lithium-diffusion process within carbon electrode, is not notably affected by different additive. The inflexion point of the incline and the semicircle is believed to be the total electric resistance of the electrode materials, electrolyte resistance and electric leads [10]. It is very clear that the electric resistance of electrode with B-CNTs added is much smaller than electrode with CB or MWCNTs added. The electric resistance of electrode is 9.3, 17.1 and 28.0Ω when B-CNTs, CB or MWCNTs is added, respectively. We also investigated series EIS spectra at different open circle voltage. The data scanned from 0.1 V to 1.2 V with a step of 0.1 V are coincident. These observed effects could be attributed to two factors. The first one, B-CNTs has high electron transfer kinetic due to oxygen functional groups [7] and edge-plane-like sites. In the HRTEM image of B-CNTs, many exposures of edge-plane-like sites can be observed along the tube. We consider that the electrolyte may be easier to get into the cavities of B-CNTs than CNTs with integrated hollow cylindrical structure, so the charge-transfer kinetics could be enhanced. The second, it is well agreed with the previous work [5,11], which has been confirmed that the CNTs can form three-dimensional electric conductive network and the electric conductive property can be greatly increased.

3.3. B-CNTs as anode material

Fig. 4 displays the electrochemical performance of B-CNTs and MWCNTs (slurry 2) as anode materials. As shown in Fig. 4a, B-CNTs shows capacity of 710 mAh g^{-1} at the first charge process, which is less than that of MWCNTs. Both of them show very low initial cycle efficiency. The initial cycle efficiency of B-CNTs is 17.3% and MWCNTs is 17.6%. Fig. 4b displays the cycle properties of B-CNTs and MWCNTs. The reversible capacity of B-CNTs at 10th cycle is 131 mAh g^{-1} while MWCNTs is 200 mAh g^{-1} . Both of them show

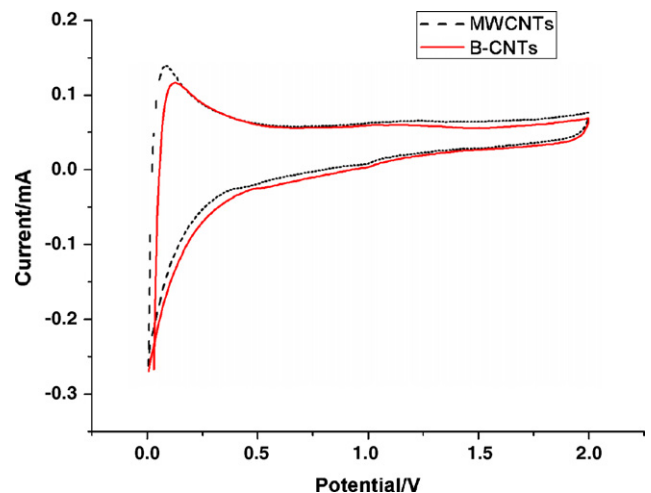


Fig. 5. Cyclic voltammetry measurement of B-CNTs and MWCNTs at 0.1 mVs^{-1} of 10th cycle.

good cycle stability. The notable difference in reversible capacity may be explained that the separated cavities in B-CNTs could offer lithium ion storage spaces [6] as the integrated hollow cylindrical structure in MWCNTs, but the inner bending graphite sheets make the transfer process of lithium ion more difficult. Furthermore, there is no plateau in the charge/discharge curves of B-CNTs (Fig. 4a). Similar profile is shown by MWCNTs. It demonstrates that though the inner B-CNTs possesses notable graphite-like structure, graphite intercalation compounds (GICs) mechanism is not the key mechanism of lithium storage in B-CNTs. It also confirmed by cyclic voltammetry (CV) measurement. Fig. 5 shows the CV curves of MWCNTs and B-CNTs. They are very similar. No evident peak corresponding to Li-GICs reaction could be observed in the CV curves, which is well agreed with the charge/discharge curves.

4. Conclusion

B-CNTs has been prepared via CVD process. The potential application of B-CNTs as electric conductive additive and anode materials for lithium ion batteries was explored. B-CNTs shows low reversible capacity of 135 mAh g^{-1} and very low initial cycle efficiency of 17.3%, which indicates that B-CNTs is not suitable for anode material in lithium ion batteries. However, the EIS spectra prove that B-CNTs is better electric conductive additive than MWCNTs and

traditional CB. The electric resistance of the electrode is decreased around 20Ω when B-CNTs is used instead of CB. The cycle stability is also enhanced. B-CNTs is promising electric conductive additive in electrode for lithium ion batteries.

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