

EFFECT OF CARBON NANOTUBES ADDITION ON THE ANODE PERFORMANCES OF FLAKE GRAPHITE FOR LITHIUM-ION BATTERY

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Abstract

A comparative investigation was carried out on carbon black and multiwalled carbon nanotubes as conductive additives in spherical natural flake graphite as an anode material for rechargeable lithium-ion batteries. Scanning electron microscopy images showed that carbon nanotubes interlaced graphite powders in series to form a three-dimensional network structure. The constant current charge-discharge experiment showed that carbon nanotubes were more effective to improve reversible capacity and cycle stability. The discharge capacity was improved to be 384 mAh/g in the first cycle. The cycle stability was improved 47.5% compared with the bare sample. The research is of potential interest to the application of carbon nanotubes as a conductive additive in anode materials for high-power lithium-ion battery.

Keywords: carbon nanotubes; electrochemistry; anode; lithium ion battery

Introduction

In the field of lithium ion battery, electrode materials are undergoing extensive and innovative developments. But these researches are focused on the lattice doping and surface coating on the electrode-active particles [1, 2]. However, the conducting network throughout the electrode materials is rarely investigated. As the traditional conductor, carbon black is used to fill the interspace among particles and plays an important role in the performances of the composite electrode as a whole. In fact, the content and microstructure of carbon conductor affected a lot the utilization of active materials and energy density of electrode [3].

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As a new carbon conductor, carbon nanotubes are superior to amorphous carbon black in many ways, such as high conductivity, tubular shape and layered structure. Yang et al. reported that electron conductivity of multiwalled carbon nanotubes (MWCNTs) thin film was around $(1-4) \times 10^2$ S/cm along the nanotube axis and (5-25) S/cm perpendicular to the axis, respectively [4, 5]. The conducting connections will be improved when MWCNTs are used in the anode preparation. Here we report the novel composite anode of natural flake graphite with MWCNTs in order to improve electronic connecting network and energy density of anode materials.

Experimental

Natural spherical flake graphite powders were provided from Hengyuan Tianzhuang Graphite Company (Shandong Province, China). MWCNTs were prepared by hydrogen arc discharge method in normal atmosphere at room temperature. MWCNTs were soaked in nitric acid at 80 °C for 10 h and then washed by distilled water until pH value of the filtrate reached 7.0. Prior to measurements and cathode preparation, carbon black and MWCNTs were heated at 150 °C for 12 h under vacuum to remove surface-adsorbed species, such as H₂O and hydrocarbons.

Raman spectra data of carbon black and MWCNTs were collected at room temperature using Jobin-Yvon, ISA T6400 Raman spectrometer. The morphologies of the composite materials were observed by scanning electron microscopy (SEM) using JSM-6460 LV. Microstructure of carbon black and MWCNTs was analyzed by high-resolution transmission electron microscopy (HRTEM) using JEM-2010F. Specific surface area were measured by the Brunauer, Emmett and Teller method using nitrogen gas and automatic specific surface area measuring equipment (NOVA 4000).

The anode slurry was prepared by mixing graphite, polyvinylidene fluoride binder (PVDF) and carbon black or MWCNTs in the weight ratio 90:5:5 in N-methyl-2-pyrrolidone (NMP) solvent. The slurry was coated on Cu foil, dried at 100 °C for 2 h, roller pressed into desired thickness and then punched into circular strips. The strips were dried under vacuum at 120 °C for 12 h before assembling. The Charge-discharge characteristics were examined in CR2032 coin cells, assembled in an argon-filled glove box. These cells were composed of a lithium foil as the anode, 1 M LiPF₆ in volume ratio 1:1 ethyl carbon (EC)/diethyl carbonate (DEC) as the electrolyte, microporous polyethylene separator (Celgard 2400) and the prepared anode. These cells were charge-discharged galvanostatically on LAND 2001 CT battery tester. Cyclic voltammetry (CV) was carried out at 0.1 mV/s scanning rate in 0-2.0 V vs. Li/Li⁺ potential range with Zahner elektrik (IM6ex).

Results and Discussion

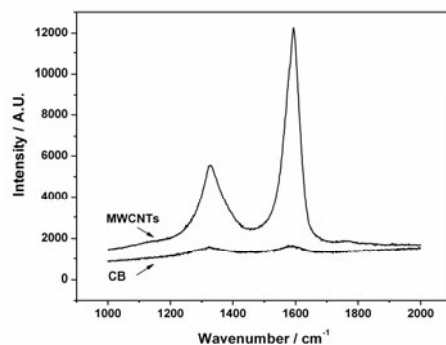


Figure 1. Raman spectra of carbon black and MWCNTs.

In Figure 1, the strong peak at 1580 cm^{-1} is responding to E_{2g2} vibration mode in the graphitic region of carbon materials (G-band) and the peak at 1330 cm^{-1} shows an A_{1g} mode arising from the disordering in carbon (D-band). The ratio of D-band to G-band intensity, $R (=I_D/I_G)$ indicates the degree of surface disordering of graphite powders [6]. R value of carbon black is 0.937, which is bigger than that of MWCNTs ($R=0.429$). In addition, HRTEM photograph in Figure 2 confirmed that MWCNTs have turbulence layered structure.

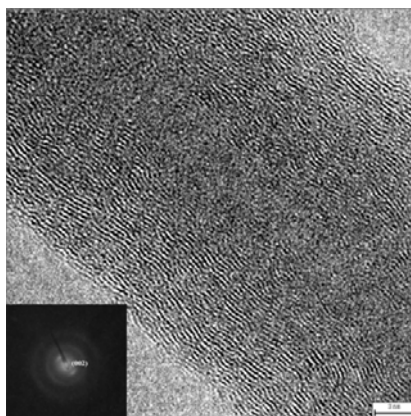


Figure 2. HRTEM image of MWCNTs.

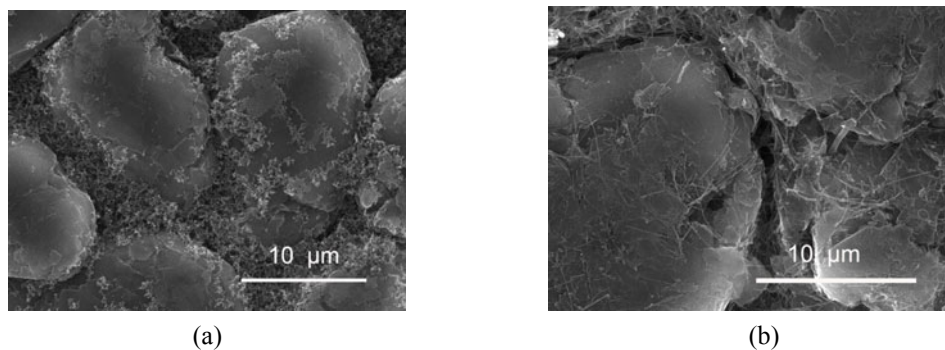


Figure 3. SEM images of the anode mixing with carbon black (a) and MWCNTs (b).

Figure 3 (a) illustrates that some of carbon black distribute on the surface, but more of them agglomerate in the interval space among particles. MWCNTs connect graphite particles together to form a network wiring as shown in Figure 3 (b).

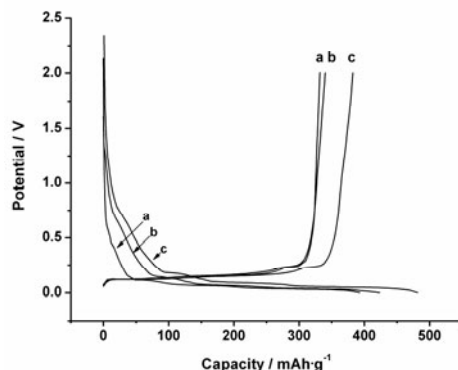


Figure 4. Charge-discharge curves of the anode electrode (a: graphite; b: graphite/carbon black; c: graphite/MWCNTs) in the first cycle at C/10 rate at the cutoff voltage of 0-2.0 V vs. Li/Li^+ .

In Figure 4, in the charge process, the prominent potential plateau in the potential range from 0.6-0.2 V vs. Li/Li^+ is believed to be the solvated lithium intercalation and the formation of SEI on the surface of graphite, leading to the irreversible capacity loss in the first cycle. In the case of carbon black addition, the potential plateau was enlarged because the specific surface area of the anode was increased due to carbon black addition. Thus more of solvated lithium was consumed on the formation of SEI. As shown in Figure 4, the irreversible capacity loss was increased and the discharge plateau was enlarged when MWCNTs was added. MWCNTs possessed ordered layer structure and disordered graphene structure as well. The irreversible capacity loss became bigger when the solvated lithium intercalate into the disordered part of MWCNTs. The precious result proved that the prominent potential plateau in the potential range from 0.6-0.2 V vs. Li/Li^+ was observed in the first charge curve of MWCNTs [7].

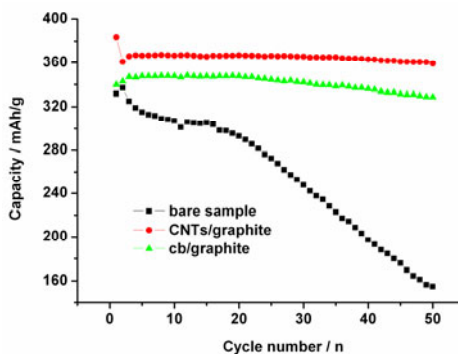


Figure 5. Plots of discharge capacity of the anode with carbon black and MWCNTs addition as a function of the cycle number in 1 M LiPF_6 / EC-DEC (1:1 in v/v) at 20 °C at C/10 rate (current density: 15 mA/g) in the potential range from 0.0 to 2.0 V vs. Li/Li^+ in the first 50 cycles

In Figure 5, both the reversible capacity and cycle stability were improved remarkably when carbon conductor was used. MWCNTs were more effective to improve the cycle behaviors in comparison with carbon black, for the discharge capacity of graphite/MWCNTs composite kept at 366 mAh/g in cycles and the cycle stability was improved to be 93.8 %. The intercalation-deintercalation reactions essentially depend on electron conducting, for the process of lithium ions insertion-deinsertion is accompanied by electron removal simultaneously [8]. And the diffusion of lithium ions in the solid state is improved because MWCNTs are metallic conducting comparing with carbon black. Additionally, the conductive network structure by MWCNTs wiring can increase the contact area of graphite particles, which could transport ions and electrons in mass immediately. Therefore, MWCNTs wiring is an effective method to improve the cycle efficiency and rate capability of cathode materials.

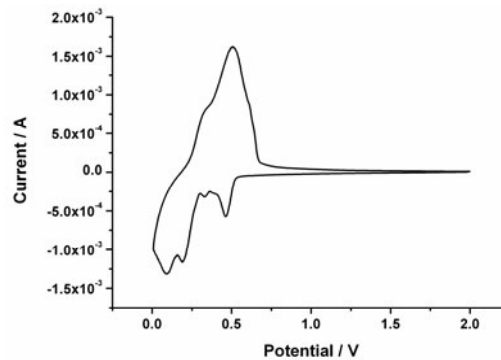


Figure 6. Cyclic voltammogram for the composite of graphite/MWCNTs in the 10th cycle at 0.1 mV/s scanning rate in a sweep range between 0.0 - 2.0V vs. Li/Li⁺.

As seen from Figure 6, the sharp peak at 0.15V was attributed to the insertion and extraction of lithium into and from the layers of the crystallites having a graphite-like structure because the CV of well graphitized carbon shows a sharp strong peak in the same potential region [9]. The clearly separated peaks in the potential range of 0.2-0.5 V can be ascribed to the intercalation and deintercalation of Li⁺ in the so-called disordered sites, or more accurately, such as cavity, turbulence structure and edge space. When the composite of graphite/MWCNTs was scanned from the positive to the negative direction, Li⁺ is believed to store in the disordered sites at first and then in the crystallites.

Concluding Remarks

A novel composite anode material for rechargeable lithium ion battery with high capacity was successfully prepared by adding MWCNTs into natural flake graphite powder. The comparative investigation on the conductor of carbon black and MWCNTs revealed that MWCNTs wiring could increase reversible capacity and cycling stability remarkably.

This study is of potential interest to the application of MWCNTs as a conducting additive in anode materials for high-power lithium rechargeable batteries, which will facilitate the development of high-power lithium ion batteries for hybrid electric vehicles.

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