



## Short communication

Effect of carbon nanotube on the electrochemical performance of C-LiFePO<sub>4</sub>/graphite battery

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## ARTICLE INFO

## Article history:

Received 18 December 2007  
 Received in revised form 3 March 2008  
 Accepted 4 March 2008  
 Available online 16 March 2008

## Keywords:

LiFePO<sub>4</sub>  
 Carbon nanotube  
 Cyclic performance  
 Rate capability  
 Cyclic voltammograms  
 AC impedance

## ABSTRACT

This paper describes the fabrication and testing of C-LiFePO<sub>4</sub>/graphite battery with different conductive carbon additives: carbon nanotube (CNT) or carbon black (CB). The discharge capacity, rate capability and cyclic performance of the battery were investigated. Compared with the batteries with CB additive, those with CNT additive show better electrochemical performances with capacity retention ratio of 99.2% after 50 cycles, and the ratio of discharge capacity at 0.1 C rate to that at 1 C rate is 94.6%. The reason for the difference in electrochemical property was studied with cyclic voltammograms and AC impedance. It was found that, with CNT additive, the polarization voltage was decreased from 0.3 to 0.2 V, and the impedance was decreased from 423.2 to 36.88 Ω. The structures of active materials after cycling were characterized using XRD. The better crystal retaining of LiFePO<sub>4</sub> was found in the active materials with CNT added.

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## 1. Introduction

Since phospho-olivines were first reported as cathode materials for rechargeable lithium batteries in 1997 [1], intensive studies have been focused on the LiFePO<sub>4</sub> material with olivine structure owing to its particular advantages with regard to low cost, nontoxicity, environmental friendliness and high safety. Although it possesses so many advantages, LiFePO<sub>4</sub> as a cathode material still meets some obstacles for its practical application. One is the low electronic conductivity and slow lithium ion diffusion across the LiFePO<sub>4</sub>/FePO<sub>4</sub> boundary due to its intrinsic character [1]. To improve the conductivity, many methods such as coating carbon on the surface of LiFePO<sub>4</sub> [2–4], reducing the particle size [5,6] and doping [7–9] were used.

Intensive attention was paid to the LiFePO<sub>4</sub> battery fabrication [10]. Conductive additive is an important element affecting the performance of LiFePO<sub>4</sub> battery [11,12]. Li et al. [11] and Thorat et al. [12] conclude that good conductive additives such as carbon fibre can improve rate capability and cycle efficiency. Carbon nanotube (CNT) with excellent electrical conductivity has been intensively studied since its discovery by NEC Co. Ltd. in 1991. In this paper, we report the effect of CNT on the C-LiFePO<sub>4</sub>/graphite

battery performance compared with normal carbon black (CB).

## 2. Experimental

## 2.1. Structure and surface analysis

The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement (Cu Kα radiation at 40 kV, 50 Ma, 0.02°) was employed to identify the crystalline phase of LiFePO<sub>4</sub> at a speed of 2° min<sup>-1</sup> from 10° to 90°.

The particle size and morphology of the LiFePO<sub>4</sub> powders and carbon black were measured by scanning electron microscope (SEM, JEOL, JSM-5600LV) with an accelerating voltage of 20 kV.

## 2.2. Battery preparation

Commercially available LiFePO<sub>4</sub> powders (provided by Changs Ascending Enterprise Co. Ltd.), carbon nanotube (CNT) or carbon black (Super P provided by TIMCAL Group, Switzerland), LA133 binder and H<sub>2</sub>O were mixed together at certain ratio in a high-speed mixer, and then the viscous slurry was coated onto an aluminum foil current-collector and dried at 120 °C under vacuum for 24 h. The cathode was then pressed and divided into small patch. The cathode and anode were assembled through convoluting, then enclosed in stainless steel can, and dried at 70 °C under vacuum

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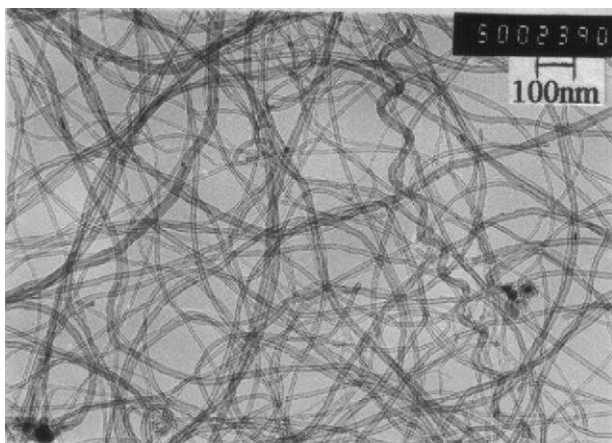


Fig. 1. The TEM of the CNT.

for 36 h. Celgard 2400 microporous membrane as separator with 1.0M LiPF<sub>6</sub> in mixture of EC, EMC, DMC (1:1:1) electrolyte.

### 2.3. Electrochemical performance test

The cyclic performance and rate capability of LiFePO<sub>4</sub> battery were tested at BK-7064. The charge/discharge voltage region was 2.2–3.8V, and the current was 0.1C, 1/3C and 1C rate. Electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) measurements of the cell were carried out using CHI660A (Chenghua, Shanghai). The amplitude of the AC signal was 5 mV over the frequency range between 100 kHz and 0.01 Hz. The sweep rate of CV was 0.1 mV s<sup>-1</sup> over a volt of 2.5–4.2 V.

## 3. Results and discussion

Fig. 1 shows the TEM of CNT. The diameter of the CNT is about 10–20 nm. Fig. 2 shows the SEM of carbon black. The BET specific surface area is 62 m<sup>2</sup> g<sup>-1</sup>.

Fig. 3 shows the X-ray diffraction (XRD) patterns of the cathode material LiFePO<sub>4</sub>. All the diffraction peaks can be indexed on the orthorhombic structure with the space group *Pnmb*. Reflection peak of impurity cannot be found in Fig. 3 indicating the high purity of the raw materials.

Fig. 4 shows the SEM images of the powders. The average second-particle size of the LiFePO<sub>4</sub> sample is 2–3 μm. The small particle size is in favor of the lithium ion diffusion [13]. The carbon coated on the particles surface can also be observed in Fig. 4.

Fig. 5 shows the first discharge curves of two different electrodes at the discharge current of 1/3C rate. The capacities of cathodes with

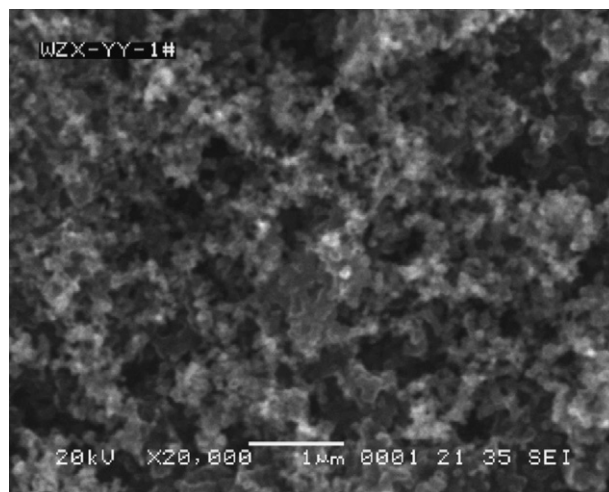


Fig. 2. The SEM of carbon black.

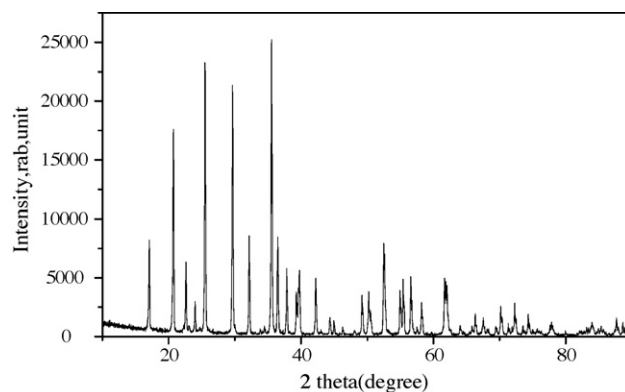


Fig. 3. The XRD of LiFePO<sub>4</sub> sample.

the introduction of CNT and CB are 109 and 105 mAh g<sup>-1</sup>, respectively. This indicates that the CNT additive is in favor of increasing the capacity of cathodes discharged at 1/3C rate. This is because that the CNT additive improves the conductivity of the cathode, in favor of the lithium ion diffusion with the result of capacity increasing.

The rate capability of LiFePO<sub>4</sub> cathodes were shown in Fig. 6. The capacities of cathodes added with CNT are 113 and 107 mAh<sup>-1</sup> discharged at 0.1C and 1C rate, respectively. And the capacities of cathodes added with CB are 113 and 102 mAh g<sup>-1</sup>, respectively. The data in Fig. 6(a) show 94.7% of discharge retention at 1C versus 0.1C rate, and that of Fig. 6(b) is 90.2%. The results show that the CNT additive obviously improves the rate capability of LiFePO<sub>4</sub> cathode.

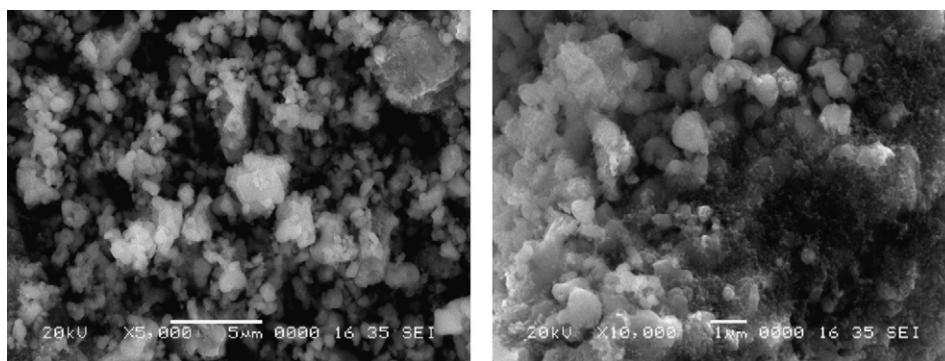


Fig. 4. The SEM of LiFePO<sub>4</sub> sample.

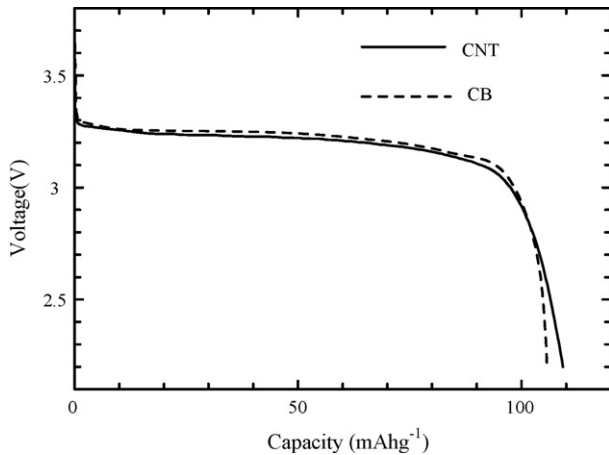


Fig. 5. The discharge curves of LiFePO<sub>4</sub> with the different conductive additives.

Fig. 7 shows the SEM of LiFePO<sub>4</sub> cathode with different conductive additives. In Fig. 7(a), the cathode not containing CNT was intended a control or baseline from which to compare the influence of the fibers. The pictures show the cathode to be well-mixed on the microscale. The cathodes containing CNT show the fibers quite clearly. The CNT appears to be in good contact with other particles. The fibers are believed to enhance the electrical conduction and contact throughout the cathode and also provide mechanical strength for the solid matrix.

The discharge curves also show that the capacities of cathodes added with CNT or CB are all 113 mAh g<sup>-1</sup> discharged at 0.1C rate,



Fig. 8. The sketch map of cathode.

but the capacities are not the same discharged at 1C rate. This can be explained by fellow mechanism.

Fig. 8 is the sketch map of cathode. After components of cathode were dispersed by high-speed mixer, the CNT was dispersed among the LiFePO<sub>4</sub> particles and also between the LiFePO<sub>4</sub> particles and aluminum foil. The transfer of lithium ion among the LiFePO<sub>4</sub> particles, and between the LiFePO<sub>4</sub> particles and aluminum foil is greatly improved because the contact resistance is reduced by the CNT. We suggest that the lithium ion diffusion in the LiFePO<sub>4</sub> particles is the rate-limiting step for the whole diffusion process, when the cathode is discharged at small current such as 0.1C rate. The conductivity of cathode improved by CNT is not embodied. The capacities of LiFePO<sub>4</sub> cathodes with different conductive additives discharged at 0.1C rate are the same. However, the transfer of lithium ion among the LiFePO<sub>4</sub> particles, and between the LiFePO<sub>4</sub> particles and aluminum foil is the rate-limiting step when the cathode discharged at large current such as 1C rate. The capacities discharged at 1C rate are different. The contact resistance among the LiFePO<sub>4</sub> particles and between the LiFePO<sub>4</sub> particles and aluminum foil is reduced by the CNT. The transfer of lithium ion was improved, resulting in the improved rate capability.

Fig. 9 shows the cyclic voltammograms of LiFePO<sub>4</sub> measured at a sweep rate of 0.1 mV s<sup>-1</sup> at room temperature. The CV curve of LiFePO<sub>4</sub> containing CB shows two pair peaks. Anodic and cathodic

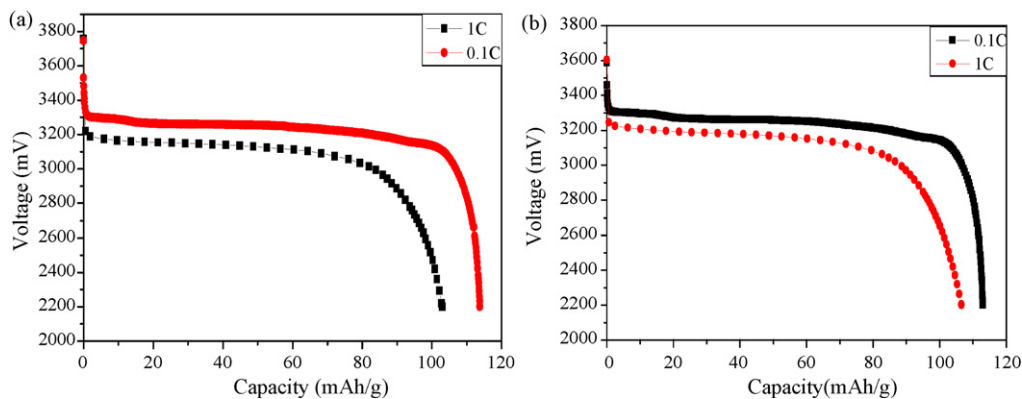


Fig. 6. The rate capacity of LiFePO<sub>4</sub> (a = CB, b = CNT).

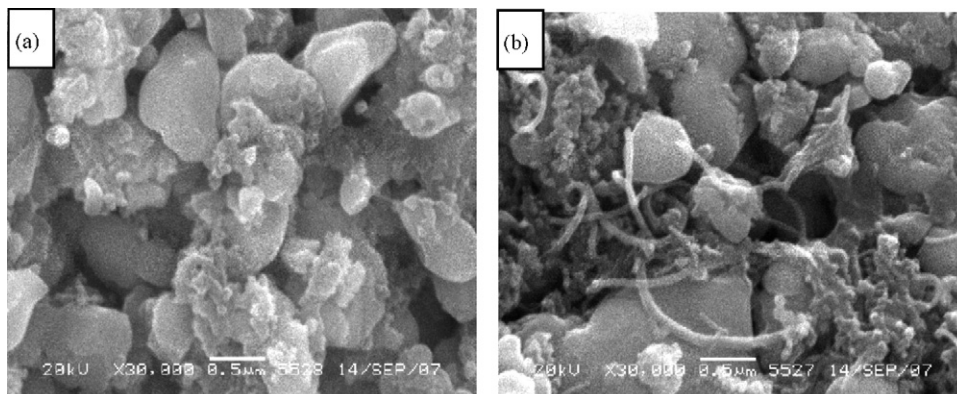


Fig. 7. SEM images of LiFePO<sub>4</sub> cathode (a) CB added and (b) CNT added.

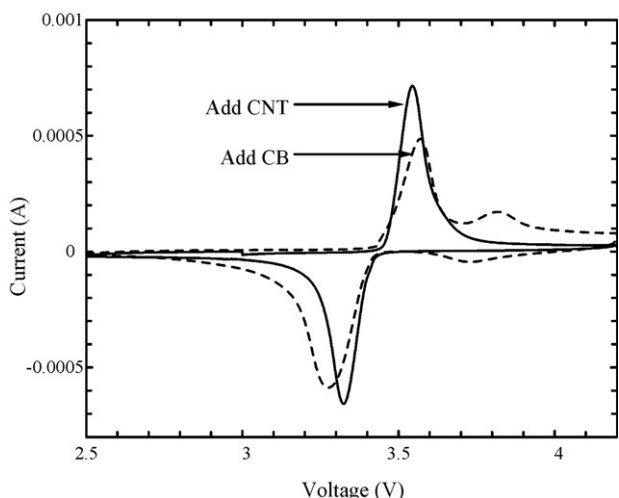


Fig. 9. The cyclic voltammograms curves of LiFePO<sub>4</sub> electrode.

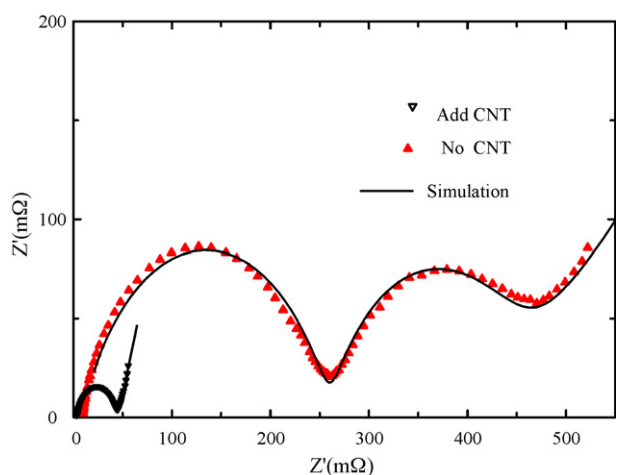


Fig. 10. AC impedance and simulate result of LiFePO<sub>4</sub> electrode with different conductive additives.

peaks appear at ~3.6 and ~3.3 V, which correspond to the two-phase charge–discharge reaction of the Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple. Other pair peaks, which are not indexed, appear at ~3.8 and ~3.7 V. The CV curve of LiFePO<sub>4</sub> containing CNT shows one pair peaks, and the pair peaks at ~3.8 and ~3.7 V disappear. Anodic and cathodic peaks appear at ~3.55 and ~3.35 V. The redox current for LiFePO<sub>4</sub> with CB (0.59 mA) is smaller than that for LiFePO<sub>4</sub> with CNT (0.65 mA). These results indicate that the CNT additive improves the electronic conductivity of anode and simultaneously decreases the polarization. However, the reason for the disappearance of the pair peaks at ~3.8 and ~3.7 V is still unknown at present.

To compare the effect of different conductivity additives in more detail, AC impedance measurement was carried out using three-electrode configuration. In Fig. 10, the impedance spectra of LiFePO<sub>4</sub> with CB added are combinations of two depressed semicircles in high frequency region and a straight line in low frequency region. An intercept at the Z<sub>real</sub>-axis in high frequency region corre-

Table 1  
Impedance parameters of equipment circuit

Conductivity additives	R <sub>s</sub> (Ω)	R <sub>ct</sub> (Ω)	R <sub>f</sub> (Ω)
CB	8.537	173.1	250.1
CNT	3.268	36.88	

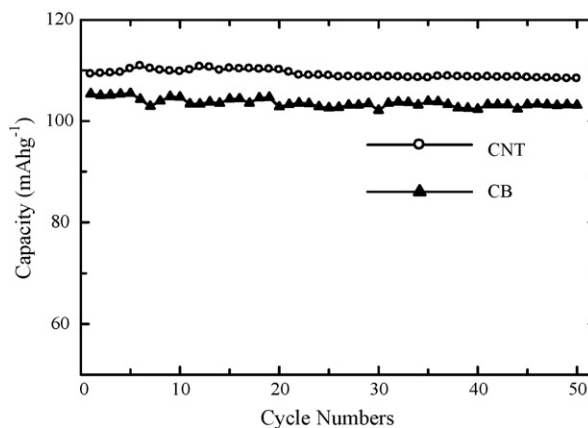


Fig. 12. The cyclic performance of LiFePO<sub>4</sub>.

sponded to the ohmic resistance (R<sub>s</sub>). The depressed semicircle in the high frequency range is related to the Li-ion migration resistance (R<sub>f</sub>) through the SEI film formed on the cathode surface. The second semicircle in the middle frequency range indicates the charge transfer resistance (R<sub>ct</sub>). The inclined line in the lower frequency represented the Warburg impedance (W), which is associated with lithium-ion diffusion in the LiFePO<sub>4</sub> particles. However, the impedance spectra of LiFePO<sub>4</sub> with CNT added are combinations of a depressed semicircle and a straight line, which indicate that CNT improves the electrical conductivity of anode and results in the disappearance of Li-ion migration resistance through the SEI film and the decrease of charge transfer resistance.

A simplified equivalent circuit models was constructed to analyze the impedance spectra in Fig. 10. The parameters of equipment circuit and impedance spectra were simulated by Zview 2.0. The parameter results are listed in Table 1, and the simulated impedance spectra are shown in Fig. 11.

The cyclic performance of LiFePO<sub>4</sub> cathode added with CB and CNT was shown in Fig. 12. The discharge current is 1/3C rate. The capacities of the LiFePO<sub>4</sub> cathodes added with CB and CNT are still 103 and 108 mAh g<sup>-1</sup>, respectively, and the retaining ratios are 97.7% and 99.2%, respectively, after 50 cycles. The LiFePO<sub>4</sub> cathode added with CNT exhibits improved capacity retention without significant capacity fading, indicating the better cyclic performance with CNT additive than CB additive.

Fig. 13 shows the X-ray diffraction patterns of LiFePO<sub>4</sub> cathodes before and after cycling. The intensity of all LiFePO<sub>4</sub> (after cycling) diffraction peaks are weakened, especially those added with CB. Several impurity peaks are observed after cycling. The intensity of impurity peaks in the LiFePO<sub>4</sub> added with CNT is lower than that of LiFePO<sub>4</sub> added with CB. This indicates that the crystal structure of LiFePO<sub>4</sub> is less affected by adding CNT than adding CB after cycling. The crystal lattice parameters were measured by XRD.

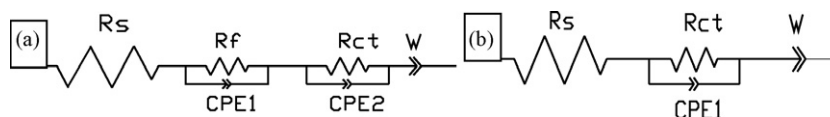


Fig. 11. Equivalent circuit for the LiFePO<sub>4</sub> electrode with different conductive additives (a) CB added and (b) CNT added.

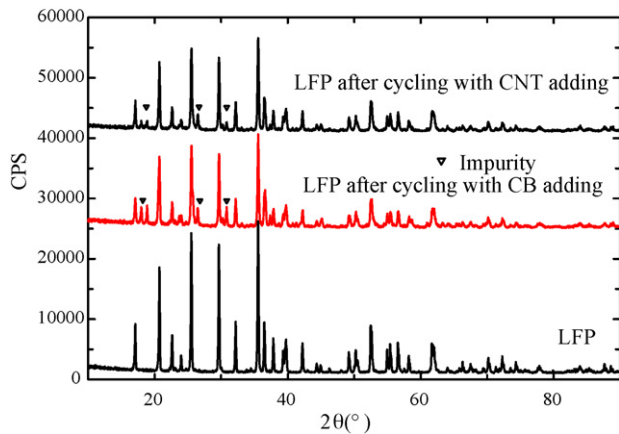


Fig. 13. The XRD of  $\text{LiFePO}_4$  before and after cycling.

The lattice parameters of the  $\text{LiFePO}_4$  with CNT and CB added are  $a = 10.328 \text{ \AA}$ ,  $b = 6.006 \text{ \AA}$  and  $c = 4.687 \text{ \AA}$ , and  $a = 10.330 \text{ \AA}$ ,  $b = 6.009 \text{ \AA}$  and  $c = 4.685 \text{ \AA}$ , respectively. Thus, the difference in cyclic performance may be ascribed to the difference in electrical conductivity and crystal structure retaining.

#### 4. Conclusion

The full battery was produced with commercial  $\text{LiFePO}_4$  as cathode and graphite as anode. Different conductive carbon additives including CNT and CB were used in the battery. The discharge performance, rate capability and cyclic performance were tested. Compared with the batteries with CB additive, those with CNT

additive show better electrochemical performances with capacity retention ratio of 99.2% after 50 cycles, and the ratio of discharge capacity at 1C rate to that at 0.1C rate is 94.6%. It was found that the polarization voltage was decreased from 0.3 to 0.2V by adding CNT. The CNT improves the electrical conductivity of anode and results in Li-ion migration resistance through the SEI film disappearing and the charge transfer resistance decreasing. The crystal structure of  $\text{LiFePO}_4$  changed less after cycling with CNT than with CB. Better crystal structure retaining and improved electronic conductivity are mainly responsible for the superior cyclic performance.

#### Acknowledgement

The project was sponsored by National Basic Research Program of China (973 Program, 2007CB613607).

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