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# Synthesis and electrochemical properties of LiFePO<sub>4</sub>/MWCNT nanocomposites for rechargeable lithium-ion batteries

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LiFePO<sub>4</sub>/multi-walled carbon nanotube (MWCNT) nanocomposites were synthesized by a hydrothermal method. MWCNT as a conductive additive were added to improve the electronic conductivity of pure LiFePO<sub>4</sub> nanoparticles. The crystal structure and electrochemical properties of LiFePO<sub>4</sub>/MWCNT nanocomposites were investigated using X-ray diffraction, scanning electron microscopy, cyclic voltammetry, and charge/discharge tests. It is found that the electrochemical performance of pure LiFePO<sub>4</sub> nanoparticles is increased due to the incorporation of MWCNT where LiFePO<sub>4</sub>/MWCNT nanocomposite (5 wt % MWCNT) shows the highest discharge capacity and stable cyclability at room temperature, and its discharge capacity is 142 mAh g<sup>-1</sup> at a discharge current density of 0.05 mA cm<sup>-2</sup>.

Key words: Nanocomposite, Lithium-ion battery, Multi-walled carbon nanotube.

#### Introduction

It is widely agreed that one of the most important power sources is the rechargeable lithium-ion batteries in a variety of applications such as in mobile phones, laptop computers, digital cameras, electrical vehicles and hybrid electrical vehicles. In rechargeable lithium-ion batteries, the cathode material is a key component mainly relating to the performance of the batteries. Among the well-known cathode materials, layered LiCoO<sub>2</sub> and LiNiO<sub>2</sub>, spinel LiMn<sub>2</sub>O<sub>4</sub>, and other cathode materials such as elemental sulfur have been studied extensively [1-9]. Nowadays, LiCoO<sub>2</sub> is being used as the cathode material for commercial lithium-ion batteries. However, due to the toxicity and the high cost of cobalt, a novel cathode material must be developed not only in relation to battery performance but also in relation to safety and cost.

Recently, lithium transition metal phosphates proposed by Goodenough and co-workers with an ordered olivinetype structure, LiMPO<sub>4</sub> (M = Fe, Mn, Ni, and Co), have attracted extensive attention due to a high theoretical specific capacity (170 mAh g<sup>-1</sup>) [10-20]. The potential of the M<sup>3+</sup>/M<sup>2+</sup> redox couple versus Li/Li<sup>+</sup> of LiMPO<sub>4</sub> is as follows; 3.5 V for LiFePO<sub>4</sub>, 4.1 V for LiMnPO<sub>4</sub>, 5.2-5.4 V for LiNiPO<sub>4</sub>, and 4.8 V for LiCoPO<sub>4</sub>. Among these phosphates, LiFePO<sub>4</sub> is the most attractive because of its high stability, low cost and high compatibility with the environment. However, it is difficult to attain its full capacity because its electronic conductivity is very low, which leads to an initial capacity loss and poor rate capability, and diffusion of Li<sup>+</sup> ion across the LiFePO<sub>4</sub>/FePO<sub>4</sub> boundary is slow due to its intrinsic character [10]. The electronic conductivity of LiFePO<sub>4</sub> is  $\sim 10^{-9}$  S cm<sup>-1</sup> [10], which is much lower than those of  $LiCoO_2$  (~10<sup>-3</sup> S cm<sup>-1</sup>) [21] and LiMn<sub>2</sub>O<sub>4</sub> ( $2 \times 10^{-5}$ -5 × 10<sup>-5</sup> S cm<sup>-1</sup>) [22]. There are two methods to improve the electronic conductivity. One method is to introduce conductive additives including a carbon coating [23] and supervalent cation doping [24]. Another method is to control the particle size by optimizing the synthesis conditions [25, 26]. LiFePO<sub>4</sub> can be synthesized by different methods such as a solid-state reaction [27, 28], a sol-gel method [29, 30], a co-precipitation method [31], and a hydrothermal method [32-36], and so forth. Among these methods, hydrothermal synthesis is a useful method to prepare fine particles, which has some advantages such as a simple synthesis process and low energy consumption compared to the high firing temperature and long firing time during the solid-state reaction used conventionally.

In this contribution, LiFePO<sub>4</sub>/multi-walled carbon nanotube (MWCNT) nanocomposites were prepared by a hydrothermal method. Different contents of MWCNT as a conductive additive were incorporated to improve the electronic conductivity of pure LiFePO<sub>4</sub> nanoparticles. The structural and electrochemical properties of LiFePO<sub>4</sub>/MWCNT nanocomposites were analyzed by means of scanning electron microscope (SEM), X-ray diffraction (XRD), cyclic voltammetry (CV) and charge/discharge experiments.

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Pure LiFePO<sub>4</sub> nanoparticles synthesized hydrothermally

**Experimental** 

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at 170 °C for 10 h without ball-milling and annealing further at 500 °C for 1 h were prepared from starting materials of LiOHH<sub>2</sub>O (Aldrich, 99.95%), FeSO<sub>4</sub>7H<sub>2</sub>O (Aldrich, 99%), (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>3H<sub>2</sub>O (Wako, 99%) and C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> (Aldrich, 99%), as described previously [35]. MWCNT (5 wt% or 10 wt%) were incorporated into the mixture of the above LiFePO<sub>4</sub> nanoparticles and N-methylpyrrolidinone (NMP) to improve its low electronic conductivity, and then the mixture was ball-milled for 10 h using a shaker type of ball mill (Planetary Mono Mill). The ball-to-powder weight ratio was 20:1. After drying at 90 °C for 12 h, the powders were pelleted and further heated at 500 °C for 1 h in a nitrogen atmosphere. After cooling to room temperature, the mixture of NMP and LiFePO4/MWCNT nanocomposite was ball-milled again for 10 h. Finally, the mixture was dried at 90 °C for 12 h. For comparison, pure LiFePO<sub>4</sub> nanoparticles were also prepared by the hydrothermal method followed by high-energy ball-milling which is a promising method for synthesizing cathode materials [37]. During the high-energy ball-milling process, the powder particles undergo repeated welding, fracturing and rewelding in a dry high-energy ball-milling vessel, which results in pulverization and intimate powder mixing. An improvement in electronic conductivity of LiFePO<sub>4</sub>/ MWCNT nanocomposites prepared by the high-energy ball-milling process can be expected due to the very fine nanoparticles and their large specific surface area.

The crystalline phases were identified with XRD (Dmax/ 1200, Rigaku) with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) and powder morphologies were observed by SEM (JEOL JSM-5400).

Composite electrodes were prepared by mixing pure LiFePO<sub>4</sub> nanoparticles or LiFePO<sub>4</sub>/MWCNT nanocomposite with carbon black and polyvinylidenefluoride in a weight ratio of 70:25:5 in NMP. The slurry was coated onto aluminum foil and dried at 90 °C for 1 h before rollpressing, and then the electrodes were cut into  $2 \times 2$  cm sections and dried again at 110 °C for 24 h under a vacuum. The testing batteries were assembled in an argon-filled glove box using lithium as the anode and 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate/dimethyl carbonate (1:1) as the electrolyte. The charge/discharge tests were performed using an automatic charge/discharge equipment (WBCS3000, WonATech) in a potential range of 2.0-4.5 V at various C-rates ranging from C/2 to 10C (1C = 170 mA  $g^{-1}$ ) at room temperature. A rate of nC corresponds to a full discharge in 1/n h. A WBCS3000 battery testing system was also used for measurements of CV at a scan rate of 0.1 mV s<sup>-1</sup> from 2.0 to 4.5 V. The electronic conductivity of the samples was measured by a four-point probe method.

## **Results and Discussion**

The XRD patterns for LiFePO<sub>4</sub>/MWCNT nanocomposites with different MWCNT contents are shown in Fig. 1. All the patterns can be indexed to a single-phase material having an orthorhombic olivine-type structure with a space



Fig. 1. The XRD patterns for (a) pure  $LiFePO_4$  nanoparticles, (b)  $LiFePO_4/MWCNT_{5.0}$  and (c)  $LiFePO_4/MWCNT_{10}$  nanocomposites.

group *Pnma*, which is the same as the one listed in the X-ray powder diffraction data file (JCPDS card number 81-1173, *Pnma* (62), a = 10.332 Å, b = 6.01 Å, c = 4.692 Å,  $V = 291.35 \text{ Å}^3$ ) by the American Society for Testing Materials as standard. The crystallite size D was calculated by Scherrer's equation:  $D = 0.9\lambda/\beta \cos\theta$ , from the fullwidth-at-half-maximum  $\beta$  of four strong and well-resolved reflection peaks corresponding to (101), (111), (211) and (311) crystallographic plane and the mean value was calculated [38, 39]. As shown in Table 1, D = 34 nm for pure LiFePO<sub>4</sub> nanoparticles, D = 19 nm for the LiFePO<sub>4</sub>/ MWCNT<sub>5.0</sub> nanocomposite and D = 21 nm for the LiFePO<sub>4</sub>/  $MWCNT_{10}$  nanocomposite respectively where the subscripts of MWCNT denote wt % MWCNT. Thus, the D value of the LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite is the smallest. There is no impurity in LiFePO4/MWCNT nanocomposites such as  $Fe_2O_3$ ,  $Li_3Fe_2(PO_4)_3$ , and  $Li_3PO_4$ . The addition of L-ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) as a reducing agent to the precursor is useful in prohibiting the conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> during the hydrothermal reaction. There is no obvious carbon diffraction peaks due to its low content and amorphous state. As demonstrated in Table 2, the lattice parameters 'a', 'b' and 'c' are slightly increased on increasing

 Table 1. The properties of LiFePO<sub>4</sub>/MWCNT nanocomposites with different MWCNT contents

|  | MWCNT content       |                     |                     |
|--|---------------------|---------------------|---------------------|
|  | 0%                  | 5%                  | 10%                 |
| Average crystal size <sup>a</sup> (nm)       | 34                  | 19                  | 21                  |
| Particle size range <sup>b</sup> (nm)        | 50-200              | 20-100              | 100-150             |
| Eletronic Conductivity (S cm <sup>-1</sup> ) | $5.86\times10^{-9}$ | $1.08\times10^{-1}$ | $9.17\times10^{-1}$ |

<sup>a</sup>Calculated from XTD data

<sup>b</sup>Estimated from SEM data

|                |         |              | -       |
|----------------|---------|--------------|---------|
|                | l       | MWCNT conter | nt      |
| -              | 0%      | 5%           | 10%     |
| Cell constants |         |              |         |
| <i>a</i> (Å)   | 10.3037 | 10.4006      | 10.4308 |
| b(Å)           | 5.9808  | 6.0058       | 6.0158  |
| <i>c</i> (Å)   | 4.6977  | 4.7240       | 4.7486  |
| $V(Å^3)$       | 289.49  | 295.08       | 297.97  |
|                |         |              |         |

**Table 2.** The lattice constants of LiFePO<sub>4</sub>/MWCNT nanocomposites with different MWCNT contents calculated from the XRD patterns

the MWCNT content. The crystal structure of LiFePO<sub>4</sub>/ MWCNT nanocomposites does not change compared to pure LiFePO<sub>4</sub> nanoparticles.

The SEM images of LiFePO4/MWCNT nanocomposites with different MWCNT contents are shown in Fig. 2. SEM observations show that the grain size of pure LiFePO<sub>4</sub> nanoparticles is around 50-200 nm. Furthermore, the grain sizes of LiFePO4/MWCNT5.0 and LiFePO4/MWCNT10 nanocomposites are around 20-100 and 100-150 nm, respectively. The MWCNT intertwine with LiFePO<sub>4</sub> nanoparticles together to form a three-dimensional network. The dispersed MWCNT provide pathways for electron transference. Therefore, the electronic conductivity of LiFePO<sub>4</sub>/MWCNT nanocomposites is improved. As shown in Table 1, the electronic conductivity  $\sigma$  values for pure LiFePO<sub>4</sub> nanoparticles, LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> and LiFePO<sub>4</sub>/ MWCNT<sub>10</sub> nanocomposites are  $5.86 \times 10^{-9}$ ,  $1.08 \times 10^{-1}$ and  $9.17 \times 10^{-1}$  S cm<sup>-1</sup>, respectively. Hence,  $\sigma$  increases as the MWCNT content increases. In particles with a small diameter, lithium ions diffuse over smaller distances between the surfaces and center during lithium intercalation and de-intercalation, and LiFePO<sub>4</sub> nanoparticles near the particle center contribute very little to the charge/discharge reaction. This is helpful to enhance the electrochemical properties of LiFePO<sub>4</sub>/MWCNT nanocomposites due to the increase in the quantity of LiFePO<sub>4</sub> nanoparticles that can be used.

The cyclic voltammograms of LiFePO<sub>4</sub>/MWCNT nanocomposites with different MWCNT contents at a scan rate of 0.1 mV S<sup>-1</sup> are shown in Fig. 3. As shown in Fig. 3(a), oxidation and reduction peaks in the initial cycle are located at around 3.55 and 3.30 V, respectively. The voltage difference between two peaks is 0.25 V. The oxidation peak decreases and shifts to a higher potential after six cycles, the corresponding reduction peak also decreases and shifts to a lower potential. This is due to an increase in the internal impedance of the battery upon charge/discharge cycling. Furthermore, in the case of LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite, the oxidation and reduction peaks in the initial cycle are located at around 3.48 and 3.34 V, respectively. The corresponding voltage difference is 0.14 V, being obviously smaller than that of pure LiFePO<sub>4</sub> nanoparticles. The oxidation and reduction peaks hardly shift to higher or lower potential after six cycles, and this shows the good overlap of the first, the second and the sixth cycles. The redox peak profiles of the LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite are more symmetric



**Fig. 2.** The SEM images of (a) pure LiFePO<sub>4</sub> nanoparticles, (b) LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> and (c) LiFePO<sub>4</sub>/MWCNT<sub>10</sub> nanocomposites.

and spiculate than that of pure LiFePO<sub>4</sub> nanoparticles. This demonstrates that the reversibility and reactivity of the LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite are better than that of pure LiFePO<sub>4</sub> nanoparticles.

The initial discharge curves of  $LiFePO_4/MWCNT$  nanocomposites with different MWCNT contents at various C-rates ranging from C/2 to 10C at room temperature are shown in Fig. 4. The characteristic flat discharge plateau at around 3.4 V, which represents a two-phase reaction



Fig. 3. The cyclic voltammograms of (a) pure LiFePO<sub>4</sub> nanoparticles and (b) LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite at a scan rate of  $0.1 \text{ mV S}^{-1}$ .



**Fig. 4.** The initial discharge curves of (a) pure LiFePO<sub>4</sub> nanoparticles and (b) the LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite at various C-rates ranging from C/2 to 10C at room temperature. A rate of *n*C corresponds to a full discharge in 1/n h.

in the electrode, is observed in the two samples. As shown in Fig. 4(a), the initial discharge capacities of pure LiFePO<sub>4</sub> nanoparticles obtained at C/2, 1C, 3C, 5C and 10C are 127, 111, 75, 53 and 26 mAh g<sup>-1</sup>, respectively. The potential plateau remains flat even for the 1C curve except for a slight decrease. Furthermore, in the case of the LiFePO<sub>4</sub>/ MWCNT<sub>5.0</sub> nanocomposite, the initial discharge capacities obtained at C/2, 1C, 3C, 5C and 10C are 128, 121, 104, 95 and 76 mAh g<sup>-1</sup>, respectively. The potential plateau remains flat even for the 10C curve except for a slight decrease. In light of the above results, it is concluded that the battery can operate at relatively high rates up to 10C, confirming the improved kinetics of LiFePO<sub>4</sub>/ MWCNT<sub>5.0</sub> nanocomposite. Meanwhile, it is also demonstrated that the discharge rate capability of the LiFePO<sub>4</sub>/ MWCNT<sub>5.0</sub> nanocomposite is better than that of pure LiFePO<sub>4</sub> nanoparticles due to an increase in the electronic conductivity and a decrease in the crystallite size, as demonstrated in Table 1, which is consistent with the XRD results in Fig. 1 and the CV results in Fig. 3. It is evident that the initial discharge capacity decreases while the overpotential increases with an increase in the C-rate. This phenomenon can be explained in terms of the electric polarization due to an increase in the IR drop, where I is the current passing through the battery and R is the battery impedance.

The cycling performance of LiFePO<sub>4</sub>/MWCNT nanocomposites with different MWCNT contents at a discharge current density of 0.05 mA cm<sup>-2</sup> at room temperature is shown in Fig. 5. The charge/discharge tests at various C-rates ranging from C/2 to 10C at room temperature were performed, and the results are shown in Fig. 6. As shown in Fig. 5(a), the initial discharge capacity of pure LiFePO<sub>4</sub> nanoparticles is 143 mAh g<sup>-1</sup>, and decreases to 128 mAh g<sup>-1</sup> after 30 cycles. As shown in Fig. 5(b) and 5(c), the discharge capacities of LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> and



**Fig. 5.** The cycling performance of (a) pure LiFePO<sub>4</sub> nanoparticles, (b) LiFePO<sub>4</sub>/MWCNT<sub>50</sub> and (c) LiFePO<sub>4</sub>/MWCNT<sub>10</sub> nanocomposites at a discharge current density of 0.05 mA cm<sup>-2</sup> at room temperature.



**Fig. 6.** The cycling performance of (a) pure LiFePO<sub>4</sub> nanoparticles and (b) LiFePO<sub>4</sub>/MWCNT<sub>50</sub> nanocomposite at various C-rates ranging from C/2 to 10C at room temperature. A rate of *n*C corresponds to a full discharge in 1/n h.

LiFePO<sub>4</sub>/MWCNT<sub>10</sub> nanocomposites after 30 cycles are 142 and 140 mAh g<sup>-1</sup>, respectively. It is demonstrated that the discharge capacities of the LiFePO<sub>4</sub>/MWCNT nanocomposites do not change upon cycling and the cycling performance of LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite is the best due to its smallest crystallite size, which is consistent with the XRD results in Fig. 1 and the CV results in Fig. 3. Fig. 6 demonstrates that the high-rate discharge properties of the LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite are better than that of pure LiFePO<sub>4</sub> nanoparticles especially at 5C and 10C.

## Conclusions

LiFePO<sub>4</sub>/MWCNT nanocomposites have been synthesized successfully by a hydrothermal method. The electronic conductivity of the LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposite is  $1.08 \times 10^{-1}$  S cm<sup>-1</sup>, which is eight orders of magnitude higher than that of pure LiFePO<sub>4</sub> nanoparticles. The incorporation of MWCNT obviously improves the high-rate discharge capability of LiFePO<sub>4</sub>/MWCNT<sub>5.0</sub> nanocomposites especially at 5C and 10C.

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