

## Structural and Electrochemical Characterization of LiFePO<sub>4</sub> Synthesized by Hydrothermal Method

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Phospho-olivine LiFePO<sub>4</sub> cathode materials were prepared by hydrothermal reaction. Carbon black was added to enhance the electrical conductivity of LiFePO<sub>4</sub>. The structural and morphological performance of LiFePO<sub>4</sub> and LiFePO<sub>4</sub>-C powders were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). LiFePO<sub>4</sub>/Li and LiFePO<sub>4</sub>-C/Li cells were characterized electrochemically by cyclic voltammogram (CV), charge/discharge experiments and ac impedance spectroscopy. The results showed that the discharge capacity of LiFePO<sub>4</sub>/Li cell was 147 mAh/g at the first cycle and 118 mAh/g after 30 cycles, respectively. The discharge capacity of LiFePO<sub>4</sub>-C/Li cell with 5wt% carbon black was the largest among LiFePO<sub>4</sub>-C/Li cells, 133 mAh/g at the first cycle and 128 mAh/g after 30 cycles, respectively. It was demonstrated that cycling performance of LiFePO<sub>4</sub>-C/Li cell with 5wt% carbon black was better than that of LiFePO<sub>4</sub>/Li cell.

**Keywords :** LiFePO<sub>4</sub>, Carbon black, Cathode material, Hydrothermal method

### 1. Introduction

Since the commercialization of rechargeable lithium-ion batteries by Sony Energy Tech.[1] 15 years ago, they have been widely utilized as the power sources in a wide range of applications, such as mobile phones, laptop computers, cameras, electrical vehicles (EV), and hybrid electrical vehicles (HEV). In the rechargeable lithium ion batteries, cathode material is the key component, and mainly devoted to the performance of the batteries. Among the known cathode materials, the layered LiCoO<sub>2</sub>, LiMnO<sub>2</sub> and LiNiO<sub>2</sub>, spinel LiMn<sub>2</sub>O<sub>4</sub>, and elemental sulfur have been studied extensively[2-10]. LiCoO<sub>2</sub> has been nowadays utilized for commercial lithium-ion batteries. However, 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 with an ordered olivine-type 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)[11]. 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 discharge plateau for LiCoPO<sub>4</sub>. Among these phosphates, LiFePO<sub>4</sub> is the most attractive because of its high stability, low

cost, high compatibility with environment[12-13]. However, it is difficult to attain its full capacity because its electronic conductivity is very low, and diffusion of Li<sup>+</sup> ion in the olivine structure is slow. It is found that small amount of Fe<sup>2+</sup> is oxidized to Fe<sup>3+</sup> during hydrothermal process or annealing process[14-15]. There are two methods to improve the electronic conductivity. One method is to introduce conductive additives including carbon coating[16-20] and supervalent cation doping[21-22]. Another method is to control the particle size by optimizing the synthesis conditions[23].

In this study, phospho-olivine LiFePO<sub>4</sub> was prepared by hydrothermal reaction. In order to enhance the electrical conductivity of LiFePO<sub>4</sub>, carbon black was added. LiFePO<sub>4</sub>/Li and LiFePO<sub>4</sub>-C/Li cells were fabricated in an argon-filled glove box and their electrochemical properties were analyzed by means of CV, ac impedance and charge-discharge experiments.

### 2. Experimental

LiFePO<sub>4</sub> was prepared with starting materials of LiOH·H<sub>2</sub>O (Aldrich Co. 99.95%), FeSO<sub>4</sub>·7H<sub>2</sub>O (Aldrich Co. 99+%), H<sub>3</sub>PO<sub>4</sub> (Aldrich Co. 99.999+%) and C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> (Aldrich Co. 99+%). After LiOH·H<sub>2</sub>O was dissolved in distilled water to obtain 1M solution, H<sub>3</sub>PO<sub>4</sub>

and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  powders were added to LiOH solution in a molar ratio for Li:Fe:P =3:1:1. Addition of ascorbic acid as a reducing agent to the precursor was useful in prohibiting the conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  during the hydrothermal reaction and generation of  $\alpha\text{-Fe}_2\text{O}_3$  during the annealing process. The mixed solution was heated at 150 °C. After being cooled to room temperature, the solution was filtered to separate the precipitate powder, the powder was washed with ultrapure water. The obtained powder was dried at 100 °C for 1 h under vacuum. The dried powders were further dried at 400 °C for 1 h in nitrogen atmosphere. In order to improve low electron conduction of  $\text{LiFePO}_4$ , carbon black with different content (5wt%, 10wt% and 15wt%) was added.

The crystalline phases were identified with X-ray diffraction (XRD, Dmax/1200, Rigaku). The X-ray diffraction pattern was collected by a step-scanning mode in the range of 10°~80° with a step time of 5°/min. Powder morphologies were observed by SEM (JEOL JSM-5400) and TEM (JEOL JEM-2000 FXII). A composite electrode was prepared by mixing  $\text{LiFePO}_4$  or  $\text{LiFePO}_4\text{-C}$  with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 70:25:5. This mixture was coated onto an Al-foil, cut into 2×2 cm sections and heated at 110 °C for 24 h under vacuum. A lithium foil was used as an anode. Electrolyte was 1M  $\text{LiPF}_6$  dissolved in ethylene carbonate/dimethyl carbonate (EC:DMC=1:1). The beaker-type cells were fabricated for the electrochemical tests. Charge/discharge testing was performed using automatic charge/discharge equipment (WBCS3000, WonaTech Co.) in a potential range of 2.5-4.3 V at a constant current density of 0.1 mA/cm<sup>2</sup>. Electrochemical impedance measurements were performed using an IM6 impedance system (Zahner Elektrik Co.). The spectrum was potentiostatically measured by applying an ac voltage of 10 mV over the frequency range from 2 MHz to 10 mHz. The WBCS3000 (Wonatech) Battery Tester System was also used for measurements of cyclic voltammetry at a scan rate of 0.1 mV s<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Crystal structure

XRD patterns of  $\text{LiFePO}_4\text{-C}$  powders are shown in Fig. 1. All the patterns can be indexed to a single-phase material having an orthorhombic olivine-type structure (space group Pmnb), which are the same as the theoretical value. No impurity is found in all the  $\text{LiFePO}_4\text{-C}$  powders.

#### 3.2. SEM and TEM

SEM and TEM images of  $\text{LiFePO}_4\text{-C}$  powders are shown in Fig. 2 and Fig. 3, respectively. As can be seen from Fig. 2a,

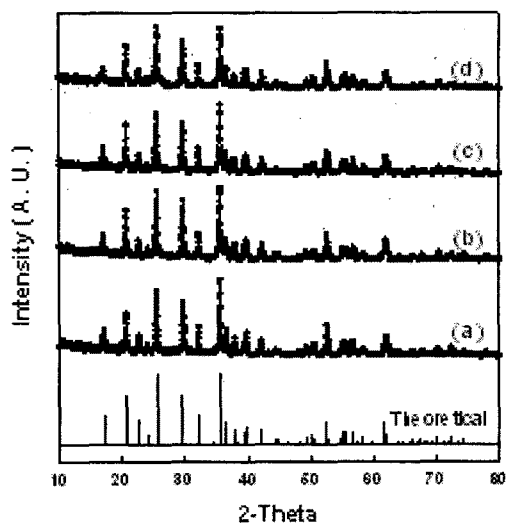


Fig. 1. XRD patterns of  $\text{LiFePO}_4$  (a),  $\text{LiFePO}_4\text{-5%}$  (b),  $\text{LiFePO}_4\text{-10%}$  (c) and  $\text{LiFePO}_4\text{-15%}$  carbon black (d).

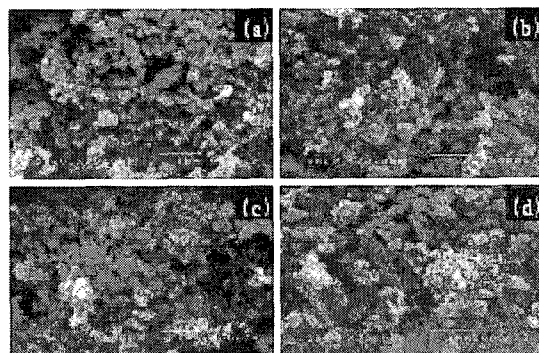


Fig. 2. SEM images of  $\text{LiFePO}_4$  (a),  $\text{LiFePO}_4\text{-5%}$  (b),  $\text{LiFePO}_4\text{-10%}$  (c) and  $\text{LiFePO}_4\text{-15%}$  carbon black (d).

the average particle size of  $\text{LiFePO}_4$  is around 500 nm. It is shown from Fig. 2b, Fig. 2c and Fig. 2d that the average particle size of  $\text{LiFePO}_4\text{-C}$  powders with 5wt%, 10wt% and 15wt% is around 150, 200 and 250 nm, respectively. It is obvious that the average particle size of  $\text{LiFePO}_4\text{-C}$  powders is much smaller than that of  $\text{LiFePO}_4$  powders. This demonstrates that carbon black in the mixture retards the particle growth during calcination. When carbon content is 10% and 15%, the particles agglomerate and form the secondary particles. The smaller particles, which shorten the lithium ions diffusion distances between the surfaces and center during lithium intercalation and de-intercalation, are expected to

contribute the enhanced electrochemical performance of the carbon-coated  $\text{LiFePO}_4$ .

As can be seen from Fig. 3a, an amorphous layer is clearly observed for the hydrothermally synthesized  $\text{LiFePO}_4$ , but this amorphous layer is crystallized by heat-treatment at  $400\text{ }^\circ\text{C}$ , as shown in Fig. 3b, Fig. 3c and Fig. 3d. To confirm how carbon black is dispersed in  $\text{LiFePO}_4$ -C powders, a part of  $\text{LiFePO}_4$  powders which contain 5wt% carbon (Fig. 3b) is magnified, as shown in Fig. 3e. It is obvious from the image that the surfaces of  $\text{LiFePO}_4$  powders are coated by carbon coating layer.

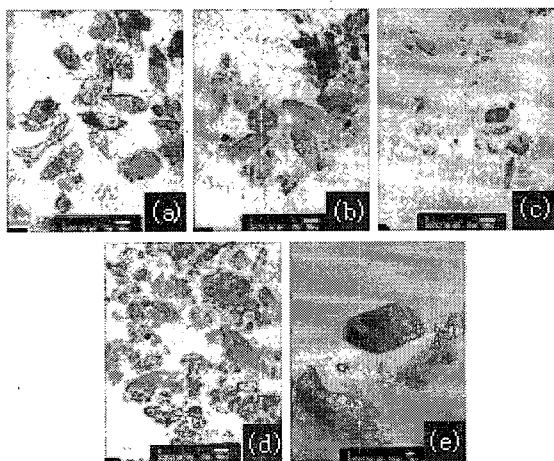


Fig. 3. TEM images of  $\text{LiFePO}_4$  (a),  $\text{LiFePO}_4$ -5% (b),  $\text{LiFePO}_4$ -10% (c),  $\text{LiFePO}_4$ -15% (d) and magnified  $\text{LiFePO}_4$ -5% carbon black (e).

### 3.3. Cyclic voltammetry

Cyclic voltammetry of  $\text{LiFePO}_4/\text{Li}$  and  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5 wt% carbon black is shown in Fig. 4. As can be seen from Fig. 4a, reduction and oxidation peak positions for  $\text{LiFePO}_4/\text{Li}$  cell appear at 3.375 and 3.54 V vs  $\text{Li}/\text{Li}^+$ , respectively. It is shown from Fig. 4b that reduction and oxidation peak positions for  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5wt% carbon black appear at 3.32 and 3.54 V vs  $\text{Li}/\text{Li}^+$ , respectively. It is obvious that the reduction and oxidation peak currents of  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell are greater than that of  $\text{LiFePO}_4/\text{Li}$ . It is demonstrated that the reversibility of  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5 wt% carbon black is better than that of  $\text{LiFePO}_4/\text{Li}$ .

### 3.4. Charge/discharge properties

Cycling performance of  $\text{LiFePO}_4/\text{Li}$  and  $\text{LiFePO}_4\text{-C}/\text{Li}$  cells is shown in Fig. 5. As can be seen from Fig. 5, the discharge capacity of  $\text{LiFePO}_4/\text{Li}$  cell is 147 mAh/g at the first cycle and 118 mAh/g after 30 cycles, respectively. The initial discharge capacity of  $\text{LiFePO}_4$  with 5wt%, 10wt% and 15wt% carbon black is 133, 115 and 105 mAh/g, respectively. After 30 cycles, the

discharge capacity of  $\text{LiFePO}_4$  with 5wt%, 10wt% and 15wt% carbon black is 128, 112 and 106 mAh/g, respectively. It is demonstrated that cycling performance of  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell is better than that of  $\text{LiFePO}_4/\text{Li}$  cell and the discharge capacity is the largest when carbon content is 5 wt%. It is consistent with the CV results in Fig. 4.

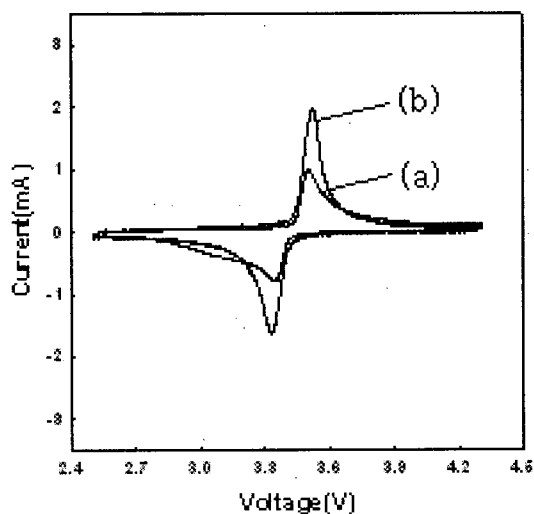


Fig. 4. Cyclic voltammetry of  $\text{LiFePO}_4/\text{Li}$  (a) and  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5 wt% carbon black (b).

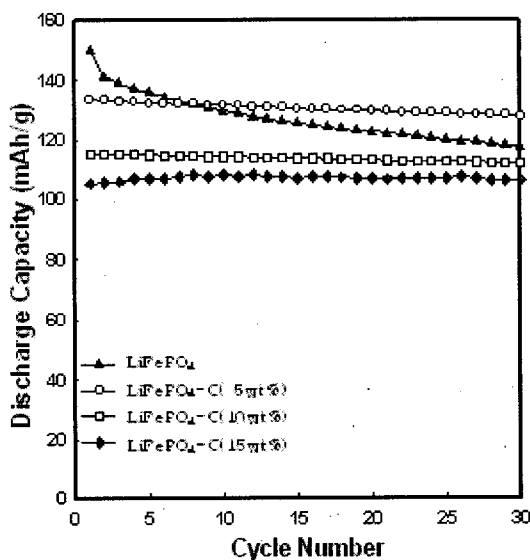


Fig. 5. Cycling performance of  $\text{LiFePO}_4/\text{Li}$  and  $\text{LiFePO}_4\text{-C}/\text{Li}$  cells.

### 3.5. Impedance properties

Impedance spectra of  $\text{LiFePO}_4/\text{Li}$  and  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5 wt% carbon black upon cycling are shown in Fig. 6. It is noted that the ac impedance response of the cell forms a broad semicircle and a line to the real axis in the lowest frequency range. The semicircle in the high frequency is mainly related to the complex reaction process at the electrolyte/cathode interface including resistance of SEI film formed on the surface  $\text{LiFePO}_4$  particles, the particle-to-particle contact resistance, charge transfer resistance, and corresponding capacitances. The inclined line in the lower frequency is attributed

to the Warburg impedance, which is associated with lithium ion diffusion in  $\text{LiFePO}_4$  electrode. As can be seen from Fig. 6a, the resistance is  $20\ \Omega$  at the first cycle,  $25\ \Omega$  after 3 cycles,  $30\ \Omega$  after 5 cycles,  $31\ \Omega$  after 7 cycles and  $38\ \Omega$  after 9 cycles, respectively. It is obvious that  $\text{LiFePO}_4/\text{Li}$  cell resistance increases upon the cycling. As can be seen from Fig. 6b, the resistance is  $19\ \Omega$  at the first cycle,  $20\ \Omega$  after 3 cycles,  $21\ \Omega$  after 5 cycles,  $21\ \Omega$  after 7 cycles and  $22\ \Omega$  after 9 cycles, respectively. It is obvious that  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5 wt% carbon black resistance hardly changes upon the cycling. It is noted that the length of the inclined line in  $\text{LiFePO}_4/\text{Li}$  cell is longer than that of the inclined line in  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5 wt% carbon black, that is to say, lithium ion diffusion in  $\text{LiFePO}_4\text{-C}$  electrode is faster than that in  $\text{LiFePO}_4$  electrode, therefore, as can be seen from Fig. 5, cycling performance of  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell is better than that of  $\text{LiFePO}_4/\text{Li}$  cell.

### 4. Conclusions

Phospho-olivine  $\text{LiFePO}_4$  cathode materials were prepared by hydrothermal reaction. Carbon black was added to enhance the electrical conductivity of  $\text{LiFePO}_4$ . The average particle size of  $\text{LiFePO}_4\text{-C}$  powders is much smaller than that of  $\text{LiFePO}_4$  powders. The discharge capacity of  $\text{LiFePO}_4/\text{Li}$  cell is  $147\ \text{mAh/g}$  at the first cycle and  $118\ \text{mAh/g}$  after 30 cycles, respectively. The discharge capacity of  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell with 5wt% carbon black is the largest among  $\text{LiFePO}_4\text{-C}/\text{Li}$  cells,  $133\ \text{mAh/g}$  at the first cycle and  $128\ \text{mAh/g}$  after 30 cycles, respectively. It is demonstrated that cycling performance of  $\text{LiFePO}_4\text{-C}/\text{Li}$  cell is better than that of  $\text{LiFePO}_4/\text{Li}$  cell.

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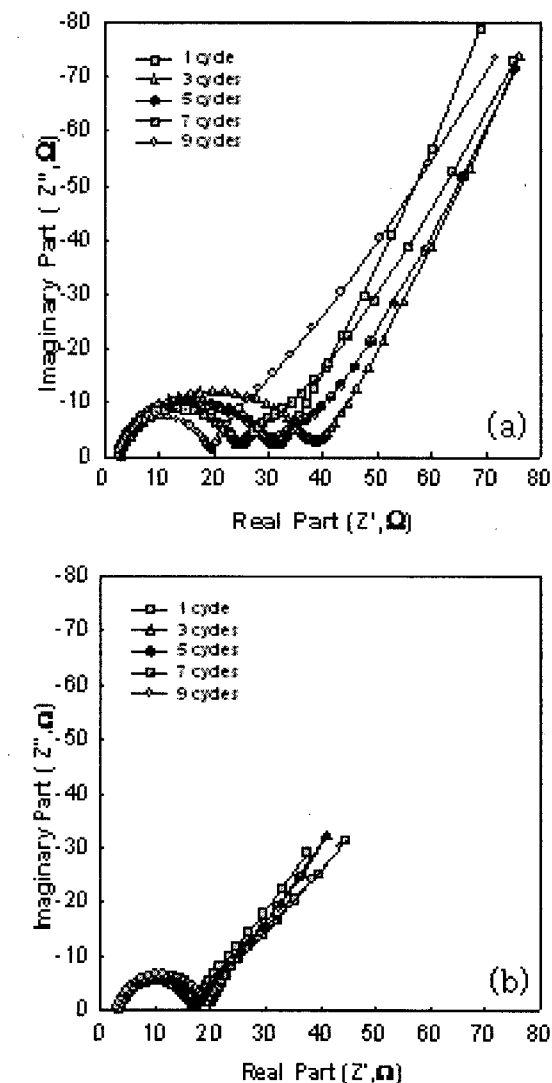


Fig. 6. Impedance spectra of  $\text{LiFePO}_4/\text{Li}$  (a) and  $\text{LiFePO}_4\text{-C}$  cell with 5 wt% carbon black (b) upon cycling.

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