

Electrochemical properties of LiFePO₄ cathode materials by hydrothermal route

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Abstract : Phospho-olivine LiFePO₄ cathode materials were prepared by hydrothermal reaction at different temperatures. The structural performance of LiFePO₄ powders were characterized by X-ray diffraction (XRD). LiFePO₄/Li batteries were characterized electrochemically by charge/discharge experiments. The XRD results demonstrate that LiFePO₄ powder has an orthorhombic olivine-type structure with a space group of Pnmb. Among the synthesized cathode materials, LiFePO₄ synthesized at 170 °C and subsequently annealed at 500 °C shows the best electrochemical properties. It shows initial discharge capacity of 167 mAh g⁻¹ (98% of the theoretical capacity) close to the theoretical capacity of LiFePO₄ (170 mAh g⁻¹) at 0.1 C rate, which is ascribed to the enhanced degree of crystallinity, better phase purity, more spherical and more finely dispersed nanoparticles, crystallization and activation of small amount impurity.

Key Words : Olivine; Lithium-ion batteries; Cathode; Orthorhombic; Hydrothermal method

1. Introduction

Lithium transition metal phosphates with an ordered olivine-type structure, LiMPO₄ (M = Fe, Mn, Ni, and Co), have attracted extensive attention due to a high theoretical specific capacity (170 mAh/g) [1]. The potential of the M³⁺/M²⁺ redox couple versus Li/Li⁺ of LiMPO₄ is as follows; 3.5 V for LiFePO₄, 4.1 V for LiMnPO₄, 5.2-5.4 V for LiNiPO₄, and 4.8 V discharge plateau for LiCoPO₄. Among these phosphates, LiFePO₄ is the most attractive because of its high stability, low cost, high compatibility with environment [2]. However, it is difficult to attain its full capacity because its electronic conductivity is very low, which leads to initial capacity loss and poor rate capability, and diffusion of Li⁺ ion in the olivine structure is slow. There are two methods to improve the electronic conductivity. One method is to introduce conductive additives including carbon coating [3] and supervalent cation doping [4]. Another method is to control the particle size by optimizing the synthesis conditions [5]. LiFePO₄ can be synthesized by different methods including solid-state reaction [1], emulsion-drying method [6], co-precipitation method [7] and hydrothermal method [8]. The hydrothermal synthesis is a useful method to prepare fine particles, which has some advantages such as simple synthesis process and low energy consumption.

In this study, phospho-olivine LiFePO₄ was prepared by hydrothermal reaction. LiFePO₄/Li batteries were fabricated in an argon-filled glove box and their electrochemical properties were analyzed by means of SEM, XRD, CV, and charge-discharge experiments.

2. Experimental

LiFePO₄ was prepared from starting materials of LiOH·H₂O, FeSO₄·7H₂O, (NH₄)₃PO₄·3H₂O and C₆H₈O₆. After LiOH·H₂O was dissolved in distilled water to obtain 1M solution, (NH₄)₃PO₄·3H₂O and FeSO₄·7H₂O powder were added to LiOH solution in a molar ratio for Li:Fe:P = 2.5:1:1. Addition of ascorbic acid as a

reducing agent to the precursor was useful in prohibiting the conversion of Fe²⁺ to Fe³⁺ during the hydrothermal reaction and generation of α-Fe₂O₃ during the annealing process. The mixed solution was heated at 170 °C for 10 h. After being cooled to room temperature, the solution was filtered to separate the precipitate powder, the powder was washed with distilled water. The obtained powder was dried at 110 °C for 1 h under vacuum. The powders are coded as LFP17. The dried powders were subsequently dried at 400 °C for 0.5 h and 500 °C for 1 h in nitrogen atmosphere, respectively. These two powders are coded as LFP174 and LFP175, respectively.

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). A composite electrode was prepared by mixing LiFePO₄ with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 70:25:5. This mixture was coated onto an aluminum 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 LiPF₆ 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 2.0-4.5 V at different C rates ranging from 0.1 to 5 C (1 C=170 mA g⁻¹) at 25 °C. The WBCS3000 Battery Tester System was also used for measurements of cyclic voltammetry at a scan rate of 0.1 mV s⁻¹.

3. Results and discussion

XRD patterns for LiFePO₄ powders synthesized in nitrogen atmosphere at various temperatures 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 group of Pnmb, which is identified by JCPDS file (40-1499). No impurity is found

in the LiFePO_4 powders.

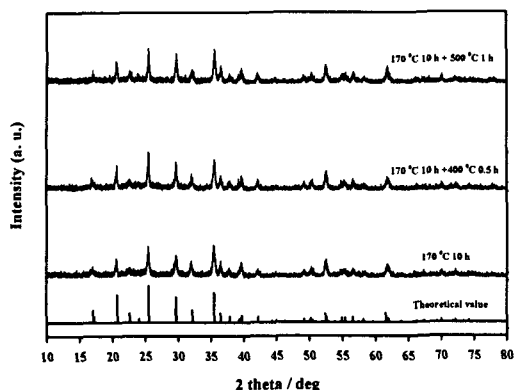


Figure 1. XRD patterns of LiFePO_4 synthesized at various temperatures.

The discharge curves of LiFePO_4 are presented in Fig. 2. The discharge plateaus appear at around 3.4 V (versus Li/Li^+) after initial charging. As shown from Fig. 2a, the discharge capacity of as-prepared LFP17 is 110 mAh g^{-1} in the first cycle, the amount of cycled lithium is limited to $x = 0.65$, 94% of the initial capacity can be remained after 5 cycles. As shown from Fig. 2b, the discharge capacity of LFP174 is 150 mAh g^{-1} (88% of the theoretical capacity) in the first cycle, the amount of cycled lithium is limited to $x = 0.88$, 94% of the initial capacity can be remained after 5 cycles.

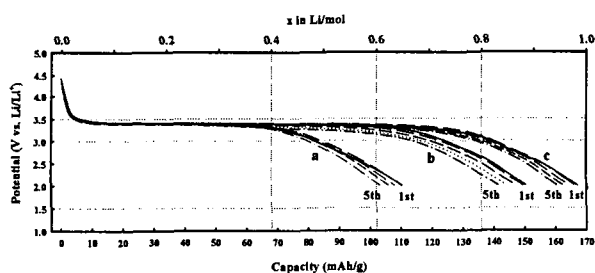


Figure 2. The discharge curves of (a) LFP17, (b) LFP174 and (c) LFP175.

It is noted that the discharge capacity of LiFePO_4 subsequently annealed is larger than that of as-prepared LiFePO_4 . This is due to the amorphous layer, which is electrochemically inactive and involved in the as-prepared LiFePO_4 . After the annealing, it may be crystallized and activated.

As shown from Fig. 2c, the discharge capacity of LFP175 is 167 mAh g^{-1} (98% of the theoretical capacity) close to the theoretical capacity of LiFePO_4 (170 mAh g^{-1}) in the first cycle, which indicates that the active material utilization is very close to the theoretical value, the amount of cycled lithium is limited to x

$= 0.98$, 96% of the initial capacity can be remained after 5 cycles.

Conclusions

Phospho-olivine LiFePO_4 cathode materials were successfully prepared by hydrothermal reaction at different temperatures. The XRD results demonstrate that LiFePO_4 synthesized at $170 \text{ }^\circ\text{C}$ and subsequently annealed at $500 \text{ }^\circ\text{C}$ has an orthorhombic olivine-type structure with a space group of Pnmb and average particle size of 200 nm . Its discharge capacity is 167 mAh g^{-1} (98% of the theoretical capacity) at 0.1 C rate, which is the largest compared to other samples.

Acknowledgments

The participants in this research received supporting funds from the second-stage BK 21.

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