

Formation of impurities on phospho-olivine LiFePO_4 during hydrothermal synthesis

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Abstract

Phospho-olivine LiFePO_4 as a cathode material of rechargeable lithium battery was synthesized from LiOH , FeSO_4 , and $(\text{NH}_4)_3\text{PO}_4$ by hydrothermal process at 170°C . The optimized molar ratio of $\text{Li}:\text{Fe}:\text{P}$ in the starting solution was 2.5:1:1. The charge and discharge capacities at 3.5 V versus Li/Li^+ of hydrothermally synthesized LiFePO_4 were 65 mAh g^{-1} . The additional heat treatment was carried out to improve the charge–discharge performance of hydrothermally synthesized LiFePO_4 . Raman spectroscopy revealed that existence of $\alpha\text{-Fe}_2\text{O}_3$ on the particle surface of LiFePO_4 annealed at 400°C . The charge and discharge capacities of the annealed LiFePO_4 were 150 mAh g^{-1} . Two plateaus at 3.5 and 2.5 V were observed in the charge–discharge curves, and the 2.5 V plateau was correlated with the Li^+ insertion into $\alpha\text{-Fe}_2\text{O}_3$. © 2005 Elsevier B.V. All rights reserved.

Keywords: Phospho-olivine LiFePO_4 ; Hydrothermal synthesis; Rechargeable lithium batteries; Cathode materials; Raman spectroscopy

1. Introduction

Rechargeable lithium batteries have been utilized in a wide range of applications, such as electronic devices. High temperature behavior of a rechargeable lithium battery is a key issue, because it can be heated inadvertently. However, present cathode materials, such as Li_xCoO_2 , are metastable, and oxygen evolution occurs during decomposition of Li_xCoO_2 at elevated temperatures [1]. On the other hand, phospho-olivine LiMPO_4 ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{or Ni}$) have been intensively investigated because of their high stability [2]. They have a highly stable three dimensional framework due to strong P–O covalent bonds in $(\text{PO}_4)^{3-}$ polyanion, which prohibits the liberation of oxygen [3]. These characteristics provide an excellent safety and a stable operation of battery even under unusual conditions [4–7]. Moreover, LiFePO_4 is a low cost material and highly compatible to environment.

LiFePO_4 can be synthesized by normal solid-state reaction. Unfortunately, it is very difficult to achieve the theo-

retical capacity of LiFePO_4 , because of its low electronic conductivity and slow diffusion of Li-ion in the olivine structure [3,4,8]. So far, several alternative synthetic methods have been applied to preparation of LiFePO_4 . Recently, it has been reported that the control of LiFePO_4 particle size is effective to increase the charge and discharge capacities [4]. It has been also reported that highly dispersed conductive substances such as carbonaceous materials and some metals in the cathode composite electrode enhance the charge–discharge performance of LiFePO_4 [9–15]. Furthermore, Chung et al. reported that substitution of small fraction of Fe in LiFePO_4 by other metals increases the electronic conductivity of LiFePO_4 , and it improved the charge–discharge rate performance of LiFePO_4 [8].

In this work, hydrothermal synthesis was employed for preparation of phospho-olivine LiFePO_4 . The hydrothermal synthesis is a useful method to prepare fine particles, which has some advantages such as simple synthesis process and low energy consumption. Yang et al. have already demonstrated the hydrothermal synthesis of LiFePO_4 [16]. In the present paper, the optimized hydrothermal condition was explored to obtain single phase of LiFePO_4 . The additional heat

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treatment was carried out to improve the charge–discharge performance. The obtained LiFePO_4 was characterized by X-ray diffraction (XRD) and Raman spectroscopy. The electrochemical properties of obtained LiFePO_4 were evaluated by constant current charge–discharge measurements.

2. Experimental

Phospho-olivine LiFePO_4 was prepared by hydrothermal process with $\text{LiOH}\cdot\text{H}_2\text{O}$ (High Purity Chemicals), $\text{FeSO}_4\cdot x\text{H}_2\text{O}$ (Aldrich) and $(\text{NH}_4)_3\text{PO}_4\cdot 3\text{H}_2\text{O}$ (Wako). $\text{LiOH}\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{PO}_4\cdot 3\text{H}_2\text{O}$ were dissolved into purified water, and FeSO_4 solution was added subsequently. The molar ratio of the $\text{Li}:\text{Fe}:\text{P}$ was $x:1:1$ ($2 \leq x \leq 3$), and the concentration of FeSO_4 was controlled to be 0.1 mol dm^{-3} . The mixed solution of 40 mL was put into a Teflon-lined Parr reactor (inner volume: 120 mL), and it was heated at 170°C for 12 h. During this hydrothermal process, precipitation took place inside the reactor. After the hydrothermal reaction, the solution was cooled down to room temperature. This solution was filtered to separate the precipitated powder in the solution. The powder was washed with ultra pure water and acetone. Then the obtained sample was dried at 100°C for 1 h under vacuum. The thermogravimetry (TG, DTG-60, Shimadzu) was performed to investigate the thermal stability of the hydrothermally synthesized LiFePO_4 . XRD (RINT-UltimaII, Rigaku Co.) measurements with $\text{Cu K}\alpha$ radiation, and Raman spectroscopy (NRS-1000, Jasco) with 532 nm laser radiation were carried out to identify crystallographic phases of the prepared samples.

A beaker-type cell was fabricated for the electrochemical tests. A composite electrode was prepared by mixing the obtained sample, Ketjen black, and polytetrafluoroethylene (PTFE) in weight ratio of 80:15:5. This mixture was rolled into thin sheet with uniform thickness, and it was cut into pellet. This pellet was pressed to a titanium mesh with a pressure of 1500 kg cm^{-2} . A mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) containing $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ was used as an electrolyte. A lithium foil was used as anode, and electrochemical measurements were performed with two-electrode system. Charge–discharge test was performed using automatic charge–discharge equipment (HJR-110mSM6, Hokuto Denko) in a potential range of 2.0–4.5 V at 0.1°C rate (17 mA g^{-1}). All electrochemical experiments were conducted in an argon-filled glove box at room temperature.

3. Results and discussion

The scanning electron microscopy revealed that the particle size of hydrothermally synthesized samples were about $0.5 \mu\text{m}$. Fig. 1 shows the XRD patterns for the products synthesized with various mixed ratios of the starting materials. When the molar ratios of $\text{Li}:\text{Fe}:\text{P}$ were 2:1:1 and

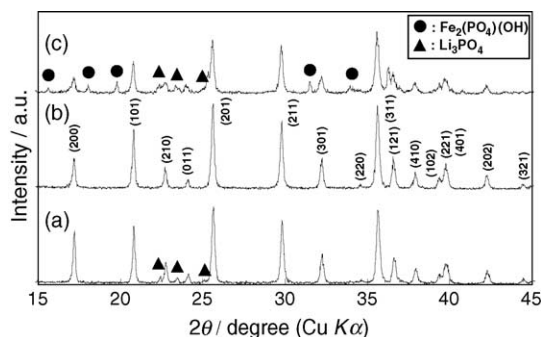


Fig. 1. XRD patterns of hydrothermally synthesized LiFePO_4 with various molar ratios of $\text{Li}:\text{Fe}:\text{P}$ of starting materials. (a) 2.0:1:1, (b) 2.5:1:1, and (c) 3.0:1:1.

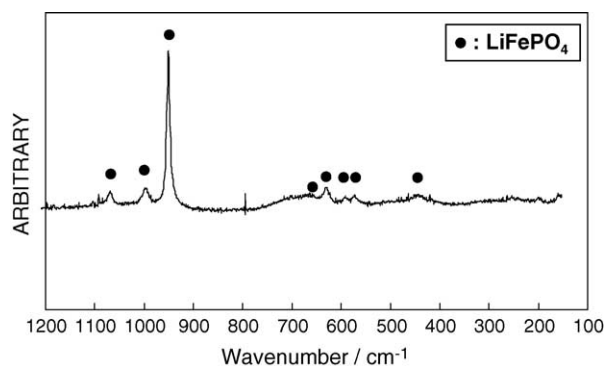


Fig. 2. Raman spectrum of hydrothermally synthesized LiFePO_4 with the molar ratio of $\text{Li}:\text{Fe}:\text{P} = 2.5:1:1$.

3:1:1 of starting solution, the peaks due to impurities such as Li_3PO_4 and $\text{Fe}_2(\text{PO}_4)\text{OH}$ appeared besides the XRD pattern of LiFePO_4 . On the other hand, no peak due to impurity components was observed for the sample synthesized with the molar ratio 2.5:1:1 of $\text{Li}:\text{Fe}:\text{P}$. Fig. 2 shows Raman spectrum of the LiFePO_4 synthesized by using the molar ratio of $\text{Li}:\text{Fe}:\text{P} = 2.5:1:1$. The peaks observed in Fig. 2 agree very well to the assignments reported in the literature [17].

Fig. 3 shows charge and discharge curves of the LiFePO_4 synthesized by using the molar ratio of $\text{Li}:\text{Fe}:\text{P} = 2.5:1:1$. The very flat charge and discharge curves were observed at

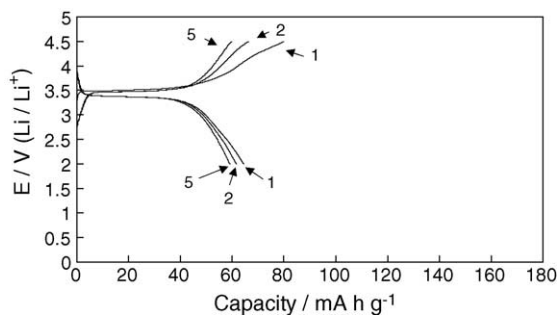


Fig. 3. Charge and discharge curves of hydrothermally synthesized LiFePO_4 with the molar ratio of $\text{Li}:\text{Fe}:\text{P} = 2.5:1:1$.

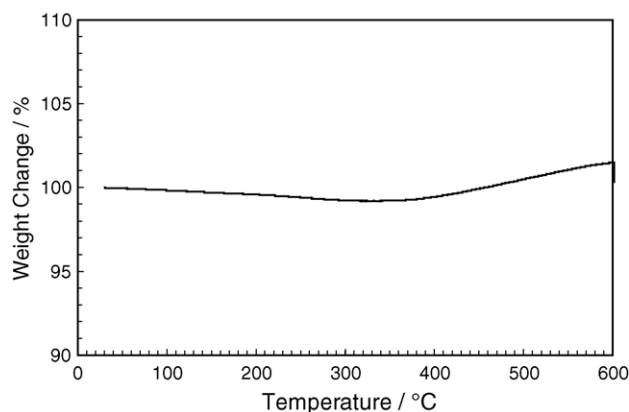


Fig. 4. TG curve of hydrothermally synthesized LiFePO₄. TG measurement was carried out under N₂ atmosphere, and heating rate was 5 °C min⁻¹.

3.5 V versus Li/Li⁺, which was an intrinsic electrochemical property of LiFePO₄ [3]. The theoretical capacity of LiFePO₄ is 170 mAh g⁻¹. However, the discharge capacity was estimated to be 64 mAh g⁻¹, which was considerably smaller than the theoretical one. This result indicates that the hydrothermally synthesized LiFePO₄ sample contains electrochemically inactive impurities, which were detected by neither XRD nor Raman spectroscopy. Such impurities should be amorphous.

Fig. 4 shows the TG result of the hydrothermally synthesized LiFePO₄. TG measurement was carried out under nitrogen atmosphere. The weight change was less than 1% in the range from 50 to 400 °C. Therefore, significant decomposition of LiFePO₄ did not take place in this temperature range, and the sample did not contain any crystal water. The oxidation of the sample might take place at higher than 400 °C due to residual oxygen in the furnace. In order to confirm the existence of amorphous phase in the hydrothermally synthesized LiFePO₄, the sample was annealed at 400 °C for 1 h in argon atmosphere. The XRD pattern of the annealed sample (not shown here) was very similar to Fig. 1(b). On the other hand, the Raman spectrum of annealed LiFePO₄ shown in Fig. 5(a) was different from that of non-annealed one (Fig. 2). There are several peaks in the ranges of 200–500 cm⁻¹ and 600–800 cm⁻¹, which were not observed for non-annealed

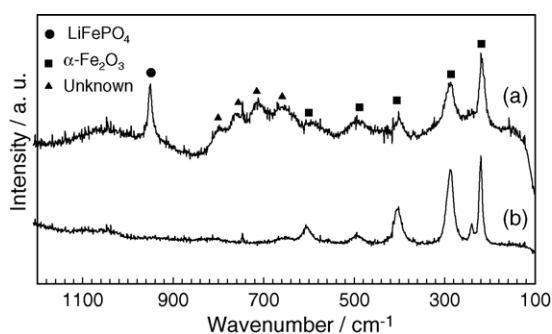


Fig. 5. Raman spectra of LiFePO₄ annealed at 400 °C (a) and pure α-Fe₂O₃ (b).

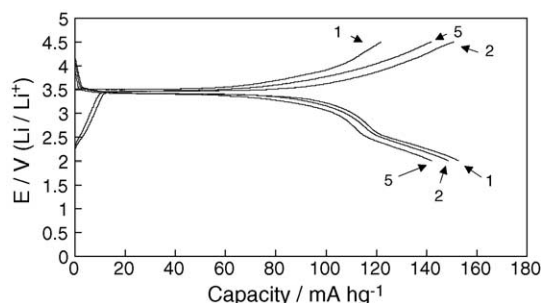


Fig. 6. Charge and discharge curves of LiFePO₄ annealed at 400 °C.

LiFePO₄. The peaks between 600 and 800 cm⁻¹ cannot be assigned at present. The peaks between 200 and 500 cm⁻¹ can be attributed to small amount of α-Fe₂O₃. The Raman spectrum of pure α-Fe₂O₃ is shown in Fig. 5(b) as a reference. The assignments of Raman peaks of LiFePO₄ and α-Fe₂O₃ were documented in the literatures [17,18]. Raman spectroscopy is sensitive to the surface of materials compared with XRD. It was considered that a small amount of α-Fe₂O₃ existed on the particle surface. This indicated that small amount of Fe²⁺ was oxidized to Fe³⁺ during hydrothermal process and/or annealing process. The amorphous phase including Fe³⁺ might be generated on the particle surface. Probably, this amorphous phase was crystallized during the heat treatment at 400 °C.

Fig. 6 shows the charge and discharge curves of the annealed LiFePO₄. The charge and discharge capacities were 150 mAh g⁻¹, which was larger than that of the non-annealed LiFePO₄. However, besides 3.5 V plateau, another plateau at 2.5 V appeared. This electrochemical behavior may be due to impurity phase. The discharge capacity at 3.5 V plateau was about 110 mAh g⁻¹, and it was still larger than that of non-annealed LiFePO₄ (Fig. 3). This suggests that the additional heat treatment increases the charge and discharge capacities of hydrothermally synthesized LiFePO₄ probably due to the crystallization of amorphous Li–Fe–PO₄ compounds. The plateau observed at 2.5 V can be attributed to the charge–discharge of α-Fe₂O₃. In fact, the first discharge capacity of the annealed sample was larger than the first charge capacity. It has been reported that Li⁺ ion can be inserted into α-Fe₂O₃ [19,20]. Li⁺ ion was inserted into α-Fe₂O₃ in the first discharge at 2.5 V, while the Li⁺ ion did not exist in the structure of α-Fe₂O₃ of the pristine electrode. The Li⁺ ion insertion and extraction took place reversibly in the subsequent cycles.

4. Conclusion

Phospho-olivine LiFePO₄ was synthesized from LiOH, FeSO₄, and (NH₄)₃PO₄ by hydrothermal process at 170 °C. The optimized molar ratio of Li:Fe:P in the starting solution was 2.5:1:1. The charge and discharge capacities at 3.5 V of hydrothermally synthesized LiFePO₄ were 65 mAh g⁻¹.

The additional heat treatment at 400 °C in argon atmosphere was effective to crystallize the amorphous phase on the particle surface of hydrothermally synthesized LiFePO₄. Raman spectroscopy revealed that the existence of α-Fe₂O₃ on the particle surface of the annealed LiFePO₄. The charge and discharge capacities of the annealed LiFePO₄ were 150 mAh g⁻¹. Two plateaus at 3.5 and 2.5 V were observed in the charge–discharge curves for the annealed LiFePO₄. The 2.5 V plateau was correlated with the Li⁺ insertion into α-Fe₂O₃. Further efforts to prepare high performance LiFePO₄ via hydrothermal process and analysis of the surface state of LiFePO₄ are underway, and it will be reported in due course.

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