

Short communication

Electrochemical properties of LiFePO_4 prepared via hydrothermal route

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Available online 17 November 2006

Abstract

LiFePO_4 as a cathode material for rechargeable lithium batteries was prepared by hydrothermal process at 170 °C under inert atmosphere. The starting materials were LiOH , FeSO_4 , and $(\text{NH}_4)_2\text{HPO}_4$. The particle size of the obtained LiFePO_4 was 0.5 μm . The electrochemical properties of LiFePO_4 were characterized in a mixed solvent of ethylene carbonate and diethyl carbonate (1:1 in volume) containing 1.0 mol dm^{-3} LiClO_4 . The hydrothermally synthesized LiFePO_4 exhibited a discharge capacity of 130 mA h g^{-1} , which was smaller than theoretical capacity (170 mA h g^{-1}). The annealing of LiFePO_4 at 400 °C in argon atmosphere was effective in increasing the discharge capacity. The discharge capacity of the annealed LiFePO_4 was 150 mA h g^{-1} .

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Keywords: Hydrothermal synthesis; LiFePO_4 ; Lithium batteries

1. Introduction

Phosphates LiMPO_4 ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{or Ni}$) have been investigated intensively as promising cathode materials for lithium batteries [1–15]. Among this series of materials, LiFePO_4 is a low cost material and highly compatible to the environment. LiFePO_4 has 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. These characteristics provide an excellent safety under abuse conditions of the batteries [3]. LiFePO_4 can be synthesized using conventional solid-state reactions [1]. However, it is difficult to attain its full capacity, because its electronic conductivity is very low, and diffusion of Li^+ ion in the olivine structure is slow [1,8]. Several alternative synthetic methods have been applied to the preparation of LiFePO_4 . It has been reported that the control of particle size is useful in increasing the charge and discharge capacities of LiFePO_4 [5,6]. In addition, highly dispersed conductive substances such as carbonaceous materials and some metals in the cathode composite electrode were reported as being efficient additives [5–10].

The hydrothermal synthesis is a useful method for preparing fine particles. It also has other advantages such as a simple process and energy efficient. Yang et al. have already demon-

strated the hydrothermal synthesis of LiFePO_4 [16,17]. We have prepared LiFePO_4 via a hydrothermal route and reported that the surface impurity on the LiFePO_4 particle gives a significant influence on its electrochemical properties [18–20]. The impurity was amorphous phase containing Fe^{3+} , which was formed on the particle surface during the hydrothermal process. It has been also reported that the addition of ascorbic acid to the precursor as a reducing agent is useful in prohibiting undesirable oxidation of Fe^{2+} during hydrothermal process [19]. In the present study, LiFePO_4 was hydrothermally synthesized under strictly controlled inert atmosphere, and its electrochemical behavior was characterized.

2. Experimental

LiFePO_4 was prepared by hydrothermal process from $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{HPO}_4$. $\text{LiOH}\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were dissolved into purified water, and then FeSO_4 aqueous solution was added subsequently. In order to prohibit the conversion of Fe^{2+} to Fe^{3+} , the water was degassed by N_2 gas bubbling for 30 min prior to preparing the starting solution, and the mixing process was carried out under nitrogen atmosphere. The concentration of Fe^{2+} in the precursor solution was controlled to be 0.5 mol dm^{-3} . The molar ratio of the Li:Fe:P in the precursor solution was $x:1:1$ ($1 \leq x \leq 3$). The precursor solution of 40 mL was put into a Teflon-lined Parr reactor (inner volume: 120 mL) with nitrogen gas, and the reactor was heated at 170 °C

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in an oven for 12 h. During this hydrothermal process, precipitation took place inside the reactor. After the hydrothermal reaction, the reactor was cooled down to room temperature. The precipitated powder was washed with ultra pure water and acetone. Then the obtained powder was dried at 110 °C for 1 h under vacuum. In some cases, heat treatments for hydrothermally synthesized LiFePO_4 were carried out in an electric tube furnace under purified argon gas flow (200 mL min^{-1}). The crystalline phases were identified with X-ray diffraction (XRD, RINT-2000, Rigaku Co.) with $\text{Cu K}\alpha$ radiation. The morphology of particle was observed with a scanning electron microscope (SEM, JSM-5310, JEOL). The thermogravimetry (TG, DTG-60, Shimadzu) was performed to investigate the thermal stability of the hydrothermally synthesized LiFePO_4 .

The performance of the LiFePO_4 as cathode was evaluated using a coin-type cell (size: 2016) with a lithium metal anode. A composite electrode was prepared by mixing the LiFePO_4 , Ketjen black, and polytetrafluoroethylene (PTFE) in weight ratio of 80:15:5. This composite was rolled into a thin sheet with uniform thickness (ca. $150 \mu\text{m}$), and it was cut into a circle shape (13 mm diameter). The mass of LiFePO_4 contained in the composite cathode was ca. 12 mg cm^{-2} . The electrolyte was a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v) containing $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$. Galvanostatic charge and discharge tests were performed using an automatic charge–discharge equipment (HJR-110mSM6, Hokuto Denko Co.) in the voltage range of 2.0–4.2 V at various rates ranging from 0.1 to 5 C ($1 \text{ C} = 170 \text{ mA g}^{-1}$). All electrochemical measurements were carried out at 25 °C.

3. Results and discussion

Fig. 1 shows XRD patterns of hydrothermally synthesized LiFePO_4 . The XRD patterns of samples prepared with $x = 1$ and 2 agree very well with that of phospho-olivine LiFePO_4 [13,14], and no impurity phase was detected. Yields of the hydrothermal process were very good. Although all solid products could not be collected, yields were about 95% for both cases of $x = 1$ and 2. This suggested that almost all the Fe^{2+} species in the precursor solutions were converted to LiFePO_4 . In the case of $x = 3$, Li_3PO_4 and $\text{Fe}_2(\text{PO}_4)\text{OH}$ were obtained as impurities due

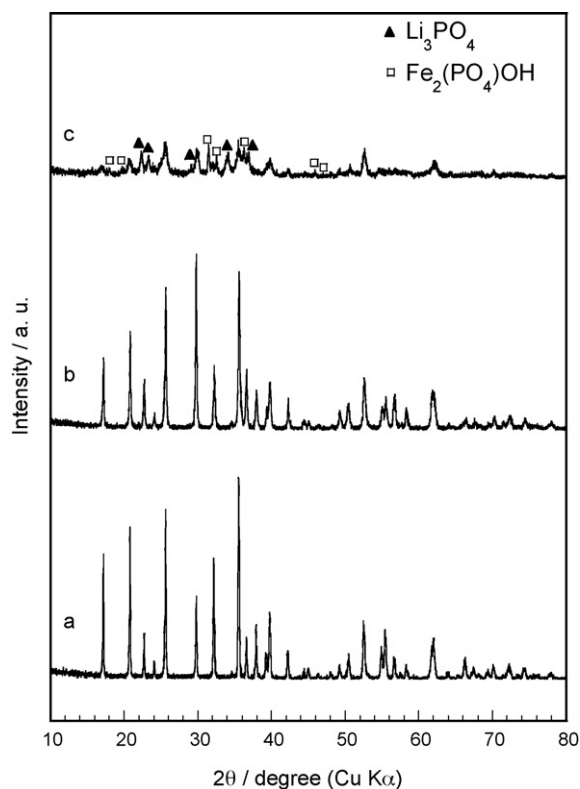


Fig. 1. XRD patterns of the materials prepared by hydrothermal method at 170 °C. The molar ratios of Li:Fe:P in the precursor solutions were 1:1:1 (a), 2:1:1 (b), and 3:1:1 (c).

to the strong basic condition. The pH values of the precursor solutions of $x = 1, 2,$ and 3 were 8.04, 8.99, and 9.54, respectively. This suggests that slightly basic or neutral conditions are preferable for hydrothermal synthesis of LiFePO_4 [20,21]. Fig. 2 displays SEM images of the prepared LiFePO_4 powders. The obtained powders were composed of agglomerated particles. The primary particle sizes of samples of $x = 1$ and 2 were 3 and $0.5 \mu\text{m}$, respectively. The primary particle size decreased as increasing the concentration of LiOH in the precursor solution.

Fig. 3 shows the TG result of the hydrothermally synthesized LiFePO_4 ($x = 2$). TG measurement was carried out under nitrogen atmosphere. The weight change was less than 2.5% in the

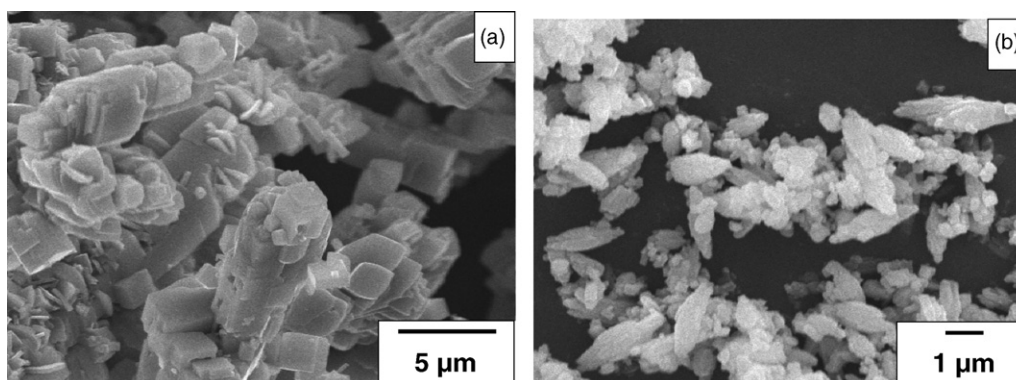


Fig. 2. SEM images of LiFePO_4 prepared by hydrothermal method at 170 °C. The molar ratios of Li:Fe:P in the precursor solutions were 1:1:1 (a) and 2:1:1 (b).

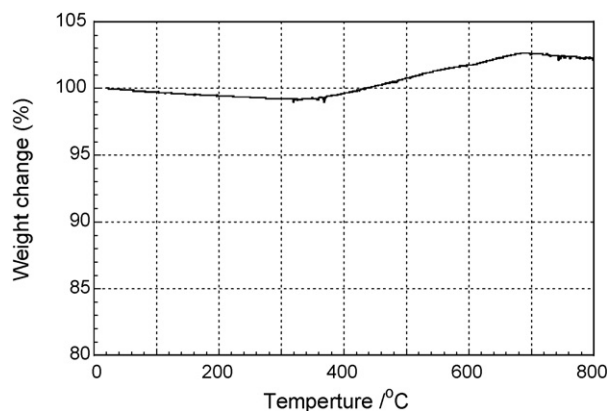


Fig. 3. TG curve of hydrothermally synthesized LiFePO_4 . TG measurement was carried out under N_2 atmosphere, and heating rate was 5°C min^{-1} .

range from 50 to 800°C . The sample prepared with $x=1$ showed the similar thermal behavior. Therefore, significant decomposition of LiFePO_4 did not take place in this temperature range, and the sample hardly contained any crystal water. Some oxidation of the sample might take place at higher than 400°C due to residual oxygen in the furnace.

The charge and discharge curves of hydrothermally synthesized LiFePO_4 samples ($x=1$ and 2) are shown in Fig. 4. The charge and discharge were carried out at 0.1 C (17 mA g^{-1}). In both cases, the plateaus were observed in the charge and discharge curves at the potential of 3.5 V versus Li/Li^+ . This electrochemical behavior corresponded to the solid-state redox of $\text{Fe}^{2+/3+}$ in the LiFePO_4 accompanying with Li^+ ion extraction and insertion [1]. The discharge capacity of the sample of $x=1$ was 30 mA h g^{-1} , which was considerably smaller than the theoretical capacity (170 mA h g^{-1}). On the other hand, the discharge capacity of the sample of $x=2$ was 130 mA h g^{-1} . The small discharge capacity of the sample of $x=1$ was due to the relatively large particle size. The electronic conductivity of LiFePO_4 is very low, and diffusion of Li^+ ion in the olivine structure is slow [1,5,8]. The smaller particle size, which is helpful for accessibility of the redox centers, is preferable to achieve larger capacity.

In order to enhance the charge–discharge performance of the LiFePO_4 , a heat treatment was carried out. The hydrothermally synthesized LiFePO_4 ($x=2$) was annealed at 400°C under argon

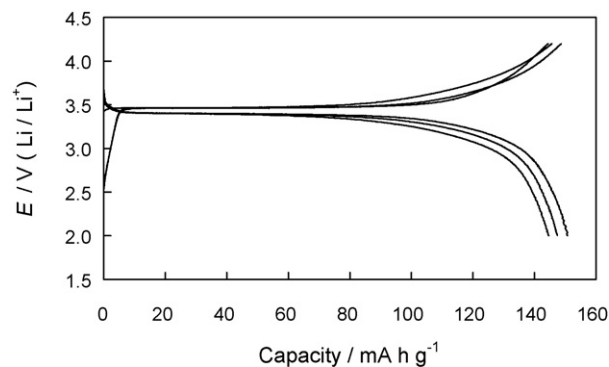


Fig. 5. Charge and discharge curves of LiFePO_4 annealed at 400°C in Ar. LiFePO_4 was prepared from the precursor of $\text{Li:Fe:P}=2:1:1$. The charge–discharge measurements were carried out at 0.1 C rate.

gas flow for 1 h. The XRD pattern and the particle morphology of the annealed LiFePO_4 (not shown here) were very similar to those of non-annealed sample. In fact, the particle morphology changed at higher than 500°C because of grain growth, and heat treatment at higher temperature was avoided. Fig. 5 shows the charge and discharge curves of the annealed LiFePO_4 . The charge and discharge capacities were increased by the annealing. The discharge capacity was about 150 mA h g^{-1} , which was 88% of the theoretical capacity. This result shows a good agreement with our previous work [19]. It was considered that small amount impurity, which was electrochemically inactive, was involved in the hydrothermally synthesized LiFePO_4 . The impurity was assumed to be amorphous, because no impurity phase was detected by XRD (Fig. 1(b)). The amorphous component might exist on the particle surface and be non-conductive layer. After the heat treatment, it might be crystallized and activated.

Finally, the rate capability of the annealed LiFePO_4 ($x=2$) was evaluated. Fig. 6 shows discharge curves of the LiFePO_4 measured at various rates. The electrode was charged up to 4.2 V at 0.1 C rate prior to each discharge. The annealed LiFePO_4 exhibited a good rate capability, and the discharge capacity at 1 C (2 mA cm^{-2}) rate was ca. 110 mA h g^{-1} . This good rate capability was due to the small particle size of the LiFePO_4 as discussed above. So far, extensive studies have been conducted to enhance the electronic conductivity of the material by using some carbon coating techniques [5–11]. Carbon coating on the particle is effective in decreasing the impedance of the cathode [11], which

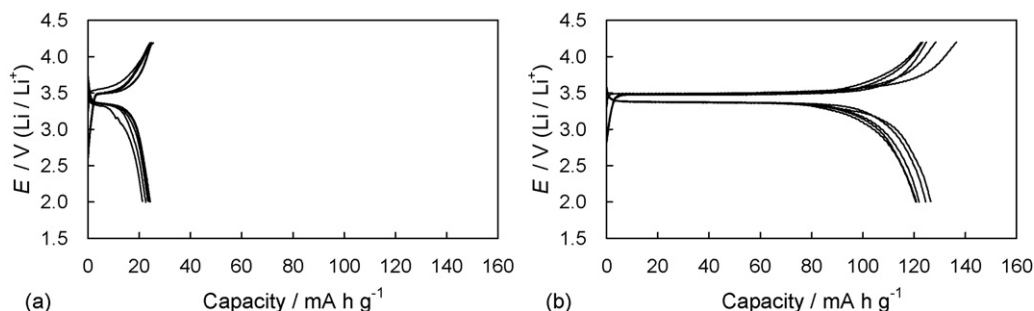


Fig. 4. Charge and discharge curves of LiFePO_4 prepared by hydrothermal method at 170°C . The molar ratios of Li:Fe:P in the precursor solutions were 1:1:1 (a) and 2:1:1 (b). The charge–discharge measurements were carried out at 0.1 C rate.

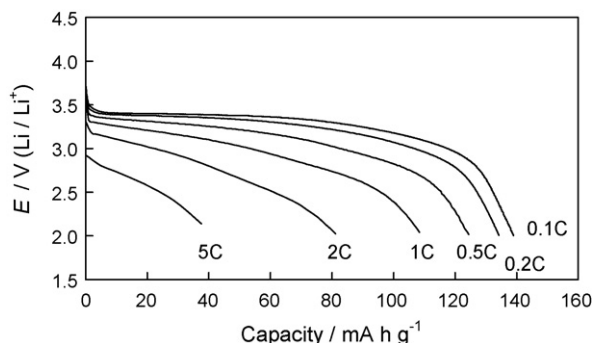


Fig. 6. Discharge curves of LiFePO_4 annealed at 400°C in Ar. LiFePO_4 was prepared from the precursor of $\text{Li}:\text{Fe}:\text{P} = 2:1:1$. The electrode was charged up to 4.2 V at 0.1 C rate prior to each discharge and discharged at various rates.

may further enhance the charge–discharge performance of the LiFePO_4 prepared via the hydrothermal route. Further efforts to improve the charge–discharge performance of the hydrothermally synthesized LiFePO_4 are underway in our group, and it will be reported in due course.

4. Conclusions

LiFePO_4 was hydrothermally synthesized from LiOH , FeSO_4 , and $(\text{NH}_4)_2\text{HPO}_4$ under inert atmosphere at 170°C . The control of pH and concentration of the precursor solution was important to obtain LiFePO_4 as a main product by hydrothermal process. The particle size of the obtained LiFePO_4 was $0.5\ \mu\text{m}$. The discharge capacity of hydrothermally synthesized LiFePO_4 was $130\ \text{mA h g}^{-1}$. Annealing of the LiFePO_4 at 400°C in argon atmosphere was effective in improving the charge–discharge performance. The discharge capacity of the annealed LiFePO_4 was $150\ \text{mA h g}^{-1}$.

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