

Short communication

Synthesis of olivine-type LiFePO_4 by emulsion-drying method

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Abstract

Olivine-type, orthorhombic, LiFePO_4 powders with small particle size have been successfully synthesized by the emulsion-drying method. The electronic and crystal structure is analyzed by X-ray absorption spectroscopy (XAS) and X-ray diffraction Rietveld refinement. The powder calcined at 750°C shows the highest discharge capacity of 125 mAh g^{-1} with excellent cycle stability. The discharge capacity of this powder increases to 154 mAh g^{-1} on increasing the addition of carbon black as a conductive agent up to 40 wt.%. In a rate capability test, the discharge capacity is completely recovered and retained up to the 700th cycle.
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1. Introduction

Padhi [1] was the first to demonstrate that orthorhombic LiFePO_4 could be used as a positive electrode (cathode) for rechargeable lithium batteries. This compound having a theoretical capacity of 170 mAh g^{-1} , is environmentally benign and inexpensive, and shows good cycle stability due to the structural similarity between the charged and the discharged states. In particular, LiFePO_4 exhibits very good thermal stability [2,3]. These properties make it an attractive candidate for large batteries that are to be required for electric and hybrid electric vehicles.

The drawback with this material is its low electrical (electronic and ionic) conductivity, which limits the electrochemical properties according to the charge–discharge rate and operating temperature [4]. Many studies have been performed to overcome this problem, and it has been found that particle-size reduction and electronic conductivity enhancement by means of conducting agents are both effective [5–8]. These factors are largely affected by the method of preparation, that is, LiFePO_4 has a large range of electrochemical properties that depend on the synthesizing conditions. Therefore, to produce commercially available LiFePO_4 , a proper preparative method is an urgent research target.

Up to now, several processes have been adapted to make LiFePO_4 . Solid-state reactions have been used in most

cases [1,3]. Carbothermal reduction and mechanochemical activation methods that can be classified as solid-state reactions have been reported to be effective in enhancing the electrochemical properties [9,10]. The first production of LiFePO_4 was achieved via hydrothermal synthesis, but encountered the problem that some iron ions resided on the lithium sites and thereby deteriorated cell performance [10]. In such liquid-phase synthesis, a solid phase is usually formed through a chemical reaction in the liquid phase. Hence, compared with solid-state reaction methods, some advantages such as homogeneous mixing, lower calcination temperature and smaller particle sizes are expected for the resultant powders.

In this study, an emulsion-drying method has been employed as a new liquid-phase synthesis route for making olivine-type LiFePO_4 .

2. Experimental

The orthorhombic LiFePO_4 was synthesized by direct calcination of a dried emulsion precursor. LiNO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were used as the starting materials and details of the synthesis route have been reported previously [11]. The dried emulsion precursor powders were calcined under argon flow at a heating rate of 5°C per minute to various temperatures.

X-ray diffraction (XRD) patterns of the calcined powders were obtained with an X-ray powder diffractometer (Cu $\text{K}\alpha$ radiation). The data were collected in steps of 0.03° (2θ)

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over the range $10\text{--}120^\circ$ (2θ) with a constant counting time of 30 s per step. Rietveld refinements were performed using the FullProf 2000 program [12]. Scanning electron microscopy (SEM) was performed in order to examine the effect of calcination temperature on powder morphology. X-ray absorption spectra at the Fe K-edge for the samples were recorded at the 3Cl beam lines of PLS (Pohang Light Source, Korea) with a Si(1 1 1) double-crystal monochromator. The storage ring was operated with the electron energy of 2 GeV and a current from 100 to 120 mA. The data were collected in the transmittance mode with a step size of 0.03 eV in ionization chambers filled with 75% N₂ and 25% Ar gas. Energy calibration was conducted before all measurements using the Fe metal foil.

Electrochemical studies were carried out in Li|LiClO₄ in PC|LiFePO₄ cells. The positive electrodes were prepared by blending the active material with carbon black and PVDF (polyvinylidene fluoride) in NMP. The slurry was spread on 1 cm² nickel ex-met, and then dried in a vacuum oven at 120 °C for 2 days. The cells were assembled in a glove-box filled with argon. Various current densities were applied in charge–discharge experiments over a voltage range of 4.0–3.0 V versus Li using a WBCS3000 (Wonatech, Korea) battery cycle tester.

3. Results and discussion

The dried emulsion precursor was calcined at different temperatures, viz., 650, 750 and 850 °C. The XRD patterns of the resulting LiFePO₄ compounds are given in Fig. 1.

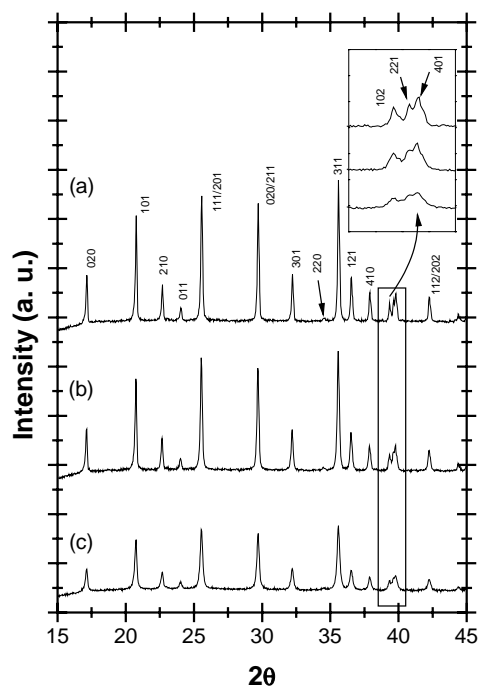


Fig. 1. XRD patterns for LiFePO₄ compounds calcined at (a) 850 °C, (b) 750 °C and (c) 650 °C.

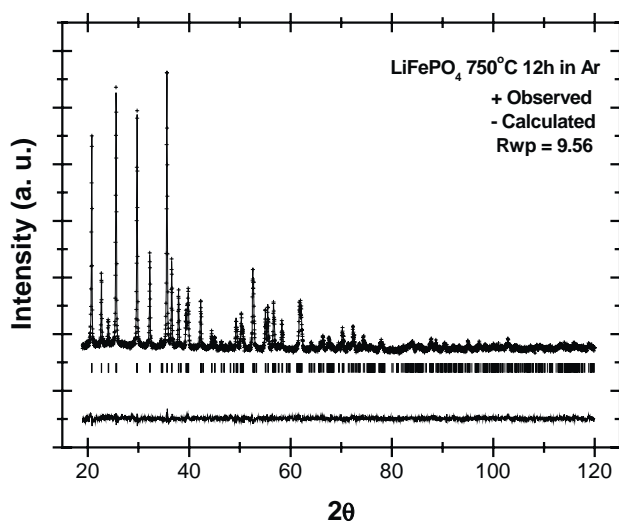


Fig. 2. X-ray Rietveld refinement fitting of LiFePO₄ compound calcined at 750 °C.

Single-phase LiFePO₄ was obtained for all compounds. The Rietveld refinement result for LiFePO₄ calcined at 750 °C is given in Fig. 2. A space group of Pnma was chosen as the best refinement model. The observed and calculated patterns match very well. The same refinement was also conducted for compounds calcined at 650 and 850 °C. The results are summarized in Table 1. The reliability factors (R_{wp}) for all the compounds were good, i.e., around 9%. The change in lattice parameters with increasing calcination temperature is shown in Fig. 3. Between 650 and 750 °C, there is a jump in the 'a' and 'b' lattice parameters but virtually no change in the lattice parameter 'c'. On increasing the temperature from 750 to 850 °C, the lattice parameters 'a', 'b' and 'c' are slightly increased. These variations in lattice parameters with increasing temperature are considered to be caused either by a change in crystallinity or by a variation in the valence state of iron ions. The ionic radius of divalent iron (Fe²⁺, 0.770 Å) is somewhat larger than that of trivalent iron (Fe³⁺,

Table 1
Results of structural analysis obtained from X-ray Rietveld refinement of LiFePO₄

Formula	LiFePO ₄		
Space group	Pnma		
Calcination temperature (°C)	650	750	850
Cell constant (Å)	$a = 10.3168(5)$	$a = 10.3263(4)$	$a = 10.3269(3)$
	$b = 6.0014(3)$	$b = 6.0056(2)$	$b = 6.0067(2)$
	$c = 4.6909(2)$	$c = 4.6909(2)$	$c = 4.6919(1)$
Fe–O ₁	2.2167(8)	2.2286(7)	2.2365(7)
Fe–O ₂	2.0877(7)	2.1129(7)	2.0962(7)
Fe–O ₃	2.0907(6)	2.0928(5)	2.0955(5)
Fe–O ₃	2.2397(6)	2.2522(6)	2.2541(5)
Fe–O (average)	2.1609	2.1719	2.1720
R_{wp} (%)	9.19	9.53	9.73

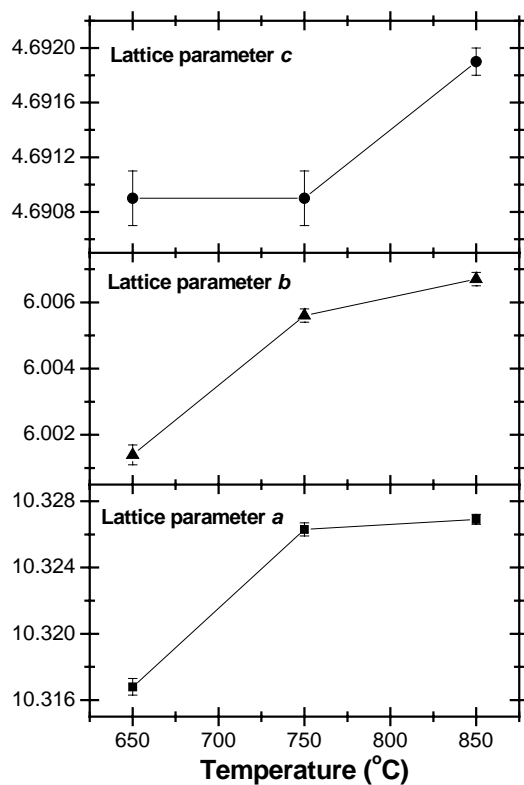


Fig. 3. Variation of lattice parameters of LiFePO₄ compounds with increasing calcination temperature.

0.645 Å). Therefore, if the iron ion is reduced from Fe³⁺ to Fe²⁺, the lattice parameters will increase. This appears to be plausible because Fe(NO₃)₃·9H₂O was used as an iron source in which the valence state of iron is 3. The results of Fe K-edge XANES for iron ions in compounds with different calcination temperatures are presented in Fig. 4. FeC₂O₄ and Fe₂O₃ were used as a standard for divalent and trivalent iron, respectively. No change in the valence state of the iron

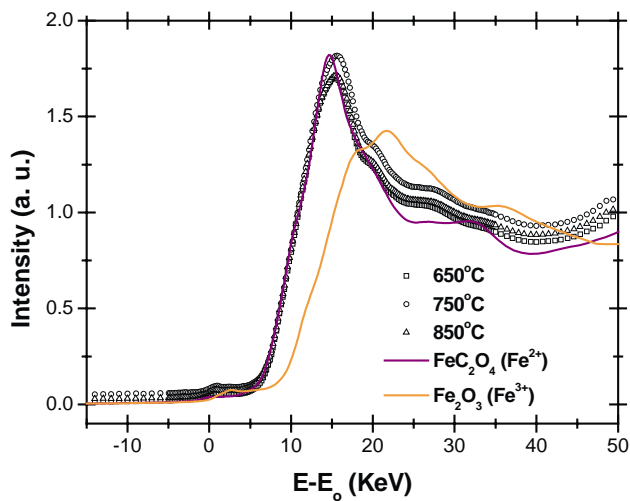
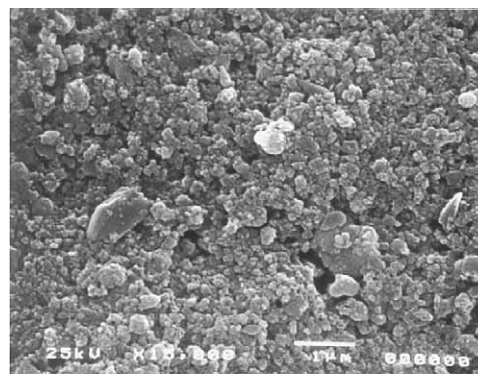


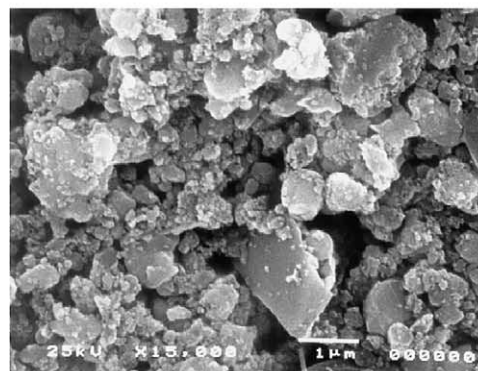
Fig. 4. Fe K-edge XANES spectra of LiFePO₄ compounds ($E_0 = 7112$ eV).

ions with heat-treatment conditions is observed. Thus, the variation in lattice parameters with temperature between 650 and 750 °C can be related to a change in crystallinity. The inset in Fig. 1 shows a jump of crystallinity between 650 and 750 °C.

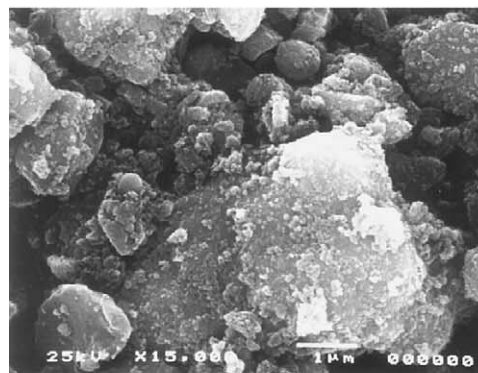
Scanning electron micrographs of compounds with different calcination temperatures are presented in Fig. 5. Obviously, increasing the calcination temperature leads to crystal growth. The particle size for the compound calcined at 650 °C is less than 400 nm. By contrast, the particle size of the compound calcined at 850 °C ranges from 1 to 3 μm.



(a)



(b)



(c)

Fig. 5. Electron micrographs of LiFePO₄ compounds calcined at (a) 650 °C, (b) 750 °C and (c) 850 °C.

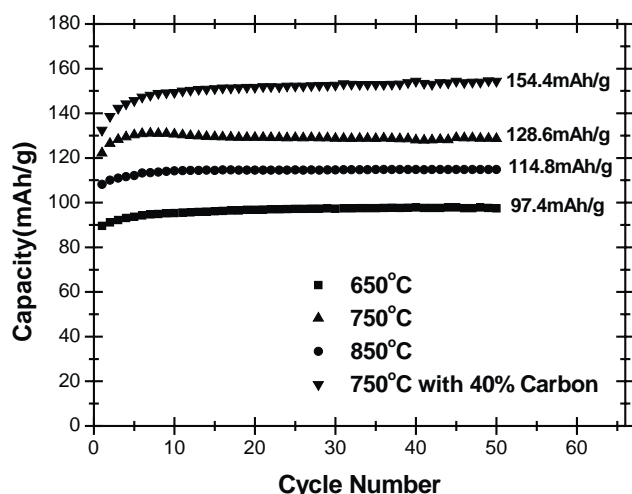


Fig. 6. Cycle performance LiFePO_4 compounds calcined at various temperatures.

The cycle performance of LiFePO_4 compounds prepared at various temperatures is given in Fig. 6. The experiments were performed in the range 3.0–4.0 V at a current density of 20 mA g^{-1} . For all compounds, the discharge capacities increase up to about the 10th cycle, and then stabilize. In spite of its small particle size, the compound calcined at 650°C for 12 h delivered the lowest capacity. For LiFePO_4 , small particle size is important for enhancing the electrochemical properties [8]. In this study, however, it appears that the ef-

fect mentioned above can dominate the particle-size effect. The capacity obtained from the compound calcined at 750°C is higher than that obtained at 850°C due to the particle-size effect. Therefore, calcination at 750°C is a good compromise between crystallinity and particle-size effects.

The cycle performance of the LiFePO_4 powder calcined at 750°C with 40 wt.% carbon black as a conductive agent is also given in Fig. 6. The initial discharge capacity is 132.5 mAh g^{-1} , and increases to 151 mAh g^{-1} at the 10th cycle. This behavior could be caused by an enhancement in conductivity through the use of a large amount of conducting medium, as reported previously [6,7].

The dependence of electrochemical performance on current density is shown in Fig. 7. When 100 mA g^{-1} was applied, a discharge capacity of 110 mAh g^{-1} was obtained. After 100 cycles, current density had increased to 300 mA g^{-1} , which resulted in a capacity loss about 18.2%. Capacity loss increased by 24.1% at a current density of 400 mA g^{-1} , but when 100 mA g^{-1} was applied again after the 300th cycle. The discharge capacity completely recovered and remained constant up to the 700th cycle.

4. Conclusions

Olivine-type, orthorhombic, LiFePO_4 with small particle size has been prepared by the emulsion-drying method. Structural analysis by X-ray Rietveld refinement and SEM observations reveal that 750°C is the best calcination temperature to obtain a well-crystallized LiFePO_4 compound with relatively small particle size. This compound exhibits excellent cycleability and rate capability up to 700 cycles. Therefore, it is concluded that the emulsion-drying method is a promising means for the synthesis of olivine-type, orthorhombic LiFePO_4 .

Acknowledgements

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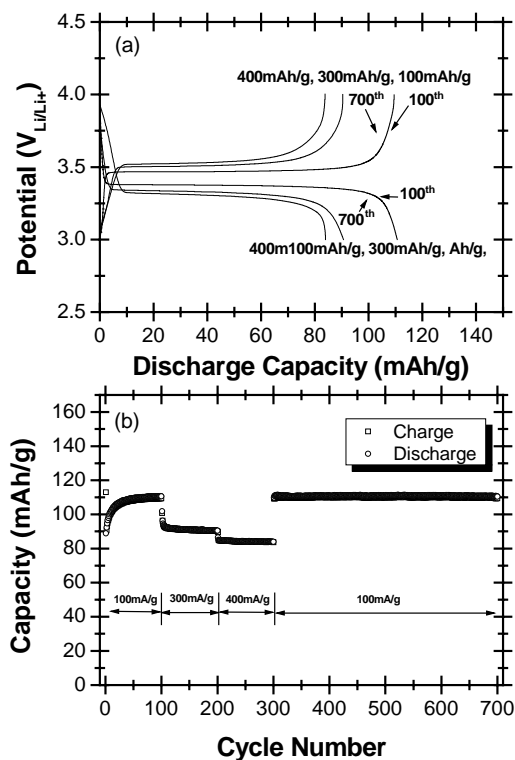


Fig. 7. (a) Charge–discharge curves and (b) cycle stability of LiFePO_4 compound calcined at 750°C with applied current.

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