Hydrothermal Processing and Characterization of LiFePO₄ Crystalline Particles

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Abstract: LiFePO₄ particles have been synthesized via the hydrothermal process from LiOH·H₂O, FeSO₄·7H₂O and H₃PO₄ as starting materials and characterized as cathode materials for lithium ion secondary batteries. However, LiCoO₂ has many problems such as high cost and amount of global resources. Recently, lithium iron phosphate (LiFePO₄) has been receiving great attention under the consideration of cost and resource issues [1]. Moreover, LiFePO₄ has a three dimensional framework due to strong P-O covalent bonds in (PO₄)³⁻ polyanion, which prohibit the dissociation of oxygen in its structure. This provides an excellent safety and stable operation of battery even under unusual conditions [2].

In this study, hydrothermal process was employed for the preparation of LiFePO₄, because this method has advantages such as simple aqueous system and low energy consumption [3]. The additional heat treatment in inert gas atmosphere was examined to improve the charge-discharge performance of LiFePO₄. Moreover, size-controlled LiFePO₄ particles were prepared and the effect of the particle size on several properties was also investigated.

2. EXPERIMENTAL
2.1. Synthesis and material characterization
LiOH·H₂O, FeSO₄·7H₂O and H₃PO₄ were selected as starting materials. The mixing ratio (Li:Fe:P) before hydrothermal treatment was set at 3:1:1. First of all, FeSO₄ aqueous solution and H₃PO₄ were mixed together. LiOH aqueous solution was then added to the mixed solution, yielding a slate-blue suspension. The resulting suspension was transferred in a Teflon-lined stainless steel autoclave and hydrothermally treated under various conditions. After the hydrothermal treatment, the precipitate was filtered and the resulting precipitate powder was rinsed with acetone. Then, the obtained powder was dried at 80°C for 15 h. The annealing treatment was carried out at 400°C for 2 h under N₂ atmosphere in order to improve the crystallinity. In addition, hydrothermally prepared LiFePO₄ powder was ball-milled from 30 min to 1 h in ethanol to reduce its particle size.

X-ray diffraction (XRD) measurement using CuKα radiation with a monochromator was performed to identify crystallographic phases of resultant products. The morphology of the samples was observed by scanning electron microscopy (SEM). The specific surface areas of LiFePO₄ powders were measured by Brunauer-Emmett-Teller (BET) technique.

2.2. Electrochemical characterization
The charge-discharge capacities were characterized by fabricating a coin-type cell. LiFePO₄ powder was mixed with carbon (LiFePO₄:carbon = 2:1.3) and binder solution (polyvinylidene fluoride (PVDF):N-methylpyrrolidone = 2:23). The resulting paste was cast on an Al foil to prepare a cathode. Li-metal was used as an anode material. The liquid electrolyte used was 1M LiPF₆ dissolved in a 3:7 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The coin-type cell was assembled using these electrodes and electrolyte. The charge-discharge measurements were carried out in the 3.0-4.3V ranges at a current density of 5 mA/g.

3. RESULTS AND DISCUSSION
Fig. 1(a) shows the XRD patterns of products synthesized for a constant time of 24 h. LiFePO₄ particles were synthesized at 150°C. When the treatment temperature was higher than 170°C, the diffraction lines of unknown phases began to emerge clearly with LiFePO₄ phase. On the other hand, Fig. 1(b) shows the XRD patterns of products synthesized at a constant temperature of 150°C. Although the diffractions of unknown phases were

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slightly observed, LiFePO$_4$ particles were obtained when the duration time of treatment was longer than 8 h.

Fig. 2 shows SEM images of LiFePO$_4$ powders synthesized under various hydrothermal conditions. When the treatment temperature was raised from 150°C to 190°C, no significant change in the morphology of LiFePO$_4$ particles was observed. On the other hand, increase of the treatment time leads to grain growth. However, when the treatment time was longer than 24 h, LiFePO$_4$ particles having similar morphology were reproducibly observed. LiFePO$_4$ particles synthesized at 150°C for 24 h had the particle size of about 5 μm and the specific surface area of around 3 m$^2$/g. The charge-discharge performance was examined after annealing at 400°C for 2 h in a N$_2$ flow. However, this sample showed a poor charge-discharge capacity (10-12 mAh/g). It may be attributable to the difficulty of the lithium ion diffusion through the LiFePO$_4$/FePO$_4$ interfaces in large particles [4].

Next step, the planetary ball milling was carried out in order to reduce particle size of LiFePO$_4$ powders. Fig. 3 shows SEM images of LiFePO$_4$ powders well-ground by the planetary ball milling. The average particle size was found to be below 1 μm. The milling time of 1 h was sufficient to decrease the particle size around 1 μm maintaining the LiFePO$_4$ phase. The specific surface area of about 13 m$^2$/g was obtained and increased by more than four times. The charge-discharge property was examined after annealing at 400°C for 2 h in N$_2$.

Fig. 4 shows the charge-discharge curves of LiFePO$_4$ powder from 3.0 to 4.3V. The charge-discharge capacity of LiFePO$_4$ particles after milling was improved compared to that before milling treatment. This is due to the effect of reduction of particle size by the planetary ball milling. As the particle size becomes smaller, the reactive area for diffusion of lithium ions increases effectively improving charge-discharge properties. However, the charge-discharge capacity of the LiFePO$_4$ powder synthesized in this study was not sufficiently high compared with the theoretical value (170 mAh/g) [1] and those reported by other researchers [5,6]. The formation of the unknown secondary phase and the low capacities may be due to the fluctuation of lithium content in synthesized LiFePO$_4$ particles. Therefore, further optimization of the synthesis conditions, particularly precise control of the chemical composition (Li:Fe:P in LiFePO$_4$), is required to improve the electrochemical properties and it is currently under investigation.

**Fig. 2.** SEM images of LiFePO$_4$ powder after hydrothermal treatment, for 24 h at (A) 150°C, (B) 170°C and (C) 190°C, for (a) 15 h, (b) 24 h and (c) 48 h at 150°C.

**Fig. 3.** SEM images of LiFePO$_4$ powders, (a) before and (b) after planetary milling for 1 h in ethanol.

**Fig. 4.** Charge-discharge curves of LiFePO$_4$ powder after planetary milling and annealing at 400°C in N$_2$.

**4. CONCLUSIONS**

LiFePO$_4$ particles were successfully synthesized via the hydrothermal treatment using LiOH·H$_2$O, FeSO$_4$·7H$_2$O and H$_3$PO$_4$ as starting materials. LiFePO$_4$ particles were synthesized at 150°C for 24 h having the particle size of around 5 μm and the specific surface area of about 3 m$^2$/g. The specific surface area of LiFePO$_4$ powders increased by more than four times through the planetary ball milling for 1 h. The charge-discharge capacity of the LiFePO$_4$ was found to be improved by this milling treatment followed by the annealing at 400°C in N$_2$.

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**REFERENCES**