Hydrothermal Reaction by Microwave Heating for Synthesis of LiFePO_4 as Cathode Material

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LiFePO_4 was synthesized by a microwave hydrothermal heating (MH) method. The particle size of the product prepared by the MH method is in the range from 200 to 300 μm . The LiFePO_4 cathode materials thus obtained had a higher discharge capacity and better cycle performance than those of the LiFePO_4 samples prepared by a conventional hydrothermal reaction.

Key words: Hydrothermal reaction, Microwave, LiFePO_4 , Cathode material,

1. INTRODUCTION

Lithium-ion batteries [1] have been applied in many portable electronic devices because of a high energy density. Layered LiCoO_2 [2][3] is one of the earliest developed cathode materials, and its good performance and stability make itself one of the most commercially used cathode materials despite its toxicity and high cost. Recently, iron-related cathode materials have attracted attention. Iron compounds are very attractive materials. The potential use of various iron phosphates as active cathode materials in low-cost, rechargeable batteries is a special case of this. Lithium ion phosphate (LiFePO_4) is a promising candidate as a cathode material for lithium ion batteries [4]-[12]. LiFePO_4 with an ordered olivine structure has useful features; environment-friendly, inexpensive, abundant, relatively large theoretical capacity of 170 mAhg^{-1} , good thermal stability etc. In many studies, LiFePO_4 was synthesized by solid state methods, hydrothermal methods, and solution methods [13].

A drawback of LiFePO_4 is low electrical conductivity (10^{-9} - 10^{-10}Scm^{-1}). In order to overcome this disadvantage and utilize it as positive electrode material, two approaches have been widely in progress; minimizing the particle size and/or introducing conductive additives [18]. Small size particles have a larger active surface and effective diffusion volume. Therefore, appropriate particle sizes are important for LiFePO_4 cathode materials to reach both high energy density and good electrochemical performances [17].

Application of microwave heating technique to inorganic materials technology has been advanced in the field of sintering and joining of ceramics [14]. Characteristics of microwave heating involve internal heating, selective heating, rapid heating rates, and promotive diffusion effect. In a view of environmental and energy saving issues, microwave heating is promising technology. Therefore, we have paid our attention to the microwave hydrothermal (MH) heating reaction. It is known to have rapid heating rate, advance of convection, high crystallization rate, and often kinetics of chemical reactions is also different [15] due

to an essentially non-equilibrium process [16].

2. EXPERIMENTAL

2.1 Synthesis of LiFePO_4

The starting materials for the MH method were $\text{LiOH} \cdot \text{H}_2\text{O}$ (99% Koujyundo Chemical), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99.9% Kanto Chemical) and H_3PO_4 (85wt% solution Kamto Chemical). $\text{LiOH} \cdot \text{H}_2\text{O}$ was dissolved in a distilled water to obtain 1 mol dm^{-3} solution, and then H_3PO_4 solution and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ powder were added to the LiOH solution in a molar ratio for $\text{Li:Fe:P}=3:1:1$. First, we heated a mixture of these materials in the Teflon vessel at 150°C for 20min by a microwave digestion system (BERGHOF speedwave MWS-2). Later, the sample was engaged in suction filtration and was parched for the vacuum drying at 110°C for 1hr. The dried sample was used for the following measurements.

2.2 Characterization

The crystal structure of the sample powders were characterized by a powder X-ray diffractometer (MAC science, MXLabo) using a $\text{Cu K}\alpha$ radiation.

The microstructure of the sample powders were examined by an electron microscope (JEOL, JSM-5800) and a transmission electron microscope (JEOL, JEM-1200EX). Specific surface areas were measured with a Micromeritics (Shimazu, GA, USA) Fowsorb II 2300 system according to the BET multi-point method by nitrogen physisorption at 77K.

The cathodes used for electrochemical characterization were fabricated by blending the prepared active material powders with acetylene black and polytetrafluoroethylene (PTFE) binder in a weight ratio of 70 : 25 : 5. Two-electrode electrochemical cells consisting of a lithium metal foil as a negative electrode, a polypropylene separator, and an electrolyte of 1 M LiClO_4 in propylene carbonate / dimethyl carbonate (1 : 1 in volume) were assembled in an argon-filled glove box. The electrochemical tests of cells were performed using an automatic galvanostatic charge-discharge unit (Hokutodenko, HJ-101M6) between 2.5 and 4.5 V at a

current density of 0.2 C rate.

3. RESULT AND DISCUSSION

Figure 1 shows the X-ray diffraction profiles of the LiFePO_4 samples synthesized by the MH heating method and a conventional hydrothermal method. The diffraction pattern of the material synthesized by the MH method have a single phase LiFePO_4 as well as the sample synthesized by a conventional hydrothermal method. Both the samples have no impurity. In the MH heating method, a single phase of LiFePO_4 is obtained in a quite short time.

Figure 1. X-ray diffraction patterns for LiFePO_4 , (a) synthesized by the MH method, (b) synthesized by the conventional hydrothermal, (c) simulation.

Electron micrographs of the LiFePO_4 products prepared by the MH method and the conventional hydrothermal method are presented in Figure 2. The particles of the sample prepared by the MH method (Figure 2 (a)) are very small and agglutinated. On the other hand, the particle size of the product prepared by the conventional hydrothermal method (Figure 2 (b)) is around 500 nm–2 μm in diameter. Diamond-shaped plate crystals were observed in the product by the conventional hydrothermal method although the sample have a broad size distribution.

Figure 3 shows TEM images of LiFePO_4 . The particle size of the sample synthesized by the MH method is around 200–300 nm in diameter. On the other hand, the sample by the conventional hydrothermal method have large sizes with 500 nm–2 μm . The BET surface area of the sample synthesized by the MH heating method was $17 \text{ m}^2\text{g}^{-1}$ while that of the synthesized by the conventional method was $4.9 \text{ m}^2\text{g}^{-1}$. Consequently, the sample synthesized by the MH heating method is thought to be a good method to give small average particle diameters and narrow size distributions.

Charge/discharge performance for the cathodes prepared by these samples was investigated at a constant current 0.2C rate in a range between 2.5 and 4 vs. Li/Li^+ .

Figure 2. SEM images for LiFePO_4 synthesized by (a) MH method and (b) conventional hydrothermal

Figure 3. TEM images for LiFePO_4 synthesized by (a) MH method and (b) conventional hydrothermal

Typical electrochemical charge/discharge profiles are shown in Figure 4 for the samples prepared at 150 $^{\circ}\text{C}$

for 20 min by the MH heating method and Figure 5 for the sample prepared at 150°C for 3 hr by the conventional hydrothermal reaction. The initial discharge capacity of the sample synthesized by the MH heating method as a lithium ion battery was achieved to 117 mAhg⁻¹, which corresponds to about 68.8% of the theoretical capacity. On the other hand, that of the sample synthesized by the conventional method have 138 mAhg⁻¹, which corresponds to about 81% of the theoretical capacity. At the 10th cycle, the discharge capacity of the MH prepared sample was achieved to 106 mAhg⁻¹, and that of the sample synthesized by the conventional method was achieved to 113 mAhg⁻¹. When comparing them to the theoretical capacity, the efficiencies of 62.4% and 66.5% were obtained and there is no great difference. The decrease of discharge capacity from 1st cycle to 10th cycle is 8.1% in the MH heated sample, and that of the sample heated by the conventional method is 14.5%. In the sample synthesized by the MH heating method, there is less capacity deterioration on charge/discharge cycle, compared with the sample synthesized by the conventional hydrothermal method. This is because of that the MH heated sample has a small particle size distribution which make the lithium diffusion path reduced.

Figure 4. Charge/discharge performance of LiFePO₄ prepared by MH method

Figure 5. Charge/discharge performance of LiFePO₄ prepared by conventional hydrothermal method

The cycle performance for the samples prepared by the MH heating method and the conventional hydrothermal method are shown in Figure 6. The decrease in discharge capacity from 1 to 10 cycles of the sample synthesized by the MH method was 23 mAh/g. Compared with this, that of the sample synthesized by the conventional hydrothermal method was 10 mAh/g. The sample prepared by the conventional hydrothermal method has the rate of decrease of 13.5%, and the sample prepared by the MH method has the rate of a decrease of 5.9% compared with the theoretical capacity. The good cycle performance observed in the products synthesized by the MH method. Small size LiFePO₄ particle leads this excellent cycling characteristics.

Figure 6. Cycle performance of LiFePO₄

In this study, the sample with a much better performance than that with the sample synthesized by the conventional hydrothermal method was obtained using the MH method. Furthermore, the MH heating method is environmental-friendly so that synthesis time is largely shortened within 20 min in comparison with 3 hr for conventional hydrothermal methods. However, further efforts are needed to increase discharge capacity of LiFePO₄.

4. CONCLUSION

LiFePO₄ particles with quite small size were prepared by the MH method at a temperature of 150°C for 20 min. The obtained LiFePO₄ particle was very fine of 200-300 nm, and their agglutinate was observed. The initial discharge capacity of the obtained LiFePO₄ exhibited 117 mAh/g. The sample prepared by the MH method have a good cycle performance. LiFePO₄ with a good performance, which may be due to small particle sizes by given the MH method.

5. REFERENCES

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