

Synthesis and Evaluation of Olivine Material Coated with Carbon

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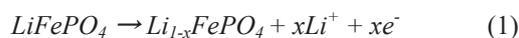
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Abstract. Lithium iron phosphate, LiFePO₄, was synthesized by hydrothermal process and subsequently coated with carbon by the thermal decomposition of acetylene gas. The products were characterized by XRD, SEM, and TG-DTA. As-synthesized LiFePO₄ was submicron sized plate-like particle. After heating at various temperature in nitrogen atmosphere, the particle size and the crystalline sizes were grown with increasing the heating temperature. Above 700°C, the grain growth was remarkably. Carbon coating temperature was set at 500-600°C because of fine particle and good crystallinity. As a carbon raw material, acetylene gas was flowing to the as-synthesized LiFePO₄ in nitrogen atmosphere, and the LiFePO₄/C composite was obtained. TG curves showed weight loss above 500°C, which was thought to be associated with carbon layer composition.

1 Introduction

LiCoO₂ has been used as a cathode material for lithium ion batteries. Usage of cobalt prohibits to reduce the material costs because of scarcity. The amount of needed lithium ion battery increases significantly for the application of EV and energy storage system. Then, the development of Co-free cathode material is quietly important. Lithium iron phosphate, LiFePO₄, is the material, in which iron having high number of Clark is rich in resources, and is inexpensive. Padhi et al. reported that polyanion material like as LiFePO₄ and Li₂FeSiO₄, showed the charge-discharge property as cathode for LIB. [1] LiFePO₄ shows 3.5 V v.s. Li of reversible potential and 170 mAhg⁻¹ of theoretical capacity. These values are the energy density comparable to LiCoO₂.

LiFePO₄ has orthorhombic crystal olivine type structure. The crystal structure of LiFePO₄ is showed in Figure 1. FeO₆ octahedra and PO₄ tetrahedra have the structure that a ridge shared one side, and Li arranges it in a b-axis. PO₄ tetrahedra is strongly connected by covalent bond, and it restrains the oxygen decomposition. The structure stability of produce for LiFePO₄ the safety. On the other hand, ionic conduction for LiFePO₄ is difficult because a Li ion in structure is localized electronically. The discharge reaction of LiFePO₄ is showed in the following equation.



In the discharge reaction, FePO₄ phase is formed by deintercalation of the lithium ion. With the biphasic reaction of LiFePO₄ and FePO₄, equilibrium potential is seen in around 3.5V. Both structure is similar, and cycle capability with charge-discharge reaction is good because the symmetricalness of both does not change. As a model

of these reaction, domino-cascade model is proposed. [2] In a border between LiFePO₄ and FePO₄ with the disorder of the atom placement, electronic conductivity is relatively high, and it is thought that Li⁺ is deintercalated from there. The conductivity of 10⁻⁸-10⁻⁹ S/cm for LiFePO₄, however, is very lower than that of 10⁻² S/cm for LiCoO₂. [3] Therefore, the problem for commercial use is this low conductivity, and the improvement of conductivity can lead to the good rate capability. In order to improve the conductivity, many researchers have been tried. First, focused on the material composition, it reported that the multi cation doped LiFePO₄ showed the good rate capability. It was because that the doped cations, such as Mg²⁺, Al³⁺, Zr⁴⁺, Nb⁵⁺ and W⁶⁺, reduce the volumetric resistance. [4] On the other hand, the microstructure for the electrode materials is also important. If the electrode material makes a fine particle, its reactivity increases due to the improvement of the specific surface area. In addition, the diffusion length of the ion is shortened by microparticulation, and this is quietly advantageous. There were the reports focused on the morphology with high performance. [5] In order to obtain the finer particle, a various synthesis method has been examined. A. Yamada reported that the optimization of solid state reaction conditions produced a fine particle, and it showed a good performance. [6] However, the diffusion necessary for a complete reaction needs the condition at high temperature for long-time. As the synthesis method at lower temperature, many methods such as hydrothermal method [7], sol-gel method [8, 9], and splay pyrolysis method [10] are reported. In this study, using the hydrothermal process, the synthesis of LiFePO₄ composed of a fine particle was attempted.

In order to cope with high rate charge-discharge reaction, LiFePO₄ needs not only the microparticulation but also

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the composition with conductive assistant. Coating on LiFePO_4 particle surfaces is suitable to make a little conductive assistant in the composition methods. The conduction layer has two kinds of an electronic conduction and the ionic conduction. B. Kang reported the ionic conduction layer. [11] The amorphous $\text{Li}_4\text{P}_2\text{O}_7$ phase as the ionic conduction layer was precipitated by making non-stoichiometric composition. This amorphous phase prohibit the grain growth, and finer particle would be obtained. As the result, the obtained active material showed good property with 130 mAh/g of the discharging capacity at high rate. On the contrary, as the electronic conduction layer, carbon coating has been examined. There are various kinds of raw carbon material and that composition methods. Then, the LiFePO_4/C composite produced by heating the mixture of the active material and ractose in inert atmosphere [12], and depositing carbon from heat decomposition of propylene gas. [13] The products by wet method are easy to be affected to the crystallinity and the grain growth among heating process. In this research, LiFePO_4 was synthesized by hydrothermal method, and the products was coated with carbon by the thermal decomposition of acetylene gas. The influence of carbon coating process to LiFePO_4 was examined.

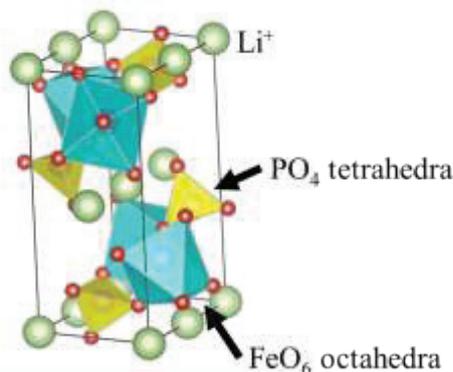


Figure 1. Olivine-type structure of LiFePO_4 .

2 Experimental procedure

2.1 Synthesis

2.1.1 Synthesis of LiFePO_4 by hydrothermal process

$\text{LiOH}\cdot\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (Wako Chemical) were used as starting materials. Each starting materials were weighted to become a molar ratio of Li: P: Fe = 2: 1: 1. After measurement, they were put into distilled water in Teflon vessel and vigorously mixed for a few minutes. Teflon vessel with mixed solution was encapsulated into autoclave and was hydrothermally treated at 200°C for 24 hours. Obtained slurry was filtrated and then dried at 50°C for overnight.

2.1.2 Heat treatment of LiFePO_4

LiFePO_4 synthesized by hydrothermal treatment was heated in nitrogen atmosphere. 0.5g of LiFePO_4 was measured, and it was put in carbon crucible. Carbon crucible was moved in a furnace. After the furnace was evacuated slowly, nitrogen gas was carried out with flow 5L/min for 30min. Then, the flow quantity of nitrogen gas was controlled 0.2L/min. The furnace was raised up to target temperature ($T=400 - 800^\circ\text{C}$) with heat rate of $4^\circ\text{C}/\text{min}$ and kept it for 2 hours.

2.1.3 LiFePO_4/C composites by thermal decomposition

Rotary kiln (Takasago Industry Co., Ltd.) showed in Figure 2 was used for the manufacture of the LiFePO_4/C composite. 5g of LiFePO_4 was measured, and it was put in carbon capsule for product. Capsule was rolled at the rate of 1rpm. In order to reduce the oxygen concentration in the capsule, N_2 gas was carried out with flow of 5L/min for 15min. Then, 0.2 L/min of acetylene gas was flowing to the capsule through a pipe of the alumina. The capsule was heated externally at 550°C and 600°C for 1 hour, respectively.

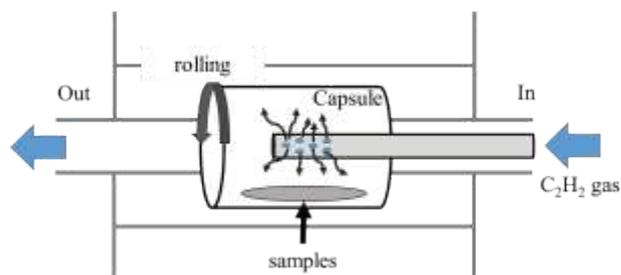


Figure 2. Schematic rotary kiln

2.2 Evaluation

The crystal phase of samples was indexed by XRD (UltimaIV, Rigaku Co., Japan). Scans were performed at $2\theta = 10-40^\circ$ with scan rate of $4^\circ/\text{min}$ using $\text{Cu-K}\alpha$ radiation. In order to estimate the lattice parameter of samples, internal reference method was used using pure Si powder. The morphology was observed by FE-SEM (s-4500, Hitachi, Japan) with applied voltage of 15 kV. Thermal gravimetric analysis was carried out under air atmosphere between room temperature and 700°C , and the flow rate of the synthetic air was 2 mL/min.

3 Results and discussions

3.1. Synthesis of LiFePO_4 by hydrothermal process

LiFePO_4 was synthesized by hydrothermal process at 200°C for 24h. XRD patterns of the products were showed in Figure 3. The diffraction peaks attributed to olivine-type structure (JCPDS#83-2092) were shown, and the other peaks considered the secondary phase like Li_3PO_4 and Fe_2P were not confirmed. So, the products by hydrothermal method was identified as olivine-type

structure. The lattice parameter estimated by inter reference method was $a=10.336\text{\AA}$, $b=6.002\text{\AA}$, $c=4.695\text{\AA}$. This result was good agreement with JCPDS value ($a=10.3340\text{\AA}$, $b=6.0100\text{\AA}$, $c=4.6930\text{\AA}$). In the case of hydrothermal process, it was reported that the lattice parameter of LiFePO_4 depended on the reaction condition, especially reaction temperature. [14] At higher reaction temperatures, the unit cell volume was closer to the value of 290.5\AA^3 . The unit cell volume of the products by hydrothermal process was 291.3\AA^3 . As this difference was thought to be case by the crystal purity, the products by hydrothermal process in this study would have the relatively high crystallinity. In addition, the crystalline from (311) plane was 35 nm. Therefore, using of this as-synthesized LiFePO_4 , the heat-treatments for LiFePO_4 and the subsequent synthesis of LiFePO_4/C composite was attempted.

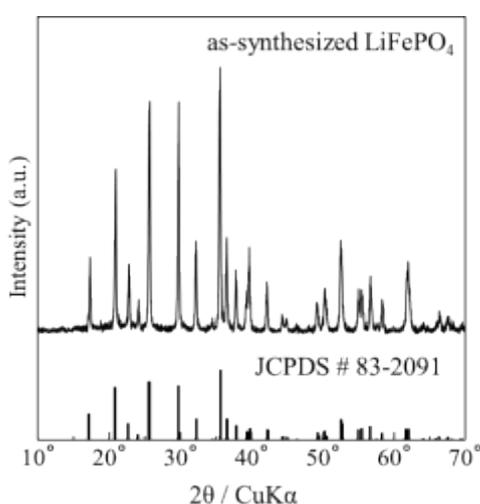


Figure 3 XRD patterns of the product synthesized by hydrothermal process.

3.2 Heat treatments of LiFePO_4

The as-synthesized LiFePO_4 was heated at 400-800°C in nitrogen atmosphere. Heating process is affected to the crystalline and the grain growth, so that is important role to influence the last products. The influence of heating process was examined. In Figure 4, the crystal phase of the products heated at various temperature in N_2 atmosphere was identified by XRD analysis. After heating, no diffraction peaks of the secondary phases except the peaks attributed olivine-type phase was appeared. In addition, the peak intensity increased with the higher temperature. Therefore, it was thought that the decomposition of LiFePO_4 or the phase transformation due to heating process was not occurred, after heat-treatments, but the crystallinity was well done. Next, the crystalline sizes were estimated by Scherer equation with the following, and the result was plotting in Figure 5.

$$D = K\lambda / \beta \cos\theta \quad (2)$$

The peaks belonged to nine lattice plane, (200), (101), (210), (201), (020), (301), (311), (121) and (410), were used for analysis. In (311) plane, the crystalline size was

41nm at 400°C larger than that of as-synthesized LiFePO_4 . The crystalline size tended to be increased linearly with heating temperature. At 800°C, 84nm of the crystalline size was estimated. Similarly, the same tendency was seen with the other diffraction peaks. In addition, the remarkable difference was appeared in the range of 600°C to 700°C.

In Figure 5, SEM images of the heated products was shown. The particle size of the as-synthesized LiFePO_4 was about $0.5\mu\text{m}$ and the morphology was plate-like particle. Finer particles were also observed in a part. There was no effect of particle size on longer reaction time, so no growth particle was generated during heat-treatments. Next, the size of samples at 400°C was about $0.5\mu\text{m}$ similar to no-heated samples and the shape became the round particle without finer particles. In addition, the particle size increased remarkably with heated temperature above 600°C. At 800°C, the coarse particle was observed, and the particle size was up to $1\mu\text{m}$. From these observation, it was thought that the grain growth occurred above 600°C.

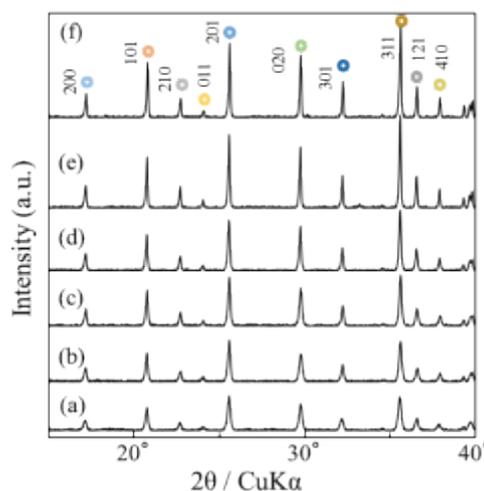


Figure 4 XRD patterns of the olivine products annealed in N_2 atmosphere at 400°C, 500°C, 600°C, 700°C, 800°C

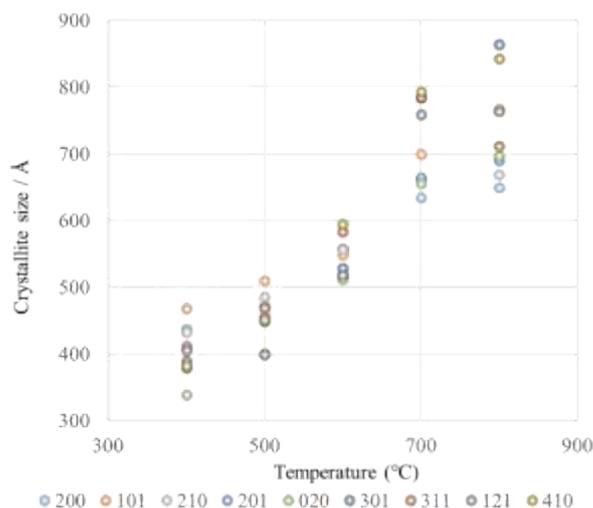


Figure 4 Crystalline sizes estimated by Scherer equation at each annealed temperature.

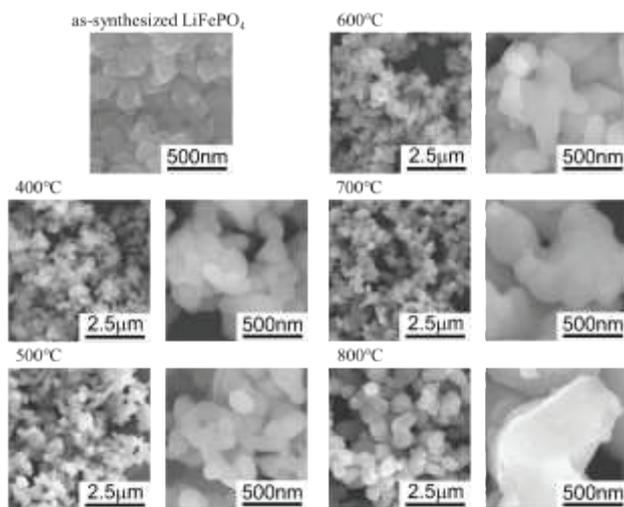


Figure 5 SEM images of the olivine products annealed in N₂ atmosphere at 400°C, 500°C, 600°C, 700°C, 800°C

As a result, heating process led to the improvement of the crystallinity. Below 600°C, amorphous phase or amorphous layer on particle surface was crystallized and the grain growth was not remarkable. Above 600°C, the grain growth was occurred, and it led to crystalline improvement.

3.3 LiFePO₄/C composites by thermal decomposition

The LiFePO₄/C composite was synthesized by the thermal decomposition of acetylene gas. With flowing of acetylene gas, the as-synthesized LiFePO₄ was heated at various temperature for 1 hour. The reaction temperature was settled at 550°C and 600°C which the crystallinity was improved and no grain growth occurred. XRD patterns of the products thermal-decomposed at 550°C and 600°C with flow of acetylene gas were showed in Figure 6. The diffraction peaks were attributed to olivine-type structure, and the secondary phase were not appeared. During this thermal decomposition, no oxidation was occurred for obtained olivine. SEM images were shown in Figure 7. The particle size was about 0.6µm. At both 550°C and 600°C, no grain growth during thermal decomposition was occurred remarkably. But, whereas the round particle was observed for samples at 550°C, the square shape was appeared partially at 600°C. The thermal decomposition of acetylene gas was exothermal reaction of 228kJ/mol. The morphology change of samples that morphology of squared shapes was similar to that at higher reaction temperature was thought to be related with exothermal reaction.

Thermal stability characterization of the obtained LiFePO₄/C composite was examined in air condition. TG-DTA curves were draw in Figure 8. In air, LiFePO₄ was oxidized with following the reaction. [15]



Estimated total weight gain is 4.2%. In case of the as-synthesized LiFePO₄, after initial weight loss associated to loss of water under 250°C, TG curves showed weight

gain of 2.8%. From DTA curves, the exothermic peak was observed at around 300°C, and the oxidation would be occurred. On the other hand, initial weight loss was not appeared for LiFePO₄/C products. Then, weight gain associated to the oxidation started at around 300°C and weight loss started at around 500°C. This weight loss was thought to be caused by the burning of carbon phase. Therefore, the LiFePO₄/C composite were successfully synthesized. In addition, the oxidation starting temperature was different from the LiFePO₄/C heated at 550°C in that heated at 600°C. Thus, it was thought that the oxidation reaction was dependent on coated carbon layer on LiFePO₄/C composites.

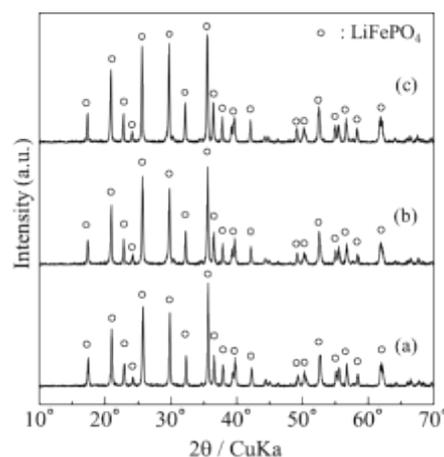


Figure 6 XRD patterns of LiFePO₄/C composite samples annealed in N₂ atmosphere. (a) as-synthesized LiFePO₄, (b) annealed at 550°C with flow of acetylene gas and (c) annealed at 600 °C with flow of acetylene gas.

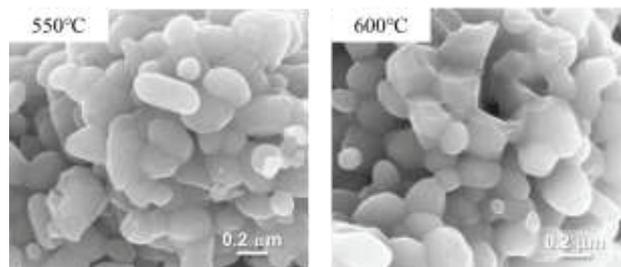


Figure 7 SEM images of LiFePO₄/C composite samples annealed in N₂ atmosphere at 550 °C, 600 °C

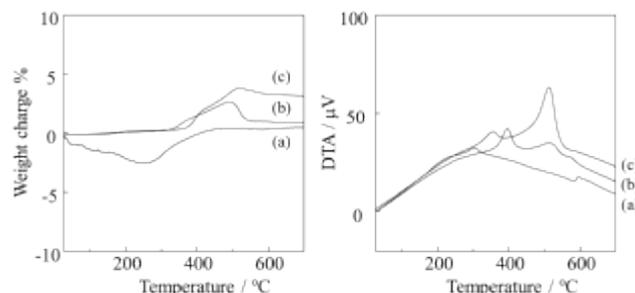


Figure 8 TG-DTA analysis of the LiFePO₄/C composite samples: (a) as-synthesized LiFePO₄, (b) annealed at 550°C and (c) annealed at 600°C.

4 Conclusion

In this study, LiFePO_4 was synthesized by hydrothermal method, and the products was coated with carbon by the thermal decomposition of acetylene gas. The influence of carbon coating process to LiFePO_4 was examined. The obtained LiFePO_4 samples was crystalline phase and lattice parameter was $a=10.336\text{\AA}$, $b=6.002\text{\AA}$, $c=4.695\text{\AA}$. Heating process was influenced to the microstructure and the crystallinity. Below 600°C , amorphous phase or amorphous layer on particle surface was crystallized. Above 600°C , the grain growth was occurred, and it led to crystalline improvement. Carbon coating temperature settled at $500\text{-}600^\circ\text{C}$ because of fine particle and good crystallinity. TG-DTA curves of the LiFePO_4/C products showed weight loss above 500°C , and it thought to be associated with carbon layer composition.

References

1. A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1609 (1997)
2. C. Delmas, M. Maccario, L. Croguennec, F. Le Cras and F. Weil, *Nature materials*, **71**, 665 (2008)
3. D. Morgan, A. Van der Ven and G. Ceder, *Electrochem. and Solid-State Lett.*, **7(2)** A30-A32 (2004)
4. S. -Y. Chung, J. T. Blocking and Y. -M. Chiang, *Nature Mater.*, **2**, 123 (2002)
5. H. Deng et al. , *Journal of Power Sources*, **220**, 342-347 (2012)
6. A. Yamada, S. C. Chung and K. Hinokuma, *J. Electrochem. Soc.*, **148**, A224 (2001)
7. J. Ni, M. Morishita, Y. Kawabe, M. Watada, N. Takeshi and T. Sakai, *Journal of Power Sources*, **195**, 2877-2882 (2010)
8. Y. Xu, Y. Lu, L. Yan, Z. Tang and R. Yang, *J. Power Sources*, **160**, 570 (2006)
9. Z. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong and M. Liu, *Electrochim. Acta*, **54**, 3206 (2009)
10. M. Konarova and J. Taniguchi, *J. Power Sources*, **195**, 3661 (2010)
11. B. Kang and G. Ceder, *Nature*, **458**, 190 (2009)
12. K. Zaghbi, A. Mauger, F. Gendron and C. M. Julien, *Chem. Mater.*, **20**, 462 (2008)
13. I. Belharouak, C. Johnson and K. Amine, *Electrochem. Commun.*, **7**, 983 (2005)
14. O. Xiuqin, P. Lin, G. Haichen, W. Yichen and L. Jianwei, *J. Mater. Chem.*, **22**, 9064 (2012)