LiFePO₄ is a promising cathode material for lithium-ion batteries which has attracted much attention because of its high energy density, low cost and superior safety. LiFePO₄ is synthesized using the citrate process in the oxygen and nitrogen atmospheres, and the crystal structure is analyzed by X-ray diffraction. The LiFePO₄ synthesized in the nitrogen atmosphere shows the single phase of Olivine structure but the second phase of Fe₂O₃ in the oxygen atmosphere. The microstructure observation indicates that the porous flower-like particles appears in the nitrogen and oxygen atmospheres but more clear structure of LiFePO₄ synthesized in nitrogen atmosphere. This study also compares the synthesis result of LiFePO₄ depending on the existence of the Chelate process after nitrogen phase of Olivine structure but the second phase of Fe₂O₃ in the oxygen atmosphere. The microstructure observation indicates that the porous flower-like particles appears in the nitrogen and oxygen atmospheres but more clear structure of LiFePO₄ synthesized in nitrogen atmosphere. This study also compares the synthesis result of LiFePO₄ depending on the existence of the Chelate process after nitrogen fixation of synthesis process. The LiFePO₄ with the addition of Chelate process shows the single phase but spherical particles are observed. The electrochemical characteristics of LiFePO₄ are evaluated using the coin cells. The LiFePO₄ with no additional chelate process shows the maximum discharge capacity of 160 mAh/g at 0.2C and 155 mAh/g at 1C. The capacity shows no reduction after the cycle test of 45 times with the current rate of 1C. Meanwhile, after chelate process, the LiFePO₄ shows 150 mAh/g at 0.2C and 108 mAh/g at 1C, which indicates substantial difference. After 5 cycles, its capacity has reduced more than 40 mAh/g.

Key-words : Citrate process, Lithium iron phosphate, Lithium ion battery, Cathode material, Flower-like shape

1. Introduction

The application of cathode material LiCoO₂, most commonly used in the lithium secondary battery, has been limited to mobile devices due to the limited Co deposits. This has led to numerous studies on alternative materials of LiCoO₂ such as LiFePO₄ and LiMnPO₄. Among them, LiFePO₄ of Olivine structure has been studied as possible alternatives of LiCoO₂ because of its low cost and rich deposits of Fe.

LiFePO₄ holds the voltage of 3.4 V and high discharge capacity of 170 mAh/g, and is suitable for the hybrid vehicle, hybrid electric vehicle and electric vehicle because it enables to produce larger capacity battery with low manufacturing cost. Also, it shows structure similarities between LiFePO₄ and FePO₄ during the process of lithium ion intercalation/deintercalation. However, the disadvantage of LiFePO₄ is a slower traveling rate of lithium ions in the charge and discharge process due to low electronic conductivity. Studies on the synthesis of nano-scale LiFePO₄ have been performed to overcome such a disadvantage. Moving distance of lithium ions are getting shorter with the particle size decrease during charge and discharge. This study seems to overcome slow rate of lithium ion. However, nano particles give a substantial increase in battery volume.

Synthesis methods of LiFePO₄ include the solid phase and liquid phase methods. The former may achieve highly pure substance but its problem is that it takes longer due to repeated synthesis processes and leads to larger particle size due to high calcination temperature. The latter includes the sol-gel and hydrothermal syntheses but these methods have difficulties in maintaining the stoichiometric composition of several metals in the synthesized powder even if the size of particles is smaller. This study is to synthesize LiFePO₄ by the citrate process using the citric acid. The citrate process is a method that manufactures the ceramic powder through the polymer precursor from the organic solvent containing the metallic salt of the end-oxide. Unlike existing liquid methods, this synthesis method can achieve a more uniform multicomponent complex oxide where the chain-structured polyester fixes metal ions. LiFePO₄ is synthesized and its electrochemical properties are analyzed by optimizing the chelate process and heat treatment process with the citrate process in this study.

2. Experimental

2.1 LiFePO₄ synthesis by citrate process

Ethylene glycol (HOCH₂CH₂OH, 99%), DAEJUNG CHEM), Citric acid [HOC(COOH)(CH₂COOH)₂, 99.5%, DAEJUNG CHEM], Lithium Carbonate (Li₂CO₃, 99%, JUNSEI), Ammonium Phosphate [(NH₄)HPO₄, 99%, JUNSEI], and Iron Chloride (FeCl₃, 98%, DAEJUNG CHEM) were used in this study.

1 mol of citric acid is added to the ethylene glycol of 4 mol heated to 90°C, dissolved by the agitation for 1 h at 200rpm and then 0.1 mol of lithium carbonate and 0.1 mol of ammonium phosphate are added at 30-min interval. After the complete dissolution, 0.1 mol of iron chloride is added and reacted for 30 min. The synthesized liquid is evaporated for 2 h at 300°C in the heating mantle to produce the black powder. The black powder undergoes the primary heat treatment for 2 h at 400°C to remove the remaining organic substance. Here, the heat treatment is provided in a nitrogen atmosphere to inhibit the Fe oxidation unlike the existing citrate process. After removing the organic substance, the powder goes through the secondary heat treatment for 5 h in N₂ or O₂ atmosphere at 600°C. The experiment procedure is schematically depicted in Fig. 1.
All the starting materials are dissolved and stirred at 200 rpm for 5 h at 130°C to compare the influence on the chelate process. As mentioned above, the synthesized solution is heated for 2 h at 300°C with the heating mantle to produce the black powder and the LiFePO4 powder is synthesized through the heat treatment process.

2.2 Analysis of the synthesized LiFePO4 powder

TG-DTA (SHMADZU, 60H, Japan) is used to analyze the thermal behavior of the synthesized LiFePO4 powder. The powder crystal phase is analyzed with the XRD (Rigaku, D-max-2500, Japan) and the microstructure is observed using the SEM (Jeol, JSM-6701F, Japan). The specific surface area of the powder is measured with the BET adsorption method (Micromeritics, TRISTA II 3020, USA).

The coin cell is manufactured to measure the electrochemical features of LiFePO4 synthesized by the citrate process. The slurry is prepared by mixing the active material (LiFePO4), electric conductor (Acetylene black) and bonding agent [6% polyvinylidine fluoride (PVDF)] with the ratio of 75:15:10 into the NMP (N-Methyl pyrrolidone, Aldrich) solvent. Then the slurry is applied to the Al foil with the thickness of 300 μm using doctor blade and then dried for 2 h at 120°C to evaporate the NMP. The dried pole plate is used as the cathode after punching with the pressure of 200 kPa. The electrolyte includes LiPF6, Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) and Diethyl Carbonate (DEC). Li metal is used as the anode. Such manufactured cells are used to perform the charge and discharge tests. The tests set up 1C rate as 150 mAh/g and the charge and discharge are provided with the current density of 0.2 C and 1C within the voltage range of 2.5–4.3 V.

3. Results and discussion

3.1 Heat treatment process optimization

The thermal behavior is analyzed with the TG-DTA to set up the primary heat treatment process to remove the organic substance from the black powder synthesized by the citrate process as shown in Fig. 2(a). The heat treatment process is required to remove the organic substance, accompanied with the starting material, before the heat treatment process to form the crystal phase in the citrate process. The exothermic peak in the range of 326–490°C results from the burning of the remaining organic substance. It means that the peak is associated with the ethylene glycol evaporation in the black powder, citric acid dissemble and organic substance combustion. Another exothermic peak appears around 560°C, assuming that the LiFePO4 phase is formed at the temperature. The primary heat treatment is provided at 400°C for the combustion of organic substances in the black powder and the secondary heat treatment temperature is determined to be 600°C according to the above results, the estimated forming temperature of 560°C.

Figure 2(b) shows the TG-DTA result of LiFePO4 after the heat treatment process as determined above. It shows that there exists almost no weight loss and no exothermic and endothermic peaks, indicating that no physical property change is found until 800°C. It means that the final output, LiFePO4, is in the thermal stability.

The secondary heat treatment is performed for the crystal phase formation of LiFePO4 with the black powder after the primary heat treatment at 400°C for 2 h under the nitrogen atmosphere. Here, the test is provided at two different atmospheric conditions (O2 and N2). Figure 3 shows the analysis of powders after the primary and secondary heat treatments.

As shown in Fig. 3(a), only the single phase of LiFePO4 exists after the primary heat treatment under the N2 atmosphere but the
secondary phase of Fe₂O₃, as well as LiFePO₄, are formed under the O₂ atmosphere. Figure 3(b) shows that the Fe₂O₃ is formed under the O₂ atmosphere in the powder which has completed secondary heat treatment. The existing synthesis study on LiFePO₄ shows that Fe is easily oxidized and forms Fe₂O₃ when it meets the oxygen. This means that an inert gas, not oxygen, shall be used for the entire heat treatment process to obtain the single phase of LiFePO₄.

Figure 4 shows the observation result of microstructure of LiFePO₄ depending on each heat treatment atmosphere. Spherical particles are mainly observed in the previous LiFePO₄ synthesis studies but flower-like shape particles are observed in all the conditions when heat treated at each atmosphere. The porous structure with a flower-like shape is observed between 3 and 7 μm combined with webbed-like particles with the size of 200 to 400 nm. A flower-like shape is clearly obtained in N₂ atmosphere even though the shape and size of the synthesized powder show little difference.

3.2 Effects of the chelate process

The effect of chelate process is investigated on the LiFePO₄ synthesis in the citrate process. The chelate process uniformly distributes metal ions of starting materials into the resin phase to form the metal-chelate complex and manufacture the polymeric resin through the poly-esterification reaction at the proper temperature (90–100°C). The previous experiment manufactured the black powder with such polymeric resin. However, the general citrate process additionally requires the chelate process for 2–5 h at the temperature between 120 and 130°C to form harder and more stable array of the polymeric resin. All the starting materials are dissolved and stirred at 200 rpm and 130°C for 5 h to compare the effects of chelate process. Other conditions remain the same.

Figure 5 shows the XRD analysis result of synthesized LiFePO₄ powders. The result shows that only single phase of LiFePO₄ is observed and its peak intensity is similar at all conditions regardless of the chelate process. Figure 6 shows the microstructure of the synthesized LiFePO₄ according to the chelate process. It is observed that the particle size and shape completely change despite insignificant differences in the crystal phase. In the previous test, the porous structure with flower-like shape was observed without the chelate process but spherical particles observed with the size between 200 and 400 nm after the chelate process. The specific surface areas of such powder are 97.9 m²/g for LiFePO₄ and become 94.1 m²/g before and after the chelate process, respectively. Such result suggests that the LiFePO₄ without chelate process contains relatively high capacity and is effective for the electrochemical assessment when manufacturing a cell of the same volume.

According to references, a flower-like shape is known as the particle type for the Fe₂O₃. In this study, a flower-like shape and spherical LiFePO₄ appeared depending on the existence of the reaction process even though no Fe₂O₃ phase was in the end-product. It is assumed that such flower-like shape is formed as the
aggregate state in the nucleation process to minimize the surface energy of metallic ions after the hydrolysis in the dissolution process, grows as webbed-shaped particles and finally forms the porous LiFePO₄ with the flower-like shape.

Earlier studies on a flower-like shape reported that the particles of a needle, round or plate-like shapes were self-assembled, rather than a webbed shape. It has never been reported that LiFePO₄ grows to particles of a webbed shape and then becomes a flower-like shape. It is assumed that the synthesis is performed without complete fixing process of metal ions by reducing the reaction time required for chelate process to fix and stabilize ions in the citric acid dissolved in ethylene glycol in comparison with the normal citrate process. This facilitates the electrolyte particle penetration into such porous LiFePO₄ and affects the electrochemical assessment.8)

3.3 Electrochemical assessment of LiFePO₄

The coin cell is prepared to examine the electro-chemical features of LiFePO₄ synthesized by the citrate process. (Fig. 7) The measurement is performed in the range of 2.5–4.3 V with the current rate of 1C and 0.2C.

The voltage and discharge capacity measured were 3.4–3.5 V and 155–160 mAh/g respectively at 1C and 0.2C current rate during the charge and discharge tests of LiFePO₄ without the chelate process. This figure is approximate to 170 mAh/g, a theoretical capacity of LiFePO₄, meaning that the efficiency reaches about 91–94% of excellent Coulomb efficiency. Mean-while, it is observed that the discharge capacity rapidly drops to 105 mAh/g at 1C even though the capacity is 150 mAh/g at 0.2C in the charge and discharge tests of LiFePO₄ with the chelate process.

The result may be related to the shape of LiFePO₄ of a flower-like structure in the microstructure observation as mentioned above. The porous LiFePO₄ with a flower-like shape is decided to show high efficiency because it has easier structure in the intercalation and deintercalation process of the lithium ions compared to the LiFePO₄ of a spherical shape.9)

It was confirmed that the LiFePO₄ of a flower-like shape synthesized by the hydrothermal or solvothermal liquid methods in the existing papers showed the discharge capacity from 90 to 145 mAh/g at the current rate of 1C. This value was lower than the results of charge and discharge tests (less than 10 mAh/g), indicating that a flower-like LiFePO₄ synthesized by the citrate process showed relatively better discharge capacity than the powder synthesized by another method.

Figure 8 shows the result of charge and discharge cycle tests using the two cells above. The cell made by the LiFePO₄ without the chelate process shows little capacity drop even after 45 charge and discharge tests at the current rate of 1C. Meanwhile, after the chelate process, the capacity of LiFePO₄ cell sharply drops more than 40 mAh/g after 5 cycles and continuously drops after that. The LiFePO₄ without the chelate process shows excellent electrochemical features of the discharge capacity and cycle behavior.
It would be difficult to make a direct comparison of AC impedance spectra for both particles with different morphologies because the spectra are affected by active surface of both particles [R1]. The higher capacity of flower-like LiFePO₄ can be reasonably explained by its unique morphology because the open porous structure can offer a large active surface and short diffusion length of Li⁺ during cycles, directly affecting electrochemical performance [R2]. Another possible reason is the limited electrolyte wettability of dense particles. The open porous structure allows sufficient electrolyte pathway, leading to a better performance.

4. Conclusion

In this study citrate process is used to synthesize LiFePO₄, cathode active material of the lithium-ion battery. The LiFePO₄ powder was formed after the primary heat treatment which removes organic substances from the synthesized powder and the secondary heat treatment which forms the crystal phase at 600°C. It is found out that all the heat-treated powders in O₂ and N₂ atmosphere show flower-like shapes. However, the heat-treated powder in O₂ atmosphere shows the Fe₂O₃ phase as well as the LiFePO₄ phase. It shows that the heat treatment shall be performed under an inert atmosphere to synthesize the LiFePO₄ in a single phase.

Microstructure and crystal phase of LiFePO₄ are investigated with the addition of chelate process under the heat treatment atmosphere of N₂. The crystal phase showed no difference but drastic microstructural change is shown from flower-like particles to spherical ones with the chelate process. The specific surface areas are 97.9 and 94.1 m²/g, respectively, which indicate slight differences according to the shape difference.

The charge and discharge test show that the LiFePO₄ without the chelate process holds the discharge capacity of 160 mAh/g, the approximate theoretical value. Also, it is confirmed that the capacity does not drop for 45 charge and discharge cycle tests. Meanwhile, the LiFePO₄ with the chelate process shows low discharge capacity of 105 mAh/g at 1C and the capacity suddenly drops more than 30 mAh/g in the cycle test. It is found out that the porous and flower-like LiFePO₄ without the chelate process shows better electrochemical features.

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