

The preparation and characterization of olivine LiFePO_4 by a solution method

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Abstract

Composite LiFePO_4/C cathode materials were prepared with a novel solution method followed by heat-treating at various temperatures. The compositions, crystalline structure, and morphology of the prepared powders were investigated with AA, EA, XRD, SEM, and EPMA. The electrochemical properties as cathode material for lithium batteries were studied by capacity retention study. Among the prepared composite cathode materials, the sample heat-treated at 700°C for 12 h shows better cycling performance than those of others. It shows initial specific discharge capacities of 165 and 130 mAh g^{-1} at 30°C with C rates of C/10 and 1C, respectively.

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1. Introduction

Among the promising candidates of the cathode material for large-sized secondary lithium batteries, such as LiMn_2O_4 [1–3], $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ [4–6], $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [7,8], and LiFePO_4 [9], olivine LiFePO_4 shows advantages in cost, safety, and cycling performance. However, LiFePO_4 is suffered from its low electronic conductivity at ambient temperature. Padhi et al. found that the electrochemical extraction of lithium in LiFePO_4 is limited to about 0.6 Li per formula unit [10]. The capacity exhibited by the material is strictly related to the current density used. From the observation that the capacity is restored when reducing the discharge current indicates that the loss in capacity is a diffusion-limited phenomenon within a single grain. Takahashi et al. used cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to investigate the influence of cell temperature on the lithium diffusion process that occurs during the extraction/insertion of Li^+ ions into/from LiFePO_4 [11]. They confirmed that the increase in the LiFePO_4 capacity as the cell temperature rose was caused mainly by the increasing lithium diffusion rate. Andersson and Thomas proposed the

mechanism for lithium extraction/insertion within a given particle for the LiFePO_4 system with two possible models [12]. In both models, the limiting process is a combination of low lithium-ion diffusion rate and low electronic conductivity in the FePO_4 phase, which prevents the full conversion of LiFePO_4 to FePO_4 , and back again.

Ways to promote the LiFePO_4 electrochemical properties are not limited to increase the operation temperature. Other possible means of improving the rate performance of the LiFePO_4 materials are those of enhancing its ionic/electronic conductivity by minimizing the particle size and the carbon coating by suitable preparation procedures. In this report, a solution method was employed to prepare small particle-sized olivine LiFePO_4/C composite powders. The cycling performance of the prepared LiFePO_4 cathode powders were examined with capacity retention studies performed with various C rates and at various temperatures.

2. Experimental

According to the stoichiometry, iron metal, LiNO_3 , and $(\text{NH}_4)_2\text{HPO}_4$ were mixed in an aqueous acidic solution. After the starting materials were dissolved, adequate amount of sucrose was added to the solution then heated at 150°C

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to evaporate water. Thermal decomposition and crystallization temperatures of the resulting powder were investigated by TGA/DTA (Simultaneous SDT2960, TA instruments Ltd., USA), which were performed between ambient and 900 °C with heating rate of 5 °C min⁻¹ under the flowing air and nitrogen, respectively. By following the results of DTA/TGA, the solid residue was calcined at 350 °C for 8 h and then heat-treated at temperatures between 400 and 800 °C for 12 h in N₂. The crystalline structure of the prepared LiFePO₄ powders were studied by a X-ray diffractometer (XRD-6000, Shimadzu Corporation, Japan), with Cu K α radiation at 40 kV, 30 mA, step size of 0.02°, and a count time of 4 s per step between 2 θ = 15° and 60°. Thus obtained patterns were used to calculate the lattice parameters of the olivine structure with computer software CELREF Version 3. AA (spectra 300 Plus, Varian Australia Pvt. Ltd., Australia), EA (Heraeus, Germany), EPMA (JXA-8600SX, JEOL Ltd., Japan), SEM (JSM-5600L, JEOL Ltd., Japan) were used to analyze the compositions and morphology of the prepared powders.

The prepared LiFePO₄ powders were mixed with acetylene carbon black and polyvinylidene fluoride (PVDF) in weight ratio of 83:10:7 in adequate amount of *N*-methyl-2 pyrrolidinone (NMP) and stirred for 24 h for mixing sufficiently. Then the mixtures were tape-cast on aluminum foil with a doctor-blade and placed in an oven at 110 °C for 24 h to remove the residual solvent. Finally, the dried tape was punched into round plates with diameter of 10.0 mm as the cathode electrodes. Thus prepared cathodes and Celgard 2400 separator (diameter of 16.0 mm) were placed into an argon-filled glove box and assembled into the 2032 coin-type cells with lithium anode, electrolyte of 1 M LiPF₆ in EC-DEC (1:1 vol.%), and the other components of the coin-type cell. For capacity retention study, the cells were placed at various temperatures (10, 20, 30, 40, and 50 °C) and cycled with various C rates (C/10, C/5, C/3, 1C, and 2C) on a 48-channel battery tester between 2.5 and 4.5 V for 30 cycles.

3. Results and discussion

The TGA/DTA results of the LiFePO₄ precursor performed under flowing air or nitrogen are shown as Fig. 1. While the broaden endothermic peaks attributed to water evaporation and dehydration of sucrose are found at temperatures between 60 and 170 °C, the small endothermic peaks at 240 °C caused by nitrate decomposition are also observed in both curves carried out under flowing air and nitrogen. Whereas the solely petite exothermic peak exhibited at 480 °C in the DTA curve accomplished under flowing nitrogen is due to the crystallization of LiFePO₄ [13], there are three exothermic peaks in addition to the LiFePO₄ formation peak shown at 505 °C in the curve obtained under air atmosphere. The exothermic peaks appear at 290 and 390 °C are assigned to the oxidation of organic acids and carbon. The peak shown at 630 °C reveals the formation of Li₃Fe₂(PO₄)₃ under flowing air [14]. It suggests that the precursor should

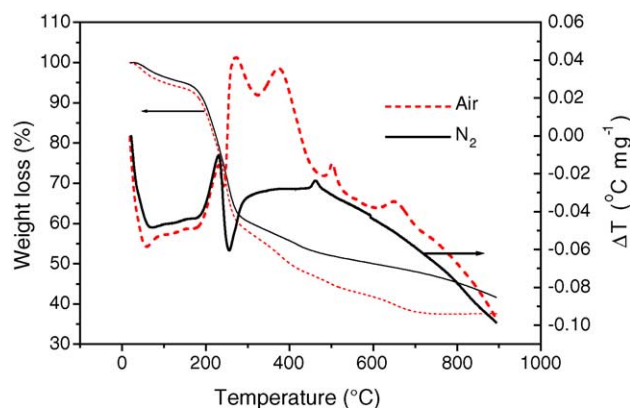


Fig. 1. TGA/DTA curves for the LiFePO₄ precursor recorded over the temperatures range from ambient to 900 °C at a heating rate of 5 °C min⁻¹ under flowing air or nitrogen. The gas flow rate is 100 mL min⁻¹.

be heat-treated in nitrogen atmosphere to avoid oxidation of Fe²⁺.

Identical TGA curves are observed for both experiments accomplished under flowing air and nitrogen between room ambient and 230 °C. The weight loss at temperature 60 and 170 °C is due to water vaporization and dehydration of sucrose, and the steep weight loss at temperatures between 180 and 230 °C is caused by the decomposition of nitrate. As the temperature higher than 230 °C, the sample placed in flowing air exhibits higher weight loss than that placed in flowing nitrogen. It is found that the residual organic compounds and carbon in the sample are oxidized in flowing air and no more weight loss is found after temperature higher than 700 °C, whereas carbon lost gradually by sublimation in the sample placed under flowing nitrogen [15].

From the results of composition analysis by atomic absorption spectrometer, it is found that the Li/Fe ratios are near the value of stoichiometry for powders prepared at temperatures between 500 and 800 °C for 12 h. The XRD patterns of the prepared samples are shown in Fig. 2. It is found that olivine phase formed, though not so obvious, in the sample

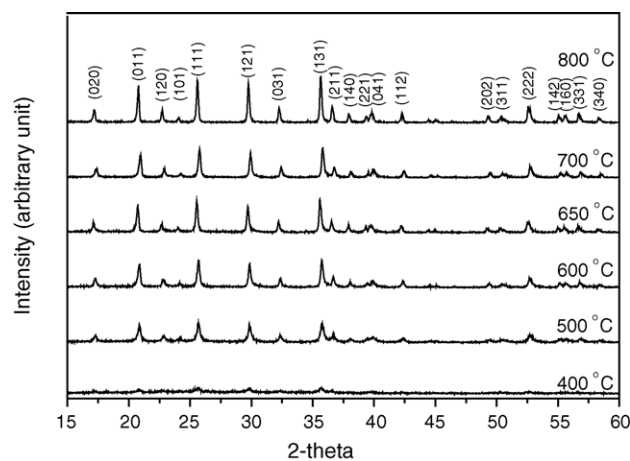


Fig. 2. XRD patterns of the powders heat-treated under nitrogen atmosphere at various temperatures for 12 h.

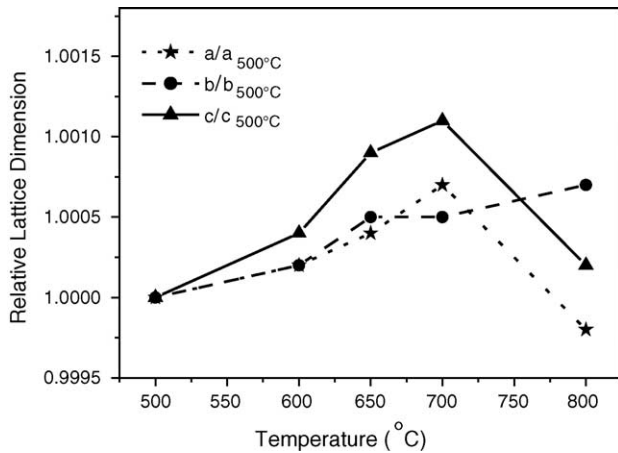


Fig. 3. Variation of the relative lattice dimensions with heat-treatment temperature for powders prepared at various temperatures for 12 h.

heat-treated at 400 °C that is in consistent with the DTA/TGA results shown in Fig. 1. The diffraction peaks corresponding to the olivine structure become prominent and the peak intensities increase with heat-treatment temperature for samples heat-treated at temperatures higher than 500 °C. Olivine phase is observed exclusively without other second phase in the samples heat-treated at temperatures between 400 and 800 °C. The crystallinity, which was estimated with software in company with Shimadzu XRD 6000, increased from 31% in 500 °C sample to 35% in 600 °C sample, 46% in 700 °C sample, and 75% in 800 °C sample.

The relative lattice dimensions were defined as the lattice parameters divided, respectively by those of 500 °C prepared powder. Variations of these dimensions with the heat-treatment temperature are illustrated in Fig. 3. It is found that the relative lattice dimension in b axis, b/b_{500} , increases

slightly and linearly with the temperature whereas the dimensions in a and c axes increase with temperature as the heat-treatment temperatures lower than 700 °C and exhibit maximum values at 700 °C. The 700 °C powder exhibits lattice parameters of 10.348, 6.012, and 4.706 Å in a , b , and c axes, respectively. According to the suggestion of Ouyang et al. [16], enlargement in the lattice parameter c will enhance the intercalation/de-intercalation of Li^+ ions.

The SEM photographs of the prepared powders are shown in Fig. 4. There are two types, plank and porous shapes, of particle in the powders. As the temperature of heat-treatment rising, the fraction of plank shape particle decreases. From the results of SEM mapping (not shown in the report), it is found that Fe and P atoms are distributed uniformly in the plank and porous particles. By comparing the results of EPMA (not shown in the report), it is found that the amount of carbon cover on the particle surface is reduced by raising heat-treatment temperature from 600 to 800 °C. The results of EA analysis for prepared samples also reveal that carbon content decreases with increasing temperature of heat-treatment. The carbon loss by rising heat-treatment temperature causes the formation of porous powder in the high temperature samples. For the 12 h heat-treated samples, it was found that the specific surface area determined by BET method decreased linearly from 54 to 22 m² g⁻¹ as the heat-treatment temperature increased from 500 to 800 °C.

The results of the capacity retention study for the cells prepared with powders heat-treated at various temperatures are shown Fig. 5. These experiments were accomplished by cycling the coin-type cells with 1 C rate between 2.5 and 4.5 V at 30 °C. The 700 °C prepared composite LiFePO₄/C sample manifests the best cycling performance among the 12 h heat-treated powders with initial specific capacity of 129 mAh g⁻¹ and capacity fading rate of 0.4 mAh g⁻¹ cycle⁻¹. This may

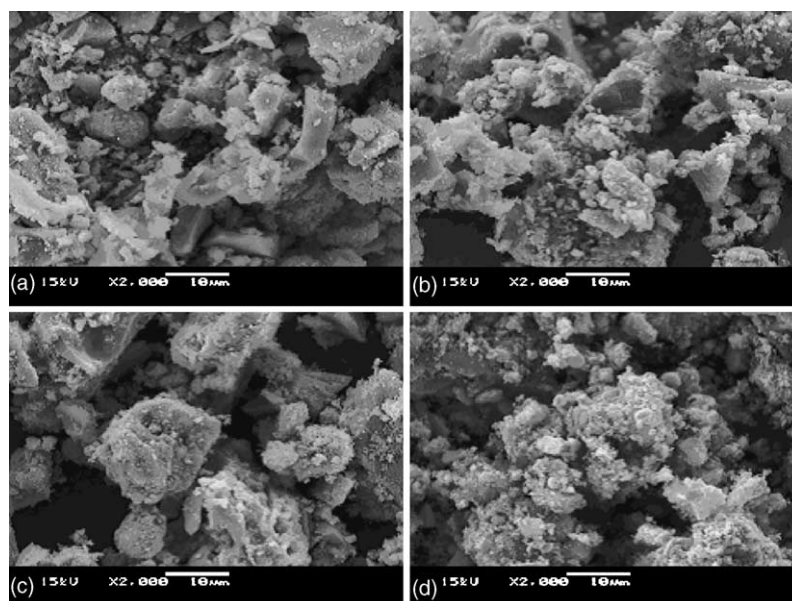


Fig. 4. SEM photographs of LiFePO₄ powders prepared at (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C.

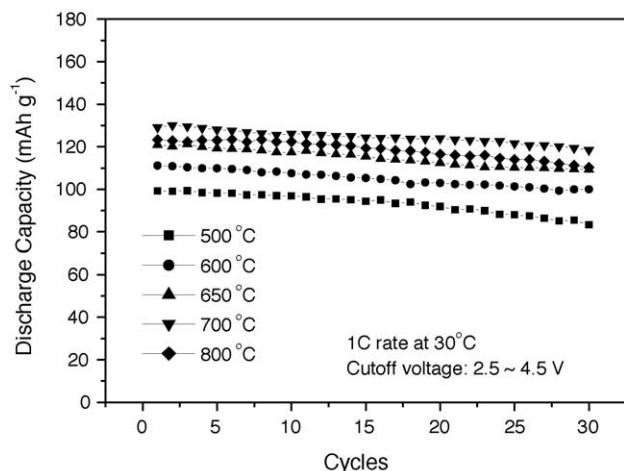


Fig. 5. The results of the capacity retention studies which were performed with 1 C rate and cutoff voltages of 2.5 and 4.5 V at 30 °C for the powders heat-treated at various temperatures for 12 h.

be attributed to the 700 °C prepared powder has higher crystallinity than those of the samples prepared at lower temperatures and has smaller particle size than that of 800 °C sample. This is in agree with the suggestion given by Yamada et al. that the LiFePO₄ have to be heated at an appropriate temperature to prevent the undesirable particle growth and the presence of a noncrystalline phase for better cycling performance [17]. Furthermore, the 700 °C sample shows the largest lattice parameters in *a* and *c* axes among the prepared powders. Since the diffusion of Li⁺ ions in LiFePO₄ was proved to be along *a* and *c* axes [8,16].

From the results of the capacity retention study performed with various C rates at 30 °C, shown in Fig. 6, it is found that the initial specific discharge capacity decreases with increasing C rate. The 700 °C prepared LiFePO₄/C cathode exhibits initial specific discharge capacity of 165 mAh g⁻¹, which is

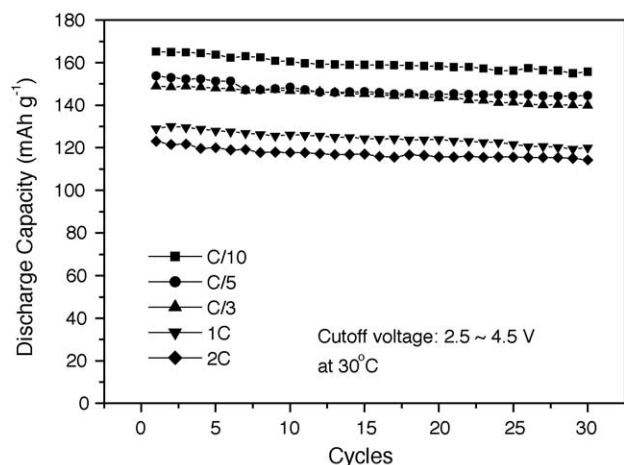


Fig. 6. Results of the capacity retention studies performed with various C rates for the LiFePO₄ powder prepared at 700 °C for 12 h under flowing nitrogen. The coin-type cells were cycled within the cutoff voltages of 2.5 and 4.5 V at 30 °C.

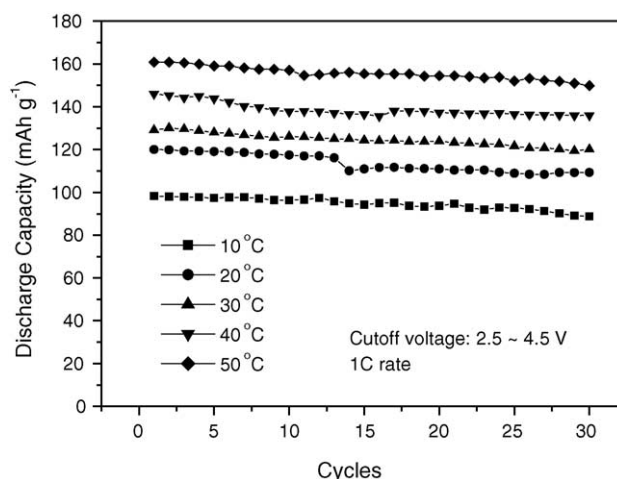


Fig. 7. Results of the capacity retention studies performed at various temperatures for the LiFePO₄ powder prepared at 700 °C for 12 h under flowing nitrogen. The coin-type cells were cycled with 1 C rate within the cutoff voltages of 2.5 and 4.5 V.

near the theoretical value of 170 mAh g⁻¹ as the cell was cycled with rate of C/10, the cell shows specific discharge capacity of 123 mAh g⁻¹ at 2C rate. It may due to its low lithium ion diffusion rate in olivine such that LiFePO₄ shows lower specific capacity as it is cycled with higher C rates [11]. Since it would allow the Li⁺ ions intercalated/de-intercalated more completely as the cell was cycled with low C rate, while the polarization would increase by cycling the cell with high C rate and thus the specific capacity within a given potential window would decrease. The percent capacity loss in 30 cycles increases with increasing C rate of cycling. In comparison with the results reported previously [18–20], the composite LiFePO₄/C cathode powder prepared by this solution method is proved to be high C rate applicable.

The cycling performances of the 700 °C prepared LiFePO₄/C cathode powder at various operating temperatures were also investigated and the results are shown in Fig. 7. It reveals that the specific discharge capacity increases with increasing operating temperature. The cell cycled at 50 °C displays initial specific discharge capacity of 160 mAh g⁻¹ whereas 98 mAh g⁻¹ is obtained for the cell cycled at 10 °C. Moreover, the percent capacity loss during the first 30 cycles decreases with increasing operation temperature. These results also support the suggestion of Takahashi et al. [21], since the diffusion rate of lithium ion in LiFePO₄ is enhanced by rising temperature and thus the specific capacity increases and percent capacity loss decreases.

4. Conclusions

Olivine LiFePO₄ cathode material can be prepared successfully from the low cost start materials by the solution method. Among the prepared composite LiFePO₄/C powders, the sample heat-treated at 700 °C for 12 h shows better

cycling performance than others. It shows initial specific discharge capacities of 165 and 130 mAh g⁻¹ at 30 °C with C rates of C/10 and 1C, respectively.

Acknowledgements

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