

Solid Chemical Reaction by Microwave Heating for the Synthesis of LiFePO₄ Cathode Material

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LiFePO₄ has been synthesized using FeC₂O₄·2H₂O, LiOH·H₂O and NH₄H₂PO₄ as raw materials by a temperature controllable microwave heating oven. The products were characterized by X-ray diffraction, scanning electron microscope and electrochemical methods. Measurement of dielectric properties of individual raw materials and products at a constant microwave frequency revealed that the starting mixture preheated at 320°C as well as added acetylene black were well microwave absorbers. Single phase olivin-type LiFePO₄ with uniform and fine particle sizes was successfully synthesized by microwave heating at 350°C in 15 min. The LiFePO₄ cathode materials thus obtained had a higher discharge capacity and better cycle performance than those of the LiFePO₄ sample by a conventional solid-state reaction.

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Introduction

Low cost rechargeable lithium ion batteries are key components of the large-scale applications such as backup power systems and hybrid electric vehicles. Layered LiCoO₂ is one of the earliest developed cathode materials, and its good performance and stability make itself the most commercially used cathode material despite its toxicity and high cost. Recently, ionic bonding compounds containing polyoxoanion frameworks built of (XO₄)ⁿ⁻ have been investigated intensively as a potential cathode material for rechargeable lithium ion batteries.¹⁾⁻⁶⁾ Padhi et al.³⁾ first employed LiFePO₄ as a cathode material, and evaluated its electrochemical properties. This work made following numerical study activated.⁷⁾⁻¹³⁾ Orthorhombic LiFePO₄, which has an ordered olivine structure, has attracted features; environmentally being, inexpensive, abundant, relatively large theoretical capacity of 170 mAh g⁻¹, good thermal stability etc. In many studies, LiFePO₄ was synthesized by a solid state reaction using an electric furnace, which required a high temperature and a long time. In a view of environmental and energy saving issues, a new synthetic method is expected to reduce energy consumption and processing time.

Application of microwave heating technique to inorganic materials technology has been advanced in the field of sintering and joining of ceramics.¹⁴⁾ There are several advantages in microwave heating compared with conventional heating techniques, in view of potentials for energy saving and shorter processing time, improved product uniformity and yields, improved or unique microstructures, and formation of new functional materials. Recently, there have been growing interests in the use of the microwave heating for synthesis of cathode materials of lithium ion battery such as LiFePO₄,¹⁵⁾⁻¹⁷⁾ LiMn₂O₄,^{18),19)} LiMn_{2-x}Cr_xO₄,²⁰⁾ LiNiO₂²¹⁾ and LiCoO₂.^{22),23)} In such studies, however, the process control of microwave heating was carried out only by irradiation time, sometimes accompanied with generation of by-product materials and melting of starting materials.^{2),17),18)} These are often due to an overload of irradiation of microwave. Therefore, the synthetic process of microwave heating should be proceeded by paying attention to dielectric properties of materials under the control of temperature.

In the microwave heating, an important phenomenon that one should consider, that is "thermal runaway". At temperatures above a critical temperature, the relative dielectric loss factor (ϵ'') of some of materials rises very rapidly. In such case, thermal runaway sometimes is observed. When the dielectric loss factor once begins to increase rapidly, the material can absorb microwave energy more efficiently. As a result, the heating system would be out of temperature control so as to make the material melted and/or decomposed. For the microwave heating, at least one component that can absorb microwaves well must be contained in starting raw materials to obtain sufficiently high temperatures necessary for initiating the reaction. Since the degree of microwave absorption is dependent on the dielectric properties of materials, the measurement of the dielectric properties is very important not only for the starting materials but also for the product.

In this paper, we have investigated the optimum conditions for microwave heating synthesis of LiFePO₄. The dielectric properties of raw materials and products were measured at a constant microwave frequency. The synthesis temperature were monitored and controlled precisely

Experimental

The starting materials for the LiFePO₄ were FeC₂O₄·2H₂O (98.5%, Kanto Chemical), LiOH·H₂O (95%, Kanto Chemical) and NH₄H₂PO₄ (99%, Kanto Chemical). These raw materials were weighed in a stoichiometric ratio and thoroughly mixed using a ball miller (Friche, Pulverisette6) with an agate ball in an agate container. The raw mixture was first pre-heated at 320°C for 5 h in N₂ flow to decomposed and expel the gases. This pre-heating is quite useful because the raw mixtures do not expand when the microwave was irradiated.

Acetylene black powders were then added to the pre-heated mixtures if necessary. The prepared starting material was then pelletized to the dimensions of 15 mm in diameter and about 10 mm in thickness. In order to deduce an escape of heat from the surface of the pellet, the pellet was surrounded by the pre-heated powder of 0.2 g. The sample was then put in an insulator vessel made of silica wool. The temperature was measured and controlled using a pyrometer and a controller equipped with a thermocouple which was sheathed in a stainless steel

tube and located on the sample pellet. To prevent oxidation of the iron, the insulator vessel was placed in a quartz tube where Ar gas was flowed at a rate of 100 ml min^{-1} . The quartz tube was placed in a domestic microwave oven (Sharp, RE-T55) operated at 2.45 GHz, with a maximum power level of 500 W. The heating time was 15 or 45 min. Details of the microwave heating method were described in the previous study.²⁴⁾ For comparison, LiFePO_4 synthesized by a conventional solid state reaction using an electric furnace at 600°C for 15 h in Ar flow was also prepared.

The crystal structure of the sample powders were characterized by X-ray diffraction (MAC Science, MXLabo) using $\text{Cu K}\alpha$ radiation. The microstructure of the sample powders were examined by an electron microscope (JEOL, JSM-5300). The dielectric properties of individual components of the starting materials and products were measured by an automated network analyzer (Hewlett Packard, 8753A) equipped with a dielectric probe kit (Hewlett Packard, 85070BB) at 25°C .

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 75 : 20 : 5. Two-electrode electrochemical cells consisting of lithium metal foil as a negative electrode, 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 3.0 and 4.0 V at a current density of 0.2 C rate.

Results and discussion

Table 1 shows the relative dielectric loss factors ϵ'' measured for the various raw materials used in this study and the product of LiFePO_4 . Both the raw materials and the pre-heated mixture showed a considerably small ϵ'' value, almost smaller than the value detectable in our analyzer. This fact implies that those materials do not work on heating by microwave irradiation. In contrast, the preheated mixture obtained previously by heating the raw mixtures at 350°C for 5 h under nitrogen atmosphere showed a ϵ'' to some extent up to 0.09. In fact, such partially decomposed product obtained from the raw mixture behaves as a microwave absorber. In addition, addition of 2 mass% of acetylene black to the preheated mixture was drastically effective for increase in the loss factor. High electrical conductivity of acetylene black should be responsible for such an increase in ϵ'' . These results confirmed that the added acetylene black is a well microwave absorber, which can effectively provide a rise of temperature to the preheated mixture.

Figure 1 shows the X-ray diffraction profiles of various LiFePO_4 products synthesized by the microwave heating method at temperatures ranging from 350 to 700°C for 15 min without adding acetylene black. The preheated powder (Fig. 1 (a)) is almost amorphous with only a small amount of olivine LiFePO_4 phase. Interesting, a LiFePO_4 phase (JCPDS 40-1499) crystallized even at a quite low temperature of 350°C (Fig. 1 (b)). When the heating time was elongated to 45 min, a well crystallized phase was also obtained (the results is not shown). At all the heating temperatures above 350°C , the reaction product was the single phase of LiFePO_4 without impurity. Since the diffraction peak intensity become intensive only a little, heating temperature does not seem to give so much influence on the crystalline particle growth. This may be understandable because of a quite short-time reaction period

Table 1. Relative Dielectric Loss Factor ϵ'' of raw Materials and Product at 2.45 GHz (25°C)

Materials	ϵ''
$\text{LiOH} \cdot \text{H}_2\text{O}$	<0.01
$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	<0.01
$\text{NH}_4\text{H}_2\text{PO}_4$	<0.01
Raw Mixture ^{*1}	<0.01
Preheated mixture ^{*2}	0.09
Acetylene black added preheated mixture ^{*3}	66.52
LiFePO_4 (Product)	0.04

*1: $\text{LiOH} \cdot \text{H}_2\text{O}:\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}:\text{NH}_4\text{H}_2\text{PO}_4=1:1:1$ (molar ratio).

*2: Material obtained by heating the above raw mixture at 320°C for 5 h in N_2 .

*3: Acetylene black of 2 mass% was added to the preheated mixture.

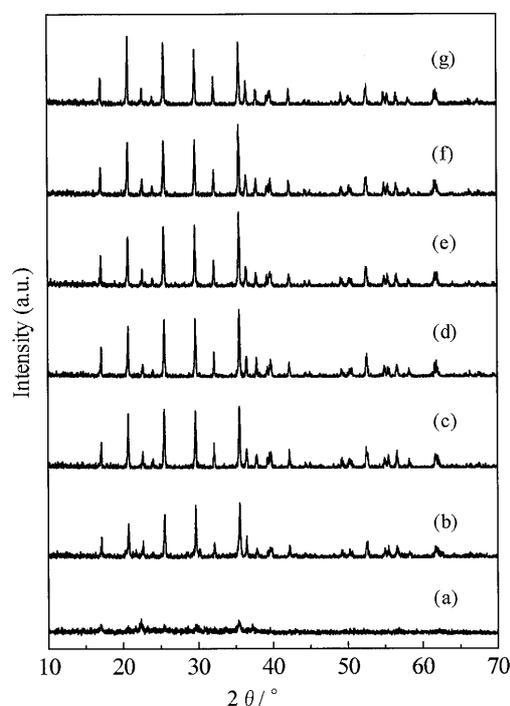


Fig. 1. Evolution of X-ray powder diffraction patterns of LiFePO_4 with heating temperature. (a) preheated mixture; (b) 350°C ; (c) 400°C ; (d) 450°C ; (e) 500°C ; (f) 600°C ; (g) 700°C .

of 15 min in this microwave synthetic method. Higuchi et al.¹⁷⁾ reported that a $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ by-product and a melted material were produced by irradiation of microwave of 500 W for 20 min using similar starting materials. Probably, this is due to their method without temperature-controlled condition. Therefore, control of the sample temperature is the crucial condition for obtain the crystalline single phase of LiFePO_4 . It seems that this become possible by control of sample temperature precisely. **Fig. 2** shows the X-ray diffraction profile of LiFePO_4 synthesized by the microwave heating method at 350°C for 15 min for the acetylene black added preheated mixtures. The single phase of LiFePO_4 was obtained for the mixtures with acetylene black contents from 2 to 30 mass%. The sample prepared from the mixture with 2 mass%

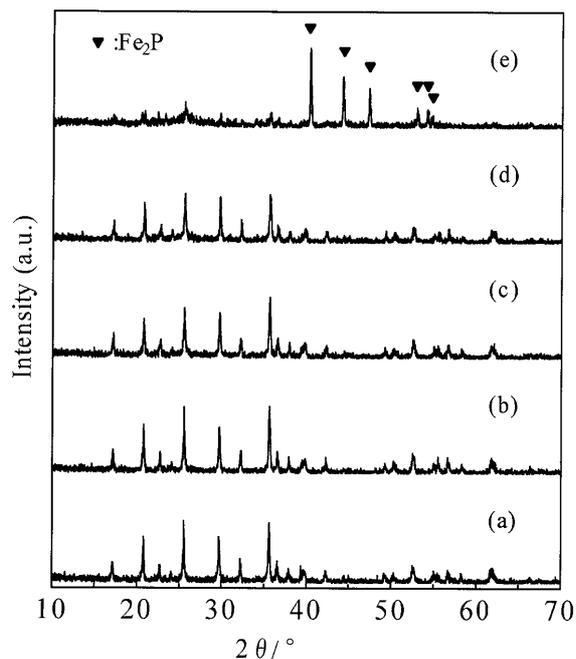


Fig. 2. Evolution of X-ray powder diffraction patterns LiFePO_4 with amount of added acetylene black. (a) 2%; (b) 10%; (c) 20%; (d) 30%; (e) 35%.

acetylene black (Fig. 2(a)) shows much better crystalline LiFePO_4 phase compared with the sample from the mixture without carbon (Fig. 1(b)). However, an excess amount of carbon gave low crystallinity to the product as seen in the case of the mixtures with 20 mass% and 30 mass%. This seems to be due to the less contact among the raw materials for the production of LiFePO_4 . Finally, in the case of the mixture with 35 mass% carbon, the main product was only a Fe_2P phase which resulted from the reduction by the excess carbon added. The similar results were reported by Kim et al. on the synthesis of LiFePO_4 by a mechanical alloying method using Fe_2O_3 , $\text{LiOH}\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{H}\cdot\text{PO}_4$ as raw materials.²⁵⁾

Figure 3 shows the time vs. temperature profile of the various raw mixtures, upon the irradiation of microwave. The raw mixture (Fig. 3(a)) shows a low heating rate up to 200°C , followed by a rapid increase in temperature. It took 6.5 min to get to 200°C , corresponding to the rate of 0.46 deg s^{-1} . Such a slow heating rate region seems to be required for the mixture to decompose to an intermediate material which is a microwave absorber. The preheated mixture (Fig. 3(b)) also shows a two-step temperature increase profile similar to the case of the raw mixture, but the rate of the first step is considerably fast with 1.2 deg s^{-1} . Compared with these cases, the carbon added preheated material (Fig. 3(c)) shows an almost one-step profile with the very fast heating rate of 4.3 deg s^{-1} , followed by a well-controlled temperature region. Addition of conductivity materials to starting mixture, such a case of the carbon-added preheated mixture, is very useful for obtaining a well-controlled temperature profile by microwave heating. It should be also noted that the preheated mixture can give a fairly good temperature profile though it has only a small ϵ'' (Table 1).

Electron micrographs of the LiFePO_4 products prepared by the microwave heating method and a conventional method are presented in Fig. 4. The particle size of the product prepared by the microwave heating method is in the range from 0.1 to

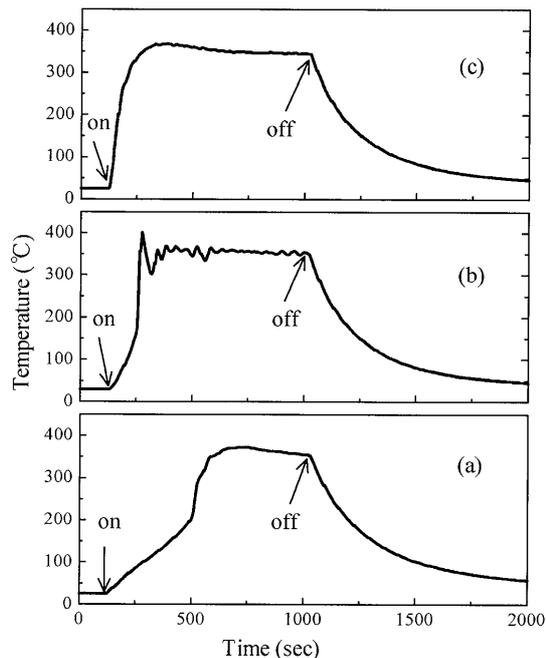


Fig. 3. Time vs. temperature profile for (a) raw mixture, (b) preheated mixture, and (c) carbon added preheating mixture irradiated by microwave.

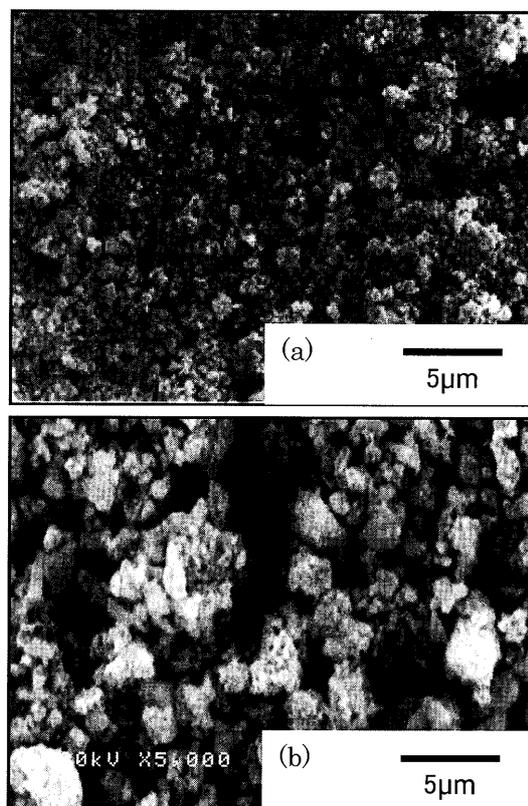


Fig. 4. SEM images of LiFePO_4 synthesized by (a) microwave heating at 350°C for 45 min and (b) conventional heating at 600°C for 15 h.

$1\ \mu\text{m}$ while that of the product prepared by the conventional method is around $1\text{--}3\ \mu\text{m}$ without uniform distribution. It is

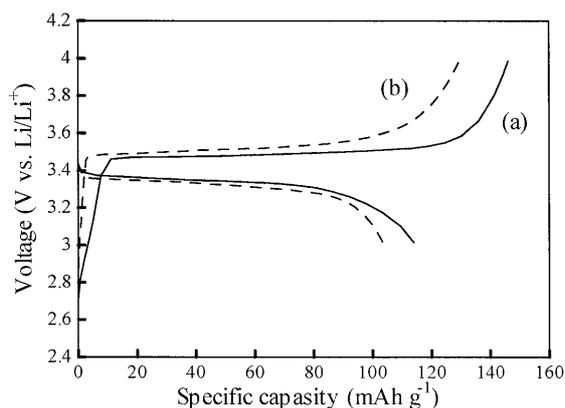


Fig. 5. Charge and discharge curves of Li/LiFePO₄ cells synthesized by (a) microwave heating at 350°C for 45 min and (b) conventional heating at 600°C for 15 h.

noted that the comparison of the difference in particle morphology should not be discussed between the two synthetic methods because of the differences in heating temperature and heating time. Nevertheless, the small particle sizes and good particle distribution provided by the microwave heating are very attractive, in particular, for the synthesis of cathode materials whose electrochemical performance is quite influenced by such characteristics.

The electrochemical properties were evaluated by performing charge-discharge tests for the samples prepared from the carbon added preheated mixture by the microwave heating method at 350°C for 45 min. **Figure 5** shows the first charge-discharge curves of the LiFePO₄ product by microwave-heating the 10 mass% carbon added mixture, and also shows that of the product prepared by the conventional heating, for comparison. A typical two-phase reaction between LiFePO₄ and FePO₄ at a 3.4 V plateau was observed in both samples. The discharge capacity and polarization behavior of the microwave heated sample is both superior to those of the conventional heated one. The cycle performance for the sample prepared from the carbon added preheated mixtures with various amount of acetylene black are shown in **Fig. 6**. The products with relatively low amounts of carbon exhibit a fairly good performance. A gradual decrease in cycle performance observed in those products is well known behavior for LiFePO₄ cathode materials without optimized surface modification such as carbon-coating treatment.^{2),26)} The optimization of carbon-coating over cathode particles is also necessary in the microwave synthetic method. The low capacity and poor cycle performance observed in the products with higher amounts of carbon may be due to their low crystallinity as shown in **Fig. 2**.

Conclusion

Single phase olivine-type LiFePO₄ was successfully synthesized at a low-temperature of 350 °C and for a short-time of 15 min by the precisely temperature-controlled microwave heating method. For the synthesis of LiFePO₄/C composites by the microwave heating, the amount of added carbon should be less than 30 mass% in order to obtain a simple phase product without Fe₂P impurity. The microwave heating product preheated by optimized conditions had a higher discharge capacity of 115 mAh g⁻¹ (at 25°C). The microwave heating method could be the one of the variable methods to produce olivine-type LiFePO₄ for lithium rechargeable batteries under en-

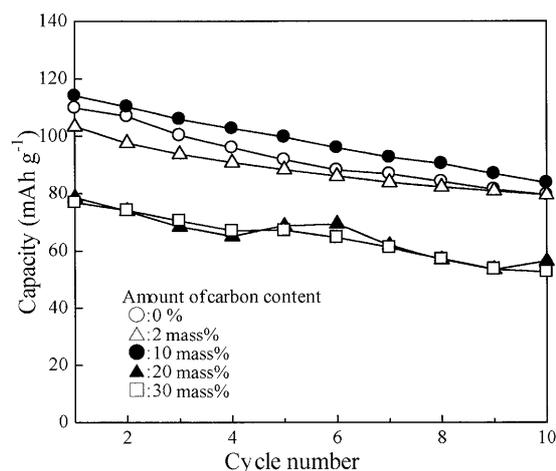


Fig. 6. Relationships between capacity and cycle number of the Li/LiFePO₄ cells.

vironmentally preferable and energy saving conditions.

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