

# Synthesis of $\text{LiFePO}_4$ cathode material by microwave processing

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## Abstract

We report on a novel synthetic method of microwave processing with a domestic microwave oven to prepare  $\text{LiFePO}_4$  cathode materials. We also studied and report on the electrochemical properties of the resultant products. XRD revealed that a single phase  $\text{LiFePO}_4$  powder can be synthesized quickly and easily by microwave processing. The initial discharge capacity of a cell assembled with the powder was 125 mAh/g at 60 °C. The  $\text{LiFePO}_4$  obtained has a high electrochemical capacity and good cycle ability. These results indicate that microwave processing is a promising method for preparing  $\text{LiFePO}_4$  cathode materials.

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## 1. Introduction

Olivine-type  $\text{LiFePO}_4$  is very interesting as a cathode material for lithium ion batteries in terms of its high theoretical capacity of 170 mAh/g and its abundance, and because its environmentally benign. Padhi et al. first prepared  $\text{LiFePO}_4$  and evaluated its electrochemical properties, and a number of researchers have actively studied its battery performance [1–9]. In all of these studies,  $\text{LiFePO}_4$  was synthesized by a solid state reaction using electric furnaces [10–12], which required a lengthy firing at 300–800 °C. A new synthetic method is needed to reduce the energy consumption, cost, and processing time required.

Microwave processing is a self-heating process that occurs through the absorption of electromagnetic energy. Since the microwave energy is directly absorbed by the sample, uniform and rapid heating can be achieved within a short period of time, and at temperatures lower than that required for furnace heating. This processing has been applied in the preparation of many ceramics as a novel sintering method, such as PZT, an oxide superconductor, and other ceramics [13,14]. For preparing the  $\text{LiMn}_2\text{O}_4$  cathode

material, Yan et al. conveniently used microwave energy to calcine the starting materials [15]. One of the instruments to radiate microwave power is a domestic microwave oven normally used for cooking. Domestic microwave ovens are inexpensive and convenient, and they require very little energy to operate. Therefore, microwave processing using a domestic oven is presumed to be a very economical synthetic method that can be expected to produce various inexpensive ceramic powders with homogeneous microstructures and fine grain size.

Here, we describe microwave processing with a domestic microwave oven to prepare  $\text{LiFePO}_4$  cathode materials. We also describe the electrochemical properties of the resultant products.

## 2. Experimental

The starting materials were  $\text{Li}_2\text{CO}_3$  (99%, Wako Pure),  $\text{NH}_4\text{H}_2\text{PO}_4$  (99%, Kanto), and iron acetate (95%, Aldrich,  $\text{Fe}(\text{CH}_3\text{COO})_2$ ) or iron lactate (98%, Soekawa  $\text{Fe}(\text{CH}_3\text{CHOHCOO})_2 \cdot 2\text{H}_2\text{O}$ ). These materials were weighed in stoichiometric ratios, dispersed into ethanol, and thoroughly mixed using an agate mortar. The mixed powder was dried at 60 °C and pressed at a pressure of 98 MPa into pellets. Each pellet was covered with glass wool and then placed in

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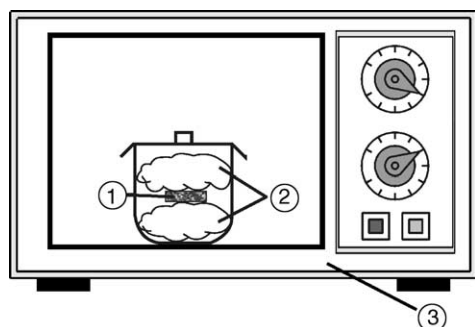


Fig. 1. Schematic of an apparatus used in this experiment. (1) Pellet, (2) glass wool, (3) domestic microwave oven.

Table 1  
Synthetic conditions for the preparation of  $\text{LiFePO}_4$  by microwave processing

Li source	$\text{Li}_2\text{CO}_3$
Fe source	$\text{Fe}(\text{CH}_3\text{COO})_2$ or Fe and $\text{Fe}(\text{CH}_3\text{CHOHCOO})_2$
P source	$\text{NH}_4\text{H}_2\text{PO}_4$
Li/Fe/P (molar ratio)	1.0/1.0/1.0
Microwave oven conditions power (W)	500
Frequency (GHz)	2.45
Irradiation time (min)	5–20
Atmosphere	Argon

an alumina crucible with a lid, as shown in Fig. 1. The microwave irradiation to the crucible was conducted with a domestic microwave oven that operated at 2.45 GHz, with a maximum power level of 500 W. These synthesis conditions are given in Table 1.

The phases in the synthesized products were determined by X-ray diffraction analysis (XRD; PW1370, Philips) with  $\text{Cu K}\alpha$  radiation. The microstructure of all products was observed by scanning electron microscopy (SEM; S-3500H, Hitachi).

We measured the electrochemical properties of the products synthesized using a microwave oven. A cathode was prepared by mixing the products with acetylene black and polytetrafluoroethylene (PTFE) powder with a weight ratio of 80:16:4. The mixture was rolled into a sheet around 0.14 mm thick, and then cut into pellets. Li foil was used as an anode, and a mixture of ethylene carbonate and diethyl carbonate in a molar or weight ratio of 1:1 and  $\text{LiPF}_6$  was used as the electrolyte. These three parts were assembled into a 2030 type coin cell in an argon atmosphere. The electrochemical properties of the cell were measured at a current of 10 mA/g, with a charge–discharge voltage limit of 2.0–4.3 V.

### 3. Results and discussion

#### 3.1. Preparation of $\text{LiFePO}_4$ using microwave processing

Products were obtained by changing the Fe source and microwave processing conditions such as irradiation time.

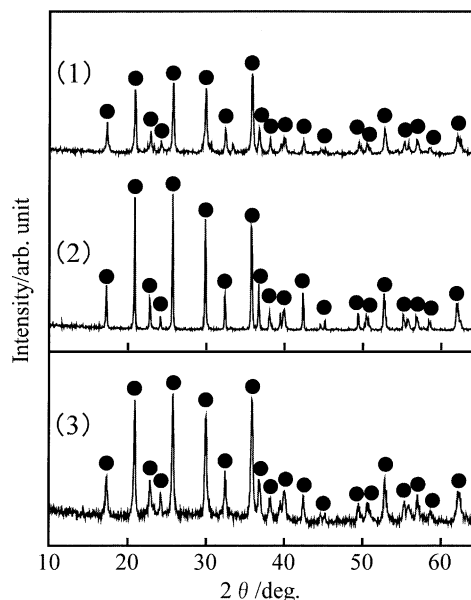


Fig. 2. XRD patterns of  $\text{LiFePO}_4$  synthesized by microwave processing using (1) iron lactate with iron metal powders or (2) iron acetate, as iron source, and by (3) solid-state reaction firing at 400 °C for 24 h in argon atmosphere. (●):  $\text{LiFePO}_4$ .

Typical XRD patterns of the  $\text{LiFePO}_4$  synthesized by microwave processing or solid-state reaction are given in Fig. 2. When we used iron acetate as the Fe source, the product obtained after 10 min of irradiation was black, and we identified it as a single phase  $\text{LiFePO}_4$ , as shown in Fig. 2(1). When iron lactate was used, no reaction was observed in the pressed pellet, even in the case of more than 30 min of irradiation. It is generally believed that microwave susceptors, which absorb microwave rays, are mandatory for microwave processing [16]. No reaction occurred in the pellets made from  $\text{Li}_2\text{CO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  with microwave irradiation when a Fe source was not included in the preparing powders. When iron acetate or iron lactate was used as a Fe source in preparing the powder, the pre-experiment revealed that iron acetate acts as a susceptor, but iron lactate did not act as a susceptor in this preparation. However, iron lactate is more convenient to use than iron acetate because of its reasonable cost and low deliquescence. Therefore, in order to synthesize  $\text{LiFePO}_4$  using iron lactate, we tried combining iron lactate with a small amount of iron metal powder as a microwave susceptor. We were able to synthesize  $\text{LiFePO}_4$ , as shown in Fig. 2(2). Fig. 2(3) shows  $\text{LiFePO}_4$  obtained by a solid-state reaction, firing at 400 °C for 24 h in argon atmosphere using an electric furnace, identified by JCPDS file (40-1499). The diffraction lines of the single phase  $\text{LiFePO}_4$  obtained from microwave processing were in very good agreement with the  $\text{LiFePO}_4$  obtained by solid-state reaction, and we therefore conclude that  $\text{LiFePO}_4$  can be synthesized successfully by microwave processing for a short irradiation time of 10 min.

Fig. 3 shows XRD patterns of the products synthesized by changing the irradiation time.  $\text{LiFePO}_4$  was not confirmed in

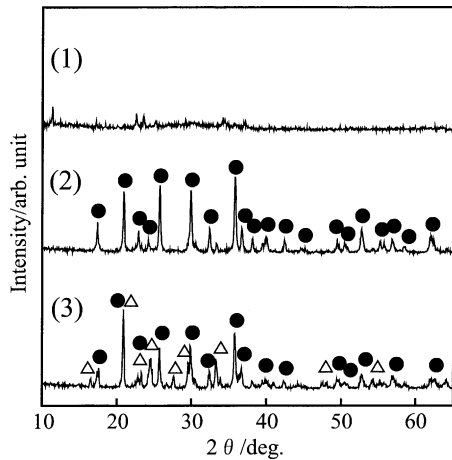


Fig. 3. XRD patterns of the products synthesized by using irradiation times of (1) 5, (2) 10, and (3) 20 min. (●):  $\text{LiFePO}_4$ ; (△):  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ .

the case of 5 min of irradiation, but the formation of a single phase  $\text{LiFePO}_4$  was confirmed in the case of 10 min of irradiation. In addition to  $\text{LiFePO}_4$ , a large amount of  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  was formed as a by-product when products were synthesized for 20 min. Products that were irradiated for 30 min or above melted. These results indicate that the product is formed into some lithium iron phosphate phases or melts, because longer irradiation increases the temperature of samples. Therefore, microwave irradiation for the optimum short time is required to successfully synthesize a single-phase  $\text{LiFePO}_4$ .

Fig. 4 shows the microphotograph of the synthesized  $\text{LiFePO}_4$ . It demonstrates many agglomerations of small particles that have a particle size of less than one micrometer.

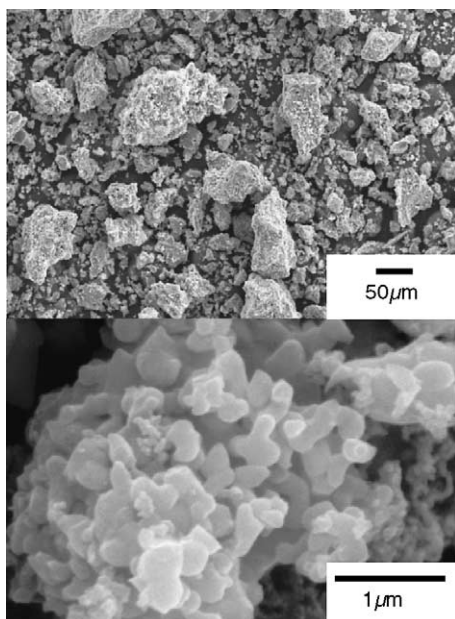


Fig. 4. SEM photographs of  $\text{LiFePO}_4$  synthesized by microwave processing.

However, particles of this powder display nonuniformity, and their characteristics have not been sufficiently studied.

### 3.2. Electrochemical properties of synthesized $\text{LiFePO}_4$

The charge and discharge curves of the cells with  $\text{LiFePO}_4$  as a cathode for the first cycle at 25 and 60 °C are shown in Fig. 5. Voltage plateaus at around 3.4 V observed in all the curves indicate that the charge and discharge reaction proceeds as a two-phase reaction. The initial discharge capacity of the  $\text{LiFePO}_4$  synthesized from iron lactate with iron metal powders was 100 mAh/g at 25 °C and 115 mAh/g at 60 °C. When iron acetate was used as a Fe source, the initial discharge capacity decreased to 95 mAh/g at 25 °C and 125 mAh/g at 60 °C. Many papers have already reported that the discharge capacity of  $\text{LiFePO}_4$  increases at an elevated temperature because of the higher Li diffusion rate in  $\text{LiFePO}_4$  particles [9,17]. The measured electrochemical characteristics of  $\text{LiFePO}_4$  synthesized in this study are similar to those of  $\text{LiFePO}_4$  obtained by solid-state reaction [18].

Variations of the discharge capacity with increasing cycles for the synthesized two products measured at 60 °C are shown in Fig. 6. The  $\text{LiFePO}_4$  obtained from iron lactate with Fe metal powders after a 10 min irradiation showed better cycling stability. Fig. 7 shows the rate capability of  $\text{LiFePO}_4$  obtained from iron lactate with the iron metal powders. At both low (C/1) and medium (C/2) rates,

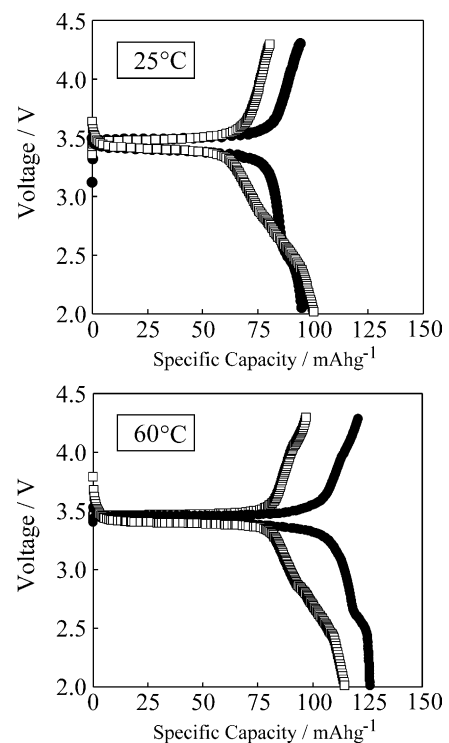


Fig. 5. The charge and discharge curves of the synthesized  $\text{LiFePO}_4$  for the first cycle. (●):  $\text{LiFePO}_4$  obtained from iron acetate; (□):  $\text{LiFePO}_4$  obtained from iron lactate with iron metal powders.

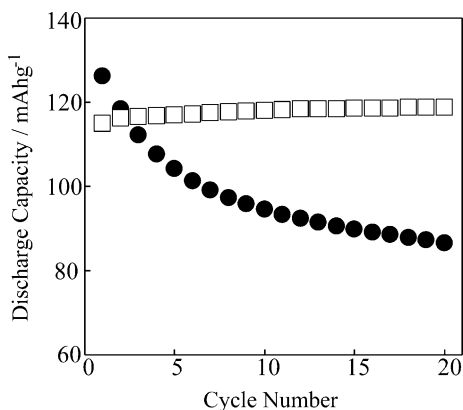


Fig. 6. The variations in the discharge capacity with increasing cycles for the synthesized two products measured at 60 °C. (●): LiFePO<sub>4</sub> obtained from iron acetate; (□): LiFePO<sub>4</sub> obtained from iron lactate with iron metal powders.

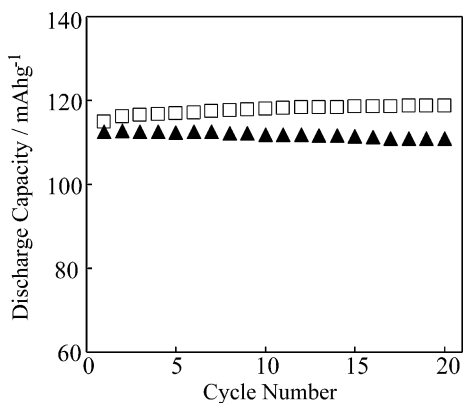


Fig. 7. The rate capability of LiFePO<sub>4</sub> obtained from the iron lactate with iron metal powders. (□): low (C/11) rate; (▲): medium (C/2) rate.

the products showed excellent cycling stability. However, the capacity of the product from iron acetate decreased as the cycle number increased, and the capacity decreased to about 85 mA/g. The different behavior of these two samples might be related to the addition of iron metal powders, or the crystallization of LiFePO<sub>4</sub> after the charge–discharge reaction. As described above, the use of iron metal powders affected the formation of LiFePO<sub>4</sub> and improved the electrochemical properties, and that may have caused these variations. This mechanism has not been sufficiently clarified.

#### 4. Conclusions

Single phase LiFePO<sub>4</sub> can be synthesized quickly and easily by microwave processing. The initial discharge capacity was about 125 mA/g at 60 °C. The LiFePO<sub>4</sub> obtained has a high electrochemical capacity and good cycleability. These results indicate that microwave processing is a promising method for preparing LiFePO<sub>4</sub> cathode materials.

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