Synthesis of olivine LiFePO$_4$ cathode materials by mechanical alloying using iron(III) raw material

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Abstract

Olivine LiFePO$_4$ has been produced using Fe$_2$O$_3$ raw material by mechanical alloying (MA) and subsequent firing. X-ray diffraction (XRD) and Mössbauer spectroscopy analysis revealed that LiFePO$_4$ prepared by MA had a well-ordered olivine-type LiFePO$_4$ structure with an ionic state of Fe^{2+} by the reduction of Fe^{3+} precursor. It showed a maximum discharge capacity of 160 mAh g^{-1} at C/20 (8.5 mA g^{-1}) when cycled from 2.5 to 4.3 V. Compared to the LiFePO$_4$ prepared by conventional solid-state method, MA synthesized LiFePO$_4$ a displayed higher charge/discharge capacity and more stable cycle life because of the improvement of the electronic conductivity. It was originated from uniformly distributed fine particles and an increased specific surface area by MA process.
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Keywords: LiFePO$_4$; Cathode material; Olivine-type iron phosphate; Mechanical alloying

1. Introduction

Olivine-type LiFePO$_4$ have been known as an interesting cathode material for lithium ion batteries since it was first proposed by Padhi et al. [1] because of its low cost and safety. The early drawback with LiFePO$_4$ was its extremely low electronic conductivity. Many works have been reported that the poor electrical conductivity of LiFePO$_4$ can be overcome by adding conductive carbon and by treating the particle surface with nanocrystalline carbon [2–5]. But these approaches of adding conductive carbon led to a loss in energy density due to the electrochemically inertness of the carbon. Also the use of the Fe^{2+} precursor compound is relatively high cost and has problems for mass production.

Recently, Barker et al. [6] reported that LiFePO$_4$ and LiFe$_{0.9}$Mg$_{0.1}$PO$_4$ were synthesized by a carbothermal reduction (CTR) technique, which is based on the C → CO transition, starting with Fe$_2$O$_3$ that is very cheap and readily available. In the present study, the same concept has been applied to the technique of mechanical alloying (MA)

process. Previously, we have reported on the effectiveness of synthesizing LiFePO$_4$ and LiFePO$_4$/C composite from a Fe^{2+} precursor by mechanical alloying (MA) [7]. In this work, LiFePO$_4$ was synthesized from Fe(III) by MA and subsequent firing under the assumption that the following reaction occurred:

$$LiOH \cdot H_2O + 0.5(Fe_2O_3) + (NH_4)_2H \cdot PO_4 + 0.5C$$
$$\rightarrow LiFePO_4 + 3H_2O + 2(NH_3) + 0.5CO \quad (1)$$
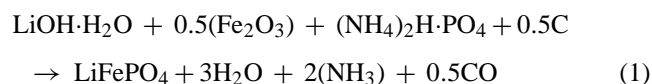
The electrochemical properties and cycle life of prepared powders were investigated and compared with those of a sample synthesized by the conventional solid-state reaction.

2. Experimental

LiOH·H$_2$O (Aldrich, ≥98%), Fe$_2$O$_3$ (Aldrich, ≥99%), (NH$_4$)$_2$H·PO$_4$ (Aldrich, ≥99%), and acetylene black powders were used as starting materials. The MA process was carried out for 4 h under argon atmosphere using a shaker type ball miller (SPEX 8000 M) rotating at around 1000 rpm. Detailed MA conditions were described in a previous study

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[7]. The mechanical-alloyed powders were then fired from 500 to 900 °C for 30 min in a tube-type vacuum furnace at a pressure 10^{-6} Torr. For comparison, another LiFePO$_4$ sample was prepared by the solid-state reaction under different firing condition. The mixture, which the same starting materials were thoroughly mixed in an agate mortar, was first decomposed at 450 °C for 5 h and then reground and fired at 900 °C for 10 h (denoted as SS450 + 900), which was the two-step firing condition employed in the conventional solid-state reaction process.

The crystal structures of the prepared sample powders were characterized by X-ray diffraction (Rigaku D-MAX 3000) using Cu Kα radiation. The Mössbauer spectra were recorded (Austin Science, Inc., USA) using ^{57}Co in Rh matrix as the source of radiation at room temperature. The powder morphology and particle size distribution were investigated by field emission scanning electron microscopy (FE-SEM), and a particle size analyzer (PSA). The specific surface area of the powder particles was measured by Brunauer–Emmett–Teller (BET), and the electrical conductivity of the prepared samples was also measured by a four-point probe method.

The cathodes used for electrochemical characterization were fabricated by blending the prepared active material powders with carbon black and polytetrafluoroethylene (PTFE) binder in a weight ratio of 75:20:5. Two-electrode electrochemical cells consisting of lithium metal foil as the negative electrode, polypropylene separator, and an electrolyte of 1 M LiPF$_6$ in EC:DMC (1:1, vol.) were assembled in an argon-filled glove box. The electrochemical cycle tests were performed using an automatic galvanostatic charge–discharge unit (Maccor series 4000) at various C rates, C/x (x = 1, 5, 10, 20) (1C = 170 mA g^{-1}) between 2.5 and 4.3 V at ambient temperature (25 ± 2 °C).

3. Results and discussion

As for the MA variables, optimum MA time to produce a crystalline LiFePO$_4$ phase was decided to 4 h in the previous study [7]. To obtain a single phase olivine-type LiFePO$_4$, the mechanical-alloyed powders were then fired at temperatures ranging from 500 to 900 °C for 30 min. The XRD patterns for the resulting their structural an evolution with increasing firing temperature are shown in Fig. 1. The sample prepared at 500 °C (Fig. 1(a)) mainly consists of Fe$_2$O$_3$ with a minor LiFePO$_4$ peaks. With increasing temperature above 500 °C the peaks of Fe$_2$O$_3$ were diminishing, whereas the LiFePO$_4$ peaks became sharper and more intense. Fig. 1(e) shows that well-ordered olivine structure without heterogeneity was obtained on firing at 900 °C for only 30 min (will be referred to as MA900). It indicates that the reduction of Fe$_2$O$_3$ starts from at 500 °C and completely finishes at 900 °C. This result is out of accordance with Barker's experiment, which is synthesized at 750 °C for 8 h using LiH$_2$PO$_4$ and Fe$_2$O$_3$ [6], because the starting materials is different and unsuitable re-
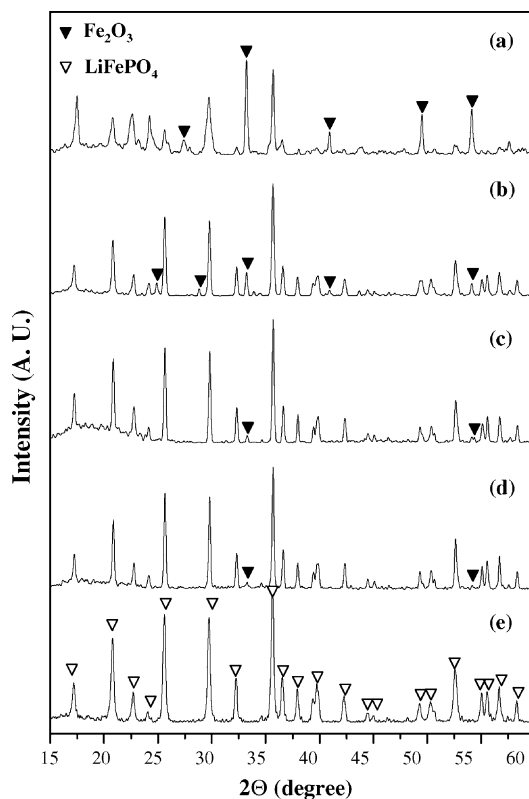

Fig. 1. XRD patterns of LiFePO$_4$ prepared from Fe$_2$O$_3$ raw material at various firing temperatures: (a) 500 °C; (b) 600 °C; (c) 700 °C; (d) 800 °C; (e) 900 °C.

duction reaction may be blocked by the short time firing as 30 min.

Although XRD pattern of MA900 revealed a single phase LiFePO$_4$, complete transfer of Fe^{3+} to Fe^{2+} had to be confirmed. For this reason, the ionic state of Fe was investigated by Mössbauer spectroscopy. Mössbauer spectroscopy measurements for LiFePO$_4$ prepared by the MA method at 800 and 900 °C are shown in Fig. 2. For sample fired at 800 °C, the six-line patterns were analyzed with isomer shift (IS) = 0.37 mm s^{-1} and quadropole split (QS) = −0.09 mm s^{-1}. The IS and QS values indicate that the Fe ions in the sample are predominantly composed of Fe^{3+}. For the sample fired at 900 °C, however, the spectra was observed by only one symmetric doublet with IS = 1.25 mm s^{-1} and QS = 2.95 mm s^{-1}, typical for those of ionic compounds with bare Fe^{2+} ions [5]. These results mean that the electrochemically inactive Fe^{3+} would be reduced to active Fe^{2+} at higher temperature to form LiFePO$_4$, and eventually a single phase of olivine could be produced at 900 °C.

It is well known that LiFePO$_4$/C composite containing carbon or carbon coated LiFePO$_4$ can improve the low electronic conductivity of LiFePO$_4$ and show excellent cathode performance [2–5]. In our previous work LiFePO$_4$/C composite compound containing no impurities was successfully synthesized by MA using Fe^{2+} precursor. However, in the cur-
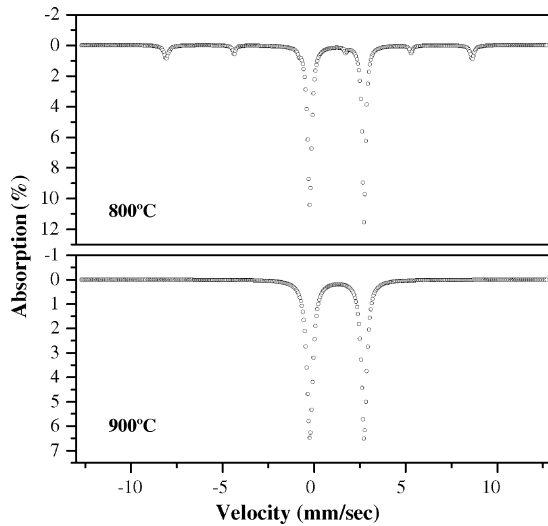
Fig. 2. Mössbauer spectra of the LiFePO$_4$ prepared by MA and subsequent fired at 800 and 900 °C, respectively.

rent study, the specimen prepared with 3 wt.% carbon using Fe$_2$O$_3$ raw material revealed the presence of second phase of Fe$_2$P as shown in Fig. 3(a). When a large amount of carbon is added in excess of 12 wt.%, most of the LiFePO$_4$ disappeared and iron phosphide was predominantly produced (Fig. 3(b)). It seemed that carbon in excess of the stoichiometric amount shown in Eq. (1) reduced the phosphate and generated Fe$_2$P as follows Eq. (2).

$$Fe_2O_3 + PO_4 + 7C \rightarrow Fe_2P + 7CO \qquad (2)$$
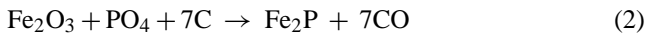
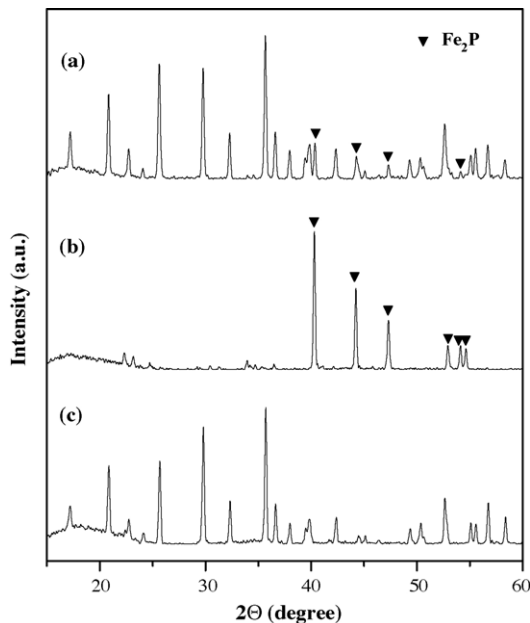On the other hand, SS450 + 900 prepared by convention solid-state method through two-step and long time heat treat-

Fig. 3. XRD patterns of (a) LiFePO$_4$/C composite compound (3 wt.%) and (b) LiFePO$_4$/C composite compound (12 wt.%), (b) LiFePO$_4$ prepared conventional solid-state reaction method.
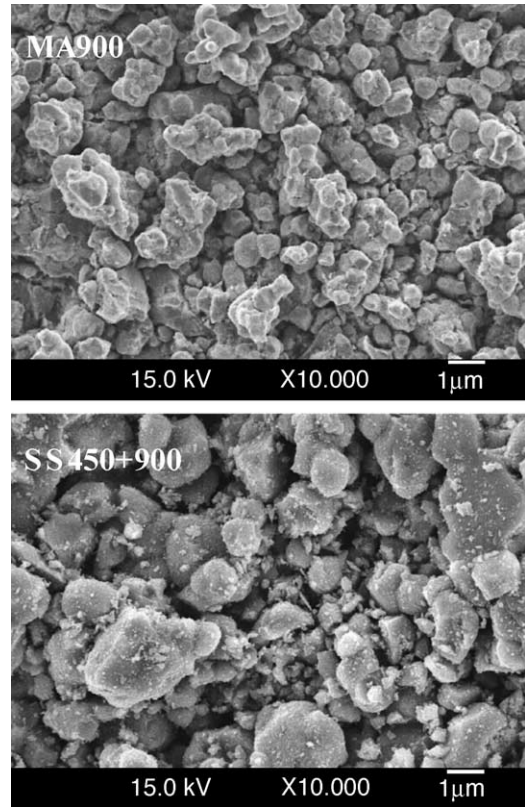

Fig. 4. SEM images of MA900 and SS450 + 900.

ment produced single phase LiFePO$_4$ with no second phase (Fig. 3(c)).

Electron micrographs of LiFePO$_4$ prepared by the MA and SS methods are presented in Fig. 4. The particle size distribution of MA900 ranged from 0.1 to 2 μm, while that of the SS450 + 900 ranged from around 1–10 μm with non-uniform morphology. The particle size distributions of the samples were in good agreement with the results determined by PAS. The results of the mean particle size determined by PSA, surface area by BET, and electronic conductivity for MA900 and SM450 + 900 are summarized in Table 1. The MA900 particle size was much smaller, whereas their surface area and electronic conductivity were higher than SS450 + 900 particles. It is considered that MA process can reduce the particle size by the high energy ball milling and by a markedly reduced firing time. This would cause the surface area of LiFePO$_4$ to increase, which would enhance the electronic conductivity. These results correspond well with the study of Yamada et al. [5] who reported that improvements in the conductivity could be achieved by synthesizing small and homogeneously sized powders.

The second charge and discharge curves of the Li/LiFePO$_4$ cells obtained from the MA and SS methods are shown in Fig. 5. The cells were cycled between 2.5 and 4.3 V at a current density of C/20 (8.5 mA g^{-1}) rate. Typical two-phase reactions between LiFePO$_4$ and FePO$_4$ with a 3.4 V plateau were observed in both samples [1]. The discharge capacity

Table 1
The powder properties of LiFePO$_4$ prepared by different synthesis method

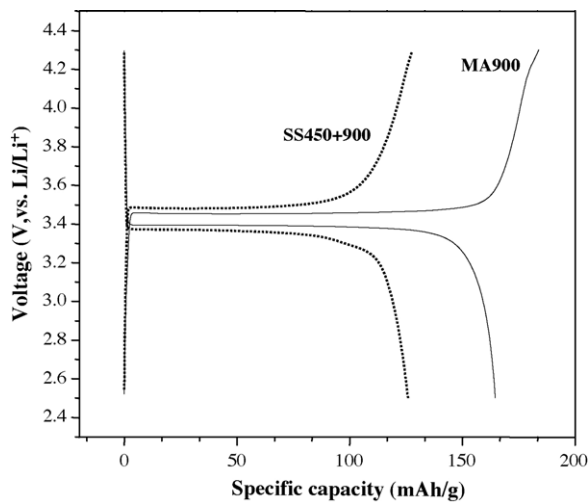| Sample ID	Synthesis condition	Surface area (m^2 g^{-1})	Ave. particle size (μm)	Electronic conductivity (S cm^{-1})
MA900	MA+ 900 °C, 30 min	8.5	1.45	1.2×10^{-7}
SS450 + 900	Simple mixture (450 °C, 5 h + 900 °C, 10 h)	1.2	5.78	1.7×10^{-9}

Fig. 5. The charge/discharge curves of MA900 and SS450 + 900 at C/20 rate.

of the SS450 + 900 sample was 130 mAh g^{-1}, which is 76% level of the theoretical capacity. On the other hand, MA900 exhibited excellent cell performance with a discharge capacity of 160 mAh g^{-1}, which is 94% level of the theoretical capacity. The discharge capacity of MA900 is similar or higher discharge capacity than LiFePO$_4$/C composite compound reported in the recent studies [8–11].

Fig. 6 shows the variation of the specific discharge capacity with the number of cycles. The charge/discharge current density was relatively high at the C/5 rate with a cut-off voltage of 2.5–4.3 V at room temperature. The sample prepared
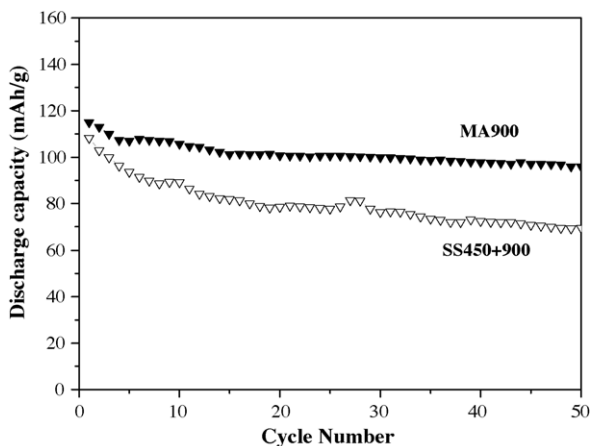
by MA has a higher discharge capacity and a more stable cycle life than the conventional solid-state synthesized sample. The cycling retention rate of MA900 after 50 cycles was about 89% of its maximum capacity, whereas the retention rate for SS450 + 900 was 62%. Consequently, it could be concluded that mechanical alloying enhanced the electronic conductivity and improved the cell performances of LiFePO$_4$ prepared from Fe^{3+} precursor.

4. Conclusion

Olivine-type LiFePO$_4$ was successfully synthesized from Fe$_2$O$_3$ by MA method, and subsequent firing at 900 °C for only 30 min. A single phase LiFePO$_4$/C composite could not be produced with carbon in excess of the stoichiometric amount because the Fe$_2$P was created by a reduction reaction of phosphate at high temperature. The well-crystallized lithium iron phosphate consisting of uniformly and fine particles had a higher discharge capacity of 160 mAh g^{-1}, and better electrochemical cycling behavior compared to LiFePO$_4$ prepared by the conventional solid-state reaction. It is reconfirmed that the MA process could be the one of the viable methods to produce olivine-type LiFePO$_4$ for lithium rechargeable batteries.

Acknowledgement

Fig. 6. Cycle life of LiFePO$_4$ prepared by the MA method and solid-state reaction method (cycle between 2.5 and 4.3 V, C/5).

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