

Synthesis and electrochemical properties of olivine LiFePO_4 as a cathode material prepared by mechanical alloying

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Received 23 February 2004; accepted 27 May 2004

Abstract

Pure olivine LiFePO_4 and LiFePO_4/C composite powders are synthesized by using mechanical alloying (MA) and subsequent firing. The powder properties and the electrochemical characteristics of the prepared samples are investigated in comparison with those of a sample obtained by the conventional solid-state reaction. The olivine LiFePO_4 prepared by MA shows a maximum discharge capacity of 135 mA h g^{-1} at the C/20 rate (8.5 mA g^{-1}) when fired at a relatively low temperature of 600°C . A LiFePO_4/C composite compound prepared by the MA process under optimum firing conditions has a high capacity of 156 mA h g^{-1} at the C/20 rate, i.e. 92% of the theoretical capacity. The composite also displays a better rate capability, a higher charge–discharge capacity and a more stable cycle-life than when produced by the conventional solid-state method. The improved electrode performance of MA samples originates mainly from very fine particles of sub-micron size and with a rough surface morphology. These powder characteristics increases the surface area of LiFePO_4 particles and maximizes the contact area with the conductor additive, which results in enhanced electronic conductivity. Consequently, the MA technique offers a promising synthetic process to overcome the disadvantages of olivine-type LiFePO_4 and LiFePO_4/C composite cathode materials for rechargeable lithium batteries.

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Keywords: LiFePO_4 ; Cathode material; Mechanical alloying; Rate capability; Rechargeable lithium battery

1. Introduction

Recently, LiFePO_4 has been identified as an interesting cathode material for lithium-ion batteries since it was first proposed by Padhi et al. [1]. Olivine-type LiFePO_4 has a relatively large theoretical specific capacity of 170 mA h g^{-1} based on a two-phase reactions with discharge plateau voltage of around 3.4 V versus Li/Li^+ . In addition, the material exhibits good thermal stability in the highly charged state, and has low-cost and environmental benefits. The material does, however, have the disadvantage of poor electronic conductivity. Consequently, its poor rate capability has been attributed to low electronic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) and/or slow diffusion of lithium ions across the two-phase boundary. Recent research has suggested that this limitation of conductivity can be overcome by adding a conductive material [2–4], doping transition metal ions [5] on synthesizing the powder with very fine particles [6]. Yamada et al. [6]

reported that increase in the specific surface area resulting from very fine and uniform particles gives good electrochemical cycle performance. Ravet et al. [2] found that LiFePO_4 exhibits a high discharge capacity of 160 mA h^{-1} C rate (80°C) when coated with 1 wt.% carbon. Also, Huang et al. [3] manufactured LiFePO_4/C composite compounds (about 15 wt.% C) of high discharge capacity by mixing carbon gel with raw material powder prior to heat treatment. These approaches, however, suffer from the problems of complex manufacturing processes and firing at high temperature for long periods in order to obtain a single-phase olivine-type LiFePO_4 .

Other studies have shown that mechanical alloying (MA) offers a promising method for synthesizing LiFePO_4 . We have already reported the effectiveness of MA to synthesize HT- LiCoO_2 and spinel LiMn_2O_4 [7–9]. During the MA process, the powder particles undergo repeated welding, fracturing and rewelding in a dry high-energy, ball-milling vessel. This results in pulverization, intimate powder mixing, and then solid-state reaction to a new phase. Accordingly, when the MA process is applied to the synthesis of LiFePO_4 ,

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an improvement in electronic conductivity can be expected due to the very fine particles and their large specific surface area also, on synthesizing LiFePO₄/C composite with carbon black the MA process, it can show excellent cell performance.

In this study, therefore, we describe first the influence of firing conditions followed by MA on the powder characteristics of pure LiFePO₄ particles. Then an attempt is made to synthesize directly the LiFePO₄/C composite by MA and subsequent firing under optimum conditions. The electrochemical cycling properties of the resulting samples are investigated and compared with those of samples prepared by the conventional solid-state reaction.

2. Experimental

Olivine LiFePO₄ powders were prepared by the MA process using LiOH·H₂O (Aldrich, ≥98%), FeC₂O₄·2H₂O (Aldrich, ≥99%), and (NH₄)₂HPO₄ (Aldrich, ≥99%) powders as starting materials of which the particle sizes were smaller than 500 μm. The MA process was carried out for 4 h under an argon atmosphere using a shaker type of ball mill (SPEX 8000M) that rotated at around 1000 rpm. The starting materials were charged in stoichiometric amounts into a hardened steel vial that had two steel balls (12.7 mm in diameter) and was located in a glove-box under an argon atmosphere. The ball-to-powder weight ratio was 15:1. The mechanically alloyed powders were then fired at 600, 700 and 800 °C for 10 h in a tube-type vacuum furnace. The pure LiFePO₄ samples synthesized in this way are referred to as MA600, MA700, and MA800, respectively. In order to increase the electronic conductivity, surface carbon coating of the LiFePO₄ powders was undertaken under optimized MA conditions using a mixture of the same starting materials and 7.8 wt.% carbon black. A LiFePO₄/C composite was then synthesized with the same firing conditions for MA600 (denoted as MA600C). For comparison, two more LiFePO₄/C composites were synthesized by the conventional solid-state reaction with different firing conditions. The same starting materials and carbon black (7.8 wt.%) were first thoroughly mixed in an agate mortar. Thereafter, one was fired at 600 °C for 10 h (denoted as SS-1), which are the same firing conditions as for the MA600 sample, the other was decomposed first at 350 °C for 5 h and then re-ground and fired at 600 °C for 10 h (denoted as SS-2), which are the conventional two-step firing conditions employed in the conventional solid-state reaction process.

The crystal structures of the prepared samples were characterized by X-ray diffraction (Rigaku D-MAX 3000) using Cu Kα radiation. The powder morphology and particle size distribution were investigated by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and particle size analysis (PSA). The specific surface area of the powder particles was measured by the Brunauer–Emmett–Teller (BET) method. The electrical

conductivity of the prepared samples was also measured by a four-point probe method.

Cathodes 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 were assembled with lithium metal foil as the negative electrode, a polypropylene separator, and an electrolyte of 1 M LiPF₆ in EC:DMC (1:1 vol.%) in an argon-filled glove box (EC = ethylene carbonate; DMC = dimethyl carbonate). 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

3.1. LiFePO₄ prepared by mechanical alloying and subsequent firing

In our previous studies [7–9], it was found that the cathode materials for lithium rechargeable batteries, such as HT-LiCoO₂ and LiMn₂O₄, should be directly synthesized by an optimized mechanical alloying (MA) process, although subsequent firing was required for good electrochemical performance. In this study, however, preliminary experiments have shown that single-phase cannot be obtained by the MA process alone because of the limitation in the selection of starting materials and a completely sealed reaction vessel. Nevertheless, it has been confirmed that the MA process still provides an effective means in terms of homogeneity and particle size.

Typical XRD patterns for LiFePO₄ samples prepared by MA and subsequent one-step firing at various temperatures are presented in Fig. 1. All samples reveal a single-phase LiFePO₄ with a well-ordered olivine structure. No impurities are detected in the XRD patterns. The crystallinity increases with increasing temperature. This means that the firing conditions become simpler than conventional firing schedules, since the MA process enhances the solid-state reaction between the raw materials.

Scanning electron micrographs of LiFePO₄ samples fired at (a) 600, (b) 700 and (c) 800 °C are shown in Fig. 2. With increasing the temperature, a significant increase in particle size and a smoother particle surface are observed. The particle size of samples fired below 700 °C ranged from 0.1 to 2 μm. The BET surface areas of the three samples are 7.6, 4.8 and 2.1 m² g⁻¹, respectively. These values of surface area are two to four times greater than that of the sample synthesized by the conventional solid-state reaction [10].

The second charge and discharge curves of the samples fired at 600, 700 and 800 °C are shown in Fig. 3. The cells were cycled between 2.5 and 4.3 V at a current density of C/20 (8.5 mA g⁻¹) rate. In all three samples, the

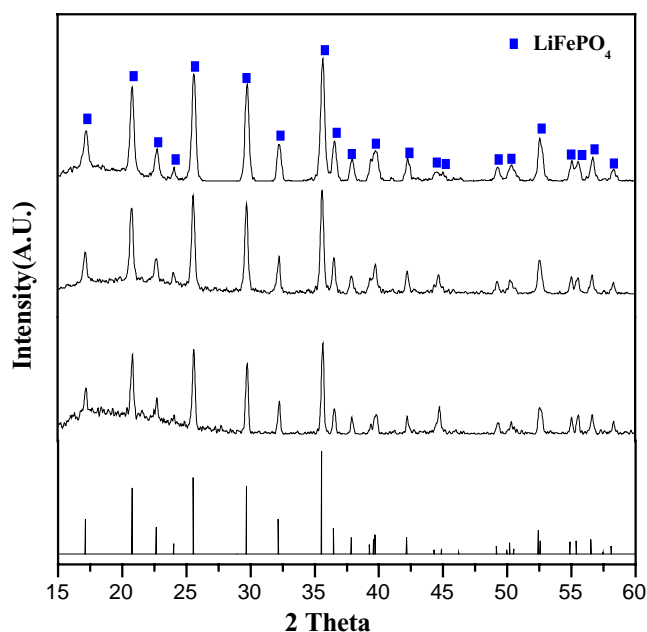


Fig. 1. XRD patterns of samples after mechanical alloying for 4 h followed by firing at temperatures for 10 h. (a) MA600 (600 °C, 10 h); (b) MA700 (700 °C, 10 h); (c) MA800 (800 °C, 10 h); (d) theoretical pattern.

plateau voltages are almost the same to 3.4 V (versus Li/Li⁺) regardless of the firing temperature, this indicates a typical two-phase reaction between LiFePO₄ and FePO₄ [1]. The discharge capacity, however, increases with decreasing preparation temperature and reaches 133 mA g⁻¹ for the sample fired at 600 °C. This value of discharge capacity is similar to that reported by Padhi et al. [1], despite the fact that the current density applied in this study is four times greater. The variation of discharge capacity with preparation temperature is consistent with previous studies [6,10]. According to Padhi et al. [1], the surface area (i.e., particle size) is a critical factor in determining the cell performance of LiFePO₄, because the charge–discharge process is controlled by lithium transport across the LiFePO₄|FePO₄ interface. Consequently, the largest discharge capacity for the MA600 sample can be explained in terms of particle size and specific surface area.

The variation of the first discharge capacity of MA600, MA700 and MA800 with discharge rate which illustrates the rate capability is presented in Fig. 4. The capacity of MA600 decreases from 135 mA h g⁻¹ at the C/20 rate to 87 mA h g⁻¹ at the 1C rate, which are the largest values for the three samples over the entire range of C rates. By contrast, the decrease in capacity with increasing C rate is similar in all samples. Thus, since all the LiFePO₄ samples produced by the MA process consists of sufficiently small particles, the rate capability is about the same in all samples. In general, the rate capability of olivine LiFePO₄ is inferior to that of other cathode oxides, as well as to that of surface-modified olivine due to its poor electronic conductivity. Therefore, the discharge capacity and rate capability of MA600 are still

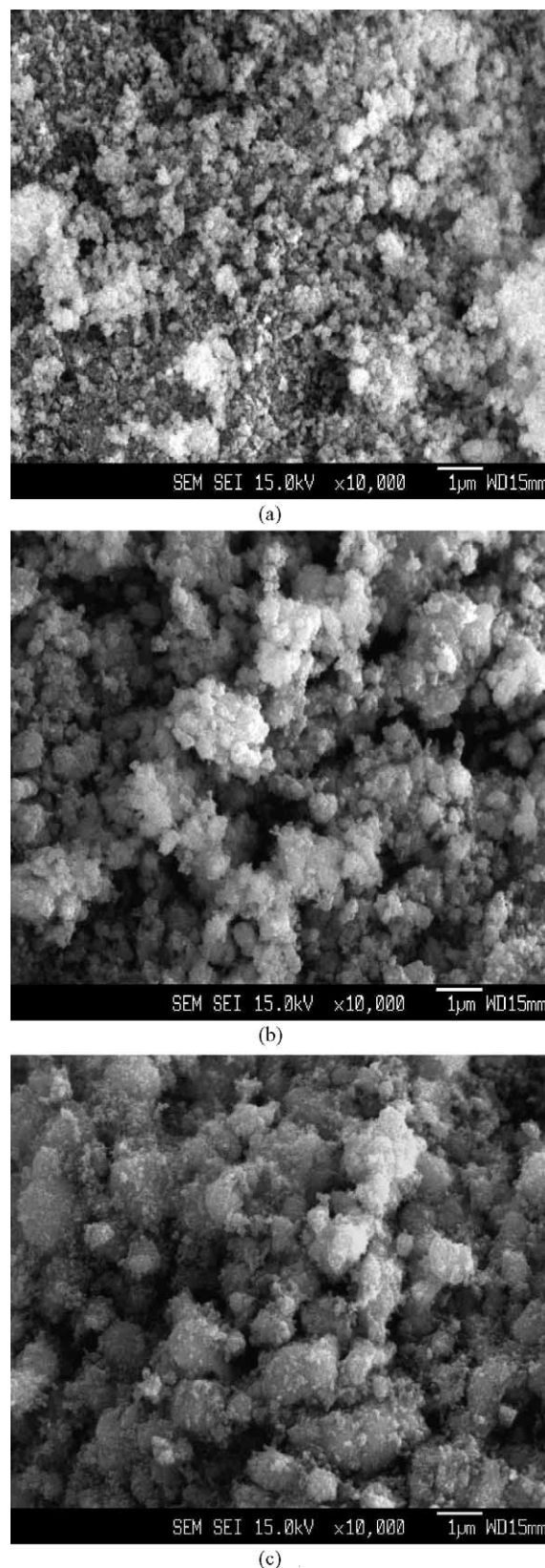


Fig. 2. Scanning electron micrographs of LiFePO₄ prepared by MA after firing at various temperatures: (a) MA600; (b) MA700; (c) MA800.

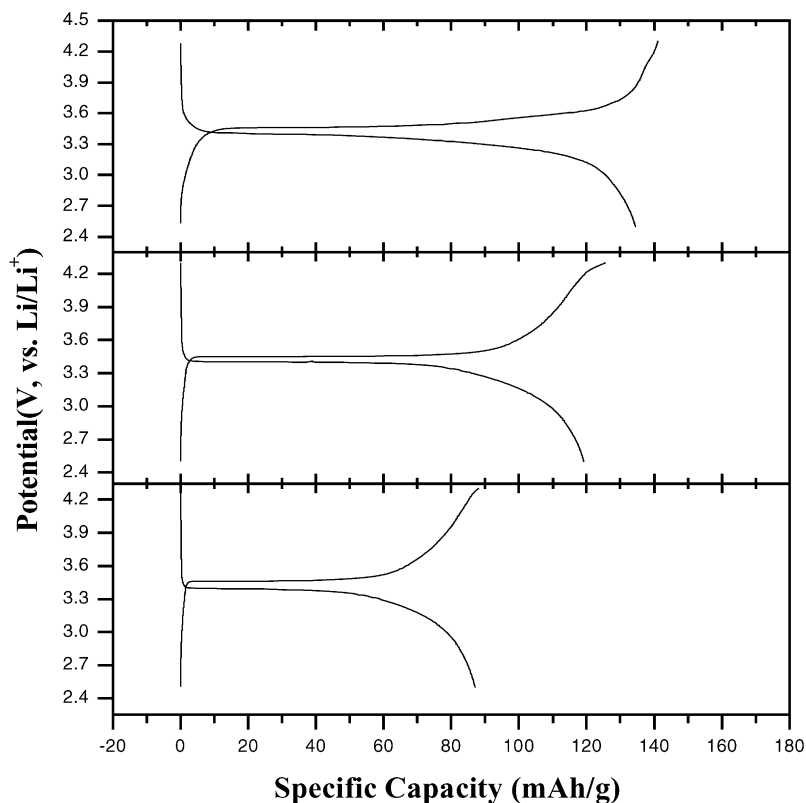


Fig. 3. Charge–discharge curves of second cycle of LiFePO_4 at $C/20$ rate prepared by mechanical alloying method, showing effect of firing temperatures: (a) MA600; (b) MA700; (c) MA800 (cycled between 2.5 and 4.3 V).

lower than those reported in recent investigations [11–13], although the particle size is minimized to a sub-micron size. Accordingly, the effect of carbon coating on LiFePO_4 using MA process is investigated.

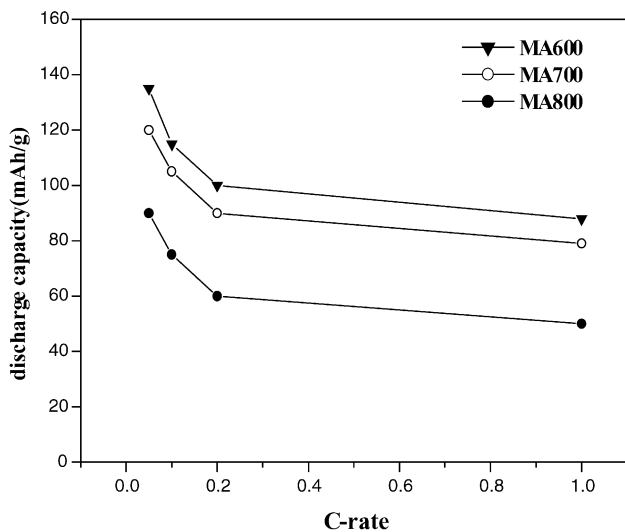


Fig. 4. Rate capability as function of current rate for samples prepared by MA and firing at different temperatures (cycled between 2.5 and 4.3 V).

3.2. LiFePO_4/C composite prepared by MA

In order to increase the electronic conductivity, a LiFePO_4/C composite containing 7.8 wt.% carbon was directly synthesized by MA from a mixture of the starting materials and carbon black, and subsequent firing at 600°C . It has been reported [2,3,5,6] that the diffusion limitation and the poor electronic conductivity of LiFePO_4 can be overcome by minimizing the particle size, doping the cation or introducing the conductive additives. As for the conductive additive, the surface coating and dispersion effect of the carbon black has played a beneficial role in obtaining samples with small and uniform particle size, as well as in enhancing their overall electronic conductivity. Huang et al. [3] have synthesized a LiFePO_4/C composite using a carbon gel, and concluded that both particle size minimization and intimate carbon contact are required to optimize the rate capability. Chen and Dahn [4] also reported that the rate capability of carbon-coated LiFePO_4 is dependent on the preparation method. In this study, therefore, the MA process is evaluated as a method for synthesizing LiFePO_4/C composites.

The XRD patterns of LiFePO_4/C composites prepared by MA and the conventional solid-state reaction method are presented in Fig. 5. The MA600C sample prepared by the MA process shows single-phase LiFePO_4 and no im-

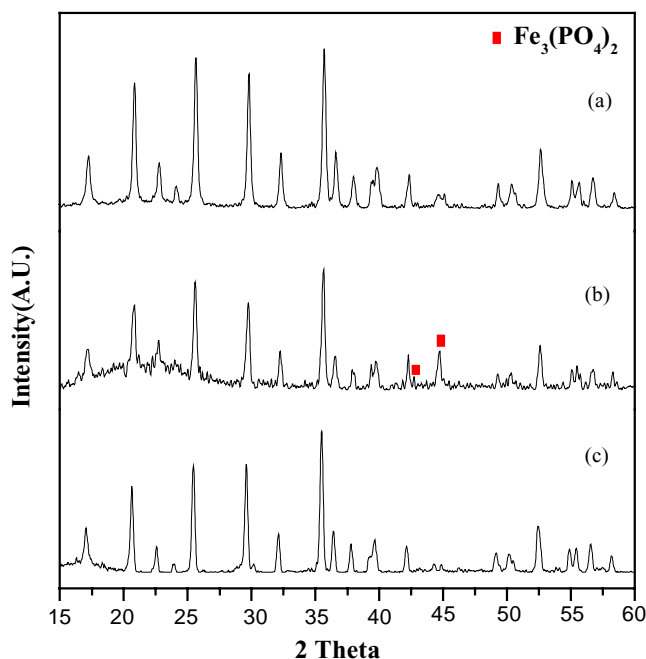


Fig. 5. XRD patterns of LiFePO₄ composite prepared either by MA method or by conventional solid state reaction method: (a) MA600 (600 °C, 10 h, add carbon black); (b) SS-1 (600 °C, 10 h add carbon black); (c) SS-2 (350 °C, 5 h + 600 °C, 10 h add carbon black).

purity phases (Fig. 5(a)). The added carbon is not detected in the XRD patterns due to the amorphous characteristics. On the other hand, for the SS-1 sample (Fig 5(b)) synthesized by the solid-state method with one-step firing, an impurity phase of Fe₃(PO₄)₂ is observed. This intermediate phase arises from insufficient mixing and reaction time. By using the two-step firing condition (Fig. 5(c)), the impu-

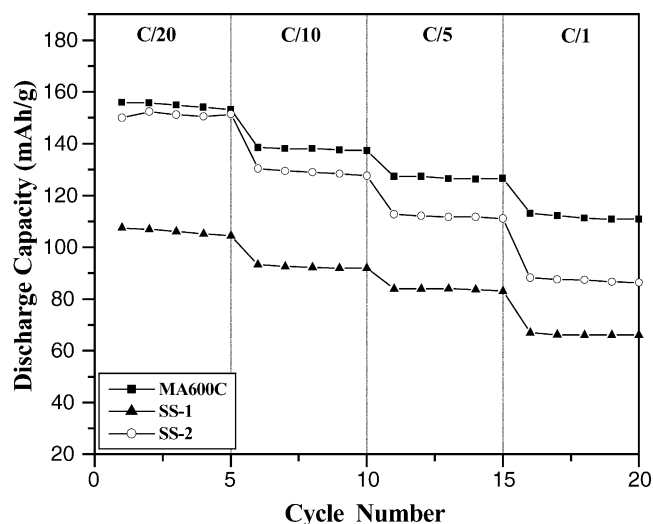
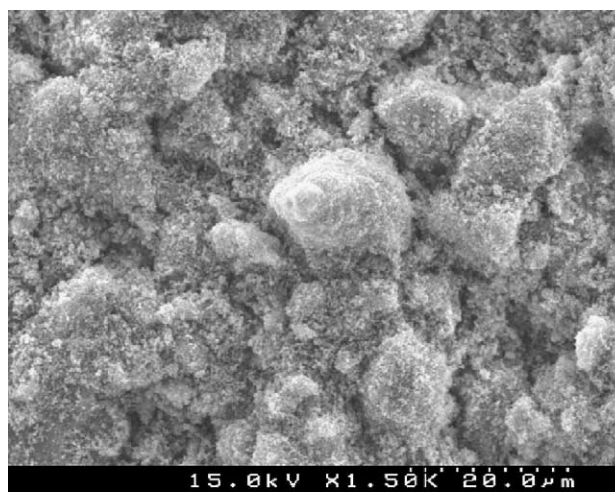


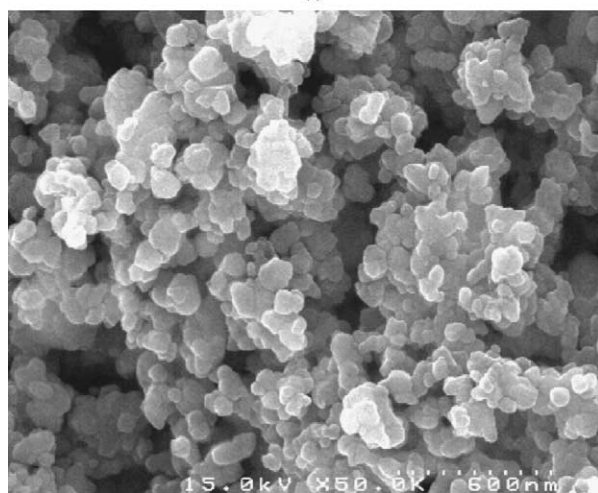
Fig. 6. Discharge capacity as function of cycle number at various rates (C/20, C/10, C/5, C/1) compared with samples prepared by MA method and solid-state reaction method (cycled between 2.5 and 4.3 V).

rities disappear and a well-ordered olivine single phase is obtained. This indicates that two-step heat treatment with intermittent grinding is required to synthesize pure olivine LiFePO₄ in the case of the conventional solid-state reaction method.

A comparison of the discharge capacity as a function of cycle number for the samples prepared by MA method and conventional solid-state reaction method is given in Fig. 6. The samples were cycled between 2.5 and 4.3 V at various rates (C/20, C/10, C/5, 1C). The discharge capacity for SS-1 is most inferior compared with those of the other samples over the entire range of C rate, since single-phase olivine could not be obtained. On the other hand, the discharge capacity of both MA600C and SS-2 is larger than that of pure LiFePO₄ (MA600) at all rates. In the case of MA600C, the initial discharge capacity is 156 mA h g⁻¹ at the C/20 rate, which is 92% of theoretical capacity while SS-2 gives 89% of theoretical capacity with 152 mA h g⁻¹ at the C/20 rate. This confirms that the



(a)



(b)

Fig. 7. Morphologies of LiFePO₄/C prepared by MA method: (a) ×1500; (b) ×50,000.

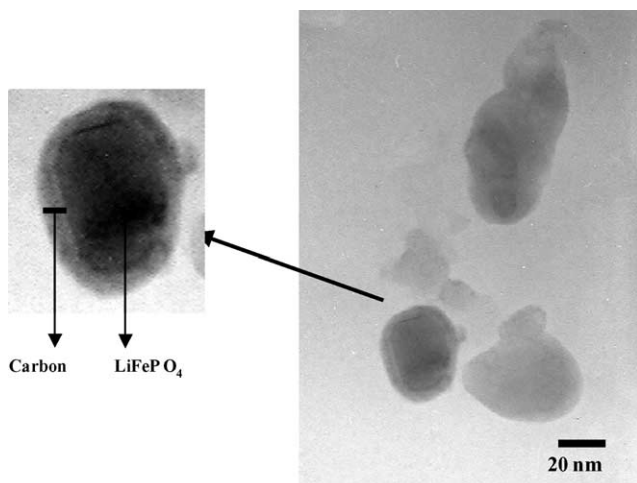


Fig. 8. TEM observation of LiFePO_4/C composite prepared by MA method.

addition of carbon black during the synthesis of LiFePO_4 improves the electrochemical performance of the material in terms of practical capacity and charge–discharge rate [14]. Despite showing a high discharge capacity at C/20, the maximum discharge capacity of SS-2 (86 mA h g^{-1}) was much lower than that of MA600C (110 mA h g^{-1}) at the 1C rate. This indicates that the performance of the cell at a high current rate is enhanced due to the improvement in electronic conductivity. This improvement is due to the production of uniform and fine particles via the MA process, which increases the surface area of the LiFePO_4 particles and maximizes the contact area with the conductor materials.

The mean particle size (as determined by PSA) and electronic conductivity of MA600C, SS-2, and MA600 (pure LiFePO_4) is listed in Table 1. The particle size is smallest and the electronic conductivity for MA600C. For example, the value of the conductivity is at least two orders of magnitude larger than that for SS-2. On the other hand, MA600 (pure LiFePO_4) has low conductivity, even though its particle size is similar to that of MA600C. Consequently, the LiFePO_4/C composite prepared by the MA process can be enhanced in electronic conductivity, unlike that obtained by the solid-state reaction method.

Fig. 7 is a scanning electron micrograph of the sample obtained on adding 7.8 wt.% carbon black to the starting

Table 1
Particle size and electronic conductivity of samples prepared under various conditions

Sample ID	Mean particle size (μm)	Electronic conductivity (S cm^{-1})
MA600C	0.1–1	1.8×10^{-4}
SS-2	0.5–50	1.4×10^{-6}
MA600 (pure LiFePO_4)	0.1–2	1.5×10^{-8}

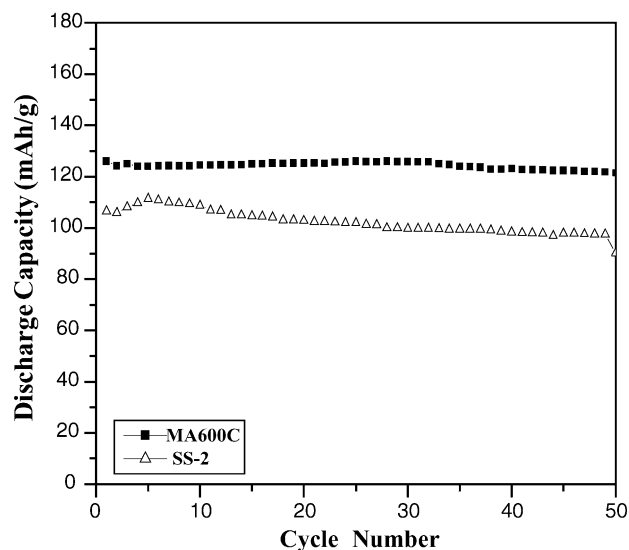


Fig. 9. Cycle-life of LiFePO_4/C composite prepared by MA method and solid-state reaction method (cycled between 2.5 and 4.3 V, C/5).

materials and then using the MA method with subsequent firing. The LiFePO_4 phase is seen to be spherically agglomerated with a primary crystallite size of 60–100 nm, and the carbon black is uniformly dispersed between particles. Transmission electron microscopy (TEM) was also used to observe the morphology of the carbon coating on the LiFePO_4/C composite compound. Powder morphologies for MA600C with a particle size about 70 nm are presented in Fig. 8. These show that carbon black particles completely cover the surface of the LiFePO_4 particles. Accordingly, it is confirmed that carbon particles uniformly displayed between LiFePO_4 particles under the influence of the MA process can prevent particle coalescence and therefore enhance the electronic conductivity.

The cycle-life of MA600C and SS-2 at the C/5 rate to a cut-off voltage of between 2.5 and 4.3 V is shown in Fig. 9. The sample prepared by the MA method yields a higher discharge capacity and stable cycle-life, compared with the sample manufactured by means of the conventional solid-state reaction method. After 50 cycles, the discharge capacity of MA600C is about 96% of its maximum capacity, but only 88% for SS-2.

Finally, to evaluate the electrochemical performance as a function of applied current density, discharge curves for MA600C and SS-2 at various discharge rates are compared in Fig. 10. With increasing current density, the discharge voltage and the plateau voltage are rapidly reduced in both samples. In fact, however, MA600C exhibits smaller ratio of decrease than SS-2, although the two samples show roughly a similar capacity at a slow discharge rate of C/20. Consequently, it could be concluded that the reduced crystallite size and particle size achieved by MA enhance the electronic conductivity and improved electrode performance.

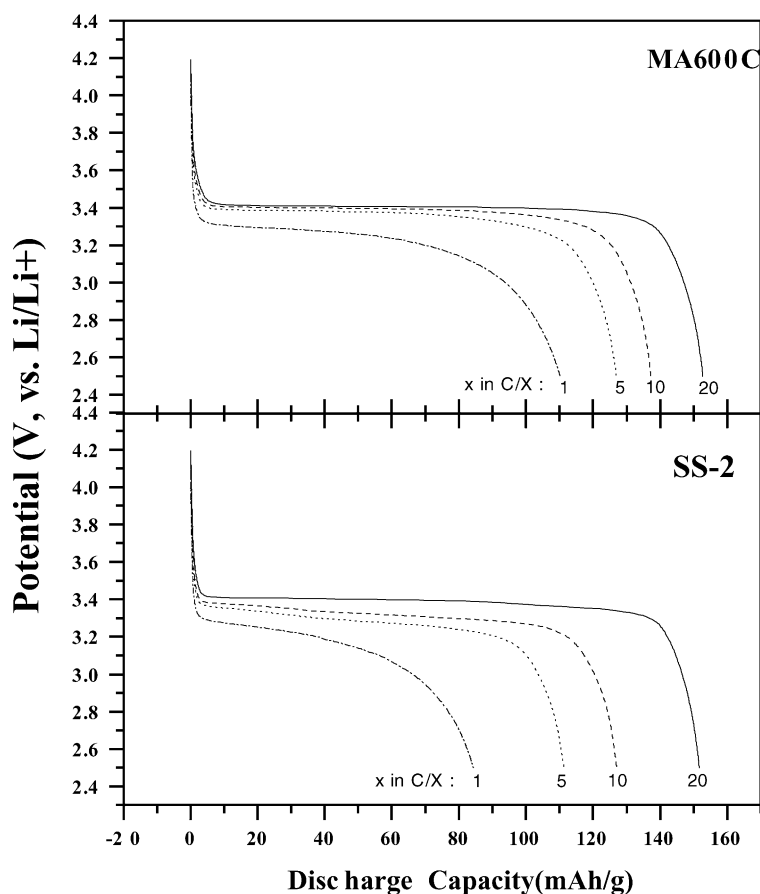


Fig. 10. Discharge curves of LiFePO_4/C composite compound at various rates prepared by MA method and solid-state reaction method.

4. Conclusions

A mechanical alloying (MA) method is used to manufacture cathode material of olivine-type phosphate with uniform and fine particles. Such alloyed powder, obtained through the MA process and subsequent firing at an optimum temperature of 600°C for 10 h gives a higher discharge capacity and rate capability than samples prepared at temperatures above 600°C . A LiFePO_4/C composite compound is found to exhibit excellent electrode properties with a discharge capacity of 156 mA h g^{-1} at C/20. In addition, it shows a higher charge–discharge capacity and a more stable cycle-life at a high current rate than that prepared by the conventional solid-state method. It is concluded that fine particle size and uniformly dispersed carbon black between the particles achieved with the MA process increases the electronic conductivity.

Acknowledgements

This work has been supported by a Korea Research Foundation Grant (KRF-2002-041-D00299).

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