Short communication

Simple and fast synthesis of LiFePO$_4$-C composite for lithium rechargeable batteries by ball-milling and microwave heating

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Abstract

A very simple and rapid method for synthesizing LiFePO$_4$-C composite has been developed by vibrant type ball-milling for 30 min and microwave heating for 2–4 min. X-ray diffraction and Mössbauer spectroscopy verify that well-crystallized LiFePO$_4$ without Fe^{3+} impurities is obtained. From laser particle size analysis and transmission electron microscopy, it is confirmed that a LiFePO$_4$-C composite with fine and uniform particle size (mean particle size $\leq 0.640 \,\mu m$, D75 in volume distribution $\leq 0.592 \,\mu m$) and with extremely uniform carbon distribution is prepared by vibrant type ball-milling and microwave heating. The LiFePO$_4$-C delivers a high initial discharge capacity of 161 mAh g^{-1} at C/10 and shows very stable cycling behaviour.
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1. Introduction

LiFePO$_4$ is a very promising cathode material for rechargeable Li batteries used in large-size appliances such as hybrid electric vehicles (HEVs), electric vehicles (EVs), power tools and e-bikes, due to its advantages of excellent thermal stability, low cost of the starting materials, high reversibility of Li insertion/extraction, and no toxicity [1–6]. LiFePO$_4$, however, has the problems of low electronic conductivity and low lithium diffusivity [7,8], as well as the difficulty in synthesizing a single-phase material due to the easy oxidation of Fe^{2+} to Fe^{3+} [5,9]. Therefore, numerous studies have been carried out to solve these problems.

The strategies of electronically conductive carbon coating (carbon composite) [10–13], particle size reduction [9,14] and supervalent cation doping [15] have contributed to an improvement in the rate-capability of LiFePO$_4$. Various synthetic methods such as solid-state reaction, mechanochemical activa-tion, sol–gel route, hydrothermal reaction, co-precipitation have been successfully used for these strategies and for the synthesis of single-phase LiFePO$_4$ [9–17].

To the best of our knowledge, except for the three investigations applying microwave heating [18–20] almost all efforts to develop LiFePO$_4$ have adopted furnace heating (thermal diffusion process), and consequently, it has taken more than several hours or 1 day to synthesize LiFePO$_4$. Although the precursor materials of LiFePO$_4$ are relatively inexpensive, it is essential to reduce the production cost of LiFePO$_4$ by developing a simple and fast synthetic method.

Microwave heating can achieve very fast and uniform heating through a self-heating process that arises from the direct absorption of microwave energy into the materials. Furthermore, microwave heating makes it possible to synthesize the target materials at temperatures lower than those required for furnace heating [18]. Therefore, compared with furnace heating, microwave heating is an economic and very fast procedure for the synthesis of LiFePO$_4$.

Park et al. [19] reported that single-phase LiFePO$_4$ was synthesized without reductive gas flow by microwave irradiation

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for 4 min (cf., Higuchi et al. [18]: 10 min; Wang et al. [20]: 9 min) using carbon as a microwave absorber and a reducing agent. In their work, however, the employment of complex and time-consuming co-precipitation to mix the precursor materials diminished the advantages of microwave heating, and the use of a mortar and pestle to mix carbon with the precursor mixture obtained by co-precipitation could not achieve very uniform distribution of carbon through the precursor mixture. (In situ carbon mixing during co-precipitation is very difficult because carbon itself does not disperse well in the aqueous solution.)

Carbon distribution has a strong effect on the particle size of $LiFePO_4$ because carbon plays an additional role as a barrier layer that hinders particle growth during microwave heating. In addition, carbon distribution affects the electronic conductivity of $LiFePO_4$. Therefore, the mixing step of precursor materials and carbon, which mainly decides the degree of carbon distribution and the particle size of the precursor materials, is very important to the improvement of the electrochemical perfor-

mance of $LiFePO_4$. After the mixing step, the particles certainly grow during microwave heating, but the degree of the particle growth is much smaller than that experienced during furnace heating due to the very short heat-treatment time of microwave heating [21]. Hence, particularly in a microwave heating process using carbon, the effect of the mixing step on the final morphology of $LiFePO_4$ is much more significant.

In order to obtain a $LiFePO_4$-C composite with a fine particle size and a uniform carbon distribution more simply and quickly, an attempt has been made in the work reported here to mix precursor materials with carbon using vibrant type ball-milling (high-energy ball-milling) and then perform microwave heating. This approach has been adopted because high-energy ball-milling is a simple and fast process that is effective in mixing and grinding materials [22]. This ball-milling process provides the advantage of reducing the two-step process, composed of co-precipitating precursor materials followed by mixing them with carbon, to one-step process of ball-milling precursor mate-
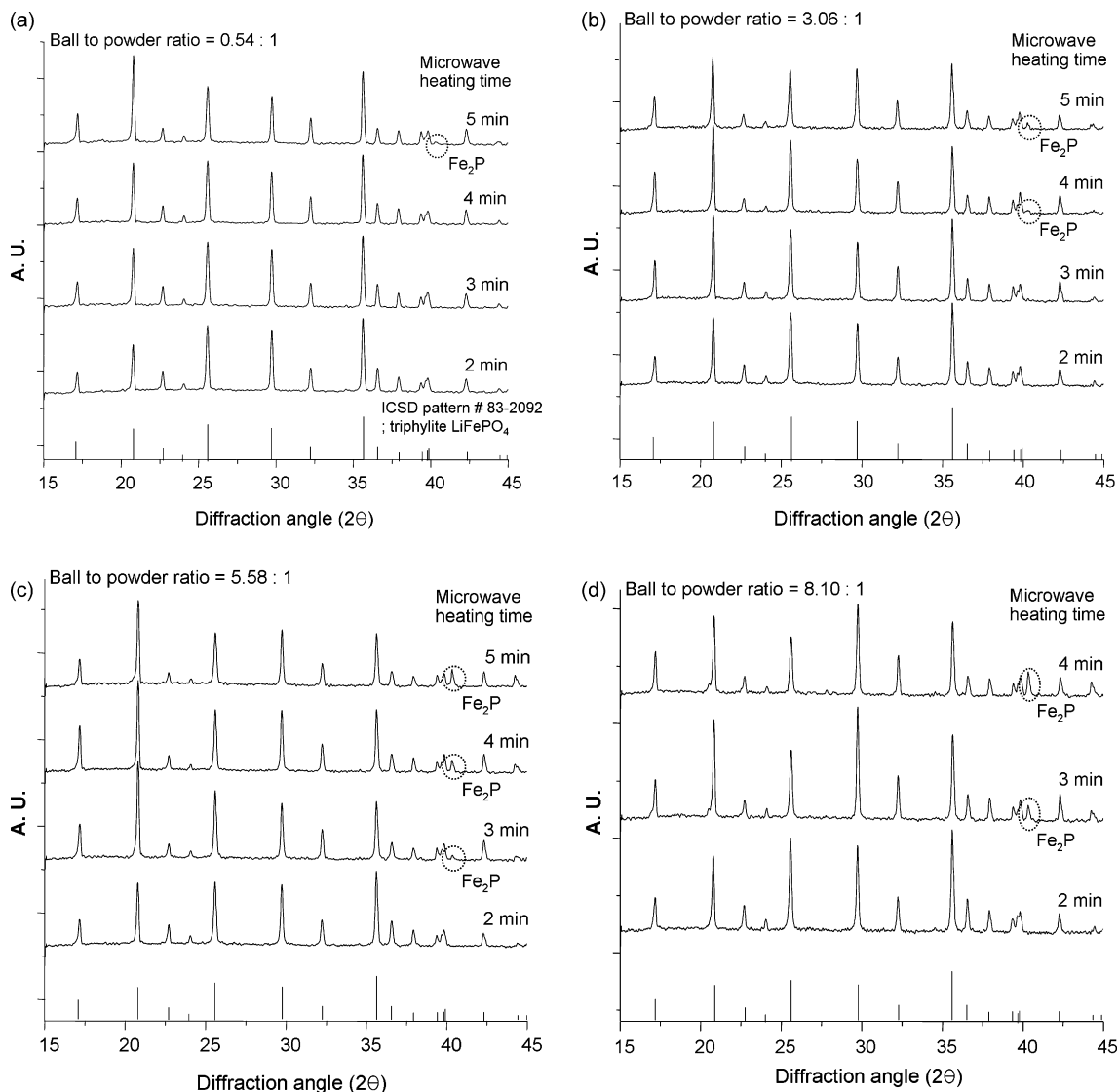

Fig. 1. X-ray diffraction patterns of LiFePO4-C and inorganic crystal structure database (ICSD) reference pattern, #83-2092 in JADE5 software. Ball-to-powder ratio: (a) 0.54:1; (b) 3.06:1; (c) 5.58:1; (d) 8.10:1.

rials with carbon. Hence, an examination has been made of the effects of vibrant type ball-milling and microwave heating on the synthesis and microstructure of a $LiFePO_4$-C composite.

2. Experimental

2.1. Preparation and characterization of $LiFePO_4$-C

$LiFePO_4$-C was prepared by ball-milling and subsequent microwave heating. Li_3PO_4 (Aldrich) and $Fe_3(PO_4)_2 \cdot 8H_2O$ (Kojundo) were used as precursor materials for $LiFePO_4$. Stoichiometric amounts of Li_3PO_4 and $Fe_3(PO_4)_2 \cdot 8H_2O$ (1:1, molar ratio) were weighed and placed in a ball-milling jar with 5 wt.% acetylene black. Ball-milling at various ball-to-powder ratios (weight ratios) was carried out under an argon atmosphere for 30 min using a vibrant type mill (SPEX8000 mixer/mill). The ball-milled mixture was pressed into a pellet and then put inside a quartz crucible that was filled with activated carbon (Aldrich, 20–40 mesh). The quartz crucible was put in the middle of a domestic microwave oven (750 W) and microwaves were irradiated for several minutes (2–5 min). During that treatment, carbon generated heat through the direct absorption of microwave energy and thereby made a reductive atmosphere by carbothermal reaction. After microwave irradiation, $LiFePO_4$-C was obtained.

The structure of $LiFePO_4$-C was examined by X-ray diffraction analysis (Rigaku, Cu Kα radiation, $1° \text{ min}^{-1}$ scan rate) and JADE5 software (Materials Data Inc.). Fe^{3+} impurities existing in the $LiFePO_4$-C were detected by Mössbauer spectroscopy (MR351, FAST) with a ^{57}Co γ-ray source. Velocity calibration was carried out using the spectrum of α-Fe at room temperature. The morphology of the $LiFePO_4$-C was observed by transmission electron microscopy (TEM, JEOL) operating at 300 kV, and the particle size was measured by a laser particle size analyser (LPSA, LS230 System/Small Volume Module, Beckman Coulter) equipped with a PIDS detector and a 116 channel detector for detecting 0.4–0.04 μm size particles effectively. In order to investigate the temperature at which $LiFePO_4$ was synthesized, differential thermal analysis (DTA, SDT Q600, TA) was performed at a heating rate of $5 °C \text{ min}^{-1}$.

2.2. Cell fabrication and electrochemical testing

A slurry of $LiFePO_4$-C cathode was prepared by mixing 75 wt.% $LiFePO_4$-C and 17 wt.% acetylene black, and then adding N-methyl-2-pyrrolidene (NMP) solution containing 8 wt.% polyvinylidene fluoride (PVdF) to the mixture. The slurry was coated on to an Al foil substrate and then dried at 120 °C for 12 h in a vacuum oven. Subsequently, the cathodes were cut into a disc shape of 1.3 cm in diameter and then pressed. 2016 coin-type cells (Toyo system) were assembled in an argon-filled glove box (M-braun MB 20G) by stacking a microporous polypropylene (Celgard 2400) separator containing a liquid electrolyte of 1 M $LiClO_4$ in 1:1 EC/DMC (Merck) between the cathode and the lithium metal foil anode (Cyprus Foote Mineral, 99.98%, USA). The cells were charged and discharged galvanostatically between 2.5 and 4.3 V (versus
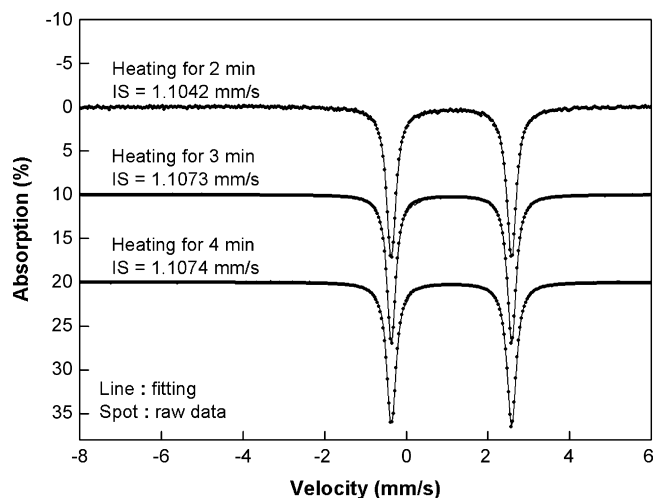

Fig. 2. Mössbauer spectra of $LiFePO_4$-C (ball-milling at a ball-to-powder ratio of 0.54:1; microwave heating for 2–4 min) at room temperature.
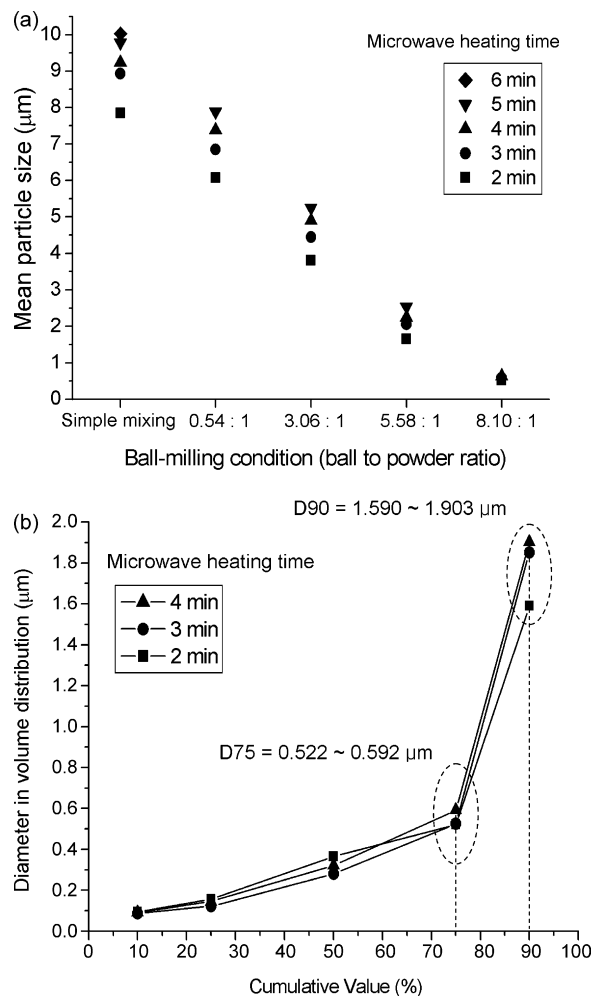

Fig. 3. Particle size of $LiFePO_4$-C measured by laser particle size analyzer: (a) mean particle size of $LiFePO_4$-C; (b) particle diameter of $LiFePO_4$-C (ball-milling at a ball-to-powder ratio of 8.10:1; microwave heating for 2–4 min) in volume distribution as a function of cumulative value. In case of the group of particles cumulated up to n (vol%) in the sequence of particle diameter from low to high, Dn means the diameter of the largest particle in that group.

Li/Li$^+$) at 27 °C by means of a Toscat-3100u battery tester (Toyo System). The rest time between charging and discharging was 10 min.

3. Results and discussion

The X-ray diffraction patterns of LiFePO$_4$-C prepared by ball-milling at various ball-to-powder ratios for 30 min and microwave heating for 2–5 min are presented in Fig. 1. It is evident that well-crystallized LiFePO$_4$-C with an olivine type structure is successfully synthesized by ball-milling for 30 min followed by microwave heating within 5 min. The Fe$_2$P phase, a byproduct formed in a strong reductive atmosphere

[9], is formed at a later stage at each ball-to-powder ratio, as confirmed in Fig. 1(a–d). The reason for this phenomenon will be discussed later.

Very small amounts of Fe^{3+} impurities that may exist in the LiFePO$_4$-C cannot be detected by X-ray diffraction analysis as pointed out by Yamada et al. [5]. Using Mössbauer spectroscopy, they demonstrated that a very small amount of Fe^{3+} impurity, not detected by X-ray diffraction analysis, reduced the capacity of LiFePO$_4$ significantly. Hence, Mössbauer spectroscopy, which is more sensitive than X-ray diffraction, was used to detect Fe^{3+} impurities. Mössbauer spectra of LiFePO$_4$-C synthesized by ball-milling at a ball-to-powder ratio of 0.54:1 and microwave heating for 2–4 min are presented in Fig. 2. It can be seen that one symmetric doublet exists in all the spectra. Their isomer
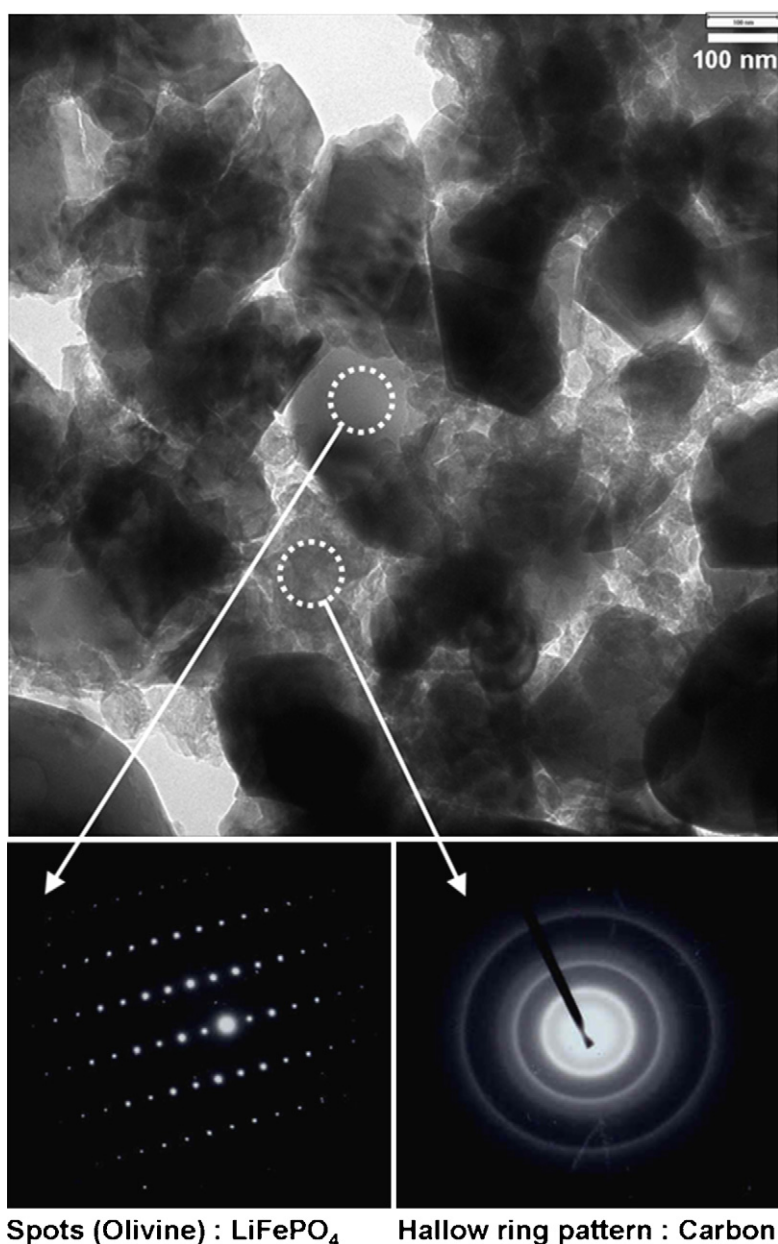

Fig. 4. Transmission electron micrograph of LiFePO$_4$-C (ball-milling at a ball-to-powder ratio of 8.10:1, microwave heating for 2 min) and the corresponding selected area diffraction patterns (SADPs) (polygonal particles: LiFePO$_4$, cotton-like particles: carbon).

shift (IS) values are 1.1042, 1.1073 and 1.1074 mm s^{-1}, respectively, and these are typical of those of ionic compounds with bare Fe^{2+} ions [5,23]. From Mössbauer spectroscopy, it is therefore confirmed that a composite of single-phase $LiFePO_4$ and carbon is successfully synthesized by ball-milling for 30 min and microwave heating within 4 min.

In this work, $LiFePO_4$-C without Fe^{3+} impurities is synthesized even in 2 min by microwave heating. which is the shortest microwave heating time that has ever been reported for the synthesis of $LiFePO_4$ by microwave heating. This result is due to the fact that the microwave power (750 W) applied in this work is higher than 550 W [18] and 650 W [19] in other studies because we found from X-ray diffraction analysis (not shown in this paper) of $LiFePO_4$-C prepared by simple mixing and microwave heating that $LiFePO_4$-C was also produced in 2 min by microwave heating without ball-milling.

The mean particle size of the $LiFePO_4$-C was measured by LPSA (Fig. 3(a)). As the ball-to-powder ratio (i.e., ball-milling power) increases, the mean particle size decreases, as shown in Fig. 3(a). When applying ball-milling at the highest ball-to-powder ratio (8.10:1), the mean particle size of the $LiFePO_4$-C produced by microwave heating for 2–4 min is 0.530, 0.585 and 0.640 μm, respectively. Thus, the mean particle size is much smaller than that (~1 μm) reported by Park et al. [19]. The particle size of $LiFePO_4$-C prepared by ball-milling at a ball-to-powder ratio of 8.10:1 and microwave heating for 2–4 min is presented in Fig. 3(b) in the form of the particle diameter in volume distribution as a function of the cumulative value. It is known from the D75 value that 75% of the total volume of $LiFePO_4$-C is composed of particles with a diameter of 0.522, 0.526 and 0.592 μm, and less. Besides, the gentle slope from D10 to D75 means that the particle size of $LiFePO_4$-C is fairly uniform.

Transmission electron micrograph of $LiFePO_4$-C and its selected area diffraction patterns (SADPs) are given in Fig. 4. Two distinctive morphologies, namely, polygonal particles and cotton-like particles, are observed in the micrograph. These particles are identified as $LiFePO_4$ and amorphous carbon, respectively, by SADPs. It is seen in Fig. 4 that almost all the particles of $LiFePO_4$ are connected by amorphous carbon, and the particles of $LiFePO_4$ and carbon are very homogeneously mixed at a nanometer scale.

Examining the results of the particle size analysis and TEM studies, the emergence of the Fe_2P phase more quickly with the ball-to-powder ratio can be explained. The Fe_2P phase has been reported to be formed by so a strong reductive atmosphere that it can break the covalent bond between phosphorous and oxygen in the PO_4^{3-} polyanion [9]. Therefore, it is reasonable that when microwave heating is performed for a long time, Fe_2P phase appears, because the reductive atmosphere generated by the carbothermal reaction becomes stronger with temperature. Based on this consideration and the results of Fig. 1(a–d), it can be concluded that a higher temperature is reached in the same microwave heating time by a higher ball-milling power. The DTA curves of the ball-milled mixtures before microwave heating are given in Fig. 5. The data show that the exothermic peak position corresponding to the temperature where $LiFePO_4$-C is synthesized is shifted from 650 to 527 °C with ball-milling power. This phenomenon implies that the exothermic reaction
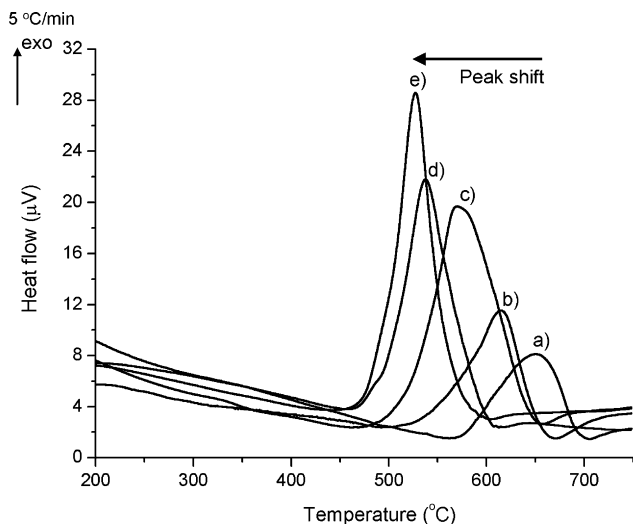

Fig. 5. Differential thermal analysis of mixtures ball-milled at various ball-to-powder ratios: (a) simple mixing (no ball-milling); (b) 0.54:1; (c) 3.06:1; (d) 5.58:1; (e) 8.10:1.
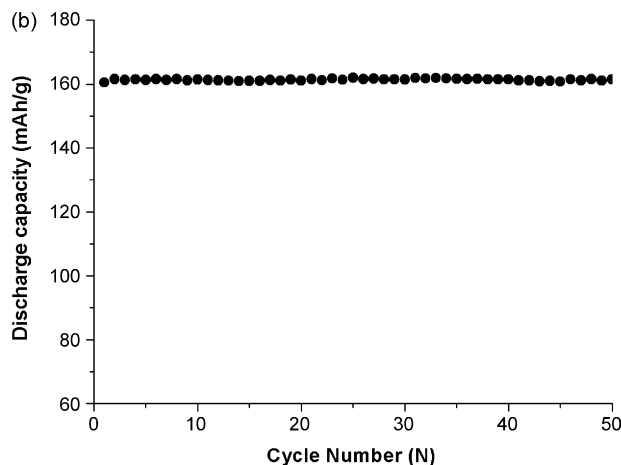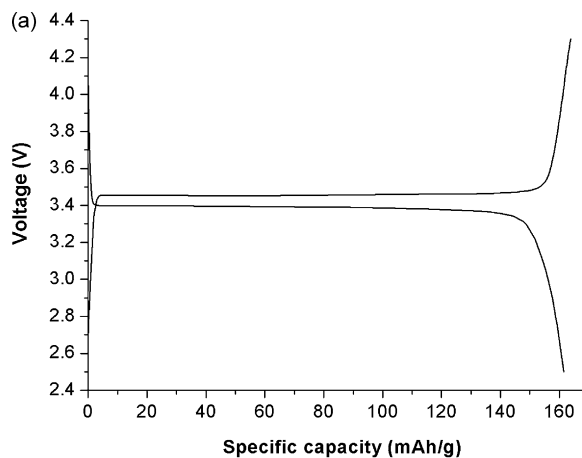

Fig. 6. (a) Initial charge–discharge curve of $LiFePO_4$-C (ball-milling at ball-to-powder ratio of 8.10:1; microwave heating for 2 min) at 27 °C (charge: C/30, discharge: C/10); (b) cycling performance at 27 °C.

takes place earlier during microwave heating. In addition to DTA results, it can be inferred from Figs. 3(a) and 4 that an increased contact area between the precursor mixture and the carbon by ball-milling enhances the efficiency of microwave heating. Consequently, it is concluded that in the case of the precursor mixture processed at a higher ball-to-powder ratio, the reductive atmosphere is stronger in the same microwave heating time due to a higher temperature because the exothermic reaction occurs earlier and the microwave heating efficiency is also higher.

The initial charge–discharge curve of $LiFePO_4$-C produced by ball-milling at ball-to-powder ratio of 8.10:1 and microwave heating for 2 min is presented in Fig. 6(a). In the discharge curve, a long flat voltage-plateau appears and then the voltage sharply falls to the cut-off value (2.5 V). This behaviour results in a high discharge capacity of 161 mAh g (95.0% of the theoretical capacity of $LiFePO_4$). Furthermore, the $LiFePO_4$-C gives a very stable cycling performance (Fig. 6(b)). These electrochemical properties are better than those reported previously for microwave heating [19].

It is expected that $LiFePO_4$-C with Fe_2P will have better electrochemical properties than $LiFePO_4$-C without Fe_2P because Fe_2P (metallic compound, σ: 10^{-1} S cm^{-1}) has been already reported to increase the conductivity of $LiFePO_4$ drastically to around 10^{-2} S cm^{-1} [13]. Electrochemical testing of $LiFePO_4$-C with Fe_2P is in progress and it is planned to disclose the results at the first available opportunity.

4. Conclusions

A very simple and rapid method has been developed for the synthesis of a $LiFePO_4$-C composite with fine and uniform particle size (mean particle size $\leq 0.640\,\mu m$, D75 in volume distribution $\leq 0.592\,\mu m$), and with extremely uniform carbon distribution. The procedure involves vibrant type ball-milling for 30 min and microwave heating for 2–4 min. $LiFePO_4$-C synthesized by ball-milling at a ball-to-powder ratio of 8.10:1 and microwave heating for 2 min has better electrochemical properties (high discharge capacity of 161 mAh g^{-1} at C/10, very stable cyclic performance) than those reported in previous studies of the application of microwave heating.

The higher microwave heating power (750 W) employed in this work shortens to 2 min the microwave heating time required to synthesize well-crystallized $LiFePO_4$ without Fe^{3+} impurities. This is the shortest microwave heating time that has ever been reported for the synthesis of $LiFePO_4$ by microwave heat-

ing. The ball-milling process lowers the synthetic temperature of $LiFePO_4$ and increases the microwave heating efficiency in addition to the advantages of reducing the particle size and distributing carbon uniformly. Ball-milling precursor materials with carbon are both simpler and faster than the previous two-step process of co-precipitation and carbon mixing.

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