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Electrochemical properties of single-phase LiFePO$_4$ synthesized using LiF as Li precursor and hydrogen and carbon gel as reducing agents

Y. Z. Dong · Y. M. Zhao · H. Duan · L. Chen · Z. F. He · Y. H. Chen

Abstract LiFePO$_4$ samples have been synthesized by mixing stoichiometric amounts of $(NH_4)_2HPO_4$, $FeC_2O_4 \cdot 2H_2O$, and LiF. During synthesis, carbon gel was used as the carbon source. Single-phase LiFePO$_4$ can be formed when the heating temperature ranges from 650 to 800 °C and it is decomposed into $Li_4P_2O_7$, Li_3PO_4, Fe_2P, and Li_3P_7 when the temperature comes to 850 °C. We find that the ratio of the lattice parameter (a/c) decreases with the increasing temperature, thereby increasing the Li$^+$ diffusion channel length. Both the decrease of a/c and the abrupt crystal growth are expected to contribute to the monotonic decrease of the initial capacity of the samples. The sample heated at 650 °C with a smaller uniform particle size and relative higher specific surface area (8.2 m^2/g) shows an excellent electrochemical performance. The initial specific capacity of 156.7(3) mAh/g is obtained at the rate of C/10.

Keywords Lithium ion cells · LiFePO$_4$ · LiF · Li precursor · Carbon gel

Introduction

In recent years, lithium ion batteries have been of great potential application in electric vehicles, hybrid electric vehicles, dispersed energy storage systems, and other uses such as space batteries. The cost, safety, environmental friendliness, and long operational life of the cathode materials are of major concerns for the application of large-scale lithium ion batteries. Commercial lithium ion batteries utilize generally cobalt-based oxides as the positive electrode [1, 2], but its high cost and toxicity prevent it from large-scale or biomedical applications. Manganese-based materials are attractive because of both their low cost and low toxicity. However, they suffer from remarkable capacity fading during cycling, especially at high temperatures. As part of an intensive search for alternative materials, lithium transition metal phosphates (LiFePO$_4$) have become of great interest as storage cathodes for rechargeable lithium ion batteries because of its high energy density (around 170 mAh/g), low raw material cost, environmental friendliness, and safety. In addition, because of its structural similarity between the charged and discharged states, it shows good cycle stability.

A cathode material is required to be a mixed ionic and electronic conductor. In this respect, the phosphates are not ideal cathode material due to their low electronic conductivities. For example, the pristine form of LiFePO$_4$ has an electronic conductivity of only 10^{-9}–10^{-10} S cm^{-1} and exhibits very poor electrochemical performance [3].

In order to improve the electrochemical performance of a lithium iron phosphate sample, many different material processing approaches were reported in the earlier work, such as reducing the crystal size of LiFePO$_4$ [4, 5], carbon addition [6–9], metal powder addition [10], and doping with supervalent ions [3, 11]. In these methods, especially the carbon addition was a very promising approach. Conductive carbon, added during the synthesis, interfere with the grains coalescence determining grain size reduc-

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tion. Both particle size minimization and intimate carbon contact have been proved to optimize the electrochemical performance.

The LiFePO$_4$ compound can be prepared by solid-state reaction synthesis, where Li$_2$CO$_3$ is usually used as the Li precursor [12–14]. Impurities often exist unless the heating temperatures are increased to 800 °C. However, the higher heating temperatures can cause the abrupt growth of particles, which has a negative influence on the electrochemical performances, and thus a synthesis routine using other Li precursors instead of Li$_2$CO$_3$ should be developed. LiF is usually regarded as a stable compound and rarely used to prepare the lithium-containing electrode materials. Wang et al. [15] successfully synthesized LiFePO$_4$ using LiF as the lithium source at 600 °C. The heating temperature is lower than that using Li$_2$CO$_3$ and other Li salts as the lithium source and thus avoids the abrupt growth of particles.

Based on the above discussion, here, we synthesized LiFePO$_4$ compounds using LiF as lithium source and carbon gel as carbon source. The properties of LiFePO$_4$ compounds were investigated. The solid-state reaction mechanism was analyzed by X-ray diffraction (XRD). The temperature ranges for the single-phase LiFePO$_4$ were obtained. The heating temperature dependences of the lattice parameters ratio a/c and the electrochemical properties of LiFePO$_4$ have been investigated.

Experimental

LiFePO$_4$ samples were made by mixing stoichiometric amounts of (NH$_4$)$_2$HPO$_4$, FeC$_2$O$_4$·2H$_2$O, and LiF with carbon gel (the synthesis procedure is described below) as the carbon source [16]. The total amounts of carbon gel was 10 wt.% for the final LiFePO$_4$ product. The precursors were dispersed into acetone and ball-milled for 7 h in a planetary mill. After evaporating acetone, the mixture was first decomposed at 350 °C in a N$_2$ atmosphere for 10 h to evaporate H$_2$O and NH$_3$. The reagents were re-ground prior to heating in a sealed tube furnace. The samples were heated at a rate of 2 °C/min to the temperatures ranging from 600 to 850 °C and held for 10 h under a stream of a gas mixture of 95% Ar+5% H$_2$. Before removal from the furnace, the samples were slowly cooled down to room temperature.

As the carbon source, the carbon gel was prepared firstly by sol–gel method, following literature procedure [16], using C$_6$H$_6$O$_2$ (resorcinol, 98%), CH$_2$O (formaldehyde, 37% in water), and Na$_2$CO$_3$ (sodium carbonate, 99.8%) as starting materials. A solution containing 5% (w/v) solids was prepared, in which the mole rate of C$_6$H$_6$O$_2$:CH$_2$O: Na$_2$CO$_3$ was fixed at 1:2:0.02. Na$_2$CO$_3$ was only used as

the catalyst. The solution was sealed in a flask and magnetically stirred for 30 min, followed by 1 day of curing in an oven at 85 °C (no stirring). After curing, the gel was removed from the oven and cooled to room temperature. The gel was washed with acetone. Then, the washed gel was dried at 110 °C under N$_2$ in a tube furnace for 5 h. Finally, the carbon gel was formed by pyrolysis of the dried gel at 1,050 °C for 3 h in a N$_2$ atmosphere with both heating and cooling rates set at 5 °C min^{-1}.

The initial characterization of the material was carried out using powder XRD, using a MAX 18A-HF diffractometer with rotating anode, which had an 18 kW X-ray generator and CuK$_\alpha$ radiation. A graphite monochromator was used for diffracted beams. The power of 12 kW (300 mA, 40 kV) was used in our experiment. All the diffraction intensity data for Rietveld refinement analysis were collected by a step-scan mode with a scanning step of 0.02° and a sampling time of 2 s. Rietveld refinement was performed using the FullProf program to obtain the crystal structure parameters. Scanning electron microscopy (SEM) images were carried out with a LEO 1530VP (LEO, Germany) electron microscope in order to examine the effect of the heating temperature on powder morphology. The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method (Micromeritics FlowsorbIII). The carbon content was determined by a CHN analyzer (MT-5, Yanaco) as 9.12 wt% (referred to LiFePO$_4$).

For electrochemical measurements, the LiFePO$_4$ electrodes were prepared by mixing with a conductive carbon, acetylene black, and a binder, PVDF-HFP copolymer. The electrode constituents were mixed into a slurry with acetone to achieve homogeneity. The resulting slurry was coated on the aluminum foil current collector. After the acetone was evaporated, the electrode composition was 85:10:5 for active material, carbon, and binder, respectively. The electrode was then dried at 50 °C for 24 h and pressed (5 MPa), respectively. The fabricated electrodes were dried again at 80 °C for 12 h in a vacuum and cut into pieces of 1×1 cm with ~5 mg of active materials on it. Two-electrode electrochemical cells were assembled in a Mikrouna glove box filled with high-purity argon. The lithium metal foil, Celgard® 2320, and 1 M LiPF$_6$ in EC:DMC (1:1 vol.%) were used as anode, a separator, and an electrolyte, respectively. The electrochemical capacity measurements were performed in the voltage range between 2.5 and 4.2 V, and the electrochemical capacity of samples was evaluated based on the active materials.

Result and discussion

The XRD pattern of the carbon gel sample is shown in Fig. 1. A broad peak with the width of 10° at $2\theta=44°$ is
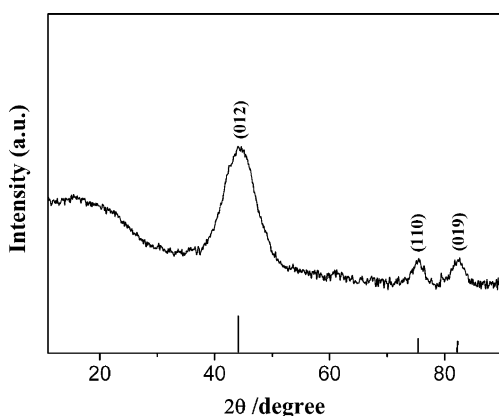
Fig. 1 XRD pattern of the carbon gel sample. The *short lines* indicate the data of the crystalline carbon from JCPDS card (No.: 50-1083)

observed, which reveals that the carbon gel was an amorphous.

Figure 2 shows the XRD patterns of LiFePO$_4$ synthesized by the solid-state reaction with LiF as Li precursor at different temperatures: (a) 600 °C, (b) 650 °C, (c) 700 °C, (d) 750 °C, (e) 800 °C, and (f) 850 °C. Obviously, the impurity phase Fe$_3$(PO$_4$)$_2$ exists although LiFePO$_4$ is the dominant phase at 600 °C (Fig. 2, pattern a). When the temperature was higher than 650 °C, single-phase LiFePO$_4$ with orthorhombic structure appeared (Fig. 2, pattern b–e). It should be noted that the temperature to get single-phase LiFePO$_4$ with orthorhombic structure in our experiments (650 °C) is higher than that reported by Wang et al. [15]. The difference is due to different experimental procedures. On the other hand, the single-phase LiFePO$_4$ starts to decompose into Li$_4$P$_2$O$_7$, Li$_3$PO$_4$, Fe$_2$P, and Li$_3$P$_7$ when the heating temperature reaches 850 °C as shown in

Fig. 2, pattern f. Thus, we can conclude that single-phase LiFePO$_4$ compounds may be existent only in the heating temperature regions from 650 to 800 °C under our experimental conditions.

The XRD patterns of LiFePO$_4$ compounds were successfully indexed with orthorhombic lattice using the program Dicovl. The space group of LiFePO$_4$ compounds was derived to be Pnma based on the reflection conditions. In order to verify the contamination of Fe$_2$P or other compounds as the impurity phases and whether iron atoms exist in the lithium lattice site of our products, the single-phase model Rietveld refinement of the powder XRD data of LiFePO$_4$ compounds was performed for the samples prepared with the heating temperatures ranging from 650 to 800 °C. The space group of Pnma was chosen as the refinement model. In this orthorhombic structure, each unit cell contains four chemical formula units of LiFePO$_4$. There is one lithium position [4a], one iron position [4c(1)], one phosphorus position [4c(2)], and three oxygen sites [4c (3), 4c(4), 8d]. Our Rietveld refinement results reveal that 4 (a) positions are occupied by 4Li, 4c(1) by 4Fe, 4c(2) by 4P, and 4c(3) and 8d by 12O, respectively. A typical refinement result of the LiFePO$_4$ compound heated at the temperature of 650 °C is shown in Fig. 3. The reasonably small R_{wp} factors (11.90~9.81%) suggest that single-phase LiFePO$_4$ had been obtained at the heating temperatures ranging from 650 800 °C. A test refinement on a multiple-phase model had been also performed with the impurity phases Fe$_2$P or Fe$_3$(PO$_4$)$_2$. The refinement results indicate that no impurity phases of Fe$_2$P or Fe$_3$(PO$_4$)$_2$ can be detected under the resolution of our X-ray diffractometer. Our results are in contrast with [17], where Franger et al. concluded that the solid-state reactions are not convenient for preparation of pure LiFePO$_4$ by comparing different LiFePO$_4$ synthesis routes. In addition, the refinements were
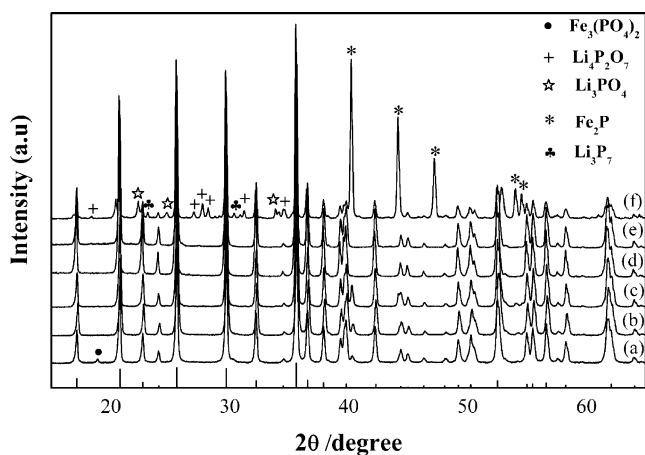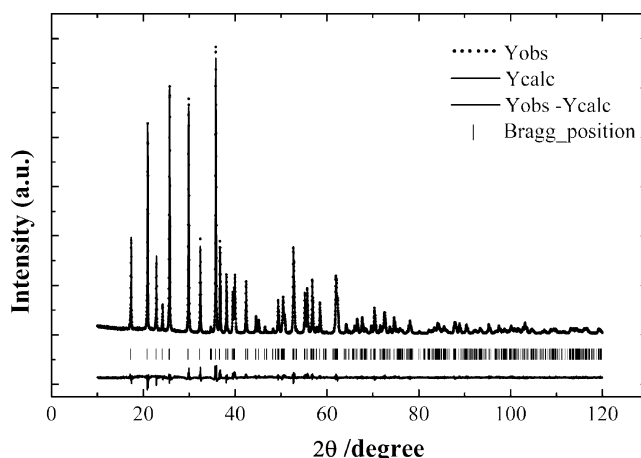

Fig. 2 XRD of LiFePO$_4$ compounds synthesized at different temperatures: (*a*) 600 °C, (*b*) 650 °C, (*c*) 700 °C, (*d*) 750 °C, (*e*) 800 °C, (*f*) 850 °C. The *short lines* indicate the data of the crystalline LiFePO$_4$ with orthorhombic structure from JCPDS card (No.: 81-1173)

Fig. 3 X-ray Rietveld refinement fitting of LiFePO$_4$ compound heated at 650 °C

Table 1 Lattice constants (*a*, *b*, and *c*) and reliability factors (R_p (%), R_{wp} (%), and R_{exp}(%)) obtained from the Rietveld refinement for LiFePO₄ compounds heated at different temperatures (*T*). (Experimental details of X-ray powder diffraction and Rietveld refinement are listed)

T	650°C	700°C	750°C	800°C
a (Å)	10.3009 (2)	10.3011 (1)	10.3011 (3)	10.3014 (7)
b (Å)	6.0043 (5)	6.0063 (2)	6.0095 (7)	6.0116 (5)
c (Å)	4.6919 (2)	4.6999 (4)	4.7035 (3)	4.7144 (2)
R_p (%)	8.68	8.58	6.62	6.24
R_{wp}(%)	11.61	11.12	8.38	9.68
R_{exp}(%)	5.46	5.37	5.25	5.44

Diffractometer, MAX 18A-HF; radiation type, CuK$_\alpha$; wavelength (Å), 1.5418; profile range (2θ), 10° to 120°; step size (2θ), 0.02°; step scan time (s), 2

Fig. 5 Initial charge/discharge curves of LiFePO₄ compounds synthesized at different temperatures with a low current rate (C/10): (*a*) 600°C, (*b*) 650°C, (*c*) 700°C, (*d*) 750°C, (*e*) 800°C, (*f*) 850°C

also performed, where we exchanged some iron atoms with the lithium atoms site and refined the isotropic temperature parameters and/or occupation numbers for Li and Fe atoms. Either negative values of thermal parameters of Li and Fe or higher R_{wp} (>18%) were obtained, which implies that there is no mixed occupation of Li and Fe occurring in our single-phase LiFePO₄ compounds. The cell parameters *a*, *b*, and *c*, as well as the reliability factors obtained from the result of the Rietveld refinement are summarized in Table 1. The experimental details of X-ray powder diffraction and Rietveld refinement are also listed.

From Table 1, we can find that with increase of the heating temperature from 650 to 800°C the lattice parameters *a* and *b* slightly increase, but there is a relative greater increase of lattice parameters *c*. These variations in lattice parameters with increasing temperature are expected to be caused by the change in crystallinity [18]. Because lithium
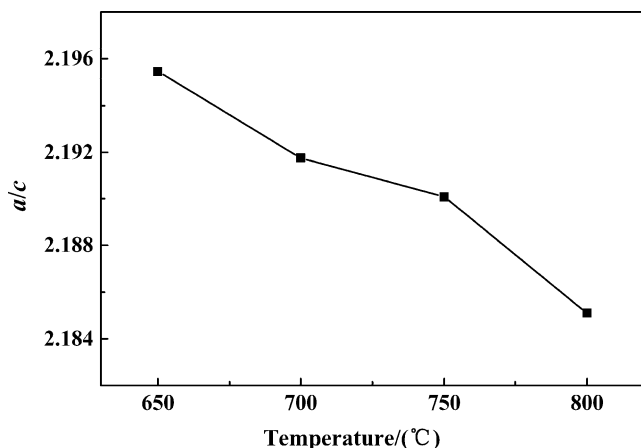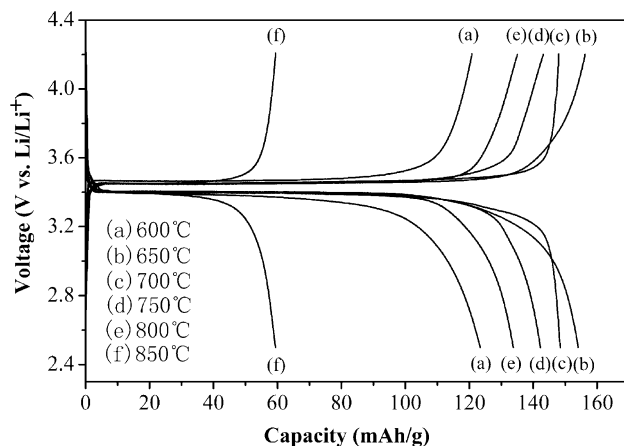
diffusion in olivine-type LiFePO₄ is one-dimensional along *c* directions [19], the ratio *a/c* is an important factor relating to the electrochemical performance of the LiFePO₄. A smaller value of *a/c* is corresponding to a better electrochemical performance. As shown in Fig. 4, the values of *a/c* decreased monotonically from 2.1955(2) at 650°C to 2.1850(3) at 800°C.

Figure 5 shows the initial charge/discharge curves measured at C/10 rate for LiFePO₄ compounds synthesized at different temperatures. The initial capacity of 123.5(2) mAh/g was obtained for the samples prepared at the temperatures of 600°C. Based on the XRD data, a little Fe₃(PO₄)₂ existed as impurity in this sample (Fig. 2 pattern a). Higher capacity was obtained for the single-phase samples synthesized from 650 to 800°C. A small capacity was found for the samples prepared at the temperatures of 850°C, where the LiFePO₄ started to decompose. It implies
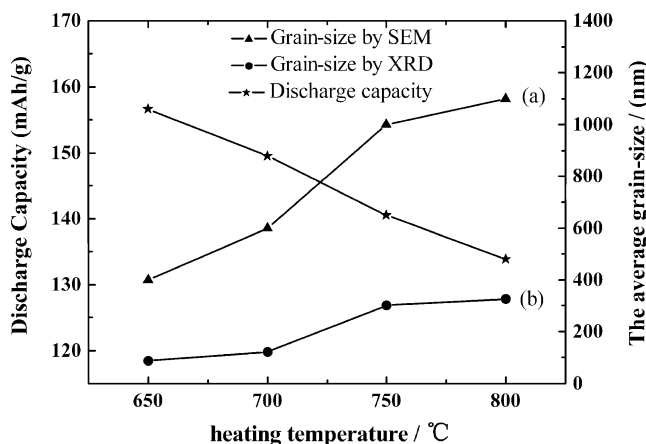

Fig. 4 Ratios of lattice parameters *a/c* of LiFePO₄ as a function of the synthesizing temperature

Fig. 6 The heating temperature dependences of the discharge capacity (first discharge at C/10 rate) and the average grain size (observed by SEM (*a*) and by XRD (*b*))

that a small amount of impurity can affect the electrochemical properties remarkably.

The discharge capacity of single-phase LiFePO$_4$ as a function of the heating temperature is represented in Fig. 6. The initial capacity decreases monotonically with the increase of the heating temperature. The sample synthesized at 650°C exhibit the highest initial capacity of 156.7(3) mAh/g at the rate of C/10.

In order to elucidate what happens for the morphology of the samples obtained at the temperatures ranging from 650 to 800°C, Fig. 7a–d show the SEM images for the samples heated at the different temperatures. The heating temperature dependences of the particle size, D_s, obtained from SEM images are shown in Fig. 6. Obviously, a higher heating temperature leads to better crystal growth. The particle size for a compound heated at 650°C is less than 500 nm, and it grows up to around 1.1 μm for the compound heated at 800°C. We can also calculate the average grain size D_x from the XRD peaks using the Scherrer formular, $D = 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength employed, θ is the diffraction angle of the most intense peaks ((2 0 0), (1 0 1), (1 1 1), (2 1 1) and (3 1 1)), and β is defined as $\beta^2 = \beta_m^2 - \beta_s^2$. Here, β_m is the experimental full width at half maximum (FWHM) and β_s is the FWHM of a standard silicon sample. The as-obtained D_x are presented in Fig. 6. Although the particle sizes observed by SEM are several times larger than those calculated by XRD, which indicates that each particle

observed by SEM consists of several crystallized grains, a similar grain growth trend can be found from Fig. 6. Furthermore, the specific surface areas of the four samples are 8.2, 7.1, 5.7, and 4.2 m^2/g, respectively. The change trend is consistent with SEM measurements.

From Fig. 7, we can see that the sample with smaller uniform particle size and relative higher specific surface area (8.2 m^2/g) can be obtained at the heating temperature of 650°C, where a better electrochemical performance can be presented, as shown in Fig. 5. In contrast, with the increase of heating temperature from 650 to 800°C, the particles with increasing non-uniformity and particle size monotonically can also be observed in Fig. 7, where the abundance of increasing grain boundary with increasing heating temperature leads to poor connection of LiFePO$_4$ particles. Furthermore, in particles with a larger diameter and a relative lower specific area, considering its inferior electronic conductivity, the electronics have to diffuse over greater distance between the surface and center during lithium insertion or extraction, and the active materials near the center of particle contribute very little to the charge/discharge reaction [20]. Our experimental results suggest that the best performance can be obtained with optimizing the powder characteristic at a relative lower temperature of 650°C. The small uniform particles with the diameter of about 400 nm (Fig. 7), which have a relative larger specific area (8.2 m^2/g), can bring on the better performance. Both the abrupt increase of particle size and the decreasing of the ratio of a/c at the heating

Fig. 7 SEM images of the LiFePO$_4$ compounds synthesized at different temperatures: **a** 650°C, **b** 700°C, **c** 750°C, **d** 800°C
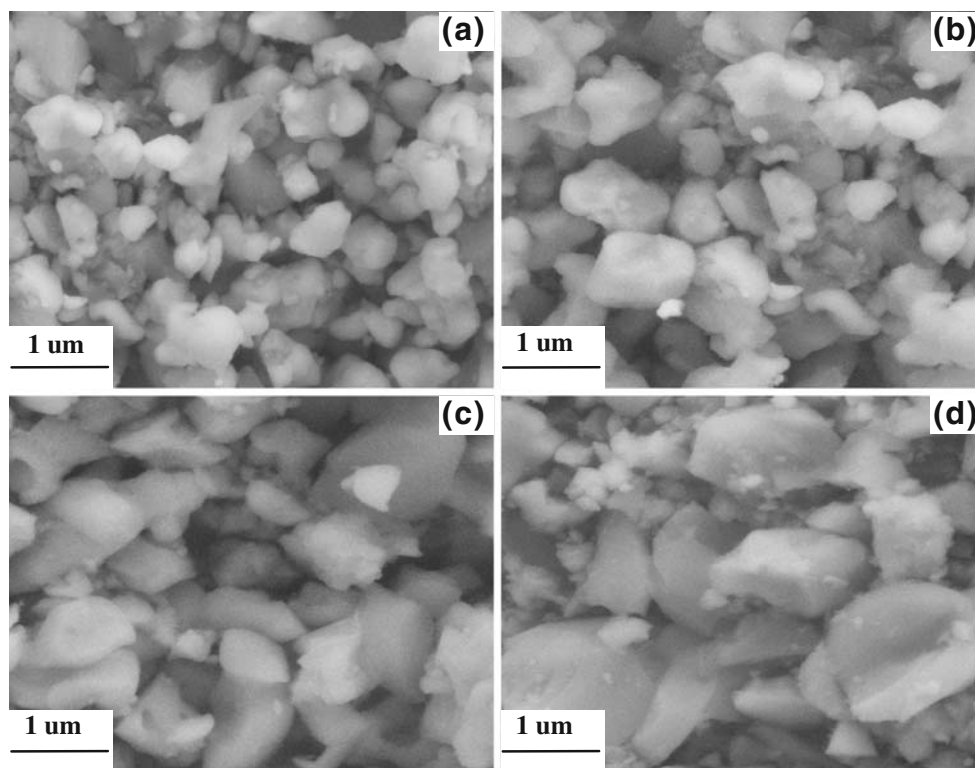
temperature higher than 650 °C may be responsible for the decreasing of the initial capacity monotonically.

The cycle performances of LiFePO$_4$ prepared from LiF at the temperatures ranging from 600 to 850 °C are shown in Fig. 8. The charge/discharge rate is 0.1C. The samples prepared using LiF as the Li precursor exhibit good capacity retention after 50 cycles. A relative sustained cycling behavior is observed for the samples heated at temperatures of 650 °C with the initial specific capacity of 156.7 mAh/g. The LiFePO$_4$ compound prepared at 650 °C shows higher initial specific capacity than those prepared at the temperatures higher than 650 °C in our experiment process. At the 50th cycle, the discharge capacities between 2.5 and 4.2 V are 92.6(3) (74.2% of initial capacity), 151.2 (6) (96.5% of initial capacity), 138.0(2) (92.3% of initial capacity), 122.2(3) (86.1% of initial capacity), 110.5(4) (82.6% of initial capacity), and 48.5(1) mAh/g (71.2% of initial capacity) for the samples heated at 600, 650, 700, 750, 800, and 850 °C, respectively.

It is well known that the rate capability is very important for the commercially viable systems. Rate capability refers to the ability of an electrode material to retain its capacity when discharged in different rates. In our experiment, the LiFePO$_4$ compound heated at 650 °C exhibits good rate performance as shown in Fig. 9. The cells were discharged at different rates C/10, C/5, and C/2 between 2.5 and 4.2 V, and the initial discharge capacities of 156.7(3), 151.9(2), and 144.3(4) mAh/g can be obtained, respectively. At C/10 rate, the mean fade of capacity is 0.07% per cycle. Even when the rate was increased to 1C, the specific capacity of 138.8(4) mAh/g still remained between 2.5 and 4.2 V, and the capacity fade per cycle is only 0.09%.

In our experimental procedure, LiFePO$_4$ compound heated at 650 °C shows the better specific capacity data as well as a better cycle and rate performance. It has been reported that
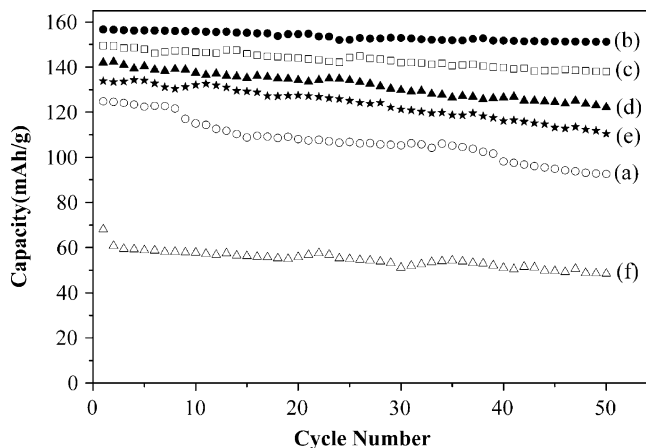

Fig. 8 The cycle performances LiFePO$_4$ compounds synthesized at various temperatures: (a) 600 °C, (b) 650 °C, (c) 700 °C, (d) 750 °C, (e) 800 °C, (f) 850 °C (cycled between 2.5 and 4.2 V, 0.1C)
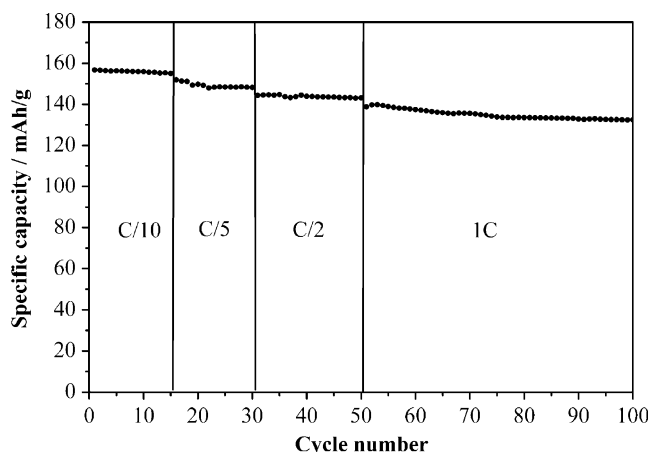

Fig. 9 Cycle performance of LiFePO$_4$ compound synthesized at 650 °C with different discharge rates

the residual carbon left over from the reactant is expected to be beneficial for electrochemical properties [21]. It has been shown that well-dispersed carbon can have a profound influence on the electrochemical insertion capacity [22]. In addition, it is also clear from morphological studies that high surface area carbon acts as a nucleation site for material growth, suppressing extensive grain growth in the product [23]. Although the temperature of 650 °C in our experimental procedure is higher than that reported by Wang et al. [15], the relative higher initial capacity of 156.7(3) mAh/g at the rate of C/10 can still be obtained in our experiment.

Conclusion

LiFePO$_4$ samples have been synthesized by mixing stoichiometric amounts of $(NH_4)_2HPO_4$, $FeC_2O_4 \cdot 2H_2O$, and LiF in an Ar–H$_2$ flow. In this reaction, the carbon gel was used as the carbon source. Single-phase LiFePO$_4$ can be only formed between 650 and 800 °C. When the heating temperature is higher than 800 °C, the single-phase LiFePO$_4$ is decomposed into $Li_4P_2O_7$, Li_3PO_4, Fe_2P, and Li_3P_7. The XRD results show that the ratio of a/c decreases when the heating temperature increases from 650 to 800 °C. The sample heated at 650 °C has the highest initial specific capacity, the best cycle performance, and a good rate behavior. Based on the XRD analysis and SEM images, the better electrochemical properties of the sample prepared at 650 °C are owing to the relative uniform particles, smaller particle size (about 400 nm), and relative higher ratio of a/c.

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