Int. J. Electrochem. Sci., 13 **(2018)** 2236 – 2247, doi: 10.20964/2018.03.17

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Synthesis of $LiFePO_4$/C with Fe_3O_4 as Iron Source by High Temperature Ball Milling

Qing Zhao[1,2], *Xuetian Li*[2,*], *Zhongbao Shao*[2], *Binshi Xu*[2], *Chengjun Liu*[1,2], *Maofa Jiang*[1,2], *Ron Zevenhoven*[3], *Henrik Saxén*[3]

[1] Key Laboratory for Ecological Metallurgy of Multimetallic Minerals (Ministry of Education), Northeastern University, Shenyang 110819, China
[2] School of Metallurgy, Northeastern University, Shenyang 110819, China
[3] Thermal and Flow Engineering Laboratory, Åbo Akademi University, Åbo/Turku 20500, Finland
[*]E-mail: xuetian.li@163.com

Received: 3 November 2017 / *Accepted:* 3 January 2018 / *Published:* 5 February 2018

$LiFePO_4$/C cathode material was prepared with Fe_3O_4 as iron source by a high temperature ball milling (HTBM) method and the effects of milling temperature were experimentally investigated in this work. The results indicated that high milling temperature improved the crystallinity of $LiFePO_4$, but that an unfavorable crystal agglomeration and the phase transformation from $LiFePO_4$ into $LiFeP_2O_7$ could occur when the temperature becomes too high. $LiFePO_4$/C synthesized by HTBM at 650°C exhibited the optimal electrochemical performance: the initial discharge capacities were 152.7, 146.6, 140.3, 130.0, 119.1 and 108.3 $mAhg^{-1}$ at rates of 0.5, 1.0, 2.0, 5.0 and 10C, respectively; after 50 cycles, the capacities of $LiFePO_4$/C sample were 147.0, 135.0, 126.4, 115.4, 105.6 and 95.3 at rates of 0.1, 0.5, 1.0, 2.0, 5.0 and 10C, and their capacity retention were 96.3%, 92.1%, 90.0%, 88.8%, 88.7% and 88.1%, respectively. No obvious capacity decay was observed demonstrating the excellent electrochemical performance of the product prepared by this work.

Keywords: $LiFePO_4$/C; Fe_3O_4; High temperature ball milling method; Electrochemical performance

1. INTRODUCTION

The electrochemical performance requirements and standards for batteries have rapidly become more stringent and demanding with the fast development of industry and applications in recent decades. Li-ion batteries have attracted more attention and are regarded to be an excellent choice because of attractive characteristics such as high operating voltage, high particle density, long cycle life, low self-discharge, and no memory effect [1]. Olivine-type $LiFePO_4$ is widely seen as a promising material for a Li-ion battery due to its high capacity (theoretically around 170 $mAhg^{-1}$), stable charge/discharge platform, low cost, environmental benignity and cycling stability [2-6]. To overcome the drawbacks of low electric conductivity and low lithium ion diffusion rate of the $LiFePO_4$ [7, 8], the material is usually coated with carbon [9, 10] or doped with some metal iron [11, 12].

Many methods, including high temperature solid phase methods [13,14], carbothermic reduction [15], co-precipitation [16,17], hydrothermal methods [18], microwave methods [19], sol-gel methods [20, 21], spray-pyrolysis [22] and emulsion drying methods [23] can be used to synthesize the $LiFePO_4$, although the product purity, production cost and efficiency are still unsatisfactory for industrial scale manufacture. A method of high temperature ball milling (HTBM) using a high-temperature ball-mill was employed in our earlier study [24], by which advanced materials can be prepared in an economical and efficient way [24-26].

Iron sources have a significant effect on the performance of $LiFePO_4$/C. The relatively high cost of Fe^{2+} raw material limits its industrialized application, and Fe^{3+} raw material requires large numbers of reducing agent. Therefore, Fe_3O_4 is regarded to be a promising iron sources to synthesize the $LiFePO_4$/C.

In this work, $LiFePO_4$ powder was prepared by the HTBM method with Fe_3O_4 [27], and the effects of milling temperature (600°C, 650°C, 700°C and 750°C) on crystallization behavior, phase transformation, and electrochemical properties of $LiFePO_4$/C were investigated.

2. EXPERIMENTAL

2.1. Preparation $LiFePO_4$/C

Analytical grade reagents including lithium dihydrogen phosphate (LiH_2PO_4), glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$) and magnetite (Fe_3O_4) were used as raw materials to produce a precursor for $LiFePO_4$/C. A mass of 1.2mol lithium dihydrogen phosphate and 45.5 g glucose monohydrate (mass ratio of $LiFePO_4$-to-C was 100:5) were dissolved in 250mL deionized water, after that 0.388mol magnetite with a molar ratio of $n_{Li}:n_{Fe} = 1.03:1$ [28] was added into the solution, which was agitated for 4 h for intensive mixing. The precursor for $LiFePO_4$/C was obtained after drying the product slurry at 120°C for 12h. The precursor was poured into a jar with some milling balls at a ball-to-powder mass ratio of 15:1 [29] followed by sealing of the mill with a very low rate of injection of pure nitrogen (> 99.99 %). The samples were firstly roasted at 350°C for 1 hour for glucose carbonization, and then heated to the set temperatures (600°C, 650°C, 700°C and 750°C) for 8h. A flow sheet of the process route was given in Fig.1

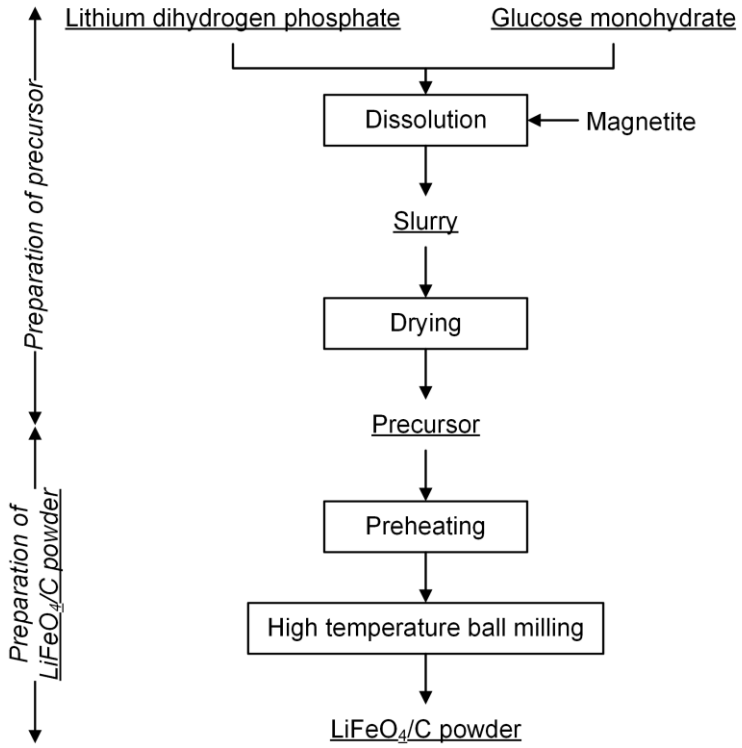


Figure 1. Flow sheet of the process route

2.2 Characterization of LiFePO$_4$/C

The structure of the LiFeO$_4$/C product was characterized by X-ray diffraction (XRD, Rigaku D/max-RB). The morphology was determined by scanning electron microscopy (SEM, HITACHI S-3000H) analysis, and the coating of carbon on LiFePO$_4$ was studied by transmittance electron microscopy (TEM, JEM-2100F) analysis.

2.3. Electrochemical Characterization

For the electrode preparation, LiFeO$_4$/C powder, carbon black and polyvinylidene fluoride (PVDF) binder were weighted with the mass ratio of 80:10:10 and mixed, followed by adding some N-methyl pyrrolidone (NMP), giving rise to an electrode slurry. The electrode slurry was coated on an aluminum foil and was then heated at 110℃ under vacuum for 12 h, the coated Al foil was cut into electrode disks (CR14 mm), which was used as an anode in the button battery assembling process that was conducted in an argon filled glove box. A lithium plate (CR16 mm) was used as the anode, and Celgard 2400 porous polypropylene screen was used as a membrane, 1 M LiPF$_6$/EC+DEC+EMC (1:1:1 in volume) as liquid electrolyte in the battery, respectively.

Battery-testing system (Neware Co., Ltd., China) was used to test the cycle charge-discharge behavior for button battery product at different rates from 2.5 to 4.2V (1C equals to 170mAhg^{-1}). The electrochemical impedance spectra (EIS) measurement was carried out on a CHI660E electrochemical work-station from 0.1HZ to 100 KHZ with amplitude of 5 mV. The cyclic voltammetry (CV) test was performed using CHI660E electrochemical work-station at a scan rate of 0.5 mV·s^{-1} at room temperature.

3. RESULTS AND DISCUSSION

3.1. Crystallization behavior and phase transformation

Fig. 2 shows the XRD patterns of $LiFePO_4$/C synthesized at the milling temperatures of 600, 650, 700 and 750°C for 8 h by HTBM. Obvious diffraction peaks of $LiFePO_4$ (olivine structure) were found in the four patterns, which are well indexed to an orthorhombic, *Pnmb* space group (JCPDS Card NO. 40-1499). Some $LiFePO_4$ was produced at 600°C HTBM but the synthesis reaction was incomplete, which was concluded from the co-existence of diffraction peaks of $LiFePO_4$ and intermediate Li_3PO_4. When the ball milling temperatures were 650 and 700°C, the diffraction peaks of Li_3PO_4 disappeared. Furthermore, some $LiFeP_2O_7$ was generated when the ball milling temperature reached 750°C as a result of the condensation of $LiFePO_4$, causing a decrease of conversion into $LiFePO_4$. The intensity of the diffraction peaks of $LiFePO_4$ was enhanced when the milling temperature increased from 600 to 750°C, showing the strong effect of the heating on the crystallinity of the $LiFePO_4$ in the milling process.

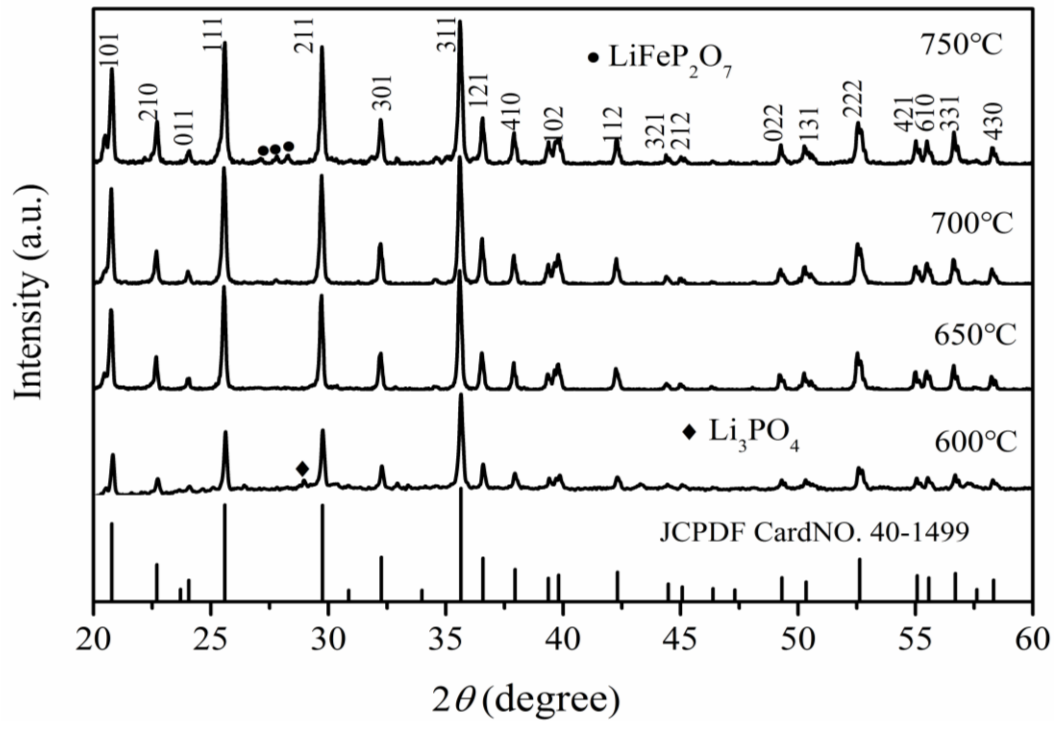


Figure 2. XRD patterns of samples prepared at different milling temperatures (600-750°C)

SEM images of the products prepared at the milling temperatures are shown in Fig. 3. Spherical $LiFePO_4$/C particles were obtained at the four milling temperatures, and a majority of the grain sizes of the powders were around 0.5 μm and often smaller. When the HTBM was conducted at 600°C the product had lower crystallinity, agreeing with the results of XRD analysis. The crystallinity increased and the grain size decreased when increasing the milling temperature from 600°C to 750°C, suggesting that a high temperature promotes crystal growth and grain purity. However, a severe crystal agglomeration phenomenon occurred when the ball milling process was performed at 750°C, which also has a negative effect on the electrochemical performance of the $LiFePO_4/C$ material. Therefore, the optimal milling temperature range for preparing fine $LiFePO_4/C$ powder obtained in the current study is in the range of 650-700°C, and the following investigations of the effect of milling duration on the $LiFePO_4/C$ product were therefore carried out at 650°C.

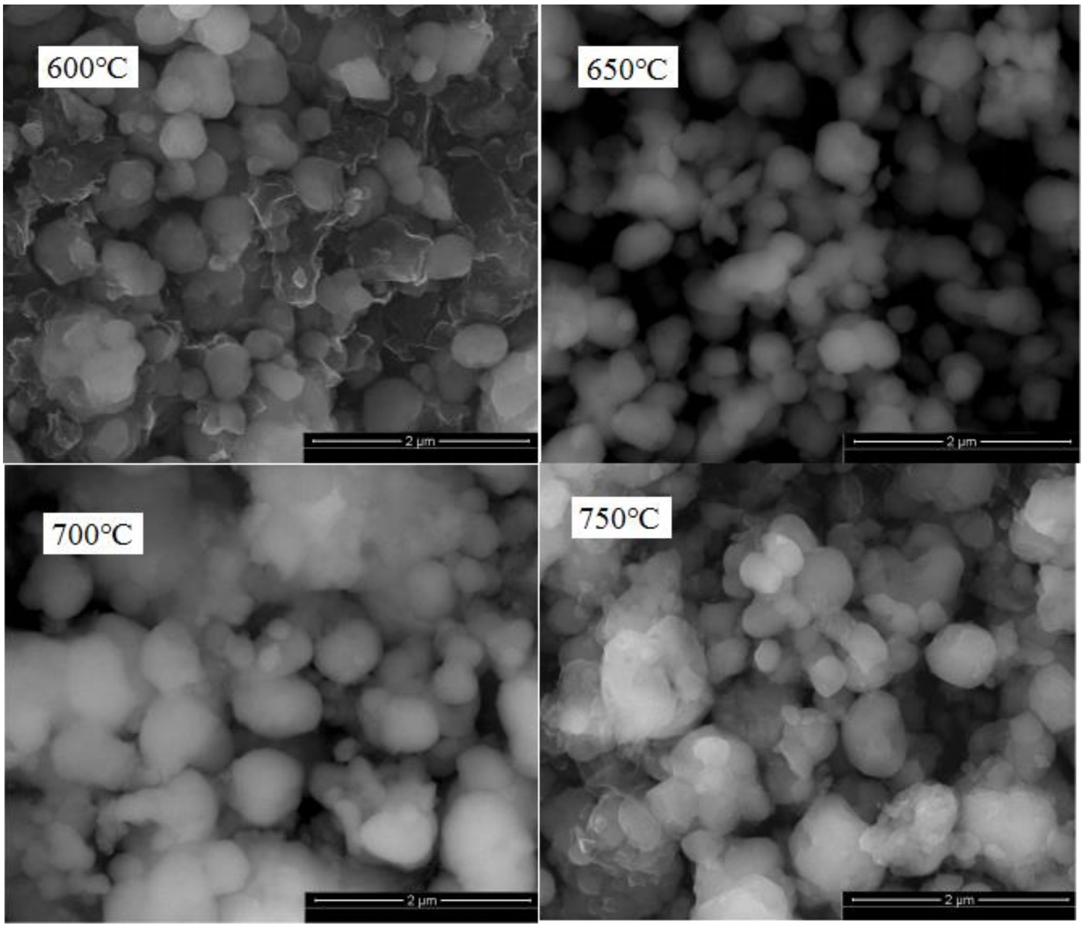


Figure 3. SEM images of samples prepared at different milling temperatures (600-750°C)

3.3. Coating results

In order to study the results of the coating of carbon on the $LiFePO_4$, TEM analysis was conducted on the product prepared by HTBM at 650°C for 8h, with an example presented in Fig. 4. It could be clearly observed that some carbon (dark color) has uniformly coated the surface of the $LiFePO_4$ particles, and other carbon (light color) combined with the $LiFePO_4/C$ clusters giving rise to a conductive network. Researchers have reported that the carbon films can inhibit the growth of the covered $LiFePO_4$ crystal and improve the electrical conductivity of the $LiFePO_4$ particles, which is very beneficial for obtaining a high performance $LiFePO_4/C$ cathode material [30, 31].

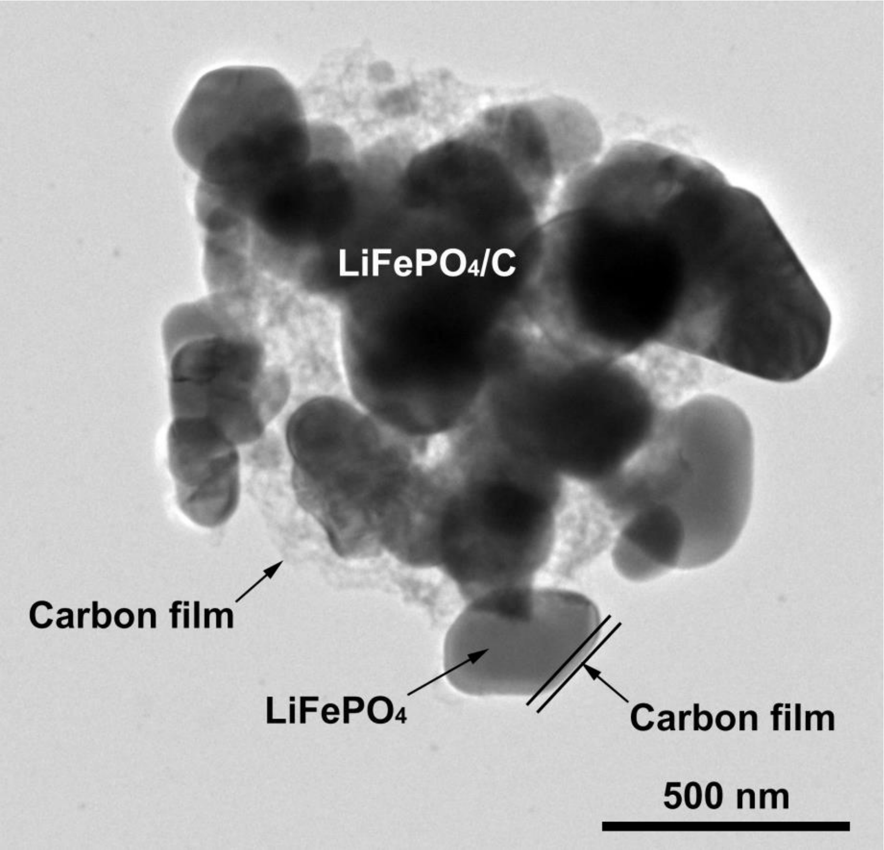
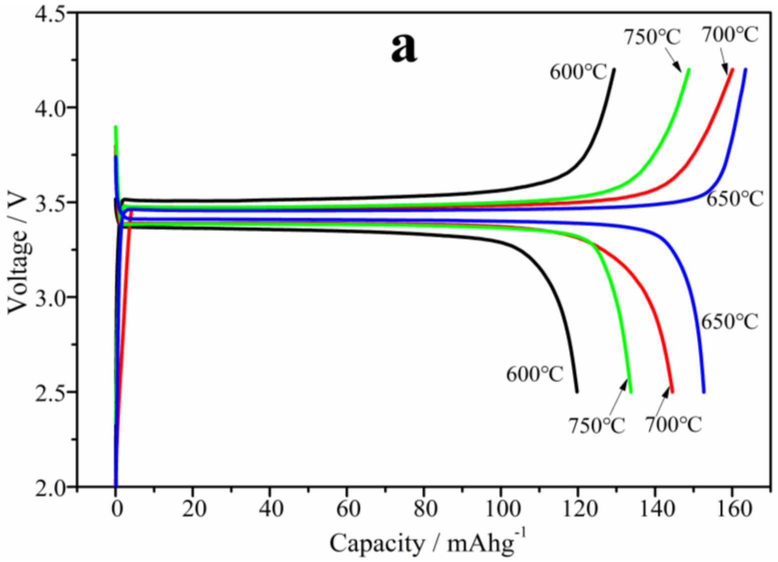


Figure 4. TEM image of the sample prepared by HTBM at 650°C

3.4. Electrochemical performance

Fig. 5 (a) shows charge/discharge curves of the batteries with $LiFePO_4$/C cathode materials that prepared by various temperatures at 0.1C-rate from 2.5 to 4.2 V (Li^+/Li). The initial discharge capacities of samples were 119.8, 152.7, 144.5 and 133.7mAhg^{-1} at 0.1C-rate, respectively.



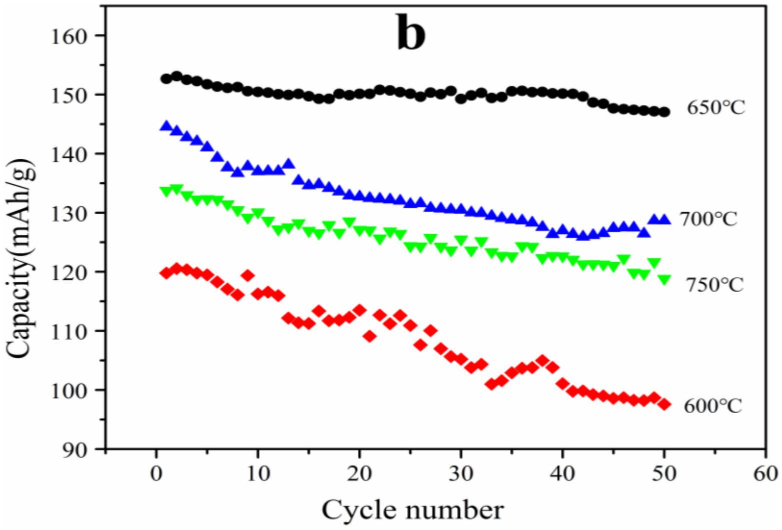


Figure 5. (a) Charge/discharge curves and (b) cycling performance at 0.1C-rate of $LiFePO_4$/C prepared at different temperatures

Fig.5 (b) shows the cycling performances of $LiFePO_4$/C prepared with various ball milling temperature at 0.1C-rate. After 50 cycles, the discharge capacities of the samples were 97.6, 147.0, 128.7 and 118.8 mAhg^{-1}, and their capacities retention were 81.5, 96.3, 89.0 and 88.8%, respectively. It could be found that the milling temperature had a significant on the capacity of battery. The sample which was synthesized at 650°C had the highest capacity with the longest discharge voltage plateau, which could be primarily attributed to the high purity and crystallinity of the cathode material (cf. Fig. 1). On the basis of the XRD and SEM results, the explanation of this finding is proposed as follows: when the milling temperature was 600°C, the crystallinity of the product is insufficient compared with that of 650°C, so its capacity is relatively lower, while when the milling temperature were increased to 700°C and 750°C, the crystal agglomeration became serious limiting the electrochemical performance of the $LiFePO_4$/C. Therefore, 650°C is the optimal milling temperature to prepare of $LiFePO_4$/C cathode materials.

Fig. 6 (a) provides the charge/discharge curves of the button battery with a $LiFePO_4$/C cathode material that prepared at 650°C at various currents. Its initial discharge capacities were 146.3, 140.4, 130.0, 119.1 and 108.3mAhg^{-1} at the rates of 0.5, 1.0, 2.0, 5.0 and 10C, respectively. $LiFePO_4$/C sample prepared at 650°C for 8 h exhibited an excellent rate performance.

Fig. 6 (b) shows the cycling performances of $LiFePO_4$/C cathode material that prepared at 650 °C for 8 h. After 50 cycles, the discharge capacities of the sample were 135.0, 126.4, 115.4, 105.6 and 95.3 mAhg^{-1} at rates of 0.5, 1.0, 2.0, 5.0 and 10C, and their capacity retentions were 92.1%, 90.0%, 88.8%, 88.7% and 88.1%, respectively. No significant capacity decay was observed demonstrating the excellent electrochemical performance of the product prepared with Fe_3O_4 as iron source by the high temperature ball milling method.

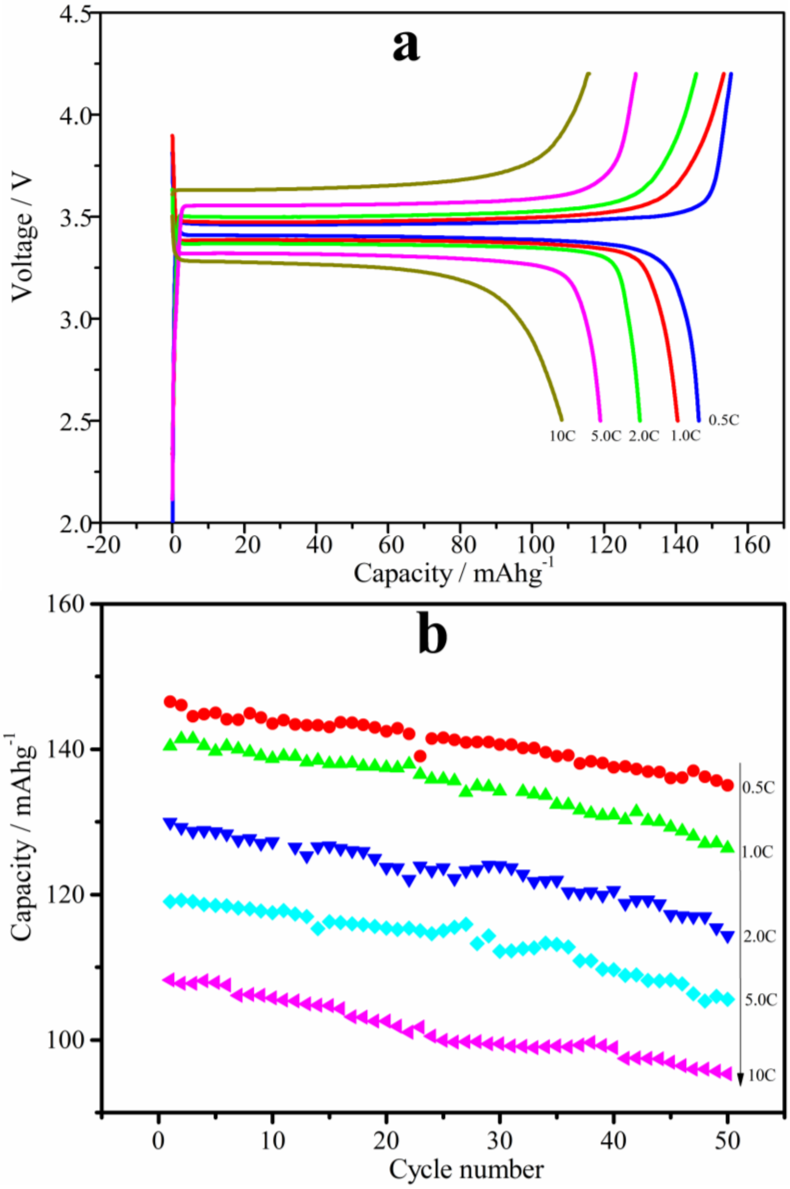


Figure 6. (a) Charge/discharge curves and (b) rate cyclic performance of the button battery with a $LiFePO_4$/C cathode material that prepared for 650 °C for 8 h at various currents

As shown in Fig.7 (a), The Nyquist plots for all four samples were composed of a concave semicircle in the high mid-frequency region and a straight line in the low frequency range. The semicircles were related to the charge transfer resistance of lithium ions at the electrolyte interface [32]. The detailed results of these samples were summarized in Table 1.

The initial R_s of the four electrodes are nearly the same (Table 1). However, the $LiFePO_4$/C sample synthesized at 650°C has a smallest charge-transfer resistance (99.72Ω) than other samples, meaning that the polarization of the sample synthesized at 650°C was less than that of others. This phenomenon could be attributed to the homogeneous particle distribution and thin carbon coating layer, which could improve the electrical conductivity. The lithium ion diffusion coefficient (D_{Li}, cm^{2}s^{-1}) of the electrodes was calculated by equation (1)

$$D_{Li} = R^2T^2/(2A^2n^4F^4C^2\sigma^2) \quad (1)$$

where *R* is the gas constant (8.314$JK^{-1}mol^{-1}$), *T* is the room temperature(298K), *A* is the surface area of the electrode (1.539×10^{-4} m^2), *n* is the number of the electrons per molecule attending the electronic transfer reaction is 1, *F* is the Faraday constant (96500 $Cmol^{-1}$), *C* is the concentration of lithium ion in $LiFePO_4$ electrode, which is 6.339×10^3 $molm^{-3}$ here, σ is the slope of the line $Z' \sim \omega^{-1/2}$ which can be obtained from Fig.7 (b).

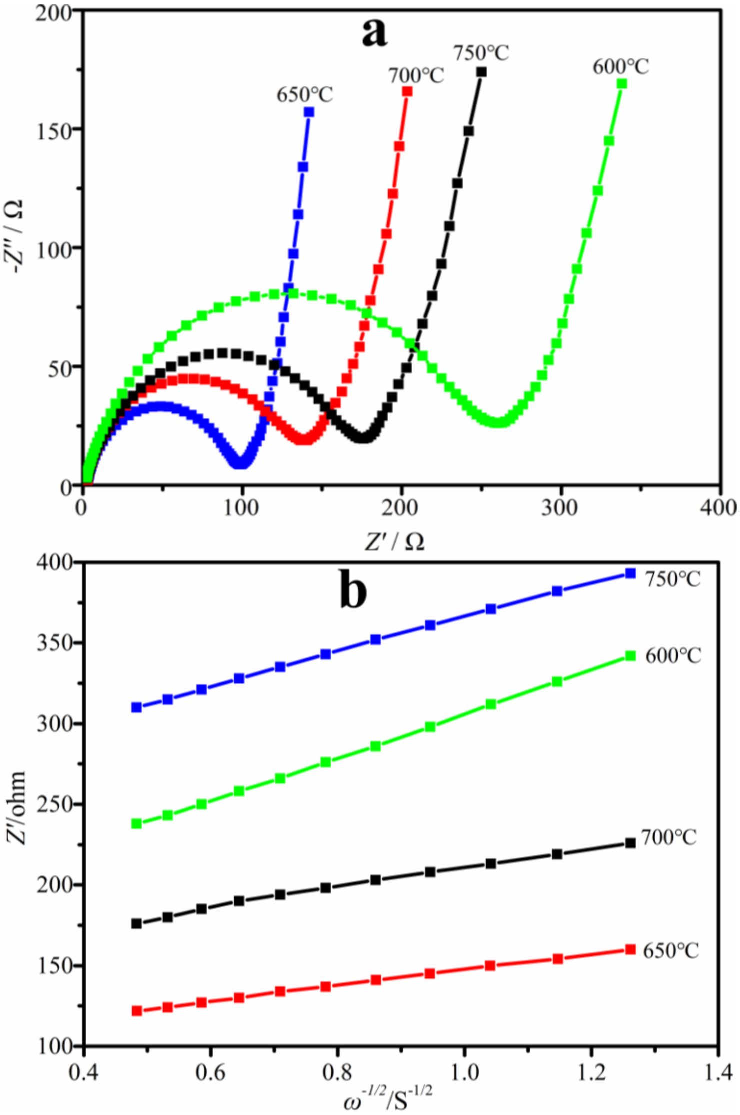


Figure 7. (a) Nyquist plots and (b) the relationship between *Z* ' and square root of frequency ($\omega^{-1/2}$) in the low-frequency region of $LiFePO_4$/C samples obtained with the different synthesis temperatures

Table 1. The simulation results of electrochemical impedance

Milling temperature (°C)	R_{s}(Ω)	R_{ct}(Ω)	σ
600	2.41	260.35	134.82
650	2.95	99.72	49.25
700	2.67	138.11	62.63
750	2.30	177.12	107.93

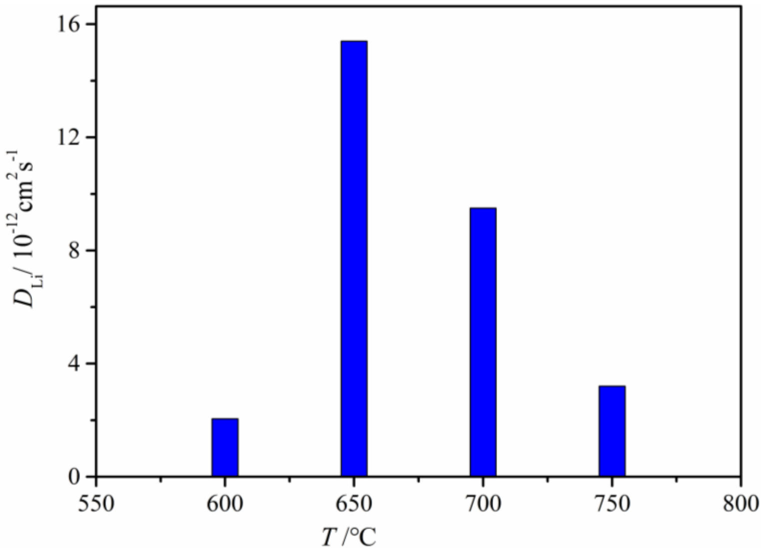


Figure 8. The relationship between lithium ion diffusion coefficient and synthesis temperatures

As shown in Fig.8, the calculated D_{Li} of sample synthesized at 650°C was 1.54×10^{-11}, while that of synthesized at 600, 700 and 750°C were only 2.05×10^{-12}, 9.49×10^{-12} and 3.19×10^{-12}. The reasons of these phenomenons are attribute to the smaller primary particle and more subtle pore structure of sample prepared at 650°C. Experimental results demonstrated that the $LiFePO_4$/C synthesized by high temperature ball milling at 650°C possesses excellent electrochemical performances, and the Fe_3O_4 is a suitable iron source for $LiFePO_4$/C production.

$LiFePO_4$/C products were synthesized by different methods and the related electrochemical data were summarized in Table 2. It was reported that the initial discharge capacity of the $LiFePO_4$/C synthesized by solid-state reaction using Li_2CO_3, $NH_4H_2PO_4$, $FeC_2O_4\cdot2H_2O$ and DEG as raw materials was 58 mAhg^{-1} at 0.1C-rate [14], and that of the samples prepared via carbothermic reduction using LiH_2PO_4, Fe_2O_3 and Super P carbon as raw materials was 125 mAhg^{-1} at 0.35C-rate [15]. As for the hydrothermal method, the initial discharge capacities of samples reached 157, 140, 130, 114 and 98 mAhg^{-1} at the rates of 0.2, 1.0, 2.0, 5.0 and 10C, respectively [18]. When sol-gel route method was used to synthesize $LiFePO_4$/C with $C_2H_3LiO_2$, $C_4H_6FeO_4$, $H_9N_2O_4P$ and citric acid as raw materials, the initial discharge capacity of the sample was reported to be 133mAhg^{-1} at 0.1C-rate [20].

In this work, $LiFePO_4$/C powders were prepared by HTBM with Fe_3O_4, LiH_2PO_4 and $C_6H_{12}O_6\cdot H_2O$ as raw materials, and the initial discharge capacities were 152.7, 146.6, 140.3, 130.0, 119.1 and 108.3 mAhg^{-1} at rates of 0.5, 1.0, 2.0, 5.0 and 10C, respectively. After 50 cycles, the capacities were 147.0, 135.0, 126.4, 115.4, 105.6 and 95.3 mAhg^{-1} at rates of 0.1, 0.5, 1.0, 2.0, 5.0 and 10C, showing an excellent electrochemical performance.

Compared with $LiFePO_4$/C synthesized using different iron sources , Fe^{2+}raw material is relatively high cost and limits its industrialized application, Fe^{3+}raw material need large numbers of reducing agent. Fe_3O_4 as iron source is low-cost and easily-available, high temperature ball milling method is simple eco-friendly green process.

Table 2. Comparison of $LiFePO_4/C$ prepared by different synthesis methods

Synthesizing method	Raw materials	Rate capacity ($mAhg^{-1}$)	References
High temperature ball milling	Fe_3O_4; LiH_2PO_4; $C_6H_{12}O_6 \cdot H_2O$	152.7 (0.1C); 146.3 (0.5C); 140.4 (1.0C); 130.0 (2.0C); 119.1 (5.0C); 108.3 (10C)	As prepared
Solid-state reaction	Li_2CO_3; $NH_4H_2PO_4$; $FeC_2O_4 \cdot 2H_2O$; DEG	58 (0.1C)	[14]
Carbothermic reduction	LiH_2PO_4; Fe_2O_3; Super P carbon	125 (0.35C)	[15]
Hydrothermal method	$FeSO_4 \cdot 2H_2O$; H_3PO_4; $LiOH \cdot H_2O$; Grapheme	157 (0.2C); 140 (1.0C); 130 (2.0C); 114 (5.0C); 98 (10C)	[18]
Sol-gel route	$C_2H_3LiO_2$; $C_4H_6FeO_4$; $H_9N_2O_4P$; Citric acid	133 (0.1C)	[20]

4. CONCLUSIONS

In this work, $LiFePO_4/C$ was produced with Fe_3O_4 as iron source by high temperature ball milling method. The effects of milling temperature on the $LiFePO_4/C$ were investigated. Experimental results showed that increasing milling temperature from 600 to 750°C improved the crystallinity of $LiFePO_4$, while a severe crystal agglomeration phenomenon and the phase transformation from $LiFePO_4$ into $LiFeP_2O_7$ occurred when the temperature reached 750°C. Some button batteries were assembled with the high temperature ball milling products as a cathode material, and the electrochemical performance results indicated that the $LiFePO_4/C$ synthesized at milling temperature of 650°C exhibited the optimal electrochemical performance.

ACKNOWLEDGMENTS
The authors gratefully acknowledge supports by the National Natural Science Foundation of China (No. 51704068), the National Key R&D Program of China (No. 2017YFC0805100), the China Postdoctoral Science Foundation (No. 2017M610184), and the Postdoctoral Foundation of Northeastern University (No. 20170305).

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