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Two-step synthesis of nanocomposite LiFePO_4/C cathode materials for lithium ion batteries

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Abstract

A two-step method for the preparation of nanocomposite LiFePO_4/C cathode materials for lithium ion batteries. Water is used as a solvent in the sintering process, with $\text{Fe}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and H_3PO_4 as the raw materials and citric acid as the carbon source. Synthesis of the resultant grain-size precursor is then performed at 700 °C for 1 h in order to obtain a lithiation reaction precursor via ball milling. The crystal structure and morphology of the samples are characterized using X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The electrochemical properties of the material are assessed using charge-discharge and cyclic voltammetry testing. Based on the test results, the discharge capacity of the LiFePO_4/C reaches 163.3 mAh/g in the first cycle, exhibiting a discharge capacity close to the theoretical value (170 mAh/g). After 50 charge-discharge cycles, a capacity of 154.4 mAh/g is obtained. The capacity retention ratio is 94.5%.

Keywords: Lithium-ion batteries; LiFePO_4 ; Cathode materials; Electrochemical performance; synthesis technique

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1. Introduction

Typical olivine-structured LiFePO_4 has a relatively high theoretical capacity (170 mAh/g) with a 3.4–3.5-V discharge voltage platform, as well as other advantages such as abundant raw materials, low environmental impact, low price, and good thermal stability[1-3]. In 1997, the Goodenough[4] research team first reported the use of LiFePO_4 cathode materials in lithium batteries; this report attracted considerable public attention. The high rate performance of LiFePO_4 is expected to be render it suitable for use in batteries in electric vehicles[5-7]; however, the low electronic conductivity and ion diffusion of this material greatly restricts its wide application[8-12]. Therefore, considerable research has been focused on the development of synthesis methods and techniques to improve the electrochemical properties of the LiFePO_4 cathode material in recent years. These approaches have involved, for example, the use of carbon-coated surfaces[13-15], metal ion doping[16-18], and nanotechnology[19-20]. Currently, the preparation of a LiFePO_4 variant is the most prominent technique, and involves both the high-temperature solid-phase and sol-gel methods. Yamada et al. have used the solid-phase method with Fe^{3+} as raw material, and successfully reduced the synthesis realization difficulty[21]. However, it is difficult to control particle growth and agglomeration during the synthesis process, which affects the electrochemical properties of the resultant material significantly.

As stated above, the conventional sol-gel method is one step in the synthesis process of precursors with very good uniformity. However, lithium salt can also be added to increase the particle growth and agglomeration[22-24]. In the paper, the combination of the conventional sol-gel method with the high-temperature solid-phase method inspires the two-step pyrophosphate synthesis technique, revealing a new method for the synthesis of LiFePO_4 . In the first step of this two-step process, in order to prepare for the subsequent lithium reaction, carbon coated with intermediates effectively controls any excessive particle growth. This is part of a sol-gel method used to prepare a precursor, which is conducted under specific conditions. In the second step, uniform nanosized LiFePO_4/C is sintered. This paper presents the two-step pyrophosphate synthesis technique and evaluates the electrochemical performance of LiFePO_4/C cathode materials prepared using this approach.

2. Experimental

2.1. Synthesis

LiFePO₄ powder is prepared using two-step synthesis of pyrophosphate. A stoichiometric amount of Fe(CH₃COO)₂·4H₂O, H₃PO₄ and 20 wt% of carbon (with citric acid as the carbon source) are used as the starting materials, and are dissolved in 10 ml of deionized water. An ultrasound reaction slurry is then prepared, which contains 80–90% active ingredients. This slurry is placed in a protective argon gas in a tube furnace and calcined at 700 °C for 1 h. Subsequent testing (described below) confirms that is synthesized, with controlled nanomaterial grain sizes. Then, certain molar ratios of LiOH and precursor are added to a planetary ball mill, which is operated at a set speed of 500 rpm for 5h, with a powder quality:deionized water:bead mass ratio of 1:1:4. After evaporation of the deionized water, the mixture is placed in a tube furnace under argon protection and sintered 12 hours. For the purposes of this study, the characteristics of the materials obtained for furnace temperatures of 600, 700, and 800 °C were investigated.

2.2. Characterization

The identification of the LiFePO₄ phase was conducted using powder X-ray diffraction (XRD, Bruker D2) with Cu K- α radiation. The diffraction data were collected using the step mode over an angular range of 10–70°, with a step size of 0.02° at 30 kV and 10 mA. Scanning electron microscopy (SEM, Germany Zeissm Supra 55VP) images were collected at 20 kV. Transmission electron scanning electron microscopy (TEM, Philips CM10) images of the samples were collected at an accelerating voltage of 200 kV.

For electrochemical measurements, a cathode was fabricated by mixing 80-wt% active material, 15-wt% acetylene black, and 5-wt% polytetrafluoroethylene (PTFE) in deionized water. The obtained slurry was coated on Al foil, and then dried at 80 °C for 12 h in vacuum. The loading density of the active material was approximately 2–3 mg/cm².

All the cells used in the charge-discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy(EIS) testing were composed of a cathode, separator (polypropylene porous film), electrolyte, and a lithium foil anode. The electrolyte was 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 by volume). The charge-discharge measurements were conducted on a battery test system (LAND Wuhan, China CT-2001A), in the 2.5–4.3-V range in the constant voltage mode at a rate of 0.5C at room temperature. The CV tests were conducted using an electrochemical workstation (China Tianjin, LK2005A) before the charge-discharge test. The CV curves were recorded in the 2.5–4.3-V potential range at a scan rate

of 0.1 mV/s at room temperature. And the electrochemical impedance spectroscopy (EIS) measurements were carried out at frequencies ranging from 0.01 Hz to 0.1 MHz.

3. Results and discussion

Figure 1 shows the XRD patterns of LiFePO_4 pyrophosphate samples produced using the two-step synthesis technique at different temperatures. In addition, the XRD patterns of an intermediate product and the standard LiFePO_4 card (JCPDS 40-1499) are shown. Comparison between the patterns shown in Figure 1(a) shows the emergence of $\text{Li}_4\text{P}_2\text{O}_7$ and Li_3PO_4 hybrid peaks at the sintering temperature of 600 °C; this indicates that the lithiation reaction is incomplete. The Figure 1(b) focuses on the peaks in the range of 18–25° of the XRD patterns of the hybrid samples. As the temperature increases up to 800 °C, the peak intensities of the $\text{Li}_4\text{P}_2\text{O}_7$ and Li_3PO_4 gradually decrease. For the sample prepared at 800 °C, the XRD pattern is consistent with that of the standard card. Hence, a prolonged high-temperature process time can promote the formation of LiFePO_4/C crystals. Furthermore, citric acid was used as a carbon source, but it is not detected in the synthesized LiFePO_4/C carbon phase; this indicates that the carbon produced from the citric acid is amorphous, and its presence does not affect the LiFePO_4/C crystal structure.

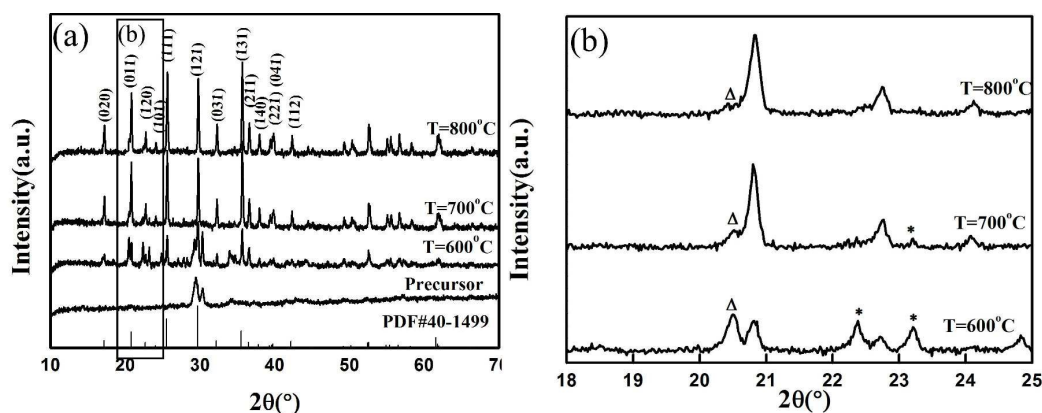


Fig.1(a) XRD patterns of: LiFePO_4 pyrophosphate samples synthesized at different temperatures; intermediate product ; and standard card (PDF# 40-1499). Fig.1(b)XRD patterns in the 18–25° 2θ range for LiFePO_4 pyrophosphate samples synthesized at different temperatures.

The morphology and particle size of the two-step-synthesized LiFePO_4/C material were observed using SEM and TEM micrographs, such as those shown in Figure 2. As can be seen from these images, the pyrophosphate-step synthesis using deionized water as a solvent yields large

particle clusters that agglomerate during the synthesis of the LiFePO_4/C material. Specifically, irregular spherical nanoparticles having grain diameters of approximately 50–100 nm are obtained from Figure 2 (a) , 2 (b) and 2 (c). This indicate that the method is effective for the material to get to the smaller particle size. The lithium-ion charging and discharging process of the transmission path is shortened large extent by the morphology of nano materials, which is more conducive to the lithium-ion escape and embedding. It also can be clearly observed from Figure 2 (d) of the HRTEM photograph of synthetic material to the surface of the particles coated with a layer of about 2-5 nm thick amorphous carbon film, which is the precursor uniformly distributed carbon-containing compounds at high temperatures thermal decomposition carbonization, the tight uniform crystal particles deposited on the surface of LiFePO_4 . Carbon parcels not only prevent crystal grains of LiFePO_4 continuing to grow, helping to reduce the particle size, but also can improve the conductivity of the sample[25].

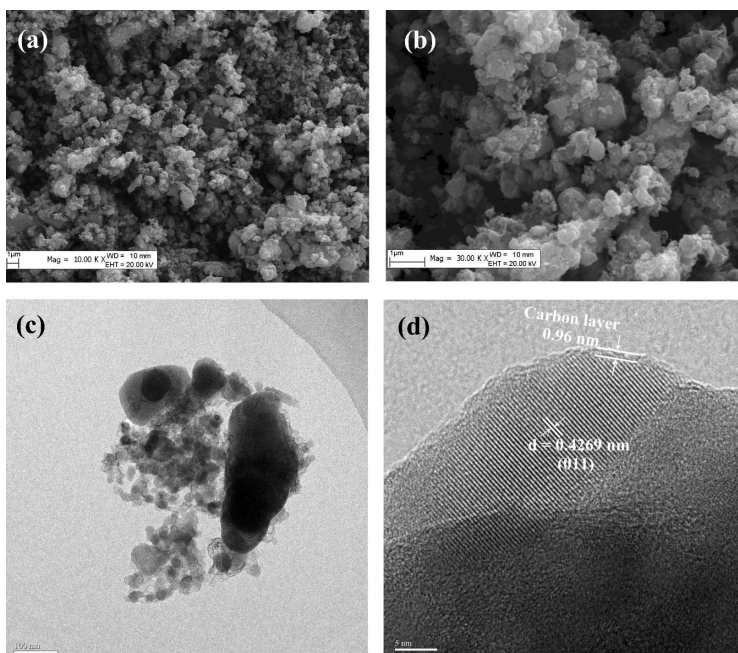


Fig. 2 SEM and TEM images of LiFePO_4/C material.

Figure 3(a) shows that the charge-discharge curve of the LiFePO_4/C material in the range of 2.5–4.3-V at a 0.5 C rate and room temperature exhibits a significant 3.3–3.5 V charge-discharge plateau voltage. The discharge capacity of the LiFePO_4/C nanocomposites in the first cycle reaches 163.3 mAh/g, which is close to the theoretical capacity (170 mAh/g). After 50 charge-discharge cycles, a capacity of 154.4 mAh/g is obtained, which corresponds to a slight

performance decay. This may be related to the material morphology, as the nanomaterials have large specific surface areas; thus, after assembly of the battery through the electrolyte infiltration and lithium ion deintercalation process, its structure is more susceptible to charging. Also, the electrochemical cycle life figure shown in Figure 3 (b) demonstrates that the sample exhibits good cycle stability. The charge and discharge profiles of LiFePO_4/C measured at various rates with cut out voltage between 2.5 and 4.3 V are shown in Figure 3 (c). The LiFePO_4/C material presents an initial discharge capacity of 163.3 mAh/g at 0.5 C. Even with increase in the current rate to 5 C and 10 C, the capacity still remains at 135.5 and 95.9 mAh/g, respectively. The charge and discharge curves evidence that the excellent properties are likely a result of compositing with the two-step synthesis technique. Figure 3 (d) shows the cycle performances of the LiFePO_4/C at different charge-discharge rates of 0.5, 1, 5 and 10 C. The cycle performance of LiFePO_4 is observed to excellent electrochemical performance of LiFePO_4/C at the low discharge rate of 0.5 C and at the high rate of 10 C, respectively. Furthermore, when the current density is reverted to 0.5C from 10 C, the discharge capacity of LiFePO_4/C returns to 147.3 mAh/g, illustrating that the structure of LiFePO_4 remains stable after cycling.

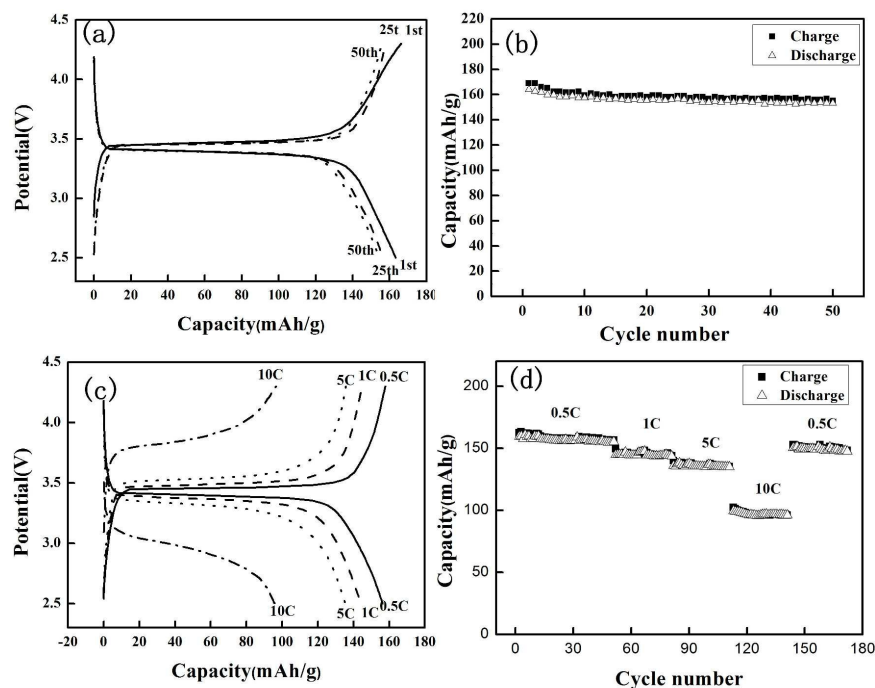


Fig. 3 Charge-discharge curve and electrochemical cycle life of LiFePO_4/C material.

Cycle voltammety curves subjected to 50 cycles of the LiFePO_4/C material is displayed in

Figure 4. Here, the emergence of a pair of redox peaks is evident in the 2.5–4.3 V test range; this indicates that the testing process only identifies one redox process, corresponding to the charge-discharge characteristics of graphs shown on the Internet. It can also be observed that the three consecutive test cycles almost completely overlap within the figure, indicating that the material does not exhibit significant attenuation capacity and the circulation is good. Moreover, a peak potential difference of 0.15 V can be seen between the oxidation and reduction peaks, with both peaks being of considerable size; this indicates that the irreversible capacity of the material charge-discharge process is small.

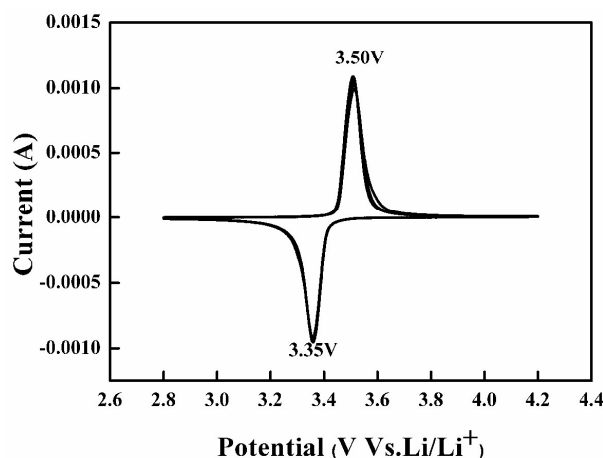


Fig. 4 Cyclic voltammetry curves of LiFePO₄/C material.

The Nyquist plots of the electrochemical impedance spectra (EIS) analyses are shown in Fig.5. Table 1 shows the calculated electrochemical parameters for the sample. All plots consist of both a semicircle in the high-frequency region and a slope in the low-frequency region. The semicircles, which are to some extent overlapped, have a high-frequency cutoff that identifies the ohmic resistance of the electrolyte and electrodes. At lower frequencies, the resistance is related to the complex reaction process of charge transfer between the electrolyte and the active material, i.e. migration of the Li⁺ ions at the electrode/electrolyte interface and interparticle contact resistance. The electrode reaction process is primarily controlled by a mixed process of lithium ion diffusion (Warburg impedance, which is inversely proportional to the diffusion coefficient D_{Li^+}) and the surface electrochemical reaction at a temporary steady state of EIS. The results show that the reaction impedance and warburg impedance of original state are all larger than the charge to 3.48V (approach the fully charge state) and the discharge to 3.31V (approach the fully discharge state), which indicates that electrochemical reaction is relatively easy to occur under the fully charged and fully discharged states. This is to say, using

this new synthesis method of preparation of LiFePO_4/C material has good electronic and ionic conductivity. Moreover, The fitting results in table 1 show that the reaction impedance and warburg impedance of the charge state is a little more than the discharge state, which indicates that the electrochemical intercalation of lithium ions is relatively easy to the deintercalation. However, the two kinds of state basic close to impedance values, the implies that the electrochemical reversibility of the materials is better in process of circulation. This is consistent with the test result of the cyclic voltammograms.

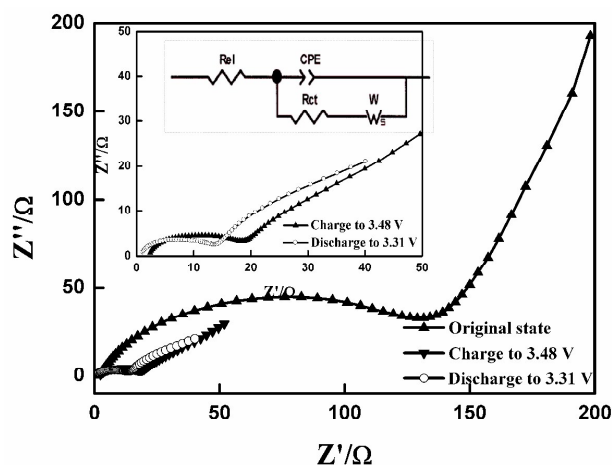


Fig. 5 electrochemical impedance spectroscopy curves of LiFePO_4/C material.

Table 1 Calculated electrochemical parameters from the AC impedance spectra of the LiFePO_4/C sample using ZView 2.8 software.

Sample	R_{ct} (Ω)	W_s (Ω)	CPE
Original state	151.76	126.50	2.96×10^{-6}
Charge to 3.48 V	28.41	59.71	9.47×10^{-4}
Discharge to 3.31 V	23.64	52.69	1.83×10^{-4}

Note: R_{ct} represents the charge-transfer resistance, CPE represents the constant phase element, and W_s represents the Warburg impedance.

4. Conclusions

A two-step for the synthesis of LiFePO_4/C composite material for lithium ion batteries based on the derivative sol-gel method was reported, which can effectively control grain growth and produce nanomaterials. XRD analysis confirmed that the lithium ion cathode material LiFePO_4/C was successfully synthesized via the two-step synthesis of pyrophosphate at 800 °C. TEM results showed that the particle sizes of this material were approximately 50–100 nm, indicating that the proposed method effectively controlled the grain size. The initial discharge capacity of the sample prepared at 800 °C reached 163.3 mAh/g, the discharge capacity was 154.4 mAh/g after 50 cycles,

and the capacity retention ratio was 94.5%. These results indicate stable electrochemical performance and controllability with inseparable grains. Thus, this study has shown that the cathode material grain size can be effectively controlled using the new two-step pyrophosphate synthesis technique, because of the controlled carbon coating process employed in the first step of the technique. In future, we will continue to develop this synthesis method, focusing on the structure and grain morphology of the synthesized material, and work to further improve the electrochemical performance of LiFePO_4 .

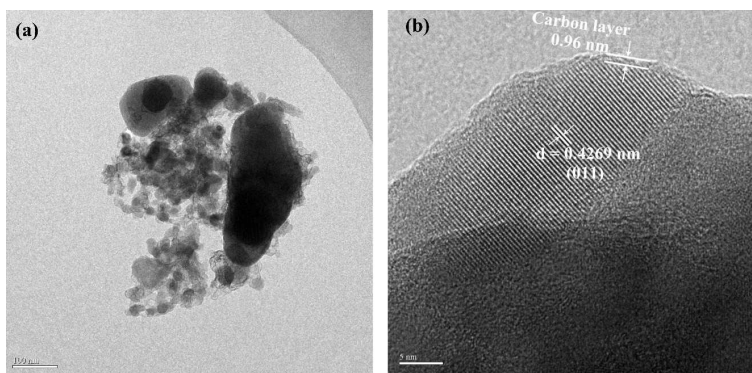
Acknowledgement

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LiFePO₄/C nanocomposite was fabricated via a novel two-step method , which effectively controlled the particle size .