

LiFePO₄/C Nanocomposites Synthesized from Fe₂O₃ by a Hydrothermal Reaction-calcination Process and Their Electrochemical Performance

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Abstract: LiFePO₄ nanoparticles coated with a carbon layer were synthesized by a hydrothermal reaction-calcination process, using Fe₂O₃ as an iron source and ascorbic acid as carbon source. The amount of ascorbic acid have an effect on the structure, phase and carbon amount of the final product. With 1 g ascorbic acid used in the reaction, the particle sizes of synthesized LiFePO₄/C nanocomposites are in a range of 220–280 nm. Using as the cathode materials for the lithium-ion batteries, the as-prepared material shows high capacity and good cycle stability (159 mAh/g at 0.1C over 500 cycles), as well as good rate capability.

Key words: lithium ion battery; lithium iron phosphate; Fe₂O₃; hydrothermal method

Since from the pioneering work by Padhi^[1], the olivine LiFePO₄ has attracted extensive interest as a potential candidate of cathode materials for high power lithium ion batteries, owing to its numerous appealing features, such as high theoretical capacity, acceptable operating voltage (3.4 V vs Li⁺/Li), high safety, environmental benignity and low cost. The major limitation of LiFePO₄ is the poor electronic and ionic conductivity, so considerable efforts have been made by metal doping, carbon coating and co-synthesizing with carbon by solid-state methods^[2–5].

There are lots of methods to prepare LiFePO₄, such as high temperature solid-state, microwave, hydrothermal, Sol-Gel and co-precipitation^[6–12]. Hydrothermal synthesis routes are increasing being pursued as energy-savvy ways, as opposed to conventional solid-state synthesis, to produce fine particles. And the carbon introduced by the hydrothermal synthesis can be more homogeneously dispersed than physical mixing of solid chemicals. It should be noted that many previous studies involving the synthesis of LiFePO₄ employ Fe²⁺ or Fe³⁺ salts as the precursors in the hydrothermal or solvothermal method, which increase the cost of the LiFePO₄. As far as we know, there is few works done on the hydrothermal synthesis of LiFePO₄ from Fe₂O₃. And Fe₂O₃ is often used as the iron source in the conventional solid state synthesis of LiFePO₄^[13]. Therefore the preparation of LiFePO₄/C nanocomposites from Fe₂O₃ would be of great interest.

Herein, a hydrothermal reaction-calcination process has

been reported for the synthesis of LiFePO₄ coated with carbon in the water medium using inexpensive and stable Fe₂O₃ as the iron source, ascorbic acid as the antioxidant and carbon source. And the electrochemical behaviors of the LiFePO₄/C composites prepared with different amount of the ascorbic acid were then investigated.

1 Experimental

1.1 Preparation of LiFePO₄/C nanocomposites

In a typical synthesis, reagent-grade Li₂SO₄ (0.15 mol), P₂O₅ (0.05 mol), Fe₂O₃ (0.05 mol) and ascorbic acid (1 g) were added into 40 mL deionized water and stirred for 30 min at room temperature, then the mixture was placed in a PTFE-lined stainless steel autoclave and maintained at 200 °C for 24 h. After being cooled naturally to room temperature, the deep green precipitates were collected by centrifugation without further washing and then dried at 80 °C in vacuum overnight before heat-treatment at 600 °C in Ar/H₂ (95 and 5 mL/min) atmosphere for 10 h. To investigate the effects of ascorbic acid on the morphology and phase purity of products, the amount of the ascorbic acid were changed to 0 or 0.5 g, while keeping other parameters constant. The synthesized samples are named as LFP-*x*, and the value of *x* is based on the amount of the ascorbic acid used.

1.2 Characterization

Fourier transform infrared (FT-IR) spectra (4000–

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400 cm^{-1}) were obtained from KBr pellets using a Nicolet FT-IR Impact 400 system. Raman spectrum was taken under ambient condition by using a RM 2000 microscope confocal Raman spectrometer in the range of 400–2000 cm^{-1} . Powder X-ray diffraction (XRD) was carried out through a Bruker AXS D8 diffractometer using Cu K α radiation. The carbon content was measured in a Thermogravimetric analyzer (TGA) with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ to 600 $^{\circ}\text{C}$ in air. The structures were analyzed using a JSM-5610LV scanning electron microscope (SEM, JEOL) and a JEM 2010-FEF transmission electron microscope (TEM, JEOL).

1.3 Electrochemical measurements

Electrochemical performances of LiFePO_4/C nanocomposites were characterized using CR2016 coin-type cell. A composite electrode was fabricated with the active material, super P carbon back and polyvinylidene fluoride (PVDF) with a weight ratio of 75:15:10 using *N*-methylpyrrolidinone (NMP) as solvent. The slurry was then pasted onto an Al foil and the NMP was evaporated at 120 $^{\circ}\text{C}$ for 12 h in vacuum. Each individual electrode has an area of 0.65 cm^2 and contains 4–6 mg/cm^2 of active materials. A disk cut from Al foil coated with LiFePO_4/C nanocomposites was used as the tested electrode. The electrolyte was 1 mol/L LiPF_6 dissolved in ethyl carbonate, diethyl carbonate and dimethyl carbonate (volume ratio, 1:1:1). The coin cells were composed of LiFePO_4/C as the cathode, lithium metal as the anode and a microporous polypropylene sheet as the separator. The cells were charge/discharged between 4.2 V and 2.5 V at room tem-

perature with a rate of 0.1C–10C using a charge/discharge apparatus.

2 Results and discussion

Figure 1(a) presents the morphology of the pristine Fe_2O_3 with an average size of 500 nm. When there is no ascorbic acid in the reaction system, the prepared product exhibits a cone-shaped structure with the edge length of about 1.5 μm (Fig. 1(b)). When the amount of the ascorbic acid is 0.5 g, there are cone-shaped particles accompanied with some smaller irregular particles in the product. However, with 1 g ascorbic acid added into the reaction, the product is composed of nanoparticles with the size in the range of 200–300 nm, as shown in Fig. 1(c). Compared with Fe_2O_3 , the sample synthesized without ascorbic acid has a larger size, while the sample synthesized with 1 g ascorbic acid has a smaller size. The results indicate that Fe_2O_3 may experience a dissolution and recrystallization process, and the addition of the ascorbic acid into the reaction medium may restrict the growth of the product. This phenomenon can be explained by the space steric effect, which increased the diffusion activation energy of the reactants and slowed down the growth rate of grains^[14]. It can be found from the high resolution TEM image (Fig. 1(e) and (f)) that both of the primary crystallite of the sample LFP-0.5 and LFP-1 are coated by a fine carbon layer. But, LFP-1 shows a much higher carbon coating with a thickness of 2 nm. The selected area electron diffraction of LFP-1 reveals that the single particle is well crystallized. The fine carbon layer is produced from the

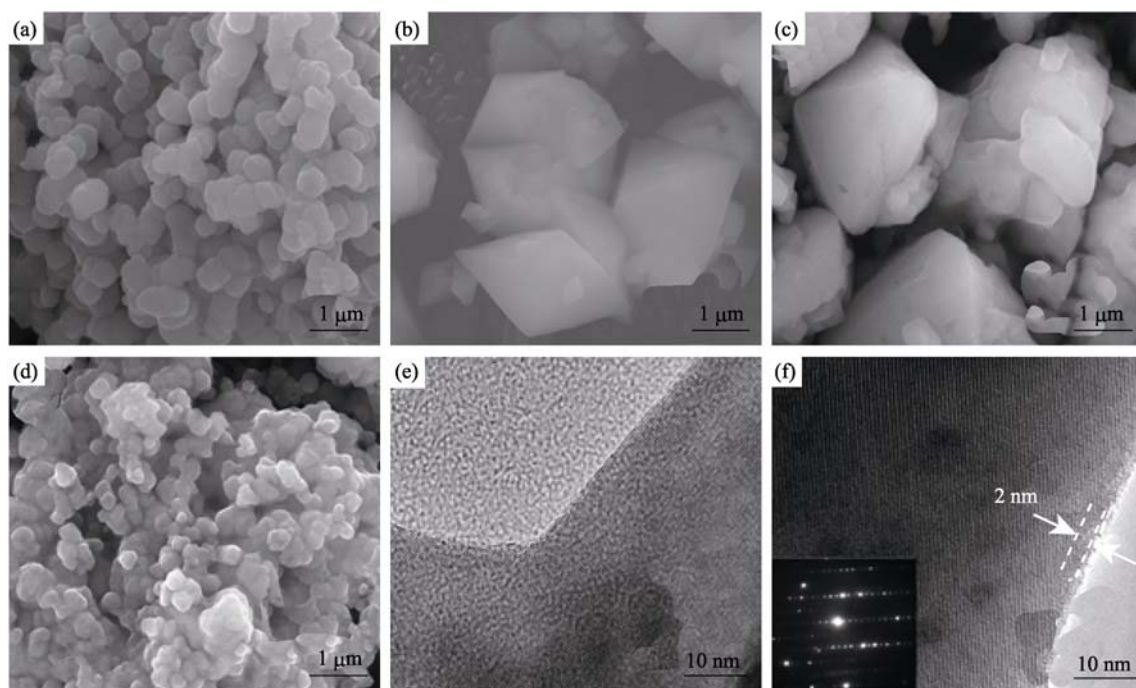


Fig. 1 SEM (a–d) and TEM (e, f) images of the samples
(a) pristine Fe_2O_3 ; (b) synthesized without ascorbic acid; (c) and (e) LFP-0.5; (d) and (f) LFP-1

decomposition of the ascorbic acid during heat treatment process, through which Li⁺ can easily intercalate into the framework of the synthesized crystal. Although the presence of agglomerated particles usually decreases tap density, the present heat treated samples show relatively high tap density of 1.4 and 1.1 g/cm³ for LFP-0.5 and LFP-1, respectively.

XRD patterns of the products synthesized with different conditions are displayed in Fig. 2. The peaks of the pristine material synthesized without ascorbic acid can be indexed as a mixture of Fe₂O₃ and Fe₃(PO₄)₂(OH)•2H₂O phase (Fig. 2(a)). As for the pristine material prepared with 1 g ascorbic acid (Fig. 2(b)), the Fe₂O₃ phase is vanished, whereas the peaks of the Fe₃(PO₄)₂(OH) phase turn up. After annealed at 600°C in H₂/Ar atmosphere, the phases of pure LiFePO₄ are obtained and the sharp diffraction peaks illustrate the highly crystalline nature (Fig. 2(c)). As indicated by Fig. 2(d), when adding 0.5 g ascorbic acid the products after heat treatment also show a pure LiFePO₄ phase. However, after heat-treated at 600°C, the product prepared without ascorbic acid exhibits a mixture phase of Fe and LiFePO₄ (Fig. 2(e)), in which Fe should be ascribed to the reduction of Fe₂O₃ by H₂. It should be noted that the precipitates collected after the hydrothermal reaction need not be washed to obtain a pure LiFePO₄ phase. Together with the images shown in Fig. 1, ascorbic acid in the system can be considered not only as structure director, but also as an anti-oxidation source to favor the formation of pure LiFePO₄. And the peaks corresponding to carbon are not visible, owing to its amorphous structures.

The FT-IR absorption spectra of the pristine and

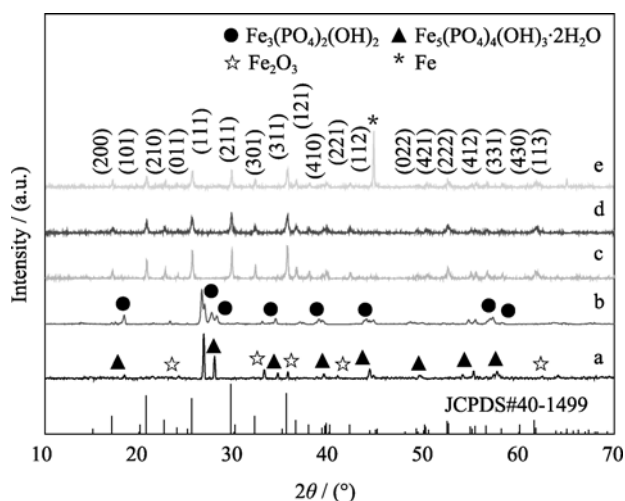


Fig. 2 XRD patterns of the samples prepared under different conditions

Pristine sample synthesized with 0 (a) and 1 g (b) ascorbic acid; the heat treated sample synthesized with 1 g (c), 0.5 g (d) and 0 (e) ascorbic acid, respectively

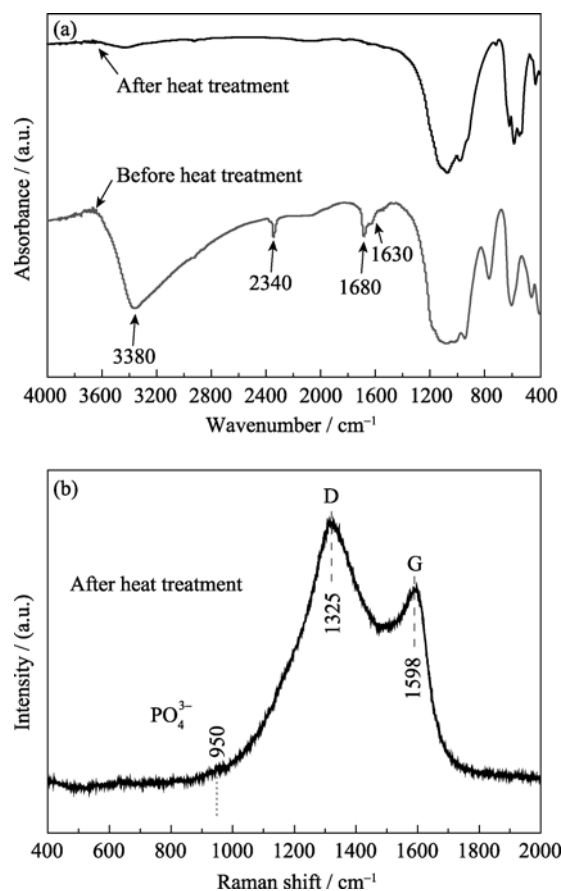


Fig. 3 FT-IR (a) and Raman (b) spectra of the LiFePO₄/C nanocomposites prepared with 1 g ascorbic acid

heat-treated samples synthesized with 1 g ascorbic acid are shown in Fig. 3(a). Except for the similar bands located in the region of 1200–700 cm⁻¹ and 630–540 cm⁻¹ assigned to the PO₄³⁻ groups^[15-16], several additional absorption peaks exist in the pristine sample without heat treatment. The bands at 3400 and 1634 cm⁻¹ are attributed to the stretching vibrations of hydroxyls and bending modes of absorbed water, respectively. The band at 2340 cm⁻¹ originates from a un-deprotonated P–OH group^[17]. The absorption peak at 1680 cm⁻¹ is attributed to the stretching vibration of C=C in ascorbic acid^[18], which confirms that the amorphous carbon layer around the LiFePO₄ crystal lattice seen in the TEM image (Fig. 1(f)) possibly due to carbon resulting from pyrolyzed ascorbic acid. A typical Raman spectrum of the carbon coated LiFePO₄ is shown in Fig. 3(b). The carbon layer makes it difficult to see the details of the spectrum of the olivine structure of LiFePO₄ due to the attenuation of the signal and the overlapping of the spectral bands^[19]. Only a very weak signal at 945 cm⁻¹ related to PO₄³⁻ anion symmetric stretching (the strongest peak in the olivine LiFePO₄ spectrum) is observed. Two peaks at 1600 and 1358 cm⁻¹ correspond to the D and G bands of carbon, respectively. The

D band arises because of the disorder induced in sp^2 -bonded carbon, whereas the G band arises from the in-plane vibration of sp^2 carbon atoms. The results further reveal that the synthesized sample is composed of $LiFePO_4$ and amorphous carbon.

Thermogravimetric (TG) measurement was used to estimate the carbon content in the final product. Figure 4 gives the TG curve of the sample in air. As can be seen from Fig. 4, the prepared nanocomposite has a high thermal stability below 260°C . Olive $LiFePO_4$ can be oxidized into $Li_3Fe_2(PO_4)_3$ and Fe_2O_3 in the temperature range of $250\text{--}500^\circ\text{C}$, corresponding to a theoretical weight gain of $5.07\text{wt}\%$ ^[20]. When the sample is heated above 350°C , the carbon in the mixture is oxidized into CO_2 gas. Finally, taking into account the theoretical weight gain ($5.07\text{wt}\%$) of pure $LiFePO_4$ during TGA measurement in air, the amount of coated carbon for the synthesized sample is calculated to be $2.06\text{wt}\%$.

Figure 5(a) shows the cyclic voltammetry curves of the LFP-1. As can be seen, no peak appears at 2.63 V (characteristic of Fe^{3+} in Fe_2O_3), indicating that all the iron atoms in the $LiFePO_4/C$ nanocomposites are Fe^{2+} ^[21]. The couple of redox peaks are observed between 3.2 and 3.6 V (vs Li^+/Li), which should be attributed to the Fe^{2+}/Fe^{3+} redox

couple reaction, corresponding to lithium extraction and insertion in $LiFePO_4$ crystal structure. Figure 5(b) shows that a flat discharge potential plateau was observed for $LiFePO_4/C$ sample at around 3.4 V , suggesting that the two-phase redox reaction proceeds *via* a first-order transition between $FePO_4$ and $LiFePO_4$.

Long-term cyclic discharge performances of the samples are shown in Fig. 5(b) and (c). After 500 cycles at $0.1C$, it demonstrates high cycling stability of LFP-1 by

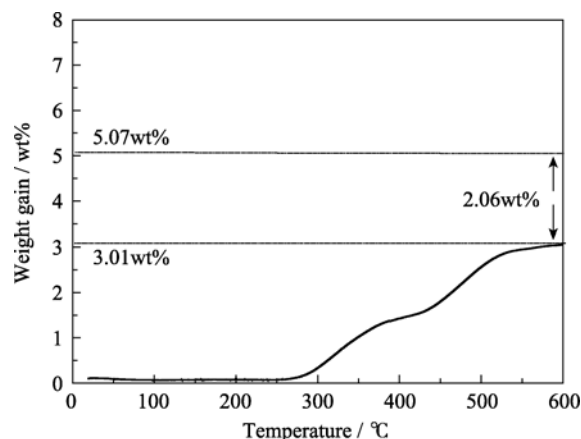


Fig. 4 TGA curve of the $LiFePO_4/C$ sample prepared with 1 g ascorbic acid

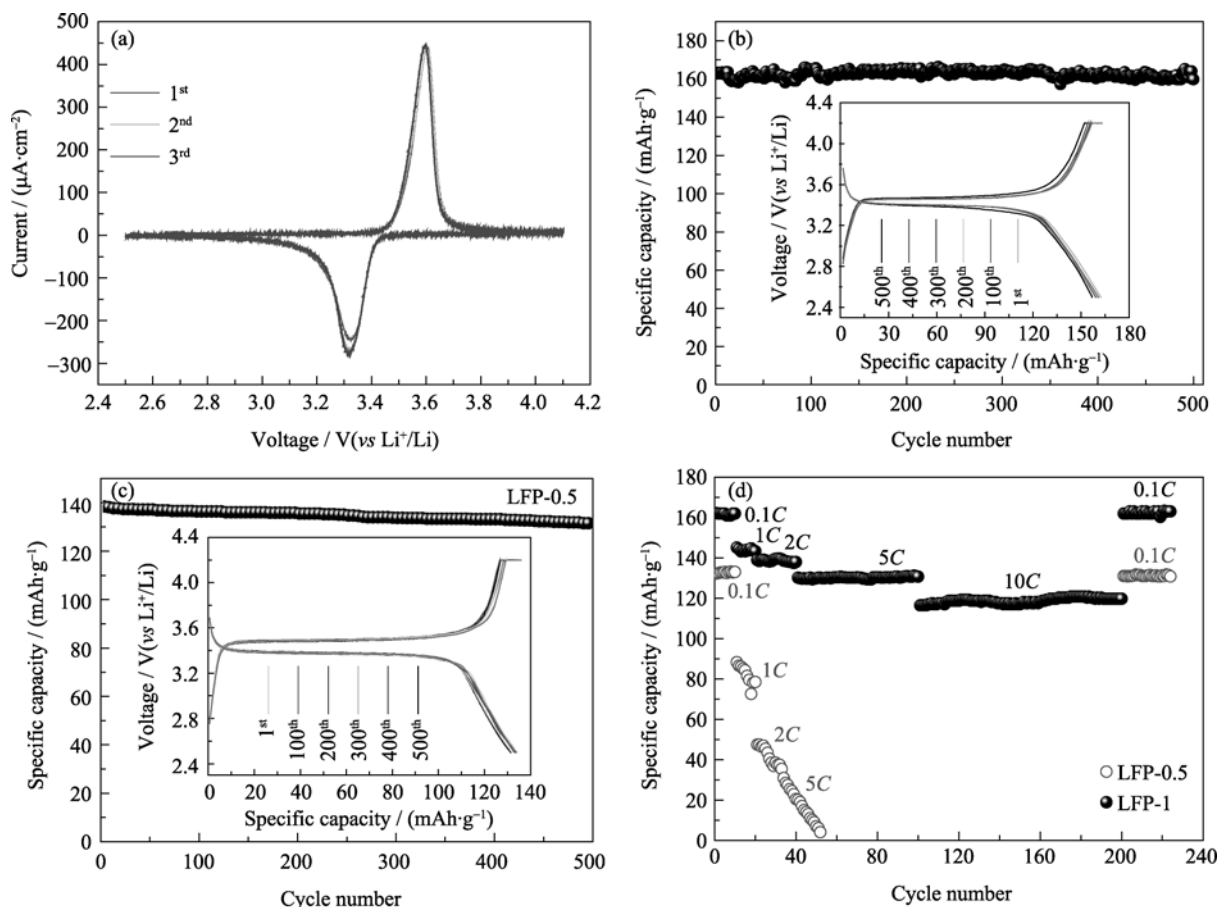


Fig. 5 Cyclic voltammograms (a), cyclability (b, c) and rate performance (d) of $LiFePO_4/C$ nanocomposites

delivering the discharge capacity of 159 mAh/g with a capacity retention of 97.5%, while LFP-0.5 exhibit a specific capacity of 129 mAh/g with capacity retention of 92.8%. And the charge/discharge curves inserted in the Fig. 5(b) and (c) indicated that the reversible capacities are relative stable at low rate. Although Fe₂O₃ is used in the hydrothermal system, the typical discharge plateau at 0.75 V corresponding to Fe₂O₃^[22-23] does not appear, which could further indicate the phase purity of the prepared materials.

To study the rate capabilities of the fabricated electrodes, the cells were charged and discharged at various current rates. As shown in Fig. 5(d), charge/discharge measurement was firstly conducted at a rate of 0.1C, and then increased to 10C stepwise and finally returned back to 0.1C. There is a decrease in the discharge capacity of the prepared sample with the current rates increasing. The initial discharge capacities of LFP-1 at a rate of 0.1C are 163 mAh/g and the columbic efficiency is 97%, while that of LFP-0.5 is 136 mAh/g and 96%, respectively. However, the discharge capacity for the LFP-1 at 10th cycle decreases to 144 and 140 mAh/g at current rates of 1C and 2C, respectively. Although the specific capacity of electrode decreases drastically when the sample is cycled at higher rates from 1C to 10C, the initial capacity of the composite is retained if returning to the low current rate (0.1C). As exhibited in Fig. 5(d), there is a striking difference between the prepared samples when discharged at high rates. There is almost no capacity retention when LFP-0.5 discharged over 2C rate. But the initial specific capacity can be retained after the current change to 0.1C rate. These results indicate that the capacity loss at high charge/discharge rate is mainly caused by the low diffusion rate of lithium ions within the electrode materials due to the larger particle size of sample LFP-0.5^[21, 24].

3 Conclusions

A hydrothermal reaction-calcination process for the synthesis of LiFePO₄/C nanocomposites in the water medium was developed using inexpensive and stable Fe₂O₃ as the iron source, ascorbic acid as the antioxidant and carbon source. It is found that the amount of ascorbic acid has an effect on the structure, phase and carbon amount of the final product. With 1 g ascorbic acid used in the reaction, the particle size of synthesized LiFePO₄/C nanocomposites is in a range of 220–280 nm. When used as the cathode materials for the lithium-ion batteries, the as-prepared material shows high capacity and good cycle stability (159 mAh/g at 0.1C rate over

500 cycles), as well as good rate capability. Its excellent cycling behavior make it a promising cathode material for the lithium-ion batteries.

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以 Fe_2O_3 为原料通过水热–高温煅烧法合成 LiFePO_4/C 纳米复合材料及其电化学性能研究

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摘 要: 采用三氧化二铁(Fe_2O_3)为铁源, 抗坏血酸作碳源, 通过在 200°C 下水热反应并经煅烧后合成出 LiFePO_4/C 纳米复合材料. 抗坏血酸在水热反应体系中不但作为最终反应产物的碳源, 而且还起到了限制 LiFePO_4 颗粒生长的作用. 抗坏血酸的用量对产物的形貌、结构、碳含量有重要影响, 进而影响产物的电化学性能. 当抗坏血酸用量为 1 g 时, 制得的 LiFePO_4/C 纳米复合材料的粒径在 $220\sim 280\text{ nm}$. 该材料用作锂离子电池的正极材料时, 在 0.1 C 的电流密度下循环 500 次后其放电容量仍保持 159 mAh/g , 并且具有较好的倍率性能.

关 键 词: 锂离子电池; 磷酸铁锂; Fe_2O_3 ; 水热法

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