

Modified carbothermal reduction method for synthesis of LiFePO_4/C composite

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Abstract: With $\text{LiAc}\cdot 2\text{H}_2\text{O}$ as Li precursor, pure olivine phase LiFePO_4/C was synthesized at a relatively low temperature (650°C) and short sintering period (4 h) by molten salt carbothermal reduction method. Scanning electron micrograph shows that particle size of the product is about $1\mu\text{m}$, smaller than that of the sample synthesized with Li_2CO_3 as Li precursor. Electrochemical measurements prove that LiFePO_4/C obtained from $\text{LiAc}\cdot 2\text{H}_2\text{O}$ shows high capacity. The initial discharge capacities are $148\text{ mA}\cdot\text{h/g}$ at $0.5C$ rate and $115\text{ mA}\cdot\text{h/g}$ at $5C$ rate, respectively. After 50 cycles, the capacity retention ratios are 93% and 89% at $0.5C$ rate and $5C$ rate, respectively.

Key words: LiFePO_4/C composite; molten salt; carbothermal reduction; β -cyclodextrin

1 Introduction

Recently, olivine-structured LiFePO_4 proposed by PADHI et al [1] has received particular interest as a candidate cathode material for rechargeable lithium ion batteries. This kind of material has merits, such as high energy density, low cost, environmental friendliness and safety. However, the very poor electronic conductivity and Li-ion diffusion coefficient of LiFePO_4 lead to its poor rate capability, which limits its industrial application to great extent. Therefore, research on LiFePO_4 is mostly devoted to enhance its conductivity by metal doping [2,3], coating with the electronically conductive materials like carbon, metal and conductive polymer [4–6] or minimizing the particle size by modifying synthesis conditions [7,8].

As is known to all, synthesis methods would significantly affect the electrochemical performance of material. Up to now, several processing methods have been developed, such as high-temperature solid-state reaction, sol-gel reaction, hydrothermal method, co-precipitation and microwave heating [9–11]. Solid-state reaction is considered the suitable method for mass production of LiFePO_4 because of the relatively

simple processing procedure. However, the solid-state reaction has shortcomings, such as high energy consumption and poor uniformity of the product. Other soft-chemistry methods require complicated synthetic techniques, hard-controlled synthesis condition and relatively high cost of Fe(II) precursor. In recent years, the solid-state carbothermal reduction (CTR) method has been widely explored in the preparation of LiFePO_4 [12,13]. This method has a lot of advantages, such as low cost raw materials, simple synthesis process and easy mass production application. However, as the traditional solid-state reaction, the uniformity of the product is hard to be controlled and the energy consumption is relatively high.

Recently, the molten salt method has been widely employed to manufacture cathode materials for lithium-based secondary batteries [14]. Small particles can be obtained at relatively low temperatures due to the high ion diffusion rates between reaction components in the molten media. But the traditional molten salt method must introduce NaCl [14], which acts as molten salt and must be washed off after the reaction. This will increase the complexity of the producing process. It is urgent to develop a simple, cheap and efficient method for the mass production of LiFePO_4 cathode material.

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In this work, with $\text{LiAc}\cdot 2\text{H}_2\text{O}$ as lithium source and molten media, β -cyclodextrin as carbon sources and reducing agent, a modified carbothermal reduction method (which is called as molten salt carbothermal reduction method) is used to produce LiFePO_4 at a lower sintering temperature in a shorter reaction period. It is well known that the melting point of $\text{LiAc}\cdot 2\text{H}_2\text{O}$ is as low as 53–56 °C. During the reaction process, the molten $\text{LiAc}\cdot 2\text{H}_2\text{O}$ can offer liquid environment with high ion diffusion rate and strong dissolving capability, which is benefit for the ionic diffusion and can accelerate the reaction. Another merit is that the product does not need washing because $\text{LiAc}\cdot 2\text{H}_2\text{O}$ also acts as reactant. As comparison, the synthesis and characteristic of LiFePO_4/C composite materials by ordinary carbothermal reduction route using Li_2CO_3 as lithium source are also presented.

2 Experimental

LiFePO_4/C composites were prepared by the modified carbothermal reduction method using $\text{LiAc}\cdot 2\text{H}_2\text{O}$ (AR), $\text{NH}_4\text{H}_2\text{PO}_4$ (AR) and Fe_2O_3 (AR) as starting materials. Stoichiometric $\text{LiAc}\cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, Fe_2O_3 and a certain amount β -cyclodextrin (9%, in mole fraction) were dissolved in de-ionized water and thoroughly mixed. After that, the mixture was dried in an oven at 80 °C for 8 h in air to form solid paste. Then the precursors were pressed into pellets and heated to 350 °C for 4 h and then to 550 °C, 600 °C and 650 °C for 4 h in nitrogen atmosphere, respectively. Samples with different temperatures of 550, 600 and 650 °C were named as a, b and c respectively. As comparison, LiFePO_4/C composite materials were synthesized by ordinary carbothermal reduction method using the same pretreatment process. Among raw materials, only lithium source was changed to Li_2CO_3 . The resulting precursors were sintered at 650 °C for 4 h and 700 °C for 10 h, which were nominated as samples d and e.

Thermal studies were carried out by means of thermogravimetric-differential analysis (TG–DTA) using a thermal analyzer system (Shimadzu DT–40) at a heating rate of 5 °C/min up to 700 °C in a N_2 flow. XRD patterns were obtained from a Bruker AXS D8 X-ray diffractometer with Cu K_α radiation at 40 kV and 40 mA. SEM (AMARY–1000B) was used to observe the particle morphology.

Electrochemical performance of LiFePO_4/C composites was characterized using CR2016 coin-type cell. The as-prepared powder was blended with acetylene and polyvinylidene fluoride (PVDF) with a mass ratio of 80:10:10, following the mixing with N-methylpyrrolidinone (NMP) to form slurry. The slurry was then pasted onto an Al foil and the solvent was

evaporated at 110 °C for 10 h under vacuum and finally pressed under 0.3 MPa. A disk cut from Al foil pasted with LiFePO_4/C (about 0.02 mm thick) was used as the test electrode. Lithium metal was used as counter and reference electrodes. Ethylene carbonate (EC), dimethyl carbonate (DMC) and 1 mol/L LiPF_6 were used as electrolyte. The coin cells were assembled in the glove box (ZKX3, Wuhan). Charge–discharge and cycling were carried out on a battery test system (CT2001A LAND, Wuhan). Normally the cells were cycled galvanostatically and the cut-off voltage was controlled between 2.5 and 4.2 V. The electrochemical impedance spectroscopy (EIS) and the cyclic voltammetry (CV) analyses were both carried out using a CHI660B electrochemical work station (Chenhua, Shanghai). The amplitude of AC signal was 5 mV over the frequency range of 0.1 Hz– 10^5 Hz. The scan rate of CV was 0.01 mV/s in the voltage range of 2.5–4.3 V. All tests were performed at room temperature.

3 Results and discussion

Figure 1 shows the TG–DTA curves of the precursor containing $\text{LiAc}\cdot 2\text{H}_2\text{O}$ from room temperature to 700 °C with a heating rate of 5 °C/min in a N_2 flow. It shows that there are various stages of mass losses. In the range of 50–160 °C, an initial mass loss and two weak endothermic peaks are observed. This continuous mass loss may correspond to the removal of physi-sorbed water, crystal water and melting of $\text{LiAc}\cdot 2\text{H}_2\text{O}$, respectively. From 150 to 275 °C, there appear two mass loss steps (6.578% and 11.84%) and a strong endothermic peak in the DTA–TG curves, which can be ascribed to the thermal decomposition of LiAc and $\text{NH}_4\text{H}_2\text{PO}_4$. Between 275 and 650 °C, the DTA plot shows two wide exothermic peaks with two mass losses of 9.539% and 8.223%, which can be attributed to the decomposition, carbonization, oxidation of β -cyclodextrin and crystallization of LiFePO_4 [15–17].

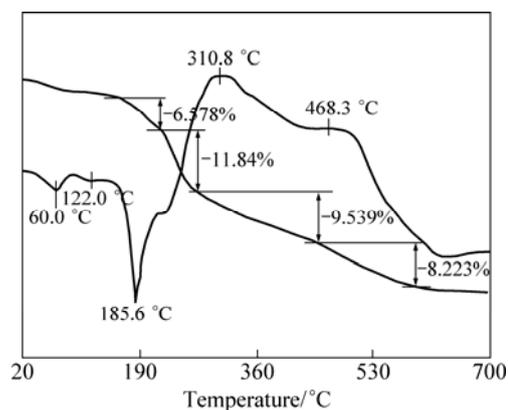


Fig. 1 TG–DTA profiles for precursor of LiFePO_4/C using $\text{LiAc}\cdot 2\text{H}_2\text{O}$ as lithium source

There is no mass loss for further increase of temperature. Therefore, we choose three different synthesis temperatures, 550 °C, 600 °C and 650 °C to obtain LiFePO₄/C composites.

The XRD patterns of LiFePO₄/C composites sintered at different temperatures using the modified (a–c) and ordinary (d–e) carbothermal reduction methods are shown in Fig. 2. With the increase of temperature, the intensity of the diffraction peaks of LiFePO₄ phase becomes stronger and stronger, indicating the increase of phase purity and crystallinity of LiFePO₄. When the temperature is higher than 650 °C, all the diffraction patterns show a single and well-crystallized LiFePO₄ phase with an olivine structure and a space group of *Pnma*. The diffraction peak intensity of Sample c is higher than that of Sample e (synthesized at 700 °C for 10 h [18, 19]) and is similar to that of Sample d. The results prove that the modified carbothermal reduction method can reduce the synthesis temperature and reaction time compared with the ordinary method. The reason is attributed to the high ion diffusion rate and strong dissolving capability of molten LiAc·2H₂O.

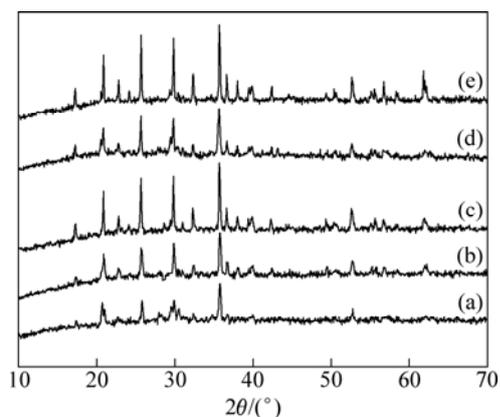


Fig. 2 XRD patterns of LiFePO₄/C samples sintered at different temperatures using modified and ordinary solid state carbothermal reduction: (a) 550 °C, 4 h, LiAc as Li source; (b) 600 °C, 4 h, LiAc as Li source; (c) 650 °C, 4 h, LiAc as Li source; (d) 650 °C, 4 h, Li₂CO₃ as Li source; (e) 700 °C, 10 h, Li₂CO₃ as Li source

Scanning electron micrographs of LiFePO₄/C composites synthesized by the modified carbothermal reduction method at 650 °C and ordinary one at 700 °C are presented in Fig. 3. It can be seen that particle size of LiFePO₄/C composites synthesized by the modified method is much smaller than that of the ordinary one. The former with quasi-spheric shape shows a uniform and narrow size distribution of around 1 μm. However, the latter with irregular appearance shows a wide particle size distribution ranging from 1 to 5 μm. It is well known that in addition to crystallinity, the particle morphology, particle size and particle size distribution of cathode

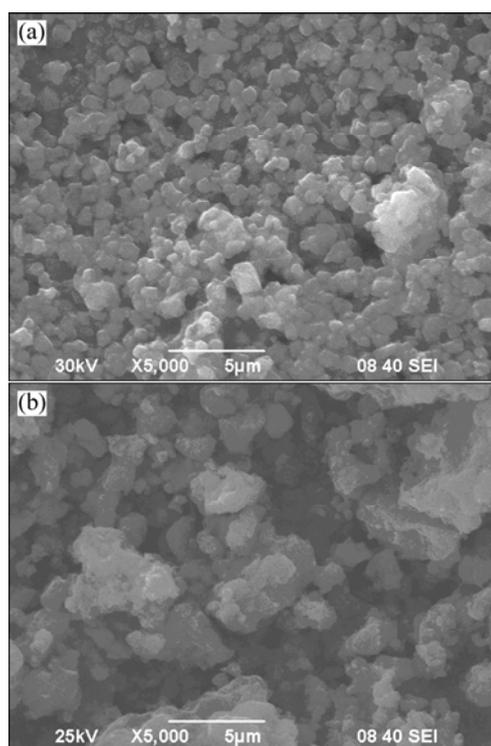


Fig. 3 SEM images of LiFePO₄/C samples sintered at different temperatures using modified and ordinary solid state carbothermal reduction: (a) Sample c; (b) Sample e

materials are of great importance to the performance of batteries. Smaller particle size and narrower particle size distribution are benefit for Li ion diffusion and improvement of its electrochemical performance.

Figures 4 and 5 show the charge and discharge curves of the LiFePO₄/C electrodes at various current rates. For the LiFePO₄/C composites synthesized by the modified method, the reversible capacity was 148 mA·h/g at 0.5C and 115 mA·h/g at 5C rate. While for the ordinary one, the reversible capacity was 122 mA·h/g at 0.5C and 61 mA·h/g at 5C rate. It should also be noticed that polarization of the LiFePO₄/C composites synthesized by the modified method is slighter than that synthesized by the ordinary method at 5C rate. This can be attributed to the relatively good particle morphology, small particle size and narrow particle size distribution of the former. During the charge–discharge processes, the diffusion of Li ion is more harder inside the particle than outside. Therefore the utilization ratio of Li ion in large particles is lower than that in small particles, especially when the current density is not too low. This can explain why the discharge capacity of LiFePO₄/C synthesized by the modified method is higher than that of samples synthesized by the ordinary method.

Figure 6 shows the CV profiles of LiFePO₄/C electrode synthesized by modified and ordinary carbothermal reduction methods sintered at 650 °C and 700 °C, respectively. It can be seen that the anodic and

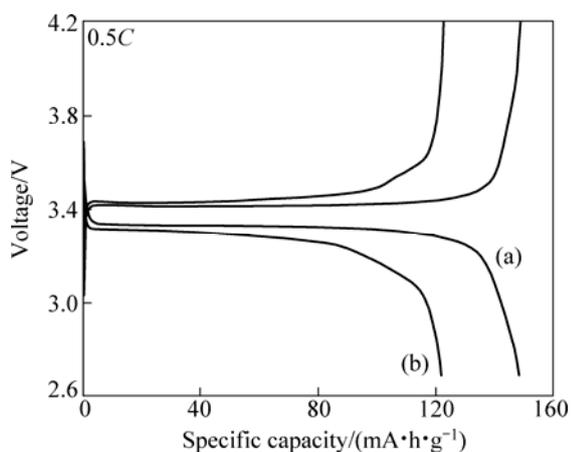


Fig. 4 Charge–discharge profiles of LiFePO_4/C samples prepared by modified and ordinary solid state carbothermal reduction at 0.5C rate: (a) Sample c; (b) Sample e

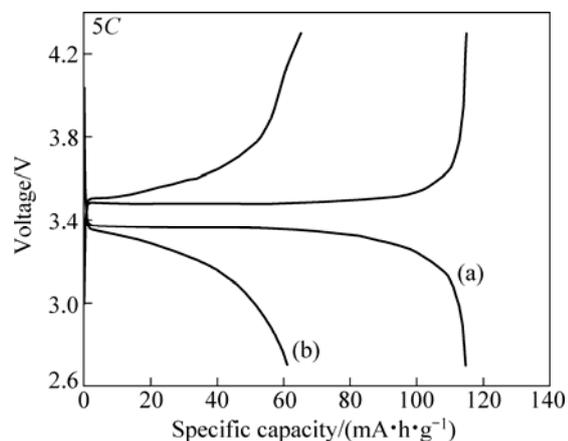


Fig. 5 Charge–discharge profiles of LiFePO_4/C samples prepared by modified and ordinary solid state carbothermal reduction at 5C rate: (a) Sample c; (b) Sample e

cathodic peaks on CV curve of Sample c are more symmetrical and sharper than those of Sample e, and the amplitude of the peak current of the former is almost twice that of the latter. For Sample c the peak potential difference between cathodic and anodic peaks is 0.27 V, whereas for Sample e, it is 0.34 V. The well-defined peaks and the smaller peak potential difference on CV curve of Sample c suggest the higher reversibility of the electrode reaction.

AC impedance of the electrodes with different sintering time using modified and ordinary carbothermal reduction methods is shown in Fig. 7. All profiles exhibit a semicircle in the high frequency and a straight line in the low-frequency region. The values of the cross point of the semicircle on the horizontal axis represent the charge transfer resistance (R_{ct}). The straight line represents the Warburg impedance, which is associated with the lithium-ion diffusion in the inner of LiFePO_4 particles. The smaller numerical value of the diameter of

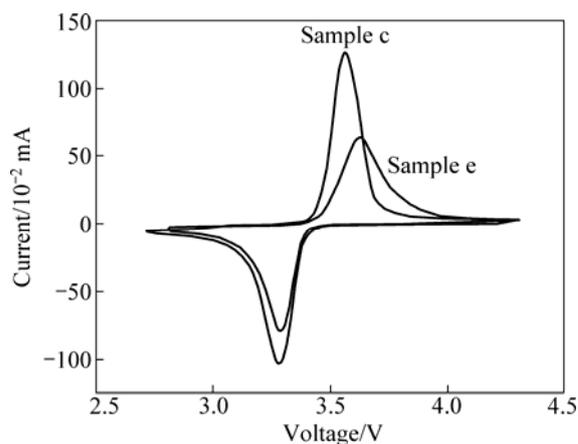


Fig. 6 Cyclic voltammograms of the LiFePO_4/C samples prepared by the modified and ordinary solid state carbothermal reduction methods

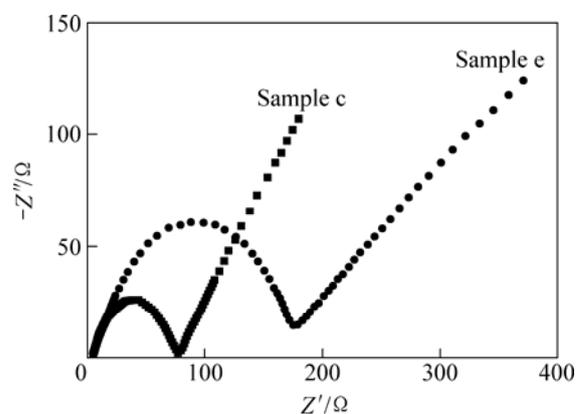


Fig. 7 AC impedance plots of LiFePO_4/C samples prepared by modified and ordinary solid state carbothermal reduction methods

the semicircle along the Z' axis means smaller charge-transfer resistance and thus better reaction kinetics of lithium ion. From Fig. 7 it is obvious that R_{ct} of Sample c is remarkably smaller than that of Sample e, indicating the increase of conductivity of Sample c, which explains its excellent electrochemical performance.

Figure 8 shows the cycling performance of LiFePO_4/C samples at different current rates. It can be clearly seen that sample c shows much better cycling ability. At 0.5C rate, the initial discharge capacity of Sample c is 148 mA·h/g, and after 50 cycles it is 137 mA·h/g with a capacity retention up to 93%. For Sample e, the initial discharge capacity is 122 mA·h/g and the capacity retention is only 86%. At 5C rate, the capacity retentions of Samples c and e are 89% and 81%, respectively. According to the results of WANG et al [20], the formation of cracks in LiFePO_4 particles after cycling would lead to poor electric contact and capacity fading. From literature, large particles with higher

internal strain during Li-extraction/insertion process, crack more easily than smaller ones. So, the relatively small particle size and high electric conductivity explain the high capacity and excellent cycling performance of Sample c.

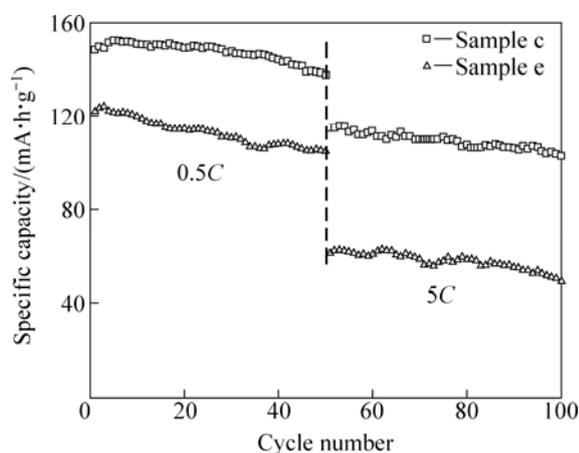


Fig. 8 Cycling performance of LiFePO₄/C samples at different current rates

4 Conclusions

1) LiFePO₄/C composites with pure olivine phase were synthesized using the modified carbothermal reduction method with LiAc·2H₂O as Li-precursor. The sintering temperature and time (650 °C, 4 h) are reduced compared with the ordinary method using Li₂CO₃ as Li source (usually higher than 700 °C for at least 10 h).

2) As cathode material for Li-ion batteries, it can deliver a high capacity of 148 mA·h/g at 0.5C rate and 115 mA·h/g at 5C rate. After 50 cycles, the capacity retention ratios are 93% and 89% at 0.5C rate and 5C rate, respectively.

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改进的碳热还原法合成 LiFePO_4/C 材料

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摘 要: 采用 $\text{LiAc}\cdot 2\text{H}_2\text{O}$ 作为锂源, 利用熔盐碳热还原方法在较低的烧结温度和较短的烧结时间内($650\text{ }^\circ\text{C}$, 4 h)合成纯相 LiFePO_4/C 材料。扫描电镜照片显示这种方法合成的材料粒径大约为 $1\text{ }\mu\text{m}$, 小于用 Li_2CO_3 作为锂源合成的材料。电化学测试表明, 采用 $\text{LiAc}\cdot 2\text{H}_2\text{O}$ 作为锂源合成的材料表现出了高的放电容量和良好的倍率循环性能: 在 0.5C 和 5C 倍率下, 其首次放电容量分别为 $148\text{ mA}\cdot\text{h/g}$ 和 $115\text{ mA}\cdot\text{h/g}$; 50次循环后, 容量保持率分别为93% 和89%。

关键词: LiFePO_4/C ; 熔盐; 碳热还原; β -环糊精

(Edited by LI Xiang-qun)