



Short communication

The cycling performance of LiFePO₄/C cathode materials

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ABSTRACT

Olivine LiFePO₄/C cathode materials were synthesized by carbothermal reduction method at different temperatures. The samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), particle size analysis and charge–discharge test. The results showed that both the crystallization degree and particle size increased remarkably with the synthesis temperature increasing. The LiFePO₄/C synthesized at 750 °C showed a highest initial discharge specific capacity of 145 mA hg⁻¹ at 1C rate, which decreased to 60 mA hg⁻¹ after 500 cycles. However, the sample prepared at 850 °C exhibited a lower initial discharge capacity of 135 mA hg⁻¹ at 1C rate, whose capacity could also reach 105 mA hg⁻¹ after 500 cycles. The material synthesized at lower sintering temperature had lower crystallization degree and plenty of nano-sized microstructure, leading to its higher electrochemical activity and initial discharge capacity. But at the same time, the lower sintering temperature also leads to the instability of the crystal structure and the solution of active materials, which results in the degradation of discharge capacity on long-time cycling. In short, synthesizing the material with perfect crystallization degree and moderate particle size is an effective way to improve the cycling performance of LiFePO₄/C cathode materials.

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1. Introduction

Lithium-ion rechargeable batteries offer an operative voltage and energy density higher than those of the other rechargeable battery systems, and have various application ranges from electronic devices to electric vehicles. Among several components in the lithium-ion batteries, cathode materials have attracted much attention since they determine the initial capacity of a battery and play important roles in fading resistance. Recently, olivine LiFePO₄ cathode materials have attracted particular interest due to their good features, such as abundance in raw materials, environmental friendliness, safety and so on [1–4]. However, the relatively poor ionic and electronic conductivity is a disadvantage for the compound [5–7]. Currently, several research groups made efforts to overcome the low conductivity of LiFePO₄ by carbon coating [8–10], synthesizing small particles [11,12] and metal-ion doping [13–16], through which, the electrochemical performance of LiFePO₄ cathode material, including initial discharge capacity, rate capability and energy density, been improved.

The olivine LiFePO₄ should show an excellent reversibility on cycling since LiFePO₄ and delithiated FePO₄ have the same space group with only small changes in the unit cell parameters. However, the capacity gradual fading of LiFePO₄ was observed by many

researchers [17–21]. Especially under conditions of high discharge rate, the capacity fading is so fast that it cannot be used in some fields which need long-life battery.

In this work, the reason causing the poor cycling performance of LiFePO₄/C cathode materials at high discharge rate was systematically investigated and an effective way to improve their cycling performance was put forward.

2. Experimental

LiFePO₄/C powders were synthesized by carbothermal reduction method using Fe₂O₃ (A.R.), LiH₂PO₄ (A.R.) and glucose as raw materials. The above materials were weighed in stoichiometric ratio, ground uniformly in a mortar with acetone, then transferred to a tubular furnace and calcined at 750, 800 and 850 °C for 9 h in a nitrogen atmosphere, and the samples were denoted as L750, L800 and L850, respectively.

The morphology and microstructure of the prepared sample powders were observed using scanning electron microscopy (SEM) with an FEI SIRION microscope. The crystal structures were analyzed by X-ray diffraction (XRD) on a Rigaku-D/MAX-2550PC diffractometer with Cu K α radiation. The particle size distribution of the sample was determined by Laser Particle Sizer (LS800).

The electrochemical measurement was made with the CR2430 pattern. The cathode electrode was made in the following way. The LiFePO₄/C powder was mixed with acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 80:15:5, then rolled

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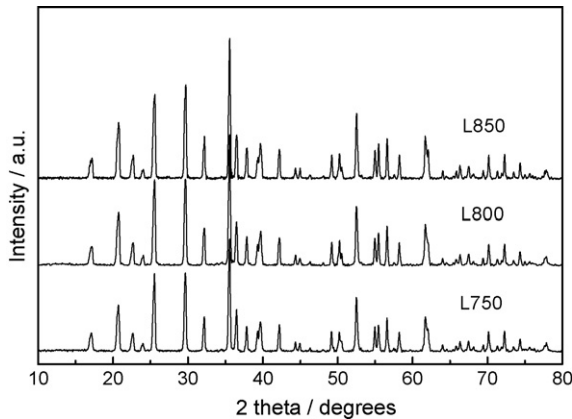


Fig. 1. XRD patterns of LiFePO_4/C composites synthesized at different temperatures.

the mixture into a 0.16 mm thick sheet and cut into pellets. With the natural graphite as the anode, a Celgard 2400 microporous membrane as the separator, and 1 mol L^{-1} LiPF_6 in ethylene carbonate (EC)-dimethyl carbonate (DMC; 1:1 in volume) as the electrolyte, the cell were assembled in an nitrogen-filled ($\text{RH} < 3\%$) glove box. The charge–discharge test was performed between 2.3 and 4.2 V with LAND batteries testing system.

3. Results and discussion

The XRD diffraction patterns of LiFePO_4/C powder prepared at different temperatures are shown in Fig. 1. The XRD patterns show that the main phase of all the samples can be identified as LiFePO_4 with an ordered olivine structure indexed to orthorhombic $Pnmb$. No impurities are detected in the XRD patterns. From Fig. 1 we can also see that the peak intensity of LiFePO_4 increases slightly with increasing the synthesis temperature from 750 to 850 °C, indicating that the crystallization degree increases with synthesis temperature increasing. On the other hand, there is no additional diffraction peaks associated with crystal modification by carbon, which indicates that the carbon generated from glucose

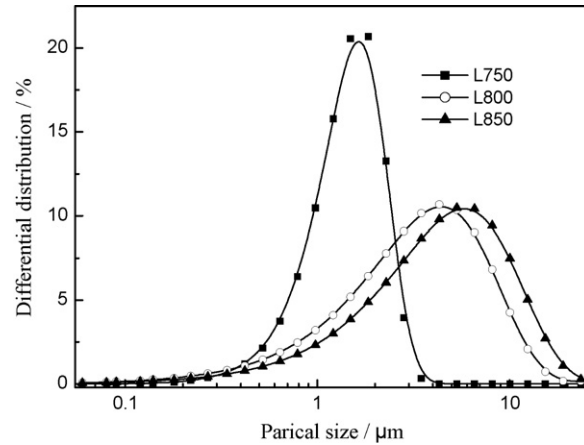


Fig. 3. The particle size distribution curves of LiFePO_4/C composites synthesized at different temperatures.

is amorphous and its presence does not influence the structure of LiFePO_4 .

Fig. 2 shows the SEM images of LiFePO_4/C samples. With the increase of the temperature, a significant increase in particle size and a smoother particle surface are observed. Sample L750 has a homogeneous particle size of about 100–200 nm with a rough surface as a result of lower crystallization degree. And there are plenty of nano-sized microstructure on the surface of the particles. However, Sample L800 has a particle-agglomerated morphology. When the temperature increases to 850 °C, the powders show a glossy surface, whose average particle size is about 1 μm . The disappearance of nano-sized microstructure on the particles surface and the increase in particle size can be attributed to the higher crystallization degree of the samples prepared at high temperature.

The particle size distribution curves in Fig. 3 also indicate the increase of particle size with the increase of synthesis temperature. The narrower distribution curve of sample L750 indicates a homogeneous particle size distribution of the powders. However, Samples L800 and L850 show a broadened distribution curve

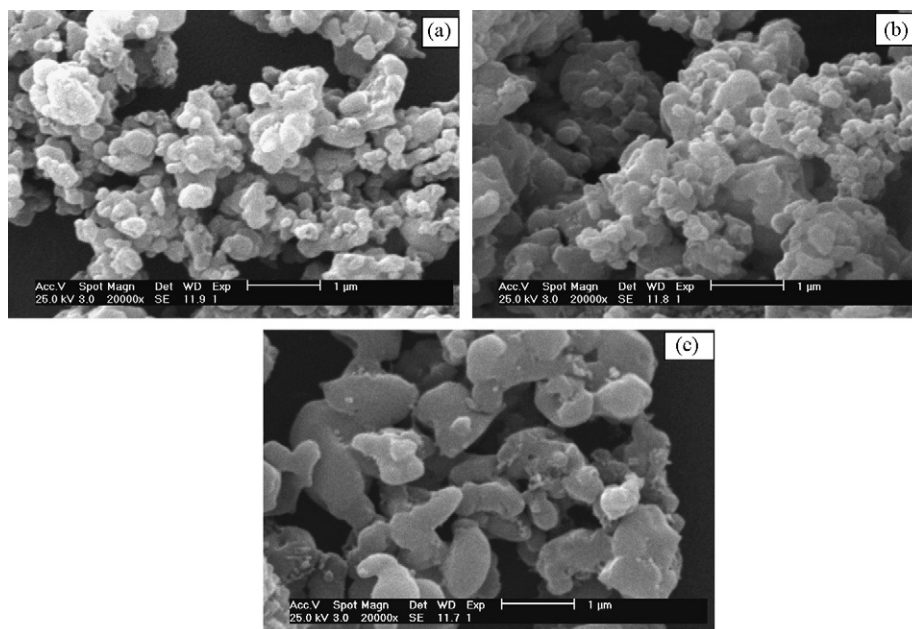


Fig. 2. SEM images of LiFePO_4/C composites synthesized at different temperatures: (a) L750, (b) L800 and (c) L850.

Table 1
The D_{50} values of LiFePO_4/C composites synthesized at different temperatures

Samples	D_{50} (μm)
L750	1.33
L800	3.08
L850	4.03

due to the inhomogeneous particle size distribution caused by the agglomeration of some small particles into larger ones. The values of particle size at 50% cumulative population (D_{50}) are listed in Table 1. We can see that the D_{50} values of samples synthesized at different temperatures are 1.33 μm (L750), 3.08 μm (L800) and 4.03 μm (L850), respectively.

The initial charge–discharge curves of LiFePO_4/C samples synthesized at different temperatures at 0.2C rate are illustrated in Fig. 4. As shown in Fig. 4, the initial discharge capacities of LiFePO_4 samples synthesized at 750, 800 and 850 $^\circ\text{C}$ are 154, 151 and 144 mA h g^{-1} , respectively. According to several reports [22,23], the particle size is a critical factor in determining the electrochemical performance of LiFePO_4 , because the charge–discharge process is controlled by lithium transport across the $\text{LiFePO}_4\text{-FePO}_4$ interface. Consequently, the highest discharge capacity for sample L750 can be explained in terms of particle size. On the other hand, the samples synthesized at lower temperatures have lower crystallization degree, which means that metastable structure may be contained in the material, thus leading to its higher electrochemical activity and higher initial capacity.

Fig. 5 shows the cycling performance curves of all the samples at 1C rate. From Fig. 5, we can see that the LiFePO_4/C synthesized at 750 $^\circ\text{C}$ shows a highest initial discharge capacity of 145 mA h g^{-1} at 1C rate, which decreases to 60 mA h g^{-1} after 500 cycles. However, the sample prepared at 850 $^\circ\text{C}$ exhibits a lower initial discharge capacity of 135 mA h g^{-1} at 1C rate, which could also remain 105 mA h g^{-1} after 500 cycles. It is clear that the cycling performance is improved with the increase of synthesis temperature.

The charge–discharge curves at 1st, 100th, 300th and 500th cycles for sample L750 are shown in Fig. 6. It is clear that the voltage difference between charge and discharge plateau increases remarkably with the cycle number increasing. In addition, a decrease of initial discharge voltage is also observed with the cycle number increasing. All these results indicate an increase in polarization of electrode during cycling, which results in a decrease of charge–discharge capacity. To better understand the reason of the

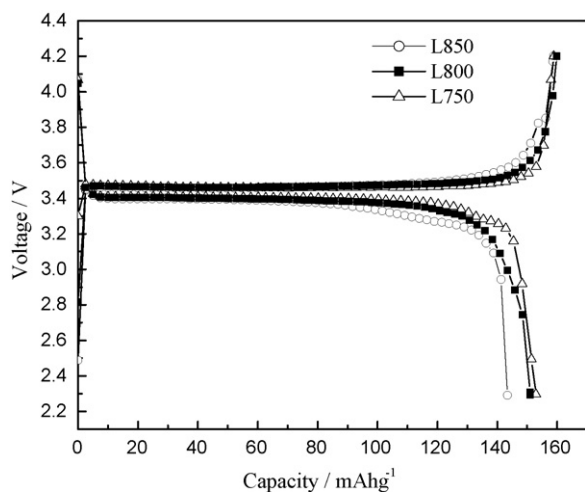


Fig. 4. Initial charge–discharge curves of LiFePO_4/C composites synthesized at different temperatures at 0.2C rate.

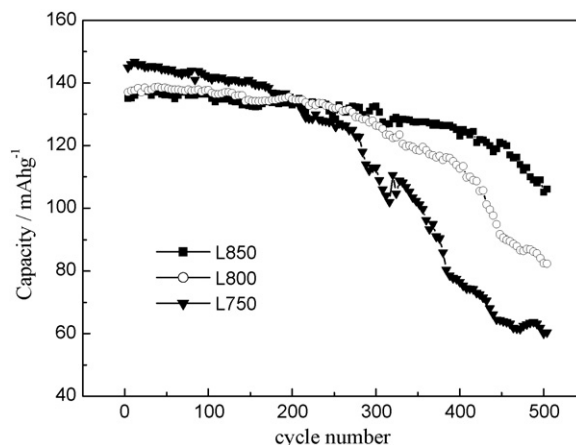


Fig. 5. Cycling performance curves of all the samples at 1C rate.

increase of cell polarization, we disassemble the testing cell after cycling more than 500 times, the chemical compositions of the anode is analyzed by EDS and the iron element is detected. The iron element in the anode can be considered as the product of chemical dissolution of LiFePO_4 . Since $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1) is used as the electrolyte in the testing cell, the LiFePO_4/C composite reacts with the residual HF inevitably, thus leading to the dissolution of iron from the cathode material. It is believed that the chemical dissolution of LiFePO_4 causes the loss of contacting between active materials and conductive carbon, thus leading to the increased polarization of electrode. Fig. 7 shows a sketch of the possible mechanism of the increased polarization. For the initial cycle, there exists a firm contact between active materials and conductive carbon, and both the Li^+ ions and electrons have to be available at the same spot. With the cycle number increasing, LiFePO_4 dissolves gradually. In particular, as to the nano-sized microstructure on the rough surface, the dissolution of active materials may be more serious due to its larger contact areas with the electrolyte, leading to the separation of active material from conductive carbon. The electrons have to go through the material body to these spots, thus causing additional polarization. So it is very important to suppress the dissolution of active material to improve the cycling performance of the LiFePO_4/C composite.

The stability of the three samples in electrolyte is investigated as follows: 1 g LiFePO_4 powder was dispersed in 10 mL electrolyte,

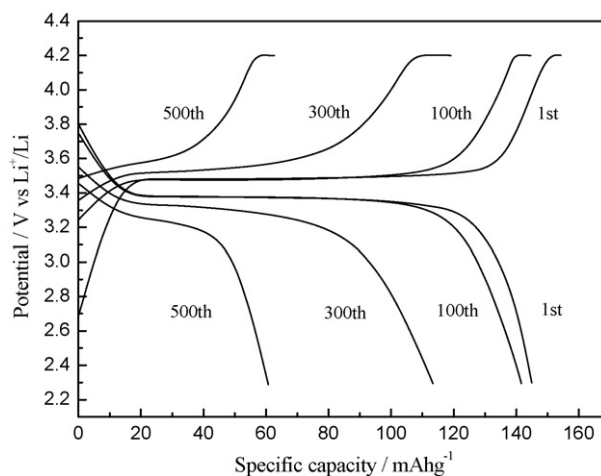


Fig. 6. Charge–discharge curves at 1st, 100th, 300th and 500th cycles for sample L750.

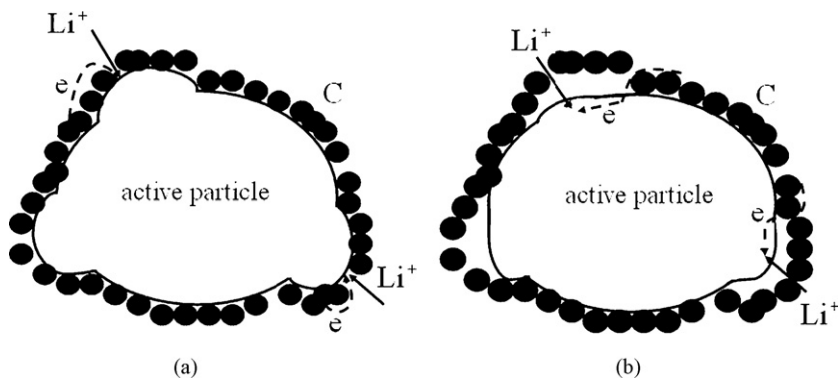


Fig. 7. A sketch of the possible mechanism of the increased polarization: (a) for the initial cycle, there exists a firm contact between active materials and conductive carbon; (b) the contact between active materials and conductive carbon is broken after long-time cycling.

and then the mixture was sealed and stored for 7 days. In order to accelerate the dissolution rate, the test was performed at 55 °C. Iron concentration in the electrolyte was analyzed using a 721 visible spectrophotometer. At the end of the aging process, the iron concentrations in the electrolyte for the three samples are 48.6 ppm (L700), 14.7 ppm (L800) and 4.9 ppm (L850), respectively, indicating that the stability of the samples increases with the synthesis temperature increasing. It is believed that the material synthesized at lower temperature has lower crystallization degree and lots of metastable structure, thus leading to its higher electrochemical activity and initial discharge capacity. But at the same time, the lower synthesis temperature leads to the instability of the crystal structure, which results in the incidental dissolution of active material, thus leading to the degradation of discharge capacity on long-time cycling. On the contrary, the material synthesized at higher temperature has good crystallization degree and smooth surface, thus leading to its better stability in the electrolyte and excellent cycling performance. In a word, synthesizing the material with perfect crystallization degree and moderate particle size is an effective way to improve the cycling performance of LiFePO_4/C cathode materials.

4. Conclusion

The chemical dissolution of LiFePO_4 causes the loss of contacting between active materials and conductive carbon, thus leading to the increasing polarization of electrode and worse cycling performance. It is very important to suppress the dissolution of active material to improve the cycling performance of LiFePO_4/C composites. The better stability in the electrolyte and excellent cycling performance of the material synthesized at higher temperature can

be contributed to higher crystallization degree and smaller specific surface area. Synthesizing the material with perfect crystallization degree and moderate particle size is an effective way to improve the cycling performance of LiFePO_4/C cathode materials.

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