Effect of particle size on electrochemical performance of lithium iron phosphate materials

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Abstract: LiFePO₄ material has many virtues, such as rich raw materials, low price, excellent high temperature cycling performance and safety property. Lithium ion battery with LiFePO₄ as positive electrode active material is the most promising. However, compared with other positive electrode active materials, LiFePO₄ material has the inherent disadvantage of poor electrical conductivity, it greatly limits its dynamic characteristics at low temperature. In this paper, the effect of particle size of LiFePO₄/C material on the low temperature performance prepared via solid-state method is systematically investigated. The structure and morphology of the samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The electrochemical properties of cathode materials were studied by Land2001.

1. Introduction

With the increasing prominence of energy and environmental problems, the new generation of safe and green lithium ion batteries are widely used [1-4]. Relative to the traditional lithium ion battery materials, Lithium iron phosphate (LFP) has the advantages of low price, environment friendly, good thermal stability, abundant resources, good safety and so on [5,6,7]. At present, the synthesis methods of lithium iron phosphate have solid state method with high temperature calcine, carbothermal way, microwave synthesis, sol-gel, hydrothermal method and so on. The application of LFP materials is restricted by its low electron conductivity and low lithium ion diffusion coefficient. In addition, the low temperature performance can not meet the current requirements.

Based on the above problems, coating and doping methods are generally used for modification LiFePO₄. In this paper, nanocrystallization is used to enhance the properties of LFP. Using LiH₂PO₄ and Fe₂O₃ as raw materials, the preparation process of low cost, high efficiency and clean LiFePO₄ for industrial application was studied. And citric acid is added as carbon source. The particle size of the material is controlled by ball milling time and milling process.
2. Experimental

2.1 Apparatus and Reductant
Lithium dihydrogen phosphate was manufactured by Tangshan abundant south area into feng technology co., LTD. Iron oxide is produced by Tianjin zhengyuan haoye. Citric acid is produced by Tuosheng Chemical Co., Ltd.

Scanning electron microscopy (SU8020, Hitachi), X-ray diffraction (BRUCKER D8 ADVANCE), Electrothermal blowing dry box (150-1B, Shanghai), Electronic balance (BSA423S-CW, Sartorius), Glovebox (FG1200/750 Vigor (CHINA) CO., LTD), MICROTRAC HRA (Topsizer plus, OMCC)

2.2 Synthesis and characterization
Lithium iron phosphate was prepared by carbothermal reduction using lithium dihydrogen phosphate and iron oxide as raw materials. Add citric acid as carbon source. According to the following synthesis steps to prepare. The molar ratio of lithium dihydrogen phosphate (AR), Fe₂O₃(AR), citric acid (AR) were blended in acetone and ball milled under the speed of nearly 400r/minute for 4h, 6h, 8h and 10h, respectively. Then, the mixture was dried at 105°C in the oven for 5h. Then the drying materials were put in an atmosphere furnace and was calcined in Ar atmosphere at 300°C for 5h, then 700°C for 10h, the rate of elevated temperature was 3°C/min. The composite electrode material was prepared by atmosphere tube furnace (GELISI Luoyang). Then the particle size of materials was measured by laser particle size analyzer.

The pureness and construction of the samples were tested by X-ray diffraction (XRD) (BRUCKER D8 ADVANCE) using Cu Kα radiation. Scanning electron microscopy (SU8020, Hitachi) was used to observe the particle morphology.

3. Results

3.1 Particle size analysis
Table.1 illustrates the particle size of the LiFePO₄/C samples at different balling mix time. It can be seen from Table 1 that the particle size reaches the minimum when the milling time is 4h. And the D50 is 1.50μm at 4h. The reduction of particle size is beneficial to shorten the transport path of lithium ions and allow more facile Li⁺ ions intercalation/deintercalation process.

| Samples  | Particle size (μm) |
|----------|--------------------|
|          | D10    | D50    | D90    |
| LFP-4h   | 0.78   | 1.50   | 1.94   |
| LFP-6h   | 1.10   | 2.04   | 2.12   |
| LFP-8h   | 1.05   | 1.90   | 2.01   |
| LFP-10h  | 1.24   | 2.31   | 2.54   |

3.2 X-ray diffraction Discussion
Fig. 1 demonstrates the XRD spectra of LiFePO₄/C samples prepared at four different ball milling times. Each diffraction peak is consistent with the position that corresponding to the diffraction angle of standard card JCPDF (40-1499). There is no impurity peak in XRD pattern, indicating that the composite electrode materials are pure. In addition, there is no diffraction peak of carbon in the figure, indicating that the amorphous carbon formed after high temperature pyrolysis of citric acid, and the crystal structure of LiFePO₄ olivine was not affected.
3.3 SEM analysis of the material

Fig. 2 SEM images of the material (A-4h, B-6h, C-8h, D-10h)

Fig. 2 shows the SEM images of materials obtained at various milling time. The SEM images of LiFePO₄ obtained by various ball milling times are composed of irregular particles. From Fig. 2, we can see that the particles in Figure 2A are smaller than those in Fig. 2B 2C and 2D. And the particles in Figure 2A are relatively uniform than other samples.

3.4 Electrochemical performance of the material

Figure. 3 illustrates the initial charge and discharge curves of LiFePO₄/C material at different milling time. From the Fig. 3 it can be seen that all samples at 0.2C have a long flat discharge plateau at around 3.4V, which indicates that the two-phase redox reaction proceeds via a first-order transition between LiFePO₄ and FePO₄[8,9]. The specific discharge capacities of the samples obtained at different milling times are 158.6mAh/g, 157.3mAh/g, 155.6mAh/g and 152.4mAh/g, respectively. The best milling time is 4h. These results indicate that the ball milling time has a certain effect on the granular size of the sample, thus affecting the electrochemical properties of the sample.
4. Conclusion
In this paper, the influence of different ball milling time on the particle size of the material was researched by high temperature solid phase method, using lithium dihydrogen phosphate and iron oxide as raw materials and citric acid as carbon source. The results show that the microstructure and size of the particles are affected by different milling time. And the smaller of the particle size, the more conducive to the deintercalation of the lithium ions. Thus the material with small particle size has better electrochemical properties.

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