Study on the Preparation of Lifepo4 by Hydrothermal Method

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Abstract. A simple hydrothermal process combined with carbon coating is attempted to prepare nano particle LiFePO₄ cathode materials for Li-ion batteries. A carbon coating process with glucose is used to make LiFePO₄/C composites. The structure, morphology and electrochemical properties of the materials are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and constant current charge/discharge. The X-ray diffraction pattern indicates that the pure phase LiFePO₄ material could be prepared at different reaction temperatures, and the pure phase LiFePO₄ material could not be prepared with the reaction time of 6 h. SEM test shows that the dispersion of LiFePO₄ particles become better with the increase of reaction temperatures and the morphology is more regular with the increase of reaction temperature. But when the reaction temperature increases to 200 °C, LiFePO₄ particles reaggregate severely. As the reaction time increases, the particles of the sample gradually grow. The electrochemical performance indicates that the sample synthesized at 180 °C for 10 h has the highest specific capacity of 139.5 mAh·g⁻¹ at 0.1 C. This study shows that proposed process can be a potential promising way to prepare high performance LiFePO₄ cathode materials.

1. Introduction

The olivine lithium iron phosphate(LiFePO₄) has been regarded the most promising lithium ion batteries cathode material because of the advantages of excellent energy density, good cycling performance, high operating voltage, low-cost and environment friendly [1-4]. Nowadays LiFePO₄ has been applied in all areas of our life [5]. However, the low electronic and ionic conductivity of single phase LiFePO₄ result in poor electrical properties and awful thermostability, especially the slow lithium ion diffusivity of pristine LiFePO₄ at lower temperature which severely restrict its extensive application in practice [6-8]. In order to improve the properties of LiFePO₄, a lot of researches have been done to overcome the defects of lithium iron phosphate by decreasing particle size, optimizing the microcosmic morphology, doping other metal ions [9-11]. The morphology of LiFePO₄ is the key factor to achieve high specific capacity and cycling performance. Choosing appropriate preparation method can not only improve microstructure, but also make the powder particle size reach nano-sized [12, 13]. Moreover, the sample particle has the advantages of good uniformity and dispersity which shortens lithium ion diffusion as well as improves electron transfer efficiency and then improves the performance of LiFePO₄ cathode material [14].

High temperature solid state reaction method is the conventional approach to synthesis LiFePO₄ due to the advantages of simple synthesis process and convenient control [15-17]. However, the product particle size is thick and large, and the most serve defects are the lower purity and poor uniformity [18]. Compared with state reaction method, hydrothermal synthesis method has the advantages of high crystallinity, uniform particle, simple process, low energy consumption and short period [19, 20].
In this paper, we select hydrothermal synthesis method to prepare LiFePO$_4$ cathode material, and investigate the effect of temperature and time on the performance of LiFePO$_4$ cathode material.

2. Experimental

2.1. Sample preparation
The sample powders were synthesized via hydrothermal synthesis method, using LiOH·H$_2$O, FeSO$_4$·7H$_2$O, and H$_2$PO$_4$ as raw materials. They were dissolved into deionized water according to the stoichiometric amounts of LiFePO$_4$ and stirred at room temperature for several minutes to form LiFePO$_4$ precursor. In particular, the above process was conducted in Ar atmosphere. The obtained precursor solution was transferred into a autoclave and kept at 140 °C, 160 °C, 180 °C and 200 °C for 10 h. Then the solution was washed with deionized water for several times and filtered. Subsequently, the filtered powders were dried in the oven at 80°C and then milled in an agate mortar. Then was heated at 650 °C for 6 h which filled with Ar gas. The LiFePO$_4$ powders were synthesized. Choose appropriate temperature and set the hydrothermal reaction time to 6 h, 8 h, 10 h, 12 h, 15 h and repeated above process.

2.2. Phase structure and morphology characterization
The crystal structures of all LiFePO$_4$ were analyzed by XRD (D/Max2500, Japan). The microstructure of as-prepared samples was examined by SEM (FESEM, JEOL, 6300/7001).

2.3. Electrochemical characterization
LiFePO$_4$ was used as cathode electrode active material, acetylene black as a conductive agent, polyvinylidene fluoride (PVDF) as a binder. According to the mass ratio of LiFePO$_4$ : acetylene black : PVDF is 8:1:1. NMP is added as solvent to make it fully mixed. Then the slurry was coated on the foil and dried in vacuum at 100 °C for 24 h. Sliced and assembled the button cell in a vacuum glove box. Lithium metal was used as the negative electrode and Celgard 2400 (polypropylene) was used as the separator. Constant current charge and discharge experiments were tested from 2.5 V to 4.5 V by using Blue Electronic battery test system.

3. Results and discussion
In the process of synthesizing LiFePO$_4$, the temperature and time of hydrothermal reaction are important factors. When the reaction temperature is low, the iron and lithium dislocations are generated easily in the crystal lattice, which affects the electrochemical properties. When the temperature is raised, the precipitation and grain growth of the crystal during hydrothermal process can be enhanced. Figure 1 shows the XRD patterns of the LiFePO$_4$ particles obtained at various reaction temperatures at a fixed reaction time of 10 h. It can be seen from Figure 1 that the XRD patterns of all the samples are consistent with the JCPDS (81-1173) standard, and no diffraction peaks of any impurity phases are detected in each sample, indicating that high-purity LiFePO$_4$ samples are prepared successfully. The peaks of the sample obtained at 180 °C are sharper, indicating that the crystallinity of the material is better and the degree of crystallization is higher when the hydrothermal temperature is 180 °C. As shown in Figure 2, all of the LiFePO$_4$ particles are tiny cuboids over the entire temperature range. The particle size prepared at 200 °C is uneven obviously, and some large particle size can be seen. That may be because the temperature is higher to affect the nucleation reaction of the material. The other samples are monodisperse at lower temperatures, but the sheet-like LiFePO$_4$ nanoparticles with a smaller size appear at 180 °C. With the increase of the reaction temperatures, the dispersibility of the LiFePO$_4$ particles become better and the morphology is more regular until 180 °C. The LiFePO$_4$ particles agglomerated when the temperature is 200 °C.
Figure 3 is the first charge/discharge diagram of LiFePO$_4$ prepared at different reaction temperatures at 0.1 C rate. The charge/discharge curve platform is stable, corresponding to the two-phase transformation process of LiFePO$_4$/FePO$_4$. With the reaction temperatures rising from 140 ºC to 200 ºC, the specific capacities of samples are 28.5, 69.2, 139.5 and 111.6 mAh·g$^{-1}$. The specific capacity of the samples increase with the temperature from 140 ºC to 180 ºC, but the specific capacity decreases at 200 ºC. The sample prepared at 180 ºC has the highest specific capacity. From all of the above analysis, the comprehensive performance of the material at 180 ºC is the most superior.

Figure 4 is the XRD patterns at different reaction times at 180 ºC. It can be seen that the sample with reaction time of 6 h does not correspond to the standard patterns, indicating that LiFePO$_4$ cannot be synthesized. The other XRD patterns of the reaction time are consistent with the standard card. The peaks are sharp and no impurity peaks. That indicates the high-purity samples are prepared at other time. The half-peak width of the sample at 10 h is narrow, indicating that the crystallinity increases.

The SEM images at different reaction times is shown in Figure 5. As the reaction time increases, the average particle size gradually increases. No obvious particles are observed at 6 h. This should be caused by the hydrothermal reaction time is too short to form LiFePO$_4$ which matches with the XRD. When the time is 8 h, the particle is small and agglomerates together. At 10 h, the particles have good dispersibility and become uniform with lathing shape. At 12 h, the particle size increases significantly. At 15 h, the particles start to grow and change their shapes. This is because the essence of the hydrothermal reaction is the process of dissolution-crystallization-regeneration of the material. First, the relatively large particles begin to dissolve into smaller particles, and the dispersibility is improved, and
then the dissolved small particles are continuously crystallized again. As the reaction time increases, the crystallized particles undergo a regrowth process and grow into large particles.

![Figure 5. SEM images of LiFePO₄/C prepared at different reaction times: (a) 6 h, (b) 8 h, (c) 10 h, (d) 12 h, (e) 15 h.](image)

Figure 6 shows the first charge/discharge diagram of the samples at different reaction times. The specific capacities of samples at 0.1C rate are 127.9, 129.6, 139.6, 112.3 and 48.5 mAh·g⁻¹. As the reaction time increases, the specific capacity increases first and then decreases. The specific capacity of the sample at 15 h is lowest. That may be because the reaction time is too long to make the particle size large. At 10 h, the sample with a larger specific surface area leads to increase in the contact area with the electrolyte, resulting in a highest charge/discharge capacity.

![Figure 6. First charge and discharge diagram of LiFePO₄/C prepared at different reaction times.](image)

4. Conclusion
LiFePO₄ cathode materials were prepared by simple hydrothermal method. The structure, morphology and electrochemical properties of the materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and constant current charge/discharge. The effect of reaction temperatures and times on the structure, morphology and electrochemical properties of LiFePO₄ were investigated. The results show that the pure phase LiFePO₄ nanoparticles can be prepared at a reaction temperature of 180 °C. When the reaction time is 10 h, the prepared LiFePO₄ has high purity and good crystallinity. Therefore, the final preparation process was determined to be 180 °C for 10 h. In particular, LiFePO₄ particles prepared by this hydrothermal process exhibit a reversible capacity of 139.5 mAh·g⁻¹, so the hydrothermal process is a promising strategy for industry production of LiFePO₄ with high performance.

5. References
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